Oxygen reduction reaction of Pt/Ti_4O_7 nanoparticles

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Abstract: Ti_4O_7 nanoparticles synthesized by microwave heating were used as a cathode catalyst support for polymer electrolyte fuel cell. Electron microscopic observation confirmed that Ti_4O_7 nanoparticles had a particle size of approximately 30 nm. Thin films prepared by applying Ti_4O_7 nanoparticles to GC electrodes showed a high electrochemically surface area. Further, the activity and durability of the oxygen reduction reaction using a Pt/Ti_4O_7 catalyst were investigated.

Keywords: magneli phase, microwave, Catalyst support

1. Introduction

Oxygen reduction reaction (ORR) in a polymer electrolyte fuel cell (PEFC) system requires a high activity and a high durability. Carbon has been used as a support for PEFC catalysts due to its large surface area and high electrical conductivity, but one of the causes of deterioration in PEFC systems is the corrosion of carbon supports. Reduced titanium oxide (TiOx) is a well-known electrode material because it has good electrical conductivity and high potential stability, and the nanomaterial has recently been used as a catalyst and a catalyst support in electrolysis and fuel cells.[1,2] Among the reduced titanium oxides, Ti_4O_7 has a particularly high electric conductivity and is highly likely to be used as a catalyst carrier for PEFC. Ioroi et al. reported that the Pt/Ti_4O_7 cathode catalyst is chemically more stable than Pt/C under high potential conditions.[3] Ti_4O_7 having a high surface area with a nanoparticle size is required as a catalyst support, but there is a problem that particles are sintered and the particle size increases during reduction process of titanium oxide at a high temperature. Nano-sized Ti_4O_7 has been synthesized using microwave heating.[4] In this study, Ti_4O_7 nanoparticles synthesized by microwave heating are used as a catalyst support for a fuel cell catalyst, and oxygen reduction activity and durability are studied.

2. Experimental

Rutile type TiO_2 nanoparticles and PVP K30 were put into pure water, irradiated with ultrasonic waves for 30 minutes and then dried to prepare a precursor of Ti_4O_7. The precursor was heated at 950 °C for 30 minutes with the 2.45 GHz microwave irradiation under Ar flow to prepare Ti_4O_7 nanoparticles.

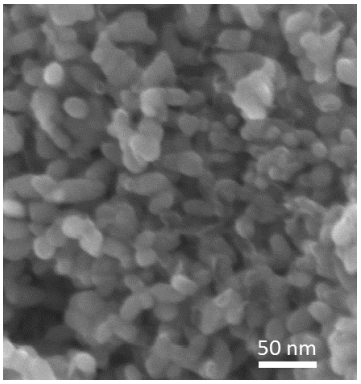

Figure 1. SEM image of Ti_4O_7 nanoparticles

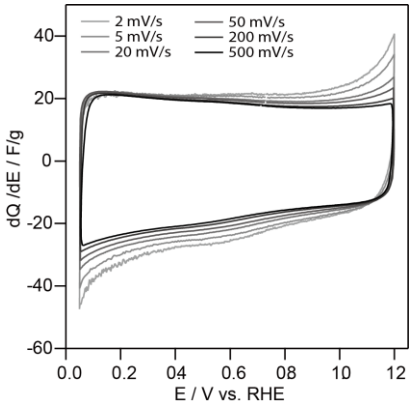

Figure 2. Cyclic Voltammetry of Ti_4O_7 nanoparticles

3. Results and discussion

Figure 1 shows SEM images of Ti_4O_7 nanoparticles obtained by microwave heating. The obtained sample was a plate-like particle having a diameter of approximately 30 nm, and it was shown that the starting titanium oxide nanoparticles of 30 nm were reduced without particle growth. It was also found that the particle form of the starting material was maintained even when the starting material particles were changed to titanium oxide of 50 nm. Cyclic voltammogram of the Ti_4O_7 (Figure 2) showed that the shape does not change significantly even when the scanning rate of the potential is changed, and the charge is accumulated at the charged electrode/electrolyte interface (electric double layer). The charge storage amount of 18.9 F g^{-1} was calculated as 31 m^2 g^{-1} with the accumulation amount per unit area of the metal oxide (60 μF cm^{-2}). The electrochemically surface area is in good agreement with the surface area obtained from the nitrogen adsorption measurement, indicating that Ti_4O_7 nanoparticles have a large surface area.

Figure 3A shows a TEM image of Pt/Ti_4O_7 nanoparticles. It was observed that platinum nanoparticles (particle size of 2.6 ± 0.5 nm) were uniformly supported on Ti_4O_7 nanoparticles. Figure 3B shows the initial LSV at each rotational speed of Pt/Ti_4O_7. From a Koutecky-Levitch plot at 0.90 V vs. RHE (Figure 3C) the initial mass activity (334 A $g_{\text{-Pt}}^{-1}$) of Pt/Ti_4O_7 showed 1.4 times higher activity than Pt/C (233 A $g_{\text{-Pt}}^{-1}$).

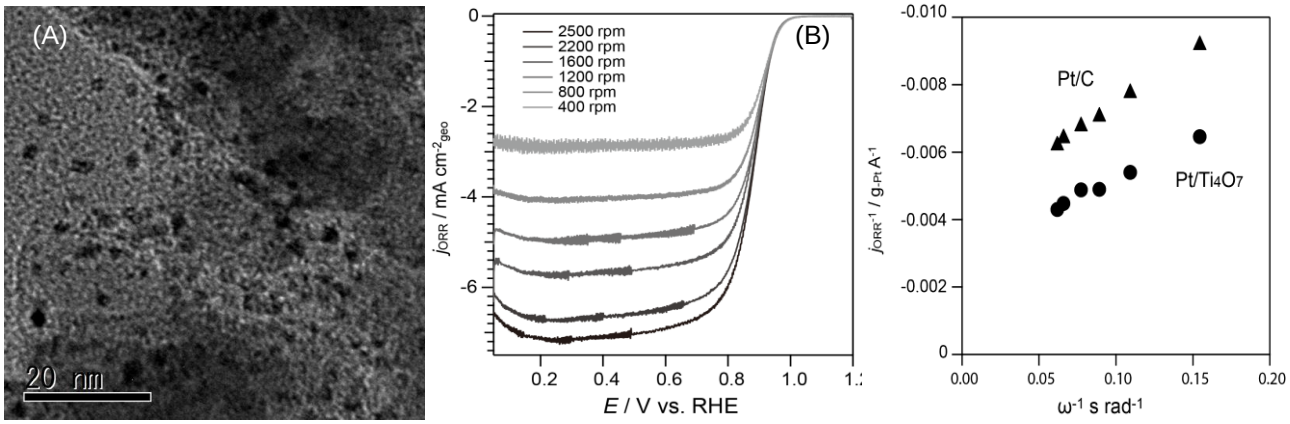

Figure 3. (A) TEM image of Pt/Ti_4O_7, (B) Linear sweep voltammograms in 0.1 M $HClO_4$ (25 °C) at various rotation rates for Pt/Ti_4O_7 catalysts (C) Koutecky-Levitch plots at 0.9V vs RHE on LSV curves of Pt/Ti_4O_7 and Pt/C.

To evaluate the influence on the oxygen reduction activity of the accelerated durability test, a load cycle acceleration durability test (0.6-1.0 V, 5000 cycles) was performed. Pt/Ti_4O_7 remained at 76% relative to the initial ECSA after 5000 cycles, whereas Pt/C had a residual of 58%. When the durability test of Pt/Ti_4O_7 was carried out for 10,000 cycles, the residual ratio of 60% was exhibited, thus the Ti_4O_7 support had doubled durability as compared with the carbon support.

4. Conclusions

Ti_4O_7 nanoparticles prepared by microwave heating reduction method were used as supports and applied to fuel cell catalysts. The Ti_4O_7 nanoparticles inhibited grain growth of platinum as an electrode material having an electrochemically large surface area, and it became possible to use it as a support with high durability.

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