Nanosized titanium oxides as electrocatalyst for oxygen reduction reaction toward PEFC

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Introduction

Platinum, which was used as electrocatalysts for PEFCs, have many problems such as small amount of resources, high cost and instability. In particular, a large amount of Pt is used as cathode of PEFCs. For real commercialization of PEFC, we have to develop non-platinum electrocatalysts.

We have focused on group 4 and 5 transition metal oxides which had large amount of resources, low cost and high stability in acidic media. Titanium has the largest amount of resources among group 4 and 5 metals. We showed that titanium oxide-based catalysts, with a particle size of submicrometer, had some catalytic activity for oxygn reduction reaction(ORR) in acidic media[1)].

In this study, we tried to prepare nano-sized titanium oxide-based catalysts to increase the ORR activity by using new starting materials, nitrogen-containing organic meal complexes.

Experimental

First, submicron titanium carbonitride powders with the elemental composition $TiC_{0.82}N_{0.23}O_{0.06}$ were used as starting material. This powder was oxidized in 0.5%O_2 + 2%H_2/N_2 gas by rotary electrical furnace. This material was thermally-treated under NH_3 atmosphere and mixed with CNTs as conductive materials(Ti-CNO(CN))[1)].

On the other hand, to obtain nanosized electrocatalyst, two organic meal complexes (oxytitanium phthalocyanine(TiOPc) and oxytitanium tetrapyrazinoporphyrazine (TiOTPPz)) were used as starting materials. After CNTs were mixed with TiOPc and TiOTPPz respectively, these powders were oxidized in 0.5%O_2 + 2%H_2/N_2 gas(Ti-CNO(Pc) and Ti-CNO(TPPz)). These catalysts were observed by SEM and TEM.

These activities toward ORR were evaluated by using electrochemical cell which had RHE as a reference, GC plate as a counter electrode and GC rod supporting catalysts as a working electrode. As pre-treatment, the potential was scanned 300 cycles from 0.05 V to 1.2 V with a scan rate of 150 mV s^{-1} in O_2 atmosphere. After this, the potential was scanned 3 cycles from 0.2 V to 1.2 V with a scan rate of 5 mV s^{-1} in both O_2 and N_2 atmosphere, and the cathodic density of 3rd cycle was used for the evaluation of the ORR activity.

Results and discussion

Fig.1 shows *i*-*E* curves of Ti-CNO(CN), Ti-CNO(Pc) and Ti-CNO(TPPz) The small ORR current of the Ti-CNO(CN) was observed under 0.80 V vs. RHE, indicating that the Ti-CNO(CN) had poor ORR activity. On the other hand, ORR current of both Ti-CNO(Pc) and Ti-CNO(TPPz) were higher than that of Ti-CNO(CN). In particular, ORR current of Ti-CNO(TPPz) was about 56 times higher than that of Ti-CNO(CN). Therfore, Ti-CNO(TPPz) and Ti-CNO(Pc) had higher ORR activities than Ti-CNO(CN).

Fig.2 shows SEM images of Ti-CNO(CN) and TEM images of Ti-CNO(Pc). About Ti-CNO(CN), it was about 500 nm in diameter and catalyst particles were not well dispersed on CNTs. In contrast, Ti-CNO(Pc), which showed higher ORR activities than Ti-CNO(CN), had a diameter of about 10 nm and catalyst particles were well dispersed on CNTs.

Thus, we obtained nanosized titanium-oxide based catalyst by using nitrogen- containing organic metal complexes and their ORR activities was larger than that of submicron titanium-oxide based electrocatalysts.

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References

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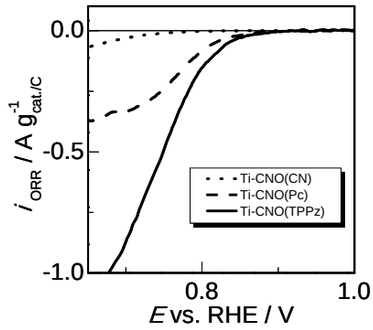

Fig.1 *i* – *E* curves of Ti-CNO(CN), Ti-CNO(Pc) and Ti-CNO(TPPz)

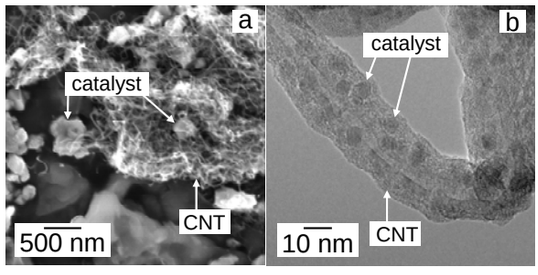

Fig.2 a) SEM image of Ti-CNO(CN) and b) TEM image of Ti-CNO(Pc).