

Motivations & Objectives

- Insights into oxygen reduction reaction (ORR) process in a dense LSM-type cathode system have been provided to better understand polarization-induced cathode kinetics.
- Reveal detailed surface processes (diffusion & local reactions) and parallel reaction pathways (3PB & 2PB)
- Evaluate the influencing factor for 3PB/2PB competition & transition under polarization
- Analyze spatial domain and coupling relationship of oxygen species (surface oxygen & bulk vacancy)
- A one-dimensional continuum model combining with close-packing theory takes into account the effect of cathode microstructure.
- Predict the interaction between electrode particle size and ORR behavior
- Demonstrate the influence of electrode particle size on oxygen species distribution
- Correlate electrode kinetics, mass transport process and microstructural design of cathode materials

Model Set-Up

Driving forces:

$$\chi_S = \phi_e(M)_B - \phi_e(M)_s = FC_{O_{ad}} / C_S \quad \eta_{app} = (\bar{\mu}_{e,R/M} - \bar{\mu}_{e,R/M}^0) / F = \eta_{2PB}$$

$$E_{2PB} = \phi_e(M)_B - \phi_e(Y) \quad \Delta\chi_{3PB} = 2\eta_{2PB} - \Delta\chi_S = 2\eta_{app} - \Delta\chi_S$$

$$\chi_{3PB} = \phi_e(M)_S + \phi_e(M)_B - 2\phi_e(Y)$$

Reaction rate equations:

$$r_{S1} = r_{S1s} \left(\exp(-\alpha_s f \Delta\chi_s) - \frac{C_{O_{ad}}}{C_{O_{ad,eq}}} \exp[(1-\alpha_s) f \Delta\chi_s] \right)$$

$$r_{S2} = r_{S2s} \left(\frac{C_{O_{ad}}}{C_{O_{ad,eq}}} \exp(-\alpha_s f \Delta\chi_s) - \exp[(1-\alpha_s) f \Delta\chi_s] \right)$$

$$r_{B3} = r_{B3s} \left(\frac{C_{O_{ad}}}{C_{O_{ad,eq}}} \frac{C_{V_{MEC,s}}}{C_{V_{MEC,eq}}} \exp(\alpha_s f \Delta\chi_s) - \exp[-(1-\alpha_s) f \Delta\chi_s] \right)$$

$$r_{B4} = r_{B4s} \left(\exp(-2\alpha_s f \Delta\chi_s) - \frac{C_{V_{MEC}}}{C_{V_{MEC,eq}}} \exp[2(1-\alpha_s) f \Delta\chi_s] \right)$$

Governing formula:

$$\frac{\partial C_{O_{ad,s}}}{\partial t} = D_{s,chem} \left(\frac{\partial^2 C_{O_{ad,s}}}{\partial x^2} \right) + r_{S2} - r_{B3} \quad \frac{\partial C_{V_{MEC,s}}}{\partial t} = D_{b,chem} \left(\frac{\partial^2 C_{V_{MEC,s}}}{\partial x^2} \right) - \left(\frac{\Delta S}{\Delta V} \right)_{ads} r_{B3}$$

Geometric factors & solutions:

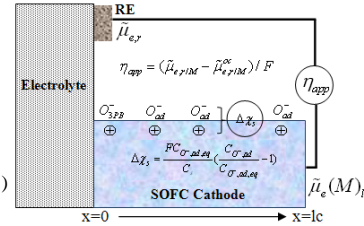
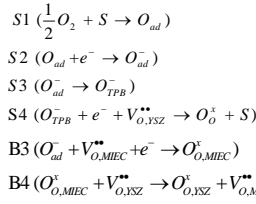
$$i_{3PB} = -2FS_{spB} \left[D_{s,chem} \left(\frac{\partial C_{O_{ad}}}{\partial x} \right) \right]_{x=0} + \left(\frac{rS2 - rB3}{\Delta S / \Delta V} \right)_{ads} i_{2PB} = 2FD_{b,chem} \left(\frac{\partial C_{V_{MEC}}}{\partial x} \right)_{x=0}$$

$$S_{spB} = S_{spB,0} \left(1 - \frac{\varepsilon - \varepsilon_{fc}}{1 - \varepsilon_{fc}} \right) \frac{d_g^3}{d_s^3} \quad \left(\frac{\Delta S}{\Delta V} \right)_{ads} = \frac{6}{d_g} (1 - \varepsilon)$$

$$i_{cathodic} = 2F \frac{r_{S2,0} \exp(-\alpha_s f \Delta\chi_s) / r_{B3,0} \exp[-(1-\alpha_s) f \Delta\chi_s]}{r_{S2,0} \exp(-\alpha_s f \Delta\chi_s) + r_{B3,0} \exp[-(1-\alpha_s) f \Delta\chi_s]} \Rightarrow 2F(rS2 - rB3) = i_{anodic} - i_{cathodic}$$

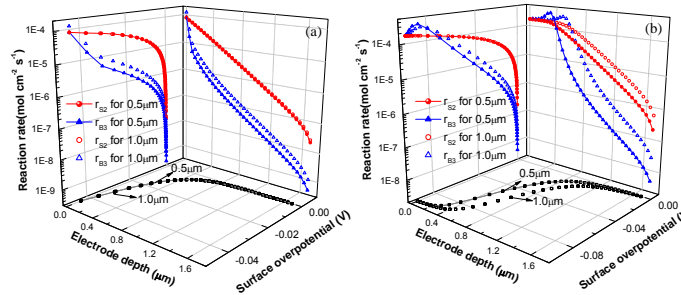
$$i_{anodic} = 2F \frac{r_{S2,0} (C_{O_{ad}} / C_{O_{ad,eq}}) \exp(-\alpha_s f \Delta\chi_s) / r_{B3,0} (C_{O_{ad}} / C_{O_{ad,eq}}) (C_{V_{MEC}} / C_{V_{MEC,eq}}) \exp(\alpha_s f \Delta\chi_s)}{r_{S2,0} (C_{O_{ad}} / C_{O_{ad,eq}}) \exp(-\alpha_s f \Delta\chi_s) + r_{B3,0} (C_{O_{ad}} / C_{O_{ad,eq}}) (C_{V_{MEC}} / C_{V_{MEC,eq}}) \exp(\alpha_s f \Delta\chi_s)}$$

Reaction Mechanism

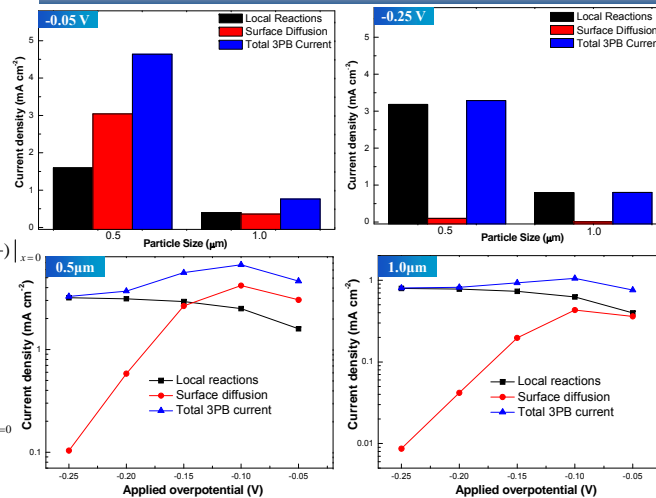


- Multi-stepped charge transfer reactions with two parallel pathways (3PB & 2PB)
- 1-D diffusion and space coupling of single charged surface adsorbates and bulk vacancies
- Competition of surface reaction kinetics between adsorption and incorporation

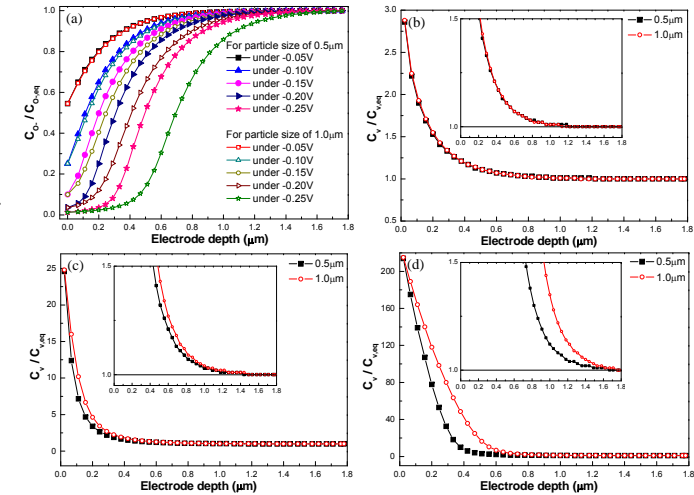
Characteristics of Surface Kinetics



Detailed 3PB behavior

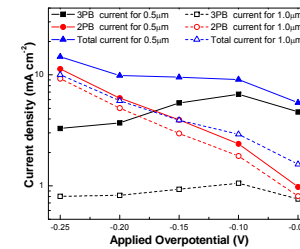


Concentration distribution of Oxygen



Concentration profiles along electrode depth of (a) surface oxygen adsorbates in the applied overpotential from -0.05 V to -0.25 V, and (b) bulk oxygen vacancies at applied overpotential of -0.05 V, (c) -0.15 V and (d) -0.25 V.

I-V features



The decrease in particle size of cathode,



- Current density and ORR kinetics increase
- Global transport resistance decreases
- 3PB/2PB transition potential shifts to more negative

Summary

- Observed shifts in relative rates and species concentrations are the result of competing processes described by the coupled transport and reaction equations, and do not arise from fundamentally altered energies associated with the uncoupled processes.
- As compared to the electrode with smaller particles, the surface limitation of the electrode using bigger particles leads to 3PB/2PB transition under less negative cathodic polarization.
- Depending on particle size of cathode materials, different optimization strategies are recommended. For relatively smaller particles, emphasis should be put on enhancing ionic conductivity and decreasing oxygen incorporation resistance. Surface modification for obtaining high catalytic activity is more effective to improve the electrochemical properties of SOFC cathode using bigger particles.

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