

Improvement of Zr oxide based cathode for polymer electrolyte fuel cells

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Introduction

Polymer electrolyte fuel cells are expected for the residential and transportable applications, due to their high power density and low operating temperature. The ENEFARMS (home co-generation system using 1 kW PEFC system) are operating more than 30,000 units in Japan. Fuel cell vehicles will be commercialized in 2015.

However, a significant cost reduction is needed especially for fuel cell vehicles. And the estimated amount of Pt reserve is too small to supply for the huge number of fuel cell systems. In order to commercialize the fuel cell systems widely, the development of a non-precious metal cathode is strongly required.

We think that new non-precious metal cathodes should have both high stability and high catalytic activity for the ORR. In particular, we believe that high stability in cathode condition is essentially required for the cathode catalyst. Some transition metal oxides could be used for the cathode of PEFC. However, most of the transition metal oxides are not stable in the acidic and oxidative atmosphere.

We started this study by searching stable materials in acid and in oxygen. Group 4 and 5 metal oxides, which are well known as valve metals, are stable even in acidic and oxidative atmosphere. However, these oxides are generally insulator. In order to get some electrical conductivity, these oxides should be modified by the formation of the oxygen vacancy and/or the substitution of foreign atoms.

We have reported that partially oxidized group 4 and 5 metal carbonitrides were stable in an acid solution and had a definite catalytic activity for the oxygen reduction reaction (ORR) (1-5). We have tried to apply group 4 and 5 metal oxide-based compounds to the cathode catalyst.

In this paper we will report our recent results of Zr oxide based cathode for PEFCs.

Experimental

Powders of Zr compounds (carbonitride or metal complexes that contain nitrogen) were heat-treated at 800-1200°C under different flowing rate of the H₂/N₂ gas mixtures that containing small amount of oxygen to obtain specimens with different oxidation state. After heat treatment, the compounds changed to oxides that contained small amount of carbon and nitrogen.

Heat treated powder was mixed with alcohol, Ketjen Black and Nafion. The mixture was dipped on a glassy carbon rod (5 mm diameter) and the working electrode was made. All electrochemical measurements were examined in 0.1 M H₂SO₄ at 30°C under atmospheric pressure using a conventional 3-electrode cell. The RHE was used for the reference in the same solution. Slow

scan voltammetry (scan rate: 5 mVs⁻¹) was performed under O₂ and N₂ atmosphere to obtain the current for the oxygen reduction reaction (ORR). The onset potential was defined as the electrode potential at the ORR current density of -0.2 μA cm⁻².

Results and Discussion

The catalytic activity of our material strongly depended on the degree of oxidation (DOO) for these compounds. An appropriate oxidation is essential to have a definite catalytic activity for the ORR.

The onset potentials of partially oxidized Zr carbonitride (Zr-CNO) were 1.05 V vs RHE that is the onset potential of commercial Pt-C. Significant cost reduction is possible with our materials.

In order to improve the current density especially at high potentials we have tried to use metal complexes that have nitrogen as starting materials. More than 100 times improvements have been obtained using these materials. Although there is still some difference in the ORR activity from Pt/C catalyst, we should say these materials have great potential for PEFC cathode.

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References

- (1) A.Ishihara, K.Lee, S.Doi, S.Mitsushima, N. Kamiya, H.Hara, K.Domen, K.Fukuda, K.Ota, *Electrochem. and Solid-State Lett.*, **8**, A201. (2005)
- (2) A.Ishihara, Y.Shibata, S.Mitsushima, K.Ota, *J.Electrochem. Soc.*, **155**, B400.(2008)
- (3) A.Ishihara, Y.Ohgi, K.Matsuzawa, S.Mitsushima, K.Ota, K. *Electrochim. Acta*, **55**, 8005. (2010)
- (4) Y.Ohgi, A.Ishihara, K.Matsuzawa, S.Mitsushima, K. Ota, *J. Electrochem. Soc.*, **157**, B885. (2010)
- (5) K.Ota, Y.Ohgi, K.D.Nam, K.Matsuzawa S. Mitsushima, A. Ishihara, *J. Power Sources*, **196**, 5256-5263 (2011).