



Ni–P coated Ni foam as coking resistant current collector for solid oxide fuel cells fed by syngas

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ABSTRACT

Ni–P amorphous alloy coatings with different P content are coated onto porous Ni foam by means of electroless plating. The plated Ni foams exhibit excellent carbon deposition resistance and structure stability in syngas at elevated temperature when P content is higher than 6.5 wt% in the coating. Anode supported solid oxide fuel cells fabricated using a spin coating process have a maximum power density of $\sim 1.3 \text{ W cm}^{-2}$ in H_2 at 850°C and $\sim 0.8 \text{ W cm}^{-2}$ in syngas at 800°C . The H_2 -fueled cells with naked and plated Ni foam current collector have very similar internal ohmic resistance and power density, which confirm the good electronic conductivity of the coatings. The syngas-fueled cells with Au mesh and plated Ni foam current collector reach almost identical power density and internal resistance, and the latter has no apparent degradation of power output during extended fuel cell stability testing. Thus Ni–P is a promising carbon deposition resistant coating of current collector for syngas-fueled solid oxide fuel cells.

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1. Introduction

Syngas, a mixture of hydrogen and carbon monoxide ($\text{H}_2 + \text{CO}$), has gained increasingly interest as fuel for solid oxide fuel cells (SOFC) as it has lower price and wider availability than pure H_2 [1–4]. When SOFC design is based on electrode support rather than electrolyte support, the optimum operating temperature is decreased to $\sim 750^\circ\text{C}$ from $\sim 1000^\circ\text{C}$, which makes the use of metallic current collectors (i.e., the interconnect) economically feasible [5]. However, the use of metallic components in syngas fuel at elevated temperature may lead to severe coking, also known as metal dusting, resulting in performance degradation during long term operation [6,7].

Great efforts have been made to protect metals against metal dusting in carbon containing atmospheres [8–10]. For example, carbon deposition is suppressed when H_2S is present in feeds such as syngas or natural gas [8]; however, H_2S poisons Ni anode catalyst [11]. Dense, uniform oxide layers have been applied in attempts to provide protections [9], but commonly their low electronic conductivity does not meet the requirements for use as current collector. Although electroplated Cu is effective in protecting Ni [10], it is difficult to form uniformly thick deposits on a highly porous matrix such as Ni foam. Also, a high Cu/Ni ratio is needed to inhibit carbon deposition.

Electroless plating of Ni–P coatings is a well-known commercial process which has been applied in many fields due to its excellent capability to provide coatings with good corrosion resistance, high uniformity of the deposits on complex shapes, low cost and outstanding compatibility with the metal matrix [12,13]. However, there are no reports describing the application of Ni–P as coking resistant coating for current collectors. In this work, Ni–P alloy was electrolessly plated onto Ni foam current collectors. The resistance to carbon deposition of plated Ni foam was studied and the performance of syngas SOFC with plated current collector was also investigated.

2. Experimental

2.1. Ni foam electroless plating

The Ni foam used is a commercial product (1.7 mm thick, 0.51 g cm^{-2}), INCOFOAM® from Vale Canada Ltd. It was cut into $1 \text{ cm} \times 1 \text{ cm}$ squares and treated with ultrasonic bath in ethanol for 30 min, then those samples were washed with de-ionized water ultrasonically for 10 min.

Both homemade and commercial electroless plating solutions from Alfa Aesar were adapted in this experiment to achieve different compositions of the coating. The composition of homemade solution was: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 0.23 mol L^{-1} ; $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ 0.17 mol L^{-1} and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 0.27 mol L^{-1} . Before plating, Ni foam samples were immersed into plating solution and evacuated ($< 20 \text{ kPa}$) for 5 min to remove bubbles that formed on the foam. Then

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the solution was heated up to 85 °C in a water bath at which it was held for 10–30 min during the plating process. After plating all the plated samples were rinsed with de-ionized water and dried in a stream of air.

2.2. Fuel cell fabrication

The most widely used anode supported SOFC design was selected in this experiment [14–16]. To fabricate the anode support substrate, 33 wt% YSZ (yttria stabilized zirconia; TZ-8Y, Tosoh Corporation), 45 wt% NiO and 22 wt% corn starch initially were mixed in ethanol for 24 h using a ball-milling process. After drying the milled slurry, the powder was sieved through a 150-mesh screen to produce a uniform and fine particle mixture. The resulting powder was pressed into discs of 2.54 cm in diameter and then sintered at 1100 °C for 2 h to obtain strong substrates.

The composition of anode functional layer starting materials was chosen as 50 wt% NiO + 50 wt% YSZ. The powder mixture was produced by ball-milling for 24 h. The electrolyte material was YSZ. The cathode material was a mixture of 50 wt% $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-x}$ (LSM-20, Fuel Cell Materials) and 50 wt% YSZ. The anode functional layer and YSZ electrolyte thin film were applied sequentially onto the pre-sintered anode support using spin coating. Then the half-cell was sintered at 1400 °C for 4 h. Finally, the composite cathode layer was coated onto the densified electrolyte using spin coating and then sintered at 1150 °C for 2 h.

2.3. Materials characterization and performance tests

The phases presented in the Ni–P coatings were identified using a Rigaku Rotaflex X-ray diffractometer (XRD) with Cu K α radiation. Morphologies of samples were determined using a Hitachi S-2700 scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDS).

Both plated and naked Ni foam samples were put into a quartz tube and treated with syngas (60% CO + 40% H₂). The weight gains, which corresponded to the amounts of carbon deposits were determined as a function of temperature and duration of exposure.

Plated Ni foam and Au mesh were used as anode and cathode current collectors during fuel cell tests. The SOFC test set-up system was described in our previous work [10]. The active area of the button cell was 0.47 cm², anode fuel flow rate was 50 mL min⁻¹ and cathode air flow rate was 100 mL min⁻¹. During testing each membrane electrode assembly (MEA) was heated to the selected operating temperature and then impedance and current–voltage characteristics were determined using a Solartron 1287 electrochemical interface together with a 1255B frequency response analyzer. The impedance spectra of cells were obtained under open circuit with AC amplitude of 10 mV and the frequency range from 0.1 Hz to 100 kHz.

3. Results and discussions

3.1. Characterization of Ni–P coatings

Fig. 1 shows the XRD patterns of samples before and after high temperature treatment in H₂ for 6 h. The diffraction peaks in XRD patterns for samples were wide before high temperature operation, indicating that the initial Ni–P coatings on Ni foam were amorphous. However, after high temperature treatment, the meta-stable phase transformed into more stable Ni and Ni₃P crystalline phases. Thus, the surface composition of plated Ni foam current collector comprised mainly metallic Ni and Ni₃P during SOFC operation at elevated temperatures. EDX analysis showed that the P content of different coatings depended on the plating conditions as shown in

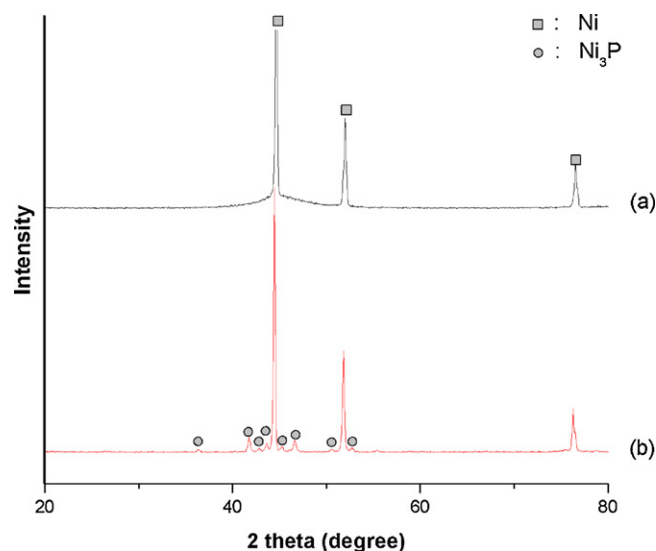


Fig. 1. XRD patterns of (a) plated Ni foam before heat treatment; (b) plated Ni foam after heat treatment in H₂ at 750 °C for 6 h.

Table 1
P content of coatings.

Sample	P content in the coating (wt%)
Ni–P–L	1.2
Ni–P–M	6.5
Ni–P–H	10.7

Table 1. After electroless plating, the porosity of plated Ni foam decreased to 52.3% from original 66.2% based on the weight gains.

3.2. Carbon deposition tests

Fig. 2 shows photographs of samples with different P content in the coatings after treatment in syngas at 750 °C for 24 h. Both naked Ni foam and the plated Ni foam with 1.2 wt% P (sample: Ni–P–L) turned black and brittle whereas there was no apparent surface change for the plated Ni foams with higher P content of 6.5 wt% (sample: Ni–P–M) and 10.7 wt% (sample: Ni–P–H). The weight gains of the samples of naked Ni foam and Ni–P–L each were more than 50%, resulting from high carbon deposition, whereas there was very little weight change for Ni–P–M and Ni–P–H. XRD patterns (Fig. 3)

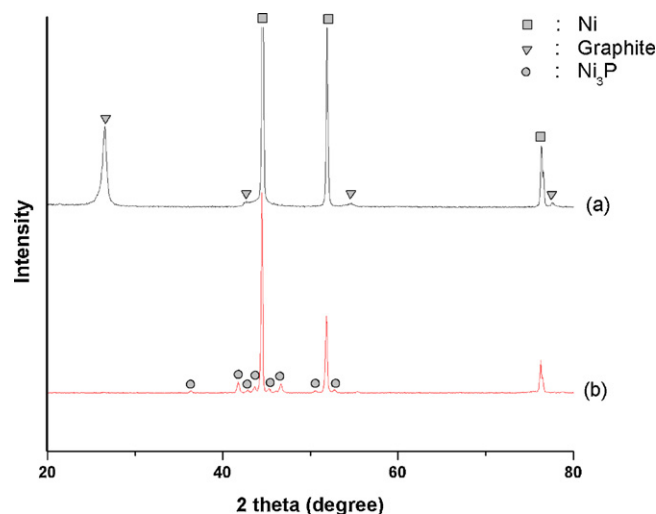


Fig. 2. XRD patterns of (a) naked Ni foam; (b) plated Ni foam, after treatment in syngas at 750 °C for 24 h.

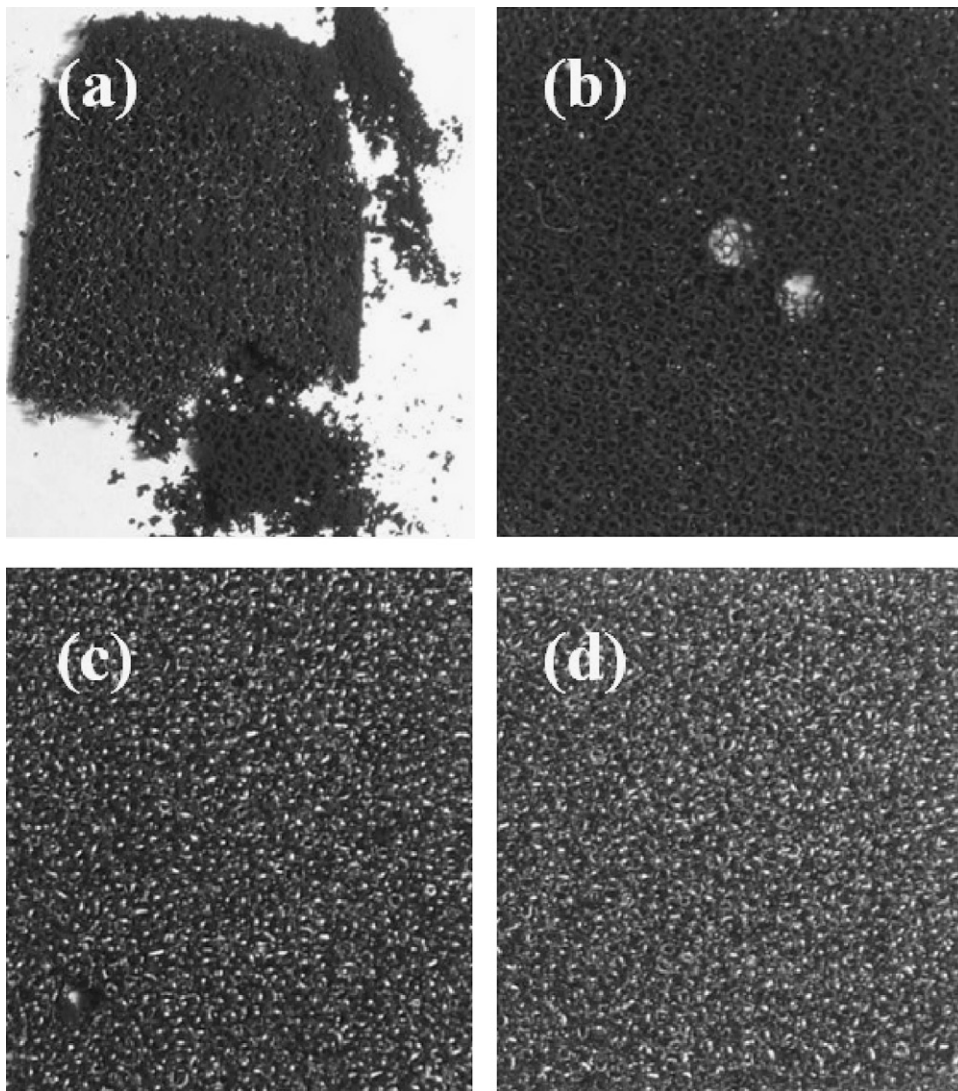
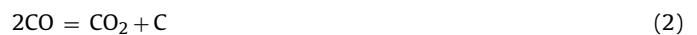


Fig. 3. Photographs of (a) naked Ni foam; (b) Ni-P-L; (c) Ni-P-M; (d) Ni-P-H, after treatment in syngas at 750 °C for 24 h.

also confirmed that no carbon was deposited on Ni-P-M. Thus the sample of Ni-P-M was chosen as the coating for the following parametric studies.

The amount of carbon deposition from syngas on both naked Ni foam and Ni-P-M was determined as a function of temperature and duration of exposure. SEM images (Fig. 4) showed that the surface of naked Ni foam was fully covered with graphite, and the sample became brittle and lost its integrity after treatment in dry syngas at 750 °C for 24 h. In contrast, the plated Ni foam was still shiny with no detectable carbon deposits on the surface and no apparent mechanical strength loss. Fig. 5 shows the weight gain as a function of time for naked Ni foam and Ni-P-M after exposure to dry syngas for at 750 °C. The amount of coking on naked Ni foam increased dramatically and there was a 247% weight gain after 48 h treatment in syngas. In contrast, there was no obvious weight change for plated Ni foam during the same exposure time. Fig. 6 demonstrates the superior carbon deposition resistance of plated Ni foam when compared to naked Ni foam in dry syngas for 24 h at temperatures between 600 °C and 800 °C.

Carbon deposition on metallic Ni in syngas was studied by many researchers e.g. [7,17]. There are two main reactions that are sources of carbon:



Reaction (1) was believed to be the predominant reaction due to its faster kinetics [17]. The carbon formed on the metal surface from reactions of gaseous phases diffused into the bulk and the Ni foam structure was destroyed by direct inward growth of carbon [18]. The coking resistance mechanism of Ni-P coatings is attributable to dilution or poisoning of Ni surface active sites at which C is formed through deposition of inert Ni₃P. This inert phase changes the type and structure of chemisorbed species from syngas. Similar mechanisms have been reported for coking free catalysts such as sulfur-passivated Ni and copper-diluted Ni [19–21].

3.3. Fuel cell tests

Fig. 7 shows an SEM image of a fuel cell cross-section after testing. The thicknesses of the respective layers were: (1) Ni-YSZ anode support substrate: ~800 μm; (2) Ni-YSZ anode functional layer: ~15 μm; (3) YSZ electrolyte ~10 μm; (4) LSM/YSZ composite cathode: ~30 μm. The YSZ electrolyte was essentially dense, which was also proved by the open circuit potential (OCV) (Fig. 8; >1.15 V in H₂). The fuel cell had a low area specific resistance (ASR; Fig. 9) and exhibited maximum power densities of 0.38 W cm⁻², 0.59 W cm⁻², 0.94 W cm⁻² and 1.32 W cm⁻² at 700 °C, 750 °C, 800 °C and 850 °C,

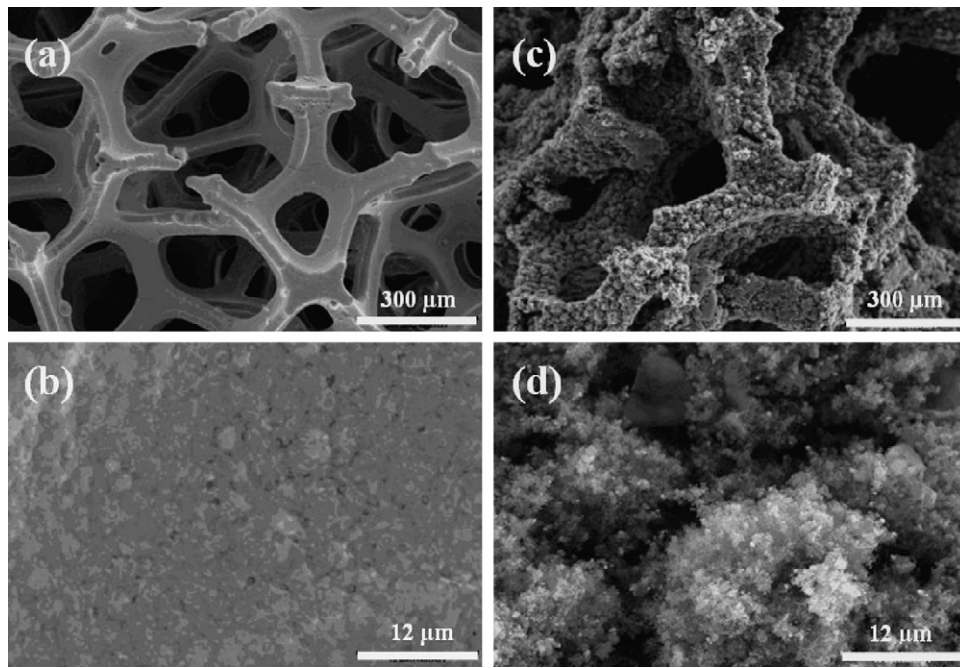


Fig. 4. SEM images of (a, b) Ni-P-M; (c, d) naked Ni foam, after treatment in syngas at 750 °C for 24 h.

respectively (Fig. 8). Thus the low ASR fuel cells provided a good platform for comparison testing of current collectors since their performances were very sensitive to system internal ohmic resistance changes.

Fig. 10 shows the voltage–current characteristics and power density curves of two fuel cells tested at 800 °C in H₂ using Ni-P-M and naked Ni foam current collector, respectively. Both cells had good power densities (>900 mW cm⁻²) and low ohmic resistance (Fig. 11), indicating good electronic conductivity of both naked and plated Ni foams. From the IV curve of the plated Ni foam group, it was observed that the small decrease in porosity after plating had little influence on fuel transport. The different shape of EIS curve for naked Ni foam group was caused by extra water present in the electrode originated from leakage. However, the EIS curves revealed that Ni-P-M had slightly higher ohmic resistance. The cause might be either higher contact resistance, as plated Ni foam is more rigid

than naked Ni foam [22], or the small overall increase in thickness of the material.

For comparison of plated Ni foam with a current collector of known performance, the performances of otherwise identical fuel cells fed with humidified syngas at 800 °C also were determined using Au mesh and Ni-P-M as anode current collectors. The Au current collector was chosen for the comparison since it has high conductivity and stability in syngas at elevated temperature [10]. The peak power densities for cells with Au mesh and plated Ni foam current collector were high and almost identical (~800 mW cm⁻²) as shown in Fig. 12. From the EIS curves (Fig. 13) it was found that the internal ohmic resistance of cell with Ni-P-M collector was very close to that with Au mesh current collector in syngas, which suggested that plated Ni foam had similar excellent conductivity when used in the syngas at the cell's operating temperature.

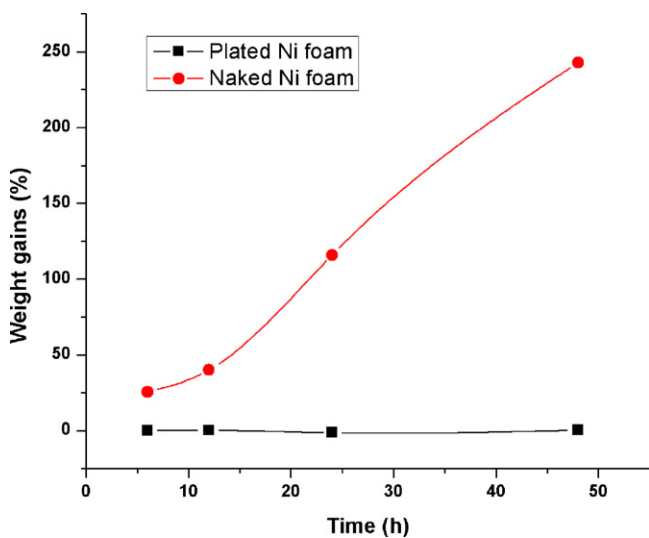


Fig. 5. Weight gains of naked and plated Ni foam after treatment in syngas at 750 °C for 48 h.

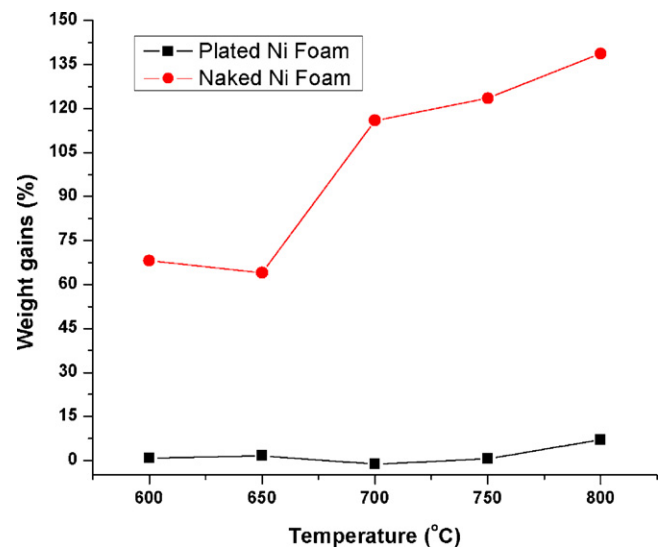


Fig. 6. Weight gains of naked and plated Ni foam after treatment in syngas for 48 h as a function of temperature between 600 °C and 800 °C.

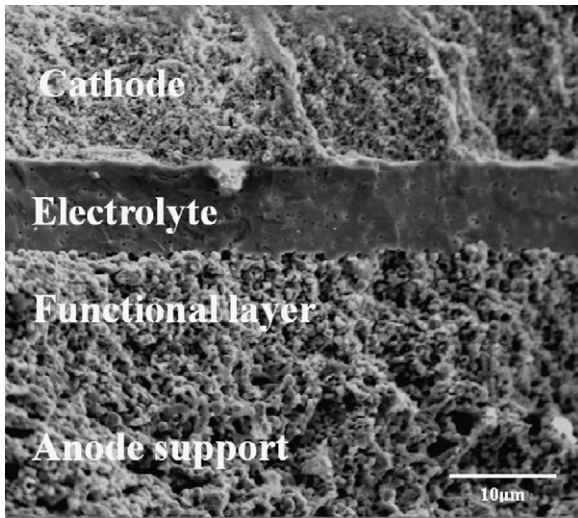


Fig. 7. SEM cross-section image of a typical tested fuel cell.

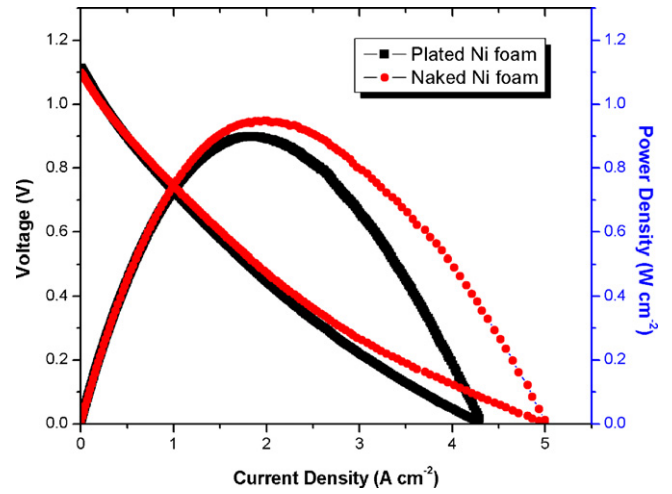


Fig. 10. Comparison of current–voltage characteristics and power densities of SOFC with plated and naked Ni foam anode current collectors in H₂ at 800 °C.

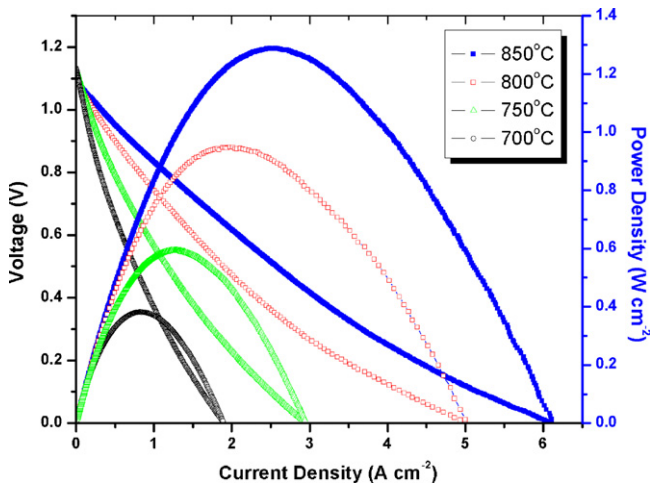


Fig. 8. Current–voltage characteristics and power densities of a typical SOFC fuel cell tested in H₂ at different temperatures.

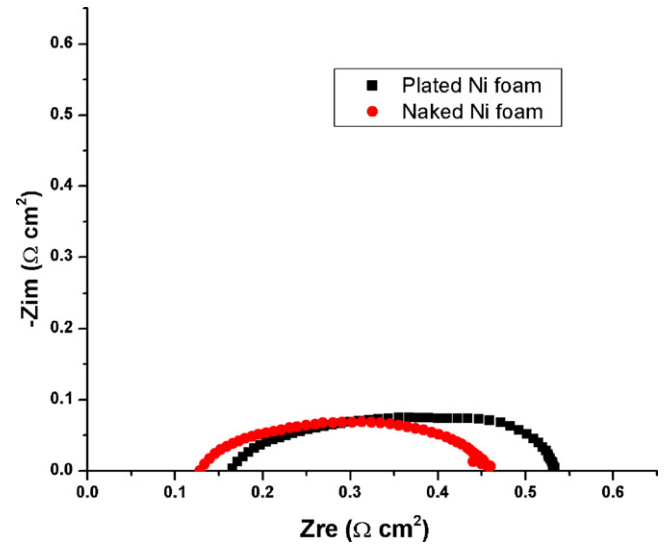


Fig. 11. Comparison of electrochemical impedance spectra of SOFC with plated and naked Ni foam anode current collectors in H₂ at 800 °C.

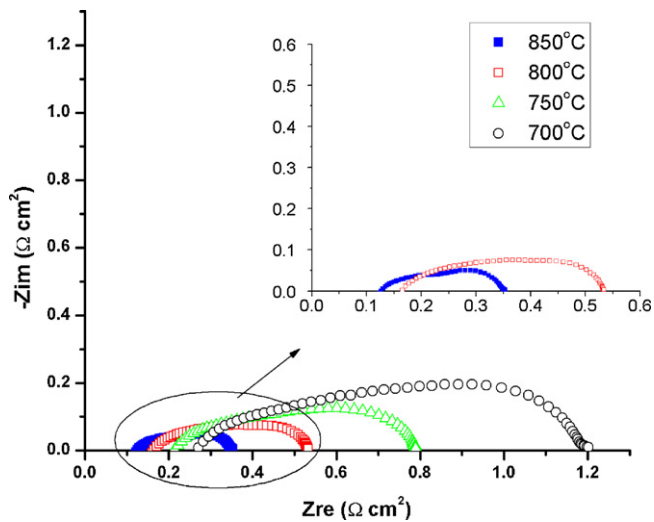


Fig. 9. Electrochemical impedance spectra of a typical SOFC fuel cell tested in H₂ at different temperatures.

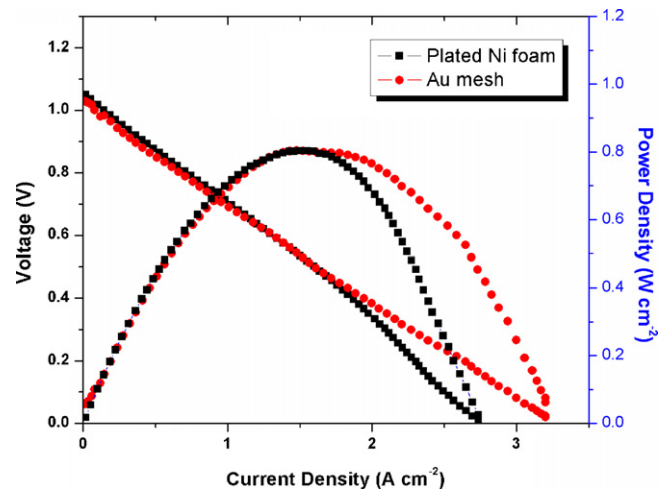


Fig. 12. Comparison of current–voltage characteristics and power densities of SOFC with plated Ni foam and Au mesh anode current collectors in syngas at 800 °C.

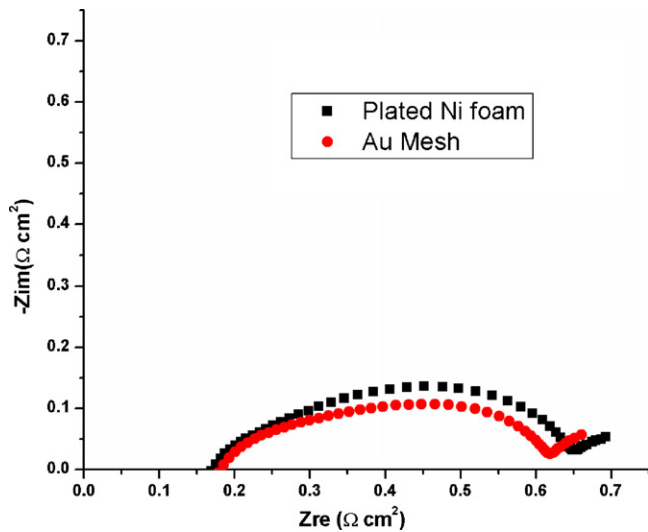


Fig. 13. Comparison of electrochemical impedance spectra of SOFC with plated Ni foam and Au mesh as anode current collectors in syngas at 800 °C.

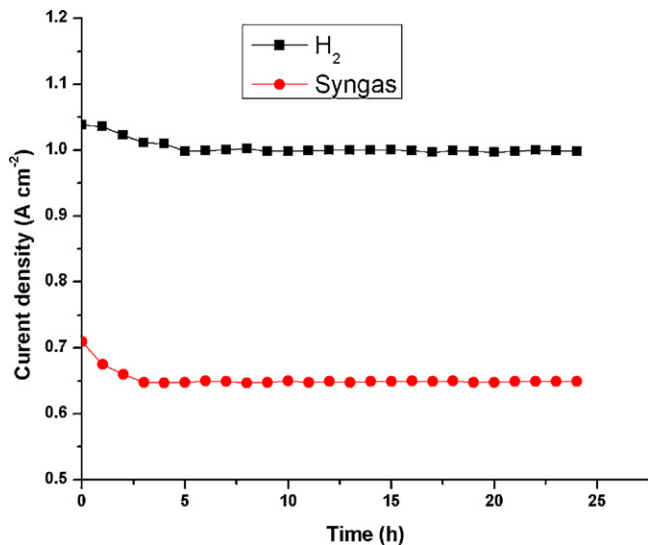


Fig. 14. Stability of SOFC with plated Ni foam anode current collector in H₂ and syngas at 0.75 V and 800 °C over 24 h.

Although the behaviors and stabilities of plated Ni foams had been evaluated by heating in syngas in the quartz tube, it also was necessary to evaluate their performances as current collectors in an operating fuel cell system because the working fuel cell environment is more complex: (1) the current collectors are in contact with the cell electrodes at high temperature, thus the pressure might damage the coatings and there might be reactions between syngas and current collectors; and (2) the electrochemical reaction products (CO₂ and H₂O) in the cell also may cause deterioration of the current collectors. Fig. 14 shows stability test curves of cell with plated Ni foam current collector discharging at 0.75 V and 800 °C for 24 h in either H₂ or humidified syngas. The respective power

densities were $\sim 750 \text{ mW cm}^{-2}$ in H₂ and $\sim 490 \text{ mW cm}^{-2}$ in humidified syngas, and no apparent degradation was observed during each 24 h test. After test, no carbon deposits, structural damages or products of reaction with anode were observed by SEM on plated Ni foam. Thus Ni–P plated Ni foam current collectors have excellent stability during fuel cell operation under working conditions.

4. Conclusions

Electroless plating of Ni–P onto Ni foam provides an easy, quick and inexpensive method to produce a highly uniform protective coating comprising mainly Ni and Ni₃P at SOFC working temperatures (>600 °C). Plated Ni foams with coatings having P content higher than 6.4 wt% have much better coking resistance and structure stability in syngas at various temperature (600–800 °C) than either naked Ni foam or the same foam coated with Ni–P with lower P content. SOFC for current collector test has a maximum power density exceeding 1.3 W cm^{-2} in H₂ at 850 °C and 0.8 W cm^{-2} in syngas at 800 °C. The SOFC system with plated Ni foam anode current collector has performance substantially as good as the one using naked Ni foam in pure H₂ and the one using Au mesh in syngas. They also exhibits high and stable power outputs during stability test using either H₂ or humidified syngas as fuels. Thus Ni–P plated Ni foam is a promising anode current collector in the syngas SOFC system.

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