The Mechanism of Direct Formic Acid Fuel Cell Using Pd, Pt and Pt-Ru

Nobuyuki Kamiya Non-member (Yokohama National University)

Yan Liu Non-member (Yokohama National University)

Shigenori Mitsushima Non-member (Yokohama National University)

Ken-ichiro Ota Non-member (Yokohama National University)

Yasuyuki Tsutsumi Member (Electric Power Development Co., Ltd.)

Naoya Ogawa Non-member (Electric Power Development Co., Ltd.)

Norihiro Kon Non-member (Ibaraki University)

Mika Eguchi Non-member (Ibaraki University)

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Slow scan voltammogram (SSV) and chronoamperometry measurements showed that the activity of formic acid oxidation increased in the following order: Pd black > Pd 30wt.%/C > Pt50wt.%/C > 27wt.%Pt-13wt.%Ru/C. A large oxidation current for formic acid was found at a low overpotential on the palladium electrocatalysts. These results indicate that formic acid is mainly oxidized through a dehydrogenation reaction. For the oxidation of 2-propanol and methanol, palladium was not effective, and 27wt.%Pt-13wt.%Ru/C showed the best oxidation activity.

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1. Introduction

The anodic oxidation of formic acid was studied using Pt catalysts⁽¹⁾⁽²⁾. Though the performance was considerably improved by the under-potential deposited Pb on the Pt surface⁽³⁾, the performance of the direct formic acid fuel cell (DFAFC) was lower than that of the direct methanol fuel cell (DMFC).

R. Masel's group of Illinois University showed a good result of DFAFC by Pd electrocatalyst⁽⁴⁾. In Fuel Cell Seminar 2004, they reported a high performance (0.7V-0.2Acm⁻², at 20°C) of the DFAFC with Pd anode catalyst⁽⁵⁾⁽⁶⁾. In addition, they gave the prototype of a cellular phone equipped with a direct formic acid fuel cell⁽⁵⁾. They indicated that the improved cell performance was as high as that of H₂-O₂ fuel cell. The cell performance of the DFAFC, i.e., the open circuit voltage and the maximum power density were raised to 0.9V and 0.172Wcm⁻², respectively⁽⁷⁾. Although the cell performance was increased by improving the cell assembly, the open circuit voltage did not exceed 1.23V, i.e., the theoretical electromotive force of the H₂-O₂ fuel cell.

Although the precise mechanism of the oxidation of formic acid has not been clarified yet, the total oxidation reaction on the anode

and the reduction of oxygen on the cathode would take place through the following Eqs. (1)-(3).

The theoretical oxidation potential of formic acid at the anode is -0.24V vs. RHE, and the electromotive force of the DFAFC is 1.47V, which is larger than those of the hydrogen-oxygen fuel cell, 1.23V, and of DMFC, 1.21V.

Although the anodic reaction finally takes place according to Eq. (3), the reaction mechanism could change depending on the electrode catalysts. One possible path is through formation of CO_{ads} or COH_{ads} (Eq. (4) or Eq. (5)) that adsorbs on the Pt surface and seriously decreases the catalytic activity of Pt.

In order to avoid catalyst poisoning by CO_{ads} or COH_{ads}, an attempt was made to hinder the adsorption of CO species on Pt. The linear and the bridge type CO species occupy one and two active sites, respectively. On the other hand, the COH species has

* Yokohama National University

79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501

** Electric Power Development Co., Ltd.

1-9-88, Chigasaki, Chigasaki-shi 253-0041

*** Department of Biomolecular Functional Engineering, Faculty of Engineering, Ibaraki University
4-12-1, Nakanarusawa-cho, Hitachi 316-0033

three bonding points and adsorbs on at most three active sites of Pt. Underpotential-deposited Pb on Pt showed a good effect on formic acid oxidation⁽¹⁾. In this case, Pb is deposited underpotentially on Pt at the potential range where the formic acid is oxidized. The Pb deposit occupies 2 to 3 consecutive active sites of Pt and decreases the number of the free sites on Pt. Therefore, the adsorption of CO species on the Pt active sites is hindered and the oxidation of formic acid is enhanced⁽¹⁾.

On the contrary, such poisoning phenomena do not take place on Pd⁽⁸⁾. On the Pd surface, another path (Eq. (6)) would also occur. If formic acid attaches to the surface of Pd, hydrogen is strongly extracted from the formic acid into the Pd lattice. Thus occluded hydrogen would be oxidized in the same way as in hydrogen-oxygen fuel cells. In this case, the electrode does not suffer from the poisonous CO_{ads}⁽⁸⁾.

As mentioned above, R. Masel et al. showed good performance of the direct formic acid fuel cell, and the performance was as high as that of the H₂-O₂ fuel cell⁽⁵⁾. If the formic acid is oxidized according to the Eq. (1), the open circuit potential or the open circuit cell voltage would exceed 1.23V. Actually, none of the results for the electromotive force were larger than 1.23V. These results indicate the another reaction path way.

Pd is well-known to occlude hydrogen. This has been used for cold fusion studies that utilized Pd as the cathode, where electrochemically generated hydrogen is occluded in the Pd lattice⁽⁹⁾. Based on the result, Pd is expected to extract hydrogen from formic acid through the dehydrogenation reaction and occlude hydrogen inside the Pd lattice. The direct dehydrogenation (Eq. (6)) and the dehydration path followed by the oxidation of adsorbed CO (Eq. (4)) are considered to occur competitively on the surface of the solid catalyst⁽¹⁰⁾⁽¹¹⁾. These reactions take place independently of the metallic components and the surface structure⁽¹²⁾. Since the Gibbs' energy change of dehydrogenation of formic acid (Eq. 6) is -33.0kJmol⁻¹⁽¹³⁾, the dehydrogenation and occlusion of hydrogen in the Pd lattice would take place rather easily.

The dehydrogenation reaction also takes place on Pt⁽¹⁴⁾ and Ru⁽¹⁵⁾⁽¹⁶⁾. In the former case, the reaction occurs chiefly on the surface of Pt (111)⁽¹⁴⁾. On the other hand, the dehydrogenation reaction and the dehydration takes place at 1:1 on the surface of Ru (100)⁽¹⁵⁾ and Ru (001)⁽¹⁶⁾. However, the extent of the dehydrogenation reaction is far slower than that on Pd. The precise information on the dehydrogenation has not been obtained; therefore, we investigated the effect of the Pd catalyst on the dehydrogenation reaction using fuels other than formic acid.

The anodic oxidation reaction controls the performance of the formic acid fuel cell. Many studies of oxidation reactions such as those using methanol, 2-propanol, and formic acid that use Pt or the Pt-Ru catalyst have already been reported. The Pt catalyst, the Pt-Ru catalyst, and methanol are the most popular catalysts and fuel. On the other hand, 2-propanol is known to undergo the following dehydrogenation-oxidation reaction on Pt and Ni (Eq. (7)). The Gibbs' energy change of dehydrogenation of 2-propanol (Eq. (8)) is 27.6kJmol⁻¹⁽¹³⁾, therefore spontaneous dehydrogenation and occlusion of hydrogen in Pd catalyst would not occur so easily.

Platinum is widely used for the cathode catalyst of PEFC or DMFC. However, it is also a good catalyst for methanol oxidation at such high potential as the oxygen reduction, therefore in case of methanol crossover of DMFC, the Pt cathode represents the mixed potential in the methanol contaminated condition and causes the decrease of the cell performance. On the contrary, Pd is almost inactive for methanol oxidation in the same methanol contaminated condition and the higher cathode potential was obtained⁽¹⁷⁾.

Considering the characteristics of these catalysts and the fuel reactivities, it is quite important to clear the reaction mechanism of formic acid, 2-propanol and methanol on Pd, Pt and Pt-Ru electro-catalysts in developing a high performance fuel cell.

2. Experimental

2.1 Preparation of a Powder Coated Electrode Thirty wt.% Pd/C (Aldrich), 96.8wt.% Pd black, 50wt.% Pt/C, and 27wt.% Pt-13wt.% Ru/C (N. E. Chemcat) powder catalysts were applied to the end face of a 6mmφ glassy carbon. Here /C indicates that the catalysts are dispersed on the supporting carbon particles. For the powder application, the catalyst is mixed with water. The catalyst ink was stirred by a supersonic wave mixer for 30 minutes and was applied to the glassy carbon edge. The amount of the catalysts was kept 0.1mgcm⁻². Water was evaporated at 80°C under a nitrogen atmosphere, and the electrode surface was coated with 1% Nafion® solution. Thereafter, it was heat-treated for 1 hour at 80°C and then at 120°C for 30 minutes under a nitrogen gas atmosphere, and the catalyst-coated glassy carbon electrode was used for the studies.

2.2 Electrochemical Measurements A three-electrode cell was used for the electrochemical measurements. The characteristics of the prepared electrode were evaluated by cyclic voltammetry (CV) in a 0.1 M (M=mol·dm⁻³) H₂SO₄ solution. The oxidation ability of the fuel was evaluated using slow scan voltammetry (SSV) and potentiostatic chronoamperometry in 0.1 M H₂SO₄ + 5 M HCOOH, 0.1 M H₂SO₄ + 1 M 2-propanol and 0.1 M H₂SO₄ + 1 M methanol solutions at 30°C under a nitrogen atmosphere. The current density is displayed as the current for each unit mass of Pt or Pd. The mass activity; i_m, and the catalytic activity were evaluated.

2.3 Preparation of Fuel Cell Assemblies A thin film MEA was prepared by the decal method, i.e., first the anode and cathode catalyst ink were sprayed on PTFE (polytetrafluoroethylene) sheets separately and the catalyst layers were transferred on an electrolyte membrane by means of a heat pressing procedure. Thus prepared anode and cathode catalyst layer was sandwiched by gas diffusion layers to a MEA. The amounts of Pt in the cathode and of Pd in the anode were 0.96mgcm⁻², and 0.74mgcm⁻², respectively. Nafion® 117 was used for the electrolyte membrane. The area of the catalyst layer was 5×5cm². The flow rate of the fuel for 10M formic acid at the anode was 2.5mlmin⁻¹, the dry air to the cathode was 800mlmin⁻¹, and the H₂ gas to the cathode and anode was 200mlmin⁻¹.

3. Results and Discussion

3.1 Dehydrogenation of Formic Acid and Occlusion of Hydrogen in Palladium Pd and Pt smooth wires were

examined whether they dehydrogenate formic acid and occlude hydrogen in the metals. First, these metallic wires were dipped in formic acid for 10 minutes and then washed with deionized water. They were transferred into 0.1M H_2SO_4 solution, and a potential step-chronoamperometric examination was carried out under nitrogen. Figure 1 shows the oxidation current decay curves of the Pd and Pt electrodes after the potential was stepped to 0.3V. The apparent surface area was applied to determine the current density. The Pt electrode showed almost no current during the experimental time period. This indicates that the smooth Pt did not occlude a significant amount of hydrogen. On the other hand, the Pd electrode showed a large oxidation current which lasted for a long time. These facts support that formic acid is dehydrogenated and hydrogen is occluded in Pd during the dipping step in the formic acid solution.

The same hydrogen gas occlusion was observed for Pd after being dipped in sulfuric acid solution with bubbling hydrogen gas. A large oxidation current of occluded hydrogen was detected with Pd catalyst as seen with the formic acid, nevertheless Pt showed no such current under the same condition. Under a nitrogen gas atmosphere, no such oxidation current was observed on both Pd and Pt.

From these results, dehydrogenation of formic acid and occlusion of hydrogen must occur on Pd surface. According to the reaction scheme (6), the open circuit voltage of the DFAFC would be at highest the electromotive force of the $\text{H}_2\text{-O}_2$ fuel cell. Since the oxidation reaction of methanol does not proceed in a significant rate on $\text{Pd}^{(17)}$, the formic acid oxidation according to the reaction scheme (4) or (5) would be far slower than the rate of dehydrogenation⁽⁸⁾. Even though such intermediate species, or any other organic intermediates form and adsorb on the Pd surface, they would be oxidized rapidly under the transfer stage from dipping step to the potential step – chronoamperometric experiment. Under the transfer stage, the surface of the Pd is placed in the air condition, therefore even a strong adsorbate, i.e., CO is instantly oxidized. The oxidation of strongly adsorbed poisonous CO by mixed very low pressure of oxygen in the reformed hydrogen fuel is generally carried out in the fuel cell operation. To avoid the decline of the cell performance by ppm order of CO contaminant and recovery of Pt surface are well known as the air bleed method in the fuel cell operation.

Even a small amount of the occluded hydrogen in the Pd lattice

Fig. 1. Chronoamperometry (Potential: 0.3 V vs. RHE) of Pd and Pt electrodes in 0.1 M H_2SO_4

is oxidized under the transfer stage, the rest occluded hydrogen in the Pd lattice does not come out to the Pd surface in a short time, and therefore the large amount of the remained hydrogen is oxidized under the potential step – chronoamperometric experiment.

With hydrazine, the same large oxidation current was also observed by dipping - chronoamperometric method. In this case, the Gibbs' energy change of hydrazine decomposition is as large as $-149.4 \text{ kJ mol}^{-1}$ ⁽¹³⁾, decomposition of hydrazine and occlusion of hydrogen in Pd would take place easily.

3.2 Influence of Catalyst on Formic Acid Oxidation Reaction Figure 2 shows SSV of formic acid solution using 96.8wt.%Pd black, 30wt.%Pd/C, 50wt.%Pt/C, and 27wt.%Pt-13wt.%Ru/C catalysts. The scanning rate was 5 mVs^{-1} . The scanning range was 0.05V~0.8V (vs. RHE), except for the Pt-Ru/C, and 0.05V~0.7V (vs. RHE) for the Pt-Ru/C. The onset potential of formic acid oxidation increased in the order of Pd black (ca.0.05V) < 30wt.%Pd/C (ca.0.05V) < 50wt.%Pt/C (ca.0.2V) < 27wt.%Pt-13wt.%Ru/C (ca.0.35V). A high oxidation current began to flow with two previous types of catalysts at a significantly low potential. The onset potential of formic acid oxidation on these catalysts is nearly 0V and the polarization is small.

On Pt/C and Pt-Ru/C catalysts, formic acid oxidation occurs at more positive potential than on Pd catalysts and a fairly large polarization curves are observed. On the Pt-Ru/C catalyst, the oxidation current began to increase rapidly at 0.5V or more positive potential. This trend was seen with methanol oxidation.

The time decay of formic acid oxidation is shown in Fig. 3. The electrode potential was maintained for ten seconds at 1.0V (vs. RHE). Thereafter, it was stepped to 0.3V (vs. RHE), and the potentiostatic chronoamperometry was operated. To evaluate the catalyst's activity, the current was divided by the amount of the catalysts, here the term was represented as the mass activity. Although the mass activity for each catalyst decreased with time, the mass activity of formic acid oxidation was clearly in the order of Pd black ($112 \text{ mA} \cdot \text{mg}^{-1}$) > 30wt.%Pd/C ($55 \text{ mA} \cdot \text{mg}^{-1}$) > 50wt.%Pt/C ($12 \text{ mA} \cdot \text{mg}^{-1}$) > 27wt.%Pt-13wt.%Ru/C ($0.5 \text{ mA} \cdot \text{mg}^{-1}$).

As shown in Fig. 2, the activity of Pt-Ru was larger than Pt at higher overpotential region than 0.5V. However, at 0.3V, the

Fig. 2. Slow scan voltammogram of Pd black, Pd 30 wt% / C, Pt-Ru/C, Pt/C electrodes in 0.1 M H_2SO_4 + 5 M formic acid under N_2 , Scan rate: 5 mVs^{-1}

Fig. 3. Chronoamperometric activity (Potential: 0.3V vs. RHE) of Pd black, Pd30wt%/C, Pt-Ru/C, Pt/C electrodes in 0.1M H₂SO₄+5M formic acid under N₂ atmosphere

current density for Pt was larger than for Pt-Ru even after 30 min.

On the Pd catalyst, the oxidation reaction of the formic acid starts at a low overpotential, and the current value is also large. On the contrary, the oxidation of formic acid on Pt/C or Pt-Ru/C requires much overpotential. The Pt-Ru/C catalyst is considered to be most effective for CO_{ads} oxidation, however, the reaction (4) or (5) will start at more positive potential than 0.3V. Therefore the dehydrogenation on Pd predominates over these enhancement effect by Pt/C or Pt-Ru/C at this potential region.

3.3 Influence of Catalyst on 2-Propanol and Methanol Oxidation Reaction To investigate the oxidation catalyst ability of the fuel, slow scan voltammetry (SSV) of Pd black, Pd/C, Pt-Ru/C, and the Pt/C electrocatalysts in 2-propanol and methanol are shown in Figs. 4 and 5, respectively. The oxidation catalytic activity for the alcohols was in the following order.

27wt.%Pt-13wt.%Ru/C > 50wt.%Pt/C > Pd black 30wt.%Pd /C
The Pd activity was found to be extremely low for the oxidation of 2-propanol and methanol unlike that for formic acid. The catalytic ability for oxidation by Pt-Ru/C was the highest among these electrocatalysts for the oxidation of 2-propanol and methanol. When the Pt-Ru/C catalyst was used, the onset potential of the oxidation of 2-propanol, known as a dehydrogenation reaction type fuel, was very low, at less than 0.1V. This phenomenon was similar to that with the formic acid using the palladium catalyst. However, the oxidation current of 2-propanol using a palladium catalyst was extremely low. The Gibbs' energy change of the dehydrogenation reaction of 2-propanol is positive⁽¹³⁾, therefore the reaction does not take place spontaneously even on Pd surface. Instead the oxidation of C-OH in 2-propanol would proceed significantly fast on Pt or Pt-Ru catalyst.

The onset oxidation potential of the Pt-Ru catalyst for methanol was about 0.4 V, which was 0.1V more negative than that for the Pt catalyst. Preferential effect of Pt-Ru for methanol oxidation is known as a characteristic of the methanol fuel cell. On the other hand, the palladium catalyst which acts effectively in the formic acid oxidation, was ineffective for the oxidation of the methanol. Pd has no activity of oxidation of C-OH or CO_{ads} in oxidation of 2-propanol and methanol.

3.4 Performance and Polarization Char-Acteristic of Formic Acid Fuel Cell A single cell using a palladium

Fig. 4. Slow scan voltammogram of Pd black, Pd 30 wt%/C, Pt-Ru/C, Pt/C electrodes in 0.1M H₂SO₄+1M 2-propanol under N₂ atmosphere. Scan rate:5mVs⁻¹

Fig. 5. Slow scan voltammogram of Pd black, Pd 30 wt%/C, Pt-Ru/C, Pt/C electrodes in 0.1M H₂SO₄+1M MeOH under N₂ atmosphere. Scan rate:5mVs⁻¹

Fig. 6. Performance and polarization characteristic of formic acid fuel cell at 25°C

catalyst was constructed according to the 2.3's procedure, and the performance of the formic acid fed fuel cell was examined. Figure 6 shows the performance of the formic acid-air fuel cell (FA-Air : ◆) and a hydrogen-air fuel cell (H_2 -Air : ■), together with an electrolyser feeding formic acid-hydrogen (FA- H_2 : ▲), and hydrogen-hydrogen (H_2 - H_2 : ●) using the same cell setup and under the same operating temperature of 25°C. The performance of the formic acid-air fuel cell at 25°C was equivalent to that of the Pt-Ru catalyst methanol fuel cell at 100°C⁽¹⁸⁾. The formic acid-air fuel cell at the ambient temperature of 25°C had a higher performance compared to the methanol fuel cell at 30°C⁽¹⁹⁾.

Because the polarization for the hydrogen oxidation and the proton reduction at the hydrogen electrode are much smaller than those for methanol or formic acid oxidation, it is possible to consider the hydrogen electrode as the reference electrode. Therefore, the performance of the hydrogen-air fuel cell shows the approximate cathode polarization based on the RHE, and the performance of the formic acid-air fuel cell includes both the approximate anode polarization, i.e., oxidation of formic acid and the cathode polarization. The measured voltage difference of both fuel cells is approximately equal to the polarization of the formic acid oxidation.

As for the formic acid-hydrogen and hydrogen-hydrogen electrolyzers, the current was input from the outer power source. Therefore the cell performance increased with increase of the current density. The open circuit voltage of the formic acid- H_2 electrolyser was +0.06V for the theoretical electromotive force of -0.24V. Based on these data, the anode overpotential of the DFAFC was calculated to be $0.06 - (-0.24) = 0.3V$ under the open circuit condition. The difference between the performances of formic acid-hydrogen and hydrogen-hydrogen electrolyzers indicates the difference between the anodic polarization of formic acid and hydrogen, which is nearly equivalent to the difference observed in hydrogen-air and formic acid-air fuel cells.

As discussed in Fig. 1, the palladium occludes hydrogen inside its lattice and the potential of the Pd electrode was near that of hydrogen after the Pd electrode was dipped in the formic acid solution. However, the amount of hydrogen occluded in the Pd lattice would be much smaller than that obtained in a pure hydrogen atmosphere. If the direct anodic oxidation of formic acid takes place, the open circuit potential of the anode may be more positive as seen in the DMFC⁽²⁰⁾. Considering these results, the open circuit anode potential, i.e., 0.6V for formic acid oxidation, strongly indicates to be due to the dehydrogenation reaction at the Pd electrode. In the DMFC, the open circuit potential of the anode is also more positive, i.e., the larger overpotential being due to the slow anodic reaction and poisoning phenomena.

However, more studies are required to clarify the reaction mechanism of the formic acid oxidation.

4. Conclusion

The reaction mechanism of DFAFC has been discussed by means of Pd, Pt, Pt-Ru electrocatalysts. The ability of occlusion of hydrogen in Pd is high enough to extract hydrogen from formic acid and thus occluded hydrogen is oxidized on Pd anode. The enhanced and H_2 - O_2 FC like cell characteristics of DFAFC by Pd would be due to the dehydrogenation effect. Pt and Pt-Ru showed only low activity on the oxidation of formic acid.

On the other hand, 2-propanol was not oxidized easily on Pd surface and the dehydrogenation reaction of 2-propanol on Pd was

not considered to take place. Instead, Pt and Pt-Ru electrocatalysts are effective for the oxidation of 2-propanol. These catalysts would assist the oxidation of C-OH of 2-propanol. The oxidation paths of formic acid on Pd and 2-propanol on Pt and Pt-Ru was found to be different each other.

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Nobuyuki Kamiya

(Non-member) was born in Aichi, Japan, on April 22, 1941. Received Ph.D. in Chemical engineering from Tokyo Institute of Technology in 1969, he joined Electrochemical Research Group of Yokohama National University. His major research field is electrolyses and fuel cells. He was promoted to Professor of the Graduate School of Yokohama National University in 2000.

Yan Liu

(Non-member) was born on April 1, 1974. Received B. S. degree from Beijing University of Aeronautics & Astronautics, China in 1996, she entered Graduate School of Yokohama National University in 2001, and finished her Ph. D course in 2006. She is now Assistant Prof. of Peking University, Institute of Physical Chemistry, College of Chemistry & Molecular Engineering, China.

Shigenori Mitsushima (Non-member) was born on September 24, 1963. Received Master degree in Material Engineering from Yokohama National University (YNU) in 1989, he joined Hitachi, Ltd. He received Doctor of Engineering from YNU in 1998, and moved to YNU as Research Associate in 2000. His major research field is fuel cells and industrial electrolysis. He has been Associate Professor of YNU since 2006.

Ken-ichiro Ota (Non-member) was born in Hyogo 1945 and got Dr of Engineering, Graduate School of Engineering, the University of Tokyo. He is now a professor of Yokohama National University, Graduate School of Engineering. His research field is applied electrochemistry, especially fuel cells.

Yasuyuki Tutsumi (Member) was born on January 18, 1938. Graduated from Department of Electric Engineering, Kyushu University in 1960, he joined Hitachi, Ltd. Retired there, he moved to Ibaraki University as Professor of Faculty of Engineering in 1989. He retired the Institute and was promoted Emeritou Professor in 2003. He has been worked as the chief researcher at Electric Power Development Co., Ltd. His measure research field is phosphoric fuel cell and dimethyl ether fuel cell.

Naoya Ogawa (Non-member) was born in Hiroshima, Japan, on September 14, 1969. Graduated from Department of Electric Engineering Tokyo University of Agriculture and Technology in 1993. He has been as the chief engineer at Advanced Technology Development Group of Electric Power Development Co. Ltd. (JPOWER) His major research field is the improvement of Membrane Electrode Assembly (MEA) for DMFC, PEFC and Fuel cell systems.

Norihiro Kon (Non-member) was born on July 5, 1982. Graduated from Ibaraki University, Department of Materials Science, Faculty of Engineering in 2005, he entered ENAX, Inc.

Mika Eguchi (Non-member) was born in Tokyo, Japan, on April 10, 1966. Received Ph.D. in Applied Chemistry from Keio University in 1995, she started in National Institute Post Doctoral Fellowship. She joined Department of Materials Science, Faculty of Engineering, Ibaraki University in 1998. Her major research field is lithium batteries and fuel cells. She has been Assistant Professor of the Ibaraki University since 2006.