Preparation of LiCoO₂ films from spent lithium-ion batteries by a combined recycling process

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A new process is described for recovering and regenerating lithium cobalt oxide from spent lithium-ion batteries (LIBs) by a combination of dismantling, detachment with N-methylpyrrolidone (NMP), acid leaching and re-synthesis of LiCoO₂ from the leach liquor as a cathode active material. The leach liquor, obtained from spent LIBs, is used as electrolyte to regenerate LiCoO₂ crystals on nickel plate at constant current in a single synthetic step using electrochemical deposition technology. The crystal structure and surface morphology of regenerated LiCoO₂ were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. LiCoO₂ phase with preferred (104) orientation was electro-deposited on nickel substrate at current density 1 mA cm⁻² for 20 h, and found to have good characteristics as a cathode active material in terms of charge and discharge capacity, and cycling performance. The particle size and layer thickness of the regenerated LiCoO₂ crystalline powder were 0.5 μm and 0.2 mm, respectively. After 30 cycles, the capacity had decreased by less than 4% compared with the first cycle. This process involves simple equipment and could be feasible for recycling LIBs in large scale.

1. Introduction

Since LIBs were first marketed by Sony in 1991, they have replaced Ni-Cd and Ni-MH batteries in many applications due to their high energy density, high voltage, very low self-discharge rate, safe handling and good cyclicity (Freitas and Garcia, 2007). LIBs are extensively used in laptops, mobile phones, video cameras and other portable electronic devices, and the lithium battery market is increasing significantly. The worldwide consumption of LIBs in 2000 and 2004 was about 500 and 700 million cells, respectively, and their production is estimated to be 7.0 billion in 2015. The annual amount of spent LIBs, containing 5–15 wt.% Co and 2–7 wt.% Li, has been estimated to be 200–500 MT (Lee and Rhee, 2003; Li et al., 2010; Paulino et al., 2008).

The more LIB waste that is produced, the more attention should be focused on dealing with the waste in the coming years. Although LIBs have been progressively introduced into the consumer market, and are taking the place of the more polluting and less well-performing Ni-Cd batteries, LIBs have a limited life. When they reach the end of their practical life, they produce environmental pollutants; and therefore proper post-treatment of spent LIB materials is required (Castillo et al., 2002; Contestabile et al., 1999; Lain, 2001). LIBs contain heavy metals, organic chemicals and some plastics. The metal residues are normally found at very high concentration levels, sometimes even higher than in natural ores. By analysis of the metal content of LIBs, it’s found that valuable metals such as aluminum, cobalt, lead and lithium were the main species needed to be separated. (Dorella and Mansur, 2007). LiCoO₂ is a favored material for LIB cathodes due to its good performance, and needs large amounts of Co to meet the market demand. Moreover, Co and Li are not only rare and precious metals, but are also toxic to the environment. From the viewpoint of environmental protection, the recycling of spent LIBs is highly desirable at present or in the future; in addition, it can bring economic benefits (Bernardes et al., 2004; Espinosa et al., 2004; Mantuano et al., 2006).

The current status of the recycling process has been reviewed in several studies, and it is important that good recoveries are obtained during recycling of spent battery materials. Most of the proposed processes are based on hydrometallurgical chemistry and have been developed on a laboratory scale, mainly with the aim of recovering valuable metals from the cathode. Recycling plants and protocols are appearing in several developed countries, and we considered it to be important to devise an efficient collection system to receive and recycle spent LIBs worldwide (Contestabile et al., 2001; Li et al., 2009; Zhang et al., 1998).

Unlike other batteries, LIBs often explode during the recycling process due to the vigorous oxidation of metallic lithium, which is formed on the graphite anode by overcharging and abnormal
deposition. There are two problems to be solved during recycling LIB waste: disposal of harmful waste and the prevention of explosions (Lee and Rhee, 2002).

At the present time, two basic classes of recycling processes, physical and chemical, are used for the separation or recovery of cobalt, lithium and other components from spent LIBs (Xu et al., 2008). Recovery and separation of valuable metals were mainly achieved by the recycling process. Re-synthesis of electrode materials or synthesis of other reactive materials from the spent LIBs has also been studied in many investigations. A new hydrometallurgical process was proposed to obtain valuable metals from spent LIBs (Kang et al., 2009). A new combined recovery process comprising reductive leaching, chemical precipitation and solvent extraction has been proposed for obtaining valuable metals from spent LIBs (Kang et al., 2010).

Electrochemical technology is used in the recycling process due to the low energy consumption, and safe and less recycling steps. A new process for recycling LIBs was developed, in which layered LiCoO$_2$ phase was recovered and renovated in a single synthetic step using Etoile–Rebatt technology (Ra and Han, 2006). The recovered LiCoO$_2$ exhibited significant electrochemical activity. It was reported that cobalt ions, extracted from waste LiCoO$_2$ using a nitric acid leaching solution, were potentiostatically transformed into hydroxide on a titanium electrode, and cobalt oxide was then recovered via a dehydration procedure (Myoung et al., 2002).

The aim of the present work was regeneration of LiCoO$_2$ films on nickel plate, as cathode active materials, from leach liquor via electrochemical technology. The process has the advantages of low energy consumption and less recycling steps, and be feasible for recycling LIBs in large scale.

2. Experimental

We recently successfully fabricated LiCoO$_2$ films by an aqueous solution reaction combined with electrochemical–hydrothermal reactions. The following reaction pathway to LiCoO$_2$ phase has been proposed (Tao et al., 2006, 2007):

\[ \text{Co(OH)}_2\text{(suspending)} \rightarrow \text{HCOO}^- \rightarrow \text{CoOOH} \rightarrow \text{LiCoO}_2 \]  \hspace{1cm} (1)

\[ \text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{HCOO}^- + \text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{HCOO}^- \rightarrow \text{CoOOH} + \text{e}. \]  \hspace{1cm} (3)

The re-synthesis mechanisms of LiCoO$_2$ are shown in Fig. 1. If we control the reaction conditions for electrochemical deposition, regeneration of LiCoO$_2$ can be accomplished without any additional chemical impurities. After nitric acid leaching of waste LiCoO$_2$ electrode, the pH = 11 was adjusted by adding fresh 4 M LiOH solution. Then electrolysis was performed under galvanostatic conditions with current density 1.0 mA cm$^{-2}$ at 100 °C for 20 h. In the 4 M LiOH solution the suspended Co(OH)$_2$ was dissolved as HCOO$^-$ ions, which migrated to the anode (nickel plate) in the electric field. As the consequence, while the concentration of HCOO$^-$ ions reached saturation in the vicinity of the anode, the HCOO$^-$ ions precipitated on the nickel plate as Co(OH)$_2$. At the same time, one electron transfer from Co(OH)$_2$ to the electrode, with the oxidation state of Co changing to +3, generated a thin film of CoOOH. In the highly concentrated LiOH solution Li$^+$/H$^+$ exchange occurred to give LiCoO$_2$ due to its Gibbs energy being less than zero (Larcher et al., 1997); the reaction can be represented as:

\[ \text{Li}^+ + \text{CoOOH} \rightarrow \text{LiCoO}_2 + \text{H}^+. \]  \hspace{1cm} (4)

2.1. Dismantling and preparation of the electrodeposition solutions

Spent LIBs were dismantled to eliminate package, protection circuit module, etc. The recycling procedure, as schematized in the flow chart of Fig. 2, consists of six steps: dismantling, discharging, separation, detachment, leaching and recycling treatment. The unit cells were completely discharged for safety reasons, then anode, separator, electrolyte and cathode were separated. The discharge capacity for the positive electrode of the cell dismantled for recycling is about 91 mAh g$^{-1}$. Black pastes were separated from the cathode by applying ultrasonic energy together with NMP. The cathode active material was then obtained by combustion of carbon and residual binder at 800 °C for 2 h. The resulting LiCoO$_2$ powder was leached at 80 °C for 1 h with 1 M HNO$_3$ containing 1.0 vol.% H$_2$O$_2$ in a reactor, in which the initial S:L (Solid: Liquid) ratio was 20 g L$^{-1}$.

2.2. Preparation of LiCoO$_2$ by electrochemical method

Preparation of LiCoO$_2$ films was performed in a hermetically sealed 80 ml polytetrafluoroethylene vessel. The electrochemical deposition experiments were carried out with a nickel plate as the anode and
platinum as cathode. The electrolyte was an alkaline solution composed of 20 ml leaching liquor, whose pH was adjusted to 11 with 30 ml LiOH solution. Fig. 3 shows schematically the apparatus used for the electrochemical deposition of LiCoO₂ material from the leaching liquor. During the electrolysis process, the current was maintained at 1.0 mA/cm², the temperature was 100 °C and electrochemical reaction duration was 20 h. After preparation, the LiCoO₂ samples were washed with doubly distilled water, then dried at 80 °C for 24 h.

2.3. Material characterization

XRD analysis was carried out using a D Max-RD12Kw diffractometer with Cu Kα radiation. The scan data were collected in the 2θ range 10–90° at scan rate 1°min⁻¹. Scanning electron microscopy (SEM) was performed using a Quanta 600 instrument.

Electrochemical properties of the samples were examined in CR2025 coin type cells. The cathode was regenerated LiCoO₂ film and lithium foil was used as anode. The electrolyte was 1 M LiPF₆/EC+DMC (1:1 by volume). The cells were assembled in an argon-filled glove box, then aged for 12 h before electrochemical cycling between 2.8 and 4.5 V (versus Li/Li⁺) using a CT2001A Land instrument. Cyclic voltammograms (CV) were obtained at 5 mV s⁻¹ with a CHI660a instrument.

3. Results and discussion

3.1. SEM micrographs and EDX analysis

SEM micrographs of regenerated LiCoO₂ crystals are shown in Fig. 4, which shows fine particles. The size of the regenerated, homogenously distributed LiCoO₂ crystals is about 5 μm (from Fig. 4(b)). The grains

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**Fig. 2.** Schematic of waste Li ion battery recycling steps using a combined recycling process.

**Fig. 3.** Schematic of the recycling instrument using electrochemical deposition.
are closely integrated, with a large number of micropores between them. Spherical LiCoO₂ particles grew in a laminar fashion and formed a compact film. The cross-sectional SEM image of LiCoO₂ grown on a nickel substrate (Fig. 4(c)) shows that the material was composed of small, well-defined grains growing in layers with thickness 0.2 mm. The regenerated LiCoO₂ film electrode had the characteristics of a porous electrode.

Fig. 4. SEM images of (a) surface (500×), (b) surface (10,000×), and (c) cross-section (400×) of the LiCoO₂ electrode prepared at 1 mA cm⁻² and 100 °C, for 20 h.

3.2. Material structure analysis

During the recycling of waste LiCoO₂, the formation of a dark-gray layer was visually observed on the nickel plate. Fig. 6 shows the XRD pattern of the regenerated LiCoO₂ material. By comparison with the Committee on Powder Diffraction Standards (JCPDS), the cathode material from spent LIBs consisted of LiCoO₂, Co₃O₄ and carbon. The presence of Co₃O₄ is due to the LiCoO₂ solid-state reaction that occurs during the charge–discharge cycles. The molar ratio of Li:Co becomes unbalanced and the characteristics are changed during the charge–discharge processes. The reaction that occurs can be represented by (Yamaki et al., 2003):

\[
\text{Li}_0.5\text{CoO}_2 \rightarrow 0.5\text{LiCoO}_2 + \frac{1}{6}\text{Co}_3\text{O}_4 + \frac{1}{6}\text{O}_2. \tag{5}
\]

In the XRD pattern of recovered LiCoO₂ (Fig. 6(b)) some peaks correspond to metallic Ni and others to LiCoO₂. No other chemical component was detected. Apart from the Ni diffraction peaks (from the nickel plate), the (003), (101), (006), (104), (108) and (101) reflections from LiCoO₂ were observed. The (104) peak had the highest intensity, indicating that the preferred orientation of LiCoO₂ crystals is the (104) plane, which can be explained as follows. (1) The calculated a and c lattice parameters are 2.72 and 13.32 Å, respectively based on the (003) and (104) peak positions. The c/a ratio is 4.897, which is in good agreement with a reported value (4.991) for bulk

Fig. 5. EDX spectroscopy of regenerated LiCoO₂ material.

Fig. 6. X-ray diffraction patterns for (a) cathodic material after dismantling and calcination at 800 °C for 2 h; (b) LiCoO₂ material regenerated using electrochemical technology.
material (Reimers and Dahn, 1992), proving a well-defined layered structure. (2) The atom arrangement of the Ni(111) plane is close to that of the LiCoO$_2$ (104) plane and different from that of the (003) plane. Thus the preferred LiCoO$_2$ (104) texture is presumably induced by the Ni(111) orientation (Xia and Lu, 2007).

3.3. Electrochemical properties

Fig. 7 shows voltage versus capacity profiles for the used and regenerated LiCoO$_2$ at 0.1 C rate. The charge potential plateau is reduced, and the discharge potential plateau is elevated by comparison with the used materials. The initial charge and discharge capacities were 130.8 and 127.1 mAh g$^{-1}$, respectively.

The cyclic voltammograms (5 mV s$^{-1}$) of the LiCoO$_2$ electrode, shown in Fig. 8, were used to investigate the redox behavior of the material. The anodic peak at 4.2 V corresponds to de-intercalation, and the cathodic peak at 3.7 V is associated with intercalation of Li ions into LiCoO$_2$ on discharging. The cycle curves are in good coincidence, and the loss of capacity is small with increasing number of cycles. Fig. 9 shows after 30 cycles, the discharge capacity of the LiCoO$_2$ electrode was 122.9 mAh g$^{-1}$ and the charge efficiency was 99.1%. Thus the regenerated LiCoO$_2$ has good characteristics as a cathode active material in terms of cycling performance.

4. Conclusions

Spent LIBs potentially could be important raw materials such as lithium, cobalt, aluminum and copper, and also the environmental benefits are obvious in recycling spent LIBs. In this paper, using electrochemical technology the re-synthesized LiCoO$_2$ film on nickel plate from leach liquor exhibited preferred (104) orientation. The regenerated LiCoO$_2$ material had good electrochemical characteristics, with initial discharge capacity of 127.2 mAh g$^{-1}$ and charge efficiency of 97.2%. The regenerated material had good cycling performance. After 30 cycles, the discharge capacity decreased by less than 4% compared with the first cycle, and charge efficiency was 99.1%. The proposed recovery/regeneration process is simple, environmentally benign and adequate for the recovery of valuable metals from spent LIBs.

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