Fundamental Studies of Electrodes for SOFCs

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Outline

- Technical Issues Addressed
- Objectives & Approach
- Recent Progress (Since May 2004)
  - QM Calculations
  - Probing and mapping gas-surface interactions
  - Cells with Patterned Electrodes: TPB width/thickness
  - Fabrication of Porous Electrodes
- Applicability to SECA
- Activities for the next 6-12 Months

Critical Issues

1. **Why one particular electrode material is better than others?**
   - Origin of intrinsic catalytic properties
   - Effect of surface defects/Nano-struture
   - Role of ionic and electronic transport
2. **Why a particular electrode architecture is more efficient than others?**
   - Quantify microscopic features important to electrodes
   - Predictive models for design of better electrodes
3. **How to fabrication FGE with desired microstructure and composition cost effectively**

Objectives

- To develop novel tools for probing and mapping surface reactions
  - In-situ experimental measurements (FTIR, SERS, TERS, μ-IS) under practical conditions
  - Ex-situ measurements under well-controlled conditions (ESD/PSD)
  - Computational approaches
- To apply this tools to investigations of important reactions in SOFCs
  - Oxygen reduction, Cr-poisoning, S-poisoning
  - MIEC active regions, Bonding sites / mechanisms
  - Rate-limiting steps, surface reaction rates, bulk diffusion coefficients
- To establish scientific basis for rational design of better electrodes

Recent Progress (Since May 2004)

- **QM Calculations**
- **Experimental: Probing and mapping gas-surface interactions**
- **Cells with Patterned Electrodes: TPB width/thickness**
- **Fabrication of Porous Electrodes**

Computational Approach
QM Calculation of Gas-Surface Interactions

Quantum Mechanical (QM) methods

↓

Geometrical Configuration for reactants, intermediates, transition states and products

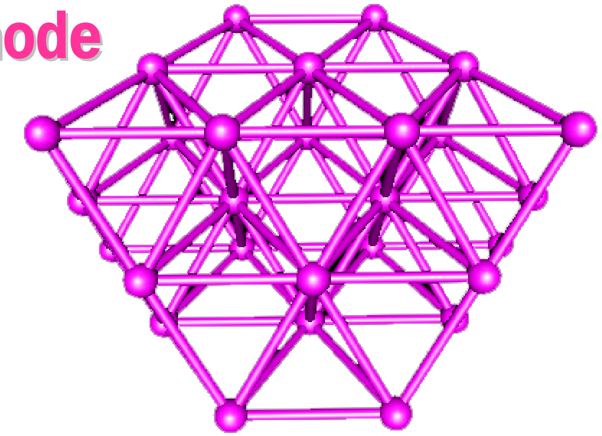
Vibrations → **FTIR/Raman Spectroscopy**

Energetics → **Reaction mechanism: Favorable reaction pathways**

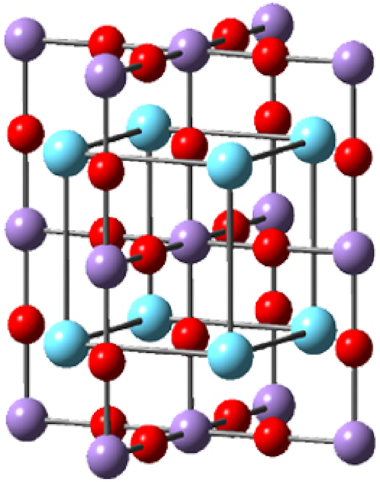
Modeling in Different Length Scale

Atomic-Level View

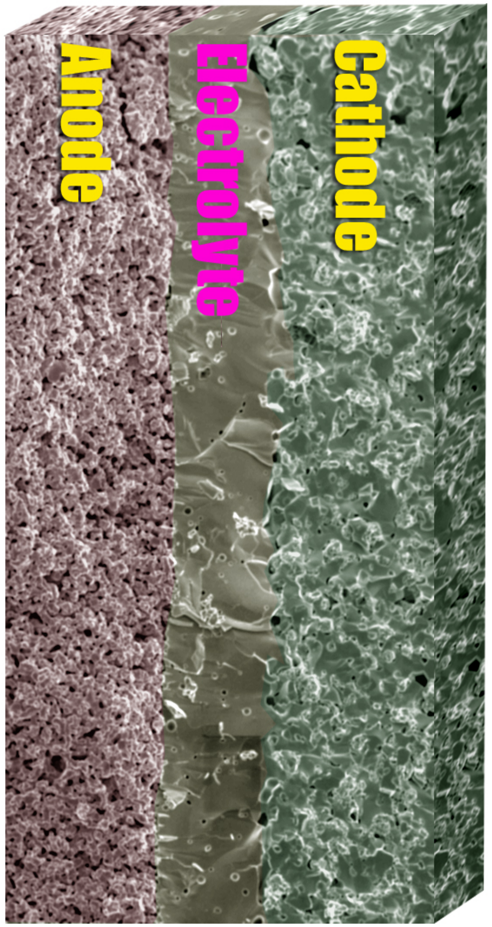
Ni Anode



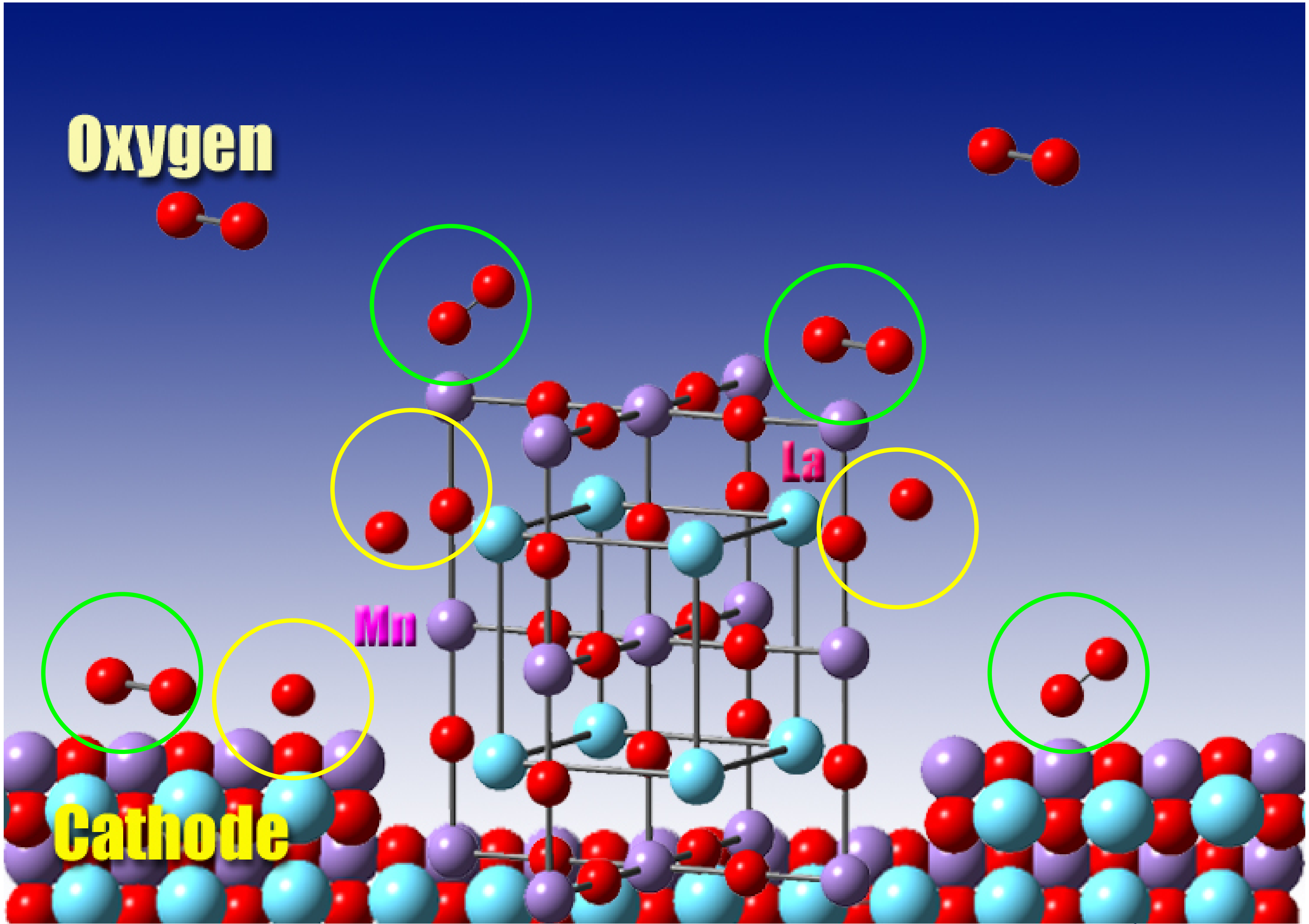
LSM Cathode



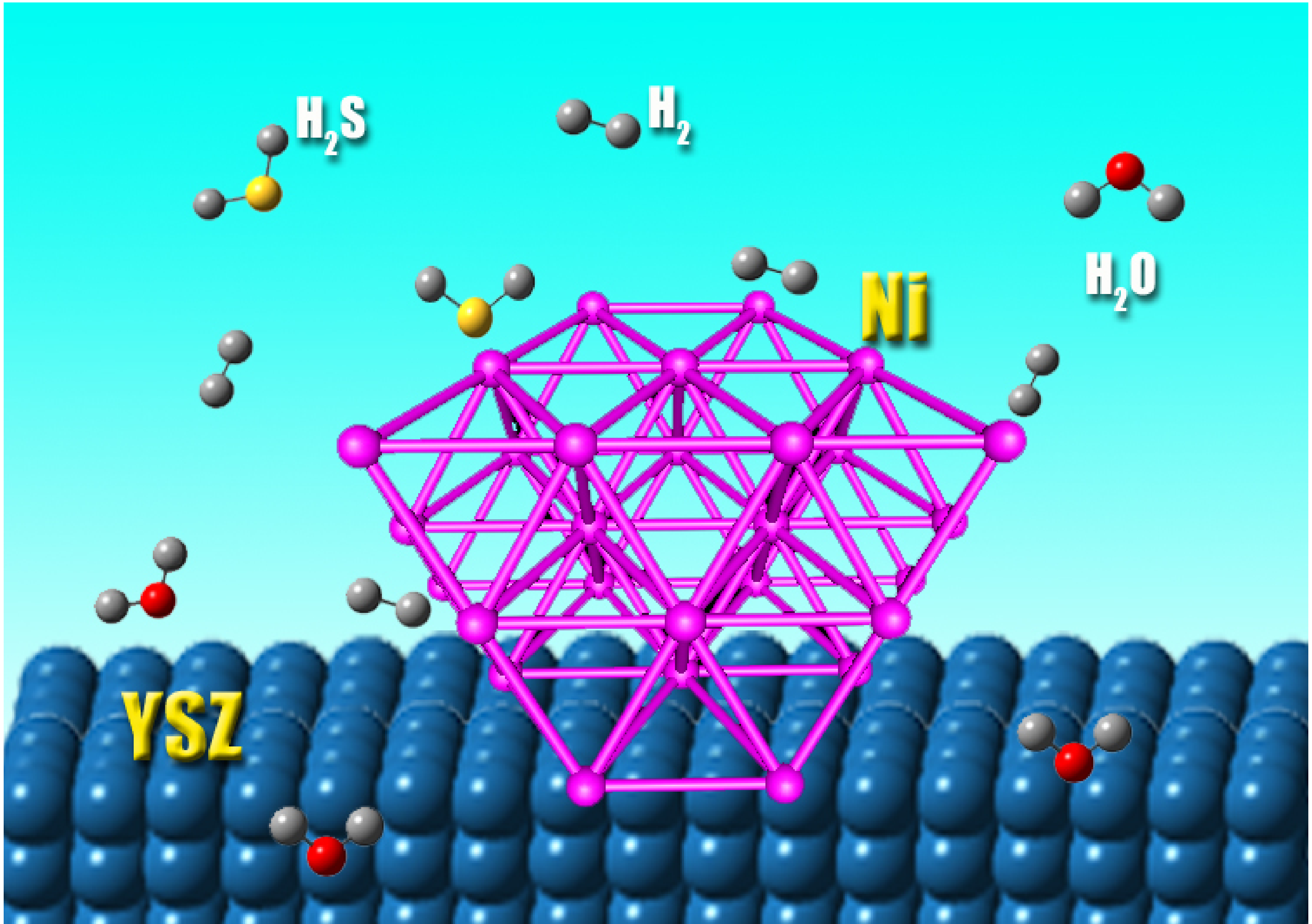
Macro-level view



Cathode: O_2–LSM Interactions



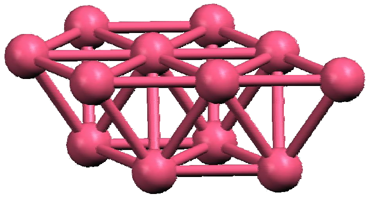
Anode: H_2S–Ni Interactions



Models for QM calculations of gas-surface interactions

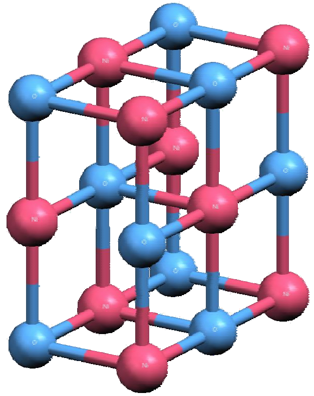
1. Cluster model: Gaussian 03 code

a. bare-cluster model: metal



Ni(111)

b. embedded-cluster model: metal oxide ionic solid

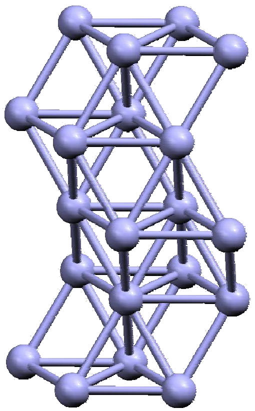


NiO

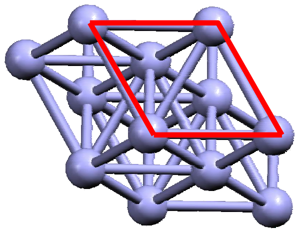
- **an array of point charges to represent the surrounding ions**

2. Slab model: VASP code

Super cell



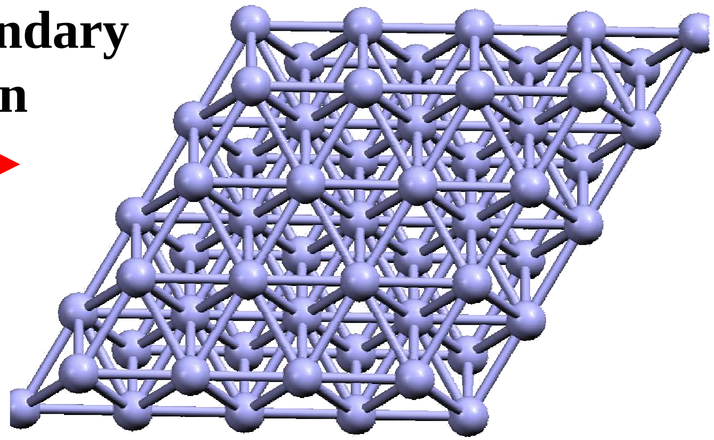
side view



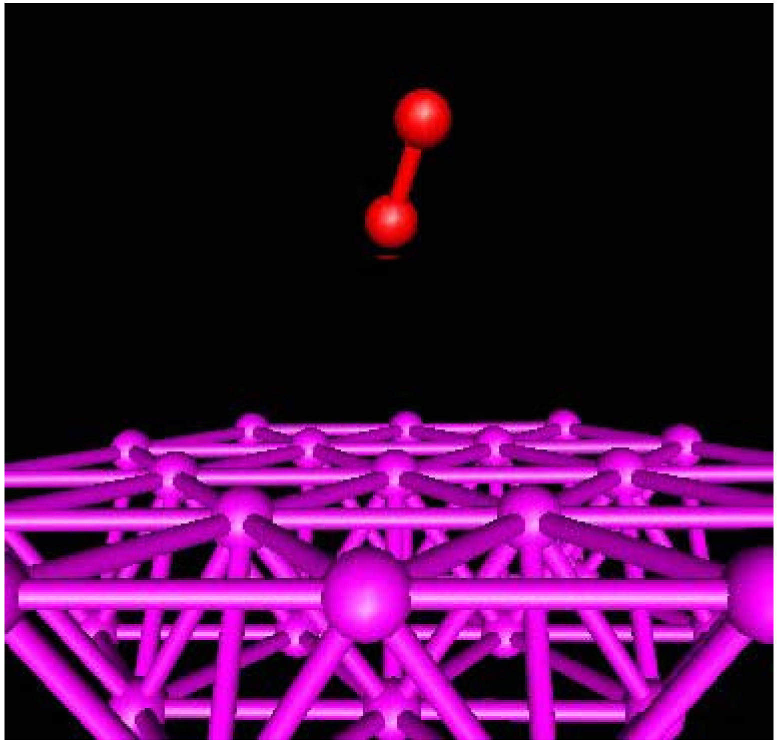
top view

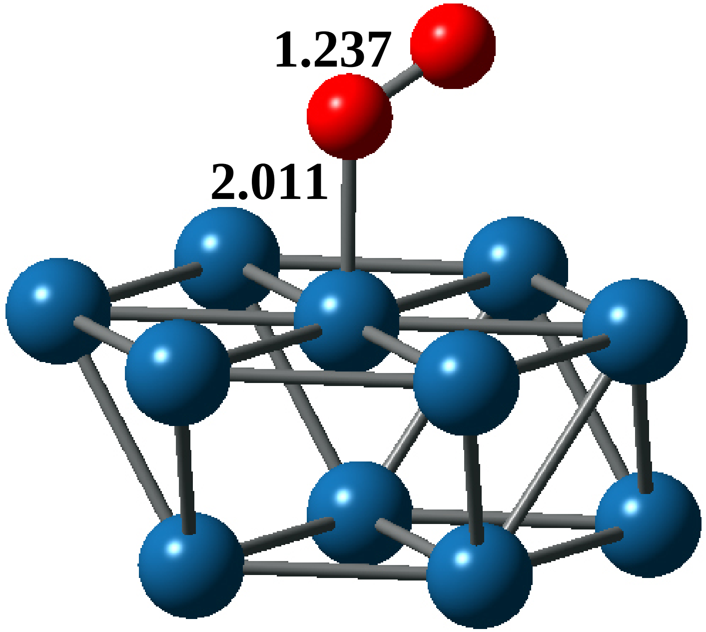
Periodic Boundary Condition

Ni(111) Bulk



O_2 Adsorption on Pt(111)





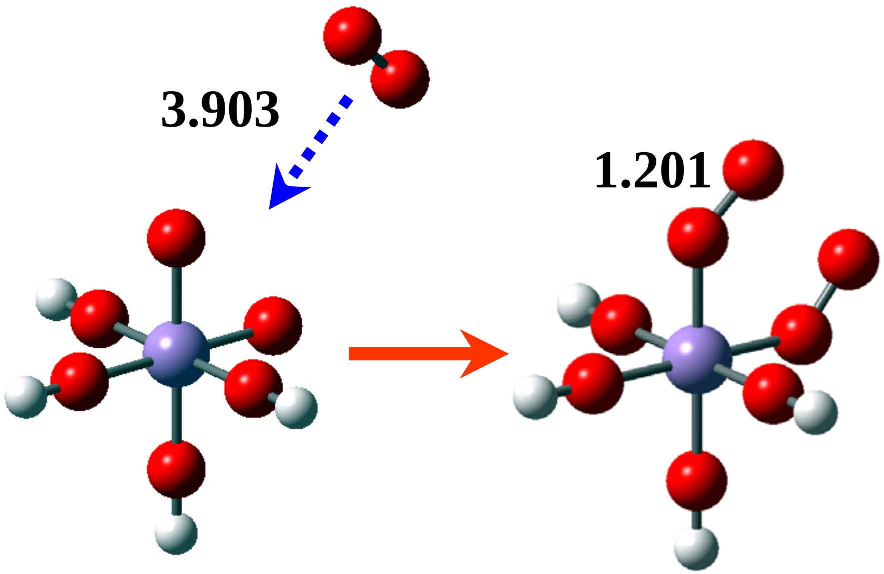
	Surface	Gas phase
v(Pt-O)	478 cm^{-1}	853 cm^{-1}
v(O-O)	1305 cm^{-1}	1633 cm^{-1}
r(Pt-O)	2.011 Å	1.751 Å
r(O-O)	1.237 Å	1.206 Å

- **Pt atom: B3LYP/Lanl2DZ**
- **O atom: B3LYP/6-311+G(d)**

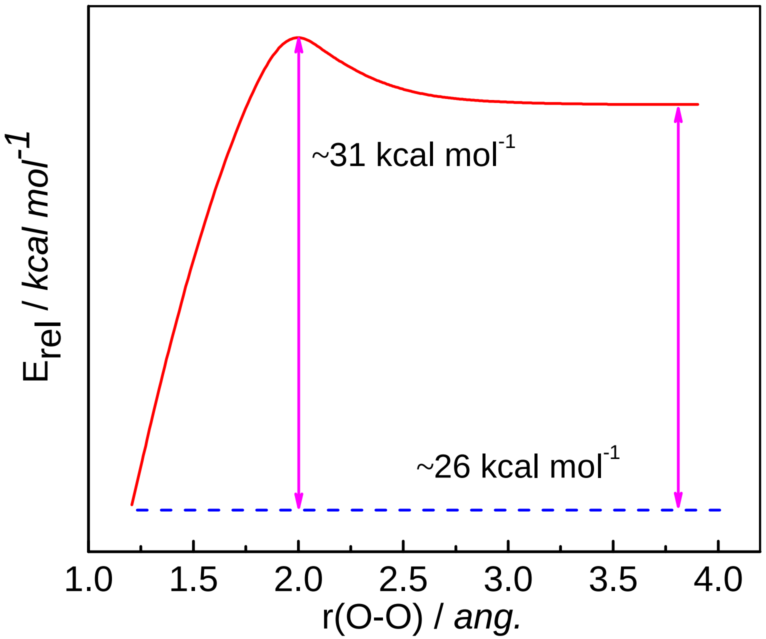
- **The O-O stretching of the superoxo end-on geometry is in line with experimental IR frequencies (1040 – 1190 cm^{-1}).**

Dissociative Adsorption of O_2 on Metal Oxide

- **$Mn(OH)_4O_2$: A cluster model for LSM**
- **B3LYP/6-311+G(d)**

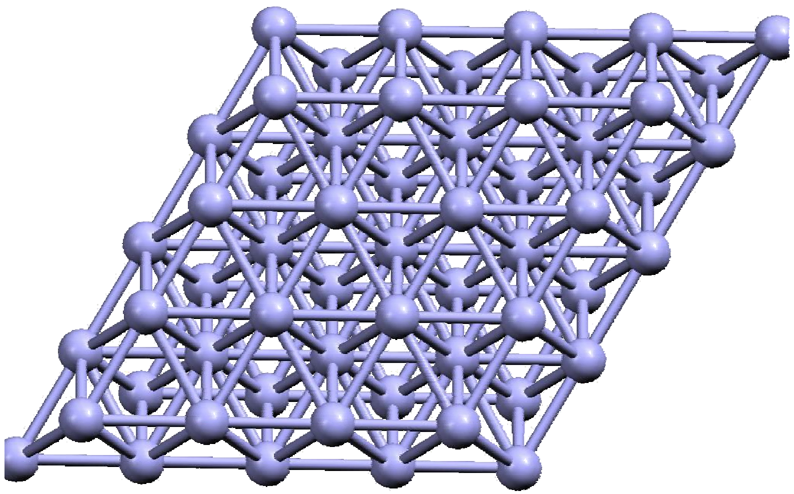


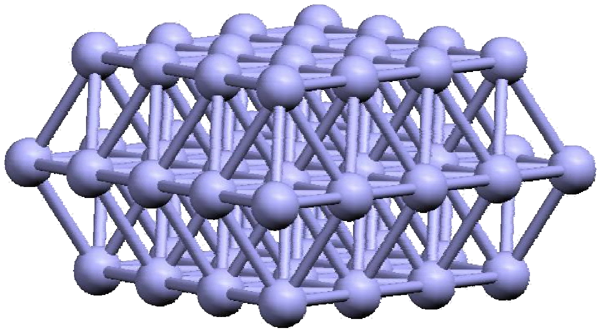
v(O-O^{-1}) = 1100 cm^{-1}

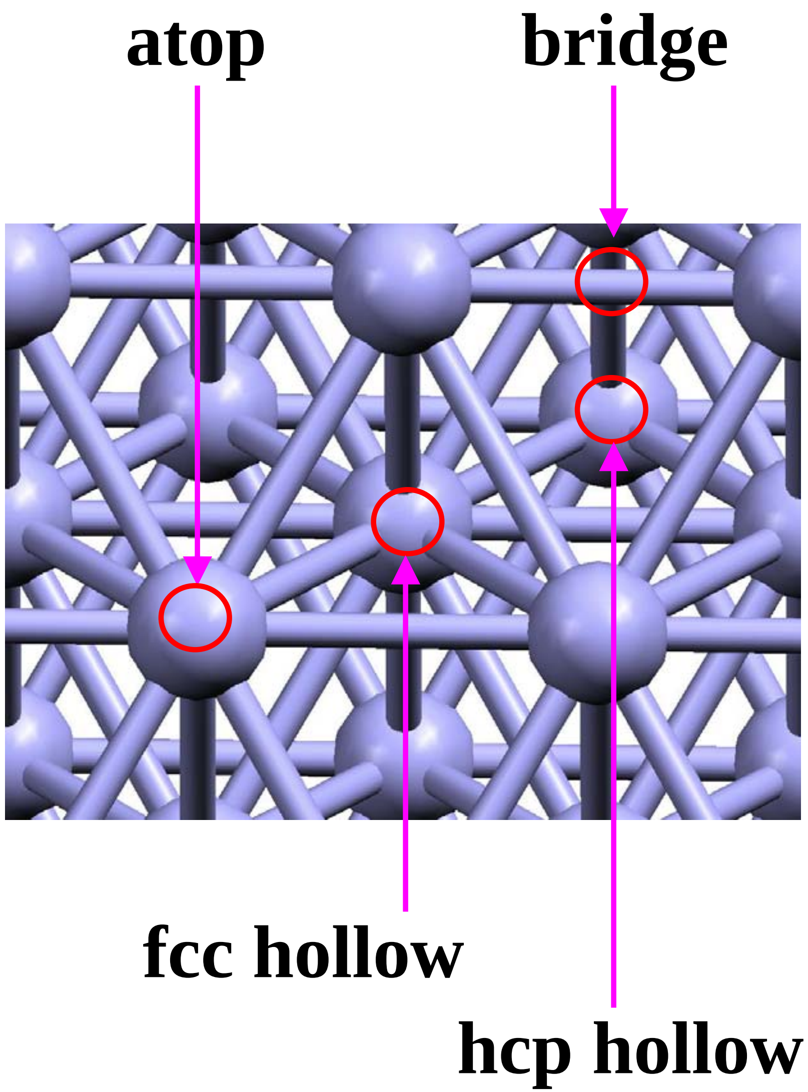


- **Comparing with experimental bands using FT-IR (1124 cm^{-1}), it may be assigned to be superoxide ion.**

Ni(111) Surface and Adsorption Sites







Summary – QM Calculations

- Constructed Pt, Ni, Cu, and $LaMnO_3$ surfaces for QM calculations
- Predicted some adsorbed oxygen species on cathode surfaces
- Calculated dissociative adsorption of oxygen molecules on manganese oxide
- Detailed mechanistic studies of O_2 reduction and S-poisoning are still in progress

Conclusions

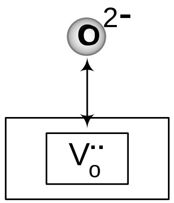
- **QM calculations provide important insight into mechanisms of fuel cell reactions: geometric configurations and energetics;**
- **Computations complement measurements (FTRI/Raman): experimental design and data interpretation**
- **Super-cell models are needed to represent real systems**

Work in Progress

Extension of the small cluster model to a super-cell model to mimic real system

Cathode

- **Oxygen reduction on real cathode materials (LSM, LSC…)**
- **MD: Oxygen diffusion on surfaces & across interfaces on electrodes**
- **Oxygen or vacancy transport through lattice**

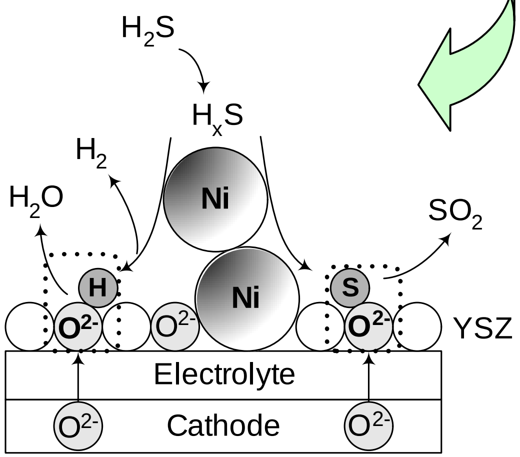


Work in Progress

Super-Cell Model

Anode

- H_2S interaction with Ni-YSZ surface to provide a reliable reaction mechanism
- S-H-O interactions on other anode materials
- Vibration frequency
  Energetics
  Sulfur poisoning



Recent Progress (Since May 2004)

- Computational: QM Calculations
- Experimental: Probing and mapping gas-surface interactions
- Cells with Patterned Electrodes: TPB width/thickness
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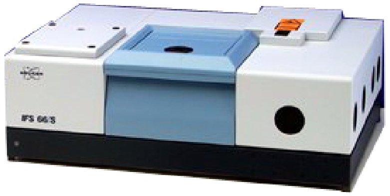
In-Situ Characterization Techniques

FTIR



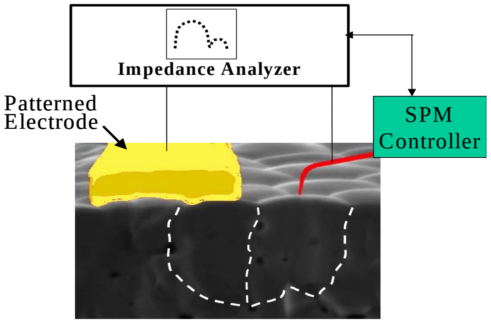
pd-FTIR: Electrically-induced species

Rapid Scan (120 spectra/s): Surface reaction kinetics/bulk transport properties

Raman

SERS: Dramatically enhanced sensitivity (with enhancement factor up to 10^8) to surface species: adsorbates/intermediates

TERS (Raman+SPM): Dramatically enhanced spatial resolution (~dimension of the SPM tip size), nano-scale mapping of surfaces species



Micro-Impedance Spectroscopy:

To measure the impedance of a single grain, a grain boundary, or a TPB

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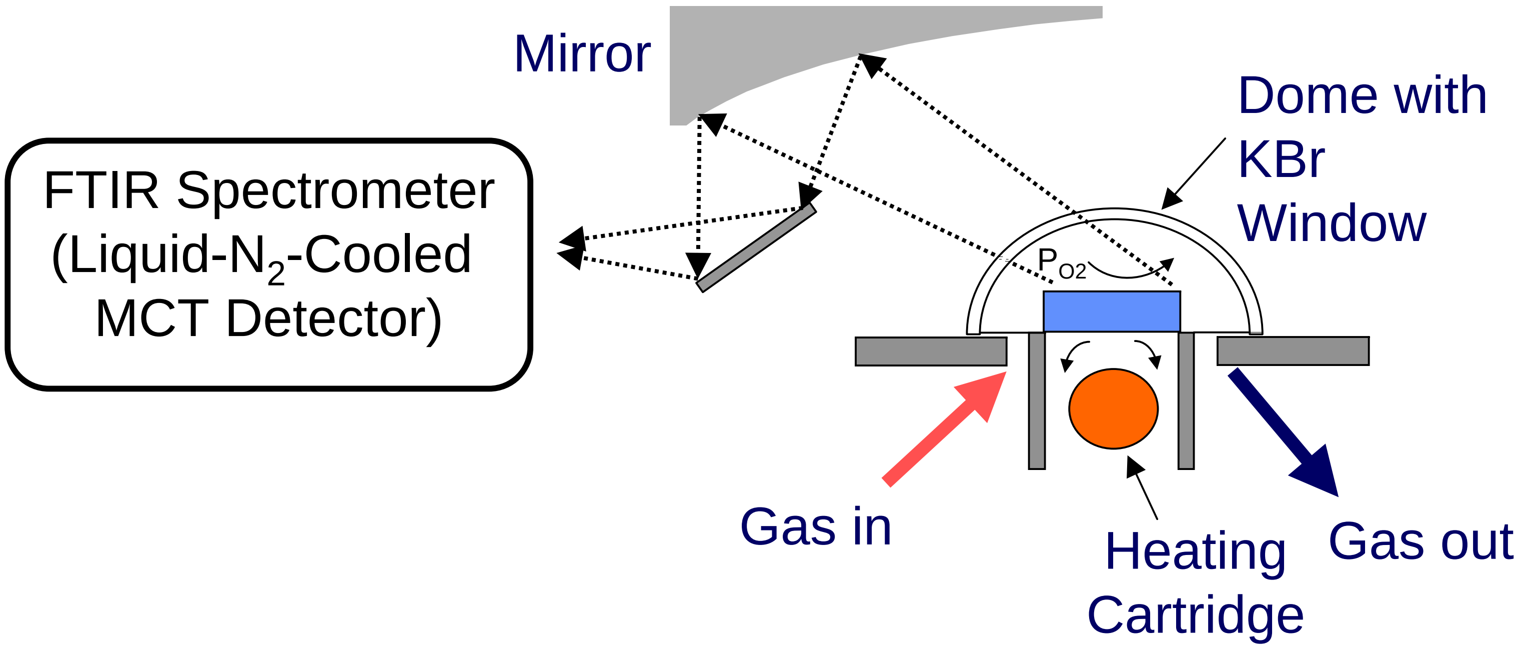
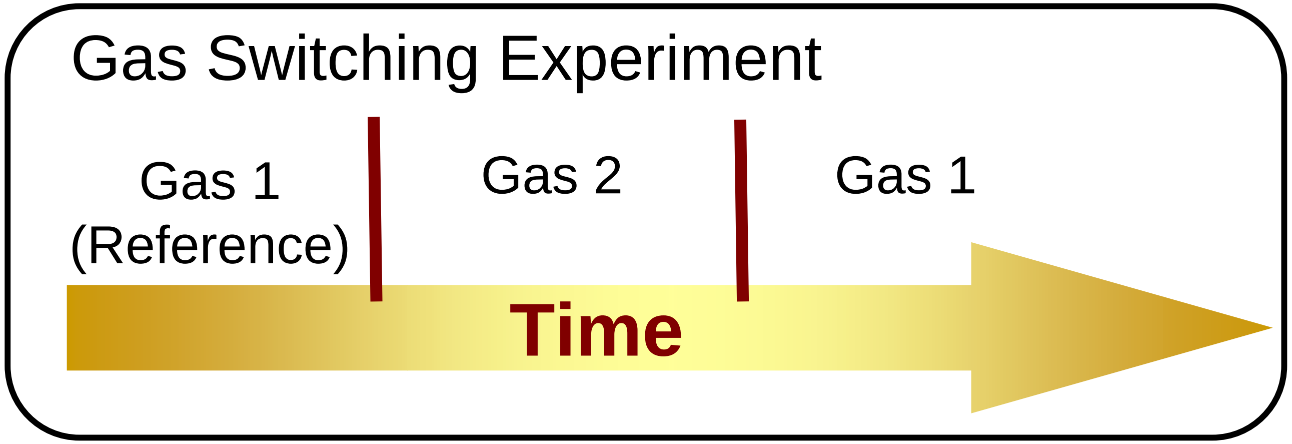
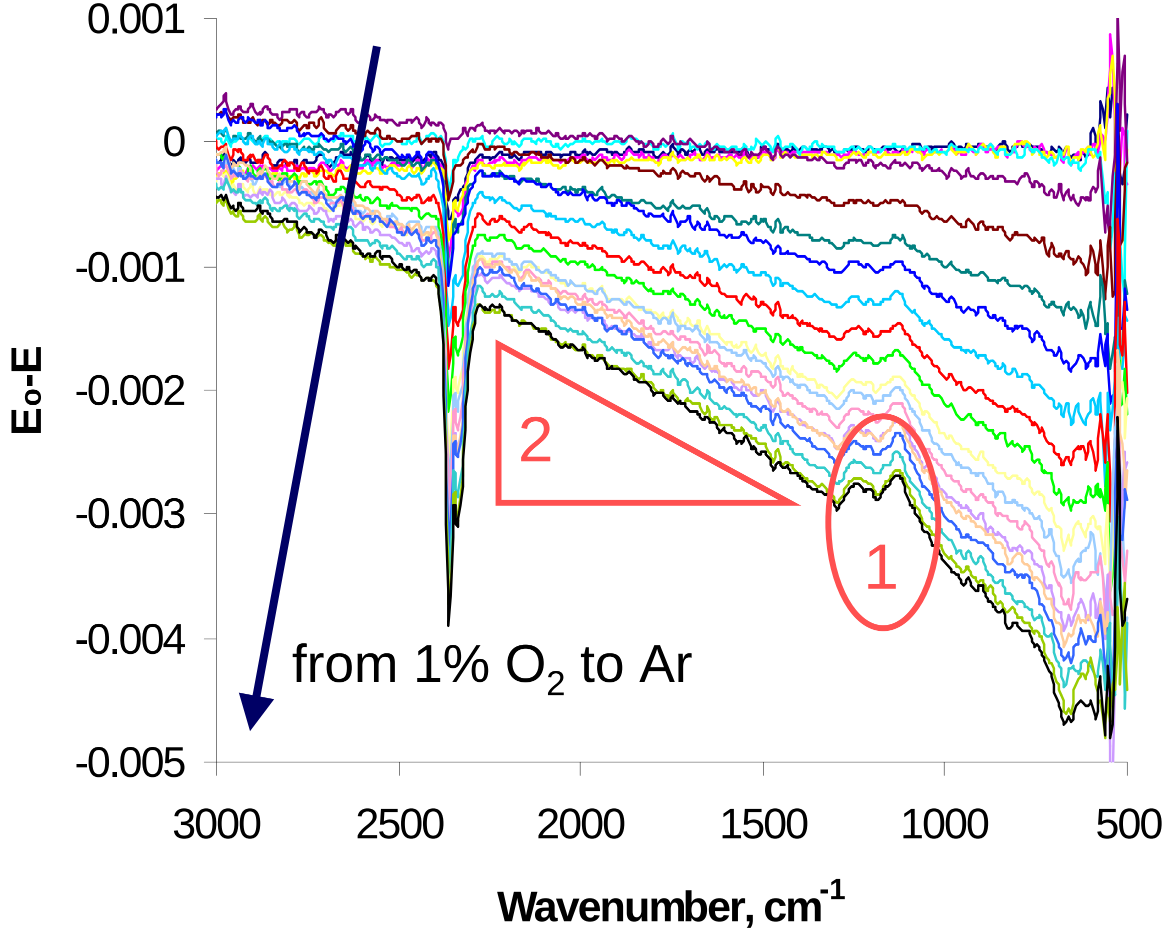
FTIR-ES Setup



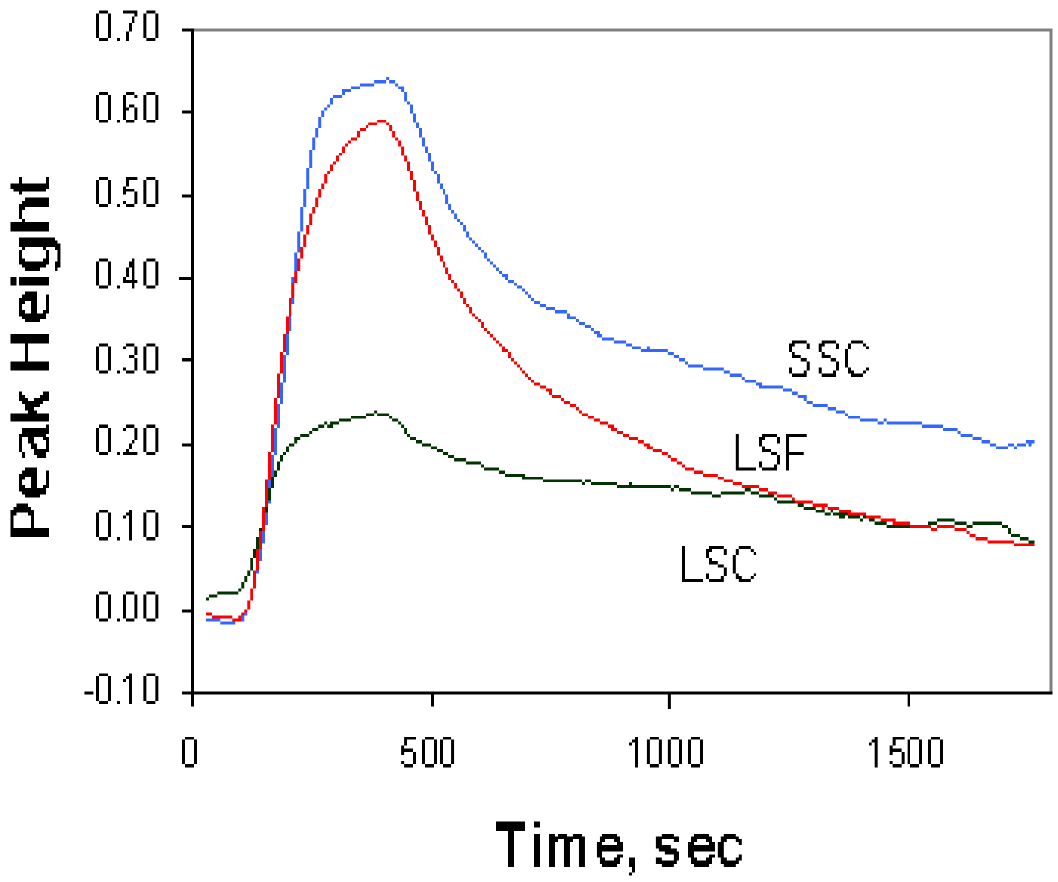


FTIR – Gas Switching Experiments



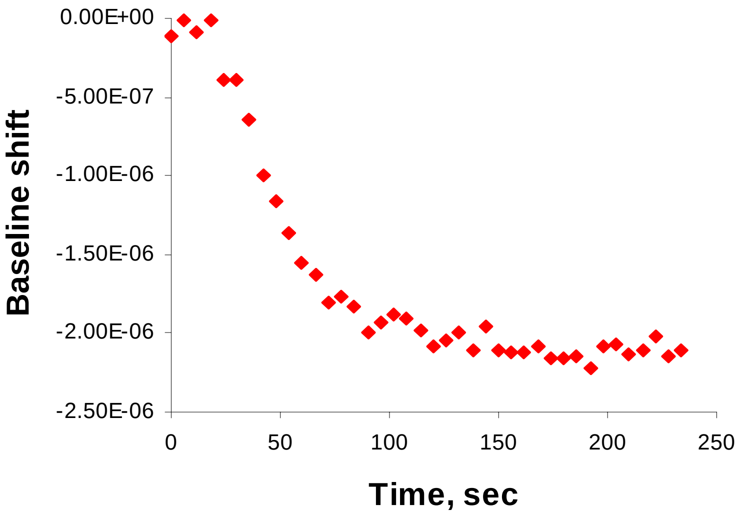
- 1 = Reduced surface oxygen species
- 2 = Change in bulk emissivity

Results – Kinetics: Superoxide peak height

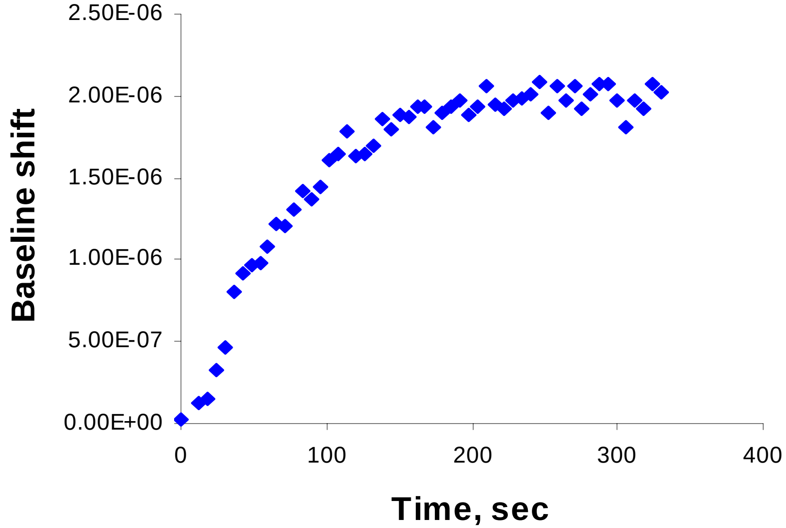


- SSC has higher concentration of surface species
- Adsorption much faster than desorption

Results – Kinetics: Baseline shift



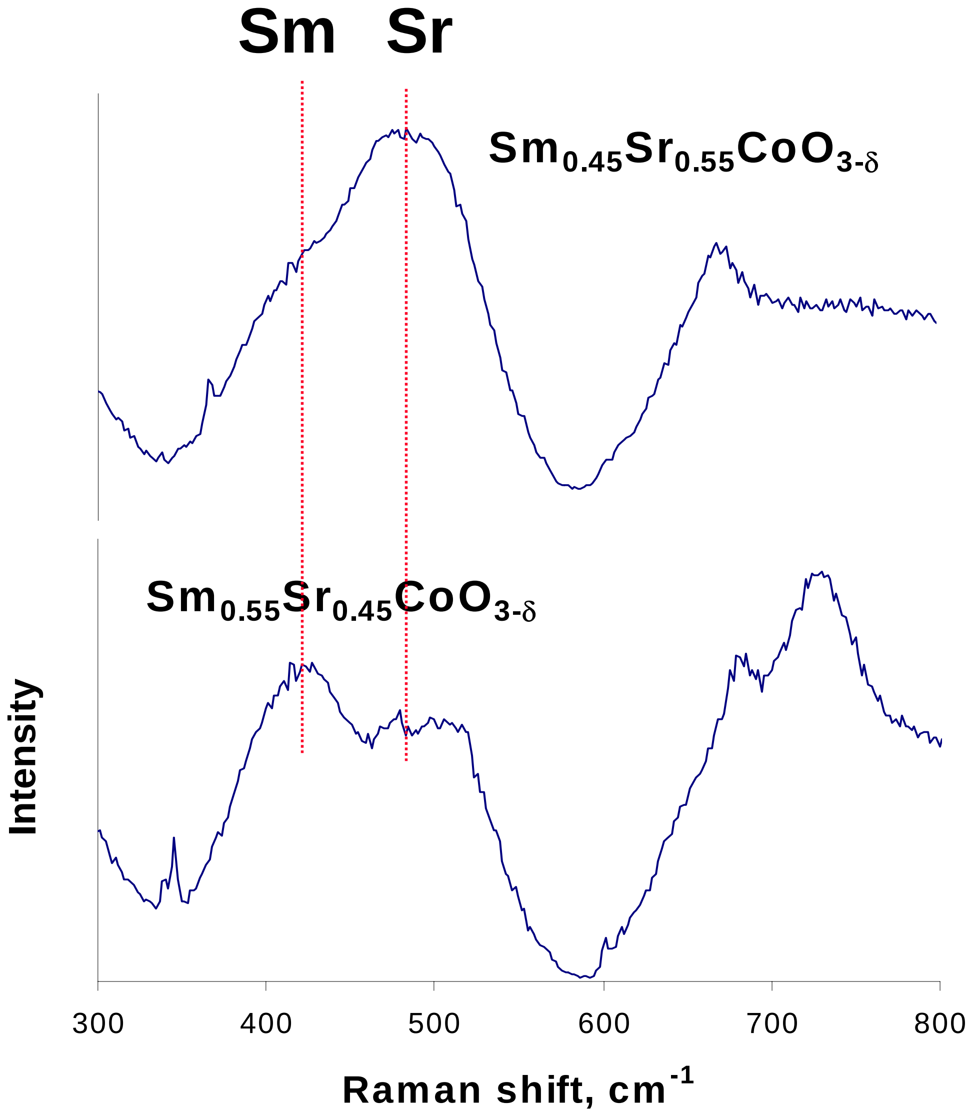
From Ar to 1% O_2



From 1% O_2 to Ar

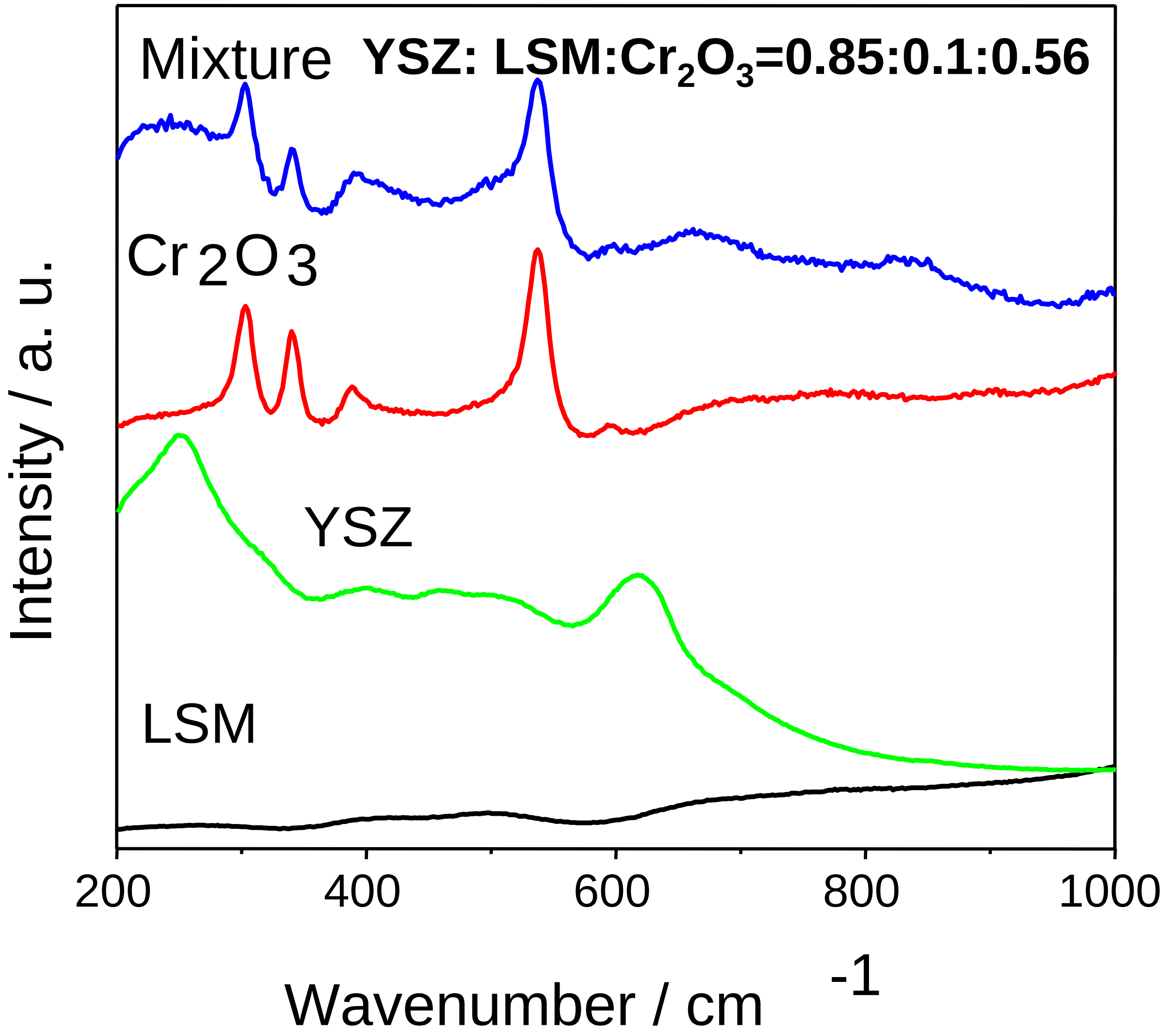
Material response dictated by surface + bulk kinetics

Raman Microspectroscopy



- Raman spectroscopy sensitive to composition and structure
- May be used to map the inhomogeneity of electrode materials
- In-situ under conditions similar to fuel cell operation

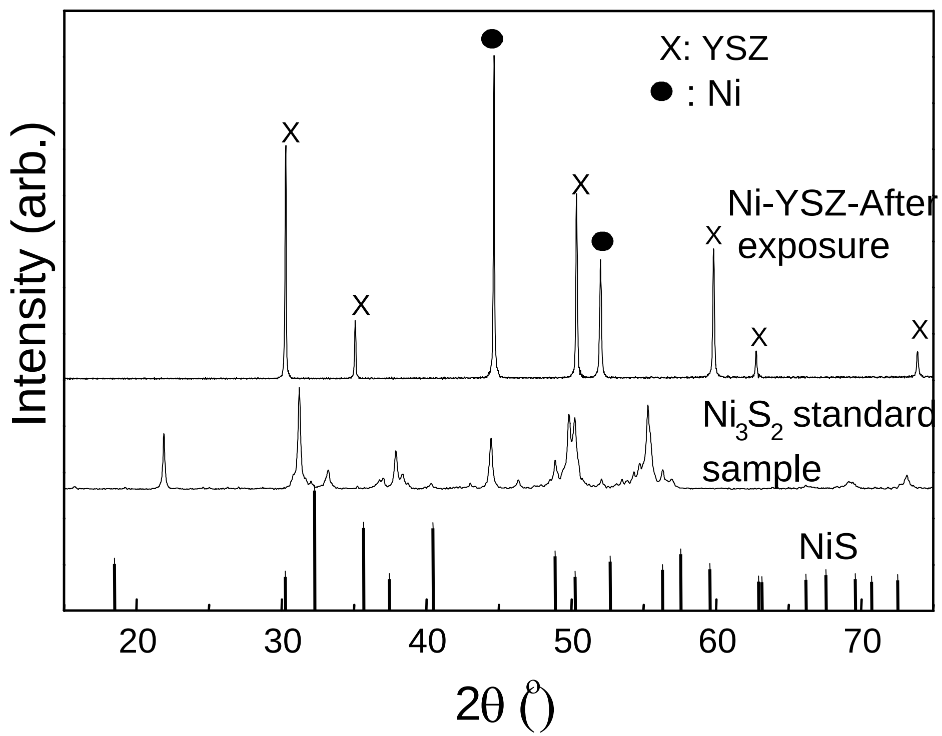
Phases Relevant to Cr-Poisoning

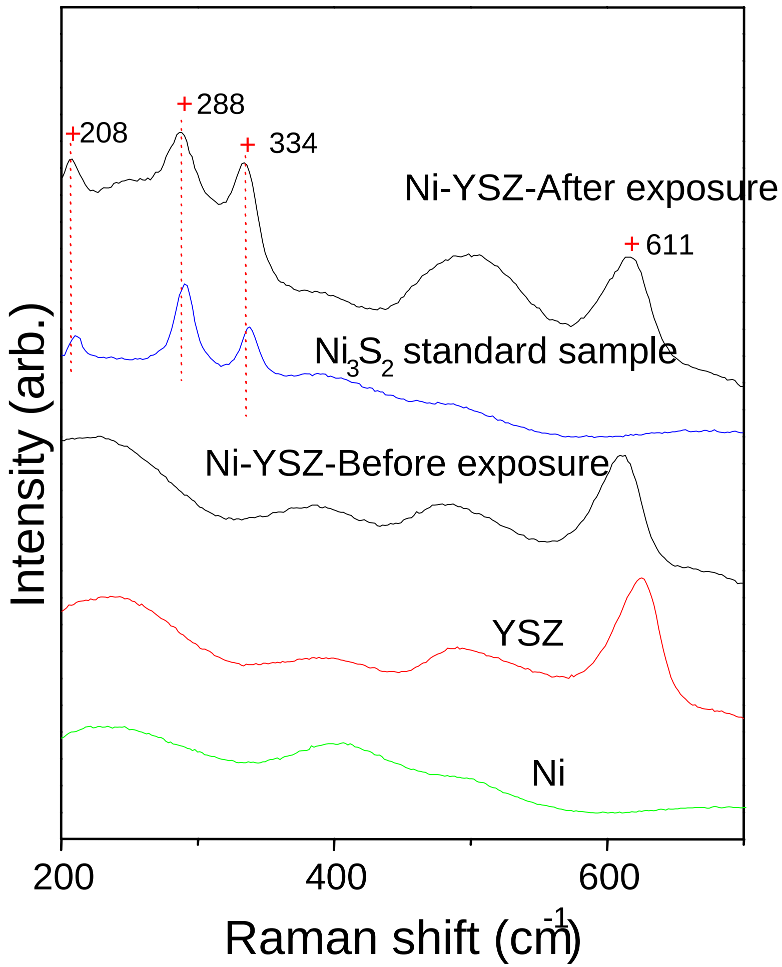


Raman Spectra in Air at 600ºC

In addition to pre-/post-test analysis, possibly for in-situ probing and mapping of Cr2O3 to elucidate Cr-poisoning mechanism, providing critical info for design of Cr-tolerant cathode

Sulfur-Ni Interactions

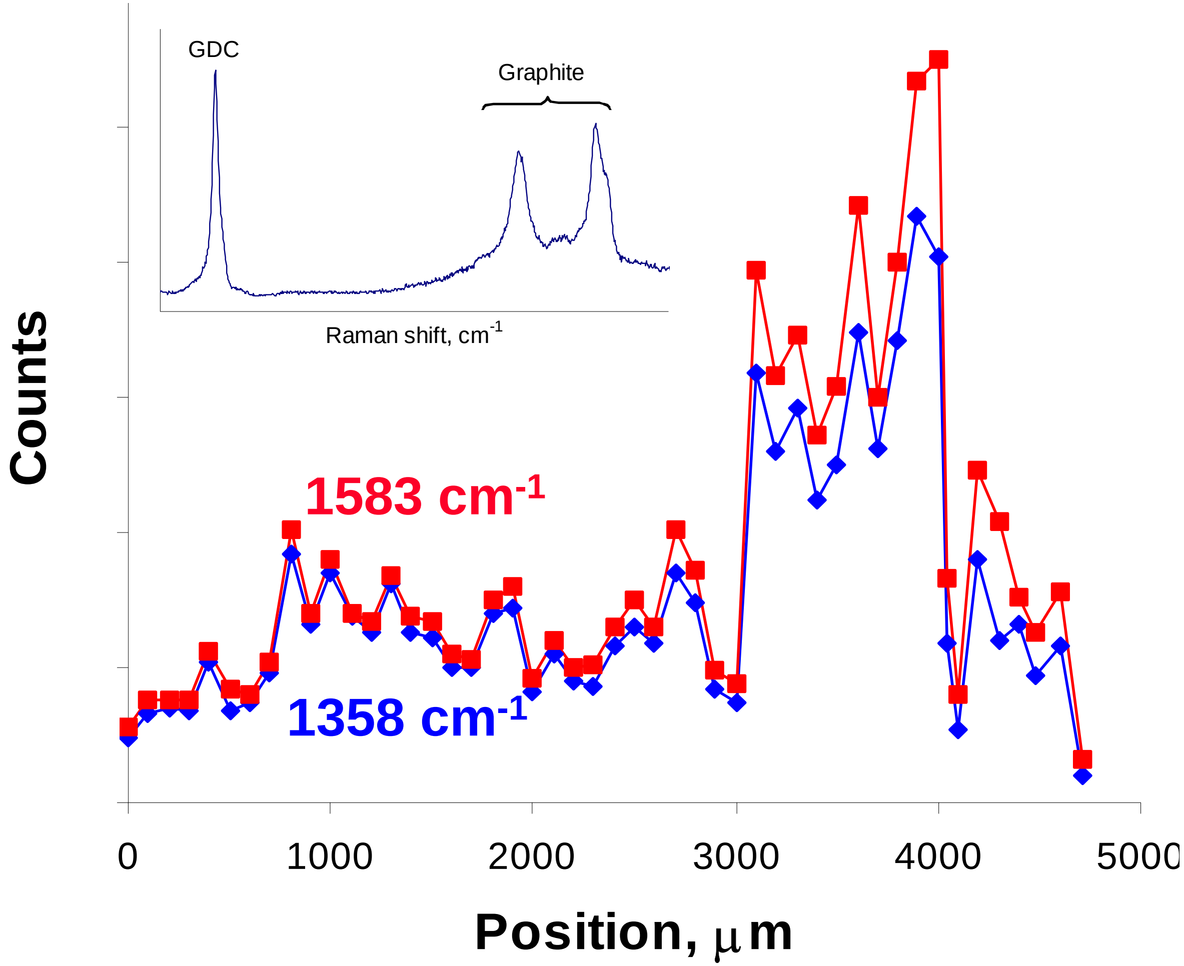




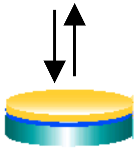
Ni-YSZ cermet was exposed to humidified hydrogen containing 100 ppm H_2S at 727°C for 5 days.

Possibly for in-situ probing and mapping (patterned sites) of NiSx to elucidate S-poisoning mechanism → S-tolerant anodes

Raman microspectroscopy



Button Cell
Run on CH_4



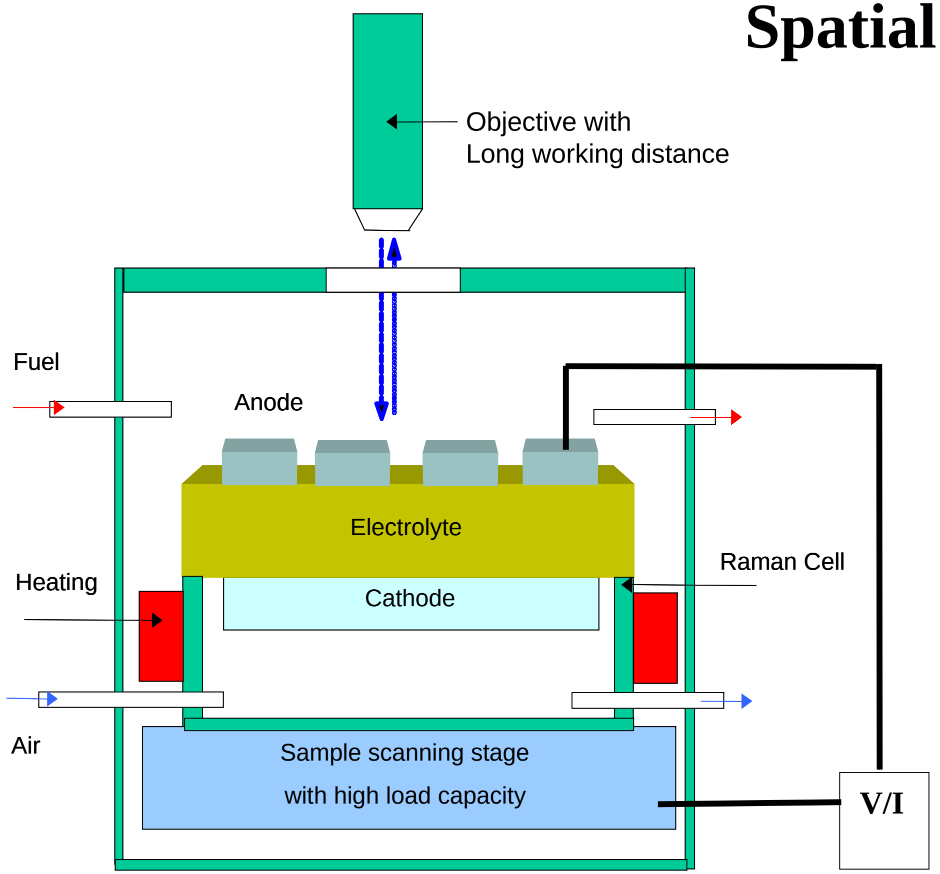
Raman sensitive to carbon compounds

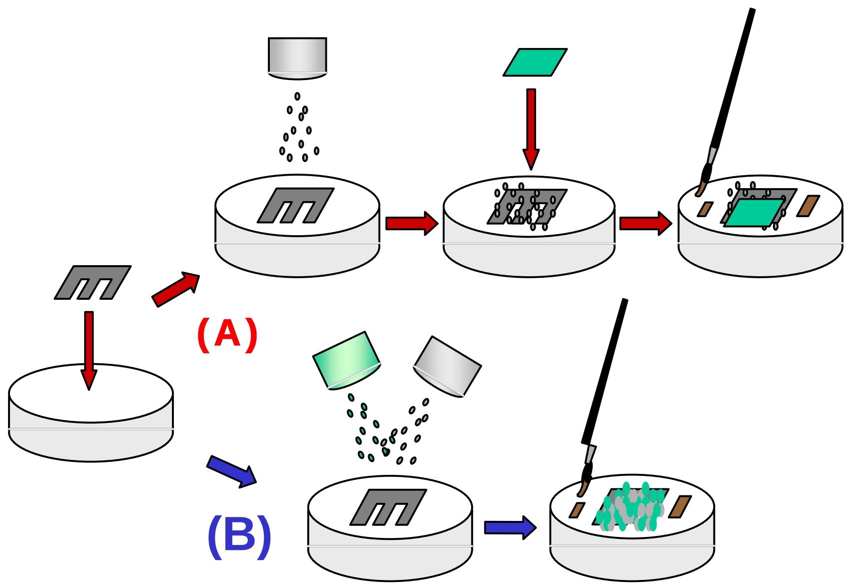
Motorized stage allows for controlled surface mapping

Carbon deposition at distance from anode center

Surface Enhanced Raman Scattering (SERS)

Extremely sensitive to surface species
Spatial resolution: ~ μm





In-Situ SERS

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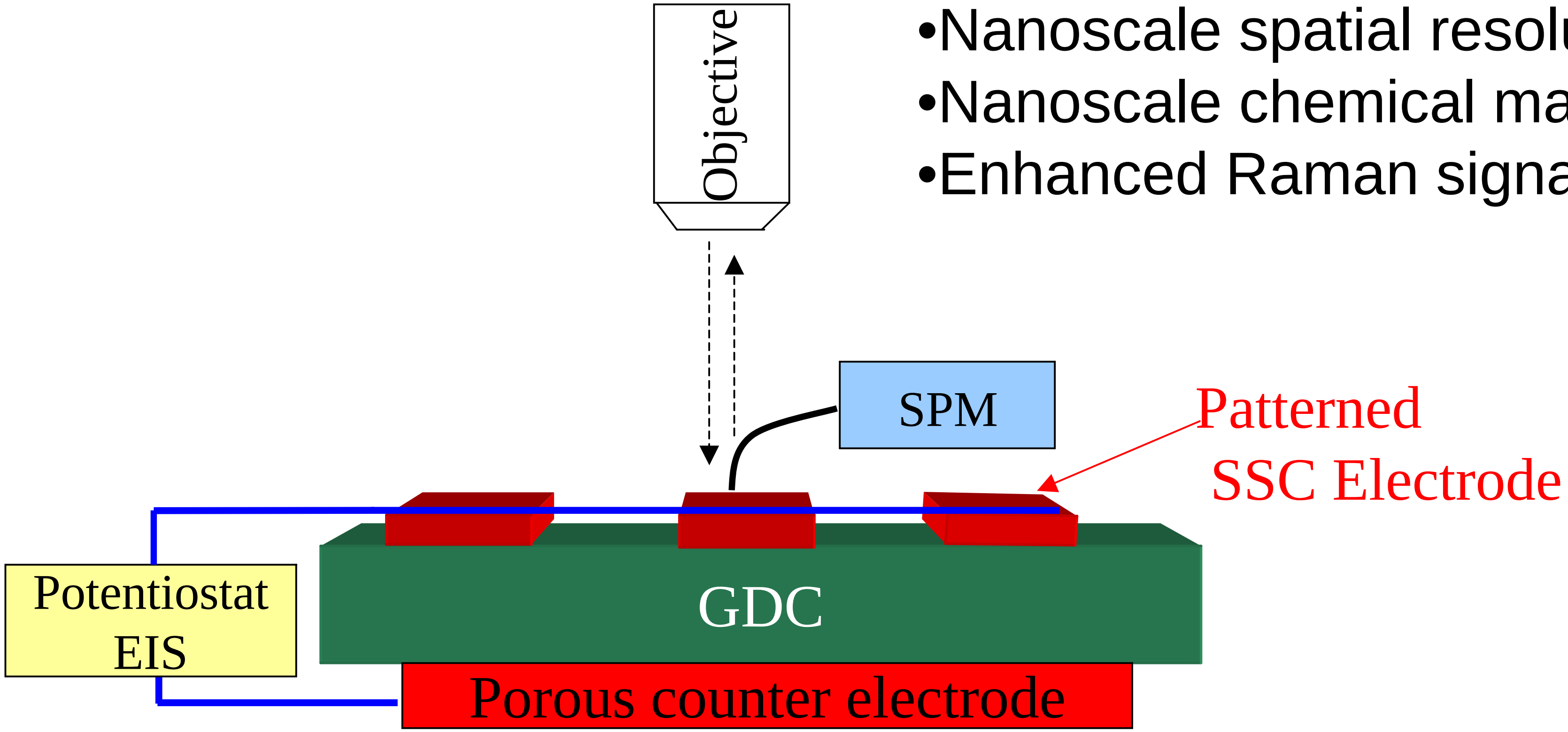
Tip Enhanced Raman Scattering

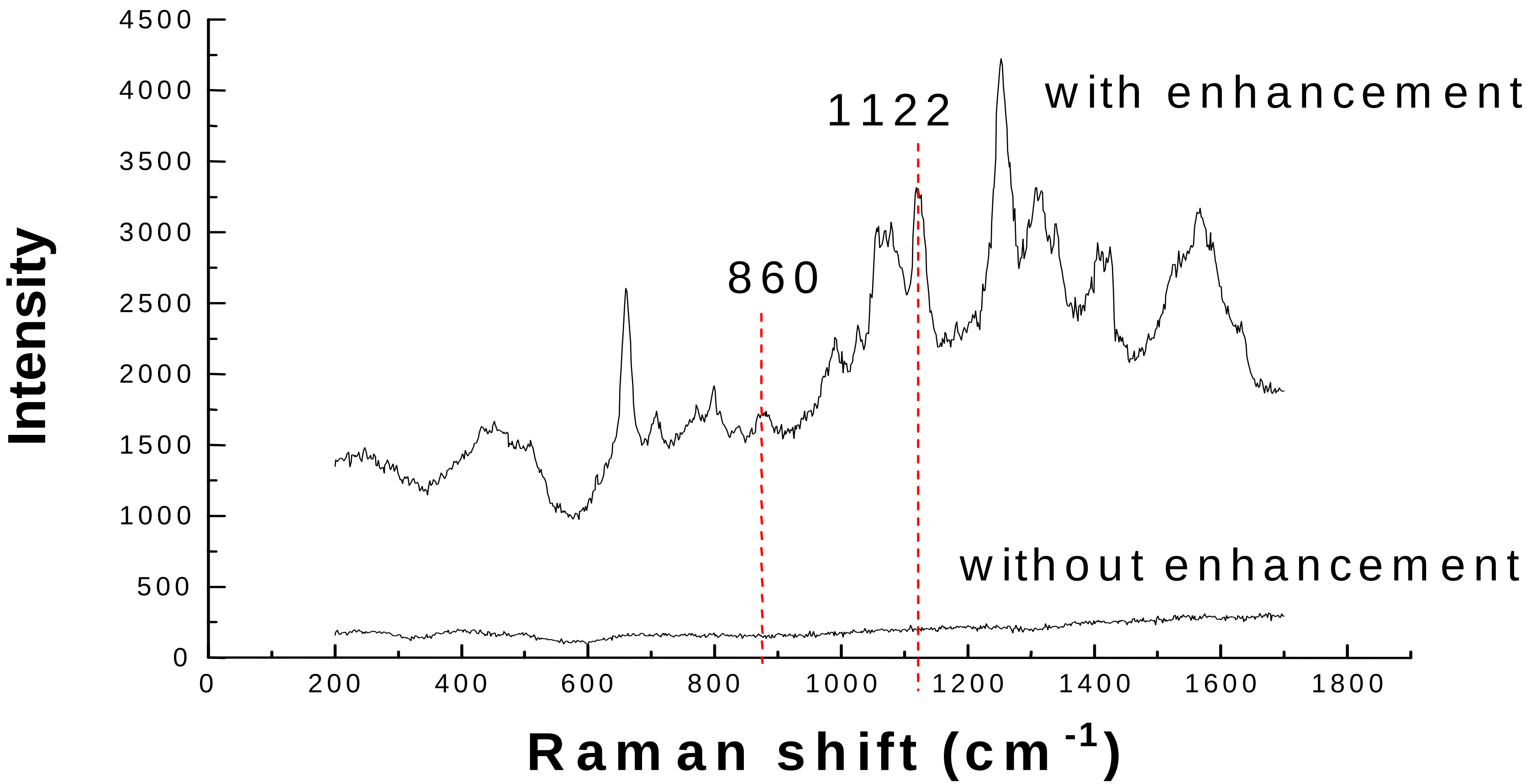


- Nanoscale spatial resolution
- Nanoscale chemical mapping
- Enhanced Raman signal

In-situ TERS for study of oxygen reduction/evolation processes under various practical testing conditions:

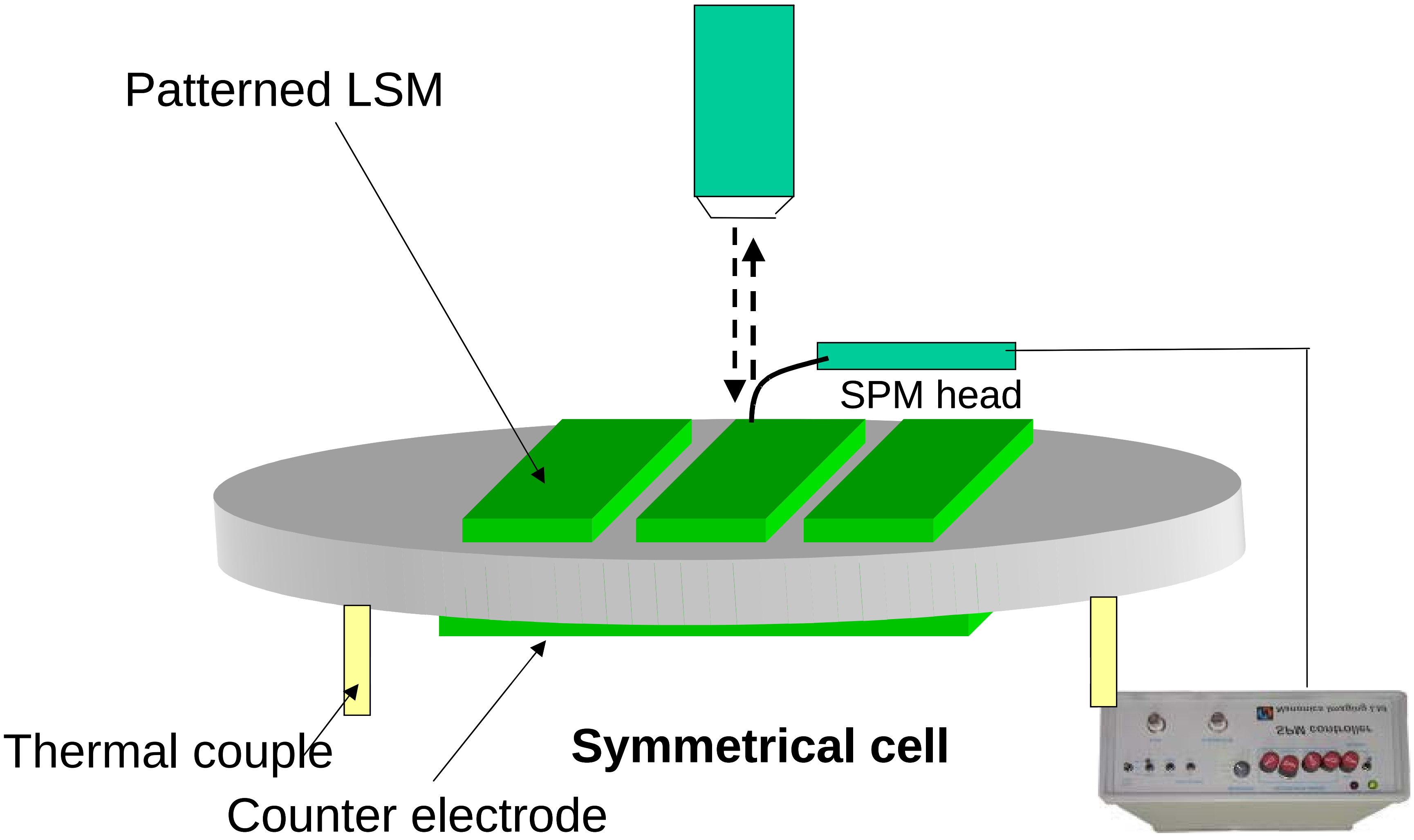
Temperature, pO2, current/voltage

TERS – SSC in Air

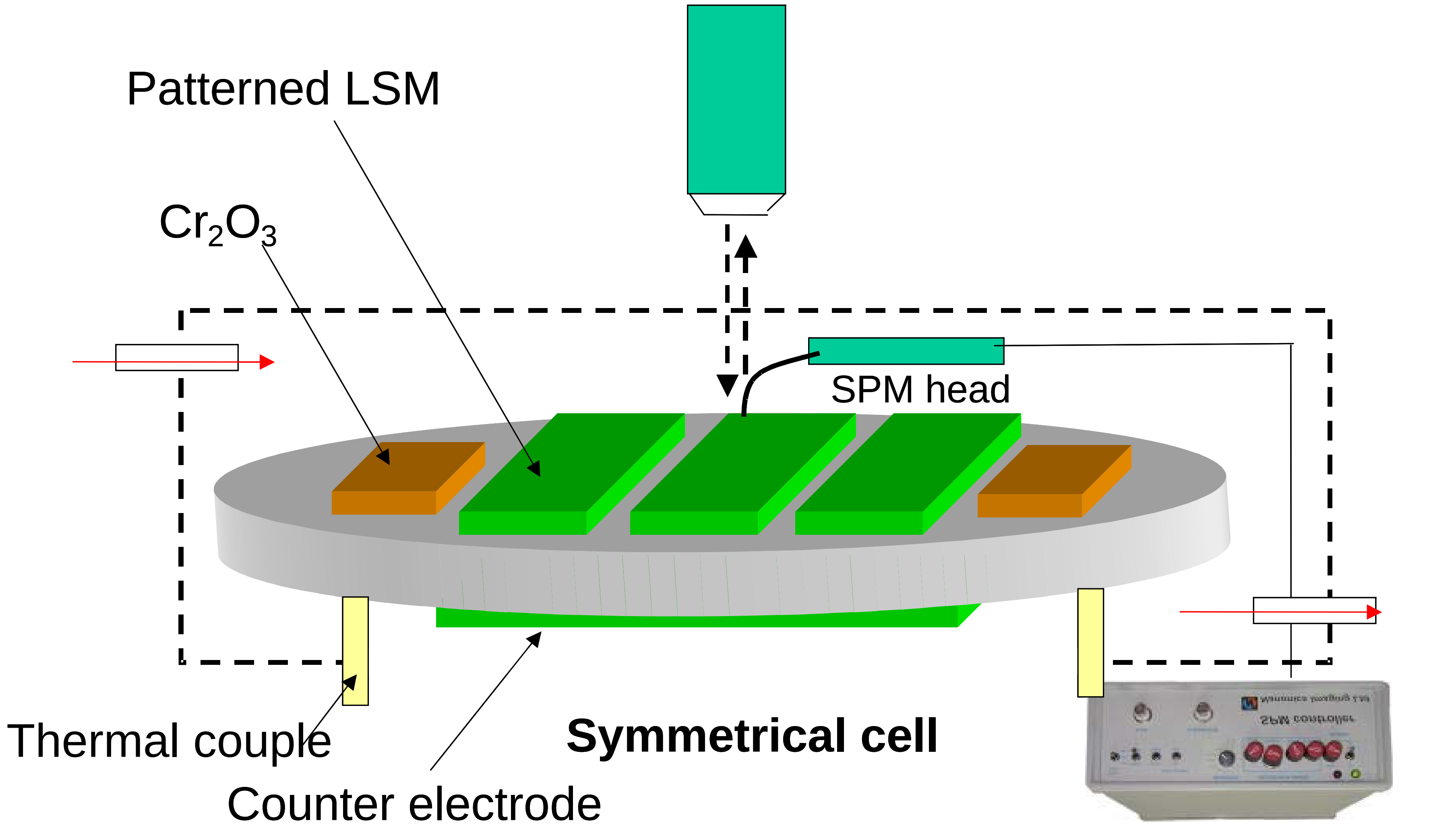


- Surface signal greatly enhanced
- Confirms FTIR data
- Additional peaks are yet to be interpreted, M-O

Ex-situ Characterization of Cr-poisoning process



In-situ characterization of Cr-poisoning process



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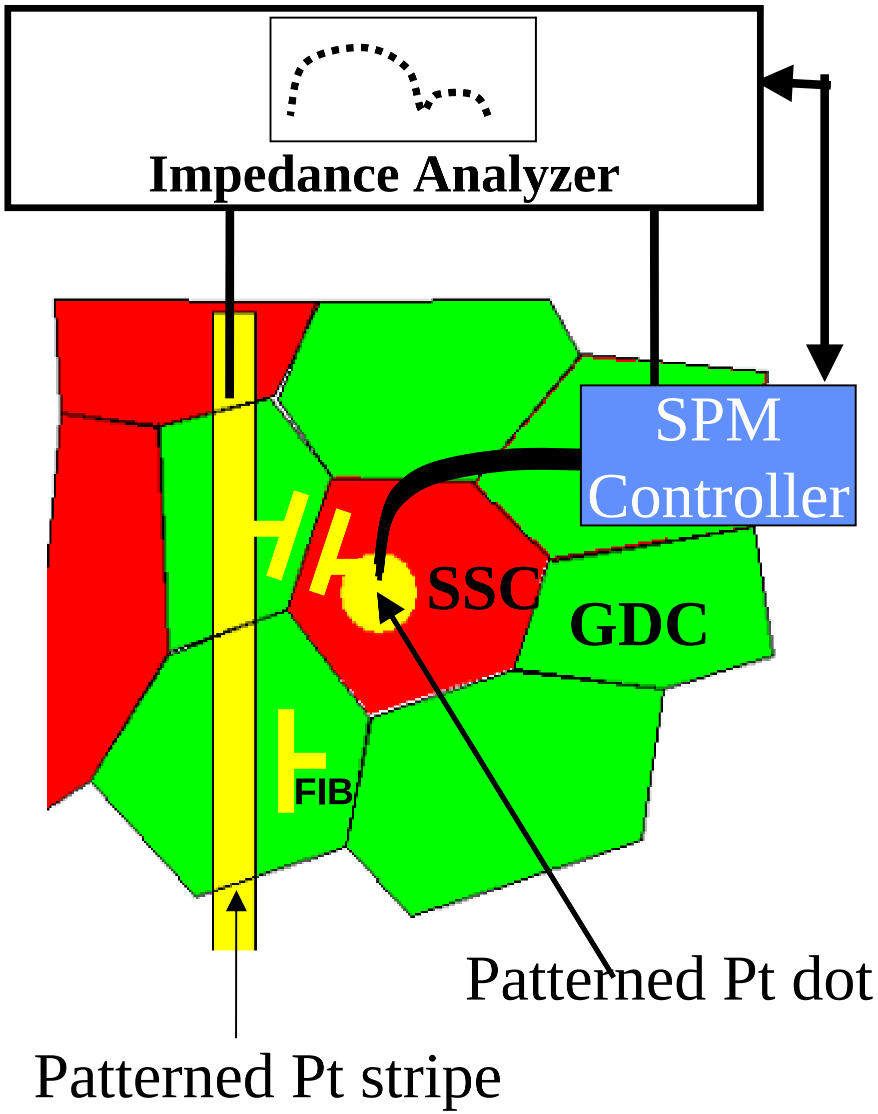
High-Temperature μ-IS

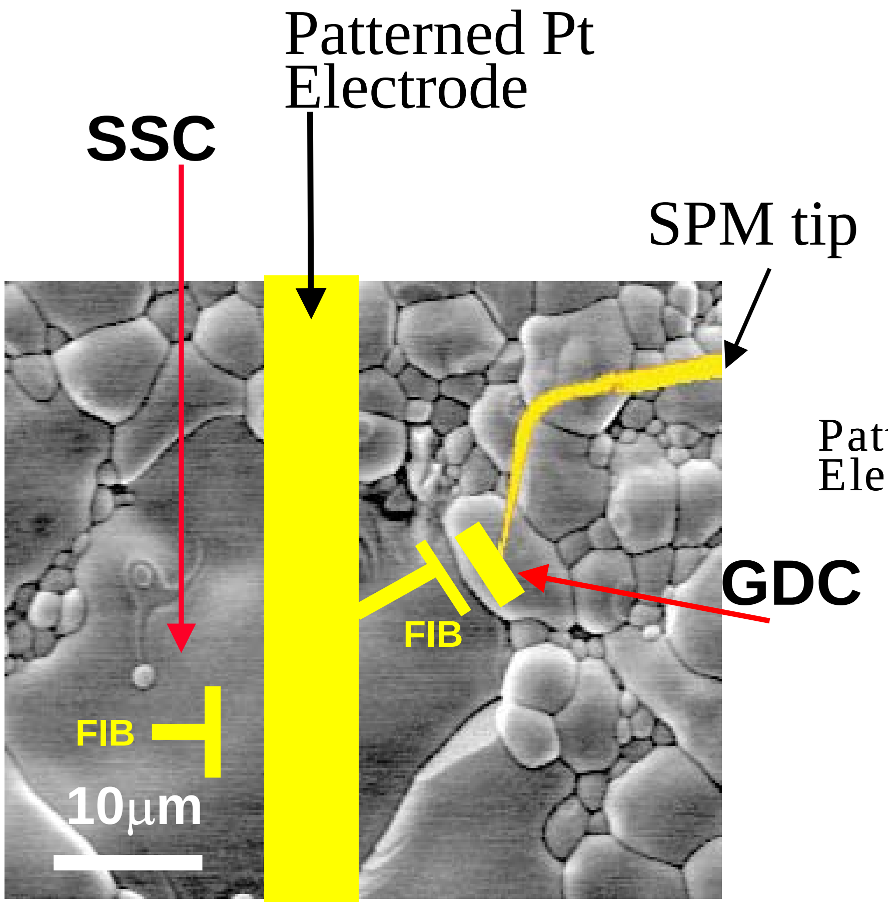


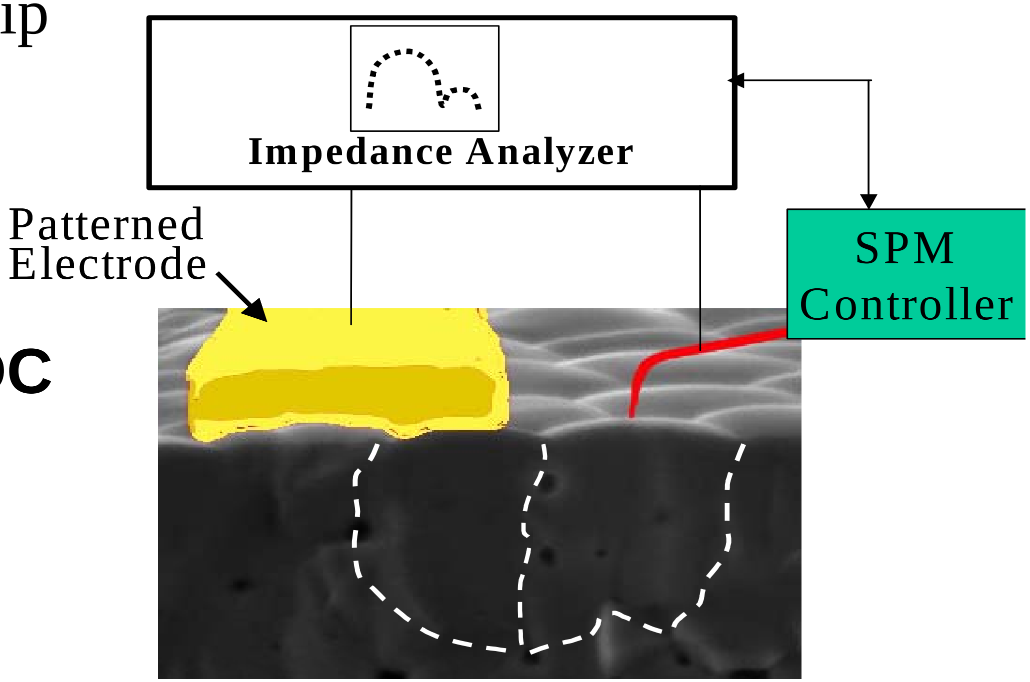
Advantage: simplicity

- No complications due to sheet resistance or m.t. in gas phase
- Simple modeling and simulation
- May be directly correlated with TERS or Raman mapping, in-situ, under various conditions: T, pO2, I/V

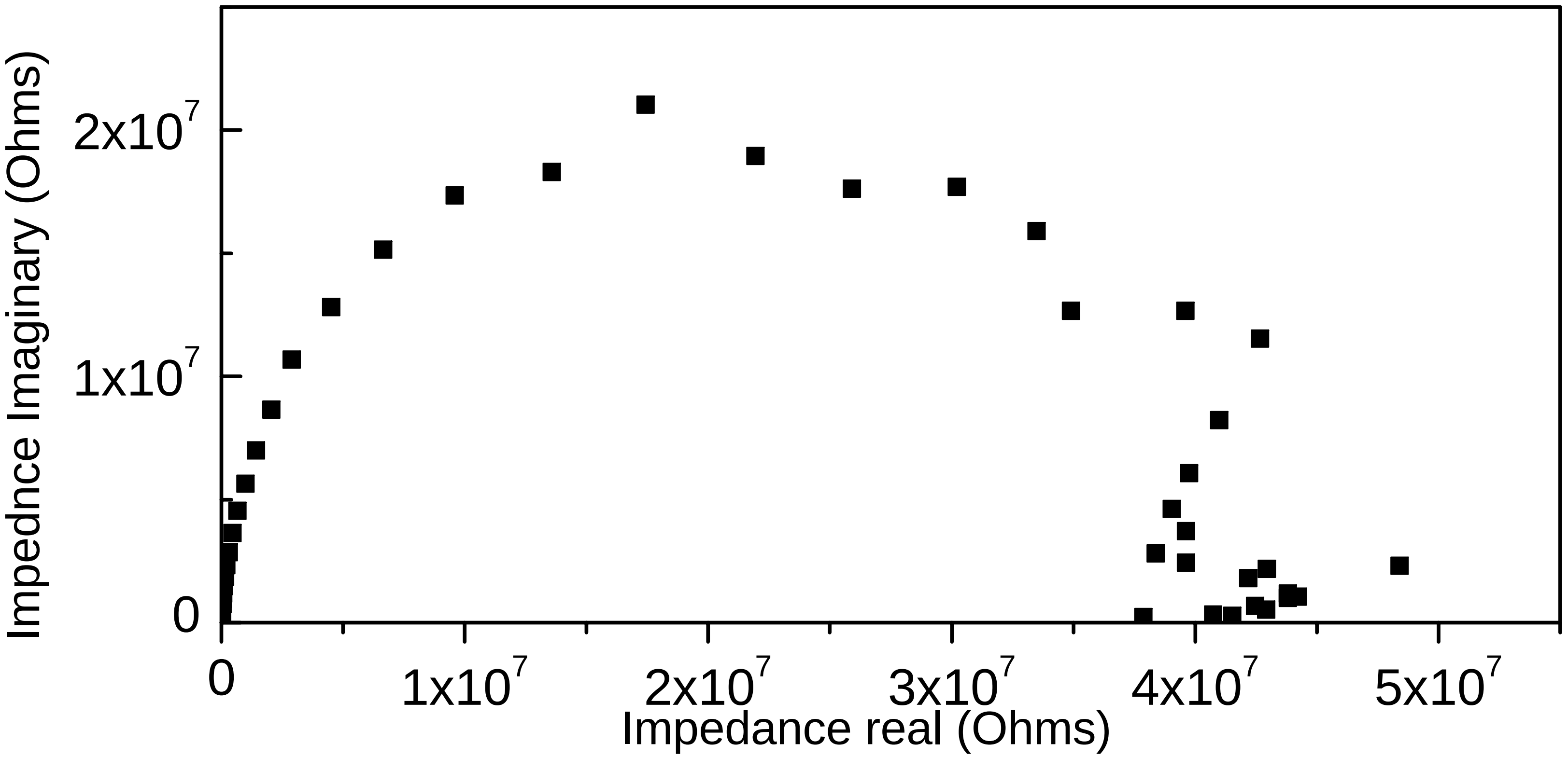
Study of a single grain, gb, or TPB

Patterned Electrodes
SPM tip
Electrodes by FIB





μ-IS at 290ºC



Impedance spectra collected inside one SSC grain at 290ºC, Au coated W tip

Conclusions - FTIR

- For studied MIEC cathode materials in studied operating conditions, initial adsorption and reduction of oxygen is not rate-limiting
- SSC shows greater activity for oxygen reduction than LSF, LSC, LSCF, and LSM at lower operating temperatures
- FTIR-ES can be used to simultaneously identify surface species and measure kinetic parameters

Conclusions - Raman

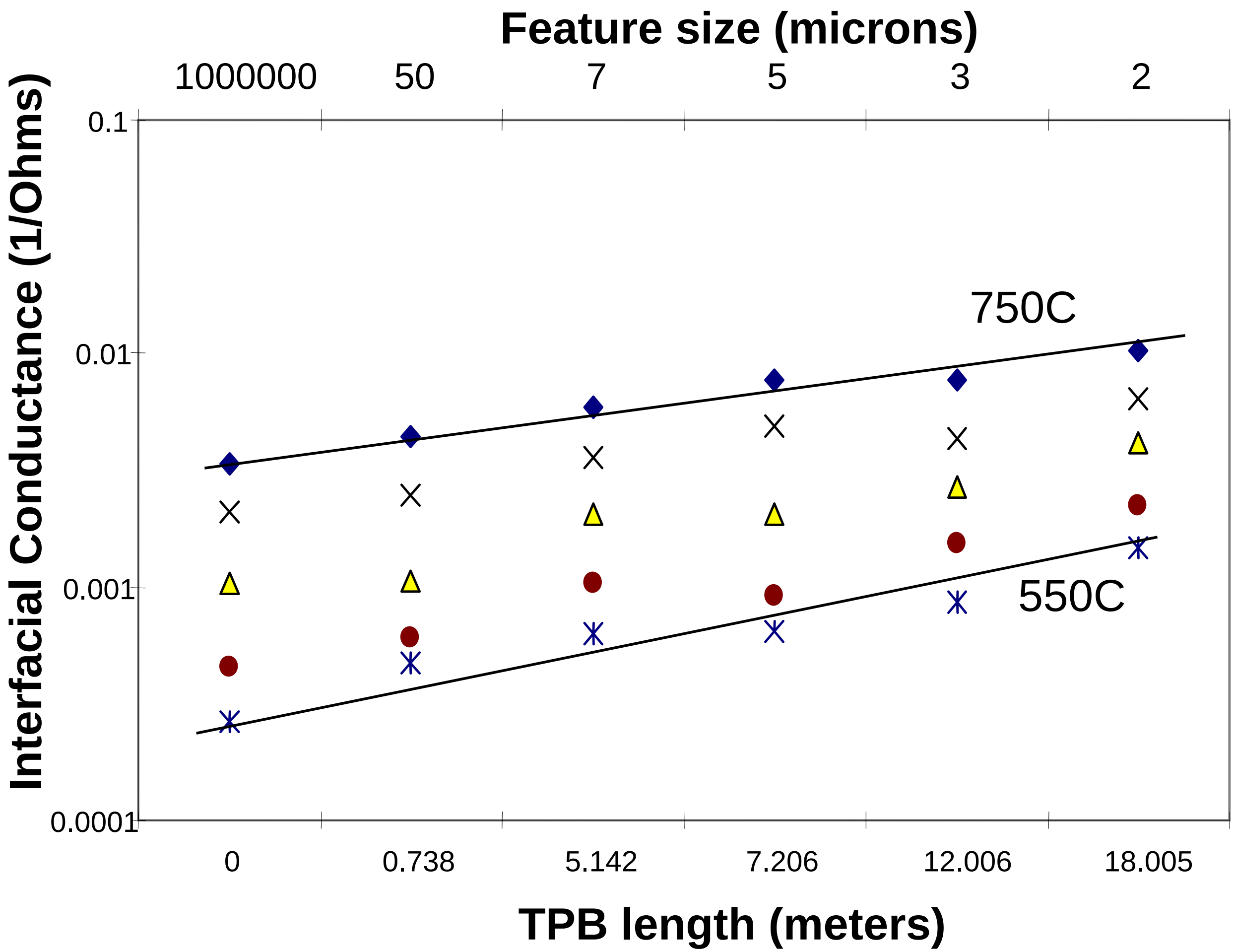
- **SERS and TERS offer extremely high sensitivity and spatial resolution in probing and mapping surface species on electrodes of SOFCs;**

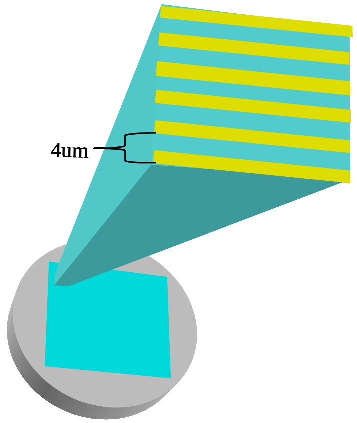
- **Surface species associated with sulfur-poisoning, Cr-poisoning, and carbon deposition are detected by Raman spectroscopy (characteristic peaks), offering possibilities of probing and mapping these species to elucidate the poisoning mechanisms;**

Recent Progress (Since May 2004)

- Computational: QM Calculations
- Experimental: Probing and mapping gas-surface interactions
- **Cells with Patterned Electrodes: TPB width/thickness**
- Fabrication of Porous Electrodes

Dependence of Interfacial Resistance on TPB Length

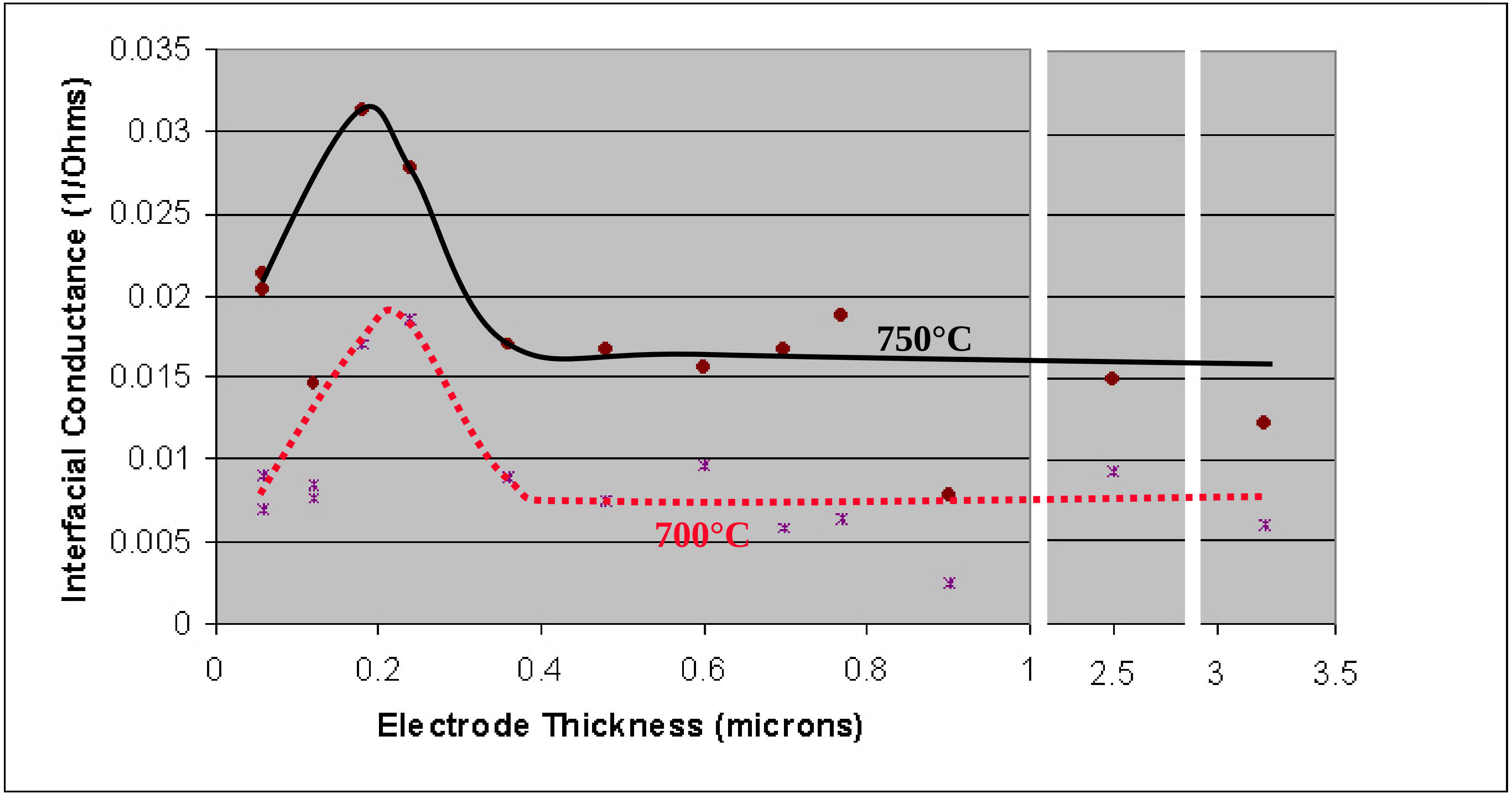




Effective TPB Width?

The effective width of TPB is less than 1 μm → Scale of porous LSM

Effect of MIEC Electrode Thickness



Effect of Electrode Thickness

- Electrode thickness dramatically influence on the catalytic properties of MIEC electrode stripes
- Impedance data demonstrate a clear peak performance (around 0.18μm at 750°C). For electrodes thicker than this critical value, the performance drops rapidly with thickness, approaching the value associated with the activity of the TPB (e.g., performance drops to less than 30% of the maximum near L=0.4 μm).
- For electrodes thinner than the critical value, the performance drops as it gets thinner because of the sheet resistance of the electrode, which makes part of the electrode no longer active.
- Electronic conductivity sets the minimum electrode thickness while ionic conductivity sets the upper limit of electrode thickness.

Recent Progress (Since May 2004)

- Computational: QM Calculations
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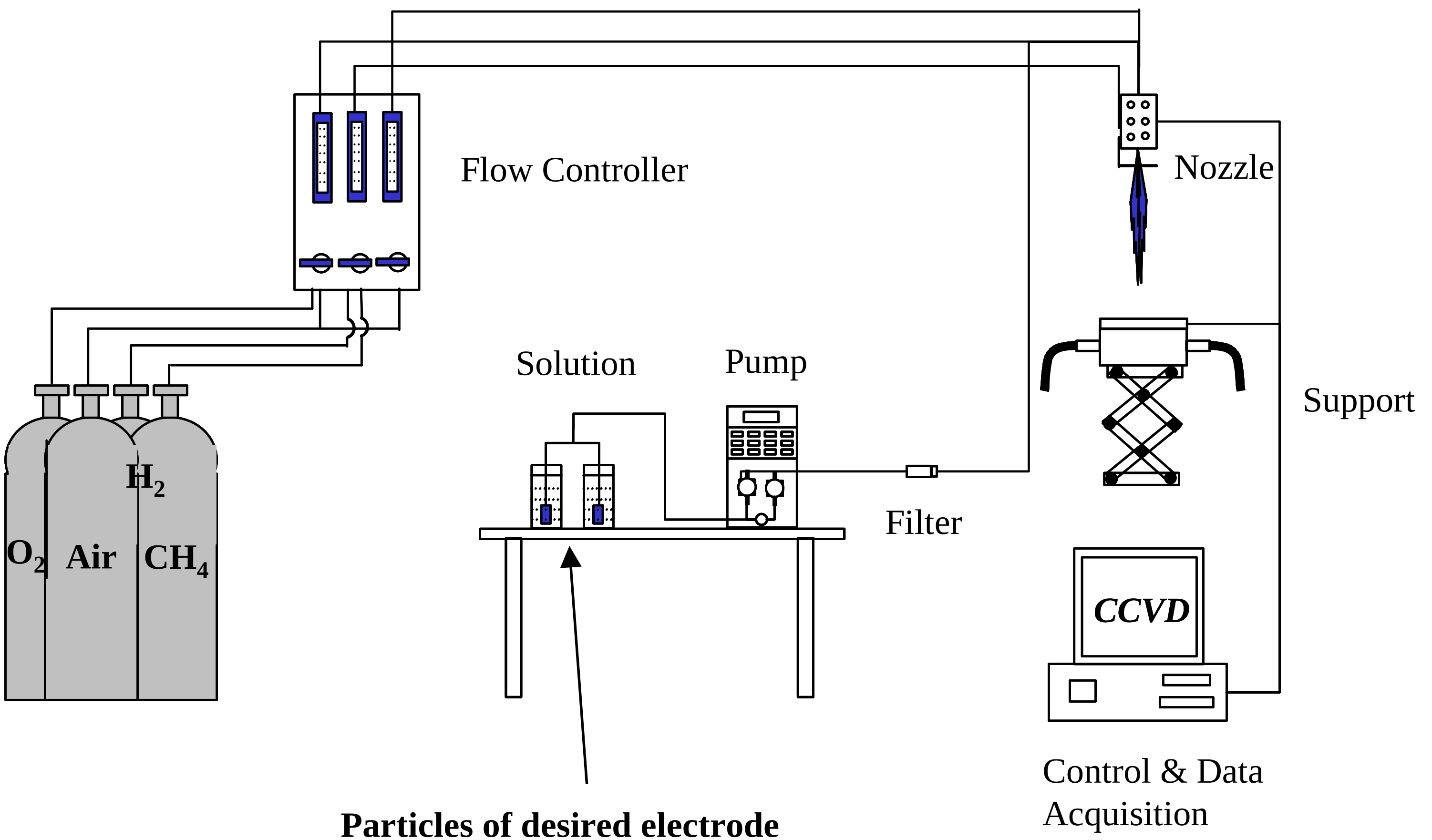
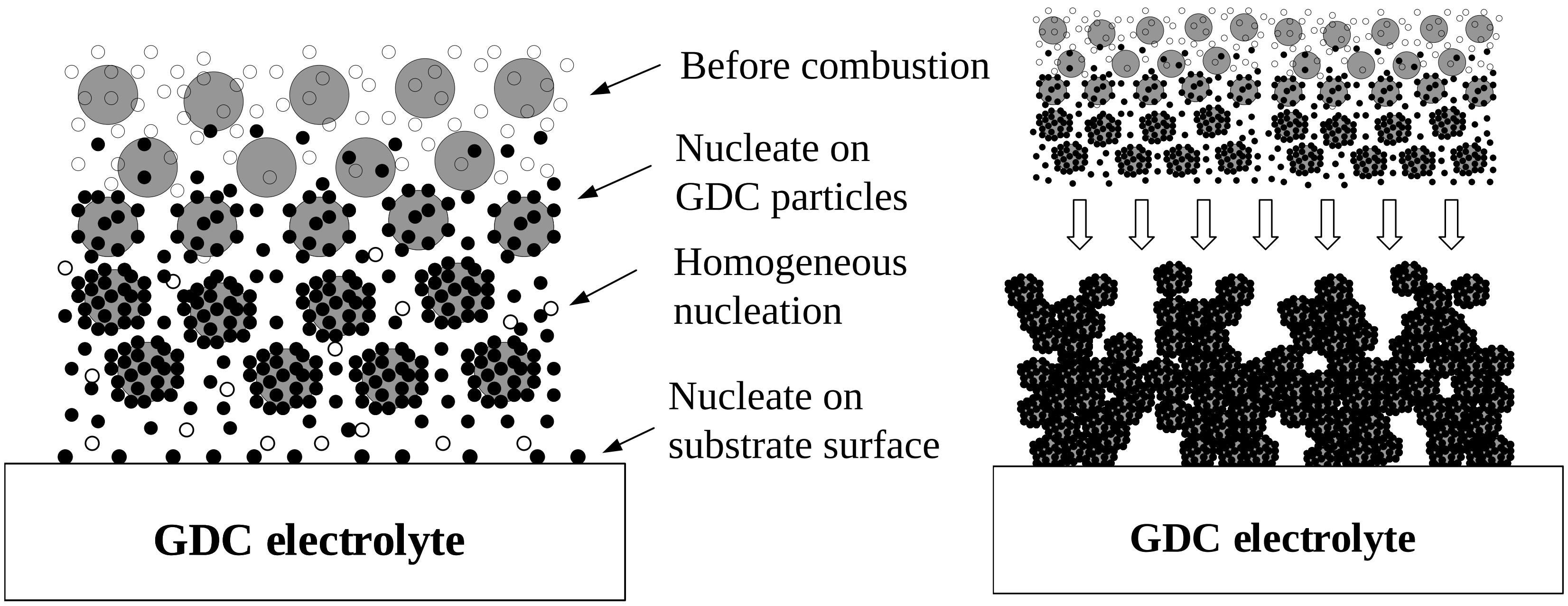
- Cells with Patterned Electrodes: TPB width/thickness
- **Fabrication of Porous Electrodes**

Particle-Solution Spraying Process



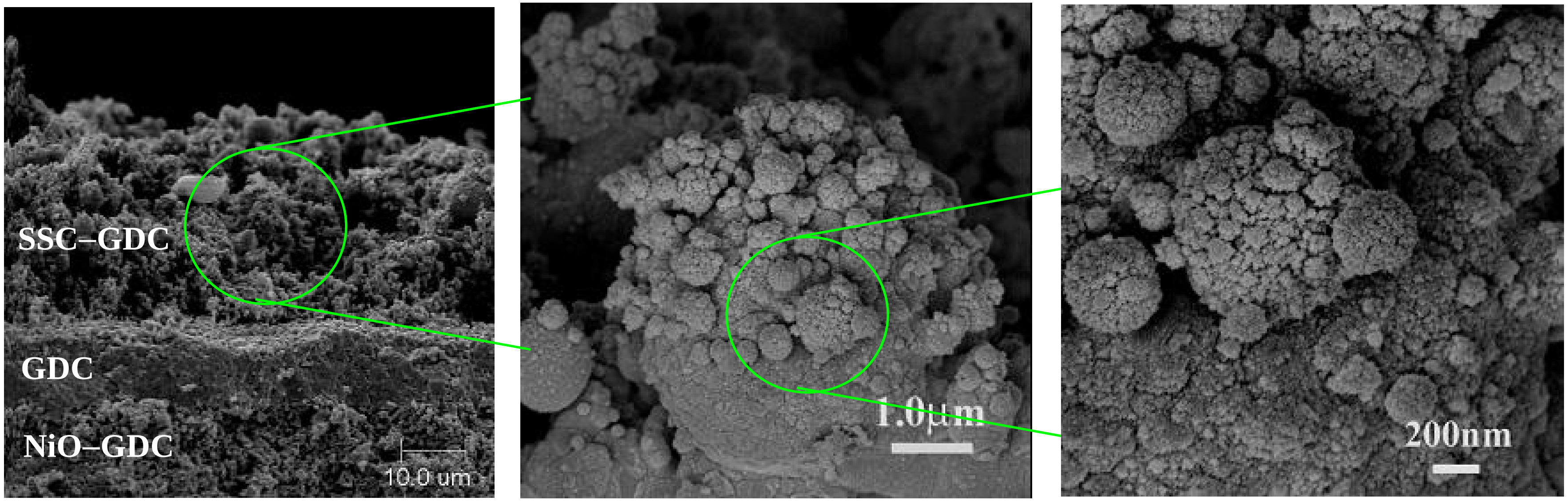
Particles of desired electrode materials are dispersed in a sol of the same electrode material

Formation of Porous Nanocomposite Electrodes in a Particle-Solution Spraying Process



- Liquid droplet containing Sm, Sr, Co nitrates
- SSC solid particle
- GDC solid particle

Nanocomposite Cathodes Fabricated Using Particle-solution Spraying Process



- Sm, Sr, Co nitrates for $Sm_{0.5}Sr_{0.5}CoO_3$(**SSC**) phase
- $Gd_{0.1}Ce_{0.9}O_{1.95}$ (**GDC**) solid powders, 0.5 µm
- Deposition temperature: 1200°C for 10 min.

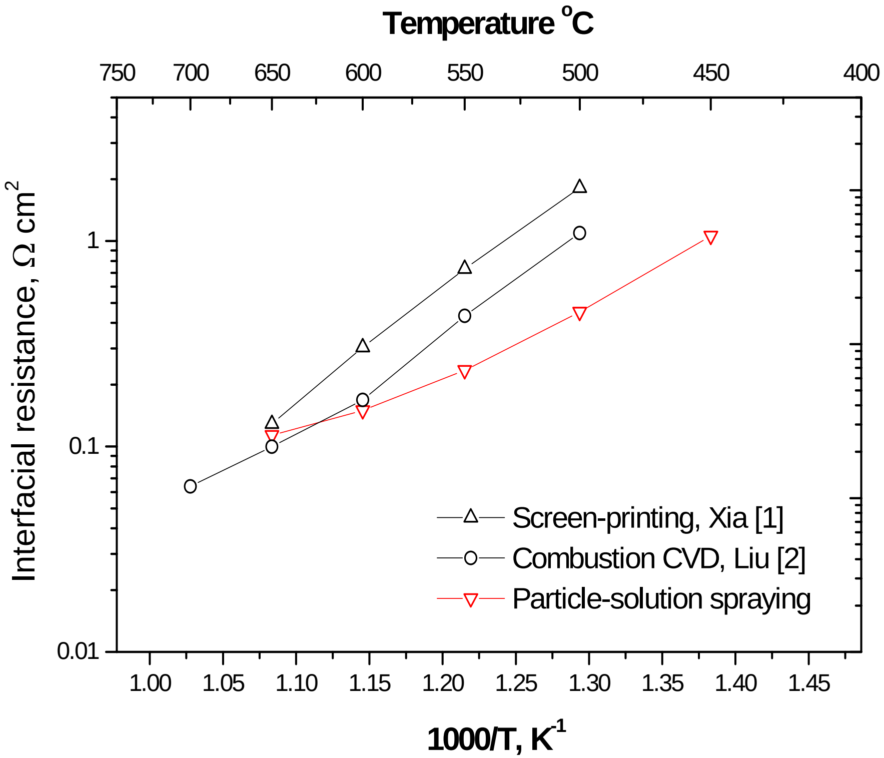
* Y. Liu, S. Zha, M. Liu, *Chem. Mater*. **16** (2004)3502.

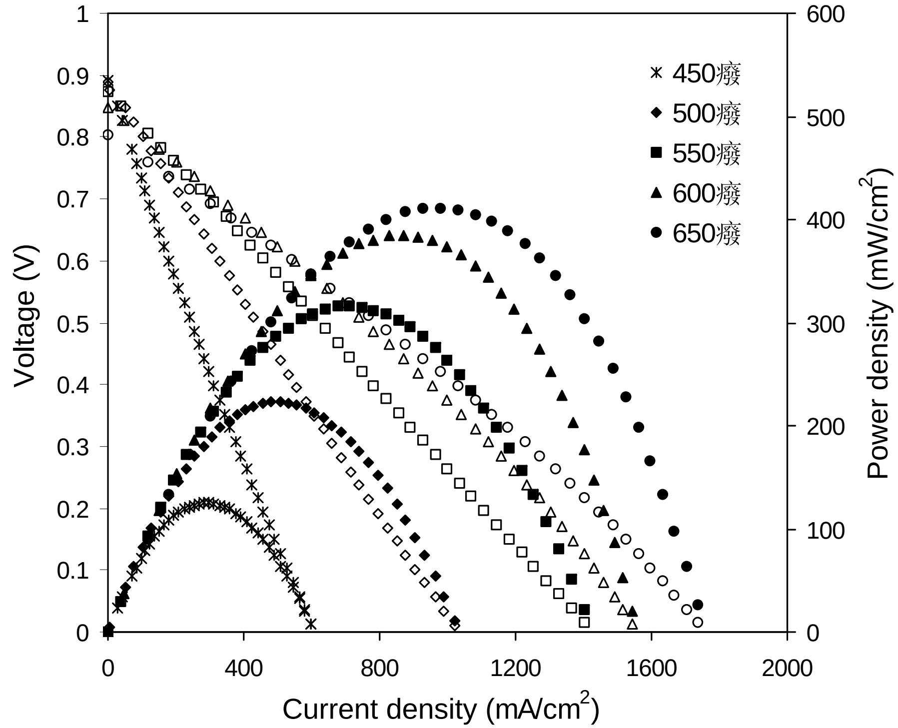
Potential Applications of Particle-Solution Spraying Process for Composite Electrodes

PSSP can virtually be employed to fabricate all kinds of composite electrodes (cathodes and anodes) by minor modifications:

- **Both phases are synthesized from solutions.**
- **To avoid formation of undesired phases, two spray nozzles are used. Each phase is formed separately and then sprayed onto the substrate.**
- **One phase can be introduced as solid particles while the other phase is formed from solution.**
- **Both phases are solid particles before spray.**

Electrochemical Performance of SOFC with Fractal-structured Nanocomposite Cathodes

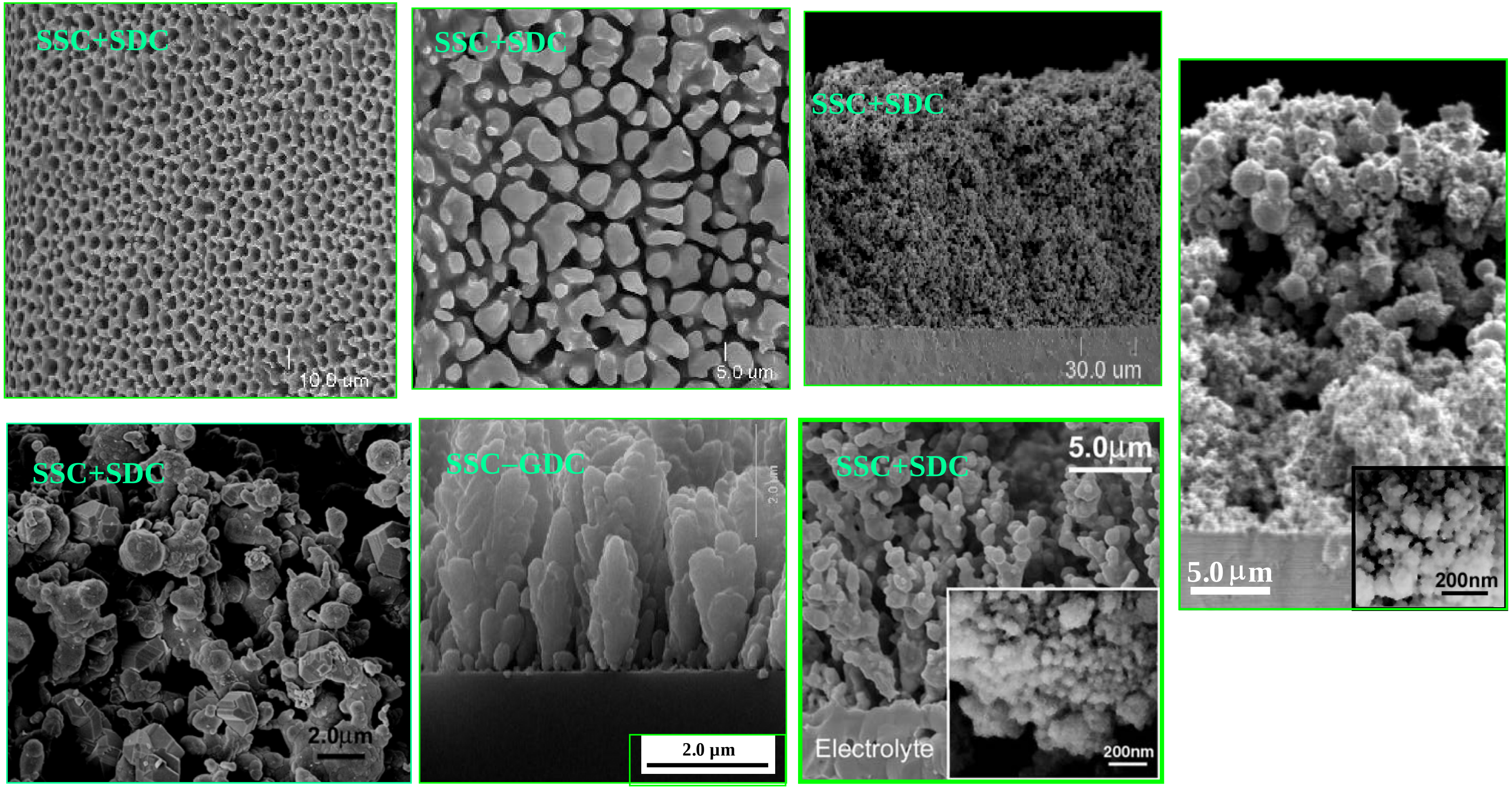




1. C. Xia, M. Liu, *Solid State Ionics* **144** (2001) 249.

2. Y. Liu, S. Zha, M. Liu, *Adv. Mater.* **16** (2004) 256.

Porous Electrodes Created by Combustion CVD



Applicability to SOFC Commercialization?

- **Do we really understand why one electrode material is better than the other?**
  - **Not yet; we still do not have a complete picture of the processes. However, we do know them better.**
- **Benefits to the SECA team?**
  - **Basic understanding does have technological implications; e.g., effective TPB width and max thickness are critical to design of MIEC electrodes**
  - **New tools for in-situ determination of electrode properties under practical conditions**
  - **Mechanistic understanding may help rational design of efficient electrodes (S- and Cr-poisoning)**

Activities for the Next 6-12 Months

- QM computations using super-cell models to better represent real systems
- Couple QM calculations with TERS experiments to characterize surface
- Finalize the design and construction of TERS, μ-IS and TPD systems, including tip preparation for μ-IS and TERS
- Identification of surface species relevant to oxygen reduction, S-poisoning, and Cr-Poisoning under various electrochemical conditions using SERS/TERS

Activities for the Next 6-12 Months

- **Investigation of local impedance of a single TPB, MIEC surface, and electrolyte surface using μ-IS under in-situ conditions**
- **FTIR - Vary thickness of cathode for gas switching experiments**
  - Find sampling depth of emission spectroscopy
  - Separate surface reaction from bulk diffusion
- **Resolve FTIR kinetic data with EIS data**
- **Characterize effect of cathode composition on surface activity and bulk properties**

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