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Preparation and Characterizations of NiYSZ-based Anode for Solid Oxide Fuel Cells and Solid Oxide Electrolyser Cells

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ABSTRACT
Solid Oxide Fuel Cells (SOFCs) offer their ability to directly convert hydrocarbon fuel into electricity via internal dry reforming. NiYSZ-based SOFC anodes were manufactured via aqueous tape casting. Raw materials such as NiO and yttria-stabilized ZrO_2 powders, glycerol, polyvinyl alcohol (PVA), and water were weighed and mixed. The obtained slurry was ball milled for 12 hours, de-gassed, tape-cast, and dried at ambient temperature to obtain smooth, crack-free, elastic, and easy to remove green tapes. The good green tapes were then sintered at 1200˚C. The sintered tapes were characterized for their morphology, topography, and composition by using SEM/EDX. The hardness uses Vickers hardness tests while the electrical conductivity at 600-800ºC uses a special furnace and a multimeter. On the other hand, the porosity is being tested by the Archimedes method. The results showed that good SOFC anode tapes were obtained after degassing in the range of 32 - 125 hours depending on the amount of PVA and water added to the mixture. The resulting morphology and topography of the anode tapes were comparable with those of the reference anode tape, with pore sizes ranging from 100ηm-1μm and 28% porosity (pore volume). The tapes' hardness after sintering was in the range of 170.3 HV and 212.2 HV. Under the condition, their conductivities were 0.098 Siemens and 0.529 Siemens at 750ºC and 800ºC respectively. The successful attempts to make NiYSZ-based SOFC anodes using locally available materials and equipment are promising as the initial steps for further development of SOFC manufacturing in Indonesia. The developed SOFC will be further tested as a Solid Oxide Electrolyser Cell (SOEC) to produce hydrogen.

Keywords: *solid oxide fuel cells; Ni-YSZ anodes; aqueous tape casting.*

1. INTRODUCTION

The pressure to use renewable energy and the need to convert fuel with high efficiency increase sharply as our awareness towards environmental protection becomes real and spreading. Fuel cell technology is most likely to be the right solution for the future of energy challenges. It is due to the ability of the fuel cell which can convert fuel directly into electricity with such a high efficiency of 60-85%. Solid Oxide Fuel Cell can even use hydrocarbon and biogas as fuel [1], [2] Biogas which contains CH_4 and CO_2 is a by-product of anaerobic digestion (AD) of organic wastes. In Indonesia, biogas is not maximally utilized. Biogas utilization has been seen for fuel in steam engines or for direct burning for cooking on gas stoves. Making biogas as fuel for fuel cells offers the opportunity to obtain electricity with a neutral carbon footprint so that it will provide both economic and environmental benefits. Other advantages of converting energy by using fuel cells are quiet, minimal maintenance, and can be designed in a modular manner. They can be built on a small scale (hundreds of Watts, such as for home needs) or large (MWatt as for industrial needs) with similar efficiency. As Indonesia moves towards more renewable energy-based electricity, there will be places where renewable electricity is in surplus that needs the electricity storage. An electrolyser can be utilized for the electrolysis of water (or steam) to produce hydrogen which can then be stored in tanks or other forms to be used later or this hydrogen can also be transported to other places. A solid oxide fuel cell that can be operated as an electrolyser cell (hence SOEC) will have the benefits of simple operation as well as space-saving and low capital costs. As generally understood, the manufacturing costs remain the main barrier to commercialization of SOFC and SOEC. However, the research continuity, more case studies, and production scale-up are potential ways to reduce costs [3][4][5]. Anode plays an important role in solid oxide fuel cells' operation. It serves as the site for electrochemical oxidation of the fuels. Generally, anode needs to be porous for the gas fuels to diffuse through; it has to be electron-conducting for the electrons produced from the electrochemical oxidations to travel from inner to outer layers and the current collectors; it has to be mechanically strong to withstand impacts from daily operation [6][7]. Specifically, anode needs to be catalytically active for the specific desirable reactions to occur, and resistant to coke formations especially for operations on hydrocarbons [8][9][10].

2. MATERIALS AND METHODS

An *aqueous tape casting* method for preparing SOFC anodes developed at the University of Birmingham UK [11] was adopted in this work. It is an environmentally friendly method that avoided the use of organic solvents throughout the preparation procedure. NiO and YSZ powders were used as the base materials with the addition of aqueous solvent, binder, and plasticizers.

2.1. Tape casting

The materials for preparing anode slurry were weighed into a 100 mL plastic bottle. Zirconia milling beads were added to the mixture. The bottle was placed in a ball milling machine and set for 12 hours slow milling at 120rpm. Then, the bottle (with the lid open) was placed in a desiccator to allow for any air bubble formed during milling to escape. This stage is called degassing which was done at ambient temperature and pressure. The obtained slurry was carefully cast over a flat glass surface (10x20cm) lined with a layer of parafilm. Before casting, the four edges of the flat glass were lined with several layers of dark cello tapes to give approximately 1mm thick wet cast. The wet cast was placed in a suitable plastic box (with the lid half-open) to avoid contamination from bags of dust while slow drying for 24-48 hours. The dried tapes were examined for visual appearances such as surface smoothness, flexibility/elasticity, and appearance of (micro) cracks. The tapes with high scores were chosen for sintering.

2.2. Sintering

Sintering was carried out by gradually heating the dried anode tapes in a chamber furnace at 1200^{o}C for 90 minutes. Then the sintered anode tapes were examined for visual appearances such as surface smoothness, cracks, and the presence of curvature [12]–[14].

2.3. Physical property tests

Characterizations of sintered SOFC anode comprise morphology, topography, chemical composition, electrical conductivity, and hardness. Morphology and topography tests were performed using Scanning Electron Microscopy at a magnification of 5000-15000 while the hardness test was carried out using Hardness Testing Machine -122. A porosity test was carried out using the Archimedes method. Meanwhile, the conductivity test on the anode plate is carried out by measuring the resistance read by a multimeter which is then converted to conductivity at 600^{o}C - 800^{o}C.

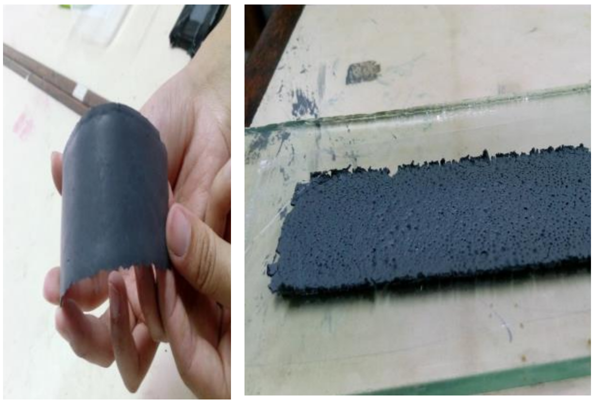
3. RESULTS AND DISCUSSION

Thirteen batches of SOFC anode (coded A – M) were made. According to the results, the optimum composition is presented in Table 1.

Table 1. SOFC anode material used, their function and composition

Material	Function	Weight %
NiO	Electron-conducting phase	25-25
8YSZ	Ion-conducting phase	22
Aquadest	Solvent	45-47
Poly Vinyl Alcohol	Binder	2-3
PEG 400	Plasticizer	3
Glycerol	Plasticizer	1

A good anode surface can be seen in Figure 1a. It is a smooth, flexible, and non-fractured plate. An example of anode tape with a rough surface that shows insufficient degassing time is presented in Figure 1b. It was noted that the composition of the material which acts as plasticizer and binder is of primary importance to obtain a good, flat, and strong half-cell. In addition, homogenization of the slurry before casting is important.



(a) (b)

Figure 1 (a) a flexible anode tape with no cracks and (b) a rough anode surface resulted from insufficient degassing time

Only the good anode tapes are suitable for sintering at 1200ºC. At the beginning of the sintering process (temperature 100-200ºC), water contained on the anode surface evaporates. Further heating (at temperatures around 600ºC) will burn organic compounds (such as PEG, PVA) and subsequently, (at 800-1200ºC) sintering unifies a part of the inter-molecule NiYSZ allowing the connection of the Ni-Ni phase (as an electron conductor) and the YSZ-YSZ phase as O^{2-} conductor. Sintering also leaves a continuous pore as a place for gas mixing and reactions. Sintering provides a triple-phase boundary, which is the place where chemical and electrochemical reactions occur, as well as the formation of the conduction pathway of three reactant species (electrons, O^{2-} and gas) at the SOFC anode. This sintering stage is very critical. Failures often occur at this stage. Among the failures were caused by cracks or curved layers (either convex or concave). Normally, sintering with a heating rate that matches the nature of the sintered material is successful.

3.1. Morphology and topography of anode surface

Morphology and topography of the sintered anode tapes were compared to those of the reference anode. Pore volume, size, and connectivity are among the important parameters to be collected from micrographs. Besides, the appearance of microcracks, the shapes of the grains, and grain boundaries are useful for comparisons with those of the reference materials. Micrographs of a reference anode were taken from commercially available SOFCs of the same type (Ni-YSZ- based) with the prepared SOFC prototype. Figure 2 shows a micrograph of clearly porous reference anode surface whereas Figure 3 shows a micrograph of batch K prototype anode surface.

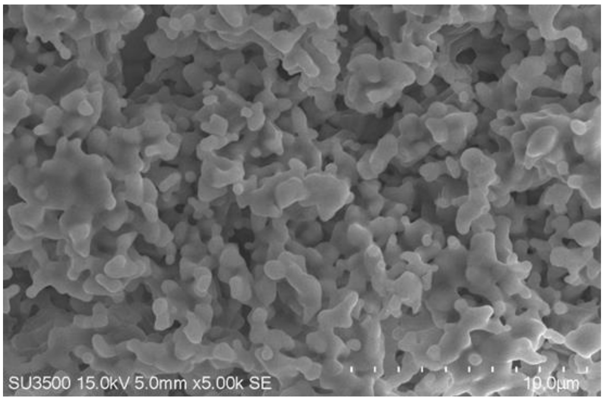


Figure 2 shows a typical porous anode surface

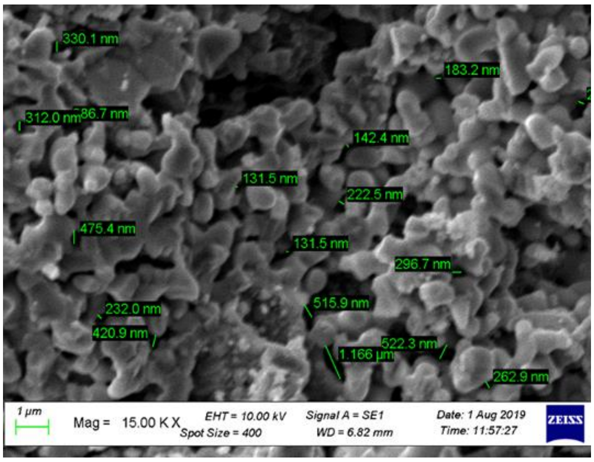


Figure 3 Micrograph of anode surface of batch K shows different pore sizes.

Figure 4. is an EDX map of batch K anode which clearly shows that Ni and Zr are evenly distributed with Ni-YSZ grains size of 130nm-1.1µm.

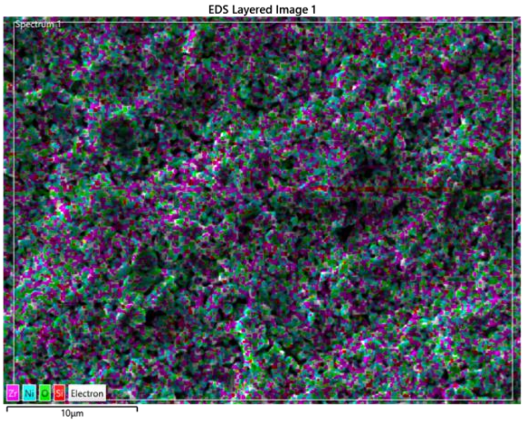


Figure 4 An EDX map of SOFC anode surface

3.2. Chemical composition according to EDX

According to EDX results which were carried out to three sample batches namely K, L, and M, the chemical composition of the main elements in the three batches were expected. The results are presented in Table.2.

Table 2. Chemical composition of a SOFC Anode measured by EDX

Batch Id	Main elements					
	Ni		Zr		Y	
	Wt %	At %	Wt %	At %	Wt %	At %
Batch K	21.95	11.80	32.33	11.19	4.80	1.70
Batch L	39.83	25.59	27.76	11.48	4.51	1.91
Batch M	34.87	21.32	30.58	12.03	4.89	1.97

3.3. Conductivity

The electrical conductivity of the anode layer is one of the important characteristics of the anode. The anode's ability to conduct the electricity at SOFC operating temperatures is one of the determinants of SOFC performance. Conductivity is measured after the SOFC anode layer was reduced by H_2 gas at the measured temperature. The results of conductivity measurements are presented in Table 3. When H_2 has not yet flowed, the anode layer practically does not deliver electrons as evidenced by the very high resistance. However, after H_2 was introduced, the anode showed increasing conductivity as the temperature was increased. Ideally, the expected anode conductivity values range from 10-20 S/cm at 800ºC or around 20-40 times the conductivities shown in Table 3.

Tabel 3. Conductivity at 600–800ºC

No	Temp (˚C)	*Batch* K		*Batch* L	
		(Ω.cm)	(S/cm)	(Ω.cm)	(S/cm)
1	800 (no H_2 flow)	6325	0.00016	73000	0.0000
2	600	2213.3	0.00045	2790	0.0004
3	650	1890	0.00053	1630	0.0006
4	700	198	0.00505	435	0.0023
5	750	50	0.02000	10.19	0.0981
6	800	.89	0.52910	5.93	0.1686

3.4. Hardness

The hardness of the anode tape represents the mechanical strength which is very important for the SOFC when it is in operation. It is shown that the Vickers hardness of the anode tapes was higher than the reference anode tape. This is a promising sign that the prepared anode tapes will make a mechanically strong anode. This is very important as these anode tapes will be used as anode supported SOFC types.

Table 4. Hardness (Vickers)

Batch	Load (g)	HV
K	0,2	170,3
L		187,8
M		212,2
Reference		144,2

3.5. Anode porosity

The anode porosity was measured using the Archimedes method. A certain area of the anode (approximately 3cm^2) was weighed in dry condition. Then it was immersed in a beaker glass containing pure water for 5 hours. This is then heated to boiling point for one minute and left to cool at ambient temperature for 24 hours. Then, the anode sample was taken out of the water and carefully dried off the dripping water before re-weighing. The difference of the anode weight before and after immersion was converted into volume (Vp). Porosity was calculated by finding Vp/Total anode volume (represented in %). It was found that the pore volume is 28 % which is within the acceptable range of 20-40%.

4. CONCLUSION

A first attempt to prepare and characterize the SOFC anode using the aqueous tape casting method was carried out at Politeknik Negeri Bandung. The results were promising that the tapes produced at 500-700 microns thickness were suitable for sintering at 1200ºC without any visible sign of cracks and bending. The morphology, pore-volume, and pore sizes are like those of the reference anode and the values are within the acceptable range. Further work is to continue for preparing the electrolyte-anode layer half cells and their characterizations.

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