Fabrication of alloy foam-supported solid oxide electrolysis cell (SOEC) for hydrogen production

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Abstract. Alloy foam-supported SOEC is fabricated. Nickel-iron (Ni-Fe) alloy foam (Porosity: 5-130 ppi) is used for cell support. Single thin-cell composed of Ni- Sco.1Ce0.05Gd0.05Zr0.89O2 (SCGZ) cathode, SCGZ electrolyte and Ba0.5Sr0.5Co0.8Fe0.2O3- δ (BSCF) anode is fabricated. Electrode powders are mixed with additives forming as slurry for wet chemical coating. 70%weight content of cermet provides smooth surface and sufficient viscosity to prevent slurry sweep through the porous foam. However, severe cracking is clearly seen on the surface of the cell because of mismatching of thermal expansion coefficient (TEC) during sintering. Therefore, the cell with three cathode layers having TEC gradient (13.83, 13.62 and 13.40 ppmK⁻¹) and %weight content of cermet gradient (70%, 60% and 50%weight) is fabricated. Heating rate and steps are controlled at 0.5°C/min (600 °C), 3°C/min (800 °C) and 1°C/min (1,300°C, 4 h) to burn off additives before sintering.

1 Introduction

Hydrogen is a promising a carrier for clean and sustainable energy. It is also used as a feedstock for various chemical production. The demand tends to increase continuously. Steam electrolysis through solid oxide electrolysis cell (SOEC) can produce high purity hydrogen. Challenge remains for SOEC development is to improve performance and durability of the cell. There are various strategies for SOEC development such as material selection, sealant development, and optimized operating condition. The reduction of cell's resistance by making cell thinner is one among strategies. In general, the cell requires a support from a thick electrode and is called as cathode- or anode-supported cell [1-3]. Therefore, to fabricate a thin cell, metal support is extensively studied to reduce ohmic resistance in thick electrode and increase strength in cell. Nevertheless, metal support SOEC is still facing high fabrication cost and poor durability in long-term operation due to metal oxidation under high steam containing environment. Using an alloy as a support to

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fabricate a thin cell can provide lower resistance and oxidation rate and help enhance mechanical properties of cell [4-7].

In this study, alloy-foam supported SOEC was fabricated. Nickel-iron (Ni-Fe) alloy foam (Porosity: 5-130 ppi) was used for the cell support. Single thin-cell composed of Ni-Sc_{0.1}Ce_{0.05}Gd_{0.05}Zr_{0.89} (SCGZ) cathode, SCGZ electrolyte and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ}(BSCF) anode was fabricated. The morphology of the cell was characterized by scanning electron microscopy (SEM). The electrochemical performance of the SOEC is measured under H₂O/H₂ feed with varied steam content in a controlled temperature from 600°C to 900 °C.

2 Experimental

2.1 Substrate Preparation

NiFe foam (Tmax Battery Equipments Limited, China) having porosity of 5-130 ppi and 3 mm thickness was used as substrate. The foam was cut into 25 mm diameter with a thickness of 3 mm. After that, the foam was uniaxially pressed at 62.5 psi and for 30 s to produce smoother surface, ready for electrodes layer deposition.

2.2 Slurry Preparation

2.2.1 Cathode Slurries

NiO (Sigma-Aldrich, USA) and Sco₁Ce_{0.05}Gd_{0.05}Zr_{0.89}O₂ (SCGZ, Kceracell, Republic of Korea) were used as cermet starting powders for fabrication of cathode slurry. The powders were mixed using ball-milling in solvent consisting of toluene and ethanol at room temperature for 24 h. Then, plasticizer and dispersant were added into the mixture and the compositions were mixed for another 24 h. Polyethylene glycol 400 (PEG 400) and α -terpineol were used as plasticizer and dispersant, respectively. Cermet content in slurry was varied between 40-80 wt%. NiO content in cermet was 66-75 wt%.

2.2.2 Electrolyte Slurries

Electrolyte slurry was obtained by well mixing of SCGZ powder, solvents and additives at 70°C for 24 h. Xylene and Butyraldehyde were used as solvent. Additives were included Polyvinyl butyral (B-98, Sigma-Aldrich), PEG 400 and Polyvinylpyrrolidone (PVP, Sigma-Aldrich) as binder, plasticizer and dispersant, respectively. 0.5 wt% CuO (Sigma-Aldrich) was added into the electrolyte slurry as sintering additive to help decrease sintering temperature. The effect of CuO sintering additive on sinterability and electrochemical performance of the cell was reported in our previous work [8].

2.2.3 Anode Slurries

Ba0.5Sr0.5Co0.8Fe0.2O3- $_{\delta}$ (BSCF, Kceracel, Republic of Korea) were used as anode material. The anode powder was mixed with α - terpineol in weight ratio 1:1 to form anode paste.

2.3 Fabrication of NiFe-alloy-foam-supported SOEC

Cathode slurries were deposited onto foam substrate by tape-casting technique. The green tape were dried at room temperature and fired at 1100°C for 2 h. Then, SCGZ thin layer was coated by electrolyte slurry dip-coating, followed by sintering at 1250-1300°C for 4 h. Heating rate and steps which were 3 condition were investigated at 1) 2°C/min (300°C, 5 h) and 3°C/min (1250°C, 4 h), 2) 1°C/min (300°C, 5 h) and 2°C/min (1250°C, 4 h), 3) 0.5°C/min (600°C), 3°C/min (800°C) and 1°C/min (1250°C 4 h). Anode slurry was screen printed on the sintered cell. The schematic drawing of the cell is shown in Fig 1. Microstructural images of sintered cell was taken by using SEM (Hitachi S-3400N JEOL model S-3400, Japan).



Fig. 1 Schematic drawing of Alloy foam-supported solid oxide electrolysis cell (SOEC); (a) top view, (b) side view.

2.4 Electrochemical Performance Measurement

The fabricated cell was installed in test station consisting of cell holder with high temperature sealant (Ceramabond 552, Aramco) inside a furnace (Chavachote). Platinum (Pt) conductive paste (70 wt% Pt, Nexceris), mesh and wire (Kceracell) were attached on the fabricated cell for electrical connection. The electrochemical performance was measured at 600-900°C with feed containing 60-80 vol% of steam and constant hydrogen content (balanced N₂). Deionized water was supplied for steam generation by high performance liquid chromatography pump (Teledyne SSI, USA). A heated-tube was used as steam generator. Linear sweep current techniques was applied to generate current/voltage (I/V) curves. A potentiostat (PG310 Metrohm Autolab, Netherlands) was used to control the potential from 0.4 V to 1.8 V with a scan rate of 20 mVs⁻¹.

3 Results and Discussion

3.1 Cermet content in cathode slurry

Unfired cathode with 60 wt% Ni / 40 wt% SCGZ on NiFe-alloy foam with varied cermet content in cathode slurry are shown in Fig. 2. After casting the cathode, it was found that 70 wt% cermet in slurry provided smooth surface and sufficient viscosity to prevent slurry sweeping through the porous foam.



Fig. 2 Unfired Ni-SCGZ cathode on NiFe-alloy foam with vary cermet content in cathode slurry: (a) 40%wt, (b) 50%wt, (c) 70%wt, and (d) 80%wt cermet content

Electrolyte was coated on fired cathode and sintered at 1300°C. Sintered half cell with 70 wt% cermet content in cathode slurry and the SEM image are shown in Fig. 3. Fig. 3 reveal that thin SCGZ electrolyte was deposited on cathode layer. However, severe cracking was clearly found all over the surface of the cell. This was likely due to mismatching of thermal expansion coefficient (TEC) among electrolyte (10.65 ppm/K), cathode (13.40 ppm/K), and substrate (14.62 ppm/K). Gondolini et al.[6] investigated Ni-GDC layer deposition on NiCrAl foam for SOFC application. It was reported that sintered layer which is accompanied by a certain shrinkage lead to crack formation due to TEC mismatching. To overcome this problem, cathode was divided into three layers with vary cermet content in slurry (70 wt%, 60 wt% and 50 wt%) and NiO content in cermet content (75 wt%, 70 wt% and 66 wt%). Three slurries were formulated for fabrication of cathode layers as presented in Table 1.

Layers Properties	NiO- SCGZ 1	NiO- SCGZ 2	NiO- SCGZ 3
TEC (ppm/K)	13.83	13.62	13.40
Viscosity (Pa·s) at shear rate 10 s ⁻¹	Undefined	702.1	578.3
Cermet content in slurry	70%wt	60%wt	50%wt

Table 1. 1 Cathode slurries properties



Fig. 3 Sintered half cell of Ni-SCGZ/SCGZ on NiFe-alloy foam: (a) Surface image and (b) SEM image

3.2 Heat treatment in sintering process

Heating treatment in electrolyte sintering process is one of the important factors for cell fabrication. The effect of heating rate during sintering was compared. Sintered half cells in different heating rate are shown in Fig. 4.



Fig. 4 Sintered half cell of Ni-SCGZ/SCGZ on NiFe-alloy foam using different heating rate: a) 2° C/min (300°C 5 h) and 3° C/min (1250 °C 4 h), (b) 1° C/min (300 °C 5 h) and 2° C/min (1250 °C 4 h), (c) 0.5° C/min (600 °C), 3° C/min (800 °C) and 1° C/min (1250 °C 4 h)

Fig. 4 reveals that fast heating rate dominated the crack on the cell surface, corresponding to the work of Jin et al.[9] who studied the fabrication of Ni-SSZ porous anode for anode-supported SOFC fabricated by tape casting and co-firing technique. It was proposed that low heating rate could suppress the defect formation and delamination. The mismatch in shrinkage of anode and electrolyte were accelerated at faster heating. In this study, slow heating and steps to burn off additives were applied in heat treatment.

3.3 Microstructure of alloy-foam supported SOEC

The NiFe-alloy-foam/Ni-SCGZ/SCGZ/BSCF was successful fabricated by adjusting TEC in cathode, using suitable heat treatment during sintering process, and preparing foam substrate. Cathode was divided into three layers with different composition to form different TEC. Fig. 5 shows the cell during preparation and Fig. 6 presents the cell's morphology. SEM images revealed well attachment between all layer (electrolyte, electrolyte, and substrate). However, as can be seen in Fig. 6 (a), some porosity on electrolyte layer was observed due to insufficient electrolyte densification.



Fig. 5 NiFe alloy foam/Ni-SCGZ/SCGZ/BSCF SOEC: (a) Cathode layer deposition, (b) sintered cathode, (c) electrolyte deposition, (d) sintered electrolyte, (e) anode deposition, and (f) side view of the cell after heat treament



Fig. 6 SEM images of compressed NiFe-foam supported solid oxide electrolysis cell: a) SCGZ electrolyte sintered at 1,300 °C, (b) and (c) Anode/Electrolyte/Cathode/Support layers

3.4 Electrochemical Performance measurement

The electrochemical performance of the alloy-foam supported SOEC was measured at 800°C with 80% steam content using linear sweep current techniques (Fig. 7). Open circuit voltage (OCV) of cell (~0.5V) was dropped below theoretical value. Lenser et al.[10] were reviewed that OCV is either decreased by the external load powered by the cell (SOFC) or increased by an external power source (SOEC) and loss of concentration of reactant. In this study, low OCV was likely due to insufficiently densified electrolyte which was sintered at 1,300°C. Ohmic resistance of cell in SOEC mode was also higher than SOFC mode. The current density at 1.1 V which is operating voltage in SOEC was consumed 0.3 A/cm².



Fig. 7 I-V Curve in 80%H2O and 20%H2 for NiFe foam/ Ni-SCGZ/ SCGZ/ BSCF

4. Conclusion

NiFe-alloy-foam supported Ni-SCGZ/SCGZ/BSCF solid oxide electrolysis cell was fabricated by wet chemical coating of electrodes slurry. There were various parameters affected the fabrication process such as heat treatment and slurry composition. The TEC mismatching among cathode, electrolyte, and substrate was found, leading to a crack in the cell after heat treatment. Therefore, cathode layers were designed to obtain TEC gradient to suppress TEC mismatching in the cell. Three layers of cathode with different compositions were formed. Moreover, fast heating rate during sintering was found to dominate the shrinkage behaviour and led to the cell defect. Slow heating rate with a step to burn off the additives could decrease the defect in sintered cell. However, microstructure of fabricated cell revealed some porous in electrolyte layer and likely to be the cause of OCV dropping during electrochemical performance measurement. Sintering temperature at 1,300°C for electrolyte slurry having 0.5%wt CuO as sintering additive was insufficient for the electrolyte densification.

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