Direct alcohol fuel cell—relation between the cell performance and the adsorption of intermediate originating in the catalyst-fuel combinations

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Abstract

Since a direct alcohol fuel cell (DAFC) can be downsized and can operate at room temperature, it is expected as a power source for mobile applications. On the other hand, cost reduction is also expected, because Pt is used in the electrocatalyst. In this study, the use of base metals for Pt was investigated by combined with the 2-propanol fuel that had an advantage compared to methanol in terms of oxidability.

The various base metal catalysts were compared to the Pt catalyst as an anode electrocatalyst in the DAFC performance. The Ni catalyst showed the highest open circuit voltage (V_{oc}) among the base metal catalysts. The V_{oc} reflected the hydrogen abstraction activity of the metal species. The Ni catalyst was a match for the Pt catalyst in the V_{oc}. However, the Ni catalyst could not reach to the Pt catalyst in the cell performance. The relation between the catalyst and the fuel was investigated in both the Ni and the Pt catalyst. The suitable catalytic performance was observed depending on each fuel. The Ni catalyst was suitable for the 2-propanol, while the Pt catalyst was suitable for the methanol fuel. The stripping voltammetry indicated that the DAFC showed better performance as the adsorbate could be removed easily and the easiness depended on the fuel-catalyst combinations.

Considering the catalyst cost and the possibility of the improvement in the catalyst, Ni is the potential candidate for the anode catalyst by combined with the 2-propanol fuel in the DAFC for the mobile applications.
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1. Introduction

A secondly cell have been made rapid progress for prolonging an operating duration in one charge. Recently a polymer electrolyte fuel cell (PEFC) that can work at room temperature have been being investigated as a substitute of the secondly cell. Especially direct methanol fuel cell (DMFC) that methanol can be directly supplied without a reformer can be miniaturized [1]. Additionally, a liquid fuel like methanol is suitable for a mobile instrument due to its high energy density.

The DMFC is usually operated below 120 °C because of a limitation of a thermal tolerance of the polymer membrane, and the limitation needs a quite active catalyst, the Pt-based catalyst. Pt has been known for its superior oxidation activity, while its scarcity and high cost have been requiring an alternative catalyst without precious metals. Pt price is extremely higher by several thousands times than a base metal such as nickel, copper or iron. The base metal catalysts have been investigated as a substitution for Pt. All of those studies were performed with a half-cell in an aqueous solution, not with a fuel cell itself [2–4]. The DMFC have been studied also in terms of a fuel aspect [5–7]. The alternatives for methanol did not show enough performance in all cases, however, it was found that 2-propanol began to be oxidized at lower potential than methanol. Besides, the oxidation current of 2-propanol was superior to that of methanol up to a relatively high potential [6,7]. Since the mobile instruments do not require a large current density, there is some possibility of that the base metal catalyst combined with 2-propanol would be applicable for the DMFC. In this study, several catalysts with base metal were evaluated at room

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temperature and were compared in a reaction on the anode electrode with the Pt catalyst.

2. Experimental

2.1. Preparation of catalyst

Various base metals were supported on activated carbon (M/C, M: Pt, Ni, Cu, Co, Mn) and used as an anode catalyst. The anode catalysts were prepared with the following manner. In case of the Pt modified carbon catalyst (Pt/C), 100 mg of activated carbon power (Ketjen black EC carbon black, Lion Co., BET surface area 800 m^2/g, average particle size 31 nm) was dispersed in 10 ml of water and stirred. Water was purified with a Milli-Q system (Millipore) after distillation. Unless otherwise specified, the water purified with above manner was used. 94 mg of reagent grade sodium hydrogen carbonate (Wako Pure Chemical, Inc.) was added to the slurry with vigorously agitating and the slurry was raised to 100 °C. A solution of 100 mg platinum as tetraammineplatinum(II)chloride hydrate in 5.0 ml the water was dropped to the slurry little by little and the slurry was boiled. 110 μl of formaldehyde was diluted to 1 ml with the water and dropped to the slurry [8] then the slurry was dried up. The catalyst was ground with a mortar, washed and filtrated several times to eliminate sodium. The catalyst powder was ground again and reduced at 573 K for 2 h in 1% H$_2$ (Argon balance) atmosphere (50 wt.% Pt/C catalyst). The 50 wt.% M/C catalysts (M: Ni, Cu, Co, Mn) were also prepared with the same manner as the Pt/C catalyst. Since it is difficult to conform the various characteristics of the catalysts like a crystalline size of the supported metals at once, the preparation conditions of the catalyst were conformed. Metal nitrates were used as precursors and aqueous solution of them was added to the carbon-dispersed slurry. These metal modified carbon catalysts were provided to XRD analysis (MAC Science MXP18 II). As a cathode catalyst, purchased Pt/C catalyst was used. (Tanaka Kikin-zoku Kogyo Co., TEC10E50E, Pt = 45.7 wt.%). In all the catalysts, reagent grade chemicals were used.

2.2. Fabrication of membrane/electrode assembly

Electrodes were prepared as follows. 2000 mg of 5 wt.% Nafion-aliphatic alcohol solution (Aldrich) was poured into 6000 mg of butyl acetate (Wako Pure Chemical, Inc.). 100 mg of the catalyst powder was dispersed to the dispersant with ultrasonic for 30 min [9]. The resultant paste was applied to carbon papers (Teflon treated Toray Paper, 190 μm) so as for the metal loading to be 2.0 mg/cm^2 and was dried in air.

The working electrodes with 5.0 cm^2 were placed on either side of a polymer electrolyte (Dupont, Nafion 117®) as shown in Fig. 1. Direct bonding between electrodes and polymer electrolytes were achieved by pressing at 10 MPa for 5 min at 403 K.

2.3. Fuel cell performance

The fabricated membrane/electrode assembly (MEA) was settled in a housing block (Electrochem, Inc. FC-05-01SP-2REF) that was placed in a drying oven. Alcohol was diluted to 2.0 M and fed to the anode by 1.0 ml/min through a liquid-feed pump (Shimazu, LC-10AT VP) and pure oxygen was fed to the cathode by 100 ml/min as shown in Fig. 1(a). Current was controlled with a galvanostat (Hokuto denko Ltd., HA-104) and potential was measured. The measurement was waited for two or three hours until the potential was stabilized.

2.4. Electrochemical measurements (stripping voltammetry)

Stripping voltammetry was conducted to investigate adsorbates on the catalyst. For the simulation of the half-cell test, a continuous stream of hydrogen was supplied to the counter electrode (Pt/C) instead of oxygen as drawn in
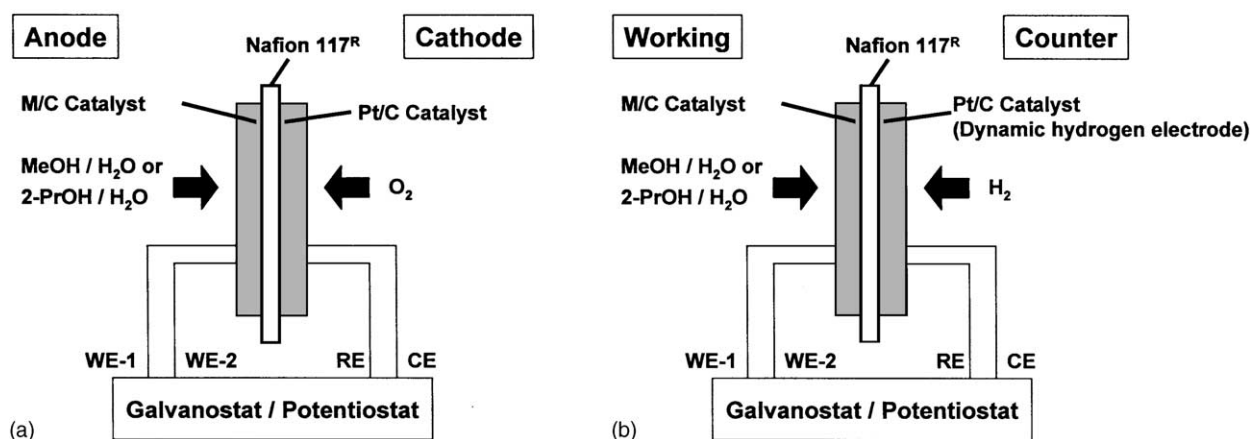

Fig. 1. Illustration of cell structure and test conditions. (a) Current–potential test, (b) stripping voltammetry, M: Pt, Ni, Cu, Co, Mn.

Fig. 1(b) [10]. In this case, the homemade M/C (M: Pt or Ni) electrode and the purchased Pt/C electrode behave as a working and a counter electrode, respectively. Thus, the electrochemical measurement with the half-cell can be simulated on the MEA mounted on the housing block [11]. The working electrode was held at 700 mV for 30 min with the flow of the alcohol aqueous solution. Then the fuel was switched to the water and the anode was soaked for 15 min without applying the potential. The stripping voltammetry was carried out with a continuous stream of hydrogen to the counter side and the potential was scanned between 0 and 1300 mV with 2 mV/s. The potential were controlled by the POTENTIOSTAT/GALVANOSTAT 2000 potentiostat and FG-02 function generator (Toho Technical Research).

3. Results and discussion

3.1. Fuel cell performance

The fuel cell performance with the various anode catalysts was evaluated by using 2-propanol or methanol. The 2-propanol fuel needed much longer time for a relaxation than the methanol fuel. Fig. 2 shows a typical relaxation curves of the cell voltage at 1.0 mA/cm^2 at 25 °C in case of Pt catalyst. The fuel cell with the 2-propanol fuel showed high cell voltage just after applying current and then gradually declined. Finally, the 2-propanol fuel was inferior to the methanol fuel. Consequently, sometimes the measurement had to be waited for a few hours.

Fig. 3(a) compares an open-circuit voltage (V_{oc}) among the various catalysts. The Ni catalyst showed the highest V_{oc} among the base metal catalysts, which reached to almost 350 mV in case of a 2-propanol fuel even at 25 °C. The V_{oc} of the Cu or the Co catalyst was approximately 55 mV, while the V_{oc} of the Mn catalyst was negative regardless of the fuel.

As shown in Fig. 3(c), all base metal catalysts showed little cell performance in case of the methanol fuel. Base metals could not enough oxidize methanol and Pt was essential to oxidize methanol as was expected. In contrast with the methanol fuel, the Ni catalyst combined with the 2-propanol fuel showed better performance as shown in Fig. 3(b). This would be derived from the advantage in the 2-propanol oxidability. On the other hand, the base metals except Ni did not show the difference between methanol and 2-propanol. Here, Cu and the VIII group elements, especially Ni, have been known for their high hydrogen abstraction activity. Mn belongs to the VII group and does not have high hydrogen abstraction activity. It is thought that the V_{oc} and the cell performance faithfully reflected the activity of the hydrogen abstraction. The catalysts were observed by XRD. While Cu was metal state (Cu$^{(0)}$), the others were oxide state (Ni$^{(II)}$O, Co$^{(II)}$O and Mn$^{(II)}$O). The Co catalyst contained trivial Co$^{(0)}$. Crystalline sizes of them estimated by Scherrer's equation were 16, 21 and 17 nm in the Cu, Ni and Co catalysts, respectively. Their crystalline sizes were almost equivalent, however, their oxidation activities of 2-propanol were difference. The Ni catalyst was quite superior in the performance than the Co catalyst even though both the Ni and the Co were oxide state. Based on these facts, it was indicated that the V_{oc} and the cell performance depended on the hydrogen abstraction activity rather than the crystalline size or the oxidation state. The crystalline size of Mn was 48 nm and significantly larger than that of others. Nevertheless, the no performance in the DAFC with the Mn catalyst would almost result from the poor hydrogen abstraction activity.

The Ni catalyst showed the better performance by using the 2-propanol fuel. Then, the Ni catalyst was compared with the Pt catalyst. The cell performances and the V_{oc} of them were summarized in Fig. 4 and Table 1. The estimated Pt crystalline size was 36 nm. The V_{oc} values of the Pt
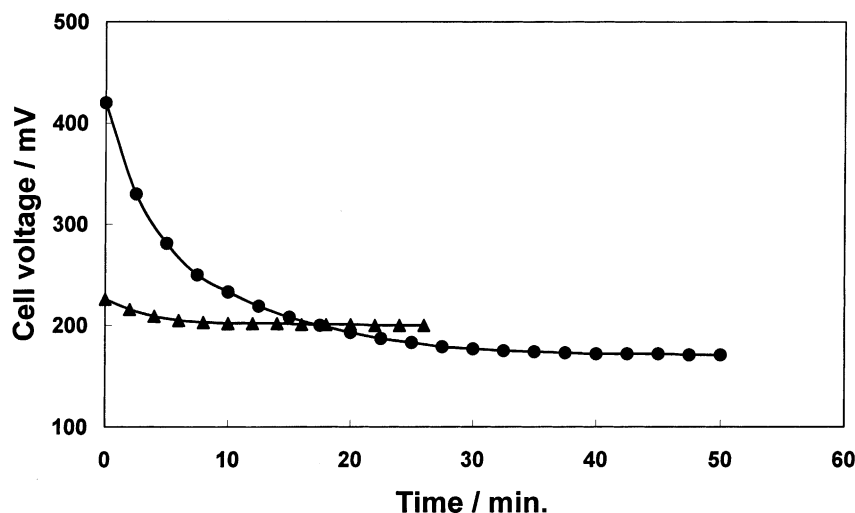

Fig. 2. Comparison of cell voltage relaxation between the 2-propanol and the methanol fuel Pt catalyst, 1 mA/cm^2, temperature: 25 °C, (●) 2-propanol fuel, (▲) methanol fuel.
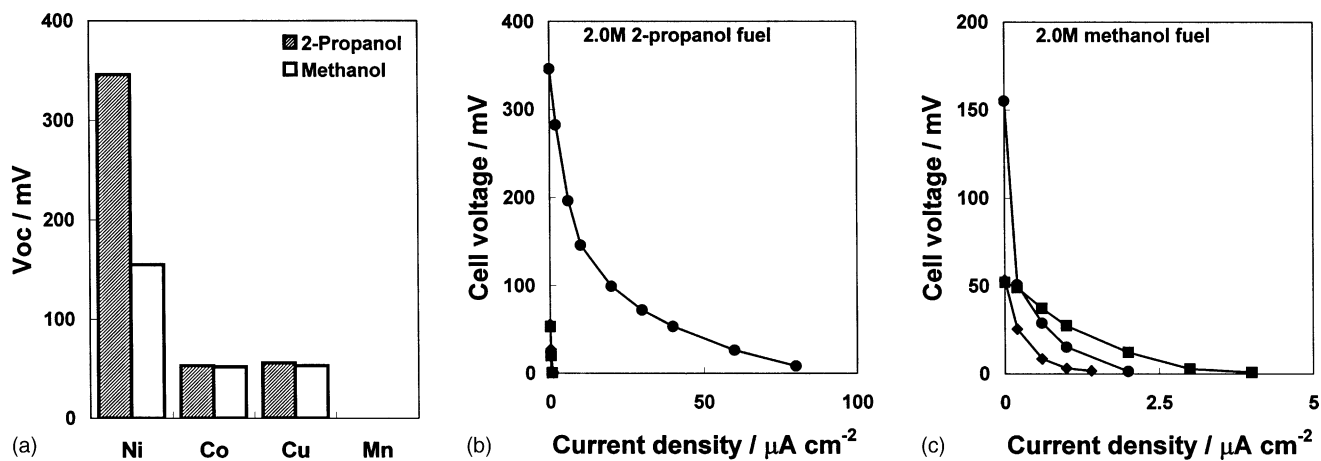
Fig. 3. Cell performance with base metal catalysts (a) cell voltage of open circuit (b) *I–V* curves in 2-propanol fuel (c) *I–V* curves in methanol fuel, temperature: 25 °C, (●) Ni, (■) Co, (◆) Cu, V_{oc} of the Mn catalyst was negative value.
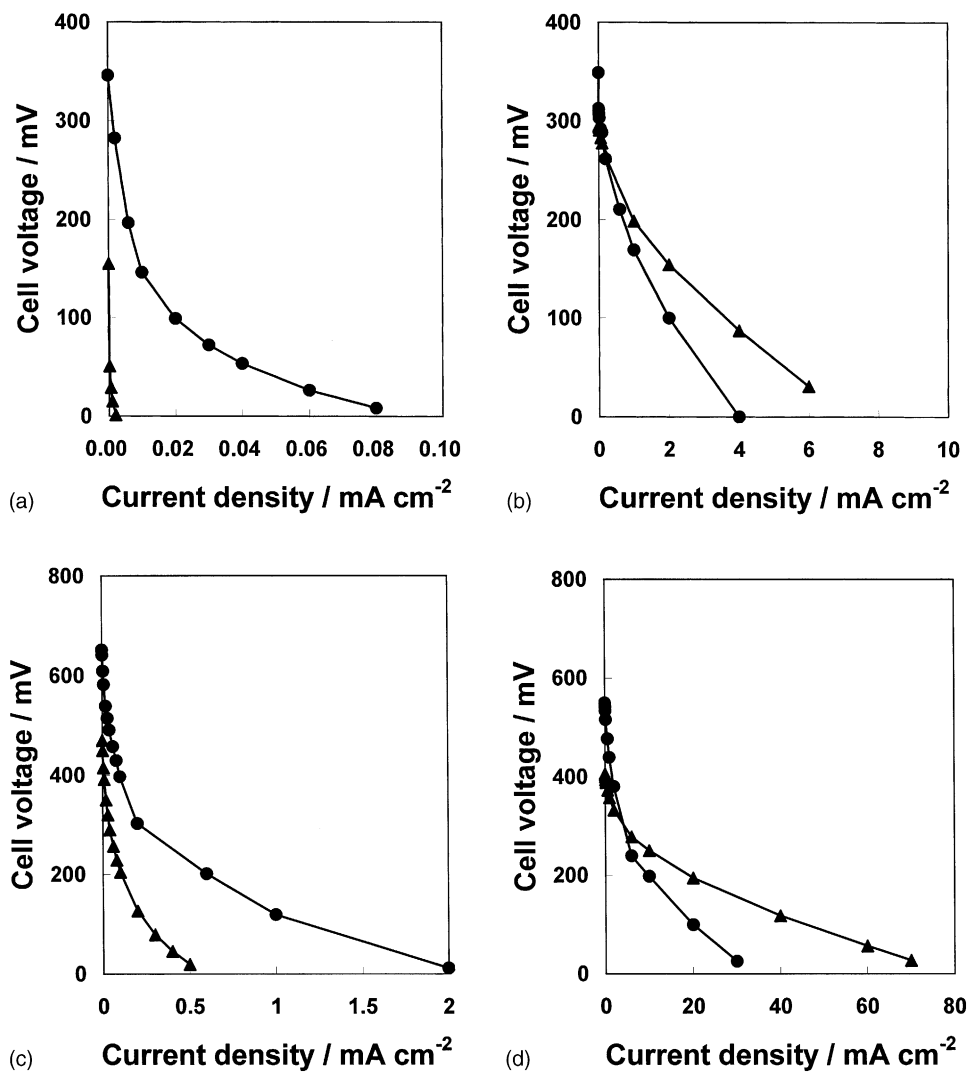

Fig. 4. Cell performance of the DAFC (a) Ni catalyst at 25 °C (b) Pt catalyst at 25 °C (c) Ni catalyst at 80 °C (d) Pt catalyst at 80 °C (●) 2-propanol fuel, (▲) methanol fuel.

Table 1
Open circuit cell voltage

	25 °C		80 °C	
	2-Propanol	Methanol	2-Propanol	Methanol
Ni Catalyst	346	155	651	470
Pt Catalyst	349	295	549	406

catalyst were 295 and 349 mV at 25 °C in the methanol and the 2-propanol fuels, respectively. In case of the 2-propanol fuel, the Ni catalyst was equivalent in the V_{oc} to the Pt catalyst. The V_{oc} of the Ni catalyst, 346 mV was larger than the V_{oc} of the Pt catalyst in the methanol fuel, 295 mV. On contrary to the 2-propanol fuel, the Ni catalyst was inferior to the Pt catalyst in the methanol fuel. Although the hydrogen abstraction activity of Ni is inferior to Pt, the Ni catalyst showed equivalent V_{oc} to the Pt catalyst in the 2-propanol fuel. This would result from the advantage in the oxidability of 2-propanol [7]. At 80 °C, the V_{oc} of the Ni catalyst was higher than that of the Pt catalyst in both fuels. As to the V_{oc}, the Ni catalyst was superior to the Pt catalyst except in the methanol fuel at 25 °C. The cell performance of the Ni catalyst, however, was much lower than the Pt catalyst. From the viewpoint of the fuels, the 2-propanol fuel was more favorable than the methanol fuel in case of the Ni catalyst, while the advantage was limited in the low potential in case of the Pt catalyst. What is interested is that there was a difference in a tendency of oxidation of the fuel between the Ni and Pt catalyst. In case of the Ni catalyst, the 2-propanol fuel brought higher cell performance than the methanol in overall potential range, while the advantage became small in the Pt catalyst.

3.2. Electrochemical measurement

In order to understand the relation between the catalysts and the fuels, the property of the adsorbate was analyzed by the stripping voltammetry. Usually cyclic voltammetry is carried out by using a half-cell, however, this experiment was conducted by using the MEA under hydrogen. The hydrogen was fed to the counter electrode instead of the oxygen. Since the overpotential of the counter electrode is negligible according to the previous work [11], the counter electrode works as a dynamic hydrogen electrode and the half-cell test can be simulated with the MEA mounted on the housing block. Fig. 5 shows an oxidation current originating in the adsorbate on the catalyst. In case of the methanol fuel, the Ni catalyst showed the large oxidation peak around 850 mV. The corresponding peak in the Pt catalyst was much smaller than that of the Ni catalyst and appeared at lower potential region, around 700 mV. The oxidation current corresponds to CO or COH oxidation originating in methanol [12,13]. Fig. 5 indicates that the Ni catalyst is poisoned more seriously than the Pt catalyst and the CO oxidation activity of Ni is poorer than Pt. On the other hand, the adsorbate on the Ni catalyst is less than that of the Pt catalyst in the 2-propanol fuel. According to the previous works, it is reported that the electrooxidation products of 2-propanol are acetone and negligible CO_2 [14,15]. The formed acetone strongly adsorbed on the Pt catalyst and severely deteriorates the Pt catalytic activity [16]. Finally, adsorbed acetone on Pt is oxidized to CO_2 and the acetone diffuses to bulk [17]. In contrast with Pt, Ni was not degraded by acetone in severe and the Ni catalyst showed the cell performance at some level. The characteristics of the adsorbate on the catalyst well agree to the cell performance.

Consequently, the relations between the catalysts and the fuels were figure out. In case of the methanol fuel, no base metal could indicate the potential alternating for Pt because of poor hydrogen abstraction activity and serious CO poisoning, i.e. poor CO oxidation activity. However, at least Ni was a match for Pt in the V_{oc} by using the 2-propanol fuel and demonstrated the potential of the alternative catalyst for Pt.
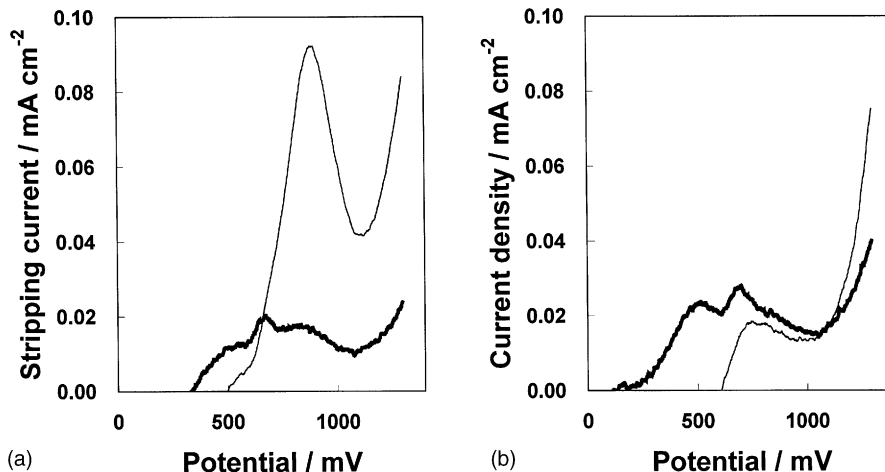

Fig. 5. Stripping voltammetry (a) Ni catalyst (b) Pt catalyst, temperature: 25 °C, scan rate: 2 mV/s, (━) 2-propanol fuel, (—) methanol fuel.

4. Conclusions

Under the limitation in the mobile instrument application, the possibility of a base metal in the anode catalyst of the DAFC was investigated by using the advantage in 2-propanol oxidability. In order to study the relation between the catalysts and the fuels, the effect of the adsorbate on the catalyst was investigated by stripping voltammetry.

The Ni catalyst showed the best cell performance among the base metal catalysts. The cell performance approximately agreed with the hydrogen abstraction activity of the metals. Their performance except the Ni catalyst was far less than of the Pt catalyst. Then, the cell performance with the Ni catalyst was investigated by comparing to the Pt catalyst and it was found that the suitable catalytic performance was observed depending on each fuel. The Ni catalyst was suitable for the 2-propanol. In case of the 2-propanol fuel, the Ni catalyst was a match for the Pt catalyst in the V_{oc} especially at the low temperature, however, the Ni catalyst could not compete with the Pt catalyst in the cell performance. In contrast with the Ni catalyst, the Pt catalyst was suitable for the methanol fuel. The compatibility between the catalyst and the fuel was explained by the stripping voltammetry. The Ni catalyst was seriously poisoned by CO or COH originating in methanol compared with the Pt catalyst. On the other hand, the formed acetone remained on the Pt catalyst more than the Ni catalyst.

The Ni catalyst was match for the Pt catalyst in the open circuit voltage in case of 2-propanol fuel, while the cell performance with the Ni catalyst could not compete with that of the Pt catalyst. Considering the catalyst cost and the possibility of the improvement in the catalyst, Ni is the potential candidate for the anode catalyst by combined with the 2-propanol fuel in the DAFC for the mobile applications. There is concern that Ni is corrodes on the acidic cation-exchange membrane and affects the membrane. The impact should be also assessed in the future catalyst investigations.

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