Economical Synthesis and Promotion of the Electrochemical Performance of Silicon Nanowires as Anode Material in Li-Ion Batteries

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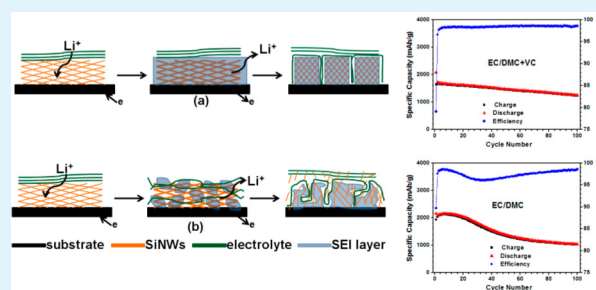
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Ⓢ *Supporting Information*

ABSTRACT: Silicon is considered as one of the most promising anodes alternative, with a low voltage and a high theoretical specific capacity of ~4200 mAh/g, for graphite in lithium-ion batteries. However, the large volume change and resulting interfacial changes of the silicon during cycling cause unsatisfactory cycle performance and hinder its commercialization. In this study, electrochemical performance and interfacial properties of silicon nanowires (SiNWs) which are prepared by the Cu-catalyzed chemical vapor deposition method, with 1 M LiPF$_6$/EC + DMC (1:1 v/v) containing 2 wt % or no vinylene carbonate (VC) electrolyte, are investigated by using different electrochemical and spectroscopic

techniques, i.e., cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) techniques. It is shown that the addition of VC has greatly enhanced the cycling performance and rate capability of SiNWs and should have an impact on the wide utilization of silicon anode materials in Li-ion batteries.

KEYWORDS: *Cu catalyst, solid-state interphase, cycling performance, rate capability*

1. INTRODUCTION

The future development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has put forward high-level requirements for lithium-ion batteries. Silicon has a theoretical specific capacity of ~4200 mAh/g at the fully lithiated state Li$_{22}$Si$_5$, which is 10 times higher than that of conventional carbon anode. In addition, Si has a low Li–Si electrochemical reaction potential, which is slightly higher than carbon anode.[1] It is believed that silicon is a most promising anode alternative for carbon to obtain high energy density and good safety performance lithium-ion batteries. There have been a great deal of studies on silicon-based materials involving nanosized particles, various composite electrodes such as silicon–carbon, silicon–metal composites, and so on.[2–8] However, the lithiation and delithiation process of the material causes a large volume change (>300%) of silicon,[9] introduces a great deal of mechanical stress, and causes pulverization of silicon and detaches active materials from the current collector. Finally, it results in a rapid capacity decrease and fast cycle performance degradation of the materials, which has hindered the commercial application of silicon in lithium-ion batteries for a long time.

Silicon nanowires (SiNWs) have the advantage of efficient electron transfer pathways, short Li-ion diffusion distances, and moderate stress relaxation,[10] which are promising to meet the

demand for high-capacity lithium-ion batteries. The chemical vapor deposition (CVD) method is a useful way to prepare SiNWs, with Au or Au-based materials as the most commonly used catalyst.[11] However, Au is a noble metal and also has an adverse effect on the electrochemical properties of silicon.[12] In this study, the Cu-catalyzed CVD method has been used to synthesize SiNWs on a stainless steel (SS) substrate. It is believed that Cu which is compatible with Si as a cheap catalyst for SiNW preparation,[13–15] should be beneficial for their large-scale production in the future.

Although SiNW electrodes are able to maintain a high reversible capacity in several dozen cycle numbers, the huge volume change can also cause electrode failure in long-term cycles. Therefore, surface coating, proper electrode binders, and functional electrolytes with additives have been investigated and reported as some efficient ways to improve long cyclic performance of Si and Si composite material.[16–25]

In the literature, there are several studies on the effects of a film-forming additive such as vinylene carbonate (VC) on the electrochemical performance of silicon thin films and nano-particle electrodes,[20–23] as well as an investigation of a solid

electrolyte interface (SEI) on SiNWs without electrolyte additives.[24] However, there is only one report about studies of VC effects on electrochemical performance of SiNWs in ionic liquid electrolyte.[25] Generally, a stable and flexible SEI layer could help to bind the Si particles and may suppress surface pulverization and ensure good electric contact between Si and the current collector. Then, these effects could improve the cycle ability of Si materials. In this study, the effects of a common film-forming additive such as vinylene carbonate (VC) in organic electrolytes on the electrochemical performance of SiNWs has been investigated in detail. Since SiNWs have much higher specific surface area than that of the Si thin film,[10] we hope to explore the underlying relationship between interfacial properties and electrochemical performance of SiNWs and have a deep understanding of the effects of additives on the electrochemical performance of SiNWs as anode materials.

2. EXPERIMENTAL SECTION

Synthesis of SiNWs on a SS Substrate. Silicon nanowires were synthesized using the CVD method on stainless steel substrate (~15 mm diameter) by a Cu catalyst (~10 μg/cm^2), which was deposited on a SS substrate by radio frequency magnetron sputtering, with Ar-diluted 5% SiH$_4$ gas (10 sccm flow) as the precursor, 99.999% pure H$_2$ gas (30 sccm flow) as the carrier gas, and protective gas under a reducing atmosphere at 670 °C for 1 h. The SiNWs obtained were ~600 μg/cm^2. The SiNW mass was measured using a microbalance with 1 μg resolution (Mettler Toledo XS3DU).

Characterization and Electrochemical Measurement. The morphology and structure of the obtained samples were examined by scanning electron microscopy (SEM, HITACHI S-4800) with an energy-dispersive X-ray spectrometer (EDX), transmission electron microscopy (TEM, PHILIPS JEM-2100), and X-ray photoelectron spectroscopy (XPS PHI Quantum-2000). Electrochemical measurements were performed by coin-type cells (CR2025) that were assembled in a glovebox (Mbraun, LabMaster 100, Germany) under an argon atmosphere by directly using the as-synthesized SiNWs as the anode. The counter and reference electrodes were lithium metal foil (15 mm diameter), and the electrolyte solution was a 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) with 2 wt % vinylene carbonate (VC). A galvanostatic cycling test of the assembled cells was carried out on a Land CT2001A system at room temperature between 0.01 and 2.5 V (versus Li$^+$/Li). The discharge capacity of the material referred to here is the total charge inserted into the SiNW per mass unit. Cyclic voltammetry (CV) was recorded on a four-channel multifunctional electrochemical workstation (VersaSTAT MC, America) at a scan rate of 0.2 mV/s, as well as the electrochemical impedance spectroscopy (EIS) measurement at the delithiation stage from 100 kHz to 1 Hz with a 5 mV amplitude ac signal. Surface characterization for the cycled electrodes in delithiation state was performed after taking the SiNW electrodes from the coin cells in the glovebox, immersing and washing them in DMC solvent to remove the residual electrolyte, and leaving them for solvent evaporation thereafter.

3. RESULTS AND DISSCUSSION

3.1. Improved Electrochemical Performance of Cu-Catalyzed SiNWs by a VC Additive. A large quantity of SiNWs (~600 μg/cm^2) were prepared on a stainless steel substrate by using a Cu-catalyzed CVD method with SiH$_4$ gas as the precursor, H$_2$ as the carrier gas, and protective gas under a reducing atmosphere. The SEM image in Figure 1 shows a structure of coexistence of straight and curly SiNWs, which are crystalline with a diameter of 50−100 nm (Figure S1, Supporting Information). As we know, the eutectic temperature of Cu−Si is 802 °C, and at a growth temperature of 670 °C,
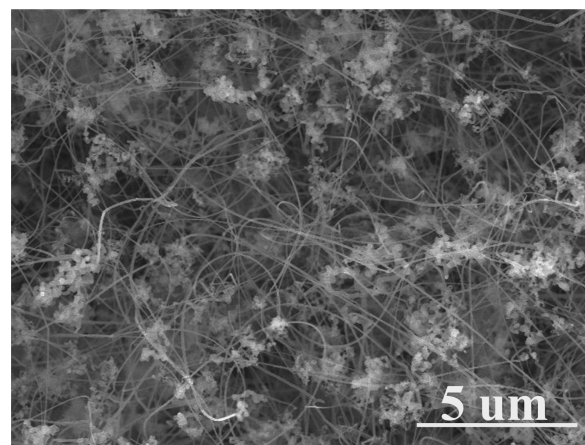

Figure 1. SEM image of SiNWs on a stainless steel substrate synthesized by the Cu-catalyzed CVD method at 670 °C.

both VLS (Vapor−Liquid−Solid) and VSS (Vapor−Solid−Solid) growth processes may occur at the same time,[14,15] which contributes to the rich morphology of SiNWs.

To examine the electrochemical performance of SiNWs, the as-synthesized SiNW electrodes were assembled with a Li foil directly, with no binders or conducting additives. A galvanostatic test from 0.01 to 2.5 V (vs. Li$^+$/Li) at a current density of 840 mA/g (0.2 C rate) shows a high initial Coulombic efficiency of 89% with first discharge (lithiation) capacity of 2160 mAh/g (Figure 2a). The first discharge curve has an obvious different shape from the following cycles, with a long sloping plateau in the discharge curve (Figure S2a, Supporting Information) which corresponds to the sharp peak at ~0.10 V on the dQ/dV curves (Figure S2b, Supporting Information). The sharpness of this peak indicates the coexistance of two phases, that is unreacted c-SiNWs and lithiated a-Li$_x$Si, which has been reported as an electrochemically driven solid-state amorphization.[26]

It has been generally recognized that the c-Si transforms into a-Li$_x$Si in the first discharge process, and then the a-Li$_x$Si turns to a-Si after delithiation in the first charge process; so, SiNW electrodes show typical lithiation/delithiation behaviors of a-Si in the following cycles.[1] In the second cycle, we can see that lithiation of the a-Si shows two major sloping regions in the discharge curves (Figure S2a, Supporting Information), with two broad peaks at ~0.25 V (A) and ~0.10 V (B) in the dQ/dV curve (Figure S2b, Supporting Information), corresponding to different lithiation degrees of a-SiNWs into a-Li$_{x'}$Si and Li$_{x'+x''}$Si, respectively,[1] while delithiation from the amorphous Li−Si alloy also shows two major sloping regions in the charge curves (Figure S2a, Supporting Information), with two broad peaks at ~0.30 V (D) and ~0.45 V (E) in the dQ/dV curve (Figure S2b, Supporting Information), corresponding to different delithiation degrees of a-Li$_{x'+x''}$Si into a-Li$_{x'}$Si and a-Si, respectively.[1] In addition to the obvious peaks, there is also a small tail peak below ~0.05 V (C) during lithiation on the dQ/dV curves (Figure S2b, Supporting Information), which has been considered as the fast crystallization of highly lithiated amorphous Li−Si alloy into c-Li$_{15}$Si$_4$, and it will turn into a-Si during delithiation.[27] As can be seen from Figure 2b and d, the SiNWs show some behavior similar to that of the second cycle in the thrid and following cycles in the dQ/dV curves. The delithiation of c-Li$_{15}$Si$_4$ may occur nearly at the same voltage as the deep delithiation of the amorphous Li−Si alloy,
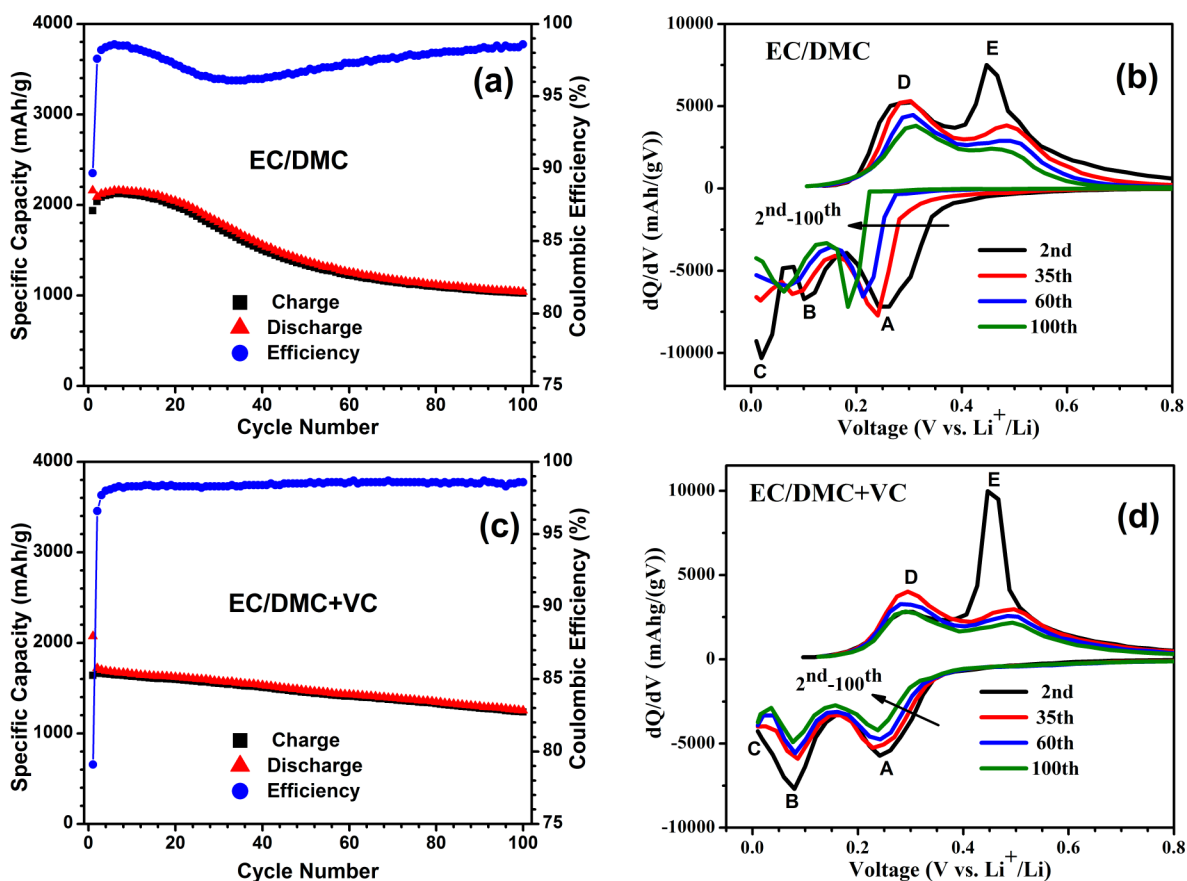
Figure 2. Cycling performance ((a), (c)) with corresponding dQ/dV curves ((b), (d)) of SiNWs cycled at 0.2 C during 0.01−2.5 V (vs Li$^+$/Li) without or with VC electrolyte additive.

which is confirmed by the fact that the ∼0.45 V (E) broad peak may become sharp sometimes (Figures 2b, 2d, and 3b) in the dQ/dV curves when the formation of the c-Li$_{15}$Si$_4$ peak during lithiation is obvious, which may indicate a two-phase coexistence of c-Li$_{15}$Si$_4$ and a-Si. To gain a clear understanding of the above reaction processes, the electrochemical reactions[1,26,27] of SiNWs during lithiation and delithiation cycling are summarized in Scheme 1.

Though the SiNW electrodes can maintain a stable capacity of ∼2000 mAh/g in several dozens of cycles, Figure 2a shows a fast degradation of capacity with a low Coulombic efficiency from around 30 cycles. Its corresponding dQ/dV curve (Figure 2b) shows that the lithiation peaks (A, B, C) move towards lower potentials and delithiation peaks (D, E) towards higher potentials, which means that the electrochemical polarization increases with cycling times. According to Ohm's Law "$R = \Delta V/I$",[28] this means that the electrode resistance increases during the cycling process, indicating the deterioration of the contact between active materials or active materials with the current collector. In fact, from the XRD experiment (Figure S3, Supporting Information), after the initial charge−discharge cycle, the XRD patterns of SiNW electrodes still show the existence of c-Si, which may be because only some part of SiNWs form a lithium-rich Li$_x$Si layer on the surface and leave some unreacted c-SiNWs.[29] However, more and more unreacted c-SiNWs will be involved in the reaction during cycling; therefore, it can only see SS substrate peaks from the XRD pattern after 30 cycles test and no additional fresh c-SiNWs to compensate the capacity. While from a low-
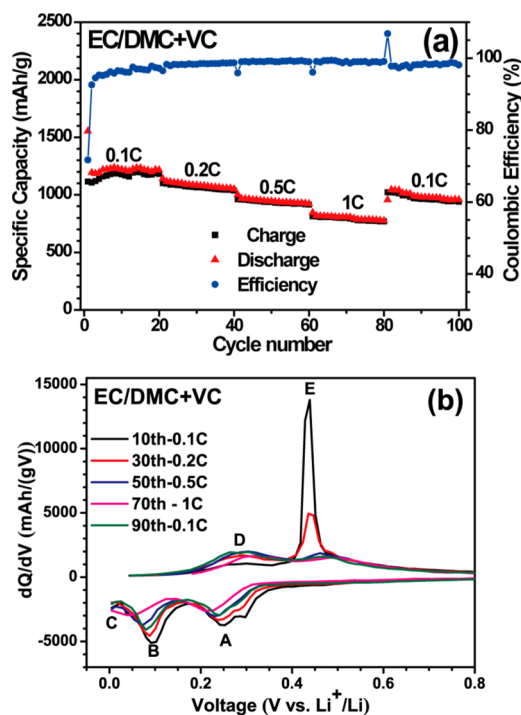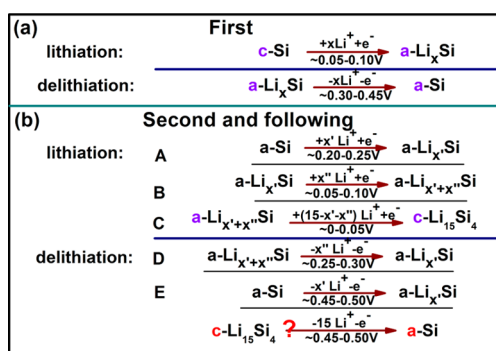

Figure 3. Rate capability (a) and corresponding dQ/dV curves (b) of SiNW electrodes in VC-containing electrolyte at different current densities.

Scheme 1. Summarized Electrochemical Reactions during Lithiation and Delithiation Cycling[1,26,27]

Figure 4. Initial cyclic voltammetry curve comparison of blank SS electrode (a) and SiNW electrode (b) in VC-containing and VC-free electrolyte at a scan rate of 0.2 mV/s.

magnification SEM image (Figure S4, Supporting Information) the SiNW electrode cracks into multiple islands after 30 cycles, though most of the active materials still maintain contact with the current collector, some part of the electrode structures become loose and collapse with some of the active materials detaching from the current collector, resulting in the decrease of practical active materials and fast capacity degradation. It is of great importance to maintain a good electrical contact between active materials and the current collector to improve the cycling performance of SiNWs. Apparently, stable SEI which is mostly determined by the reduction of solvents and additives in the electrolytes should be a useful way to achieve this target.

Then, we started to investigate the effect of vinylene carbonate (VC) on the electrochemical performance of SiNWs. At a same current density of 0.2 C, the initial charge and discharge capacity are 1640 and 2073 mAh/g (Figure 2c), with a Coulombic efficiency of 79%, which is slightly lower than in the VC-free electrolytes. However, from the dQ/dV curves (Figure 2d), the potential polarization during cycling is much lower with a VC additive. It can be seen that the lithiation peaks (A, B, C) and delithiation peaks (D, E) nearly remain at the same potentials as that of the second cycle. After 100 cycles galvanostatic test, the capacity of the SiNWs still remains at about 1300 mAh/g with a stable Coulombic efficiency of 98−99%, and the average capacity fading is only 0.25% per cycle. Apparently, the charge/discharge rate capability has also been improved by the addition of a VC additive. SiNWs were tested continuously at 0.1, 0.2, 0.5, and 1 C for 80 cycles, then back to the 0.1 C for another 20 cycles. Figure 3a shows that SiNWs maintain about 84% and 72% at 0.5 and 1 C rate, respectively, of the initial capacity at 0.1 C rate, which is much higher than in the VC-free electrolytes (Figure S5a, Supporting Information). The dQ/dV curve in Figure 3b exhibits smaller potential polarization at higher current densities than the VC-free one (Figure S5b, Supporting Information). After 80 cycles following the 1 C rate, the capacity could restore to 86% of the initial capacity at 0.1 C.

3.2. Further Electrochemical and Interfacial Characterization of the SiNW Electrode with and without Electrolyte Additives. To further evaluate the VC additive impact on the electrochemical performance of the SiNW electrode, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies have been conducted, with SiNW electrodes as the work electrode and Li foil as the reference and counter electrode. Figure 4a shows the initial CV curve comparison of SiNWs in different electrolytes. There is
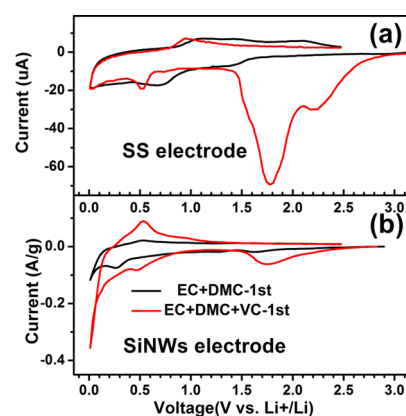
an additional reduction peak at ~1.8 V with VC additives, besides a reduction peak at ~0.3−0.7 V for SiNWs with or without VC, which is similar with the blank SS substrate electrode (Figure 4b). This fact indicates that VC reduction reaction occurs at ~1.8 V, which may play a role in the formation of a stable SEI layer, and other component contributions such as EC or DMC decompose at ~0.3−0.7 V.[30] However, due to reasons such as kinetic limitations,[31] the lithiation peaks of SiNWs are not obvious in the initial CV curve, and SiNWs show an activation process in the following cycles (Figure S6, Supporting Information). The EIS spectra before cycling, after 5, 35, 60, and 100 cycles, have been measured and simulated (Figure S7, Supporting Information). We use an equivalent circuit inset in Figure 5a, with R_s as the solution resistance, R_{SEI} as the solid-state interphase resistance, R_{ct} as the charge-transfer resistance, W as the Warburg resistance, and CPE representing the constant-phase element in place of a capacitor to compensate for nonhomogeneity in the system such as a rough or porous surface.[20] From these results, it is observed that the impedance of R_{SEI} maintains as almost constant, and the increase of R_{ct} has been suppressed in a certain number of cycles in VC-containing electrolyte. Both R_{SEI} and R_{ct} have been increasing during cycling in the absence of VC (Figure 5b, c, d). Therefore, it is easily concluded that the addition of VC has helped form and maintain the stable SEI layer.

The SEM images of the SiNW electrode surface after 100 cycles galvanostatic test are shown in Figure 6. In VC-free electrolyte, the electrode surfaces are mostly loose regions, with a morphology which is similar with the original SiNWs before cycling, while in the VC-containing electrolyte, the surfaces are mostly compact regions with porous lamellar structure, which may be beneficial for proper electrolyte penetration and maintain the structure stability during charge−discharge cycles. From typical EDS and XPS spectra (Figure S8, Supporting Information), and the atomic composition of the SiNW surface in different electrolytes after 100 cycles in Figure 7, it is obvious that Li, C, and O are the major elements and the C/O atomic ratio in the presence of VC is higher than in VC-free ones. From the high-resolution C 1s spectra (Figure 8a), there are several peaks at ~284.5 eV associating the presence of $\underline{C}H_2$, ~286 eV associating the presence of $\underline{C}-OR$, ~288 eV associating the presence of $\underline{C}=O$, and ~290 eV associating the presence of $\underline{C}O_3^{2-}$, which may be from the reduction of

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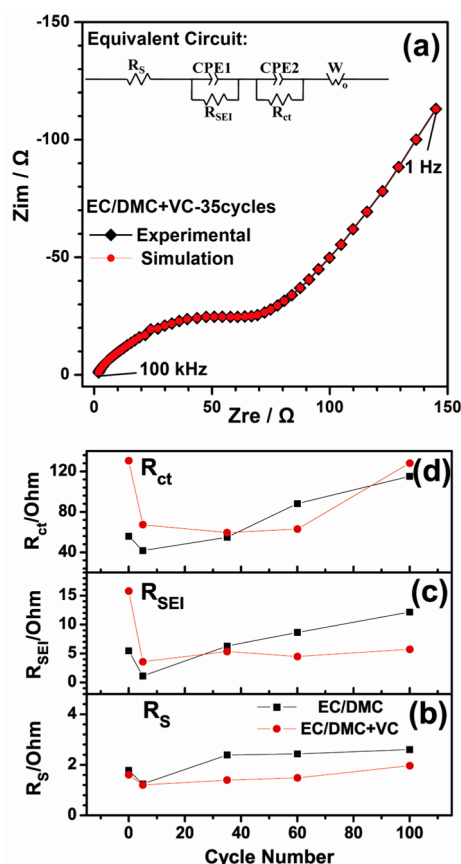dx.doi.org/10.1021/am302731y | *ACS Appl. Mater. Interfaces* 2013, 5, 1681−1687

Figure 5. Experimental data and simulation electrochemical impedance spectroscopy example (a). The equivalent circuit has been inserted as shown, and a comparison of fitted (b) R_S, (c) R_{SEI}, (d) R_{ct} results during cycling of SiNW electrodes in VC-free or VC-containing electrolytes.
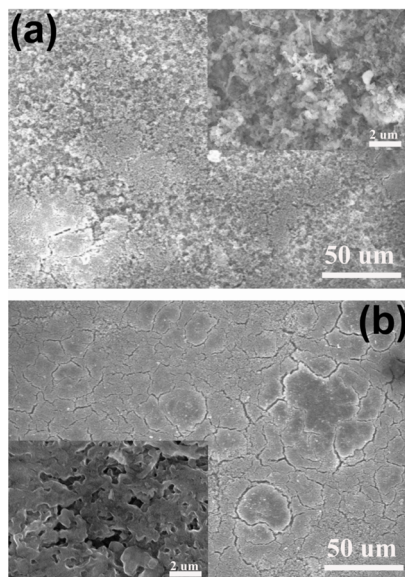

Figure 6. SEM images of SiNW electrodes after 100 cycles galvanostatic charge−discharge test at 0.2 C rate in (a) VC-free and (b) VC-containing electrolyte, and insets are the magnified images.

VC-derived species (usually polymers or oligomers), alkyl lithium carbonate such as $ROCO_2Li$, which is the reduction and decomposition of VC or other components such as EC in
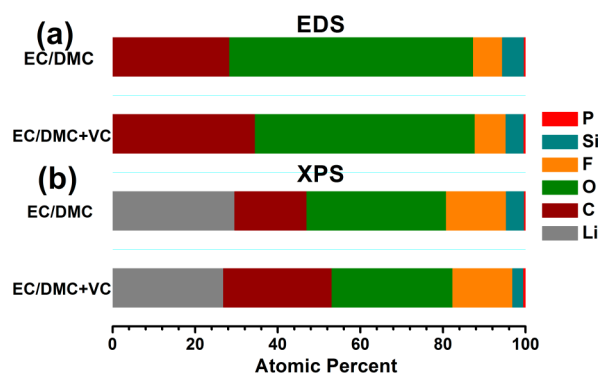

Figure 7. Atomic composition determined by (a) EDS and (b) XPS survey scan of the SiNW electrode surface after 100 galvanostatic cycles in VC-free or VC-containing electrolytes at 0.2 C.

organic electrolyte, and Li_2CO_3, respectively.[20,32] In the high-resolution O 1s spectra (Figure 8b), there are several peaks at ∼530.5 eV (Li_2O or LiOH etc.), ∼531.5 eV (Li_2CO_3), ∼532.5 eV (C=$\underline{O}$ of alkyl lithium carbonate or SiO_x), and ∼533.5 eV (C−$\underline{O}$ of alkyl lithium carbonate).[20,24] The Li 1s, F 1s, Si 2p, and P 2p XPS spectra (Figure S9, Supporting Information) also show the presence of LiF, a certain amount of SiO_x, and a trace amount of $LiPF_6$ or LiP_xF_y.[19] These results are similar with that reported for graphite and other types of silicon electrode in the literature.[20,22,24,32,33] However, the C 1s spectra in Figure 8a show a much higher peak intensity ratio of ∼284.5 eV (VC-derived species) to ∼290 eV (Li_2CO_3) in VC-containing electrolyte than VC-free electrolyte, combined by the higher EDS and XPS C/O atomic percent results in Figure 7. Combining with analysis of XPS and the surface morphology of SiNWs after long cycling in Figure 6, it is recognized that the presence of VC helps the formation of a VC-derived species that contains more carbon species, which may be more dense and less permeable to solvent transport, thus maintaining the stability of SiNW surface structure and keeping good electrical contact with the current collector, which as a result can substantially improve the electrochemical performance of SiNWs. The schematic illustration in Figure 9 shows that with VC a good SEI layer is formed between the SiNW active materials and the electrolyte, and even though active materials may lose direct contact with the current collector due to large volume change after delithiation, they will still be bound together by a compact SEI layer and keep a close contact with the current collector (Figure 9a). Without a VC additive, the inferior SEI layer formed cannot seriously inhibit the direct reaction between active materials and the electrolyte during the cycling process. Some SiNWs will lose contact with the current collector and also with other nanowires, and some may even be detached into the electrolyte, causing high electrochemical polarization or loss of active material during the cycling process (Figure 9b), which deteriorates the cell capacity and cycling performance.

■ CONCLUSIONS

In summary, we have synthesized SiNWs on stainless steel foil by the Cu-catalyzed CVD method and studied the electrochemical performance of the as-prepared SiNWs. The SiNWs as-prepared show a high Coulombic efficiency of 89% at first cycle with a high specific capacity over 2000 mAh/g in several dozens of cycles. However, the electrochemical polarization becomes larger and larger with cycling process, and some of the
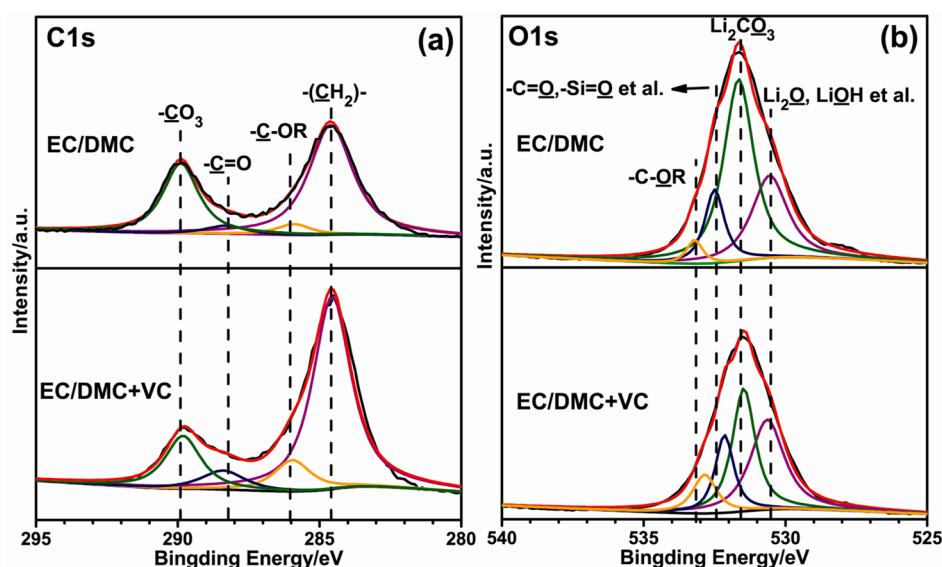
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Figure 8. (a) C 1s and (b) O 1s XPS spectra of SiNW electrode surface after 100 galvanostatic cycles in VC-free or VC-containing electrolytes at 0.2 C.
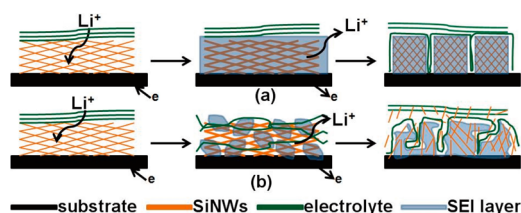

Figure 9. Schematic illustration of the role of (a) a good SEI layer formed with VC additive and (b) an inferior SEI layer formed without VC during lithiation and delithiation of SiNWs.

active materials even detach from the current collector due to the huge volume change of the lithiation/delithiation process. As a result, there is a fast capacity fading with a lower Coulombic efficiency from around 30 cycles. The introduction of VC additives into electrolytes has been confirmed to greatly improve the cycle performance and rate capability of the SiNWs and show a slow capacity degradation of 0.25% per cycle during 100 cycles test. A variety of electrochemical and spectroscopic characterization techniques have been used to investigate the possible acting mechanism of VC additives on the SiNW electrodes, such as cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy, X-ray energy dispersive spectroscopy, and X-ray photoelectron spectroscopy. It is shown that the reduction of VC occurs at ∼1.8 V (vs Li$^+$/Li); the impedance of the SEI layer maintains almost constant during cycling with the VC additive; and the major components of surface species are VC-derived polymer or oligomer species, Li$_2$CO$_3$, LiF, and so on. However, the VC-derived SEI layer has some advantages which helps to improve the stability and integrity of the SiNW structure, which is an important factor for the enhancement of electrochemical performance of the SiNWs in the electrolytes with VC as an additive.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Additional information as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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