

Short communication

Fabrication by electrolytic deposition of platinum black electrocatalyst for oxidation of ammonia in alkaline solution

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Abstract

Platinum (Pt) black electrode was fabricated by electrolytic deposition for oxidation of ammonia. The electrocatalytic activity of the fabricated platinum black was characterized by cyclic voltammetry and atomic force microscopy observation. Pt black electrocatalyst enhances significantly the electro-oxidation of ammonia. The increased catalytic activity of Pt black electrode is attributable to both an increased effective surface area and the enhanced electron transfer reaction. However, the latter is predominant throughout the ammonia oxidation processes. The electrolytic depositing parameters affect the electrocatalytic activity of Pt black electrode. In particular, there is an optimal depositing potential to maximize the electrocatalytic activity. With the increasing depositing time and elevated bath temperature, the electrocatalytic activity of Pt black electrode increases continuously in this work.

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1. Introduction

Electrocatalytic technique for ammonia oxidation has attracted much attention since it eliminates environmental concerns of ammonia emission into air and, furthermore, offers a significant advantage in cost and convenience over pure hydrogen as an alternative fuel for clean energy supply [1–3]. Platinum and its alloys have been acknowledged to own unparalleled advantages over other noble metals for catalytic electro-oxidation of ammonia [4–9]. In authors' previous work [10], it was found that bright platinum could be used as an effective electrocatalyst for ammonia oxidation, with the cell efficiency for ammonia electrolysis up to 45%. Increasing ammonia and KOH concentrations further increased the electrolytic cell efficiency. Furthermore, it was confirmed that the ammonia electro-oxidation on Pt was controlled by the mass-transfer process of ammonia towards the electrode surface. However, the adsorption and desorption of N_xH_y intermediates

played important roles in ammonia oxidation and hydrogen evolution. Determination of the ammonia electro-oxidation kinetics depended on a comprehensive consideration of mass-transfer and adsorption/desorption processes.

It was reported [9] that the electrocatalytic activity for oxidation of ammonia could be significantly enhanced by fabricating platinum black electrode with an appropriate surface roughness. The increasing ammonia-oxidative current density was ascribed to the increase of the effective surface area for ammonia adsorption and oxidation. However, the overpotential for ammonia oxidation reaction was relatively high on Pt black, resulting in a high-energy input.

In this work, electrolytic deposition technique was used to fabricate Pt black electrode. The electrocatalytic activity of the fabricated Pt black electrocatalyst was characterized by cyclic voltammetry. Electrolytic depositing parameters, including depositing potential, temperature and depositing time, were adjusted to optimize the electrocatalyst performance. The surface morphology of Pt black electrode was characterized by atomic force microscope (AFM) to establish the correlation between the improved catalytic activity of Pt black electrocatalyst and the surface roughness of the electrode.

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2. Experimental

2.1. Fabrication of Pt black electrode

A platinum rod with a diameter of 0.13 cm (purity >99.999%, VWR Chemicals) was point-welded to a copper wire and then mounted by epoxy (BUEHLER) at 60 °C for 90 min. The electrode was consequently polished with 9, 6, 3 and 1 μm Al_2O_3 polishing suspensions (BUEHLER), and then cleaned by ethanol and deionized water.

The bath solution for electrolytic deposition of Pt black electrode was prepared with 4 mM H_2PtCl_4 (ACRÖS Organics) + 1 M HCl (analytical reagent, BDH Inc.). During electrolytic deposition, the Pt rod electrode was used as cathode, and a pure Pt wire (VWR Chemicals) as anode. The deposition was controlled potentiostatically.

2.2. Cyclic voltammogram measurements

Electrocatalytic activities of the fabricated Pt black electrodes were characterized by measurements of cyclic voltammograms (CVs). A three-electrode cell was used to measure CV through a PAR Model 263 potentiostat. The Pt black electrode was used as the working electrode, a platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The CV was measured in 0.1 M ammonia (extra pure, ACRÖS Organics) + 1 M KOH (analytical reagent, BDH Inc.) solution with a potential sweep rate of 5 mV s^{-1} .

Prior to and during tests, the solutions were purged with high-purity nitrogen gas (99.999%). Tests were performed at ambient temperature with the exception that the effect of temperature was investigated. The temperature of the solution was controlled through an OMEGA LHS-730 series digital hot plate/stirrer.

2.3. AFM characterization

The morphology of the fabricated Pt black electrode was characterized by a NanoWizard AFM (JPK Instruments AG, Berlin, Germany). Silicon cantilevers (Type BS-ElectriTap300, Budget Sensors, Sofia, Bulgaria) with a chromium/platinum conductive coating, a resonant frequency of 300 kHz, and a force constant of 40 N m^{-1} were used. Images of the sizes $15 \mu\text{m} \times 15 \mu\text{m}$ and $5 \mu\text{m} \times 5 \mu\text{m}$ were taken at a line rate of 0.2 Hz and a pixel density of 512×512 .

3. Results

3.1. CVs measured on Pt and Pt black electrodes

Fig. 1 shows the CVs measured on bright Pt and the fabricated Pt black electrodes in 0.1 M ammonia + 1 M KOH solution. It is seen that an anodic current peak was observed at -0.35 V (SCE). In particular, the peak current measured on Pt black, $2.25 \times 10^{-2} \text{ A cm}^{-2}$, was nearly 45 times higher than that measured on bright Pt of about $5.05 \times 10^{-4} \text{ A cm}^{-2}$. Furthermore, the cathodic current density was much higher on Pt black than on bright Pt electrode.

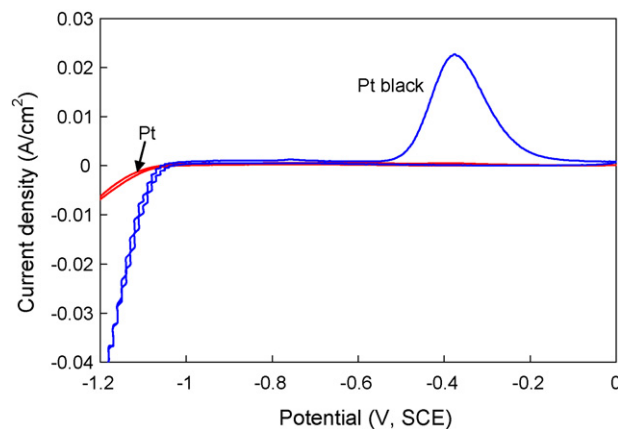


Fig. 1. CV measured on bright Pt and the fabricated Pt black electrodes in 0.1 M ammonia + 1 M KOH solution.

3.2. Effects of electrodeposition potential

Fig. 2 shows the CVs measured on Pt black electrodes fabricated at various depositing potentials for 20 min at room temperature. It is seen that the anodic current peak at -0.35 V (SCE) measured on Pt black electrode was dependent on the depositing potential. There was a maximum of anodic current when the depositing potential was -0.2 V (SCE). In particular, when the depositing potential was -0.1 V (SCE), the cathodic/anodic polarization behaviours were quite similar to those measured on bright Pt electrode. At -0.3 V (SCE), accompanying with the decrease of anodic current peak, the cathodic reductive current density decreased as well.

3.3. Effects of electrodeposition time

Fig. 3 shows the CVs measured on Pt black electrodes fabricated at -0.2 V (SCE) with the various depositing times at room temperature. It is seen that, with the increase of electrodeposition time, both the anodic current peak and the cathodic current density increased. The present result showed a continuous increase of current density with time within the test time period of 40 min.

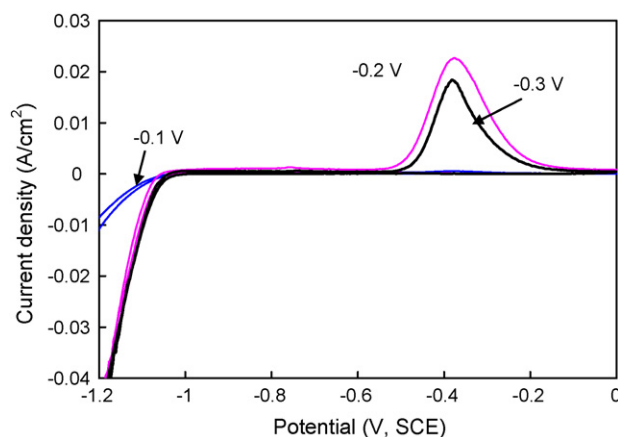


Fig. 2. CVs measured on Pt black electrodes fabricated at the various depositing potentials for 20 min at room temperature.

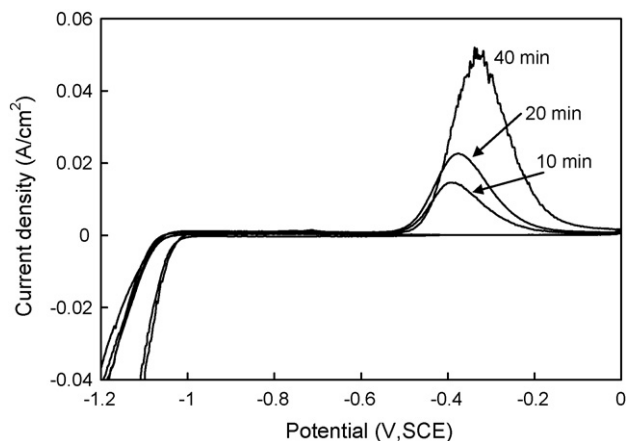


Fig. 3. CVs measured on Pt black electrodes fabricated at -0.2 V (SCE) with the various times at room temperature.

3.4. Effects of electrodeposition temperature

Fig. 4 shows the CVs measured on Pt black electrodes fabricated at -0.2 V (SCE) for 20 min at the various temperatures. It is seen that the anodic current peaks at -0.35 V (SCE) and the cathodic current density increased continuously with the elevated temperature.

3.5. AFM characterization of Pt black electrodes

Fig. 5 shows the AFM images of bright Pt and the fabricated Pt black electrodes with the various depositing times. It is apparent that the surface roughness of Pt black electrode was quite different from that of bright Pt. Furthermore, the AFM images indicate that the shape of Pt nuclei was generally three-dimensionally conical. At 5 min of electrodeposition, the deposited Pt nuclei were small and randomly distributed on the Pt electrode surface. After 10 and 20 min, Pt nuclei grew with many more additional nuclei initiated. After 40 min of deposition, the island-shaped growth of deposited Pt was observed, and the Pt electrode surface was completely covered by the deposited Pt.

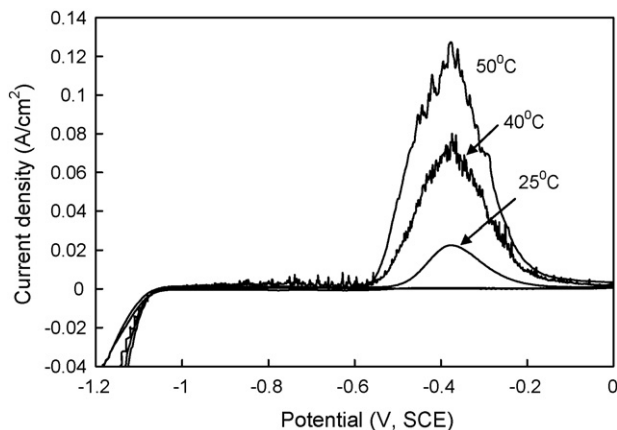


Fig. 4. CVs measured on Pt black electrodes which were fabricated at -0.2 V (SCE) for 20 min at the various temperatures.

4. Discussion

4.1. Electrocatalytic activity of Pt black electrode for the ammonia oxidation

It has been acknowledged [7,11,12] that the anodic current peak at -0.35 V (SCE) is attributed to the oxidation of ammonia to N_2 . Moreover, the oxidative reaction activity can be enhanced by utilizing electrode with an elevated surface roughness [13–15], which is due to the electrode scaling effect that is relevant to the increasing effective surface area for electrode reaction. Table 1 shows the fitted surface areas of Pt black electrodes fabricated at the various depositing times through a WSxM 4.0 software from the AFM images in Fig. 5. It is clear that the effective surface area for electro-oxidation reaction of ammonia increases with the depositing time.

To confirm the surface scaling effect, the effective surface areas fitted at a $50 \mu\text{m} \times 50 \mu\text{m}$ scale were chosen, and the relationship between surface area and the electrodeposition time is shown in Fig. 6. An approximately linear relationship was observed, indicating that the kinetic roughening during electrolytic deposition of Pt black obeyed a simple scaling law [11].

A further observation and comparison of the increasing effective surface area (Table 1) with the enhanced ammonia-oxidative current density (Fig. 1) shows that, from bright Pt to Pt black electrode depositing for 40 min, the effective surface areas of the electrodes increase from 1.02 to 1.12 times, while the peak current density increases from 5.24×10^{-4} to 2.27×10^{-2} A cm^{-2} , a 43-fold difference. Apparently, the enhanced electrocatalytic activity of Pt black electrode is not solely dependent on increase of the effective surface area.

The mechanism of the ammonia electro-oxidation, as proposed by Gerischer and Maurer [16], involves the diffusion, adsorption of NH_3 and then dehydrogenation steps of $NH_{3,ads}$ to N_{ads} as well as the recombination of two $NH_{x,ads}$, where partially dehydrogenated species of $NH_{2,ads}$ and NH_{ads} are active intermediates to give the final product of N_2 . It is believed that the diffusion of ammonia will not be affected by using Pt black as electrocatalyst. The increasing effective area of Pt black electrode enhances the ammonia adsorption, but at a minor level, as confirmed by AFM data fitting in Table 1. Therefore, the significant enhancement of electrocatalytic activity for oxidation of ammonia on Pt black electrode is due to its effect on the ammonia oxidation reaction, i.e., the interfacial electron transfer reaction.

The anodic Tafel slope for the ammonia oxidation reaction, b_a , is related to the charge-transfer coefficient, α , by

$$|b_a| = \frac{2.303RT}{\alpha nF} \quad (1)$$

where R is the gas constant, T is the temperature, n is the number of electrons exchanged in the electrode reaction, and F is the Faraday's constant. The charge-transfer coefficient α refers to the proportion of energy to overcome the activation energy barrier for occurrence of the anodic ammonia oxidation reaction under applied anodic polarization. The larger the coefficient, i.e., the smaller the absolute value of anodic Tafel slope, the more

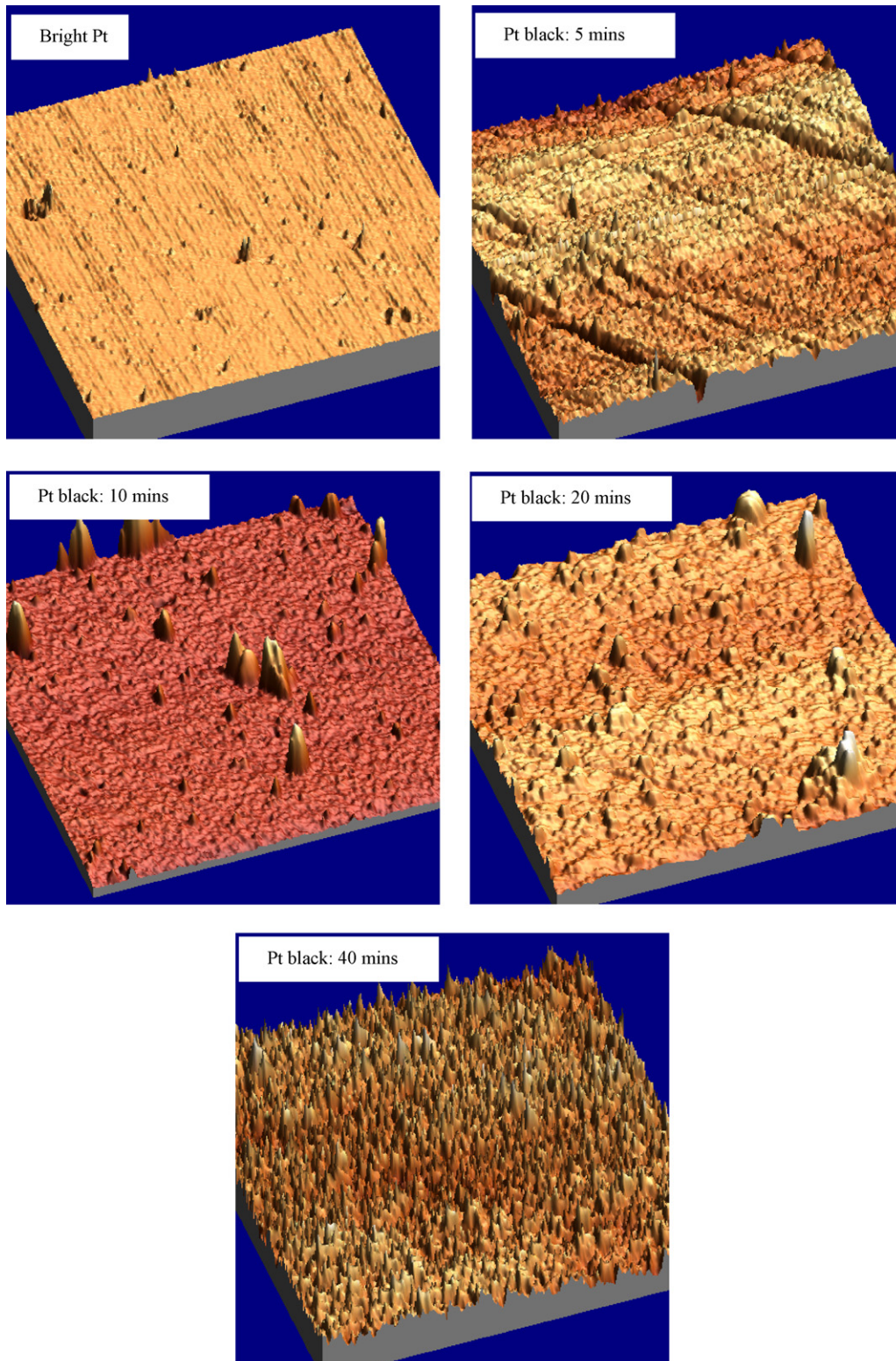


Fig. 5. AFM images of the bright Pt and the fabricated Pt black electrodes with the various depositing times.

the proportion of applied anodic polarization used for ammonia oxidation. Fig. 7 shows the anodic portions of the polarization curves measured on bright Pt and Pt black electrodes. The electron transfer coefficients were fitted from the curves to obtain 0.058 and 0.59 on bright Pt and Pt black electrodes, respectively.

Apparently, the activity for oxidation reaction on Pt black is up to 10 times higher than that on bright Pt electrode. Therefore, the significant improvement of electrocatalytic activity of Pt black electrode is attributable to both an increased effective electrode surface area and the enhanced electron transfer reaction.

Table 1
Effective surface area (μm^2) of the Pt and Pt black electrodes with various depositing times at 25 °C

	Bright Pt	Pt black 5 min	Pt black 10 min	Pt black 20 min	Pt black 40 min
50 $\mu\text{m} \times 50 \mu\text{m}$	2507.70	2512.17	2532.04	2547.69	2568.86
20 $\mu\text{m} \times 20 \mu\text{m}$	402.711	405.599	408.011	415.637	447.109
5 $\mu\text{m} \times 5 \mu\text{m}$	25.2509	26.7171	27.3591	27.4122	28.3553

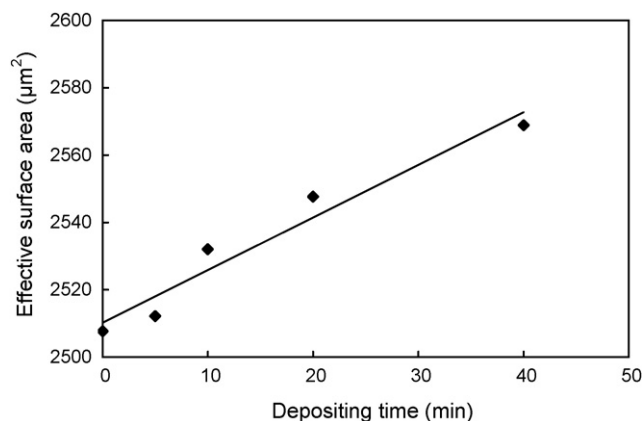


Fig. 6. Relationship between the surface area and electrodeposition time.

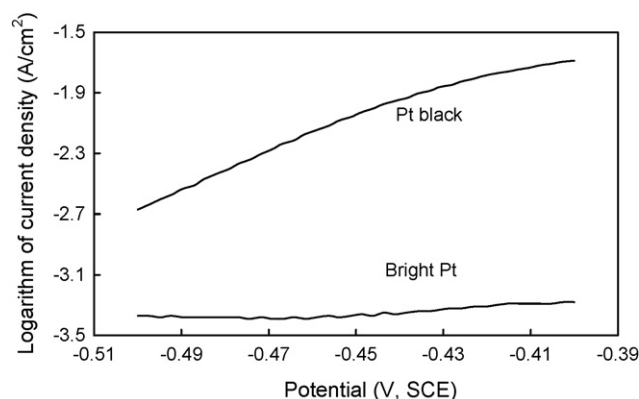


Fig. 7. The anodic portions of polarization curves measured on bright Pt and Pt black electrodes.

In particular, the latter is predominant in the ammonia oxidation processes.

4.2. Effects of the depositing parameters on electrocatalytic activity of the fabricated Pt black electrode

The present work shows that, when Pt black electrode was fabricated at -0.1 V (SCE) , the measured CV behaviour was identical to that measured on bright Pt electrode, indicating that there exists a threshold potential for electrolytic deposition of Pt black. Below the threshold value, the reduction of Pt ions and the deposit of Pt black will not occur because the required energy barrier is not overcome. The threshold potential is dependent on the Pt ion concentration and depositing temperature. However, when the depositing potential was sufficiently negative, such as -0.3 V (SCE) , the energy criterion becomes less important and the Pt depositing layer thickness increases. It is assumed that, accompanying the continuous deposition of Pt

layer on the previous layer, the Pt film becomes more compact, resulting in a decrease in effective surface area. Thus, the electrocatalytic activity of the deposited Pt black electrode decreases. Apparently, there is an optimal cathodic depositing potential, which is essential to maximize the electrocatalytic activity of the fabricated Pt black electrode in the present system.

It is also found in this work that the electrocatalytic activity of Pt black electrode increases with the depositing time. As shown in AFM images, with the increasing time, there are more Pt nuclei generating on the electrode, and furthermore, the deposited Pt nuclei grow and distribute to the whole electrode surface. It is thus expected that a saturation of Pt nucleation will be achieved after a certain time of electrodeposition, resulting in a relatively steady value of ammonia-oxidative current density in CVs.

The catalytic activity of Pt black electrode is enhanced when it is fabricated at an elevated temperature. In general, the increase of electrodeposition bath temperature accelerates both mass-transfer of Pt ions from the bulk solution towards the electrode surface (mass-transfer effect) and the reduction reaction on the electrode (activation effect), resulting in the enhancement of electrocatalytic activity of the electrode.

5. Conclusion

Fabrication by electrolytic deposition of Pt black electrocatalyst enhances significantly the electrocatalytic activity for the ammonia oxidation. The improved catalytic activity of Pt black electrode is attributable to both an increased effective surface area of the electrode and the enhanced electron transfer reaction. In particular, the latter is predominant in the ammonia oxidation processes.

The depositing parameters affect the electrocatalytic activity of the fabricated Pt black electrode. There is an optimal depositing potential to maximize the electrocatalytic activity of Pt black electrode. With the increasing depositing time and bath temperature, the electrocatalytic activity of Pt black electrode increases.

Acknowledgements

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