



Recovery of valuable metal ions from the spent lithium-ion battery using aqueous mixture of mild organic acids as alternative to mineral acids



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ABSTRACT

A well characterized cathode material (LiCoO₂) recovered from spent lithium-ion battery is dissolved in aqueous mixture of citric acid (chelating agent) and ascorbic acid (reductant) at 80 °C. The dissolution proceeds with a reductive-complexing mechanism, and complete dissolution occurs in about 6 h when stoichiometric amount of C/A is used. The dissolution rate constants (k) are $3.1 \times 10^{-3} \text{ min}^{-1}$ for Li and $0.8 \times 10^{-3} \text{ min}^{-1}$ for Co ions as determined by 'cubic rate law' plots. The formation of Co(III)– to Co(II)–citrate during the dissolution is confirmed from the UV–Vis spectra. The dissolved solution was subjected for selective precipitation of cobalt as Co-oxalate and lithium as LiF using oxalic acid and NH₄F, respectively. The present study has a merit when compared to literature reports as we make use of mild organic acids as alternatives to mineral acids.

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1. Introduction

Recovery of commercially important metal ions like Co and Li from spent Li-ion batteries is advantageous considering the limited availability of these metal ions and environmental regulations. LiCoO₂ as cathode materials was discovered by the research group of Goodenough in 1980 at Oxford University, which established a rechargeable cell within the 4 V range using LiCoO₂ as cathode and lithium metal as anode material (Mizushima et al., 1980). LIBs have been introduced to the market by Sony Corp. in 1991 (Zou et al., 2013; Georgi-Maschler et al., 2012; Nishi, 2001). These batteries have substituted Ni–Cd and Ni–MH batteries in many applications due to their high energy density, low auto-discharge rate, and excellent cycle life. Presently, lithium-intercalating material, typically graphitic carbon is used as anode (negative electrode) and LiCoO₂ is the most used cathode (positive electrode) material in LIB due to their good performance (Armstrong and Bruce, 1996; Freitas and Garcia, 2007; Xin et al., 2009; Nan et al., 2005), although several other oxides such as Ni, Mn-doped LiCoO₂, LiMn₂O₄ and LiFePO₄ have been investigated (Castillo et al., 2002). Also, significant improvements in electrolyte (liquid and polymer) system are also underway. For instance, Nanini-Maury et al. (2014) have reported new liquid

electrolytes stable at high potential with greater ionic conductivity than polymer electrolytes.

LIBs are put to use in all personal computers, cellular phones, cameras and many other modern-life appliances (Ra and Han, 2006; Nan et al., 2005; Lizuka et al., 2013; Wee, 2007; Swain et al., 2007) and recently in electric vehicles. Thus, LIB consumption is considerably high around the world. For instance, the household battery industry in the USA is estimated to be a US \$ 2.5 billion industry with annual sales of nearly 3 billion batteries. These batteries, also known as dry cells, are used in over 900 million battery-operated devices. In Europe, 5 billion units of batteries were produced in year 2000 (Bernardes et al., 2004). In the USA and Europe, the consumption of batteries is estimated to be 8 billion units per year. In Japan, around 6 billion batteries were produced in 2004, while almost 1 billion units are consumed every year in Brazil (Georgi-Maschler et al., 2012; Xu et al., 2008; Salgado et al., 2003; Gupta and Manthiram, 1996). World LIB production reached 500 million units in 2000 and almost 4.6 billion in 2010. Therefore, equally large amounts of spent LIBs have to be handled after their lifetime.

The increasing public concern on environmental sustainability in the last decade has resulted in stricter regulations worldwide, for the adequate destination of hazardous residues from electronic waste, including LIBs. These regulations have impelled the society to look for technical solutions such as e-waste management and resource recycling techniques. Consequently, the spent LIB material has become an

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environmental burden. In China, consumer battery waste amounted to 200–500 t/year from 2002 to 2006 with significant amounts of metals, organic chemicals and plastics in the following proportions: 5–20% Co, 5–10% Ni, 5–7% Li, ~15% organic chemicals and ~7% plastics. This composition varies slightly with different manufacturers (Li et al., 2010a, 2010b, 2013; A.K. Jha et al., 2013; Sun and Qiu, 2011). The use of cobalt in LIBs has grown from 700 to 1200 tpa during the year 1995–2005, which is ~25% of cobalt demand globally. The other important metal, lithium, has a current demand of 110,000 tpa and is expected to rise three fold within ten years (M.K. Jha et al., 2013; Al-Thyabat et al., 2013; Dewulf et al., 2010; Georgi-Maschler et al., 2012). A typical LIB contains about 27.5% LiCoO₂, 24.5% steel/Ni, 14.5% Cu/Al, 16% carbon, 3.5% electrolyte and 14% polymer (Li et al., 2013). Thus, toxic but commercially important metals and flammable compounds (LiBF₄ and LiPF₆ dissolved in organic solvent) present in these spent LIBs must be treated for resource recycling due to limited availability of these natural resources and also to meet the environmental regulations. It is impervious to note that there is hardly any natural resource of lithium in India.

The existing methods for recycling spent LIBs are mainly pyrometallurgical and hydrometallurgical processes (Xu et al., 2008; Georgi-Maschler et al., 2012). In the pyrometallurgical processes, organic electrolytes and binder are burnt off and make leaching of valuable metals more easy (Li et al., 2010a; Freitas et al., 2010; Wang et al., 2009; Chen et al., 2011). In the hydrometallurgical processes, the dismantled electrodes are first dissolved in concentrated acids followed by recovery of metal ions by precipitation (Castillo et al., 2002; Shin et al., 2005; Ferreira et al., 2009; Li et al., 2010b; Espinosa et al., 2004; Contestabile et al., 1999; Chagnes and Pospiech, 2013). Therefore, recycling of constituent metal ions in LIBs has become inevitable towards the development of green technologies and to achieve some economical benefits.

There are many studies on the dissolution of active cathode materials from spent LIBs using strong acids viz., 2 M H₂SO₄ (A.K. Jha et al., 2013; Chen et al., 2011; Contestabile et al., 2001), 4 M HCl (Contestabile et al., 2001) and 1 M HNO₃ (Lee and Rhee, 2002) as leaching agents. The leaching efficiency of Co is highest in HCl when compared to H₂SO₄ and HNO₃ at 80 °C. However, on adding H₂O₂ (5–20 vol.%) to H₂SO₄ and HNO₃, the leaching efficiency was increased (Chen et al., 2011; Mantuano et al., 2006; Lee and Rhee, 2003) because H₂O₂ acts as a reducing agent in acidic medium. Recently, a novel method to recycle mixed cathode materials for LIBs has been reported by Zou et al. (2013). The authors have dissolved mixtures of LiCoO₂, LiMn₂O₄, Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O₂ and LiFePO₄ in 4 M H₂SO₄ + 30 wt.% H₂O₂ at 70–80 °C for 2–3 h. The dissolved ions were precipitated as metal hydroxides at different pH and the Li as Li₂CO₃ at 40 °C. Finally, they have succeeded in preparing the same active cathode material, Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O₂, by decomposing these metal hydroxides. There are few studies on the use of mild organic acids viz., 1.25 M citric acid (Li et al., 2010b), 1.0 M oxalic acid (Sun and Qiu, 2012), 1.5 M aspartic acid (Li et al., 2013) and 1.5 M malic acid (Li et al., 2010a) to leach metal ions from spent LIBs. All of these reagents have not shown complete dissolution of Co and Li ions, however, the dissolution was enhanced by adding 1–6 vol.% of H₂O₂ (reducing agent).

To develop environmentally benign process i.e. to avoid using the mineral acids, we have formulated an aqueous mixture of mild organic acids containing reductant (ascorbic acid) and chelating cum buffering agent (citric acid). We believe such a mild formulation should be of great help in the recovery of metal ions from spent LIBs and/or electronic gadgets, especially during large scale treatment. In fact, it is shown here that the leaching or chemical extraction efficiency is not compromised with this mild formulation. This is because of the availability of stoichiometric amounts of H⁺ ions from these reagents during dissolution. In the next step, we have succeeded in selective precipitation of cobalt as Co-oxalate and lithium as LiF towards the recycling of active cathode material. The details on dissolution behavior of cathode material

from a typical spent LIB and the selective precipitation of constituent metals are reported here. To the best of our knowledge, the present study is the first report for the dissolution of LiCoO₂ using ascorbic acid as reductant.

2. Experimental

Several spent Li-ion batteries of BL-5CA (Nokia) series available in the local market were collected. For safe handling, they were discharged completely and then dismantled to separate the cathode and anode materials coated on Al- and Cu-foil, respectively. The cathode material was scrubbed carefully and heated at 700 °C for 2 h to burn off the organics such as polyvinylidene fluoride (Li et al., 2010b). More than 90% of the this cathode material was found to be LiCoO₂ based on X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The remaining 5–10% is expected to be carbon residue formed due to organic burn off.

The above cathode material was subjected for chemical dissolution using mild chemical formulation, an aqueous mixture of citric acid and ascorbic acid (C-A). In a typical stoichiometric case, 20 mM metal ion worth of LiCoO₂ sample (0.2 g) was added to 100 ml water containing 100 mM of citric acid and 20 mM ascorbic acid (C-A) at 80 °C. The mixture was kept stirred for about 6 h. The pH of the formulation before and after dissolution was 2.05 and 2.66, respectively. The periodically collected samples were syringe filtered (0.2 μm) and estimated for Co and Li ions using atomic absorption spectrometer (AAS). Also, the UV-Vis absorption spectra of the formulation during dissolution (as it turned pink color) were recorded to know the complexation behavior of Co ions. At the end of dissolution, the undissolved black carbon residue was separated by filtration.

On adding stoichiometric amount of oxalic acid to the above dissolved solution, selective precipitation of Co as Co-oxalate occurred. It was separated by filtration, and NH₄F (100 mM) was added to the filtrate to precipitate Li as LiF. The recovery of Co and Li from the dissolved solution was estimated by analyzing the filtrate solution for Co and Li by AAS.

3. Results and discussion

Fig. 1 shows the XRD pattern of the cathodic active material obtained from the spent LIBs. All the peaks could be indexed to rock-salt structured LiCoO₂ (JCPDS 44-0145). The SEM/EDX analysis (not shown here) confirmed the residual carbon, 5–10 wt.%, present along with this cathode material due to organic burn off. The origin for such carbon might be from the acetylene black (used to ensure the electronic conductivity in the cathodes) and polyvinylidene fluoride (used as a binder to ensure the electrode cohesion).

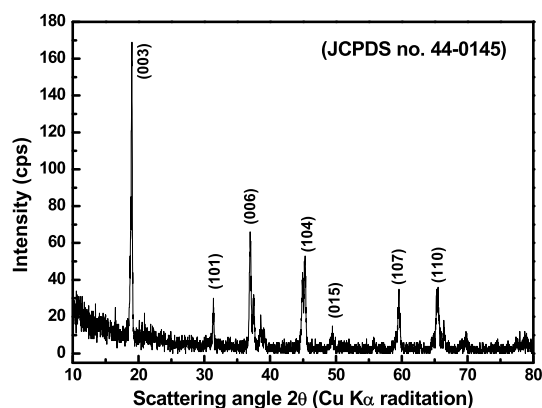


Fig. 1. Powder XRD patterns of the cathodic material (calculated at 700 °C for 2 h) from a spent LIB.

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