

Improving ORR activity of group 4 and 5 metal oxide-based cathodes for PEFCs

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Introduction

Group 4 and 5 metal oxide-based cathodes have been attracting a great deal of attention as a non-platinum-group oxygen reduction reaction (ORR) catalyst, which exhibits a high onset potential that is comparable to those of platinum-based catalysts. Recently, we successfully prepared nano-sized oxide-based particles by new synthesis method with nitrogen-containing organic complexes as precursors. Although the size of primary particles was approximately 10 nm, secondary particle size was very large, indicating that the primary particles existed in the secondary particles did not act as active sites for the ORR. Therefore, the secondary particles must be cracked to obtain high actual surface area of oxides. In addition, the density of active sites also must be increased for drastic increase in the ORR current. In this study, some trials such as ball mill and nitridation of oxides were performed.

Experimental

We used oxy-metal phthalocyanines (MeOPc) as precursors. MeOPc was supported on multi-walled carbon nanotube (MWCNT) to prepare MeOPc/MWCNT. MeOPc/MWCNT powders were ball milled to crack secondary particles. These powders were heat-treated at 900°C under N₂ containing 2% H₂ + 0.5 or 0.05% O₂ to prepare oxide-based catalyst powder.

All electrochemical measurements were performed in 0.1 mol dm⁻³ H₂SO₄ at 30°C with a 3-electrode cell. A reversible hydrogen electrode (RHE) and a glassy carbon plate were used as a reference and a counter electrode, respectively. A slow scan voltammetry was performed at a scan rate of 5 mV s⁻¹ from 0.2 to 1.2 V under O₂ and N₂ atmosphere. A current density was based on the amounts of catalyst powder with carbon support. The catalysts were characterized by an X-ray diffractometer and Transmission Electron Microscope (TEM).

Results and discussion

Figure 1 shows the TEM (a, b) and SEM (c, d) images of zirconium oxide-based compounds. These particles had ZrO₂ (tetragonal) structure according to XRD pattern. The primary particles size was approximately 10 nm as shown in Fig.1 (a) and (b),

indicating that nano-sized oxide-based particles were successfully obtained. However, as shown in Fig.1 (c), the secondary particle size of the heat-treated powder without ball mill was so large. On the other hand, as shown in Fig.1 (d), the secondary particles were cracked by ball mill to reduce the particle size.

Figure 2 shows the effect of the ball mill on the potential – ORR current curves in 0.1 M H₂SO₄ at 30°C. The ORR current was increased by ball mill. The current increase was responsible for the increase in actual surface area of oxide-based compounds. Other elements such as tantalum and titanium oxide-based compounds showed similar effect. Therefore, the cracking of the secondary particles were useful to improve the ORR activity of the oxide-based compounds made from the organic complexes.

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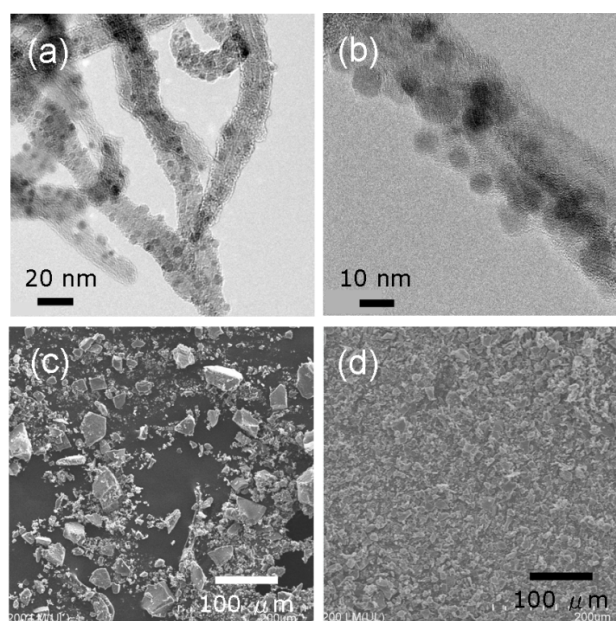


Fig.1 TEM (a, b) and SEM (c, d) images of zirconium oxide-based cathodes. (a) and (b): Primary particles, (c): Secondary particles without ball mill, (d): Secondary particles with ball mill.

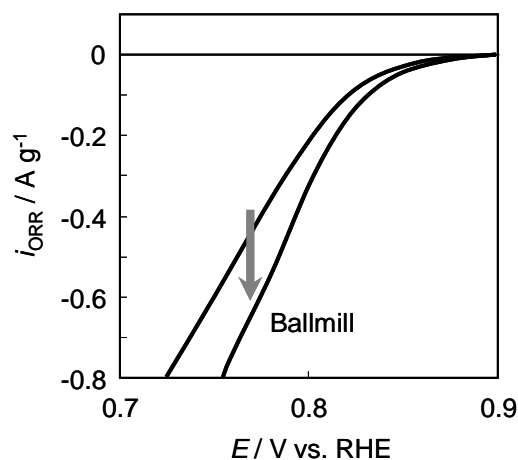


Fig.2 Effect of ball mill on potential – ORR current curves of zirconium oxide-based compounds in 0.1 M H₂SO₄ at 30°C.