Chemical-hydrogenation Functionalized Flow-Field in Toluene Direct Electro-hydrogenation Electrolyzer for Energy-carrier Synthesis System

Kensaku NAGASAWA,a,b Yuki SAWAGUCHI,a Akihiro KATO,c Yoshinori NISHIKI,c and Shigenori MITSUSHIMAa,b

a Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
b Green Hydrogen Research Center, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
c De Nora Permelec, Ltd., 2023-15 Endo, Fujisawa 252-0816, Japan

*Corresponding author: nagasawa-kensaku-st@ynu.ac.jp

ABSTRACT

The toluene-methylcyclohexane organic hydride has been expected to be a candidate of the hydrogen energy carrier system for the effective utilization of renewable energy. We have developed an electrocatalyst for the toluene electro-hydrogenation electrolyzer. However, hydrogen evolution as the side reaction decreases the current efficiency by inhibiting the toluene mass transfer. In this study, we demonstrated the effect of the toluene-methylcyclohexane chemical-hydrogenation by the loading of Pt nanoparticles in the carbon-paper as a porous flow-field. The loaded Pt in the flow-field functioned as the toluene hydrogenation catalyst with the generated hydrogen gas. This simultaneous functioning of chemical- and electro-hydrogenation in the flow-field and the catalyst layer was designed to enhance the overall apparent current efficiency. Based on the electrochemical measurement, the Pt-loaded carbon paper flow-field showed an outstanding enhancement of the current efficiency without a decrease in performance for the Pt loading from 0.5 to 0.02 mg cm

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1. Introduction

The effective utilization of renewable energy such as wind, solar, geothermal heat and wave power has been needed as a solution of the global environment issue, because it provides an essentially clean system. However, the geographical distance and overseas transportation between the areas of energy supply and demand on a global scale are realistic problems regarding energy loss and installation with the electric grid transportation. For the solution of these problems, the large-scale storage and transportation technology of hydrogen as the secondary energy converted from renewable energy have been expected. The organic hydride system, which works as the hydrogen energy carrier, is an attractive candidate for filling this demand.1,2 Especially, the toluene-methylcyclohexane system has the advantages of a high energy density and easy handling due to its the low toxicity and the existence of a liquid state at the ambient temperature and pressure.3-5 Generally, the toluene hydrogenation reaction occurs by the following two-step reactions. 2H2O(l) = O2(g) + 4H+(aq) + 4e− (1st step, anode) (1) 2H+(aq) + 2e− = H2(g) (1st step, cathode) (2) C6H4(CH3)l + 3H2(g) → C6H11CH3(l) (2nd step) (3) Meanwhile, we have studied the electrocatalytic one-step reaction by the direct hydrogenation process using a proton exchange membrane (PEM).6-11,14 which can be used at the same time for the toluene hydrogenation and the water splitting as shown by the following reactions. 2H2O(l) = O2(g) + 4H+(aq) + 4e− (anode) (4) C6H4CH3(l) + 6H+(aq) + 6e− = C6H11CH3(l) (cathode) (5) This process has the advantages of no exothermic heat loss by the hydrogenation reaction of Eq. (3) with a lower theoretical decomposition voltage from 1.23 of the water electrolysis according to Eqs. (1) and (2) to 1.08 V of the electrohydrogenation of Eqs. (4) and (5).14,15,16 In this system, if toluene is not sufficiently supplied to the cathode catalyst, the hydrogen gas is generated from the adsorbed hydrogen by the following side reaction instead of reaction (5). 2H+(aq) + 2e− = H2(g) (cathode) (6) This reaction is a dominant factor that decreases the current efficiency for the toluene direct electrocatalysis hydrogenation, because by-products, such as methylcyclohexadienes and methylcyclohexenes, which produce the current efficiency loss, were not detected for this one-step reaction in our previous study.11,12 Hydrogen gas disturbs the toluene transportation to the electrocatalyst, and lead to the hydrogen evolution reaction. In this study, we have developed a new functionalized toluene flow-field, which involves the toluene hydrogenation catalyst using a generated hydrogen gas from the side reaction, to demonstrate the improvement in the apparent current efficiency.

2. Experimental

Figure 1 shows a schematic drawing of the toluene direct hydrogenation electrolyzer used for the chemical-hydrogenation functionalized flow-field. As the electrolyzer components, an oxygen evolution anode and PEM used a DSE® electrode for the oxygen evolution (De Nora Permelec, Ltd.) and Nafion®117 (DuPont), respectively. The flow-fields had the parallel and the porous structure for anode and cathode, respectively.14 The Ti web,
which was held between the anode DSE and Ti plate worked as a uniform membrane-pressure component by its elasticity with the function of the current corrector. Hence, this electrolyzer has a zero-gap structure for the porous-carbon flow-field, electrode and membrane between the Ti end plates. The cathode was fabricated by the following method. The catalyst ink was made by mixing 5.1 wt.% of Pt-Ru/C (Pt: 30 wt.% Ru: 23 wt.% TEC61E54, Tanaka Kikinzoku Kogyo), 6.1 wt.% of pure water, 38.1 wt.% of 5% NaFon® solution (DuPont) and 50.7 wt.% of 1-propanol (Wako Pure Chemical Industries, Ltd.), and ball-milled using a 100 mL pot and 3.0 mm balls at 200 rpm for 10 min. The prepared ink was applied on the cathode carbon paper (10BC, thickness: 420 µm, porosity: 34.6%, mean pore diameter: 2.92 µm, SGL Carbon, Ltd.) with a 0.5 mg-Pt cm⁻² loading amount. This result would mean that the increase in the Pt particle size was the highest. The Pt particle number of 0.02 mg-Pt cm⁻² was then the highest of all the samples by that loading amount, though the Pt particle size was the highest. The Pt surface area of 0.5 mg-Pt cm⁻² was 2.7 nm, the size increased with the Pt loading amount using a bar coater. After drying, this cathode was hot-pressed on the PEM at 1 MPa for 3 min. The anode side of the PEM was roughened by emery paper (#2000) as a hydrophilic treatment.

In the above process, the chemical-hydrogenation catalyst loaded carbon paper was prepared by the following impregnation method. The carbon paper with the size of 10 cm² was immersed in 10 mL from 0.97 to 25.5 mmol L⁻¹ of H₂PtCl₆·6H₂O at 10 mL min⁻¹ for both flow rates, respectively, and the operating temperature was 60°C. The electrochemical measurements were conducted by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronopotentiometry (CP) and current efficiency measurement. The Nyquist plot of the EIS measurement was analyzed by the ZView® program. The current efficiency was measured by the following method. The volume ratio of the generated hydrogen gas and toluene-methylecyclohexane solution obtained at the outlet of the cathode chamber was measured at the constant voltage from 1.0 to 2.5 V. The current efficiency was then calculated by Faraday’s law. Conversion from toluene to methylecyclohexane was defined as a one-pass condition in the electrolyzer injected with 100% toluene at the inlet. The solution sampled at the cathode outlet of electrolyzer was measured by gas chromatography (GC, GC-2014, Shimadzu Co.). During the GC sampling, the current density was 0.4 A cm⁻² and the flow rates were 10, 5, 2.5, 1 and 0.5 mL min⁻¹.

3. Results and Discussion

Table 1 shows the Pt loading, particle size, particle number and surface area for the carbon papers before applying the Pt-Ru/C catalyst. The Pt loadings of the XRF were almost the same as that of the weight change and the expected value from the H₂PtCl₆·6H₂O amount. The Pt particle size was evaluated by the Scherrer equation from the XRD pattern (Figure S1). Though the particle size for the loading of 0.02 mgPt cm⁻² was 2.7 nm, the size increased with the loading amount. This result would mean that the increase in the H₂PtCl₆·6H₂O amount during preparation affected the growth of the particle size. The Pt particle number of 0.02 mgPt cm⁻² was 5–6 times that of the others. The Pt surface area of 0.5 mgPt cm⁻² was then the highest of all the samples by that loading amount, though the Pt particle size was the highest.

Figure 2 shows the LSV curves for the 0, 0.5, 0.1 and 0.02 mgPt cm⁻² carbon paper flow-fields with 100 and 10% toluene at 60°C. The concentrations of 100 and 10% toluene simulated the conditions of the cathode in the vicinity of the inlet and outlet regions for a several m² class electrolyzer of practical use, respectively. These curves did not show the continuous change in the Pt loading amount. The orders of the cell voltages at 0.4 A cm⁻² were 0.5 mgPt cm⁻² < No loading < 0.1 mgPt cm⁻² < 0.02 mgPt cm⁻² in both the 100 and 10% toluene. The 0.5 mgPt cm⁻² loaded flow field cell showed the lowest cell voltage of 1.92 V at 0.4 A cm⁻² with 100% toluene. Especially, the LSV curve for 0.5 mgPt cm⁻² showed a minimum of 3.3 V.

Table 1. Pt loading, particle size, particle number and surface area for carbon paper samples before applying the Pt-Ru/C catalyst.

| Sample                                      | No loaded | 0.02 mg cm⁻² | 0.1 mg cm⁻² | 0.5 mg cm⁻² |
|---------------------------------------------|-----------|--------------|-------------|-------------|
| Pt loading (XRF, mg cm⁻² geo⁻²)             | —         | 0.02 (0.01¹) | 0.08 (0.02¹) | 0.40 (0.06¹) |
| Pt loading (Weight change, mg cm⁻² geo⁻²)   | —         | 0.03         | 0.14        | 0.50        |
| Pt particle size (XRD, nm)                  | —         | 2.7          | 7.4         | 12.6        |
| Pt particle number (cm⁻²)                   | 9.0 × 10¹³| 1.7 × 10¹³   | 1.8 × 10¹³  |             |
| Pt surface area (cm²)                       | 21        | 30           | 89          |             |

¹) standard deviation for 5 × 5 measurement points on carbon paper by XRF thickness measurement.
²) values calculated from Pt loading by XRF.
a behavior different than the other loadings. The reason, which did not show the continuous order in cell voltages for the Pt loading amount, will be discussed later in impedance analysis section. These results will be discussed later in the impedance analysis section. Basically, in the low toluene concentration, the hydrogen gas generates at the cathode side as a side reaction described by reaction (6). However, in Fig. 2, the concentration overvoltage due to the diffusion resistance was not observed in the 10% toluene for all cells. In this study, the electrolyzer had a zero-gap structure as described in the experimental section. This structure would be free from any ionic conduction interruption by the generated oxygen bubbles, which increases not only the ionic resistance, but also the electrode reaction overpotentials due to turbulence caused by the current flow.

Figure 3 shows the current efficiency for the 0, 0.5, 0.1 and 0.02 mg Pt cm⁻² of the carbon paper flow-field with 100 and 10% toluene at 60°C. With the 100% toluene, all the cells showed a 100% current efficiency until 0.4 A cm⁻². This means that the hydrogen gas did not generate at the cathode. On the other hand, as the remarkable characteristic with the 10% toluene, the Pt nanoparticle loaded carbon paper flow-field significantly enhanced the current efficiency compared to the Pt free flow-field. It is considered that this advantage exhibited a chemical-hydrogenation effect, which is the reaction of the generated hydrogen gas and toluene on the Pt catalyst of the carbon paper flow-field to produce methylcyclohexane based on the following reactions.

$$C_6H_5CH_3(l) + 3H_2 = C_6H_{11}CH_3(l) \quad (\text{Pt surface})$$  \hspace{1cm} (7)

A schematic drawing of this process is described in Fig. 4 (The simple demonstration of toluene hydrogenation with H₂ and toluene by Pt nanoparticle catalyst shows in Figure S2). If the toluene supply to the cathode catalyst is sufficient, the toluene direct electro-hydrogenation reaction without hydrogen evolution occurs as shown in Fig. 4(a). However, the shortage of toluene to the catalyst by the diffusion limit leads to hydrogen evolution as shown in Fig. 4(b). In this case, a hydrogen bubble would disturb the toluene supply from the flow field to the catalyst layer. In this situation, Pt nanoparticles on the carbon paper flow-field work as the chemical-hydrogenation

![Figure 2](image1.png)  \hspace{1cm} ![Figure 3](image2.png)  \hspace{1cm} ![Figure 4](image3.png)

**Figure 2.** LSV curves for 0, 0.5, 0.1 and 0.02 mg Pt cm⁻² loaded diffusion layer with (a) 100 and (b) 10% toluene at 60°C.

**Figure 3.** Current efficiency for 0, 0.5, 0.1 and 0.02 mg Pt cm⁻² loaded diffusion layer with 100 and 10% toluene at 60°C.

**Figure 4.** Schematic drawing of (a) toluene electro-hydrogenation, (b) generating hydrogen by limited supply of toluene to catalyst and (c) chemical-hydrogenation function at Pt loaded diffusion layer.
catalyst for the reaction of toluene and the generated-hydrogen to remove the hydrogen bubble as shown in Fig. 4(c). As a result, this process with the loaded Pt nanoparticles on the carbon paper flow-field contributes to enhancement of the apparent current efficiency.

In Fig. 3, the current efficiency was measured with an increase in the current density. The onset current density from 100% of the current efficiency was around 0.15 A cm\(^{-2}\) for all the cells. This means that there was no significant difference in the catalyst layers with and without Pt loading on the flow-field, because this current efficiency area had no hydrogen bubbles. However, over 0.15 A cm\(^{-2}\), the decrease in the current efficiency for the Pt free flow-field cell was significantly greater than the Pt loaded flow-fields. It is considered that this difference originated from the chemical-hydrogenation effect, which suppressed the toluene transfer interruption with hydrogen bubbles. This tendency ensured the occurrence of reaction (7). On the other hand, the measured conversions for the Pt loaded carbon paper were significantly different for the Pt particle number and Pt surface area than the others as shown in Table 1, respectively. However, the difference from 0.5 to 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\) for the samples hardly showed in the current efficiency curves. This result means that the 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\) loading had a sufficient Pt surface area for the chemical hydrogenation, and it was suggested the possibility that the chemical-hydrogenation effect functioned even if the Pt loading amount was lower than 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\). At least, the loading amounts of 0.5 and 0.1 mg\(\text{Pt} \times \text{cm}^{-2}\) were in excess regarding the current efficiency. Additionally, it should be noted that the large Pt particle size over 10 nm for 0.5 mg\(\text{Pt} \times \text{cm}^{-2}\) maintained the effect of the current efficiency enhancement the same as the small particle size of 2.7 nm for 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\), and the change in the Pt particle number also did not affect.

Figure 5 shows the measured conversion and cell voltage during the chronopotentiometry as a function of the setting conversion that was controlled by the flow rate of 100% toluene at 0.4 A cm\(^{-2}\) under a one-pass condition at 0.5, 0.1 and 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\) of the carbon paper flow field cells at 60°C. Conversion was defined by the methylocyclohexane ratio in the outlet solution of the electrolyzer for the inlet of 100% toluene under one-pass condition of solution. The dotted line in Fig. 5 represents the ideal conversion from the setting conversion, the value of which corresponds to 100% of the current efficiency. This mean is following. In this measurement, the current density fixed at 0.4 A cm\(^{-2}\) during the stabilization time of conversion at a constant flow rate and the sampling of outlet solution. In this time, the conversion of outlet solution depends on the value of the flow rate. Because, even if the current efficiency of the electrolyzer system is 100%, the conversion depends on by the average existence time of toluene in cathode chamber, and it is decided by the flow rate. Hence, if the flow rate is higher, theoretical conversion is lower. And the conversion has the upper limit in the condition of the 100% current efficiency. That limit defined the setting theoretical conversion. It was calculated using Faraday’s law as follows:

\[
\text{Setting theoretical conversion (\%)} = \frac{100ltM}{3FpQ} \tag{8}
\]

where, \(I\), \(t\), \(M\), \(z\), \(f\), \(\rho\) and \(Q\) are the load current (A), time (=60(s)), molecular weight of methylocyclohexane (g mol\(^{-1}\)), electron number of hydrogenation (=0), Faraday constant, density of methylocyclohexane (g mL\(^{-1}\)) and flow rate (mL min\(^{-1}\)), respectively. In Fig. 5, the measured conversion of the no Pt loading sample began to decrease for the theoretical conversion from less than 1.0 mL min\(^{-1}\), while it showed 55% of the theoretical conversion at 0.5 mL min\(^{-1}\). On the other hand, the measured conversions for the Pt loaded carbon paper flow-field almost corresponded to the theoretical conversion line. Especially, in the vicinity of 0.5 mL min\(^{-1}\), which is the theoretical conversion of nearly 100%, the measurement conversions showed outstanding values from 92 to 96% (Figure S3). These results showed that the chemical hydrogenation effect by loading the Pt catalyst apparently functioned in this measurement. Additionally, it means that the electrolyzer in this study achieved almost the complete toluene-hydrogenation function under the condition of one-through operation at 0.4 A cm\(^{-2}\) using a 100 cm\(^{-2}\) class electrode area. During the conversion measurement, the cell voltages for all the samples showed a constant behavior for the variation in the flow rate under 0.4 A cm\(^{-2}\). Generally, the gas generation from the electrode would increase the cell voltage by interruption of the current distribution in the electrolyte solution. In our electrolyzer, if the flow rate decreased, the volume ratio of hydrogen gas in the cathode chamber would increase because of the significantly low liquid supply rate, while keeping a high current efficiency. However, our result indicated that the increase in the gas volume in the cathode chamber did not affect the cell voltage. This desirable property would be caused by the cell composition of the zero-gap structure as described in the section for Fig. 2.

Figure 6 shows the impedance spectra of the Pt free flow-field cell fed 100% toluene at 1.5, 1.7 and 1.9 V cell voltages as the Nyquist plots with an inset of the equivalent circuit for the impedance analysis with the resistance \(R_1\) and constant phase element \(CPE\). \(R_1\), \(R_2\) and \(R_3\) represent the internal resistance, cathodic and anodic charge transfer resistance, which provided the intercept of the real axis at a high frequency, semi-circle of the high and low frequency sides, respectively.\(^{14,18}\) The \(R_1\) and \(R_2\) were assigned as the cathodic and anodic charge transfer resistances in the experimental and theoretical way in our previous study, respectively.\(^{10,14}\) In fact, the semicircle on the low frequency side was not the diffusion resistance, because the value of \(R_1\) decreased as the cell voltage or current increased.

Figure 7 shows \(R_1\), \(R_2\) and \(R_3\) as a function of the current density for 0, 0.5, 0.1 and 0.02 mg\(\text{Pt} \times \text{cm}^{-2}\) of the carbon paper flow-field with 100 and 10% toluene at 60°C, respectively. For all the resistances, the influence of the toluene concentration between 100 and 10% on the resistances was not clearly confirmed. This tendency was as same as the behavior for the cell voltage in Fig. 2. The \(R_1\) values of all the Pt loaded samples were lower than that of the no Pt loaded sample. This tendency would originate from the decrease in the contact resistance between the Ti end plate and the Pt loaded carbon paper. The difference in the \(R_2\) for each sample was not low,
but it did not clearly show the tendency for loading. The lowest cell voltage for 0.5 mg-Pt cm$^{-2}$ in Fig. 2 originated from the low $R_1$ and $R_2$, because the $R_{3s}$ for all the samples did not change. The differences in $R_{3s}$ and $R_{3s}$ would originate from the difference of contact resistance by the slight variation of cell fabrication and the slight effect of the mass transfer by the variation in the catalyst layer fabrication, respectively. However, for the difference of $R_{3s}$, the current efficiency and conversion in Figs. 3 and 5 were almost the same results for the Pt loaded samples, respectively. It is considered that the chemical-hydrogenation in the flow-field reduced the difference in the electro-hydrogenation performance in the PtRu/C catalyst layer for each sample.

Consequently, the loading change from 0.02 to 0.5 mg-Pt cm$^{-2}$ focusing on the cell voltage and conversion indicated no significant difference from the effect of the Pt loading. From the analogizing of our result, the electrochemical properties of the sample over 0.5 mg-Pt cm$^{-2}$ would not also change significantly. On the other hand, reducing the Pt consumption amount is also a significant issue from the aspect of cost or resource in industry. Regarding this point, the lowest Pt loaded sample of 0.02 mg cm$^{-2}$ would have the advantage according to the results in this study.

4. Conclusion

For improving the performance of the toluene direct electro-hydrogenation electrolyzer, Pt nanoparticles, functioning as the toluene chemical-hydrogenation catalyst, were loaded on the carbon-paper as the flow-field. LSV measurement of the 0.5 mg-Pt cm$^{-2}$ sample showed the lowest cell voltage with the 100 and 10% toluene concentrations. On the other hand, the current efficiency for all the Pt loaded samples indicated the significant enhancement compared to the no-loaded sample. This result demonstrated that the toluene chemical-hydrogenation reaction effectively functioned in the carbon paper flow-field. The conversion from toluene to methylcyclohexane by the one-pass using the electrolyzer of this component showed 92–96% at the flow rate of 100% setting conversion, and the cell voltage maintained a constant value for the change in flow rate. Impedance analysis determined the internal, cathodic and anodic charge transfer resistance for all samples. Consequently, the 0.02 mg-Pt cm$^{-2}$ loading was the best loading in this study from the aspect of reducing the Pt consumption amount.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.18-00055.

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