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Short communication

Electrodeposition of cobalt from spent Li-ion battery cathodes by the electrochemistry quartz crystal microbalance technique

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ABSTRACT

Information about the cobalt electrodeposition mechanism at different pH values was obtained using an electrochemistry quartz crystal microbalance (EQCM) technique as well as potentiodynamic and potentiostatic techniques. Potentiodynamic and potentiostatic electrodeposition of ionic cobalt at pH 5.40 occurs via a direct reduction mechanism. The mass/charge relation was found to be 33.00 g mol^{-1}. At pH 2.70, electrodeposition under potentiodynamic conditions occurs via a mechanism of cobalt reduction with the formation of adsorbed hydrogen. Potentiostatic analysis verified that cobalt reduction occurs simultaneously via direct reduction and with the formation of adsorbed hydrogen. The ratio mass/charge (M/z) is 13.00 g mol^{-1} for potentiodynamic conditions and 26.00 g mol^{-1} for potentiostatic conditions and potentiodynamic conditions. The cobalt electrodissolution occurs directly to Co^{2+} in pH 2.7 and through of the intermediary Co^{+} that is oxidized to Co^{2+} in pH 5.4.

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1. Introduction

Li-ion batteries were brought onto the consumer market by Sony Corp. in the early 1990s [1]. Desirable characteristics, such as high energy density, low auto-discharge rate, and high potential difference, made these batteries preferable to the typical Ni–Cd and Ni–MH batteries for many applications. Moreover, Li-ion batteries are less harmful to the environment. For Li-ion batteries, the main materials used are $LiCoO_2$ in the cathode and carbon in the anode [2]. High potentials obtained with these batteries (approximately 3.70 V) hinder the utilization of aqueous electrolytes so that a mixture of lithium organic solvents and inorganic salts is usually required.

Li-ion battery production has been continually increasing since the 1990s, accompanying the consumption growth of portable devices (e.g., cellular phones, microcomputers, and toys). World production of Li-ion batteries increased from 250 to 700 million units between 1998 and 2004 [3]. Residues generated by Li-ion batteries remained at 200–500 tons year^{-1} from 2002 to 2006. Cobalt constitutes between 5 and 20% (m/m) of this residue, while lithium constitutes 2–5% (m/m) of it [3]. The price of cobalt increased from \$15 to \$54 per kilogram between 2003 and 2004 [4]. Li-ion battery recycling is of great importance for environmental protection; however, economic factors should also be considered. In the USA, Japan, France, Germany, and Sweden, battery recycling is a successful practice. For these regions it is useful to study the established recycling processes of Li-ion batteries [5]. The spent batteries can be recycled by pyrometallurgical or hydrometallurgical processes. The pyrometallurgical process is not desirable due to the emission of toxic gases into the environment. The hydrometallurgical process is thus more favorable from an environment conservation viewpoint. In the hydrometallurgical process, after battery dismantling occurs, the electrodes are dissolved in concentrated acids. After this stage, the resultant solution, which contains metal ions, can be recovered in one of three forms: precipitation, extraction, or electrodeposition. Electrochemical recycling is a viable process to produce cobalt metallic films, alloys, and multilayer deposits with controlled structure and morphology. For this reason, part of cobalt electrochemical recycling is the study of its electrodeposition mechanism. In order to study electrochemical recycling, it is necessary to analyze the mechanism of cobalt electrodeposition at different solution pH.

The production of metallic cobalt is accomplished predominantly via electrodeposition in an aqueous solution [6]. It has been suggested that cobalt electrodeposition at pH < 4.00 occurs together with a hydrogen detachment reaction [6–12]. During this electrodeposition, a rich hydrogen phase can be adsorbed in the deposits, as represented by Eqs. (1)–(4):

$$Co_{(aq)}{}^{2+} + 2e^{-} \rightarrow Co_{(s)}; \tag{1}$$

$$H_{(aq)}{}^{+} + Co_{(s)} + e^{-} \rightarrow CoH_{(ads)}; \tag{2}$$

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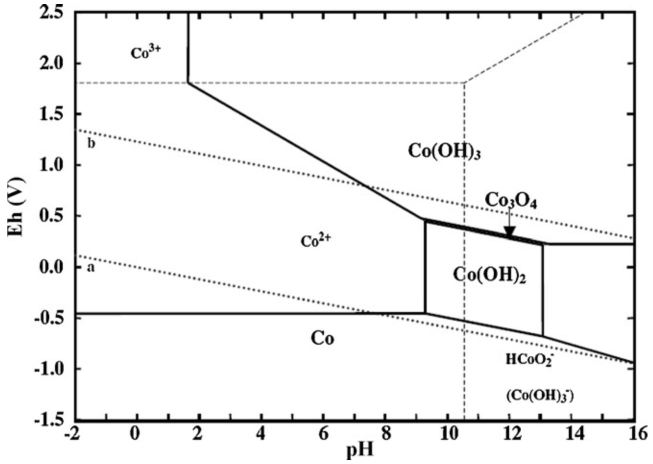

Fig. 1. Pourbaix diagram for Cobalt–H_2O system.

$$H_{(aq)}{}^{+} + CoH_{(ads)} + e^{-} \rightarrow Co_{(s)} + H_{2(ads)}; \tag{3}$$

$$\text{Total equation}: \ Co_{(aq)}{}^{2+} + 2H^{+} + 4e^{-} \rightarrow Co_{(s)} + H_{2(ads)}. \tag{4}$$

At pH > 4.00, the electrodeposition of cobalt occurs via $Co(OH)_2$ forming in the interface electrode solution (chemical stage). In the cobalt electrodeposition process the interface electrode solution becomes alkaline due to the water reduction (Eq. (5)). The local alkalization that occurs in the interface electrode solution can provoke the precipitation of the $Co(OH)_2$ as showed in Pourbaix diagram (Fig. 1). The presence of cobalt hydroxide was confirmed with an electrochemistry quartz crystal microbalance (EQCM) technique, as done by Matsushima et al. [11].

H_3BO_3 was added to the cobalt electrodeposition solution to avoid pH variations in the interface electrode solution. In this case, the electrodeposition of cobalt occurs directly, owing to Eq. (1) [12]. Eqs. (5)–(8) describe the electrodeposition process through formation of a cobalt hydroxide intermediate:

$$2H_2O + 2e^{-} \rightarrow 2OH_{(aq)}{}^{-} + H_{2(g)}; \tag{5}$$

$$Co_{(aq)}{}^{2+} + 2OH_{(aq)}{}^{-} \rightarrow Co(OH)_{2(s)}; \tag{6}$$

$$Co(OH)_{2(s)} + 2e^{-} \rightarrow Co_{(s)} + 2OH_{(aq)}{}^{-}; \tag{7}$$

$$\text{Total equation}: \ Co_{(aq)}{}^{2+} + 2H_2O + 4e^{-} \rightarrow Co_{(s)} + 2OH^{-} + H_{2(g)}. \tag{8}$$

The EQCM technique supplies detailed information about variations in electrodeposition and electrodissolution mass for fine films, as caused by oxidation and reduction processes [13–20]. According to Sauerbrey's equation, frequency variation (Δf) of the quartz crystal can be correlated with the mass variation (Δm) and can be written according to Eq. (9):

$$\Delta f = \left(\frac{-2f_0^2 \Delta m}{A\sqrt{\mu_i \rho_i}} \right) = -\Delta m K \tag{9}$$

where f_0 is the resonance frequency of the quartz crystal, A is the piezoelectric active area, μ_i is the quartz shear modulus, K is the experimental mass coefficient, and ρ_i is the density of quartz.

The current work is a continuation of previous work that studied the electrochemical recycling of cobalt from the spent cathodes of Li-ion batteries [8]. In this work, a greater efficiency for cobalt electrodeposition was found at a potential equal to −1.00 V at all pH values tested (1.50, 2.70, and 5.40). It was observed that the charge efficiency of cobalt electrodeposition decreased with a decrease in the pH of the solution. The cobalt nucleation process was investigated with the help of mathematical models proposed by Scharifker and Hills [21]. In the present work, the electrodeposition mechanism of cobalt thin films has been studied. For this reason the electrochemical quartz crystal microbalance technique was used together with potentiodynamic and potentiostatic techniques to obtain information about the electrodeposition mechanism for cobalt from the cathodes of spent Li-ion batteries. This technique is very effective in the study of the mechanism of metal electrodeposition for thin films. However, deviations from the Sauerbrey's equation occur for thick films. The study of the electrodeposition mechanism is key in electrochemical recycling because it correlates with the structure, morphology, and properties of the cobalt film. The current work aims to clarify the cobalt electrodeposition mechanism as a function of pH. It follows then that the study of the cobalt electrodeposition process is of paramount importance in the electrochemical recycling of cobalt.

2. Experimental

2.1. Electrodeposition solution preparation

Li-ion batteries were manually dismantled and physically separated into their different parts, including the anode, cathode, steel, separators, and current collectors. Electrodes were dried at 80 °C for 24 h and then washed in distilled water at 40 °C for 1 h under agitation to eliminate organic solvents, propylene carbonate (PC), and ethylene carbonate (EC). This procedure also facilitates the detachment of active material from the respective current collectors. Active material was filtered, washed with distilled water at 40 °C to remove potential lithium salts (e.g., $LiPF_6$ and $LiCl_4$) and Cu (from anode current collector), and then dried in air for 24 h. A total of 9.17 g of positive electrode material was dissolved in a solution containing 470.00 ml of HCl 3.00 mol l^{-1} and 30.00 ml of H_2O_2 (30%, v/v). This system was maintained under constant magnetic agitation at 80 °C for 2 h. Cathode dissolution efficiency increases with increasing acid concentration and temperature. The addition of H_2O_2 was necessary to increase cathode dissolution efficiency [22]. H_2O_2 reduces cobalt from a +III oxidation state, which is insoluble in aqueous systems, to a +II oxidation state, which is soluble in aqueous systems. For an active material consisting of $LiCoO_2$, the cathode dissolution reaction is represented by Eq. (10):

$$LiCoO_{2(s)} + 1/2H_2O_{2(l)} + 3HCl_{(aq)} \rightarrow CoCl_{2(aq)} + 1/2O_{2(g)} + LiCl_{(aq)} + 2H_2O_{(l)} \tag{10}$$

The cathode composition was found to be $LiCoO_2$, Co_3O_4, Al, and carbon [8]. The cathode can be contaminated with electrolyte or anode material. Therefore, the leaching solutions used were characterized by atomic absorption spectroscopy (AAS) to detect the presence of lithium, copper, and cobalt. The cobalt and lithium concentrations were both equal to 0.10 mol l^{-1}. The ionic copper concentration was not detected. The ionic lithium does not influence the cobalt electrodeposition because its reduction occurs at a more cathodic potential (−3.02 V). Solutions were buffered using H_3BO_3 at 0.10 mol l^{-1} to maintain the electrodeposition bath pH.

2.2. Electrochemistry quartz crystal microbalance measurements

For ECQM Experiments, a 50.0 ml Pyrex® cell was used. The cover was made of Teflon® and included holes for the introduction of saturated Ag/AgCl/NaCl reference and platinum auxiliary electrodes, with a geometric area of 0.50 cm^2. The working electrode was introduced at the bottom of the cell. Working electrodes were composed of quartz crystal covered with platinum of

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