Int. J. Electrochem. Sci., 12 **(2017)** 10749 – 10762, doi: 10.20964/2017.11.84

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of prop-1-ene-1,3-sultone on the Performances of Lithium Cobalt Oxide/Graphite Battery Operating Over a Wide Temperature Range

Wenfeng Song[1,2] , *Bo Hong*[1,*], *Shu Hong*[1,*] *Yanqing Lai* [2], *Jie Li*[2], *Yexiang Liu*[2]

[1] School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China
[2] School of Metallurgy and Environment, Central South University, Changsha Hunan 410083, China；
[*]E-mail: miaoshoushu1234@163.com and bop_hong@163.com

Received: 30 July 2017 / *Accepted:* 19 September 2017 / *Published:* 12 October 2017

In this paper, we find that prop-1-ene-1,3-sultone (PES) must be a promising additive for the lithium ion battery operating over a wide temperature range. The effect of PES on the graphite anode and $LiCoO_2$ cathode is systematically studied by cyclic voltammetry (CV), charge-discharge test, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The results demonstrate that PES could be reduced prior to the ethylene carbonate (EC) and formed a more stable SEI film on the graphite anode. Meanwhile, the PES could also form a film on $LiCoO_2$ electrode. For these reasons, the $LiCoO_2$/ artificial graphite (AG) battery using PES additive exhibits an excellent high temperature performances. The battery with PES additive could bear 2C charge/discharge cycle under 70°C and the capacity retention could reach 90.1% after 300 cycles. Although PES additive will little increase the resistance of $LiCoO_2$/AG cells and harm its low temperature performance, the discharge capacity retention of the battery with 1% PES can still reach 75% at -40°C. This demonstrates that PES must be a very promising additive for the battery operating over a wide temperature range.

Keywords: Lithium-ion battery, Electrolyte additive, Prop-1-ene-1,3-sultone, low temperature performance, high temperature performance, wide temperature range

1. INTRODUCTION

Nowadays, lithium-ion batteries begin to apply in some new fields, such as special weapons ordnance device, aircraft power vehicle, and deep-sea equipment due to its high capacity and power. These fields have higher application standards on the temperature performances of the power supply. For instance, the military batteries are required to steady run at 70°C and deliver 70% of the room temperature capacity at -40°C. Unfortunately, most of the commercial lithium battery batteries cannot work well at this wide temperature rang.

New electrolyte with high conductivity at low temperatures was turned out to be a effective way to improve the low temperature performance of batteries [1]. U.S. Army Research Laboratory [2-4] and Jet Propulsion Laboratory [5, 6] did lots of works in this field. A high proportion of ethyl (-methyl-) carbonate (EMC) was added to the electrolyte and resulted in good discharge capacity when the temperature dropped to -40°C [5,7]. Plichta [8] also found that the battery in electrolyte with 1.0M $LiPF_6$ EC/ DMC/EMC(1:1:1, by weight) has a good room temperature performance, and the conductivity of the electrolyte reached to 1.0 mS/cm at -40°C. Xiao reported the cells with 1.0 M $LiPF_6$ in EC/DMC/EMC (8.3:25:66.7, by weight) electrolyte obtained 90.3% capacity retention at -40°C with 0.1C current [9]. However, the cells using these electrolytes will be not available at temperatures above 55°C. The capacity fades rapidly in the charge-discharge cycle process owing to the poor thermal stability of the solid electrolyte interphase (SEI) [10]. There is abundant evidence that using additives improving the properties of the SEI was the most effective approaches to advance the cycling durability at high temperatures [11, 12]. These additives usually contain $-S(=O)_2-$ (sulfone group), -O-S(=O)-O- (sulfite group), or –O-C(=O)-C(=O)-O- (oxalate group) [13], which would preferentially reduce compared with the electrolyte solvent and produce a more stable SEI layer enduring high temperatures. Such additives reported by literatures are vinylene carbonate (VC) [14, 15], propane sultone (PS) [16], methylene ethylene carbonate (MEC) [17], methylene methanedisulfonate (MMDS) [18, 19], tris(trimethylsilyl)phosphate (TMSP) [20], lithium bis(oxalate)borate (LiBOB) [21, 22]. And improved cycling stabilities at elevated temperature (45°C-60°C) were also reported while these additives were incorporated into lithium ion batteries. But most of these additives create a barrier hindering lithium ion migration which raise cell impedance and cause capacity reduction at low temperature.

From the above analysis, we think that combination of EC/DMC/EMC(1:1:1) solvents with high temperature film additives may be a feasible program for developing battery operating with a wide temperature range from -40°C to 70°C. In particular, the additives are vitally important for this purpose.

Prop-1-ene-1,3-sultone (PES) is a relative novel additive which has a better anode SEI film forming property than the propane sultone (PS) when it applied to the cells with propylene carbonate (PC) based electrolyte, reported by Li *et al.* [23, 24]. PES can decompose and form a passive film on both of the anode and cathode surfaces. The decomposition products of PES mainly contained sulfite compounds, such as organic RSO_3Li and inorganic Li_2SO_3. Due to the high stability of sulfite compounds in the SEI layer, the capacity retention of this battery increased to 90% after 400 cycles [25,26]. Then, Dahn *et al.* [27, 28] found that the PES additive could improve the high voltage cycling life of Li $[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$/artificial graphite (AG) battery. Recently, Xia et al. [29] combined the PES with VC in EMC:EC (7:3 by weight) electrolyte and found that there is almost no gas of NMC(311)/AG pouch cells with 2% PES for 500 h storage. Nelson et al. [30] also demonstrated that 4% or 6% PES adding will be beneficial to decrease gas production and promote the storage stability at the cost of a large resistance increase.

In this paper, 18650 $LiCoO_2$/AG battery using 1.0M $LiPF_6$ EC/DMC/EMC(1:1:1, wt.%) electrolyte adding different concentrations of PES were assembled. The battery's performances at different temperature (-40 °C to 70 °C) were researched. Effects of the PES on the AG anode, $LiCoO_2$ cathode were also systematically studied by cyclic voltammetry (CV), Transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), and so on.

2. EXPERIMENTAL

The blank electrolyte (1.0 M $LiPF_6$/EC:DMC:EMC (1:1:1, wt.%)) was purchased from Dongguan Shanshan Battery Material Co., Ltd., China. The additive, PES, was purchased from Fujian Chuangxin Science and Technology Develops Co., Ltd., China. 1.0 or 3.0 wt.% PES were added in blank electrolyte in an argon-filled glove box with oxygen and water content below 5ppm. $LiCoO_2$/AG 18650 batteries (design capacity: 1500mAh), AG/Li and $LiCoO_2$/Li half-cells were prepared. In order to prepare the anode electrode, 94.0 wt.% AG and 2.0 wt% conductive carbon (super P) were suspended in a solution of 1.5wt.% carboxymethyl cellulose (CMC) and 2.5 wt.% styrene butadiene rubber (SBR) in distilled water and spread on the copper foil. Cathode electrode contains 89 wt.% $LiCoO_2$, 2.2 wt.% PVDF binder and 3.8 wt.% super P.

Cyclic Voltammetry (CV) of coin cells was performed by a Princeton 2273 electrochemical working station to investigate the reductive and oxidative decomposition of PES. The scanning rate was 0.05 $mV\cdot s^{-1}$ and scanning region was between 0 V to 3.0 V vs. Li^+/Li. Battery performance tests were conducted on a Neware cell test system (CT 3008W). To analyze the composition and microstructure of the electrodes, the 18650 full cells were discharged to 2.5V then dismantled in an argon-filled glove box. The electrodes were subsequently rinsed with DMC for 5 times to remove residual electrolyte and dried in a vacuum for 12 h at normal atmospheric temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed with a K-Alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, UK). The depth of the analyzed layer was approx. 3.5-4 nm.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry test

In order to investigate the electrochemical performances of the PES additive when in Lithium battery, the cyclic voltammetry was performed on the AG/Li and $LiCoO_2$/Li coin cells.

Fig. 1 shows the voltammograms of AG/Li coin cells in the electrolytes without (a) or with 1 wt.% PES (b). For the blank electrolyte, the reduction peak (C_1) around 0.68 V at the first cathodic potential sweep is attributed to the decomposition of EC. This reduction peak (C_1) can also be observed at the second sweep though the current is smaller than that of the first cycle. It suggested that the passive layer formed on graphite electrode during the first cycle, does not availably suppress further decomposition of EC during the following cycle which may cause extra irreversible capacity loss. However, in the electrolyte with 1 wt.% PES, a new reduction peak can be observed at 1.21 V (vs. Li^+/Li), as shown in Fig. 1b. This new reduction peak is attributed to the decomposition of PES on the graphite electrode.

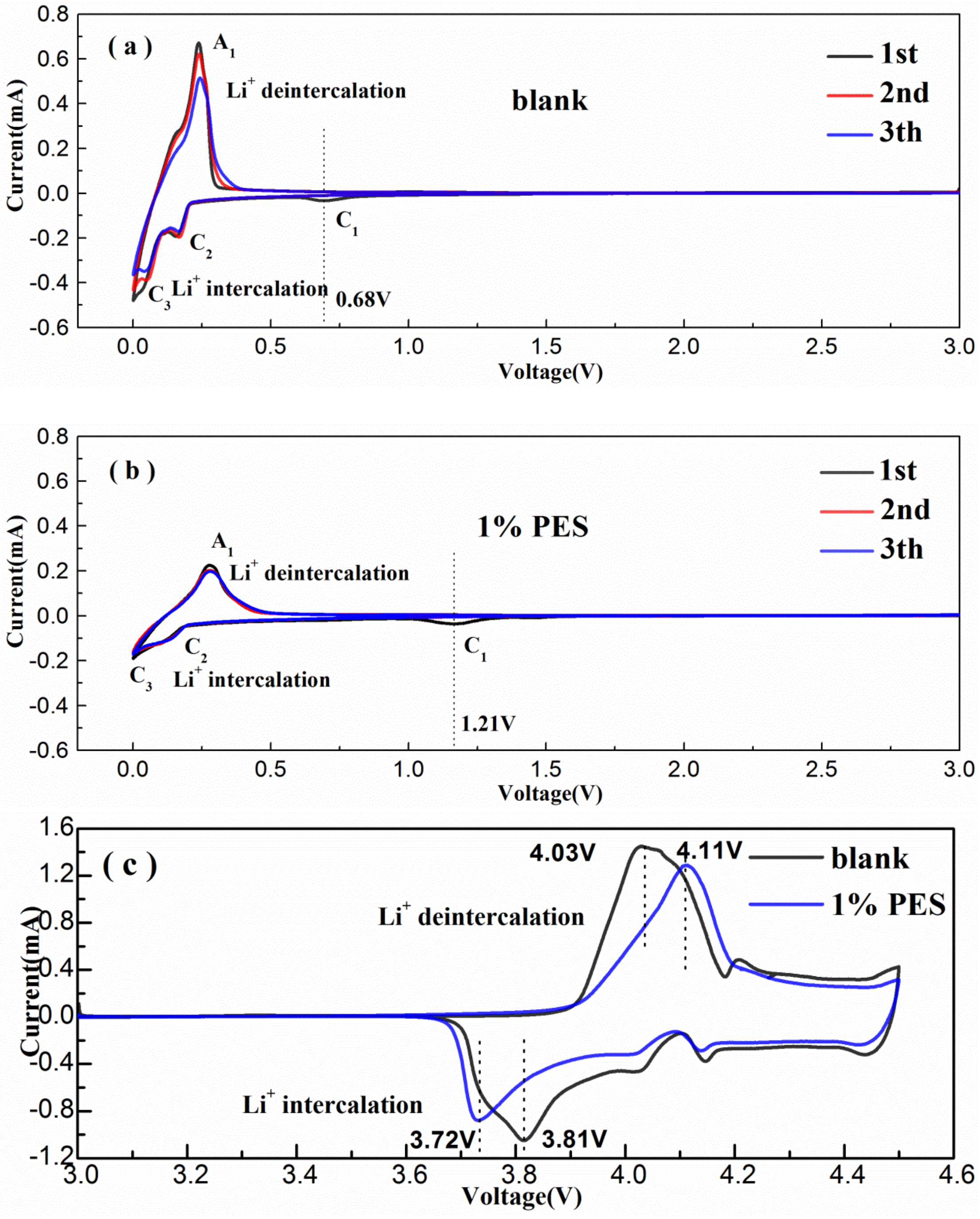


Figure 1. Cyclic voltammetry curve of AG/Li and $LiCoO_2$/Li coin cells in 1 M $LiPF_6$/EC:DMC: EMC (1:1:1) electrolyte without and with PES, (a) AG/Li cell in blank electrolyte, (b) AG/Li cell in electrolyte containing 1 wt.% PES (scan range: 0V to 3.0V, scan rate: 0.05 $mV{\cdot}s^{-1}$), (c) $LiCoO_2$/Li cells in electrolyte without and with 1 wt% PES (scan range: 3.0V to 4.5V, scan rate: 0.05 $mV{\cdot}s^{-1}$).

It can be observed that there is no observable reduction peak at 0.68 V. It suggests that PES additive can effectively suppress EC decomposition on the graphite anode surface. The reduction peak of PES is not observed in the second or third cycles, which confirmed that a stable anode SEI was formed by PES additive. It was noted that the reduction current density of the electrode cycled in the electrolyte with 1% PES (C_1 in Fig. 1b) is stronger than that in blank electrolyte (C_1 in Fig. 1a). This result indicated that, due to the preferential reduction of PES to EC, more degenerated production of PES are incorporated into the SEI than that of EC. But we also noted that the peak intensity of the lithium intercalation/ deintercalation cycled in PES-containing electrolyte (A_1, C_2 and C_3 in Fig. 1b) is much weaker than that in blank electrolyte (A_1, C_2 and C_3 in Fig. 1a). It indicates that SEI formed by PES may hinder the lithium-ion's intercalation/ deintercalation on the AG surface.

Fig. 1c shows the voltammograms of $LiCoO_2$/Li coin cells in the electrolytes without (a) or with 1 wt. % PES (b). That is a typical CV curve of $LiCoO_2$ electrode at EC-content electrolyte. The highest oxidation and reduction peaks related to the deintercalation and intercalation of Li ions. Other oxidation and reduction peaks are difficult to identify, it often be considered as the reactions of other metallic elements、solvents or impurities. According to the picture, the Li^+ deintercalation potential positive shift and Li^+ intercalation potential negative shift when PES added. This indicates that PES may oxidize on the $LiCoO_2$ electrode surface and formed a barrier layer, which will block Li-ion's migration. However, the oxidization peak of PES is not observed on CV curves. We guess that the PES's oxidization potential may approach the Li^+ deintercalation potential, so it was covered by Li^+ deintercalation peak.

3.2 SEI characterization

To analyze the composition and structure of the SEI derived from PES on $LiCoO_2$ and graphite electrodes. The 18650 $LiCoO_2$/AG batteries were constructed containing 1.0M $LiPF_6$/ EC:DMC:EMC (1:1:1) electrolyte with or without PES additive. After initial formation cycling (three charge-discharge cycling between 3.0V and 4.2V at 0.5C rate), the batteries were chrarge – discharge with 1C current at room temperature for 3 cycles. Then the cells were discharged to 2.5V and disassembled in the N_2 atmosphere. The electrodes were subsequently cleanout with DMC to obliterate residual electrolyte and dried under vacuum for 12 h at normal temperature for TEM and XPS tests.

(1) TEM

The surface structrue analyses were performed by transmission electron microscope (TEM). Fig. 2a and Fig. 2b shows the TEM images of $LiCoO_2$ electrodes after 3 cycles in the electrolyte with or without PES. In the electrolyte without PES, it is observed that there is a very thin film (about 2~3nm) on the $LiCoO_2$ particle's surface. This film comes from the oxidation and deposition of the solvents, it is not uniform and discontinuity. However, a much more thicker film (about 8~10nm) is formed when 1 wt.% PES added, It confirmed that PES can oxidize on the $LiCoO_2$ surface and form a passivation layer. It is the film who blocks Li-ion's migration on $LiCoO_2$ surface. TEM images of graphite electrodes is shown in Fig. 2c and Fig. 2d. It is clearly seen a SEI layer formed on the graphite particle's surface both in 1M $LiPF_6$/EC:EMC:DMC (1:1:1) electrolyte with and without PES additive.

The thickerness of the SEI layer formed in blank electrolyte is about 20~150nm. The homogeneity is relatively poor. However, the thickerness of the SEI film formed in electrolyte with 1 wt.%PES is about 50~80nm which seems more uniformity. This suggests that 1 wt.%PES addition may not increase the thickness of SEI on graphite surface. The hindrance to the lithium-ion's intercalation/ deintercalation on the AG surface should be blamed on the transformation of the SEI chemical structure when PES added.

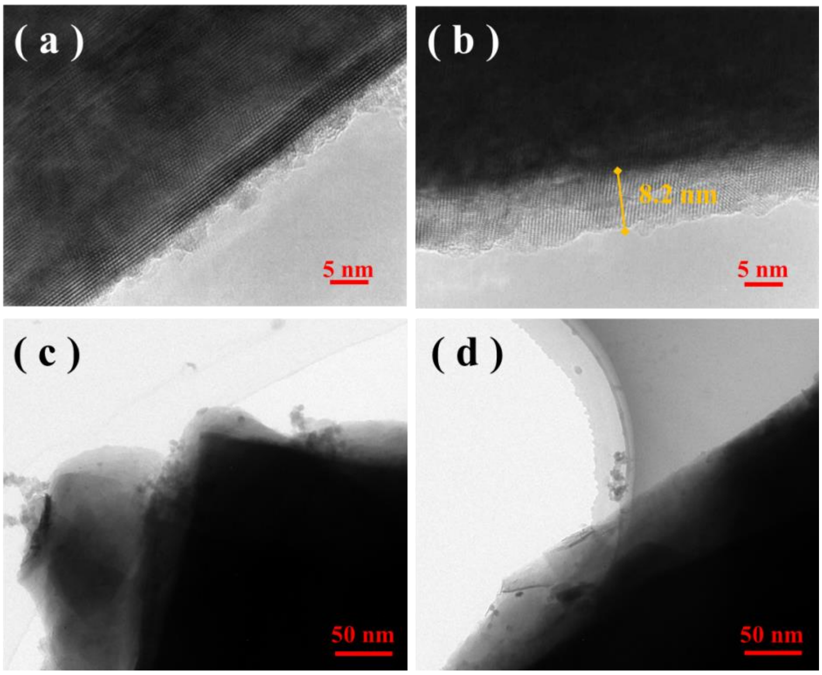


Figure 2. TEM graph of $LiCoO_2$ and graphite particles after 3 cycles in the electrolyte with or without PES, (a) $LiCoO_2$ electrode in the electrolyte without PES, (b) $LiCoO_2$ electrode in the electrolyte with 1 wt.% PES, (c) graphite electrodes in the electrolyte without PES, (d) graphite electrode in the electrolyte with 1 wt.% PES

(2) XPS analysis

XPS was adopted here to investigate the compositional variation of the SEI when PES added. The SEI films were all analyzed after 3 charge-discharge cycles.

Graphite negative electrodes.—The graphite electrode showed four C 1s core components at 284.7, 286.4, 288.8 and 290 eV related to the C=C bonds of the graphite, C-C/C-H of the $ROCO_2Li$, C=O of the Li_2CO_3 and C-F of PVDF/other fluoride. The intensity of the peaks at 284.7ev increased and the peaks at 286.6, 288.8, 290eV decreased slightly when 1 wt.% PES added. In the O 1s core spectra, the graphite electrode displayed two O 1s core components at 531.6, 532.7eV. The peak at 531.6 eV is related to oxygen of carbonate compounds such as Li_2CO_3 [31].

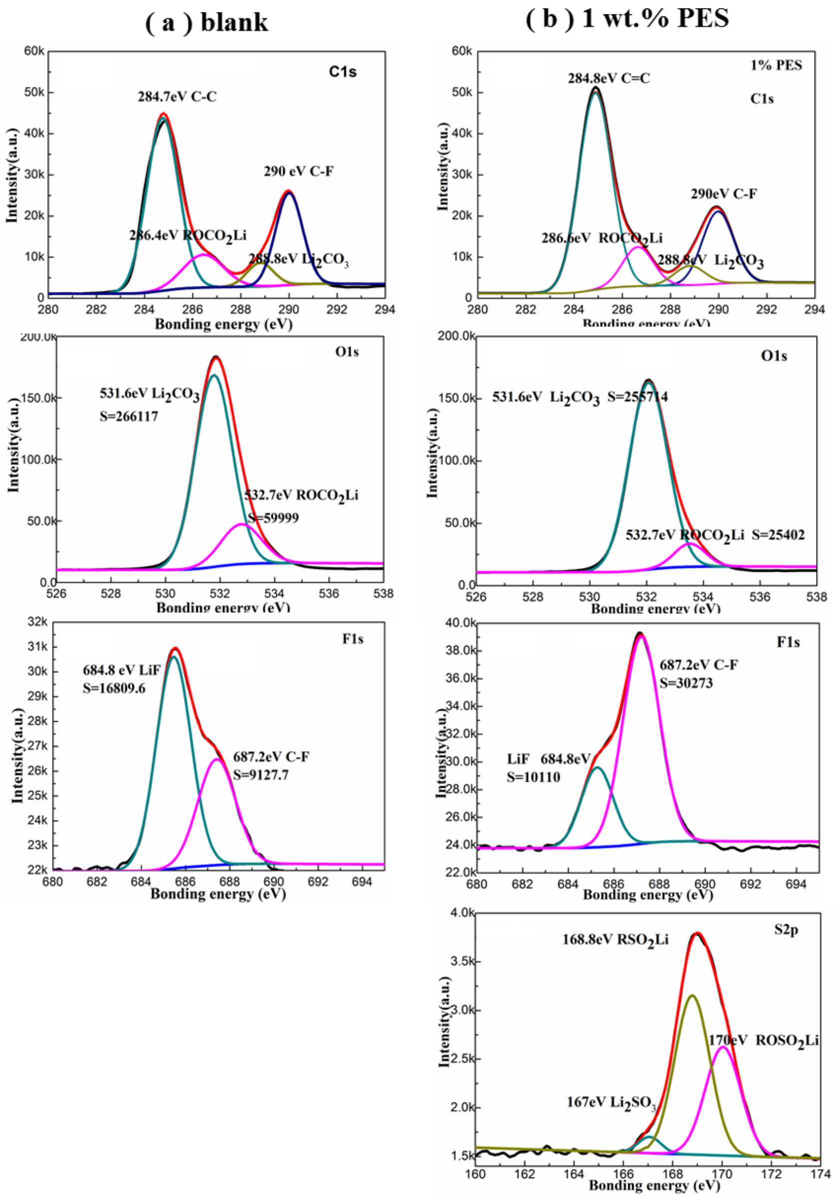
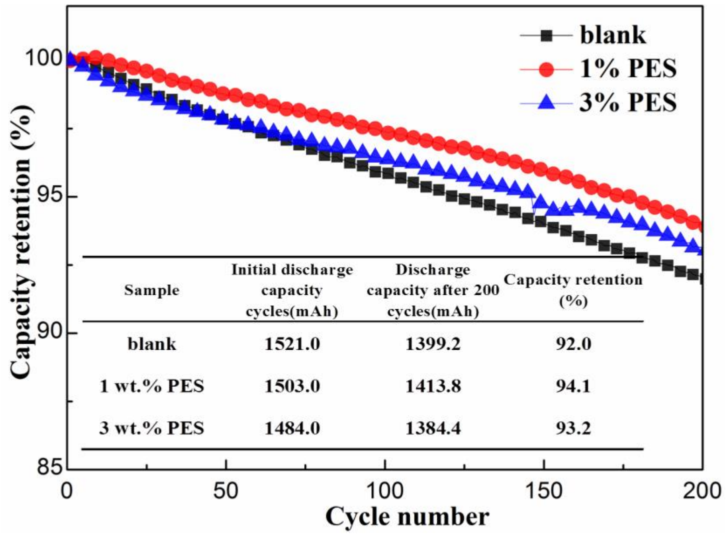


Figure 3. XPS spectra of graphite anode in 1M $LiPF_6$ /EC:EMC:DMC (1:1:1) electrolyte containing no additive (a) or 1wt.% PES (b).

The second peak at 532.7 eV is attributed to -C-O- bonds of $ROCO_2Li$[32]. It can be observed that the content of $LiCO_3$ is basically equal but $ROCO_2Li$ is much lower at the graphite surface for PES-containing electrolytes. There is two F 1s core components at 684.8eV and 687.2eV in the F 1s core spectra. The peak at 684.7 eV is attributed to LiF and the peak at 687.2 eV may be attributed to Li_xPF_y or other F-containing compunds. It is noted that the content of LiF is significantly lower of the 1% PES electrode compared with the blank one. L. Madec attributed the reduction of LiF to the suppression of the $LiPF_6$ degradation by PES at the graphite surface, because LiF mainly generated by PF_6^- anion's reduction at the charge process. The S 2p core spectra is shown in Figure 3d. The peak at 168.8 and 170eV are related to organic sulphur compounds (RSO_3) such as $ROSO_2Li$ and/or RSO_3Li. The peak at 167 eV can be attributed to inorganic Li_2SO_3[33].

3.3 Performance at room temperature

The 18650 $LiCoO_2$/AG batteries were constructed containing 1.0M $LiPF_6$/ EC:DMC:EMC (1:1:1) electrolyte with or without PES additive. After initial formation cycling (three charge-discharge cycling between 3.0V and 4.2V at 0.5C rate), the batteries were chrarge – discharge with 1C current at room temperature for 200 cycles. Fig. 7 shows the cyclical behavior of the batteries. The initial capacity of the battery with the blank electrolyte is 1521.0 mAh, this value decreased to 1399.2 mAh after 200 cycles. It shows an average capacity fading of 0.6 mAh each cycle. Since the higher impedance of the film formed by PES on the both anode and cathod surface, the battery with 1 wt.% and 3 wt.% PES additive shows a lower initial capacity of 1503.0mAh and 1484.0mAh, repectively. But when after 60 cycles, the capacity with 1 wt.% PES additive has exceeded the blank cell. And after 200 cycles, its capacity retains 1413.8mAh, the capacity fading rate is only 0.4 mAh each cycle. Note that the battery with PES exhibits better cyclic performance which is agreeable with Bin Li's reports[24].



Sample	Initial discharge capacity cycles(mAh)	Discharge capacity after 200 cycles(mAh)	Capacity retention (%)
blank	1521.0	1399.2	92.0
1 wt.% PES	1503.0	1413.8	94.1
3 wt.% PES	1484.0	1384.4	93.2

Figure 4. Cyclical behavior of lithium-ion batteries at 25℃ with 1M $LiPF_6$ /EC:EMC:DMC (1:1:1) electrolyte containing no additive, 1wt.% PES, 3wt.% PES. The batteries were cycled over 3.0V~4.2V range with 1C current.

3.4 High temperature performances

(1) High temperature storage performance

After initial formation cycling, the batteries were stored at 45 ℃ for 7 days or stored at 70 ℃ for 48 h to evaluate the high temperature storage stability. Fig. 5a and Fig. 5b shows the capacity retention of the batteries after storage. It can be noted that battery without PES additive retained only 80.7 % capacity after 45 ℃ storage and 70.9% capacity after 70 ℃ storage, while battery with added 1 wt.% PES retained 91.9% and 81.0% of their initial storage capacity, and the battery with 3 wt.% PES additive, these value is 93.8% and 85.6%. These test results suggests that PES additive can significantly improve the high temperature storage stability of the $LiCoO_2$/AG battery as the SEI formed by PES has better thermal stability than that formed by EC. The more content of PES, the better thermal stability of the batteries.

(2) Cycling performance at elevated temperature

To further evaluate the high temperature performances, $LiCoO_2$/AG batteries were charged and discharged with 2 C current betwwen 3.0 V and 4.2 V for 300 cycles under 70 °C. Test results shows in Fig. 5c. It can be observed that the battery without PES additive has 16.1 wt.% capacity loss under 70 °C by 300th cycles. However, the cells containing 1.0 wt% and 3.0 wt% PES shows only 11.8% and 9.9% capacity loss, respectively. This suggests that PES is an excellent thermal stabilizing additive for lithium-ion battery. Little addition of PES can markedly promote the battery performances when worked at elevated temperature. On a separate note, the higher PES content, the better the high temperature cycling performance of the battery.

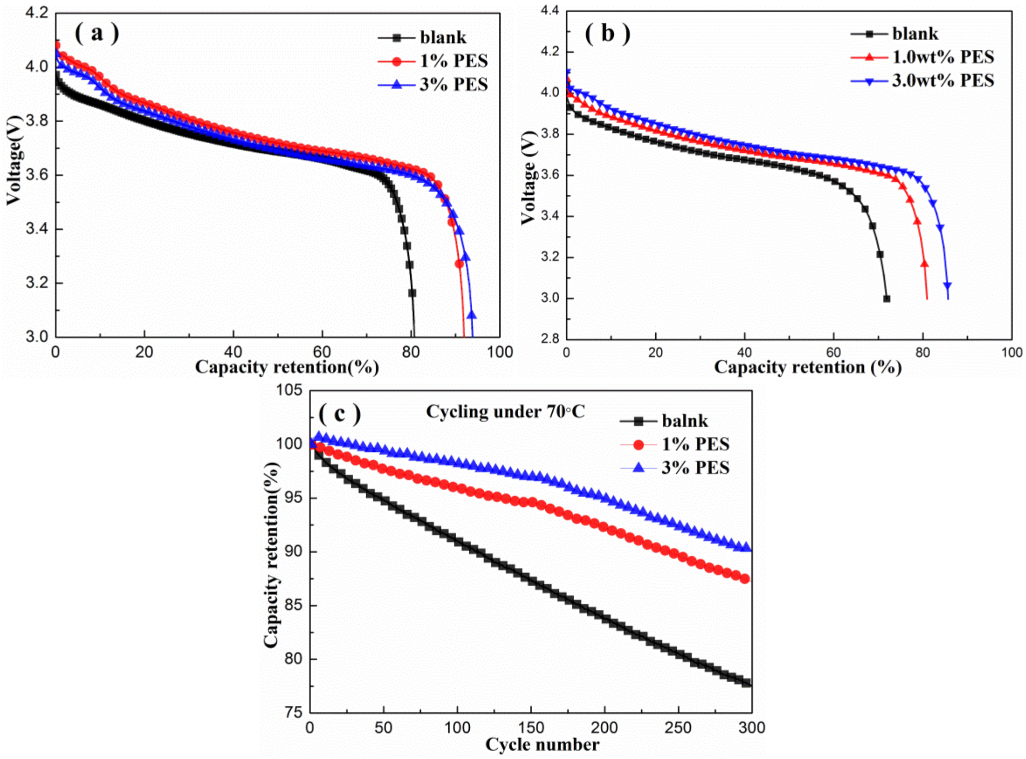


Figure 5. Capacity retention of lithium-ion batteries with 1M $LiPF_6$/ EC:EMC:DMC (1:1:1) solution containing no additive, 1 wt.% PES and 3 wt.% PES after storage (a) at 45 °C for 7 days (b) at 70 °C for 48h, (c) Cycling performance of lithium-ion batteries with 1M $LiPF_6$/EC:EMC:DMC (1:1:1) solution containing no additive, 1 wt.% PES, 3 wt.% PES under elevated temperature (70 °C). The batteries were cycled over 3.0 V~4.2 V range with 2C current.

It is generally believed that degradation of SEI layer on anode is the leading causes of capacity loss. In order to understand how PES additive inhibits the capacity fading when battery worked under high temperature environment, the 18650 cells were discharged to 2.5 V after 300 cycles and disassembled in N_2 atomsphere. The SEM photograph of graphite electrode before/after 300 cycles under 70 °C in 1M $LiPF_6$/EC:EMC:DMC (1:1:1) electrolyte without or with 1 wt.% PES are shown in

Fig. 10. From observation of Fig. 10a and Fig. 10b, the graphite particles all have smooth surface and sharp edges before cycles. However, the graphite particle seems adhering each other after cycles as SEI layer becomes more and more thicker with the cycles running. In the elctrolyte without PES, it is observed that lots of scattered particles on the electrode surface which may stem from exfoliation of graphite's shallow surface. This exfoliation must be the main reason which lead to capacity fading of the battery. But in the elctrolyte with 1 wt.% PES, the surface of the electrode is much better. Graphite exfoliation phenomenon was obviously inhibited. It suggests that the SEI formed by PES has better stability at elevated temperature.

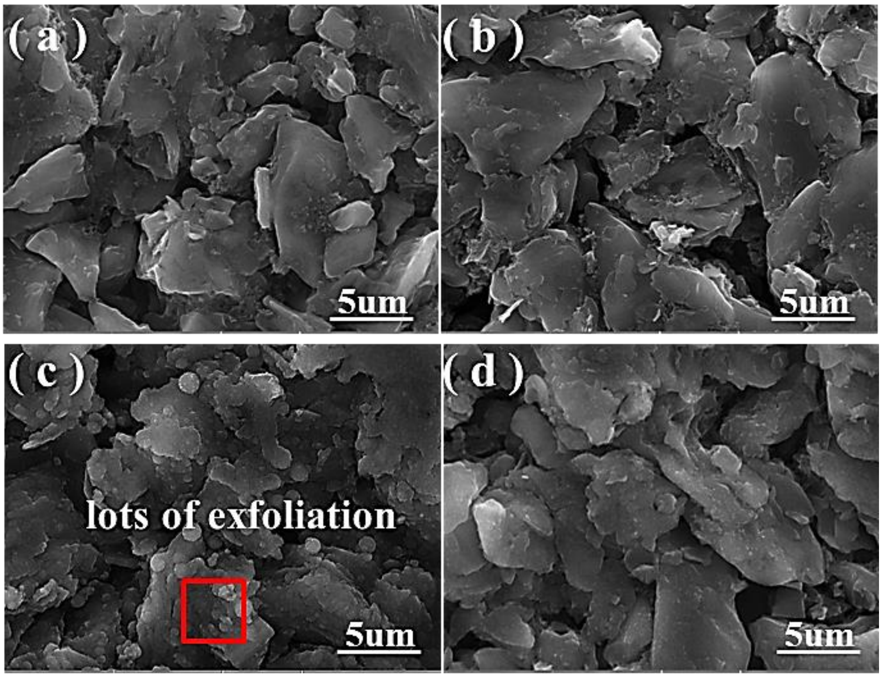


Figure 6. The SEM photograph of graphite electrode after before/after 300 cycles under 70 ℃ in 1M $LiPF_6$/EC:EMC:DMC (1:1:1) electrolyte without or with 1 wt.% PES (a) before cycle in electrolyte without PES, (b) before cycle in electrolyte containing 1 wt.% PES, (c) after 300 cycles in electrolyte without PES, (d) after 300 cycles in electrolyte containing 1.0 wt.% PES

3.5 Low temperature performances

The batteries were stored at -40 ℃ for 2 h, then dicharge with 0.2 C or 0.5 C current with a 2.5 V cutoff voltage to evaluate the discharge performance at low temperature. It is observed that the initial discharge voltage and discharge capacity both dramatically dropped with decreasing of the temperature. According to the Fig. 7, such a cell with 1 wt.% PES retained 75.6% (0.2 C rate) and 70.3% (0.5 C rate) of relative capacity, and the battery with 3 wt.% PES retained 73.2% (0.2 C rate) and 66.0% (0.5 C rate), while the value of the blank cell is 78.2% (0.2 C rate) and 76.9% (0.5 C rate). Although PES additive increased the resistance of both $LiCoO_2$ and graphite electrodes, the discharge capacity retention of the battery with 1 wt.% PES still reached 75% at -40℃. It suggests that little PES addition never gravely impair the low temperature performance of the $LiCoO_2$/AG battery.

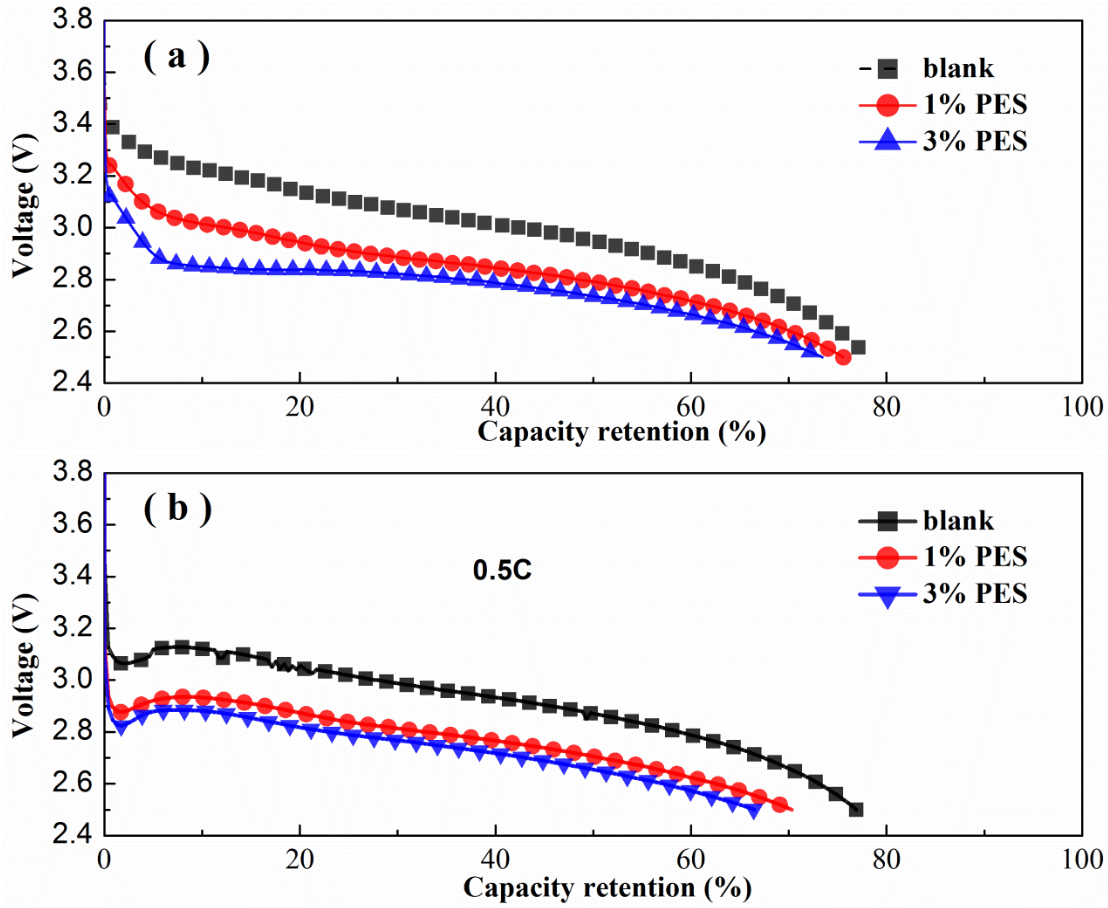


Figure 7. Capacity retention of lithium-ion batteries with different electrolyte discharge at -40 ℃, (a) with 0.2 C discharge current, (b) with 0.5 C discharge current.

Battery performance degradation can be imputed to the polarization when cells operate at cold temperatures, because the impedance containing electric resistance (R_b) and electrochemical reaction resistance (R_{ct}) would be both increased with temperature negative shift [34]. To further study the effect of PES on the battery's low temperature performances, electrochemical impedance spectroscopy (EIS) of 18650 $LiCoO_2$/AG full cells possessing various electrolytes after full charged (100% SoC) were tested at different temperatures. The Nyquist plots of $LiCoO_2$/AG half cells are shown in Fig. 8, which are composed of a distinct semicircle at the high frequency and a straight line at the low frequency, each separately represents the electrochemical reaction resistance (R_{ct}) and Warburg impedance (W_0). The electric resistance on $LiCoO_2$ electrode surface can not be measured as its impedance is too low in full cells. It indicates that increasing of electrochemical reaction resistance (R_{ct}) is the major reason for the polarization of lithium battery under low temperature. Similar to our results, SS. Zhang's reported that electrochemical reaction resistance is more sensitive to temperature changes than electric resistance[35]. The impedance of the 18650 cells rapidly decreased with temperature decline. The resistance value of the cell with 1 M $LiPF_6$/EC:EMC:DMC (1:1:1) electrolyte increased by two orders of magnitude from 25 ℃ to -40 ℃. Compared with the blank cells, we note that the impedance of the cell with 1 wt.% PES is just a little increase at 25 ℃ but two times at -40 ℃. When PES added to 3 wt.%, the impedance of the battery increase to 2.5 times at 25℃ and more than 5 times at -40 °C. For this reason, the batteries with PES additive shows a little higher polarization and lower discharge capacity at -40 °C. Considering the low temperature performance of the battery, amount of PES additive can not exceed 3 wt.%.

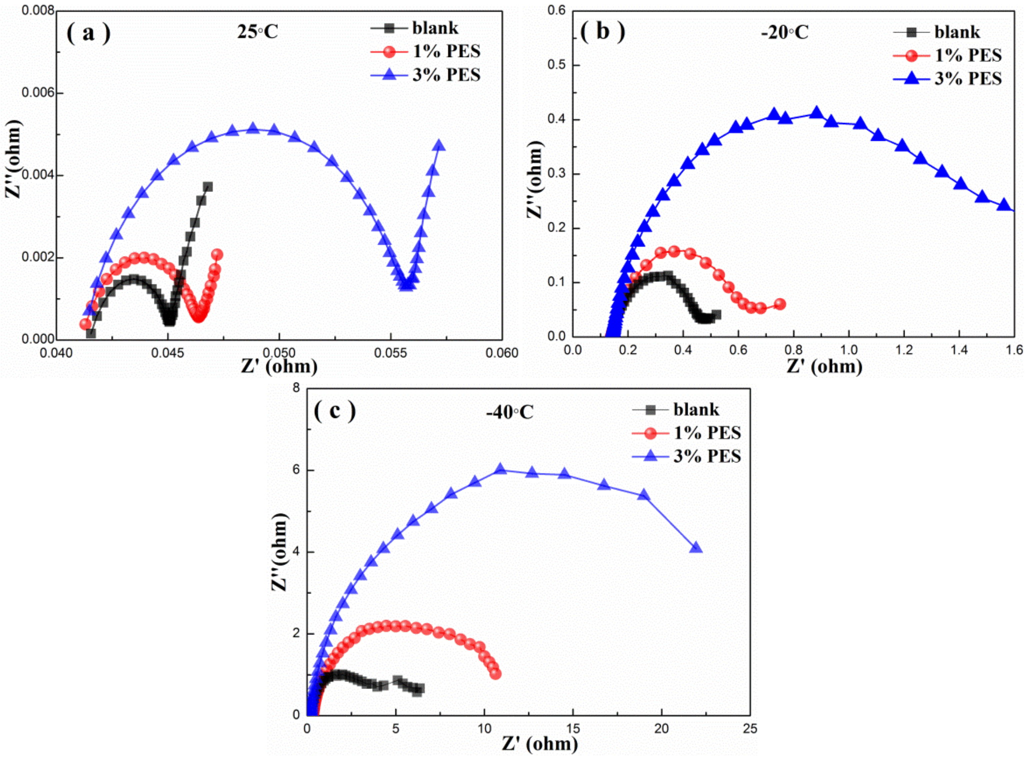


Figure 8. Electrochemical impedance spectroscopy (EIS) of $LiCoO_2$/AG full cells without or with PES additives in electrolyte under different temperatures, (a) 25 °C, (b) -20 °C, (c) -40 °C.

4. CONCLUSIONS

For this paper, the advantages and disadvantages of PES additive in lithium cobalt oxide/AG battery were analyzed in detail. Prop-1-ene-1, 3-sultone (PES) could be reduced prior to ethylene carbonate (EC) and formed a more stable solid electrolyte interphase (SEI) film on the graphite anode. Meanwhile, PES also can form a film on $LiCoO_2$ electrode and improve its stability. For these reasons, the $LiCoO_2$/AG battery using PES additive exhibits an excellent high temperature performance. The battery with PES additive could bear 2 C charge/discharge cycles under 70 ℃ and the capacity retention could reach 90.1 % after 300 cycles. But SEI formed by PES may hinder the lithium-ion's intercalation/ deintercalation and increase the resistance of the battery, then harm the battery's rate capability and low temperature performance. Considering the low temperature performance of the battery, amount of PES additive must not exceed 3 wt.%. And, for the special touch, the 18650 $LiCoO_2$/AG battery with 1.0 M $LiPF_6$/EC: DMC: EMC (1:1:1, wt.%) + 1wt% PES could work well at a wide temperature rang from -40℃ to 70℃. This demonstrates that PES must be a very promising additive for the battery operating over a wide temperature range.

ACKNOWLEDGEMENTS
Project(51222403) supported by the National Natural Science Foundation of China, Project(13JJ1003) supported by the Natural Science Foundation of Hunan Province;

References

1. M. S. Ding, K. Xu, S.S. Zhang, K. Amine, G.L. Henriksen, T.R. Jow, *J. Electrochem. Soc*., 148 (2001) A1196.
2. S.S. Zhang, K. Xu, T.R. Jow, *J. Power Sources,* 115 (2003) 137.
3. S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta*, 49 (2004) 1057.
4. S.S. Zhang，K. Xu，J.L. Allen, T.R Jow, *J. Power Sources,* 110 (2002) 216.
5. M.C. Smart, J.F. Whitacre, B.V. Ratnakumar, K. Amine, *J. Power Sources,* 168 (2007) 501.
6. M.C. Smart, B.V. Ratnakumar, L.D. Whitcanack, K.B. Chin, S. Surampudi, H. Croft, D. Tice and R. Staniewicz, *J. Power Sources*, 119 (2003) 349.
7. S.S. Zhang，T.R. Jow，K. Amine，G.L Henriksen, *J. Power Sources,* 107 (2002) 18.
8. E.J. Plichta，W.K. Behl, *J. Power Sources*, 88 (2000) 192.
9. L.F. Xiao, Y.L. Cao, X.P. Ai, H.X. Yang, *Electrochim. Acta*, 49 (2004) 4857.
10. T.R. Jow, M.S. Ding, K. Xu, S.S. Zhang, J.L. Allen, K. Amine, G.L. Henriksen, *J. Power Sources,* 192 (2003) 343.
11. A.M. Haregewoin, A.S. Wotango, B.J. Hwang, *Energy & Environmental Science*, 9 (2016) 1955.
12. S. Herreyre, O. Huchet, S. Barusseau, E. Perton, J.M. Bodet and Ph. Biensan, *J. Power Sources,* 97-98 (2001) 576.
13. P. Jankowski, W. Wieczorek, P. Johansson, *Journal of molecular modeling*, 23 (2017) 6.
14. Broussely, Ph. Biensan, F. Bonhomme, Ph. Blanchard, S. Herreyre, K. Nechev and R.J. Staniewicz, *J. Power Sources,* 146 (2005) 90.
15. M.C. Smart, B.L. Lucht, B.V. Ratnakumar, *J. Electrochem. Soc*., 155 (2008) A557.
16. M.Q. Xu, W.S. Li, B.L. Lucht, *J. Power Sources* 193 (2009) 804.
17. D. Chalasani, J. Li, N.M. Jackson, M. Payne, B.L. Lucht, *J. Power Sources,* 208 (2012) 67.
18. T. Huang, M.X. Wu, W.G. Wang, Y. Pan, G.H. Fang, *J. Power Sources,* 262 (2014) 303.
19. X.X. Zuo, C.J. Fan, X. Xiao, J.S. Liu, J.M. Nan, *J. Power Sources,* 219 (2012) 94.
20. G.C. Yan, X.H. Li, Z.X. Wang, H.J. Guo, C. Wang, *J. Power Sources,* 248 (2014) 1306.
21. J. Ufheil, M.C. Baertsch, A. Wursig, P. Novak, *Electrochim. Acta,* 50 (2005) 1733.
22. K. Xu, S.S. Zhang, T.R. Jow, W. Xu, C.A. Angell, *Electrochem. Solid State Lett*., 5 (2002) A26.
23. B. Li, M. Xu, T. Li, W. Li, S. Hu, *Electrochemistry Communications*, 17 (2012) 92.
24. B. Li, M. Xu, B. Li, Y. Liu, L. Yang, W. Li, S. Hu, *Electrochim. Acta*, 105 (2013) 1.
25. R. Petibon, L. Madec, L.M. Rotermund, J.R. Dahn. *J. Power Sources*, 313 (2016) 152.
26. B. Li, Y. Wang, W. Tu, Z. Wang, M. Xu, L. Xing, W. Li, *Electrochim. Acta,* 147 (2014) 636.
27. J. Xia, L. Ma, C.P. Aiken, K.J. Nelson, L.P. Chen, J. R. Dahn, *J. Electrochem. Soc*., 161 (2014) A1634.
28. J. Self, D.S. Hall, L. Madec, J.R. Dahn. *J. Power Sources,* 298 (2015) 369.
29. J. Xia, L. Ma, C. P. Aiken, K. J. Nelson, L. P. Chen, J. R. Dahn, *J. Electrochem.Soc*., 161 (2014) A1634.
30. K. J. Nelson, J. Xia, J. R. Dahn, *J. Electrochem. Soc*., 161 (2014) A1884.
31. M. Nie, D. Chalasani, D. P. Abraham, Y. Chen, A. Bose, B. L. Lucht, *J. Phys. Chem*. C, 117 (2013) 1257.
32. W. Li, A. Xiao, B.L. Lucht, M.C. Smart, B.V. Ratnakumar, *J. Electrochem.Soc*., 155 (2008) H648.
33. L. Madec, R. Petibon, J. Xia, J.-P. Sun, I. G. Hill, J. R. Dahn, *J. Electrochem.Soc*., 162 (2015) A2635.
34. J.C. Panitza, U. Wietelmann, M. Wachtler, S. Ströbele, M.W. Mehrens, *J. Power Sources*, 153

(2006) 396.
35. SS. Zhang, K. Xu, T.R. Jow, *Electrochemistry communications,* 4 (2002) 928-932.