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Effective and environmentally friendly recycling process designed for $LiCoO_2$ cathode powders of spent Li-ion batteries using mixture of mild organic acids

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ABSTRACT

An effective and environmentally friendly recycling process designed for $LiCoO_2$ cathode powders of spent Li-ion batteries using mixture of mild organic acids, citric acid (CA), tartaric acid (TA) and ascorbic acid (AA), to recover the metals. Almost complete dissolution of Li and nearly 90% dissolution of Co occurred in at 80 °C for 6 h. The reducing agent, ascorbic acid (AA), converts the dissolved Co(III) to Co (II) thereby selective recovery of Co as Co(II)-oxalate is possible. The formation of Co(III)–and Co(II) complex is evident from the UV–Vis spectra of the dissolved solution as a function of dissolution time. Thus, the reductive-complexing dissolution mechanism is proposed here. These mild organic acids are environmentally benign unlike the mineral acids.

1. Introduction

The ever budding technology in the electrical and electronic segment has resulted in upsurge of Waste Electrical and Electronic Equipment (WEEE). Safe disposal of this WEEE is imperative meanwhile it comprises over a thousand resources, much of which are extremely toxic. Right now 95 % of e-Waste continues to be recycled unceremoniously with little or no precautions to human health and the environment (Freitas and Garcia, 2007; Chen et al., 2011; Fouad et al., 2007a,b; Liu et al., 2006). Spent Li-ion battery (LIB) is one, comes under e-Waste which can be used in portable electronic devices viz., mobile phones, personal computers, cameras and recently in electric vehicles due to their favorable characteristics such as high energy density, high voltage, long storage life, low self-discharge rate and wide temperature range of use (Chagnes and Pospiech, 2013; Gonclaves et al, 2015, Thyabat et al., 2011). After the life time failure of these LIBs, the safe disposal is a serious problem because these comprise of organic chemicals, number of valuable metals and plastics. In addition, these too contain toxic and flammable organic electrolyte dissolved in organic solvent (Shin et al., 2005; Fouad et al., 2007a,b, Kang et al., 2010; Paulino et al., 2008). Hence, the recycling of these spent LIBs and recovery of major components is believed to be advantageous to avoid environmentally hazardous waste. Presently there is no conventional system for disposing of or recycling these huge, environmentally hazardous spent LIB systems. At present, the traditional recycling methods being used cannot support increasing electric vehicles (EV) market as they are inefficient and uneconomical. Since, these traditional methods for recycling allow only the recovery of battery's metal constituents in a relatively low worth form. Hence tailoring of a new recycling technique would be greatly beneficial to the society in general.

$LiCoO_2$ is the most widely used cathode material in LIBs due to its good performance. This $LiCoO_2$ need to be treated properly in view of the economic, environmental toxicity and availability of Co also simultaneously the lack of Li availability. Consequently the recycling and recovery of these metals from spent LIBs would be advantageous to all of us through a proper method. Till now, a number of studies have been reported for the recovery and recycling of metals from the spent LIBs through pyrometallurgy,

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hydrometallurgy or bio-hydrometallurgy methods (Xu et al., 2008; Bernardes et al., 2004; Al-Thyabat et al., 2013; Sun and Qiu, 2012). Among these, hydrometallurgical method is beneficial as of ecological viewpoint (Lee and Rhee, 2003; Swain et al., 2007).

Till now there are several studies on recycling of spent LIBs using strong acids like HCl (Mantuano et al., 2006), H_2SO_4 (Chen et al., 2011) and HNO_3 (Lee and Rhee, 2002; Li et al., 2011) as well as mild acids like ascorbic acid (Li et al., 2012), citric acid (Li et al., 2013; Nayaka et al., 2015), malic acid, aspartic acid (Li et al., 2013; Qi et al., 2018), oxalic acid (Sun and Qiu, 2012), DL-maleic acid (Li et al., 2010a,b; Li et al., 2018a), succinic acid (Li et al., 2015), tartaric acid (Nayaka et al., 2016a), iminodiacetic acid (Nayaka et al., 2016b), glycine (Nayaka et al., 2016c), phosphoric acid Qi et al., 2017; Xiangping et al., 2017) and acetic acid (Li et al., 2018a; Wenfang et al., 2018) as dissolution agents with the addition of reducing agents like H_2O_2, ascorbic acid and glucose (Qi et al., 2017, 2018). These studies have proved that the use of mild acids are advantageous than strong acids as they are safe to handle and emit less toxic gases than strong acids. These mild acids have proved as good dissolution agents without compromise in the results, which can give almost complete dissolution.

Here in this study, we focused on to explore an efficient and environmentally friendly dissolution media using mixture of mild acids; citric acid, tartaric acid and ascorbic acid (CTA). The details on dissolution performance of $LiCoO_2$ cathode material from a typical spent LIBs and the selective precipitation of constituent metals are reported here.

2. Experimental

The spent LIBs used in this work were collected from different mobile phones and were dismantled through a manual procedure. To prevent short-circuiting and self-ignition, the spent LIBs were discharged completely and dismantled to separate plastic, steel shells, cathode and anode materials coated on curled Al- and Cu-foil, respectively. To separate the cathode material coated, Al- foil was uncurled and cut in to small pieces (about 1 cm × 1 cm). These pieces were immersed in 100 mL concentrated N–Methyl pyrrolidone (NMP) solvent and exposed for ultrasonic washing using ultrasonic bath (Model- SUG-321, S. No. 90933) at about 1 hr. After ultrasonic washing the active cathode material was separated from Al–foil was filtered and heated at 700 °C for 2 h to burn off the organics such as carbon and polyvinylidene fluoride. As leaching is an interfacial reaction between the solid and the liquid, the boundary area of the two phases can affect the reaction rate significantly (Li et al., 2018b). Therefore, the powder was then ground for 30 min to obtain smaller particles with higher surface to increase dissolution efficiency. Based on the X–ray diffraction (XRD) study, scanning electron microscopy (SEM) and energy dispersive X–ray (EDX) analysis, the cathode material was found to be rocksalt structured $LiCoO_2$ and was found to contain 5–10 wt. % of residual carbon, due to organic burn off. The source for such carbon is from the acetylene black used to ensure the electronic conductivity in the cathodes.

The $LiCoO_2$ cathode material (0.2 g) obtained was subjected for dissolution using mild chemical organic acids, an aqueous mixture of 0.1 M (2.1 g) citric acid (CA), 0.1 M (1.5 g) tartaric acid (TA) and 0.02 M (0.325 g) ascorbic acid (AA) were taken in a three necked round-bottomed flask with volume of 100 mL and the flask was placed in a water bath to control the reaction temperature during the dissolution. The flask was fitted with vapor condenser and a magnetic stirrer at 80 °C for 6 h. During the dissolution process, a series of samples with a volume of approximate 1 mL were taken out from the dissolution mixture and filtered by using syringe filters (0.2 μm) to get the dissolution rate of metal ions for further analysis. After 6 h dissolution, the solution and insoluble residue were separated by filtration by using membrane filter paper of 0.2 μm and washed with deionized water, yielding a pink colored filtrate and a black residue. All the reagents used in this study were of analytical grade, and all the solutions were prepared in deionized water.

The pH of the formulation before (pH = 3) and after (pH = 4) dissolution was measured using digital pH meter (Systronics 335). The UV–Vis spectrum of the dissolved solution was also recorded using UV–Visible spectrophotometer (Ocean optics, DH-2000 BAL). The concentration of metal ions (Li and Co) in the dissolved solution was determined by using atomic absorption spectrophotometer

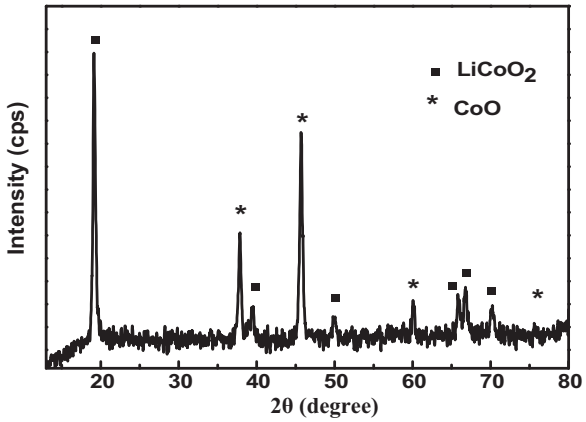

Fig. 2. XRD patterns of the cathode material from a spent LIB, after calcinations and grinding.

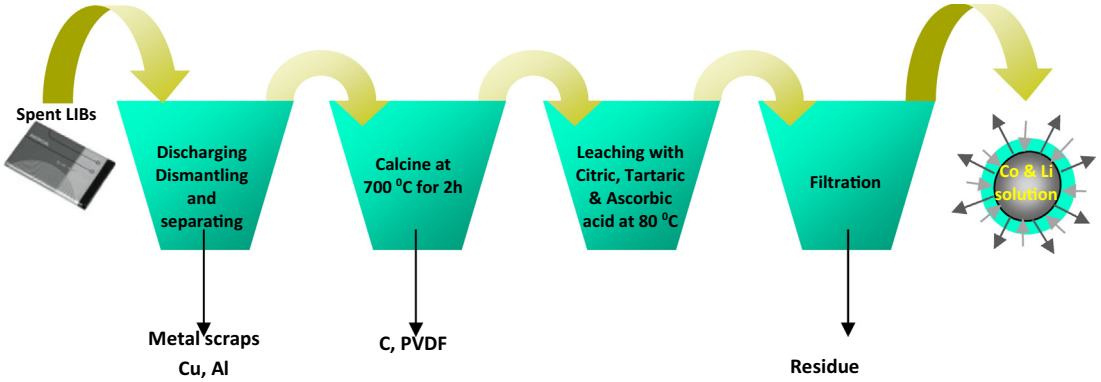

Fig. 1. Flow sheet for the recovery of Co from active cathode material ($LiCoO_2$) in spent LIBs using mixture of citric acid, tartaric acid and ascorbic acid.