Electrochemistry and Conductivity Determination of PB

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Electrochemistry and Direct Conductivity Determination of Thin Films of Prussian Blue
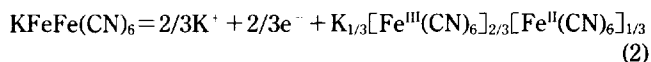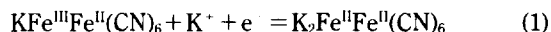
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Received February 13, 1995

Since much studies have been performed concerning the electrochemical behaviors and the practical applications of PB based devices, little has yet reported to investigate the best condition for the preparation for PB thin films. As considered some factors (peak shape, peak current, and peak separation) from the i-V curves, the optimal condition in the film growth were investigated under various immersion solutions. An electron-transfer processes of Fe^{2+}/Fe^{3+} and $Fe(CN)_6^{3-/4-}$ redox couples were considered by measuring the observed currents as a function of the rotation velocity. The standard heterogeneous electron-transfer rates for these films and bare Au disc electrode in 10^{-3} M Fe^{2+}/Fe^{3+} solution, applied at $+0.65$ V *vs.* SCE, were 6.14×10^{-3} and 7.78×10^{-3} cm/s, respectively, obtained using a rotating disc electrode. In case of the addition of potassium ion, the rate constants for these Fe^{2+}/Fe^{3+} system on thin films of PB and bare electrode were given a little high values. The electron transfer rates for 10^{-3} M $Fe(CN)_6^{3-/4-}$ were 4.55×10^{-3} and 6.84×10^{-3} cm/s, respectively. The conductivity as directly determined during obtained the voltammogram, was 2.2×10^{-7} $(\Omega \cdot cm)^{-1}$. This value is similar magnitude to that calculated from bulk sample.

Introduction

Prussian Blue (PB) is presently well-known material among the polynuclear transition metal hexacyanides. Since the first study of thin films of PB on various metal and semiconductor substrates was performed,[1] a variety of researches in the electrochemistry of PB and related hexacyanometallates have been carried out.[2~5] The thin films of PB can be reduced (-0.2 V *vs.* SCE) and oxidized ($+0.9$ V *vs.* SCE) in the solution containing potassium ion. Reduction of PB yields the colorless Everitt's salt (ES) and oxidation of PB to Berlin Green (BG) as shown in equation (1) and (2):

$$KFe^{III}Fe^{II}(CN)_6 + K^+ + e^- = K_2Fe^{II}Fe^{II}(CN)_6 \qquad (1)$$

$$KFeFe(CN)_6 = 2/3K^+ + 2/3e^- + K_{1/3}[Fe^{III}(CN)_6]_{2/3}[Fe^{II}(CN)_6]_{1/3} \qquad (2)$$

These reduced films can be electrochemically oxidized back to PB and cycled in electrolyte between the oxidized and reduced states with great stability. Several of PB analogues

are presumed to be the very similar structure because of their physical and chemical properties. These materials have the great potentiality of practical applications such as electrochromic devices,[6~8] electro-optical devices,[9,10] secondary solid cell,[11] highly reversible battery,[12~14] potassium ion-selective electrodes,[15~17] and electrocatalysts.[18~20] Further investigations are required to expand other technology areas and determine the best film growth of PB.

In this study the best condition for the preparation of PB thin films will be discussed. The rate constants of electron transfer for simple redox couples (Fe^{2+}/Fe^{3+} and $Fe(CN)_6^{3-/4-}$) on thin films of PB, electrochemically deposited under the optimal condition, will be described. The conductivity will be directly determined by measuring both the differential potentials and currents between the working electrode and the auxiliary electrode on simple redox couple (Fe^{2+}/Fe^{3+}).

Experimental

All experiments were carried out in a three electrode system consisting of working electrode, auxiliary electrode, and

reference electrode. The chemicals used were reagent grade and were not further purified. The Au disc electrode was used as the working electrode. The Saturated Calomel Electrode (SCE) and a Pt wire were used as a reference electrode and an auxiliary electrode, respectively. All solutions were freshly prepared with triply distilled water and deoxygenated with nitrogen for the electrochemical experiments. The rotating disc electrode (RDE) was prepared from 1 mm diameter Au wire fitted in a teflon rod with an external diameter of 1/4 inch and attached to a stainless steel rod. The electrodes were cleaned inserted in 0.5 M H_2SO_4 for electrochemical pretreatment and polished with alumina powder (0.3 μ) on a 8″ polishing cloth and rinsed thoroughly in an ultrasonic bath before measurements.

The growth of PB thin films have been performed galvanostatically (current density of 2 μA/cm^2) and potentiostatically instead of $FeCl_3$-$K_3Fe(CN)_6$ conventional system on the Au disc electrode. The immersion solutions are consisted of $Fe(NO_3)_3$-$K_3Fe(CN)_6$ changed different amounts in the range of 0.01 M to 0.03 M. The films were light blue and usually dried in air for 1 hr before measurements. The film thickness, estimated from the total charge for the reduction, was approximately 1000 A. Infrared spectra of thin films, deposited on conducting indium tin oxide (ITO) glass, were obtained by Nicolet 740 FT-IR spectrometer. The ITO glasses were obtained from LXD Inc., Bedford, OH, USA.

The kinetics of electron transfer rates for some redox couples (Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$) on PB thin films were performed using a Au rotating disc electrode of our laboratory design. The RDE was placed vertically in a solution and stirred by a variable speed motor controlled in the range of 1,000-7,000 rpm. The performance of these RDEs constructed in our lab was carried out to compare the rate constant for the iron (II/III) couple on a platinum RDE in 0.1 M H_2SO_4 of 3.9×10^{-3} cm^2/s with recent literature value of 4.3×10^{-3} cm^2/s.[21] The rotation speeds were continuously changed until the currents achieved stationary currents. The currents (as a function of rotation speed) were measured on the potentionstat after steady state conditions were achieved in the considered systems. All measurements were employed at room temperature. The electron transfer rates are calculated from the plot of the observed currents *vs.* the angular velocities.[22] The conductivity of thin film in the supporting electrolyte was first investigated during obtaining conventional voltammograms. All electrochemical measurements were made with a PAR model 273 potentiostat. The voltammograms were recorded by using a Linseis LY 1600 XY recorder.

Results and Discussion

The depositions of PB thin films have been considered with a variety of influencing factors which include galvanostatic method, potentiostatic method, molar concentration of ferric ion and ferricyanide solution, pH of the mixture solutions, and supporting electrolyte. The films deposited one of two procedures, potentiostatically at +0.5 V *vs.* SCE and galvanostatically with the low current density of 2 mA/cm^2, were confirmed the uniformly growth on conducting substrates by EDX (Energy Dispersion X-ray Analysis) and scan-

Table 1. Various immersion solutions for the investigation of the best preparation of PB thin film

Concentration	molar ration of $Fe(NO_3)_3$ and $K_3Fe(CN)_6$	solns adjusted at pH=2	solns adjusted at pH=3	solns no adjusted at pH=7
0.01 M	1:1	O	O	O
0.02 M	1:1	O	O	O
0.03 M	1:1	O	O	O
	1:5	×		O
	1:3	×		O
0.01 M	1:2	O		O
	3:1	O		O
	5:1	×		×

o: deposited film. x: failed to deposit the film.

ning electron micrographs.[23,24] The molar concentration and the composition of the supporting electrolyte based on the mixture solutions of $Fe(NO_3)_3$-$K_3Fe(CN)_6$ was little affected the film growth. So, We attempted to focus on some of the key factors effected on the film deposition. In this study, the films prepared at the constant current of 2 μA/cm^2 were rinsed with triply distilled water and dried in air over night. The mixture solutions of $Fe(NO_3)_3$-$K_3Fe(CN)_6$ were selected instead of the conventional system ($FeCl_3$-$K_3(CN)_6$) because of the removal of possible chloride contamination in the film growth. The EDX measurements were shown the presence of chloride ion which might be coordinated with ferric ion in the films and not an interstitial sites.[23,24] The presence of chloride ion demands an additional cation charge in the film growth which may be counterbalanced by K^+ or protons from acidic immersion solution. The molar concentration of the mixture solutions were employed in the range of 0.01 M to 0.03 M and different amounts of the solutions also applied. There are listed of these variable factors in Table 1. The mixture solutions were controlled neutral (no adjustment) and some acidic number (2 and 3) adjusted with 0.1 M HCl.

The voltammogram prepared under the best condition taken in 0.1 M KNO_3 is shown in Figure 1. The voltammograms for PB on Au disc electrode were obtained in the potential ranges of +0.6 V to −0.4 V with the scan rate of 10 mV/s. The mid-peak potential between cathodic and anodic peaks is found to be 0.45 V. As considered some factors (peak shape, peak currents, and peak separation) from the i-V curves, the optimal condition in the film growth were investigated. We have known that the films deposited in acidic mixture solutions are quite stable in the supporting electrolyte because the formation of $Fe(OH)_3$ above pH 6.4 may inhibit the film growth. Surprisingly, the films formed in neutral solution are also quite stable as those in acidic solution, but shown a large film resistance. These result can be accountable that incorporation of the protons into the lattice may be prohibited the film growth from exchanging of some resident ions or entering an interstitial sites. The mid-peak potential for these films, produced under various immersion
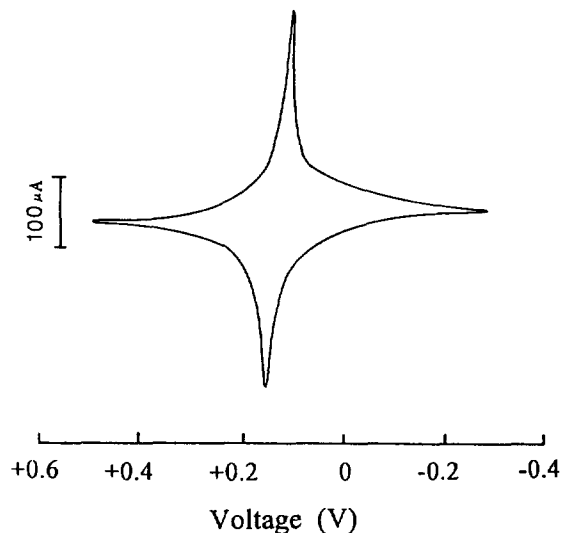
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Figure 1. Voltammogram of a PB thin film, prepared under the optimal condition, on a Au disc electrode in 0.1 M KNO_3. The scan rate was 10 mV/s.
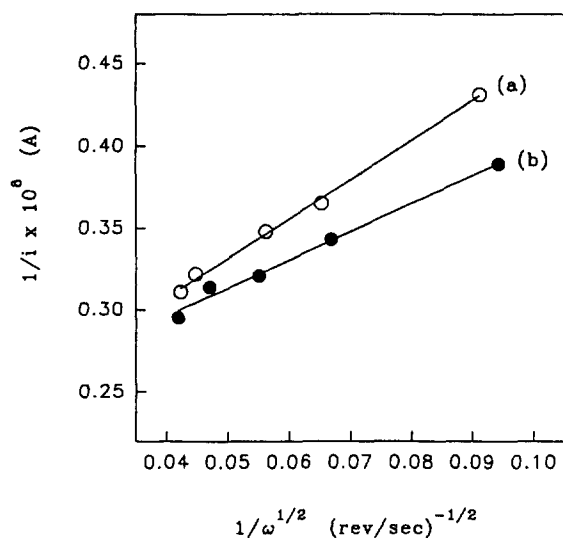

Figure 2. A plot of $1/i$ *vs.* $1/\omega^{1/2}$ obtained for both (a) PB thin film (b) bare Au disc electrode, applied at 0.65 V *vs.* SCE, in 10^{-3} M Fe^{3+}/Fe^{2+} solution.

Table 2. The heterogeneous electron transfer rate constants for some simple redox couples on both PB thin film and bare Au disc electrode

system	applied potential (V *vs* SCE)	thin film or bare Au disc electrode	k_s (cm/sec)
10^{-3} M Fe^{3+}/Fe^{2+}	0.65	with PB	6.14×10^{-3}
		bare Au	7.78×10^{-3}
	0.9	with PB	1.52×10^{-2}
		bare Au	1.91×10^{-2}
10^{-3} M Fe^{3+}/Fe^{2+} with 0.1 M KNO3	0.65	with PB	8.72×10^{-3}
		bare Au	1.14×10^{-2}
	0.9	with PB	2.28×10^{-2}
		bare Au	3.35×10^{-2}
10^{-3} M $Fe(CN)_6^{3-/4-}$	0.65	with PB	4.55×10^{-3}
		bare Au	6.84×10^{-3}
10^{-3} M $K_3Fe(CN)_6$	-0.2	with PB	2.28×10^{-2}
		bare Au	2.38×10^{-2}
10^{-3} M $K_4Fe(CN)_6$	0.65	with PB	1.13×10^{-2}
		bare Au	1.27×10^{-2}

solution, are almost same but the shapes and half-widths are a slightly different. In an attempt to define a good film, a sharp voltammogram with a small magnitude of the half-width at a scan rate of 1 mV/s was selected.[2] Finally, we should note that the best condition is selected with an excess of ferricyanide solution. The molar ratio of Fe^{3+} and $Fe(CN)_6^{3-}$ is given as 1 : 3 and the molarity of each solutions are 0.01 M. For the reduction process in Figure 1, the half-width is 29 mV for the cathodic scan and 41 mV for the anodic scan. This slight difference in half-width is characteristic and always observed. The peak shape in Figure 1 is similar to that of PB thin films prepared in conventional system.[2] The good films prepared under optimal condition should be influenced the improvement of any prac-

tical applications of PB based devices.

The oxidation of PB undergoes to BG at +0.9 V or higher positive potentials in supporting electrolyte. This process means the oxidation of ferrocyanide to ferricyanide. The infrared spectrum of PB prepared on conducting ITO glasses was shown the characteristic stretching frequency of CN at 2045 cm^{-1}. We investigated to get the spectra of completely oxidized state of BG as soon as the film was oxidized to hold at +0.9 V for 3 mins. Unfortunately, it is really hard to confirm the wholly oxidized form because BG is not quite stable and quickly back to PB. In case of BG, there are two extinctive bands in the IR spectrum; the CN stretching bands of ferricyanide at 2064 cm^{-1} and that of ferrocyanide at 2161 cm^{-1}. There are slightly some variations in the IR spectra of PB and BG in the stretching domain, compared to the published paper,[2] because the films were electrodeposited on different conducting substrates.

The kinetics of simple redox couples at both thin films and bare Au disc electrodes have been studied using a rotating disc electrode. The Fe^{2+}/Fe^{3+} and $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ redox couples were chosen to consider the electron transfer processes at the thin film/electrode interface and those in an ordinary reaction at the electrode/solution interface. Both cases are not catalytic but may be regarded as a single electron transfer medium. The electron transfer rate constants are calculated from the RDE experimental data obtained to be considered by both the diffusion and the electron transfer. A plot of the observed currents as a function of the angular velocities, shown in Figure 2, provide the electron transfer rate constants. The kinetic data are listed in Table 2. The standard heterogeneous electron-transfer rate constants for PB films and bare electrode, obtained in 10^{-3} M Fe^{2+}/Fe^{3+} under the control of the applied potential
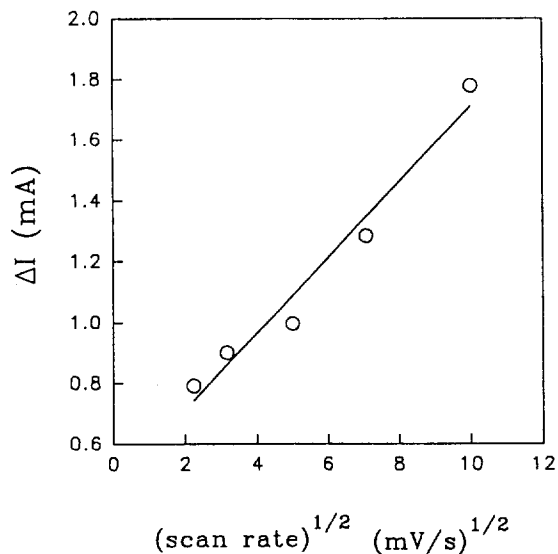
Figure 3. Differential currents *vs.* (scan rate)$^{1/2}$ for a PB thin film in 0.1 M KNO_3.

Table 3. The difference of potentials and currents between PB thin film and bare Au disc *vs.* scan rate in the mixture solution of 10^{-3} M Fe^{3+}/Fe^{2+}

Scan rate	Differences between PB and Au bare electrode	
(mV)	ΔI (μA)	ΔV (mV)
5	79.1	5
10	88.9	6
25	99.6	8
50	128.3	10
100	177.8	13

ΔI *vs* (scan rate)$^{1/2}$ has shown a good linearity in Figure 3. Some values of potentials and currents with the change of the scan rate, summarized in Table 3, are simultaneously measured by a Digital Voltmeter and a potentiostat. The conductivity, as calculated from the difference of potentials and currents at 0.5 V *vs.* SCE, is given as 2.2×10^{-7} $\Omega^- \cdot cm^{-1}$. The conductivity, directly obtained from thin film electrochemistry in simple redox couple (10^{-3} M Fe^{+2}/Fe^{+3}), has shown similar magnitude compared to that observed from bulk sample.[28] Therefore, this measurement can be applied one of the conductivity determination in thin film.

(+0.65 V *vs.* SCE), were 5.81×10^{-3} cm/s and 6.39×10^{-3} cm/s, respectively. Both in the presence of potassium ion and application a little high potential, the rate constants were shown slightly high values compared to that in Fe^{2+}/Fe^{3+} system. As considered a high conductivity in the presence of potassium ion,[25] the presence of potassium ion might be closely related to a freely easier electron transfer process at the film/electrode interface. The rate constants, obtained as applying at both -0.2 V in 10^{-3} M $K_3Fe(CN)_6$ and 10^{-3} M $K_4Fe(CN)_6$ may be much associated with the composition of ES and PB state, respectively. In case of $Fe(CN)_6^{3-}/$ Fe $(CN)_6^{4-}$, the rates were given as 5.81×10^{-3} cm/s and 6.39×10^{-3} cm/s, respectively. The rate constants of electron transfer obtained with PB thin films are slightly less than that obtained for the ordinary reaction at the bare Au disc electrode. The rate constants obtained on the bare Au disc electrode are concordant with earlier works.[26,27] Observing within an experimental error of ± 5%, it may be concluded that the redox electron transfer rate is essentially indifferent to whether the electrode are PB thin films or whether it is a bare metal substrate.

Direct determination of the conductivity in thin film electrochemistry has not previously investigated. The basic idea of the method is that the peak current increases approximately as the square root of the scan rate in the range between 5 and 100 mV/s and the film thickness might be constant value so that the conductivity will be directly evaluated if the current differences and the potential differences between the electrode and the solution as changing the scan rates were determined. There are two connections: one is related to be general connection to a potentiostat for determining the differential currents and the other included an external connection to the voltmeter for observing the differential potentials. The measurements of the differences of potentials and currents between thin films and bare Au disc are employed by the connection with the working electrode and auxiliary electrode while the voltammetry are undergoing in the conventional three electrode system. A plot of

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Structure and Physical Properties of YSe₁.₈₃

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Structure and Physical Properties of YSe₁.₈₃

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Received February 13, 1995

YSe₁.₈₃ was synthesized by vapor transport technique and its crystal structure was determined. The structure was isostructure of LaTe₂₋ₓ, which was layered structure consisting of two-atom thick layers of YSe with distorted NaCl-type structure and one-atom thick layer of Se. The substructure of YSe₁.₈₃ was tetragonal with space group of P4/nmm and $a = 4.011(2)$ and $c = 8.261(3)$ Å with final $R/R_w = 6.4/6.9\%$. The superstructure with $a_{super} = 2a$, $b_{super} = 6b$ and $c_{super} = 2c$ was found. The measurements of electronic and magnetic properties of this compound indicate that it is an electronic insulator and diamagnet.

Introduction

Layered transition-metal dichalcogenides have been extensively studied for their interesting low-dimensionality and resulting anisotropic properties.[1,2] Many phases of layered structures lead to rich intercalation chemistry with many potential applications. The electronic and magnetic properties of some dichalcogenide MX_2 (M = V, Nb, Ta, X = chalcogen), especially d^1 compounds, are closely related to structural transitions. It has been known that the structural transition in d^1 transition metal dichalcogenides is related with CDW (Charge Density Wave) instability and the single d-electron coupled with two-dimensional character was found to be the driving force for CDW.[3,4]

However, rare earth compounds such as DySe₂ and GdSe₂ are inverse analogies of d^1 transition metal dichalcogenides, since there is one hole in Se p-band. Many rare earth diselenides and ditellurides display nonstoichiometry owing to deficiencies of chalcogen sites. Some supercells[5] due to the ordering of chalcogen vacancies in this nonstoichiometric compounds were also reported. In a previous study, an incommensurate superstructure in DySe₁.₈₃ was found and it was assigned to be the CDW type.[6]

During the investigation of YSe system to find new low-dimensional compounds, a new phase, YSe₁.₈₃, was found. The structure of YSe₁.₈₃ is closely related to LaTe₂ and NdTe₃.[7] The structure of NdTe₃ can be described as consisting of two-atom thick layers of NdTe with distorted NaCl-type and

two-atom thick layers of Te with sequence of layers along the c axis being ··· Te NdTe, NdTe, Te, Te, NdTe, NdTe, Te ···. However, the LaTe₂ structure consists of the sequence of layers, ··· Te LaTe, LaTe, Te, LaTe, LaTe, Te ···. It has been known that the LaTe₂ phase displays a solid solution region up to near LaTe₁.₇ and that there is the tellurium deficiency resulted from the removal of Te from pure tellurium layers.

In the Weissenberg and rotation photographs of the titled compound, superstructure reflections were indicated, but these reflections were not strong enough to refine structure. Thus, only the substructure is reported in this work. The electronic and magnetic properties are also reported.

Experimental

Sample of overall composition Se/Y = 1.83 was prepared directly from elemental yttrium (99.9% Strem Chemicals) and selenium (99.999% Aldrich chemicals). The mixture of two elements was sealed in a evacuated quartz tube and heated at 800 ℃ for two weeks. The product obtained was homogeneous platelike polycrystals with reddish metal luster.

Single crystals of YSe₁.₈₃ were grown by chemical vapor transport technique with iodine. The starting elements, yttrium and selenium with the ratio of Se/Y = 2.0, and iodine (~1 mg/cm³) were sealed in a evacuated quartz tube, which then were placed in a two-zone furnace with temperature gradient of 30 ℃. The starting materials were placed at high