

in situ XAS study of temperature effect on the oxygen reduction reaction of Pt-Pd/C core-shell catalyst

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Introduction

Environment and global warming issue is one of the main global issues around the world. The polymer electrolyte fuel cells (PEFCs) supposed to be one of the main devices used in the global renewable energy system and pure hydrogen energy society in the future. PEFC cathode catalyst requires an excess amount of platinum due to the degradation of oxygen reduction reaction (ORR) activity. High performance, high durability and low cost cathode catalyst is expected for the wide use of PEFC devices. Therefore, it is important to reduce the use of platinum in the catalyst and improve its catalytic activity as well as durability.

Core-shell structure catalyst is one of the solutions to achieve a higher catalytic activity and less use of platinum. Compare with the common used platinum catalyst, Pd-core/Pt-shell catalyst is one of the promised catalyst to use less platinum, reduce the cost and possess high performance. However, the factor of controlling ORR activity in core-shell catalyst still has not well understood such as potential/temperature-dependent surface structures and oxidation states of platinum.

Experimental methods

In this research, we synthesized the 1 mono-layer Pt shell on carbon-supported palladium(Pd) core by copper under potential deposition (Cu-UPD) method, investigated its oxygen reduction reaction (ORR) activity and reaction rate constant k_{app} at various temperatures and the oxygen coverage of platinum by rotating disk electrode (RDE) electrochemical measurements and *operando* X-ray absorption fine structure (XAFS) respectively. Through the results of electrochemical measurements and XAFS, the relationship among ORR activity and oxygen coverage of the surface Pt shell at different temperature, the change of electronic structure and local structure of Pt atoms in Pt-Pd/C core-shell catalyst at different temperature in the same condition with electrochemical measurement (N₂-saturated) and real working condition (O₂-saturated) have been discussed.

Results and discussion

The result of electrochemical measurements shows Pt-Pd/C core-shell catalyst possess higher ORR activity and lower oxygen coverage than common Pt/C catalyst. In the high temperature (50~70°C), the ORR activity of Pt-Pd/C catalyst decrease with the increase of oxygen coverage and temperature, shows the decrease of active sites on the surface of Pt shell and the change of mechanism or structure of Pt-Pd/C catalyst.

The result of XAFS shows the core-shell catalyst possess compressive strain and less Pt-Pt bond distances than common Pt/C catalyst in N₂-saturated electrolyte, the expand of Pd core and Pt-Pt bond extend occurs at high temperature, explained the high ORR activity and less oxygen coverage of Pt-Pd/C core-shell catalyst in room temperature and the activity loss in the high

temperature. In O₂-saturated electrolyte, XAFS result shows Pt-O bond formation is dramatically increase and in the high temperature almost all the Pt shell oxidized to PtO₂, Pt-Pd bond remarkable extends, shows the loss of ORR activity of the Pt-Pd/C catalyst in high temperature (60°C) in O₂-saturated condition.

Conclusion

This research do the analysis of Pt on the reaction surface of catalyst, connect the change of local structure and ORR activity on Pd core-Pt shell with the change of temperature.

Gratitude

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