Influence of the Applied Potential and Temperature on the Electrodeposition of the Lead Dioxide

Taha Yaseen Khalaf

Department of Biomedical Engineering / Al-Khawarizmi College of Engineering / University of Baghdad
Email: Taha_y9@yahoo.com

(Received 21 May 2013; accepted 11 September 2013)

Abstract

The excellent specifications of electrodes coated with lead dioxide material make it of great importance in the industry. So it was suggested this study, which includes electrodeposition of lead dioxide on graphite substrate, knowing that the electrodeposition of lead dioxide on graphite studied earlier in different ways.

In this work the deposition process for lead dioxide conducted using electrolytic solution containing lead nitrate concentration 0.72 M with the addition of some other material to the solution, such as copper nitrate, nickel nitrate, sodium fluoride and cetyl trimethyl ammonium bromide, but only in very small concentrations. As for the operating conditions, the effect of change potential and temperature as well as the time on the deposition process was studied.

The results shown at the end of the experiments that the change in the applied potential to the cell and electrolytic solution temperature had the greatest influence on the cell current, anodic current density, anodic overpotential and the amount of lead dioxide deposited on the anode.

Keywords: Electrodeposition; Lead dioxide; Alpha-lead dioxide.

1. Introduction

Electrodeposition, electroplating or electrochemical deposition is the process by which an applied current or potential is used to deposit a film of metal or alloy from by the reduction of metallic ions onto a conductive substrate [1 - 2]. In the case of electrochemical metal phase formation creating crystalline metal deposits, the process is known as electrocrystallization. More generally, the term electrodepositionis used [2]. Electrodeposition is the application of a coating to conducting surfaces by electrochemical processes, and is usually confined to metallic coatings, although other materials such as metal-oxides are also possible [3]. The heterogeneous transfer of electrons from the solution environment is clearly a key process in electrodeposition [2]. The electrodeposition of particulates along with a metal or alloy leads to the formation of a composite [1].

The pulse electrodeposition is a modified form of electrodeposition in which either pulse current or pulse potential is applied to the electrode for a given duration of time. Metal deposits obtained by pulse plating show distinct advantages like improved deposit distribution, minimized edge effect, pinhole free deposit, less hydrogen uptake, uniform thickness, better adhesion and lower impurity content compared to conventional dc electrodeposition. The characteristics of the films deposited by pulse electrodeposition are controlled by factors like on-time, off-time and current density [4].

2. Lead Dioxide Electrodeposition

During the past decade, lead dioxide (PbO₂) anodes sparked a worldwide interest and were used frequently in industry because of their excellent properties such as high electronic conductivity, high over oxygen evolution, high
Also highly recognized [8] platinum. Its use inorganic electrosynthesis is that can substitute noble materials such as some ions, for example Bi\textsuperscript{+3} can often been hanced greatly by incorporation of reactions in acidic media. However, this activity electrocatalytic activity toward various anodic demonstrated to exhibit a moderate PbO\textsubscript{2} stability in medium, good electrocatalytic activity and relatively high service life [5 - 6]. A great number of applications for lead dioxide such as positive active material in lead acid batteries, electrochemical sensors, electrowinning of metals, oxidation of organic compounds in waste water, oxidation of glucose, ozoneevolution, oxidation of phenol and Cr\textsuperscript{+3} has been reported [6 - 7]. The substantial growth in new avenues such as telecommunication networks, electronics, computers etc., has raised new challenges for PbO\textsubscript{2} batteries [7]. It is a cheap alternative material that can substitute noble materials such as platinum. Its use inorganic electrosynthesis is also highly recognized [8].

Electrodeposited pure lead dioxide was demonstrated to exhibit a moderate electrocatalytic activity toward various anodic reactions in acidic media. However, this activity can often been hanced greatly by incorporation of some ions, for example Bi\textsuperscript{+3}, As\textsuperscript{+3}, Fe\textsuperscript{+3}, Cl\textsuperscript{-}, F\textsuperscript{-}. There is much less information on effects of polyelectrolyte and surfactantadditives on the process of oxide electrodeposition and the physicochemical properties of the resulting materials. It was shown that both polyelectrolytes and anionicsurfactants are adsorbed on PbO\textsubscript{2} and that the composition materials prepared from plating solutions containing those additives have new physicochemical properties [9 - 10].

In practice, the materials with large O\textsubscript{2} overpotential are commonly chosen as the anode. Metal oxides are probably the most interesting material for use in electrocatalysis. There are a number of oxides electrodes (RuO\textsubscript{2}, IrO\textsubscript{2}, SnO\textsubscript{2} and PbO\textsubscript{2}) that may be used as anode materials for the oxidation of organic compounds [11].

There are two forms of PbO\textsubscript{2}; α-PbO\textsubscript{2}(orthorhombic structure) and β-PbO\textsubscript{2}(tetragonal structure). Electrochemically α-PbO\textsubscript{2} is readily prepared in weakly acidic or alkaline solution by the oxidation of Pb(II) whilst β-PbO\textsubscript{2} can be easily prepared by the electrooxidation of Pb(II) from acidic solutions [6 - 11]. β-PbO\textsubscript{2} also has higher stability in acidic conditions than α-PbO\textsubscript{2}. Different electrocatalytic activities of α and β forms of PbO\textsubscript{2} were reported in many studies. It was concluded that porous structured PbO\textsubscript{2} with a high degree of crystallinity is more active and has influenced the electrocatalytic properties of the material. The porous structure of β-PbO\textsubscript{2} provides a greater surface area for anodic applications; therefore, the increased in the active surface area will increase the formation of OH radicals and will favour the degradation of organic compounds. The advantage of using of such electrodes is their high surface area and high mass transfer coefficient and hence high rate of electrochemical conversion [11].

3. Mechanism and Kinetic of Electrodeposition

The prerequisite for the creation of new composite lead dioxide-based materials with specified electrocatalytic properties is the development of notions concerning the basic regularities that govern the lead dioxide electrodeposition process. There is a considerable body of works devoted to studying the regularities that govern the lead dioxide electrodeposition reaction. Despite this fact, at present there is no universal kinetic scheme of the lead dioxide electrodeposition process, which would satisfactorily describe the entire collection of experimental data [12]. According to recent data, in nitric acid the rate of PbO\textsubscript{2} electrodeposition process can be limited by an electron transfer or a diffusion stage and the reaction mechanism is described by the following scheme [12 - 15].

\[
\begin{align*}
H_2O & \rightarrow OH_{ads} + H^+ + e^- \quad \ldots(1) \\
Pb^{+2} + OH_{ads} & \rightarrow Pb\text{ (OH)}^{+2} \quad \ldots(2) \\
Pb\text{ (OH)}^{+2} + H_2O & \rightarrow PbO_{2} + 3H^+ + e^- \quad \ldots(3)
\end{align*}
\]

The first stage is the formation of oxygen-containing species such as chemisorbed OH\textsuperscript{-}, followed by a chemical stage in which these particles interact with the lead species forming soluble intermediatespecies, likely to contain Pb(III), which is then oxidized electrochemicallyforming PbO\textsubscript{2}[14].

The potential \(E\) of the \(M^{2+}/M\) electrode is a function of the activity of metal ions in the solution according to the Nernst equation,

\[
E = E^0 + \frac{RT}{zF} \ln \alpha(M^{2+}) \quad \ldots(4)
\]

or converting the natural logarithm into the decimal logarithm yields

\[
E = E^0 + 2.303 \frac{RT}{zF} \log \alpha(M^{2+}) \quad \ldots(5)
\]

where \(E^0\), \(R\), \(T\), \(z\), and \(F\) are the relative standard electrode potential of the \(M^{2+}/M\) electrode, gas constant, absolute temperature, number of electrons involved in reaction and Faraday’s constant (96487 C), respectively [16 - 17].
For any electrodeposition to take place, a current has to flow through an electrochemical cell. When a net current flows through an electrochemical cell, the electrode potential deviates from its equilibrium value. The difference between the actual electrode potential \( E_a \) and the equilibrium potential \( E \) is called the overpotential \( \eta \). It can be expressed by\[18, 19\],

\[
\eta = E_a - E
\]  
...(6)

For large negative values of overpotentials \( \eta \geq 100 \text{ mV} \), the current density \( i \) \( (i = I/S, \text{where} \ S \text{ is the surface area of the electrode}) \) increases exponentially with the overpotential \( \eta \) according to the following equation \[20\],

\[
i = i_o e^{-a \eta}
\]  
...(7)

and for large positive values of overpotential (anodic processes) according to the following equation,

\[
i = i_o e^{(1-a) \eta}
\]  
...(8)

where \( i_o \) is the exchange current density \( (i_o = i \text{ when} \ \eta = 0) \), \( a \) the transfer coefficient, and

\[
f = \frac{F}{RT}
\]  
...(9)

The general form of the current–potential characteristics which takes into account both forward and reverse processes, when expressed in terms of overpotential assumes therefore the following form:

\[
i = i_o \left\{ \exp \left[-\frac{aF\eta}{RT}\right] - \exp \left[-\frac{(1-a)F\eta}{RT}\right] \right\}
\]  
...(10)

This is the so-called Butler–Volmer (B–V) equation. The first term describes the partial current density of the cathodic process and the second that of the anodic one. \[19\].

The activation overpotential is dependent upon the number of ions present in solution. The relationship between activation overpotential and the current density can be shown by the Tafel equation \[20 - 21\],

\[
\eta = a \mp b \log|i|
\]  
...(11)

where \( a \) and \( b \) are constants and \( |i| \) is the absolute value of the current density. The sign holds for anodic and cathodic processes, respectively. The theoretical value of the constant \( a \) for the anodic process, is

\[
a = -\frac{2.303RT}{(1-a)xF} \log
\]  
...(12)

and that of \( b \) is

\[
b = \frac{2.303RT}{(1-a)xF}
\]  
...(13)

The objective of the present study was to develop a practical PbO\(_2\) anode that could be used in industrial electrolyte processes. Therefore, the graphite was selected as a substrate of lead oxide in the experiments due to it is cheap. In particular we evaluated the influence of temperature of solution and applied voltage on polarization of anode and cathode.

Faraday’s law indicates that the weight of the metal deposited in an electrolytic process is proportional to the current, plating time and its chemical equivalent. Thus:

\[
W = It e
\]  
...(14)

Where \( W \) is the weight (in grams) of metal deposited, \( I \) is the current (A), \( t \) is time (Sec) and \( e \) is the chemical equivalent. The product of current and time \( (It) \), is the quantity of electricity passed. For a given coulomb, the weight of an element discharged is proportional to its chemical equivalent. One Faraday \( (F) \) deposits a gram-equivalent of an element of atomic weight, A \[22\]. Thus:

\[
W = \frac{ItA}{xF}
\]  
...(15)

4. Experimental Work

4.1. Assembly Cell

The cell consisted of a glass beaker pyrex-type with a capacity of 250 ml covered with a piece of poly vinyl chloride material. Two rectangular copper plates area each one 1.6 cm\(^2\) and a sheet of graphite \[23\] were used as the cathode and anode, respectively.

4.2. Anode

A graphite electrode \( (2 \text{ cm} \times 0.3 \text{ cm} \times 1.5 \text{ cm}) \) served as anode. It was placed in the center between the two copper plates of the cathode. Before electrode graphite was placed in solution electrolytic than should be a pretreatment, where surface graphite using sand paper and washing the sheet with water and liquid soap to remove fatty substances and impurities that may be present on the surface. Later, it was immersed in distilled water for \( 1/2 \) to 1 hour at a temperature of 25 to 30 \( ^\circ \text{C} \), so water-filled pores. Upon removal from the immersing bath, the substrate is immediately transferred to the electrolyte.
4.3. Solution

Electrolytic solution plating PbO\(_2\) could be prepared by dissolving lead nitrate in water to produce an aqueous solution with a concentration of 0.72M. Aqueous solution had also some materials and certain concentrations, as follows: 10 g/L nickel nitrate, 14 g/L copper nitrate, 0.75 g/L cetyl trimethyl ammonium bromide and 0.75 g/L sodium flouride.

4.4. Electrolysis

Operating conditions for the deposition process were identified by several factors as follows: First, the applied potential was changed from 2, 2.5, 3, 3.5 to 4 Volts, knowing that the time required for coating a single sample is 45 minutes. Second, the temperature of the deposition solution was changed when the values 32, 46, 61 and 76\(^\circ\)C. In addition to the above, the value of the pH of the solution before starting the deposition must be adjusted to 3.5 ± 0.2 and the electrolytic solution must be mixed at a rate regularly using magnetic stirrer so as to remove any bubbles that may be present on the surface of graphite electrode.

The objective of the present study was to develop a practical PbO\(_2\) anode that could be used in industrial electrolyte processes. Therefore, the graphite was selected as a substrate of lead oxide in the experiments due to it is cheap. In particular we evaluated the influence of temperature of solution and applied voltage on polarization of anode and cathode.

5. Results and Discussion

5.1. Effect of Deposition Time and Temperature on The Cell Current

Figure 1 shows the relationship between the current with deposition time when deposition lead dioxide from an aqueous solution containing lead nitrate (0.72M), while the temperature change between 32 and 76\(^\circ\)C. The change of the current appeared as a function of temperature when the rate mixing was fixed. The cell current increases with increasing temperature. In addition to that, there was no effect of deposition time on the cell current when the applied potentials were fixed or were very small.

5.2. Effect of Applied Potential and Temperature on The Cell Current

Results are displayed in Figure 2 shows that the cell current proportional to the applied potential when the temperature difference. It is obvious that in all the experiments that the cell current increases with increasing applied potential. The logical explanation for that the increased applied potential leads to an increase in concentration of reactants around the electrodes and thus increases the amount of the deposit, which consequently leads to an increase in cell current.

In addition to the above, it can be seen two types of shapes, at a temperature of 32 and 61\(^\circ\)C on the one hand and at temperatures of 46 and 76\(^\circ\)C on the other. First at a temperature of 32
and 61°C, it is noted that the cell current is increasing according to the law of the straight line. Either in second form, the cell current increases are straight in the early stages. And then in the applied potential range 2.4 and 4, the cell current is increasing according to an exponential law, knowing that the values of applied potentials confined within this range are the most commonly used values in previous research [24].

5.3. Effect of Applide Potential and Temperature on The Anodic Current Density

For the purpose of obtaining more information, we will study the current term anodic current density versus applied potential and this is what is shown in Figure 3 where the anodic current density increases with the applied potential and temperature. The results showed the process of deposition of lead dioxide on graphite electrode that increasing the applied potential leads to increase the amount of material deposited on the electrode, as well as increase the anodic current density.

5.4. Effect of Overpotential on The Anodic Current Density

To understand the behavior of the polarization curve of the anode, we calculated the overpotential of the cell using the basic equations mentioned earlier in paragraph mechanism and kinetics of electrodeposition, and then through the Tafelequation of the anode, the data is plotted with the log current density of the anode versus overpotentialas shown in Figures 4(a), (b), (c) and (d), while varying the temperature between 32 and 76°C.

The increase of temperature of the electrolytic solution lead to change the physical properties of the solution, such as density and viscosity. In addition, the increase in temperature will lead to increase the kinetic energy of the ions and make it move more quickly and therefore it will be helpful to increase the speed of precipitation reactions, and this whole is the main reason for the increase in anodic current density.
These figures show the variation of overpotential as a function of anodic current density at constant temperatures in each experiment. It was observed that the overpotential increases with increasing anodic current density.

The plot of the overpotential versus log anodic current density is non-linear. We note that the overpotential increases exponentially with the log anodic current density according to the equation 8, for large positive values of overpotential (anodic processes).

5.5. Effect of Temperature and Applied Potential on the Overpotential

Fig. 5 shows the variation of overpotential versus temperature in the electrodeposition process for the various applied potential.

We note from this figure that the overpotential not affected when increasing temperature, but the fact is that decrease very little in the overpotential at increasing temperature cannot distinguish clearly in figure because of the narrow range of temperature and this is what can be detected clearly when you apply the Nernst equation. As for the effect of applied potential on the overpotential it is clear from the figure that the increase in the applied potential leads to an increase of the overpotential.

5.6. Effect of Temperature and Applied Potential on the Log Anodic Current Density

Figure 6 shows the effect of temperature on the log anodic current density at changing the values of the applied potential, as we have noted that the increase in temperature leads to an increase anodic current density and the reason for this is due to the increase in temperature reduces the viscosity of the solution, which leads to reduced resistance to movement of ions that make up the current.
Fig. 6. Effect of Temperature and Applied Potential on the Log Anodic Current Density.

5.7. Effect of Applied Potential and Temperature on the Deposition Weight

Figure 7 shows the weight of deposited lead dioxide from an aqueous solution containing lead nitrate (0.72M) on graphite for varying applied potentials. It seems from this figure that the weight deposited increases with increase in the applied potential and also increases when the temperature increases.

The experimental data in figure explain to us the amount of material deposited on the anode when the applied potential is changed making it easier for us to identify one of the most important operational conditions in the electrodepositing process and thus the possibility to control the amount of material deposited with the times.

Fig. 7. Effect of Applied Potential and Temperature on the Deposition Weight.

5.8. Effect of Temperature and Applied Potential on the Deposition Weight

The effect of temperature on deposition weight for the various applied potential is shown in Figure 8.

Fig. 8. Effect of Temperature and Applied Potential on the Deposition Weight.

The weight deposited increases with increasing temperature electrolytic solution, which means that the electrodeposition process can be improved by increasing the temperature.

6. Conclusion

This work demonstrates the influence of applied potential and temperature of solution on the performance of the lead dioxide deposition on a graphite electrode from lead nitrate solutions. The following conclusions were reached:

1. The increase in the deposition time had very little effect on the cell current, but in general, the increase in the time of deposition led to an increase in the weight of lead dioxide deposited.
2. The increase in applied potential during the deposition process lead dioxide had the greatest influence on the current and current density, which led to an increase in overpotential as well as the increase in the weight of deposited.
3. The results showed that the increase in the temperature of the electrolytic solution worked to improve the performance of the deposition process, as well as to increase the weight of the deposited.
7. References


تأثير الجهد المسلط ودرجة الحرارة على الترسب الكهربائي لثاني أكسيد الرصاص

طه ياسين خلف
قسم هندسة الطب الحيكي / كلية الهندسة الخوارزمي / جامعة بغداد
البريد الالكتروني: Taha_y9@yahoo.com

الخلاصة

المواصفات الممتازة للأقطاب الكهربائية المطلية بمادة ثاني أكسيد الرصاص جعل منها ذات أهمية كبيرة في الصناعة. لذلك اقترحنا هذه الدراسة، والتي تتضمن الترسب الكهربائي لمادة ثاني أكسيد الرصاص على ركزة من الكرايفيت، مع العلم أن عملية الترسيب الكهربائي لمادة ثاني أكسيد الرصاص على الكرايفيت تمتد دراستها سابقاً بطرق مختلفة.

في هذا العمل أجرينا عملية الترسيب لمادة ثاني أكسيد الرصاص باستخدام محلول الكتربوليتكي كهربائي حتوى على مادة نترات الرصاص يتركز 0.72 M مع إضافة بعض المواد الأخرى إلى المحلول الكتربوليتكي، مثل مادة نترات الحساس، ومادة نترات الليثيوم، ومادة فلوريد الصوديوم ومادة مبتئل تراي إيثيل بروميدي الأمونيوم. علماً أن هذه الاضافات كانت تتركز قليلة جداً، أما بالنسبة للظروف الفنية، فقد قمنا بدراسة تأثير تغير الجهد المسلط ودرجة حرارة محول وكذلك الزمن على عملية الترسيب الكهربائي.

بينت النتائج عند انتهاء التجربة بأن التغير في الجهد المسلط على الخليه الكتربوليتية وكذلك التغير لدرجة حرارة المحول كان لهما التأثير الأكبر على تيار الخلية، وكذلك التيار الأندوبي، فوق الجهد الأندوبي وكذلك أيضاً على كمية ثاني أكسيد الرصاص المرسبة على الأندو.