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Enhancement of oxygen reduction at Fe tetrapyridyl porphyrin by pyridyl-N coordination to transition metal ions

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ABSTRACT

One of the promising candidates as noble-metal-free electrode catalysts for polymer electrolyte fuel cells (PEFCs) is a carbon material with nitrogen atoms coordinating iron ions embedded on the surface ($Fe—N_x$ moiety) as the active site, although the activity is insufficient compared to conventional platinum-based electrocatalysts. In order to obtain fundamental information on the activity enhancement, a simple model of the $Fe—N_x$ active site was formed by adsorbing 5,10,15,20-Tetrakis(4-pyridyl)-21*H*,23*H*-porphine iron(III) chloride (FeTPyPCl) on the basal plane of highly oriented pyrolytic graphite (HOPG), and cathodic oxygen reduction was investigated on the surface in 0.1 M $HClO_4$. The catalytic activity for oxygen reduction was enhanced by loading transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}) together with FeTPyPCl. The X-ray photoelectron spectrum of the surface suggested that the metal was coordinated by the pyridine-N. The enhancement effect of the transition metals was supported by two different measurements: oxygen reduction at HOPG in 0.1 M $HClO_4$ dissolving FeTPyPCl and the metal ions; oxygen reduction in 0.1 M $HClO_4$ at the subsequently well-rinsed and dried HOPG. The ultraviolet–visible spectrum for the solution also suggested the coordination between the pyridyl-N and the metal ions. The oxygen reduction enhancement was attributed to the electronic interaction between the additional transition metal and the Fe center of the porphyrin through the coordination bonds. These results implied that the improvement of the activity of the noble-metal-free catalyst would be possible by the proper introduction of the transition metal ions around the active site.

1. Introduction

A polymer electrolyte fuel cell (PEFC) has attracted much attention for many years as a new, efficient, and basically pollutant-free energy conversion system based on electrochemical reactions [1,2]. Practical use of the PEFC has just started recently in electric vehicles and co-generation systems for domestic electricity and heating, although a try for its dissemination suffers from resource limitation and potential cost inflation of platinum used conventionally as catalysts in the electrodes.

An effective way to solve these problems is to use catalysts free from noble metals; thus, there are currently increasing studies to develop noble-metal-free catalysts [3–20]. One of the most promising and extensively studied noble-metal-free catalysts is a carbon material with nitrogen atoms coordinating iron ions embedded on the surface ($Fe—N_x$ moiety) as the active site for cathodic O_2 reduction. Quite recently, it has been reported that a PEFC formed using the carbon material with the $Fe—N_x$ moiety as the cathode catalyst generated current approaching with that generated at a PEFC with a typical Pt-based cathode [21]. Nevertheless, the current was still smaller than that at the Pt-based PEFC. Thus there is room for the enhancement of the catalytic activity for O_2 reduction, which leads to realize practical use of the noble-metal-free catalysts and the PEFC dissemination.

The factors for the activity enhancement are the following: (1) increase in the activity per active site; (2) increase in the amount of the active site in the carbon material; (3) exposure of the active site to the pore surface inside the carbon material; (4) increase in the availability of O_2 molecules for the individual active site by pore development inside the carbon material [22]. Several studies have been reported about the activity enhancement by the addition of transition metals to the carbon material, in which the added metals were different from those functioning at the center of the active site [23–27]. The enhancement would be associated with the increase in the activity per active site and various possible mechanisms were proposed to explain the enhancement [27]; however, the detailed mechanism has not been clarified yet.

In order to obtain fundamental information on the activity enhancement mechanism, a simple model of the active site was formed by adsorbing 5,10,15,20-Tetrakis(4-pyridyl)-21*H*,23*H*-porphine iron(III) chloride (FeTPyPCl) on the basal plane of highly oriented pyrolytic graphite (HOPG) and the effects of the addition

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of transition metal ions on cathodic oxygen reduction was investigated on the surface in this study. The porphyrin with the pyridyl group as the substituent was chosen because the coordination of the pyridyl-N to the added metal ion and its contribution to the oxygen reduction were expected. Useful information was obtained in this study, which would lead to formation of active noble-metal-free cathode catalysts.

2. Experimental

2.1. Electrode/electrolyte system (A)

Three kinds of electrode/electrolyte systems were used to finely investigate the oxygen reduction at Fe porphyrin. An outline of the systems is summarized in Table 1 and the details are described below. FeTPyPCl was synthesized according to the methods reported previously [28–30]. An aliquot of 17 mm^3 of 1 μM FeTPyPCl aqueous solution was pipetted on 0.283 cm^2 of the basal plane of HOPG (Mikromasch, ZYB grade), which was carefully cleaved by adhesive tape and masked using an adhesive tape made of polytetrafluoroethylene (PTFE) with a hole of 6 mm in diameter to expose the HOPG surface of 0.283 cm^2. An aliquot of 17 mm^3 of highly purity water, 1 μM $FeCl_2$, 1 μM $CoCl_2$, 1 μM $NiCl_2$, or 1 μM $CuCl_2$ aqueous solution was immediately added to the drop on the HOPG surface and dried overnight to form the electrodes. They are hereafter called FeTPyP-M/HOPG, in which M is –, Fe, Co, Ni, and Cu, respectively. For comparison, an aliquot of 17 mm^3 of 1 μM 5,10,15,20-Tetrakis(4-pyridyl)-21*H*,23*H*-porphine (TPyP) dimethylformaide (DMF) solution and an aliquot of 17 mm^3 of 1 μM $CuCl_2$ DMF solution were pipetted on 0.283 cm^2 of the basal plane of HOPG and dried overnight to form the electrode without the porphyrin center Fe, which is hereafter called TPyP-Cu/HOPG. The surface was characterized by X-ray photoelectron spectroscopy (XPS) using a PHI ESCA 5700 system (Physical Electronics) with Al Kα radiation (1486.6 eV).

The electrochemical measurements including cyclic voltammetry, the measurements of the oxygen reduction current–potential relationships, and electrochemical impedance spectroscopy were performed using Autolab PGSTAT 20 (Eco Chemie) and a three-electrode glass cell. The glass cell was cleaned by soaking in a 1:1 mixture of concentrated H_2SO_4 and 33% H_2O_2, followed by soaking in boiling high-purity water obtained from a Milli-Q system (Millipore). The electrolyte was 0.1 M $HClO_4$ prepared by diluting 70% $HClO_4$ (Merck, Suprapur) with high-purity water. The counter electrode was a Pt wire, and the reference electrode was a reversible hydrogen electrode (RHE). All potentials were referred to the RHE. The RHE potential vs the standard hydrogen electrode was −0.06 V.

2.2. Electrode/electrolyte system (B)

The oxygen reduction was investigated at bare HOPG for dissolved FeTPyPCl in 0.1 M $HClO_4$ with and without the metal salt mentioned above. The bare HOPG as the working electrode was masked in the same way as the electrode/electrolyte system (A). The concentrations of FeTPyPCl and the metal salt were 1 μM. Ultraviolet–visible (UV–vis) spectroscopy was performed for the electrolyte using Cary 50 (Varian). The electrolyte containing 1 μM TPyP and 1 μM $CuCl_2$ in 0.1 M $HClO_4$ was also used.

2.3. Electrode/electrolyte system (C)

After the experiment of the electrode/electrolyte system (B) using the electrolyte containing FeTPyPCl with and without $CuCl_2$, the HOPG electrode was taken out from the electrolyte, rinsed with high-purity water, and dried overnight. The oxygen reduction was investigated at the electrode in 0.1 M $HClO_4$ to correlate the experiments of the electrode/electrolyte systems (A) and (B).

3. Results and discussion

3.1. Cyclic voltammograms for electrode/electrolyte system (A)

Fig. 1 shows the typical cyclic voltammograms in the Ar-saturated electrolyte for FeTPyP-M/HOPG. The voltammograms were similar for all the electrodes except for the intensities of the peaks at 0.3 V. The peaks at 0.3 V were attributed to the $Fe^{2+/3+}$ redox reactions in the center of the porphyrin [31]. The charge involved in the redox reactions calculated by the peak area was 1.7–2.8% of the value corresponding to the amount of FeTPyPCl loaded on HOPG, indicating that a part of the iron porphyrin was electrochemically active. The similar behavior has also been reported for metal porphyrins [31,32] and metal phthalocyanines adsorbed on carbon materials [33]. This partial contribution of the adsorbed metal porphyrins and phthalocyanines to be electrochemically active was explained by the inhomogeneity on the carbon support based on the fact that the electron transfer rates are very slow at the HOPG basal plane and can be greatly improved by the introduction of surface defects [31]. The difference of the fraction of the electrochemically active species on the carbon surface was then associated with the difference in the kind of the carbon support: 10% for carbon black, Vulcan XC-72R [31]; 30% for high surface area carbon,

Table 1
Outline of experimental conditions of three kinds of electrode/electrolyte systems.

Electrode/electrolyte system	Electrode	Electrolyte
(A)	HOPG loaded with: (A-1) FeTPyPCl (A-2) FeTPyPCl + $FeCl_2$ (A-3) FeTPyPCl + $CoCl_2$ (A-4) FeTPyPCl + $NiCl_2$ (A-5) FeTPyPCl + $CuCl_2$ (A-6) TPyPCl + $CuCl_2$ (Solute, 1 μM Solution volume, 17 mm^3 Dried overnight)	0.1 M $HClO_4$
(B)	HOPG	(B-1) 0.1 M $HClO_4$ + 1 μM FeTPyPCl (B-2) 0.1 M $HClO_4$ + 1 μM FeTPyPCl + 1 μM $CoCl_2$ (B-3) 0.1 M $HClO_4$ + 1 μM FeTPyPCl + 1 μM $NiCl_2$ (B-4) 0.1 M $HClO_4$ + 1 μM FeTPyPCl + 1 μM $CuCl_2$ (B-5) 0.1 M $HClO_4$ + 1 μM TPyPCl + 1 μM $CuCl_2$
(C)	(C-1) HOPG used in (B-1) (C-2) HOPG used in (B-4) (Rinsed and dried overnight)	0.1 M $HClO_4$