TRANSITION METAL B-SITE SUBSTITUTED LANTHANUM MANGANITE SOFC CATHODE MATERIALS

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ABSTRACT

The properties of some B-site substituted (Co, Cr), alkali-earth doped lanthanum manganites were studied. Submicron powders were synthesised using the standard glycine-nitrate combustion method, and characterised using XRD. High temperature conductivity of dense samples were measured using the standard 4 probe DC method. Electrochemical properties of spray coated thin films on YSZ substrates were examined using the current interruption technique. The reactivity of powdered samples of these binary solid solutions with YSZ at temperatures from 1000°C to 1300°C was also studied. Low level Cr doping of A-site deficient La(Ca,Sr)MnO₃ resulted in a material with morphological stability and decreased oxygen overpotential, without extensive detriment to the electronic conductivity. Co-doped La(Ca,Sr)MnO₃, however, showed decreased morphological stability and poor compatibility with the YSZ substrate.

INTRODUCTION

In high temperature solid oxide fuel cell (SOFC) applications, cathode materials must have material properties compatible with other components in the cell such as the electrolyte, generally 8 mol% yttria stabilized zirconia (YSZ). The high operating temperature, typically 1000°C, is generally determined by the electrolyte, where its oxide ion conduction becomes realistically acceptable. Thus, the operating temperature imposes many limitations on the cathode materials that can be successfully utilised.

The perovskite-type cathode Laₓ₋₁ₓAₓMnO₃ (A = Sr, Ca), has been the popular choice, being compliant with requirements such as similar thermal expansion, high electronic conductivity, good oxygen reduction catalysis, chemical stability etc. In the ABO₃ perovskite structure, doping of the A-site, with the alkali earth metals mentioned, essentially increases the charge carrier concentration, and reasonable p-type conductivity is observed at high temperature in an oxidising environment.

Many properties of the perovskite-type oxides are primarily influenced by the B-site ion, especially when transition metals are present and mixed valencies are observed. A-site substitution can affect electronic conductivity via charge compensation, by increasing the extent of mixed valent states. The work here, examines some effects of Cr and Co substitution on the B-site of A-site doped lanthanum manganite. In the
example of Cr doping, the undoped composition was A-site deficient which has shown low reactivity (7) and very good electronic conductivity. However, high sinterability (2), is undesirable in a cathode that requires a large triple phase boundary area for oxygen reduction. By using Cr in the B-site, the sinterability of the A-site deficient manganite should be retarded (as LaCrO$_3$ is ill-sinterable) allowing for a stable electrode with good morphology. Although the electronic conductivity of this system may be compromised to an extent, the reaction with YSZ at 1000°C is expected to be low. It has also been shown that degradation of the electrode, during high fabrication temperatures, and subsequent increase of overvoltage can be minimised with low level Cr doping (3).

Doping with Co involves material design directed at increasing reaction kinetics of the cathode. Because LaCoO$_3$ is a mixed conductor, doping at levels up to 50 mol%, in the LaMnO$_3$, system increases the oxygen self diffusion (4) and O$_2^-$ ion migration. This would effectively increase and extend the triple phase boundary to the entire surface area of the cathode, therefore markedly increasing efficiency. Unfortunately, some reaction at high fabrication temperatures, with the more reactive Co (1) present, may cause secondary phases to be produced at the cathode-electrolyte interface. These secondary phases would most likely be SrZrO$_3$ (in the Sr doped case), La$_2$Zr$_2$O$_7$ and cobalt oxide, all having a detrimental effect on the cathode performance due to their high resistivities (5). It was the primary focus of this work to investigate reactivity of these systems with YSZ, using sub-micron powders produced by the glycine-nitrate synthesis, and observe the effect of B-site doping on the conductivity, and the effect of annealing temperature on the cathodic overpotential.

**EXPERIMENTAL PROCEDURE**

Compositions La$_{1-x}$A$_x$Mn$_{1-y}$Co$_y$O$_3$ (A = Ca, x = 0.5 ; A = Sr, x = 0.2, and y = 0-0.5) and (La$_{1-x}$A$_x$)$_0.9$Mn$_{1-y}$Cr$_y$O$_3$ (A = Ca, x = 0.5 ; A = Sr, x = 0.2, and y = 0-0.15) (labelled LSMCo, LCMCo, LSMCr and LCMCr, respectively) were prepared. Synthesis of these powders was carried out using a self-propagating combustion method (6) with glycine as a fuel, and annealing at 900-1000°C to ensure perovskite formation. Characterisation of the powders was performed using X-ray powder diffraction (XRD) on a Rigaku RC (12kW) system with monochromated Cu Kα radiation and a scintillation detector.

Rectangular bars (approximately 3.5 x 10mm) were uniaxially pressed and sintered at temperatures from 1350 to 1400°C for measurement of electrical conductivity, as a function of temperature, using the standard 4-probe DC method. Measurements were progressively made from room temperature to 1000°C, and also on cooling back to room temperature.

Pellets of 8 mol% YSZ (Tosoh) for use in polarization measurements, were prepared from a pressed disk (12mm Ø and 2mm thick), sintered at 1450°C for 6 hours. These were then treated by etching with HF at 70°C for 30 minutes. Oxygen reduction polarization measurements were performed on a 3-electrode cell using the current interruption technique (7) allowing removal of the I-R drop contribution. Cathodic overpotential measurements were performed at 900°C and 1000°C in an air atmosphere.
The cell was comprised of a spray-coated perovskite powder, fired at various temperatures from 1150 to 1300°C for 4 hours, as the working electrode. Platinum paste was painted on to the reverse side and provided the counter and reference electrodes.

Reactivity of the perovskite powders with YSZ was checked by mixing in a 1:1 weight ratio, and grinding until a homogenous mixture was obtained. Pellets were uniaxially pressed under a pressure of 2500kg cm⁻² and then fired at various temperatures. Examination was completed using XRD after the sintered sample had been crushed and ground.

RESULTS AND DISCUSSION

The electrical conductivity of solid sintered bodies shows conductivities as seen in Figures 1 and 2, where conductivity is plotted against reciprocal temperature for measurements from 1000°C to room temperature. Generally, for all compositions, a reduction in the conductivity and increase in the activation energy occurred with B-site doping. The LSMCo samples showed fairly close electronic conductivity at 1000°C, although activation energies were seen to increase generally with increasing Co content. At low dopant levels (between 10 and 20 mol%) in the LCMCo samples, conductivity was found to slightly increase at 1000°C. The decrease in conductivity reversed with 40 mol% Co showing the same result as for 20 mol%.

Doping on the B-site with Cr showed a greater deviation from conductivity values for the undoped system at high temperature, due to the decrease in Mn sites which are thought to dominate the conduction process. The LSMCr systems displayed semiconductive behaviour with best conductivity at 1000°C shown by the 15 mol% Cr sample, although activation energy was higher than that with lower dopant levels. The LCMCr samples also showed that 15 mol% Cr was the optimum dopant percentage for best conductivity at 1000°C. This sample, and the undoped Ca containing manganite, showed metallic conduction above 1000°C.

The overpotential of Co doped samples should decrease and oxygen reduction activity increase, because oxygen vacancies are created with Co doping on the B-site (8, 9). Spray-coated thick films, approximately 15μm thick, were poorly adhered to the electrolyte pellets, possibly due to greater thermal mismatch of Co containing perovskites with the YSZ (9), although sintering within the film was improved with increasing anneal temperature, consequently, acceptable measurements could not be achieved. However it was obvious from absolute values obtained from the coated samples that overpotential increased slightly with Co doping, although this could be attributed to the poor cohesion between electrolyte and electrode and also the resistive reaction products found with the Co doped samples.

Cr doping effectively decreased the overpotential in both the Sr and Ca doped systems. This was probably caused by increased adhesion and morphological variation. Annealing to optimise the oxygen reduction activity showed that temperatures of 1150°C and 1200°C gave best results for the Sr and Ca doped compositions, respectively. This can be seen in Figures 3(a) and (b).
Reaction of these electrode materials, with YSZ, at high temperature was expected to occur to some extent with the Co containing perovskites, but was expected to be retarded for the Cr containing compositions. XRD patterns for various anneal temperatures, between 1000°C and 1300°C for 96 hour periods, are shown in Figures 4 and 5. The LSMCo compositions showed reaction products La2Zr2O7, SrZrO3 and only small amounts of CoO appearing at 1000°C after annealing for 96 hours. Quantitatively, the reaction products were greater with increasing Co concentration, although at up to 50 mol% the measured CoO was significantly smaller, which is in agreement with Ivers-Tiffée et al. (9, 10). LCMCo showed only small amounts of CoO appearing after annealing at 1200°C for 96 hours and CaZrO3 appearing after treatment at 1250°C. This is almost the opposite to the result of Takeda et al. (11) for non B-site doped manganites annealed at 1200°C for 2 hours. The Cr containing compositions showed virtually no reaction after annealing at 1300°C for 96 hours, except for the Sr containing samples where very small amounts of La2Zr2O7 were detected after treatment at 1250°C.

CONCLUSIONS

Transition metal (Cr, Co) doped La(Sr, Ca)MnO3 show reasonable electronic conductivity at high temperature with dopant levels less than 15 and 50 mol% for Cr and Co, respectively. Cr doping effectively decreases the overpotential due to morphological stabilization. Co doping appears to create a morphologically unstable, poorly adhered electrode, consequently showing very poor overpotential behaviour than that expected. Reaction with a YSZ electrolyte material occurs with Co doped systems, especially Sr A-site doped. Cr doping creates a stable morphology with no reaction seen at high temperatures, with anneal periods up to 96 hours. These results suggest Cr doped lanthanum manganite is a good candidate for a SOFC cathode material. The Co doped system, however, requires further examination to optimise desirable properties and produce a morphologically stable mixed conducting cathode.

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Fig. 1. Temperature dependence of electrical conductivity for (a) $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$ and (b) $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$. 
Fig. 2. Temperature dependence of electrical conductivity for (a) \((\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3\) and (b) \((\text{La}_{0.5}\text{Ca}_{0.5})_{0.9}\text{Mn}_{1-y}\text{Cr}_y\text{O}_3\).
Fig. 3. Overpotential data for (a) (La$_{0.8}$Sr$_{0.2}$)$_{0.9}$Mn$_{1-y}$Cr$_y$O$_3$ and (b) (La$_{0.5}$Ca$_{0.5}$)$_{0.9}$Mn$_{1-y}$Cr$_y$O$_3$ annealed at various temperatures, measured at 900°C in air.
Fig. 4. XRD patterns of (a) $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1.4}\text{Co}_2\text{O}_3$ and (b) $\text{La}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1.2}\text{Co}_2\text{O}_3$ with YSZ annealed at various temperatures.
Fig. 5 XRD patterns of (a) \((\text{La}_{0.8}\text{Sm}_{0.2})_{0.9}\text{Mn}_{1.1-y}\text{Cr}_{y}\text{O}_{3})\) and (b) \((\text{La}_{0.5}\text{Ca}_{0.5})_{0.9}\text{Mn}_{1.1-y}\text{Cr}_{y}\text{O}_{3})\) with YSZ annealed at various temperatures.