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Formation of Nanoporous Platinum by Selective Anodic Dissolution of PtZn Surface Alloy in a Lewis Acidic Zinc Chloride-1-Ethyl-3-methylimidazolium Chloride Ionic Liquid

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Nanostructured metals with a high surface area are of considerable interest for various applications in catalysis,[1] fuel cells,[2] chemical sensors,[3] etc. Among these materials, nanostructured platinum films deserve special attention because of the excellent properties of platinum in electrochemical applications. A nanoporous platinum electrode is expected to exhibit much higher surface area than a polished platinum electrode. This feature is very advantageous in the study of electrochemical reactions involving adsorption. We report here a simple strategy to fabricate nanoporous platinum electrodes.

Several investigations that were concerned with the preparation of nanoporous platinum can be found in the literature. A mesoporous platinum film was prepared by electrodeposition of platinum into the hexagonally packed cylindrical pores of the self-assembled liquid crystal surfactant octaethyleneglycol monohexadecyl ether.[4−6] Alternatively, nanoporous platinum was recently produced by electrochemical de-alloying, that is, selective dissolution of Cu from the $Cu_{0.75}Pt_{0.25}$ binary alloy in 1 M H_2SO_4.[7] The surfactant techniques have the advantages of control over the size of the porous structure but are generally difficult and time-consuming to implement. The electrochemical de-alloying method is relatively easy but the preparation of the binary alloy requires special attention during arc melting of the Cu and Pt at 1000 °C. The de-alloying method had also been found to produce other porous materials such as Au in a report by Newman and co-workers.[8]

We describe herein a method for fabrication of nanoporous platinum by electrochemical deposition and dissolution of ZnPt alloy in zinc chloride-1-ethyl-3-methyl chloride ($ZnCl_2$-EMIC) ionic liquid. In recent years, ambient temperature ionic liquids have attracted enormous attention as green solvents for organic synthesis, separation, catalysis, and electrochemical applications.[9,10] The most well-known ionic liquid system is the one that consists of aluminum chloride anions and certain dialkylimidazolium cations. Although the aluminum chloride-based ionic liquids have found wide applications, they are highly moisture/air-sensitive. This problem is circumvented by replacing the aluminum chloride anion with other anions such as zinc chloride to produce ionic liquids that are water/air-stable.[11] The Lewis acidity of the $ZnCl_2$-EMIC ionic liquid can be

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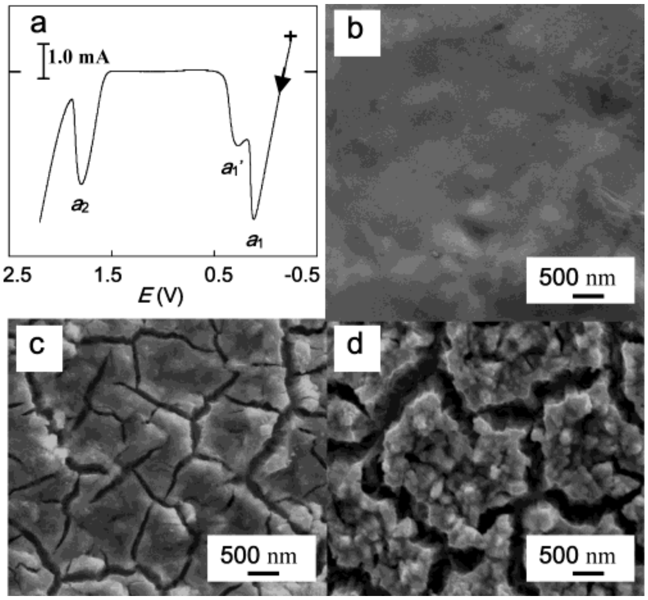

Figure 1. (a) A linear scan stripping voltammogram recorded for a Pt electrode that had been electrodeposited with Zn at −0.22 V for 100 s, in the 40−60 mol % $ZnCl_2$-EMIC (the reference electrode was a Zn wire placed in a separate fritted glass tube containing pure 50.0−50.0 mol % $ZnCl_2$-EMIC melt). Waves a_1 and a_1' are correlated to the stripping of Pt whereas the wave a_2 is due to the stripping of the Zn-domain PtZn alloy. SEM images of platinum wire: (b) a polished platinum wire, (c) and (d) de-alloyed Pt wires that were electrodeposited with Zn until a quantity of electricity $Q_c = 0.36$, and 0.72 C/cm^2, respectively at 120 °C followed by de-alloying at 1.2 V to remove the surface PtZn alloy.

rendered basic or acidic by varying the ionic liquid composition. It has been shown that the Lewis acidic $ZnCl_2$-EMIC ionic liquids (which contain more than 33 mole percent (mol %) $ZnCl_2$) are potentially useful for the electrodeposition of zinc-containing alloys.[12−15]

We have been investigating the formation of PtZn alloy on a platinum surface by electrodeposition of zinc on the platinum substrate from a Lewis acidic 40.0−60.0 mol % $ZnCl_2$-EMIC. The linear scan voltammogram shown in Figure 1a reveals that the resulting PtZn surface alloy could be anodically stripped off the platinum surface. The stripping process creates nanosized channels on the platinum surface depending on the amount of PtZn alloy that was formed during the deposition of Zn. This fact is useful in fabricating a highly porous network of pure platinum. Polished platinum wires (1 cm, $r = 0.1$ cm) which have been immersed in 0.2 M NaOH solution and rinsed with deionized water with a specific resistivity of 18.2 MΩ·cm were cathodically treated in the 40.0−60.0 mol % $ZnCl_2$-EMIC ionic liquid at 120 °C at a potential (−0.22 V versus Zn(II)/Zn) where bulk deposition of zinc occurs. During the electrodeposition of zinc, the color of the platinum electrode surface remained silver white. Subsequent anodic treatment was conducted at 1.2 V, where the PtZn alloy was stripped, until the anodic current dropped to zero. The PtZn-coated electrode surface turned black immediately after the start of the anodic treatment, indicating the formation of a porous surface. During anodic treatment, the PtZn alloy was selectively dissolved from the platinum electrode, resulting in the formation of nanochannels on the platinum surface. The microstructure of the electrode was examined with SEM. Figure 1b shows the SEM image of a polished platinum electrode surface before the electrochemical treatment. Figure 1c shows the microstructure of a de-alloyed platinum electrode surface that had been electrodeposited with 0.36 C/cm^2 zinc. For this sample, nanochannels approximately 40-nm wide are distributed uniformly on the electrode surface. The merit of fabricating nanoporous platinum by electrochemical formation and dissolution of a ZnPt surface alloy is that the channel size produced on the resulting porous platinum surface is easily tunable by the amounts of the electrochemically generated PtZn surface alloy. Figure 1d shows the microstructure of a platinum surface after anodic stripping of the PtZn surface alloy that was produced by electrodeposition of 0.72 C/cm^2 zinc on the pure platinum. This figure reveals that, in comparison with Figure 1c, an increase in the PtZn surface alloy during the electrodeposition step produces a more porous surface with larger channels, 100−500 nm, as well as channels of smaller size, 40−100 nm, after de-alloying. The distribution of the channel widths of the nanostructured platinum surface shown in Figure 1c,d are presented in the histograms shown in Figure 2.

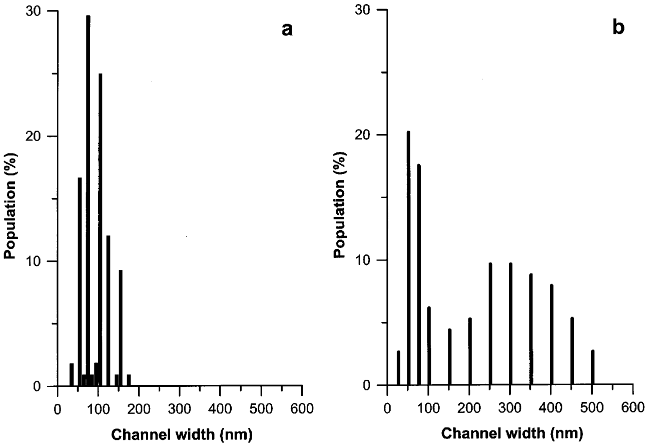

Figure 2. Histograms show the channel width distribution of nanopores of the Pt films shown in Figure 1, (a) part c and (b) part d.

Cyclic voltammograms of our nanostructured and polished platinum electrodes in 2 M H_2SO_4 at 200 mV s^{-1} from 1.4 to −0.15 V (vs Ag/AgCl) are shown in Figure 3a. The fine peaks corresponding to the formation and removal of platinum oxide and hydride are clearly resolved on the nanostructured platinum electrodes. Because the nanostructured platinum electrodes have much higher surface area, they exhibit current responses approximately 600 times higher than that of the polished platinum electrode. From the area under these current−potential curves, the roughness factor of the nanostructured platinum electrodes shown in Figure 1b,c were estimated[16,17] to be 456 and 950, respectively. Table 1 summarizes the roughness factors of the films produced with three different cathodic charges. For each

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Table 1. Roughness Factors of Nanoporous Platinum

cathodic charge of zinc (c/cm^2)	0.32			0.16			0.10		
sample no.	I	II	III	I	II	III	I	II	III
roughness factor	356	335	348	121	133	127	76	69	81
roughness factor (avg.)		346 ± 10.6			127 ± 6.0			75 ± 6.0	

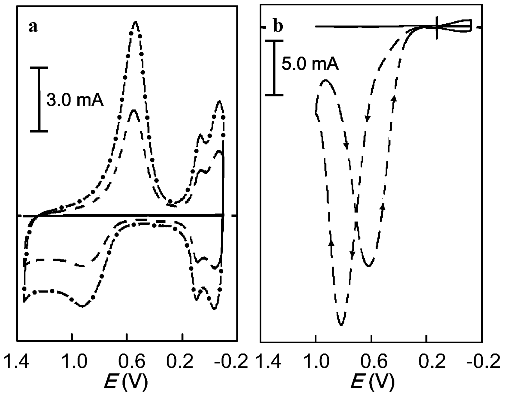

Figure 3. Cyclic voltammograms recorded (a) at (−, in the neighborhood of 0 mA) the electrode in Figure 1b; (- - -) electrode in Figure 1c; (-•-) electrode in Figure 1d in a 2 M H_2SO_4 solution at 200 mV s^{-1} between −0.15 and +1.35 V (vs Ag/AgCl); (b) at (−, in the neighborhood of 0 mA) the electrode in Figure 1b; (- - -) electrode in Figure 1d in a 2 M H_2SO_4 solution containing 0.5 mM methanol at 200 mV s^{-1} between −0.15 and +1.0 V (vs Ag/AgCl).

cathodic charge, roughness factors were estimated from three independent films. The data shown in this table indicate that the reproducibility of the films is fairly good.

The fabricated nanostructed platinum electrode was also tested for the electrooxidation of methanol. Typical cyclic voltammograms showing the electrooxidation of 0.50 mM methanol in 2 M H_2SO_4 is presented in Figure 3b. The voltammograms exhibit the same features as the reported electrochemical behavior of methanol on polished polycrystalline platinum.[18,19] The potential scan was started from −0.2 V toward 1.0 V and then reversed. Methanol oxidation commences at about 0.50 V, giving a peak at about 0.80 V. On the reverse negative-going scan, however, an oxidation peak occurs at about 0.55 V, and no reduction current was observed. This kind of anomalous behavior was attributed[18,19] to the adsorption and interactions of various intermediate species, such as CO_{ads} and OH_{ads}, at the electrode surface. As can be seen in Figure 3b, the much higher current density observed on the nanostructured platinum electrode compared with that on the polished platinum electrode indicates that the former has a much higher surface area. The mechanical strength of the nanostructured pt electrode was tested by sonicating it for a period of 20 min. No changes were observed in the cyclic voltammogram of a 2 M H_2SO_4 solution recorded at the electrode before and after the sonication, indicating a good mechanical strength of the nanostructured pt electrode.

Our results show that the electrochemical deposition and de-alloying of PtZn alloy in an acidic $ZnCl_2$-EMIC ionic liquid can provide a simple yet effective way to fabricate nanostructured platinum electrode with high surface area. Some of the general advantages of the method include (1) the nano-channel size can be manipulated by varying the quantity of PtZn surface alloy through the electrodeposition charge, (2) no corrosive acids or bases were used for the de-alloying, (3) extremely high working temperature is not required, and (4) applicability to any other system that forms surface alloy with Zn. This last characteristic we have begun exploring by performing the same kind of plating/de-alloying experiments on palladium. Upon de-alloying PdZn, we produced a highly porous Pd surface.

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