Fabrication and microstructure of porous alumina tubular support for SOFC by extrusion

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Abstract – In this study, porous alumina supporting tubular cell for solid oxide fuel cell (SOFC) was produced using an extrusion method. This research focused on a suitable alumina dough composition composed of cassava starch and methylcellulose binders in water-based solvent system. The alumina dough with 35% water, 3wt%starch and 2wt%methylcellulose that showed good flow ability for extrusion. The sample was then sintered at 1300°C-1600°C for 1 h. A scanning electron microscope (SEM) was determined microstructure of the samples with various sintering temperatures. Porosity and pore size of the tubes tended to decrease slightly with increasing sintering temperature due to improvement in densification. Therefore, the flexural strength of alumina-supported tubular cell was further enhanced with increasing temperature due to the decrease of porosity. Although the alumina tubes sintered at 1600°C for 1 h showed the maximum flexural strength (63.66 MPa) but low porosity level (27.21%) affected on the decrease gas permeability. The optimum porosity (44.18 %) and flexural strength (25.85 MPa) of porous alumina supporting tubes was achieved after sintered at 1500°C for 1 h. However, the dense second phase of NiAl2O4 was observed at interlayer of the coated NiO-GDC on alumina substrate after sintered at 1350°C. This second phase is main problem to reduce surface area for gas permeability. Therefore, it will possibly improved by addition NiO in Al2O3 structure to generate the complete NiAl2O4 phase.

Keyword: Porous alumina support, NiO-GDC, Screen printing technique, Tubular, Extrusion, SOFC
1. Introduction

Solid oxide fuel cell (SOFC) has been recognized as one of the most promising renewable energy production devices that can convert the chemical energy of a reaction directly into electrical energy without combustion and releasing toxic gases [1]. The two major designs can be classified as planar and tubular. Although planar design has higher power density than tubular design but it has the problems of low mechanical properties and limitation of seal and interconnect cell requirement. Tubular design has shown many desirable characteristics over the planar system such as high mechanical properties, thermal stability, good thermal shock resistance and simple seal requirement [2].

The cell configurations are categorized according to the supporting types. Electrolyte-supported cell configuration has desirable mechanical properties because of the densed electrolyte layer. However, ohmic loss of electrolyte is the main problem that hinders the operation of SOFC at the intermediate temperature (600-800°C). The ohmic loss can be improved by two ways [3]. The first way is the reduction of thickness of the conventional yttria stabilized zirconia (YSZ), while the other way is the new materials with faster ionic conduction than YSZ such as ceria-based materials. The anode-supported cell is an excellent configuration to solve the ohmic loss problem because it can fabricate a thin electrolyte layer. However, the main problems of the anode supported cells are that gas transport through the thick anode may contribute to polarization losses [4]. Moreover, Michael et.al [5] reported that electrolyte layer of anode-supported cell cracked after rapid thermal cycling due to the tension from the large volume expansion associated with the oxidation of Ni [5]. Recently, many researchers have been focused on the external-supported cell configuration such as FeCr metal to fabricate thin cell component. Metal-supported cell is another excellent configuration that shows high electrical conductivity and high corrosion resistance in oxidizing atmosphere (air) as well as in a reducing atmosphere (hydrogen) [6]. Unfortunately, metallic substrate such as FeCr is easily converted to metal oxide (Fe₂O₃, Fe₃O₄ and Cr₂O₃), leading to high electrical resistance [7]. Such problem could be overcome by choosing another type of support with better oxidation resistance.

In this study, the alumina tubes were fabricated by an extrusion process to use as supporting cells for SOFC because the excellent properties of alumina are high hardness, high strength, high abrasive resistance, and high thermal shock resistance. Moreover, it is chemically stable in reducing and oxidizing environments [8]. Cassava starch was used as a water soluble binder due to its low environment impact and low cost. However, the only cassava starch binder cannot produce sufficient green strength for the extrusion. Therefore, methylcellulose is selected to use jointly with cassava starch to increase green strength. The suitable microstructure characterization and porosity of alumina tubes were studied to select the optimum processing conditions.

2. Experimental procedures

Alumina powder (Cernic international Co, Ltd) was mixed with total of methyl cellulose and cassava starch at 5% total weight in water using high speed milling (80-80s/120-120s, MHS-100, Japan). The alumina dough was then pressed by a triple roll mill (EXAKT, Germany). The homogeneous alumina dough was fed into vacuum kneader and extruder (FM-30-1, Miyasaki iron works, Japan) with a 0.66 mm diameter stainless steel die. The extruded alumina tube was dried at 80°C to increase green strength. The sintering temperatures were varied in the range of 1400-1600°C for 1 h. Phase transformation at interlayer of the NiO-GDC and alumina tube was analyzed by X-ray diffraction technique (PANalytical (X’Pert PRO MPD). Microstructure was observed under a scanning electron microscope (SEM) (JEOL, JSM-5410LV). Apparent densities and porosity of the sintered alumina tubes were measured based on the Archimedes principles by the standard test method of C373-88 [9]. A maximum pore size determination was studied in accordance with the standard of American society for testing and materials (ASTM) E 128-89 [10]. This method determined by immersing the porous samples in water and applying air pressure until the first bubble of air pass through the surface of porous samples. The maximum pore size (D) can be calculated by the relation:

\[ D = \frac{30 \gamma}{p} \]  

(1)

Where \( \gamma \) is surface tension of test liquid in dynes/cm and \( p \) is pressure (mmHg). The flexural strength (\( \sigma_{\text{max}} \)) of alumina tubes were tested from standard test method for ultimate strength of advance ceramics with diametral compression C-ring specimens in accordance with the standard of American society for testing and materials (ASTM) C1323-96 [11]. The C-ring samples of this test were compressed to find the maximum applied compressive load (\( P \)). It was then calculated by the relation:

\[ \sigma_{\text{max}} = \frac{PR}{btr_0} \left[ \frac{r_0 - r_t}{r_0 - R} \right] \]  

(2)

Where \( b \) is specimen width, \( r_o \) is the outer C-ring radius, \( r_i \) is the inner C-ring radius, \( t \) is specimen thickness \( R = r_0 + r_i / \ln (r_0 / r_i) \) and \( r_0 = r_0 + r_i / 2 \).
3. Results and Discussions

Figure 1 shows the particle size distribution of alumina powders by using laser diffraction method. The \(D_{4,3}\) of alumina powder was about 2.49 \(\mu m\). However, SEM micrograph in Figure 2 is clearly explained the particle size distribution of alumina powders. It was found that small particle size (< 2 \(\mu m\)) of alumina powders were agglomerated to the large size.

All green alumina tubes were prepared from alumina powders with different amounts of organic binders (methyl cellulose and cassava starch) to obtain proper dough with uniformity during die filling. The effects of water content on the quality of alumina dough are presented in Table 1. It was observed that alumina dough in formula 1 and 2 was hard and crumbly due to the deficiency water content. On the other hand, the alumina dough in formula 4 was highly stuck that was difficult to push through die because the water content exceeded the optimum limit. The optimum 35% water content in formula 3 was obtained the good plasticity and fluidity. The alumina dough with 35% water content was then studied the effects of cassava starch and methyl cellulose binders on green strength, as be illustrated in Table 2. The amount of binders significantly affected on the fluidity of alumina dough. In formula 5, the alumina dough with 5%wt cassava starch binder could be comfortably flown but it was continually flown. Besides, it was observed that the green alumina tube was bent and creaked after extrusion due to the low green strength of alumina dough, as be shown in Figure 3a. This effect was explained that the cassava starch binder was less adhesively than methyl cellulose binder, so 1%wt methyl cellulose binder was insufficient for the stability of shape. Therefore, the methyl cellulose was more added to assist green strength of alumina tubes for the alumina dough in formula 6 and 7. It was found that the replaced methyl cellulose (≥2%wt) could be improved green strength of alumina during extrusion process (Figure 3b). Although both alumina dough in formula 6 and formula 7 could be extruded continually and protected the problems of the bending and cracking, however, the alumina dough in formula 6 was selected to study in next part due to low cost production of cassava starch.

Table 1. The effects of water content on preparation alumina dough

<table>
<thead>
<tr>
<th>Formula</th>
<th>A</th>
<th>W</th>
<th>C</th>
<th>Dough</th>
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<tr>
<td>1</td>
<td>70</td>
<td>25</td>
<td>5</td>
<td>Hard/Crumbly</td>
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<tr>
<td>2</td>
<td>65</td>
<td>30</td>
<td>5</td>
<td>Hard/Crumbly</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>35</td>
<td>5</td>
<td>Soft</td>
</tr>
<tr>
<td>4</td>
<td>55</td>
<td>40</td>
<td>5</td>
<td>Stick</td>
</tr>
</tbody>
</table>

*A=A=Alumina, W=Water, C=Cassava starch

Table 2. The effects of cassava starch and methyl cellulose on preparation alumina dough

<table>
<thead>
<tr>
<th>Formula</th>
<th>A</th>
<th>W</th>
<th>M</th>
<th>C</th>
<th>Dough</th>
<th>Extrusion</th>
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<tbody>
<tr>
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<td>60</td>
<td>35</td>
<td>1</td>
<td>4</td>
<td>Soft</td>
<td>Not continually</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>35</td>
<td>2</td>
<td>3</td>
<td>Proper</td>
<td>Success</td>
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<td>60</td>
<td>35</td>
<td>3</td>
<td>2</td>
<td>Proper</td>
<td>Success</td>
</tr>
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*A=A=Alumina, W=Water, C=Cassava starch, M=Methyl cellulose
Figure 3. Extrusion of alumina dough with (a) 5% cassava starch and (b) 2% cassava starch and 3% methyl cellulose.

Figure 4 shows the SEM micrographs and the thickness of the sintered alumina tubes at different temperatures. At 1400°C, intergranular pores were still largely observed and the thickness of alumina tube was about 1.84 mm (Figure 4a). With increasing sintering temperature at 1500°C and 1600°C, the pore content was slightly reduced while the agglomerated particles were larger, as be observed in Figure 4b and 4c. About the thickness of the sintered alumina tube, it was seen that the thickness of the sintered alumina tube at 1500°C and 1600°C were about 1.62 mm and 1.52 mm, respectively. The thinner thickness of the sintered alumina tubes were related with the increased shrinkage because of the higher sintering temperatures.

To understand the sintering mechanism of alumina tubes better, the relative density and apparent porosity with different sintering temperatures are shown in Figure 5. The plot shows the low relative density (87.53%) and the high apparent porosity (52.13%) for the sintered alumina tubes at 1400°C. The relative density of the sintered alumina tubes were increased corresponding with the lower apparent porosity when the sintering temperatures were increased. At 1600°C, the sintered alumina tubes had the minimum apparent porosity and the maximum relative density about 29.80% and 89.26%, respectively. The maximum pore size of the sintered alumina tube was further studied to explain about the development of microstructure, as be presented in Figure 6. At 1400°C, the maximum pore size was about 1.01 µm. The maximum pore size was slightly reduced about 0.88 µm and 0.69 µm with increasing temperatures from 1500°C to 1600°C, respectively. It was found that the maximum pore size tended to reduced when the sintering temperatures were increased because of the neck growth behavior of alumina particles.
From the results of the porosity and pore size results, it was directly affected on the flexural strength (Figure 6). At 1400, the flexural strength showed the lowest about 16.75 MPa because it was observed high apparent porosity and the largest of maximum pore size. It was found that the flexural strength was improved with increasing sintering temperatures due to the lower porosity and the smaller pore size. The maximum flexural strength (63.66 MPa) was obtained in the sintered alumina tubes at 1600°C for 1h. Although this temperature could produce the maximum flexural strength but the supporting cell for SOFC should has low porosity for gas transportation. Besides, the low porosity of the sintered alumina tube at 1600°C was affected on the deteriorated adherence of the coated NiO-GDC anode by screen printing technique. Therefore, the optimum sintering condition of the alumina tube was achieved at 1500°C that had the high porosity about 44% and the excellent flexural strength at 25.85 MPa. Furthermore, the coated NiO-GDC anode could be adhered and fully coated on the sintered alumina tube (1500°C) after sintered at 1350°C. However, it was observed the problem of dense second phase at interlayer of the coated NiO-GDC (Figure 7) because it reduced surface area for gas transportation. To investigate the formation of this dense second phase, this dense second phase was indicated by XRD pattern showing in Figure 8. It was found that this second phase presented the crystal structure of Ni-spinel (NiAl2O4). It was explained that the oxygen vacancies were generated from the substitution of Al3+ ions by Ni2+, leading to the higher oxygen vacancies diffusion during sintering process. Similar to the literature [12], it was reported that the substitutions of aliovalent dopant in the lattice sites to observe point defect such as vacancies that could be cased for the increased diffusion mechanism during sintering process.

For all results, the porous alumina should be improved the problem of dense second phases when it was coated by NiO-GDC anode. However, it is believed that addition of exceed NiO in the Al2O3 structure to form NiAl2O4 and the remaining NiO phases that will be improved the problem of second phase because of the complete substitution of Ni in Al2O3 structure. It has been attentively studied in the future work.

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4. Conclusions

Porous alumina tube was obtained by the extrusion of alumina powders with both binders of methyl cellulose and cassava starch in water solvent. The suitable composition of alumina dough for extrusion depended on the quantity of water and binder to prepare an appropriate level of fluidity. In this study, 35%wt water was found to be the good solvent for extrusion. Both binders could be assisted to increase green strength. However, methyl cellulose showed better binding ability than the cassava starch. Therefore, 2%wt methyl cellulose was replacing in 5%wt cassava starch to improve green strength of alumina dough during extrusion process. With increasing temperatures, the relative density tended to increase while the porosity and the maximum pore size were decreased. The flexural strength was related to the densification, the porosity and pore size. Flexural strength was enhanced with higher density, lower porosity and pore size. The optimum sintered alumina tube was achieved at 1500°C. In the part of NiO-GDC coating, it was observed the problem of dense NiAl2O4 phase at interlayer that affected on the reduced surface area for gas transportation. However, the addition of exceed NiO in Al2O3 to form the complete NiAl2O4 and the remaining NiO will protect Ni2+ diffusion from NiO-GDC layer.
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References


