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ELECTROCHEMICAL GROWTH OF Pt ULTRAMICROPARTICLES IN NAFION FILMS ON GLASSY CARBON ELECTRODES

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The electrodeposition of platinum (Pt) into Nafion films on glassy carbon electrode is described. The Pt particles are dispersed three-dimensionally throughout the Nafion layer. The specific surface area of the particles is surprisingly large, suggesting that the Pt particles are highly dispersed into the Nafion film. The average crystal size of the platinum clusters is on a range of 100 to 200 Å.

It is well known that the highly dispersed platinum (Pt) catalyst has been widely employed for the air-cathode in fuel cells. Recently, the deposition of metal particles onto polymer modified electrodes and Nafion membranes has gained wide interest for catalytic purposes.[1-5] Using a polymer (vinyl acetic acid (PVAA)), it has recently been discovered by Kuwana et al.[4] that metals can be electrodeposited as microparticles. Although various types of polymers have previously been examined,[1-4] polyperfluorosulfuric acid (Nafion) is one of the most interesting materials for both scientific and technological research.

This paper will discribe an electrodeposition of Pt into Nafion films on a GC electrode. A 3% solution of Nafion (equivalent weight 1000) in ethanol was used to prepare electrode coatings. The working electrode was a Teflon-shrounded GC disk electrode (Tokai Carbon-3G;diameter 0.30 cm). Cyclic voltammetry (CV) was applied to deposit Pt into the Nafion film. Freshly prepared solutions of K_2PtCl_6 in 1 M (M=mol dm^{-3}) H_2SO_4 were used. A typical procedure was employed for the deposition as follows; the potential limits for the first cycle were 0.7 and -0.22 V vs. SCE and 0.7 and 0.2 V vs. SCE for the successive potential cycles, respectively. Under this condition, the nucleation occurs only on the first potential cycle and Pt particles grow on the successive repeated scan. The loading levels of Pt were calculated from the charge consumed on the successive repeated scans.

Figure 1 shows an example of the SEM cross section of the Nafion film (thickness 4000 Å) on GC with a loading level of 42 μg cm^{-2}(GC). It is clearly seen that the Pt particles are almost spherical and randomly distributed throughout the Nafion film. The diameter of the Pt particles seems to be on the

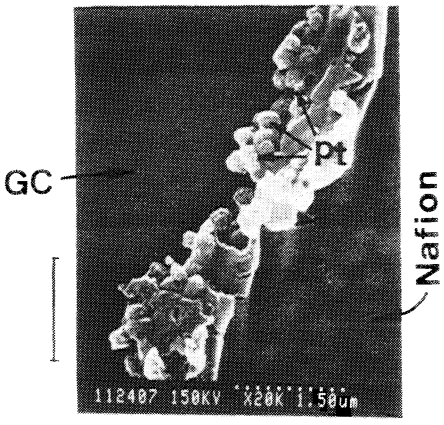

Fig. 1. SEM cross section. The bar is 1.5 μm.

Table 1. Mass specific surface area (σ_m) and crystal size (d)

Pt loading	Q_H	σ_m	d
$\mu g\ cm^{-2}(GC)$	$mC\ cm^{-2}(GC)$	$m^2 g^{-1}$	Å
3.02	0.086	15.8	150
10.3	0.31	17.0	140
18.4	0.53	16.0	150
44.8	1.53	19.4	120

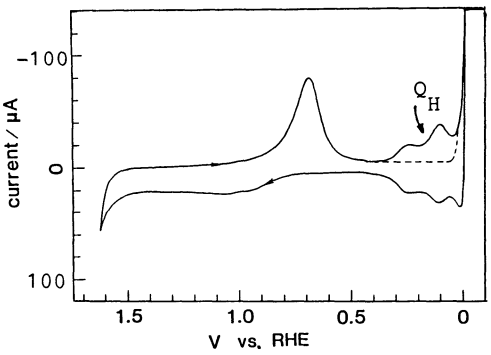

Fig. 2. CV curve at Nafion(Pt)/GC with a loading level of 44.8 $\mu g\ cm^{-2}(GC)$ in 1 M H_2SO_4. The scan rate was 50 mV s^{-1}.

order of 1500-2000 Å.

Kuwana et al. reported that the adsorption-desorption fine structure of hydrogen on Pt/PVAA/GC was ill-defined for determination of the active Pt surface area.[4] However, we found in this work the fine structure on the Pt dispersed Nafion-GC electrode (Nafion(Pt)/GC) as shown in Fig. 2. The loading level of Pt was limited to values less than 50 $\mu g\ cm^{-2}(GC)$ in which all the Pt particles were grown only in the Nafion film. The active Pt surface area was measured by the charge (Q_H) required for the adsorption of hydrogen (dashed line shown in Fig. 2).

From the values of the loading level and the active Pt surface area, the mass specific surface area (σ_m;$m^2\ g^{-1}$) can be calculated as listed in Table 1. The σ_m was calculated by an assumption that the average density of Pt atoms at the surface is 1.12×10^{15} atoms $cm^{-2}(Pt)$.[6] These extraordinary large values of the σ_m strongly suggest that the electrodeposited Pt particles are highly dispersed into the Nafion film. The σ_m obtained in this work can be translated into an average crystal size by assuming that the crystal is a cube of side d.[6] The average crystal size (d) is on a range of 100 to 200 Å. The value of d is considerably smaller than that of the Pt particle image observed under SEM. This suggests that the particles observed under SEM are formed as coalesced ultramicro Pt clusters. It might be expected that each Pt particle observed under SEM has 1000 - 8000 ultramicro Pt clusters! We have examined oxygen reductions in 1 M H_2SO_4 at Nafion(Pt)/GC electrodes. An oxygen reduction wave was clearly observed at 0.45 V vs. SCE (peak potential) under a potential scan of 20 mV s^{-1}. The height of the peak current was almost the same as that observed at a bare Pt electrode.

It is expected that the present electrode can be used as a cathode in a fuel cell. Electrodepositions such as Au, Pd, and Ag are under an investigation.

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