Performance and Durability of Ni-Fe-Cr Alloys Hydrogen Electrode of Solid Oxide Electrolysis Cells for Steam Electrolysis

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Abstract

The conventional Ni-YSZ cathode suffers from oxidation after exposed to steam during electrolysis for prolonged operation. The Ni-Cr-Fe alloys with various compositions are introduced to improve cathode oxidation resistance. This study aims to study the effect of alloy contents and determine suitable fabrication method for SOEC cathode. The alloy containing cathode should satisfy both high electrochemical performance and low degradation rate. The content of Fe and Cr are varied in the range of 0-20%wt when the weight ratio of metal to YSZ is maintained constantly at 60:40. The SOEC having Ni-Cr-Fe alloy cathode are fabricated. The oxidation resistances are studied using thermogravimetric analysis (TGA). The electrochemical performance is carried out using current/potential characteristic curve and electrochemical impedance spectroscopy (EIS). The operating temperature is controlled between 600-900 °C with the feed containing varied steam to hydrogen (60:40, 70:30 and 80:20).

Keywords: Solid oxide electrolysis cells, Nickle alloy electrode, Hydrogen production, Steam electrolysis, Oxidation tolerance

1. Introduction

The requirement for clean and sustainable fuel sources has encouraged great interests in electrochemical technologies such as high temperature solid oxide electrolysis cell (SOEC). Hydrogen can be produced through steam electrolysis using SOEC which operates in the range of 700 – 1000 °C. The advantage of using high temperature electrolysis is the improvement of electrochemical reaction rates and reduction of electrical energy demand. However, high operating temperature also accelerates oxidation of electrode under high steam environment (Keane, Fan et al. 2014, Grieshammer et al. 2015). The electrolyte material which has been widely used is yttria-stabilized zirconia (YSZ) because it shows a good thermal and chemical stability and performs as a good oxide-ion conductor with enough mechanical strength (Ni, Leung et al. 2008). Nickel-yttria stabilized zirconia (Ni-YSZ) is generally used as

hydrogen electrode in SOEC because of their good thermal compatibility (Moçoteguy and Brisse 2013); nevertheless, the material shows low durability due to Ni oxidation under high steam partial pressure, resulting in lowered electronic conductivity and catalytic activity of the electrode. The Ni-Cr-Fe alloys are introduced to improve the hydrogen electrode oxidation resistance**.** These alloys are used as an interconnect of solid oxide fuel cell (SOFC). The oxidation resistance was reported to improve with the increasing of alloys contents (Church et al. 2007, Simonsen, Muhl et al. 2019). The material properties of metal alloys have been described by Church et al.; the two most critical properties are a similar thermal expansion matching with electrolyte and high oxidation resistance in the operating environment of the SOEC.
In this study, the effects of chromium and iron additions to a Ni based alloy on thermal expansion behavior, oxidation rate in air at 800 °C and electrochemical performance was investigated. The properties of the powders and their application as the hydrogen electrode of SOEC were also investigated.

2. Experimental procedure

2.1 Preparation and characterization of Ni-Cr-Fe alloys powder

Compositions of the Ni–Cr–Fe/YSZ samples have been grouped as binary with constant to total metal content [NixFe, NixCr]. The contents (x) were ranging from 0-20 %wt. as shown in table 2.1 and 2.2. The weight ratio of YSZ to Ni alloys was controlled at 40:60 %wt. All the powders were mixed in ethanol. The mixture was ball-milled for 24 hours to form a uniform slurry followed by drying and grinding.
The oxidation resistances were studied by thermogravimetric analysis (TGA).

Table 2.1 composition of Ni-Fe-YSZ

Composition	Conventional (%wt)	Sample 1 (%wt)	Sample 2 (%wt)	Sample 3 (%wt)	Sample 4 (%wt)
Ni	60	55	50	45	40
Fe	0	5	10	15	20
YSZ	40	40	40	40	40

Table 2.2 composition of Ni-Cr-YSZ

Composition	Sample 5 (%wt)	Sample 6 (%wt)	Sample 7 (%wt)	Sample 8 (%wt)
Ni	55	50	45	40
Cr	5	10	15	20
YSZ	40	40	40	40

2.2 Fabrication of solid oxide electrolysis cells

Ni-based alloys cathode was prepared by dry pressing process. Starch was added as a pore former to form an adequate porosity of porous cathode. The mixed powder was pressed into a disc with diameter of 2.54 cm under of 2-5 MPa for 30s. The green disc was pre-sintered at 1100 °C for 2 hours. Then, electrolyte was deposited on one side of the pre-sintered cathode using dip-coating technique. The electrolyte slurry composition is shown on Table 2.3. After depositing electrolyte, the cell was sintered at 1450 °C for 4 hours to form dense layer of YSZ. The BSCF oxygen electrode was deposited using doctor blade technique and sintered at 900 °C for 2 hours to form a thin layer on the sintered YSZ with effective area of 0.5 cm^2.

Table 2.3 electrolyte slurry composition

YSZ powder (g)	Solvent System		Polyvinyl butyral resin (butar98) (g)	Polyethylene glycol (g)	Polyvinylpyrrolidone (g)
	Xylene (ml)	Buthanale (ml)			
10	36.3	11	0.3	0.002	0.5

2.3 Fabrication of SOEC having Ni alloy containing cathode

To prevent oxidation of Ni in electrode, the SOEC having Ni alloy containing cathode was fabricated.

2.3.1 Fabrication of SOEC having Ni alloy cathode

Ni alloy: containing 72%wt Ni, 14-16%wt Cr and 6-10%wt Fe with the ratio of Ni alloy to YSZ at 60:40 %wt. were used to fabricate the hydrogen electrode. The powders were pressed and sintered using the same condition as used for the fabrication of Ni-YSZ hydrogen electrode.

2.3.2 Fabrication of SOEC having Ni-alloy wash-coated Ni-YSZ cathode. The Alternative method to prevent the oxidation while minimizing thermal expansion issue was to wash-coating conventional Ni-YSZ cathode with Ni alloy slurry. The sintered Ni-YSZ was wash-coated by the alloy slurry. The slurry was prepared with the composition in Table 2.4.

Table 2.4 wash-coated slurry composition

Ni-Alloy (commercial) (g)	Solvent System		Polyvinyl butyral resin (butar98) (g)	Polyethylene glycol (g)	Polyvinylpyrrolidone (g)
	Xylene (ml)	Buthanale (ml)			
10	36.3	11	0.3	0.002	0.5

2.4 Electrochemical performance measurement

Single cell polarization curves were generated using linear sweep techniques. A potentiostat was used to control the voltage between 0.5 and 1.8 V with a scan rate of 20 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were functioned using a sinusoidal signal amplitude of 20 mV_{rms}, across the frequency range of 100 kHz to 0.1 Hz. The feed contained humidified hydrogen at cathode chamber using varied steam to hydrogen (60:40, 70:30 and 80:20) when operating temperature was maintained at 800 °C (see Table 2.5).

The electrical connection was made to the cell electrodes via platinum wires and paste. The cell ridge was sealed using gas sealant to create a separation of the gas environment of two electrodes. Fig. 1 shows the experimental set-up for the delivery of the gas to the cell in the furnace. The feed of H_2, H_2O and N_2 with various of composition were allowed to be introduced to the H_2 electrode. N_2 was used to balance the gas flow and control the steam ratio in the gas compositions. Deionized water was transferred using an HPLC liquid pump. Steam was generated in a heated tube and mixed with the N_2 and H_2 lines.

Table 2.5 steam to H_2 ratio of operating condition

Steam to H_2 ratio	H_2 flow (ml/min)	N_2 flow (ml/min)	Steam flow (ml/min)	Total flow (ml/min)
60:40	20	100	30	150
70:30	20	83	47	150
80:20	20	50	80	150

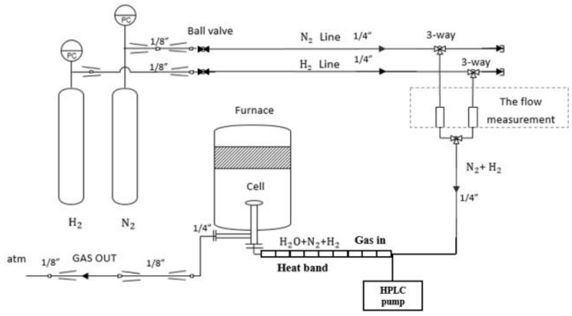

Fig. 1 Schematic drawing of the test system

3. Progressed result and discussion

3.1 Oxidation resistance measurement

The metal alloys were tested under extremely condition in air at operating temperature of 800 °C. The oxidation resistance was observed through TGA. Fig. 2 and Fig. 3 show the thermal behaviour of binary metal and ceramic of Ni-Fe/YSZ and Ni-Cr/YSZ, compared to conventional Ni-YSZ respectively. Increasing Fe content reduced oxidation rate of the cathode. For Ni-Cr/YSZ, 5 %wt Cr addition increase the oxidation resistance of the cathode when compared to conventional Ni-YSZ. The oxidation of Ni-Cr-Fe/YSZ is presented in Fig.4.

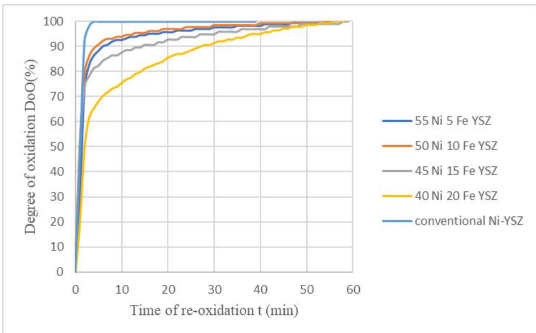

Fig. 2 Degree of oxidation (%) for Ni-Fe-YSZ compared to conventional Ni-YSZ in air atmosphere at 800°C

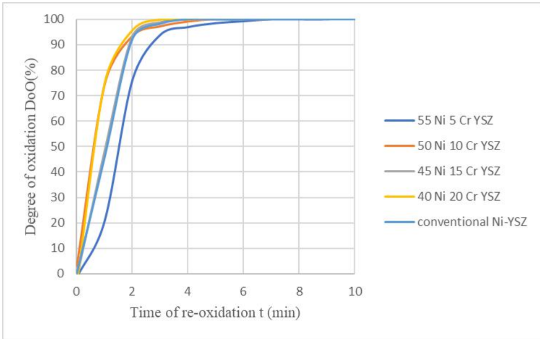

Fig. 3 Degree of oxidation (%) for Ni-Cr-YSZ compared to conventional Ni-YSZ in air atmosphere at 800°C

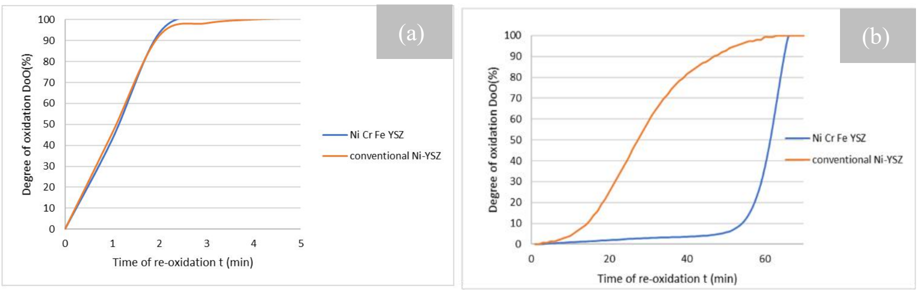

Fig. 4 Degree of oxidation (%) for Ni-Cr-Fe-YSZ compared to conventional Ni-YSZ in air atmosphere: (a) at 800°C, and (b) ramping from room temperature to 800°C

3.2 Fabrication of hydrogen electrode

The Ni alloys / YSZ powder was used to fabricate the hydrogen electrode (see 2.3.1). Dry pressing process was selected to minimize the cost of fabrication. After sintering at 1100 °C for 2 hours, it was observed that the electrode bent, likely due to rather high thermal expansion of the material (Fig. 5). The surface cracked and peeled off. Therefore, Ni alloys / YSZ power could not directly fabricated into the cathode. Development has been made by wash-coating Ni alloys solution into Ni-YSZ cathode (see 2.3.2).

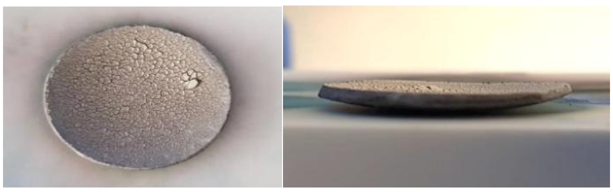

Fig. 5 The fabrication of hydrogen electrode using commercial NiFeCr-YSZ as a material

3.3 Electrochemical performance

The electrochemical performance of Ni alloys wash-coated Ni-YSZ/YSZ/LSM-YSZ was studied. The effects of various steam to H_2 ratio are shown in Fig. 6. The electrochemical performance were similar in different various steam to H_2 ratio (Fig. 6).

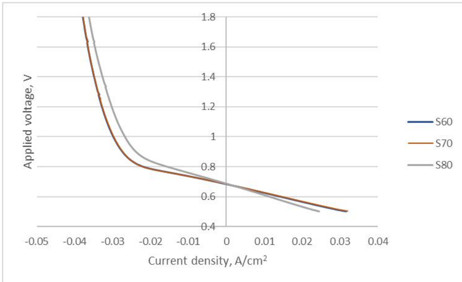

Fig. 6 Effect of steam to H_2 ratio (operating temperature at 800 °C)

The effect operating temperatures were investigated between 650 and 900 °C as shown in Fig. 7. Increasing temperature increased the cell performance. Electrochemical impedance analysis is shown in Fig. 8. Mass transportation resistance of the operation in SOEC mode (1.1 V) was significantly larger than SOFC mode (0.6 V) while activation resistance was comparable. This result corresponded to the I/V curve which presented increasing slope at a higher current density.

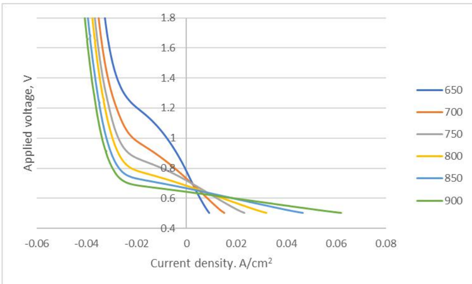

Fig. 7 Comparison of the electrochemical performance of various operating temperature and steam to H_2 ratio at 70:30

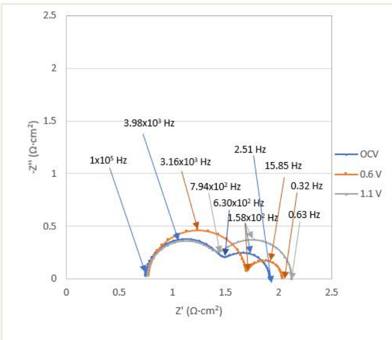

Fig. 8 Electrochemical impedance response of the Ni alloy wash-coated Ni-YSZ/YSZ/LSM-YSZ at different applied voltage at a constant operating temperature of 800 °C ($H_2O:H_2 = 70:30$)

4. Conclusions

Ni-Fe-Cr alloy could help improving an oxidation resistance of the SOEC cathode. However, fabrication of the cathode should be considered in term of both oxidation resistance and thermal expansion. Fabrication of the Ni-alloy/YSZ electrode was rather difficult due to thermal expansion. The electrode was bent after sintering process. The Ni-YSZ was therefore washed coated by Ni-alloy solution. Ni alloy wash-coated Ni-YSZ/YSZ/LSM-YSZ was fabricated and tested for electrochemical performance.

5. References

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