Novel Electrodes for Low-Temperature SOFCs

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DOE/NETL – University Coal Program

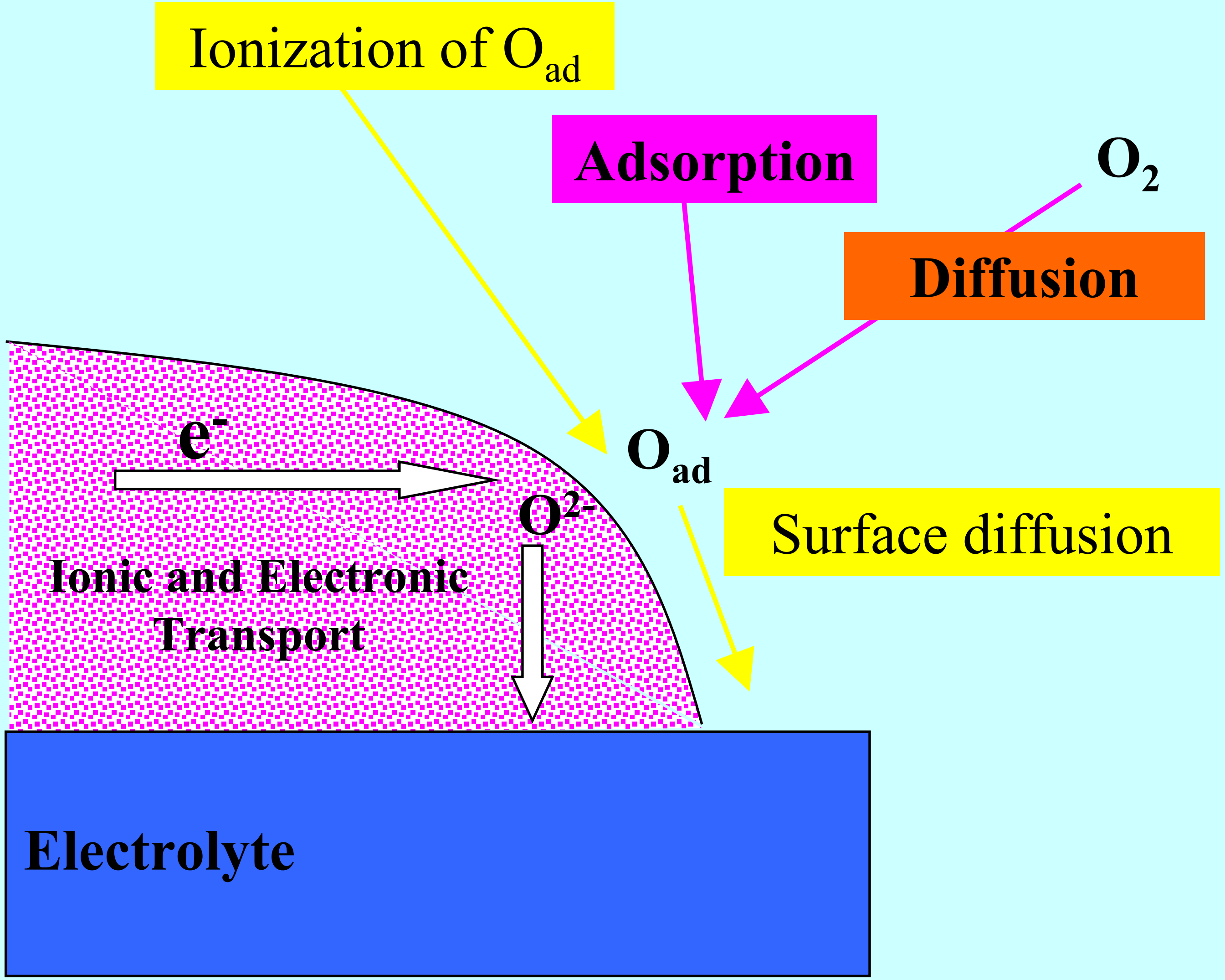
DARPA/DSO - Palm Power Program

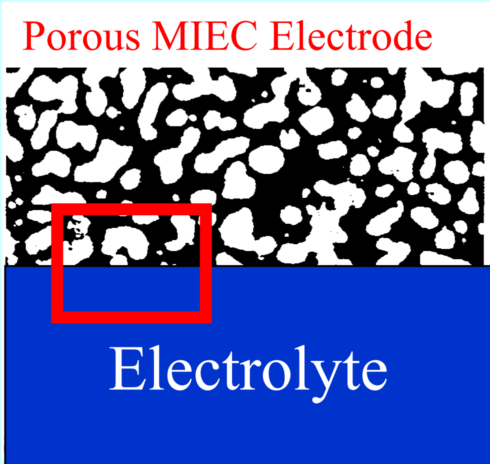
Outline

- **Introduction**
- **Program Objectives**
- **Technical Approach**
- **Results to Date**
  - Combustion CVD
  - In-situ potential dependent FTIR emission spectroscopy
  - Functionally Graded Electrodes
- **Summary**
- **Future Work**

Introduction: Electrode Processes

$$2e'(_{electrode}) + V_O^{\bullet\bullet}(_{electrolyte}) + \frac{1}{2}O_2(_{gas}) \rightarrow O_O^X$$





Modeling of Porous MIEC Electrodes

- In the Solid MIEC

$$J_k = -z_k F\left(\frac{u_k}{\tau_s}\right)\left[(1-p)c_k\right]\left(\nabla\mu_k + z_k F\nabla\phi\right)$$

- Through the Pores of MIEC

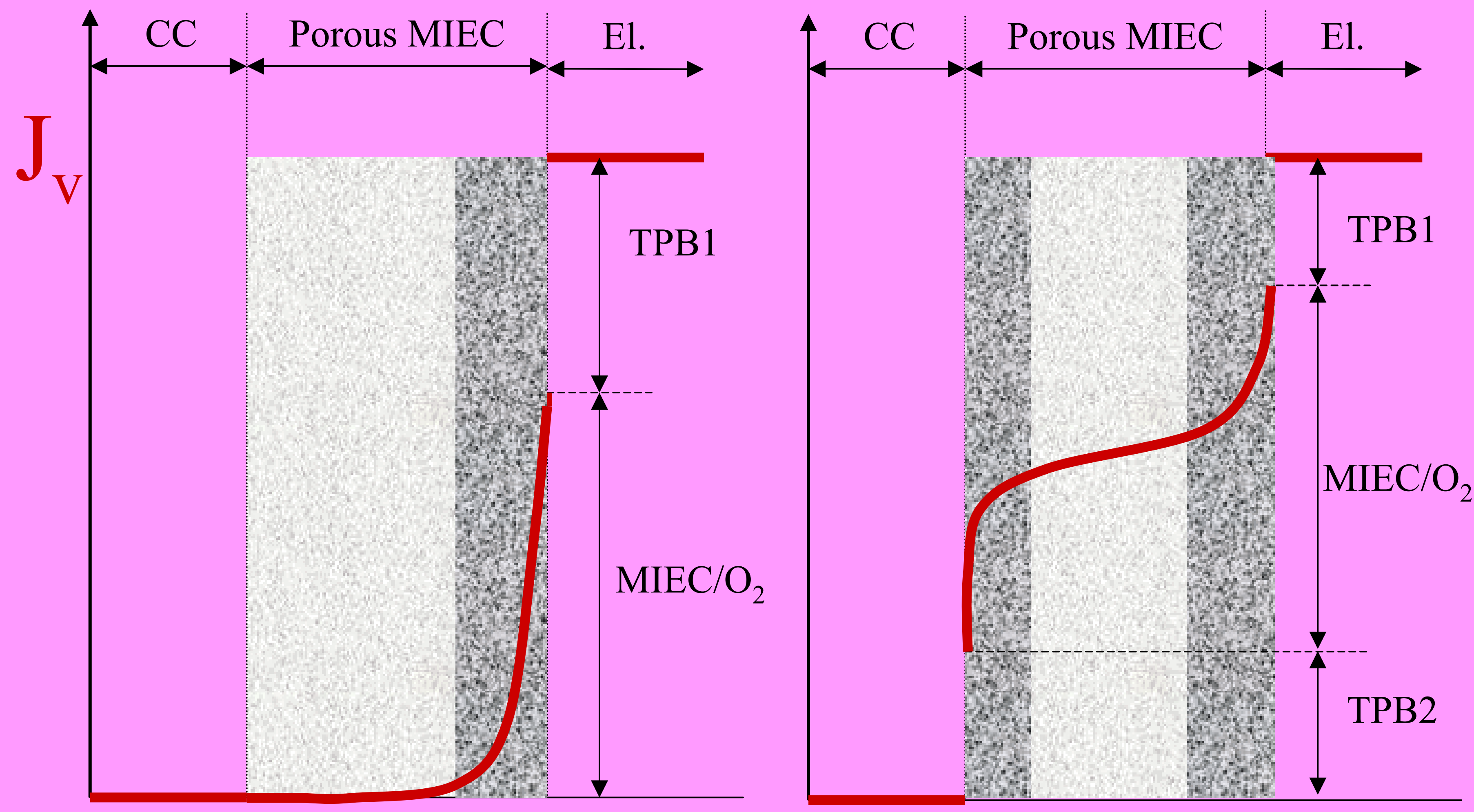
$$N_{O_2} = \left[-\left(\frac{u_{O_2}}{\tau_g}\right)\nabla\mu_{O_2} + v\right]\left(pc_{O_2}\right)$$

- At the MIEC/O_2 Interface & TPBs

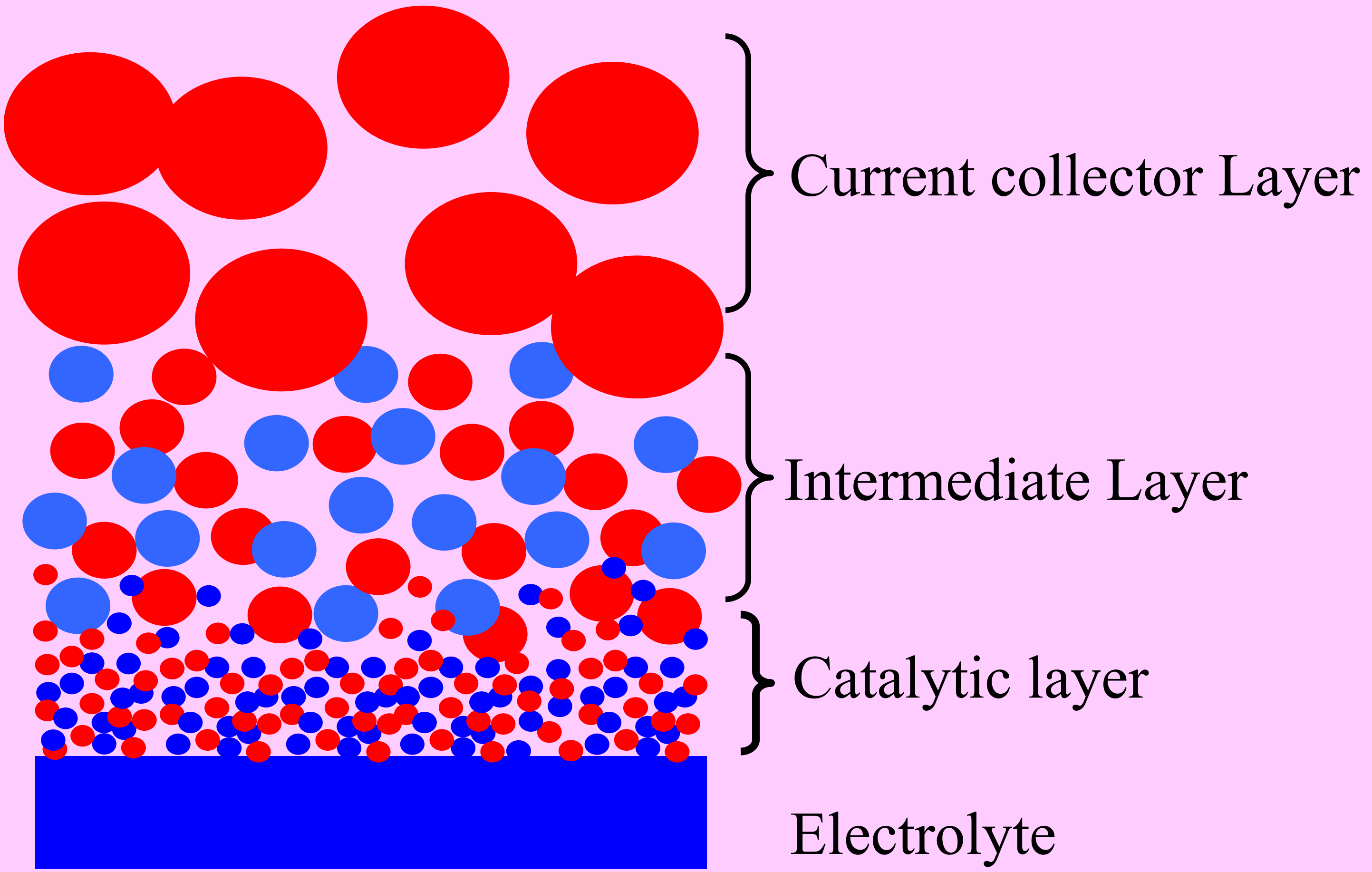
$$J_V = J_{0,V}\left\{\left(\frac{c_V^*}{c_V}\right)\exp\left(\frac{\alpha_a \Delta\tilde{\mu}_e}{RT}\right) - \left(\frac{p_{O_2}}{p_{O_2}^*}\right)^{\frac{1}{2}}\exp\left(\frac{\alpha_c \Delta\tilde{\mu}_e}{RT}\right)\right\}$$

Distribution of Reaction Rate

Useful Thickness



Functionally Graded Electrode



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Objectives

- To develop highly efficient electrodes at low temperatures
  - Inexpensive metallic components may be used
  - Greater system reliability & longer optional life
  - Potential for mobile applications
- To develop simple and cost-effective processes for fabrication of electrodes with desired microstructures

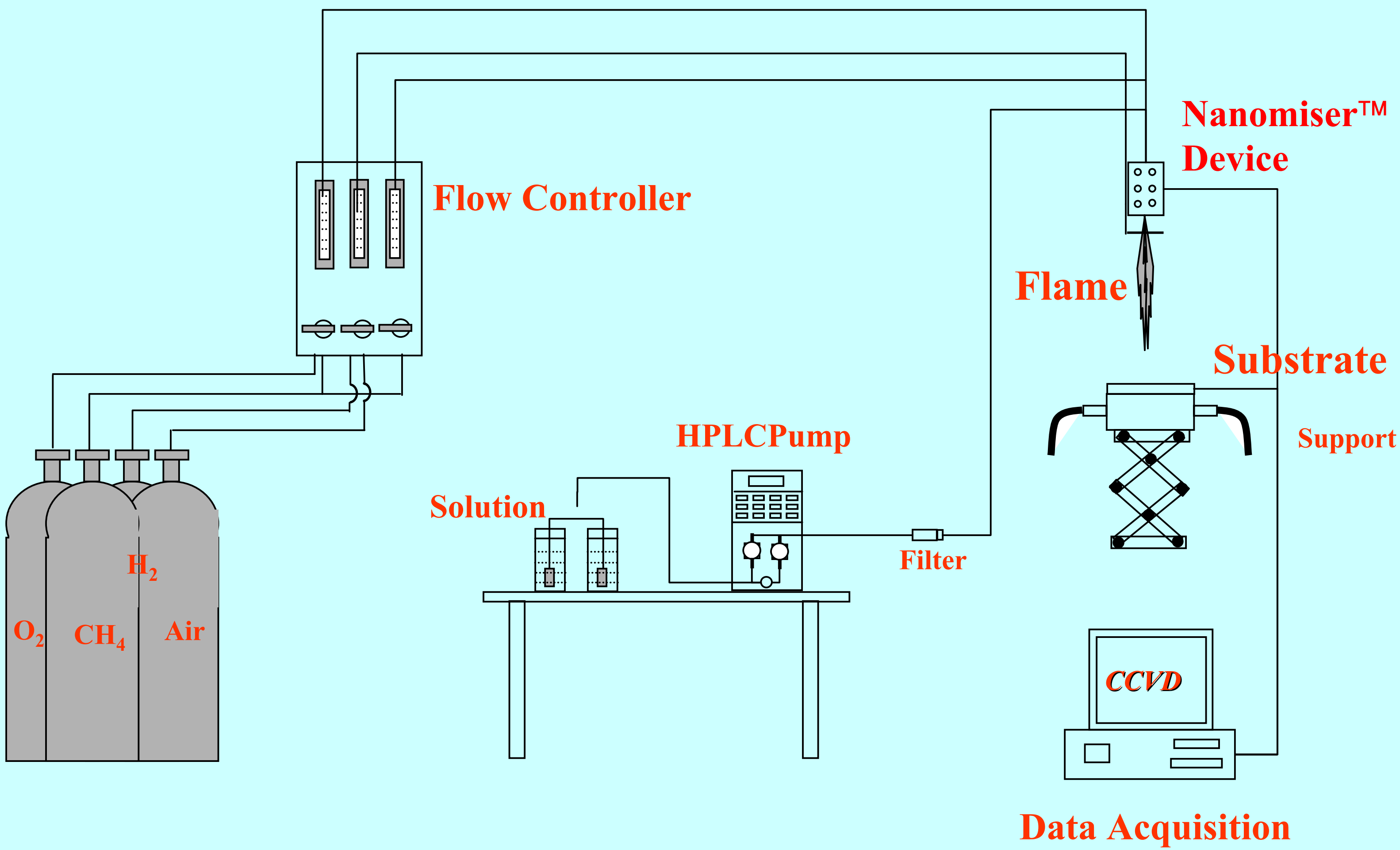
Technical Approaches

- Rational design of functionally graded electrodes
- In-situ characterization of electrode processes using FTIR emission spectroscopy and impedance spectroscopy (IS)
- Investigating effect of geometry (TPB & surfaces) using micro-fabricated patterned electrodes
- Fabrication of electrodes by combustion CVD

Results to Date

- Nano-particles fabricated by combustion CVD and electrodes modified by CCVD
- In-situ pd-FTIR emission spectroscopy and IS
  - Cathode: mechanism of oxygen reduction
  - Anode: Sulfur tolerance and carbon deposition
- Functionally graded electrodes on extruded honeycomb cells

Combustion CVD System



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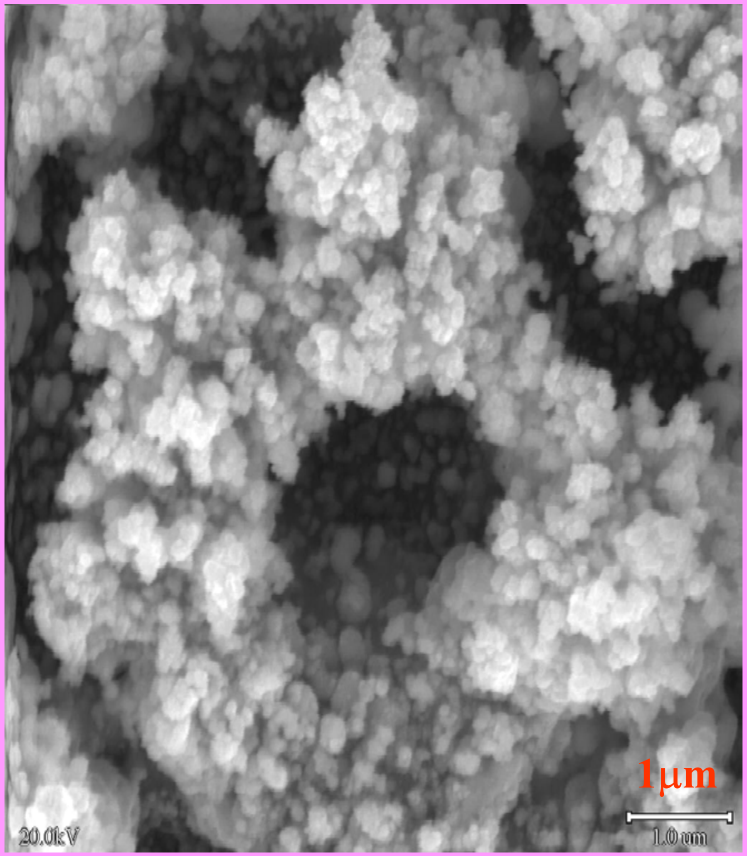
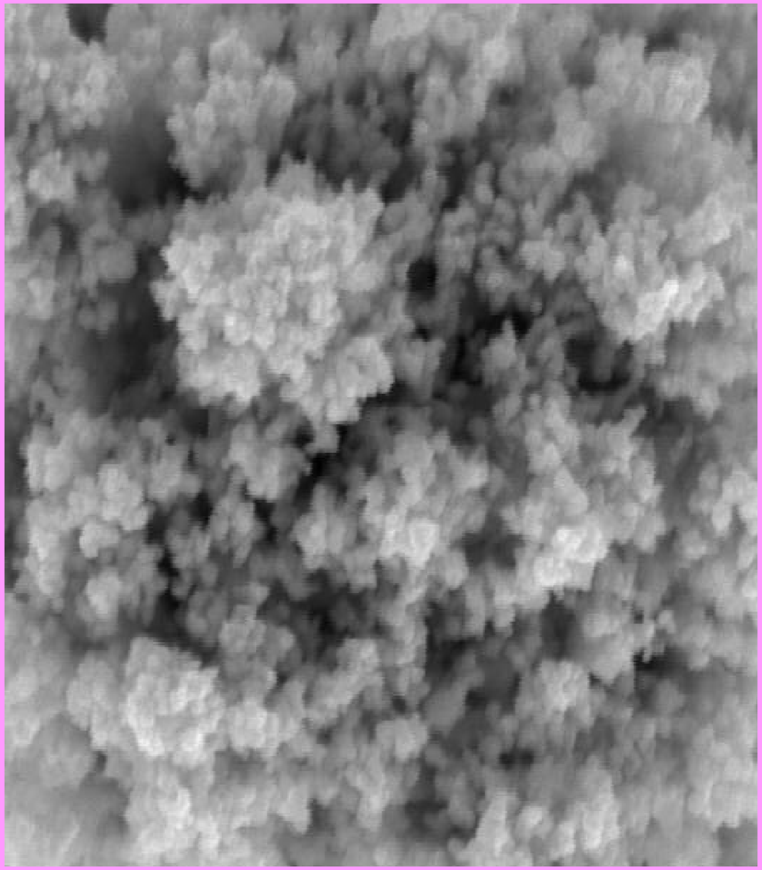
A Composite Electrodes





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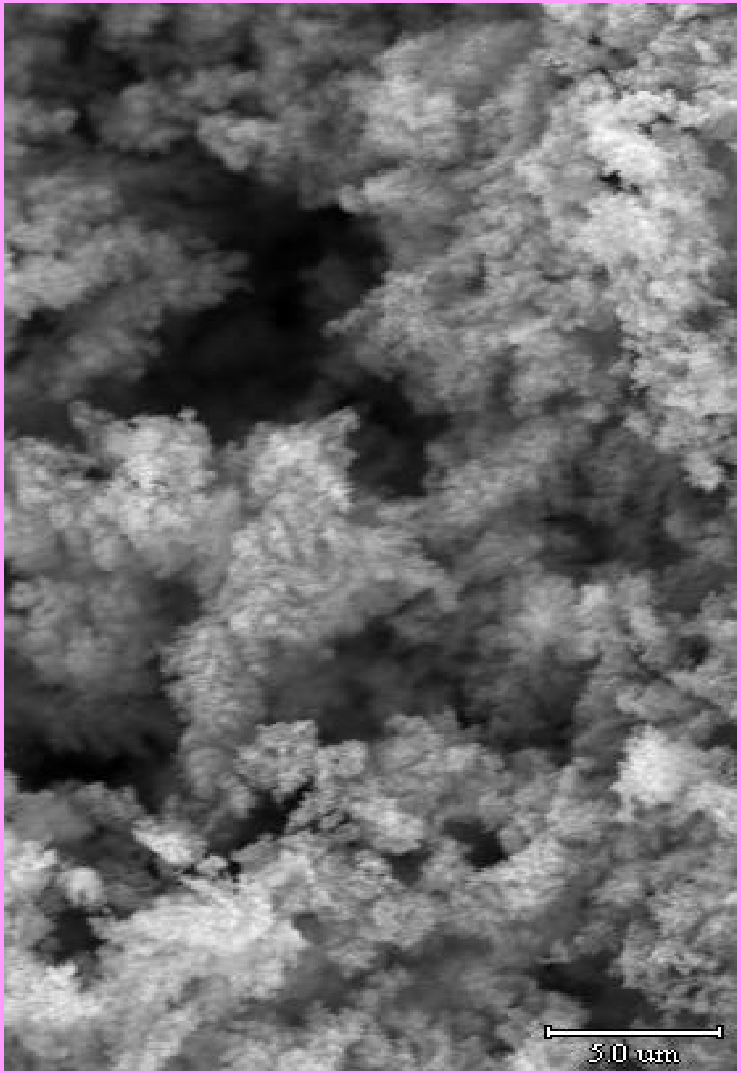
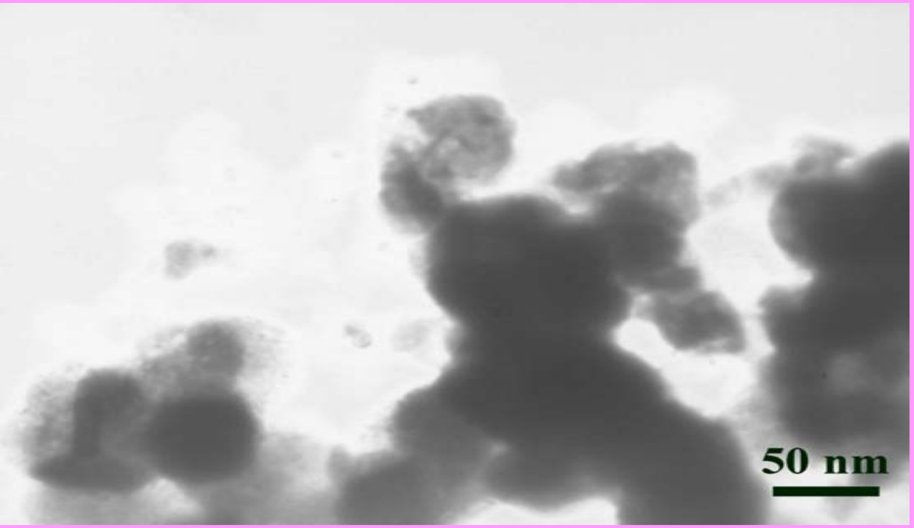
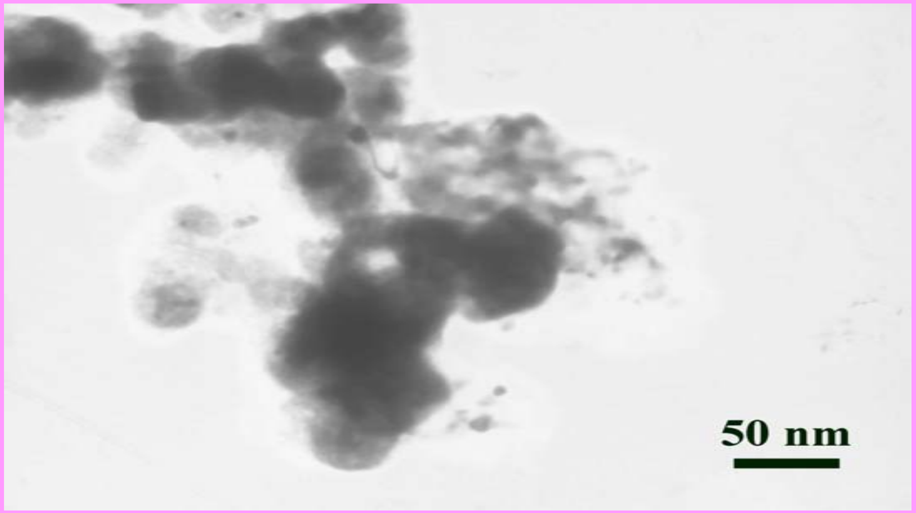
Nano-Structured Electrodes







In-situ Characterization of SOFCs using pd-FTIR ES and IS

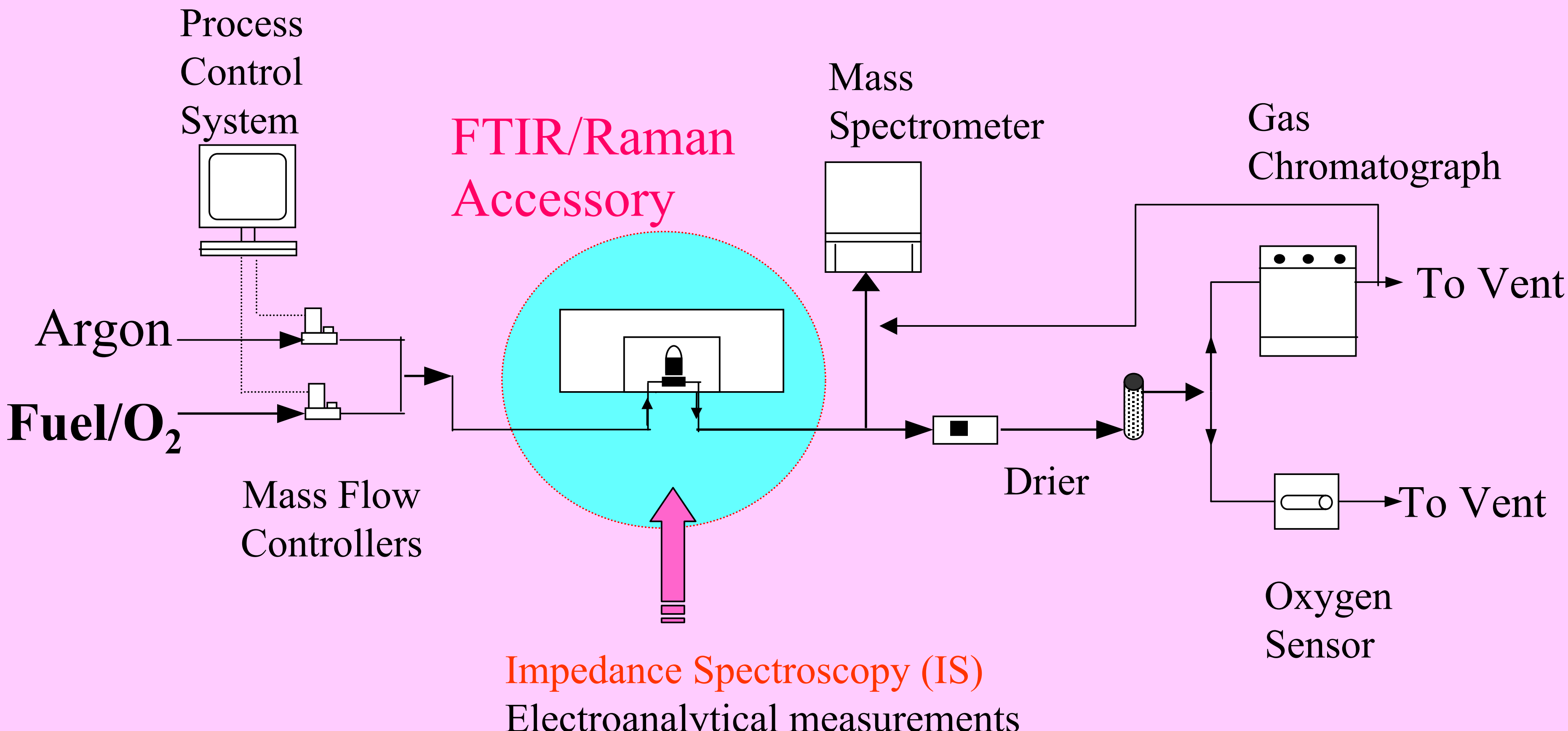
To understand elementary steps involved in electrode reactions in SOFCs;

To provide surface structural details under conditions for actual fuel cell operation; and

To rationalize the pd-FTIRES and Impedance spectra correlated to other data with the types of the intermediate species found at the functional interfaces.

Experimental Arrangements for

Investigations into SOFC Reactions Using *in-situ* FTIR-ES, Raman, MS/GC, and IS



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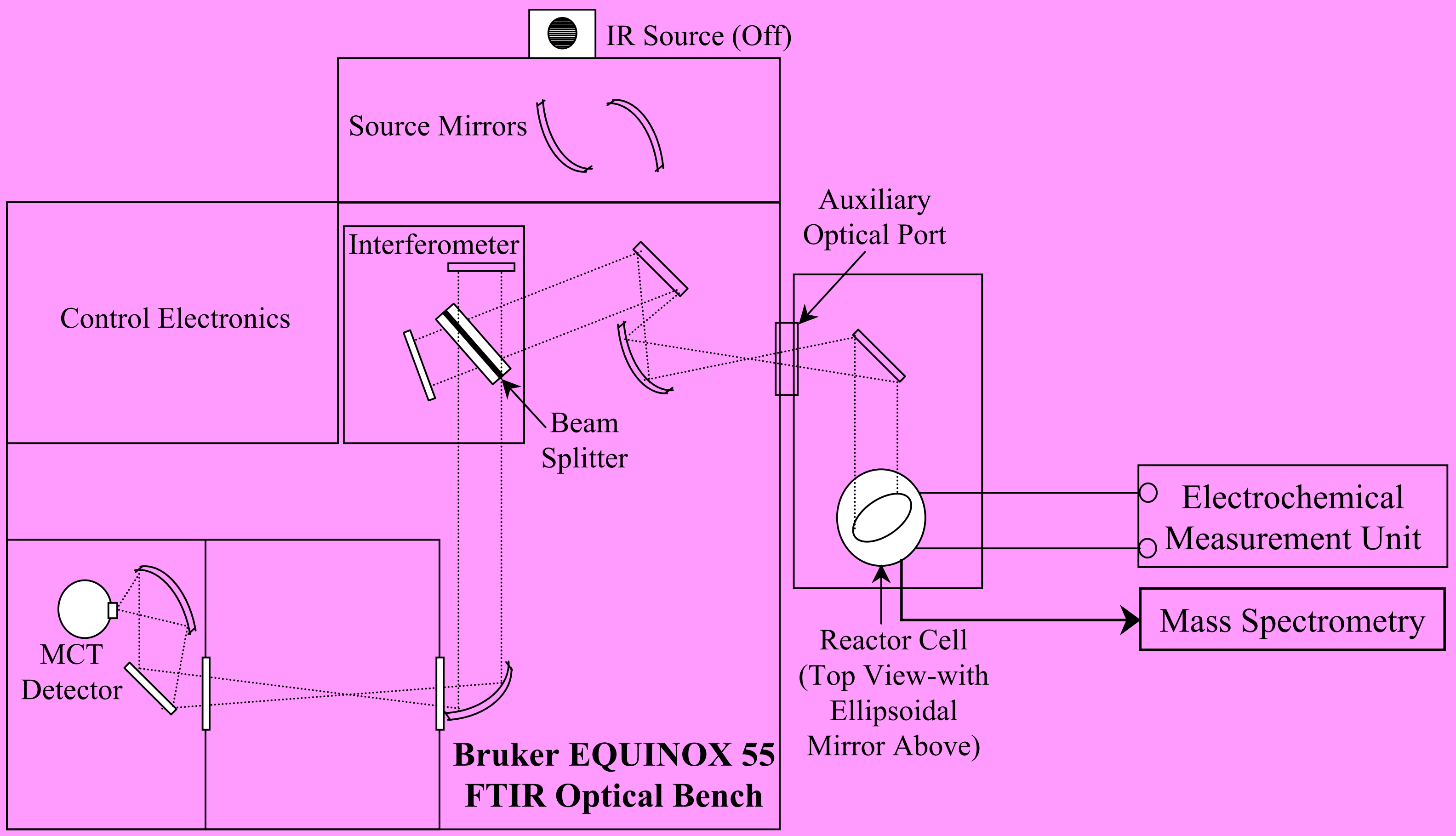
Optical Bench
for *In-situ* pd-FTIR Spectroscopy



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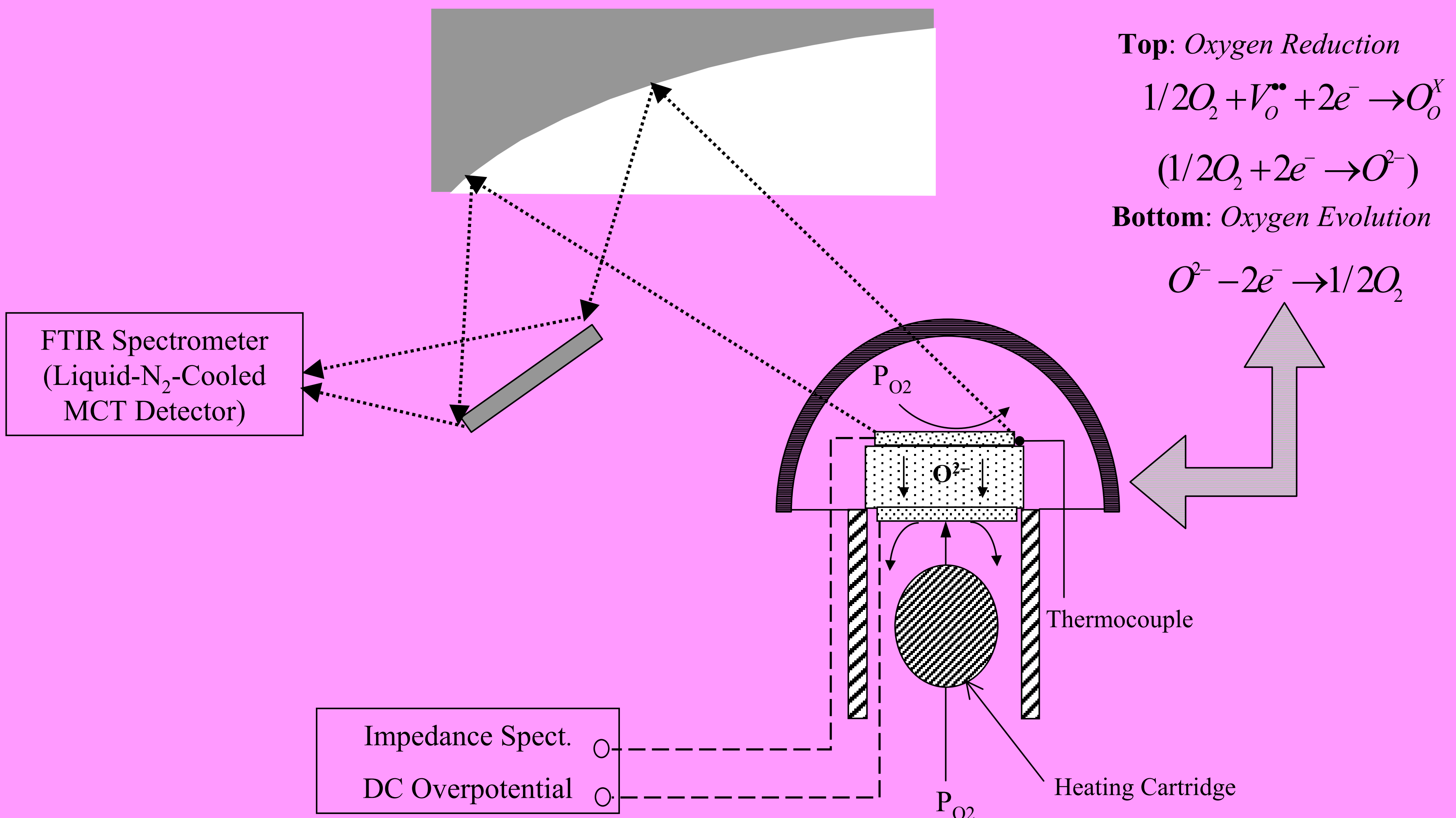
Optical Configuration for *In-Situ* pd-FTIR Emission Spectroscopy



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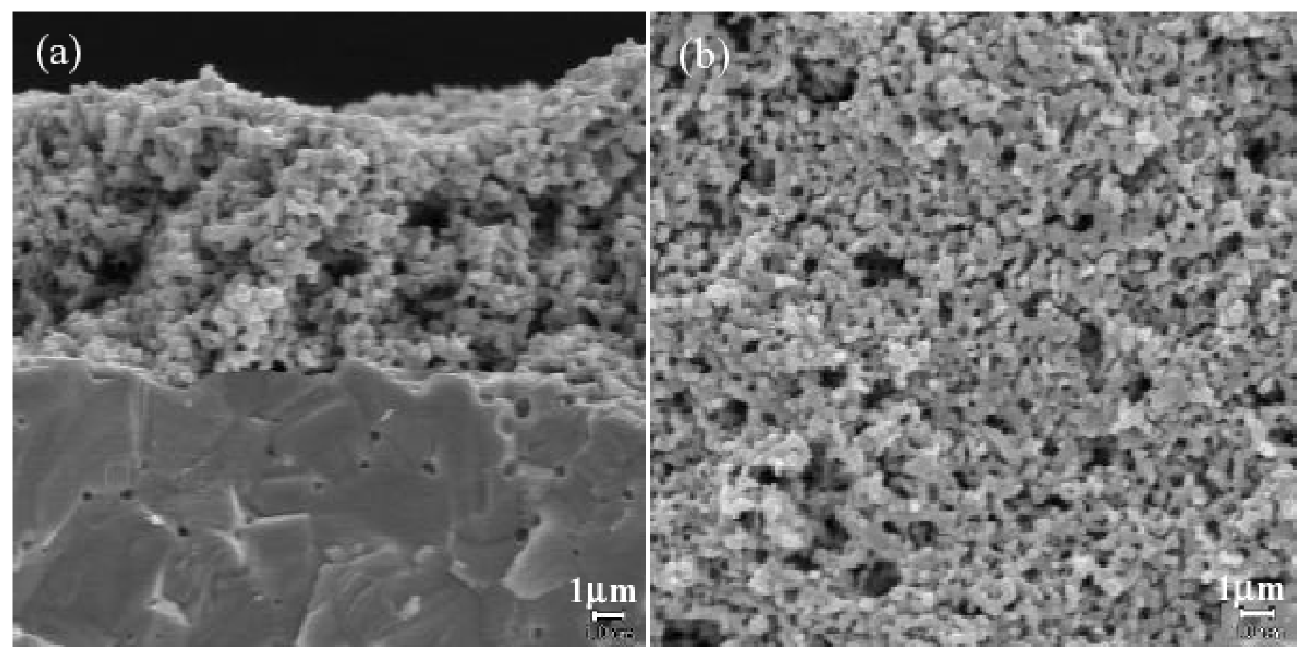
Microstructure of The SSC/SDC Interface



Glycine-nitrate process:

Cathode: $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)

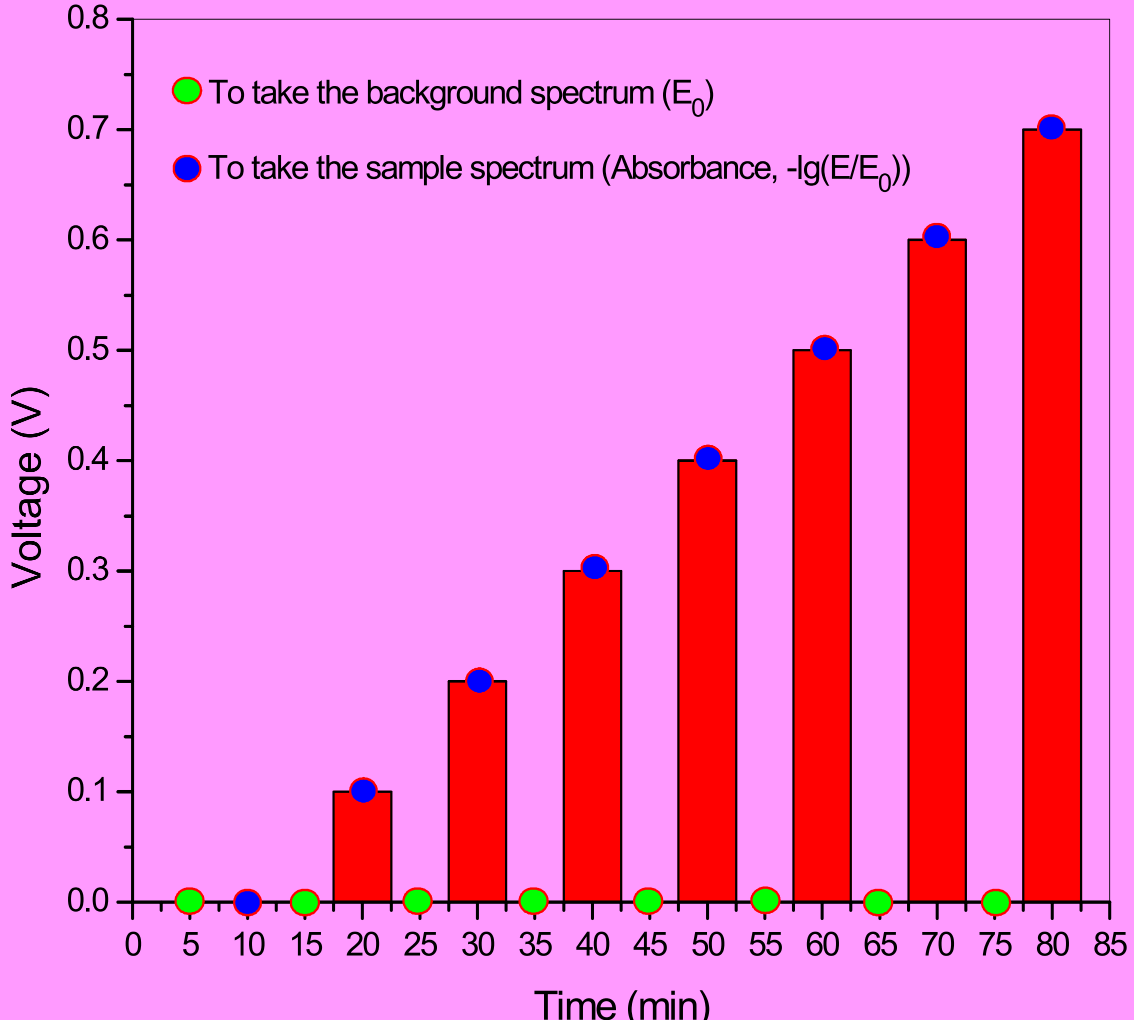
Electrolyte: $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)

A symmetrical cell: SSC/SDC/SSC

Dry pressing SDC and screen-printing SSC

Conditions for Spectra Collection

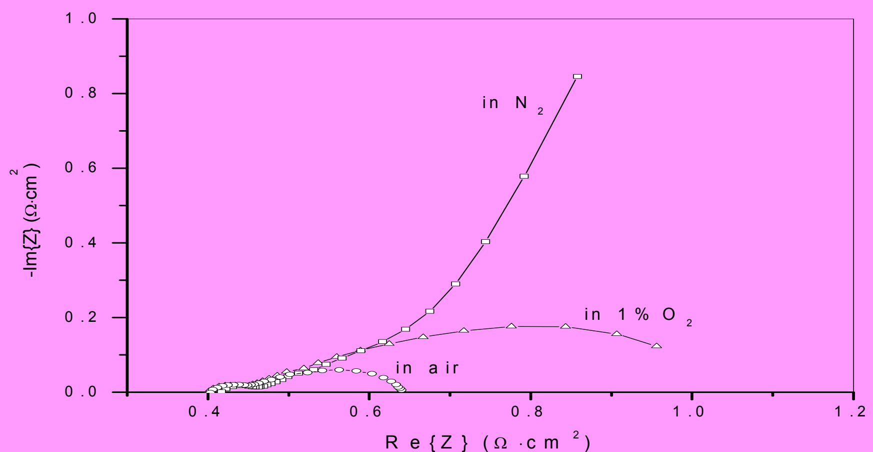
In-Situ pd-FTIR Emission Spectroscopy

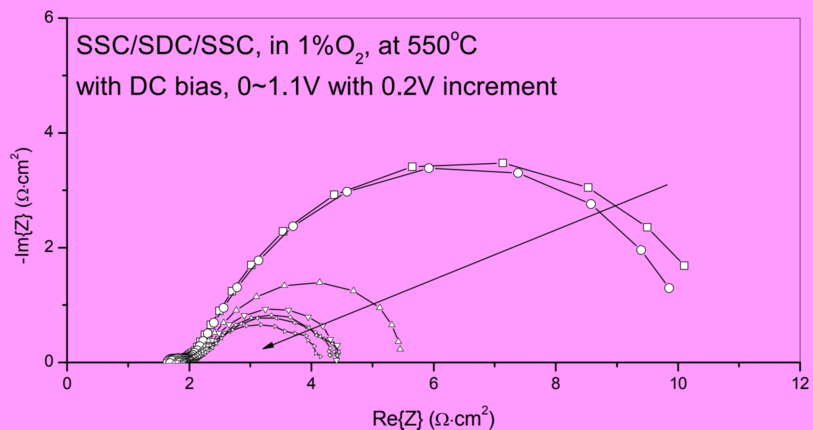


Do not need *blackbody* background.

By normalizing as E/E_0 (%), the *greybody emission* (emission when no potential applied) is removed.

Electrochemical Measurements
(Impedance and DC Performance)





	Applied voltage (V)	Overpotential (mV)	Current (mA)
air	0.0	0	0.0
R_B=6.4 O	-0.1	-38	-9.7
	-0.3	-109	-29.9
	-0.5	-174	-50.9
	-0.7	-232	-73.1
	-0.9	-277	-97.3
	-1.2	-317	-138.0
	-1.5	-323	-184.0
1% O_2 in N_2	0.0	0	0.0
R_B=6.4 O	-0.1	-61	-6.2
	-0.3	-178	-19.0
	-0.5	-295	-32.1
	-0.7	-420	-43.7
	-0.9	-584	-49.3
	-1.0	-672	-51.2
	-1.1	-758	-53.5
N_2	0.0	0	0.0
R_B=6.6 O	-0.2	-199	-0.1
	-0.3	-299	-0.2
	-0.4	-399	-0.2
	-0.5	-498	-0.3
	-0.6	-597	-0.5
	-0.7	-693	-1.0

$$\frac{1}{2}O_2 + \{V_O^{\cdot\cdot} + 2e'\} \rightarrow O_O^X$$

Controlled by charge transfer

Possible Elementary steps/Reaction pathways

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

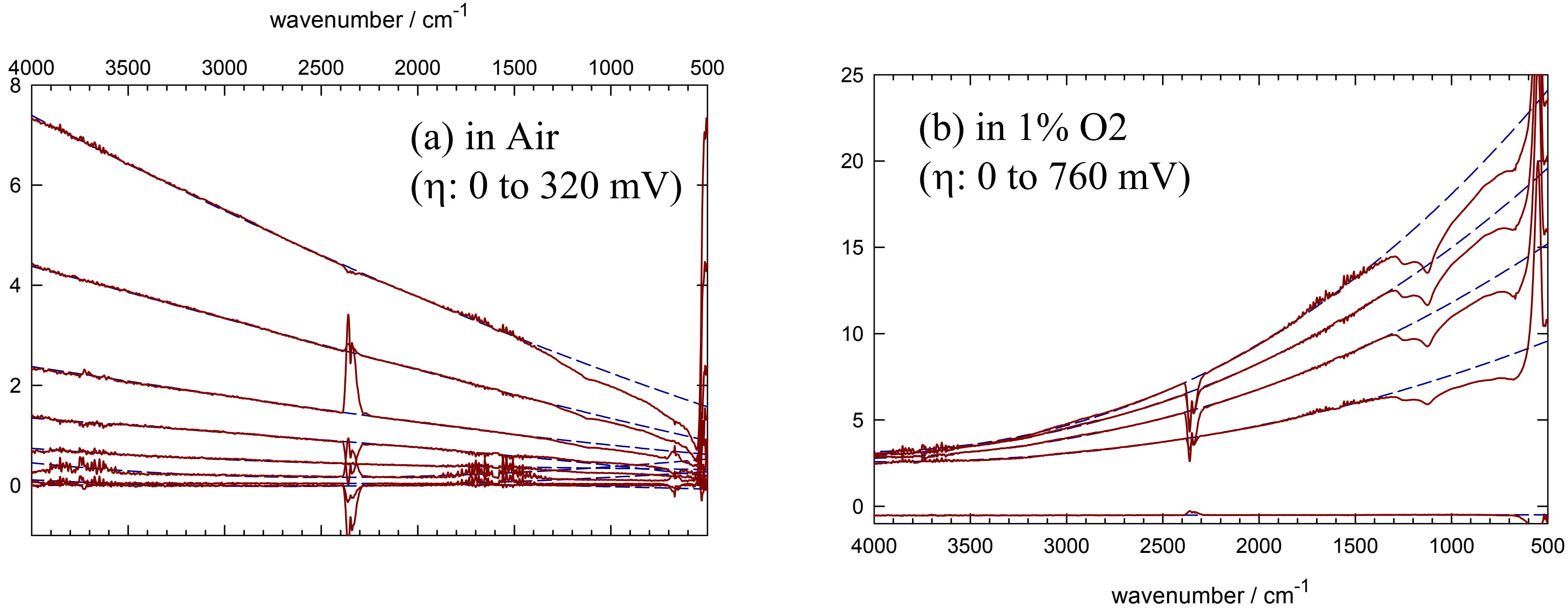
Charge Transfer Steps

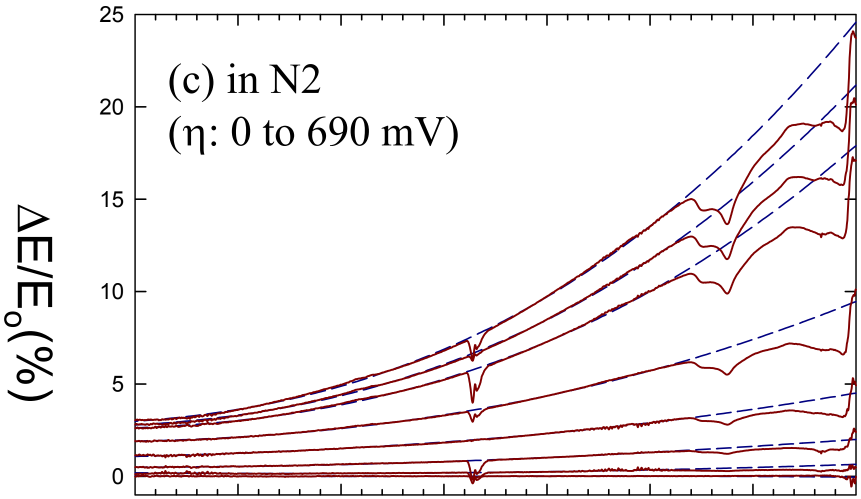
$$O_{2,ad} + e' \rightarrow O^{-}_{2,ad}$$

$$O^{-}_{2,ad} + e' \rightarrow O^{=}_{2,ad} \rightarrow O^{-}_{ad}$$

$$O^{-}_{ad} + e' \rightarrow O^{=}$$

In-Situ pd-FTIRES Spectra

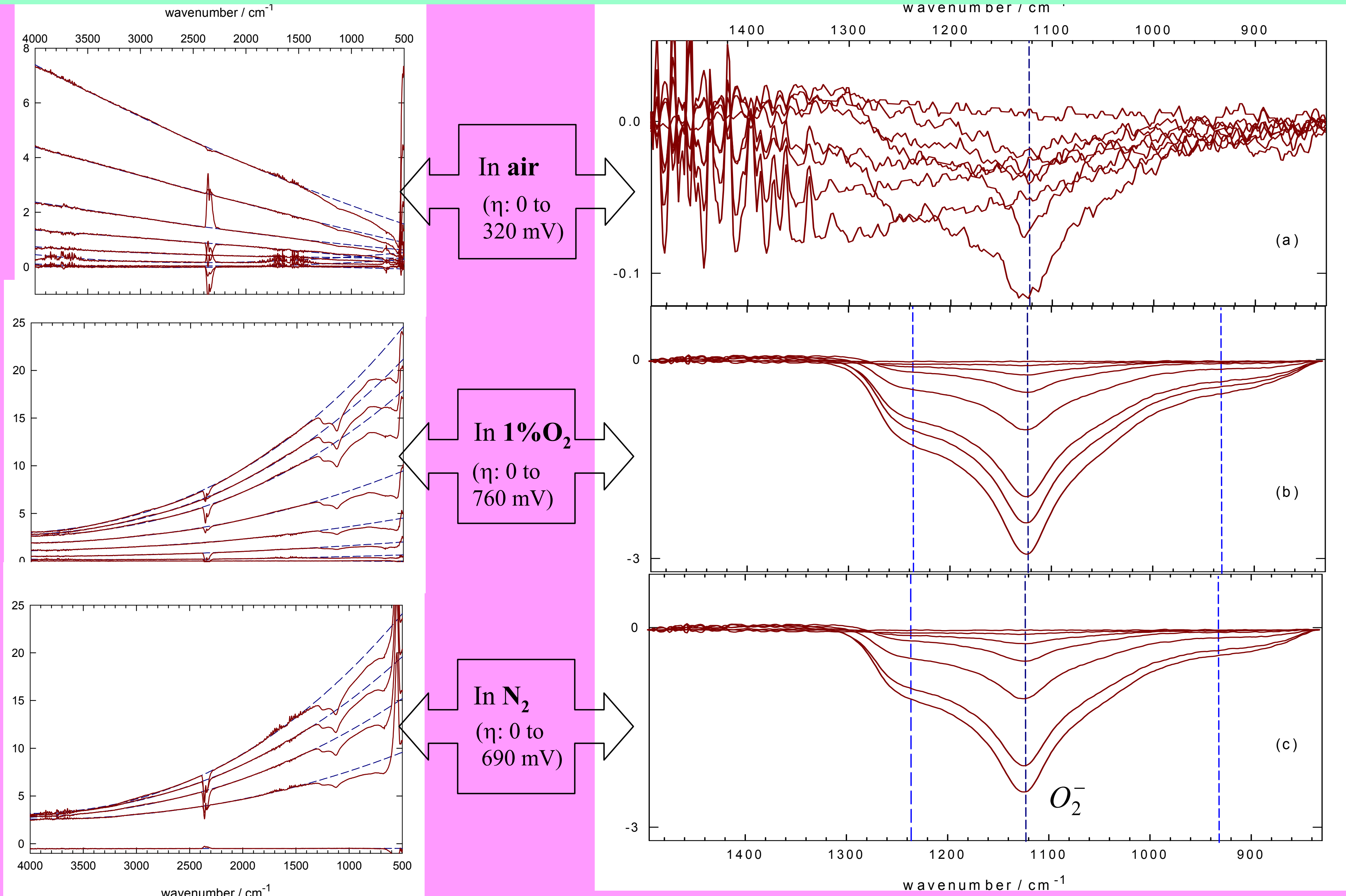




Comparison of pd-FTIRE spectra for three different feed gas conditions: (a) air, (b) 1% O_2 in N_2, and (c) N_2.

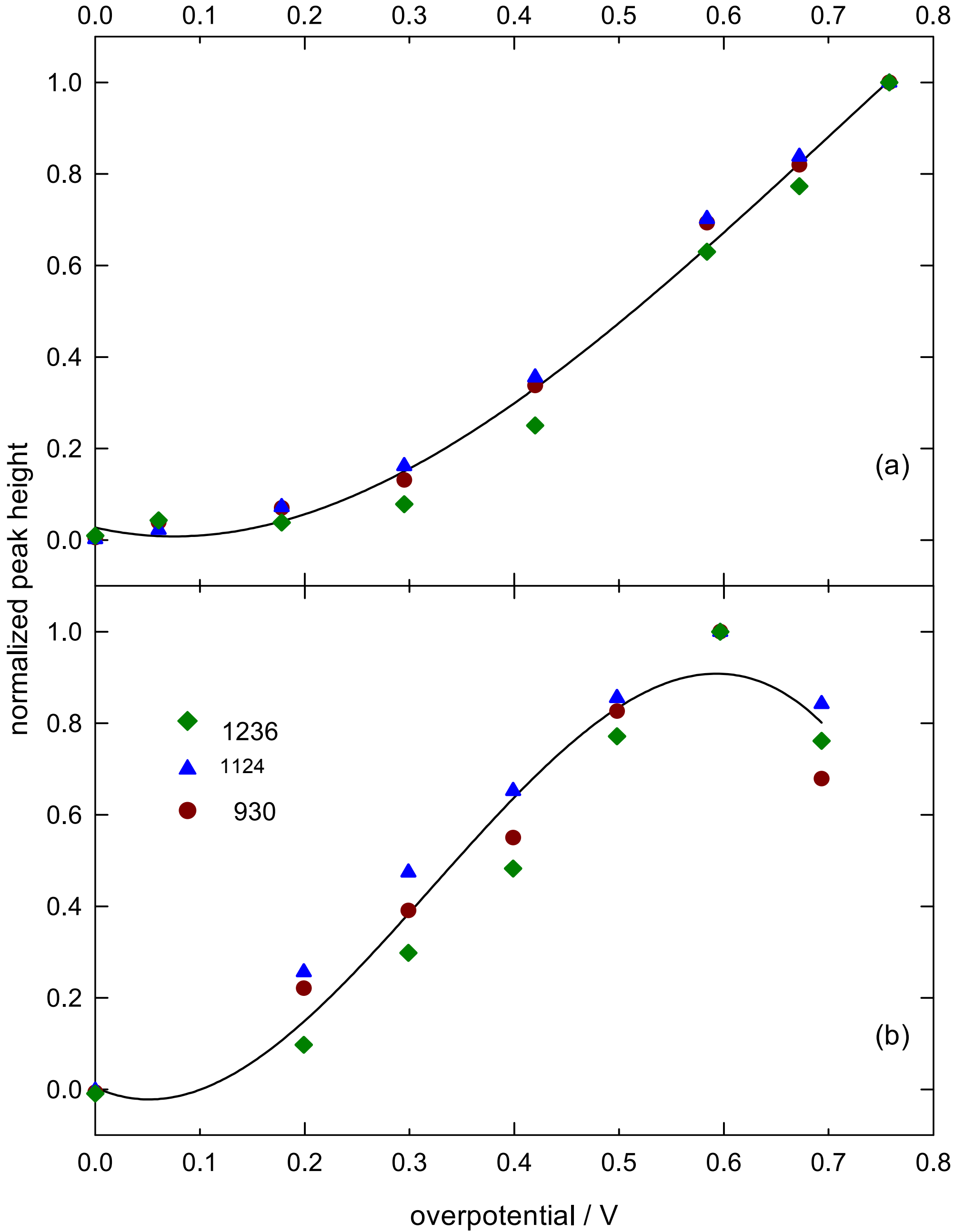
Dashed lines indicate cubic fit to baseline. Electrochemical characteristics are listed in Table 1.

In-Situ Pd-FTIRES Spectra - After local baseline correction



After local baseline correction

Peak Heights v.s. DC Overpotential



(a) in 1% O_2

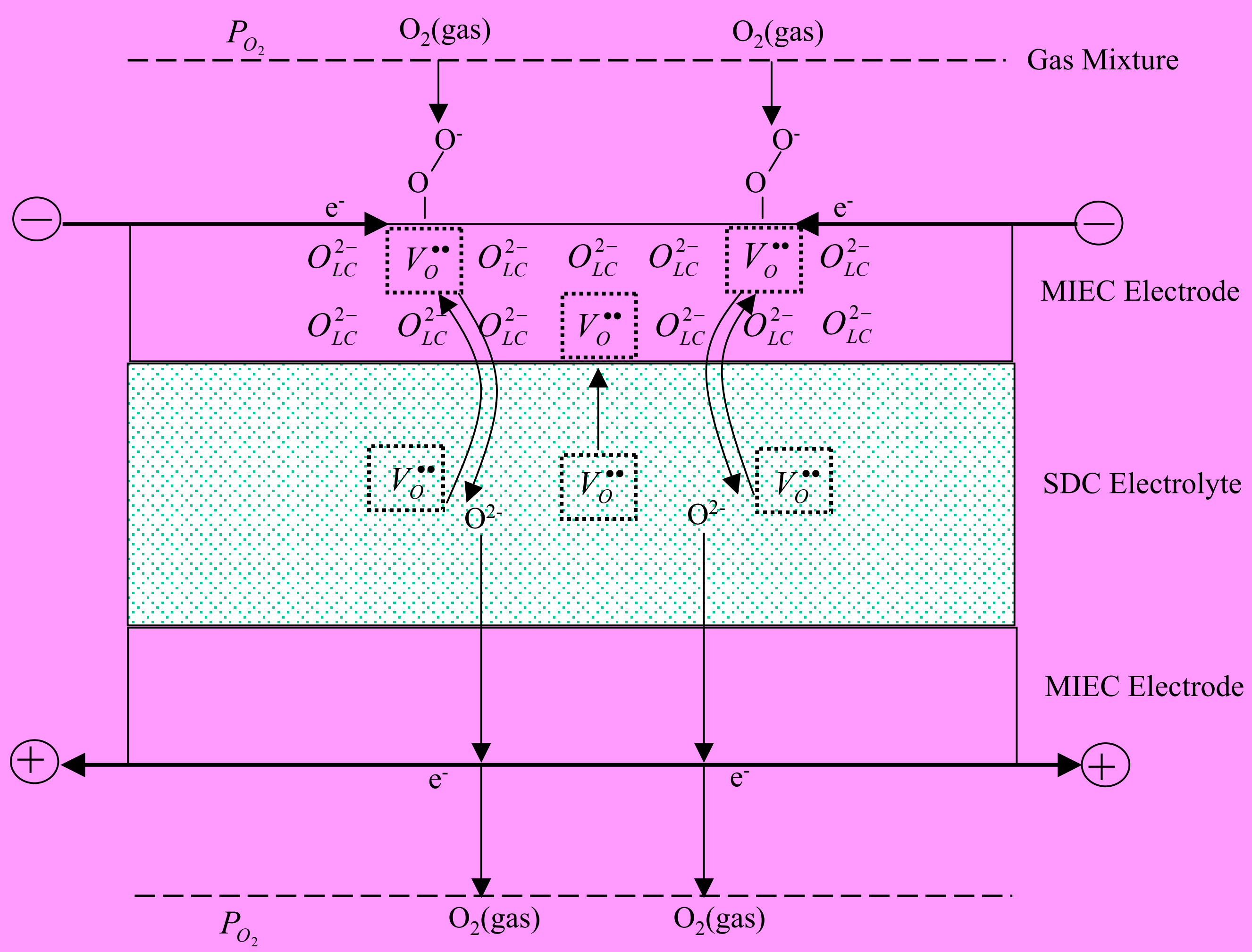
- 1236 cm^{-1}, perturbed O_2^-
- 1123 cm^{-1}, O_2^-
- 930 cm^{-1}, O_2^{2-}

(b) in N_2

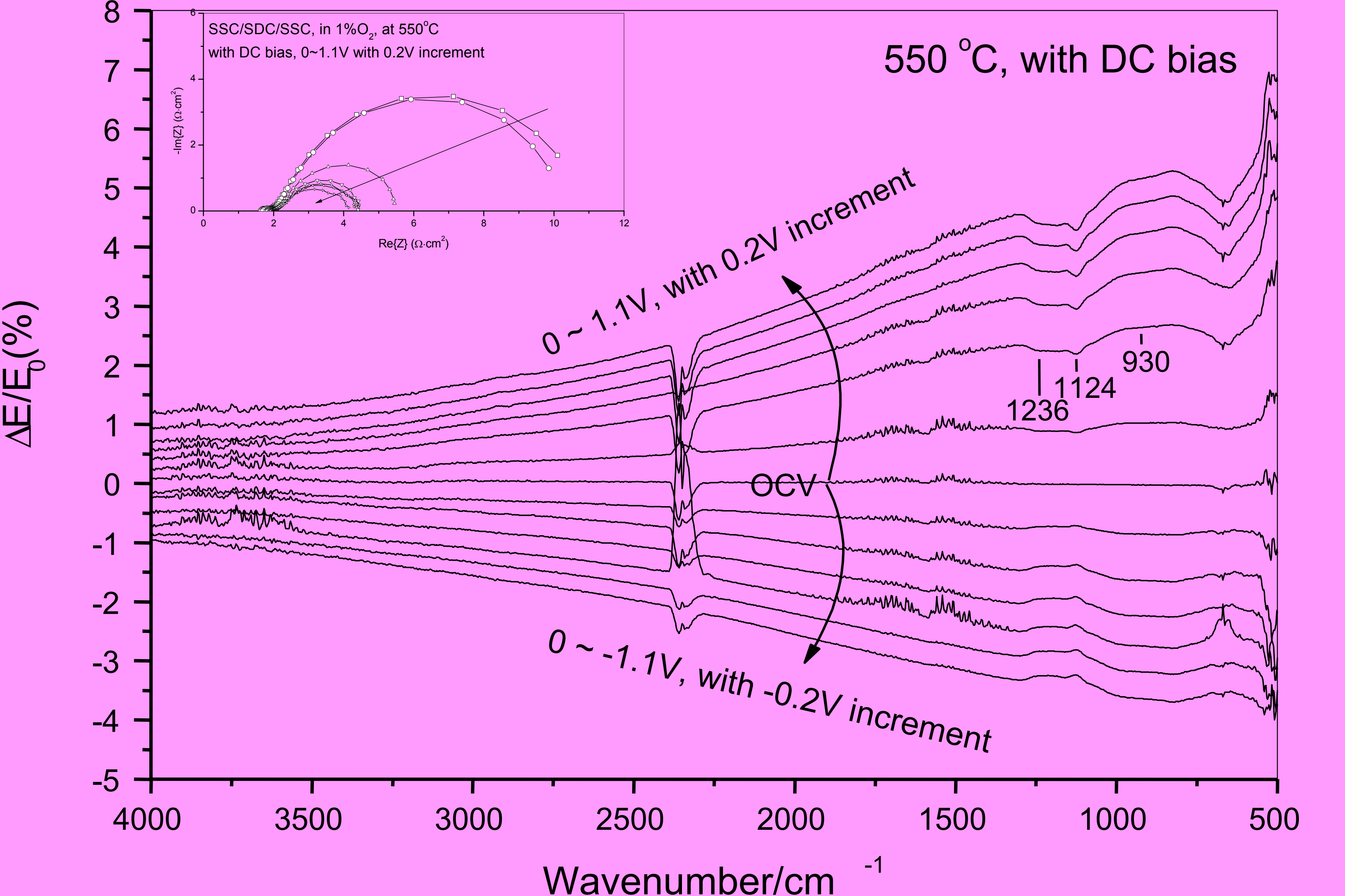
Effect of mass trafer observed at high overpotentials

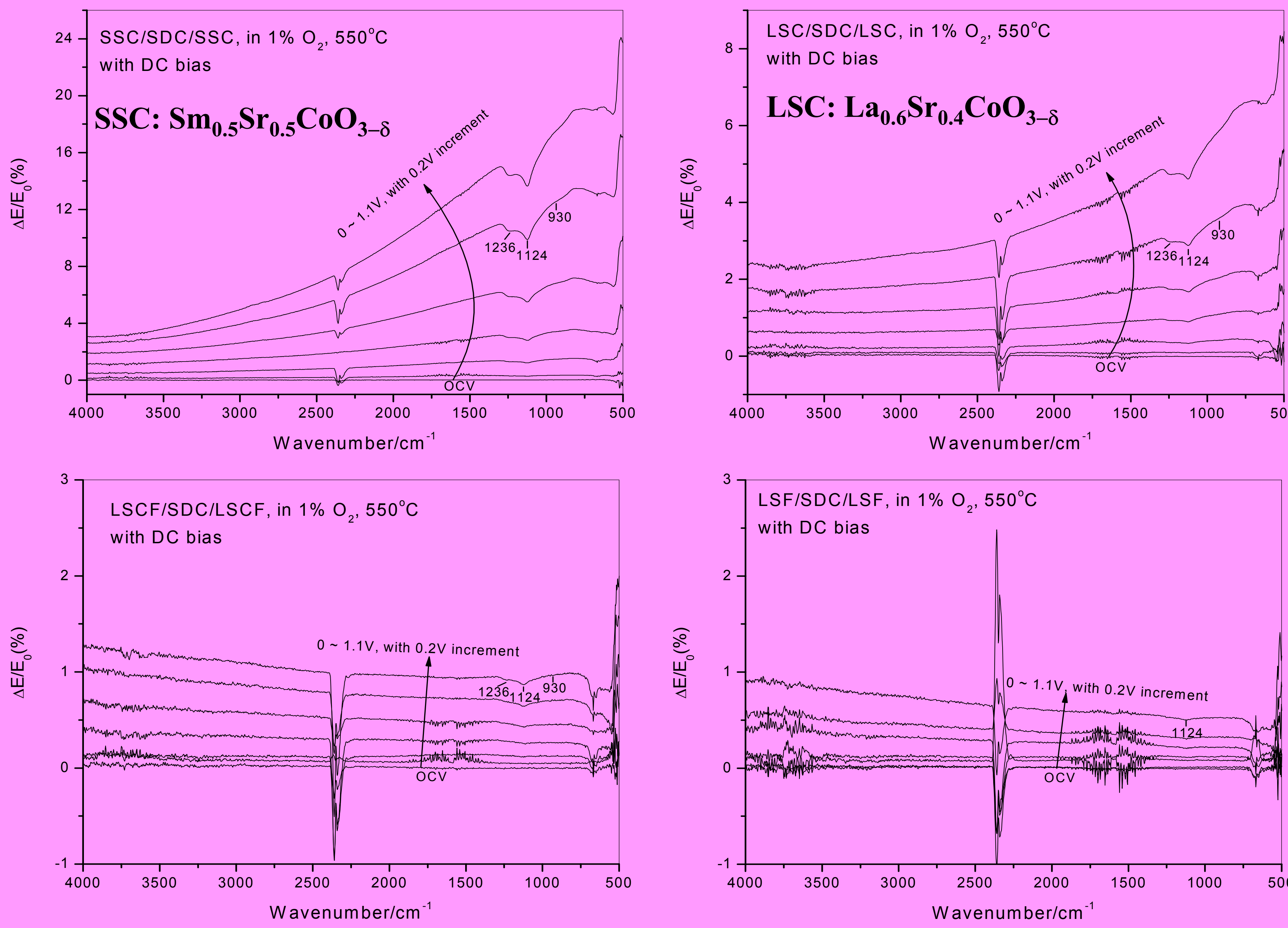
Proposed Reaction Mechanism for Oxygen Reduction

Rate-determining step (rds): $O_{2,ad}^{-} + e' \rightarrow O_{2,ad}^{=}$



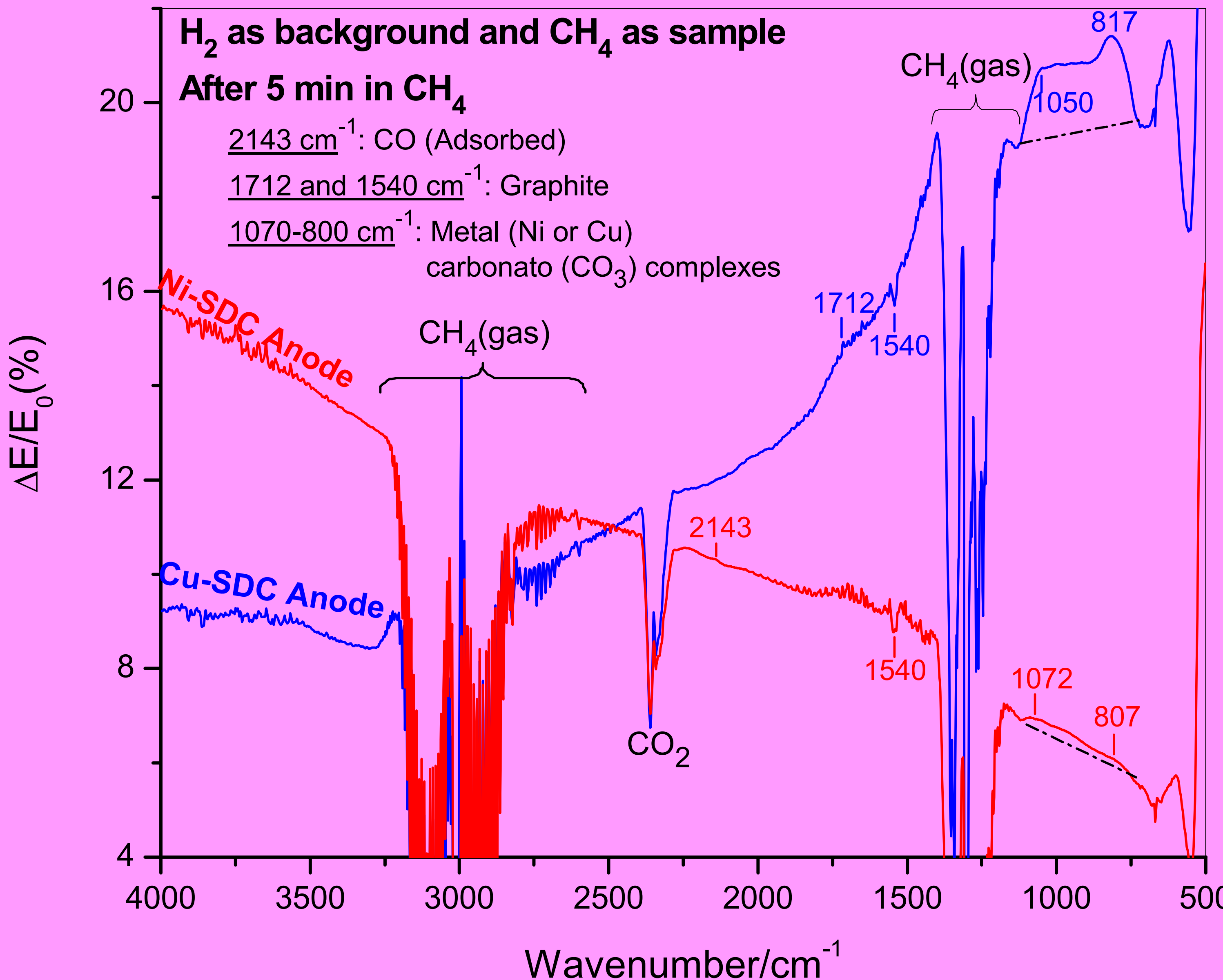
Evolution of Oxygen - SSC/SDC/SSC, in 1% O_2 at 500°C



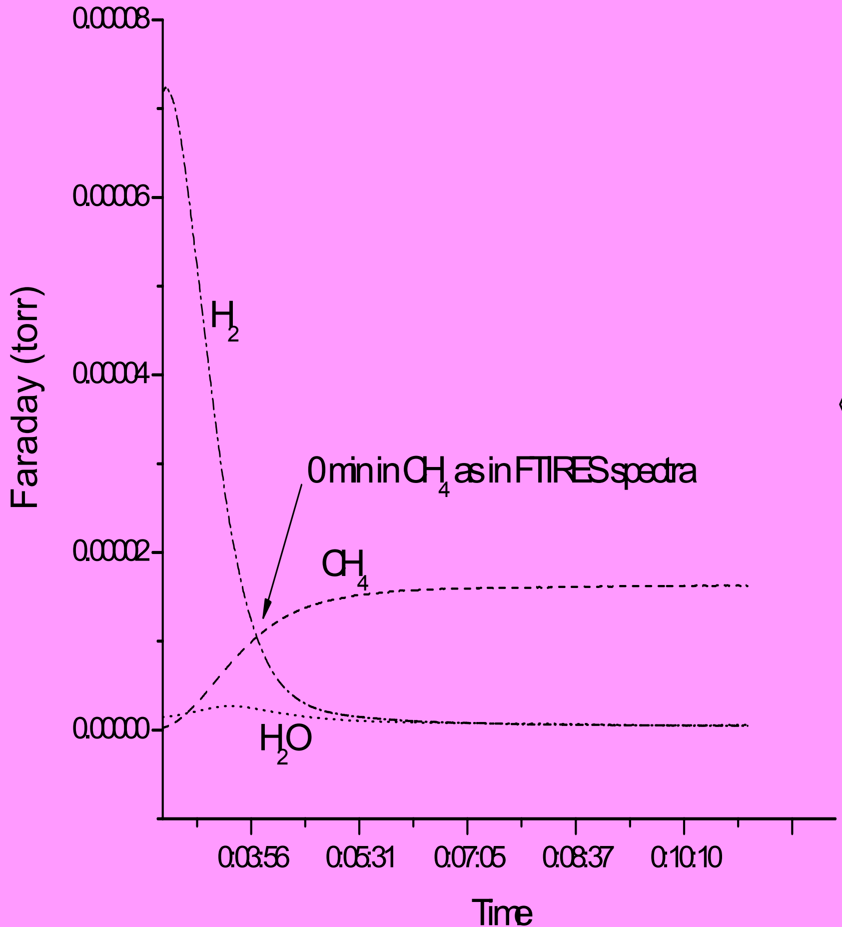


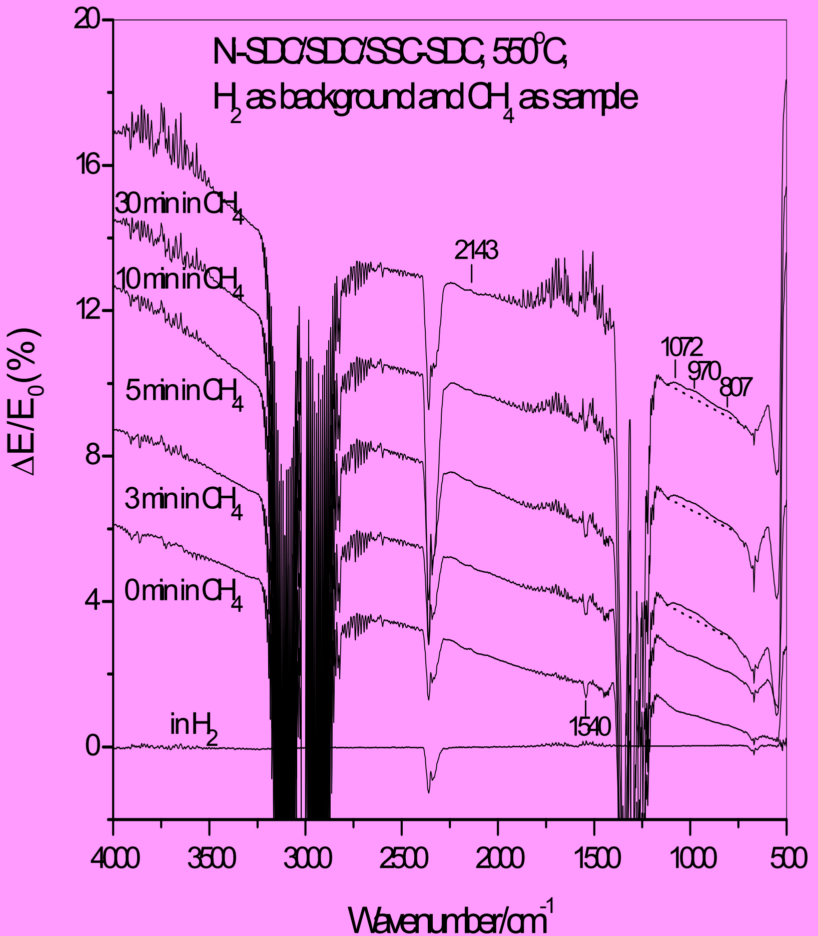
SSC: $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ **LSC**: $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ **LSCF**: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ **LSF**: $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ **SDC**: $Sm_{0.2}Ce_{0.8}O_{1.9}$

In-situ FTIRES – Anodes in SOFCs

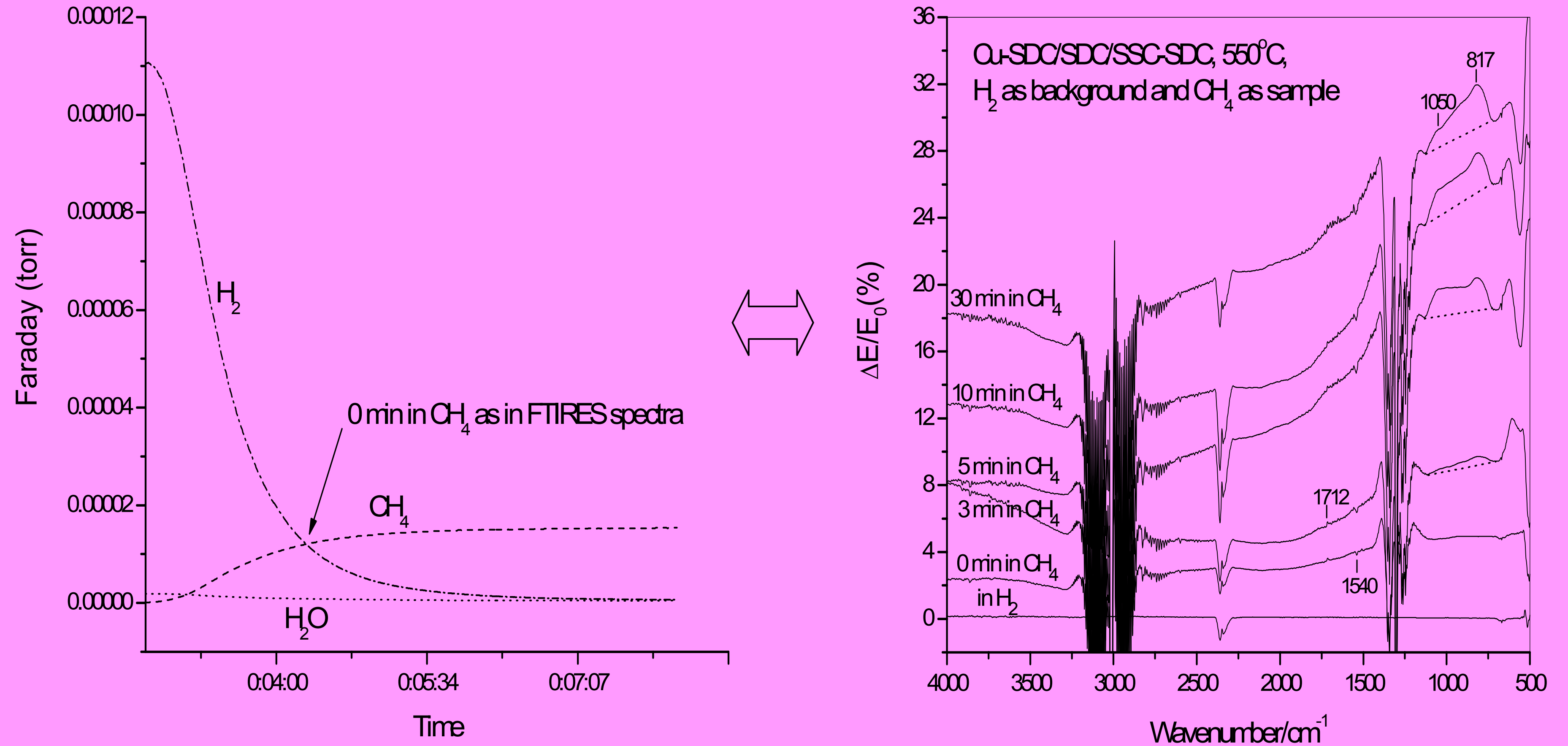


Ni-CeO$_2$ Based Anodes





Cu-CeO$_2$ Based Anodes

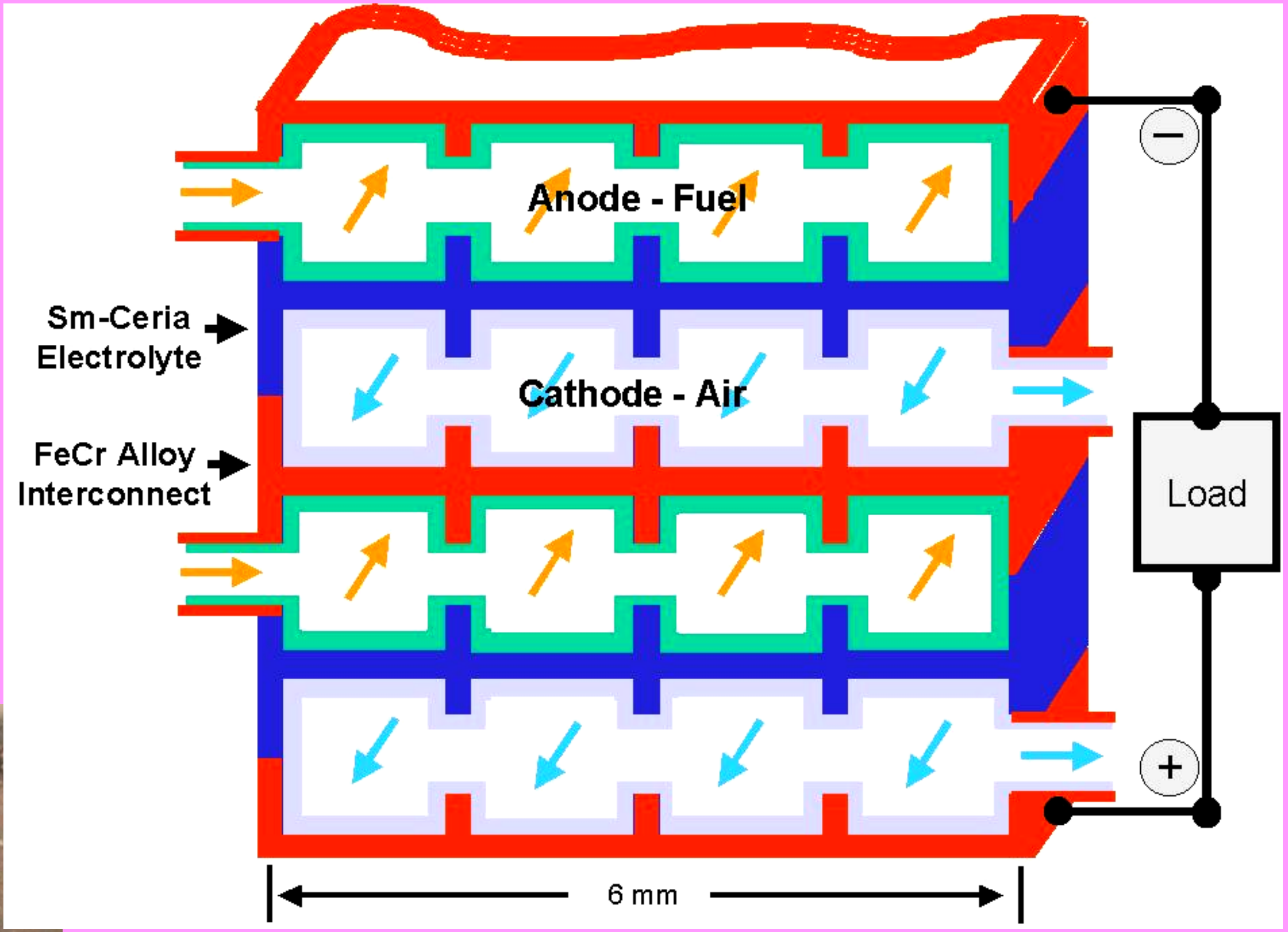


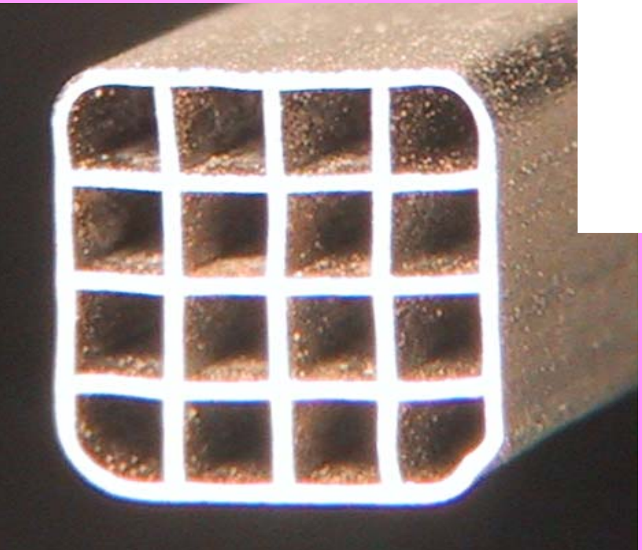
SUMMARY – FTIR Studies

- *A strong adsorption band at 1124 cm^{-1} (O_2^-), two weak adsorption bands at 1236 cm^{-1} (perturbed O_2^-) and 930 cm^{-1} (O_2^{2-}) were observed on oxygen reduction.*
- *The rds is the charge transfer step,* $O_{2,ad}^{-} + e' \rightarrow O_{2,ad}^{=}$
- *Broad spectral features (baseline shifts), **infrared electro-emission effect**, is induced by electrochemical polarization.*
- *The emission difference spectra of Ni-SDC and Cu-SDC cermet anodes at 550^{o}C unveiled the nature of intermediate species when methane was used as the fuel. Graphite peaks were found at 1712 and 1540 cm^{-1}. The broad bands at 1070-800 cm^{-1} were possibly metal (Ni or Cu) carbonato (CO_3) complexes.*

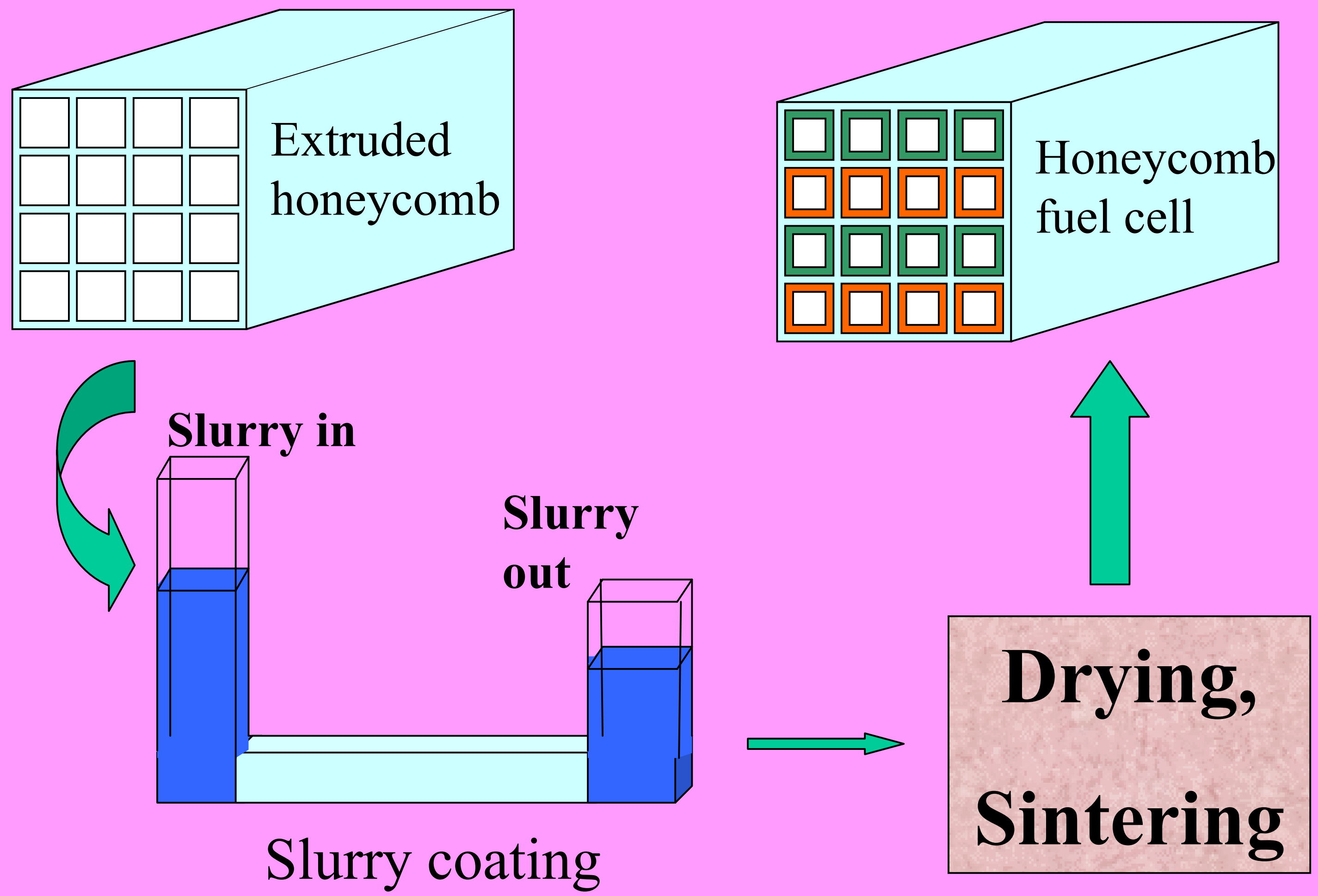
Functionally Graded Electrodes on Honeycomb Cells

Hybrid Metal/Electrolyte Monolithic Low Temperature SOFCs





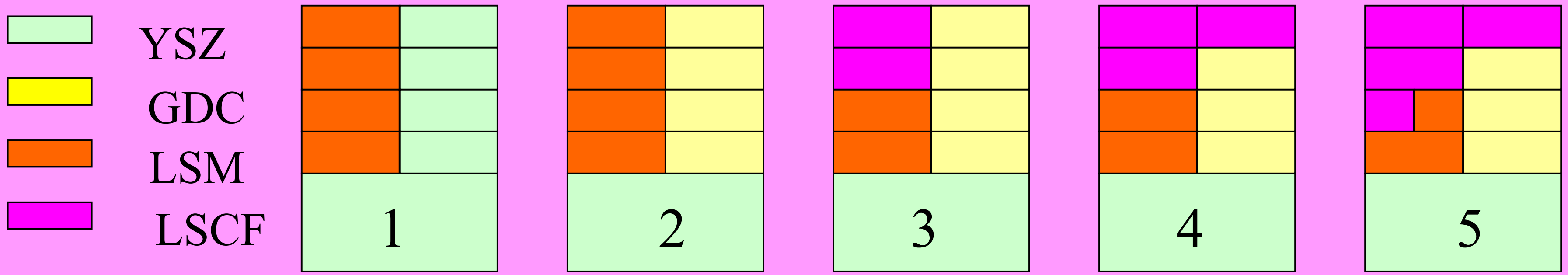
Electrode Processing

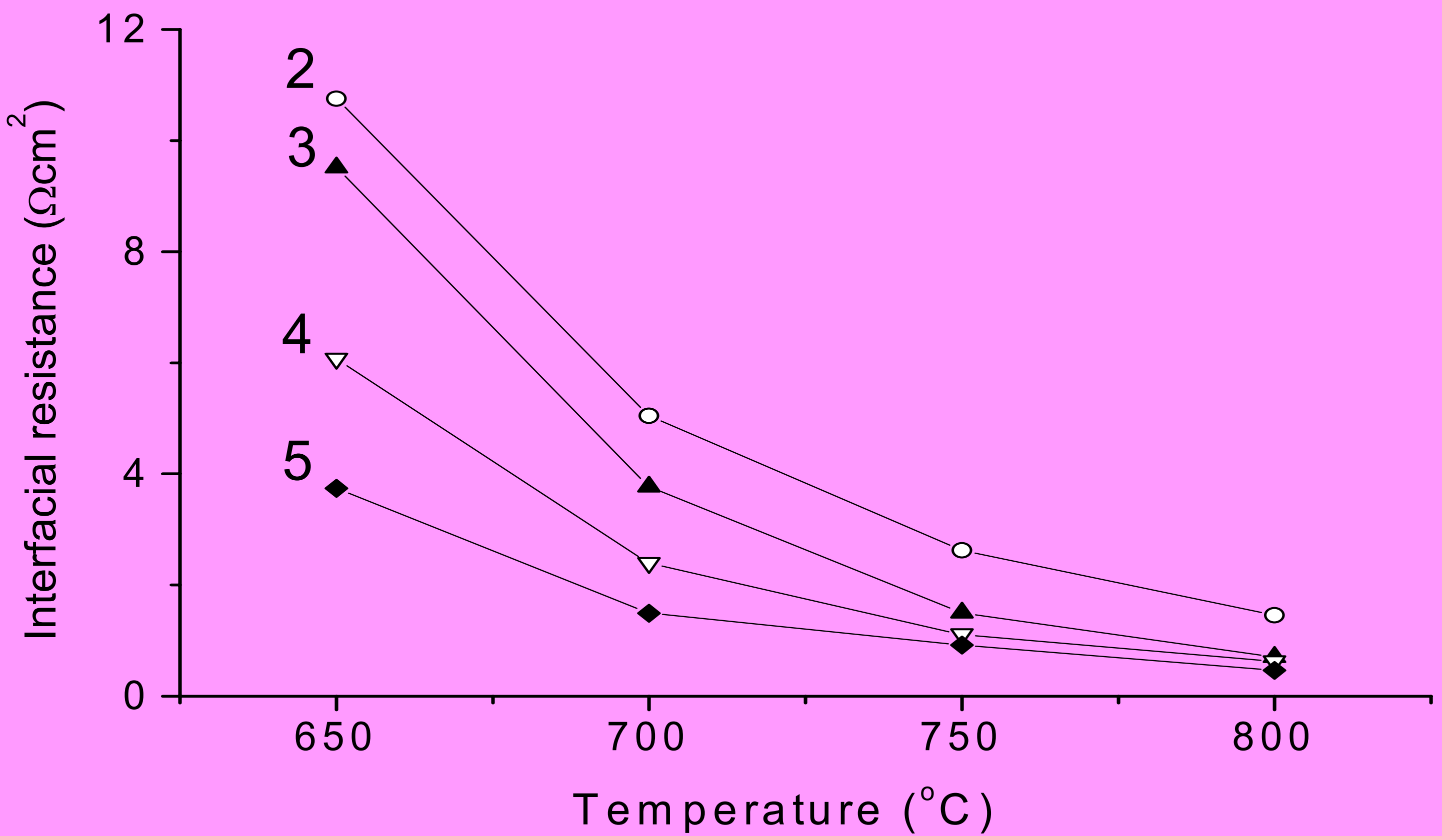


Cathode for YSZ Fuel Cells

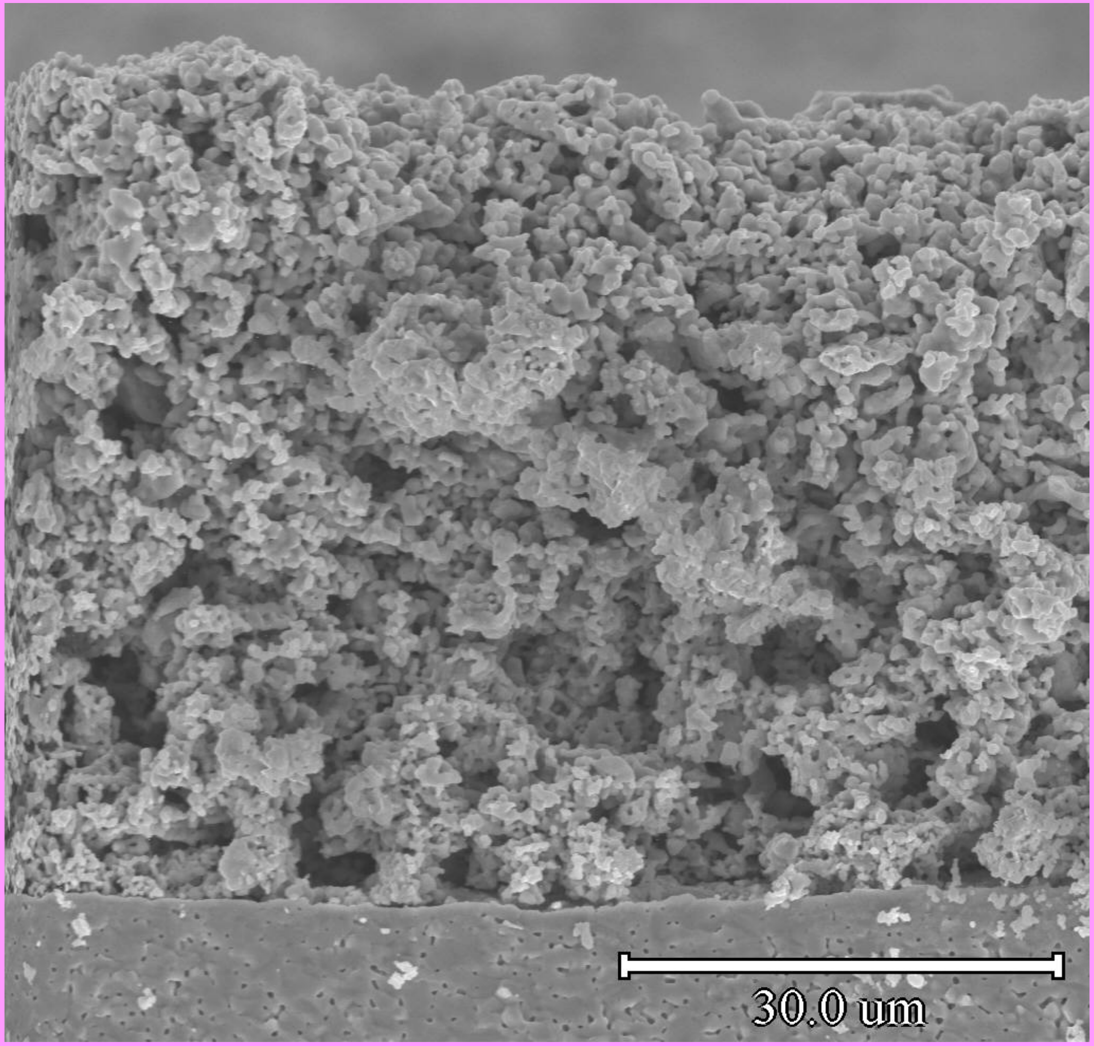
- **LSM-YSZ**
  - Efficient performance above 800^{o}C
  - 1.31 Ωcm^{-2} at 750^{o}c
  - E. Murray, solid state Ionics 2001
- **LSM-GDC**
  - Improved performance below 800^{o}C
  - 0.49 Ωcm^{-2} at 750^{o}C
  - E. Murray, solid state Ionics 2001
- **Graded composites of LSM-LSC**
  - Much better performance
  - 0.2 Ωcm^{-2} at 750^{o}C
  - NT Hart, J. Power sources 2002
  - P. Holtappels, J. Euro. Cer. Soc. 2002

Functionally Graded Electrodes





Sample 5: LSM/GDC/LSCF



LSCF

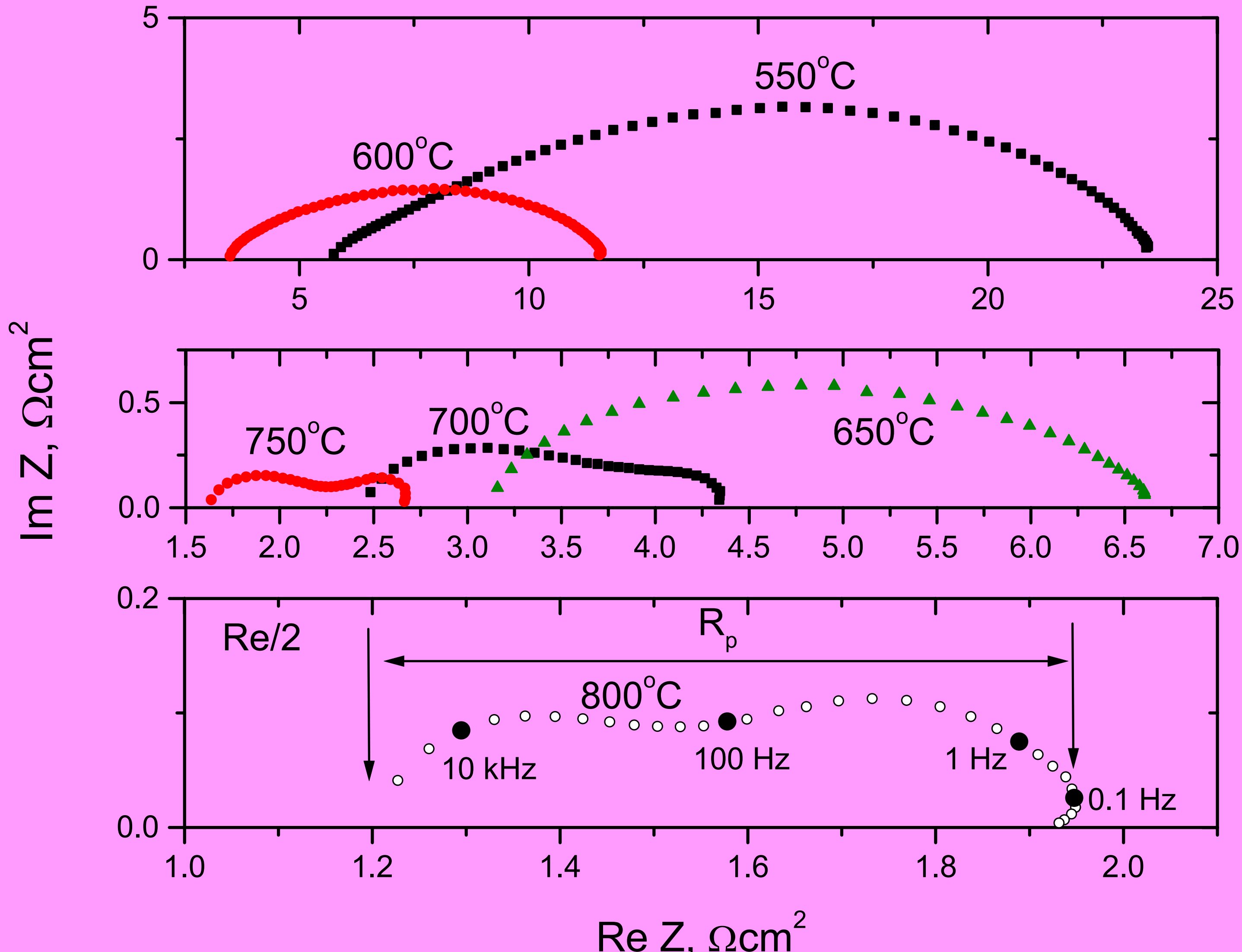
LSCF50+GDC50

LSM25+LSCF25+
GDC50

LSM50+GDC50

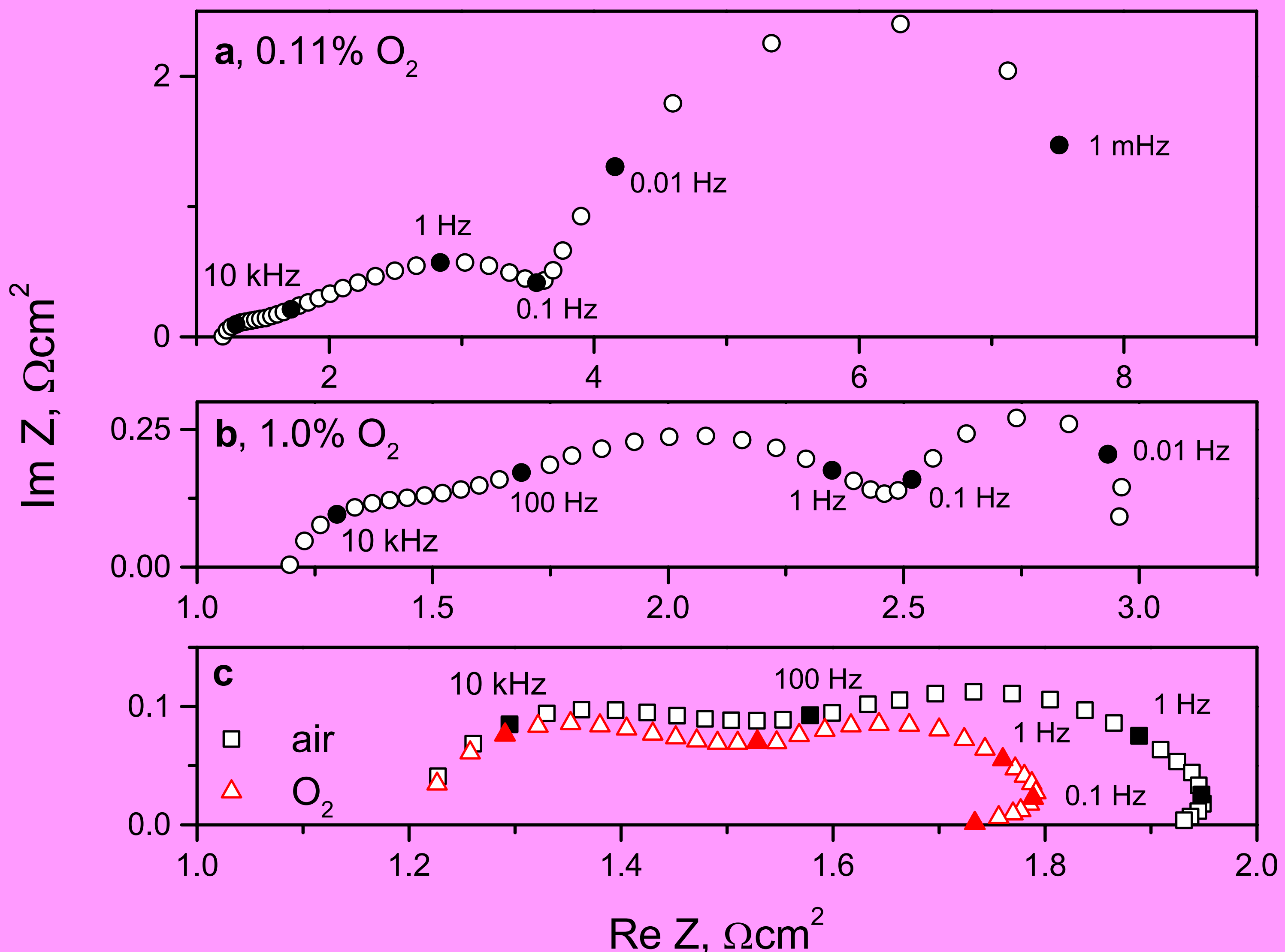
YSZ

IS for Graded Electrodes



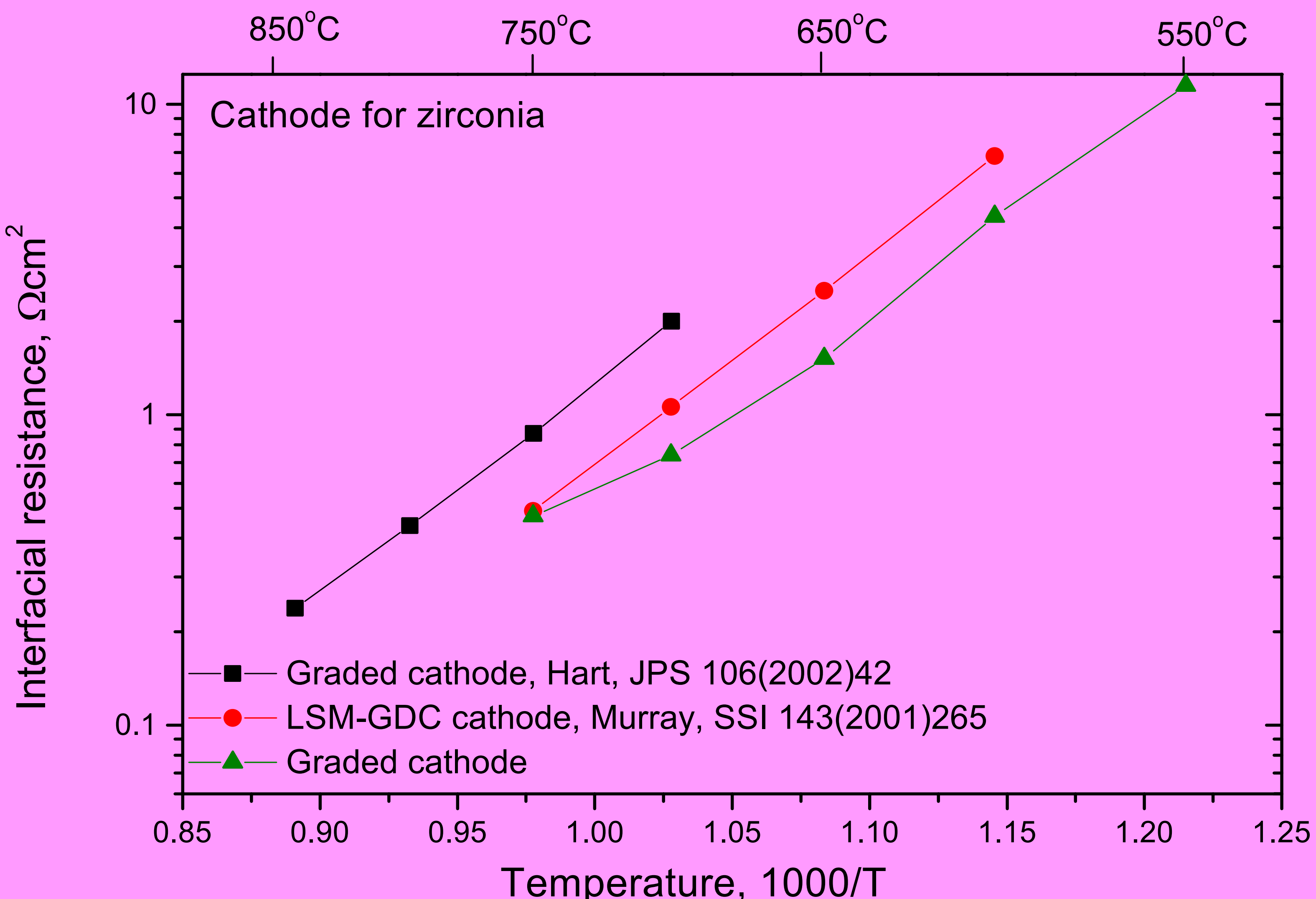
Fired at 1100 °C, measured in air

IS for Graded Electrodes



Fired at 1100 ºC, tested at 800 ºC

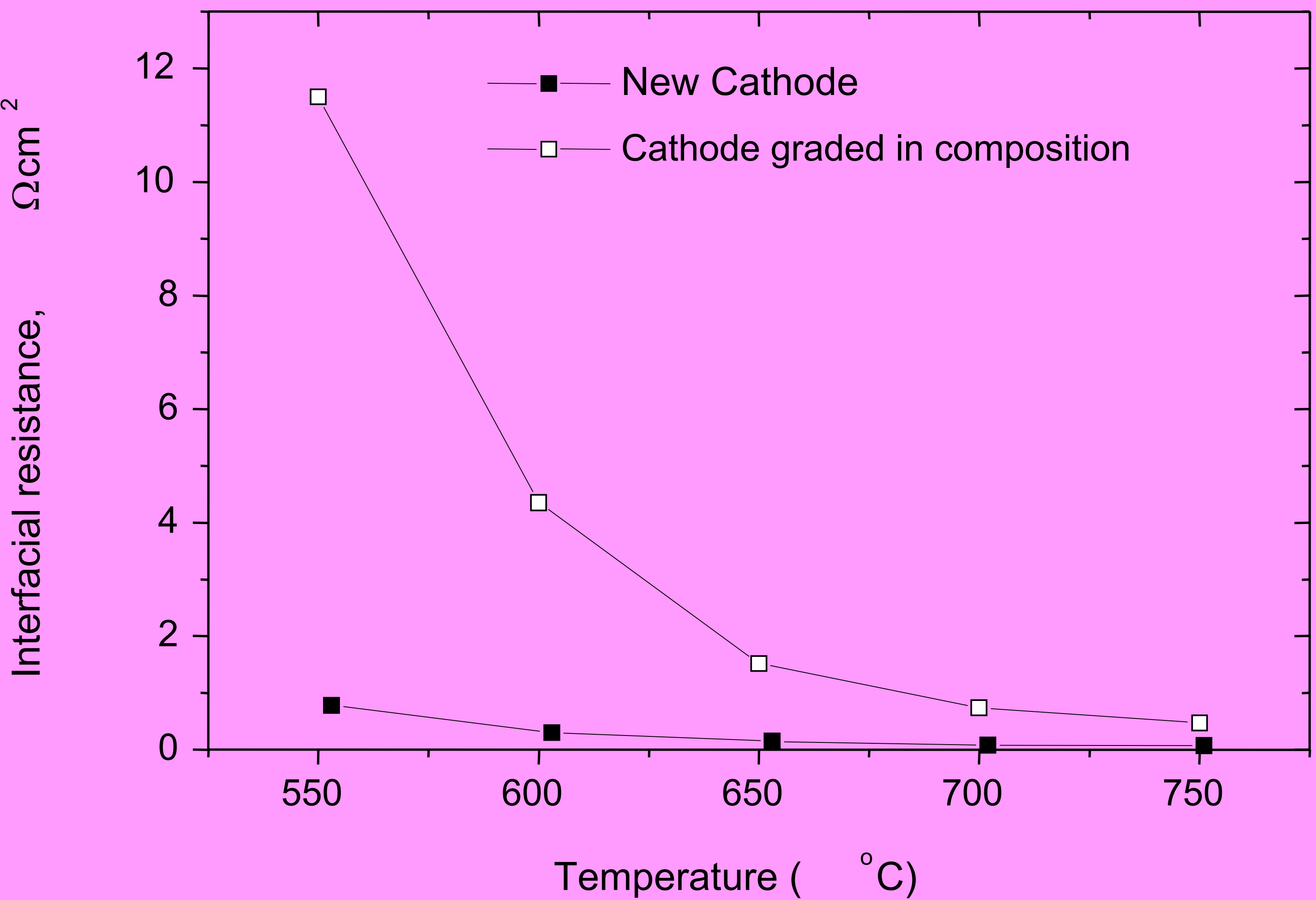
Cathodes for YSZ Honeycomb Fuel Cells



Electrodes of High-Catalytic Activities

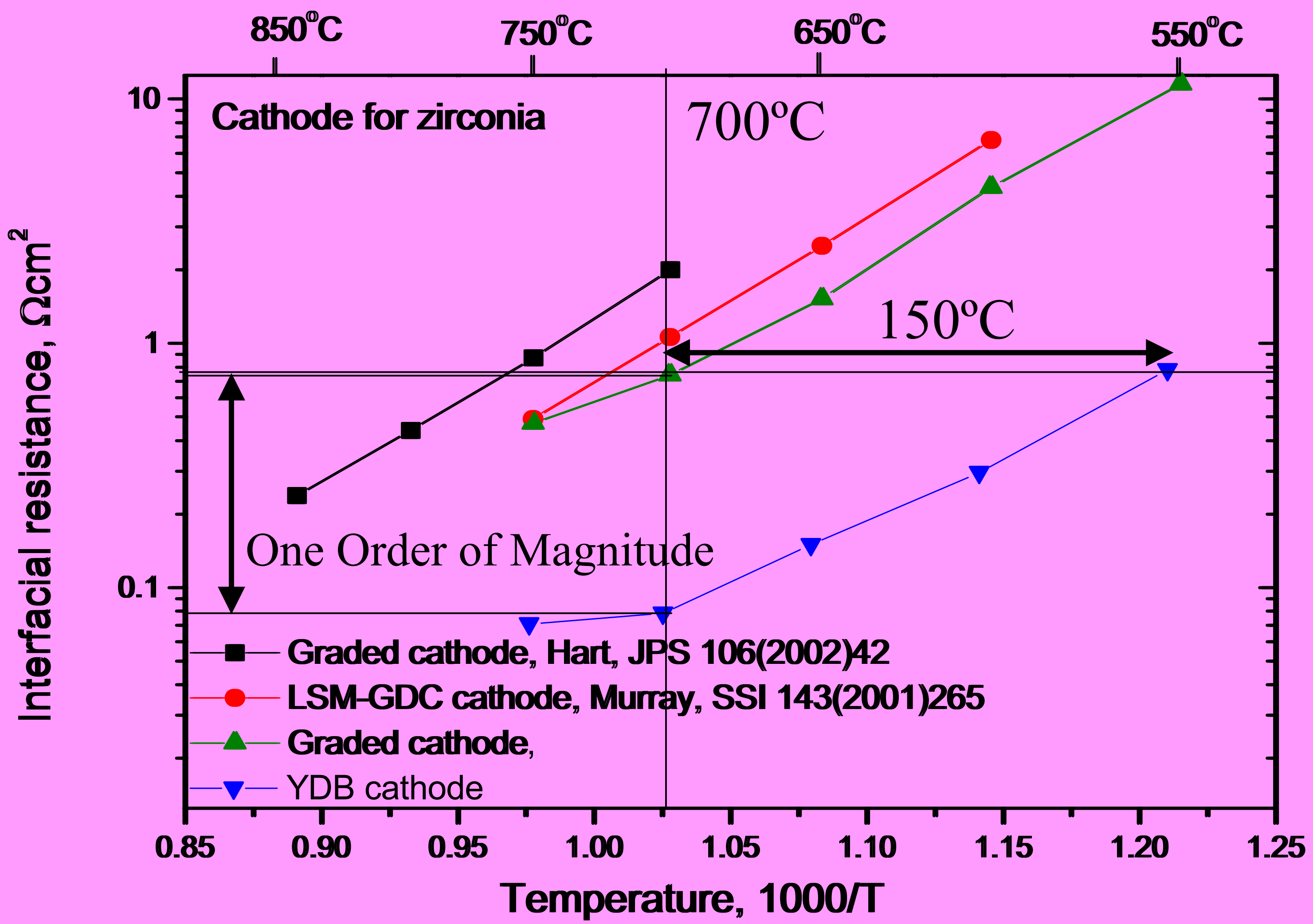
- High catalytic properties for oxygen reduction
- High catalytic properties for direct oxidation of hydrocarbon fuels or reforming of hydrocarbon fuels

Cathodes for Zirconia Honeycomb Fuel Cells

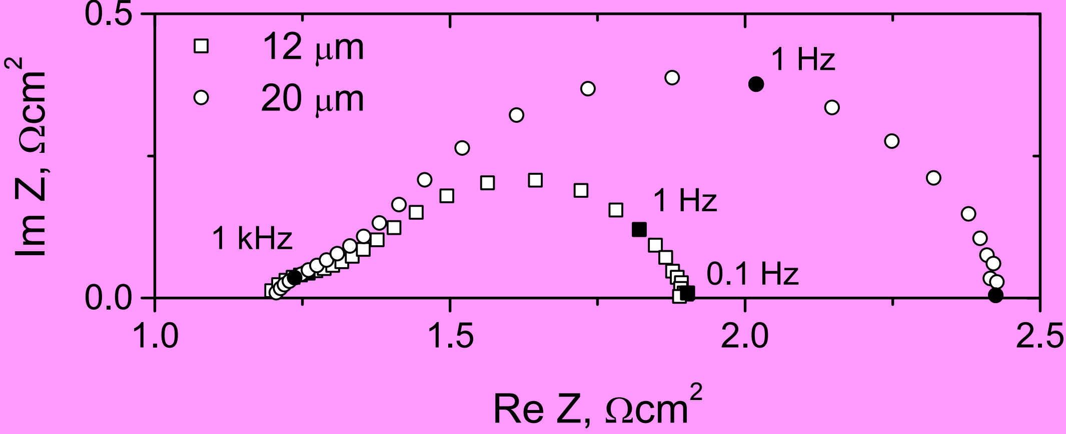


Comparison of a new cathode and a cathode graded in composition

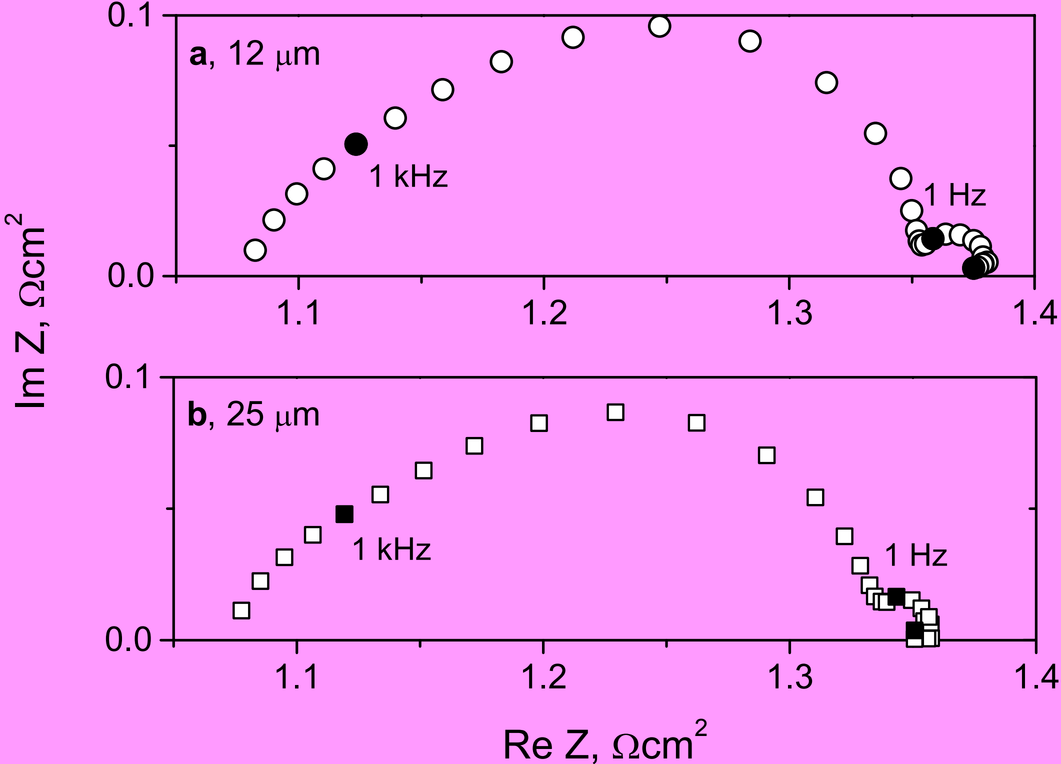
Cathodes for Zirconia Fuel Cells



Effect of Firing Temperature/Thickness - Measured at 600^{o}C



Fired at 850°C/2 hrs



Fired at 750°C/2 hrs

R_p can be further reduced by microstructure optimization

Summary - Electrode Development

- Cathodes graded in composition show interfacial resistances about 10 times lower than that of a conventional LSM-YSZ cathode;
- The performances are dependent on the microstructures, and is favored by low-temperature sintering;
- Interfacial resistance of graded cathodes as low as 0.47 Ωcm^2 was achieved at 750°C. However, it increased to 4.1 Ωcm^2 at 600°C;
- A new cathode showed much lower interfacial resistances than the graded cathodes, **0.30 Ωcm^2 at 600°C,** about 10 times better; and
- **High performance: >600 mW/cm^2 at 600°C**

Future Work

- Mathematical Modeling of Functionally Graded Electrodes

  → The Best design

- In-situ pd-FTIRES, IS, and MS

  → High **Catalytic Activity** for fast reactions

  - Cathode: Mechanism of oxygen reduction
  - Anode: Sulfur tolerance and carbon deposition

- Patterned electrodes

  →Optimal **Architecture** for Rapid Mass Transport

- Combustion CVD → **Nano-Structure**