



## Porous Ni–Fe alloys as anode support for intermediate temperature solid oxide fuel cells: I. Fabrication, redox and thermal behaviors



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### H I G H L I G H T S

- Redox behaviors of porous Ni–Fe alloys are systematically investigated.
- Thermal expansion/cycling behaviors are systematically investigated.
- A modified oxidation kinetics equation for porous metal was proposed.

### A R T I C L E I N F O

#### Article history:

Received 25 July 2014

Received in revised form

16 September 2014

Accepted 3 October 2014

Available online 29 October 2014

#### Keywords:

Metal-supported solid oxide fuel cell

Porous Ni–Fe alloy

Oxidation resistance

Redox

Thermal cycles

### A B S T R A C T

Porous Ni–Fe anode supports for intermediate solid oxide fuel cells are prepared by reducing the sintered NiO-(0–50 wt. %) Fe<sub>2</sub>O<sub>3</sub> composites in H<sub>2</sub>, their microstructure, redox and thermal expansion/cycling characteristics are systematically investigated. The sintered NiO–Fe<sub>2</sub>O<sub>3</sub> composites are consisted of NiO and NiFe<sub>2</sub>O<sub>4</sub>, and are fully reducible to porous metallic Ni–Fe alloys in H<sub>2</sub> at temperatures between 600 and 750 °C. The porous structure contains pores in bimodal distribution with larger pores between the sintered particles and smaller ones inside the particles. The oxidation resistance of the Ni–Fe alloy anode supports at 600 and 750 °C is increased by the addition of Fe, their oxidation kinetics obeys a multistage parabolic law in the form of (Percentage weight gain/Specific surface area)<sup>2</sup> =  $k_p \cdot t$ , where  $k_p$  is the rate constant and  $t$  the oxidation time. The dimension of the Ni–Fe anode supports is slightly changed without disintegrating their structure, and Fe addition is beneficial to the redox stability. The TEC of the Ni–Fe alloy anode supports decreases with the increase of Fe content. The anode supports containing Fe is less stable in dimension during thermal cycles due to the continuous sintering, but the dimension change after thermal cycles is within 1%.

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### 1. Introduction

Reducing the operating temperature of solid oxide fuel cells (SOFCs) from near 1000 °C to the intermediate temperature (IT) range between 500 and 800 °C allows metallic materials to be utilized as cell and stack components, such as cell support [1] and interconnect [2]. The idea of metal-supported SOFC was firstly proposed in 1960s [3], however, less attention has been paid to it until late 1990s [4]. Since then metal-supported SOFC has been extensively investigated as the advantages of the metallic support, including reliable mechanical structure, excellent thermal/

electrical conductivity and reduced material cost, have been recognized by the SOFC community [5].

Ferritic stainless steels with body-centered-cubic structure are the primary material choice for the anode support, such as SUS 430 [6–11], Crofer22 [12–15] and ZMG 232 [15], since they possess relatively high resistance to oxidation in IT-SOFC environments and are well matched to the cell components in thermal expansion behavior. Austenitic stainless steels [16–18] and high temperature alloys [7,19] have also been considered as the candidate materials due to their excellent resistance to oxidation, even though the thermal expansion coefficient (TEC) of them is significantly higher than that of the ceramic cell. Other than the above mentioned commercial stainless steels and superalloys, porous Ni has been used for the cell support [20–23] as well, because metallic Ni is inert in the anode atmosphere of IT-SOFCs. The TEC of Ni

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( $16.5 \times 10^{-6} \text{ k}^{-1}$ ) is not well matched with those of other cell components ( $10\text{--}13 \times 10^{-6} \text{ k}^{-1}$ ), which causes difficulties in cell fabrication and operation. Adding Fe into Ni decreases the TEC of Ni [24], therefore Ni–Fe alloy has attracted increasing attention as another kind of alternative support materials [25–34].

Porous Ni–Fe alloy anode support is usually made by sintering NiO–Fe<sub>2</sub>O<sub>3</sub> in air at a high temperature, followed by reduction in H<sub>2</sub> at a lower temperature. A variety of NiO–Fe<sub>2</sub>O<sub>3</sub> compositions approximately between 10 and 70 wt. % Fe<sub>2</sub>O<sub>3</sub> have been studied by Ishihara et al. [25–33] and Park et al. [34]. High performance has been obtained at intermediate temperatures with cells prepared either by plasma laser ablation or slurry printing. The purpose of the present study is to systematically investigate Ni–Fe alloy anode support itself and provide experimental results related to the redox and thermal behaviors. The results related to the performance of Ni–Fe alloy supported cells will be reported elsewhere in near future.

## 2. Experimental

### 2.1. Fabrication of Ni–Fe alloy anode support

Porous Ni–Fe alloy anode supports were fabricated by reducing (in H<sub>2</sub>) the as-sintered NiO–Fe<sub>2</sub>O<sub>3</sub> composites containing 0, 10, 30 or 50 wt. % of Fe<sub>2</sub>O<sub>3</sub>, designated as NF0, NF10, NF30 and NF50, respectively. The starting NiO (~0.3 μm, Inco, type standard) and Fe<sub>2</sub>O<sub>3</sub> (~0.3 μm, Sinopharm Chemical Reagent) powders were mixed proportionally and ball-milled for 24 h in an organic solution consisting of xylene and anhydrous ethanol with fish oil as the dispersant and corn starch as the pore former. After the addition of plasticizer (polyethylene glycol) and binder (polyvinyl butyral), the slurry was ball-milled for another 24 h and then tape cast using an in-house made tape caster. Disc specimens (φ25 × 1 mm) were cut from the green tape, and sintered in air at 1470 °C for 4 h. In practical cell fabrication, cell components such as functional anode and electrolyte are built on the sintered NiO–Fe<sub>2</sub>O<sub>3</sub> substrate. Subsequent cell reduction procedure, especially the reduction temperature, is critical for maintaining cell integrity. Therefore herein two different reduction procedures, at 650 and 750 °C in H<sub>2</sub> for 3 h, respectively, were adopted to obtain metallic Ni–Fe alloy substrates.

### 2.2. Evaluation of redox and thermal behaviors

To understand the redox behavior of the Ni–Fe alloy substrates, they were subjected to oxidation in flowing air at 600 or 750 °C for 2 h in a thermogravimetric analyzer (Diamond TG, PerkinElmer Instruments) and re-reduction in flowing H<sub>2</sub> for 2 h in an atmosphere-controlled furnace at the same temperature. The weight gain of the specimen caused by oxidation was recorded, and the dimension of the specimen at each stage was measured with a digital caliper.

For TEC measurement and thermal cycling test, rod specimens (φ8 × 10 mm) were prepared as required by press-forming and sintering in air at 1470 °C for 4 h, followed by reduction in H<sub>2</sub> for 5 h. The specimens for TEC measurement were reduced at a higher temperature of 850 °C to diminish the sintering effect during the measurement, and those for thermal cycling were reduced at 650 or 750 °C to simulate the procedure of cell fabrication. A thermo-mechanical analyzer (TMA Q400EM, TA Instruments-Waters LIC) was employed for TEC measurement at a heating of 5 °C min<sup>-1</sup> up to 800 °C and thermal cycling at a rate of 5 °C min<sup>-1</sup> between 200 and 600 or 750 °C in Ar environment.

### 2.3. Characterization of specimens

The phases in the specimens were identified by X-ray diffraction (XRD, X'Pert Pro, PANalytical B.V. Corporation, Holland). The microstructures of the specimens were examined by using a scanning electronic microscope (SEM, Quanta 200, FEI Corporation, Holland). The porosity of the specimens was measured by the Archimedes method. The pore size distribution was determined by Mercury Porosimetry (Poromaster GT/60, Quantachrome).

## 3. Results and discussion

### 3.1. Phase and microstructure

Fig. 1 shows the XRD patterns of the as-sintered and reduced disc substrates with various Fe contents. In the sintered state the substrate was consisted of NiO (JCPDS file 01-071-1179) and NiFe<sub>2</sub>O<sub>4</sub> (JCPDS file 01-074-2081), after the reduction in H<sub>2</sub> for 3 h at 650 °C, the substrates were fully reduced to a single phase Ni–Fe alloy with an FCC crystal structure (JCPDS file 01-070-0989). The observed peak shift towards smaller 2θ angle is caused by the addition of Fe. Similar diffraction patterns were obtained from the specimens reduced in H<sub>2</sub> for 3 h at 750 °C. In general, the above results are consistent with those reported previously [30,34].

Fig. 2 demonstrates the cross-sectional microstructure of the as-sintered and reduced disc substrates with various Fe contents. The sintered substrates were porous, but gradually densified with the increase of Fe content, which suggests that adding Fe<sub>2</sub>O<sub>3</sub> into NiO enhances the sinterability of NiO–Fe<sub>2</sub>O<sub>3</sub> composite due to the formation of NiFe<sub>2</sub>O<sub>4</sub>. The reduced substrates were also porous and densified with the increase of reduction temperature. The pore structure tends to a bimodal distribution with larger pores between sintered particles and smaller pores inside one particle, except for NF50 reduced at 750 °C due to the simultaneous sintering during reduction. This observation is confirmed by the results from Mercury Porosimetry as shown in Fig. 3. Table 1 lists the porosity and specific surface area of all the specimens in different states. The porosity in reduced specimens was in the range between 34.88 and 52.54%, which meets the requirement for an anode support that is capable of transporting adequate fuel to the functional anode. The specific surface area decreased as the reduction temperature

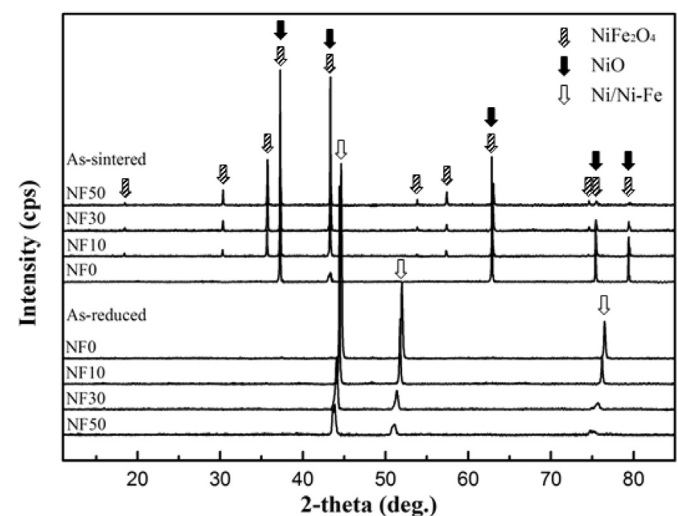


Fig. 1. XRD patterns of the disc Ni–Fe anode supports before and after reduction in H<sub>2</sub> at 650 °C for 3 h.

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