



Dissolution of cathode active material of spent Li-ion batteries using tartaric acid and ascorbic acid mixture to recover Co



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ABSTRACT

Environmentally benign hydrometallurgical dissolution process is investigated for the recovery of cobalt from the cathode active materials of spent lithium-ion batteries (LIBs). A mixture of tartaric acid and ascorbic acid is used to dissolve the LiCoO₂ collected from spent LIBs. The reductive-complexing mechanism led to >95% dissolution with 0.4 M tartaric acid and 0.02 M ascorbic acid in about 5 h at 80 °C. The dissolved Co was separated as cobalt oxalate from the mixture.

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1. Introduction

Li-ion batteries (LIBs) are widely used as rechargeable power suppliers because of their high capacity, high energy density, light weight and small size (Chagnes and Pospiech, 2013; Bertuol et al., 2015; Shin et al., 2015). Consequently, large quantities of spent LIBs are disposed as solid waste. Since they contain heavy metals like Co and other toxic organic matters, they are hazardous to environment (Shapek, 1995). Hence, it is imperative to recycle the valuable metals present in spent LIBs (Cai et al., 2014; Dunn et al., 2012; Wang et al., 2014). Thus, the recovery of Co and Li from cathode active materials and Al and Cu from metallic components is important considering their uses in commercial, industrial and military devices (Zhao et al., 2011; Swain et al., 2007; Nan et al., 2005). On the other hand, it is highly desirable to prevent environmental pollution from these elements, Co in particular. In view of the ever increasing consumption of metallic resources, resources recycling techniques/process have gained much importance. In addition to many basic R & D works, there are few companies viz., AEA Technology (U.K.), SNAM (France), Toxco (Canada), Umicore (Belgium) etc. which have developed the processes of recycling valuable metals from the cathode of spent LIBs (Cai et al., 2014).

In order to recover the metal ions from spent LIBs, the cathode material is usually dissolved in leaching agents followed by separation and recovery of metal salts from the solution in different steps. The conventional techniques for recycling spent LIBs mainly involve pyrometallurgical

process, hydrometallurgical process or the combination of both (Bernardes et al., 2004; Al-Thyabat et al., 2013). Pyrometallurgical process involves more energy consumption, high cost, low efficiency, loss of materials and emission of hazardous gases (Jha et al., 2013; Sun and Qiu, 2012; Chen et al., 2011; Joulie et al., 2014). Hence, recent studies have shown that the hydrometallurgical process is advantageous to recover valuable metals from spent LIBs (Swain et al., 2007; Lee and Rhee, 2003). Many studies have reported on the leaching of active cathode material (LiCoO₂) using mineral acids such as HCl, HNO₃, H₂SO₄ etc. (Espinosa et al., 2004; Fouad et al., 2007; Paulino et al., 2008; Granata et al., 2012). However, these processes introduce significant amount of secondary pollutants such as emission of Cl₂, SO₃ and NO_x. Also, the recovery processes become more complex due to series of separation and purification steps for Li, Co and other components (Sun and Qiu, 2012).

To reduce such secondary pollution, without compromising leaching efficiency, there are reports on using mild organic acids such as citric acid, ascorbic acid, malic acid, oxalic acid, aspartic acid, succinic acid etc. (Li et al., 2010, 2012, 2013, 2015; Sun and Qiu, 2012) on adding H₂O₂ as reducing agent. Overall these mild organic acids are as effective as mineral acids. Recently, we have reported (Nayaka et al., 2015) using mixture of citric acid (chelating agent) and ascorbic acid (reducing agent). In this process, although Co was separated successfully as Co-oxalate, the Li separation as LiF was not advantageous. Hence, we have investigated on alternative mineral acids such as mixture of tartaric acid (chelating cum buffering agent) and ascorbic acid (reductant). The details on dissolution behavior and separation of Co from dissolved mixture of Co and Li ions are reported here.

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2. Experimental

The spent LIBs (BL-5CA Nokia series) collected from the local market was discharged completely (to prevent self-ignition and short-circuiting), and manually dismantled to separate the cathode and anode parts. The cathode material coated on Al-foil was uncurled and cut to small parts. Upon ultrasonication in N-methyl-2-pyrrolidone (NMP), all the oxide deposit was separated from Al-foil. After removing Al metal part, the oxide powder was collected by filtration. It was heated to 700 °C for 2 h to burn off the organics such as carbon and polyvinylidene fluoride. It was ground to fine powder for higher surface area to increase the leaching efficiency. Fig. 1 shows the flow sheet of the process followed in this work. As reported in our previous study (Nayaka et al., 2015), the oxide thus obtained was found to be LiCoO₂ based on XRD, SEM/EDXA and FT-IR.

The rocksalt structured LiCoO₂ was found to contain residual carbon, 5–10 wt.%, 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.

The above cathode material (LiCoO₂, 0.2 g) was subjected for chemical dissolution in 100 ml aqueous mixture of tartaric acid (TA) and ascorbic acid (AA). TA concentration was varied from 0.1–0.5 M by keeping fixed concentration of AA (0.02 M). The dissolution was monitored for about 5 h at 80 °C by collecting the samples periodically. During sampling, the insoluble residue was separated by filtration through 0.2 μm syringe filter. The concentration of Li and Co metal ions in the dissolved solution was determined by using atomic absorption spectrophotometer (Model: AA-7000F). The results obtained here are found to carry a maximum of about 5% error. The UV–vis spectrum of the dissolved solution was also recorded using UV–visible spectrophotometer (Ocean optics, DH-2000 BAL).

3. Results and discussion

The amount of LiCoO₂ used here (0.2 g) is worth of 0.02 M Co and 0.02 M Li. Thus, stoichiometrically, the tartaric acid (TA, 0.1–0.5 M)

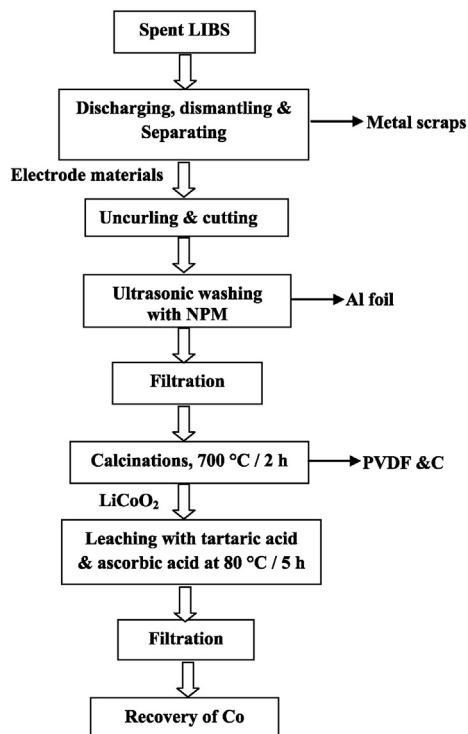


Fig. 1. Flow sheet for the recovery of Co from active cathode material (LiCoO₂) in spent LIBs.

used here is much higher in concentration. TA acts as a chelating agent while the ascorbic acid (AA, 0.02 M) acts a reducing agent during the dissolution process. As shown in Fig. 2, rapid dissolution to the extent of 80% occurred in about 30 min. Thereafter, marginal increase in dissolution occurred over a period of 3–5 h as it reached to complete dissolution. As shown in Fig. 3, on increasing the concentration of TA from 0.1 to 0.5 M, overall there was about 15% increase of Co and about 5% increase in Li release. It is clear that 0.4 M TA is enough to bring complete dissolution and further increase in TA is not advantageous. The chelating agent is responsible to leach the Co and Li ions from the lattice through complexation process. As the lattice gets disturbed, both Co and Li ions are released from the LiCoO₂. The metal ions thus released are stabilized in the solution by complexation with tartarate (Sun and Qiu, 2012; Ferreira et al., 2009). Since Co is present as Co³⁺ in the oxide lattice, Co(III)-tartarate is expected to build-up with dissolution time. However, the AA can reduce the Co(III)- to Co(II)-tartarate, and hence most of the Co is present as Co(II)-tartarate as the end of dissolution. The dissolution process can be shown as



Li et al. (2010, 2012, 2013, 2015) have clearly shown that leaching efficiency is enhanced by using reducing agent. However, in the present study, the reducing agent AA is not found to increase the dissolution, nevertheless, reduces the dissolved Co(III)- to Co(II)-L. This is useful for subsequent recovery of Co as Co(II)-oxalate. Manjanna and Venkateswaran (2001, 2002) have shown that AA can reduce the lattice metal ions such as Fe³⁺ in the dissolution of Cr-substituted hematite and it was essential to initiate the dissolution. However, such a

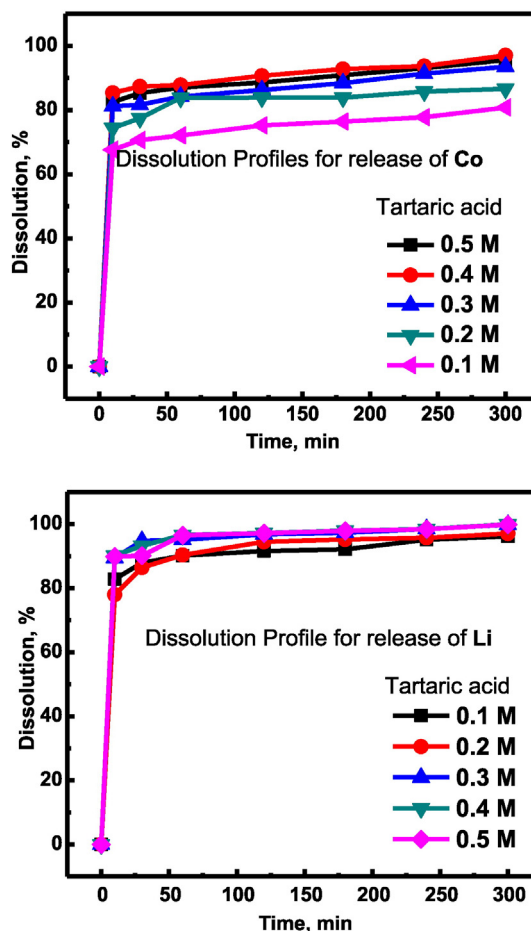


Fig. 2. Dissolution of Co and Li as a function of time in aqueous mixture of tartaric acid (0.1–0.5 M) and ascorbic acid (0.02 M) at 80 °C.

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