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Acid reducing leaching of cathodic powder from spent lithium ion batteries: Glucose oxidative pathways and particle area evolution

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ABSTRACT

Co and Li recovery by acid-reducing leaching of lithium ion battery powder was investigated evidencing that glucose efficiency changes depending on leaching procedure. Postponing glucose addition metal extractive yields were higher (88% for Co and 92% for Li) than adding glucose at the beginning (60% for both). Chromatographic analyses evidenced that glucose degradation occurred preferentially via glucaric acid when its addition is postponed, while gluconic via is favored if glucose is added initially. Dynamic evolution of particle area showed particle fragmentation occurring during acid preleaching determining an increase of specific surface area available for further reaction when glucose is added.

1. Introduction

Lithium ion batteries (LIB) are widely used as electrochemical power sources in modern electronic equipments due to their high energy density, high cell voltage, long storage life, low self discharge rate and wide temperature range of usage [1].

European Guideline 66/2006 declared the necessity of reducing pollutant effects due to spent batteries. Mandatory collection rates and material recovery targets were then established: 25% and 45% collection rates within 2012 and 2016, respectively, and 50% material recovery for LIB [2]. LIB electrodic powder contains interesting amounts of strategic metals, mainly Co and Li (but also Mn and Ni can be present according to the cathodic materials used). In fact LIB electrodic powder is generally made up of graphite pasted on copper foils (anode) and $LiCoO_2$ pasted on aluminum foils (cathode) [3].

Raw material depletion, market expansion and European guidelines determined together new research interest toward metal recovery from spent LIB. In particular, research has been mainly focused on the optimization of leaching conditions for metal extraction from electrodic powder. It is noteworthy that acid-reducing leaching conditions should be used because Co in electrodic powder can be present as Co(II) and Co(III) but only Co(II) can be extracted by acid leaching, while Co(III) needs a reducing agent to be dissolved.

Most works reported experimental results of acid leaching with sulfuric acid in the presence of hydrogen peroxide as reducing agent [4–9]. In this leaching system the simultaneous dissolution of Li and Co occurred according to the following overall reaction:

$$LiCoO_2 + 1.5H_2O_2 + 1.5H_2SO_4 = CoSO_4 + 0.5Li_2SO_4 + O_2 + 3H_2O \tag{1}$$

Reagent concentrations ranged from 2 to 3 M for acid and 2–15% for H_2O_2 at temperature from 60 to 75 °C gaining recovery from 88 to 100%. Other works reported leaching experiments using only sulfuric acid [10,11]: in this case similar acid concentrations were used but at higher leaching temperature (80 °C) in order to achieve metal extraction ranging from 80 to 99%.

Zhang and coworkers [12] investigated three acids (nitric, sulfuric and hydrochloric) and evaluated the effect of acid concentration, temperature, leaching time and solid/liquid ratio. They found that hydrochloric acid gave the best performance in agreement with experimental results reported by [13].

Organic reducing agents can be also used such as citric acid [14], malic acid [15], ascorbic acid [16], oxalic acid [17] and glucose [3].

Among these organic reducing agents carbohydrates are low cost and non-hazardous chemicals. Their use has been proposed either in pure form or as component of industrial wastes for Mn

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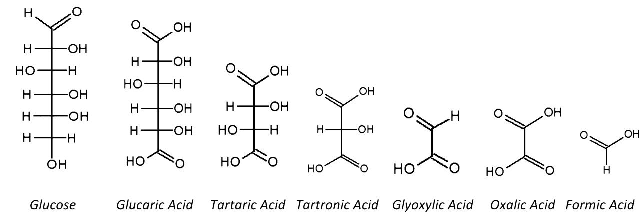
First oxidative pathway via glucaric acid (strong oxidation conditions)



Second oxidative pathway via gluconic acid (mild oxidation conditions)

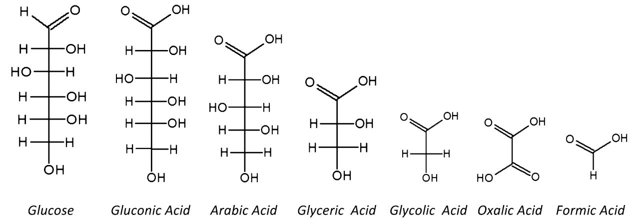


Fig. 1. Oxidative pathways of glucose.

reducing leaching of pyrolusite ores [18–22] and alkaline batteries [23]. The analysis of glucose intermediates in acid-reducing leaching of MnO_2 ores denoted the presence of high concentrations of formic acid along with mono-carboxylic poly-hydroxyacids such as glyceric and glycolic acids [24]. These data suggested that, during leaching, glucose carbon chain is shortened to lower aldaric acids by the detachment of formic acid via the formation of mono-carboxylic poly-hydroxyacids.

The accepted mechanism of glucose oxidation consists of oxidation at C1 atom ([25] and references within). Reaction proceeds via aldonic oxidation to give CO_2 and aldoses with five carbon atoms [26]. The first step of oxidation can give different products depending on the operating conditions: as an example glucaric acid or glucuronic acid can form in ozonization of glucose depending on ozone concentration (glucaric for high concentrations) [27].

In summary, oxidation products of glucose may be polyhydroxyacids, aldonic and aldaric acids, aldoses, formic acid and CO_2. Fig. 1 shows two possible schemes of glucose oxidation elaborated on the base of literature survey.

The aim of this work is the optimization of the operating conditions for acid reducing leaching of cathodic powder from LIB using sulphuric acid and glucose. The reductive efficiency of glucose was assessed by comparing tests performed with initial and postponed glucose addition at two concentrations. Experimental data were analyzed in terms of Li and Co extraction, glucose intermediate's formation, and particle area dynamic evolution.

The main novelty aspect of this work is the study of the effect of addition time on glucose performances in leaching of Li-ion batteries powders also considering the alternative oxidation pathways of this carbohydrate. In fact, even though one work was already published using glucose as reducing agent for Li-ion batteries leaching [3], neither the effect of addition time nor the dynamic evolution of oxidation products was reported. Another novelty aspect is the determination of particle area evolution during leaching in the different operating conditions which contributes to the understanding of the chemico–physical mechanisms occurring in the system.

2. Materials and methods

2.1. Cathodic material preparation

A sample of 10 kg of spent Li ion batteries furnished by a collection point in Italy was preliminary grinded by knife mill (Retsch, SM100). Aluminum foils with pasted cathodic materials were manually recovered from milled wastes and treated by alkaline leaching (solid/liquid ratio = 1:20) with NaOH (2 M) in order to dissolve Al. Residual solid containing mainly the cathodic component ($LiCoO_2$) was washed with distilled water until neutral pH, dried in an oven at 60 °C, sieved in order to eliminate the particles with dimensions larger than 500 μm, and stored in closed box for further tests.

NaOH pellets with reagent grade purity were bought by Sigma–Aldrich and used for preparing alkaline leaching solution.

2.2. Acid digestion

Total metal concentration in cathodic powder was determined by acid digestion using an acid solution made with HNO_3 (65%, w/w) and HCl (36%, w/w) with a volume ratio 1:3 (aqua regia). Samples (2 g) of cathodic powder were digested with aqua regia (solid/liquid ratio = 1:20) at 80 °C for 2 h under magnetic stirring. After 2 h, H_2O_2 was added (2 ml of 35, vol.% solution) and digestion was continued for another hour. Concentrations of dissolved metals were determined by an Inductively Coupled Plasma Optical Emission Spectrophotometer Varian Vista-MPX CCD Simultaneous (ICP/OES). Acid digestions were performed in triplicate.

All chemicals used for digestion (HNO_3, HCl and H_2O_2) were bought by Sigma–Aldrich as reagent grade purity.

2.3. Leaching tests

Leaching tests were performed using 2 g samples of cathodic powder put in contact with leaching solutions prepared with 27 ml of sulfuric acid (2 mol/l), 5 ml (or 10 ml) of glucose solution (50 g/l), and 25 ml (or 20 ml) of distilled water. Glucose solution was added at the beginning or after 2 h of acid leaching according to Table 1. Each jacketed reactor was kept under magnetic stirring and thermostated at 80 °C by forced recirculation of heated water in the jacket using a thermostatic bath with external recirculation (Falc, SB5). During leaching tests suspension samples were collected and, after solid–liquid separation by centrifugation (Hettich, EBA 21), metal concentrations in liquids were analyzed by ICP-OES. Leaching tests were performed in duplicates.

Reagent grade chemicals used for leaching experiments (H_2SO_4, glucose) were bought by Sigma–Aldrich.

2.4. Analyses of glucose intermediates

Glucose intermediates were analyzed by High Performance Liquid Chromatography (HPLC Thermo Spectra System) with Aminex hpx-87 h column (Biorad) operated at 30 °C using H_2SO_4 (0.008 mol/l) as mobile phase (0.6 ml/min) with a UV detector (210 nm). Standard chemicals (all analytical grade purity from Sigma–Aldrich) used for calibration along with calibration curve, coefficient of correlation R^2, and elution times were reported in Table 2. Leach liquor samples (2 ml) were collected during leaching experiments, filtered (0.45 μm filter of cellulose nitrate), cooled at 5 °C, and analyzed by HPLC.

Table 1
Operating conditions in leaching tests.

Test	Glucose (ml of 50 g/l solution)	Time of glucose addition (h)
1	5	0
2	10	0
3	5	2
4	10	2