

Preparation and Characterization of Cu/YSZ Composite for High Temperature Electrolysis

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ABSTRACT: The Cu/YSZ (Y_2O_3 stabilized ZrO_2) composite for high temperature electrolysis (HTE) was successfully prepared by high-energy ball-milling method. Thus the synthesized Cu/YSZ composite was characterized using various analytical tools such as XRD, SEM and laser diffraction and scattering method. The Cu/YSZ cermet was composed of crystalline Cu and YSZ, in a sub-micron scale and had even distribution without aggregated particle. Electrical conductivity of sintered Cu/YSZ cermet pellet thus prepared was measured by 4-probe technique and compared with that of conventional Ni/YSZ cermet. The effect of composites composition on the electrical conductivity was investigated and the marked increase in electrical conductivity for copper contents greater than 40 vol% in the composite was explained by percolation threshold. Therefore, hydrogen production performance is expected better than Ni/YSZ cermet as result that measured a electrical conductivity.

Keywords: hydrogen, electrode, high temperature electrolysis (HTE), mechanical alloying

1. INTRODUCTION

Hydrogen is usually made by steam reforming and the partial oxidation of natural gas or oil fractions of petroleum oil. However, the processes of hydrogen production emit green house gases into the atmosphere. High-temperature electrolysis of steam (HTES) is recognized a technology capable of producing hydrogen for a future hydrogen economy, because HTES do not emits green house gas and can produce hydrogen using less electric power than conventional water electrolysis[1-3]. Ni/YSZ (8 mol% Y_2O_3 -stabilized ZrO_2) composite powder is the most common cathode material for HTES due to its low cost and chemical stability in $\text{H}_2\text{O}/\text{H}_2$ mixture. But Copper(Cu) has recently been

introduced as an anode material in SOFC technology, due to its low resistivity, low cost, and high electro- and stress-migration resistance[4,5]. As HTES is reverse reaction of SOFC technology, Cu applied to HTES's cathode material. In cathode cermet, YSZ constitutes a framework for the dispersion of metal (Ni, Cu) particles and acts as an inhibitor for the sintering and coarsening of metal powders at high temperature. Additionally, it offers a significant part of ionic contribution to the overall conductivity, thus broadening the triple phase boundary (TPB) where cathode, electrolyte and pores for reaction gas meet. The thermal expansion coefficient of cathode can be managed to match with those of HTES components as YSZ is mixed with metal in an arbitrary ratio[6,7].

In this study, modified Ni/YSZ and Cu/YSZ cermets for HTES have been directly synthesized by the high-energy ball milling of Ni and YSZ powder or Cu and YSZ powder. The synthesized cermets analyse with microstructure and electrical conductivity.

2. EXPERIMENTAL

Fig. 1. showed process of fabrication of HTE cathode composite. The Ni/YSZ composite was synthesized by mechanical alloying of Ni and YSZ powder. Nickel (Johnson Matthey, Alfa Aesar, $< 3 \mu\text{m}$) and 8 mol% Y_2O_3 stabilized ZrO_2 (YSZ, Tosoh Co., TZ-8Y, $< 0.3 \mu\text{m}$) were used as starting materials with appropriate volume ratios of Ni powder for final composition of 60 vol.% Ni-balance YSZ. Mechanical alloying was carried out in planetary ball mill (Fritsch Pulverisette 6) under air atmosphere. The ball milling media consisted of ZrO_2 balls (2mm in diameter) and a ZrO_2 bowl (250 mL). The ball to powder weight ratio was 15 to 1 and the rotating speed was 400 rpm. For comparison, Cu/YSZ cermet was synthesized from Cu (Sigma Aldrich, dendritic type, $< 3 \mu\text{m}$) and YSZ powder. The Cu and YSZ powders were ball milled in α -Terpineol (90%, Aldrich) and then the ball-milled powder were baked at 110°C in air for 10 h. The Ni/YSZ and Cu/YSZ composites powder thus prepared were pressed into pellet shape ($\varnothing 10 \text{ mm} \times 2 \text{ mm}$) and subsequently sintered at 900°C under flowing Ar-5% H_2 reductant gas mixture for 2 h in a conventional horizontal quartz tube furnace. The morphology of the composite particles was observed by scanning electron microscopy (SEM, Model LEO SUPRA 55, Carl Zeiss, Germany) and transmission electron microscopy (TEM, Model JEM 3010, Japan) with energy dispersive analysis (EDS) of X-rays in each step of the cermet synthesis process. Ball-milled particle size distribution was quantitatively characterized using laser diffraction and scattering method.

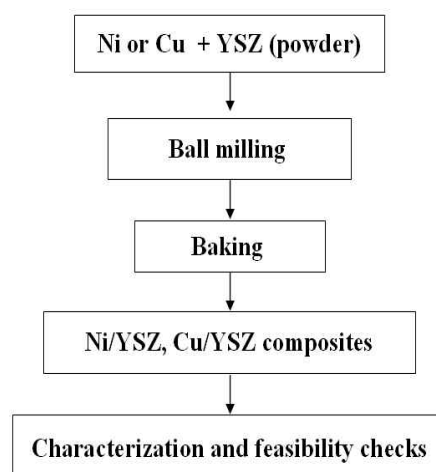


Figure 1: Schematic diagram of preparation procedure for Ni/YSZ and Cu/YSZ composites.

The crystal structure of the prepared composite was determined by X-ray diffraction (XRD, Model M18XHF-SRA, Mac Science, Japan). Electrical conductivity of sintered Ni/YSZ and Cu/YSZ cermet pellets was measured using 4-probe technique at room temperature and the effect of material composition on the electrical conductivity investigated.

3. RESULTS AND DISCUSSION

The XRD patterns of the Ni/YSZ and Cu/YSZ composite are shown in Fig. 2. The XRD patterns show that not only the ball-milled Ni/YSZ composites consisted of crystalline Ni, YSZ but also Cu/YSZ composite was composed of crystalline Cu and YSZ particles and the pattern does not change but some oxidized portion of copper powder in the form of CuO. Regarding the copper oxide occurring in the planetary ball mill, while the high energy ball-milling is advanced Cu, YSZ powder and the ball which is charged with the fact that CuO where is caused by with the high temperature and producing high energy and mechanical impulse occurs.

Copper oxide will be able to decrease with electric conductivity. Reducing

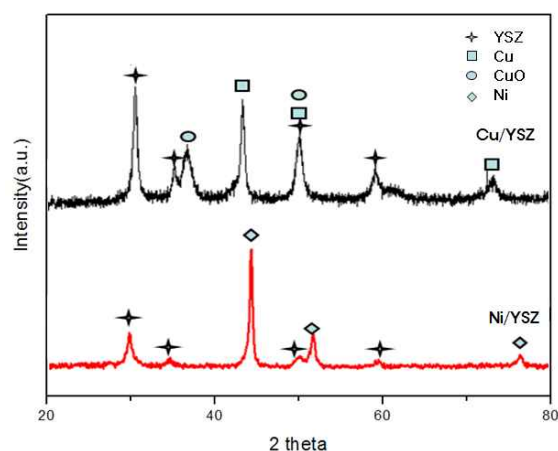


Figure 2: XRD patterns of Ni/YSZ and Cu/YSZ composite powder.

process enhances the electrical conductivity of the composite. A possible explanation for the particles to become denser and more closely packed enhanced better electron migration. Fig. 3. shows the SEM photographs of Ni/YSZ(a) and Cu/YSZ(b) composite particles prepared by the mechanical alloying method. It was also obvious from Fig. 3. (a) and (b) that Ni and Cu powder was ground finer particles. As a result of SEM-EDAX analysis in high magnification, it was observed that the ground Ni and Cu particles were partially covered with YSZ fine particles.

Average particles sizes of the ground Ni and YSZ were about 0.2 and 7 μm in this figure, respectively. This is qualitatively investigated using laser diffraction and scattering method and the results depicted in Fig. 4. The high-energy ball-milling of Ni-balance YSZ at 400 rpm for 24 h yielded high-energy ball-milled powder with minuter particle size distribution while high-energy ball milled Cu-balance YSZ powder mainly consisted of 5 μm average particle size. It shows that composite particles less than 10 μm were successfully fabricated by the mechanical method using high energy ball milling. Confirmed through SEM images Ni or Cu particles and YSZ particles high-energy ball mill puts out from with the alloy powder and in compliance with a

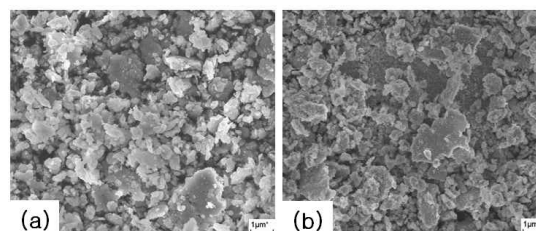


Figure 3: SEM images of the Ni/YSZ(a) and Cu/YSZ(b) composite powder prepared by high-energy ball-milling.

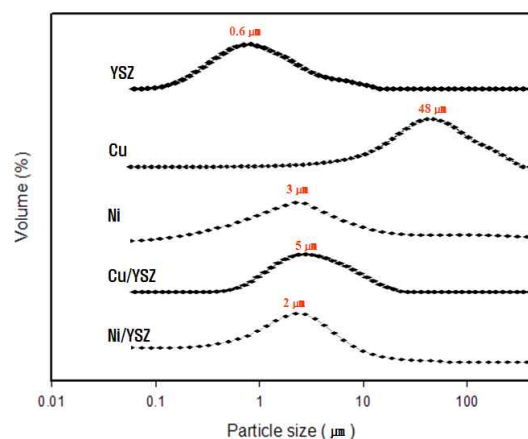


Figure 4: Average particle size distribution of ball-milled Ni/YSZ and Cu/YSZ composite as analyzed by laser diffraction and scattering method.

break and the pressure welding which are repetitive changed most spherical form and part below 1 μm existing in thin plate form during a high energy balling process.

Fig. 5. displayed TEM image of Ni/YSZ(a) and Cu/YSZ(b) composite. Ni/YSZ composite could confirm that exist by composite that YSZ was distributed evenly to Ni particle and that YSZ particle of Cu/YSZ composite was distributed to Cu particle with Ni/YSZ evenly through EDS analysis result. Thus improve electrical conductivity and ion conductivity act by important electrode characterization in hydrogen production uniform ingredient distribution of particle improves YSZ connection degree that is Ni, Cu and ion conductivity material that is electricity

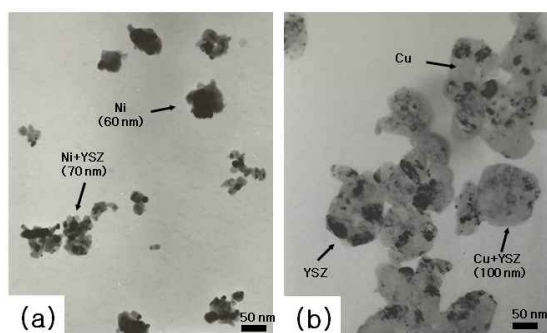


Figure 5: TEM images of the Ni/YSZ(a) and Cu/YSZ(b) composites powder prepared by high-energy ball-milling.

conductibility material. Fig. 6. shows schematic diagram of electron and ionic migration along with SEM images of sintered cermet pellets. Also, through selected area diffraction (SAD) pattern, confirmed that exist by composite of profitable crystalline in electrical conductivity.

The electrical conductivity of the Ni/YSZ and Cu/YSZ composites measured at room temperature. The electrical conductivity of the ball-milled Ni/YSZ composite was about $0.5 \times 10^3 \text{ S cm}^{-1}$ compared with the Cu/YSZ composite fabricated had a higher value of $1.8 \times 10^3 \text{ S cm}^{-1}$. A possible explanation for the large difference in electrical conductivity may be due to difference of the inherent electrical conductivity of the Ni and Cu materials.

Fig. 5. shows that YSZ particles were randomly distributed over the surface of the Ni particles of the Ni/YSZ composite. This is similar to surface of the Cu particles of the Cu/YSZ composite electrical conductivity changes according to content of Ni and Cu and connection degree of particle that is electrical conduction material. And electrical conductivity decreases temperature is higher, because electrical conductivity is not smooth electron's flowing by thermal vibrations of metal crystalline. Therefore, electrical conductivity is expected to be lower than during operating high temperature electrolysis. Cu/YSZ composite is estimated

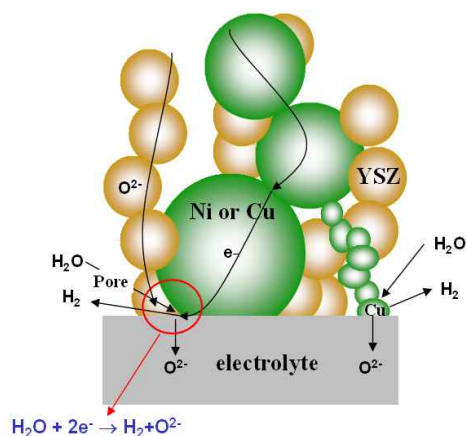


Figure 6: Electron and ionic migration paths for composites along the electronic conductor and YSZ particles.

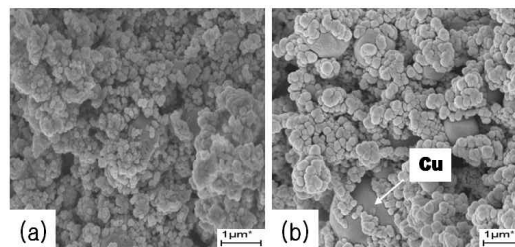


Figure 7: SEM images of 900 °C sintered Ni/YSZ(a) and Cu/YSZ(b) composites.

by method that it produces hydrogen when electrical conductivity is the highest that reducing heat treatment in condition that heat treatment temperature with temperature of reactor because sintering of Cu particle goes well is higher. Ni/YSZ and Cu/YSZ composites observed section of HTE cathode using scanning electron microscope to analyze microstructure. Fig. 7. (a) and (b) showed that Ni/YSZ and Cu/YSZ composite coated SEM picture, respectively. Cu/YSZ confirmed that formed by structure of open-pore and porosity to size of $1 \mu\text{m}$ in form that Cu was cohered. But, Ni/YSZ pore was formed smaller than Cu/YSZ and confirmed that exists with the structure which is composed with $0.1 \mu\text{m}$ dense particles. This Ni/YSZ pore structures of the electrode inside intercept the passageway of vapour and three phases boundary where the

possibility electrolysis reaction occurs brings about a decrement.

Thus that is expected to contribute in hydrogen production performance elevation because securing three phases boundary extensively because with the fact that the pore quality of Cu/YSZ composite is superior.

4. CONCLUSIONS

The cathode of high temperature electrolysis material in order to estimate a apply possibility with Ni/YSZ and Cu electrode materials which fabricated Cu/YSZ by mechanical alloying. Particle size of the Ni/YSZ finer than Cu/YSZ but after reducing the Cu of Cu/YSZ as much as YSZ connections, pore characterization and electric conductivity was superior. The cathode of high temperature electrolysis cell operates with the characterization where the mixture conductivity, pore characterization and electric conductivity are important in hydrogen production. As a result, hydrogen production efficiency is possible to predict with the fact that Cu/YSZ composite will be better than Ni/YSZ composite. And is estimated to be used for cathode material because has superior high temperature electrolysis if improve high temperature stability and durability of Cu.

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