CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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Introduction

The awareness of environmental factors and limited energy resources has driven the search for new energy supplies and technologies even though the fossil and nuclear sources can remain adequate for the next few decades. The new energy technologies have to be cleaner, cheaper, smaller and more efficient, such as fuel cells or solar cells.[1] The development of solid oxide fuel cells has been extensively performed from both industrial and experimental points of view. Over the past few years, work has been focused on the solid oxide fuel cells operated at intermediate temperature regime (500 – 700ºC), which seems mandatory if the cells can be commercialized. Compared to the conventional high temperature cell operation (>800ºC), the intermediate temperature operation requires an extremely strict material selection, which allows for similar electrode kinetics and internal resistance as those at high temperature. This article treats the cathode in particular. $La_{0.80}Sr_{0.20}MnO_3$, the currently preferred cathode material, has proven to be unsuitable for use below 800ºC due to very low oxygen vacancy concentration. Therefore, research work is required if a cathode is to be developed which will be suitable for use in the intermediate temperature range. Current studies have tried three ways to address this problem: (1) replacing La with Pr, Nd, Sm or Gd; (2) partial or complete substituting of Mn by Fe, Co and/or Ni; (3) combination of (1) and (2). From these studies, ferrites and cobaltites have shown reasonably good, stable performance, and in addition have displayed lower have activation energy, smaller areal resistance, higher oxygen vacancy level and faster kinetics for interfacial oxygen transfer reaction, compared to manganite. Thus it appears that there may be solutions to the cathode problem, but in order to develop the fundamental knowledge required to resolve a number of the practical and fundamental problems, experiments have to be conducted from the viewpoints of materials selection, defect chemistry, and electric, magnetic and catalytic properties. In this paper, the oxygen vacancy level was determined from electrical conductivity, thermogravimetric analysis, and neutron diffraction. Valence states of Fe/Co in $Ln_{1-x}Sr_xFe_{1-y}Co_yO_3$ (where Ln = La and Sm; $0 \le x, y \le 1$) and magnetic properties were achieved by analyzing the results from ^{57}Fe Mössbauer, SQUID and neutron diffraction. Nanocrystalline cathode particles and thin films were used to study the size effect.

Experimental

The Pechini method was used to synthesize nanocrystalline particles[2] . A polymeric solution which was formed by a chelating reaction between cations and chelants was used to prepare thin films by spin coating the polymer onto a substrate followed by annealing at elevated temperatures.[3] Electrical conductivity was measured by the four-probe method at temperatures and oxygen activities ranging from 150 – 1000ºC and 10^{-25} to 1, respectively. The thermogravimetric analysis was conducted at 1000 and 1200ºC in O_2, air, and Ar. Mössbauer and neutron diffraction were performed at room temperature on the sintered and quenched specimens.

Results and Discussion

Initial experiments focused on the synthesis and electrical properties of the $La_{1-x}Sr_xFeO_3$ (LSF) series, which is being considered as the cathode candidates. The perovskite phase was formed at 600ºC for x = 0.1 to 0.9. The particles from the Pechini method exhibited a specific surface area of 18 m^2/g for $La_{0.60}Sr_{0.40}FeO_3$ at 600ºC, from which the full dense LSF ceramics were formed by sintering at 1300ºC for 6 hours. Figure 1 illustrates the fracture surface of a sintered specimen with an average grain size ~ 4μm.

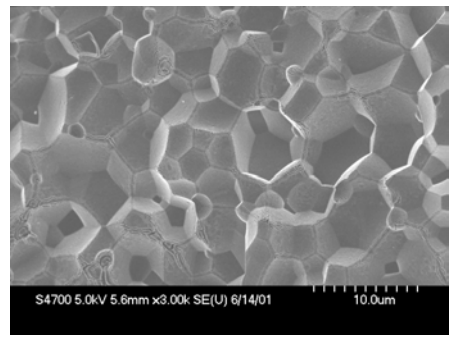

Figure 1. SEM image of fracture surface of $La_{0.60}Sr_{0.40}FeO_3$ sintered at 1300ºC for 6 hours.

Electrical conductivity measurements were performed on sintered bars of LSF. Figure 2 shows the plots of log(σ) vs. 1/T for $La_{0.60}Sr_{0.40}FeO_3$ measured in air, 2% O_2 and 0.1% O_2 from 200ºC to 1000ºC. A maximum conductivity around 600ºC was observed for all gas atmospheres with a σ ~ 182 S/cm in air. $La_{0.60}Sr_{0.40}FeO_3$ is a p-type of conductor with the holes as the majority carriers. The electroneutrality condition was given in the Kröger-Vink notation as $[Sr_{La}^{'}]=2[V_O^{\circ\circ}]+[h^{\circ}]$, where $[Sr_{La}^{'}]$ is the dopant concentration, $[V_O^{\circ\circ}]$ is the oxygen vacancy concentration and $[h^{\circ}]$ is the hole concentration.[4] The oxygen vacancies are generated at high temperature due to loss of oxygen, which results in a higher $[V_O^{\circ\circ}]$ and a lower hole concentration, assuming $[Sr_{La}^{'}]$ is constant. Therefore, $\sigma = \mu\, p\, q$, where p is the carrier concentration and q is the carrier charge, at elevated temperature, the mobility is increased whereas the carrier concentration, p, is decreased, which results in a maximum in the conductivity. This type of phenomenon was also observed in manganite and benefits the cells operated at intermediate temperature because of the maximum conductivity is around 600ºC.

Further study was then performed on the electrical conductivity of $La_{0.60}Sr_{0.40}FeO_3$ at the low pO_2, in which oxygen vacancy concentrations were increased. Figure 3 shows the plot of log(σ) vs. log(pO_2) at various temperature (from 700ºC to 1000ºC) with a control over the oxygen activity being made by using a mixture of CO/CO_2, from which the pO_2 can be determined thermodynamically. In figure 3, a transition from p-type to n-type of conductor is obvious at relative low pO_2, at which the majority carriers changed from the holes to electrons because of the valence state decreases in Fe due to the further loss of oxygen.

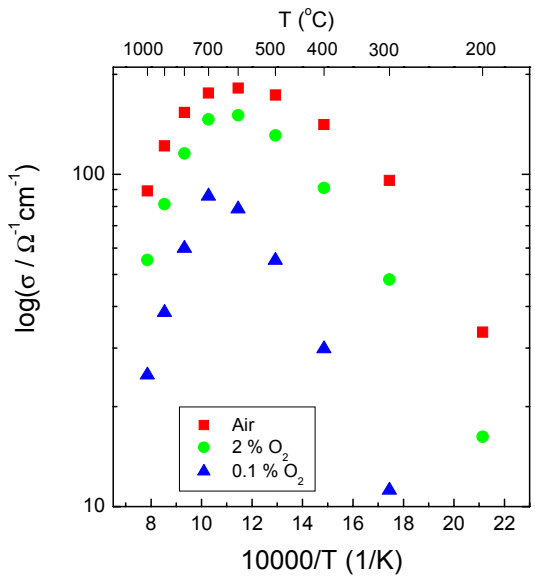

Figure 2. Plots of log(σ) vs. 1/T for $La_{0.60}Sr_{0.40}FeO_3$ in air, 2% O_2, and 0.1% O_2 from 200ºC to 1000ºC.

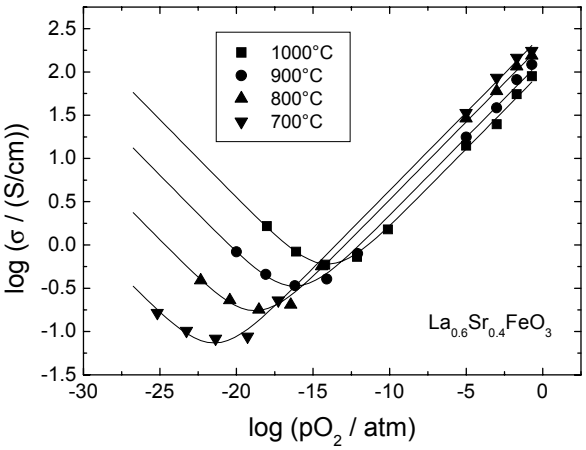

Figure 3. Plots of log(σ) vs. log(pO_2) for $La_{0.60}Sr_{0.40}FeO_3$ at various temperatures.

In addition to the conductivity, oxygen vacancy concentration also plays a key role in the function of cathodes, in particular in the catalytic properties. Determination of the oxygen vacancy level has been performed by thermogravimetric analysis (TGA) and neutron diffraction. TGA simply measures the weight changes with the variable being time, gas environment and temperatures. Neutron diffraction was performed on the samples which were quenched at 1000ºC from different oxygen activities. A large decrease in 3-δ was observed when the was gas changed from 90%CO to 99%CO. XRD results showed that $La_{0.60}Sr_{0.40}FeO_3$ decomposed in the 99% CO atmosphere. The consistence results between TGA and neutron diffraction confirmed that the quenching experiment could be used to study the ferrites under reducing conditions.

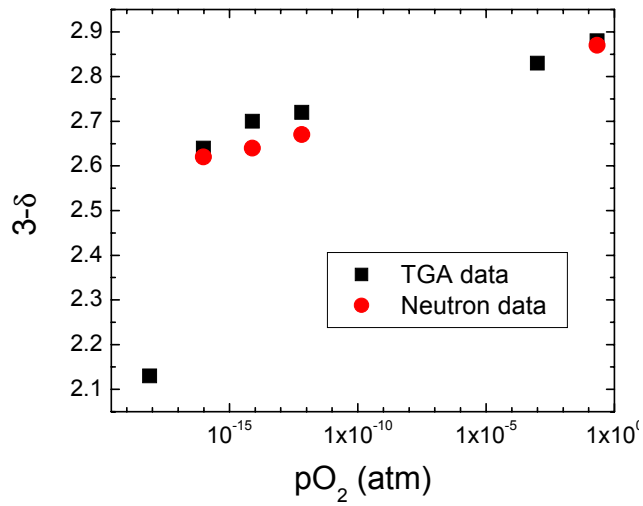

Figure 4. Oxygen vacancy levels in $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ determined from TGA and neutron diffraction at various oxygen activities

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References:

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(4) Kröger, F. A., The Chemistry of Imperfect Crystals, John Wiley and Sons: New York, 1962.