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Short communication

Enhanced electrochemical properties of $LiFePO_4$ (LFP) cathode using the carboxymethyl cellulose lithium (CMC-Li) as novel binder in lithium-ion battery

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ABSTRACT

Novel water-based binder CMC-Li is synthesized using cotton as raw material. The mechanism of the CMC-Li as a binder is reported. Electrochemical properties of batteries cathodes based on commercially available lithium iron phosphate ($LiFePO_4$, LFP) and CMC-Li as a water-soluble binder are investigated. CMC-Li is a novel lithium-ion binder. Compare with conventional poly(vinylidene fluoride) (PVDF) binder, and the battery with CMC-Li as the binder retained 97.8% of initial reversible capacity after 200 cycles at 176 mAh g^{-1}, which is beyond the theoretical specific capacity of LFP. Constant current charge–discharge test results demonstrate that the LFP electrode using CMC-Li as the binder has the highest rate capability, follow closely by that using PVDF binder. The batteries have good electrochemical property, outstanding pollution-free and excellent stability.

Binder is indispensable to bond electrode materials in lithium-ion batteries, and it plays an important part in improving the performance of lithium-ion battery, especially in the cycle life (Li et al., 2013). To meet the demand for the higher-energy density and improve cycle performance of batteries, then a great deal of attempt has been made to develop a new battery binder in recent years (Masquelier & Croguennec, 2013). In commercial Li-ion batteries, polyvinylidene fluoride (PVDF) has been widely used as the binder for both the negative and positive electrodes in current collectors and commercial Li-ion batteries, because of its good electrochemical stability and high binder to electrode materials. Nonetheless, PVDF as a binder easily reacts exothermically with anode lithium metal and forms LiF. Besides, using in batteries, it requires the organic solvent *N*-methyl pyrrolidone (NMP), which is expensive, non-eco-friendly and inflammable, as a dispersant (Qiu, Shao, Liu, et al., 2014). Moreover, accidents that cause by low energy efficiency of lithium battery and NMP are often reported. In order to improve these problems and make lithium battery more efficient, some scholars proposed the method of substituting water-based binder for PVDF in batteries (Lestrie, Bahri, Sandu, Roue, & Guyomard, 2007). Aqueous binders have more merits, such as eco-friendliness, lower cost and better safety. Moreover, they can make an electrode simply, with water as a dispersant. For example, at present, as a water-based binder, the sodium carboxymethyl cellulose (CMC-Na) in lithium-ion battery has been reported with good performance (Li et al., 2011), as it can prevent an exothermic reaction between commercial 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.

Novel binder CMC-Li is based on cotton as raw material and synthesized by a unique two-step method (Qiu, Shao, Wang, Zhang, & Cao, 2013). CMC-Li with a unique molecular structure is a polyhydroxy water soluble cellulose derivative polymer (see in ESI Figs. S1 and S2). When such a solution reaches a certain concentration, the adhesiveness of CMC-Li is strong enough to act as a binder. The studied show that CMC-Li is also an effective ion-conductive polymer, and ionize to obtain lithium ions, which can increase the contents of freely moving lithium ions in lithium-ion batteries (see in Fig. S3), short the diffusion pathway to the cathode particle surface (Qiu, Shao, Yang, et al., 2014). It can also enhance the efficiency of extraction and insertion of lithium ions between the anode and cathode electrode, thus improving the charge and discharge

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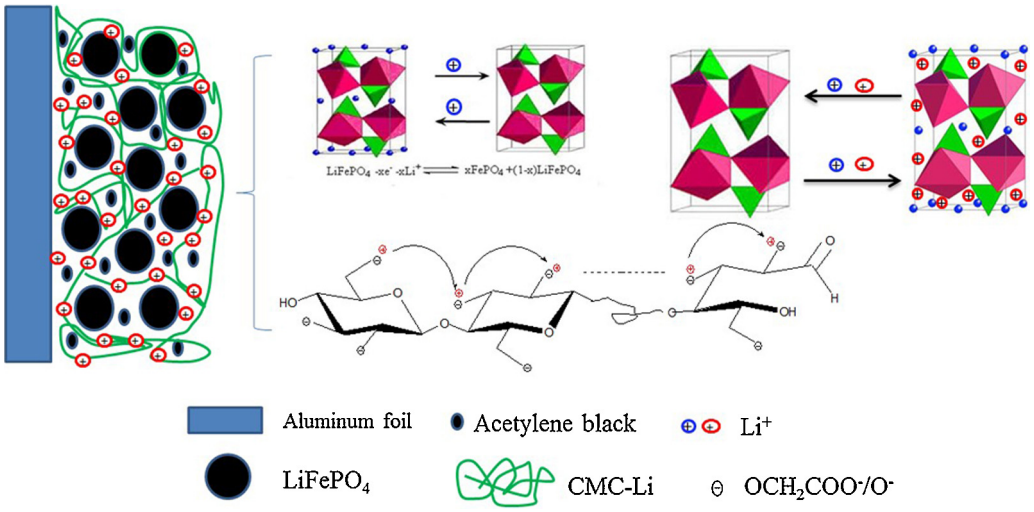

Fig. 1. Preliminary investigation of the mechanism of the CMC-Li binder in LFP cathode. Active substances react with lithium-ions on the molecular chain of CMC-Li adjacent to the active center of active substances.

capacity of the whole lithium-ion battery (Hu, Wu, Lin, Khlobystov, & Li, 2013). Meanwhile, excepting the advantages of CMC-Na, 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. Moreover, CMC-Li can prevent an exchange reaction between the Na-ion deposited on the carbon anode surface and the Li-ion, and the decomposition of the electrolyte solution. Since the conductive efficiency of CMC-Na is weak, it is difficult for the lithium battery to exhibit its merits, such as small volume, light quality and extraordinary energy (Lacey, Jeschull, Edstrom, & Brandell, 2013). Therefore, a current development allows applying the CMC-Li binder directly to the lithium battery, with a very broad range of potential applications.

In our paper, CMC-Li as a binder greatly increase the actual specific capacity of batteries. The first charge and discharge specific capacity reach the maximum value 183 mAh g^{-1}. After 200 cycles, the maximum charge and discharge capacity loss is merely 4.49%, and the battery capacity is still 176 mAh g^{-1}. It can conclude that CMC-Li as the binder increase the contents of lithium ions in the whole battery, improve the efficiency of extraction and insertion of lithium ions between anode and cathode electrode, as well as the diffusion coefficient. Furthermore, it can also enhance the charge and discharge platform of the battery and conductive efficiency of ions, and reduce the degree of polarization between electrode materials as well as film impedance on the surface of electrode material. All the above excellent properties showed that CMC-Li as a new efficient binder can be applied in lithium batteries and further extended to preparation of other electrode materials.

Fig. 1 shows the distribution of CMC-Li in the LFP-based electrode. The performance of CMC-Li can be ascribed to strong hydrogen bonds resulting from the action of the —OH groups, which contributed to form an efficient network. In addition, the hydrophilic CMC-Li binder is insoluble in organic electrolytes and does not swell in a cell. It has strong adhesion, thus maintaining the stability of the electrode structure. Furthermore, CMC-Li is a good lithium-ion conductive binder as there are various functional groups on the macromolecular chain of CMC-Li. During the discharge process, the active substances reacted with lithium-ions on the molecular chain of CMC-Li adjacent to the active center of active substances.

The reactions between carboxymethyl and hydroxyl groups from the CMC-Li binder and the lithium-ions will form the coordination bonds. Under an electric field force, lithium-ions can be transmitted along the same molecular chain or adjacent molecular chains, without destroying the structure of the molecular chain. Eventually, lithium-ions will be combined with the LFP particles, and the CMC-Li binder raises the transport efficiency of lithium-ions, the utilization rate and discharge capacity of LFP. The anode lithium reacts with the —CH_2COOH and —OH groups of CMC-Li to form the —CH_2COOLi and —OLi, respectively. This reaction is irreversible so as to reduce the initial coulomb efficiency (Xie et al., 2012). Therefore, the first discharge capacity of LFP electrode with CMC-Li for binder is higher than that of PVDF for the binder. Moreover, the increase in content of —CH_2COOLi equates to improvement of the degree of substitution (DS) of CMC-Li. Adhesive coating layer formed on the surface will be more stable. In addition, the increase in the carboxymethyl anion also contributed to the transport of Li^+.

Different electrodes are different in the position of the oxidation reduction peak (Figs. 2 and S4). The CV curves of battery with CMC-Li as cathode material and binder show the weaker electricity, which proves that CMC-Li had some electrochemical performances and thus laying the foundation for applying it to batteries. In addition, the difference in voltage of the oxidation reduction peak of the electrode with water-based binder is less than that with PVDF as binder, and the CV curves of electrodes with the water-based binder are sharper than those with PVDF binder. The distance between the discharge and charge curves of the former is smaller than that of the latter and minimum value reach 0.22 V, which shows that the polarization of the former is weaker than the latter and increases the activity of electrochemical reaction. This may be explained by the fact that most of the active materials are coated with PVDF binder, causing poor ionic conductivity of PVDF, so that PVDF hinder the diffusion of lithium in the charge and discharge process of the battery, and reduce the electrochemical activity of electrode material. While the active material is coated with CMC-Li binder to form an effective ionic conductivity layer, which provide a diffusion pathway for Li^+ to reach the active particle surface and enhance the activity of electrochemical reaction, reversibility of Li-ions and cycle performance.

The first discharge specific capacity of battery with CMC-Li as the binder is higher than that with PVDF as the binder, LFP as cathode material, which prove that the utilization rate of LFP in battery with water-soluble binder is increased (Figs. 3, S5 and S6). Moreover, the first charge specific capacity of battery with high DS CMC-Li as the binder is beyond the theoretical specific capacity 170 mAh g^{-1} of LFP, and reaches 180 mAh g^{-1}, which is increased by 17.6% relative

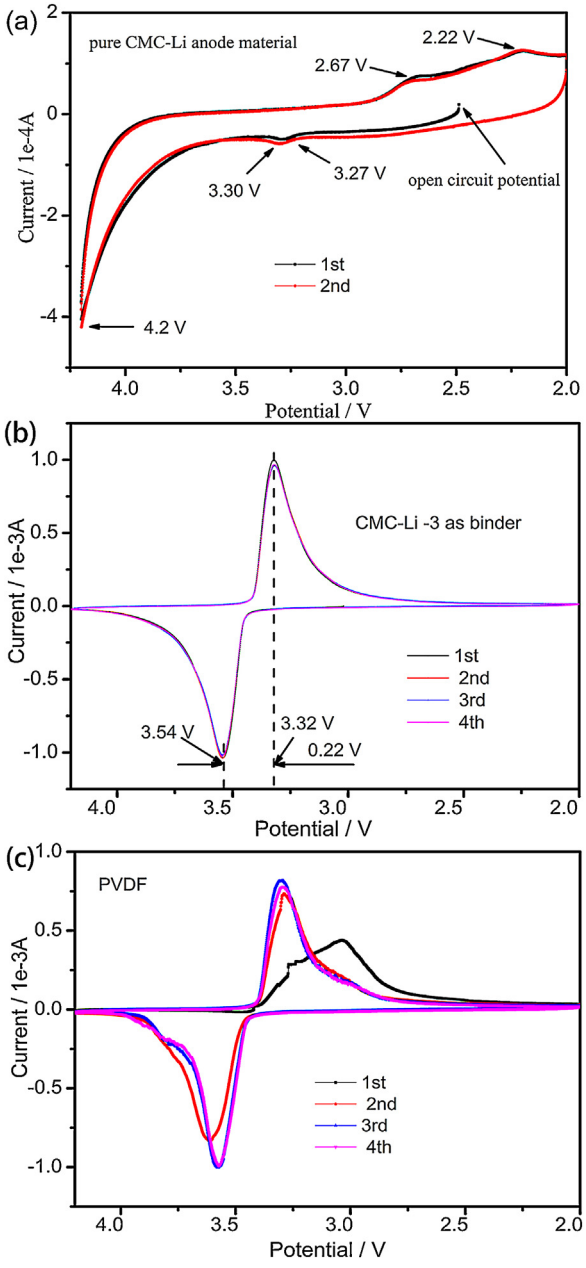

Fig. 2. CV tests of batteries with different electrode material. CV curves of (a) batteries with pure CMC-Li as cathode material and binder. (b) Batteries with LFP as cathode material and CMC-Li as the binder. (c) Batteries with LFP as cathode material and PVDF as the binder.

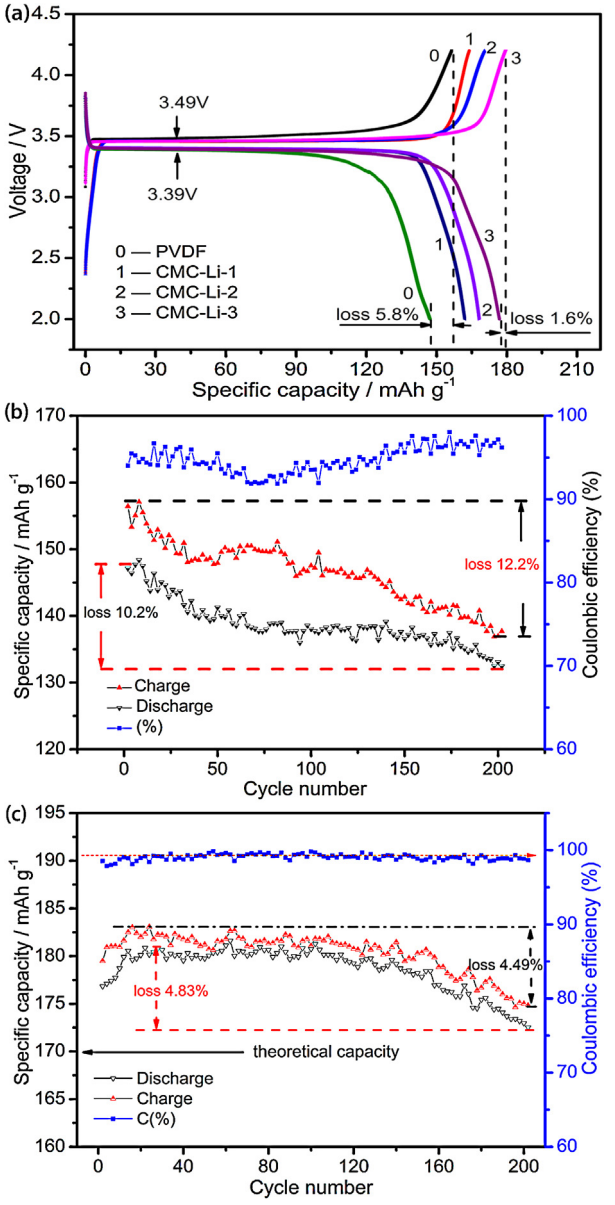

Fig. 3. Charge and discharge and cycle life curves of different binders. (a) The first charge and discharge curves of battery with different binder. (b) After 200 cycles, the life curves of battery with PVDF as the binder. (c) After 200 cycles, the life curves of battery using CMC-Li-3 as the binder. CMC-Li as a water-based binder can significantly improve the performance of electrode material and reduce the degree of polarization, and it can also promote the efficiency and the diffusion rate of Li-ions.

While the active material is coated with CMC-Li binder to form an effective ionic conductivity layer, which provides a diffusion pathway for Li^+ to reach the active particle surface and enhance the activity of electrochemical reaction, reversibility of Li-ions and cycle performance.

to the battery with PVDF as the binder. After 200 cycles, the specific capacity of all batteries with CMC-Li as the binder is higher than that with PVDF as the binder. The capacity loss of the latter is up to 12.2%, and the discharge capacity reach 132 mAh g^{-1}. However, the capacity loss of battery with CMC-Li-3 as the binder is merely 3.8%, and discharge specific capacity reach 173 mAh g^{-1}, which is still beyond the theoretical specific capacity of LFP. All of this show that CMC-Li as a water-based binder can significantly improve the performance of electrode material and reduce the degree of polarization, and it can also promote the efficiency and the diffusion rate of Li-ions. In addition, the increase in the carboxymethyl anion also contributed to the transport of Li^+. Meanwhile, the study of the molecular structure of CMC-Li shows that the battery with high DS CMC-Li as a binder has the superior performance than that with low DS CMC-Li.

In summary, the study using cotton, as a raw material, synthesized CMC-Li by a unique two-step method. CMC-Li is applied in Li-ion batteries. CMC-Li can increase the content of Li-ions in the whole batteries. The discharge platform of the battery is high, and the degree of polarization is small, which exhibit the excellent electrochemical performance. After 200 cycles, the specific capacity of the battery is still higher, and the loss is very little, so the performance is stable. Finally, we conclude that the performance of CMC-Li with high DS is superior to that with low DS. Meantime, the CMC-Li is cheaper, more eco-friendly and easily degraded, safer, and it is also applied in the field of other related materials.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.05.027.

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