

ANALYTICAL AND EXPERIMENTAL STUDY OF OXYGEN REDUCTION MECHANISM ON OXYGEN ELECTRODES OF SOFCs: Case study on $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$

Bilge Yildiz, Gerardo Jose la O', Yang Shao-Horn
 Electrochemical Energy Laboratory
 Massachusetts Institute of Technology,
 77 Massachusetts Ave., Cambridge, MA02139

Introduction

The power of a solid oxide fuel cell (SOFC) is limited by the current associated with oxygen reduction at the cathode under a given operating voltage. The current can in general be treated as the combination of charge transfer in the cathode from two pathways, as shown in Figure 1. The first is the adsorption and reduction of oxygen at the cathode surface followed by bulk diffusion of the ions that yield the charge transfer at electrode/electrolyte interface at the 2PB (Figure 1a). The second is the surface- adsorption and transport of oxygen that leads to the reduction of oxygen and charge transfer at the 3PB region (Figure 1b). A theoretical model that takes into account the defined combined current behavior to simulate physically the cell I-V characteristics is necessary to understand the electrochemical behavior of the SOFC cathode under different operating conditions and for optimizing the properties of cathode materials.

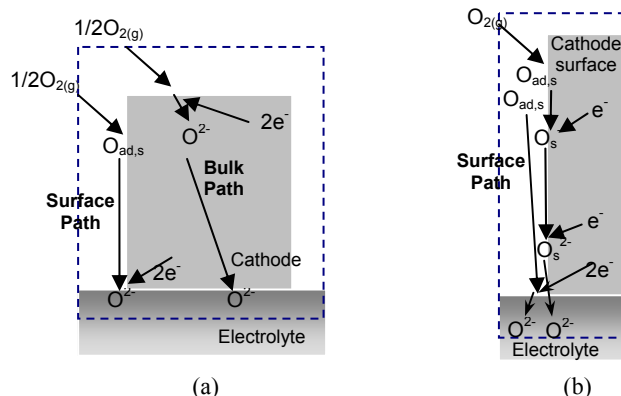


Figure 1. (a) Bulk and surface as the main charge transfer pathways on an SOFC cathode. (b) Parallel charge transfer schemes for the surface pathway of an SOFC cathode.

Although this two-pathway charge transfer behavior and modeling of SOFC cathodes has been studied in literature, a comprehensive physical model that takes into account the effect of both pathways has not been developed. A theoretical model for understanding the I-V characteristic of SOFC electrodes has initially been developed by Adler et al. [1] and this work provides important insights for charge transfer characteristics in SOFC electrodes. However, the model considers only the bulk process followed by 2PB vacancy exchange and it is limited to mixed ionic and electronic conducting electrodes with bulk ionic transfer much faster than surface charge transfer. Although there have been few recent studies that model both bulk and surface pathways [1-4], both pathways are not treated in a single coupled consistent model. For example, the overpotential have been treated as an independent variable rather than being coupled to the oxygen reaction on cathode [2,3].

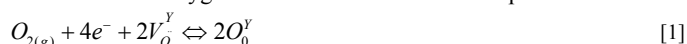
To further complicate our understanding of oxygen reduction at the cathode, there is lack of consistent experimental evidence to explain the surface reaction characteristics, even for the most commonly used cathode $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_{3+\delta}$ (LSM) system [5,6]. While the surface path typically dominates the cell current for porous LSM electronic conductor electrode, the oxygen ion diffusion along the bulk path of LSM is shown to control the current in dense thin film LSM

electrodes. In addition, under high cathodic polarization (typically $<-200\text{mV}$) the LSM system becomes a mixed electronic and ionic conductor [7] and allows the bulk path of charge transfer in LSM to be a major contributor to cell current. Therefore, it is essential to develop a physical model to analyze the charge transfer characteristics of SOFC cathodes from both surface and bulk pathways under different operating conditions and electrode configurations.

In our study, we plan to develop a two dimensional continuum model that handles the surface and bulk charge transfer pathways in a coupled and consistent way for SOFC cathodes. We first model the surface charge transfer characteristics - the rate determining pathway and the rate determining steps (rds), of LSM cathode as our initial case study. This paper presents the analytical and experimental study of oxygen reduction on LSM under different temperature and voltage conditions. The reaction pathway on the surface and rate limiting step revealed in this study will be used to determine the oxygen reduction rate along the surface path required in the coupled continuum model.

Theoretical Analysis

The overall oxygen reduction reaction can be represented as



where V_O^Y and O_0^Y refer to vacancies and oxygen ions in the electrolyte YSZ lattice, respectively. This reaction consists of multiple consecutive steps, one or more of which may be rate determining. Two surface dominated schemes for oxygen reduction on LSM are first considered in this work, as presented in Table 1. Both pathways can occur in parallel to contribute to the cathode current. Other surface models that include 2 electron charge transfer at one step or the transport of totally reduced oxygen (O^-) on the LSM surface away from the 3PB are not considered in this preliminary study.

The rate equations of the proposed reaction steps in each model are written as a function of rate constants and concentrations of species for each step. We assume that the steps that are not rds occur much faster than the rds and thus the net rate of these steps is taken as zero provided that they are in equilibrium. This approach allows the determination of the overall rate of oxygen reduction, r , without computing intermediate species concentrations, and the final rate expression consists of the following parameters: P_{O_2} , temperature, overpotential, and a combination of rate constants that can be correlated with the exchange current density for the cathode.

Table 1. Selected Reaction Models for Oxygen Reduction on LSM

STEPS	EQUATION	PROCESS / LOCATION
Model 1		
1	$\text{O}_{2(g)} \leftrightarrow 2\text{O}_{ad,s}$	Dissociative adsorption on LSM surface
2	$\text{O}_{ad,s} + e^- \leftrightarrow \text{O}_s^-$	Partial reduction of $\text{O}_{ad,s}$ on the surface or the extended 3PB
3	$\text{O}_s^- \leftrightarrow \text{O}_{3PB}^-$	Diffusion of intermediate oxygen species O_s^- along the surface to 3PB
4	$\text{O}_{3PB}^- + e^- \leftrightarrow \text{O}_{3PB}^{2-}$	Complete reduction of intermediate oxygen species at 3PB
5	$\text{O}_{3PB}^{2-} + V_O^Y \leftrightarrow \text{O}_0^Y$	Transfer of O^{2-} at 3PB into YSZ lattice
Model 2		
1	$\text{O}_{2(g)} \leftrightarrow 2\text{O}_{ad,s}$	Dissociative adsorption on LSM surface
2	$\text{O}_{ad,s} \leftrightarrow \text{O}_{3PB}$	Diffusion of $\text{O}_{ad,s}$ to 3PB along the surface
3	$\text{O}_{3PB} + e^- \leftrightarrow \text{O}_{3PB}^-$	Partial reduction of O_{3PB} at 3PB or extended 3PB
4	$\text{O}_{3PB}^- + e^- \leftrightarrow \text{O}_{3PB}^{2-}$	Complete reduction of intermediate oxygen species O_{3PB}^- at 3PB
5	$\text{O}_{3PB}^{2-} + V_O^Y \leftrightarrow \text{O}_0^Y$	Transfer of O^{2-} at 3PB into YSZ lattice

The current from each pathway is then expressed as follows:

$$i_m = -n_e F r_m \quad [2]$$

$$\text{and } i_m = i_{m,a} - i_{m,c} \quad [3]$$

where

$$i_{m-a} = 1 / \sum_j (1 / i_{m-a,j}) \quad \text{and} \quad i_{m-c} = 1 / \sum_j (1 / i_{m-c,j}) \quad [4]$$

$$\text{Total current from each possible scheme: } i = \sum_m i_m \quad [5]$$

In Eq.'s 2-5, the subscripts *a* and *c* represent anodic and cathodic reactions as shown in Table 1, respectively. The parameters *m* and *j* stand for each model and for each of the rds in the model, respectively. In this work, *m* stands for Model 1 and Model 2 in Table 1. Surface diffusion and oxygen ion transfer to YSZ are considered as the rate limiting steps in both models.

As the cathode current is expressed a function of overpotential or cell voltage, one can derive the impedance *Z* for the oxygen reduction process from:

$$Z(\omega) = \frac{FFT(\eta(\omega, t))}{FFT(I(\omega, t))} \quad [6]$$

where η , *I*, *FFT*, ω and *t* represent overpotential, cell current, fast Fourier transform, frequency and time respectively.

The exchange current density expressions for the surface transport of oxygen and the vacancy transfer at LSM/electrolyte interface were obtained from Chen et al [8]. Figure 2 shows the cell resistance calculated from Eq. 6 plotted against the reciprocal of temperature. The slope of the plot is then used to calculate the activation energy, *E_a*, of the rds, which is 1.55 eV in this case. This value suggests the rate determining [10-12] mechanisms of dissociative adsorption or surface diffusion on LSM.

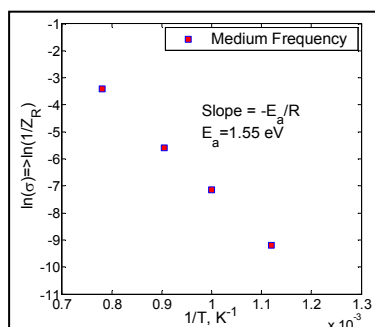


Figure 2. Calculated reciprocal resistances as a function of temperature at 1 atm based on theoretical evaluation (0.1 – 500 Hz)

Experimental Analysis

The $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_{3+\delta}$ with *x*=0.2 cathode and 8YSZ electrolyte samples were prepared by RF sputtering on a single crystal silicon wafer. AC impedance measurements were performed at 0V DC (OCV) with 20mV of amplitude using a Solartron 1260 frequency response analyzer in the frequency range of 0.01 to 10^7 Hz in the temperature range from 450°C to 550°C and at atmospheric pressure. Preliminary AC impedance data showed two semicircles, which became more distinct at lower temperatures, in Figure 3. The resistances in the AC impedance spectra at different temperatures were calculated and the dependence of the reciprocal of resistance was used to find the activation energy of the rate determining process(es), as shown in Figure 4.

The activation energy of 1.1eV was found for the high frequency arc, which is close to values reported for the transfer of oxide ions from LSM to YSZ lattice as $1\text{eV}^{[11]}$.

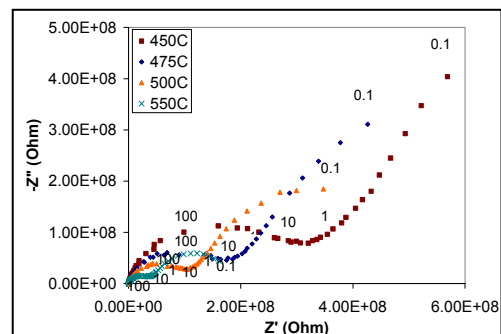


Figure 3. Impedance data obtained for LSM/YSZ at OCV

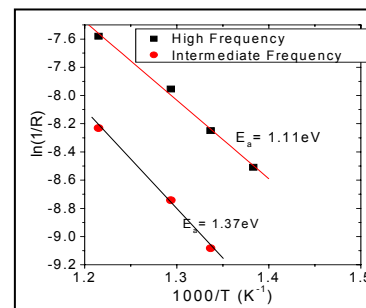


Figure 4. Calculated reciprocal resistances as a function of temperature at 1 atm based on impedance measurements.

The activation energy of 1.37eV was found for the intermediate frequency arc, which could be associated with the dissociative adsorption or the surface diffusion of oxygen species on LSM. The range of activation energy for these processes, although widely studied, greatly varies in the literature - the overall range of *E_a* for these processes reported falls from 1.5 to 2 eV [10-11]. It should be noted that, the 1.55 eV value for *E_a* obtained from theoretical impedance analysis having surface diffusion as one of the rds is similar to the *E_a* found experimentally for the intermediate frequency arc. This preliminary result suggests that the surface diffusion, not the dissociative adsorption, is one of the rds for the oxygen reduction in our experiments.

Additional experiments under changing *P_{O2}* and temperature conditions and modeling work are underway to probe surface reaction mechanisms for LSM, which is essential to develop continuum models of the SOFC cathodes in two-dimensional geometry.

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