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Electrochemical coupling of benzene hydrogenation and water electrolysis

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Abstract

To establish an efficient process for hydrogenation of benzene to cyclohexane as one of the candidates for transportable, chemical hydrogen carriers, a combined scheme of water electrolysis and hydrogenation in the polymer electrolyte cell was proposed.

A Rh–Pt electrode, which was found to be more active for electrochemical hydrogenation of benzene, was formed on a polymer electrolyte (Nafion, Du Pont) by means of soaking-reduction. Using an electrochemical cell, hydrogen pumping rate, electrochemical hydrogenation of benzene and water electrolysis were investigated at temperatures 25–70°C and atmospheric pressure, followed by combined electrochemical hydrogenation of benzene and water electrolysis.

It became clear that benzene could be electrochemically hydrogenated on the cathode with hydrogen (proton), which was produced by water electrolysis at the anode and then pumped. The combined effects were recognized as a drop in decomposition voltage of water as well as a rise in current.

Keywords: Polymer electrolyte; Water electrolysis; Hydrogenation; Benzene

1. Introduction

1.1. Hydrogen transportation by chemicals

Hydrogen is recently revived as a secondary clean and renewable energy source (fuel) to be able to generate thermal power without discharging carbon dioxide, which is closely related to the global warming. There are large international projects to assess the most efficient (economical) way of producing, transporting and utilizing a large amount of hydrogen by using renewable energy resources such as solar, geothermal, wind and hydro-power. One is the Euro-Quebec Hydro-Hydrogen Pilot Project (EQHHPP), a corporation between Canada and EC countries since 1986 [1]. Another is the “World Energy Network (WE-NET)” project started since 1993 as a part of the New Sunshine program led by the Ministry of International Trade and Industry (MITI), Japan. An overview is presented in Fig. 1. In these projects, hydrogen is planned to be produced mainly by means of electrolysis in areas blessed with natural energy resources. Of all, hydropower left undeveloped is promising and amounts to 13×10^{12} kWh per year. Gaseous hydrogen thus obtained should be transformed to either liquid hydrogen or liquid chemical carriers, and then transported by sea. As the candidate of chemical hydrogen carriers, cyclohexane was selected as well as methylcyclohexane, methanol and ammonia. Cyclohexane can evolve hydrogen according to the

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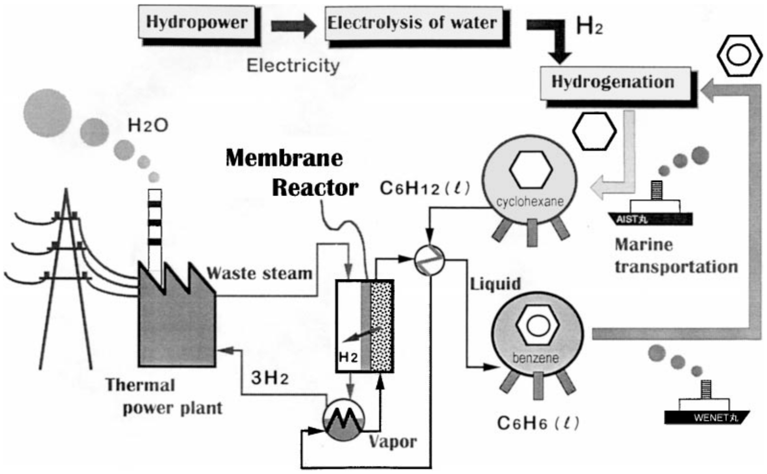

Fig. 1. Hydrogen storage and transportation system using liquid chemical carrier in the WE-NET project in Japan.

following reversible reaction whereas benzene produced will be sent back to the area rich in renewable energy.

$$C_6H_{12} = C_6H_6 + 3H_2$$

A common problem existing in such chemical carrier systems is that the hydrogen evolution (dehydrogenation) reactions are limited thermodynamically and therefore also a limited conversion is obtained. To solve such inevitable problems, we have been developing a novel type of reactor, that is, a palladium membrane reactor, which can improve the dehydrogenation conversion via selective separation of hydrogen produced during the reaction through palladium membranes. It has been demonstrated that the palladium membrane reactor makes it possible to obtain 100% conversion even at 175°C for the dehydrogenation of cyclohexane [2]. This means that a highly energy-efficient system utilizing worthless low-temperature waste heat for dehydrogenation may be established, and therefore the possibility of utilizing liquid chemicals as hydrogen carriers increases.

The next target is the hydrogenation process, in which hydrogen will be supplied from water electrolysis using a polymeric electrolyte. An idea postulated in this study is to combine the water electrolysis and hydrogenation in a polymer electrolyte cell. Fig. 2 represents the principle schematically. Such a direct hydrogenation process is expected to be more efficient because the hydrogen generated on the cathode during water electrolysis can be utilized in-situ.

1.2. Chemical reaction using polymer electrolyte cell system

A series of perfluorosulfonic-acid based membranes (Nafion®, Du Pont) is well known as cation exchange membranes. These membrane have high thermal resistance (<300°C), exceptional chemical stability and excellent proton conductivity. The

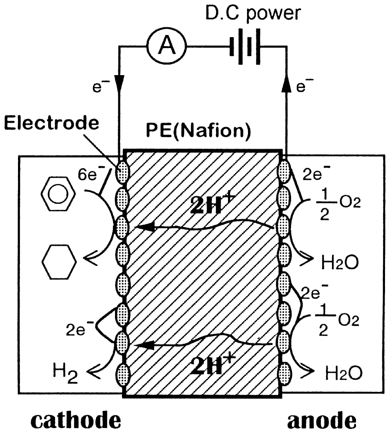

Fig. 2. Principle of combined water electrolysis and electrochemical hydrogenation of benzene in a solid polymer electrolyte cell.

membranes have been used as a solid polymer electrolyte (PE) in fuel cells, NaCl electrolyzers, water electrolyzers, as well as gas sensors. Compared with other cell systems using alkali, phospheric acid and carbonate, it is pointed out that a PE cell has many advantages such as simple structure, light weight, high current density, and additionally no loss of electrolyte itself. There are numerous researches and developments on the PE cell to improve the cell efficiency much more. Also, investigations on production of H_2 by water electrolysis using the PEs have been carried out, and higher performance has been achieved compared to traditional alkali electrolysis technology [3].

On the other hand, electrochemical reactions in the PE cell have been attempted on the basis of the working principle similar to that of the PE fuel cell. Metallic electrodes were in general coated on the Nafion membrane by chemical plating method. As examples of gas-phase reactions, the reduction of N_2 to NH_3 on the Ru electrode [4], O_2 to H_2O_2 on the Au, Pd, and Pt electrodes [5,6], CO_2 to CH_4 on the Cu electrode [7,8], and the partial oxidation of methanol to $HCOOCH_3$ and HCHO on the Pt, Pd and Au electrodes [9–13] have been investigated. As an example of liquid-phase systems, reduction of benzaldehyde to benzyl alcohol [14] on the Ag/Nafion membrane was attempted.

In the present study, we tried to apply the PE cell to the combined electrochemical hydrogenation reaction and water electrolysis, where benzene hydrogenation was taken as a test reaction. Such a combined system would expect to reduce the decomposition voltage of water ($E = -1.23$ V) because benzene hydrogenation, a spontaneously driven reaction with positive potential ($E = 0.17$ V), is coupled in a cell as follows

$$\text{at anode}: \quad H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \quad (E^0 = -1.23\,\text{V}) \tag{1}$$

$$(H_2 \rightarrow 2H^+ + 2e^-, \quad \text{when } H_2 \text{ is supplied}) \tag{2}$$

$$\text{at cathode}: \quad C_6H_6 + 6H^+ + 6e^- \rightarrow C_6H_{12} \quad (E^0 = 0.17\,\text{V}) \tag{3}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

2. Experimental

2.1. Deposition of electrode

Nafion 117 membrane (Du Pont, equiv. wt. = 1100, H^+ ion form, 0.19 mm thick) was used in this study. The membrane surface was initially roughened with sandpaper, followed by washing with water. Then the membrane was treated with a 10 wt.% aqueous solution of H_2SO_4 for 1 h at 80°C and subsequently washed with boiling water for 30 min. Platinum deposition was carried out by means of soaking-reduction, in which the membrane was first soaked in a $0.05\,\text{mol}\,\text{l}^{-1}$ H_2PtCl_6 aqueous solution and then reduced in a 5 wt.% $NaBH_4$ aqueous solution. Although there was a report claiming that platinum was effective for the electrochemical hydrogenation of benzene [15], a preliminary test in this study revealed that the catalytic activity of such a thin Pt layer was very low. Then, a Rh layer was further coated over the Pt layer in the same way by using a $5\,\text{g}\,\text{l}^{-1}$ Rh solution (Rhodex, Tanaka Kikinzoku K.K). The obtained PE membrane with Rh–Pt electrode was finally rinsed in water.

2.2. Cell assembly and method

Details of a glass-made cell used is shown in Fig. 3a. The anode and cathode compartments are separated by the PE membrane, which has an effective geometric surface area of $7.07\,\text{cm}^2$, and is fixed to the cell together with a current collector using a silicon rubber gasket. Fig. 3b shows a schematic diagram of the experimental apparatus. The cell and water-saturators are placed in a thermostat which is kept at a constant temperature ranging from 25 to 70°C. The electric resistance between the electrodes, which was determined by passing hydrogen on the both sides, was 0.925 ohm. This suggested that the contact between the metal electrodes and the PE was satisfactory. The inlet gases, supplied at a constant rate through mass-flow controllers, were saturated with water vapor prior to entering the reaction cell. The gas composition at the outlet on the cathode was analyzed with an on-line gas chromatograph.

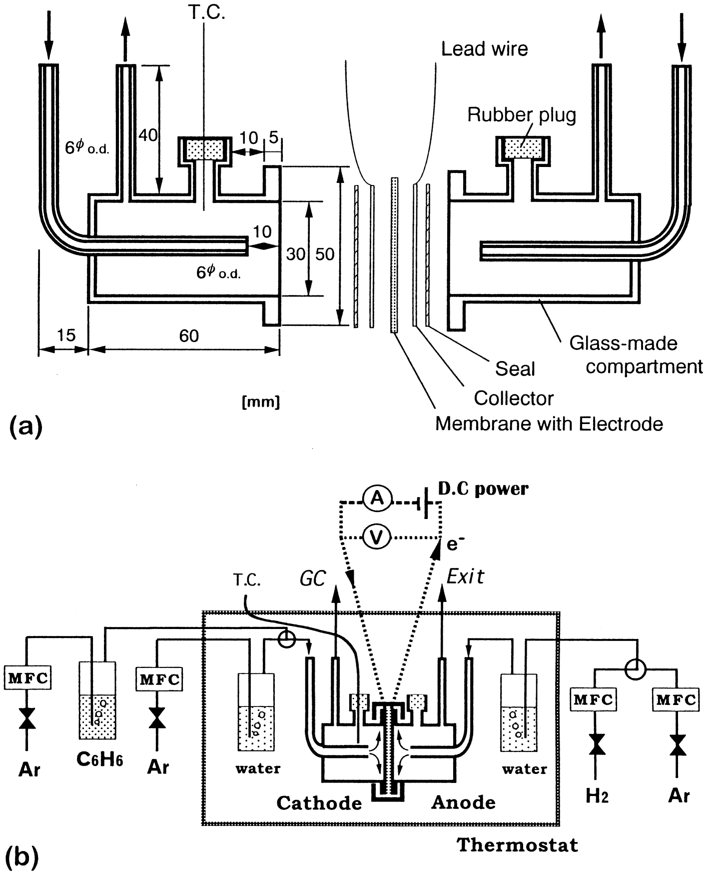

Fig. 3. Details of an electrochemical cell (a) and schematic diagram of the experimental apparatus (b).

3. Results and discussion

3.1. Electrochemically driven hydrogen permeation

Prior to water electrolysis, experiments with electrochemically driven hydrogen permeation were carried out by passing hydrogen gas of 10 $cm^3 min^{-1}$ to the anode-side and argon of 10 $cm^3 min^{-1}$ to the cathode-side compartment, respectively. The amount of hydrogen permeating in the molecular form corresponded to about 2.4 mA in current, which was considerably small compared with that being pumped under applied voltage. At the same time when the circuit between the anode and cathode was shorted, current started flowing and hydrogen pumping from the anode to the cathode side was observed. Fig. 4 shows changes of the short-circuit current at different temperatures. The current became stable within 5 min after shorting the circuit and was kept almost constant during the experiments. At room temperature (25°C), the current was about 16.5 mA, and increased with a rise in cell temperature, but decreased a little at 70°C. Such a decrease in current might be partially due to a decrease in hydrogen partial pressure caused by an increase in the saturated water vapor pressure at higher temperatures.

The pumping rate of hydrogen was examined when a DC voltage between anode and cathode was applied. Fig. 5 shows that the current increased proportionally to the applied voltage, accompanying in an increase of hydrogen pumping rate. The linear relationship between the pumping rate of hydrogen and the current is found as plotted in Fig. 6, in which the theoretical line calculated by Faraday's law is also drawn together. It

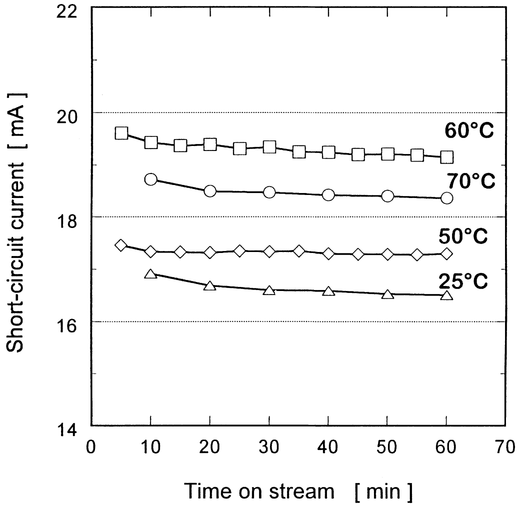

Fig. 4. Changes of the current after short-circuiting (anode, H_2; cathode, Ar).

is seen that the experimental data are located a little lower than the theoretical line. The current efficiency, defined as a ratio of the current calculated from the hydrogen pumping rate to the current recorded, at the temperatures tested was between 75 and 80%.

3.2. Electrochemical hydrogenation of benzene

Hydrogenation of benzene may take place not only electrochemically but also non-electrochemically. The former proceeds according to Reaction (3), while the latter by the catalytic reaction with hydrogen molecules in the cathode compartment, probably on the metal electrode. To make a difference between the two ways, benzene was supplied together with hydrogen gas to the cathode compartment, where no electrical circuit was connected (gas phase reaction mode). The result can be seen in Fig. 7, showing that a part of the benzene supplied was hydrogenated to cyclohexane even in gas-phase reaction. This fact means that

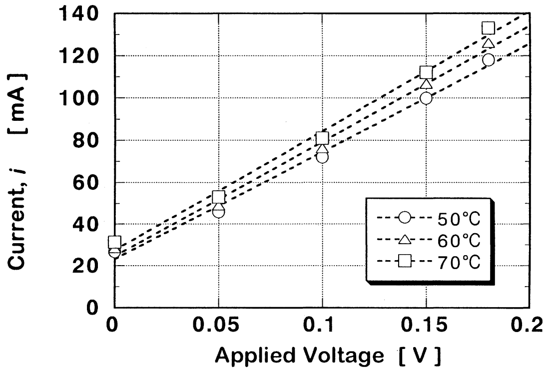

Fig. 5. Relation between current and applied voltage.

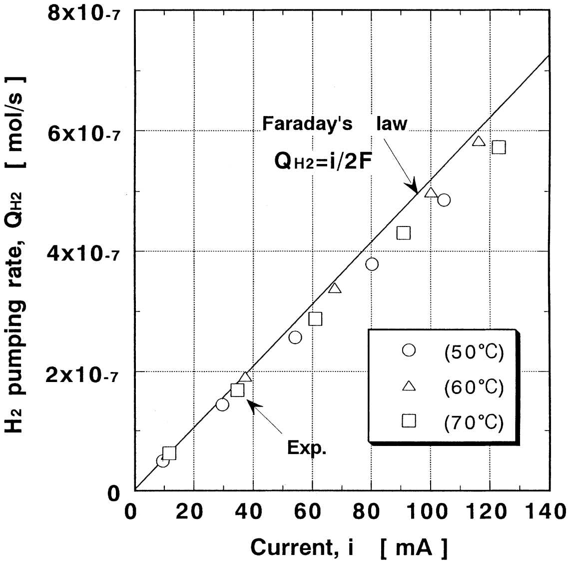

Fig. 6. Correlation between the pumping rate of hydrogen observed on the cathode and the current.

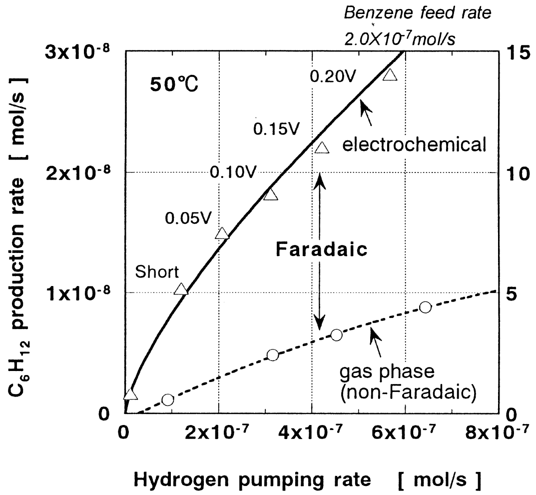

Fig. 7. Electrochemical hydrogenation compared with non-Faradaic gas-phase reaction.

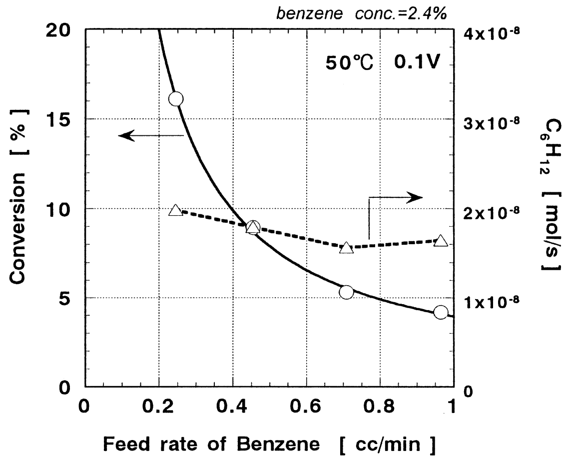

Fig. 8. Effects of benzene feed rate on the conversion and the production rate of cyclohexane.

the Rh–Pt electrode can function as catalyst. Moreover, it is evident that much higher production rates of cyclohexane could be obtained by reacting with hydrogen pumped electrochemically, where the pumping rate was increased by increasing the applied DC voltage as noted in Fig. 7. Therefore, one can regard that the difference between the two rates corresponds to an increment of the production rate due to the Faradaic (electrochemical) hydrogenation.

Next, effects of benzene supplying rate on the conversion as well as the cyclohexane production rate were examined at a fixed pumping rate of hydrogen (0.1 V applied), where the concentration of benzene was kept constant (2.4%). Fig. 8 shows that as the feed rate of benzene increases, the conversion decreases but the decrease in the cyclohexane production rate is slight. This is possibly explained by considering that the number of active sites on the electrode for the hydrogenation of benzene molecule is fixed, and therefore the production rate of cyclohexane is nearly constant regardless of the proton concentration under the hydrogen-excess conditions.

3.3. Water electrolysis

Water electrolysis in the polymer electrolyte cell system produces oxygen on anode and hydrogen on cathode. It has been reported that the purity of hydrogen obtained is 99.999% and the current efficiency reaches as high as 95% [16]. In this study, a voltage exceeding 1.42 V was required to electrolyze water vapor as shown in Fig. 9a, whereas the theoretical decomposition voltage of water is 1.23 V. It can be seen that the hydrogen evolution rate was very low at applied voltages up to 1.5 V and increased by increasing the applied voltage. Fig. 9b shows a relation between the current and the evolution rate of hydrogen. Similarly to the case of electrochemical hydrogen pumping mentioned above, the evolution rate of hydrogen is proportional to the current but a little lower than that estimated by Faraday's law. The reason is not clear at present, so that further studies with cell assembly, experimental errors, etc. is necessary.

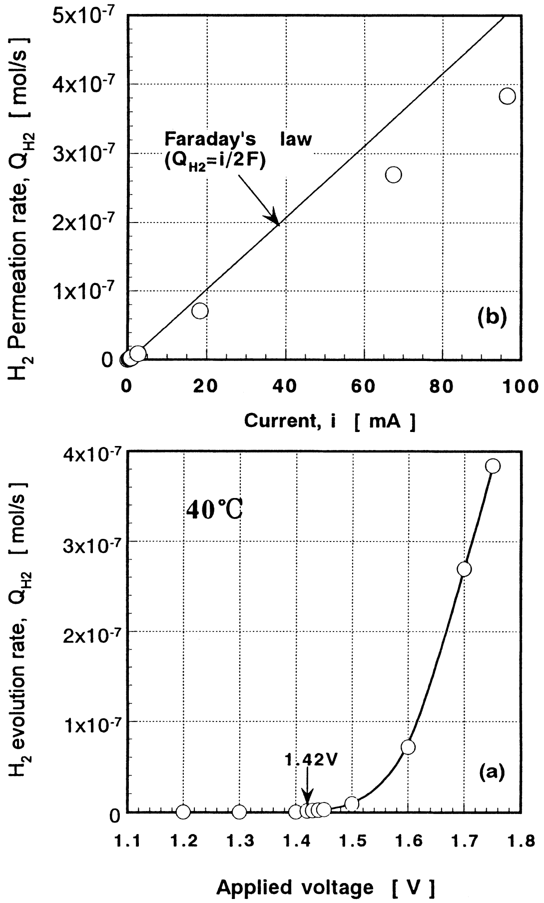

Fig. 9. Hydrogen evolution rate when the applied voltage for water electrolysis was successively increased (a) and its relationship against current (b).

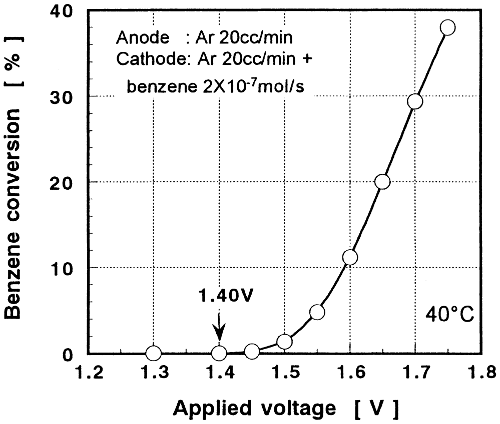

Fig. 10. Changes in benzene conversion when water electrolysis was carried out at various applied voltages.

3.4. Combined water electrolysis and benzene hydrogenation

It should be possible to bring about the hydrogenation with the protons produced by water electrolysis instead of using pumped hydrogen as described in Section 3.2. Electrochemical hydrogenation of benzene on the cathode and water electrolysis on the anode were simultaneously carried out in the cell. The result is shown in Fig. 10. Similar results were also obtained at other temperatures (50, 60, and 70°C). Experimentally, substantial current is found to be observed when the applied voltage is 1.40 V as marked in Fig. 10. This voltage is 0.02 V lower than that of water electrolysis (Fig. 9). Although further study should be needed to confirm whether such a slight drop is due to the combined effect, it is noted that the electrochemical combination of water electrolysis and benzene hydrogenation, the most important objective of this study, has been realized.

The effect of introducing benzene during water electrolysis taking place at 1.6 V of applied voltage was investigated. In Fig. 11, changes in current are recorded with time. The current tends to decrease little by little with time — this is probably because the activity of the cathode for the hydrogenation was gradually lowered by some deactivation process. However, a sudden rise in current when benzene was introduced to the cathode side was observed. This could be elucidated as that the reaction between benzene and protons on the cathode made the proton concentration lower, thereby accelerating the pumping rate of protons through the polymer electrolyte. Such an increase, although not so large, means that water electrolysis as well as hydrogenation are enhanced compared with the case that each takes place independently. Therefore, the combined system would be advantageous especially when the efficiency of hydrogen energy transportation becomes a key factor as in the WE-NET (Japan) and EQHHPP (Europe–Canada) projects.

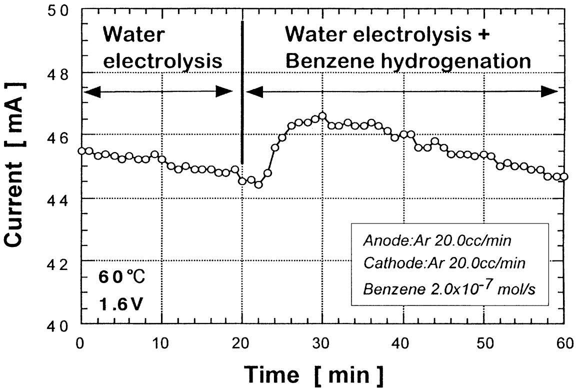

Fig. 11. Changes in current before and after benzene was introduced to the cathode.

4. Conclusion

An efficient way for producing a chemical hydrogen carrier (e.g. cyclohexane), which was obtained by a hydrogenation reaction between a dehydrogenated compound (e.g. benzene) and hydrogen produced by water electrolysis utilizing hydroelectric power, was discussed. A combined scheme of water electrolysis and hydrogenation in the polymer electrolyte cell was proposed as one of the promising ways.

It was found that a Rh–Pt electrode, which was formed on a polymer electrolyte (Nafion, Du Pont) by means of soaking-reduction was more active than a Pt one for electrochemical benzene hydrogenation. Hydrogen pumping rate measured with an electrochemical cell assembled, almost agreed with that calculated from the Faraday's law.

Benzene could be electrochemically hydrogenated on cathode with hydrogen (proton), pumped from anode using pure hydrogen, while a part of benzene was converted to cyclohexane by a catalytic (non-Faradaic) reaction with hydrogen. The similar result could be achieved for the electrochemical hydrogenation of benzene with protons produced by water electrolysis, where the combined effects, although not so large, were recognized as a drop in decomposition voltage of water as well as a rise in current.

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