Rechargeable PEM Fuel Cells using Organic Hydrogen Reservoirs(OHR). Electric Power Generation by Electrooxidation of Cyclohexane or 2-Propanol and Power Storage with Water Electrolysis.

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Recently, the direct fuel cell systems using "organic hydrogen reservoirs (OHR)" such as cyclohexane, decalin, and 2-propanol which release and absorb hydrogen reversibly by dehydrogenation and hydrogenation reactions have been proposed[1]. Different from methanol and hydrocarbons, reaction of OHR emits no CO_2 for producing hydrogen, and the dehydrogenated reservoirs can be hydrogenated at high efficiency for recycle use and saving surplus hydrogen. Since electrochemical dehydrogenation and hydrogenation of the OHR is reversible[2], the "rechargeable" direct PEMFC is available by combination with electrolysis of H_2O and electrochemical hydrogenation of OHR. In this paper, we report the details of the electro-oxidation of typical OHR and electro-reduction of acetone with electrolysis of water in PEM FC. (Figure 1, Scheme 1).

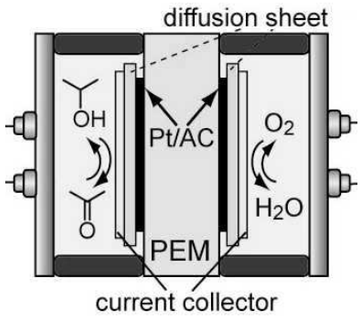
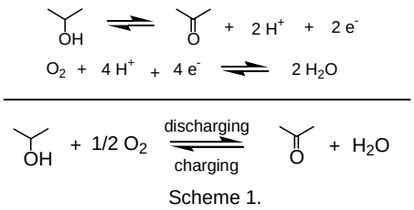


Figure 1. Rechargeable FC



Scheme 1.

Figure 2 shows the I-V curves on the Pt / Pt MEA for cyclohexane, 2-propanol, and cyclohexanol with feeding rate of 5.0 mmol min^{-1}, at 100 ^oC. The best performance was obtained for 2-propanol among the three fuels. The cell performance of 2-propanol has an open circuit voltage (OCV) of 720 mV and maximum power density was 37 mW cm^{-2}. The higher cell performance for 2-propanol was obtained by using PtRu $_{anode}$ / Pt $_{cathode}$ MEA, due to the high C-H bond cleavage ability of the PtRu catalysts. The cell performance of cyclohexane has an open circuit voltage (OCV) of 920 mV and maximum power density was 14 mW cm^{-2}.

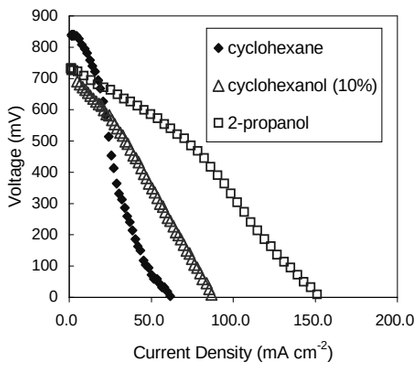


Figure 2. I-V curves of cyclohexane, cyclohexanol, 2-propanol at 100 ^oC.

The amount of crossover fuel was estimated[3] by applying positive voltage and measuring crossover currents (data not shown). The crossover current of cyclohexane and 2-propanol were smaller than that of methanol. Therefore cyclohexane and 2-propanol PEMFC may be one of the promising systems with lower crossover; in other words, higher fuel efficiency and fuel cell performances.

Figure 3 shows the I-V curves for the electro-reduction of acetone and water electrolysis mediated by the PEM on the several MEA at 80 ^oC (charging process). Using Pt/C, PtRu/C and Pt black catalysts, formations of 2-propanol (on cathode side) and oxygen (on anode side) were observed. Conversions of acetone were as low as 1 – 3 %, however, by improvement of the catalytic activity and the reactor design, the efficiency will be increased.

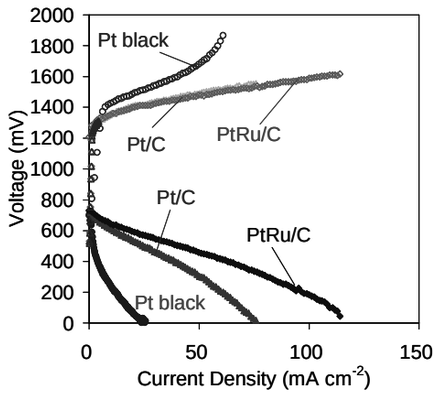


Figure 3. I-V curves for 2-propanol on Pt/Pt and PtRu/Pt MEA at 80 ^oC.

In conclusion, the present work is the first example of a direct fuel cell system using cyclic hydrocarbons, and a "rechargeable" fuel cell system using 2-propanol and acetone. Further improvement of catalytic activity on anode, studies of the reaction mechanisms, reaction of other rechargeable fuels such as cyclohexylbenzene, are under progress.

1) N. Kariya, A. Fukuoka, M. Ichikawa, *Chem. Commun.*, 2003,690-691.
2) J. L. Rodrígues and E. Pastor, *Electrochim. Acta.*, 2000, **45**, 4279-4289.
3) Z. Qi and A. Kaufman, *J Power Sources,* **112**, 121 (2002).