



## Improvement of cyclability of Si as anode for Li-ion batteries

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### ABSTRACT

Silicon working as anode for Li-ion batteries has attracted much attention due to its high capacity ( $\sim 4200 \text{ mAh g}^{-1}$ ). However, due to the large volume expansion during lithiation, the capacity of silicon fades very fast. In this systematic study, we focus on the issue to fight the capacity fading. Results show that Si with sodium carboxymethyl cellulose (Na-CMC) as a polymer binder exhibits a better cyclability than that with poly(vinylidene fluoride) (PVDF). Yet differing from the system used in PVDF, the addition of vinylene carbonate (VC) does not improve or even worsens the performance of the system using Na-CMC. In addition, the small particle size of Si, a large amount of carbon black (CB), the good choice of electrolyte/conducting salt and charge–discharge window also play important roles to enhance the cyclability of Si. It is found that electrode consisting of 40 wt.% nano-Si, 40 wt.% carbon black and 20 wt.% Na-CMC (pH 3.5) displays the best cyclability, and in the voltage range from 0 to 0.8 V, after 200 cycles, its capacity can still keep  $738 \text{ mAh g}^{-1}$  (C/2, in 1 M LiPF<sub>6</sub> ethylene carbonate/diethyl carbonate electrolyte, with VC-free), almost twice as that of graphite.

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### 1. Introduction

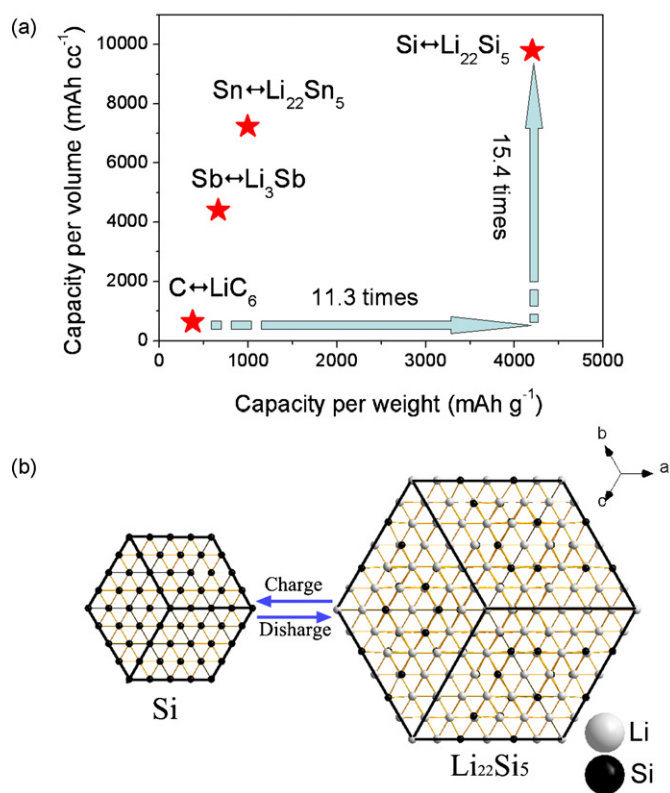
Li-ion batteries are the most successful energy storage devices invented in the past two decades and have dominated the portable electronic market. Meanwhile, with the development of high performance of central processing unit in laptops and the use of 3D techniques in cellular phones, we should seek higher-power and longer-life batteries. To meet these requirements, it is necessary to find higher capacity electrode materials. However, at present, the most widely used anode material is graphite, whose theoretical capacity is only  $372 \text{ mAh g}^{-1}$  [1]. Another disadvantage of graphite is its low energy density ( $508 \text{ mAh cc}^{-1}$ ). Compared with graphite, elemental materials that can alloy with lithium, such as Si ( $4200 \text{ mAh g}^{-1}$ ) [2], Sn ( $994 \text{ mAh g}^{-1}$ ) [3] and Sb ( $660 \text{ mAh g}^{-1}$ ) [4], are promising alternative candidates due to their markedly higher capacities. And among them, silicon delivers the highest capacity of  $\sim 4200 \text{ mAh g}^{-1}$ , more than 10 times that of graphite. Fig. 1a shows the comparison of these anode materials in mass capacity and energy density (their capacities are calculated based on de-lithiated samples). Though Si seems to be a good candidate of anode material, due to the huge volume expansion in lithiation/de-lithiation, its capacity fades very fast during cycling [2]. Fig. 1b displays the illustration of volume change from Si to

the full-discharge state of Li<sub>22</sub>Si<sub>5</sub> and in the whole charge and discharge process, the volume of Si undergoes a volume change of about 300% (expansion in discharge and contraction in charge). This huge volume change will cause the electrode to lose contact and to increase electronic resistance. Therefore, the main issue of improvement of Si cyclability is how to overcome the volume change.

The first promising way is the use of nano-Si. The density of nano-materials is usually very low, a large number of pores are left to accommodate the volume change during cycling, therefore, under the same condition, nano-Si displays more excellent cyclability than Si of large scales [5,6]. It should be mentioned that though some Si films prepared by vacuum deposition or other techniques exhibit an excellent electrochemical performance [7,8], considering the handling process, the rigid films are easily broken and not suitable for industrial applications. Therefore, our study is only focused on Si powders. The second widely used way is to coat carbon on Si surface [9], using the soft carbon to tolerate the volume change and enhance the electronic conductivity. Similar to the function of carbon, the addition of a secondary phase, such as Si–M alloys/composites (M=Fe, Zn, Ag, Sn and so on) can also enhance the Si cyclability [10–14]. The third way that is easily achieved is to add more carbon black (CB) in the electrode preparation [15]. Beattie et al. [16] have demonstrated by geometrical calculation that the electrode is better made with  $\leq 20\%$  Si (calculated with 270% volume expansion, forming Li<sub>15</sub>Si<sub>4</sub>). However, the addition of a large amount of CB decreases the energy density. Another way is the use of an elastomeric polymer binder instead of the traditional

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**Fig. 1.** (a) Comparison of graphite, Si, Sn and Sb as anode materials in mass capacity and energy density. (b) Illustration of Si volume expansion during charge and discharge.

binder poly(vinylidene fluoride) (PVDF), which is a stiff polymer. Compared with PVDF, the elastomeric polymers, such as styrene butadiene rubber (SBR), can overcome the volume change to some degree [17]. Recently, Li et al. [18] have reported that sodium carboxymethyl cellulose (Na-CMC), despite as a stiff polymer, can also significantly improve the cyclability of Si. The reason is due to the esterification between hydroxyl on Si surface and carboxyl in CMC [19]. This effect results in that Si particles in CMC system contact much closer than that in PVDF system [20]. In addition, to enhance the esterification, pH value of CMC should be adjusted to obtain more carboxyl functional group. One of our targets in this study is to find the optimal pH value.

Up to now, all aspects mentioned above are only associated with electrode. Besides electrode, electrolyte also plays a crucial role in improving cyclability. For example, recently, Aurbach and co-workers [21] have reported that thin film silicon electrode exhibits an exciting performance with a stable capacity of about 3000 mAh g<sup>-1</sup> in the ionic liquid 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (MPPpTFSI) containing 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). The choice of appropriate electrolyte additives to enhance the formation for solid electrolyte interface (SEI) can also improve the Si cyclability, such as vinylene carbonate (VC), vinyl ethylene carbonate (VEC), vinyl acetate (VA), and so on [22,23].

In this study, we have systematically investigated all these aspects mentioned above and optimized the choice of silicon particle size, the amount of carbon black, polymer binder and electrolyte/conducting salt/additive. Our results show that after optimization, the cyclability of Si as anode can be significantly improved, and after 100 cycles at C/2 rate, the cell can still deliver a capacity of more than 1000 mAh g<sup>-1</sup>.

## 2. Experimental

Si powders with two different average particle sizes, micro-Si (Sinopharm Chemical Reagent Co., Ltd., 200 mesh) and nano-Si powder (Aldrich, 98%, average particle size: 50 nm), were used as the active materials of electrodes. In one of the optimized conditions, the electrode was comprised of 40 wt.% nano-Si, 40 wt.% CB and 20 wt.% Na-CMC (pH 3.5, dissolved in 5 wt.% distilled water, adjusted by formic acid). The electrolyte was a solution of 1 M LiPF<sub>6</sub> dissolved in EC/DEC (1:1 w/w) where EC and DEC stood for ethylene carbonate and diethyl carbonate, respectively. Lithium metal was chosen as the counter electrode. Coin cells (CR 2032 type) were assembled in an argon-filled dry-box (MBraun Labmaster 130) with a porous polypropylene membrane (Celgard 2400) as the separator.

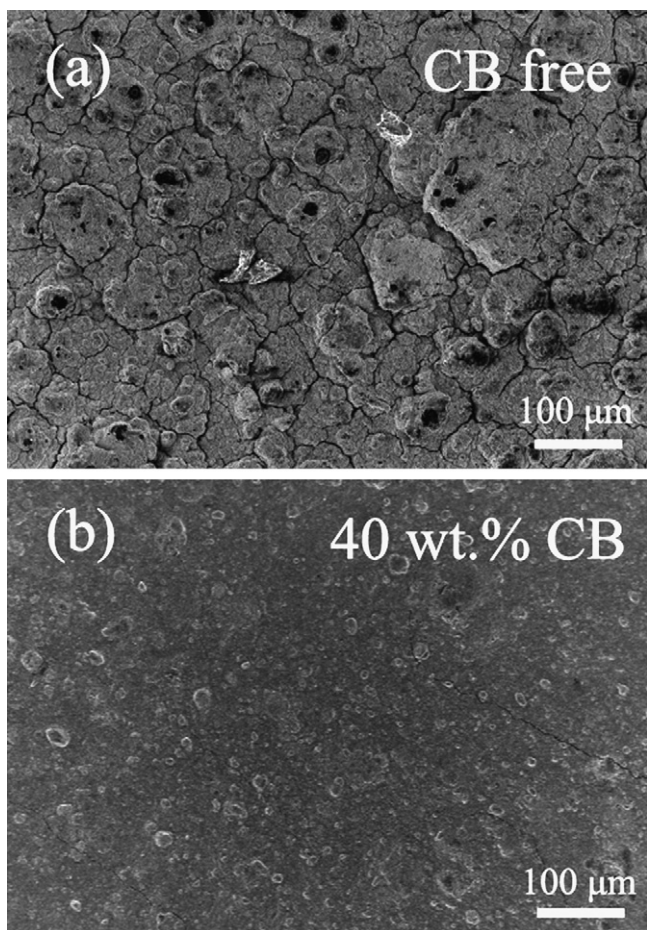
The cells were cycled on a multi-channel battery system (NewareBTS2300, Shenzhen) at two different rates: C/10 and C/2, herein, 1C means that the cell is full-discharged in 1 h. Electrochemical impedance spectra (EIS) were measured on CHI 604 Electrochemical Workstation in the frequency range from 100 kHz to 100 mHz. The open circuit voltage (OCV) in EIS measurements was controlled to 0.2 V. In order to achieve an equilibrium state, all cells for EIS were relaxed for 2 h before measurement. After discharged, the cells were disassembled in an argon-filled glove box. The electrodes were washed with anhydrous dimethyl carbonate (DMC) to remove the electrolyte residues. The morphologies of electrodes were characterized by field-emission scanning electron microscopy (FE-SEM, LEO 1530 Gemini), immediately after the electrodes were taken out of the glove box (less than 10 min).

Carbon-coated nano-Si was synthesized by mixing nano-Si and sucrose in a weight ratio of 1:1, and then the mixture is decomposed under Ar/H<sub>2</sub> flow at 750 °C for 5 h. The residual carbon is estimated to 23 wt.% in the final product. The electrode of carbon-coated nano-Si is composed of 80 wt.% carbon-coated nano-Si and 20 wt.% Na-CMC (pH 3.5), without adding CB.

## 3. Results and discussion

### 3.1. Optimizing the amount of carbon black

Fig. 2 shows the SEM images of nano-Si electrodes with and without CB after the first cycle (discharge to 2500 mAh g<sup>-1</sup>). The volume change of the electrode without CB is huge (Fig. 2a), and its surface is accidented. Moreover, among these “heaves”, the electrode film seems to be cracked and undergoes mechanical failure. This failure leads the electrode to lose contact and to increase the resistance. In comparison with the CB-free electrode, the electrode with 40 wt.% CB can distinctly tolerate the volume change of Si during lithiation, after lithiation, the surface of the electrode is still as smooth as before (Fig. 2b). Adding more CB can fight against the volume change but also decreases the energy density due to the low density of CB. Therefore, it is necessary to find a balance between cyclability and energy density. In an ideal condition, the CB particles should just cover all Si particles and form a mono-CB layer. However, it is difficult to evaluate its amount due to the aggregation of CB particles. Recently, the study of Tarascon's group has shown that the electrode with 33.3 wt.% Si and 33.3 wt.% CB shows the best cyclability [16]. Our results also reveal that the cycling performance of the electrode containing 40 wt.% CB is better than that containing 10 wt.% CB (Fig. 3, the coulombic efficiency in the first cycle, CE1, is also given). Thus, in our following study, the amount of Si, CB and polymer binder is fixed in the weight ratio of 2:2:1. In addition, a large initial capacity loss (ICL) of Si is observed in the first cycle, which comes from three aspects: (1) the formation of solid-state electrolyte interface (SEI) film; (2) the irre-



**Fig. 2.** SEM images of nano-Si electrodes with (a) CB-free and (b) 40 wt.% CB in the first cycle (discharge to 2500 mAh g<sup>-1</sup>).

versible capacity of carbon black; and (3) the oxidation layer on the Si surface. According to the studies of graphite, the ICL attributed to the formation of SEI film should be less than 100 mAh g<sup>-1</sup> [24], whereas the ICL resulting from carbon black is about 100 mAh g<sup>-1</sup> [25]. However, in our case, the ICL is extremely high, which can even reach 1500 mAh g<sup>-1</sup>. Thus the third effect (the oxidation layer on Si), instead of carbon black, plays a crucial role in causing the

ICL [26]. In fact, such a high ICL is usual for silicon-based anode materials [16,21].

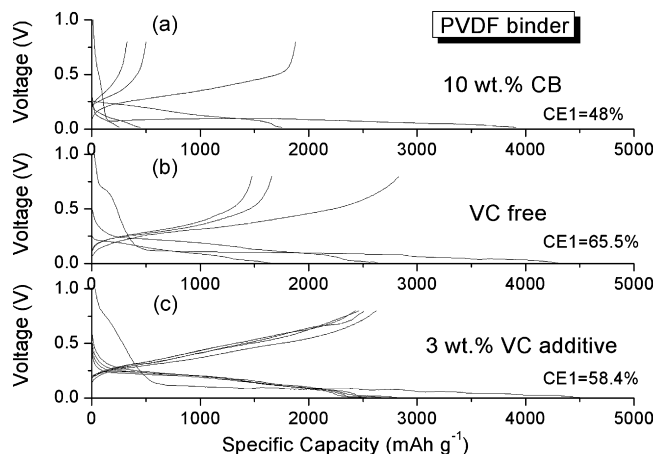
### 3.2. Optimizing the polymer binder

The capacity of the electrode using PVDF as a binder fades very fast (Fig. 3b). Though CMC is also a stiff polymer, there is an extra connection by the esterification between hydroxyl on Si surface and carboxyl in CMC. Thus, the connection of Si and CMC has been strengthened (Fig. 4) [20]. This effect can make CMC better tolerate the volume change. However, pure CMC is insoluble in water; hence CMC is usually replaced by the soluble Na-CMC. Furthermore, during the preparation of the electrode, the viscosity of binder should be also considered. Na-CMC is dissolved in distilled water with a concentration of 5 wt.% (pH 6.7). To find the optimization condition, formic acid was used to adjust the pH values to 5.4, 4, 3.5, 3.1 and 2, respectively. The galvanostatic charge–discharge curves of Si using Na-CMC binders at different values are shown in Fig. 5. In all cases, the electrodes deliver a discharge capacity of more than 4200 mAh g<sup>-1</sup> in the first cycle, and in the following charge process, the reversible capacities are about 3000 mAh g<sup>-1</sup>. Comparing these voltage profiles with different pH values, obviously, the best pH value is between 3.1 and 4. For long time cycling, the cell with Na-CMC (pH 3.5) shows the best capacity retention (Fig. 6).

### 3.3. Nano-Si and drying temperature

The large surface and short diffusion path usually cause the nano-sized electrode materials to display more excellent performance than micro-sized materials [27]. The cycling performances of micro-Si and nano-Si are shown in Fig. 7a. Nano-Si exhibits a better cyclability and after 200 cycles, still keeps a capacity of 738 mAh g<sup>-1</sup>, whereas, for micro-Si, its capacity drops to 249 mAh g<sup>-1</sup>, only one third of nano-Si. It is also found that in the first 40 cycles, the capacity of nano-Si fades a little faster than that of micro-Si, which is probably associated with the formation of SEI layer on the interface. Due to the large surface of nano-Si, it consumes more lithium and needs a longer time to form a stable SEI layer. The Nyquist plots of micro-Si and nano-Si in the 60th cycle are shown in Fig. 7b. The plots consist of two depressed semicircles in the high- and intermediate-frequency region and the Warburg-type element (the sloping line) in the low-frequency region, respectively. The first semicircle results from the SEI layer forming on the interface between electrolyte and electrode and the second semicircle corresponds to the charge transfer process. The impedance of SEI layer on nano-Si is about 2 Ω larger than that on micro-Si. Nevertheless, due to the quite low Li<sup>+</sup> ions diffusion coefficient in Si (~10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>) [8,28], the limiting process of the electrode reaction should be the Li<sup>+</sup> ion diffusion in Si. In this case, the large surface of nano-Si increases the contact area with electrolyte and the small particles of nano-Si decrease the Li<sup>+</sup> ion diffusion path, thus, nano-Si shows a smaller impedance of charge transfer and displays a higher capacity than micro-Si. Furthermore, the cycling performance of carbon-coated nano-Si is also tested (Fig. 7a). Though its capacity is lower than nano-Si, its cyclability has been improved. In addition, the conducting carbon in the electrode of carbon-coated nano-Si is only 23 wt.%, which is available to the energy density.

In addition to the composition of electrode, in the electrode preparation, one more process, drying, especially the drying temperature should be considered, for Si is not stable and its surface is easily oxidized to SiO<sub>x</sub>. Though the layer of SiO<sub>x</sub> is good for the connection between CMC and Si, if it is too thick, the layer would definitely affect the electrochemical performance of Si. Four drying temperatures (70, 100, 120 and 150 °C) were studied, the results show that the electrode drying at 70 °C exhibits the best cyclability



**Fig. 3.** Galvanostatic charge–discharge curves of nano-Si with PVDF binder containing (a) 10 wt.% CB and 40 wt.% CB in 1 M LiPF<sub>6</sub> EC-EDC based electrolyte with (b) VC-free and (c) 3 wt.% VC as the additive.

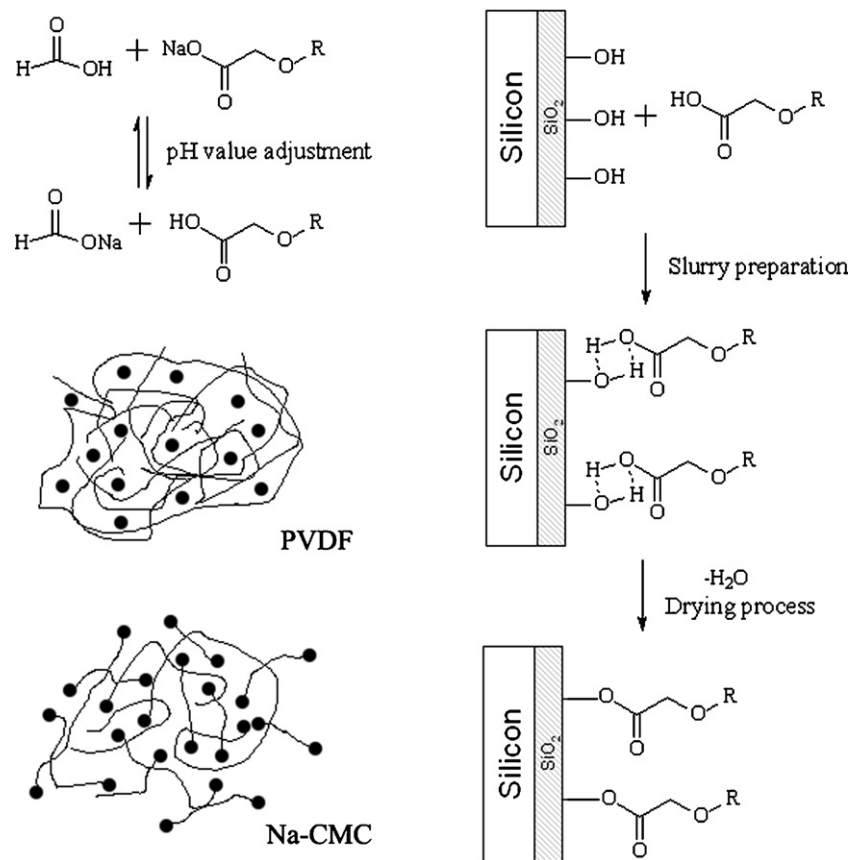


Fig. 4. Illustration of the esterification between hydroxyl on Si surface and carboxyl in CMC. This effect strengthens the connection between Si and CMC.

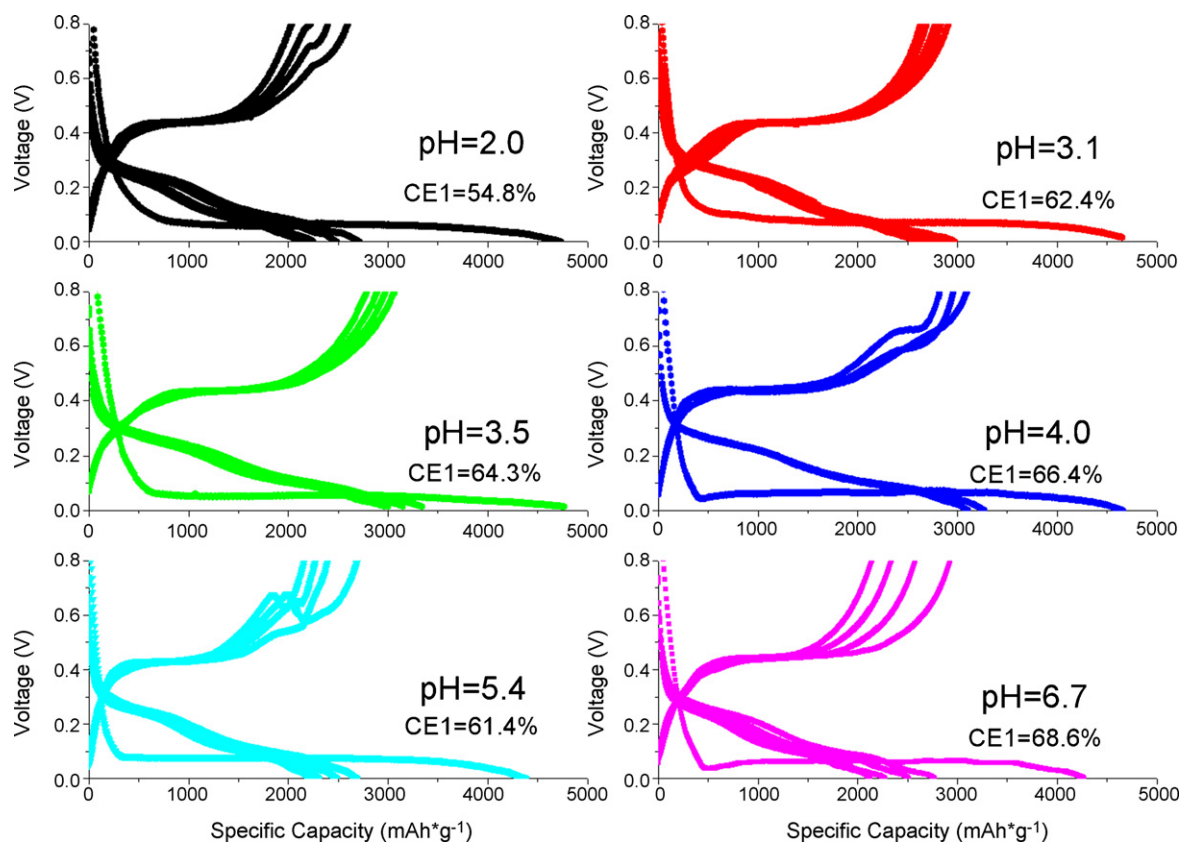


Fig. 5. Galvanostatic charge–discharge curves of micro-Si with Na-CMC binders in 1 M  $\text{LiPF}_6$  EC-EDC based electrolyte. Na-CMC was dissolved in distilled water with a concentration of 5 wt.% (pH 6.7) and the pH values were adjusted by formic acid to 5.4, 4, 3.5, 3.1 and 2, respectively.

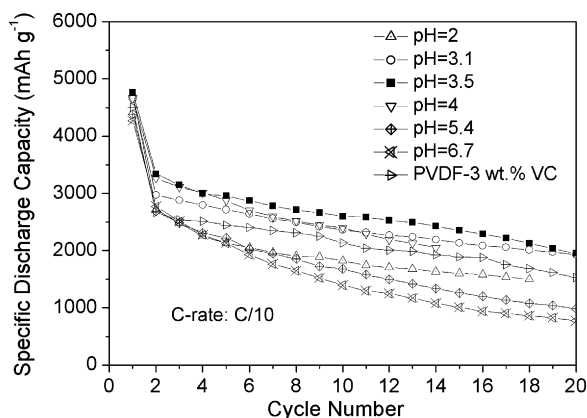


Fig. 6. Cycling performance of micro-Si with Na-CMC binders at different pH values and with PVDF binder.

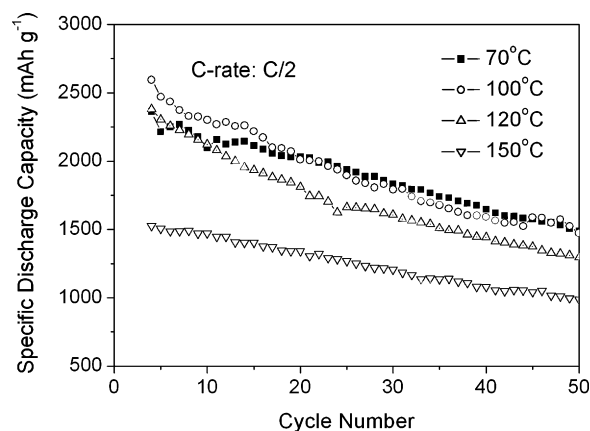


Fig. 8. Cycling performance of nano-Si electrodes drying at 70, 100, 120 and 150 °C.

(Fig. 8). With the temperature increase to 150 °C, the capacity drops to about 1600 mAh g<sup>-1</sup>. In addition, it is found that if the Na-CMC solution dried at 120 °C for a long time, the color of Na-CMC turns brown, probably indicating the decomposition/conglomeration of Na-CMC. To avoid these defects, the drying temperature is set at 70 °C.

### 3.4. Optimizing the electrolyte

Choosing an appropriate electrolyte, including organic solvent, conducting lithium salt and additive can also improve the electrode performance and enhance its cyclability. For example, due to the

low melting point of propylene carbonate (PC, -49 °C), PC based electrolyte is very suitable for batteries working at low temperatures; on the other hand, the melting point of EC is above 37 °C, thus EC-DEC based electrolyte leads to a poor battery performance at low temperatures. However, graphite can not be cycled in PC based electrolyte with LiPF<sub>6</sub> as the conducting salt, as PC molecule can insert into the graphite at a low potential around 0.9 V vs. Li and finally destroys its layer structure [29]. Then what about Si, if it can be cycled in PC based electrolyte? And it is also interesting to study whether the addition of a large amount CB will affect the Si cyclability. Fig. 9a shows the galvanostatic charge–discharge curves of

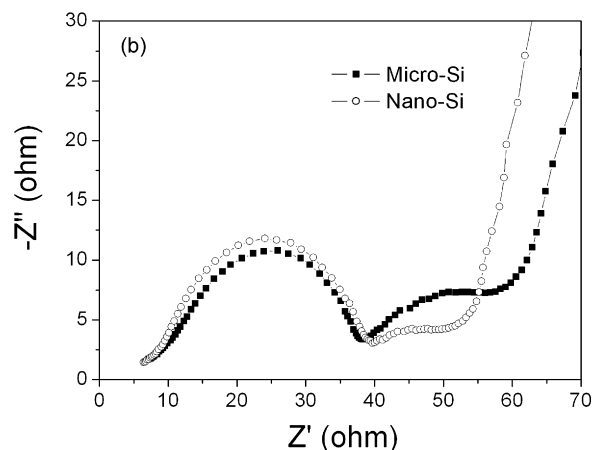
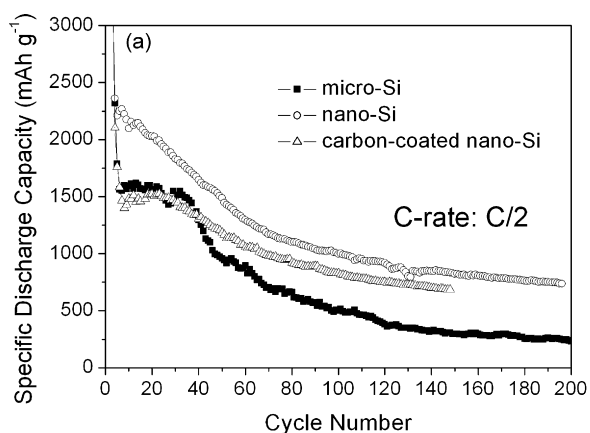


Fig. 7. (a) Cycling performance of micro-Si, nano-Si and carbon-coated nano-Si with Na-CMC binder (pH 3.5). (b) Nyquist plots of micro-Si and nano-Si in the 60th cycle.

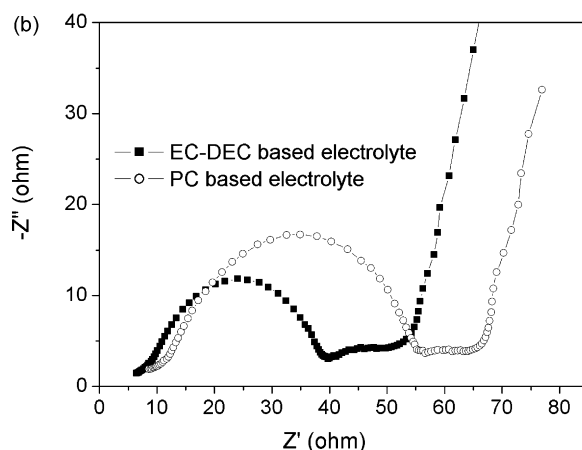
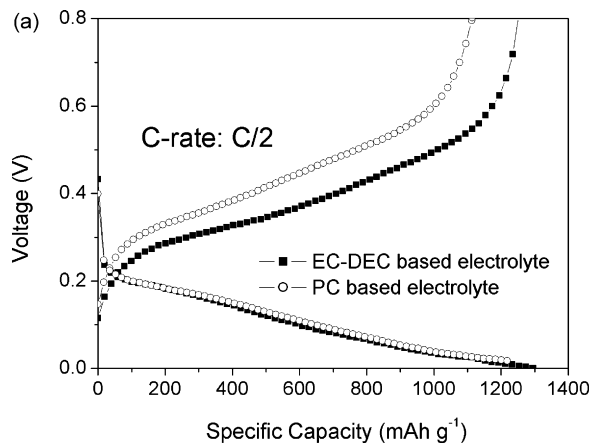
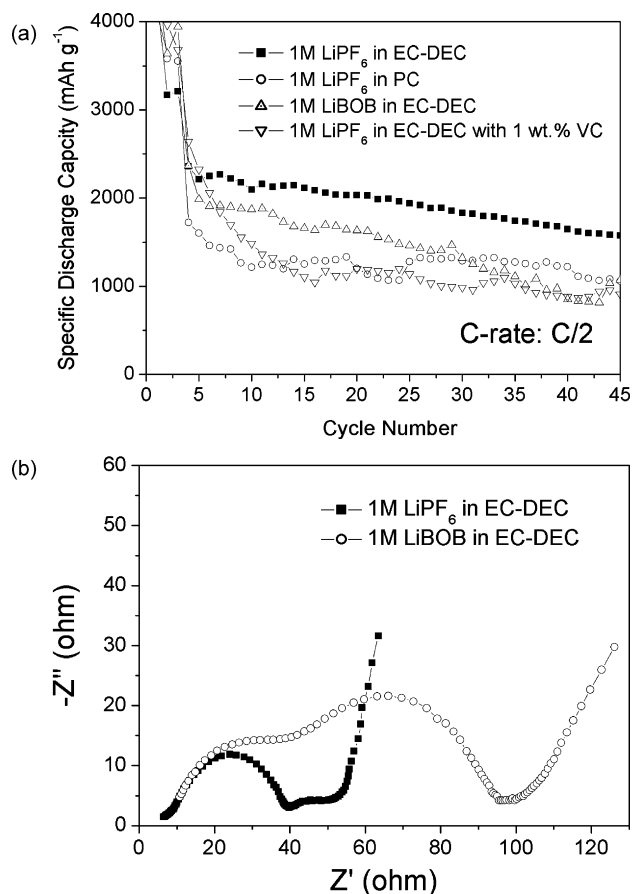


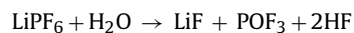
Fig. 9. (a) Galvanostatic charge–discharge curves and (b) Nyquist plots (in the 60th cycle) of nano-Si cycled in EC-DEC and PC based electrolytes.



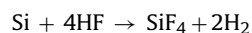
**Fig. 10.** (a) Cycling performance of nano-Si electrodes in EC-DEC and PC based electrolytes with  $\text{LiPF}_6$  and  $\text{LiBOB}$  as conducting salts. The performance of the electrolyte with VC as additive is also given; (b) Nyquist plots (in the 60th cycle) of nano-Si cycled in EC-DEC based electrolytes with  $\text{LiPF}_6$  and  $\text{LiBOB}$  as conducting salts.

nano-Si in EC-DEC and PC based electrolytes. The charge voltage of PC based electrolyte is 0.1 V higher than that of EC-DEC based electrolyte, indicating the larger impedance of the cell using PC based electrolyte. Moreover, the cell using PC based electrolyte exhibits a larger irreversible capacity loss (low coulombic efficiency), which is associated with the side reaction between the electrolyte and the electrode material. The Nyquist plots of nano-Si using two electrolytes in the 60th cycle are shown in Fig. 9b. Obviously, the cell using PC based electrolyte has larger impedance of SEI layer (first semicircle). The formation of SEI layer is due to the decomposition of electrolyte. Thus, though Si can be cycled in PC based electrolyte, the side reaction between PC and CB leads to the electrode with a lower capacity and damage the cyclability (Fig. 10a). If possible (not working at a low temperature), EC-DEC based electrolyte is a better choice than the PC based.

Until now, all electrolytes in our experiment use  $\text{LiPF}_6$  as the lithium conducting salt. However, in the batteries,  $\text{LiPF}_6$  can undergo such a reaction even if there is trace amount of water:

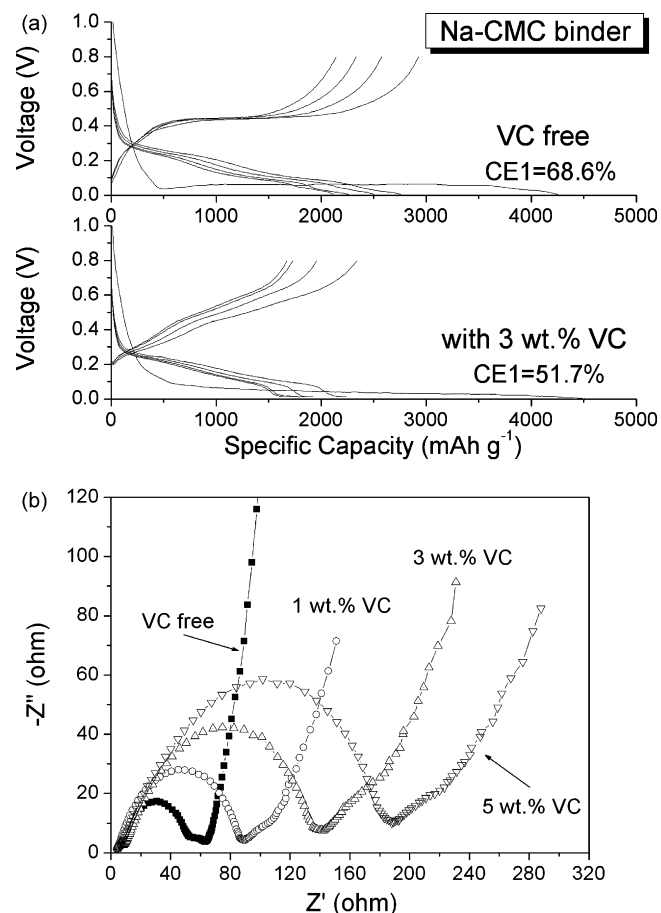


and the resulting hydrofluoric acid (HF) can further react with Si:



Then can we may need to find a better lithium salt than  $\text{LiPF}_6$  to avoid the above reaction.

One candidate salt is lithium bis(oxalato)borate ( $\text{LiBOB}$ ). Xu et al. [30] have reported that  $\text{LiBOB}$  shows an extraordinary ability to form SEI layer and even can stabilize graphite in PC-based



**Fig. 11.** (a) Galvanostatic charge-discharge curves of nano-Si with Na-CMC binder (pH 6.7) and (b) Nyquist plots (in the 50th cycle) of micro-Si with Na-CMC binder (pH 3.1) cycled in EC-DEC based electrolyte with VC-free and containing.

electrolyte. In addition to enhancing the SEI formation,  $\text{LiBOB}$  also exhibits a better stabilization than  $\text{LiPF}_6$  and can improve the cell cyclability at a high temperature [31]. The cycling performance of nano-Si with 1 M  $\text{LiBOB}$  in EC-DEC based electrolyte is shown in Fig. 10a. However, the results show that the replacement of  $\text{LiPF}_6$  with  $\text{LiBOB}$  does not improve the cyclability significantly and even sacrifices the capacity. In addition, EIS study shows that the cell using  $\text{LiBOB}$  as the conducting salt exhibits impedance about two times higher than that using  $\text{LiPF}_6$  due to the lower conductivity of  $\text{LiBOB}$  and the enhancement of SEI layer formation (Fig. 10b). Therefore,  $\text{LiBOB}$  seems not to be a good candidate of lithium salt for Si anode. Considering the fact that other conducting salts, such as  $\text{LiTFSI}$ , can etch the cathode current collector in the industrial application [32],  $\text{LiPF}_6$  is still the optimum salt for Si anode.

A slight presence of electrolyte additives can improve the cycling performance of the electrodes. And among them, VC is a good SEI formation additive and has been extensively studied. In PVDF binder system, the addition of VC can significantly enhance the cyclability of Si electrode, as shown in Fig. 3c. However, in Na-CMC binder system, VC does not play a positive role and even worsens the performance (Fig. 11a). The voltage profiles of Si in VC-free and VC containing electrolytes with Na-CMC binder are shown in Fig. 10a. The charge voltage plateau with the VC containing electrolyte is about 0.1 V higher than that with the VC-free electrolyte, indicating the larger cell impedance. Moreover, after 50 cycles, the impedance (SEI layer) in the VC-free electrolyte is only 50  $\Omega$ , whereas in the VC containing electrolyte, the impedance is 85, 137, 184  $\Omega$ , corresponding to the VC concentration of 1, 3, 5 wt.%, respectively (Fig. 11b). The larger impedance of VC containing electrolyte is a definitely

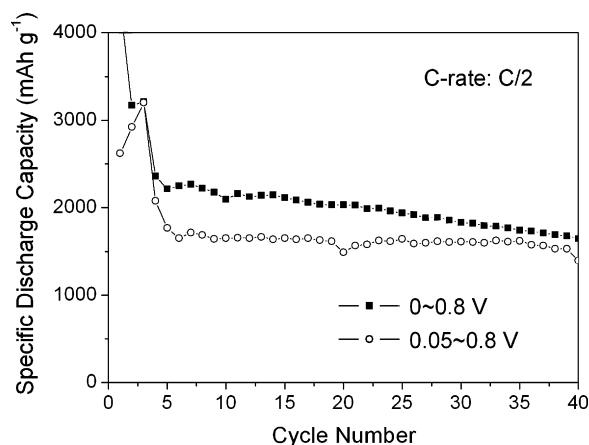


Fig. 12. Cycling performance of nano-Si electrodes with 0–0.8 and 0.05–0.8 V charge–discharge windows.

undesirable. Thus, VC seems not to be compatible with Na-CMC binder. One plausible explanation is that the decomposition of VC can destroy the connection between CMC and Si and cause the Si particles to lose contact.

### 3.5. Optimizing the charge–discharge window

Charge–discharge window is also an important factor to affect the Si cyclability. At the low voltage ( $\sim 50$  mV), Si undergoes a phase

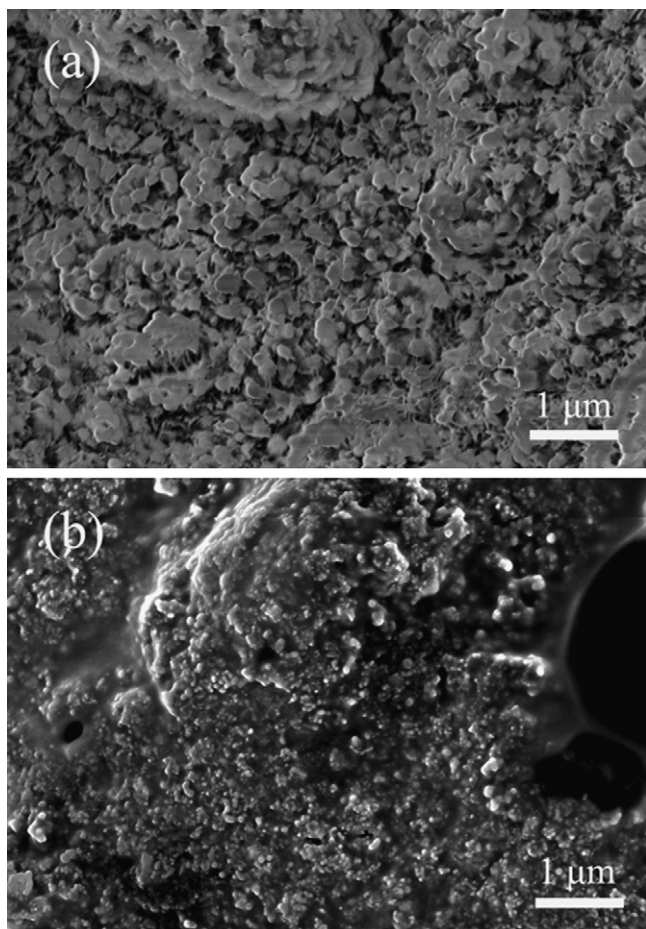


Fig. 13. SEM images of nano-Si electrodes discharged to (a) 3000 mAh g<sup>-1</sup> and (b) 3500 mAh g<sup>-1</sup>.

transition from amorphous to crystalline Li<sub>15</sub>Si<sub>4</sub>. Though XRD study has shown that the diffraction peaks of crystalline Li<sub>15</sub>Si<sub>4</sub> disappear during charge and can reversibly appear in the next discharge process [33], the cyclability of nano-Si can be significantly enhanced by setting a greater lower-cut-off voltage to avoid the formation of crystalline Li<sub>15</sub>Si<sub>4</sub> (Fig. 12) [34]. SEM images show that in the first discharge process, when the capacity reaches 3000 mAh g<sup>-1</sup>, the diameter of nano-Si particles increases from 50 to 120 nm (Fig. 13a), whereas, when the cell is deeply discharged to 3500 mAh g<sup>-1</sup>, corresponding to the formation of crystalline Li<sub>15</sub>Si<sub>4</sub>, the particles are broken into 40 nm size, instead of further volume expansion (Fig. 13b). This effect might be due to the increase of inner stress in crystal lattice when Li<sub>15</sub>Si<sub>4</sub> crystallizes. In addition, according to the study of Kang et al. [34] the upper-cut-off voltage also should be lower than 1 V to obtain a good cyclability.

## 4. Conclusions

Silicon particle size, the amount of carbon black, types of polymer binder and electrolyte/conducting salt/additive have been systematically investigated and optimized to fight the capacity fading of Si anode. It is found that nano-Si displays a better electrochemical performance than micro-Si and the large amount of carbon black can make the electrode better tolerate the volume change. For the binder, Na-CMC binder exhibits a more excellent performance than PVDF binder due to the esterification between hydroxyl on Si surface and carboxyl in CMC. To enhance the esterification, in the preparation of the electrode, the pH value of Na-CMC should be adjusted to 3.5. It is also found that Si can still be cycled in PC based electrolyte, even with a large amount of CB. However, the cycling performance is not as good as in EC-DEC based electrolyte. Though LiBOB has been thought to be a better salt for Si anode, the result of this study contradicts to this idea. The best conducting salt is still LiPF<sub>6</sub>, at least in EC-DEC based electrolyte. VC additive can be used in the electrode with PVDF binder and improve the cycling performance, but VC is not compatible with CMC binder. Finally, to improve the cyclability, the lower-cut-off voltage should be set to above 50 mV vs. Li<sup>+</sup>/Li to avoid the formation of crystalline Li<sub>15</sub>Si<sub>4</sub>.

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