

# Morphology-controlled preparation of lead powders by electrodeposition from different PbO-containing choline chloride-urea deep eutectic solvent

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## ABSTRACT

Lead powders with different morphologies, including corals, rods, wires, needles, ferns and dendritic forms, are prepared by electrodeposition onto a stainless steel substrate from different PbO-containing (10–60 mM) choline chloride-urea deep eutectic solvent at cell voltage 2.5 V and 343 K for 2 h. The electrochemical behavior of the PbO dissolved in this solvent is investigated with cyclic voltammetry. It is demonstrated that the increasing of PbO concentration makes the reduction potential  $E_{\text{Pb(II)/Pb}}$  shift positively and facilitates the electrodeposition of lead from PbO in the deep eutectic solvent. According to the analysis of the morphological and crystallographic characteristics of lead powders, the predominant origin of the growth layers is turned away from centre type towards the edge and corner types with the increase in PbO concentration. Due to the large number of growth centres at higher PbO concentration, fine and irregular grains are observed on the surface of formed particles which results in the development of primary and secondary branches in dendrites.

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## 1. Introduction

Lead powders have been acknowledged as a favorable material in acid battery plates [1], gas and oil exploration, radiological medical protective clothing, industrial X-ray shield, golf club manufacture, and anti-friction products [2,3]. Other applications of lead are in containers used to transport corrosive substance and in corrosion protection on steel alloys under industry atmospheres [4]. These prospective applies are calling for the preparation of lead powders with homogeneous chemical composition and uniform particle size. A number of physical and chemical methods have been reported in literatures for preparing lead powders, such as mechanic commutating and liquid metal atomization techniques [5,6]. Typically, electrodeposition technique is a suitable way to obtain lead powders due to the low energy consumption, easy operation and high purity deposits. With this method, the metallic powders can be produced in many forms including flakes,

needles, wires, spongy forms and dendritic forms, and so on [2,7]. The surface morphology is one of the most important properties of electrodeposited metals and mainly depends on the kinetic parameters of the deposition process and the overpotential or current density [8]. Moreover, the type of used electrolyte also is one of the important factors to affect the morphology of deposit [9–11]. The electrolytes for lead electrodeposition are usually acidic such as fluorosilicate [12], chloride [13], nitrate [14], bromide [15], etc. Although this water based electrodeposition process is readily available and clean, however, it is fraught with inherent problem such as non-uniform morphology and particle size of the products. To overcome these shortcomings, it is necessary to find a new electrolyte for the electrochemical reduction process. In this case, deep eutectic solvents (DESs), which are a unique class of multicomponent solvent systems formed through hydrogen bond interactions, have been developed as promising electrolytes for electrodeposition application. Because of their low melting points, nontoxicity, chemical inertness with water, and easy to prepare, DESs have been applied in organic synthesis [16], material chemistry [17], electrochemistry [18–20] and the like. In addition, DESs are capable of dissolving various metal oxides and can be used as electrolytes to recover metals through electrowinning [21–24]. This method is valuable not only from the point view of low capital investment and

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operational costs, but also for the easy operation and high purity of the deposits. In our previous studies [25,26], sub-micrometer lead wires were electrodeposited from PbO-choline chloride (ChCl)-urea solution on stainless steel substrate. The effects of existence form and concentration of PbO on the electrical conductivity and viscosity of ChCl-urea DES were also examined [27].

In this paper, lead powders with different morphologies are prepared by electrodeposition through varying PbO concentration (10–60 mM) in ChCl-urea DES at cell voltage 2.5 V and 343 K for 2 h. Cyclic voltammetry is carried out at different PbO concentrations to further analyze the electrochemical behavior of the PbO dissolved in ChCl-urea DES. Based on experimental evidences, the relationship between morphological and crystallographic characteristics of lead powders is studied.

## 2. Experimental

### 2.1. Chemicals

All the chemicals used in this work were purchased commercially with analytical grade (purity > 99.90%) from Chemical Reagent Co., Shanghai, China. ChCl ( $C_5H_{14}NOCl$ ) and urea ( $CO(NH_2)_2$ ) were recrystallized twice and dried under vacuum. PbO was dried under vacuum for 48 h at 353 K. Prior to use, platinum wire (99.95%) and silver wire (99.95%) were polished with emery paper, cleaned with acetone, treated with deionized water and dried.

### 2.2. Synthesis of ChCl-urea DES

The ChCl-urea DES was synthesized by mixing ChCl and urea (mole ratio 1:2) together at 353 K until a homogeneous, colorless liquid formed, as reported by Abbott et al. [24]. Then different amounts of PbO (10–60 mM) were added into the ChCl-urea DES under dry argon atmosphere. The resulted suspension was heated in an oil bath and the accuracy of temperature was  $\pm 1$  K. The complete dissolution of PbO was within 4 h at 353 K.

### 2.3. Electrolysis and electrochemical measurements

All electrochemical measurements were carried out by using a CHI760D electrochemical workstation (Shanghai CH Instruments Company, China). Electrochemical studies were based on the analysis of cyclic voltammetric measurements. A conventional three-electrode cell was used for these experiments. The working electrode was a stainless steel sheet. Every sheet was sealed with epoxy resin, with the remaining portion as the efficient working area ( $0.15\text{ cm}^2$ ). A silver wire and a platinum wire were used as quasi-reference and counter electrodes, respectively. Before each experiment, the stainless steel sheet electrode was polished successively with fine grade emery papers, degreased with anhydrous ethanol in an ultrasonic bath for 10 min, washed with doubly distilled water and finally dried. Cyclic voltammetric experiments were carried out under argon condition from the initial potential of  $-0.10\text{ V}$  to the final potential of  $-1.00\text{ V}$  at a constant scan rate of  $10\text{ mV s}^{-1}$  at 343 K.

Small-scale potentiostatic electrolysis experiment was performed in a  $50\text{ cm}^3$  plexiglass cell by chronoamperometric measurements. A stainless steel sheet and a graphite rod (1 cm in diameter) were used as the cathode and anode, respectively. The interelectrode distance was 1.0 cm. Lead was deposited on the cathode with an effective area of  $3\text{ cm}^2$ . All the electrolysis experiments were conducted for 2 h with the concentration of PbO varying from 10 to 60 mM at cell voltage 2.5 V and 343 K. After electrolysis, the cathode was removed from the cell and washed thoroughly with ethanol and dried.

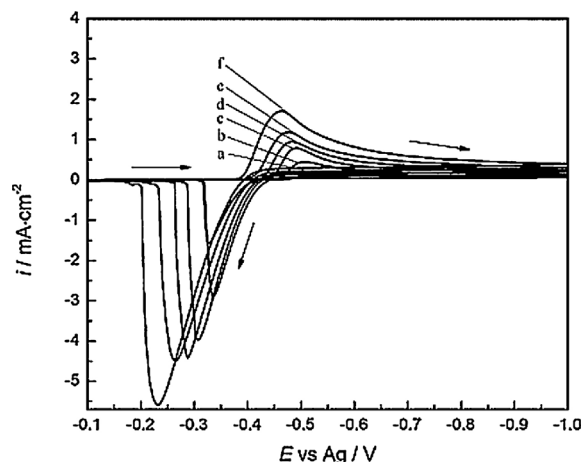


Fig. 1. Cyclic voltammograms of stainless steel electrode for different PbO concentration in ChCl-urea DES at 343 K. (a) 10 mM, (b) 20 mM, (c) 30 mM, (d) 40 mM, (e) 50 mM, (f) 60 mM. Scan rate:  $10\text{ mV s}^{-1}$ .

### 2.4. Measurement and characterization

The morphology and particle size of deposits were examined by SEM (XL 30 ESEM TMP model). The deposits were analyzed by XRD (D/Max-2200 model) with Cu-K $\alpha$  radiation at a scan rate of  $10^\circ/\text{min}$  in the range of  $2\theta = 10\text{--}90^\circ$ .

## 3. Results and discussion

### 3.1. Cyclic voltammetry

In order to clarify the effect of PbO concentration on the electrodeposition of lead onto stainless steel electrode from PbO-ChCl-urea solution, a set of voltammograms were conducted at 343 K, as shown in Fig. 1, from which the variation of cathodic peak potential  $E_{pc}$  and peak current density  $i_{pc}$  with PbO concentration  $C_{PbO}$  is obtained (Table 1). The cyclic voltammograms are initiated from the open circuit potential  $-0.10\text{ V}$  and the electrochemical window of ChCl-urea DES was determined in our previous study [26]. A promotion effect can be noticed because the deposition potential of Pb(II)/Pb  $E_{Pb(II)/Pb}$  and cathodic peak potential  $E_{pc}$  both shift to more positive values with the increasing of PbO concentration. This can be attributed to the fact that the reduction potential is changed with the PbO concentration of the solution. The anodic peak potential  $E_{pa}$  shifts to more positive values and the corresponding peak current density  $i_{pa}$  increases as the concentration increases. The difference in peak potentials  $\Delta E_p (=|E_{pa} - E_{pc}|)$  are in the range of 180–230 mV, which are much larger than the theoretical values of  $2.3RT/nF$  (34 mV) in reversible process (Table 1) [28]. Furthermore, good linear correlation between  $i_{pc}$  and  $\nu^{1/2}$  is obtained at 343 K in our previous study [26] which demonstrates that the reduction of Pb(II) in ChCl-urea DES is a diffusion controlled quasi-reversible process at various PbO concentration investigated in the present study.

At the initial stage of the redox reaction, there is little difference in Pb(II) concentration between the bulk solution and the electrode surface, i.e.  $C_{Pb(II)} \approx C'$  Pb(II). When the diffusion of Pb(II) is the controlling step of reduction rate, the reduction potential of Pb(II)/Pb on the electrode surface in PbO-ChCl-urea solution is given as follows [28,29].

$$\begin{aligned} E_{Pb(II)/Pb} &= E_{Pb(II)/Pb}^0 + \frac{RT}{2F} \ln (\gamma_{Pb(II)} \times C_{Pb(II)}) \\ &= E_{Pb(II)/Pb}^0 + \frac{RT}{2F} \ln (\gamma_{Pb(II)} \times C_{Pb(II)}) \end{aligned} \quad (1)$$

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