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Performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ prepared from spent lithium-ion batteries by a carbonate co-precipitation method

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ABSTRACT

Spherical $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode particles were resynthesized by a carbonate co-precipitation method using spent lithium-ion batteries (LIBs) as a raw material. The physical characteristics of the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor, the $(Ni_{1/3}Co_{1/3}Mn_{1/3})_3O_4$ intermediate, and the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material were investigated by laser particle-size analysis, scanning electron microscopy–energy-dispersive spectroscopy (SEM-EDS), thermogravimetry–differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), inductively coupled plasma–atomic emission spectroscopy (ICP-AES), and X-ray photoelectron spectroscopy (XPS). The electrochemical performance of the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was studied by continuous charge–discharge cycling and cyclic voltammetry. The results indicate that the regenerated $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor comprises uniform spherical particles with a narrow particle-size distribution. The regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ comprises spherical particles similar to those of the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor, but with a narrower particle-size distribution. Moreover, it has a well-ordered layered structure and a low degree of cation mixing. The regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ shows an initial discharge capacity of 163.5 mA h g^{-1} at 0.1 C, between 2.7 and 4.3 V; the discharge capacity at 1 C is 135.1 mA h g^{-1}, and the capacity retention ratio is 94.1% after 50 cycles. Even at the high rate of 5 C, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ delivers the high capacity of 112.6 mA h g^{-1}. These results demonstrate that the electrochemical performance of the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is comparable to that of a cathode synthesized from fresh materials by carbonate co-precipitation.

1. Introduction

Lithium-ion batteries (LIBs) have excellent electrochemical properties and are extensively used in consumer electronics and electric vehicles (EVs); with the further development of EVs, the use of LIBs will substantially increase. Because of the limited cycle lifetime of LIBs, many have entered the waste stream. The quantity and weight of spent LIBs in China alone is expected to exceed 25 billion units and 500 thousand metric tons by 2020, respectively [1]. Spent LIBs contain toxic heavy metals and corrosive electrolytes; improper battery disposal poses an unacceptable hazard to the environment and human health [2]. This waste also contains large quantities of valuable metals [3], which are vital secondary resources with proper recycling. Consequently, the recycling of spent LIBs is important for achieving sustainable development.

Current processes and technologies available for recycling spent LIBs have been reviewed in several studies [4–6]. The hydrometallurgical process consists of discharging and dismantling, separating active materials and current collectors, leaching valuable metals, and extracting these metals. The leaching systems used in the recovery of spent LIBs mainly include inorganic acids (HCl [7,8], HNO_3 [9,10], and H_2SO_4 [11,12]), organic acids (citric acid [13] and L-tartaric acid [14]), and bioleaching [15]. The main methods reported for the separation and extraction of metals from the leachate include chemical precipitation [8,16,17], solvent extraction [18–20], and electrodeposition [21,22]. The complete separation of Ni, Co, and Mn from the leachate is difficult because of the similarity of the metals and requires complicated separation processes, which significantly increases the cost of recycling.

The inexpensive $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material, which exhibits outstanding electrochemical performance and high thermal stability, is widely used in commercial LIBs [23–25]. To avoid unnecessary separation procedures during recycling, many researchers have recently focused on the direct synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from spent LIBs by NaOH co-precipitation [26–29]. However, the resulting $Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_2$ precursor is unstable; $Mn(OH)_2$ is easily oxidized to

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MnOOH and/or MnO_2 during co-precipitation, thereby reducing the uniformity of the precursor [30]. In contrast, the Na_2CO_3 co-precipitation method retains the oxidation state of Mn^{2+} and generates a more homogeneous carbonate precursor that can be used to produce cathode materials with good electrochemical properties [30–34]. Moreover, the Na_2CO_3 precipitation process is less expensive than NaOH precipitation.

In this study, a novel recycling process based on the Na_2CO_3 co-precipitation method was developed for the resynthesis of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material from spent LIBs. After manual dismantling, ultrasonic cleaning, leaching, and molarity adjustment, the leachate obtained from spent LIBs was used as the feed solution for the production of a $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor with uniformly spherical particles, which was then used to resynthesize the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material. The physical characteristics and electrochemical performance of the regenerated precursor, intermediate, and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material were studied in detail.

2. Experimental

2.1. Resynthesis of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material from spent LIBs

The overall closed-loop process for the resynthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from spent LIBs is shown in Fig. 1. First, the collected spent LIBs were fully discharged and manually dismantled to obtain the cathodes. Ultrasonic cleaning [35] was used to separate the cathode materials (active material and conductor) from the Al foil. The obtained cathode materials were then dissolved in a solution of 1-M H_2SO_4 and 1 vol% H_2O_2. The molar ratio of Ni:Co:Mn in the leachate was adjusted to 1:1:1 by adding analytically pure $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$, and $MnSO_4{\cdot}H_2O$. The concentrations of the various metals in the leachate and the leachate pH before and after molarity adjustment are listed in Table 1. After molarity adjustment, the leachate was used as the raw solution to prepare the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor.

The regenerated leachate (1.8 M), aqueous Na_2CO_3 (1.8 M), and a specific amount of $NH_3{\cdot}H_2O$ were simultaneously pumped into a continuous stirred-tank reactor. The pH of the reaction solution was carefully maintained at 7.5 for 12 h. A stirring speed of 700 rpm and a temperature of 60 °C were maintained during the carbonate co-precipitation process. The regenerated $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor was collected by filtration, washed with deionized water, and then dried at 120 °C for several hours under vacuum. The $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ was calcined at 500 °C in air for 5 h to obtain the $(Ni_{1/3}Co_{1/3}Mn_{1/3})_3O_4$ intermediate. This metal oxide was then thoroughly mixed with Li_2CO_3 at a Li/M (M = sum of Ni, Co, and Mn) molar ratio of 1.06. The mixture was finally preheated at 500 °C for 5 h and then sintered in air at 900 °C for 12 h to obtain the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

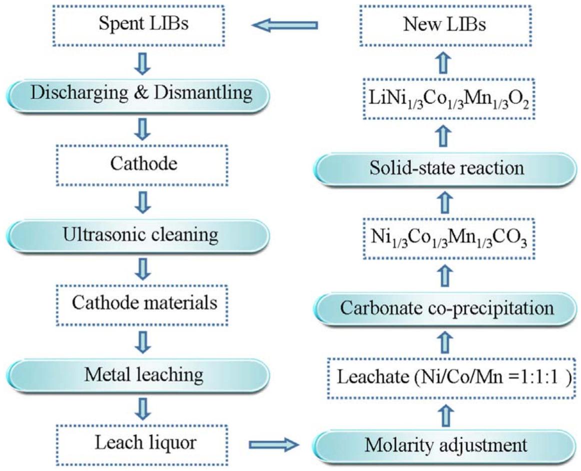

Fig. 1. Flow diagram for the resynthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ from spent LIBs.

Table 1
Metal concentrations and pH of the leachate before and after molarity adjustment.

Leachate	Elemental concentration (M)				pH
	Li	Ni	Co	Mn	
Before molarity adjustment	0.408	0.091	0.266	0.066	0.45
After molarity adjustment	0.296	0.597	0.593	0.594	0.37

2.2. Sample characterization

The morphologies and element distributions of the samples were analyzed by scanning electron microscopy (SEM, Quanta250, FEI) and associated energy-dispersive spectroscopy (EDS, Genesis-SiLi, EDAX). The particle distributions of the samples were determined using a laser particle-size analyzer (MS3000, Malvern). The thermal behaviors of the samples were examined by thermogravimetry and differential scanning calorimetry (TG-DSC, SDT-Q600, TA instruments) at a 10 °C/min heating rate. The crystal structures and compositions of the samples were analyzed by X-ray diffraction (XRD, D/max-2550V, Rigaku) and inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Arcos FHS12, Spectro), respectively. The valencies of the Ni, Co, and Mn present in the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher).

2.3. Electrochemical measurements

The electrochemical performance of the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was tested in CR2025 coin cells, which were assembled in an Ar-filled glove box. The active material mixture consisted of the regenerated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (10 wt%), which was made into a slurry and smoothly coated onto Al foil. The cathode was then dried at 120 °C for 24 h under vacuum to completely remove the solvent. After drying, the cathode was punched into small rounds and pressed into thin slices. Metallic Li served as the anode and Celgard 2400 was used as the separator. $LiPF_6$ (1 M) dissolved in a 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) was used as the electrolyte. Charge and discharge tests were performed at room temperature between 2.7 and 4.3 V using an electrochemical workstation (Parstat 4000, Princeton Instruments); the 1 C rate was assumed to be 160 mA h g^{-1}. Cyclic voltammetry curves were recorded on the electrochemical workstation in the 2.7–4.8 V voltage range at a scan rate of 0.1 mV s^{-1}.

3. Results and discussion

3.1. Mechanism for the formation of the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

During carbonate co-precipitation, the recovery efficiencies of Ni, Co, and Mn were 97.78%, 99.16%, and 99.12%, respectively. The recovery efficiencies for the recycling process, including pretreatment, leaching, and carbonate co-precipitation, were determined as 96.13% for Ni, 96.83% for Co, and 97.45% for Mn. The preparation of the $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ precursor involved the two stages of crystal nucleus formation and crystal growth. The added $NH_3{\cdot}H_2O$ acted as a chelating agent to maintain the balance between the rates of nucleation and crystal growth, thereby generating homogeneous spherical particles [30,32,36]. The mechanism for the formation of $Ni_{1/3}Co_{1/3}Mn_{1/3}CO_3$ is explained by the following equations [30]: