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Activity and Stability of Sub-Stoichiometric Titanium Oxide Supported Pt Nano-Particles

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Improvement of the stability of electrocatalyst materials used in polymer electrolyte fuel cells (PEFCs) is one of the most important issue to develop PEFC systems with high efficiency, durability and low cost. Carbon-supported platinum (Pt/C) catalysts are widely used as anode and cathode catalyst materials, however, it is pointed out that carbon corrosion is accelerated by Pt particles, may be one of causes of catalyst degradation, especially at high potential conditions [1].

Sub-stoichiometric titanium oxides (TiOx), which are known as Magnéli phases are attractive material as a corrosion-resistant and conductive catalyst support [2]. As reported previously, TiOx-supported Pt catalysts shows superior stability under high potential conditions as high as 1.5 V vs RHE [2]. In addition, improved activity for oxygen reduction reaction (ORR) can be obtained by simultaneous alloying of Pt with Ti, which is diffused from TiOx support during reduction process of Pt precursor.

On the other hand, to maximize the mass activity of the catalyst (efficient utilization of Pt), it is very important to minimize the diameter of the Pt particle. To prepare supported Pt catalyst particles with smaller diameter, lowering temperature of the heat treatment is effective. However, for the titanium oxide support system, rather higher annealing (~900^{o}C) is favorable to develop intimate contact between Pt particle and TiOx support, so that preparation of Pt/TiOx catalyst with smaller Pt particles is very difficult by the conventional wet chemical processes, such as impregnation-reduction method. In order to prepare TiOx-supported Pt nano-particles of which the diameter is comparable to that of the conventional Pt/C, arc plasma deposition (APD) process was applied for Pt/TiOx. In the APD process, metal clusters created by arc discharge have rather higher kinetic energy than that of electron beam deposition, so that metal clusters collide more violently to make a more intimate contact between metal and the substrate [3]. In this work, Pt nano-particles were deposited by APD process on TiOx (APD-Pt/TiOx), and activity and stability of Pt NPs on TiOx support were examined with comparing that of Pt/C and Pt-Ti alloy/TiOx catalysts.

TiOx support was prepared by reducing fine TiO_2 particles using Nd:YAG laser operated at λ = 355 nm. After UV laser irradiation to TiO_2 particles (BET: 20m^2/g, 70 nm diameter), spherical TiOx particles with a diameter around 50~300 nm were obtained. Figure 1 shows a typical TEM image of the prepared 10%APD-Pt/TiOx catalyst particles. Pt nano-particles with diameter of 2-3 nm are uniformly deposited on the TiOx surface. Crystal structure and electronic state of the deposited Pt particles were also examined by XRD and XPS.

Electrochemical activity of the catalyst was examined by using rotating disk electrode (RDE) under 0.1M $HClO_4$ solution at 25^{o}C. Figure 2 shows Tafel plots of APD-Pt/TiOx, Pt-Ti/TiOx, and conventional Pt/C in O_2 saturated solution. Comparing the kinetic current density at 0.9 V, Pt-Ti/TiOx catalyst shows higher activity than Pt/C as reported previously, however, activity of the APD-Pt/TiOx is almost the same with that of the Pt/C.

Durability tests (potential cycles between 1.0/1.5V at sweep rate of 500 mV/s; FCCJ protocol [4]) were carried out to examine catalyst stability under high potential conditions. Even after 10,000 potential cycles, APD-Pt/TiOx kept almost the same specific activity for ORR and showed slightly reduced electrochemical area (ECA retention: ca. 80%).

To evaluate the actual performance of the catalyst as a cathode, APD-Pt/TiOx MEA was operated under constant current load condition (@300 mA/cm^2, 80^{o}C, H_2/O_2) for > 1000 hrs. It was found that the cell voltage was fairly stable during the operation. Details about catalyst characterization, electrochemical activity and stability will be discussed at the meeting.

References

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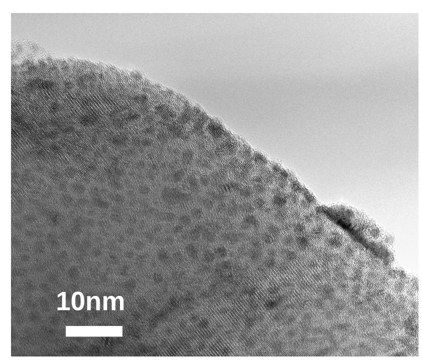

Fig. 1 TEM image of a 10%Pt/TiOx catalyst particle prepared by arc plasma deposition.

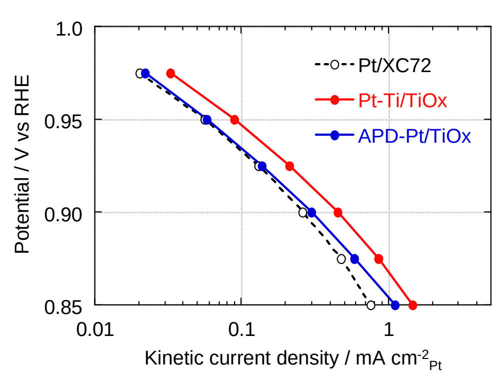

Fig. 2 Tafel plots of 10%APD-Pt/TiOx, 10%Pt-Ti/TiOx, and 40%Pt/XC72 catalysts in O_2-saturated 0.1M $HClO_4$ (25^{o}C).