Fundamental Characterization and Modeling of Infiltrated SOFC Cathode

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Acknowledgement

- Technical Contributors
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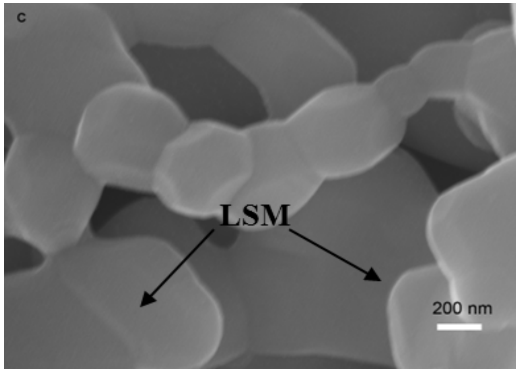
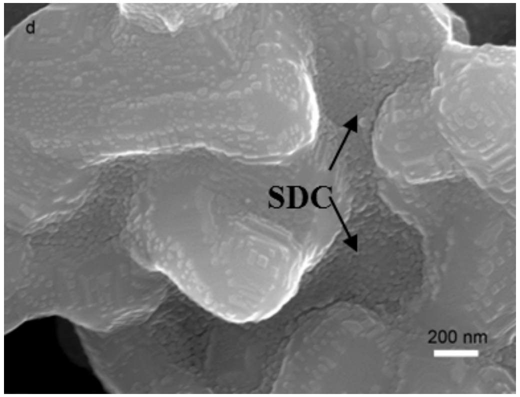
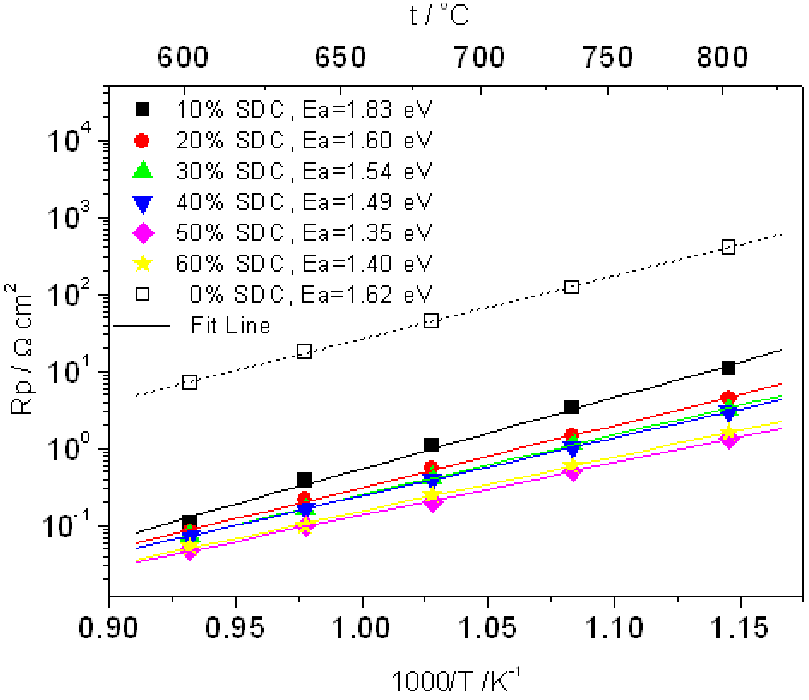
  - Kirk Gerdes, Randall Gemmen – NETL
- SECA Program Management Team
  - Dan Driscoll, Shailesh Vora, Briggs White, Joe Stoffa

Infiltrated SOFC Cathode

Principal Assumption: Infiltrants having high oxygen absorption capabilities enhance oxygen flux into the cathode and thus improve the cathode performance





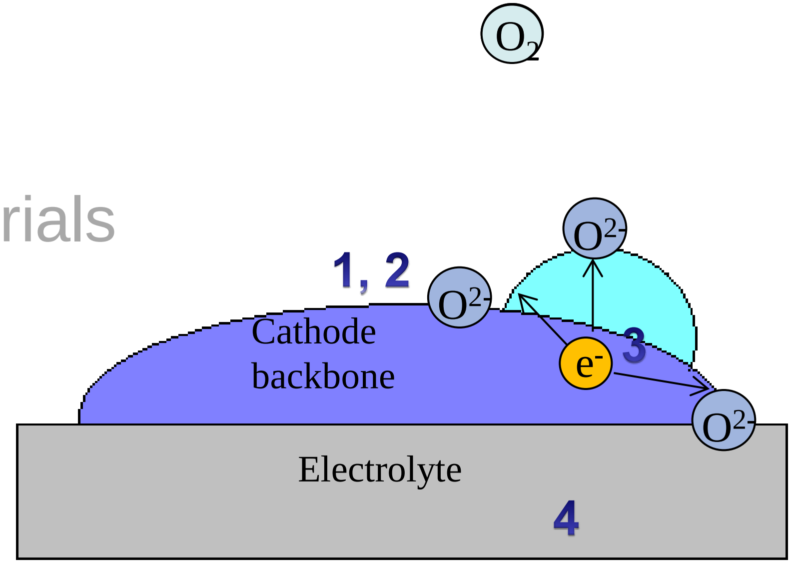


Strategies: (1) Catalysts on MIEC
(2) IC/EC on EC/IC
(3) Self-infiltration to increase TPB

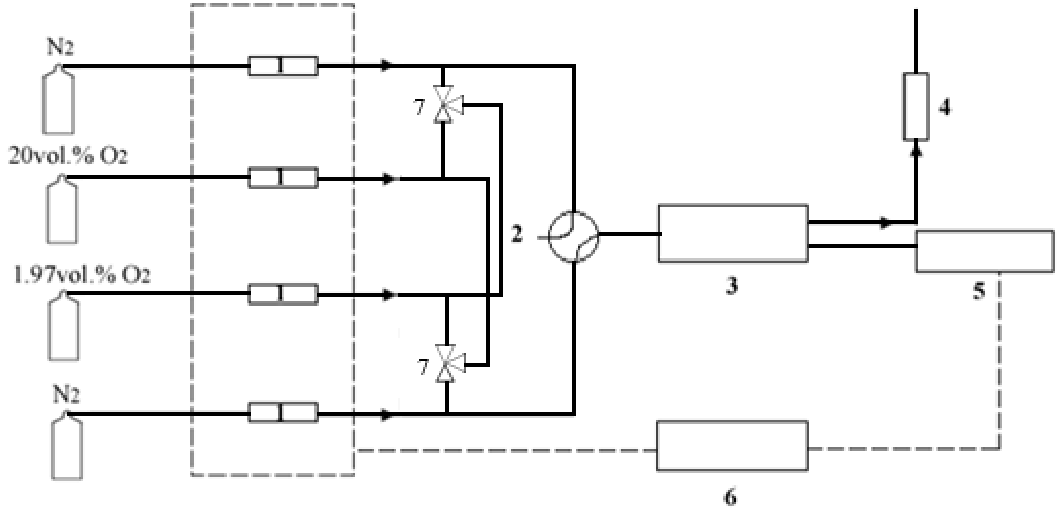
Dong Ding, Mingyang Gong, Chunchuan Xu, Nicholas Baxter, Yihong Li, John Zondlo, Kirk Gerdes, **Xingbo Liu***: Electrochemical characteristics of samaria-doped ceria infiltrated strontium-doped LaMnO3 cathodes with varied thickness for yttria-stabilized zirconia electrolytes, *Journal of Power Sources 196 (2011) 2551-2557*

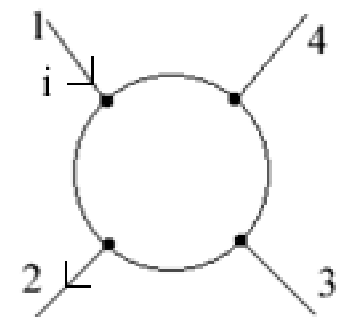
Fundamental Issues in SOFC Cathode

- **Improving the data analysis method for ECR**
- **Understanding the kinetic parameters obtained from ECR**
- Develop ECR application for infiltrated cathode materials
- Infiltrated cathode model



ECR Testing System Setup





van der Pauw Method

$$\sigma = \frac{\ln 2}{a\pi R}$$

Schematic representation of the conductivity relaxation set-up
1.Mass flow controller 2. Four-way valve 3. Furnace 4. Oxygen analyzer
5. Nano-voltemeter and current source meter 6. Computer 7. Three way valve

Theoretical Background of ECR Method

- Assume a small oxygen partial pressure changing step:

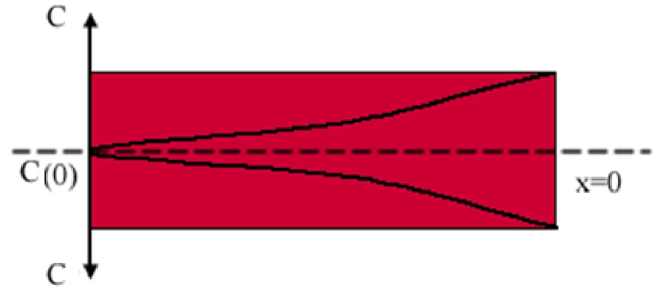
$$\frac{C(t)-C(0)}{C(\infty)-C(0)}=\frac{\delta(t)-\delta(0)}{\delta(\infty)-\delta(0)}=\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}$$

$$\Delta \log P_{O_2} \leq 1$$

- Diffusion equation and solution:

$$\frac{\partial \phi}{\partial t}=D\frac{\partial^2 \phi}{\partial x^2}$$

$$-D\partial C/\partial x\Big|_{x=\pm a}=k[C(\infty)-C(t)]$$



C(∞): is in equilibrium surface concentration under certain oxygen pressure

C(t): real time surface concentration

$$\frac{C(t)-C(0)}{C(\infty)-C(0)}=1-\sum_{n=1}^{\infty}\frac{2L^2\exp(-\beta_n^2 Dt/a^2)}{\beta_n^2(\beta_n^2+L^2+L)}$$

$$L=\frac{ak}{D}=\frac{a}{l_c}=\beta_n \tan\beta_n$$

Characteristic length

Data Analysis

❖ *Get initial value of k*

$$\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}=1-\exp[-\frac{k(t-t_0)}{a}]$$

❖ *Get initial value of D*

$$\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-\frac{(2n+1)^2\pi^2 D(t-t_0)}{4a^2}]$$

❖ *Calculate L*

$$L=\frac{ak}{D}$$

If L>1, use fitting parameters (D, b_1, t_0)

If L<=1, use fitting parameters (k, b_1 , t_0)

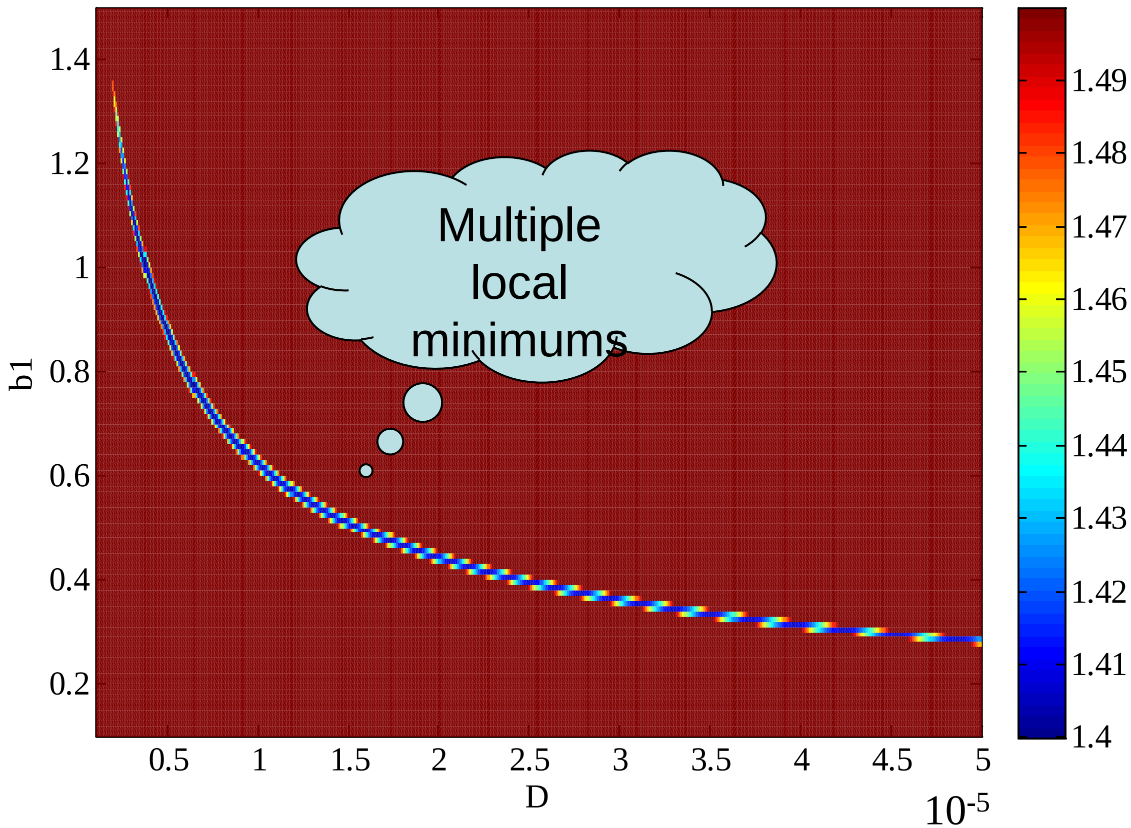
Chang-Rock Song, Han-Ill Yoo. Chemical diffusivity of $BaTiO_{3-\delta}$: I. Experimental determination. Solid State Ionics, 1999; 120(1-4): 141-153.

Fitting *D* and *k*

- Problem of the reported method

With 2% noise

D [cm²/s]	k [cm/s]
5×10^{-6}	1×10^{-4}
t_0 [s]	b_1 [-]
0	0.8603
a [cm]	L [-]
0.05	1

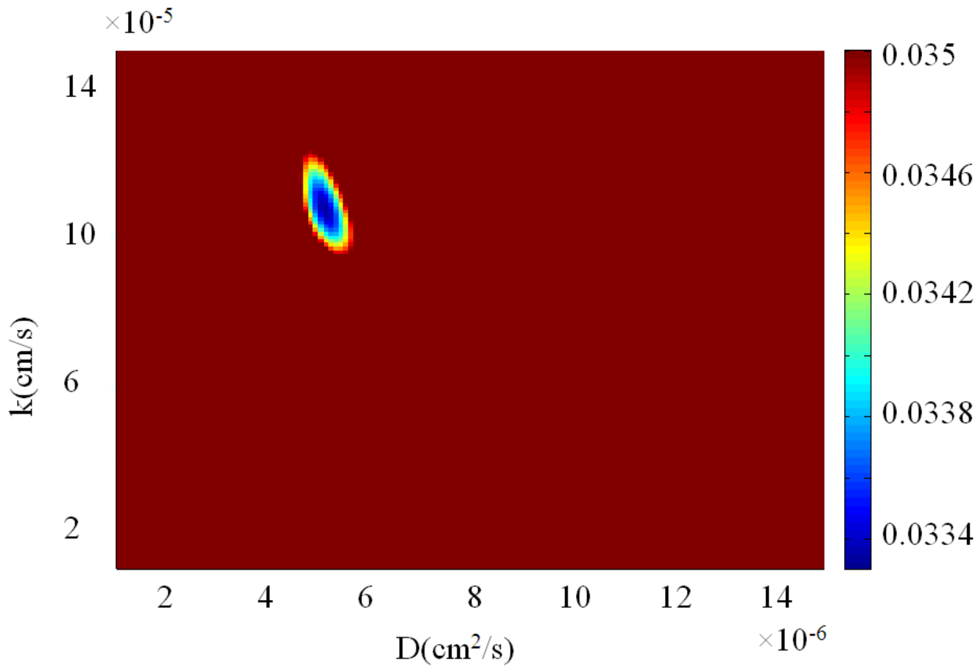


Improved Method

- Analyze two relaxation data sets

D [cm^2/s]	k [cm/s]
5×10^{-6}	1×10^{-4}
t_0 [s]	b_1 [-]
0	0.8603
a_1 [cm]	L_1 [-]
0.05	1
a_2 [cm]	L_2 [-]
0.50	10

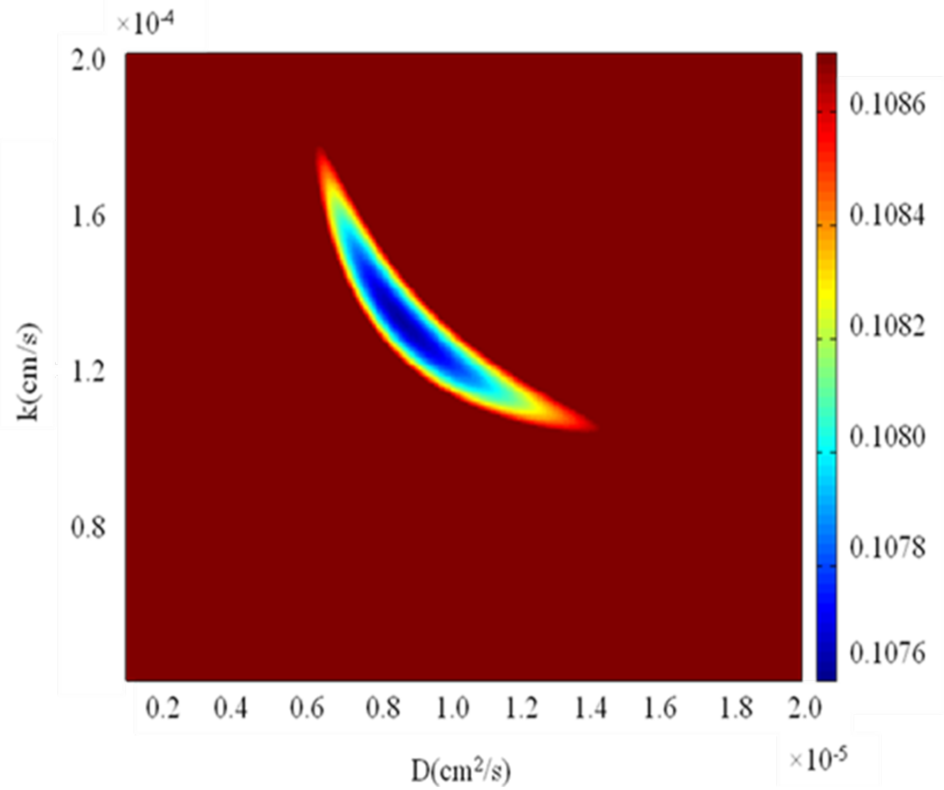
$$f = \sqrt{\frac{F_1^2}{T_1} + \frac{F_2^2}{T_2}}$$



The estimation error for oxygen surface exchange coefficient was decreased by 80% within a 5% variation of minimum error band

Yihong Li, Kirk Gerdes, **Xingbo Liu***: An Improved Method to Increase the Predictive Accuracy of the ECR Technique, *Solid State Ionics 204-205 (2011) 104-110*

Oxygen Transport in LSCF Cathode



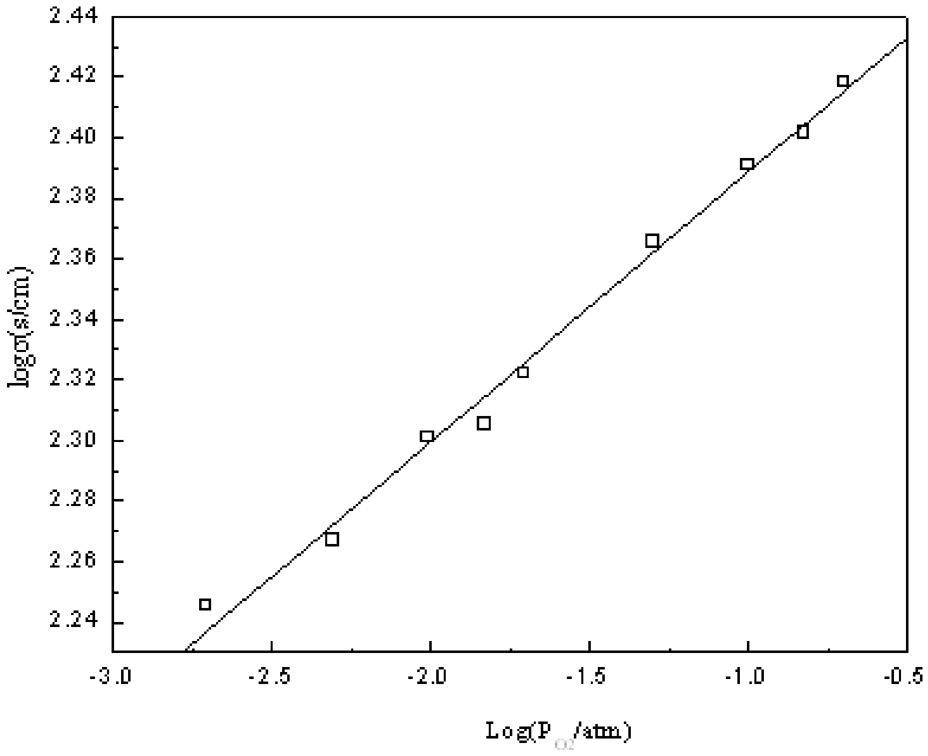
0.20atm→0.18atm

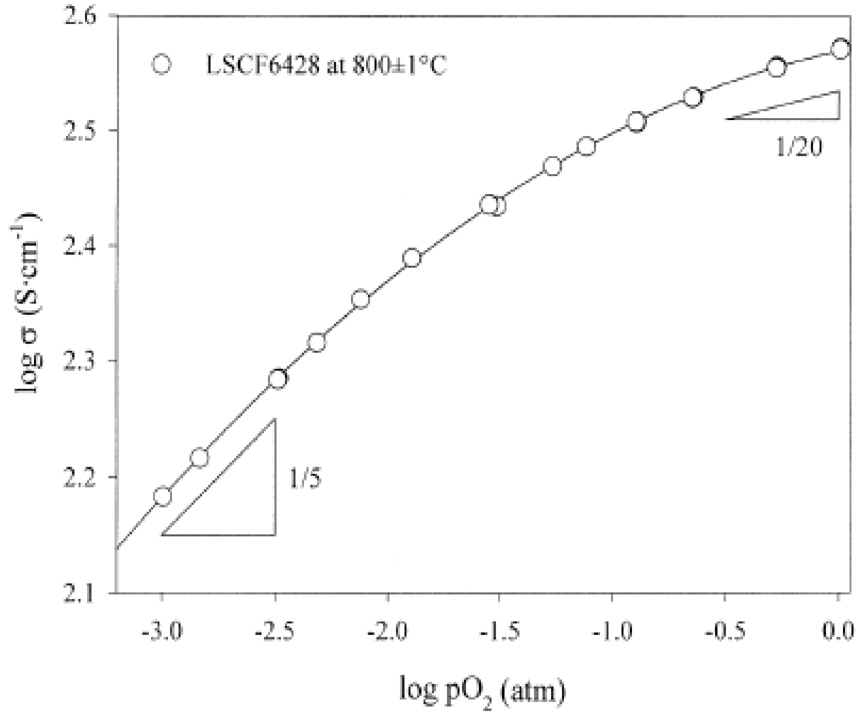
❖ Testing conditions:

- Gas flow rate: 400sccm
- Temperature: 800C
- Constant current: 40mA
- Oxygen partial pressure: 0.20atm~0.018atm
- Oxygen partial pressure step change: $|\Delta \log P_{O2}| < 0.1$

Oxygen Transport in LSCF Cathode

❑Conductivity of LSCF





J.A. Lane, J.A. Kilner / Solid State Ionics 136–137 (2000) 997–1001

Oxygen Transport in LSCF Cathode

- Oxygen partial pressure effects

Oxygen reduction reaction

$$\frac{1}{2}O_2 + 2e^- + V_o^{\cdot\cdot} \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_o^x$$

Surface exchange coefficient

$$k_1 P_{O_2}^{1/2}[V_o^{\cdot\cdot}]' - k_2 C_s = k[C(\infty) - C_s]$$

$$k = \frac{k_1 P_{O_2}^{1/2}[V_o^{\cdot\cdot}]' - k_2 C_s}{[C(\infty) - C_s]} = k_1 P_{O_2}^{1/2} + \frac{k_1 P_{O_2}^{1/2}[V_o^{\cdot\cdot}] - k_2 C_s}{[C(\infty) - C_s]}$$

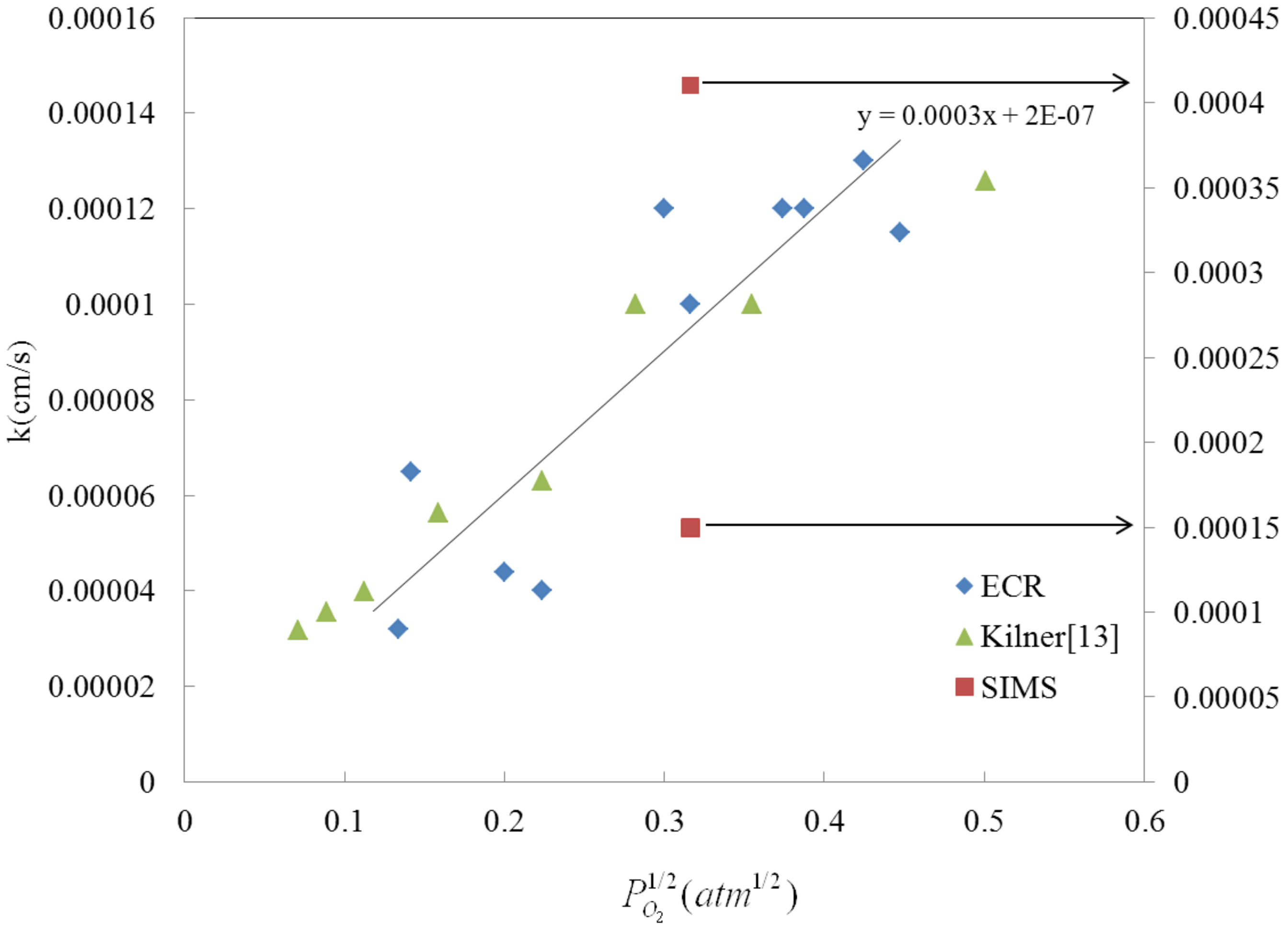
$$k_1 P_{O_2}^{1/2}[V_o^{\cdot\cdot}] = k_2 C(\infty)$$

$$= k_1 P_{O_2}^{1/2} + \frac{k_2 C(\infty) - k_2 C_s}{[C(\infty) - C_s]} = k_1 P_{O_2}^{1/2} + k_2$$

$$[V_o^{\cdot\cdot}]' = [V_o^{\cdot\cdot}] + C(\infty) - C_s$$

$$k = k_1 P_{O_2}^{1/2} + k_2$$

ECR vs. IE



Yihong Li, Kirk Gerdes, Teruhisa Horita, **Xingbo Liu***: Surface Exchange and Bulk Diffusivity of LSCF as SOFC Cathode: Electrical Conductivity Relaxation and Isotope Exchange Characterizations, *Journal of The Electrochemical Society 160 (2013) F343-F350*

Fundamental Issues in SOFC Cathode

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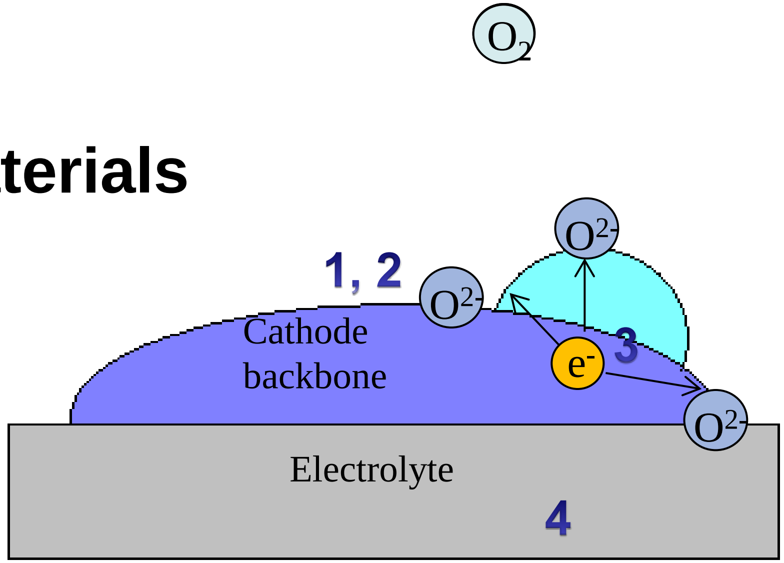
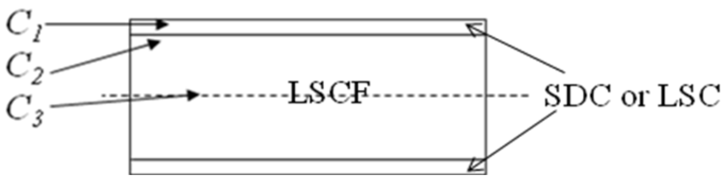


Oxygen transport in Infiltrated SOFC Cathode

- Characterize oxygen exchange coefficient at infiltrated/cathode backbone interface



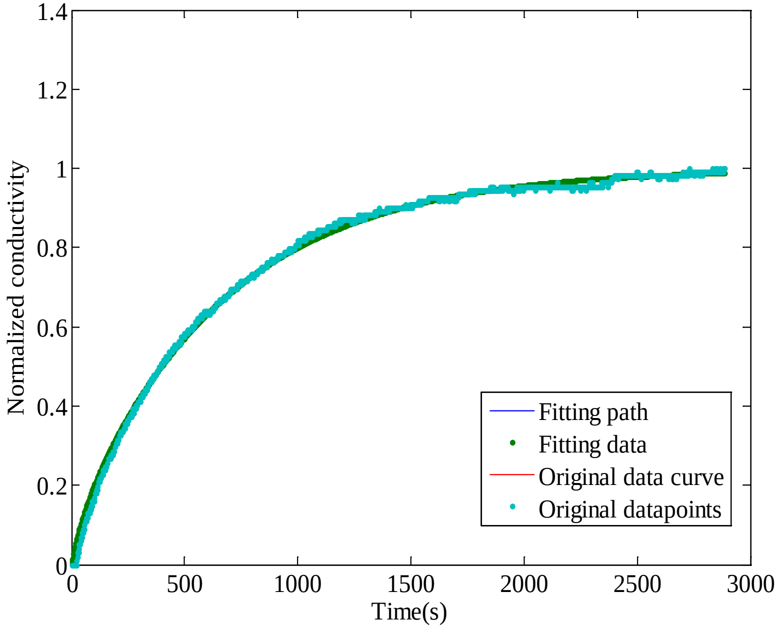
$$C_1 - C'_\infty = \frac{J}{k_{surface}}$$

$$C_2 - C_\infty = \frac{J}{k_{interface}}$$

$$C_3 - C_2 = \frac{Ja}{D}$$

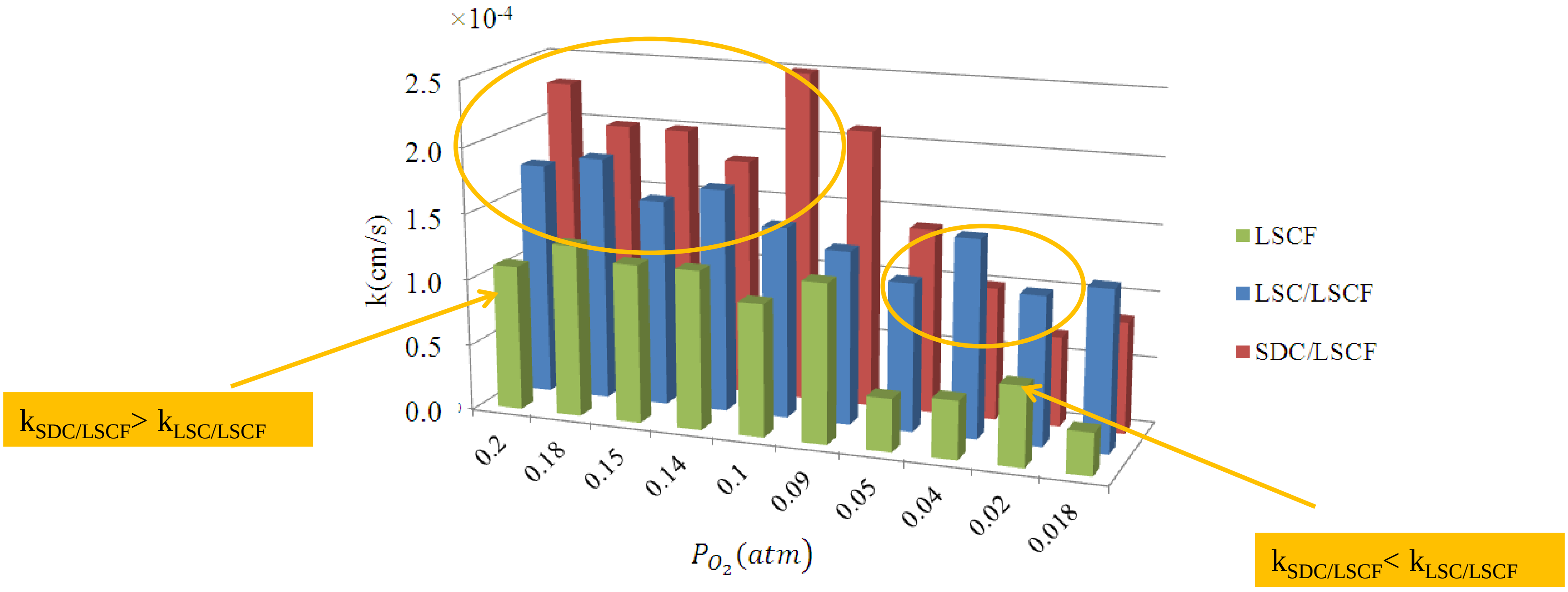
$$\frac{1}{k} = \frac{1}{k_{interface}} + \frac{1}{k_{surface}}$$

Total surface exchange coefficient 3.3×10^{-4}cm/s
Interface exchange coefficient: 3.7×10^{-4}cm/s



Normalized conductivity and fitting curve of spin coated LSC with oxygen partial pressure changing from 0.05atm to 0.04atm

Oxygen Transport in Infiltrated SOFCs Cathode



Surface exchange coefficients of single phase LSCF and infiltrated cathodes

Yihong Li, Kirk Gerdes, **Xingbo Liu*:** Oxygen Transport Kinetics in Infiltrated SOFCs Cathode by Electrical Conductivity Relaxation Technique, *Journal of The Electrochemical Society 160 (2013) F554-559*

Fundamental Issues in SOFC Cathode

- Improve the data analysis method for ECR
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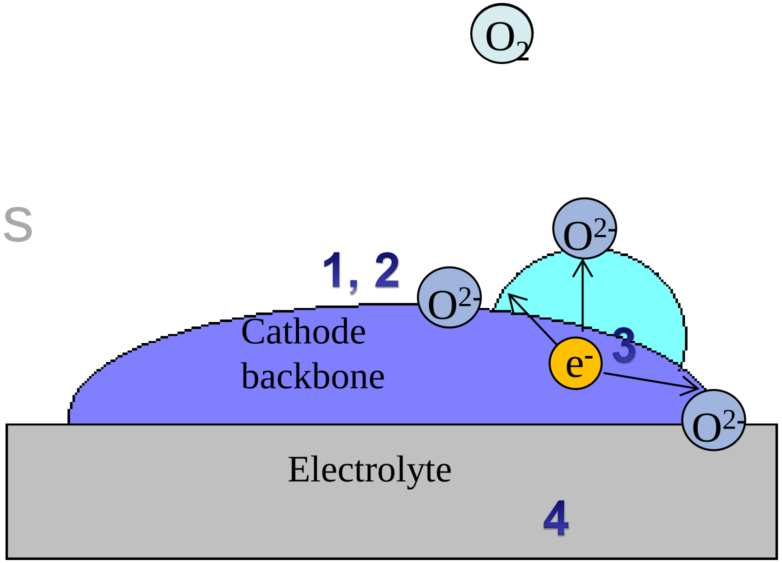
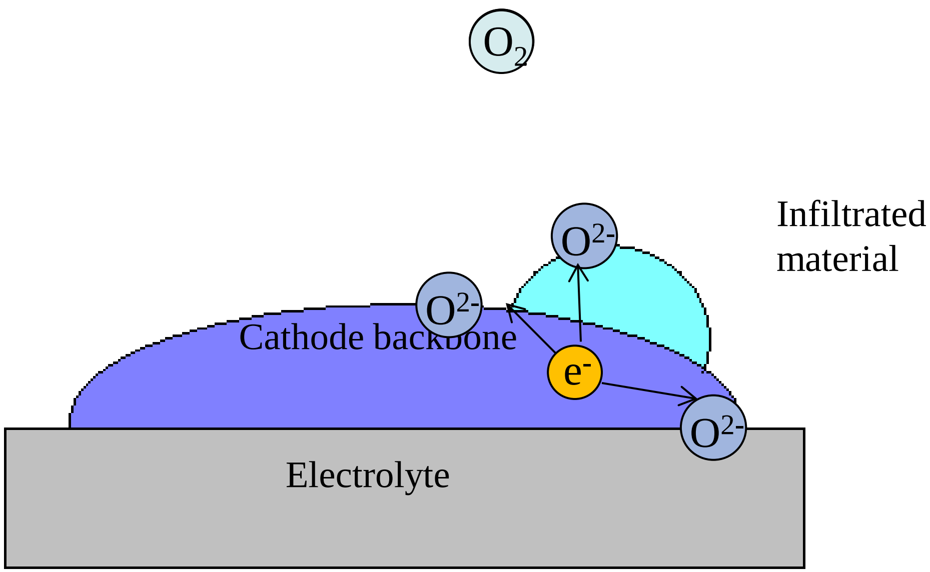
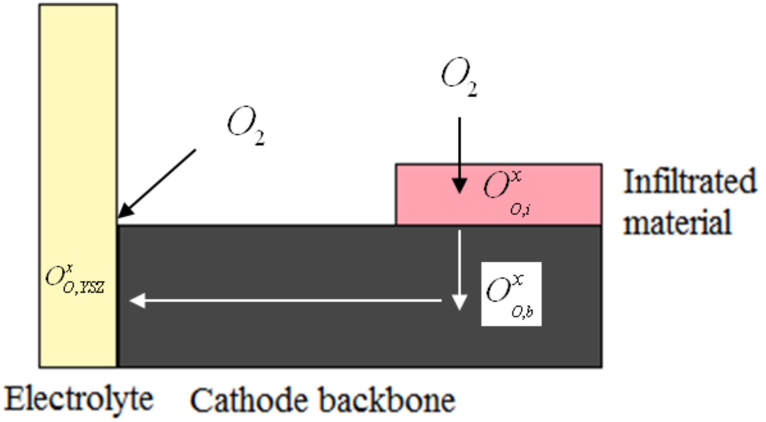
- Develop ECR application
for infiltrated cathode materials
- **Infiltrated cathode model**



Infiltrated Cathode Modeling

- Physical mechanism





$$O_2 + s \underset{k_1^-}{\overset{k_1}{\rightleftarrows}} O_{2,ad}$$

$$O_{2,ad} + 2V_{O,I}^{\cdot\cdot} \underset{k_2^-}{\overset{k_2}{\rightleftarrows}} 2O_{o,I}^x + 4h^{\bullet} + s$$

$$O_{O,I}^x + V_{O,LSCF}^{\cdot\cdot} \underset{k_3^-}{\overset{k_3}{\rightleftarrows}} V_{O,I}^{\cdot\cdot} + O_{O,LSCF}^x$$

$$O_{O,LSCF}^x + V_{O,YSZ}^{\cdot\cdot} \underset{k_4^-}{\overset{k_4}{\rightleftarrows}} O_{O,YSZ}^x + V_{O,LSCF}^{\cdot\cdot}$$

Infiltrated cathode modeling

- Basic equations

$$O_2 + s \underset{k_1^-}{\overset{k_1}{\rightleftarrows}} O_{2,ad}$$

$$O_{2,ad} + 2V_{O,I}^{\cdot\cdot} \underset{k_2^-}{\overset{k_2}{\rightleftarrows}} 2O_{o,I}^{x} + 4h^{\cdot} + s$$

$$O_{O,I}^{x} + V_{O,LSCF}^{\cdot\cdot} \underset{k_3^-}{\overset{k_3}{\rightleftarrows}} V_{O,I}^{\cdot\cdot} + O_{O,LSCF}^{x}$$

$$O_{O,LSCF}^{x} + V_{O,YSZ}^{\cdot\cdot} \underset{k_4^-}{\overset{k_4}{\rightleftarrows}} O_{O,YSZ}^{x} + V_{O,LSCF}^{\cdot\cdot}$$

Governing Equation

$$\frac{\partial C_{V,LSCF}}{\partial t} = D\frac{\partial^2 C_{V,LSCF}}{\partial x^2} - \frac{\Delta S}{\Delta V} r_3 = D\frac{\partial^2 C_{V,LSCF}}{\partial x^2} - \frac{\Delta S}{\Delta V} r_{3,0}\left(\frac{C_{V,LSCF}}{C_{V,LSCF,eq}} - 1\right)$$

Initial Condition

t=0, $C_{V,LSCF} = 1\times10^{-4}$ mol/cm³

Boundary conditions

x=0

$$D\frac{\partial C_{V,LSCF}}{\partial x} = -r_4 = -r_{4,0}[\exp(-2\alpha_{2PB} f\eta) - \frac{C_{V,LSCF}}{C_{V,LSCF,eq}}\exp[2(1-\alpha_{2PB}) f\eta]$$

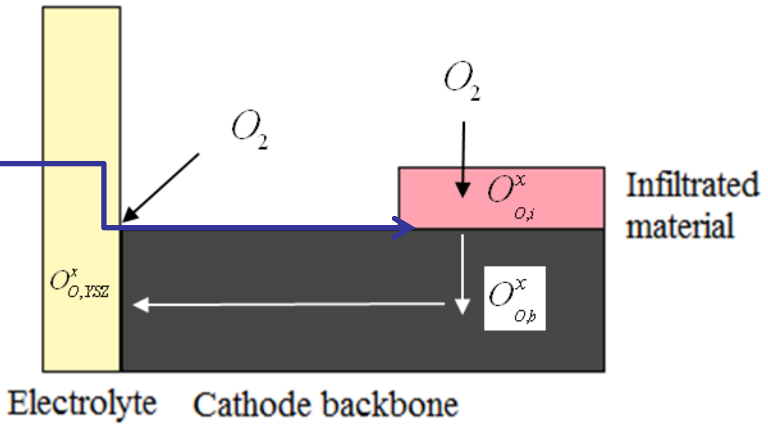
x=l_c

$$\frac{\partial C_{V,LSCF}}{\partial x} = 0$$

Infiltrated Cathode Modeling

- ECR measurement application

$$O_{O,I}^{x} + V_{O,LSCF}^{\cdot\cdot} \underset{k_3^-}{\overset{k_3}{\rightleftharpoons}} V_{O,I}^{\cdot\cdot} + O_{O,LSCF}^{x}$$



$$r_3 = k_3 C_{V,LSCF} - k_3^- C_{V,I}$$

$$k_{interface}(C_{V,LSCF} - C_{V,LSCF,eq}) = k_3 C_{V,LSCF} - k_3^- C_{V,I}$$

$$r_{3,0} = k_3 C_{V,LSCF,eq} = k_3^- C_{V,I}$$

$$r_{3,0} = k_3 C_{V,LSCF,eq} = k_3^- C_{V,I} = k_{interface} C_{V,LSCF,eq}$$

$$k_{interface} = \frac{k_3 C_{V,LSCF} - k_3^- C_{V,I}}{C_{V,LSCF} - C_{V,LSCF,eq}}$$

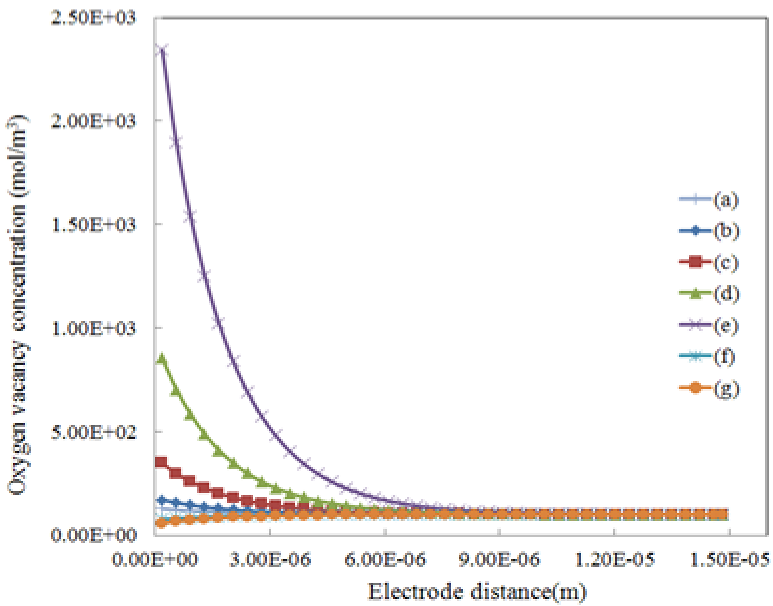
$$= \frac{k_3^- C_{V,I} \dfrac{C_{V,LSCF}}{C_{V,LSCF,eq}} - k_3^- C_{V,I}}{C_{V,LSCF} - C_{V,LSCF,eq}}$$

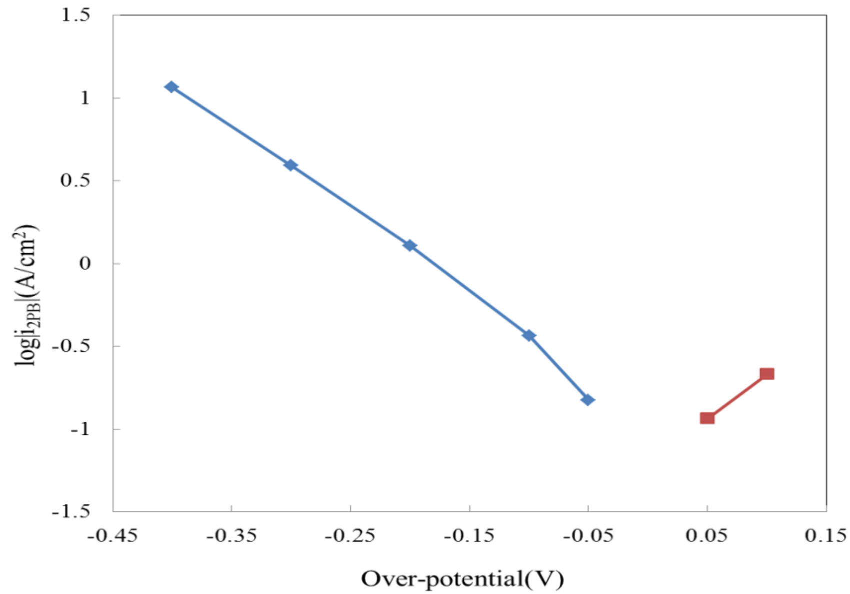
$$= \frac{k_3^- C_{V,I}}{C_{V,LSCF,eq}}$$

Infiltrated Cathode Modeling

- Over-potential effects

$$i_{2PB} = i_4 = 2FD_{backbone}\left(\frac{\partial C_{V,MIEC}}{\partial x}\right)\Big|_{x=0}$$





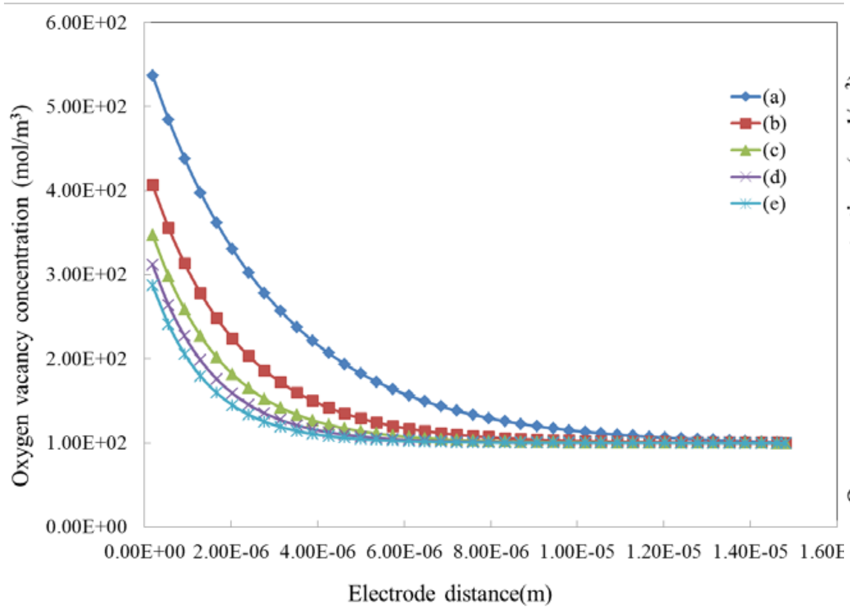
$r_{3,0}$ (mol/cm²·s) = 3×10^{-8}

(a)-0.05V (b) -0.1V (c) -0.2V (d) -0.3V (e) -0.4V (f) 0.05V (g)0.1V

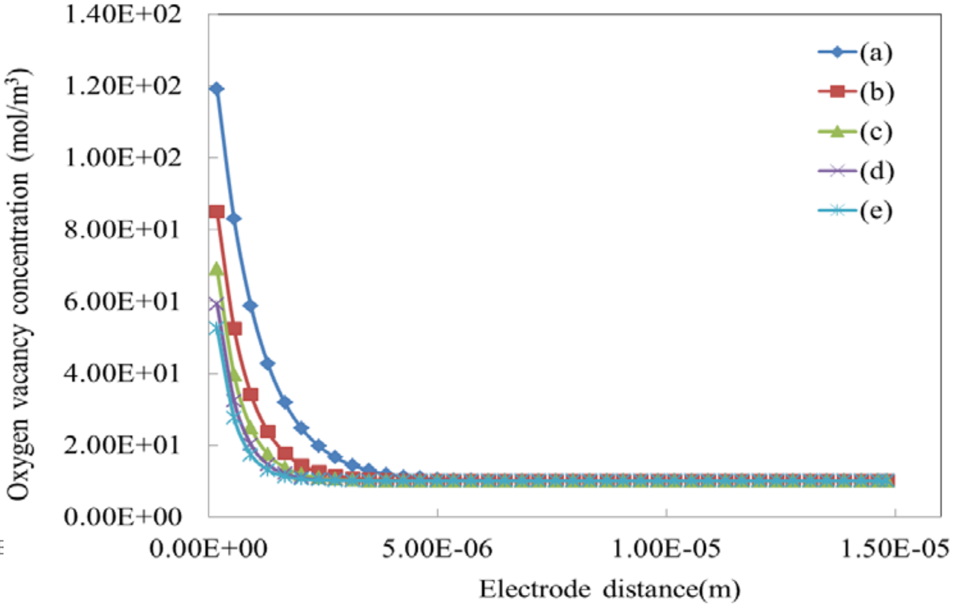
Exchange current = 0.14A/cm²

Infiltrated Cathode Modeling

- Cathode backbone effects



$C_{v,eq}$ (mol/cm³) = 1×10⁻⁴



$C_{v,eq}$ (mol/cm^3) = 1×10^{-5}

η=-0.2V

$r_{3,0}$ (mol/cm^2·s) value is: (a) 1×10^{-8} (b) 2×10^{-8} (c) 3×10^{-8} (d) 4×10^{-8} (e) 5×10^{-8}

Summary

❖ Improve ECR data fitting method

- Fix the initial relaxation time by assuming the reactor is an ideally stirred tank reactor
- Using weight average error function to fitting two data sets together

❖ Investigate oxygen transport in LSCF

- Oxygen surface exchange coefficient depends on the final oxygen partial pressure following the law
- Deduce oxygen reduction reaction constants and the results revealed that it is easier for oxygen to enter LSCF lattice than to leave at 800° C

❖ Develop ECR technique for Infiltrated SOFCs cathode

- LSC infiltrated cathode materials possess higher oxygen surface exchange rate compared to single phase LSCF material

❖ Cathode Modeling

- The characteristic length of the cathode decreased with the increasing interface oxygen ion exchange rate.

Take Home Message

- Infiltrants
  - Surface Exchange Rate Limiting Step
  - Strain Effect
  - Size vs. Characteristic Length
- Hetero-Interface
  - Nature of the Interface
  - Oxygen Transport Mechanisms
- Stability Issues
  - Backbone
  - Reaction between Backbone and Infiltrants
  - Infiltrants growth
- Overall ORR Kinetics


THANK YOU