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Pulse electrodeposition of Prussian Blue thin films

P. Najafisayar, M.E. Bahrololoom *

Department of Materials Science and Engineering, School of Engineering, Shiraz University, 71348-15939 Shiraz, Iran

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ABSTRACT

The effects of pulse electrodeposition parameters like peak current density and frequency on the electrochemical properties of Prussian Blue thin films were investigated. Electrochemical Impedance Spectroscopy, Cyclic Voltammetry and Chronoamperometry tests were carried out on Prussian Blue thin films which were pulse electrodeposited on Indium Tin Oxide coated glass substrates. The results showed that increase in the peak current densities and using higher pulsating frequencies during electrodeposition decreases the charge transfer resistance of the thin films while the diffusion coefficient of electroactive species in the films is increased as a consequence of using the same pulsating parameters. In addition, pulse electrodeposition technique does not alter deposition mechanism and morphology of the Prussian Blue thin films.

1. Introduction

Application of Prussian Blue (PB) dates back to the 18th century when a German paint maker synthesized it chemically as very fine blue particles for applications such as pigment in paint production [1]. This material exists as a slightly soluble and also an insoluble compound in water with chemical formulae of $KFe^{III}[Fe^{II}(CN)_6]$ and $Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3$ respectively. Many years later, researchers showed in1978 that it was possible to create a thin film of PB compound on the surface of a conductive substrate using electrochemical techniques. This may be regarded as the onset of modern application of PB, rather than simple paint filler, based on its electrochemical properties [2,3]. It may include electrocatalytic and electrochromic properties of PB thin films which make it a good candidate in the production of biological sensors and are use in electrooptical applications.

The insoluble PB or ferric hexacyanoferrate compound has a cubic structure in which Fe^{III} ions are coordinated with N atoms and Fe^{II} ions are linked with C atoms, in this way the whole cubic framework is formed by Fe^{II}–C–N–Fe^{III} sequences. It should be noted that the insoluble PB is a hydrated compound in which water molecules are located in N vacancies or interstitial sites in its structure while soluble PB contains interstitial K^+ ions [4]. With such a structure which contains both low spin (Fe^{II}) and high spin (Fe^{III}) centers, PB can undergo redox reactions accompanied with color changes. It occurs as a result of changes in applied potential on a PB thin film while it is in contact with a solution containing electroactive species (K^+ or other compatible cations). This behavior is known as an electrochromic property in the literature and the reactions that contribute to electrochromism in PB are as follows [5]

$$KFe^{III}[Fe^{II}(CN)_6] + K^+ + e^- \Rightarrow K_2Fe[Fe(CN)_6] \quad (1)$$

$$Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3 + 4K^+ + 4e^- \Rightarrow K_4Fe_4[Fe(CN)_6]_3 \quad (2)$$

Blue — Colorless

$$Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3 + 3A^- \Rightarrow Fe^{III}[Fe^{III}Fe^{II}(CN)_6A]_3 + 3e^- \quad (3)$$

Blue — Green

Eqs. (1) and (2) describe the redox electrochromic reactions under which PB is reduced electrochemically to Prussian White (PW) compound at about 0.2 V applied potential with respect to Ag/AgCl reference electrode for soluble and insoluble PB respectively. Eq. (3) describes the electrochemical oxidation of PB to Prussian Green (PG) which occurs around an applied potential of 0.9 V with respect to Ag/AgCl reference electrode. In this equation A^- represents the anion which is in the electrolyte solution and can diffuse into PB thin film structure (like Cl^-). This behavior makes the PB compound to be considered as a suitable candidate in construction of solid state electrochromic devices [6,7].

As seen, electrochromic behavior of PB thin film is closely related to its electrochemical properties. So far, many researches have been conducted to investigate electrochemical characteristics of PB thin films. In majority of these cases, PB thin films were electrodeposited on conductive substrates using conventional three electrode Cyclic

Abbreviations: PB, Prussian Blue; PW, Prussian White; PG, Prussian Green; ITO, Indium Tin Oxide; EIS, Electrochemical Impedance Spectroscopy; CV, Cyclic Voltammetry; SEM, Scanning Electron Microscopy.

* Corresponding author. Tel.: +98 711 6133139; fax: +98 711 2307293.
E-mail addresses: pnajafi@shirazu.ac.ir (P. Najafisayar), bahrolom@shirazu.ac.ir (M.E. Bahrololoom).

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Voltammetry in solutions containing Fe^{III} and $Fe(CN)_6^{3-}$ ions [8–10]. In some cases thin films were also electrodeposited potentiostatically or galvanostatically [11–13]. On the other hand, some recent publications have demonstrated that application of pulsed currents in the electrodeposition process would affect the properties of the electrodeposited material [14]. For example, previous studies that were conducted by Najafisayar and Bahrololoom have shown that modification of pulse plating conditions in nickel electroplating process may result in some beneficial properties in electrodeposited coatings [15,16]. In this regard, and given the fact that current research works which are concerned with pulse electrodeposition of PB thin films would not be sufficient, so, in the present work it was tried to investigate the possible effects of pulsating conditions on electrochemical properties of electrodeposited PB thin films.

2. Experimental details

2.1. Thin film electrodeposition

PB thin films were electrodeposited on Indium Tin Oxide (ITO) coated glass ($A = 8\ cm^2$, $R < 90\ \Omega \cdot cm^{-2}$) using pulse electrodeposition technique. A square wave (on-off) pulsating current was utilized at various peak current densities of 15, 30, 60 and 120 $\mu A \cdot cm^{-2}$ at pulsating frequencies of 0.1 Hz, 100 Hz, 1 kHz and 10 kHz respectively. In order to investigate the effect of pulse electrodeposition technique on the resulting electrochemical properties of PB thin films, galvanostatic electrodeposition technique was also used in PB thin film preparation at current densities of 15, 30, 60 and 120 $\mu A \cdot cm^{-2}$ for 1500, 750,325 and 160 s respectively. The duty cycle in all pulse electrodeposition experiments was 50% and the deposition time was adjusted in each experiment in order to achieve approximately the same resulting film thickness. All PB thin films were electrodeposited from a bath containing 10 mM $FeCl_3 \cdot 6H_2O$, 10 mM $K_3Fe(CN)_6$ and 0.1 M HCl with pH of 2 at room temperature. A graphite rod was used as the anode in all electrodeposition processes. After electrodeposition, the samples were rinsed well with distilled water and stored in air for more investigation.

2.2. Electrochemical characterization

Electrochemical tests like Cyclic Voltammetry (CV), Chronoamperometry and Electrochemical Impedance Spectroscopy (EIS) were carried out in order to investigate electrochemical properties of PB thin films electrodeposited under various conditions. All electrochemical tests were carried out in a 0.1 M HCl:0.1 M KCl solution at room temperature using a potentiostat/galvanostat model Solartron 1287 in conjunction with a Solartron 1260 Impedance-Gain/Phase Analyzer (equipped with Corrware/Corrview 3.3a and Zplot/Zview 3.3a software). In all tests, a conventional three electrode cell was used with PB thin films on ITO glass as the working electrode, Ag/AgCl (3.0 M KCl) as the reference electrode and a Pt rod as the counter electrode. All as-deposited PB thin films were cycled 5 times between −0.2 V and 1.2 V at 20 mV/s scan rate before performing the electrochemical tests. For each specimen, EIS spectra were taken at a frequency range of 0.1 Hz to 10^5 Hz at 0.6 V DC potential with the amplitude of 10 mV. Cyclic Voltammetry tests were performed at a scan rate of 5 mV/s in order to investigate redox properties of PB thin films.

2.3. Particle size investigation

A dynamic light scattering particle size analyzer model Horiba LB-550 was used in order to investigate the size distribution of PB particles. To do so, 0.03 g of electrodeposited PB particles, which were scratched from the ITO glass substrate, added to 30 ml distilled water and ultrasonicated for 10 min to breakup agglomerates and obtain a uniform suspension. The selected refractive index for PB and dispersant were 1.606 and 1.333 respectively. Micrographs were taken from deposited PB thin films using a Cambridge S-360 Scanning Electron Microscope (SEM) at 20.0 kV operating voltage.

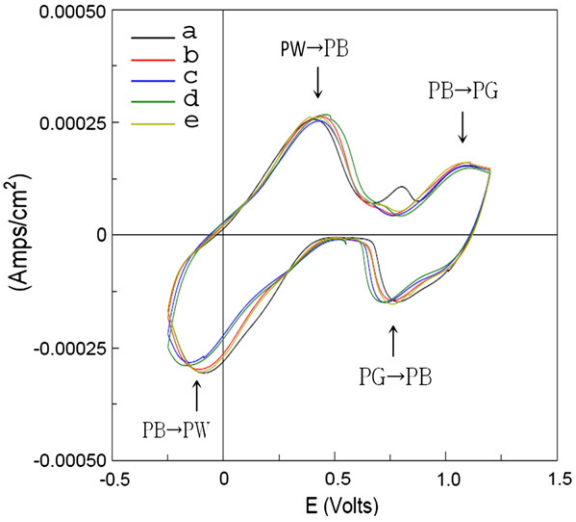

Fig. 1. Cyclic voltammograms of the PB thin films electrodeposited at a) 15 $\mu A \cdot cm^{-2}$ DC, b) 15 $\mu A \cdot cm^{-2}$, 0.1 Hz, c) 30 $\mu A \cdot cm^{-2}$, 100 Hz, d) 60 $\mu A \cdot cm^{-2}$, 1 kHz, and e) 120 $\mu A \cdot cm^{-2}$, 10 kHz. The curves were obtained after 5 cycles at 5 mV/s scan rate in 0.1 M HCl:0.1 M KCl solution.

3. Results and discussion

3.1. Cyclic Voltammetry

In general, during the electrodeposition process of Prussian Blue thin films, PB particles, that were formed as a result of electrochemical reduction of $FeFe(CN)_6$ and subsequent cation association in the electroplating bath, were attached to the surface in a colloidal manner

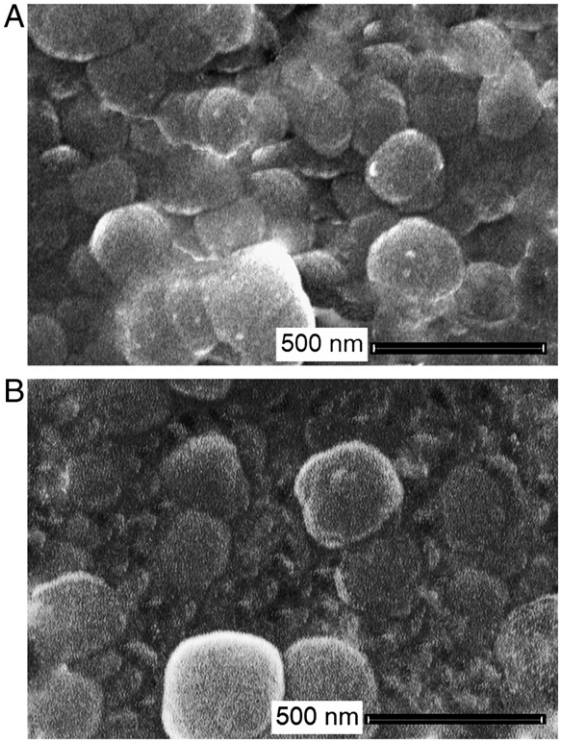

Fig. 2. SEM micrographs of the PB thin films electrodeposited at A) 15 $\mu A \cdot cm^{-2}$, 0.1 Hz and B) 60 $\mu A \cdot cm^{-2}$, 1 kHz.