Influence of Degree of Substitution of Carboxymethyl Cellulose on High Performance Silicon Anode in Lithium-Ion Batteries

Xinxin WANG, Jian LIU,* Zhengliang GONG, Chaofan HUANG, Shuaishuai HE, Lubing YU, Lihui GAN, and Minnan LONG

College of Energy, Xiamen University, Xiamen 361005, China

* Corresponding author: jianliu@xmu.edu.cn

ABSTRACT

Binder is one of the key materials which affect the electrochemical performance of the Li-ion batteries. As a promising binder, carboxymethyl cellulose (CMC) is a derivative of cellulose, in which the hydroxyl (3 per unit) is replaced by the carboxymethyl group. It attains more and more attention. However, few studies have been carried out on CMC with the degree of substitution (DS). In this study, CMC with different DS was synthesized by a specially designed method. The raw materials and products were characterized with FT-IR, 1H-NMR, 13C-NMR and XRD. A series of CMC with different DS were prepared as silicon-based binder of anode of lithium-ion batteries. Electrical tests, including galvanostatic charge-discharge, cyclic voltammetry, AC impedance and rate capability were performed to evaluate the silicon-based anode. Results showed that the discharging specific capacity of silicon-based anode using CMC of DS = 0.55 in the first and 50th cycle were 2917.0 mAh/g and 1607.6 mAh/g, and the electrochemical performance was superior to those using CMC with lower (0.23 and 0.43) or higher (0.72 and 0.86) DS. The current study confirms that DS of CMC has strongly affected battery performance parameters such as deliverable capacity, power, cycle-life and storage performance etc. The working mechanism is also investigated on why the CMC with the best DS is compatible with the silicon-based anode.

Keywords : Silicon-based Anode, CMC, Degree of Substitution, Binder

1. Introduction

Binder is a critical material in the preparation of electrodes for lithium-ion batteries to connect current collector, conductive components and active components. It plays an important role in the improving performance of lithium-ion battery, especially cyclic performance. Currently, oil-based binder polyvinylidene fluoride (PVDF) is popular in most commercial batteries. However, PVDF has its own shortcomings. It is attributed to the disabled binder, which makes active materials fall off and then invalids the electrode. Meanwhile, the binder tends to generate LiF in the cycle process which does harm to the battery. Moreover, as the corresponding dispersant to PVDF, N-methyl pyrrolidone (NMP) is expensive, flammable, explosive and hazardous, and may give rise to environmental pollution. Therefore, development of a new type of green water-based alternative binder to replace organic solvent-PVDF is of far-reaching significance, and has gradually become a hot topic to meet the modern social demand for green energy saving production.

Carboxymethyl cellulose (CMC), as the carboxymethylation derivative of cellulose, is a water-absorbing expansible polymer. As an aqueous binder, it is relatively cheaper, environment-friendly. Furthermore, another great advantage is its easy disposability at the end of life of battery. CMC consists of blinked glucose monomeric units with 0.6 to 1.2 carboxymethyl side groups per unit. The predominant functional group is hydroxyl (3 per unit), being replaced by the carboxymethyl group during derivatization. The number of carboxymethyl groups per unit is defined as the degree of substitution (DS), which is responsible for the physic-chemical property of CMC relative to original cellulose. The cellulose is an insoluble macromolecule with rigid backbone structure due to the nature of the polysaccharide chain but the derivatization changed it. As an aqueous binder, CMC with a certain DS can dissociate in water to form carboxylate anionic functional groups. Moreover, the DS influences viscosity and hydrophobicity of CMC, and provides unknown electrochemical property in lithium-ion battery deserving research.

Liu et al. applied CMC/SBR as the binder on Si and carbon coated Si (carbon content about 27 wt%) electrode, and studies have shown that the cycle performance of SBR/CMC electrode was improved significantly compared with those of PVDF electrode. Buqa et al. studied CMC/SBR used in a Si/C anode containing 10 wt% Si and found that the cyclic performed better than PVDF electrodes with the specific capacity remaining around 550 mAh/g after 150 cycles. Guo et al. developed the slurry spray technique to build a polymer scaffold CMC structure for high capacity silicon anode of lithium-ion battery. Unfortunately, the above researches are limited on the application of water-based CMC binder in lithium-ion batteries, but the study carried out with the DS of CMC is rare.

In this paper, microcrystalline cellulose was used as raw material in solvent slurry process with a large slurry ratio by repeated alkalinization and etherification to prepare CMC with different DS. The nano-silicon with theoretical capacity as high as 4200 mAh/g was used as the anode material of lithium-ion battery. The effects of CMC with different DS on the electrochemical performance of silicon anode were investigated and related functional mechanism was also discussed.

2. Experimental

2.1 Preparation of CMC

The synthetic process of CMC is as follows: 80 ml of ethanol, 26.67 g of 15% NaOH solution and 5.00 g of microcrystalline cellulose (MCC) powder were mixed in a florence flask with stirring for alkalinize at 30°C for 0.5h. And then 6.00 g of sodium chloroacetate was added at the end of alkalinization, raising the temperature to 60°C and etherizing for 1 h, neutralizing the solution with glacial acetic acid at the end of reaction. The sample was
Table 1. DS and viscosity of prepared samples.

| Sample | DS | Viscosity (mPa·s) |
|--------|----|------------------|
| CMC-1  | 0.23 | 10.30 |
| CMC-2  | 0.43 | 7.08  |
| CMC-3  | 0.55 | 6.78  |
| CMC-4  | 0.72 | 6.42  |
| CMC-5  | 0.86 | 5.16  |

washed with 80% ethanol for 3 times, filtered and dried to obtain CMC-1. The above alkalization and etherification process was repeated for (n-1) times with CMC-1 to obtain CMC-n (CMC-2, CMC-3, CMC-4 and CMC-5).

DS was determined by acidity meter method according to the literature. DS was calculated with the following formula:

\[
DS = \frac{B}{m - 0.08B} \tag{1.2}
\]

In which, B: mmols of carboxymethyl in each gram of sample, mmol/g; \( V_1 \): volume of sulfuric acid volumetric solution (Shanghai, Guoyao), mL; \( c_1 \): concentration of sulfuric acid volumetric solution, 0.0566 mol/L; \( m \): weight of purified sample, g.

Viscosity was measured according to the reported method. Viscosity of samples are summarized in Table 1.

2.2 Battery preparation

Each aqueous solution containing 2.5% of dissolved CMC was subjected to ball mill at 300 rpm for 0.5 h and then 500 rpm for 3.0 h with a ratio of nano-silicon (100 nm, 99%, Alfa, Shanghai): acetylene black: CMC = 7.0:1.5:1.5 to make a slurry. The slurry was coated on the copper foil (thickness is 0.08 mm, and diameter is 14 mm) and dried at 80°C in a vacuum oven for 24 h. The button batteries were prepared in a glove box with lithium as the counter electrode, Celgard 2400 membrane as the separator and 1 mol/L LiPO4/EC+DMC (volume ratio 1:1, battery grade)/10% FEC as the electrolyte.

2.3 Test and analysis

The structure of CMC was characterized with FT-IR spectroscopy, NMR and XRD. The cyclic performance and rate capability of the material were inspected with LAND battery testing system. The cyclic voltammetry and AC impedance were tested with electrochemical workstation (ChenHua, ShangHai). The structure of the material were inspected with LAND battery testing system. The structure of CMC was characterized with FT-IR spectroscopy (Shanghai, Guoyao). The cyclic performance and rate capability of the material were inspected with LAND battery testing system. The cyclic voltammetry and AC impedance were tested with electrochemical workstation (ChenHua, ShangHai). The structure of the surface of the electrodes was observed by SEM.

3. Results and Discussion

3.1 Synthesis and analysis of CMC

In order to understand how DS regulates effect of CMC binder, a series of samples with different DS were produced. It is shown in Fig. 1 that the diffraction peak appears at \( 2\theta = 15.7^\circ \) is the typical crystal form I of cellulose and the strong diffraction peak at \( 2\theta = 22.5^\circ \) is the 002 crystal phase of cellulose. As the characteristic spectrum of cellulose, the diffraction peak at \( 2\theta = 15.7^\circ \) disappears. Meanwhile, the strong diffraction peak at \( 2\theta = 22.2^\circ \) shifts to 20.0°, as the process of alkalization and etherification destroys the crystalline form of cellulose and some hydrogen bonds are opened, indicating the generation of CMC.

The IR spectra of MCC and CMC are shown in Fig. 2. The absorption peaks at 3410 cm\(^{-1}\), 1100 cm\(^{-1}\) and 1000 cm\(^{-1}\) correspond to the stretching vibration of –OH, C–O and C–O–C in the molecular skeleton of cellulose and CMC. But CMC shows the characteristic absorption peaks at 1604 cm\(^{-1}\), 1430 cm\(^{-1}\) and 1324 cm\(^{-1}\), assigned to the asymmetric and symmetric stretching vibration of –COO– and the stretching vibration of C–H in carboxymethyl group, which is the major difference between CMC and MCC. It clearly indicates that a certain amount of carboxymethyl group have generated in the synthesized CMC after alkalization and etherification in the derivatization process.

The \(^1\)H-NMR spectrum is provided in Fig. 3a. The peaks with chemical shifts between 3.0 and 5.0 are assigned to the characteristic peak of H in CMC, but the structure of CMC cannot be elucidated directly with this spectrum. The \(^13\)C-NMR spectrum in Fig. 3b and 3c shows that peaks with chemical shifts of 108–100 and 63–58 correspond to the characteristic peaks of 1 C and 6 C, and peaks with chemical shifts between 90–70 are assigned to the characteristic peaks of 2 C, 3 C, 4 C, 5 C and 7 C, respectively. The peak of chemical shifts of 182–175 in Fig. 3c, which is caused by carbon on the substituent, indicates the formation of carboxymethyl. The naming rule of carbon atoms in the structure of CMC is shown in Fig. 3d. It has been confirmed in the experiment that carboxymethyl group are connected to the molecular chain of cellulose, so that CMC with a certain DS can be produced with MCC by this specially designed process in a large slurry ratio.

3.2 Electrochemical performance

In order to investigate the effects of DS on the electrochemical
performance, the prepared CMC (CMC-1 to CMC-5) were employed as the binders in silicon anodes. It can be seen from Fig. 4 that the electrode using CMC with DS of 0.55 showed the best cyclic performance. The specific capacity of all the 5 electrodes saw a severe capacity fading in the first 3–5 cycles, but the downtrend of the best sample (DS = 0.55) tended to slow after the 3rd cycle and remained 1407.2 mAh/g in the 100th cycle, while those of the others were 531.4 mAh/g, 877.2 mAh/g, 980.7 mAh/g and 559.6 mAh/g, respectively. The degree of cycling degradation by different degree of substitution is shown in Fig. 5. The sample of DS = 0.55 gives the best result. As a contrast, the electrode using PVDF showed poor cyclic performance, and the capacity tends to be zero after the 20th cycle. In literature reports, the cyclic stability of the electrode tends to monotonously increase with the DS of CMC due to more functional groups enforcing viscidity. However, the DS of 0.55 gives the best cyclic performance in this research. It seems that the former common understanding on the function of binder is questionable. Since the carboxymethyl group is highly hydrophilic, it is concluded that excessive functional carboxymethyl groups may reduce the hydrophobicity and weaken the hydrophobic bond between binder and silicon powder.

The capacity retentivity of the electrode using CMC with different DS within the voltage range of 0.0–3.0 V are shown in Fig. 6. The capacity reversibility and retentivity of the prepared batteries were investigated under a relative low rate of 0.1 C in 5 cycles, and then the rate was raised to the interval of 0.1 C to 2.0 C (147 mA/g to 2940 mA/g) to evaluate the rate capacity. Based on Fig. 6, all the 5 electrodes using different CMC showed a high reversible capacity of 2500 mAh/g–3000 mAh/g, but the capacity of the electrodes using CMC with DS of 0.23, 0.43, 0.72 and 0.86 attenuated rapidly in the first 5 cycles, but those with DS of 0.55 attenuated relative slowly. When the rate were 0.2 C, 0.5 C, 1.0 C and 2.0 C, the average reversible capacity reduced to 1736.5 mAh/g, 1576.7 mAh/g, 1412.9 mAh/g and 1172.0 mAh/g, successively. Nevertheless, as the rate decreased to 0.1 C again, the reversible
capacity of those with DS of 0.55 returned to 1883.3 mAh/g and maintained a stable level of 1766.2 mAh/g, 64.06% of the reversible capacity in the first cycle. Therefore, the best rate capacity of the electrode is available by using CMC with DS of 0.55.

AC impedance graph in open circuit state of electrodes using CMC with different DS is shown in Fig. 7. It can be seen that after the first charge-discharge cycle, the following curve consists of a high-frequency semicircle region and a diagonal line of low-frequency region. The semicircle of high-frequency region represents the superposition of impedance of lithium ion through SEI membrane and charge transfer resistance, and the line of low-frequency region reflects the diffusion impedance of lithium ion in silicon electrodes.\(^\text{17}\) Compared with the others, the impedance of lithium ion through SEI membrane and the charge transfer impedance of electrodes using CMC with DS of 0.55 were relative lower, while those of the others showed no obvious difference. It is concluded that because of the existence of suitable covalent bonds and hydrophobic forces, CMC with DS of 0.55 can transmit lithium ions more efficiently, so the charge transfer impedance is smaller, this speculation is similar to the principle that guar gum is capable of transmitting lithium ions efficiently.\(^\text{18}\) In addition, the presence of these forces makes the silicon particles not break easily, so the generated SEI membrane are stable and uniformity, therefore the membrane impedance is relative small. While the SEI membrane formed in other samples is unstable and its conductivity is poor.

Therefore, the membrane impedance and charge transfer impedance are larger.

Figure 8 shows the respective cyclic voltammetry of electrodes using CMC of DS = 0.23 (a), 0.55 (b) and 0.86 (c) at a scanning rate of 0.001 mV s\(^{-1}\).

Figure 6. Rate capacity of electrodes using CMC with different degree of substitution.

Figure 7. Impedance graph of the electrodes prepared with 5 types of CMC.

Figure 8. Respective cyclic voltammetry of electrodes using CMC of DS = 0.23 (a), 0.55 (b) and 0.86 (c) at a scanning rate of 0.001 mV s\(^{-1}\).
became smaller in the 2nd cycle and latter cycles, describing relative poor structure stability. The formation of SEI film consumes some lithium ions, which makes the irreversible capacity of first cycle increase, and reduces the charge and discharge efficiency of electrodes. It explains why the charge and discharge efficiency of electrode with CMC of DS = 0.55 (62.06%) is lower than those of 0.23 (70.76%) and 0.86 (69.63%). The embedding reaction of lithium ion into silicon occurred with a voltage under 0.80 V and two oxidizing peaks appeared around 0.32 V and 0.52 V during the anode scanning process, which were related to the escaping reaction of lithium ion from Li\(_x\)Si alloy. The current density of two oxidizing peaks increases after the activation process. The peak electric current in CV curve reflects the activity (reaction speed) of the electrode reaction. The peak electric current of samples with CMC of DS = 0.23, 0.55 and 0.86 are 511.1, 548.5 and 431.2 mAg\(^{-1}\) in the 4th cycle, respectively. Comparing the CV curve of electrode, it is also found that the peak electric current of DS = 0.55 was larger than those of DS = 0.23 or 0.86, showing a higher reaction activity.

Based on the above results, CMC with DS of 0.55 has a certain advantage in the improvement of the electrochemical performance of lithium-ion battery, and the related function mechanism is inferred as follows.

The superiority of CMC electrode is due to that carboxymethyl group on the surface of CMC molecule forms a covalent bond (Si–O–CO–R) with the hydroxyl group absorbed on the surface oxidation layer of Si-based electrode.\(^2\) It is interesting to note that in common sense, CMC with a higher DS has more active points to form chemical bond with the surface of Si particles. Increasing DS to a certain extent may enhance the connection between CMC and Si particles,\(^2\) thus improved the cyclic performance of lithium-ion battery. But excessive high DS tended to result in self-bonding and coiling of CMC inside particles, which may have a negative impact on the binding performance between anode materials.\(^2\)

The hydrophobicity of binder also affects the electrochemical performance.\(^2\) The higher the hydrophobicity is, the stronger the interaction between the binder and the hydrophobic silicon particles becomes, and the better the electrochemical performance shows. The measured contact angles of CMC with different DS are 58°, 39°, 32°, 24° and 20°, as shown in Fig. 9. With the increase of DS, the hydrophobicity of CMC decreases. Compared with those of 0.72 and 0.86, the CMC with DS of 0.55 is easier to combine with the hydrophobic Si.

Therefore, the reason for the excellent electrochemical performance of CMC of DS = 0.55 is the synergistic action of covalent bonds and hydrophobic bonds. When the number of covalent bonds and hydrophobic bonds are kept at a suitable level, the electrochemical performance of the binder is optimal.

Another worth noting potential reason is that the sodium ions associated with carboxymethyl groups are also known to cause volume effect in the electrolyte, which may further destroy crystal structure and impact the cycle stability. Therefore, the electrode using optimized CMC has a stronger skeleton and better performance.

The surface structure of electrodes prepared by different DS before the charge discharge cycle is shown in Fig. 10. When 0.55 is the binder, the electrode materials uniformly disperse, and the porous electrode structure is clear. However, the electrode material on the surface is reunion more or less when CMC of other four DS are used as binder. It may be associated to covalent bonds and hydrophobic bonds.
In this work, CMC of different DS was prepared with solvent slurry method in a large slurry ratio by a repeated alkalization and etherification process, and characterized by XRD, IR and NMR. The effects of CMC with different DS on the electrochemical performance of Si-based anode were investigated, including cycle performance, multiplier performance, impedance performance and cyclic voltammetry. Compared with the Si-based electrodes using CMC with DS of 0.23, 0.43, 0.72 and 0.86, those with DS of 0.55 had a higher specific capacity and a better cyclic performance, and showed the best specific capacity of 1407.2 mAh/g at the 100th cycle. Its electrochemical performance was also superior to those of both lower DS (0.23, 0.43) or higher DS (0.72, 0.86). The experimental results show that DS have a great influence on the capacity and cycle life of lithium ion battery. As the key binder component in an electrode, CMC with the optimized DS can promote cycle life and avoid irreversible capacity loss. Therefore, it is going to play a more crucial role in the fabrication of electrodes and their electrochemical performance.

Acknowledgments

This work was supported by the President Fund of Xiamen University (No. 20720150090), and the Energy development Foundation of Energy College, Xiamen University (No. 2017NYFZ02).

References

1. L. L. Chai, L. Zhang, and Q. T. Qu, Chemistry, 76, 299 (2013).
2. N. S. Hochgatterer, M. R. Schweiger, and S. Koller, Electrochem. Solid-State Lett., 11, A76 (2008).
3. S. S. Zhang, K. Xu, and T. R. Jew, J. Power Sources, 138, 226 (2004).
4. M. Hossein, G. P. Deng, and K.-H. Inna, J. Electrochem. Soc., 147, 4470 (2000).
5. J. L. Wan, L. Zhao, and L. Xie, Battery Bimonthly, 42, 81 (2012).
6. J. R. He, H. X. Zhong, and D. Shao, Advance In New And Renewable Energy, 3, 231 (2015).
7. A. Gueith, M. Kaneko, and M. Peitcnler, J. Power Sources, 163, 1047 (2007).
8. S. F. Lux, F. Schappacher, A. Balducci, S. Passerini, and M. Winter, J. Electrochem. Soc., 157, A320 (2010).
9. W. N. Liu, M. H. Yang, and H. C. Wu, Electrochem. Solid-State Lett., 8, A100 (2005).
10. H. Buqaa, M. Holzapfel, and F. Krumeich, J. Power Sources, 161, 617 (2006).
11. J. C. Guo and C. S. Wang, Chem. Commun., 46, 1428 (2010).
12. X. Wang, Y. Zhai, and W. Zhan, J. Food Safety and Quality, 6, 3145 (2015).
13. Standardization administration of the people’s republic of China, Food additive – sodium carboxymethyl cellulose GB1904-2005, China standard press (2005).
14. M. P. Adinugraha, D. W. Marseno, and Haryadi, Carbohydr. Polym., 62, 164 (2005).
15. J. Zhao, Z. Li, and Y. Y. Qian, New Chem. Mater., 42, 87 (2014).
16. L. Xie, L. Zhao, J. Wan, and Z. Shao, J. Electrochem. Soc., 159, A499 (2012).
17. M. Q. Li, M. Z. Qu, and X. Y. He, Electrochim. Acta, 54, 4506 (2009).
18. Y. N. Sudhakar, M. Selvakumar, and D. K. Bhat, Mater. Sci. Eng., B, 180, 12 (2014).
19. W. Li, R. Yang, X. Wang, T. Wang, J. Zheng, and X. Li, J. Power Sources, 221, 242 (2013).
20. Y. Zhang, J. Gao, L. J. Fu, L. C. Yang, Y. P. Wu, and H. Q. Wu, J. Mater. Chem., 17, 1321 (2007).
21. J. S. Bridel, T. Azais, and M. Morcrette, Chem. Mater., 22, 1229 (2010).
22. J. H. Lee, U. Paik, V. A. Hackley, and Y. M. Choi, J. Electrochem. Sci., 147, 249 (2005).