Influence of NiO to SDC ratio on the properties of Ni-SDC cermet prepared via reduction process

Salmie Suhana Che Abdullah¹,² * and Siti Sarah Ismail¹

¹ School of Materials Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, 02600 Arau, Perlis, Malaysia
² Centre of Excellence Frontier Materials Research, Universiti Malaysia Perlis, Seriab, 01000 Kangar, Perlis, Malaysia

Abstract. This work presents the preparation of Ni-Ce₀.₈Sm₀.₂O₁.₉ (Ni-SDC) ceramic-metal from reduction of NiO-Ce₀.₈Sm₀.₂O₁.₉ (NiO-SDC) ceramics for application of solid oxide fuel cell. NiO-SDC powder with different weight percentage of NiO and SDC (100% NiO + 0% SDC), (80% NiO + 20% SDC), (70% NiO + 30% SDC) and (60% NiO + 40% SDC) was pelletized and sintered at 1400 °C for 4 hours. Then, pellet samples were undergone reduction process using mixed gas of hydrogen and nitrogen gas with concentration of 40% H₂ and 60% N₂ at 800 °C for 2 h. Phase analysis was done using X-ray Diffraction and it was found that for all samples, NiO was completely reduced to Ni, meanwhile SDC was remained in its phase. The density of the samples decreased after reduction, results in more porous samples were obtained. It was found that increasing NiO content lead to sample with higher porosity. The surface morphology of the samples was observed by using the Scanning Electron Microscopy.

1 Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device that can generate electricity directly from chemical reaction. It has many advantages such as high efficient, low emission, and fuel flexibility. For that reason, it has been a subject for extensive research, both in development of materials, as well as for the systems [1].

One of the most important parts of SOFC is the anode. Anode materials must possesses good electrochemical activity to oxidize fuels, high electronic conductivity, and having thermal expansion compatibility with other components in SOFC. Furthermore, it is known that fine particle size, large surface area, adequate porosity and sufficient content of Ni in the anode are essential to achieve high performance [2-4]. Although common anode material for SOFC consist of NiO and yttria stabilized zirconia (YSZ), researchers found that anode material that consist of NiO and ceria (CeO₂) based oxide offer better performance than NiO-YSZ due to higher catalytic activity, has mixed electrical conductivity, less polarized and offer more stable operation [5-7].

Performance of anode dependence on its preparation method. Several techniques have been exploited to produce porous anode structure. Macropores promote rapid gas transport

* Corresponding author: salmie@unimap.edu.my
through the porous electrode and nanopores provide a high surface area for gas adsorption or desorption. Available techniques that are frequently uses are ultrasonic spray pyrolysis [8, 9], plasma sprayed method [10-11], addition of pore-forming agent [12-14], using porous scaffolds [15, 16], and phase inversion [17]. An alternative approach to prepare anode is via reduction process. Reduction process is a simple, low cost and effective method to produce metal from ceramic metal oxide. Reduced ceramic metal oxide to metal during reduction process increases the porosity due to volume contraction between metal oxide and metal, resulted in high electrical conductivity and sufficient electrochemical activity of the anode due to high nickel activity for H2 oxidation [18-20]. It has been reported that, NiO shows structural transformation when reduce under H2, and the transformation of the metal oxide to metal is able to achieved in a very short time [21].

Properties of the reduced Ni powder are dependent on many parameters such as the temperature, holding time, and hydrogen gas flow [22]. Therefore, the aim of this study is to synthesis porous Ni-SDC cermet anode material from NiO-SDC by reduction process using H2 gas. The influence of the ratio of NiO to the SDC on the phase transformation, porosity and microstructure was investigated.

2 Methodology

2.1 Sample preparation

2.1.1 Preparation of Ce0.8Sm0.2O1.9 (SDC) powder

Stoichiometric Ce0.8Sm0.2O1.9 (abbreviated as SDC) powder was prepared from Cerium Oxide, CeO2 (Acros Organics, purity of 99.9%) and Samarium Oxide, Sm2O3 (purity of 99.95%). Raw materials were ground using agate mortar for 1 h with addition of ethanol to obtained homogeneous powder. Then, mixed powder was calcined at 800, 900 and 1000 °C for 3 h.

2.1.2 Preparation of NiO-SDC pellet

| Sample        | Ratio (wt. %) |
|---------------|---------------|
|               | NiO | SDC |
| 100NiO-0SDC   | 100 | 0   |
| 80NiO-20SDC   | 80  | 20  |
| 70NiO-30SDC   | 70  | 30  |
| 60NiO-40SDC   | 60  | 40  |

As prepared SDC powder was mixed with NiO (Acros Organics, purity of 97%) with various composition, as can be seen in Table 1. These powder were mixed using mortar for 1 h, and ethanol was used as mixing aid. Homogeneous powder were pelleted using uniaxial press under 3.44 MPa with holding time of 5 min, followed by cold isostatic press under 103
MPa for 5 min. The green pellets has dimension of 15 mm in diameter and 4-5 mm in thickness. Then, pellets were sintered at 1400 °C for 4 h.

2.2 Reduction process

Pellet samples were heated up to 800 °C with heating rate of 10 °C/min. Once furnace temperature reached 800 °C, H₂ and N₂ gases were supplied to the samples for 2 h. Concentration of gas mixture was fixed at 40% H₂ and 60% N₂ with total mass flow of 100 ml/min.

2.3 Characterization

2.3.1 Phase identification

X-ray Diffraction, XRD (Bruker D2 Phaser) was used to identify the phase of all pellet samples before and after reduction process. The scan range and scan rate is 20-80° and 1s/step, respectively.

2.3.2 Density

Apparent density of the samples before and after reduced under H₂ gas was measured using Archimedes method. Apparent density ($\rho$), theoretical density ($\rho_{th}$) and relative density ($\rho_r$) were obtained by using Equation (1), (2) and (3), respectively. Then percentage of density change after reduction process was calculated.

\[
\rho = \rho_L \times \left( \frac{W}{W - (W_s - W_L)} \right) \quad (1)
\]

\[
\rho_{th} = \frac{M \times Z}{N_A \times V} \quad (2)
\]

\[
\rho_r = \frac{\rho}{\rho_{th}} \quad (3)
\]

where, $\rho_L$ density of water, $W$ is sample mass, $W_S$ is sample mass in water, $W_L$ is water mass, $M$ is molecular weight, $Z$ is number of atoms in unit cell, $N_A$ is Avogadro’s number and $V$ is volume of unit cell.

2.3.3 Morphology observation

Scanning electron microscopy (JEOL JSM-6460LA) was used to observe the morphology of the samples. The samples were ground and coated with platinum by putter coating before tested. The morphology of the sample was viewed and recorded in 5000× magnification.

3 Results and discussion

3.1 Phase identification

3.1.1 Ce₀.₈Sm₀.₂O₁.₉ (SDC)

XRD patterns of SDC powder calcined at different temperature which are 800, 900 and 1000 °C are shown in Fig. 1. Analyzed data show that four main peaks belongs to CeO₂ (ICCD file no: 01-080-5549). No significant peak shifting detected when calcination increased indicating that no changes in lattice parameter can be found. As all calcination temperatures could produce identical result, for the low energy consumption reason, lower calcination temperature, i.e 800 °C was chosen as calcination temperature for SDC powder in this work.
3.1.2 NiO-SDC before and after reduction

Phase confirmation was done for all samples before and after reduction. The results are shown in Fig. 2 (a)-(c). For all samples, before undergo reduction process, main peaks that corresponding to NiO (ICDD file no: 00-001-1239) at 37°, 43°, and 63° and CeO$_2$ (ICDD file no: 01-080-5548) at 28°, 33°, 47°, and 56° were detected. No additional peak for new compound is found. It shows that there is no reaction occur between NiO and CeO$_2$ to produce new compound and NiO and SDC remain in separate phase even though the samples were sintered at 1400 °C. After undergo reduction process using 40% H$_2$-60% N$_2$ gases at 800 °C for 2 h, phase identification was done to the same samples once again. For all samples, peaks that corresponding to CeO$_2$ remained. Meanwhile, peaks that corresponding to NiO was completely disappeared, and new main peaks that corresponding to Ni (ICDD file no: 01-088-2326) was identified at 45° and 52°.

Fig. 1. XRD patterns of Ce0.8Sm0.2O1.9 (SDC) powder calcined at 800, 900 and 1000 oC for 3 h. ▼ indicates main peaks belong to ICDD 01-080-5549.
Fig. 2. XRD patterns of (a) 80NiO-20SDC, (b) 70NiO-30SDC, and (c) 60Ni-40SDC pellet before and after reduction at 800 °C for 2 h under 40% H2 and 60% N2 gas.

From these results, for transformation of NiO to Ni under H2 gas, overall reaction can be written as follow:

$$NiO + H_2 \rightarrow Ni + H_2O$$

(4)

This reaction can be interpreted as, firstly, H2 is dissociated, and then adsorption of hydrogen atom on nickel atom occurs, followed by diffusion of hydrogen atom. Desorption of H2O take place after dissociation of nickel-oxygen bond, and finally, leave the nickel metal [19, 20, 23]. It has been reported that reaction between NiO and hydrogen gas adsorbed on NiO, and reaction at the boundary between the two solid phases NiO and Ni with hydrogen adsorbed on nickel occur simultaneously [24]. In addition, when increased NiO ratio, peak shifting to lower angle especially at 28° and 45° was observed, therefore it is expected that there was a small change in lattice parameter.
3.2 Density

Relative density of samples before and after undergo reduction process was calculated, and the result is tabulated in Table 2. Sintered pellets are sufficiently dense in the range of 92-96 % of theoretical density.

Table 2. Relative density and density change of samples before and after reduction process.

| Sample       | Relative density, % |
|--------------|---------------------|
|              | Before reduction    | After reduction |
| 80NiO-20SDC  | 94.9                | 78.0            |
| 70NiO-30SDC  | 95.5                | 80.9            |
| 60NiO-40SDC  | 92.0                | 80.3            |

Fig. 3 shows the percentage of density change before and after reduction for samples with different NiO and SDC content. From this Fig., it can be seen that the percentage of density change decreased gradually with decreasing the NiO content. This result indicates that gas permeability is directly proportional with the NiO content. Similar result was found for NiO-YSZ where, it is reported that for samples with low NiO content, reduction only occur at the surface of the sample [26]. The density change resulted from density change in NiO only, when NiO is reduced to Ni. Meanwhile, it is believed that the SDC compound does not involve in the density change of sample. This is proven by the XRD data where after reduction process, SDC remained in the SDC phase.
3.3 Morphology

Morphology observation were done with magnification ×5000, and the images are shown in Fig. 4. In general, for all samples, unreduced samples shows less pore compared to reduced samples showing that density of the unreduced samples is higher that the reduced samples. These results are in agreement with the density value shown in Table 2. Significant morphology change can be observed for sample that contain 100% of NiO, where unreduced sample possesses dense structure with only few pores. Meanwhile, for reduced sample, small pores were detected on the entire surface of the sample.

![SEM images of NiO-SDC samples](image)

Fig. 4. SEM images of (a-i) unreduced 100NiO, (a-ii) reduced NiO, (b-i) unreduced 80NiO-20SDC, (b-ii) reduced 80NiO-20SDC, (c-i) unreduced 70NiO-30SDC, (c-ii) reduced 70NiO-30SDC, (d-i) unreduced 60NiO-40SDC, (d-ii) reduced 60NiO-40SDC.

4 Conclusions

Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) was successfully synthesized via conventional method and calcination process at as low as 800 °C. NiO-SDC with different NiO to SDC ratio was sintered at 1400 °C. All pellet NiO-SDC samples show identical phase which is mixture of NiO and SDC phase. Reduction of NiO-SDC at 800 °C for 2 h using 40% H₂- 60% N₂ completely reduced NiO to Ni. Larger NiO ratio to SDC resulted in higher percentage of density change. The porosity of the samples after reduction process is in the range that is required by SOFC anode material.

This work was partially supported by Short Term Grant: Anugerah Kecemerlangan Universiti Malaysia Perlis (Grant Number: 9009-00055).

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