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Electrochemical performance of $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag composite cathodes in intermediate temperature solid oxide fuel cells

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Abstract

The electrochemical performances of $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag composite cathodes have been investigated in intermediate temperature solid oxide fuel cells. The $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag cathodes prepared by ball milling followed by firing at 920 °C show the maximum performance (power density: 0.15 W cm^{-2} at 800 °C) at 3 wt.% Ag. On the other hand, the $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag composite cathodes with 0.1 mg cm⁻² (~0.5 wt.%) Ag that were prepared by an impregnation of Ag into $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag composite cathodes with 0.1 mg cm⁻² (~0.5 wt.%) Ag that were prepared by an impregnation of Ag into $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ followed by firing at 700 °C (but the electrolyte– $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ assembly was prepared first by firing at 1100 °C) exhibit much better performance (power density: 0.27 W cm⁻² at 800 °C) than the composite cathodes prepared by ball milling, despite a much smaller amount of Ag due to a better dispersion and an enhanced adhesion. AC impedance analysis indicates that the Ag catalysts dispersed in the porous $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ cathode reduce the ohmic and the polarization resistances due to an increased electronic conductivity and enhanced electrocatalytic activity. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

There has been considerable effort in recent years to reduce the operating temperature of solid oxide fuel cells (SOFC) to an intermediate range of 500-800 °C [1]. However, the reduced operating temperature leads to a decrease in the catalytic activity of the cathode for the oxygen reduction reaction [2]. For example, the currently used $La_{1-x}Sr_xMnO_3$ perovskite cathode does not provide adequate catalytic activity at the targeted intermediate temperatures due to its poor oxide ion conductivity [3,4]. In this regard, the Sr-doped lanthanum cobaltite ($La_{1-x}Sr_xCoO_{3-\delta}$) has been investigated as an alternative due to its high electronic and oxide ion conductivities [5,6], but it suffers from a large thermal expansion coefficient (TEC) and high chemical reactivity with the yttria-stabilized zirconia (YSZ) electrolyte [7,8]. With an aim to reduce the TEC, various strategies such as the replacement of La by other smaller lanthanides or the substitution of Co by Fe have been pursued [9-13]. For instance,

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we recently reported that the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} composition exhibits a smaller TEC (16.7 × 10⁻⁶ °C⁻¹) [14] than La_{0.6}Sr_{0.4}CoO_{3- δ} (21.3 × 10⁻⁶ °C⁻¹) [15] due to the substitution of both Nd for La and Fe for Co, but its electrocatalytic activity is lower than that of La_{0.6}Sr_{0.4}CoO_{3- δ} due to the reduced electronic and ionic conductivities [14].

It is well known that the addition of precious metals such as Pt into porous cathodes enhances the electrocatalytic activity [16-19]. Ag is also known to improve the electrocatalytic properties for the oxygen reduction reaction [20], and several oxide-Ag cermet cathodes have been found to show good electrochemical performance [21-24]. With an aim to improve the electrocatalytic activity of $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ while taking advantage of its lower TEC [14], we present here the fabrication and electrochemical performance of the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-δ}-Ag composite cathodes for the oxygen reduction reaction in intermediate temperature SOFC. The electrochemical performances of SOFC single cells having the composite cathodes that were prepared by a ball milling and an impregnation methods followed by firing at different temperatures are compared.

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2. Experimental

The Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} powder was synthesized by a coprecipitation method. Required amounts of Nd₂O₃, SrCO₃, Co(CH₃COO)₂·4H₂O, and Fe(CH₃COO)₂ were dissolved in dilute nitric acid and the metal ions were coprecipitated as carbonates and hydroxides by adding a mixture of KOH and K₂CO₃. The coprecipiate was washed with deionized water, dried, fired at 500 °C for 5 h, ground, and finally fired at 1200 °C for 24 h. The composite cathode powders were then prepared by ball milling the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} powders with various amounts of Ag₂O for 24 h using a zirconia ball medium. The particle sizes of Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} and Ag₂O after ball milling were, respectively, 0.3 and 0.5 µm as estimated from the line broadening of the X-ray diffraction peaks using the Scherrer equation [25]:

Particle size =
$$\frac{0.9\lambda}{FW \cdot \cos\theta}$$
 (1)

where λ is the wavelength of the incident radiation and FW is the full width at half maximum in radians. NiO–Ce_{0.9}Gd_{0.1}O_{1.95} (GDC) cermet (Ni:GDC = 70:30 vol%) anode was synthesized by the glycine-nitrate combustion method [26]. The La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8} (LSGM) electrolyte that has higher oxide ion conductivity than YSZ at intermediate temperatures was prepared by firing required amounts of La₂O₃, SrCO₃, Ga₂O₃, and MgO at 1100 °C for 5 h, followed by pelletizing and sintering at 1500 °C for 10 h.

The single cells for electrochemical evaluations were fabricated by screen printing the slurries prepared with the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-δ}-Ag₂O composite cathode powders prepared by ball milling or the NiO-GDC cermet anode powders and an organic binder (Heraeus V006) onto an 0.8 mm thick LSGM electrolyte pellet, followed by firing for 3h at 920 °C for the cathode and 1200 °C for the anode. The ball milled $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag₂O composite transformed to Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-δ}-Ag composite on firing at 920 °C. With an aim to have a better dispersion of the Ag particles, the $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ -Ag composite cathodes were also fabricated by an impregnation method. In this case, the porous $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ cathodes were first prepared by screen printing on to the LSGM electrolyte, followed by firing at 1100 °C for 3 h. The porous $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ cathodes were then impregnated with an aqueous AgNO3 solution, followed by firing at 700 $^\circ C$ for 3 h. The amount of Ag particles loaded in the impregnation method was $0.1\,\mathrm{mg\,cm^{-2}}$ (∼0.5 wt.%).

Microstructural characterizations were carried out with a Hitachi field emission scanning electron microscope (SEM). AC impedance analysis was carried out with a potentiostat having a frequency response analyzer using a three electrode configuration. Pt paste was used as both the counter and the reference electrodes. The detailed single cell configuration has been described elsewhere [27]. The geometrical area of the working and the counter electrodes was, respectively, 0.25 and 0.49 cm². The applied frequency was in the range of 0.5 mHz to 1 MHz with the voltage amplitude of 10 mV. Current–voltage

(I-V) measurements of the single cells were carried out also with the three electrode configuration, which allowed for separating and monitoring the cathode over-potentials during the cell operation. The test cell configuration was same as that used for the AC impedance measurement. The geometrical area of both the cathode and anode was 0.25 cm^2 . Pt paste was used as the reference electrode. Humidified H₂ (~3% H₂O at 30 °C) and air were supplied as fuel and oxidant, respectively, at a rate of $100 \text{ cm}^3 \text{ min}^{-1}$.

3. Results and discussion

The *I*–*V* curves and the over-potentials at 800 °C for the composite cathodes containing different amounts of Ag that were prepared by ball milling the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} powders with required amounts of Ag₂O are compared in Fig. 1. The open-circuit voltage value at 800 °C is typically about 1.1 V, which is close to the theoretical value. The cathode



Fig. 1. Electrochemical performance data at 800 °C of Nd_{0.6}Sr_{0.4}Co_{0.5} Fe_{0.5}O_{3- δ}-Ag/LSGM/Ni-GDC single cells with various amount of Ag incorporated into the cathode by ball milling followed by firing at 920 °C: variations of (a) the *I*-*V* curves and (b) cathode over-potential.



Fig. 2. Variations of the power density and cathode over-potential with Ag content at 0.24 A cm⁻² and 800 °C. The cathodes were fabricated by ball milling followed by firing at 920 °C as in Fig. 1.

with 3 wt.% Ag shows the best electrochemical performance. Fig. 2 shows the effect of Ag incorporation on the power density and over-potential at $0.24 \,\mathrm{A \, cm^{-2}}$. The power density increases with the Ag content, reaches a maximum at 3 wt.% Ag, and then decreases, with the over-potential correspondingly reaching a minimum at 3 wt.% Ag. The performance of the cathodes is strongly influenced by both the electronic and oxide ion conductivities of the electrode. The initial improvement in the electrochemical performance with Ag incorporation (up to $\sim 3 \text{ wt.}\%$) is due to an increase in the electronic conductivity and catalytic activity while maintaining adequate amount of reaction sites, e.g. the three-phase boundary (TPB), Air/Ag/Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}. However, with >3 wt.% Ag, the continuity of the oxide ion conducting paths within the $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ network may be interrupted by the Ag particle, which is not an oxide ion conductor, resulting in blocking of oxide ion conduction and consequent decrease in electrochemical performance despite an increase in the overall electronic conductivity.

Fig. 3 compares the AC impedance spectra recorded at 800 °C in air of the ball milled Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}-Ag cathodes containing various amount of Ag after firing at 920 °C. The ohmic resistance R_b (left intercept on Z_{re} axis), total resistance R_{tot} (right intercept on Z_{re} axis) and polarization resistance R_p ($R_{tot} - R_b$) at 800 °C in air that were calculated from the AC impedance spectra are given in Table 1. While the ohmic resistance decreases with increasing Ag content, the polarization resistance decreases significantly at 3 wt.% Ag and then

Table 1

The ohmic resistance R_b , total resistance R_{tot} , and polarization resistance R_p of the ball milled Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}-Ag composite cathodes at 800 °C in air

| Ag content (wt.%) | $R_{\rm b} (\Omega {\rm cm}^{-2})$ | $R_{\rm tot} (\Omega {\rm cm}^{-2})$ | $R_{\rm p} (\Omega {\rm cm}^{-2})$ |
|-------------------|--------------------------------------|--|--------------------------------------|
| 0 | 0.97 | 3.02 | 2.05 |
| 3 | 0.86 | 1.73 | 0.87 |
| 5 | 0.78 | 2.34 | 1.56 |



Fig. 3. Typical AC impedance spectra recorded at 800 °C in air of the ball milled Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}-Ag cathodes with various amount of Ag after firing at 920 °C for 3 h.

increases again at 5 wt.% Ag. This result is consistent with the single cell performance data in Figs. 1 and 2. The data suggest that the ohmic resistance decreases due to an increase in electronic conductivity and better adhesion with the addition of Ag, while the polarization resistance decreases first due to an increase in catalytic activity at 3 wt.% Ag, but increases then due to an interruption of the oxide ion conduction by the Ag particles at 5 wt.% Ag.

The main drawback with the above ball milled Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-δ}-Ag composite cathodes is a poor adhesion between the cathode and the LSGM electrolyte due to the low firing temperature (920 °C) employed, which is dictated by the melting point of Ag (961 °C). Impregnation is known to be an effective method to incorporate highly dispersed fine particles into porous electrode structures without interrupting the matrix network [28]. Fig. 4 compares the back-scattered SEM micrographs of the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathodes with and without Ag after firing at various temperatures for 3 h. The cathodes with and without Ag after firing at 920 °C (Fig. 4a and b) show only point contact between the particles and poor adhesion between the cathode and the electrolyte. On the other hand, the cathodes without Ag after firing at $1100 \,^{\circ}\text{C}$ (Fig. 4c) and the cathodes with impregnated Ag followed by firing at 700 °C (but the LSGM—Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} assembly was prepared first by firing at 1100 °C) (Fig. 4d) show good area contact and adhesion with the electrolyte with similar microstructures, suggesting that the impregnation of Ag does not affect the microstructure adversely. However, it was not possible to visualize the Ag particles in the impregnated cathode by SEM due to the very small amount of Ag (~ 0.5 wt.%). Uhlenbruck et al. [23] have also reported similar difficulties with the La_{0.65}Sr_{0.3}MnO₃-Ag composite system containing 1 wt.% Ag.

Fig. 5 compares the AC impedance spectra recorded at 800 °C in air of the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathodes without Ag after firing at 1100 °C and the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathodes after firing at 1100 °C for 3 h followed by impregnating



Fig. 4. Back-scattered SEM micrographs of the cathodes after firing at various temperatures for 3 h: (a) $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ without Ag (920 °C), (b) $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ with 3 wt.% Ag (920 °C), (c) $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ without Ag (1100 °C), and (d) $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ mipregnated with 0.1 mg cm⁻² Ag (1100 °C). The temperature in (d) refers to the firing of the LSGM— $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ assembly before impregnating Ag.

0.1 mg cm⁻² (~0.5 wt.%) of Ag and finally firing at 700 °C for 3 h. Both the ohmic and polarization resistances of the cathodes at 800 °C are reduced by the impregnation of Ag. The temperature dependences of the ohmic (R_b) and polarization (R_p) resistances are shown in Fig. 6. While the ohmic resistance of



Fig. 5. Typical AC impedance spectra recorded at 800° C in air of the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode without Ag after firing at 1100 °C for 3 h and the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode after firing at 1100 °C for 3 h followed by impregnating with 0.1 mg cm⁻² of Ag and finally firing at 700 °C for 3 h.

the cathode with Ag at any temperature is only slightly lower than that of the cathode without Ag, the polarization resistance is much lower than that of the cathode without Ag. Especially, the polarization resistance at 650 °C is reduced by about 40% with 0.5 wt.% impregnated Ag. This observation suggests that the Ag catalyst within the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode works more effectively at lower temperatures.

Fig. 7 shows the effect of the firing temperature and Ag impregnation on the electrochemical performance. The single cells with and without Ag cathode fired at 1100 °C show better electrochemical performance compared to those fired at 920 °C. The better performance of the former cathodes is due to the good area contact among the cathode particles as well as the good adhesion between the cathode and electrolyte, as seen in Fig. 4. More importantly, with the same firing temperature of 920 or 1100 °C, the cathodes impregnated with 0.1 mg cm^{-2} (~0.5 wt.%) Ag exhibit better electrochemical performance compared to those without Ag. The cathode impregnated with 0.1 mg cm⁻² (\sim 0.5 wt.%) Ag with a firing temperature of 1100 °C exhibits the highest performance with a power density of $0.27 \,\mathrm{W \, cm^{-2}}$ at 800 °C. This indicates that even a small amount of Ag dispersed in the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode could enhance the cell performance significantly without major microstructural changes. Based on the AC impedance analysis (Figs. 5 and 6), the reduction in the cathodic overpotential caused by Ag impregnation could be attributed possibly to the high catalytic activity of Ag rather than simply



Fig. 6. Temperature dependence of (a) ohmic (R_b) and (b) polarization (R_p) resistances of the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode without Ag after firing at 1100 °C for 3 h and the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode after firing at 1100 °C for 3 h followed by impregnating with 0.1 mg cm⁻² of Ag and finally firing at 700 °C for 3 h. The results were derived from the impedance data.

to the reduction in the ohmic resistance. It has been reported that nanosize Pt promotes surface reaction at the boundary between Pt and La(Sr)CoO₃ [19]. Also, Wang et al. [24] have reported that Ag coating improves the oxygen exchange reaction in the La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃-Ce_{0.8}Gd_{0.2}O_{1.9}-Ag cathode. Thus, the Ag catalyst presumably helps the surface exchange step (the dissociative adsorption of O₂ molecules to O_{ad} and/or the exchange reaction between the oxygen atoms (O_{ad}) and oxide ion vacancies in the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} lattice). Additionally, Ag can provide electrons readily through the cathode surface due to its high electronic conductivity. Therefore, with respect to surface exchange and charge transfer, the oxygen reduction reaction at the boundary of Air/Ag/Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} could be more effective than



Fig. 7. Electrochemical performance data at 800 °C of the single cells fabricated with Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- $\delta}$ cathodes with and without Ag after firing at 920 or 1100 °C for 3 h: variations of (a) the *I*–V curves (open symbols) and power density (closed symbols) and (b) cathode over-potentials. In the case of 1100 °C firing temperature with impregnated Ag, the LSGM—Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- $\delta}$ assembly was first fired at 1100 °C before impregnating Ag followed by firing at 700 °C for 3 h.}}

at the boundary of Air/Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}, and consequently the electrochemical performance is enhanced by the impregnation of Ag catalyst.

4. Conclusions

The Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ}-Ag composite cathodes containing ~0.5 wt.% impregnated Ag exhibit higher catalytic activity for the oxygen reduction reaction in intermediate temperature SOFC compared to the Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} cathode due to the increased electronic conductivity and electrocatalytic activity contributed by Ag. The incorporation of Ag into porous Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3- δ} offers the advantage of enhancing the catalytic activity while keeping the TEC low. The study demonstrates that cathodes prepared by impregnating the less expensive Ag may offer an attractive strategy to develop successful cathodes with a combination of low TEC and high electronic and ionic conductivities for intermediate temperature SOFC. However, further long-term stability investigation by operating over an extended period (>100 h) may be needed to verify the effect of Ag diffusion.

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