ALTERING THE EQUILIBRIUM CONDITION IN Sr-DOPED LANTHANUM MANGANITE

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ABSTRACT

The material of choice for a solid oxide fuel cell cathode based on a yttria-stabilized zirconia (YSZ) electrolyte is doped lanthanum manganite, (La, Sr)MnO₃. It excels at many of the attributes necessary for a system to work at the required operating temperature and is flexible enough to allow for materials optimization. Although strontium-doping increases the electronic conductivity of the material, the ionic conductivity of the material remains negligible under operating conditions. Studies have shown that the internal equilibrium of the material heavily favors oxidation of the manganese rather than the loss of lattice oxygen as a charge compensation mechanism. This lack of oxygen vacancies in the structure retards the ability of the material to conduct oxygen ions; thus the optimized system requires a large number of engineered triple point boundary locations to work efficiently. We have successfully doped the host LSM lattice to alter the internal equilibrium of the material to increase its ionic conductivity and thus lower the cathodic overpotential of the system. Our paper discusses these new materials, the results of cell tests, and a number of characterization experiments performed.

INTRODUCTION

In recent years, fuel cell technology has emerged as a major area of research with anticipated uses in electric vehicles, remote power generation, and large-scale power supplies. Because of the many diverse applications for fuel cells, many different types have been developed to respond to different markets and available working conditions. For instance, polymer-electrolyte membrane (PEM) fuel cells are under study by the transportation industries because they are capable of operating at low temperatures (80°C), while solid oxide fuel cells (SOFC), which offer higher efficiency and the option of self-reforming their fuel, require higher operating temperatures (around 1000 °C) but are better suited as a stand-alone power unit. The typical SOFC is constructed of an Ni/YSZ anode, a yttria-stabilized zirconia (YSZ) electrolyte, and an (La, Sr)MnO₃ (LSM) cathode. In general, an SOFC cathode has to have three important properties: (1) good
electrical conductivity, (2) catalytic properties for oxygen disassociation, and (3) acceptable ionic conductivity. Specifically, LSM has been found to have very good electrical conductivity and catalytic properties, but poor ionic conductivity. This is not totally surprising since ionic conductivity and electrical conductivity work by opposite mechanisms. As LaMnO$_3$ is doped with strontium, the charge can be compensated for, either by oxidizing the manganese cations (good electrical conductivity) or by creating oxygen vacancies (good ionic conductivity).

$$La_{1-x}Sr_x((Mn^{4+})_{1-x}(Mn^{3+})_{1-x})O_3 \leftrightarrow La_{1-x}Sr_x(Mn)O_{3-x/2}$$

Previous studies have shown that under most conditions, the favored mechanism is cation oxidation (1,2). In the actual SOFC, this limitation can be addressed by engineering the cathode so that a large number of triple boundary points take advantage of the LSM’s good surface exchange coefficient for oxygen (3,4,5). These are points where the electrolyte, air, and the cathode come together, minimizing the distance the created oxygen anions must travel. In order to improve the efficiency of SOFCs, the ionic conductivity properties of the cathode must be improved upon without a significant decrease in its catalytic and electrical properties. In this paper, we will discuss our recent efforts to increase the ionic conductivity of LSM by selective B-site doping.

**EXPERIMENTAL**

**Materials Synthesis and Characterization**

All materials in this study were synthesized by a glycine nitrate method. In a typical reaction, predetermined amounts of La(NO$_3$)$_3$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_3$, and $M_x(NO_3)_m$ (M = Al, Ga, In) were mixed in aqueous solution to yield the final stoichiometry $(La_{1-x}Sr_x)_{0.99}(Mn_{1-y}M_y)O_3$. Once dissolved, glycine was added and the solution was boiled until the mixture ignited. The resulting fine powder was pressed into a pellet and calcined at 1250°C for one hour. The pellet was ground into powder and submitted for X-ray diffraction (XRD) analysis.

**Electrode Preparation and Cell Testing**

After a single-phase synthesis of the desired powders was determined, a few grams of the powder were ball-milled in methanol for 7-10 days. The mixture was subsequently slurry coated onto a YSZ electrolyte disk (200 $\mu$m) and sintered in air at temperatures of about 1000-1300°C for one hour before testing. A symmetric cell configuration (see Figure 1) was employed with each electrode having a reference. Platinum mesh was used as current collector, and all measurements were performed at 1000°C in air.

Both AC impedance spectroscopy and DC polarization techniques were used for the characterization of the cathode materials. Cathodic polarization resistance ($R_c$)
at/near the open circuit potential (OCV) condition was determined by impedance spectroscopy. The polarization curve was obtained using a galvanostatic method while simultaneously measuring the impedance with an applied constant current. For this study, the cathodic overpotential was examined as a function of dopant concentration.

![Diagram of cell configuration](image)

**Figure 1.** Cell configuration for half-cell test in air at 1000°C

**RESULTS**

A series of compositions with the formula \((\text{La}_{1-x}\text{Sr}_x)(\text{Mn}_{1-y}\text{M}_y)\text{O}_3\) were synthesized varying both the amounts of Sr and dopant M (M = Al, Ga, In). Strontium is on the A-site and dopant M on the B-site. Both dopant concentrations were varied \((0 < x < 45 \text{ mol} \% ; 0 < y < 60 \text{ mol} \% )\) in order to obtain a single-phase material. It was found that a balance between A-site and B-site doping was required in order to obtain a single-phase material under our experimental conditions. Single-phase materials only exist when one dopant concentration differs significantly from the other. At high Sr concentration (40-50 mol %), single-phase materials could only be obtained when the B-site dopant concentration was less than 30 mole percent. When the Sr concentration was low (< 20%), the solubility of the B-site dopant increased up to 40 mole percent.

For the single phase materials, a series of half-cell tests was used to determine the effect of the B-site doping on the overall cell performance. These data are plotted in Figure 2 showing the change of cathodic overpotential of air electrode with Ga doping at two constant current densities after current conditioning. For comparison, LSM with no dopants on B-site was also synthesized and examined under the same conditions. The results are also shown in the figure by the three points at zero dopant concentration, which correspond to the electrode compositions of \(\text{La}_{0.54}\text{Sr}_{0.45}\text{MnO}_3\) (LSM5), \(\text{La}_{0.59}\text{Sr}_{0.4}\text{MnO}_3\) (LSM6) and \(\text{La}_{0.79}\text{Sr}_{0.2}\text{MnO}_3\) (LSM8) respectively. Although the overpotential varies with Sr content in LSM without Ga doping, it is obvious that there is an optimum doping concentration, which gives lowest overpotential at both current densities.
Figure 2. Effect of gallium concentration on the cathodic overpotential of LSM cathodes. Open circles were run at 250 mA/cm², while filled circles were run at 100 mA/cm².

For this series of compounds, a minimum in the curves at approximately 5% dopant is indicative of a significant drop in the cathodic overpotential when compared to the standard materials, usually reported to be around 60mV.

**DISCUSSION**

In the near future, SOFCs may offer an attractive alternative to other power sources because of the intrinsic advantages that include fuel adaptability, reliability, and low emission levels. One of the main system limitations identified to date is the low ionic conductivity of the cathode. As stated above, the intrinsic internal equilibrium of LSM strongly favors manganese oxidation over oxygen loss as a charge compensation mechanism. Studies by Kuo, Anderson, and Sparlin (2) have shown that the internal equilibrium lies far to the left, that is, favoring manganese oxidation until oxygen partial pressures of $10^{12}$ atm are used. The strong tendency of manganese cations to oxidize rather than reduce coordination number under these conditions lies at the heart of the ionic conductivity problem. In our studies we have used B-site doping to selectively alter this equilibrium. By doping LSM with a small amount of an element that prefers a coordination number lower than six, the system has an alternative to cation oxidation as strontium is added in place of lanthanum. For this study gallium was chosen because of its comparable size and charge to manganese, stability in the perovskite structure, and strong preference for tetrahedral coordination in ternary (or higher) oxides. Considering these elements’ valence electron count and periodic table position this is not an unexpected observation (6). It is the tendency for gallium to have four-coordination that lies at the heart of the ionic conductivity of LSGM, $(\text{La, Sr})(\text{Ga,Mg})\text{O}_{3-x}$ (7,8) Because there is no other
charge compensation mechanism other than loss of oxygen, a significant number of vacancies can be formed when the material is doped correctly (9,10). When this concept is applied to LSM, the added gallium should seed vacancies into the framework, slightly altering the internal equilibrium to include some oxygen vacancies as a charge compensation mechanism, especially at the higher operating temperatures. To a first approximation, the addition of a gallium cation into the framework should not affect the overall stability of the perovskite lattice. The diagram in Figure 3 shows that the addition of gallium at a low concentration into an ideal perovskite layer has the effect of making the manganese cations around it adopt a square pyramidal coordination as they share vacancies. With its Jahn-Teller d⁴-electron configuration, manganese has a variety of choices for its coordination environment. In this case, square pyramidal coordination is a common secondary observation for manganese (III) cations. For instance, in the oxygen-deficient perovskite CaMnO₂.₅, all of the manganese cations are square pyramids (11). This material is made by the controlled removal of oxygen from the perovskite CaMnO₃. As oxygen is removed, and manganese is reduced formally to +3, structural studies indicate the formation and ordering of vacancies around the manganese. As long as clustering of the gallium cations can be averted so as not to have all of the vacancies tied up around the dopant cation, a measurable

Figure 3. A [100] layer from an ABO₃ perovskite showing the effect of adding a tetrahedral cation to the coordination geometry of the surrounding cations.

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number of vacancies should reside on the manganese cation lattice. In instances
where high gallium concentrations are used on the B-site, several studies have noted
their tendency to cluster to form ordered brownmillerite-type and related phases,
notably the oxygen-deficient perovskites LaSrCuGaO$_5$ and LaSrCuAlO$_5$ (12,13,14).
In our studies of gallium-doped LSM, we observed in our XRD studies no significant
changes in the unit cell volumes of the materials until approximately 10 mol % of the
B-site was gallium. This break point also corresponded to a significant drop-off in
performance. As can be seen in Figure 2, a minimum around 5% Ga on the B-site led
to the lowest observed cathodic overpotential. We attribute this increase in
performance to an increase in the ionic conductivity of the sample. We are in the
process of expanding these studies by performing secondary ion mass spectrometry
(SIMS) and various X-ray absorption spectroscopy (XAS) studies of these materials
to determine the new oxygen diffusion numbers. It should be noted that on the same
figure, the undoped samples are plotted and perform as expected for LSM-type
materials, but not as well as the doped materials.

Additional studies where aluminum was substituted into the samples resulted in
very similar results, with a minimum on the curve in roughly the same position. An
interesting alternative experiment substituting indium for manganese produced the
expected negative results, as indium has little predilection for tetrahedral
coordination.

When applying this theory to other systems, similar conclusions can be drawn.
An extensive study by Carter et al. of several doped cobaltites and manganites
showed that vacancy formation and oxygen self-diffusion increased by several orders
of magnitude, depending on the concentration of lower-coordination-number species
(15). In their studies of LSM, (La, Sr)(Mn$_{0.8}$Co$_{0.2}$)O$_{3-x}$, (La, Sr)(Mn$_{0.46}$Co$_{0.12}$Ni$_{0.4}$)O$_3$,
and (La,Sr)(Co$_{1-x}$Fe$_x$)O$_{3-x}$ they observed that higher rates in the cobaltites were seen
as the amount of the coordinatively unsaturated d$^5$ Co$^{4+}$ cation was formally formed
(16). A recent study by Mineshige et al. on La$_{0.7}$Sr$_{0.3}$CoO$_{3-x}$ also shows that even at
this A-site dopant level, 3% of the charge compensation was attributable to oxygen
vacancies at oxygen partial pressure of 2 x 10$^{-3}$ atm (17). In Carter’s work, some of
the best performances were observed in samples where extra strontium (or calcium)
was added to the A-site in addition to the iron on the B-site. This increase in average
B-site oxidation state increases the amount of formally tetravalent d$^4$ iron or formally
d$^5$ Co$^{4+}$. If the tetravalent iron is less stable than the tetravalent cobalt, more of the
burden is also on the cobalt, which has the option to lower its coordination number
because of its electronic configuration.

For manganite materials used by Carter et al., small increases in oxygen self-
diffusion were obtained with their cobalt-doped materials at high Sr-doping levels.
However significant increases, 2-3 orders of magnitude, were observed when d$^8$
Ni$^{2+}$ was added to the B-site. In this instance, nickel has a very strong preference for
4-coordinate square planar configuration in oxides. A relevant example is the
reduction of the perovskite LaNiO$_3$ to the oxygen deficient perovskite LaNiO$_{2.5}$ (18).
This material contains all square planar nickel cations within its framework. In Carter's materials, adding a significant amount of nickel resulted in a large number of oxygen vacancies and a significant increase in the oxygen self-diffusion constant. This explanation is also supported by several recent reports where adding nickel (II) was seen to increase the ionic conductivity of the materials and the oxygen non-stoichiometry (19,20,21,22). Additionally a series of crystal structures of several doped oxygen-deficient manganese-doped lanthanum nickelates have shown that a large concentration of the oxygen defects was around the nickel cations (23).

CONCLUSIONS

We have investigated a new series of gallium-doped LSM materials and explained their superior performance to a B-site dopant mechanism where gallium seeds the LSM lattice with oxygen vacancies. This theory is supported by our obtaining similar results with other dopant cations that prefer tetrahedral coordination and is consistent with other recent literature studies using divalent nickel or iron cations as a dopant.

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