Carbohydrate Polymers 112 (2014) 532–538

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Novel polymer Li-ion binder carboxymethyl cellulose derivative enhanced electrochemical performance for Li-ion batteries

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ARTICLE INFO

Article history:
Received 9 May 2014
Received in revised form 11 June 2014
Accepted 13 June 2014
Available online 20 June 2014

Keywords:
Lithium battery
Lithium iron phosphate
Water-based binder
Sodium carboxymethyl cellulose
Lithium carboxymethyl cellulose

ABSTRACT

Novel water-based binder lithium carboxymethyl cellulose (CMC-Li) is synthesized by 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 water-soluble binder are investigated. Sodium carboxymethyl cellulose (CMC-Na, CMC) and CMC-Li are used as the binder. After 200 cycles, compared with conventional poly(vinylidene fluoride) (PVDF) binder, the CMC-Li binder significantly improves cycling performance of the LFP cathode 96.7% of initial reversible capacity achieved at 175 mA h g^{-1}. Constant current charge–discharge test results demonstrate that the LFP electrode using CMC-Li as the binder has the highest rate capability, followed closely by those using CMC and PVDF binders, respectively. Electrochemical impedance spectroscopy test results show that the electrode using CMC-Li as the binder has lower charge transfer resistance than the electrodes using CMC and PVDF as the binders.

1. Introduction

The lithium-ion battery (LIB) is one of the most promising energy storage systems for mobile devices, portable computers, plug-in hybrid-electric vehicles, and hybrid-electric vehicles (HEVs) (Fei et al., 2013; Lu, Huang, Mou, Wang, & Xu, 2010; Wang et al., 2014; Zhang, Uchaker, Candelaria, & Cao, 2013). There have been extensive studies on electrode materials (Yang & Leung, 2013), electrolytes (Masquelier & Croguennec, 2013), additives (Seh et al., 2013), membranes (Zhao et al., 2014), and binders to attain improvement of the battery performance (Qiu, Shao, Yang, et al., 2014). Compared with the significant progress on most of these components for the LIB; however, recent works show that the choice of binder is very important to stabilize the cycling performance of electrodes for Li-ion batteries, which display large-volume changes (Li, Yang, & Qin, 2013; Lu et al., 2014; Xun, Song, Battaglia, & Liu, 2013). To make electrode sheets for lithium-ion (Li-ion) anodes or cathodes with appropriate mechanical properties, generally have to be blended with specific polymeric binders (Lestrie, Bahri, Sandu, Roue, & Guyomard, 2007; Li et al., 2011). Binders are electrochemically inactive materials which, however, can have an important influence on the electrode performance (Mancini, Nobili, Tossici, & Marassi, 2012). In commercial Li-ion batteries, PVDF has been widely used as the binder for both the negative and the positive electrodes in current collectors and commercial LIBs, because of its good electrochemical stability and high binder to electrode materials (Lee & Oh, 2013; Xu, Chou, Gu, Liu, & Dou, 2013). Nonetheless, PVDF binder is expensive, not easy to recycle, and involved the use of volatile organic compounds such as the environmentally harmful and toxic *N*-methyl-2-pyrrolidone (NMP) for its processing (Sethuraman et al., 2013). Moreover, accidents that caused by low-energy efficiency of lithium battery and NMP were 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. Nevertheless, the need for eco-friendliness, low cost, better electrode performance, and solvent recycling has led to recent investigations aiming at switching from a non-aqueous-based to an aqueous-based system (Courtemanche, Pinter, & Hof, 2011; Lacey, Jeschull, Edstrom, & Brandell, 2013).

CMC, which is produced from the insertion of carboxymethyl groups into natural cellulose, is the commonly used binder for anodes and cathodes of Li-ion batteries (Sivasankaran et al., 2011). CMC has a strong shear-thinning behavior that adjusts the slurry rheology (Qiu, Shao, Liu, et al., 2014). CMC is a weak polyacid that dissociates to form carboxylate anionic functional groups. Because CMC is very stiff, having a small elongation at break (<8%), it could

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http://dx.doi.org/10.1016/j.carbpol.2014.06.034
0144-8617/

not function as the elastomeric binder (Qiu, Shao, Yang, et al., 2013; Wach, Kudoh, Zhai, Muroya, & Katsumura, 2005). Thus, the reasons why a brittle polymer like CMC can give good results for electrodes must be explored. Nevertheless, the need for providing the lithium ion, eco-friendliness, low cost, better electrode performance, and solvent recycling has led to designing new binder as switching from a no-provide the lithium-ion to provide the lithium-ion (Qiu, Shao, Xiang, et al., 2014).

Novel water-based binder CMC-Li with a unique molecular structure is a polyhydroxy water soluble cellulose derivative polymer as CMC (Qiu, Shao, Wang, Zhang, & Cao, 2013). When such a solution reaches a certain concentration, the adhesiveness of CMC-Li is strong enough to act as a binder. The studies show that except some advantages of other water-based binders, CMC-Li was also an effective ion-conductive polymer, and ionized to obtain lithium ions, which could increase the contents of freely moving lithium ions in lithium-ion batteries, shorten the diffusion pathway to the cathode particle surface (Augustyn et al., 2013; Gibot et al., 2008). It could also improve the efficiency of extraction and insertion of lithium ions between the cathode and anode electrode, and improving the charge and discharge capacity of the whole LIB. Meanwhile, excepting the advantages of CMC, this method, by substituting lithium for sodium, can avoid the decline of charge and discharge efficiency, as well as the cycle capacity performance of the battery, with CMC 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 was weak, it was difficult for the lithium battery to exhibit its merits, such as small volume, light quality, and extraordinary energy (Qiu, Shao, Liu, et al., 2014; Qiu, Shao, Yang, et al., 2014). Therefore, a current development allows applying the CMC-Li binder directly to the lithium battery, with a very broad range of potential applications.

In this investigation, water-soluble binders CMC-Li and CMC are applied to prepare the LFP cathode. Compared with PVDF, CMC-Li, and CMC, which have two functional groups, carboxylate anion, and hydroxyl, are well known as an effective dispersion and thickener agent for aqueous suspension. CMC-Li, as a binder, greatly increased the actual specific capacity of batteries. The first charge and discharge specific capacity achieved a maximum value 183 mA h g^{-1}. After 200 cycles, the maximum charge and discharge capacity losses were merely 3.31%. It can conclude that CMC-Li as the binder increased the contents of lithium ions in the entire battery, improved the efficiency of extraction and insertion of lithium ions between cathode and anode electrode, as well as the diffusion coefficient. Furthermore, it can also enhance the charge and discharge platform of 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.

2. Experimental

2.1. Powder preparations

The preparation process of CMC and CMC-Li can be clarified by the slurry process in a solution of isopropyl alcohol in our laboratory (Qiu, Shao, Wang, et al., 2013). CMC-Lis with the different degree of substitution (DS) were prepared by selecting the DS of CMC and the amount of $LiOH{\cdot}H_2O$. In this paper, CMC and CMC-Lis with two different DS values were prepared, respectively. CMC-Na-1 (DS = 0.68, Mw = 110,000 g mol^{-1}), CMC-Na-2 (DS = 1.22, Mw = 370,000 g mol^{-1}), CMC-Li-1 (DS = 0.65, Mw = 90,000 g mol^{-1}), CMC-Li-2 (DS = 1.25, Mw = 350,000 g mol^{-1}).

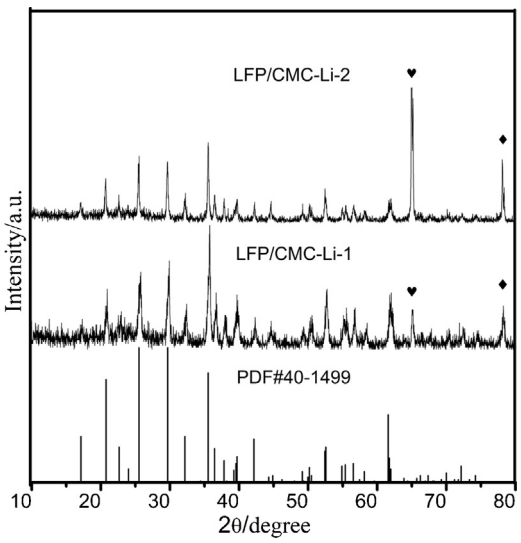


Fig. 1. XRD patterns for the electrode slices with CMC-Li as a binder (PDF no. 40-1499 is standard XRD of $LiFePO_4$, "♥" is standard XRD of Li_3P (1 1 4) and "♦" is standard XRD of Li_2O_2 (1 1 4)). It shows that CMC-Li as a binder maybe increases the contents of lithium ions in the entire battery.

2.2. Structural characterization and electrochemical measurements

XRD diffraction experiments were performed with an Inel Cps 300 diffractometers using the Cu K radiation (−1.54056 Å).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results were obtained with electrochemical workstation CHI660E from Shanghai Chen Hua Instruments Co., Ltd. The coin cells (CR2025) were assembled to test the electrochemical performance of the as-prepared LFP:acetylene black:binder is 80:10:10, using 1.0 M $LiPF_6$ ethylene carbonate (EC):diethyl carbonate (DEC):dimethyl carbonate (DMC) = 1:1:1 by volume as the electrolyte and a Li foil as the counter electrode. The cells were charged and discharged galvanostatically in the fixed potential window from 2.0 to 4.2 V on a Shenzhen Neware battery cycle (China) at 25 °C. The calculated capacity was based on the entire mass of the cathode electrodes. EIS was measured by applying an alternating potential of 5 mV over the frequency ranging from 10^{-1} to 10^5 Hz after 5 cycles. CV was conducted in a cell at 0.1 mV s^{-1} and performed from 4.2 to 2.0 V.

3. Results and discussion

3.1. Electrode characterization

XRD patterns obtain from the LFP electrode using CMC-Li as the binder (Fig. 1). Typical LFP peaks are observed for these samples. In addition, CMC-Li as the binder samples presents typical diffraction peaks at 2 theta of about 65.7°, 78.6°, corresponding to the (1 1 4) planes of Li_3P and Li_2O_2 crystals, respectively. All of these show that CMC-Li as a binder maybe increases the contents of lithium ions in the entire battery, and improves the effectiveness of extraction and insertion of lithium ions between Li-ions, thus, improving the diffusion efficiency and specific capacity.

3.2. Charge and discharge curves of LFP electrode using different binders

The first discharge specific capacity of battery with CMC-Li as the binder was higher than that with CMC and PVDF as the binder when electricity density was 0.2 mA cm^{-2}, respectively. LFP as

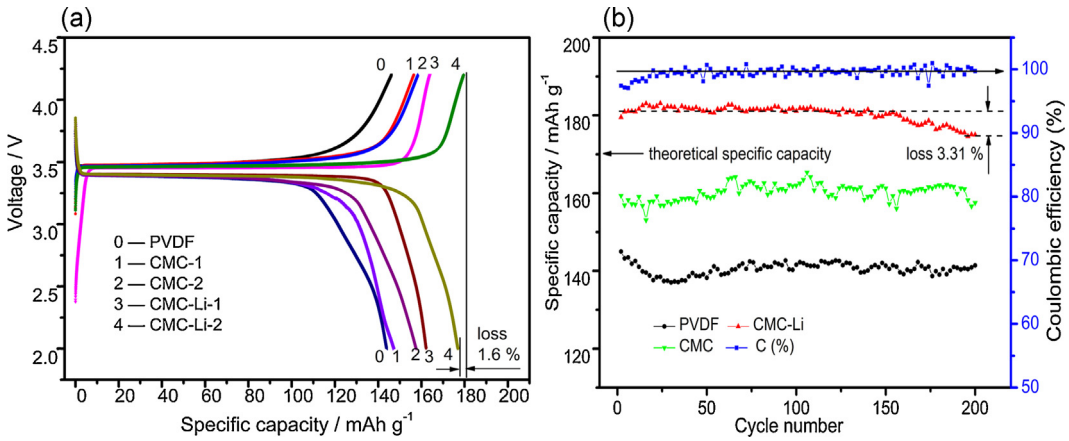


Fig. 2. (a) Initial charge and discharge curves of LFP electrode using different binders. (b) Specific capacity versus the cycle number for the LFP electrodes with CMC-Li, CMC, and PVDF binder at 0.1 C charge and discharge at room temperature. CMC-Li as a water-based binder can significantly improve 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.

cathode material, which proves that the utilization rate of LFP in battery with a water-soluble binder is increased (Fig. 2a). Moreover, the first charge specific capacity of battery with high DS of CMC-Li as the binder reaches 181 mA h g^{-1}, which increases by 19.3% relative 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 CMC and PVDF as the binder, respectively (Fig. 2b). The capacity loss of the PVDF as a binder is up to 19.4%, and the discharge capacity reaches 141 mA h g^{-1}. However, the capacity loss of battery with CMC-Li-2 as the binder is merely 3.31%, and discharge specific capacity reached 175 mA h g^{-1}. All these 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 (Armstrong, Lyness, Panchmatia, Islam, & Bruce, 2011; Hu, Wu, Lin, Khlobystov, & Li, 2013). 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.

3.3. Electrical and electrochemical properties

To further investigate the electrode electrochemical impedance spectra (EIS), Fig. 3 shows the Nyquist plots of the electrodes with different binders in the discharged state of 3.50 V (vs. Li/Lit) at room temperatures after charge–discharge for five cycles. All the impedance curves of LFP with different binders show one semicircles in the medium frequency and the low-frequency regions, which could be assigned to the lithium ion diffusion through the solid electrolyte interphase (SEI) film (R_g) and the charge transfer resistance (R_{ct}), respectively, and an unclear ~110° inclined line in the low-frequency range with CMC-Li as the binder, which could be considered to be a Warburg impedance (Z_w). The R_{ct} is calculated using the equivalent circuit shown in the inset of Fig. 3. The equivalent circuit model also includes electrolyte resistance (R_s), a constant phase element (CPE1) and a non-ideal constant phase element (CPE2). LFP electrode with CMC-Li binder had the smallest R_{ct} values, below those of CMC binder and PVDF binder, respectively, indicating the enhancement of the kinetics and the consequent improvement in the rate capability of LFP using CMC-Li binder. These results indicate that the interfacial properties between LFP electrode and electrolyte are improved by using CMC-Li as the binder to increase the electrochemical reaction and dynamic performance. CMC-Li is played a positive role in the charge transfer process. For CMC-Li with different DS, the polar group numbers carry by unit mass of CMC-Li with high DS are greater than those carry by CMC-Li with low DS. The repellence of CMC-Li with high DS is better, and the LFP layer form on the active grain surface is more stable. The charge-transfer resistance of the cell using CMC-Li with high DS is obviously lower than that with low DS.

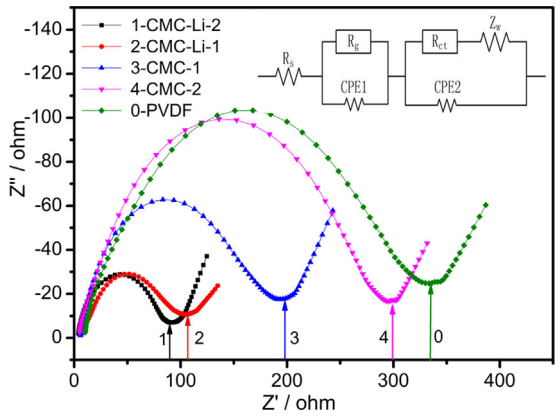


Fig. 3. Nyquist plots of LFP electrodes using CMC-Li, CMC, and PVDF as the binder at the discharged state of 3.50 V (vs. Li/Lit) at frequencies from 100 kHz to 100 mHz. The insets show the equivalent circuit. The interfacial properties between LFP electrode and electrolyte are improved by using CMC-Li as the binder to increase the electrochemical reaction and dynamic performance.

Different electrodes are different in the position of the oxidation reduction peak (Fig. 4). The CV curves of battery with CMC-Li as cathode material and binder show the weaker electricity, which proves that CMC-Li has some electrochemical performances and thus laying the foundation for applying it to batteries (Fig. 4a). In addition, the difference in voltage of the oxidation reduction peak of the electrode with water-based binder is lower 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 CMC-Li as the binder are smaller than that of the CMC and PVDF as the binder, and the minimum value reaches 0.22 V (Fig. 4b–d), 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 hinders the diffusion of lithium in the charge and discharge process of the battery, and reduces the electrochemical activity of electrode material. While the active material is coated with CMC-Li binder to form an effective ionic conductivity layer, it provides a diffusion pathway for Li^+ to reach the active particle surface and

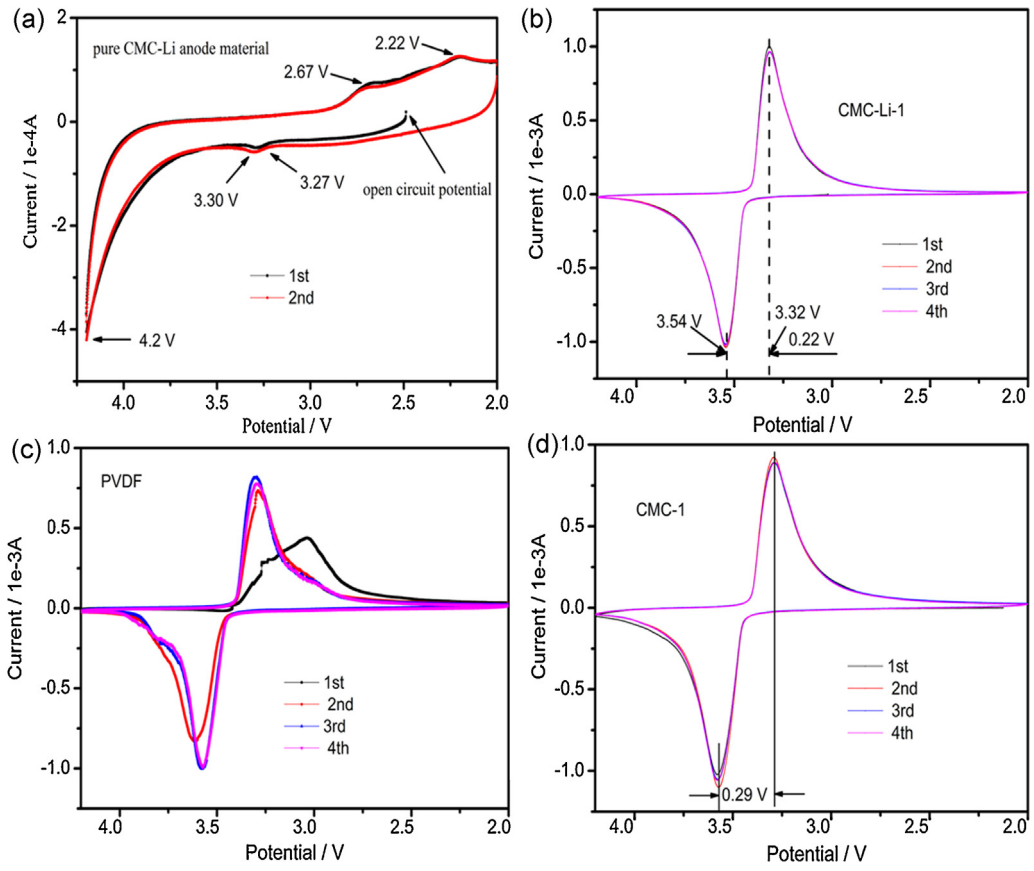


Fig. 4. (a) CV curves of battery with pure CMC-Li as cathode material and binder. (b–d) CV curves of the LFP cathodes at a scanning rate of 0.1 mV s^{-1} using different binders: (b) CMC-Li, (c) PVDF, and (d) CMC. While the active material is coated with CMC-Li binder to form an effective ionic conductivity 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.

enhances the activity of electrochemical reaction, reversibility of Li-ions, and cycle performance.

It can be seen from Fig. 5 that the rate performance and cycle property of electrode material with CMC-Li-2 as the binder is excellent. At a discharge rate of 0.2 C, the discharge capacity is up to 171.5 mA h g^{-1}. When discharge rate increases to 0.5 C, discharge capacity decreases to 158.2 mA h g^{-1}. Even at a rate of 1 C, the capacity is still up to 139.8 mA h g^{-1}, which shows that the discharge capacity presents linear variation with the increment of rate performance. This depends on the diffusion of Li-ions in material. It is because CMC-Li as the binder can be uniformly distributed on the surface of LFP material, the ionized Li-ions can short its transmission distance between cathode and anode electrode, and can enhance the transmission efficiency and conductivity, which causes the material to have relatively good rate performance and cycle property.

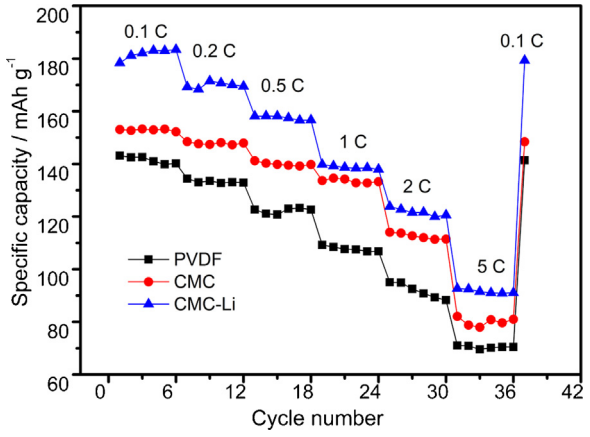


Fig. 5. Rate performance of LFP electrodes with different binders at 0.1 to 5 C. It is because CMC-Li as the binder can be uniformly distributed on the surface of LFP material, the ionized Li-ions can short its transmission distance between cathode and anode electrode, and enhance the transmission efficiency and conductivity, which causes the material to have the relatively good rate performance and cycle property.

3.4. SEM images of LFP cathode materials with different binders

Fig. 6 shows that we successfully synthesize a new binder CMC-Li (Fig. 6a). Related product characterization is presented in our previously published articles (Qiu, Shao, Liu, et al., 2014; Qiu, Shao, Xiang, et al., 2014; Qiu, Shao, Yang, et al., 2014). SEM images of electrode prepare by different binder and LFP as cathode material after 200 cycles (Fig. 6b–f). SEM photo of electrode slice of PVDF as binder (Fig. 6b) shows the image that the particle of electrode material is big and distributed non-uniformly, and the gathering phenomenon among particles is more significant. SEM images of the electrode slice of CMC as a binder (Fig. 6c) show that the particle is bigger and distribution is more uniform than that with PVDF as binder, and the immersion process of electrolyte is better. SEM images of electrode slice of CMC-Li as binder (Fig. 6d–f) present that the particle is the smallest with no significant aggregation of particles, and the distribution is uniform and the immersion process of electrolyte is best. Moreover, there exist many "black holes" on the surface of electrode slice and the inside crystal structure presents the regular change. The "black hole" phenomenon may be the reason for improving the charge and discharge specific capacity

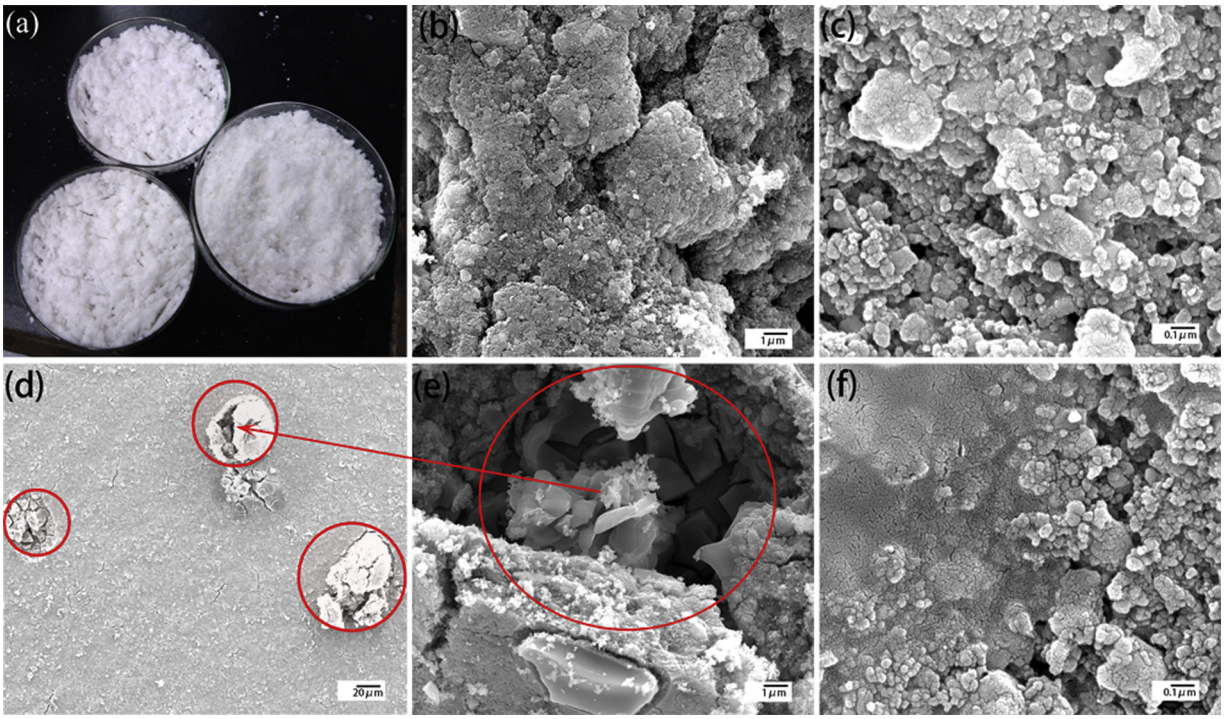
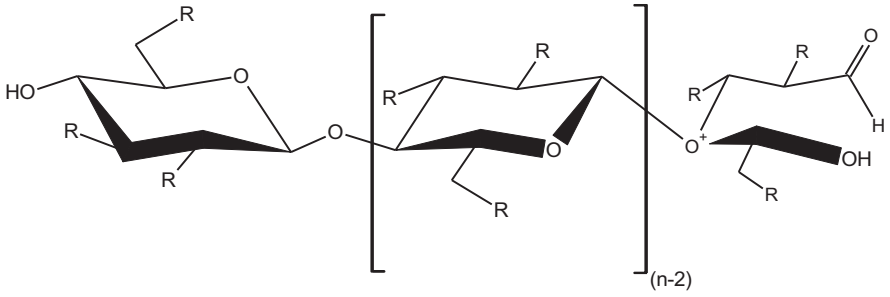


Fig. 6. SEM images of LFP cathode materials with different binders at the end of the 200th cycles charge–discharge. (a) Digital pictures of CMC-Li, (b) PVDF as binder, (c) CMC as binder, (d–f) CMC-Li as binder. "Black hole" phenomenon may be the reason for improving the charge and discharge specific capacity of battery.

of battery. The formation of the "black hole" may benefit the extraction and insertion efficiency of Li-ions between anode and cathode, as well as the extraction and insertion time of Li-ions to form fast lanes, thus increasing the ionic conductive efficiency and electronic conductive efficiency in order to improve the performance of the whole battery.

3.5. The investigation of the mechanism of the CMC-Li as the binder in LFP battery

The preparation process of CMC-Li can be clarified by the following schematic equation:



Cellulose (R=OH, Cell-$(OH)_3$)

$$\text{Cell-(OH)}_3 \xrightarrow[\text{ClCH}_2\text{COOH}]{\text{NaOH}} \text{Cell-(OH)}_{3-x}(\text{ONa})_{x-n}(\text{OCH}_2\text{COO}^-\text{Na}^+)_n(\text{Cell-CH}_2\text{COONa})$$

$$\text{Cell-CH}_2\text{COONa(CMC-Na)} \xrightarrow{\text{HCl}} \text{Cell-CH}_2\text{COOH(CMC-H)} \xrightarrow{\text{LiOH}} \text{Cell-CH}_2\text{COOLi(CMC-Li)}$$

$$\text{Cell-(OH)}_{3-x}(\text{ONa})_{x-n}(\text{OCH}_2\text{COO}^-\text{Na}^+)_n(\text{Cell-CH}_2\text{COONa}) \xrightarrow{\text{HCl}} \text{Cell-(OH)}_{3-x}(\text{OH})_{x-n}(\text{OCH}_2\text{COO}^-\text{H}^+)_n$$
$$(\text{Cell-CH}_2\text{COOH}) \xrightarrow{\text{LiOH}\cdot\text{H}_2\text{O}} \text{Cell-(OH)}_{3-x}(\text{OLi})_{x-n}(\text{OCH}_2\text{COO}^-\text{Li}^+)_n(\text{Cell-CH}_2\text{COOLi})$$

CMC is prepared by the slurry process in a solution of isopropyl alcohol in our laboratory, after alkalization, etherification, neutralization, and washing on cellulose, we can get the CMC for this article, and DS is measured by the method of gray alkali. DS of CMC-Li and CMC-H depends on the DS of raw materials CMC.

Fig. 7 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 contribute 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

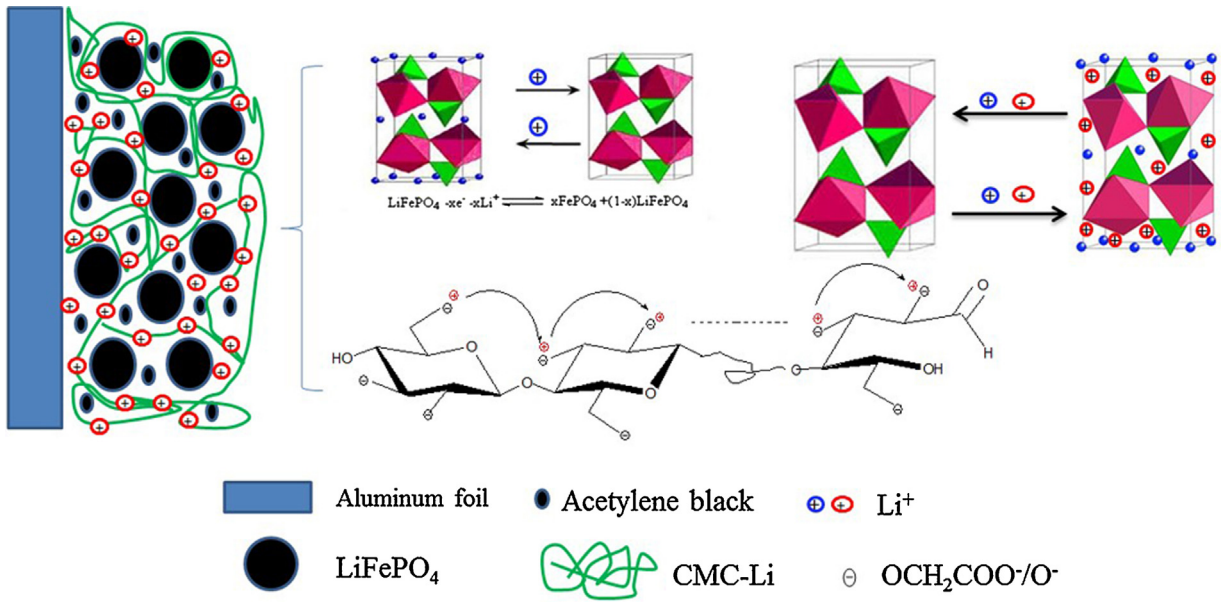


Fig. 7. Preliminary investigation of the mechanism of the CMC-Li binder in LFP battery. Active substances react with lithium-ions on the molecular chain of CMC-Li adjacent to the active center of active substances.

the electrode structure (Ryou et al., 2013). 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 react with lithium-ions on the molecular chain of CMC-Li adjacent to the active center of active substances (Liang, Zhang, & Chen, 2013).

The reactions between carboxymethyl and hydroxyl groups from the CMC-Li binder and the lithium-ions will form the coordination bonds (Qiu, Shao, Wang, et al., 2013). 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, during the processing on charge–discharge of lithium-ion batteries, lithium-ions will be combined with the LFP particles and the carboxymethyl and hydroxyl groups from the CMC-Li. So the CMC-Li binder raises the transport efficiency of lithium-ions, the utilization rate, and discharge capacity of LFP (Armand et al., 2009; Young, Ransil, Amin, Li, & Chiang, 2013). In addition, the $-CH_2COOH$ and $-OH$ groups of CMC-Li can easily react with anode lithium metal and form the $-CH_2COOLi$ and $-OLi$, respectively. This reaction is irreversible so as to reduce the initial coulomb efficiency. Therefore, the initial discharge capacity of LFP electrode with CMC-Li for binder is higher than that with CMC and PVDF as the binder. Moreover, the increase in content of $-CH_2COOLi$ equates the improvement of the DS of CMC-Li (Gibot et al., 2008). Adhesive coating layer on the surface will be more stable. In addition, the increase in the carboxymethyl anion also contributes to the transport of Li^+.

4. Conclusion

In summary, we are using water-soluble CMC-Li, CMC instead of traditional PVDF as a binder for the LFP cathode. The CMC-Li cathode exhibits a reversible capacity of 175 mA h g^{-1} after 200 cycles, the specific capacity of the battery is still higher than the theoretical specific capacity of LFP, and the loss is very little, showing remarkably improved cyclability as compared with the traditional PVDF cathode. The battery delivers high capacity which consists of the results of EIS measurement showing a low internal resistance and low charge transfer impedance for the CMC-Li cathode, due to an efficient electronic conductivity. It indicates that the CMC-Li binder can provide an effective electronically conductive network and a stable interface structure for the cathode. Our results clearly show that the cheap and environment-friendly CMC-Li as a highly efficient binder for the LFP cathode can improve the electrochemical performance. The present findings open new prospects for the electrode performance optimization via better understanding the role of the binder.

Acknowledgements

Financial support from the special programs of graduate students' scientific and technological innovation activities of Beijing Institute of Technology (3090012241302) and Youth Science and Technology Innovation Projects of North Chemical Industry Co., Ltd. (QKCZ-BIT-04).

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