IV.A.8 Functionally Graded Cathodes for Solid Oxide Fuel Cells

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Objectives

- Qualitatively evaluate the importance of sheet resistance of thin-film electrodes in fundamental studies of electrode properties.
- Quantitatively estimate the bulk defect structure of the cathode material $La_xSr_{1-x}MnO_{3\pm\delta}$ (LSM) at low temperatures in order to better determine thermodynamic and transport properties of LSM.

Accomplishments

- Achieved qualitative correspondence between continuum models featuring sheet resistance in thin films of LSM and experimental studies.
- Developed a new model for bulk defects in LSM at low temperatures, quantitatively validated the model against experimental nonstoichiometry data, and attained quantitative estimates for model parameters.

Introduction

The cathode reaction in solid oxide fuel cells (SOFCs) is the largest single source of polarization resistance in the cell at low temperatures. Optimization of cathode microstructure – likely in the form of functionally graded electrodes, wherein the composition of the cathode changes through its thickness in order to best facilitate the overall oxygen reduction process – is therefore paramount to achieving better performing fuel cells at lower operating temperatures and lower cost. However, optimization is hindered by a lack of quantitative and qualitative knowledge regarding the oxygen reduction process in SOFC cathodes. LSM is the most widely used cathode material in SOFCs. Our work this year has focused on acquiring knowledge about two aspects of oxygen reduction on LSM cathodes that are important for optimization of the microstructure. The first is the propensity to encounter power losses due to sheet resistance – or losses due to transport of electrons and electron holes through LSM, as opposed to losses due to transport of oxygen ions or that due to slow chemical reactions – for certain cathode geometries. The second is the quantitative bulk defect structure of LSM at low temperatures. Bulk defects influence the rate of transport of oxygen ions as well as the rate of chemical reactions on the electrode. Existing defect models for LSM were derived and applied for high-temperature situations, and are not appropriate for low-temperature operation [1-5].

Approach

For the sheet resistance study, we developed a continuum model based on the well-known Nernst-Planck equation, but we could not use the approximations typically employed for high electronic conductivity mixed ionic electronic conductors (MIECs) that preclude any consideration of electronic resistance. We were therefore forced to develop computational simulation methods, which we applied to two-dimensional renderings of thin-film LSM cathodes. We used the best available literature data to estimate model parameters. We then compared our results with experiments on dense, thin-film LSM cathodes.

For the determination of bulk defect structure, we developed a computational method for quantitatively comparing bulk defect models with nonstoichiometry experiments. These experiments are designed to investigate defect structure by comparing the weight change of the material as the atmosphere in contact with the material changes composition. The computational methods we developed allow for validation of the model as well as quantitative parameter estimation.

Results

Qualitative comparisons to electrochemical experiments on LSM thin films show that these films very likely experience significant sheet resistance effects. The model successfully replicated these effects, as shown in Figure 1. The plot shows both the current density and the utilization of the electrode versus applied potential. Utilization is the total fraction of the electrode that is active; it is 1.0 when there is zero sheet resistance but drops as sheet resistance becomes more prominent. Note that the current density curve, plotted logarithmically versus potential, consists of two approximately straight-line regions, and that the point

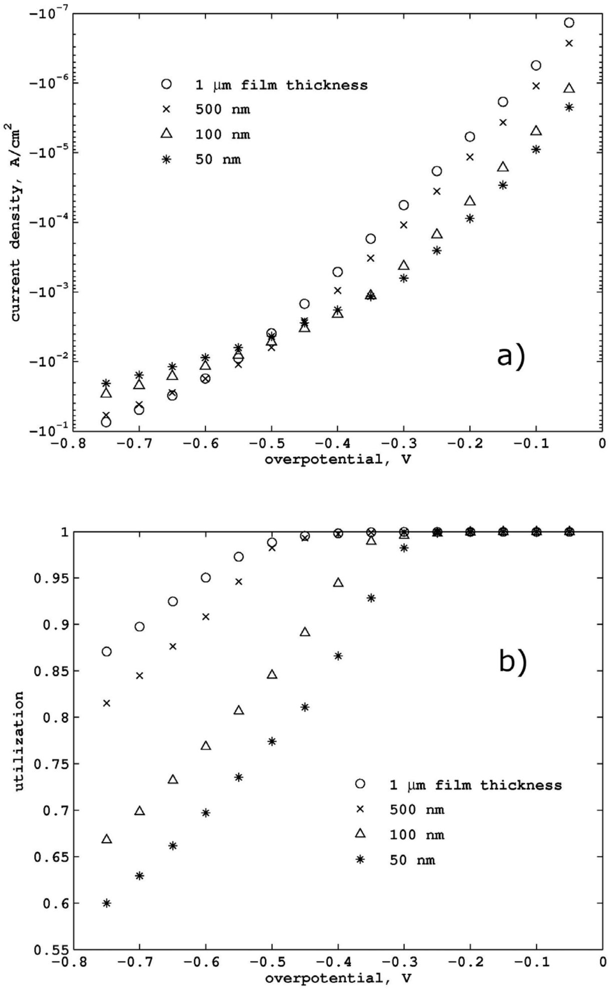

FIGURE 1. a) Current-Voltage and b) Total Film Utilization for Model LSM Thin Films of Different Thicknesses

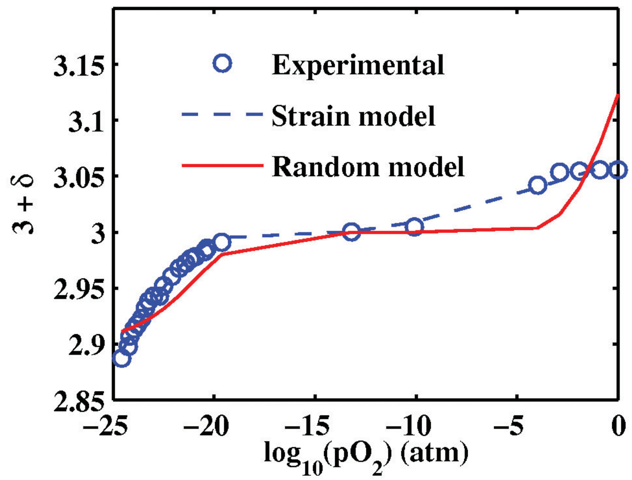

FIGURE 2. Fits to LSM nonstoichiometry data for the previous bulk defect model (Random) and a new model including strain interaction between cation defects developed by the authors. The ordinate indicates a measure of the ratio between oxygen and manganese in LSM.

of inflection between these regions occurs at the point where the utilization curve drops significantly below 1. The existence of a similar shape in current-potential curves reported for thin films in the literature is a strong indication that sheet resistance is an issue in these thin films.

Using the procedures we developed for rigorous, quantitative comparison between experiment and model, we definitively showed that the best existing model for bulk defects in LSM failed to adequately describe the behavior of nonstoichiometry experiments at temperatures below 800°C, a temperature that is now generally considered to be too high for economical operation of SOFCs. We modified the model and used our techniques to show the resulting good correspondence between the model and experiment at temperatures as low as 600°C (see Figure 2).

We additionally estimated the well-defined parameters of the model, enabling straightforward calculation of the defect structure of LSM at any temperature.

Conclusions and Future Directions

The analysis of sheet resistance clearly shows that designers of LSM cathodes must take sheet resistance into account. This becomes especially important as structures become finer in scale, as is anticipated in terms of the development of nanostructured morphologies. We have an approximate idea of the types of morphologies that will encounter sheet resistance effects, and we are using this knowledge in the development of new cathode designs. We are also endeavoring to gain a more quantitative understanding of sheet resistance in LSM.

Since the bulk defect structure critically influences many aspects of cathode operation, the work in bulk defects provides a foundation for more quantitative investigation of LSM using the same computational parameter estimation methods that we have developed in the past year. We are currently turning our sights on quantitatively estimating bulk oxygen transport properties in LSM along with rate constants for some of the key chemical-electrochemical reactions taking place in the material. Our objective is to produce cathode microstructures that display higher performance than current state-of-the-art composite cathodes at low temperatures (600-750°C). Both microstructure and composition of the composite cathodes will be optimized to achieve better performance.

FY 2007 Publications/Presentations

Publications

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2. Mebane, D. S., Liu, Y. J. and Liu, M. L. "A two-dimensional model and numerical treatment for mixed conducting thin films: the effect of sheet resistance," *Journal of the Electrochemical Society* 154 (5) A421–A426, 2007.

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5. Mebane, D. S., Liu, Y. J. and Liu, M. L. "Refinement of the Bulk Defect Model for $La_xSr_{1-x}MnO_{3\pm\delta}$," *Solid State Ionics*, submitted.

Presentations

1. Mebane, D. S., Liu, Y. J. and Liu, M. L., "Quantitative Understanding of Oxygen Reduction on LSM," Exploratory Workshop-I/UCRC for Fuel Cells at USC-GT, Georgia, February 2007.

2. Lynch, M., Mebane, D. S. and Liu, M. L., "Modeling of Porous SOFC Cathodes," Exploratory Workshop-I/UCRC for Fuel Cells at USC-GT, Georgia, February 2007.

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