## **R&D of Nano-size Composite Electrode Catalysts for Durable Polymer** Electrolyte Fuel Cells

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Key words: Polymer Electrolyte Fuel cells, Electrode Catalyst, Durability

In order to solve the intricate problems such as energy crises and global warming, electrochemical energy conversion systems, which can directly convert between chemical energy and electrical energy, have been investigated for decades.

Fuel cells are a representative of such systems and are operated through oxygen reduction reaction (ORR) to H<sub>2</sub>O at the cathode and hydrogen oxidation reaction (HOR) at the anode; therefore, these are attracted attention as a leading player in sustainable and zero-emission society where hydrogen is used as a power source. In particular, polymer electrolyte fuel cells (PEFCs in Japan), which is employed proton exchange membranes as electrolytes, have been developed intensively of house-hold cogeneration systems (ENE•FARM in Japan), FCHVs (fuel cell hybrid electric vehicles) and FCVs (pure fuel cell vehicles) because of unique advantages such as compactness, low operation temperature, high power density and etc.

The power density of PEFCs is mainly determined by reaction kinetic of ORR under normal operation condition; in the other words, the cathode material is very important to increase the cell performance of PEFCs. Platinum is the best catalyst for ORR itself despite its rarity. In fact, *ca.* 100 g of Pt is served for each FCHV due to keep power density as well as to ensure the durability; on the other hand, depletion of platinum is

severely in the near future. Hence, further reduction in Pt usage is one of an international issue for establishment the sustainable and zero-emission society based on PEFCs. For decrease in Pt usage, nano-sized platinum particles (2 nm in diameter) are dispersed on carbon blacks employed as the electrode catalysts, which is typical "nano-technology" for PEFCs. Thus, "nano-technology" is a key to solve this issue.

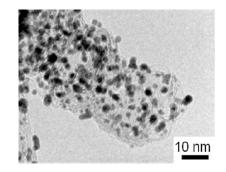


Fig. 1 A typical TEM image of the electrode catalyst purchased by TKK.

The electrode catalysts of PEFCs are launched from several manufactures. Figure 1 shows typical TEM image of the catalysts purchased from TKK in Japan. The carbon support is Ketjen black. The size of Pt particles is ca. 2 nm and has been made smaller from 5 nm to 2 nm in less than 10 years by improve the preparation procedures such as Pt precursor and carbon supports employed, giving steep increase in the power density as well as a decrease in the cell cost. Ironically, a decrease of particle size induced to decrease in the durability, which is one of the serious problems for commercialization of PEFCs. In fact, Pt particles of 2 nm are grown to be 5 nm under the continuous operation conditions and the growth rate is accelerated under vehicle conditions. The several degradation mechanisms such as Ostwald ripening, sintering on the supports and oxidation of the supports are proposed [1], but it is not determined yet.

Recently, core-shell type catalysts have been developed. This type of catalyst was firstly prepared by the research group of Prof. Adzic [2]. This has quite high ORR activity per unit weight of Pt because Pt exists only on the skin of each catalyst particles. Nowadays, R&D of this type of catalysts has been carried out by the various groups.

## http://pubs.acs.org/doi/abs/10.1021/jp055634c

An increase in durability of the electrode is also important to reduce Pt usage. Although it had not been considered seriously that carbon materials were stable, the theoretical oxidation potential of carbon to  $CO_2$  and CO is *ca*. 0.2 V and *ca*. 0.5 V at 25°C, respectively, which are much lower than cathode potential of PEFCs. In fact, it was found that carbon supports were oxidized to  $CO_2$  at the cathode in the course of "driving-idling" cycles. Then, not only alternative materials as metal oxide but also utility of graphitize carbons and carbon nano tubes (CNT) has been intensively developed. On the other hand, stabilization of the surface of carbon supports is essential since carbon oxidation reaction takes place on the surface of carbon materials. In this presentation, recent R&D of Oita University with regard to nano-size composite electrode between metal oxide and carbon for durable PEFCs will be also mentioned. *References* 

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