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Formation of Soluble Intermediate During the Electrochemical Crystallization of Lead Dioxide

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Details on the electrochemical formation of lead dioxide from aqueous plumbous ion are studied by measuring current-time behavior with potential step method at a rotating platinum electrode. A cubic law without induction period can be applied to the crystallization of lead dioxide in both acetate and nitrate media. In the course of the mechanistic study, the presence of a soluble intermediate during the nucleation step is clearly observed with a rotating ring-disk electrode. Decrease in the anodic ring current due to the reduction of soluble species formed during the anodic crystallization of lead dioxide at disk is detected.

Introduction

Lead dioxide has been used as the positive plate in lead-acid battery and as an inert electrode for various anodic processes. There are numerous monographs and papers including several reviews¹⁻⁷ concerning the behavior of this electrode.

Electrochemical kinetics for the formation of lead dioxide have been studied in terms of nucleation and crystal growth⁸⁻¹⁵. Fleischmann and Thirsk have reported that the current-time relationship on the formation and growth of lead dioxide by the oxidation of PbSO₄ in potentiostatic condition obeys a cubic law as⁹

$$i = ABN_0 t^3 / 3$$

where A is the potential dependent nucleation rate constant, B is the potential dependent rate constant of crystal growth, N_0 is the maximum number of nuclei, and t is time. Derivation of the cubic growth law can be made by assuming that the crystal grows three-dimensionally and that there is a uniform probability for the formation of nuclei⁸. These assumptions are proven to be acceptable by morphological studies with scanning electron microscope (SEM)¹³⁻¹⁶.

Fleischmann and Liler⁸ investigated the kinetics of deposition of α -PbO₂ from acetate solution on a platinum substrate. The cubic growth law could also be applied in this case, however, an induction period, t_0 , before nucleation had to be introduced as following to fit the experimental data,

$$i = ABN_0(t - t_0)^3 / 3$$

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It was also shown that the current varied as the square of time

$$i = BN_s t^2$$

when the nuclei were preformed at a relatively high potential. Fleischmann *et al.* tested this mechanism by applying repetitive square pulses of potential. So a series of potential dependent relaxation time for the nucleation and crystal growth processes were obtained¹².

Barradas and Contractor^{13,14} have examined the cubic growth of electrodeposited PbO₂ on a glassy carbon electrode in acetate medium. No induction period appeared to be necessary to account for their results in terms of cubic law. Ramamurthy and Kuwana¹⁵, however, had to introduce the induction period to fit their data to cubic law. They also used a glassy carbon electrode as a substrate in acetate solution. But, they interpreted the induction period as the time span in the constant current region during nucleation. This concept is quite different from that of others mentioned above.

These different results on the crystallization of lead dioxide prompted us to look into this system and in this paper, we report that no induction period is necessary to explain the current-time behavior in acetate and nitrate media. Also we report the experimental evidence of the presence of soluble intermediates in the anodic crystallization of PbO₂ from plumbous ion using rotating platinum electrode. Even though we are not able to point the exact chemical nature of the soluble species at the moment, Pb(OH)₂²⁺ can be one of possible candidates. This Pb(IV) species has been suggested as an intermediate in their proposed mechanism without any experimental details by Fleischmann *et al.*¹¹. Recently, Chang and Johnson have noticed the presence of soluble species of Pb(IV) at a gold electrode in perchloric acid solution^{17,18}.

Experimental

Reagents

Nitric acid (25%) was Merck's Guaranteed Reagent (GR) grade and was used without further purification. Lead nitrate was Wako (Japan) GR grade and was purified by recrystallization in doubly distilled water. All solutions used in this study were prepared with the doubly distilled water. The second distillation was made from dilute alkaline permanganate with a water-droplet trap.

Electrodes

Working electrode. A rotating platinum ring-platinum disk electrode (DT6, Pine Instrument Co., Grove City, PA) was mainly used in this experiment. Its geometrical measurements were $r_1 = 0.764$ cm, $r_2 = 0.802$ cm, and $r_3 = 0.846$ cm with collection efficiency of 0.170.

The surface of electrode was polished with a silicon carbide paper and with the slurry of α -alumina and doubly distilled water on a polishing cloth (Microcloth, Buehler). The size of alumina used in the final polishing was 0.05 μ m and the electrode was always polished before each experiment.

Reference electrode. A reference electrode with β -form of lead dioxide deposited on platinum wire was prepared in 0.25 M lead nitrate and 1 M nitric acid. The β -lead dioxide was electrochemically deposited primarily with 1 mA anodic current for one second followed by repetitive application of 110 μ A anodic and 100 μ A cathodic currents alternatively with the interval of one second each for an

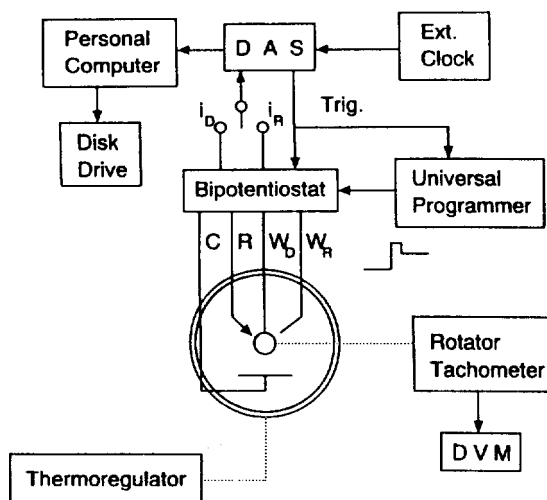


Figure 1. Schematic Diagram of the Experimental Setup for Rotating Ring-Disk Electrode.

hour. The reversible potential of the reference electrode in 0.25 M lead nitrate and 1 M nitric acid was +1.28 V *vs.* SCE at 25°C.

Counter electrode. A platinum foil of about 4 cm² was used as the counter electrode.

Instrumental setup

A laboratory-built potentiostat was used for potential step experiments and an EG & G Princeton Applied Research Corporation (Princeton, NJ) model 173 potentiostat and a model 175 universal programmer were used for linear sweep voltammetry. A home-made bipotentiostat assembly was attached to the model 173 for the measurement of ring current when rotating ring-disk electrode (RRDE) experiments were performed. For the rotating experiment, an ASR 2 rotator (Pine Instrument Co.) was employed.

All measurements were made with a data acquisition system (DAS)¹⁹ built in the laboratory, which was interfaced with a personal computer for data storage and process. All necessary software were programmed in the laboratory.

Figure 1 shows the instrumental setup for RRDE studies. The DAS was used for a main control unit, which triggered the potential jumping circuit in the potentiostat when the acquisition was needed. The acquired data in the DAS were transported to floppy disk for further processing. The rotation speed of RRDE was varied from 400 to 4,000 rpm.

When the double potential step experiments were performed, the universal programmer was used as a potential source and was synchronized with the DAS. The cell was thermostated at 25.0 ± 0.1°C with a thermoregulator (Haake E52).

Results and Discussion

As shown in Figure 2, crystallization rate, $k = ABN_s/3$, depends upon the rotation speed in case of potential step experiments. When the rotation speed increases to 4,000 rpm from stationary electrode, the total current flowing is not only small at a given time but the rate itself is slow. Figure 3 shows the effect of prenucleation time at the potential of +400 mV *vs.* β -PbO₂, growing potential of +200 mV with the rotation speed of 400 rpm. Almost no increase in current

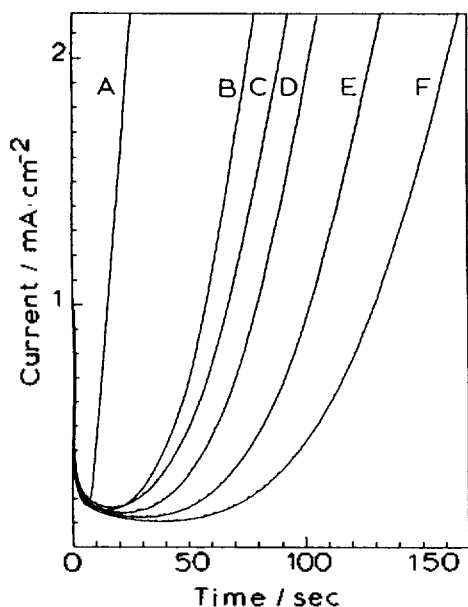


Figure 2. Dependence of Current-Time Behavior at Platinum Disk Electrode on Rotation Speed. Solution; 0.25 M $\text{Pb}(\text{NO}_3)_2$ and 1 M HNO_3 , Applied Potential; +200 mV vs. $\beta\text{-PbO}_2$, Acquisition Rate; 5 Hz, Rotation Speed; A) 0 rpm, B) 400 rpm, C) 600 rpm, D) 1,000 rpm, E) 2,000 rpm, and F) 4,000 rpm.

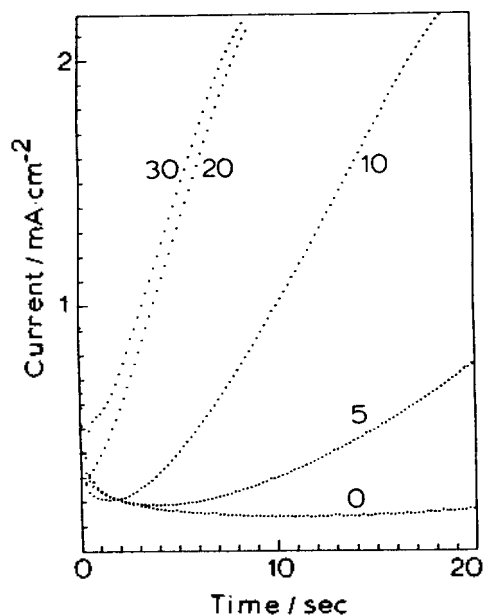


Figure 3. Effect of Prenucleation Time on Current-Time Behavior at Platinum Disk Electrode. Prenucleation at +400 mV, Crystal Growth at +200 mV vs. $\beta\text{-PbO}_2$, Rotation Speed; 400 rpm, Solution; 0.25 M $\text{Pb}(\text{NO}_3)_2$ and 1 M HNO_3 . Numbers are the corresponding prenucleation time in msec.

is observed within 20 seconds at the electrode without prenucleation. A rapid increase of current, however, appears with a short prenucleation period but no further increase of the growing rate with prenucleation made longer than

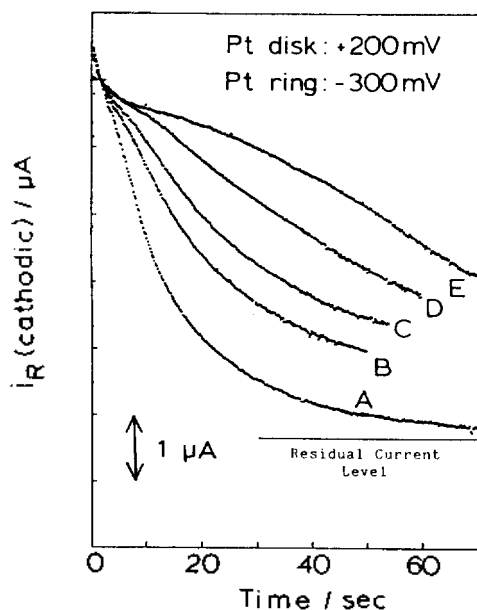


Figure 4. Variation of Ring Current against Time in RRDE. Disk Potential; +200 mV vs. $\beta\text{-PbO}_2$, Ring Potential; +300 mV vs. $\beta\text{-PbO}_2$, Solution; 0.25 M $\text{Pb}(\text{NO}_3)_2$ and 1 M HNO_3 , Rotation Speeds are A) 400, B) 600, C) 1,000, D) 2,000, and E) 4,000 rpm.

20 msec. Therefore, nucleation sites is believed to be saturated when the prenucleation period is longer than 20 msec.

Also it is observed that the rotation speed does not give any effect on the crystal growing rate, $k' = BN_o$, once the electrode is covered with a sufficiently large number of nuclei. Since the number of available nucleation sites, N_o , is independent of the rotation speed, it is clear that ω -dependent variable is only in the nucleation rate constant, A . Because the growing rate constant, B , in the cubic law equation is found to be independent of the rotation speed, the nucleation becomes difficult with increasing rotation speed.

The crystallization rate, $k = ABN_o/3$, can be calculated from the cubic growth law,

$$i = k(t - t_o)^3 + i_o$$

where i ; current observed at time t
 t_o ; induction period
 i_o ; residual current

and k varies from $0.45 \times 10^{-9} \text{ A sec}^{-3} \text{ cm}^{-2}$ at 4,000 rpm to $4.4 \times 10^{-9} \text{ A sec}^{-3} \text{ cm}^{-2}$ at 400 rpm. The decreasing rate of crystallization with rotation speed can be explained by the mechanism in which soluble intermediates are produced by heterogeneous reactions at the surface of electrode. The soluble species, thus, can be dispersed away from the electrode to the bulk solution by rotation²⁰.

The induction period is found to be almost zero in all rotation speeds in this experiment. Since the induction period is time needed for the reorientation of surface for the nucleation of lead dioxide, little such reorientation of Pt surface is believed to be necessary. The reported induction periods vary from zero to almost 300 seconds depending on the experimental conditions. Fleischmann *et al.* obtained the induction period of some tens of seconds in acetate solution at

the overpotential of +200 mV⁸. Chang and Johnson observed rather long induction periods of 1.5 to 5 minutes at gold electrode in perchloric acid solution¹⁷. Barradas and Contractor, however, have reported that no induction period is necessary to account for their results in acetate solution at glassy carbon electrode^{13,14}. Zero induction time was also observed at glassy carbon electrode in the course of crystallization of lead dioxide in nitric acid media¹⁹.

The existence of soluble intermediates is confirmed by rotating ring-disk electrode (RRDE) experiments where both ring and disk are made of platinum. Since the ring potential is held at -300 mV vs. Pb²⁺/PbO₂, the residual current at this potential in the absence of any disk electrode reaction is slightly anodic because of the formation of surface oxide and oxygen evolution at the ring electrode. Figure 4 shows that the cathodic ring current, however, immediately increases when the disk potential jumps to +200 mV from zero. And then the ring current is gradually recovered back to the initial residual value with time while the anodic deposition is in progress at the disk electrode.

The anodic ring current due to the oxidation of platinum surface and oxygen evolution can not be shielded by the anodic reaction at disk electrode because both of them are not controlled by bulk diffusion but controlled rather by charge transfer reaction²¹. Furthermore, it is unlikely that the reduction of oxygen which is produced at the disk to occur at this ring potential. Actually the background current in 1 M HNO₃ solution without lead nitrate changes only about 0.1 μA when the disk potential is changed from -280 mV to +220 mV while the ring potential is held at -280 mV.

It is, therefore, reasonable to believe that the flow of cathodic current is caused by the reduction of the soluble intermediate produced at the disk electrode. The rate of recovery to initial state also decreases with increasing rotation speed as in the case of the rate of crystallization at the disk electrode by single potential step. Because no cathodic ring current is observed at the electrode completely covered with PbO₂, the soluble intermediate is produced only at the platinum substrate. This means that the soluble intermediate is produced in the early stage of nucleation. Since the formation of PbO₂ nuclei is strongly hindered by the rapid rotation of the disk due to the convective diffusion of soluble intermediates, the slow increasing of the disk current with increasing rotation speed is observed. This is because of the slow nucleation rate at the fast moving electrode. The slower is the nucleation rate, the harder the electrode substrate can be covered with PbO₂. This is why the cathodic ring current decreases rapidly with the rotation speed of 400 rpm (Figure 4, A) compared to the slow decay in the case of 4,000 rpm (Figure 4, E). Recently, evidences of the soluble intermediate product of the nucleation process in the deposition of PbO₂ in perchloric acid solution have been clearly demonstrated by RDE¹⁷ and RRDE¹⁸ experiments. They have observed the rotation rate dependence of the induction period as well as the steady-state current value. The main difference with this study is that they have employed a rather low cathodic ring potential (0.2 V vs. SCE compared to 0.96 V in this study). Not only any soluble intermediate formed during the nucleation process, but also gold oxide can be reduced at the gold ring electrode at this potential.

Therefore, the transient behavior of the ring current provides little information on the deposition process. No cathodic current other than that from the soluble intermediate, however, in this study is observed.

Conclusions

No induction period is necessary to fit the current-time behavior into a cubic law, which indicates little reorientation of Pt surface is needed in the nucleation of lead dioxide. Also a soluble intermediate can be detected at the ring electrode in the course of electrochemical crystallization of lead dioxide with a RRDE. The soluble intermediate is observed only during the nucleation step.

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