

Polymer Electrolyte Fuel Cell free from Acid Leaching  
shows Remarkably High Durability under High  
Temperature Operation

**Tsuyohiko Fujigaya**<sup>a,b</sup>, **M. R. Berber**<sup>a</sup>, **Naotoshi Nakashima**<sup>a,b,c</sup>

<sup>a</sup>Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Motoooka 744, Fukuoka 819-0395, Japan

<sup>b</sup>World Premier International (WPI), International Institute for Carbon-Neutral Energy Research, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

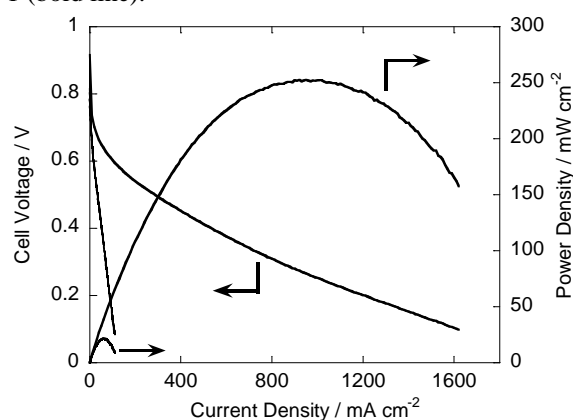
<sup>c</sup>Japan Science and Technology Agency (JST), Core Research of Evolutional Science & Technology (CREST), 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

In the current PEFC systems, water-assisted proton conduction in the conventional polyelectrolytes limit the operation temperature below 100 °C(1). The limitation of operating temperature originated from the poor proton conductivity of the conventional polyelectrolytes such as Nafion at temperatures above 100 °C(1), thus the development of a new polyelectrolyte with a high proton conductivity at high temperature has been strongly desired. To overcome this temperature limitation problem, the use of polymer membrane doped with a non-volatile liquid acid as a polymer electrolyte membrane (PEM) has been proposed(2), in which the mobile acid is responsible for the proton conduction through the vehicle mechanism. Especially, phosphoric acid-doped polybenzimidazoles (denoted PA-doped PBIs) have been considered as the most promising substitutive polyelectrolytes(3) and the PEFC employing PA-doped PBIs not only in PEM but also in the catalyst layers (Cat-L) have been developed for high temperature operation(4, 5). However, recent studies have revealed that leaching of liquid PA from PEM(6) and Cat-L(7) causes inhomogeneous PA distribution that results in deterioration of PEFC performance during long-term operation.

In this study, in order to prevent acid leaching from the high temperature PEFC system, we used poly(vinylphosphonic acid) (PVPA)-doped PBI membrane in place of PA-doped PBI membrane because PVPA is a polymeric acid and is stably bound to the PBIs via multipoint acid-base reactions(8). We then carried out single cell durability test for a membrane-electrode assembly (MEA) fabricated from our materials. The PVPA is known to form a hydrogen-bonding network with the neighboring phosphonic acid groups(9, 10); consequently, it forms an effective proton pathway after blending with the PBIs. As for the electrocatalyst in Cat-L, novel electrocatalyst assembled with carbon nanotubes (CNTs), PBI and platinum (Pt) nanoparticles as an electron-conducting supporting material, Pt binder on CNT, and metal catalyst, respectively, was employed in MEA. The power density was found as low as 20 mWcm<sup>-2</sup> probably because the low proton conductivity in Cat-L caused by the absence of acid leaching (Fig. 1: thin line).

Therefore, we doped our electrocatalyst (CNT/PBI/Pt) with PVPA, where bottom-up assembly of nanometer-thick PVPA-doped PBI layer around CNTs is expected to serve as an effective proton conduction pathway via the Grotthuss mechanism. This is the first report to employ PVPA-doped PBI not only for PEM but also for the electrocatalyst in Cat-L to fabricate the MEA (PVPA-doped MEA) and to operate the MEA under non-

humidified condition at above 100 °C. As a result, the power density was improved to 250 mWcm<sup>-2</sup> as shown in Fig. 1 (bold line).



**Fig. 1** Polarization and power density curves of the PVPA-doped MEA (bold line) and PVPA-non-doped MEA (thin line).

One may expect a high durability in such a leaching-free MEA. Thus, we tested the durability of the PVPA-doped MEA by following the protocol proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ)(11). As a comparison, the durability of a PA-non-doped MEA was tested. While the cell voltage of the PA-doped MEA drastically decreased upon repeated cycling, the PVPA-doped MEA exhibited a gradual decrease; namely, the high cell voltage is still remained even after 400,000 cycles. Such an extremely high durability was only achieved by the PVPA doping onto the PBIs in both the PEM and Cat-L, which are free from acid leaching.

- 1 H. Zhang and P. K. Shen, *Chem. Rev.*, **112**, 2780 (2012).
- 2 J. A. Asensio, E. M. Sanchez and P. Gomez-Romero, *Chem. Soc. Rev.*, **39**, 3210 (2010).
- 3 D. Mecerreyes, H. Grande, O. Miguel, E. Ochoteco, R. Marcilla and I. Cantero, *Chem. Mater.*, **16**, 604 (2004).
- 4 E. Quartarone and P. Mustarelli, *Energy Environ. Sci.*, **5**, 6436 (2012).
- 5 K. Matsumoto, T. Fujigaya, K. Sasaki and N. Nakashima, *J. Mater. Chem.*, **21**, 1187 (2011).
- 6 Y. Oono, T. Fukuda, A. Sounai and M. Hori, *J. Power Sources*, **195**, 1007 (2010).
- 7 Y. Oono, A. Sounai and M. Hori, *J. Power Sources*, **189**, 943 (2009).
- 8 Ü. Akbey, R. Graf, P. P. Chu and H. W. Spiess, *Aust. J. Chem.*, **62**, 848 (2009).
- 9 Y. J. Lee, B. Bingöl, T. Murakhtina, D. Sebastiani, W. H. Meyer, G. Wegner and H. W. Spiess, *J. Phys. Chem. B*, **111**, 9711 (2007).
- 10 L. Yan, Q. Feng, L. Xie and D. Zhang, *Solid State Ionics*, **190**, 8 (2011).
- 11 A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida and A. Daimaru, *ECS Transactions*, **41**, 775 (2011).