

Short communication

Effect of vinylene carbonate (VC) as electrolyte additive on electrochemical performance of Si film anode for lithium ion batteries

Libao Chen^a, Ke Wang^b, Xiaohua Xie^{b,c}, Jingying Xie^{b,c,*}

^a *Micro-Nano Technologies Research Center, Hunan University, Changsha 410082, China*

^b *Energy Science and Technology Laboratory, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China*

^c *Graduate school of Chinese Academy of Sciences, Beijing 100049, China*

Available online 28 June 2007

Abstract

The effect of VC as electrolyte additive on the electrochemical performance of Si film anode was studied in this paper. The charge/discharge test, scanning electron microscopy (SEM), electrochemical impedance spectrum (EIS), Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to investigate the cycle performance and SEI layer of Si film anode. It was found that the SEI layer formed in VC-containing electrolyte possessed better properties. It was impermeable to electrolyte and its impedance kept almost invariant upon cycling. The presence of VC in electrolyte brought out the VC-reduced products and decreased the LiF content in SEI layer. The major components of SEI layer were similar in VC-free and VC-containing electrolytes, which contained lithium salt (e.g. ROCO_2Li , Li_2CO_3 , LiF), polycarbonate and silicon oxide. It was newly found that silicon oxide could be formed in SEI layer of Si film anode due to the reaction of lithiated silicon with permeated electrolyte in both VC-free and VC-containing electrolytes.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Vinylene carbonate; SEI layer; Si film; Anode; Lithium ion battery

1. Introduction

Graphitized carbon has been commonly used as the anode material for commercial lithium ion batteries. However, the graphitized carbon cannot meet the energy density requirement of batteries needed for portable electric devices and (hybrid) electrical vehicles due to its restricted theoretical capacity of 372 mAh g^{-1} [1]. Thus, some new anode materials (e.g. Si, Sn, Sb, Al, etc.) with high volumetric and gravimetric capacity have been studied extensively [2–5]. Among them, Si has attracted much attention because it has the highest specific capacity (4200 mAh g^{-1}) for any of anode materials studied to date [6]. But, Si undergoes a dramatic volume change during Li^+ insertion and extraction. This causes the pulverization of Si particles and loses contacts between silicon particles and current collector, resulting in the mechanical instability and poor cyclability. To improve the electrochemical performance, many attempts have focused on reducing the particle size of Si and synthesizing Si-based composites to minimize and buffer the mechanical

stress caused by volume change of Si [7–10]. Although, these solutions are desirable, they still have some problems related to irreversible capacity loss and cyclability for practical applications.

Recently, Si film anode prepared by various deposition methods including CVD, sputtering and evaporation, has been developed by many research groups due to its excellent capacity and cycle performance [11–16]. The electrochemical performance of Si film anode is decided by many factors, such as thickness of film, roughness of substrate and parameters of deposition. However, the effect of electrolyte on electrochemical performance of Si film anode is rarely reported so far. For graphite anode, it has been reported that electrolyte additive played an important role on improving the electrochemical properties. A slight presence of electrolyte additive can result in a critical difference in electrochemical behavior of graphite anode, as evidenced by the well-known example of VC, VEC, VA, and so on [17–19]. In this paper, we studied the effect of the presence of VC in electrolyte on the electrochemical performance of Si film anode prepared by ion beam sputtering deposition, and investigated the difference of SEI layer of Si film anode formed in VC-free and VC-containing electrolytes.

* Corresponding author. Tel.: +86 21 62511070; fax: +86 21 62131647.
E-mail address: jyxie@mail.sim.ac.cn (J. Xie).

2. Experimental

Si films were prepared by ion beam sputtering deposition from a N-type Si target on 18 μm thickness Cu foils (14 mm diameter) as current collector. The working pressure was 4.5×10^{-3} Pa in Ar atmosphere, and the sputtering angle was 45° . The surface roughness of the Cu foils is 0.4 μm (RMS). The thickness of Si film is about 150 nm.

To evaluate the electrochemical properties of Si film anode, the 2025-type half-cells containing testing electrode, separator, electrolyte and lithium foil as counter electrode were assembled in a glove box filled with pure Ar. The electrolytes used in the experiments were 1 M lithium hexafluorophosphate (LiPF_6) in a 1:1 (v/v) mixture solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with or without 1 wt.% VC additive. Cycle performance was carried out using Land battery test system with the cut off potentials being 0 V versus Li/Li^+ for discharge and 1.5 V versus Li/Li^+ for charge. After different cycles, electrochemical impedance spectroscopy (EIS) measurements were performed using electrochemical workstation (Shanghai Chenhua Instrument Co., China). The impedance spectra were measured after the cell had been discharged to 0 V and the voltage were in equilibrium. The frequency used for the impedance measurements was 1 mHz to 100 kHz, and the signal amplitude was 5 mV.

After electrochemical test, the Si film anode in the state of Li^+ deinsertion was removed from the coin cell and rinsed with highly purified DMC to remove electrolyte. After drying under vacuum for 5 h, the Si film anode was moved with a transfer vessel for surface measurements. The surface morphologies of Si film before and after the first cycle were observed by scanning electron microscopy (S-3000N, HITACHI, Japan). The organic components of the SEI layers were characterized by an FTIR spectrometer (NEXUS 470, NICOLET, USA). XPS experiments were carried out on a PHI-5000C ESCA system (Perkin-Elmer, USA) with Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The XPS spectra were analyzed and fitted using Xpspeak software (Version 4.1). The C 1s region was used as a reference for surface charging and was set at 284.6 eV. A mixture of Lorentzian and Gaussian functions was used for the least-squares curve fitting procedure.

3. Results and discussion

In order to know the contribution of additive to the cycle performance of Si film, 1% VC by weight was added to blank electrolyte. Fig. 1 shows the cycle performance and efficiency of Si film anode in VC-containing and VC-free electrolytes. For the VC-containing electrolyte, Si film exhibits superior cycle performance, which reversible capacity keeps over 50% of the first charge capacity even up to 500 cycles. The efficiency that is around 70% in initial cycle reaches to about 100% after three cycles, and maintains stable in subsequent cycles. The irreversible capacity loss in the first cycle is attributed to the formation of solid electrolyte interphase (SEI) layer due to the decomposition of the electrolyte on the surface of Si film anode. In contrast, in VC-free electrolyte, severe capacity fade occurs upon cycling. The electrode cannot cycle at all after 200 cycles.

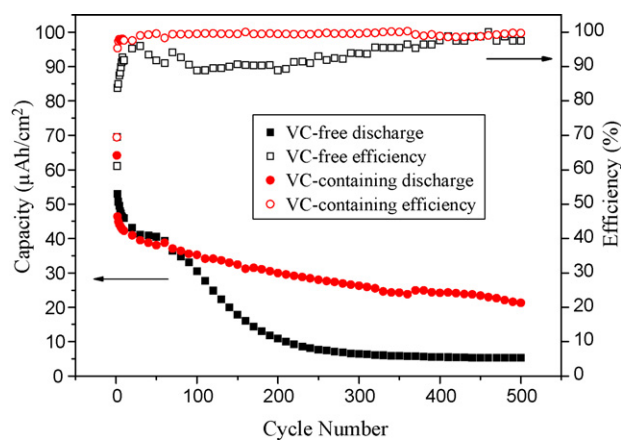


Fig. 1. Comparison of cycle performance and efficiency of Si film anode in VC-containing and VC-free electrolytes.

Furthermore, Si film whose initial efficiency is 61% shows a larger irreversible capacity loss in the first cycle. The efficiency can only increase to 95%, and fluctuates during cycling. The difference on cycle performance and efficiency of Si film anode in VC-containing and VC-free electrolytes may be attributed to the different properties of SEI layer formed in initial several cycles. The properties of SEI layer formed in these two kinds of electrolytes are analyzed in the following paragraphs.

Fig. 2 shows the SEM images of Si film anodes before and after cycling in different electrolytes. Fig. 2a exhibits that the surface of Si film is clean before cycling, though it is rough due to the surface roughness of Cu foil substrate (Fig. 3). After the first cycle, SEI layer can be formed on the surface of Si film. The SEI layer formed in VC-free electrolyte is non-homogeneous and embeds with some spherical crystallites, as shown in Fig. 2b. Andersson and Edstrom [20] had also shown the similar SEI morphology on the surface of graphite anode after three cycles and elevated temperature storage. They verified that the crystallites were LiF crystals. And they thought that isolated LiF crystals that were permeable to electrolyte caused the degradation of graphite electrode. Therefore, we speculate that the spherical crystallites appeared on the surface of SEI layer are LiF crystals, too. The SEM image of the SEI layer formed in VC-containing electrolyte shows a smooth and uniform morphology, as seen in Fig. 2c. No spherical crystallite appears on the surface of SEI layer. However, the SEI layer appears a series of cracks in the valleys between the hills. We think that the cracks are caused by the shrinkage of Si film during lithium ions extraction. When the lithium ions extract from Si electrode, most of the contraction of Si layer must be in vertical direction to the substrate. The SEI layer in the valleys cannot bear the contraction stress of two sides of walls of the valley, resulting to the cracks. These cracks can be cured in the subsequent charging course. It is concluded that the presence of VC in electrolyte resulted in quite different surface morphology of the SEI layer and configuration of LiF .

It is well known that electrochemical impedance could detect Li^+ conductivity of SEI layer. The lower the impedance value is, the faster Li^+ transports through SEI layer. So we performed impedance measurements of the cells after different cycles in the

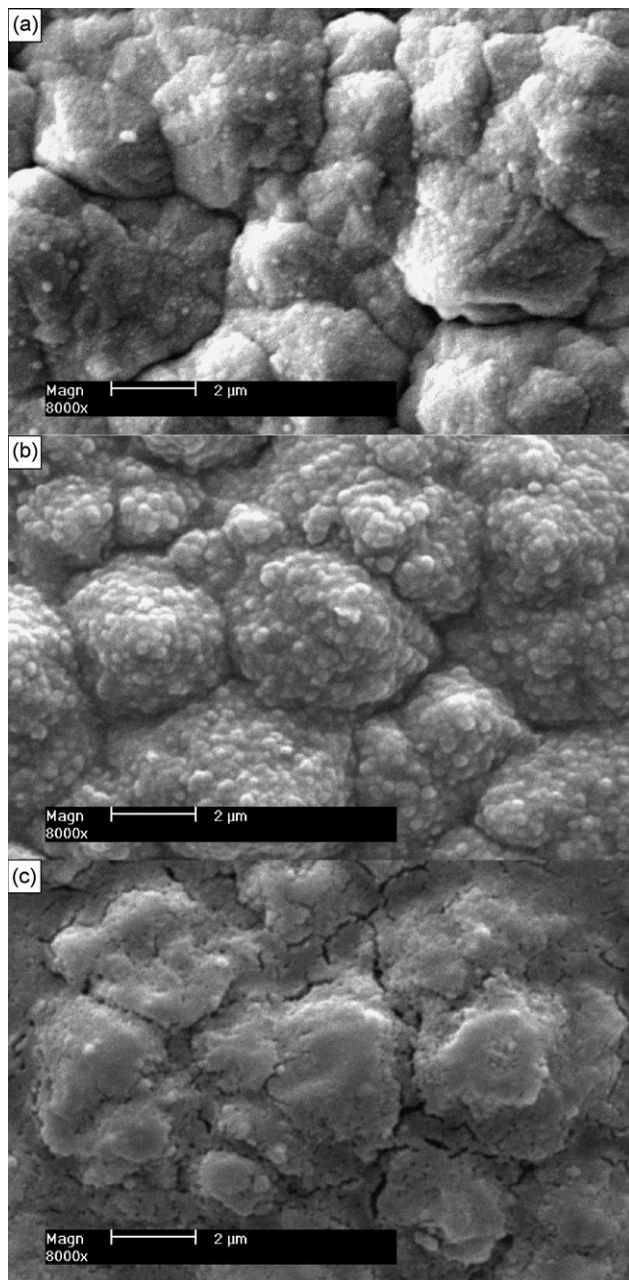


Fig. 2. SEM images of Si film anodes before and after cycling in different electrolytes: (a) before cycling; (b) after the first cycle in VC-free electrolyte; (c) after the first cycle in VC-containing electrolyte.

state of Li^+ deinsertion at equilibrium potentials. Fig. 4 shows the changes of impedance spectra of Si film anode upon cycling in VC-free and VC-containing electrolytes. As already discussed in detail [21], the high frequency semicircle relates to resistance for Li^+ migration through SEI layer, and the medium frequency semicircle relates to charge transfer resistance between SEI layer and electrode interface, and the low frequency is attributed to Warburg impedance (diffusion of Li^+ in the electrode) and insertion capacitance (accumulation of Li^+ in the electrode). As seen in Fig. 4a, the diameters of high frequency semicircles increase dramatically with the increasing of cycling times in VC-free electrolyte. The increasing of SEI layer impedance

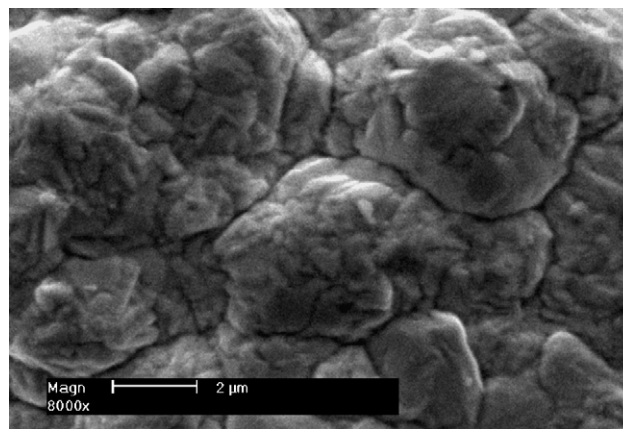


Fig. 3. SEM image of Cu foil substrate.

may be attributed to the increasing of SEI layer thickness. Fig. 4b shows the pronounced impact of VC on the impedance behavior of Si film electrodes. Both the overall SEI layer impedance and its fluctuations upon cycling are smaller in VC-containing electrolyte.

The equivalent circuit shown in Fig. 5 is used to model the impedance spectra. This circuit is basically similar to that used for graphite materials [22]. Because the semicircles are

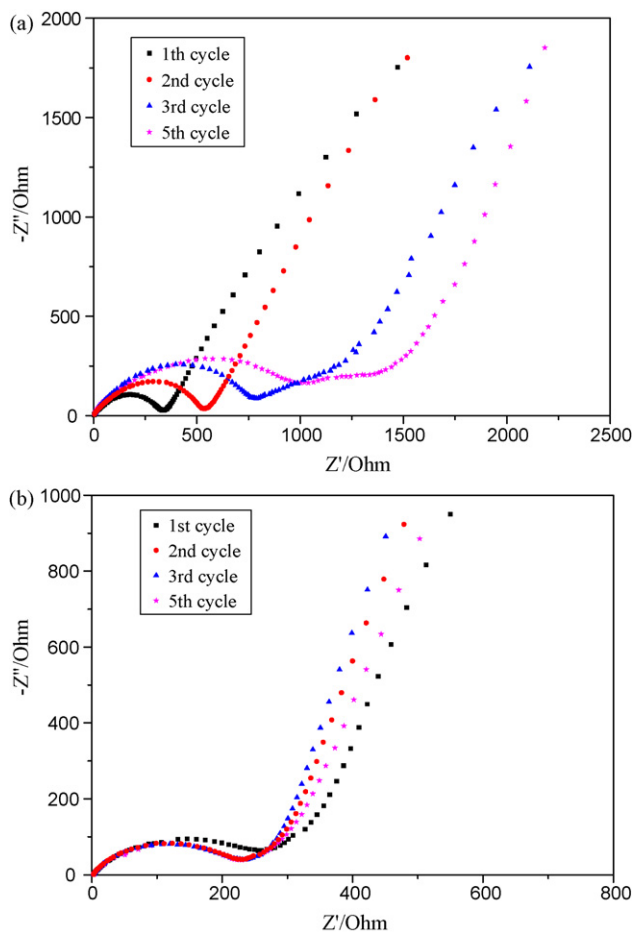


Fig. 4. Nyquist plots for changes of impedance spectra of Si film anode upon cycling in VC-free (a) and VC-containing (b) electrolytes.

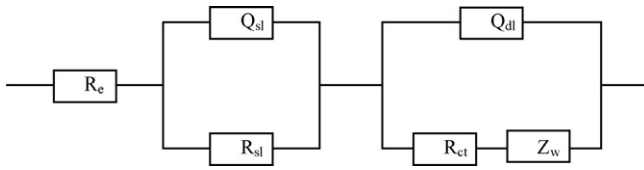


Fig. 5. Equivalent circuit used to model the impedance spectra of Fig. 4.

depressed, constant phase element (Q) is used to replace double layer capacitance in equivalent circuit. The equivalent circuit comprises a R_e , representing the resistance of the bulk electrolyte, and an R_{sl} – Q_{sl} parallel circuit where R_{sl} is the resistance for Li^+ conduction in the SEI layer, and Q_{sl} describes the space charge capacitance of the SEI layer. The final component is a parallel circuit of R_{ct} and Q_{dl} , which represent charge transfer resistance and double layer capacitance at the electrode surface, respectively. Z_w , representing Warburg impedance, is connected in series to R_{ct} .

R_{sl} that is the only interested parameter to us is obtained from the simulation of the data according to the equivalent circuit. Fig. 6 summarizes the changes of area-normalized R_{sl} on cycling in VC-free and VC-containing electrolytes. R_{sl} increases almost linearly at initial five cycles in VC-free electrolyte, while it maintains invariant in VC-containing electrolyte. Because the chemical components of the SEI layer are similar upon cycling on the same electrode, the increasing of R_{sl} is attributed to the change of thickness of SEI layer in VC-free electrolyte. As known on the above paragraphs, isolated LiF crystals are formed in the SEI layer in VC-free electrolyte. The electrolyte can permeate the SEI layer upon cycling. Therefore, new SEI layer is formed constantly on the surface of Si film in each cycle, resulting in the increasing of the SEI layer thickness. And then, this causes the increasing of anode polarization, which degrades the electrochemical performance of Si film. In the VC-containing electrolyte, however, R_{sl} keeps constant in values of about $360 \Omega \text{ cm}^2$ in initial five cycles. It indicates that impermeable SEI layer is formed on the surface of Si film, and it maintains stable upon cycling.

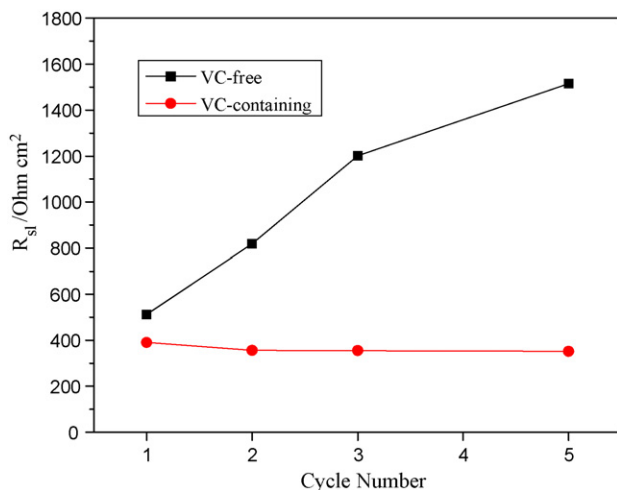


Fig. 6. Changes of R_{sl} of SEI layer upon cycling in VC-free and VC-containing electrolytes.

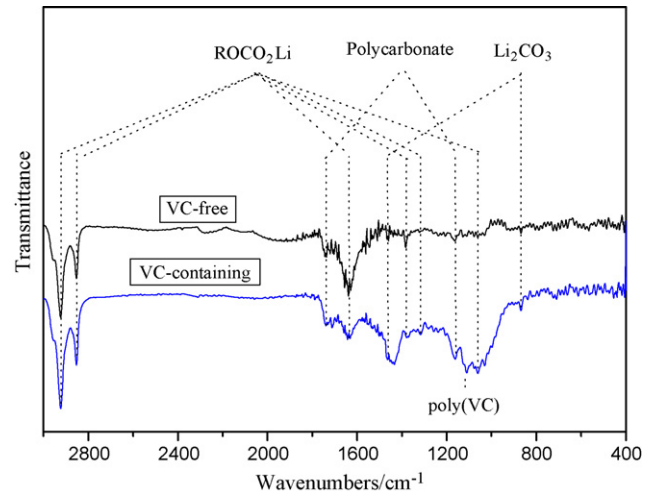


Fig. 7. Comparison of FTIR spectra of SEI layers formed on Si film anode in VC-containing and VC-free electrolytes.

In order to obtain information on the chemical component of the SEI layer, FTIR and XPS spectra of the SEI layers formed in two kinds of electrolytes were measured. Fig. 7 shows the comparison of FTIR spectra of SEI layers formed in VC-containing and VC-free electrolytes. The pronounced peaks at $2960\text{--}2800 \text{ cm}^{-1}$ ($\nu_{\text{C-H}}$), 1643 cm^{-1} ($\nu_{\text{C=O,as}}$), 1381 cm^{-1} (δ_{CH_2}), 1316 cm^{-1} ($\nu_{\text{C=O,s}}$), and 1061 cm^{-1} ($\nu_{\text{C-O}}$) are attributed to ROCO_2Li , which are the major reduction products of EC [23]. Another two peaks at 1162 and 1738 cm^{-1} may relate to polycarbonates that are formed by some polymerisation of EC and DMC [17]. Spectra contain peaks around $1500\text{--}1420 \text{ cm}^{-1}$ and 869 cm^{-1} that should be attributed to Li_2CO_3 [23]. Spectrum related to the SEI layer formed in VC-containing electrolyte contains not only the typical above-mentioned peaks of ROCO_2Li , polycarbonate and Li_2CO_3 but also a poly(VC) peak at 1111 cm^{-1} [24] that is absent in spectrum of SEI layer formed in VC-free electrolyte. The spectral differences of the SEI layers described above are attributed to the possible polymerization of VC and/or the VC reduction products via their double bond. From the SEM images, it is clear that VC considerable influences the surface reactions of the Si film electrodes with electrolyte. The double bond in VC, which adds more strain to this molecule compared to EC, makes it more reactive on the surface of electrode at slightly higher reduction potential than that of EC. The reduction mechanisms of VC were suggested in Ota's literature [24].

Fig. 8 shows the C 1s and O 1s XPS spectra for SEI layers formed on Si film anodes in VC-free and VC-containing electrolytes. The SEI layer formed in VC-free electrolyte (Fig. 8a and b) shows peaks related to ROCO_2Li at 291.1 eV (CO_3), 287.5 eV (CH_2O), and 285.8 eV ($\text{CH}_2\text{CH}_2\text{O}$) in the C 1s spectrum and at 533.5 eV (C-O-C) and 532.5 eV (C=O) in the O 1s spectrum. A strong peak at 284.6 eV in C 1s spectrum can be assigned to the absorbed carbon from the atmosphere. Another peaks at 289.9 eV in C 1s spectrum and 531.5 eV in O 1s spectrum may be attributed to Li_2CO_3 . Fig. 8c and d show the C 1s and O 1s XPS spectra for SEI layer related to VC-containing electrolyte. It can be found that the SEI layer has the same components as

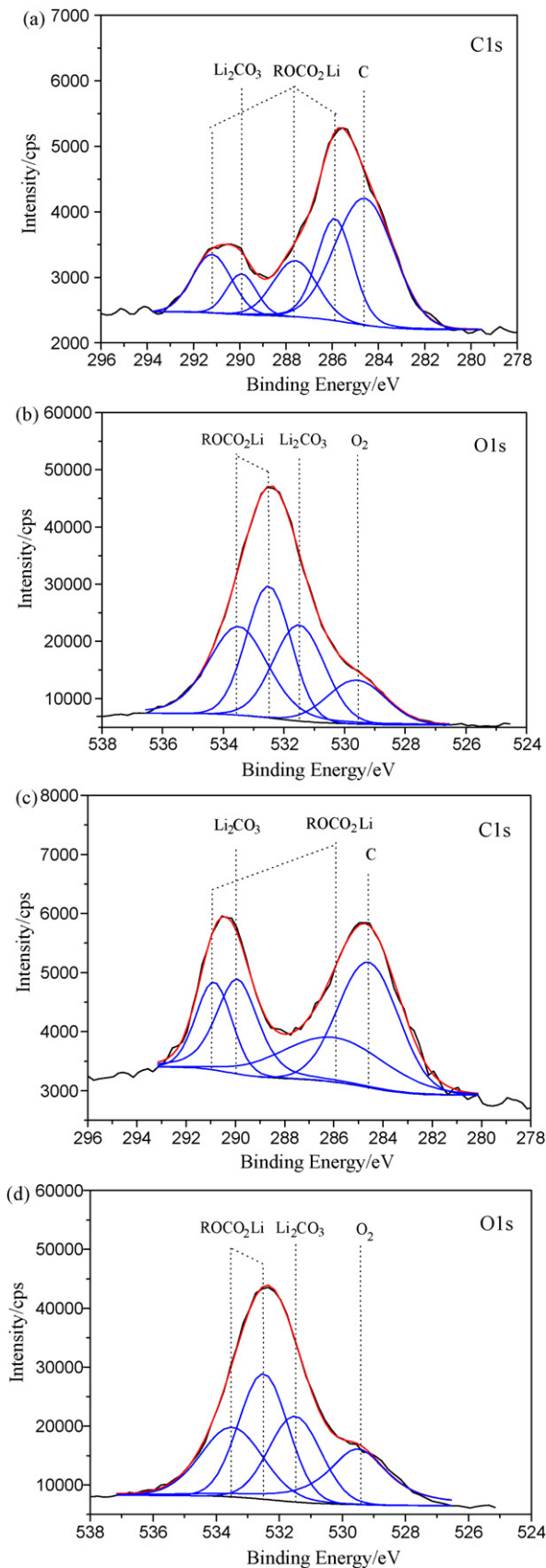


Fig. 8. C 1s and O 1s XPS spectra for SEI layer of Si film formed in VC-free (a and b) and VC-containing (c and d) electrolytes.

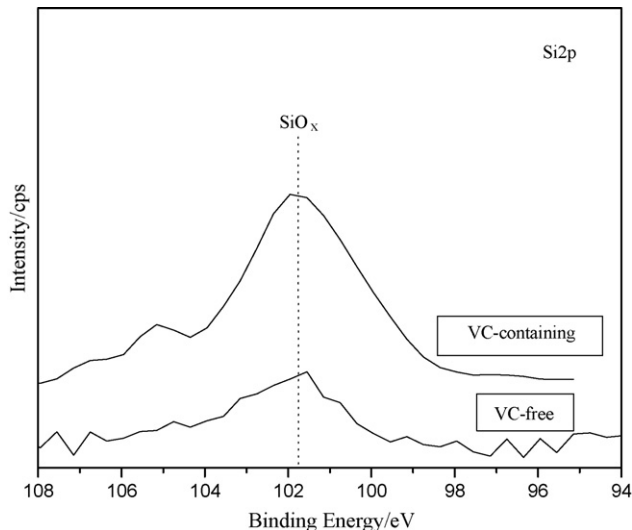


Fig. 9. Si 2p XPS spectra of SEI layer formed in VC-free and VC-containing electrolytes.

the SEI layer formed in VC-free electrolyte. The peaks related to poly(VC) or VC reduction products cannot be observed in XPS spectra, which can be detected from FTIR spectrum. It is most likely that the VC-derived products lie in the inner layer of SEI layer due to its higher reduction potential. But, the XPS can only detect the components on the top surface of SEI layer.

It is interesting that the silicon oxide appears in SEI layers formed in both VC-free and VC-containing electrolytes. Fig. 9 shows the Si 2p XPS spectra. Because the concentration of silicon oxide is very low in the top surface of SEI layers, the intensity of the spectra is weak and the shape is irregular due to the accuracy of XPS instrument. After fitting, the peaks are located at 102 eV, which can be assigned to SiO_x . The formation mechanism of SiO_x in the SEI layer on Si anode has not been reported in the literature. We think that the mechanism may be very similar to the formation mechanism of SnO_x on Sn film electrode suggested by Shieh et al. [25], but the formation process is different. The possible reaction can be interpreted as follows:



It is likely that the formation of silicon oxide is undergone mainly in the Li^+ insertion process. In the first Li^+ insertion process, the initially formed SEI layer is cracked due to the expansion of silicon. As a result, the electrolyte permeates through the damaged SEI layer and reacts with lithiated silicon to form silicon oxide. In the Li^+ deinsertion process, the SEI layer is broken in the valleys as described in SEM image, and silicon oxide can also be formed in the cracks.

A semiquantitative analysis of the XPS spectra is carried out based on atom sensitivity factor. The comparison of atomic concentration of various elements in SEI layers formed in VC-free and VC-containing electrolytes is shown in Fig. 10. The atom concentration of F in SEI layer formed in VC-containing electrolyte is obviously lower than that in VC-free electrolyte. The possible components containing F are LiF and PF_5 in the SEI layer. Because the content of P that derived from PF_5 is very

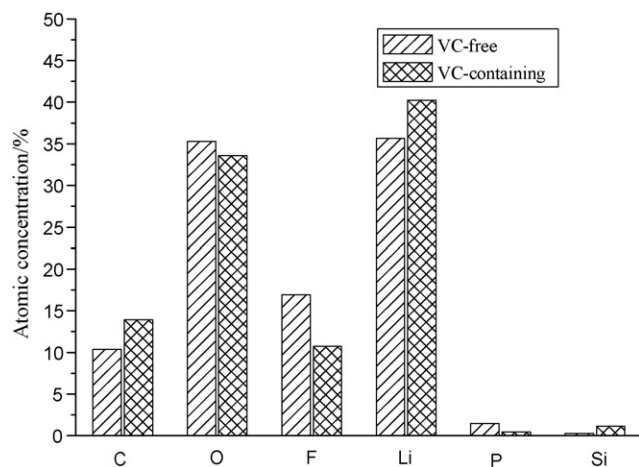


Fig. 10. The comparison of atomic concentration of various elements in SEI layers formed in VC-free and VC-containing electrolytes.

low, it indicates that the content of LiF decreased greatly in the SEI layer formed in VC-containing electrolyte. This has positive effect on the properties of SEI layer of Si film anode.

4. Conclusion

In this paper, the effect of VC as electrolyte additive on the electrochemical performance of Si film anode was studied in details. The cycle performance and efficiency of Si film anode were enhanced significantly with the presence of VC in electrolyte. The reversible capacity kept stable even up to 500 cycles. The superior electrochemical performance of Si film in VC-containing electrolyte was attributed to the advanced properties of SEI layer formed in initial several cycles. The SEI layer formed in VC-containing electrolyte showed smooth and uniform morphology. R_{SEI} of the SEI layer kept almost invariant upon cycling because SEI layer was impermeable to electrolyte. The presence of VC brought out the VC-reduced products and reduced the LiF content in SEI layer, which resulted in the better properties of SEI layer. However, in VC-free electrolyte, the impedance of SEI layer increased constantly upon cycling due to the increasing of SEI layer thickness and high content of LiF. And then, this caused the increasing of anode polarization, which resulted in the degradation of cycle performance and efficiency of Si film anode. The components of SEI layer of Si film anode were mainly lithium salt (e.g. ROCO_2Li , Li_2CO_3 , LiF) and polycarbonate, and the major components of SEI layer were similar in VC-free and VC-containing electrolytes. It was newly found that silicon oxide was formed in SEI layer of Si film anode due to the reaction of lithiated silicon with permeated electrolyte.

Acknowledgement

This study was supported by National High-Tech Research and Development Program of China.

References

- [1] M. Yoshio, H. Wang, K. Fukuda, Y. Hara, Y. Adachi, J. Electrochem. Soc. 147 (2000) 1245–1250.
- [2] J.H. Ryu, J.W. Kim, Y.E. Sung, S.M. Oh, Electrochem. Solid-State Lett. 7 (2004) A306–A309.
- [3] M. Wachtler, J.O. Besenhard, M. Winter, J. Power Sources 94 (2001) 189–193.
- [4] X.B. Zhao, G.S. Cao, C.P. Lv, L.J. Zhang, S.H. Hu, T.J. Zhu, B.C. Zhou, J. Alloy Compd. 315 (2001) 265–269.
- [5] Y.C. Su, J. Yan, P.T. Lu, J.T. Su, Solid State Ionics 177 (2006) 507–513.
- [6] M.N. Obrovac, L. Christensen, Electrochem. Solid-State Lett. 7 (2004) A93–A96.
- [7] H. Li, X.J. Huang, L.Q. Chen, Z.G. Wu, Y. Liang, Electrochem. Solid-State Lett. 2 (1999) 547–549.
- [8] J. Yang, B.F. Wang, K. Wang, Y. Liu, J.Y. Xie, Z.S. Wen, Electrochem. Solid-State Lett. 6 (2003) A154–A156.
- [9] G.X. Wang, J.H. Ahn, J. Yao, S. Bewlay, H.K. Liu, Electrochem. Commun. 6 (2004) 689–692.
- [10] S.M. Hwang, H.Y. Lee, S.W. Jang, S.M. Lee, S.J. Lee, H.K. Baik, J.Y. Lee, Electrochem. Solid-State Lett. 4 (2001) A97–A100.
- [11] S. Bourderau, T. Brousse, D.M. Schleich, J. Power Sources 81/82 (1999) 233–236.
- [12] H. Jung, M. Park, Y.G. Yoon, G.B. Kim, S.K. Joo, J. Power Sources 115 (2003) 346–351.
- [13] T.D. Hatchard, J.R. Dahn, J. Electrochem. Soc. 151 (2004) A838–A842.
- [14] K.L. Lee, J.Y. Jung, S.W. Lee, H.S. Moon, J.W. Park, J. Power Sources 129 (2004) 270–274.
- [15] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, J. Power Sources 136 (2004) 303–306.
- [16] J.B. Kim, H.Y. Lee, K.S. Lee, S.H. Lim, S.M. Lee, Electrochem. Commun. 5 (2003) 544–548.
- [17] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423–1439.
- [18] Y.S. Hu, W.H. Kong, H. Li, X.J. Huang, L.Q. Chen, Electrochem. Commun. 6 (2004) 126–131.
- [19] K. Abe, H. Yoshitake, T. Kitakura, T. Hattori, H.Y. Wang, M. Yoshio, Electrochim. Acta 49 (2004) 4613–4622.
- [20] A.M. Andersson, K. Edstrom, J. Electrochem. Soc. 148 (2001) A1100–A1109.
- [21] K. Dokko, Y. Fujita, M. Mohamedi, M. Umeda, I. Uchida, J.R. Selman, Electrochim. Acta 47 (2001) 933–938.
- [22] E. Barsoukov, J.H. Kim, J.H. Kim, C.O. Yoon, H. Lee, Solid State Ionics 116 (1999) 249–261.
- [23] G.A. Nazri, G. Pistoia, Lithium Batteries Science and Technology, Kluwer Academic Publishers, Boston, 2004, pp. 208–218.
- [24] H. Ota, Y. Sakata, A. Inoue, S. Yamaguchi, J. Electrochem. Soc. 151 (2004) A1659–A1669.
- [25] D.T. Shieh, J.T. Yin, K. Yamamoto, M. Wade, S. Tanase, T. Sakai, J. Electrochem. Soc. 153 (2006) A106–A112.