Self-Regeneration Pd-Perovskite Anode for SOFC

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A Pd doped perovskite La0.85Sr0.15Cr0.9Ni0.05Pd0.05O3 (LSCNP) was investigated as a candidate for a metal-free anode material of solid oxide fuel cell in comparison with La0.85Sr0.15Cr0.9Ni0.1O3 (LSCN). The performance of anodes of LSCNP and LSCN with and without mixing Sm doped Ceria (SDC) was measured using H2 and dry-CH4 as fuel. The maximum current density of the cell in H2 increased approximately twofold by the doping of Pd for the anode with or without SDC. The rate of the anodic reaction in H2 was enhanced mainly by the catalytic activity of LSCNP and additionally by SDC. When dry-CH4 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 CH4. 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) have been developed. 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 LaFe0.57Co0.38Pd0.05O3 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 La0.85Sr0.15Cr0.9Ni0.05Pd0.05O3 (LSCNP) has been studied as a candidate for SOFC anode.

1. Experimental

1.1 Powder Preparation

La0.85Sr0.15Cr0.9Ni0.05Pd0.05O3 (LSCNP) and La0.85Sr0.15Cr0.9Ni0.05O3 (LSCN) has been prepared using citric acid complex method. Nitrates of each metal, La(NO3)3·6H2O (99.99%, Kanto Chemical Co., Inc.), Sr(NO3)2 (99.5%, Kanto Chemical Co., Inc.), Cr(NO3)3·9H2O (99.99%, Kanto Chemical Co., Inc.), Ni(NO3)2 (99.5%, Kanto Chemical Co., Inc.), and Pd(NO3)2 (99.9%, Kanto Chemical Co., Inc.) were dissolved in distilled water. Then an aqueous solution of citric acid 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.
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 Sm0.5Sr0.5CoO3 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 × 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-oxidation 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 H2 as fuel at (a) 900, (b) 800, and (c) 700°C.
enhancement effect on the performance. The rate of the anodic reaction in H₂ 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 CH₄ as fuel. In dry CH₄, the cells showed lower performances compared to the cells operated in H₂. 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-CH₄ as fuel. The maximum current density was approximately 250 mA/cm² 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 CH₄. 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 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-CH₄. Therefore, the rate determining step of the electrochemical oxidation of dry-CH₄ 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-CH₄. It was only when LSCNP was in the anode that the initial oxidation of CH₄ occurred, and presumably the produced H₂O enhanced the anodic reaction of CH₄.

After using methane as fuel, the performance of the cell in H₂ was measured again. Figure 6 shows the comparison of terminal voltage vs. current density of the cell with LSCNP-SDC anode in H₂, before and after the operation in CH₄. The change in the performance was negligible at 700 and 800°C. However, a slight decrease was observed at 900°C, indicating a
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 H₂ and dry-CH₄ as fuel. The maximum current density of the cell in H₂ increased approximately twofold by the doping of Pd for the anode with or without SDC. The rate of the anodic reaction in H₂ was enhanced mainly by the catalytic activity of the perovskite and additionally by SDC. When dry-CH₄ 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 CH₄. 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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Literature Cited