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Novel Functional Material Carboxymethyl Cellulose Lithium (CMC-Li) Enhanced Performance of Lithium-Ion Batteries

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Novel Functional CMC-Li was synthesized by cotton as raw material. The new method modified electrode materials with CMC-Li by electrospinning, and CMC-Li as the novel binder was used in battery, which was beyond the theoretical specific capacity of LFP. The batteries have good electrochemical property, outstanding pollution-free, excellent stability.

Lithium batteries, as a main power source or back-up power source for mobile communication devices, portable electronic devices and the like, have received increasing attention in the scientific and industrial fields due to their high electromotive force and high-energy density.[1] To meet the demand for the higher-energy density and improved cycle characteristics of batteries, a great deal of attempt has been made to design new structures of electrode materials and develop a new battery binder in recent years.[2] Aqueous binders have more merits, such as eco-friendliness, lower cost and better safety, with water as a dispersant, thus, it became the ideal binder for safety and environmental lithium ion battery.[3] In this study, for the first time, we used cotton as a raw material and synthesized a new linear ionic cellulose ether carboxymethyl cellulose lithium (CMC-Li) by a unique two-step method. Next, for the first time, we utilized electrospinning technology to obtain composite nanofibers, and then $LiFePO_4$ (LFP) was coated and further carbonized to obtain CNF/LFP/Li (CLL) composite nanofibers, which reached the goal of modifying for LFP by nanocrystallizing, carbon-covering and ion doping. Besides, for the first time, CMC-Li as a new binder was applied in the batteries. Then, we found that the first charge and discharge specific capacity was beyond the theoretical specific capacity of LFP, the charge and discharge platform was high and the battery polarization degree is small, thus, improving battery performance. After 200 cycles, the loss of charge and discharge specific capacity was little, which was still beyond the theoretical specific capacity of LFP and achieved better results. Moreover, for the first time, we specifically compared the CMC-Li with different DS and found the relevant research rules. Furthermore, the above research method can be applied in the study on other batteries, cellulose and nano materials, which provide a good idea and assistance for relevant scholars in this field.

CMC-Li with a unique molecular structure is a polyhydroxy water soluble derivative polymer.[4,5] Since it is difficult to find a solvent suitable for water-soluble polysaccharide ionic polymer to be electrospun at present,[6] thus the study on electrospinning for water soluble ionic cellulose ether is always a problem in the related field,

Fig.1 Schematic illustration of assembling battery. (a) The magnified details of as-spun fibers which consist of CMC-Li as the polymer agent and dispersed LFP nano-particles. (b) Mechanism of formation of CMC-Li/LFP and CLL electrospun nanofibers has been proposed.

especially it is a blank in the study on electrospinning for CMC-Li. Based on a large number of experiments, we proposed an electrospinning method suitable for water soluble ionic cellulose ether CMC-Li.[7] Then we obtained water soluble CMC-Li nanofiber by electrospinning, and further studied on the functional fiber material, which broke through the difficulty in related research. Meanwhile, the fiber materials also can be applied in film materials,[8] mesoporous materials[9] and drug embedding.[10] In our work, CMC-Li was applied to modify lithium battery electrode materials by electrospinning.[11] This unique method not only meets the demand for carbonizing and modifying electrode material by electrospinning, but also uniquely increased contents of freely moving lithium ion in electrode material and the efficiency of prolapsing and embedding of lithium ion between anode and cathode electrode. C, Li^+ and

electrode material formed fully stable network structure model, thus improving the charge and discharge capacity of the whole lithium-ion battery (See Fig. S1).[12]

Binder is indispensable to bonding electrode materials in a lithium-ion battery, and it plays an important role in improving the performance of lithium-ion battery.[13] However, batteries with polyvinylidene fluoride (PVDF) as a binder easily react exothermically with anode lithium metal and forms LiF.[14] Besides, used in batteries, it requires the organic solvent *N*-methyl pyrrolidone (NMP), which is expensive, non-eco-friendly and inflammable, as a dispersant for PVDF.[15] Currently, as a water-based binder, the ionic cellulose ether CMC-Na in lithium-ion battery has been reported with good performance,[16] as it can prevent an exothermic reaction between battery with PVDF as a binder and anode lithium metal, and a series of insecurity with NMP as dispersants. Additionally, carboxymethyl cellulose salt is cheaper, and its performance is better than that of PVDF.[5] Results from the electronic conductivity tests of the binder films showed that carboxymethyl cellulose salt films had better electronic conductivity and performance than PVDF films.[7]

CMC-Li is a water-soluble cellulose derivative, and when such a solution reaches a certain concentration, the adhesiveness is strong enough to work as a binder in lithium-ion battery.[18] The study showed that sharing some advantages of other water-based binders, CMC-Li is also an effective ion-conductive polymer.[5] Specifically, the Li^+ carried by CMC-Li can shorten the diffusion pathway to the cathode particle surface, and increase the contents of freely moving lithium ions in lithium-ion batteries.[7] It can also improve the efficiency of prolapsing and embedding of lithium ions between the anode and cathode electrode, thus improving the charge and discharge capacity of the whole lithium-ion battery. Meanwhile, sharing the advantages of CMC-Li, this method, by substituting lithium for sodium, can prevent the decline of charge and discharge efficiency, as well as the cycle capacity performance of the battery, with CMC-Na for a binder.[19] Moreover, CMC-Li can prevent an exchange reaction between the Na-ion deposited on the carbon anode surface and the Li-ion, and further promotes the decomposition of the electrolyte solution. Since the conductive efficiency of CMC-Na was low, it was difficult for the lithium battery to exhibit its merits, such as small volume, light quality and extraordinary energy. Therefore, a current development allows applying the CMC-Li binder directly to the lithium battery, with a very broad range of potential applications.

We used cotton as raw material and then successfully synthesized CMC-Li products with different DS and molecular weight (Fig. 1 and S2, S3). Next, CMC-Li/LFP composite fiber coated with LFP and CMC-Li nanofibers were successfully obtained by electrospinning, and LFP was uniformly distributed in fibers. Then, CMC-Li/LFP nano-composite fiber was carbonized under nitrogen at a high temperature, after that, it not only obtained the modified LFP electrode material with uniform carbon coating, namely CNF/LFP, but also increased the contents of Li-ions in electrode material and formed CLL composite nanofibers as cathode material. Finally, we used CLL and unmodified LFP as cathode material of battery, respectively, PVDF as a binder to assemble button battery for the performance testing and comparing. Meanwhile, we used CLL as cathode material for the battery, and CMC-Li with different DS as binder, water as dispersant to prepare the pole piece of the battery, further assembled 2025 button batteries for testing and comparison.

The particle of unmodified LFP electrode material was smaller, and some particle was gathering (Fig. 2a). CMC-Li nanofiber was successfully obtained by electrospinning (Fig. 2b). It can be seen that the surface of the fiber was relatively smooth, the diameter was small. The dispersion was relatively uniform, and there was no formation of the larger links or particularly of messy breakpoints.

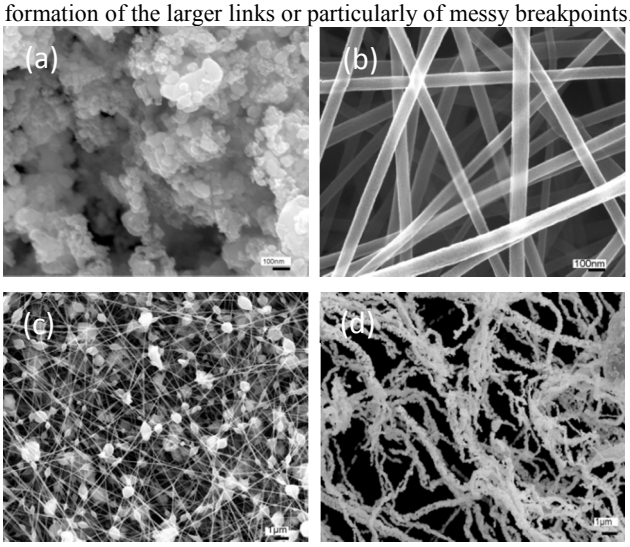

Fig.2 Scanning electron microscope (SEM) analysis of preparing CLL electrode. SEM images of (a) LFP particles, (b) CMC-Li nanofiber by electrospinning, (c) LFP/CMC-Li composite nanofibers by electrospinning, (d) CLL composite nanofiber as electrode after carbonization at a high temperature.

All of these proved that the spinning process was more stable. Thus laying a good foundation for studying on functional water soluble ionic polymer materials by electrospinning. The particle of LFP was uniformly dispersed in fibers (Fig. 2c), and formed the LFP/CMC-Li composite nanofibers with excellent morphology and structure. Under the protection of nitrogen, the composite fiber was carbonized at a high temperature (600 ^oC) to obtain CLL composite fiber (Fig. 2d). The CLL maintained the skeleton structure of nanofiber, and the particle of LFP was more uniformly distributed and coated with carbon nanofibers. The combination was better among carbon, LFP, Li-ion, and a study is being conducted with CLL as cathode material in lithium battery (Fig. S1).

In our experiment, CMC-Li with different DS was electrospun to obtain different CLL as cathode material for lithium-ion battery, and combined with PVDF to assemble button batteries, which is compared with performance of button battery assembled by unmodified LFP as cathode material. It is found that the first charge and discharge specific capacity of batteries using CLL as cathode material was higher than that using unmodified LFP as cathode materials (Fig. 3a and S4a). Among them, the highest one is the battery with CLL-3 as an electrode material, and the value reached 168 mAh g^{-1} and 161 mAh g^{-1}, respectively, which was improved by 15.1 % and 11.8 % than which with unmodified LFP as electrode material. Moreover, the first charge and discharge loss was only 4.1 %. Meantime, the charge and discharge platform are high, which showed that it enhanced the conductivity of cathode materials, shortened the diffusion path of Li-ion, reduced the degree of polarization between the electrodes and increased electrochemical performance (Fig. S5a). After 200 cycles, specific capacity loss of battery with CLL as electrode material was less than that with unmodified LFP as electrode material when the cycle efficiency was nearly close to 100 %. Among them, the least one is the battery with CLL-3 as electrode material, which is almost close to the zero and have the best performance (Fig. 3b). All of these proved that the unique method using CMC-Li to modify electrode material is of significance to improve the capacity of the battery. Furthermore, the battery using CMC-Li with high DS has superior capacity and better

electronic conductivity and electrochemical properties than that with low DS (Fig. 3a and S5a).

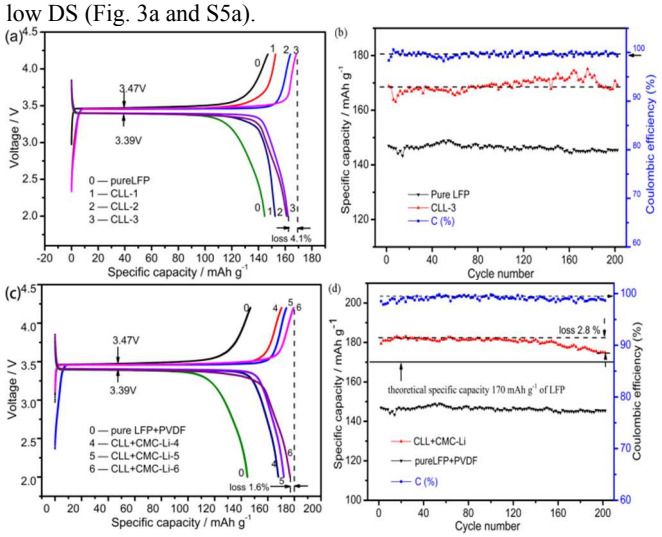

Fig. 3 The cycle comparison chart of the modified composite electrodes. (a) The first charge and discharge curves of different cathode material. (b) The efficiency of battery with CLL-3 and LFP as cathode material after 200 cycles. (c) The first charge and discharge curves of battery with CLL as cathode material and with different CMC-Li as a binder. (d) The capacity of battery with CLL as cathode material and with CMC-Li as a binder after 200 cycles.

In the further experiment, the battery pole pieces using CLL-3 as cathode material, Meantime, the battery with CMC-Li-6 as a binder possesses the highest charge and discharge capacity and best cycle performance, and the platform is higher, thus leading to the better discharge rate, electronic conductivity and electrochemical properties (Fig. 3c and S6, S7, S4b). Moreover, its first charge and discharge specific capacity is up to 180 mAh g^{-1} and 176 mAh g^{-1}, which is increased by 23.3 % and 22.2 % relative to the battery with unmodified LFP as cathode material and PVDF as a binder, and the first charge and discharge specific capacity loss was merely 1.6 %. After 200 cycles, when the cycle efficiency was nearly close to 100 %, the charge and discharge specific capacity loss of battery is only 2.8 % and 2.2 %, the value reached 175 mAh g^{-1} and 172 mAh g^{-1}, respectively, which was 97.8 % of the initial value, and still far higher than the theoretical specific capacity 170 mAh g^{-1} of LFP (Fig. 3d and S5b, S4b). Subsequently, the CV test of these batteries showed that the difference between the REDOX peak value was small, merely 0.22 V (Fig. S6b). Meanwhile, electrochemical performance was quite stable, and the cures were nearly coincided with each other, the reversibility was superior. Moreover, it also can increase the conductivity and ionic diffusion coefficient of electrode material (Fig. S7b). Furthermore, the test showed that the batteries using CMC-Li with higher DS as the binder has the taller charge and discharge capacity, the better cycle performance and fewer impedances (Fig. S3b). All of these showed that CMC-Li as a water-based binder is safe and environmental, pollution-free and easily degraded, and it can also well shorten the prolapse and embedding path of Li^+, reduced the polarization distance and increased the capacity of a lithium battery. Thus, CMC-Li can be preferable as a new binder to apply in the lithium battery.

In summary, the study used cotton, as a raw material, synthesized new functional materials water-soluble ionic cellulose ether CMC-Li by unique two-step chemical reactions. Considering the characteristics of CMC-Li, we proposed an electrospinning method for water soluble ionic cellulose ether nanometer CMC-Li and it can also provide a good idea for scholars who specialized in water soluble film materials, tissue engineer scaffold materials and biological medicine embedding materials. CMC-Li was applied to modify LFP as cathode material of battery, which caused the first charge and discharges specific capacity to be approximate to the theoretical specific capacity of LFP. Next, we applied the CMC-Li as the water-based binder in batteries, and found that the first charge specific capacity increased by 23.3 %, up to 180 mAh g^{-1}. After 200 cycles, specific capacity is still higher than the theoretical specific capacity of LFP. Besides, the combination resulted in taller charge and discharge platform, smaller degree of polarization, better reversibility, superior electrochemical performance, increased the diffusion coefficient of Li-ion and exhibited excellent battery performance. This synthesis of novel functional material and application new binder for high power lithium- ion batteries were unique. Furthermore, we concluded that the performance of CMC-Li with high DS was superior to that with low DS. Meantime, the CMC-Li is cheaper, more eco-friendly and easily degraded, safer, and it was also applied in the field of other related materials as a new advanced functional material.

Notes and references

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† Electronic supplementary information (ESI) available: Experimental details, IR, ^{1}H-NMR analysis of CMC-Li and XRD, EIS and different charge and discharge rate test of battery with CMC-Li as a binder.

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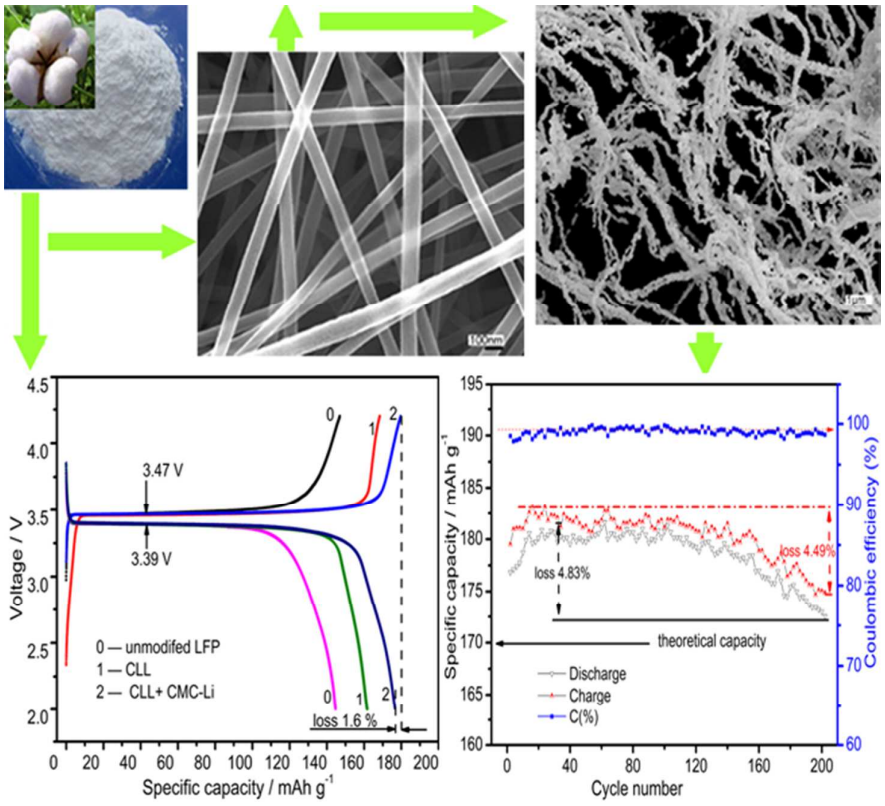

Cotton as raw material and synthesized new functional material CMC-Li. The new method modified electrode materials with CMC-Li by electrospinning, and CMC-Li as the novel binder was used in battery. The battery with this method retained 97.8 % of initial reversible capacity after 200 cycles at 176 mAh g^{-1},which was beyond the theoretical specific capacity of LFP. The batteries have good electrochemical property, outstanding pollution-free, excellent stability