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Preparation of Platinum Implanted Glassy Carbon Electrode and Electro-oxidation of Formic Acid and Formaldehyde

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Abstract: The glassy carbon substrates were bombarded with 5×10^{17} ions/cm^2 of platinum. The surface composition of implanted electrode and concentration-depth profiles of various elements were measured by AES. The chemical state of Pt in glassy carbon electrode implanted with platinum (Pt/GC) was detected by X-ray Photoelectron Spectroscopy (XPS). The electro-oxidation of HCOOH and HCHO have been investigated on Pt/GC and smooth Pt electrodes. The results show that the platinum implanted into glassy carbon is much more active than the smooth platinum metal for electro-oxidation of HCOOH and HCHO.

Keywords: Ion implantation, electro-oxidation, formic acid, formaldehyde.

Electrocatalytic oxidation of small organic molecules has attracted considerable attention in system of fuel cell[1-4]. In this research field, Parsons[4] pointed out that the electrodes which were prepared from non-noble substrates modified by excellent dispersal noble metal particles and which still exhibited better catalytic activity should be studied. Ion implantation is a technique with unique advantage and has been used in many electrochemical research fields[5,6]. The present study is an attempt to use ion implantation technique for producing catalytically active electrode surface and to study electro-oxidation of formic acid and formaldehyde.

Experimental

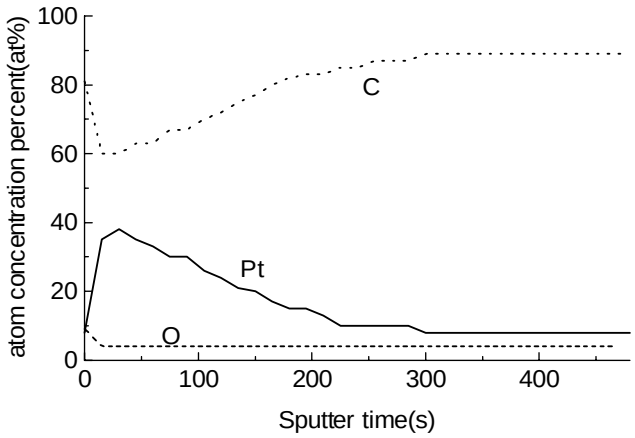
The implantation of Pt (99.95%) was carried out by using a metal vapor vacuum arc (MEVVA) source ion implanter. The extracting voltage and beam current of Pt ion beam were 40KeV and 1.2mA, respectively. The implanted dose of Pt is 5×10^{17} ions/cm^2. The surface composition of implanted electrode and concentration-depth profiles of various elements were measured by PHI-610/SAM AES. The chemical state of platinum in Pt/GC electrode was detected by PHI-5300 XPS. Analyser energy is 35.75 eV, Al α X-ray. Electrochemical measurements were performed by a CHI705A Analyzer. The working electrode was Pt/GC electrode or smooth Pt metal. The exposed apparent area was about 0.14cm^2.

Results and Discussion

1 Surface Analysis

The measured concentration-depth profile of platinum in Pt/GC was approximately Gaussian distribution (**Figure1.**). The maximum concentration and the outermost surface concentration of platinum on the profiles are about 38at% and 8 at%, respectively. The recorded results of Pt 4f XPS from Pt-implanted GC indicated that Pt is mainly in atom form.

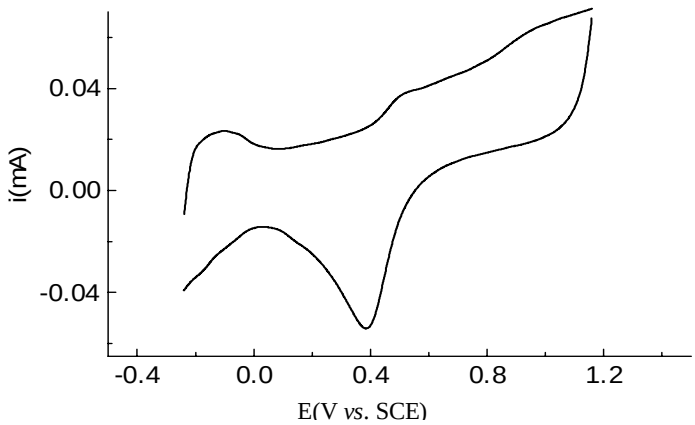
Figure 1. Auger depth profiles of platinum in Pt implanted GC



2 Oxidation of Formic Acid on Pt/GC Electrode

The cyclic voltammogram(CV) obtained from the Pt/GC electrode in 0.5mol.l^{-1}$HClO_4$ solution was shown in **Figure 2.**

Figure 2. Cyclic voltammogram of Pt/GC electrode in 0.5mol.l^{-1}$HClO_4$, scan rate 0.05V/s

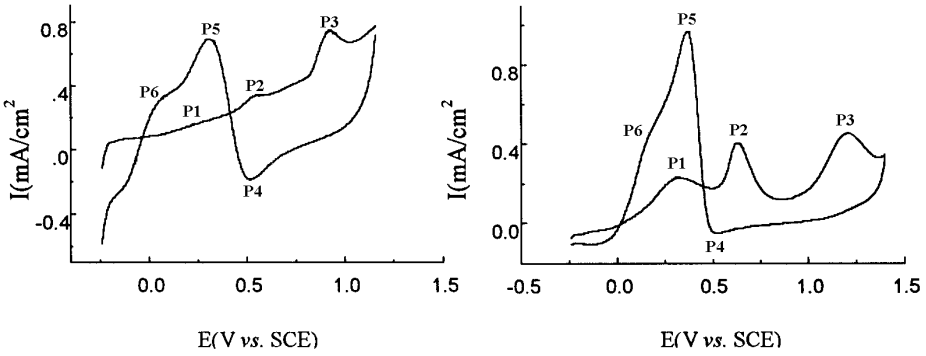


This CV curve is very similar to that of platinum electrode in the same electrolyte. It is evident that platinum implanted GC electrode has been changed in character. **Figure 3a.** shows CV curves of the anodic oxidation of 0.1 mol.l^{-1} HCOOH in 0.5mol.l^{-1}$HClO_4$ on Pt/GC electrode. On the anodic sweep, there are three peaks occurring at 0.2-0.3V, 0.65V and 0.89V, which will be termed the P_1, P_2 and P_3 anodic peaks, respectively. On the return sweep there are one cathodic peak P_4 and two anodic peaks (P_5 and P_6) which occur at approximately the same potential as the P_1 and P_2 anodic peaks. By comparing the overall shape of this curve with that from Pt (**Figure 3b.**), it was found that oxidation of HCOOH on the two kinds of electrodes was similar.

In order to compare real current density, the real surface areas of platinum on implanted electrode and smooth Pt electrode were measured by integration of the i-E response to CV curves in 0.5mol.l^{-1}$HClO_4$ solution[7]. The data show that the real surface area of Pt clusters on Pt/GC electrode and of the smooth Pt electrode are about 0.247cm^2 and 2.745cm^2, respectively.

Figure 3a. CV of oxidation of 0.1mol.l^{-1} HCOOH in 0.5mol.l^{-1}$HClO_4$ on Pt/GC electrode, scan rate 0.05V/s apparent area 0.14cm^2

Figure 3b. CV of oxidation of 0.1mol.l^{-1} HCOOH in 0.5mol.l^{-1}$HClO_4$ on Pt electrode, scan rate 0.05V/s, apparent area 0.14cm^2



The calculated results indicated that the real current density of each peak obtained for HCOOH oxidation on Pt/GC was greater than that of smooth Pt electrode. The platinum implanted into GC is much more active than the smooth platinum metal for the HCOOH oxidation.

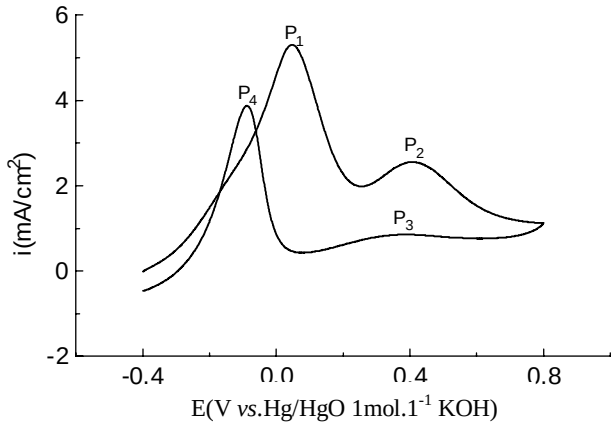
3 Oxidation of Formaldehyde on Pt/GC Electrode

CV curves of electro-oxidation of 0.1 mol.l^{-1} HCHO on Pt/GC electrode was shown in **Figure 4.** On the anodic sweep, the two peaks P_1 and P_2 appeared successively. On the return sweep, the two peaks P_3 and P_4 were observed. At lower OH^- concentration, the mechanism of reactions was suggested elsewhere[3]. The P_1 was corresponding to the first electron transfer reaction, while P_2 was corresponding to the second electron transfer reaction. The reaction of P_4 and P_3 should be the same reactions as P_1 and P_2, respectively.

The calculated results indicated that the real current density of each peak obtained for HCOOH oxidation on Pt/GC was greater than that of smooth Pt electrode. In addition, the long-term stability of the implanted samples is excellent.

The reason for the high activity of the implanted platinum is not clear yet and requires additional investigations. Possible explanation is precipitation of active platinum clusters during and after bombardment. It was observed by SEM that there were a large number of Pt clusters on the surface of Pt .

Figure 4. Cyclic voltammogram of 0.1mol.l^{-1}HCHO in 0.5mol.l^{-1} Na_2CO_3 solution on Pt/GC electrode, scan rate 0.05V/s, apparent area 0.14cm^2



Conclusions

Platinum implanted into glassy carbon produced marked effects with respect to the electrocatalytic activity for the oxidation of formic acid in perchloric acid solution and formaldehyde in sodium carbonate. The reason is believed to be precipitation of active platinum clusters during and after bombardment.

Acknowledgments

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