

Preparation and performance characterization of the Fe–Ni/ScSZ cermet anode for oxidation of ethanol fuel in SOFCs

Bo Huang*, S.R. Wang, R.Z. Liu, T.L. Wen

Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China

Received 10 January 2007; received in revised form 27 February 2007; accepted 28 February 2007

Available online 12 March 2007

Abstract

An anodic cermet of Fe–Ni alloy and scandia stabilized zirconia (ScSZ) has been investigated for a solid oxide fuel cell (SOFC) running on ethanol fuel. Composite anodes having alloy compositions of 0, 12.5, 25, 37.5, 50 and 100 wt.% Ni were exposed to ethanol stream at 700 °C for 12 h to demonstrate that carbon formation is greatly suppressed on the Fe–Ni alloys compared to that of pure Ni. Then the short-term stability for the cells with the Ni/ScSZ and Fe_{0.5}Ni_{0.5}/ScSZ anodes in ethanol stream at 700 °C was checked over a relative long period of operation. Open circuit voltages (OCVs) increased from 1.03 to 1.1 V, and power densities increased from 120 to 460 mW cm² as the operating temperature of a SOFC with Fe_{0.5}Ni_{0.5}/ScSZ anode was increased from 700 to 850 °C in ethanol stream. Electrochemical impedance spectra (EIS) illustrated that the cell with Ni/ScSZ anode exhibits slightly less total impedance than that observed for the cell with Fe_{0.5}Ni_{0.5}/ScSZ anode. The performance of a fuel cell made with the Ni/ScSZ and Fe_{0.5}Ni_{0.5}/ScSZ anodes was tested in ethanol stream for 48 h and showed a significant decrease in polarization resistance with time. Impedance spectra of similar fuel cells suggest that small carbon deposits are formed with time and that the decrease in polarization resistance is due to enhanced electronic conductivity in the anode.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Anode; Carbon deposition; Electrochemical impedance spectroscopy; Ethanol; Solid oxide fuel cell (SOFC)

1. Introduction

Solid oxide fuel cells (SOFCs) will inevitably exert a great impact on the development of the next generation energy technology and the hydrogen economy as fossil fuels are running out. At present, it has been launched into primeval stage of commercial manufacture in some developed countries. One of the challenges to commercializing them is the fact that SOFCs require that the fuel be H₂, which is almost always produced by reforming hydrocarbons. This adds an additional level of complexity to the overall system. However, direct oxidation of hydrocarbons is theoretically possible in SOFCs and has been demonstrated by a number of groups [1–3]. It is well known that Ni–YSZ (yttria stabilized zirconia) cermet anodes of SOFC have excellent catalytic properties and stability for the H₂ oxidation at SOFC operation conditions [4,5]. However, since Ni is a good catalyst for hydrocarbon cracking reaction, the use of

hydrocarbon fuels in a SOFC with Ni-based anode results in carbon deposition and rapid, irreversible cell degradation [6–10]. Ni–YSZ cermet anodes can only be directly used for hydrocarbon fuels if excess steam is present to ensure the complete fuel reforming and to suppress the carbon deposition [7,11]. Therefore, the development of an anode material for SOFCs that operate on hydrocarbons is widely recognized to be an important technical objective.

Gorte et al. focused their attention on developing carbon resistant anodes by replacing Ni with Cu and CeO₂ [12–16]. Compared to Ni, Cu is not catalytically active for the carbon deposition but effective as current collector, while ceria provides a high catalytic activity for hydrocarbon reforming due to its special mixed conductivity. Since the melting points of both copper and copper oxide are significantly less than the sintering temperature of ca. 1500 °C which is necessary for densification of electrolytes, it is not possible to prepare Cu–YSZ cermets by high temperature sintering technology. Therefore, an alternative method for preparing Cu–YSZ cermets was developed in which a porous YSZ matrix was prepared first, and then adding both Cu and CeO₂ through wet impregnation [13,15].

* Corresponding author. Tel.: +86 21 52411520; fax: +86 21 52413903.
E-mail address: huangbo2k@hotmail.com (B. Huang).

Another approach for enhancing the activity and stability of Ni-based anodes running on hydrocarbons involves replacing Ni with other metals such as Cu, Co and Fe [17,18]. Since the melting temperature of Cu–Ni alloys increases almost linearly with Ni content. Indeed, the Cu–Ni alloys have been used for the anodes in molten carbonate fuel cells [19]. The reactivity of Ni for alkane hydrogenolysis and dehydrogenation, reactions which are likely to be related to anode coking reactions, is greatly modified by formation of an alloy with Cu [20–22]. For example, Sinfelt and co-workers [20] demonstrated that the hydrogenolysis activity of a series of Cu–Ni catalysts dropped by five orders of magnitude as the Cu content increased from 0 to 60%. Ringuedé et al. reported [17] that by adding Co to the Ni–YSZ composite anode the cell performance was improved. Dokiya and coworkers studied [23] the oxidation and steam reforming of CH₄ on Ni/YSZ and Fe/YSZ cermet anodes under the condition of $0 \leq \text{H}_2\text{O}/\text{CH}_4 \leq 1$. The results indicated that the steam reforming activity of CH₄ on Ni/YSZ was much higher than on Fe/YSZ at open circuit. However, Fe/YSZ anode had excellent carbon-resistant performance. Alqahntany also confirmed [24] that Fe showed high catalytic activity without degradation, while Ni showed rapid degradation due to coking. Therefore, it is not appropriate to use the Fe/YSZ cermets as an anode in the hydrocarbon fuel condition because of its low activity. However, Fe can be used for controlling the hydrocarbon reforming reaction if it is applied as a coating or mixed with Ni/YSZ cermet anode.

In this work, a tape casting method was presented to prepare SOFCs with a series of Fe_{1-x}Ni_x/ScSZ ($x=0, 0.125, 0.25, 0.375, 0.5, 1.0$) composite anodes. Tape casting is favorable for preparing very thin electrolyte films, and multi-layer structures. We adopted this process to prepare a thin dense film of ScSZ (scandia stabilized zirconia) electrolyte, supported by a thick porous ScSZ layer which serves as the framework of the final anode. Ammonium oxalate ((NH₄)₂C₂O₄·H₂O) was used as the pore former. In order to study the influence of different amount of Fe and Ni on fuel oxidation, we fabricated, measured and compared anodes with different ratios of Fe versus Ni. We have focused our efforts on the investigation of a Fe–Ni alloy–ScSZ catalyst formulation as a suitable combination in terms of catalytic activity and tolerance to carbon deposition.

2. Experimental

2.1. Preparation of the porous ScSZ anode matrix

The procedure for obtaining the porous ScSZ anode matrix by tape casting samples comprising the preparation of a slurry containing scandia-stabilized zirconia Zr_{0.89}Sc_{0.1}Ce_{0.01}O_{2-x} (ScSZ, 99.99% pure, Daiichi Kigenso Kagaku Kogyo, Japan) powder, azeotropic mixture of butanone and ethyl alcohol absolute as solvent; Triethanolamine as a kind of zwitterionic dispersant to reduce the interfacial tension between the surface of the particle and the liquid; Polyethylene glycol (PEG 200) as plasticizer to increase the flexibility of the tapes; Poly-vinyl-butyl (PVB) as binder to provide their strength after the evaporation of the solvent and ammonium oxalate ((NH₄)₂C₂O₄·H₂O, 200 mesh) as pore former to increase the

porosity of the ScSZ anode matrix. The PVB binder was supplied as a free flowing fine-grained powder and the PEG plasticizer was obtained in a liquid form. All the organic additives were supplied by Shanghai Chem. Ltd., China. The amount of ammonium oxalate pore formers was 40 wt.% of the ScSZ powders. Start materials were weighed, mixed and ball milled, then a homogeneous slurry was obtained. The slurry was degassed using a vacuum pump (pressure: 200 mbar absolute) and cast on to glass surface. The green tapes were allowed to dry at room temperature for 48 h. They were then sintered in air at 1450 °C for 3 h. The porosities of the sintered ScSZ layers were determined using either Hg porosimetry (Pore Sizer 9320) or a standard test method based on Archimedes' principle by measuring the mass of water that could be absorbed into the porous ScSZ layer [25]. Thus a disk-shaped anode substrate, or a fuel electrode, having a diameter of about 3.0 cm, a thickness of 1 mm, and a porosity of about 66%, was then produced.

2.2. Fabrication of unit-cells

Anode-supported SOFCs were fabricated using a dual tape cast layers of ScSZ, one containing pore formers (the porous anode matrix) and the other without pore formers (the electrolyte layer). The electrolyte layer was cast first and then allowed to dry at room temperature for 48 h. A second layer of ScSZ which contained pore formers was then cast on top of the electrolyte green tape and allowed to dry overnight. The composite structure was then co-sintered in the air at 1450 °C for 3 h. The cathode with 1.54 cm² area was fabricated by screen-printing a slurry containing (Pr_{0.7}Ca_{0.3})_{0.9}MnO₃ (PCM) onto the surface of the dense ScSZ electrolyte and then sintered at 1200 °C for 3 h. SEM images showed that the thicknesses of the dense ScSZ electrolyte layer and PCM cathode layer of the single cell used in this study were about 15 and 20 μm, respectively.

2.3. Fe–Ni coating

The Fe_{1-x}Ni_x/ScSZ anodes were prepared by impregnating the porous ScSZ layer with aqueous solutions of Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·H₂O into the anode matrix having the desired Fe:Ni ratio, followed by low temperature calcinations at 450 °C to decompose the nitrates. For these cells the total amount of Fe and Ni in the Fe_{1-x}Ni_x/ScSZ anode was held constant at 40 wt.%, while the ratio of Fe to Ni in the anode was varied. The Fe³⁺ concentration in the transparent solution was 4 mol dm⁻³. The porous anode layer ScSZ of anode-supported cell was completely dipped in the above solution and evacuated using a vacuum pump set to an absolute pressure of 200 mbar for 30 min so that the solution filled the pores of the ScSZ layer. Then it was dried at 75 °C, followed by calcination at 450 °C for 2 h. This procedure was repeated several times to have a uniform coating. The impregnated Fe–Ni weight loading in the ScSZ anode matrix was calculated from the weight change of the ScSZ anode matrix before and after the impregnation treatment. The amounts of Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·H₂O were controlled such that the Ni content in the Fe–Ni alloy will be 0, 12.5, 25, 37.5, 50 and 100 wt.% after reduction. We made several kinds

of cells with different ratios of 8:0 (40 wt.%Fe–0 wt.%Ni/ScSZ, denoted as Fe/ScSZ), 7:1 (35 wt.%Fe–5 wt.%Ni/ScSZ, denoted as $\text{Fe}_{0.875}\text{Ni}_{0.125}/\text{ScSZ}$), 5:3 (25 wt.%Fe–15 wt.%Ni, denoted as $\text{Fe}_{0.625}\text{Ni}_{0.375}/\text{ScSZ}$), 4:4 (20 wt.%Fe–20 wt.%Ni, denoted as $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$) and 0:8 (0 wt.%Fe–40 wt.%Ni, denoted as Ni/ScSZ).

2.4. Characterization of anode performance and single cell performance

Experimental techniques, apparatus and the electrochemical cell assembly for SOFC tests have been described previously [26]. A Pt mesh and lead wire were attached to the surface of the cathode using a Pt ink, followed by sintered at 950 °C for 0.5 h. On the anode side, a Au mesh and lead wire were used as the current collector and were attached using a Au ink applied to the edges of the Au mesh, followed by sintering at 850 °C for 0.5 h. The anode side of the structure was then attached to an alumina tube using Au ink and the edges were sealed using a ceramic adhesive. All the anodes were evaluated with the same testing procedure. The anodes were fully reduced in H_2 atmosphere at 850 °C for 2 h prior to cell testing. Hydrogen or gasified ethanol–water mixture (with volume ratio 2:1) were used as fuel and oxygen was used as oxidant. The fuel and oxidant flow rate were all controlled at 25 mL min^{-1} , and the liquid fuel was vaporized by water bath (70 °C) and then brought into the anode surface by nitrogen. The current–voltage curves and electrochemical impedance spectroscopy (EIS) were obtained using an Electrochemical Workstation IM6e (Zahner, GmbH, Germany). These measurements were started after stabilized under a constant discharge voltage of 0.7V for 4 h in order to obtain a sufficiently stabilized system necessary for a cell testing experiment. Then the current was switched off and the impedance spectra of the electrochemical cell were recorded under open circuit from time to time with amplitude of 20 mV over the frequency range 0.02 Hz to 100 KHz. The measurement was carried out in the temperature range of 700–850 °C in steps of 50 °C. The ohmic resistance of the electrolyte, the cathode and the anode (R_{Ω}) was estimated from the high frequency intercept of the impedance curves and the overall electrode polarization (interface) resistance (R_E) was directly measured from the differences between the low and high frequency intercepts on the impedance curves.

3. Results and discussion

3.1. Microstructural characterization

To demonstrate the effect of Fe–Ni alloy composition on the propensity of the anodes to form carbon, we made a series of cermets with varied Fe:Ni ratios, reduced them in H_2 at 850 °C for 3 h, and then exposed them to flowing ethanol stream at 700 °C for 12 h. The results are shown in the photograph in Fig. 1. These porous ScSZ/dense ScSZ were identical to cells used in fuel cell testing, except that the cathode layer was not attached on the reverse side. The cermet made with only Fe was almost unaffected by the treatment in ethanol stream, showing no evidence

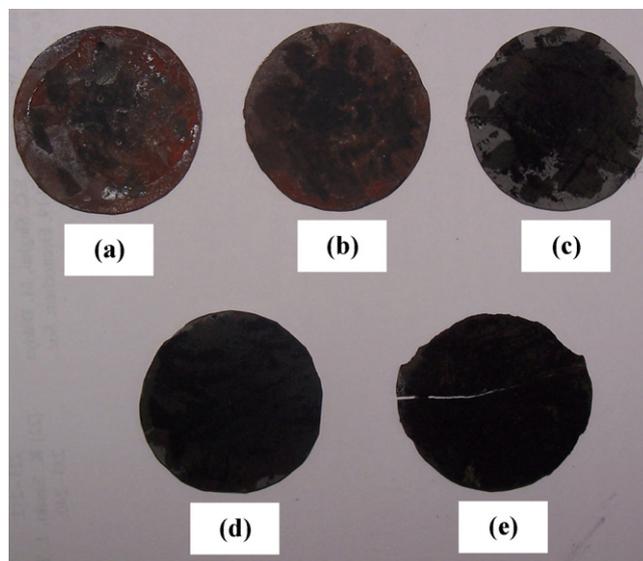


Fig. 1. Photograph of cermets having 40 wt.% metal after reduction in H_2 at 850 °C, for 3 h and exposure to ethanol steam at 700 °C for 12 h. The photographs are shown for the following metal compositions: (a) Fe/ScSZ; (b) $\text{Fe}_{0.875}\text{Ni}_{0.125}/\text{ScSZ}$; (c) $\text{Fe}_{0.625}\text{Ni}_{0.375}/\text{ScSZ}$; (d) $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$; (e) Ni/ScSZ.

for carbon formation. By contrast, the cermet made with only Ni formed large amounts of black carbon. The Fe–Ni alloys all showed some carbon formation, as evidenced by the black powder on each sample, but the amount of carbon deposited on the samples increased with the increase of Ni content in the Fe–Ni alloy cermets. For the alloy with a Fe: Ni ratio of 7:1, only small amounts of carbon formed.

The effect of composition on the Fe–Ni alloy cermets is quantified in Table 1. In these experiments, we made a series of cermets with varied Fe:Ni ratios, reduced them in H_2 at 850 °C for 3 h, exposed them to flowing ethanol stream at 700 °C for different time, and then weighed to determine the amount of carbon that was deposited. For the Fe/ScSZ sample, almost no weight change was observed upon exposure to ethanol stream at 700 °C for 12 h. Significant weight gains were observed with the 5:3 and 4:4 Fe–Ni alloys and the gains were larger on the

Table 1
The effect of metal compositions of Fe–Ni alloys on carbon formation

Samples	Exposure time (h)	Weight gain (g/g)
Fe/ScSZ	12	0.005
	48	0.008
$\text{Fe}_{0.875}\text{Ni}_{0.125}/\text{ScSZ}$	12	0.204
	48	0.212
$\text{Fe}_{0.625}\text{Ni}_{0.375}/\text{ScSZ}$	12	0.270
	48	0.293
$\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$	12	0.324
	48	0.315
Ni/ScSZ	12	0.481
	48	0.510

Cermet samples having 40 wt.% metal after reduction were reduced in H_2 at 850 °C for 3 h and then exposed to flowing ethanol steam at 700 °C for the time shown.

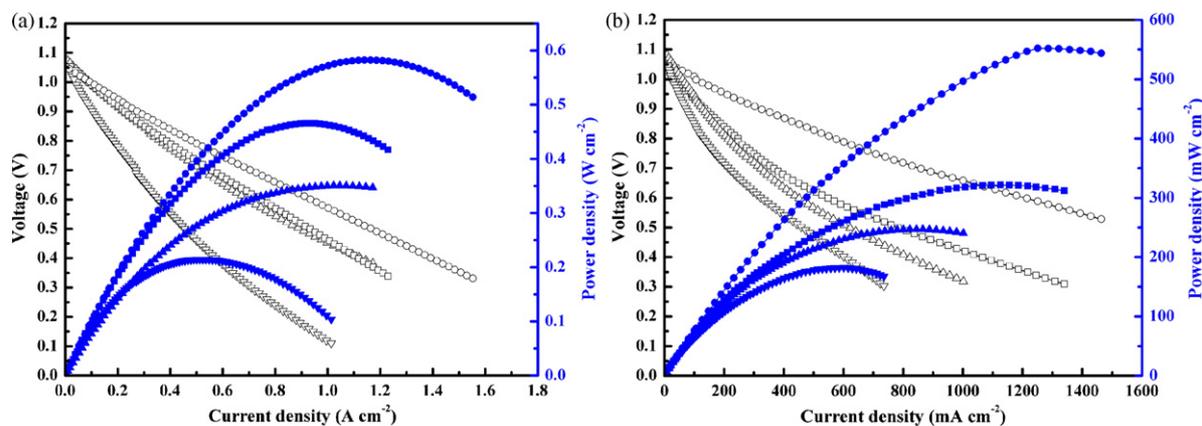


Fig. 2. Voltage and power density vs. current density for a SOFC with Ni/ScSZ anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperature: (○, ●) 850 °C (□, ■) 800 °C (▲, △) 750 °C (▼, ▽) 700 °C.

sample having more Ni. It was noted that the amount of carbon deposited on the alloys did not increase linearly with time, but seemed to approach a constant value after long time.

3.2. Performances of single cells

To determine whether the Fe–Ni alloys might be useful as anodes for direct oxidation of ethanol fuel, we made a model fuel cell with an alloy anode having a Fe:Ni ratio of 4:4 ($\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$). Figs. 2 and 3 show typical voltage and power density versus current density of a SOFC with Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes while operating on humidified hydrogen (a) and ethanol stream (b), respectively. We could find that the open circuit voltage (OCV) for H_2 and $\text{C}_2\text{H}_5\text{OH}$ were, respectively, 1.02–1.12 V and 1.030–1.1 V in the temperature range, which were all slightly below the theoretical OCV. It revealed that the ScSZ electrolyte was not dense enough that resulted in decreased value of OCV. The data show a slightly decrease in performance of a SOFC with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode than that of a SOFC with Ni/ScSZ anode while running on humidified hydrogen and ethanol stream. The performance of the cell with Ni/ScSZ anode while operating on humidified hydrogen

was modest with a maximum power density of 584, 466, 345 and 212 mW cm^{-2} at 850, 800, 750 and 700 °C, respectively, and whereas the corresponding values were 466, 385, 254 and 149 mW cm^{-2} for the cell with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode. The highest power density of the cell with Ni/ScSZ anode while operating on ethanol stream was 545, 321, 246 and 181 mW cm^{-2} at 850, 800, 750 and 700, respectively. The counterpart of the cell with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode while operating on ethanol stream was 460, 265, 165 and 120 mW cm^{-2} at 850, 800, 750 and 700 °C, respectively. Since the electrolyte and cathode were prepared identically, the performance of the two cells depended strongly on the anode composition.

In an attempt to examine the reason for the two cell performances in Figs. 2 and 3, we measured the impedance spectra of the two cells while running on humidified hydrogen and ethanol stream at different temperature. Figs. 4 and 5 show a comparison of typical EIS results, from cells with Ni/ScSZ anode and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode operated in humidified hydrogen and ethanol stream under open circuit at different temperature, respectively. The high-frequency intercept of the impedance spectra corresponds to the ohmic resistance of the cell, including ohmic resistance of the ScSZ electrolyte, ohmic resistance of

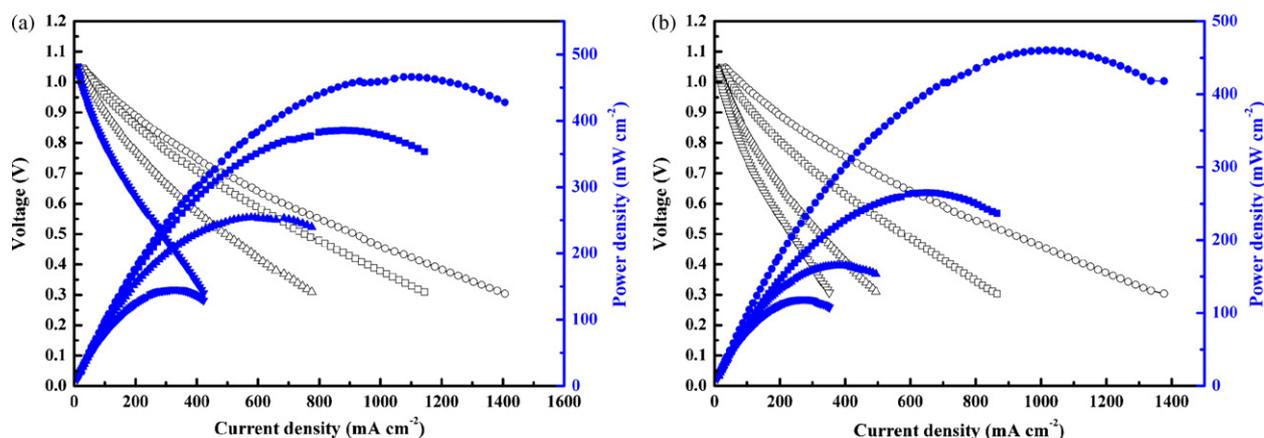


Fig. 3. Voltage and power density vs. current density for a SOFC with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperature: (○, ●) 850 °C (□, ■) 800 °C (▲, △) 750 °C (▼, ▽) 700 °C.

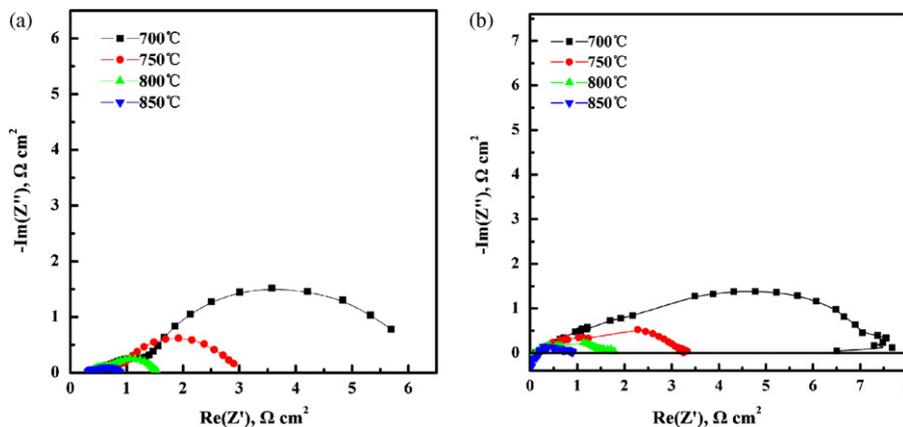


Fig. 4. Electrochemical impedance spectra for a SOFC with Ni/ScSZ anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperature under open circuit.

the Fe–Ni/ScSZ anode and the PCM cathode, contact resistance at the electrode/electrolyte interface, and contact resistance between the electrodes and current collector [27]. The high-frequency and low-frequency depressed arcs are due to the different electrode polarization processes. As above-mentioned, the compositions and preparation conditions for the electrolyte and cathode, as well as the single cell fabrication steps, were identical for the two single cells; therefore, the cathodic polarization resistance and total ohmic resistance of the cells should be the same. Since the high-frequency arc remained essentially constant for the different cells, it was assigned to be from the cathode. On the other hand, the low-frequency arc changed significantly as the anode composition varied; therefore, it was related to the anodic process. As could be expected through examination of Figs. 4 and 5, the cell with Ni/ScSZ anode exhibits slightly less total impedance than that observed for the cell with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode. The slow electrochemical oxidation of humidified hydrogen and ethanol steam at these temperatures was due to the anodes employed in these SOFCs, which combined Ni/ScSZ with Fe. Impedance measurements taken in humidified hydrogen or ethanol steam for Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes indicated that the Fe caused the interfacial resistance to increase.

3.3. Cell stability tests

The stabilization and the degradation of the two cells with Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes were also investigated in ethanol steam at 700°C during the measurements. The electrochemical impedance spectra were measured during the aging process. Fig. 6 depicts the electrochemical impedance spectra for the two cells with Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes at 700°C under open circuit at different operating time. As can be seen from Fig. 6, the overall electrode polarization (interface) resistance (R_E) is decreasing with time. This implies that, in the case of two anode materials, the electrochemical reaction rates are increasing with time. The variation of the overall electrode polarization resistance with time for the two cells with Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes indicates that the electrochemical oxidation reaction of ethanol steam are not taking place under constant conditions, rather the conditions at the anode surface are modified with the time of exposure to ethanol steam. These surface modifications affect electrochemical performance of anode samples. The changes in the impedance spectra can be assumed to be due to carbon deposition in the anode shown in Fig. 1. Visual inspection of the cell after the end of the test revealed carbon deposition on the anode material and the surroundings. The

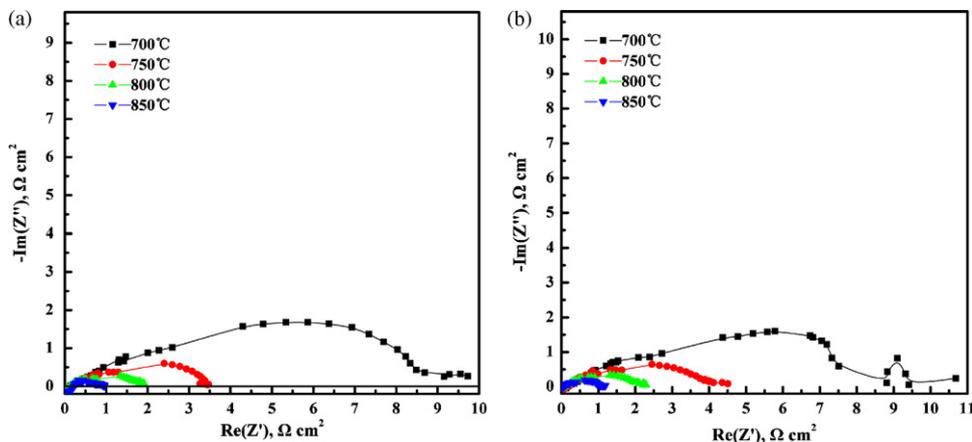


Fig. 5. Electrochemical impedance spectra for a SOFC with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode while running on humidified hydrogen (a) and ethanol steam (b) at different temperature under open circuit.

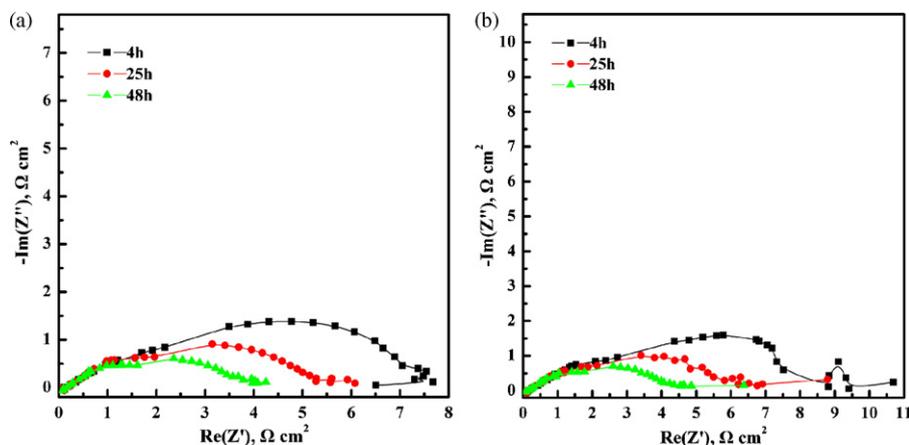


Fig. 6. Electrochemical impedance spectra of (a) Ni/ScSZ anode and (b) $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode in ethanol steam at 700°C under open circuit during the aging process.

decrease of the R_E after carbon deposition can be understood by the model similar to that proposed by Gorte and coworkers [28]. Metal Fe–Ni in the anode acts also for the efficient current collection. Some metal particles are expected to be not connected to the outside circuit and can not assist in the removal of electrons. Therefore, the entire region under the isolated metal particle is ineffective for the electrochemical reaction. With the addition of moderate levels of carbon, these isolate metal particles could become electronically connected to the outside circuit. Because more of the anode surface is now involved in the electrochemical reaction, the effect of using a higher fraction of the surface will be an apparent decrease in polarization resistances. Further work will be required to do to verify the activity and stability of Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes in ethanol stream in a long term.

4. Conclusions

Fe–Ni/ScSZ composite anodes have been studied as anode materials for SOFC running on ethanol fuel. We have demonstrated that carbon formation is greatly suppressed on SOFC anodes based on Fe–Ni alloys compared to Ni-based anodes. A mixing between Ni and Fe appears to be a suitable approach to achieve a good compromise between proper catalytic activity and the suppressing of the carbon deposition. The present results show that SOFC with $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anode can be operated directly with ethanol fuel, yielding high power densities. The performance of a fuel cell made with the Ni/ScSZ and $\text{Fe}_{0.5}\text{Ni}_{0.5}/\text{ScSZ}$ anodes was tested in ethanol stream for 48 h and showed a significant decrease in polarization resistance with time. Impedance spectra of similar fuel cells suggest that small carbon deposits are formed with time and that the decrease in polarization resistance is due to enhanced electronic conductivity in the anode. Also, the fact that carbon deposition was clearly observed after these tests indicates that the cells are not likely to be stable over time. So, again, inclusion of some longer-term data for cells operating at a realistic current/voltage condition would be a more appropriate way to conclude this report.

Acknowledgements

The authors thank the Shanghai Institute of Ceramics Chinese Academy of Sciences, the Postdoctoral Foundation of Shanghai (Grant No. 06R214156) and the Postdoctoral Foundation of China (2006) for the grants that support this research.

References

- [1] E. Perry Murray, T. Tsai, S.A. Barnett, *Nature* 400 (1999) 649.
- [2] S. Park, J.M. Vohs, R.J. Gorte, *Nature* 404 (2000) 265.
- [3] B.C.H. Steele, I. Kelly, H. Middleton, R. Rudkin, *Solid State Ionics* 28 (1988) 1547.
- [4] S.P. Jiang, S.H. Chan, *Mater. Sci. Technol.* 20 (2004) 1109–1118.
- [5] S.P. Jiang, S.H. Chan, *J. Mater. Sci.* 39 (2004) 4405–4439.
- [6] C.H. Bartholomew, *Catal. Rev. Sci. Eng.* 24 (1982) 67–70.
- [7] R.T.K. Baker, *Carbon* 27 (1989) 315–323.
- [8] B.C.H. Steele, *Solid State Ionics* 86–88 (1996) 1223–1234.
- [9] K. Hernadi, A. Fonseca, J.B. Nagy, A. Siska, I. Kiricsi, *Appl. Catal. A* 199 (2000) 245–255.
- [10] J.H. Koh, Y.-S. Yoo, J.-W. Park, H.C. Lim, *Solid State Ionics* 149 (2002) 157–166.
- [11] R.J. Farrauto, C.H. Bartholomew, *Fundamentals of Industrial Catalytic Processes*, first ed., Blackie Academic & Professional, London, 1997, pp. 341–343.
- [12] S. Park, J.M. Vohs, R.J. Gorte, *Nature (London)* 404 (2000) 265–266.
- [13] R.J. Gorte, S. Park, J.M. Vohs, C. Wang, *Adv. Mater.* 12 (2000) 1465–1469.
- [14] S. Park, R. Craciun, J.M. Vohs, R.J. Gorte, *J. Electrochem. Soc.* 146 (1999) 3603–3605.
- [15] S. Park, R.J. Gorte, J.M. Vohs, *J. Electrochem. Soc.* 148 (2001) A443–A447.
- [16] H. Kim, C. daRosa, M. Boaro, J. MVohs, R.J. Gorte, *J. Am. Ceram. Soc.* 85 (2002) 1473–1476.
- [17] A. Ringuedé, D.P. Fagg, J.R. Frade, *J. Eur. Ceram. Soc.* 24 (2004) 1355.
- [18] M. Shinagawa, T. Ishihana, A. Kawakami, H. Nishiguchi, Y. Takita, *The Electrochemical Society Proceedings Series*, Pennington, NJ, 2005, p. 1331.
- [19] EG&G Services, Parsons, Inc., and Science Applications International Corporation, *Fuel Cell Handbook*, Rev. 5, U.S. Department of Commerce, Springfield, VA, 2000, pp. 138.
- [20] J.H. Sinfelt, J.L. Carter, D.J.C. Yates, *J. Catal.* 24 (1972) 283.
- [21] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, *J. Catal.* 140 (1993) 16.

- [22] L.B. Avdeeva, O.V. Goncharova, D.I. Kochubey, V.I. Zaikovskii, L.M. Plyasova, B.N. Novgorodov, Sh.K. Shaikhutdinov, *Appl. Catal. A* 141 (1996) 117.
- [23] T. Horita, N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya, *J. Electrochem. Soc.* 143 (4) (1996) 1161–1168.
- [24] H. Alqahntany, D. Eng, M. Stoukides, *J. Electrochem. Soc.* 140 (1993) 1677.
- [25] R. Morrel, *Handbook of Properties, Technical and Engineering Ceramic, Part 1*, NPL, 1986.
- [26] X.-F. Ye, B. Huang, S.R. Wang, Z.R. Wang, L. Xiong, T.L. Wen, *J. Power Sources* 164 (2007) 203–209.
- [27] Y. Leng, S. Chan, K. Khor, S. Jiang, *Int. Hydrogen Energy* 29 (2004) 1025.
- [28] H. Kim, C. Lu, W.L. Worrell, J.M. Vohs, R.J. Gorte, *J. Electrochem. Soc.* 149 (3) (2002) A247–A250.