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PEM Fuel Cell Freeze and Rapid Startup Investigation

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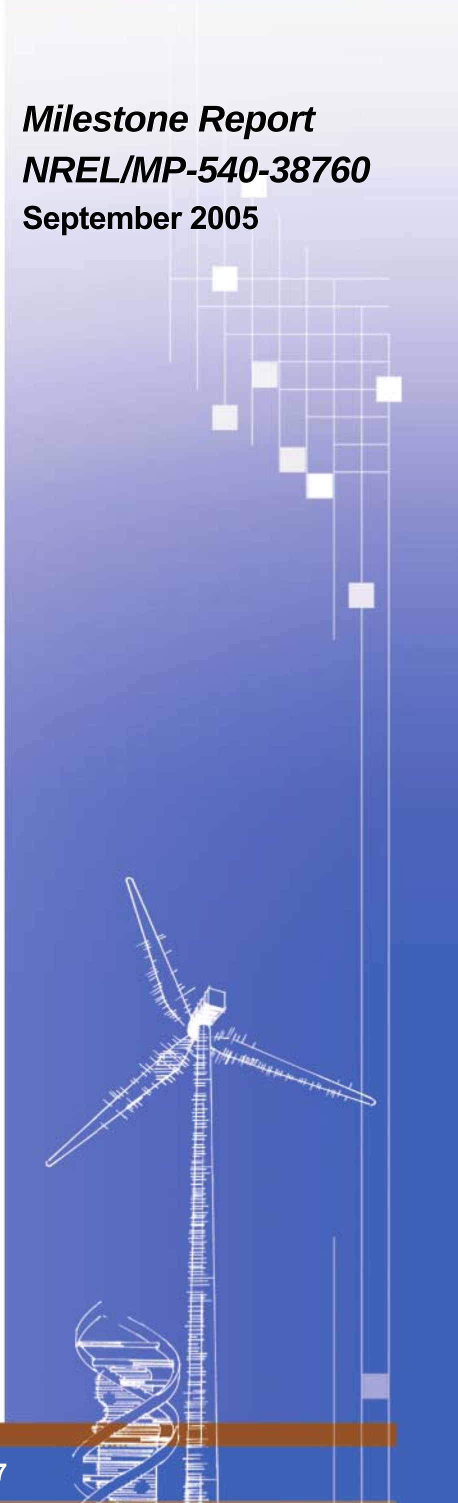
Milestone Report
NREL/MP-540-38760
September 2005



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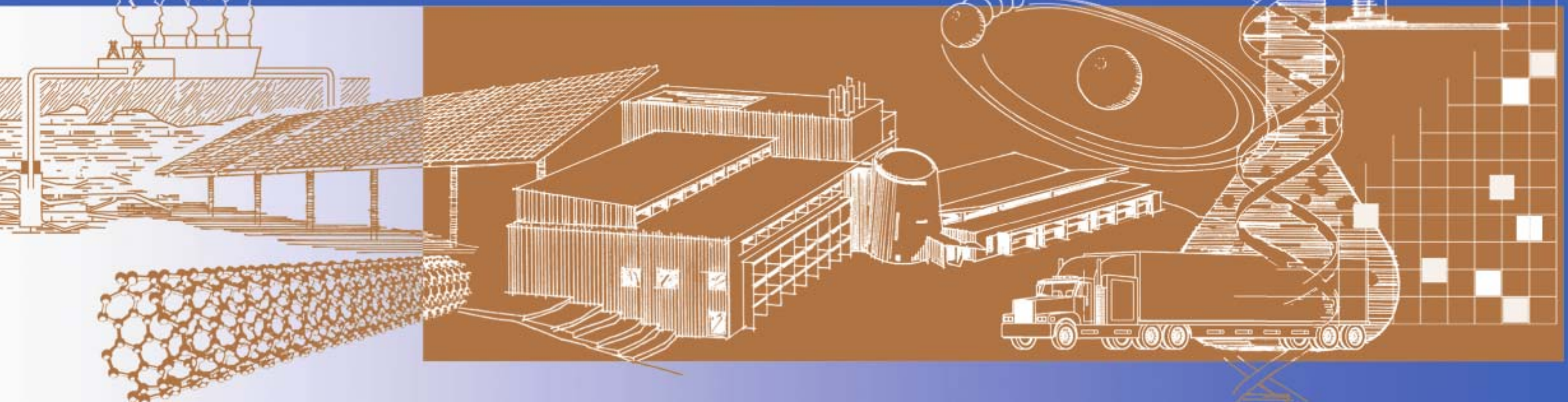

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Preface

This report documents completion of the August 2005 milestone as part of NREL's 2005 Hydrogen, Fuel Cell and Infrastructure Technologies (HFCIT) Annual Operating Plan with the U.S. Department of Energy (DOE). The objective of the work was to investigate the issue of rapid startup of PEM fuel cells from sub-freezing temperatures and solutions that could address them. This supports the DOE/FreedomCAR target of rapid startup of a fuel cell vehicle to 90% rated power soaked at –20°C in less than 30 seconds in 2010 with less than 5 mega Joules of energy.

This work had three major elements: 1. Literature and patent search of concepts proposed by industry and academia and analysis and categorization of the concepts; 2. Analysis of the concepts in relation to U.S. weather patterns and driving cycles as well as estimating the energy and power needs for startup from -20°C; 3. Estimation of energy and power needs at startup from sub-freezing temperatures. This report contains the results of a literature search including related patents in pdf format, and PowerPoint presentations for different meetings.

The Center for Transportation Technologies and Systems and the Center for Electric and Hydrogen Technologies and Systems at the National Renewable Energy Laboratory (NREL) performed this work. This report supports the goals of the FreedomCAR Program in addressing barriers of durability, operation and rapid startup, and water and thermal management for PEM fuel cells and supports the rapid startup targets set by the FreedomCAR Program.

The Fuel Cell Program of the DOE Hydrogen, Fuel Cell and Infrastructure Technologies Office funded this work. We wish to thank our sponsors Nancy Garland and Valri Lightner from the DOE Office HFCIT, and George Sverdrup (NREL HFCIT Technology Manager) for their support. We also would like to express our appreciation for the technical support provided by Keith Wipke (NREL Fuel Cell Task Leader), Doug Wheeler (NREL Consultant), and Cory Welch (NREL) during the course of this project.

Ahmad Pesaran

Fuel Cell Vehicle Systems Subtask Leader

Executive Summary

The Proton Exchange Membrane Fuel Cell (PEMFC) is considered a major power source for future clean transportation and zero emission vehicles. However, survivability, durability, operation, and rapid startup of fuel cell vehicles under sub-freezing temperatures are barriers to the technology that should be addressed before mass-market penetration of hydrogen powered PEMFC vehicles. The objectives of the project are to identify fact-based strategies for rapid start-up of PEM fuel cells from sub-freezing temperatures and to investigate the proposed solutions using system and other analysis tools to aid in evaluating and identifying strategies. In support of the objectives we performed the following activities:

- Conducted a detailed literature and patent search to identify freeze issues and potential solutions to them.
- Participated in the DOE fuel cell freeze workshop.
- Categorized the ideas found in the literature.
- Evaluated the merits of various concepts/solutions using component/system level analysis.
- Performed component-level energy analysis to bracket energy/power requirements for startup from sub-freezing temperatures.
- Collected data on weather patterns and frequency of sub-freezing temperatures across the United States to evaluate the effectiveness of each proposed concept.
- Prepared a record of inventions to document new ideas developed during the course of this project.

The main PEMFC freeze and rapid start issues of concern are preventing system damage caused by freezing and properly managing the energy/power production and distribution for rapid startup in a subfreezing environment. Data and information on these topics were collected through a literature search and discussions with fuel cell experts. The disclosed ideas in numerous patents were categorized by solution approaches. The proposed solutions were categorized into two main strategies according to whether the system uses energy during vehicle parking or mostly at vehicle start: “Keep-Warm” and “Thaw and Heat at Startup.” The successful implementation of either strategy will require developing the corresponding supporting technology groups.

The initial step towards evaluating the various freeze-start solutions and supporting technologies was to conduct an analytical investigation of FC stack cooling time. This analysis was then extended to include the effects of potential FC vehicle use patterns and ambient temperature variation. Given the significant link between ambient and stack temperature variation, the weather analysis was expanded to evaluate the frequency of occurrence of the DOE target -20 ºC cold-soak condition at locations across the United States. This analysis found that a large portion of populated locations rarely experience cold-soak durations at this temperature threshold.

The next part of the analysis involved calculating the energy, power, and stack temperature performance for potential freeze protection and thaw strategies. A refined examination of thaw requirements at a component level highlighted the importance of strategies that minimize the amount of water allowed to freeze in the system, as well as strategies that target heating only to areas absolutely requiring thaw prior to system start-up. Due to the significant system thaw energy requirements (order of 1-6 mega Joules), and the short time period desired for freeze start (less than 30 seconds), a high heating power (order 33 – 200 kW) would be required for the thaw-at-start strategy. Because such high heating power will be difficult to apply uniformly, it is important to include 3-D modeling analysis that goes beyond the lumped heating approximation done here. We have performed preliminary analysis with such a fuel cell modeling tool designed for use at temperatures above freezing, and have made plans to work with the program's developers at the University of South Carolina to expand the capability for rigorous fuel cell simulation at sub-freezing temperatures.

Based on our research and analysis of several freeze management supporting technologies, it seems likely that some combination of different technologies will best address the challenge of PEMFC freeze and rapid-start. It is, however, possible that the added complexity of multiple approaches will increase the cost for operation and installation of the system. It also seems promising that less rigorous interim freeze management solutions will satisfy the requirements of many parts of the country, and could be a transition path to accelerate the introduction of fuel cell vehicles. During this transition period, full deep-freeze management devices could be offered as an add-on option in much the same way as was done with air conditioning before it became a standard option in nearly all vehicles today. This is also similar to "cold-weather packages" (including block heater, heated seats, and heated rear-view mirrors) or "thawing packages" that are being offered in vehicles for cold climates or special purpose uses.

In FY06, emphasis will be placed on expanding analyses begun in FY05 and increasing industry collaboration. One major effort will involve adding freeze modeling capability to the StarCD three-dimensional modeling package and performing rigorous 3-D freeze-start simulation on the interior of a fuel cell stack. Another major project will be creating a PEMFC vehicle freeze management tool that will allow a system designer to combine their specific system inputs with information on potential temperature variation, vehicle use, and management strategies in order to generate the best freeze solution for their application. Finally, we are planning to investigate, test, and evaluate novel rapid startup solutions that we came up with during the course of this project and filed in two records of invention.

1. Introduction

The Proton Exchange Membrane Fuel Cell (PEMFC) has been proposed as a power source for zero emission vehicles. PEMFC systems are particularly well suited for vehicle applications since they do not require the use of hazardous fluids, and they enjoy high power densities and low operating temperatures. However, cold start issues should be resolved for a successful vehicle application of PEM fuel cells. Key issues of concern are to maintain the "integrity" of the fuel cell system and "convenience" for vehicle users.

Table 3.4.3 in the DOE/FreedomCAR Hydrogen, Fuel Cell and Infrastructure Technologies (HFCIT) Program R&D Multi-year Plan identifies the 2010 technical target for cold startup time to 90% of rated power to be less than 30 (or 15) seconds at –20°C (or 20°C) ambient temperatures. The survivability target is –40°C, which means that performance targets must be achieved at the end of an 8-hour cold-soak at temperature http://www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf. Additionally in a May 2005 pre-solicitation document, DOE identified the following updated requirements/targets for freeze-capable fuel cells: "To be competitive with internal combustion engine vehicles, a fuel cell vehicle must be able to start from -20°C and drive away at 50% power within 30 seconds. Furthermore, the fuel consumption to start the vehicle should not exceed approximately 5 mega Joules of additional energy for startup from negative 20°C." One of the goals of the solicitation is to have a fuel cell stack delivered that must, without suffering performance degradation, survive repeated soaking at -40ºC (at least 8 hours) and start unassisted in 30 seconds from -20ºC and produce 50% rated power http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/sow_draft.pdf. Although these are aggressive targets, they need to be met in the long term to make fuel cell vehicles competitive with internal combustion engine vehicles.

Pure water is formed at the cathode as a result of electric power production in the fuel cell, and the polymer electrolyte membrane (PEM) should be well hydrated to maintain high proton conductance and low internal resistance. The inherent presence of water in PEMFC systems creates a problem when vehicles using these power sources are parked in sub-freezing ambient weather conditions. Freeze/thaw cycles can create a durability issue for the fuel cell system (such as related to internal ice expansion), and create a convenience problem for the vehicle user if a long warm-up period or large energy input is required before the vehicle may be driven. Even though the detailed mechanism of the rate reduction is not well known, it is believed that either the proton conductivity of the PEM becomes poor at these temperatures or that the effectiveness of the catalyst is so poor that a sufficient amount of current cannot be drawn.

The objectives of this FY 2005 PEM Fuel Cell Freeze and Rapid Start research at the National Renewable Energy Laboratory (NREL) were to establish a fact-based strategy for finding solutions for these freeze-related issues, particularly with rapid startup. We investigated potential approaches for achieving DOE's fuel cell freeze-start technical targets, and we used system and component analysis tools to analyze and investigate specific solution techniques. We also estimated the energy need for FC start from –20°C.

Participation in the DOE Fuel Cell Freeze Workshop.

NREL supported DOE's workshop on "fuel cell operations at sub-freezing temperatures" (hosted by LANL) in Phoenix, AZ on February 1-2, 2005. NREL's Keith Wipke and Doug Wheeler, as organizing committee members, supported LANL and DOE in planning the event. Keith Wipke, Doug Wheeler, George Sverdrup and Ahmad Pesaran of NREL participated at the Workshop. The Workshop consisted of a series of presentations provided by industry, academia, and national laboratories. Doug Wheeler moderated a session and Ahmad Pesaran of NREL presented an update of the literature search, patent search, and some preliminary analysis on energy and power requirements for warming up fuel cell stacks quickly. (A copy of his presentation is included in the companion CD and can be accessed by linking to FC19_Pesaran.pdf.) Several of the Workshop participants expressed interest in the patent search and analysis including 3M, GM, and Penn State. Following the information exchange part of the workshop, there were two parallel brainstorming sessions to identify the key gaps for addressing the fuel cell freeze issue in automotive applications. Further information on the workshop can be found on the HFCIT website
http://www.eere.energy.gov/hydrogenandfuelcells/fc_freeze_workshop.html
A copy of the presentations and summary of the meeting is included in the companion CD and can be accessed by getting into the FC_Freeze_WorkShop subfolder. The workshop provided an opportunity to look at the freeze issues from fundamental and applied aspects and follow-on research and development needed for addressing the durability and rapid startup issues. Further discussions of the workshop are found in Section 2.1.2.1 of this report.

Excerpts from the minutes of the meeting from LANL further outlines the scope of the workshop: "*The workshop focused on identifying the potentially adverse effects of freezing temperatures on fuel cell operation and planning research and development activities to mitigate these effects. Based on the identified technical challenges/barriers, R&D needs were developed as potential components of a comprehensive R&D plan that is responsive to the findings of this workshop. The needs were prioritized on the basis of potential impact to support the primary objective of the workshop – develop a fuel cell system that will start at sub-freezing temperature rapidly, repeatedly, reliably and without performance degradation.*" Among the top R&D needs was developing fuel cell designs to permit rapid startup that included: minimize power requirements to delay onset of freezing, incorporating materials with low thermal mass, and using advanced design and control strategies for integrating stack, and balance of plant components including humidifiers. This R&D need could be addressed using system tools. Another top R&D need was to develop modeling tools that focus on partially frozen, low-temperature conditions, particularly developing 3D models describing water movement and distribution during freezing and startup. Y. S. Kim, et al, [1], discussed a summary of the workshop at the 2005 DOE Hydrogen Program Merit Review Meeting held in Washington D.C. on May 23-26, 2005. A copy of the presentation is included in the companion CD and can be accessed by linking to FC41_Kim.pdf. This presentation summarizes the findings of the workshop very well. Sub-freezing temperatures lead to ice formation, large thermal mass, delimitation or physical breakdown, which in turn causes:

- *Delayed fuel cell system startup and drive away*
- *Temporary loss of fuel cell system performance.*
- *Irreversible and reversible performance degradation.*
- *Loss of fuel efficiency and increased fuel consumption.*
- *Physical degradation of membrane allowing crossover of gases.*
- *Lowered MEA transport and degraded kinetic properties.*
- *Clogging due to water and icing in pores and flow channels*
- *Reactant starvation and/or imbalance at low temperature operation.*
- *Increased mechanical stresses on fuel cell components and morphological changes.*
- *Loss of thermal and electrical interfacial contact.*
- *Adverse effects in balance of plant components, due to freezing water.*
- *Increased system costs due to the requirement for freeze mitigation strategies.*

This report is organized to discuss the results of our literature and patent search, categorization of ideas/solutions, analysis of concepts/solutions, estimating energy and power requirements for startup from sub-freezing temperatures; weather patterns and frequency of sub-freezing temperatures across the United States, conclusions, and future work.

2. Literature Search

The foundation of our approach was to conduct a thorough investigation of the techniques being pursued by experts in the field working to develop a PEMFC cold start strategy. This research helped indicate the subset of strategies and specific techniques deserving of detailed energy and power analysis. Our modeling and analysis has helped to bracket the requirements for sub-freezing startup and to evaluate the merits of various proposed solutions. We interacted with experts in the field by presenting and receiving feedback on our findings at the FC Freeze Workshop and Hydrogen Program Merit Review. Data and information were collected through discussions with NREL experts and completion of a comprehensive literature and patent search.

2.1. Articles from Open Literature

Not many articles on the FC cold start issue have been published through academic journals. Most of the journal articles listed in this section are quite new. For successful portable/automotive applications of PEMFC, the cold start problem has lately attracted considerable attention in academic research areas as well as in industry. There are many more patents filed than public articles; obviously the community was more interested in protecting their ideas through patents rather than disclosing them in public forums. The subjects of the listed findings of journal articles could be categorized as following.

- Study on proton conductivity of PEM at low temperature
- Study on performance degradation by freezing
- Study on cold start experiments and modeling
- Study of bootstrapping (self-starting) fuel cell at subfreezing temperatures

2.1.1 Journal Articles

Saito et al. [*JA*1, 2005] evaluated the ionic conductivity and water self-diffusion coefficient of the membrane, and investigated the temperature dependence of these transport properties. Cappadonia et al. [*JA*2, 1995] investigated the conductance of Nafion as a function of temperature by means of impedance spectroscopy. Impedance spectroscopy at 80°C was also used by Cho et al. [*JA*3, 2003] to determine changes in single fuel cell characteristics by exsitu thermal cycling. The author concludes that the contact resistance in the fuel cell increased after thermal cycles because of worse contact between the membrane and the electrode, whereas the membrane ionic conductivity itself is not affected. Cho et al. [*JA*4, 2004] also studied the effect of water removal on the performance of a PEMFC repetitively brought down to −10°C. They concluded that the observed performance degradation can be reduced by removing the water from the cell by supplying dry gases or an antifreeze solution into the cell before the cell temperature fell below 0°C.

Hishinuma et al. [*JA*5, 2004] studied the performance of the fuel cell below the freezing point by experiments and simulation. They concluded that it is necessary to heat the cell with an additional heat source in order to start the fuel cell below -5°C. Oszcipok et al. [*JA*6, 2005] performed isothermal, potentiostatic single cell experiments to investigate the basic cold start behavior, and the results are analyzed using statistical software. Sundaresan and Moore [*JA*7, 2005] developed a layered stack model revealing the effect of the endplate thermal mass on the end cells, and accommodated the evaluation of internal heating methods that may mitigate this effect. McDonald et al. [*JA8*] conducted studies to understand the physical and chemical changes in fuel cell membranes that result from Freeze/Thaw (F/T) cycling which might occur in electric vehicles. Nafion® membranes and membrane electrode assemblies (MEA) were subjected to 385 temperature cycles between +80°C and -40°C over a period of three months to examine the effects on key properties. Although no catastrophic failures were seen, the analytical results shed some light on the relationship of temperature cycling to membrane structure, water management, ionic conductivity, gas permeability and mechanical strength [McDonald et al].

There have been several studies regarding the state of water at freeze in the Perfluorosulfonic Acid Copolymer (Nafion®). Yu Seung Kim et al. [*JA9,* 2003] discussed the state of water in Nafion® and proposed that the state of water in the membrane plays a significant role in determining the membrane transport properties. The state of water has been generally defined as follows: (1) *nonfreezing water*, water that is strongly bound to the polymer chain and has a role in effective glass transition reduction (plasticization); (2) *freezable loosely bound water*, water that is weakly bound to the polymer chain or interacts weakly with nonfreezing water and displays relatively broad melting endotherms; and (3) *free water*, water that is not intimately bound to the polymer chain and behaves like bulk water, i.e., a sharp melting point at 0°C. M. Cappadonia, etal. [*JA10*, 1994] studied proton conduction of Nafion® 117 membrane between 140 K and room temperature and found two different water environments can be identified in the membrane, and a relationship between the water content and the conductance could be observed. Sivashinsky and Tanny [JA11, 1981] studied the state of water in swollen ionomers containing sulfonic acid salts and reported that only a part of the water present in Nafion and chlorosulfonated polyethylene undergoes freezing, while no transition was observed for water in sulfonated polysulfone for temperatures down to minus 60°C. Wilson, et. al [*JA*12, 1995] studied platinum loading of electrodes in PEM fuel cells and suggested durability of the catalyst layer and the integrity of the catalyst layer/membrane interface is provided by the high tolerance of such fuel cells to shut-down/start-up and freeze-thaw cycles. De Francesco and Arato [*JA* 13, 2002] developed a transient, lumped stack model using for evaluating various startup strategies considered for hybrid fuel cell bus.

[*JA*1]

Title: Temperature dependence of ion and water transport in perfluorinated ionomer membranes for fuel cells

Author: Saito, Morihiro (Natl. Inst. Adv. Indust. Sci./T., AIST Tsukuba Center 5); Hayamizu, Kikuko; Okada, Tatsuhiro

Source: *Journal of Physical Chemistry B*, v 109, n 8, Mar 3, 2005, p 3112-3119

Abstract: The temperature dependence of the transport properties of perfluorinated ionomer membranes was investigated, to understand thermal properties of polymers. The ionic conductivity and water self-diffusion coefficient in the membranes were evaluated and discussed for ions and water transport mechanisms. The freezing and nonfreezing water in the membranes at low temperatures and the interaction energy between the cation species and water molecules were estimated by DSC and DFT calculations. The results suggest that the water content and the ratio of freezing and nonfreezing water depend strongly on the cation species penetrating into the membrane.

[*JA*2]

Title: Conductance of Nafion 117 membranes as a function of temperature and water content

Author: Cappadonia, Marcella (Research Cent Juelich (KFA)); Erning, J. Wilhelm; Saberi, Seyedeh M.; Stimming, Ulrich

Source: *Solid State Ionics*, v 77, Apr, 1995, p 65-69

Abstract: The conductance of Nafion membranes was investigated by means of impedance spectroscopy as a function of temperature and of sample treatment. In addition to other treatments, the hot pressing of Nafion membranes was also considered, because of its relevance for making membrane-electrode assemblies (MEA) for proton exchange membrane fuel cells (PEMFC). An Arrhenius-type analysis of the conductance shows two regimes, with a change in activation energy observed at transition temperatures between 225 and 260 K, which depends on the water content.

[*JA*3]

Title: Characteristics of the PEMFC repetitively brought to temperatures below 0°C

Author: Cho, EunAe (Fuel Cell Research Center, Korea Inst. of Sci. and Technology); Ko, Jae-Joon; Ha, Heung Yong; Hong, Seong-Ahn; Lee, Kwan-Young; Lim, Tae-Won; Oh, In-Hwan

Source: *Journal of the Electrochemical Society*, v 150, n 12, December, 2003, p A1667-A1670

Abstract: Freezing of water in a polymer electrolyte membrane fuel cell (PEMFC) may cause severe problems in driving a fuel cell vehicle during the winter time. Characteristics of PEMFC which suffered low temperatures below zero celsius were examined with thermal cycles during which the temperature of the environment chamber was cycled from 80 to -10°C. With the thermal cycles, the cell performance was degraded due to the phase transformation and volume changes of water. Effects of freezing of water in a PEMFC on the electrode structure and polarization resistance were examined by Brunauer, Emmett, Teller analysis, cyclic voltammetry, and ac impedance spectroscopy.

[*JA*4]

Title: Effects of water removal on the performance degradation of PEMFCs repetitively brought to less than or equal 0°C

Author: Cho, EunAe (Fuel Cell Research Center, Korea Inst. of Sci. and Technology); Ko, Jae-Joon; Ha, Heung Yong; Hong, Seong-Ahn; Lee, Kwan-Young; Lim, Tae-Won; Oh, In-Hwan

Source: *Journal of the Electrochemical Society*, v 151, n 5, 2004, p A661-A665

Abstract: For the mobile application, performance of polymer electrolyte membrane fuel cells (PEMFCs) should be maintained with being exposed to subzero temperatures in the winter time. To simulate the situation, a PEMFC was operated at 80°C, stopped, cooled to and kept at -10°C for 1 h, and heated to 80°C for the next operation. With the thermal cycle, cell performance was measured and found to degrade at a degradation rate of 2.3% based on current density at a cell voltage of 0.6 V. The degradation was attributed to freezing of water that was produced during operation and remained in the PEMFC after the operation. To prevent the performance degradation, water was removed from the PEMFC by supplying dry gases or an antifreeze solution to the PEMFC before the cell temperature fell to below 0°C, By using the gas-purging and the solution-purging method designed in this work, the performance degradation rate was successfully reduced to 0.06 and -0.47%, respectively.

[*JA*5]

Title: The design and performance of a PEFC at a temperature below freezing

Author: Hishinuma, Yukio (Department of Mechanical Science, Hokkaido University); Chikahisa, Takemi; Kagami, Fumio; Ogawa, Tomohiro

Source: *JSME International Journal, Series B: Fluids and Thermal Engineering*, v 47, n 2, May, 2004, p 235-241

Abstract: At temperatures below freezing, air humidity becomes lower and produced water at the cathode freezes on the surface of catalyst, and it is difficult to start a PEFC (Polymer Electrolyte Fuel Cell) at a cold district. The object of the work is to study the performance of the fuel cell below the freezing point by experiments and simulation. To investigate the characteristics of the starting of a temperature below freezing the performance of a single cell was measured at temperatures from -3 to -25°C and pressures from 1 to 2 atm. The results of the experiments and simulation indicate that the performance of a PEFC decreases at higher current densities and pressures, and lower cell temperatures because of ice more produced on the reactive area of the cathode. To maintain the cell performance below freezing point, it is effective to adjust the current densities and gas flow rate to balance the produced and removed water. However at -5°C, heat generated in the fuel cell is effective to warm the cell and make self-starting possible. These results shows that it is necessary to heat the cell with an additional heat source in order to start the fuel cell below -5°C.

[*JA*6]

Title: Statistic analysis of operational influences on the cold start behavior of PEM fuel cells

Author: M. Oszcipok, D. Riemann, U. Kronenwett, M. Kreideweis and M. Zedda

Source: *Journal of Power Sources, In Press, Corrected Proof, Available online 29 April 2005*

Abstract: For portable fuel cell systems a multitude of applications have been presented over the past few years. Most of these applications were developed for indoor use, and not optimized for outdoor conditions. The key problem concerning this case is the cold start ability of the polymer electrolyte membrane fuel cell (PEMFC). This topic was first investigated by the automotive industry, which has the same requirements for alternative traction systems as for conventional combustion engines. The technical challenge is the fact that produced water freezes to ice after shut-down of the PEMFC and during start-up when the temperature is below 0 ◦C. To investigate the basic cold start behavior isothermal, potentiostatic single cell experiments were performed and the results are presented. The cold start behavior is evaluated using the calculated cumulated charge transfer through the membrane, which directly corresponds with the amount of produced water in the PEMFC. The charge transfer curves were mathematically fitted to obtain only three parameters describing the cold start-up with the cumulated charge transfer density and the results are analyzed using the statistical software Cornerstone 4.0. The results of the statistic regression analyses are used to establish a statistic-based prediction model of the cold start behavior, which describes the behavior of the current density during the experiment. The regression shows that the initial start current mainly depends on the membrane humidity and the operation voltage. After the membrane humidity has reached its maximum, the current density drops down to zero. The current decay also depends on the constant gas flows of the reactant gases. Ionic conductivity of the membrane and charge transfer resistance were investigated by a series of ac impedance spectra during potentiostatic operation of the single cell at freezing temperatures. Cyclic voltammetry and polarisation curves between cold start experiments show degradation effects by ice formation in the porous structures, which lead to significant performance loss.

[*JA*7]

Title: Polymer electrolyte fuel cell stack thermal model to evaluate sub-freezing startup

Author: M. Sundaresan and R.M. Moore

Source: *Journal of Power Sources, In Press, Available online 26 April 2005*

Abstract: For passenger fuel cell vehicles (FCVs), customers will expect to start the vehicle and drive almost immediately, implying a very short system warmup to full power. While hybridization strategies may fulfill this expectation, the extent of hybridization will be dictated by the time required for the fuel cell system to reach normal operating temperatures. Quick-starting fuel cell systems are impeded by two problems: (1) the freezing of residual water or water generated by starting the stack at below freezing temperatures and (2) temperature-dependent fuel cell performance, improving as the temperature reaches the normal range. Cold start models exist in the literature; however, there does not appear to be a model that fully captures the thermal characteristics of the stack during sub-freezing startup conditions. Existing models lack the following features: (1) modeling of stack internal heating methods (other than stack reactions) and their impact on the stack temperature distribution and (2) modeling of endplate thermal mass effect on end cells and its impact on the stack temperature distribution. The focus of this research is the development and use of a sub-freezing thermal model for a polymer electrolyte fuel cell stack. Specifically, the work has focused on the generation of a model in which the fuel cell is separated into layers to determine an accurate temperature distribution within the stack. Unlike a lumped model, which may use a single temperature as an indicator of the stack's thermal condition, a layered model can reveal the effect of the endplate thermal mass on the end cells, and accommodate the evaluation of internal heating methods that may mitigate this effect.

[*JA*8]

Title: Effects of deep temperature cycling on Nafion® 112 membranes and membrane electrode assemblies

Author: McDonald, R.C., Mittelsteadt, C.K., and Thompson, E.L.

Source: *Fuel Cells, v 4, n 3, August, 2004, 2nd European PEFC Forum, July 2003, Lucerne, Switzerland, p 208-21. 3ISSN: 1615-6846, John Wiley and Sons Ltd*

Abstract: A study was conducted to understand the physical and chemical changes in fuel cell membranes that result from Freeze/Thaw (F/T) cycling which might occur in electric vehicles. Nafion® membranes and membrane electrode assemblies (MEA) were subjected to 385 temperature cycles between +80°C and -40°C over a period of three months to examine the effects on key properties. These studies were done on both compressed and uncompressed materials in the un-humidified state. Although no catastrophic failures were seen, the analytical results shed some light on the relationship of temperature cycling to membrane structure, water management, ionic conductivity, gas permeability and mechanical strength. Changes in water swelling behavior and dry densities were noted and the effect on ionic conductivity and cell performance was examined. The impact on catalyst activity and structural integrity of MEAs was evaluated electrochemically.

[*JA*9]

Title: State of Water in disulfonated poly(arylene ther sulfone) copolymers and a perfluorosulfonic acid copolymer (nafion) and its effect on physical and electrochemical properties

Author: Yu Seung Kim, Limin Dong, Michael A. Hickner, Thomas E. Glass, Vernon Webb, and James E. McGrath

Source: *Macromolecules*, 36, 17, 6181 (2003)

Abstract: It is proposed in this paper that the state of water as it is confined in the membrane plays a more significant role in determining the membrane transport properties than previously suggested. The state of water in polymers has been extensively studied, but mainly in the context of hydrogels. It has been generally defined as follows: (1) *nonfreezing water*, water that is strongly bound to the polymer chain and has a role in effective glass transition reduction (plasticization); (2) *freezable loosely bound water*, water that is weakly bound to the polymer chain or interacts weakly with nonfreezing water and displays relatively broad melting endotherms; and (3) *free water*, water that is not intimately bound to the polymer chain and behaves like bulk water, i.e., a sharp melting point at 0 °C

[*JA*10]

Title: Proton conduction of Nafion® 117 membrane between 140 K and room temperature

Author: M. Cappadonia, J. Wilhelm Erning and Ulrich Stimming

Source: *J. Electroanal. Chem*, 376,189 (1994)

Abstract: Nafian® 117 membranes were investigated by measuring the impedance response of the Au/membrane/Au cell between 140 K and room temperature in the frequency range 10^{-2} and 10^{6} Hz. The conductance and its activation energy were obtained for membrane aged either in air or in water after different pretreatments. Two different water environments can be identified in the membrane, and a relationship between the water content and the conductance has been observed.

[*JA*11]
Title: State of Water in Swollen Ionomers Containing Sulfonic Acid Salts
Author: Sivashinsky, N. and Tanny, G. B.
Source: *Journal of Applied Polymer Science*, v 26, n 8, Aug, 1981, p 2625-2637

Abstract: In the reported experiments, the proton magnetic resonance relaxation times and heat capacity of water in perfluoroethylene sulfonic acid (Nafion), chlorosulfonated polyethylene (SPE), and sulfonated polysulfone (SPS) were measured as a function of temperature. Only the relaxation data for water present in Nafion conformed to the BPP model. The data indicate that the presence of fine pores, approximately equals 12 Å in diameter, causes water-surface interactions to play a significant role. For materials with the same pore size, a difference in spin-lattice relaxation time T may be correlated to the Flory-Huggins parameter chi calculated for the interaction of water with the neutral portion of the polymer backbone. Only a part of the water present in Nafion and SPE undergoes freezing, while no transition was observed for water in SPS for temperatures down to minus 60 degree C. For Nafion and SPE, the heat of fusion DELTA Hf calculated from combined FID data and the DSC study was congruent 20 cal/g.

[*JA*12]
Title: Low Platinum Loading Electrodes For Polymer Electrolyte Fuel Cells Fabricated Using Thermoplastic Ionomers
Author: Wilson, Mahlon S., Valerio, Judith A. and Gottesfeld, Shimshon
Source: *Electrochimica Acta*, v 40, n 3, Feb, 1995, p 355-363

Abstract: Low platinum loading catalyst layers for polymer electrolyte fuel cells (PEFCs) consist of a thin film of highly inter-mixed ionomer and catalyst that is applied to the electrolyte membrane. High performances are achieved with loadings as low as 0.12 mgPt cm^{-2} at the cathode and even lower loadings are required at the anode. However, the long-term performance of these fuel cells depends upon the structural integrity of the recast, ionomer-bound catalyst layers. The discovery that the inclusion of large cations through a simple ion-exchange process renders perfluorosulfonate ionomers moderately melt-processable is exploited to significantly improve the structural integrity of the catalyst layers. When the thermoplastic form of the solubilized ionomer is used in the membrane catalyzation process, the reproducibility is greatly improved and the long-term performance losses are quite low. Overall, the fuel cells demonstrate less than 10% loss in maximum power over almost 4000 h. An indication of the durability of the catalyst layer and the integrity of the catalyst layer/membrane interface is provided by the high tolerance of such fuel cells to shut-down/start-up and freeze-thaw cycles. Various other aspects of endurance testing and overall operation of such PEFCs are also discussed.

[*JA*13]
Title: Start-up analysis for automotive PEM fuel cell systems
Author: De Francesco, M. and Arato, E.
Source: *Journal of Power Sources*, v 108, n 1-2, Jun 1, 2002, p 41-52

Abstract: The development of fuel cell cars can play an important role in resolving transport problems, due to the high environmental compatibility and high efficiency of this kind of vehicle. Among the different types of fuel cells, proton-exchange membrane fuel cells (PEMFCs) are considered the best solution for automotive applications at the moment. In this work, constructive criteria are discussed with the aim of obtaining a power generation module adaptable to a wide range of cars. A particular problem in accomplishing the overall project is represented by the definition of the compressor system for air feeding. In this work, the design approach to the problem will be delineated: some options are reviewed and the best solution is analyzed. The transient response of the system (fuel cell and compressor) is investigated in order to optimize the start-up running through a model of a fuel cell stack and a compressor simulation. The model and its results are proposed as a work procedure to solve the problem, by varying external conditions: in fact, to perform the system start-up under stable conditions, the air relative humidity and temperature must be maintained in a proper range of values. The approach here presented has been utilized for the definition of the characteristics of the power module and layout of a middle-size hybrid city bus in the framework of a project promoted by the European Union.

2.1.2 Conference Articles/Presentations

There has been a number of more recent conference papers that deal with system issues and solutions of freeze and rapid startup. M. Gummalla et al. [*CA1,* 2004] from United Technologies Research Center discusses dynamic modeling and analysis of PEM fuel cells for startup from subfreezing temperatures. This work presents the results of a study of <u>bootstrap</u> start using a physics-based dynamic model representing the strongly coupled reaction-transport phenomena, including transport through the various sub-layers in a PEM fuel cell, namely the gas diffusion layers, catalyst layers and the polymer membrane. Bootstrap start simulations depict the key factors limiting bootstrap startup performance, in particular the onset of flooding at the cell cathode. Comparisons of model predictions and experimental data for voltage response during bootstrap start show reasonable agreement, validating the modeling approach. R. Balliet of UTC Fuel Cells [*CA2*, 2005] has discussed PEM fuel cell startup performance in subfreezing conditions. Q. Yan and J. Wu of Mississippi State University [*CA3*, 2005] studied the performance of a PEM fuel cell stack at sub-freezing conditions. Means to mitigate freeze startup are investigated. A fuel cell stack with ten cells is used in the initial experimental studies both before and after low temperature cycling.

The following papers are from the AIChE 2005 Annual Meeting. R. Bradean et al. from Ballard [*CA4,* 2005] studied modeling of freeze start of fuel cell stacks. To speed up the development of the optimum freeze start strategy for a fuel cell stack, a freeze start model is developed that includes critical effects of ice and water management during startup as well as the temperature effects on the critical performance parameters. The fuel cell stack performance during freeze start is found to be in reasonable agreement with the model results. R. Bradean, et al. from Ballard [*CA5*, 2005] present models for predicting MEA water content during fuel cell operation and after shutdown. This work presents models for predicting the MEA water content that are used to provide input into the design of operating strategies of fuel cell stacks. A. Pandy from United Technologies Research Center [*CA6*, 2005] discusses dynamic modeling and analysis of PEM fuel cells for startup from subfreezing temperatures. Parasitic power, space and cost constraints make bootstrap start an attractive option, wherein the fuel cell is started up on its own without external heating. Several factors – total ice hold-up, water movement, history of freeze -- determine the success of a bootstrap start from subfreezing temperatures and the subsequent performance decay. Mathematical modeling used to understand the phenomenon occurring during a bootstrap start could help developing better fuel cell stacks for the automotive industry. Using a validated model, several bootstrap start strategies were simulated and the sensitivity of different parameters on the fuel cell performance during the startup were investigated.

[*CA*1]
Title: Dynamic Modeling and Analysis of PEM Fuel Cells for Startup from Subfreezing Temperatures
Author: Mallika Gummalla et al. (United Technologies Research Center)
Source: AIChE 2004 Annual Meeting, November 7 - 12, 2004, Austin, TX

Abstract: Presented in this work is a study of bootstrap start using a physics-based dynamic model that represents the strongly coupled reaction-transport phenomena, including transport through the various sub-layers in a PEM fuel cell, namely the gas diffusion layers, catalyst layers and the polymer membrane. Bootstrap start simulations depict the key factors limiting bootstrap startup performance, in particular the onset of flooding at the cell cathode. Comparisons of model predictions and experimental data for voltage response during bootstrap start show reasonable agreement, validating the modeling approach. The model was then deployed to analyze the startup behavior from sub-freezing conditions. The start-up power density obtained from the fuel cell is found to be strongly dependent on the ease of species transport across the various layers and the rate of heat generation. Finally, the dynamic model was used to predict the start-up temperature dynamics and the voltage response, and the results are in good comparison with the test data.

[*CA*2]

Title: PEM FC Startup Performance in Subfreezing Conditions

Author: Ryan Balliet (UTC Fuel Cells)

Source: *Fuel Cells,* Bryant University, Smithfield, RI, July 17-22, 2005

The author and conference organizers did not disclose paper content because of Gordon Conference policy.

[*CA*3]

Title: Performance of A PEM Fuel Cell Stack at Sub-Freezing Conditions

Author: QianguYan and Junxiao Wu (Mississippi State University)

Source: 208th ECS Meeting - Los Angeles, California, October 16-21, 2005

Abstract: One major obstacle that must be overcome is the start-up difficulties that arise when fuel cell operation is initiated under sub-zero temperatures. One hypothesis for this difficulty is that the water generated, initially at the cathode, will freeze. This, in turn, can block the penetration of reactants into the catalyst from the gas diffusion layer. Water may freeze both on the catalyst and in the gas diffusion layers. Improvements in fuel cell response to low temperatures and thermal cycling is the focus of the present work. Experimental studies are directed towards identifying the impact of thermal variations through changes in fuel cell performance and by examination of fuel cell components after loss of performance has been established. In these initial experiments, a fuel cell stack is employed. An additional technical concern is the non-uniformity of temperature distribution during startup of a fuel cell stack at sub-freezing conditions. During startup the interior cells warm at a faster rate, while the cells located adjacent to either end of the stack warm more slowly. This compromises the performance of the fuel cell stack during initial startup and is not acceptable to the consumer. Means to mitigate this effect is investigated. A fuel cell stack with ten cells is employed in initial experimental studies both before and after low temperature cycling. Operation of the stack at 80°C will allow baseline performance to be established through measurement of open circuit potential, polarization curve, cyclic voltammetry, and membrane conductivity. These baseline performance data will then be available for comparison with data gathered during operation after thermal cycling to sub-freezing temperatures. This comparison will reveal significant changes that have occurred and impacted performance. The fuel cell stack system will be housed in an environmental chamber that will allow the system to be subjected to temperatures ranging from sub-freezing to those encountered during normal operation. Care will be taken to ensure that the entering feed gas streams have sufficient residence time to thermally equilibrate at the temperature in the environmental chamber.

[*CA4*]

Title: Modeling Freeze Start of Fuel Cell Stacks

Author: Radu Bradean, Chris Richards and Herwig Haas (Ballard Power Systems)

Source: AIChE 2005 Annual Meeting, October 30 - November 4, 2005, Cincinnati, OH

Abstract: Freeze start is a key requirement for fuel cell stacks that operate in locations with potentially cold climate. Recent achievements in the design of fuel cell stacks and operating strategies made possible very fast freeze starts with little or no performance loss. To speed up the development of the optimum freeze start strategy for a fuel cell stack, a freeze start model is developed that includes critical effects of ice and water management during startup as well as the temperature effects on the critical performance parameters. The fuel cell stack performance during freeze start is found to be in reasonable agreement with the model results.

[*CA5*]

Title: Models for Predicting MEA Water Content During Fuel Cell Operation and After Shutdown

Author: Radu Bradean, et al. (Ballard Power Systems)

Source: AIChE 2005 Annual Meeting, October 30 - November 4, 2005, Cincinnati, OH

Abstract: Effective fuel cell operation requires the optimization of the water content of the membrane electrode assembly (MEA) such that to meet targets for performance, freeze start, durability and reliability. In this work we present models for predicting the MEA water content that are used to provide input into the design of operating strategies of fuel cell stacks. The measurements of MEA water content during fuel cell operation, stack purging after shutdown, or natural cooling after shutdown are in good agreement with the model results.

[*CA6*]

Title: Dynamic Modeling and Analysis of PEM Fuel Cells for Startup from Subfreezing Temperatures

Author: Arun Pandy, Arvind Raghunathan, Nikunj Gupta, Mallika Gummalla, Cynthia York and Sergei Burlatsky (United Technologies Research Center)

Source: AIChE 2005 Annual Meeting, October 30 - November 4, 2005, Cincinnati, OH

Abstract: One of the key challenges to the development of commercially viable automotive PEM fuel cells (Polymer Electrolyte Membrane) is the start-up of the fuel cell from frozen conditions. Parasitic power, space and cost constraints make bootstrap start an attractive option, wherein the fuel cell is started up on its own without external heating. Several factors – total ice hold-up, water movement, history of freeze -- determine the success of a bootstrap start from subfreezing temperatures and the subsequent performance decay. Mathematical modeling can be used to understand the phenomenon occurring during a bootstrap start and help to develop better fuel cell stacks for the automotive industry. In this work, t a one-dimensional mathematical model that captures the coupling between transport phenomena, phase change and fuel cell electrochemistry is proposed. The transport phenomena include mass, momentum and energy transport through various porous layers of the PEM fuel cell. Phase change of water into ice under sub freezing conditions, and evaporation of water, are accounted for in each of the porous layers. The electrochemistry is modeled using a Tafel-type equation for oxygen reduction reaction. A performance curve of the fuel cell during normal operating conditions was simulated with this model and was validated against experimental data. Using this validated model we simulate several bootstrap starts and study the sensitivity of different parameters on the fuel cell performance during the start-up. The parameters that are varied are the total water content in the fuel cell prior to freeze, differential drainage of water on anode and cathode sides prior to freeze, and temperature to which the cell is frozen. Results from these simulations will be presented and discussed.

2.1.3. Presentations from DOE Meetings

2.1.3.1 DOE Fuel Cell Freeze Workshop

The following presentations made at Fuel Cell Freeze Workshop provide up-to-date information on PEM FC freeze. Further information on the workshop could be found in HFCIT websitehttp://www.eere.energy.gov/hydrogenandfuelcells/fc_freeze_workshop.html. A copy of the presentations and summary of the meeting is included in the companion CD and can be accessed by getting into FC_Freeze_WorkShop subfolder.

- DOE Program/Targets and Workshop Objectives, Nancy Garland, DOE Hydrogen Program
- Automotive PEM Stack Freeze Requirements & Suggested Fundamental Studies, Glenn Skala, General Motors
- Fundamental Issues in Subzero PEMFC Startup and Operation, Jeremy Meyers, UTC Fuel Cells
- PEMFC Freeze Start, Ballard Power Systems
- Stationary Applications and Freeze/Thaw Challenges, Richard Gaylord, Plug Power
- Low Temperature Proton Conductivity, Tom Zawodzinski, Case Western Reserve University
- Membranes and MEAs at Freezing Temperatures, Phil Ross, Lawrence Berkeley National Lab
- MEA and Interfacial Issues in Low Temperature Fuel Cells, Bryan Pivovar, Los Alamos National Lab
- Startup of PEFC Stacks From Sub-Freezing Temperatures, R. K. Ahluwalia and X. Wang, Argonne National Lab
- A Study on Performance Degradation of PEMFC by Water Freezing, EunAe Cho, Korea Institute of Science and Technology
- 3-D modeling of Fuel Cells using PEMFC StarCD, John Van Zee, University of South Carolina
- Fuel Cell Freeze Startup and Landscape of FC Freeze Patents, Ahmad Pesaran, Tony Markel, Gi-Heon Kim, Keith Wipke, National Renewable Energy Lab

2.1.3.2 DOE 2005 Hydrogen Program Review Meeting

Three presentations at the 2005 Hydrogen Program Review Meeting discussed some aspects of freeze issues. These presentations could be found in the HFCIT website www.hydrogen.energy.gov and also contained in the companion CD.

- Sub-Freezing Fuel Cell Effects Yu Seung Kim, Rangachary Mukundan, Fernando Garzon and Bryan Pivovar, Los Alamos National Laboratory Institute
- Fuel Cell Systems Analysis R. K. Ahluwalia, X. Wang, E. Doss, R. Kumar, Argonne National Laboratory
- Fuel Cells Vehicle Systems Analysis - Fuel Cell Freeze Investigation, Ahmad Pesaran, Gi-Heon Kim, Jeff Gonder, Keith Wipke, National Renewable Energy Laboratory

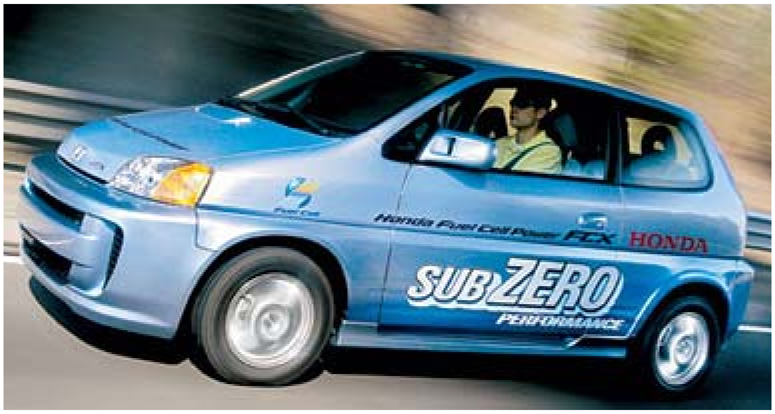
2.1.4 Thesis (M.S. or Ph.D.)

M. Sundaresan of University of California/Davis has written her Ph.D. dissertation on the topic of thermal modeling to evaluate sub-freezing startup for PEM FC vehicles. The focus of this research was the development and use of a sub-freezing thermal model for a polymer electrolyte fuel cell stack and system designed for integration within a direct hydrogen hybrid FCV. The stack is separated into individual cell layers to determine an accurate temperature distribution within the stack. Unlike a lumped model, which may use a single temperature as an indicator of the stack's thermal condition, a layered model can reveal the effect of the endplate thermal mass on the end cells, and accommodate the evaluation of internal heating methods that may mitigate this effect. Major research findings include the following recommendations for the best startup strategies based on model parameter values and assumptions: 1) use internal heating methods (other than stack reactions) below 0ºC, 2) circulate coolant for uniform heat distribution, 3) minimize coolant loop thermal mass, 4) heat the endplates, and 5) use metal such as stainless steel for the bipolar plates. The full text of this dissertation could be accessed from the University of California/Davis publication site http://www.its.ucdavis.edu/publications/2004/UCD-ITS-RR-04-05.pdf.

Title: A thermal model to evaluate sub-freezing startup for a direct hydrogen hybrid fuel cell vehicle polymer electrolyte fuel cell stack and system
Author: Sundaresan, Meena.
Publication: Institute of Transportation Studies, University of California, Davis,
Year: 2004

2.1.5 News and Press Releases

Honda Motor Co. has announced since late 2003 that its new fuel cell vehicle equipped with Honda FC stack could be started successfully from subfreezing temperatures (such as -20°C) without any problems. The announcement has been reiterated several times and reported by many web newsletters. It is reported that room temperature starts will take 5 to 10 seconds, but startup from freezing conditions may take up to 45 seconds. Details on how this works have not been disclosed.



Honda takes next step in fuel cells, from Chicago Tribune, May 30, 2005
www.fuelcellsworks.com/Supppage2746.html

Excerpts: The hydrogen-powered Honda FCX, a four-door hatchback, boasts the first fuel cell that works in subzero temperatures. After sitting out one sub-20 degree night, the check lasted about 37 seconds. The process took about 18 seconds after the car sat in subfreezing temperatures for more than 24 hours, and the heater provided warm air less than a minute after startup.

Honda FCX demonstrates cold-start performance, from HONDA Motor Co. Fuel Cells Bulletin; Apr2004, Vol. 2004 Issue 4, p5, 1p

Abstract: Japanese automaker Honda Motor Co has conducted a successful public cold-weather demonstration of its FCX fuel cell car equipped with the company's new Honda FC Stack. The tests displayed the vehicle's cold-weather driving performance, as well as its ability to start in sub-freezing temperatures. ISSN:1464-2859

Honda Develops Fuel Cell Scooter Equipped with Honda FC Stack, from Honda Press Release, October 2003 http://world.honda.com/news/2004/2040824_03.html

Abstract: Honda announced the development of the Honda FC Stack, a next-generation fuel cell capable of starting at subfreezing temperatures. Honda plans to deliver the Honda FC Stack-equipped FCX in the second half of 2004 to customers in the United States, and in 2005 to customers in Japan.

Honda FCX Proves Its Cold-Start Capabilities in Public Test, from AutoWeb www.autoweb.com.au/cms/A_100885/newsarticle.html

Abstract: Honda FCX Proves Its Cold-Start Capabilities in Public Test. The Honda FCX is the first fuel cell vehicle to be certified for regular commercial use.

Honda FCX: Honda proves it's ready for a 'hydrogen economy.' Now, where's the hydrogen? from Car and Driver**,** July 2005, Dave Vanderwerp.
www.caranddriver.com/article.asp?section_id=3&article_id=9640&page_number=1

Excerpts: "To start, turn the key to the run position and wait. A bar graph displays how long it will take to boot up—much like starting the Windows routine on a computer. During our time with the FCX, temperatures were quite mild and startup took just 5 to 10 seconds, but when parked overnight in freezing conditions, that can be more like 45 seconds. After a handful of clicks and whirs, a "Ready to Drive" message is displayed. Put the gearshift lever in "D" just like any automatic, but in this case the transmission is a single set of gears, i.e., no shifting, making acceleration buttery smooth."

Ballard Power Systems has announced significant progress in three areas crucial to the commercialization of automotive fuel cell stack technology- freeze start capability, durability and cost reduction - without compromising performance. Ballard scientists and engineers have demonstrated a stack design that can start repeatedly from -20 degrees C (-4 degrees F) and operate for more than 2,000 hours at a substantially reduced cost with no performance trade-off (February 2005).
http://www.h2cars.biz/artman/publish/article_667.shtml
http://www.fuelcellmarkets.com/article_default_view.fcm?articleid=7386&subsite=2843

Ballard's Technology Hat Trick - Driving Fuel Cell Innovation, from Ballard Website, http://www.ballard.com/be_informed/fuel_cell_technology/hat_trick
Ballard demonstrated freeze starts from -20°C. The test lowered the fuel cell stack and its supporting systems to -20°C and then subjected the unit to a drive cycle test from start-up through power down. The unit was then allowed to cool to -20°C and the test was repeated. Fifty consecutive freeze start cycles were conducted with no degradation in performance or damage to the stack. While we have a future goal of operating at -30°C, a -20°C temperature is well within the operating requirements for most of North America and Europe. Water generation is a by-product of fuel cell operation. As such, managing water within fuel cells presents a substantial challenge in freezing temperatures and has been a key hurdle in the commercialization of the technology.

Ballard's Fuel Cell Technology "Road Map" Shows Freeze Start Capability, from Ballard Website http://www.ballard.com/be_informed/fuel_cell_technology/roadmap. Managing the water produced by fuel cells presents a challenge in freezing temperatures and, as such, to the commercialization of fuel cell technology. Ballard has already achieved fuel cell stack start-up at -20°C, within 100 seconds, to 50% of the rated power for the stack. Ballard's 2010 target for stack freeze start is -30°C, in 30 seconds, to 50% rated power.

UTC Fuel Cells, a business unit of UTC Power develops a freeze-capable fuel cell power plant and integrate it into a new Hyundai fuel cell vehicle. http://www.utcpower.com/fs/com/bin/fs_com_Page/0,5433,03554,00.html

General Motors reports that it has made great strides in solving many of the challenges inherent in fuel cell technology, including the tendency to freeze and stop working in cold weather. The GM fuel cell's freeze start-up time has decreased to less than 15 seconds for 100% power at minus 20 degrees Celsius. http://www.gm.com/company/gmability/adv_tech/400_fcv/

DaimlerChrysler Fuel Cell Vehicles Operate in Freezing Temperature**s.** In January 2005, with winter in full swing, the time and place to test fuel cell vehicles in a cold environment was Detroit. DaimlerChrysler had fuel cell vehicles operating daily with customers in snowy conditions. One of the environments that the company was collecting operational data from is extreme cold. http://www.autointell-news.com/News-2005/Jan-2005/Jan-2005-4/Jan-26-05-p6.htm

DaimlerChrysler Fuel Cell Vehicles Run In Freezing Temperatures. DaimlerChrysler has fuel cell vehicles operating daily with customers in snowy conditions. http://www.autoemirates.com/International/2005/0129FuelCellMBINT.asp

Hyundai and UTC Fuel Cells collaborate on all-weather fuel cell vehicle. Hyundai's second generation fuel cell vehicle aimed at overcoming sub-zero degree start up challenge. http://www.csrwire.com/article.cgi/1935.html

2.2. Patent Search

A detailed search of the time period from January 1988 to June 2005 yielded more than 1350 patents related to fuel cell freeze/thaw. Further mapping and analysis of the patent database and deletion of references to items such as reformers led to tabulation and categorization of the more than 160 most relevant patents. A list of all the relevant patents is provided in Table A.1 in Appendix A. The patents in PDF format are provided on a companion CD attached to the back of this report or could also be downloaded from the NREL Fuel Cell and Hydrogen Program website under the Fuel Cell Projects at http://www.nrel.gov/hydrogen/proj_fuelcells.html. Each PDF file is linked to the Patent number in Table A.1

After reviewing and categorizing each patent, we developed a Solution Category Chart for PEMFC Freeze and Rapid Startup Methods shown in Figure 1. As indicated by the chart, the proposed solutions can be categorized into two main strategies according to whether the system uses energy during vehicle parking or mostly at vehicle start. The successful implementation of either strategy will require developing the corresponding supporting technology groups.

The first, so-called "Keep-Warm" method, does not allow the system to freeze. With this strategy, the system consumes energy/fuel in order to remain above a certain threshold temperature. In this method, since the fuel cell system is not allowed to freeze, the moisture does not need to be drained from the system. The energy/fuel consumption requirements are highly dependent on difficult-to-predict parking time and ambient temperature variables. The heat/energy (Q) added in the Keep-Warm method does not depend on the mass of the fuel cell system, but the heat loss rate from the system to keep it above freezing ($T_{surface}$) makes this method dependent on the surface area (A) and volume.

$$Q = h\,A * (T_{surface} - T_{ambient})$$

Supporting technologies for the Keep-Warm method include system insulation, using a continuous low-power energy source (from a battery or hydrogen fuel converter), and sensing and control for energy/fuel management during heated parking. Preliminary analysis indicated that this method is effective for short-term parking and/or for mild sub-freezing vehicle storage temperatures.

The method of "Thaw and Heat-up at Start" does not use energy/fuel during vehicle parking. This technique instead requires high power at system start. Supporting technologies include water drainage from the fuel cell stack at shut-down, re-humidification at system start, ice management in the system components, and design of the thawing/heating power source. This method depends on the mass of the system and particularly the mass of water that needed to be melted.

$$m_{system} C_p \frac{\partial T}{\partial t} = h\,A * (T_{surface} - T_{ambient}) + m_{water} * h_{fg} / \Delta t$$

Although various combinations of different technologies appear to provide promising solutions to the sub-freezing parking issue, the added complexity of multiple strategies will increase the operation and installation costs of the system. The categories could be divided in the following way:

- Keep-Warm method includes
    - Insulation (stack and balance of plant)
    - Adding heat continuously or intermittently
        - Resistive heat using DC current from batteries
        - Heat of reaction of hydrogen
            - Catalytic reaction
            - Combustion in a burner
            - Operating the fuel cell (waste heat and charging battery)
    - Sensing and controls and energy management
- Thaw-Heating at Start method included
    - Adding heat from external sources
        - Resistive heat using DC current from batteries
        - Heat of reaction of hydrogen
            - Catalytic reaction
            - Combustion in a burner
    - Adding heat from fuel cell operation
        - Hot air from compressor
        - Waste heat from fuel cell
        - Resistive heating in the fuel cell
    - Re-humidification
    - Sensing, control, and energy management

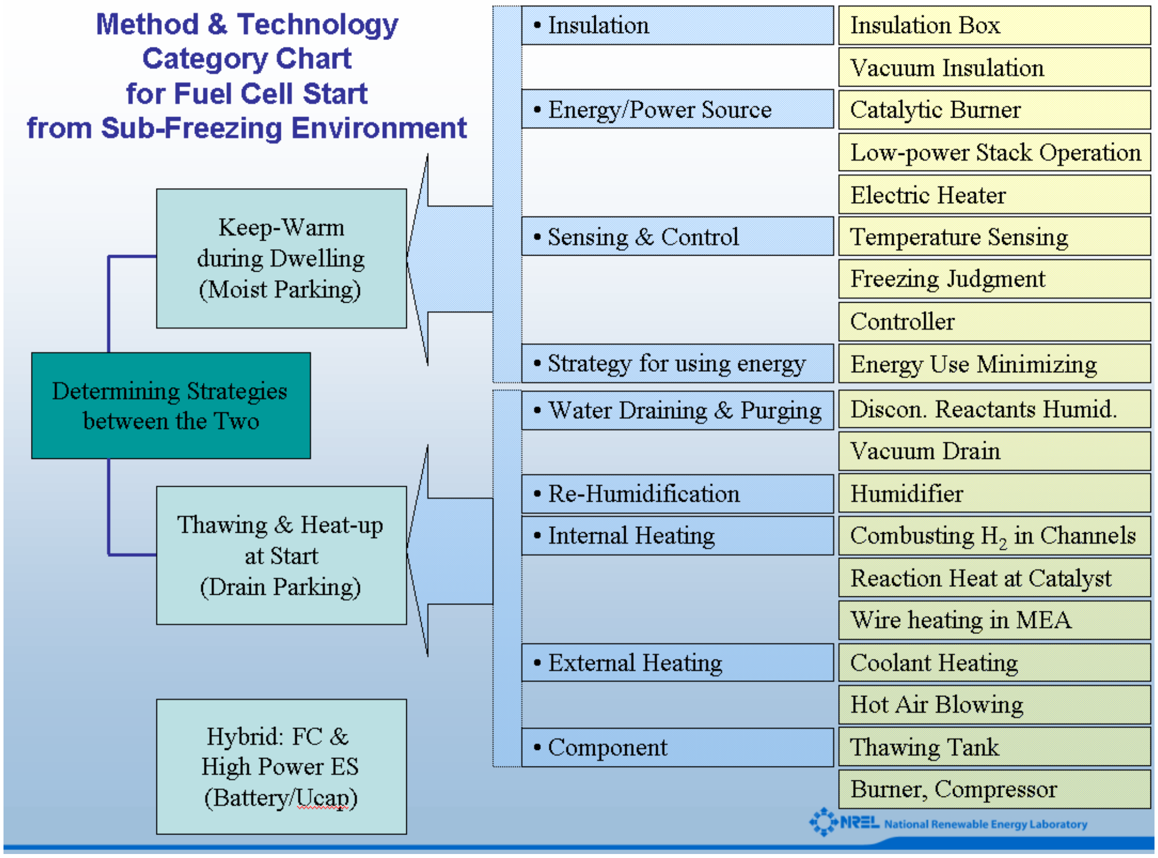


Figure 1. Solution Category Chart for PEM Fuel Cell Freeze Start Methods

2.2.1. Technology Categorization

Identified patents addressing the PEM Fuel Cell cold start issues were classified according to the categories proposed in the previous section. Even though some technologies do not clearly fall under a certain category and many of the patents use combined technologies from several categories, it is useful to investigate the different potential solution approaches to PEMFC freeze start.

2.2.1.1 Keep-Warm Strategy

This approach potentially prevents damages that may be caused when the fuel cell stack remains in a dwell or off-mode at sub-freezing ambient temperatures for a long time or go through a warm-up and freeze cycle. In accordance with a keep-warm system, thermal insulating enclosures are usually provided to prevent freeze-sensitive portions of the power plant (such as the cell stack assembly and the water management system) from freezing.

Problems: This system generally requires insulation, continuous or intermittent use of energy from a battery or hydrogen source, and a control and management system—therefore it could be costly. This approach demands energy and therefore would require great fuel consumption over a long time, which limits the storage protection time available.

Related Examples:

Publication		***Title*** Summary
Patent Number	US06727013	**Fuel cell energy management system for cold environments** An energy management system controls the temperature of a fuel cell system while a vehicle is not running. The energy management system includes a fuel cell stack, a blower that provides air to the fuel cell stack, a water supply, and a hydrogen supply. A hydrogen supply valve is connected between the hydrogen supply and the fuel cell stack. A heater is connected to an output of the fuel cell stack. A controller controls the hydrogen supply valve and the blower to power the heater to warm the fuel cell stack and the water supply. The controller starts the blower and opens the hydrogen supply valve if heating is necessary and if a tank level signal exceeds a first tank level value. The controller activates a purge, drains water from the water supply, and inhibits vehicle startup if the tank level signal does not exceed a first tank level value.
Assignee	General Motors Cooperation	
Category	System, Control, Component	
Publication		***Title*** Summary
Patent Number	EP1414090A1	**Freeze protected fuel cell system** A fuel cell system has a heater for heating water in the fuel cell system; and a controller for controlling the heater. The controller executes a stop mode having the smaller energy consumption of a temperature maintenance mode where water in the fuel cell system is maintained to a temperature greater than freezing point in a period after a shutdown the fuel cell system until a scheduled start-up date-time and a defrost start-up mode where frozen water in the fuel cell system is melted when the fuel cell system undergoes a start-up operation. The controller stores a historical external temperature data for a period prior to the shutdown of the fuel cell system. The historical external temperature data is used for predicting the external temperature for the scheduled start-up date-time. The controller calculates the energy consumption in the defrost start-up mode based on the predicted external temperature.
Assignee	Nissan Motor Co, LTD	
Category	System, Control	
Publication		***Title*** Summary
Patent Number	US06797421B2	**Method and apparatus for preventing water in fuel cell power plants from freezing during storage** A keep warm system for a fuel cell, power plant, typically of the PEM type, prevents freeze-sensitive portions of the power plant, such as the cell stack assembly (CSA) and the water management system from freezing under extreme cold external temperatures, during extended storage (CSA shut-down) periods. Pre-stored and pressurized fuel, typically hydrogen, normally used to fuel the anode of the CSA, is used as fuel for a catalytic oxidation reaction at a catalytic burner to produce heated gas that convectively passes in heat exchange relation with the freeze sensitive portions of the power plant. The convective flow of the heated gases induces the airflow to the burner, obviating the need for parasitic electrical loads. Thermal insulating means substantially enclose the freeze-sensitive CSA and/or the water management system, and the convective flow of the heated gas from the catalytic burner, to improve system thermal efficiency.
Assignee	UTC Fuel Cells, LLC	
Category	System,	

Comments: US6727013 assigned to General Motors Corporation, proposes that the controller opens the hydrogen supply valve and powers the blower to run a fuel cell if heating is necessary during dwell times. A heater to warm the fuel cell stack or the water supply is connected to an output of the fuel cell stack. On the other hand, US6797421B2 assigned to UTC Fuel Cells, LTC, suggests a catalytic burner; eliminating the need for parasitic electrical loads to produce heated gas. EP1414090A1 assigned to Nissan Motor Co, LTD, proposes that the controller could determine a stop mode as a temperature maintenance mode or a defrost start-up mode according to the historical external temperature data and user input of estimated dwelling time.

2.2.1.2. Thermal Insulation

The insulation is often integrated with the fuel cell stack casing in order to keep susceptible components such as the stack, humidifier, and water tank from freezing. This approach occasionally used with Keep-Warm strategy.

- Insulation Enclosure
- Vacuum Insulation
- Variable-Conductance Insulation

Problems: The insulation increases stack volume and weight as well as the thermal mass of the system. Additional weight adversely impacts vehicle performance, installed power requirements, and cost.

Related Examples:

Publication		***Title*** Summary
Patent Number	US06756143	**Fuel cell system and method for starting a fuel cell system** A fuel cell system, particularly for a motor vehicle, includes at least one fuel cell and a device for supplying at least one fuel cell with hydrogen or a hydrogen-containing gas. Particularly during start-up or a cold start of the system, individual components of the device or at least one fuel cell can be supplied thermal energy with cooling water contained in a cooling water system. The cooling water system is equipped with an insulating device for storing cooling water in a thermally insulated manner.
Assignee	Ballard Power Systems AG	
Category	System, Water-system Insulation	

Publication		***Title*** Summary
Patent Number	JP2004241303A2	**FUEL CELL** PROBLEM TO BE SOLVED: To provide a vehicular fuel cell allowing effective warming-up of the fuel cell in stopping it, and capable of reducing its starting time, and of preventing usage stop due to freeze. SOLUTION: This vehicular fuel cell equipped with a piping system associated with a cooling system, an air system, a hydrogen system and the like is provided with a warming-up system for a stack body of the fuel cell. The fuel cell is characterized by that the warming-up system is equipped with a heat insulation box for housing at least a part of the stack body and the piping system of the fuel cell in its inside, and has a vehicular air conditioner incorporated; and the air warmed by a heat exchanger provided for a heat pump cycle of the air conditioner is supplied to the heat insulation box.
Assignee	Denso Corp	
Category	System, Warming-Up System	

Publication		***Title*** Summary
Patent Number	JP2004234892A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To prevent freezing of a fuel cell when operation is stopped. SOLUTION: A fuel cell is stored in a sealed state inside a case and a gas layer is provided in between the case and the fuel cell. When a system is stopped, the interior of the gas layer is made vacuum by operating a vacuum pump and the fuel cell and the outside of the case are insulated.
Assignee	Nissan Motor Co LTD	
Category	System, Vacuum Insulation	

Comments: The insulating container suggested by US6756143 assigned to Ballard Power System AG, is equipped with a burner, water heater, or latent heat storage unit. US6797421 assigned to UTC Fuel Cells, LLC, presents the system insulation incorporated with the Keep-Warm method using a catalytic burner. US5433056 and US5175975, assigned to NREL, propose compact vacuum insulation, which can provide the insulation volume reduction with variable conductance (on-and-off) thermal insulation apparatus.

2.2.1.3. Low Power Heat Source

In order to keep the FC stack and freeze sensitive system components above a pre-determined threshold temperature, a low-power heating source is required. In the invention US6727013 assigned by General Motors Cooperation, the fuel cell is operated in a low power mode to provide electricity to the heaters in the system. Energy storage devices such as a battery are often integrated with fuel cell systems, and may be used to supply some of the energy for the heaters during parking. The fuel cell can, therefore, operate intermittently to recharge the on-board battery as needed and directly operate the heaters. Instead of turning on a fuel cell during vehicle parking, US6797421, assigned by UTC Fuel Cells LLC, suggests using a catalytic burner, which does not require great flow rates of fuel and air.

2.2.1.4. Sensing & Control

One of the supporting technologies for the Keep-warm Method is sensing and control for energy/fuel management during heated parking. Various strategies appear in many inventions, such as WO04004035A3, WO04082053A1, EP1429409A1, and WO04004056A1.

2.2.1.5. Minimizing the Use of Water Coolant

Some PEMFC cooling systems may employ de-ionized water in order to avoid electrically shorting the fuel cell stack with more traditional coolants that are electrically conductive. One solution to mitigate this freeze problem is to develop a low freezing temperature, non-electrically conductive heat transfer fluid to replace (or be used as an additive with) pure water as a coolant. Another option to minimize the use of pure water coolant is to operate with separate stack and radiator coolant loops thermally coupled with heat exchanger.

- Electrically-non-conducting Anti-freeze Coolant
- Separated Coolant Loops

Problems: Problems include: Difficulty in developing and maintaining purity of non-conducting heat transfer fluids. Possibility of water-containing portions of coolant system freezing under long-term storage in a subfreezing environment, thus requiring excessive time and energy to be melted for start-up. Separating coolant loops with additional liquid-liquid heat exchanger adds cost, weight, and volume.

Related Examples:

Publication		***Title*** Summary
Patent Number	EP1416563A1	**Fuel cell and fuel cell coolant composition** This invention is directed to coolant compositions, particularly coolant compositions useful in fuel cells, and to fuel cells containing such coolant compositions. The coolant compositions or heat transfer fluids of this invention have and retain low electrical conductivity through extended periods of use. These coolants or heat transfer fluids are composed of a base composition and an additive package which imparts the property of retaining low electrical conductivity for extended periods of time. The base composition can be de-ionized water (DI water) alone or a mixture of DI water and a freezing point depressant of the types well known in the art (e.g., propylene glycol). The additive package contains an organic corrosion inhibitor and a polymeric ion suppressant. The use of both components of the additive package is important.
Assignee	Advanced Fluid Technologies, Inc.	
Category	Material, Coolant	
Publication		***Title*** Summary
Patent Number	US0224201A1	**Antifreeze cooling subsystem** Liquid cooled systems having coolant circulation loops must often operate in below freezing conditions. For instance, in various applications certain fuel cell systems must be able to tolerate repeated shutdown and storage in below freezing conditions. Conventional glycol-based coolants typically used for internal combustion engines are generally unsuitable for use in the associated fuel cell cooling subsystems due to the presence of additives and/or inhibitors, which are normally included to deal with problems relating to decomposition of the glycol. With additives or inhibitors present, the coolant conductivity can be sufficiently high as to result in electrical shorting or corrosion problems. However, provided the purity of the coolant is maintained, a pure glycol and water coolant mixture may be used as a fuel cell system coolant to obtain suitable antifreeze protection. Adequate purity can be maintained by including an ion exchange resin unit in the cooling subsystem.
Assignee	Ballard Power System Inc.	
Category	Material, Antifreeze	
Publication		***Title*** Summary
Patent Number	WO04053015A1	**COOLANT BASED ON AZOLE DERIVATIVES CONTAINING 1,3-PROPANEDIOL FOR FUEL CELL COOLING SYSTEMS** The invention relates to an anti-freeze concentrate for the cooling systems of fuel cell drives, from which ready-to-use
Assignee	BASF AKTIENGESELLSCHAFT	

Category	Material, Antifreeze	aqueous coolant compositions with a maximum conductivity of 50 ?S/cm can be produced, based on 1,3-propanediol or mixtures of 1,3-propanediol with alkylene glycols and/or derivatives thereof, comprising one or more five-membered heterocyclic compounds (azole derivatives) with two or three heteroatoms from the group nitrogen or sulphur which comprise no or a maximum of one sulphur atoms and which can have an aromatic or saturated six-membered annealed ring.

Comments: JP2004172049A2 assigned to Honda Motor Co LTD, proposes that the fuel cell product water can be made into antifreeze by supplying alcohol to an evaporator fitted halfway through a cathode air supply channel.

2.2.1.6. Removing Water from FC Stack at System Shut-Down

Much effort has also been given to techniques of reducing the amount of water that remains in the fuel cell system at shutdown. This is done in order to prevent system damage resulting from ice expansion during freezing, and to minimize the energy requirement to reheat the system from sub-freezing temperatures. The majority of the liquid water within the fuel cell stack can be removed at system shut down using gravity self-drain. Residual water within the stack can be removed by blowing dry air through the fuel cell stack. Water can be removed from the FC stack prior to powering off the system by air.

- Vacuum evaporation
- Air purging
- Discontinuing reactant humidification, and
- Fuel starvation.

Problems: After drying out the stack at shutdown, it becomes very important to quickly re-humidify the FC membranes during startup.

Related Examples:

Publication		***Title*** Summary
Patent Number	JP2004193102A2	**FUEL CELL OPERATING METHOD, AND FUEL CELL OPERATING DEVICE** PROBLEM TO BE SOLVED: To provide a fuel cell operating method capable of preventing freezing of a reaction gas passage, and minimizing energy necessary for drainage by draining water in a system only when it is necessary. SOLUTION: In the operating method for a fuel cell, gaseous hydrogen and air are supplied as reaction gases to each reaction gas passage, and power generation is carried out by electrochemical reaction. It is characterized by that water in the reaction gas passages are drained and operation of the fuel cell is stopped by cutting off electric power supply from the fuel cell, detecting an outside air temperature, and supplying the reaction gases to the reaction gas passages in response to the outside air temperature.
Assignee	Honda Motor Co LTD	
Category	System, Operation Method	

Publication		***Title*** Summary

Patent Number	JP2004111196A2	**OPERATION METHOD OF FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To provide an operating method for a fuel cell system which can prevent its being frozen after the stop of the operation and whose starting time is shortened. SOLUTION: When the fuel cell is stopped operating, a control device changes over three-way valves into bypass passages, and an output current smaller than in the normal operating condition is taken out of a fuel cell stack while a dried hydrogen and dried air are supplied to the fuel cell stack so as to purge the excessive water/moisture, and the fuel cell stack is prevented from drying of MEA (Membrane Electrode Assembly) with a minute quantity of produced water.
Assignee	Nissan Motor Co LTD	
Category	System, Operation Method	

Comments: US6358637 assigned to General Motors Cooperation suggests evaporating the water out of the fuel cell with a vacuum while it is still warm from use (before it is rendered inactive between uses). However, this method is not useful in fuel cells utilizing porous water transport plates, because there is too much water to be removed simply by slow evaporation into a vacuum stream. WO04017444A2 assigned to General Motors Corporation presents a freeze-start method that includes discontinuing reactant humidification before shutting down the fuel cell stack. The anode and cathode are purged with the dry reactants, and electrical current draw from the stack is regulated based on cell voltage measurements.

2.2.1.7 Rapid Heat-Up

Even if the fuel cell can start at sub-freezing temperatures, product water at cathode can freeze to block the gas passage. Rapid heat-up at start can raise the stack temperature above the freezing point of water and prevent such blockage from occurring. In addition, fluid and gas delivery systems must be heated, and humidifiers may require rapid heating to prevent damaging the membranes from dry operation. In order to thaw and start up a frozen PEM fuel cell system in such a rapid manner, high power heat must be supplied and distributed properly. In some, so-called “external heating” methods, heat is generated outside the stack and delivered into the stack and other components through a heat transfer medium. In other “internal heating” methods, heat is generated within the stack such as through use of reaction heat at the catalyst layers or combustion of hydrogen within the flow channels. We have categorized the proposed rapid heat-up methods by the heat sources used with each approach.

- Combustion Heat of Hydrogen
- Catalytic Reaction Heat
- Hot Air Blowing
- Embedded Electric Resistance Wire
- Waste Heat of Fuel Cell Stack

2.2.1.7. 1 Using Combustion Heat from Hydrogen/Air

Advantages of using combustion heat include the generation of a large amount of high-quality heat, relatively rapidly. Waste heat can be used to warm the passenger compartment.

Problems: Decrease in fuel economy and requirement for the hydrogen/air burners that add weight, volume, and cost to the fuel cell system.

Related Examples:

Publication		***Title*** Summary
Patent Number	JP2004111243A2	**WARM-UP SYSTEM OF FUEL CELL** PROBLEM TO BE SOLVED: To surely prevent condensed water from freezing as at the time of start-up below freezing point. SOLUTION: A fuel cell, a combustor combusting fuel gas and air, and a heat exchanger for heating cooling water circulated in the fuel cell by heat exchange with reaction heat of the combustor are provided. A partial vapor pressure in exhaust gas is calculated from a fuel volume, an air volume supplied to the combustor and exhaust gas pressure. When the partial vapor pressure calculated is higher than a saturated vapor pressure at a temperature of the fuel cell at that time and a fuel cell temperature is below freezing point, it is judged that there is a fear of the fuel cell freezing, and the exhaust gas from the combustor is exhausted without guiding it into the fuel cell. When there is no more fear of freezing, it is guided into the fuel cell.
Assignee	Nissan Motor Co LTD	
Category	System, Control	

Publication		***Title*** Summary
Patent Number	JP2004047210A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To shorten time until a fuel cell is ready to generate power, and reduce fuel and power consumption for melting ice in a water container. SOLUTION: The fuel cell comprises a cell part and a humidifying part, and it is provided with the water container storing water, water feeders feeding water in the water container to the humidifying part of a fuel cell interior, and a return passage returning water not used by the humidifying part to the water container. It is provided with a combustor burning hydrogen and oxygen not used by the cell part of the fuel cell interior, burned gas feeding means for feeding gas burned by the combustor instead of the water to the humidifying part of the fuel cell interior when the water in the water container is frozen in starting of the fuel cell.
Assignee	Nissan Motor Co LTD	
Category	System	

2.2.1.7.1 Using Catalytic Reaction Heat

EP1113516B1 assigned to General Motors Corporation suggests that instead of using the reactants for combustion heating in the flow pathways, the MEA may be locally heated at the anode and cathode by the exothermal catalytic reaction between H_2 and O_2. For this method, H_2 is introduced into the O_2-rich cathode feed stream and O_2 is introduced into the H_2-rich anode feed stream.

Problems: This method also adversely affects the fuel economy.

2.2.1.7.3 Hot Air Blowing

Hot air, typically greater than 90°C, is available relatively quickly as a result of the compression process in the system's air compressor. This hot air can help to warm all portions of the cathode.

Problems: Disadvantages include the fact that not much heating power is derived from air. However, the thermal mass of the membrane electrode assembly is very low.

Related Examples:

Publication		***Title*** Summary
Patent Number	US06815103	**Start control device for fuel cell system** At a time of starting a fuel cell when solenoids of control valves such as a check valve and a discharge valve are in a frozen state, hot air obtained by adiabatic compression at an air supply portion is divisionally supplied into a warm-up box through a warm-up valve. It is determined whether the discharge valve is opened by determining whether the discharge fuel gas pressure P_{out} is reduced below a predetermined pressure while the check valve is in an opened state. After confirming that the discharge valve has been opened, it is determined whether the check valve can be closed by determining whether the pressure near the fuel supply port of the fuel cell has risen above the predetermined pressure stored in the memory. The warm-up operation of the fuel cell can thereby be efficiently conducted and the fuel cell can be reliably started.
Assignee	Honda Giken Kogyo Kabushiki Kaisha	
Category	System, Control	

Comments: Prior to using the reactants for catalytic heating, EP1113516B1 assigned to General Motors Corporation suggests first supplying high temperature fuel gas to the anode catalyst and oxidant gas to the cathode catalyst at elevated flow rates relative to typical operation. These hot, dry reactant flows can be used to melt ice on the anode and cathode catalyst surfaces, which may otherwise block H_2 and O_2 access to the catalyst sites.

2.2.1.7.4 Using Waste Heat from Fuel Cell

Perhaps the simplest way to start a frozen fuel cell stack is to supply fuel and oxidant directly to the fuel cell while drawing electrical power from the stack across a resistive load (such as one of the vehicle's auxiliary loads). This is possible because the fuel cell has some electro-chemical activity as low as –30°C. This is also called boost-strapped. Due to freezing point depression in the nano-size pores, a portion of the water in the PEM and the ionomer within the catalyst layer does not freeze.

Problems: The product of the electrochemical reaction is water, which accumulates within the porous structure of the catalyst layer and the diffusion layer until the cell temperature is above freezing. Water/ice accumulation tends to block the porous structures that are required to supply reactants to the catalytic sites. Furthermore, this approach can take an unacceptably long period of time to reach operational temperature.

Related Examples:

Publication		***Title*** Summary
Patent Number	US6777115	**Battery-boosted, rapid startup of frozen fuel cell** A fuel cell stack has an auxiliary load in series with a battery, which can selectively

Assignee	UTC Fuel Cells, LLC	be connected across the fuel cell stack in place of a main load. A method includes connecting the battery and auxiliary load across the fuel cell stack while providing fuel to the anode flow field; in one embodiment, oxidant is provided to the cathode flow fields initially; in a second embodiment, oxidant is withheld from the cathode flow for a predetermined time or until a threshold voltage is reached.
Category	System, Battery-boosted Startup	

Comments: US6777115 assigned to UTC Fuel Cells is identical with WO04025752. According to the invention, additional current provided by the source (battery) initially forces the weak cells in the fuel cell stack to a negative cell voltage, thus producing heat as a consequence of polarizations within the cell. As the weak cells heat up, they quickly approach typical performance of good cells.

2.2.1.8. Components

New designs and fabrication techniques for system components (such as the water tank, humidification system and hydrogen pump) are suggested to address efficient thawing and preventing deformation, blockage and clogging.

Related Examples: JP2004150298A2, US6806632, JP2004192940A2, P2004139771A2

3. Concept Evaluation Analysis

Evaluation analysis was conducted for the proposed freeze prevention and rapid startup solutions. We developed Matlab-based analysis programs to calculate energy, power, and temperature-time performance for freeze protection and thaw methods. We analyzed the impacts of insulation, heating, water drainage, de-humidification, and heated reactant flow as they related to each of the proposed methods.

3.1. Analytical Investigation of Cool-Down Time

The first step in evaluating freeze management for a PEMFC is determining the time it takes the fuel cell to approach freezing once the system is turned off and parked in a sub-freezing environment. The temperature of an operating stack is maintained at its preferable operation temperature, approximately 80ºC, regardless of the environmental temperature. We refer to the time it takes the stack to drop from this operating temperature to a defined target temperature once the system is turned off as the "cool-down time." Assuming a constant ambient temperature, derivation of an analytical solution for a lumped stack transient thermal model results in the following equation:

$$t_{cd} = \frac{mc_p}{A}\left(\frac{1}{h} + \frac{l}{k}\right)\ln\left(\frac{T_o - T_a}{T_t - T_a}\right)$$ **Equation 1**

In this equation, cool-down-time t_{cd} is given as a function of the mass * heat capacity of the stack (mc_p), the heat transfer surface area (A), the heat transfer coefficient to ambient (h), the thermal conductivity of insulation around the stack (k), the insulation thickness (l), the stack normal operating temperature (T_o), the ambient temperature (T_a) and a target temperature (T_t).

Figure 2 presents the cool-down time of a stack as a function of insulation thickness at different ambient temperatures. The mass of the modeled stack was 160 *kg* with 10 *l* of water added. The heat transfer coefficient and surface area were assumed to be 10 $W/m^{2}\cdot K$ and 1.4 m^2, respectively. The selected initial and target temperatures of the stack were 80ºC and 5ºC, respectively. Thermal conductivity of the insulation material was chosen to be 0.036 $W/m\cdot K$, a typical value for a common insulation material such as glass-fiber. As the figure illustrates, insulation greatly affects the stack cool-down time, especially at mild ambient freezing temperatures. This implies that particularly for moderately cold climates, insulation could be used as a helpful supplementary means for cold start management of automotive PEMFC systems.

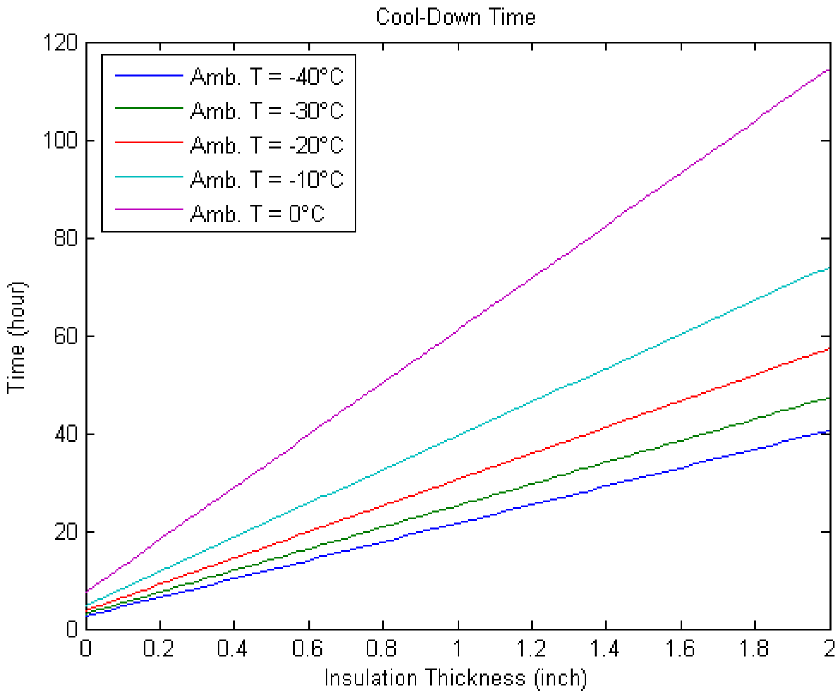


Figure 2. Cool-down time (from 80 to 5 ºC) as a function of insulation thickness at different ambient temperature conditions.

Patent US20050031914 suggested a method to increase cool-down time even further through bypassing the heat exchanger in order to raise the sensible heat of the stack prior to shutdown. The effect of this approach is shown in Figure 3 for the different insulation cases. The ambient temperature was assumed to be –20ºC. The figure shows that raising the initial stack temperature does provide a small increase in cool-down time (by roughly 13% for a temperature rise from 80 to 100ºC), and that the absolute magnitude of the impact increases with greater insulation thicknesses.

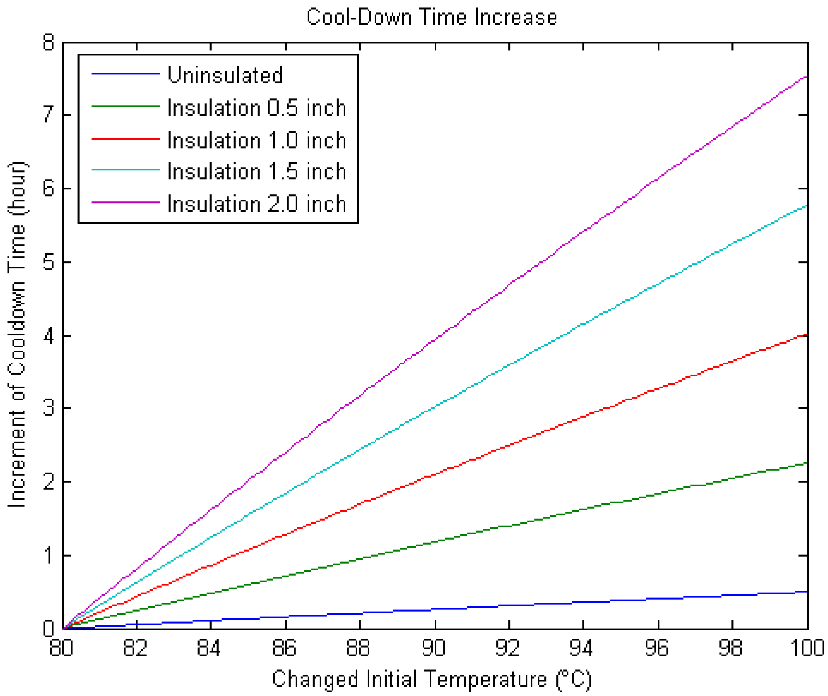


Figure 3. Time increments for Cool-down (from 80 to 5ºC) as a function of initial stack temperature for different insulation cases.

Figure 4 shows the actual variation of FC stack temperature with time when the vehicle is stored at –20ºC ambient temperature with different insulation thickness cases. As with Figure 2, this graph implies that the required fuel consumption for the Keep-Warm strategy could be remarkably reduced by incorporating insulation around the system. However, using insulation can also increase the system volume and weight, which will adversely impact vehicle performance, installed power requirements, and cost.

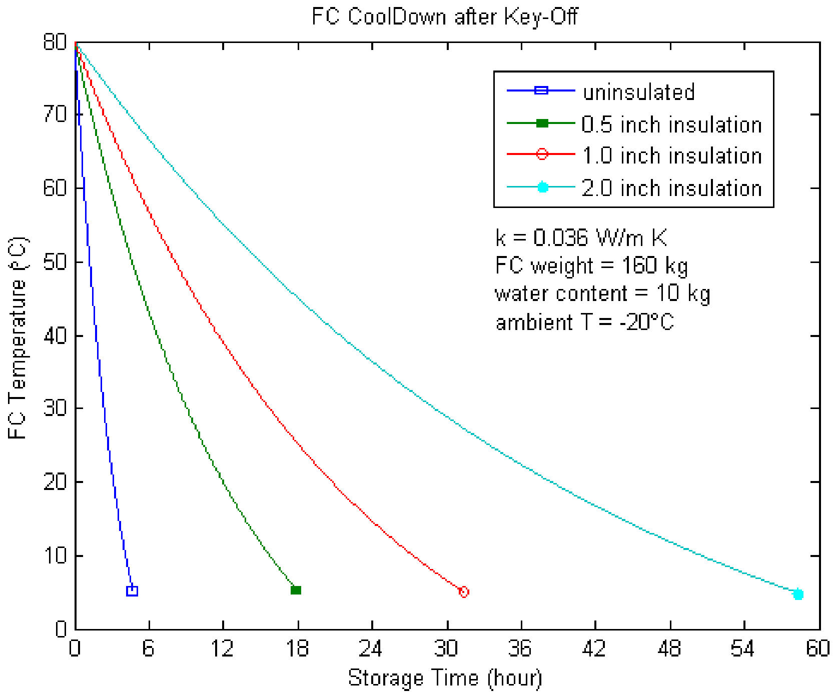


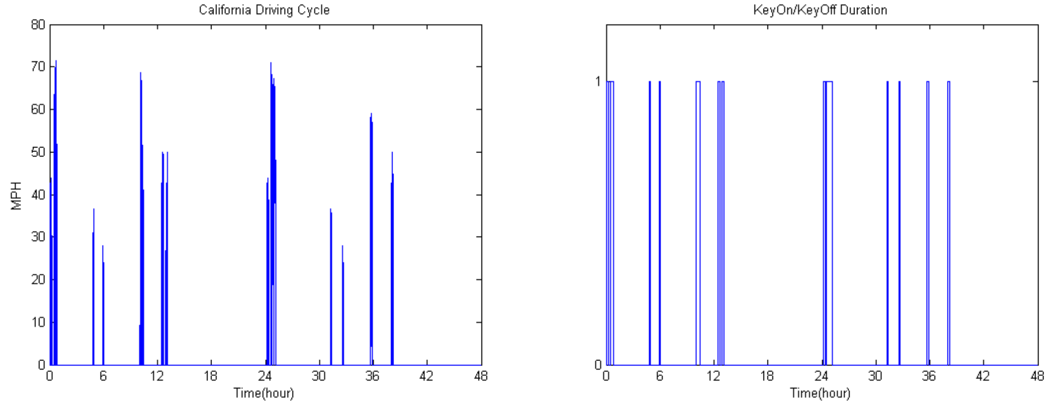
Figure 4. Stack temperature variation during FC cool-down after Key-Off

3.2. Effects of Typical Weather and Driving Patterns

Two more important inputs for making PEMFC system freeze management decisions are the actual ambient temperature variation and the expected operating pattern for the vehicle. Relative to a constant temperature during long-term parking analysis, these additional parameters lead to a more accurate portrayal of the freezing conditions a vehicle will likely experience. One key output from this improved analysis will be the number of expected freeze-thaw cycles, which is an important phenomenon to consider since repeated freezing is believed to deteriorate the stack structure and directly decrease fuel cell life.

The temperature variation for different locations used in this analysis was extracted from Typical Meteorological Year (TMY) weather data. To generate TMY data for a given station location, each “typical” calendar month is selected from actual data taken over a 30-year period from 1961-1990. The data is then smoothed at the start and end of each month in order to link the months into a “typical” year. Each TMY month is selected based on how well several meteorological measures represent typical observations over the 30-year period for that particular month [1].

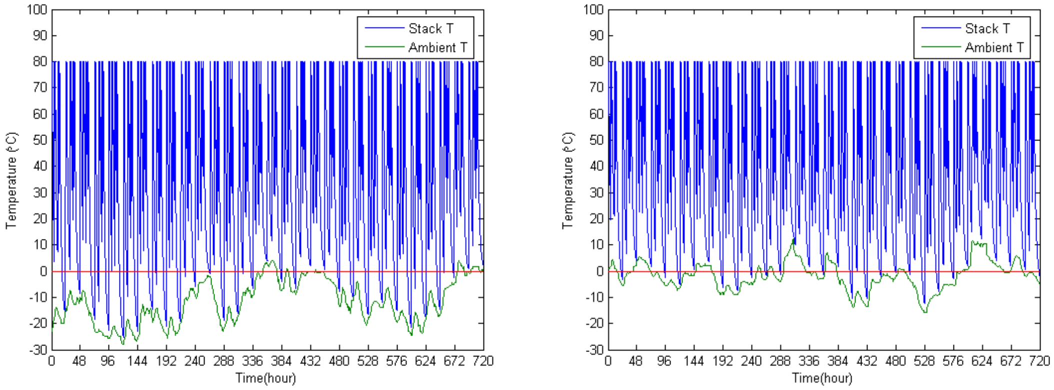
Figure 5 shows the key-on/key-off cycle for 2 days extracted from a California Driving Cycle. The FC system is operated 13 times for 2 days, and this cycle is repeated 15 times to simulate one month of operation. Figure 6 presents the temperature variations for a typical January in both Minneapolis and New York City (green line) and the resulting FC stack temperature (blue line) if the stack were to operate with the on/off duty cycle presented in Figure 5. During the system "on" operation periods the stack is assumed to go to 80ºC. The Januarys selected as "typical" for Minneapolis and New York City were from the years 1988 and 1976, respectively.



(a) California Driving Cycle

(b) Corresponding "On/off Cycle I."

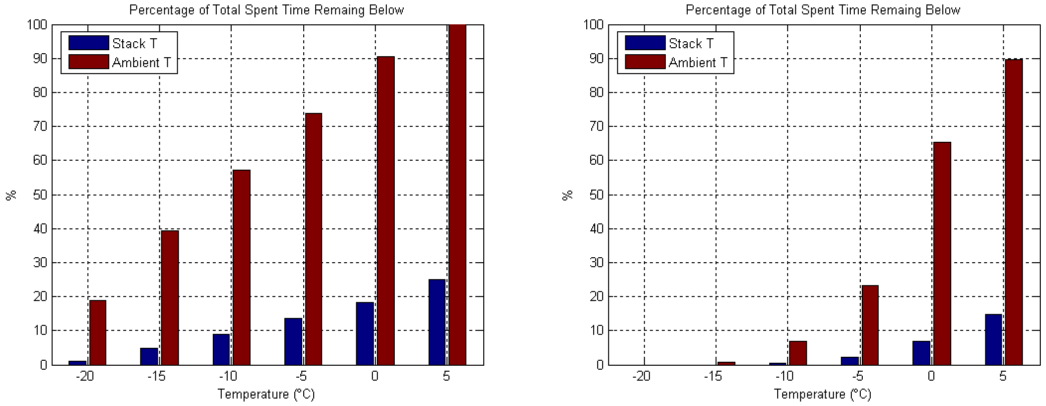
Figure 5. California Driving Cycle (a), and extracted key-on/key-off cycle.

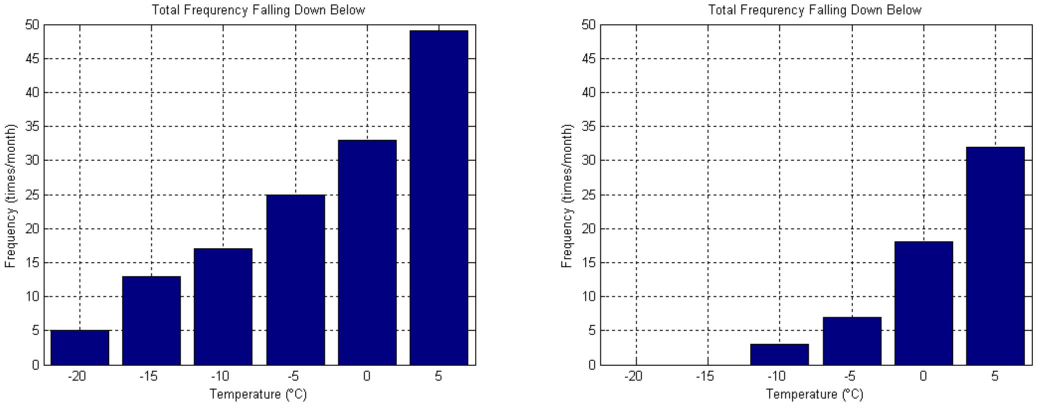


(a) Minneapolis, un-insulated

(b) NY, un-insulated

Figure 6. Temperature variation of FC stack operated with on/off cycle presented in Figure 5 for a typical January in (a) Minneapolis and (b) New York City.


(a) Minneapolis, % of time below given temps. **(b) NY, % of time below given temps.**


(c) Minneapolis, occurrence frequency go-below **(d) NY, occurrence frequency go-below**

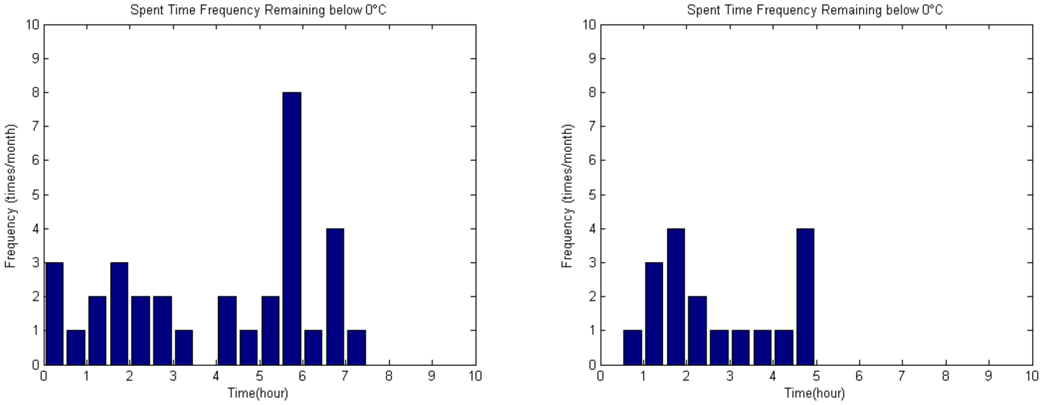
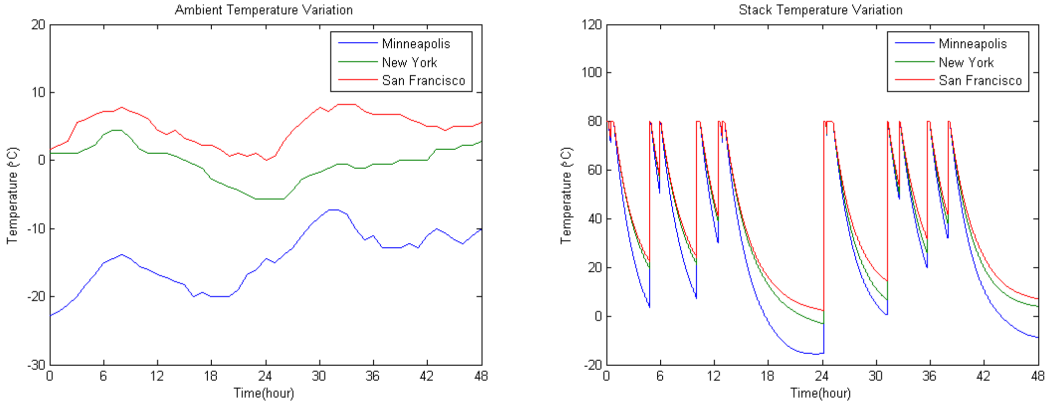
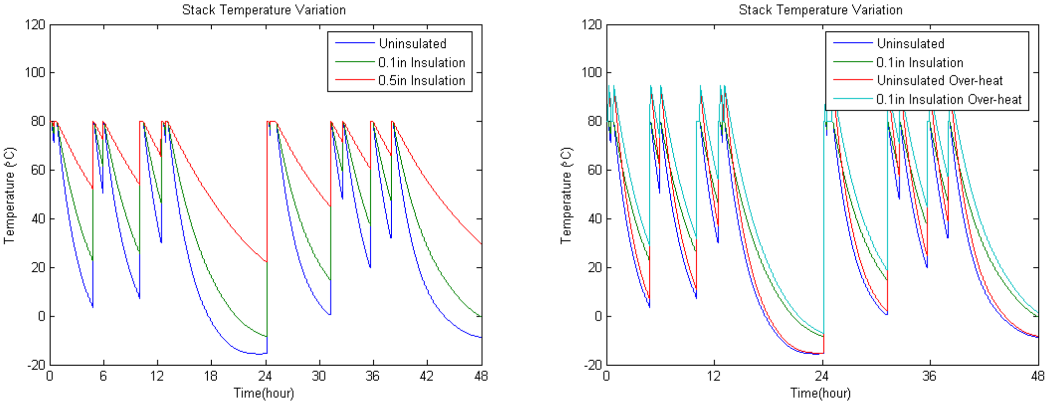

(e) Minneapolis, occurrence frequency lasting **(f) NY, occurrence frequency lasting**

Figure 7. Statistical information on the stack temperature variations evaluated from the simulation shown in Figure 6; Percentage of total spent time remaining below the given temperatures for a stack and ambient temperature in typical January of (a) Minneapolis and (b) New York, Occurrence frequency of stack temperature going down below the given temperatures in typical January of (c) Minneapolis and (d) New York, Occurrence frequency of stack temperature remaining for a certain period of time below 0^{o}C in typical January of (e) Minneapolis and (f) New York.

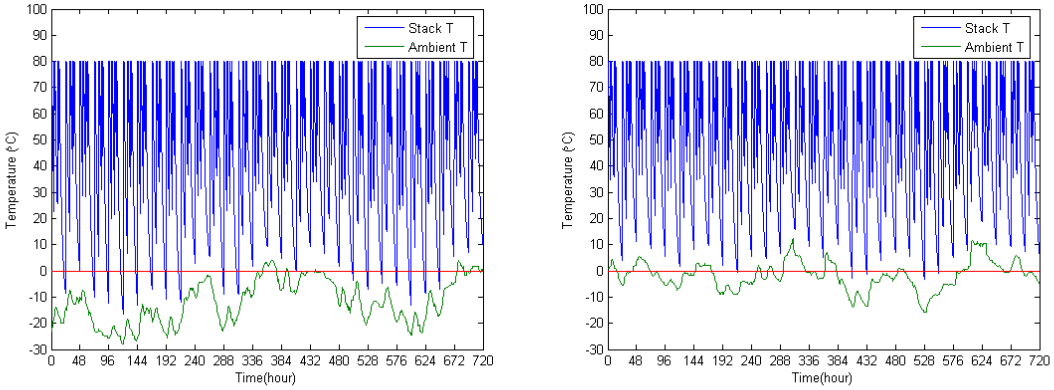

(a) Ambient Temperature

(b) Ambient temperature effects

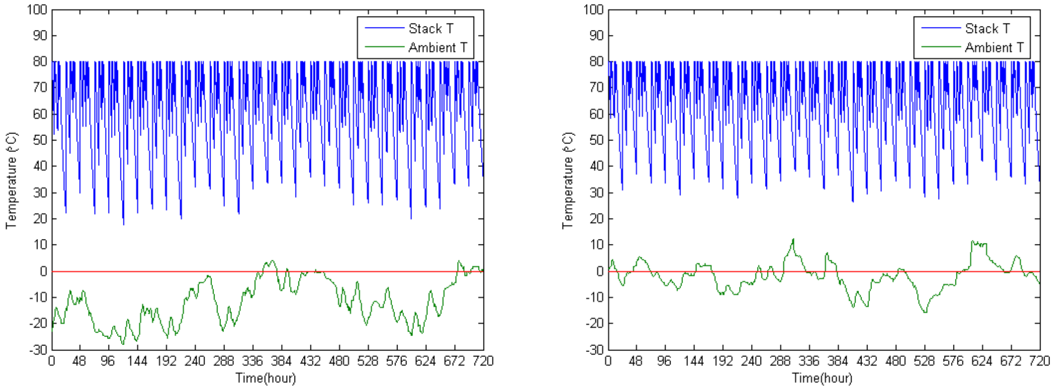

(c) Minneapolis, insulation impact

(d) Minneapolis, over-heat impact

Figure 8. Comparison of stack temperature variations for the first two days of simulation; (a) two-day ambient temperature variations used for the simulations (in Minneapolis, New York and San Francisco); (b) Comparison of stack temperature variation for the different cities. Impact in Minneapolis of (c) insulation and (d) stack over-heat at shutdown on the stack temperature variation.


(a) Minneapolis, 0.1 inch insulation

(b) NY, 0.1 inch insulation


(c) Minneapolis, 0.5 inch insulation

(d) NY, 0.5 inch insulation

Figure 9. Temperature variation of FC stack operated with on/off cycle presented at Figure 5 during a typical January in Minneapolis for (a) 0.1 inch insulation case, and (c) 0.5 inch insulation case. The same cases are given in (b) and (d), respectively, for a typical January in New York City.

Figure 7 presents statistical information on the stack temperature variations evaluated from the simulation shown in Figure 6. These statistics are highly dependent on the key-on/key-off cycle and ambient temperature variation. Figure 7 (a) & (b) indicate how much time the stack spends below given temperatures in a typical January for Minneapolis and New York. Statistics are provided both for the stack and for the ambient temperature. According to figure, the stack operated with the duty cycle extracted from the California Drive Cycle ("On/off cycle I.") spends about 18% of the total time (corresponding to 4 hours and 20 minutes a day) below 0ºC in typical Minneapolis January. In New York, the percentage is about 7% (corresponding to 1 hour and 40 minutes a day). Since the repeated phase change of water in the stack is believed to degrade fuel cell performance, the frequency of occurrences when the stack drops below freezing is also important. Figure 7 (c) & (d) show that the stack temperature goes down below 0ºC 33 times in a typical January for Minneapolis and 18 times for New York. Figure 7 (e) & (f) presents another kind of occurrence frequency graph showing how long and how frequently freezing conditions occur in Minneapolis and New York, respectively. For example, most frequent duration of stack freezing in Minneapolis is 5.5-6 hours.

Potential cold start strategies and methods, as well as the on/off operating cycle and ambient temperature variation can greatly affect the stack temperature behavior. In order to better observe the stack temperature effects, a zoomed-in view of the first two days of the simulation are shown in Figure 8. On/off cycle I was used for these comparisons. Figure 8(a) shows the two-day ambient temperature variation in different cities (Minneapolis, New York and San Francisco). The corresponding stack temperature variations are compared at Figure 8(b) to show the impact of the location in the country. Figure 8(c) & (d) show insulation effects and stack overheat effects on the stack temperature variation in Minneapolis, the coldest city among those selected. As indicated in the graph, insulation makes a big difference in the stack temperature profiles. The stack never drops below freezing with 0.5 inch insulation in Minneapolis (if it is operated with on/off cycle I). As indicated in the previous section, the overheat method does not have nearly as large an impact on increasing cool-down time. The impact of insulation on stack temperature variation is clearly seen at Figure 9 for the FC operated by the on/off cycle I. Figure shows that integrating only 0.1-inch insulation can address the most freezing cases in New York City which could occur if the insulation is not incorporated. If a stack is insulated with 0.5 inch thickness, the temperature of the stack operated with on/off cycle I would stay high enough and never be cooled-down near freezing temperature in both cities tested.

Figure 10 shows another FC operation scenario ("on/off cycle II") to be used for the examining the effects of the on/off duty cycle on stack temperature. In on/off cycle II, the FC is turned on every other day for 15 minutes. This type of duty cycle can represent either the operating pattern for a relatively seldom-used vehicle, or a control strategy for preventing deep freeze of the FC system. Several patents suggested this technique of periodic FC turn-on during storage in a sub-freezing environment in order to provide heating power directly or to recharge the system's energy storage devices.

Figure 11 presents the stack temperature variation for operation with on/off cycle II during a typical January in Minneapolis and New York with ((a) & (b)) no insulation, ((c) & (d)) 0.5 inch of insulation, and ((e) & (f)) 1.0 inch of insulation. In the un-insulated cases, the stack temperature follows the ambient temperature most of the time. However, integration of insulation results in a significant reduction in the number of times the stack freezes, and in the amount of time it remains at a subfreezing temperature. As shown in Figure 11 (f), a system operated every other day during a typical January in New York will never freeze if it uses 1.0 inch of insulation (even without application of additional heating). This impact can also be seen in Figure 12, which presents the influence of insulation on the percentage of time the stack (relative to the displayed ambient temperature statistics) remains below given thresholds during a typical January in Minneapolis and New York.

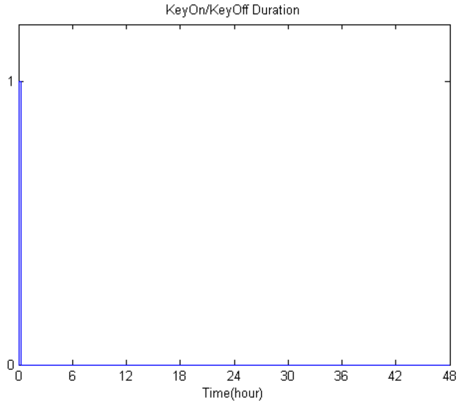
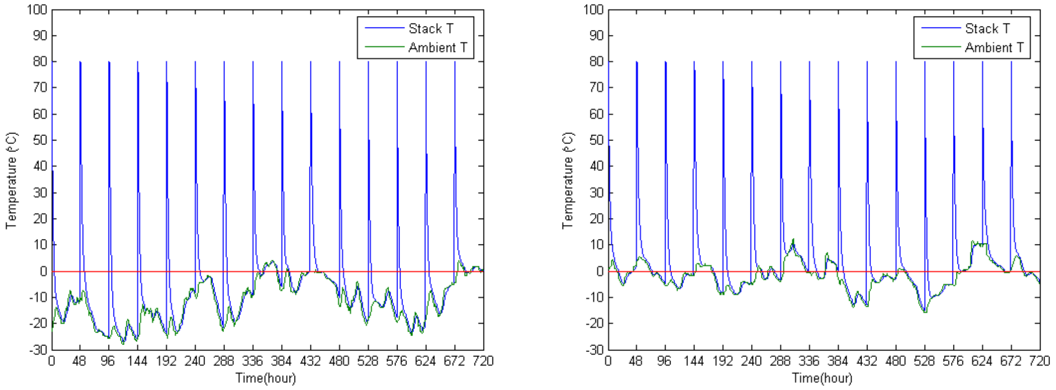
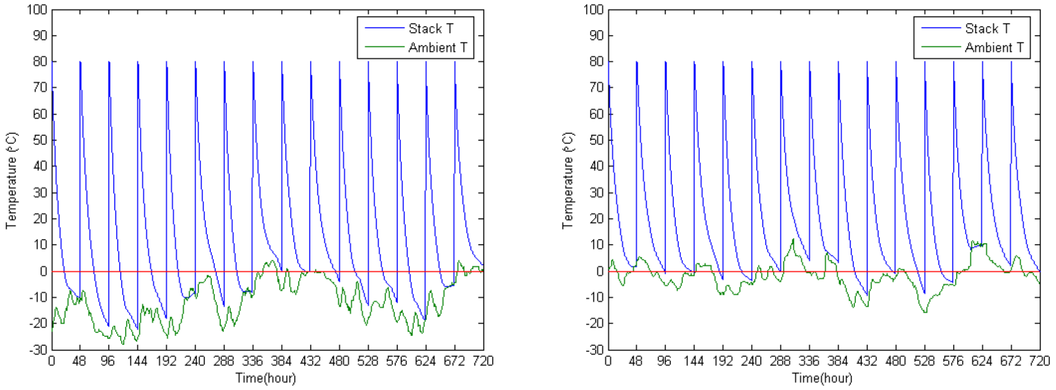


Figure 10. Key-on/key-off cycle for repeated two-day parking: "On/off cycle II."


(a) Minneapolis, un-insulated **(b) NY, un-insulated**


(c) Minneapolis, 0.5 inch insulation **(d) NY, 0.5 inch insulation**

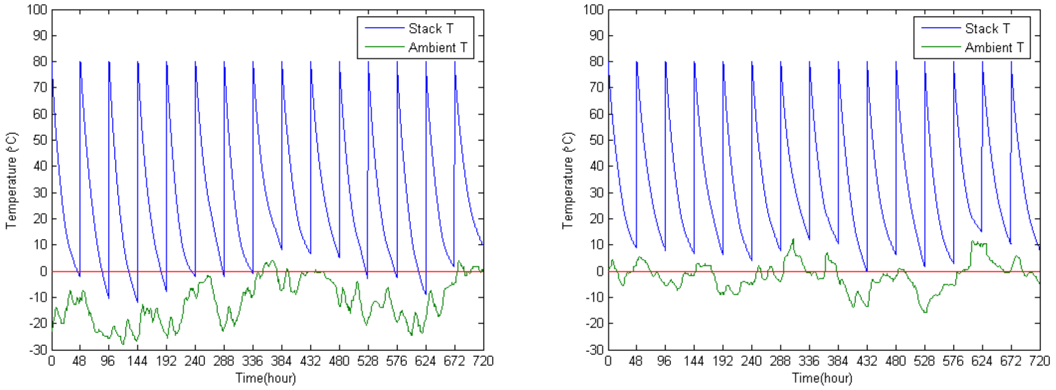
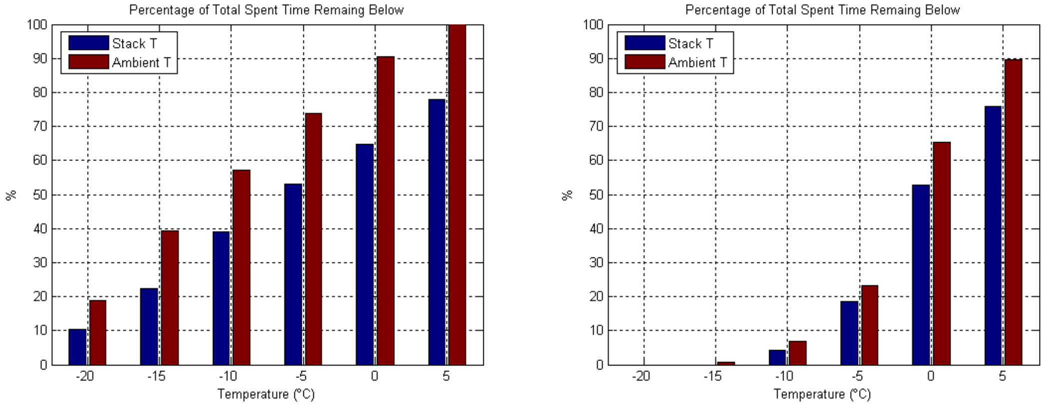
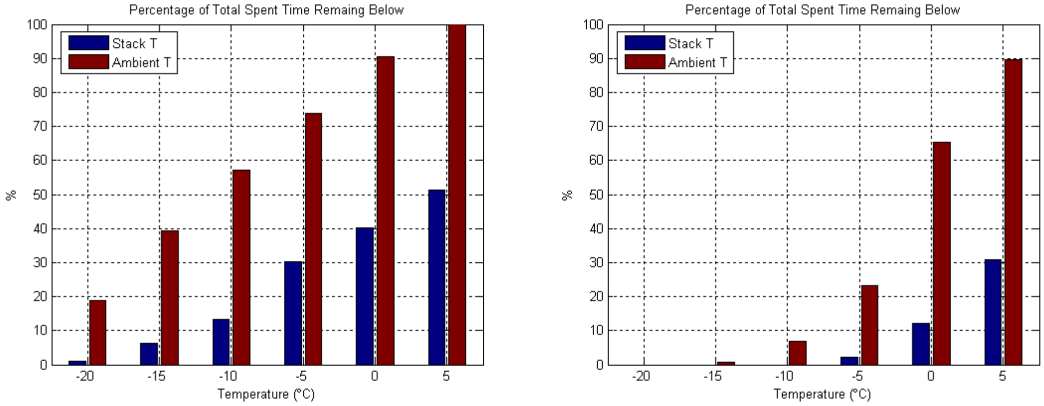

(e) Minneapolis, 1.0 inch insulation **(f) NY, 1.0 inch insulation**

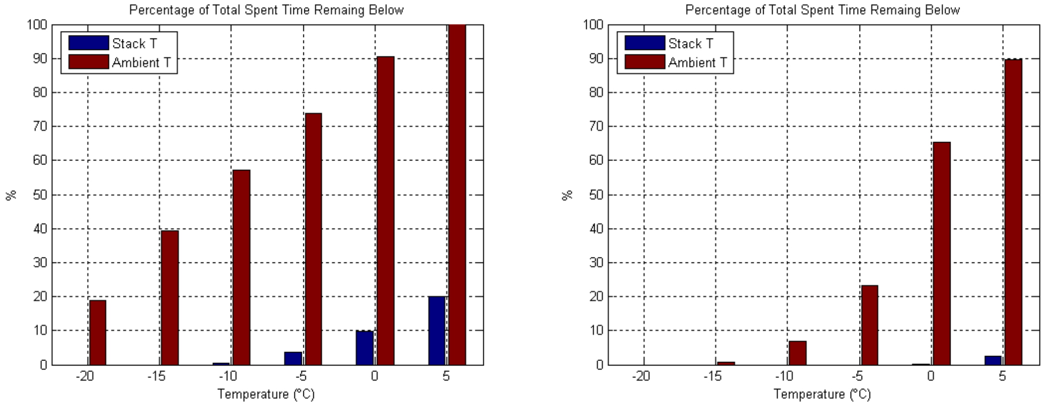
Figure 11. Temperature variation of FC stack operated with on/off cycle presented at Figure 10 during a typical January in Minneapolis for (a) un-insulated stack case, (c) 0.5 inch insulation case, and (e) 1.0 inch insulation case. The same cases are given in (b), (d) and (f), respectively, for a typical January in New York City.


(a) Minneapolis, un-insulated

(b) NY, un-insulated


(c) Minneapolis, 0.5 inch insulation

(d) NY, 0.5 inch insulation


(e) Minneapolis, 1.0 inch insulation

(f) NY, 1.0 inch insulation

Figure 12. Statistical information on the stack temperature variations evaluated from the simulation shown in Figure 11: Percentage of total time the stack and ambient temperature remain below given thresholds during a typical January in Minneapolis for (a) un-insulated stack case, and (c) 0.5 inch insulation case, and (e) 1.0 inch insulation case. The same cases are given in (b), (d) and (f), respectively, for a typical January in New York City.

3.3. National Analysis of -20 ºC Cold-Soak Condition

Having examined the typical winter weather behavior in a few cities, we next expanded the analysis to examine historic temperature observations on a national level. The objective of the analysis was to examine the frequency of occurrence for the -20ºC cold-soak condition in locations across the United States. The results can help evaluate if a more stringent cold-soak condition would be appropriate (automakers have recently suggested that a -40ºC cold-soak should be the requirement), or if a more relaxed cold-soak requirement would be appropriate for PEMFC vehicles during the transition period leading up to mass market introduction. In order to develop an effective systems-level approach to the freeze-start issue it is important to understand the actual temperature conditions the vehicle will experience.

The database used for the analysis included roughly 230 weather stations that collected hourly temperature data over the same time period as the TMY analysis from the previous section. However, because of problems with the data archive for a few of the stations during 1989 and 1990, the time period used for this analysis was shortened to 28

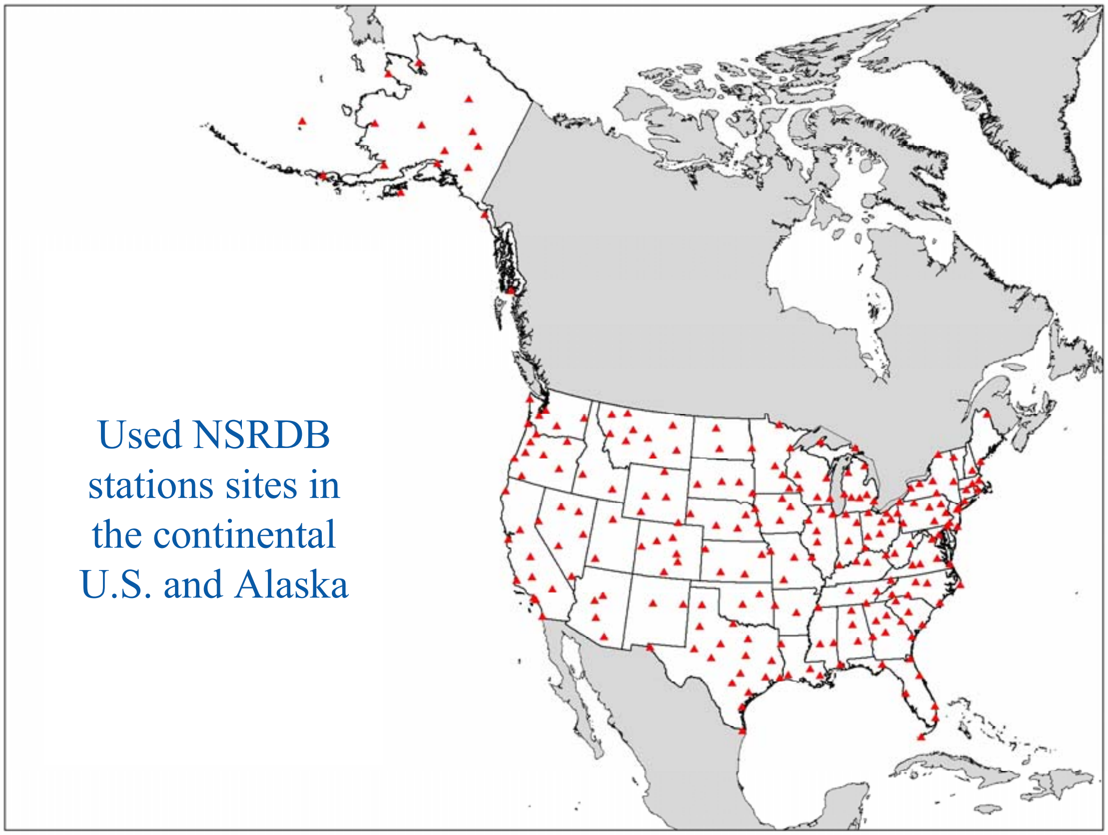


Figure 13. Weather stations used for -20 ºC cold-soak investigation years (1961-1988)

Figure 13 shows the spatial distribution of the stations used, which were all located in the continental U.S. and Alaska. The analysis criteria examined for each station was the number of consecutive hours that the station recorded temperatures at or below -20 ºC.

To give a context for the time period required for cold-soak, we refer back to the analysis of Figure 4, which showed the stack temperature profile over time for different insulation thicknesses. In Figure 14 we extend the temperature profiles to indicate the time required for the stack to equalize with the assumed constant ambient temperature of -20ºC. Note that this extended profile neglects the additional time contribution for the phase change of any water contained in the stack (which could be significant). However, caveats to keep in mind for the weather data comparison include that the ambient temperature could be colder during the "consecutive hours at or below -20ºC" period, and that the ambient temperature may still be below freezing before and after the consecutive hours period. Depending on these actual temperatures and when the fuel cell system is turned off relative to the consecutive hours time period, the time to achieve cold-soak could be reduced.

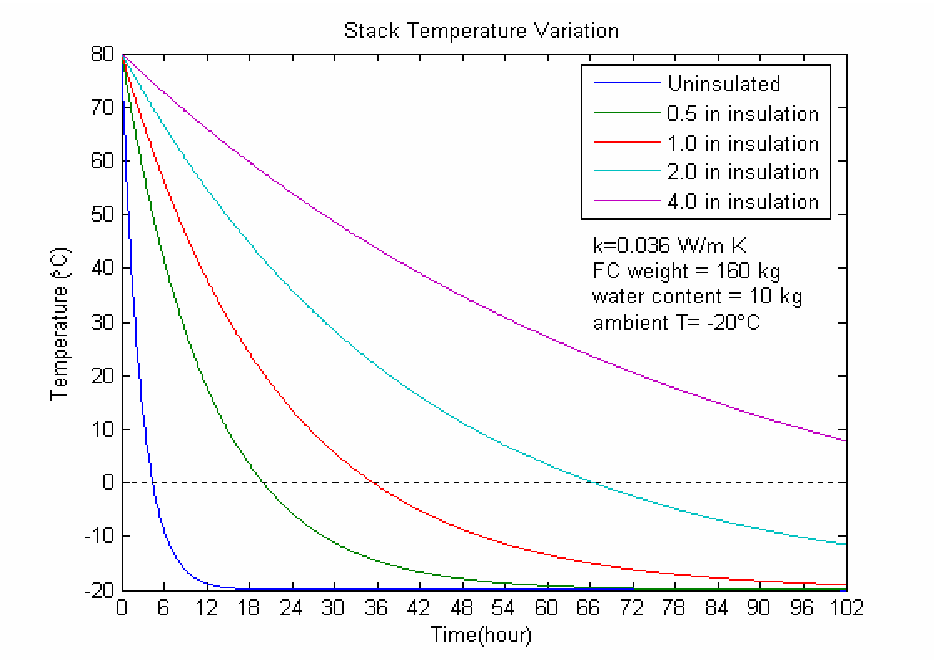


Figure 14. Temperature profiles for stacks with various insulation thicknesses to equilibrate with -20ºC ambient temperature (neglects additional time required for water content phase change at ~0ºC).

The first step for the national weather stations analysis was to establish a worst-case for the longest consecutive time period that each station recorded temperatures at or below -20ºC over the entire 28-year period of record. Figure 15 presents an interpolation of the maximum consecutive hours results recorded at each station during some time between 1961 and 1988. The figure shows most northern, inland parts of the country experiencing temperatures at or below -20 ºC for 24 or more consecutive hours at least once during the 28-year period. Far northern inland states and much of Alaska experience quite long extreme periods at or below -20 ºC.

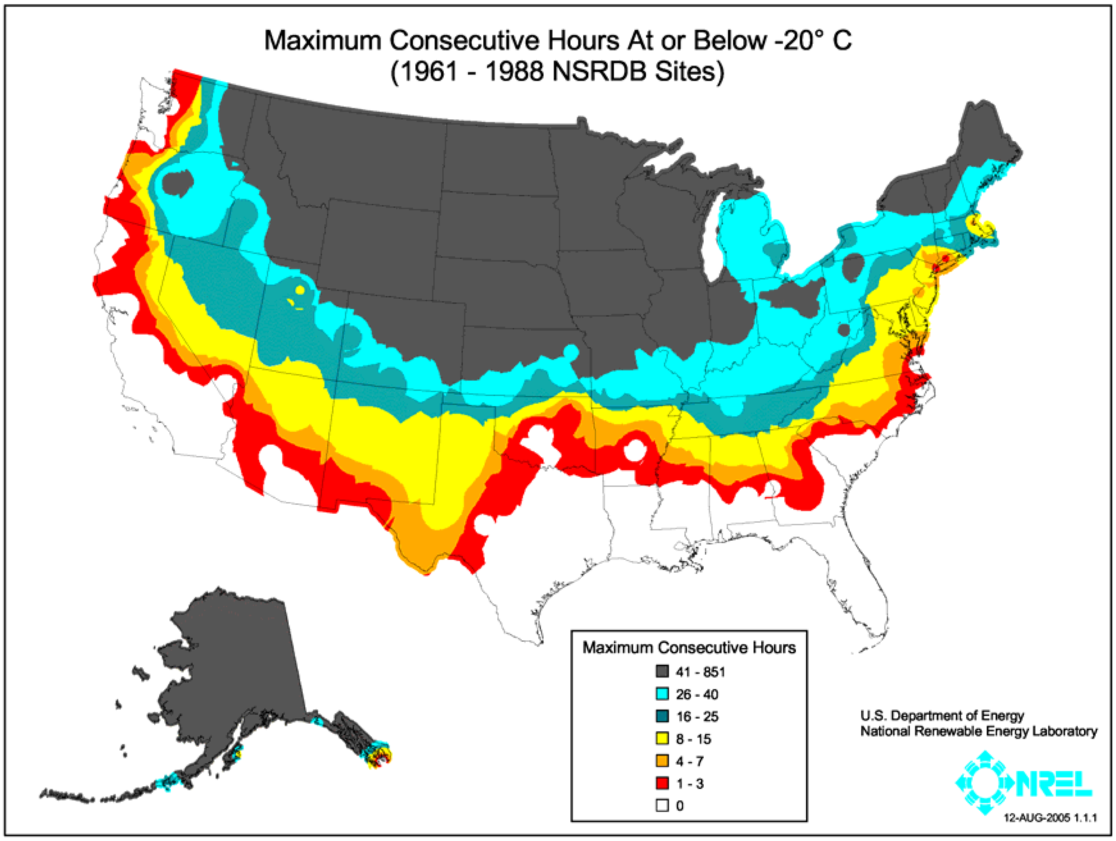


Figure 15. Worst case consecutive number of hours at or below -20 ºC for each location over the 28-year data record.

Having identified the extreme cold-soak time periods, the next step was to examine the frequency of occurrence for different cold-soak scenarios. Figure 16 provides an interpolation based on the number of occurrences over the 28-year period that each station observed an hourly temperature measurement at or below -20ºC. Once again, the total distribution of occurrences seems quite extensive. However, with reference to the profiles in Figure 14, the stack temperature will remain relatively high after just one hour parked in an ambient -20ºC temperature. Figure 17 (a) presents a more useful number of occurrences distribution for a longer time period of 15 consecutive hours at or below -20ºC. Next to this image, Figure 17 (b) highlights the location on the reference stack temperature profile from Figure 14 after 15 hours parked at -20ºC. A similar pair of figures is presented in Figure 17 (c) & (d), (e) & (f), (g) & (h), and (i) & (j) for 25, 40, 72, and 96 consecutive hours, respectively.

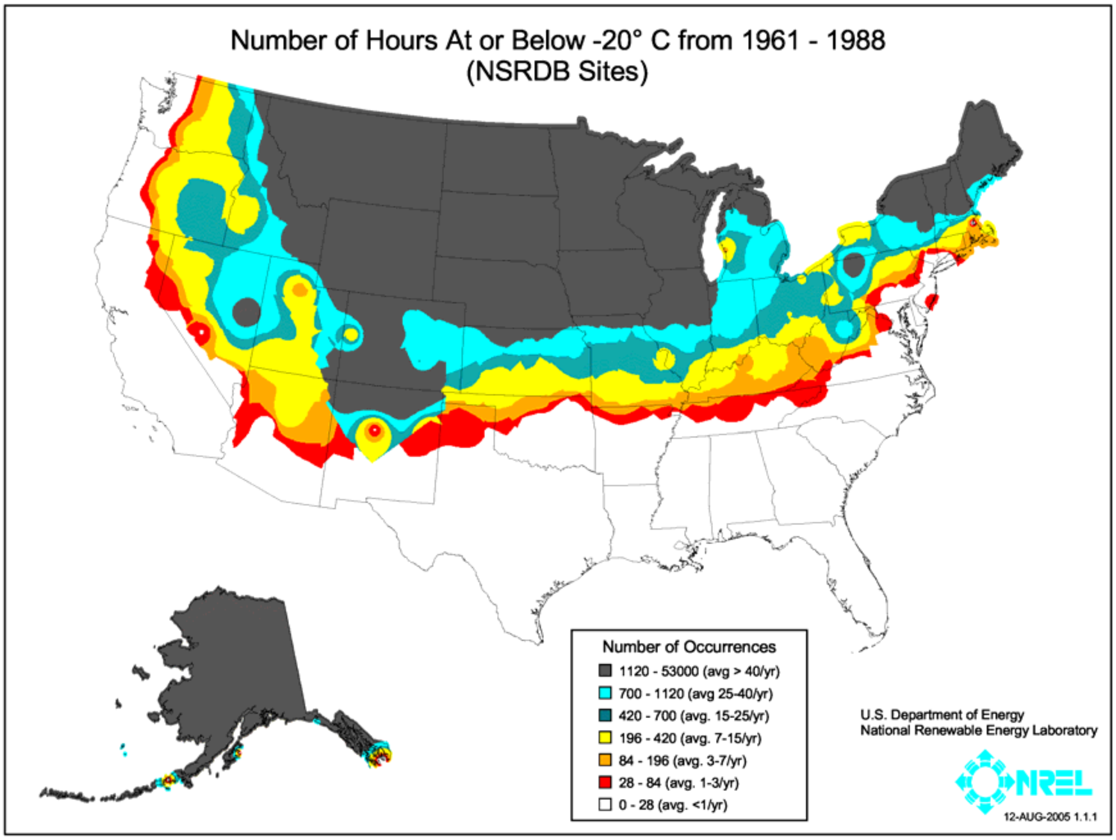
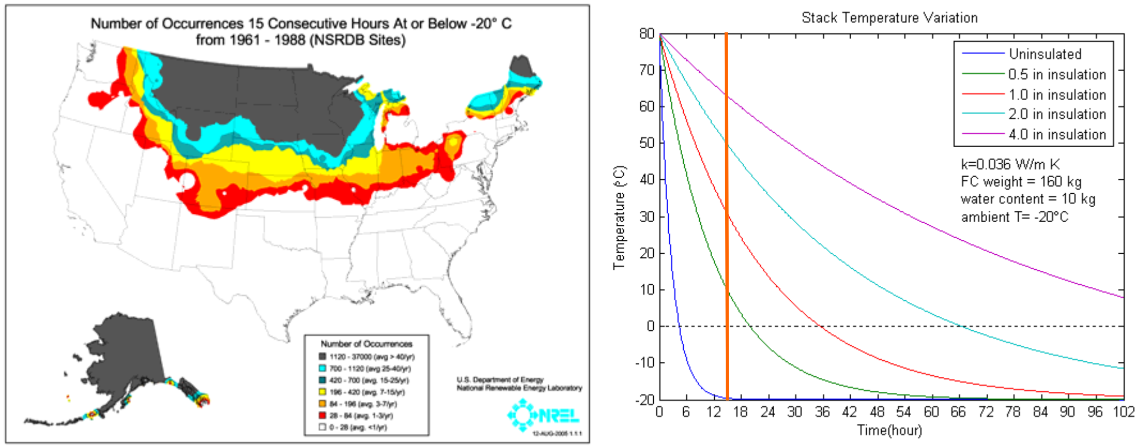
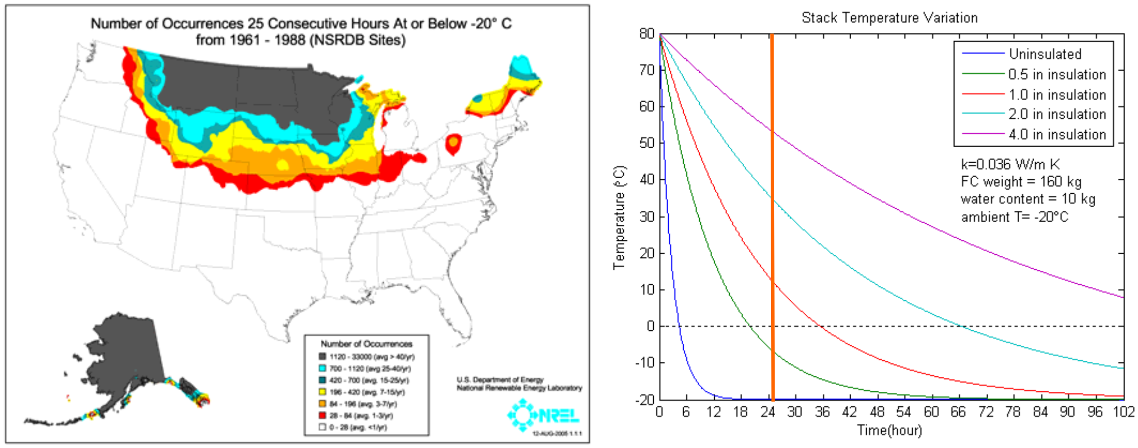


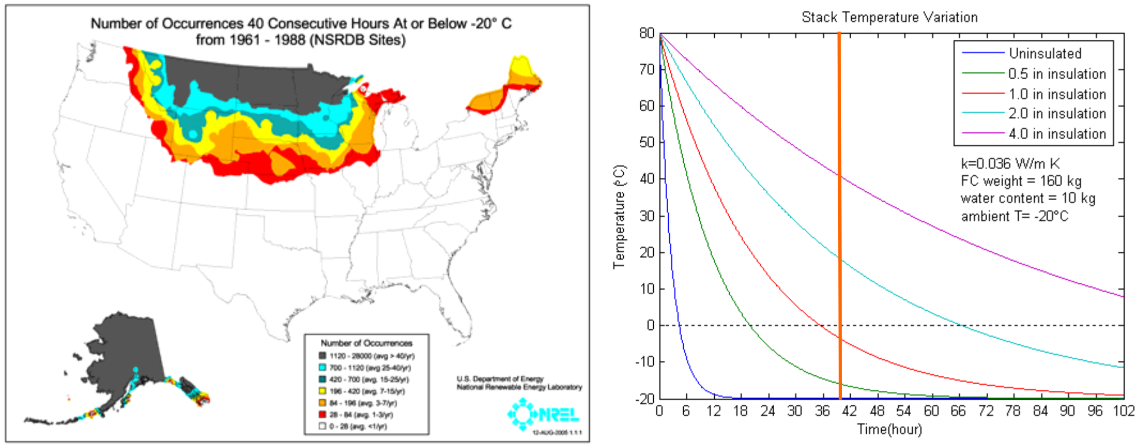
Figure 16. Total number of Concurrences (hours and Average #/ year) that Ambient Temperature Fall below –20°C



(a) Frequency of occurrence 15 consecutive hours **(b) Reference temp. profile at 15 hours**

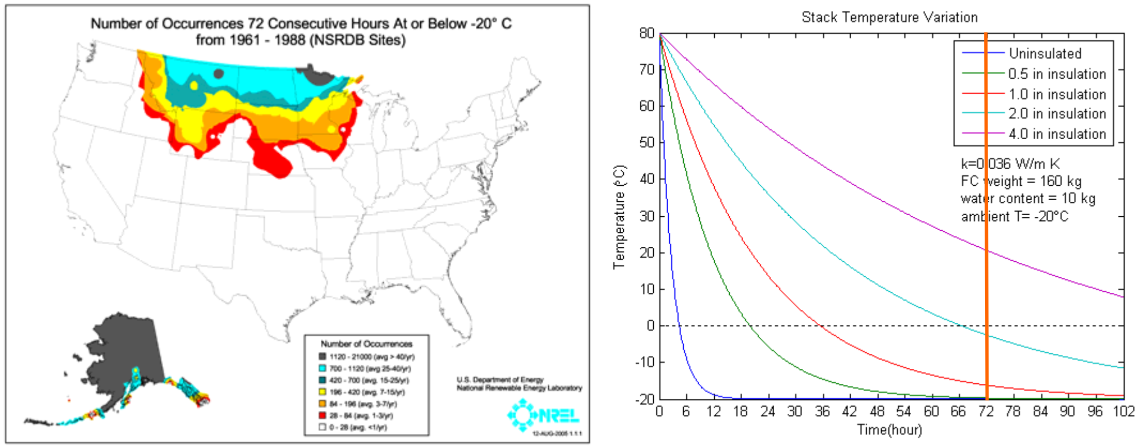


(c) Frequency of occurrence 25 consecutive hours **(d) Reference temp. profile at 25 hours**

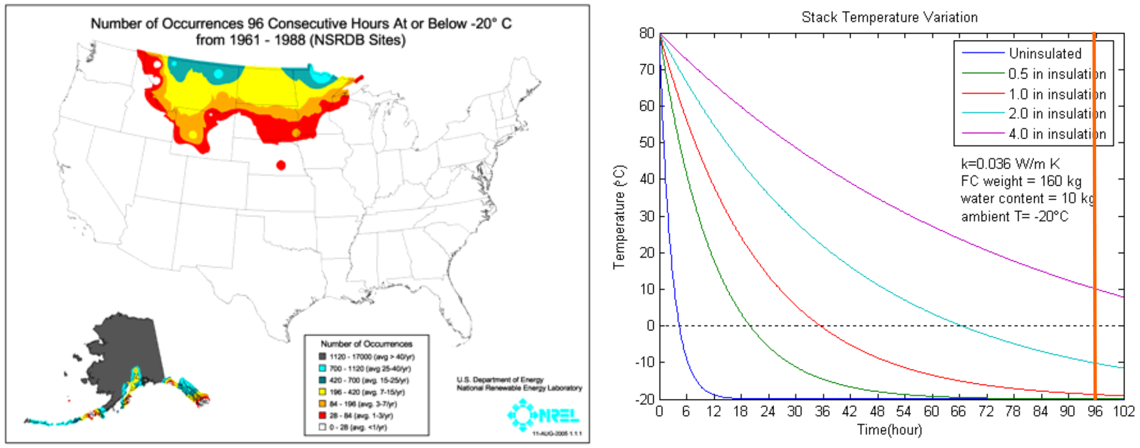


(e) Frequency of occurrence 40 consecutive hours **(f) Reference temp. profile at 40 hours**

Figure 17. Diminishing frequency of occurrence for longer cold-soak periods; shown next to highlight of hours duration on reference stack temperature profile figure.



(g) Frequency of occurrence 72 consecutive hours **(h) Reference temp. profile at 72 hours**



(i) Frequency of occurrence 96 consecutive hours **(j) Reference temp. profile at 96 hours**

Figure 17 -Continued. Diminishing frequency of occurrence for longer cold-soak periods; shown next to highlight of hours duration on reference stack temperature profile figure.

While considering the results presented in Figure 17, keep in mind that different PEMFC system configurations will result in different cool-down times, and that a vehicle parked long enough will eventually equalize with the surrounding ambient temperature. The map results also reflect the average number of freeze events for a given year, but some years will be warmer and some will be colder than the average. Nevertheless, the analysis reveals that a technique of slowing a FC system's temperature drop in a cold ambient environment may be one effective component of a system-level freeze management strategy. The analysis further shows that only a relatively small portion of populated parts of the country experience very many extended periods below -20ºC in a given year (as shown in US population density map in Appendix C). The data analysis may easily be repeated in order to investigate the extent to which different cold-soak threshold temperatures apply in different parts of the country. This analysis may be used to indicate parts of the country where less extensive freeze start strategies would be acceptable for initial market introductions. It could also be used to determine how frequently an extreme freeze start strategy may be required in other parts of the country. System developers can more effectively make trade-off decisions related to efficiency, cost, etc if they understand exactly how frequently or infrequently a particular strategy may be called upon.

3.4. Power and Energy Requirements for Potential Freeze Strategies

Having to this point analyzed FC system response to cold ambient temperatures, potential FC vehicle use patterns and actual temperature variation in different parts of the country, we next examine the effect of these variables on the power and energy requirements for the various freeze management strategies identified in the Technology Assortment section of this report. We begin by evaluating the requirements for the keep-warm strategy. Figure 18 shows the heat loss rate as a function of insulation thickness, when the system remains at 5°C for a given ambient temperature. The analysis does not consider the radiative heat transfer. The graph indicates that the required power/energy for keeping warm the stack could be greatly saved with installing insulation around it.

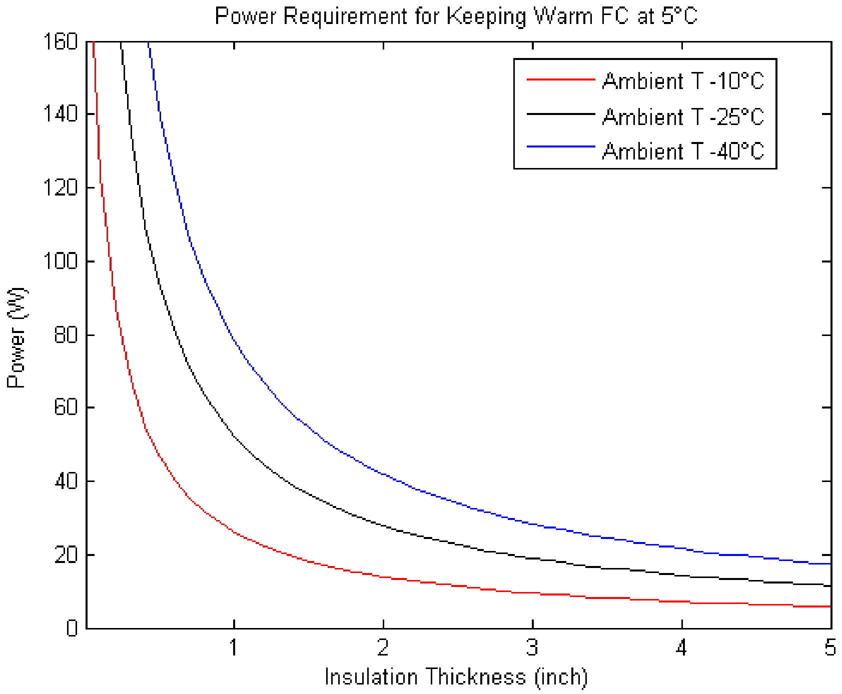
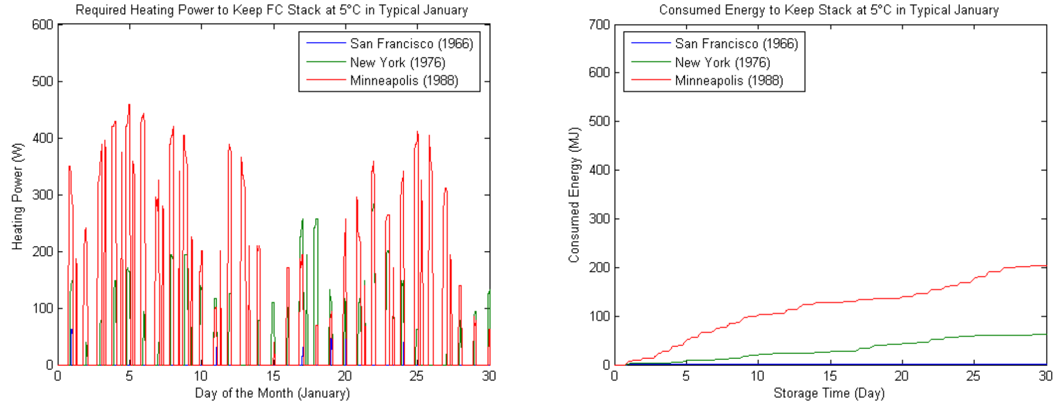


Figure 18. Power Requirement for Maintaining System Temperature at 5°C

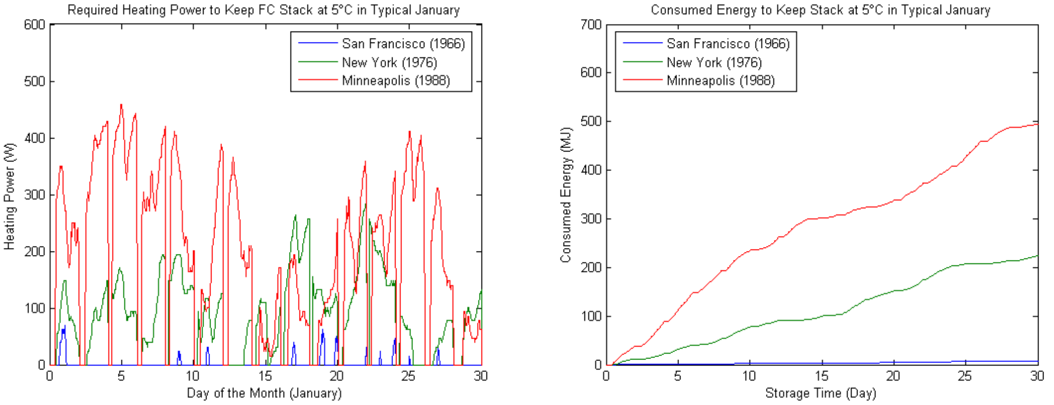
Power for heating and required energy for using keep-warm strategy are highly dependent on ambient temperature variation and on/off cycle of FC operation. FC on/off cycle impact on heating power and cumulative consumed energy for keeping warm FC system is presented in Figure 19. Comparisons are made for the un-insulated FC system operated in different cities using TMY weather data. Figures indicate that the maximum power requirement for keeping warm the un-insulated system is about 470 *W* in Minneapolis and about 270 *W* in New York regardless of the FC on/off operation cycle. However, total cumulative energy consumption is affected directly by the on/off cycle with which the FC is operated. On/off cycle III indicated at Figure 19 (e),(f) is for one-month-long vehicle storage without operation.

On the other hand, Figure 20 presents the impact of insulation on heating power requirement and cumulative consumed energy for keeping warm FC system for the fixed operating scenario, on/off cycle II. Both the power and the energy requirement for system heating can be greatly reduced by adopting insulation into the system. Insulation acts in two other ways for this power/energy requirement reduction. Increasing cool-down time decreases required heating time. In addition, adding insulation cuts down the power for heating by reducing the rate of heat loss to ambient.



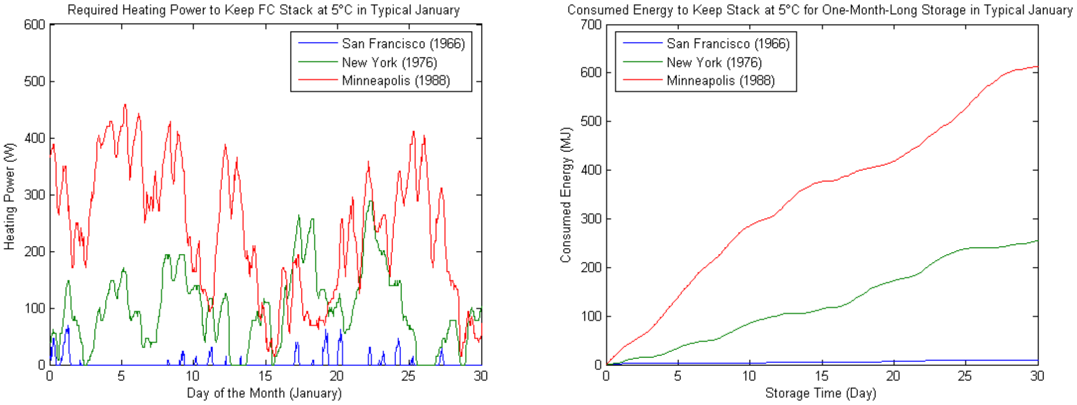
(a) Heating Power, on/off cycle I

(b) Energy Consumption, on/off cycle I



(c) Heating Power, on/off cycle II

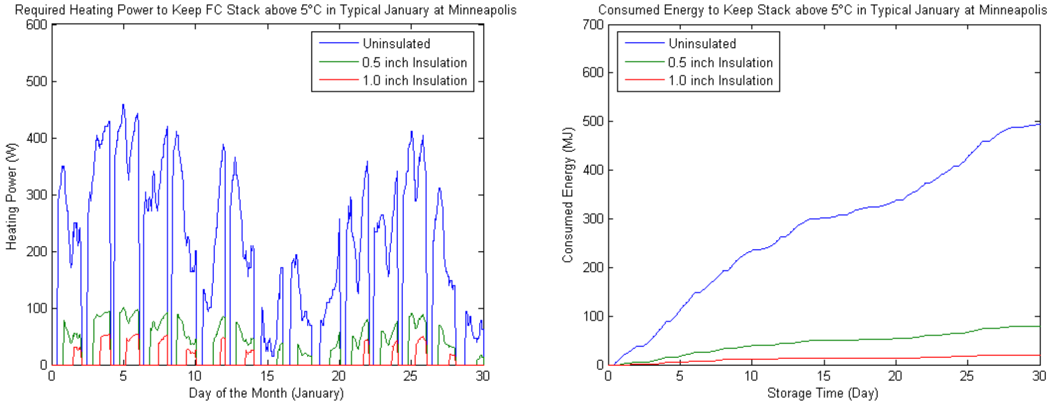
(d) Energy Consumption, on/off cycle II



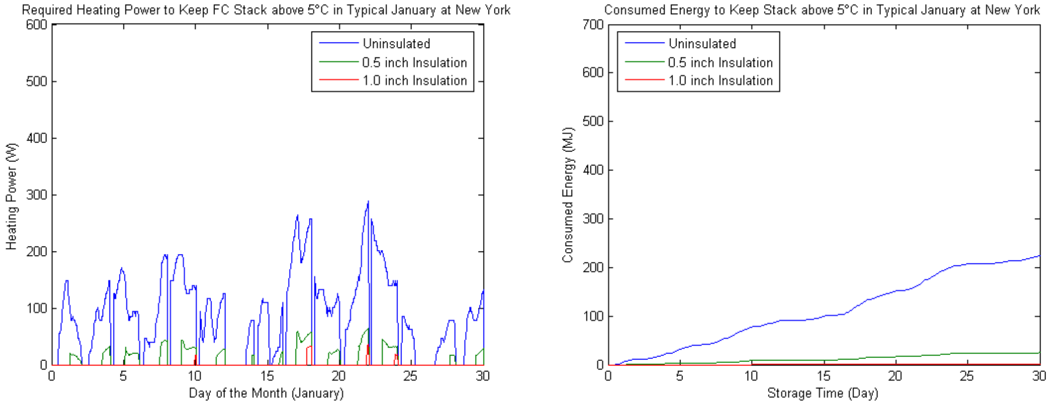
(e) Heating Power, on/off cycle III

(f) Energy Consumption, on/off cycle III

Figure 19. FC on/off cycle impact on heating power and consumed energy for keeping warm FC system. Comparisons are made for the un-insulated FC operated in different cities.



(a) Heating Power, Minneapolis **(b) Energy Consumption, Minneapolis**



(a) Heating Power, NY **(b) Energy Consumption, NY**

Figure 20. Insulation impact on heating power and consumed energy for keeping warm FC system. Comparisons are made for the differently insulated FC operated in Minneapolis and New York.

Figure 21 provides a required energy comparison between the Keep-Warm method using one-inch of insulation and the Thaw at Start method using no insulation (which assumes the system is started from the given cold-soaked temperature). The calculations for each method apply only to the fuel cell stack, and assume uniform stack temperatures. While the thawing energy requirements do not vary with vehicle storage time, the keep-warm requirements show a positive slope since this method continuously consumes energy. There is therefore a break-even parking duration where one method becomes more advantageous than the other with respect to required energy consumption.

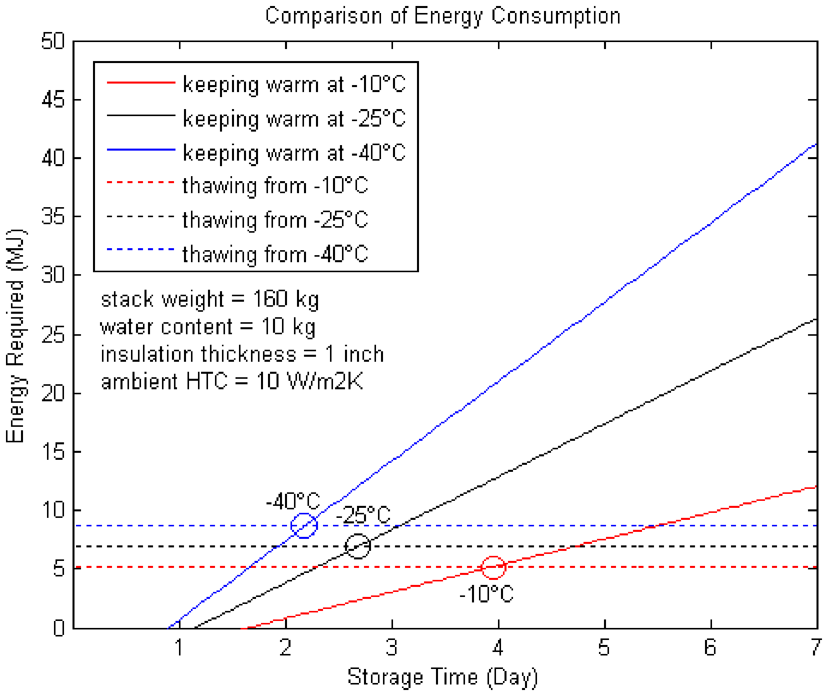


Figure 21. Energy Consumption Comparison Between Keep-Warm and Thaw at Start methods.

3.5. Energy Requirement Analysis at Startup

This analysis sought to estimate a range of energy requirements for complete fuel cell system thawing based on assumptions about the system's constituent components. This approach expands upon the analysis that just took a representative specific heat value to determine the thaw energy requirement for the fuel cell stack alone. The analysis approach involved scaling available manufacturer data on an actual fuel cell system, and making additional assumptions to generate mass, water content, and specific heat values for each major component in a hypothetical 80 kW net fuel cell system. The component specific heat (C_p) values were determined by taking a mass-weighted average of the C_p values for the constituent raw materials that were assumed to make up each part. For instance, to represent the backing plates, flow channels, current collectors, MEA's, etc. making up the fuel cell stack, assumptions were made as to the mass percent composition of stainless steel, graphite, polymer, aluminum, etc. in the stack. Table 1 presents the assumed values for the composition materials used to generate the estimated C_P value for the fuel cell stack, and Table 2 provides a summary of the similarly-determined property estimates for each component.

Table 1. Composition values used to estimate representative C_P value for the fuel cell stack.

Material	C_P (J/(kg*K))	% mass	Mass (kg)
Stainless Steel	480	21.5	16.2
Aluminum	875	20	15.0
Copper	385	10	7.5
Graphite	711	38.5	28.8*
PTFE	1010	10	7.5
Average for FC Stack	**~700**	**100**	**75**

***Consistent with 2004 DOE-stated technology status for weight of bipolar plates (0.36 kg/kW * 80 kW = 28.8 kg) [2]**

Table 2. Summary of Component Property Estimates

	Component	Mass (kg)	Water Mass Proportion		Average Non-Water c_P (J/(kg*K))
			Low Case	High Case	
FC Stack Module	-FC Stacks	75	0.5%	10%	700
	-Enclosure & Misc	23	0%	0%	750
	-Coolant & Plumbing	12	0%	50%	550
	-Electronics	6	0%	0%	650
System Module	-Air Compressor Sys	22*	0%	0%	550
	-Enclosure	24	0%	0%	750
	-Condenser	14	5%	30%	750
	-Humidifiers	18	5%	40%	800
	-DI Water Handling/ Accumulator	18	5%	50%	550
	-Other	24	0%	20%	600

***Consistent with 2004 DOE-stated technology status for weight of air compressor system in an 80 kW fuel cell engine [2]**

The component properties from Table 2 was used to calculate the energy requirements for heating the system from a cold-soaked temperature of -20ºC to a threshold temperature level of +5ºC. It was assumed that the stack would not contribute internal waste heat generation during this warm-up, and any heating losses to the environment were neglected. With these assumptions, the equation for determining the lumped heat input requirement for each component is:

$$\mathbf{Q = (m_{comp} \cdot c_{P,comp} + m_{ice} \cdot c_{P,ice}) \cdot \Delta T_1 + m_{ice} \cdot h_f + (m_{comp} \cdot c_{P,comp} + m_{water} \cdot c_{P,water}) \cdot \Delta\, T_2}$$

Equation 2

In this equation,

- "comp" refers to non-H_2O portions of the component
- ΔT_1 & ΔT_2 represent heating from -20 to 0 ºC and from 0 to +5 ºC, respectively
- h_f is used to determine the heat requirement to melt the ice in the component

Please note that the Q in Equation 2 is the heat that is needed for warming the components. The electrical energy for pumps, compressor/blower is additional at startup and must be added to this energy. However, the energy for compressor/blower and pumps for the short startup time of 30 seconds in not significant (order of 0.1 to 0.5 MJ) and we have neglected it compared to heat energy needed for thaw. See Figure 22 for estimation of the energy required for various cases.

Compressor Power	Humidification Power	Duration	Energy		
kW	kW	Seconds	kJ	MJ	Whr
10	2	60	720	0.72	200
5	1	30	180	0.18	50
3	0.5	30	105	0.11	29

In addition to calculating the "bulk" energy requirements for heating every component (and all the water each component contains) in the low and the high water content cases, further assumptions were made to determine the "localized" heating requirements for a more sophisticated targeted-heating approach. In the localized heating cases, we assumed that the wet fuel cell stack still required full heating, but that the system would be able to start itself without applying full heating to the other components. We specifically assumed that no heat needed to be applied to non-water containing components, and that only 10% of the water in the other components (in addition to those components themselves) needed to be heated. It was assumed that the other 90% of the water could be separately thawed later using waste heat from the stack.

Figure 22 presents the results of the energy analysis for the four different heating cases considered: Bulk Heating for both the Low and the High Water Content Cases, and Localized Heating for both the Low and the High Water Content Cases. The results of the analysis show that the thaw energy required for each low-water content case can satisfy the DOE target of no more than 5 MJ [3]. It is also observed that adopting technology-specific strategies to target heating only where it is really needed prior to starting a frozen system has the potential to significantly reduce thaw energy requirements. Another major opportunity to reduce thaw energy requirements is with the shutdown water management strategy. Due to the high heat capacity and latent heat requirements to melt ice, every amount of water that can be removed when the system is parked can result in significant energy savings during thaw.

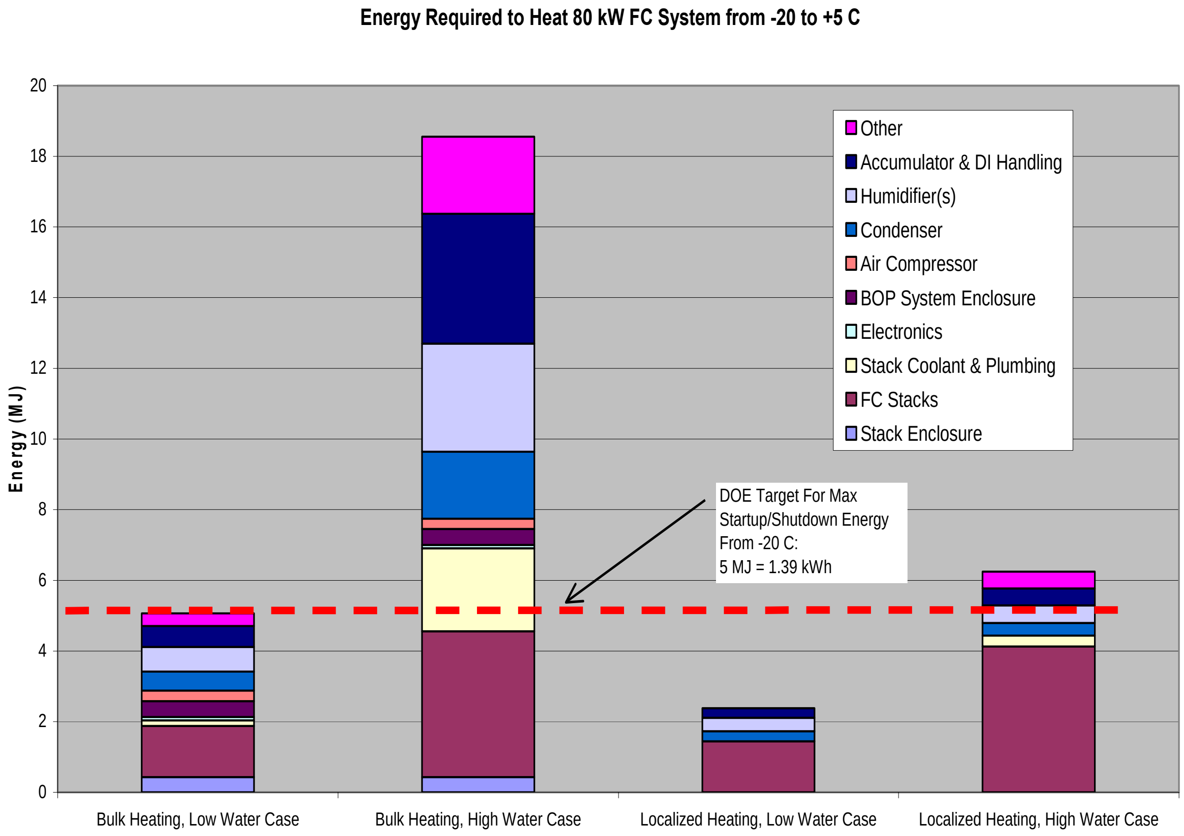


Figure 22. Component-level thaw energy requirements results

It should be noted that the exact numerical results of this analysis are only applicable to actual fuel cell systems insofar as those systems' properties match the property assumptions presented. Important considerations for tailoring the analysis to a specific system about which detailed information is known include: actual components, mass, heat capacity, and water content information; the required threshold temperature for system "boot-strap" or self-start; the stack's warm-up efficiency and heat generation characteristics; actual components requiring heating in order to start; environmental heat loss characteristics; the shutdown water management strategy; and the stack humidification requirements during freeze-start.

3.6. Three-Dimensional Modeling Analysis

In previous sections, we have presented the useful analysis results from lumped FC models. Even though a lumped analysis can provide lots of information for designing FC cold start strategies, this kind of approach has inherited limitations in predicting some critical design inputs such as distributions of heat and water inside system.

Three dimensional modeling and analysis are inevitable to predict such distributions. The stack should be rapidly heated up to prevent the blockage by the ice from production water. Fluid and gas delivery system must be heated. Humidifier should be rapidly heated up to prevent the membrane from drying-out. Therefore, in order to thaw and start up a frozen PEM Fuel Cell system, high power heat must be supplied. This technology requires information about proper distribution of a supplied heat inside stack and system, as well as the power/energy requirement prediction. Lower temperature near the end plate (than the temperature of middle of stack) is one of the important issues being addressed in many disclosed technologies. In many revealed inventions, water is suggested to be removed from the FC stack by air purging, evaporating with a vacuum, or discontinuing reactant humidification prior to powering off the system. For these suggestions, it is important to figure out how the residual water would be distributed in the stack.

There are many components and layers in PEM fuel cells. And, a couple of processes occur in each component. But, three key processes have the greatest impact on PEM fuel cell performance: the electro-chemical reactions in the catalyst layers, proton migration in the polymer electrolyte membrane layer, and mass transport within all regions of the PEM fuel cell. Even though the detailed mechanism of the rate reduction is not well known, it is believed either that the proton conductivity of PEM becomes poor at these temperatures or that the effectiveness of catalyst is so poor that sufficient amount of current can not be drawn. So, if the proper models for proton conduction in MEA and for catalytic chemistry at freezing temperatures are applied, the stack behavior at low temperatures could be predicted.

We evaluated several commercial fuel cell modeling software packages for more rigorous three-dimensional analysis of FC. Out of the various packages considered, we selected the PEMFC module in StarCD, and have established a working relationship with that program's developers at the University of South Carolina. Figure 23 shows the StarCD mesh for a five-channel serpentine flow field PEMFC. Current density contours at the MEA are also presented for a humidified feed case and for a dry cathode feed case. The average values of current density are 0.61 A/cm^2 and 0.55 A/cm^2 respectively for the given geometry and conditions.

Hot air (typically greater than 90°C) is available relatively quickly as a result of the compression process in the system's air compressor. Even though the hot air supplied to the stack does not contain a large heat capacity, the thermal mass of the MEA is rather small and does not require much heating power. Figure 24 presents the results of a heat-up model via hot air blowing that we developed using StarCD. The model features include transient multi-stream flow, porous media flow and conjugate heat transfer. The cell is initially soaked at a temperature of –25°C and then heated with the hot air. Comparisons are made for co-flow heating and counter flow heating by showing the temperature contours of channels and MEA's after 0.4 sec and 0.6 sec of heating. Counter flow heating appears to result in more favorable even heating of the fuel cell stack.

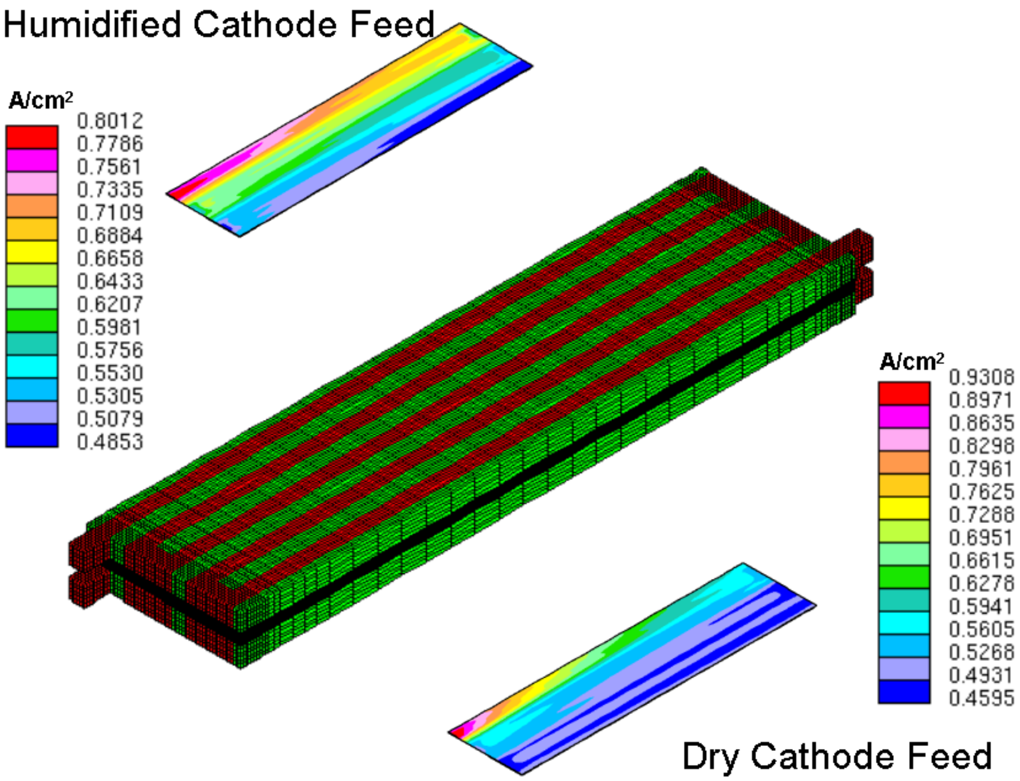


Figure 23. Five-channel serpentine flow field PEMFC mesh and current density contours for humidified cathode feed case and dry cathode feed case.

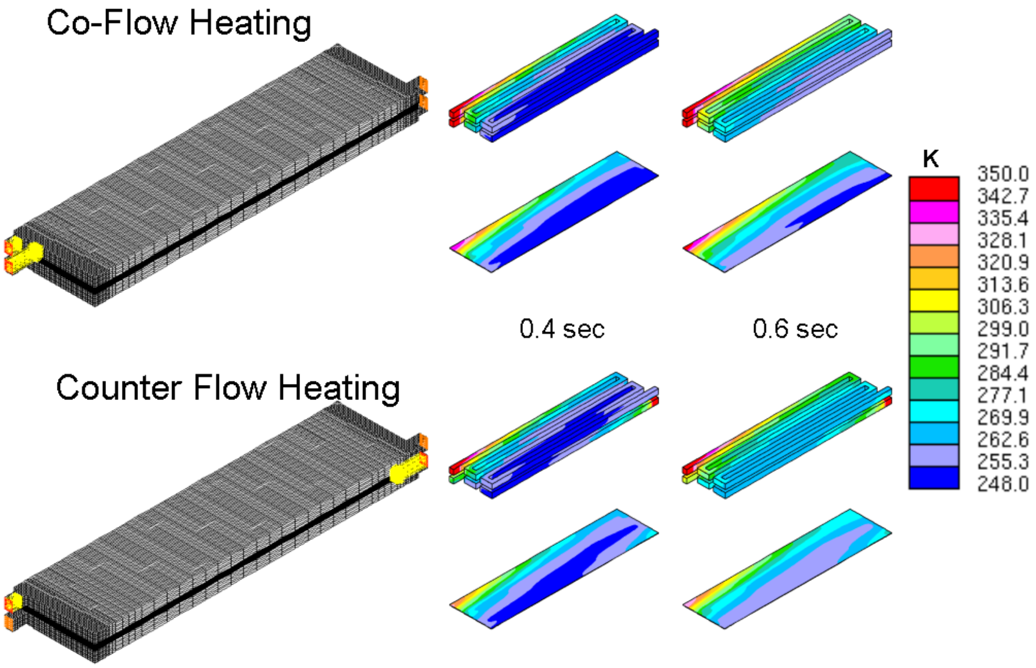


Figure 24. Comparison of hot air heating model results for co-flow heating and counter flow heating: Meshes and temperature contours of channels and MEA's at 0.4 sec and 0.6 sec.

4. Conclusions and Future Work

Conclusions

There are many system and component-level approaches to resolve the freeze protection and rapid cold startup issues in PEMFC vehicles. We researched and categorized more than 100 patents related to these issues and investigated the effects of actual cold-climate ambient temperature variation on FC stack freeze conditions. We then conducted energy and power analysis on the most promising of the identified solution approaches. The following summarizes our accomplishments:

- We found that many patents, more so than journal articles have been published on fuel cell freeze and rapid start, and we categorized the ideas disclosed in the patents in order to systematize the solution approaches.
- We identified the “keep-warm” method (in which the FC is never allowed to freeze) and the “thaw-at-start” method as two top-level categories for the various patented strategies.
- We performed an analytical investigation of stack cool-down, and found that use of insulation could potentially delay the onset of stack freezing up to several days following system turn-off. Overheating the stack prior to turn-off will delay freezing to a smaller extent.
- Given the effectiveness of insulation at delaying freezing, we found that for typical winter temperature variation in New York City and (to a lesser extent) in Minneapolis, regular use of the vehicle would routinely raise the FC to its operating temperature and virtually eliminate freezing events.
- When analyzing the frequency of occurrence of the -20ºC cold-soak condition at locations throughout the United States, we found that a significant portion of populated areas do not experience temperatures at or below this level for sufficient durations to cold-soak the stack to -20ºC. This suggests that a less rigorous freeze-start strategy may be acceptable in many areas for an initial vehicle introduction. Similarly, a less-than ideal deep-freeze management strategy may be acceptable for other areas given how infrequently it will need to be used.
- Given vehicle use and ambient temperature profiles, we developed several Matlab-based simulation programs to calculate energy, power, and temperature-time performance for the Keep Warm and rapid Thaw at Start methods. The keep-warm method seems to be effective short-term storage and/or for mild sub-freezing temperatures, but could be inefficient for long-term storage. The thaw-at-start method does not require as much energy for long-term storage, but does require high-power and potentially re-humidification at system start.
- Investigating the thaw method from a component level perspective highlights the major contributors to the energy requirement, and the importance of minimizing the amount of water allowed to freeze in the system. Targeting heating only to those areas that absolutely need it for start-up will similarly help minimize the required thaw energy input.
- Because the thaw method requires high power heat input, 3-D modeling is needed to evaluate the potential imbalance of heating, humidification and current generation

within the fuel cell stack. We have performed initial modeling with PEMFC module in StarCD (developed by CD-adapco and the University of South Carolina, and will continue collaboration with developers to add freeze modeling capabilities into the PEMFC module in FY06.

- As a result of our analysis we conclude that a combination of multiple technologies and strategies will provide the most promising solution to the fuel cell freeze problem. However, we recognize that the added complexity of multiple strategies may increase the operation and installation costs of the system.

Future Directions

The following highlight some of the areas we have identified for expanding this work in FY06 and beyond:

- Expand the national temperature variation investigation to evaluate other cold-soak target temperatures (-40°C, -30°C, -10°C, and 0°C) and consider the resulting impact on selecting freeze protection and rapid startup solutions.
- Overlay GIS information on population/vehicle registration onto the weather analysis in order to better view the percentage of vehicle users who would be impacted by different freeze-start criteria.
- Perform energy and power requirement calculations for various PEMFC vehicle configurations, use profiles and freeze management strategies based on operation during the coldest month in 3-4 select cities during the period from 1961-1988.
- Obtain updates to the national hourly temperature database to include statistics from the past 15 years.
- Add freeze analysis capability to the PEMFC module in StarCD, and perform more rigorous evaluation of freeze-start technologies and methods using 3D FC stack simulation models.
- Create general tool containing both information libraries and user input capabilities for the following parameters:
    1. FC system characteristics (including effective heat capacities, insulation, electricity and heat generation as a function of temperature, etc);
    2. Ambient temperature variation for the location where the vehicle will be used (could be typical winter, worst case, etc);
    3. Vehicle use patterns (daily driving, long-term parking, etc); and
    4. Potential strategies and add-on technologies for freeze protection and rapid cold-start (including any temperature, start-up time, energy and power restrictions).

  The tool would be able to feed back to a user the resulting energy and power requirements for different situations, the number of expected yearly freeze/thaw cycles, typical temperature and heat flux profiles experienced by the stack, etc. Partner with industry (to include receiving input on development of the above tool) to evaluate and implement innovative freeze management approaches.
- Present results at conferences and meetings.
- Investigate, evaluate, and test the novel rapid startup concepts and ideas we developed under this task and filed in two records of invention.

References

1. Marion, W. and Urban, K. *User's Manual for TMY2's: Typical Meteorological Years.* National Renewable Energy Laboratory, June 1995.

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3. U.S. Department of Energy – Energy Efficiency and Renewable Energy. *Draft Funding Opportunity Announcement: Research and Development of Polymer Electrolyte Membrane (PEM) Fuel Cells for the Hydrogen Economy.* Topic 5: Freeze-capable stack. April 25, 2005.

Appendix A

List of Relevant Fuel Cell Freeze and Thaw Patents

Click here to link to the table.

Table A.1 List of Patents Regarding Fuel Cell Freeze
(January 1991 – June2005)

Publication	Title Abstract	Assignee	Pub. Date
US20050112424A1	**Fuel cell system** A fuel cell system includes a fuel cell stack, a hydrogen flowing passage, an air flowing passage and a control valve. At least one of the gas flowing passages includes a bypass, a selecting means, a gas flowing means and a control unit. The bypass allows a gas to flow through so as to detour the fuel cell stack and the control valve. The selecting means selects one of a passage which passes through the fuel cell stack and the bypass. The gas flowing means flows the gas to the bypass. In the control unit, the through passage is selected by the selecting means when the system is operated, The bypass is selected by the selecting means when the operation of the system is stopped. The gas is flowed to the bypass by operating the gas flowing means when the control valve is frozen thereby heating the control valve.		2005-05-26
US20050112418A1	**Apparatus for improving the cold starting capability of an electrochemical fuel cell** An electric power generation system has elements that improve the cold start capability and freeze tolerance of a constituent fuel cell stack cooperate to reduce the amount of water remaining within the passages of the stack. The system includes a purge system that is connectable to the oxidant supply, fuel supply and/or coolant passages upstream of the stack. When the stack is shut down, the stack is disconnected from an external circuit, and purge fluid is transmitted by the purge system through the stack before the stack falls below the freezing point of water. In systems where fuel and/or oxidant streams are humidified prior to entry into the stack, a humidifier bypass system may be provided in place of the purge system. The humidifier bypass system transmits reactant fluid to the stack in fluid isolation from the humidifier, so that the inlet reactant streams are un-humidified.		2005-05-26
US20050095477A1	**Freeze tolerant fuel cell power plant with a direct contact heat exchanger** A power plant (10) includes at least one fuel cell (12), a coolant loop (18) including a freeze tolerant accumulator (22) for storing and separating a water immiscible fluid and water coolant, a direct contact heat exchanger (56) for mixing the water immiscible fluid and		2005-05-05

Publication	Title Abstract	Assignee	Pub. Date
	the water coolant within a mixing region (72) of the heat exchanger (56), a coolant pump (21) for circulating the coolant through the coolant loop (18), a radiator loop (84) for circulating the water immiscible fluid through the heat exchanger (56), a radiator (86) for removing heat from the coolant, and a direct contact heat exchanger by-pass system (200). The plant (10) utilizes the water immiscible fluid during steady-state operation to cool the fuel cell and during shut down of the plant to displace water from the fuel cell (12) to the freeze tolerant accumulator (22).		
US20050095476A1	**Freeze tolerant fuel cell power plant with a direct contact heat exchanger** A freeze tolerant fuel cell power plant (10) includes at least one fuel cell (12), a coolant loop (18) including a freeze tolerant accumulator (22) for storing and separating a water immiscible fluid and water coolant, a direct contact heat exchanger (56) for mixing the water immiscible fluid and the water coolant within a mixing region (72) of the heat exchanger (56), a coolant pump (21) for circulating the coolant through the coolant loop (18), a radiator loop (84) for circulating the water immiscible fluid through the heat exchanger (56), and a radiator (86) for removing heat from the coolant. The plant (10) utilizes the water immiscible fluid during steady-state operation to cool the fuel cell and during shut down of the plant to displace water from the fuel cell (12) to the freeze tolerant accumulator (22).		2005-05-05
US20050095475A1	**Freeze tolerant fuel cell power plant with a two-component mixed coolant** A freeze tolerant fuel cell power plant (10) includes at least one fuel cell (12), a coolant loop (42) having a porous water transport plate (44) secured in a heat and mass exchange relationship with the fuel cell (12) and a coolant pump (46) for circulating a coolant through the plate (44) and for transferring water into or out of the plate (44) with the coolant. A coolant heat exchanger (52) removes heat from the coolant, and an accumulator (66) stores the coolant and fuel cell product water and directs the product water out of the accumulator (66). The coolant is a two-component mixed coolant liquid circulating through the coolant loop (42) consisting of between 80 and 95 volume percent of a low freezing temperature water immiscible fluid component and between 5 and		2005-05-05

Publication	Title Abstract	Assignee	Pub. Date
	20 volume percent of a water component.		
US20050084735A1	**Reducing PEM fuel cell hard freeze cycles** The reactant gas manifolds (12 - 15) of a PEM fuel cell are modified to provide insulated manifolds (14 a) having inner and outer walls (30, 31) closed off by a peripheral wall (35) to provide a chamber (36) which may be filled with a vacuum, a low thermal conductivity gas, a VIP (59) or a GFP (63). Single walled manifolds (14 d , 14 e) may have VIPs or GFPs inside or outside thereof. An insulation panel (40) similarly has inner and outer walls (42, 43) closed with a peripheral wall (45) so as to form a chamber (46) that may contain a vacuum, a low thermal conductivity gas, a VIP or a GFP. The tie rods 9 a may be recessed 50 into the pressure plate 11 a of the fuel cell stack to allow a flush surface for the insulation panel 40.		2005-04-21
US20050084732A1	**Fuel cell stack having an improved current collector and insulator** A fuel cell stack (10) includes a reaction portion (20) having an end cell (12) secured adjacent to a current collector (30). The collector (30) has a sensible heat no greater than a sensible heat of the end cell (12) and an electrical resistivity no greater than 100 micro-ohms centimeters. An insulator (40) is secured adjacent the collector (30) and has a thermal conductivity that is no greater than 0.500 Watts per meter per degree Kelvin. Because of the low sensible heat of the current collector (30) and low rate of heat transfer of the insulator (40), heat does not readily leave the end cell (12) resulting in a rapid heating of the end cell (12), thereby avoiding freezing and accumulation of product water in the end cell (12) during start up in subfreezing conditions.		2005-04-21
US20050058865A1	**Self -thawing fuel cell** Electrical resistance heating elements recessed in the terminal plates, or the cell end plates, of a fuel cell stack at the interfaces therebetween are energized by electricity generated by the stack to heat the end cells during start-up of a frozen stack. The flow of current in the heating elements is ended when the temperature of the end cell(s) reach(es) a prescribed above-freezing temperature.		2005-03-17
US20050053807A1	**Method of operating a fuel cell system under freezing conditions** A fuel cell system having a stack of proton exchange membrane fuel cells is operated in		2005-03-10

Publication	Title Abstract	Assignee	Pub. Date
	sub-freezing temperatures by draining any liquid water from the fuel cell water flow passages upon or after the previous shut-down of the stack before freezing can occur, and, thereafter a) starting-up the stack by directing fuel and oxidant reactants into the cell and connecting a load to the stack; b) using heat produced by the stack to increase the operating temperature of the stack to melt ice within the stack; and, c) upon the stack operating temperature reaching at least 0° C., circulating anti-freeze through stack coolers to maintain the temperature of the stack low enough to maintain a sufficiently low water vapor pressure within the cells to prevent cell dry out for at least as long as there is insufficient liquid water to circulate through the water flow passages.		
US20050051754A1	**Corrosion inhibiting compositions and methods for fuel cell coolant systems** Carboxylic acids or the salts thereof are suitable for use in cooling systems where low electrical conductivity is required. The compositions are of particular use in fuel cell stacks. The preferred salts are those of amines. The salts can be used with a liquid alcohol freezing point depressant such as monoethylene glycol. Thiazoles and/or triazoles may be included, as well as other corrosion inhibitors known in the art.		2005-03-10
US20050035127A1	**Pure water tank for fuel cell system** A pure water tank reduces stress to be applied to the tank when pure water in the tank freezes, to thereby prevent the deformation or breakage of the tank without thickening the wall of the tank. The tank has inner side-walls to define a pure water zone. On the outer side of the inner side-walls, an antifreeze zone is defined. The antifreeze zone holds antifreeze having a freezing point lower than a lowest temperature of a service temperature range of the tank. The density of the antifreeze increases as the temperature thereof decreases. The width of the antifreeze zone is set to satisfy D>=alpha loge(H)+d0, where H is the height of the antifreeze zone.		2005-02-17
US20050031914A1	**PEM fuel cell with high porosity water transport plates and temperature increase before shut down in subfreezing conditions** A fuel cell stack (50) includes fuel cells (16, 18, 19) with anode and cathode water transport plates (23, 31, 34, 37) having		2005-02-10

Publication	Title Abstract	Assignee	Pub. Date
	porosity of at least 50%, thereby to significantly increase the amount of water stored within the water transport plates when the stack is shut down, which doubles the heat of fusion as the ice in the pores melts during a startup following freeze. This extends the period of time before the water in the pores reaches a hard freeze at -20° C. from 180 hours to 280 hours. A controller (60) controls the bypass (55) of a heat exchanger (54) to cause the temperature of the stack to reach a temperature sufficient to raise the sensible heat of the stack by 20%-40% above what it is with the fuel cell power plant operating steady state, prior to being shut down, thereby increasing the hours required for the fuel cell to cool down to 0° C. in -20° C. environment from 60 hours to 90 hours, allowing easier startups when shut down for less than 90 hours.		
US20050019628A1	**Low temperature fuel cell power plant operation** A fuel cell power plant system includes the ability to operate an enthalpy recovery device even under cold conditions. A bypass arrangement allows for selectively bypassing one or more portions of the enthalpy recovery device under selected conditions. In one example, the enthalpy recovery device is completely bypassed under selected temperature conditions to allow the device to freeze and then later to be used under more favorable temperature conditions. In another example, the enthalpy recovery device is selectively bypassed during a system startup operation. One example includes a heater associated with the enthalpy recovery device. Another example includes preheating oxidant supplied to one portion of the enthalpy recovery device.		2005-01-27
US20050003261A1	**Porous fuel cell separator, method of manufacture thereof, and solid polymer fuel cell** A porous fuel cell separator which is shaped as a porous plate composed of an electrically conductive material and a resin and which has gas flow channels on at least one surface thereof contains a far-infrared radiating material. Even when the separator is exposed to sub-freezing temperatures, the presence of the far-infrared radiating material prevents water within the pores from freezing, and can thus prevent a decline in the power generating efficiency of the fuel cell when it is restarted.		2005-01-06

Publication	Title Abstract	Assignee	Pub. Date
WO05048376A2	**Freeze Tolerant Fuel Cell Power Plant with a Two-Component Mixed Coolant** A freeze tolerant fuel cell power plant (10) includes at least one fuel cell (12), a coolant loop (42) having a porous water transport plate (44) secured in a heat and mass exchange relationship with the fuel cell (12) and a coolant pump (46) for circulating a coolant through the plate (44) and for transferring water into or out of the plate (44) with the coolant. A coolant heat exchanger (52) removes heat from the coolant, and an accumulator (66) stores the coolant and fuel cell product water and directs the product water out of the accumulator (66). The coolant is a two-component mixed coolant liquid circulating through the coolant loop (42) consisting of between 80 and 95 volume percent of a low freezing temperature water immiscible fluid component and between 5 and 20 volume percent of a water component.	UTC FUEL CELLS, LLC	2005-05-26
WO05045954A2	**Freeze Tolerant Fuel Cell Power Plant with a Direct Contact Heat Exchanger** A freeze tolerant fuel cell power plant (10) includes at least one fuel cell (12), a coolant loop (18) including a freeze tolerant accumulator (22) for storing and separating a water immiscible fluid and water coolant, a direct contact heat exchanger (56) for mixing the water immiscible fluid and the water coolant within a mixing region (72) of the heat exchanger (56), a coolant pump (21) for circulating the coolant through the coolant loop (18), a radiator loop (84) for circulating the water immiscible fluid through the heat exchanger (56), and a radiator (86) for removing heat from the coolant. The plant (10) utilizes the water immiscible fluid during steady-state operation to cool the fuel cell and during shut down of the plant to displace water from the fuel cell (12) to the freeze tolerant accumulator (22).	UTC FUEL CELLS, LLC	2005-05-19
WO05043645A2	**FUEL CELL STACK HAVING AN IMPROVED CURRENT COLLECTOR AND INSULATOR** A fuel cell stack (10) includes a reaction portion (20) having an end cell (12) secured adjacent to a current collector (30). The collector (30) has a sensible heat no greater than a sensible heat of the end cell (12) and an electrical resistivity no greater than 100 micro-ohms centimeters. An insulator (40) is secured adjacent the collector (30) and has a thermal conductivity that is no greater than 0.500 Watts per meter per degree Kelvin.	UTC FUEL CELLS, LLC	2005-05-12

Publication	Title Abstract	Assignee	Pub. Date
	Because of the low sensible heat of the current collector (30) and low rape of heat transfer of the insulator (40), heat does not readily leave the end cell (12) resulting in a rapid heating of the end cell (12), thereby avoiding freezing and accumulation of product water in the end cell (12) during start up in subfreezing conditions. L'invention concerne un empilement de piles à combustible (10) qui comprend une partie de réaction (20) munie d'une cellule d'extrémité (12) montée à proximité d'un collecteur de courant (30). Ce collecteur (30) présente une chaleur sensible qui n'est pas supérieure à une chaleur sensible de la cellule d'extrémité (12) et une résistivité électrique qui ne dépasse pas 100 micro-ohms-centimètres. Un isolateur (40) fixé à proximité du collecteur (30) présente une conductivité thermique qui ne dépasse pas 0,500 Watts par mètre par degré Kelvin. En raison de la faible chaleur sensible du collecteur de courant (30) et du faible taux de transfert de chaleur de l'isolateur (40), la chaleur ne sort pas facilement de la cellule d'extrémité (12), ce qui entraîne une chauffage rapide de la cellule d'extrémité (12) et permet d'éviter la congélation et l'accumulation d'eau produite dans la cellule d'extrémité (12) lors d'une mise en marche dans des conditions de surgélation.		
WO05038955A2	**REDUCING PEM FUEL CELL HARD FREEZE CYCLES** The reactant gas manifolds (12-15) of a PEM fuel cell are modified to provide insulated manifolds (14a) having inner and outer walls (30, 31) closed off by a peripheral wall (35) to provide a chamber (36) which may be filled with a vacuum, a low thermal conductivity gas, a VIP (59) or a GFP (63). Single walled manifolds (14d, 14e) may have VIPs or GFPs inside or outside thereof. An insulation panel (40) similarly has inner and outer walls (42, 43) closed with a peripheral wall (45) so as to form a chamber (46) that may contain a vacuum, a low thermal conductivity gas, a VIP or a GFP. The tie rods (9a) may be recessed (50) into the pressure plate (11a) of the fuel cell stack to allow a flush surface for the insulation panel (40). Les collecteurs de gaz réactifs (12-15) d'une pile à combustible PEM sont modifiés pour obtenir des collecteurs isolés (14a) dotés de parois intérieures et extérieures (30, 31) fermées par une paroi périphérique (35) pour former une chambre (36) pouvant être isolée	UTC FUEL CELLS, LLC	2005-04-28

Publication	Title Abstract	Assignee	Pub. Date
	par le vide, par un gaz à faible conductivité thermique, par un panneau VIP (59) ou par un panneau GFP (63). Les collecteurs à paroi simple (14d, 14e) peuvent comprendre des VIP ou des GFP, à intérieur ou à l'extérieur. De même, un panneau isolant (40) comporte des parois intérieures et extérieures (42, 43) fermées par une paroi périphérique (45) pour former une chambre (46) pouvant contenir un vide, un gaz à faible conductivité thermique, un panneau VIP (59) ou un panneau GFP. Les tirant d'assemblage (9a) peuvent être encastrés (50) dans la plaque de pression (11a) de l'assemblage de piles à combustible pour conférer au panneau isolant (40) une surface lisse.		
WO05027238A3	**METHOD OF OPERATING A FUEL CELL SYSTEM UNDER FREEZING CONDITIONS** A fuel cell system (10) having a stack of proton exchange membrane fuel cells (12) is operated in sub--freezing temperatures by draining any liquid water from the fuel cell water flow passages (40) upon or after the previous shut-down of the stack before freezing can occur, and, thereafter a) starting-up the stack by directing fuel (50) and oxidant (52) reactants into the cell and connecting a load (23) to the stack; b) using heat produced by the stack to increase the operating temperature of the stack to melt ice within the stack; and, c) upon the stack operating temperature reaching at least O'C, circulating anti-freeze through stack coolers (18) to maintain the temperature of the stack low enough to maintain a sufficiently low water vapor pressure within the cells to prevent cell dry out for at least as long as there is insufficient liquid water to circulate through the water flow passages. L'invention concerne un dispostif de piles à combustible comportant un empilage de piles à combustible à membrane échangeuse de protons, ledit dispositif étant utilisé à des températures inférieures au point de congélation par évacuation de toute l'eau des passages de circulation de l'eau des piles à combustible dès ou après l'arrêt antérieur de l'empilement avant que la congélation puisse avoir lieu. Le procédé comporte ensuite a) le démarrage de l'empilement par l'alimentation de la pile à combustible en réactifs de combustible et en réactifs oxydants et la connexion d'une charge à l'empilement; b) l'utilisation de la chaleur produite par	UTC FUEL CELLS, LLC	2005-03-24

Publication	Title Abstract	Assignee	Pub. Date
	l'empilement pour augmenter la température d'utilisation de l'empilement afin de faire fondre la glace dans l'empilement et c) dès que la température d'utilisation de l'empilement atteint au moins 0 DEG C, la mise en circulation d'antigel dans les refroidisseurs du pile à combustible afin de garder la température de l'empilement assez basse pour maintenir une tension de vapeur d'eau assez basse dans les cellules afin d'empêcher le séchage des cellules au moins pendant qu'il n'y a pas assez d'eau liquide pour circuler dans les passages de circulation d'eau. [continued...]		
WO05027238A2	**METHOD OF OPERATING A FUEL CELL SYSTEM UNDER FREEZING CONDITIONS** A fuel cell system (10) having a stack of proton exchange membrane fuel cells (12) is operated in sub--freezing temperatures by draining any liquid water from the fuel cell water flow passages (40) upon or after the previous shut-down of the stack before freezing can occur, and, thereafter a) starting-up the stack by directing fuel (50) and oxidant (52) reactants into the cell and connecting a load (23) to the stack; b) using heat produced by the stack to increase the operating temperature of the stack to melt ice within the stack; and, c) upon the stack operating temperature reaching at least O'C, circulating anti-freeze through stack coolers (18) to maintain the temperature of the stack low enough to maintain a sufficiently low water vapor pressure within the cells to prevent cell dry out for at least as long as there is insufficient liquid water to circulate through the water flow passages. L'invention concerne un dispostif de piles à combustible comportant un empilage de piles à combustible à membrane échangeuse de protons, ledit dispositif étant utilisé à des températures inférieures au point de congélation par évacuation de toute l'eau des passages de circulation de l'eau des piles à combustible dès ou après l'arrêt antérieur de l'empilement avant que la congélation puisse avoir lieu. Le procédé comporte ensuite a) le démarrage de l'empilement par l'alimentation de la pile à combustible en réactifs de combustible et en réactifs oxydants et la connexion d'une charge à l'empilement; b) l'utilisation de la chaleur produite par l'empilement pour augmenter la température d'utilisation de l'empilement afin de faire fondre la glace dans l'empilement et c) dès que	UTC FUEL CELLS, LLC	2005-03-24

Publication	Title Abstract	Assignee	Pub. Date
	la température d'utilisation de l'empilement atteint au moins 0 DEG C, la mise en circulation d'antigel dans les refroidisseurs du pile à combustible afin de garder la température de l'empilement assez basse pour maintenir une tension de vapeur d'eau assez basse dans les cellules afin d'empêcher le séchage des cellules au moins pendant qu'il n'y a pas assez d'eau liquide pour circuler dans les passages de circulation d'eau. [continued...]		
WO05018036A1	**PEM FUEL CELL WITH HIGH POROSITY WATER TRANSPORT PLATES AND TEMPERATURE INCREASE BEFORE SHUT DOWN IN SUBFREEZING CONDITIONS** A fuel cell stack (50) includes fuel cells (16, 18, 19) with anode and cathode water transport plates (23, 31, 34, 37) having porosity of at least 50% thereby to significantly increase the amount of water stored within the water transport plates when the stack is shut down, which doubles the heat of fusion as the ice in the pores melts during a startup following freeze. This extends the period of time before the water in the pores reaches a hard freeze at -20EC from 180 hours to 280 hours. A controller (60) controls the bypass (55) of a heat exchanger (54) to cause the temperature of the stack to reach a temperature sufficient to raise the sensible heat of the stack by 20%-40% above what it is with the fuel cell power plant operating steady state, prior to being shut down, thereby increasing the hours required for the fuel cell to cool down to OEC in-20EC environment from 60 hours to 90 hours, allowing easier startups when shut down for less than 90 hours. L'invention concerne une batterie de piles à combustible (50) comprenant des piles à combustible (16, 18, 19) constituées de plaques de transport d'eau anodiques et cathodiques (23, 31, 34, 37) ayant une porosité d'au moins 50 %, ce qui, d'une part, augmente sensiblement la quantité d'eau stockée dans les plaques de transport d'eau lorsque la batterie est arrêtée et, d'autre part, double la chaleur de fusion lorsque la glace dans les pores fond lors d'un démarrage après un gel. Cette caractéristique permet de faire passer de 180 heures à 280 heures le temps nécessaire avant que l'eau dans les pores n'atteigne la température de solidification de 20 DEG C. Un contrôleur (60) contrôle le circuit de dérivation (55) d'un échangeur de chaleur (54) de façon que la température de la	UTC FUEL CELLS, LLC	2005-02-24

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	batterie atteigne une température suffisante pour augmenter la chaleur sensible de la batterie de 20-40 % en-dessus de la valeur correspondant à un état de fonctionnement stable de la centrale à pile à combustible, avant qu'elle ne soit arrêtée. Ce procédé permet de faire passer de 60 heures à 90 heures le temps nécessaire pour que la pile à combustible redescende à 0 DEG C dans un environnement à 20 DEG C, ce qui permet un redémarrage plus facile après un arrêt de moins de 90 heures. [continued...]		
WO05011020A3	**LOW TEMPERATURE FUEL CELL POWER PLANT OPERATION** A fuel cell power plant system (22) includes the ability to operate an enthalpy recovery device (40) even under old conditions. A bypass arrangement allows for selectively bypassing one or more portions of the recovery device under selected conditions. In one example, the enthalpy recovery device (40) is completely bypassed under selected temperature conditions to allow the device to freeze and then later to be used under more favorable temperature conditions. In another example, the enthalpy recovery device (40) is selectively bypassed during a system startup operation. One example includes a heater (60) associated with the enthalpy recovery device (40). Another example includes preheating oxidant supplied to one portion of the enthalpy recovery device (40).	UTC FUEL CELLS, LLC	2005-02-03
WO05011020A2	**LOW TEMPERATURE FUEL CELL POWER PLANT OPERATION** A fuel cell power plant system (22) includes the ability to operate an enthalpy recovery device (40) even under old conditions. A bypass arrangement allows for selectively bypassing one or more portions of the recovery device under selected conditions. In one example, the enthalpy recovery device (40) is completely bypassed under selected temperature conditions to allow the device to freeze and then later to be used under more favorable temperature conditions. In another example, the enthalpy recovery device (40) is selectively bypassed during a system startup operation. One example includes a heater (60) associated with the enthalpy recovery device (40). Another example includes preheating oxidant supplied to one portion of the enthalpy recovery device (40). Un système de centrale à piles à combustibles (22) possède la capacité d'utiliser un dispositif de récupération par enthalpie (40) même dans des conditions de basses	UTC FUEL CELLS, LLC	2005-02-03

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	températures. Un dispositif de dérivation permet le contournement sélectif d'une ou plusieurs parties du dispositif de récupération par enthalpie dans des conditions sélectionnées. Dans un exemple, le dispositif de récupération par enthalpie (40) est intégralement contourné dans des conditions de températures sélectionnées afin de permettre au dispositif de geler et d'être ensuite utilisé dans des conditions de température plus favorables. Dans un autre exemple, le dispositif de récupération par enthalpie (40) est contourné pendant l'opération de démarrage du système. Dans un exemple, un organe de chauffage (60) associé au dispositif de récupération par enthalpie (40) est prévu. Dans un autre exemple, un oxydant de préchauffage est fourni à une partie du dispositif de récupération par enthalpie (40).		
US6864000	**Shutdown procedure to improve startup at sub-freezing temperatures** A method for shutting down a fuel cell system including a plurality of fuel cells arranged in a stack, includes cooling the fuel cells to a shutdown temperature while maintaining a substantially uniform water vapor pressure through the fuel cells whereby migration of water within the fuel cells during cooling is reduced.	UTC Fuel Cells, LLC	2005-03-08
US6899969	**Fuel cell system and freezing prevention method thereof** In a fuel cell system, a temperature sensor detects an internal temperature of a fuel cell. A cooling water pump is controlled so that it is stopped when the internal temperature of the fuel cell is equal to or lower than 0 degrees. A driving amount of the cooling water pump increases according to a rise in internal temperature of the fuel cell when the internal temperature is higher than 0 degrees. A degree of increase in driving amount is restrained when the internal temperature of the fuel cell is between 0 degrees and a predetermined temperature higher than 0 degrees.	Toyota Jidosha Kabushiki Kaisha	2005-05-31
US20050109979A1	**Coolant composition for fuel cell** The present invention relates to a coolant composition used for cooling a fuel cell, in particular to a coolant composition used for cooling a fuel cell having low conductivity, anti-freeze properties, and excellent anti-corrosion properties for a metal, especially an aluminum based material, for use in the cooling system	Shishiai-Kabushikigaisha	2005-05-26

Publication	Title Abstract	Assignee	Pub. Date
	of fuel cell and, further, exhibiting no significant increase in conductivity even after long term use. The coolant composition according to the invention is characterized by comprising a base agent and an additive for sustaining low conductivity of the coolant composition, the anti-corrosive additive being such a substance as suppressing oxidation of the basic agent or blocking ions eluting into a cooling system to prevent conductivity of the coolant composition from increasing.		
EP1501140A1	**COOLING LIQUID COMPOSITION FOR FUEL CELL** The present invention relates to a coolant composition used for cooling a fuel cell, in particular to a coolant composition used for cooling a fuel cell having low conductivity, anti-freeze properties, and excellent anti-corrosion properties for a metal, especially an aluminum based material, for use in the cooling system of fuel cell and, further, exhibiting no significant increase in conductivity even after long term use. The coolant composition according to the invention is characterized by comprising a base agent and an additive for sustaining low conductivity of the coolant composition, the anti-corrosive additive being such a substance as suppressing oxidation of the basic agent or blocking ions eluting into a cooling system to prevent conductivity of the coolant composition from increasing.	Shishiai-Kabushikigaisha	2005-01-26
EP1494300A1	**Porous fuel cell separator, method of manufacture thereof, and solid polymer fuel cell** A porous fuel cell separator which is shaped as a porous plate composed of an electrically conductive material and a resin and which has gas flow channels on at least one surface thereof contains a far-infrared radiating material. Even when the separator is exposed to sub-freezing temperatures, the presence of the far-infrared radiating material prevents water within the pores from freezing, and can thus prevent a decline in the power generating efficiency of the fuel cell when it is restarted.	NISSHINBO INDUSTRIES, INC.	2005-01-05
CA2472831AA	**POROUS FUEL CELL SEPARATOR, METHOD OF MANUFACTURE THEREOF, AND SOLID POLYMER FUEL CELL** A porous fuel cell separator which is shaped as a porous plate composed of an electrically conductive material and a resin and which has gas flow channels on at least one surface thereof contains a far-infrared radiating material, Even when the	NISSHINBO INDUSTRIES, INC.	2005-01-04

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	separator is exposed to sub-freezing temperatures, the presence of the far-infrared radiating material prevents water within the pores from freezing, and can thus prevent a decline in the power generating efficiency of the fuel cell when it is restarted.		
CA2473213AA	**METHOD OF STARTING UP OPERATION OF FUEL CELL AT LOW TEMPERATURE** When it is detected that the temperature of the fuel cell stack is at the freezing temperature of water or less (step S1), an operation mode using a freezing temperature starting up operation control map is selected (step S2). Freezing temperature starting up operation of the fuel cell stack is performed according to the freezing temperature starting up operation control map (step S3). Then, when it is detected that the temperature of the fuel cell stack exceeds the freezing temperature (step S4), the operation mode using the freezing temperature starting up operation control map is switched to an operation mode using a normal starting up operation control map (step S5). Thus, normal starting up operation is performed according to the normal starting up control map (step S6).	HONDA MOTOR CO., LTD.	2005-01-09
US20050053809A1	**Method of starting up operation of fuel cell at low temperature** When it is detected that the temperature of the fuel cell stack is at the freezing temperature of water or less (step S1), an operation mode using a freezing temperature starting up operation control map is selected (step S2). Freezing temperature starting up operation of the fuel cell stack is performed according to the freezing temperature starting up operation control map (step S3). Then, when it is detected that the temperature of the fuel cell stack exceeds the freezing temperature (step S4), the operation mode using the freezing temperature starting up operation control map is switched to an operation mode using a normal starting up operation control map (step S5). Thus, normal starting up operation is performed according to the normal starting up control map (step S6).	Honda Motor Co., Ltd.	2005-03-10
WO05038947A2	**SELF-THAWING FUEL CELL** Electrical resistance heating elements recessed in the terminal plates, or the cell end plates, of a fuel cell stack at the interfaces therebetween are energized by electricity generated by the stack to heat the end cells during start-up of a frozen stack. The flow of current in the heating	GENERAL MOTORS CORPORATION	2005-04-28

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	elements is ended when the temperature of the end cell(s) reach(es) a prescribed above-freezing temperature. L'invention concerne des éléments chauffants de résistance électrique, encastrés dans les plaques terminales ou les plaques terminales de piles d'un paquet de piles à combustible, qui sont alimentés aux interfaces situées entre, par de l'électricité produite par le paquet de piles pour chauffer les piles terminales pendant le démarrage d'un paquet de piles gelées. Le flux de courant circulant dans les éléments chauffants s'arrête lorsque la température de la (des) pile(s) terminale(s) atteint une température hors gel prescrite.		
US6887598	**Control system and method for starting a frozen fuel cell** A method for starting a frozen fuel cell stack includes discontinuing reactant humidification before shutting down the fuel cell stack. The anode and cathode are purged with the dry reactants. The fuel cell stack is soaked at freezing temperatures. During subsequent startup, dry reactants are initially delivered. An outlet temperature of the anode and a current load of the fuel cell stack are measured. The dry reactants are shut off when the temperature of the anode outlet or the current load reach predetermined values. The open circuit voltage potential of the fuel cells is monitored and compared to a first voltage value. When the open circuit voltage exceeds the first value, the fuel cell stack begins supplying current load. The current load of the fuel cell stack is increased or decreased based on a difference between the minimum voltage and a second voltage value.	Generals Motors Corporation	2005-05-03
US6884529	**Method of heating up a solid polymer electrolyte fuel cell system** A method is disclosed to heat a direct methanol fuel cell stack system at start-up without using any external energy source. During the start-up period, the fuel cell stack is at open circuit state so that the fuel cell stack is not connected to any external circuit. The methanol solution introduced at the anode side of the fuel cell stack will diffuse through the proton conductive membrane to the cathode side of the fuel cell stack. The methanol diffused from the anode side will be oxidized at the cathode side by oxygen in the air stream. This oxidation reaction generates heat that heats up the fuel cell stack and the system. The concentration of methanol in the methanol	E. I. du Pont Canada Company	2005-04-26

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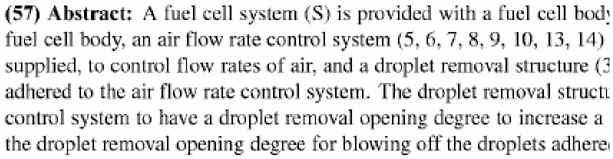
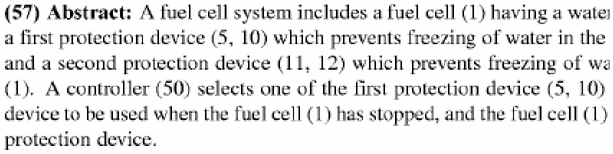
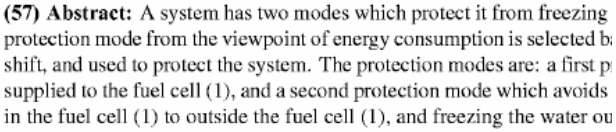
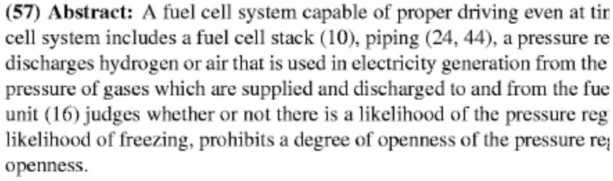
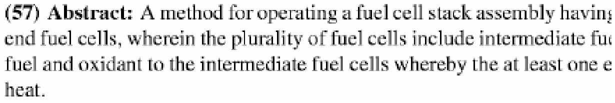
	solution can be varied depending on the initial stack temperature. The lower the initial stack temperature, the higher the concentration of the methanol solution required. At an initial stack temperature of -40° C., a solution having 40 wt % methanol is preferred to avoid freezing of the solution. If the initial stack temperature at start-up is above the freezing point of water, the methanol concentration in the solution can be in a range of 0.5 to 25 wt %, with a more preferred concentration range being from 3 to 10 wt % of methanol. The methanol solution and air feed rates can also be varied to control the rate at which heat is generated in the stack.		
US6855444	**Fuel cell system** Provided is a fuel cell system capable of activating a fuel cell even under low-temperature environments. The fuel cell system detects an outside air temperature in the vicinity of the fuel cell to, after the fuel cell enters a deactivated state, estimate a transition of outside air temperature on the basis of a variation of the detected outside air temperature, and makes a decision as to whether or not the estimated outside air temperature falls below a predetermined freezing temperature at which moisture freezes. When a decision is made that the estimated outside air temperature falls below the predetermined freezing temperature, freezing prevention processing is conducted to prevent moisture from freezing in the interior of the fuel cell. The estimation of the outside air temperature transition is made by time-differentiating a variation of outside air temperature.	Denso Corporation	2005-02-15
WO05048386A1	**FUEL CELL SYSTEM WHICH CAN BE USED IN A MOBILE MANNER WITH AN ADSORPTION ACCUMULATOR** The invention relates to fuel cell system which can be used in a mobile manner with a fuel cell unit (1) in order to produce electric energy, and an adsorption accumulator (3) which is associated with a fuel cell unit (1). Said adsorption accumulator (3) is used to release heat and interacts in a thermal manner with a heat exchanger (2) which is arranged downstream from the fuel cell unit (1) in a cooling circuit (4,5) associated with the fuel cell unit. The invention also relates to a method for operating said type of fuel cell system, especially during a cold start.	DAIMLERCHRYSLER AG	2005-05-26

Publication	Title Abstract	Assignee	Pub. Date
EP01505678A1	**Fuel cell system** Disclosed is a fuel cell system provided with a fuel cell (1), a water tank (2) which stores water to be supplied to the fuel cell, and a heating device (10) which defrosts the water inside the tank during activation of the fuel cell. The fuel cell system has a switch (19) which signals activation of the fuel cell; at least one temperature sensor (13, 14) which detects a temperature inside the water tank; a pump (3) which conveys water from the water tank to the fuel cell; a heater (12) which warms the pump; and a controller (15). The controller (15) is programmed to read a start temperature from said at least one temperature sensor (13, 14) upon reception of a signal from the switch (19); calculate on the basis of the read start temperature a first arm-up period (tw) required for the water inside the water tank (2) to reach a predetermined temperature (Tw) greater than zero degrees centigrade; calculate on the basis of the read start temperature a second warm-up period (tH) required to defrost ice inside the pump (3) using the heater; set a start time (t2) for warm-up of the pump (3) using the heater on the basis of a difference (Dt) between the first warm-up period (tw) and the second warm-up period (tH); and control the heater to begin generating heat at the start time (t2) for warm-up of the pump (3).	Nissan Motor Co., Ltd.	2005-09-02
US6727013B2	**Fuel Cell Energy Management System for Cold Environments** An energy management system controls the temperature of a fuel cell system while a vehicle is not running. The energy management system includes a fuel cell stack, a blower that provides air to the fuel cell stack, a water supply, and a hydrogen supply. A hydrogen supply valve is connected between the hydrogen supply and the fuel cell stack. A heater is connected to an output of the fuel cell stack. A controller controls the hydrogen supply valve and the blower to power the heater to warm the fuel cell stack and the water supply. The controller starts the blower and opens the hydrogen supply valve if heating is necessary and if a tank level signal exceeds a first tank level value. The controller activates a purge, drains water from the water supply, and inhibits vehicle startup if the tank level signal does not exceed a first tank level value.	General Motors Corporation	2005-04-27
WO03058740A1	**Fuel Cell System and Method of Removal**	Nissan	2003-07-17

Publication	Title Abstract	Assignee	Pub. Date
	of Water During Shutdown for Improving Freeze Tolerance  **(57) Abstract:** A fuel cell system (S) is provided with a fuel cell bod fuel cell body, an air flow rate control system (5, 6, 7, 8, 9, 10, 13, 14) supplied, to control flow rates of air, and a droplet removal structure (adhered to the air flow rate control system. The droplet removal struct control system to have a droplet removal opening degree to increase a the droplet removal opening degree for blowing off the droplets adhere	Motor Co., Ltd.	
WO03073547A2	**A Fuel Cell System, and Method of Protecting a Fuel Cell from Freezing**  **(57) Abstract:** A fuel cell system includes a fuel cell (1) having a wate a first protection device (5, 10) which prevents freezing of water in the and a second protection device (11, 12) which prevents freezing of wa (1). A controller (50) selects one of the first protection device (5, 10) device to be used when the fuel cell (1) has stopped, and the fuel cell (1) protection device.	Nissan Motor Co., Ltd.	2003-09-04
WO03081704A2	**Fuel Cell System and Protection Method Thereof**  **(57) Abstract:** A system has two modes which protect it from freezing protection mode from the viewpoint of energy consumption is selected b shift, and used to protect the system. The protection modes are: a first p supplied to the fuel cell (1), and a second protection mode which avoids in the fuel cell (1) to outside the fuel cell (1), and freezing the water ou	Nissan Motor Co., Ltd.	2003-10-02
WO2004091022A2	**Fuel Cell System**  **(57) Abstract:** A fuel cell system capable of proper driving even at ti cell system includes a fuel cell stack (10), piping (24, 44), a pressure re discharges hydrogen or air that is used in electricity generation from the pressure of gases which are supplied and discharged to and from the fue unit (16) judges whether or not there is a likelihood of the pressure reg likelihood of freezing, prohibits a degree of openness of the pressure re openness.	Toyota Jidosha Kabushiki Kaisha	2004-10-21
WO2004064182A3	**Fuel Cell Stack with Passive End Cell Heater** (57) Abstract: A fuel cell system comprising a passive end cell heater for heating an end cell or cells within a fuel cell stack is disclosed. The fuel cell system comprises a fuel cell stack and a resistive heatable element connected in parallel to the fuel cell stack, wherein the resistive heatable element is adapted to heat an end cell of the fuel cell stack. A method for heating an end cell in a fuel cell stack is also disclosed.	Ballard Power Systems INC.	2004-07-29
WO2004086534A2	**System and Method for Starting a Fuel Cell Stack Assembly at Sub-Freezing Temperature**  **(57) Abstract:** A method for operating a fuel cell stack assembly havin end fuel cells, wherein the plurality of fuel cells include intermediate fu fuel and oxidant to the intermediate fuel cells whereby the at least one e heat.		2004-10-07
WO2005027238A2	**Method of operating a fuel cell system under freezing conditions** A fuel cell system having a stack of proton exchange membrane fuel cells is operated in sub-freezing temperatures by draining any liquid water from the fuel cell water flow passages upon or after the previous shut-down	UTC Fuel Cells, LLC	2005-03-24

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	of the stack before freezing can occur, and, thereafter a) starting-up the stack by directing fuel and oxidant reactants into the cell and connecting a load to the stack; b) using heat produced by the stack to increase the operating temperature of the stack to melt ice within the stack; and, c) upon the stack operating temperature reaching at least 0° C., circulating anti-freeze through stack coolers to maintain the temperature of the stack low enough to maintain a sufficiently low water vapor pressure within the cells to prevent cell dry out for at least as long as there is insufficient liquid water to circulate through the water flow passages.		
EP1416563A1	**Fuel cell and fuel cell coolant composition** This invention is directed to coolant compositions, particularly coolant compositions useful in fuel cells, and to fuel cells containing such coolant compositions. The coolant compositions or heat transfer fluids of this invention have and retain low electrical conductivity through extended periods of use. These coolants or heat transfer fluids are composed of a base composition and an additive package which imparts the property of retaining low electrical conductivity for extended periods of time. The base composition can be de-ionized water (DI water) alone or a mixture of DI water and a freezing point depressant of the types well-known in the art (e.g., propylene glycol). The additive package contains an organic corrosion inhibitor and a polymeric ion suppressant. The use of both components of the additive package is important.	Advanced Fluid Technologies, Inc.	2004-05-06
CA2447174AA	**Fuel Cell and Fuel Cell Coolant Compositions** This invention is directed to coolant compositions, particularly coolant compositions useful in fuel cells, and to fuel cells containing such coolant compositions . The coolant compositions or heat transfer fluids of this invention have and retain low electrical conductivity through extended periods of use. These coolants or heat transfer fluids are composed of a base composition and an additive package which imparts the property of retaining low electrical conductivity for extended periods of time. The base composition can be de-ionized water (DI water) alone or a mixture of DI water and a freezing point depressant of the types well-	Advanced Fluid Technologies, Inc.	2004-04-30

Publication	Title Abstract	Assignee	Pub. Date
	known in the art (e.g., propylene glycol). The additive package contains an organic corrosion inhibitor and a polymeric ion suppressant. The use of both components of the additive package is important.		
WO04015796A2	**Energy Storage System** A closed loop energy storage system configured with a hydrogen tank, an oxygen tank, a fuel cell stack and an electrolyzer. A heat exchanger freeze-dries the hydrogen and oxygen prior to their storage in their respective tanks. The heat exchanger also uses excess fuel cell heat to preheat streams of hydrogen and oxygen coming from the tanks. Phase separators serve both to separate water from hydrogen and oxygen, and to store the water. A thermal management system encloses all the system components except the tanks. An airfoil-shaped shell covers the system, and the larger of the two tanks extends substantially across the shell at its point of greatest camber thickness. The tanks are composed of polymer liners integral with composite shells.	AEROVIRONMENT, INC.	2004-02-19
US06756143	**Fuel cell system and method for starting a fuel cell system** A fuel cell system, particularly for a motor vehicle, includes (1) at least one fuel cell and (2) a device for supplying at least one fuel cell with hydrogen or a hydrogen-containing gas. Particularly during start-up or a cold start of the system, individual components of the device or at least one fuel cell can be supplied thermal energy with cooling water contained in a cooling water system. The cooling water system is equipped with an insulating device for storing cooling water in a thermally insulated manner.	Ballard Power Systems AG	2004-06-29
US20040224201A1	**Antifreeze cooling subsystem** Liquid cooled systems having coolant circulation loops must often operate in below freezing conditions. For instance, in various applications certain fuel cell systems must be able to tolerate repeated shutdown and storage in below freezing conditions. Conventional glycol-based coolants typically used for internal combustion engines are generally unsuitable for use in the associated fuel cell cooling subsystems due to the presence of additives and/or inhibitors which are normally included to deal with problems relating to decomposition of the glycol. With additives or inhibitors present, the coolant conductivity can be sufficiently high as to	Ballard Power Systems Inc.	2004-11-11

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	result in electrical shorting or corrosion problems. However, provided the purity of the coolant is maintained, a pure glycol and water coolant mixture may be used as a fuel cell system coolant to obtain suitable antifreeze protection. Adequate purity can be maintained by including an ion exchange resin unit in the cooling subsystem.		
WO04053015A1	**Coolant Based on Azole Derivatives Containing 1,3-Propanediol for Fuel Cell Cooling Systems** The invention relates to an anti-freeze concentrate for the cooling systems of fuel cell drives, from which ready-to-use aqueous coolant compositions with a maximum conductivity of 50 ?S/cm can be produced, based on 1,3-propanediol or mixtures of 1,3-propanediol with alkylene glycols and/or derivatives thereof, comprising one or more five-membered heterocyclic compounds (azole derivatives) with two or three heteroatoms from the group nitrogen or sulphur which comprise no or a maximum of one sulphur atoms and which can have an aromatic or saturated six-membered annelated ring.	BASF AKTIENGESELLSCHAFT	2004-06-24
EP1464588A1	**Freeze-proof pure water tank for fuel cell system** A pure water tank reduces stress to be applied to the tank when pure water in the tank freezes, to thereby prevent the deformation or breakage of the tank without thickening the wall of the tank. The tank has inner side-walls to define a pure water zone. On the outer side of the inner side-walls, an antifreeze zone is defined. The antifreeze zone holds antifreeze having a freezing point lower than a lowest temperature of a service temperature range of the tank. The density of the antifreeze increases as the temperature thereof decreases. The width of the antifreeze zone is set to satisfy D≥ɑloge(H)+d0, where H is the height of the antifreeze zone.	Calsonic Kansei Corporation	2004-10-06
JP2004273322A2	**Pure Water Tank of Fuel Cell** PROBLEM TO BE SOLVED: To provide a compact pure water tank of a fuel cell with a heightened pure water thawing property. SOLUTION: A heating media tank 3, introducing a heating medium, surrounding the outside of a tank main body 2 for storing the pure water, is arranged in the pure water tank of the fuel cell. Further, a thawed water tank 4 introducing the pure water thawed in the tank main body 2 is arranged so as to contact with	CALSONIC KANSEI CORP	2004-09-30

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	the outside of the heating media tank 3. The pure water tank 1 can be integrally made in a compact structure, and a thawing efficiency can be heightened by transferring the pure water thawed in the tank main body 2 to the thawed water tank 4, and by keeping the pure water in a state of contacting with an outside wall receiving heat from the heating media tank 3 at all times.		
US06743538	**Fuel cell system and method for operating same** A fuel cell system has an anode space and a cathode space with a separating proton-conducting membrane. A cathode feed line is used to feed oxygen-containing gas to the cathode space, and an anode line is used to feed and discharge an operating medium into the anode space. A representative temperature is determined for the system, and metered amounts of operating medium are passed to the cathode space as a function of this temperature. Increasing in the operating medium concentration in the cathode space in this manner causes a reduction in the freezing point and, when the system is started, an exothermic catalytic reaction.	DaimlerChrysler AG	2004-06-01
JP2004241303A	**Fuel Cell** PROBLEM TO BE SOLVED: To provide a vehicular fuel cell allowing effective warming-up of the fuel cell in stopping it, and capable of reducing its starting time, and of preventing usage stop due to freeze. SOLUTION: This vehicular fuel cell equipped with a piping system associated with a cooling system, an air system, a hydrogen system and the like is provided with a warming-up system for a stack body of the fuel cell. The fuel cell is characterized by that the warming-up system is equipped with a heat insulation box for housing at least a part of the stack body and the piping system of the fuel cell in its inside, and has a vehicular air conditioner incorporated; and the air warmed by a heat exchanger provided for a heat pump cycle of the air conditioner is supplied to the heat insulation box.	DENSO CORP	2004-08-26
JP2004228038A	**Fuel Cell System** PROBLEM TO BE SOLVED: To provide a fuel cell system rising the temperature of a fusel cell at cold start, capable of obtaining a prescribed output within a short period at cold start.	DENSO CORP	2004-08-12

Publication	Title Abstract	Assignee	Pub. Date
	SOLUTION: In the case that the output during temperature decrease is lower than the output during temperature increase, during warming-up, a thermal medium is circulated only at a part of respective cells 10a, and the part of respective cells 10a are intensively heated up to the temperature at which the ratio of the output during the temperature increase to the output during the temperature decrease reaches over a prescribed value, afterwards, remaining part of respective cells 10a are heated. Thus, the partial portions of respective cells 10a are quickly controlled to an environment suitable for a power generation operation, and it becomes possible to execute a stable power generation with a high output density within a short period at a partial position.		
JP2004103367A	**Fuel Cell System** PROBLEM TO BE SOLVED: To obtain the maximum cell output in a short time when starting a fuel cell system at low temperatures. SOLUTION: Since the temperature in the vicinity of an air electrode and a fuel electrode of a fuel cell 10 is higher than the cooling water outlet temperature, the temperature of the air electrode and the fuel electrode is above 0°C when the cooling water outlet temperature exceeds 0°C, and the fuel cell 10 is in a temperature condition wherein moisture is not frozen. Therefore, if humidification is started when the cooling water temperature has exceeded 0°C, an electrolyte film in the fuel cell 10 can be humidified while avoiding freezing of moisture in the fuel cell 10 when starting it at low temperatures, and the maximum cell output can be obtained in a short time even when starting the fuel cell system at low temperatures. COPYRIGHT: (C)2004,JPO	DENSO CORP	2004-04-02
JP2004022198A US2003232226A1	**Fuel Cell System** PROBLEM TO BE SOLVED: To provide a fuel cell system capable of starting a fuel cell even in a low temperature environment. SOLUTION: The fuel cell system comprises an outside air temperature detecting means 25 for detecting an outside air temperature in the vicinity of the fuel cell 1, an outside air temperature forecast means S11 for forecasting the transition of the outside air temperature based on the changes of the outside air temperature detected by the outside air temperature detecting means 25 after the stop of the fuel cell 1, a freeze	DENSO CORP	2004-01-22

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	determination means S 12 for determining whether or not the forecast outside air temperature forecast by the outside air temperature means S 11 drops below a prescribed water freezing temperature, and a freeze prevention means S14 for preventing the freezing of water inside the fuel cell when the forecast outside air temperature is determined to drop below the prescribed water freezing temperature by the freeze determination means S 12. The outside air temperature forecast means S11 time-differentiates the change of the outside air temperature and forecasts by computing the transition of the outside air temperature.		
EP01113516B1	**Method of cold start-up of a PEM fuel cell** [From equivalent EP1113516A1] A method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H2 and O2 on the anode and/or cathode catalysts. To their end, H2 is introduced into the O2-rich cathode feed stream and/or O2 is introduced into the H2-rich anode feed stream.	General Motors Corporation	2004-04-28
US06727013B2	**Fuel cell energy management system for cold environments** An energy management system controls the temperature of a fuel cell system while a vehicle is not running. The energy management system includes a fuel cell stack, a blower that provides air to the fuel cell stack, a water supply, and a hydrogen supply. A hydrogen supply valve is connected between the hydrogen supply and the fuel cell stack. A heater is connected to an output of the fuel cell stack. A controller controls the hydrogen supply valve and the blower to power the heater to warm the fuel cell stack and the water supply. The controller starts the blower and opens the hydrogen supply valve if heating is necessary and if a tank level signal exceeds a first tank level value. The controller activates a purge, drains water from the water supply, and inhibits vehicle startup if the tank level signal does not exceed a first tank level value.	General Motors Corporation	2004-04-27
WO04017444A3	**Control System and Method for Starting a Frozen Fuel Cell** A method for starting a frozen fuel cell stack includes discontinuing reactant humidification before shutting down the fuel cell stack. The anode and cathode are purged with the dry	General Motors Corporation	2004-02-26

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	reactants. The fuel cell stack is soaked at freezing temperatures. During subsequent startup, dry reactants are initially delivered. An outlet temperature of the anode and a current load of the fuel cell stack are measured. The dry reactants are shut off when the temperature of the anode outlet or the current load reach predetermined values. The open circuit voltage potential of the fuel cells is monitored and compared to a first voltage value. When the open circuit voltage exceeds the first value, the fuel cell stack begins supplying current load. The current load of the fuel cell stack is increased or decreased based on a difference between the minimum voltage and a second voltage value. Cette invention concerne une méthode de lancement d'une pile à combustible gelée consistant à interrompre l'humidification du réactif avant de couper ladite pile. Un réactif sec est utilisé pour purger l'anode et la cathode. La pile à combustible est noyé à des températures sub-zéro. Au moment du démarrage suivant, on administre d'abord des réactifs secs. On mesure la température de sortie de l'anode et la charge de courant de la pile à combustible. L'alimentation en réactifs secs est coupée lorsque la température en sortie d'anode ou la charge de courant atteint des valeurs prédéterminées. La différence de potentiel en circuit ouvert de la pile à combustible est surveillées et comparée. Lorsque la tension en circuit ouvert dépasse la première valeur, la pile à combustible commence à débiter du courant. La charge de courant de la pile à combustible augmente ou diminue en fonction de l'écart entre la tension minimum et la seconde valeur de tension.		
WO04017444A2	**Control System and Method for Starting a Frozen Fuel Cell** A method for starting a frozen fuel cell stack includes discontinuing reactant humidification before shutting down the fuel cell stack. The anode and cathode are purged with the dry reactants. The fuel cell stack is soaked at freezing temperatures. During subsequent startup, dry reactants are initially delivered. An outlet temperature of the anode and a current load of the fuel cell stack are measured. The dry reactants are shut off when the temperature of the anode outlet or the current load reach predetermined values. The open circuit voltage potential of the fuel cells is monitored and compared to a first voltage	General Motors Corporation	2004-02-26

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	value. When the open circuit voltage exceeds the first value, the fuel cell stack begins supplying current load. The current load of the fuel cell stack is increased or decreased based on a difference between the minimum voltage and a second voltage value.		
US6815103	**Start control device for fuel cell system** At a time of starting a fuel cell when solenoids of control valves such as a check valve and a discharge valve are in a frozen state, hot air obtained by adiabatic compression at an air supply portion is divisionally supplied into a warm-up box through a warm-up valve. It is determined whether the discharge valve is opened by determining whether the discharge fuel gas pressure Pout is reduced below a predetermined pressure while the check valve is in an opened state. After confirming that the discharge valve has been opened, it is determined whether the check valve can be closed by determining whether the pressure near the fuel supply port of the fuel cell has risen above the predetermined pressure stored in the memory. The warm-up operation of the fuel cell can thereby be efficiently conducted and the fuel cell can be reliably started.	Honda Giken Kogyo Kabushiki Kaisha	2004-11-09
US6808832	**Fuel cell Humidifying System** The fuel cell humidifying system is to prevent freezing and clogging of a water permeable type humidifier by providing a gas passage switching device for changing the gas flow paths communicating with the humidifier. To direct the flow of dry air exiting from the supercharger to the exhaust passage in the humidifier, the gas passage switching device includes a first three-way valve, a second three-way valve, a flow adjusting valve and a sweep piping. In this system, water vapor in the humidifier which causes freezing can be swept off by flowing dry air through the exhaust gas passage in the humidifier, and therefore, clogging caused by ice particles which plug up the pores of the hollow thread membrane in the humidifier can be prevented.	Honda Giken Kogyo Kabushiki Kaisha	2004-10-26
JP2004193102A	**Fuel Cell Operating Method and a Fuel Cell Operating Device** PROBLEM TO BE SOLVED: To provide a fuel cell operating method capable of preventing freezing of a reaction gas passage, and minimizing energy necessary for drainage by draining water in a system only when it is necessary. SOLUTION: In the operating method for a fuel	Honda Motor Co., Ltd.	2004-07-08

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	cell 1, gaseous hydrogen and air are supplied as reaction gases to each reaction gas passage 5 and 6, and power generation is carried out by electrochemical reaction. It is characterized by that water in the reaction gas passages 5 and 6 are drained and operation of the fuel cell 1 is stopped by cutting off electric power supply from the fuel cell 1, detecting an outside air temperature, and supplying the reaction gases to the reaction gas passages 5 and 6 in response to the outside air temperature.		
JP2004178950A	**Fuel Cell with Start Warm-Up Mechanism** PROBLEM TO BE SOLVED: To provide a fuel cell with a start warm-up mechanism aimed at shortening of a start warm-up period of the fuel cell at low temperature (including a temperature below freezing point), uniformity of internal temperature distribution, and reduction of energy necessary for the start warm-up. SOLUTION: The fuel cells 1, 1' is formed by further accumulating cells each formed by laminating a separator 4, at a sheet-shaped end surface of which, a plurality of ribs conducting supply gas are arranged, an MEA 5 composed of a polymer electrolyte film, a catalyst, and a diffusion layer, and a separator 4, at the sheet-shaped end surface of which, a plurality of air conducting ribs are arranged, in a superposed state. The fuel cell 1 has an inside heating means for warming up the device when starting by selectively induction heating the polymer electrolyte film, moisture remained in the polymer electrolyte film, and the separator by a high frequency power source impressing a prescribed voltage on the fuel cell 1.	Honda Motor Co., Ltd.	2004-06-24
JP2004172049A	**OPERATION METHOD OF POWER GENERATION SYSTEM AND FUEL CELL** PROBLEM TO BE SOLVED: To continue power generation by avoiding freezing of product water even when a fuel cell is made started below freezing point. SOLUTION: The power generation system is provided with a fuel cell 1 equipped with an anode and a cathode on either side of a solid polymer electrolyte film and generating power as the anode is supplied with hydrogen and the cathode is supplied with air. When the fuel cell 1 is started or stopped below 0°C, product water produced in accordance with power generation is made antifreeze, by supplying	Honda Motor Co., Ltd.	2004-06-17

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	alcohol to an evaporator 3 fitted halfway through an air supply channel 21 and supplying alcohol vapor together with air to the cathode of the fuel cell 1.		
JP2004152599A	**Controlling Equipment of Fuel Cell** PROBLEM TO BE SOLVED: To provide a control device for a fuel cell maintaining the starting property of the fuel cell well. SOLUTION: A fuel cell 2 loaded on a car 1, a starting means 5 and a shutdown means of the fuel cell 2 which can be operated manually, a means 8 to inhibit energizing stop of the fuel cell 2 until the temperature of the fuel cell 2 exceeds a specified value when the fuel cell 2 is started in a sub zero temperature, and purge means 4a and 4b are provided.	Honda Motor Co., Ltd.	2004-05-27
JP2004150298A2	**HYDROGEN PUMP AND FUEL CELL SYSTEM USING THE SAME** PROBLEM TO BE SOLVED: To provide a hydrogen pump and a fuel cell system using the hydrogen pump capable of protecting the hydrogen pump from locking due to freezing without lowering pump performance. SOLUTION: In the hydrogen pump, hydrogen gas is sucked and exhausted into a casing 12 with the rotation of an impeller 14. A groove is cut in the end face 19 of the impeller 14 or the inside face 20 of the casing 12 opposed to it.	Honda Motor Co., Ltd.	2004-05-27
EP1385223A3	**Fuel cell system with anti-freezing Operation Modes** A fuel cell system comprises a reformer for reforming a feed material to generate a reformed gas containing hydrogen, a material feed means for feeding the feed material to the reformer, a heater for heating the reformer, a fuel cell for generating a power by reacting the reformed gas supplied from the reformer with an oxidizing gas, and a temperature detector for detecting a temperature at a predetermined position in the fuel cell system, and in a first antifreezing operation mode, when the detector detects a temperature which is not higher than a threshold, the feed material heated in the reformer by the heater is caused to flow through flow passages of the reformed gas.	MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.	2004-04-07
JP2004071539A2	**System with Small Generator to Melt Frozen Metal Plate Placed in Device for Reacting Oxygen and Hydrogen of Fuel Cell Vehicle** PROBLEM TO BE SOLVED: To enable travelling of a fuel cell vehicle which is considered unable to travel in a cold district. SOLUTION: The system with a small generator	MISAWA NOBUHIRO	2004-03-04

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	to melt a frozen metal plate placed in a device for reacting oxygen and hydrogen of a fuel cell vehicle mounts the small generator (of which the fuel is alcohol or benzene) on the vehicle to prevent the vehicle from becoming unable to travel due to a malfunction of the device in the vehicle for reacting oxygen and hydrogen of the vehicle as a result that the metal plate placed in the device is frozen when a temperature of outside air drops below freezing because the metal plate is always covered with water to introduce hydrogen, and the metal plate is melted by feeding a current supplied from the generator to the metal plate. The system can promote a full-scale actual use of the vehicle.		
EP1490923A2	**FREEZE PROTECTED FUEL CELL SYSTEM**	Nissan Motor Co., Ltd.	2004-12-29
EP1479123A2	**FREEZE-PROTECTED FUEL CELL SYSTEM AND METHOD OF PROTECTING A FUEL CELL FROM FREEZING**	Nissan Motor Co., Ltd.	2004-11-24
EP1472752A1	**FREEZE PREVENTION OF A FUEL CELL POWER PLANT**	Nissan Motor Co., Ltd.	2004-11-03
EP1414090A1	**Freeze protected fuel cell system** A fuel cell system has a heater (10,11) for heating water in the fuel cell system; and a controller (100) for controlling the heater. The controller (100) executes a stop mode having the smaller energy consumption of a temperature maintenance mode where water in the fuel cell system is maintained to a temperature greater than freezing point in a period after a shutdown the fuel cell system until a scheduled start-up date-time and a defrost start-up mode where frozen water in the fuel cell system is melted when the fuel cell system undergoes a start-up operation. The controller (100) stores a historical external temperature data for a period prior to the shutdown of the fuel cell system. The historical external temperature data is used for predicting the external temperature for the scheduled start-up date-time. The controller (100) calculates the energy consumption in the defrost start-up mode based on the predicted external temperature.	Nissan Motor Co., Ltd.	2004-04-28
JP2004234892A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To prevent freezing of a fuel cell when operation is stopped. SOLUTION: A fuel cell 1 is stored in a sealed state inside a case 3 and a gas layer 7 is	Nissan Motor Co., Ltd.	2004-08-19

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	provided in between the case 3 and the fuel cell 1. When a system is stopped, the interior of the gas layer 7 is made vacuum by operating a vacuum pump 31 and the fuel cell 1 and the outside of the case 3 are insulated.		
JP2004207110A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To provide a fuel cell system using pure water, preventing pure water from freezing during system shutdown period. SOLUTION: When shutting down the system, pure water is introduced from a humidifying device 4 to a pure water tank 11, if water freezing is suspected. Hydrogen gas is introduced from a high pressure hydrogen tank 22 as a fuel tank for the fuel cell 2 to the pure water tank 11 to pressurize inside the tank. When starting the system, a heater 26 is activated to heat the pure water inside the pure water tank 11 to a temperature higher than a freezing point under the atmospheric pressure to release the pressured status.	Nissan Motor Co., Ltd.	2004-07-22
JP2004192940A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To reduce a thawing time of frozen water in a water tank to improve starting performance of a fuel cell system. SOLUTION: This fuel cell system is so structured that a gas carrying means composed of a gas pump 26, a suction pipe 27 and a discharge pipe 28 is installed on the water tank 22; gas in the water tank 22 is sucked by the gas carrying means to discharge it into the water tank 22 in thawing the frozen water in the water tank 22, and the frozen water and the unfrozen water in the water tank 22 are stirred by the discharged gas.	Nissan Motor Co., Ltd.	2004-07-08
JP2004186028A2	**WATER TANK FOR FUEL CELL VEHICLE** PROBLEM TO BE SOLVED: To provide a water tank for a fuel cell vehicle in which a thawing time can be shortened and energy required to thaw can be saved. SOLUTION: A pure water thawing tank 1 capable of freezing the pure water safely has a tapered protrusion 2 rising from the bottom face at its center part. An electric heater 10 as a heating means is installed at the pure water thawing tank 1, a thawing water storage tank 4 to temporarily store the thawing water, a diaphragm pump 5, and a piping 7. In the case the ice in the pure water thawing tank 1 is thawed, it is heated by supplying electricity to the electric heater 10. Because the water	Nissan Motor Co., Ltd.	2004-07-02

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	thawed in the pure water thawing tank 1 promptly flows down to the thawing water storage tank 4, contact of the ice with the wall face of the pure water thawing tank 1 is maintained, and thermal conductivity becomes superior. The water of the thawing water storage tank 4 is sprinkled on the ice in the pure water thawing tank 1 from a water spray port 8 via the diaphragm pump 5, a switching valve 6, and the piping 7, and the ice can be thawed quickly.		
JP2004171837A2	**THAWING TANK AND FUEL CELL SYSTEM USING THIS** PROBLEM TO BE SOLVED: To provide a thawing tank in which an ice can be promptly thawed by effectively transmitting the heat of the heating means to the ice when the stored water is frozen and become ice. SOLUTION: One of the heat sinks 3, 4 with which a heater is incorporated is movement freely arranged in the water tank 1. When the water 2 stored in the water tank 1 is frozen and become ice 11, this ice 11 is pinched by the heat sinks 3, 4 and the heat of the heater incorporated with the heat sinks 3, 4 is transmitted to the ice 11 and the ice is thawed. When thawing of the ice 11 is progressed and the ice becomes small, the heat sink 4 is moved so as to narrow the space between the heat sinks 3, 4, and to make the not thawed ice 11 always contact the heat sinks 3, 4. Thereby, the heat of the heater is transmitted effectively to the ice 11 not thawed and prompt thawing can be performed.	Nissan Motor Co., Ltd.	2004-06-17
JP2004146187A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To provide a fuel cell system in which precision for determining the frozen state of water in a water tank is enhanced. SOLUTION: A pressure sensor 23 to detect the pressure of the water is installed in a through conduit of piping 21 in which the pressure of the water is regulated by a pressure control valve 22, and based on the pressure detection result of the pressure sensor 23, the frozen state of the water in the water tank 18 is determined.	Nissan Motor Co., Ltd.	2004-05-20
JP2004139771A2 WO2004036675A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To prevent unnecessary power and fuel consumption of a fuel cell other than is used for power generation as an intended purpose. SOLUTION: The system, provided with a	Nissan Motor Co., Ltd.	2004-05-13

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	fuel cell (1) generating power by a reaction of hydrogen and air supplied to each electrode of a cell part, a humidifier (34) humidifying supply gas with the use of water from a water tank (31), and coolant temperature adjustment means (21, 22, 25, 26, 27, 28, 51) making temperature adjustment of a coolant flown inside the fuel cell (1) for controlling temperature of the fuel cell (1), is further provided with an ice thawing device (61) for thawing ice inside the water tank (31) with the use of the coolant rising in temperature by heat exchange inside the fuel cell (1) with waste heat occurring from the power generation of the fuel cell (1).		
JP2004134220A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To carry out humidification effectively with minimum energy even at low temperature starting when there is a possibility of freezing of water, and realize small sizing of the system for humidification. SOLUTION: This system comprises a cooling system which circulates cooling water containing anti-freeze solution to the fuel cell 1, humidifiers 3, 7 which humidify the fuel and air to be supplied to the fuel cell 1, a heat exchanger 8 which recovers the moisture in the exhaust gas, a pure water tank 27 which stores the recovered water, a pure water separation means 18 which separates and extracts the pure water from a part of the cooling water, a heater 19 which heats the pure water separation means 18, a pump 20 which sends the pure water from the pure water tank 27 and the pure water separation means 18 to the humidifiers 3, 7, and a sensor 29 which detects the temperature of the pure water tank 27. When freezing of the pure water is presumed, the pure water separated by the pure water separation means 18 is supplied for humidification, and when freezing is released, separation of the pure water at the pure water separation means 18 is stopped, and the pure water from the pure water tank 27 is supplied for the humidification.	Nissan Motor Co., Ltd.	2004-04-30
JP2004119308A2	**WATER TANK AND FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To provide a water tank capable of obtaining water for humidification in a short time by quickly melting frozen ice, and a fuel cell system with a short start-up time. SOLUTION: The water tank 1 is cone-shaped with its tip facing downward. A heat medium tube 4 as a heating means is fitted	Nissan Motor Co., Ltd.	2004-04-15

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	around and in contact with a cone-shaped tank wall 2. A heat medium 5 heated by combustion heat of hydrogen combustor is circulated in the heat medium tube 4 to melt ice in the water tank 1. A liquid water exhaust tube 3 is communicated with the tip part of the cone of the tank wall 2 and serves as an exhaust outlet for water.		
JP2004111243A2	**WARM-UP SYSTEM OF FUEL CELL** PROBLEM TO BE SOLVED: To surely prevent condensed water from freezing as at the time of start-up below freezing point. SOLUTION: A fuel cell 1, a combustor 3 combusting fuel gas and air, and a heat exchanger 4 for heating cooling water circulated in the fuel cell 1 by heat exchange with reaction heat of the combustor 3 are provided. A partial vapor pressure in exhaust gas is calculated from a fuel volume, an air volume supplied to the combustor 3 and exhaust gas pressure. When the partial vapor pressure calculated is higher than a saturated vapor pressure at a temperature of the fuel cell at that time and a fuel cell temperature is below freezing point, it is judged that there is a fear of the fuel cell freezing, and the exhaust gas from the combustor 3 is exhausted without guiding it into the fuel cell. When there is no more fear of freezing, it is guided into the fuel cell 1.	Nissan Motor Co., Ltd.	2004-04-08
JP2004111196A2	**OPERATION METHOD OF FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To provide an operating method for a fuel cell system which can prevent its being frozen after the stop of the operation and whose starting time is shortened. SOLUTION: When the fuel cell is stopped operating, a control device 49 changes over three-way valves 7, 11, 31, and 35 into bypass passages 13 and 37, and an output current smaller than in the normal operating condition is taken out of a fuel cell stack 21 while a dried hydrogen and dried air are supplied to the fuel cell stack 21 so as to purge the excessive water/moisture, and the fuel cell stack 21 is prevented from drying of MEA (Membrane Electrode Assembly) with a minute quantity of produced water.	Nissan Motor Co., Ltd.	2004-04-08
JP2004087301A2 US2005118473A1	**FUEL CELL APPARATUS** PROBLEM TO BE SOLVED: To efficiently and quickly defrost frozen ice in a water tank. SOLUTION: During normal travel, an antifreeze flows between a fuel cell stack 1 and an	Nissan Motor Co., Ltd.	2004-03-18

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	radiator 11, and radiates the heat absorbed from the fuel cell stack 1 through the radiator 11. At cold start, a 3-way valve 13 switches so that the antifreeze flows between fuel cell stack 1 and a heat exchanger 17. A water tank 5 is disposed on the lower stream side of the fuel cell stack 1, and a hot medium flow path 25 where antifreeze flows is formed at the outer periphery of the water tank 5. The antifreeze heated by the heat exchanger 17 heats the fuel cell stack 1 and the water tank 5. The heated water tank 5 defrosts the frozen ice. The water in the water tank 5 is used for humidifying the fuel cell stack 1, etc.		
JP2004055378A2	**FUEL CELL SYSTEM FOR VEHICLE INSTALLATION** PROBLEM TO BE SOLVED: To provide a fuel cell system capable of being humidified even at extremely low temperatures without freezing. SOLUTION: In this fuel cell system, a gas supplied to a fuel cell stack 14 is humidified by pure water. The fuel cell system is provided with: a film module 22 equipped with a pervaporation film 22c for selectively filtering and separating pure water from a nonfreezing solution in a decompressed atmosphere; a nonfreezing solution supply system 21 for supplying the nonfreezing solution to the film module 22; and humidification means 26, 13 and 31 for mixing, in the supply gas supplied to the cell stack 14, the pure water filtered by applying the decompressed atmosphere to the film module 22. The supply gas is humidified by using the pure water separated and extracted from the nonfreezing solution by the film module 22.	Nissan Motor Co., Ltd.	2004-02-19
JP2004047210A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To shorten time until a fuel cell is ready to generate power, and reduce fuel and power consumption for melting ice in a water container. SOLUTION: The fuel cell 1 comprises a cell part and a humidifying part, and it is provided with the water container 5 storing water, water feeders 6 and 8 feeding water in the water container 5 to the humidifying part of a fuel cell 1 interior, and a return passage 11 returning water not used by the humidifying part to the water container 5. It is provided with a combustor 2 burning hydrogen and oxygen not used by the cell part of the fuel cell 1 interior, burned gas feeding means 3, 8, 21, 22 and 23 for feeding gas burned by the combustor instead of the water to the		

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	humidifying part of the fuel cell 1 interior when the water in the water container 5 is frozen in starting of the fuel cell 1.		
WO04004035A3	**FUEL CELL STACK DEFROSTING** A fuel cell power plant comprises a fuel cell stack (1) constituted by a plurality of fuel cells which perform electric power generation by means of a reaction of hydrogen and oxygen. A controller (16) determines whether or not moisture inside the fuel cell stack (1) is frozen, and if the moisture is frozen, the controller (16) causes the fuel cell stack (1) to perform intermittent electric power generation via an inverter (27) while continuing to supply oxygen to the fuel cell stack (1). The fuel cell stack (1) generates heat as a result of the electric power generation, whereby moisture is generated in a cathode (9) During the periods in which electric power generation is not performed, the oxygen which is supplied to the cathode (9) of the fuel cells scavenges the generated moisture, thereby ensuring the supply of oxygen to the cathode (9) during electric power generation.	Nissan Motor Co., Ltd	2004-01-08
US20040005489A1	**Fuel cell system** A fuel cell system has a heater (**10,11**) for heating water in the fuel cell system; and a controller (**100**) for controlling the heater. The controller (**100**) executes a stop mode having the smaller energy consumption of a temperature maintenance mode where water in the fuel cell system is maintained to a temperature greater than freezing point in a period after a shutdown the fuel cell system until a scheduled start-up date-time and a defrost start-up mode where frozen water in the fuel cell system is melted when the fuel cell system undergoes a start-up operation. The controller (**100**) stores a historical external temperature data for a period prior to the shutdown of the fuel cell system. The historical external temperature data is used for predicting the external temperature for the scheduled start-up date-time. The controller (**100**) calculates the energy consumption in the defrost start-up mode based on the predicted external temperature.	Nissan Motor Co., Ltd	2004-01-08
JP2004207093A2	**FUEL CELL SYSTEM AND ITS OPERATION METHOD** PROBLEM TO BE SOLVED: To prevent a fuel cell system from being broken by freezing, even if the fuel cell is mounted in a place where outdoor air temperature is low. SOLUTION: The fuel cell system 400	SANYO ELECTRIC CO LTD	2004-07-22

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	comprises a fuel cell 406, and a water supply line (such as piping 467, a water tank 411, 412) for supplying water to the fuel cell 406. The fuel cell system 400 further comprises a control part 455. The control part 455 performs an antifreeze process for preventing the water in the water supply line from freezing, if the outdoor air temperature of a casing 534 storing the fuel cell 406 is a predetermined degree or lower, for example, approximately 4°C or lower, while power generation of the fuel cell 405 is not performed.		
WO04091022A2	**FUEL CELL SYSTEM** A fuel cell system capable of proper driving even at times of low temperature, below freezing or the like. The fuel cell system includes a fuel cell stack (10), piping (24, 44), a pressure regulator (30, 48), and a control unit (16). The piping (24, 44) discharges hydrogen or air that is used in electricity generation from the fuel cell stack (10). The pressure regulator (30, 48) regulates pressure of gases which are supplied and discharged to and from the fuel cell stack in accordance with the size of a load. The control unit (16) judges whether or not there is a likelihood of the pressure regulator (30, 48) freezing, and when it is judged that there is a likelihood of freezing, prohibits a degree of openness of the pressure regulator (30, 48) from going below a predetermined degree of openness.	TOYOTA JIDOSHA KABUSHIKI KAISHA	2004-10-21
WO04082053A1	**FUEL CELL SYSTEM** A gas/liquid separator (60) is provided, as a freezing judging mechanism, with electrodes (100a, 100b), an iron core (101), a magnet attractor (110a) installed under water, and guides (102a, 102b) for controlling the operation of the magnet attractor (110a). A control unit applies a voltage to the electrodes and changes the iron core (101) to an electromagnet (101) by a magnetic field produced between the electrodes. During a non-freezing time, the electromagnet (101) and the magnet attractor (110a) attract each other to close contacts (A, B) and produce a conduction state. During freezing time, the magnet attractor (110) is difficult to float up due to the presence of ice between the electromagnet (101) and the magnet attractor (110a) even if they attract each other. The control unit, when a conduction state is not detected a specified time after the application of voltage to the	TOYOTA JIDOSHA KABUSHIKI KAISHA	2004-09-23

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	electrodes, judges that water (Wa) in the gas/liquid separator (60) is frozen.		
EP1429409A1	**Fuel cell system and method of starting the frozen fuel cell system** The fuel cell system is provided which detects a freeze among specific components and portions thereof by evaluating various conditions upon starting operation of the fuel cell system. If a freeze is detected through those evaluations, the start of the system is prohibited in order to prevent some deterioration in the fuel cell system.	TOYOTA JIDOSHA KABUSHIKI KAISHA	2004-06-16
US20040106026A1	**Fuel cell system and method of controlling the same fuel cell system** The fuel cell system is provided which detects a freeze among specific components and portions thereof by evaluating various conditions upon starting operation of the fuel cell system. If a freeze is detected through those evaluations, the start of the system is prohibited in order to prevent some deterioration in the fuel cell system.	TOYOTA JIDOSHA KABUSHIKI KAISHA	2004-06-03
JP2004172025A2	**FUEL CELL SYSTEM** PROBLEM TO BE SOLVED: To avoid degradation and breakage of a fuel cell system by activating when freezing. SOLUTION: When a starting operation of the fuel cell system is performed, a shut bulb 21 is opened and temperature is measured with a temperature sensor 102. When the measured temperature is below a specified value, the pressure value is judged whether normal or not by a pressure sensor 54. When it's normal, a discharge valve 26 is opened and the amount of decreased pressure measured by the pressure sensor 54 is judged whether normal or not. Then, the discharge valve 26 is closed, and the pressure increasing amount measured by the pressure sensor 54 is judged whether normal or not. Then, a hydrogen pump 45 is started and rotational speed is judged whether normal or not. Then, a compressor 41 is activated and the pressure value measured by a pressure sensor 53 is judged whether normal or not. In the above decision, if there is at least one abnormality, it is judged that there is a frozen part and activation of the system is prohibited.	TOYOTA MOTOR CORP	2004-06-17
US6797421	**Method and apparatus for preventing water in fuel cell power plants from freezing during storage** A keep warm system for a fuel cell, power plant (10), typically of the PEM type, prevents	UTC Fuel Cells, LLC	2004-09-28

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	freeze-sensitive portions of the power plant, such as the cell stack assembly (CSA) (12) and the water management system (28, 30), from freezing under extreme cold external temperatures, during extended storage (CSA shut-down) periods. Pre-stored and pressurized fuel, typically hydrogen (25), normally used to fuel the anode (16) of the CSA, is used as fuel for a catalytic oxidation reaction at a catalytic burner (66) to produce heated gas that convectively passes in heat exchange relation with the freeze sensitive portions (12, 28, 30) of the power plant (10). The convective flow of the heated gases induces the air flow to the burner (66), obviating the need for parasitic electrical loads. Thermal insulating means (64) substantially enclose the freeze-sensitive CSA (12) and/or the water management system (28, 30), and the convective flow of the heated gas from the catalytic burner (66), to improve system thermal efficiency.		
US6777115	**Battery-boosted, rapid startup of frozen fuel cell** A fuel cell stack (7) has an auxiliary load (30) in series with a battery (29) which can selectively (25) be connected across the fuel cell stack in place of a main load (24). A method includes connecting the battery and auxiliary load across the fuel cell stack while providing fuel (13) to the anode flow fields (8, 10); in one embodiment, oxidant (17) is provided to the cathode flow fields (16) initially; in a second embodiment, oxidant is withheld from the cathode flow for a predetermined time or until a threshold voltage is reached.	UTC Fuel Cells, LLC	2004-08-17
US6773840	**Configuration enabling rapid fuel cell power from sub-freezing initial condition** A start system for enabling rapid fuel cell power from sub-freezing initial conditions in a fuel cell power plant which comprises heating an antifreeze coolant source and melting ice in the sump of a cell stack assembly with the heated antifreeze to effect start up.	UTC Fuel Cells, LLC	2004-08-10
US6699612	**Fuel cell power plant having a reduced free water volume** The invention reduces free water volume in a fuel cell power plant so support systems of the plant are freeze tolerant. The fuel cell power plant includes a coolant system having a sealed cooler plate that circulates an antifreeze coolant in heat exchange with a fuel cell and	UTC Fuel Cells, LLC	2004-03-02

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	that collects fuel cell water; a water vapor removal system that removes water vapor from the antifreeze coolant to regulate the antifreeze concentration; and a start-up system having a start-up heat exchanger and a start-up valve that selectively direct heated antifreeze coolant into the cooler plate for a start-up procedure. The plant may also include a fuel processing system that utilizes the removed water vapor, and that is in heat exchange with the start-up heat exchanger. The antifreeze coolant is a low vapor pressure solution, such as an alkanetriol or polyethylene glycol.		
US6673481	**Initiating operation of an electric vehicle or other load powered by a fuel cell at sub-freezing temperature** A vehicle (150) includes a fuel cell stack (151) started when the stack is below freezing, by connection (158) to the vehicle propulsion system (159) within a few seconds of starting the flow of fuel (179) and oxidant (173), or when open circuit voltage (155, 156) is detected. The fuel is in excess of stochiometry requirement and the oxidant is in excess of at least twice stochiometric requirement, either may be at about atmospheric pressure or at 4 kPa (0.6 psi) or more above the pressure of any water in said water passages, and either may be below freezing. Water transport plates (84, 86, 88, 89) have water passages connected to a water circulation loop (170) including a reservoir (164) having an auxiliary heater (161) connected (160) to the stack. Warming of cell stack materials and ice in the water transport plates, heat of fusion of melting ice, warming of melted water, and evaporative cooling of water melted in the water transport plates keep the fuel cell cool until liquid coolant can be circulated.	UTC Fuel Cells, LLC	2004-01-06
WO04107839A2	**MAINTAINING AND RESTORING PEM FUEL CELL PERFORMANCE DESPITE SUB-FREEZING BOOT STRAP AND FREEZE/THAW CYCLES** Temperature of cathodes (34, 92) of fuel cells (16, 80) are maintained at sufficient temperatures above temperatures of corresponding anodes (24, 90) either before, during or after cold starts and after freeze thaw cycles to cause migration of water from cathodes to anodes, thereby to preserve or restore performance. Temperatures may be controlled by heaters (48, 49, 54) or by heating (91, 96) process air, by flowing air through just the anode to be	UTC FUEL CELLS, LLC	2004-12-16

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	cooled by vaporization, by flowing air through both anodes and the cathodes, the cathode's air being warmer, or by bleeding (120) H2 into cathodes momentarily.		
WO04073133A3	**FUEL CELL STACK MELTING OF COOLANT WATER DURING FROZEN STARTUP** A PEM fuel cell system (19) has a multifunction oxidant manifold (98) disposed contiguously beneath a fuel cell stack (20), serving as coolant accumulator (28). An electric heater (45) is powered by the fuel cell electrical output (47, 51) during frozen startup. Auxiliary pump (54) and conduits (55, 57, 58) forces water (28) above oxidant pressure in upper coolant manifold (41), into the oxidant flow fields to be warmed before flowing from the oxidant exhaust to the accumulator to melt additional ice. Alternatively, melted coolant is forced by oxidant pressure into coolant channels for heating. Conduit (61) conducts coolant from the coolant flow fields to the accumulator. A condensing heat exchanger (65) embedded in accumulator coolant receives oxidant exhaust. A condensing heat exchanger (70) has cold inlet air (75) and warm moist oxidant exhaust (72) on opposite sides, condensing liquid into the accumulator. Melting of coolant may be started by a heater (45) powered by a battery (80) or by circulating externally heated (83) glycol.	UTC FUEL CELLS, LLC	2004-08-26
WO04073133A2	**FUEL CELL STACK MELTING OF COOLANT WATER DURING FROZEN STARTUP** A PEM fuel cell system (19) has a multifunction oxidant manifold (98) disposed contiguously beneath a fuel cell stack (20), serving as coolant accumulator (28). An electric heater (45) is powered by the fuel cell electrical output (47, 51) during frozen startup. Auxiliary pump (54) and conduits (55, 57, 58) forces water (28) above oxidant pressure in upper coolant manifold (41), into the oxidant flow fields to be warmed before flowing from the oxidant exhaust to the accumulator to melt additional ice. Alternatively, melted coolant is forced by oxidant pressure into coolant channels for heating. Conduit (61) conducts coolant from the coolant flow fields to the accumulator. A condensing heat exchanger (65) embedded in accumulator coolant receives oxidant exhaust. A condensing heat exchanger (70) has cold inlet air (75) and warm moist oxidant exhaust (72) on opposite sides, condensing liquid into the accumulator. Melting of coolant may be started by a heater	UTC FUEL CELLS, LLC	2004-08-26

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	(45) powered by a battery (80) or by circulating externally heated (83) glycol.		
WO04025752A3	**BATTERY-BOOSTED, RAPID STARTUP OF FROZEN FUEL CELL** A fuel cell stack (7) has an auxiliary load (30) in series with a battery (29) which can selectively (25) be connected across the fuel cell stack in place of a main load (24). A method includes connecting the battery and auxiliary load across the fuel cell stack while providing fuel (13) to the anode flow fields (8,10); in one embodiment, oxidant (17) is provided to the cathode flow fields (16) initially; in a second embodiment, oxidant is withheld from the cathode flow for a predetermined time or until a threshold voltage is reached.	UTC FUEL CELLS, LLC	2004-03-25
WO04025752A2	**BATTERY-BOOSTED, RAPID STARTUP OF FROZEN FUEL CELL** A fuel cell stack (7) has an auxiliary load (30) in series with a battery (29) which can selectively (25) be connected across the fuel cell stack in place of a main load (24). A method includes connecting the battery and auxiliary load across the fuel cell stack while providing fuel (13) to the anode flow fields (8,10); in one embodiment, oxidant (17) is provided to the cathode flow fields (16) initially; in a second embodiment, oxidant is withheld from the cathode flow for a predetermined time or until a threshold voltage is reached.	UTC FUEL CELLS, LLC	2004-03-25
WO04004056A1	**SHUTDOWN PROCEDURE TO IMPROVE STARTUP AT SUB-FREEZING TEMPERATURES** A method for shutting down a fuel cell system including a plurality of fuel cells arranged in a stack, includes cooling the fuel cells to a shutdown temperature while maintaining a substantially uniform water vapor pressure through the fuel cells whereby migration of water within the fuel cells during cooling is reduced.	UTC FUEL CELLS, LLC	2004-01-08
WO04109822A2	**MAINTAINING PEM FUEL CELL PERFORMANCE WITH SUB-FREEZING BOOT STRAP STARTS** The fuel cells (16, 18) adjacent or near the end plate (15) of a fuel cell stack (14) are warmed either by (a) a heater wire (48, 50) within the fuel cell (16) adjacent to the end plate, (b) heater wires (53) disposed in a heater element (52) located between the end plate and the fuel cell closest to the end plate (15), (c) one or more heaters (56) are disposed in holes (55) within the end plate (15), (d) a catalytic heater (61) disposed	UTC FUEL CELLS, LLC.	2004-12-16

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	on the inner surface of the end plate, or (e) catalytic burner (78, 100) disposed adjacent a current collector (70) between an end cell (16) and insulation (81) on an end plate (82). The fuel cells (16, 18) may be heated before or during startup at sub-freezing temperatures to prevent loss of fuel cell performance.		
US20040247967A1	**Maintaining PEM fuel cell performance with sub-freezing boot strap starts** The fuel cells (16, 18) adjacent or near the end plate (15) of a fuel cell stack (14) are warmed either by (a) a heater wire (48, 50) within the fuel cell (16) adjacent to the end plate, (b) heater wires (53) disposed in a heater element (52) located between the end plate and the fuel cell closest to the end plate (15), (c) one or more heaters (56) are disposed in holes (55) within the end plate (15), (d) a catalytic heater (61) disposed on the inner surface of the end plate, or (e) catalytic burner (78, 100) disposed adjacent a current collector (70) between an end cell (16) and insulation (81) on an end plate (82). The fuel cells (16, 18) may be heated before or during startup at sub-freezing temperatures to prevent loss of fuel cell performance.		2004-12-09
US20040247965A1	**Maintaining PEM fuel cell performance with sub-freezing boot strap starts** The fuel cells (16, 18) adjacent or near the end plate (15) of a fuel cell stack (14) are warmed either by (a) a heater wire (48) within the fuel cell (16) adjacent to the end plate, (b) heater wires (53) are disposed in a heater element (52) located between the end plate and the fuel cell closest to the end plate (15), (c) one or more heaters (56) are disposed in holes (55) within the end plate (15), (d) electric heating elements (59) on a surface of the end plate (15), or (e) a catalytic heater (61) disposed on the surface of the end plate. The fuel cells (16, 18) may be heated before or during operation at sub-freezing temperatures to prevent loss of fuel cell performance, or may be heated after operation at sub-freezing temperatures to restore fuel cell performance.		2004-12-09
US20040224191A1	**Vacuum assisted startup of a fuel cell at sub-freezing temperature** A vehicle (150) includes a fuel cell stack (151) started below freezing, by connection (158) to the vehicle propulsion system (159) within a few seconds of starting the flow of fuel (179) and oxidant (173), or when open circuit voltage (155, 156) is detected. The fuel in		2004-11-11

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	excess of stochiometry requirement and the oxidant in excess of at least twice stochiometric requirement, are at atmospheric pressure and at 4 kPa (0.6 psi) or more above the pressure of any water in said water passages due to a water passage vacuum pump 205, and may be below freezing. Water transport plates (84, 86, 88, 89) have water passages connected to a water circulation loop (170) including a reservoir (164) having an auxiliary heater (161) connected (160) to the stack. Warming of cell stack materials and ice in the water transport plates, heat of fusion of melting ice, warming of melted water, and evaporative cooling of water melted in the water transport plates keep the stack cool until liquid coolant is circulated.		
US20040219401A1	**Operation method and purging system for a hydrogen demand/delivery unit in a fuel cell system** The invention pertains to a process for preventing the freezing of water in a structural component containing at least one moving part in the anode cycle of a fuel cell system, characterized by the fact that at the time of a switching-off process the structural component is scavenged by a dry scavenging gas in order to remove a quantity of water present there.		2004-11-04
US20040209135A1	**Cold start pre-heater for a fuel cell system** A fuel cell system with fuel cells displaying cooling channels (26) assembled to form a fuel cell stack (10), with a coolant cycle (16) in which coolant is circulated by a pump (72) in a main cycle (70) which includes the cooling channels and a cooler (74) and with a heat storage unit (100) and a heating device (104) is characterized by the fact that the heat storage unit (100) is arranged in a branch (102) on the coolant cycle (16) parallel to the cooler (74), that a heat exchanger (106) that can be heated by the heating device (104) is arranged in a second branch (108) parallel to the heat storage unit (100), that a second pump (110) in the first branch (102) is arranged in front of the heat storage unit (100), that a two-way switching valve (112) is provided which displays a first connection (114) arranged in a first branch (102) in front of the second pump (110), a second connection (116) arranged in the first branch (102) in front of the second pump (110) and a third connection (118) which is arranged in the second branch (108) in front of the heat exchanger (106), and that a T connection		2004-10-21

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	(120) is provided between the first branch (102), the second branch (108) and the main cycle (70).		
US20040191581A1	**System and method for starting a fuel cell stack assembly at sub-freezing temperature** A method for operating a fuel cell stack assembly having a plurality of fuel cells arranged in a stack to define opposed end fuel cells, wherein the plurality of fuel cells include intermediate fuel cells between the opposed end fuel cells, including feeding fuel and oxidant to the intermediate fuel cells whereby the at least one end fuel cell transports hydrogen across the cell and produces heat.		2004-09-30
US20040166388A1	**Fuel cell energy management system for cold environments** An energy management system controls the temperature of a fuel cell system while a vehicle is not running. The energy management system includes a fuel cell stack, a blower that provides air to the fuel cell stack, a water supply, and a hydrogen supply. A hydrogen supply valve is connected between the hydrogen supply and the fuel cell stack. A heater is connected to an output of the fuel cell stack. A controller controls the hydrogen supply valve and the blower to power the heater to warm the fuel cell stack and the water supply. The controller starts the blower and opens the hydrogen supply valve if heating is necessary and if a tank level signal exceeds a first tank level value. The controller activates a purge, drains water from the water supply, and inhibits vehicle startup if the tank level signal does not exceed a first tank level value.		2004-08-26
US20040157094A1	**Fuel cell stack melting of coolant water during frozen startup** A PEM fuel cell system (19) has a multifunction oxidant manifold (98) disposed contiguously beneath a fuel cell stack (20), serving as coolant accumulator (28). An electric heater (45) is powered by the fuel cell electrical output (47, 51) during frozen startup. Auxiliary pump (54) and conduits (55, 57, 58) forces water (28) above oxidant pressure in upper coolant manifold (41), into the oxidant flow fields to be warmed before flowing from the oxidant exhaust to the accumulator to melt additional ice. Alternatively, melted coolant is forced by oxidant pressure into coolant channels for heating. Conduit (61) conducts coolant from the coolant flow fields to the		2004-08-12

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	accumulator. A condensing heat exchanger (65) embedded in accumulator coolant receives oxidant exhaust. A condensing heat exchanger (70) has cold inlet air (75) and warm moist oxidant exhaust (72) on opposite sides, condensing liquid into the accumulator. Melting of coolant may be started by a heater (45) powered by a battery (80) or by circulating externally heated (83) glycol.		
US20040001982A1	**INITIATING OPERATION OF AN ELECTRIC VEHICLE OR OTHER LOAD POWERED BY A FUEL CELL AT SUB-FREEZING TEMPERATURE** A vehicle (**150**) includes a fuel cell stack (**151**) started when the stack is below freezing, by connection (**158**) to the vehicle propulsion system (**159**) within a few seconds of starting the flow of fuel (**179**) and oxidant (**173**), or when open circuit voltage (**155, 156**) is detected. The fuel is in excess of stochiometry requirement and the oxidant is in excess of at least twice stochiometric requirement, either may be at about atmospheric pressure or at 4 kPa (0.6 psi) or more above the pressure of any water in said water passages, and either may be below freezing. Water transport plates (**84, 86, 88, 89**) have water passages connected to a water circulation loop (**170**) including a reservoir (**164**) having an auxiliary heater (**161**) connected (**160**) to the stack. Warming of cell stack materials and ice in the water transport plates, heat of fusion of melting ice, warming of melted water, and evaporative cooling of water melted in the water transport plates keep the fuel cell cool until liquid coolant can be circulated.		2004-01-01
US20040001981A1	**Shutdown procedure to improve startup at sub-freezing temperatures** A method for shutting down a fuel cell system including a plurality of fuel cells arranged in a stack, includes cooling the fuel cells to a shutdown temperature while maintaining a substantially uniform water vapor pressure through the fuel cells whereby migration of water within the fuel cells during cooling is reduced.		2004-01-01
WO00059058A1	**Fuel Cell Battery With a Heating Element and Improved Cold-Start Performance and Method for Cold-starting a Fuel Cell Battery** The invention relates to a PEM or a PAFC fuel cell battery with a heating element and improved cold start performance. The	Siemens Aktiengesellschaft (DE/DE), München, DE	2000-10-05

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	invention also relates to a method for cold-starting such a battery. The heating element, e.g., a wire, heats a minimal area of a fuel cell unit. The entire battery can then be auto-thermally heated up starting at said area.		
WO00103217A1	**Assembly for heating/cooling a fuel cell and a fuel cell system** The invention relates to a fuel cell system (10), comprising a fuel cell (20) and an assembly (30) for heating/cooling said fuel cell (20). The assembly (30) enables the fuel cell (20) and the streams of gas which are fed to the fuel cell (20) to be preheated and to be rapidly brought up to the ideal operating temperature, in particular, during a rapid start-up of the fuel cell system (10). A flow line (31) for a heating/cooling medium is provided for this purpose, which is connected or can be connected to the fuel cell (20) in such a way that a thermal exchange occurs or can occur between the fuel cell (20) and the heating/cooling medium. At least one heat sink (35;36) is also provided in the flow line (31) which is/can be connected to a supply line for the fuel (21) and/or a supply line for the oxidation agent (23) for the fuel cell (20) in such a way that a thermal exchange occurs/can occur between the heat sink(s) (35; 36) and the fuel and/or the oxidation agent for the fuel cell (20). The inventive assembly (30) also enables the waste heat, which is generated in the fuel cell (20) to be used to heat the fuel and/or the oxidation agent. A heating device (42), configured as a burner, is also provided for the additional heating of the heating/cooling medium, for example during a cold-start of the fuel cell system (10).	ATECS Mannesmann AG (DE/DE), Düsseldorf, DE	2001-01-11
WO00122515A1	**Method and system for starting a fuel cell stack of a fuel cell arrangement** The invention enables to electrically cold-start a stack by simply applying a voltage to the electrodes of at least one cell and by leading hydrogen into the cathode chamber. The electrodes and the membrane are then quickly and electrically heated without corrosion problems occurring.	Siemens Aktiengesellschaft (DE/DE), München, DE	2001-03-29
WO00152339A1	**Liquid-Fuel-Cell System** The invention relates to a fuel cell system comprising an anode chamber (2) a cathode chamber (3), which are separated from one another by a proton-conductive membrane (4). A gas containing oxygen flows through the	DaimlerChrysler AG (DE/DE), Stuttgart (DE)	2001-07-19

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	cathode chamber. A liquid fuel/coolant mixture, preferably a mixture of methanol and water is guided in a circuit through the anode chamber. To provide greater frost-protection and improved cold-starting capability, a temperature in the fuel cell system is monitored, even when said system is at a standstill and if a drop in temperature occurs, the concentration of fuel in the anode circuit is increased.		
WO00186745A2	**Method for cold starting fuel cells of a fuel cell facility and corresponding fuel cell facility** Cold starting is carried out by directly converting process gas into thermal energy by means of a catalytic reaction. The thermal energy is used to heat up the fuel cell stack, wherein the process of heating up the fuel cell stack is carried out separately from the operation of the fuel cell facility. To this end, heating elements (20/40) form separate components in the fuel cell stack (10/30), which are mounted in a predetermined order in said fuel cell stack.	Siemens Aktiengesellschaft (DE/DE), München (DE)	2001-11-15
WO00186745A3	**Method for cold starting fuel cells of a fuel cell facility and corresponding fuel cell facility** Cold starting is carried out by directly converting process gas into thermal energy by means of a catalytic reaction. The thermal energy is used to heat up the fuel cell stack, wherein the process of heating up the fuel cell stack is carried out separately from the operation of the fuel cell facility. To this end, heating elements (20/40) form separate components in the fuel cell stack (10/30), which are mounted in a predetermined order in said fuel cell stack		2001-11-15
WO03015200A2	**Method for operating a fuel cell system** The invention relates to a method for operating a fuel cell system. Said system comprises a fuel cell unit, which is supplied with fuel and an oxidant, in addition to a gas generation system, in which the fuel is obtained from the combustion agent and is cleaned in subsequent components. To initiate the system, in a first phase, a combustion agent is supplied to the reforming reactor and fuel is produced from said agent. The reforming reactor, which is at least partially filled with fuel is intermittently impinged by oxygen and the fuel is burnt catalytically in the reforming reactor, whereby said reactor heats up to an operating	OMG AG & CO. KG (DE/DE), Hanau-Wolfgang (DE)	2003-02-20

Publication	Title Abstract	Assignee	Pub. Date
	temperature.		
WO03015200A3	**Method for operating a fuel cell system** The invention relates to a method for operating a fuel cell system. Said system comprises a fuel cell unit, which is supplied with fuel and an oxidant, in addition to a gas generation system, in which the fuel is obtained from the combustion agent and is cleaned in subsequent components. To initiate the system, in a first phase, a combustion agent is supplied to the reforming reactor and fuel is produced from said agent. The reforming reactor, which is at least partially filled with fuel is intermittently impinged by oxygen and the fuel is burnt catalytically in the reforming reactor, whereby said reactor heats up to an operating temperature.	OMG AG & CO. KG (DE/DE), Hanau-Wolfgang (DE)	2003-02-20
WO03067694A1	**Freeze prevention of a fuel cell power plant** A fuel cell power plant comprises a water circulation passage (5), which circulates the cooling water in a fuel cell stack (4). Sodium hydroxide, which lowers the melting point of water is mixed with water in the water circulation passage (5) to prevent freezing of the water in the water circulation passage (5). Electrodes (11, 12) are disposed in the water. When the fuel cell stack (4) is running, a voltage is applied between the electrodes (11, 12) such that the positive electrode (11) attracts sodium ions, thereby removing sodium ions from the cooling water supplied to the fuel cell stack (4). When the fuel cell stack (4) stops running, sodium ions, which are attracted to the positive electrode (11), are made to diffuse into the cooling water by ceasing to apply the voltage to the electrodes (11, 12).	Nissan Motor Co., Ltd. (JP/JP), Kanagawa (JP)	2003-08-14
WO04021493A1	**Fuel cell device and related control method** A fuel cell device and related control method are disclosed wherein a water tank (5) is disposed downstream of a fuel cell stack (1) and a hot medium flow passage (25) is formed on an outer periphery of the water tank (5) to pass antifreeze solution. During cold start-up, a three-way vale (13) is switched over to allow antifreeze solution to flow through the fuel cell stack (1) and a heat exchanger (17), by which antifreeze solution is heated and supplied to the fuel cell stack (1) and the water tank (5) to heat these components, whereby the water tank (5) is heated to thaw frozen ice.	Nissan Motor Co., Ltd. (JP/JP), Kanagawa (JP)	2004-03-11

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WO04045012A2	**Fuel cell system** A fuel cell system comprises a hydrogen supply system (2) which supplies hydrogen to a fuel cell (1), a heating medium supply system (4) which adjusts a temperature of the fuel cell (1) by causing a heating medium to recirculate into the fuel cell (1), a burner (5) which generates high-temperature combustion gas by burning hydrogen, a heat exchanger (6) which warms the fuel cell (1) during a cold start-up operation by providing the heating medium with the heat of the combustion gas such that the heating medium is heated, a purging valve (13) which causes gas inside the hydrogen supply system (2) to flow into the burner (5), and an exhaust three-way valve (21) for discharging the combustion gas without allowing the combustion gas to pass through the heat exchanger (6). During hydrogen purging, the combustion gas is discharged by the exhaust three-way valve (21) so as to bypass the heat exchanger (6).	Nissan Motor Co., Ltd. (JP/JP), Kanagawa (JP)	2004-05-27
US006358638B1	**Cold Start-up of a PEM Fuel Cell** A method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalysts. To their end, H_2 is introduced into the O_2-rich cathode feed stream and/or O_2 is introduced into the H_2-rich anode feed stream.	General Motors Corporation , Detroit, MI (US)	2002-03-19
US006444345B2	**Fuel Cell System** A fuel cell system includes at least one fuel cell unit which is accommodated in a fuel cell enclosure. A cathode gas delivery line, cold-start gas delivery line, a cathode off-gas return line, anode off-gas return line may also be provided. According to the invention, the system is equipped with at least one Coanda flow amplifier in order to amplify the airstream for the purpose of ventilating the fuel cell enclosure, a cathode gas stream, a cold-start gas stream, a recirculated cathode off-gas stream or a recirculated anode off-gas stream. This may be equipped with a ventilating means for a housing outside the fuel cell enclosure. In the housing are components of the fuel cell system, said ventilating means including a Coanda flow amplifier.	Xcellsis GmbH, Kirchheim/ Teck-Nabern (DE)	2002-09-03
US006548200B2	**Cold Starting of Gasoline Fueled Fuel Cell** A fuel cell power plant has a fuel cell (38) receiving hydrogen (37) from a fuel processing system (12) which employs a vaporizer (19) to vaporize clean gasoline from a source (13). A conventional start burner (22) and startup	UTC Fuel Cells, LLC, South Windsor, CT (US)	2003-04-15

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	heat exchanger (28) are utilized to convert water (31) from the fuel processing system (12) and fuel cell (38) into stream (32); but during sub-zero startup, an aqueous antifreeze solution (46) is provided to the heat exchanger (28) to produce the stream (32) for starting the vaporization of gasoline in the vaporizer (19).		
US006632555B2	**Proton Electrolyte Membrane Fuel Cell with Anti-Freeze Coolant and Humidifiers** A fuel cell system comprising a closed coolant path within a fuel cell; a humidifier comprising a humidification fluid flow path and a fuel and air gas supply passage continuous in, through, and out of the humidifier; the humidification fluid flow path and the fuel and air gas supply passage separated by a water permeable membrane that is impervious to organic materials allowing water from the humidification fluid flow path to enter the fuel and air gas supply passage; and the humidifier connected to the fuel cell by a humidified air and fuel passageway. The water permeable membrane can be a keggin ion pillared a-ZrP composite material. The coolant can be water and organic material mixture, such as glycol, thus allowing the coolant flow in temperatures below the freezing point.	Ballard Power Systems, Inc. Burnaby, CA	2003-10-14
US006660415B2	**Method for Improving the Light-Off Performance of Mobile Fuel Cell Systems** In a method for improving cold starting of a catalytically active component in gas generation systems for a mobile fuel cell system, a temporary store is arranged directly in the starting-material gas stream. During cold starting, the temporary store stores gaseous constituents from the gaseous starting material, which constituents cause problems when starting, and releases such constituents (which have been stored during the cold-start phase) again as a result of the heating which takes place as operation of the system continues.	Ballard Power Systems, AG Kirchbeim, DE	2003-12-09
US210024747A1	**Fuel Cell System** A fuel cell system includes at least one fuel cell unit which is accommodated in a fuel cell enclosure. A cathode gas delivery line, cold-start gas delivery line, a cathode off-gas return line, anode off-gas return line may also be provided. According to the invention, the system is equipped with at least one Coanda flow amplifier in order to amplify the air stream for the purpose of ventilating the fuel	N/A	2001-09-27

Publication	Title Abstract	Assignee	Pub. Date
	cell enclosure, a cathode gas stream, a cold-start gas stream, a recirculated cathode off-gas stream or a recirculated anode off-gas stream. This may be equipped with a ventilating means for housing outside the fuel cell enclosure. In the housing are components of the fuel cell system, said ventilating means including a Coanda flow amplifier.		
US210055707A1	**Apparatus for Improving the Cold Starting Capability of an Electrochemical Fuel Cell** An electric power generation system has components that improve the cold start capability and freeze tolerance of a constituent fuel cell stack. The components cooperate to reduce the amount of water remaining within the passages of the stack. The system includes a purge system that is connectable to the oxidant supply, the fuel supply and/or the coolant passages upstream of the stack. When the stack is shut down, the stack is disconnected from an external circuit, and purge fluid is directed by the purge system through the stack before the stack falls below the freezing point of water. In systems where the fuel and/or oxidant streams are humidified prior to their introduction into the stack, a humidifier bypass system may be provided in place of the purge system. The humidifier bypass system directs reactant fluid to the stack in fluid isolation from the humidifier, so that the inlet reactant streams are unhumidified.	N/A	2001-12-27
US220009623A1	**Methods and Apparatus for Improving the Cold Starting Capability of a Fuel Cell** Apparatus and methods of ceasing operation of an electric power generating system improve the cold-starting capabilities of the system. The system comprises a fuel cell stack connectible to an external circuit for supplying electric current to the external circuit. The stack comprises at least one solid polymer fuel cell and the system further comprises a fuel passage for directing a fuel stream through the stack and an oxidant passage for directing an oxidant stream through the stack, a sensor assembly connected to the stack for monitoring a parameter indicative of stack performance, a controller for controlling at least one operating parameter of the stack, and a control system communicative with the sensor assembly and operating parameter controller. The method comprises adjusting at	N/A	2002-01-24

Publication	Title Abstract	Assignee	Pub. Date
	least one fuel cell stack operating parameter to cause the stack to operate under a drying condition that causes a net outflux of water from the stack, operating the stack under the drying condition until the water content in the stack has been reduced, and interrupting supply of electric current from the stack to the external circuit.		
US220068202A1	**Method for Cold-Starting a Fuel Cell Battery, and Fuel Cell Battery Suitable for This Method** The invention relates to a PEM or PAFC fuel cell battery with heater element and improved cold-starting performance, and to a method for cold-starting such a battery, in which the heater element initially heats up a minimal area of a fuel cell unit, from which auto-thermal heating-up of the entire battery then becomes possible.	N/A	2002-06-06
US220071972A1	**Fuel Cell Battery with Heating and an Improved Cold-Start Performance, and Method for Cold-Starting of a Fuel Cell Battery** A fuel cell battery is described with a heater and an improved cold-start performance, and to a method for cold-starting of a battery of this type. The heater, such as for example a reformer, is started first, and the operating heat from the heater is utilized to heat the fuel cell stack.	N/A	2002-06-13
US220119353A1	**Integrated Fuel Cell System** The invented system includes a fuel cell system comprising a fuel cell that produces electrical power from air (oxygen) and hydrogen, and a fuel processor that produces hydrogen from a variety of feedstocks. One such fuel processor is a steam reformer which produces purified hydrogen from a carbon-containing feedstock and water. In the invented system, various mechanisms for implementing the cold start-up of the fuel processor are disclosed, as well as mechanisms for optimizing and/or harvesting the heat and water requirements of the system, and maintaining desired feed ratios of feedstock to water in the fuel processor and purity of the process water used in the system.	N/A	2002-08-29
US220122966A1	**Cold Start and Temperature Control Method and Apparatus for Fuel Cell System** A fuel cell which provides improved performance during a cold start. Several	N/A	2002-09-05

Publication	Title Abstract	Assignee	Pub. Date
	embodiments are provided to enable the controlled introduction of fuel into the cathode of the fuel cell such that oxidation occurs, heat is released and the temperature of the fuel cell is raised. Such fuel may be introduced into the cathode directly or may be introduced into the anode and allowed to crossover an electrolytic membrane. Alternatively, the fuel may be directed through a special conduit which allows oxidation of some of the fuel as it flows through.		
US220132146A1	**Method and System for Starting a Fuel Cell Stack of a Fuel Cell Installation** The fuel cell stack can be electrically cold-started by simply applying a voltage to the electrodes of at least one cell, in combination with the introduction of hydrogen into the cathode chamber. The electrodes and the membrane are then rapidly heated electrically without corrosion problems.	N/A	2002-09-19
US230072984A1	**System and Method for Rapid Preheating of an Automotive Fuel Cell** A system for selectively and rapidly preheating one or more vehicle fuel cells during cold start or freezing conditions. The system includes a bypass valve, a controller, vehicle sensors, and a bypass conduit. The controller monitors vehicle attribute data by use of sensors to determine whether a cold start condition exists. Based upon the attribute data, controller may signal valve to bypass heat exchanger, and cause compressed air to be delivered directly to fuel cells, thereby heating the fuel cells.	N/A	2003-04-17
US230077487A1	**Methods for Improving the Cold Starting Capability of an Electrochemical Fuel Cell** Temperature dependent methods can be used to improve the cold start capability of fuel cell electric power generation systems. A method of ceasing operation of an electric power generation system improves the cold start capability and freeze tolerance of a fuel cell stack by reducing the amount of water remaining within the passages or the stack. The method involves purging one or more of the fuel cell stack oxidant and fuel passages at shutdown prior to allowing the fuel cell stack to drop to temperatures below the freezing point of water. Preferably purging at shutdown is conducted at a temperature below the stack operating temperature. Another method, used at start-up, involves directing a coolant fluid stream to the fuel cell stack only after a	N/A	2003-04-24

Publication	Title Abstract	Assignee	Pub. Date
	predetermined temperature above the freezing temperature of water is exceeded. Preferably, after freezing the fuel cell stack is heated to a temperature above its normal operating temperature before operation is commenced.		
US23162063A1	**Fuel Cell System and Method of Protecting a Fuel Cell from Freezing** A fuel cell system includes a fuel cell having a water passage and passage for gas required for power generation, a first protection device which prevents freezing of water in the fuel cell by maintaining the temperature of the fuel cell, and a second protection device which prevents freezing of water in the fuel cell by discharging the water in the fuel cell. A controller selects one of the first protection device and the second protection device as the protection device to be used when the fuel cell has stopped, and the fuel cell is protected from freezing of water by operating the selected protection device.	Nissan Motor Co., Ltd.	2003-08-28
US230190507A1	**Fuel Cell and Method for Cold-Starting Such a Fuel Cell** A fuel cell includes an electrolyte electrode assembly having a cathode disposed on a first side and an anode disposed on a second side of the electrolyte electrode assembly, a first flow module disposed adjacent the cathode, and a second flow module disposed adjacent the anode. At least one of the first and second flow modules includes a material suitable for exothermal hydride formation. In addition, a method for cold-starting such a fuel cell that includes flooding at least one of the first and second flow modules with a hydrogen-containing gas so as to induce the exothermic hydride formation and release heat; and heating the fuel cell using the heat.	DaimlerChrysler AG, Stuttgart (DE)	2003-10-09
US230207162A1	**Battery-Boosted Rapid Startup of Frozen Fuel Cell** A fuel cell stack has an auxiliary load in series with a battery which can selectively be connected across the fuel cell stack in place of a main load. A method includes connecting the battery and auxiliary load across the fuel cell stack while providing fuel to the anode flow fields; in one embodiment, oxidant is provided to the cathode flow fields initially; in a second embodiment, oxidant is withheld from the cathode flow for a predetermined time or until a threshold voltage is reached.	N/A	2003-11-06
US230209484A1	**Filter Cartridge for Liquid Media at Risk for Freezing, Particularly for Use in Fuel**	Hydraulik-Ring,	2003-11-13

Publication	Title Abstract	Assignee	Pub. Date
	Cell Operated Vehicles and In Internal Combustion Engines A filter cartridge for liquid media at risk for freezing employed in fuel cell operated vehicles and internal combustion engines has a housing and a filter lid connected to the housing for closing the housing. A filter insert is inserted into the housing and provided with a t least one filter element and terminal parts. The filter element is positioned between the terminal parts. The filter insert also has at least one pretensioning part for axially pretensioning at least one filter element. At least one reinforcement part is provided that has at least one profiled section. It is inserted into the filter element and receives at least one of torque and axial forces. This prevents twisting of the filter element and improves the sealing action and the filter function.	Gmbh, Nurtingen (DE)	
US240053096A1	**Freeze Prevention of a Fuel Cell Power Plant** A fuel cell power plant comprises a water circulation passage which circulates the cooling water in a fuel cell stack. Sodium hydroxide, which lowers the melting point of water is mixed with water in a water circulation passage to prevent freezing of the water in the water circulation passage. Electrodes are disposed in the water. When the fuel cell stack is running, a voltage is applied between the electrodes such that the positive electrode attracts sodium ions, thereby removing sodium ions from the cooling water supplied to the fuel cell stack. When the fuel cell stack stops running, sodium ions which were attracted to the positive electrode are made to diffuse into the cooling water by ceasing to apply the voltage to the electrodes.	N/A	2004-03-18
US006068941A	**Start Up of Cold Fuel Cell** A proton exchange membrane fuel cell has methanol or ethanol fed into the coolant passages during shut down so as to prevent water trapped therein from freezing in sub-freezing environments. Upon start-up, a controlled amount of air is fed through the cathode reactant flow field so that alcohol diffusing to the cathode catalyst is oxidized, producing heat which will raise the temperature of the fuel cell above freezing, and to a normal operating temperature. A heat exchanger in the coolant water circulating loop may be bypassed during start-up.	International Fuel Cells, LLC, South Windsor, Conn.	2000-05-30
US006103410A	**Start Up of Frozen Fuel Cell**	Internation	2000-08-15

Publication	Title Abstract	Assignee	Pub. Date
	During start up, a fuel cell is warmed to operating temperature by introducing a dilute hydrogen/air mixture into the normal process oxidant channels of the fuel cell where it reacts with a noble metal or noble metal alloy catalyst to produce heat at subflame temperatures. In one embodiment, catalyst is provided in a structure between the cathode and the process oxidant channels; if the structure is not sufficiently hydrophobic to allow the hydrogen/fuel mixture to reach it, such structure may be specially produced with hydrophobic regions to assure ice-free passages; in a structure with sufficient hydrophobic regions, only the catalyst need be added. In embodiments with a hydrophobic cathode, no structural modification is required; or a hydrophilic cathode may be provided with hydrophobic regions.	al Fuel Cells, LLC, South Windsor, Conn.	
US006127056A	**Start Up of Proton Exchange Membrane Fuel Cell** A proton exchange membrane fuel cell has a noble metal or noble metal allow catalyst disposed in its air inlet manifold. During startup, a fuel cell is warmed to operating temperature by introducing a small amount of hydrogen into a flow of air to the air inlet of the fuel cell where they react with the catalyst to produce heat at subflame temperatures. The adiabatic temperature rise of the gas stream is limited to about 150°F by limiting the hydrogen to about one volume percent of the fuel/oxidant mixture, thereby to be capable of raising the fuel cell temperature, for instance, from -40°C to about +45°C (+113°F) without flame, explosion or drying out of the membrane.	International Fuel Cells, LLC, South Windsor, Conn.	2000-10-03
US006277509B1	**Hydride Bed Water Recovery System for a Fuel Cell Power Plant** The invention is a hydride bed water recovery system for a fuel cell power plant that has at least one fuel cell having an electrolyte between anode and cathode electrodes for producing an electric current from a reducing fluid and an oxidant stream. A coolant loop directs a coolant fluid from a coolant reservoir through a coolant passage to the fuel cell and back to the reservoir. A process exhaust passage receives a cathode exhaust stream from the fuel cell and directs the stream away from the fuel cell and into a hydride bed cooler that passes the stream in heat exchange relationship with a condensing hydride bed of the cooler so that the bed cools the process	International Fuel Cells, LLC, South Windsor, Conn.	2001-08-21

Publication	Title Abstract	Assignee	Pub. Date
	exhaust stream to condense water out of the stream. In a preferred embodiment, the hydride bed cooler is a two-pair hydride bed cooler that includes a first pair and a second pair of hydride beds, and each pair includes a high temperature hydride bed, and a low temperature hydride bed so that each pair of hydride beds operates in alternating regeneration and cooling modes.		
US06376114B1	**Reformate Fuel Treatment System for a Fuel Cell Power Plant** The invention is a reformate fuel treatment system for a fuel cell power plant that includes at least one fuel cell for generating electricity from process oxidant and reducing fluid reactant streams; fuel processing components including a steam supply and a reformer for producing a hydrogen enriched reformate fuel for the fuel cell from a hydrocarbon fuel; and an ammonia removal apparatus that treats the reformate fuel to make it appropriate for supplying hydrogen to an anode electrode of the fuel cell. The ammonia removal apparatus may be a disposable ammonia scrubber, an ammonia scrubbing cool water bed and an ammonia stripping warm water bed, a pair of first and second regenerable scrubbers, and a single regenerable ammonia scrubber.	UTC Fuel Cells, LLC, South Windsor, Conn.	2002-04-23
US006387555B1	**Selective Oxidizer in Cell Stack Manifold** An integrated fuel cell stack assembly and selective oxidizer bed assembly is provided. The fuel cell stack assembly also includes a number of fuel cells. A fuel inlet manifold and fuel inlet plenum to cell stack manifold are arranged in fluid communication with the fuel stack assembly for supplying to and exhausting from, respectively, the fuel supply in the fuel cells in the fuel stack assembly. The bed resides in said fuel inlet manifold. The bed includes a selective oxidation catalyst with a heat exchange fluid conduit routed therethrough. Oxygen-containing gas is supplied into the bed via the input plenum. The temperature of the internal selective oxidizer bed is controlled by the fluid conduit in the bed to reduce carbon monoxide in the fuel.	UTC Fuel Cells, LLC, South Windsor, Conn.	2002-05-14
US6207309B1	**Environmental Compensation methods and apparatus for a fuel cell assembly** An environmental compensation apparatus for an electro-chemical fuel cell assembly, wherein a compressible material is dispersed within a coolant flow of the fuel cell assembly and is utilized to compensate for the expansion of the	UTC Fuel Cells, LLC, South Windsor, Conn.	2001-03-27

Publication	Title Abstract	Assignee	Pub. Date
	coolant when said fuel cell assembly is subjected to harsh environmental conditions. The compressible material is formed as a plurality of either polymeric or elastomer microspheres, each microsphere having a diameter larger than the pores of an anode or cathode flow field plate, yet smaller than the diameter of a coolant channel.		
US6479177B1	**Method For Improving The Cold Starting Capability Of An Electrochemical Fuel Cell** A method of ceasing operation of an electric power generation system improves the cold start capability and freeze tolerance of a fuel cell stack by reducing the amount of water remaining within the passages of the stack. The method involves purging one or more of the fuel cell stack oxidant and fuel passages at shutdown prior to allowing the fuel cell stack to drop to temperatures below the freezing point of water. Preferably purging at shutdown is conducted at a temperature below the stack operating temperature.	Ballard Power Systems Inc. Burnaby(CA)	2003-11-12
US5482790	**Fuel Cell Power Generation System** To generate electric energy to a load such as an electric car or the like, a fuel cell power generation system includes a fuel cell composed of a fuel electrode and an oxygen electrode with an electrolytic layer interposed therebetween so as to continuously supply electric power to the load, a secondary cell for supplying a required quantity of electric energy to the load at least during the initial time until the generation of electric energy is started with the fuel cell and a shifting unit serving to shift the power source of electric energy to the load from the fuel cell main body to the secondary cell or from the secondary cell to the fuel cell. An electrolytic layer constituting the fuel cell is composed of a film of high molecular material having ionic conductivity and a secondary cell is a secondary lithium cell consisting of a non-aqueous solution based material or a solid electrolyte based material or a solid electrolyte based material as an electrolyte.	Kabushiki Kaisha Toshiba	1996-01-09
US5605770	**Supply System for Fuel Cells of the S.P.E. Type for Hybrid Vehicles** A supply system for fuel cells of the solid polymer electrolyte type for vehicles, including a primary cooling and humidifying circuit with demineralized, pressurized water with a small volumetric capacity and a secondary liquid cooling circuit with plate exchangers for	Finmeccanica S.p.A. Azienda Ansaldo	1997-02-25

Publication	Title Abstract	Assignee	Pub. Date
	cooling the demineralized water of the primary circuit and air/liquid exchangers for cooling compressed air for supply to the cells, the system further including an electric heater for heating the liquid in the secondary circuit so that the cells can be put into service quickly and means for recycling hydrogen leaving the cells to make the optimum use of the fuel.		
US5798186	**Method and Apparatus for Commencing Operation of a Fuel Cell Electric Power Generation System Below the Freezing Temperature of Water** A method and apparatus are provided for starting and operating an electric power generation system comprising an electrochemical fuel cell stack for supplying electric current to an external electrical circuit. The stack comprises at least one fuel cell comprising a membrane electrode assembly comprising an anode, a cathode, and a water permeable ion exchange membrane interposed between the anode and the cathode. A fuel stream and an oxidant stream are each flowable to the fuel cell. At least a portion of the membrane electrode assembly has a temperature below the freezing temperature of water. The supply of electric current to the external circuit from the fuel cell stack is commenced such that the temperature of the membrane electrode assembly exceeds the freezing temperature of water.	Ballard Power System Inc.	1998-08-25
US5858568	**Fuel Cell Power Supply System** A power supply system for enhancing the economic viability of different modes of transportation that incorporate fuel cells to generate electricity. For example, the power supply system of the present invention provides for the off-board use of the electric power generated by an on-board power plant, such as a fuel cell, of a mobile vehicle power system, such as an electric car. Off-board use, or use remote from the vehicle, of the electrical power includes the delivery of power to a remote site. Off-board stations are provided for delivery of fuel to the vehicle and/or for receiving the electrical power generated by the fuel cell. The off-board station and the vehicle are appropriately equipped for quick and easy interconnection such that electrical power is drawn from the fuel cell for off-board use.	Ztek Corporation	1999-01-12
US6007930	**Method for Initiating a Fuel Cell** The present invention provides a method for	Ford Global Technologi	1999-12-28

Publication	Title Abstract	Assignee	Pub. Date
	initiating a fuel cell power system by directly introducing a gas containing oxygen into the fuel cell stack. A gas storage source provides oxidizer to the fuel cell such that there is enough initial power to generate a load. The air compressor is started electrically by a portion of the load, and begins to supply compressed air to the cathode. The fuel cell stack thereby obtains a further quantity of oxidizer from the compressed air. The air system valve then operates to transfer the fuel cell stack from the gas storage source to the air compressor.	es, Inc.	
US6087028	**Fuel-Cell System and Method of Regulating Temperature in Fuel Cell System** In a fuel-cell system, cooling water circulating through a cooling water flow path is heated by heat exchanger, carried out in fuel cells, subsequently cooled down by a radiator, and fed again to the fuel cells. A cooling water pump gives a driving force used for circulating the cooling water through the cooling water flow path. A control unit of the fuel-cells system measures an inlet cooling water temperature (T1) and an outlet cooling water temperature (T2) of the fuel cells and calculates a difference (ΔT) between the observed temperatures T1 and T2. When the difference ΔT is not less than a reference value set equal to 5°C, the control unit determines that a distribution of internal temperature of the fuel cells is in a predetermined non-uniform state. The control unit then increases the driving voltage of the cooling water pump to equalize the internal temperature of the fuel cells.	Toyota Jidosha Kabushiki Kaisha	2000-07-11
US6186254	**Temperature Regulating System for a Fuel Cell Powered Vehicle** A temperature regulating system for a fuel cell powered electric motor vehicle assists in maintaining the temperature of the fuel cell stack within a temperature range that provides satisfactory fuel cell performance.	Xcellis Fuel Cell Engines Inc.	2001-02-13
US6248462	**Method and Apparatus for Thermal Management of a Fuel Cell Assembly** An apparatus for the thermal management of an electro-chemical fuel cell assembly, wherein a plurality of thermal management loops in contact with the fuel cell assembly are utilized to maintain the fuel cell assembly above freezing or, alternatively, raise the fuel cell assembly above freezing. The thermal	International Fuel Cell, LLC	2001-06-19

Publication	Title Abstract	Assignee	Pub. Date
	management loops are in thermal communication with the fuel cell assembly as well as each other, but are diffusably isolated from one another.		
US6276473	**Hybrid Vehicle Having a an Internal-Combustion Engine, A Fuel Cell System and An Electric Drive Motor** A vehicle has an internal combustion engine drive and a fuel cell drive system. Liquid fuel is used to supply energy to the internal combustion engine drive and the fuel cell system. The internal combustion engine drive is used for starting the vehicle and for permitting its immediate movement after start of the internal combustion engine, as well as for heating the fuel cell system to a working temperature. After the working temperature is reached, the fuel cell is started. Subsequently, an electric driving motor, which is fed by the fuel cell system, alone or together with the internal combustion engine drive, drives the movement of the vehicle.	XCELLSIS GmbH	2001-08-21
US6416891	**Operating System for a Direct Antifreeze Cooled Fuel Cell Power Plant** An operating system for a direct antifreeze-cooled fuel cell power plant is disclosed for producing electrical energy from reducing and process oxidant fluid reactant streams. The system includes at least one fuel cell for producing electrical energy from the reducing and oxidant fluid streams; fuel processing components for processing a hydrocarbon fuel into the reducing fluid; a thermal management system that directs flow of a cooling fluid for controlling heat within the plant including a porous water transport plate adjacent and in fluid communication with a cathode catalyst of the fuel cell; a direct antifreeze solution passing through the water transport plate; and a split oxidant passage that directs the process oxidant stream into and through the fuel cell.	UTC Fuel Cells, LLC	2002-07-09
US6440595	**Fuel Cell System** Disclosed is a fuel cell system comprising a fuel cell which includes a feed line for a fuel and a feed line for an oxidant. To ensure adequate moistening of the fuel cell membrane even during the start-up phase of the fuel cell, a fluid reservoir containing a fluid is provided, via which the fuel and/or the oxidant are humidified before entering the fuel cell. Thus adequate moistening of the fuel cell membrane is ensured even during the start-up phase of the fuel cell. To prevent the fluid from freezing	Siemens AG;Vodafone AG	2002-08-27

Publication	Title Abstract	Assignee	Pub. Date
	at low temperatures, mixing of the fluid with an antifreeze is provided for. To ensure that the antifreeze will not pass into the fuel cell, the fluid drawn from the fluid reservoir is heated sufficiently by a heating means for evaporation of the antifreeze and separation from the fluid to take place. The heating means can include a flow conduit designed as a closed system. The flow conduit has a heating medium flowing through it which, prior to giving off heat to the fluid, is heated via a burner.		
US6467698	**Vehicles Containing Water-Producing Fuel Cells, and Methods for Using Water Produced by the Fuel Cells** A vehicle includes a fuel cell that generates electricity and water, which fuel cell includes a first end, a second end electrically coupled to the first end, and a water outlet. The water outlet of the fuel cell is connected to at least one of a washing system, a cooling system, a humidification system, and combinations thereof. In addition, a method is described for utilizing water produced by a fuel cell that includes generating water from the fuel cell and conveying a first portion of the generated water to a component of a vehicle, which component, upon actuation, transfers a liquid comprising a portion of the first portion from the component to a point distal therefrom.	Visteon Global Technologies, Inc.	2002-10-22
WO00/65676	**Freeze Tolerant Fuel Cell System and Method** A freeze tolerant fuel cell system and method of operating the freeze tolerant fuel cell system is disclosed. The freeze tolerant fuel cell system is realized by separating the coolant loop from the active membrane through the use of gaskets interposed between the collector cell plates. A method of operating the freeze tolerant fuel cell system is disclosed which comprises flowing a coolant fluid other than pure water having a sufficiently low freezing point though the coolant loop. A method for startup and shutdown of the freeze tolerant fuel cell system is also disclosed	Energy Partners, L.C.	200-11-02
WO01/24296	**Methods for Improving the Cold Starting Capability of an Electrochemical Fuel Cell** Temperature dependent methods can be used to improve the cold start capability of fuel cell electric power generation system. A method of ceasing operation of an electric power generation system improves the cold start capability and freeze tolerance of a fuel cell	Ballard Power Systems Inc.	2001-04-05

Publication	Title Abstract	Assignee	Pub. Date
	stack by reducing the amount of water remaining within the passages of the stack. The method involves purging one or more of fuel cell stack oxidant and fuel passages at shutdown prior to allowing the fuel cell stack to drop to temperatures below the freezing point of water. Preferably purging at shutdown is conducted at a temperature below the stack operating temperature. Another method, used at start-up, involves directing a coolant fluid stream to the fuel cell stack only after a predetermine temperature above the freezing temperature of water is exceeded. Preferably, after freezing the fuel cell stack is heated to a temperature above its normal operating temperature before operation is commenced.		
WO02/081367	**Method an Apparatus for the Operation of a Cell Stack Assembly During Subfreezing Temperatures** A cell stack assembly coolant comprises a coolant exhaust conduit unit in fluid communication with a coolant exhaust manifold and a coolant pump. A coolant inlet conduit enables transportation of the coolant to the coolant inlet manifold. The coolant system further included a bypass conduit in fluid communication with the coolant exhaust manifold and the coolant inlet manifold, while a bleed valve is in fluid communication with the coolant exhaust conduit and a source of gas. Operation of bleed valve enables venting of the coolant from the coolant channels, and through a shut down conduit. An increased pressure differential between the coolant and reactant gases forces water out of the pores in the electrode substrates. An ejector prevents air form inhibiting the pump. Pulsed air is blown through the coolant channels to remove more water.	UTC Fuel Cells, LLC	2002-10-17

Appendix B

Highlight Summary Presentations

NREL Presentation at 2005 Fuel Cell Freeze Workshop

NREL Presentation at 2005 Hydrogen Merit Review

NREL Presentation for Updating to DOE, August 2005

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

Fuel Cell Freeze Startup and Landscape of FC Freeze Patents

DOE Workshop on Fuel Cell Operations at
Sub-Freezing Temperatures

Phoenix, Arizona

February 1, 2005

Ahmad Pesaran
Tony Markel
Gi-Heon Kim
Keith Wipke

NREL is operated by Midwest Research Institute • Battelle

Content

- NREL's FC Freeze Project
- Patent Search – Initial Results
- System Perspective Evaluation
- Summary
- Appendix (Supporting Slides)

NREL's FY05 FC Freeze Project

As part of a Task in the FY05 AOP to DOE's HFCIT.

Objective

- Investigate and evaluate strategies for rapid startup of PEM fuel cells from sub-freezing temperatures.

Approach

- Collect data/information through literature search and collaborations
  - Patent search
- Perform energy analysis to bracket energy/power requirements for startup.
- Use component/system models to evaluate merits of various solutions from fuel efficiency and other factors within a vehicle.

Issues Found with Freeze & Rapid Startup of PEM Fuel Cells

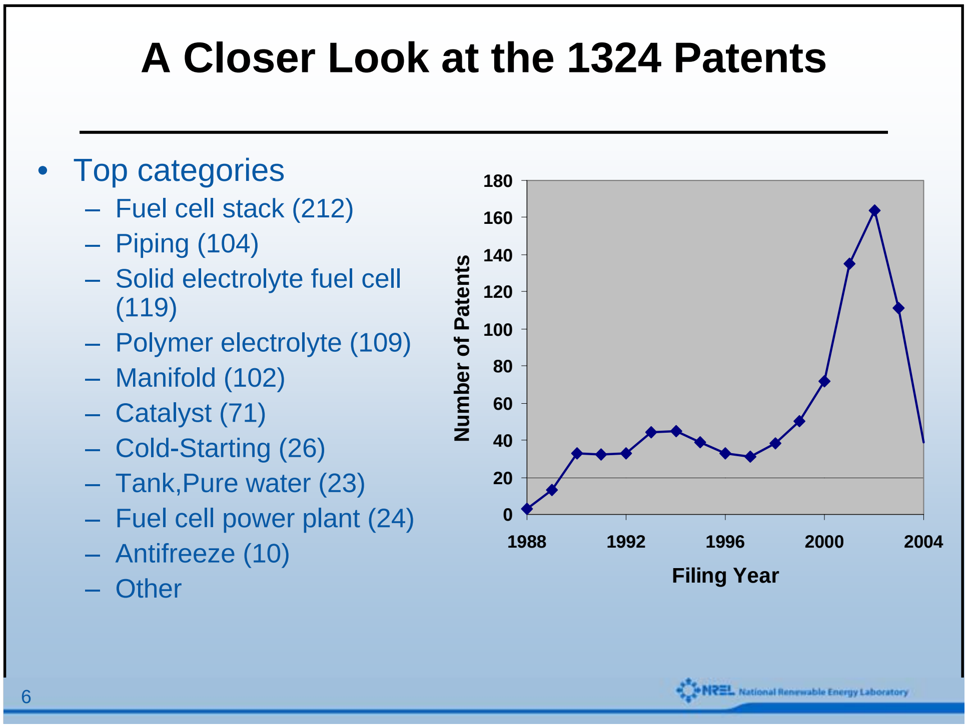
A fuel "cell" can startup at sub-freezing temperatures, but product water may form ice if local sub-freezing still exist.

- Maintaining membrane integrity
- Fuel starvation (Elimination of water droplets from flow fields)
- Cathode ice formation
  - Product water forms ice on electrode and blocks air flow
  - Ice formation in cathode flow fields
- Rapid heat up of cell/cell manifolds to prevent ice formation
  - System heating issue:
    - Where is heat coming from and how much and how fast?
    - What is impact on energy consumption and overall efficiency?
  - Rapid heat up of humidifier to prevent membrane dry out
- Balance-of-plant: Heating of fluid/gas delivery systems
  - Prevent ice blockage
  - Thermal shock to mechanical components
  - Rapid startup and protection of components

Majority of these issues appears to be system related

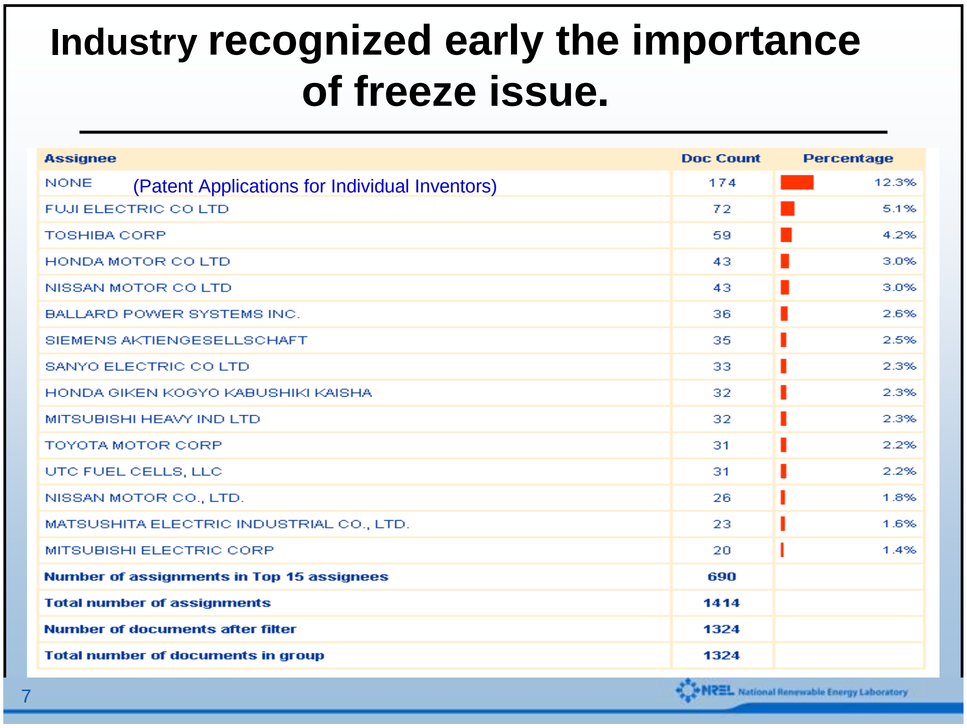
Initial Patent Search

- Search included US, Japan, and world patents
- Period of January 1988 to January 2005
- In the initial round, we used “Fuel Cell” and “Freeze” and/or “Thaw”
  - We found 1324 patents
  - Some related to reformer startup and other type of FC
- Further restricting the research to PEM and non-reformer and <u>rapid startup</u>
  - Reduced the number of patents to 177 (with some duplication in US, Japan, and world)
- Number of articles in “academic” literature less than 15, indicating that industry recognized early the importance of freeze and rapid startup.



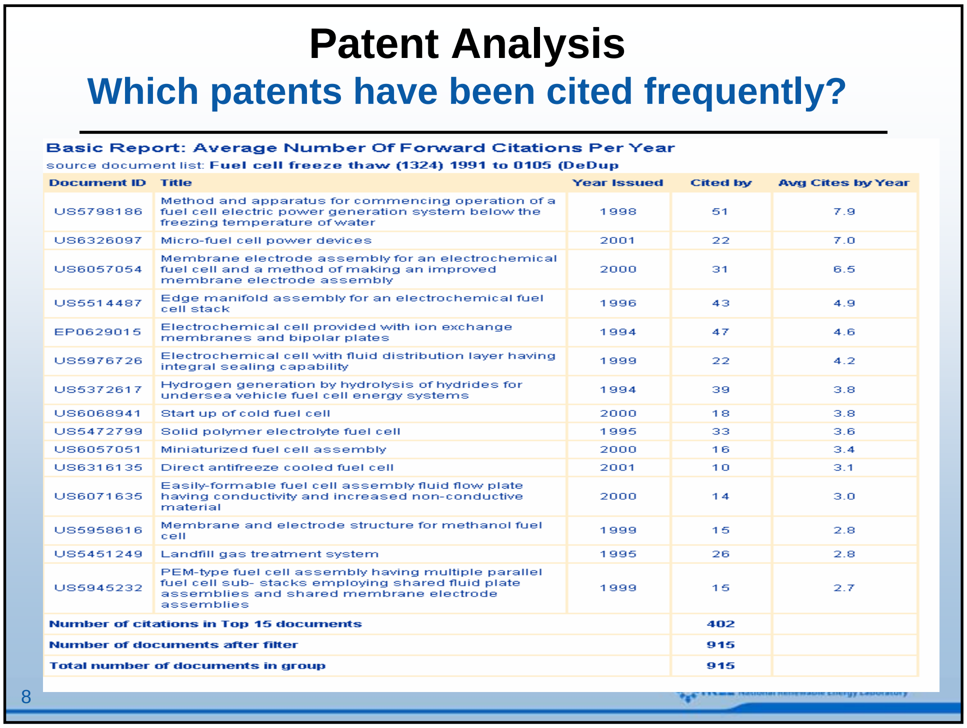
A Closer Look at the 1324 Patents

- Top categories
  - Fuel cell stack (212)
  - Piping (104)
  - Solid electrolyte fuel cell (119)
  - Polymer electrolyte (109)
  - Manifold (102)
  - Catalyst (71)
  - Cold-Starting (26)
  - Tank,Pure water (23)
  - Fuel cell power plant (24)
  - Antifreeze (10)
  - Other



Industry recognized early the importance of freeze issue.

Assignee	Doc Count	Percentage
NONE (Patent Applications for Individual Inventors)	174	12.3%
FUJI ELECTRIC CO LTD	72	5.1%
TOSHIBA CORP	59	4.2%
HONDA MOTOR CO LTD	43	3.0%
NISSAN MOTOR CO LTD	43	3.0%
BALLARD POWER SYSTEMS INC.	36	2.6%
SIEMENS AKTIENGESELLSCHAFT	35	2.5%
SANYO ELECTRIC CO LTD	33	2.3%
HONDA GIKEN KOGYO KABUSHIKI KAISHA	32	2.3%
MITSUBISHI HEAVY IND LTD	32	2.3%
TOYOTA MOTOR CORP	31	2.2%
UTC FUEL CELLS, LLC	31	2.2%
NISSAN MOTOR CO., LTD.	26	1.8%
MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.	23	1.6%
MITSUBISHI ELECTRIC CORP	20	1.4%
Number of assignments in Top 15 assignees	**690**	
Total number of assignments	**1414**	
Number of documents after filter	**1324**	
Total number of documents in group	**1324**	



Patent Analysis

Which patents have been cited frequently?

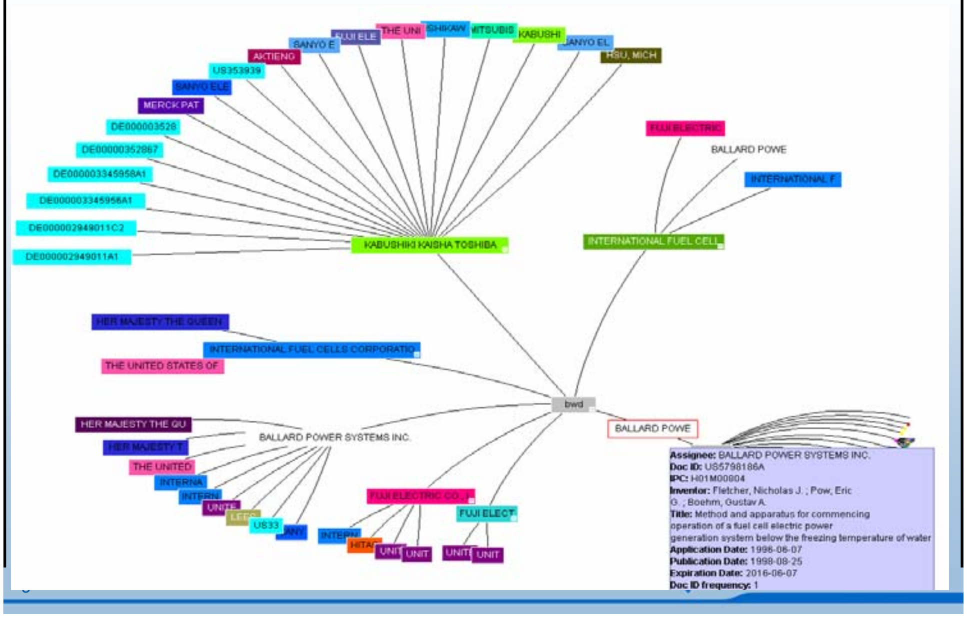
Basic Report: Average Number Of Forward Citations Per Year

source document list: **Fuel cell freeze thaw (1324) 1991 to 0105 (DeDup**

Document ID	Title	Year Issued	Cited by	Avg Cites by Year
US5798186	Method and apparatus for commencing operation of a fuel cell electric power generation system below the freezing temperature of water	1998	51	7.9
US6326097	Micro-fuel cell power devices	2001	22	7.0
US6057054	Membrane electrode assembly for an electrochemical fuel cell and a method of making an improved membrane electrode assembly	2000	31	6.5
US5514487	Edge manifold assembly for an electrochemical fuel cell stack	1996	43	4.9
EP0629015	Electrochemical cell provided with ion exchange membranes and bipolar plates	1994	47	4.6
US5976726	Electrochemical cell with fluid distribution layer having integral sealing capability	1999	22	4.2
US5372617	Hydrogen generation by hydrolysis of hydrides for undersea vehicle fuel cell energy systems	1994	39	3.8
US6068941	Start up of cold fuel cell	2000	18	3.8
US5472799	Solid polymer electrolyte fuel cell	1995	33	3.6
US6057051	Miniaturized fuel cell assembly	2000	16	3.4
US6316135	Direct antifreeze cooled fuel cell	2001	10	3.1
US6071635	Easily-formable fuel cell assembly fluid flow plate having conductivity and increased non-conductive material	2000	14	3.0
US5958616	Membrane and electrode structure for methanol fuel cell	1999	15	2.8
US5451249	Landfill gas treatment system	1995	26	2.8
US5945232	PEM-type fuel cell assembly having multiple parallel fuel cell sub- stacks employing shared fluid plate assemblies and shared membrane electrode assemblies	1999	15	2.7
Number of citations in Top 15 documents			**402**	
Number of documents after filter			**915**	
Total number of documents in group			**915**	

Citation Analysis

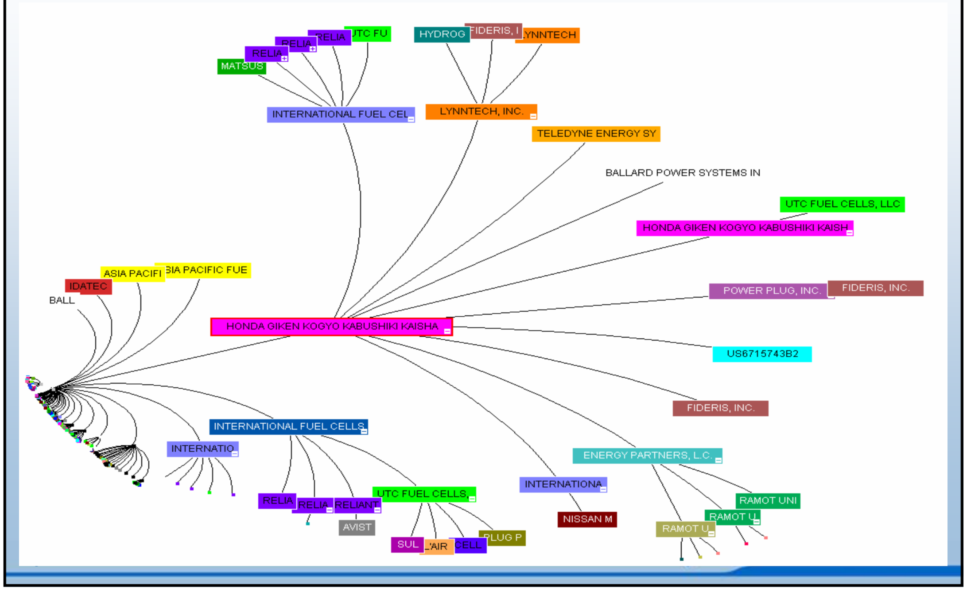
(Where patents are cited?)



Assignee: BALLARD POWER SYSTEMS INC.
Doc ID: US5798186A
IPC: H01M00804
Inventor: Fletcher, Nicholas J. ; Pow, Eric G. ; Boehm, Gustav A.
Title: Method and apparatus for commencing operation of a fuel cell electric power generation system below the freezing temperature of water
Application Date: 1996-06-07
Publication Date: 1998-08-25
Expiration Date: 2016-06-07
Doc ID frequency: 1

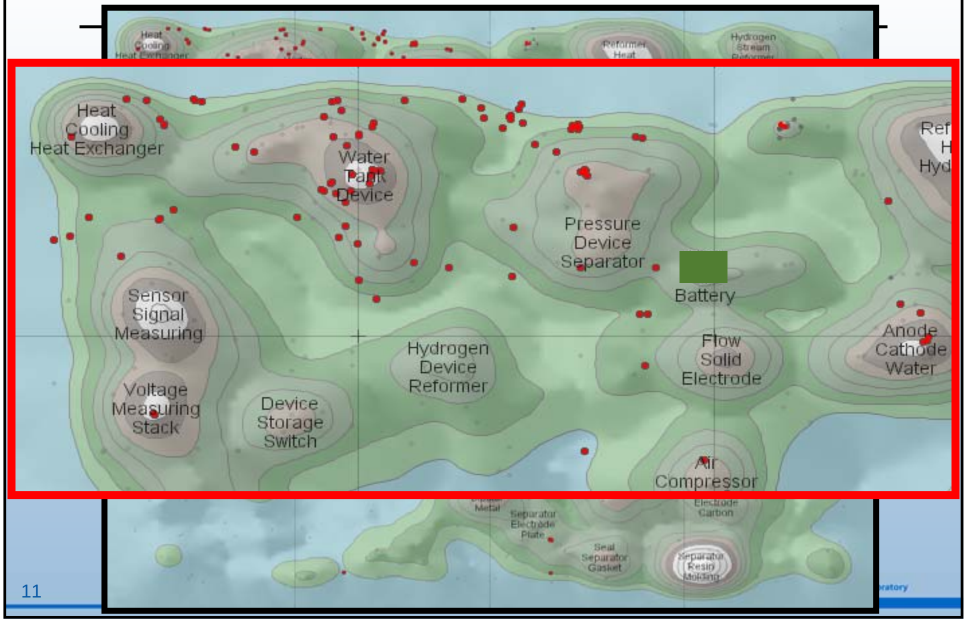
Citation Analysis

(Who is Citing who?)



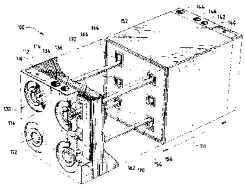
Fuel Cell Patent Map (January 2001 – March 2004)

Freeze-Thaw Patents Highlighted in Red



Example of Results

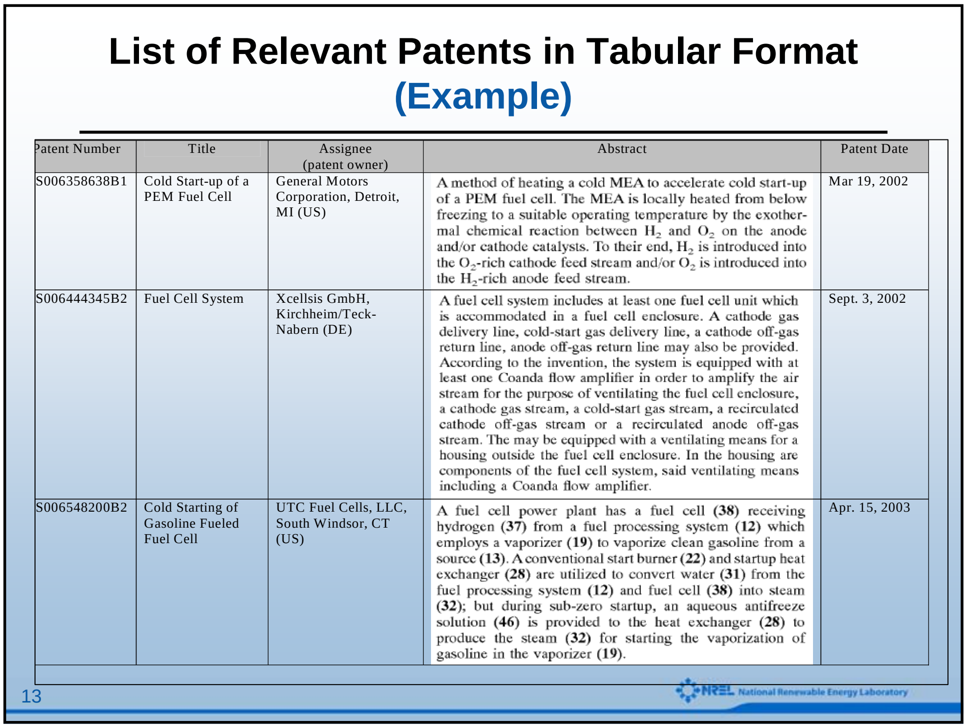
Method and apparatus for commencing operation of a fuel cell electric power generation system below the freezing temperature of water



A method and apparatus are provided for starting and operating an electric power generation system comprising an electrochemical fuel cell stack for supplying electric current to an external electrical circuit. The stack comprises at least one fuel cell comprising a membrane electrode assembly comprising an anode, a cathode, and a water permeable ion exchange membrane interposed between the anode and the cathode. A fuel stream and an oxidant stream are each flowable to the fuel cell. At least a portion of the membrane electrode assembly has a temperature below the freezing temperature of water. The supply of electric current to the external circuit from the fuel cell stack is commenced such that the temperature of the membrane electrode assembly exceeds the freezing temperature of water.

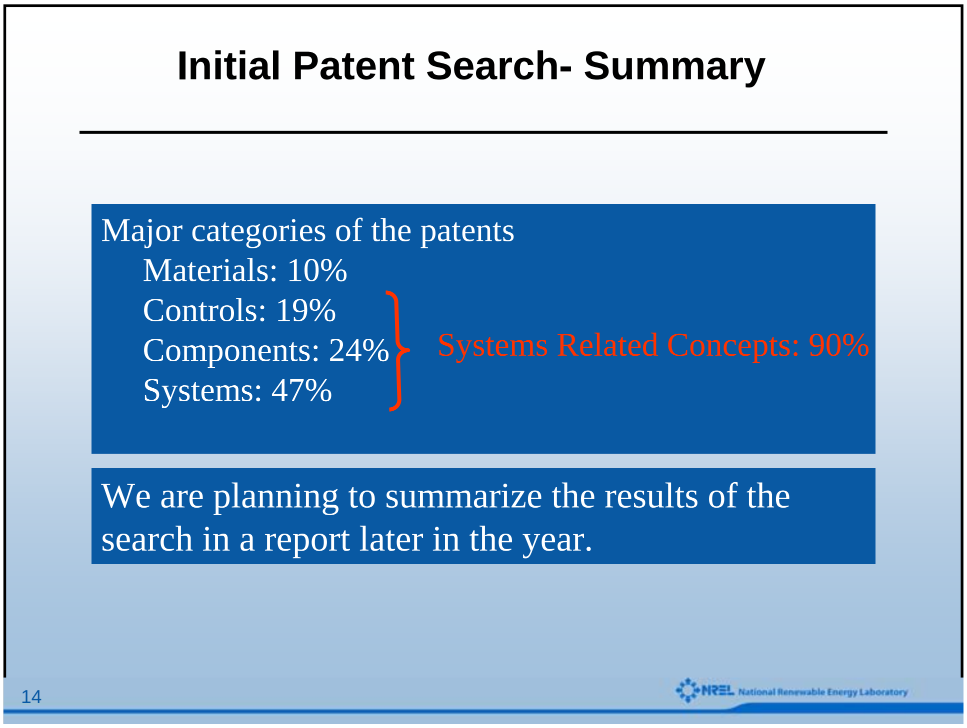
Ballard Power Systems Inc.

Fletcher, Nicholas J.
Pow, Eric G.
Boehm, Gustav A.



List of Relevant Patents in Tabular Format
(Example)

atent Number	Title	Assignee (patent owner)	Abstract	Patent Date
S006358638B1	Cold Start-up of a PEM Fuel Cell	General Motors Corporation, Detroit, MI (US)	A method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalysts. To their end, H_2 is introduced into the O_2-rich cathode feed stream and/or O_2 is introduced into the H_2-rich anode feed stream.	Mar 19, 2002
S006444345B2	Fuel Cell System	Xcellsis GmbH, Kirchheim/Teck-Nabern (DE)	A fuel cell system includes at least one fuel cell unit which is accommodated in a fuel cell enclosure. A cathode gas delivery line, cold-start gas delivery line, a cathode off-gas return line, anode off-gas return line may also be provided. According to the invention, the system is equipped with at least one Coanda flow amplifier in order to amplify the air stream for the purpose of ventilating the fuel cell enclosure, a cathode gas stream, a cold-start gas stream, a recirculated cathode off-gas stream or a recirculated anode off-gas stream. The may be equipped with a ventilating means for a housing outside the fuel cell enclosure. In the housing are components of the fuel cell system, said ventilating means including a Coanda flow amplifier.	Sept. 3, 2002
S006548200B2	Cold Starting of Gasoline Fueled Fuel Cell	UTC Fuel Cells, LLC, South Windsor, CT (US)	A fuel cell power plant has a fuel cell **(38)** receiving hydrogen **(37)** from a fuel processing system **(12)** which employs a vaporizer **(19)** to vaporize clean gasoline from a source **(13)**. A conventional start burner **(22)** and startup heat exchanger **(28)** are utilized to convert water **(31)** from the fuel processing system **(12)** and fuel cell **(38)** into steam **(32)**; but during sub-zero startup, an aqueous antifreeze solution **(46)** is provided to the heat exchanger **(28)** to produce the steam **(32)** for starting the vaporization of gasoline in the vaporizer **(19)**.	Apr. 15, 2003



Initial Patent Search- Summary

Major categories of the patents

- Materials: 10%
- Controls: 19%
- Components: 24%
- Systems: 47%

Systems Related Concepts: 90%

We are planning to summarize the results of the search in a report later in the year.

System Perspective Evaluation

Examples of Fuel Cell Freeze Systems Level Questions NREL will Answer this Year.

- How much water is needed to operate during a warm-up from -30°C to 0°C, and then 80°C?
- How long does it take to get from –30°C to 0°C, and then to 80°C?
- How long does it take to get to 50% of rated power when starting at –30° C or 0°C? 90% of rated power?
- For minimal drive cycle performance degradation what kind of battery requirements and roles be needed?
- What is the fuel economy impact of the energy needed to warm-up the system?
- What components/parts are most critical to heat in a rapid-start strategy?
- What are the thermal response of each component?
- Impact of any non-consumed reactants in the stack at startup?
- What are source of energy for heating and cost/weight/FE impacts?

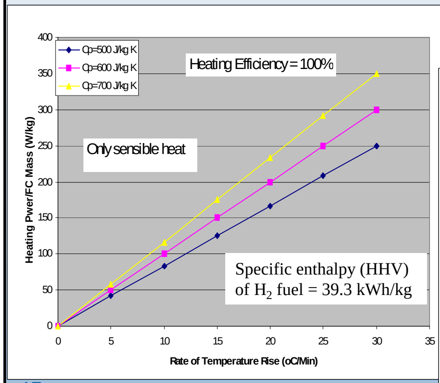
Energy Need for Heating a Frozen FC could be Reasonable, but How about Power?

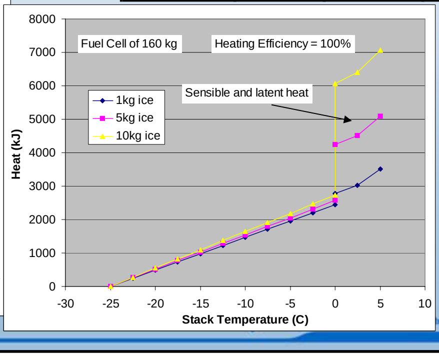
$E_{heating} = m\, C_p\, \Delta T \qquad P_{heating} = m\, C_p\, \Delta T/\Delta t$

- Parametric assumptions
  - Heat capacity ranging from all stainless steel to all graphite
  - FC specific power ranging from 400 W/kg to 1000 W/kg
  - Water content ranging from 0.5 lit to 10 lit

160kg FC with 5kg water contents

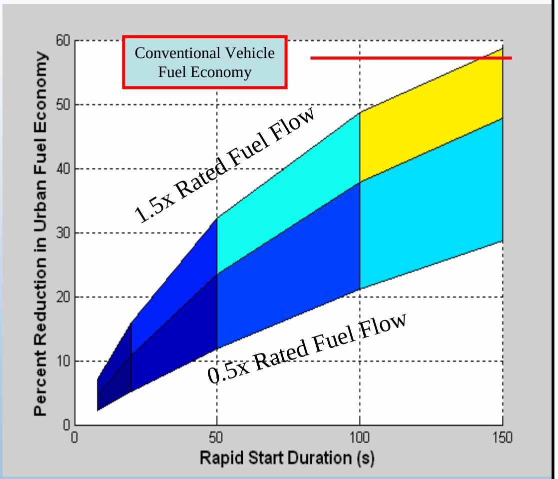
	-25C to 0C		-25C to 5C
	Sensible	Sens+Latent	Sens+Latent
Energy (kJ)	2567	4237	5091
Energy (Whr)	713	1177	1414
	Power (kW)		
for 1 sec	2567	4237	5091
for 10 sec	257	424	509
for 60 sec	42.8	70.6	84.9
for 120 sec	21.4	35.3	42.4
for 240 sec	10.7	17.7	21.2





Rapid-Start Process from a Cold-Soak Needs to be Optimized to Minimize Fuel Consumption Impacts

- Assumptions
  - System power output linearly ramps from 0 to 50% of rated power during the rapid start duration
  - Normal operation and fuel consumption assumed after reaching 50% of rated power
- Significance
  - To maintain reasonable vehicle fuel efficiency it is critical to minimize the duration and energy required for fuel cell rapid start



Summary

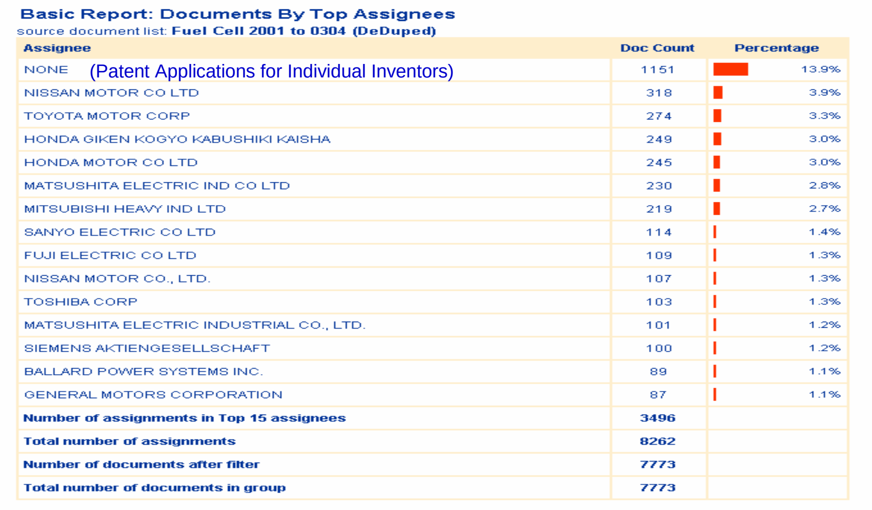
- There is high level of world wide activity in fuel cell freeze and startup issues.
- There are many more patents than published articles on the topic of fuel cell freeze and startup.
- The majority of proposed concepts/solutions is from system level perspective.
- Although many concepts are proposed, effectiveness and feasibility are not clear.
- There is a need to evaluate ideas with a systematic approach.
- NREL will use its system tools to evaluate these/other solutions.
- NREL will continue analyzing patent search results and disseminating them.

Appendix

(Supporting Slides)

Patent Search for "Fuel Cell"

Invention Assignees (until 03/04)



Basic Report: Documents By Top Assignees

source document list: **Fuel Cell 2001 to 0304 (DeDuped)**

Assignee	Doc Count	Percentage
NONE (Patent Applications for Individual Inventors)	1151	13.9%
NISSAN MOTOR CO LTD	318	3.9%
TOYOTA MOTOR CORP	274	3.3%
HONDA GIKEN KOGYO KABUSHIKI KAISHA	249	3.0%
HONDA MOTOR CO LTD	245	3.0%
MATSUSHITA ELECTRIC IND CO LTD	230	2.8%
MITSUBISHI HEAVY IND LTD	219	2.7%
SANYO ELECTRIC CO LTD	114	1.4%
FUJI ELECTRIC CO LTD	109	1.3%
NISSAN MOTOR CO., LTD.	107	1.3%
TOSHIBA CORP	103	1.3%
MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.	101	1.2%
SIEMENS AKTIENGESELLSCHAFT	100	1.2%
BALLARD POWER SYSTEMS INC.	89	1.1%
GENERAL MOTORS CORPORATION	87	1.1%
Number of assignments in Top 15 assignees	**3496**	
Total number of assignments	**8262**	
Number of documents after filter	**7773**	
Total number of documents in group	**7773**	

* None = Patent Applications or Individual Inventors

Example of Assumptions for FC Rapid Cold Start Fuel Consumption Impacts

- Durations: 8s, 50s, 150s (from Ballard presentation)
- Fueling rate: 0.5x, 1.0x, 1.5x
- System rated power: 85kW
- Stack rated power: 105kW
- Hydrogen flow at rated power: ~1.7g/s
- Oxygen flow at rated power: ~13.4g/s

NREL's Systems Capabilities

- Modeling – components and systems
- Testing equipment
- Access to major freeze facilities for vehicles
- Vehicle and industry's perspective (relationships)
- Previous programs with freeze & rapid start-up
  - Batteries for hybrid electric vehicle
  - Solar water heaters
  - PV system durability
- Experience in addressing issues such freeze from system's perspective for vehicles

---

NREL's Modeling Capabilities
Modeling - Components and Systems

Tools/Software

- ADVISOR™ vehicle simulator
- Fuel cell model in Matlab/ADVISOR™
- Water and heat management in fuel cell systems
- Heat and mass transfer and fluid flow codes (e.g, ANSYS, FLUENT, StarCD, SINDA/FLUINT)
- Thermal and system analysis (FlowMaster, ASPEN+)

Recent Related Projects

- Predicting the Fuel Economy Impact of "Cold-Start" for Reformed Gasoline Fuel Cell Vehicles (for OHFCIT)
- Effect of Material and Manufacturing Variations on Membrane Electrode Assembly Pressure Distribution (with Plug Power)
- Energy Storage System Requirements Analysis for Hybridized Fuel Cell Vehicles (for USABC and FreedomCAR Tech Teams)
- Dynamometer Testing of Insight and Prius Hybrid Vehicles, **Froze a Honda Insight** (for OFCVT)

NREL's Testing Capabilities

Battery and Power Testing Units

5- 440 V (1- 150 kW)
ABC-150 power conditioning units

Unique large
calorimeter
-30°C to 100°C

0- 70 V (0-21 kW)
six Power conditioning units

Energy Storage lab at TTF for power/energy evaluation of devices

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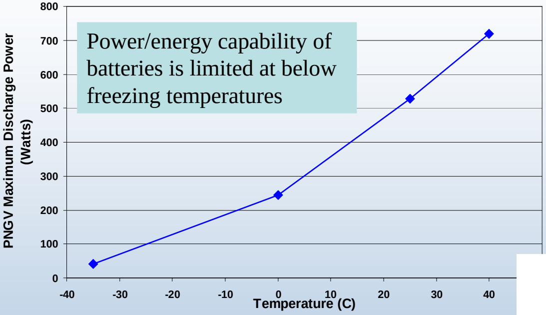
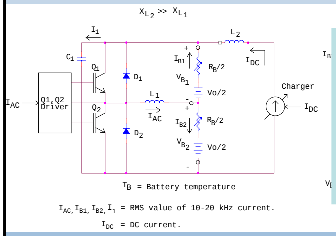
NREL's Rapid Heating of Batteries in Cold Climates

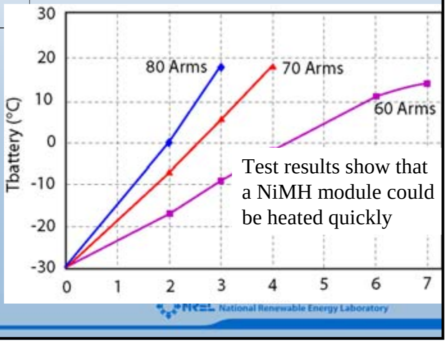
(OFCVT Energy Storage Program)



Power/energy capability of batteries is limited at below freezing temperatures



Circuit for applying high frequency alternating current power to battery and other power devices.



Test results show that a NiMH module could be heated quickly

NREL’s Testing Capabilities

Environmental and freeze chambers (capability to go to – 40°C)

Environmental chamber for durability due to weather variations & freeze (at NREL’s OTF)

Environmental chambers for battery cold and freeze studies (at NREL’s TTF)

NREL’s Complimentary Testing Capabilities

Freeze rooms along with dynamometer (at ETC, a private vehicle testing lab)

Ability to go down to - 30°C

Cold Temperature Hybrid Vehicle Testing Experience

- Performed data collection on both Insight and Prius starting from cold (32 F)
- Data available at
  http://www.ctts.nrel.gov/analysis/hev_test/index.shtml

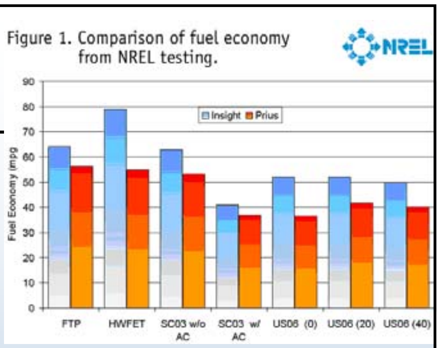
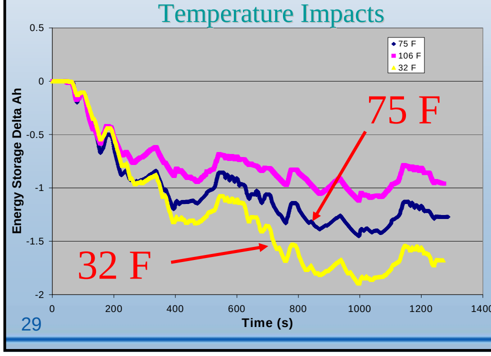


Figure 1. Comparison of fuel economy from NREL testing.

Honda Insight Testing Temperature Impacts



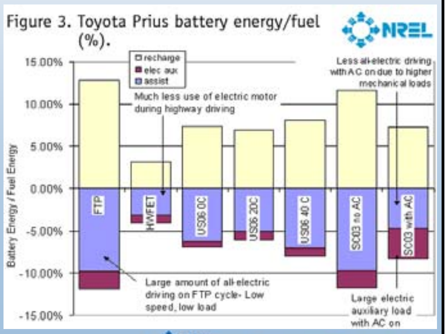


Figure 3. Toyota Prius battery energy/fuel (%).

Cold Temperature Hybrid Vehicle Testing Experience

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- Data available at
  http://www.ctts.nrel.gov/analysis/hev_test/index.shtml

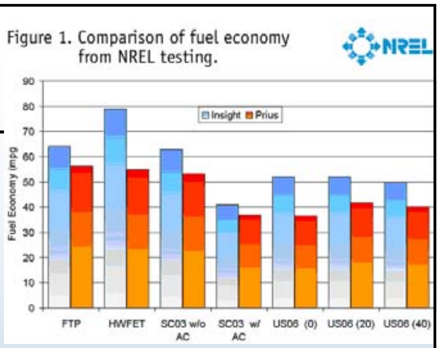
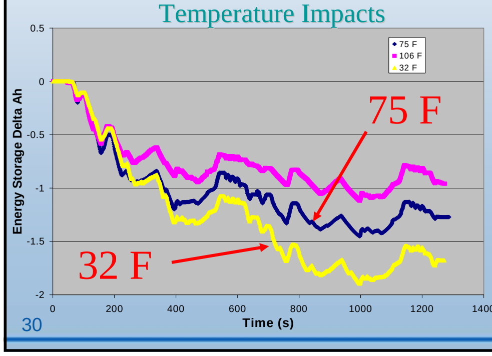


Figure 1. Comparison of fuel economy from NREL testing.

Honda Insight Testing Temperature Impacts



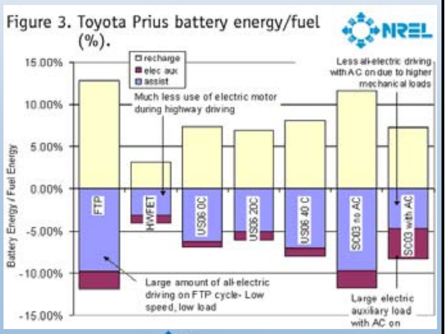
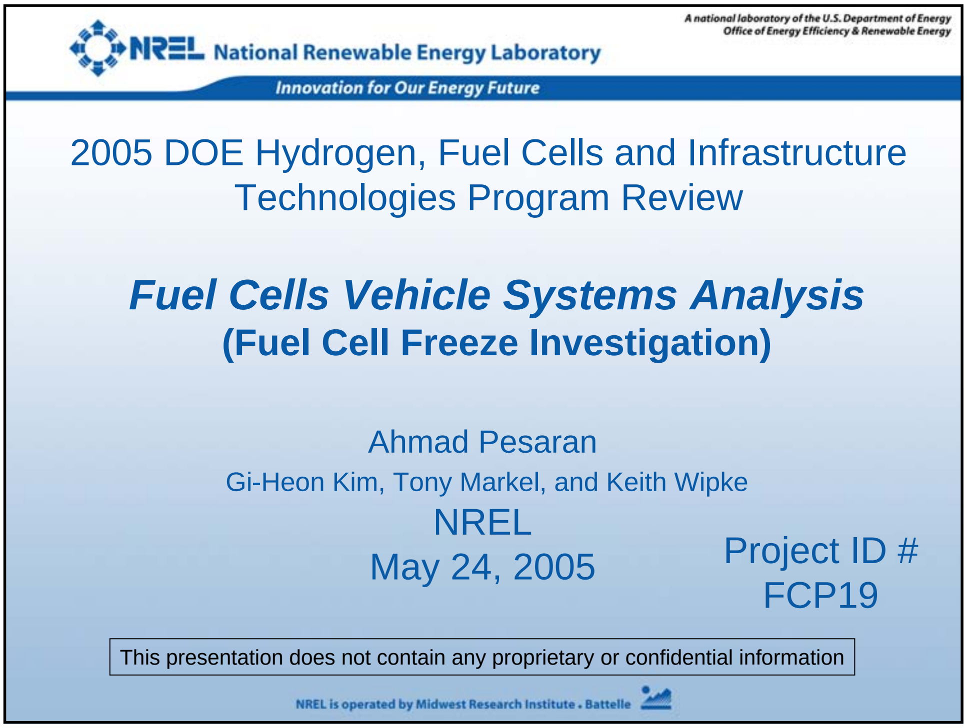


Figure 3. Toyota Prius battery energy/fuel (%).


A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

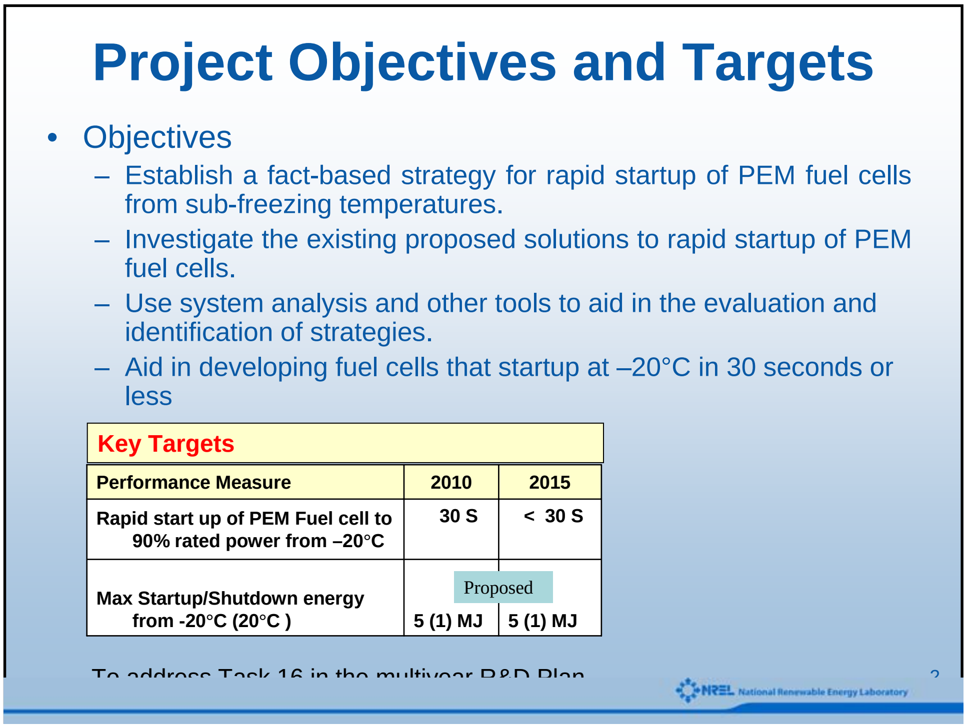
2005 DOE Hydrogen, Fuel Cells and Infrastructure
Technologies Program Review

Fuel Cells Vehicle Systems Analysis
(Fuel Cell Freeze Investigation)

Ahmad Pesaran
Gi-Heon Kim, Tony Markel, and Keith Wipke
NREL
May 24, 2005

Project ID #
FCP19

NREL is operated by Midwest Research Institute • Battelle


Project Objectives and Targets

- Objectives
  - Establish a fact-based strategy for rapid startup of PEM fuel cells from sub-freezing temperatures.
  - Investigate the existing proposed solutions to rapid startup of PEM fuel cells.
  - Use system analysis and other tools to aid in the evaluation and identification of strategies.
  - Aid in developing fuel cells that startup at –20°C in 30 seconds or less

Key Targets

Performance Measure	2010	2015
Rapid start up of PEM Fuel cell to 90% rated power from –20°C	30 S	< 30 S
Max Startup/Shutdown energy from -20°C (20°C)	Proposed 5 (1) MJ	5 (1) MJ

To address Task 16 in the multiyear R&D Plan

Project Overview

Timeline

- Project start: FY04
- Project end: FY07
- ~20% complete

Budget

- NREL FY04 funding (for Freeze): $100K
- NREL FY05 funding: $104K

Fuel Cell Barriers

A. **Durability** – Operation below freezing could damage the fuel cell.

D. **Thermal, air and water management** – Addressing freeze is critical in water management of fuel cells.

J. **Startup Time/Transient Operation**– Fuel cell power plant is required to start rapidly and flow the transient loads.

Partners/Customers

- General Motors
- 3M
- University of South Carolina

Project Approach

- Collect data/information through literature search and collaborations.
- Conduct a detailed patent search and document the findings.
- Perform energy analysis to bracket energy/power requirements for startup.
- Use component/system models to evaluate merits of various solutions from fuel efficiency and other factors within a vehicle.
- Participate in the DOE fuel cell freeze workshop.

Issues Found with Freeze & Rapid Startup of PEM Fuel Cells

A fuel “cell” can start up at sub-freezing temperatures, but product water may form ice if local sub-freezing still exists.

- Maintaining membrane integrity
- Fuel starvation (Elimination of water droplets from flow fields)
- Cathode ice formation
  - Product water forms ice on electrode and blocks air flow
  - Ice formation in cathode flow fields
- Rapid heat up of cell/cell manifolds to prevent ice formation
  - System heating issue:
    - Where is heat coming from and how much and how fast?
    - What is impact on energy consumption and overall efficiency?
  - Rapid heat up of humidifier to prevent membrane dry out
- Balance-of-plant: Heating of fluid/gas delivery systems
  - Prevent ice blockage
  - Thermal shock to mechanical components
  - Rapid startup and protection of components

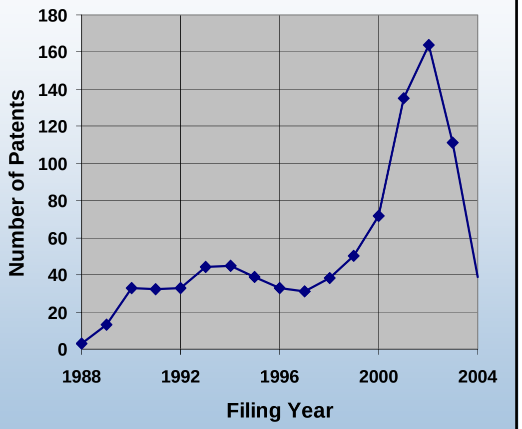
Majority of these issues are system related.

Accomplishments: Results of Patent Search

- Search included US, Japan, and world patents
- Period of January 1988 to January 2005
- In the initial round, we used “Fuel Cell” and “Freeze” and/or “Thaw”
  - We found 1324 patents
  - Some related to reformer startup and other types of FC
- Further restricting the research to PEM and non-reformer and rapid startup
  - Reduced the number of patents to 177 (with some duplication in US, Japan, and world)
- Number of articles in “academic” literature less than 15, indicating that industry recognized early the importance of freeze and rapid startup.

Results:
A Closer Look at the 1324 Patents

- Top categories
  - Fuel cell stack (212)
  - Piping (104)
  - Solid electrolyte fuel cell (119)
  - Polymer electrolyte (109)
  - Manifold (102)
  - Catalyst (71)
  - Cold-Starting (26)
  - Tank,Pure water (23)
  - Fuel cell power plant (24)
  - Antifreeze (10)
  - Other



Findings: Industry recognized early the importance of freeze issue.

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NONE (Patent Applications for Individual Inventors)	174	12.3%
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TOSHIBA CORP	59	4.2%
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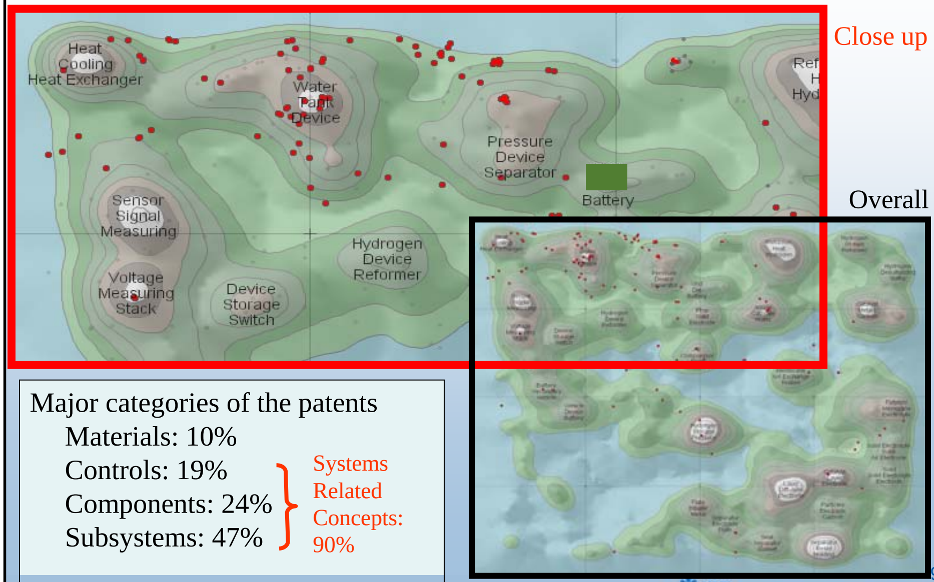
Fuel Cell Patent Map With Freeze-Thaw Patents Highlighted in Red

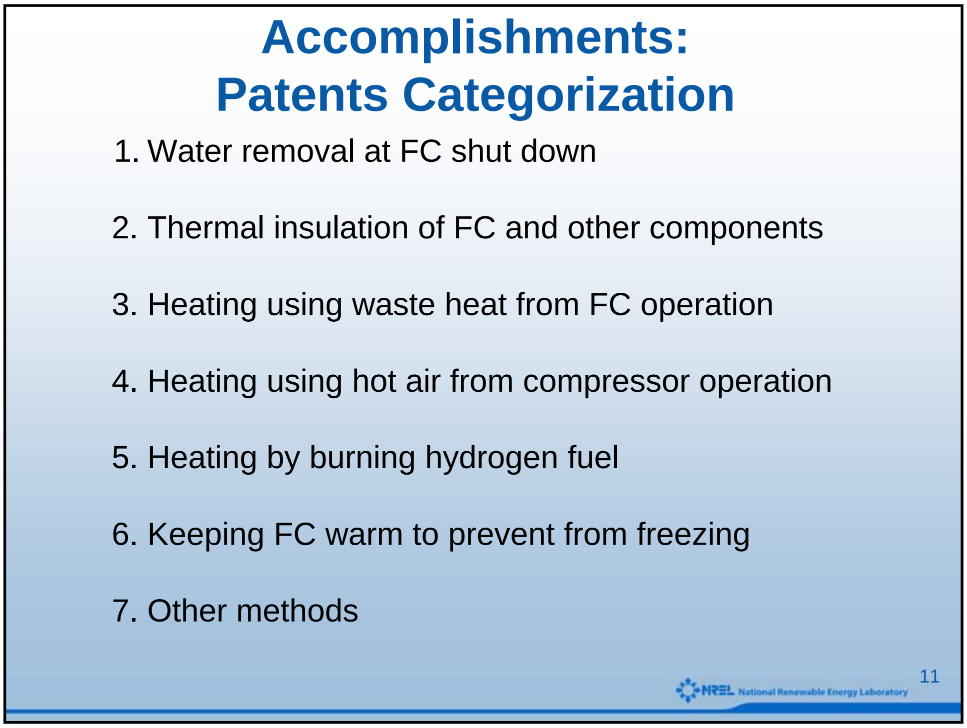


Major categories of the patents
- Materials: 10%
- Controls: 19%
- Components: 24%
- Subsystems: 47%

Systems Related Concepts: 90%

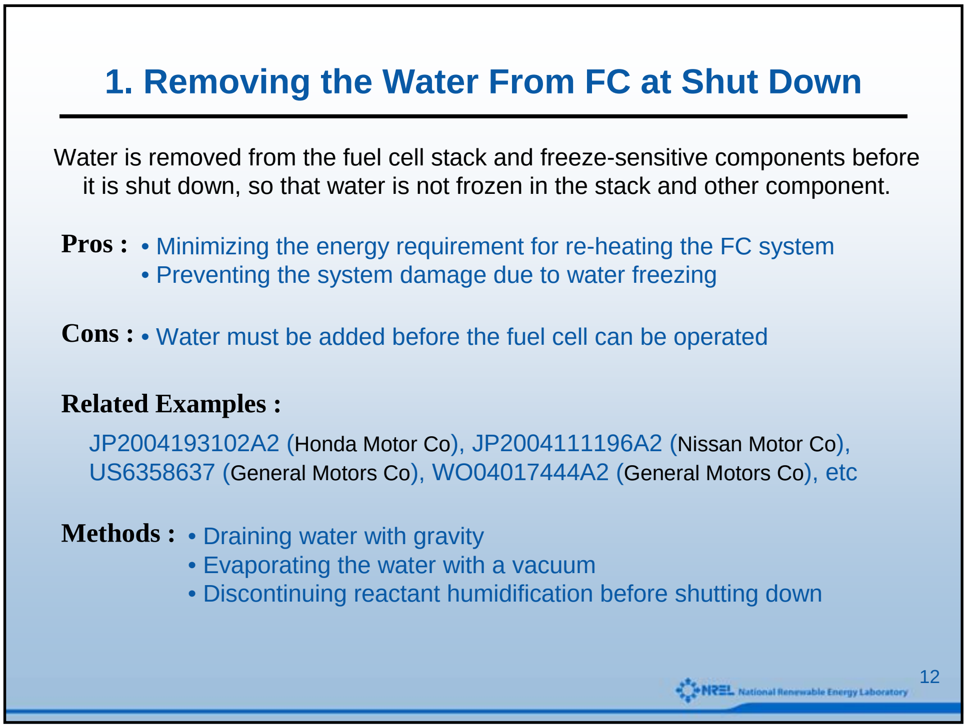
Accomplishments: Prepared List of Relevant Patents in Tabular Format

atent Number	Title	Assignee (patent owner)	Abstract	Patent Date
S006358638B1	Cold Start-up of a PEM Fuel Cell	General Motors Corporation, Detroit, MI (US)	A method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalysts. To their end, H_2 is introduced into the O_2-rich cathode feed stream and/or O_2 is introduced into the H_2-rich anode feed stream.	Mar 19, 2002
S006444345B2	Fuel Cell System	Xcellsis GmbH, Kirchheim/Teck-Nabern (DE)	A fuel cell system includes at least one fuel cell unit which is accommodated in a fuel cell enclosure. A cathode gas delivery line, cold-start gas delivery line, a cathode off-gas return line, anode off-gas return line may also be provided. According to the invention, the system is equipped with at least one Coanda flow amplifier in order to amplify the air stream for the purpose of ventilating the fuel cell enclosure, a cathode gas stream, a cold-start gas stream, a recirculated cathode off-gas stream or a recirculated anode off-gas stream. The may be equipped with a ventilating means for a housing outside the fuel cell enclosure. In the housing are components of the fuel cell system, said ventilating means including a Coanda flow amplifier.	Sept. 3, 2002
S006548200B2	Cold Starting of Gasoline Fueled Fuel Cell	UTC Fuel Cells, LLC, South Windsor, CT (US)	A fuel cell power plant has a fuel cell **(38)** receiving hydrogen **(37)** from a fuel processing system **(12)** which employs a vaporizer **(19)** to vaporize clean gasoline from a source **(13)**. A conventional start burner **(22)** and startup heat exchanger **(28)** are utilized to convert water **(31)** from the fuel processing system **(12)** and fuel cell **(38)** into steam **(32)**; but during sub-zero startup, an aqueous antifreeze solution **(46)** is provided to the heat exchanger **(28)** to produce the steam **(32)** for starting the vaporization of gasoline in the vaporizer **(19)**.	Apr. 15, 2003



Accomplishments:
Patents Categorization

1. Water removal at FC shut down
2. Thermal insulation of FC and other components
3. Heating using waste heat from FC operation
4. Heating using hot air from compressor operation
5. Heating by burning hydrogen fuel
6. Keeping FC warm to prevent from freezing
7. Other methods



1. Removing the Water From FC at Shut Down

Water is removed from the fuel cell stack and freeze-sensitive components before it is shut down, so that water is not frozen in the stack and other component.

Pros :
- Minimizing the energy requirement for re-heating the FC system
- Preventing the system damage due to water freezing

Cons :
- Water must be added before the fuel cell can be operated

Related Examples :

JP2004193102A2 (Honda Motor Co), JP2004111196A2 (Nissan Motor Co), US6358637 (General Motors Co), WO04017444A2 (General Motors Co), etc

Methods :
- Draining water with gravity
- Evaporating the water with a vacuum
- Discontinuing reactant humidification before shutting down

2. Thermal Insulation around FC and other Components

Insulation is used to keep the fuel cell stack and other freeze-sensitive components such as humidifier and water tank from freezing. Insulation is often integrated with the casing.

Pros : • Increase of cool down time after shut-down in sub-freezing environment

Cons : • Increase of stack volume and weight affecting vehicle performance, installed power requirements, and cost

Related Examples :

US6756143 (Ballard Power System), JP2004241303A2 (Denso Corp), JP2004234892A2 (Nissan Motor Co), US6797421(UTC Fuel Cells, LLC), etc

Comments :
- This approach occasionally used with Keep-Warm method
- US5433056 and US5175975, assigned to NREL, present compact vacuum insulation which can provide the insulation volume reduction with on-and-off thermal insulation apparatus

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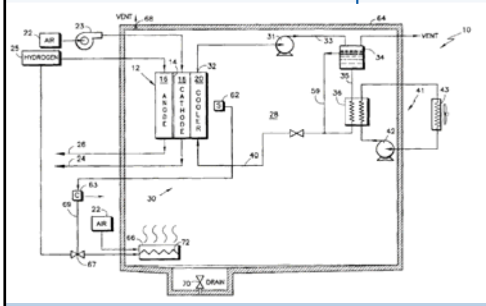
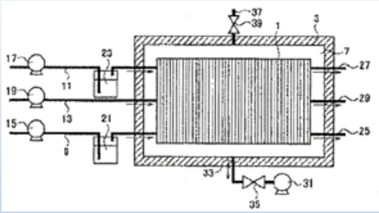
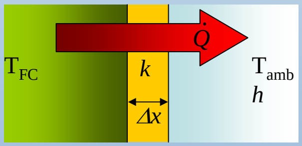
Analysis Approach

2. Thermal Insulation around FC and other Components

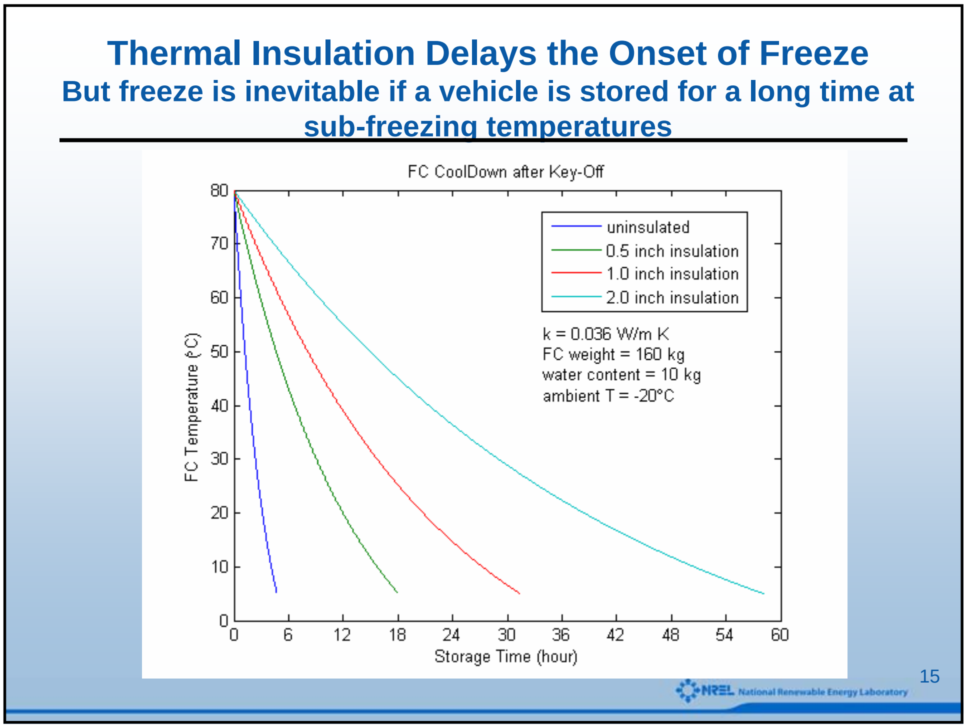
Method Evaluation : Estimating Energy & Power Requirement from Thermal Properties and Heat Transfer







Assumptions & Parameters
- Not Considering Radiative Heat Transfer
- Uniform Temperature inside FC
- Ambient Heat Transfer Coefficient: 10 $W/m^2 \cdot K$
- Surface Area of Insulation Box: 1.4 m^2
- Insulation Thermal Conductivity: 0.036 $W/m \cdot K$
- System Temperature: 5^oC



Thermal Insulation Delays the Onset of Freeze

But freeze is inevitable if a vehicle is stored for a long time at sub-freezing temperatures

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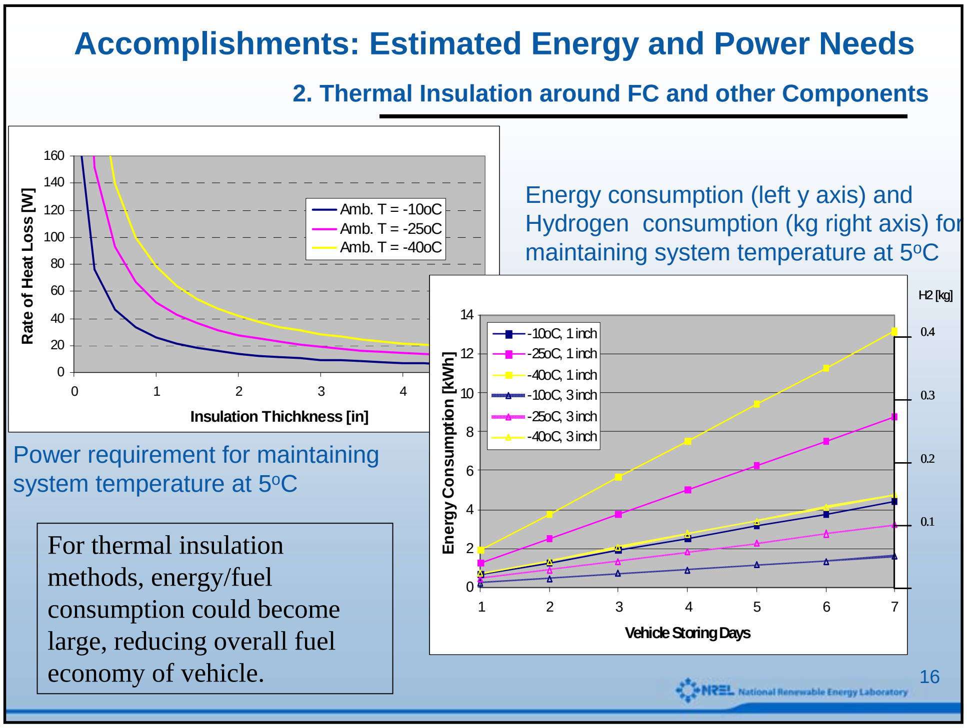

Accomplishments: Estimated Energy and Power Needs

2. Thermal Insulation around FC and other Components

Power requirement for maintaining system temperature at 5ºC

Energy consumption (left y axis) and Hydrogen consumption (kg right axis) for maintaining system temperature at 5ºC

For thermal insulation methods, energy/fuel consumption could become large, reducing overall fuel economy of vehicle.

3. Heating Using Waste Heat from FC Operation

Supply fuel and oxidant directly to the fuel cell while drawing electrical power from the cell stack across a resistive load while the fuel cell stack is still in the frozen state.

Pros :
- Relatively simple design that typically requires no system changes

Cons :
- The product water accumulates within catalytic and diffusion layers and ices up at freezing temperatures blocking the porous structures
- This approach takes several minutes to reach operational temperature

Related Examples :

US6777115, WO04025752 (UTC Fuel Cells, LLC), etc

Comments :

- According to the invention(US6777115), additional current provided by the battery initially forces the weak cells to a negative voltage which produces heat. Therefore, the performance of the weak cells quickly approaches typical performance of good cells.

4. Heating Using Hot Air from Compressor

Hot air is generated by the compression of air by the compressor. The heat is available relatively quickly and could be supplied to cathode side, which warms all portions of the MAE and starts melting any ice.

Pros :
- Hot air typically greater than 90°C is available relatively quickly
- Hot air warms all portions of the cathode and/or anode

Cons :
- Not much heating power is derived from air. However, the thermal mass of the membrane electrode assembly is very low.

Related Examples :

US6815103 (Honda Giken Kogyo Kabushiki Kaisha), EP1113516B1 (General Motors Co), etc

Comments :

- EP1113516B1 suggests that the dry fuel gas and oxidant gas are warmed and passed through the associated flow field for a sufficient time to de-ice the catalyst before introducing the O_2 and H_2 into the fuel or oxidant streams for catalytic heating.

5. Heating by Burning Hydrogen Fuel

A small amount of hydrogen is burned with air, either in a combustion chamber or catalytically to provide high quality heat to the manifold, MEA and other components.

Pros :
- Generation of a large amount of high-quality heat
- Waste heat can be used to warm the passenger compartment

Cons :
- Decrease in fuel economy
- Requirement for the hydrogen/air burners that add weight, volume and cost

Related Examples :

JP2004111243A2 (Nissan Motor Co), JP2004047210A2 (Nissan Motor Co), WO0148846A1 (PTC Int. App.), etc

Comments :
- US6797421B2 suggests that instead of using the reactants for heat by combustion, the system is heated by the exothermal catalytic reaction from a catalytic burner.
- EP1113516B1 suggests that the MEA is locally heated from catalytic reaction between H_2 and O_2 on the anode and cathode catalysts.

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6. Keeping FC Warm to Prevent Freezing

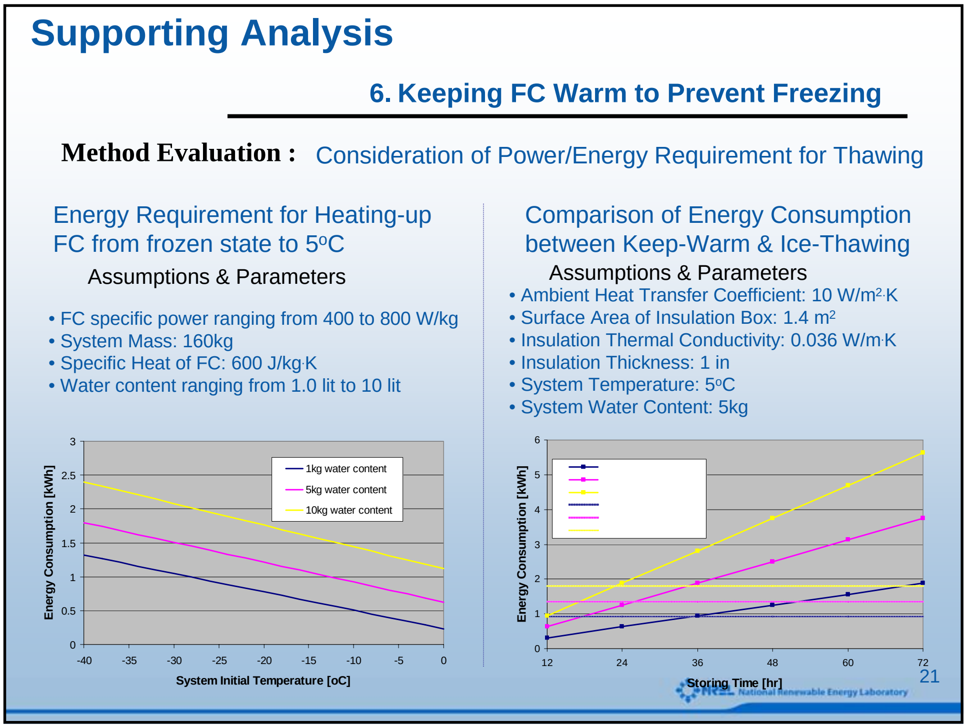
FC system is kept warm by insulation, adding heat or combination of the two to keep the FC and other components from freezing while the vehicle is stored in subfreezing environment

Pros :
- Addresses damages that may be caused when the fuel cell stack remains in a dwell or off-mode at low ambient temperatures

Cons :
- Requires complex, and therefore costly, energy demanding control schemes
- Requires great fuel consumption which limits the storage protection time available

Related Examples : US6727013B2(General Motors Co), EP1414090A1(Nissan Motor Co), US6797421B2(UTC Fuel Cells. LLC), etc

Methods :
- US6727013B2 presents a heater to warm the fuel cell stack or the water supply, being connected to an output of the fuel cell stack.
- US6797421B2 suggests a catalytic burner obviating the need for parasitic electrical loads to produce heated gas.
- EP1414090A1 presents the controller determining a stop mode as a temperature maintenance mode or a defrost start-up mode.



Supporting Analysis

6. Keeping FC Warm to Prevent Freezing

Method Evaluation : Consideration of Power/Energy Requirement for Thawing

Energy Requirement for Heating-up FC from frozen state to 5°C

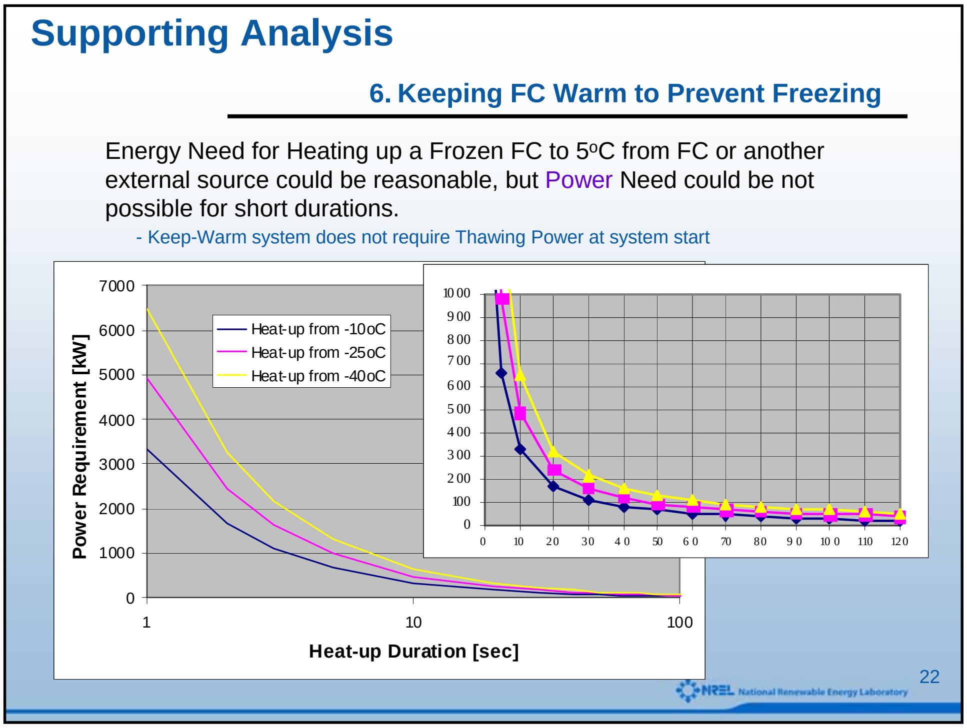
Assumptions & Parameters

- FC specific power ranging from 400 to 800 W/kg
- System Mass: 160kg
- Specific Heat of FC: 600 J/kg·K
- Water content ranging from 1.0 lit to 10 lit

Comparison of Energy Consumption between Keep-Warm & Ice-Thawing

Assumptions & Parameters

- Ambient Heat Transfer Coefficient: 10 W/m^2·K
- Surface Area of Insulation Box: 1.4 m^2
- Insulation Thermal Conductivity: 0.036 W/m·K
- Insulation Thickness: 1 in
- System Temperature: 5°C
- System Water Content: 5kg

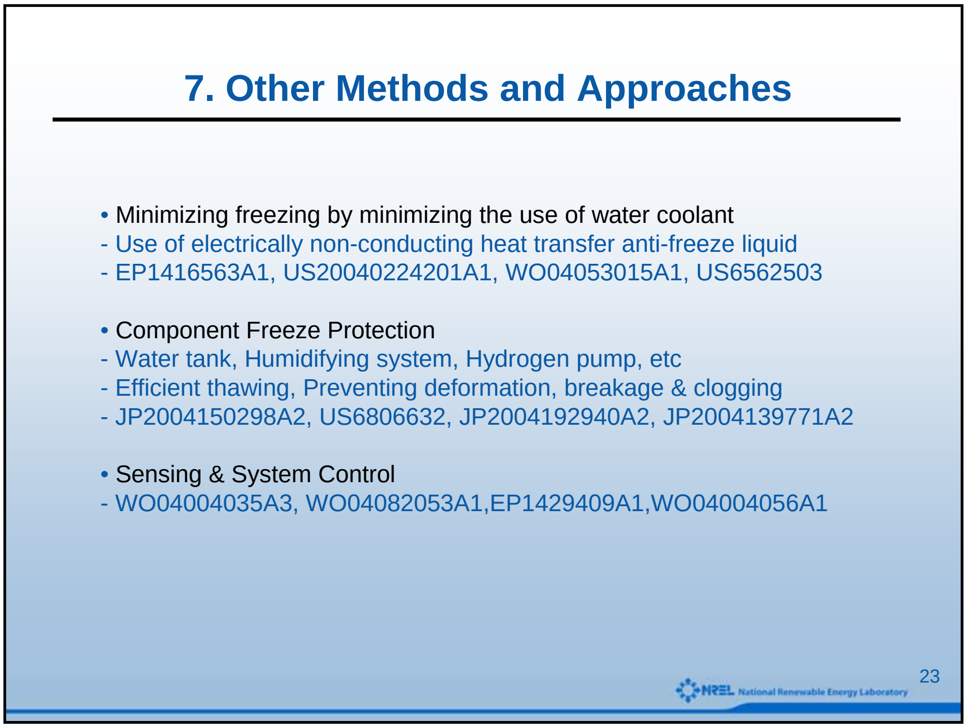


Supporting Analysis

6. Keeping FC Warm to Prevent Freezing

Energy Need for Heating up a Frozen FC to 5°C from FC or another external source could be reasonable, but Power Need could be not possible for short durations.

- Keep-Warm system does not require Thawing Power at system start

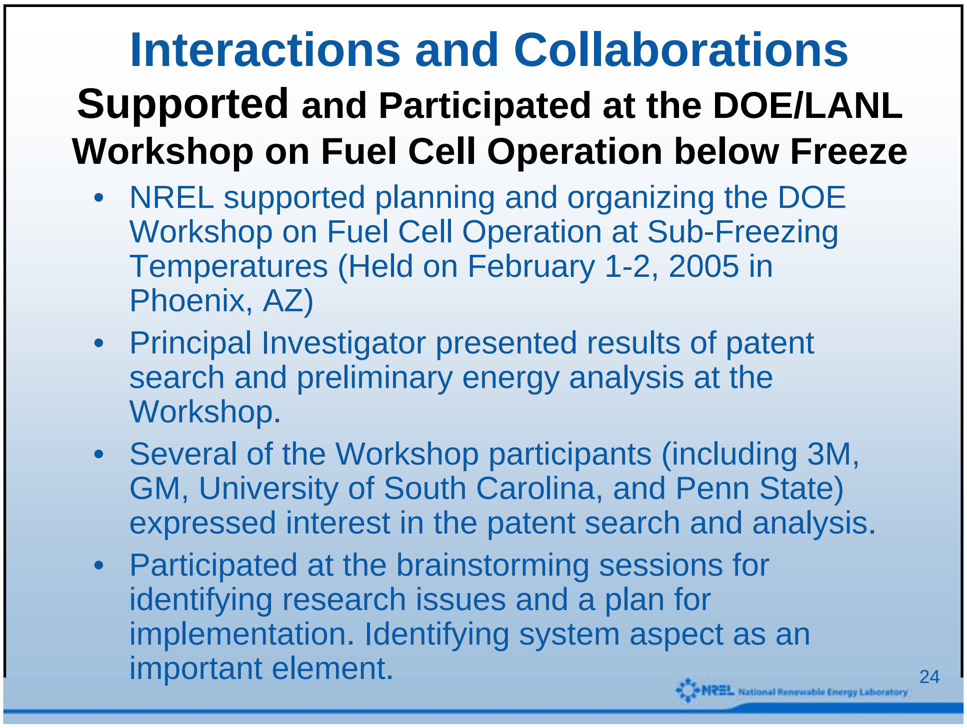


7. Other Methods and Approaches

- Minimizing freezing by minimizing the use of water coolant
  - Use of electrically non-conducting heat transfer anti-freeze liquid
  - EP1416563A1, US20040224201A1, WO04053015A1, US6562503

- Component Freeze Protection
  - Water tank, Humidifying system, Hydrogen pump, etc
  - Efficient thawing, Preventing deformation, breakage & clogging
  - JP2004150298A2, US6806632, JP2004192940A2, JP2004139771A2

- Sensing & System Control
  - WO04004035A3, WO04082053A1,EP1429409A1,WO04004056A1



Interactions and Collaborations

Supported and Participated at the DOE/LANL Workshop on Fuel Cell Operation below Freeze

- NREL supported planning and organizing the DOE Workshop on Fuel Cell Operation at Sub-Freezing Temperatures (Held on February 1-2, 2005 in Phoenix, AZ)
- Principal Investigator presented results of patent search and preliminary energy analysis at the Workshop.
- Several of the Workshop participants (including 3M, GM, University of South Carolina, and Penn State) expressed interest in the patent search and analysis.
- Participated at the brainstorming sessions for identifying research issues and a plan for implementation. Identifying system aspect as an important element.

Responses to Previous Year Reviewers’ Comments

Note: Last year, the focus was on system analysis to investigate oxygen enrichment. This year, we have focused on the fuel cell freeze issues so the effort is new.

- Comment: “Increase interactions with industry teams.”
  - We have worked with industry teams through participating and organizing the Workshop on Fuel Cell Freeze.
  - We are interacting with GM and others on the patent search.
- Comment: “Investigate more extreme environment in the next steps.”
  - We have focused on sub-freezing temperatures particularly very cold temperatures of –20°C and below.
- Comment: “Depth of analysis of individual questions (not specific components) could improve the impact of this project.”
  - We are addressing an the important issue of rapid startup of fuel cells from sub-freezing temperatures.

Summary

- Operating fuel cell at sub-freezing temperatures quickly and energy efficiently without durability impacts is a key barrier for fuel cell vehicles.
- We found that many patents, more than published articles, have been issued on fuel cell freeze and rapid startup.
- The majority of proposed concepts/solutions in these patents are from system level perspective. We performed preliminary analysis of some of these solutions.
- We analyzed and categorized these patents: “keep-warm” or “thaw/heating” methods are two major categories.
- “Keep-warm” methods do not allow the system to freeze. This method uses is effective for short-term storage and/or for mild sub-freezing temperatures, but could be in-efficient for long-term storage.
- “Thawing/heating” methods require high power and humidification at startup but do not consume a lot of energy.
- Some combinations of different technologies maybe promising to address rapid startup issues

Future Work

- Remainder of FY05
  - Complete the analysis patent search
  - Prepare a report summarizing the results of patent search
  - Perform energy analysis to evaluate different rapid startup methods
  - Use system and component tools to evaluate and define various strategies for rapid cold starts
- FY06 and beyond
  - Perform more rigorous evaluation for the “freeze start technologies and methods” using 3D PEM Fuel Cell models
  - Present results at conferences and meetings
  - Partner with industry to evaluate and implement and new approaches.
  - Perform system-wise analysis for the possible combinations of promising technologies

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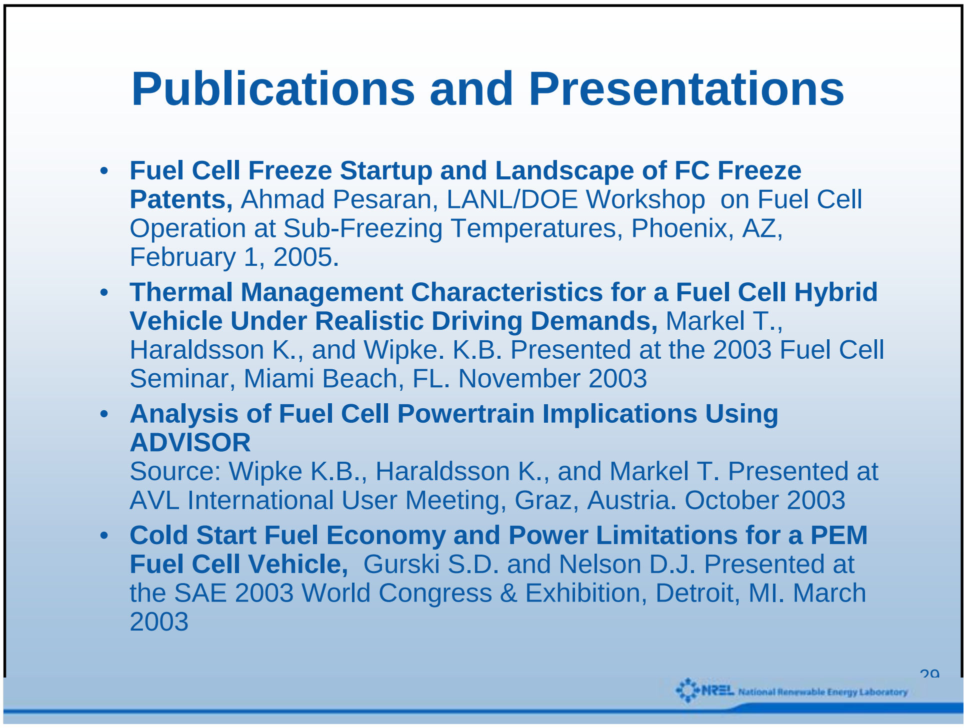
Project Safety

- **There is no hazard associated with this project.**



Publications and Presentations

- **Fuel Cell Freeze Startup and Landscape of FC Freeze Patents,** Ahmad Pesaran, LANL/DOE Workshop on Fuel Cell Operation at Sub-Freezing Temperatures, Phoenix, AZ, February 1, 2005.
- **Thermal Management Characteristics for a Fuel Cell Hybrid Vehicle Under Realistic Driving Demands,** Markel T., Haraldsson K., and Wipke. K.B. Presented at the 2003 Fuel Cell Seminar, Miami Beach, FL. November 2003
- **Analysis of Fuel Cell Powertrain Implications Using ADVISOR**
  Source: Wipke K.B., Haraldsson K., and Markel T. Presented at AVL International User Meeting, Graz, Austria. October 2003
- **Cold Start Fuel Economy and Power Limitations for a PEM Fuel Cell Vehicle,** Gurski S.D. and Nelson D.J. Presented at the SAE 2003 World Congress & Exhibition, Detroit, MI. March 2003

NREL National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

Fuel Cells Vehicle Systems Analysis
(Fuel Cell Freeze Investigation)

A progress report to DOE
Hydrogen, Fuel Cell, and Infrastructure Technologies

August 15, 2005

Ahmad Pesaran
Gi-Heon Kim
Jeff Gonder
Keith Wipke

NREL is operated by Midwest Research Institute • Battelle

Project Objectives and Targets

- Objectives
  - Establish a fact-based strategy for rapid startup of PEM fuel cells from sub-freezing temperatures.
  - Investigate the existing proposed solutions to rapid startup of PEM fuel cells.
  - Use system analysis and other tools to aid in the evaluation and identification of strategies.
  - Aid in developing fuel cells that startup at –20°C in 30 seconds or less

Key DOE Targets

Performance Measure	2010	2015
Rapid start up of PEM Fuel cell to 90% rated power from –20°C	30 S	< 30 S
Max Startup/Shutdown energy from -20°C (20°C)	Proposed 5 (1) MJ	5 (1) MJ

To address Task 16 in the multiyear R&D Plan

Project Overview


January 2005 Ice Storm in Geneva

Addressing Barriers

A. **Durability** – Operation and storage below freezing could damage the fuel cell.

D. **Thermal, air and water management** – Addressing freeze is critical in water management of fuel cells.

J. **Startup Time/Transient Operation**– Fuel cell power plant is required to start rapidly and follow the transient loads.

Project Approach

- Collect data/information through literature search and collaborations.
- Conduct a detailed literature search and document the findings.
- Participate in the DOE fuel cell freeze workshop.
- Perform energy analysis to bracket energy/power requirements for startup.
- Use component/system models to evaluate merits of various solutions from fuel efficiency and other factors within a vehicle.
- Study impact of weather patterns on freeze solutions.
  (Response to comments from DOE H_2 Merit Review)

Accomplishments until FC Freeze Workshop (February 2005)

- Reviewed freeze issues in a couple of brainstorming sessions and generated ideas for addressing freeze;
- Performed a comprehensive literature and patent search (1991- 2004);
- Mapped and analyzed the patent data base;
- Collected and tabulated all the relevant patents;
- Developed an idea and a record of invention for "alternating current heating of fuel cells at sub-freezing temperature";
- Presented our progress at the Fuel Cell Freeze Workshop in February.

Accomplishments until Hydrogen Program Review Meeting (May 2005) - 1

- Reviewed 177 relevant patents to identify novel solutions;
- Separated the ideas in the patents into several categories
- Performed energy and power analysis for the most interesting of these categories
- Analyzed the impact of insulation and heating on keeping fuel cell warm and rapid thaw for startup;
- Developed a Matlab-based simulation program to calculate energy, power, and temp-time performance for the keep warm and rapid thaw method;

Accomplishments until Hydrogen Program Review Meeting (May 2005) - 2

- Investigated several commercially available fuel cell modeling software for freeze evaluation
- Acquired a 30-day free trial license to evaluate whether the PEMFC module is capable of addressing the performance of fuel cells.
- Concluded that combination of methods (removing water at shutdown, keeping warm, and heating at start) seem to address the fuel cell system (stack and other components) freeze.
- Prepared and presented a poster for the HFCIT Review, where we received many good comments/ideas for our continued analysis.

Accomplishments Since May Hydrogen Program Review Meeting

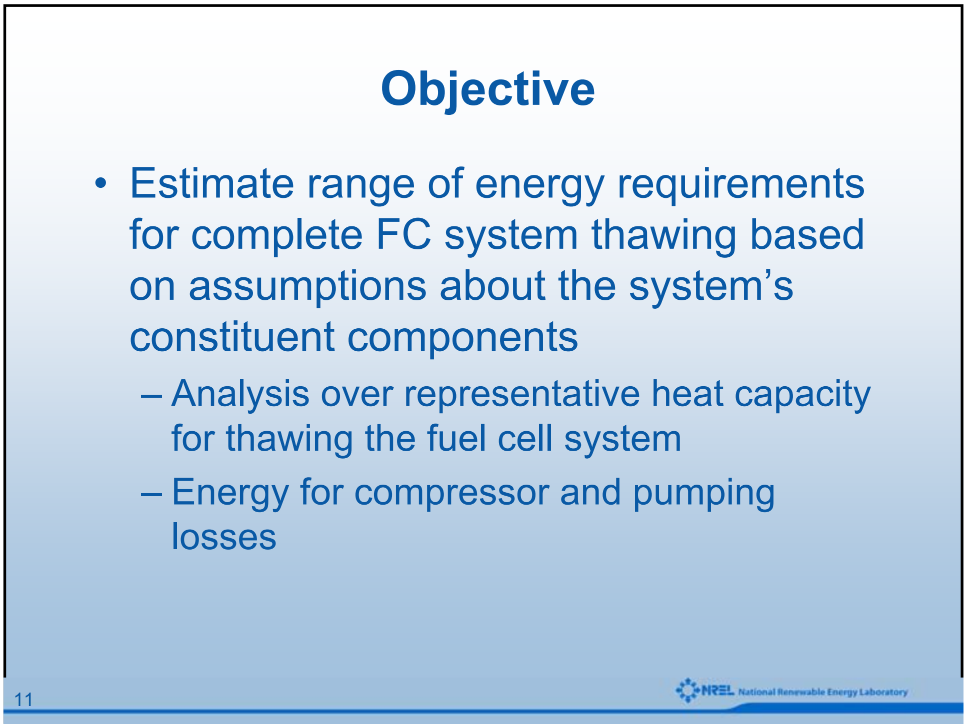
- Estimated energy and power requirements for fuel cell startup from component-level perspective
- Mapped time and spatial distribution of -20ºC freezing occurrences across U.S.
- Performed energy analysis to investigate the impact of weather patterns (from U.S. TMY) and driving profiles on freeze solutions.
- Negotiated purchase of StarCD PEMFC software for 3D analysis of freeze (collaboration with USC)
- Prepared first draft of August milestone report for internal review.

Presentations for this meeting

- Literature/Patent Search
- Thaw/Startup Energy Estimation
- Concept Analysis – Weather Patterns
- Weather Mapping and FC Freeze Targets
- 3D Fuel Cell Model (StarCD)
- FY06 Proposed Work

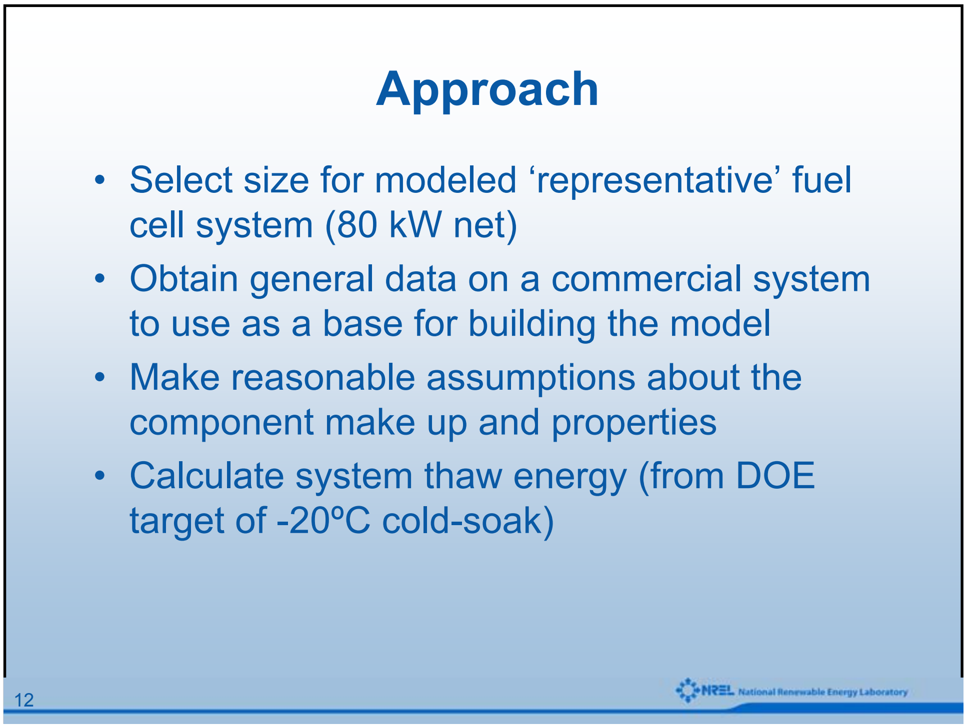
Fuel Cell System Thaw Energy Requirements

(A Component-Level Analysis Approach)



Objective

- Estimate range of energy requirements for complete FC system thawing based on assumptions about the system's constituent components
  - Analysis over representative heat capacity for thawing the fuel cell system
  - Energy for compressor and pumping losses

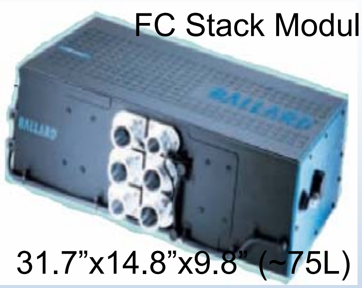


Approach

- Select size for modeled 'representative' fuel cell system (80 kW net)
- Obtain general data on a commercial system to use as a base for building the model
- Make reasonable assumptions about the component make up and properties
- Calculate system thaw energy (from DOE target of -20ºC cold-soak)

Base Data

FC Stack Module



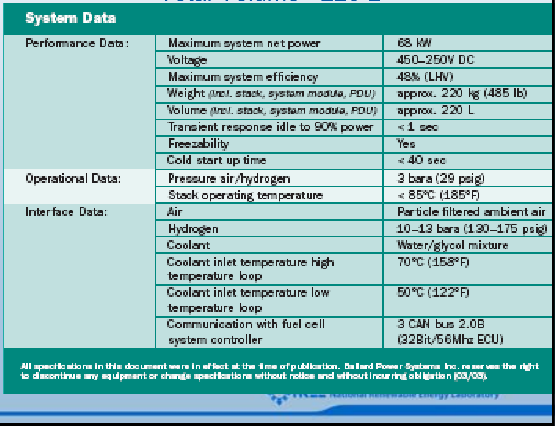
31.7”x14.8”x9.8” (~75L)

System Module (BOP)

31.5”x23.6”x9.6” (~117 L)

Ballard-provided specs from Xcellsis HY-80 data sheet

- Max Net Power = 68 kW
- Total Mass ~ 220 kg
- Total Volume ~220 L



System Data

Performance Data:	Maximum system net power	68 kW
	Voltage	450–250V DC
	Maximum system efficiency	48% (LHV)
	Weight *(incl. stack, system module, PDU)*	approx. 220 kg (485 lb)
	Volume *(incl. stack, system module, PDU)*	approx. 220 L
	Transient response idle to 90% power	< 1 sec
	Freezability	Yes
	Cold start up time	< 40 sec
Operational Data:	Pressure air/hydrogen	3 bara (29 psig)
	Stack operating temperature	< 85°C (185°F)
Interface Data:	Air	Particle filtered ambient air
	Hydrogen	10–13 bara (130–175 psig)
	Coolant	Water/glycol mixture
	Coolant inlet temperature high temperature loop	70°C (158°F)
	Coolant inlet temperature low temperature loop	50°C (122°F)
	Communication with fuel cell system controller	3 CAN bus 2.0B (32Bit/56Mhz ECU)

All specifications in this document were in effect at the time of publication. Ballard Power Systems Inc. reserves the right to discontinue any equipment or change specifications without notice and without incurring obligation (03/03).

Mass Distribution Assumptions

- Stack Module will have higher packing factor & density than System Module (Balance of Plant)
- Scaled upwards for 80 kW net system (Target) and assigned component mass breakdown

	%	Mass (kg)		%	Mass (kg)
FC Stack Module	**100**	**115**	**System Module**	**100**	**120**
-FC Stacks	65	75	-Air Compressor Sys	30	36
-Enclosure & Misc	20	23	-Enclosure	20	24
-Coolant & Plumbing	10	12	-Condenser	10	12
-Electronics	5	6	-Humidifiers	10	12
			-DI Water Handling/ Accumulator	10	12
			-Other	20	24

Component Property Assumptions

- FC Stacks will include endplates, moist MEA’s, current collectors, flow fields & gas distribution layers, bolts or other fasteners, coolant channels, etc.
- Assumed material distribution to generate “average” property for component:

Material	c_P (J/(kg*K))	% mass
Stainless Steel	480	20
Aluminum	875	15
Copper	385	10
Graphite	711	45
PTFE	1010	10
Average for FC Stack	**~700**	**100**

Component Property Estimate Summary

	Component	Water Mass Content		Average Non-Water
		Low Case	High Case	c_P (J/(kg*K))
FC Stack Module	-FC Stacks	0.5%	10%	700
	-Enclosure & Misc	0%	0%	750
	-Coolant & Plumbing	0%	50%	550
	-Electronics	0%	0%	650
System Module	-Air Compressor Sys	0%	0%	550
	-Enclosure	0%	0%	750
	-Condenser	5%	30%	750
	-Humidifiers	5%	40%	800
	-DI Water Handling/ Accumulator	5%	50%	550
	-Other	0%	20%	600

Additional Assumptions

- Supply external heat until components reach +5 ºC threshold temperature at which point the FC system will generate net power
- Neglect internal FC stack heat generation at below +5 ºC (only external heating up to this T)
- Neglect heating losses to environment (100% heat application efficiency)
- Electric power for compressor and humidifier is added until +5 ºC after which no external electric power is in needed (E = P * Δtime)

Compressor Power	Humidification Power	Duration	Energy		
kW	kW	Seconds	kJ	MJ	Whr
10	2	60	720	0.72	200
5	1	30	180	0.18	50
3	0.5	30	105	0.11	29

Analysis

- Mass, water content and property estimations used to calculate required heat energy input for thawing each component:

$$Q = (m_{comp} \cdot c_{P,comp} + m_{ice} \cdot c_{P,ice}) \cdot \Delta T_1 + m_{ice} \cdot h_f$$
$$+ (m_{comp} \cdot c_{P,comp} + m_{water} \cdot c_{P,water}) \cdot \Delta T_2$$

  - "comp" refers to non-H_2O portions of the component
  - ΔT_1 & ΔT_2 represent heating from -20 to 0 ºC and from 0 to +5 ºC, respectively
  - h_f, enthalpy of melting, used to determine heat requirement to melt the ice in the component

- Total energy is the thaw heating energy plus the compressor/pump energy

$$E_{total} = Q + E$$

Bulk Heating Calculations (Scenario 1)

- Results for bulk thaw requirements (heating entire mass of all components & water)
- Large difference between high and low water content cases due to high heat capacity and latent heat requirements to melt the ice

(Energy Given in MJ)

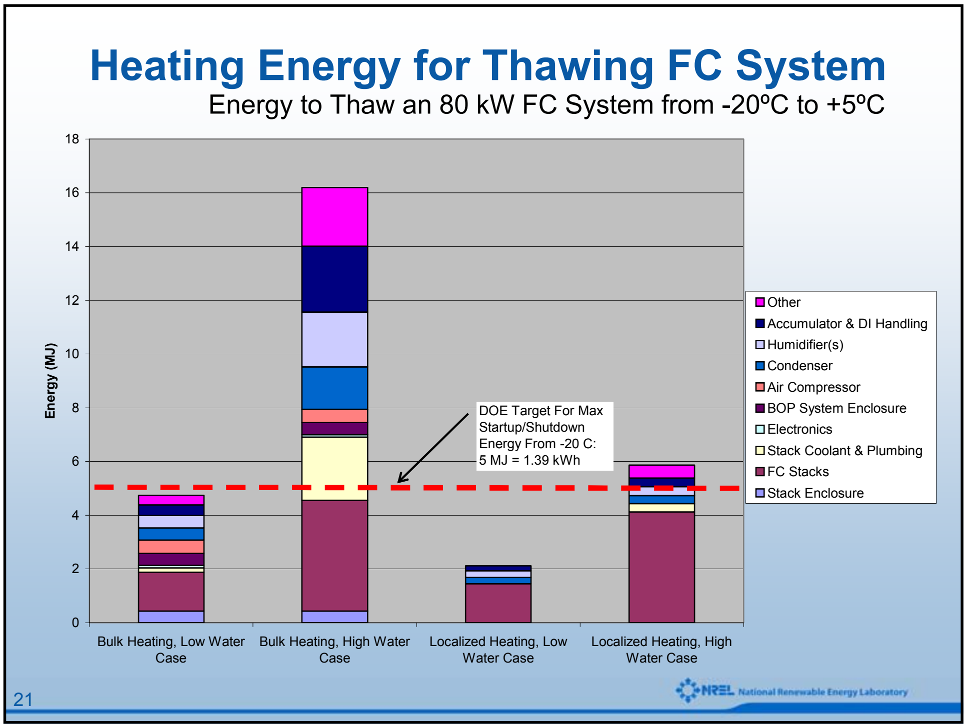
	Component to Heat	Low Case	High Case
FC Stack Module	-FC Stacks	1.45	4.13
	-Enclosure & Misc	0.43	0.43
	-Coolant & Plumbing	0.16	2.35
	-Electronics	0.09	0.09
System Module	-Air Compressor Sys	0.50	0.50
	-Enclosure	0.45	0.45
	-Condenser	0.45	1.58
	-Humidifiers	0.46	2.04
	-DI Water Handling/ Accumulator	0.39	2.45
	-Other	0.36	2.18
Total Energy Input		**4.75**	**16.19**

Localized Heating Calculations (Scenario 2)

- Assumptions targeted heating only to localized areas requiring thaw prior to FC System start:
  - Full heating still applied to FC stack
  - No heating applied to components not containing water
  - Assume that only 10% of H_2O in other components must thaw prior to start, & that other 90% could be separated and later thawed using FC waste heat

(Energy Given in MJ)

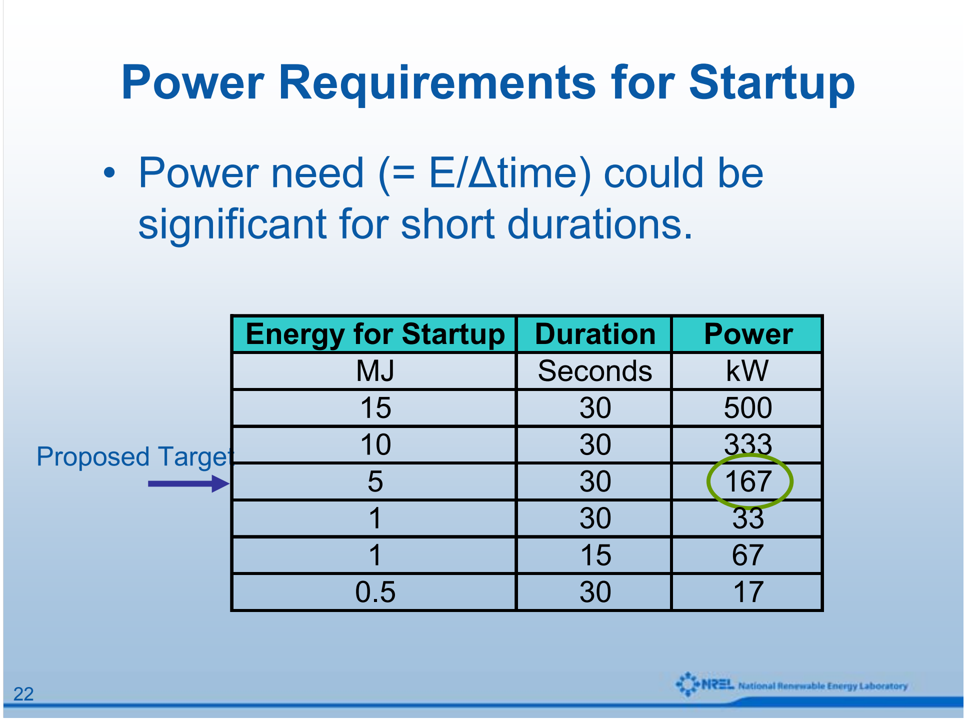
	Component to Heat	Low Case	High Case
FC Stack Module	-FC Stacks	1.45	4.13
	-Enclosure & Misc	0	0
	-Coolant & Plumbing	0	0.31
	-Electronics	0	0
System Module	-Air Compressor Sys	0	0
	-Enclosure	0	0
	-Condenser	0.24	0.30
	-Humidifiers	0.25	0.33
	-DI Water Handling/ Accumulator	0.18	0.32
	-Other	0	0.48
Total Energy Input		**2.12**	**5.86**



Heating Energy for Thawing FC System

Energy to Thaw an 80 kW FC System from -20ºC to +5ºC

DOE Target For Max Startup/Shutdown Energy From -20 C: 5 MJ = 1.39 kWh



Power Requirements for Startup

- Power need (= E/Δtime) could be significant for short durations.

Energy for Startup	Duration	Power
MJ	Seconds	kW
15	30	500
10	30	333
5	30	167
1	30	33
1	15	67
0.5	30	17

Proposed Target

Limitations of Findings

- Results only relevant to actual systems insofar as assumptions match those systems' properties
- Many potential system variations
  - Components, mass & heat capacities
  - Required temp for rapid "boot-strap" or self-start
  - Stack warm-up efficiency and heat generation
  - What components actually need heating
  - Shutdown water management/drain strategy

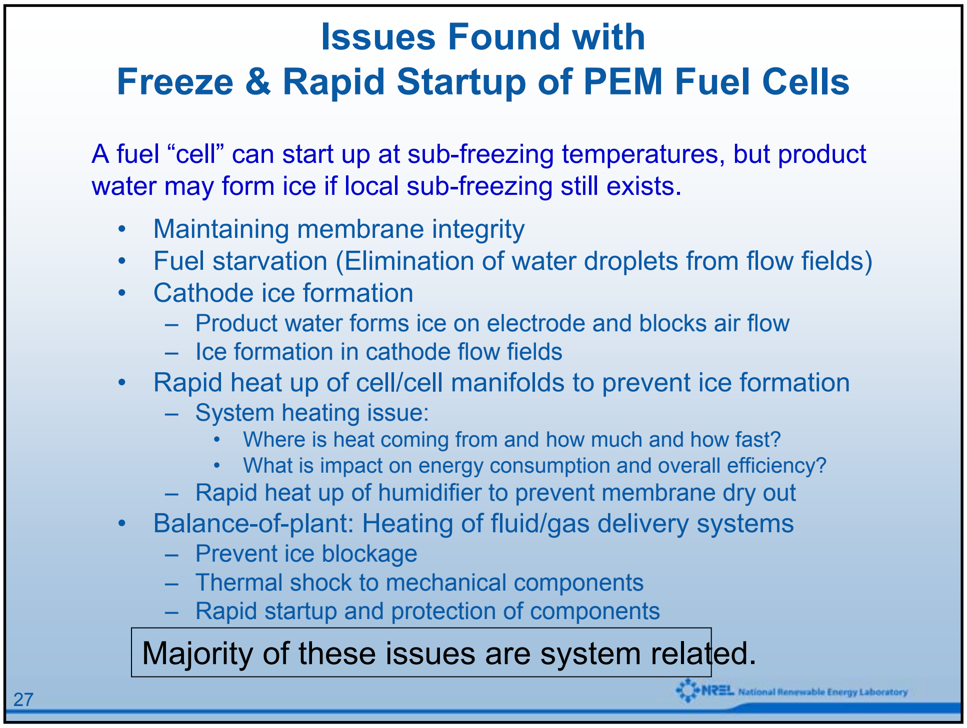
Summary – Startup Energy Need

- Analysis indicates that heat energy required for low-water content case (a system with water removed at shut-down) is below DOE target of 5 MJ
- Localized heating (or technology-specific strategies) less intensive than bulk heating of the entire system have potential for even lower energy requirements
- The electric energy for compressor and pump startup is much smaller than heat energy for thaw.
- Effectiveness of shutdown water management can greatly impact freeze-start energy requirement.
- Findings can vary based on specific properties and conditions associated with various actual systems.
- Power needs for startup is very high for proposed targets.

Suggestions for FY06 Work

- Gauge industry interest in development of a tool that would make this type of analysis more relevant to their particular systems
  - Obtain additional input specific to each design (mass, volume, surface area, electricity & heat generation characteristics with temperature, heat input strategy, insulation characteristics, etc)
  - Tool would help determine heating energy required for different strategies, and startup times
- Develop a more advanced FCV Freeze-Startup useful to developers to predict the expected system behavior & number of freeze/thaw cycles for a particular trial vehicle introduction
  - FC system characteristics (as said in previous slide)
  - Weather information (worst case and normal hourly temperature variation for possible driving locations)
  - Vehicle use patterns (running vs. parked data for a particular user or for average users in a given area)

Literature/Patent Search

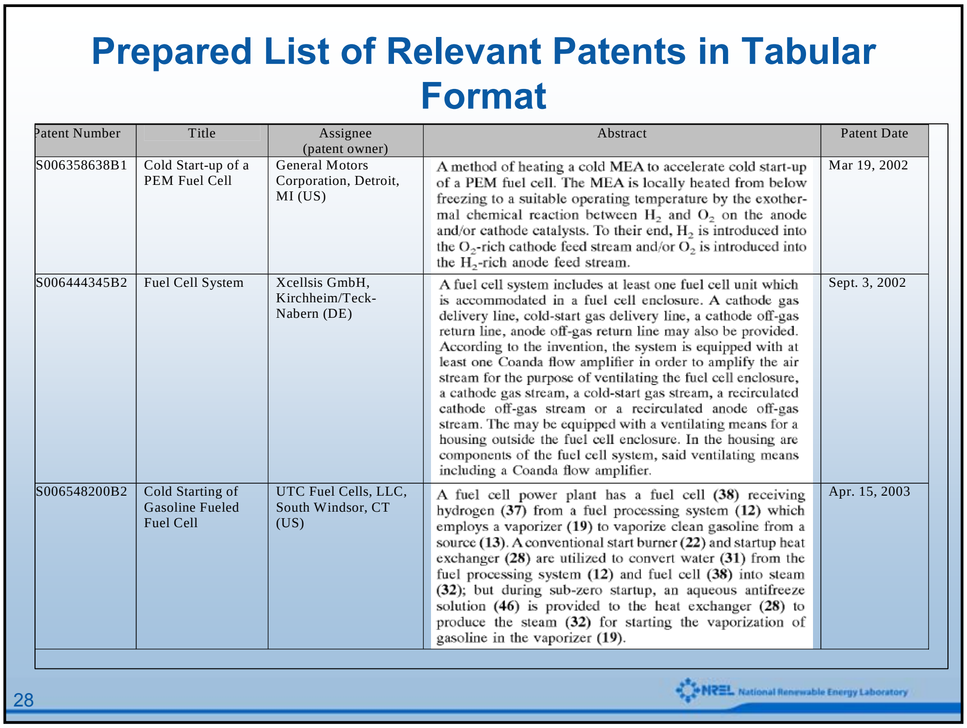


Issues Found with Freeze & Rapid Startup of PEM Fuel Cells

A fuel "cell" can start up at sub-freezing temperatures, but product water may form ice if local sub-freezing still exists.

- Maintaining membrane integrity
- Fuel starvation (Elimination of water droplets from flow fields)
- Cathode ice formation
  - Product water forms ice on electrode and blocks air flow
  - Ice formation in cathode flow fields
- Rapid heat up of cell/cell manifolds to prevent ice formation
  - System heating issue:
    - Where is heat coming from and how much and how fast?
    - What is impact on energy consumption and overall efficiency?
  - Rapid heat up of humidifier to prevent membrane dry out
- Balance-of-plant: Heating of fluid/gas delivery systems
  - Prevent ice blockage
  - Thermal shock to mechanical components
  - Rapid startup and protection of components

Majority of these issues are system related.



Prepared List of Relevant Patents in Tabular Format

atent Number	Title	Assignee (patent owner)	Abstract	Patent Date
S006358638B1	Cold Start-up of a PEM Fuel Cell	General Motors Corporation, Detroit, MI (US)	A method of heating a cold MEA to accelerate cold start-up of a PEM fuel cell. The MEA is locally heated from below freezing to a suitable operating temperature by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalysts. To their end, H_2 is introduced into the O_2-rich cathode feed stream and/or O_2 is introduced into the H_2-rich anode feed stream.	Mar 19, 2002
S006444345B2	Fuel Cell System	Xcellsis GmbH, Kirchheim/Teck-Nabern (DE)	A fuel cell system includes at least one fuel cell unit which is accommodated in a fuel cell enclosure. A cathode gas delivery line, cold-start gas delivery line, a cathode off-gas return line, anode off-gas return line may also be provided. According to the invention, the system is equipped with at least one Coanda flow amplifier in order to amplify the air stream for the purpose of ventilating the fuel cell enclosure, a cathode gas stream, a cold-start gas stream, a recirculated cathode off-gas stream or a recirculated anode off-gas stream. The may be equipped with a ventilating means for a housing outside the fuel cell enclosure. In the housing are components of the fuel cell system, said ventilating means including a Coanda flow amplifier.	Sept. 3, 2002
S006548200B2	Cold Starting of Gasoline Fueled Fuel Cell	UTC Fuel Cells, LLC, South Windsor, CT (US)	A fuel cell power plant has a fuel cell **(38)** receiving hydrogen **(37)** from a fuel processing system **(12)** which employs a vaporizer **(19)** to vaporize clean gasoline from a source **(13)**. A conventional start burner **(22)** and startup heat exchanger **(28)** are utilized to convert water **(31)** from the fuel processing system **(12)** and fuel cell **(38)** into steam **(32)**; but during sub-zero startup, an aqueous antifreeze solution **(46)** is provided to the heat exchanger **(28)** to produce the steam **(32)** for starting the vaporization of gasoline in the vaporizer **(19)**.	Apr. 15, 2003

Results of Patents Categorization

1. Water removal at FC shut down
2. Thermal insulation of FC and other components
3. Heating using waste heat from FC operation
4. Heating using hot air from compressor operation
5. Heating by burning hydrogen fuel
6. Keeping FC warm to prevent from freezing
7. Other methods

REMOVING WATER FROM FC AT SHUT DOWN

- Water is removed from the fuel cell before it is shut down

Pros :
- Minimizing the energy requirement for re-heating the FC system
- Preventing the system damage due to water freezing from occurring

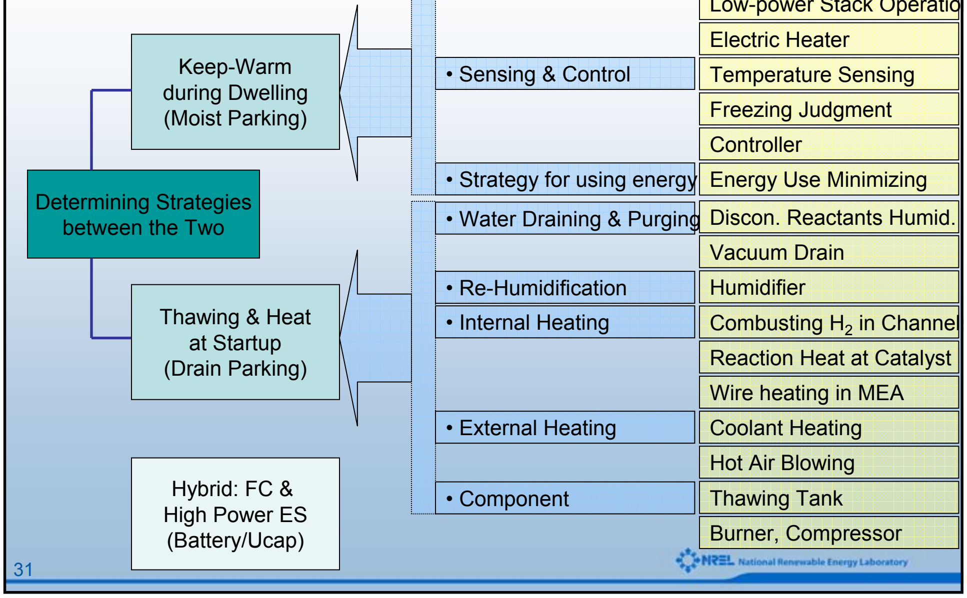
Cons :
- Water must be added before the fuel cell can be operated

Related Examples :

JP2004193102A2(Honda Motor Co), JP2004111196A2(Nissan Motor Co), US6358637(General Motors Co), WO04017444A2 (General Motors Co), etc

Methods :
- Draining water with gravity
- Evaporating the water with a vacuum
- Discontinuing reactant humidification before shutting down

Method & Technology Category Chart for Fuel Cell Start from Sub-Freezing Environment



Keep-Warm during Dwelling (Moist Parking)

Determining Strategies between the Two

Thawing & Heat at Startup (Drain Parking)

Hybrid: FC & High Power ES (Battery/Ucap)

• Insulation	Insulation Box
	Vacuum Insulation
• Energy/Power Source	Catalytic Burner
	Low-power Stack Operatio
	Electric Heater
• Sensing & Control	Temperature Sensing
	Freezing Judgment
	Controller
• Strategy for using energy	Energy Use Minimizing
• Water Draining & Purging	Discon. Reactants Humid.
	Vacuum Drain
• Re-Humidification	Humidifier
• Internal Heating	Combusting H_2 in Channel
	Reaction Heat at Catalyst
	Wire heating in MEA
• External Heating	Coolant Heating
	Hot Air Blowing
• Component	Thawing Tank
	Burner, Compressor

Keep-Warm
INSULATION

- The insulation is often integrated with the fuel cell stack casing to protect freeze-sensitive portions of fuel cell system

Pros : • Increase of cool down time after shut-down in sub-freezing environment

Cons : • Increase of stack volume and weight affecting vehicle performance, installed power requirements, and cost

Related Examples :

US6756143(Ballard Power System), JP2004241303A2 (Denso Corp), JP2004234892A2(Nissan Motor Co), US6797421(UTC Fuel Cells, LLC), etc

Comments : This approach occasionally used with KEEP-WARM technologies
• US5433056, US5175975, assigned to NREL, presents compact vacuum insulation which can provide the insulation volume reduction with on-and-off thermal insulation apparatus

Thaw and Heat at Startup
HOT AIR BLOWING

- Employing hot air to melt ice in the anode and cathode flow channels and to warm the MEA during operation and/or as part of the start-up process

Pros :
- Hot air typically greater than 90°C is available relatively quickly
- Hot air warms all portions of the cathode and/or anode

Cons :
- Not much heating power is derived from air. However, the thermal mass of the membrane electrode assembly is very low.

Related Examples :

US6815103(Honda Giken Kogyo Kabushiki Kaisha), EP1113516B1(General Motors Co), etc

Comments :

- EP1113516B1 suggests that the dry fuel gas and oxidant gas are warmed and passed through the associated flow field for a sufficient time to de-ice the catalyst before introducing the O_2 and H_2 into the fuel or oxidant streams for catalytic heating.

Thaw and Heat at Startup
USING WASTE HEAT FROM FC

- Operating the fuel cell to produce waste heat that is to heat the fuel cell stack as part of the startup process

Pros :
- Relatively simple design that typically requires no system changes

Cons :
- The product water accumulating within catalytic and diffusion layers and blocking the porous structures
- This approach takes several minutes to reach operational temperature

Related Examples :

US6777115, WO04025752(UTC Fuel Cells, LLC), etc

Comments :

- According to the invention(US6777115), additional current provided by the battery initially forces the weak cells to a negative voltage which produces heat. thereby, the performance of the weak cells quickly, approaches typical performance of good cells.

Thaw and Heat at Startup
BURNING HYDROGEN FUEL

- Using the heat from hydrogen/air combustion to heat the FC system

Pros :
- Generation of a large amount of high-quality heat
- Waste heat can be used to warm the passenger compartment

Cons :
- Decrease in fuel economy
- Requirement for the hydrogen/air burners that add weight, volume and cost

Related Examples :

JP2004111243A2(Nissan Motor Co), JP2004047210A2(Nissan Motor Co), WO0148846A1(PTC Int. App.), etc

Comments :
- US6797421B2 suggests that instead of using the reactants for heat by combustion, the system is heated by the exothermal catalytic reaction from a catalytic burner
- EP1113516B1 suggests that the MEA is locally heated from catalytic reaction between H_2 and O_2 on the anode and cathode catalysts

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Keep-Warm
Other Patents

- Burn hydrogen <u>occasionally</u>
- Use a battery to electrically heat the fuel cell and other components
- Run the fuel cell <u>occasionally</u> to warm the stack and charge the battery
- Run the FC after key-off to make stack warmer to take longer to cool down
- Combine the above concepts with insulation

Summary – Literature Search

- We found that many patents, more than published articles, have been issued on fuel cell freeze and rapid startup.
- The majority of proposed concepts/solutions in these patents are from system level perspective.
- “Keep-warm” or “thaw/heating” methods are two major categories.
- Removing water from fuel cell system at shut-down is critical.
- “Keep-warm” methods do not allow the system to freeze. This method is effective for short-term storage and/or for mild sub-freezing temperatures, but could be consume a lot of energy for long-term parking.
- “Thaw/heating” methods require high power and humidification at startup but do not consume a lot of energy.
- Some combinations of different technologies may be promising to address rapid startup issues

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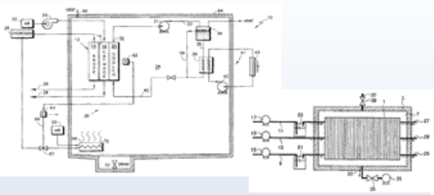
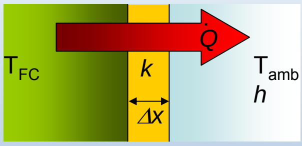
Analysis of Concepts for FC Freeze Solutions

Placing Thermal Insulation around FC

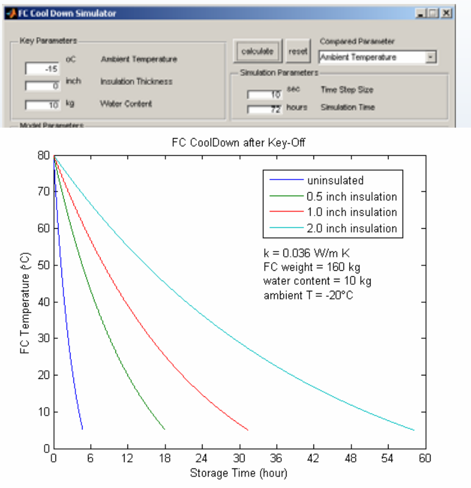




$$m_{FC}c_p\frac{\partial T}{\partial t}=\dot{Q}=A_{surf}(T_{FC}-T_{amb})/(\frac{\Delta x}{k}+\frac{1}{h})$$

Lumped Analysis

- Not Considering Radiative Heat Transfer
- Uniform Temperature inside FC
- Constant Ambient Heat Transfer Coefficient



FC Cool Down Simulator

Key Parameters

-15 oC Ambient Temperature

0 inch Insulation Thickness

10 kg Water Content

Compared Parameter: Ambient Temperature

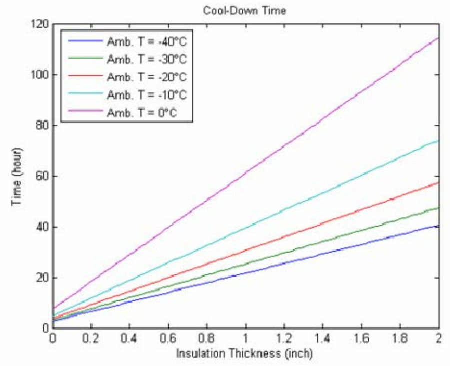
Simulation Parameters

10 sec Time Step Size

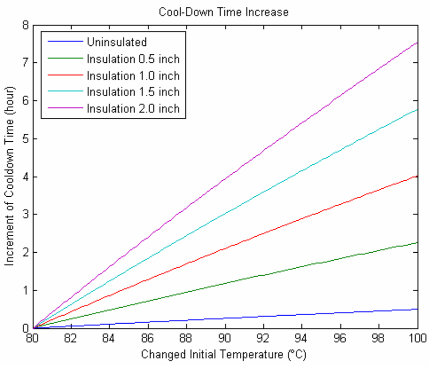
72 hours Simulation Time

FC Cool-Down Time after Key-Off

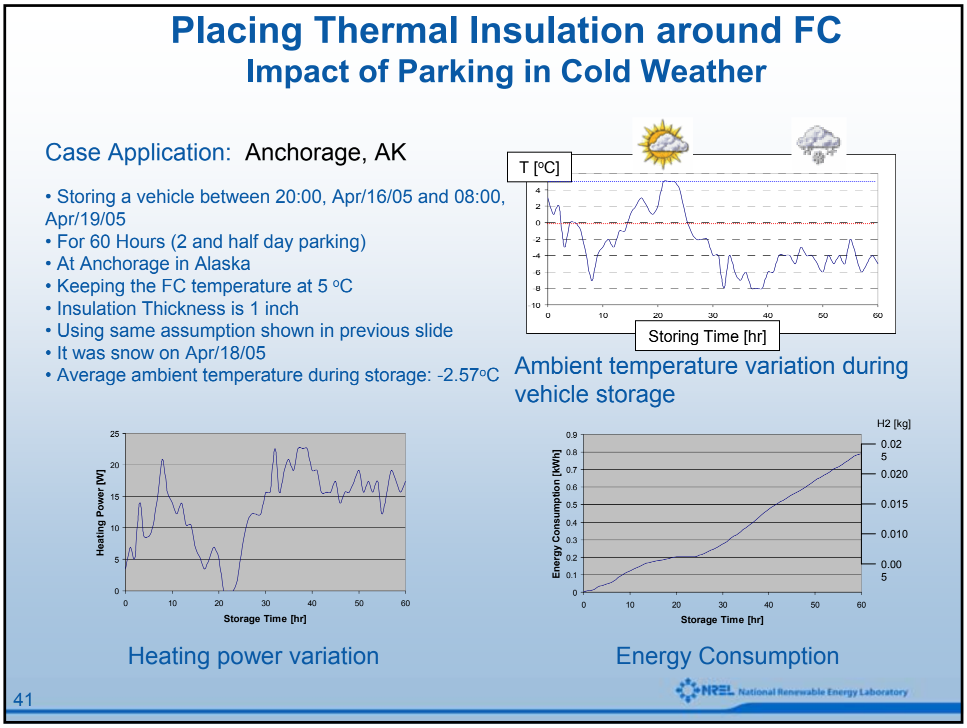
Delaying Cooling Down of FC Stack



US6756143 and JP2004241303A2 suggest adding insulation



Patent US20050031914 suggested a method to increase cool-down time even further through bypassing the heat exchanger in order to raise the sensible heat of the stack prior to shutdown.



Placing Thermal Insulation around FC

Impact of Parking in Cold Weather

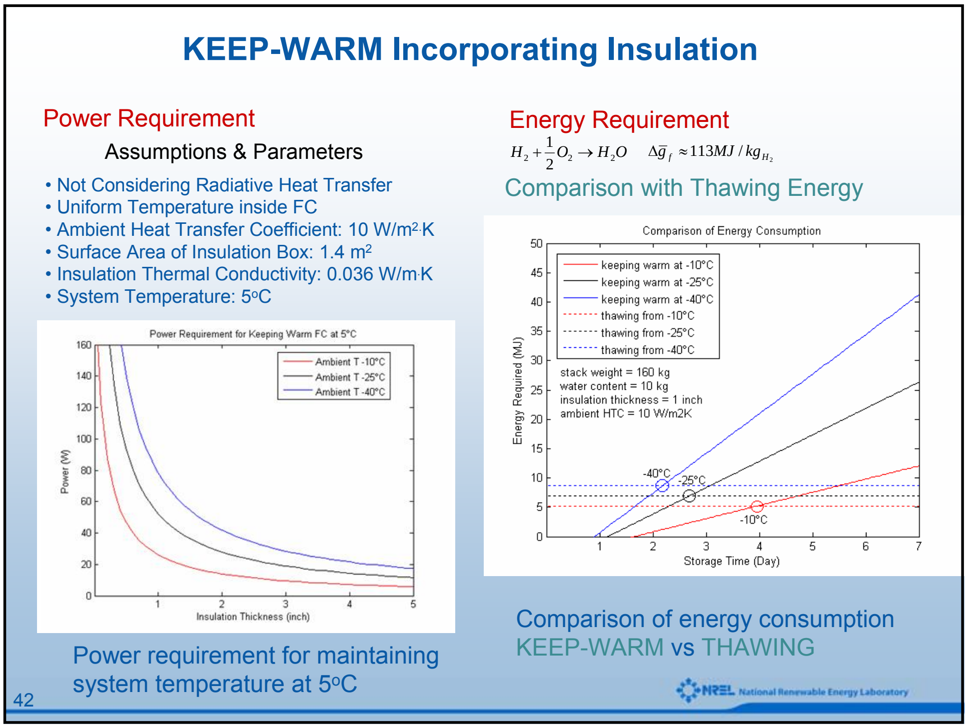
Case Application: Anchorage, AK

- Storing a vehicle between 20:00, Apr/16/05 and 08:00, Apr/19/05
- For 60 Hours (2 and half day parking)
- At Anchorage in Alaska
- Keeping the FC temperature at 5 ^{o}C
- Insulation Thickness is 1 inch
- Using same assumption shown in previous slide
- It was snow on Apr/18/05
- Average ambient temperature during storage: -2.57^{o}C

Ambient temperature variation during vehicle storage

Heating power variation

Energy Consumption



KEEP-WARM Incorporating Insulation

Power Requirement

Assumptions & Parameters

- Not Considering Radiative Heat Transfer
- Uniform Temperature inside FC
- Ambient Heat Transfer Coefficient: 10 W/m^{2}·K
- Surface Area of Insulation Box: 1.4 m^{2}
- Insulation Thermal Conductivity: 0.036 W/m·K
- System Temperature: 5^{o}C

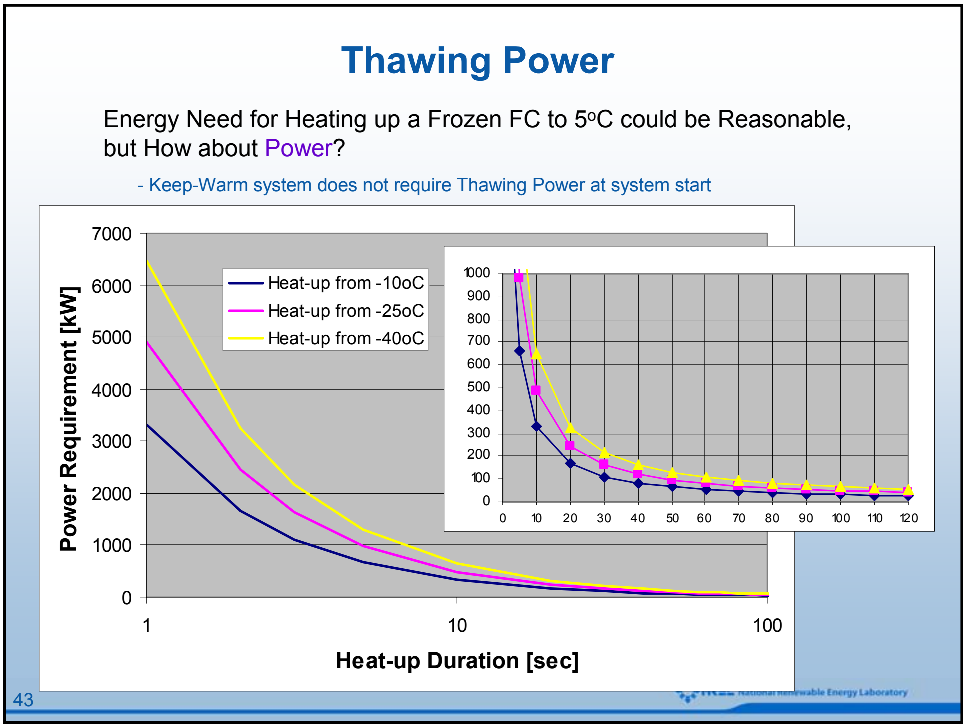
Power requirement for maintaining system temperature at 5^{o}C

Energy Requirement

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta\bar{g}_f \approx 113 MJ/kg_{H_2}$$

Comparison with Thawing Energy

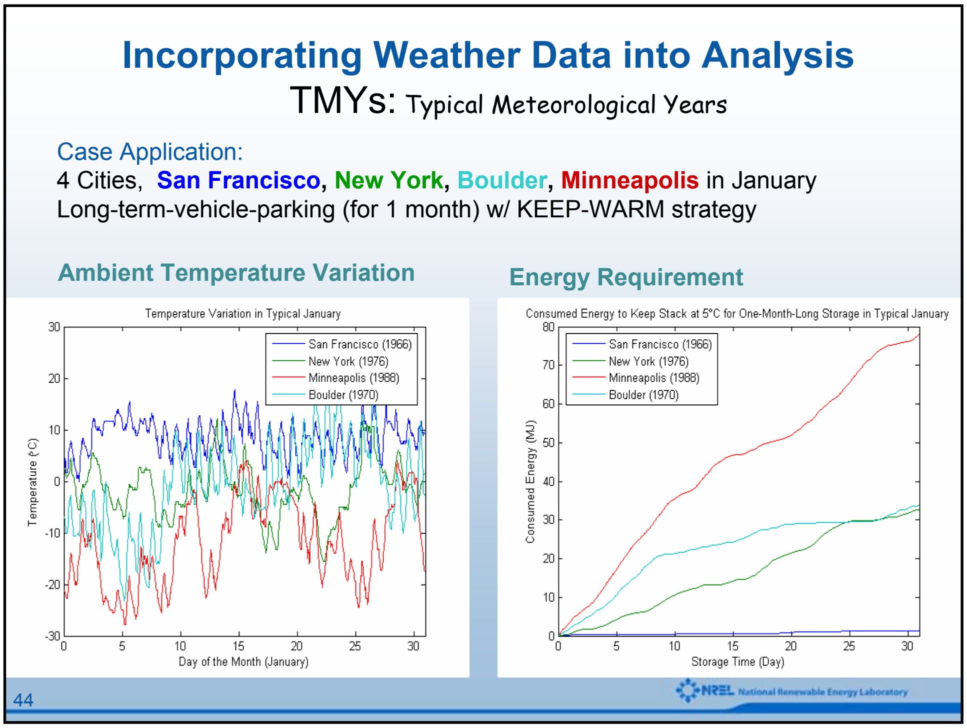
Comparison of energy consumption KEEP-WARM vs THAWING



Thawing Power

Energy Need for Heating up a Frozen FC to 5°C could be Reasonable, but How about Power?

- Keep-Warm system does not require Thawing Power at system start



Incorporating Weather Data into Analysis

TMYs: Typical Meteorological Years

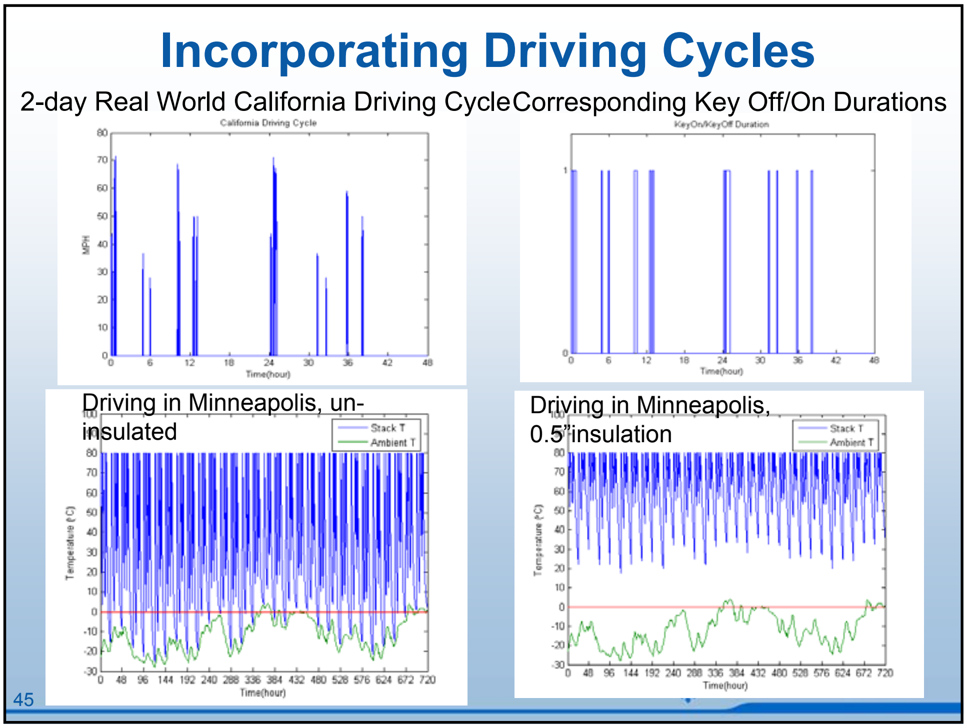
Case Application:

4 Cities, **San Francisco**, **New York**, **Boulder**, **Minneapolis** in January

Long-term-vehicle-parking (for 1 month) w/ KEEP-WARM strategy

Ambient Temperature Variation

Energy Requirement



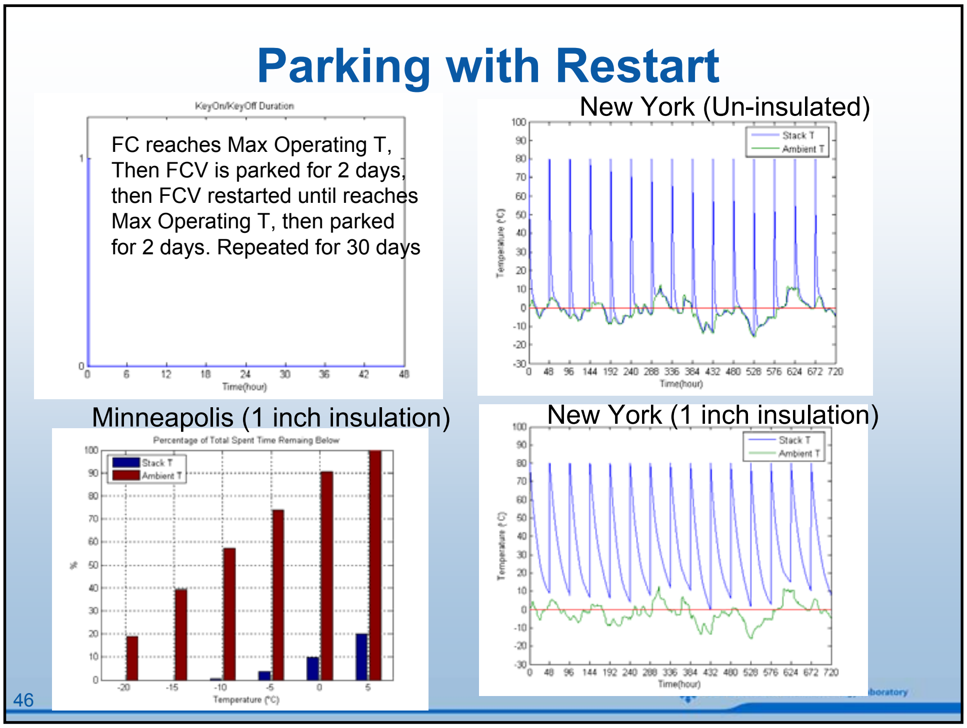
Incorporating Driving Cycles

2-day Real World California Driving Cycle

Corresponding Key Off/On Durations

Driving in Minneapolis, un-insulated

Driving in Minneapolis, 0.5"insulation



Parking with Restart

FC reaches Max Operating T, Then FCV is parked for 2 days, then FCV restarted until reaches Max Operating T, then parked for 2 days. Repeated for 30 days

New York (Un-insulated)

Minneapolis (1 inch insulation)

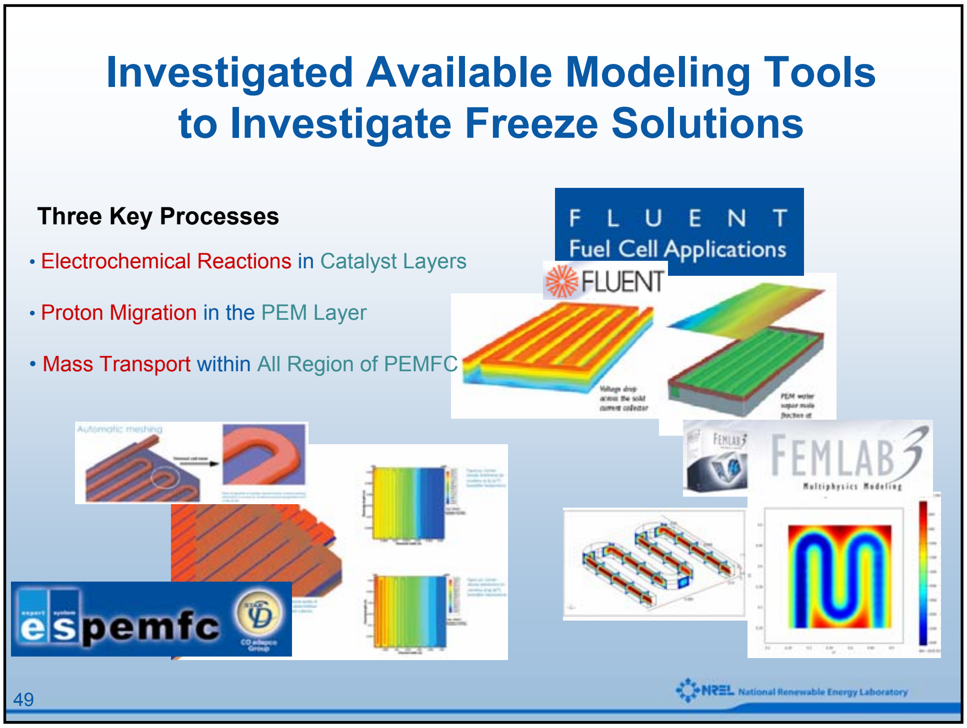
New York (1 inch insulation)

Summary – Concept Evaluation

- We analyzed “keep-warm” and “thaw/heating” methods
  - Investigated impact of insulation
  - Estimated amount heat needed to be added to keep FC above 5ºC
  - Included drive cycles and parking times
  - Investigated impact of weather pattern
- “Keep-warm” is effective for short-term storage and/or for mild sub-freezing temperatures, but could be inefficient for long-term storage.
- “Thawing/heating” methods require high power and humidification at startup but do not consume a lot of energy.
- Some combinations of different technologies may be promising to address rapid startup issues.
- Some simples solutions may be good enough for a large number of conditions

3D Computer Aid Engineering Tools for Modeling Fuel Cell Freeze

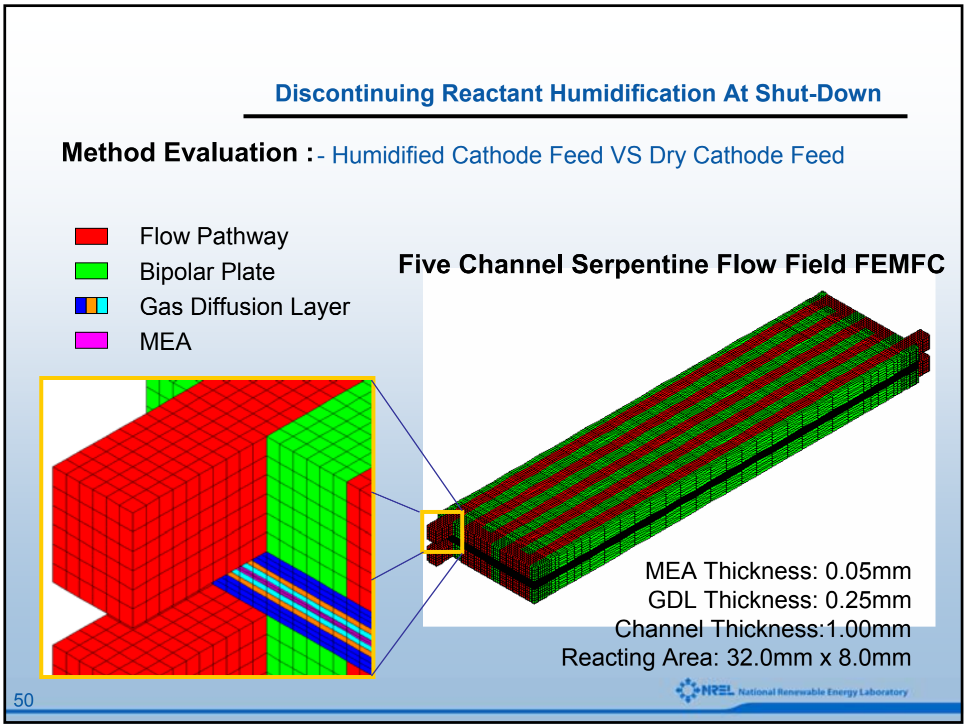
(Examples from StarCD PEMFC)



Investigated Available Modeling Tools to Investigate Freeze Solutions

Three Key Processes

- Electrochemical Reactions in Catalyst Layers
- Proton Migration in the PEM Layer
- Mass Transport within All Region of PEMFC



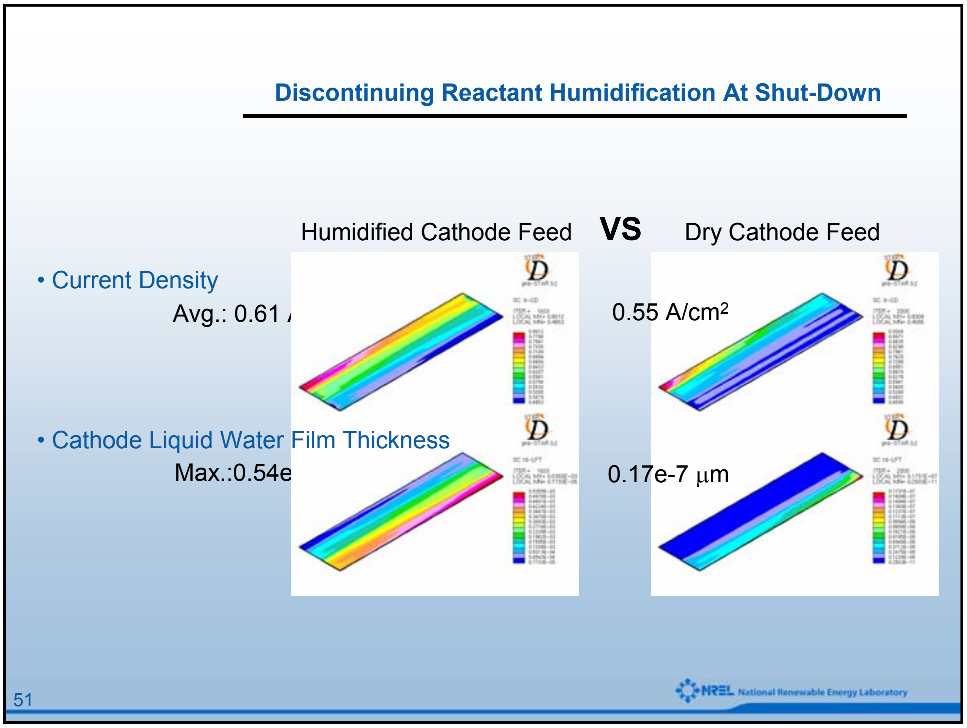
Discontinuing Reactant Humidification At Shut-Down

Method Evaluation : - Humidified Cathode Feed VS Dry Cathode Feed

🟥 Flow Pathway
🟩 Bipolar Plate
▨ Gas Diffusion Layer
🟪 MEA

Five Channel Serpentine Flow Field FEMFC

MEA Thickness: 0.05mm
GDL Thickness: 0.25mm
Channel Thickness:1.00mm
Reacting Area: 32.0mm x 8.0mm



Discontinuing Reactant Humidification At Shut-Down

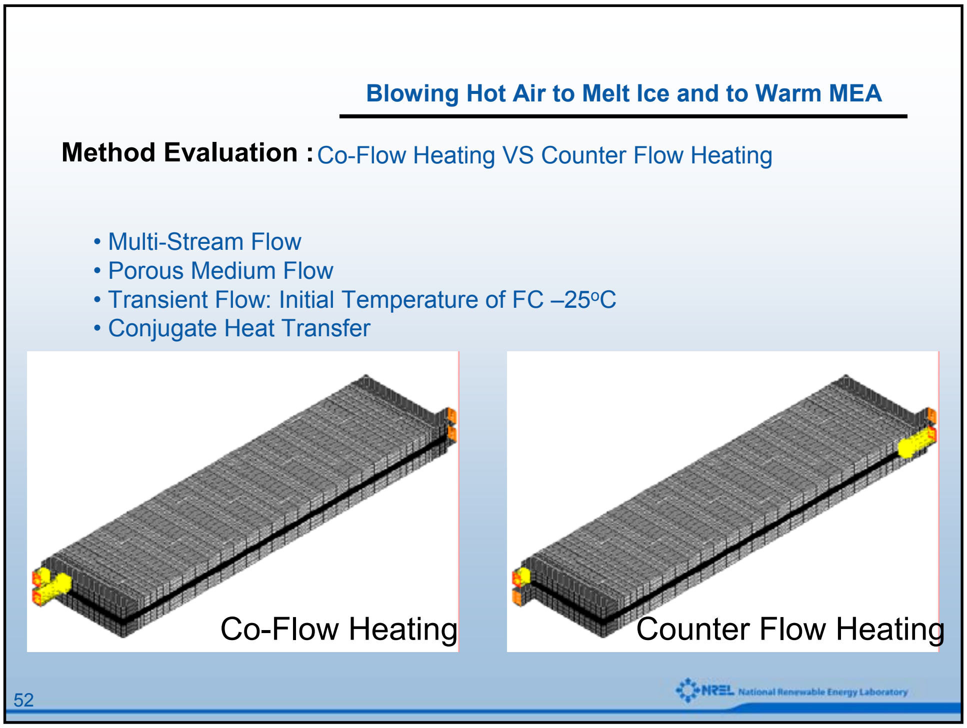
Humidified Cathode Feed **VS** Dry Cathode Feed

- Current Density

  Avg.: 0.61 0.55 A/cm^2

- Cathode Liquid Water Film Thickness

  Max.:0.54e 0.17e-7 μm



Blowing Hot Air to Melt Ice and to Warm MEA

Method Evaluation : Co-Flow Heating VS Counter Flow Heating

- Multi-Stream Flow
- Porous Medium Flow
- Transient Flow: Initial Temperature of FC –25^{o}C
- Conjugate Heat Transfer

Co-Flow Heating

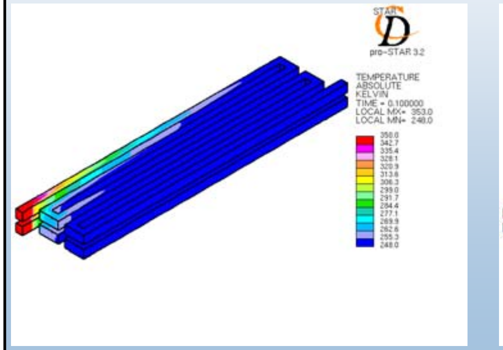
Counter Flow Heating

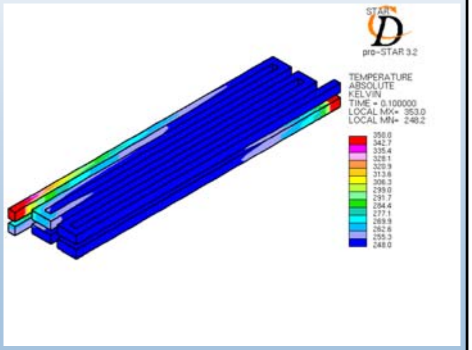
Blowing Hot Air to Melt Ice and to Warm MEA

Channel Temperature

Co-Flow Heating

Counter Flow Heating

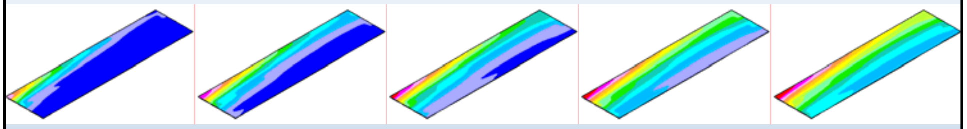




Blowing Hot Air to Melt Ice and to Warm MEA

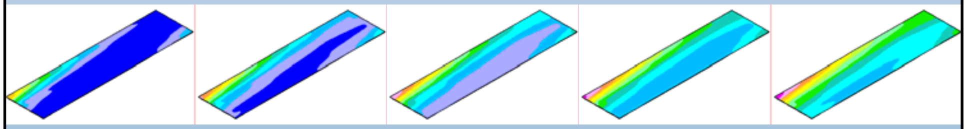
MEA Temperature

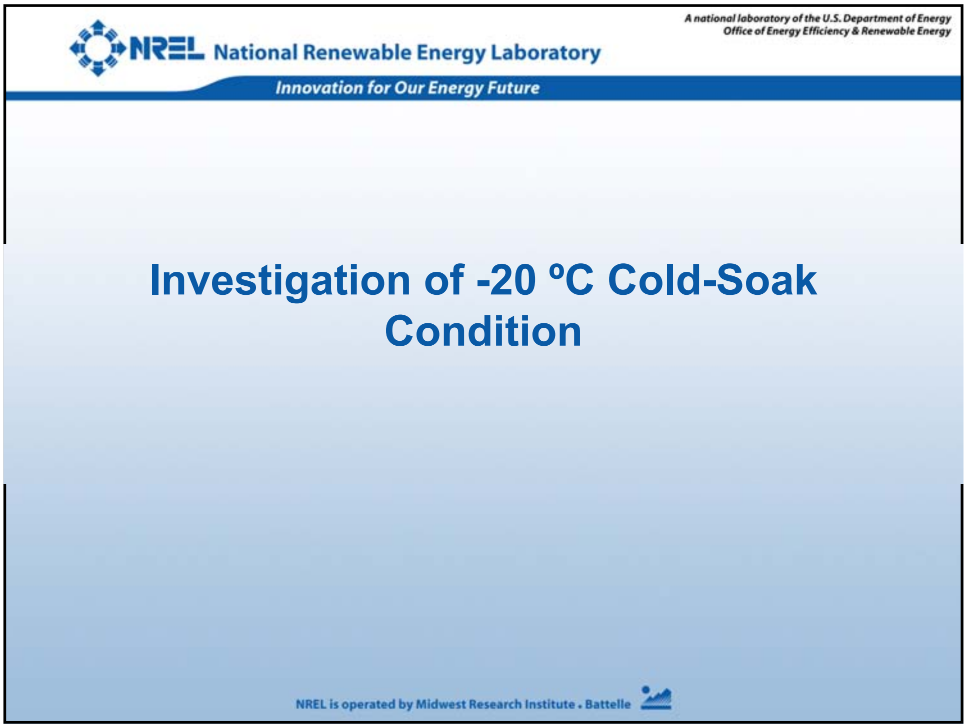
Co-Flow Heating



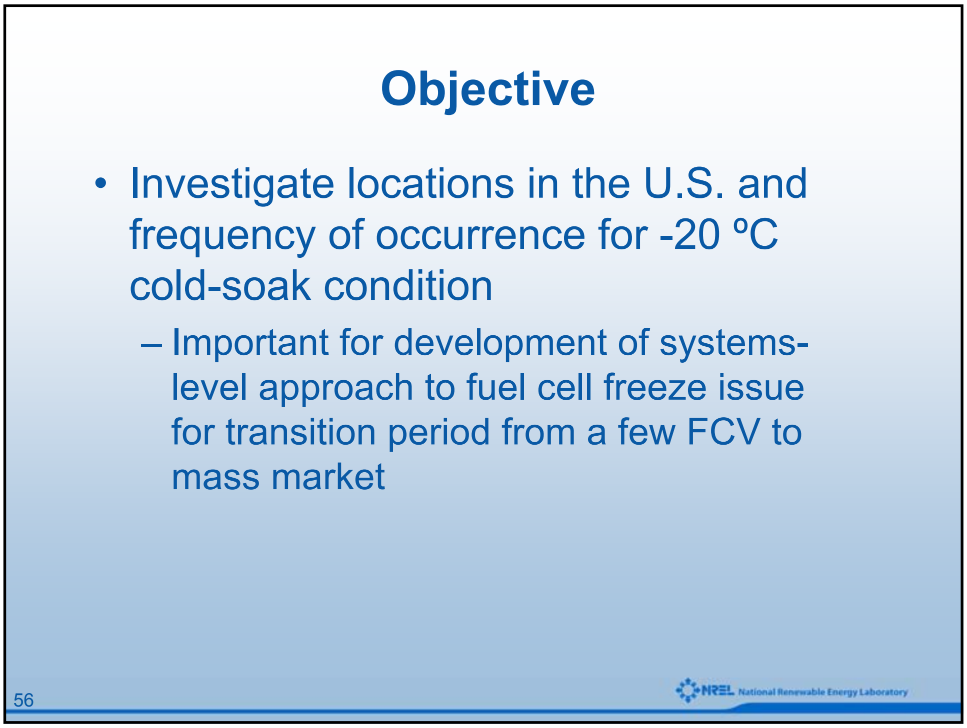
0.2sec 0.4sec 0.6sec 0.8sec 1.0sec

Counter Flow Heating





Investigation of -20 ºC Cold-Soak Condition



Objective

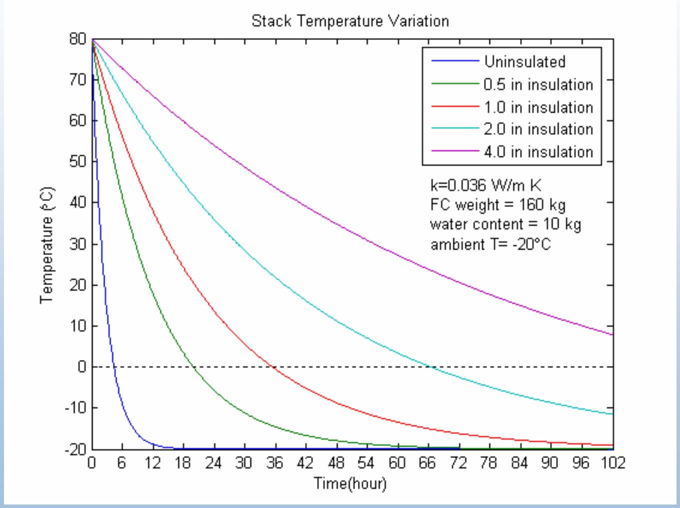
- Investigate locations in the U.S. and frequency of occurrence for -20 ºC cold-soak condition
  - Important for development of systems-level approach to fuel cell freeze issue for transition period from a few FCV to mass market

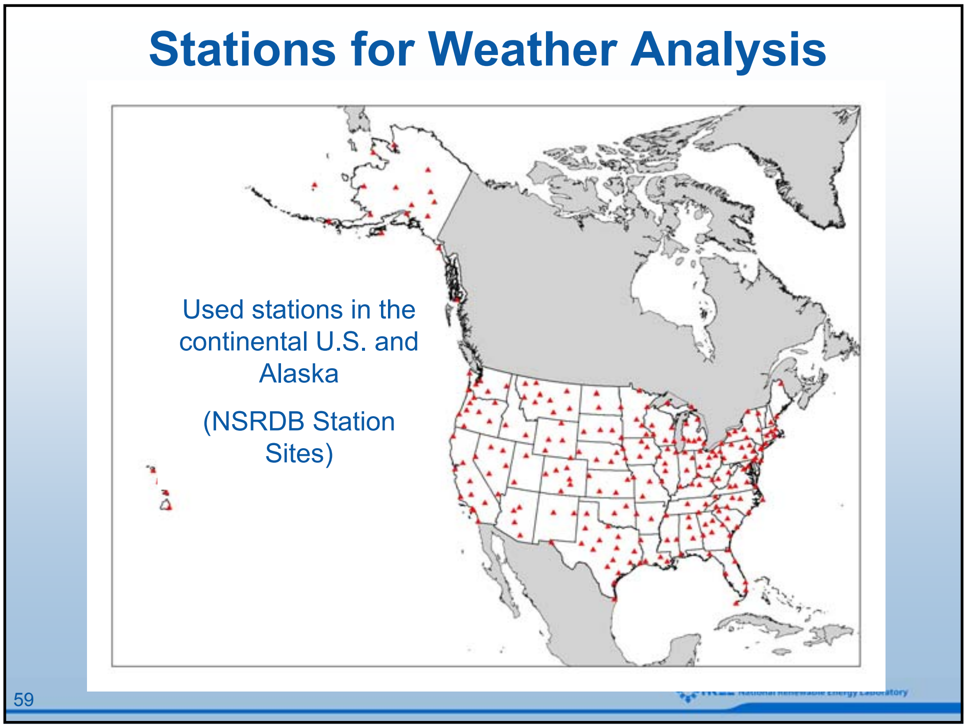
Approach

- Establish context for stack to achieve -20 ºC cold-soak
  - Baseline analysis calculating cool-down time from stack operating temperature
- Use database of ~230 weather stations across the U.S. to collect hourly temperature data for 28 year period from 1961-1988
- Determine longest consecutive hours each station measured temperatures below -20 ºC
- Determine total number of hours each station measured temperatures below -20 ºC
- Determine total number of times each station measured temperatures below -20 ºC for 2, 3, 4, … max consecutive hours (and calculate resulting average number of occurrences per year)

Results: Stack Cool-Down From 80 ºC

- Significant effect of insulation on cool-down time
- Figure ignores additional time required for water content phase change at ~0 ºC

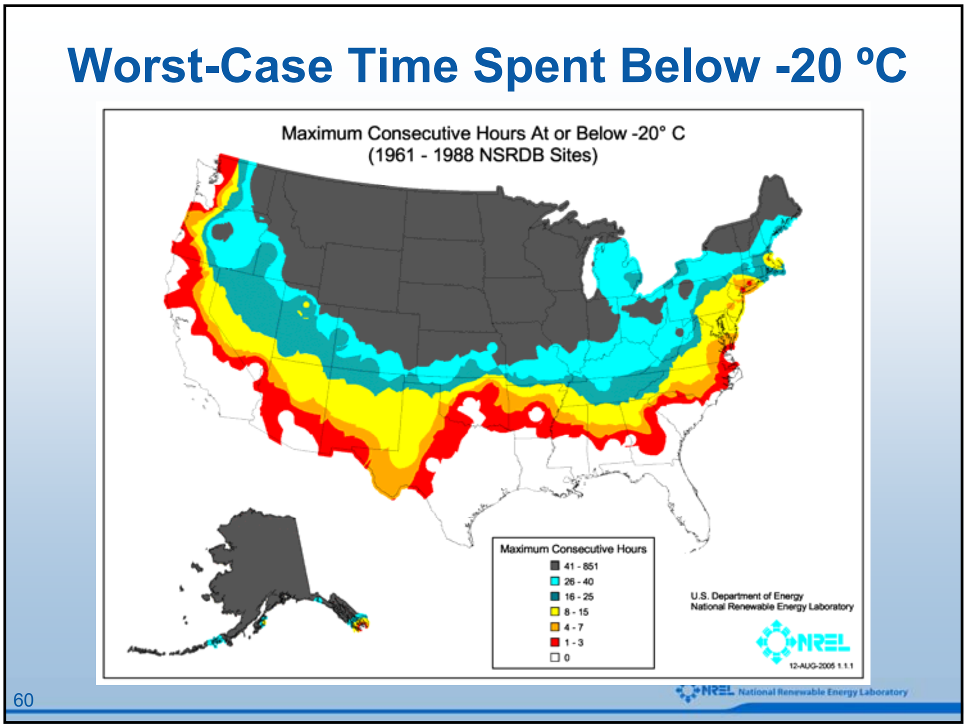




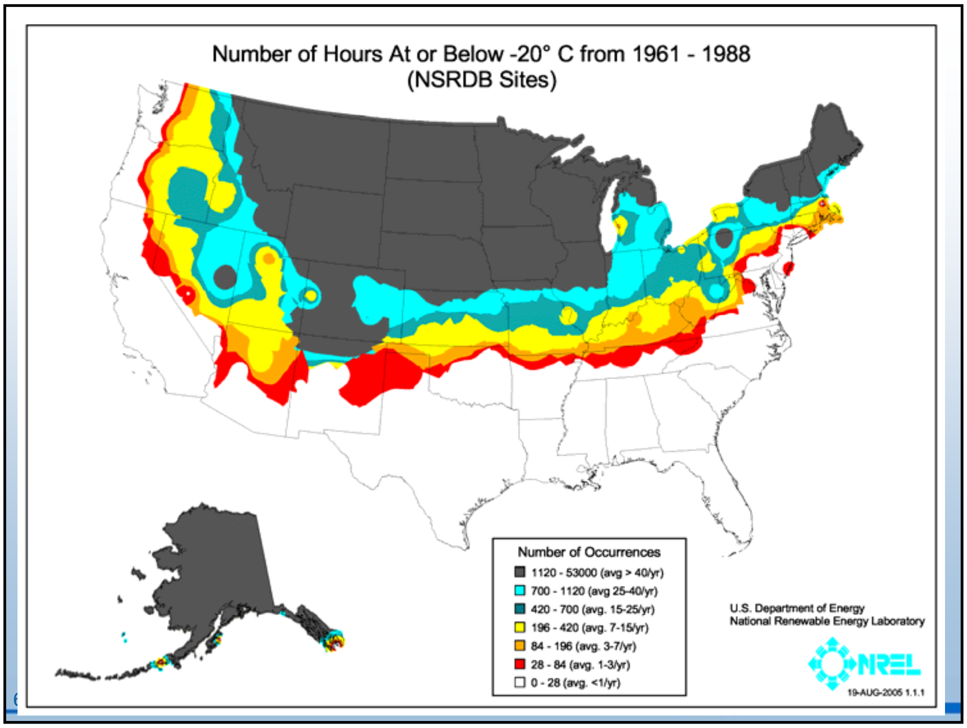
Stations for Weather Analysis

Used stations in the continental U.S. and Alaska

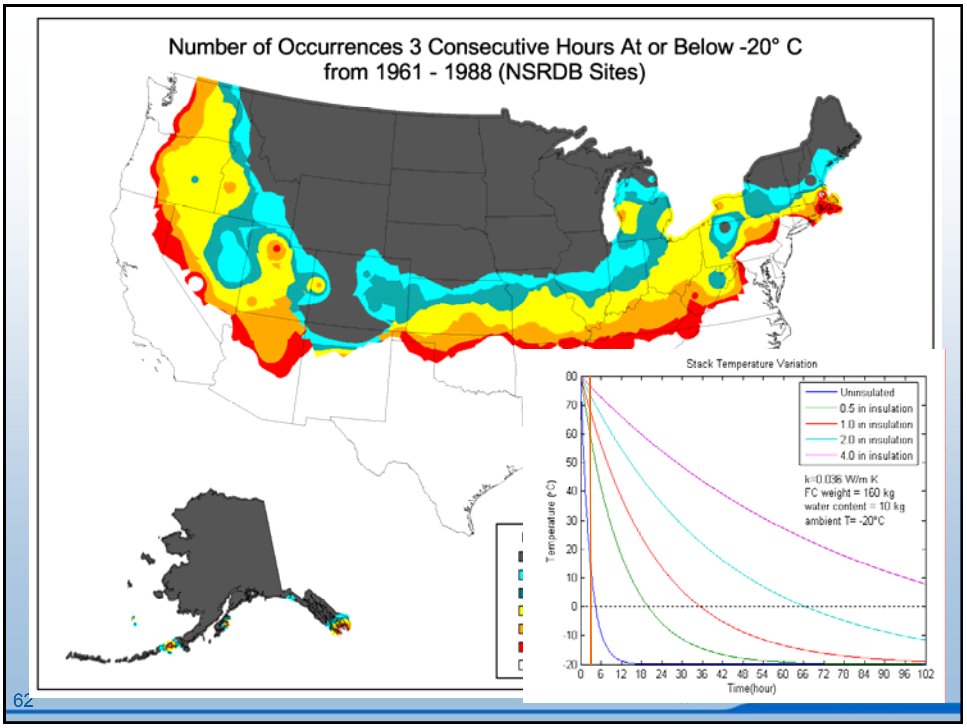
(NSRDB Station Sites)



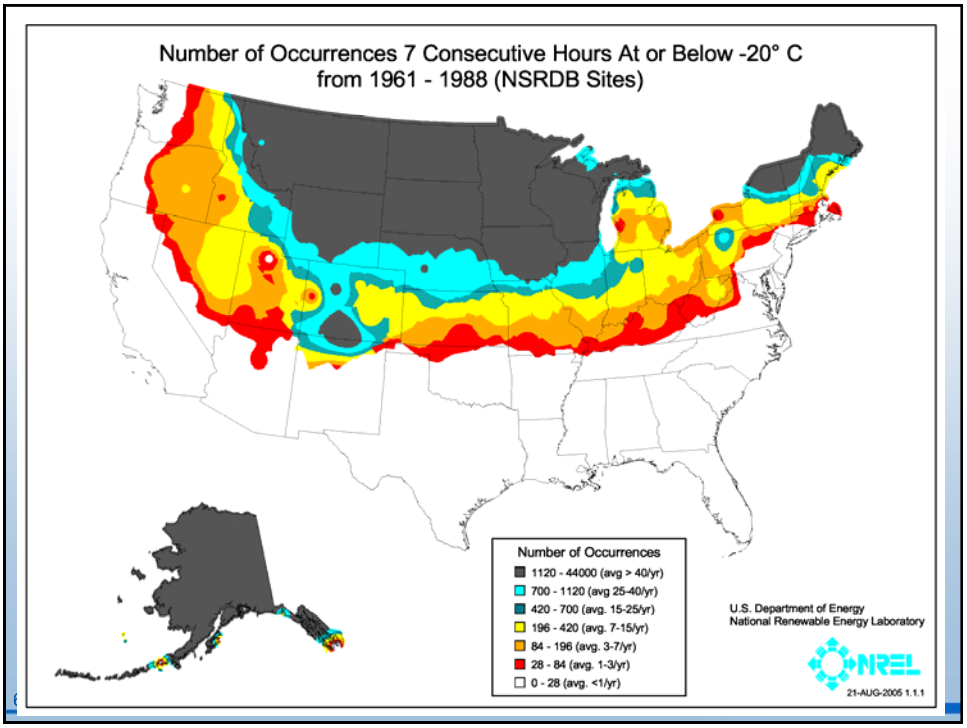
Worst-Case Time Spent Below -20 ºC



Number of Hours At or Below -20° C from 1961 - 1988 (NSRDB Sites)



Number of Occurrences 3 Consecutive Hours At or Below -20° C from 1961 - 1988 (NSRDB Sites)



Number of Occurrences 7 Consecutive Hours At or Below -20° C
from 1961 - 1988 (NSRDB Sites)

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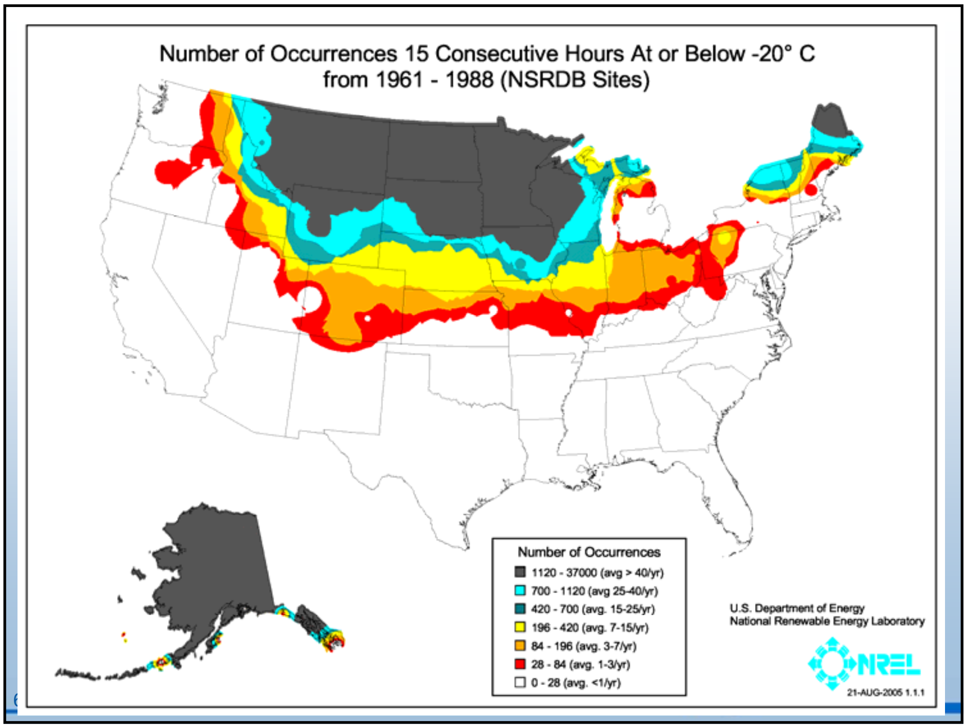
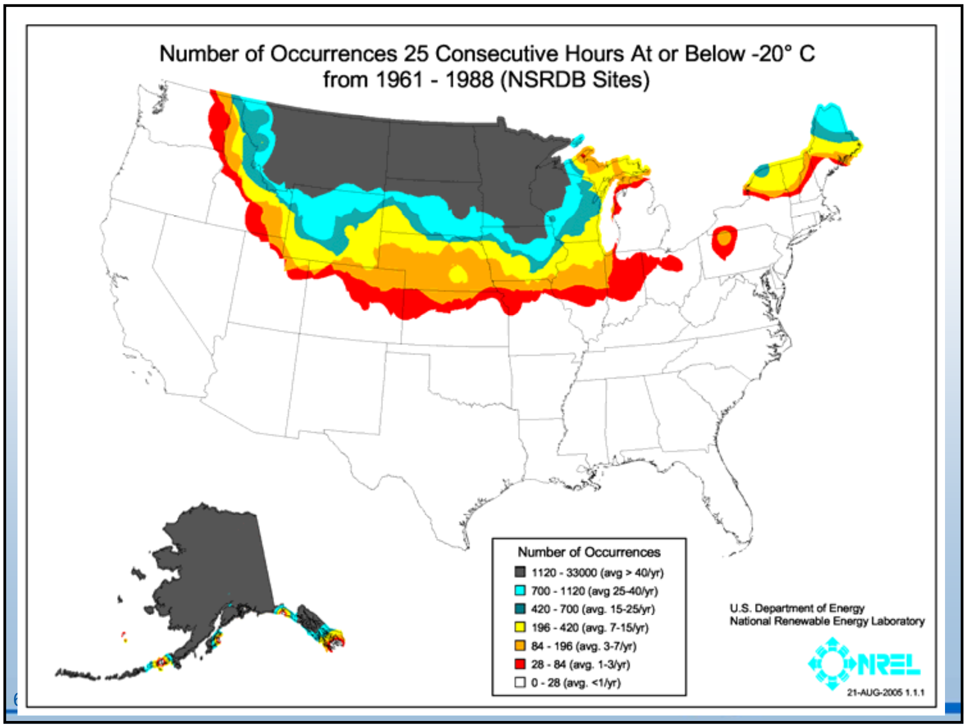


Number of Occurrences 15 Consecutive Hours At or Below -20° C
from 1961 - 1988 (NSRDB Sites)

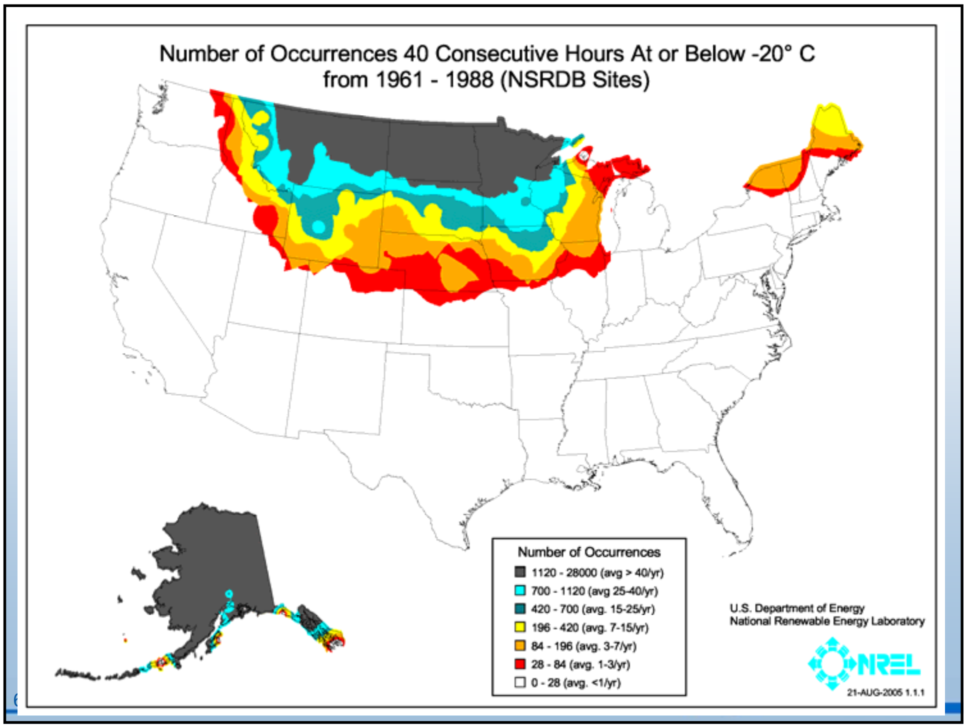
U.S. Department of Energy
National Renewable Energy Laboratory

NREL

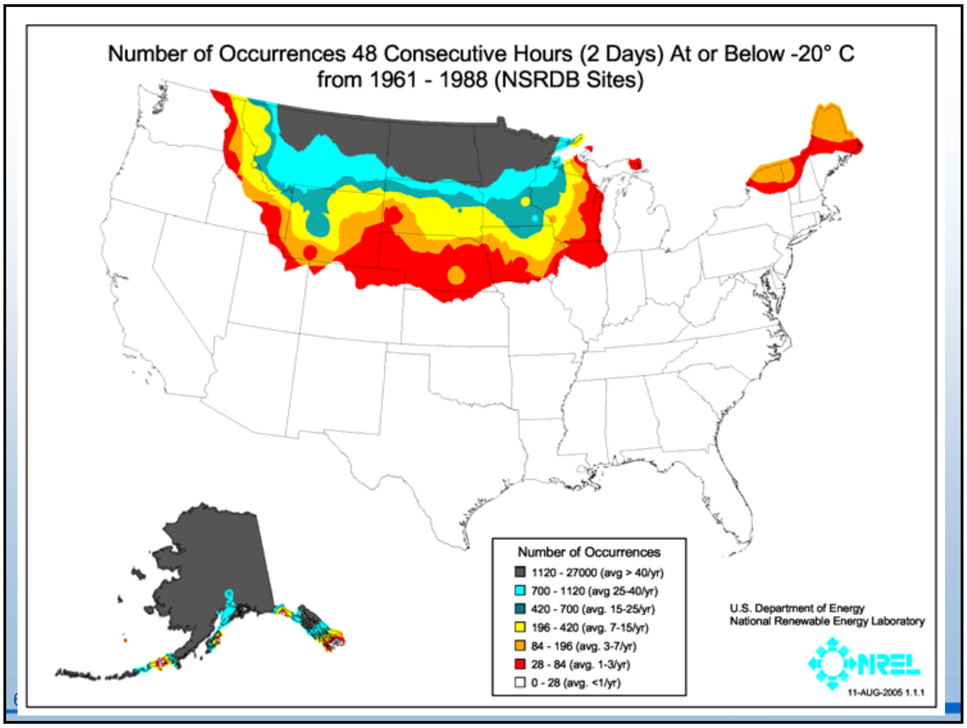
21-AUG-2005 1.1.1



Number of Occurrences 25 Consecutive Hours At or Below -20° C
from 1961 - 1988 (NSRDB Sites)



Number of Occurrences 40 Consecutive Hours At or Below -20° C
from 1961 - 1988 (NSRDB Sites)



Number of Occurrences 48 Consecutive Hours (2 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

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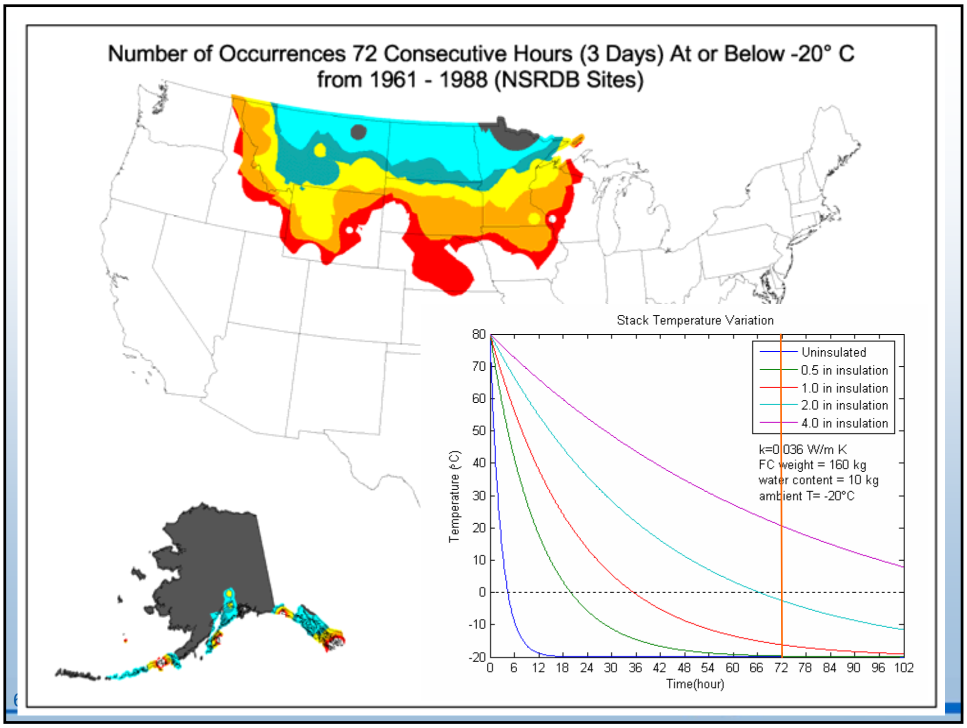
National Renewable Energy Laboratory

NREL

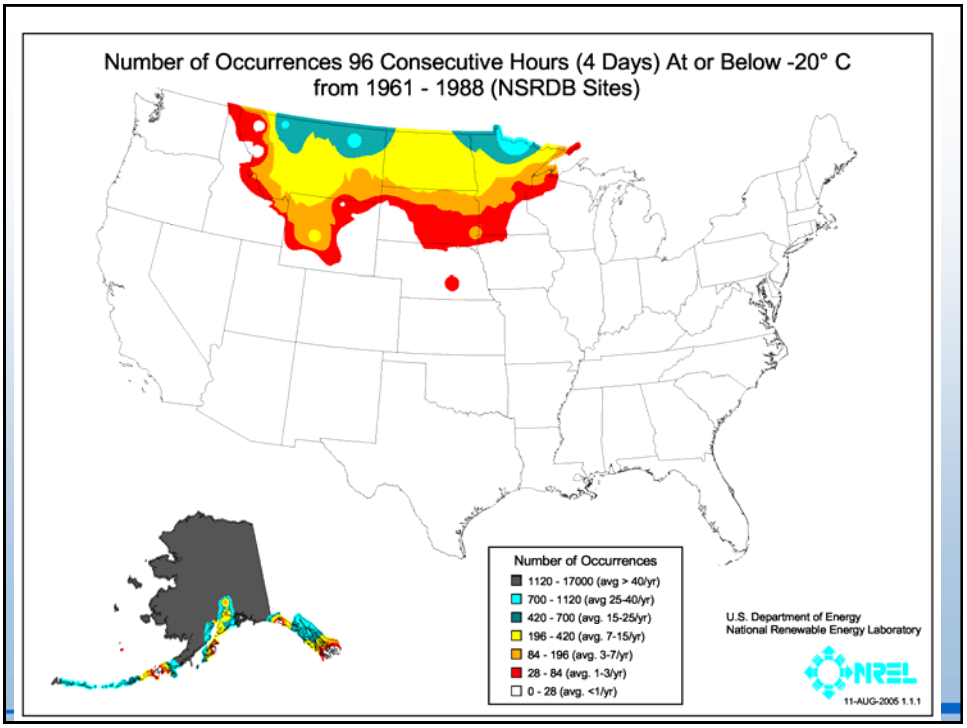
11-AUG-2005 1.1.1



Number of Occurrences 72 Consecutive Hours (3 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

Stack Temperature Variation

k=0.036 W/m K
FC weight = 160 kg
water content = 10 kg
ambient T= -20°C



Number of Occurrences 96 Consecutive Hours (4 Days) At or Below -20° C
from 1961 - 1988 (NSRDB Sites)

Number of Occurrences
- ■ 1120 - 17000 (avg > 40/yr)
- ■ 700 - 1120 (avg 25-40/yr)
- ■ 420 - 700 (avg. 15-25/yr)
- ■ 196 - 420 (avg. 7-15/yr)
- ■ 84 - 196 (avg. 3-7/yr)
- ■ 28 - 84 (avg. 1-3/yr)
- ☐ 0 - 28 (avg. <1/yr)

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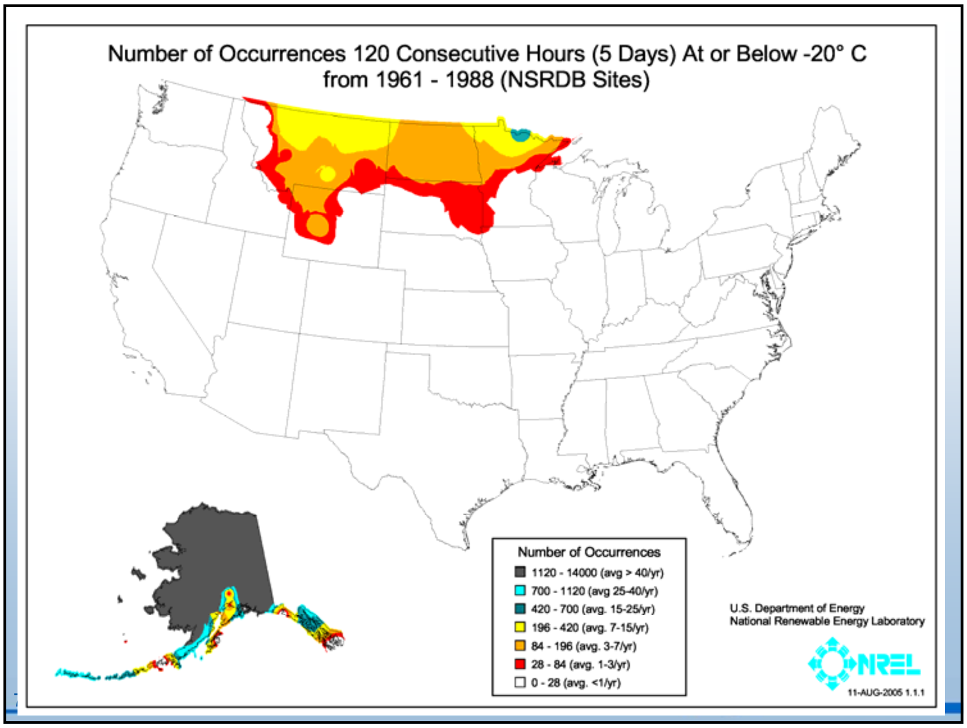

Number of Occurrences 120 Consecutive Hours (5 Days) At or Below -20° C
from 1961 - 1988 (NSRDB Sites)

Number of Occurrences
- ■ 1120 - 14000 (avg > 40/yr)
- ■ 700 - 1120 (avg 25-40/yr)
- ■ 420 - 700 (avg. 15-25/yr)
- ■ 196 - 420 (avg. 7-15/yr)
- ■ 84 - 196 (avg. 3-7/yr)
- ■ 28 - 84 (avg. 1-3/yr)
- ☐ 0 - 28 (avg. <1/yr)

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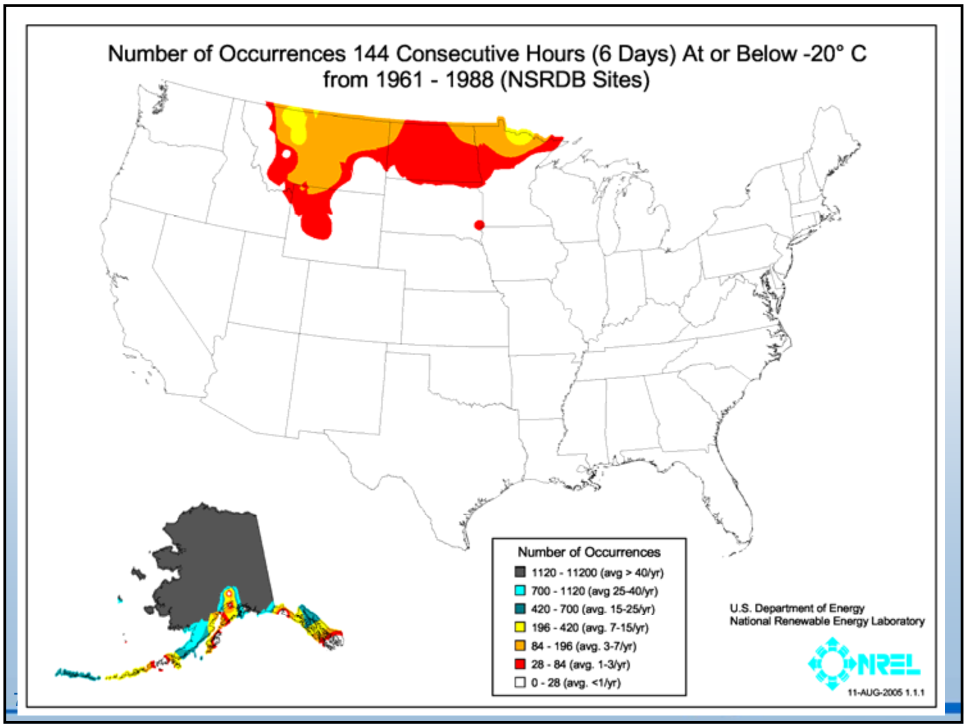
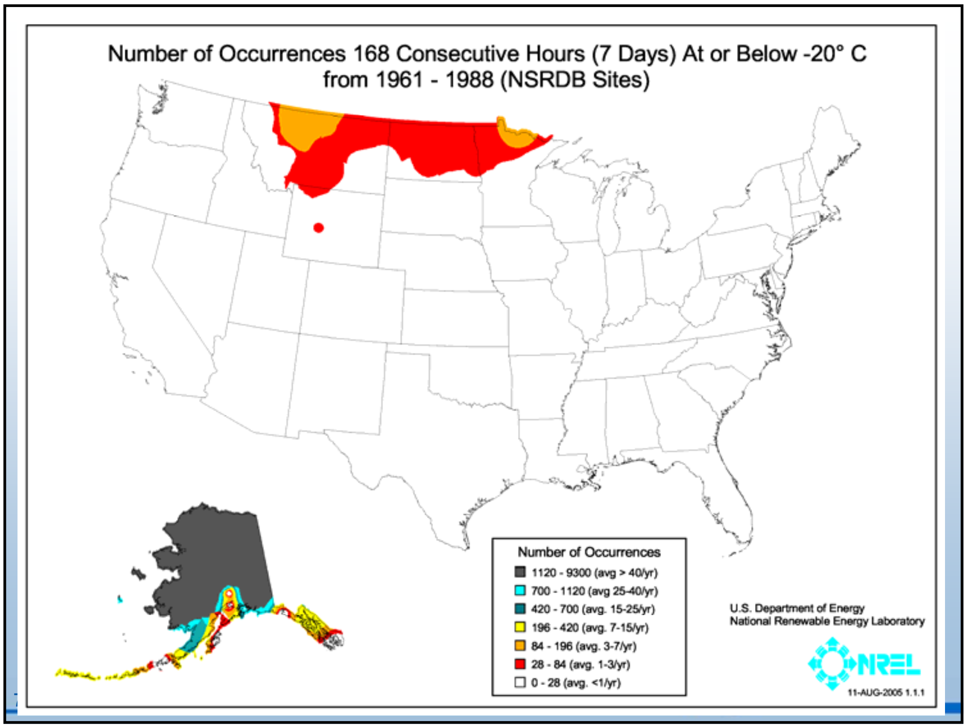
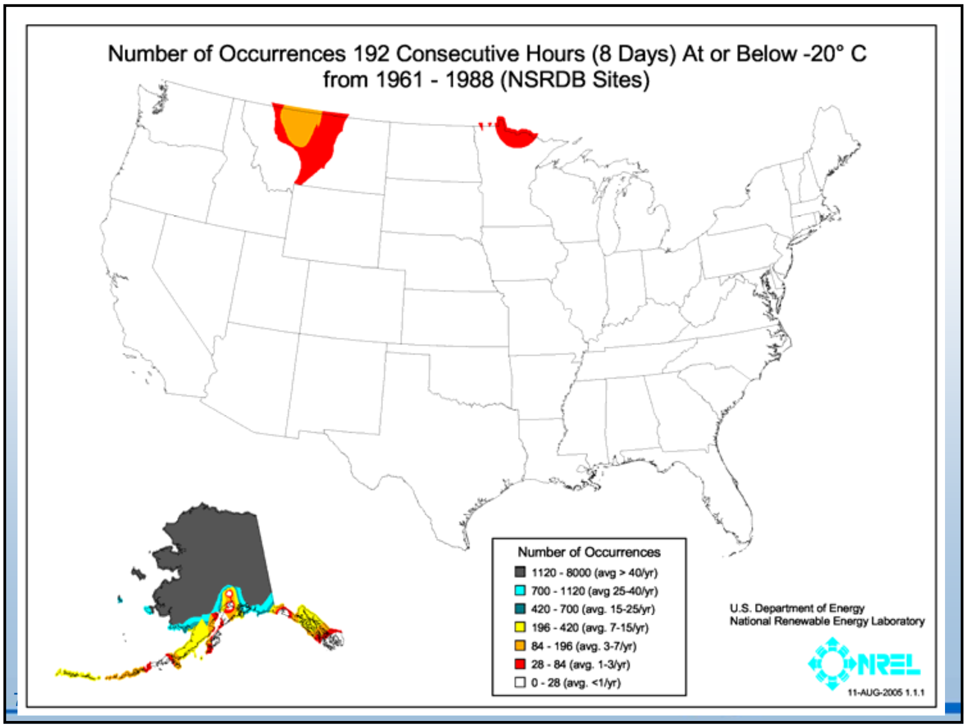
11-AUG-2005 1.1.1

Number of Occurrences 144 Consecutive Hours (6 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

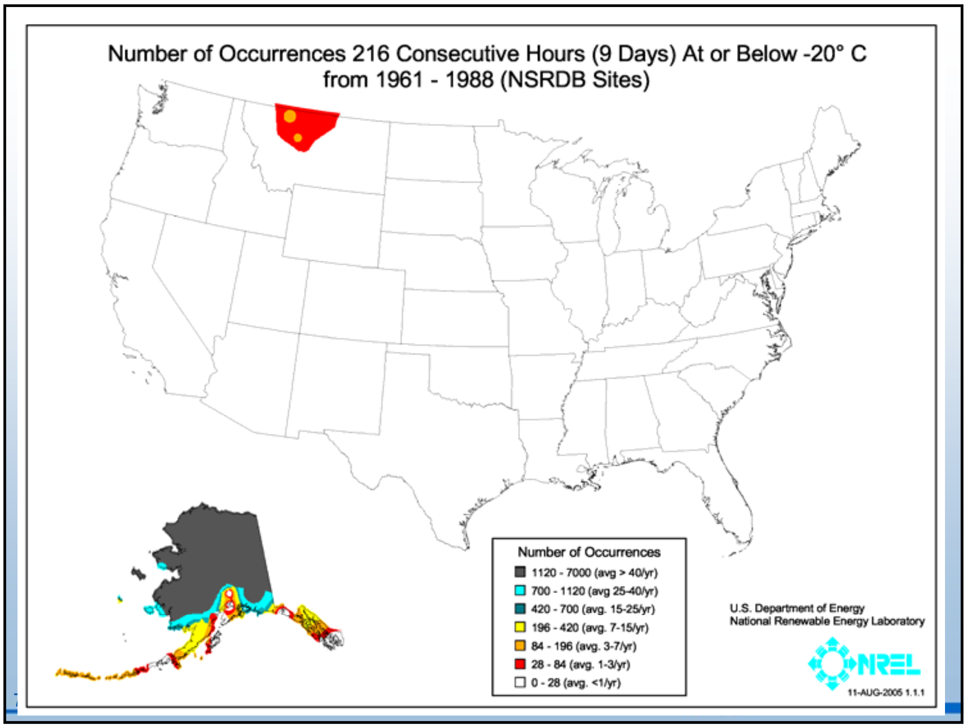


Number of Occurrences 168 Consecutive Hours (7 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

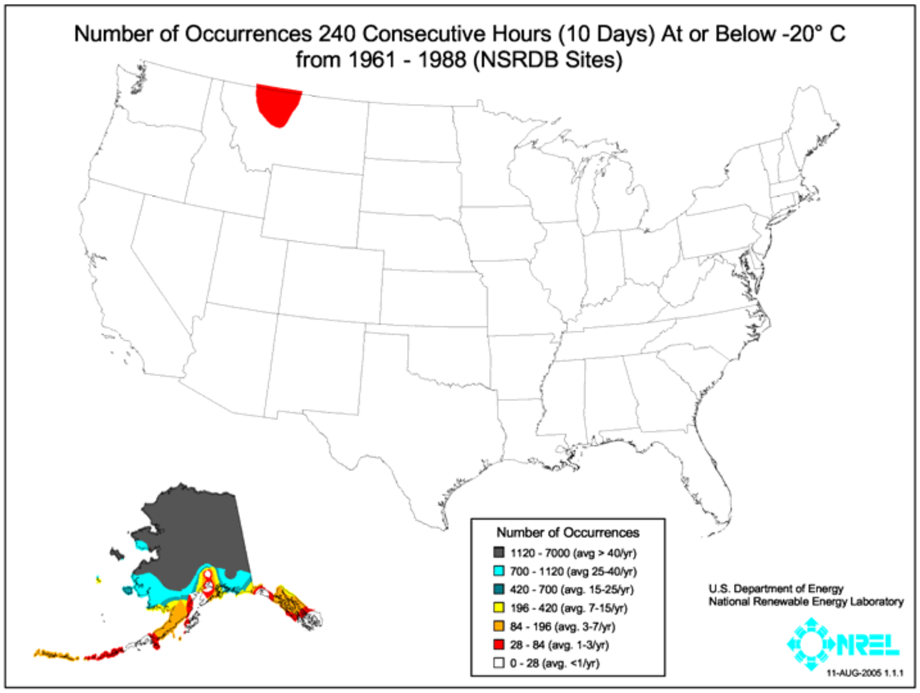




Number of Occurrences 192 Consecutive Hours (8 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

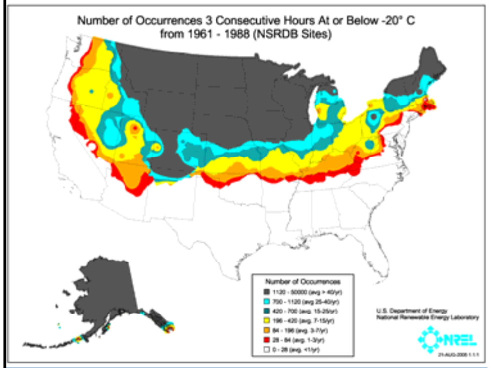


Number of Occurrences 216 Consecutive Hours (9 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

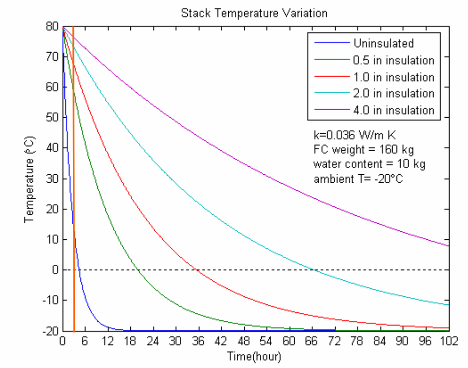


Number of Occurrences 240 Consecutive Hours (10 Days) At or Below -20° C from 1961 - 1988 (NSRDB Sites)

-20 ºC Soak Condition "Melts Away"



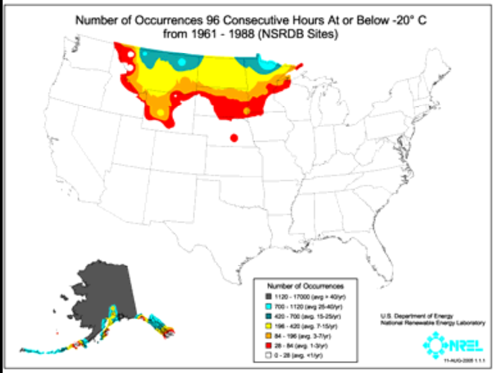
Number of Occurrences 3 Consecutive Hours At or Below -20° C from 1961 - 1988 (NSRDB Sites)

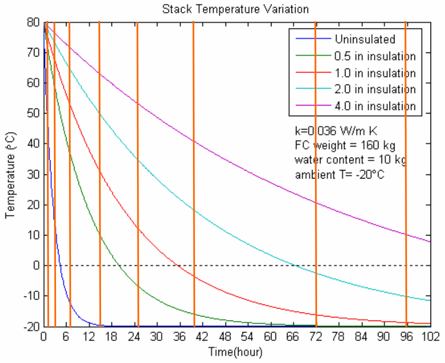


Stack Temperature Variation

Note stack behavior if ambient temperature is constant at -20 ºC for given period of time

-20 ºC Soak Condition “Melts Away”





Note stack behavior if ambient temperature is constant at -20 ºC for given period of time

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Caveats to Analysis Comparison

- Constant ambient at -20 ºC for stack temperature profile, but ambient could be lower during consecutive hours in weather map and could still be below 0 ºC following consecutive period
- Different fuel cells will have different temperature profiles
- Map presents average events per year, but some years will be worse than others
- If parked for long periods, the stack will eventually reach the ambient temperature

Discussion

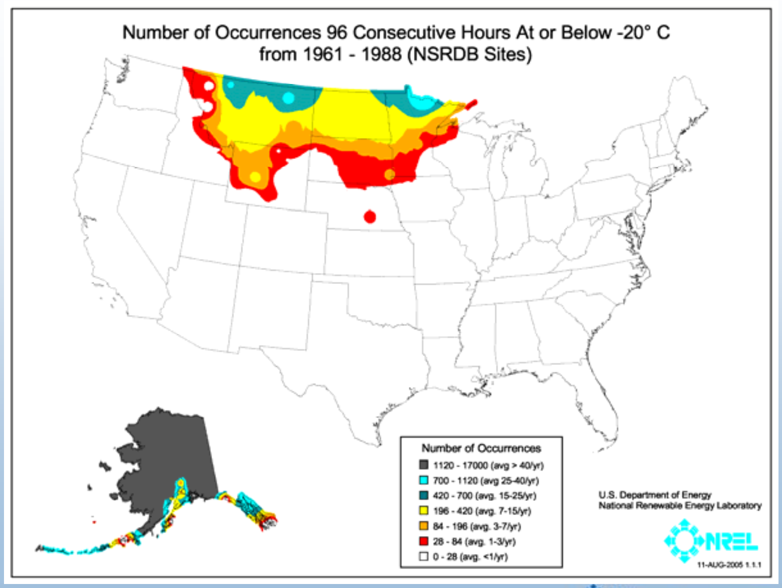
- Analysis useful for determining actual energy requirements for different strategies (e.g. – thaw vs. keep-warm)
- Can determine how frequently and widespread worst-case conditions below -20 ºC occur, and how well different thresholds would represent actual temperature observations around the country
- When combined with driving pattern information, can be used to estimate number of freeze/thaw cycles
- Analysis can point to areas of US that FC Freeze is NOT important in early market penetration and which solutions may be sufficient

Future Work

- Further calculations using hourly temperatures for worst-case coldest month in different locations
- Run number of occurrences analysis at different threshold temperatures
- Further analyze regional impacts of sub-freezing temperatures by considering population/registered vehicle distribution
- Integrate national temperature profile database into general tool for inputting PEMFC & drive cycle parameters in order to determine freeze behavior

Extra stand-alone animation slide

Cold-Soak Animation



Summary and FY06 Work – 3D Modeling

- Among the commercial software for 3D modeling fuel cell, StarCD PEMFC seems to be the most advanced
- Our evaluation runs indicated it is suitable for FC freeze evaluation.
- Collaborate with CD-adapco and University of South Carolina to develop 3D freeze modeling capability for the PEMFC module of StarCD
- Perform rigorous evaluation for the “freeze start technologies and methods” using 3D PEM Fuel Cell models

Interactions and Collaborations

Supported and Participated at the DOE/LANL Workshop on Fuel Cell Operation below Freeze

- NREL supported planning and organizing the DOE Workshop on Fuel Cell Operation at Sub-Freezing Temperatures (Held on February 1-2, 2005 in Phoenix, AZ)
- Principal Investigator presented results of patent search and preliminary energy analysis at the Workshop.
- Several of the Workshop participants (including 3M, GM, University of South Carolina, and Penn State) expressed interest in the patent search and analysis.
- Participated at the brainstorming sessions for identifying research issues and a plan for implementation. Identifying system aspect as an important element.

Summary

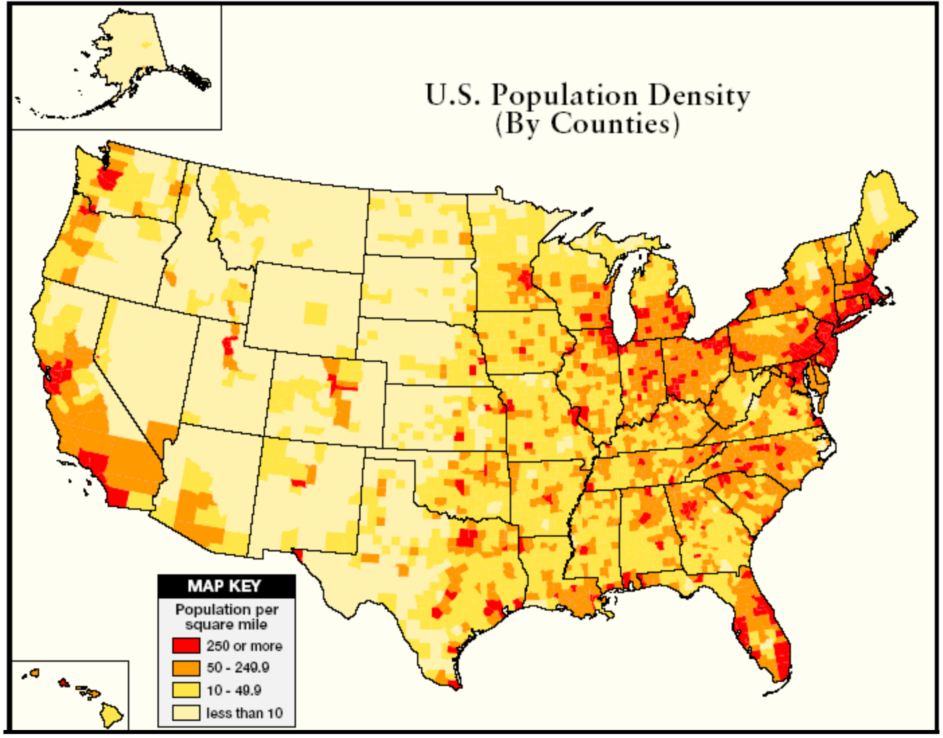
- Operating fuel cell at sub-freezing temperatures quickly and energy efficiently without durability impacts is a key barrier for fuel cell vehicles.
- We found that many patents, more than published articles, have been issued on fuel cell freeze and rapid startup.
- The majority of proposed concepts/solutions in these patents are from system level perspective. We performed preliminary analysis of some of these solutions.
- We analyzed and categorized these patents: “keep-warm” or “thaw/heating” methods are two major categories.
- Removing water from fuel cell system at shut-down is critical.
- “Keep-warm” methods do not allow the system to freeze. This method is effective for short-term storage and/or for mild sub-freezing temperatures, but could be inefficient for long-term storage.
- “Thawing/heating” methods require high power and humidification at startup but do not consume a lot of energy.
- Some combinations of different technologies may be promising to address rapid startup issues

Future Work

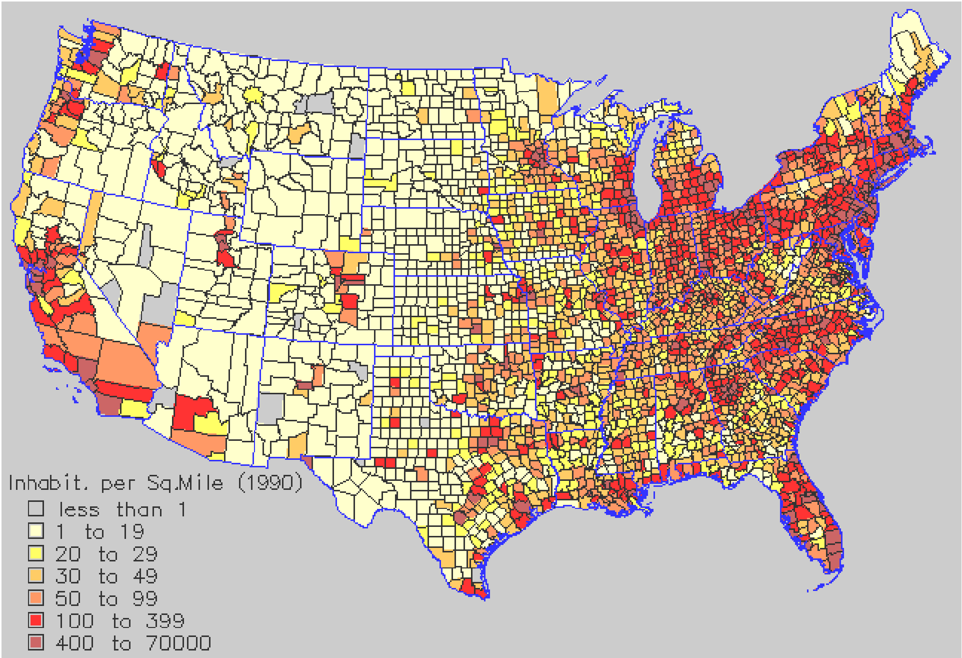
- FY06 and beyond
  - Collaborate with CD-adapco and University of South Carolina to develop 3D freeze modeling capability for the PEMFC module
  - Perform more rigorous evaluation for the “freeze start technologies and methods” using 3D PEM Fuel Cell models
  - Partner with industry to evaluate and implement and new approaches. (Response to H2 Merit Review)
  - Develop an advanced tool for estimating energy and power requirements for FC startup from freeze with ability for developer to provide input specific to their system
  - Perform system-wise analysis for the possible combinations of promising technologies
  - Present results at conferences and meetings

Appendix C

Population Density Map in the United State



2000 Population Density in USA
(www.census.gov/dmd/www/pdf/512popdn.pdf)



1990 Population Density in USA
(http://www.cast.uark.edu/local/catalog/national/html/Population.htmldir/USpop1990.html)