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Development of non-enzymatic glucose sensor using recycled cobalt from cell phone Li-ion batteries



Sicele A. Gonçalves^a, Eric M. Garcia^{a,*}, Hosane A. Taroco^a, Rodrigo G. Teixeira^a, Kassílio J. Guedes^a, Honória F. Gorgulho^b, Patrícia B. Martelli^b, Antônio P.L. Fernandes^c

^a University of São João Del Rei – Sete Lagoas Campus/DECEB, MG 424- Km 45, Sete Lagoas, MG 35701-970, Brazil
^b University of São João Del Rei/DCNAT, Praça Dom Helvecio 74, Fábricas, São João Del Rei, MG 36301-160, Brazil
^c Federal University of Minas Gerais, Department of Chemistry, Av. Antônio Carlos, 6627, Minas Gerais, Brazil

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ABSTRACT

This article aims to present an alternative to recycling of spent Li-ion batteries applied to electrochemical sensor manufacturing. The cobalt, from cathode of Li-ion batteries, was recovered by electrodeposition onto AISI 430 stainless steel substrate and applied as glucose sensor. The composition of cathode utilized was obtained by AAS measures and corresponds to $\text{LiNi}_{0,40}\text{Co}_{0,60}\text{O}_2$. Despite this composition, in the cobalt electrodeposition onto AISI 430 stainless steel the Ni is less of 1.7% (w/w) due the anomalous electrodeposition. The sensitivity of cobalt electrode for glucose detection is 70.2 μ A/mmol cm² and the linear range is 1–10 mmol/L. This result shows that the Co electrodeposited onto AISI 430 stainless steel is a promissory and low-cost non-enzymatic glucose sensor.

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1. Introduction

The Li-ion battery promoted a great technological revolution in electronic equipment in mid 1991 (Tao et al., 2014). Among the many advantages of Li-ion batteries can be highlighted the high energy density, long lifespan and light weight (Eric et al., 2014; Zhang et al., 2014). The numbers of Li-ion batteries are expressive. In 2012 the Li-ion batteries were responsible for 60% of total portable battery market what corresponds to \$11.8 billion dollars (Eric et al., 2014). The large consumption of mobile phones contributes enormously to circulation of Li-ion batteries in the market. In 2010 consumers of mobile phones overcome 5.2 billions, what is extremely alarming considering the toxic waste generated (Tao et al., 2014). Although the Li-ion batteries are less environmentally harmful than their predecessor NiCd batteries, they still have in their composition potential toxic metals such as Co, Li, Ni and Mn (Joulié et al., 2014; Schneider et al., 2014). Thus, it is extremely necessary scientific studies focused on the recycling of Li-ion batteries (Xihua et al., 2014; Zhang et al., 2013). In this context, the cathode of Li-ion batteries is the part most valuable and the most researched due the cobalt presence in form of LiCoO₂ and $LiCo_xNi_{(1-x)}O_2$ (Joulié et al., 2014; Mariana et al., 2015). By other hand, the metallic cobalt reached US\$ 30.2 kg in 2014 (Barbieri et al., 2014). Moreover, recycling of cobalt is necessary due to its toxicity. The recent studies in animals demonstrated an incidence of alveolar/bronchial neoplasms and pheochromocytomas by exposure to soluble cobalt (Mamta et al., 2015). In literature is described the recycling of Li-ion batteries cathode in the production of pseudocapacitors (Barbieri et al., 2014) and in the production of catalysts for environmental decontamination (Mariana et al., 2015). The recycling process proposed in this study aims the application of cobalt and nickel, obtained from spent cathode, as electrochemical sensor of glucose. Thus, another aspect of the recycling of Li-ion batteries, focused on environmental analytical chemistry can be developed. The electrochemical sensor of glucose has attached much interest over the years due its low cost, response time, sensitivity and selectivity compatible with enzymatic sensors (Fei-Fei et al., 2015; Jiao and Jianbin, 2015). Despite being a current theme, no work proposes the application of recycled Co as glucose sensor. In this way, the aim of this paper is to show the potential application of Co from spent Li-ion battery cathode as glucose sensor. To this end, spent Li-ion battery cathode was dissolved in sulfuric acid for prepare the electrodeposition bath (Iha et al., 2013). The Co was obtained by potentiostatic electrodeposition. The electrochemical behavior of Co in front of glucose was made by cyclic voltammetry and chronoamperometry in NaOH solution.

^{*} Corresponding author. *E-mail address:* ericmgmg@hotmail.com (E.M. Garcia).

2. Material and methods

2.1. Preparation and characterization of lixiviation solution of spent cathode of Li-ion batteries

The Li-ion battery was manually dismantled and the spent cathode in tape form was separated. The cathode tape was heated to 200 °C for 5 h to remove organic solvents before use (Li et al., 2010). The spent Li-ion battery cathode tape was scraped from the current collector (Al) for elemental analysis (Fig. 1-a). One battery yielded a powder mass of 8.39 g (Fig. 1-b). The powder was dissolved in 1000 mL of 2.0 M sulfuric acid and 6 mL of H₂O₂ 36% v/v (Fig. 1-c) (Eric et al., 2012; Freitas et al., 2009). In Li-ion batteries the most common binder is polyvinylidene-fluoride (PVDF). This part was included in the manuscript "In Li-ion batteries the most common binder is polyvinylidene-fluoride (PVDF). This compound can act in complexation of Co ions working as additive (Eric et al., 2012). The resulting solution was filtred and analyzed by atomic absorption spectrophotometry (AAS) on a Hitachi-Z 8200 (Fig. 1-d and e). The crystalline structure of the spent Li-ion battery cathode tape was characterized by X-ray diffraction on a 200 B Rotaflex-Rigaku with Cu K_{α} irradiation, a Co filter, and scanning speed of 0.02° min⁻¹. The morphology of the spent Li-ion battery cathode tape was observed by Field-Emission Scanning Electron Microscopy on a IEOL IXA model 8900 RL.

2.2. Electrochemical measurements

Electrochemical measurements were made using an AUTOLAB PGSTAT 30 power supply. The working electrode was made of AISI 430 stainless steel. The composition of working electrode is shown in the Table 1. The samples were prepared as wire with 0.50 mm in spiral shape. The auxiliary electrode, with an area of 3.75 cm², was

Table 1

The elementary composition of 430 AISI stainless steel obtained by atomic absorption spectophotometry.

	С	Mn	Si	Р	S	Cr	Fe
%(w/w)	0.06	0.02	0.4	0.040	0.030	17.0	Balance

made of platinum. A saturated Ag/AgCl reference electrode was used. The working electrodes were sanded with 600-grit sandpaper before each measurement and washed with distilled water. All the electrochemical measurements were performed without solution agitation, at 25 °C.

2.2.1. Co-Ni electrodeposition onto 430 AISI stainless steel

The voltammetry of 430 AISI stainless steel was realized in lixiviation solution in pH = 2 for determination of better potential for Co and Ni electrodeposition. The scan rate was 50 mV s⁻¹ and the interval of potential was -0.40 V (rest potential) up to -1.50 V (Eric et al., 2012). For electrodeposition of Co-Ni alloy was utilized the potentiostatic method. The stair of potential applied was 0.0 V, 10 s, -1.0 V, 30 s and 0.0 V, 10 s. This experiment was used for charge efficiency($Q_{\%}$) calculation (Eq. (1)). For preparation of sensor based on Co, the potentiostatic electrodeposition was performed during 1000 s in -1.0 V. The pH of bulk and interface electrode solution varies during electrodeposition due water reduction. However, due to the relatively acidic pH on electrodeposition bath used in this study (pH = 2), the solution not was buffered.

$$Q_{\%} = \frac{\int i_c dt}{\int i_a dt} \times 100 \tag{1}$$

The Ni and Co composition was made by dissolution of electrodeposits in HNO₃ 1 M and determinate by AAS measure.



Fig. 1. (a) Cathode powder scraped from the current collector. (b) Powder mass of 8.39 g of cathode. Dissolution of cathode powder in 2 M sulfuric acid and 6 mL of H₂O₂ 36% v/v (c).

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