

Short Communication

Preparation of Ternary Cathode Materials from Spent Lithium Batteries at Low Temperature

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In order to avoid the shortcomings of long process and low recovery rate during the existing recycling of spent lithium-ion batteries. A novel process was developed for regeneration of spent $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode in Li^+ molten salt solution at low temperature under atmospheric pressure. Based on regeneration at low temperature, the initial discharge capacity of the regenerated cathode material is $169.1 \text{ mAh}\cdot\text{g}^{-1}$, and the capacity retention rate is 89.36% after 200 cycles. The regenerated NCM523 sample changed from $165.9 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1C to $137.35 \text{ mAh}\cdot\text{g}^{-1}$ at 5C and the rate capacity measured at the current density of 0.1 C is almost as the same as the original capacity. The original composition and crystal structure of NCM523 cathode are regenerated, which makes the capacity, cycle stability and rate capability reached the level of original material.

Keywords: Ternary materials; Lithium ion battery; Regeneration; Low temperature lithium addition; $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material

1. INTRODUCTION

Electricity is a widely used clean energy to cope with resource shortage and environmental pollution. As the development of urbanization, people have put forward higher and higher requirements on the degree of environmental pollution caused by the mode of transportation [1]. Environmental friendly electric vehicles has become the first choice for people to travel. Lithium ion batteries (LIBs) have attracted more and more attention due to the low cost, long service life, low toxicity and high energy density [2]. It has been widely used in the field of new energy vehicles and various energy storage devices [3]. LIBs can provide high energy density, high coulomb efficiency and long life, which make them the primary power source for portable electronic devices and electric

vehicles (EVS) in contemporary society. It is estimated that the global manufacturing capacity of LIBS will reach several hundred gigawatts per year over the next five years [4]. Accordingly, recovery of spent LIBs will become a non-negligible subject after their several years of operation life [5].

According to different failure modes of lithium ion batteries, the recovery methods of spent lithium ion batteries can be roughly divided into indirect regeneration and direct regeneration two types [6]. The indirect regeneration method includes pyro-metallurgy, hydrometallurgy and biological methods. Pyro-metallurgy processes require high temperature melting and multi-step purification or separation processes, which will produce a lot of spent gas and other problems [7]. The hydrometallurgy process mainly includes pretreatment, leaching, co-precipitation and other processes. It has the advantages of high metal recovery rate and low environmental pollution. Hydrometallurgical processes require acid leaching and subsequent complex pretreatment steps to prepare precursors for regeneration of new cathode materials [8]. The indirect regeneration methods would have to completely destroy secondary particle structures of spent cathode materials [9]. Therefore, the direct regeneration process has been developed to repair the spent cathode materials, including water heat treatment and short-term high temperature calcination. During direct regeneration process, lithium source was added into the cathode materials directly followed by high temperature sintering process. The direct regeneration can repair structure defects and deactivated lithium in spent cathode materials without leaching steps [10]. The regenerated cathode materials performance high specific capacity, high cycle stability and high rate capability. Therefore, the direct regeneration for recycling of spent cathode materials has become an important research hotspot.

Herein, a novel direct regeneration was developed for recycling of spent cathode materials at low temperature with mixed lithium salt. The recovery process of low-temperature lithium is analyzed by the phase diagram and thermogravimetric with mixed lithium salt as the lithium source. Based on XRD and TEM analysis, the phase and crystal structure of the regenerated material was analyzed. The electrochemical properties of regenerated cathode materials were analyzed by electrochemical measurement. The results showed that the novel direct regeneration could achieve recycling of spent cathode materials at low temperature.

2. EXPERIMENTAL

2.1 Regeneration of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ material

Firstly, the spent cathode material of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was obtained by manual dismantling [11]. Then, 5g spent NCM523 material was weighed and then mixed with an excess of 5% Li_2CO_3 and LiOH at a molar ratio of 4:1 in the mortar. The mixture was placed in the muffle furnace with the heating rate of $3\text{ }^\circ\text{C min}^{-1}$. The temperature of the first stage was 430°C and heated for 4 h. The temperature continued to rise to $850\text{ }^\circ\text{C}$ for 12 h. After cooling to room temperature, the regenerated $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was obtained.

2.2 Characterization analysis

The samples were analyzed by X-ray diffraction (XRD) and atomic absorption spectrometry (AAS, Ice3000, USA). The morphology and elemental composition of the samples were analyzed by scanning electron microscopy (SEM, tescan vega3, CZE).

2.3 Electrochemical performance testing

Firstly, the cathode electrode material was mixed with polyvinylidene fluoride and conductive carbon black at the mass ratio of 8:1:1 with adding a certain amount of NMP in the mortar for 20 min [12]. The mixed slurry was evenly spread on the aluminum foil with a thickness coater of 0.25mm. The cathode plate was put it into a drying oven to dry for 10 hours. Then, the electrodes was obtained by cutting 14 mm wafers from the plate pressing machine. The battery was assembled with negative lithium metal plates in a glove box filled with argon [13]. Finally, the prepared cathode electrode sheet, lithium plate, diaphragm and electrolyte were packed in a sealed glove box and placed for 8 hours in argon atmosphere. The battery charge and discharge test was conducted at 25 °C using Rand CT 2001a battery.

3. RESULTS AND DISCUSSION

The regenerated NCM523 cathode material was recovered at low temperature through mixed melt salts. Generally, a wide range of mixed melt salts could be formed by mixing of Li_2CO_3 and LiOH . The lower melting point of 432 °C would be obtained at the molar ratio of 4:1 for LiOH and Li_2CO_3 . The mixed melt salt with high Li^+ concentration can be beneficial for effectively regeneration of spent cathode material without any additional pressure [14]. As shown in Fig. 1, the spent NMC523 materials with Li vacancy are mixed with Li_2CO_3 and LiOH . Then, the mixture was heated to 430 °C and kept for 4 hours, which can provide enough time for lithium ions to diffuse through the particles.

As shown in Fig. 2, the heat absorption peak at 250 °C corresponds to the loss of crystal water from LiOH due to LiOH is very easy to absorb water from the air, which corresponds to the reduction of the weight of the first segment. The second heat absorption peak at 432 °C corresponds to the melting of eutectic molten salt with unchanged the weight of the mixture. Therefore, the reaction between the spent NCM523 cathode material and mixed lithium salt mainly occurs at 430 °C based on the above TGA analysis. Therefore, the temperature of 430 °C is selected for conducting lithium addition and regeneration process.

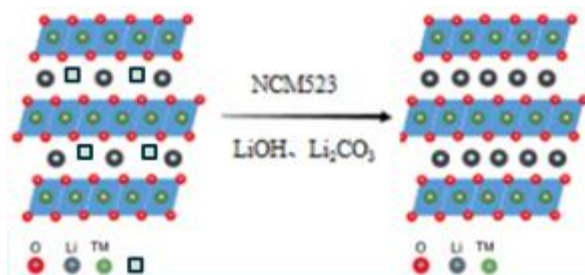


Figure 1. Regeneration process diagram of spent cathode materials at low temperature

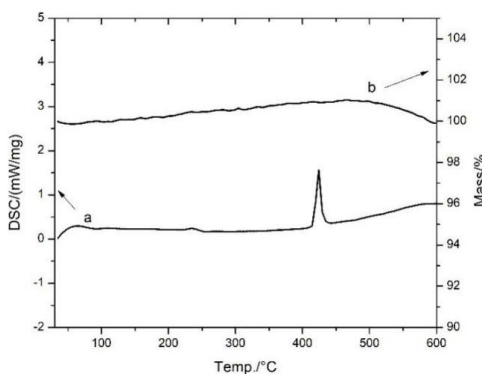


Figure 2. TGA and DSC curves of spent NCM523 cathode material and mixed lithium salt.

Figure 3 shows the XRD pattern of the spent NCM523 and the regenerated NCM523 samples after lithium addition. The two sample has typical α - NaFeO_2 structure and R3m spatial group [15]. With the increase of the c lattice, the (003) peak moves to a lower angle in the lithium absence state, which was caused by electrostatic repulsion between oxygen layers in the direction of c . After the cycle, the spacing between the $(006)/(102)$ and $(108)/(110)$ bimodal will be increased, which compensates for the lattice parameter reduction caused by the fact that the effective ion radius of Ni^{3+} is smaller than Ni^{2+} . The spent cathode material has a good layered structure. After extensive cycling and severe degradation of the cathode material, the spinel phase diffuses from the surface to the bulk phase, which can be detected in the XRD spectrum. The peak of the material (003) moved to a higher angle after regeneration. The decreasing of $(108)/(110)$ bimodal and the separated $(006)/(102)$ bimodal indicates the recovery of layered crystal structure [16].

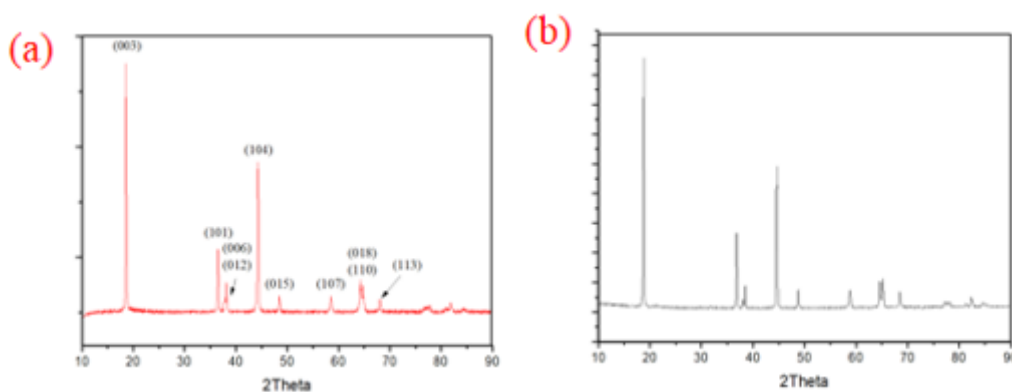


Figure 3. XRD patterns of the spent NCM523 samples and the regenerated NCM523 samples.

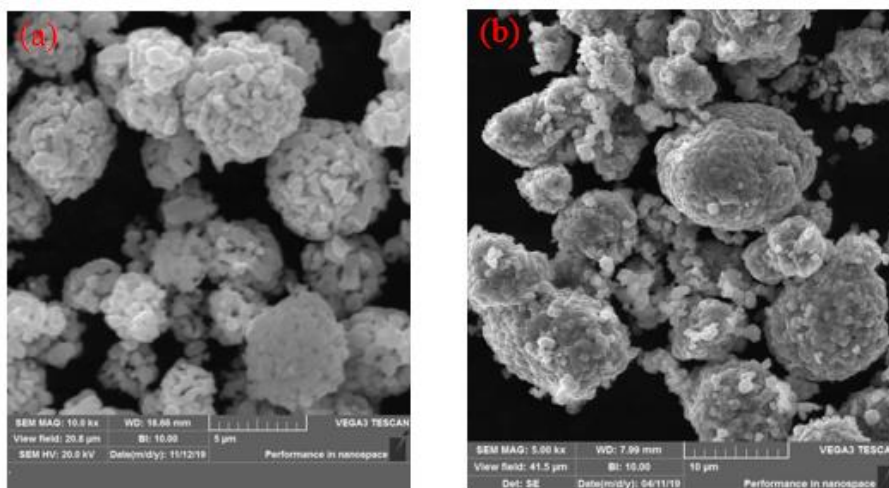


Figure 4. The SEM diagram of (a) spent NCM523 samples and (b) the regenerated NCM523 samples.

The SEM of the spent NCM523 and the regenerated NCM523 samples after calcination were shown in Fig. 4. The spherical particles of the regenerated NCM523 sample were maintained in good condition after lithium supplementation. Fig. 4 (a) shows the surface of spent NCM523 sample is rough without void. Fig. 4(b) shows the surface of regenerated NCM523 materials becomes smoother after lithium supplementation. Meanwhile, the primary particles are uniform in size with scattered spherical particles, which are beneficial for perfect electrochemical performance of the regenerated materials.

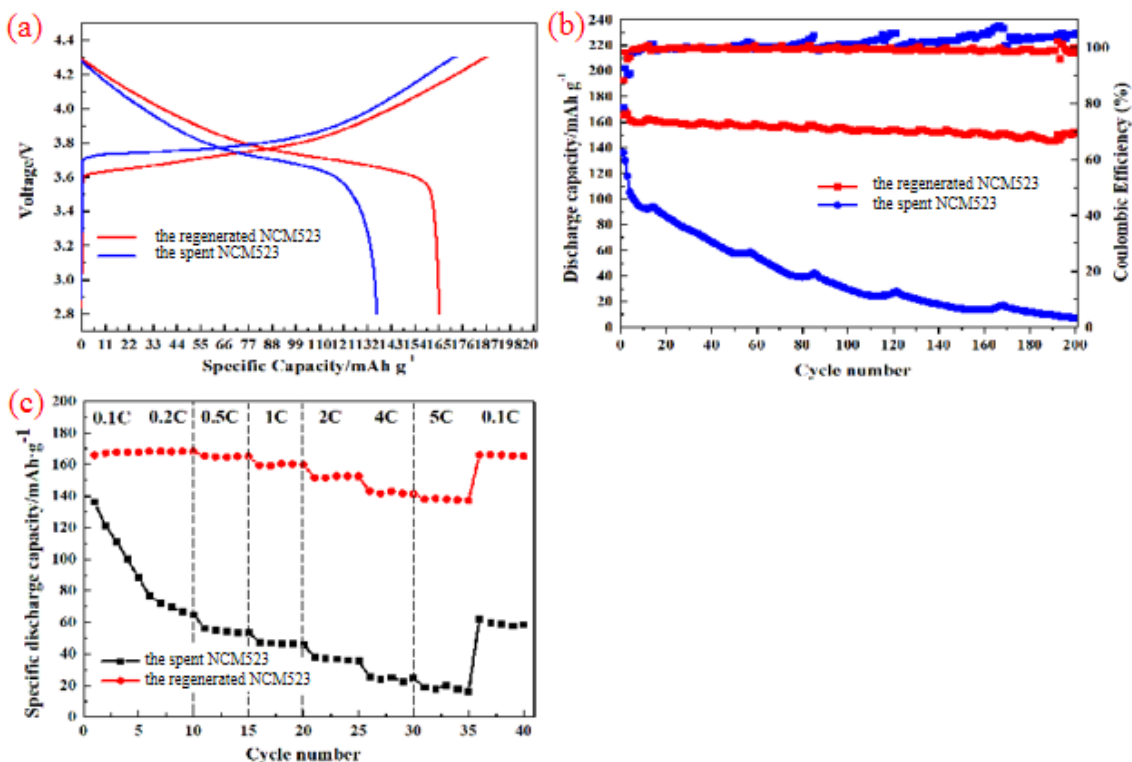


Figure 5. Electrochemical performance of spent NCM523 and regenerated NCM523. (a) Initial charge and discharge curves; (b) Cycle performance diagram; (c) Rate performance test.

The electrochemical performance with the voltage range of 2.8-4.3V at current density of 0.1C and ambient temperature of 25 °C is shown in Fig. 5. The initial discharge capacity of the regenerated sample is 165.9 mAh·g⁻¹ with the coulomb efficiency of 88.33%, which shows that the charging and discharging properties and coulomb efficiency were improved by the direct lithium addition due to structural restoration caused by mixture lithium salt [17]. The reversibility of Li⁺ de-intercalation is higher than that of the spent NCM523 cathode material. The charging-discharging cycle performance curves of spent NCM523 and regenerated NCM523 within the voltage range of 2.8-4.3V at 1C are shown in Fig. 5(b). The discharge capacity of regenerated NCM523 sample after lithium addition was 169.1 mAh·g⁻¹ at the first cycle. The discharge capacity was 151.1 mAh·g⁻¹ after 200 cycles and the capacity retention rate was 89.36%. The discharge capacity of the spent NCM523 sample is 136.3 mAh·g⁻¹ at the first cycle and 7.2 mAh·g⁻¹ after 200 cycles with the capacity retention rate of 5.28%, which is caused by stable material structure [18]. It can be seen that the properties of cathode materials are effectively improved after lithium addition. Rate capability is shown in Fig. 7(c). The spent NCM523 and the regenerated NCM523 samples were tested for 5 times at each current density at 0.1C, 0.2C, 0.5C, 1C, 2C, 4C and 5C respectively, and finally returned to 0.1C current density for 5 times. The discharge capacity of the spent NCM523 sample decreased seriously from 136.9 mAh·g⁻¹ at 0.1C to 16.1 mAh·g⁻¹ at 5C with the increase of current density. However, the regenerated NCM523 sample after lithium addition decreased from 165.9 mAh·g⁻¹ at 0.1c to 137.35 mAh·g⁻¹ at 5C, which is close to commercial material level [19]. The specific discharge capacity measured is almost the same as the original capacity under the current density of 0.1C. It can be seen that the regenerated NCM523 cathode material after lithium addition has better rate performance.

4. CONCLUSIONS

In this paper, LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ was directly regenerated at low temperature using mixed lithium salt as lithium source. The initial charge and discharge capacity of the regenerated cathode materials is 165.9 mAh·g⁻¹ and 136.8mAh·g⁻¹, which shows the charge-discharge and coulomb efficiency are improved compared with those of the spent cathode materials. Meanwhile, the rate performance test indicates that the regenerated NCM523 cathode material has better rate performance throughout directly regeneration with mixed lithium salt. The novel direct regeneration could achieve recycling of spent cathode materials at low temperature.

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