

# Zero-CO<sub>2</sub> emission and low-crossover 'rechargeable' PEM fuel cells using cyclohexane as an organic hydrogen reservoir

Nobuko Kariya, Atsushi Fukuoka and Masaru Ichikawa\*

Catalyst Research Centre, Hokkaido University, Sapporo 060-0811, Japan.

E-mail: michi@cat.hokudai.ac.jp; Fax: 81 11 706 4957; Tel: 81 11 706 2919

Received (in Cambridge, UK) 27th November 2002, Accepted 30th January 2003

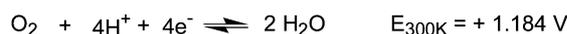
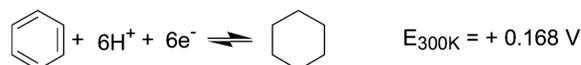
First published as an Advance Article on the web 12th February 2003

High performance (open circuit voltage = 920 mV, maximum power density = 14–15 mW cm<sup>-2</sup>) of the PEM fuel cell was achieved by using cyclohexane as a fuel with zero-CO<sub>2</sub> emission and lower-crossover through PEM than with a methanol-based fuel cell.

Fuel cell (FC) power systems have received increased attention in recent years because of their potential for high fuel efficiency and lower emissions. Direct proton exchange membrane fuel cells (D-PEMFCs) employing organic fuels are attractive because of their considerable weight and volume advantage over 'indirect' FC, in which the fuel is reformed into hydrogen prior to use.

In D-PEMFC, methanol has shown relatively high performance, and methanol fuel cell systems have already proved to be feasible for portable applications.<sup>1</sup> However, there are still some drawbacks<sup>1–5</sup> in the direct methanol fuel cells (DMFC) as follows: (a) low electrocatalytic activity of the anodes, (b) poisoning due to strong CO adsorption on Pt-based anode catalysts, and (c) high degree of permeation of methanol through the PEM. To overcome these problems, various organic chemicals with short chains such as ethanol,<sup>6</sup> 2-propanol<sup>7</sup> were applied as fuels for D-PEMFC. However, all these studies were limited to the use of alcohols,<sup>8,9</sup> glycols,<sup>9,10</sup> ethers,<sup>11</sup> and acetals.<sup>12</sup> To our knowledge, there has been no report on the electro-oxidation of cyclic hydrocarbons under the conditions of PEMFC working at *ca.* 100 °C.

Recently, we have proposed the utilization of dehydrogenation–hydrogenation of cyclic hydrocarbons such as cyclohexane<sup>†</sup> and decalin to store and transport hydrogen, and achieved an efficient supply of hydrogen by the dehydrogenation of cyclic hydrocarbons using a spray-pulse mode reactor without CO, CO<sub>2</sub> or other by-products.<sup>13,14</sup> Cyclic hydrocarbons have relatively high weight and volume contents of hydrogen, high boiling points (bp = 80–190 °C), and are compatible with the existing petroleum infrastructure. Additionally, the dehydrogenation and hydrogenation of cyclic hydrocarbons is reversible and the fuels are regenerative and recyclable, thus the 'rechargeable' D-PEMFC is available by combination with electrolysis of H<sub>2</sub>O and electrochemical hydrogenation of hydrocarbons.<sup>15</sup> Based on this background, we applied cyclic hydrocarbons to D-PEMFC, and observed the polarization curves of the electro-oxidation of cyclic hydrocarbons (Scheme



Scheme 1

1). In this communication, we report the performance of direct-cyclic hydrocarbon fuel cells.

The experiments were performed using a 4 cm<sup>2</sup> single cell with stainless steel punching sheets as the current collector. The fuels were vaporized and fed with N<sub>2</sub> carrier gas into anode (Fig. 1), where the N<sub>2</sub> gas was saturated with vapour by passing through a saturator in a thermostat. A gas mixture of O<sub>2</sub> and N<sub>2</sub> (O<sub>2</sub>:N<sub>2</sub> = 1:4) was similarly saturated with water vapour and introduced to the cathode. Membrane electrode assemblies (MEAs) of Pt<sub>anode</sub>/Pt<sub>cathode</sub> were prepared by hot-pressing<sup>16</sup> 20 wt% Pt catalyst supported on active carbon (Ishifuku Metal Industry Co., Ltd) onto Nafion 117 for 3 min at 125 °C (Pt loadings 1.5 mg cm<sup>-2</sup>). The atomic ratio in the bimetallic anode Pt/M is 5 for PtRu<sub>anode</sub>/Pt<sub>cathode</sub>, PtRh<sub>anode</sub>/Pt<sub>cathode</sub>, and PtPd<sub>anode</sub>/Pt<sub>cathode</sub>. The product composition in the gas phase was periodically analysed by a TCD-GC (Agilent Micro GC, detection limit of CO<sub>2</sub> > 20 ppm). Potentials were scanned by a galvanostat in the anodic direction at a scan rate of 10 mA min<sup>-1</sup> for the polarization measurements in the potential range 0–1000 mV. The polarization curves of all experiments were reproducible within 10% error.

Fig. 2 shows the polarization curves of cyclohexane, methylcyclohexane, and tetralin (feeding rate = 5.0 mmol min<sup>-1</sup>) over Pt<sub>anode</sub>/Pt<sub>cathode</sub> MEA at 100 °C. The best performance of the single cell was obtained for cyclohexane among the three substrates. The cell performance of cyclohexane has an open circuit voltage (OCV) of 920 mV and maximum power density was 14 mW cm<sup>-2</sup>. It is noteworthy that cyclohexane has a high OCV even at 100 °C while non-electrochemical catalytic dehydrogenation of cyclohexane is performed at above 300 °C.<sup>13,14</sup> During the electro-oxidation of cyclohexane, only cyclohexane and benzene were observed in exhausted gas from the anode, and no CO and CO<sub>2</sub> production was detected from the anode or cathode by GC analysis.

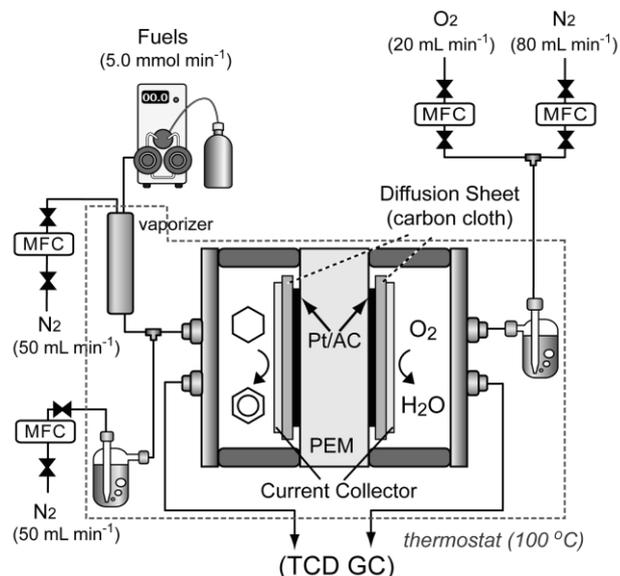
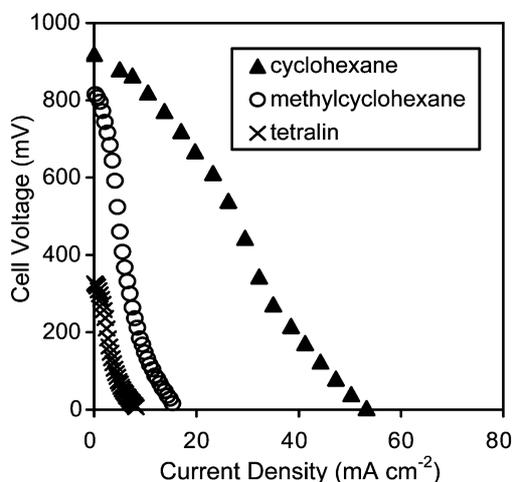
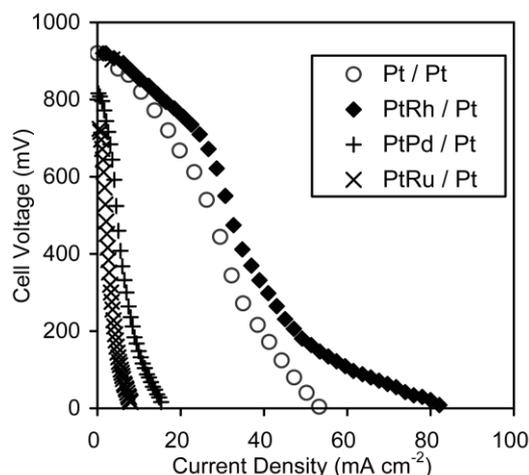


Fig. 1 Direct-cyclohexane PEM FC.



**Fig. 2** I–V curves of cyclohexane, methylcyclohexane, and tetralin in Pt/Pt D-PEM FC at 100 °C. Feeding rate of fuels = 5.0 mmol min<sup>-1</sup>.



**Fig. 4** I–V curves of cyclohexane over Pt, PtRh, PtPd, and PtRu anode catalysts at 100 °C. Feeding rate of fuels = 5.0 mmol min<sup>-1</sup>.

Therefore the crossover of cyclohexane is significantly small, presumably due to the hydrophobicity of cyclohexane. This is different behaviour from that found for methanol in DMFC.

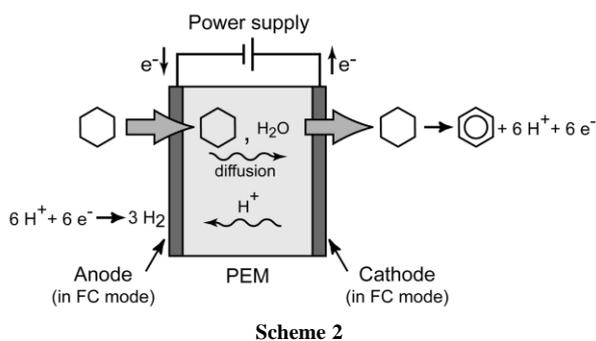
The crossover current was estimated by the method reported in refs. 3 and 7, applying positive voltage and measuring crossover currents on the ‘cathode side’ in FC mode (Scheme 2). The crossover current for methanol and 2-propanol are also measured for comparison. As shown in Fig. 3, the crossover current of cyclohexane (0.08 mA cm<sup>-2</sup>) at 900 mV was 930 times smaller than that of methanol (75 mA cm<sup>-2</sup>). Considering that both the oxidation of cyclohexane and methanol involves 6-electron transfer, the amount of crossover molecules for cyclohexane is *ca.* 1/930 of that of methanol. These results are probably due to the hydrophobicity and the large molecule size of cyclohexane. Therefore cyclohexane D-PEMFC may be one

of the most promising systems with lower crossover; in other words, higher fuel efficiency and fuel cell performances.

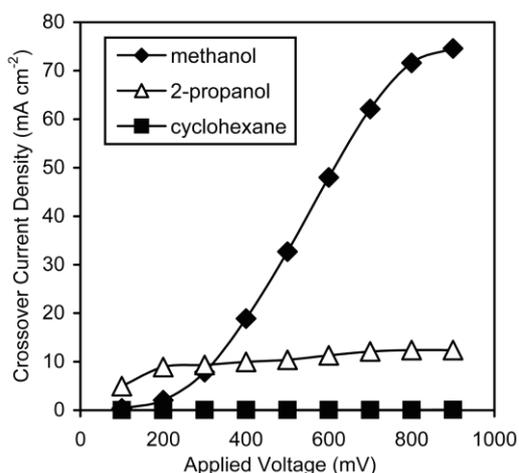
In Fig. 4, cell voltages are compared for several anode catalysts, Pt, PtRu, PtPd, and PtRh, in the electro-oxidation of cyclohexane at 100 °C. The PtRh anode showed the best performance (maximum power density = 16 mW cm<sup>-2</sup>), while PtRu and PtPd gave lower activity toward cyclohexane than Pt. PtRu has higher activity in the methanol electro-oxidation and is widely used for DMFC; however, it showed negative effects for the reaction of cyclohexane.

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

This study was partly supported by NEDO, New Energy and Industrial Technology Development Organization under Grant no. 12S1001.



**Scheme 2**



**Fig. 3** Crossover current density vs. applied voltage for methanol, 2-propanol and cyclohexane D-PEM FC at 80 °C. Feeding rate of fuels = 2.5 mmol min<sup>-1</sup>. Nitrogen flow rate = 100 mL min<sup>-1</sup>.

## Notes and references

† The toxicity of benzene may be problematic in utilization of cyclohexane as hydrogen storage media. However, it is not hazardous by means of a tightly sealed cell.

- 1 S. Wasmus and A. Kuver, *J. Electroanal. Chem.*, 1999, **461**, 14–31.
- 2 V. M. Barragán and A. Heinzel, *J. Power Sources*, 2002, **104**, 66–72.
- 3 Z. Qi and A. Kaufman, *J. Power Sources*, 2002, **110**, 177–185.
- 4 P. N. Ross, Jr., in *Electrocatalysis*, ed. J. Lipkowski and P. N. Ross, Wiley–VCH, Inc., USA, 1998, Cap. 2, p. 43.
- 5 T. D. Jarvi and E. M. Stuve, in *Electrocatalysis*, ed. J. Lipkowski and P. N. Ross, Wiley–VCH, Inc., USA, 1998, Cap. 3, p. 75.
- 6 J. Wang, S. Wasmus and R. F. Savinell, *J. Electrochem. Soc.*, 1995, **142**, 4218–4224.
- 7 Z. Qi and A. Kaufman, *J. Power Sources*, 2002, **112**, 121–129.
- 8 C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau and J–M. Léger, *J. Power Sources*, 2002, **105**, 283–296.
- 9 C. Lamy, E. M. Belgsir and J. M. Léger, *J. Appl. Electrochem.*, 2001, **31**, 799–809.
- 10 E. Peled, T. Duvdevani, A. Aharon and A. Melman, *Electrochem. Solid–State Lett.*, 2001, **4**, A38–A41.
- 11 S. R. Narayanan, E. Vamos, S. Surampudi, H. Frank, G. Halpert, G. K. Surya Prakash, M. C. Smart, R. Knieler, G. A. Olah, J. Kosek and C. Cropley, *J. Electrochem. Soc.*, 1997, **144**, 4195–4201.
- 12 O. Savadogo and X. Yang, *J. Appl. Electrochem.*, 2001, **31**, 787–792.
- 13 N. Kariya, A. Fukuoka and M. Ichikawa, *Appl. Catal. A.*, 2002, **233**, 91–102.
- 14 N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, *Appl. Catal. A.*, 2003, in press.
- 15 N. Ito, W. C. Xu, S. Hara and K. Sakaki, *Catal. Today*, 2000, **56**, 307–314.
- 16 X. Ren, M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, 1996, **143**, L12–15.