Investigation of Sheet Resistance in Thin-Film SOFC Mixed Conductors

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Introduction

- Thin-film mixed ionic-electronic conductors (MIEC)
  - Serve as working electrodes in test cells
  - Provide simplification of reaction pathways present in porous SOFC cathodes
  - Useful for isolating and studying cathode electrochemical processes in detail
  - Examples include $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM) and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF)

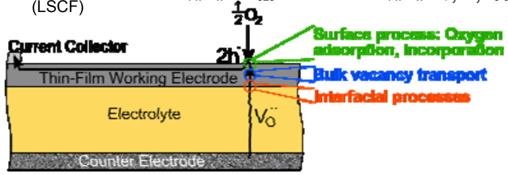

Figure 1: Schematic representation of a thin-film SOFC cathode test cell. The test cell aids the evaluation of intrinsic surface, bulk, and interfacial processes. However, the long-range electronic transport causes sheet resistance.

- Sheet resistance distorts the experimentally observable properties of a test cell
  - Caused by long-range transport of electronic charge to the current collector (CC) from heterogeneous reaction sites on the MIEC surface
  - Continuously variable film potential causes continuously variable local processes and thus the measured macroscopic properties are not representative of the intrinsic material properties
- Uniform potential across the film is the ideal case for measuring intrinsic material properties
  - Sheet resistance must be mitigated to achieve this goal
  - Current collector placement must be appropriately designed
    - Porous layers mitigate sheet resistance but interfere with electrochemical measurements
    - Mesh and patterned CCs do not interfere as much, but should be placed appropriately

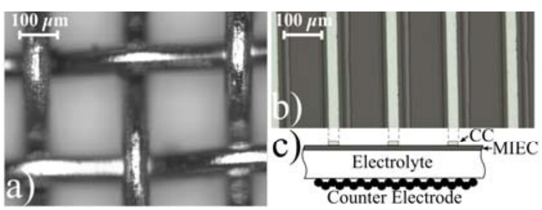

Figure2: a) Optical micrograph of a typical woven current collector mesh. Note the likelihood of producing regularly spaced discrete-diameter circular contacts as opposed to a continuous contact grid. b) Optical micrograph (top view) and c) schematic diagram (cross-sectional view) of a continuous LSM thin-film test cell with patterned, parallel platinum current collectors deposited on top. The LSM appears dark while the CCs appear silver.

Model

- Electrostatic potential distribution
  - 2D MIEC thin film: $$0 = \nabla \cdot (\sigma_m t_m \nabla \phi_m) + i_{bdry}$$
  - 3D bulk electrolyte: $$0 = \nabla \cdot (\sigma_e \nabla \phi)$$

- Electrostatic polarization due to oxygen reduction
  - Oxygen reduction reaction: $$\frac{1}{2}O_2 + V_O^{\cdot\cdot} = O_O^x + 2h^{\cdot}$$
  - Classical, phenomenological kinetics: $$i = nF\left[k_l\left(\prod_i^l c_i\right)\exp\left(\frac{(1-\beta)nF}{RT}\eta\right) - k_r\left(\prod_j^r c_j\right)\exp\left(\frac{-\beta nF}{RT}\eta\right)\right]$$
  - Low-polarization (linear) approximation: $$i_{bdry} = \frac{\eta_{local}}{R_p}$$
  - High-polarization (Tafel) approximation $$i_{bdry} = i_0\left[\exp\left(\frac{(1-\beta)nF}{RT}\eta_{local}\right) - \exp\left(\frac{-\beta nF}{RT}\eta_{local}\right)\right] \qquad i_0 = \frac{1}{R_p}\frac{RT}{nF}$$

- The linear case has wide applicability because its parameters are simple, empirical, and available from common measurements
- The Tafel case provides an estimation of the upper bound of sheet resistance because mass-transfer effects are not considered
- Simulation of sheet resistance performed using the finite element method (FEM), on a domain formed by the symmetry of the cell

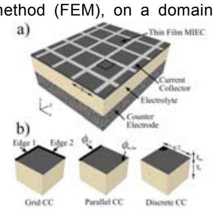

Figure 3: a) Schematic illustration of thin-film test cell geometry. The CCs are deposited onto the MIEC in the "grid" configuration. b) Domain for FEM simulation, reduced by symmetry along the dashed line. In the "grid" configuration, a constant potential is applied along Edge 1 and 2. In the "parallel" configuration, a potential is applied along Edge 1 only. In the "discrete" configuration, a constant potential is applied within and on the boundaries of the quarter-circle region.

Impact of Experimental Factors

The model is used to evaluate the contribution of various geometric and experimental factors to the sheet resistance manifested in the test cell.

$$\text{Relative Potential} = \frac{\phi_{m,far}}{\phi_{CC}}$$

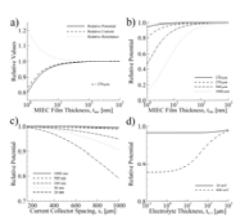

Figure 4: a) Relative values of electrostatic potential, current, and resistance as a function of various experimental parameters for the discrete CC configuration. a)-c) cell voltage = 0.010 V, d) t_m = 20 nm and. In all cases, R_p, R_Ω, σ_m, σ_e, and t_e are representative of an LSCF thin-film working electrode and s = 270 μm.

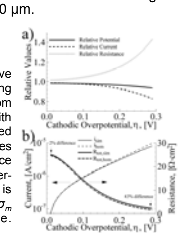

Figure 5: a) Relative values of potential, cell current, and relative resistance, R_{tot}, as a function of nominal cathodic overpotential using the discrete CC configuration. All of the simulated values deviate from the "homogeneous" (the case with no sheet resistance) values, with the strongest deviation appearing in *resistance*. b) Area-normalized cell current and calculated resistance, R_{tot}. The actual current varies from the ideal Tafel behavior and the relative difference in resistance becomes large (43%) at high polarization. In both a) and b), Butler-Volmer kinetics are assumed locally with β=0.5, the electrolyte is assumed vanishingly thin, t_m = 20 nm and s = 270μm, local R_p and σ_m are representative of a thin-film LSCF working electrode.

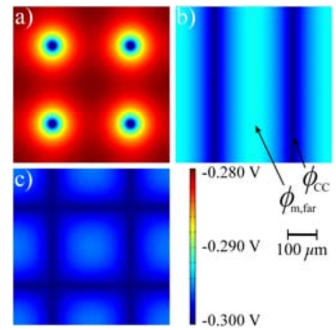

Figure 6: Distribution of electrostatic potential in a mixed conducting film for three different current collector configurations: a) 20-μm diameter discrete contacts from e.g. a woven mesh; b) linear and c) grid configurations deposited by e.g. photolithography and physical vapor deposition. R_p and σ_m are representative of LSCF, the electrolyte is assumed very thin, t_m = 20 nm, s = 270 μm, cell voltage = 0.300 V.

General Cell Design

The following figure is a set of maps for the critical current collector spacing leading to 90% reduction of potential under low cathodic polarization under different combinations of material properties. Similar plots may be constructed for different requirements on the potential drop and under high cathodic polarization. These maps may be used as selection charts for the spacing of current collectors in an arbitrary test cell.

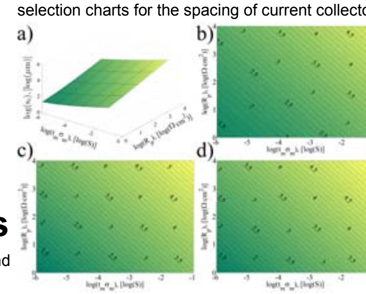

Figure 7: a) 3D surface of log(s_c) for the discrete CC configuration under low cathodic polarization. s_c is the critical CC spacing at which the electrostatic potential in the MIEC film falls to no less than 90% of the value applied at the current collector, given the combination of the independent parameters polarization resistance, R_p, and the product of electronic conductivity and film thickness, ($t_m\sigma_m$).

b)-d): Contour plots of log(sc) for the b) 20-μm diameter discrete, c) parallel CC, and d) grid CC configurations. The contours denote the level sets of log(sc).

Summary and Future Work

- Current collectors designed to minimize sheet resistance in the MIEC film will yield better measurements and more accurate conclusions about the intrinsic material properties studied by the experiments
- This general and empirical model for sheet resistance is useful to candidate SOFC materials and uses easily accessible measurements
- CC spacing maps can be used to limit the drop in potential across the film prior to the fabrication of the test cell by estimating properties
- Use of this model for CC design will aid the design of experiments within our research group as we investigate SOFC cathode processes

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