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Electrocatalytic performances of Ni/SDC anodes fabricated with EPD techniques for direct oxidation of CH_4 in solid oxide fuel cells

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ABSTRACT

The electrochemical performances and the morphologies of Ni/SDC anodes fabricated by EPD technique were investigated for direct oxidation of dry CH_4 in solid oxide fuel cells (SOFCs). Ni/SDC(EPD) anode with both 20 wt% of Ni content and 20 μm of thickness exhibited the lowest overpotential and the highest maximum power density for dry CH_4–air SOFC at 973 K. The power density of the cell with Ni/SDC(EPD) anode was higher than that with Ni/SDC fabricated by a conventional slurry coating method. It was found that Ni/SDC(EPD) anode having dense structure suppressed carbon deposition and exhibited a stable cell operation in SOFC using dry CH_4.

1. Introduction

Solid oxide fuel cell (SOFC) offers good fuel flexibility, allowing a variety of hydrocarbon fuels to be utilized. Due to its high operating temperature, the internal reforming process of hydrocarbon fuels with H_2O or CO_2 proceeds on the anode of SOFC [1–3]. Recently, the direct oxidation of hydrocarbons with oxygen ions transporting from the cathode side to the anode side has been reported [4,5]. Among SOFCs using the hydrocarbon fuels, direct oxidation of dry CH_4 over composite anode in SOFCs has attracted much attention because natural gas is available.

In order to realize direct oxidation of dry CH_4 in SOFCs, much effort has been devoted to developing functional anodes with high electrocatalytic performances. For example, it is demonstrated that SOFCs with Ni-based anodes such as Ni/CeO_2–Sm_2O_3(Ni/SDC) [6,7] and Ru–Ni/CeO_2–Gd_2O_3 [8] can be operated with dry CH_4 fuel. However, the serious problem that the coke was formed on Ni-cermet anode still remains for direct oxidation of dry CH_4 in SOFCs. The coke formation often gives the damage of electrocatalytic performance of anodes. Therefore, the development of anode suppressing coke formation is required.

The electrocatalytic performances of Ni/SDC anode has been reported to depend on the microstructure of anode. Wang et al. [6] studied Ni/SDC anodes for direct oxidation of CH_4 in SOFCs and they claimed that the optimized distribution and connection between Ni–Ni, SDC–SDC, and Ni–SDC particles in anodes are important factors to obtain high performance of fuel cell. Suzuki et al. [9] reported that low overpotential of Ni/SDC was achieved by depositing fine Ni particles on SDC support. Here we wish to report the electrochemical performances of Ni/SDC anodes fabricated by the electrophoretic deposition (EPD) techniques for direct oxidation of dry CH_4 in SOFCs. This technique has been reported to be applicable to the fabrication of electrolyte film [10]; however, little is known about the application to electrode fabrication.

2. Experimental methods

Scandium-stabilized zirconia (ScCSZ) powder with the composition $(ZrO_2)_{0.81}(CeO_2)_{0.01}(ScO_{1.5})_{0.18}$ was supplied from Daiichi Kigenso Kagaku Kogyo Co., Ltd. ScCSZ powder was pressed at 14.7 MPa and sintered at 1773 K for 10 h to yield the electrolyte pellet with 8 mm in diameter and 2.5 mm in thickness.

SDC support ($(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$) was prepared by the co-precipitation method reported previously [7]. The mixed cerium and samarium hydroxides were obtained by the addition of ammonia solution to the mixed aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Wako, 98.0% pure) and $Sm(NO_3)_3 \cdot nH_2O$ (Wako, >99% pure). The mixed hydroxides were calcined at 623 K for 4 h to yield SDC powder. The other supports, LDC ($(CeO_2)_{0.8}(LaO_{1.5})_{0.2}$) and CeO_2, were prepared by the similar procedure. X-ray powder diffraction (XRD) analysis using a Rigaku RINT2200HF diffractometer with Cu Kα radiation demonstrated that SDC, LDC, and CeO_2 supports possessed a single fluorite structure.

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NiO was supported on CeO_2-based oxides by the impregnation method with the $Ni(NO_3)_2 \cdot 6H_2O$ (Wako, >99% pure) solution, followed by the calcination at 973 K for 10 h. Supported NiO samples were deposited on one surface of electrolyte by EPD technique as follows [11]. The supported NiO samples after ball-milling for 24 h were added to acetylacetone containing I_2 as a charging agent and sonicated for 30 min. A constant voltage of 30–50 V was applied for 3–6 min between stainless electrode and electrolyte with carbon-coated surface. The thickness of electrode was controlled by changing voltage and time. As a reference, supported NiO anode was fabricated by a slurry coating (SC) technique [7]. The anodes fabricated by both techniques were finally heat-treated at 1173–1473 K. Prior to electrochemical measurement, the supported NiO anode was reduced by H_2 at 973 K to yield metallic Ni. The obtained anode is abbreviated as Ni(20)/SDC(EPD) [Ni(Ni content/wt%)/support (fabrication technique)], here-in-after.

The following dry CH_4–air fuel cell was used to evaluate the electrochemical performances (*I–P* characteristics and anodic overpotential) at 973 K:

$$CH_4(P_{CH_4} = 1.0\,\text{atm}), \text{anode}|\text{ScCSZ}|\text{Pt}, \text{air}(P_{O_2} = 0.21\,\text{atm})$$

CH_4 was supplied to the anode compartment at a flow rate of $50\ cm^3\ min^{-1}$, while air was supplied to the cathode compartment with a flow rate of $50\ cm^3\ min^{-1}$. In order to evaluate the power density and the anodic overpotential in a steady state, their measurements were carried out after the operation of dry CH_4–air SOFC at $0.01\ mA\ cm^{-2}$ of current density for 24 h to avoid the unexpected initial change in anodic performance [12,13], unless otherwise stated. Details of the construction of SOFC and the current interruption method for measuring anodic overpotential were reported elsewhere [14]. The amount of carbon deposited on anode during cell operation was determined by subtracting a weight of cell before operation from that after operation of dry CH_4–air SOFC.

3. Results and discussion

3.1. Electrochemical performances of dry CH_4–air SOFC with Ni/SDC(EPD) anode

The electrochemical performances of SOFC with Ni/SDC(EPD) anodes were investigated as functions of Ni content, heat-treatment temperature, kind of support material, and thickness of electrode. The effects of Ni content in Ni/SDC(EPD) anode on power density and anodic overpotential of SOFC are shown in Fig. 1(A) and (B), respectively. The maximum power density of *ca.* $28\ mW\ cm^{-2}$ for Ni(20)/SDC(EPD) anode was larger than those for Ni(10)/SDC(EPD) and Ni(40)/SDC(EPD) anodes. The anodic overpotential of Ni/SDC(EPD) decreased with Ni content, reached a minimal value at 20 wt%, and increased with further increasing Ni content. A similar dependence of Ni content on anodic overpotential was reported for Ni/SDC(SC) anodes [7]. Note that Ni content giving the lowest overpotential for Ni/SDC anode was smaller than that for Ni/YSZ cermet electrode (40–60 wt% of Ni content) [6]. This is due to the fact that SDC shows the mixed ion conductivity under a reducing atmosphere, that is, the formation of Ni network for electron migration is not necessary for Ni/SDC electrode.

Fig. 2(A) and (B) show the power density and anodic overpotential of SOFC, respectively, with Ni(20)/SDC(EPD) anodes heat-treated at the different temperatures. Although the maximum power density of Ni(20)/SDC(EPD) heat-treated at 1173 K was higher than that heat-treated at 1473 K, no or less change in anodic overpotential was observed between them. This result suggests that the ohmic resistance of anode rather than anodic overpotential is influenced by heat-treatment. Zhang et al. [15] reported that the anodic overpotential of Ni(50)/SDC fabricated by a screen printing method increased with increasing the heat-treatment temperature due to the decrement of the triple phase boundary by sintering. Taking above report into consideration, Ni(20)/SDC(EPD) anodes were found to have high thermal stability for anodic overpotential.

We have reported that the overpotentials of Ni(20)/$(CeO_2)_{0.8}(LnO_{1.5})_{0.2}$ (Ln = La, Pr, Nd, Sm, Gd, Yb, and none) anodes fabricated by SC method were strongly influenced by the kind of support [7]. Therefore, the influence of support material of Ni-anodes fabricated by EPD was examined. Fig. 3 shows the power density and the anodic overpotential of the cell with Ni(20)/SDC(EPD), Ni(20)/LDC(EPD), and Ni(20)/CeO_2(EPD) anodes. The maximum power density decreased in the order of Ni(20)/SDC(EPD) > Ni(20)/CeO_2(EPD) > Ni(20)/LDC(EPD). On the other hand, the anodic overpotential was less dependent on the kind of support material. Thus, the difference in the maximum power density may originate from that in the conductivity of support, as pointed out previously [7].

The influence of thickness of Ni(20)/SDC(EPD) anode heat-treated at 1173 K on electrochemical performances of dry CH_4–air SOFC is illustrated in Fig. 4. Ni(20)/SDC(EPD) anodes with 9, 20, and

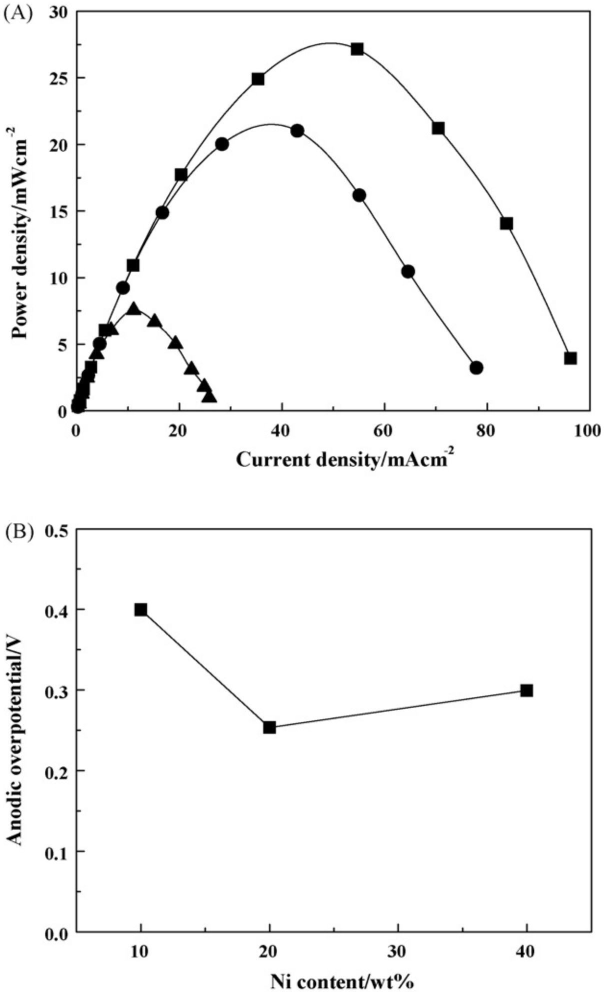

Fig. 1. (A) Power density and (B) anodic overpotential of SOFC with (▲) Ni(10)/SDC(EPD), (■) Ni(20)/SDC(EPD), and (●) Ni(40)/SDC(EPD) anodes heat-treated at 1173 K. The applied voltage and time of EPD method were 30 V and 3 min, respectively. The anodic overpotential was measured at $0.01\ A\ cm^{-2}$.

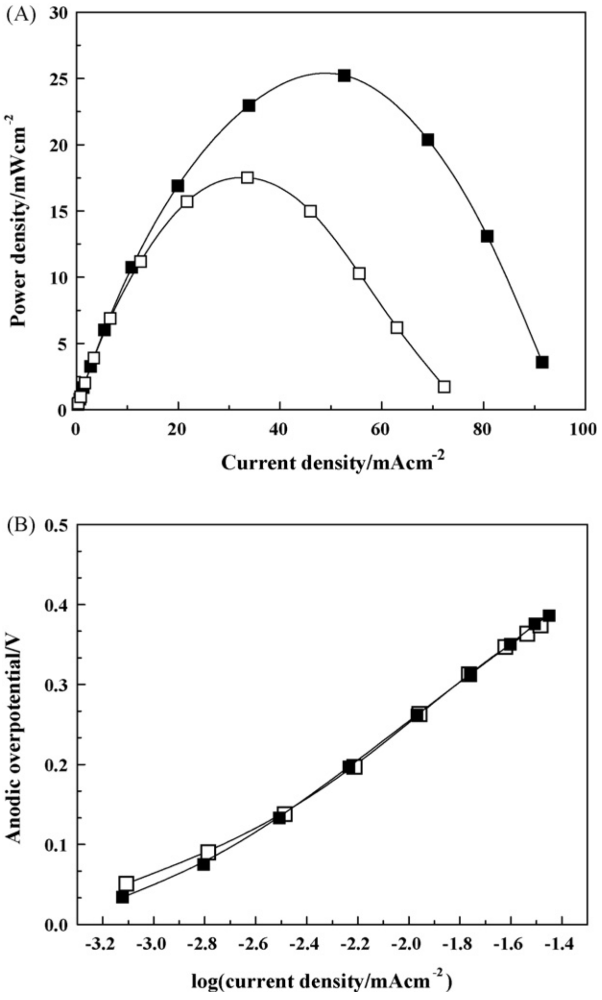

Fig. 2. (A) Power density and (B) anodic overpotential of SOFC with Ni(20)/SDC(EPD) anode heat-treated at (■) 1173 and (□)1473 K. The applied voltage and time of EPD method were 30 V and 3 min, respectively.

36 μm in thickness were obtained by applying 30 V for 3 min, 50 V 3 min, and 50 V 6 min, respectively, in EPD process, and the thickness was determined by SEM measurement. The power density of SOFC with Ni(20)/SDC(EPD) anode with 20 μm in thickness was higher than that with Ni(20)/SDC(EPD) anode with 9 μm in thickness. This may be due to an increase in the number of catalytically active Ni site and/or a decrease in the ohmic resistance of anode with increasing thickness. The former assumption was supported by the fact that the anodic overpotential of Ni(20)/SDC(EPD) anode with 20 μm in thickness was lower than that of Ni(20)/SDC(EPD) anode with 9 μm in thickness, as shown in Fig. 4(B). It should be noted that the usage of thicker anode resulted in the decrease in the power density. This cannot be explained by the reason mentioned above. In a separate experimental, we measured the amounts of carbon formed on Ni(20)/SDC anodes with different thickness after the operation of SOFC with outer load (1 kΩ) at 973 K for 6 h. The results are summarized in Table 1 together with the total amount of O^{2-} supplied from cathode to anode for the same time. When the amount of O^{2-} supplied was unified to be *ca.* 1.0×10^{-5} mol, the amount of carbon deposition increased with increasing thickness of anode; especially a remarkable increment of amount of carbon formed was observed for Ni(20)/SDC(EPD) anode with 36 μm in thickness. Therefore, it is considered that the decrease in power density of Ni(20)/SDC(EPD) anode with 36 μm in thickness anode is related with an increase in amount of carbon deposition. In order to sustain the electrocatalytic activity and stability of anodes in fuel cells, sufficient O^{2-} supply rate from the cathode is required to oxidize CH_4 fuel completely [13]. In other words, the insufficient O^{2-} supply rate of thick anodes may result in the carbon deposition, which would deactivate the cells.

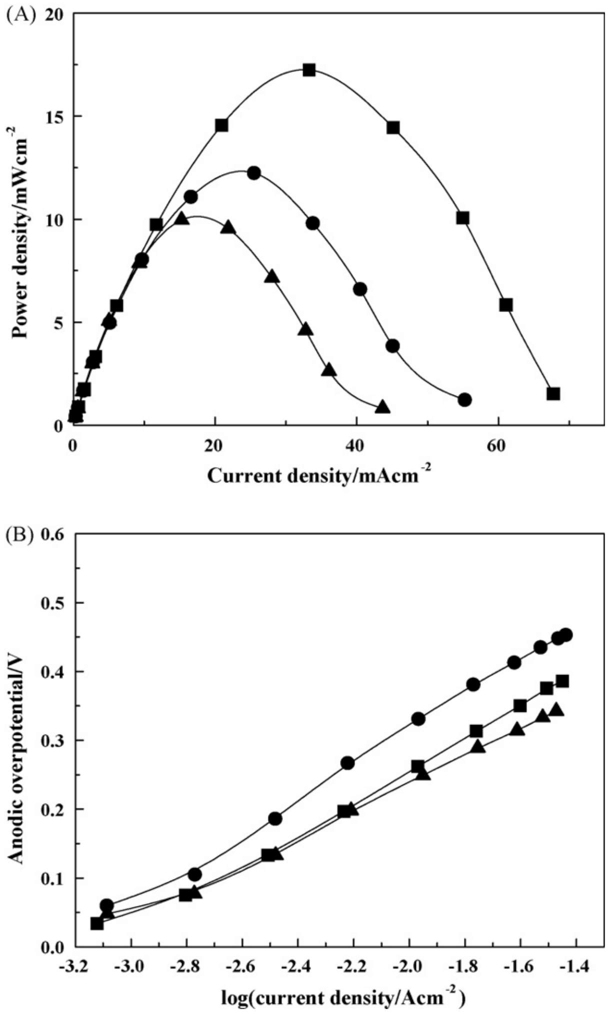

Fig. 3. (A) Power density and (B) anodic overpotential of SOFC with (■) Ni(20)/SDC(EPD), (▲) Ni(20)/LDC(EPD), and (●) Ni(20)/CeO_2(EPD) anodes heat-treated at 1173 K. The applied voltage and time of EPD method were 30 V and 3 min, respectively.

The present results of electrochemical performances of Ni/SDC(EPD) anodes as functions of Ni content, heat-treatment temperature, kind of support material, and thickness of electrode lead us to conclude that Ni(20)/SDC(EPD) anode with 20 μm in thickness is the best anode under the present experimental condition. However, the other factors such as partial pressure of

Table 1
Amounts of O^{2-} supplied from cathode to anode and carbon deposited on Ni/SDC(EPD) anodes with different thickness during 6 h operation at 973 K

Anode thickness (μm)	O^{2-} supplied (10^{-5} mol)	Amount of carbon deposition (mg)
9	1.07	≈0
20	0	3.7
	1.06	0.8
	7.35	≈0
36	1.01	12.3

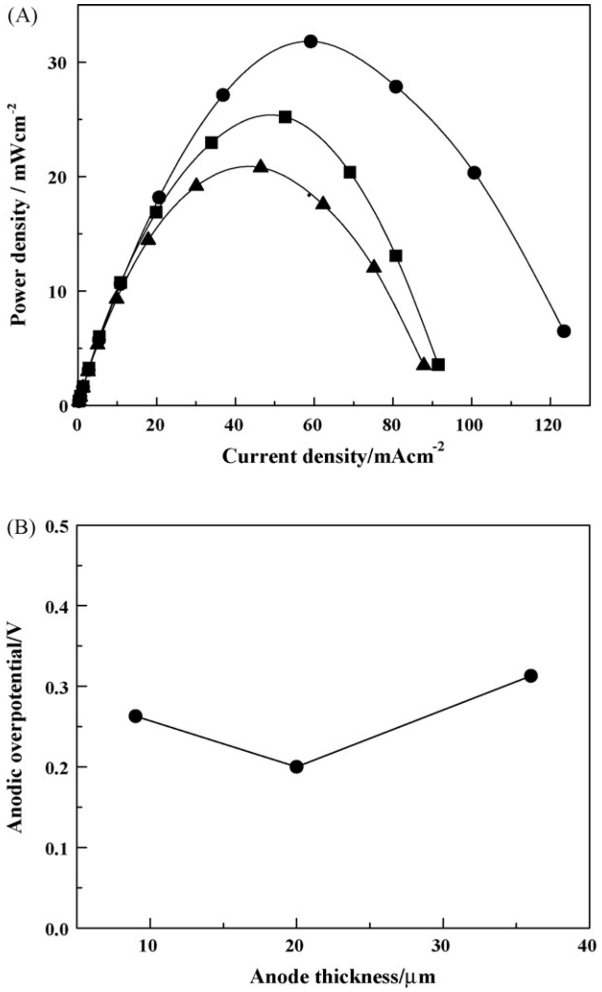

Fig. 4. (A) Power densities of SOFCs with Ni(20)/SDC(EPD) anodes with different anode thickness; (■) 9 μm, (●)20 μm, and (▲) 36 μm. (B) Anodic overpotential of Ni/SDC(EPD) calcined at 1173 K as a function of anode thickness. The anodic overpotential was measured at 0.01 A cm^{-2}.

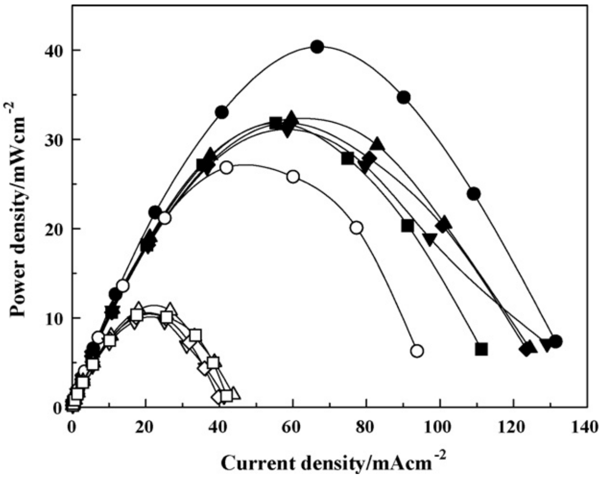

Fig. 5. *I–P* characteristics of SOFC with (closed symbols) Ni(20)/SDC(EPD) and (open symbols) Ni(20)/SDC(SC) anodes at (●, ○) 0, (▲, △) 12, (▼, ▽) 24, (◆, ◇) 36, and (■, □) 48 h after dry CH_4 was introduced into anode compartment. The thicknesses of Ni(20)/SDC(EPD) and Ni(20)/SDC(SC) anodes were 20 and 50 μm, respectively. The heat-treatment temperature was 1173 K. The cell was continuously operated at 0.01 A cm^{-2} of current density.

CH_4, flow rate of CH_4, and the kind of electrolyte are expected to affect the electrochemical performances of anode; further studies in this direction are needed to optimize the performance of SOFCs that oxidized CH_4 directly.

3.2. Comparison between Ni/SDC(EPD) and Ni/SDC(SC) anodes

As mentioned in previous section, Ni(20)/SDC(EPD) anode with 20 μm in thickness was found to exhibit the lowest overpotential at 973 K for the direct oxidation of dry CH_4 in SOFC. In this section, the electrochemical performance of Ni(20)/SDC(EPD) anode was compared with that of Ni(20)/SDC(SC) anode. The power generating curves of both Ni(20)/SDC(EPD) and Ni(20)/SDC(SC) anodes were depicted in Fig. 5. The fuel cell was continuously operated at *ca.* 0.01 mA cm^{-2} of the current density and the data were collected at 0, 12, 24, 36, and 48 h after the introduction of CH_4 to anode side. The maximum power density of 40 mW cm^{-1} for Ni(20)/SDC(EPD) anode decreased in the beginning 12 h. However, after 12 h continuous services, the maximum power density showed the constant value. The drop of the maximum power density in initial period may be due to the deactivation of anode associated with the carbon deposition. Similarly the maximum power density for SOFC using Ni(20)/SDC(SC) anode also remarkably decreased for initial 12 h.

Fig. 5 allows us to give further information that the maximum power density of SOFC with Ni(20)/SDC(EPD) anode was higher than that with Ni(20)/SDC(SC) anode. This may be related with the difference of morphologies between Ni(20)/SDC(EPD) and Ni(20)/SDC(SC) anodes. Fig. 6(A) and (B) show the SEM images of the

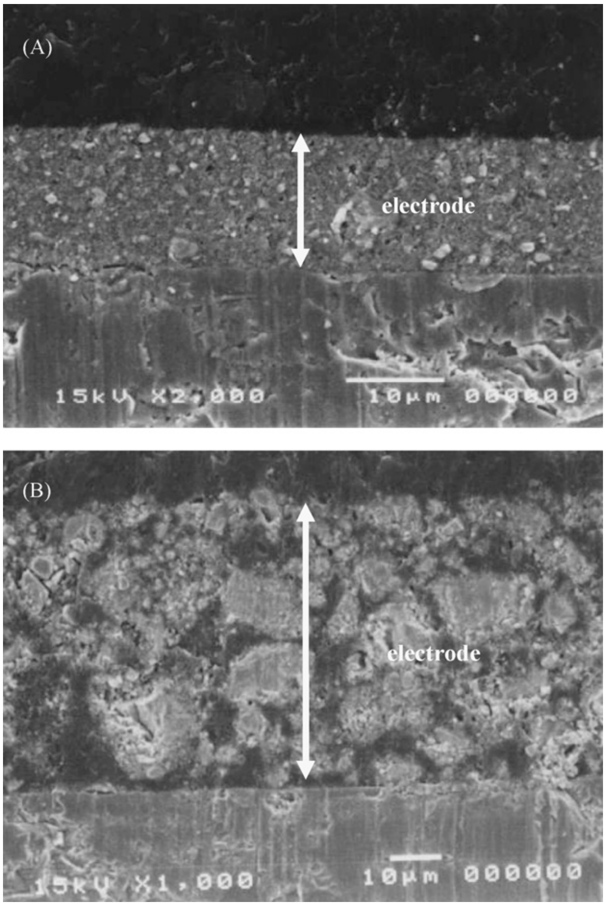

Fig. 6. SEM images (cross-section) of (A) Ni(20)/SDC(EPD) and (B) Ni(20)/SDC(SC) anodes heat-treated at 1173 K.

cross-section of Ni(20)/SDC(EPD) and Ni(20)/SDC(SC) anodes heat-treated at 1173 K, respectively. EPD techniques provided the Ni/SDC anodes with many small pores, as shown in Fig. 6(A). This suggests that the appropriate electronic network was formed between Ni/SDC particles, providing the low ohmic resistance. In contrast to Ni/SDC(EPD) anode, Ni/SDC(SC) anode possessed the microstructure containing both small and large pores, as shown in Fig. 6(B). It is expected that the gaseous reactants and products easily diffuse into Ni/SDC(SC) anode, compared with Ni/SDC(EPD) anode; however, the ohmic resistance of the former electrode is lower than that of the latter one. From there results, the higher maximum power density of SOFC with Ni/SDC(EPD) anode is probably due to the lower ohmic resistance of anode.

The carbon deposition on Ni/SDC(EPD) and Ni/SDC(SC) anodes will be discussed briefly. When dry CH_4–air SOFC with Ni/SDC(SC) anode was operated at 973 K for 24 h, carbon was noticeably deposited on Ni/SDC(SC) anode. On the other hand, carbon deposition on Ni/SDC(EPD) anode was scarcely recognized. Such a difference in the amount of carbon deposited suggests that Ni/SDC(EPD) anode conduces to maintaining of the higher power density than Ni/SDC(SC) in SOFC using dry CH_4. The quantitative analysis shown in Table 1 allows us to conclude that Ni/SDC(EPD) possesses high resistant to carbon deposition. The amount of carbon deposited on Ni/SDC(EPD) anode decreased with increasing the amount of O^{2-} supplied. Similar results have been reported by Koh et al. [16] and Lin et al. [17]. As can be seen in Fig. 6, the microstructure of Ni/SDC(EPD) anode was denser than that of Ni/SDC(SC) so that in the former electrode the sufficient amount of O^{2-} can easily supply to whole Ni particles due to the low ohmic resistance. Such a sufficient supplement of O^{2-} is considered to lead the complete oxidation of CH_4 on Ni particles, resulting in the inhibition of carbon deposition. Therefore, SOFC with Ni/SDC(EPD) anode provides a steady cell operation and a good performance.

4. Conclusion

In the present study, Ni/SDC anodes fabricated with EPD techniques were applied to the direct oxidation of dry CH_4 in SOFCs. The electrochemical performances of SOFC with Ni/SDC(EPD) anodes were investigated as functions of Ni content, heat-treatment temperature, kind of support material, and thickness of electrode. The power density of SOFC with Ni/SDC(EPD) anode was influenced by all the factors investigated; the optimized conditions were 20 wt% for Ni content, 1173 K for heat-treatment temperature, SDC for the kind of support material, and 20 μm for anode thickness. It is found that Ni(20)/SDC(EPD) heat-treated at 1173 K was the potential candidate under the present experimental condition.

The electrochemical performance of Ni(20)/SDC(EPD) anode was compared with that of Ni(20)/SDC(SC) anode. The maximum power density of SOFC with the former anode was higher than that with the latter anode. It was found that Ni/SDC(EPD) anode with less than 20 μm in thickness suppressed the carbon deposition because the sufficient amount of O^{2-} is supplied to whole catalytically active sites (Ni particles) in anode to oxidize CH_4 completely.

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