



Elementary kinetics of the oxygen reduction reaction on LSM-YSZ composite cathodes



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ABSTRACT

A multi-physics based transient, continuum model of a solid oxide half-cell comprising of a porous LSM-YSZ composite cathode sintered to a dense YSZ electrolyte was developed to investigate the oxygen reduction reaction kinetics. The model coupled species, electron and ion transport through the porous cathode to surface and electro-chemistry. The electrochemical reduction of O_2 was modeled using three candidate elementary kinetic mechanisms. Each mechanism included parallel surface and bulk pathways for O_2 reduction and was driven by three different electric phase potentials. The mechanisms were compared against three sets of electrochemical impedance spectra and polarization curves measured by Barbucci et al. (2009), Cronin et al. (2012) and Nielsen and Hjelm (2014) over a wide range of operating temperatures (873–1173 K), inlet O_2 concentrations (5–100%) and overpotentials (–1 V to +1 V). Two of the three mechanisms were able to quantitatively reproduce the three sets of experiments by only tweaking the microstructural parameters for each individual set. Yet on analyzing their kinetic and thermodynamic parameters, the mechanism postulating the chemisorption of gas-phase O_2 on LSM to form the superoxo-like adsorbate O_2^- was determined to be the most realistic. A model-based sensitivity analysis revealed that ionic transport in the YSZ phase, O_2 dissociation in conjunction with surface to bulk charge transfer in the LSM phase and charge transfer at the three phase boundary were the rate limiting steps throughout the operating space. Additionally, the bulk pathway was found to be insignificant.

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) offer an efficient, decentralized and clean alternative to conventional power generation systems. However, one of the major stumbling blocks toward commercialization is the optimal design of cathodes and selection of materials that readily catalyze the oxygen reduction reaction (ORR) [1]. In fact, cathodic polarization due to slow ORR kinetics is widely acknowledged to be the dominant source of losses especially in the low-intermediate temperature range [2,3]. Acceptor-doped transition metal oxides with high electron conductivities serve as attractive low cost alternatives to noble metals for use as cathodes owing to their superior oxygen exchange coefficients [4,5]. Lanthanum strontium manganite (LSM) is one such material. Although newer materials have been developed with superior catalytic activity toward O_2 reduction, LSM remains technologically relevant due to its excellent blend of catalytic activity, thermal and mechanical stability, and compatibility with yttria-stabilized zirconia (YSZ), a traditional SOFC electrolyte [2]. However, owing to its poor ionic

conductivity, the active area for catalytic reaction is insufficient in single phase LSM cathodes. A potential solution is the introduction of an ionic YSZ phase resulting in a porous LSM-YSZ composite. The state of the art LSM-YSZ composite cathodes perform significantly better than the single phase LSM cathodes due to a much larger utilization region [6–8].

A vital component in improving the design and performance of LSM-YSZ composite cathodes is a deeper understanding of the underlying ORR mechanism. To that end, electrochemical impedance spectroscopy (EIS) has emerged as a powerful measurement technique to spell out the fundamental processes occurring in an electrode. Numerous experimental studies employing EIS, as reviewed comprehensively by Adler [2], have been performed to try and gain deeper insights into the reaction pathways and rate-limiting steps for oxygen reduction on SOFC cathodes. However, the measured spectra are complex, influenced by many factors and thus difficult to interpret, especially for composite electrodes [9].

From a modeling standpoint, various quantum chemical and molecular dynamics studies have been conducted on non-stoichiometric oxides in general [10–12], and LSM in particular [13–15], to try and uncover oxygen reduction kinetics from first

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principles. While these studies are crucial in determining the stability and energy of different transition states and reaction intermediates, the microscopic particle simulations are unable to simulate macroscopic measures of performance like impedance spectra and polarization curves. This limitation of the quantum chemical approach is overcome by continuum scale models that serve as a bridge between microscale molecular simulations and macroscale impedance measurements. Multi-physics based continuum models, employing elementary kinetics informed by density functional theory (DFT), have already been used to simulate impedance spectra and polarization curves for a few anodes and cathodes [16–19]. The micro-kinetic mechanisms are akin to detailed mechanisms commonplace in the fields of homogeneous and heterogeneous catalysis. Yet, owing to the complex role of the porous microstructure, none of these mechanisms have been demonstrated to be ‘intrinsic’, i.e. capable of reproducing large sets of experimental data from distinct and independent sources for a given reaction system.

The use of elementary kinetics is not without its own challenges. Kinetic rate constants comprising of pre-exponential factors and activation energies for all elementary steps must be specified, alongside thermodynamic parameters like enthalpies and entropies of all reacting species, to ensure a thermodynamically consistent mechanism. Therefore, it is important to select reaction systems which have a sizeable repository of kinetic and thermodynamic data published in the literature, as candidates for detailed mechanistic models. Since, LSM-YSZ composites are a staple of the SOFC community, O_2 reduction on LSM-YSZ composites has been investigated for well over ten years [2]. It is a well characterized reaction system (both numerically and experimentally) and is ideally suited to elementary kinetic modeling as demonstrated in this study.

To help develop a detailed micro-kinetic mechanism for O_2 reduction on LSM-YSZ composites, the present study integrates ORR elementary kinetics into a fully transient continuum model of a LSM-YSZ half-cell. The half-cell consists of a porous LSM-8YSZ (8 mol% Ytria in Zirconia) composite cathode sintered to a dense 8YSZ electrolyte. In addition to an elementary kinetic ORR model, the model also incorporates species and charge transport through the porous cathode and dense electrolyte. The coupled transport and kinetic model so developed is then used to simulate three separate experimental studies conducted by Barbucci et al. [20], Cronin et al. [21] and Nielsen and Hjelm [22] to ensure realistic kinetic and thermodynamic parameters for the ORR mechanism. The data sets consist of transient electrochemical impedance spectra and steady-state Tafel plots measured over a temperature range of 873–1173 K and an oxygen partial pressure (p_{O_2}) range of 0.05–1 atm. Three separate ORR mechanisms, each including parallel surface and bulk reaction pathways driven by three different electric phase potentials, are modeled to identify the mechanism which best describes the three sets of experiments. The rate limiting steps for each mechanism are also identified with the aid of a sensitivity analysis.

2. Modeling description

The computational model presented in this study is based on a framework previously published [23,24]. The model simulates the path of the oxygen molecules after they enter the porous cathode from the bulk stream. Ordinary and Knudsen diffusion along with bulk (Darcy) flow drives the O_2 molecules through the microporous network comprised of spherical LSM and YSZ particles. Within the composite network, an O_2 molecule may adsorb on the surface of a LSM particle and be electrochemically reduced to O^{2-} by consuming electrons offered up by the LSM bulk. The O^{2-}

ion is then transferred to a neighboring YSZ particle before being transmitted to the electrolyte through the YSZ cluster. A schematic representation of the modeling domain detailing the involved physics is shown in Fig. 1.

In formulating the mathematical model, the following assumptions were made:

1. The sintered composite cathode can be approximated as a homogeneous continuum of spherical particles with random percolating clusters of LSM and YSZ.
2. The modeling domain (cathode + electrolyte) is isothermal.
3. The species and charge transport through the modeling domain is assumed to be one-dimensional along the thickness.
4. The thin current collector mesh has no impact on the gas transport at the bulk stream-cathode interface.
5. The current collector and the dense electrolyte are assumed to be pure electronic and ionic conductors respectively.
6. The principle of electroneutrality holds in the cathode.
7. Diffusive fluxes due to electron-hole and oxygen vacancy concentration gradients within the LSM and YSZ phases respectively are negligible, i.e. electronic transport in the LSM bulk and ionic transport in the YSZ bulk are due to electrostatic migration only.
8. The counter electrode is ideal and the potential drops across the current collector-cathode and electrolyte-counter electrode interfaces are neglected, i.e. the cell voltage, E_{cell} , is equal to the sum of the potential drops across the cathode and electrolyte.
9. ORR is modeled using an elementary kinetic mechanism, i.e. by resolving the global reaction into a series of reversible steps involving reaction intermediates with each step being thermodynamically consistent and obeying the law of mass action. The chemical activities of the reacting species are set equal to their concentrations which are evaluated using a mean-field approximation.

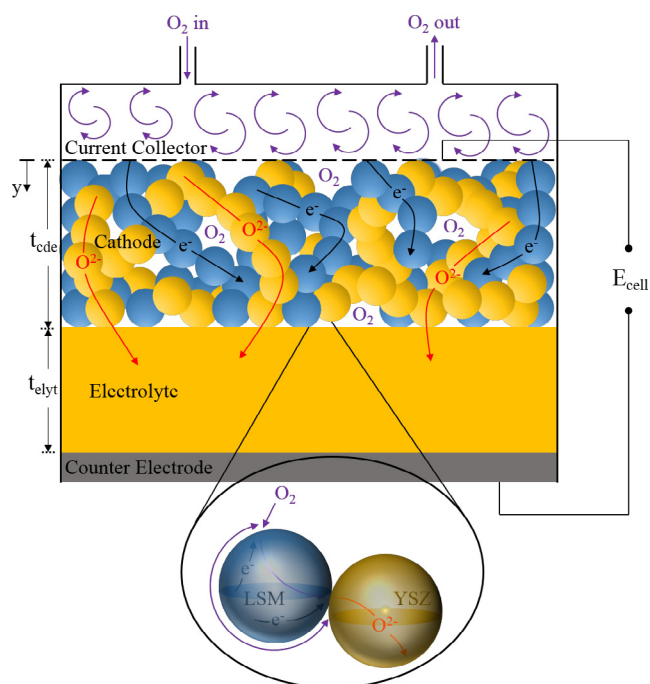


Fig. 1. Schematic of the modeling domain illustrating the various transport phenomena and oxygen reaction pathways through the LSM and YSZ particles.

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