Electrocatalytic oxidation of methanol on platinum modified polyaniline electrodes

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Abstract

Electrocatalytic oxidation of methanol on Pt modified polyaniline electrodes was investigated with the aim of developing highly active composite electrodes for direct methanol fuel cells. Cyclic voltammetry and chronoamperometry were used to evaluate the catalytic activity in sulfuric acid solutions containing methanol. Pt / polyaniline modified carbon electrodes showed higher catalytic activity towards oxidation of methanol than Pt deposited carbon electrodes. The effect of different protonic acids used in the electrochemical preparation of polyaniline on the oxidation current of methanol was studied. Largest oxidation current was obtained for polyanilines prepared in sulfuric acid solutions.

Key words: Electrochemical methods, Polyaniline and derivatives, Fuel cells

1. Introduction

The preparation of highly active electrodes for the electrocatalytic oxidation of methanol is important to develop direct methanol fuel cells. Conjugated polymers provide the possibility of higher surface areas of dispersed metallic particles and are conducting in the potential range where C1 organic molecules are oxidized. 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 [2,3]. 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 N_2 atmosphere at 25 °C. The protonic acids used were H_2SO_4, HCl, HNO_3, HBF_4 and $HClO_4$.

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The thickness of PAn films were controlled by measuring the quantity of electricity passed. 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 modified 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 $\mu g/cm^2$.

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.

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

Pt deposited	Current (mA/ cm^2)*	
($\mu g/cm^2$)	Pt / C Electrode	Pt / PAn / C Electrode
179	0.70	2.32
268	1.06	3.23

* Measured at +0.5 V (vs. SCE)

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 a sulfuric acid solution and the amount was 169 $\mu g/cm^2$. As listed in Table 2, the current densities due to methanol oxidation of Pt / PAn electrode was much higher than those of Pt / C electrode up to 30 minutes.

Hereafter, chronoamperometry was used to evaluate the catalytic activity of Pt dispersed PAn electrodes.

Table 2
Change of electrolytic current due to methanol oxidation during controlled potential electrolysis

Time	Current (mA/cm^2)	
(min)	Pt / C Electrode	Pt / PAn / C Electrode
5	0.344	2.461
10	0.153	0.910
15	0.100	0.465
20	0.074	0.293
25	0.057	0.206
30	0.049	0.159

Pt deposited ; 179 $\mu g/cm^2$

3.3. Effect of anions in polymerizing solution

It is known that PAn prepared in $HClO_4$ or HBF_4 aqueous solution has a fibril structure, while PAn prepared in H_2SO_4 or HNO_3 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 summarized in Table 3. PAn's prepared in sulfuric and nitric acid solution were more effective in the electrocatalytic oxidation of methanol, indicating that a granular structure is suitable for higher dispersion of Pt particles.

Table 3
Effect of anions in polymerizing solution on catalytic activity of Pt / PAn / C electrodes

Acid	Current density (mA/cm^2)*
H_2SO_4	0.910
HNO_3	0.547
$HClO_4$	0.258
HBF_4	0.170
HCl	0.161

* Values after 10 min, Pt deposited = 179 $\mu g/cm^2$

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/cm^2 (Table 4).

Table 4
Effect of polymerizing current on electrocatalytic current of methanol oxidation at Pt / PAn / C electrode

Polymerizing current (mA/cm^2)	Current ratio (after 15 min)
0.30	1.00*
1.49	1.19
7.43	1.14
44.6	1.07

* This current value was taken as unity

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (C) and by a Grant-in-Aid for Scientific Research on Priority Area of " Electrochemistry of Ordered Interfaces " from the Ministry of Education, Science, Sports and Culture. Financial support by the Electric Technology Research Foundation of Chugoku is also acknowledged.

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