Synthesis of cathode material with different dosage of maleic acid-leachate of spent lithium-ion batteries

Liuye Sun, Borui Liu, Tong Wu, Guange Wang and Qing Huang*

School of Materials Science and Engineering, Beijing Institute Technology University, Beijing, China

*Corresponding author e-mail: huangqing3121@sina.com

Abstract. In this paper, LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cathode materials were synthesized by sol-gel with different dosage of maleic acid-leachate of spent lithium ion batteries (LIBs). Electrochemical performance test was performed on the re-synthesised materials to explore the effect of leachate dosage. The results show that the degree of Li^+/Ni^{2+} mixing increased while initial discharge capacities and capacity retention decreased significantly with leachate dosage increasing. Therefore, the leachate dosage is preferably 65% which can achieve a win-win situation in economy and performance when the LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cathode materials were synthesized with maleic acid-leachate of spent LIBs in our work.

1. Introduction

In the last few years, owing to environmental pollution and energy consumption lithium-ion batteries (LIBs) develop rapidly [1]. Therefore, a large number of spent LIBs need to be disposed properly. The cathode materials of spent LIBs contain many value metals such as Li and Co that are important raw materials for synthesizing industrial LIBs cathode materials. In addition, the content of value metals in spent LIBs is higher than in natural minerals [2]. Thus, the recovery of spent LIBs cathode materials especially the most commercialized materials (LiCoO_2) is particularly important.

At present, the hydrometallurgical process is preferred for recycling of spent LIBs cathode materials, and the vital step of hydrometallurgical process is acid leaching, which converts the cathode material from solid to liquid with inorganic acids or organic acids[3], [4]. In the past, researchers used inorganic acid, which was easy to produce secondary pollution. In recent years, some researchers have paid more attention to green organic acids. The common treatment methods for leachate are extraction, chemical precipitation, and electrodeposition[5]. These methods are complicated to operate and increase recycling costs. Therefore, some researchers consider using the leaching solution to directly synthesize the cathode material to avoid the steps of separation and purification[6]-[8]. The organic acid leachate contains raw materials like Li, Ni, Co and Mn and complexing agent, which can synthesize cathode materials [9].

Although there were some studies on the synthesis of cathode materials with acid-leachate, which mainly focuses on how to use acid-leachate to synthesize Ni-rich cathode materials, the research about the amount of acid-leachate on the performance of synthesized cathode materials is still very limited. In this paper, to study the influence of the dosage of acid-leachate, maleic acid and H_2O_2 were...
employed as leaching agents to recycle the spent LiCoO₂. The raw materials with different amount acid-leachate containing Li and Co were employed to synthesize cathode material by the sol-gel.

2. Experimental

2.1. Materials.
Spent LIBs (from Zhongguancun Electronic Market, Beijing, China), maleic acid and H₂O₂ were used to obtain acid-leachate. NH₃·H₂O was applied to regulate pH of solution. CH₃COOLi·2H₂O, (CH₃COO)₂Co, (CH₃COO)₂Ni·4H₂O and (CH₃COO)₂Mn·4H₂O were used to synthesize cathode materials.

2.2. Methods.
According to previous research work, maleic acid was applied as a leaching acid to obtain acid-leachate under the optimal parameters from spent LiCoO₂ materials [3]. CH₃COOLi·2H₂O, (CH₃COO)₂Co, (CH₃COO)₂Ni·4H₂O and (CH₃COO)₂Mn·4H₂O were added to acid-leachate to adjust the ratio of Li⁺, Mn²⁺, Co²⁺ and Ni²⁺ to 1:0.5:1:3:1/3:1/3:1/3, and NH₃·H₂O was added to solution until pH=7. Then the solution was stirred with magnetic stirrer at 80 °C until that a gel was obtained. The gel was dried at 110 °C for 24 h and was grinded into powder. The gel powder was calcined at 450 °C for 5 h and then calcined at 850 °C for 8 h in muffle furnace to obtain LiNi₁/₃Co₁/₃Mn₁/₃O₂. The Ni and Mn in the synthetic LiNi₁/₃Co₁/₃Mn₁/₃O₂ all come from the reagents, while the Li and Co come from the acid-leachate and raw materials, respectively. In this paper, the Co_leachate/(Co_leachate+Co_raw) was set as 0, 35%, 65% and 100%. According to the dosage of maleic acid-leachate, the synthesized cathode materials were marked as L-0, L-35, L-65 and L-100. The specific experimental flow chart is shown in Fig. 1.

![Fig. 1. The flow sheet of synthesizing LiNi₁/₃Co₁/₃Mn₁/₃O₂ with different dosage maleic acid-leachate.](image)

2.3. Characterization
The phase characterization of materials was analyzed by X-ray diffraction (XRD). The surface appearance of the cathode materials was investigated with Scanning Electron Microscopy (SEM).

3. Results and discussion

3.1. XRD of the re-synthesis cathode materials
To study the influence of the acid-leachate dosage on the phase characterization of synthesised cathode materials, X-ray diffraction (XRD) was employed. It can be known from Fig. 2 that the characteristic peaks of the four synthetic materials are basically the same, meanwhile, every diffraction peak of re-synthesis cathode materials belongs to the α-NaFeO₂ structure, R₃̅m space.
group. There is no obvious impurity peak indicating that high-purity materials were obtained [6]. The double peaks (006)/(102) and (108)/(110) of the re-synthesis materials L-0, L-35 and L-65 were apparent splitting which indicate that they have a highly ordered layered structure [5], while double peaks of L-100 was not as obvious as the other three materials.

In addition, because the ionic radius of Li$^+$ and Ni$^{2+}$ is close, cation mixing in the cathode materials is likely to occur [10]. The intensity ratio of (003)/(104) peaks shows the degree of cation distribution and the degree of cation mixing of materials [11]. Generally speaking, the larger the ratio of I (003)/I (104) is, the better order of the the material is. Especially, the ratio of I (003)/I (104) is greater than 1.2 demonstrating that the degree of cation mixing is considerably low [11, 12]. The I (003)/I (104) ratios of L-0, L-35, L-65, L-100 (as shown in table 1) are 1.48, 1.36, 1.33 and 1.23 respectively, which were all greater than 1.2. These results indicated that the an increase in the amount of leachate which contain some impurities in re-synthesis materials might lead to the increase of Li$^+$/Ni$^{2+}$ mixing [13].

**Table 1.** I (003)/I (104) ratio of four materials with different ratios of leachate

| sample | I (003)/I (104) |
|--------|----------------|
| L-0    | 1.48           |
| L-35   | 1.36           |
| L-65   | 1.33           |
| L-100  | 1.23           |

3.2. **SEM of the re-synthesis cathode materials**

To explore the influence of leachate dosage on the morphology of re-synthetic materials, SEM was applied to analyze the morphology of the materials. It showed from Fig. 3 that the four materials have little difference in morphology and size. The four materials were formed by the secondary particles which were about 300-500 nm. As we know that the smaller of the particle size, the easier the particle could contact with the electrolyte which might reduce the deintercalation path of Li, improving the electrochemical performance of materials [14]. The results showed that with leachate dosage increased, the particles of the material increase slightly, thus, in our work, the leachate dosage has little effect on the morphology of the cathode material synthesized by the sol-gel.
3.3. Electrochemical Performance of re-synthesis cathode material

We tried to assemble the battery for testing with L-0, L-35, L-65 and L-100 to explore the influence of leachate dosage of re-synthesized materials. Figure 4(a) shows the cycling characteristics of the four materials at a rate of 0.2 C, and the cycling voltages of all batteries are between 2.8 and 4.3 V. Observing the cycle performance of different batteries in the figure, it is found that the initial discharge capacities of L-0, L-35, L-65 and L-100 are 159.5, 156.1, 158.2 and 141.7 mAh g\(^{-1}\). After 100 cycles, the capacity retention of L-0, L-35, L-65 and L-100 were 92.72%, 92.69%, 84.07% and 86.52%, respectively. The coulombic efficiency of the four materials is basically the same, all of which are above 98%. While the capacity retentions after 100 cycles of L-0, L-35, L-65 and L-100 at 1 C (shown in Fig. 4(b)) were 87.9%, 82.41%, 82.28% and 73.40%. These results indicated that when the amount of leachate was less than 65%, the first week discharge capacity of the re-synthesized material would not change significantly with the increase of the amount of leachate. However, when the amount of leaching solution was greater than 65%, the first week discharge capacity of the re-synthesized material at 0.2 C and 1 C was significantly reduced. This is mainly due to the fact that the degree of Li\(^+/\)Ni\(^{2+}\) mixing was more obvious when leachate dosage was above 65% [13], [15]. The rate performance of the four materials at 0.2 C, 0.5 C, 1 C, 2 C, 5 C and 0.2 C was shown as Fig. 4(c). The discharge capacity of the re-synthesized material decreased with the increase of the leachate dose, especially above 65%. When the discharge current reached to 0.2 C, the capacities of L-0, L-35, L-65 and L-100 were 153.3, 150.1, 142.2 and 133.4 mAh g\(^{-1}\).
4. Conclusion

In summary, we synthesized LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cathode materials with different dosage of maleic acid-leachate. XRD results showed that the four materials had a highly ordered layered structure, and the ratio of I(003)/I(104) for L-0, L-35, L-65 and L-100 were 1.48, 1.36, 1.33 and 1.23. SEM results showed that the morphology of the materials was little effect by the leachate dosage. The initial cycle discharge capacities of L-0, L-35, L-65 and L-100 were 159.5, 156.1, 158.2 and 141.7 mAh g\(^{-1}\). In addition, the rate performance also decreases when the leachate dosage was above 65%. Therefore, the leachate dosage should not exceed 65% to re-synthesis LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) in our work.

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