Electrochemical characterization of platinum black electrodeposited from electrolyte including lead acetate trihydrate

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The effect of lead acetate trihydrate on platinum black coating has been examined for the electrolyte free of or including lead acetate trihydrate using cyclic potential-current curves and a multi-pulse current measurement. The current-potential curves measured with a cyclic sweep of a current density in the electrolyte including lead acetate trihydrate show that no peak assigned to the reduction of Pt (IV) to Pt (II) in the process of electrode reactions is observed. The kinetic constant, the exchange current density and the double-layer capacitance, which can be determined from the measured potential-time curves, exhibit significantly different values for H_2PtCl_6 electrolytes free of or containing lead acetate trihydrate. In particular, the exchange current density for the electrolyte including lead acetate trihydrate is much larger than that for the electrolyte free of lead acetate trihydrate. These experimental results indicate that lead acetate trihydrate significantly enhances the electrode reactions in platinum black coating by mainly lowering a height of the energy barrier for the reduction of Pt (IV) to Pt (0) and by suppressing the reduction of Pt (IV) to Pt (II).

1. Introduction

Platinum electrodeposition has attracted a number of researchers in the field of fuel cell technology [1, 2]. Additives are widely known to play an important role in electrodeposition. For instance, lead acetate trihydrate in platinum electrodeposition has been employed for platinum black coatings [3-7] because a small amount of lead acetate trihydrate makes it possible to yield platinum black. The appearance of platinum electrodeposits from $PtCl_6^{-2}$ acid solution in the absence of lead acetate trihydrate usually has a color of grey rather than black.

In spite of many efforts to make clear the mechanism of lead acetate trihydrate, the effect of lead acetate trihydrate on platinum electrodeposition has been far from full understanding. Proposed models explain that Pb^{2+} ions absorbed on surfaces are behaved as an inhibitor to the growth of Pt islands or act as sites for electron transfer between the electrode and $PtCl_2^{6-}$. However, Feltham and Spiro [4] pointed out that the electrode kinetics in the presence of lead acetate trihydrate is little understood. Lately Layson and Columbia [6] proposed a model of Pb ions adsorbed on electrode surfaces that act as nucleation centers for Pt islands using scanning tunneling microscopy. The model seems to be different from Bernard's one [8] that Pb inhibits the growth of platinum deposits.

In this preliminary paper, as a first step to understand the electrode kinetics of platinum black in the presence of lead acetate trihydrate, from a macroscopic point of view, electrochemical investigation into the effect of lead acetate trihydrate on electrode reactions is made. In particular, the electrochemical reaction from $PtCl_6^{-2}$ to Pt is studied with cyclic voltammograms. The electrochemical parameters of the electrode reaction such as kinetic constant in electro-crystallization, the exchange current density and the double-layer capacitance in the presence of lead acetate trihydrate are also examined using a multi-pulse current measurement method [9]. These results are discussed in terms of the effect of lead acetate trihydrate on the electrode reaction.

In addition, instead of conventional cyclic voltammograms [4, 9, 10], current-potential curves with a cyclic sweep of a current density are employed for the two kinds of H_2PtCl_6 electrolytes with or without lead acetate trihydrate. Because of the high H_2PtCl_6 concentration, which enables us to make the electric resistance of the electrolytes lower and to hold the concentration of H_2PtCl_6 during the measurements, a sweep rate of the potential above millivolts per unit time yields high deposition rates.

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Hence, instead of a sweep of the potential, a sweep of a current density that allows us to control the deposition rate is chosen for the current-potential curve measurements.

The purpose of the present paper shows that the effect of lead acetate trihydrate on platinum black coatings is to suppress the reduction of Pt (IV) to Pt (II) and to lower a height of the energy barrier for the reduction of Pt (IV) to Pt (0).

2. Experimental setup

Experiments were performed using two kinds of electrolytes that included the following components (mol/L): electrolyte A; $H_2PtCl_6 \cdot 6H_2O$ 0.1 and $(CH_3COO)_2Pb \cdot 3H_2O$ 0.0, electrolyte B; $H_2PtCl_6 \cdot 6H_2O$ 0.1 and $(CH_3COO)_2Pb \cdot 3H_2O$ 0.0002. The concentration of H_2PtCl_6 in the electrolyte much higher than that in other studies[1] were used to make the electrical resistance of electrolyte lower and to hold the concentration in the electrolyte during the measurements. The low concentration of lead acetate trihydrate was chosen after the previous studies [3, 4].

Poly-crystalline nickel foils of 8 mm long and 8 mm wide and carbon square plates of a 50 mm side were prepared for cathode and anode electrodes, respectively. The area of the anode electrode was about 40 times as large as that of the cathode electrode. Hence, the resistance and capacitance in series with the anode electrode in the electrolyte can be ignored. These electrodes cleaned by a wet process were located parallel in the quiescent electrolyte maintained at 300K for the multi-pulse current measurements and for the current-potential with a cyclic sweep of a current density. The experimental setup is shown in Fig.1 (a).

The multi-pulse currents through an electrochemical cell as shown in Fig.1 (b) were provided with a programmable bipolar power source. The magnitudes of currents passing through the electrodes were chosen to hold the rising potential between the electrodes at millivolts. The potentials between the electrodes were recorded with a digital oscilloscope that had an input impedance of 10MΩ.

Instead of conventional cyclic voltammetry curves, the current-potential profiles with a sweep of a current density in the electrolytes mentioned above were measured using the saturated calomel electrodes (SCE). A sweep rate of millivolts per unit time caused high deposition rates for the high H_2PtCl_6 concentration in the electrolyte. Hence, a sweep of the current density that enabled us to

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control the deposition rate was employed instead of a sweep of the potential. The current-potential profiles were also recorded with the digital oscilloscope as well as in the multi-pulse current measurements.

3. Results and Discussion

3.1 Cyclic current-potential curves measured with a sweep of current densities

There have been a great number of reports on cyclic voltammetry curves in platinum electrodeposition. We have made experiments to find out how the effect of lead acetate trihydrate emerges in the cyclic potential-current curves. As mentioned in Introduction and Experimental setup, the concentration of H_2PtCl_6 in the electrolyte is about two orders of magnitude higher than that in the other studies [1, 9-12] to make the electrical resistance of electrolyte lower and to hold the concentration in the electrolyte during the measurements. In our preliminary experiments, a sweep of potential causes high deposition rates on cathode electrodes. Hence, a sweep of the current density, which allows us to control the deposition rate, is employed instead of a sweep of the potential.

Typical plots of the potential-current curves at a sweep rate of 10 and 20 μA/s are shown in Fig.2. The shallow peak A in Fig.2 (a) can be assigned to the reduction of Pt (IV) to Pt (II) ($PtCl_6^{-2} + 2e^- \rightarrow PtCl_4^{-2} + 2Cl^-$). The plateau B can be related to diffusion-limited transport for the negatively charged ions $PtCl_6^{-2}$. This indicates the presence of the rate of diffusion of $PtCl_6^{-2}$ equal to the reduction rate of Pt (IV) to Pt (II) ions. The limiting currents for a sweep rate of 10 and 20 μA/s are 0.25 and 0.17mA, respectively. The broad peak C corresponds to the adsorption of H atoms prior to the reduction of H^+ to H_2 gas [7]. In contrast with Fig.2 (a), it can be seen that the shallow peak A and the plateau B disappear in Fig.2 (b). Hence, Fig.2 suggests that lead acetate trihydrate inhibits the reduction of Pt (IV) to Pt (II) and enhances the deposition of platinum. This result has not been reported anywhere.

3.2 Estimate of electrochemical parameters in the electrode kinetics of platinum black

We have already reported in detail the multi-pulse current measurements [9] for determining the electrochemical parameters in electrodeposition. We here briefly describe the method. The reaction process in electro-crystallization of metal ions M^{+n} is given by

$$M^{+n} + ne^- \xrightarrow{k} M,$$

(1)

where k is the rate constant. For the multi-pulse current i_t passing through the cathode and anode electrodes shown in Fig.1(a), the transient potential η across the two electrodes in electrolytes at a temperature of T and at a time of t obeys the following equation,

$$\eta = -\frac{RT \, i_t}{nFi_O}\left(1 - e^{-\frac{nF \, i_o t}{CRT}}\right) + \frac{2\nu \, RT \, k}{nF\sqrt{\pi D}}\sqrt{t},$$

(2)

where ν is the stoichiometric factor, i_t is the amplitude of the pulse current, C is the electrochemical double layer capacitance, D is the diffusion coefficient, i_o is the exchange current density, F is the Faraday constant and R is the gas constant. The exponential term on the right-hand in Eq. (2) is related to a charging process of the electrochemical double-layer and the charge-transfer reactions. The square root of time represents the movements of ions by diffusion close to the cathode electrode.

Typical plots of the potential vs. time measured for the two kinds of electrolyte are shown in Fig.3, which indicates that a small amount of lead acetate trihydrate significantly affects the behaviors of the potential, that is, the rise-time and the impedance for the applied current densities. In this study, the electrical resistance of the electrolyte can be ignored owing to the high concentration of H_2PtCl_6. In comparison with the potential-time curve for the electrolyte free of lead acetate trihydrate, the rise time in Fig.3 (b) is shorter. The impedance in the electrolyte including lead acetate trihydrate is also smaller than that in the electrolyte free of lead acetate trihydrate. Hence, Fig.3 suggests that the addition of a small amount of lead acetate trihydrate significantly changes the reaction resistance and capacitance [13] regarded as an equivalent electric circuit for the electrode reactions.

In order to analyze these results quantitatively, it is necessary to determine three electrochemical parameters such as the kinetic constant, the exchange current density and the double-layer capacitance.

We present how to derive the fundamental parameters describing the kinetic electrode reactions from the measured voltage-time curves. According to Eq. (2), as time proceeds, η should be proportional to the square root of time. Fig.4 shows a plot of η vs. $t^{1/2}$ for the two kinds of electrolytes. Here, we define η_1 and η_2 as the first and second term on the right hand side in Eq. (2). The slope best fitted to the data in Fig.4 corresponds to $2RTk/nF\sqrt{\pi D}$ in Eq. (2), from which $k/\sqrt{D}$ and η_2 curves can be calculated for the values of n=4 and ν=1. Subtracting the calculated curve η_2 from the measured voltage-time curve in Fig.3, we have an exponential-type curve η_1 that corresponds to the first term on the right-hand side in Eq. (2). Fig.5 shows that the measured voltage-time curves are divided into two curves η_1 and η_2. Certainly, the curve η_1 in Fig.5 appears to be an exponential-type function with the voltage saturation. Thus, the voltage-time function represented by Eq. (2) is justified. The three constants in Eq. (2), RTi_t/Fi_o, nFi_o/CRT and $2RTk/nF\sqrt{\pi D}$ can be determined from the results in Figs.4 and 5.

These coefficients, RTi_t/nFi_o and nFi_o/CRT can be calculated from the η_1 curve and the exchange current density i_o and the capacitance C are also determined. In the result, Fig.5 shows that the measured potential-time curves can be well described by Eq. (2). The values of $k/\sqrt{D}$, the exchange current density i_o and the capacitance C are summarized in Table 1.

It can be seen from Table 1 that a small amount of lead acetate trihydrate increases the exchange current density, the reaction rate and the capacitance. The exchange current density is given by [14]

$$i_o = i_c \exp\left(-\frac{zF\alpha\Delta\phi}{RT}\right),$$

(3)

where i_c is the constant, α is the transfer coefficient and $\Delta\phi$ is the free energy change (energy barrier) due to the electrical work done by ions across the double layer. Substituting the values of i_o in Table 1 into Eq. (3), we have for the two different electrolytes and assuming α=1/2,

$$\Delta\phi_A - \Delta\phi_B \approx 63mV,$$

(4)

where $\Delta\phi_A$ and $\Delta\phi_B$ are the energy barriers for the electrolyte free of lead acetate trihydrate and those for the electrolyte containing lead acetate trihydrate. This indicates that lead acetate trihydrate lowers the height of the energy barrier.

In general, cathodic electrodeposition favors positively charged ions rather than negatively charged ions. The electrode reactions [1] in a solution of H_2PtCl_6 involves a reduction process of $PtCl_6^{-2}$ and $PtCl_4^{-2}$. The negative charges might make it difficult to promote the electron charge transfer reactions at cathode electrodes. The negatively charged ions such as $PtCl_6^{-2}$ and $PtCl_4^{-2}$ are transported only by diffusion to electrode surfaces through the Helmholtz layer. Hence, the electrode reactions in the electrolyte free of lead acetate trihydrate are expected to go slow kinetically and the exchange current density may become small. Eq. (4) and the rate constant in Table 1 show that lead acetate trihydrate enhances the electrode reactions by lowering the energy barrier.

Table 1 also shows that lead acetate trihydrate increases the capacitance of the double layer in comparison with the capacitance in the electrolyte free of lead acetate trihydrate, which suggests that more charges of diploes and ions due to the presence of lead acetate trihydrate might be accumulated in the Helmholtz layer [15].

Thus, the effect of lead acetate trihydrate on the electrode reaction in platinum black is found to lower the height of the energy barrier. Moreover, the fairly low concentration of lead acetate trihydrate in the electrode reactions is considered to be a surface effect rather than a bulk effect. However, the mechanism of the interplays between lead acetate trihydrate and chloroplatinic acid on electrode surfaces, is unclear in this study and further study will be needed.

4. Conclusions

We have investigated the effect of lead acetate trihydrate in platinum black electrodeposition using the cyclic potential-current curves and the multi-pulse current measurement. The current-potential curves measured with the cyclic sweep of the current density in the electrolyte including lead acetate trihydrate exhibit that the shallow peak assigned to the reduction of Pt (IV) to Pt (II) in the electrode reactions disappears. The kinetic constant, the exchange current density and the double-layer capacitance exhibit the significant differences between those values for the two kinds of electrolytes.

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The exchange current density in the electrolyte including lead acetate trihydrate is much larger than that in the electrolyte free of lead acetate trihydrate. These results suggest that lead acetate trihydrate lowers the barrier of energy as the surface effect and suppresses the reduction of Pt (IV) to Pt (II).

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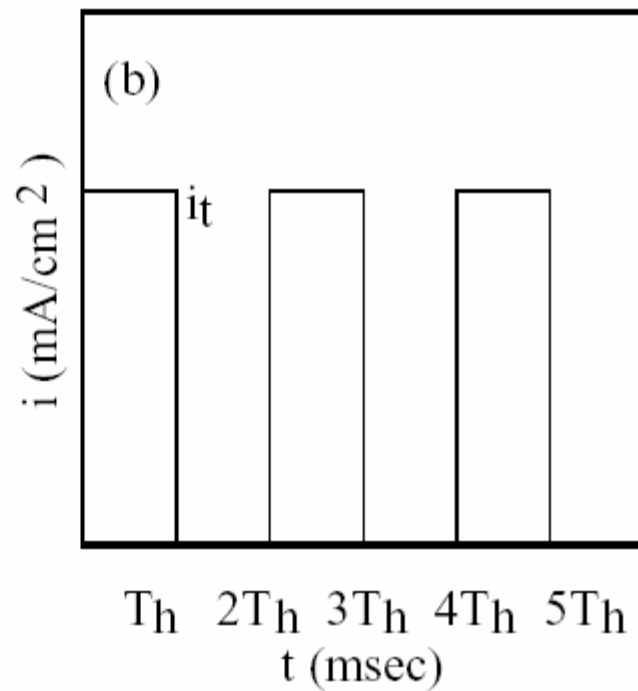
Figure Captions

Fig.1 Schematic diagram for measurements of transient potential curves for multi-pulse currents applied across the electrodes. The current densities were chosen to hold the rising potential between the nickel and carbon electrodes at millivolts.

Fig.2 Cyclic current-potential curves at various scan rates of current for the two different concentration of lead acetate trihydrate in the electrolytes. (a) in the case of the electrolyte A free of lead acetate trihydrate, (b) in the case of the electrolyte B containing lead acetate trihydrate 0.2m mol/L.

Fig.3 Typical potential-time curves for the multi-pulse currents. (a) i_t=0.0625mA/cm^2 and T_h=10msec for the electrolyte A free of lead acetate trihydrate, (b) i_t=1.79mA/cm^2 and T_h=1msec for the electrolyte B containing lead acetate trihydrate.

Fig.4 Plots of potential vs. $t^{1/2}$ for the two different concentration of lead acetate trihydrate in the electrolytes. The straight lines best fitted to the experimental data are shown. (a) in the case of the electrolyte A: lead acetate trihydrate 0.0 mol/L, (b) in the case of the electrolyte B: lead acetate trihydrate 0.0002 mol/L.

Fig.5 Plots of $t^{1/2}$ and exponential curves determined from the measured potential-time curves in Fig.3.

Table 1: Electrochemical parameters of platinum black for the two kinds of electrolytes.
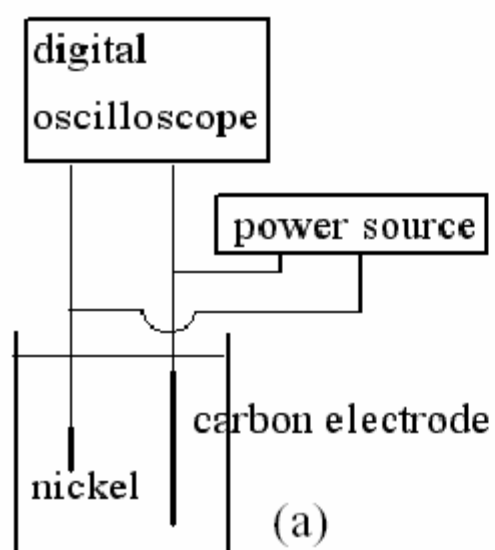
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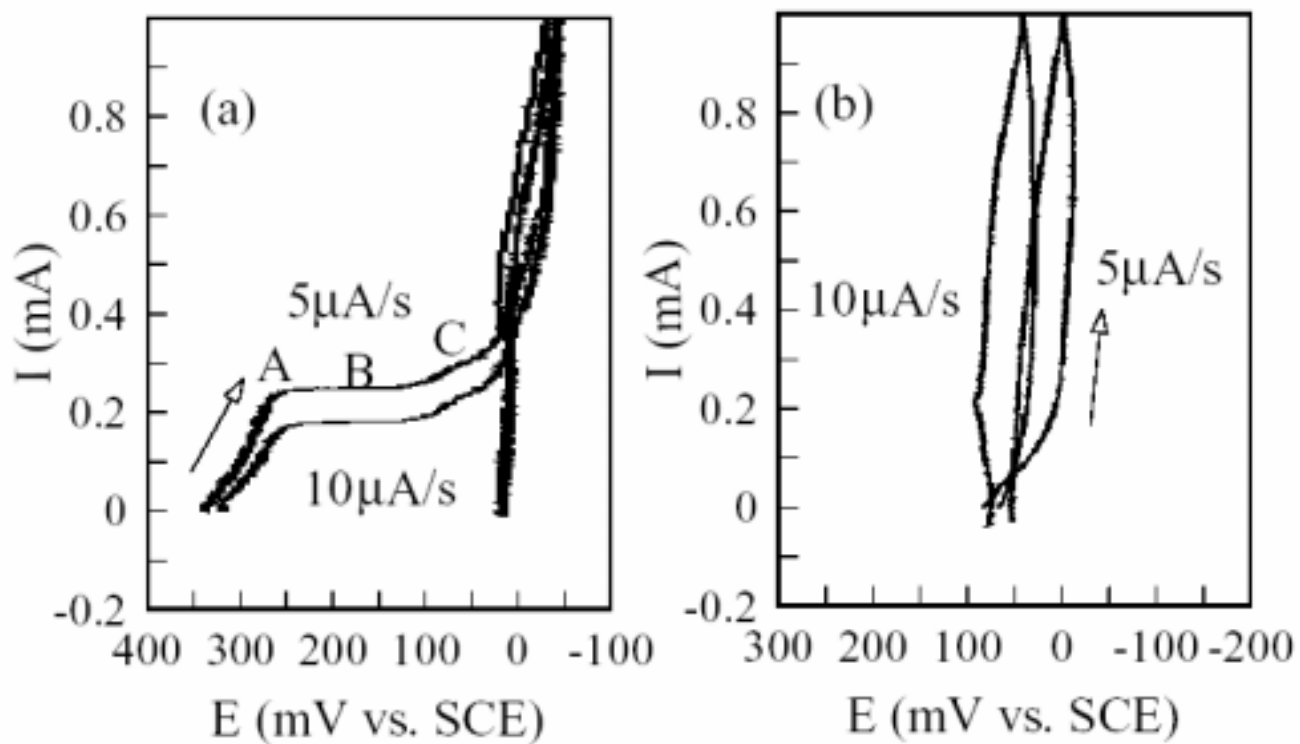
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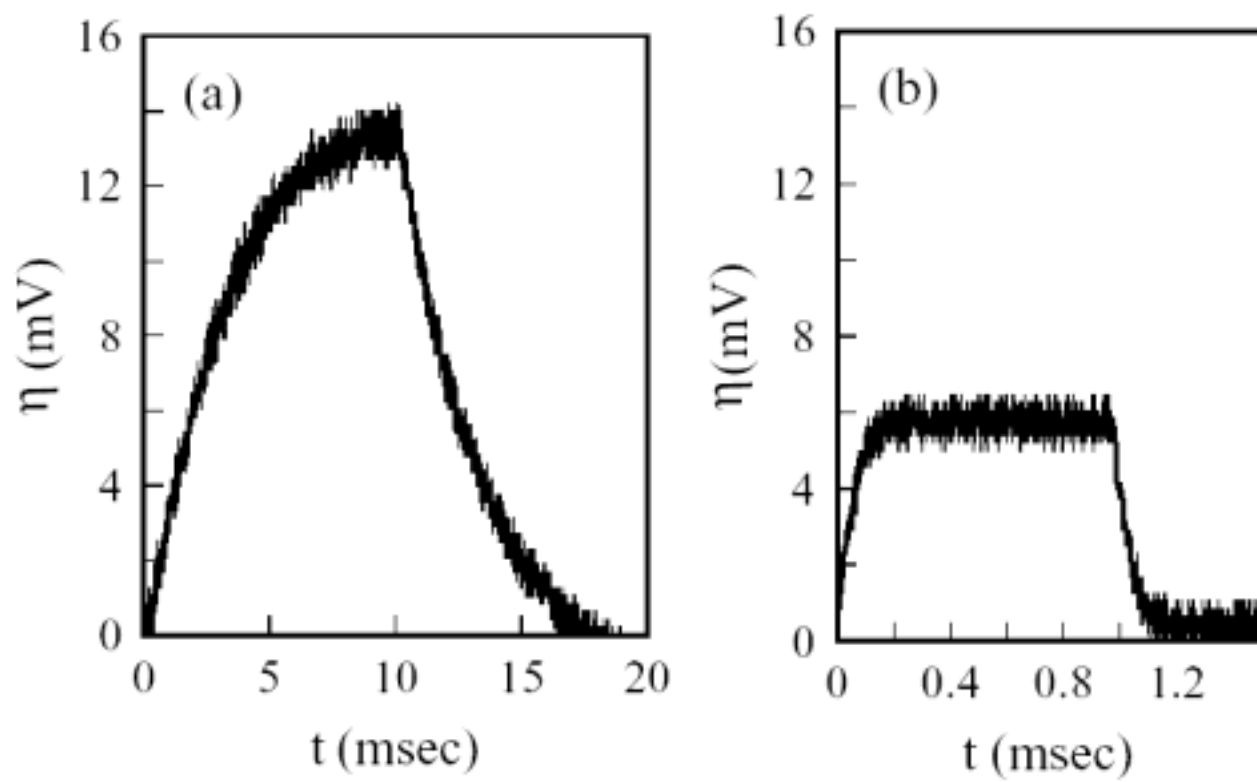
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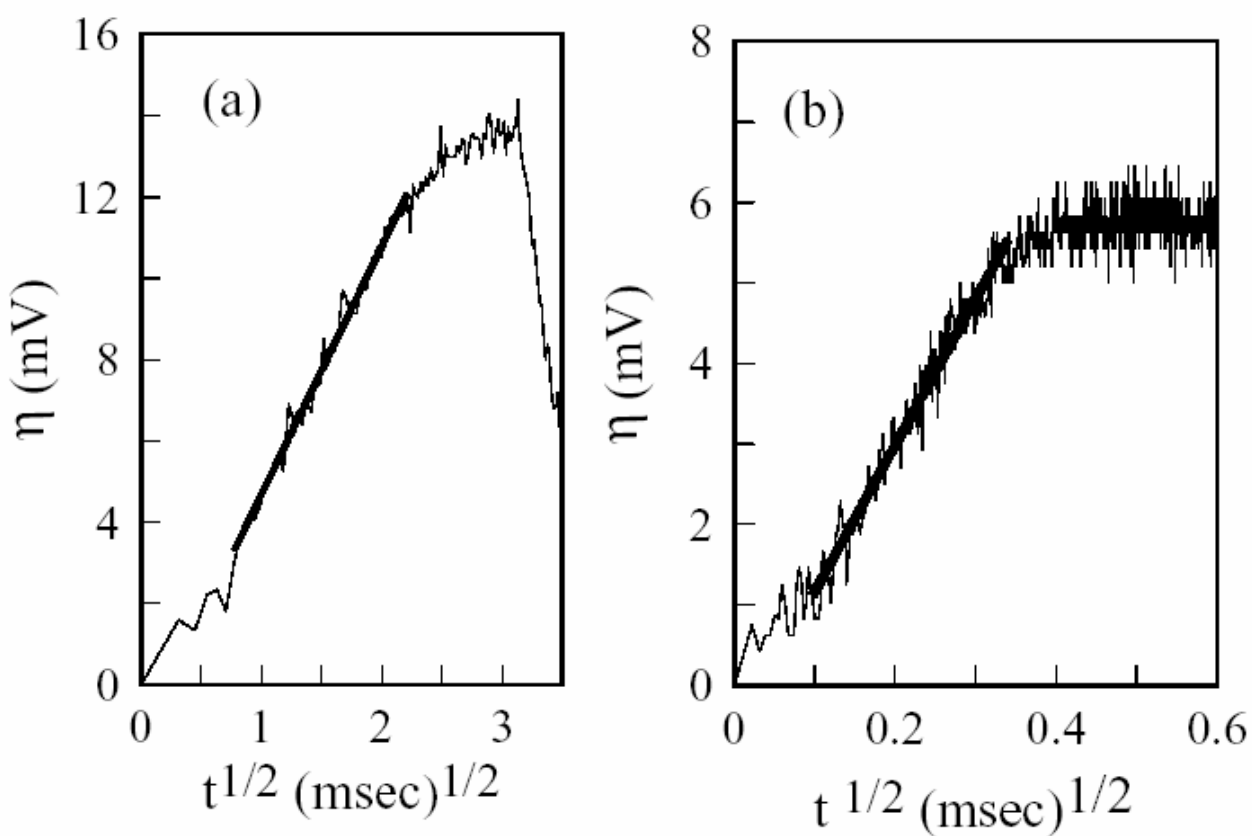
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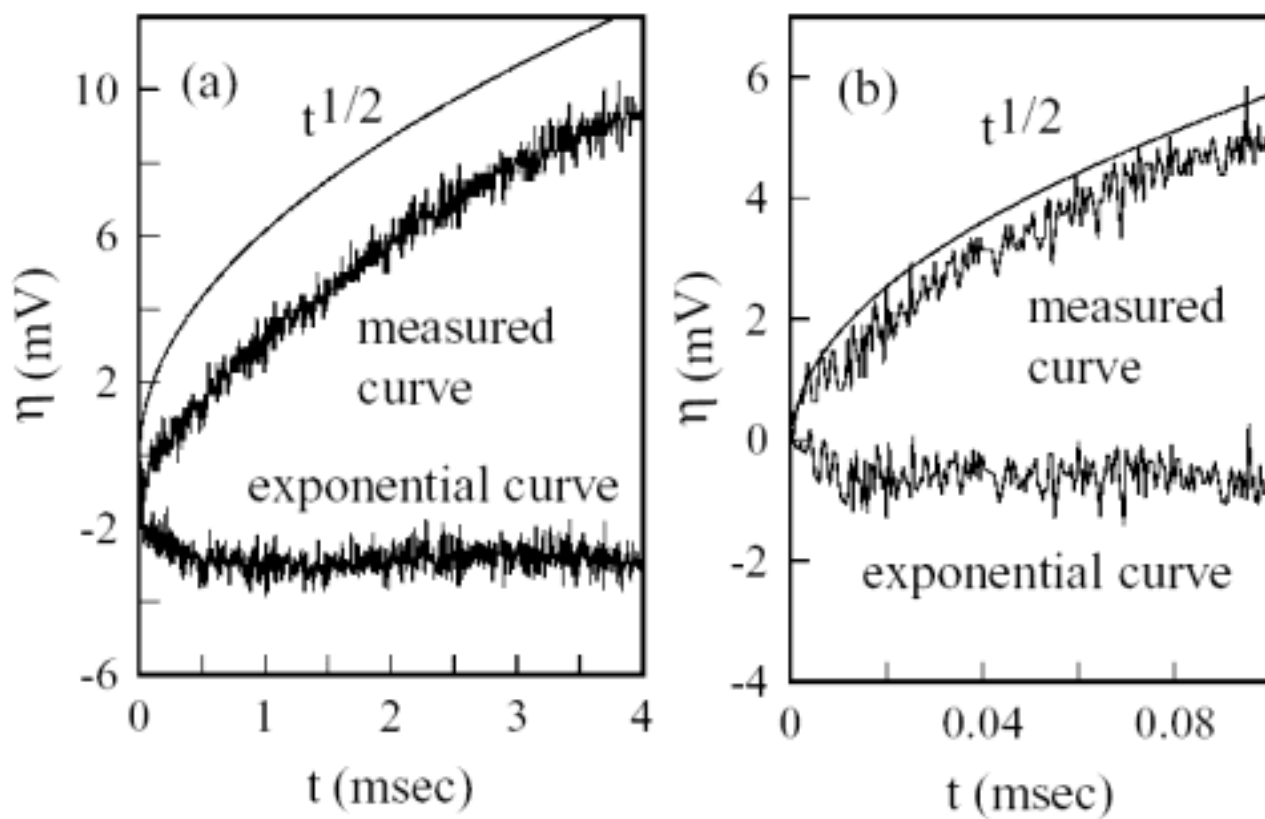
Fig.5 Plots of $t^{1/2}$ and exponential curves determined from the measured potential-time curves in Fig.3.

Electrolyte(mol/L)		$k/\sqrt{D}\left(\sec^{-1/2}\right)$	$C\left(\mu F/cm^2\right)$	$i_o\left(mA/cm^2\right)$
A:$H_2PtCl_6 6H_2O$	0.1,	24.1±0.9	2.44±0.83	0.141±0.014
$(CH_3COO)_2Pb\ 3H_2O$	0			
B:$H_2PtCl_6 6H_2O$	0.1,	78.6±3.4	18.2±6.2	18.7±1.7
$(CH_3COO)_2Pb\ 3H_2O$	0.0002			

Table 1: Electrochemical parameters of platinum black for the two kinds of electrolytes.