Factors Governing Performance of Mixed-Conducting SOFC Cathodes

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Motivation: How do we understand and improve processes limiting cathode performance?
Our Approach

• Advanced Measurement and Modeling Tools
  – Quantitative analysis of impedance data.
  – Measurement and modeling of nonlinear harmonics.
  – Microelectrodes for improved half-cell measurements.

• Studies of Porous and Dense Mixed-conductors on Samaria-Doped Ceria (SDC)
  – Common interface in composite/2-layer electrodes.
  – Less reaction between electrode and SDC than YSZ
  – Good model systems.
Outline

• Electrochemical Behavior of Porous Electrodes
  – Role of chemical and transport steps in oxygen reduction.
  – Why chemical and transport steps tend to be co-limiting.
  – How this behavior appears in impedance (faradaic capacitance).

• Studies of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ on samaria-doped ceria (SDC)
  – Role of interface vs. chemical and transport steps
  – Dependence on processing and operating conditions
  – What we can tell about possible mechanisms.
  – What steps are most sensitive to degradation, polarization, other unknown variables.

• Conclusions/Recommendations
Role of Chemical and Transport Steps in Oxygen Reduction

The length of three-phase boundary is inadequate information to explain the kinetics of SOFC cathodes.
Role of Chemical and Transport Steps in Oxygen Reduction
Role of Chemical and Transport Steps in Oxygen Reduction

Chemical & Transport Steps
(Slow response time due to faradaic accumulation)
\[ C = 10^{-3} \sim 1 \text{ F/cm}^2 \]

Interfacial Charge-Transfer
(fast response time)
\[ C = 10^{-6} \sim 10^{-4} \text{ F/cm}^2 \]
Why Chemical and Transport Steps Tend to be Co-Limiting in Porous Catalysts

Thiele Modulus: \( \phi = \frac{R}{3} \sqrt[3]{\frac{k_A a}{D_A}} \)

Steady-State Concentration

rate \( \sim R^2 c_{A0} \sqrt{k_A a D_A} \)
Co-limited Behavior in Porous Electrocatalysts

Reduction of $A$ to $A^-$

At Equilibrium
Co-limited Behavior in Porous Electro catalysts

Reduction of $A$ to $A^-$

gaseous $A$

adsorbed $A$

$C_{A0}\quad x\quad \text{catalyst surface}$

Under Polarization

$k_A\quad D_A$
Co-limited Behavior in Porous Electro catalysts

Reduction of $A$ to $A^-$

gaseous $A$

adsorbed $A$

$C_{A0}$

catalyst surface

$C_{A0}$

$C_{A}$

$C_{A1}$

$x/k_A$

$D_A$

$C_{A0}$

$x/\sqrt{D_A k_A}$
Co-limited Behavior in Porous Electrocatalysts

Reduction of A to A$^-$
gaseous $A$

adsorbed $A$

$C_{A0}$

catalyst surface

\[ \frac{C_A - C_{A0}}{C_{A1} - C_{A0}} \]

\[ \frac{C_A - C_{A0}}{\sqrt{D_A/k_A}} \]

\[ \frac{\Delta C \sqrt{k_A D_A}}{N_{A1} (\omega)} \]
Co-limited Behavior in Porous Electro catalysts

Reduction of A to A

gaseous A

adsorbed A

\[ C_{A0} \]

\[ C_A \]

\[ C_{A1} \]

\[ C_{A0} \]

\[ C_{A1} \]

\[ D_A \]

\[ x / \sqrt{D_A / k_A} \]

\[ Z(\omega) = \frac{\Delta C \sqrt{k_A D_A}}{N_{A1}(\omega)} \]

\[ \frac{C_A - C_{A0}}{C_{A1} - C_{A0}} \]
Co-limited Behavior in Porous Electrocatalysts

Reduction of A to A⁻

gaseous A
adsorbed A

catalyst surface

\[ Z(\omega) = \frac{\Delta C \sqrt{k_A D_A}}{N_{A1}(\omega)} \]

\[ \frac{C_A - C_{A0}}{C_{A1} - C_{A0}} \]
Co-limited Behavior in Porous Electro catalysts

Reduction of $A$ to $A^-$

gaseous $A$

adsorbed $A$ $C_{A0}$

catalyst surface

$LSCF$ on ceria, $700^\circ$C

(Adler, Lane, Steele, 1996)
Separating Chemical & Interfacial Timescales

Porous Pt on YSZ at 800°C

(A. Mitterdorfer, 1997)

Porous La$_{1-x}$Sr$_x$CoO$_{3-d}$ on SDC at 700°C
Materials of Interest

Porous Perovskite Electrodes:
- electrode: $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3-\delta$
- electrolyte: $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-x}$

Microelectrode Half Cells:
- WE: Working electrode
- RE: Reference electrode
- SDC: Solid dye cell
- MgO/spinel
- 1 in.
Role of Firing (Sintering) Temperature

Recall that for co-limiting reaction and transport:

\[ R_{\text{chem}} \sim \frac{1}{\sqrt{akD}} \quad \omega_{\text{chem}} \sim ak \]

\( k \) & \( D \) constant: \( R_{\text{chem}} \sim \frac{1}{\sqrt{\omega_{\text{chem}}}} \)

Surface area reduction?

Fired at 1050°C.
Role of Operating Temperature

La$_{0.8}$Sr$_{0.2}$O$_{3-\delta}$ fired on SDC at 1050°C (tested in air)

If:
\[ R_{chem} \sim \frac{1}{\sqrt{akD}} \quad \omega_{chem} \sim ak \]

Then:
\[ ak \sim \omega_{chem} \quad D \sim \frac{1}{(\omega_{chem}R_{chem}^2)} \]

At 75 kcal/mol, LSC-82 is not a stellar O$_2$ catalyst...
Dependence on Operating $P_{O_2}$

La$_{0.8}$Sr$_{0.2}$O$_{3-\delta}$ fired on SDC at 950°C
(tested at 725°C vs. $P_{O_2}$)

If: $ak \sim \omega_{chem} \sim P_{O_2}^{0.53 \pm 0.08}$

Then: $k \sim P_{O_2}^{1/2}$

Oxygen exchange rate 1/2 order in $P_{O_2}$
Several mechanisms are consistent with $k \sim P_{O_2}^{1/2}$

**Oxygen exchange limited by vacancy exchange**

$$r_{ads} = k_1 \left( \frac{1}{2} P_{O_2}^{gas} - \frac{1}{2} P_{O_2}^{solid} \right)$$

$$k \sim r_{exch} = k_1 \left( P_{O_2} \right)^{1/2}$$

**Oxygen exchange limited by dissociative adsorption**

$$r_{ads} = k_1 \left( \frac{P_{gas}^{O_2}}{P_{O_2}^{solid}} \right)^{1/2} - \left( P_{O_2}^{solid} \right)^{1/2}$$

$$k \sim r_{exch} = k_1 \left( P_{O_2} \right)^{1/2}$$

Same!
Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)
example: LSF/ceria/LSF cell at 750°C in air (10 Hz)

Time-domain data

Gaussian Apodization

Current FFT (magnitude)
1st (5x)

Voltage FFT (magnitude)
1st (5x)
3rd
5th
Nonlinear Electrochemical Impedance Spectroscopy

Vacancy exchange

\[ \frac{V_{ii}}{\eta^*} \]

\[ V_{11} \]

\[ \phi(V_{ii}) \]

\[ \omega / \omega_{chem} \]

Dissociative adsorption

\[ \frac{V_{ii}}{\eta^*} \]

\[ V_{11} \]

\[ \phi(V_{ii}) \]

\[ \omega / \omega_{chem} \]
Nonlinear Electrochemical Impedance Spectroscopy

Vacancy exchange

\[ \frac{V_{ii}}{\eta^*} \]

\[ V_{11} \]

\[ V_{22} \]

\[ V_{33} \]

\[ \phi(V_{ii}) \]

\[ \omega / \omega_{chem} \]

Dissociative adsorption

\[ \frac{V_{ii}}{\eta^*} \]

\[ V_{11} \]

\[ V_{22} \]

\[ V_{33} \]

\[ \phi(V_{ii}) \]

\[ \omega / \omega_{chem} \]
Electrode Degradation

\[ \text{La}_{0.8}\text{Sr}_{0.2}\text{O}_{3-\delta} \text{ on SDC at 725°C in air (fired at 950°C)} \]

Since \( \omega_{\text{chem}} \sim ak \), scaling suggests changes in surface area or surface kinetics.

Other observations:
- humidity dependence
- reverse direction in dry gas
- depends on test furnace?

Suggests surface kinetics are very sensitive to environment.
Dependence of the Interface on Electrolyte Polishing

Polishing of SDC prior to electrode processing degrades performance.

Electrode adhesion is noticeably worse if SDC is polished.

Re-firing of SDC surface before processing LSC recovers performance.
Polarization Effects
Conclusions

• For La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ on SDC, optimum performance is achieved when electrode firing temperature is sufficient to achieve bonding/connectivity, but not so high as to lose active surface area.

• The best performing electrodes are generally co-limited by dissociative adsorption and surface/bulk transport. LSC is not a very good oxygen reduction catalyst (75 kcal/mol).

• Interfacial resistance is sensitive to preparation of the electrolyte and polarization. Oxygen surface kinetics appear sensitive to an number of overlapping factors (humidity, exposure to impurities).
Current Efforts

• Extending NLEIS measurements to a much wider range of materials and conditions. Currently improving signal-to-noise to obtain finer detail and more information regarding interface.

• At 75 kcal/mol, oxygen dissociative adsorption appears to be the biggest bottleneck with LSC-82. Examining competitive electrocatalysts on the basis of oxygen exchange rates.

• More carefully examining electrode degradation and sensitivity factors. Will quantify the role of humidity, and other gas-born impurities on electrode performance.
Thank You