



Probing Oxygen Reduction Mechanism of Sr-doped LaMnO₃ supported on 8mol% Yttria-Stabilized Zirconia:

An Electrochemical Impedance Study of Patterned, Dense Microelectrodes

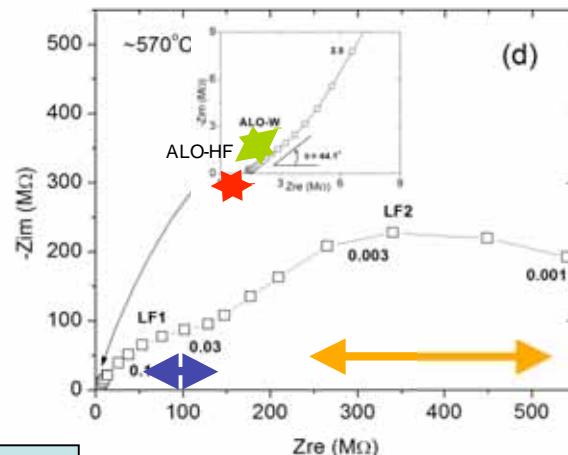
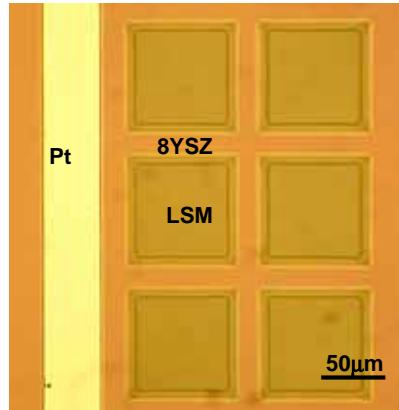
Gerardo Jose la O' and Yang Shao-Horn

*Electrochemical Energy Laboratory
Massachusetts Institute of Technology
Cambridge, MA*

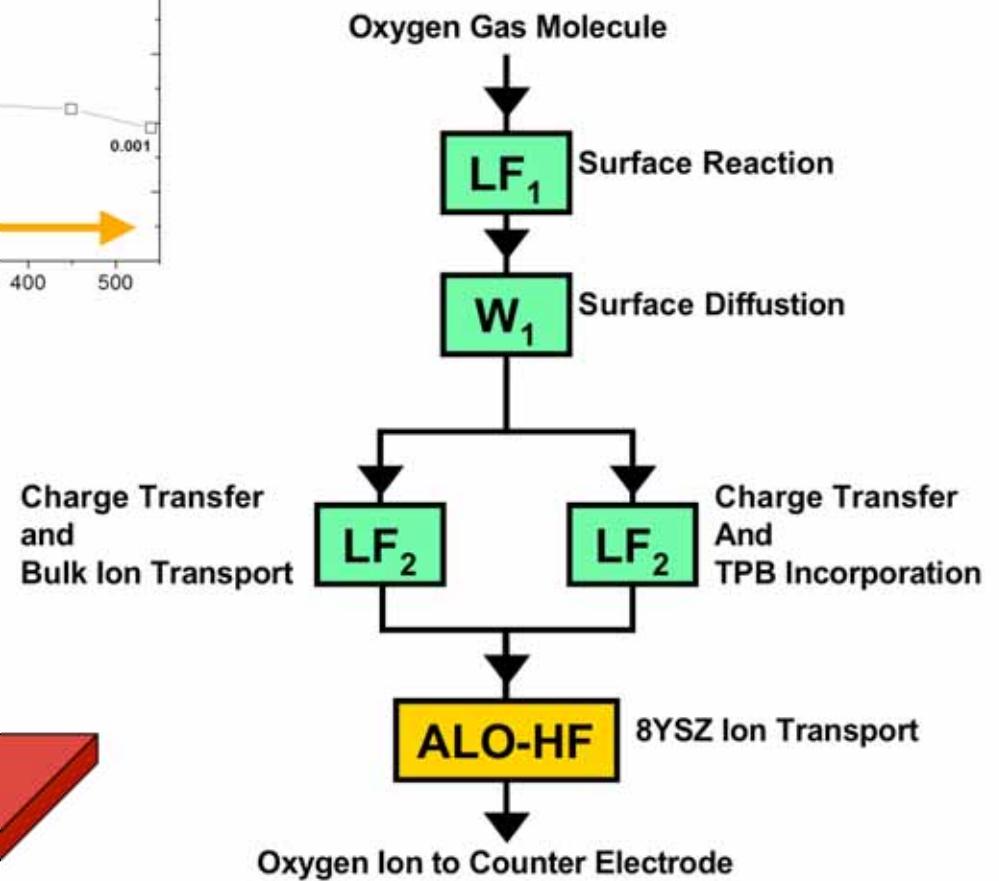
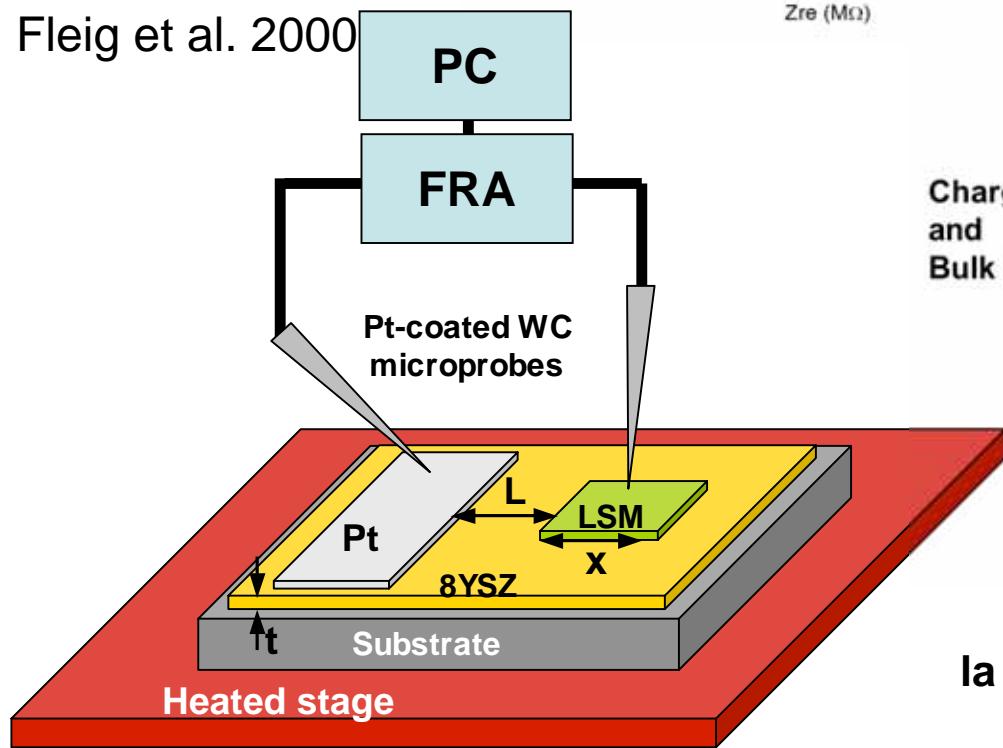
Funding: Ford-MIT Alliance and NSF



Probing Oxygen Reduction Reaction Mechanism



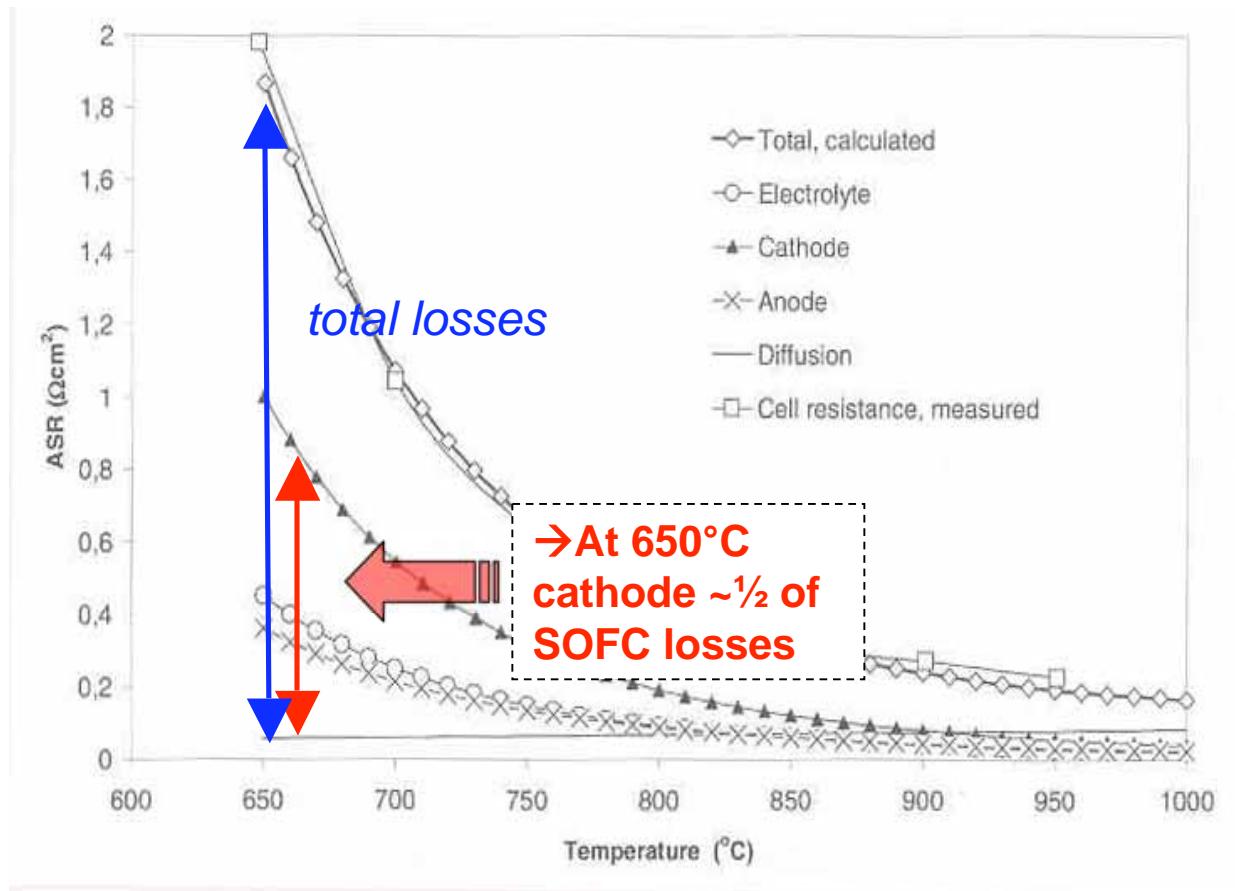
Fleig et al. 2000



Ia O', Yildiz, and Shao-Horn, submitted.

Sr-doped LaMnO₃

- La_{1-x}Sr_xMnO_{3-d} (**LSM**)
- Most widely used cathode in solid oxide fuel cell (SOFC)
- The largest contributor to voltage loss at low temperature:

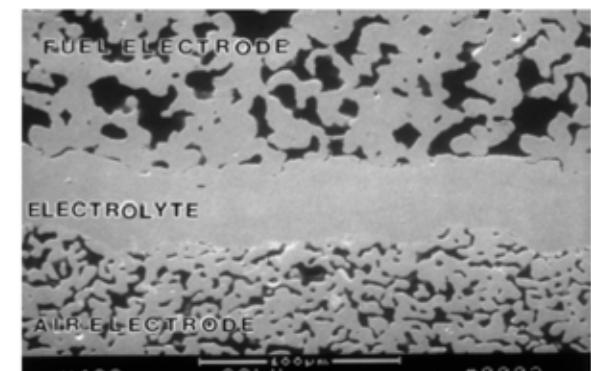


S. Singhal et al., High Temperature Solid Oxide Fuel Cells, p.280 (2003)

Current Understanding ORR in LSM

- Using Electrochemical Impedance Spectroscopy (EIS)

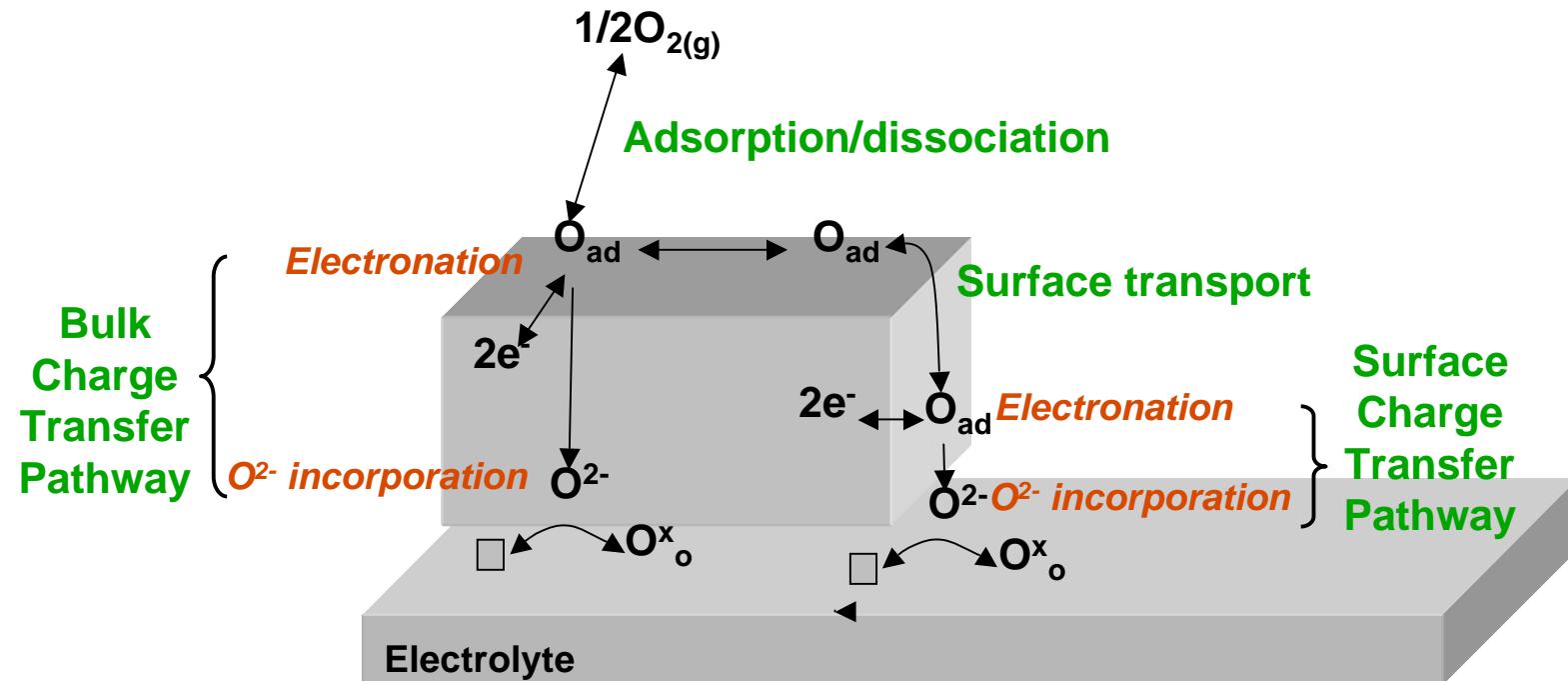
<i>Rate Limiting Attributed Process</i>	<i>Activation Energy, eV [Temperature, °C]</i>	<i>Resonant Frequency, Hz</i>	<i>References</i>
Oxygen molecule dissociation	1.8eV [680 – 970]	100 – 10	Siebert, 1995
Oxygen molecule dissociation	2.11eV [700 – 900]	10-1	Van Herle, 1996
Oxygen adsorption and dissociation	1.61±.05eV [550 – 850]	4,000 – 3,000	Murray, 1998
Dissociative adsorption, transfer to TPB, and surface diffusion	~2eV [800 - 1,050]	10,000 – 0.1	Jorgensen, 2001
Dissociation and surface diffusion	1.63 – 3.02 eV [700 – 900]	100 – 0.1	Jiang 2001, 2002
Dissociation and surface diffusion	1.61eV [700 – 950]	10	Chen, 2003



Singhal, S. C., Solid State Ionics 135 (1-4): 305-313 (2000)

- Rate-limiting mechanisms found inconsistent
- Porous electrodes undefined microstructure

Mechanisms of Oxygen Reduction on LSM/YSZ



Surface Reactions

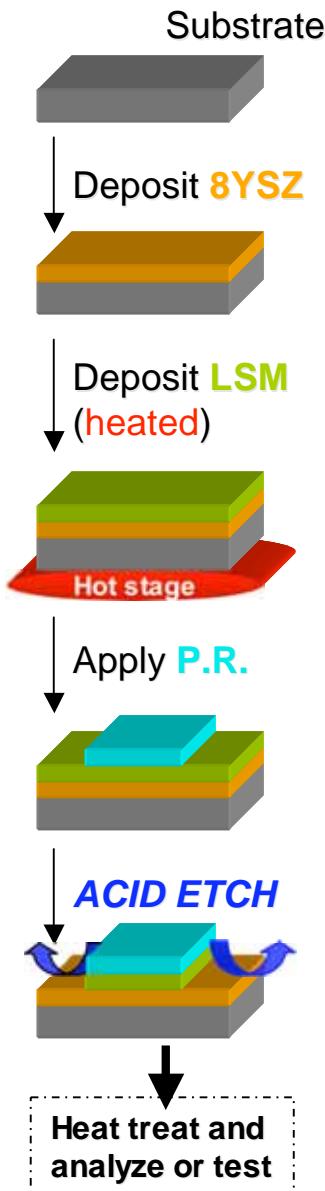
Adsorption/
Dissociation
Transport
Diffusion (bulk and surface)
Charge Transfer



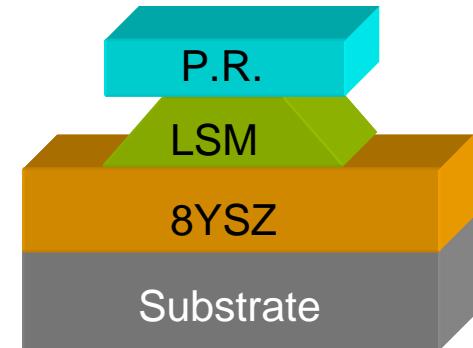
Two Current Pathways

1. Bulk Pathway
2. TPB Pathway

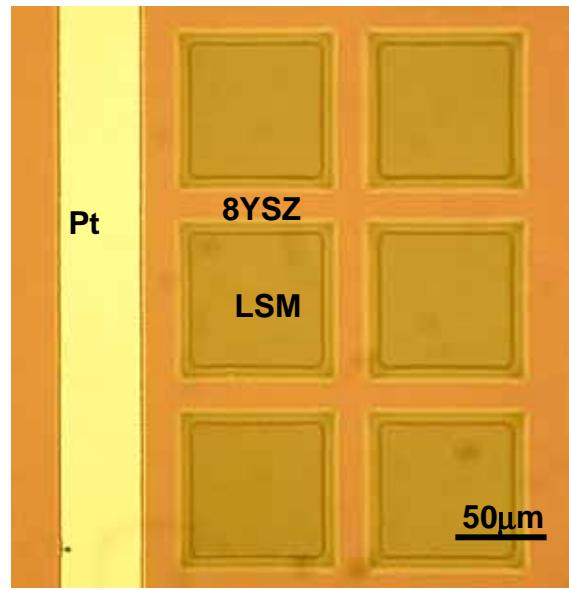
Sample Processing



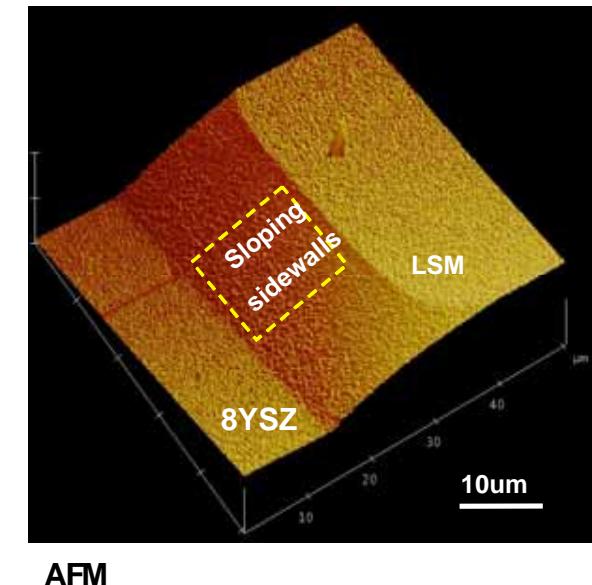
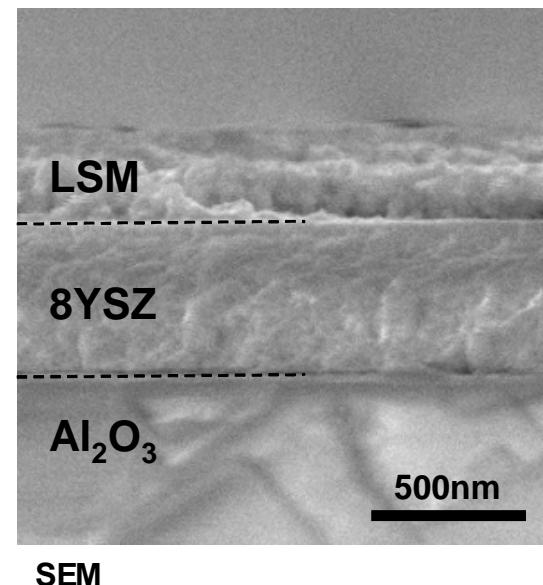
- RF Sputtered Thin Films on Al_2O_3 :
 - 8YSZ electrolyte
 - LSM cathode and Platinum counter electrode
 - Hot stage $>500^\circ\text{C}$
- Photolithography and Acid Etching LSM for patterning:
 - HCl acid etch
 - Unwanted *undercutting*
- Annealing: 800°C for 10hrs
- Sputter Pt as the counter



Microelectrodes



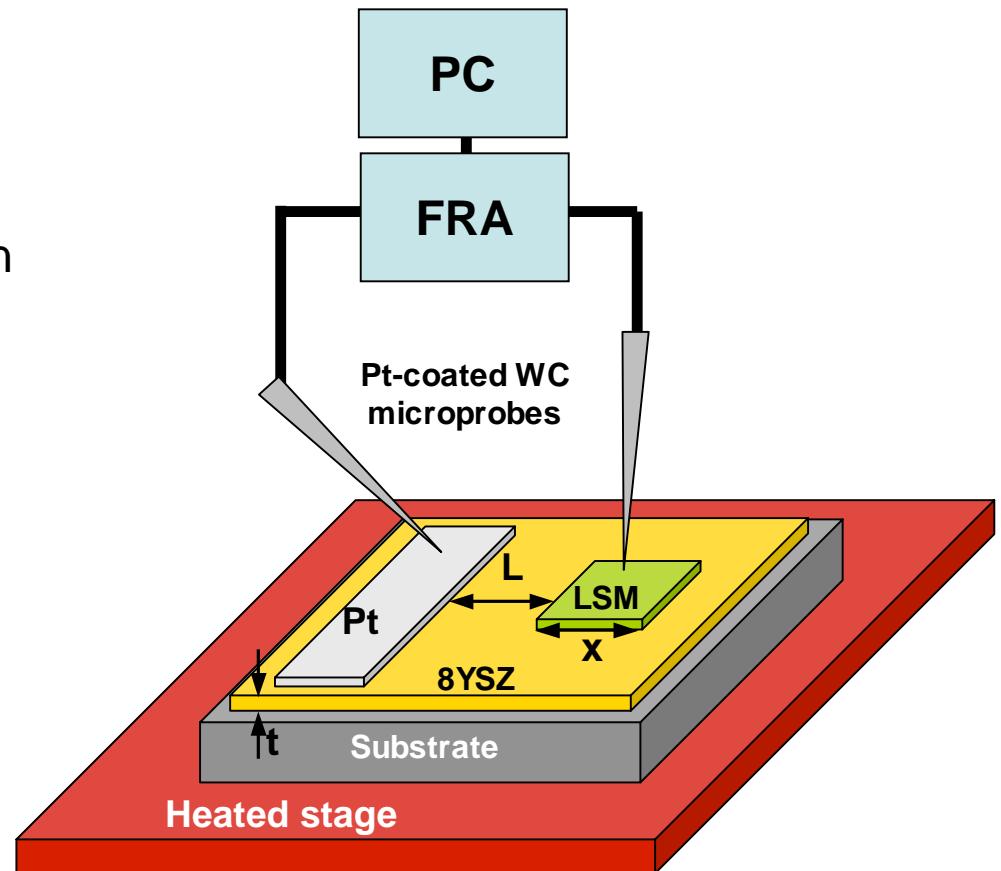
Optical Micrograph



- LSM, Pt and YSZ are dense and crack free
- Undercut clearly observed and being improved

Electrochemical Impedance Testing

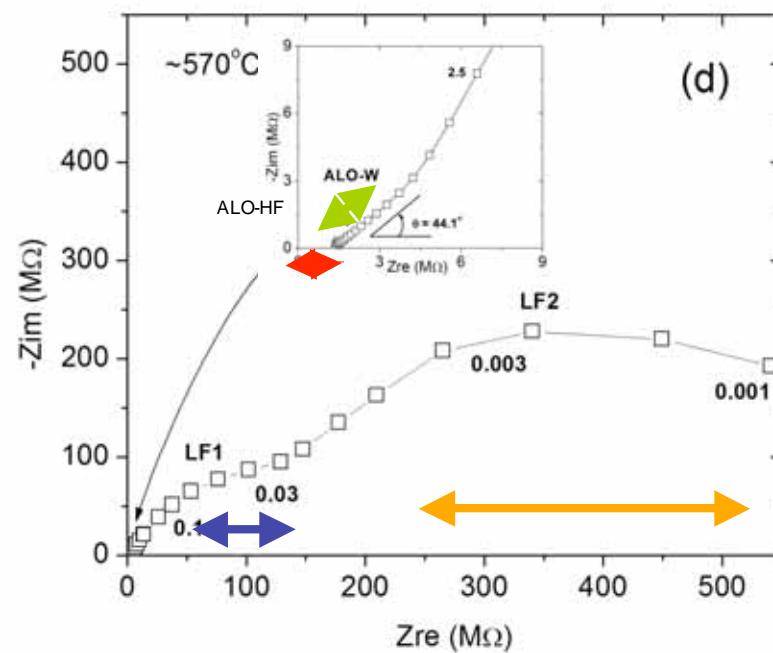
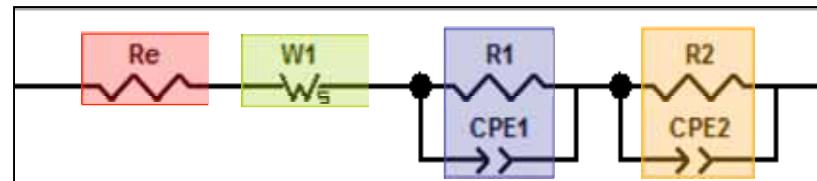
- Experimental configuration
 - Microprobe station (Karl Suss)
 - PC and Solartron 1260, 1296
 - Pt/YSZ/LSM testing configuration
- Testing Conditions
 - 2 electrode configuration
 - AC Voltage amplitude: 10mV
 - Frequency: 1MHz – 100 μ Hz
 - Air atmosphere
- Variables
 - Substrate: Al_2O_3
 - Temperature: ~790°C to ~570°C
 - Pt-LSM distance constant (L)
 - Microelectrode sizes (50-200 μ m)



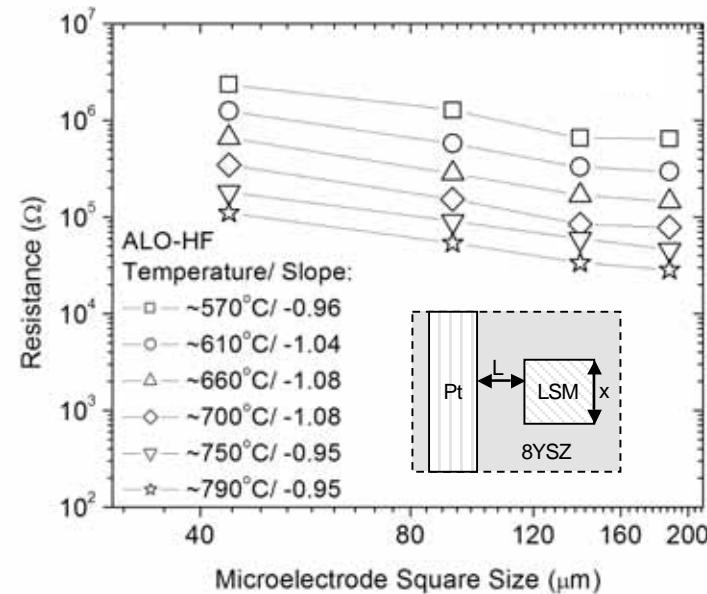
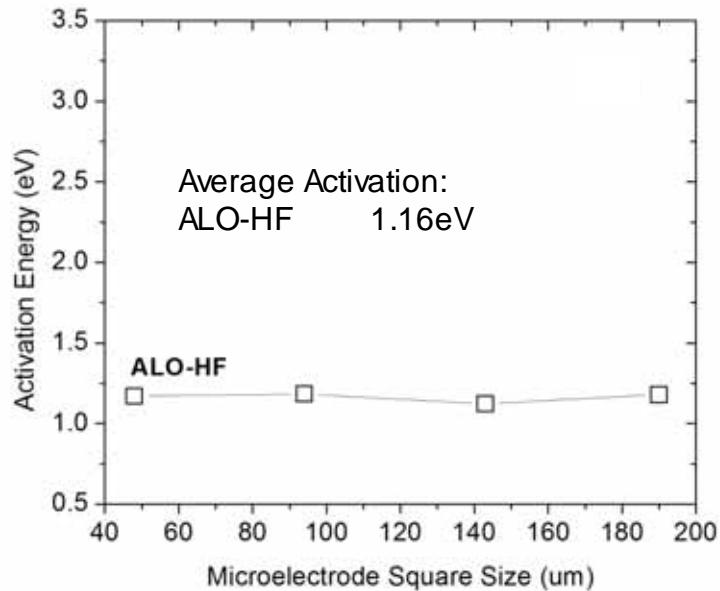
EIS Data Analysis

- Equivalent Circuit Fitting:
 - Quantify the impedance response
 - Extract resistances and capacitances

a) ALO-HF
 b) ALO-W
 c) LF1
 d) LF2



High Frequency Intercept (ALO-HF)

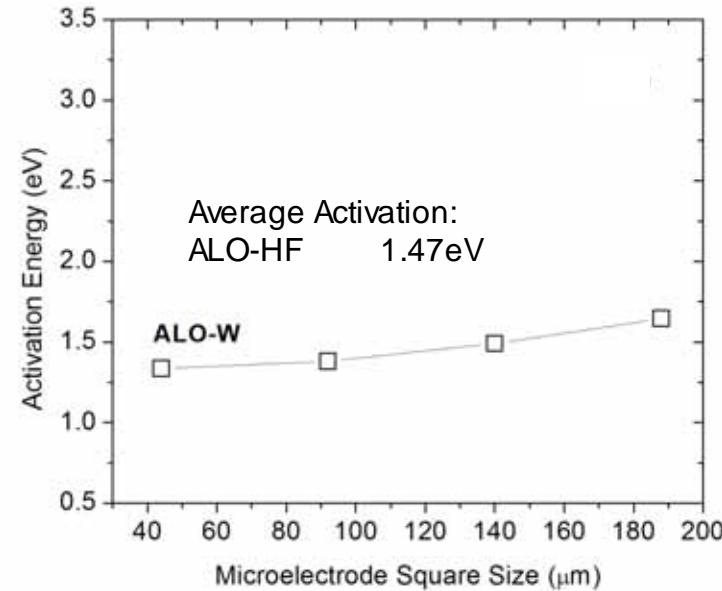
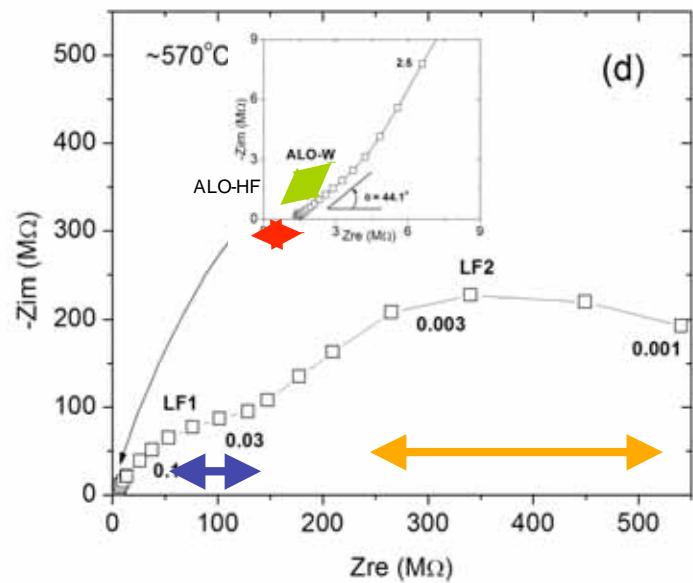


- Activation energy observed is close to reported values for 8YSZ (0.8-1.10eV)
- Correlate geometry to high-frequency resistance

$$R_{8\text{YSZ}} = \frac{L}{\sigma_{8\text{YSZ}} tx} \rightarrow R_{8\text{YSZ}} = x^{-1}$$

→ High Freq. Intercept (ALO-HF): Ion transport in 8YSZ

Linear Impedance Response (ALO-W)



- Activation Energies Reported for Surface Diffusion:

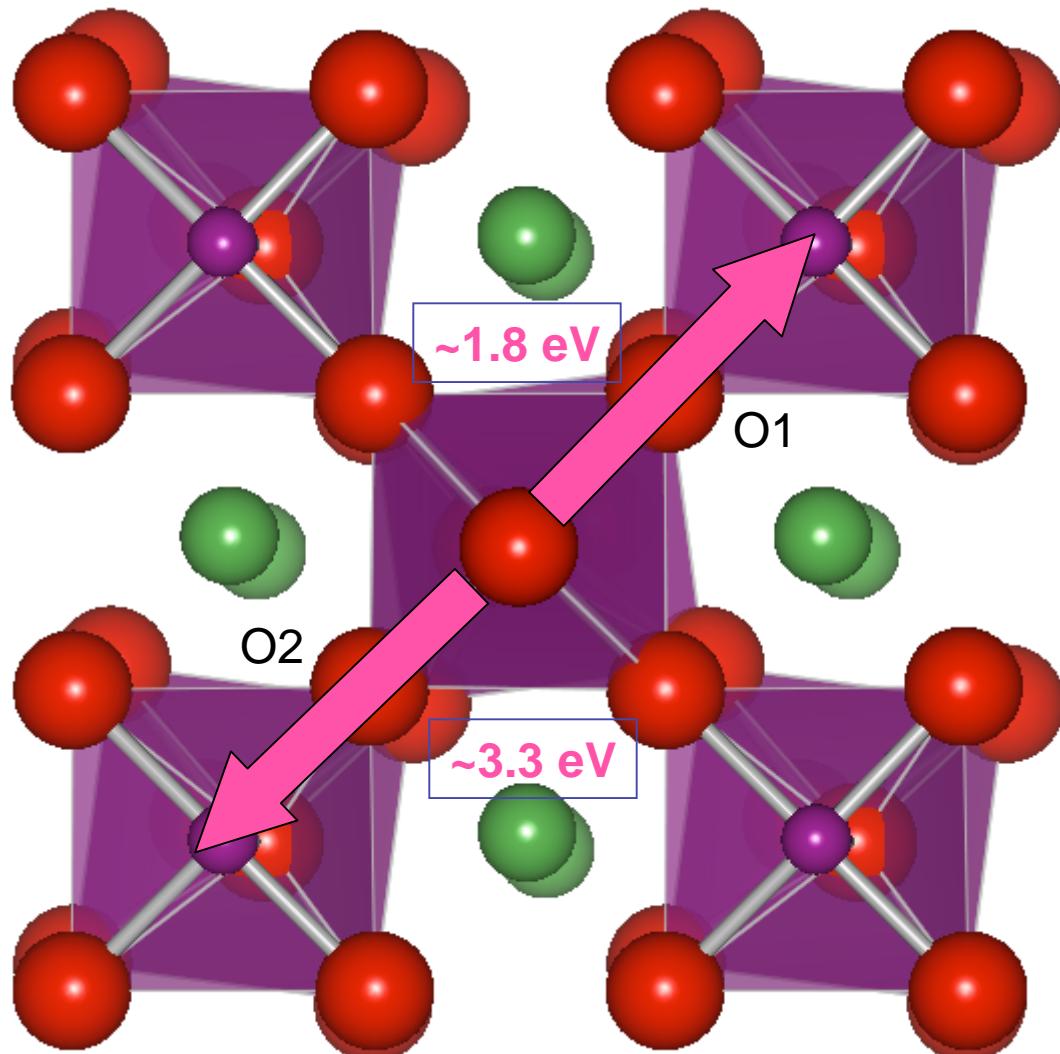
Pt (surface diffusion) 1.45 eV

LSM (surface diffusion + adsorption) 1.61 eV

- Value of R_w too small for bulk diffusion resistance

→ Linear Impedance (ALO-W) indicative of surface diffusion on LSM

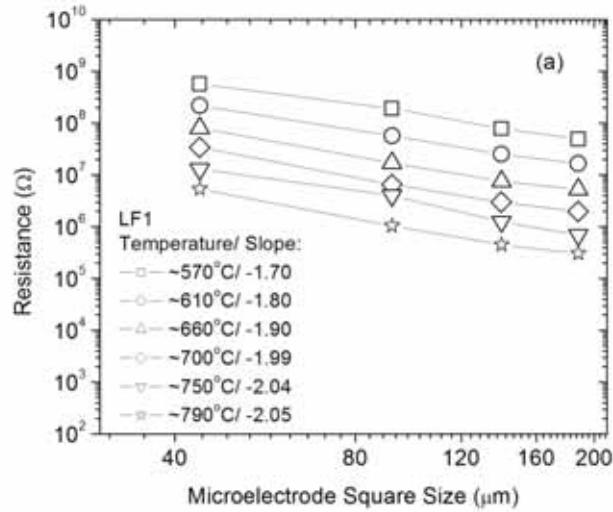
O Diffusion on LMO



- Surface process in ORR: Experimental E_A 1.34-1.65 eV (Ia O', *et al.*, Submitted '06)
- Our E_A for oxygen hopping ~ 1.8 eV

Courtesy of D. Morgan at the University of Wisconsin-Madison

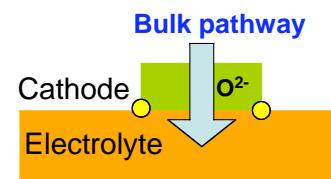
Low Frequency Semicircle (LF1)



- LF1 slope dependence of $\sim (-2)$
- Indicates a bulk/surface/interface dependence
- Activation energy ($\sim 1.83\text{eV}$) and capacitance ($3.4 \times 10^{-4}\text{F/cm}^2$) point to surface reaction*

*Siebert et al., E.Acta, 40 (1995), Van Herle et al., E.Acta, 41 (1996), Mitterdorfer, SSI, 111 (1998) and Ioroi et al., JECS, 145 (1998)

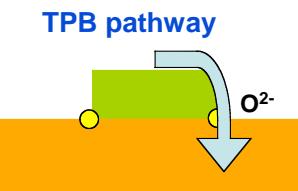
[1] Bulk (& surface or interface) path:



$$R_{b/s/int} = \frac{h}{\sigma_{LSM} x^2}$$

$$\rightarrow R_{b/s/int} \propto x^{-2}$$

[2] TPB path*:



$$R_{tpb} = \frac{1}{\sigma_e x^2}$$

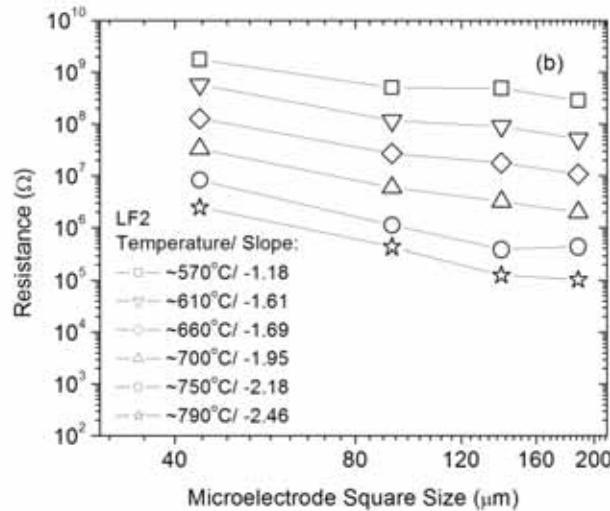
$$\sigma_e \propto x^{-1}$$

$$\rightarrow R_{tpb} \propto x^{-1}$$

*J. Mizusaki et al., SSI 22 (1987) p. 313
 σ_e = electrode interfacial conductivity

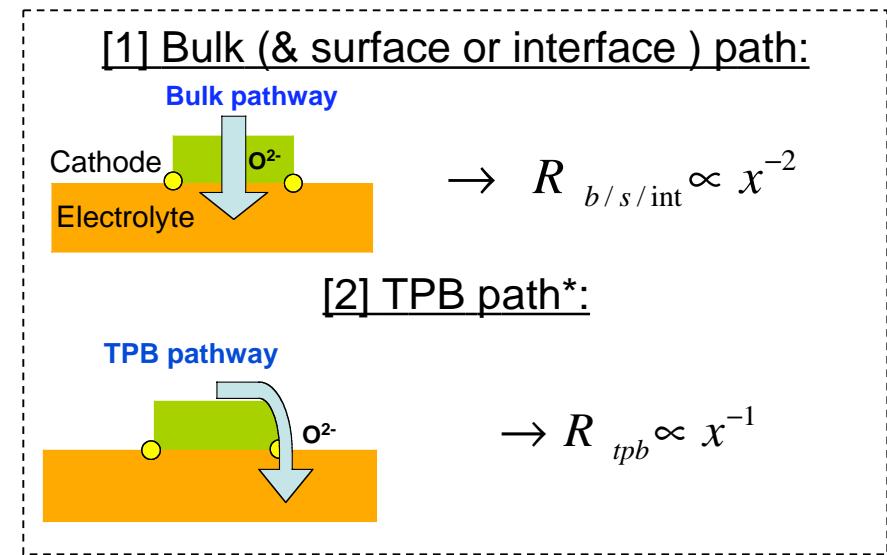
→ LF1: Surface reaction on LSM (possibly dissociative adsorption reaction as observed in previous studies)

Low Frequency Semicircle (LF2)



- LF2 slope dependence range from (-1.2) to (-2.5)
- Signify a change in dependence from low to high temperature
- Activation energy (~2.83eV) and capacitance ($3.2 \times 10^{-3} \text{ F/cm}^2$) indicate bulk transport contribution*

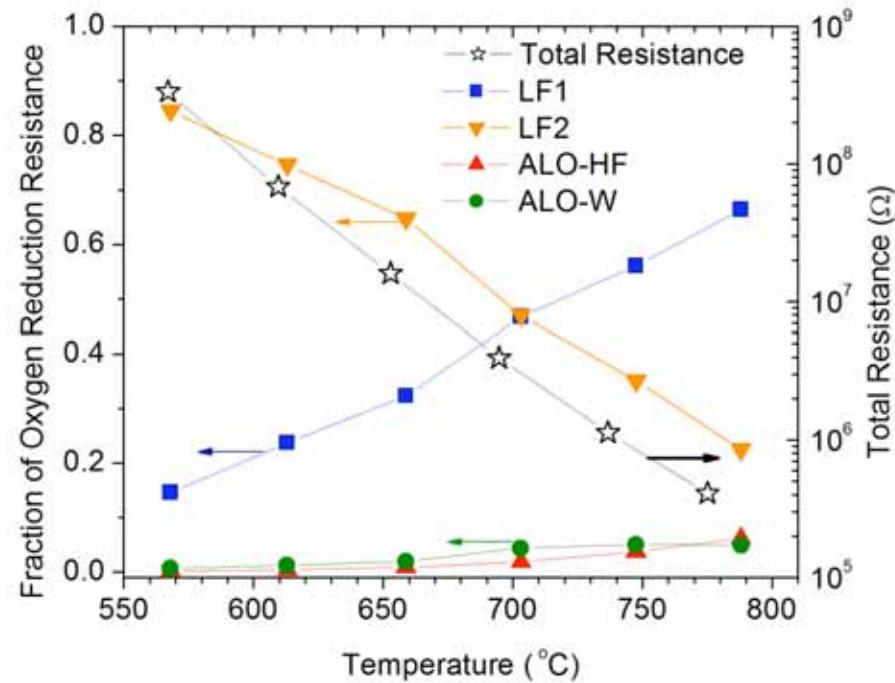
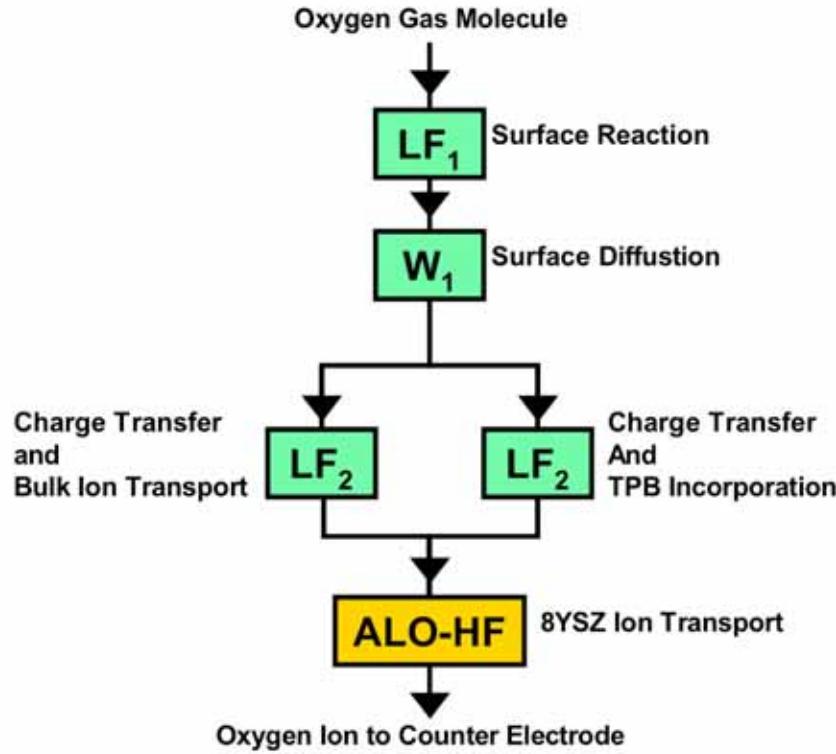
*Yasuda et al., SSI, 86-88 (1996), De Souza et al., SSI, 106 (1998), and Adler (Chem. Reviews, 104, (2004)) reports higher capacitance indicates increased bulk contribution



*J. Mizusaki et al., SSI 22 (1987) p. 313
 σ_e = electrode interfacial conductivity

→ LF2: indicative of Bulk ion transport and TPB process with dominating reaction dependent on temperature

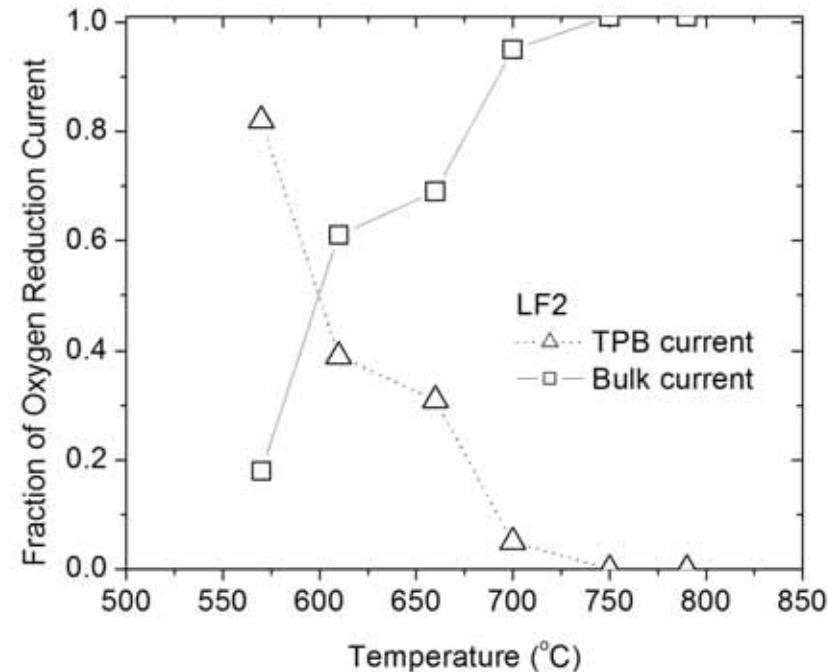
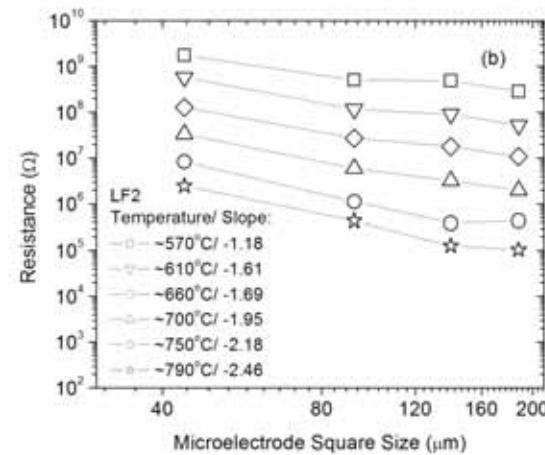
Overall Limiting Reaction(s) on LSM



- Below 700°C, **bulk/TPB charge transfer** from LF2 processes limiting
- Above 700°C, **surface reaction(s) LF1** limiting

→ *Rate limiting reaction on LSM microelectrodes is dependent on temperature*

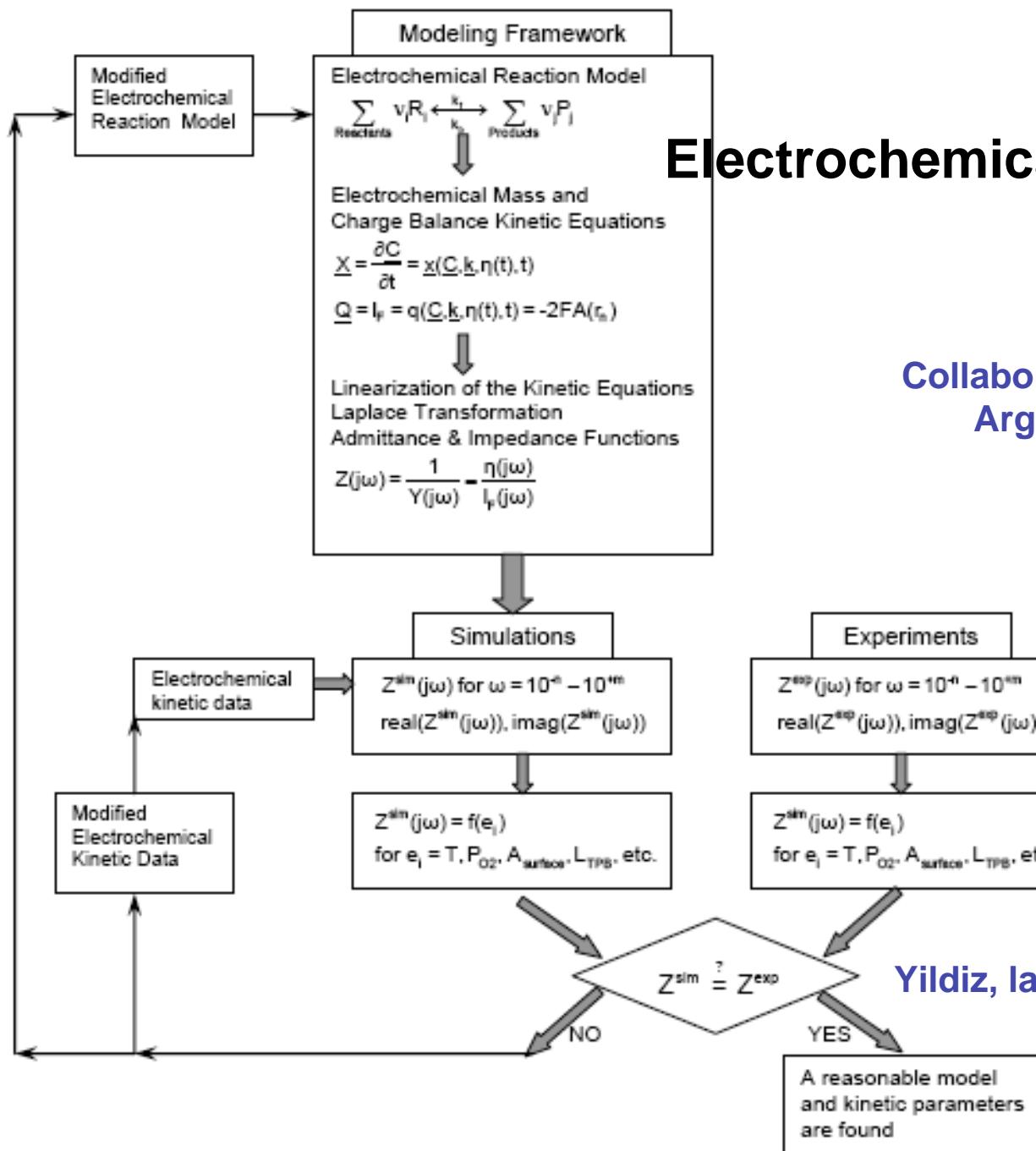
Current Path during Oxygen Reduction



- Using the LF2 slope dependence, the current path can be estimated using the relationship →

$$\ln\left(\frac{A^{1-y} B^y}{C}\right) = (y-1)\ln\left(\frac{I_{TPB}}{I_{total}}\right) + y \ln\left(\frac{I_{bulk}}{I_{total}}\right); \text{ where } 0 > y > 1$$

Extrapolating to $\sim 550^\circ\text{C}$, current primarily through the **TPB**
Insights: Nanostructured cathode ==> lowering LSM cathode polarization
Improve SOFC performance at low temperatures



Electrochemical Kinetics Modeling

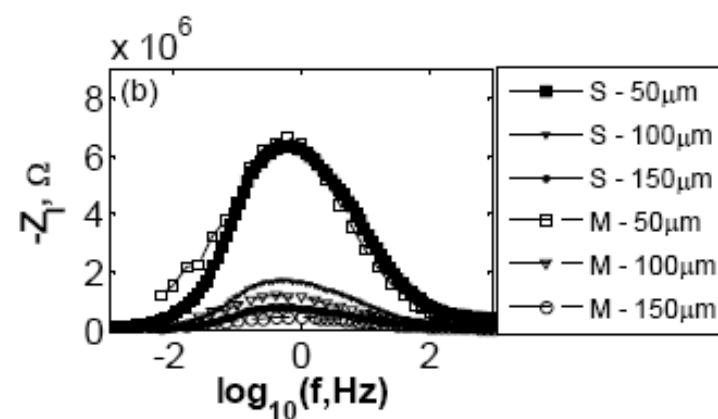
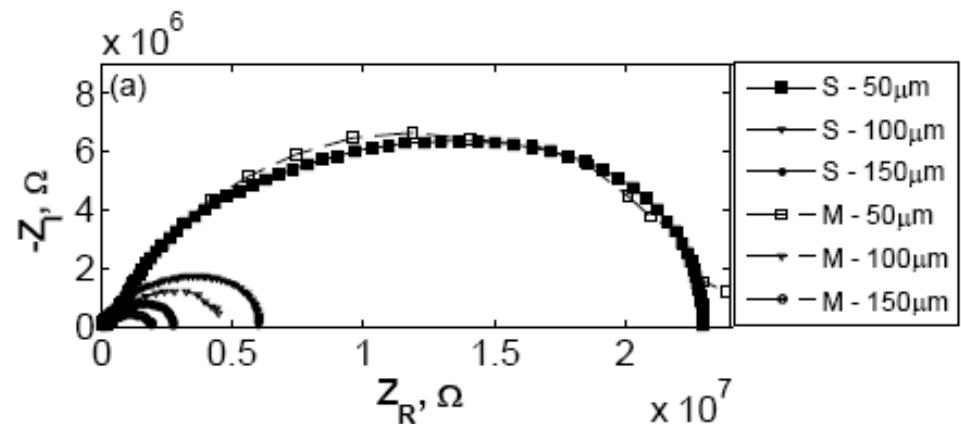
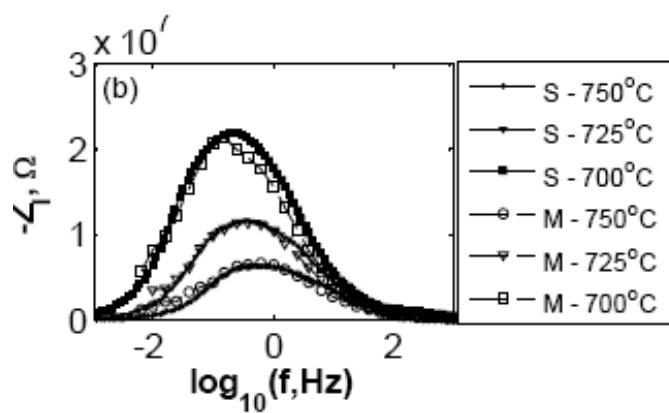
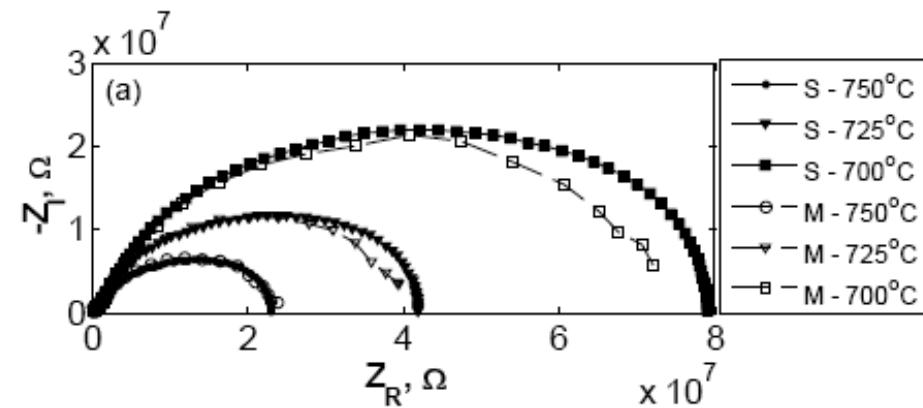
Collaboration with B. Yildiz at Argonne National lab

Modeled Oxygen Reduction Scheme

REACTION / LOCATION	REACTION PARAMETERS
$O_{2(g)} \xrightleftharpoons[k_{des}]{k_{ads}} 2O_{ad,s}$	<ul style="list-style-type: none"> - Adsorption / desorption reaction rate constants on LSM surface; k_{ads}, k_{des} - Surface coverage of oxygen on LSM; θ - Oxygen surface site concentration; N_o
$O_{ad,s} + 2e^- \xrightleftharpoons[k_{-el}]{k_{el}} O_s^{-2}$	<ul style="list-style-type: none"> - Oxygen electronation rate constants; k_{el}, k_{-el} - Surface coverage of oxygen on LSM; θ - Fraction of reduced oxygen on LSM; α
$O_s^{-2} \xrightleftharpoons{D_{Surf}} O_{3PB}^{-2}$	<ul style="list-style-type: none"> - Oxygen ion (O^-) diffusion coefficient on LSM surface; D_{surf}
$O_b^{-2} \xrightleftharpoons{D_{Bulk}} O_{2PB}^{-2}$	<ul style="list-style-type: none"> - Oxygen ion (O^-) diffusion coefficient in the bulk of LSM; D_{bulk}
$O_{3PB}^{-2} + V_O^Y \xrightleftharpoons[k_{-ts}]{k_{ts}} O_O^Y$ $O_{2PB}^{-2} + V_O^Y \xrightleftharpoons[k_{-tb}]{k_{tb}} O_O^Y$	<ul style="list-style-type: none"> - O^- transfer rate constants at LSM surface/YSZ interface and LSM bulk/YSZ interface; k_{ts}, k_{-ts}, k_{tb}, k_{-tb} - Oxygen concentration in YSZ ; O_o - Vacancy concentration in YSZ ; V_O^Y
$O_O^Y \xrightleftharpoons{D_{YSZ}} O_O^Y$	<ul style="list-style-type: none"> - Oxygen ion (O^-) diffusion coefficient in the bulk of YSZ; D_{YSZ}

Yildiz, la O' and Shao-Horn, submitted.

Simulated and Experimental Data



Simulated EIS data from the proposed ORR reaction mechanism are consistent with experimental data

Yildiz, Ia O' and Shao-Horn, submitted.



Probing Oxygen Reduction Reaction Mechanisms of Different Electrode-Electrolyte Systems

