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The Re-Synthesis of $LiCoO_2$ from Spent Lithium Ion Batteries Separated by Vacuum-Assisted Heat-Treating Method

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The $LiCoO_2$ is re-synthesized from spent lithium ion batteries by a simple process combined with vacuum-assisted heat-treating and solid state reaction at 750℃. The batteries can be fully discharged in 1wt.% NaCl solution without the leakage of case. The results show that the product after two times of heat-treatment mainly contains of Co_3O_4. The re-synthesized $LiCoO_2$ shows a reversible capacity of 106.8 mAh g^{-1} and almost no capacity degradation after 20 charge/discharge cycles. The relative low reversible capacity is ascribed to the large particle size of the raw material Co_3O_4, which can be optimized by adjusting the ball-milling parameters to ensure the fully mixture of the Co_3O_4 and Li_2CO_3.

Keywords: Lithium ion battery; recycling, lithium cobalt oxide

1. INTRODUCTION

Lithium ion battery has developed quickly due to its advantages of high energy density, long cycle life and no pollution. The so-called “green battery” only means that the compositions of lithium ion batteries is non- or low-toxic judged from material safety data sheet (MSDS), but the major pollution of lithium ion batteries mainly in the process of metal metallurgy when assessed by total life cycle analysis [1]. Furthermore, the reserve and abundance of the metal mineral used in lithium ion batteries, such as Li, Co, Ni and Cu is limited, for example, the total resources of lithium are evaluated to be more than 13 million tons [2], thus the recycling of the spent lithium ion batteries is an important solution to realize the sustainable development and the minimum environmental pollution. According to the analysis of the savings in terms of energy and cumulative energy extracted from the natural environment, the recycling of lithium ion batteries results in a 51.3% natural resource savings [3]. Thus, the recycling of lithium ion battery is necessary and feasible.

The lead acid battery has been fully recycled due to the relative simple composition (mainly contains the lead and its oxide, H_2SO_4, glass fiber separator and plastic case). But the composition of lithium ion batteries includes metal, organic compound, organism, polymer and composite, is much complex than that in the lead acid batteries, resulting in the much difficult of the recycling of the spent lithium ion batteries.

The application of lithium ion batteries for electric tools, hybrid electric vehicles and electric vehicles is just beginning and their recycling needs time. The potable lithium ion batteries have used for more than 20 years and accumulated considerable waste batteries. The recycling methods for potable and power lithium ion batteries are different mainly due to the difference of cathode material, thus this paper mainly discuss the recycling methods for potable lithium ion batteries, especially that contains $LiCoO_2$. Three recycling methods include hydrometallurgical, pyrometallurgical process and the combination of the above two processes are reported in the literatures. The hydrometallurgical process mainly includes pretreatment, leaching and precipitation. The key of hydrometallurgical are leaching and the leaching agents used include H_2SO_4 combined with H_2O_2 [4-10], HCl [11], DL-malic acid ($C_4H_5O_6$) [12], Citric acid and hydrogen peroxide [13] etc. Bioleaching shows environment friendly and low price, thus is another important potential recovery technique for lithium ion batteries [14-16]. The combination of mechanical pretreatment with hydro- and pyrometallurgical process can obtain the metals and alloys [17]. For the lithium ion batteries, the most valuable composites are the metal and its composite, thus the recycling of the metals and the re-synthesis of cathode materials have attracted much attention. Weng et al. synthesized $Li[(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}Mg_x]O_2$ by hydrometallurgy and shows a reversible capacity of 152.7 mAh g^{-1} [18]. A recycling process involving chemical, mechanical, and electrochemical steps has been applied to recover cobalt from spent lithium ion batteries and re-synthesize with a ratio of Co:Mn=10:1 to obtain the cathode active materials$LiCo_{1-x}Mn_xO_2$, which shows a discharge capacity of 156.3 mAh g^{-1} at a rate of 20 mA g^{-1} with no perceptible capacity loss [19]. The $LiCoO_2$ is re-synthesized from spent lithium ion batteries by leaching and a sol-gel method shows a discharge capacity of 137 mAh g^{-1} at the 0.1 C with the capacity retention of 88.14% after 40 cycles [20]. But these processes are based on hydrometallurgy, which need much acid and produce much waste water, which is not an ideal process as assessed from the environmental and economic points. Furthermore, most processes are only based on a lab-scale investigation, which is difficult to be scaled up.

In this paper, we developed a simple recycling route based on pyrometallurgy to recycle the metals and re-synthesize the cathode of $LiCoO_2$.

2 EXPERIMENTAL PART

2.1 The pre-treatment of the spent lithium ion batteries

The battery was put into the NaCl solution to discharge and three kinds of concentration of 10, 5 and 1 wt.% were used to analyze the effect of salt concentration on discharge time. The batteries used in this experiment are new batteries, whose state of charge is about 60% and the voltage is about 3.85V.

2.2 Flow-chart of the recycling

The process is as follows: the spent batteries were put into a 1 wt.% NaCl solution to discharge, then the discharged batteries was heat-treated at 600 ℃ in vacuum condition for 3 hours to remove the organic solvent and carbonize the binder; then the battery was cut, and ground and sieved to separate the metallic composite and powder. The powder mainly contains cathode and anode active materials. The composite then heat-treated at 800℃ to remove the carbon and the final obtained product (denoted as Co-A) was measured by atomic absorb spectroscopy to analyze the contents of Co and Li, then control the Li:Co=1.05:1 and ball-milled for 2 hrs, then the mixture was sintered at 750 ℃ for 15 hrs to obtain the $LiCoO_2$ (denoted as LCO).

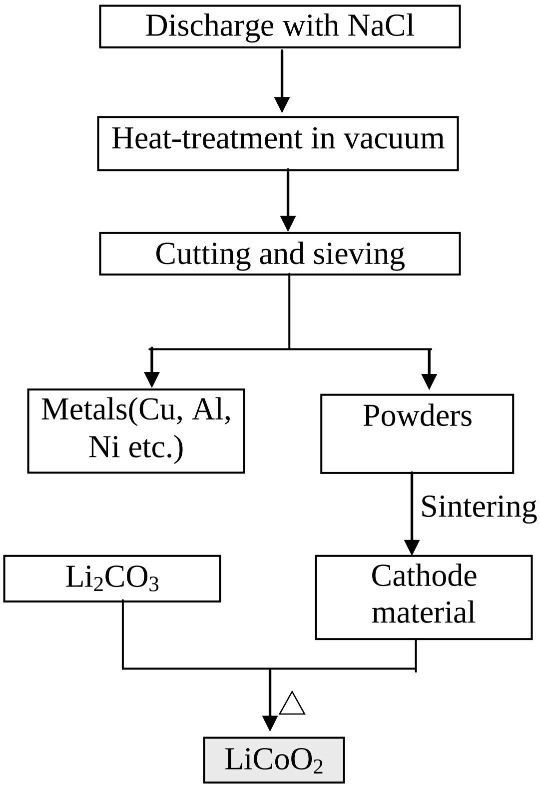

Figure 1. The flow-chart of the recycling process

The processes are summarized in Figure 1. The battery used for the recycling and re-synthesis of $LiCoO_2$ was come from the spent lithium ion batteries, whose history is un-known.

2.3 Synthesis of $LiCoO_2$

The $LiCoO_2$ was synthesized by direct reaction of the recycled Co_3O_4 and Li_2CO_3 with Li:Co=1.05:1. The reactants was mixed homogenous by ball-milling and packed in a ceramic boats and heat treated at 750 ℃ for 15 hrs under air condition.

2.4 The physical characterization

The morphologies of the samples were observed using a scanning electron microscope (SEM) (SU8010, Hitachi, Japan). The structure of the alloy was measured by X-ray diffraction (XRD) (X'pert PRO, Panalytical, Netherlands) with a scanning rate of 10 deg. min^{-1} in a range of 2θ values from 10-90^o and a step size of 0.02^o.

2.5 The Electrochemical test

The slurry of $LiCoO_2$ was prepared by ball-milling a mixture of 10 wt.% Super P (TIMCAL) carbon as conductive regent, 80 wt.% $LiCoO_2$ as active materials and 10 wt.% PVdF as binder with an adequate amount of N-methyl-2-pyrrolidone (NMP) solvent for 2 hrs. The $LiCoO_2$ slurry was coated onto Al foil with an area of 1 cm^2, then the electrodes were dried at 100 °C under vacuum (below -0.09) for more than 10 hrs to obtain an electrode for measurement. CR2025 coin-type cells were assembled in an argon-filled glove box (Etelux 2000, China), where both moisture and oxygen levels were kept at less than 1 ppm. $LiPF_6$ (1 mol L^{-1}) in ethylene carbonate and dimethyl carbonate (EC-DMC, 1:1 v/v) was used as the electrolyte and lithium foil was used as the counter electrode. Charge/discharge cycles were performed using a Neware® instrument (China) with a stable current of 0.1 C (1C=150 mA g^{-1}).

3. RESULTS AND DISCUSSION

3.1 The effect of NaCl concentration on the discharge

The batteries sent to the consumers generally contain about 60% of the rated capacity, showing a voltage about 3.85 V. But the state of charge (SOC) of the spent batteries is uncertain, whose SOC may verify from 0 to 100 %. The package and transportation of spent batteries can not be as restrict as that of the new ones, which fully separated the batteries to avoid the firing or explosion caused by the short circuit among the batteries. Thus it is important to find a cheap solution to fully discharge the spent batteries to solve the difficult of the collection of spent batteries. In this paper, we use NaCl solution to discharge the batteries and discuss the effect of concentration on the discharge time. The discharge curve of the new batteries with a voltage about 3.85 V treated by 10, 5 and 1 wt% NaCl solution are shown in Figure 2.

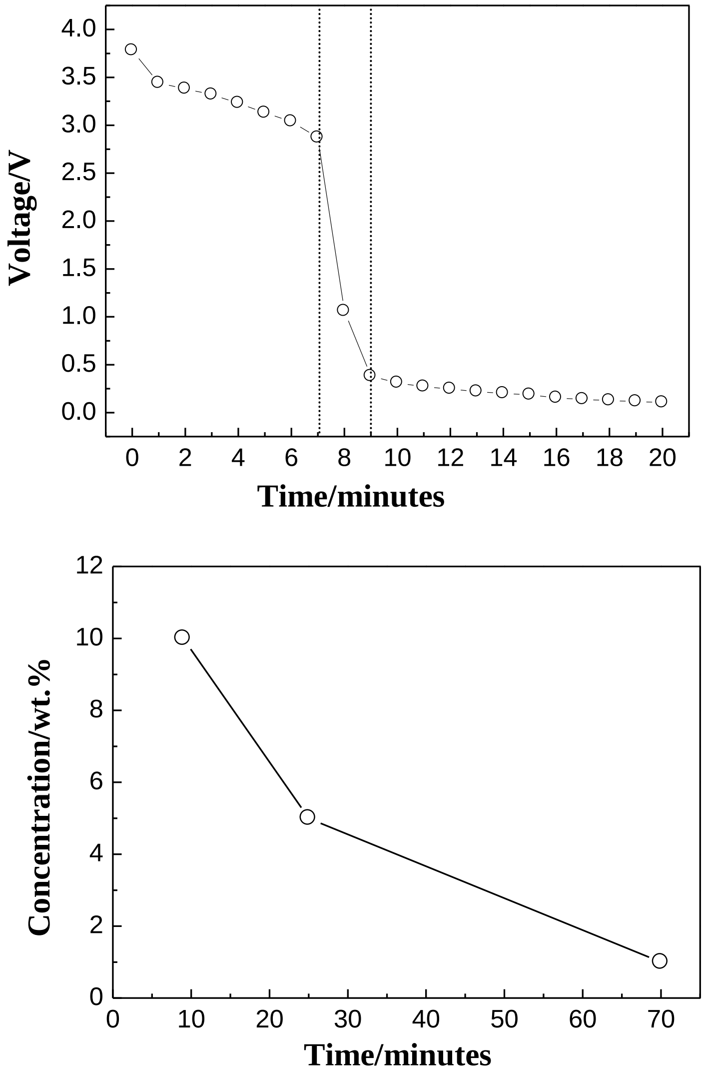

Figure 2. The discharge profile of the spent batteries in the 10 wt.% NaCl solution (a); The discharge times changes with the concentration of NaCl solution with a end voltage of 0.5V(b)

Figure 2(a) is the voltage of the batteries in 10 wt.% NaCl solution changes with time. It shows that the voltage decreases gradually with time, which is similar to the discharge curve of $LiCoO_2$, but suddenly decreases after about seven minutes due to the leakage of case at the edge place. The solution was entered into the case and makes the batteries discharge fast. The leakage results in the pollution of the electrodes inside the case by the salt solution. Furthermore, the $LiPF_6$ in the electrolyte may react with water to form HF, which will bring much negative effect on the recycling process. To decrease the reactivity during the discharge process, we select 5 wt.% and 1 wt.% NaCl solution to further investigate the effect of concentration on the discharge time. Figure 2(b) compares the discharge time to 0.5V in the three kinds of solution and the results show that the batteries can be fully discharged even in the very dilute NaCl solution of 1 wt.%, only with a relative long time of about 70 minutes. In this situation, no leakage was occurred.

The discharge is not like that using electric conductor (for example, Cu) to short-circuit the positive and negative tabs, rather than the electrolysis of the NaCl solution. The main relative reactions are as follows:

$$2NaCl \xrightarrow{Electrolysis} 2Na + Cl_2 \quad (1)$$
$$2H_2O + 2Na = 2NaOH + H_2 \quad (2)$$
$$2H_2O \xrightarrow{Electrolysis} 4H_2 + O_2 \quad (3)$$
$$\mathrm{Cl_2 + H_2O = HCl + HClO} \quad (4)$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2 \quad (5)$$
$$NaAlO_2 + HCl + H_2O = Al(OH)_3 + NaCl \quad (6)$$
$$NaOH + HCl = NaCl + H_2O \quad (7)$$

These reactions produce white foam-like $Al(OH)_3$ gathered around the battery and the leakage is arisen by the reaction (3).

3.2 The discussion of the recycling process

The spent batteries used for the recycling process are used battery, whose history and state of charge are unknown. The batteries are discharged by 1 wt.% NaCl solution, then heat treated in vacuum condition at 600 ℃ for 3 hrs. The advantage of heat-treating in vacuum is that the metal composites (Cu, Al and Ni) can not be oxidized but the binder and separator can be carbonized. Another advantage for the vacuum is the solvent can be recycled by condensation. After heat-treatment, the battery was cut into large pieces and sieved to separate the metallic composites (Al, Cu and Ni etc.) from the cathode and anode powders. The carbon in the spent lithium ion batteries possesses little value and the mixture is sintered to remove the carbon. The burning of carbon can create heat and decrease the power consuming, left a sample mainly from the cathode materials. The left sample was measured by atomic absorb spectroscopy to determine the content of Co and Li, then ball-milled and sintered to obtain the final $LiCoO_2$.

3.2 The performance of $LiCoO_2$ prepared from the recycled materials

The SEM of the Co-A and LCO is shown in Figure 3. It shows that the particle size of the Co-A is about 10 μm, while that of the LCO is similar to that of Co-A, indicating that the morphology of Co-A determines the morphology of the final $LiCoO_2$.

The XRD of the Co-A and LCO are shown in Figure 4, it shows that the Co-A shows a typical characterization of Co_3O_4 (PDF Card No. 00-043-1003). This is corresponding to the atomic absorb spectroscopy detection, which shows that the cobalt content in the composite is as high as 59.3%, while the lithium content is only 0.7%, much lower than the theoretical content in $LiCoO_2$ (7.09%). The lithium was disappeared due to the lithium ion the cathode and electrolyte was transferred to the composition of SEI, which mainly contains organic lithium composite and may evaporate during the heating process. The LCO shows a typical character of $LiCoO_2$ (PDF Card No. 01-075-0532), which indicates that the re-synthesis of the cathode material is realized.

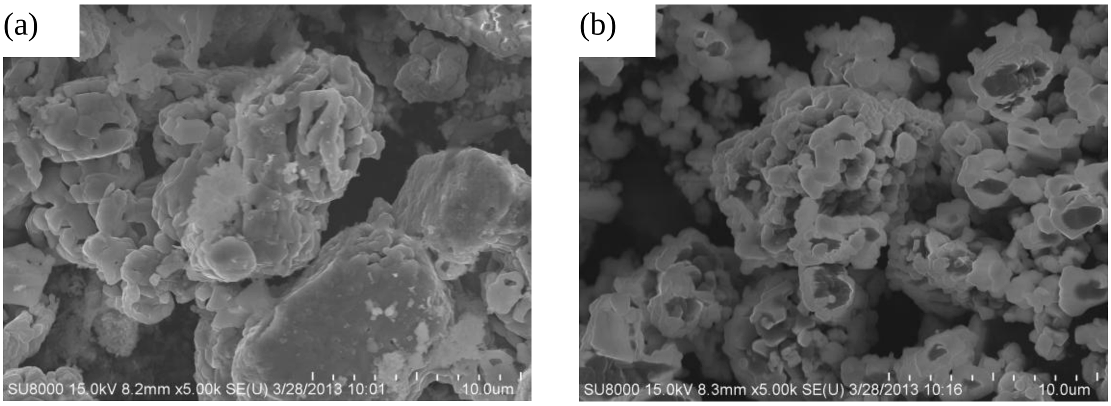

Figure 3. The SEM of the samples. (a) Co-A; (b) LCO

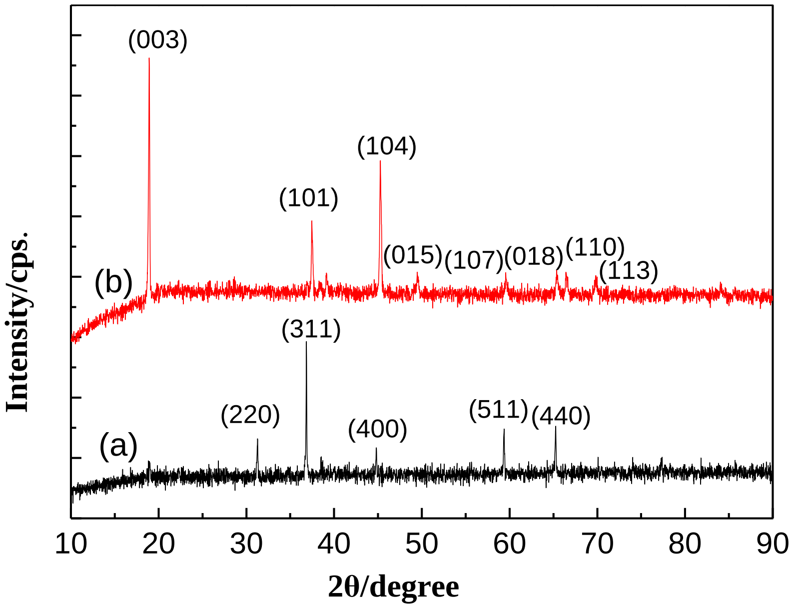

Figure 4. The XRD of the samples. (a) Co-A; (b) LCO

To further analyze the electrochemical performance of the synthesized cathode material, the charge-discharge performance is tested and shown in Figure 5. The first charge-discharge curves are shown in Figure 5(a) and the results show a typical charge discharge character of $LiCoO_2$: a discharge plateau higher than 3.7 V and small charge capacity at constant voltage stage. The first discharge capacity is 106.8 mAh g^{-1}, which is a little lower than that reported in the literature, this may be ascribed to that the particle size of the raw material is relative large and the solid-state reaction needs the fully mixture of the reactants. The reversible capacity of the sample thus prepared can be improved by increase the ball-milling time. The cycling curve shows that the capacity degradation is negligible. In summary, the reversible capacity of the sample synthesized in this paper is a little lower than that reported in the literature and can not be used in this stage, but can be improved by increase the ball-milling time, improving the heat-treating process and adjusting the composites before sintering.

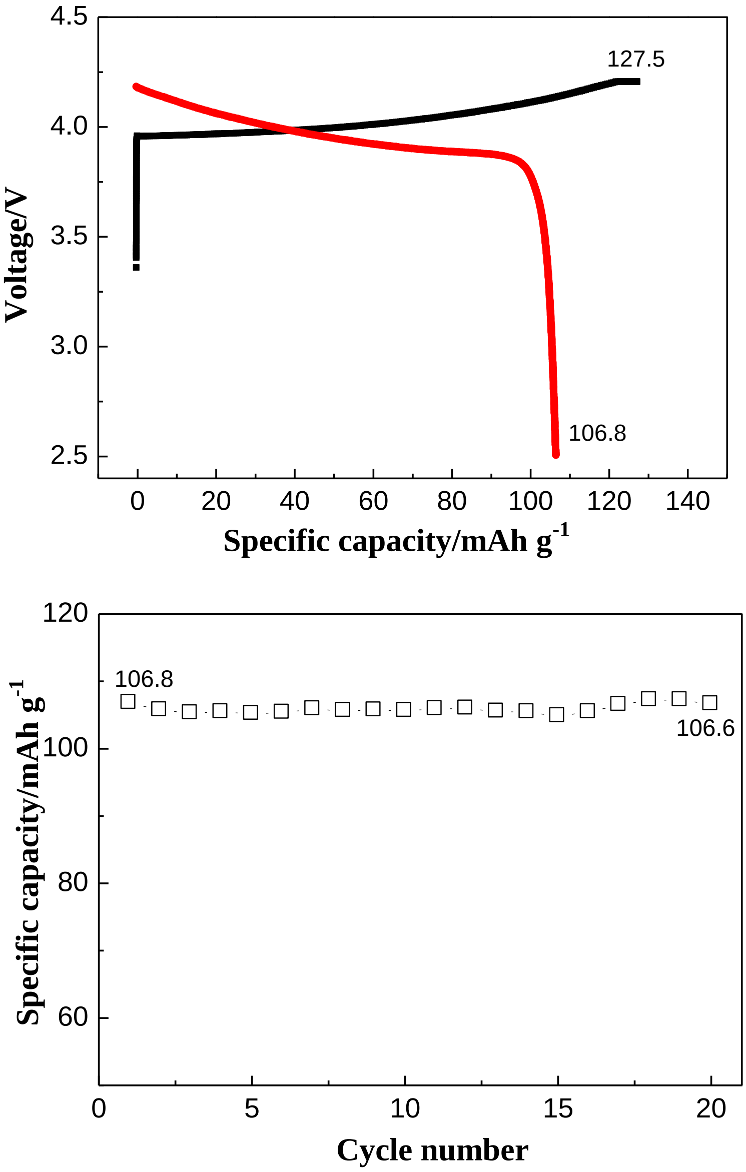

Figure 5. The electrochemical performance of the samples. (a) The first charge/discharge curves of the re-synthesized $LiCoO_2$; (b) the cycling curves of the re-synthesized $LiCoO_2$

This paper just reports the preliminary and a possible route to separate the metals and re-synthesize the cathode material. The composite in the spent lithium ion batteries may contain $LiCoO_2$ 、 $LiNi_xCo_yMn_{1-x-y}O_2$ etc, which can be treated by similar method to obtain the $LiNi_xCo_yMn_{1-x-y}O_2$ cathode.

4. CONCLUSIONS

The metallic composites in the lithium ion battery is separated and recycled by a simple vacuum-assisted pyrometallurgical process and the $LiCoO_2$ is re-synthesized. The re-synthesized

$LiCoO_2$ shows a reversible capacity of 106.8 mAh g^{-1} with negligible capacity degradation. The relative low reversible capacity is ascribed to the relative larger particle size of the raw material Co_3O_4, which can be improved be adjusting the parameters.

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