



Short communication

 $(\text{Ni}_{0.75}\text{Fe}_{0.25-x}\text{MgO})/\text{YSZ}$ anode for direct methane solid-oxide fuel cellsYan Liu^a, Yaohui Bai^a, Jiang Liu^{a,b,c,*}^a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, PR China^b The Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, 381 Wushan Road, Guangzhou 510641, PR China^c The Key Laboratory of New Energy Technology for Guangdong Universities, Department of Education of Guangdong Province, Guangzhou 510641, PR China

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ABSTRACT

$(\text{Ni}_{0.75}\text{Fe}_{0.25-x}\text{MgO})/\text{YSZ}$ samples—with a varying weight percentage x (0, 5%, 10%) of MgO with respect to $\text{Ni}_{0.75}\text{Fe}_{0.25}$ —were prepared and studied as anodes for intermediate temperature solid oxide fuel cells (SOFCs) operated on humidified methane (3% H_2O). Among the cells with different anode compositions, it was found that the cell with the $(\text{Ni}_{0.75}\text{Fe}_{0.25}-5\%\text{MgO})/\text{YSZ}$ anode showed the highest power density, giving 648 mW cm^{-2} at 800°C . The cells with MgO-doped anodes were able to operate stably for 20 h under a current density of 0.53 A cm^{-2} at 700°C without observed degradation, while the cells without MgO degraded rapidly. The mechanisms responsible for the superior performance and duration of the $(\text{Ni}_{0.75}\text{Fe}_{0.25}-5\%\text{MgO})/\text{YSZ}$ anode were analyzed.

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1. Introduction

Using solid oxide as an electrolyte, solid oxide fuel cells (SOFCs) can convert the chemical energy of fuels directly to electricity. SOFCs have been widely investigated due to their high energy conversion efficiency and fuel flexibility. SOFCs are therefore a promising candidate technology for the generation of electrical power for stationary applications such as power plants and next-generation home electricity-heat cogeneration systems [1–6]. Hydrogen, the most widely used fuel in fuel cells, is usually produced from hydrocarbon steam reforming. If hydrocarbons could be directly used as fuel, overall energy costs would be significantly reduced [7].

Ni–YSZ anodes are one of the most commonly used and extensively studied materials for SOFCs [8,9]. Ni has good electrical conductivity, and high catalytic activity towards H_2 oxidation. One function of YSZ in the anode is to provide ionic conductivity and to increase the triple phase boundary (TPB) for the anode reaction. The other function is to avoid Ni particle coarsening from sintering [10]. Though Ni–YSZ anodes show good performance in SOFCs using hydrogen fuel, coking is a fatal problem when using hydrocarbon fuel. Even for hydrogen SOFCs, there is still a strong expectation that novel anodes with better performance can be developed. It has been found that doping the Ni sites in the anode

with a small amount of Fe can improve the SOFC performance with H_2 fuel. This improvement in performance might be related to the unique electronic interaction between the Ni and Fe atoms in the Ni–Fe alloy [11]. Ding et al. [12] reported that the microstructure of the anode could be improved by doping NiO with a suitable amount of Fe (close to the mol ratio of Fe:Ni = 1:9); the improvement resulted from the fact that the loose structure of $\text{Ni}_{1-x}\text{Fe}_x\text{O}$ increased the triple phase boundary (TPB) of the anode, while the traditionally used NiO coarsened easily. Ishihara et al. [13] also found that the activation energy of the anode reaction with Fe dopant decreased, and the H_2 oxidation kinetics for the Ni-based anode changed.

Although Ni–Fe-based anodes can improve the performance of SOFCs using H_2 as fuel, a serious coking problem still remains [14–17]. To overcome this problem, substantial effort has been devoted to the development of new anode materials. For example, Cu-based anodes have been developed for direct hydrocarbon SOFCs, due to the inertness of Cu with respect to the cracking reaction of hydrocarbons [18]. However, the poor catalytic activity of Cu for fuel oxidation limits the cell's power output, and the techniques optimized for the fabrication of SOFCs with Ni-based anodes are not applicable for Cu-based anodes, because of the low melting point of Cu. Some nickel-free conducting metal oxides have also been developed as anode materials, based on a consideration of their electronic and ionic conductivities [19,20]. In many cases, however, the power densities of SOFCs using Ni-free oxide anodes are lower than those shown by conventional Ni–YSZ-supported SOFCs with thin electrolytes; this may result from the detrimental reaction between the anode materials and YSZ, or inadequate lateral conductivity [21].

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It has been demonstrated that Ni-based anodes can operate stably with hydrocarbon fuels at high currents; this is because the carbon deposited on Ni can be oxidized by the oxygen-ion flux across the electrolyte [22]. Note that carbon can be used directly as a fuel for SOFCs [23]. Carbon deposition itself should therefore not be an essential reason for anode failure. It is most likely that cracks caused by carbon deposition are the real problem; it seems that carbon deposition on Ni in the anode can cause stress in the anode, resulting in cracks [24]. This is somewhat similar to the anode degradation caused by Ni–NiO–Ni redox cycling. Some progress has been made recently towards Ni–NiO–Ni redox cycling stability, via the addition of a stable oxide (such as CaO, MgO, TiO₂ and Al₂O₃) to the anode cermet [25,26]. The improvement in anode endurance was attributed to the suppression of the physical Ni–NiO–Ni transformation during redox cycling, resulting in the reduction or elimination of internal anode stress. It is proposed that—based on a similar mechanism—the addition of these additives would allow the anode to endure the stress caused by carbon deposition, and would produce better coking tolerance than that shown by traditional Ni–YSZ anodes.

To verify the mechanism described above, (Ni_{0.75}Fe_{0.25}–xMgO)/YSZ was prepared and used as the anode material for anode-supported SOFCs. The performance of the cells was measured at intermediate temperatures, using humidified methane as fuel and ambient air as oxidant, with special attention paid to the optimal amount of MgO to be added to the bulk anode. The microstructures of the anodes were also examined and analyzed in detail.

2. Experimental

2.1. Preparation of anode

Ni_{0.75}Fe_{0.25} [27] oxide powder was prepared using the glycine–nitrate process (GNP), as reported earlier [28]. First, stoichiometric amounts of Ni(NO₃)₂·6H₂O (A.R., Guangdong Guanghua Chemical Factory Co. Ltd., Guangdong, China) and Fe(NO₃)₃·9H₂O (A.R., Tianjin Kermel Chemical Reagents Co. Ltd., Tianjin, China) were dissolved in distilled water to form a precursor solution. A suitable amount of glycine (NH₂–CH₂–COOH, A.R.) was added to the solution. The solution was then boiled to evaporate the excess water. The molar ratio of glycine to nitrate was 1:1. The resulting viscous liquid was auto-ignited and combusted, producing an ash composed of Ni_{0.75}Fe_{0.25} oxide products. The ash was then fired at 800 °C for 2 h to remove any possible carbon residues. The as-prepared Ni_{0.75}Fe_{0.25} oxide powder was then characterized with X-ray powder diffraction (XRD) on a Bruke D8 ADVANCE diffractometer (Cu K α radiation, operated at 40 kV, 40 mA). The selected 2 θ range was from 20° to 80°, scanning in increments of 0.02°. The XRD patterns were analyzed and determined with PCPDFWIN 1.10 software, along with previous correlative XRD literature [12,11,29].

The cone-shaped tubular anode substrates were prepared using a dip coating technique, as detailed in our previous work [30]. Different amounts of MgO (A.R., Tianjin Institute of Chemical Reagents, Tianjin, China) (0 wt.%, 5 wt.% and 10 wt.%) were added to the as-prepared Ni_{0.75}Fe_{0.25} oxide. The Ni_{0.75}Fe_{0.25}–xMgO and YSZ (8 mol% Y₂O₃, 6.5 m² g^{−1}, Tosoh) were thoroughly mixed with a weight ratio of 1:1. Accordingly, the three anode materials were named as Ni_{0.75}Fe_{0.25}/YSZ, (Ni_{0.75}Fe_{0.25}–5%MgO)/YSZ, and (Ni_{0.75}Fe_{0.25}–10%MgO)/YSZ. In addition, 10 wt.% carbon powder was added as a pore former, to produce sufficient porosity. Homogeneous anode slurry was achieved by ball-milling the as-prepared powders with the proper amounts of organic additives and solvent. A metal mould with a cone-shaped outline was then dipped into the slurry. After a few seconds, the mould was removed from the

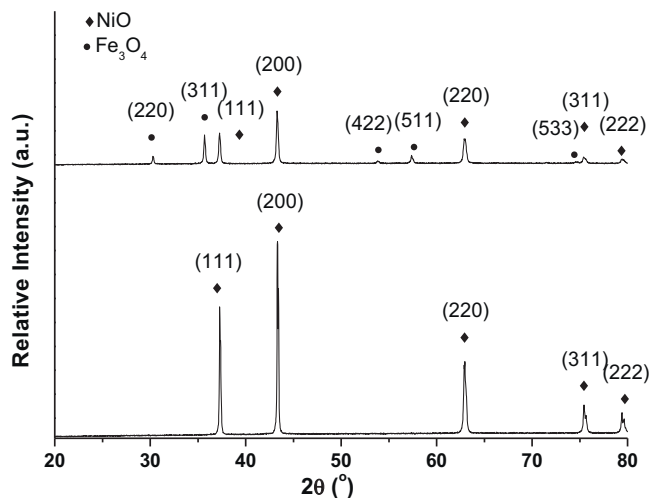


Fig. 1. XRD spectra for pure NiO and the as-prepared Ni_{0.75}Fe_{0.25} oxide powder.

slurry, and the layer of slurry coated on the mould was dried in air. This dip-coating process was repeated several times, until the required thickness was achieved. The green anode substrate was removed from the mould and pre-fired at 1200 °C for 2 h.

2.2. Single SOFC assembly and testing

The YSZ electrolyte thin film was coated on the anode substrate. The anode/electrolyte bi-layer was then co-sintered at 1400 °C for 4 h to densify the YSZ film [31,32]. Cathode powder La_{0.7}Sr_{0.3}MnO₃ (LSM, Ningbo Institute of Physical Chemistry) was mixed with YSZ (Tosoh) to a weight ratio of 6:4. A composite LSM–YSZ functional layer and a pure LSM current collector layer were then applied on the YSZ electrolyte film by brush printing, and were sintered at 1200 °C for 2 h with a heating rate of 2 °C min^{−1}. Silver paste (DAD-87, 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 ohmic loss in the silver wires. The single cone-shaped tubular SOFC was attached to one end of an alumina tube, using silver paste as a sealing and jointing material [33]. The cathode area of all the single cells was controlled to be the same, with a value of 5.7 cm².

The electrochemical performance of the cells was tested using an Iviumstat electrochemical analyzer (Ivium Technologies B.V., Netherlands). In the beginning, the cells were reduced and tested with humidified hydrogen (3 vol.% water at 25 °C, 75 ml min^{−1}) as fuel and ambient air as oxidant, in the temperature range of 600–800 °C. The temperature was then decreased to 700 °C, and the fuel was switched to humidified methane (75 ml min^{−1}). The performances of the cells were tested with methane fuel in the temperature range of 700–800 °C. After that, stability tests were performed using moist methane (75 ml min^{−1}) as fuel. Each stability measurement was taken at 700 °C under a constant current density of 0.53 A cm^{−2}. The microstructure of the cells was characterized after testing using a scanning electron microscope (Philips XL-30FEG, Holland).

3. Results and discussion

3.1. Phase identification and microstructure of the (Ni_{0.75}Fe_{0.25}–xMgO)/YSZ anodes

Fig. 1 shows the XRD spectra for pure NiO and the as-prepared Ni_{0.75}Fe_{0.25} oxide powder. The X-ray spectrum for the pure NiO clearly shows a face-centered cubic (FCC) structure. When the NiO

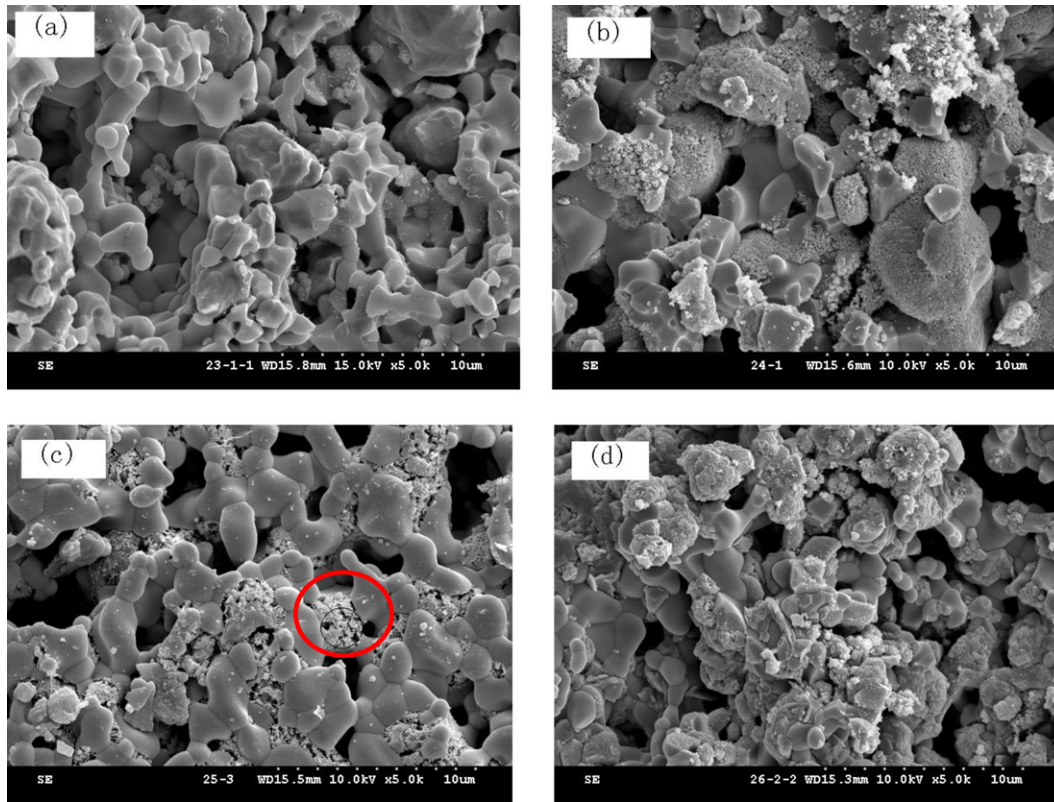


Fig. 2. SEM micrographs of the anode section after the performance and stability test. (a) Ni/YSZ; (b) $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{YSZ}$; (c) $(\text{Ni}_{0.75}\text{Fe}_{0.25}-5\%\text{MgO})/\text{YSZ}$; and (d) $(\text{Ni}_{0.75}\text{Fe}_{0.25}-10\%\text{MgO})/\text{YSZ}$.

was doped with 25 mol% Fe, the pure NiO phase still dominated, but some Fe_3O_4 phase appeared. The lattice parameter for $\text{Ni}_{0.75}\text{Fe}_{0.25}$ calculated from the Scherrer formula was 4.1797 \AA , a little larger than that for pure NiO (4.1701 \AA), indicating that Fe was doped into the crystal structure of NiO, forming a solid $\text{Ni}_{1-x}\text{Fe}_x\text{O}$ solution.

Fig. 2 shows SEM micrographs of the anode substrates of the single cells after the output performance and stability test. It can be seen that the Ni/YSZ sample was relatively dense, with some large particles. When Fe was doped into the anode the structure became more porous, which may have contributed to the improvement in the corresponding SOFC's performance. When 5 wt.% MgO (with respect to $\text{Ni}_{0.75}\text{Fe}_{0.25}$ oxide) was added to the $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{YSZ}$ anode, the resulting microstructure was almost ideal for a SOFC: the YSZ particle/grain size was small and uniform (about $1 \mu\text{m}$), and the particles were well connected through grain boundaries, forming a porous skeleton/backbone. In a poly crystal, small grain size leads to more grain boundaries, resulting in higher mechanical strength, as well as better electrical properties for oxygen-ionic conductors such as YSZ [34]. There were loose structures built in the pores of the YSZ skeleton, as circled in Fig. 2(c). The growth of carbon fibers on Ni may have been suppressed by the addition of MgO. Even if carbon fiber growth did occur on Ni, the mechanically strong YSZ-based skeleton might be able to withstand the stress, and allow the anode to survive. When the MgO content was increased to 10 wt.%, large agglomerates were formed, which is detrimental for SOFC performance. In addition to the formation of these aggregates, larger concentrations of MgO have other effects; with higher amounts of MgO (which is non-conductor) present among the YSZ and Ni particles, the electrical conductivity will be adversely affected. While the inhibiting effects of MgO on the growth of carbon fiber are

still present at higher MgO concentrations, the cell performance becomes worse with the reduced conductivity.

3.2. Cell performance

Fig. 3 shows the performances of the single SOFCs with different anodes at 700°C , using humidified methane as fuel. As can be seen, the maximum power density of the cell with a traditional Ni/YSZ anode was 170 mW cm^{-2} . When Fe was doped into the anode to form a $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{YSZ}$ anode, the power density increased to 270 mW cm^{-2} . The power density increased further to 300 mW cm^{-2} as 5 wt.% of MgO (with respect to $\text{Ni}_{0.75}\text{Fe}_{0.25}$

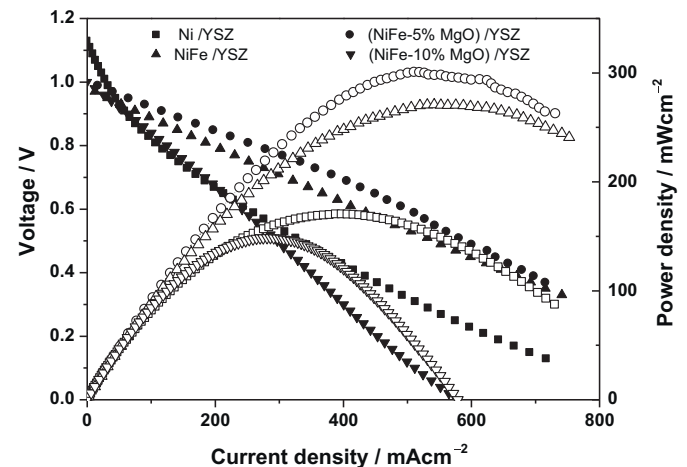


Fig. 3. Performance of single SOFCs with Ni/YSZ and $(\text{Ni}_{0.75}\text{Fe}_{0.25}-x\text{MgO})/\text{YSZ}$ ($x=0\%$, 5% , 10%) anodes at 700°C under humidified methane.

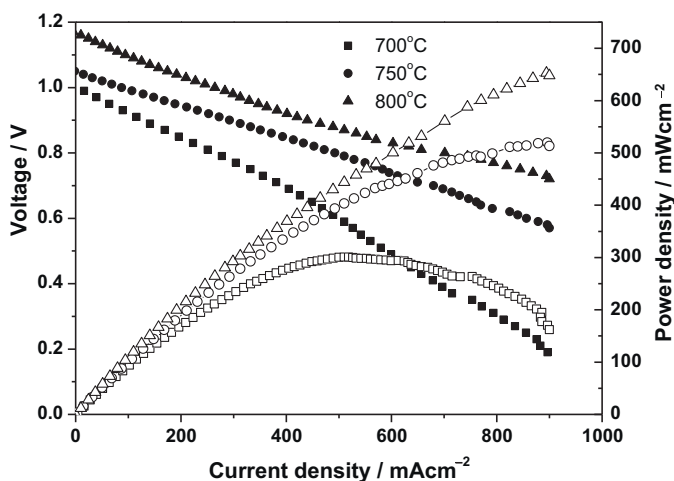


Fig. 4. Performance of the $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5\%MgO})/\text{YSZ}$ anode-supported SOFC operated on humidified methane, from 700 °C to 800 °C.

oxide) was added to the anode, while it dropped to 149 mW cm^{-2} when the MgO content in the anode increased to 10 wt.%. Since the preparation conditions and the effective area of the cathodes were identical for all the single cells, it can be presumed that the difference in performance between these cells was mainly caused by the anode properties. The above results demonstrated again that doping with a suitable amount of Fe can improve the performance of SOFC anodes [11–13]. As an impurity, stable oxide MgO particles tended to locate at the grain boundaries and interfaces of Ni and YSZ. These particles were able to suppress the growth of both Ni and YSZ particles during the calcine process and cell testing, thus giving a better microstructure with smaller grains, as in the case of $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5\%MgO})/\text{YSZ}$. Nevertheless, excess MgO may have influence the conductivity and reduced the number of catalytically active sites, resulting in a decreased power density [35,36], as in the case of $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-10\%MgO})/\text{YSZ}$.

Fig. 4 shows the cell performance of the SOFC with $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5\%MgO})/\text{YSZ}$ anode, using humidified methane (75 ml min^{-1}) as fuel and ambient air as oxidant, from 700 °C to 800 °C. The performance of this single cell was encouraging, with a power density of 648 mW cm^{-2} at 0.7 V and 800 °C. This is a relatively high value, considering that the effective area was 5.7 cm^2 , much larger than those generally reported for single cell tests. It is well known that under the same conditions, a larger effective area (which is more applicable in practical situations) will give a smaller power density value.

3.3. Stability of the $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-xMgO})/\text{YSZ}$ anode

Fig. 5 shows the stability test results for the cells with different anodes. The voltage was measured over the course of the 20 h operation time, using humidified methane (75 ml min^{-1}) as fuel, with a current density of 0.53 A cm^{-2} , at 700 °C. As expected, the cell with the $\text{Ni}_{0.75}\text{Fe}_{0.25}/\text{YSZ}$ anode failed rapidly in methane. When MgO was added into the bulk anode, the voltage remained stable over the whole period of operation.

It is well known that transition metal-based anodes promote carbon deposition when carbon-containing fuel is used in a SOFC. As carbon itself is fuel for SOFCs, it should not cause SOFC failure simply through its deposition/covering of the anode [26,37]. According to the literature, carbon deposition on metals results in a wide variety of physical and chemical structures among which carbon fiber/filaments are dominant; they are found to grow on particles made from metals such as Ni, Co, and Fe [24,38]. The fiber growth on Ni is commonly considered to occur as follows: first,

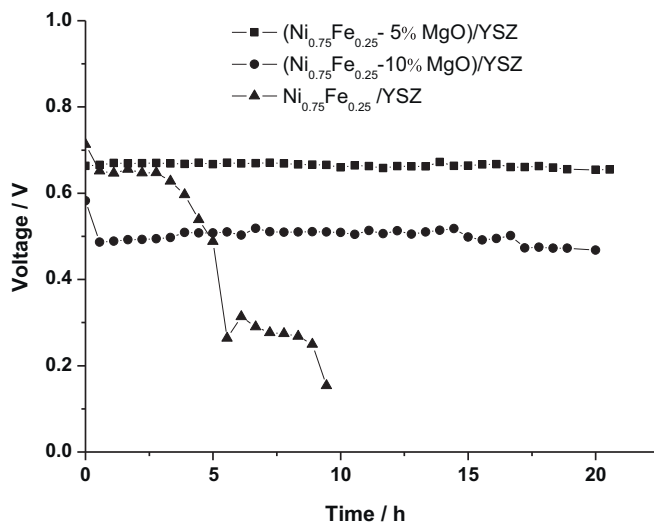


Fig. 5. Stability of SOFCs with $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-xMgO})/\text{YSZ}$ anode operated on humidified methane under a constant current density of 0.53 A cm^{-2} , at 700 °C.

carbon-containing molecules are adsorbed on the metal surface and decompose to form carbon atoms. The carbon atoms then dissolve in and diffuse through the bulk of the metal, and precipitate in the form of graphite on the other side (generally a preferred facet for metal–graphite interface) of the metal particle. The carbon precipitation displaces restructured metal crystallites from the bulk metal while carbon fibers grow, carrying with them the metal crystallite, i.e., with metal particles on the tip of the fibers, causing fragmentation of the metal [24]. This carbon fiber growth on transition metal particles can well explain the anode fracturing resulting from the operation of SOFCs with hydrocarbon fuels: first, the fragmentation of metal caused by the carbon fiber growth weakens the anode. Then, with their relatively high mechanical strength, the carbon fibers growing in the pores of the anode will cause great stress in the weakened anode, resulting in the fracture, and thus failure, of the anode.

To avoid carbon fiber growth on metal, the enhancement of metal-support interactions and the doping of the metal with oxides have been suggested [38]. The good performance of the presented anode $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5\%MgO})/\text{YSZ}$ with methane may have been related to the following factors: (1) the doping of the metal with a stable oxide may have suppressed carbon fiber growth; (2) MgO may have enhanced the metal–YSZ or metal–MgO interactions, leading to a metal–substrate interfacial free energy that was larger than the sum of that of carbon–substrate and carbon–metal, thus prohibiting carbon fiber growth on the metal [39]; (3) MgO particles located on the grain boundaries of YSZ made the YSZ skeleton strong enough to stand the stress caused by carbon fiber growth, as in the case of Al_2O_3 to YSZ [34].

4. Conclusions

$(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5\%MgO})/\text{YSZ}$ is a promising anode material for SOFCs operated using methane fuel. When doped with Fe, the microstructure of the anode was improved, leading to a much better output performance for the corresponding SOFCs than that of those using traditional Ni/YSZ anodes. It is proposed that the degradation of Ni-based anodes resulting from the use of hydrocarbon fuel or carbon-containing fuel is caused by carbon fiber growth. Doping with a small amount of MgO enabled the anode to be stably operated in methane, due to the fact that MgO strengthened the anode, allowing it to endure the stress caused by carbon fiber growth. In conclusion, high-performance and high-stability SOFCs

using hydrocarbon fuel were realized with a Ni-based anode with improved microstructure and carbon fiber growth-inhibiting properties. There may be other ways to reach the same goal; we have shown here that doping with Fe and MgO is one effective route.

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