Self-Regeneration Pd-Perovskite Anode for SOFC

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A Pd doped perovskite $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.05}\text{Pd}_{0.05}\text{O}_3$ (LSCNP) was investigated as a candidate for a metal-free anode material of solid oxide fuel cell in comparison with $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (LSCN). The performance of anodes of LSCNP and LSCN with and without mixing Sm doped Ceria (SDC) was measured using H_2 and dry- CH_4 as fuel. The maximum current density of the cell in H_2 increased approximately twofold by the doping of Pd for the anode with or without SDC. The rate of the anodic reaction in H_2 was enhanced mainly by the catalytic activity of LSCNP and additionally by SDC. When dry- CH_4 was used as the fuel, the cell with LSCNP-SDC anode was the only cell which was able to perform power generation. Both the doping of Pd to the perovskite and the mixing of SDC contributed to the ability to operate SOFC in dry CH_4 . The anode reaction did not occur when SDC was not in the anode, indicating that the supply of oxide ion was the rate determining step. Pd, which is considered to deposit from LSCNP in reducing atmosphere, seemed to be the reaction site of the electrochemical methane oxidation since the reaction rate was low for LSCN-SDC. Although slight indication of carbon deposition was observed, Pd doped perovskite would be a good candidate for metal-free SOFC anode.

Introduction

Solid oxide fuel cell (SOFC) is recently attracting much attention for its high electrical efficiency and low environmental impact. The operating temperature of SOFC is as high as 700–1000°C. This high temperature enables SOFC to be operated by hydrocarbon-based fuel without using external fuel reformer. However, the high temperature would cause agglomeration of the particle and degradation of the electrode performance. Therefore, it is necessary to develop electrode material which would maintain stable microstructure at high temperature. The state of the art anode of SOFC is a cermet anode which is composed of Ni and yttria stabilized zirconia (YSZ). However, Ni tends to sinter easily at high temperature. Moreover, the volume of the particle changes when the Ni is oxidized and reduced, which would cause the cell to crack. Recently, Ni-free electrode is being studied to avoid these problems. Novel anode materials based on perovskite such as lanthanum chromite (Sfeir *et al.*, 2001) and strontium titanate (Pudmich *et al.*, 2000) has been de-

veloped. In the meantime, a Pd doped perovskite has been studied as a self-regeneration catalyst for automotive emissions control. It has been reported (Nishihata *et al.*, 2002) that $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$ had maintained its high dispersion of precious metals by the movement of Pd inside and outside the perovskite lattice due to the structural responses to the redox fluctuations in the exhaust gas composition with gasoline engine. In the present paper, Pd-doped perovskite $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y-z}\text{Ni}_y\text{Pd}_z\text{O}_3$ (LSCNP) has been studied as a candidate for SOFC anode.

1. Experimental

1.1 Powder Preparation

$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.05}\text{Pd}_{0.05}\text{O}_3$ (LSCNP) and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (LSCN) has been prepared using citric acid complex method. Nitrates of each metal, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Kanto Chemical Co., Inc.), $\text{Sr}(\text{NO}_3)_2$ (99.5%, Kanto Chemical Co., Inc.), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.99%, Kanto Chemical Co., Inc.), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Kanto Chemical Co., Inc.), and $\text{Pd}(\text{NO}_3)_2$ (99.9%, Kanto Chemical Co., Inc.) were dissolved in distilled water. Then an aqueous solution of citric acid solution was added dropwise to the mixture which was stirred and heated at 70°C on a hot plate with magnetic stirrer. The resulting solution was evaporated by heating on a hot plate until a resin was formed.

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Fig. 1 XRD spectra of LSCNP: (a) as prepared; (b) after reduction; (c) after re-oxidation treatment

The obtained resin was calcined with an electric furnace (KM-160, ADVANTEC MFS, INC.) at 200°C for 2 h, 500°C for 2 h, and 1000°C for 18 h. The powder was ground and mixed by an agate mortar and a pestle between each calcination process. The obtained oxide was characterized by X-ray powder diffraction.

1.2 Reduction

The powder of LSCNP was heated at 800°C in a reducing atmosphere of 10% hydrogen and 90% nitrogen. The powder before and after the reduction was observed by XRD to confirm the existence of particle deposition.

1.3 Cell Preparation

SOFC cell was prepared using Sm doped Ceria (SDC) disk as an electrolyte. LSCN, LSCNP, a composite of LSCN and SDC, or a composite of LSCNP and SDC (LSCNP or LSCN:SDC = 60:40 wt%) was used as an anode and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ was used as a cathode. Mixture of α -terpinol (99% Wako Pure Chemical Industries, Ltd.) and Ethyl Cellulose (Kanto Chemical Co., Inc.) (80:20 wt%) was used as a binder. Electrodes were prepared by doctor blade method. The electrode was painted in the size of 3 mm $\times$ 3 mm. It was dried at 100°C for 10 min, and was sintered at 1100°C for 4 h using an electric furnace (SUPER-BURN SL-1415C, Motoyama Co., Ltd.). After that, the cathode was prepared in the same manner and was sintered at 1050°C for 4 h. The performance of the anode was measured using hydrogen and then methane as fuel. After using methane as fuel, the cell was oxidized using oxygen, and the performance of the cell was measured using hydrogen again. In this manner, the effect of carbon deposition was investigated.

2. Results and Discussion

Figure 1 shows the XRD spectra of the LSCNP powder, as prepared, after the reduction treatment, and after the re-oxidation treatment. It can be seen that the pattern of the spectrum changed by reduction treatment and that it returned to the same spectrum by re-oxida-

Fig. 2 Terminal voltage vs. current density of the cells with anode of LSCN and LSCNP with and without SDC using H_2 as fuel at (a) 900, (b) 800, and (c) 700°C

tion treatment, indicating the movement of Pd inside and outside the perovskite lattice due to the structural responses to the redox treatment.

Performance of SOFC cells with LSCNP, LSCNP-SDC, LSCN and LSCN-SDC anode were measured. **Figure 2** shows the terminal voltage vs. current density of the cells with each anode material using H_2 as fuel at 900, 800 and 700°C, respectively. The maximum current density of LSCNP-SDC anode was the highest and was approximately 800 mA/cm^2 at 900°C. Comparing the performance of LSCNP and LSCN, it can be seen that the addition of Pd enhanced the anode reaction. The maximum current density increased approximately twofold by the doping of Pd for the anode with or without SDC. Mixing SDC also had an

Fig. 3 Temperature dependence of the interfacial resistance of the cell for each anode material using H_2 as fuel

enhancement effect on the performance. The rate of the anodic reaction in H_2 was mainly determined by the catalytic activity of the perovskite, and was additionally enhanced by SDC.

Interfacial resistance of the anode for each material was calculated from the anode polarization, which is the voltage between the working electrode and the reference electrode. The slope of the anode polarization near OCV represented the interfacial resistance. **Figure 3** shows the temperature dependence of the interfacial resistance of each anode. The slope of the interfacial resistance changed at 800°C except for LSCNP-SDC, indicating that the rate determining step of LSCNP-SDC is different from the other electrodes at 700°C .

The cells were then operated using dry CH_4 as fuel. In dry CH_4 , the cells showed lower performances compared to the cells operated in H_2 . For the cell with LSCN-SDC anode, the OCV was as low as 100 mV at 900°C , and was approximately zero at 700°C . Moreover, the OCV of the cells with LSCNP and LSCN anode was approximately zero even at 900°C . The cell with LSCNP-SDC anode showed OCV of ca. 700 mV, and was the only cell which was able to perform power generation test. **Figure 4** shows the terminal voltage vs. current density of the cell with LSCNP-SDC anode at 900°C using dry- CH_4 as fuel. The maximum current density was approximately 250 mA/cm^2 at 900°C .

These results indicate that both the doping of Pd to the perovskite and the mixing of SDC contributes to the ability to operate SOFC in dry CH_4 . A schematic image of the reaction of each anode is shown in **Figure 5**. The supply of oxide ion was the rate determining step, since the anode reaction did not occur when SDC was not in the anode. Pd, which is considered to deposit from LSCNP in reducing atmosphere, seemed to be the reaction site of the electrochemical methane oxidation. For LSCN anode, the reaction rate of the

Fig. 4 Terminal voltage vs. current density of the cell with LSCNP-SDC anode using CH_4 as fuel at various temperature

Fig. 5 Schematic image of the anodic reaction of LSCN and LSCNP with and without SDC

anodic reaction was low even when SDC was mixed in the anode, presumably since there was no reaction site. It had been reported by Sauvet and Irvine (2004) that LSCN shows catalytic activity for methane steam reforming. However, in our study, LSCN did not show sufficient activity for anodic reaction in dry- CH_4 . Therefore, the rate determining step of the electrochemical oxidation of dry- CH_4 is considered to be different with the reaction when steam exists in the anode atmosphere. LSCN did not exhibit catalytic activity for the initial oxidation reaction of dry- CH_4 . It was only when LSCNP was in the anode that the initial oxidation of CH_4 occurred, and presumably the produced H_2O enhanced the anodic reaction of CH_4 .

After using methane as fuel, the performance of the cell in H_2 was measured again. **Figure 6** shows the comparison of terminal voltage vs. current density of the cell with LSCNP-SDC anode in H_2 , before and after the operation in CH_4 . The change in the performance was negligible at 700 and 800°C . However, a slight decrease was observed at 900°C , indicating a

Fig. 6 Terminal voltage vs. current density of the cell with LSCNP-SDC anode in H_2 at various temperature, before (●) and after (○) the operation in CH_4

slight carbon deposition at high operating temperature. Further investigation in the rate determining step and the optimization of the electrode structure would make Pd doped perovskite a good candidate for metal-free SOFC anode.

Conclusions

A Pd doped perovskite LSCNP was investigated in comparison with LSCN as a metal-free anode material of solid oxide fuel cell. The performance of anodes of LSCNP and LSCN with and without mixing SDC was measured using H_2 and dry- CH_4 as fuel. The maximum current density of the cell in H_2 increased approximately twofold by the doping of Pd for the anode with or without SDC. The rate of the anodic reaction in H_2 was enhanced mainly by the catalytic activ-

ity of the perovskite and additionally by SDC. When dry- CH_4 was used as the fuel, the cell with LSCNP-SDC anode was the only cell which was able to perform power generation. Both the doping of Pd to the perovskite and the mixing of SDC contributed to the ability to operate SOFC in dry CH_4 . The anode reaction did not occur when SDC was not in the anode, indicating that the supply of oxide ion was the rate determining step. Pd, which is considered to deposit from LSCNP in reducing atmosphere, seemed to be the reaction site of the electrochemical methane oxidation since the reaction rate was low for LSCN-SDC. Although slight indication of carbon deposition was observed, Pd doped perovskite would be a good candidate for metal-free SOFC anode.

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