

A Solid State NMR Study of Polyaniline-Fe Non-Precious Metal Cathode Catalysts for Oxygen Reduction in Fuel Cells

Shigeki Kuroki

Department of Organic and Polymeric Materials,
Graduate School of Science and Engineering, Tokyo
Institute of Technology, 2-12-1 Ookayama, Meguro-ku,
Tokyo 152-8552, JAPAN

Polymer electrolyte fuel cells (PEFCs) are attracting increasing attention as environmentally benign power sources for both stationary and mobile applications. The oxygen reduction reaction (ORR) at the cathode is a sluggish and complicated four-electron process. Carbon-supported platinum (Pt/C) is widely used in cathode catalysts for ORR[1, 2]. However, even on pure Pt, the overpotential for ORR is in excess of 300 mV. In addition, Pt is a precious metal of the lowest abundance and it is thus of great interest to develop Pt-free cathode catalysts for PEFCs.

Several Pt-free materials have been proposed as potential alternative catalysts for ORR, such as Ru/Ir-based chalcogenides[3], Pd-based alloys[4], transition metal oxides[5], and carbides and nitrides[6]. Jasinski[7] first reported that transition metal porphyrins and phthalocyanines display electrocatalytic activity towards ORR. More recently, it has been found that active ORR catalysts can be synthesized by pyrolyzing a wide variety of transition metal, carbon and nitrogen-containing precursors at high temperature [8-12].

In our previous work, iron-containing and iron-free ^{15}N labeled polyaniline (PANI) is prepared as a precursor of N-doped carbon catalysts and is pyrolyzed at several different temperatures in a nitrogen atmosphere. The iron-free pyrolyzed PANIs display quite poor catalytic activity for ORR, whilst the iron-containing pyrolyzed PANIs display better ORR activity [12].

In the present study, the evidence of the existence of iron ion (Fe^{2+} or Fe^{3+}) is found in our iron-containing PANI catalysts, and further the nitrogen of ligands is also observed in ^{15}N solid state NMR.

Acknowledgements

The authors thank the New Energy and Industrial Technology Development Organization (NEDO) and the Ministry of Education, Science, Culture and Sports of Japan(24560818) for financial support.

References

1. R. Bashyam and P. Zelenay *Nature*, 2006, **443**, 63-66.
2. L. Zhang, J. Zhang, D. P. Wilkinson and H. Wang, *J. Power Sources*, 2006, **156**, 171-182.
3. G. Liu and H. M. Zhang, *J. Phys. Chem. C*, 2008, **112**, 2058.-2065.
4. O. Savadogo, K. Lee, K. Oishi, S. Mitsushima, N. Kamiya and K. Ota, *Electrochem. Commun.*, 2004, **6**, 105-109.
5. J. H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya and K. Ota, *Electrochim. Acta*, 2007, **52** 2492-2497.
6. A. Ishihara, K. Lee, S. Doi, S. Mitsushima, N. Kamiya, M. Hara, K. Domen, K. Fukuda and K. Ota, *Electrochim. Solid-State Lett*, 2005, **8**, A201-203.
7. R. Jasinski, *Nature*, 1964, **201**, 1212-1213.

8. G. Faubert, R. Côté, J. P. Dodelet, M. Lefèvre and P. Bertrand, *Electrochim. Acta*, 1999, **44**, 2589-2603.
9. S. Ye and A. K. Vijh, *Electrochim. Commun.*, 2003, **5**, 272-275.
10. N. P. Subramanian, S. P. Kumaraguru, H. Colon-Mercado, H. Kim, B. N. Popov, T. Black and D. A. Chen, *J. Power Sources*, 2006, **157**, 56-63.
11. S. Kuroki, Y. Nabae, M. Chokai, M. Kakimoto, S. Miyata, *Carbon*, 2012, **50**, 153-162.
12. S. Kuroki, Y. Hosaka, C. Yamauchi, M. Sonoda, Y. Nabae, M. Kakimoto, S. Miyata, *J. Electrochem Soc.*, 2012, **159**, F309-F315.