

Electrocatalytic Activity of Platinum Dispersed Polyaniline Electrodes - Effect of Preparation Conditions of Polyaniline -

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1. Introduction

The preparation of highly active electrodes for the electrocatalytic oxidation of methanol is important to develop direct methanol fuel cells. Promising results have been reported for the oxidation of methanol on Pt-based particles dispersed polyaniline (PAn) electrodes [1]. The catalytic activity of metal dispersed PAn electrodes is expected to depend on the morphology and the conductivity of PAn films.

In this study, the effect of preparation conditions of PAn on the electrocatalytic activity for the oxidation of methanol was investigated, because properties of electropolymerized PAn strongly depend on polymerization conditions [2]. Special attention was paid to the effect of different protonic acids used in the electrochemical preparation of PAn.

2. Experimental

PAn was deposited by constant potential electrolysis at +0.8 V (vs. SCE) onto carbon electrodes in aqueous solutions containing 0.16 M aniline and 0.5 M protonic acid under N₂ atmosphere at 25 °C. The protonic acids used were H₂SO₄, HCl, HNO₃, HBF₄ and HClO₄.

PAn electrodes were reduced electrochemically in 0.5 M protonic acid solutions at -0.2 V until the current reached background level. Platinum particles were then incorporated by electrochemical deposition from 0.5 M protonic acid solution containing 0.01 wt% hexachloroplatinic acid at a constant potential of -0.2 V. The amount of Pt deposit was calculated from the cathodic charge passed during the deposition process.

Cyclic voltammetry and chronoamperometry were used to evaluate the catalytic activity of Pt dispersed PAn electrodes in sulfuric acid solutions containing methanol. The magnitude of current density for methanol oxidation was calculated by subtracting background current measured in the absence of methanol.

3. Results and discussion

3.1. Voltammetric study

Voltammetric evaluation of electrocatalytic activity for the oxidation of methanol was first attempted to confirm the advantage of using Pt modified PAn electrodes. Cyclic voltammograms were obtained between 0.3 and 0.8 V with a sweep rate of 20 mV/s in 1 M methanol / 0.5 M sulfuric acid solution. PAn was deposited from a sulfuric acid solution and the amount of PAn deposit was 169 µg/cm².

As shown in Table 1, the oxidation currents of Pt modified PAn electrodes are apparently higher than those of Pt dispersed carbon electrodes. Since significant current increase was not observed by the deposition of PAn on carbon surface, the remarkable effect of Pt / PAn electrode may be due to the higher dispersion of Pt particles on PAn modified carbon surface.

3.2. Chronoamperometric study

In order to know whether Pt / PAn electrodes still show high catalytic activity at longer time scale, the electrolytic current during controlled potential electrolysis at 0.8 V was measured. PAn was also deposited in sulfuric acid solution and the amount was 169 µg/cm². The current densities due to methanol oxidation of Pt / PAn electrode was much higher than those of Pt / C electrode up to 30 minutes.

3.3. Effect of anions in polymerizing solution

It is known that PAn prepared in HClO₄ or HBF₄ aqueous solution has a fibril structure, while PAn prepared in H₂SO₄ or HNO₃ solution is granular [2]. Nothing is known about the effect of protonic acids used for PAn formation, although the difference of polymer morphology should affect the catalytic activity of Pt / PAn electrodes.

The effect of anions in polymerizing solution was studied with equal anodic charge of 0.0845 C during polymerization. The results are shown in Fig. 1. PAn's prepared in sulfuric and nitric acid solution were more effective for the electrocatalytic oxidation of methanol, indicating granular structure is suitable for higher dispersion of Pt particles.

3.4. Effect of current density during polymerization

The effect of current density of polymerization was also studied, since polymerization current affect the morphology of PAn [2]. PAn was deposited from sulfuric acid solution under controlled current with equal anodic charge of 0.125 C. The catalytic current of methanol oxidation was almost unchanged, when the current density of electropolymerization of aniline was varied from 0.3 to 44.6 mA/cm².

1. H. Laborde, J-M. Leger, C. Lamy, J. App. Electrochem., **24**, 219 and 1019 (1994).
2. A. Kitani, M. Kaya, S. Tsujioka, K. Sasaki, J. Polym. Sci. Polym. Chem. Ed., **26**, 1531 (1988).

Table 1. Effect of PAn deposit on current density for methanol oxidation

Pt deposited (µg/cm ²)	Current (mA/ cm ²)*	
	Pt / C Electrode	Pt / PAn / C Electrode
179	0.70	2.32
268	1.06	3.23

* Measured at 0.5 V (vs. SCE) with voltammetry

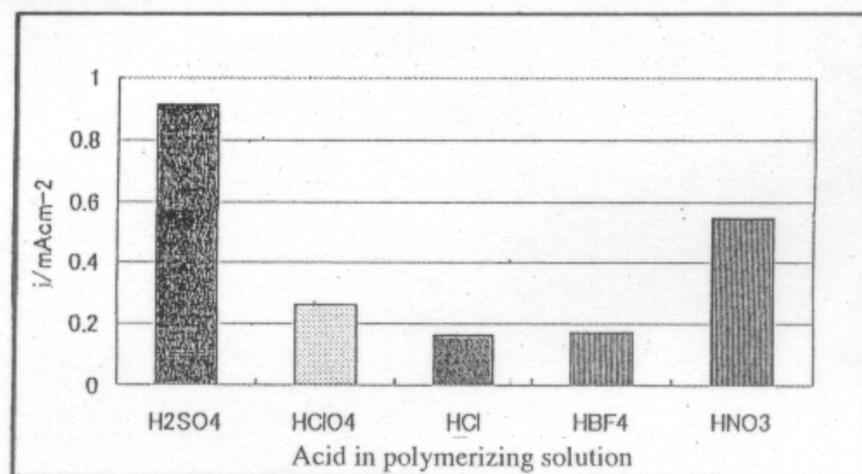


Fig. 1. Effect of anions in polymerizing solutions on catalytic activity (values after 10 min) of Pt / PAn / C electrodes.