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Fabrication and study on $Ni_{1-x}Fe_xO$-YSZ anodes for intermediate temperature anode-supported solid oxide fuel cells

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ABSTRACT

Bimetal oxides $Ni_{1-x}Fe_xO$ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) were synthesized and studied as anodes for intermediate temperature solid oxide fuel cells (SOFCs) based on yttria-stabilized zirconia (YSZ) film electrolyte. A single cell consisted of $Ni_{1-x}Fe_xO$-YSZ anode, YSZ electrolyte film, LSM–YSZ composite cathode was prepared and tested at the temperature from 600 °C to 850 °C with humidified hydrogen (75 ml min^{-1}) as fuel and ambient air as oxidant. It was found that the cell with $Ni_{0.9}Fe_{0.1}O$-YSZ anode showed the highest power density, 1.238 W cm^{-2} at 850 °C, among the cells with different anode composition. The promising performance of $Ni_{1-x}Fe_xO$ as anode suggests that bimetal anodes are worth studied for SOFCs in future.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable attention as an electrical power generating system in a friendly way primarily due to their high efficiency, low pollution and fuel flexibility [1–5]. NiO-YSZ anode has been commonly used and extensively studied as one of the anode materials for SOFCs [6], because it has good electrical conductivity and high catalytic ability towards H_2 oxidation. However, the NiO-YSZ composite anode is not absolute perfect. Coarsening of the Ni particle at high temperature may affect the overall electrical conductivity of anode, and probably also lead to decrease in triple phase boundary (TPB) length [7]. Accordingly, the performance of the cell will be reduced. To effectively obtain the high performance of the cell, it is critical to develop both anode and cathode with high catalytic activity, especially the anode of the anode-supported SOFCs. Since in the anode-supported SOFCs, the performance of single cell is mostly dependent on the anodic microstructure and its chemical catalytic activity. So it is a good method to optimize the electrochemical and catalytic properties of the anode metallic component such as partially replacing Ni with other electronic conductors such as Fe, Co, Mn and Cu [8,9] and so on. Bimetal-YSZ anode obtained by partial substitution of Ni with other metals might be an alternative to reduce coarsening of Ni particles, achieve improvements in the H_2 oxidation, and attain a better performance of the single cell.

Ringuedé et al. have reported [7,10] that the performance of the cell with bimetal-YSZ composite anode was improved. They have proved that a small amount of partial substitution of Ni with other metals have a positive effect on the anodic electrochemical and catalytic activities. Lu and Zhu [11] have studied a series ratio of Ni–Fe bimetallic anodes operating on wet H_2 fuel. Enhancement in the cell performance and the anodic property of Ni by a small fraction of Fe addition are found. Ishihara et al. [12] have found that the anodic over potential can be suppressed by addition of Fe to Ni. Many other reports also have shown that these bimetal anodes might exhibit unique anodic behaviors.

In this work, single cells with a series of bimetal $Ni_{1-x}Fe_xO$-YSZ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anode were prepared and investigated at intermediate temperature. And the performances of the cells with bimetal-YSZ anode and NiO-YSZ anode were compared from 600 °C to 850 °C using humidified hydrogen (3% water) as fuel and ambient air as oxidant. The microstructures of the anodes were examined and analyzed in detail.

2. Experimental

2.1. Starting powder preparation

$Ni_{1-x}Fe_xO$ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anode powders were synthesized by glycine–nitrate process (GNP) [13] with nitrate precursors of $Fe(NO_3)_3 \cdot 9H_2O$ (analytical reagent, A.R.) and $Ni(NO_3)_2 \cdot 6H_2O$ (A.R.). Stoichiometric amount of nitrates were dissolved in distilled water to form precursor solution. Glycine (A.R.) was then added to the solution. The molar ratio of glycine to nitrate was 1:1. The mixing solution was subsequently heated on a hot plate until it auto-ignite, producing metal-oxide 'ash'. The ash was calcined at 800 °C for 2 h to remove any possible carbon residues. Then, the as-prepared $Ni_{1-x}Fe_xO$ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2,$

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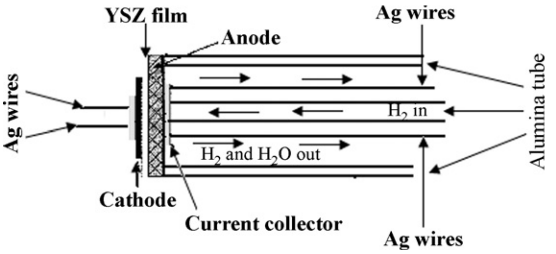


Fig. 1. Schematic diagram of the single cell testing set.

0.4, 0.5) anode powders were characterized with X-ray powder diffraction (XRD) on a Shimadzu XD-3A diffractometer (Cu Kα radiation, operated at 35 kV, 30 mA, $\lambda = 0.15406$ nm). The selected 2θ range was from 20° to 80° scanning at a step of 0.01°. The XRD patterns were analyzed and determined with PCPDFWIN 1.10 software and some correlative literatures about previous XRD work [10,11,14,15].

Cathode powder $La_{0.7}Sr_{0.3}MnO_3$ (LSM) was synthesized by citric–nitrate process [16]. Stoichiometric amounts of $Mn(NO_3)_2$ (A.R.), $Sr(NO_3)_2$ (A.R.) and La_2O_3 (99.99%) were dissolved in diluted HNO_3 (A.R.) and citric acid (A.R.) was added as the complexant. The total molar ratio of cation to citric acid was 1:1.2. The solution was evaporated at 85 °C to form a transparent gel. After drying at 100 °C for 12 h, the transparent gel changed to dry gel. Finally, the dry gel was fired at 1000 °C for 4 h to get LSM powder.

2.2. Cell fabrication

The as-prepared $Ni_{1-x}Fe_xO$ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anode powders and YSZ (TZ-8Y, Building Material Academy of China) were mixed in a weight ratio of 1:1. In addition, 10 wt% flour (bought from ordinary supermarket) was added as pore former to get sufficient porosity. After mixing and grinding, the anode powders were pressed into pellets of 13 mm in diameter and 0.5 mm in thickness under a pressure of 300 MPa. The pellets were pre-sintered at 970 °C for 4 h to get the $Ni_{1-x}Fe_xO$-YSZ anode substrates.

The YSZ electrolyte film was coated by using colloidal spray coating technique, which was reported in our previous work [17,18]. LSM–YSZ composite cathode ink was applied on YSZ electrolyte film by screen-printing and sintered at 1200 °C for 2 h with a heating rate of 2 °C min^{-1}.

2.3. Cell testing

Silver paste (Shanghai Research Institute of Synthetic Resins, Shanghai, China) was used as the current collector for both anode and cathode. A four-probe set-up was adopted to eliminate the ohmic loss in the silver wires. The single SOFC was attached to one end of an alumina tube with the anode inside by using silver paste as sealing and jointing material. Hydrogen saturated with water at room temperature (3% water) was used as fuel at the anode side at a flow rate of 75 ml min^{-1} and ambient air was used as oxidant at the cathode side. The single cell, $Ni_{1-x}Fe_xO$-YSZ/YSZ/LSM–YSZ, was tested in the temperature range of 600–850 °C. After electrochemical test, the cell was fractured and examined using a scanning electron microscope (Philips XL-30FEG, Holland). The schematic diagram of the single cell testing set was shown in Fig. 1.

3. Results and discussion

3.1. Phase identification and microstructure of the anode

Fig. 2 shows the XRD spectra of the NiO powders doped with different mole percentage of Fe. Fig. 3 shows the lattice parameter change with the amount of Fe doping into NiO anode. The X-ray spectrum for NiO doped with 1 mol% Fe (Fig. 2(a)) shows the pure NiO phase which is face-centered cubic (FCC) structure, with no second phase detected. The lattice parameter calculated for NiO doped with 1 mol% Fe is 4.1758 Å, a little larger than that for pure NiO (4.1701 Å), indicating Fe has been doped into the crystal structure of NiO, forming a solid solution $Ni_{1-x}Fe_xO$. When the Fe doping amount is 10 mol% (Fig. 2(b)), the pure NiO phase still dominates but some second phase appears. The calculated lattice parameter for NiO doped with 10 mol% Fe is 4.2100 Å, larger than that doped with 1 mol % Fe, means more Fe has been entered into the crystal lattice of NiO. The ionic radius of Fe^{2+} is 0.82 Å, larger than Ni^{2+} with an ionic radius of 0.69 Å, that explains the fact that NiO doped with Fe has a larger lattice parameter than pure NiO. While doping large amount of Fe (Fig. 2(c)), such as 50 mol% Fe, the main phase becomes Fe_3O_4. Note that Fe_3O_4 is not well conductive and cannot be reduced by hydrogen, which facts may increase the resistance of anode and cause the performance of SOFCs degraded.

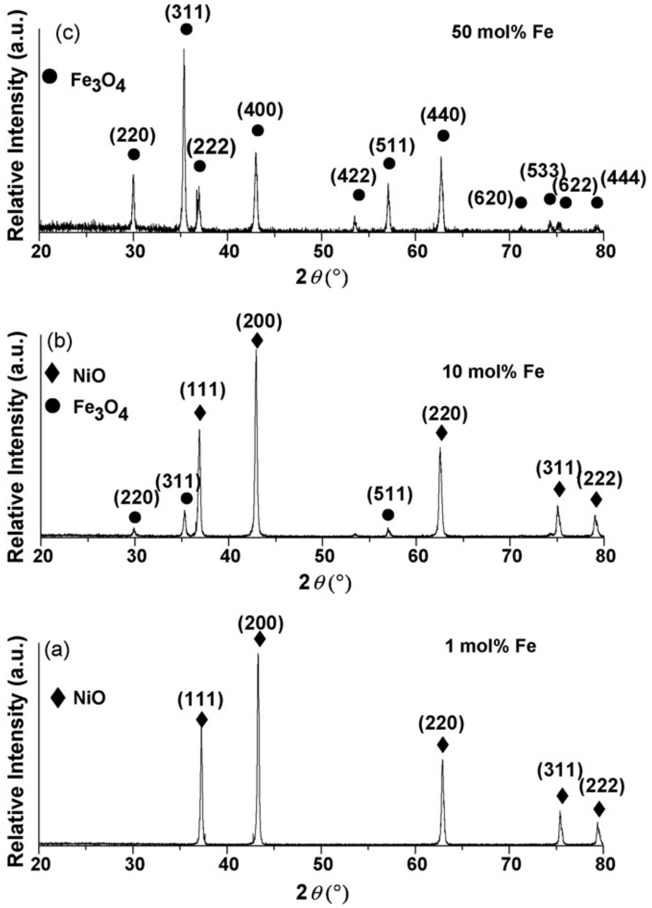


Fig. 2. XRD spectra of the NiO powders doped with different mole percentage of Fe (a) $Ni_{0.99}Fe_{0.01}O$; (b) $Ni_{0.9}Fe_{0.1}O$; (c) $Ni_{0.5}Fe_{0.5}O$.

Shown in Fig. 4(a and b) are the SEM photographs of the anode substrates with and without doped Fe after being reduced by hydrogen. Fig. 4(c–e) is the SEM picture with larger magnification and some EDX spectra of the different part of the anode. From the SEM photographs of Fig. 4(a and b), it is found that the porosity and the microstructure of the anode with doping Fe are more homogeneous than that of the anode without doping Fe. A more homogeneous

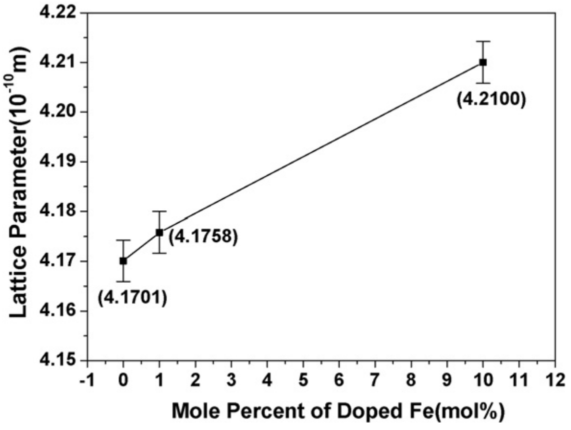
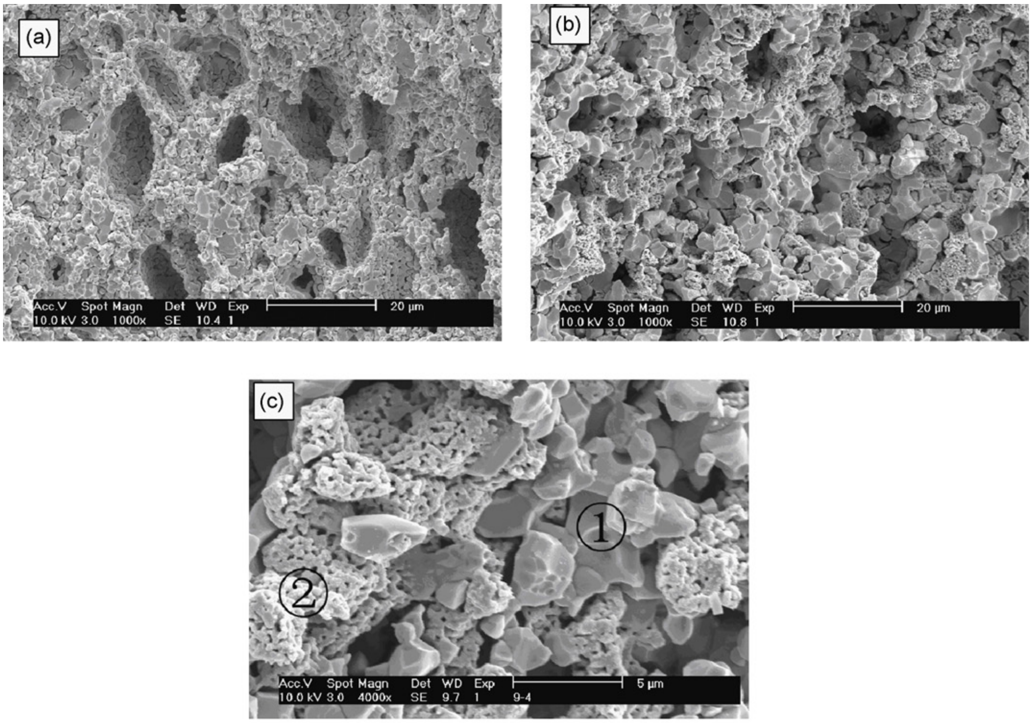
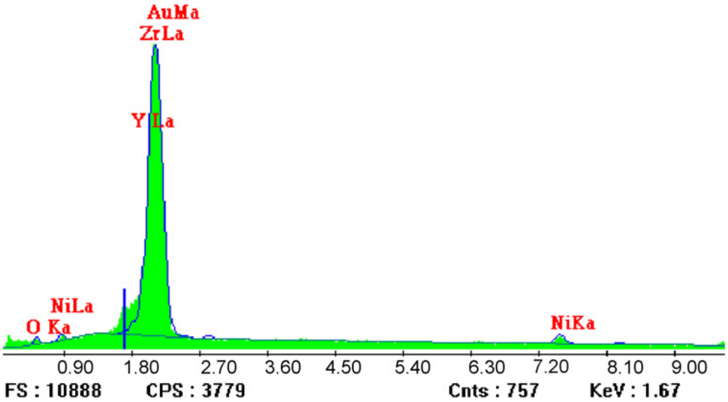


Fig. 3. The lattice parameter change with the amount of Fe doping into NiO anode.



(d) EDX of section ① in picture C:



(e) EDX of section ② in picture C:

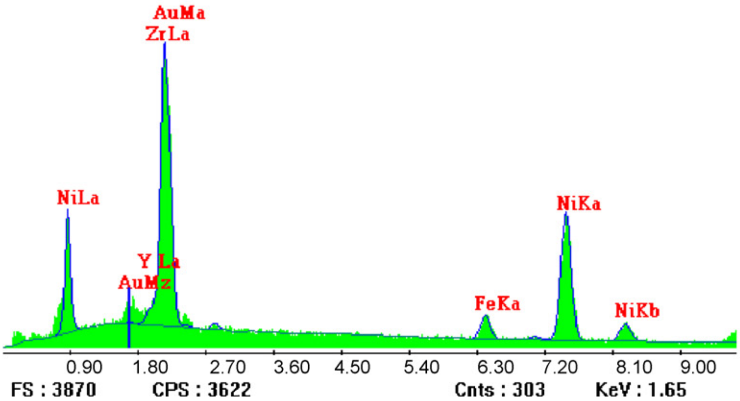


Fig. 4. SEM photographs and EDX analysis of the anode substrates after testing: (a) NiO-YSZ anode; (b) $Ni_{0.9}Fe_{0.1}O$-YSZ anode; (c–e) SEM and EDX of $Ni_{0.9}Fe_{0.1}O$-YSZ anode.

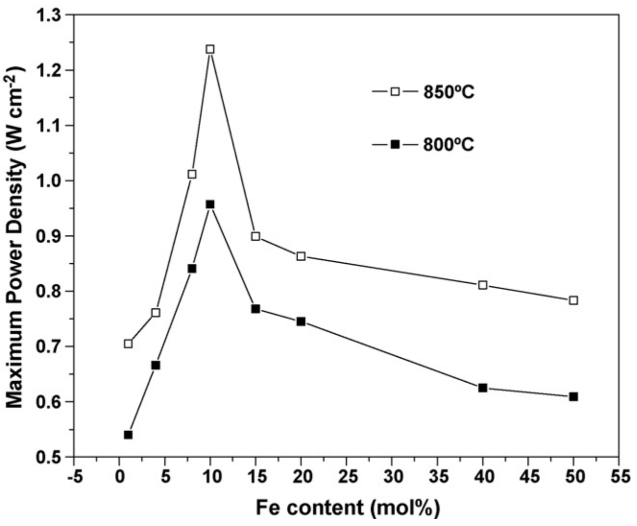


Fig. 5. Comparison of maximum power density (MPD) for single cell with $Ni_{1-x}Fe_xO$-YSZ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anode-supported SOFCs at 800 °C and 850 °C.

microstructure is better for the electrochemical reaction of the anode as the triple phase boundary (TPB) is extended. As a result, the performance of the cell is improved.

Furthermore, Fig. 4(c) suggested that there are many visible loose structures in the $Ni_{0.9}Fe_{0.1}O$-YSZ anode substrates after electrochemically testing. EDX analysis was conducted on these spots and the results were shown in Fig. 4(d and e). The EDX results of sections ① and ② indicate that Fe was found in the loose structures in the $Ni_{0.9}Fe_{0.1}O$-YSZ anode substrates while there was no Fe in the other compact spots. It is the loose structures contained Fe that increase the porosity of the anode and improve the microstructure of the anode. Accordingly, the electrochemical performance of the single cell with the anode doped Fe should be better than that without Fe.

3.2. Electrochemical performance of cell with $Ni_{1-x}Fe_xO$-YSZ anode

Shown in Fig. 5 is the comparison of maximum power density (MPD) at 800 °C and 850 °C for single cell with $Ni_{1-x}Fe_xO$-YSZ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anode-supported SOFCs. As can be seen, the performance of the cells depended strongly on Ni and Fe content. It is very clear that the highest power density is observed on the cell with $Ni_{0.9}Fe_{0.1}O$-YSZ ($x = 0.1$) anode either at 800 °C or at 850 °C. Moreover, Fig. 5 reveals a trend that the performance of the single cell increased when the metal composition gets close to this ratio. The reason may be that different metal content might change catalytic property [7,19]. Daniela et al. [20] and Li et al. [21] found that the catalytic activity was not only affected by the metal content of the anode, but also significantly influenced by the metal content balance in all parts of the anode.

Shown in Fig. 6 is the voltage and power density of the single cell with $Ni_{0.9}Fe_{0.1}O$-YSZ anode. The current–voltage (I–V) curve is not a simple linear form, which reflects polarization cannot be neglectable. The performance of the single cell is encouraging. The maximum power density reaches 1.238 W cm^{-2} at 850 °C with humidified hydrogen (3% water) as fuel and ambient air as oxidant.

3.3. Performance comparison of the single cell with $Ni_{0.9}Fe_{0.1}O$-YSZ and NiO-YSZ anode

Shown in Fig. 7 is the maximum power density comparison of the single cell with $Ni_{0.9}Fe_{0.1}O$-YSZ and NiO-YSZ anode at different temperatures. As can be seen, the maximum power density of the cell with $Ni_{0.9}Fe_{0.1}O$-YSZ anode is higher than that of the cell with NiO-YSZ anode, especially at high temperatures. Maximum power density at 850 °C for $Ni_{0.9}Fe_{0.1}O$-YSZ and NiO-YSZ anode-supported cells is 1.238 W cm^{-2} and 0.919 W cm^{-2}, respectively. It is clear that the maximum power density is increased by adding Fe to NiO anode. Since the material compositions and preparation conditions for the electrolyte and cathode, as well as the cell fabrication steps, were identical for all the single cells, it can be concluded that the performance difference of these cells is caused by the anode property. This implies that doping a proper amount of Fe to NiO anode might give a higher activity towards H_2 oxidation. Further investigation is needed to know whether the bimetal-YSZ anode can be stable enough and directly utilize hydrocarbons for application in SOFCs.

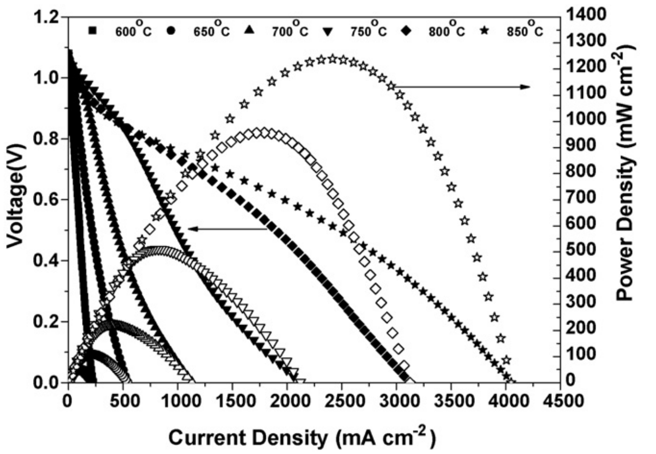


Fig. 6. Voltage and power density of the $Ni_{0.9}Fe_{0.1}O$-YSZ anode-supported SOFCs using humidified hydrogen (75 ml min^{-1}) as fuel and ambient air as oxidant from 600 °C to 850 °C.

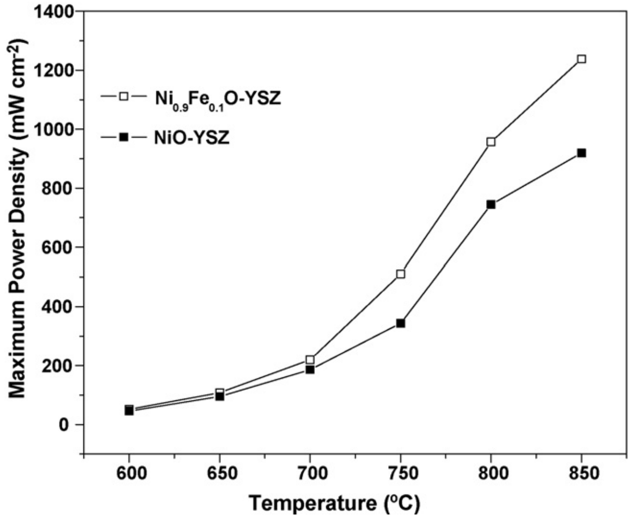


Fig. 7. Performance comparison of the single cell with $Ni_{0.9}Fe_{0.1}O$-YSZ and NiO-YSZ anode.

4. Conclusions

Bimetal $Ni_{1-x}Fe_xO$ ($x = 0.01, 0.04, 0.08, 0.1, 0.15, 0.2, 0.4, 0.5$) anodes have been studied as anode materials for intermediate temperature SOFCs. A $Ni_{0.9}Fe_{0.1}O$-YSZ anode-supported cell has shown very promising results and obtained the maximum power density of 1.238 W cm^{-2} at 850 °C with humidified hydrogen (3% water) as fuel and ambient air as oxidant. The cell performance was improved when the molar ratio was close to the mol ratio of Fe:Ni = 1:9. Compared to the cell with NiO-YSZ anode, the single cell with $Ni_{0.9}Fe_{0.1}O$-YSZ anode has better electrochemical performance. The results suggest that NiO doped with a proper amount of Fe to form a solid solution $Ni_{1-x}Fe_xO$, and its loose structure probably increases the porosity of the anode and improve the microstructure of the anode. Furthermore, it also plays a positive effect on the property of the SOFCs and achieves improvements in the H_2 oxidation. Further investigation is clearly needed to know whether the bimetal-YSZ anodes can be stable enough and directly utilize hydrocarbons for application in SOFCs anodes.

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