THE FORMATION OF TWO DISTINCT REACTION LAYERS BETWEEN TZ3Y ELECTROLYTE AND LSM

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ABSTRACT

The interfacial reactions between porous \((La_{0.8}Sr_{0.2})MnO_3\) (LSM) film and 3 mol% yttria-zirconia (TZ3Y) substrate have been investigated. Two distinct reaction layers of products, fluorite-type cubic zirconia solid solution \(c-(Zr,Mn,La,Y)O_2\) and pyrochlore \((La,Sr)\_2(Zr,Y)\_2O_7\), were observed at the interface of LSM/TZ3Y after heat treatment in the temperature range 1300-1500 °C in air. The formation mechanism of the two reaction layers has been studied. It has been found that the dissolution of Mn ions in TZ3Y caused the formation of the fluorite-type zirconia solid solution, while the interaction of La ions with TZ3Y resulted in the formation of the pyrochlore phase. The phase relations in the \((ZrY)O_2-La_2O_3-Mn_3O_4\) system have been studied and a ternary phase diagram of the system at the \((ZrY)O_2\)-rich end at 1400 °C in air is proposed based on the experimental results. The phase diagram showed that the fluorite-type zirconia solid solution phase \(c-(Zr,Mn,La,Y)O_2\), rather than the tetragonal TZ3Y, was in equilibrium with perovskite at high temperatures.

INTRODUCTION

Strontium-doped lanthanum manganese oxide, \((LaSr)MnO_3\) (LSM), and yttria stabilized or partially stabilized zirconia, \((Zr,Y)O_2\), are used as cathode and electrolyte materials respectively in a solid oxide fuel cell (SOFC) (1,2). Interactions between LSM and \((Zr,Y)O_2\), the yttria-stabilized zirconia (YSZ) in particular, have drawn great attention in recent years (3-6).

In our previous study on the interaction between strontium-doped praseodymium manganite (PSM) and partially stabilized 3 mol% yttria-zirconia (TZ3Y) (7), a fluorite-type phase of zirconia solid solution was detected between PSM and TZ3Y besides praseodymium zirconate. The formation of the fluorite-type cubic zirconia solid solution arose from the dissolution of Mn and Pr ions into the tetragonal TZ3Y. This observation has not been reported for the LSM/(Zr,Y)O_2 system so far. To confirm the existence of a fluorite-type zirconia solid solution layer as well as the pyrochlore layer in LSM/TZ3Y, and, more importantly, to understand the formation mechanism of the two reaction layers, the interactions between TZ3Y and thin porous films of LSM, lanthanum oxide and...
manganese oxide at the temperature range 1300-1500 °C in air, and the phase relations in the TZ3Y-La2O3-Mn3O4 system at the TZ3Y-rich end at 1400 °C in air were investigated in the current study.

**EXPERIMENTAL PROCEDURE**

The LSM powder with the composition (La0.8Sr0.2)MnO3 was prepared by wet chemical method and calcined at 1000 °C for 4 h in air. X-ray diffraction (XRD) pattern showed the powder to be a single perovskite phase. The TZ3Y substrate, 20 mm in diameter and 150 μm in thickness, was prepared from 3 mol% Y2O3-ZrO2 (Tosoh Corporation, Japan) by tape casting followed by sintering at 1500 °C. Powders of lanthanum oxide La2O3, calcined at 1000 °C for 2 h before use, and manganese oxide MnO2, of chemical grade, were used for solid state reaction.

The diffusion couples of LSM/TZ3Y, La2O3/TZ3Y and MnO2/TZ3Y were prepared by screen printing LSM, La2O3, MnO2 (ca. 40 μm thick) on the TZ3Y substrate respectively, and then heat-treated in the temperature range of 1300-1500 °C for various times. After heat treatments, the diffusion couples were carefully fractured and in some cases polished cross sections were prepared. To examine the surface of TZ3Y substrate at the interface, the films of perovskite, lanthanum oxide and manganese oxide were removed. The LSM film was pulled off easily from the substrate after heat treatment at temperatures up to 1400 °C. The La2O3 film became powdery two days after heat treatment due to hydration of La2O3 in air, which was wiped off easily using soft tissue. Mn3O4 was formed when MnO2 was heated at temperatures over 1000 °C (8), and was removed by dissolution in concentrated hydrochloric acid.

Powder experiments were carried out to investigate the phase relations in the system TZ3Y-La2O3-Mn3O4 at the TZ3Y-rich end at 1400 °C. The powders of TZ3Y with La2O3, MnO2 or with both of them at selected mole ratios were mixed and milled for 2 h. The powder mixtures were pressed into pellets and then heat-treated at 1400 °C for 24 h in air. The pellets were then ground to powders that were pressed into pellets again for another heat treatment at 1400 °C for 24 h to ensure complete reaction.

Scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDS) and XRD were used for microstructure and phase characterization.

**RESULTS**

**Reaction Products In Diffusion Couples**

The LSM/TZ3Y diffusion couples were heated at 1300, 1400 and 1500 °C for 4 h respectively. The LSM coating spalled off from the substrate after the heat treatment at 1300 and 1400 °C but adhered well to the substrate after 1500 °C. Fig. 1 (a) is an SEM micrograph taken from a fractured face of the specimen heat-treated at 1500 °C showing two distinct reaction layers marked “L1” and “L2” between LSM and TZ3Y. Fig. 1 (b)
Figure 1. (a) SEM micrograph of a fractured face of the specimen heat-treated at 1500 °C, and (b) the EDS spectra from (i) the first reaction layer, (ii) the upper part and (iii) the lower part of the second reaction layer. A portion of these spectra from 13 to 19 keV was expanded in Y-axis to show the K peaks of Sr and Y.
shows the EDS spectra collected from the first reaction layer “L1”–(i), and the upper part –(ii) and the lower part –(iii) of the second reaction layer “L2” respectively. A portion of these spectra from 13 to 19 keV was expanded in Y-axis to show the K peaks of Sr and Y. It can be seen from Fig. 2 that the first reaction layer “L1” contains primarily elements of Zr and La and a small amount of Sr and Y. XRD analysis confirmed the formation of a pyrochlore phase with a possible formula (La,Sr)2(Zr,Y)2O7. In the second reaction layer “L2” Mn and La were detected in addition to Zr and Y, the TZ3Y components. Mn and La ions appeared to have diffused into TZ3Y. It was confirmed from powder experiments, as shown in the following section, that the La and Mn ions have dissolved in the zirconia lattice forming a fluorite-type cubic zirconia solid solution (Zr,Mn,La,Y)O2. The La concentration decreases significantly from the upper part to the lower part of the zirconia solid solution layer, while Mn concentration varied only slightly across the second reaction layer. The two reaction layers, zirconia solid solution and pyrochlore, were also observed in the LSM/TZ3Y specimen heat-treated at 1300 and 1400 °C.

The diffusion/dissolution of Mn ions in TZ3Y was investigated by heating the MnO2/TZ3Y diffusion couple at 1300 °C for 24 h. After the heat treatment the substrate deformed slightly and became brittle. The SEM micrographs in Fig. 2 (a)–fractured face and (b)–polished cross section show a distinct reaction layer in the substrate next to Mn3O4 coating. Mn as well as Zr and Y was detected in the reaction layer. XRD analysis on the substrate surface after removal of Mn3O4 by acid treatment showed a fluorite-type zirconia solid solution phase, c-(Zr,Mn,Y)O2. From the backscattered electron image of the polished cross section in Fig. 2 (b), it can be seen that the substrate underneath the fluorite-type zirconia solid solution layer is a mixture of two types of materials. EDS analysis showed that the dark-contrast material had the same composition as that of the reaction layer, which contained a significant amount of Mn. The bright-contrast material contained relatively low levels of Mn and was probably t-(Zr,Mn,Y)O2.

Fig. 3 shows SEM micrographs of the surface of fluorite-type zirconia solid solution after removal of manganese oxide by acid–(a) and the surface of the TZ3Y before the reaction–(b) showing a completely different surface morphology of the zirconia substrate before and after the reaction with manganese oxide. Many small pores are observed on the grain surface of the cubic zirconia solid solution and the grain size is much larger than that of TZ3Y. Clearly Mn ions had dissolved in zirconia. The dissolution of Mn ions may have started from the grain boundary of TZ3Y, and hence the growth of the fluorite-type zirconia solid solution was more at the original TZ3Y grain boundary than in the center of the grain, which has resulted in many pores on the grain surface of fluorite-type zirconia solid solution. The results of the MnO2/TZ3Y diffusion test has proved that the dissolution of significant amount of Mn in TZ3Y has caused the formation of the fluorite-type zirconia solid solution and has completely changed the surface morphology of the substrate.

The diffusion/dissolution of La ions in TZ3Y was examined on the La2O3/TZ3Y specimen. The La2O3/TZ3Y diffusion couple was heated for 24 h at 1300 and 1400 °C respectively. In both cases a continuous pyrochlore layer was formed between La2O3 and TZ3Y. No other reaction layer was observed. La was not detected in TZ3Y underneath the pyrochlore layer. The results of this experiment have shown that the interaction of La
ions and TZ3Y resulted in the formation of lanthanum zirconate, but not the fluorite-type zirconia solid solution.

Figure 2. SEM micrographs of (a)—fractured face and (b)—polished cross section of the MnO2/TZ3Y diffusion couple after 24 h at 1300 °C showing a distinct reaction layer in the substrate next to the Mn3O4 coating and a mixture of probably two types of materials in the substrate underneath the fluorite-type zirconia solid solution.

The diffusion/dissolution of both Mn and La ions together in TZ3Y was studied by the following test. The La2O3/TZ3Y diffusion couple was heated at 1300 °C for 24 h to form the pyrochlore layer on the TZ3Y surface. The excess La2O3 was removed, and then a MnO2 coating was screen printed onto the pyrochlore layer. The triple layer specimen,
MnO₂/pyrochlore/TZ3Y, was heat-treated again at 1300 °C for 24 h. The SEM/EDS analysis of this specimen after heat treatment showed that the pyrochlore layer (ca. 1 µm thick) disappeared from the interface and the La ions originally in the pyrochlore phase have dissolved in the zirconia together with Mn ions. The results of this test showed that, when the amount of Mn ions is much more than that of La ions in the region of interface with TZ3Y, both Mn and La ions diffused and dissolved in TZ3Y resulting in the formation of the cubic zirconia solid solution; and the pyrochlore phase could not exist.

**Figure 3.** SEM micrographs of the surface of fluorite-type zirconia solid solution after removal of manganese oxide by acid—(a) and the surface of the TZ3Y before the reaction—(b) showing a completely different surface morphology of the zirconia substrate before and after the reaction with manganese oxide.
Powder experiments on a number of compositions were carried out. The compositions of the powder mixtures and the phases of the products after 48 h at 1400 °C are illustrated in Fig. 4, in which a ternary phase diagram of (ZrY)O$_2$–La$_2$O$_3$–Mn$_3$O$_4$ system ((ZrY)O$_2$ denotes TZ3Y in this case) at 1400 °C in air is proposed based on the results of the powder experiments. The data points of powder experiments are represented by “+” signs in the phase diagram. La$_3$MnO$_3$ is used for the formula of perovskite because of its non-stoichiometry on the A-site (9).

Two solid solution regions, c-(Zr,Mn,La,Y)O$_2$ and t-(Zr,Mn,La,Y)O$_2$, can be seen in Fig. 4. The solubility of Mn ions in tetragonal phase of zirconia is less than 3 mol%. The fluorite-type zirconia solid solution is formed when the Mn concentration in zirconia is more than 3 mol%. When the Mn concentration is more than ca. 10 mol%, the tetragonal solid solution disappears completely. Fig. 5 displays the XRD patterns of (a)–the tetragonal TZ3Y before the reaction and (b)–the reaction product of (TZ3Y)$_{0.85}$(MnO$_2$)$_{0.15}$. It can be seen that the reflections of the tetragonal zirconia phase have disappeared from the XRD trace of the product. All reflections of trace (b) in Fig. 5 belong to the phase of fluorite-type zirconia solid solution, c-(Zr,Mn,Y)O$_2$. Fig. 4 shows
that the solubility limit of Mn ions in the fluorite-type zirconia solid solution is about 24 mol%. The phase diagram also shows that La ions can be dissolved in zirconia only when a much higher concentration of Mn ions is in the solution. Between TZ3Y and La₂O₃ only pyrochlore phase is formed regardless of the initial compositions of the powder mixture.

Some important phase relations were drawn out from the phase diagram in Fig. 4, and are listed as follows: (1) TZ3Y and perovskite can not be in equilibrium with each other at 1400 °C in air; (2) The fluorite-type zirconia solid solution c-(Zr,Mn,La,Y)O₂ is in equilibrium with, respectively, pyrochlore phase, pyrochlore and perovskite, perovskite, and perovskite and manganese oxide with the increase of manganese oxide concentration; and (3) Mn₃O₄ and pyrochlore phase can not be in equilibrium with each other at 1400 °C in air.

![Figure 5. XRD patterns recorded from (a) the tetragonal TZ3Y powder and (b) the reaction product of (TZ3Y)₀.₈₅(MnO₂)₀.₁₅ showing that the tetragonal zirconia phase has disappeared completely after 48 h at 1400 °C and a fluorite-type cubic zirconia solid solution phase was formed.](image)

**DISCUSSION**

The interaction between tetragonal TZ3Y and perovskite at high temperatures has resulted in the formation of two distinct reaction layers, the fluorite-type cubic zirconia solid solution layer and the pyrochlore layer. This is different from the results of the interaction between cubic YSZ and perovskite that only one distinct reaction layer of pyrochlore phase was formed although the diffusion of Mn and La ions into zirconia occurred (6,10). Since YSZ was a fluorite-type phase by itself, the dissolution of Mn and

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La ions in its lattice had not given rise to a dramatic change in crystal structure and microstructure.

From the results of all the diffusion/dissolution tests, it is clear that the diffusion/dissolution of the Mn ions from LSM into TZ3Y is the cause for the formation of the fluorite-type cubic zirconia solid solution $c-(Zr,Mn,La,Y)O_2$ in LSM/TZ3Y, while the diffusion of La ions has caused the formation of the pyrochlore phase $(La,Sr)_2(Zr,Y)_2O_7$.

The powder experiments had not only confirmed the results obtained from the diffusion couple experiments, but also revealed the phase relations among the components involved in the interaction at the LSM/TZ3Y interface. With the phase relations drawn from the phase diagram, the driving force for the formation of the fluorite-type zirconia solid solution and the pyrochlore phase between LSM and TZ3Y can be well explained. The diffusion couple of stoichiometric LSM/TZ3Y is a non-equilibrium system at 1400 °C in air, which has the potential to change to the equilibrium state that is fluorite-type zirconia solid solution/pyrochlore/perovskite. Therefore Mn and La ions diffused through the interface and reacted with TZ3Y to form the pyrochlore phase and the fluorite-type zirconia solid solution. When a continuous layer of products was formed, the reactants LSM and TZ3Y were separated by the products, and the reaction slowed down significantly. At SOFC operating temperature range 900-1000 °C the diffusion of La and Mn ions from the perovskite to the TZ3Y is much slower than that at 1400 °C, and thus the equilibrium in the diffusion couple can hardly be reached.

When the concentration of Mn ions was much more than that of La ions in the region of interface with TZ3Y, the pyrochlore phase may not be formed, such as in MnO$_2$/pyrochlore/TZ3Y specimen. This is because pyrochlore phase could not be in equilibrium with Mn$_3$O$_4$ at high temperatures.

The effect of the formation of pyrochlore phase at the interface on the electrochemical performance is detrimental (11,12), and its formation should be avoided or at least delayed by using an A-site deficient perovskite (3). As for fluorite-type zirconia solid solution containing Mn and La ions, the phase diagram has shown that this phase would be formed eventually regardless of the stoichiometry of perovskite, although its formation may be delayed when the A-site deficiency of the perovskite is low, such as in Roosmalen and Cordfunke's experiments (13) in which the Mn diffusion was not detected. The formation of a significant layer of the fluorite-type zirconia solid solution has made the electrolyte relatively brittle, due to the low mechanical strength of cubic zirconia compared to tetragonal zirconia (1). The effect of this solid solution layer on the electrochemical performance is unknown at this stage. Nevertheless, the interaction between LSM and TZ3Y at SOFC operating temperature range 900-1000 °C in a short term is insignificant. Its effect on the performance of SOFC may become conspicuous after a long term operation.
CONCLUSIONS

Two distinct reaction layers, fluorite-type cubic zirconia solid solution and pyrochlore phase were formed at the interface of LSM/TZ3Y in temperature range 1300-1500 °C. The formation of the fluorite-type zirconia phase resulted mainly from the dissolution of Mn ions into TZ3Y, while the diffusion of La ions in TZ3Y caused the formation of the pyrochlore phase. The phase relations among the components involved at the LSM/TZ3Y interface showed that the tetragonal TZ3Y could not be in equilibrium with perovskite at high temperatures. It was the fluorite-type zirconia solid solution phase, c-(Zr,Mn,La,Y)O2, that could be in equilibrium with perovskite. It was predicted that the interaction between LSM and TZ3Y at SOFC operating temperature range 900-1000 °C in a short term is insignificant. The effect of the formation of the reaction layers on the performance of SOFC may become conspicuous after a long term operation.

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