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Influence of the type of electrolyte on the morphological and crystallographic characteristics of lead powder particles

NEBOJŠA D. NIKOLIĆ^{1*#}, VESNA M. MAKSIMOVIĆ², GORAN BRANKOVIĆ³,
PREDRAG M. ŽIVKOVIĆ⁴ and MIOMIR G. PAVLOVIĆ^{1#}

¹ICTM – Center of Electrochemistry, University of Belgrade, Njegoševa 12, P. O. Box 473, 11001 Belgrade, Serbia, ²Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia, ³Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade, Serbia and ⁴Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 3503, 11001 Belgrade, Serbia

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Abstract: Lead electrodeposition processes from basic (nitrate) and complex (acetate) electrolytes were mutually compared by scanning electron microscopy and X-ray diffraction investigation of the produced powder particles. The shape of dendritic particles strongly depended on the type of electrolyte. Dendrites composed of a stalk and weakly developed primary branches (the primary type) were predominantly formed from the basic electrolyte. Ramified dendrites composed of a stalk and of both primary and secondary branches (the secondary type) were mainly formed from the complex electrolyte. In both types of powder particles, Pb crystallites were predominantly oriented in the (111) plane. The formation of powder particles of different shapes with strong (111) preferred orientation is discussed and explained by consideration of the general characteristics of the growth of crystals in electrocrystallization processes.

Keywords: electrodeposition; lead; powder; dendrite; scanning electron microscopy (SEM); X-ray diffraction (XRD) analysis.

INTRODUCTION

The formation of metal powders by electrolysis is an economical processing method with low capital investment and operational costs. The main advantages of this method in relation to other methods of powder production (mechanical comminution, chemical reaction and liquid metal atomization) are the high purity of the produced powder, which can be easily pressed and sintered, and the low oxygen content.^{1,2} It is an environmentally friendly method of powder production that enables working in a closed-circuit.³

* Corresponding author. E-mail: nnikolic@tmf.bg.ac.rs

Serbian Chemical Society active member.

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Electrodeposited metallic powders are mainly produced in a dendritic form. Although dendritic forms are the predominant shape of powder particles, powders are also obtained as flakes or needles, fibrous or spongy, cauliflower-like forms, *etc.*, depending on the conditions of electrodeposition and on the nature of the metal.^{2,4,5}

The shape of dendritic particles also depends on the electrodeposition conditions and the nature of the metal. The shape of the dendrites of the group of normal metals,⁶ characterized by a high exchange current density ($j_0 \rightarrow \infty$) and a low melting point, T_m , such as Ag,^{2,4,7,8} Sn,⁹ and Pb,^{10,11} is completely different from those belonging to the groups of intermediate metals (moderate T_m and a medium j_0), such as Cu,^{5,12–15} Ag (complex electrolytes)^{4,8,16,17} and Au,¹⁸ or inert metals (high T_m and a low j_0), such as Co and Ni.^{19,20} The composition of electrolyte strongly affects the shape of the dendritic particles. For example, the shape of lead dendrites obtained by electrodeposition from nitrate solutions is completely different from those obtained from acetate solutions.²¹

The effect of the composition of the electrolyte and the nature of the metal, as well as other electrodeposition conditions (regime of electrolysis, temperature, type of the working electrode, *etc.*) on the morphology of the powder particles has been relatively well examined and systematized.⁷ However, there is not enough data concerning the crystallographic characteristics of powder particles, nor about the correlation between the morphology of powder particles and their crystallographic structure. An initial investigation was performed recently²² for the case of lead electrodeposition from a concentrated nitrate solution and it was shown that different morphological forms, from single crystals to branchy dendrites with a strong (111) preferred orientation, were formed. The ratio of Pb crystallites oriented in the (200), (220) and (311) planes increased with increasing overpotential of the electrodeposition. The aim of this study was to continue this investigation. The effect of the type of electrolyte on the morphological and crystallographic characteristics of lead powder particles produced by potentiostatic electrodeposition will be analyzed and discussed.

EXPERIMENTAL

The electrodeposition of lead was performed in an open cell from basic (nitrate) and complex (acetate) electrolytes. The compositions of the electrolytes were: acetate electrolyte, 0.10 M $\text{Pb}(\text{CH}_3\text{COO})_2 + 1.5 \text{ M NaCH}_3\text{COO} + 0.15 \text{ M CH}_3\text{COOH}$ and nitrate electrolyte, 0.10 M $\text{Pb}(\text{NO}_3)_2 + 2.0 \text{ M NaNO}_3$.

Doubly distilled water and analytical grade chemicals were used for the preparation of the solutions for the electrodeposition of lead. All electrodepositions were performed on vertical cylindrical copper electrodes. The geometric surface area of the copper electrodes was 0.25 cm². The counter electrode was a pure lead foil of 0.80 dm² surface area that was placed close to the cell walls. The reference electrode was a pure lead wire, the tips of which 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.

The electrodeposition of lead and polarization measurements were performed at a temperature of 22.0 ± 0.5 °C.

Polarization curve for electrodeposition of lead was recorded potentiostatically by changing the overpotential in 5 mV steps. In order to obtain a reproducible shape of the polarization curves for this reaction, the following experimental procedure,¹¹ usual for recording the polarization curves of fast electrodeposition processes, was applied. At low overpotentials (Part (I) and (II) on the polarization curves in Fig. 1), the values of the current obtained after reaching steady-state values were used for constructing the polarization curves. Since the current increased dramatically over time at overpotentials corresponding to Part (III) on the polarization curves in Fig. 1, the values recorded immediately after setting the selected overpotential were used.

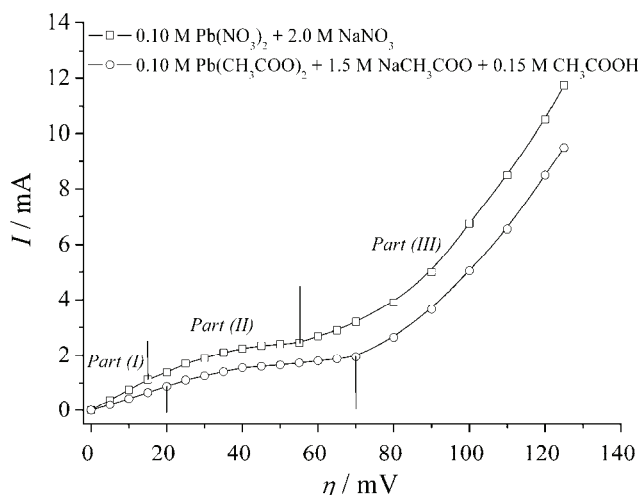


Fig. 1. The polarization curves for lead electrodeposition from $0.10 \text{ M Pb(CH}_3\text{COO)}_2 + 1.5 \text{ M NaCH}_3\text{COO} + 0.15 \text{ M CH}_3\text{COOH}$ and from $0.10 \text{ M Pb(NO}_3)_2 + 2.0 \text{ M NaNO}_3$. The surface area of the working electrode was 0.25 cm^2 .

Powder particles obtained by tapping lead deposits electrodeposited at an overpotential of 100 mV with a charge of $0.50 \text{ mA h cm}^{-2}$ were examined using a scanning electron microscope – TESCAN Digital Microscope.

X-Ray powder diffraction (XRD) analysis performed using a Rigaku Ultima IV diffractometer with $\text{CuK}\alpha$ radiation was used for examination of the crystal structures.

RESULTS AND DISCUSSION

The polarization curves for electrodeposition of lead from the basic and the complex electrolytes consisted of three parts separated by the vertical lines in Fig. 1. The characteristic of the first part (Part (I)) is the linear dependence of the current on overpotential and this part corresponds to ohmic control.^{10,11,21} The intervals of overpotentials belonging to this control of the electrodeposition were between 0 and 15 mV for the nitrate and between 0 and 20 mV for the complex electrolyte. The electrodeposition processes are diffusion-controlled in the range

of overpotentials between 15 and 55 mV for the nitrate electrolyte and between 20 and 70 mV for the complex electrolyte (Part (II) on the polarization curves). The electrodeposition processes remain diffusion controlled after the inflection points (Part (III)) and the rapid increase of the current with increasing overpotential is due to the large increase in the surface area caused by the formation and growth of dendrites.

Regular single crystals were formed in the ohmic-controlled electrodeposition and their shape did not depend on the type of the electrolyte.²¹ Dendritic growth was initiated at some overpotential belonging to the diffusion part of the polarization curve and this overpotential is denoted as the critical overpotential for dendritic growth initiation. Various morphological forms from single crystals to irregular crystals (precursors of dendrites) and dendrites were formed in the diffusion-controlled electrodeposition.²¹ Finally, the overpotentials corresponding to the inflection points on the polarization curves represent the critical overpotentials for instantaneous dendritic growth. After these overpotential values, the currents increased rapidly (Fig. 1).

Typical powder particles obtained by tapping lead deposits electrodeposited at an overpotential of 100 mV from the nitrate electrolyte are shown in Fig. 2a and b, and those from the complex electrolyte are presented in Fig. 2c and d. At first sight, a clear difference between them is evident. The powder particles obtained from the complex electrolyte were branchier than those obtained from the basic electrolyte were. In Wranglen's classic definition of dendrites,²³ a dendrite consists of a stalk and of branches (primary, secondary, *etc.*) and resembles a tree. Dendrites consisting of only the stalk and primary branches are referred as primary (P) dendrites. If the primary branches in turn develop secondary branches, the dendrite is called secondary (S).

Analysis of the shape of dendrites obtained from the nitrate electrolyte showed that they consisted of a stalk and poorly developed branches denoted as the teeth of a saw¹¹ (Fig. 2a and b). It is very clear that these poorly developed branches represent primary branches in these powder particles, and hence, these dendrites are of the P type. However, the primary branches in the powder particles obtained from the complex electrolyte were very well developed (Fig. 2c and d) and the presence of the secondary branches developed from them can be easily noticed. Hence, the dendrites formed from the complex electrolyte belonged to the S type. A common characteristic of both groups of dendrites is their two-dimensional (2D) shape.

Electrochemical aspects of the formation and growth of dendrites have been very well investigated. From the electrochemical point of view, a dendrite is defined as an electrode surface protrusion that grows under activation control, while electrodeposition to a macroelectrode is predominantly under diffusion control.^{7,24–26} Using this definition of a dendrite, the sudden and rapid increase

of the current with increasing the overpotential after the inflection point ((Part (III) in the polarization curves) could be mainly ascribed to activation-controlled electrodeposition at the tips of the formed dendrites,^{10,11,26} where the tips of both primary and secondary branches contribute to the overall control of electrodeposition process. Formation of more branchy dendrites from the complex electrolyte than from the basic electrolyte could be ascribed to the lower exchange current density for the acetate electrolyte than for the nitrate one.²¹

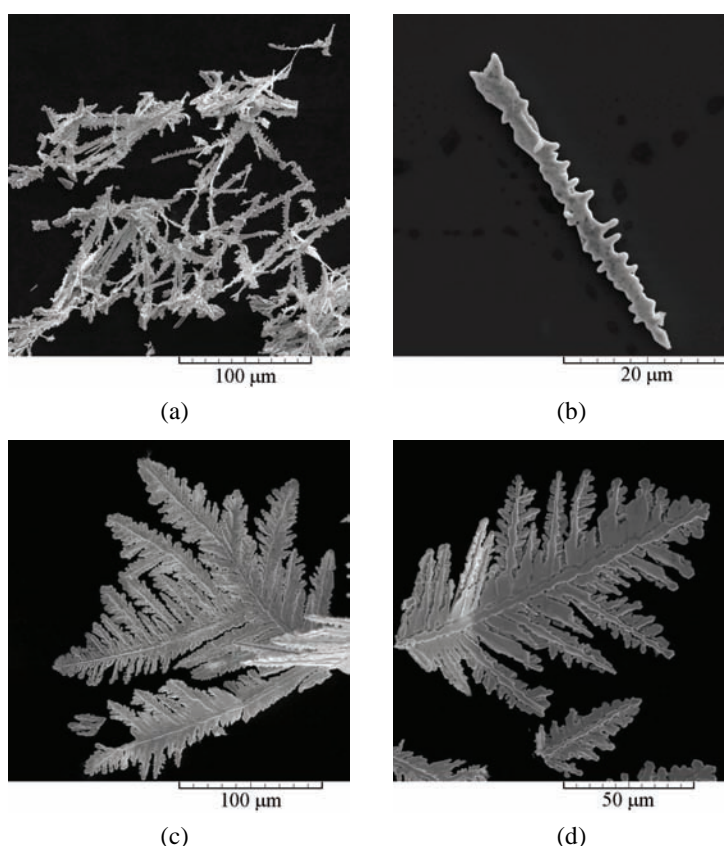


Fig. 2. Powder particles obtained by tapping the lead powder deposits formed by electrodeposition at an overpotential of 100 mV from: (a) and (b) 0.10 M $\text{Pb}(\text{NO}_3)_2$ + 2.0 M NaNO_3 , and (c) and (d) 0.10 M $\text{Pb}(\text{CH}_3\text{COO})_2$ + 1.5 M NaCH_3COO + 0.15 M CH_3COOH .

Unlike of systematized investigations of the effect of the type of the electrolyte on the morphology of powder particles, a correlation between the crystallographic structure of particles and the type of the electrolyte has not been sufficiently explored. The XRD patterns of the powder particles obtained by tapping the lead powder deposits electrodeposited from the basic and the complex elec-

trolytes are shown in Fig. 3, from which it is very clear that the presented XRD patterns were very similar to each other. Pb crystallites were predominately oriented in the (111) plane. Aside from Pb crystallites oriented in this plane, the presence of crystallites oriented in the (200), (220), (311) and (331) planes was also observed. Nevertheless, the strong (111) preferred orientation was characteristic of both types of powder particles.

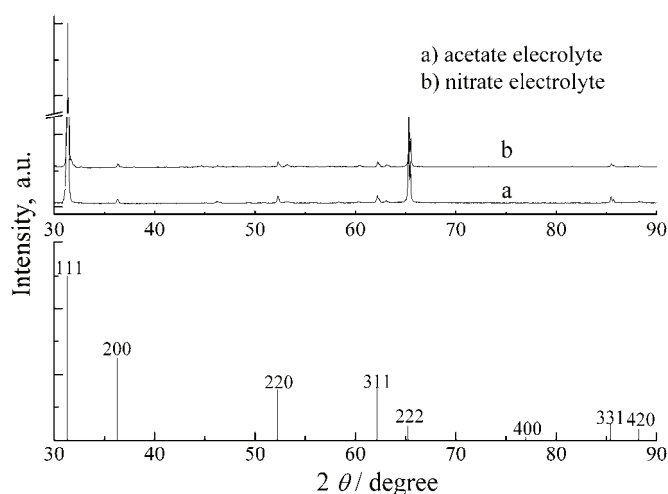


Fig. 3. The XRD patterns of the lead powder particles electrodeposited from electrolytes 0.10 M $\text{Pb}(\text{CH}_3\text{COO})_2 + 1.5 \text{ M NaCH}_3\text{COO} + 0.15 \text{ M CH}_3\text{COOH}$ and 0.10 M $\text{Pb}(\text{NO}_3)_2 + 2.0 \text{ M NaNO}_3$. The standard for Pb: 4-0686.

Formation of lead powders with the strong (111) preferred orientation could be explained as follows: lead crystallizes in a face-centered cubic (FCC) lattice. At constant overpotential, the rates of electrodeposition for this type of crystal lattice increase in the order of $(110) > (100) > (111)$.²⁷ These different deposition rates onto different faces had an important consequence; fast-growing faces tend to grow out of existence and disappear, while slow-growing faces tend to survive,²⁷ as illustrated in Fig. 4. The origin of Pb crystallites oriented in the (111) plane is the growth centers present in the interior of the crystal faces.^{22,23} This type of growth center is denoted as a “center type”. On the other hand, the origins of the Pb crystallites oriented in the (200), (220), (311) and (331) planes are the growth centers present on the edges and corners of the growing forms.²² These types of growth centers are denoted as “edge and corner types”.²³ The overpotentials and current densities responsible for crystal growth based on growth centers of the “edge and corner type” are higher than those responsible for crystal growth based on growth centers of the “center type”. This means that the current densities are higher at the tips of the growing forms than at their sides. In the

growth process, slow-growing (111) face will survive constructing all elements of dendrites (both stalk and branches), and hence, causing the predominant orientation of Pb crystallites in this plane, as confirmed in Fig. 3. In the case of lead, it is clear that the (200), (220), (311) and (331) planes are fast-growing faces. In the growth process, they will disappear which explains the considerably smaller presence of Pb crystallites in these planes than in the (111) plane.

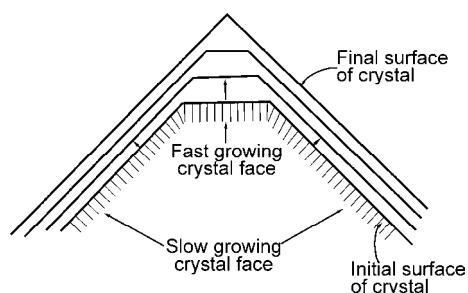


Fig. 4. The growth of a crystal, illustrating how a fast-growing face grows out of existence, while a slow-growing crystal faces remains.²⁷

These processes should not be observed independently of the effect of the current density distribution at the growing surface. The current lines are primarily concentrated at the tips of growing protrusions, causing faster growth on them than in the vicinity of the electrode surface.²⁸ As result of all these processes, dendrites of the different shape are formed.

It is very clear from the above consideration that the crystallographic (interior) structure is determined by the characteristics (nature) of the metal and it does not depend on the type of electrolyte. Unlike the approximately same crystallographic structure, the morphology of the observed powder particles strongly depended on the type of employed electrolyte. Furthermore, the dominant orientation of Pb crystallites in the (111) plane was observed in different morphological forms, from single to irregular crystals and dendrites obtained by the potentiostatic electrodeposition from the nitrate electrolyte at the different overpotentials.²² In addition, the application of both different regimes of electrolysis, such as the galvanostatic one, and the type of the working electrode, such as Cu, Ti and Al, did not affect the crystallographic characteristics of lead.²⁹

CONCLUSIONS

Powder particles obtained by potentiostatic electrodeposition from basic (nitrate) and complex (acetate) electrolytes were analyzed using the SEM and XRD techniques.

The type of electrolyte strongly affected the surface morphology of the lead powder particles. Primary type dendrites were formed from the basic (nitrate) electrolyte. This type of dendrite consists of a stalk and weakly developed branches. The secondary type of dendrites, composed of a stalk and primary and

secondary branches, was formed by electrodeposition from the complex (acetate) electrolyte. This type of dendrite was much more ramified.

In contrast to the very different morphologies of the two types of powder particles, both of them showed the dominant presence of Pb crystallites oriented in the (111) plane. It is clear that the crystallographic structure of the powder particles did not depend on the type of electrolyte, but was only determined by the nature of the metal.

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ИЗВОД

УТИЦАЈ ТИПА ЕЛЕКТРОЛИТА НА МОРФОЛОШКЕ И
КРИСТАЛОГРАФСКЕ КАРАКТЕРИСТИКЕ ПРАШКАСТИХ ЧЕСТИЦА ОЛОВА

НЕБОЈША Д. НИКОЛИЋ¹, ВЕСНА М. МАКСИМОВИЋ², ГОРАН БРАНКОВИЋ³, ПРЕДРАГ М. ЖИВКОВИЋ⁴ и
МИОМИР Г. ПАВЛОВИЋ¹

¹ИХТМ – Центар за електрохемију, Универзитет у Београду, Његошева 12, Београд, ²Институт за нуклеарне науке „Винча“, Универзитет у Београду, Београд, ³Институт за мултидисциплинарна истраживања, Универзитет у Београду, Кнеза Вишеслава 1а, Београд и ⁴Технолошко–металуршки факултет, Универзитет у Београду, Карнегијева 4, Београд

Процеси електрохемијског таложења олова из основног (нитратног) и комплексног (ацетатног) електролита су били међусобно упоређени техником скенирајуће електронске микроскопије и рендгенско-дифракционом анализом произведених честица праха. Облик дендритичних честица је снажно зависио од типа електролита. Дендрити састављени од стабла и слабо развијених грана (примарни тип) су били предоминантно формиран из основног електролита. Разгранати дендрити састављени од стабла и од примарних и секундарних грана (секундарни тип) су били углавном формиран из комплексног електролита. У оба типа прашкастих честица кристали олова су били доминантно оријентисани у (111) равни. Формирање прашкастих честица са строгом (111) оријентацијом је било дискутовано и објашњено разматрањем општих карактеристика раста кристала у процесима електрокристализације.

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