Fabrication and characterization of Intermediate-Temperature Solid Oxide Fuel Cell (IT-SOFC) single cell using Indonesia’s resources

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Abstract. Solid Oxide Fuel Cell (SOFC) is one of the promising developments in the fuel cell system. SOFC can be applied to micro-scale combined heat and power generation (micro CHP) as a power plant in housing. Recently, intermediate-temperature SOFC (500–700°C) is being widely developed since cheaper than the conventional SOFC (~1000°C). Intermediate-temperature and conventional SOFC are less developed in Indonesia due to expensive electrode and electrolyte materials, such as Yttria and Lanthanum, which are not available in Indonesia. This study aims to develop a novel disk-shaped single cell SOFC based on materials from Indonesia’s resources. Calcia Cobalt Zinc Oxide (CCZO) is an alternative cathode to replace conventional cathode such as Lanthanum Strontium Manganite (LSM). CCZO cathode was made using spray coating. Calcia can also substitute Yttria as a stabilizer of zirconia in electrolyte fabrication. Calcia-stabilized Zirconia (CSZ) electrolyte was produced using spray coating. NiO anode was fabricated through hydraulic pressing. The single cell was operated using hydrogen (125 sccm) as a fuel and ambient air (500 sccm) as an oxidant. The results showed an open-circuit voltage (OCV) of 0.577, 0.558, and 0.513 V and produced the maximum power densities of 1.4, 2.8, and 10 mW m⁻² at 500, 600, and 700°C, respectively. Measurement of the cell impedance indicated that the overall resistance decreased with increasing temperature.

1. Introduction

Electricity generations in Indonesia are still dominated by fossil fuels such as coal, oil and gas which produce greenhouse gases. Meanwhile, Indonesia’s electricity needs in 2050 will rise around 193 million tons of equivalent (TOE) according to business as usual (BAU) scenario [1]. To reduce Indonesia’s dependency of fossil fuels, utilization of new and renewable energy (NRE) is very important. Hydrogen, produced through biomass gasification, is a new energy source which can be converted into electricity. One of the methods to convert hydrogen into electricity is by using Fuel cell. Fuel cell is an electrochemical device which converts chemical energy into electricity directly without involving the process of combustion. The advantages of fuel cell are higher efficiency (40 – 60%) than heat engine (20 – 30%), quite operation, and low or zero emission [2].

Solid Oxide Fuel Cell (SOFC), a fuel cell used solid oxide electrolyte, is one of the promising developments in the fuel cell system. The advantages of SOFC are higher electrical efficiency (50 – 60%) than other types of fuel cell, higher resilience to corrosion of electrode, wider fuel flexibility and higher reduction of CO₂ emission from 90% to 35% when using hydrocarbon fuels [3]. SOFC is usually operated at 850 – 1000°C, which is called as high temperature SOFC (HT-SOFC). The requirement of
high heat and complex material such as ceramic and high temperature metal alloys make HT-SOFC expensive. The purpose of decreasing temperature is to cut material cost and decrease heat requirement. The intermediate-temperature SOFC (IT-SOFC) which operates at 500 – 800°C has been developed to be used in small scale applications such as micro combined heat and power (micro-CHP) and auxiliary power unit (APUs). IT-SOFC gives a wide range of material, rapid start-up and shut down, low corrosion rate of metallic component, improved durability and more robust construction [4].

Electrolyte material of IT-SOFC commonly used is yttria-stabilized zirconia (YSZ). Anode and cathode material of IT-SOFC commonly used is NiO cermet such as NiO-YSZ and lanthanum strontium manganite (LSM), respectively. However, these materials such as yttria, strontium and lanthanum are rare in Indonesia thus IT-SOFC is less developed in Indonesia. To replace those rare materials, cheaper and common material such as calcia (CaO) can substitute yttria as a stabilizer of zirconia in electrolyte fabrication. Indonesia has an abundant zirconia and calcia resources. Zirconia is a by-product from tin production in Bangka Belitung Island [5]. Calcia can be produced from limestone which has huge ore reserves in Indonesia, around 28.7 billion tons. [6]. Calcia-stabilized zirconia (CSZ) ionic conductivity has been investigated and it is suitable to be used for IT-SOFC electrolyte [7]. An alternative material for cathode is calcium cobalt zinc oxide (CCZO). Indonesia’s cobalt reserves in 2017 are around 180,344 tons [8]. Cobalt is a by-product from nickel production. An alternative material, NiO-CSZ, can be used as Anode material because of high electrocatalytic activity and electrically conductive [9]. Indonesia’s nickel reserves in 2017 are around 4 million tons and Indonesia is the seventh largest country of nickel production [8].

In this study, an IT-SOFC single cell was fabricated using Indonesia’s resources then characterized and evaluated its performance. NiO-CSZ anode was produced through hydraulic pressing method. In other hand, CSZ electrolyte and CCZO cathode were fabricated using spray coating method. The design of single cell was anode-supported. The single cell was evaluated on power density and impedance with different operating temperature, respectively.

2. Experimental

2.1. Material preparation
Material compositions of anode are nickel oxide (NiO), zirconia (ZrO₂), maizena flour, CaO and polyvinyl alcohol (PVA). The electrolyte was formed by ZrO₂, CaO, PVA, isopropyl alcohol (IPA) and polyethylene glycol (PEG). Meanwhile, cathode’s materials are cobalt oxide (Co₃O₄), zinc oxide (ZnO), CaO, PVA, ZrO₂, IPA and PEG. Maizena flour, PVA, IPA and PEG act as pore former, binder, dispersion agent and plasticizer, respectively. All materials except PEG and IPA was milled using ball mill for 12 hours. After ball milling, the material powders was sieved for 325 mesh.

2.2. Cell fabrication
First of all, NiO-CSZ anode as support was fabricated using hydraulic pressing method. The mass ratio between NiO and CSZ was 65:35 wt%. The function of CSZ addition is to expand an active surface area. The concentration of PVA and maizena was 3 and 15 wt%. All powders were mixed and pressed at 60 kg/cm² for 1 hour to achieve 1.5 mm in thickness. The sintering temperature of anode production was 1000°C for 1 hour. For electrolyte fabrication, ZrO₂, CaO 3 wt%, PVA 1 wt% and PEG 1 wt% were mixed and dispersed using IPA. The function of PEG addition was to increase flexibility and durability of electrolyte. A spray coating method in electrolyte production was intended to reach 20 µm in thickness. The sintering temperature of electrolyte production was 1000°C for 3 hours. In cathode fabrication, Co₃O₄, ZnO, CaO (CCZO) were mixed with CSZ. The mass ratio between CCZO and CSZ was 65:35 wt%. The concentration of PVA and PEG was 1 wt%, respectively. The method of cathode production was spray coating to achieve 50 µm in thickness. The sintering temperature of cathode production was 800°C for 5 hours. The single cell was fabricated with a disk shape of 4.3 cm in anode’s and electrolyte’s diameter, 4.2 cm in cathode’s diameter and 1.8 mm in thickness. The process flow diagram of single cell production as shown in figure 1.
2.3. Microstructure and electrochemical characterization

The single cell microstructure was examined with scanning electron microscope (SEM). This characterization aimed to determine thickness and structure of each component. The analysis was done before electrochemical characterization. To observe electrochemical measurement, SS mesh was used as current collector on the anodic and cathodic side. The electrochemical performance of single cell was tested by I-V-P curve and electrochemical impedance spectroscopy (EIS). The electrochemical measurement was carried out by Gamry V3000. The performance of single cell was observed at 500, 600 and 700°C using hydrogen as fuel and ambient air as oxidant.

3. Results and discussion

3.1. Effect of maizena on anode’s porosity and PVA concentration on anode morphology

The anode required a porous structure due to fuel diffusion to triple phase boundary (TPB). Maizena was commonly used as pore former. Testing of anode’s porosity was done by ASTM C373-88. The result showed that the porosity of NiO-CSZ anode without pore former was 6%. When a 15 wt% of maizena was added, the porosity of NiO-CSZ anode increased to 31%. The requirement of anode’s porosity was 20 – 40% because very large porosity weakened a bending strength of anode [10, 11]. A 15%wt of maizena as pore former is sufficient to reach anode’s porosity requirement while maintaining a bending strength of anode as support [12]. PVA as a binder is used to increase compact strength of NiO-CSZ anode. PVA concentrations used in this experiment were 3 and 10 wt%. The 10 %wt of PVA made a fragile structure because there are too much mass loss of PVA during sintering. Reduction of PVA concentration is used to avoid high mass loss. The 3 wt% of PVA made a strong and uniform structure of NiO-CSZ anode with the diameter of the anode was 4.4 cm after sintering, as shown in figure 2.

3.2. Effect of PVA phase to electrolyte and cathode morphology

The requirement of electrolyte is dense structure. Production of CSZ electrolyte used two phase of PVA; liquid and solid. The 1 wt% of PEG was added as plasticizer in each PVA. The 1 wt% of liquid PVA
made microcrack on surface electrolyte after sintering. The microcrack was formed by a bumpy surface which caused unequal thermal expansion in electrolyte’s surface. The 1 wt% of powder PVA and 1 wt% of PEG made the surface electrolyte uniform with the diameter of anode-electrolyte was 4.3 cm after sintering as shown in figure 3.

![Figure 3.](image)

**Figure 3.** (a) liquid (b) powder PVA effect in CSZ electrolyte fabrication (c) CCZO cathode production on surface anode-electrolyte (d) the single cell.

The composition of PEG and PVA in electrolyte fabrication was used to fabricate CCZO cathode through spray coating. The diameter of CCZO cathode was 4.2 cm which is smaller than anode-electrolyte diameter as shown in figure 3. The purpose was to avoid short circuit between anode and cathode. The single cell was successfully fabricated with 13.2 cm² in active area and 1.8 mm in thickness.

### 3.3. Microstructural characterization

Microstructure of the single cell was shown in figure 4. In figure 4a, NiO-CSZ anode as a support was thicker than the electrolyte and cathode. The thickness of anode, electrolyte and cathode was 1.65 mm, 100 µm and 50 µm, respectively. The electrolyte’s thickness was too large because the requirement of electrolyte thickness was 20 – 50 µm to reduce impedance in electrolyte [13]. Figure 4b showed the microstructure of CSZ electrolyte is less dense. It has potential to hydrogen crossover. The microstructure of CCZO cathode and NiO-CSZ anode, as shown in figure 4c and 4d, was porous structure, thus fuel and oxidant can diffuse to TPB in order to conduct oxidation and reduction reaction.

![Figure 4.](image)

**Figure 4.** A cross-sectional SEM images of (a) single cell (b) electrolyte (c) cathode (d) anode.
3.4. Electrochemical characteristic of single cell

Electrochemical tests to determine I-V-P curve and the impedance of single cell were performed at 500, 600 and 700°C, respectively. The single cell was tested using hydrogen as fuel with flow rate of 125 sccm and ambient air as oxidant with flow rate of 500 sccm. Figure 5 showed I-V-P curve of IT-SOFC single cell. The single cell had open circuit voltage (OCV) of 0.577, 0.558 and 0.513 V at 500, 600 and 700°C, respectively. The low OCV indicated that structure of electrolyte was less dense as shown in figure 4b [14]. The maximum power density of single cell at 500, 600 and 700°C was 1.4, 2.8 and 10 mW m⁻², respectively. The low power density is caused by a thick electrolyte.

![Figure 5. I-V-P curve of IT-SOFC single cell.](image)

Process of charge and mass transfer in SOFC cell was showed by Nyquist plots from EIS measurement. Nyquist plots illustrate the relationship between imaginary and real impedance. Figure 6 showed Nyquist plot of single cell was measured at OCV condition of 500, 600 and 700°C, respectively. An impedance cell was measured at frequency of 100 kHz – 0.1 Hz.

![Figure 6. Nyquist plots and equivalent circuit of IT-SOFC single cell.](image)

The first intercept on the real axis at high frequency represents the ohmic resistance (RΩ) and the second intercept on the real axis at low frequency corresponds to the total resistance of the cell. Polarization resistance (Rₚ) was determined by two different arcs where one was at high frequency range (HF, ~10⁵ Hz) and the other at medium frequency range (MF, ~10² – 10³ Hz). The Nyquist plots were fitted using equivalent circuit model of two parallel R and Q or CPE (constant phase element) and one resistor connected in series as shown in figure 6 [15]. The values from fitting was summarize in Table 1.
Table 1. Summary of values from equivalent circuit fitting of Nyquist plots.

| T(°C) | R_0 (ohm) | R_1 (ohm) | R_2 (ohm) | R_p = R_1 + R_2 (ohm) |
|-------|------------|------------|------------|-----------------------|
| 500   | 3303       | 152300     | 104700     | 257000                |
| 600   | 3452       | 44170      | 38230      | 82400                 |
| 700   | 3624       | 22750      | 31920      | 54670                 |

R_1 correlated with charge transfer process and R_2 related with mass transfer process [16]. Based on fitting result, the low performance of IT-SOFC single cell was at lower temperature (500°C). The high resistance of charge transfer happened because of a slow electrochemical kinetic of CCZO cathode when low operating temperature. The ohmic resistance was still high due to a thick electrolyte.

4. Conclusion
In this study, the IT-SOFC single cell using Indonesia’s resources was successfully fabricated using hydraulic pressing and spray coating method. Maizena as pore former can increase a porosity of anode and 3 wt% of PVA powder made anode’s structure strong and uniform surface. 1 wt% of PVA powder and 1 wt% of PEG made uniform surface of electrolyte and cathode even though the thickness of electrolyte was not fulfill a requirement of thin electrolyte fabrication. However, the process is cheap and easy to scale up. The IT-SOFC single cell exhibited the maximum power density of 10 mW m⁻² at 700°C. The total resistance was still too high because the structure of electrolyte was less dense and too thick. Moreover, the slow electrochemical kinetic of cathode at low temperature caused a high resistance. Advancement of electrolyte thickness and structure will be researched to enhance the performance of IT-SOFC single cell fabricated using Indonesia’s resources.

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