Influence of molecular structure of Carboxymethyl Cellulose on High Performance Silicon Anode in Lithium-Ion Batteries

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The study aims to the preparation of bio-based binders with optimal molecular structure for electrodes and the exploration of their influence on the electrochemical performance of electrodes. At first, a series of Carboxymethyl Cellulose (CMC) with different degree of polymerization (DP) and degree of substitution (DS) were successfully prepared using the specially designed method and their physical characteristics were also investigated. Si anodes were manufactured with the CMC binders and their electrochemical performances were evaluated and compared. As a consequence, the silicon anode containing CMC of DS= 0.38 and DP = 215 showed the best cyclic performance (71% of capacity maintained after the 100th cycle) due to its compatible molecular structure. It is assumed that the CMC with specially designed molecular structure plays a key role in binding the silicon particles during the cycles and weakened the volume effect.

Keywords: Carboxymethyl cellulose; Silicon anode; molecular structure; Lithium-Ion Batteries

1. INTRODUCTION

Lithium-ion batteries (LIB) have become a kind of widely used secondary batteries in the world due to their excellent cyclic performance, high energy density, low self-discharge rate, environmental protection and no pollution[1]. To meet ever increasing demands of energy density, [2]Silicon-based materials have the potential to replace graphite anodes because of their higher specific capacity (4200mAh/g) than the specific capacity (372mAh/g) of graphite anode. Moreover, lithium are less possible to deposit on the surface of silicon anodes during the lithiation of silicon, which lead to better safety. However in the process of lithiation and delithiation of silicon, silicon based materials

will undergo huge volume changes (400%),[3, 4] which would cause a severe damage for the intact structure of electrodes and lead to a great capacity loss. The expansion also destroys the solid electrolyte intermediate phase (SEI) on the surface of electrodes, causing the regeneration of SEI and the consumption of lithium ions.[5] Intense volume change of the electrodes could cause the deformation of battery and the malfunctions of separator, therefore leads to safety problems. [6] It is an effective way by coating a carbon layer on the surface of silicon particle to suppress volume expansion.[7]

Binders adhere the active materials and the conductive agents to the current collector in the electrode. The choice of binder has a nonnegligible impact on the cycling stability, rate performance and impedance performance of the electrode. To cope with a series of problems caused by the volume expansion of silicon anodes, many efforts have been put into the research of binders in the silicon anode battery.[8] Comparing to traditional PVDF binders, natural polymer binders such as carboxymethyl cellulose (CMC),[9] guar gum[10] and sodium alginate (SA)[11] show better effects on maintaining the structural integrity of the electrode during the dramatic volume change of silicon particle, which lead to the good contact of the particles in the electrode. Furthermore, the conduction of lithium ions is also improved.[12] The excellent performance of these binders is attributed to their abundant carboxyl groups, which contributes to forming stable hydrogen bonds or covalent bonds between silicon particles.[8] On this basis, PAA / CMC composites[13], Ca²⁺-doped-alginate[14] and other cross-linked or composite binders exhibit better mechanical properties and adhesion effect on silicon anodes.

As one of the popular binders for silicon anodes, CMC is a widely-used cellulose ether because of its solubility, biocompatibility, biodegradation and environmentally friendly. Nowadays, there are more researches on the crosslinking modification of CMC, but less research on the influence of basic properties of CMC on the electrochemical properties of silicon anodes. Although there have been a lot of studies on CMC as a binder for silicon anode electrodes,[15-17] it is still unclear that what kind of molecular structure of CMC shows the best electrochemical performance for silicon anodes electrodes.

As a kind of cellulose derivative, CMC is converted by a carboxymethyl group (-CH₂COONa) in place of a hydrogen atom on a hydroxyl group (-OH) in one unit of the cellulose strain. It is usually prepared by reacting natural cellulose with sodium hydroxide and monochloroacetic acid. The number of carboxymethyl group substitutions is defined as the degree of substitution (DS), which is a significant parameter of CMC. The DS and the degree of polymerization (DP) of CMC have a great impact on its physical properties. Therefore, it is meaningful to research the synthesized CMC with different DS and DP. To more fully explore the influence of the DP and DS of CMC on the silicon anodes, a series of cellulose with four kinds of DP were obtained by degrading the filter paper cellulose at different conditions of acid hydrolysis and 12 kinds of CMCs were synthesized by carboxymethylation of the cellulose with certain DP. All kinds of CMC were characterized and used as the binders in silicon anodes. The results provide more support for the application of CMC with difference molecular structure on silicon anodes.



Figure 1. The mechanism of the synthesis of CMC.

2. EXPERIMENTAL

2.1 Materials

Chemicals used in the study, hydrochloric acid, sodium chloroacetate, sodium hydroxide, methanol and ethanol were purchased from Aladdin. Bis(ethylenediamine)copper(II) hydroxide solution was from Sigma-Aldrich. Nano-silicon (100 nm) was from Shanghai Naiou Nano Technology Co., Ltd. Filter paper with the original DP of 845 was from Hangzhou Special Paper Industry Co., Ltd.

2.2 Methods

Preparation of cellulose with different DP: The filter paper were cut into pieces of 5*5 cm and immersed in hydrochloric acid (1 mol/L) at a ratio of 1:10 (wt/v). After that NaOH (5 mol/L) was added to end the acid hydrolysis at different temperatures. And then the filter paper was washed to neutral and dried at 105°C to obtain the cellulose of different DP.

Synthesis of CMC: 4.0 g of NaOH was dissolved in 100 mL of ethanol aqueous solution (80%, v/v). Subsequently 2.5 g of pre-swelled filter paper was added into the above alkaline solution, stirred at 30°C for 30 min, and then 5.0 g of sodium chloroacetate powder was added into the solution and stirred at 70°C for 1 h, and subjected to suction filtration. The above carboxymethylation process is repeated to obtain samples with different DS. After the reaction, the sample was cooled to room temperature, and acetic acid was added dropwise to adjust the pH of slurry to neutral. And then the sample was suction filtered and washed repeatedly with 70%(v/v) ethanol. The washed sample was dried at 60°C, lyophilized and stored for use.

2.3 Characterization

The X-ray diffraction (XRD) test was carried out by an X-ray diffractometer (Rigaku Ultima IV). The infrared spectrum was tested by a Nicolet iS5 Fourier infrared spectrometer. The DP of cellulose was calculated by the national standard of China (GBT 5888-1986).[18] The DS of CMC was

identified by the method in the literature[19]. The viscosity of CMC was tested by Brookfield viscometer.

The slurry of silicon anodes was prepared by the uniform mix of silicon powder, acetylene black and CMC powder at a weight ratio of 6:2:2 in an appropriate amount of water, and then the obtained slurry was uniformly coated on a copper foil by Automatic film applicator (AFA-II). The electrode was transferred to an oven in vacuum at 50°C for 12 h. The electrode with the silicon loading density of 1.8-1.9 mg cm⁻² was selected for the battery assembly and electrochemical performance test. The membrane of Celgard 2400 was used as the separator. The dimethyl carbonate (DMC) diethyl carbonate (DEC) and ethylene carbonate (EC) were mixed in a ratio of 1:1:1 (v/v) and dissolved with LiPF₆ (1 mol/L), and the fluoroethylene carbonate (FEC) was added to the solution and adjusted to 10 wt % to prepare the electrolyte. The assembly of the cell was operated in a glove box with dry shielding gas. The test of constant current charge discharge was carried out by the LAND-BT2013A. The cell was pre-cycled by a small current of 0.05 C for one cycle and then charged and discharged with the current of 0.1 C in the voltage range of 0.01-1.00 V versus Li/Li⁺. Cyclic voltammetry (CV) test and Electrochemical Impedance Spectroscopy (EIS) test were performed by the CHI660E electrochemical workstation. The scan rate of CV test was 0.2 mV/s. The frequency of EIS was between 0.01 and 10,000 Hz and the amplitude of EIS was 5 mV.

3. RESULT AND DISCUSSION

Temperature/	Time/min	DP of cellulose		
°C				
30	45	697		
50	60	501		
80	60	215		

Table 1. Acid hydrolysis conditions of obtained cellulose with different DP.



Figure 2. X-ray diffractometry profiles (a) and the crystallinity index (b) of cellulose with different DP.

By regulating the reaction time and temperature, the cellulose with DP of 845, 697, 501 and 215 was successfully obtained by the acid hydrolysis of filter paper cellulose. The acid hydrolysis conditions of obtained cellulose with different DP are shown in Table 1. The samples are named as DP845, DP697, DP501 and DP215. And then a series of CMC were synthesized.

For understanding the influence of acid hydrolysis on the crystallinity of cellulose, the obtained cellulose with different DP is characterized with XRD. As shown in Fig. 2(a), there are obvious characteristic peaks at $2\theta = 14.9$, 16.7, 22.7 and 34.38, corresponding to the 101, 10<u>1</u>, 002, and 040 crystal faces of cellulose I.[20-22] The crystallinity of cellulose was calculated by the method in the literature.[23] The calculation results of crystallinity are shown in Fig.2(b). The crystallinity of cellulose DP215 is the highest, 87.6%, and that of cellulose DP501 is the lowest, 85.3%. The crystallinity of the cellulose DP845 and DP697 are about 87.1%. The difference of crystallinity affects the reactive activity of cellulose, resulting in the different DS of the synthetized CMCs.

CMC was prepared through the carboxymethylation reaction of cellulose. In this study, the carboxymethylation process repeated for 3 to 5 times and more thorough reaction resulted in higher DS. Therefore, in this study, the prepared CMC with 3 or more times of carboxymethylation reaction were characterized and selected as the binders in the electrode.

Table 2. The DS of CMC.

Repetition of carboxymethylati on reactions	DP845	DP69 7	DP50 1	DP21 5
3	0.42	0.39	0.43	0.38
4	0.51	0.48	0.58	0.44
5	0.66	0.66	0.72	0.60



Figure 3. FTIR spectra of DP501 cellulose (a), and CMC with different DS (b, c, d).

The DS results of prepared CMC are shown in Table 2. The CMCs were produced from cellulose with different DP. The carboxymethylation reaction was affected by the crystallinity of cellulose. The DS of all CMCs obtained in this study ranged from 0.38 to 0.72. For DP845 and DP697, the DS of CMCs are similar because of their similar crystallinity (87.19% for DP845, 87.12% for DP697) and closer DP. Owing to the relatively low crystallinity of 85.3%, the DS of CMC prepared by DP501 is higher than those of the others. In contrast, the highest crystallinity of DP215 leads to the relatively low DS of CMC.

Since the DP of cellulose and CMC have no effect on their FT-IR results, the infrared spectra of the DP501 and CMC-DP501 with different DS were chosen to be shown in Fig.3. The broad absorption peak at 3434 cm⁻¹ was caused by the stretching frequency of the -OH group. The peak at 1329 cm⁻¹ was assigned to OH bending vibration. A band at 2920 cm⁻¹ is attributable to C-H stretching vibration. There are two visible reinforcing peaks at 1615 cm⁻¹ and 1421 cm⁻¹.[24, 25] The former is the result of the asymmetric stretching vibration peak of –COO-, while the latter is resulted from its symmetrical vibration, which indicated the successful preparation of CMC.

As a dispersant, the viscosity of CMC has a crucial influence on the electrochemical performance. It was found in the experiment that the excessive viscosity of the slurry leads to a decrease in mass transfer rate, hindering the uniform distribution of the silicon and acetylene black. If the viscosity of the slurry is too low, the layers of acetylene black and silicon are separated during the stirring process. The viscosity of CMC depends on the DP and DS. Here, the viscosity of different CMCs was tested. With the increase of DP and decrease of the DS, the viscosity of CMC solution decreases. For convenience, different CMCs are indicated by the abbreviation as shown in Table 3.

Abbreviation	DP	DS	Viscosity/mPa s
CMC-215L	215	0.38	73.3
CMC-215M	215	0.44	14.4
CMC-215H	215	0.60	10.8
CMC-501L	501	0.43	1388
CMC-501M	501	0.58	225
CMC-501H	501	0.72	29.7
CMC-697L	697	0.39	2180
CMC-697M	697	0.48	470
CMC-697H	697	0.66	45.0
CMC-845L	845	0.42	2897
CMC-845M	845	0.51	634
CMC-845H	845	0.66	66.5

 Table 3. Properties of different CMCs.

To study the reaction of silicon between 0.01 and 1.00 V versus Li/Li⁺, the cyclic voltammetry spectra of silicon anodes containing CMC-215L was characterized and the curves are shown in Fig.4. In the cathodic scan of the 2nd and 3rd cycles, the distinct peak at 0.13 V corresponds to the lithiation of the nano-silicon and the formation of LixSi.[26, 27] When the voltage rises to 0.36 and 0.55 V, the two appeared peaks are attributed to the delithiation of LixSi and the formation of nano-silicon. As the

cycle number increases, the two peaks become stronger result from the gradual activation of the electrode.[28]



Figure 4. The cyclic voltammetry spectra of Si anodes containing CMC-DP215L.



Figure 5. Long term stability of Si anodes containing different CMC with different DP. (a)DP=215; (b) DP=501; (c) DP=697; (d)845.



Figure 6. Long term stability of electrodes prepared using CMC with different DS. a)CMC-L(b) CMC-M (c) CMC-H.



Figure 7. Binding mechanism of CMC with different DP in the lithiation and delithiation of silicon.

As shown in Fig.5, the cycle stability of silicon anodes was influenced by the CMC with different molecular structures. Owing to the volume expansion of the silicon negative electrode during the lithiation process, the specific capacity of all the electrodes decreased with the increase of cycles, but the cycling stability shows a significant difference. For all the CMCs with different DP, the electrodes containing CMC with higher DS showed a more unstable cycling performance. The best cycling performance were available by using the CMC with the lowest DS, due to their more hydrophobic and more easily bonded to the same hydrophobic silicon for superior performance. Fig.6 indicates that the CMC with the DP of 215 exhibited the best cycling stability.



Figure 8. Coulomb efficiency of Si anodes containing CMC with different DP. a) DP=215; (b) DP=501; (c) DP=697; (d) DP=845.

The silicon anodes containing CMC215L showed the best cyclic performance in this study (1656mAh g⁻¹ of the capacity was maintained after 100th cycle), also better than the related researches, as shown in Table 4.

Table 4. Comparison of cyclic performance of different silicon anodes with different binders.

Binders	Loading density of silicon(mg cm ⁻²)	Current density(mA g ⁻¹)	Cycle number	Discharge specific capacity(mAh g ⁻¹)	References
Ca ²⁺ -doped-alginate	0.4–0.5	1000	300	1245	[14]
CMC-1	0.45	420	100	893	[29]
CMC-2	0.7-0.8	840	100	1544	[30]
CMC-3	0.4–0.5	1000	200	912	[14]
CMC-215L	0.8-0.9	420	100	1656	This work

The CMC with low DP first exhibited a lower viscosity, which contributes to the sufficient uniform mixing of silicon and acetylene black. The mass of CMC added in every electrode are the same, so lower DP means a bigger number of moles, or more molecular chains. As shown in Fig.7, due to the steric hindrance, the silicon combined with the long chain CMC is prone to detached during the volume expansion, but is better with the short chain CMC. Reducing the DP and increasing the number of chains is beneficial to alleviating the stress of volume expansion, thereby the application of CMC with relative lower DP is conducive to the cycle performance of silicon anode.



Figure 9. Impedance spectra of electrodes prepared using CMC with different DP at 100th cycle. (a) DP=215; (b) DP=845.

Ta	b	le 5	. I	EIS	parameters	of (electrod	les	with	different	CMCs	at	100	Əth	cy	cle.
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EIS parameters	CMC215L	CMC215M	CMC215H	CMC845L	CMC845M	CMC845H
$Rs(\Omega)$	17.3	18.7	6.4	14.1	7.3	5.8
$Rct(\Omega)$	214.5	168.7	176	125.3	109.7	120.9

The capacity of Si anodes rebounded with the increase of cycles. This is because the free silicon powder is attracted by the carboxymethyl groups on CMC[31] and re-discharged, but this unstable structure will destroy the SEI film of the electrode, resulting in the consumption of lithium ions and the unstable in coulombic efficiency as shown in Fig. 8.

To study the effect of CMC on electrode resistance, the EIS of electrodes using CMC with different DP and DS after 100th cycles was tested. As shown in Fig.9, all the curves consist of a semicircle in the high frequency region and an oblique line in the low frequency region, which correspond to the charge transfer and diffusion processes, respectively. The EIS parameters of electrodes are calculated by using Zview software and provided in Table 5. The electrodes containing CMC with lower DS showed larger impedance. It could be explained that the increase of DS favored the conduction performance of lithium ions, thereby reduced the impedance of electrode. This also shows that there is no direct relationship between impedance and cycle stability.



Figure 10. SEM micrographs of fresh (a,c,e,g) and cycled (b,d,f,h) electrodes containing CMC with different DP (a,b) DP=215; (c,d) DP=501; (e,f) DP=697; (g,h) DP=845.

The morphology and structure of the fresh electrode and electrode of CMC with different DP after the 100th cycle were characterized by SEM as shown in Fig.10. The SEM micrograph of all fresh electrodes showed a uniform and comparable morphology. The bright white spot in the SEM micrographs represent the poorly conductive silicon powder. The surface of electrodes using different CMC as the binders were different after the cycles, and the surface of all the electrodes were inevitably cracked which contribute to the volume change of silicon particle during the cycle. However, the cracks were different in the size and distribution. It can be seen that the distribution density of cracks in the electrode containing CMC215L was significantly less than the others. CMC215L exhibited better binding properties to combine active materials so that the density of cracks were tolerated in the serious volume change (Fig.10B). It is assumed that the CMC with specially designed molecular structure played a key role in binding the silicon particles during the cycles and weakened the volume effect.

4. CONCLUSION

The study presented here is trying to figure out the influence of the molecular structure of CMC on the cyclic performance of Si anodes. A series of CMCs with different DP and DS were successfully prepared by adjusting the molecule weight of cellulose and controlling the process of carboxymethylation reaction. In this study, with the increase of DS, the cyclic performance of electrode become more unstable due to the reduced hydrophobicity which contributes to lower affinity with Si NPs. Compare to the other CMCs, the electrode containing CMC of DS= 0.38 and DP = 215 shows the best cyclic performance (71% of capacity maintained after the 100th cycle) due to its more compatible molecular structure.

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