Electrochemical performance and stability of Ni$_{1-x}$Co$_x$-based cermet anode for direct methane-fuelled solid oxide fuel cells

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Abstract. Carbon deposition on Ni-based anode is well-known as a major barrier for the practical use and commercialization of hydrocarbon-fuelled solid oxide fuel cells (SOFCs). In this work, Co alloying in Ni-YSZ was studied as an alternative anode material for using CH$_4$ as a fuel. The Ni-YSZ and Ni-Co alloyed-YSZ were prepared by the traditional impregnation method without further mixing processes. After sintering and reduction in H$_2$ atmosphere, the introduced Co can completely dissolve into the Ni lattice and changed the morphology with an increase in the Ni-YSZ grain size and showed a better uniform microstructure. The Co alloying also enhanced the electrochemical performance under CH$_4$ fuel by reducing the resistance and anodic overvoltage. Moreover, the Co addition enhanced the stability of the cell with CH$_4$ a constant load current of 80 mA for 60 h. This performance related to the carbon deposition on the anode surface. The Co alloying showed a high efficiency to suppress the carbon deposition and improved the electrochemical performance of an SOFC cell operating under CH$_4$ fuel.

1 Introduction

Solid oxide fuel cells (SOFCs) are one of the most effective devices to convert chemical energy to electricity. With its high operating temperature (normally >600 °C), SOFCs can run with both hydrogen and hydrocarbon fuels, such as natural gas and ethanol. However, unsolved problems of hydrogen storage have driven a lot of researches on alternative fuels for SOFCs [1-6]. Methane (CH$_4$) is the simplest hydrocarbon, which is one of the most interested alternative fuels for SOFCs due to its high hydrogen-to-carbon molar ratio and it has a small amount of N and S impurities. Moreover, it is not only the main component of gas and coal-bed gas but also the biogas [7-10]. CH$_4$ can be therefore considered as a renewable energy.

Ni-YSZ cermet has been known as an effective anode for SOFCs due to its high electrochemical catalytic activity for hydrogen. However, Ni-YSZ cermet showed a coarsening of Ni grains at high temperatures and carbon deposition when hydrocarbons are directly used as fuels. Carbon is easy to form and deposit on a Ni-YSZ anode due to a high catalytic activity of C-H bond breaking in hydrocarbons, resulting in reduce fuel utilization but also deactivation of the anode [11]. An addition of water vapor to hydrocarbon fuels is an effective way to moderate the carbon deposition problem [12]. Unfortunately, high H$_2$O content will deactivate the cell and the system will be more complexed [13]. The replacement of Ni with electronic conductors is another way to avoid the carbon deposition. Cu was reported to avoid the coke formation in methane [14, 15]. However, the diffusion of Cu into YSZ electrolyte results in a YSZ degradation, and the low sintered temperature of Cu limits the operation temperature and decrease catalytic activity for methane conversion [16-18]. With a similar character to Ni, Co has been interested to dope in Ni anode [19]. Co alloying showed a retardation of Ni particle coarsening and enhanced the cell performance in H$_2$ [20]. Catalytic activity and stability of Ni-Co alloying was enhanced as compared to that of Ni in H$_2$ containing CO or H$_2$S as a fuel [21]. Co alloying also reduced the anodic polarization resistance and the amount of carbon deposition on Ni-GDC under a CH$_4$ fuel [22]. However, the precise mechanism of preventing carbon deposition by Co-alloying to Ni in the cermet anode is still unclear and the electrochemical performance stability has not been carefully studied. In this research, we have investigated the influence of Co alloying in conventional Ni/YSZ cermet in term of morphology and the electrochemical performance, especially the stability of the cell in dry methane.

2 Experimental

The Ni$_{1-x}$Co$_x$O-YSZ cermet (x=0 and 0.15) was prepared by the traditional impregnation method. This process was started with on appropriate amount of Ni(NO$_3$)$_2$•6H$_2$O (98% purity, Nacalai Tesque) and Co(NO$_3$)$_2$•9H$_2$O (98%
purity, Nacalai Tesque) were dissolved in distilled water, and then YSZ (8mol% Y2O3-ZrO2, 99.9% purity, Tosoh Corp.) powder was proportionately added into the solution with the composition of 60%Ni1-xCo_xO + 40%YSZ (wt.%). After dehydration, the obtained powder was calcined at 800 °C for 5 h in air to decompose the nitrate acid. To obtain fine particle, the calcined powder was manually ground for 1 h in ethanol and then dried. The ground powders of Ni1-xCo_xO-YSZ were mixed with glycerol to form a slurry and then painted as the anode on one side of the YSZ electrolyte disk (15 mm diameter and 0.3 mm thick, Nikkato) with an area of 0.28 cm². After painting, the electrode was fired at 1300 °C for 3 h. The other side of the YSZ disk was paint with La0.8Sr0.2MnO3-YSZ composite cathode slurry. The cathode slurry was prepared from the powder of 70%La0.8Sr0.2MnO3 (LSM, Seimi Chemical) + 30%YSZ (wt.%) mixed with glycerol. The cathode was fired at 1200 °C for 3 h in air. The thickness of each electrode was approximately 70 μm. The platinum paste, which used as reference electrode, was pasted as a small circle closed to working anode with a small gap (2-3 mm) on the anode side. The 0.3 mm diameter of platinum mesh (#100 mesh) was used as a current lead. A Pyrex® glass ring was used to seal between the single cells and the alumina tube. The cells were fired at 850 °C for 30 min and the anode was then reduced at 800 °C for 2 h in a H2 atmosphere prior to the measurement of the single cell performance at 750 °C under 20 v/v%CH4 in He as fuel at a total flow rate of 20 cm³/min. The cathode was fed with oxygen to use as an oxidant with the same rate as CH4.

The Ni1-xCo_x anodes at 750 °C in 20%v/vCH4 in He are shown in Fig. 2. Both anodes had a porous structure with well dispersed small metal particles. The Ni0.85Co0.15-YSZ showed a large grain size both in the metal alloy and YSZ compared to the Ni-YSZ. A coarsening of the YSZ particles was observed by Co alloying since Co3O4 can act as sintering aids [25].

### 3 Results and discussion

#### 3.1 Phase identification

Fig. 1 shows the XRD pattern of NiO-YSZ and Ni0.85Co0.15-YSZ after reduction. The reduced Ni0.85Co0.15-YSZ composite (Fig. 1(a)) exhibited the diffraction pattern of face-centered cubic (fcc) Ni metal, according to ICDD 01-070-1849, and the diffraction pattern of YSZ, according to ICDD 01-070-4431, without impurities. The 111 and 200 diffraction peaks from the fcc metal in the reduced Ni0.85Co0.15-YSZ sample (Fig. 1(b)) was slightly shifted towards the direction of low 2θ values. This result indicated that NiO and Ni0.85Co0.15O were completely reduced, and the Co was dissolved into the Ni phase and form a Ni–Co alloy. This result agreed to the binary Ni-Co phase diagram [23]. The shifts observed in the 111 and 200 peaks showed that the lattice constant of Ni was increased by Co alloying. The increase in the lattice parameters (a) was due to the ionic radius of Ni (0.69 Å), which is larger than that of Co (0.74 Å) [24].

![Figure 1](image1.png)  

**Figure 1.** The XRD patterns of (a) NiO-YSZ and (b) Ni0.85Co0.15O-YSZ after reduction under an H2 atmosphere at 800 °C for 2 h (NiO-YSZ: Ni, YSZ: Y).

#### 3.2 Microstructure of anode

The cross-sectional microstructures of reduced Ni1-xCo_x-YSZ cermet samples after sintering at 1300 °C for 3 h in air is shown in Fig. 2. Both anodes had a porous structure with well dispersed small metal particles. The Ni0.85Co0.15-YSZ showed a large grain size both in the metal alloy and YSZ compared to the Ni-YSZ. A coarsening of the YSZ particles was observed by Co alloying since Co3O4 can act as sintering aids [25].

#### 3.3 Performance of SOFC

The I-V curves and power densities for Ni-YSZ and Ni0.85Co0.15-YSZ anodes at 750 °C in 20%/vCH4 in He are shown in Fig. 3. The Ni0.85Co0.15-YSZ anode showed a significantly higher performance than the Ni-YSZ. The maximum power densities of the single cells with the Ni0.85Co0.15-YSZ anode was 136 mW/cm², which was increased from 94 mW/cm² for the Ni-YSZ, approximately 44%.

The AC impedance spectra for the Ni-YSZ and Ni0.85Co0.15-YSZ anodes at 750 °C in CH4 are compared in Fig. 4. The left intercept of the impedance spectra at high frequencies on the real axis (Re(Z)) indicated the ohmic resistance (Rθ) which was mainly contributed by the ionic resistance of the electrolyte and electrodes-electrolyte connectivity, while the right intercept on the Re(Z) corresponded to the total resistance (Rtot). The subtraction of the ohmic resistance from the total resistance (Rθ) was the polarization resistance (Rp) which is mainly generated from a charge-transfer process...
(corresponding to the electrode reaction) and a mass-

transfer process (corresponding to the gas diffusion,
adsorption and dissociation on electrodes surface process)
[26,27]. Since we used the same cathode and electrolyte,
the difference in impedance arc was influenced by the
anode resistance and its interface. The 
$R_o$ and 
$R_p$ decreased with the Co-alloying, as shown in Fig. 4,
indicating that the alloying of Co in the Ni-YSZ can
enhance the cell performance. The decrease in 
$R_o$ by Co alloying is related to the microstructural change of the
anode, as shown in Fig. 2. An improvement in the
uniformity of grain connectivity most likely contributed
to the decrease in the anode-electrolyte material
resistance. 
$R_p$ was also decreased by Co alloying, which
was probably caused the formation of porous structure
favorable for the diffusion of CH$_4$ molecules to the
reaction site with the O$^2-$ ions transported through the
electrolyte. On the contrary, the Ni-YSZ showed the
small grain size, which packed densely and provided a
small porous structure resulting in a limited CH$_4$
diffusion.

Figure 2. SEM images of (a) Ni-YSZ and (b) Ni$_{0.85}$Co$_{0.15}$-YSZ
after reduction under an H$_2$ atmosphere at 800 °C.

Figure 3. The current-voltage ($I$-$V$) curves (open symbols)
and power densities (solid symbols) for (□,■) Ni-YSZ
and (△,▲) Ni$_{0.85}$Co$_{0.15}$-YSZ anodes under an CH$_4$
atmosphere at 750 °C.

Figure 4. The impedance spectra for (■) Ni-YSZ and (▲)
Ni$_{0.85}$Co$_{0.15}$-YSZ anodes under an CH$_4$ atmosphere at 750 °C.

Figure 5. The anodic overvoltage for (■) Ni-YSZ and (▲)
Ni$_{0.85}$Co$_{0.15}$-YSZ anodes under an CH$_4$ atmosphere at 750 °C.

Fig. 5 shows a comparison of the anodic overvoltage
between the Ni-YSZ and Ni$_{0.85}$Co$_{0.15}$-YSZ. The anodic
overvoltage for the Ni$_{0.85}$Co$_{0.15}$-YSZ was significantly
lower than that for the Ni-YSZ, which corresponds to the
behavior in the cell performance and $R_p$.

3.4 Stability of SOFC

To evaluate the long-term stability of the electrochemical
performance, the impedance of the single cell for the Ni-
YSZ and Ni$_{0.85}$Co$_{0.15}$-YSZ cells in the same CH$_4$
atmosphere were investigated at 750 °C for 60 h at a
constant loaded current, 80 mA, for each cell. The ohmic
resistance ($R_o$) and the polarization resistance ($R_p$) were
plotted as a function of time, as exhibited in Fig. 6. Ni$_{0.85}$Co$_{0.15}$-YSZ showed an almost constant $R_o$ and a slight increase in $R_p$, while the Ni-YSZ showed increases in both $R_o$ and $R_p$. This result was caused by the carbon deposition onto the anode surface of Ni-YSZ, which limited the gas diffusion to the anode surface. Moreover, the carbon deposition at the triple-phase boundary (TPB) of the anode, where electrochemical reaction takes place, resulted in a decrease in the length of TPB. The surface morphologies and carbon deposition on the Ni-YSZ and Ni$_{0.85}$Co$_{0.15}$-YSZ anode were verified by SEM and a qualitative EDX analysis, respectively. The surface morphologies of the Ni-YSZ and the Ni$_{0.85}$Co$_{0.15}$-YSZ are illustrated in Figs. 7(a) and (b), while the EDX spectra of each anode were showed in the inlet of each micrograph. A significant amount of carbon was detected on the Ni-YSZ anode, whereas a very small amount of carbon was observed on the Ni$_{0.85}$Co$_{0.15}$-YSZ. This result corresponds to the previous report [22] that the rate of carbon deposition was decreased dramatically by increasing Co content in the Ni-GDC. This process was the most similar as Sn surface alloying in Ni [28] which can suppress the C-C bond formation and/or reduce the thermodynamic driving force for the nucleation and growth of graphite.

4 Conclusion

The 15 mol% Co alloying in the Ni-YSZ anode has been investigated as an alternative SOFC anode material, which can be used for an operation by methane fuels. The introduced Co was completely alloyed in the Ni metal matrix phase. The alloying of Co in Ni affected the growth of Ni grains and reduced the electrical resistance and anodic overvoltage, which consequently improved the fuel cell performance of the Ni-YSZ cermet anode in CH$_4$ atmosphere. The doping of Co improved the stability of the electrochemical performance of the Ni-YSZ cermet anode in CH$_4$ fuel at 750 °C for 60 h, which was mainly caused by reducing the carbon deposition due to a suppression of the C-C bond formation and/or reducing the required thermodynamic driving force for the nucleation and growth of graphite.

Figure 7. SEM surface micrographs and EDX spectra of Ni-YSZ and Ni$_{0.85}$Co$_{0.15}$-YSZ anodes after a stability test under an CH$_4$ atmosphere at 750 °C for 60 h.

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