Effect of CeO$_2$ addition by Atomic Layer Deposition on Surface Reactions in SOFC Cathodes

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Introduction

Improving the oxygen exchange kinetics of mixed-electronic-and-ionic conducting (MEIC) perovskites is of great interest as these materials have significant future potential in applications such as solid oxide fuel cell (SOFC) cathodes, and ion transfer membranes (ITM). In both these applications, it is vital to achieve high rates of oxygen adsorption and transport. Many studies have shown that oxygen exchange rates can be improved by the addition of promoters onto the perovskite surface. However, the mechanisms behind how the promoters are affecting surface exchange processes are not well understood. For example, various studies have reported contradicting results about the effect of adding metal catalysts like Pd and Pt. Uchida et al. found that the addition of Pt significantly enhanced the electrochemical performance of La$_0.8$Sr$_{0.2}$MnO$_3$ cathodes, while Hannappel et al. reported that neither Pd nor Pt had any effect on performance [1,2]. Similar discrepancies also exist for reported effects of infiltrated cobalt oxide [3, 4]. It is apparent that we need a better understanding of how added promoters interact with the active sites and how modifications to the surface composition affect the concentration of these sites and the kinetics of the oxygen reduction reaction.

In this study we attempt to understand the effect of surface modifications on oxygen exchange rates in SOFC cathodes through the use of atomic layer deposition (ALD) of ceria (CeO$_2$). Due to the self terminating nature of ALD, it is an extremely versatile technique for evenly depositing controlled amounts of material. By carefully controlling deposition conditions, addition of sub-monolayer coverages is possible [5]. Ceria was chosen as a model promoter as several studies have reported that addition of ceria nano-particles enhances SOFC cathode performance [6,7].

Materials and Methods

The electrochemical measurements in this study were performed using symmetric cells with La$_0.8$Sr$_{0.2}$FeO$_3$ (LSF) composite electrodes prepared by infiltration of nitrate solutions into a porous YSZ electrolyte scaffold. The cells were fabricated by laminating a porous-dense-porous structure of YSZ electrolyte wafers which were prepared by tape casting methods. A detailed description of the composition of the wafers and the details for the tape casting and lamination procedure is available elsewhere [8]. The electrodes were infiltrated with 35wt% LSF and calcined to 1123K or 1373K for 4 hours. A detailed description of the infiltration process is available elsewhere [6]. Impedance spectra of the symmetric cells were measured in ambient air with a Gamry Instruments potentiostat in the frequency range of 0.01 Hz to 300 kHz. The impedances reported have been divided by two to account for the two identical electrodes.

Ceria films were deposited by alternating exposures to oxygen (Airgas, 99.8%) and tetrakis(2,2,6,6-tetramethyle-3,5-heptane-dionato)cerium (Ce(DMP)$_4$) (Strem) using a system that was built in-house. The precursor chamber was maintained at 433K throughout the ALD process, while the sample chamber was maintained at 373K during deposition and at 673K during oxidation. The amount of ceria deposited by ALD was quantified gravimetrically as a function of ALD cycles. The measurements were performed using porous YSZ slabs (prepared using the same slurry as the porous electrode green tape) that were infiltrated with 35wt% LSF and calcined to 1123K for 4 hrs.

NO$_2$ flow titrations were used to measure the change in concentration of surface oxygen vacancies after ceria ALD. NO$_2$ is a strong oxidant which will react with oxygen vacancies to produce O(ads) and gaseous NO. The titrations were performed using LSF wafers made from the same nitrate solutions used for infiltration. 5% NO$_2$ balanced in He was passed over the LSF wafers and the exiting NO$_2$ and NO concentrations were monitored using a mass spectrometer.

Results and Discussion

ALD of Ce(DMP)$_4$ at 373K results in a coverage of 2.5x10$^{13}$ molecules/m$^2$ per cycle, which becomes roughly 2% of a ceria monolayer upon oxidation at 673K in pure oxygen. The cathode performance was analyzed as a function of the thickness of the deposited ceria film, and compared to the performance of cathodes with infiltrated ceria. Impedance spectra measured on unmodified LSF electrodes showed an initial polarization resistance of 1.1 Ω cm$^2$ at 873 K. While infiltration of ceria nano-particles decreased the polarization resistance to 0.6 Ω cm$^2$, the addition of ceria ALD coatings of less than 1 nm in thickness increased the polarization resistance by an order of magnitude (Fig. 1). The electrode impedance for the ALD cells was dominated by low-frequency processes, indicating that the electrodes were limited by slow O$_2$ adsorption. NO$_2$ flow titration measurements showed that the surface oxygen vacancy concentration decreased dramatically after deposition of ceria by ALD.

The results from this study show that the form of the added promoter matters a great deal and that the resulting change in surface oxygen vacancy concentration is much more important than the catalytic properties of the promoter. Secondly, at least for LSF, the fact that fractional monolayer coverages of ceria can significantly increase electrode impedance suggests that only a tiny fraction of this particular surface is active for O$_2$ exchange. This is consistent with the hypothesis that oxygen vacancies are the active sites for O$_2$ dissociation.

Significance

Understanding how surface modifications affect the oxygen exchange kinetics will provide critical information on how to improve the performance of SOFC cathodes and ITM.
Figure 1. Nyquist impedance plots of LSF-YSZ cathode symmetric cells calcined to 1123 K and measured at 873 K before and after ALD treatment. The impedance spectra have been offset for clarity.

References