

Enhanced electrochemical performance of submicron LiCoO_2 synthesized by polymer pyrolysis method

Lifen Xiao · Yanyan Yang · Yanqiang Zhao ·
Xinping Ai · Hanxi Yang · Yuliang Cao

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Abstract Submicron LiCoO_2 was synthesized by a polymer pyrolysis method using LiOH and $\text{Co}(\text{NO}_3)_2$ as the precursor compounds. Experimental results demonstrated that the powders calcined at 800°C for 12 h appear as well-crystallized, uniform submicron particles with diameter of about 200 nm. As a result, the as-prepared LiCoO_2 electrode displayed excellent electrochemical properties, with an initial discharge capacity of 145.5 mAh/g and capacity retention of 86.1% after 50 cycles when cycled at 50 mA/g between 3.5 and 4.25 V. When cycled between 3.5 and 4.5 V, the discharge capacity increased to 177.9 mAh/g with capacity retention of 85.6% after 50 cycles.

Keywords Submicron LiCoO_2 · Polymer pyrolysis · Lithium ion battery · Cathode material

Introduction

Currently, the hexagonal $\alpha\text{-NaFeO}_2$ type LiCoO_2 is the widely used cathode material in lithium ion batteries because of its synthetic simplicity and excellent electrochemical performance. Although LiCoO_2 has been widely used, there is still much work done to improve the performance of this material [1–14]. It is known that the crystal structure and morphology such as particle size and

size distribution play important roles in achieving high performance, and all these parameters depend strongly on the synthesis method. LiCoO_2 was originally prepared by solid-state reaction [15, 16] at elevated temperature for prolonged duration. This synthesis route inevitably suffers from uncontrollable stoichiometry due to the evaporation of lithium species and produces large particles with a broad size distribution, which significantly depress the electrochemical performance of the product. For these reasons, various wet-chemical methods including sol–gel [5–7], spray drying [8], and coprecipitation [9] have been used to synthesize uniform submicron or nano-sized LiCoO_2 powders.

Furthermore, extensive studies have been devoted to improve the specific capacity of LiCoO_2 in view of its high theoretical capacity of 274 mAh/g. The typical reversible delithiation for LiCoO_2 in commercial lithium batteries is 130–140 mAh/g with a charging voltage cutoff limit of 4.2 V, which is only corresponding to 50% utilization of its theoretic capacity. Consequently, to achieve higher reversible capacity, the upper cutoff voltage has to be raised to above 4.2 V to extract more Li^+ ions from $\text{Li}_{1-x}\text{CoO}_2$. Unfortunately, over-delithiation from LiCoO_2 will result in a phase transition and dissolution of Co^{4+} in the electrolyte, which causes a structural degradation of the host material during repeated cycling, and thereby leads to rapid capacity fades [17–20]. To overcome this problem, bulk doping [11, 12] and surface coating [13, 14] of the materials are widely studied to stabilize the layered structure of LiCoO_2 so as to give excellent capacity retention at extended voltage but often at the expense of the initial capacity values.

In our laboratory, we have synthesized submicron crystalline LiCoO_2 by adopting a novel polymer pyrolysis method [21, 22]. In this method, the precursor compounds of LiOH and Co salts can be mixed very homogeneously,

L. Xiao (✉) · Y. Yang · Y. Zhao
Department of Chemistry, HuaZhong Normal University,
Wuhan 430079, China
e-mail: lfxiao@mail.ccnu.edu.cn

X. Ai · H. Yang · Y. Cao (✉)
Department of Chemistry, Wuhan University,
Wuhan 430072, China
e-mail: ylcao@whu.edu.cn

which is advantageous to gain the pure crystalline materials with uniformly distributed size at short calcination duration. Hence, the as-prepared LiCoO_2 has displayed very good electrochemical performance even at the charge cutoff voltage of 4.5 V. It also shows that the simple synthesis procedure is time and energy saving and thus is promising for industrial production. Herein, we report the synthesis, structure and morphology, and electrochemical performance of the LiCoO_2 in depth.

Experimental

The submicron LiCoO_2 was synthesized by a polymer pyrolysis method. The synthesis process concluded a copolymerization of acrylate process, a prepyrolysis process, and a final calcination process. In the polymerization process, a stoichiometric amount of LiOH and $\text{Co}(\text{NO}_3)_2$ was dissolved in acrylic acid under stirring to form a homogeneous cation distribution. Then a small amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as initiator and 80°C heating for 2 h were applied to the solution to promote the formation of well-distributed polyacrylates of Li and Co. Afterwards, the polymer was dried at 120°C for 24 h. The as-prepared polyacrylates precursor was decomposed at 450°C for 5 h in air to get Li–Co oxides, followed by calcining at 800°C for 12 h to obtain the final product.

Thermogravimetry (TG)/thermogravimetric analysis (TGA) were carried out on a thermal gravimetric analyzer (TGA Q500, TA Instruments, USA) with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of room temperature to $1,000^\circ\text{C}$ to establish the prepyrolysis and calcination temperature. The crystal structure and morphology of the LiCoO_2 powders were characterized using X-ray diffraction (XRD; Shimadzu XRD-6000 diffractometer with $\text{Cu K}\alpha$ radiation) and a transmission electron microscope (TEM; JEM-2010FEF system).

The charge–discharge properties were measured using the test cells of a three-electrode design. The LiCoO_2 cathodes were prepared by roll-pressing the mixed paste of 85% LiCoO_2 powder, 7% acetylene black, and 8% polytetrafluoroethylene (PTFE; wt%) into approximately 0.1 mm thick film and then pressing the electrode film onto aluminum net. The counter electrodes and reference electrodes were lithium sheets. The separator was Celgard 2400 microporous membrane. The electrolyte was $1\text{ mol}\cdot\text{L}^{-1}$ LiPF_6 dissolved in a 1:1:1 mixture (by weight) of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene methyl carbonate (EMC) purchased from Shinestar battery materials (China). The cells were assembled in an argon-filled glove box. The charge–discharge measurements were carried out using a BTS-55 Neware Battery Testing System (Shenzhen, China).

Results and discussion

The thermal decomposition behavior of the copolymeric precursor of Li–Co polyacrylates was examined by TG/TGA, and the results are shown in Fig. 1. The weight loss of the copolymeric precursor occurred in three discrete steps and terminated near 420°C . The associated peaks in the TGA curves may be attributed to combustion of LiPA (Li polyacrylate) and CoPA (Co polyacrylate) into metallic carbonate and further decomposition to metallic oxides [21]. The total weight loss is 63.91%, which is in good agreement with the theoretical values of 64.8% expected from the proposed reaction schemes of $\text{P}(\text{Li,Co})(\text{AA})_3 \rightarrow \text{LiCoO}_2$, indicating the polyacrylates was formed in stoichiometry. According to the TG/TGA curve, the prepyrolysis process was settled at 450°C for 6 h to obtain the metallic oxides. As known that the heat treatment temperature should be above 800°C to obtain HT- LiCoO_2 with $\alpha\text{-NaFeO}_2$ structure, the secondary calcination is conducted at 800°C for 12 h.

The XRD patterns of LiCoO_2 calcined at 800°C for 12 h are shown in Fig. 2. As can be seen, all the diffraction peaks confirm to a single-phase hexagonal structure of $\alpha\text{-NaFeO}_2$ type with space group R3-m. The I_{003}/I_{104} intensity ratio is 1.36 indicating the good cation ordering. The (006,102) and (018, 110) peak doublets are well separated, indicative of well-ordered layered structure. The lattice parameters of a and c are calculated to be 2.8170 and 14.0547 \AA , respectively, and the c/a ratio of 4.9892 is close to the value of HT- LiCoO_2 reported in literature [1].

TEM image of LiCoO_2 powders calcined at 800°C for 12 h is shown in Fig. 3. The LiCoO_2 powders are composed of well-dispersed particles with very narrow size distribution of about 200 nm. It is inferred that such submicron-sized particles with a homogeneous size distribution prepared by the polymer pyrolysis method would

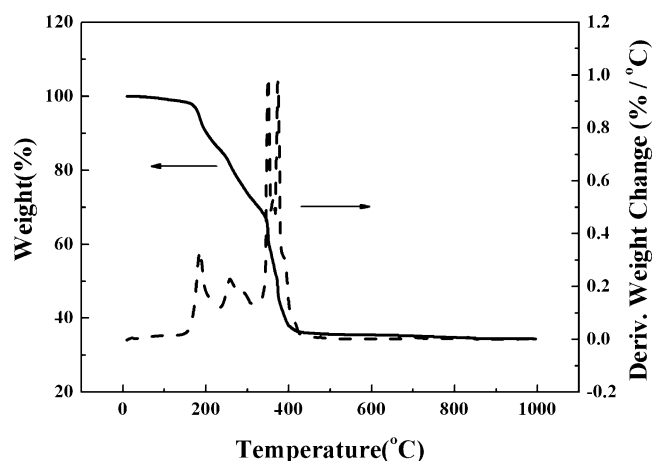


Fig. 1 TG/TGA curves of the copolymeric precursor of Li–Co polyacrylates

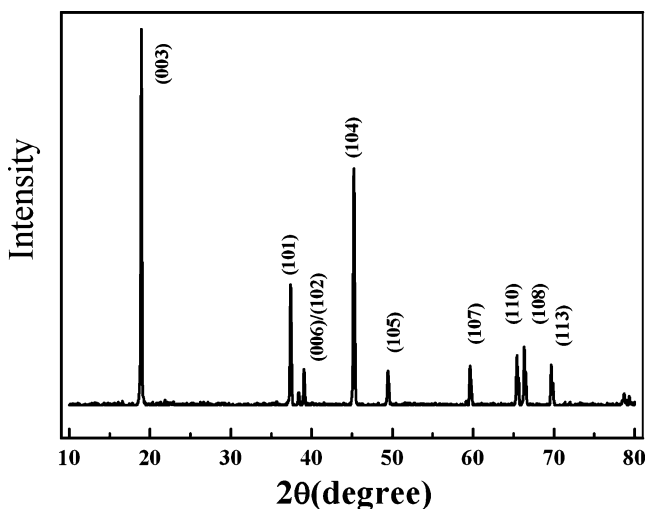


Fig. 2 XRD patterns for LiCoO₂ calcined at 800 °C for 12 h

significantly facilitate the lithium ion exchange during charge and discharge so as to improve the electrochemical performance of the product.

Figure 4 compares the initial voltage profiles of the as-prepared LiCoO₂ with commercial LiCoO₂ with average grain diameter of 8–12 μm at a specific current of 50 mA/g. Although both materials have showed smooth charge–discharge curves even on the higher cutoff voltage range, there are distinct differences in the operation voltage and capacity on charge and discharge. As can be seen, the charge voltage plateau of the LiCoO₂ as prepared is lower, while the discharge voltage plateau is higher than the commercial ones, indicating the lower polarization of the LiCoO₂. The LiCoO₂ has delivered first discharge capacity of 145.5 and 177.9 mAh/g at the upper charge cutoff voltage of 4.25 and 4.5 V, respectively, larger than the commercial materials of 135.2 and 168.8 mAh/g. These results can be well accounted for that the submicron materials have a much larger surface area than the

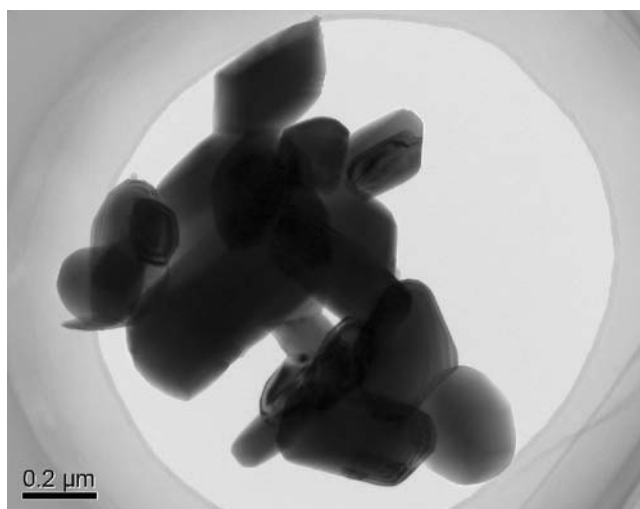


Fig. 3 TEM image for LiCoO₂ calcined at 800 °C for 12 h

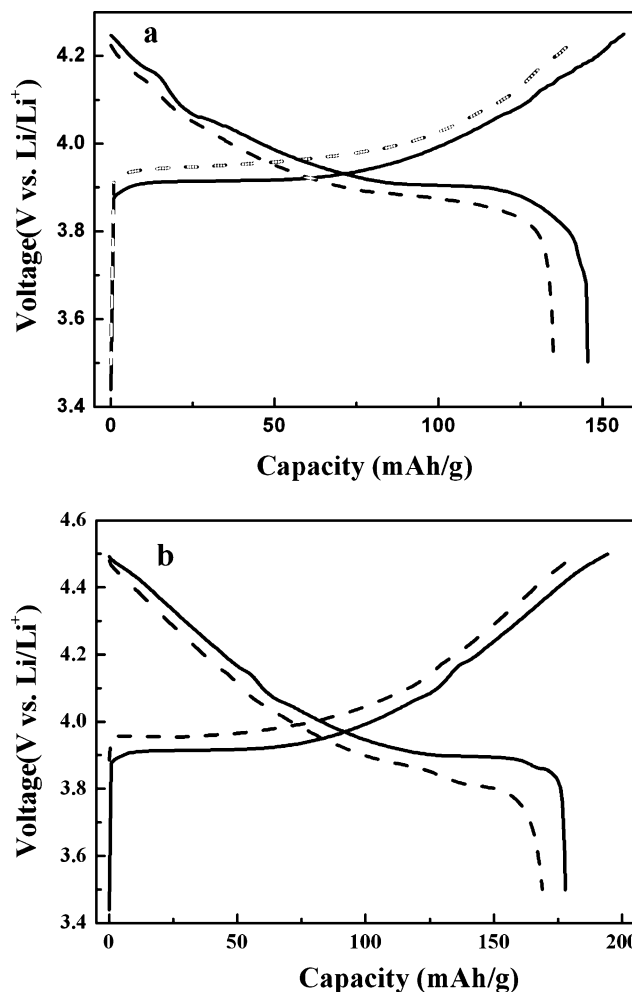


Fig. 4 Comparison of the initial voltage profiles of the as-prepared LiCoO₂ (solid line) with the commercial LiCoO₂ (dashed line), charged and discharged at 50 mA/g between **a** 3.5 and 4.25 V and **b** 3.5 and 4.5 V

micrometer powders, resulting in a shortening of the diffusion path of lithium ion in the solid phase of the materials and therefore helping to improve the spatial utilization of materials and alleviating the diffusive resistance of Li⁺ intercalation reaction. Besides, the initial coulombic efficiency is 92.3 and 91.5% for the submicron powder at the cut off voltage of 4.25 and 4.5 V, appreciably lower than that of the micron LiCoO₂ (94.1 and 92.9%).

A comparison of the cyclability of the commercial LiCoO₂ and the as-prepared samples in the voltage range of 3.5–4.25, 4.5 V vs Li/Li⁺ at 50 mA/g are given in Fig. 5. Upon cycling at upper cutoff voltage of 4.25 V, the two materials maintain their initial capacity at 86.1 and 77.1%, respectively, indicating the relatively higher structural stability of the as-prepared LiCoO₂ than the commercial one. However, increasing the charge cutoff voltage to 4.5 V leads to a drastic difference between these two electrodes, as shown in Fig. 5. The capacity fading rate of these two materials is not distinct for the initial ~6 cycles, indicating

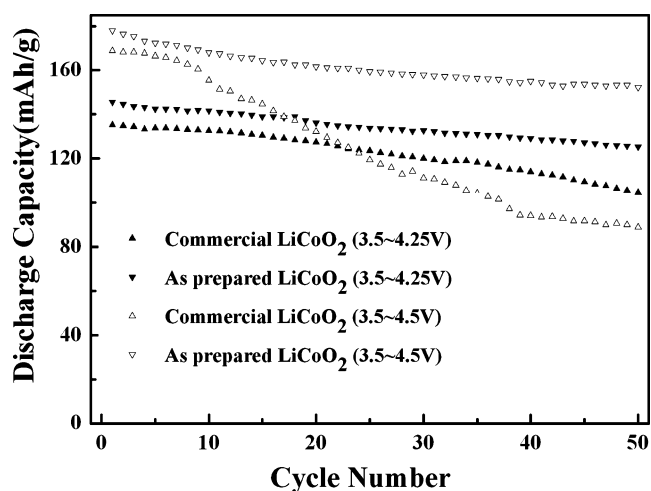


Fig. 5 The cyclability of the as-prepared LiCoO_2 with the commercial LiCoO_2 charged and discharged at 50 mA/g in the voltage range of 3.5–4.25 V and 3.5–4.5 V, respectively

the relative stable structure at the initial cycles. However, its capacity rapidly decreases to $\sim 52.6\%$ after 50 cycles for the commercial LiCoO_2 . The suggested reasons for the capacity fade of LiCoO_2 are the anisotropic expansion of the host lattice [17, 18] and/or the Co dissolution [19, 20] of the electrode material when charged above 4.2 V. The discharge capacity of the as-prepared LiCoO_2 decreases very slowly with cycling and still maintains 85.6% capacity retention, obviously suggesting the superior cyclability and structural stability in higher cutoff voltage.

To understand the structural change after extended cycling at higher charge cutoff voltage, Fig. 6 a and b compared the XRD patterns for the two kinds of LiCoO_2 electrode materials before and after the 50 cycles at 50 mAh/g between 3.5 and 4.5 V. For the fresh electrode materials, both of them show the sharp, well-defined peaks. After cycling, the peaks for the commercial powder diminish and broaden, with the lattice parameters changed from $a=2.8146 \text{ \AA}$, $c=14.0438 \text{ \AA}$ before cycle to $a=2.8112 \text{ \AA}$, $c=14.2369 \text{ \AA}$ after 50 cycles. The distinct increase in the c -axis means the structural damages occurred in this material, whereas the peaks for the as-prepared LiCoO_2 are well maintained, confirming the initial hexagonal ordered structure stabilized during cycling. The lattice parameters after 50 cycles were calculated to be $a=2.8182 \text{ \AA}$, $c=14.07420 \text{ \AA}$, which are close to the values from before cycling $a=2.8170 \text{ \AA}$, $c=14.0547 \text{ \AA}$. A little change in the lattice parameters of the as-prepared LiCoO_2 should be attributed to its short diameter, which would likely decrease the cumulative structure stress inside the particles during repeated cycling at high voltage, so as to prevent structure collapse and the Co from escaping from the structure host and therefore suppress the capacity fade of the materials during cycling.

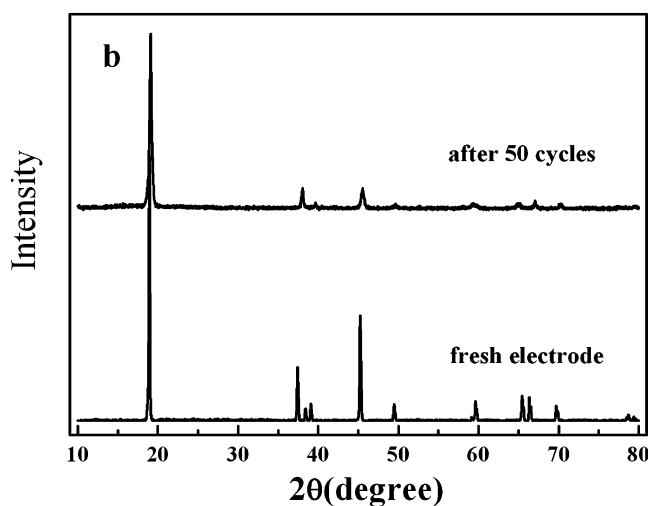
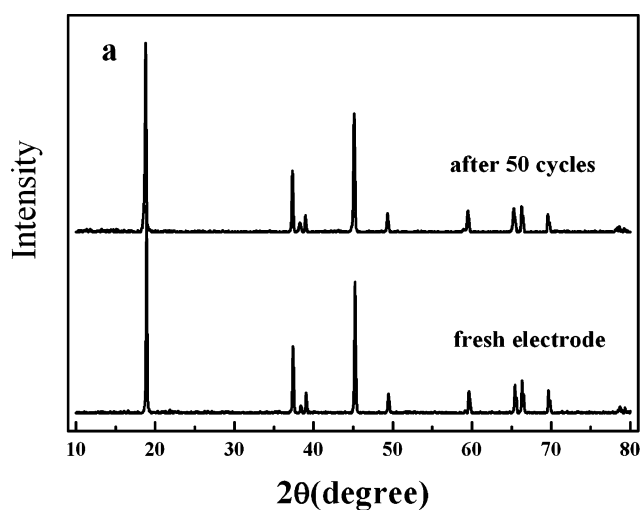


Fig. 6 XRD patterns for the fresh and 50-cycled electrodes at 50 mA/g between 3.5 and 4.5 V for a as-prepared LiCoO_2 and b commercial LiCoO_2

Conclusion

LiCoO_2 consisting of well crystallized, submicron particles with diameter of 200 nm was synthesized by a polymer pyrolysis method and tested as cathode materials for lithium ion batteries. It displayed much enhanced cyclability especially at a high upper-charge cutoff voltage of 4.5 V compared to the commercial LiCoO_2 . XRD investigation confirmed that the as-prepared material has maintained its structure when cycled at 4.5 V, whereas the commercial material has been deteriorated. This should be attributed to its short diameter, which decreases the structure stress during lithium ion intercalation and deintercalation, so as to prevent structure collapse and the Co from escaping from the structure host and therefore suppress the capacity fade of the materials during cycling.

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