



Short communication

Recycling of spent ion-lithium batteries as cobalt hydroxide, and cobalt oxide films formed under a conductive glass substrate, and their electrochemical properties



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HIGHLIGHTS

- Cobalt recycling as $\text{Co}(\text{OH})_2$ and Co_3O_4 films formed under a conductive glass.
- Morphological and structural characterization of recycled $\text{Co}(\text{OH})_2$ and Co_3O_4 films.
- Electrochemical properties of $\text{Co}(\text{OH})_2$ and Co_3O_4 films under a conductive glass.

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ABSTRACT

In this work, $\text{Co}(\text{OH})_2$ and Co_3O_4 films have been obtained using a solution to leach the cathodes of spent Li-ion batteries. The $\text{Co}(\text{OH})_2$ is electrodeposited onto conductive glass by the application of -0.85 V, with a charge density of 20 C cm^{-2} , and its efficiency is found to be 66.67%. The Co_3O_4 film is obtained by heat treatment of the $\text{Co}(\text{OH})_2$ film at 450 °C for 3 h, in an air atmosphere, with a conversion efficiency of 64.29%. The cyclic voltammetry of $\text{Co}(\text{OH})_2$, in KOH 1.0 mol L^{-1} shows: three anodic peaks in the first cycle associated with the oxidation of $\text{Co}(\text{OH})_2$ to Co_3O_4 , the conversion of Co_3O_4 into CoOOH , and the formation of CoOOH to CoO_2 and the oxidation of water. The absence of cathodic peaks shows that oxidation from $\text{Co}(\text{OH})_2$ to CoO_2 is an irreversible process. For the Co_3O_4 electrode, this verifies the existence of a redox pair associated with reversible oxidation of the Co_3O_4 to CoO_2 . The Co_3O_4 obtains a charge efficiency of 77% for the first 10 cycles (1.0 mV s^{-1}) and a specific capacitance of 31.2 F g^{-1} (1.0 mV s^{-1}) and 10.5 F g^{-1} (10 mV s^{-1}). Co_3O_4 films have promising applications as pseudocapacitors.

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1. Introduction

Worldwide economic expansion has brought about the phenomenon known as globalization, which has been facilitated by technological advances. As a result, there is a growing use of electronic devices that are dependent upon energy accumulators, especially portable devices, such as mobile devices, notebooks, smartphones, implantable medical devices, hybrid electric vehicles, etc. [1].

Today, Li-ion batteries is one of the primary models used in electronic devices because they have high energy density, low self-discharge rate, long life cycle, high electrical potential difference,

and low environmental impact [2]. The cathode of a Li-ion battery consists of a LiCoO_2 layer over an aluminum current collector. The anode consists of carbon materials over a copper current collector, and the electrolyte contains inorganic Li salt dissolved in organic solvents [3,4].

Because of the increasing demand for electronic devices, environmental and economic concerns have surfaced. One example of these concerns is the discarding of the devices when they are depleted and the shortage of raw materials used to make the devices. With that being said, the technological advances in the search for more economical, efficient, and environmentally compatible materials, as well as the development of techniques for recycling these devices, is extremely relevant to society.

The recovery of cobalt, in the form of $\text{Co}(\text{OH})_2$ and Co_3O_4 , from the cathodes of Li-ion batteries is an interesting proposal because, according to the London Metal Exchange (LME) in March 2014, the price of cobalt was US\$ 30.2 kg^{-1} [5]. Consequently, $\text{Co}(\text{OH})_2$ and

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Co₃O₄ films have received increasing attention from researchers because they have features that are compatible with various technological applications, such as supercapacitors, electrodes for batteries, electrochromic devices, as well as functioning as an additive for electrodes of Ni(OH)₂, and as a catalyst [6–18]. The Co(OH)₂ and Co₃O₄ films have been prepared via electrodeposition in solutions that contain nitrate ions for application as supercapacitors, electrochromic devices, as an additive for electrodes of Ni(OH)₂, and as a catalyst. The alkalization of the electrode/solution interface occurs due to the reduction of both nitrate and water. Then, the precipitation of Co(OH)₂ occurs, as can be seen in the following equations [19–21]:



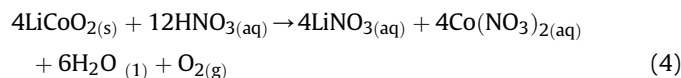
This work aims to associate the electrochemical recycling of the cobalt that is present in Li-ion depleted batteries with the properties of recycled Co(OH)₂ and the Co₃O₄ films formed under glass substrate coated with indium-doped tin oxide (ITO) for possible applications in pseudocapacitors, electrochromic windows, and as catalysts. In this study, Co₃O₄ was obtained by heat treatment of electrodeposited Co(OH)₂ on ITO. The Co₃O₄ films obtained from the heat treatment of Co(OH)₂ demonstrates good efficiency and reversibility in the voltammetric and galvanostatic charge and discharge cycles. The electrochemical behavior of the materials was evaluated by cyclic voltammetry and the charge and discharge cycles were observed. For characterization, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were applied.

2. Experimental procedure

2.1. Preparation of the electrodeposition bath

Spent Samsung Li-ion batteries were dismantled manually and separated into their basic components: cathode, anode current collector, and involucre. The cathode was dried at 120 °C for 24 h. After drying, the cathode was placed in distilled water at 40 °C for one hour. During this period, separation of the active material (LiCoO₂) from the current collector (Al) occurs. After separation from the current collector and washing, the active material was dried at 60 °C for 24 h.

For preparation of the electrodeposition bath, 10.0 of the cathode material was dissolved in 1.0 L of HNO₃ 3.0 mol L⁻¹ solution with stirring for 2 h at 80 °C. The dissolution of the cathode solution was filtered, removing the insoluble materials, such as carbon black, that make up the electrode. The dissolution process is represented by the following chemical equation:

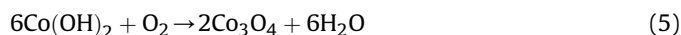


2.2. Preparation and characterization of the Co(OH)₂ and Co₃O₄ films

The pH of the dissolution of the cathode solution was 6.5 with the addition of KOH powder, and the solution was buffered with H₃BO₃ 0.1 mol L⁻¹. The working electrodes were made with glass coated with a film of indium-doped tin oxide (ITO), with an active area of 0.5 cm². The ITO substrates were washed with detergent and distilled water, and then they were placed in an ultrasound bath for

10 min. Afterwards, they were cleaned with ethanol, acetone, and isopropyl alcohol and finally dried in a room environment temperature. The counter electrode was graphite with 99% purity and an area of 3.0 cm².

The parameters for the electrodeposition of the Co(OH)₂ films under ITO were determined through cyclic voltammetry (CV), with a scan rate of 10.0 mV s⁻¹, beginning from 0.50 V and switching to the cathode potential of -1.10 V and then returning to 0.50 V vs Ag/AgCl. The electrodeposition of Co(OH)₂ on the ITO substrate was performed by applying the potential of -0.85 V vs Ag/AgCl and the charge density of 20.0 C cm⁻². A mass of 0.0032 g (66.67% relative to theoretical mass of 0.0048 g), of the Co(OH)₂ precursor material was obtained by potentiostatic electrodeposition on ITO. The mass efficiency was of 66.67% because the electrodeposition of Co(OH)₂ onto the ITO substrate occurs after alkalization of the electrode/solution interface through nitrate reduction. After alkalization of the electrode solution interface and the solubility of the product is achieved, the Co(OH)₂ film precipitates onto the ITO. The Co(OH)₂ film is nonconductive and blocks the passage of current. Therefore, only part of the charge is used to reduce the nitrate ion and subsequent precipitation of Co(OH)₂. After the Co(OH)₂ films were formed on ITO by electrodeposition, the electrodes (Co(OH)₂ films and ITO substrate) were washed and calcined at 450 °C for 3 h to obtain Co₃O₄ [22]. The chemical transformation that the calcinated material underwent can be represented by the chemical Equation (5): [19]



The efficiency of conversion of Co(OH)₂ to Co₃O₄ is 64.29% w/w due to the loss of material during washing and calcination. The mass loss could be caused by lack of adhesion between the Co(OH)₂ film and ITO substrate.

The electrochemical properties of Co(OH)₂ occurred in the range of -0.4 V to 0.6 V, and returned to -0.4 V to 0.5 V. The electrochemical properties of the Co₃O₄ electrodes were analyzed using cyclic voltammetry (CV); the initial potential of those electrodes ranged from 0.4 V to the vertex potential of 0.6 V, and then the potential was returned to 0.4 V, with rate scans of 1.0 mV s⁻¹ and 10 mV s⁻¹. The reference electrode and the counter electrode were Hg/HgO and the graphite (area 3.0 cm²), respectively. The electrolyte solution used was KOH 1.0 mol L⁻¹ without stirring at 25 °C. The galvanostatic charge and discharge cycles are made with current of 111.1 mA g⁻¹, the charge and discharge time of 60 s, and the active material mass of 0.0018 g.

All the electrochemical measurements were performed using Autolab PGSTAT 302N potentiostat/galvanostat equipment with an electrochemical impedance spectroscopy module (EIS), coupled without stirring at 25 °C.

The X-ray diffraction measurements were performed using a BRUKER model D2 PHASER[®] with Cu Kα radiation (λ = 1.5406 Å) and a scan rate of 2 min⁻¹. Scanning Electron Microscopy (SEM) of the Co(OH)₂ and Co₃O₄ were performed using a scanning electron microscope, JEOL 6610LV.

3. Results and discussion

3.1. Electrochemical formation and characterization of the Co(OH)₂ film growth on the ITO substrate

The cyclic voltammogram for the electrodeposition of the Co(OH)₂ films on the ITO substrate at a scan rate of 10 mV s⁻¹ is represented in Fig. 1. The formation of Co(OH)₂ on the surface of the electrodes occurs in the electrochemical and chemical steps. In a direct scan there is an increase in the current density from -0.6 V

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