Letter

Synthesis of High-performance $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ Cathode Material for Lithium-ion Batteries by Using a Four Times Liquid Nitrogen Quenching Method and an Al_2O_3 Coating Method

Wenyuan Yang ^{1,*}, Yinze Zuo ¹, Qi Chen ² and Yan Zhang ²

¹ National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China; yinzezuo@126.com

² Yunnan Jingxi New Material Technology Co., Ltd., Qujing 655000, China; chenqi890312@sina.com (Q.C.); cooly713@sina.com (Y.Z.)

* Correspondence: zhanghx@nju.edu.cn

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Abstract: Based on the normal co-precipitation method to synthesize $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material, we propose a novel approach using a liquid nitrogen quenching method to synthesize Al_2O_3 coated $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material. In the whole process, liquid nitrogen was used four times to quench the materials from high temperatures (50 °C, 750 °C, 90 °C, 500 °C) to −196 °C rapidly in four stages. Various characterizations proved that this method could help to improve the electrochemical performance of lithium-ion batteries. Especially at 5 C rate current, after 100 cycles, the specific discharge capacities were 24.5 mAh/g (LNCM 622), 43.8 mAh/g (LNCM 622-LN), and 53.9 mAh/g (LNCM 622-LN@ Al_2O_3). Liquid N_2 quenching increased the charge/discharge capacities and the Al_2O_3 layer increased the cycle stability at high current, to finally obtain improved electrochemical properties.

Keywords: lithium ion batteries; $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$; liquid nitrogen; Al_2O_3 ; electrochemical performance

1. Introduction

Rechargeable lithium-ion batteries are widely used for energy storage. The nickel-rich layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ materials have received significant attention because of their high reversible capacities [1]. Among them, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ is one of the most promising nickel-rich layered cathode materials [2,3], $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ is the best compromise between stability and performance aspects, also at elevated temperature [4,5]. Various methods have been applied to synthesize this material, such as the co-precipitation method [6,7] (the composition under homogeneous, synthesis conditions is easy to control), the solid-state method [8] (it is easy to introduce impurities, so the electrochemical performance is not stable), and spray-drying [9] (the uniformity of particles is better). Since the co-precipitation method is widely used in commercial production, we used it in this study to synthesis new materials. However, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ is needed to further improve its structural stability and electrochemical performance [10,11]. In this work, based on the traditional co-precipitation method, we used liquid nitrogen quenching to help synthesize a high-performance $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material.

Quenching samples into liquid nitrogen (−196 °C) is a typical technique to obtain an ultrahigh cooling rate. The cooling rate is uniform and controlled by heat transfer in the quench medium instead of heat conduction in the sample. It is widely used in the preparation of crystals [12], nanomaterials [13] and alloys [14]. Using liquid nitrogen to synthesize cathode materials for lithium-ion batteries has

been reported, such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ [15], LiFePO_4/C [16], and LiMnPO_4/C [17]. According to these reports, the liquid N_2 quenching method to prepare materials can inhibit the growth and agglomeration of particles, produce some crystal defects, which can expand the tunnels for Li-ion diffusion and shorten the diffusion distance, which are of benefit for the electrochemical performance. However, according to published reports, no one has used liquid nitrogen to help synthesize nickel-rich layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ materials; this is the first time that we have used liquid nitrogen quenching method to synthesize $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material. At the same time, using Al_2O_3 to coat $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials has been reported before [18], its electrochemical performances can be improved and the structure is not affected by the coating of Al_2O_3 . Since the liquid nitrogen quenching method and Al_2O_3 coated method are both useful for improving the electrochemical properties of cathode materials, we combined them for the whole process to synthesize high performance $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material.

2. Experimental

2.1. Preparation of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$

First, we synthesized the normal $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powder by the co-precipitation method. (1) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ powders were dissolved in deionized water to obtain 2.0 mol/L solution, with molar ratio of Ni:Co:Mn as 6:2:2. (2) The mixture was heated at 50 °C in a water bath, then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2.0 mol/L) and NaOH (2.0 mol/L) were added into the solution to control the pH between 11 and 12 under N_2 atmosphere. (3) After being stirred for 10 min and filtering the solution, the precipitated powder was washed with deionized water several times and dried at 80 °C in a vacuum oven for 24 h; this was the $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor. Then a mixture of LiOH and $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ at a molar ratio of 1.05:1 was heated at 750 °C for 15 h under a flowing oxygen atmosphere, then cooled down slowly from 750 °C to room temperature in the oven (about 5 h), and marked as LNCM 622.

As a comparison, we synthesized new $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powder with the liquid N_2 quenching and Al_2O_3 coated method. The schematic of the whole process is shown in Figure 1. First, after the $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor solution was stirred for 10 min, it was poured into liquid nitrogen quickly and the sample cooled down rapidly from 50 °C to −196 °C in 1 min; the 1st liquid nitrogen quenching, for $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$, as shown in Figure 2a. Thirty min later, the precursor powder was washed with deionized water and dried at 80 °C, then used to synthesize $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ with LiOH as described above at 750 °C for 15 h. After 15 h, the powder (at 750 °C) was taken out of the oven and immediately added quickly into liquid nitrogen, where it cooled down rapidly from 750 °C to −196 °C in 1 min; the 2nd liquid nitrogen quenching, for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, as shown in Figure 2b, marked as LNCM 622-LN.

To synthesize the 1% Al_2O_3 coated $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powder, a specified amount of $\text{CO}(\text{NH}_2)_2$ was added into deionized water to form a 1.0 mol/L solution. First 10 g LNCM 622-LN and 0.736 g $\text{Al}(\text{NO}_3)_3$ was added into deionized water and stirred at 90 °C for 30 min before adding into 2.0 mL of $\text{CO}(\text{NH}_2)_2$ solution and stirring for 4 h. After 4 h, the solution was poured into liquid nitrogen quickly and the temperature cooled down rapidly from 90 °C to −196 °C in 1 min; the 3rd liquid nitrogen quenching, for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2 @ \text{Al}(\text{OH})_3$. Sixty min later, the $\text{Al}(\text{OH})_3$ coated $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powder was washed with deionized water and dried at 80 °C. Then this sample was heated at 500 °C for 3 h. After 3 h was over, the powder (at 500 °C) was taken out of the oven immediately, rapidly poured into liquid nitrogen and cooled down rapidly from 500 °C to −196 °C in 1 min; the 4th liquid nitrogen quenching, for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2 @ \text{Al}_2\text{O}_3$. Now we obtained the 1% Al_2O_3 coated $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powder, as shown in Figure 2c, marked as LNCM 622-LN@ Al_2O_3 .

Figure 1. Synthesis method of LNCM 622-LN and LNCM 622-LN@Al₂O₃.

Figure 2. Digital photos of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (a), LNCM 622-LN (b), LNCM 622-LN@Al₂O₃ (c).

2.2. Characterization

The coin cells (type 2032) were assembled in a pure argon-filled glove box with the content of H₂O and O₂ less than 1 ppm. A mixture of 80 wt.% cathode material, 10 wt.% Super P carbon black and 10 wt.% polyvinylidene fluoride (PVDF) were mixed in N-methylpyrrolidone (NMP) to produce a slurry. The slurry was coated on aluminum foil (150 μm thickness) and dried at 80 °C for 12 h in a vacuum oven. The electrolyte was 1.0 M LiPF₆/ EC + DMC + EMC (1:1:1, volume ratio). Celgard 2400 was used as separator.

A Hitachi S-3400N field emission scanning electron microscope (SEM) was used observing at 30 kV. X-ray diffraction (XRD) powder patterns of the samples were taken on an ARL X'TRA powder diffractometer with Cu-Kα radiation (λ = 0.154 nm). The electrochemical charge/discharge properties were tested by Land CT 2001A (5 V, 50 mA) between 2.8 and 4.2 V (vs. Li/Li⁺) at different rates (1 C = 276.55 mAh/g). All the cells were charged and discharged at 0.05 C for the first 5 cycles, then a constant current was used (0.1 C, 0.5 C, 1 C, 2 C, 5 C and 10 C, separately) charged until the voltage >4.2 V, next charged at constant voltage (4.2 V) with a taper current, cut off until the taper current was less than 10% of the above constant current (less than 0.01 C, 0.05 C, 0.1 C, 0.2 C, 0.5 C and 1 C,

separately). After that, the used constant current was discharged until the voltage <2.8 V. The above cycle was repeated 50 times (0.1 C) or 100 times (other rates).

3. Results and Discussion

Figure 3 shows the SEM images of LNCM 622, LNCM-622LN and LNCM 622-LN@Al₂O₃, the particle size is about 10–20 μm in diameter. Compared with LNCM 622, the particles of LNCM 622-LN and LNCM 622-LN@Al₂O₃ are less aggregated, with more spherical morphology, but the differences are small, showing that liquid nitrogen helped the materials form more regular shapes to some extent.

Figure 3. SEM images of LNCM 622 (a), LNCM 622-LN (b), and LNCM 622-LN@Al₂O₃ (c).

Figure 4 displays the XRD patterns of the three samples. All diffraction peaks are indexed based on the α -NaFeO₂ structure (space group: *R3m*). All the XRD patterns show clear splits between the (006/012) and (108/110) peaks, especially for LNCM 622-LN and LNCM 622-LN@Al₂O₃, where the splits are clearer, meaning that the materials have a typical hexagonal structure [19,20]. Since the Al₂O₃ layer is amorphous and the content is very low, no peak of the Al₂O₃ crystal type is observed.

Figure 4. XRD patterns of LNCM 622 (a), LNCM 622-LN (b), and LNCM 622-LN@Al₂O₃ (c).

The intensity ratio of $I_{(003)}/I_{(104)}$ characterizes the degree of cation mixing of the cathode material. If $I_{(003)}/I_{(104)} < 1.2$, indicates a high degree of cation mixing, due primarily to the occupancy of other ions in the lithium region [20,21]. The higher the ratio, the lower is the level of cation mixing, which is a benefit for lithium-ion transfer. The ratio of $I_{(003)}/I_{(104)}$ increases from 1.28 (LNCM 622) to 1.37 (LNCM 622-LN) and to 1.44 (LNCM 622-LN@Al₂O₃). Especially the ratios of LNCM 622-LN and LNCM 622-LN@Al₂O₃ are greater than 1.2, showing the synthesized powders have well-ordered structures with no obvious cation mixing. This indicates that liquid N₂ quenching helped to improve the structural properties of the nickel-rich layered cathode materials.

The initial specific charge/discharge curves of the three samples between 2.8 and 4.2 V are shown in Figure 5. The initial specific discharge capacities at 0.1 C/0.5 C/1 C/2 C/5 C/10 C are 153.3/135.6/130.6/111.3/76.3/23.2 mAh/g (LNCM 622), 160.1/139.0/131.4/120.2/90.3/36.2 mAh/g (LNCM 622-LN) and 155.1/140.7/132.6/122.3/103.6/44.8 mAh/g (LNCM 622-LN@Al₂O₃), respectively. At low rate current (0.1 C), the specific discharge capacity of LNCM 622-LN is higher than the other two. However, when the rate current is higher than 0.5 C, LNCM 622-LN@Al₂O₃ performs the best of all and in any case, the specific discharge capacity of LNCM 622-LN is always higher than that of LNCM 622. This phenomenon may be due to the material having more tunnels for Li-ions diffusion, and the diffusion distance being shorter, indicating that liquid N₂ quenching could help to increase the material's electrochemical performance, similar to the work referenced above [15–17]. Although Al₂O₃ does not participate in electrochemical reactions, it could improve the cycle stability at a high rate current, so the discharge capacity of LNCM 622-LN@Al₂O₃ is lower at 0.1 C, but exhibits the highest value at the strong rate currents (0.5 C, 1 C, 2 C, 5 C and 10 C).

Figure 5. The initial specific charge/discharge curves of LNCM 622 (a), LNCM 622-LN (b), LNCM 622-LN@Al₂O₃ (c), and initial charge/discharge capacity data of the 3 samples (d).

Figure 6 shows the cycling performance of the three samples at different rate currents between 2.8 and 4.2 V. At all rates, in the last cycle, compared with LNCM 622, the specific discharge capacities

of LNCM 622-LN and LNCM 622-LN@Al₂O₃ are significantly higher, the increased proportions are about 3.66% and 0.67% (0.1 C), 9.32% and 32.58% (0.5 C), 18.36% and 28.04% (1 C), 7.25% and 19.80% (2 C), 78.78% and 120.00% (5 C), 23.40% and 101.06% (10 C), respectively. Especially at the 5 C and 10 C rate, the specific discharge capacities' values almost doubled. This means that, for LNCM 622-LN, liquid N₂ quenching increased the discharge capacities. Also for LNCM 622-LN@Al₂O₃, the increase of discharge capacities was not just due to the use of liquid N₂, the Al₂O₃ layer also improved the cycle stability of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ at high currents, finally improving the cycling performance.

Figure 6. Cycling performance of LNCM 622, LNCM 622-LN and LNCM 622-LN@Al₂O₃ at 0.1 C (a), 0.5 C (b), 1 C (c), 2 C (d), 5 C (e), and 10 C (f).

In addition, it was worthwhile to compare these materials with commercial materials. The commercial LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material was obtained from Shenzhen Kejing Star Technology Co., Ltd. (Shenzhen, China), marked as C-LNCM 622. We prepared cells and tested this material under the same conditions as mentioned above. As shown in Figure 7, at 1 C rate, the initial specific discharge capacity of C-LNCM 622 is very close to our synthesized materials. In the 30th to 50th cycle, its value was higher than LNCM 622, nearly equal to LNCM 622-LN, but lower than LNCM 622-LN@Al₂O₃. However, in the final cycle, the specific discharge capacity of C-LNCM 622 was lower than our synthesized samples. Every method has its advantages or disadvantages and compared with LNCM 622, the commercial material has a better performance in the middle cycles.

However, the liquid N₂ quenching and Al₂O₃ coated method also demonstrate many advantages in improving cycling performance.

Figure 7. Cycling performance of LNCM 622, LNCM 622-LN, LNCM 622-LN@Al₂O₃, and C-LNCM 622 at 1 C.

4. Conclusions

Using liquid N₂ to rapidly quench LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ powder and Al₂O₃ coated powder from high temperatures (50 °C, 750 °C, 90 °C, 500 °C) to −196 °C was found to be an efficient method to improve the electrochemical performance of lithium-ion batteries. In this work, we used the liquid N₂ quenching method four times over four stages, in order to make new cathode materials with better electrochemical properties, with a coated Al₂O₃ layer to obtain a better cycle stability at high currents. Compared with normal LNCM 622 and commercial LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material, LNCM 622-LN and LNCM 622-LN@Al₂O₃ have a better ordered structure with less cation mixing, higher initial charge/discharge capacities, and better cycling performance at different rates of currents. Liquid nitrogen is easy to prepare, volatilizes quickly without residue giving no pollution to the environment, and liquid N₂ quenching is a mature technology in industrial production. Therefore, this is a promising method to synthesize many other high-performance nickel-rich layered cathode materials like LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂, LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂, and LiNi_{0.85}Co_{0.1}Mn_{0.05}O₂. All the above materials could also be coated with Al₂O₃ layer by this method. We believe these cathode materials also demonstrate outstanding electrochemical properties.

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