Characterization of Steam Reforming Catalyst in Solid Oxide Fuel Cell Using Biogas

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This study described to produce hydrogen gas from recyclable biomass steadily and stably and use this resulting hydrogen effectively as an energy source of solid oxide fuel cell. We chose the steam reforming reaction as a model reaction and compared several catalytic activities with several different common and uncommon catalysts. We analyzed the amount of carbon adsorption by using scanning electron microscope and performed thermogravimetric analysis for reaction variables of several catalysts. We also used the reformed gas produced by different catalysts as energy source for solid oxide fuel cell (SOFC) and characterized the electrical properties of SOFC for the different catalysts. The comparison of three catalysts (Ru, Ni and Ni/Ru) shows that the reaction activity is higher in the order of Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ > Ni(20 wt%)/Al$_2$O$_3$ > Ru(2 wt%)/Al$_2$O$_3$. The resistance of catalyst against coking under the S/C ratio of 2.5 was turned out to be better in the order of Ru(2 wt%)/Al$_2$O$_3$ > Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ > Ni(20 wt%)/Al$_2$O$_3$. The electrical analysis of solid oxide fuel cell for the different catalysts at 750 ºC and under the S/C ratio of 2.5 shows that the initial voltage was identical for all catalysts, however, it starts to show the difference after a long operation (160 h) that the electrical property is superior in the order of Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ > Ni(20 wt%)/Al$_2$O$_3$ > Ru(2 wt%)/Al$_2$O$_3$.

Key Words: Biogas. Solid oxide fuel cell, Electrical characteristics, Scanning electron microscope, Thermogravimetric analysis.

INTRODUCTION

Since the Kyoto protocol entered into force in 2005 and the Bali road map was adopted in 2007, several countries committed themselves to reduce greenhouse gases. In contemporary society, as the energy market gets worse with depletion of fossil fuel and oil price spike, the world put forth of multilateral effort into enhancing their energy independence ratio. Particularly, as Korea has a high level of energy dependence on overseas, the national long-term policies annually set up in Korea have been guiding to establish a new policy for stable level of supply, development and utilization of renewable energy, which can replace the conventional fossil fuel.

The fuel cell has been proposed as a reliable solution that resolves the global warming and oil depletion problem because it is efficient to produce renewable energy without undergoing any combustion process and, therefore, it minimizes the cause of contaminant and the amount of contaminants emitted to air. The fuel cell, however, is not a device that stores energy but simply it is a device that transforms energy according to the supply of hydrogen gas. Thus, it is significantly important to develop efficient method and to commercialize the energy generated by fuel cell.

Most hydrogen gas is currently produced by steam reforming, thermolysis and gasification from the fossil fuel such as natural gas, oil/residue and coal. However, it is not positively considered to regard the fossil fuel as a clean energy source because the fossil fuel also accompanies generation of byproduct, greenhouse gas, during the generation of hydrogen gas which is used as secondary energy source. Massive amount of studies have been performed by researchers that the hydrogen gas production can be accomplished by thermochemical or thermoelectrical hydrolysis by using solar photovoltaic energy, wind energy, light, bioorganic waste and nuclear energy. It is anticipated that the new technic to generate hydrogen gas using alternative energy would replace the process of conventional techniques[1].

Herein, we report a method that produces hydrogen gas stably using biomass, a renewable energy, to compare the performance of different catalysts. We apply the reformed gas directly as an energy source for solid oxide fuel cell (SOFC). We use the steam reforming reaction to produce hydrogen gas by introducing Alumina-supported Ni and Ru catalyst. Also, the same catalysts but with relatively less amount of Ni and Ru are applied to the same reaction with extra amount of noble metal[2].

EXPERIMENTAL

Lab-scale experiment: Fig. 1 shows a system of Lab-scale experiment. The experimental equipment has been designed in the basis of one stack (5 cm × 5 cm) of solid oxide fuel cell. The experimental system is composed of reactant gas, mass flow controller (MFC), desulfurization device, water pump, reforming device and furnace containing the fuel cell. The single cell is a type of anode-supported (one stack, 5 cm × 5 cm), which consists of an anode made up of NiO-YSZ composition with 5:5 ratio, a cathode of LSCF series and electrolyte of TZ-8YS (8 mol % Y_2O_3 stabilized ZrO_2).

Production of hydrogen gas from biogas with steam reforming reaction: The reforming process is the core process where synthetic gas containing abundant amount of hydrogen gas is produced after the reaction of hydrocarbon and water gas. We selected the steam reforming reaction because it results in massive amount of hydrogen gas and is a relatively easy experiment to operate.

The majority of commonly used active species for hydrogen gas production can be divided into two groups, transition metal and noble metal. Nickel is representatively used as the most active catalysts among transition metal species and Ru, Rh, Pt and Pd are those among noble metal species. Ni/Al_2O_3, however, requires a pre-treatment under reduction atmosphere at high temperature (> 700 ºC) and thus, nickel is easily sintered in this process. Also, the formation of coke that has been reported as one of the main drawbacks decreases reaction activity because carbon is adsorbed onto the surface of catalyst. It has been significantly studied that the use of noble metal is one of the solutions to prevent coke formation that inactivates catalyst.

We examined a series of Ni catalysts to understand the problem in the steam reforming reaction and also compared the reaction activity of the Ni catalysts and noble metals. The commercially available FCR-4 model catalyst (NiO 12.8 wt% and Al_2O_3 87.2 wt%) and RUA model catalyst (Ru 2.02 wt% and Al_2O_3 87.2 wt%) were obtained from Sud-chemie. The noble metal catalyst, Ru-added (0.5 wt%)/Ni(20 wt%) Al_2O_3 and noble metal-added catalyst were prepared without pre-treatment process. The experimental variables in normal state of steam reforming reaction and the GC condition for reactant analysis are shown in Tables-1 and 2, respectively.

TABLE-1
EXPERIMENTAL SR CONDITIONS IN A FIXED BED REACTOR

Reaction temperature (ºC)		600-750
Inlet gas concentrations	N_2 (sccm)	50
	CH_4 (sccm)	100
Space velocity (h^{-1})		1,100

TABLE-2
ANALYSIS CONDITIONS OF GAS CHROMATOGRAPHY

Manufacture		Agilent Technologies
Detector		TCD
Column		Shin Carbon ST 100/120 mesh 2 meter × 1 mm ID micropacked
Operation conditions (ºC)	Oven temperature	40
	Gas sampling temperature	150
	Detector	250
Carrier gas		He

Resistance of catalyst against coke formation: Scanning electron microscope (SEM) was used and thermal gravimetry analysis (TGA) was performed to characterize of physical and chemical property of the catalysts used for this experiment. The electron microscope was used in order to analyze the shape and structure of the catalysts' surface before and after the reduction. The TGA was carried out to analyze the amount of active species of reduced metal catalyst as well as the amount of carbon which was adsorbed on catalyst's surface after the catalytic reaction completed under the air atmosphere.

Electrical characterization of solid oxide fuel cell for different catalysts: The electrical characterization was carried
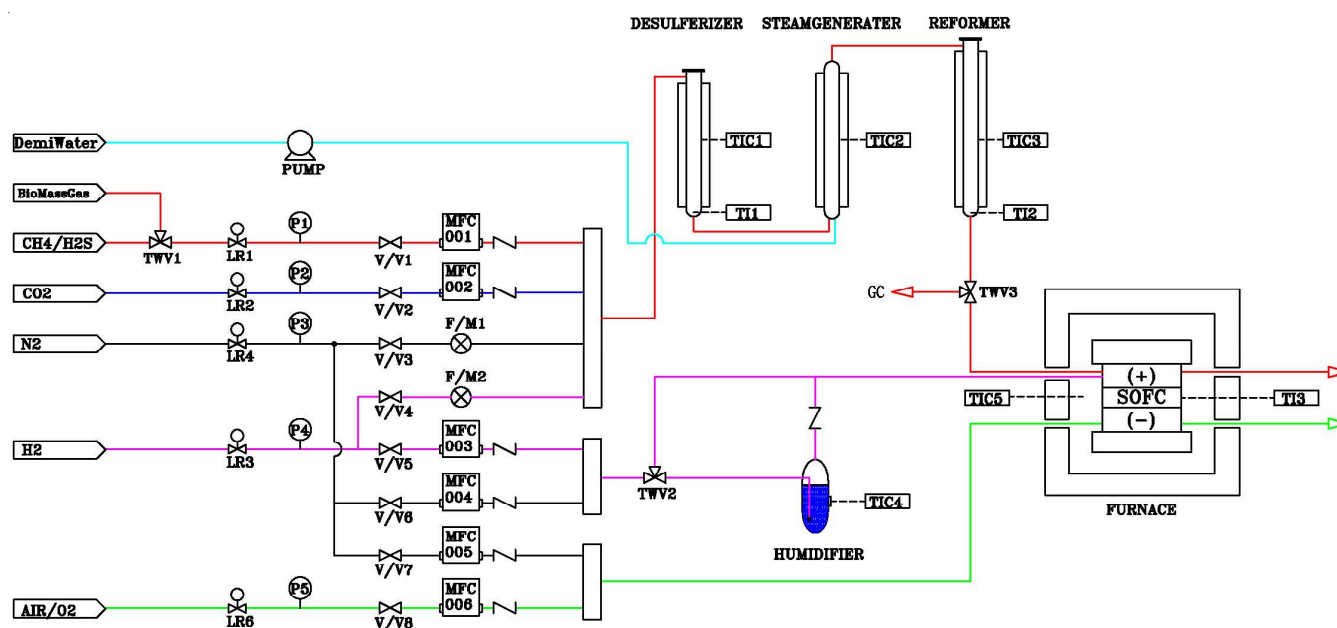

Fig. 1. Schematic diagram of solid oxide fuel cell system

out in order to evaluate the activity of NiO and noble metals for solid oxide fuel cell. The temperature of furnace was slowly elevated to 750 ºC and the gas was accurately and quantitatively provided by flow controllers. The performance and property change of the cell was monitored by changing the temperature of furnace. The measurements of I-V and impedance were analyzed by BioLogic HVP-803. The I-V tendency was measured in OCV state to 0.3 V with an interval of 10 mA/s and the impedance was analyzed in open circuit with a constant voltage (500 mV) in the range of 0.01 Hz to 20 kHz. The data of each catalyst was collected in the identical condition for comparison.

RESULTS AND DISCUSSION

Activity of the steam reforming reaction: We prepared a specific simulated gas and directly applied it to the catalytic reaction. We analyzed the conversion rate of methane after the injection of the simulated gas at 650-750 ºC with S/C ratio of 2. For Ru(2 wt%)/Al_2O_3 and Ru(0.5 wt%)/Ni(20 wt%)/Al_2O_3, we directly introduced the catalysts without hydrogen gas reduction (H_2-treatment) process. After the reaction gas was also employed to the reactor at the temperature, the initial temperature was instantly set up to 650 ºC (where the condensation of water would not occur) and the reaction was performed.

For Ni(20 wt%)/Al_2O_3, the H_2-treatment process is an essential step because the catalyst does not exhibit any activity at 650 ºC without the reduction process. However, it turned out that the catalytic activity of Ru(0.5 wt%)/Ni(20 wt%)/Al_2O_3 was better than that of Ni(20 wt%)/Al_2O_3 even though it was treated with hydrogen gas before the catalytic reaction. This result implies that Ru catalyst became self-activated at 650 ºC. On the other hand, Ru(2 wt%)/Al_2O_3 shows very low level of the conversion rate of methane compared to the other catalysts.
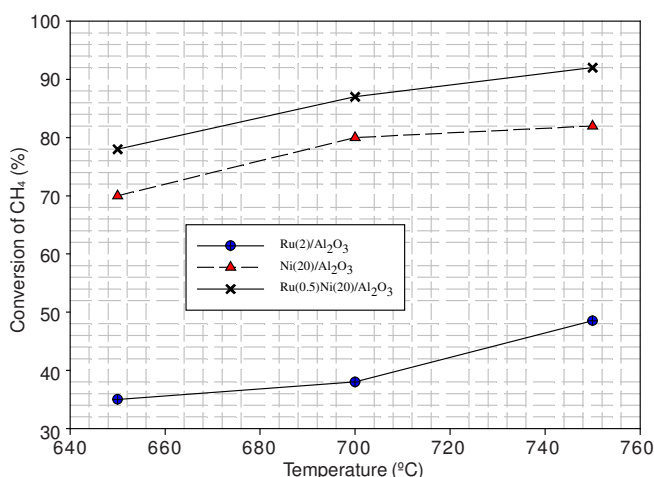

Fig. 2.   CH$_4$ conversion over the pre-reduced Ni(20)/Al$_2$O$_3$ and the Ru(2)/Al$_2$O$_3$, Ru(0.5)/Ni(20)/Al$_2$O$_3$ without pre-reduction (SR condition: 650-750 ºC, S/C ratio 2)

Resistance against coke formation: We prepared H_2-treated Ni(20 wt%)/Al_2O_3, H_2-untreated Ru(2 wt%)/Al_2O_3 and Ru(0.5 wt%)/Ni(20 wt%)/Al_2O_3 in order to compare the resistance against coking. We directly observed the surface of

catalysts with SEM and obtained the mass with TGA after the catalytic reaction at 750 ºC with S/C ratio of 2. The SEM image in Fig. 3 shows that the filamentous carbon was formed on almost every surface of Ni/Al_2O_3 and the catalyst was sintered during the reaction. The filamentous carbon is a carbon-based material that is produced at high temperature especially for catalytic reaction with Ni. For continuous and stable production of hydrogen gas through catalytic reaction, it is necessary to inhibit the growth of the filamentous carbon on the surface of catalyst because this filament-like carbon material has a high mechanical strength and it can result in breakage of catalyst[3].
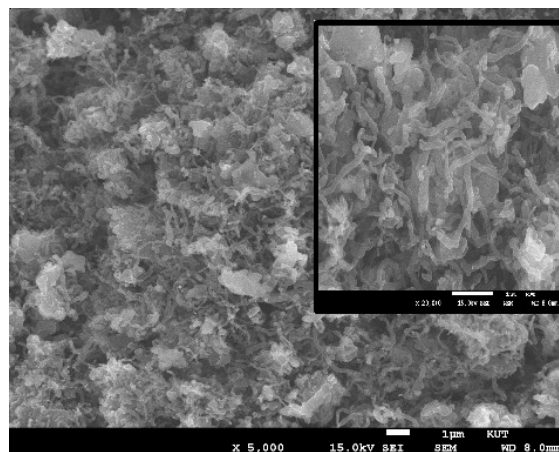

Fig. 3.   SEM micrographs of the recovered catalysts of Ni/Al$_2$O$_3$ after 160 h of reforming reaction

The SEM image shown in Fig. 4, there was almost no carbon formed on the surface of Ru(2 wt%)/Al_2O_3. The formation rate of filamentous carbon was turned out to be much slower in the reaction catalyzed by noble metals than by Ni. This result is consistent with the previously reported result, especially for Ru, that only a few atomic layers of carbon were observable on the surface of catalyst[4].
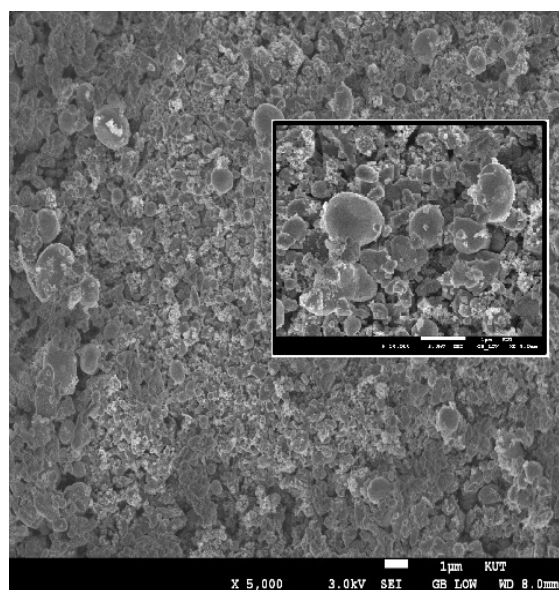

Fig. 4.   SEM micrographs of the recovered catalysts of Ru/Al$_2$O$_3$ after 160 h of reforming reaction

The SEM image (Fig. 5) represents Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ that is supported with noble metal by co-impregnation method. For Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$, only a few small size of carbon fragments can be observable. This result explains that the Ru deposited on catalyst plays a an important role that it efficiently suppresses the growth of filamentous carbon on the Ni catalyst which is reduced in the steam reforming reaction[5].
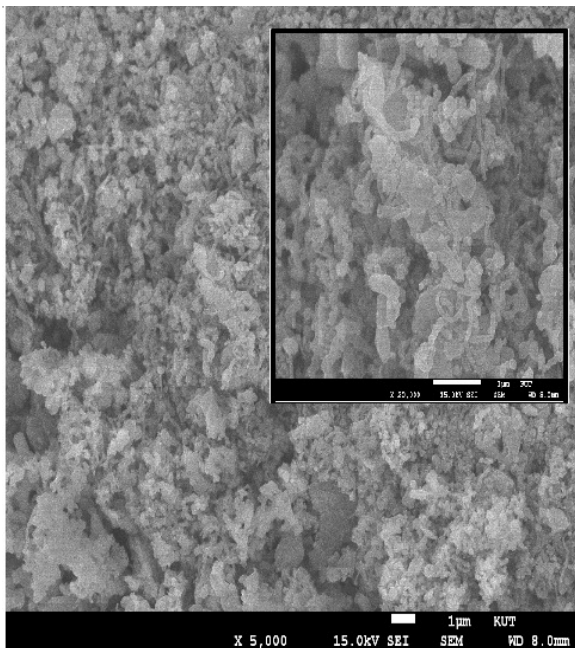

Fig. 5. SEM micrographs of the recovered catalysts of Ni/Ru/Al$_2$O$_3$ after 60 h of reforming reaction

The TGA results described in Fig. 6 shows that the steam reforming reaction leads to either increase or decrease in mass of the sample used in the reaction. The decrease in mass can be explained due to the loss of oxygen which is used to oxidize the carbon species (filamentous carbon) formed by subsequent process of decomposition and adsorption on the surface of catalyst. However, it can lead to the increase in mass due to the oxidation of reduced metal particle on the surface. The TGA curve shows that the decreased mass of Ni/Al$_2$O$_3$ in the beginning at 400-700 °C increases again. This can be explained that the catalyst was oxidized during the thermogravimetric analysis. Therefore, we calculated the mass change of adsorbed carbon species due to oxidation by subtracting the gained mass of H$_2$-treated sample after oxidation from the mass change of sample after the reaction. It turned out that the percentage of coke formation for Ni(20 wt%)/Al$_2$O$_3$, Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ and Ru(2 wt%)Al$_2$O$_3$ was 7.79, 2.275 and 0.64 wt %, respectively[6,7].

Electric characterization of solid oxide fuel cell for different catalyst: The graph (Fig. 7) shows the comparison after the electric characterization at 750 °C and S/C ratio of 2.5. The voltage applied to SOFC cell in the state of open circuit was quite similar to each other catalysts as it turned out to be 1.12, 1.10, 1.11 V for Ru(2 wt%)Al$_2$O$_3$, Ni(20 wt%)/Al$_2$O$_3$ and Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$, respectively. After the addition of the simulated gas to the cell, however, the
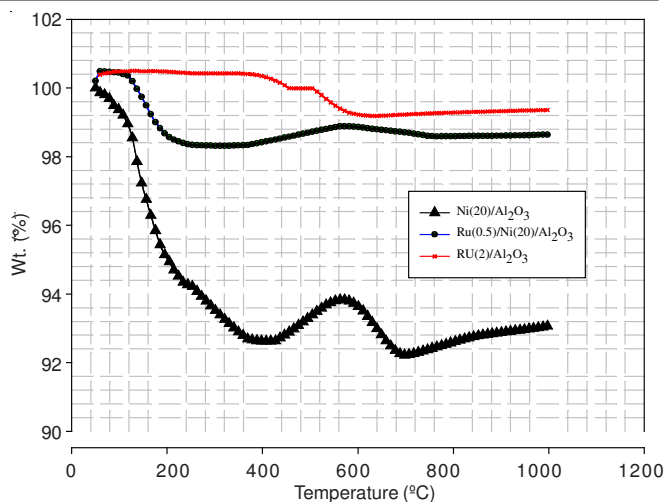

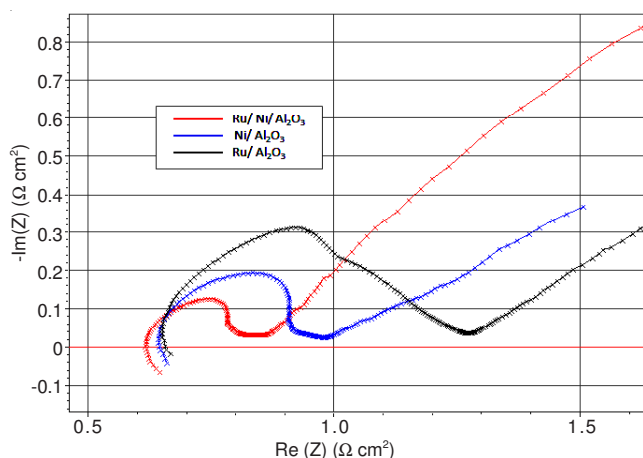Fig. 6. TGA results of Ru/Ni/Al$_2$O$_3$ Ru/Al$_2$O$_3$ and Ni/Al$_2$O$_3$ catalysts

Fig. 7. Impedance spectra change at a variation of catalyst (at 750 °C, S/C = 2.5)

voltage of SOFC catalyzed by Ni started to decrease gradually in 24 h and the voltage completely stopped flowing in further 60 h (Fig. 8). This result explains as following; the low S/C ratio facilitated coking on the surface of catalyst; the high temperature provoked sintering of catalyst, which inactivated catalytic activity dramatically and obstructed efficient supply of gas to the fuel cell. Ni (20wt %)-supported Ru (0.5 wt%) catalyst prepared by co-impregnation method[8] exhibited a superior ability to maintain its initial open circuit voltage (1.1 V) by showing the same voltage (1.0 V) even in more than 160 h.

The Ru (2 wt%) catalyst exhibited voltage drop to 1.04 V in 60 h and to 0.59 V in 160 h. Because the mass flow controller was in stable operation on flow rate of biogas to the fuel cell system, we interpreted that the catalytic efficiency decreased because of contaminants occurred with coking on the surface of Ni, which is the same material with anode. We analyzed the impedance to understand carbon deposition on the working fuel cell[9].

The impedance spectrum is divided into two regions, *i.e.*, R$_s$-region (Ohmic resistance) and R$_p$ region (polarization). The R$_s$ represents the conductivity of electrolyte and the resistivity of separator and it can be found from the x-intercept in the impedance spectrum in Fig. 7. The R$_p$ is the rest of resistivity except for the R$_s$.
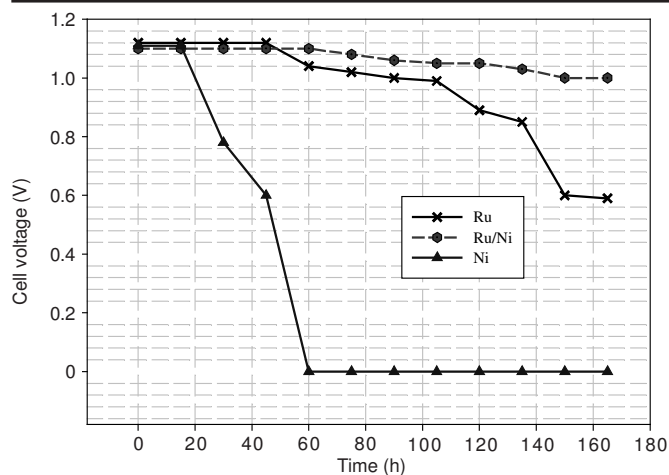
Fig. 8. Cell voltage at a variation of time (at 750 ºC, S/C = 2.5)

The impedance spectrum shown in Fig. 7 is the result obtained in 24 h after the addition of reforming gas to SOFC with different catalysts.

The Rs(Ω cm^2) for Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$, Ni(20 wt%)/Al$_2$O$_3$ and Ru(2 wt%)/Al$_2$O$_3$were 0.613, 0.659 and 0.667, respectively. This results shows that the catalytic activity of Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ is the most efficient and the high conversion rate of methane reduces the interrupted effect by electron flow[4].

The arc size of half circle in Cole-cole plot is related to the polarization resistance between cathode and anode. As polarization resistance of electrode increases and decreases, the arc size of half circle also increases and decreases. This explains the resistance of carbon deposition against electrodes. The Rp(Ω cm^2) for Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$, Ni(20 wt%)/Al$_2$O$_3$ and Ru(2 wt%)/Al$_2$O$_3$ were 0.79, 0.92 and 1.28, respectively. The Ni/Ru-supported catalyst has high conversion efficiency of hydrogen and the rate of electrochemical reaction does not decrease on the surface of electrodes. Ru (2 wt%)/Al$_2$O$_3$ has a low conversion efficiency and the performance of fuel cell decreases in case of long operation[10].

Conclusion

Ni(20 wt%)/Al$_2$O$_3$ showed the highest catalytic performance at 750 ºC and S/C ratio of 4. For Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ and Ni(20 wt%)/Al$_2$O$_3$, the H$_2$-treated Ni(20 wt%)/Al$_2$O$_3$ exhibited higher catalytic activity for methane conversion than Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ did.

For the analysis of resistance against carbon adsorption and coking, we compared H$_2$-treated Ni(20 wt%)/Al$_2$O$_3$ and H$_2$-untreated Ru(2 wt%)/Al$_2$O$_3$ and Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ at 750 ºC and S/C ratio of 2.5. The TGA result showed that 7.79, 2.275, 0.64 wt% of coke was produced on the surface of Ni(20 wt%)/Al$_2$O$_3$, Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ and Ru(2 wt%)/Al$_2$O$_3$, respectively.

The electric characterization result for SOFC showed that the catalysts used for 160 h at 750 ºC and S/C ratio of 2.5 show better electric property in the order of Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ > Ni(20 wt%)/Al$_2$O$_3$ > Ru(2 wt%)/Al$_2$O$_3$. The impedance, R$_p$ (Ω cm^2), for each catalyst was 0.79, 0.92, 1.28 (Ω cm^2), respectively.

Therefore, according to the multivariate comparison of Ni(20 wt%)/Al$_2$O$_3$ with Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$, we conclude that Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ is a more appropriate catalyst for the steam reforming reaction because it maintains stable supply of hydrogen gas to SOFC. Ru(0.5 wt%)/Ni(20 wt%)/Al$_2$O$_3$ has higher level of resistance against coke formation and shows higher activity at the high temperature as well as it does not require pre-treatment process.

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