

constant and a more negatively shifted half-wave potential. The hypersensitivity of Eu(III), which is easily measured from aqueous solution with a spectrofluorometer, may be served as a good indicator to estimate the relative strength of the complex formation of Eu(III) with a ligand and to understand the environment around Eu(III).

Conclusion

We have studied both electrochemical and fluorometric behaviors of aquo-Eu(III) and its complexes with carboxylate and sulfonate anions. Ligands, that are known to form inner sphere complexes such as acetate, propionate, and PSMA ions, form stronger complexes with Eu(III) and show more enhanced hypersensitivity of Eu(III). The increasing orders of the complex formation constant and the p value which are obtained by the electrochemical methods correlates well with the increasing order of the intensity ratio determined by spectrofluorometry.

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Mechanistic Studies on the Formation of Soluble Intermediate during the Electrochemical Nucleation of Lead Dioxide

Euijin Hwang[†], Keunchang Cho, Ho Il Kim, and Hasuck Kim*

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

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Different behavior on the formation of soluble intermediate was observed depending on the substrate employed during the nucleation of lead dioxide from plumbous ion using a rotating ring-disk electrode. It was found that no soluble intermediate was formed at glassy carbon electrode, while the presence of soluble intermediate could be detected at platinum substrate. From the different anodic behavior of two substrates, the formation of a probable Pb(III) soluble intermediate was suggested. A most probable nucleation mechanism at the platinum substrate involving a second order chemical reaction was derived on the basis of rotating disk electrode experiments.

Introduction

As mentioned in the previous paper¹, it is clear that there is a soluble intermediate during the electrochemical nucleation of lead dioxide at platinum substrate from plumbous ion. Even though some authors have suggested the nature of the intermediate, the formation mechanism of the soluble

intermediate during the nucleation has not been discussed. Fleischmann *et al.*² have suggested $\text{Pb}(\text{OH})_2^{2+}$ species as an adsorbed, not soluble, intermediate during the course of deposition of $\alpha\text{-PbO}_2$ at platinum substrate in acetate solution. Hampson *et al.*³ proposed a detailed mechanism for the formation of Pb(III) intermediate as $[\text{OH}\cdot\text{Pb}\cdot\text{OH}]^+$ during the deposition of bulk lead dioxide in perchloric acid. They also suggested $\text{PbO}_2(\text{H}^+)_2$ as an adsorbed intermediate. Recently, Chang and Johnson^{4,5} have claimed the presence of soluble species of Pb(IV) at gold electrode in perchloric acid solution.

[†]Present address: Korea Research Institute of Standards and Science, Dae Jeon 305-340, Korea

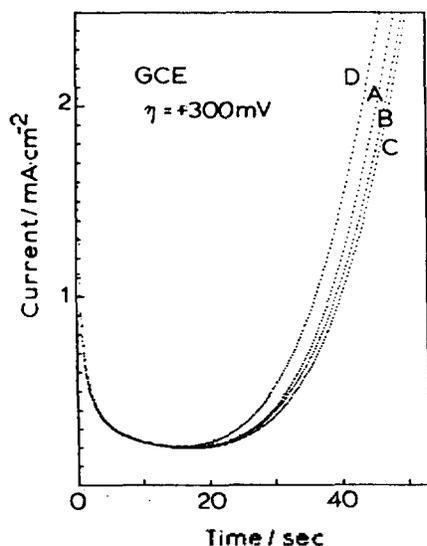


Figure 1. Current-Time Curve at Glassy Carbon RDE. Applied Potential, +300 mV vs. β -PbO₂; Solution, 0.25 M Pb(NO₃)₂ and 1 M HNO₃; A) 0 rpm; B) 400 rpm; C) 1000 rpm; D) 4000 rpm.

In this paper we discuss the different nucleation mechanism of lead dioxide involving soluble intermediates depending on the nature of substrate based on the experimental results with rotating ring-disk electrode and rotating disk electrode.

Experimental

The experimental details and apparatus were the same as those used in the previous paper¹. A rotating platinum ring-platinum disk electrode (geometrical measurements are $r_1=0.764$ cm, $r_2=0.802$ cm, and $r_3=0.846$ cm with collection efficiency of 0.170, Pine Instrument Co., Grove City, PA) and a rotating platinum ring-glassy carbon disk electrode ($r_1=0.500$ cm, $r_2=0.750$ cm, $r_3=1.000$ cm, and the collection efficiency is 0.372) were used.

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. β -form of lead dioxide deposited on platinum wire prepared in 0.25 M lead nitrate and 1 M nitric acid was used as a reference electrode. A platinum foil of about 4 cm² was used as the counter electrode. The cell was thermostated at 25.0 \pm 0.1 $^{\circ}$ C with a thermoregulator (Haake E52).

Results and Discussion

The crystallization rate of lead dioxide at platinum substrate in 0.25 M Pb(NO₃)₂ and 1 M HNO₃ was substantially reduced with increasing rotation speed of the rotating ring disk electrode (RRDE) as mentioned in the previous paper.¹ Also a soluble intermediate can be detected at ring electrode in the course of nucleation at platinum substrate. On the other hand, at the glassy carbon electrode, the crystallization

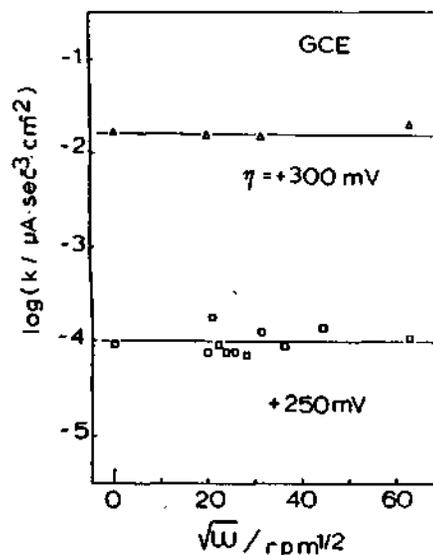


Figure 2. Effect of Rotation Speed on the Crystallization Rate Constant at Glassy Carbon RDE. Numbers are applied potential against β -PbO₂. Solution, 0.25 M Pb(NO₃)₂ and 1 M HNO₃.

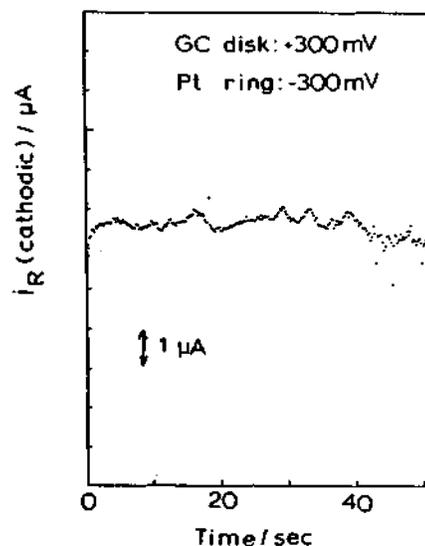


Figure 3. Variation of Ring Current against Time in RRDE. Glassy Carbon Disk and Platinum Ring; Disk Potential, +300 mV; Ring Potential, 300 mV vs. β -PbO₂; Rotation Speed, 1000 rpm; Solution, 0.25 M Pb(NO₃)₂ and 1 M HNO₃.

is not affected by the rotation speed as shown in Figure 1. The crystallization experiments at glassy carbon substrate were not as reproducible as those at platinum substrate probably because the exactly reproducible surface of glassy carbon is difficult to obtain even with repeated mechanical polishings. Figure 2 clearly shows the crystallization rate constant, k , does not change by the rotation speed, where k can be obtained from the cubic growth law ($i = kt^3$) as described in the earlier paper.¹

The variation of ring current was monitored at -300 mV vs. β -PbO₂ to check the existence of soluble intermediate during the anodic crystallization at the glassy carbon disk.

As shown in Figure 3, the ring current shows only fluctuations in residual current. It means that there is no soluble species that can be reduced at the ring. It suggests, therefore, that the process is different depending on which substrate is employed in the oxidation of Pb^{2+} either platinum or glassy carbon. This difference can be explained by the inherent characteristics of the anodic behavior of two substrates. At the anodic region of potential, platinum surface is easy to be covered with oxide layer and adsorbed hydroxyl radicals.⁶⁻⁸ The glassy carbon electrode, however, does not form such species readily.⁹⁻¹¹ Since the anodic overpotential for oxygen evolution at platinum is much smaller than that at glassy carbon and PbO_2 substrate,¹²⁻¹⁴ there is a good possibility that the formation mechanism of soluble intermediate involves the hydroxyl radical that is known as an adsorbed intermediate at platinum when oxygen evolution occurs⁶.

Some important mechanistic information can be drawn from RRDE results. If the formation rate of soluble intermediate is independent of rotation speed and the subsequent reaction is sufficiently slow, the concentration of soluble intermediate at the surface is inversely proportional to the square root of rotation speed, ω , because the mass transfer rate by diffusion is proportional to the square root of rotation speed of rotating disk electrode. Actually, the formation rate of soluble intermediate at platinum substrate turned out to be independent of the rotation speed. The transient peak of ring current at the early stage of crystallization was almost the same even though different rotation speed was used. The ring current due to the reduction of soluble intermediate was measured to about $5 \mu\text{A}$. Since the collection efficiency was 0.17 and the disk area was 0.458 cm^2 , the disk current due to the formation of intermediate must be around $60 \mu\text{A}/\text{cm}^2$. In the early stage of crystallization, the disk current is mainly due to the oxygen evolution and nucleation. The measured disk current was in the range of 100 to 200 $\mu\text{A}/\text{cm}^2$ in the early stage. That current, however, did not increase with increasing the rotation speed. It means that the formation of intermediate is not limited by the hydrodynamic diffusion of the reactant, but by kinetics of the formation reaction.

The subsequent reaction of soluble intermediate is nucleation process at the surface of platinum electrode. It is well known that the nucleation is very slow in the potential region where cubic crystal growing law can be applied.¹⁵ So it is reasonable to believe that the surface concentration of intermediate is proportional to $\omega^{-1/2}$. Because both the bulk crystal growth rate constant, B , and the number of nucleation sites at platinum substrate, N_0 , do not depend on the rotation speed, the change of overall rate constant in crystal growing, $k = ABN_0/3$, with varying ω must be due to the change of nucleation rate constant, A . If the subsequent nucleation process of the soluble intermediate is heterogeneous electrochemical reaction, the crystal growing rate constant, k , has to be proportional to the surface concentration of soluble intermediate. But, as shown in Figure 4, the plot of $\log k$ against $\log \omega$ gives a straight line with a slope of -0.93 . Thus the rate must be proportional to $(\omega^{-1/2})^2$ and the rate determining step has to be a second order chemical reaction.

One of the probable mechanisms of the second order chemical reaction in nucleation is two intermediates are for-

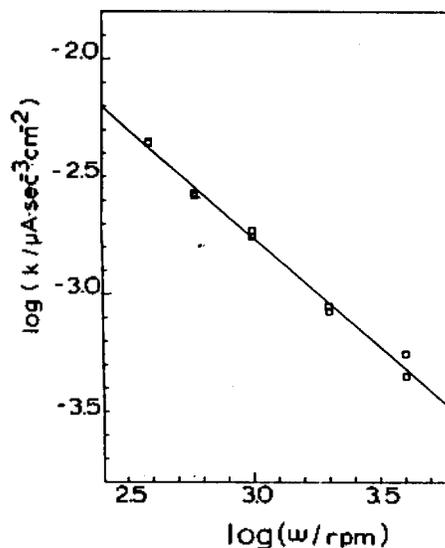
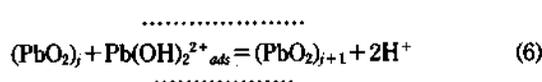
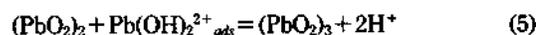
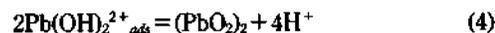
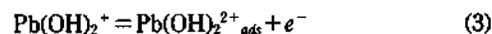
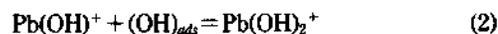
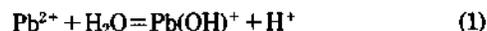


Figure 4. Plot of $\log k$ vs. $\log \omega$ at Platinum RDE. Solution, 0.25 M $\text{Pb}(\text{NO}_3)_2$ and 1 M HNO_3 ; Applied Potential, +200 mV vs. $\beta\text{-PbO}_2$.

ming a germ at the nucleation site as a nucleus that starts to exhibit the character of bulk crystal. However, it is unlikely that two soluble intermediates form a nucleus by homogeneous chemical reaction because the three-body collision at a nucleation site cannot occur with high probability. The reaction mechanism, therefore, involves the adsorbed intermediate that will form a nucleus by a second order heterogeneous chemical reaction. The presence of adsorbed intermediates such as $\text{Pb}(\text{OH})_2^{2+}$ and $\text{PbO}_2(\text{H}^+)_2$ has also been suggested by other authors.²⁻⁴ These adsorbed $\text{Pb}(\text{IV})$ intermediates can be formed by the electrochemical oxidation of the soluble $\text{Pb}(\text{III})$ intermediate or by chemical reaction of the soluble $\text{Pb}(\text{IV})$ intermediate.

Hampson *et al.*³ proposed that one of $\text{Pb}(\text{III})$ intermediates, $\text{Pb}(\text{OH})_2^+$, could be generated by the electrochemical oxidation of $\text{Pb}(\text{OH})_2$ that was in equilibrium with Pb^{2+} in solution. However, it seems reasonable to assume that the formation mechanism involves adsorbed hydroxyl radicals at platinum surface especially in the case of nucleation as mentioned above. The possible mechanism, thus, can be written as followings.



where $j = 3, 4, 5, \dots$

$\text{Pb}(\text{III})$ intermediates can be generated by the reaction step (2) and the rate determining second order chemical reaction would be the step (4). The nucleus that starts to show the

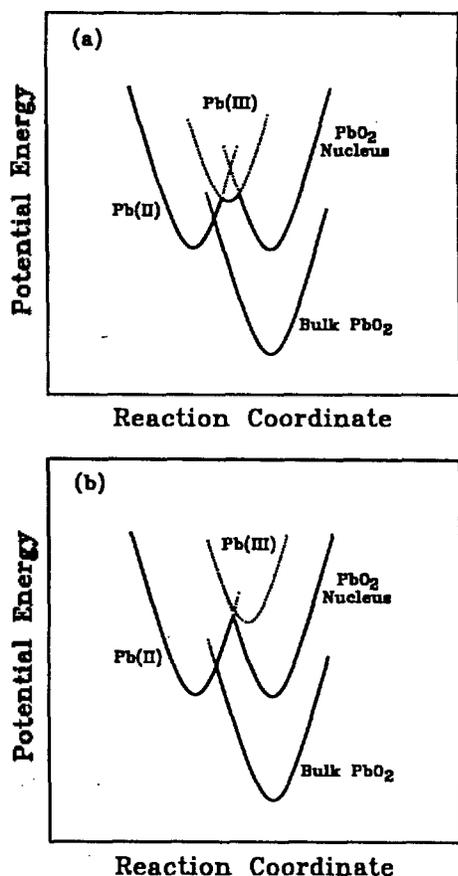


Figure 5. Reaction Models for Crystallization of Lead Dioxide (a) at Platinum and (b) at Glassy Carbon Substrate.

minimal characteristics of bulk crystal will be formed by reaction steps (4) through (6). In general, adsorbed species can go around the substrate by surface diffusion like ad atoms when metals are crystallized by the reduction of metal ions.¹⁶⁻¹⁹ The adsorbed ions are assumed to be free to wander over the surface and collide with other adsorbed ions or clusters of PbO₂ formed by preceding collisions as described in step (6). Cluster can be formed by each collision as dimer, trimer, or oligomer. Free adsorbed ions can also be formed by disintegration from clusters. Since it is very difficult to distinguish nucleus from bulk crystal, the concept of critical nucleus that has 50% probability of continuing to grow or disappearing has been introduced.^{16,20-27}

The existence of soluble intermediate during the nucleation at platinum substrate can be explained as shown in Figure 5. The potential energy of nucleus at platinum substrate is relatively higher than that of bulk lead dioxide. The soluble intermediate can exist if the potential energy of the soluble Pb(III) species is lower than the activation energy peak as shown in Figure 5(a). At glassy carbon substrate, however, the potential energy curve of soluble Pb(III) species must not meet the activation potential peak as shown in Figure 5(b) due to the lack of hydroxyl radicals at the surface.

Conclusions

A soluble intermediate can be detected only at platinum

ring electrode in the course of electrochemical crystallization of lead dioxide with a RRDE. Different mechanism must be involved in the formation of soluble intermediate because no such intermediate can be observed at glassy carbon electrode. A second order rate determining chemical reaction of two adsorbed Pb(OH)₂²⁺ to form a PbO₂ germ is proposed for a nucleation step in the electrochemical deposition of PbO₂ based on the rotation rate dependence at platinum substrate.

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Effect of Mn-addition on Catalytic Activity of Mn/In₂O₃ in Methane Activation

Jong Sik Park, Jong Ho Jun[†], Yong Rok Kim, and Sung Han Lee*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

[†]*Department of Applied Chemistry, Konkuk University, Chungju 380-701, Korea*

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Mn/In₂O₃ systems with a variety of Mn mol% were prepared to investigate the effect of Mn-addition on the catalytic activity of Mn/In₂O₃ in the oxidative coupling of methane. The oxidative coupling of methane was examined on pure In₂O₃ and Mn/In₂O₃ catalysts by cofeeding gaseous methane and oxygen under atmospheric pressure between 650 and 830 °C. Although pure In₂O₃ showed no C₂ selectivity, both the C₂ yield and the C₂ selectivity were increased by Mn-doping. The 5.1 mol% Mn-doped In₂O₃ catalyst showed the best C₂ yield of 2.6% with a selectivity of 19.1%. The electrical conductivities of pure and Mn-doped In₂O₃ systems were measured in the temperature range of 25 to 1000 °C at P_{O₂}'s of 1×10⁻⁷ to 1×10⁻¹ atm. The electrical conductivities were decreased with increasing Mn mol% and P_{O₂}, indicating the specimens to be n-type semiconductors. Electrons serve as the carriers and manganese can act as an electron acceptor in the specimens. Manganese ions doped in In₂O₃ inhibit the ionization of neutral interstitial indium or the transfer of lattice indium to interstitial sites and increase the formation of oxygen vacancy, giving rise to the increase of the concentration of active oxygen ion on the surface. It is suggested that the active oxygen species adsorbed on oxygen vacancies are responsible for the activation of methane.

Introduction

The conversion of CH₄ to C₂ hydrocarbon or to CO₂ is becoming important both for various technological applications and from a basic scientific point of view. Especially, the methane coupling reaction has become an active research area since Keller and Bhasin¹ reported the C₂ hydrocarbon production from methane over metal oxide catalyst in 1982. It has been known that high surface basicity of catalyst is required to achieve good C₂ hydrocarbon selectivity in the oxidative coupling of methane and alkali promoters can enhance the basicity of catalyst.^{2,3} The catalytic activities of metal oxides are closely linked to their nonstoichiometric composition and electronic properties. Ambigues and Teichner⁴ showed that correlations between the electrical conductivity and catalytic activity exist in metal oxide. Following their investigation of the conductivity effect of adsorbed oxygen on n-type zinc oxide, the catalytic effect on the other n-type and comparative results of p-type metal oxides led us to search for the correlations between oxide structure and catalytic activities. Therefore, it is believed that the study of catalytic activity of metal oxide in conjunction with its electrical properties is helpful to understand active sites and defects in the metal oxide. In the methane coupling reaction, a few results have been reported for the catalytic activity of metal oxide in relation to its electrical properties.

Indium sesquioxide has been known to be an n-type semiconductor and a nonstoichiometric compound with an In/O ratio larger than the ratio 2/3. Pure and impurity-doped indium sesquioxides find use in variety of applications such as electrodes in solar cells,⁵ fuel gas detectors,⁶ and heterogeneous oxidation-reduction catalysts.⁷ Otsuka *et al.*⁸ reported that In₂O_{3-x} showed an easy and reproducible redox cycle in the catalytic decomposition of water. Manganese atoms exist as multiple oxidation states in the oxide at high temperatures.⁹ It is expected that when Mn ions as impurity are doped into indium sesquioxide the oxide become either p-type or highly resistive n-type by self compensation effect in wide band gap semiconductors. In this work, Mn/In₂O₃ systems with a variety of Mn mol% were prepared to investigate the effect of Mn-addition on the catalytic activities of Mn/In₂O₃ systems in the oxidative coupling of methane. Methane conversions and C₂ selectivities of pure and Mn-doped In₂O₃ catalysts were investigated for the reaction and electrical conductivities of the catalysts were measured in the temperature range of 25 to 1000 °C at P_{O₂}'s of 1×10⁻⁷ to 1×10⁻¹ atm. XRD, XPS, SEM, DSC, and TGA techniques were used to investigate the structure and surface state of specimens. From the results, active sites on the surface and defects in the catalyst are discussed on the basis of solid-state chemistry.

Experimental Section

Mn/In₂O₃ catalysts were prepared from the mixture of In₂

*To whom correspondence should be addressed.