Digest (Extended abstract) for the
Award for Encouragement of Research in the 34th Annual Meeting of MRS-J
16th (Mon.) to 18th (Wed.) December, 2024 Yokohama , Japan

Enhancement of Oxygen Reduction and Elucidation of Activity Improvement Factors in Platinum Nanocluster Catalysts by Additive Protection

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Keywords: oxygen reduction reaction, nanoclusters, additive protection
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Abstract

In this study, we successfully prepared carbon black (CB)-supported Pt nanocluster (Pt_{NCs}: ~1 nm in size) catalysts (Pt_{NCs}/CB). Compared to commercial Pt nanoparticle (Pt_{NPs}: 2–3 nm in size) catalysts (Pt_{NPs}/CB), the prepared Pt_{NCs}/CB demonstrated 2.7 times higher mass activity (MA) for the oxygen reduction reaction (ORR) and exhibited greater durability. Furthermore, an investigation into the effect of additive protection on ORR activity and durability for Pt_{NCs}/CB revealed that the melamine-modified Pt_{NCs}/CB achieved 6.0 times higher ORR activity than Pt_{NPs}/CB and demonstrated superior durability. Density functional theory (DFT) calculations and various characterizations clarified that the improved ORR activity on Pt_{NCs} compared to Pt_{NPs} is due to the strong adsorption of melamine on Pt_{NCs}, which suppresses excessive O_2 adsorption during ORR, facilitating easier ORR progression on Pt_{NCs}.

1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) are attracting attention as energy-efficient and environmentally friendly power generation devices for automobile and house use. In PEFCs, the ORR at the cathode is the rate-determining reaction, and Pt_{NPs}/CB catalysts are widely used for such cathode catalysts. Reducing the usage of the expensive noble metal Pt is an important issue, and the use of fine Pt_{NCs} catalysts is an effective strategy to address this issue.[1)] In addition, recent studies have reported that modifying the surface of Pt_{NPs}/CB with organic compounds can improve ORR MA and durability. Notably, the addition of melamine has been shown to significantly enhance ORR activity in both Pt_{NPs}/CB and Pt alloy NPs catalysts.[2), 3)] However, the origin of the ORR activity enhancement from melamine modification remains unclear, and no research has been conducted on the effect of these organic modifications on Pt_{NCs}/CB. Therefore, in this study, we investigated whether the addition of nitrogen-containing compounds also has a significant effect on the ORR activity of Pt_{NCs}/CB and elucidated the origin of this effect.

2. Experiment (or Theory)

Based on our established method,[4)] we synthesized Pt_{NCs} ($Pt_{\sim51}(CO)_n(PET)_m$). The synthesized $Pt_{\sim51}(CO)_n(PET)_m$ was then supported on CB using an impregnation method, followed by calcination to remove organic ligands, resulting in a Pt_{NCs}-supported catalyst (Pt_{NCs}/CB). The obtained catalyst was dried on a rotating electrode, and its ORR activity and durability with/without additive protection were evaluated through electrochemical measurements. The effect of additive protection was also examined in conjunction with DFT calculations.

3. Results and discussion

3.1 Characterization & Activity

For the NCs catalysts, we successfully prepared Pt_{NCs}/CB while maintaining a fine size of approximately 1 nm (Fig. 1). Electrochemical measurements were performed on Pt_{NCs}/CB and Pt_{NPs}/CB to evaluate their ORR activities with/without organic additives (melamine and others). From the results of ORR mass activity (Fig. 2), Pt_{NCs}/CB with melamine showed 6.0 times higher mass activity than that of Pt_{NPs}/CB.

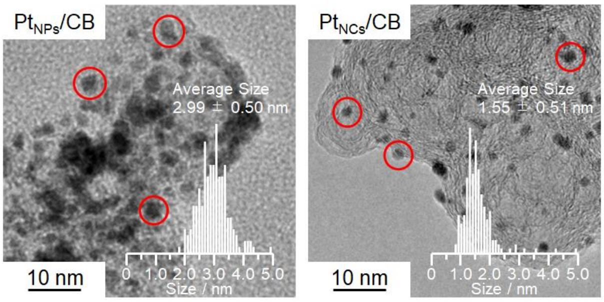

Fig.1 TEM images and the resulting Pt size histogram of Pt_{NPs}/CB and Pt_{NCs}/CB

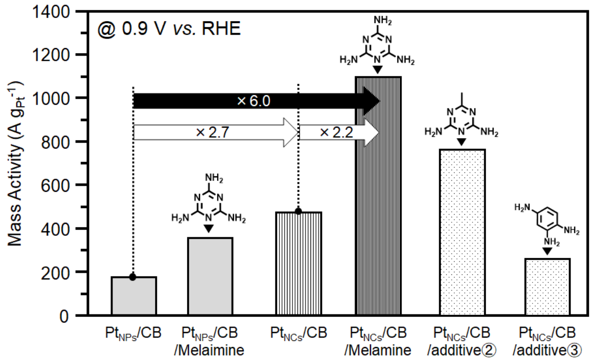

Fig.2 ORR Mass activity of Pt_{NCs}/CB and Pt_{NPs}/CB and activity enhancement by additives

3.2 Elucidation of the Activity

DFT calculations suggested a change in the charge state of Pt that facilitates the proceeding of the ORR. In fact, Pt L_3-edge X-ray absorption near edge structure (XANES) spectra revealed that the electronic state of Pt_{NCs}/CBs with melamine modification was shifted to the positive side when compared to those without the modification (Fig. 3).

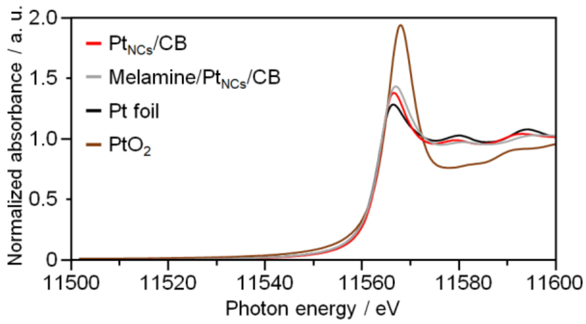

Fig.3 Pt L_3-edge XANES spectra before and after modification of melamine to Pt_{NCs}/CB. The results of Pt foil and PtO_2 powder are also shown for comparison.

4. Conclusions (or Summary)

In this study, we successfully developed a highly active catalyst through additive protection. This high activity is suggested to be due to the change of Pt particles to the electronic state where the ORR can proceed easily.

References

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