Functionally Graded Cathodes for SOFCs

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DOE National Energy Technology Laboratory

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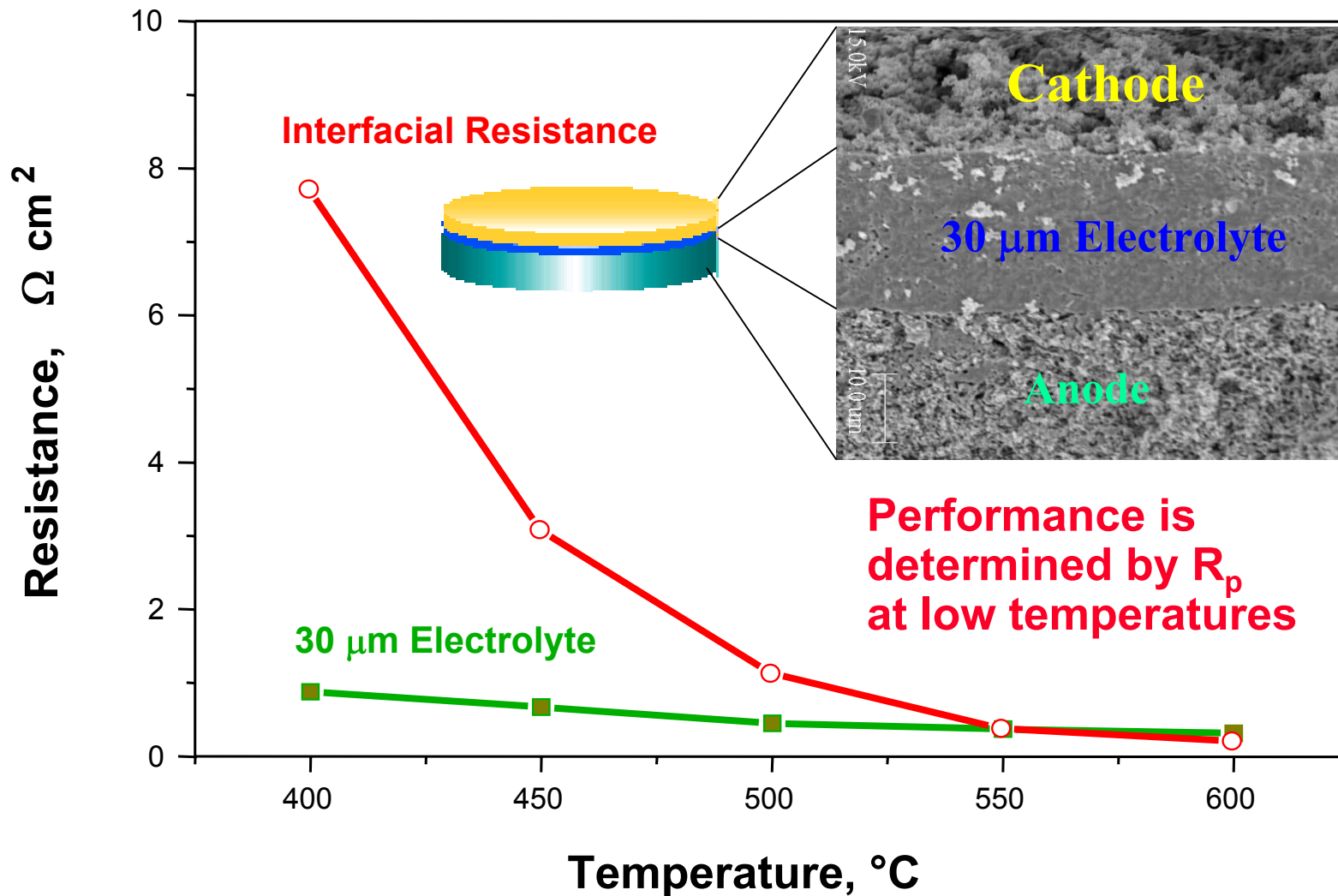
Collaborators: **T. Orlando and H. Chen**
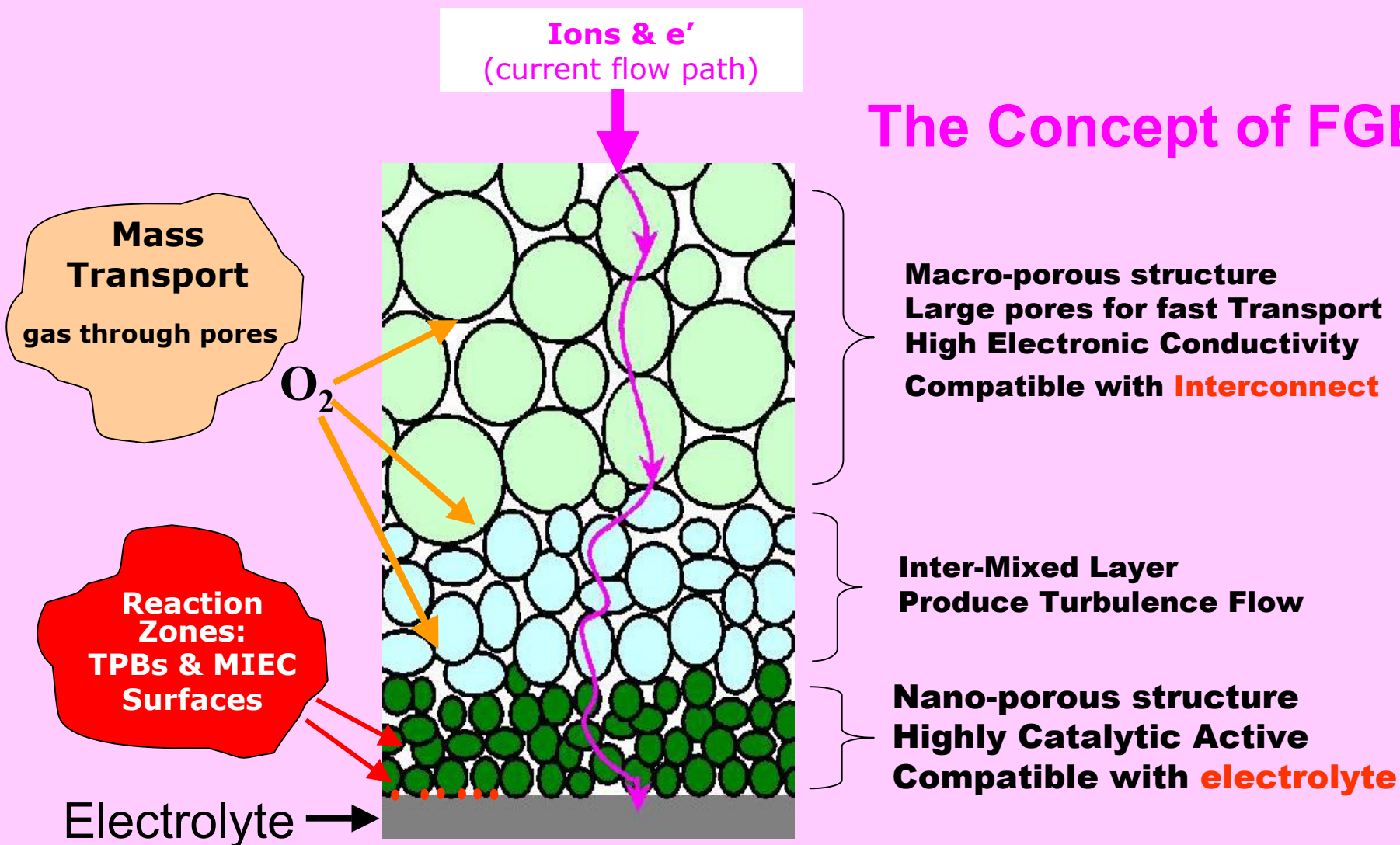Chemistry and Biochemistry, GT

May 11 – 13, 2004

Functionally Graded Electrodes

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Outline

- **Technical Issues Addressed**

- **Objectives & Approach**

- **Phase I Accomplishments**

- **Recent Results (Phase II)**
  - Further versification and interpretation of IR data
  - DFT Calculations and ESD
  - In-situ Raman and TERS
  - Patterned Electrodes with some sites selectively blocked
  - Measurement of Local (micro or nano-scale) properties
  - Fabrication of Graded Electrodes

- **Applicability to SECA**

- **Activities for the next 6-12 Months**

Functionally Graded Electrodes

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Critical Factor: Interfacial Resistance

Origin of R_P for a Porous MIEC Electrode

Ions & e'
(current flow path)

The Concept of FGE

Mass Transport

gas through pores

O_2

Reaction Zones: TPBs & MIEC Surfaces

Electrolyte ➔

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

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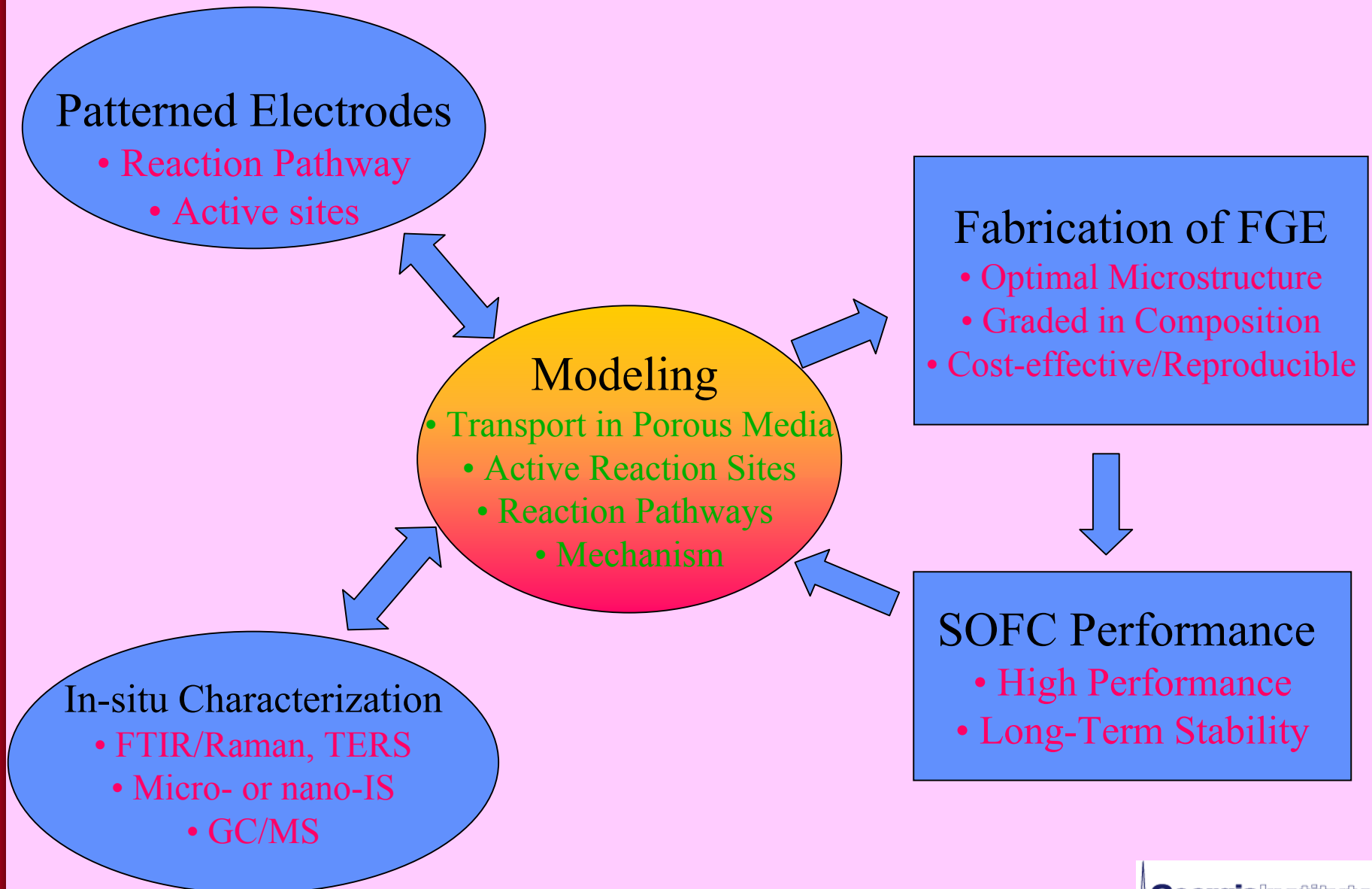
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Critical Issues

- **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**

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Objectives

- To develop tools for *in-situ* characterization of electrode reactions in SOFCs;

- To gain a profound understanding of the elemental processes occurring at cathode-electrolyte interfaces; and

- To rationally design and fabricate efficient cathodes for low temperature operation to make SOFC technology economically competitive.

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Technical Approach

Patterned Electrodes
- Reaction Pathway
- Active sites

Modeling
- Transport in Porous Media
- Active Reaction Sites
- Reaction Pathways
- Mechanism

Fabrication of FGE
- Optimal Microstructure
- Graded in Composition
- Cost-effective/Reproducible

SOFC Performance
- High Performance
- Long-Term Stability

In-situ Characterization
- FTIR/Raman, TERS
- Micro- or nano-IS
- GC/MS

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Major Phase I Accomplishments

- Successfully fabricated patterned electrodes (SSC and LSM) with well-defined geometries for determination of TPB width

- Studied SOFC cathode materials using *in-situ* FTIR emission spectroscopy under practical conditions, including Pt, SSC, LSC, LSF, and LSCF

- Characterized surface structures of SOFC materials using Raman spectroscopy

- Fabricated electrodes with vastly different microstructures and morphologies using combustion CVD and template synthesis

- Demonstrated functionally graded cathodes of low polarization resistances at low temperatures.

Functionally Graded Electrodes

Recent Progress – Phase II

- Further versification and interpretation of in-situ vibrational spectra of cathode materials (thickness and time dependence)

- DFT calculation of vibration frequencies of surface oxygen species (adsorbed O_2, O_2^-, and O_2^{2-}) – peak assignment

- Started study of electron-stimulated desorption (**ESD**) of oxygen

- Dramatically increased sensitivity and spatial resolution in probing surfaces using tip enhanced Raman scattering (**TERS**)

- Successfully fabricated patterned electrodes for specific site isolation

- Set up for local (micro or nano-scale) electrochemical measurements (IS) using **SPM tips** and patterned electrodes

- Developed processes for fabrication of electrodes graded in both composition and microstructure

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Peak assignments:

1124 cm^{-1}: O_2^-
1236 cm^{-1}: perturbed O_2^-
930 cm^{-1}: O_2^{2-}

Surface Species

CO_2

At overpotential of -0.76 V

930

1236   1124

Baseline Offset (bulk properties)

At OCV

$\Delta E/E_0$ (%)

Wave Number, cm^{-1}
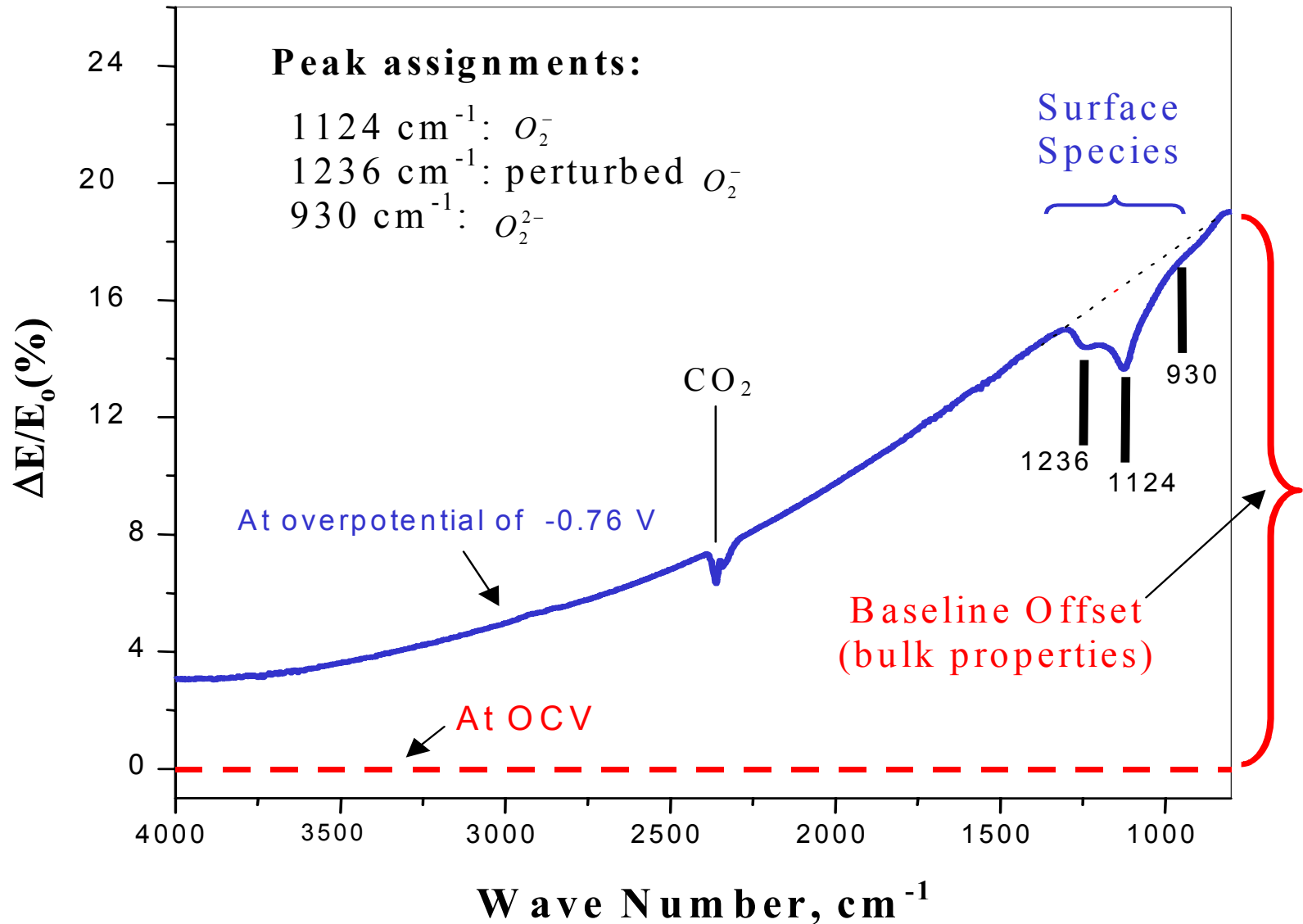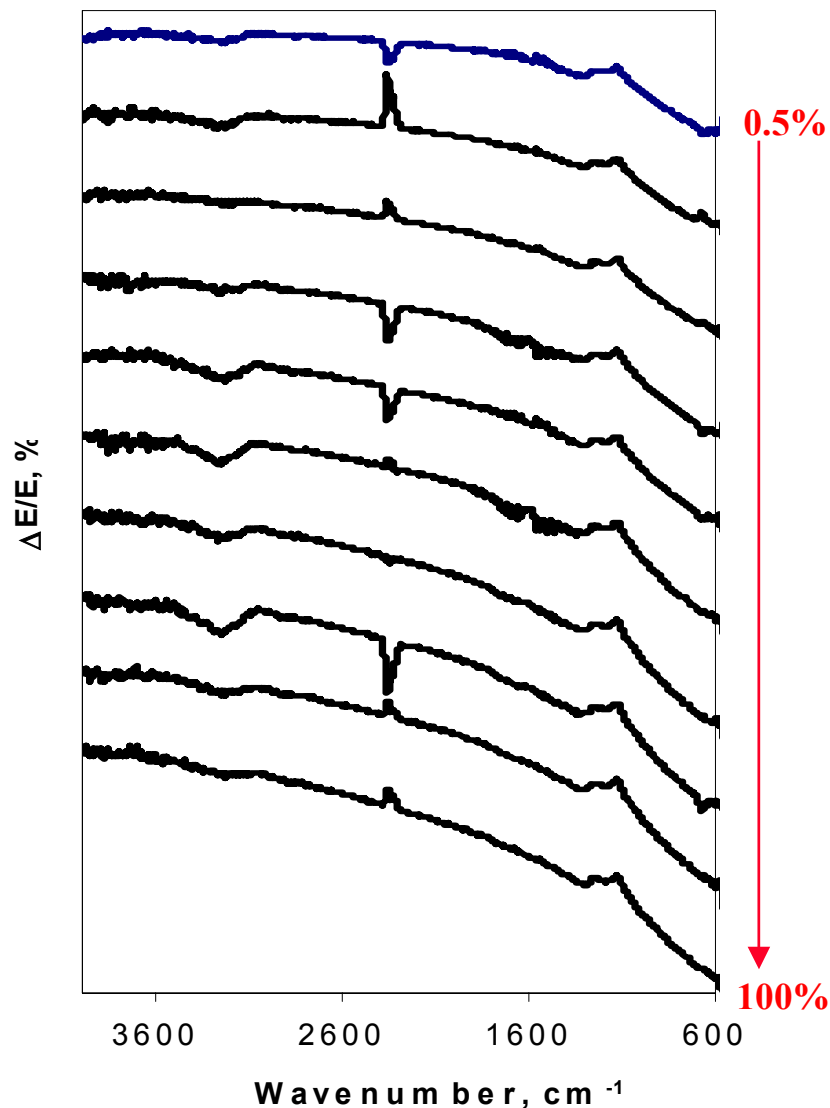
Gas switching from N_2 to a gas containing Po_2 (0.5 to 100%)

Both negative-going baseline shift and positive-going IR peak increase with the oxygen partial pressure.

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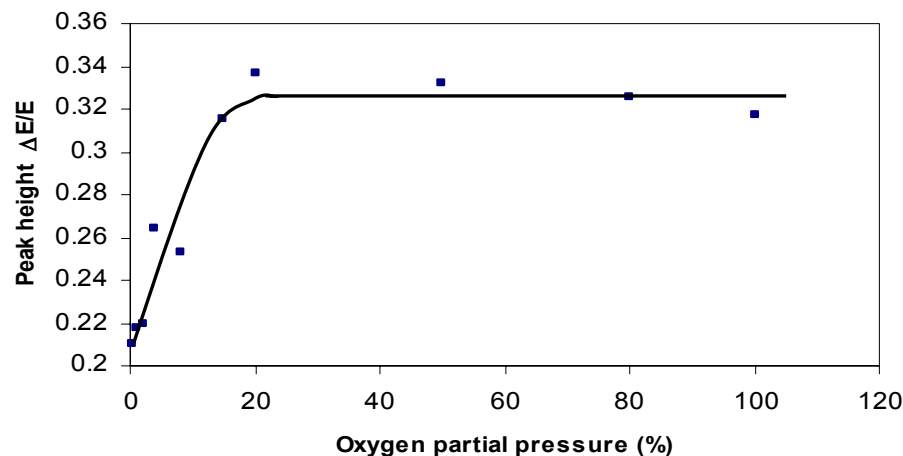
The saturated oxygen partial pressure for oxygen adsorption is about 20%.
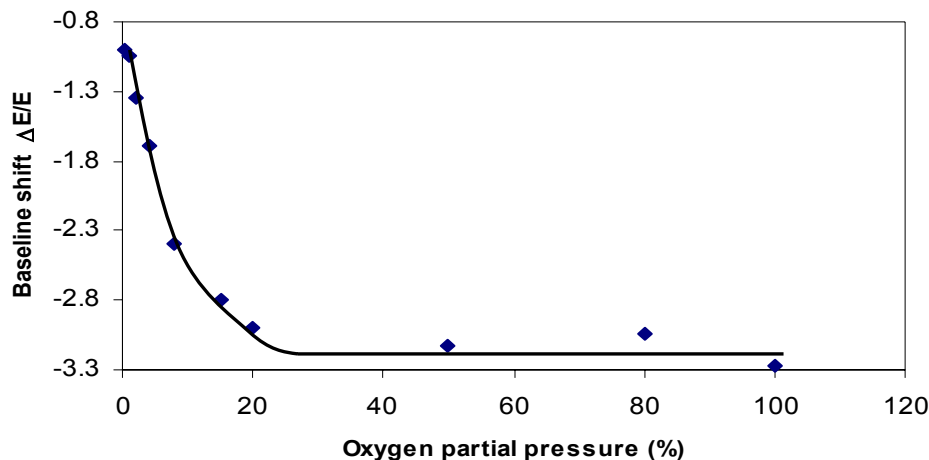
Corresponding to the IR peak height, the baseline shift at 825 cm^{-1} is also saturated when the O$_2$ is about 20%.

Baseline shift and the IR peaks seem to go together!

Lower O$_2$ pressure means higher oxygen vacancy in the bulk. Negative-going baseline shift therefore means decrease in bulk oxygen vacancy concentration

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Validity of Interpretation?

- How do we know that the peaks are corresponding to species adsorbed on surfaces, not changes in bulk properties?

- If so, can we prove that the peak assignments are correct?

- How do we know that the baseline shift is due really to changes in bulk properties, not in surface properties ?

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Thickness Dependence

Emitted IR

Adsorbed molecules

← **Active bulk < skin depth**
← **Inactive bulk**
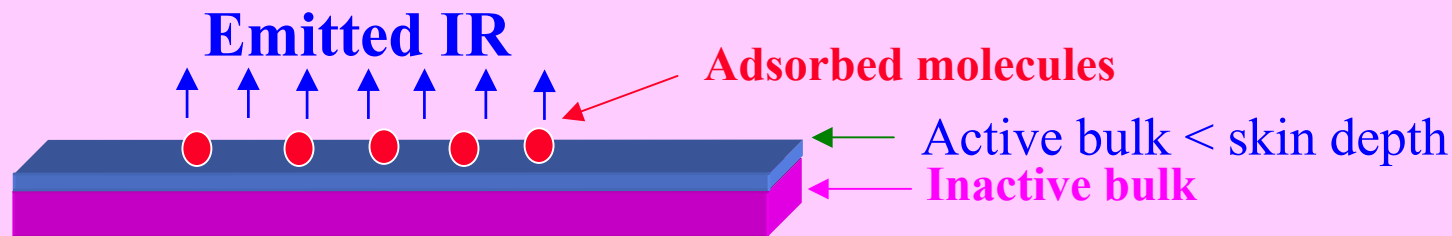
- If the peaks are corresponding to species adsorbed on surface, the heights of the peaks should be independent of film thickness.

- If the baseline shift is due really to changes in bulk properties, it should increase with thickness (until the thickness is greater than the skin depth).

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Equilibrium FITR spectra for SSC thin film electrodes
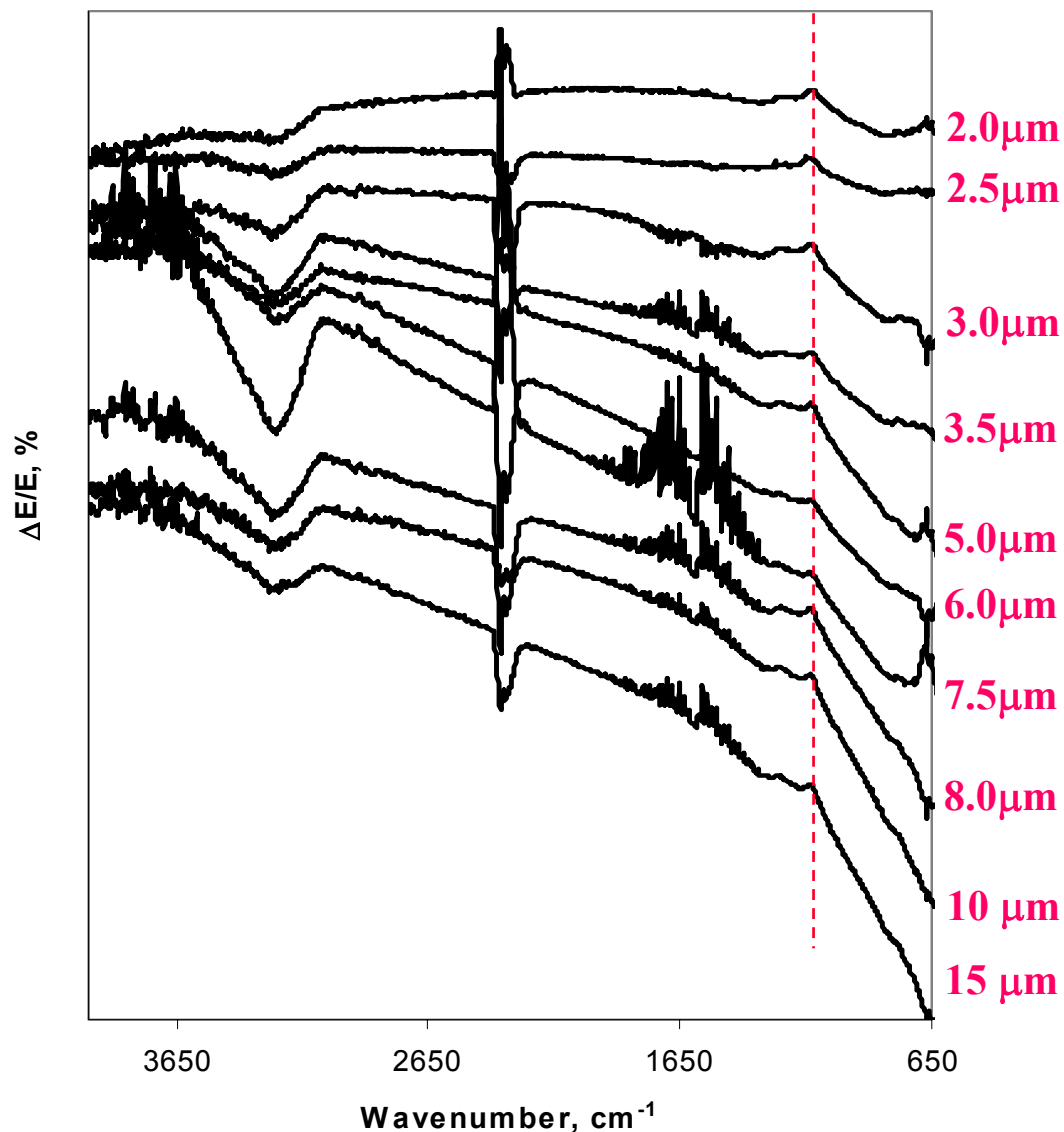
- A broad oxide adsorbent peak centered at 1124 cm^{-1}

- A negative-going baseline shift with increase thickness.

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IR peak height and baseline shift
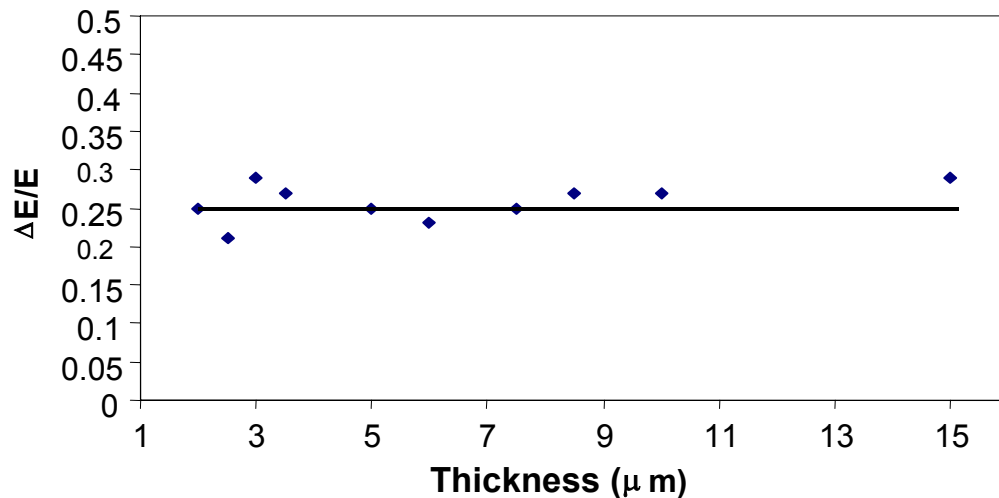
The O$_2^-$ peak height is almost independent of film thickness.
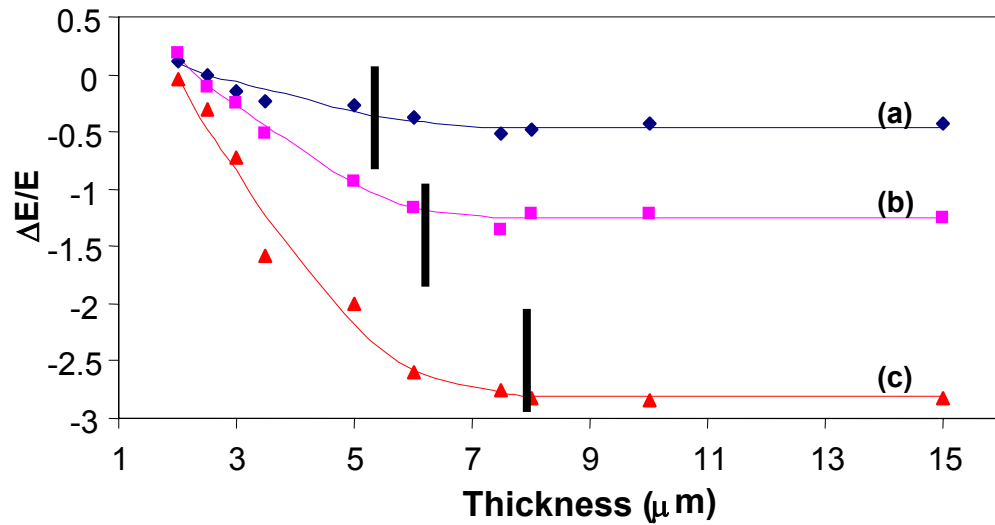
The baseline shifts at (a) 3020, (b) 2128, and (c) 825 cm^{-1} increase with film thickness.

Larger baseline shift is observed at lower wavenumber (or longer wavelength with larger skin depth).

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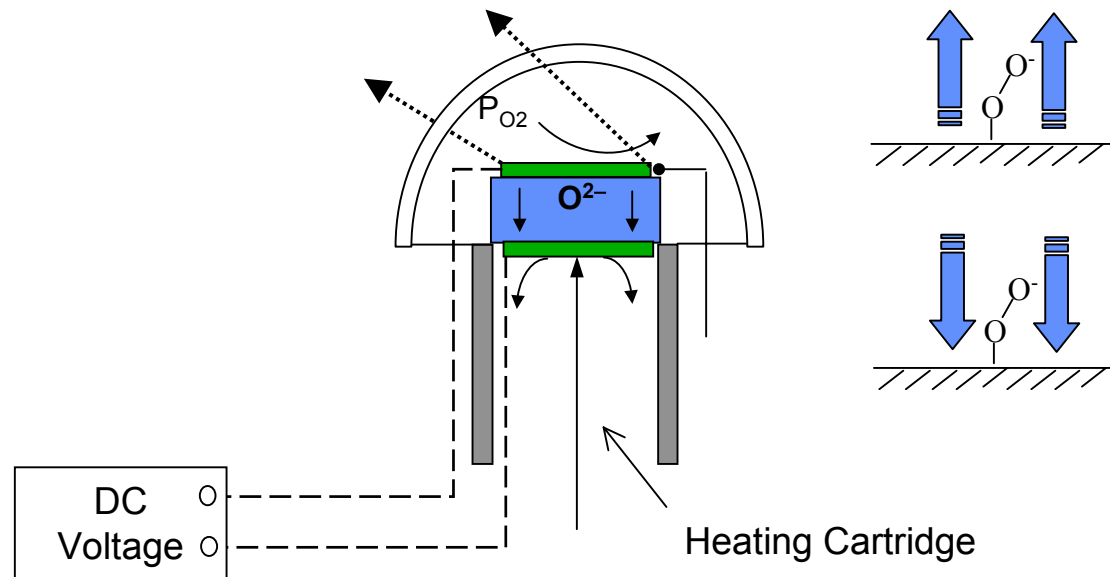
- If the peaks are corresponding to species adsorbed on surface and the baseline shift is due really to changes in bulk properties, the rate of peak height change (rate of surface reaction) should be different from that of baseline shift (the rate of bulk transport) unless the rates of the two processes are coincidently identical.

Functionally Graded Electrodes

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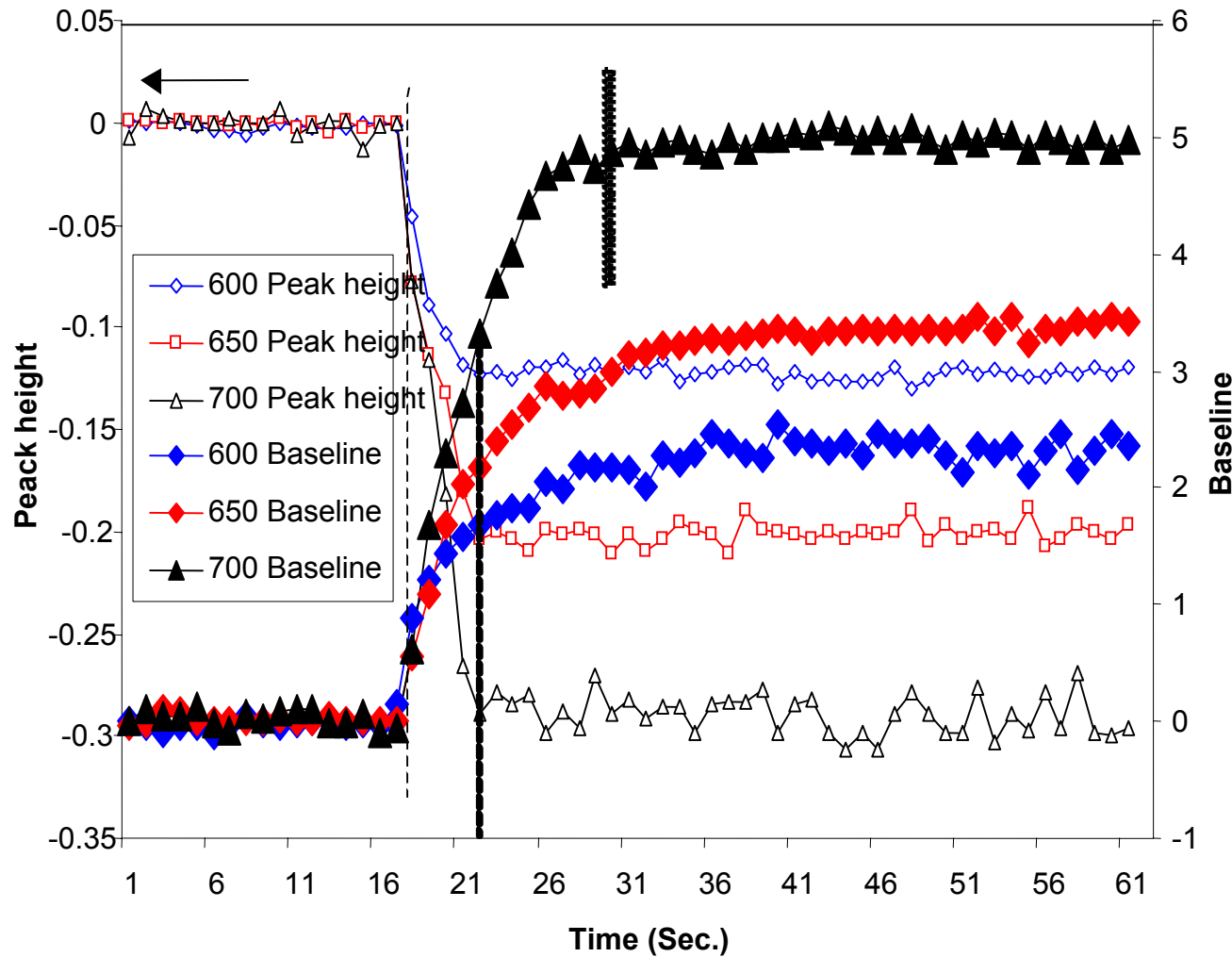
Peak height change is much faster than baseline shift, indicating again that the peak and the baseline shift correspond to different processes.

Further, it's clear that surface reaction is faster than bulk diffusion.

Electrode kinetics

Bulk diffusivity

Conclusions for FTIR Studies

- **Indeed, the IR peaks correspond to species adsorbed on surfaces or a change in surface properties;**

- **The IR baseline shift is due to a change in bulk properties of electrode material, most likely to the change in oxygen vacancy concentration in the bulk phase;**

- **However, we are still unable to conclude which peak corresponds to which species.**

  - Theoretical Calculation
  - Isotope Exchange

DFT Calculation of O-O vibrations

- Used DFT method (B3LYP) on Q-Chem software with 6-311+G(3df) basis set

- Calculated theoretical frequency of O-O bond for free O_2, O_2^-, and O_2^{2-}

Species	O_2	O_2^-	O_2^{2-}
Frequency, cm^{-1}	1592	1173	835

Effect of transition metal cation

- Began calculations of O-O vibrational frequency when bonded to cobalt cation in SSC or LSC
- Optimized geometry first, then calculated frequency

Start　　**Optimize**　　**Finish**

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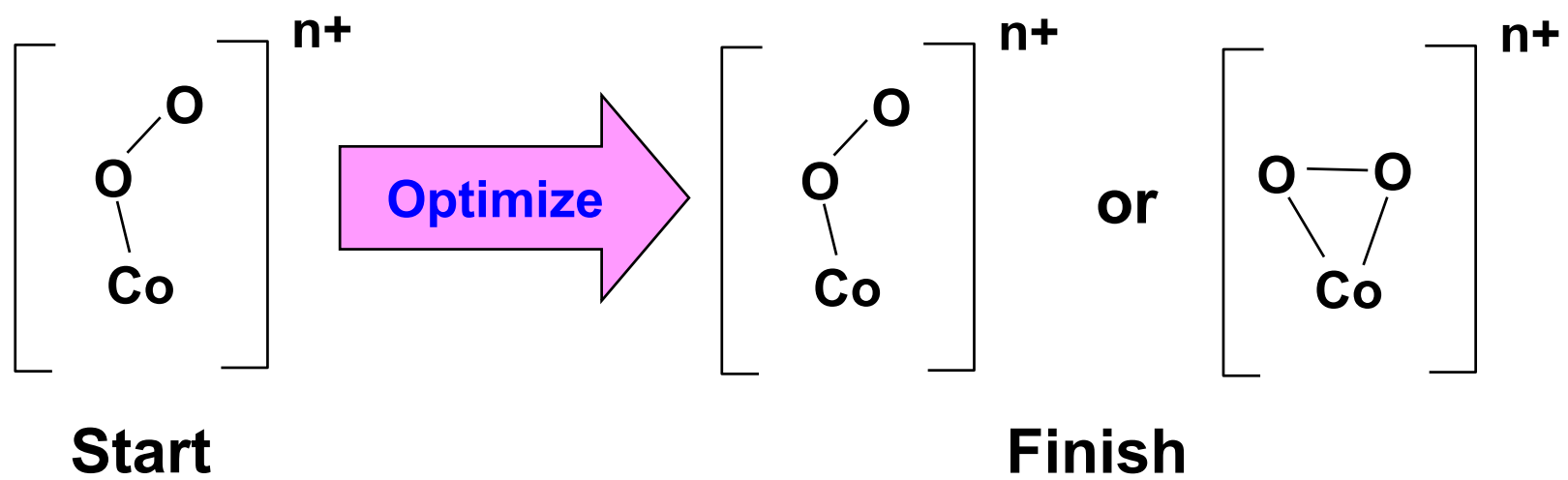
Most Probable Surface Configuration

For (101) phase
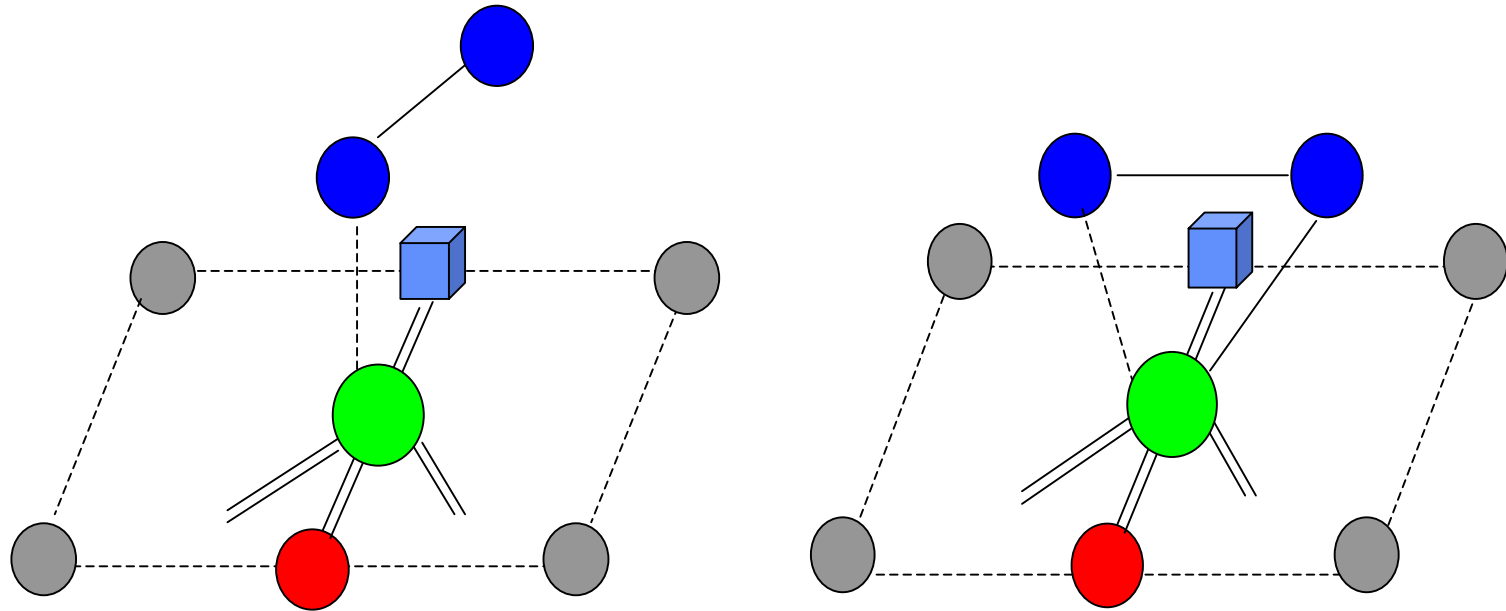
🟦 **Oxygen vacancy**   🔵—🔵 **Adsorbed Oxygen**

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Effect of transition metal cation

Species	CoO_2^+	CoO_2^{2+}	CoO_2^{3+}	CoO_2^{4+}
O-O bond, Å	1.3100	1.2074	DNC	DNC
$\angle$Co-O-O, °	141.5	70.5	DNC	DNC
O-O vibration, cm^{-1}	1487	467	N/A	N/A

*DNC denotes that geometry optimization calculation did not converge

- Calculations reveal superoxo-/peroxo- nature of oxygen species

- Frequencies unreliable – must include more of the lattice for better results

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Electron Stimulated Desorption (ESD)

Auger Electron

E-beam

e^-

X-ay

1
Ionization

2
Auger relaxation

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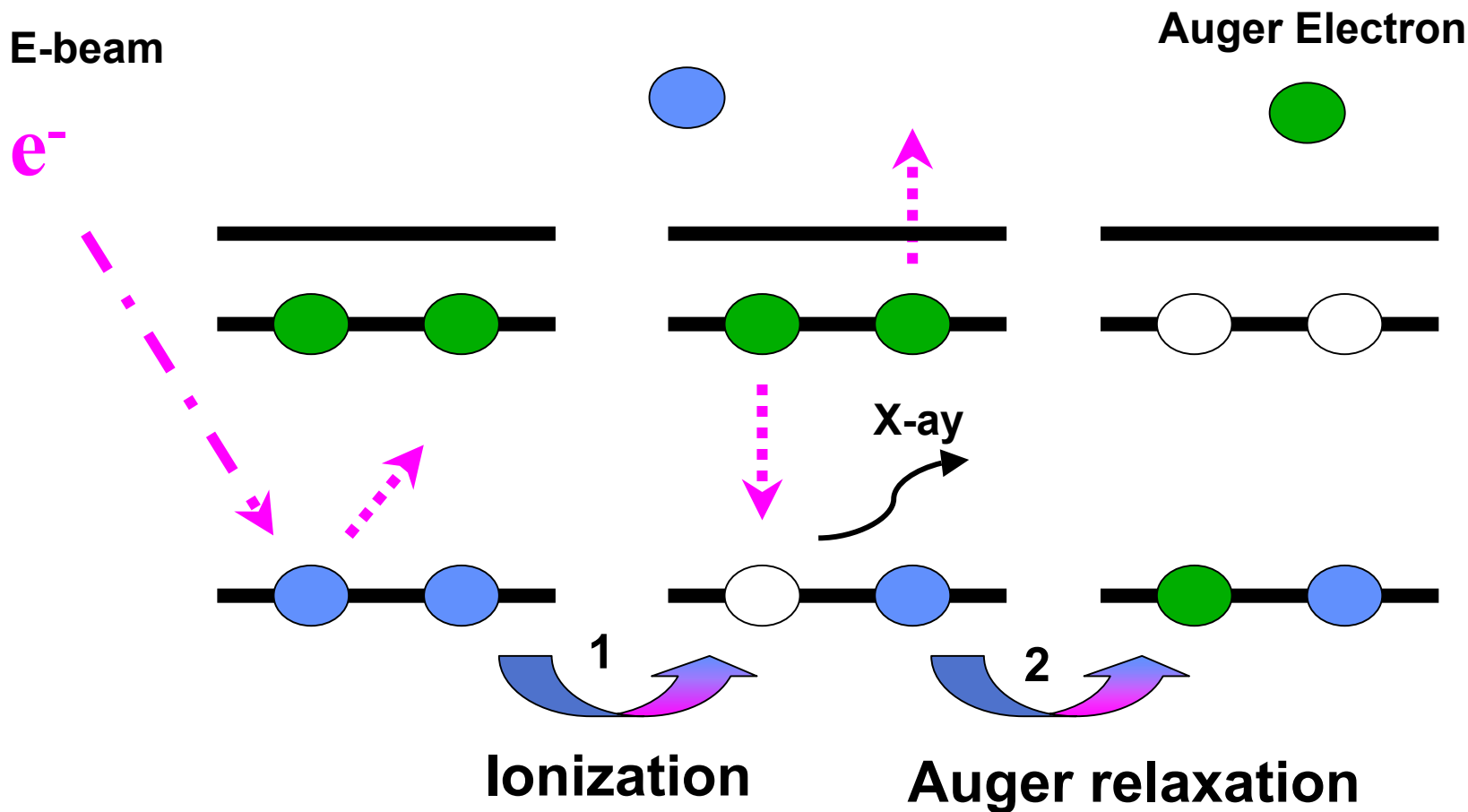
3-Step ESD Model
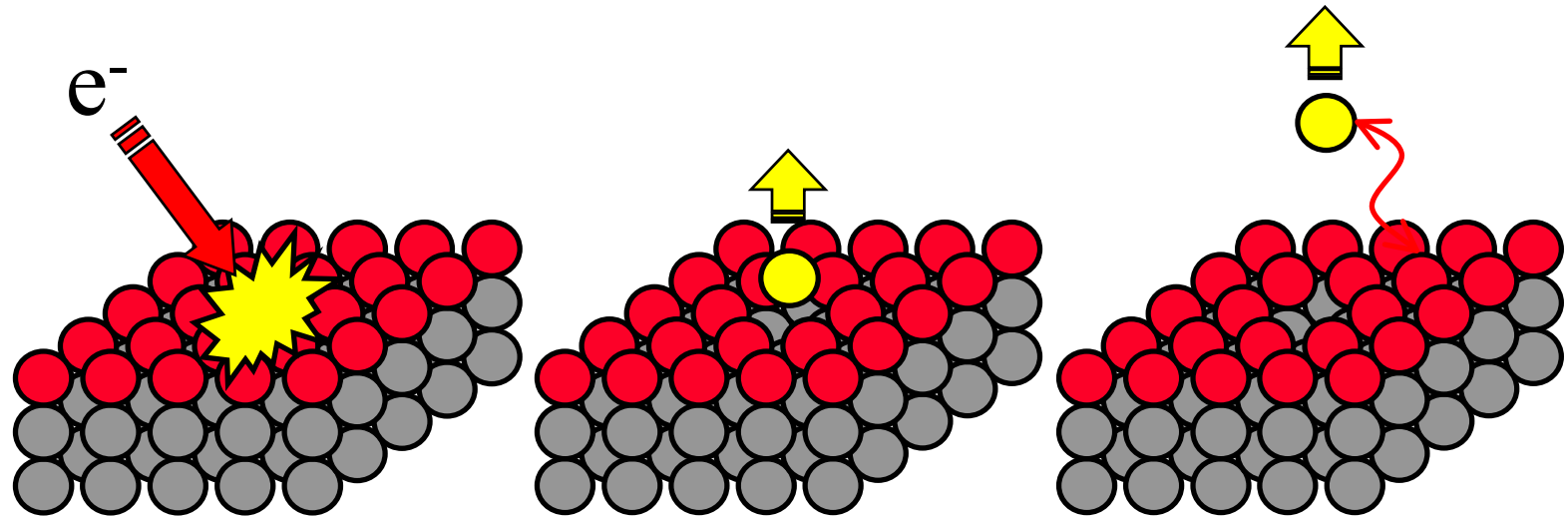
Excitation ~ 10^{-15} sec

Nuclear Separation ~ 10^{-13} sec

Desorption ~ 10^{-11} sec

- **Electron excites the target via an inelastic scattering**

- **Nuclear motion on the excited state potential surface**

- **Outgoing atom or molecule interacts with surface**

What Can ESD Offer?

- **Structures of adsorbate/adsorbent system**

  - Local bonding
  - Bonding geometry
  - Binding energy

- **Dynamics of charge transfer**

- **Site specific desorption**

  - **Defects (for example: oxygen vacancy)**
  - Local disorder

XYZ-Rotation Stage

Sample Holder   **Loading Cell**

QMS

Sample Transfer Stage

E-Gun

Turbo
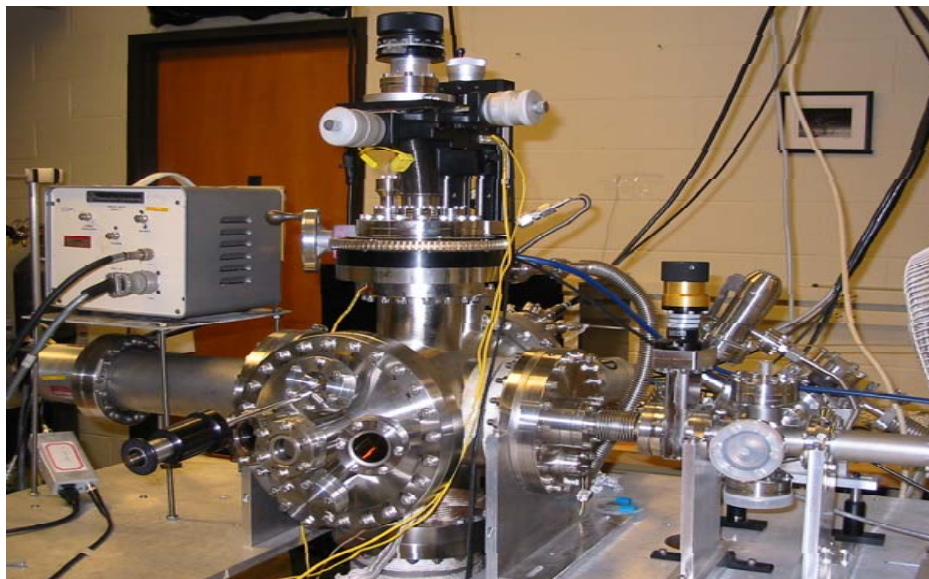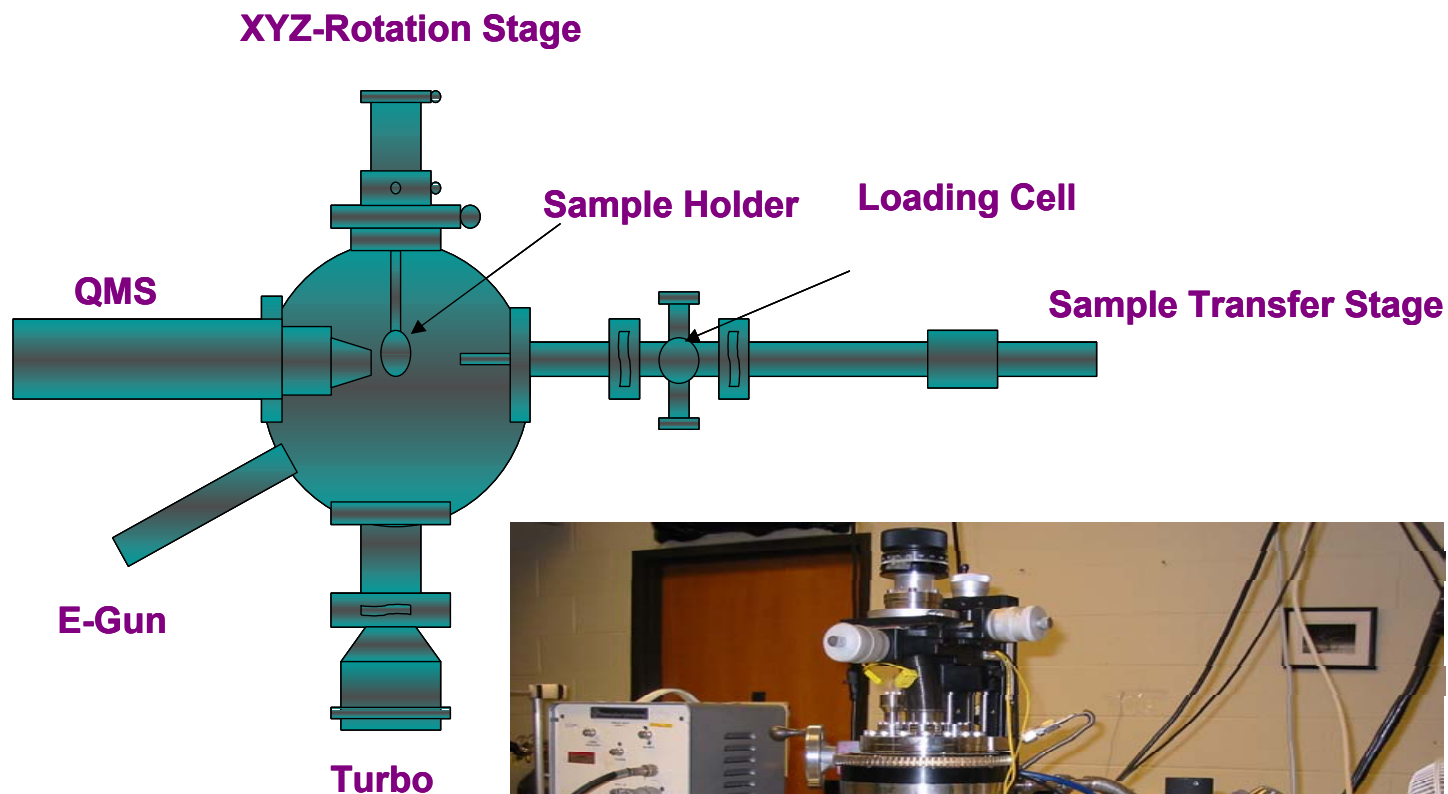
Prof. Thom Orlando
Chemistry, GT

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GDC Sample for ESD Study

Compostition :
$Ce_{0.9}Gd_{0.1}O_{1.95}$ (gadolinia doped ceria, GDC)

Preparation:
    Combustion of metal nitrate
    Calcine in air at 600ºC for 2 h
    Cold press into pellets
    Fired at 1450ºC for 5 h

Characterization:
    Relative density: 95% to 97%
    XRD: fluorite structure
    SEM: grain size about 5 μm

25.0kV   5.0 um

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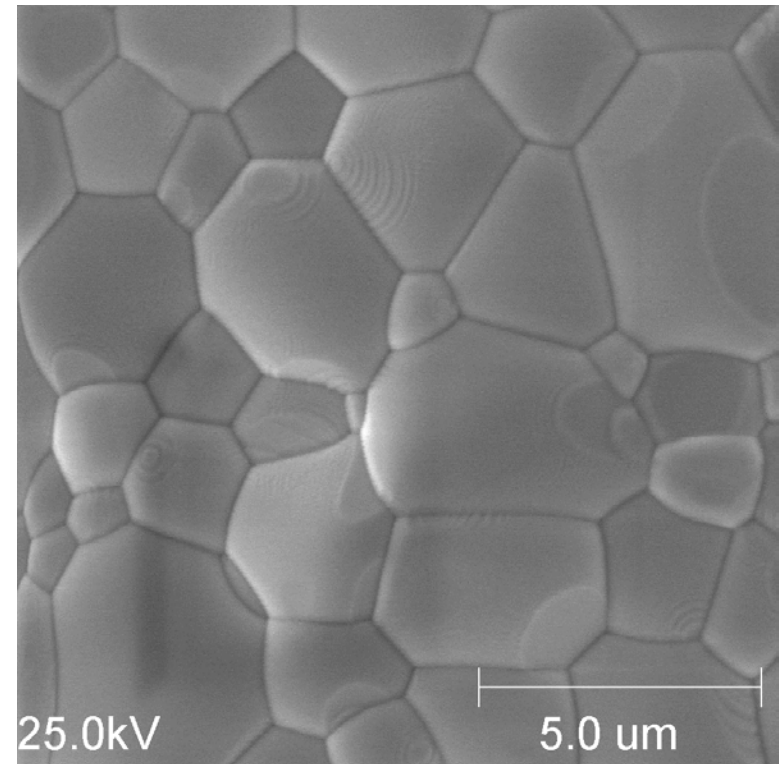
Electron Energy Dependence of ESD

O⁺

Electron Energy (eV)
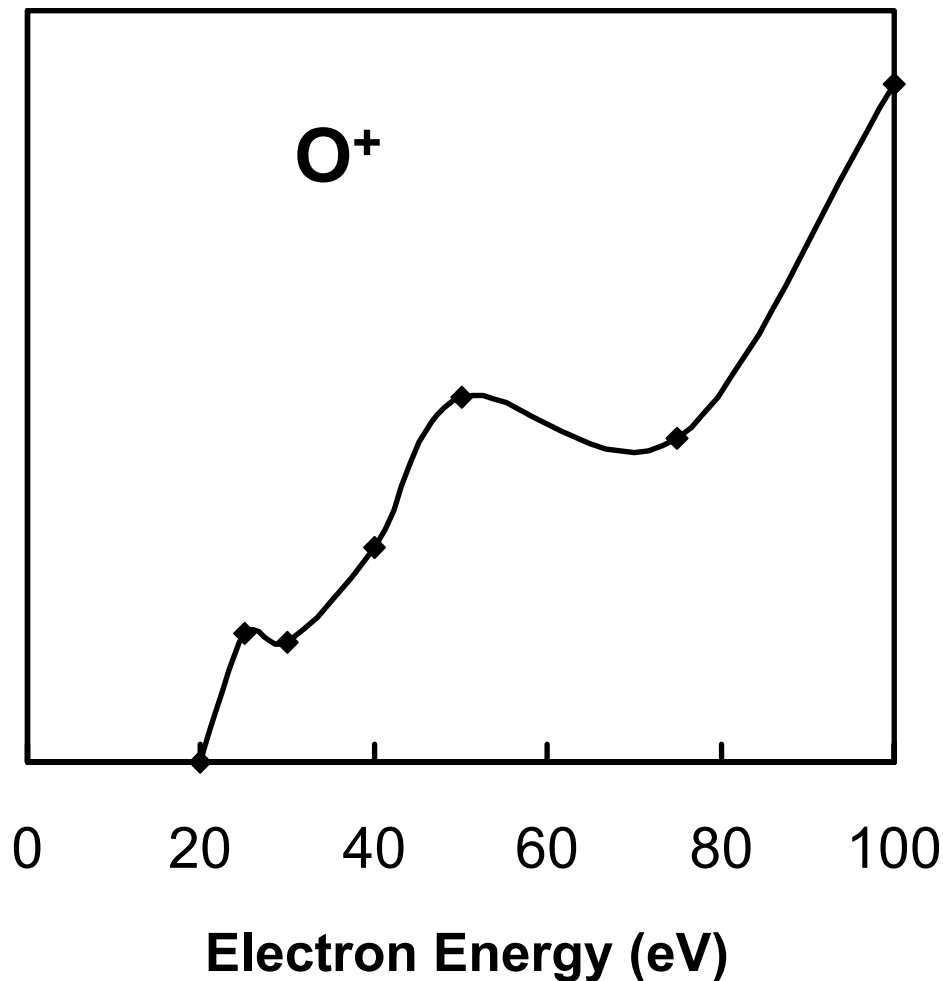
O$^+$ threshold energy is 22 eV relevant to the direct ionization of O2s level followed by an intra-atomic Auger cascade

The feature around 50 eV is related to the Auger process that involves the excitation of 5s level of cerium and gadolinium

Ready to study cathode materials (e.g, SSC)

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FTIR – Isotope Dosing

- Difficulties

  — Precise control of Po2

  — Fast oxygen exchange at high temperature

- Approach – FTIR in UHV

  — Diffuse-reflectance IR (DRIFTS) set up for low temperature FTIR measurement

  — Emission IR set up for high temperature FTIR measurement

FTIR

1P

6.02"

3"

6"

2F

1F

Sequence of mirrors

**Type of of mirrors
F: flat mirror
P: parabolic mirror**

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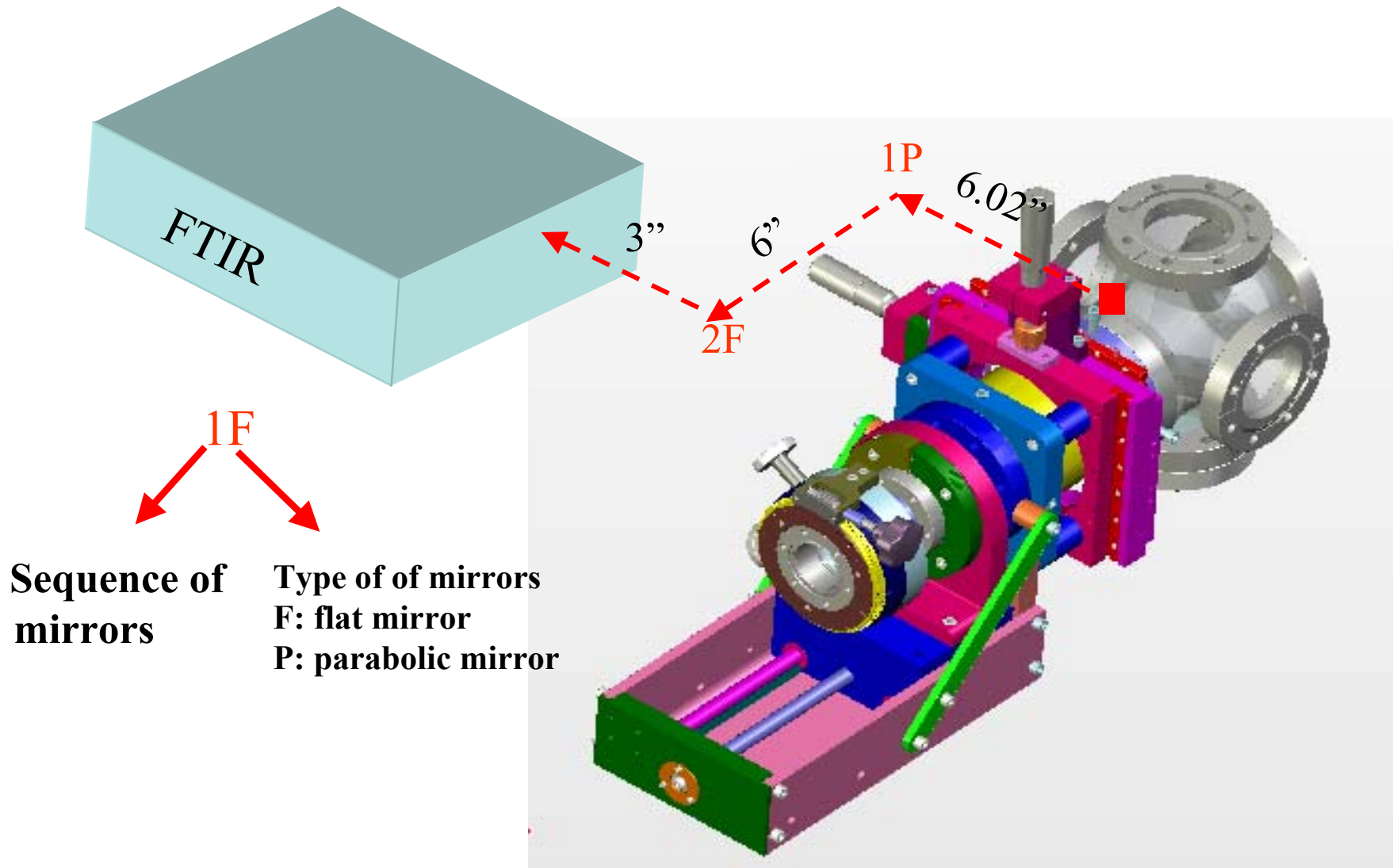
Low-Temp (LN) DRIFTS
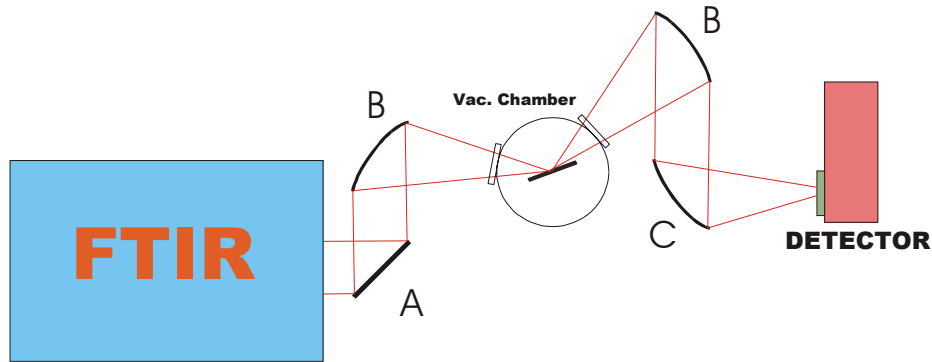
A - plain mirror

B - parabolic mirror F=69, 100, 153, 180, 220, 250, 300, 400, 418 mm

C - parabolic mirror F= 43 mm

FTIR

Vac. Chamber

DETECTOR

FTIR

3" 6" 6.02" 6.02" 3" 1.70"

1F 2P 3P 4P

Detector

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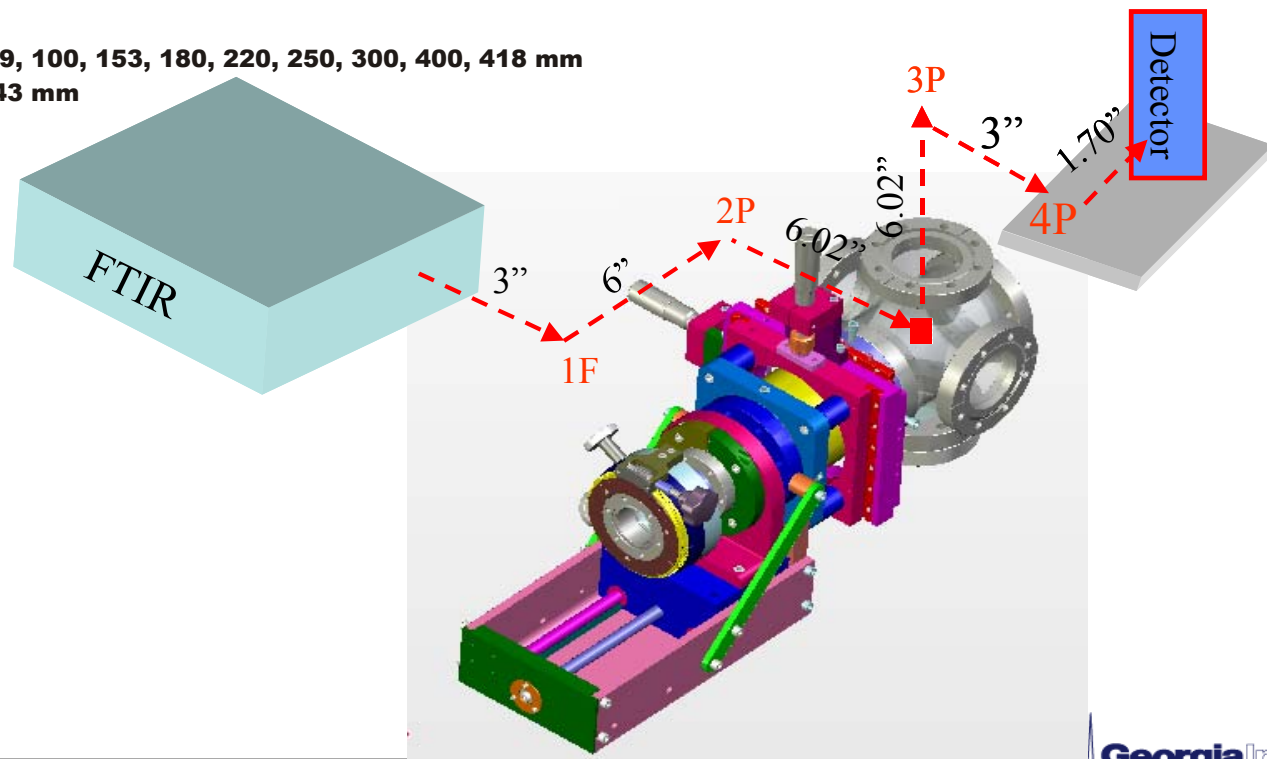
Other Tools for in-Situ Studies

- Probing and Mapping Surface Reactions using Raman Spectro-microscopy

- Tip Enhanced Raman Spectroscopy (TERS)

  – Combination of Raman and SPM

- Patterned Electrodes for Isolation of Reaction Sites
- Local (micro or nano-scale) measurement using SPM tips and patterned electrodes; TERS, Raman mapping

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Raman Spectra of LSC in a Controlled Atmosphere

Intensity (a.u.)

Wavenumber (cm^{-1})

Legend:
- O2 RT-H2
- H2 RT-H2
- H2 RT
- O2 RT
- Ar RT

200   700   1200   1700

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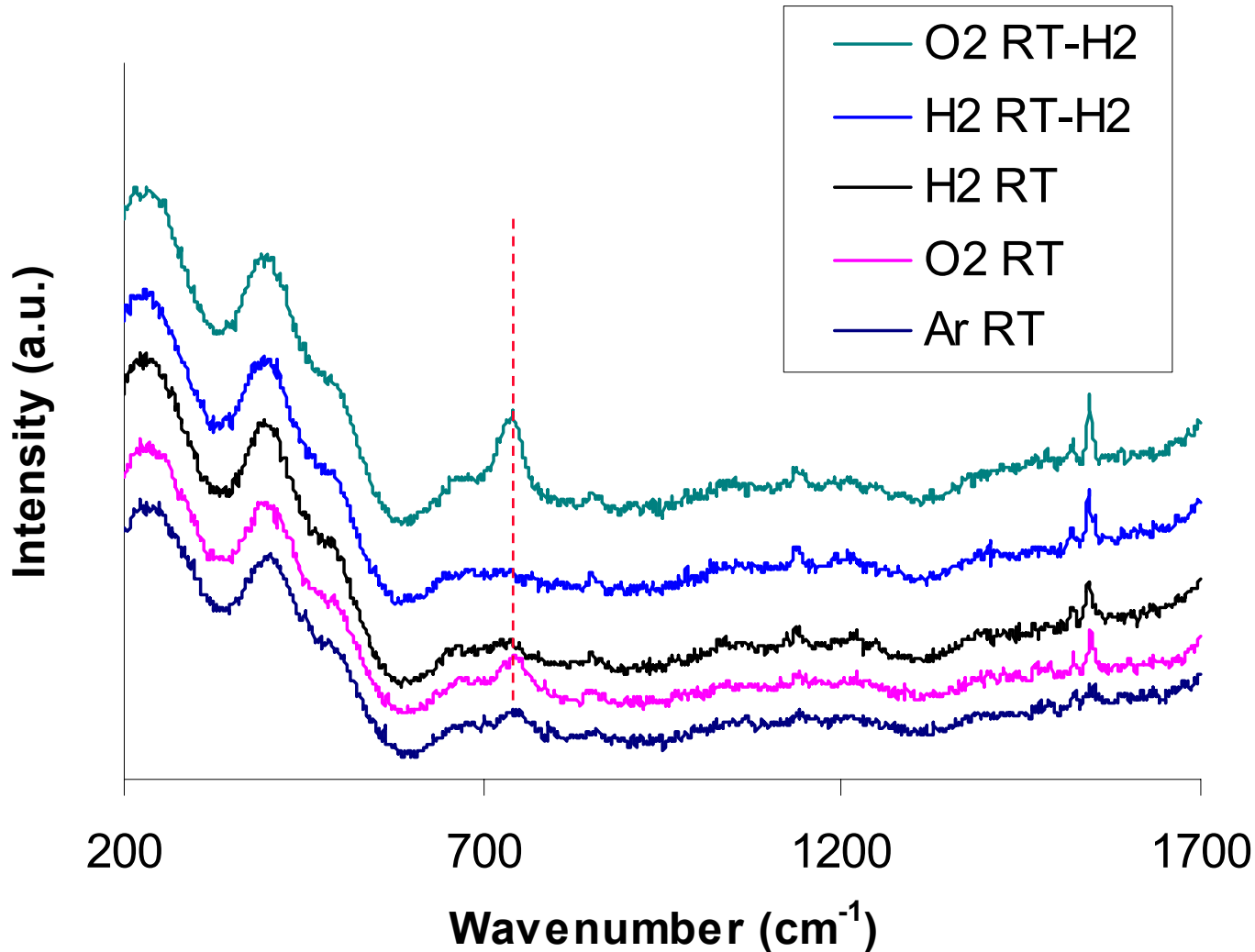
Raman Spectra of Cobalt Compounds in Air
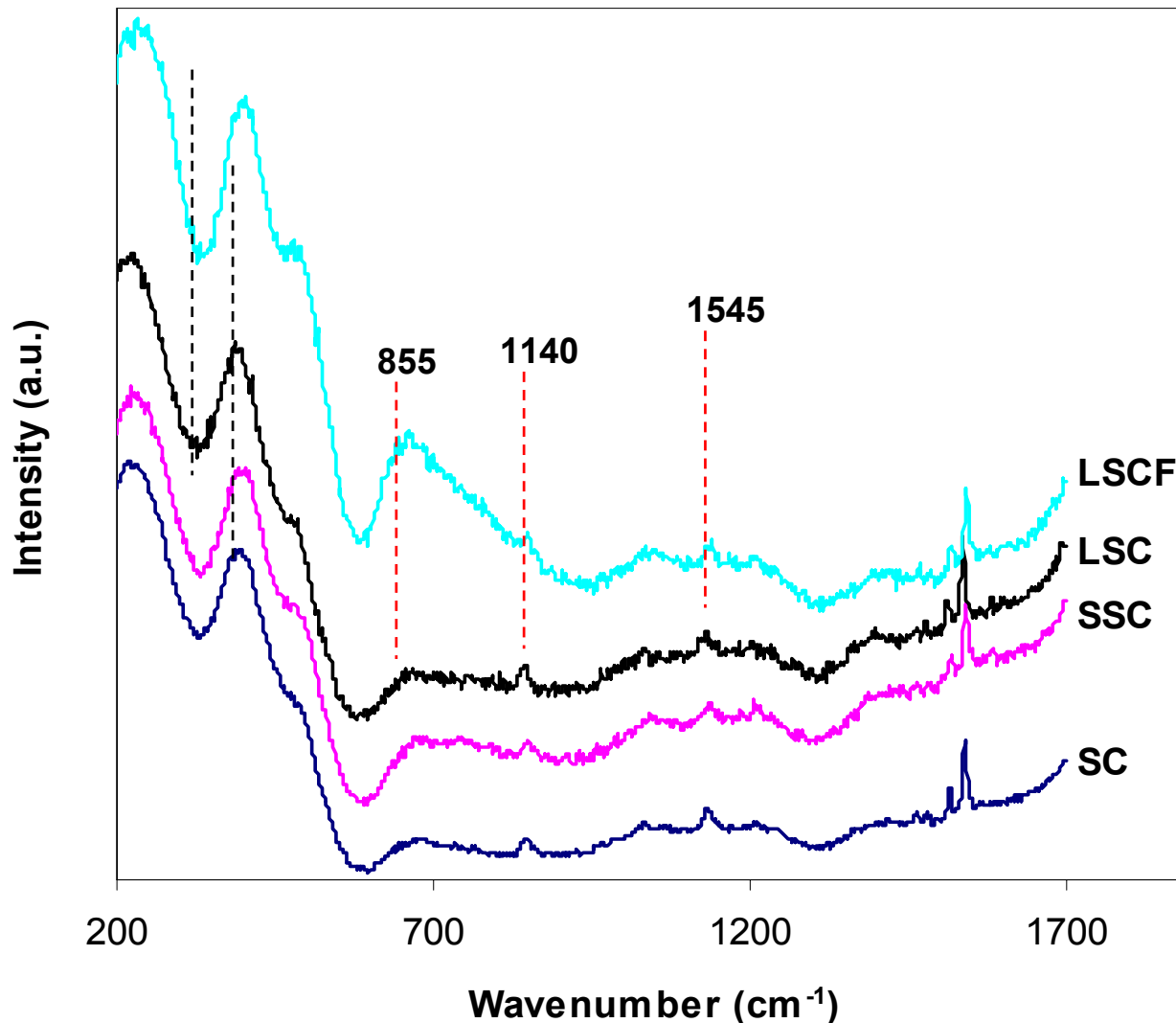
- 3 types of oxygen species are observed

- But the peaks are week

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Tip-Enhanced Raman Scattering (TERS)

Objective lens

Illumination

**Nano-sized
Au, Ag or Cu tip**

SERS

e^- e^-

Sample

SERS Mechanism

within 200 fs

e–e

adsorbed
molecules

Fermi
level

Excitation

e–p

acceleration

d-orbital
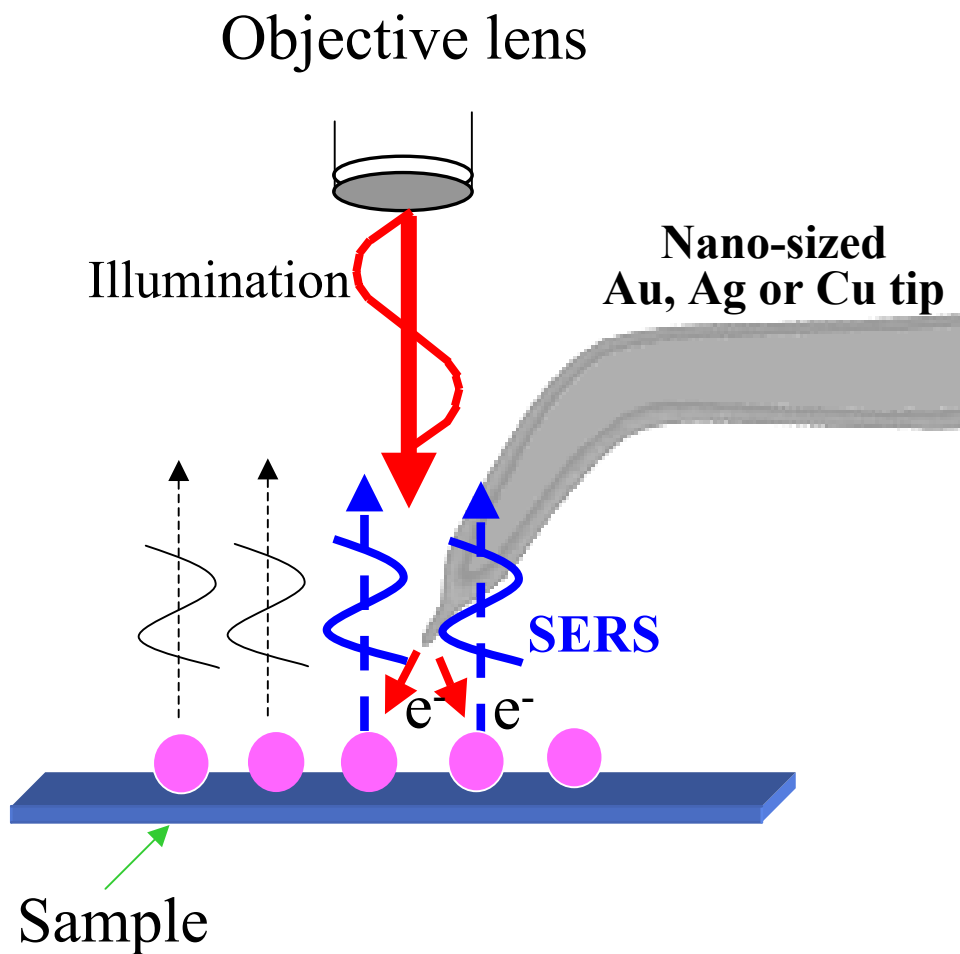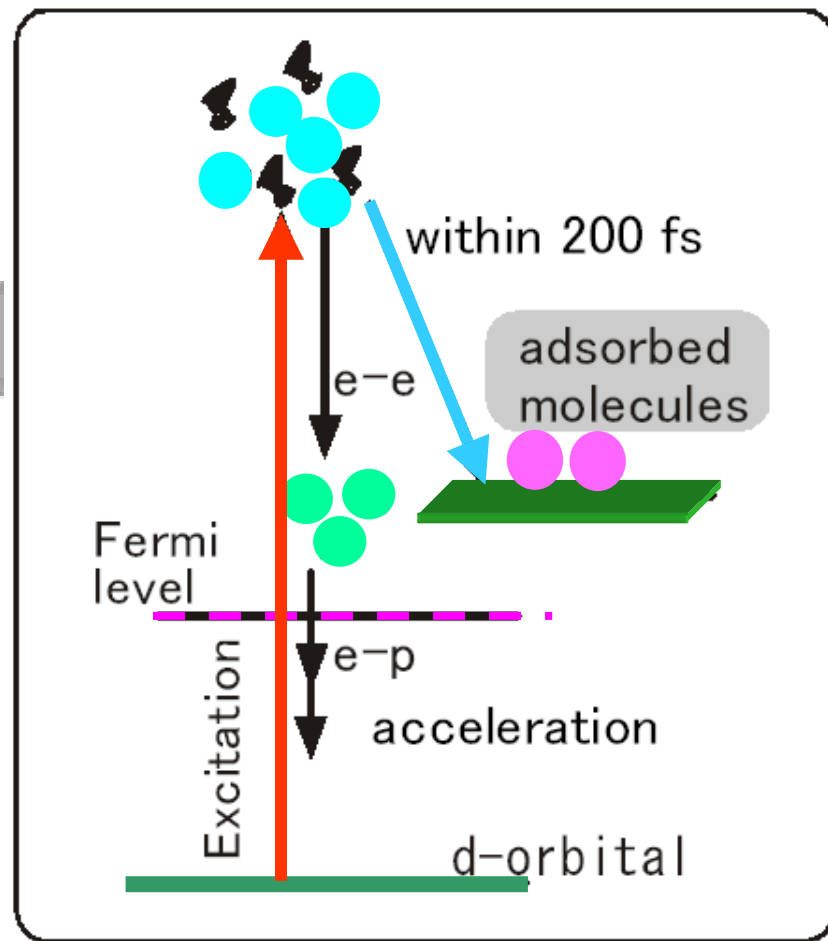
K. SHIBAMOTO, et al., ANALYTICAL SCIENCES 2001, VOL.17 SUPPLEMENT

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Objective

Scanners

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Schematic Arrangement for TERS
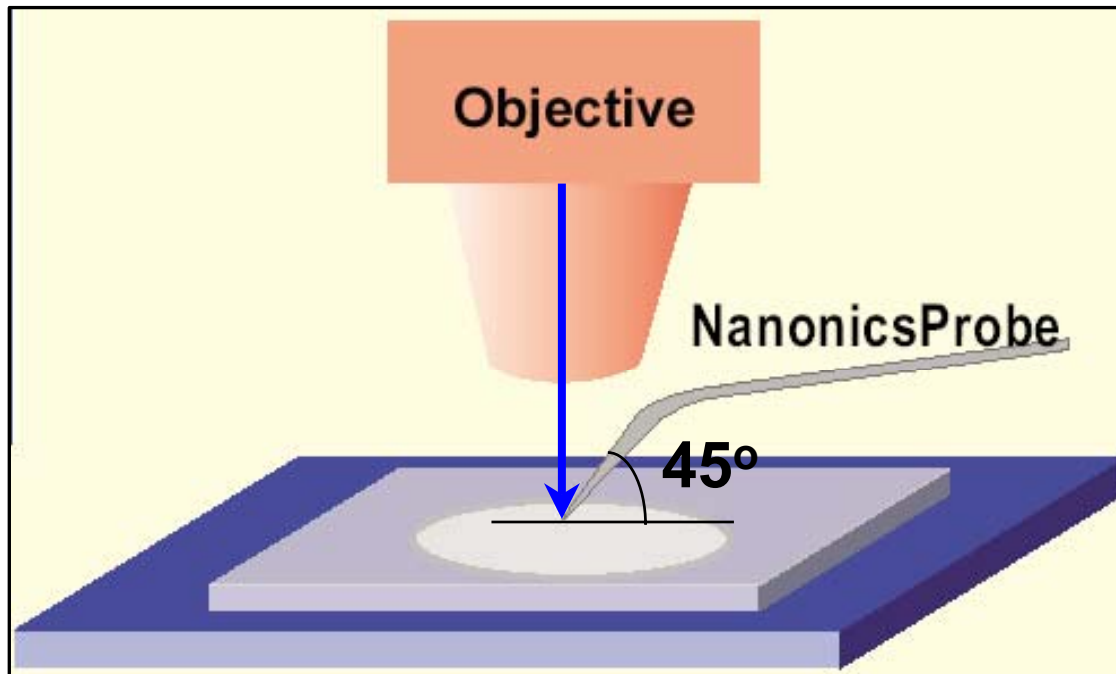
- Tip with Ag coating and small diameter (50 nm) for TERS
- Tuning fork technology removing the interruptions of other laser source

Unique Capabilities:
Spatial Resolution: up to 50 nm
Very Sensitive to the Chemical Nature of Surfaces

Functionally Graded Electrodes

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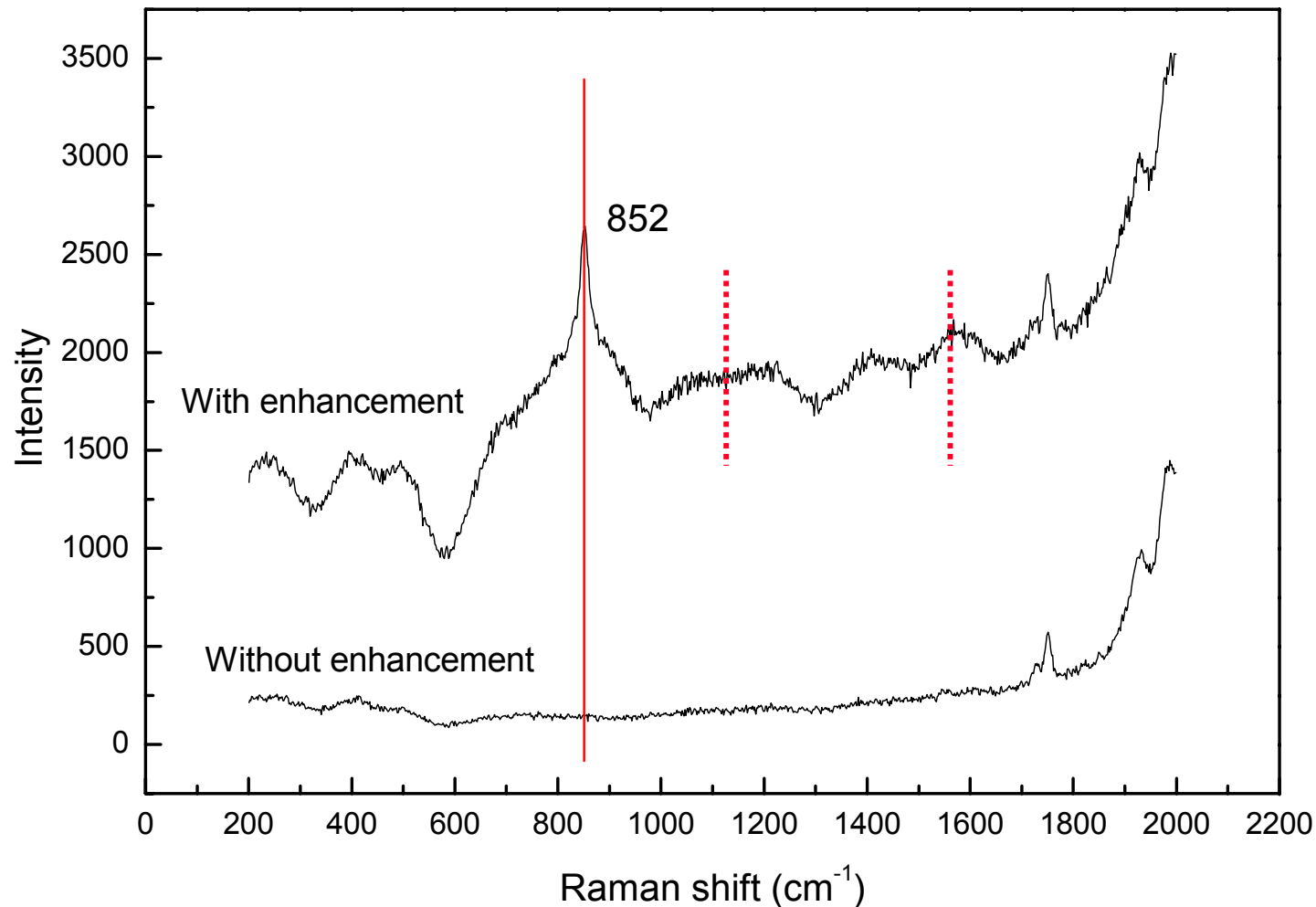
Capabilities of Our System

TERS
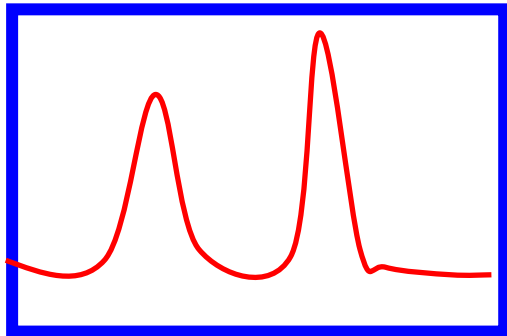
Raman Mapping

To be
Obtained
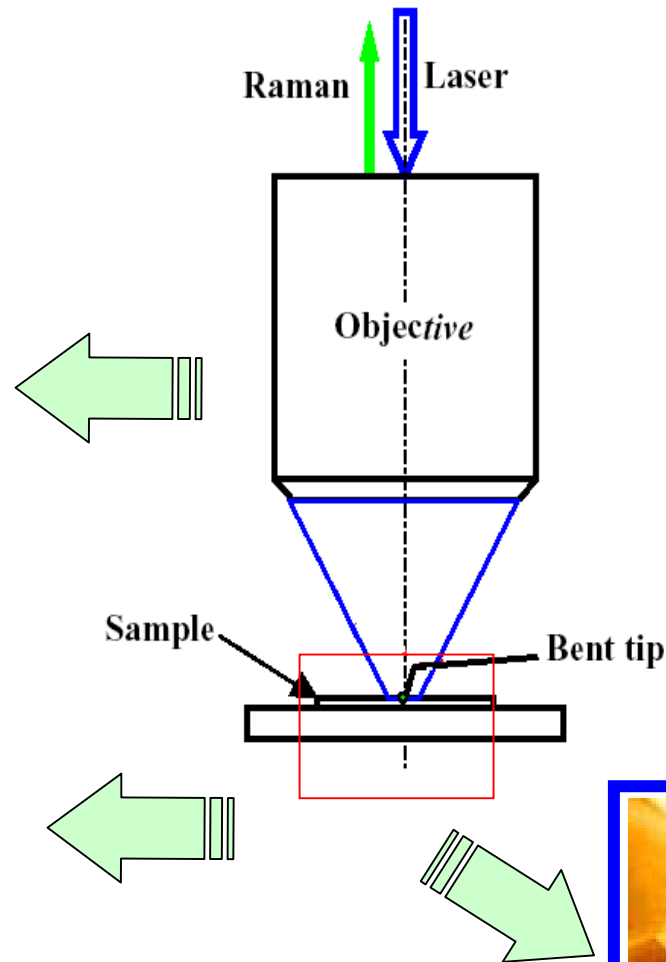
Raman   Laser

Objective

Sample   Bent tip

AFM Image
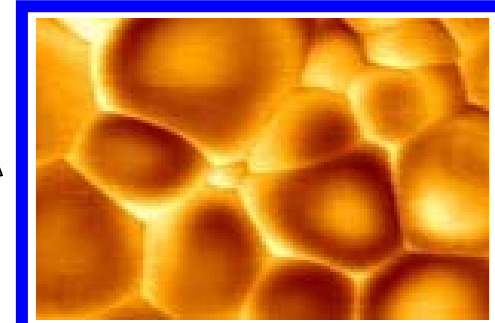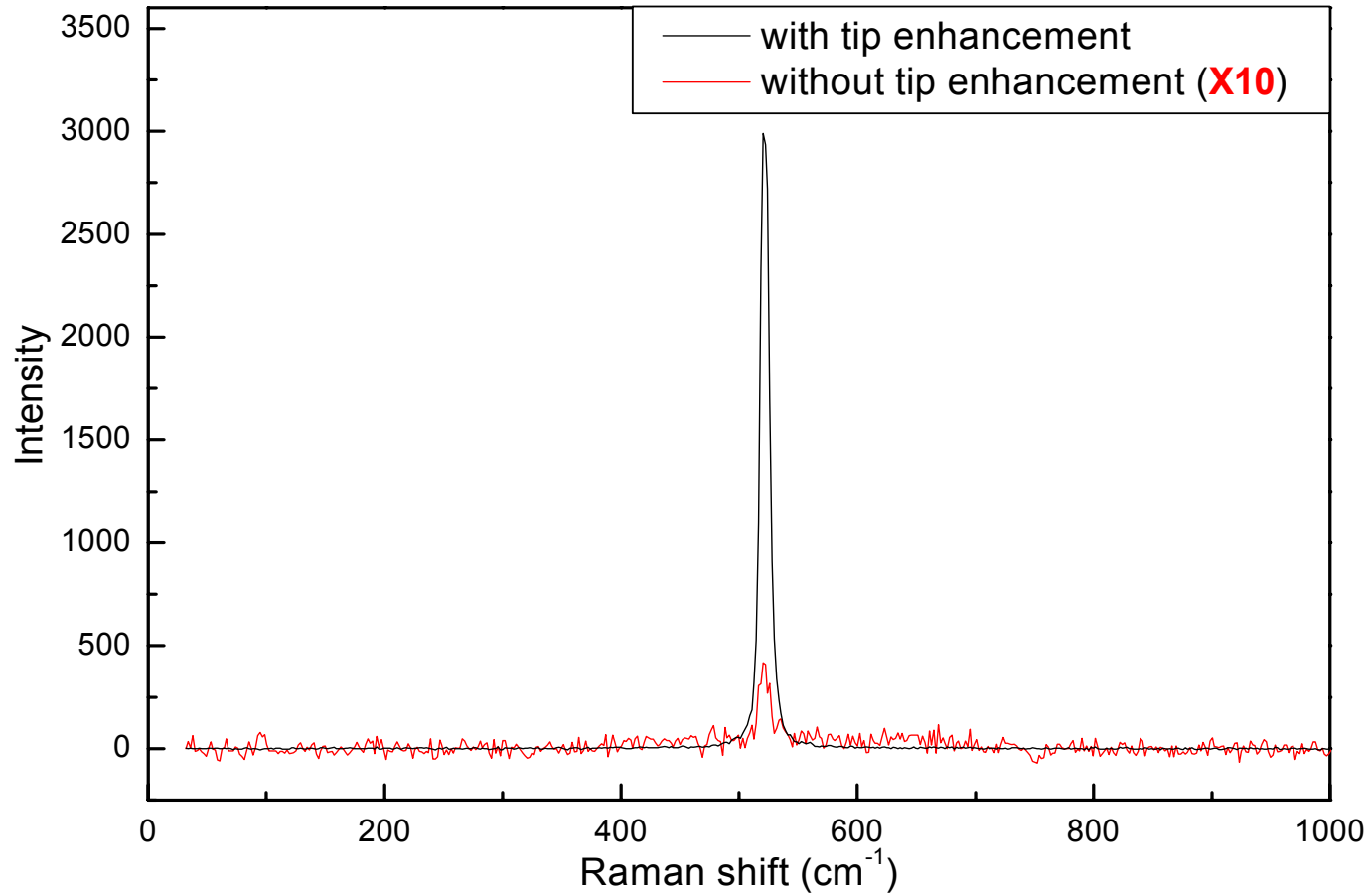
Peroxide species (O_2^{2-}) on LSM surface was **not observable with ordinary Raman or FTIR**, but **observable with TERS**. Mechanism on LSM is different from that on SSC or LSC

TERS: Carbon deposited on YSZ
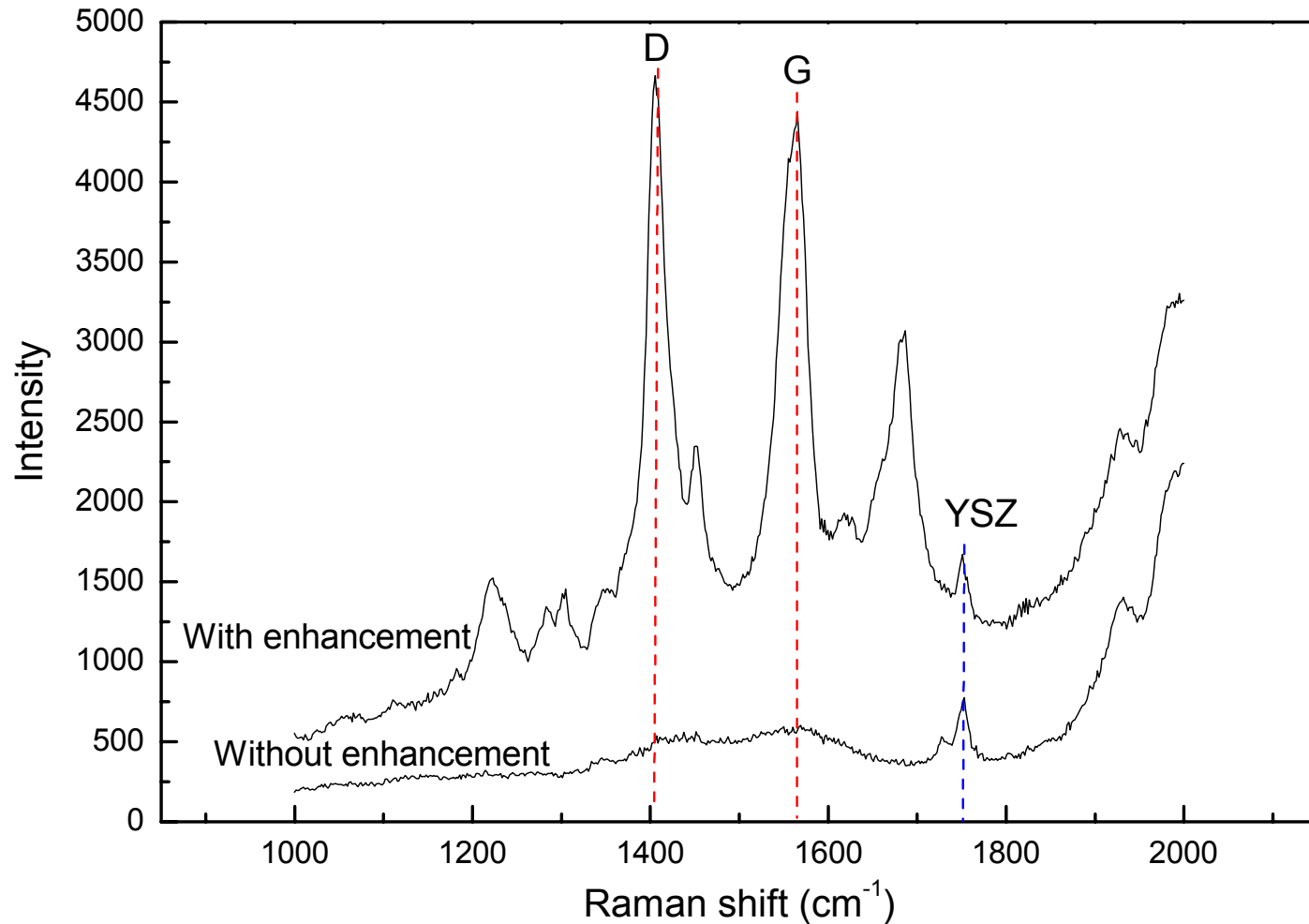
Preliminary results: The Raman intensities of the G and D mode are dramatically enhanced by the AFM tip.
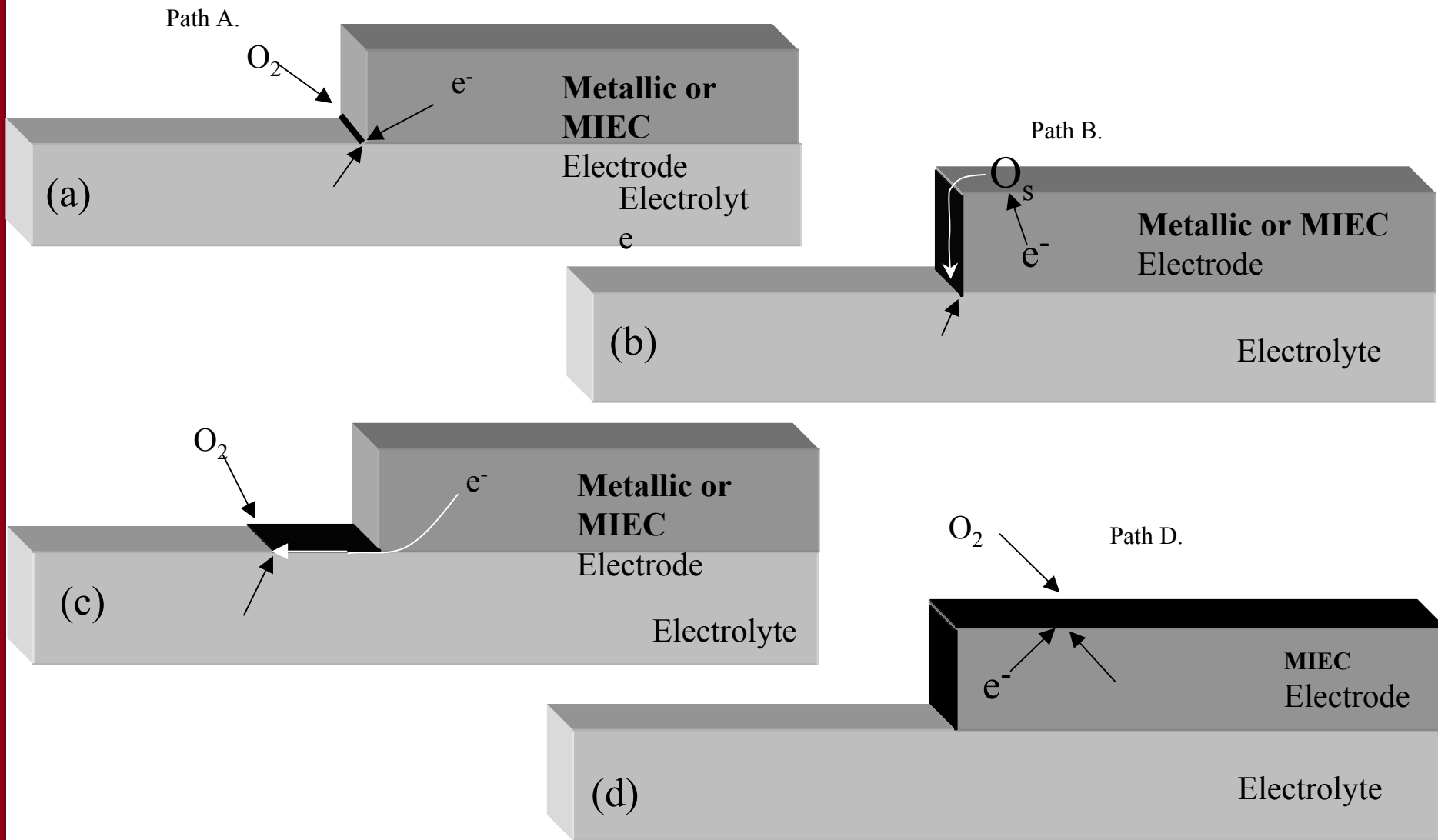
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TERS – A Sensitive Surface Probe

- Dramatically enhanced sensitivity to surface species (up to 10^8)

- Increased spatial resolution (up to 20 nm) for mapping of active sites for electrode reactions

- Unlike IR, TERS is not influenced by gas phase H_2O and CO_2 and especially sensitive to carbon and sulfur, making it a powerful tool for investigation of fuel reforming and anodes of SOFCs running on hydrocarbon fuels (e.g., gasified coal)
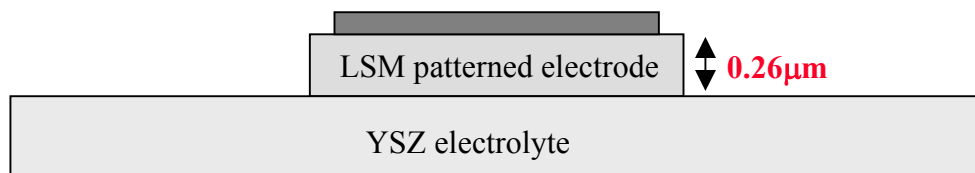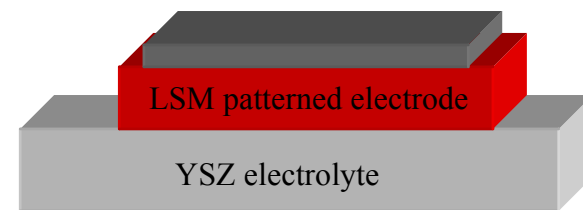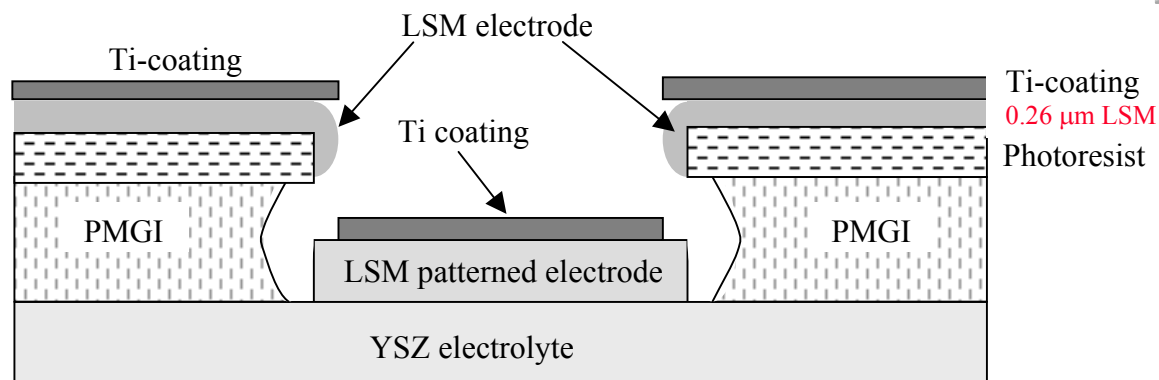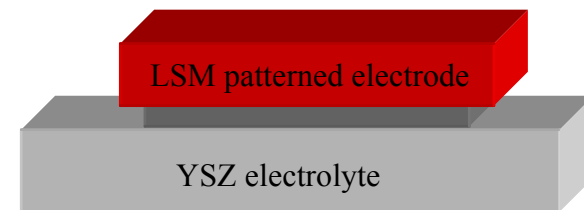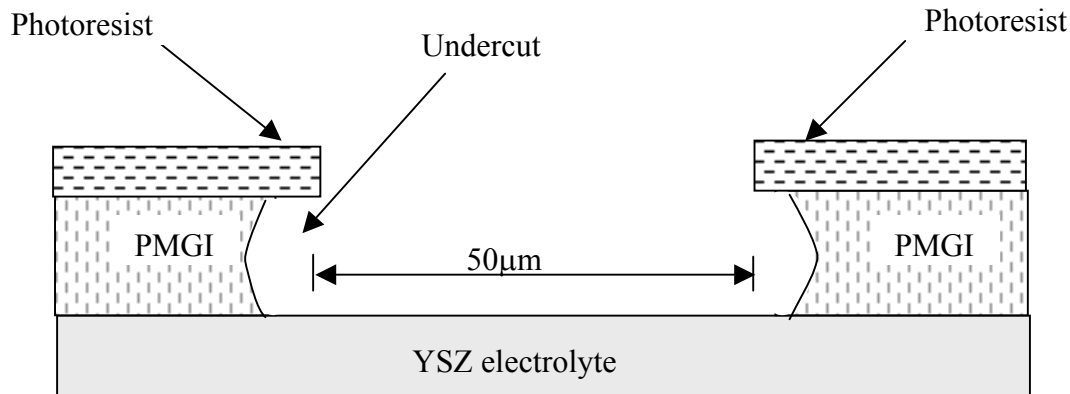
Functionally Graded Electrodes

Patterned Electrodes

- Patterned electrodes with the length of TPB varying in 4 orders of magnitudes

- Patterned electrodes with some reaction sites selectively blocked

- Combination of patterned electrodes and SPM tip for performing local (micro- to nano-scale) electrochemical measurements

Path A.

O$_2$

e$^-$
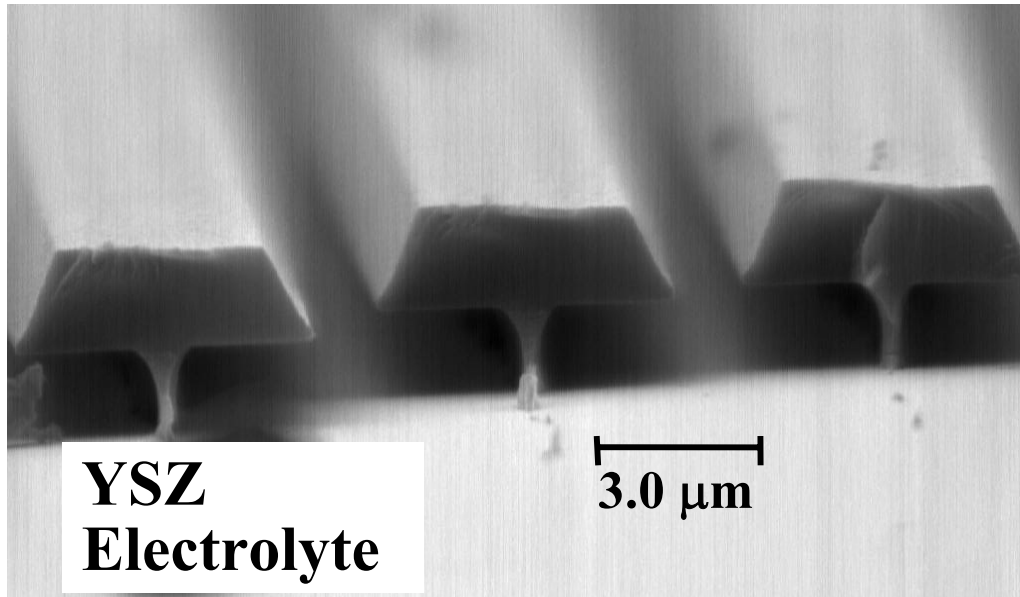
Metallic or MIEC
Electrode

Electrolyte

(a)

Path B.

O$_s$

e$^-$

Metallic or MIEC
Electrode

Electrolyte

(b)

O$_2$

e$^-$

Metallic or MIEC
Electrode

Electrolyte

(c)

O$_2$

Path D.

MIEC
Electrode

e$^-$

Electrolyte

(d)

Functionally Graded Electrodes

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A Photolithographic Process for Isolation of Reaction Sites

Photoresist

Undercut

Photoresist

PMGI

50μm

PMGI

YSZ electrolyte

LSM patterned electrode

YSZ electrolyte

LSM electrode

Ti-coating

Ti coating

Ti-coating
0.26 μm LSM

Photoresist

PMGI

LSM patterned electrode

PMGI

YSZ electrolyte

LSM patterned electrode

YSZ electrolyte

LSM patterned electrode

0.26μm

YSZ electrolyte

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Typical Micrographs

YSZ Electrolyte

3.0 μm

0.26 μm x 50 μm

TiO₂

LSM Electrode

YSZ electrolyte

15.0kV   2.0 um
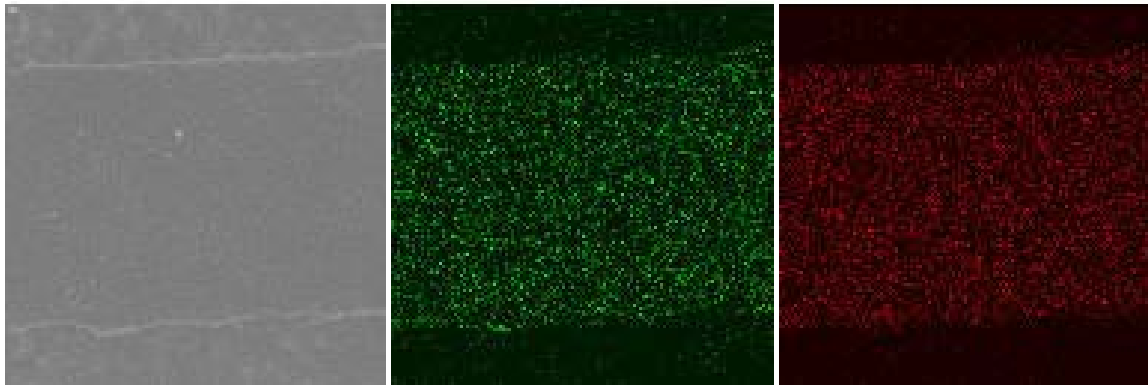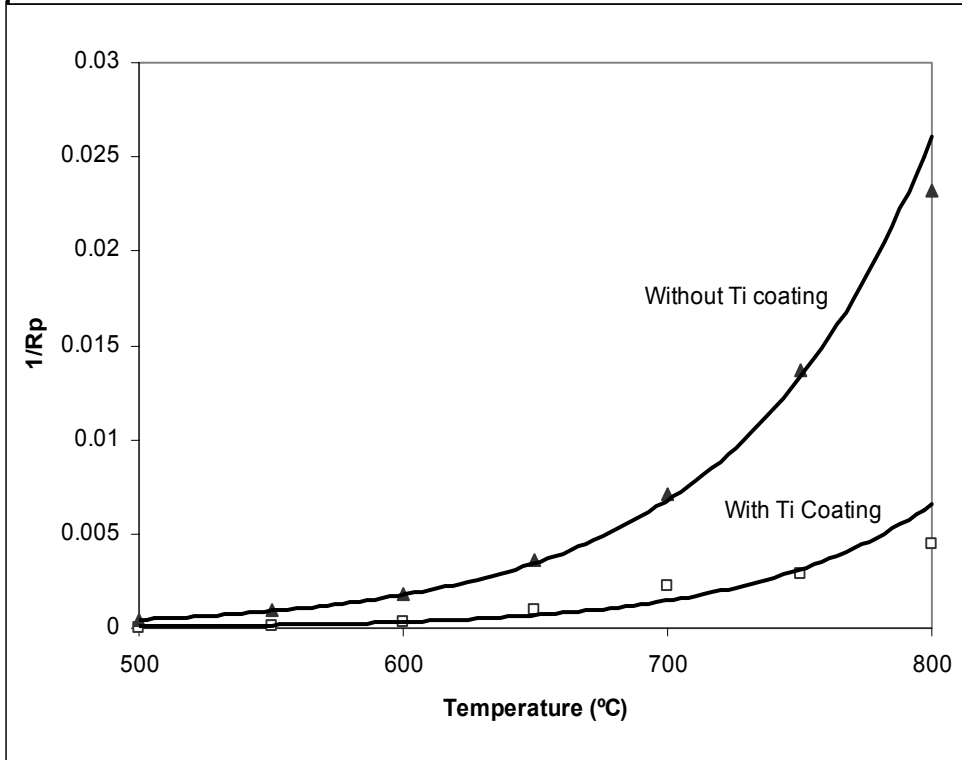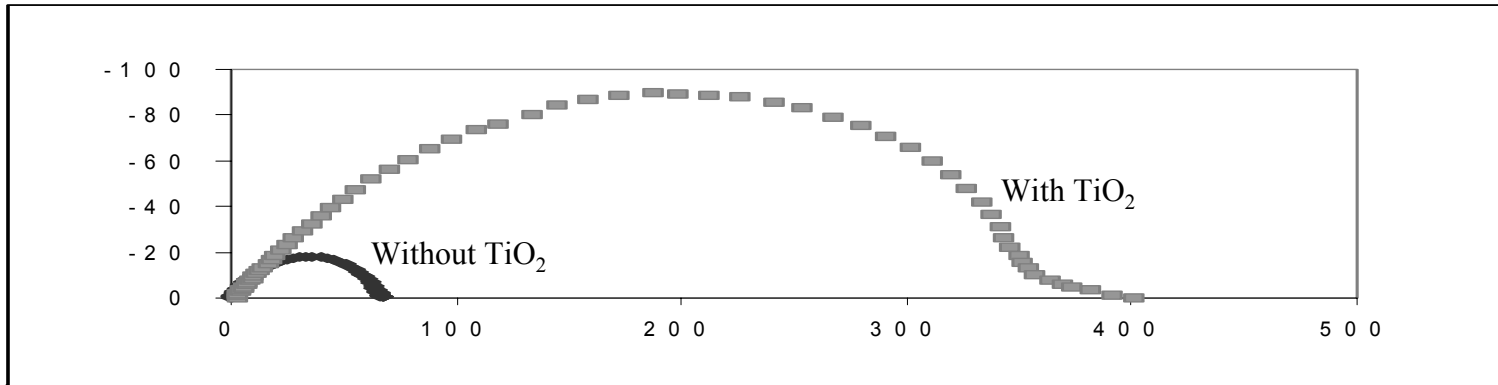
SEM   Mn   Ti

Functionally Graded Electrodes

Proof-of-Concept: Effect of Site Blocking

With TiO$_2$

Without TiO$_2$

1/Rp

Without Ti coating

With Ti Coating

Temperature (ºC)

- • The surface of the patterned (0.26x50μm) LSM electrode contributes significantly to oxygen reduction.

- • The micro-fabrication technique is effective in isolation of different reaction sites.

Functionally Graded Electrodes

Georgia Institute of Technology

Local Electrochemical Measurements

Impedance Analyzer

SPM Controller

Patterned Electrode
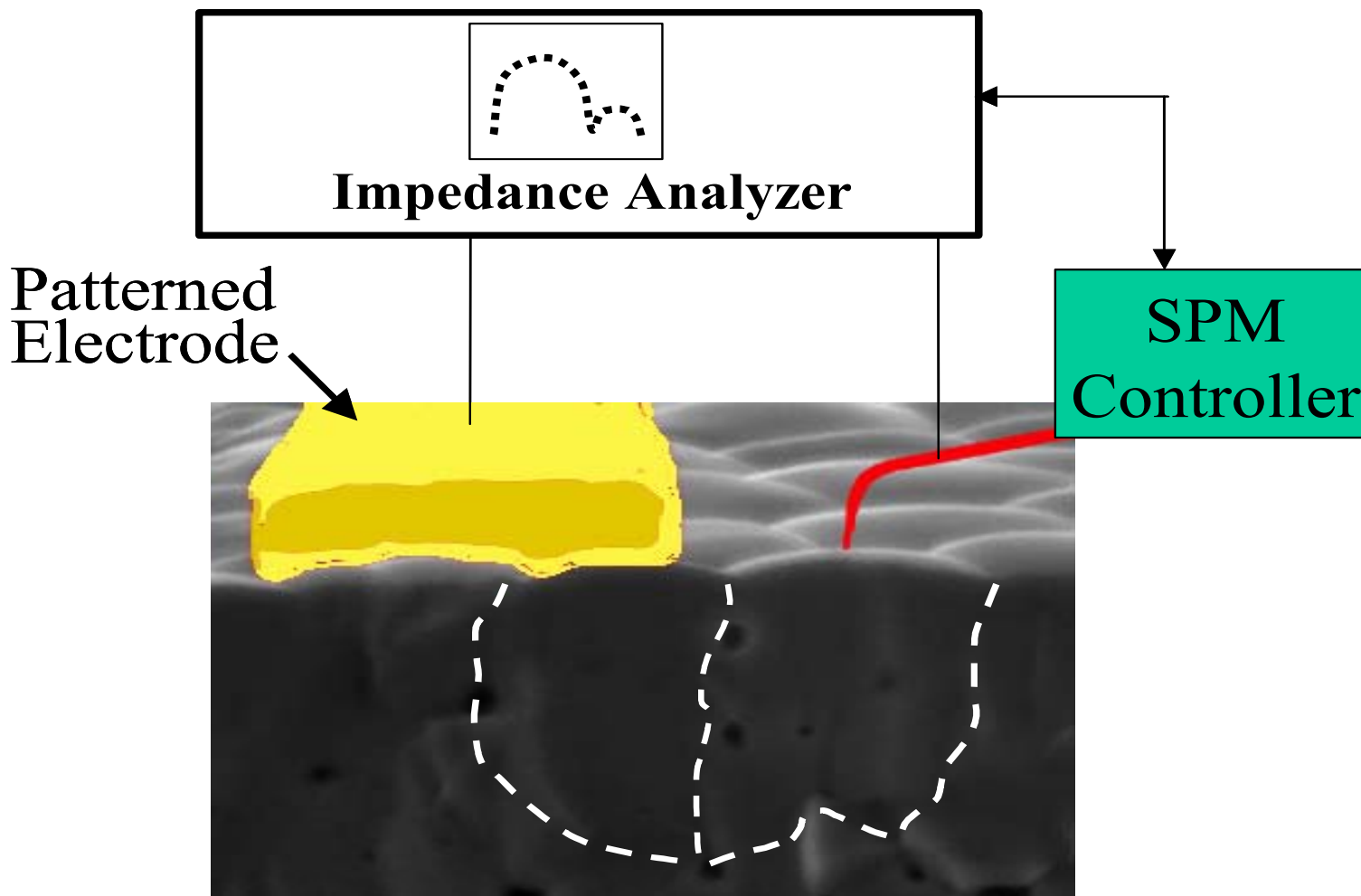
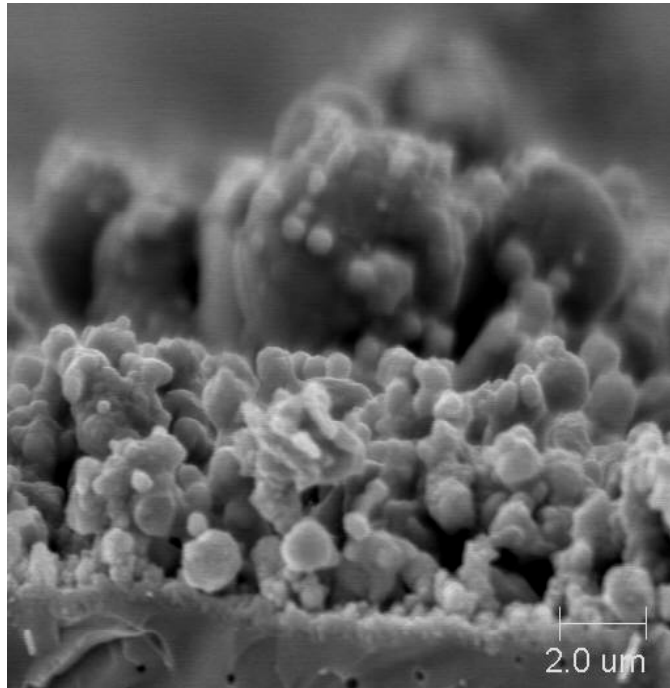**To probe local properties using impedance spectroscopy performed on an SPM tip and patterned electrodes with micro- or nano-scale spatial resolution**

Functionally Graded Electrodes

Georgia Institute of Technology

Impedance Analyzer

Patterned Electrode

1

2
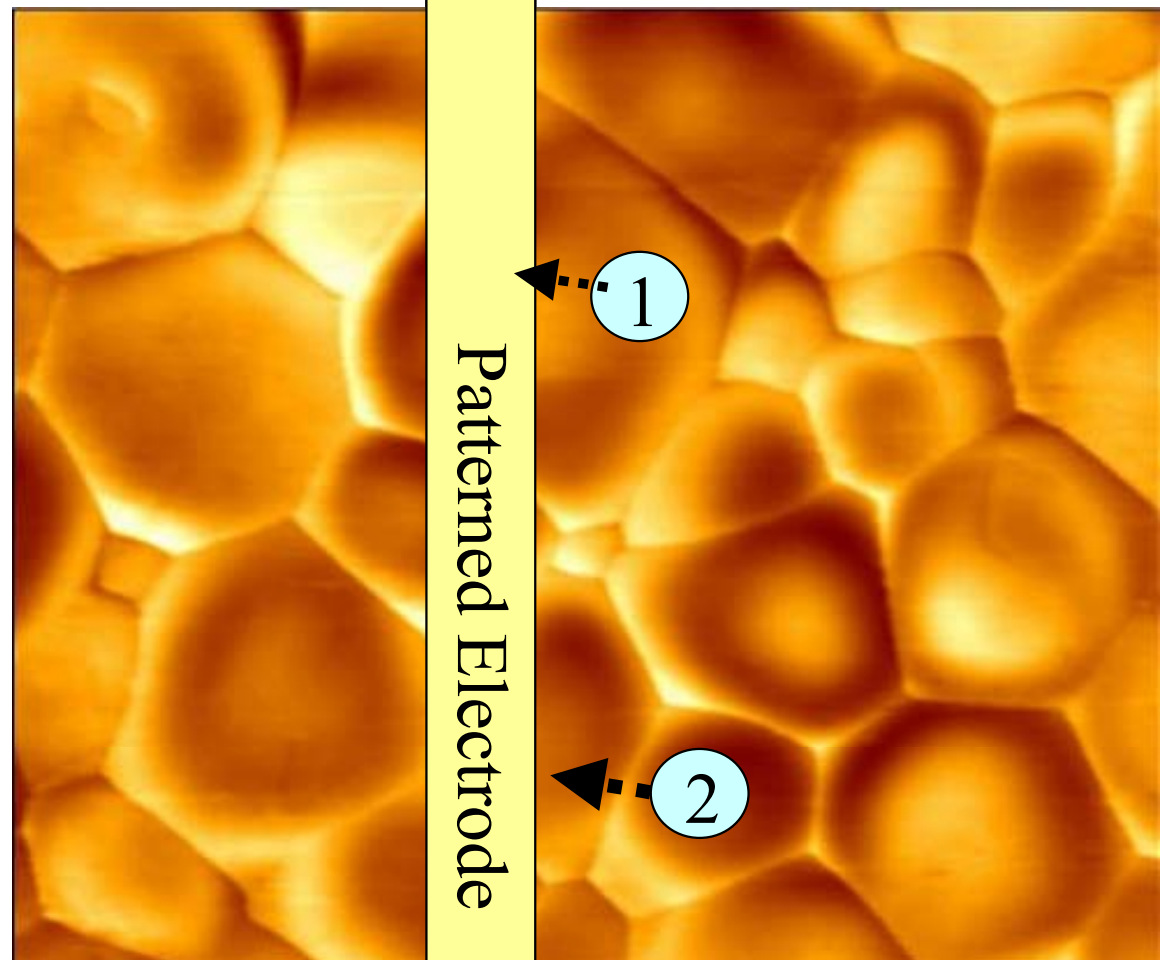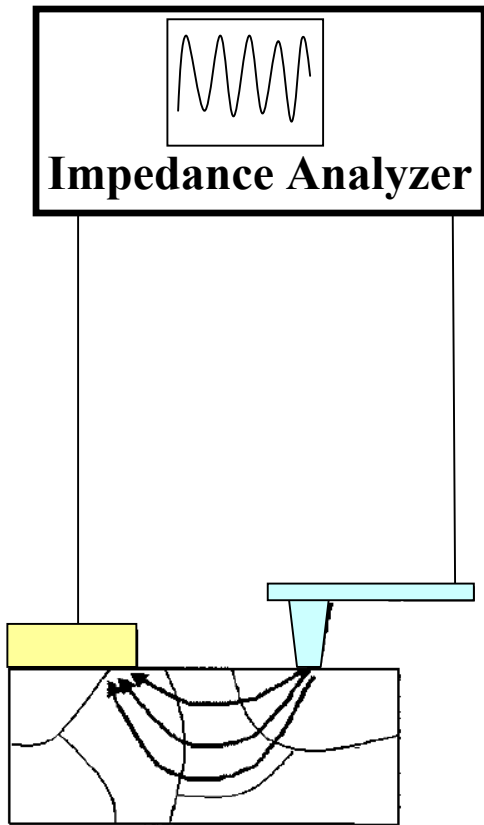
LSC

70 wt.% LSC+30 wt.% GDC

GDC

YSZ
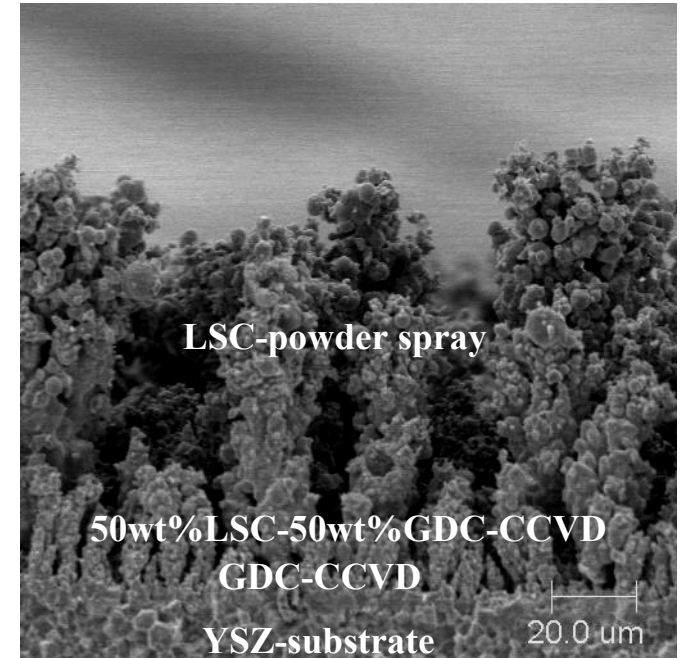
LSC-powder spray

50wt%LSC-50wt%GDC-CCVD
GDC-CCVD

YSZ-substrate

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Applicability to SOFC Commercialization

- **Generated some basic understanding of electrode reaction mechanisms**

- **Developed new tools for in-situ determination of electrode properties under practical conditions**

- **Rational design of efficient electrodes**

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Activities for the Next 12 Months

1) **Oxygen isotrope exchange experiments in UHV chamber for study of detailed reaction mechanisms using vibrational spectroscopy**

   - **FTRI, pd-FTIR, Rapid Scan FTIR**

   - **TERS and Raman Mapping**

2) **Refined calculations of vibrational spectra for different cathode materials to assist interpretation of FTIR and Raman data for different electrodes**

   - **Oxygen reaction mechanism and kinetic parameters**

   - **Bulk properties such as vacancy concentration and transport properties**

3) **Local measurements using SPM tips and patterned electrodes to probe local properties under in-situ conditions**

4) **Optimize Templated Synthesis and Combustion CVD for Fabrication of FGEs**

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Functionally Graded Electrodes

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