

The Cooperative Effect of Vinylene Carbonate and 1,3-Propane Sultone on the Elevated Temperature Performance of Lithium Ion Batteries

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Vinylene carbonate (VC) and 1,3-propane sultone (1,3-PS) have been used as the electrolyte additives to improve the high temperature safety of the lithium ion batteries. The electrochemical performance of ethylene carbonate-based binary electrolytes without and with additives on graphite electrode is studied by cyclic voltammetry and electrochemical impedance spectroscopic. The cycle performances of the graphite/LiCoO₂ batteries with two additives are measured by battery testing system at 25 °C and 60 °C. The morphology and composition of the solid electrolyte interphase are analyzed by scanning electron microscopy and X-ray Photoelectron Spectroscopy, respectively. In summary, the co-use of VC and 1,3-PS can greatly improve the cycle life and suppress swelling behavior of graphite/LiCoO₂ cells at elevated temperature.

Keywords: Vinylene carbonate; 1,3-propane sultone; Lithium ion battery; High temperature safety

1. INTRODUCTION

Lithium ion batteries have been successfully used in the portable electronic appliances and expected to apply in the hybrid electric vehicles (HEV), the electric vehicles (EV) and other large capacity storage fields due to their high energy density, high discharge voltage and long cycle life. However, its safety has attracted great attention due to the lithium-ion battery swell, fire and explosion incidents occurred throughout the world in recent years [1, 2].

The battery swell is caused by the gas evolution through the reaction of lithiated graphite with the electrolyte components, as well as through the metastable components of solid electrolyte interphase

(SEI) decomposition at elevated temperature [3, 4]. And the explosion of the batteries is due to large volume of gas release from the reaction of the carbonates with the PF_5 from LiPF_6 decomposition [5, 6]. The battery fire is usually attributed to the reaction of the inflammable organic solvents of electrolyte with the oxygen produced at the cathode active materials (such as Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, and Li_xNiO_2) at elevated temperature [7-10]. Therefore, the electrolyte plays a critical role in determining the high temperature performances of lithium ion batteries. To date, researchers commit to study the thermal stability electrolyte salts instead of unstable LiPF_6 [11-16], but research results show LiPF_6 can not be replaced in a short time. Besides the lithium salts, the electrolyte additives to the lithium ion batteries, such as vinylene carbonate (VC) [17], 1,3-propane sultone (1,3-PS) [18, 19] and fluoroethylene carbonate (FEC) [20] are used to improve the high temperature performance of lithium-ion batteries by forming stable and effective SEI film on the graphite anode because these additives generally are more easily reduced than the electrolyte. Among above additives, VC can form a stable SEI on the graphite negative electrode and improve the cycle performance of batteries, however, the effect of decreasing the gas evolution is not sufficient, especially at elevated temperature [21]. 1,3-PS is well known to suppress swelling of batteries at elevated temperature [19]. So we presume that the combination of VC and 1,3-PS will bolster each other in improvement the safety of the lithium ion batteries at elevated temperature.

2. EXPERIMENTAL PART

2.1 Electrolytes

The commercial electrolyte which was composed of 1.0 M lithium hexafluorophosphate (LiPF_6) dissolved in a solvent mixture of ethylene carbonate (EC)/ethylmethyl carbonate (EMC) with a weight ratio of 3:7, vinylene carbonate (VC) and 1,3-propane sultone (1,3-PS) were purchased from HSC (China) and Wuhan Sino-German Far East Fine Chemical Industry Co., Ltd (China) without further purification. Electrolyte preparation was carried out in a dry glove box ($\text{H}_2\text{O} < 1$ ppm) filled with high purity of argon.

2.2 Li/graphite half cells

The graphite electrode was prepared by mixing 80 wt.% artificial graphite (AG) (BTR, China), 10 wt.% conductive carbon (Super P, Timcal), and 10 wt.% polyvinylidene fluoride (Arkema, France) binder dissolved in anhydrous N-methyl-2-pyrrolidinone, then dried at 130 °C under vacuum for 12 h prior to assembly. A Celgard 2400 microporous polypropylene membrane was used as a separator. The cells (CR-2016) were assembled using lithium metal foil as the counter electrode in an argon-filled glove box (O_2 and H_2O levels less than 1 ppm). The cells were aged for overnight before the measurement to ensure percolation of the electrolyte to the electrode.

Cyclic voltammetry (CV) measurement of the Li/graphite cells contain electrolytes was performed on Gamry electrochemical workstation, and electrochemical impedance spectroscopic (EIS)

measurement was conducted on a Solartron SI 1287 electrochemical interface in the frequency range of 100 kHz to 0.01 Hz.

The cells were discharged and charged three times between 0.01 V and 2.0 V just prior to disassembly in a glove box. The graphite electrodes were carefully separated from the cells and subsequently rinsed with a dimethyl carbonate solvent in order to remove the residual electrolyte and then dried under vacuum at room temperature. The surface morphology and chemical composition of the SEI layer were analyzed by scanning electron microscope (SEM, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS, PHI-5000C, Perkin Elmer, USA), respectively.

2.3 graphite/LiCoO₂ full cells

The charge and discharge characteristics were examined by type 413952 lithium ion batteries with nominal capacity of 920 mAh. Anode was prepared by mixing artificial graphite, conductive carbon (Super P), polyvinylidene fluoride binder dissolved in anhydrous N-methyl-2-pyrrolidinone. Cathode was prepared by mixing LiCoO₂, conductive carbon (Super P), polyvinylidene fluoride (PVDF) binder dissolved in anhydrous N-methyl-2-pyrrolidinone. The batteries were cycled at a constant current-constant voltage charge and a constant current discharge with 4.2 V and 3.0 V as cutoff voltages with both charge and discharge rates of C/2. For storage performance test at high temperature, the cells of full charged state were stored at 70 °C for 48 h in a SBVO-01 (Jiang Ling, China) constant temperature oven. And the thickness of cells before and after storage was measured by vernier caliper. The swell value of cell is calculated by the following formula:

$$\text{Swell-value}(\%) = \frac{(T - T_0)}{T_0} \times 100\%$$

T_0 is the initial thickness of the cell and T is the thickness of the cell after storage.

3. RESULTS AND DISCUSSIONS

3.1 Electrochemical properties

The reduction potentials of the additives are investigated using a Li/graphite cell containing the EC-based electrolyte. When the additives are single used, the amount added to the electrolyte is 1.5 wt% based on the total amount of the electrolyte. For the combination use, each amount of the electrolyte the additive is 1.5 wt%. Fig. 1 shows the CV curves of the electrolytes containing singly used VC, 1,3-PS and co-used VC and 1,3-PS (VC+1,3-PS), respectively. In 1.0 M LiPF₆-EC/EMC solution without additives, the peak around 1.8 V can be assigned to the reduction of electrolytes. With the addition of VC a new peak appears at *ca.* 1.1 V, which is attributed to the reduction of VC. The peak of 1,3-PS-containing electrolyte appears at *ca.* 1.0 V, while the reduction of electrolytes is diminished. For comparison, the reduction behavior in the VC+1,3-PS-added electrolyte is also

presented in Fig. 1d. There are two reduction current peaks at *ca.* 1.1 V in the first scan and 0.9 V in the second scan, which correspond to the reduction of VC+1,3-PS, respectively. The reduction of electrolytes disappeared. Thus, VC and 1,3-PS maybe involved in the formation of SEI film.

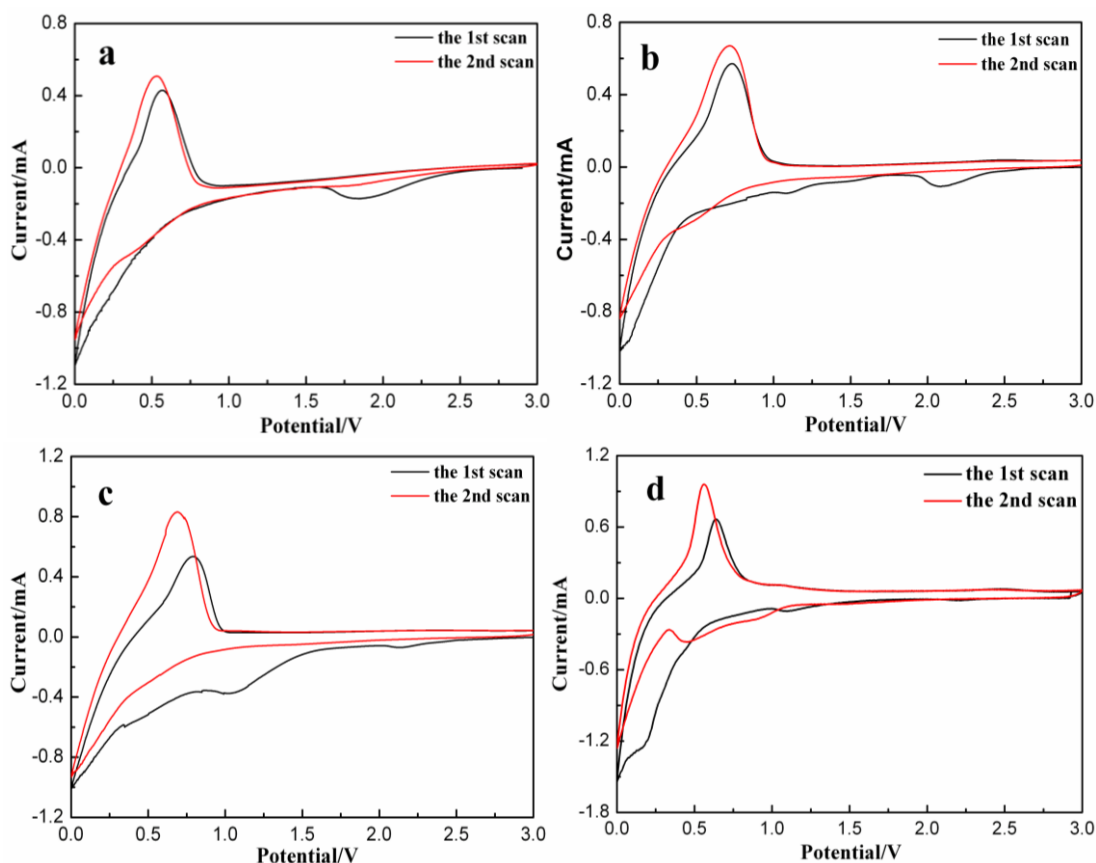


Figure 1. Cyclic voltammograms of (a) without additives; (b) with VC; (c) with 1,3-PS; (d) with VC+1,3-PS in 1.0 M LiPF₆-EC/EMC on artificial graphite with a scan rate of 1 mVs⁻¹

Electrochemical impedance spectroscopic is known to be closely associated with the lithium ion conductivity of SEI film. The impedance value is related to the lithium ion migration rate. The impedance spectra of the discharged cells before and after storage at 70 °C for 48 h are shown in Fig. 2. The figures show that electrolytes with VC and VC+1,3-PS have higher impedance values than those with 1,3-PS but without additives before and after storage. As seen in Fig. 2, the SEI film resistance of adding 1,3-PS and without additives diminish after storage, while adding VC and VC+1,3-PS increase slightly, which indicates that significant shrink of the first semicircle may result from the decomposition of the SEI film. And instead, the VC and VC+1,3-PS-induced SEI film may develop to thickness and the size of the first semicircle increases.

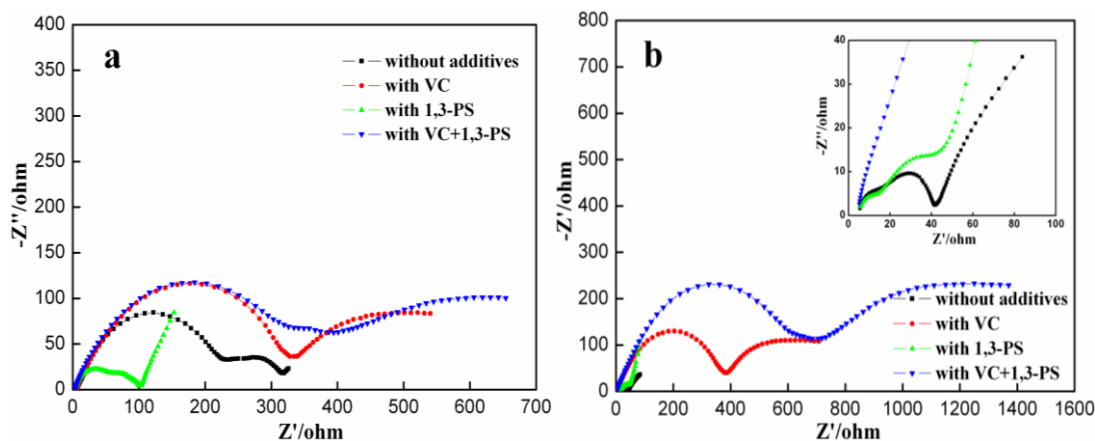


Figure 2. AC impedance of Li/AG half cells in different electrolyte systems (a) fully discharged; (b) fully discharged after storage at 70 °C for 48 h.

3.2 VC and 1,3-PS evaluation for effecting storage performance

Table 1 presents swell value of cells with various additives after storage at 70 °C for 48 h. It could be seen that the cell without additives swells 16.1%. As the VC is added into the electrolyte keeping other conditions invariable, the cell swells 18.5%. While the 1,3-PS is added into the electrolyte, the cell swells only 4.3%. The results are consistent with the study of Guo *et al.* [19] and H. Lee *et al.* [22]. Adding 1,3-PS helps to suppress the bulging of the battery. When VC and 1,3-PS are applied as electrolyte additives, the swell value of cells drops to 2.2%. The result of cooperative of VC (1.5 wt.%) and 1,3-PS (1.5 wt.%) is more effective than the co-worked LiBOB (0.10 M) and 1,3-PS (3 wt.%) [19] on suppressing bulging of battery. Because that may be the reaction between the VC and 1,3-PS for their close reduction potential, and generate the (VC)-Li⁺(1,3-PS) [23] to reduce the usage of 1,3-PS. Therefore, the cooperative of a small amount of VC and 1,3-PS can form more stable SEI film in the EC-based electrolyte to prevent the decomposition and reaction between the electrode and electrolyte at high temperature, so gas evolutions decrease and cells will swell less.

Table 1. The swell value of cells with various additives

Solvents	VC (wt.%)	1,3-PS (wt.%)	Swell value (%)
EC : EMC (3:7, wt.)	0	0	16.1
	1.5	0	18.5
	0	1.5	4.3
	1.5	1.5	2.2

3.3 Cycle performance

Fig.3 presents the cycling performance of graphite/LiCoO₂ cells without or with additives in 1.0 M LiPF₆-EC/EMC at room temperature. It can be seen from Fig.3 that the cells with EC-based electrolytes containing VC and VC+1,3-PS show higher initial discharge capacity than those without

additives and with 1,3-PS. It means that the irreversible capacity loss of the batteries with VC and VC+1,3-PS is greatly reduced. Their capacity deteriorates more slowly, where with as much as 95.8% of the initial discharge capacity maintained even beyond 250th cycle. That less irreversible capacity loss and better cycle performance confirms that the film-forming property is improved after adding VC and VC+1,3-PS to the EC-based electrolytes. The stable and efficient SEI film created by VC or VC+1,3-PS can protect the electrode material and prevent the capacity from fading with cycle times increasing at 25 °C.

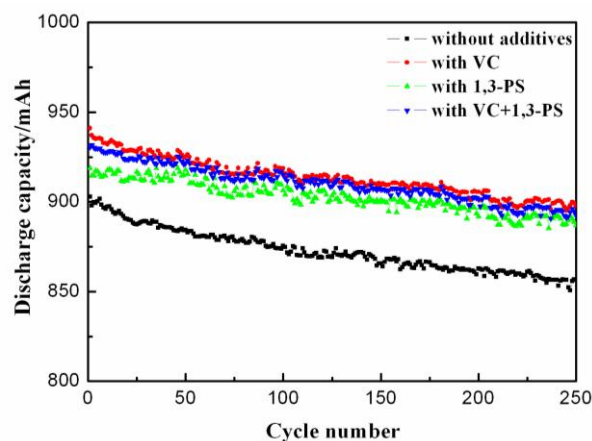


Figure 3. Cycle behavior batteries at 25 °C with 1.0 M LiPF_6 EC/ EMC without additives (-■-); with VC(-●-); with 1,3-PS (-▲-); with VC+1,3-PS (-▼-)

Fig. 4 shows the relationship between the discharge capacity and internal resistance changes and cycle number of lithium ion batteries without or with additives in 1.0 M LiPF_6 -EC/EMC at 60 °C. As showed in Fig. 4, the initial capacity of the lithium ion batteries without additives is 910 mAh, but the internal resistance increases as the cycle number increasing (initial internal resistance 60 m Ω , and even up to 103.94 m Ω).

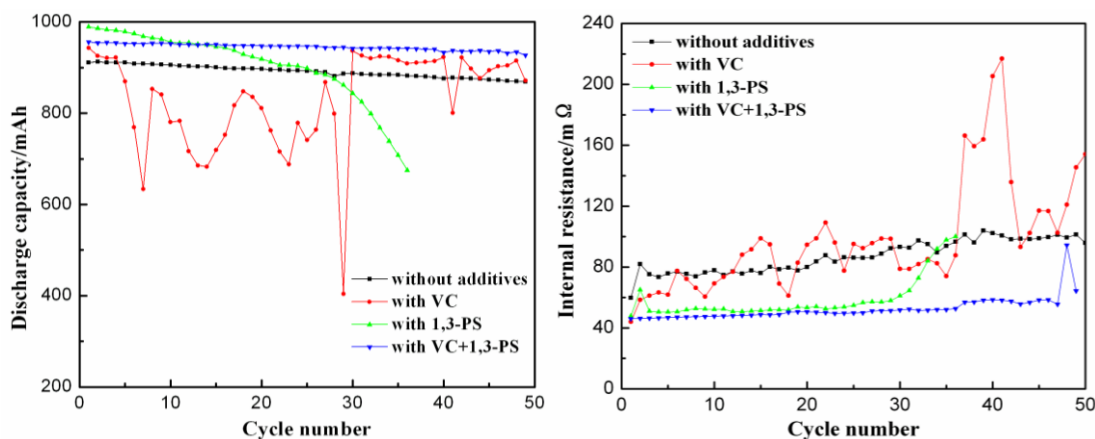


Figure 4. Cycle behavior and internal resistance of batteries at 60 °C with 1.0 M LiPF_6 -EC/EMC without additives (-■-); with VC (-●-); with 1,3-PS (-▲-); with VC+1,3-PS (-▼-)

The initial capacity of the lithium ion batteries with VC and 1,3-PS are up to 943.25 mAh and 988.89 mAh, however, the capacity and internal resistance have big changes as the cycle number increasing. At the same time, battery with the co-use VC and 1,3-PS shows a initial capacity of 956.3mAh and has good cycle performance, and the internal resistance has little changes (*ca.* 48 m Ω) as the cycle number increased. However, the batteries without additives and with single additive are found swell during the cycle process at 60 °C. Above the mentions indicate that the SEI film formed with the co-use VC and 1,3-PS has better thermal stability than the SEI film formed with other electrolytes during the cycle process at 60 °C.

3.4 Surface Morphology and SEI film composition

Fig. 5 shows a series of SEM images of the graphite electrode for with none, singly used and co-used additives. The AG surface in EC/EMC without additives is covered with a rough and loose SEI film in Fig. 5a. In image of the additives, there is a significant difference in the surface morphology of the uniformly covered film, as seen in Fig. 5b, c, and d.

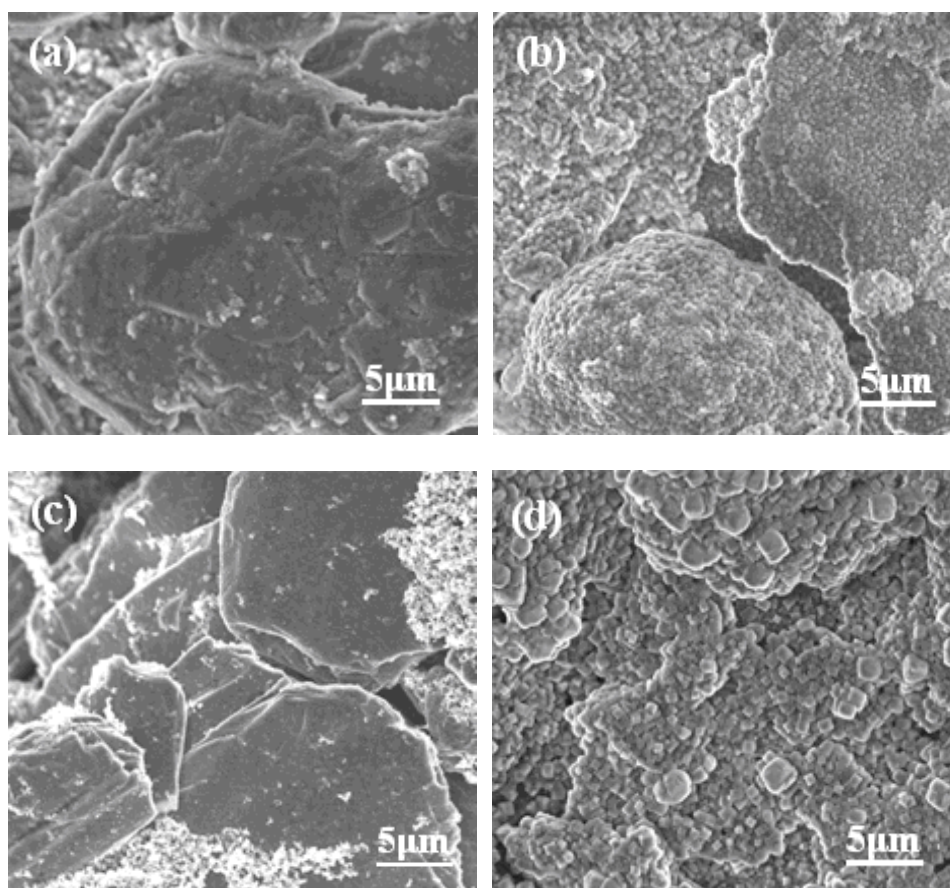
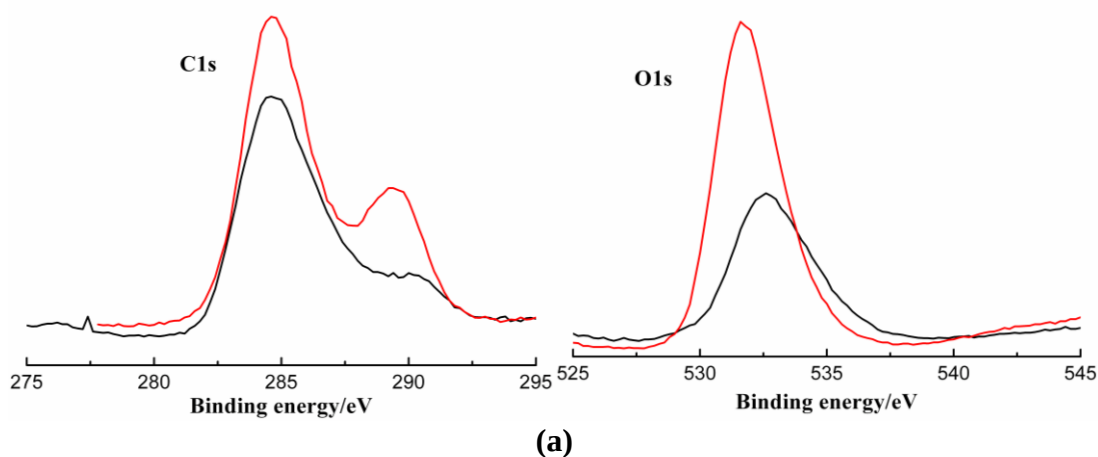
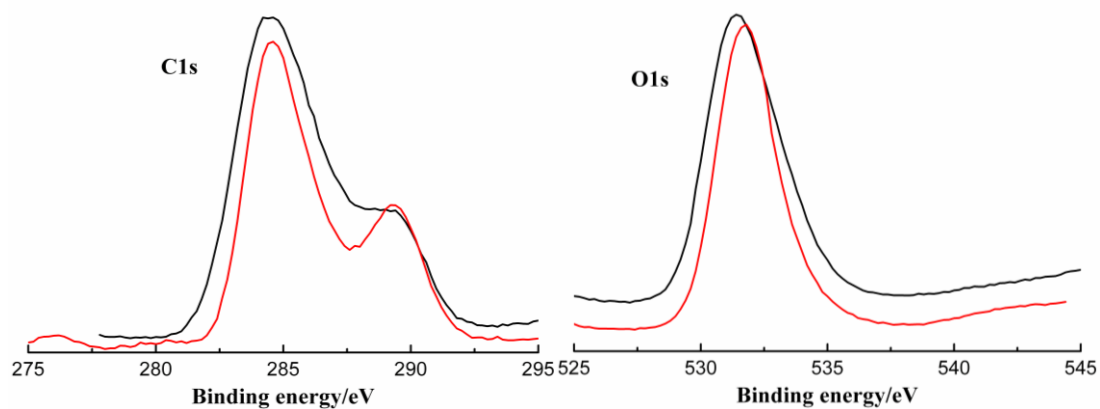


Figure 5. SEM images of the artificial graphite surface after the three charge-discharge cycles in 1.0 M LiPF₆-EC/EMC (a) without additives ; (b) with VC; (c) with 1,3-PS; (d) with VC+1,3-PS

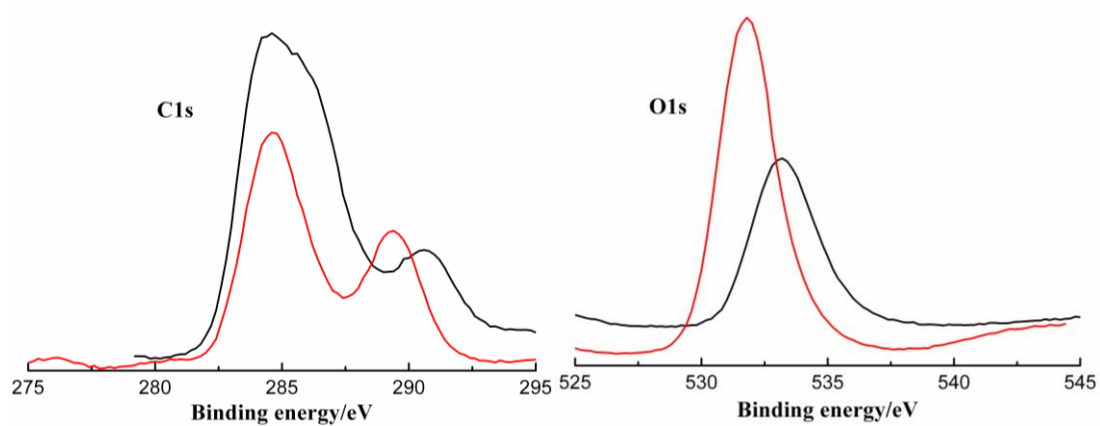
The morphology for VC-containing electrolyte (Fig. 5b) displays the graphite anode contacts with submicron balls. The morphology for 1,3-PS-containing electrolyte (Fig. 5c) displays SEI film that is much thinner and more dense than VC-containing electrolyte. When the co-use of VC and 1,3-PS, the morphology of SEI film on the graphite surface is consist of dense cubic particles (Fig. 5d). As above mentions, the SEI film of graphite electrode with VC-containing and co-used VC and 1,3-PS electrolytes are more thicker than those without additives and single used 1,3-PS. They are in good agreement with the AC impedance of the kinetic characteristics of anode electrodes. And a dense and thick SEI film is produced by VC and 1,3-PS during the charge-discharge cycles, which improves the cycleability and suppresses the gas evolution. Surface chemical compositions of graphite electrodes before and after storage at 70 °C for 48 h are analyzed by XPS as shown in Fig. 5. Analysis of the C 1s spectrum reveals that the intensity of the peak located at 284.6 eV, assigned to C-C and C-H. The surface of AG anode contains many species characteristic of electrolyte decomposition products. The electrode of VC-containing, the C 1s spectrum new peaks are observed in the 289.5 eV suggesting the presence of Li_2CO_3 (289.5 eV). The major peaks in O 1s spectra at 531.6 eV and 532.5~533.5 eV correspond to Li_2CO_3 and lithium alkyl carbonates ($\text{R-CH}_2\text{O(C=O)OLi}$ (532.5 eV) and ($\text{R-CH}_2\text{O(C=O)OLi}$ (533.5 eV) [18], respectively. For the electrode of VC-containing, the O 1s spectra peaks appear at 531.6 eV, and the other electrode of the O 1s spectra peaks are at 532.5 eV and 533.5 eV. Analysis of an AG composite anode extracted from a cell containing 1,3-PS and VC+1,3-PS addition suggests changes in surface compositions compared to anodes without 1,3-PS. The peak at 168~169 eV in the S 2p spectrum confirms that 1,3-PS participates in formation of the SEI film on the AG anode. This peak can be assigned to $\text{R-SO}_3\text{Li}$ moieties. That is, the co-use of VC and 1,3-PS, the components of the SEI are major lithium carbonate LiCO_3 and $\text{R-SO}_3\text{Li}$ moieties.

Compared to the graphite anode before the storage, the sample containing without additives and 1,3-PS appears a new C 1s peak at 289.5 eV that corresponding to LiCO_3 , while the major O1s peaks of the two samples generate migration (from 533.5 eV and 532.5 eV to 531.6 eV) (gas evolution reactions during the conversion of meta-stable SEI components lithium alkyl carbonates to stable SEI components LiCO_3). The C 1s intensity of VC-containing sample at 289.5 eV strengthen obviously. The components of co-used VC and 1,3-PS graphite surface have a little change, and are also major lithium carbonate (LiCO_3) and $\text{R-SO}_3\text{Li}$ moieties.

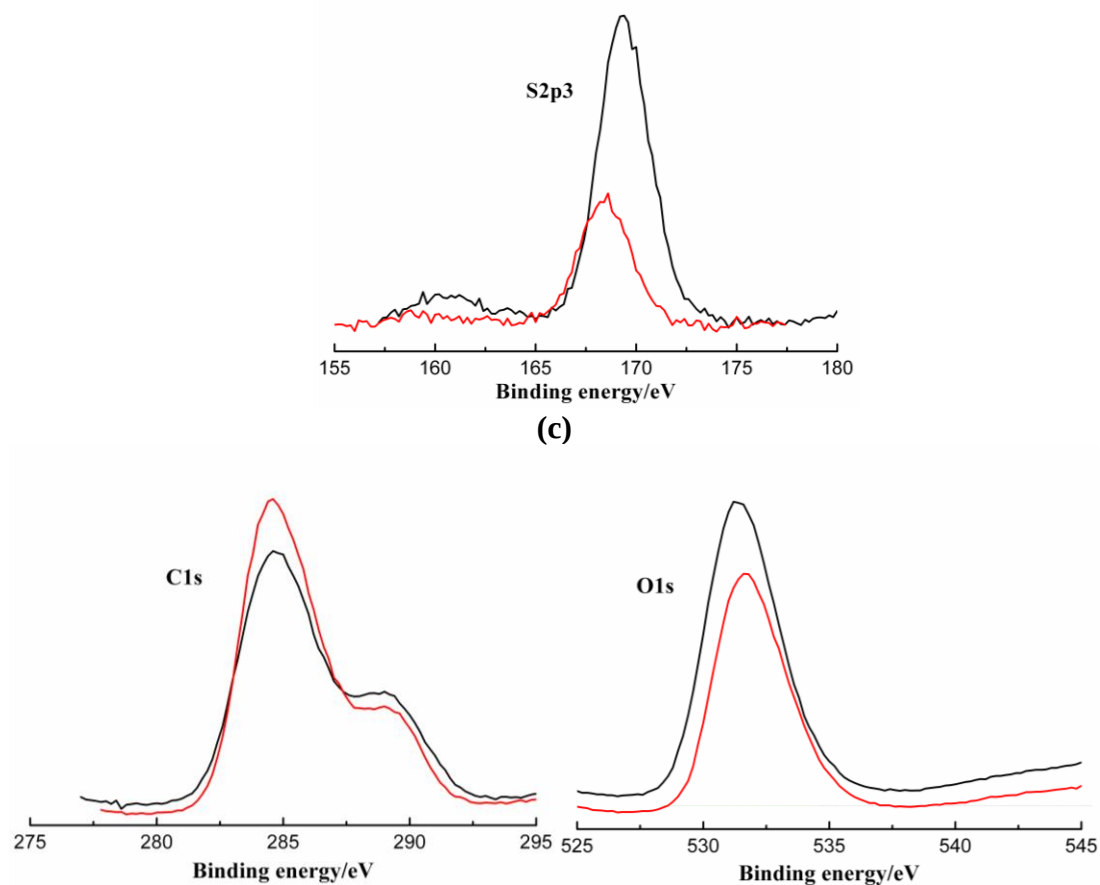




(b)



(c)



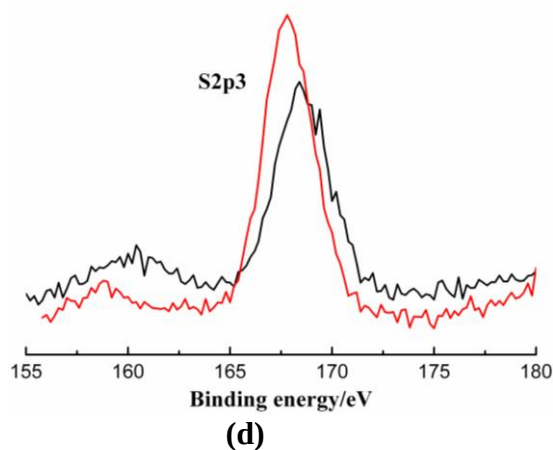


Figure 6. The C1s, O1s and S2p XPS spectra of graphite electrodes before and after storage at 70 °C for 48 h (a) without additive; (b) with VC; (c) with 1,3-PS; (d) with VC+1,3-PS

4. CONCLUSIONS

Combination of vinylene carbonate and 1,3-propane sultone as additive for the electrolytes in lithium ion batteries has effectively suppressed the swell of battery and improved the cycle performances of the battery at elevated temperature. The graphite contacting with the VC and 1,3-PS additive was demonstrated to have lithium carbonate Li_2CO_3 and $\text{R-SO}_3\text{Li}$ by XPS analysis, which maybe improve the SEI film stability.

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