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Synthesis and electrochemical performance of ropelike LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ fiber with nano-building blocks

Linsen Zhang$^*$, Zhenjiang Zhao, Xiaofeng Li, Hua Fang, Lixia Wang, Yanhua Song and Xiaodong Jia

School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002, People’s Republic of China

E-mail: hnzhanglinsen@163.com

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Abstract

A ropelike LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) fiber with superior rate capability and cycling stability was successfully synthesized via electrospinning and sintering as a cathode material for Li-ion batteries. The NCA fiber that exhibited excellent electrochemical performance as a cathode for Li-ion batteries was stacked and assembled from numerous nanoparticles. The NCA fiber delivered a high reversible capacity of 206.4 mAh g$^{-1}$ at 0.1 C, and maintained 75% capacity retention after 100 cycles at 1 C. The high rate capability and outstanding cyclic stability were due to the ropelike fiber structure that shorten the Li$^{+}$ diffusion path, improved the Li$^{+}$ diffusion coefficient, and maintained the fiber structure during cycling.

1. Introduction

Nowadays, Li-ion batteries (LIBs) have a wide application throughout all aspects of life [1, 2]. Exploiting of high-efficiency and stable electrode materials is vital to LIBs, and considerable effort has been made to enhance LIB performance, especially in electrode materials [3]. Ni-rich cathodes had been the subject of intensive study due to their high-energy density, capacity, and non-toxicity [4]. Among the Ni-rich cathodes family, ropelike LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$(NCA) had been considered a promising candidate for as a conventional cathode material due to its excellent electrochemical performance and superior thermal stability [5]. Fortunately, in recent years, the electrospinning technique was widely used in many fields as an effective and inexpensive way of truly producing 1D fibers structure from micrometer to nanometer size ranges in diameter, including the fabrication of electrode materials, especially anode and cathode materials for Li-ion batteries [6, 7].

Various unique NCA structures, such as concentration gradient [8], hierarchical hollow microsphere [9], flower-like structures [10], and microrod structures (i.e., nanofibers, nanowires, nanorods, and nanotubes), had received considerable attention due to their unique physical and electrochemical properties [11, 12]. Hence, a unique ropelike NCA fiber was successfully synthesized in this study via electrospinning and heat-treatment. The ropelike fiber could shorten the Li$^{+}$ diffusion path, improve the Li$^{+}$ diffusion coefficient, and maintain the fiber structure during cycling. Moreover, it could improve the rate capability and cyclic stability of the NAC fiber.

2. Experimental

2.1. NCA preparation

The NCA fibers were synthesized via electrospinning and heat-treatment. Stoichiometric amounts of Ni(CH$_3$COO)$_2$·4H$_2$O, Co(CH$_3$COO)$_2$·4H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, and LiCH$_3$COO·4H$_2$O were dissolved in 20 g of absolute ethanol and stirred for 12 h. Afterward, 2 g of PVP was added to the solution, stirred for 12 h to form an electrospinning solution, and transferred to a plastic syringe by using a 18 G stainless steel needle. A high-voltage generator was used for electrospinning. The fiber precursors were collected on aluminum foil and sintered at 500 °C for 5 h and 800 °C for 10 h in air with 3 °C min$^{-1}$ to obtain the final product.
temperature. The XRD patterns and lattice parameters of the NCA sample thermogravimetric analysis(TGA) was performed with a Netzsch STA449-F3 TG analyzer in air atmosphere.

2.3. Electrochemical characterization
CR2016 coin cells were assembled in a glove box by using NCA fibers as working-electrodes, Li foil as counter-electrodes, 1.0 M LiPF₆ as electrolyte, and Celgard 2400 as a separator. The charge/discharge tests were performed from 2.8 V to 4.3 V (1 C = 200 mA g⁻¹) by a NEWARE system. An electrochemical workstation (Chenhua660E, China) was employed for cyclic voltammetry (CV, 2.5–4.3 V, 0.1 mV s⁻¹) and electrochemical impedance spectroscopy (EIS, 0.01–10⁵ HZ) measurements.

3. Results and discussion

3.1. Physical characterization
TG-DTA of the fiber precursor was performed in air atmosphere figure 1(a). The results indicated that approximately 5.67 wt% weight below 250 °C, which was owing to volatilization of absorbed moisture and ethanol from the metal salt precursor. Metal salt decomposed between 280 °C and 400 °C as shown by the TG-DTA curves. The decomposition reaction was associated with approximately 42.29 wt% weight loss. The mass decomposition loss of 17.64 wt% was associated with polymers, as indicated by the endothermic peak at 530 °C. Given that quality loss was not evident at temperatures higher than 600 °C, the final product was obtained at this temperature. The XRD patterns and lattice parameters of the NCA fiber are shown in figure 1(b). All diffraction peaks could be indexed to a fine α- NaFeO₂ hexagonal layered structure with R-3m space group. No obvious impurity peak was observed, indicating that the sample was highly crystallized [13]. The ratio of c/a and I(003)/I(104) is an important parameter to the layer structure and cation mixing degree of Li⁺/Ni²⁺, respectively [14]. The values of Li⁺/Ni²⁺ and I(003)/I(104) were 4.9540 and 2.15 (figure 1(b) inset), respectively, indicating that Li⁺/Ni²⁺ possessed an excellent layered structure and lower mixing degree. The strong peak splitting of (006)/(012) and (018)/(110) demonstrated that the NCA fiber presented a highly ordered layered hexagonal structure.

The fiber precursors (figure 2(a)) possessed a smooth surface, and their diameter distribution was in the 3–5 μm range. The calcinated fiber precursors were converted to NCA fibers (figure 2(b)). The ropelike NCA fibers were stacked and assembled from the nano-building blocks (figure 2(c)). Such a unique fiber structure may be favorable for Li storage because it can shorten the Li⁺ diffusion path and increase the contact area to facilitate electrolyte penetration into the active particles. The fiber structure also reduces active particle agglomeration during cycling. The structure was further confirmed in the TEM images in figures 2(d) and (e). The NCA fibers were composed of particle matrix. The HRTEM image in figure 3(f) revealed that the 0.472 nm lattice spacing corresponded to the (003) plane of the well-crystallized hexagonal layered structures and this result was consistent with the finding of XRD analysis. Furthermore, the SAED pattern in the inset of figure 2(f) indicated that the fiber matrix demonstrated perfect crystallization.

Figure 1. (a) TG-DTA curves of the fiber precursor, (b) XRD pattern of the NCA fiber.
3.2. Electrochemical performance

Figure 3(a) shows the first charge/discharge curves of the NCA fibers. The discharge capacity reached 206.4, 180.4, and 160.2 mAh g\(^{-1}\) at 0.1, 0.5, and 1 C, respectively. The fiber specific capacities at different rate were close to that of the NCA powder [15]. The coulombic efficiency of the first cycle was relatively low, suggesting a large irreversible capacity loss. The large irreversible capacity is ascribed to the slow lithium-ion diffusion rate in the layered structure, and the 'lost capacity' could be completely recovered by discharge to low voltage at relatively slow current density [16, 17]. Figure 3(b) shows the cycling performance and coulombic efficiency of the NCA fibers at 0.5 and 1 C. After 100 cycles, the electrode delivered the reversible capacity of 147 and 120 mAh g\(^{-1}\) at 0.5 and 1 C, respectively. The discharge capacities at 0.5 and 1 C tend to decrease slowly with the increase of the cycle number. The capacities retentions at 0.5 and 1 C after 100 cycles are 81.5% and 74.9%. The coulombic efficiency after the first cycle was 100%, indicating that the NCA fibers possessed excellent reversible performance. The NCA fiber rate properties (figure 3(c)) suggested that the NCA fibers delivered a stable reversible capacity at different current densities. They regained a high discharge capacity a current density of 0.1 C. In addition, the coulombic efficiency at a different rate was maintained at 100% except during the first cycle. The CV curves of the NCA fibers in figure 3(d) show a pair of obvious redox peaks that corresponded to the redox couple of Ni\(^{2+}/\)Ni\(^{4+}\) [18]. It is clearly shown that the major anodic peak shifted from 3.930 V at the first cycle to 3.871 V and 3.841 V at the second and third cycle, respectively. However, there was no obvious difference in the cathodic peaks (3.655 V). In the last two cycles, the redox peaks were coincident, indicating that
reversibility of the NCA fiber was excellent. As such, the fiber NCA demonstrated superior electrochemical performance, which could be attributed to its unique fiber structure.

The EIS plot (figure 3(e)) and equivalent circuit model (figure 3(e) inset) of the NCA fiber were obtained after three cycles. The EIS plot shows a high-frequency intercept, two intermediate-frequency semicircles, and a low-frequency slope. The intercept at the high-frequency region was assigned to the ohmic impedance ($R_s$), the semicircles in the intermediate-frequency region were the SEI film impedance ($R_f$) and charge-transfer resistance ($R_{ct}$), and the straight line at the low-frequency region corresponded to the Warburg impedance ($W$) [19]. $W$ is related to Li$^+$ diffusion in the electrode through which the Li$^+$ diffusion coefficient ($D$) [20] could be further derived. $R_s$, $R_f$, $R_{ct}$, and $D$ are shown in the inset of figure 3(e). $D$ of the NCA fiber was $8.28 \times 10^{-10}$ cm$^2$ s$^{-1}$ and higher than that of traditional NCA particles [21, 22], indicating the excellent rate capability of the ropelike structure.

The fiber stability in cycling was further explored as shown in the SEM images of the NCA fiber electrodes after 100 cycles (figure 4). The dispersed NCA fibers were evident in the electrodes. The morphology and microstructure of the NCA fiber only changed slightly but were maintained well after cycling. Ni, Co, and Al were detected (figure 4(d)), and they exhibited a homogeneous distribution. P and F from organic electrolytes were also detected, and they showed an even distribution. The NCA structure was maintained during cycling.

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**Figure 3.** First charge/discharge profiles of the NCA fibers at 0.1 C (a), cycling performance of the NCA fibers at 0.5 C and 1 C (b), rate performance of the NCA fibers (c), CV curves of the NCA fibers (d), EIS profiles of the NCA fibers after three cycles(e), and corresponding equivalent circuit model and parameters (inset).
4. Conclusions

A ropelike NCA fiber was successfully fabricated and used as cathode material in LIBs. The NCA fiber structure exhibited excellent electrochemical performance, especially in terms of rate performance and cycling stability. The outstanding electrochemical properties could be attributed to the ropelike fiber structure that shortened Li$^+$ diffusion pathways, improved the Li$^+$ diffusion coefficient, and maintained the fiber structure.

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ORCID iDs

Linsen Zhang © https://orcid.org/0000-0002-3488-4911
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