Advanced Powder Technology xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Influence of the complex formation on the morphology of lead powder particles produced by the electrodeposition processes

Nebojša D. Nikolić [a,*], Djendji Dj. Vaštag [b], Predrag M. Živković [c], Bojan Jokić [c], Goran Branković [d]

[a] ICTM-Institute of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia
[b] Faculty of Natural Science and Mathematics, University of Novi Sad, Trg D. Obradovića 3, Novi Sad, Serbia
[c] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia
[d] Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade, Serbia

ARTICLE INFO

Article history:
Received 28 August 2012
Received in revised form 4 December 2012
Accepted 17 December 2012
Available online xxxx

Keywords:
Electrodeposition
Lead
Morphology
Powder
Scanning electron microscopy

ABSTRACT

The processes of lead electrodeposition from the basic (nitrate) and complex (acetate) electrolytes were mutually compared by the analysis of their polarization characteristics and by the scanning electron microscopic (SEM) analysis of the morphology of formed deposits. Although the polarization characteristics of lead recorded from these two electrolytes were relatively similar to each other, the shape of formed dendrites strongly depended on the type of electrolyte. The dendrites composed of stalk and weak developed primary branches (the primary (P) type) were predominantly formed from the basic electrolyte. On the other hand, the very branchy dendrites composed of stalk and of both primary and secondary branches (the secondary (S) type) were mainly electrodeposited from the complex electrolyte. Considering the fact that the application of lead powder in many technologies is closely related with its surface morphology, the special attention was given to the analysis of the type of electrolytes on formation of the different dendritic forms. It was shown that formation of more branchy dendrites from the acetate electrolyte can be ascribed to the lower exchange current density (or to the lower rate of electrochemical process) for this electrolyte than for the nitrate one due to the process of complex formation.

1. Introduction

The most important technologies of the significance for use of lead are related with the production of high purity active material for acid battery [1], for semiconductors [2,3], and the fabrication of electrochromic devices [4]. In the form of powder, lead is widely used in industries of gas and oil exploration, radiological medical protective clothing, as an industrial X-ray shield, golf club manufacture, and anti-friction products [5]. Electrodeposition technique is very suitable way to get lead in the form suitable for the application in the above mentioned technologies. For example, the advantage of use of electrodeposition technique in the production of lead in the powder form lies in the fact that lead powder is produced at low overpotentials and hence with small spent of energy. The open porous structures of lead with the extremely high surface area (the honeycomb-like ones), which are ideally situated for electrodes in electrochemical devices such as fuel cells, batteries and sensors, is also possible to get by the electrodeposition techniques [6].

Aside from the practical significance, the processes of lead electrodeposition also have the high academic significance. The academic significance is closely related with the fact that electrodeposition of lead belongs to the fast electrochemical processes characterized by $j_0 \gg j_L$ (j_0 – the exchange current density; j_L – the limiting diffusion current density) [7]. Namely, Pb belongs, together with Sn, Cd, Zn, Ag, to the group of normal metals [8], which are characterized by the large exchange current density and the low melting point. Electrodepositions of these metals occur in the conditions of the mixed ohmic-diffusion or even full ohmic control of the electrodeposition [9–12].

For the technological and academic investigations, the both the constant (potentiostatic [9–15] and galvanostatic [10,11] regimes), as well as the periodically changing regimes (such as pulsating overpotential (PO) one [16]) of electrolysis are widely used. The large number of various electrolytes found the application in lead electrodeposition processes, and they belong to the group of either acid [10–12,16–21] or alkaline electrolytes [13–15]. The most often used acid electrolytes are nitrate [10–12,18], iodide [17], bromide [17], fluoborate [19], acetate [16] and methanesulfonate [20,21] ones.

The surface morphology is probably the most important property of electrodeposited metals which depends on mainly the

* Corresponding author. Tel./fax: +381 11 337 03 89.
E-mail address: nnikolic@tmf.bg.ac.rs (N.D. Nikolić).

0921-8831/$ - see front matter © 2013 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.
http://dx.doi.org/10.1016/j.apt.2012.12.008

kinetic parameters of the deposition process and on the deposition overpotential or current density [22]. Electrodeposited metallic powders are mainly produced in a dendritic form. Also, the powders are obtained as flakes or needles, fibrous or spongy forms, etc., depending on the conditions of electrodeposition and on the nature of the metal. Also, the type of used electrolyte strongly affects the morphology of electrodeposited metal. The complex electrolytes represent the special type of electrolytes and they can be from the group of both acid and alkaline ones. In the metal electrodeposition processes, the effect of complex formation is limited not only on the polarization behavior of the metal [11,23], but to the morphology of metal deposits, as observed in the production of silver [11,23,24] and bismuth [25] powdered deposits.

The use of lead in the above mentioned technologies is strongly related with morphology of electrochemically deposited lead. In spite of the large number of available electrolytes for the electrodeposition of lead, there is no a systematic investigation about the dependences of morphology of electrodeposited lead on the type of used electrolyte. Considering the high technological significance of lead, the need for this systematic investigation is evident. For that reason, the aim of this study is to compare lead deposits obtained in the powder form from the basic (nitrate) and complex (acetate) electrolytes.

2. Experimental

Electrodeposition of lead was performed in an open cell from the following solutions:

(a) 0.10 M $Pb(CH_3COO)_2$ + 1.5 M $NaCH_3COO$ + 0.15 M CH_3COOH, and
(b) 0.10 M $Pb(NO_3)_2$ + 2.0 M $NaNO_3$.

Doubly distilled water and analytical grade chemicals were used for the preparation of the solutions for electrodeposition of lead. All electrodepositions were performed on vertical cylindrical copper electrodes. The geometric surface area of copper electrodes was 0.25 cm^2. Reference and counter electrodes were of pure lead. The counter electrode was lead foil with 0.80 dm^2 surface area and placed close to the cell walls. The reference electrode was wire of lead whose tips were positioned at a distance of about 0.2 cm from the surface of the working electrodes. The working electrodes were placed in the centre of cell, at the same location for each experiment. Electrodeposition of lead and polarization measurements were performed at a temperature of 22.0 ± 0.50 °C.

For the morphological analysis of lead deposits, lead was electrodeposited potentiostatically at overpotentials of 10, 50, 60 and 100 mV from 0.10 M $Pb(CH_3COO)_2$ + 1.5 M $NaCH_3COO$ + 0.15 M CH_3COOH and at overpotentials of 10, 50 and 100 mV from 0.10 M $Pb(NO_3)_2$ + 2.0 M $NaNO_3$ with the quantity of electrodeposited lead of 0.50 mA h cm^{-2}.

The obtained lead deposits were examined using a scanning electron microscope – TESCAN Digital Microscopy.

3. Results and discussion

3.1. Polarization characteristics of basic (nitrate) and complex (acetate) electrolytes

The polarization curves for lead electrodeposition from the basic (nitrate) and complex (acetate) electrolytes are shown in Fig. 1. The both polarization curves consist of the three parts denoted as *Part (I)*, *Part (II)* and *Part (III)* in Fig. 1.

The characteristic of the first part (*Part (I)*) is the linear dependence of the current density on overpotential and this

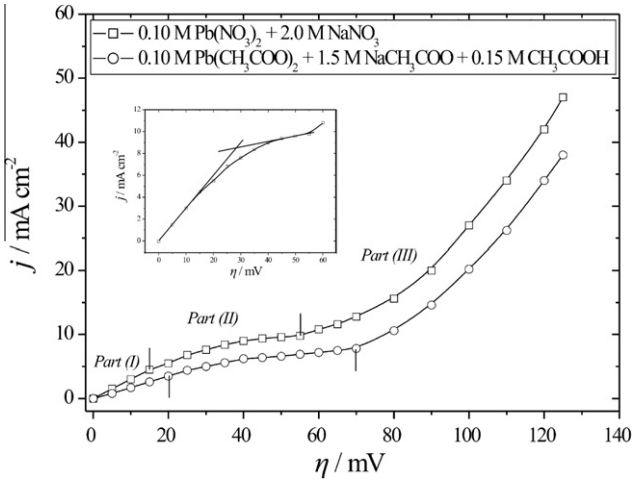

Fig. 1. The polarization curves for lead electrodeposition from 0.10 M $Pb(CH_3COO)_2$ + 1.5 M $NaCH_3COO$ + 0.15 M CH_3COOH and 0.10 M $Pb(NO_3)_2$ + 2.0 M $NaNO_3$.

linear part corresponds to the ohmic controlled electrodeposition process. With the nitrate ions used, the interval of overpotentials corresponding to the ohmic control is between 0 and 15 mV. When the acetate ion was used, the end of the ohmic control of the electrodeposition corresponded to an overpotential of 20 mV.

The second part of the polarization curves (*Part (II)*) corresponds to the diffusion controlled electrodeposition process. The ranges of overpotentials belonging to the diffusion control of the electrodeposition are from 15 to 55 mV for the basic electrolyte and from 20 to 70 mV for the complex electrolyte. The beginning of the plateau of the limiting diffusion current density is determined as intersect of straight lines joining current densities in the ohmic and diffusion control of electrodeposition, as inserted in Fig. 1. The plateaus of the limiting diffusion current density, determined in this way, were between 28.5 and 55 mV for the nitrate electrolyte, and between 33 and 70 mV for the acetate electrolyte.

The inflection point at the polarization curves denoted the ends of the plateau of the limiting diffusion current density. The fast increase of the current density after the inflection point is the characteristic of the third part of the polarization curves (*Part (III)*). The inflection point corresponds to an overpotential of 55 mV for the nitrate, and 70 mV for the acetate electrolytes.

The electrical conductivities of the electrolytes were 4.22 mS for the nitrate electrolyte and 7.06 mS for the acetate electrolyte. As seen from Fig. 1, this noticeable increase of the electrical conductivity of the acetate electrolyte of about 40% showed the strong effect on the polarization characteristics of lead electrodeposition system.

The following differences in the polarization curves obtained from the basic (nitrate) and complex (acetate) electrolytes were observed: (a) the intervals of overpotentials corresponding to the both ohmic and diffusion controls of the electrodeposition were larger for the complex than for the basic electrolytes, and (b) the plateau of the limiting diffusion current density was wider for the complex than for the basic electrolytes. The smaller value of the limiting diffusion current density for the complex electrolyte (for about 27%) is probably due to the decrease of diffusion coefficient caused by the process of complexing of Pb(II) ions.

In the next step, the polarization characteristics were correlated with morphologies of lead deposits obtained by the electrodeposition processes at overpotentials corresponding to the different positions at the polarization curves. In this way, the very important

Please cite this article in press as: N.D. Nikolić et al., Influence of the complex formation on the morphology of lead powder particles produced by the electrodeposition processes, Advanced Powder Technology (2013), http://dx.doi.org/10.1016/j.apt.2012.12.008