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Effect of 1,8-Naphthosultone Additive on High Temperature Performance of Lithium Ion Batteries

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In this paper, we calculate the Lowest Unoccupied Molecular Orbital (LUMO) level of the 1,8-naphthosultone (1,8-NS) by density functional theory. The effects of 1,8-NS on the high temperature performances of lithium ion batteries are evaluated by battery test system. The electrochemical performances are measured by cyclic voltammetry and electrochemical impedance spectroscopic. By adding 1 wt % 1,8-NS into a commercial binary electrolyte of lithium ion battery, the initial discharge capacity and cycle stability of lithium ion battery are improved significantly at 60 °C. By X-ray photoelectron spectroscopy analysis, we suggest that the improvement may be attributed to the 1,8-NS being reduced to form Li_2S, R-SO_2Li and R-SO_3Li phase on the graphite electrode. Thus, the reduction products covered on the graphite electrode may reduce the resistance of solid electrolyte interphase and suppress the battery swell.

Keywords: 1,8-naphthosultone; High temperature performance; Lithium ion battery; Solid electrolyte interphase film

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 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 state interphase (SEI) decomposition at high temperatures [3, 4]. And the explosion of the batteries is due to a large quantity of gas releasing from the reaction of the carbonates with the PF_5 from $LiPF_6$ decomposition [5, 6]. The battery burning is usually attributed to the reaction of the inflammable organic solvents of electrolyte with the oxygen produced from the decomposition of the cathode active materials (such as Li_xCoO_2, $Li_xMn_2O_4$, and Li_xNiO_2) at high temperature [7-9]. 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 $LiPF_6$ [10-15], but the research results show $LiPF_6$ cannot be replaced in a short time. Besides the lithium salts, the electrolyte additives to the lithium ion batteries, such as vinylene carbonate (VC) [16], 1,3-propane sultone (1,3-PS) [17, 18] and fluoroethylene carbonate (FEC) [19] are used to improve the high temperature performances of lithium-ion batteries by formation of a stable and effective SEI film on the graphite anode because these additives generally are more easily reduced than the electrolyte.

In our work, we choose 1,8-NS with the low LUMO level obtained by the density functional theory (DFT) calculations and a naphthalene ring structure, which is expected to be more easily reduced on the graphite anode and improve the thermal stability of the batteries. Hence the present work is to employ 1,8-NS as an additive and to study its effects on the high temperature performances of Li-ion batteries, and also to explore its possibility to be used as the high temperature additive to the Li-ion batteries.

2. EXPERIMENTAL PART

A commercial electrolyte which was composed of 1.0 M $LiPF_6$ dissolved in a solvent mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC) with a weight ratio of 3:7 was used as a reference electrolyte, and 1,8-NS (tokyokasei, Japan) was selected as an electrolyte additive to the above electrolyte.

To investigate the reductive potential of the 1,8-NS, the DFT calculation was performed using the Gaussian 09 programs package. The equilibrium and transition structures were fully optimized by B3LYP method using a 6-31G + (d, p) basis set. Cyclic voltammetry (CV) measurement of the Li/artificial graphite (AG) button cells (CR-2016) containing electrolytes with and without 1,8-NS was performed on Gamry electrochemical workstation, and electrochemical impedance spectroscopic measurement (EIS) was conducted on a Solartron SI 1287 electrochemical interface in the frequency rang of 100 kHz to 0.01 Hz.

The charge and discharge characteristics were examined by type 413952 lithium ion batteries with nominal capacity of 920 mAh at 25 °C and 60 °C, while the changes of internal resistance were measured as the batteries cycle at 60 °C. The batteries were cycled at a constant current-constant voltage charge and a constant current discharge between the voltage range of 4.2 V and 3.0 V with both charge and discharge rates of C/2. An environmental chamber (Xinrenda, China) was used to reach and maintains the desired temperature value. The cells of full charged state were stored at 70 °C for 48h in a SBVO-01 (Jiang Ling, China) constant temperature oven to test the storage performance at high temperature. And the thicknesses of the cell before and after storage test were measured by vernier caliper. The swell value of cell was calculated by the following formula:

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

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

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.

3. RESULTS AND DISCUSSIONS

3.1 The DFT calculations

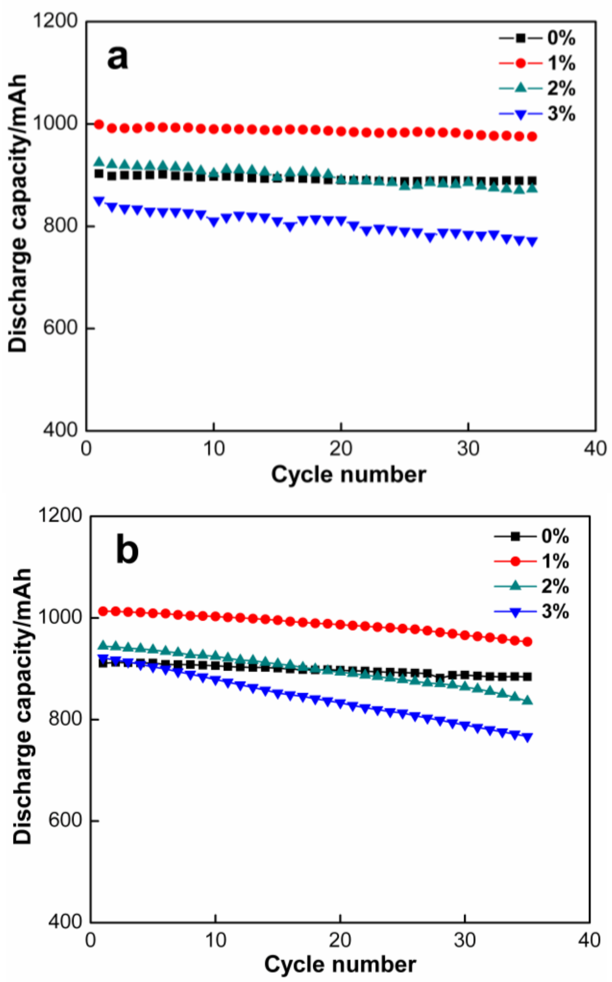
The DFT can be used to estimate the reduction and oxidation potentials of the additives, effectively screening appropriate compounds as anodic or cathodic additives for the electrolyte based on their decomposition potentials. The anodic reaction correlates to the LUMO level. The lower the LUMO level of the molecule is, the more easily the electron can be transferred into the molecule and reduced on the electrode [20]. It can be seen from Table.1 that the 1,8-NS has a low LUMO level among the solvents and additives. Thus, 1,8-NS may be more easily reduced on the anode to form the SEI film to prevent the organic solvents of the electrolyte from decomposing.

Table 1. Results of DFT calculation

Compounds	LUMO (eV)
EC	-0.02887
EMC	-0.02367
VC	-0.03907
1,3-PS	-0.02375
FEC	-0.03859
1,8-NS	-0.14493

3.2 Cycling performance of Li-ion batteries

Fig. 1 illustrates the cycle performance of lithium ion batteries without and with 1,8-NS additive in 1.0 M $LiPF_6$-EC/EMC at 25 °C and 60 °C. As shown in Fig. 1a, at 25 °C, the initial discharge capacities of the batteries without additive and with 2 wt% and 3 wt% of 1,8-NS are 899.8mAh, 919 mAh and 835.3 mAh, respectively, which are lower than normal capacity (920 mAh). However, the initial discharge capacity of the battery with 1 wt% 1,8-NS is 991.8 mAh, which indicates that adding small amount of 1,8-NS can effectively improve the initial discharge capacity. The capacities of all the cells decrease slowly as the cycle number increases, but the cell with 1 wt% 1,8-NS still maintains the highest capacity in 35 cycles. This suggests that adding the 1 wt% 1,8-NS improves the cycle performance of cells at room temperature. Furthermore, the cell with 1 wt% 1,8-NS has been found a higher initial discharge capacity and better cycle performance compared with the other tested cells at 60 °C in Fig. 1b. As shown in Fig. 1c, the internal resistances of all the cells with 1,8-NS are smaller than the cells without additive. And the cell with 1 wt% 1,8-NS has the smallest internal resistance (*ca.* 44 mΩ) and little changes as the cycle number increases in all the tested cells.



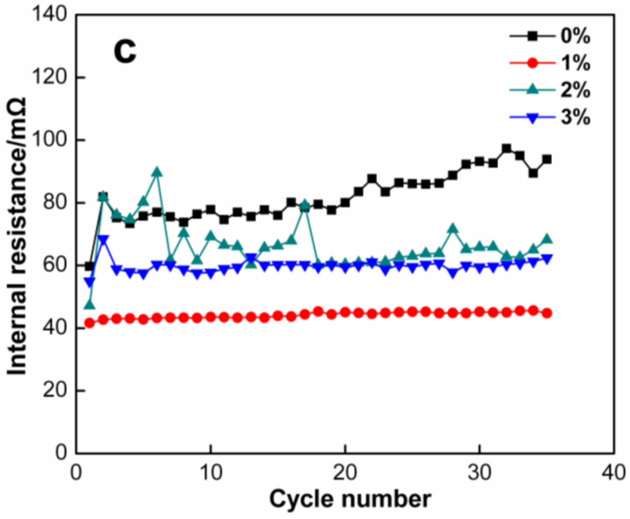
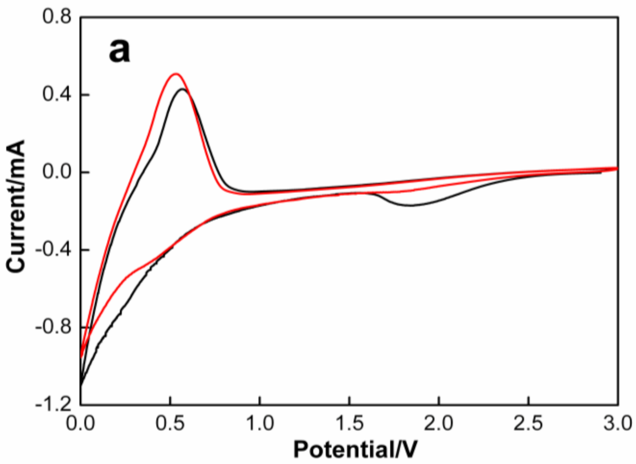


Figure 1. The cycle performance curves of 413952 lithium ion batteries using 1.0 M $LiPF_6$-EC/EMC without and with various 1,8-NS content (a) at 25 °C; (b) at 60 °C; (c) the internal resistance curves at 60 °C

3.3 CV and EIS measurements

To understand the mechanism of 1,8-NS additive on the high temperature performance of lithium ion battery**,** the CV measurement results of the 1.0 M $LiPF_6$-EC/EMC without and with 1,8-NS additive are shown in Fig. 2. During the first negative scan, the cell without additive in Fig. 2a has a reduction peak at the potential *ca.* 1.8 V, due to the reduction of electrolytes, resulting in the formation of SEI film on the graphite electrode. While the cell with 1,8-NS additive has two reduction peeks at *ca.* 2.2 V and 1.1 V (Fig. 2b, 2c and 2d) in the first scan which maybe corresponds to the reduction of electrolytes and 1,8-NS. During the second scan the two reduction peaks disappear. The results suggest that the addition of 1,8-NS additive can be reduced on the graphite electrode prior to Li intercalation and help form a SEI film.



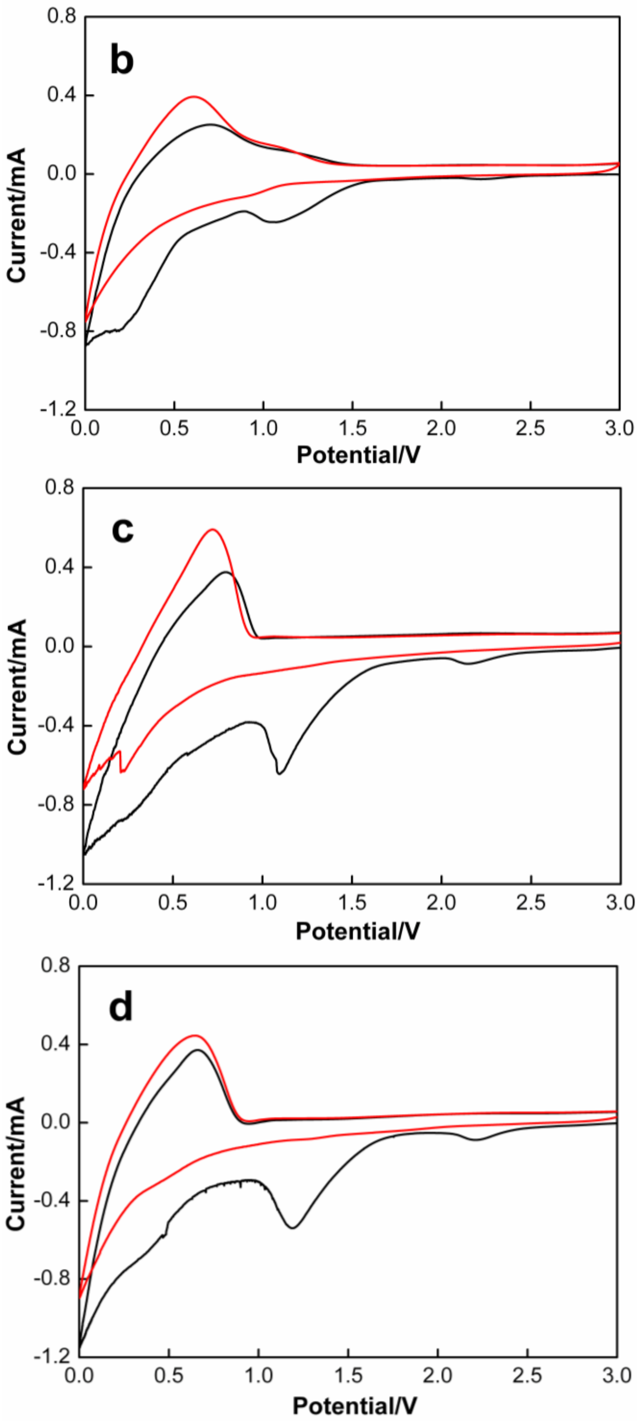


Figure 2. Cyclic voltammograms (the first scan (*black*) and the second scan (*red*)) of artificial graphite electrodes in 1.0 M $LiPF_6$-EC/EMC (a) without 1,8-NS; (b) with 1 wt% 1,8-NS; (c) with 2 wt% 1,8-NS; (d) with 3 wt% 1,8-NS, scan rate 1 mVs^{-1}.

EIS is used to investigate the kinetic characteristics of anode electrodes in different electrolyte systems in Fig. 3. Cells are firstly cycled between 0.01 V and 2.0 V for three times and then keep at the charged state. Transport behavior of lithium ions between the anode materials and the electrolytes, largely dependent on the properties of SEI layer, would determine the cell performance. As reported [21], the semicircle value in high frequency region corresponds to Li^+ migration through the SEI film and indicates the SEI film resistance. As seen in the enlargement of the high frequency semicircle in Fig. 3, the addition of 1 wt% 1,8-NS additive effectively reduce the SEI layer resistance which indicates that the 1 wt% 1,8-NS additive can help form a SEI film of higher quality to support the lithium ions transport through the interface easier.

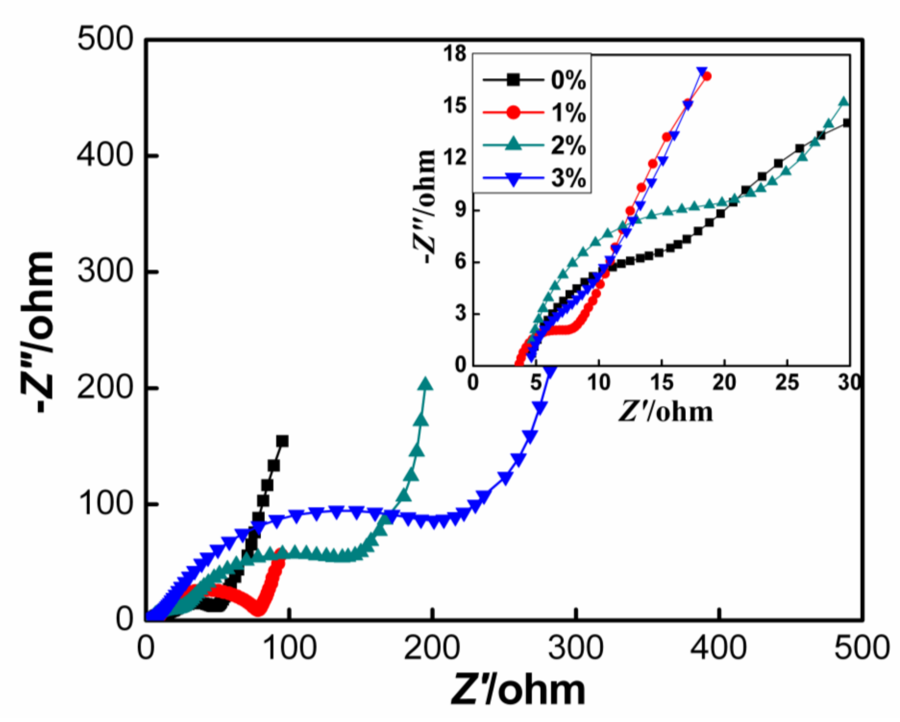


Figure 3. Electrochemical impedance of Li/AG half cells after three cycles in different electrolyte systems at 2.0 V vs. Li/Li^+

3.4 1,8-NS evaluation for effecting storage performance

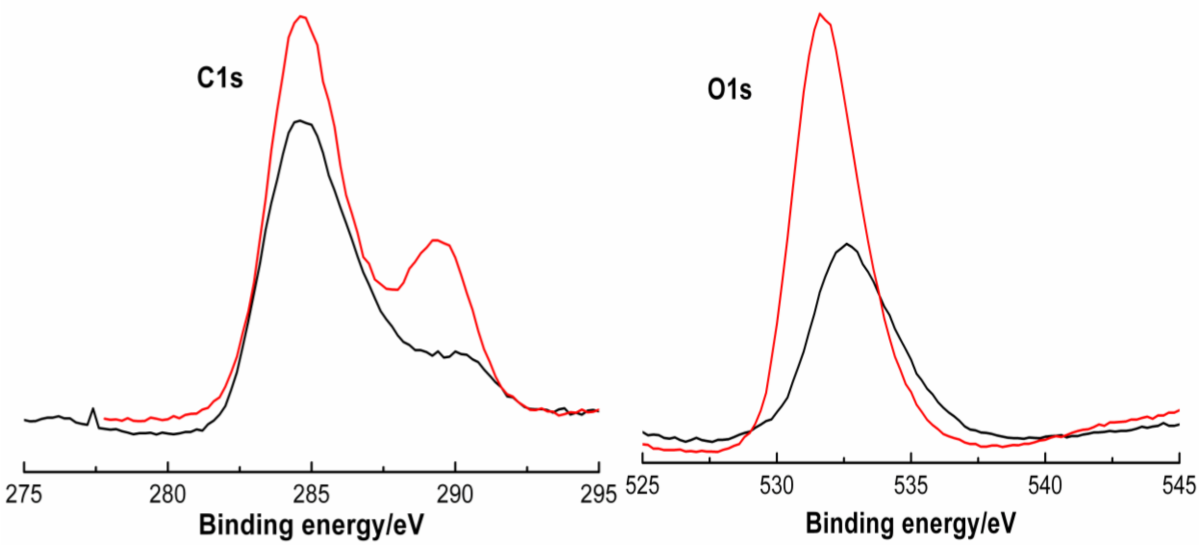
Table 2 presents swell value of cells with different amount of 1,8-NS additives after storage at 70 °C for 48 h. It could be seen that the cell without additives swells 16.1%. As the 1 wt% 1,8-NS is added into the electrolyte keeping other conditions invariable, the swell value of cell significantly reduces to 10.8%. While the addition amount of the 1,8-NS increases, the swell value of cells decreases more. Therefore, adding 1,8-NS into the electrolyte may form a stable SEI film to prevent the decomposition and reaction between the electrode and electrolyte at elevated temperature, so gas evolution decrease and cells swell less.

Table 2. The swell value of cells with various 1,8-NS content

Solvents	1,8-NS (wt %)	Swell value (%)
EC : EMC (3:7, wt.)	0	16.1
	1	10.8
	2	5.7
	3	6.9

3.5 SEI film composition

Surface chemical compositions of graphite electrodes before and after storage at 70 °C for 48 h are analyzed by XPS as shown in Fig. 4. 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 major peak in O 1s spectra at 532.5 eV correspond to lithium alkyl carbonates ($R-CH_2O(C=O)OLi$ (532.5 eV) [17]. Clearly, XPS spectra of the graphite electrode contacted with the electrolyte containing 1,8-NS exhibits the peaks of sulfide compounds. The S 2p peak at 160.8-163 eV corresponds to the Li_2S [21], the peak at 166.4 eV is assigned to $R-SO_2Li$ in Fig. 5b, respectively. As increasing the amount of 1,8-NS additive, sulfide components (C-S-C and C-S) appears at 163.6-163.9 eV [21] with 2 wt% 1,8-NS and at 168-169 eV that corresponding to $R-SO_3Li$ moiety [17] with 3 wt% 1,8-NS, respectively. So we speculate the 1,8-NS may be reduced and react with Li^+ to C-S-C, C-S, Li_2S, $R-SO_2Li$, and $R-SO_3Li$ during the charge-discharge process, and the graphite covering with these reduction products may prevent the gas evolution.



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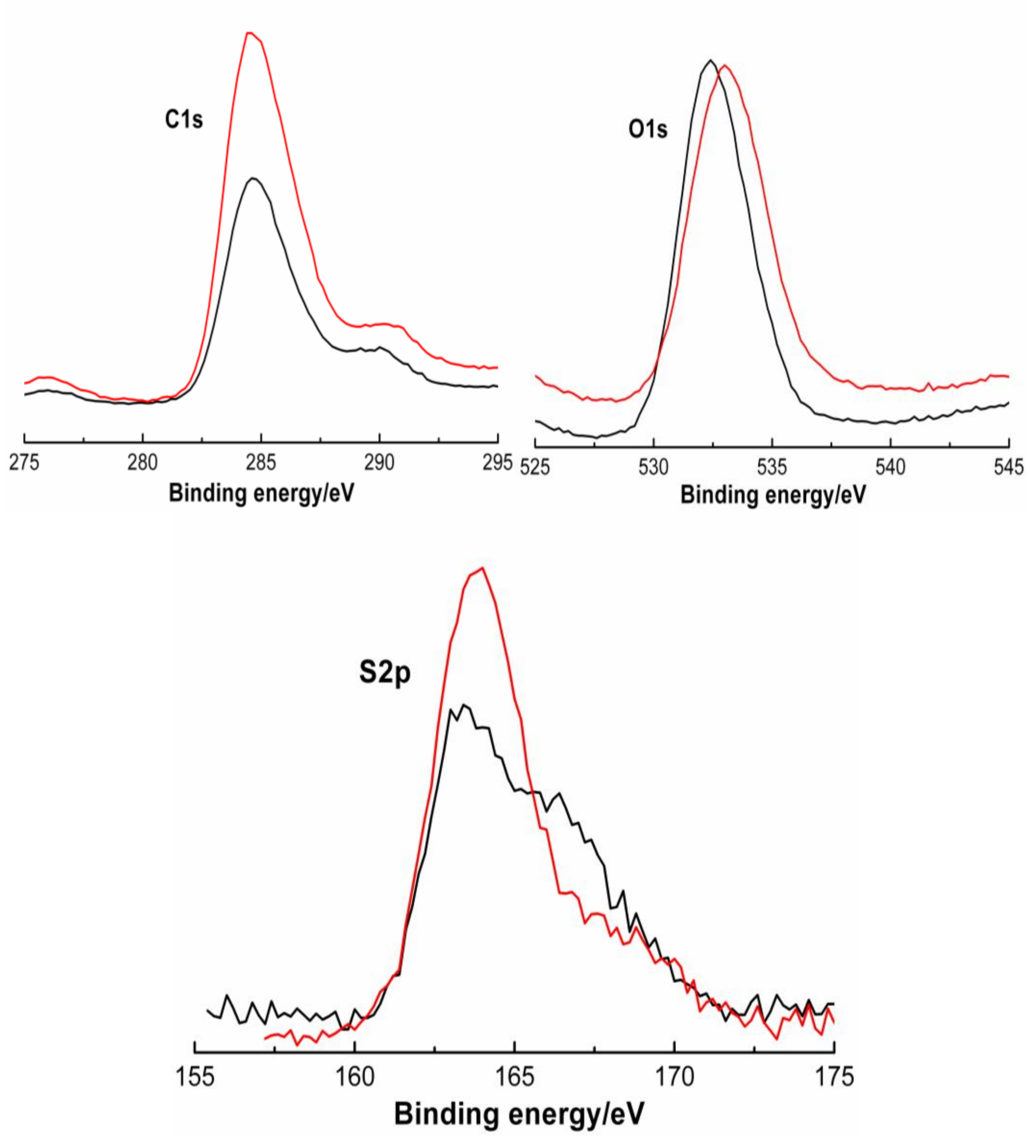
C1s
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295
Binding energy/eV
O1s
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S2p
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Binding energy/eV

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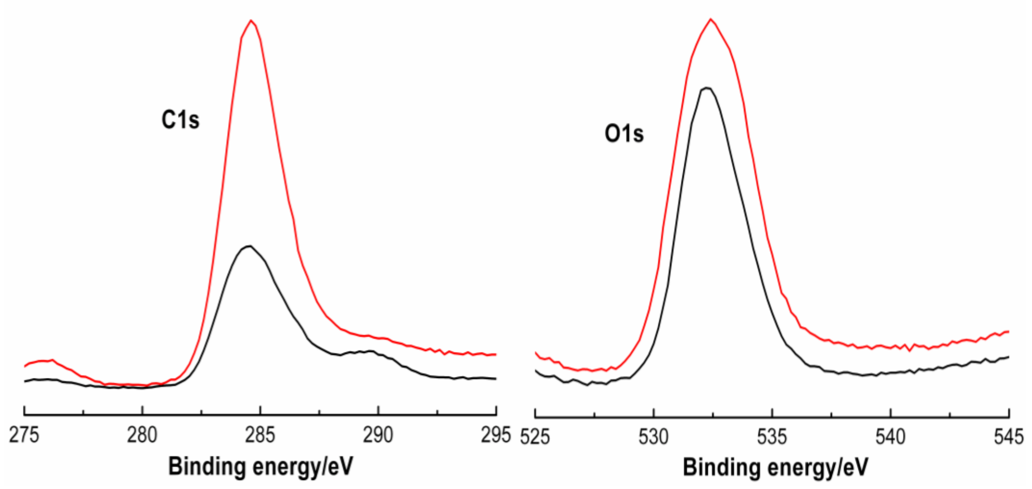
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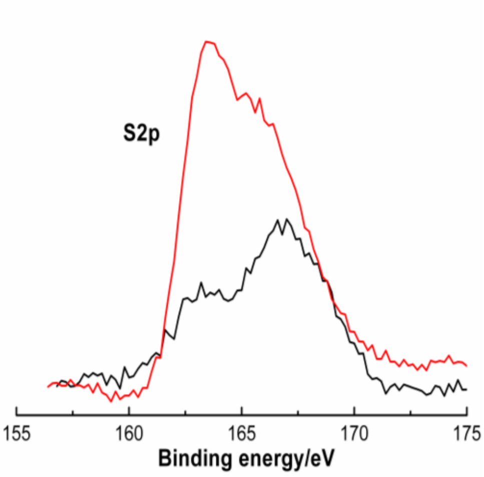

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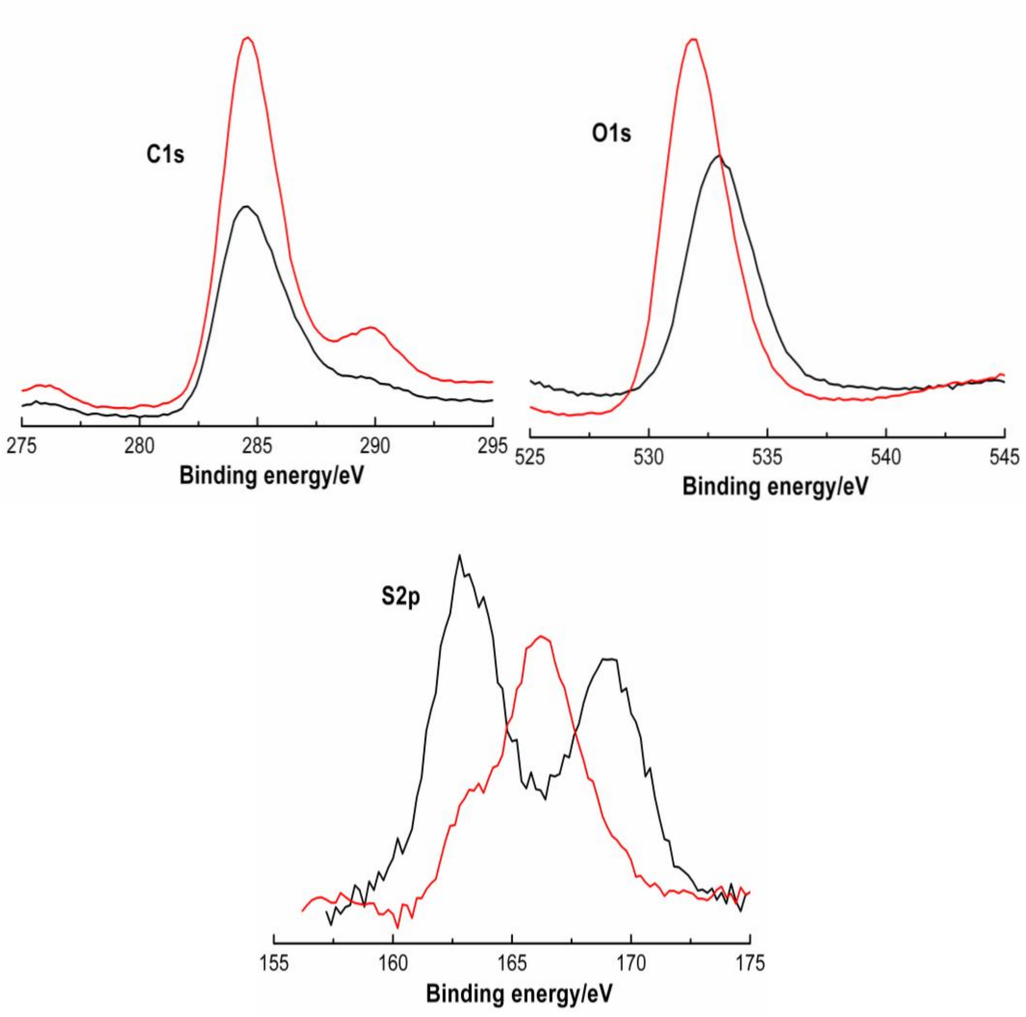

(d)

Figure 4. The C1s, O1s and S2p XPS spectra of graphite electrodes before (*black*) and after (*red*) storage at 70 °C for 48 h (a) without additive; (b) with 1 wt% 1,8-NS; (c) with 2 wt% 1,8-NS; (d) with 3 wt% 1,8-NS

Compared to the graphite anode before the storage, the samples without additives and with 3 wt% 1,8-NS appear 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 532.5 eV to 531.6 eV) (the components of the two samples surface are changed during the conversion of metastable SEI components lithium alkyl carbonates to stable components $LiCO_3$) after storage at 70 °C for 48 h.

The S 2p peaks of 1 wt% and 2 wt% 1,8-NS-containing have changed to 160.8-163 eV corresponding to the Li_2S. The components of 3 wt% 1,8-NS graphite surface have changed from Li_2S and R-SO_3Li to R-SO_2Li. The results are good agreement with the swell value of cells with 1,8-NS content.

4. CONCLUSIONS

The results indicate adding 1 wt% 1,8-NS to electrolyte effectively reduces the irreversible capacity loss and internal resistance at high temperature, because 1,8-NS is reduced to form a thin SEI film on the graphite electrode by CV and EIS analysis. Furthermore, the reduction products of 1,8-NS covered on the graphite surface is proved to be Li_2S, C-S-C, C-S, R-SO_2Li and R-SO_3Li by XPS analysis, which may be stable and suppress the gas evolution. Therefore, adding a small amount 1,8-NS to electrolyte can effectively improve the high temperature performance of the lithium-ion batteries.

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