Obtention of a cobalt-bearing coating using spent batteries as raw materials

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Abstract. The extensive use of smartphones is increasingly generating technological waste, such as the spent lithium-ion rechargeable batteries, which contains potentially toxic metals that may affect the environment. These metals can be recovered and used as raw material for new industrial applications, such as the production of metal coatings. In this work, a sample of spent lithium-ion batteries was manually disassembled, to extract transition metal-rich cathodes. The cathodes were separated and crushed in a blade mill, to obtain a cobalt-rich concentrate powder by sieving. The powder was leached using a 1.11 M citric acid solution amended with hydrogen peroxide (1.25% volume), at 74°C under stirring at 300 rpm. The obtained polymetallic liquor was analyzed for Co, Li, Mn, and Ni, then it was submitted for electrolysis to produce metal coatings over pure copper substrates. This electrochemical electrodeposition was studied by means of cyclic voltammetry and chronoamperometry, using electrolytic Cu as a working electrode (substrate), a reference electrode Ag/AgCl and an auxiliary graphite electrode. The visual appearance of the obtained coatings was analyzed by an Olympus SZ61 stereoscope, with images at a magnification of 120x. The results showed that by applying a -950 mV vs Ag/AgCl electrodeposition potential, a homogeneous coating with good adhesion and better visual appearance was obtained. In addition, at this potential, there was little influence of the reaction of hydrogen evolution reaction during the production of the coatings.

1. Introduction
Due to the mass production of electronic devices and the accelerated frequency of replacement by consumers, smartphone-related waste such as the spent lithium-ion (Li-ion) batteries is becoming a major environmental concern [1]. Researchers estimate that, by 2020, more than 25 thousand million Li-ion batteries are going to be discarded, i.e. circa 500,000 tons [2]. Discarded Li-ion batteries require proper management during final disposition because they contain a considerable amount of potentially toxic and valuable metals, such as Co, Ni, Mn, and Li. These metals may re-enter the environment, impacting mainly underground water sources and human health [3]. In this scenery, it is necessary to devise new ways to recycle these devices and in order to recover secondary raw materials for industrial applications. One of these ways is the combination of hydro and electrometallurgy processes, methods that are more efficient, environmentally friendly and consume less energy [4]. In the case of the Li-ion batteries, the materials of the cathodes can be recovered. The cathodes comprise a thin aluminum foil covered with a powder of lithium-bearing metal oxides, such as LiCoO₂, LiNiO₂, and LiMn₂O₄ [5]. For the recovery of these metals, it has been reported [4] that this cathodic powder can be leached using strong acids (HCl, H₂SO₄, and HNO₃), obtaining goods results. Nevertheless, these leaching agents may produce harmful fumes (Cl₂, SO₃, and NOₓ) and waste solutions [4] that discourage their usage. Other researchers [6] have employed combinations of citric acid (C₆H₈O₇), a biodegradable natural acid, and hydrogen...
peroxide (H₂O₂) as leaching agents, bearing in mind that this mixture would promote the formation of complex ions in solution, hence increasing over 90% the hydrometallurgical recovery efficiency. Based on the above-mentioned situation, in this work, the metal oxide bearing powder obtained from the cathodes of spent Li-ion batteries was leached using a solution containing citric acid and hydrogen peroxide. The presence of metals in the solution was verified by chemical analysis and the observed leaching efficiency was explained by the presence of complexed metal species in the solution, as determined by thermodynamic simulations. The liquors obtained were submitted to electrolysis, to produce cobalt-based metal coatings over copper substrates. Proper conditions for electrodeposition were established by means of electrochemical techniques and optical microscopy. The objective of the work was to show that spent Li-ion batteries can be successfully used as raw materials for the electro-coatings industry.

2. Experimental procedure

2.1. Extraction and analysis of the cathode powder material from the spent Li-ion batteries
The spent Li-ion batteries were obtained from the electronic waste collection stations of the Universidad Industrial de Santander, Colombia. Initially, etiquettes, plastic covers, and electric contacts were separated from the metal case of the batteries. Then, a little incision was made in the cases with a knife and the perforated batteries were immersed into a saline solution of 7 wt % NaCl during 24 h, to grant their complete discharge. Discharged batteries were then dried at 40°C for 48 hours. The next step was to separate the aluminum case and to extract the electrodes ribbons. This work only focused on the cathodes (40% of battery weight). The cathode ribbons were triturated in a blade mill and the mixture obtained was sieved, in order to separate the cathode powder (28.77% of battery weight) present in the undersize fraction [3]. The metal content of the powder was determined by atomic absorption spectroscopy (AAS), after digestion of the powder in aqua regia. The amount of hydrogen, nitrogen, and carbon in the powder was determined using a Sundy SDCHN435 elemental analyzer. The composition of the metals in the cathode powder was found to be as follows (wt %): 11.54% Co, 0.65% Li, 15.57% Mn, 2.83% Ni and 0.83% Al, as obtained by AAS. Whereas other elements such as hydrogen, nitrogen, and carbon analyzed 0.99 wt %, 0.075 wt %, and 4.92 wt % respectively. These values are in agreement with previously reported results [3].

2.2. Metals leaching and thermodynamic simulations
Once the cathode powder was obtained, it was leached in a 1.11 M citric acid solution amended with 1.25% H₂O₂ (by volume) to promote the conversion of the Co³⁺ to Co²⁺ that is more soluble and forms easily complex ions [4]. The cathode powder was added to the solution at 17.8 g/L and the leaching was performed at 74°C under stirring at 300 rpm for three hours, in a round glass reactor equipped with a condenser to prevent leachate evaporation. The solution was filtered to separate undissolved fractions (mainly carbon particles). The metal contents of the solution were evaluated by atomic absorption spectroscopy and submitted to electrolysis, as described in section 2.3. The pH of the leachate solution was measured and found to be 2.62. The results obtained from chemical analysis were used to run thermodynamic simulations employing the Hydra Medusa software to obtain species distribution and Pourbaix diagrams. Only the molar concentration of each analyzed element that takes part in reactions and their electrical charge was used in the calculations like the ionic strength (0.262 mol/L).

2.3. Synthesis and evaluation of the coatings
The coatings were synthesized in a three-electrode cell, using a graphite rod as a counter electrode, an Ag/AgCl reference electrode and an electrolytic copper wire as a working electrode. The working electrode was ground using 1500-grit sandpaper in all cases. The electrochemical study of the electrodeposition process was performed using an Autolab PGSTAT-101 potentiostat/galvanostat. The reduction of the species on the working electrode was studied by cyclic voltammetry, varying the scan rates from 10 mVs⁻¹ to 50 mVs⁻¹ and under no-stirring. Furthermore, chronoamperometric measurements
were done with a working potential between -800 mV to -1,000 mV vs Ag/AgCl during 600 s. Additionally, keeping constant the potential at -950 mV vs Ag/AgCl, the deposition was performed increasing the time from 600 s to 3,600 s. These electrodeposition experiments were done under continuous stirring at 400 rpm. The visual appearance of the obtained coatings was analyzed using an Olympus SZ61 stereoscope, with images at an original magnification of 120x.

3. Results and discussion

3.1. Metals leaching

During leaching, an insoluble mass was observed, probably due to the carbon present in the cathode material or due to other insoluble species. After filtering, the leachate was a translucent dark red solution with pH = 2.62. In Table 1 the chemical composition of this solution is shown. It can be observed that Li, Mn, and Al were totally recovered in the solution, whereas Co and Ni were partially recovered. Total recovery of Li and 90% Co have been reported in similar works [4].

| Elements | Co   | Li   | Mn  | Ni   | Al   |
|----------|------|------|-----|------|------|
| Concentration (mg/L) | 1,191.47 | 148.34 | 3,160.55 | 395.16 | 193.21 |
| %Recovery | 58.23 | 100  | 100 | 79.09 | 100 |

Citric acid is expected to form metal complexes in solution, acting as ligand aiding the dissolution of the metals contained in the cathode powder [7]. Moreover, the addition of hydrogen peroxide [7] would help to promote reductive leaching of cobalt. Figure 1. Show the species distribution diagrams for the main elements studied in the citrate-peroxide system.

Figure 1. Species distribution plots for (a) Co^{2+}/citrate, (b) Mn^{2+}/citrate, (c) Ni^{2+}/citrate and (d) Li^{+}/citrate under the conditions of the leaching system.

In Figure 1(a) at pH = 2.62, the predominant ionic (soluble) species of cobalt are quantified as follows (% mol): 55.4 Co(H_2C_6H_8O_7)^+, 1.8 Co(C_6H_8O_7)^2- and 0.3% Co^{3+}, this confirms the formation of metal complexes in the system. The remaining Co (42.5%) is present as an insoluble salt (cobalt citrate), i.e.
Co(C₆H₈O₇). That would explain the lower leaching efficiency of this metal because the cobalt citrate is a solid substance. From Table 1 it is clear that 41.77% of cobalt was not leached, so both, simulation and experiment are in close agreement. Similarly, with the others metals, in Figure 1(b), at leachate pH = 2.62, 97.77% of the available manganese is forming the soluble species Mn(H₂C₆H₈O₇)⁺ and this is in close agreement with the measured recovery of Mn (Table 1), which reached 100%. The little difference may be due to the ionic strength, for the construction of the diagrams in Figure 1 only the metal ions known were considered to estimate the ionic strength of the solution and this supposition may not be completely accurate. In the case of Ni, data in Table 1 is also consistent with Figure 1(c), which shows that 14.3% of insoluble nickel citrate is stable at the leachate pH. Finally, the thermodynamic simulation for Li showed in Figure 1(d) indicated that all the lithium present in the leachate is dissolved as Li⁺ at the leachate value of 2.62 and this is also consistent with the 100% recovery presented in Table 1 for Li.

3.2. Synthesis and evaluation of the coatings

Figure 2(a) shows cyclic voltammetry of the leachate solution on a copper electrode, varying the scan rate of 10 mVs⁻¹ to 50 mVs⁻¹. Initially can be observed that all the curves present the same behavior, no one shows additional peaks that would indicate different reactions. It is only detectable a slight increase in the values of current density when scan rate is increased, hence it can be concluded that the scan rate did not affect significantly the electrochemical process. Between the starting potential, close to the copper equilibrium potential, and -0.7 mV vs Ag/AgCl, despite small reduction currents are measured, no indication of the formation of solid products on the surface of the working electrode. For more negative potential a reduction process with exponential behavior is observed, indicating a kinetic control as predicted by Butler-Volmer equation [8]. In this region, the reduction of the metal species present in the solution are overlapped with the hydrogen evolution reaction [9], because under the experimental conditions the equilibrium potential of these metals Co²⁺ in its complexed form are more negative than the hydrogen equilibrium potential, as shown in the cobalt –citrate Pourbaix diagram showed in Figure 2(b). This behavior was seen for the other metal ions present in solution, Mn²⁺, Ni²⁺, Li⁺ and Al³⁺ (data not shown).

![Figure 2](image-url)

**Figure 2.** (a) Cyclic voltamperograms of the leachate solution on copper electrode varying the scan rate from 10 mVs⁻¹ to 50 mVs⁻¹. (b) Pourbaix diagram of cobalt/citrate system under the experimental conditions of this work.

The Figure 3(a) show the chronoamperograms for each applied potential starting at -800 mV vs Ag/AgCl and ending at -1,000 mV vs Ag/AgCl at 50 mV steps. Both limits were determined from the cyclic voltammetry, considering the stability of the working electrode and the hydrogen evolution reaction. All the curves showed the same behavior, first increasing to values more negatives of current
density and arriving at a plateau, which indicates process stability. This might be explained by the fact that, at the beginning of the electrodeposition process, a diffusion layer is built-up over the working electrode until it reaches a certain depth, which is kept constant afterward by the stirring in the system. This constant thickness of the diffusion layer, in turn, allows the steady diffusion of metal complex ions from the solution to the electrode surface, stabilizing the electrodeposition process [10]. In Figure 3(b) the respective stereoscopic photos of the coated working electrodes (copper) at 120x (original magnification) can be seen. All the images were taken on segments of the central area of the working electrode, to appreciate the change of tonality on the surface caused by the increase of the amount of coating on the copper surface. Initially, at -800 mV vs Ag/AgCl no deposition can be distinguished on the surface of the working electrode. Then, as the potential is increased up to -950 mV vs Ag/AgCl the coating covered the entire copper surface showing a good visual aspect. The last potential applied, -1,000 mV vs Ag/AgCl, showed more deposition but under these conditions the reaction of evolution of hydrogen was very high and promoted the nucleation and the growth of H₂ bubbles that adhere to the surface and hinder the process of electrodeposition of metal ions on the substrate. As a result, a heterogeneous coating with circular pores was obtained.

![Figure 3](image-url)

**Figure 3.** (a) Chronoamperograms obtained from the leachate solution from -800 mV to -1,000 mV vs Ag/AgCl during 600 seconds, under stirring at 400 rpm. (b) Respective stereoscopic photographs of the work electrodes at 120x (original magnification).

Figure 4(a) shows the chronoamperograms obtained keeping a constant potential (-950 mV vs Ag/AgCl) at different times. With the study of the coatings obtained at different times of electrodeposition, it is sought to determine the mechanism by which the coatings grow once they nucleate. In this case, it was observed that the coatings grew irregularly and accumulated on the edges of the working electrode. However, this kind growth could only be visualized when -950 mV and -1,000 mV vs Ag/AgCl potentials were applied, because those were the conditions in which a greater thickness and roughness of the deposit was seen [11]. The irregular growth of the coating means that over time the actual surface area increases with respect to the original transversal area, promoting a greater number
of active sites in which metal ions can be deposited [12]. This will be reflected in an increase in the current in the chronoaamperograms and, consequently, the charge of the process will increase as well, by the effect of the heterogeneous and three-dimensional growth of the coating. In Figure 4(b) it is possible to observe changes in the appearance of the substrates obtained when -950 mV vs Ag/AgCl was used. The coloration of the coatings became increasingly dark as the electrodeposition times increased. This effect is due to the increase of the deposit on the surface of the substrate.

4. Concluding remarks

The leaching of the powder was found to be feasible using a combination of citric acid and hydrogen peroxide, although the leaching efficiency of Co and Ni was lower than previously reported. Thermodynamic simulations indicated that the formation of insoluble citrates of these metals could have been formed under the experimental conditions tested and this would explain the lower recovery rates. Nonetheless, soluble Ni, Co and Mn species were found to be forming citrate-complex ions in the solution, which is expected to be advantageous for electrodeposition. The leachate solution obtained was successfully electrolyzed and optically satisfactory coatings were obtained on copper surfaces using a potential of -950 mV vs Ag/AgCl. The hydrogen evolution was also found to be an important drawback for the process since the application of potentials higher than -950 mV vs Ag/AgCl generated faulted coatings due to the formation of H₂ bubbles on the surface of the electrode. In conclusion, this paper showed that it was possible to reuse the cathode powder of spent lithium-ion batteries as a raw material in electrodeposition processes.

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