

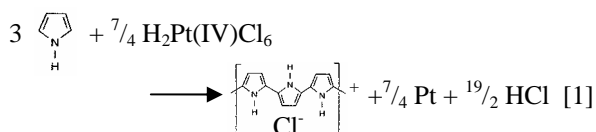
## Catalytic Activity of Pt/PPy Composite Prepared from Direct Reduction Process through Polymerization of Polypyrrole

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Polymer electrolyte fuel cells (PEFCs) have attracted enormous interest as a primary power source for electric vehicles (EVs) and a portable power source for electric devices as well as an onsite type with the cogeneration system. According to several previous research, conducting polymers (e.g., polypyrrole, polyaniline, and polythiophene) containing dispersed metal (e.g., Pt, Pd, Ru, and Sn) particles showed significant enhancement in catalytic activities toward the oxidation of small organic molecules (e.g., CH<sub>3</sub>OH and HCOOH) in comparison with bulk platinum electrodes.<sup>1, 2</sup> Previously, we succeeded preparing platinum nanoparticle/ polypyrrole (Pt/PPy) composite from platinum complex reducing by polymerization of pyrrole.<sup>3</sup>

In this study, we attempted optimization of the reaction condition of Pt/PPy composite and measured the catalytic activity for oxygen reduction. The oxidation of pyrrole into polypyrrole and the reduction of Pt(IV) to Pt(0) is proceeded using H<sub>2</sub>PtCl<sub>4</sub> by the following reaction at room temperature as shown in Eq [1]. Applying this method, the Pt catalyst can be supported simultaneously during the polymerization of PPy.



In order to evaluate of catalytic activity of the composite, a cyclic voltammogram was measured for the Pt/PPy composite samples. Nafion<sup>®</sup> solution (5 wt%, Aldrich) was added to Pt/PPy composite as a binder. The composite was supported by the glassy carbon electrode. The electrode is set into 1mol/l H<sub>2</sub>SO<sub>4</sub> aqueous solution with N<sub>2</sub> or O<sub>2</sub> bubbling.

Time dependence of Pt particle growth observed by TEM on the polymerized polypyrrole was shown in Figure 1. Pt particles were found after 30 minutes from the beginning. Monodispersed Pt particles were observed after 1 hour, and it is stably adsorbed on the surface of polypyrrole. Figure 2 shows the variation of mean size of the platinum particles with reaction period. Most Pt particles were formed after few hours. It is found that platinum complex reacts rapidly during the oxidation and polymerization of the pyrrole. According to previous study<sup>3</sup>, the characteristic bipolaron bands attributed to the formation of PPy are observed at 1210 and 930 cm<sup>-1</sup> in FT-IR spectroscopy. In this study, the bipolaron band was observed in the system reacted for 15 minutes without existence of platinum particles. It is suggested that the reduction of platinum begins after adding pyrrole immediately, and reduction of Pt ion from Pt(IV) to Pt(0) are continuously proceeded. The particle size of Pt was constant after a few hours at the range of ca. 2 nm.

We measured electrocatalytic activity of Pt particles for the oxygen reduction reaction. Figure 3 shows that cyclic voltammogram for Pt/PPy composite. For the system using the Pt/PPy composite polymerized for 45 minutes, the reduction peak assigned oxygen reduction was observed during O<sub>2</sub> bubbling, whereas no reduction peak

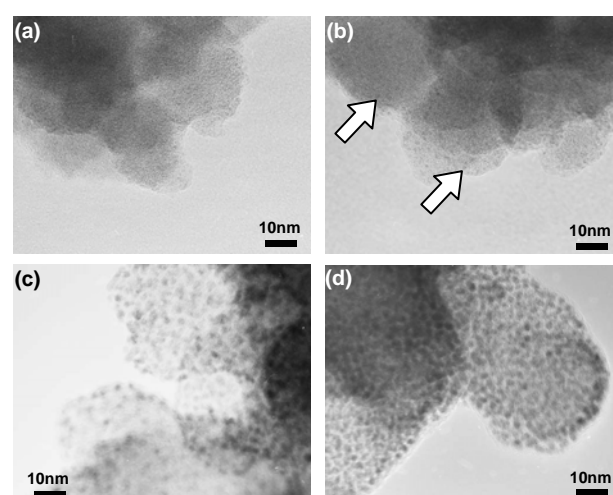
was observed during N<sub>2</sub> bubbling. The reduction peak was observed in each system containing Pt/PPy composite and its intensity depends on the reduction period of platinum species. Although the mean size of platinum particle are constant after 2 hours of reducing period, the dispersion density gradually increased. According to previous study, the conductivity of Pt/PPy composite increased with Pt loading amount which corresponded to the degree of the polymerization of pyrrole. It is suggested that the loaded platinum particles on polypyrrole keep high dispersing condition and contribute the highly ordered electrocatalytic layer.

### Acknowledgment

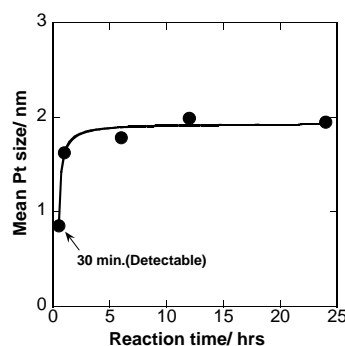
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### References

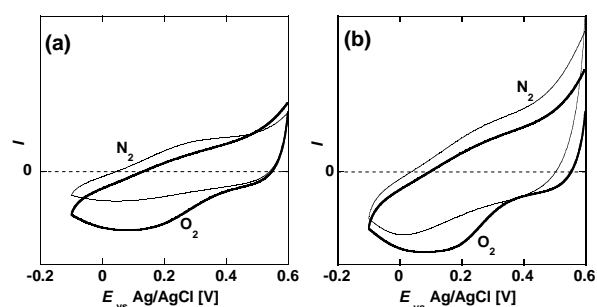
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**Figure 1.** TEM images of Pt/PPy composites. Reaction time: (a)15 min., (b)30min., (c) 1hr, and (d) 6hrs. Pt/Py= 0.6.



**Figure 2.** Variation of mean size of Pt particles with reaction period in Pt/PPy composites. Pt/Py= 0.6.



**Figure 3.** Cyclic voltammograms of Pt/PPy composite. Reaction time: (a)45 min., (b) 6 hrs. Pt/Py= 0.6.