Functionally Graded Cathodes for SOFCs

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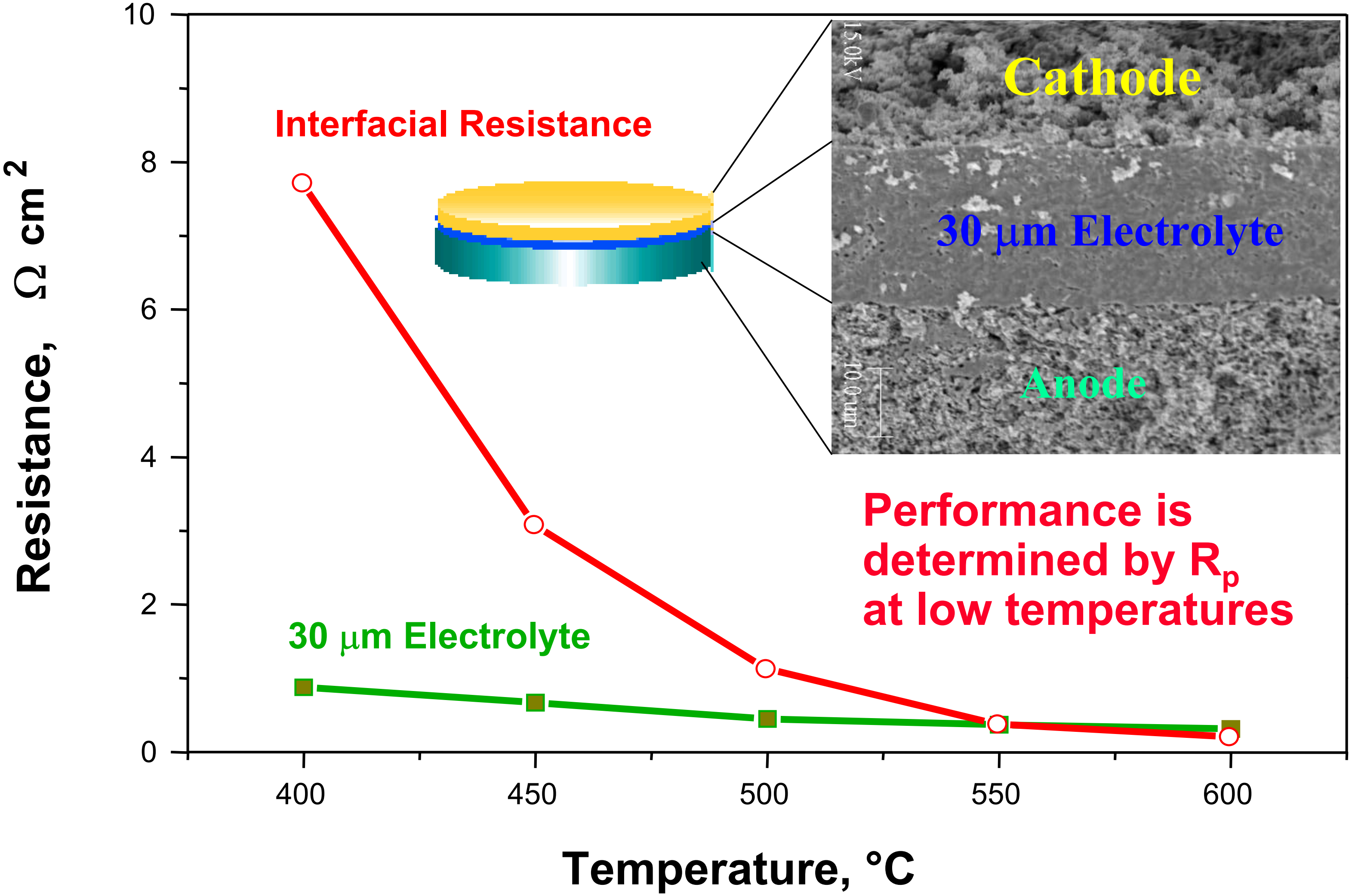
The Research Team

- Rupak Das and Robert Williams (NSF Fellow)
  - Modeling/simulation of FGE
- Erik Koep and Chuck Compson (NASA Fellow)
  - Patterned Electrodes
- Qihui Wu and Harry Abernathy (NSF Fellow)
  - In-situ Characterization: FTIR/Raman, IS, GC/MS
- Ying Liu and Yuelan Zhang
  - Fabrication of FGE and performance testing

Outline

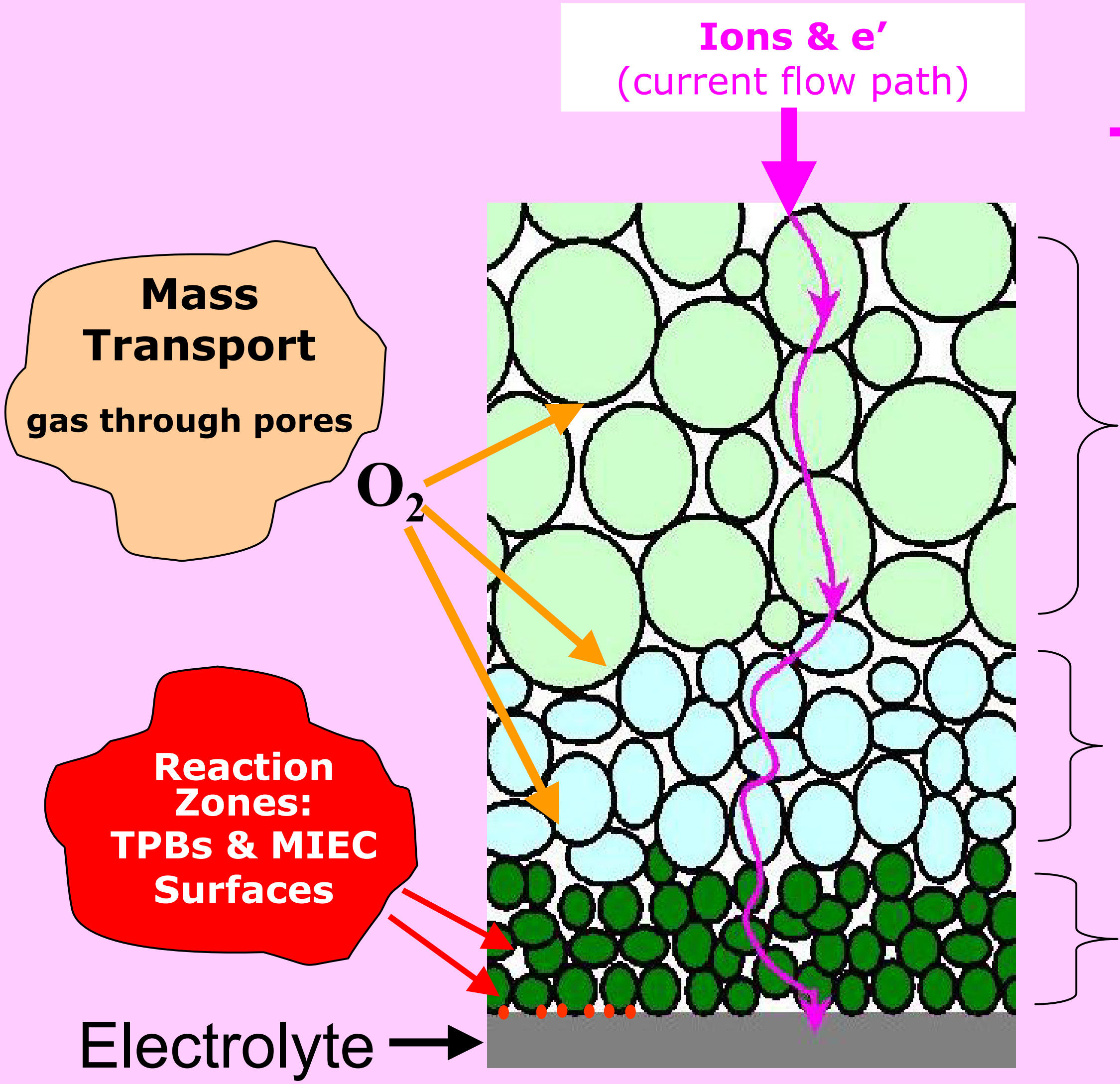
- Technical Issues Addressed
- R&D Objectives & Approach
- Results to Date
  - Modeling of Functionally Graded Electrodes
  - Patterned Electrodes
  - In-situ Characterization Techniques
  - Fabrication of Graded Electrodes
- Applicability to SOFC Commercialization
- Activities for the next 6-12 Months

Critical Factor: Interfacial Resistance



Origin of R_P for a Porous MIEC Electrode

The Concept of FGE



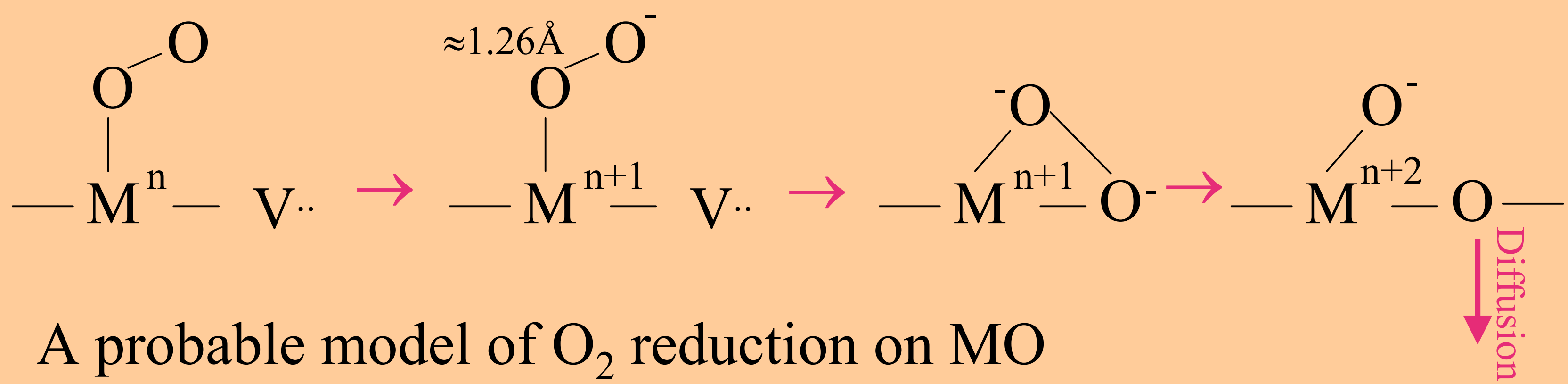
Macro-porous structure
Large pores for fast Transport
High Electronic Conductivity
Compatible with Interconnect

Inter-Mixed Layer
Produce Turbulence Flow

Nano-porous structure
Highly Catalytic Active
Compatible with electrolyte

Atomic/Molecular Level Steps Involving O_2

$$\frac{1}{2}O_{2,gas} \underset{des}{\overset{ad}{\rightleftarrows}} \left\{ \begin{array}{l} \frac{1}{2}O_{2,ad} \underset{comb}{\overset{diss}{\rightleftarrows}} O_{ad} \underset{-e'}{\overset{+e'}{\rightleftarrows}} O^{-}_{ad} \\ \frac{1}{2}\left\{ O_{2,ad} \underset{-e'}{\overset{+e'}{\rightleftarrows}} O^{-}_{2,ad} \underset{-e'}{\overset{+e'}{\rightleftarrows}} 2O^{-}_{ad} \right\} \end{array} \right\} \left\{ \begin{array}{l} \underset{-e'}{\overset{+e'}{\rightleftarrows}} O^{=}_{ad} \underset{-V_{O}^{\cdot\cdot}}{\overset{+V_{O}^{\cdot\cdot}}{\rightleftarrows}} O_{O}^{X} \\ \underset{-(V_{O}^{\cdot\cdot}+e')}{\overset{+(V_{O}^{\cdot\cdot}+e')}{\rightleftarrows}} O_{O}^{X} \end{array} \right\}$$



A probable model of O_2 reduction on MO

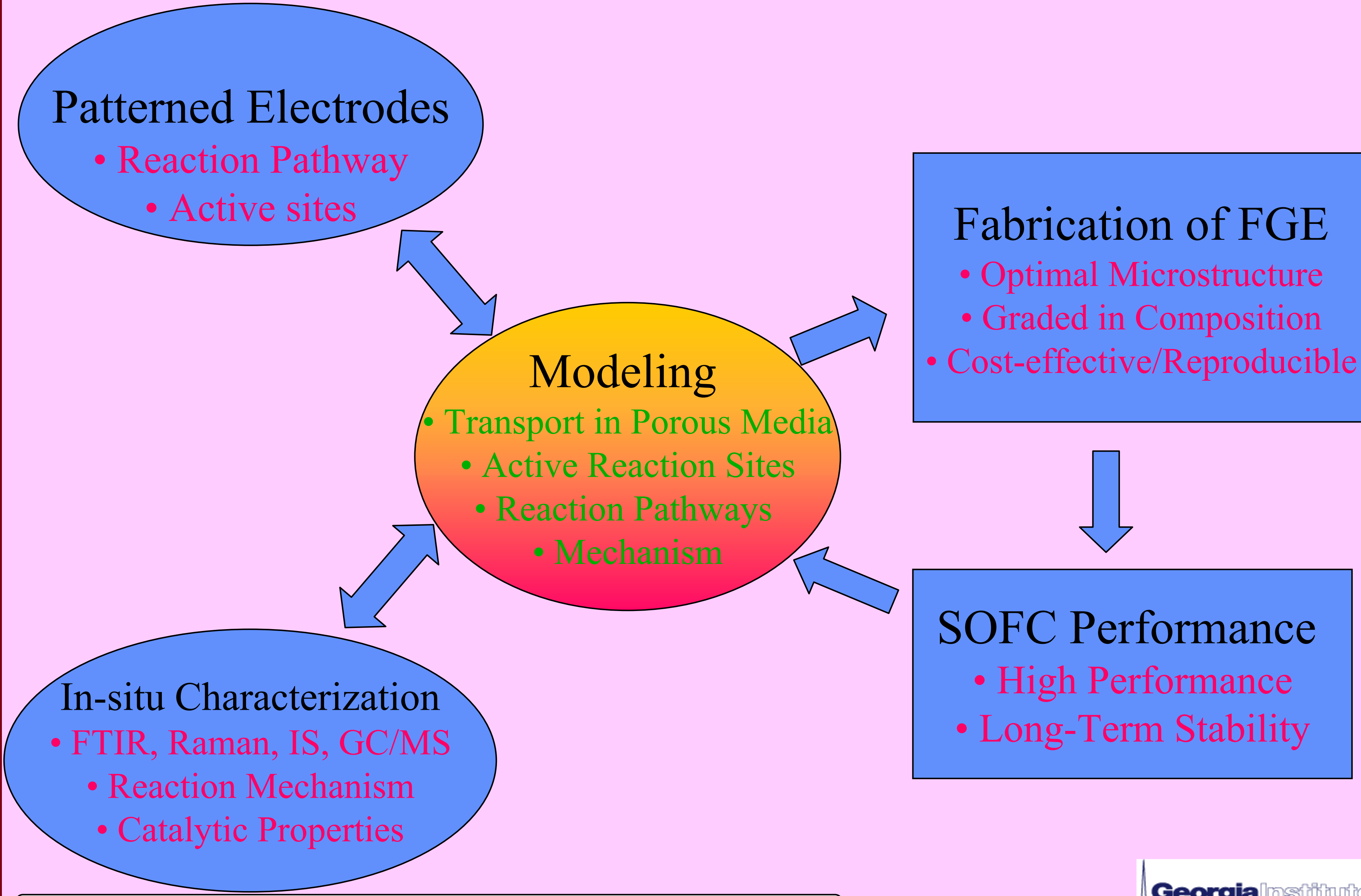
Critical Issues

- Intrinsic Properties of MIEC Cathodes
  - Fundamental processes at the surfaces?
  - Effect of surface defects/Nano-struture?
  - Effect of ionic and electronic transport?
  - In-situ characterization tools and predictive models?
- Effect of Microstructure/Architecture
  - Surface area/reaction sites
  - Rapid gas transport through pores
  - Predictive models for design of better electrodes
- Fabrication of FGE with desired microstructure and composition

Objectives

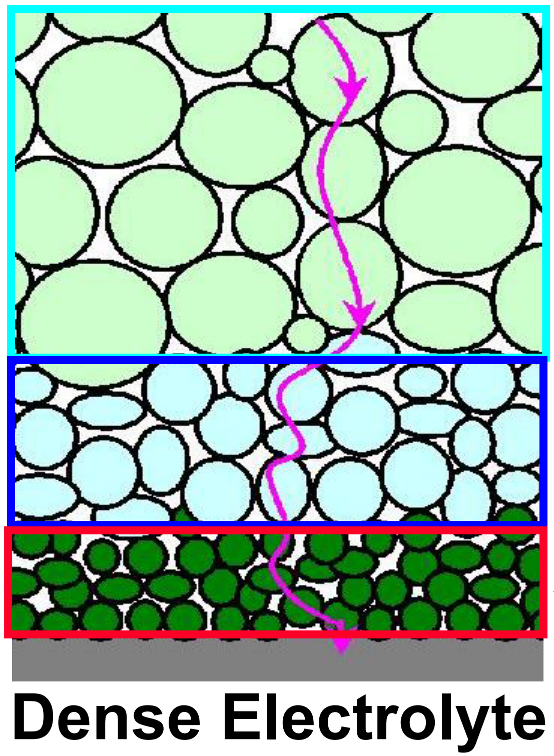
- To develop novel tools for *in-situ* characterization of surface reactions;
- To gain a profound understanding of the processes occurring at cathode-electrolyte interfaces; and
- To rationally design and fabricate efficient cathodes for low temperature operation to make SOFC technology economically competitive.

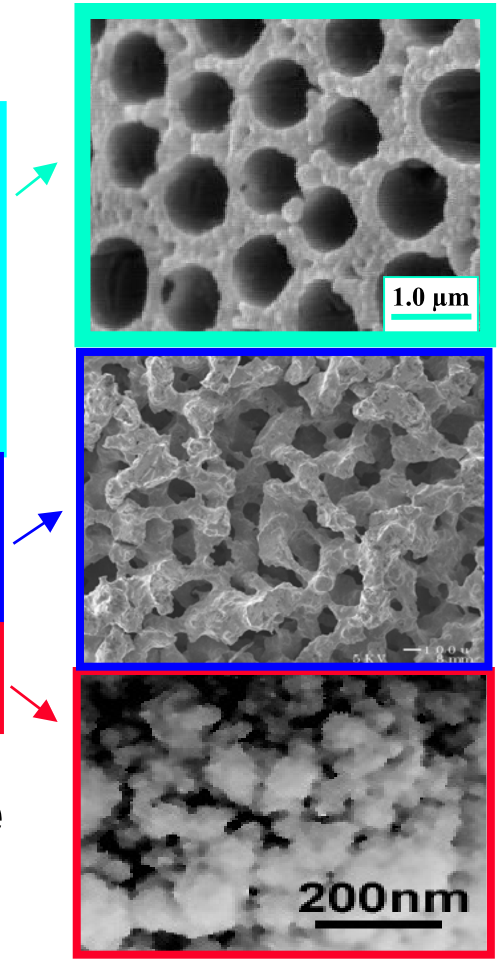
Technical Approach



Modeling of Functionally Graded Electrode

1st Order Approximation
Ionic Transport Limited





Key Input Parameters:

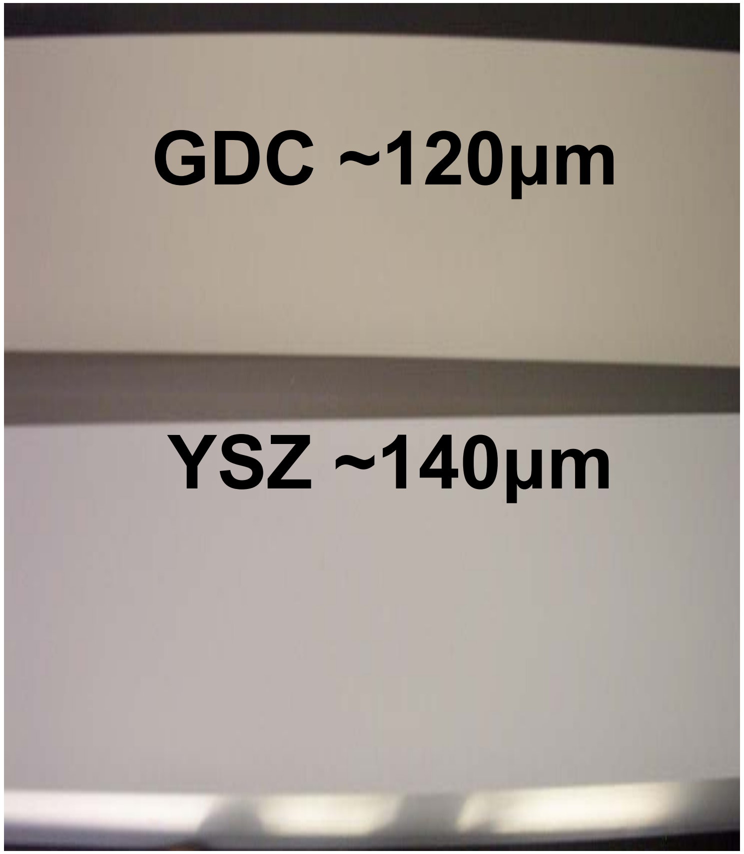
Porosity
Pore Size and Size Distribution
Grain Size and Size Distribution

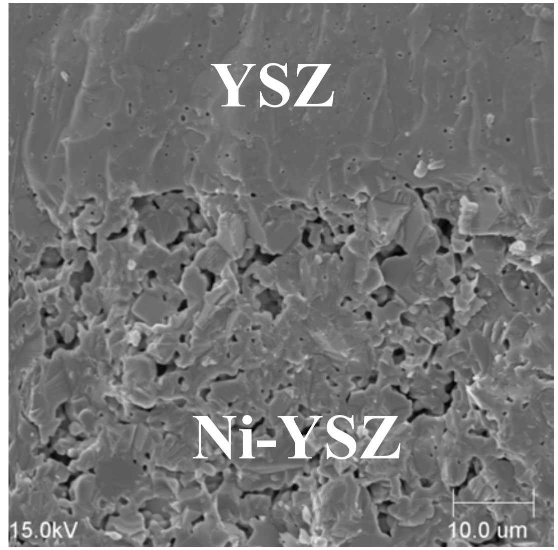
Diffusivity/Tortuosity
Knudsen Diffusion

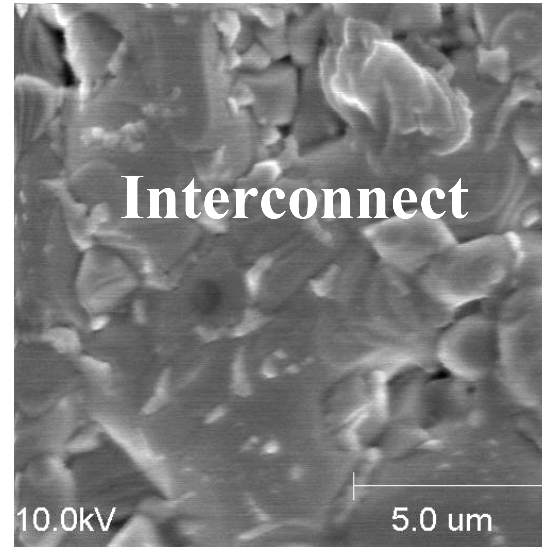
Effective Ionic Conductivity
Effective Electronic Conductivity
Ambipolar Conductivity

Exchange Current Density
Cathodic Transference Numbers

Tape Cast Substrates for Patterned Electrodes



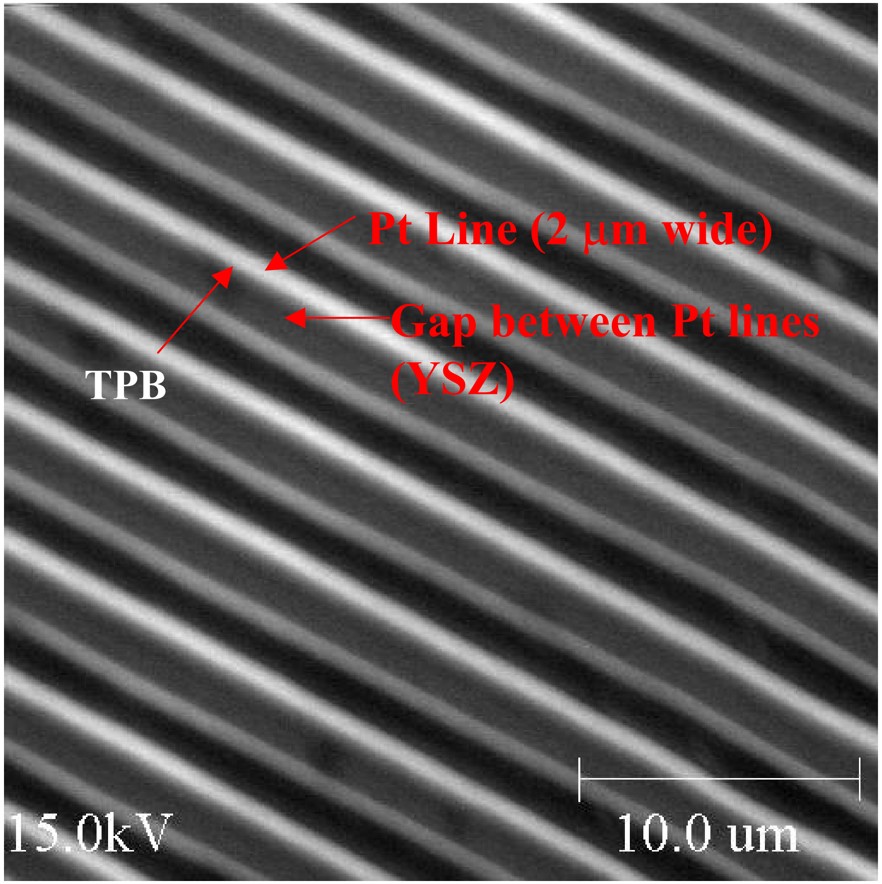




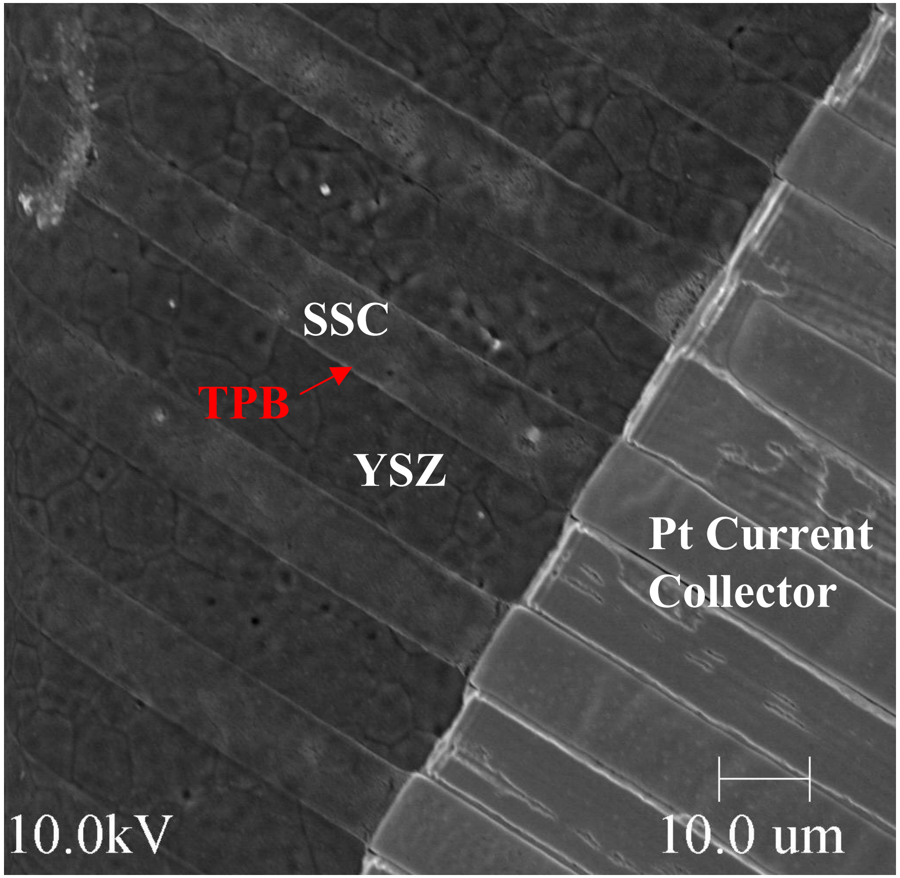
Low cost, reproducible, and easy scale-up

Great Flexibility: Co-casting of multi-layers of different materials

Microstructures of Patterned Electrodes

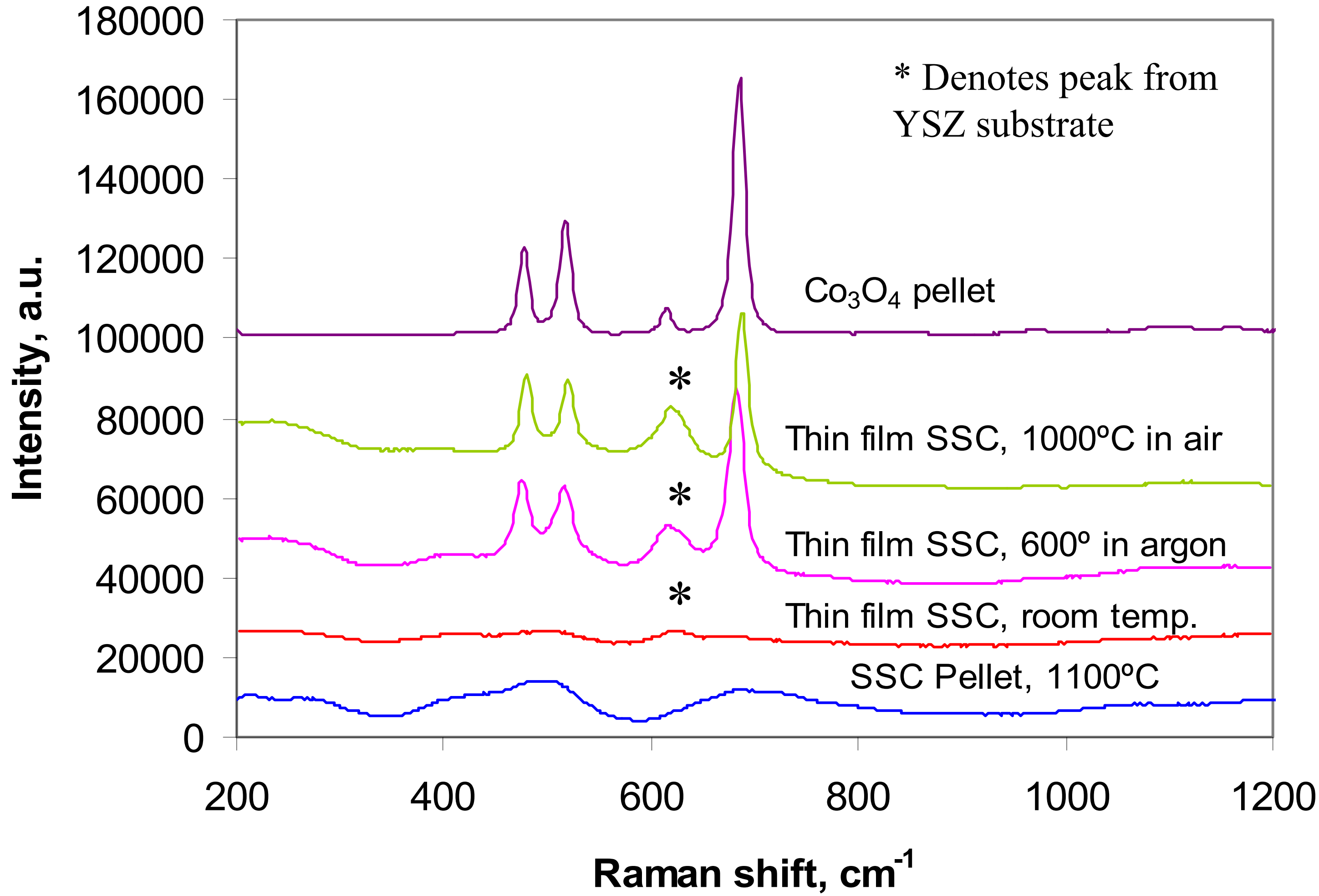


2 μm Pt Lines



10 μm SSC Lines
50 μm Pt Current Collector

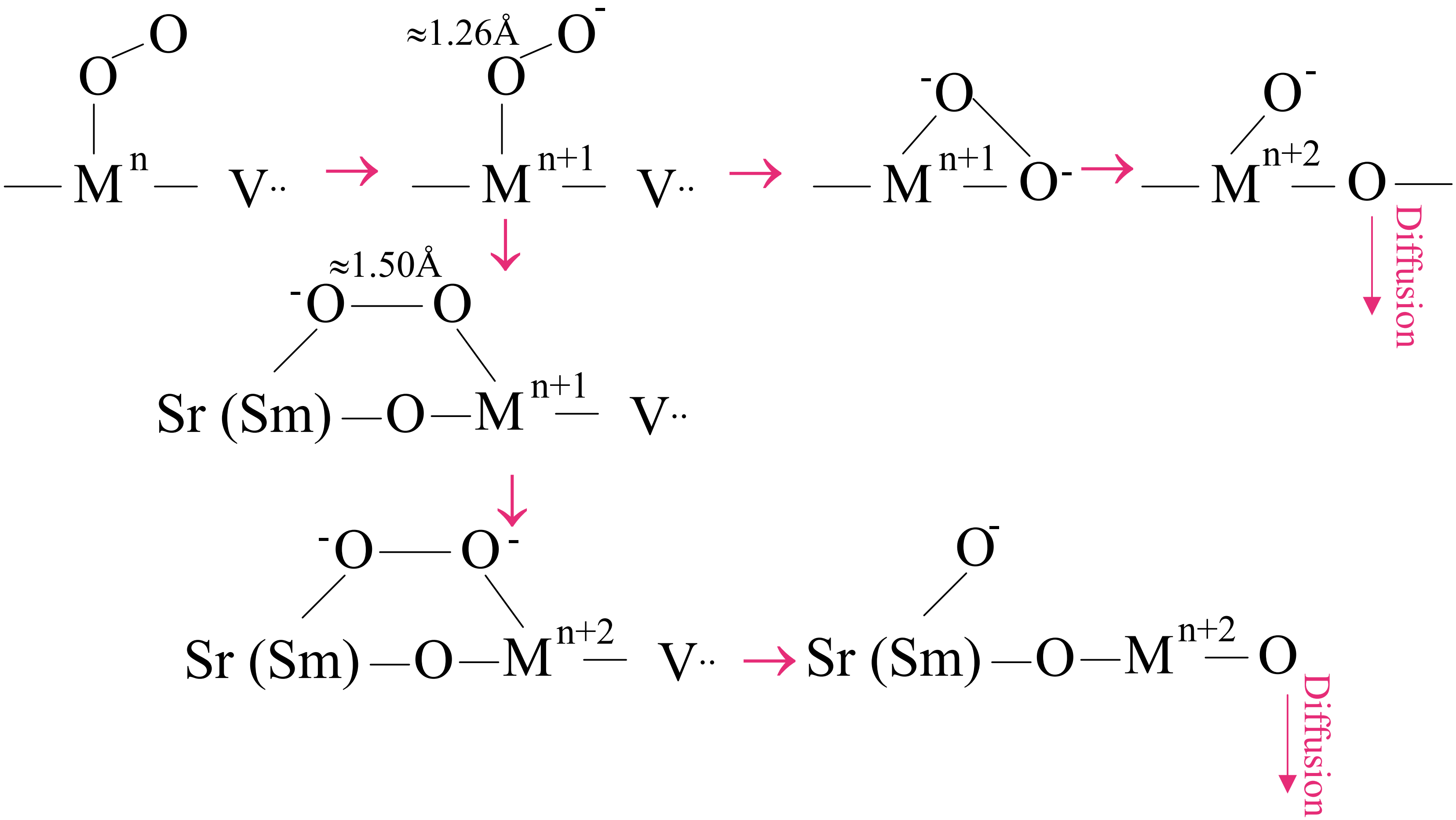
Raman Spectra of Thin Film SSC Electrodes



While initial thin film resembles SSC standard, the surface structure changes upon heating.

O_2 Reduction On a **Metal Oxide**

Probable surface reaction models



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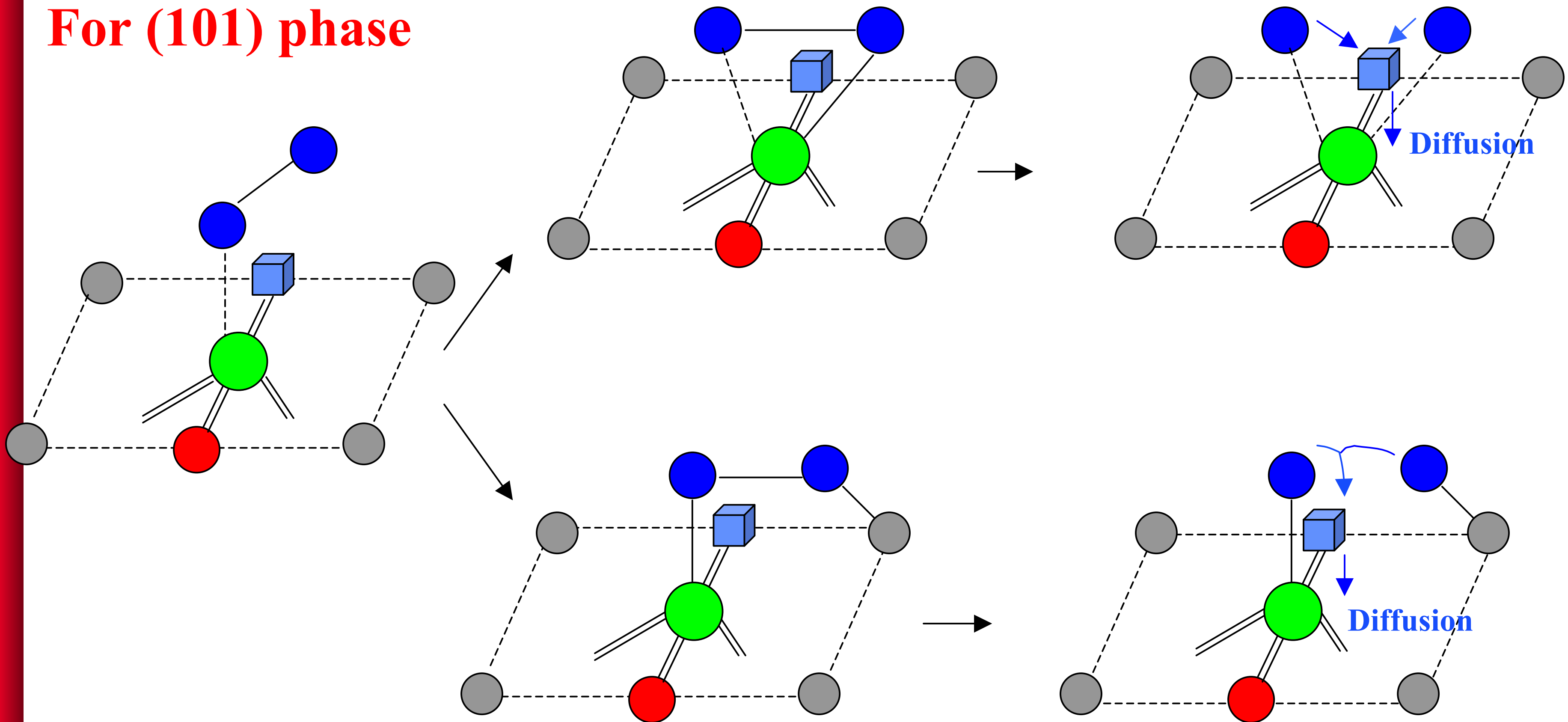
Possible Surface Reaction Processes

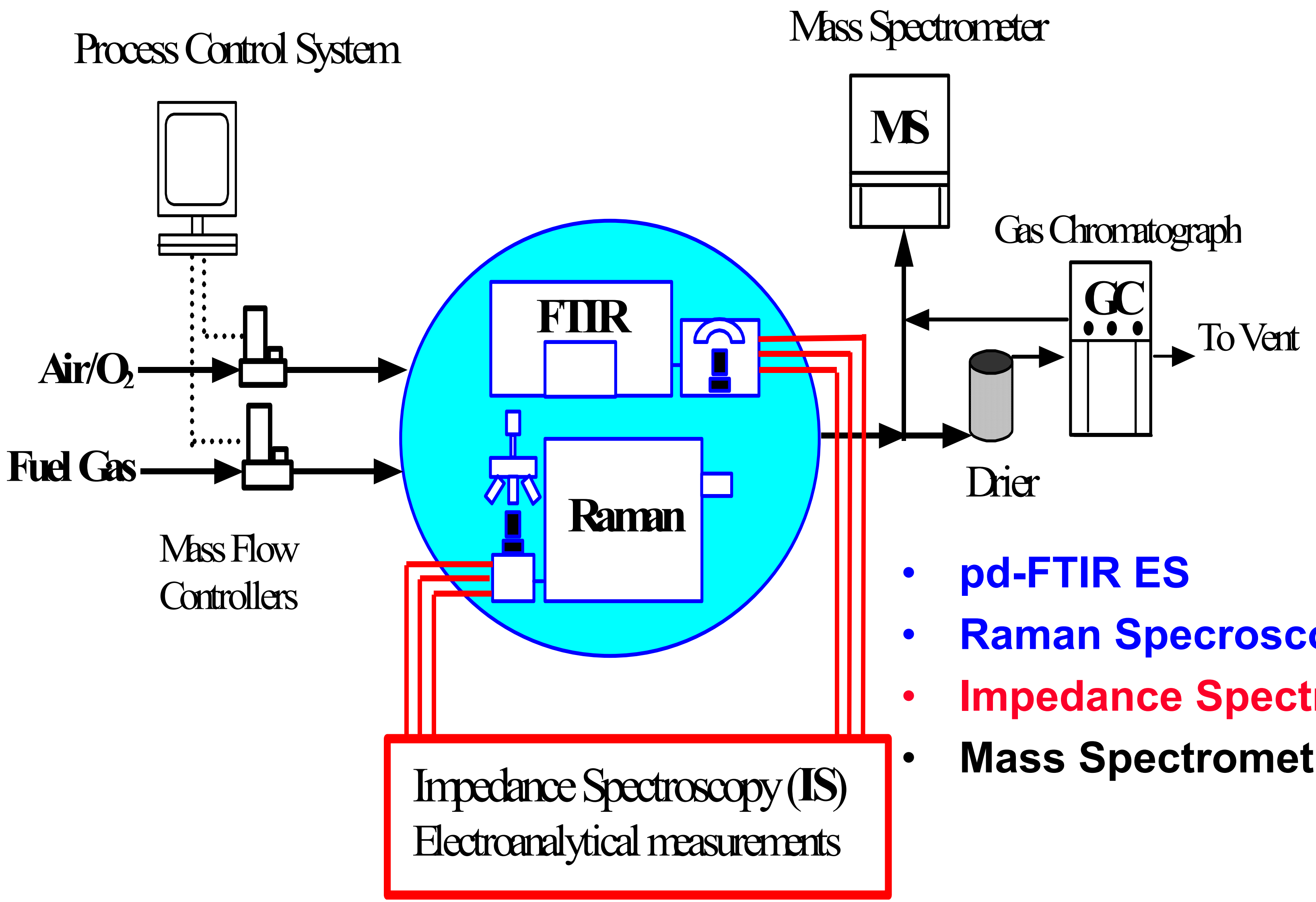
For (101) phase



Oxygen vacancy

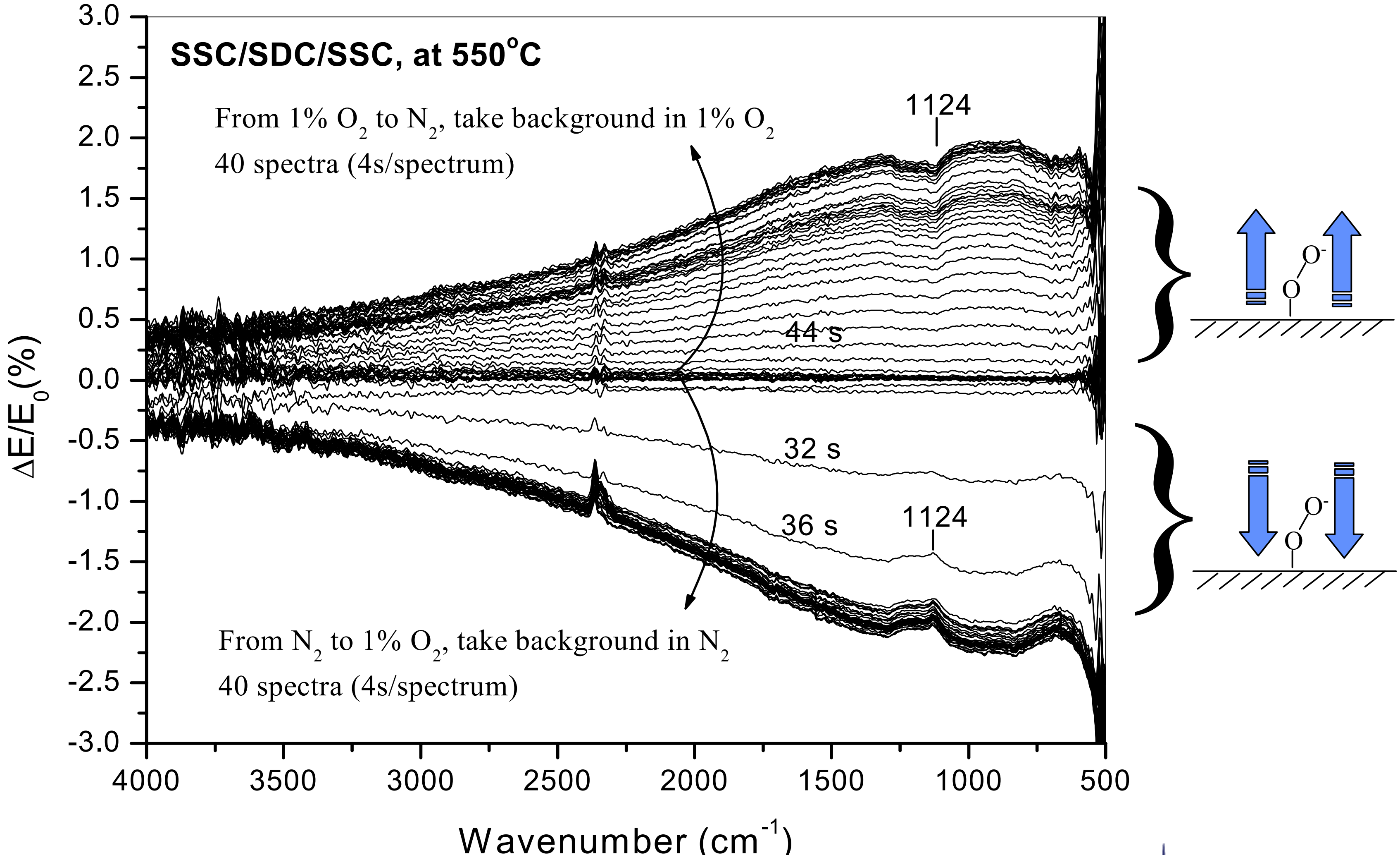
Adsorbed Oxygen

In-Situ Characterization Techniques

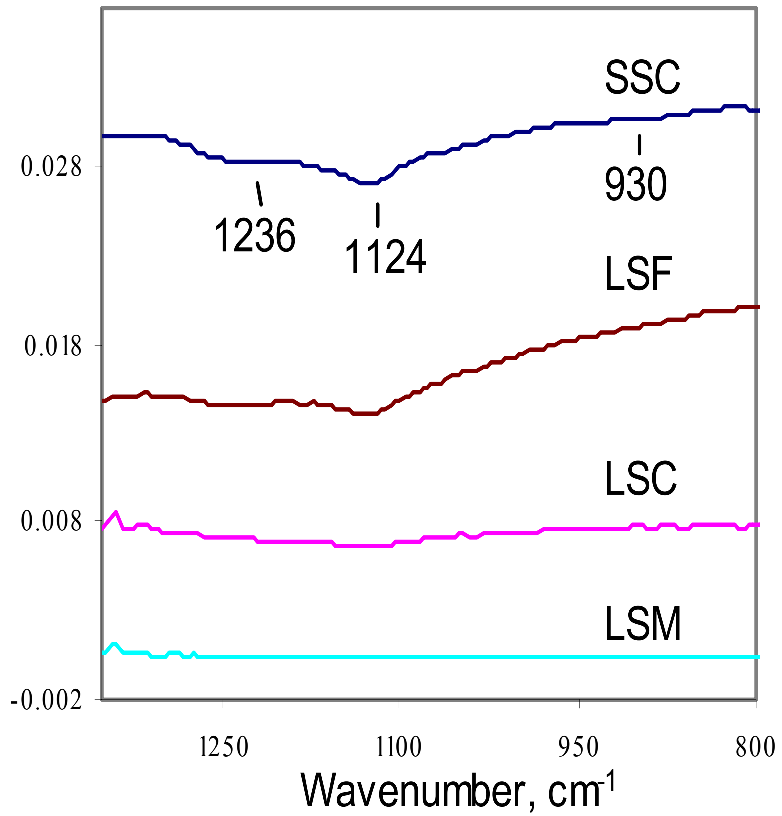


- pd-FTIR ES
- Raman Specroscopy
- Impedance Spectroscopy
- Mass Spectrometry/GC

Gas Switching Effect



Catalytic Properties of Cathode Materials



O_2^- species

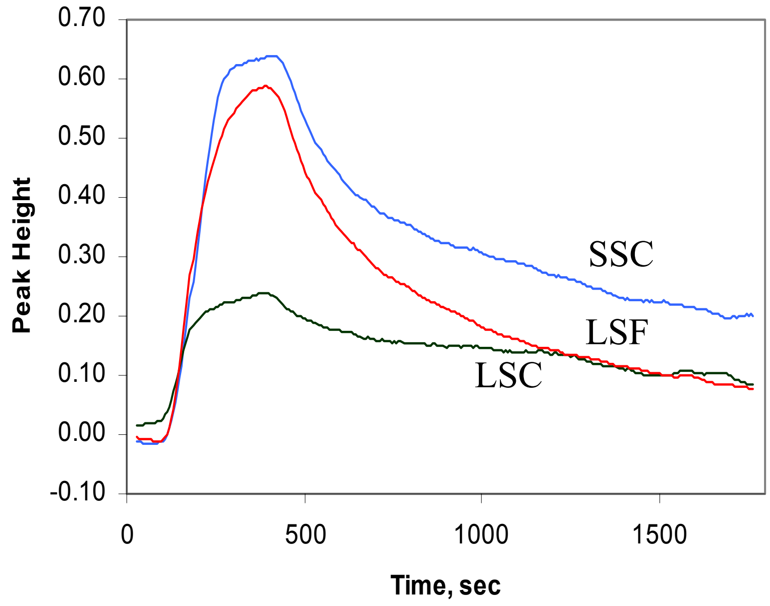
Different catalytic properties

PEAK Height:

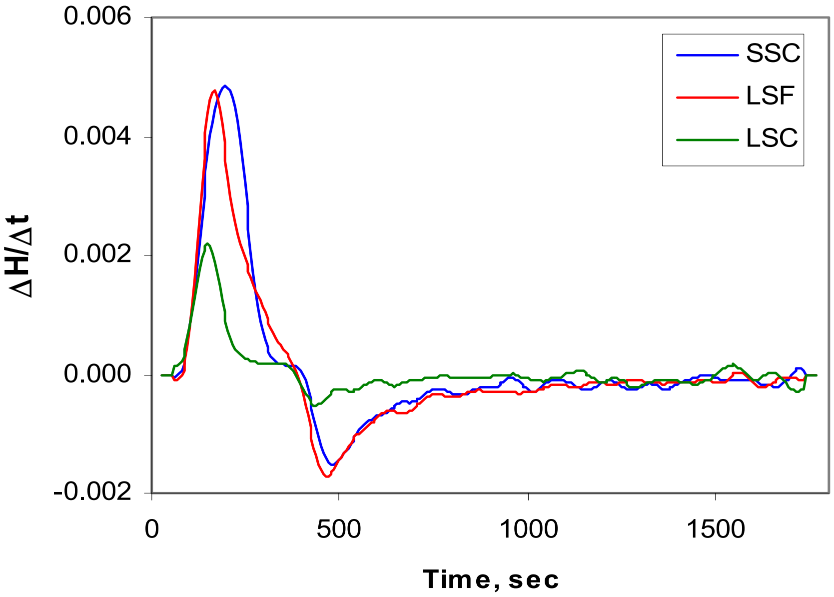
Fast Screening Tool for Materials Development

Maximum O_2^- signals for cathode materials at 600ºC in 1% O_2 atmosphere

Rates of Adsorption/Desorption



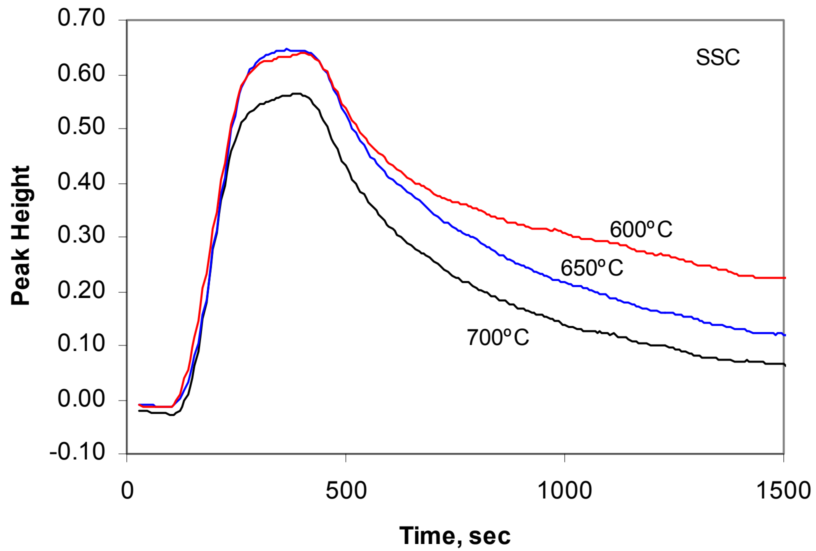
Height of 1124 cm^{-1} peak during gas witching experiment for different materials at 600ºC.



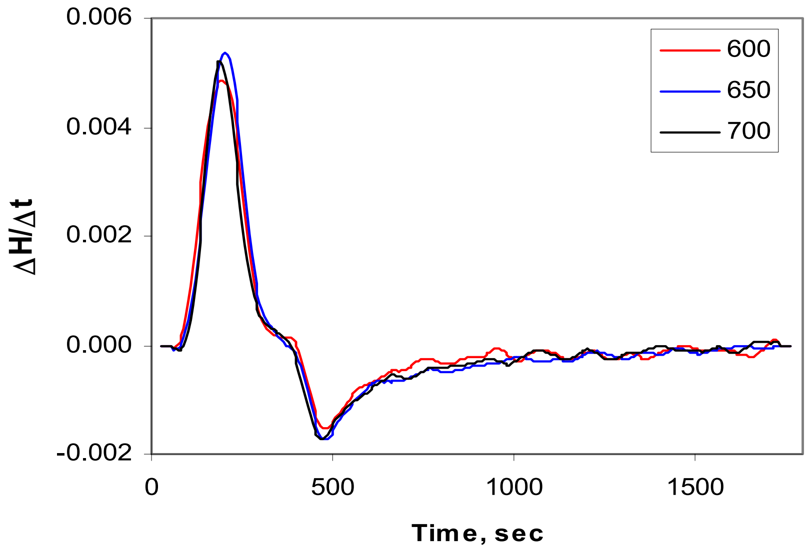
First derivative of 1124 cm^{-1} peak height vs. time curve

Reactivity for oxygen adsorption and desorption : SSC ≥ LSF > LSC

Gas Switching Effect



Height of 1124 cm^{-1} peak during gas switching experiment for SSC at different temperatures.



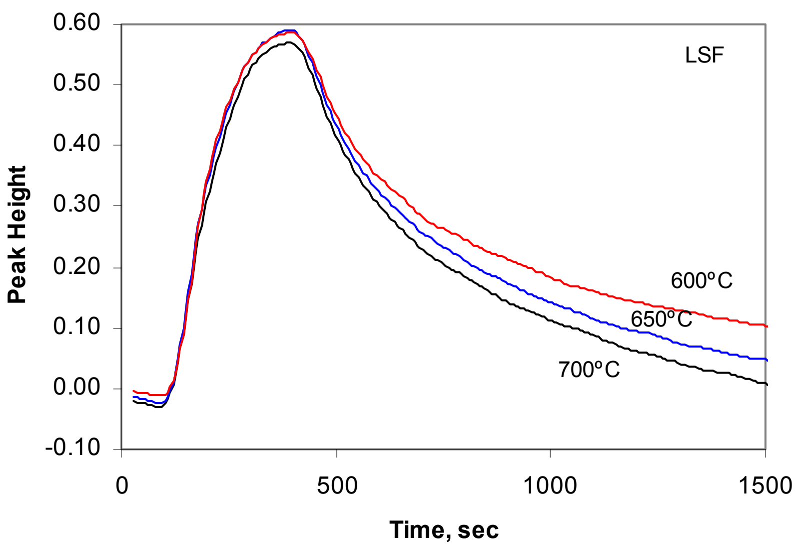
First derivative of 1124 cm^{-1} peak height vs. time curve for SSC at different temperatures

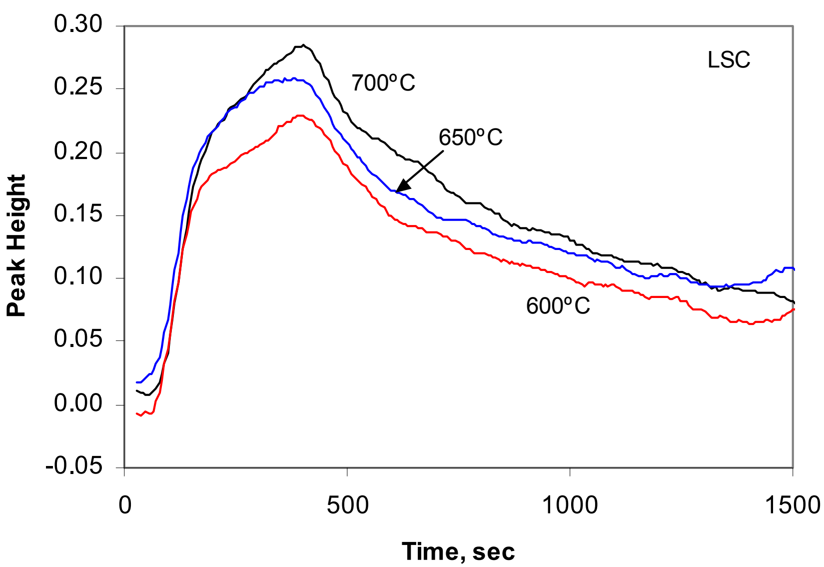
Reaction rate: 700 ≥ 650 ≥ 600

Temperature is not a significant parameter for oxygen adsorption but is for oxygen desorption

Temperature Effect

1% Oxygen

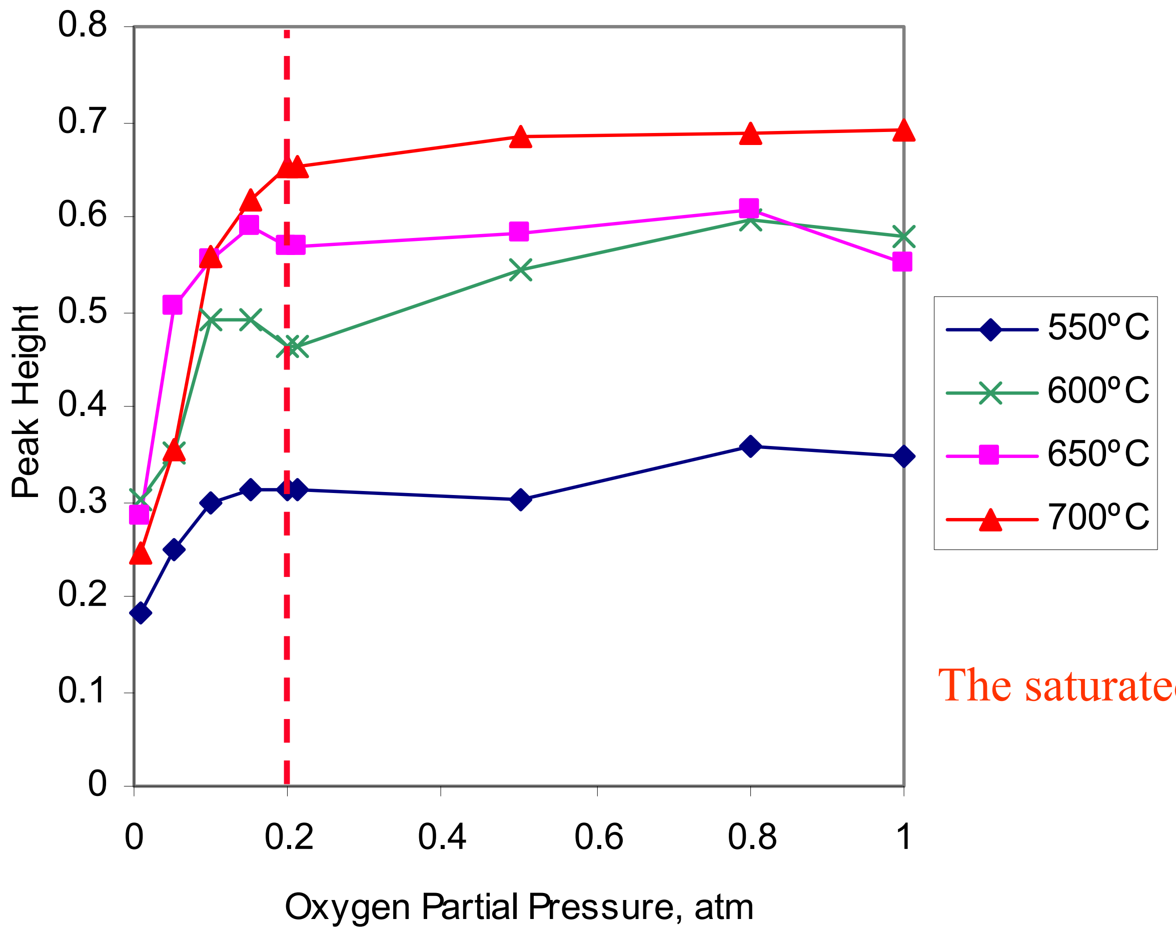




Height of 1124 cm^{-1} peak during gas witching experiment for LSF and LSC at different temperatures.

LSF and LSC show different temperature dependence for oxygen adsorption and desorption

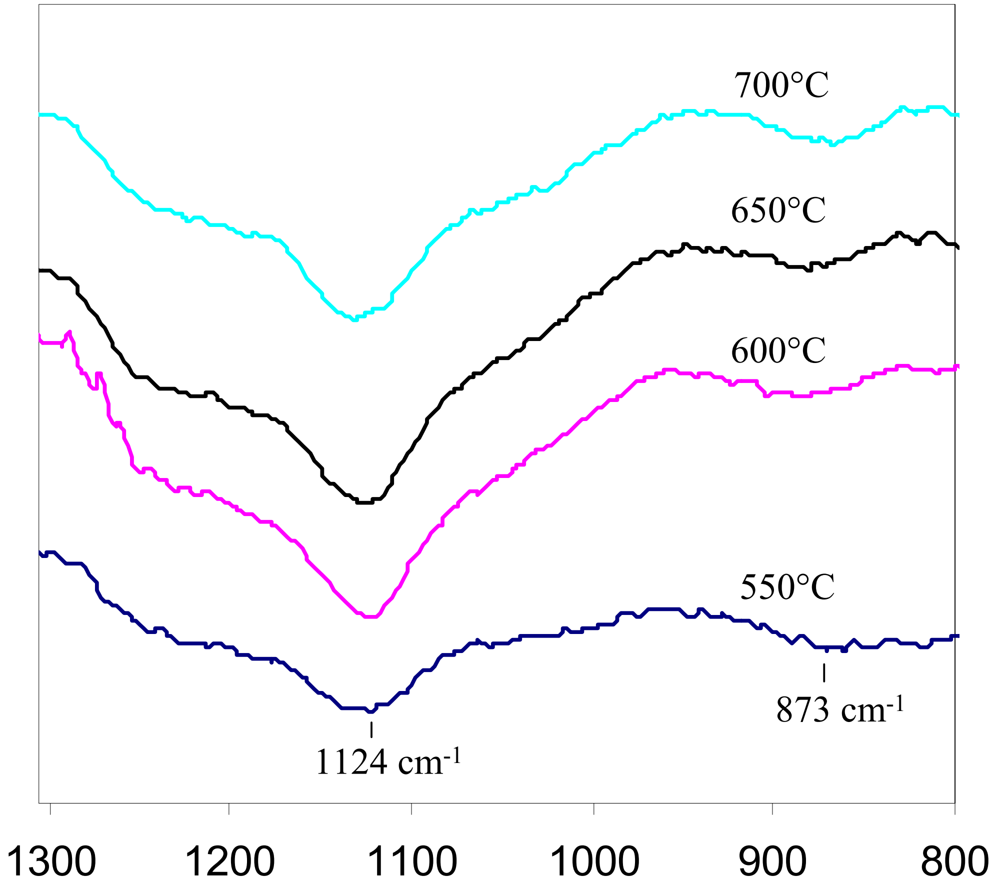
Effect of Oxygen Partial Pressure



The saturated C_{O2}: 20% (Air)

The intensity of 1124 cm^{-1} peak at different temperatures and in different atmospheres for LSF electrode

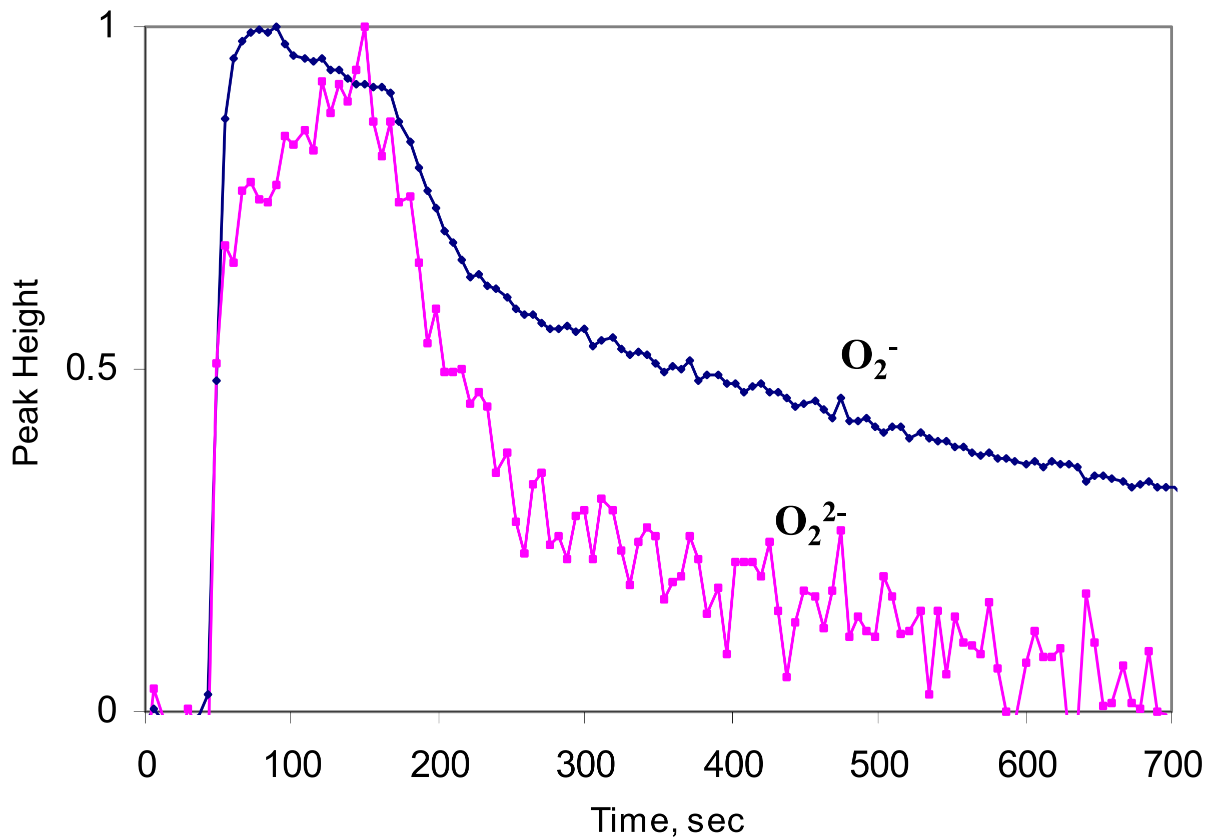
Peroxide Peak at High Po_2



The FTIR spectra of an SSC pellet at different temperatures in oxygen

High O_2 concentration → O_2^{2-}: 873cm^{-1}

Kinetics for Superoxide and Peroxide Ions



O_2^- and O_2^{2-}: fast adsorption

O_2^{2-}: slowly reach the max

Faster desorption

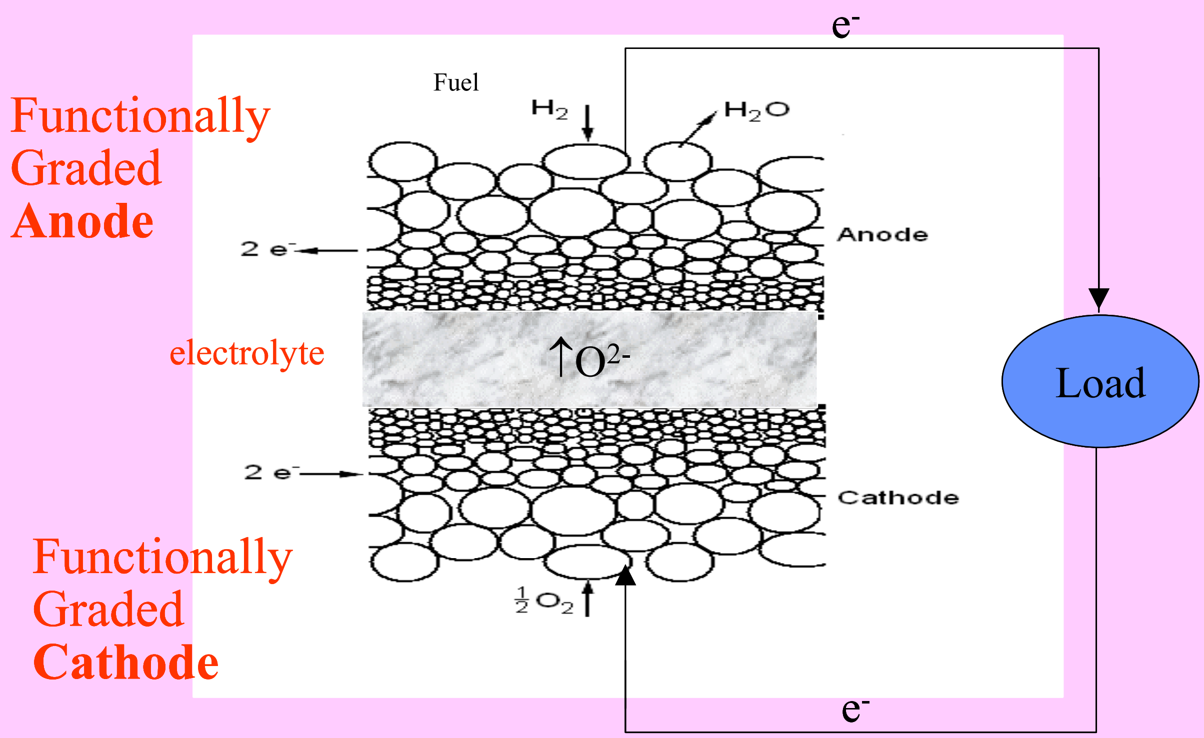
Normalized height of 1124 cm^{-1} and 875 cm^{-1} peaks during gas switching experiment from Ar to O_2 and back to Ar.

Conclusions – Time-Dependent FTIR-ES

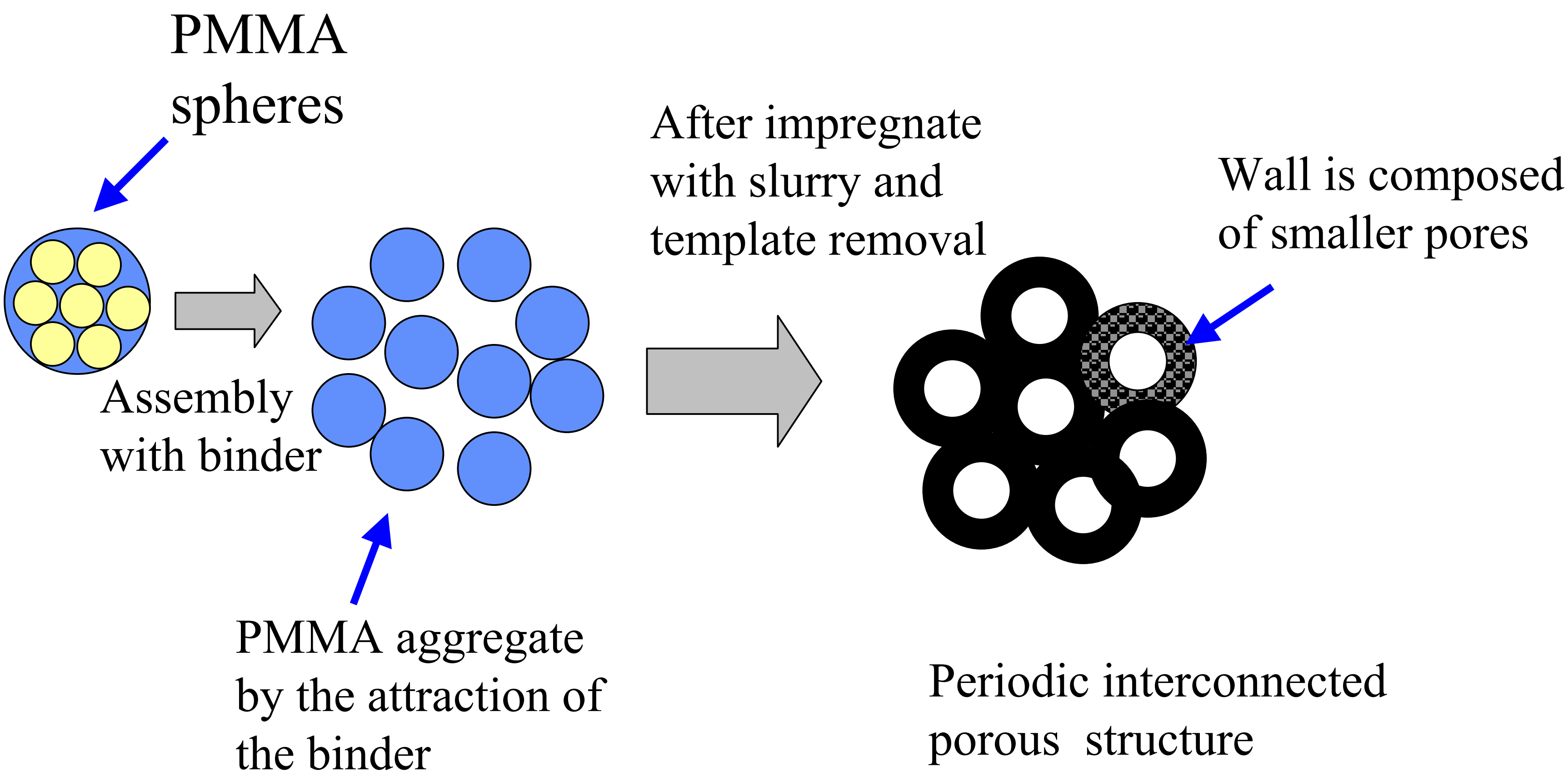
- The active sites for the oxygen reduction (oxygen adsorption) is not limited to the triple boundaries, but extended to surfaces of the MIEC electrodes.
- As expected, different cathode materials have different catalytic activity for the oxygen adsorption and desorption. In particular, SSC appears to have the highest activity for oxygen adsorption while LSF has the fastest kinetics for the oxygen desorption.
- The saturation partial pressure of oxygen is about 20% for the FTIR measurements.
- The intensity of the peroxide peaks are much weaker than those of the superoxide peak. The formation rate of peroxide species appears to be as fast as that of superoxide; however, there is some delay for peroxide to reach the maximum point. The desorption of peroxide is much faster than that of superoxide.

Fabrication of Functionally Graded Electrodes

- **Templated Synthesis**
- **Combustion CVD**

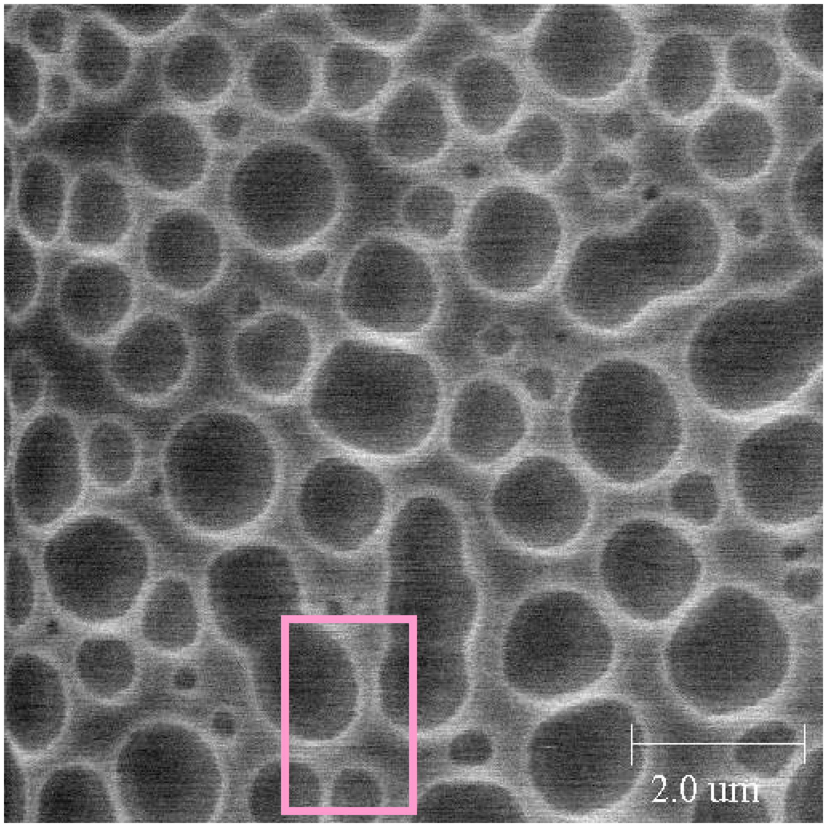


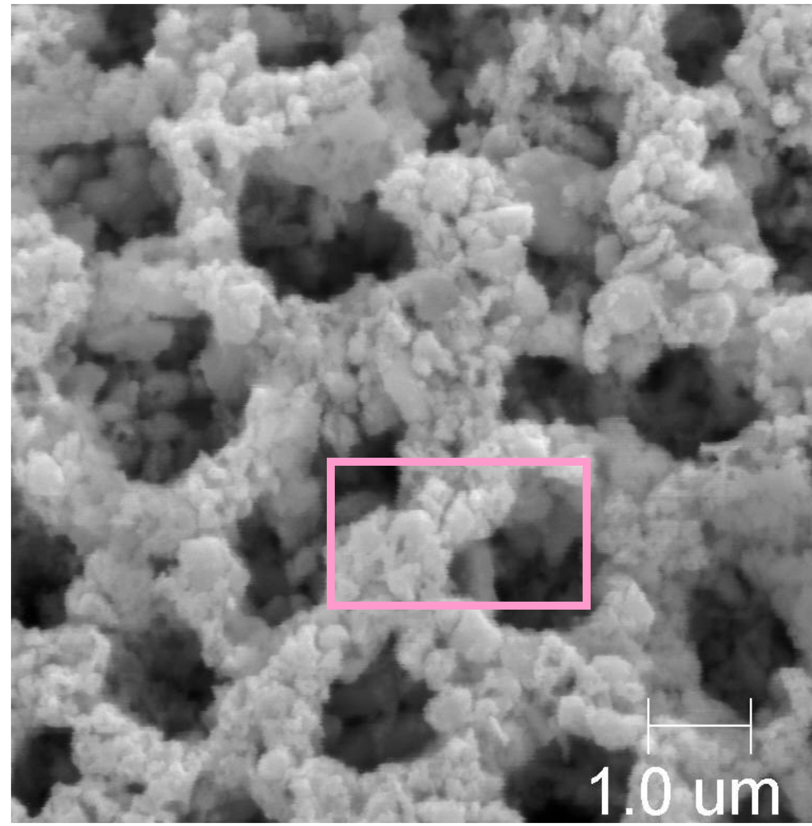
Schematics – Templated Synthesis



Preliminary Results

- SEM pictures



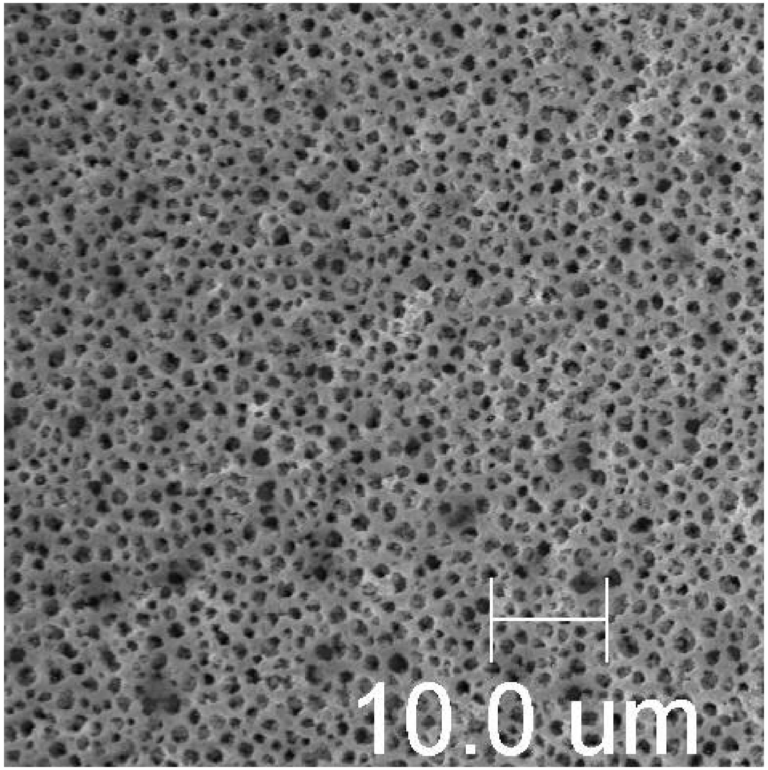


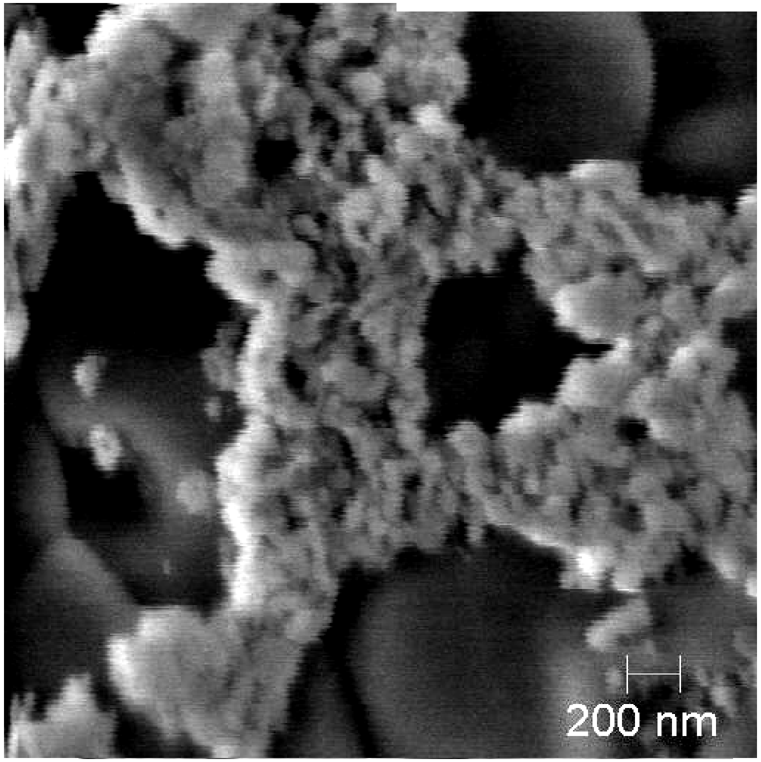
PMMA template

Porous GDC-SSC MIEC

Preliminary Results

Walls consist of particles of about 100 nm in diameter





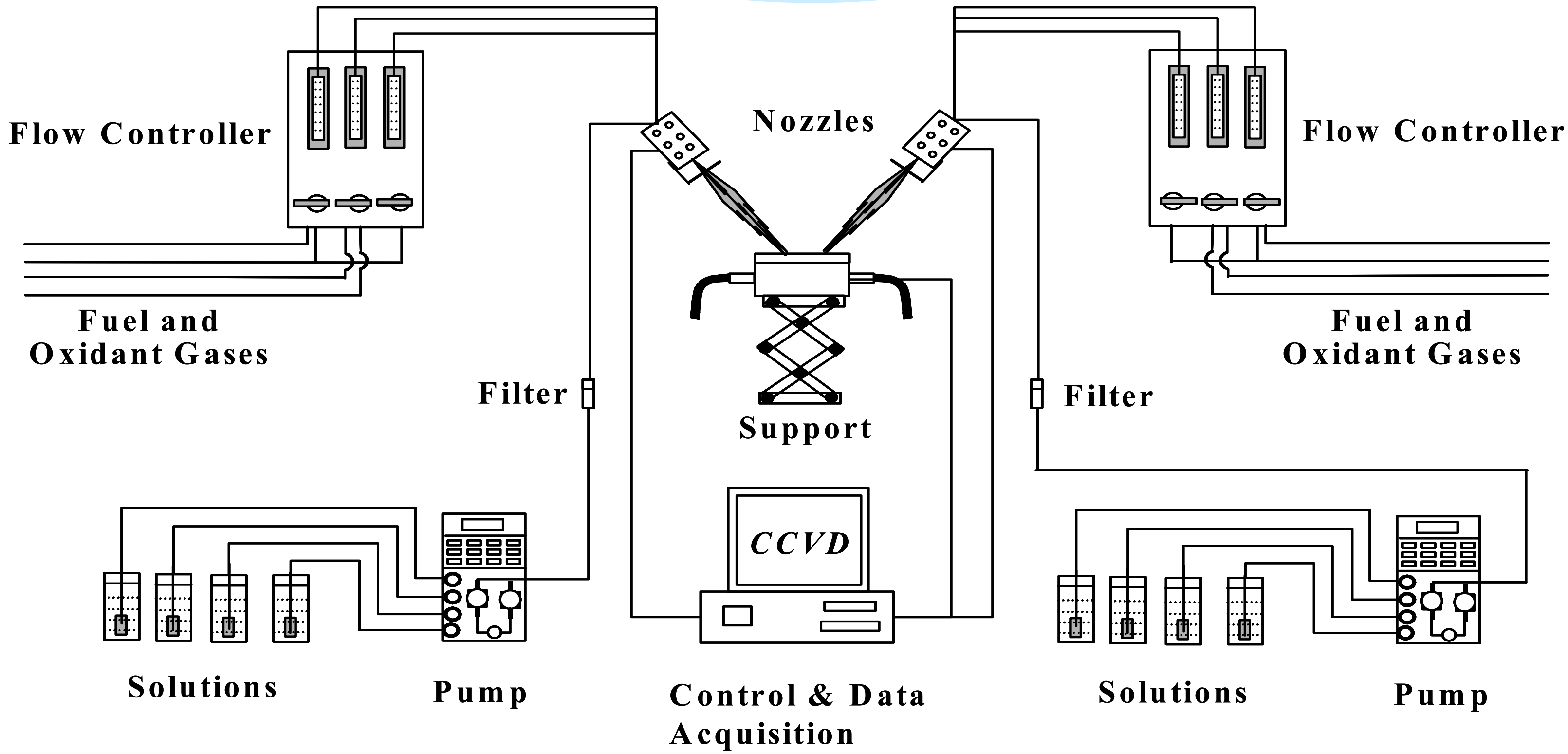
Porous GDC-NiO MIEC

Combustion CVD

High fuel-to-gas ratio
→ Reducing atmosphere

Ni GDC

Moderate fuel-to-gas ratio
→ Oxidizing atmosphere



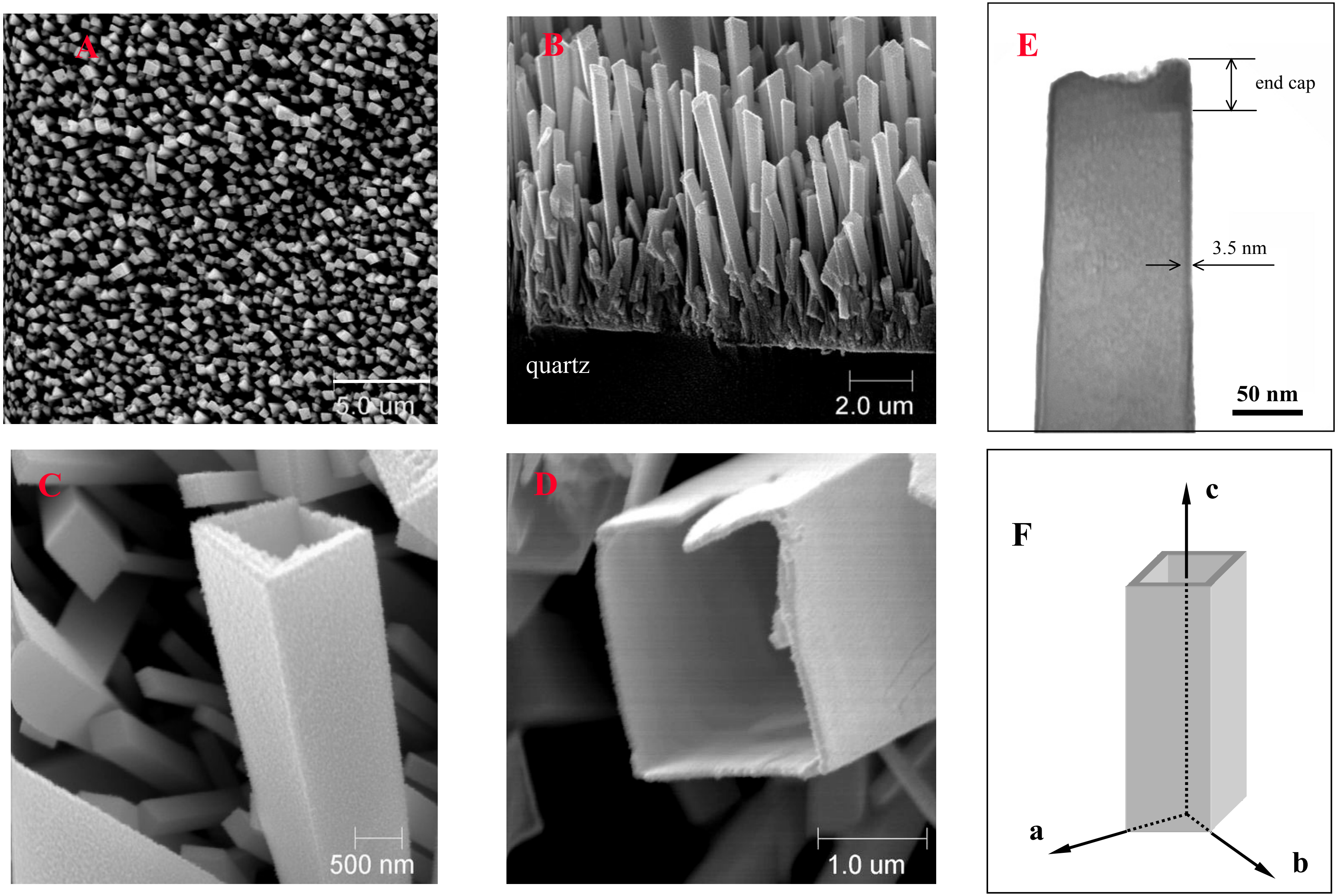
Low cost

- Open-air, flame-assisted deposition process
- No furnace or reaction chamber required
- Inexpensive precursors (e.g., metal nitrates)

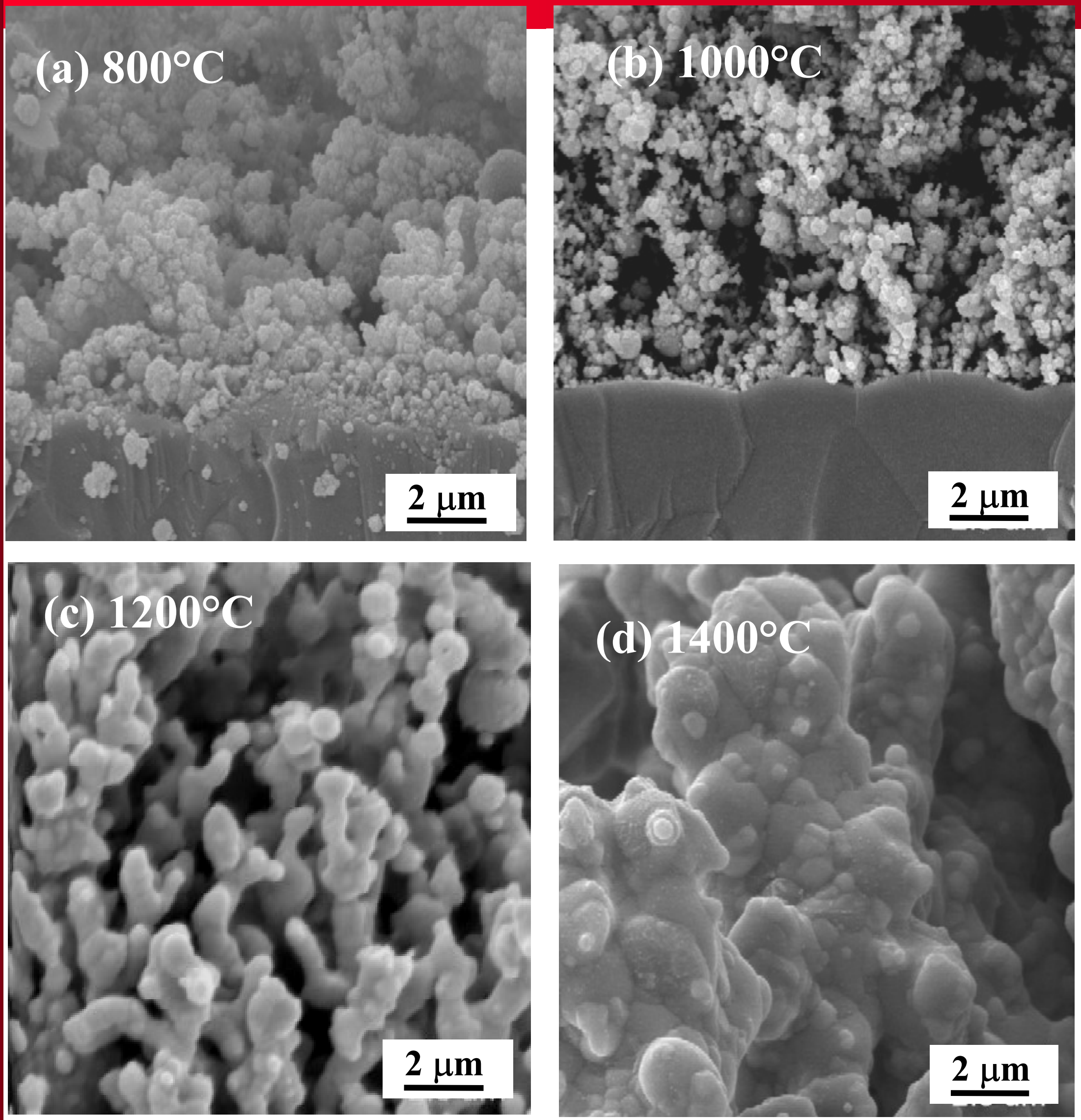
Great Flexibility

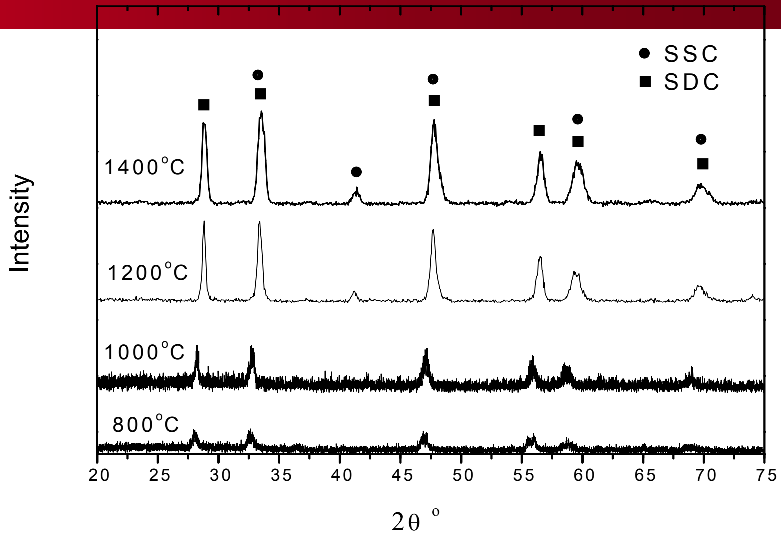
- Multi-element and/or multi-layer coating capability
- Capable of producing vastly different microstructure and morphologies;

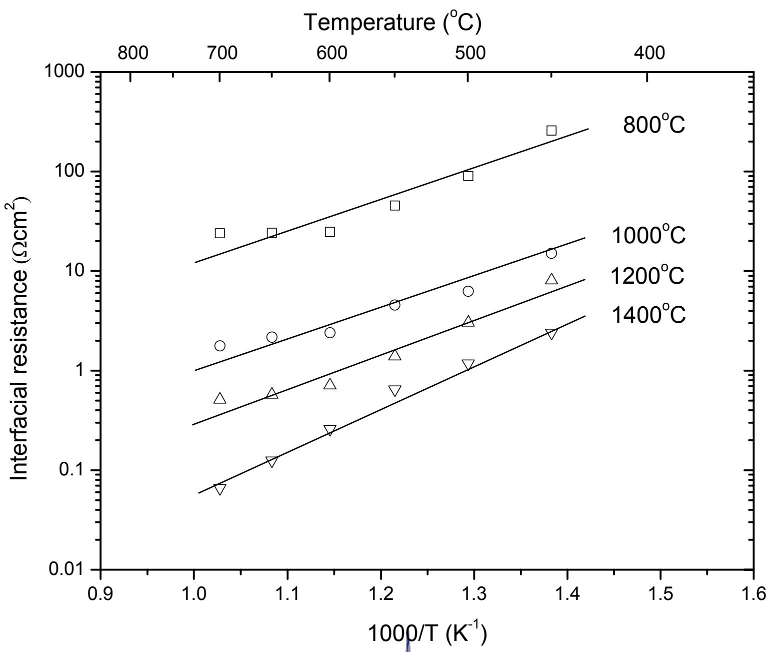
Nano Box-Beams of Semiconductor SnO_2



Effect of Deposition Temperature







Functionally Graded Electrodes

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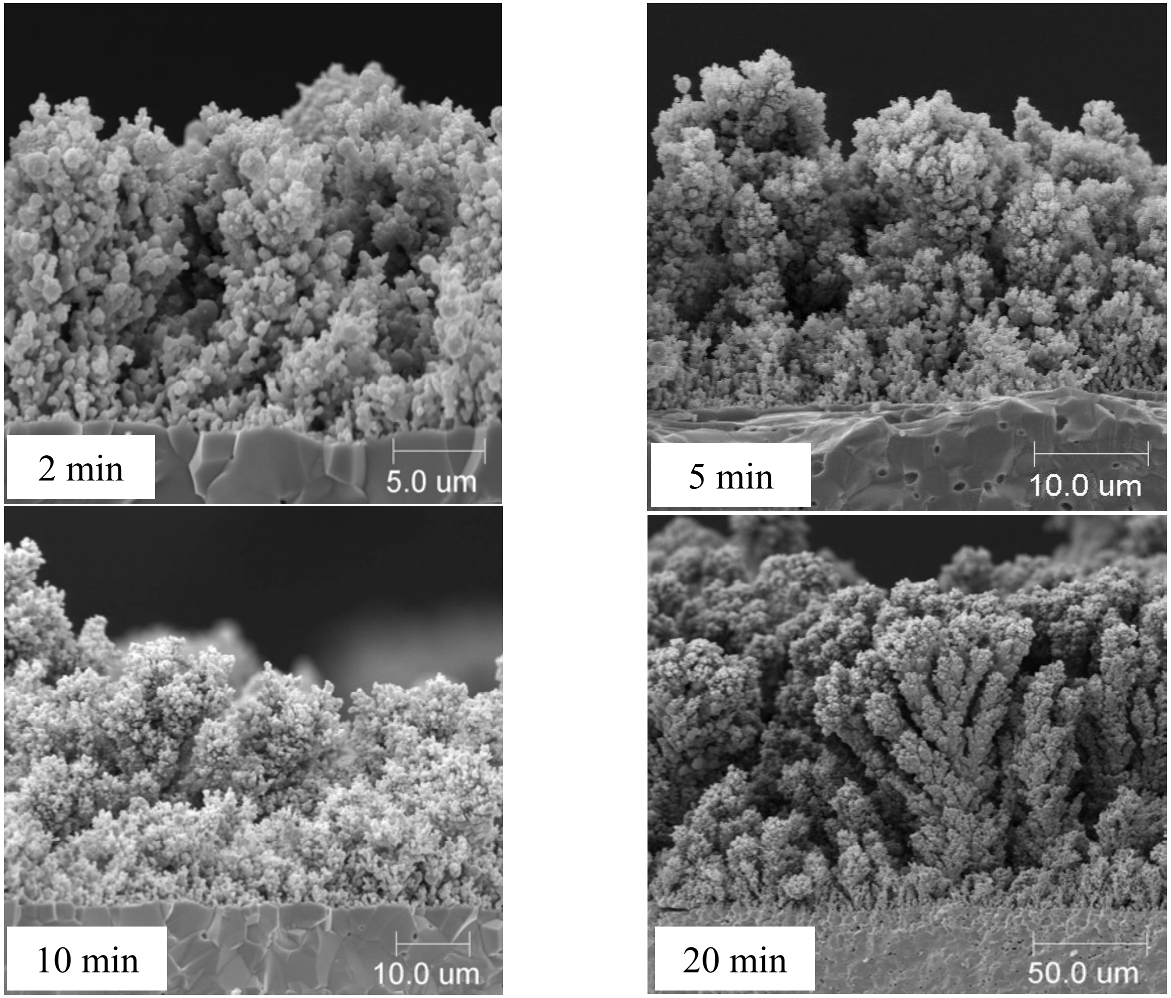
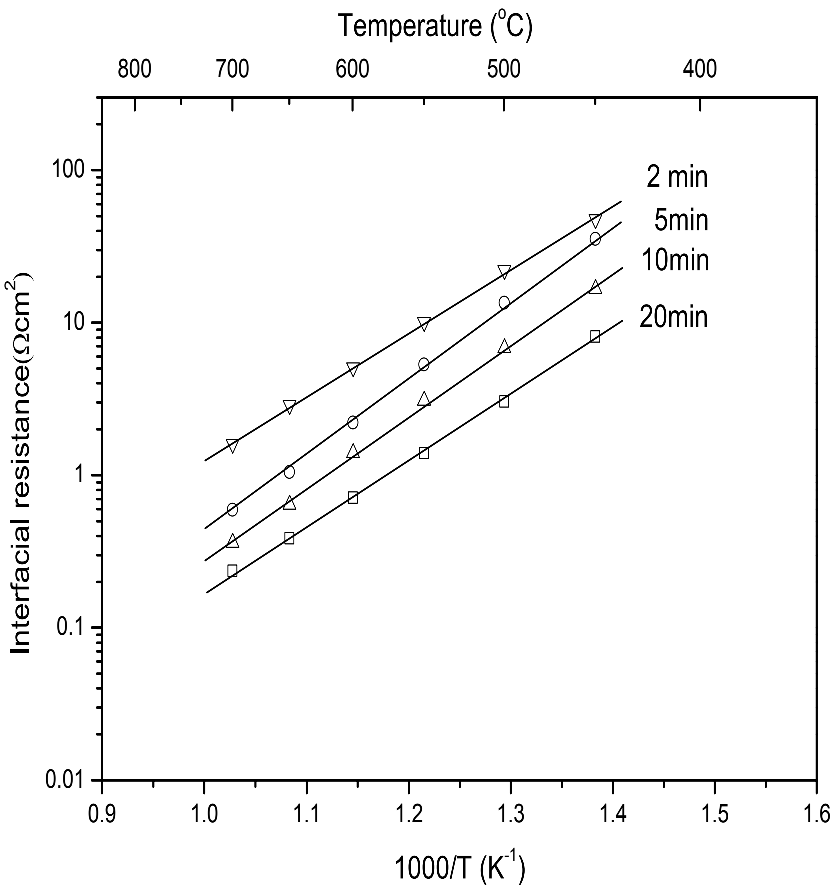
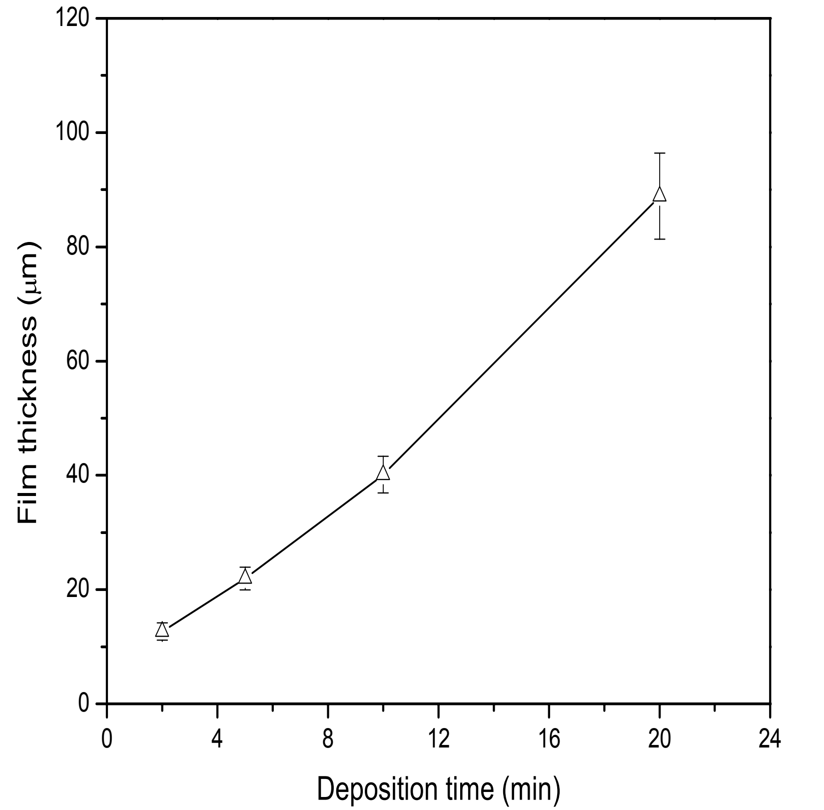
Deposition Time: Microstructures

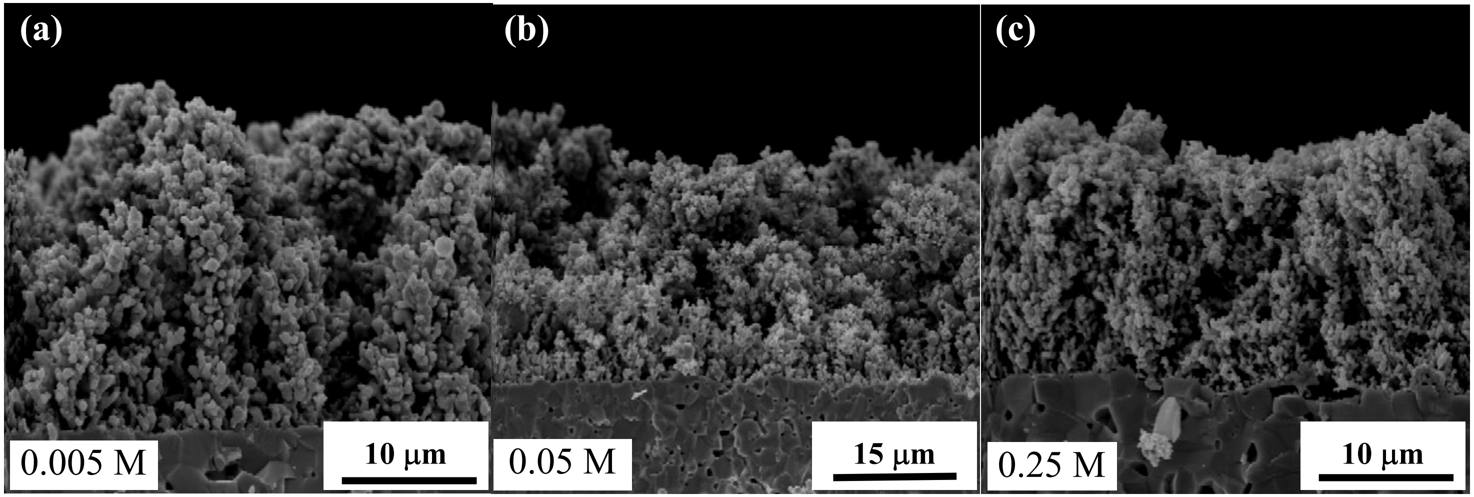


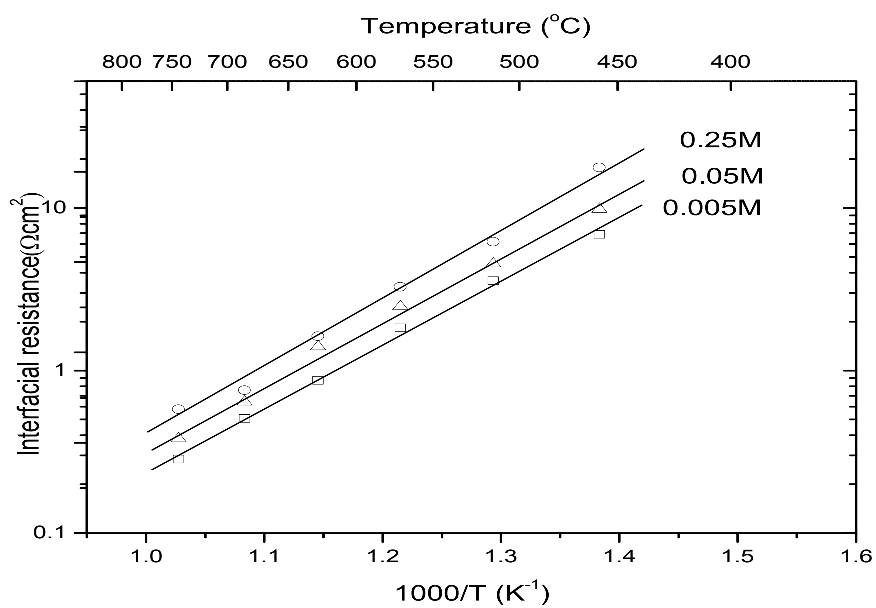
Deposition Time: Thickness and R_P



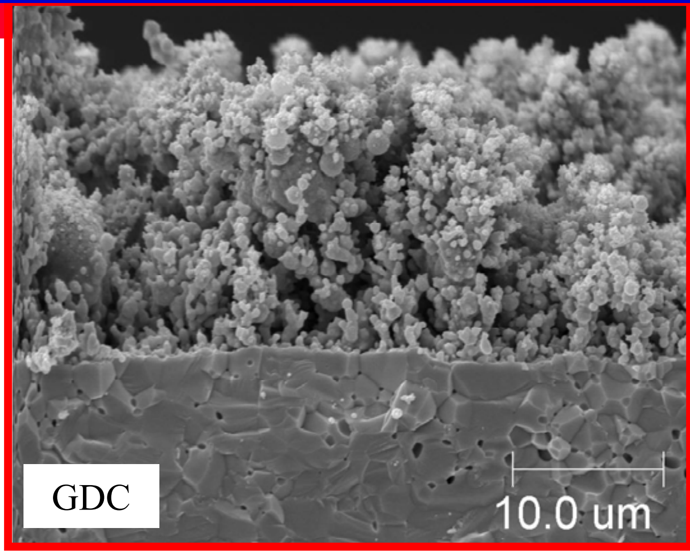


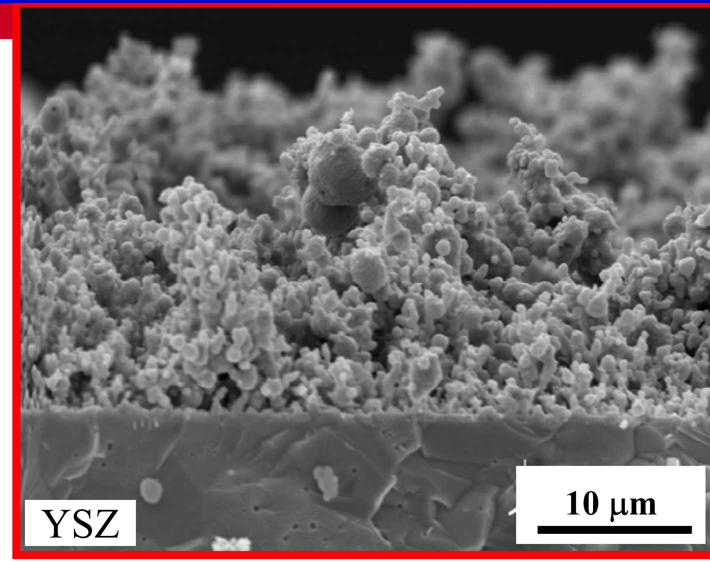
Effect of Concentration

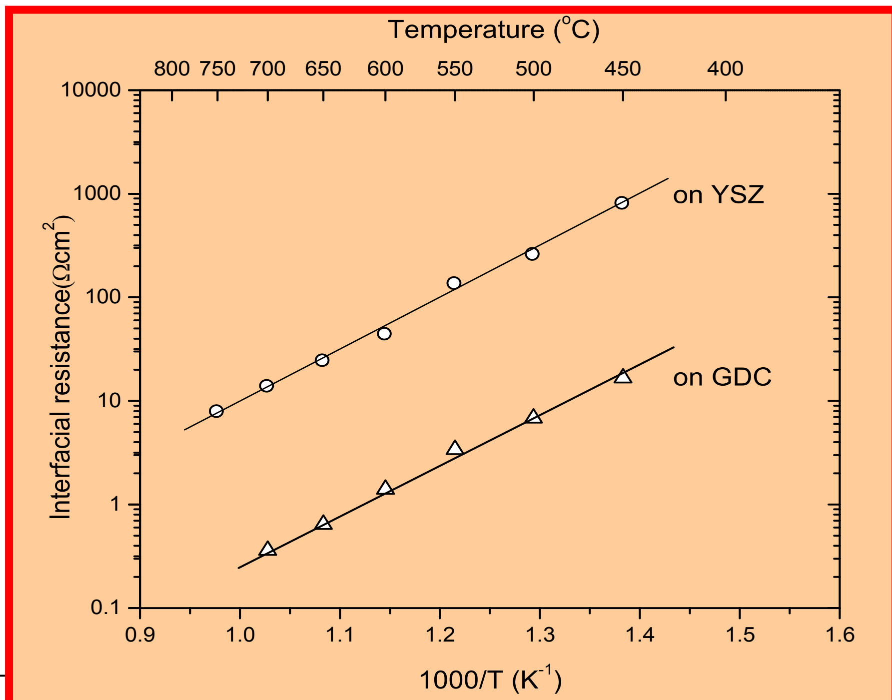




Effect of Substrate (Electrolyte)

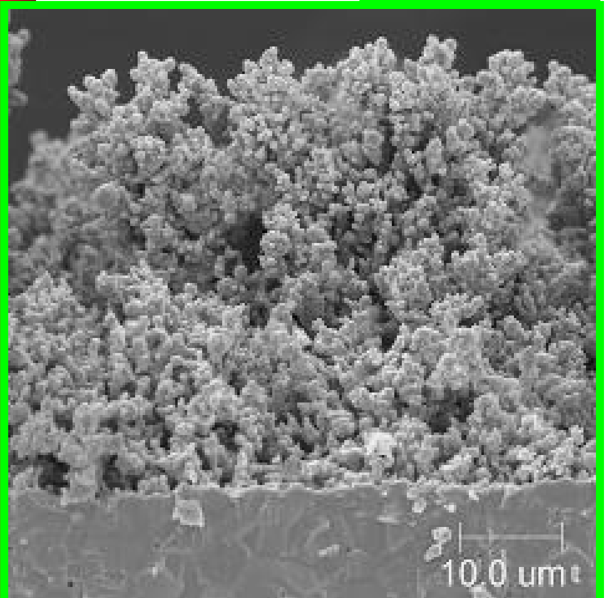


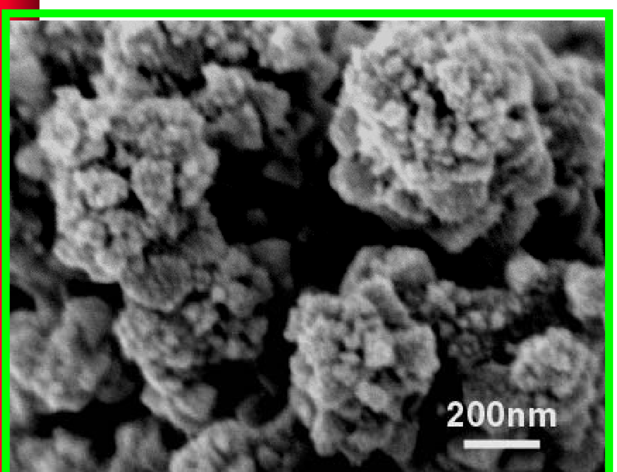


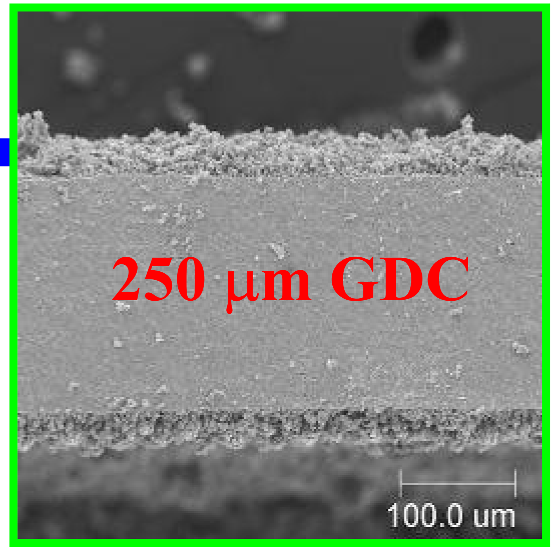


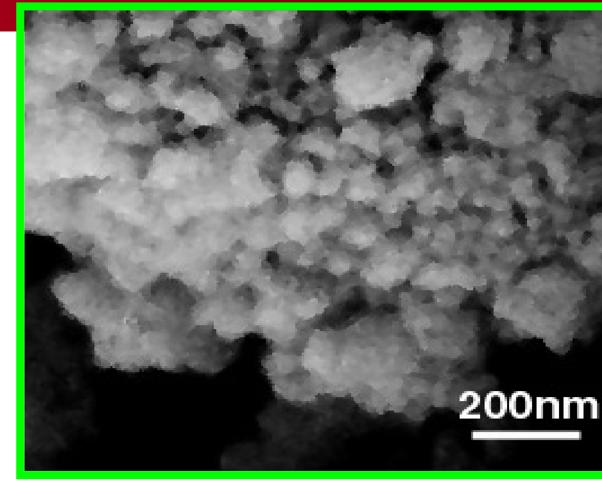
An SOFC Fabricated by CCVD

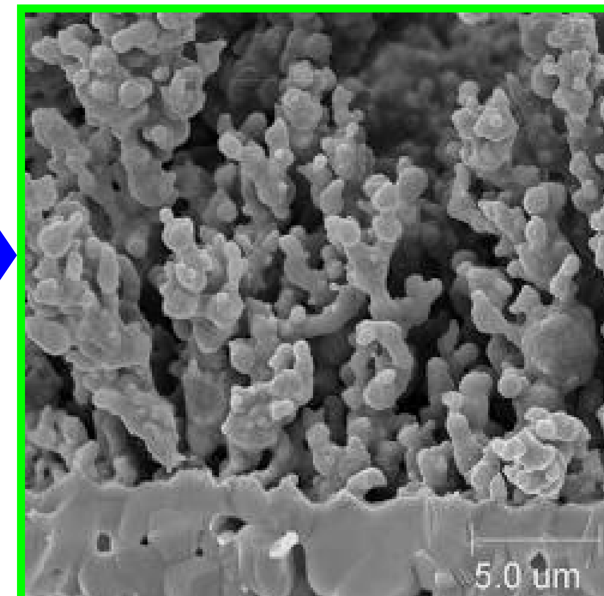
Anode
Ni +SDC









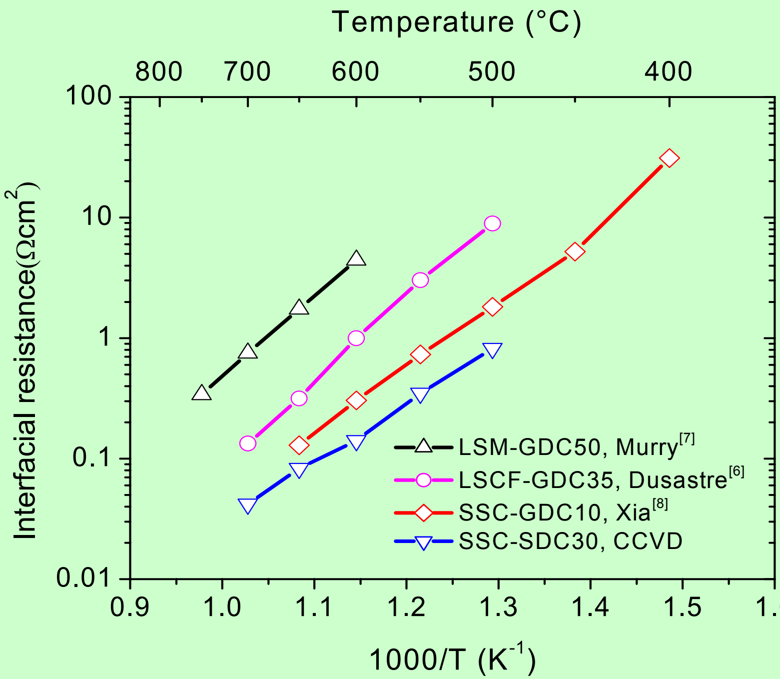


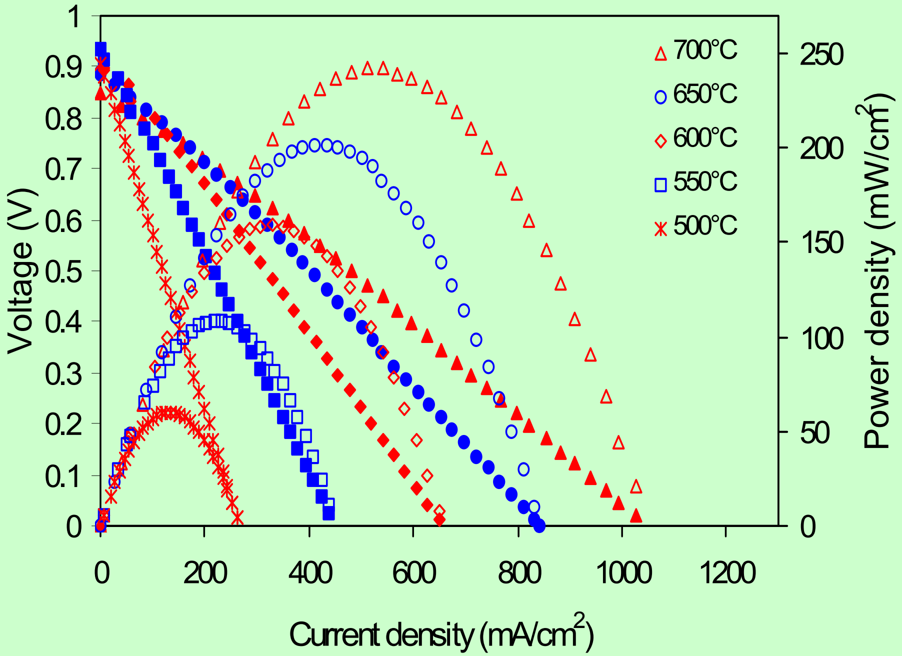
Cathode
SSC+SDC

Functionally Graded Electrodes

Interfacial Resistances and Performance

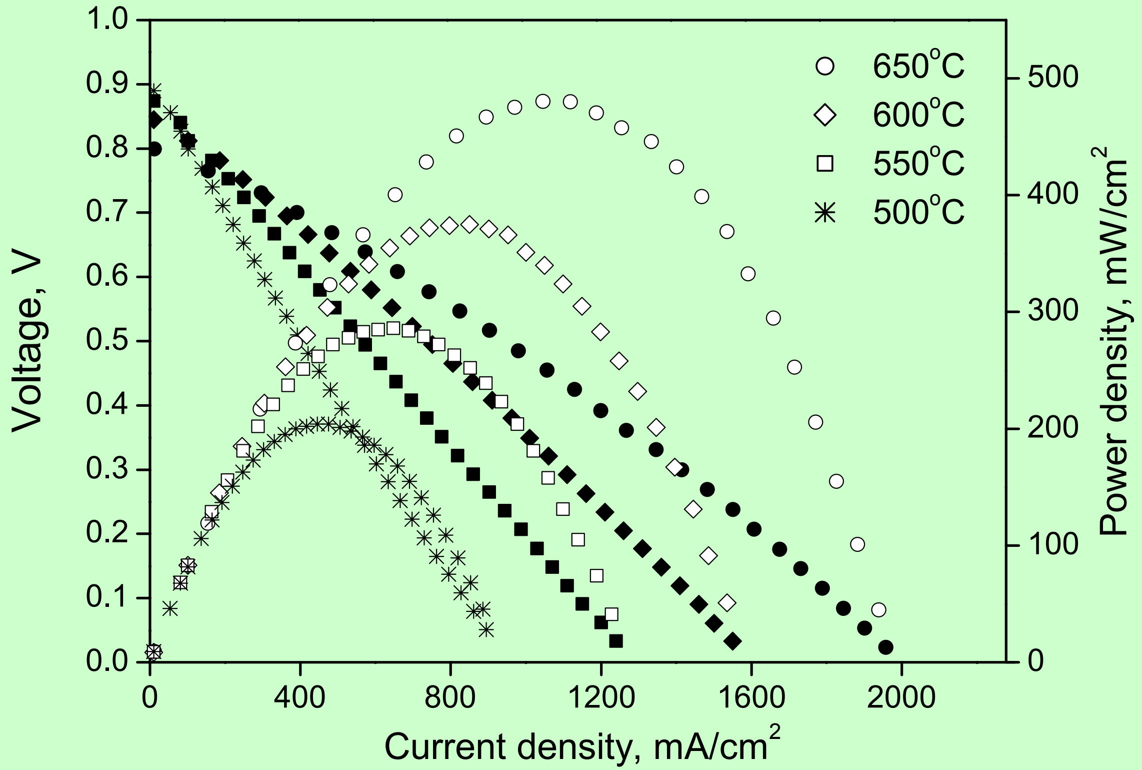
of an SOFC supported by 250 μm GDC





Performance of an Anode-Supported Cell with Cathode by CCVD

30 μm Electrolyte



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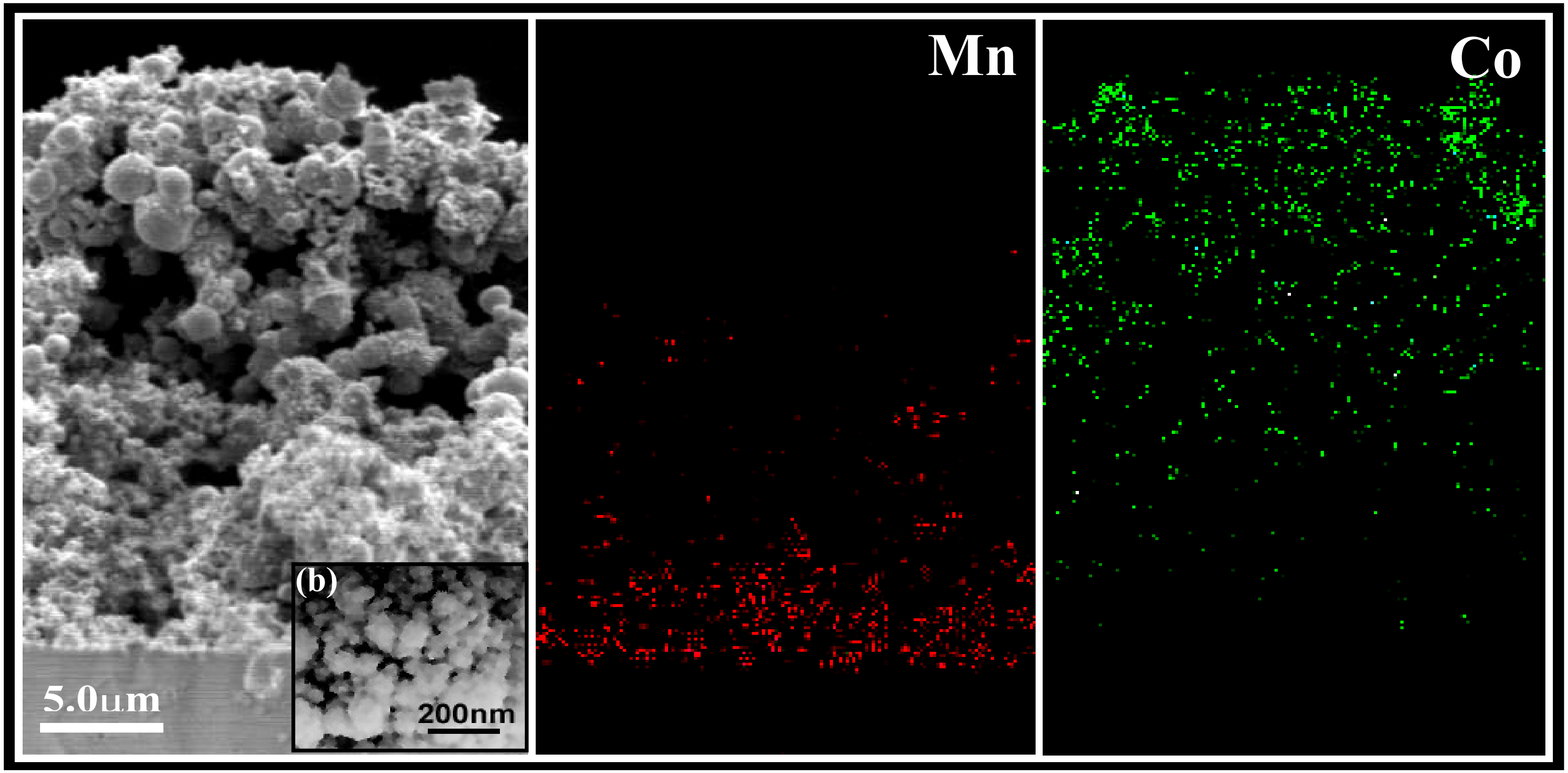
Nano-structured Electrodes by Combustion CVD



Functionally Graded Cathode (fabricated on 250µm YSZ) by CCVD, along with the EDS dot mapping of Mn and Co element distributions

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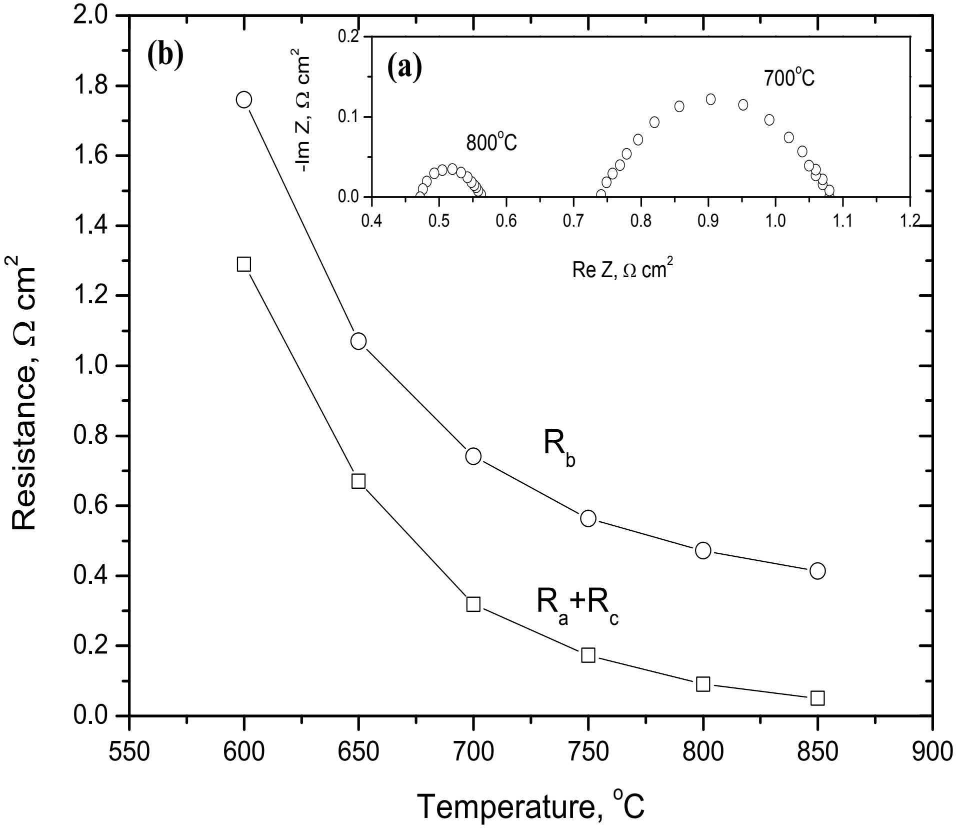
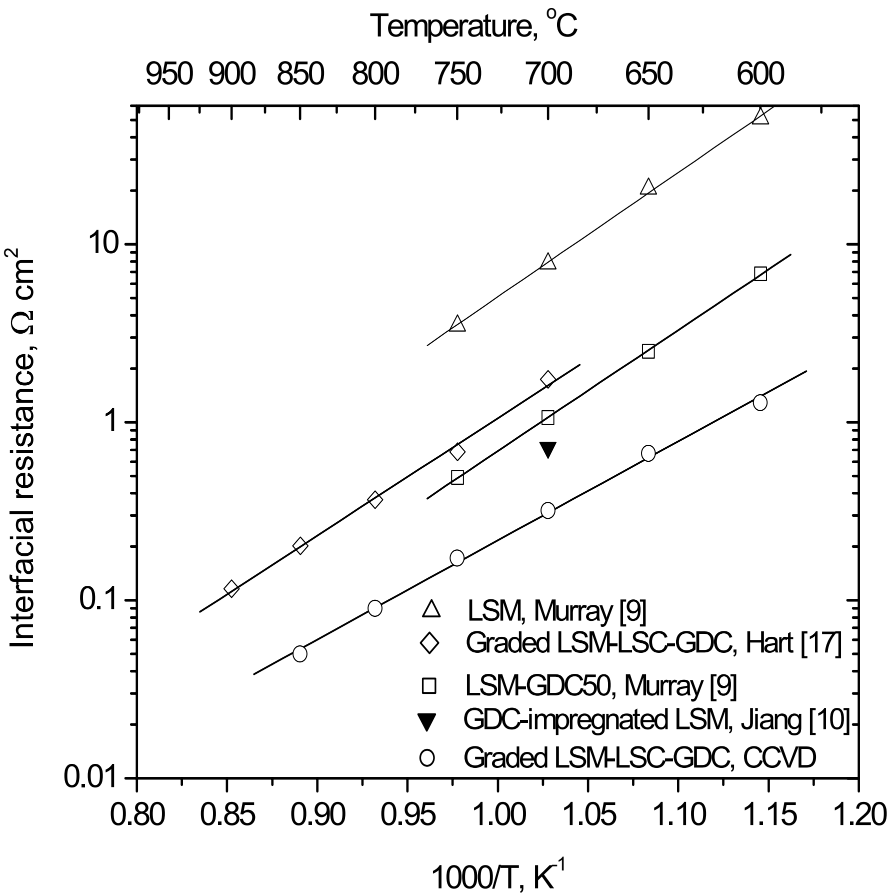
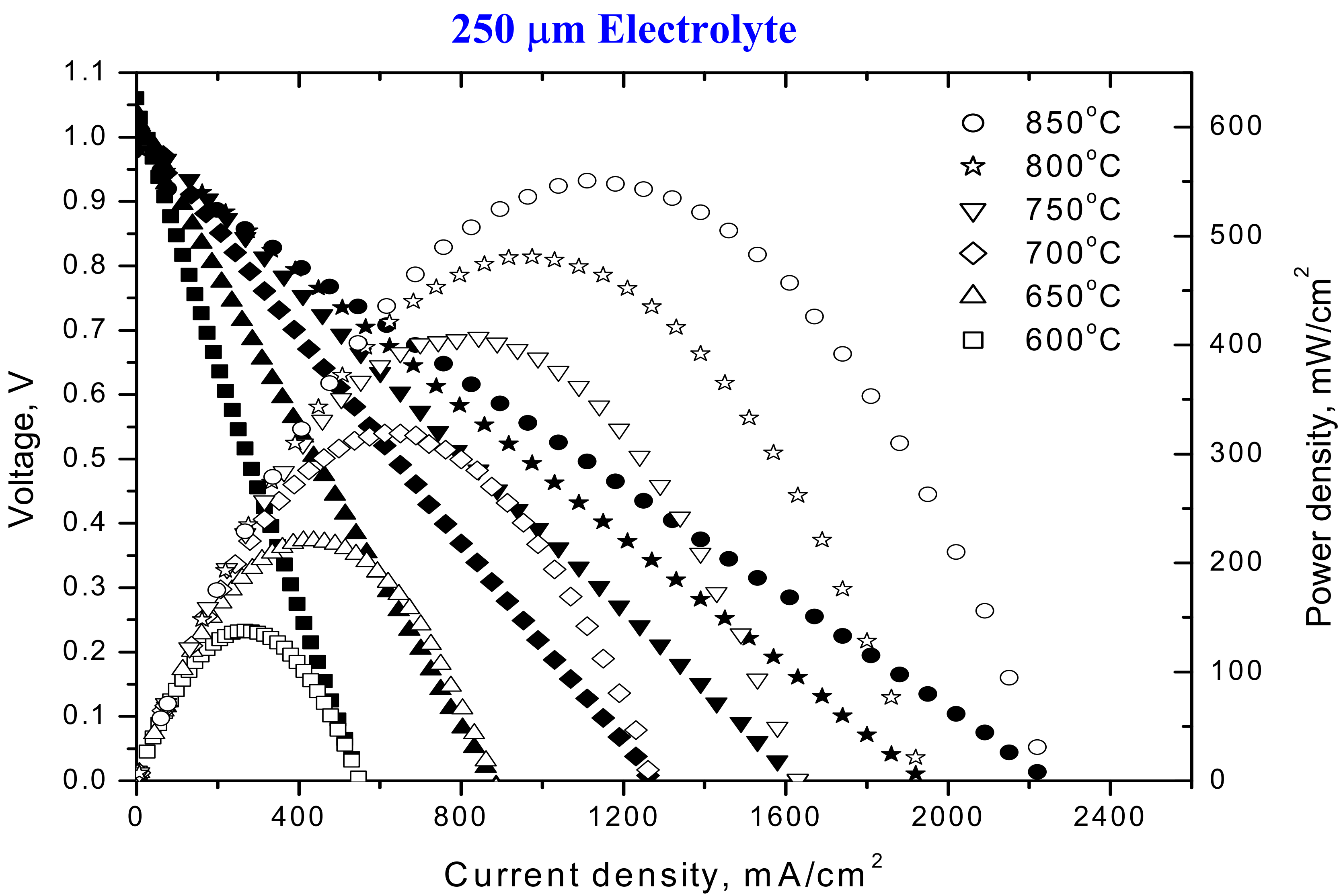
Impedance Spectra/Resistance – Combustion CVD





Fuel Cell Performance – Combustion CVD



Summary of Accomplishments

- Started 3-D Modeling of graded multi-layer cathodes
- Started Microscopic modeling of surface reaction processes
- Developed micro-fabrication techniques capable of producing MIEC electrodes (SSC and LSM) with well-defined geometries
- Understanding of reduction mechanisms on different cathode materials using in-situ characterization techniques
- Used Raman spectroscopy to better characterize surface structures of electrodes under practical operating conditions
- Used combustion CVD and templated synthesis to produce vastly different microstructure and morphologies of porous mixed-conducting electrodes
- Demonstrated cathodes of lowest polarization resistances for low temperature SOFCs

Applicability to SOFC Commercialization

- Generated some basic understanding of electrode reaction mechanisms in an effort to better design of efficient electrodes
- Developed new tools for in-situ determination of electrode properties under practical conditions
- Developed new architectures/microstructures of porous MIEC electrodes using combustion CVD and templated synthesis

Activities for the Next 6-12 Months

- **Fabrication and evaluation of patterned MIEC electrodes with active phase and finer features**

  → Reaction sites, pathway, and mechanism

- **Refine Macroscopic and Microscopic Models**

  → Optimum Microstructure/Architecture

- **Optimization of templated synthesis and combustion CVD for fabrication of FGEs**

- **Development of new in-situ characterization tools for investigation of SOFC reactions**

  → AFM/STM integrated with Raman spectro-microscope to achieve chemical mapping at nano-scale

  → AFM/STM integrated impedance spectroscopy to acquire impedance spectra of individual grains and individual grain boundaries between dissimilar materials

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