Emergence of oxygen reduction activity of titanium oxide-based compounds as non-platinum cathode for PEFCs

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Abstract: In order to create active sites for the oxygen reduction reaction, we prepared Nb-doped TiO_2 supported multi-walled carbon nanotubes by heat-treatment under 4%H_2/Ar at different temperatures. We found that the distortion of the anatase phase might be essential for the generation of the ORR activity of the titanium oxide-based cathodes.

Keywords: Oxygen reduction reaction, Oxide-based cathodes, Polymer electrolyte fuel cells.

1. Introduction

Polymer electrolyte fuel cells are expected for the residential and transportable applications, especially for the automobile use, due to their high power density and low operating temperature. In order to commercialize the fuel cell vehicles widely, the development of a non-noble metal cathode is strongly required. We focused on group 4 and 5 metal oxides, which are well known as valve metals, as stable oxygen reduction reaction (ORR) catalysts because they are stable even in acidic and oxidative atmosphere. However, these oxides are generally insulators. In order to create active sites for oxygen reduction reaction, these oxides should be modified by the formation of the oxygen vacancies and/or the substitution of foreign atoms. In this study, we have tried to apply niobium-doped titanium oxides to the cathode catalysts to clarify the generation of the ORR activity.

2. Experimental

We used multi-walled carbon nano-tubes (MWCNTs) as supports to have sufficient electronic conductivity of the catalyst powder. Nb-doped TiO_2 nano-particles were dispersed on the MWCNT by hydrolysis method to make the precursor. The weight ratio of CNT: TiO_2:Nb_2O_5 was adjusted to be 20 : 4 : 1. The precursor was heat-treated for 10 min under 4%H_2/Ar at 600, 700, 800 and 900 ^oC. The crystalline structure of the catalysts was analyzed by XRD (Rigaku Ultima IV). In order to estimate the distortion of the crystalline structure, the lattice volume of the anatase phase was calculated. The ORR activities were measured in an acidic electrolyte of 0.1 M H_2SO_4 using a three-electrode cell (reference electrode is a reversible hydrogen electrode, RHE; counter electrode is a glassy carbon).

3. Results and discussion

The catalyst without heat-treatment (precursor) had poor ORR activity. On the other hand, the heat-treatment under reductive atmosphere enhanced the ORR activity of the catalysts. Figure 1 shows the dependence of the ORR current at 0.6 and 0.7 V of the catalysts prepared at several temperatures for 10 min under 4%H_2/Ar in 0.1M H_2SO_4 at 30 ^oC. The ORR activity increased with increasing heat-treatment temperature up to 800 ^oC and decreased at 900 ^oC. The catalyst prepared at 800 ^oC showed highest ORR activity. The SEM observation indicated that the sizes of the oxide-based particles were around 20 nm for all catalysts with and without heat treatment. Therefore, the surface area of the oxide-base particles was almost the same. The dependence of the ORR activity was not responsible for the change of the surface area.

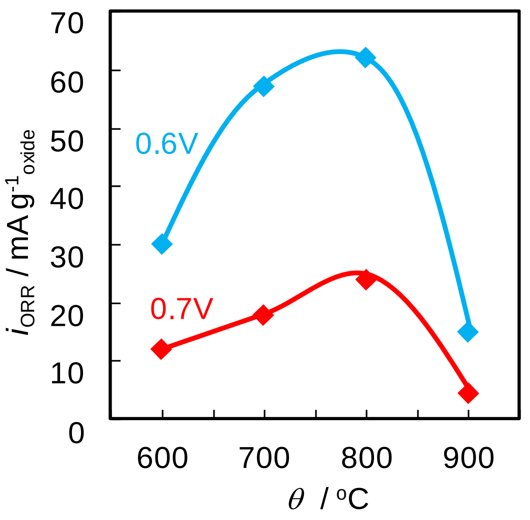

Figure 1. Dependence of ORR current at 0.6 and 0.7 V of catalysts prepared at several temperatures under 4%H_2/Ar.

The XRD patterns revealed that the catalyst without heat treatment was composed of anatase phase of TiO_2, and the peaks due to the rutile TiO_2 apparently appeared at around 700-800°C. In particular, the peaks due to anatase TiO_2 shifted at lower angular, suggesting that the niobium doped into the TiO_2 phase. We think that the crystalline distortion might affect the ORR activity. Figure 2 shows the dependence of the ORR current density at 0.7 V on the lattice volume of the anatase phase of the samples. The ORR current increased with increasing lattice volume, indicating that the distortion of the anatase phase might be essential for the generation of the ORR activity of the titanium oxide-based cathodes.

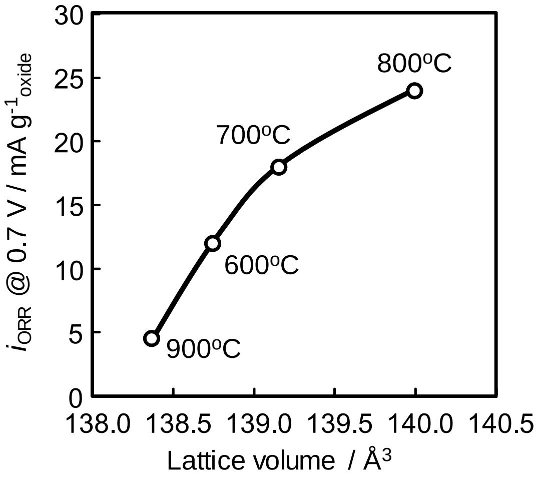

Figure 2. Dependence of ORR current at 0.7 V on lattice volume of anatase phase of Nb-doped TiO_2/MWCNTs.

4. Conclusions

In order to create active sites for the ORR, we prepared Nb-doped TiO_2 supported MWCNTs heat-treated under 4%H_2/Ar at different temperatures. We found that the distortion of the anatase phase might be essential for the generation of the ORR activity of the titanium oxide-based cathodes.

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