

Oxygen Electrochemistry at LaSrMnO₃/Yttria-Stabilized Zirconia Interfaces

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Introduction

A deeper knowledge of the oxygen reduction reaction (ORR), which occurs at the gas/electrode/solid electrolyte triple-phase boundary (TPB) in solid oxide fuel cells, is essential to optimization of fuel cell performance. Over the last few decades, the kinetics and mechanism of the ORR at LaSrMnO₃ (LSM) composite/yttrium-stabilized zirconia (YSZ) interfaces have been widely investigated using electrochemical impedance spectroscopy and dc polarization techniques. Activation energies for ORR on LSM/YSZ or LSM composite/YSZ have been reported to range between 96 and 200 kJ/mol [1] due to the different electrode preparation methods preferred by the various research groups. A range of Tafel slopes (250 to 450 mV) have also been reported in the literature for the ORR at dense and porous LSM cathodes at temperatures of 700 – 950 °C [2]. The theoretical Tafel slopes, as well as the potential range over which Tafel slopes should be obtained, is temperature dependent, a fact not commonly recognized in the literature. Indeed, the validity of the reported Tafel slopes is still under debate and often depends on the range of potential which the authors choose for their analysis.

Experimental

The LSM-YSZ composite cathode was prepared by mixing equal amounts (by weight) of (La_{0.95}Sr_{0.05})_{0.98}MnO₃ (Praxair Ceramics Inc.) with 8 % YSZ (Tosoh) in alcohol by ball milling. The slurry was screen printed (1100 mesh silk screen) on each side of a YSZ plate (2 mm in thickness). This electrode was then sintered at 1100 °C for 2 hrs, before another thin layer of LSM was screen printed on top of the composite layer to serve as the current collector. Each of these layers will be referred to as LSM/LSM-YSZ electrodes. The two sides later served as the working (WE) and counter (CE) electrodes. Pt paste (Ferro 4082) was also applied to the YSZ region on the same side as the WE, to serve as a pseudo reference electrode (RE). This procedure was followed by sintering at 1100 °C for another 2 hrs. The thickness of the LSM-YSZ electrode layer was determined using Scanning Electron Microscopy (SEM). In the CV and impedance experiments, a Pt gauze was press-contacted to the LSM/LSM-YSZ electrodes with the aid of a spring loaded ceramic cap, thus serving as a current collector.

Half-cell experiments, involving air ($p_{O_2} = 0.21$ atm) or pure oxygen, were carried out over temperatures ranging from 450 to 1000 °C in a tube furnace (Lindberg). Cyclic voltammetry (CV) measurements (sweep rates from 1 to 100 mV/s) were performed using an EG&G PARC 273 potentiostat or a Solatron 1287 interface, with control and data collection handled by Corrware software. The IR-drop originating from the electrolyte resistance was compensated using the positive feedback or current interruption compensation technique in order to establish the resistance-free I/E characteristics. For the impedance analysis, a Solartron 1255 frequency response analysis was coupled with the potentiostat. The frequency range was 0.1 Hz to 500 kHz and the measurements were made

between 0 and –0.4 V vs. the open circuit potential (OCP), using a perturbation amplitude of 10 mV. The impedance measurements and fitting analysis were controlled with commercial software (ZPLOT).

Results

In the present work, the focus has been on establishing a reliable method of determining the mechanism and kinetics of the oxygen reduction reaction (ORR) at LSM-YSZ/YSZ interfaces. Partial pressures of oxygen ranging from 0.021 to 1 atm were employed to elucidate the charge transfer resistance from the Nyquist plots.

At partial O₂ pressures above 0.5 atm, an inductive response appears at low frequencies, while the high frequency impedance response remains constant, independent of the O₂ partial pressure, indicative of an unchanging interfacial resistance. The semi-circle at mid to low frequencies of 100 – 0.1 Hz, however, increases slowly with decreasing O₂ partial pressure, indicating that this semi-circle is related to the O₂ reduction reaction. The charge transfer resistance of the ORR was then obtained from this frequency region using equivalent circuit fitting. The exchange currents for the ORR at LaSrMnO₃ cathodes, calculated from the charge transfer resistance obtained from the impedance spectra, was compared to the exchange currents obtained from low field and high field CV data. A close agreement between these values was obtained and yielded apparent activation energies ranging between 120-130 kJ/mol

In order to obtain mechanistic information about the ORR from the I/E data, the potential must be extended into the ‘exponential Tafel region’ at higher overpotentials. Based on the theoretical calculations at 800 °C, this region is > 400 mV from the OCP. This can be achieved, as unlike with Pt paste electrodes, hysteresis behavior (currents in positive scan are larger than in negative scan) is rarely seen in the CV response, even when high currents are allowed to flow (e.g., at –0.5 V, with and without IR compensation). It is seen that the experimental cathodic Tafel slopes, even after the data was IR compensated, are still significantly higher (0.59 to 0.63 and 0.94 to 1.0 V at 600 and 800 °C, respectively) than the values predicted for the case when the first electron transfer step is rate determining. This may be related to the presence of an adsorbed intermediate in a porous electrode structure. A more detailed discussion of these CV and ac impedance data and the mechanistic implications will be given in the presentation.

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