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Detection of OH radicals as the effect of Pt particles in the membrane of polymer electrolyte fuel cells

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ABSTRACT

The formation of OH radicals ($^{\bullet}$OH) for polymer electrolyte fuel cell (PEFC) was investigated with a home-made test cell by means of a fluorescence probe method for several kinds of membrane electrode assembly (MEA) consisting of Nafion. After 12-h operation under open circuit condition, $^{\bullet}$OH was detected at both the anode and the cathode sides but the amount was much larger for the anode side. The formation of $^{\bullet}$OH considerably depended on the amount of Pt/C catalyst loaded in the MEA. Dispersion of Pt particles in Nafion membranes increased the $^{\bullet}$OH formation, but Pt ions did not. Based on the results, the formation mechanism was discussed.

1. Introduction

Improvement of duration of polymer electrolyte fuel cells (PEFCs) is one of the tasks which should be attained before forthcoming practical wide applications in the world. Factors affecting the duration of PEFC may be poisoning of catalysts, dissolution of Pt catalyst, and degradation of polymer electrolyte membrane [1]. Among these factors, the degradation of membrane causes decrease of the proton conductivity, and consequently, lowering of the performance as deterioration of the membrane. For the deterioration of membranes, the decomposition with heat and the chemical reaction with active oxygen species have been acknowledged [1]. As for the active oxygen species in PEFC systems, the formation of H_2O_2 has been reported [2]. The presence of H_2O_2 was confirmed in drain water [3], exhaust gas [4], and membranes [5] during operation of PEFCs. Since the reactivity of H_2O_2 is suspected to be not so high to decompose polymer electrolytes, the formation of reactive OH radicals ($^{\bullet}$OH) from H_2O_2 has been suggested [1]. The formation of reactive $^{\bullet}$OH from H_2O_2 may be caused by electrode reduction of H_2O_2 and/or reduction with metal ions such as Fe^{2+} which are possibly present as contaminants [6]. The latter reaction is well known as Fenton reaction:

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \tag{1}$$

In recent years, the formation of Pt nano-crystallites in polymer electrolyte membrane (PEM) has been reported [7]. The dissolved Pt ions from cathode are reduced in the membrane to form Pt particles at a certain position from the cathode where the potential is less positive to reduce Pt ions to metallic Pt particles [7], which is called "Pt band". On the Pt band, O_2 leaked from the cathode may be reduced to form H_2O_2 since the potential is not so positive as the cathode. The formation of H_2O_2 at the Pt particles may produce a large amount of $^{\bullet}$OH to deteriorate membranes [8]. On the other hand, it was reported that the dispersed Pt particles in membrane scavenges H_2O_2 and the formation of $^{\bullet}$OH is suppressed [9], concluding that the Pt band functions to decrease the degradation of PEM.

Though the formation of $^{\bullet}$OH in the PEFC reaction system is suggested, there are only a few experimental researches dedicated to detect $^{\bullet}$OH [9–13]. In the literature, a spin-trapping ESR method is often used owing to the high sensitivity. In this method, a stable nitroxide radical is adducted with $^{\bullet}$OH by a trapping reagent. However, the trapping reagents or adducted radicals are sometimes not stable enough for the quantitative analysis [14]. An alternative method to sensitively detect $^{\bullet}$OH would be a fluorescence probe method [15]. This method is based on the formation of a stable fluorescent product by the reaction of $^{\bullet}$OH with a specific molecule, such as coumarin and terephthalic acid (Scheme 1). As reported previously [15], by using coumarin, we successfully detected $^{\bullet}$OH

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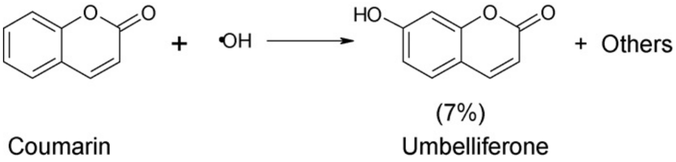

Scheme 1.

formed in the PEFC reactions for a membrane electrode assembly (MEA) supplied from a company. In the present study, we prepared several kinds of MEAs and used the fluorescence probe method to investigate the effect of the amount of Pt/C catalyst loaded in MEA and the dispersed Pt particles in PEM on the •OH formation.

2. Materials and methods

2.1. Materials

Ethanol, sodium hydroxide (Nacalai Tesque), butyl acetate, 1-pentanol, 30 wt% hydrogen peroxide (H_2O_2) solution, 20 wt% Nafion in ethanol, sulfuric acid (Wako Chemicals), coumarin, umbelliferone (Tokyo Kasei), tetra-ammine platinum(II) dichloride ($Pt(NH_3)_4Cl_2 \cdot H_2O$, Kojima Chemicals), hexa-chloro platinum(IV) acid (H_2PtCl_6, Nacalai Tesque) were used without further purification. Pt/C catalyst (46.0 wt% Pt, TEC10E50E) was purchased from Tanaka Kikinzoku. Nafion NRE-212 and Nafion 115 membranes (manufactured by DuPont) were obtained from Aldrich Chemicals. The thicknesses of the membranes are reported from the manufacturer to be 51 and 127 μm, respectively.

2.2. Preparation of MEA

The catalyst paste used in the present study was prepared with the following procedure based on the report by Uchida et al. [16]. Pt/C catalyst was dispersed in butyl acetate for 30 min by ultrasonic treatment. Into the dispersion, a 5-wt% Nafion ethanol solution and then butyl acetate were added. The mixture was agitated with ultrasonic treatment. The final weight ratio of the paste was 1:1:60 for Pt/C:Nafion(dried):butyl acetate. Carbon cloth (EC-CC1-060, Toray Co. Ltd.) was employed for the functions of a charge collecting electrode and a gas diffusion layer. The carbon cloth used was a rough cloth with the texture of 8 meshes for 10 mm. After the treatment with the 5-wt% Nafion ethanol solution, one side of the carbon cloth was coated with the catalyst paste using an air-brush spray for the area of 25 mm × 25 mm, followed by drying at 80 °C for 10 min under vacuum. This procedure was repeated until the weight of catalysts became a desired value. Finally the coated carbon cloth was dried at 80 °C for 30 min. The tested quantities of catalyst ranged from 0.1 to 1.25 $mg_{Pt}\,cm^{-2}$, but usually 0.5 $mg_{Pt}\,cm^{-2}$ was adopted. MEAs were prepared by sandwiching a PEM with the catalyst-coated carbon clothes prepared above. The contact between the PEM and the catalyst was attained by pressing the layers under 5 MPa at 150 °C for 10 min. The PEM samples used were Nafion NRE-212, acid treated NRE-212, Nafion 115, and Pt-dispersed Nafion 115.

2.3. Dispersion of Pt ions and Pt particles in Nafion

Pt-dispersed Nafion membranes were prepared with the following procedure based on the report by Hagihara et al. [17]. To prepare Pt-dispersed PEM, Nafion 115 was used instead of Nafion NRE-212 because the mechanical strength of the NRE-212 membrane after the Pt dispersion became too weak to construct a test fuel cell. A sheet (5 cm × 5 cm) of Nafion 115 membrane was treated in 100 mL of 0.26 mM $Pt(NH_3)_4Cl_2$ solution at 80 °C for 24 h to prepare an ion-exchanged membrane. This ion-exchanged membrane was used as one of the test membranes after washing by boiling pure water. To prepare a Pt particle dispersed membrane, 100 mL of 1-pentanol was mixed with the $Pt(NH_3)_4Cl_2$ solution containing ion-exchanged membrane and then the mixture was refluxed at 125 °C for 2 h. By this procedure, Pt ions in the membrane were reduced into Pt metal particles and the color of the membrane became black. The membrane was washed by boiling in pure water. According to the literature [17], the acid groups in the PEM are completely exchanged with Pt ions regardless the state of the membrane, and almost all (98%) of Pt ions are reduced to Pt metal. Under the assumption of complete exchange, the densities of Pt^{2+} and Pt are calculated to be 0.1 $mg\,cm^{-2}$.

2.4. Test cells

To apply the coumarin fluorescence probe method to the reaction occurring in a PEFC system, a test cell equipped with reservoirs for the probe solution was devised as illustrated in Fig. 1. The cell was built with two pairs of acrylic resin plates (thickness 5 and 1 mm) and shielded from gas with silicone glue. In each reservoir,

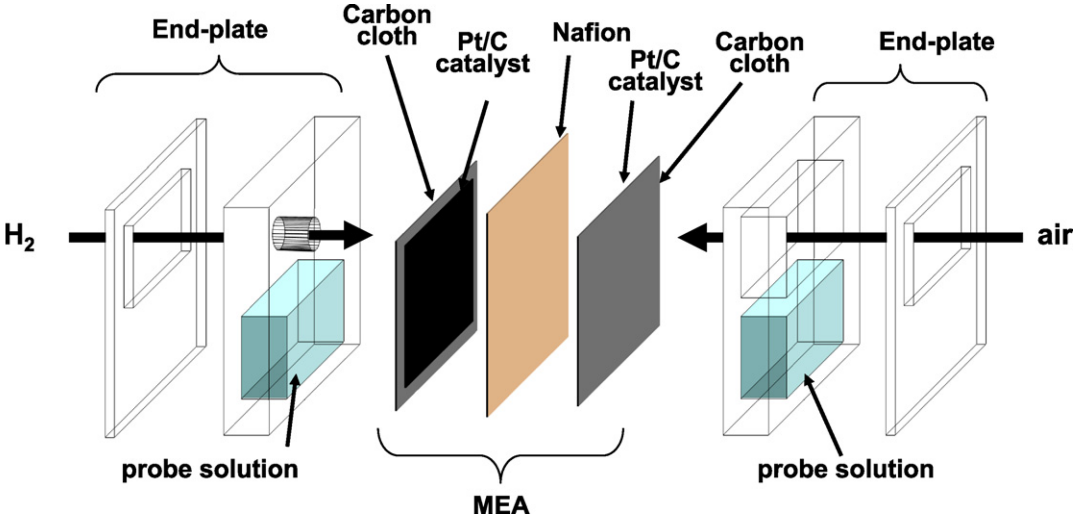

Fig. 1. Expanded illustration of the test cell. The thicknesses of the acrylic resin plates for these end-plates are 1 and 5 mm, and the dimension of the MEA is 30 mm × 30 mm. These parts were secured by four bolts of 4 mm diameter.