Electrochemical Reduction of Toluene for Energy Storage

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Introduction

Hydrogen energy systems offer benefits of low environmental impact and sustainability, and the potential for dramatic reductions in CO_2 emissions. Conventionally, hydrogen has been produced from fossil fuel, or produced using nuclear and hydroelectric power. “Green Hydrogen (hydrogen from renewable energies)” would be the ultimate goal for the sustainable growth of human society[1]. In such production schemes, hydrogen is a secondary energy that is subsequently converted into electricity. Present major hydrogen storage media are high-pressure gas cylinders, liquid hydrogen, ammonia, and organic hydride. Organic hydrides are generally easy to manage because they are liquid at room temperature, and have low toxicity. Some researchers have proposed storage methods using organic hydride that involve repeated hydrogenation and dehydrogenation. For example, methyl-cyclohexane (MCH) is able to store about 6 wt% of H_2. MCH can be dehydrogenated to toluene, which can then be converted back to MCH via hydrogenation[2]. However, there are some problems such as bulky equipments for the chemical hydrogenation process. Furthermore, gaseous hydrogen requires special handling. In addition, it is a two-step process that involves water electrolysis, and the use of that hydrogen for continuous chemical hydrogenation, which is less efficient from the standpoint of energy transport.

The authors investigated a one-step process for converting toluene into MCH, using a PEMFC-like electrolyzer, whereby liquid toluene was introduced directly into the cathode channel of the membrane-electrode-assembly (MEA) in the cell. We also studied the influence of toluene concentration on the electrochemical characteristics of the toluene reduction reaction.

Experimental

MEAs were fabricated by PFSA membranes (Nafion® NR-212, DuPont) coated Pt/C (TEC10E50E, Tanaka Kikinzoku Kogyo K.K. (TKK)) or Pt-Ru/C (TEC61E54, TKK) with an ionomer (Nafion® 2020CS, DuPont). Catalyst metal loading was 0.5 mg cm^{-2}, and the active areas of the MEAs were 25 cm^2. Single cells, which are commonly used in PEMFC performance tests, were assembled using graphite plates with a serpentine flow field. Toluene was circulated in the cathode side with a rate of 5 mL min^{-1}; humidified hydrogen was supplied to the anode that worked as a reference and counter electrode, instead of oxygen evolution reaction for the real electrolyzer system.

Result and Discussions

Figure 1 shows the steady state polarization curves for the Pt/C and Pt-Ru/C catalysts in the toluene reduction reaction at 323 K. The activity of the Pt-Ru/C catalyst was superior to that of the Pt/C catalyst, and the maximum current density was more than 400 mA cm^{-2}, which equals or exceeds that of commercial alkaline water electrolyzes. At that time, generation of hydrogen gas was not clearly observed even at -20 mV vs. RHE. The Tafel slopes of the Pt/C and Pt-Ru/C catalysts were 38 and 27 mV/dec., respectively. This difference may be due to differences in the effects of the Pt/C and Pt-Ru/C catalysts on the toluene reduction reaction, which is the rate-determining-step.

The influence of toluene concentration on the steady state polarization curve is shown in Figure 2. Each toluene concentration was determined by actual electrochemical reduction over several hours. The current densities decreased with toluene concentration, and mass-transport limitations were observed at low concentration. However, the Faraday conversion efficiency, i.e. the ratio of the actual amount of electricity passed vs. the change in concentration measured by GC, stayed above 95%. This result suggests that this electrochemical method for hydrogenation of toluene to MCH would be an alternative for the conventional chemical method.

Reference

1) K-I. Ota, A. Ishihara, K. Matsuzawa, S. Mitsushima, *Electrochemistry*, **78**, 12, 970, (2010).
2) J. Gretz, J.P. Baselt, O. Ullnann, H. Wendt, Int. *J. Hydrogen Energy*, **15**, 6, 419, (1990).

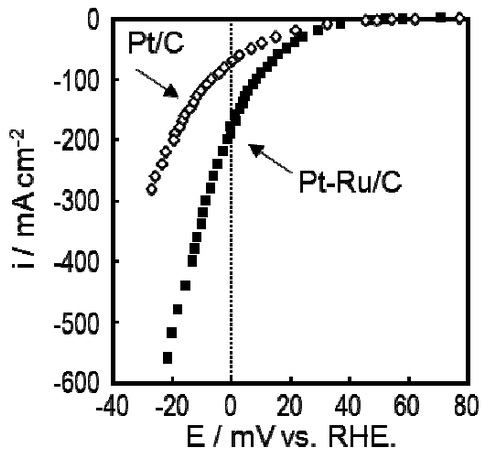

Fig.1: Steady state polarization curves for Pt/C (opened) and Pt-Ru/C (filled) in the toluene reduction reaction at 323 K. (iR-free)

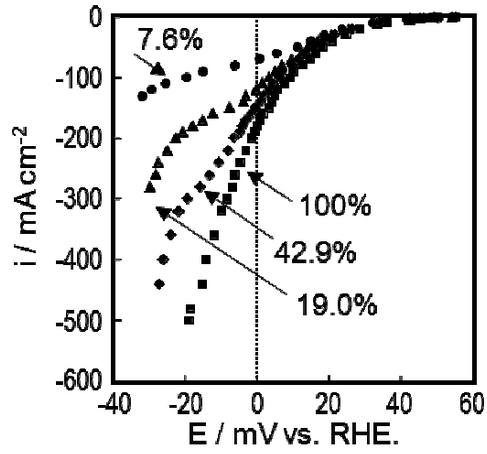

Fig.2: Influence of toluene concentration on steady state porlization curve at 323K. (Square: 100%, Diamond: 42.9%, Triangle: 19.0%, Circle: 7.6%) (iR-free)