

Short communication

GDC-impregnated Ni anodes for direct utilization of methane in solid oxide fuel cells

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Abstract

Anodes for the direct utilization of methane in solid oxide fuel cells (SOFC) are developed by ion impregnation of the electronic conducting and porous Ni electrode with oxygen ion conducting Gd-doped CeO₂ (GDC) phase. GDC-impregnated Ni anode was found to be very stable when exposed to weakly humidified (~3% H₂O) methane under open circuit at 800 °C, as compared to pure Ni and Ni/GDC cermet anodes. The stability of GDC-impregnated Ni in wet methane was further improved when an anodic current load of 20 mA cm⁻² was applied. The results indicate that GDC-impregnated Ni-based anodes could be potentially used for the direct utilization of natural gas fuel in SOFC.

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1. Introduction

Solid oxide fuel cells (SOFCs) offer significant advantages over other types of fuel cells with respect to the high fuel flexibility. Other than pure hydrogen, SOFCs can be fed with the more readily available hydrocarbon fuels such as methane (main component of natural gas). Direct utilization of methane eliminates the need for pre-reformers and greatly reduces the complexity, size and cost of the overall SOFC system. However, due to the severe carbon deposition caused by the cracking of methane, the conventional Ni-based anode is generally considered inappropriate for the direct utilization of hydrocarbons. Various strategies have been adopted, either by exploitation of new electrode materials or by continuous modification/improvement of the existing Ni-based cermets, to develop alternative anode materials for the direct utilization of hydrocarbon fuels. By partial substitution [1,2] or complete replacement [3] of Ni with Cu, Gorte et al. demonstrated the feasibility of using Cu–ceria cermet anodes for direct methane oxidation in SOFC. Other materials such as LaCrO₃-based perovskite [4] or doped ceria oxides [5] were reported to have high stability in methane atmosphere whilst their low electrical conductivity would pose special challenges in the design of the current collector.

We have recently shown that ion impregnation is a very effective method to introduce nano-sized electrocatalytic phases into porous SOFC electrode structure [6–8]. After impregnation treatment of (La, Sr)MnO₃ (LSM) cathodes with Ce_{0.8}Gd_{0.2}(NO₃)_x solution, electrode polarization resistance for the O₂ reduction at 700 °C decreased substantially from the original 26.4 Ω cm² for pure LSM electrode to 0.72 Ω cm², a reduction in the electrode polarization resistance by 36 times [6]. Significant improvement in the polarization performance is also found for the H₂ oxidation on YSZ- and GDC-impregnated Ni/YSZ and Ni anodes [7,8]. In this paper, we will present some preliminary results on the electrode behavior of GDC-impregnated Ni anodes in weakly humidified (~3% H₂O) methane under open circuit or low current load at 800 °C. The results clearly indicate that the incorporation of nano-GDC into Ni anodes not only improves the kinetics of the reaction in wet methane but also significantly reduces the degradation of the Ni anodes.

2. Experimental procedures

Disc-type electrolyte substrates were prepared by die pressing of 8 mol% Y₂O₃–ZrO₂ powder (TZ8Y, Tosoh, Japan), followed by sintering at 1500 °C for 4 h in air. NiO (J.T. Baker) powders pre-coarsened at 600 °C for 2 h in air was ball milled in propanol for 5 h. NiO electrode coating was applied to the YSZ

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electrolyte by slurry painting and sintered at 1400 °C for 2 h. Electrode coating thickness was $\sim 30 \mu\text{m}$ and electrode area was 0.5 cm^2 . Ni (70 v/o)/Gd₂O₃-doped CeO₂ (GDC) (30 v/o) cermet anodes was also prepared and sintered at 1400 °C for 2 h. GDC powder was synthesized by carbonate co-precipitation method [9].

The impregnation solution of 20 mol% Gd(NO₃)₃ + 80 mol% Ce(NO₃)₃ (Ce_{0.8}Gd_{0.2}(NO₃)_x) was prepared from Gd(NO₃)₃·6H₂O (99.9%, Aldrich) and Ce(NO₃)₃·6H₂O (99.9%, Aldrich). The metal ion concentration of the solution was 3 M. Ion impregnation was carried out by placing a drop of the solution on the top surface of NiO coating which infiltrate the porous layer by capillary action. The sample was heat treated at 850 °C in air for 1 h before the testing [7]. The impregnated GDC loading in Ni was estimated from the weight change of the electrode coating before and after the impregnation treatment. The impregnated GDC loading was 1.4–1.7 mg cm⁻² after two Ce_{0.8}Gd_{0.2}(NO₃)_x impregnation treatments. This corresponds to a loading of ~ 10 vol% GDC in the Ni anode [8].

A three-electrode arrangement was used for the electrochemical measurement. Pt paste was painted on to the opposite side of the working electrode to make counter and reference electrodes. Details of the cell configuration can be found elsewhere [8]. Hydrogen and methane humidified at room temperature ($\sim 3\%$ H₂O) were used as fuel while the counter and reference electrodes were exposed in static air. The fuel flow rate was 200 ml min⁻¹. Electrochemical performance of the specimen was characterized by electrochemical impedance spectroscopy (EIS) technique (Solartron 1260 and 1287) in the frequency range of 0.1 Hz–100 kHz. The electrode polarization resistance (R_E) was determined by the difference between high and low frequency intercepts in the impedance spectra.

All the anodes were evaluated with the same testing procedure. The anodes were reduced in 97% H₂/3% H₂O at 800 °C. After stabilized under a constant anodic current of 200 mA cm⁻², the fuel was changed to 97% CH₄/3% H₂O. The current load was kept at 200 mA cm⁻² till the electrode potential was again stabilized. Then the current was switched off and the impedance responses of the anode for the reaction in wet methane under open circuit at 800 °C were monitored from time to time for 3 h. In the case of a GDC-impregnated Ni anode, the stability of the anode in 97% CH₄/3% H₂O was also measured under a low current load of 20 mA cm⁻² at 800 °C. After testing, the fuel gas was changed back to H₂ and the specimen was cooled in H₂. The surface of the anodes was inspected and the microstructure was examined by scanning electron microscopy (SEM, Leica S360).

3. Results and discussion

Fig. 1 shows the impedance curves of pure Ni, Ni (70 v/o)/GDC (30 v/o) cermet and 1.7 mg cm⁻² GDC-impregnated Ni anodes in 97% H₂/3% H₂O at 800 °C under open circuit. For the purpose of comparison, the high frequency intercept of the impedance curve was adjusted to $\sim 1 \Omega \text{ cm}^2$ for all three anodes. The electrode polarization resistance, R_E , was $3.3 \Omega \text{ cm}^2$ for the H₂ oxidation reaction on Ni anode while on Ni/GDC

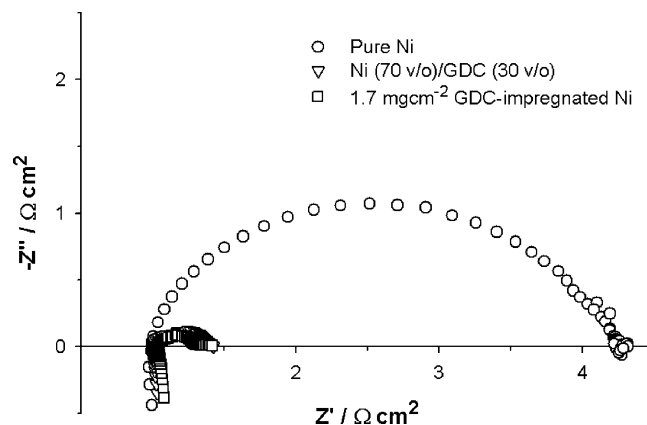


Fig. 1. Impedance curves of Ni anode, Ni/GDC cermet anode and GDC-impregnated Ni anode in 97% H₂/3% H₂O at 800 °C under open circuit.

cermet anode and GDC-impregnated Ni anode R_E was 0.44 and $0.41 \Omega \text{ cm}^2$, respectively. The low electrode polarization resistance for the reaction on Ni/GDC cermet anode and GDC-impregnated Ni anode indicates that GDC modification either by mechanical mixing or by impregnation can significantly improve the electrocatalytic activity of Ni.

Fig. 2 shows the impedance curves of Ni, Ni (70 v/o)/GDC (30 v/o) and 1.42 mg cm⁻² GDC-impregnated Ni anodes measured at 800 °C under open circuit as a function of exposure time in 97% CH₄/3% H₂O. Pure Ni anode has very poor electrocatalytic activity for the reaction in wet CH₄ (Fig. 2a). R_E was $31.8 \Omega \text{ cm}^2$, considerably higher than $3.3 \Omega \text{ cm}^2$ for the Ni anode in wet H₂. The impedance responses were not stable and increased rapidly with the exposure time. After exposure to wet CH₄ for 3 h in open circuit, R_E increased to $52.1 \Omega \text{ cm}^2$. The dramatic increase in R_E is not surprising as Ni tends to catalyze reforming reactions as well as methane decomposition. Due to the very low water content and open circuit condition, the steam reforming activity would be very low. Thus, the deposited carbon from the cracking of methane would occupy the active sites of the Ni anode, leading to the rapid degradation of electrochemical activity, as indicated by the increase in the electrode polarization resistance. The deposited carbon can also cause the disintegration of Ni anode structure by a process known as metal dusting [10]. This is confirmed by the fact that after testing, large amounts of carbon were found on the surface of the Ni anode and the Ni coating became powdery and was completely destroyed.

On the other hand, Ni/GDC cermet anode showed much higher activity and stability for the reaction in 97% CH₄/3% H₂O under the same testing conditions as compared to pure Ni (Fig. 2b). The initial R_E was $3.05 \Omega \text{ cm}^2$ and increased moderately to $3.73 \Omega \text{ cm}^2$ after exposed in wet CH₄ for 150 min under open circuit. The best performance in wet CH₄ was observed on the GDC-impregnated Ni anode (Fig. 2c). The initial R_E for the reaction in 97% CH₄/3% H₂O on the 1.42 mg cm⁻² GDC-impregnated Ni was $1.29 \Omega \text{ cm}^2$, ~ 25 times smaller than that of pure Ni and ~ 2 times smaller than that of Ni/GDC cermet anode under the same testing condition. Furthermore, the increase in the R_E values is relatively small.

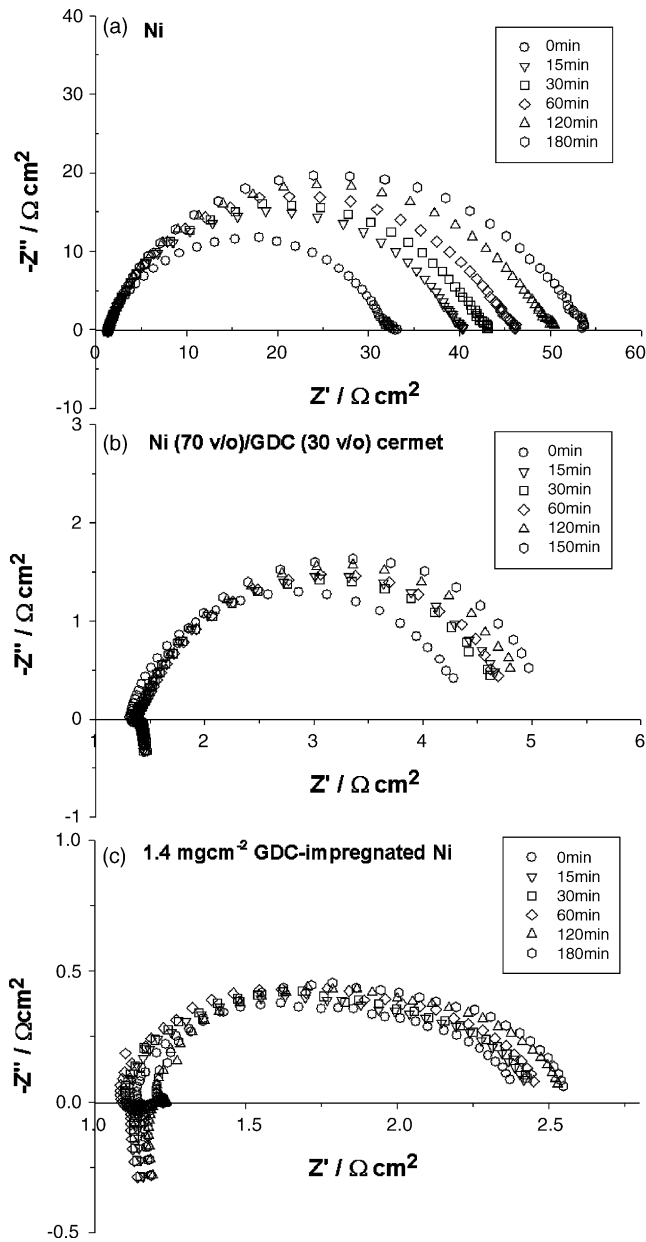


Fig. 2. Impedance curves of: (a) Ni anode, (b) Ni (70 v/o)/GDC (30 v/o) cermet anode and (c) 1.4 mg cm^{-2} GDC-impregnated Ni anode as a function of exposure time in 97% $\text{CH}_4/3\% \text{ H}_2\text{O}$ at 800°C under open circuit.

The stability of the GDC-impregnated Ni anode in wet CH_4 can be further improved with the application of an anodic current load. Fig. 3 shows the impedance responses for the reaction in 97% $\text{CH}_4/3\% \text{ H}_2\text{O}$ on a 1.4 mg cm^{-2} GDC-impregnated Ni anode under a constant current load of 20 mA cm^{-2} at 800°C . The initial R_E was $1.20 \Omega \text{ cm}^2$ and decreased to $0.9 \Omega \text{ cm}^2$ after the anodic polarization at 20 mA cm^{-2} for 3 h. It is worthy to note that the current load (20 mA cm^{-2}) used in the present work is much lower than that reported on the Ni/YSZ cermet anodes. For the reaction in wet methane, high current load ranging from 200 mA cm^{-2} to 1 A cm^{-2} is generally required to supply sufficient oxygen ions in order to suppress the carbon deposition on the Ni-based anodes [11–13]. The much lower current load in the case of GDC-impregnated Ni anode indicates the effectiveness

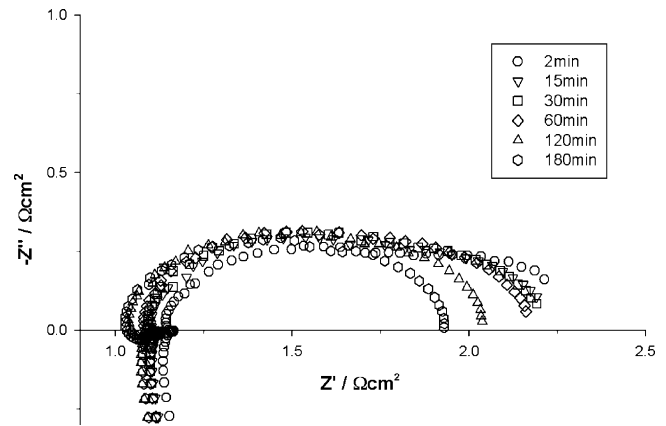


Fig. 3. Impedance curves of a GDC-impregnated Ni anode under a constant current load of 20 mA cm^{-2} as a function of exposure time in 97% $\text{CH}_4/3\% \text{ H}_2\text{O}$ at 800°C .

of the nano-sized GDC particles in the re-oxidation of deposited carbon, probably through effective distribution and dispersion of oxygen ions. Fig. 4 summarizes the stability of the electrode polarization resistance (R_E) for the reaction in wet methane on the Ni, Ni/GDC and GDC-impregnated Ni anodes under open circuit and under a current load of 20 mA cm^{-2} at 800°C . The high stability of the GDC-impregnated Ni anodes shows the potential of the GDC-impregnation in the development of Ni-based anode for SOFC based on the direct utilization of natural gas fuel.

After testing, the surface of the GDC-impregnated Ni anode was examined. A thin layer of carbon was found on the anode surface which can be easily cleaned. However, different to that of pure Ni anodes, the GDC-impregnated Ni coating adhered strongly to the YSZ electrolyte substrate. Fig. 5 shows the SEM pictures of the surface and fractured cross-section of the GDC-impregnated Ni anode with corresponding EDS patterns on GDC-covered Ni grains after testing. For comparison, the SEM picture on the surface of a freshly prepared NiO coating prior to testing is also shown. The SEM observation and EDS analysis clearly revealed the presence of fine GDC particles deposited

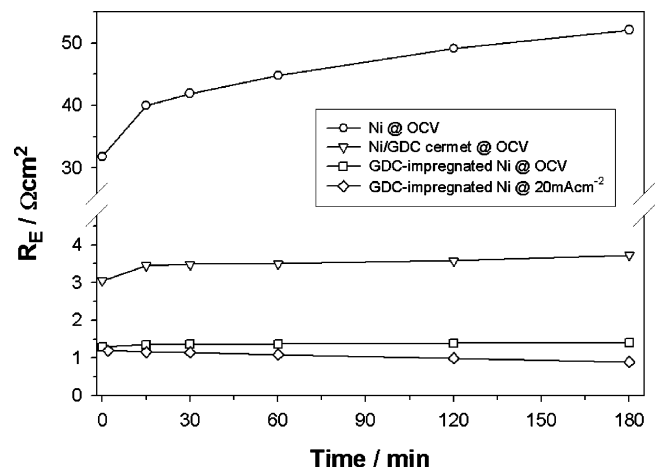


Fig. 4. Comparison of electrode polarization resistance of Ni anode, Ni/GDC cermet anode and GDC-impregnated Ni anode in 97% $\text{CH}_4/3\% \text{ H}_2\text{O}$ at 800°C .

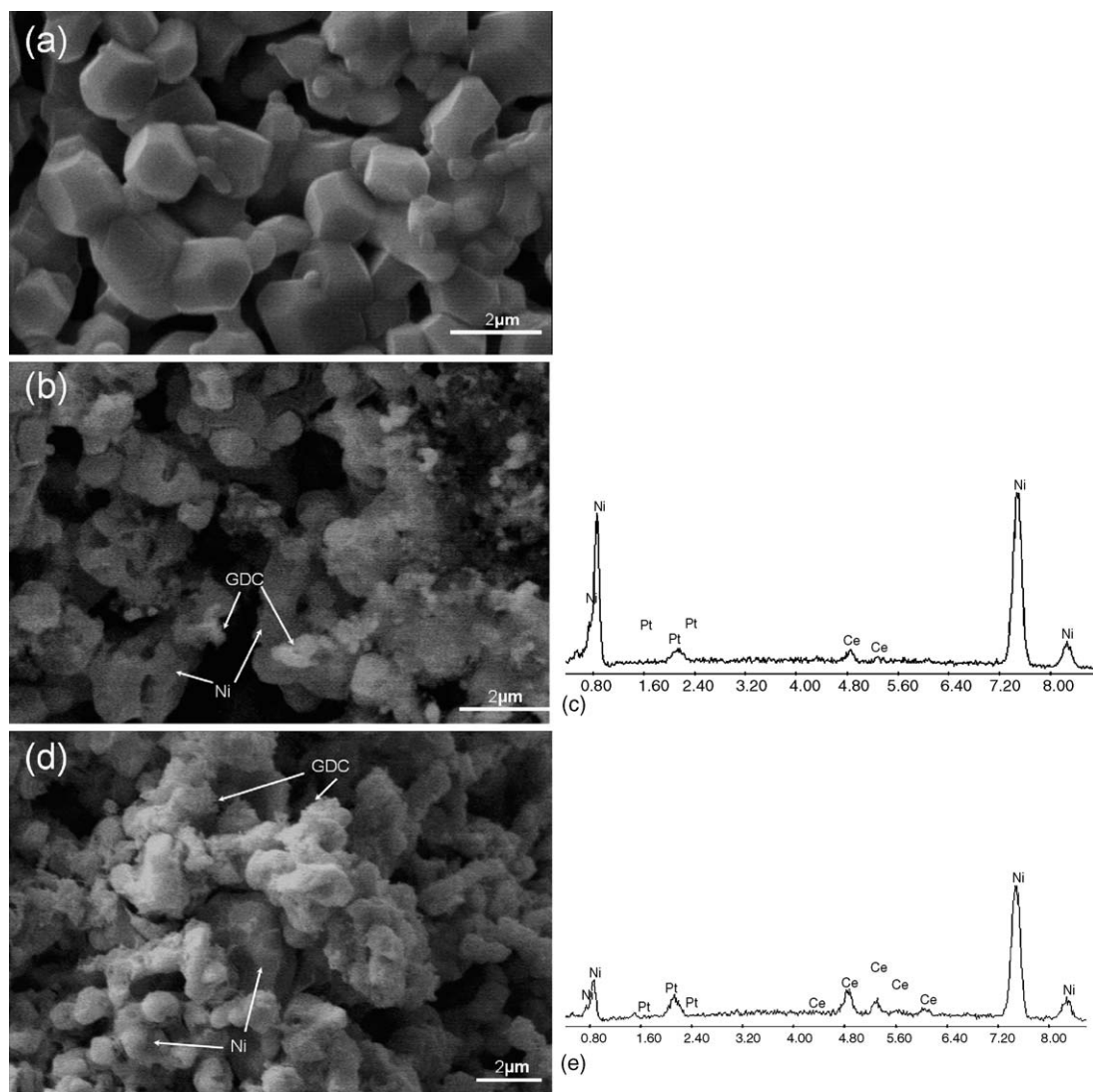


Fig. 5. SEM pictures of (a) surface of pure Ni anode before testing, (b) surface and (d) fractured cross-section of 1.42 mg cm^{-2} GDC-impregnated Ni anode after testing, and EDS patterns of the GDC-covered Ni particles (c) on the surface and (e) in the bulk of the anode coating.

around Ni grains not only on the surface but also in the bulk of the anode coating. Previous studies show that the particle size of the impregnated GDC is in the range of 100–200 nm [6–8]. It has been reported that carbon deposited on the Ni surface could dissolve into the bulk followed by precipitation as graphite on Ni surface again which would cause the metal to fracture and disintegrate [14]. The presence of nano-sized GDC particles in the impregnated Ni anode may prevent the deposited carbon from dissolving into Ni phase by the electrochemical oxidation of deposited carbon.

In the Cu–ceria systems [1–3], Cu is inert to the breaking of the C–H bonds and works primarily as current collector, while ceria is thought to act as electrocatalytic material for the direct oxidation of methane. However, as pointed out recently by Mogensen and Kammer [15], direct electrochemical oxidation of methane may not occur with appreciable rate. Instead, the conversion of hydrocarbon in the Ni-based and Cu–ceria systems is most likely via the cracking of hydrocarbons, followed by electrochemical oxidation of hydrogen and/or deposited carbon. In

this study, carbon deposition is observed on Ni, Ni/GDC cermet and GDC-impregnated Ni anodes. However, the observed rather stable impedance behavior of the GDC-impregnated Ni or Ni/GDC cermet anodes indicate that the primary function of the GDC added or impregnated in the Ni anodes is most likely to oxidize the deposited carbon due to the specific properties of oxygen storage and mobility of the oxide [16]. The much higher electrocatalytic activity of the GDC-impregnated Ni anode suggests that the impregnated nano-sized GDC particles is much more effective in aiding in the oxidation of deposited carbon as compared to the counterpart in the Ni/GDC cermet anode.

4. Conclusion

The activity and stability of the GDC-impregnated Ni anodes for the reaction in wet CH_4 were investigated. The results indicate that impregnated nano-sized GDC particles are very effective in the re-oxidation of deposited carbon on the Ni surface probably through the effective distribution and dispersion of

oxygen ions, as compared to the GDC phase in the Ni/GDC cermet anodes. The application of a low anodic current passage improved the electrode performance and stability. More studies are necessary on the polarization performance and the long-term stability of GDC-impregnated Ni anodes in weakly humidified methane.

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