Effects of Fe-Doped Electrolyte and Feed Flow Rate Evaluation in Home Made Solid Oxide Fuel Cell

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Abstract. Solid Oxide Fuel Cell (SOFC) is one type of fuel cell that has several advantages over other types of fuel cells. To achieve low cost SOFC, the materials used are nickel oxide (NiO) for the anode, Calcia Stabilized Zirconia (SCZ) for the electrolyte and Calcia Cobalt Oxide Zinc Oxide (CCZO) as cathode. Fe$_2$O$_3$ is a doping agent to form a denser electrolyte. The cell with and without Fe doping was tested using hydrogen and ambient air. Additionally, the effect of the amount of fuel flow rate is also investigated using Aspen Plus Modelling. Based on physical characterization, it is determined that 3%-mole Fe doping on the electrolyte increases the electrolyte density from 83% to 90%. Using electrochemical impedance spectroscopy, it can be concluded that SOFC with Fe doped electrolyte has a lower resistance than SOFC without Fe doping. On the other hand, using a correction factor, an equation of power correlated to fuel flow for the SOFC is generated to show increasing fuel flow enhanced SOFC performance.

1. Introduction
Energy is becoming one of the basic human needs, along with clothing, food, and shelter. Advances in technology increases the global needs of energy. With the increasing global needs of energy, clean energy improvement has to be made. Fuel cell is one of the new and alternative energy conversion technology that converts chemical energy directly into electrical energy. This technology is highly efficient, it has a wide range of fuels, and relatively environmentally friendly. Fuel cell’s unique and favorable characteristics compared to regular heat engine to produce electricity attracts the world’s attention. Research development by institutes and commercialization effort about fuel cell has been done. For fuel cell to be a commercial power generator, fuel cell has to produce power as needed while also being inexpensive. This can be done by stacking individual cells into a stacked fuel cell system [1, 2].

Solid oxide fuel cell (SOFC) is a breakthrough in clean energy conversion technology that can uses fuel that is widely available in Indonesia. The performance of SOFC is directly effected by cell fabrication methods, and one of the most important part of SOFC that requires fabrication is its electrolyte. SOFC performance will increase along with the increasing of electrolyte density and ionic conductivity[3, 4]. One of the more widely used electrolyte for SOFC is calcia-stabilized zirconia (CSZ) ceramic [5, 6]. To fabricate CSZ, calcia and zirconia powder is sintered at its eutectic temperature at 1300 °C. It is known that metal oxide doping during sintering process can lower the eutectic temperature and increase the ionic conductivity of CSZ thus increasing the overall performance of SOFC [7]. Aim
of this research is to determine the effect of Fe foping for CSZ and the evaluation of flow rate variation for single sel SOFC fueled by hydrogen.

2. Methodology
In general, this research is divided into three main sections, starting with material and equipment preparation, cell fabrication along with physical test of cell’s micro and macrostructure, and on-off cell cycle evaluation. Physical characterization of cell is carried out for cell fabrication evaluation, while the cell characteristic test is carried out using electrochemical and physical characterization. Then proceed with modeling with SOFC operation simulation using Aspen Plus simulation software.

2.1. SOFC Cell Fabrication
Anode supported SOFC fabrication starts with anode fabrication. SOFC anode used in this research was manufactured by means of dry casting. The main material of the anode used in this research was a ceramic powder made of Nickel Oxide (NiO) purchased from Changsha Easchem Co., Ltd (technical grade, Changsa, China) and zirconia purchased from Pingxiang Ball-Tec New Materials Co., Ltd (technical grade, Jianxi, China) in a ratio 65:35, into the powder polyvinyl alcohol (PVA) 1 wt% and maizena 10 wt%. To make the powder homogen, the powder was put into a ball mill for 1 hour. The mixed powder is then formed using dry casting method at 60 kN/m². The casted powder is then sintered in a furnace at 1100 °C and atmospheric pressure for 3 h to make a stable ceramic. After sintering process, the physical structure of the anode was tested. After anode fabrication, the electrolyte is made. Electrolyte used in this research is a zirconia based electrolyte with CaO purchased from Bratachem (technical grade, Bandung, Indonesia) as a stabilizer, and FeO₁.₃ purchased from Bratachem (technical grade, Bandung, Indonesia) of 3 mole% as a doping. The powder mixture is then dispersed in isopropyl alcohol (IPA). Using automated air brush sprayer, the mixture is then sprayed on the anode. The electrolyte and anode is then sintered in a furnace at 1100 °C and atmospheric pressure for 3 h. After the sintering process the physical structure sintered electrolyte and anode was tested. Cathode fabrication is the last step of SOFC fabrication. The cathode was made by using solid state reaction of calcium oxide, cobalt, and zinc. The oxide mixture was measured stoichiometrically and polyvinyl alcohol (PVA) is added into the mixture. The wet cathode mixture was then sprayed on the electrolyte using automated air brush sprayer. After the cathode was sprayed onto the electrolyte, the cell was sintered in a furnace at 900 °C and atmospheric pressure for 5 h.

2.2. SOFC Performance Test
SOFC cells are attached to main equipment set in the tubular furnace. To operate the SOFC cell, a start-up procedure is required from the cell, which is heating to a temperature of 800 °C followed by hydrogen flow into the cell to perform reduction reaction to the anode to be ready to operate. As SOFC cell is ready to operate, the electrochemical performance of the SOFC cell is checked. The SOFC cell performance testing was carried out using Gamry 3000 Potentiostat and Gamry software. Voltage and current tests on SOFCs are carried out using potentiodynamic and electrochemical impedance spectroscopy (EIS) on the potentiostat. After an hour of cell electrochemical testing, the furnace was turned off and the fuel feed flow was stopped for a period of the shutdown cycle. After the cycle off, SOFC cell is started up again, then tested for another electrochemical properties. After having tested the second time, the cells were turned off and the feed flow was stopped. After the temperature reaches ambient temperature, SOFC are removed from the furnace and tested physically using SEM to evaluate its microstructure and ASTM C373-88, standard test method for bulk density of fired whiteware products, to determine its porosity, respectively.

2.3. SOFC Simulation using Aspen Plus
SOFC was simulated using Aspen Plus software to generate voltage, current, and power production data. The simulation was adapted from a study from Doherty [8]. The flowsheet for the simulation is shown in Figure 1. In this simulation, the main blocks are prereforming, anode, cathode, and post combustion
block. For a hydrogen fueled SOFC, the prereforming and post combustion blocks is not used. To simulate an anode in Aspen Plus, RGibbs block was used. The use of RGibbs makes the fuel and oxidizing agent react according to Gibbs free energy. In the anode block, the fuel utilization is set to 85%. To simulate the cathode, separator block was used. In this block, the oxygen used in anode reaction is separated with the excess oxygen and nitrogen from air. The voltage, current, and power is calculated using Aspen Plus calculator.

![SOFC simulation process flow diagram.](image)

3. Results and Discussion

3.1. SOFC Cell Performance

The experimental result of the SOFC cell is shown with the IVP and EIS curve the cell produced. The IVP of the cell is shown in the Figure 2. From the IVP figure, it can be seen that with the same flow rate, the fuel cell with FeO\(_{1.5}\) doping has a higher maximum power than the fuel cell without FeO\(_{1.5}\) doping. The increase of maximum power happens because the Fe doping decreases resistances in the electrolyte. From the figure, it can be seen that with the increasing rate of hydrogen fuel, the maximum power also increases. This happens because the increasing rate of fuel increases the current in the SOFC system, thus increases the produced power [9].

![Experimental IVP result at 800 °C.](image)

Both electrolytes were tested by using EIS method. The EIS result, equivalent circuit model and resistance values can be seen on the Figure 3 and Table 1. Ohmic resistance (Rohm) is the bulk resistance
of the electrolyte, grain boundary resistance (R1) is the ionic resistivity, double layer resistance (R2) is the electronic resistivity of the cell. On the whole, the resistivity of the FeO$_{1.5}$ doped electrolyte is lower than the electrolyte without FeO$_{1.5}$ doping. The addition of FeO$_{1.5}$ doping also increases the oxygen vacancy thus increasing the potential of oxygen migration and lowering its grain boundary resistance [7].

![Impedance spectra of CSZ and FeCSZ at 800 °C.](image)

**Figure 3.** Impedance spectra of CSZ and FeCSZ at 800 °C.

**Table 1.** Resistance values from equivalent circuit model.

|        | Rohm | R1   | Y1     | a1   | R2   | Y2     | a2     |
|--------|------|------|--------|------|------|--------|--------|
| CSZ    | 139.60 | 53.84 | 8.84 $10^{-3}$ | 1.47 $10^{-3}$ | 83.25 | 5.93 $10^{-7}$ | 9.42 $10^{-1}$ |
| CSZ + FeO$_{1.5}$ | 84.31 | 2.51 | 1.47 $10^{-3}$ | 4.68 $10^{-1}$ | 19.63 | 1.24 $10^{-1}$ | 3.84 $10^{-3}$ |

The porosity of the cell is tested using ASTM C373-88 method. The porosity for the electrolyte without FeO$_{1.5}$ doping is 17.18% and the porosity for the electrolyte with FeO$_{1.5}$ doping is 10.12%. This indicates the increase of the electrolyte density. Both electrolytes were further tested using scanning electron microscope (SEM). The cross section of the cell can be seen on the Figure 4. From the SEM result, it can be seen that the electrolyte with FeO$_{1.5}$ doping is denser than the electrolyte without the addition of FeO$_{1.5}$ doping.

![Cross section SEM of the electrolyte without doping (left) and with Fe doping (right).](image)

**Figure 4.** Cross section SEM of the electrolyte without doping (left) and with Fe doping (right).

### 3.2. SOFC Simulation using Aspen Plus

Aspen plus simulation was used to determine the effect of different varieties of fuel. The simulation is done by adapting a simulation that was done by Doherty. The simulation was then modified until it has the same operating condition as the one from the experiment. The first comparison was the effect of recycle on the fuel cell performance. The cell performance can be seen on the Table 2.
Table 2. Comparison of using a recycled flow.

| Variation | Inlet Flowrate (kmol/h) | OCV (V) | J (A/m²) | Resistance (Volt) | Voltage (V) | Power Density (W/m²) |
|-----------|-------------------------|---------|----------|-------------------|-------------|----------------------|
|           |                         |         |          | Ohmic             | Activation  | Concentration        |                     |
| 1         | 8.54                    | 1.11    | 2035.98  | 0.20              | 0.14        | 0.11                 | 0.68                | 1392.61             |
| 2         | 4.78                    | 1.14    | 1884.03  | 0.20              | 0.13        | 0.15                 | 0.70                | 1316.94             |

From the table, it can be seen that the cell equipped with a recycling stream has a lower voltage, higher current, and higher power. The recycling stream increases the amount of fuel in the inlet side of the anode, thus according to Faraday Law, the current will increase accordingly. The decrease of voltage is because of Nernst Law, the impurity on the inlet side of the anode will decrease the OCV. The next comparison was the effect of temperature on the fuel cell performance. The increase of temperature increases the concentration resistivity of the cell, but the ionic and activation resistivity will decrease significantly. The rapid decrease of activation resistivity is because the nature of SOFC material which are semiconductors that activates at a high temperature. The effect of temperature on the resistance can be seen on the Figure 5.

Figure 5. The effect of temperature on the resistance of the cell.

The next comparison is fuel flowrate. According to Nernst equation, variation on the fuel flow will affect the OCV of the cell. The increase of fuel flow will increase the current and current density according to Faraday Law. With the increase of current density there will be an increase on the ohmic, activation, and concentration resistivity of the cell. This resistivity will decrease the voltage of the cell. The change of current is more significant than the change of current, thus the power produces increases along with the current.

3.3. Correction Factor of Experiment Results with Simulation Results
The data generated from simulations and experiments have significant discrepancy. Table 3 showed the comparison of simulation and experimental results with variations in hydrogen flow rate.
Table 3. Comparison of simulation and experimental results.

| H₂ inlet flowrate (mL/min) | P simulation (mW/cm²) | P experiment (mW/cm²) | V simulation (V) | V experiment (V) | I simulation (mA/cm²) | I experiment (mA/cm²) |
|---------------------------|-----------------------|----------------------|------------------|------------------|----------------------|----------------------|
| 500                       | 59.24                 | -                    | 0.90             | -                | 55.00                | -                    |
| 600                       | 68.71                 | 0.39                 | 0.87             | 0.27             | 66.00                | 1.46                 |
| 700                       | 77.12                 | -                    | 0.84             | -                | 77.00                | -                    |
| 800                       | 84.65                 | 0.98                 | 0.80             | 0.38             | 88.00                | 2.60                 |
| 900                       | 91.08                 | -                    | 0.77             | -                | 99.00                | -                    |
| 1000                      | 96.45                 | -                    | 0.73             | -                | 110.00               | -                    |

The table shows current has a large deviation value from the experiment. It affects the value of the activation and concentration voltage loss. Therefore, it is necessary to have a correction factor that could adjust simulation data to experimental data. The correction factor is used to assess any deviation in cell performance characteristics. In this experiment, the correction factor is considered a gradient value that manipulates the graph line equation of the current value against the flow rate. This is justified by two things, namely the Faraday Equation which shows the current value is directly proportional to the amount of fuel and the findings that show a linear trend of changes in current to flow rate with the same fuel utilization value [10]. Based on Eq (1), the current is affected by the mole of H₂ entering and fuel utilization. In this case, the experimental fuel utilization value is held constant. Using Equation 1, the value of correction factor could be determined. K value then modeled against the current data generated through the simulation to see the results of the correction.

\[
K = \frac{f(I_{percobaan})}{f(I_{simulasi})} = \frac{0.003 \, nH_2,in}{0.1319 \, nH_2,in} = 0.022744
\]  

\[y = 0.1319x\]  
\[R^2 = 1\]

\[y = 0.003x\]  
\[R^2 = 0.9827\]

\[y = 0.003x\]  
\[R^2 = 1\]

Figure 6. The effect of temperature on the performance of the cell.

Through the model line equation in Figure 6, the equation of the power density relationship with hydrogen flow rate is determined as shown in Eq (2). Using this power density value, the simulation model can show results that are closer to the experimental results.

\[
P = -1 \times 10^{-6} \left(nH_2,\text{in}\right)^2 + 0.0033 \, nH_2,\text{in}
\]  
\[(2)\]
4. Conclusion
FeO$_{1.5}$ doping on the electrolyte will lower its internal resistivity due to oxygen vacancy formation mechanism. It also increases its density because of its transformation mechanism during sintering, thus minimizing fuel cross over. Because the doping lowers the overall resistivity, it also increases the power of the SOFC. By using Aspen Plus simulation a mathematical model was made for its power generation when using 500 ml/min up to 1000 ml/min hydrogen as fuel.

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