In Situ Exsolved Ni-Decorated Ba(Ce₀.₉Y₀.₁)₀.₈Ni₀.₂O₃₋δ Perovskite as Carbon-Resistant Composite Anode for Hydrocarbon-Fueled Solid Oxide Fuel Cells

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Abstract: In this study, in situ exsolved Ni−Ba-(Ce₀.₉Y₀.₁)₀.₈Ni₀.₂O₃₋δ (Ni−BCYN+GDC) perovskite anode is studied for application in hydrocarbon-fueled solid oxide fuel cell (SOFC). The electrocatalytic activities of the oxidation reaction of anode in hydrogen and methane atmospheres are studied. The results show that the surface-exsolved Ni nanoparticles can significantly improve the electrochemical properties of the anode. The polarization resistances of the studied anode in hydrogen and methane atmospheres at 750 °C are as low as 0.0042 and 0.0054 Ω·cm², respectively. At the same time, a 36 h short-term open-circuit voltage test under a methane atmosphere confirms that the Ni−BCYN+GDC composite anode exhibits a good carbon deposition resistance. These results demonstrate that the Ni−BCYN+GDC composite anode is a potential novel anode material candidate for hydrocarbon-fueled SOFC.

1. INTRODUCTION

Solid oxide fuel cell (SOFC) can convert fuels’ chemical energy into electricity with high efficiencies. SOFC has the advantage of fuel flexibility with wide fuel options and can use hydrocarbons as fuel and hydrocarbon fuels are much cheaper and easier to be prepared, transported, and stored than hydrogen fuel. The conventional anode material for SOFC is Ni-based cermet. The Ni-based anodes have a high electrocatalytic activity for H₂ oxidation. However, Ni is prone to forming carbon filaments by a mechanism that involves carbon deposition, dissolution into the Ni particles, precipitation at the interface between the Ni particles and the substrate, and uplifting the Ni particles from the substrate. Therefore, novel alternative carbon-tolerant anode materials are highly expected. Researchers have begun to study Ni-free metal oxide based materials, such as La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ, La₀.₇₃Sr₀.₂₇Co₀.₅Mn₀.₅O₃₋δ, La₀.₇Sr₀.₃Ti₀.₃O₂₋δ, and BaZr₀.₁Ce₀.₇Y₀.₂O₃₋δ. Although these materials have a better carbon tolerance, their electrochemical performance and stability when using hydrocarbon fuels are not comparable to those of Ni-based cermets. Then, improvements in these anode materials have been attempted to enhance the electrochemical performance through nanoparticle decoration. Apart from improving Ni-based cermet anodes, the modifications may improve their carbon deposition resistance by impregnating nanoparticles on Ni-based anodes. Li et al. studied the Ni−GDC anode with impregnated BaCe₀.₉Y₀.₁O₃₋δ (BCY) nanoparticles and found excellent carbon deposition resistance performance in methane. Then in situ exsolution of metal nanoparticles on ceramic anode has also been investigated with enhanced electrochemical performance, such as Ni−Sr₀.₉ₓTixO₃₋δ, FeNiₓ−Sr₀.₉ₓTixO₃₋δ, and Ni−Ba−(Zr₀.₄Ce₀.₆Y₀.₂)₀.₈Ni₀.₂O₃₋δ (BZCYN)-infiltrated Sm₀.₂Ce₀.₈O₁.₉ (SDC) anode. In situ exsolution can obtain ceramic anode with a uniform distribution of metal nanoparticles and a larger reaction three-phase interfaces; this anode has excellent electrochemical performance.

BaCe₀.₃Y₀.₁ (BCY) has good oxygen ion and proton conductivity, which is determined by the operating temperature and working atmosphere. It has been reported in the literature that the proton conductivity of BCY is beneficial to the oxidation of hydrocarbon fuels. In this study, BCY is selected as the base perovskite phase to enhance the chemical stability and carbon deposition resistance of anode. Doping Ni into the B sites of the perovskite lattice of BCY can obtain Ba(Ce₀.₉₋ₓYₓ)₀.₈Ni₀.₂O₃₋δ (BCYN), which has better electrocatalytic activity for hydrocarbon oxidation; then, Ni is in situ exsolved on BCY by reduction. The exsolved Ni nanoparticles are in close contact with the matrix BCYN with evenly distribution, which can improve the catalytic performance of the anode and alleviate the formation of carbon deposition.

2. RESULTS AND DISCUSSION

2.1. Phase Structure. The phase composition of the calcined BCY and BCYN powders were characterized by X-ray diffraction (XRD), as shown in Figure 1a. The XRD peaks of BCYN are consistent with the ICDD file for BaCe₀.₉₀Y₀.₁ (BCY), confirming the purity of BCY phase without impure phase after calcination, which proves that Ni is doped into the perovskite lattice of BCY. However, after BCYN was reduced in 5% H₂−...
N\textsubscript{2} atmosphere for 8 h, the diffraction peaks of Ni appear, accompanied by those of BCY phase, which can prove that Ni is exsolved from BCYN. The BCYN and GDC powders were co-calcined at 1000 °C and tested by XRD. The test results are shown in Figure 1b. The result shows that no heterogeneous phase other than BCYN and GDC appears, and both BCYN and GDC are normal phases, indicating that these two materials are chemically compatible.

2.2. Microstructure Characterization. Figure 2a is the cross-sectional view of a symmetric cell supported by a GDC electrolyte. The GDC electrolyte is densely sintered and in good contact with the electrodes, with the thickness of about 230 μm. Figure 2b shows that the BCYN+GDC anode has the thickness of ~36 μm with well adherence to the electrolyte. Before working in the reducing atmosphere, the BCYN+GDC anode grains show a smooth surface. At the same time, the close connection between the grains forms a porous anode structure (Figure 2c). For the reduced anode, many isolated nanoparticles appear on smooth grains and grain boundaries (Figure 2d), which is related to the exsolved Ni nanoparticles.

The electron probe microanalyzer (EPMA) test was conducted to further investigate the distribution of Ni nanoparticles on the anode. It can be seen from the EPMA result in Figure 3 that Ni is homogeneously dispersed on the anode, and there is no O element around Ni element, so it can be concluded that Ni exists as a simple substance, which combines the evidence of the XRD patterns.

2.3. Symmetric Cell Performance in H\textsubscript{2} and CH\textsubscript{4}. Figure 4 shows the electrochemical impedance spectra (EIS) of Ni–BCYN+GDC symmetric cells in wet H\textsubscript{2} (with 3% H\textsubscript{2}O) and CH\textsubscript{4} (with 3% H\textsubscript{2}O), measured under open-circuit voltage (OCV) condition at 600–750 °C. The entire symmetric cell was placed in 5% H\textsubscript{2}–N\textsubscript{2} reducing atmosphere for 8 h before testing.

The high-frequency intercept of the impedance spectra represents the ohmic resistance (R\textsubscript{Ω}), which mainly reflects the performance of the electrolyte. Polarization impedance (R\textsubscript{P}) is the difference between low-frequency and high-frequency resistances, which mainly reflects the performance related to the electrode processes. Due to the electrochemical behavior of thermal activation, all the impedances of the cell decrease with increasing temperature. Figure 4a shows R\textsubscript{Ω} for the reaction in
Figure 4. EIS results of cell with Ni–BCYN+GDC anode under (a) wet H₂ and (b) wet CH₄ at 600–750 °C.

values of R₀ for the anode in wet CH₄ are only about 0.055, 0.018, 0.008, and 0.0054 Ω·cm⁻² at 600–750 °C, respectively. Compared with those of the anode working in a wet H₂, R₀ and Rₚ of the symmetric cells are basically the same order of magnitude in two different atmospheres, and Rₚ obtained in the two fuels is extremely small. It can be inferred that the anode has excellent oxidation performance in methane.

It can be presumed that the Ni nanoparticles on the anode can greatly increase the active site reactive. Since the precipitated particles are nanosized with a large specific surface area, more fuel gases can be contacted per unit area, thereby greatly improving the catalytic activity.

2.4. Full Cell Performance in H₂ and CH₄. Figure 5a shows the open-circuit EIS of H₂ (with 3% H₂O) oxidation reaction on anode before and after reduction at 750 °C, where the reduced curve is enlarged to an inset figure. It can be found that Rₚ decreases dramatically due to the metal Ni particles exsolved from the Ni–BCYN+GDC anode matrix. The presence of Ni nanoparticles not only increases the catalytic activity but also increases the reactive sites, so that R₀ of the cell can be significantly reduced, and the electrochemical performance is remarkably improved. The impedance results fitted by the equivalent circuit R(Rₚ)(R₀) are listed in Table 2.

Figure 5b shows EIS of the cell with BCYN+GDC anode measured in CH₄ (with 3% H₂O), where the reduced curve at 750 °C is enlarged to an inset figure. The figure shows similar results as the cell measured in H₂ (with 3% H₂O). The value of Rₚ of the cell is 4.02 Ω·cm⁻² at 750 °C before reduction but decreases sharply to 0.3 Ω·cm⁻² after reduction. There is also a remarkable decrease of R₀ from 4.15 to 1.18 Ω·cm⁻² for the cell before and after reduction.

Figure 5c is the I–V curve of the cell with Ni–BCYN+GDC anode measured in wet H₂. Also, the OCV is around 0.78 V. The low OCV of GDC is due to the electronic conductivity of GDC electrolyte at high temperature. The maximum power density is about 22 and 91 mW·cm⁻² at 750 °C before and after reduction, respectively. It can be found that the output can increase more than 4 times after Ni nanoparticle exsolution, which is consistent with the apparent decrease of Rₚ after anode reduction.

Table 1. EIS Results of Cell with Ni–BCYN+GDC Anode under Wet H₂ and Wet CH₄ at Different Temperatures

| Temperature (°C) | 750 | 700 | 650 | 600 |
|------------------|-----|-----|-----|-----|
| H₂               | Rₚ  | 0.30| 0.57| 0.67| 0.96|
|                  | R₀  | 0.0042| 0.0054| 0.01| 0.034|
| CH₄              | Rₚ  | 0.34| 0.54| 0.71| 1.05|
|                  | R₀  | 0.0054| 0.0008| 0.018| 0.055|

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Figure 5. (a) EIS of the cell with BCYN+GDC anode before and after reduction at 750 °C in H₂; (b) EIS of the cell with BCYN+GDC anode before and after reduction at 700 and 750 °C in wet CH₄; (c) I−V curve of the cell with the anode before and after reduction at 750 °C in wet H₂; (d) I−V curve of the cell before and after reduction at 700 and 750 °C in wet CH₄.

Table 2. EIS Results of BCYN+GDC and Ni−BCYN+GDC Anode in Wet H₂ and CH₄

| Anode         | H₂     | CH₄     |
|---------------|--------|--------|
|               | temperature (°C) | R (Ω·cm⁻²) | R₁ (Ω·cm⁻²) | R₂ (Ω·cm⁻²) | temperature (°C) | R (Ω·cm⁻²) | R₁ (Ω·cm⁻²) | R₂ (Ω·cm⁻²) |
| BCYN+GDC      | 750    | 3.22   | 0.68   | 0.82       | 750           | 4.15   | 1.56   | 2.46       |
| Ni−BCYN+GDC   | 750    | 1.025  | 0.05   | 0.20       | 750           | 1.18   | 0.12   | 0.18       |
|               | 700    | 4.17   | 1.62   | 4.16       | 700           | 1.928  | 0.84   | 0.58       |

Figure 6. (a) Stability of cell with Ni−BCYN+GDC anode in wet CH₄ under OCV at 750 °C for 36 h. (b) Raman spectra and (c) SEM micrograph of the anode after short-term test in wet CH₄ at 750 °C for 36 h under OCV.
SEM morphology analysis and Raman spectroscopy test were conducted about the cell after 36 h of short-term testing. The results are shown in Figure 6. In Raman spectra (Figure 6b), it can be seen that the peaks at 1350 and 1580 cm\(^{-1}\) associated with graphite are absent. Figure 6c shows the micrograph of the anode after being tested in wet CH\(_4\) for 36 h and that no carbon fibers can be found on the surface. These results confirm that Ni in situ exsolved BCYN+GDC anode is stable during 36 h test without carbon deposition.

3. CONCLUSIONS

In situ exsolved Ni-decorated Ba\((\text{Ce}_{0.9}\text{Y}_{0.1})_{0.8}\text{Ni}_{0.2}\)O\(_3\) Perovskite is studied as a composite anode for hydrocarbon-fueled SOFC. In the oxidation reaction of hydrogen and methane at 750 °C, the anode exhibits excellent electrochemical activity. The polarization resistances of the anode in a symmetrical cell are 0.0042 and 0.0054 Ω·cm\(^2\) respectively. The composite anode also exhibits good resistant to carbon deposition even under OCV test environment where carbon deposition is more likely to occur in short term. The research work verifies that in situ exsolved Ni–BCYN+GDC composite anode is a potential novel anode candidate with good carbon resistance and electrochemical properties for hydrocarbon-fueled SOFC.

4. EXPERIMENTAL SECTION

BCYN powders with the composition of Ba\((\text{Ce}_{0.9}\text{Y}_{0.1})_{0.8}\text{Ni}_{0.2}\)O\(_3\) were prepared by the sol–gel process. All raw materials were from Sinopharm, Shanghai. Ba\((\text{NO}_3)_2\), Ce\((\text{NO}_3)_3\)·6H\(_2\)O, Y\((\text{NO}_3)_3\)·6H\(_2\)O, and Ni\((\text{NO}_3)_2\)·6H\(_2\)O are used as starting materials. All compounds are first dissolved in deionized water and then ethylenediaminetetraacetic acid (EDTA) complexing agent is added to form a gel. Then, the as-prepared gel is dried and calcined at 1000 °C for 3 h to obtain BCYN powders. The BaCe\(_{0.9}\text{Y}_{0.1}\) (BCY) powders as a reference were also prepared in the same manner. Then, BCYN powders were reduced in 5% H\(_2\)−N\(_2\) at 750 °C for 8 h to study the exsolution properties of the compounds. BCYN and Gd\(_{0.1}\)Ce\(_{0.9}\)O\(_{1.9}\) (GDC) powders were mixed in a weight ratio of 1:1 and calcined at 1000 °C for 2 h to determine their chemical compatibility by XRD test. To prepare the composite anode, BCYN and GDC powders were mixed at a weight ratio of 6:4 using ball milling in ethanol. The cathode used is composed of La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.2}\)Fe\(_{0.8}\)O\(_3\)−δ (LSCF) and GDC. The XRD characterizations is also appreciated.

The GDC electrolyte supported symmetric cells and full cells (Φ12 mm × 1 mm) were made by the molding and sintering process. The GDC powders were ball-milled in ethanol and then molded into a pellet and sintered at 1550 °C for 5 h. The area of the BCYN+GDC anode is 0.5 cm\(^2\) for symmetric cells. For the symmetric cells, the BCYN and GDC mixing slurry was screen-printed on the both sides of the mechanically polished electrolyte and sintered at 1000 °C in air for 2 h. For the full cell preparation, the same process was used to print the anode only on one side of the electrolyte, while LSCF+GDC composite cathode was prepared by slurry painting using 70 wt % LSCF and 30 wt % GDC, followed by sintering at 1000 °C for 2 h. The active areas of both full cells are 0.2 cm\(^2\).

Pt paste (Sino-Platinum Metals Co., Ltd.) was painted on the anode and cathode for current collection for electrochemical measurement. A glass sealant (Ceramabond, Aremco Product Inc.) was used to seal the cells onto an Al\(_2\)O\(_3\) tube. A 5% H\(_2\)−N\(_2\) mixing gas was used to reduce the anodes in situ at 750 °C for 8 h prior to the electrochemical measurements. An electrochemical interface (Solartron 1287) and an impedance/gain phase analyzer (Solartron 1260) were adopted for the measurements. The initial EIS in wet H\(_2\) (with 3% H\(_2\)O) or wet CH\(_4\) (with 3% H\(_2\)O), and current density–voltage–power density (I−V−P) curves in wet CH\(_4\) were obtained at 600−750 °C. The carbon deposition resistant performance of the anode was studied in wet CH\(_4\) (with 3% H\(_2\)O) under OCV at 750 °C.

Phase composition was examined using X-ray diffraction (XRD), XRD-7000. Scanning electron microscopy (SEM, GeminiSEM300), environmental scanning electron microscopy (ESFM, Quanta 200), and electron probe microanalysis (EPMA-8050G) were used to analyze the morphology and composition. Raman spectrometer (LabRAM HR800) was used to detect carbon deposition.

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