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Room-Temperature Fabrication of Electrocatalyst for Oxygen Reduction Using Pt Nanoparticle-dispersed Protic Ionic Liquid with Poly(3,4-ethylenedioxythiophene)

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ABSTRACT

Mixing of a Pt-sputtered protic ionic liquid (PIL) containing 3,4-ethylenedioxythiophene and a carbon support at room temperature for 3 min produces carbon-supported Pt nanoparticles (Pt-NPs), in which the PIL acts as an adhesive. Its electrochemical oxidation generates a conducting poly(3,4-ethylenedioxythiophene) (PEDOT) network in the thin PIL layer that is present between Pt-NPs and the carbon support. The prepared material possesses high electrocatalytic activities toward oxygen reduction reaction and it exhibits high durability against carbon corrosion-inducing accelerated deterioration test.

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1. Introduction

The electrocatalyst for oxygen reduction reaction (ORR) used in the polymer electrolyte fuel cells (PEFCs) must be one of the research subjects that have been extensively investigated in the electrochemistry field.¹ From economical viewpoints, a non-platinum electrocatalyst is a subject to be researched but it is not yet practical because of its low power density.² Therefore, amelioration of carbon-supported Pt nanoparticles (Pt-NPs/C) is still of importance to solve remaining issues such as decrement of Pt usage, enhancement of catalytic activity, and prevention of deterioration. Amid various attempts to prepare Pt-NPs/C catalysts with high performance and high durability, we have developed a completely new method to synthesize Pt-NPs/C catalysts.

Ionic liquid (IL) is an anhydrous liquid salt with melting point below room temperature. Its negligible vapor pressure allowed us to conduct metal sputtering onto IL in reduced pressure, and such the bold attempt led to the invention that metal NPs with uniform particle size can be synthesized in IL.^{3,4} Furthermore, mixing of the metal NPs-dispersed IL and carbon materials while heating was found to result in adsorption of metal NPs on the carbon materials.^{5,6} The Pt-NPs/C prepared in this way exhibited high electrocatalytic activity toward ORR, and its durability was higher than that of the commercially available electrocatalyst. Analysis of the prepared Pt-NPs/C has revealed that IL works as an adhesive for the Pt NPs adsorption, i.e., a thin IL layer is present between the Pt-NPs and the

carbon support. This means that the thin IL layer, which prevents direct contact of Pt-NPs and carbon, plays the key role to suppress oxidative carbon corrosion catalyzed by Pt-NPs. As one can suppose, however, the thin IL layer hampers for electron transfer between Pt-NPs and the carbon. As a deliberate method to solve this problem, we added an electropolymerizable compound in the IL and a conducting polymer network is formed in the IL layer by electrochemical oxidation.^{7,8} This strategy effectively works when using diphenyl amine and aniline as additives, but use of some other additives regrettably resulted in a failure; pyrrole and 3,4-ethylenedioxythiophene were decomposed when heated to induce Pt-NPs adsorption. Poly(3,4-ethylenedioxythiophene) (PEDOT) prepared by oxidative polymerization of the latter compound is known well as one of the ideal conducting polymers due to its attractive properties like high conductivity (up to 300 S cm⁻¹), high environmental stability, and flexibility, especially, when composited with poly(styrenesulfonate).^{9–11}

Since our first invention as to adsorption of metal NPs onto carbon materials came from heating a mixture of the metal-sputtered IL and the carbon materials, heat treatment was considered inevitable. Quite recently, however, we found that adsorption of Pt-NPs on carbon nanotubes without heating was possible if protic IL was used.¹² This desirable circumstance prompted us to use EDOT again as the electropolymerized additive in preparation of the Pt-NPs/C catalyst. Then, in the present study a Pt-NPs/C catalyst was prepared by mixing protic IL containing EDOT and carbon

Figure 1. TEM images of (a) Pt-NPs/PIL/C, (b) Pt-NPs/PIL+EDOT/C and (c) commercial Pt-NPs/C.

black, and its electrocatalytic activity and durability were examined to confirm how the high-performance of PEDOT would be effective to improve the performance of the electrocatalyst.

2. Experimental

2.1 Preparation of carbon-supported Pt nanoparticles catalysts

Diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) was synthesized by stoichiometrically quaternizing *N,N*-diethylmethylamine (Wako Pure Chemicals) aqueous solution with trifluoromethanesulfonic acid (Tokyo Chemical Industry), followed by vacuum evaporation at 333 K. A soda glass (2.5 cm × 2.5 cm), on which [dema][TfO] (400 μL) was put and spread, was placed in a DC magnetron-sputtering system (Quick Coater SC-701HMCII, Sanyu Electron Co., Ltd.). Pt sputtering was carried out at 28 W for 15 min under 5 Pa pressure of Ar. Subsequently, carbon black (3 mg, Vulcan XC-72) and 30 μL (2.8×10^{-4} mol) EDOT were added in the resulting Pt-NPs monodispersed [dema][TfO] (400 μL), and it was mixed with a planetary centrifugal mixer (Awatori-Rentaro AR-100, THINKY) at room temperature for 3 min. Then, the mixture was ultrasonically washed with *i*-propanol and centrifuged three times, followed by drying at 333 K under vacuum for 2 h. Hereafter, the obtained catalysts without and with EDOT are abbreviated as Pt-NPs/PIL/C and Pt-NPs/PIL+EDOT/C, respectively. A commercially available catalyst (Pt-NPs/C) (TEC10V30E, Tanaka Kikinzoku Kogyo K.K.) was used for comparison. The prepared catalysts was dispersed in a mixture of *i*-propanol and water (3 : 1, w : w) by ultrasonication to prepare an electrocatalyst ink.

2.2 Electrochemical measurements

A glassy carbon (GC) rotating disk electrode (RDE; surface area = 0.196 cm²) connected to a Pine Instruments AFMSRCE electrode rotator was used as a working electrode. The electrocatalyst ink was spread onto the GC disk so as to give 15 μg cm⁻² of Pt loading, and slowly dried. The catalyst layer was coated with a very thin Nafion film by placing 5 μL of 0.1 wt% Nafion solution. Electrochemical measurements were conducted in a three-electrode glass cell with the above-mentioned GC-RDE working electrode, a Pt mesh counter electrode, and a reversible hydrogen electrode (RHE) connected to the cell by a Luggin capillary as a reference electrode. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were obtained by a computer-controlled Hokuto Denko HZ-5000 potentiostat/galvanostat. The working electrode with the electrocatalyst was electrochemically cleaned by 100 cycles of potential scanning between 0.05–1.20 V at 50 mV s⁻¹ under N₂ atmosphere prior to measurements.

Stability of the catalyst performance was examined by a start-stop test, which is one of the accelerated deterioration tests (ADT)

proposed by Fuel Cell Commercialization Conference of Japan (FCCJ). The ADT was conducted by applying continuous potential sweeps between 1.0 V–1.5 V at 0.5 V s⁻¹ to simulate the load applied at the start and stop of the fuel cell.¹³

3. Results and Discussion

Since a formation of electronic network in a thin PIL layer is essential in the present study, electrochemical polymerization of EDOT in a [dema][TfO] layer was examined by cyclic voltammetry. An indium tin oxide (ITO) glass, on which an appropriate amount of [dema][TfO] dissolving 0.66 mol L⁻¹ EDOT was put and spread, was used as a working electrode. This electrode was put in 0.1 mol L⁻¹ HClO₄ together with a Pt counter electrode and an Ag/AgCl reference electrode. Of note, the thin PIL layer stably stayed on the ITO surface without dissolution in the electrolyte solution. Potential sweepings between 0.05 and 1.2 V vs. RHE at 50 mV s⁻¹ gave cyclic voltammograms shown in Fig. S1, in which pictures of the working electrode taken before and after electrochemical oxidation are also given. The voltammograms showed increase in oxidation currents at potentials positive of 0.9 V vs. RHE and steady increase in capacitive currents with potential cycles. The [dema][TfO] layer turned light blue and then deep blue at every positive potential sweep. At the same time, electrochromic behavior of fading at negative potentials was observed. Such the electrochemical behavior allowed us to confirm electrochemical polymerization of EDOT giving PEDOT in the [dema][TfO] layer.¹⁴

TEM images of Pt-NPs/PIL/C, Pt-NPs/PIL+EDOT/C, and commercial Pt-NPs/C, are shown in Fig. 1. Although the former two samples were prepared at room temperature, the Pt nanoparticles were homogeneously immobilized on the surfaces of carbon black regardless of presence of EDOT in [dema][TfO]. Their mean particle sizes and loading amounts are given in Table S1 together with characteristic values as electrocatalysts that will be described later. The mean particle sizes estimated for Pt-NPs/PIL/C and Pt-NPs/PIL+EDOT/C were much smaller than that for the commercial Pt-NPs/C. The Pt loading amount on Pt-NPs/PIL+EDOT/C was a little smaller than Pt-NPs/PIL/C. As previously reported, PIL can induce Pt adsorption on carbon materials even at room temperature,¹² whereas use of ordinary IL requires heating at and over 200 °C. From that point of view, the ability of PIL to bring about Pt adsorption even at room temperature might be slightly weakened by addition of EDOT in PIL. However, it was already confirmed that the Pt loading amount was tunable by changing the amount of Pt-NPs dispersed in IL.⁵

Figure 2 shows cyclic voltammograms of Pt-NPs/PIL/C (a), Pt-NPs/PIL+EDOT/C (b), and commercial Pt-NPs/C (c). In each figure, voltammograms taken before/after 20,000 cycles of an ADT. It is noted that before the initial measurement, 100 times of the

Figure 2. Cyclic voltammograms of (a) Pt-NPs/PIL/C, (b) Pt-NPs/PIL+EDOT/C and (c) commercial Pt-NPs/C taken before (solid lines) and after (broken lines) 20,000 cycles of ADT, and (d) ECSA values (filled marker) and their retention rates (unfilled marker) of Pt-NPs/PIL/C (blue triangle), Pt/PIL+EDOT/C (red circle), and commercial Pt/C (black square).

potential cycling in the same potential region has been done to clean the Pt surfaces, as described in the experimental section. Therefore, EDOT in the Pt-NPs/PIL+EDOD/C catalyst should be well polymerized during the cleaning, and this was evidently supported by the fact that the voltammograms of Pt-NPs/PIL+EDOD/C showed larger capacitive currents than other catalysts.

All catalysts exhibited the typical voltammograms of Pt including current peaks due to hydrogen adsorption/desorption and those due to oxidation of Pt surfaces and their reduction at negative and positive potential regions, respectively. The electrochemically active surface area (ECSA) of all Pt nanoparticles on each catalyst was estimated on the basis of the electric charges required for the hydrogen adsorption/desorption on a polycrystalline Pt surface (210 $\mu\text{C cm}_{\text{Pt}}^{-2}$). The ECSA values of all catalysts and their retention rates, which are ratios of ECSA values at each cycle to the initial ones, are plotted as a function of cycle number, as shown in Fig. 2(d). The Pt-NPs/PIL+EDOT/C kept apparently higher ECSA value than Pt-NPs/PIL/C and Pt-NPs/C during 20,000 cycles of ADT, indicating the significant effect of the conducting PEDOT network formed in the PIL layer on increasing the number of

effectively functional Pt nanoparticles. The fact that both Pt-NPs/PIL+EDOT/C and Pt-NPs/PIL/C maintained higher retention rate than Pt-NPs/C strongly suggests that the existence of PIL between Pt-NPs and carbon supports functions for preventing the catalyst corrosion in a similar manner as that previously reported.^{5,6}

Figure 3(a) shows RDE polarization curves taken at 1,600 rpm for Pt-NPs/PIL/C, Pt-NPs/PIL+EDOT/C, and Pt-NPs/C catalysts in O₂-saturated 0.1 M HClO₄ before and after ADT. The electrocatalytic mass activities were evaluated from current values at 0.9 V vs. RHE and are given in Table S1. Apparently, the catalysts prepared with PIL in this study exhibited higher catalytic activities than the commercial Pt-NPs/C catalyst. Surprisingly, the Pt-NPs/PIL+EDOT/C catalyst possessed over twice larger initial mass activity than the Pt-NPs/C catalyst, and then 1.5 times larger mass activity value than the initial mass activity of the Pt-NPs/C catalyst was kept even after 20,000 cycles of ADT. We have previously reported enhancement of catalytic activities by adding electropolymerizable compounds like aniline and diphenyl amine in Pt-sputtered IL, as mentioned in the introduction section.^{7,8} Compared to the polymers of those compounds, PEDOT possesses the highest

Figure 3. (a) RDE polarization curves of Pt-NPs/PIL/C (blue), Pt-NPs/PIL+EDOT/C (red), and commercial Pt-NPs/C (black) at a scan rate of 10 mV s⁻¹ taken before (solid lines) and after (broken lines) 20,000 cycles of ADT, and (b) mass activities of prepared catalysts with different amount of EDOT addition. A dash line indicates mass activity of Pt-NPs/C.

conductivity. This favorable characteristic resulted in the significant enhancement of the catalytic activity.

To estimate optimized amount of EDOT in the Pt-sputtered PIL, the mass activities of Pt-NPs/PIL+EDOT/C containing different amount of EDOT were measured and the obtained values are plotted as a function of EDOT concentration, as shown in Fig. 3(b). The concentration giving the highest mass activity was 0.66 mol L⁻¹, which corresponded 1 mol EDOT/7.7 mol PIL. This molar ratio of EDOT in PIL should be appropriate for providing enough conductivity without giving unfavorable effects on Pt-NPs adsorption and catalytic activity at the Pt surfaces.

In conclusion, we successfully developed a novel method to fabricate carbon-supported Pt-NPs at room temperature; just mixing for 3 min of Pt-sputtered PIL including EDOT and carbon support. The very thin PIL layer involving the conducting PEDOT network, which is present between Pt-NPs and carbon supports, makes the catalytic activity larger than that of the commercially available catalyst and makes it extremely durable against the accelerated deterioration tests. The preparation method developed in this study that includes no chemical reactions except for the electrochemical polymerization during the initial cleaning would be the simplest among all methods to prepare the Pt-NPs/C electrocatalyst. We believe that this method, which does not involve any wasteful materials, any by-products, and heating, is undoubtedly environmentally friendly and quite practical.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-65149>.

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