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Effect of Rotation Rate on the Formation of Platinum-modified Polyaniline Film and Electrocatalytic Oxidation of Methanol

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Abstract: The oxidation of methanol was investigated on platinum-modified polyaniline electrode. Changes in the electrode rotation rates (Ω) during platinum electrodeposition remarkably affect the formation and distribution of platinum in the polymer matrix and consequently lead to different currents of methanol oxidation. The results show that platinum loading is proportional to rotation rates $\Omega^{1/2}$.

Keywords: Platinum-modified polyaniline electrode, electrode rotation rate, methanol oxidation, electrocatalytic activity.

The preparation of highly active electrodes is of considerable interest to the electrocatalytic oxidation of methanol. The routine method is to disperse, at molecular level, electrocatalytic materials, such as platinum and platinum-based alloys in the electron conductive polymers. Polyaniline (PAni), which is easy to synthesize in aqueous medium and chemically stable in air, is a very interesting support material. Many factors, such as polymerization procedure, polymerization potential, dispersity degree or particle size of platinum metals, will influence the activity of electrode. Though much work has been done on the electrocatalytic activities of platinum-modified polyaniline electrodes for the methanol oxidation reaction[1-4], few researchers have devoted to study the dependence of platinum loading and dispersity on the electrode rotation during the platinum electrodeposition. The aim of the present work is to explore the effect of electrode rotation rates on the formation and distribution of platinum particles in the polymer films and the subsequent methanol oxidation.

The Electrochemical measurements were performed with CHI650A Potentiostat / Galvanostat and ATA-1A rotating electrode apparatus. A glassy carbon (GC) rotating disc (geometric area 0.1256 cm^2) was used as working electrode. The counter electrode was a Pt plate and reference electrode was a saturated calomel electrode (SCE). The modification of the disk electrodes was performed in two steps: (a) Electropolymerization of aniline by potential cycling (15 cycles at a scan rate of 50 mV/s) between -0.2 and 0.9 V (*vs.* SCE) in aqueous solution containing 0.1 mol/L aniline + 0.5 mol/L H_2SO_4.

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The thickness of the polymer films was estimated to be 0.6 μm[1]. (b) Deposition of platinum particles into the PAni film by electroreduction of chloroplatinic acid (0.003 mol/L) in 0.5 mol/L sulfuric acid with different electrode rotation rates. Each electroreduction step involved 25 potential cycles in the range from -0.1 to 0.8 V (scan rate=50 mV/s). Cyclic voltammetry was used to evaluate the electrocatalytic effect of the platinum-modified polyaniline electrode, with different platinum loadings, on the methanol oxidation in 0.1 mol/L methanol + 0.5 mol/L H_2SO_4 solutions. All experiments were carried out at 25±1°C.

Results and Discussion

The dependence of platinum loading on rotation rates $\Omega^{1/2}$ is given in **Figure 1**. As shown in **Figure 1**, platinum loading is proportional to $\Omega^{1/2}$, showing that rotation rate has a great effect on platinum loading. The amount of loaded platinum particles was determined from the charge passed during the loading step by assuming that the reduction of Pt^{4+} to Pt^0 is 100% efficient[2]. When the rotation rate increases from 0 to 1500 r/min, the amount of platinum deposits increases from 0.14 to 1.42 mg/cm^2 (geometric area).

Figure 1 Plot of platinum loading *W vs.* rotation rates $\Omega^{1/2}$ during platinum deposition on a polyaniline-covered glassy carbon rotating disc electrode

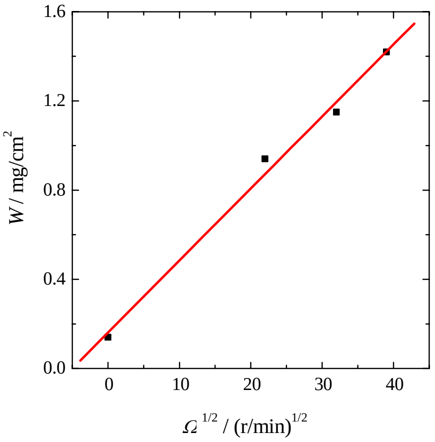
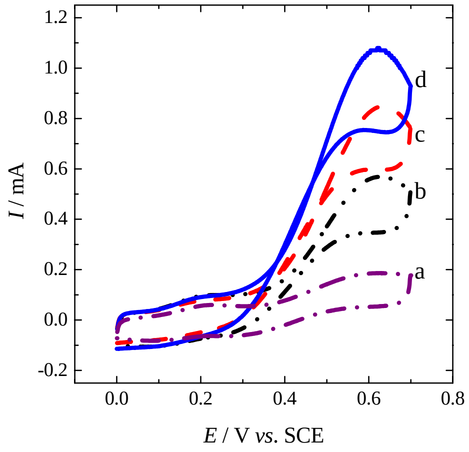


Figure 2 shows the effect of rotation rate of platinum electrodeposition on the cyclic voltammograms of methanol oxidation. From the CVs, one can see that the methanol oxidation peaks rise with the increase of rotation rates of platinum electrodeposition. One reason may be that with the increase of rotation rates, the platinum loading and particle size grow gradually, which leads to a higher electrocatalytic activity of the electrode. Another reason probably is that platinum can be dispersed sufficiently into the PAni polymer with the increase of rotation rates. Highly dispersed platinum is less susceptible to poison. The poison of the catalytic site caused by the fixation of intermediate species, which produced during methanol oxidation, is decreased[4]. Therefore, the catalytic activity of the electrode increases.

In summary, the electrode modified by platinum particles dispersed inside of the polyaniline film shows high activity with respect to methanol oxidation. Rotation rate of electrode has a great effect on the deposition of platinum. With the increase of rotation rates of platinum deposition, platinum loading increases as a function of $\Omega^{1/2}$. Moreover, platinum particles may be dispersed into the polymer homogeneously with the increase of rotation rates. More intensive work in this respect is in progress.

Figure 2 Cyclic voltammograms of methanol oxidation (Scan rate: 5 mV/ s) rotation rate during platinum deposition: a - 0, b - 500, c - 1000, d - 1500 r / min



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