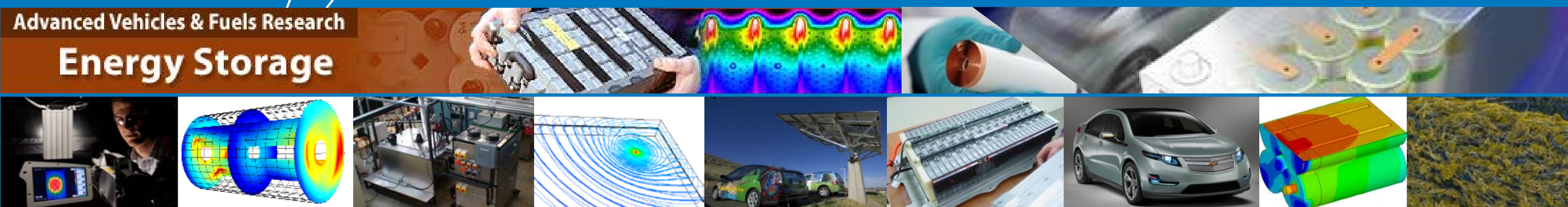
Addressing the Impact of Temperature Extremes on Large Format Li-Ion Batteries for Vehicle Applications



Ahmad Pesaran, Ph.D.
Shriram Santhanagopalan, Gi-Heon Kim
National Renewable Energy Laboratory
Golden, Colorado

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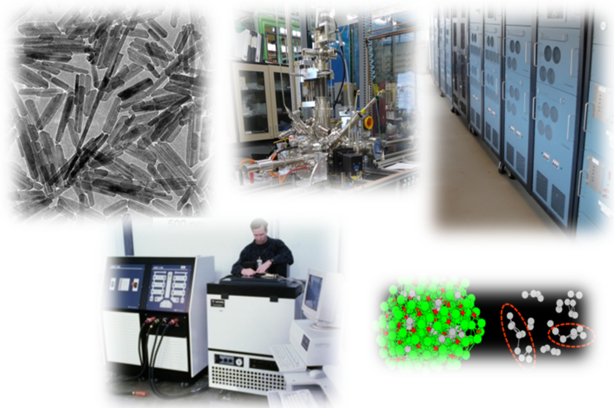
Outline

- **NREL's Projects – Focus on Temperature**
- **xEVs – Prospects & Barriers**
- **Impact of Temperature on Li-Ion Batteries**
  - Performance
  - Life
  - Safety
- **Controlling or Reducing the Impact of Temperature**
  - Material Selection
  - Cell and Module Design
  - Balance of System Design
- **Summary**

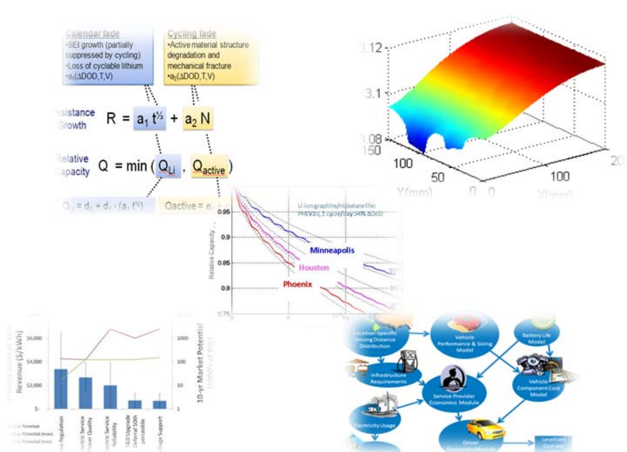
NREL Energy Storage Projects

Supporting DOE and industry to achieve energy storage targets for electrified vehicles



NREL

Energy Storage Project



Battery Material Research and Development

Component Testing and Characterization (Including Safety)

Multi-physics Battery Modeling (including Safety)

Battery Life Prediction and Trade-off

Battery System Evaluation

Working on temperature dependent issues

xEVs – Prospects

- Acceptance of hybrid vehicles by consumers
- Economic impact of high prices of oil
- Higher prices of gasoline and its volatility
- Oil peak and gap in production
- Importing oil from unstable countries
- Energy security
- Political pressure to use domestic fuel
- Environmental impact of using fossil fuel
  - Greenhouse gases
  - Climate change
- Increased interest of public in green and renewable technologies
- Regulation and policies – Upcoming Fuel Economy Standards

xEVs:

Hybrid Electric Vehicles
Plug-in HEVs
Extended Range EVs
Battery Electric Vehicles

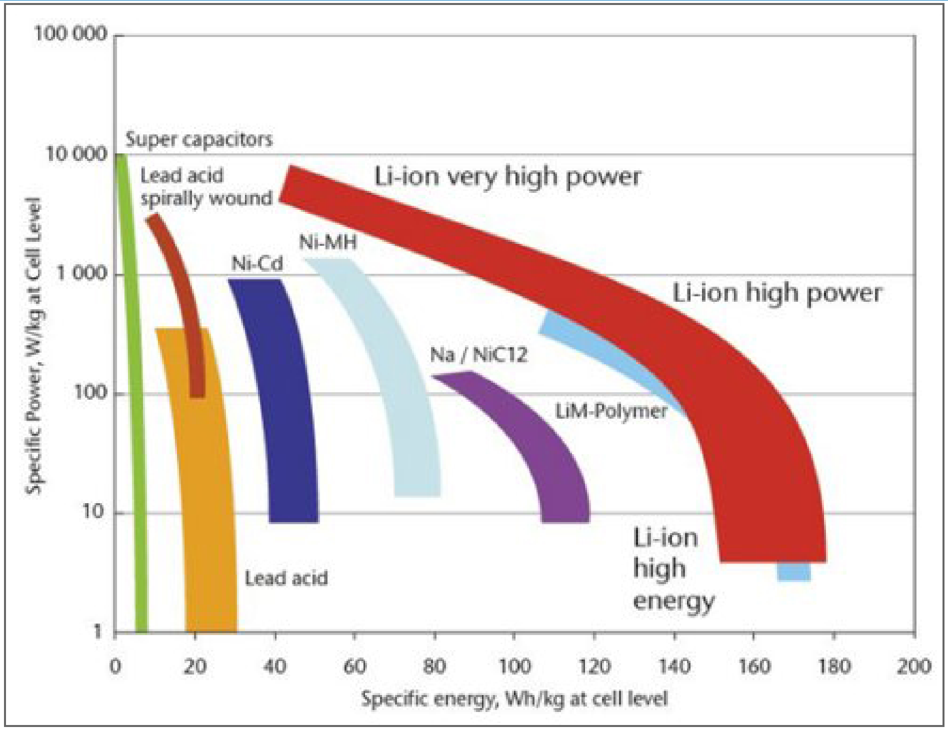
Super clean cars that run on inexpensive domestics electricity

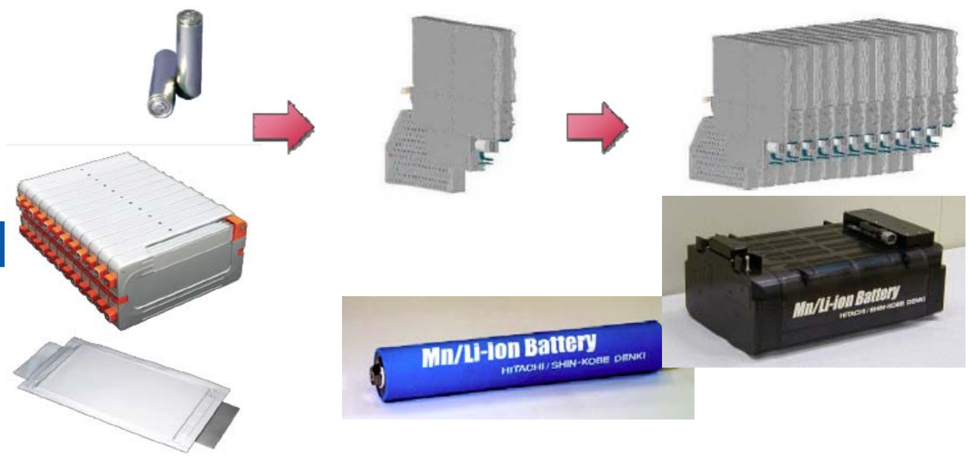
xEVs – Barriers

- Higher marginal price of xEVs relative to conventional vehicles (mostly due to battery)
- Long pay-back times of xEVs
- Low gas prices
- Improvements in fuel economy of conventional vehicles
- Interest in start-stop, micro hybrid, and electric assist vehicles
- Battery life; Cost for replacement
- Safety of lithium-ion powered xEVs
- Limited driving range of BEVs
- Charge time for PHEVs, EREVs, and BEVs
- Accessibility to large number of charge points
- Lower performance at cold and hot environments

Large Format Li-Ion Batteries for xEVs

- Lithium-ion battery technology is expected to be the energy storage choice for (xEVs) in the coming years
- Better (energy & power) performance than other existing technologies
- Trends toward large format cells
  - Higher volume &weight efficiencies and packaging
  - Lower # of connections and components
  - Lower system cost





Concerns about xEV Battery Temperature

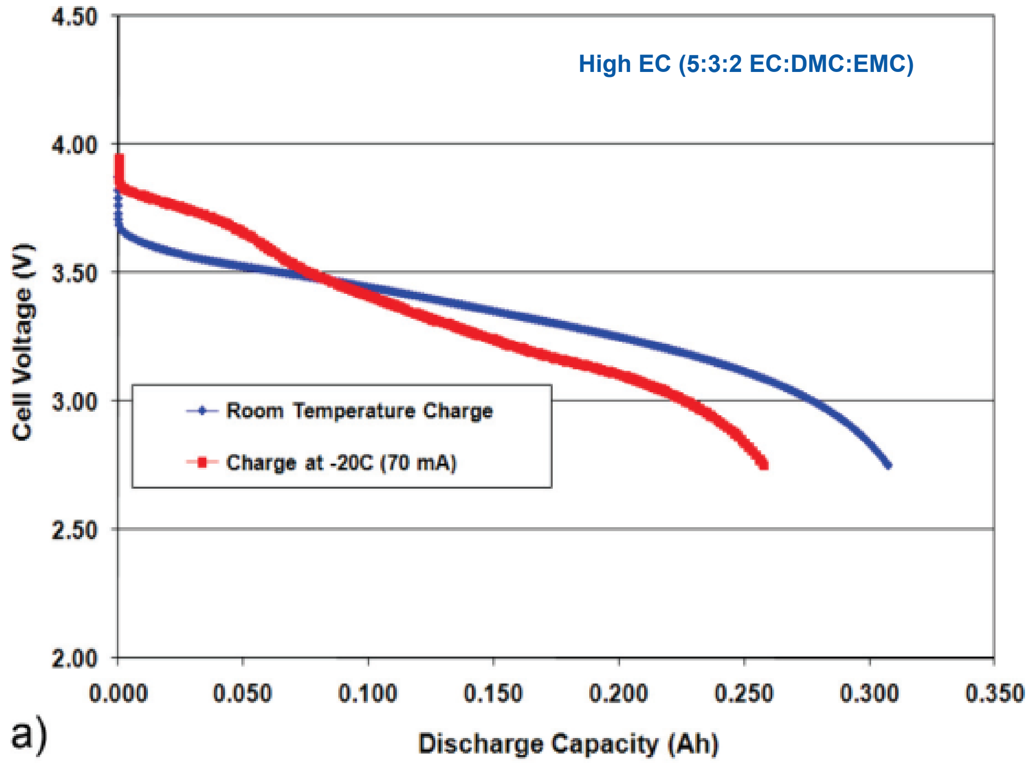
High and low temps lead to battery over-sizing and increased cost

- Cold temperature effects
  - Battery performance (power, Energy) lower due to poor ion transport
  - xEV acceleration and range are much more affected than conventional vehicles
  - Passenger heating needed, BEV range is reduced using battery energy (higher gas emissions if engine used for PHEV and EREV)
  - Charging is much more challenging as dendrite can grow and reduce life of battery and compromise safety
- Hot temperature effects
  - Side reactions happens faster so battery degrades faster
  - Faster battery degradation means higher cost for replacement
  - Passenger cooling needed, BEV range is reduce using battery energy (more pollution if engine use for PHEV and EREV)
- Very hot temperature effects
  - Potential for thermal runaway and safety incidents

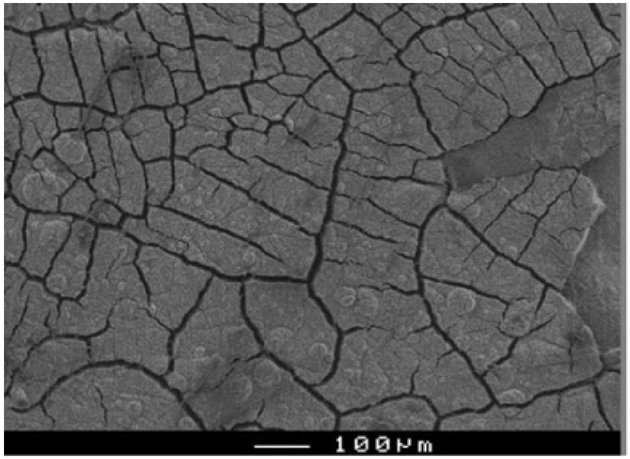
Cold Temperature Effects - 1

Physical Effects:

- Viscosity changes in the electrolyte lead to sluggish ion transport
- Polymeric components within the cell tend to become brittle (e.g., active material within the electrodes tends to fall apart due to binder failure)



a)



Poor Charge Acceptance

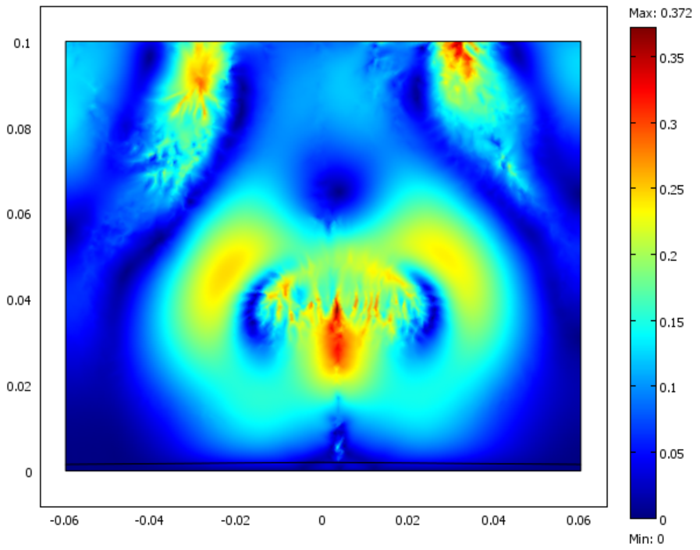
Discharge curves of MCMB-NCO Li-ion test cells with electrolytes, at 25 mA and -20°C, following charge at 70 mA at room temperature and –20°C.

M.C. Smart and B.V. Ratnakumar, JES 158(4) p. A379-A389 (2011)

Cold Temperature Effects - 2

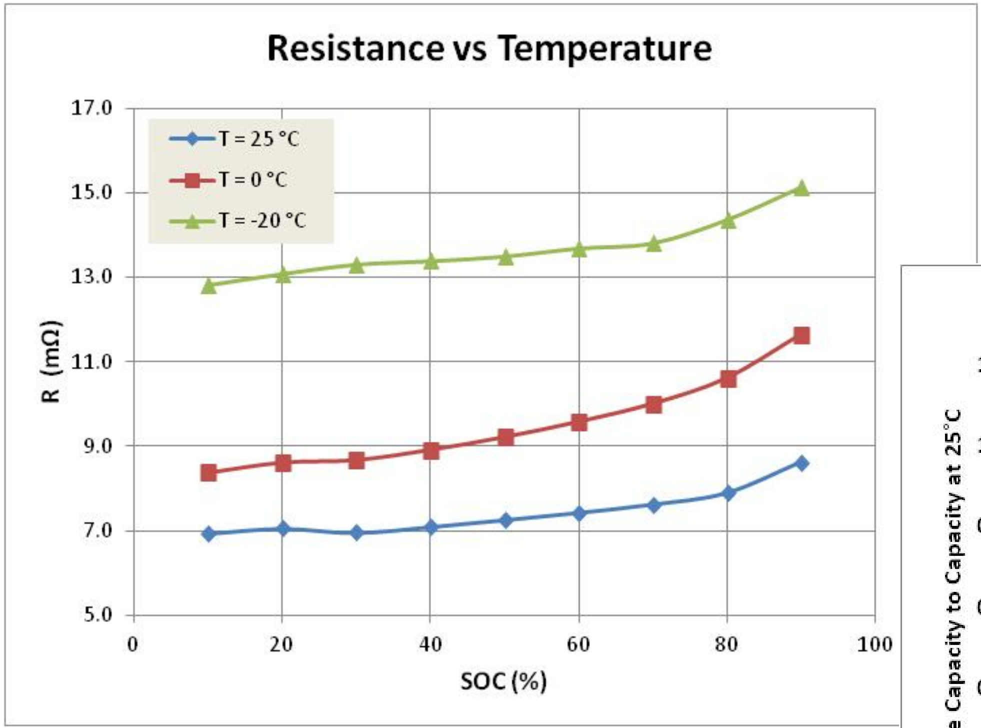
Chemical Effects:

- Type of additives used to improve low temperature performance introduce changes to the SEI properties:
  - compact, barrier-type, protective films are formed in solutions based on alkyl carbonates
  - bulky, porous, and less protective films are formed with DME additives (*Smart et al., JES 146(11) p. 3963 (1999)*)
- Resistance build-up across the SEI influences the abuse-performance of the cell

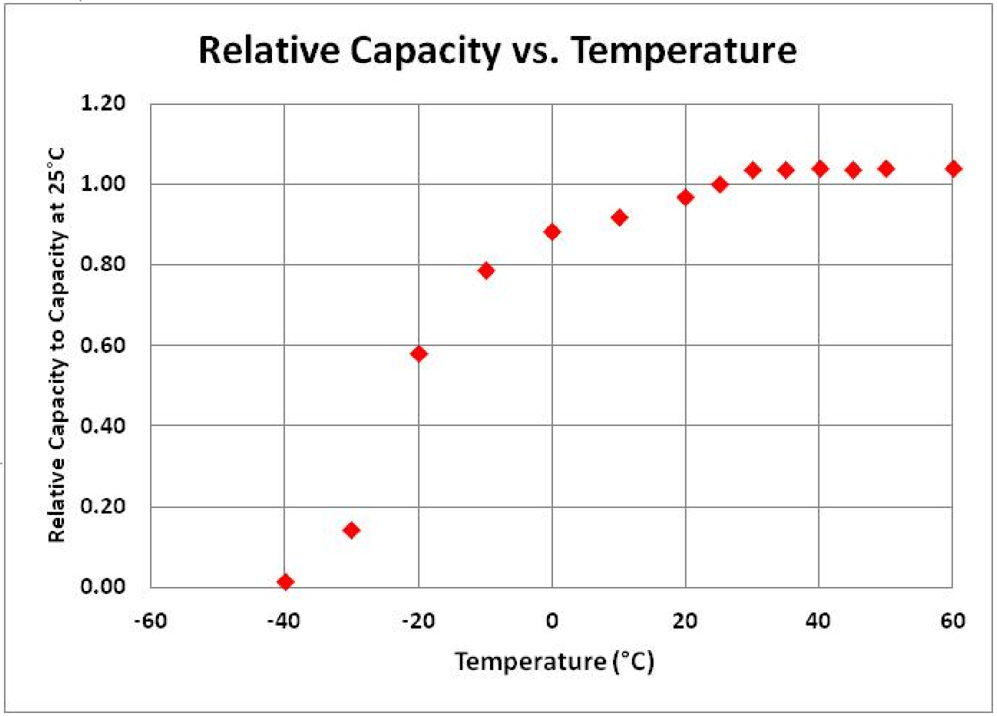


Energy and Power Lower in Cold

Battery power and energy are lower due to poor ion transport in cold temperatures



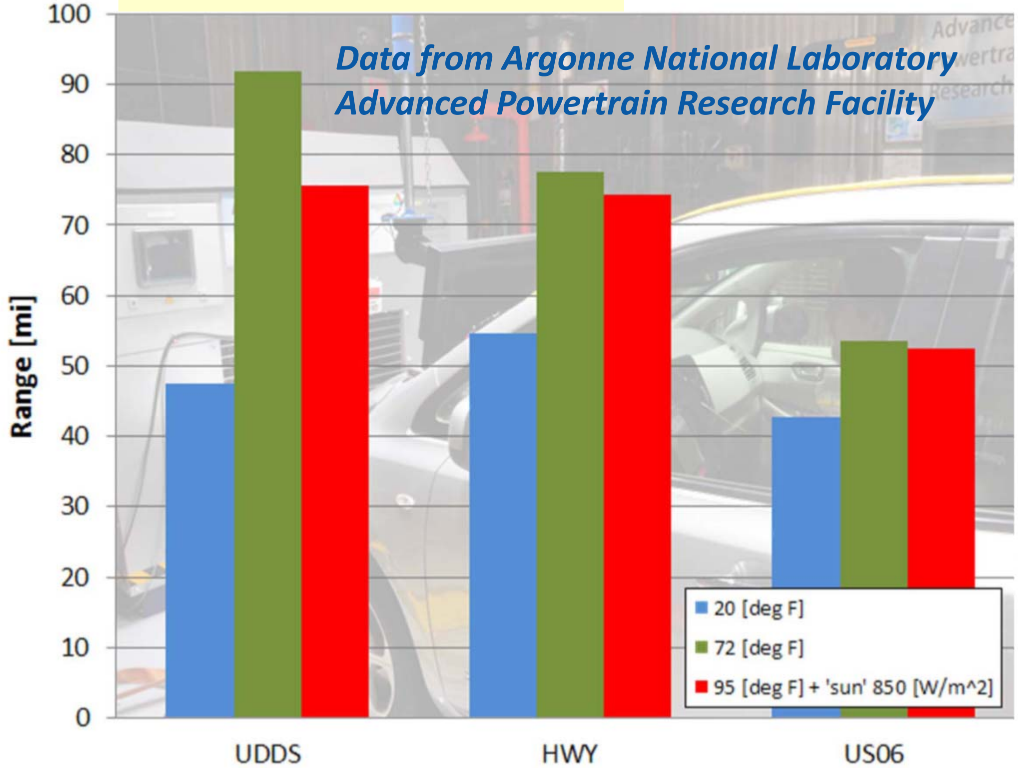
$LiFePO_4$
Graphite
Carbonates/$LiPF_6$

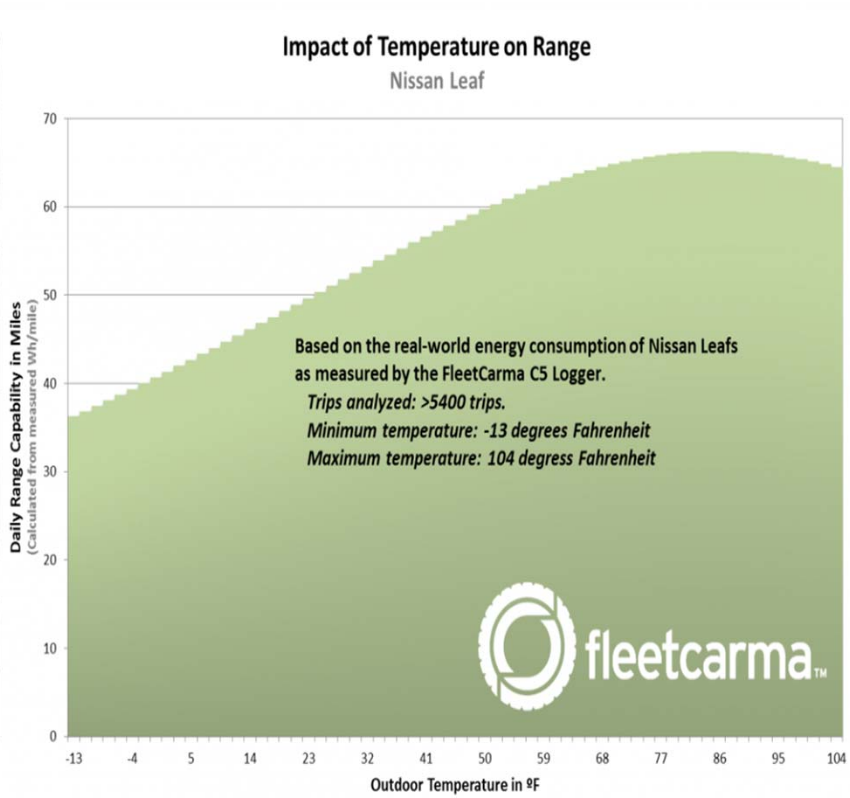


Impact of Low Temps on xEV Performance

- xEV acceleration and electric range are much more in cold temp than affected than conventional vehicles

2012 Nissan Leaf BEV





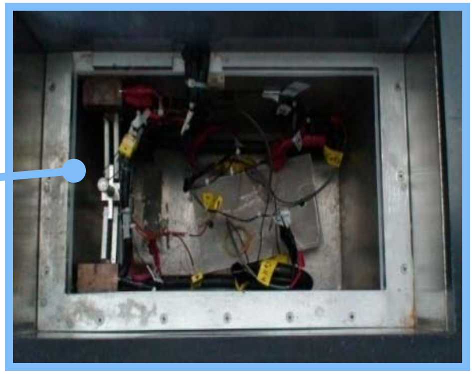
http://www.transportation.anl.gov/D3/data/2012_nissan_leaf/AVTALeaftestinganalysis_Major%20summary101212.pdf

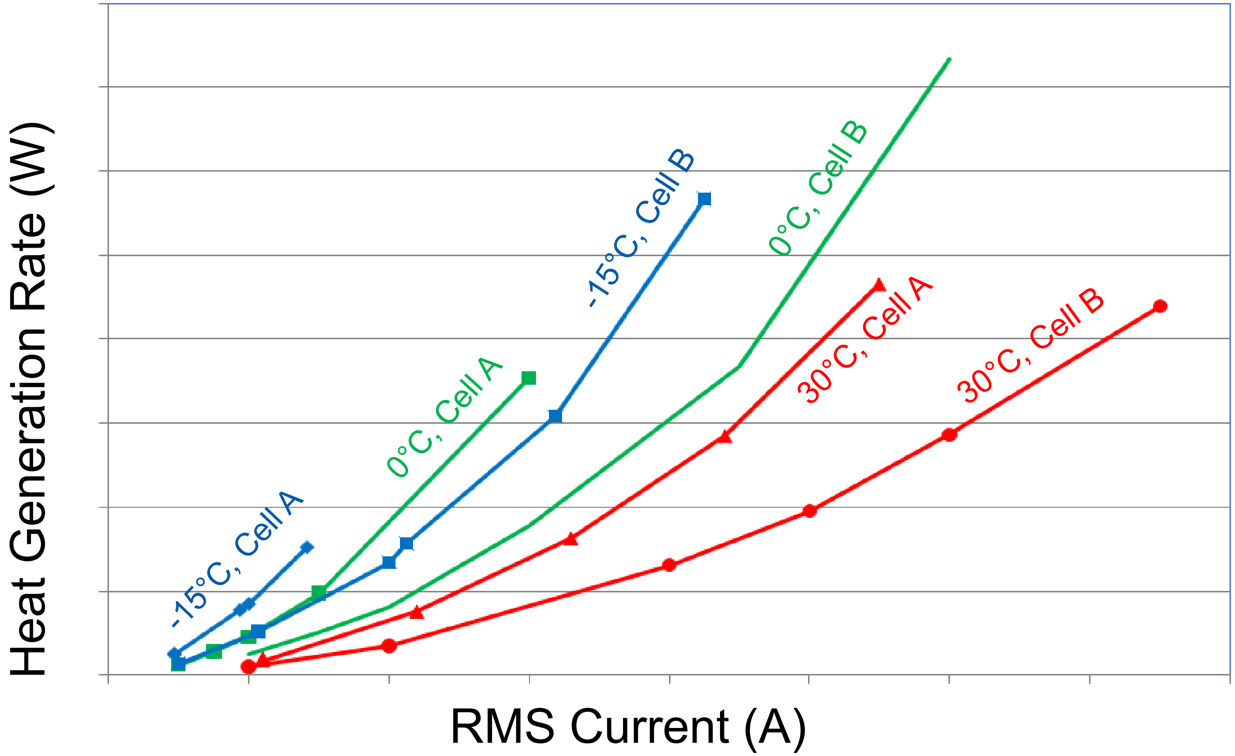
http://news.fleetcarma.com/2013/01/31/electric-car-range-in-bitter-cold/#.UQq5m_IwCVo

Impact of Temp on Cell Heat Generation

Large-Cell Calorimetry

- Profiles: USABC & US06 cycles, const. current
- Lower the temp, higher heat generation due to higher Resistance





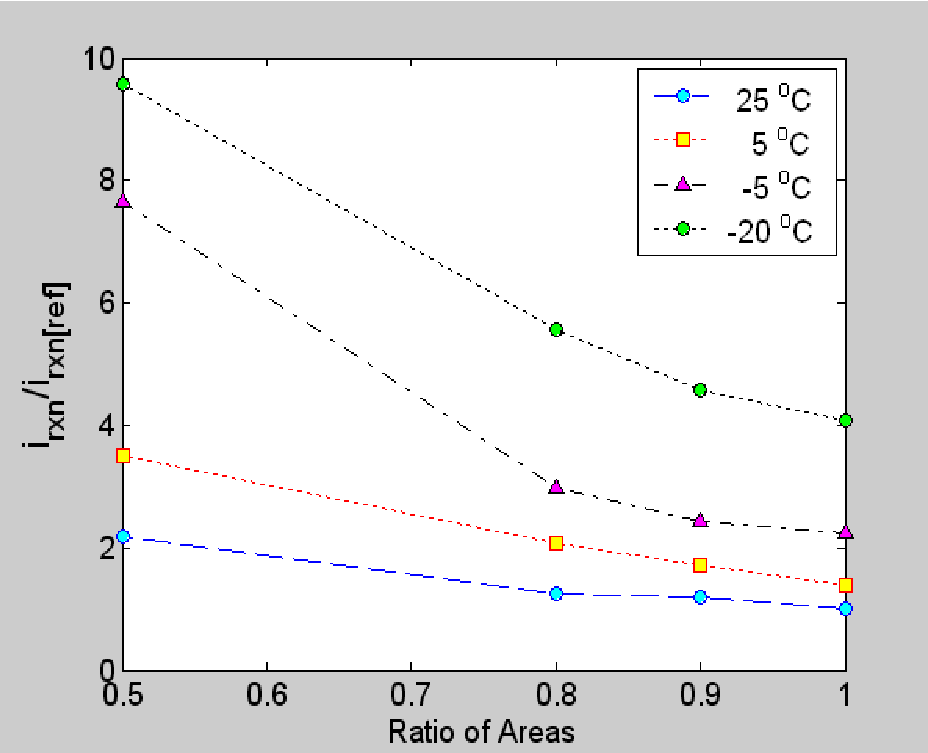
Dendrite Growth in Cold Temperatures

Charging is much more challenging as dendrite can grow and reduce life of battery and compromise safety

✓ Dendrite growth progressively worse with increase in the reacting surface area.
=> The plating reaction is accelerated by a factor of almost 10, for the worst case presented, at -20 °C.

✓Reaction rates for a given ratio of the areas, increasingly become larger with temperature:
=> Limitations from the electrolyte are more significant than the surface effects at low temperatures (esp. below -5 °C).

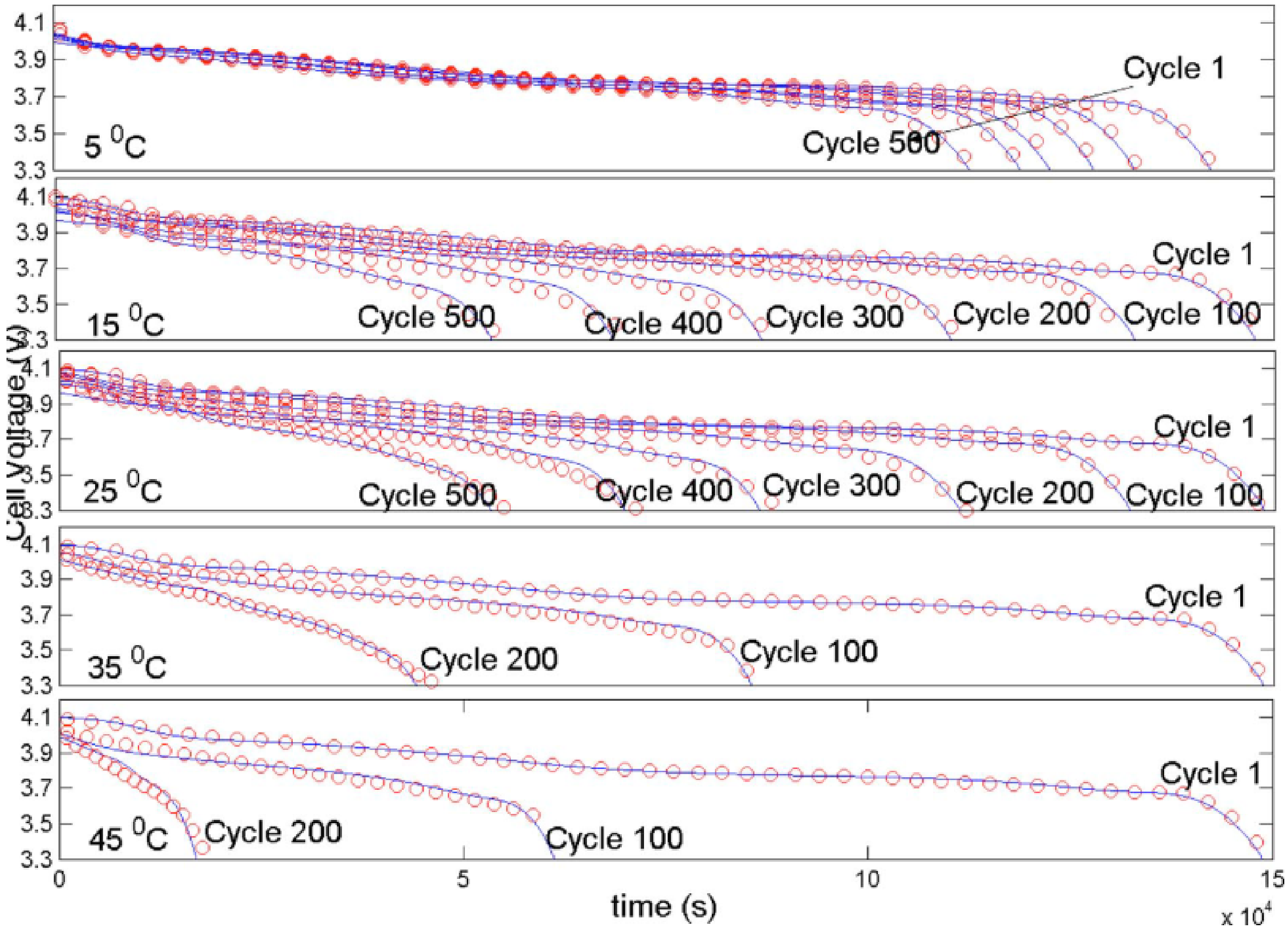
✓For the worst case, when the area of the reacting surface is double that of the reference case, the reaction rate tapers off between -5 and -20 °C despite the high over-potential
=> Bulk limitations result in non-availability of lithium at the surface.



Li-Ion battery modeling,
S. Santhanagopalan (NREL)

High Temperature Effects - 1

Poor cycle life due to loss of cyclable lithium and active material at elevated temperatures.

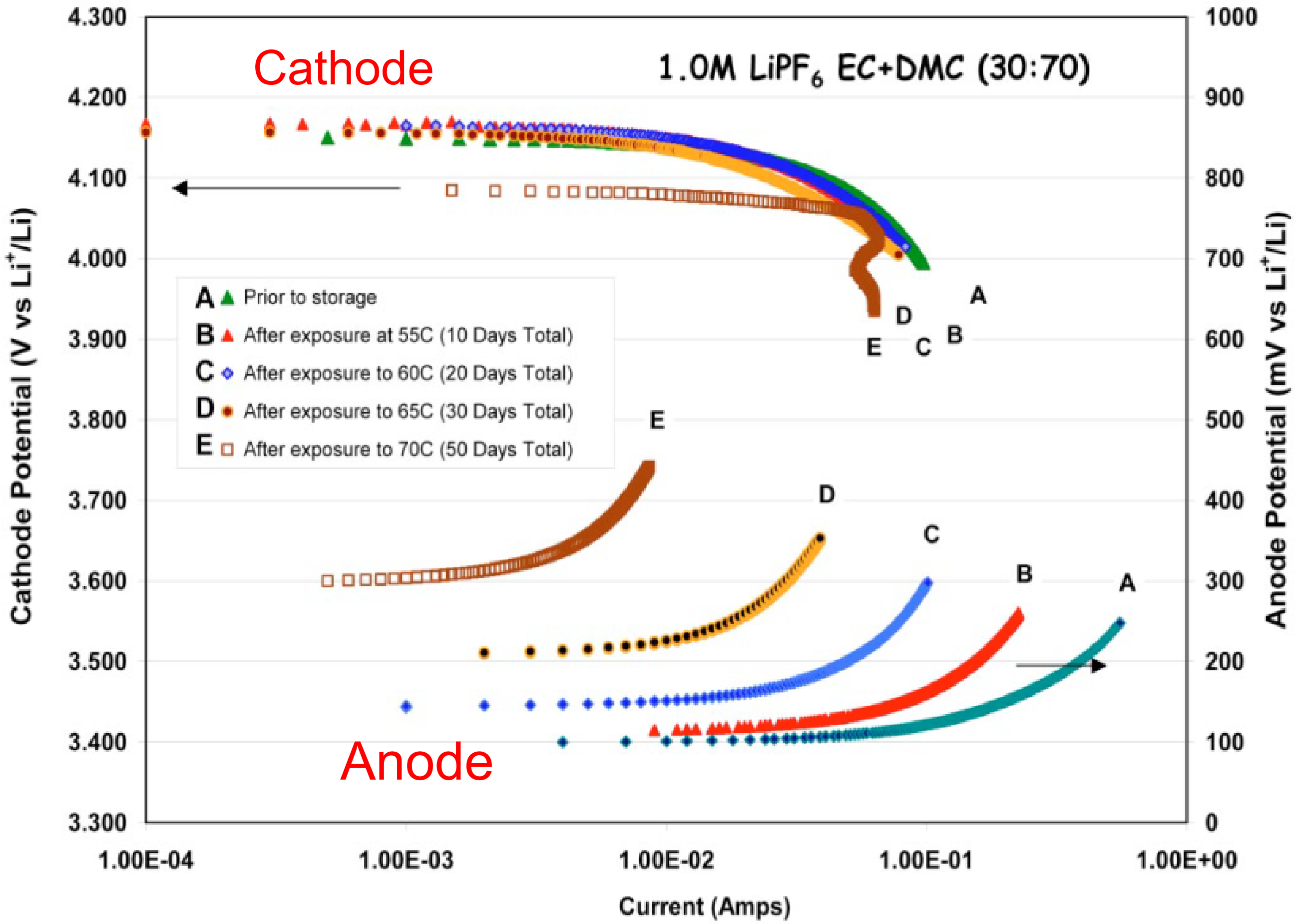


Increased rate of side-reactions results in loss of cyclable lithium and higher rate of attrition of active material at higher temperatures: the solid lines are the model results and the red circles are experimental data

Santhanagopalan et al., JES 155(4), p. A345 (2008)

High Temperature Effects - 2

- Faster Degradation
  - Side reactions happen faster on the electrode surface (esp. anode) with increase in the temperature
  - Resulting in faster build-up of the resistance at the electrode surface



Half-cell Potentials from cells subjected to aging at different temperatures: Side reactions happen faster on the electrode surface with increase in the temperature – resulting in faster build-up of the resistance at the electrode surface

Smart et al., JES V. 152(6), p. A1096 (2005)

Higher LIB Degradation at Higher Temperatures

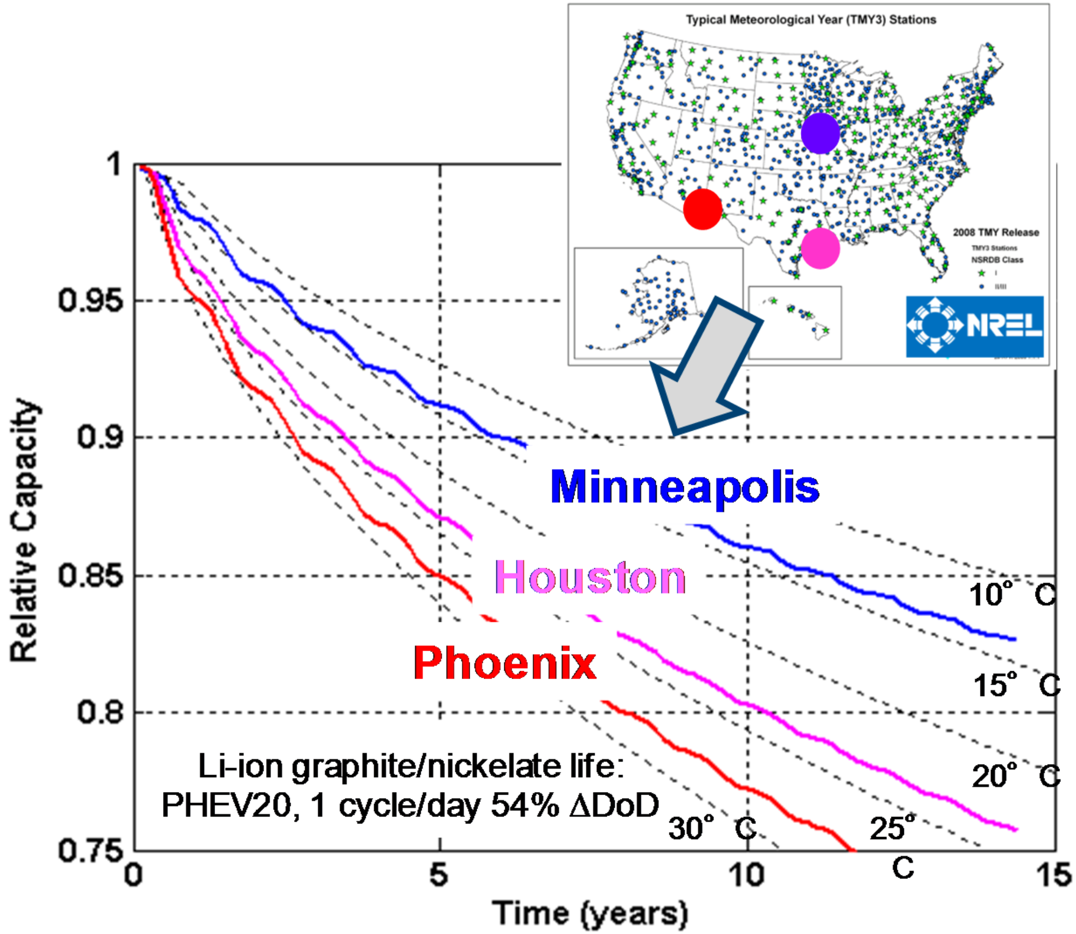
- Models have correlated the relation between capacity & temperature
- Faster battery degradation means higher cost for replacement

Cycling fade

- Active material structure degradation and mechanical fracture
- $a_2(\Delta DOD, T, V)$

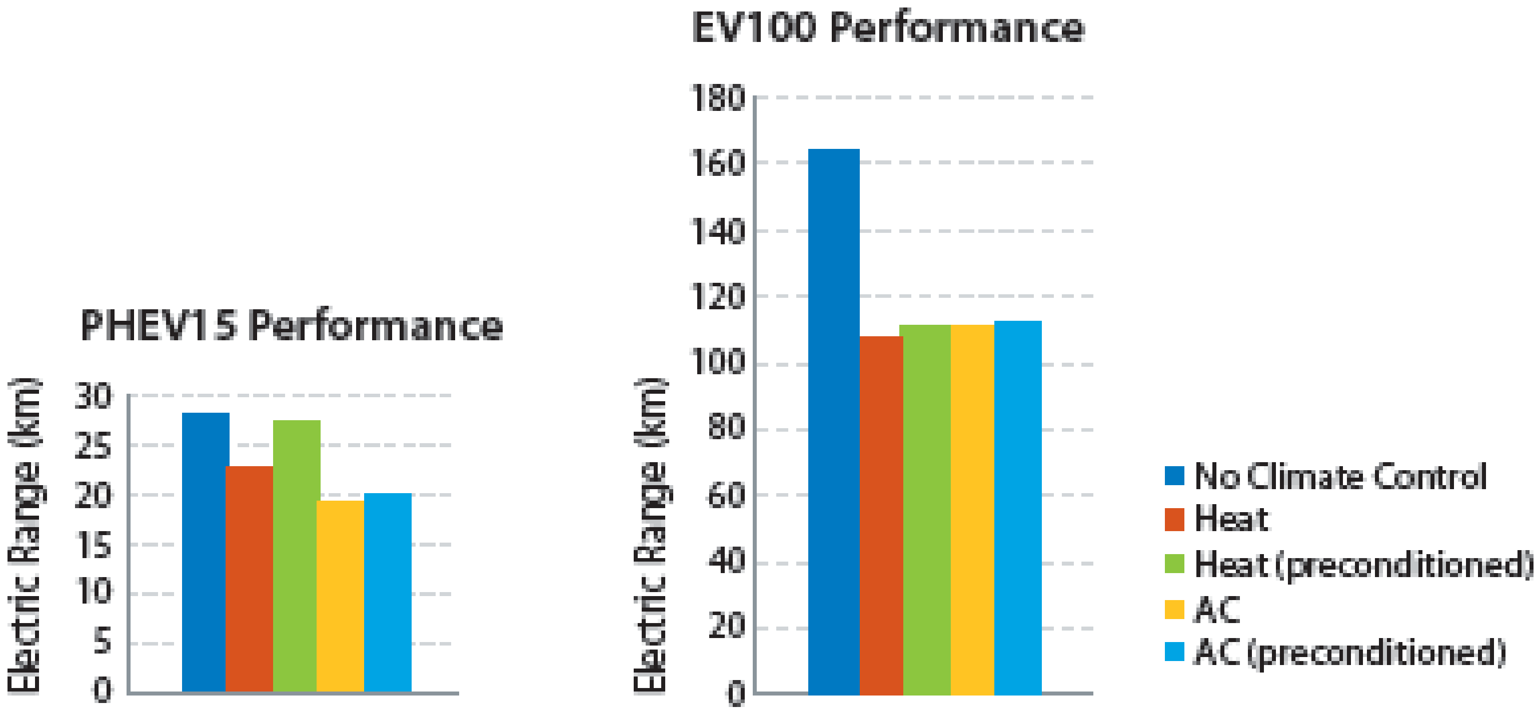
Calendar fade

- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1(\Delta DOD, T, V)$

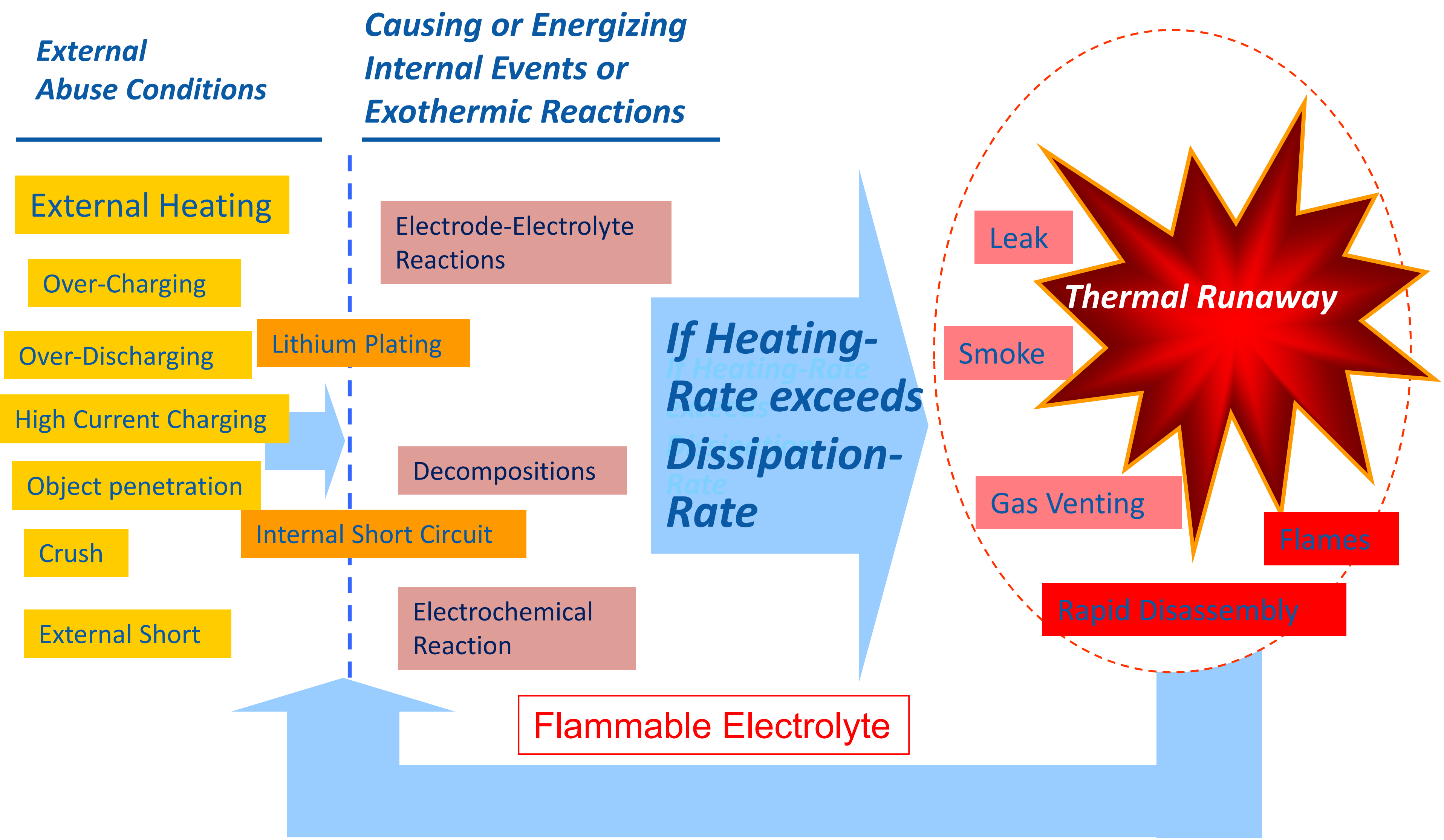


Comfort Heat/Cooling Reduces xEV Range

- Passenger heating needed, BEV range is reduced using battery energy (more pollution if engine use for PHEV and EREV)
- Passenger cooling needed, BEV range is reduced using battery energy (more pollution if engine use for PHEV and EREV)
- NREL analysis has shown that climate-control system loads can increase fuel consumption in PHEVs by as much as 61% and can decrease electric range by up to 35% in EVs.



Thermal Runaway of LIB and Safety Events



(The flammability of the vented electrolyte is a significant unresolved safety issue for LIBs.)

Thermal Runaway in Li-Ion Cells

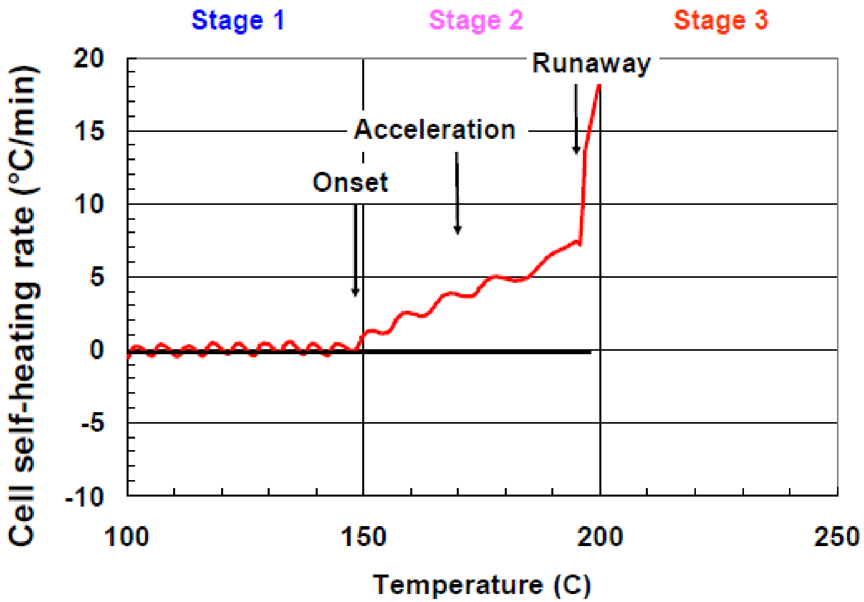
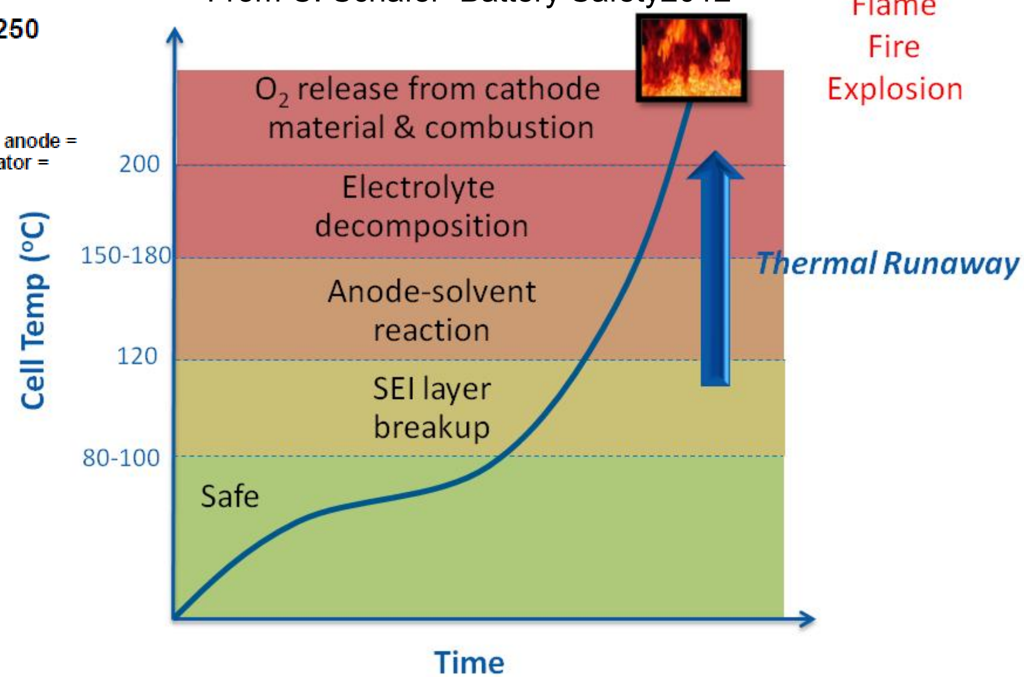


Figure 9. Cell self-heating rate during forced thermal ramp test of Li-Ion Gen 2 chemistry: anode = MCMB | electrolyte = 1.2 M $LiPF_6$ in EC:PC:DMC | cathode = $LiNi_{0.8}Co_{0.05}Al_{0.05}O_2$ | separator = Celgard 2325 trilayer.[60]

1. An external source of heat raises the temperature of the cell to the **Onset Temperature**
2. If this heat is not dissipated, the temperature will continue to rise due to exothermic reactions and the cell enters **Acceleration,** which is characterized by more rapid and accelerating heat release.

From C. Schafer Battery Safety2012

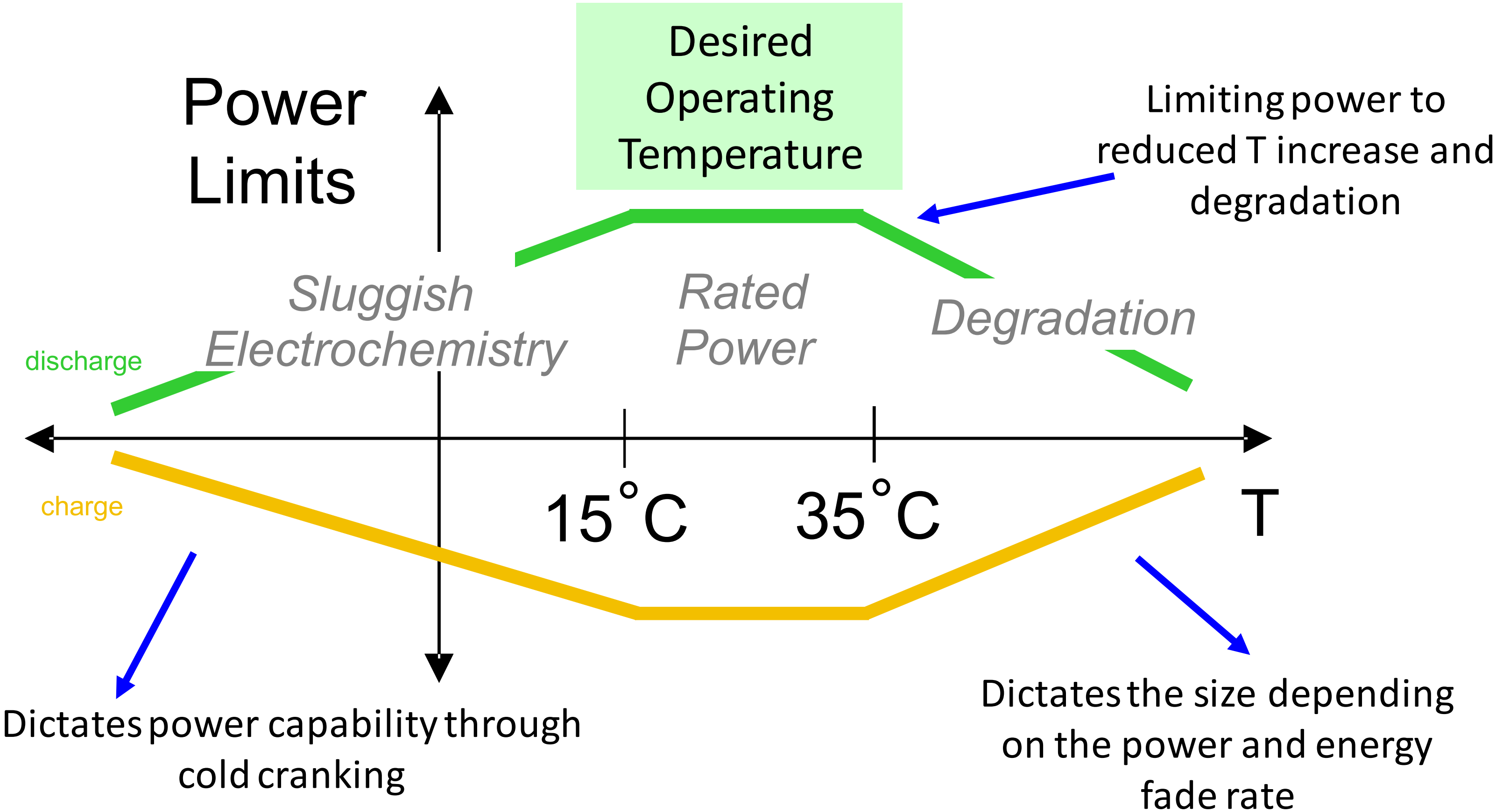


3. Additional heating causes the cell to enter **Runaway**, in which the high-rate cathode and/or anode reactions cause the temperature to rise rapidly (thermal runaway) and flame or explosion may follow.

Description of stages from Dan Doughty : http://www.nrel.gov/docs/fy13osti/54404.pdf

Battery Temperature in xEVs

- **Temperature has a significant impact on life, performance, safety, and thus cost of LIBs and eventually affordability of XEVs**

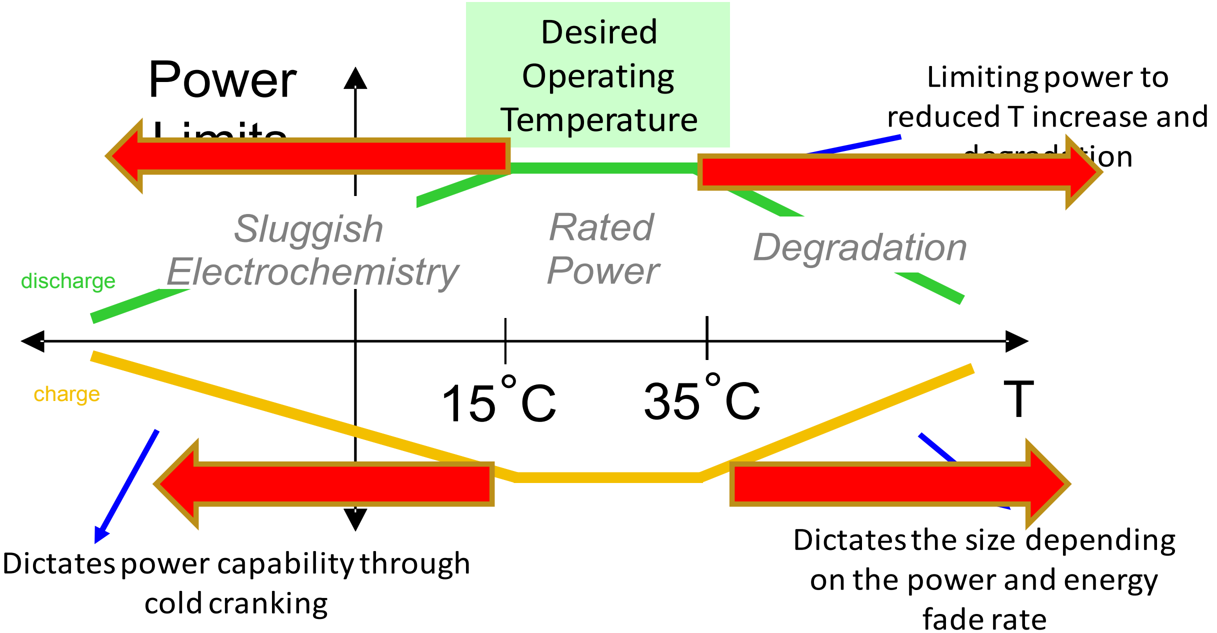


Also limits the electric driving range

Kandler Smith, NREL Milestone Report, 2008

Addressing Temperature Issues

- **Material Selection**
- **Cell and Module Design**
- **Balance of the System**

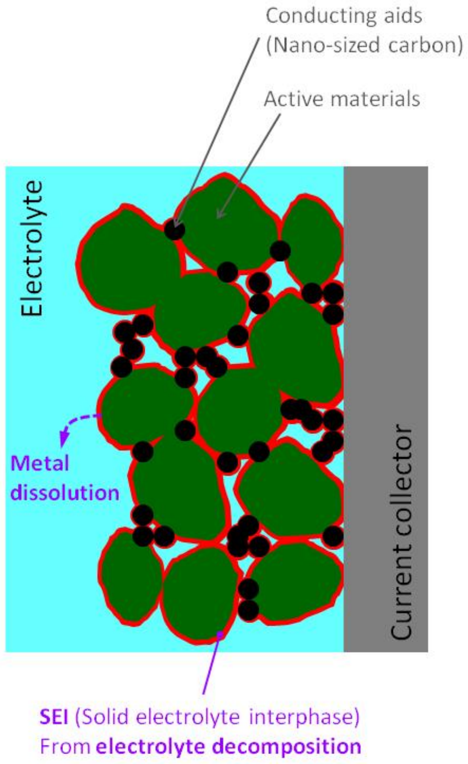


Also limits the electric driving range

Kandler Smith, NREL Milestone Report, 2008

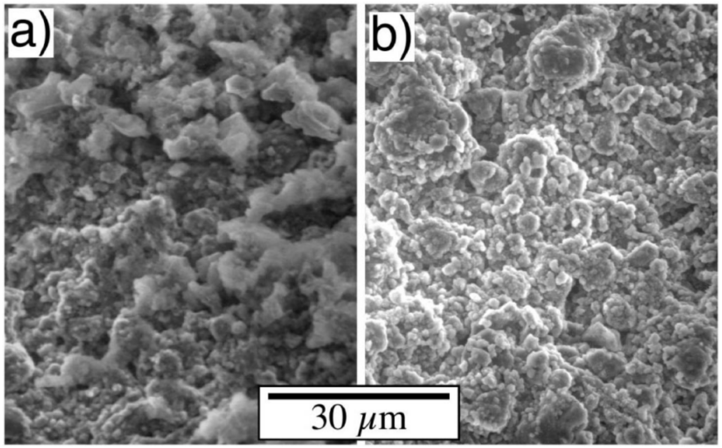
Material Selection – Performance & Life

- **Choice of cathode**
- **Choice of anode**
- **Choice of separator**
- **Choice of Electrolytes**
  - Stable at high Ts (ionic liquids?)
  - Good conductivity and low viscosity at low Ts
- **Surface morphology**
- **Binders**
- **Additives and Surface Treatments**
  - Improve stability
  - Improve conductivity
  - Coating
  - Atomic or molecular layer depositions



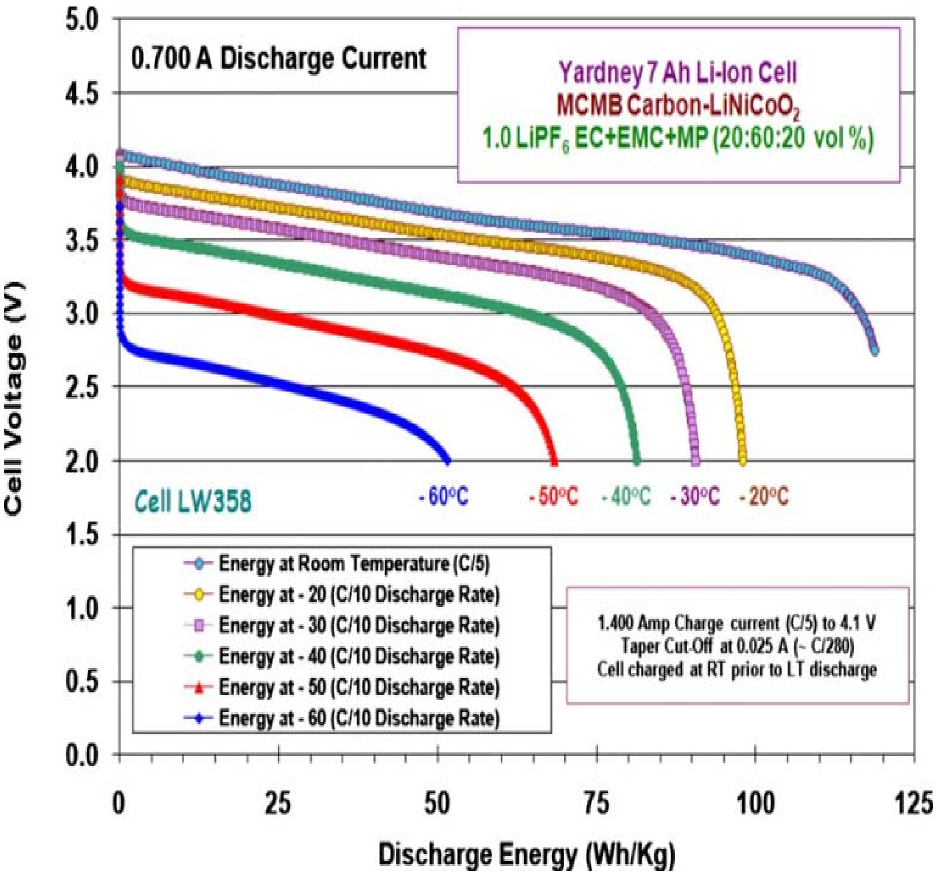
Using Materials to Address Temperature Issues

- **Performance and Life**



SEM micrographs showing the surface morphology of MCMB anode structures after testing in electrolyte with EC/DMC ratios of a) 30/70 and b) 70/30: higher EC content reduces degradation at elevated temperatures.

Smart et al., JES 152(6), p. A1096 (2005)



Additives like Methyl Propionate have been shown to enable cell operation at temperatures as low as -60°C.

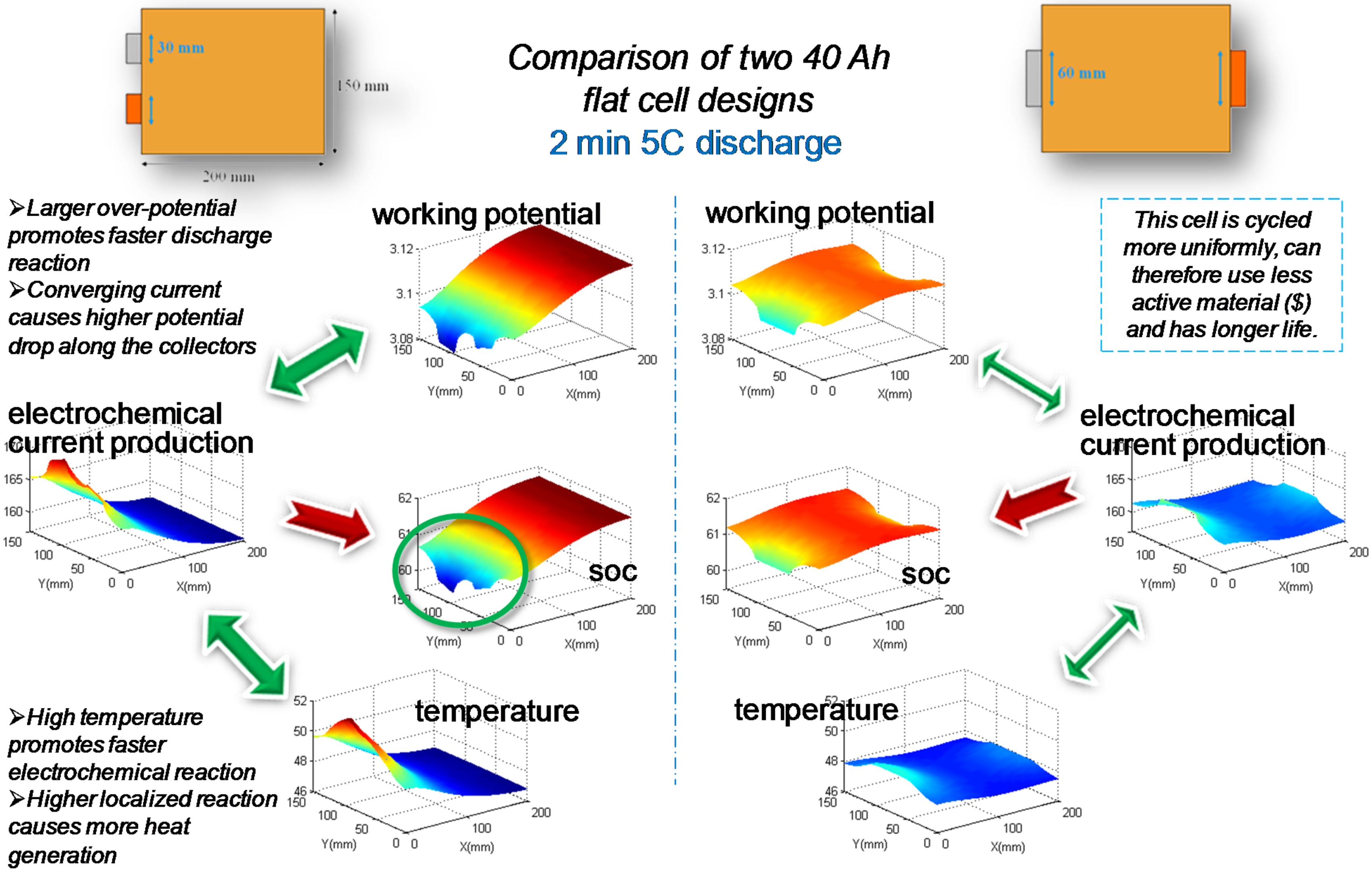
Smart et al., JES 157(12), p. 1361 (2010)

Using Materials to Address Temperature Issues

- **Safety**
  - Develop non-flammable electrolytes (Ionic liquids?)
  - Adding fire retardants additives
  - Develop high energy cathodes that do not generate oxygen
  - Develop coatings for cathodes and anodes
  - Develop artificial SEI layer for anodes
  - Develop new separators that maintain integrality and little shrinkage at high temperatures.
  - Design and placement of heat resistance layers

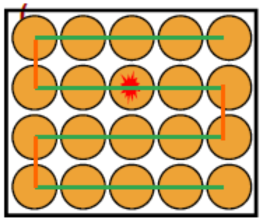
Cell and Pack Designs can Alleviate Temp Effects

- Cell design for more uniform heat distribution

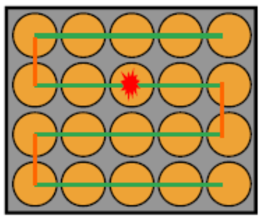


Cell & Module Design to Address Temperature Issues

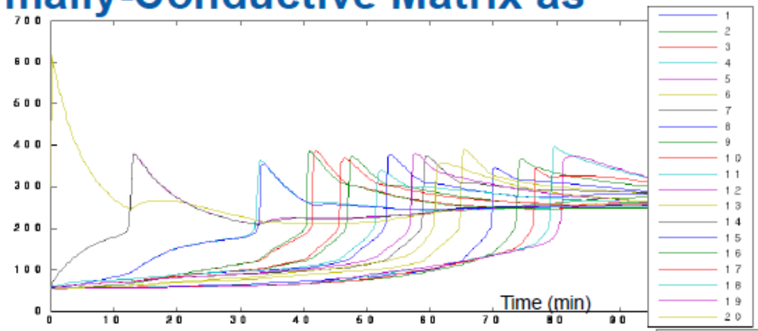
Impact of a Thermally-Conductive Matrix as Medium

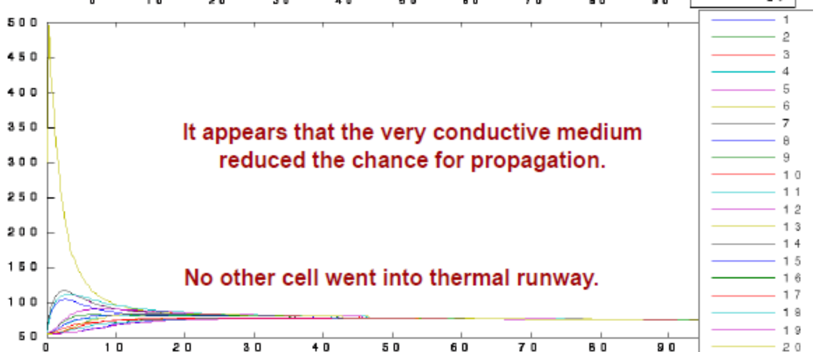


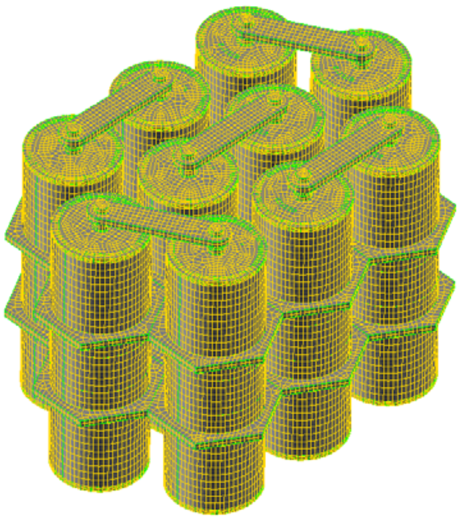
Base Case - Air



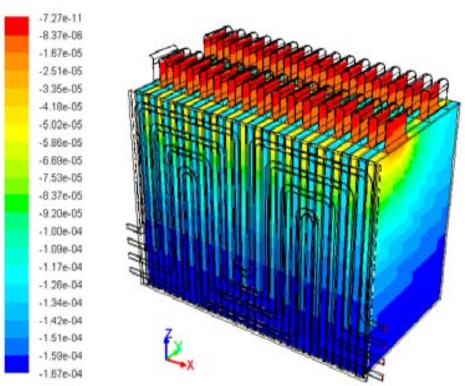
PCM/Graphite Imbedded Matrix*



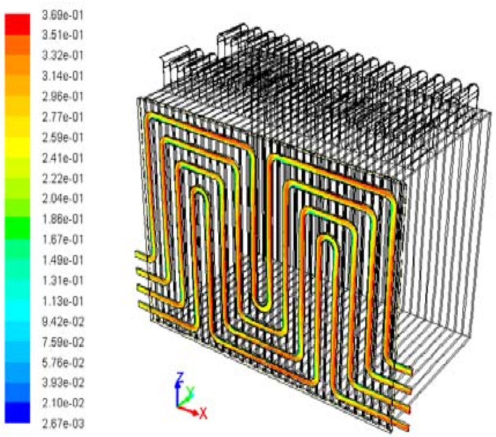




across the module

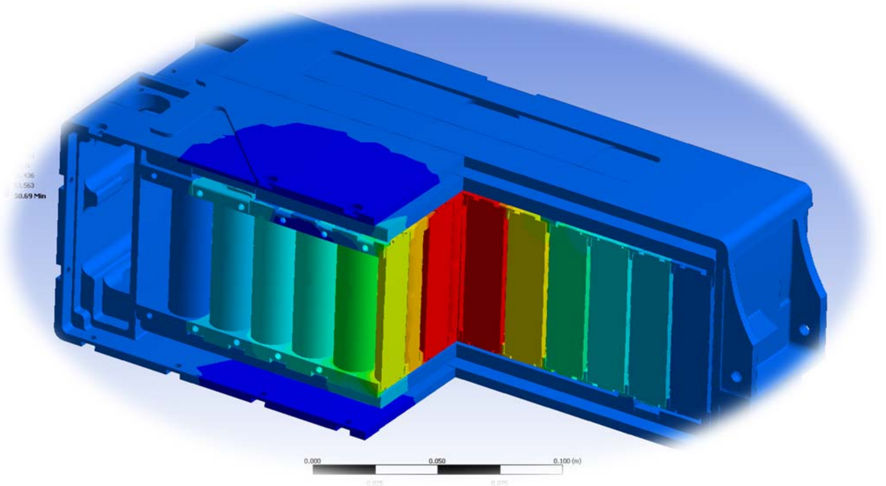


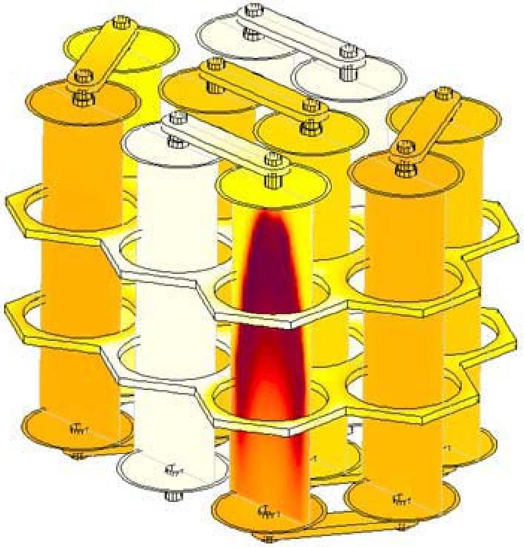
Cooling Channel Temperature



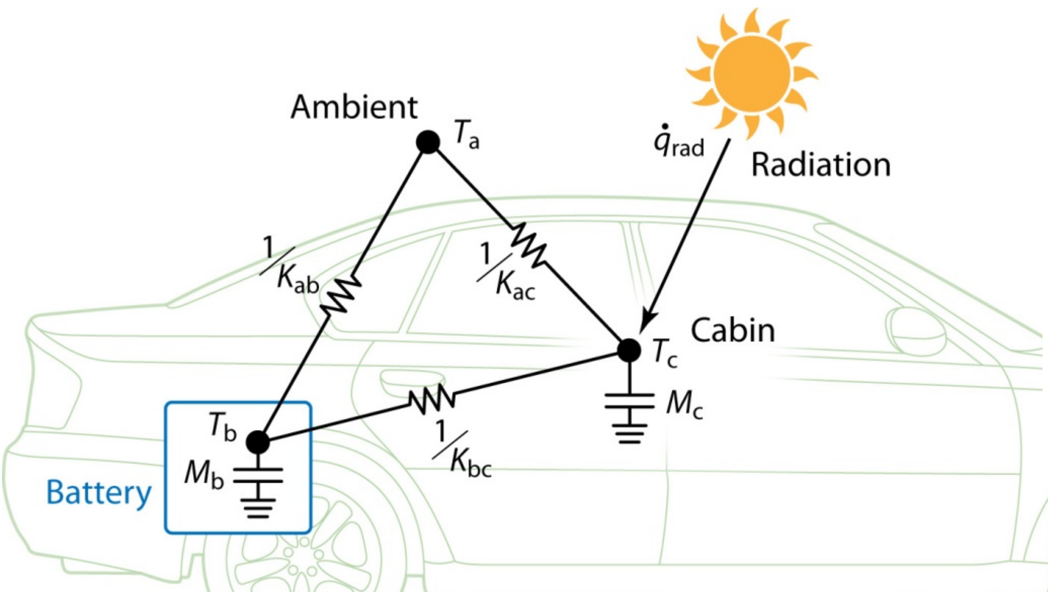
Use Balance of System to Address Temperature Issues

- Battery Thermal Management
  - Heating
  - Cooling
  - Standby or pre-conditioning cooling and heating
- Advanced Sensing
- Electrical Battery Management System and Control
  - Balancing and equalization
  - Advanced controls while maximizing range and life

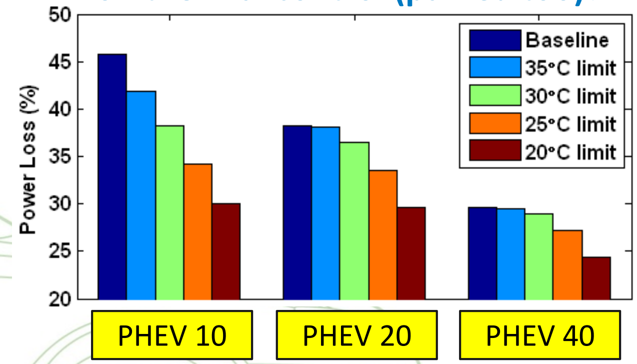




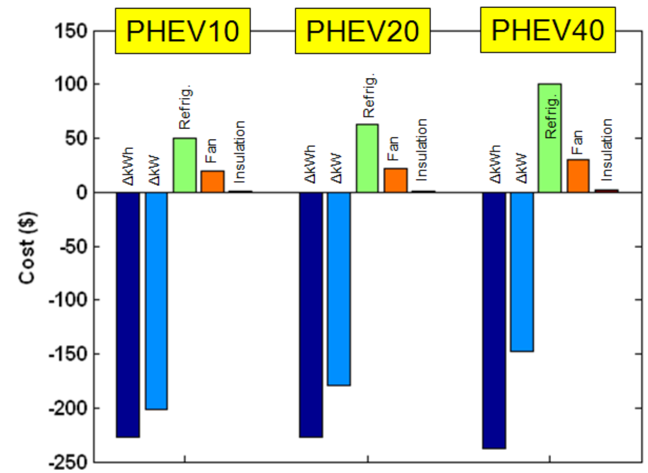
Standby Cooling in Hot Climates



How much is it worth to spend on thermal control (parked too)?



- Battery life can greatly benefit from cooling the battery during standby, i.e. while vehicle is parked & plugged in to the grid
- Refrigeration cooling systems with some insulation particularly compelling
- Slower battery degradation rate enables smaller, lower cost battery ($300-$400 savings)



Battery sized for 15 years life in Phoenix, AZ, charged nightly.

Summary

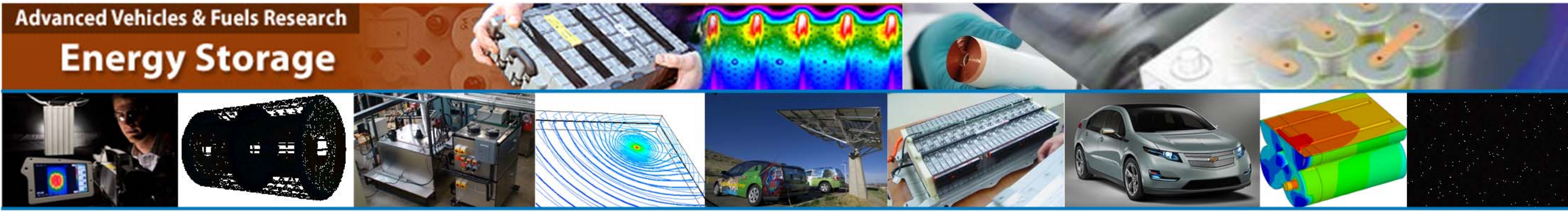
- Lithium-ion battery (LIB) technology is expected to be the energy storage of choice for electric drive vehicles (xEVs) in the coming years
- Temperature has significant impact on Li-Ion batteries
  - Performance → lower range
  - Life → higher cost
  - Safety → lower market acceptance
- Controlling or reducing the adverse impact of extreme temperature could be done through
  - Material Selection (thermal stability and electrolyte critical)
  - Cell and Module Design
  - Balance of System Design (thermal management, BMS, standby and pre-conditioning)
- NREL has developed tools and models to investigate impact of the extreme temperatures on LIB and xEVs

Acknowledgments

- Support provided by the DOE Vehicle Technologies Program
  - Dave Howell, Hybrid and Electric Systems Team Lead
  - Brian Cunningham, Energy Storage Technology Manager

- Support from NREL Energy Storage Team
  - Matt Keyser
  - Kandler Smith
  - John Ireland
  - Dirk Long

Contact Information:
Ahmad Pesaran
ahmad.pesaran@nrel.gov
303-275-4441



nrel.gov/vehiclesandfuels/energystorage