Supercritical hydrothermal synthesis of ZrO_2/C cathode catalyst without non-precious-metal for PEFCs

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Introduction

The group 4 and 5 transition metal oxide based compounds have been attracting much attention as a new class of non-precious-metal oxygen reduction electro-chemical catalysts for polymer electrolyte fuel cells (PEFCs)[1]. Although they shows the high onset potentials for oxygen reduction reaction (ORR) that is comparable with platinum-based catalysts, the ORR current remains insufficient.

Supercritical hydrothermal synthesis is able to produce high crystalline and fine particles of metal oxide, because of unique atmosphere, for example high temperature and pressurey[2]. In this study, we reported the properties of the ZrO_2/C catalysts synthesized by this measures.

Experimental

The raw slurry was prepared by mixing zirconium hydroxide and aqueous carbon source. Hydrothermal synthesis equipment shows Fig. 1, and the experimental conditions are at 380 °C(mixing point) and 30MPa. The precursor gel in this slurry was got by centrifugation and then drying in vacuum. ZrO_2/C catalysts ware synthesized by the heat treatment of precursor at 800 °C for 1 hour under nitrogen flow atmosphere.

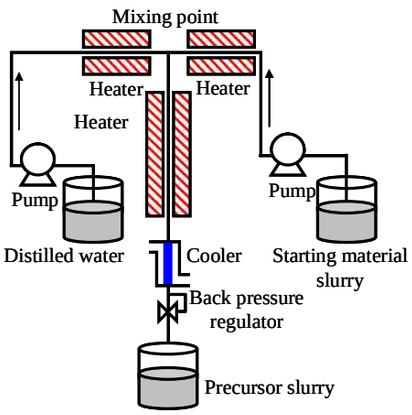

Fig.1 Apparatus for supercritical hydrothermal synthesis.

All electrochemical measurements were examined in 0.1M H_2SO_4 under atmospheric pressure using a 3-electrode cell. Slow scan voltammetry (scan rate: 5mVs^{-1}) was performed under O_2 and N_2 atmosphere at room temperature to obtain the ORR current. A current density was based on the geometric area.

The crystal phase of the catalysts were analyzed by X-ray diffraction (XRD). The morphologies of the catalysts were observed by energy - filtered transmission electron microscopy (EF-TEM). The electrical conductivity of powder samples were measured under various pressure conditions with powder resistivity measurement system.

Results and Discussion

Mixed crystal phase of monoclinic and tetragonal zirconia was observed in XRD pattern. The crystalline size calculated from XRD data was correspondent with the crystalline size measured from TEM image. The thickness of the coating carbon on the surface of zirconia was about 2-3nm (Fig.2). ZrO_2/C catalysts synthesized by supercritical hydrothermal synthesis shows a high cathodic current associated with the ORR (Fig.3).

The electrical conductivity of the ZrO_2/C catalysts synthesized by supercritical hydrothermal synthesis was 0.19 Scm^{-1} under 20 kN. These results suggest that the high electrical conductivity of the surface of the catalysts was one of the important factors which affected the catalytic activity for the ORR.

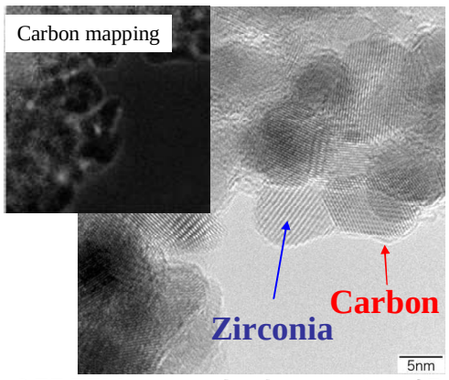

Fig.2 EF-TEM image and carbon mapping of ZrO_2/C synthesized by supercritical hydrothermal synthesis.

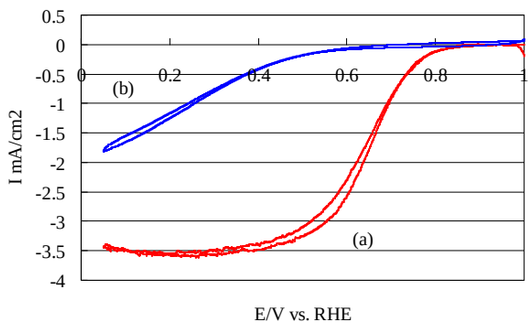

Fig.3 Potential-current curves of ZrO_2/C catalysts synthesized by (a)supercritical hydrothermal synthesis and (b)solid state synthesis for the ORR in 0.1 M H_2SO_4.

Acknowledgements

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References

[1]A. Ishihara, Y. Ohgi, K. Matsuzawa, S. Mitsushima, K. Ota, Electrochim. Acta. 55, 8005 (2010)
[2]T. Adschiri, K. Kanazawa, K. Arai, J. Am.Ceram. Soc.,75, 2615 (1992)