ELECTROCHEMICAL PROPERTIES OF La$_{1-x}$Ca$_x$MnO$_{3-z}$ AS CATHODE IN SOFC

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ABSTRACT

The electrical and electrochemical properties of the perovskite type oxide, La$_{1-x}$Ca$_x$MnO$_{3-z}$, as cathode for solid oxide fuel cells (SOFC) were examined. The substitution of Ca for La sites increased conductivity with the Ca content up to $x=0.5$, and further substitution decreased the conductivity. The oxygen reduction catalytic activity increased with increasing the Ca content. No reaction product between 8 mole% yttria stabilized zirconia (8YSZ) and La$_{2-x}$Ca$_x$MnO$_{3-z}$ ($0.3<x<0.6$) was observed for annealing at 1200°C for 2h; La$_2$Zr$_2$O$_7$ was found for the couple of La$_{0.8}$Ca$_{0.2}$MnO$_{3-z}$ and 8YSZ, and CaZrO$_3$ and Mn$_3$O$_4$ for the couple of La$_{0.3}$Ca$_{0.7}$MnO$_{3-z}$ and 8YSZ. In the La$_{1-x}$Ca$_x$MnO$_3$ system, La$_{0.5}$Ca$_{0.5}$MnO$_{3-z}$ is considered to be the most adaptable electrode for SOFC, because of high electric conductivity, high catalytic activity for oxygen reduction, and good compatibility with 8YSZ.

INTRODUCTION

Solid oxide fuel cells based on stabilized zirconia operate at around 1000°C because of the limitation of the conductivity of the electrolyte(1). The high operating temperature poses many material problems. The most significant material limitations are imposed by the cathode and the cathode leads. The cathode material has to meet the following requirements: high electrical conductivity, thermal and chemical stability, compatibility with the electrolyte, and high catalytic activity for oxygen reduction. The perovskite type oxides, La$_{1-x}$A$_x$MO$_3$ (A=Sr, Ca, Ba; M=Cr, Mn, Fe, Co) have been extensively examined, because they satisfy above requirements with regard to electrical conductivity(2,3). Among them, strontium doped lanthanum manganites, La$_{1-x}$Sr$_x$MnO$_3$, have been reported to be the most promising because of their good chemical and thermal compatibility with yttria stabilized zirconia (YSZ) and their high catalytic activity for the reduction of oxygen(4–6). However, further study is necessary for the development of improved cell performance and, long-term stability. Recently, reaction between YSZ and La$_{1-x}$Sr$_x$MnO$_3$ at a high temperature has been reported(7). La$_{1-x}$Sr$_x$MnO$_3$ ($x=0$ – 0.2) reacted with YSZ to form a solid solution of cubic zirconia with La$_2$O$_3$ and/or MnO$_x$, and then the solid solution reacted with La$_{1-x}$Sr$_x$MnO$_3$ to form La$_2$Zr$_2$O$_7$. The reaction product, La$_2$Zr$_2$O$_7$, has poor oxide ion conductivity even at
1000°C and causes degradation of the catalytic activity for oxygen reduction. In this study, an alternative cathode material, calcium doped lanthanum manganite, \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3-z \) \((x=0 - 1.0)\), has been examined. We will report the electrical conductivity, electrochemical catalytic activity of oxygen reduction, reactivity with YSZ and thermal expansion property of the lanthanum manganites over a wide range of composition. The results are discussed in the scope of their application to SOFC.

**EXPERIMENTAL**

The oxides \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3-z \) \((x=0 - 1.0)\) were prepared from \( \text{La}_2\text{O}_3 \) (preheated at 1500°C for 1h) and \( \text{CaCO}_3 \) purchased from Nakarai Chemical Ltd., Japan, and \( \text{Mn}_2\text{O}_3 \) (analyzed as \( \text{Mn}_2\text{O}_3 \)) from Mitsuwa Chemicals Ltd., Japan. The mixtures of the starting materials were ground, pressed into pellets, and fired in air at 1300°C for 24h. Cubic stabilized zirconia with 8 mole% \( \text{Y}_2\text{O}_3 \) (8YSZ) was used as the electrolyte for electrochemical tests. The 8YSZ powder, purchased from Tosoh Ltd. Japan, was pressed into pellets (12 mm dia. x 1mm thick) under a pressure of 200 MPa, and sintered at 1400°C for 3h.

The electrical conductivity of the sintered oxides was measured in air by a four-terminal method, using direct current over a temperature range from room temperature to 1000°C. The oxide powder was pressed into pellets (4x1x14 mm³) under a pressure of 200 MPa and sintered at 1300°C for 24h in air. The current interruption technique was applied for the cathodic overpotential measurements to remove the IR-drop contribution. The steady-state residual voltage (overpotential) between the working and reference electrodes was measured under a constant drain. Two platinum-pasted electrodes (Englehard 6080) were applied on the one-side of the 8YSZ tablet; one electrode of about 0.7 cm² was used as a counter-electrode and the other with a small area as a reference electrode. The platinum mesh with platinum lead was used as the current corrector, which was pressed on the electrodes by the ceramic tube. The \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3-z \) thin film working electrodes (0.3μm - 7.0μm thick) were prepared on the other side of 8YSZ tablet by RF-sputtering technique. A ULVAC-1140 RF-sputtering system was used for the film deposition. The powdered \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3-z \) target was used as the cathode. Film thickness was calculated from the weight gain and the theoretical density of the oxides. The value was in good agreement with that estimated from scanning electron microscopy (SEM) pictures. The polarization experiments were carried out in open air.

The measurements of the thermal expansion properties were conducted from room temperature to 1000°C on sintered rods (3x3x40 mm³) of \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3-z \) using a Shinku–Riko DL-7000Y-RH dilatometer. The heating rate was fixed at 200°C/h. For comparison, measurements were also carried out on a sintered YSZ rod.
RESULTS AND DISCUSSION

The X-ray diffraction patterns of the La$_{1-x}$Ca$_x$MnO$_3$-$z$ system showed that La$_{0.8}$Ca$_{0.2}$MnO$_3$-$z$ had an orthorhombic cell and this orthorhombic distortion decreased on further substitution of Ca for La. These results are in good agreement with those by Wollan and Koehler(8) and Yakel(9). The lattice parameters of the cubic cell decreased linearly with the content of Ca. This decrease in the lattice parameter may result from the smaller size of Ca$^{2+}$(1.26Å) compared La$^{3+}$(1.36Å) and/or the oxidation of Mn$^{3+}$ to Mn$^{4+}$ as well as the formation of oxide ion vacancies by substitution of Ca$^{2+}$ for La$^{3+}$. The oxygen content in La$_{1-x}$Ca$_x$MnO$_3$-$z$ was determined by the measurement of the oxidation state of manganese by iodometry. In Fig. 1, the oxygen contents, 3-$z$, are shown as a function of x. It is difficult to obtain LaMnO$_3$ with the ideal composition. By firing at 1330°C in nitrogen containing about 1% oxygen, 3-$z$ in LaMnO$_3$-$z$ was reported to be about 3.10(10). The oxygen content in La$_{1-x}$Ca$_x$MnO$_3$-$z$ decreases with increasing x up to 0.5, and then keeps a constant value. By substitution of Ca$^{2+}$ for La$^{3+}$ up to 50 mole%, the charge neutrality was maintained by the formation of oxygen vacancy and the oxidation of Mn$^{3+}$ to Mn$^{4+}$, and by the further substitution mainly by the oxidation of Mn$^{3+}$. The weight change of the samples was measured with the help of thermogravimetric analysis from room temperature to 1200°C in air. No weight change was observed for La$_{1-x}$Ca$_x$MnO$_3$-$z$ with x=0 to 0.7. The result suggests that the oxygen content in La$_{1-x}$Ca$_x$MnO$_3$-$z$ shown in Fig. 1 corresponds to that at 1000°C. The high Ca-doped lanthanum manganites such as La$_{0.8}$Ca$_{0.2}$MnO$_3$-$z$ showed a weight loss at 1000°C.

The electrical conductivity of La$_{1-x}$Ca$_x$MnO$_3$-$z$ was measured in air over a temperature range 25 to 1000°C. The results are shown in Fig. 2. The electrical conductivity of La$_{1-x}$Ca$_x$MnO$_3$-$z$ with the low content of Ca increases rapidly with increasing temperature, and at temperatures above 700°C, the conductivity becomes nearly constant with temperature. However, the electrical conductivity shows a transition from positive to negative temperature dependence as the Ca content is increased to 60 mole%. This suggests a semiconductivity to metallic transition. Similar results were also found for La$_{1-x}$Sr$_x$MnO$_3$-$z$(11, 12). The electrical conductivity at 1000°C increases with increasing the Ca content up to 50 mole% and then decreases with further increase. The maximum conductivity at 1000°C was found to be 90 S/cm for La$_{0.5}$Ca$_{0.5}$MnO$_3$-$z$.

Fig. 3 shows a top view of the surface of the sputtered La$_{1-x}$Ca$_x$MnO$_3$ on 8YSZ, where the sputtered films were sintered at 1100°C for 2h. The particle sizes of the sintered films are less than 1 μm and no significant change of the morphology with the Ca content is observed. The XRD patterns of the sputtered films showed the single phase with perovskite type structure, which were exactly same to those of the target materials. The oxygen reduction catalytic activity on the sputtered La$_{1-x}$Ca$_x$MnO$_3$-$z$ electrodes was examined at 1000°C in air. The cathodic overpotential curves showed...
the dependence on the electrode thickness. The lowest overpotential was found for the electrode with around 1.5 μm thickness. Similar result was reported for the sputtered LaCoO3 film, where the overpotential minimum was observed for the electrode with 2.0 μm thickness.(13). In Fig. 4, the cathodic polarization curves for the sputtered La1-xCa2MnO3-δ electrodes at 1000°C are shown as a function of the content of Ca, where the thickness of the electrodes was around 1.5 μm. The overpotentials decrease with increasing the Ca content in the oxide. Takeda et al. also observed the dependence of the Sr content in La1-xSr2CoO3. In this system, the lowest overpotential for oxygen reduction was found for the La0.3Sr0.7CoO3 electrode.(14). Similar results were also observed for La1-xSr2MnO3. The oxygen reduction activity increased as the content of strontium increased, and a correlation between the electrochemical activity and the conductivity of the electrode was proposed.(15). In the La1-xCa2MnO3-δ system, however, the electrode showing the highest electrochemical activity does not have the highest electrical conductivity. As shown in Fig. 1, the oxygen content decreased with the Ca content up to 50 mole%. Therefore, the oxygen reduction activity of La1-xCa2MnO3-δ is correlated with the amounts of the oxide ion vacancy and also Mn4+. The oxygen reduction mechanism on La1-xCa2MnO3-δ was examined. The relation between the electrode resistance, Re1, and oxygen partial pressure, PO2, was determined. The slope of the logRe1 vs. logPO2 curves was around 1/4 in a temperature range 1000 to 800°C for the La0.5Ca0.5MnO3. This value suggested that the rate determining step for oxygen reduction could be considered to be the charge transfer process rather than the decomposition, adsorption, or mass transport process.

The dependence of the sintering temperature of the sputtered electrodes was examined. The electrode sintered at 1200°C for 2h showed a degradation in the catalytic activity for oxygen reduction, especially the La0.3Ca0.7MnO3-δ electrode, which showed the highest activity. The perovskite oxides La1-xAxMO3(A=Ca, Sr; M=Cr, Mn, Fe, Co) are known to react with YSZ at high temperatures to form La2Zr2O7, SrZrO3 or CaZrO3.(13, 16). The sputtered La1-xCa2MnO3-δ films on YSZ were heated at 1200°C for 2h. The XRD patterns of the heated films are shown in Fig. 5. The film with the low content of Ca such as 20 mole% shows the diffractions of La2Zr2O7, and that with the high content of Ca such as 70 mole%, reacts with YSZ to form CaZrO3 and Mn3O4. The degradation of the catalytic activity for the La0.3Ca0.7MnO3-δ electrode sintered at 1200°C may be due to the formation of the low conductivity phase of CaZrO3.

The thermal expansion compatibility of La1-xCa2MnO3-δ with YSZ is required in order to avoid stresses at the interface. In Fig. 6, the relative thermal expansions of different compositions are shown along with that of YSZ. The average thermal expansion coefficient of YSZ(room temperature to 1000°C) is about 9.77x10^-6K^-1, a value which is comparable to those reported.(17). The thermal expansion coefficients of La1-xCa2MnO3-δ increased with the degree of substitution of Ca for La. The expansion characteristics of the weakly Ca–doped oxides are very close to those of YSZ. The average thermal expansion coefficients for La0.8Ca0.2MnO3-δ and La0.4Ca0.6MnO3-δ are...
calculated to be $9.92 \times 10^{-6} \text{K}^{-1}$ and $11.84 \times 10^{-6} \text{K}^{-1}$, respectively, in the temperature range from room temperature to 1000°C. No fundamental data concerning the thermal expansion has been reported, except that of $\text{La}_{0.45}\text{Ca}_{0.45}\text{MnO}_3$ was reported to be $11.4 \times 10^{-6} \text{K}^{-1}$ by Macker et al.\(17\). The present common cathode material in SOFC is $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$. This material has a thermal expansion coefficient of about $12 \times 10^{-6} \text{K}^{-1}$\(17, 18\). Ca–doped $\text{LaMnO}_3$ exhibited almost the same thermal expansion behavior to that of Sr–doped samples. The difference of thermal expansion coefficient between YSZ and doped $\text{LaMnO}_3$ does not appear to be a problem, probably due to the porosity of the cathode.

**CONCLUSIONS**

The Ca–doped lanthanum manganite shows excellent oxygen reduction catalytic activity, high electrical conductivity and good chemical stability and the thermal expansion compatibility with the yttria doped zirconia electrolyte. These properties depend on the degree of the amount of Ca. It is concluded from our results that $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_{3-x}$ is the best candidate for the cathode in SOFC.

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Fig. 1  Oxygen content of La$_{1-x}$Ca$_x$MnO$_{3-z}$

Fig. 2  Temperature dependence of electrical conductivity for La$_{1-x}$Ca$_x$MnO$_{3-z}$
Fig. 3 SEM photographs of the La$_{1-x}$Ca$_x$MnO$_3$ electrodes (about 1 μm thick) sintered at 1100°C for 2h.

Fig. 4 Cathodic polarization curves for the La$_{1-x}$Ca$_x$MnO$_3$ electrodes at 1000°C in air (sintered at 1100°C)
Fig. 5 XRD patterns of the La$_{1-x}$Ca$_x$MnO$_{3-z}$ electrodes (about 1 μm thick) sintered at 1200°C.

![XRD pattern](image)

Fig. 6 Thermal expansion of La$_{1-x}$Ca$_x$MnO$_{3-z}$ and YSZ

![Thermal expansion graph](image)