



## Short communication

## The important role of additives for improved lithium ion battery safety

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## ABSTRACT

1,3-Propane sultone (PS) additive for graphite electrodes was studied for propylene carbonate (PC) and ethylene carbonate (EC)-based electrolytes in lithium batteries. Decomposition of solvents with graphite electrodes could be remarkably suppressed by addition of the PS additive in the PC-based electrolyte, leading to improvement of electrochemical performances of the cells. The 1,3-propane sultone additive showed very interesting properties for the graphite electrode. It is predicted to give a solid electrolyte interphase (SEI) on the surface of the graphite prior to solvent decomposition and bring about effects that not only suppress lithium deposition on the graphite electrode surface, but also accelerate lithium intercalation, leading to formation of  $\text{LiC}_6$  onto graphite electrode.

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## 1. Introduction

Lithium ion batteries (LIBs) have been used as power sources for portable devices ranging from cellular phones and laptop computers to digital cameras. This is due to their high energy density and availability in a wide temperature range when compared to traditional batteries, owing to the organic solvent electrolytes. Furthermore, application of LIBs has been extended to stationary systems, battery-assisted bicycles, and more recently, Hybrid Electric Vehicles (HEV), taking direct advantage of this higher energy density. Accordingly, many research groups have focused on developing and/or improving high-voltage cathode materials, low-voltage and high-capacity anode materials, and suitable electrolyte systems for lithium ion batteries. However, as the energy density of the battery increases, so too does the chance for accidental explosion, with recent incidences of Li ion batteries exploding in laptop computers exemplifying this. The main reason for these accidents is dendrite metal impurity, including lithium metal deposition on the graphite anode [1]. Once deposited metals create a surface on the graphite, it grows until reaching the positive electrode, causing a short cut at low temperatures and high cycling rates in the battery. Graphite electrodes also have a few disadvantages: (1) active points of the graphite decompose the electrolyte and (2) the potential profile of electrode surface is not uniform, thus the Li metal can form

lower potential areas. In order to improve the cyclability of graphite anodes, additives have been developed, especially high crystalline graphite, which show the theoretical capacity of graphite [2]. Thus, the energy density of LIB is increased. The additives decompose during the first discharge process, before electrolyte decomposition. The decomposed compounds of the additives cover the active sites of the graphite anode and suppress further electrolyte decomposition at these sites on the anode [3–13]. Therefore, the surface film formed by additives on the anode plays an important role and partly replaces the solid electrolyte interphase (SEI) film formed by decomposition of the electrolyte solvents. Recently, several kinds of additives for graphite anodes have been reported, including catechol carbonate [3], imide compounds [4], double-bonded compounds like vinyl acetate [5,6], ethylene sulfide [7], butyl sultone [8], vinyl carbonate [9–12], and propane sultone (PS) [13]. Such additives have been focused on forming a high quality solid electrolyte interphase onto the various electrodes, leading to improved cyclability in lithium ion batteries. Since the introduction of such additives for graphite anodes, the capacity of the anode has been improved by modification with the SEI film and has played an important role in electrolyte research.

In this present study, we introduce a 1,3-propane sultone as the electrolyte additive for the graphite anode in lithium ion batteries and report on the electrochemical performance of the PS additive with the propylene carbonate (PC)-based electrolytes that is known to co-intercalate into graphitic layers with  $\text{Li}^+$  and exfoliate graphitic carbons without the formation of an effective SEI film. We also investigate the effect of the PS additive towards suppressing

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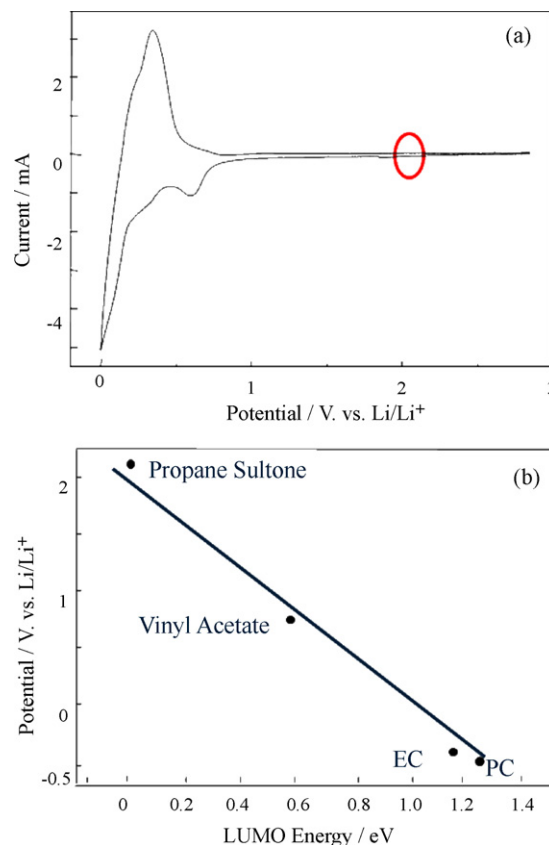
lithium deposition and lithium intercalation into graphite by *ex situ* X-ray diffraction.

## 2. Experimental

1,3-Propane sultone (PS) is commercially available from Aldrich and used without further purification. The electrolyte was a mixture of 1.0 M LiPF<sub>6</sub> in PC/diethyl carbonate (DEC) (1:1 vol., Ube Chemicals, Japan) and ethylene carbonate (EC)/DEC (3:7 vol., Ube Chemicals, Japan) alone or with the addition of 1,3-propane sultone. Electrolyte preparation was carried out under argon atmosphere in a glove box. For investigating the reductive potential of the 1,3-propane sultone, cycle voltammetry (CV) was carried out in glass cells with three electrodes. The graphite electrode served as the working electrode and lithium metal foil was applied for counter and reference electrodes with 0.5 wt% 1,3-propane sultone additive in 1.0 M LiPF<sub>6</sub>-EC/DEC (3:7 vol.). The charge and discharge characteristics of the graphite electrode were examined in a screw-type cell, comprised of a lithium metal electrode and a graphite electrode separated by a glass fiber. In order to prepare the electrode, 90 wt% graphite powder and 6 wt% acetylene black were suspended in a solution of 4 wt% carboxymethylcellulose (CMC) in distilled water and spread on the copper foil as a current collector, dried at 100 °C, pressed at 150.0 kg cm<sup>-2</sup>, and finally dried in a glass tube oven at 160 °C for 4 h. The test cell was made of an anode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by two glass fibers. The charge and discharge current densities were 0.1 mA cm<sup>-2</sup> with a cut-off voltage from 0.005 to 2.5 V. There were two test conditions, in the absence of and in the presence of the PS additive. In the absence of the PS additive, only one discharge process was carried out and kept at 0.005 V for 10 h at a temperature of -5 °C. Conversely, in the presence of the PS additive, three cycles at room temperature were conducted. After cycling at room temperature, the process in the absence of the PS additive was carried out. To investigate lithium deposition on the graphite, we conducted X-ray diffraction (XRD, MINIFlex II, Rigaku, Japan), using Cu K $\alpha$  radiation, to identify lithium deposition on the graphite anode after cycling, followed by *ex situ* XRD. The cells were disassembled and the electrodes sealed in a vinyl bag in an argon-filled glove box to prevent any reaction with moisture in the air.

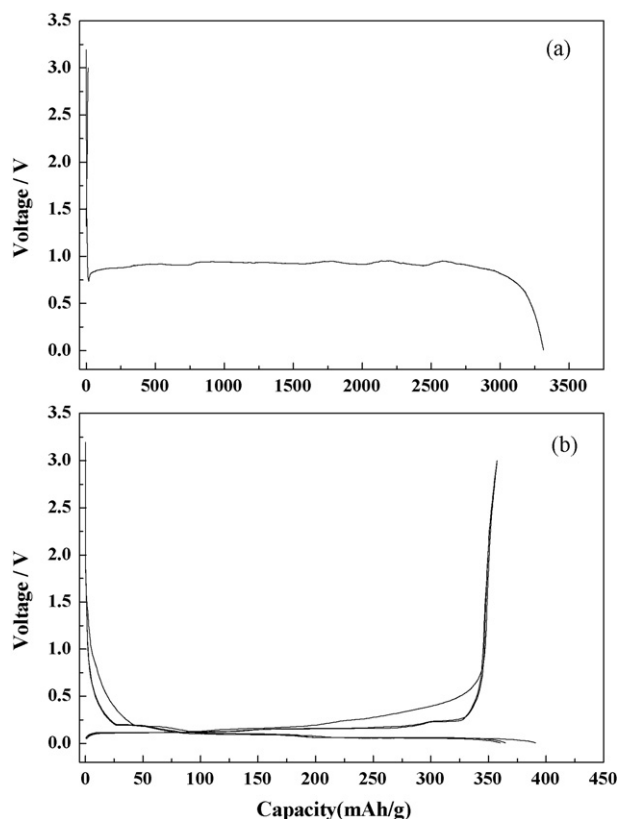
## 3. Results and discussion

Concerned about the selection of additives, we employed cyclic voltammetry, for reductive potentials, and molecular orbital (MO) calculations as the first screening method. The MO theory gives estimations of 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 lowest unoccupied molecular orbitals (LUMOs). In order to investigate the reductive potential of the PS additive, we used cyclic voltammetry. Cyclic voltammograms of PS additives on natural graphite anodes in 1.0 M LiPF<sub>6</sub>-EC/DEC (3:7 vol.) with 0.5 wt% PS of additive are shown in Fig. 1(a). The reduction potential with the graphite electrode was measured to ascertain an additive inhibiting reductive decomposition of the EC or PC solvent. Therefore, it is important that the additive should decompose on the graphite to produce the SEI film prior to EC or PC decomposition because the electrochemical decomposition of propylene carbonate on the graphite occurs during the initial lithium ion intercalation process [14,15]. As a result, additives should be easily reduced at potentials higher than the decomposition potential of the solvent, reflecting the low LUMO energy and leading to the inhibition of graphite exfolia-



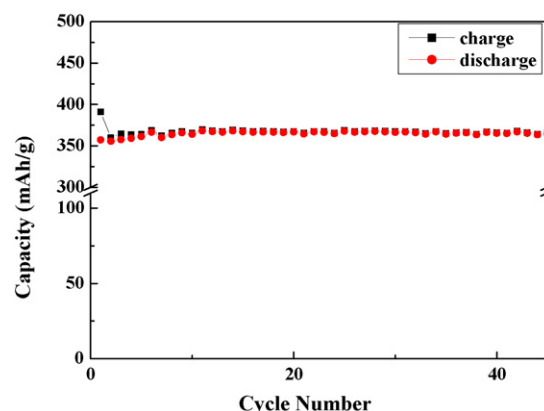
**Fig. 1.** (a) Cyclic voltammogram of 0.5 wt% of 1,3-propane sultone in 1.0 M LiPF<sub>6</sub>-EC/DEC (3:7 vol.) on natural graphite with a scan rate of 1 mV s<sup>-1</sup> and (b) correlation between LUMO energies and reduction potentials for additives and solvents at the Pt electrode.

tion through PC decomposition and effective lithium intercalation and de-intercalation processes. The reductive potential was estimated from irreversible reductive peaks of the first cycle in the cyclic voltammogram and equal to the potentials where the irreversible decomposition current began to rise drastically in the CVs. The reductive potential of 1,3-propane sultone is 2.1 V in Fig. 1(a). Fig. 1(b) shows that the decomposition potential of the compounds correlates with their LUMO energies. In our previous report [5], we found that the reduction order of additives and solvents correlated well with their relative LUMO values, thus, the additives with lower LUMO energy have higher reduction potentials and are reduced on the anode to form a passivation layer film prior to solvent decomposition. Such a straightforward relationship allows us to estimate the reductive potential of the 1,3-propane sultone additive by means of the calculated LUMO values. It is noteworthy that PC and EC decompose at approximately -0.5 V (vs. Li/Li<sup>+</sup>) on platinum electrodes, but between 0.5 and 0.8 V on graphite electrodes due to their catalytic action. Therefore, appropriate additives should decompose at potentials higher than 0.5 V vs. Li/Li<sup>+</sup>, form stable films on the graphite anodes, and prevent electrolytic decomposition due to catalytic decomposition of the solvents. In accordance with Fig. 1(b), appropriate LUMO values of the candidate anode additives should remain below 1 eV, at a reduction potential higher than the PC or EC decomposition potential at the graphite anode. We have temporarily determined that the appropriate LUMO energies of the candidate anodic additives should fall in the range from -1 to 1 eV. On the basis of the reductive potential and LUMO energy, 1,3-propane sultone is a good candidate additive for graphite.



**Fig. 2.** The charge/discharge curves of natural graphite with a current density of  $0.4 \text{ mA cm}^{-2}$ , at a cut-off voltage between 2.5 and 0.005 V in 1.0 M  $\text{LiPF}_6\text{-PC/DEC}$  (1:1 vol.): (a) in the absence of the additive and (b) in the presence of 3 wt% 1,3-propane sultone additive.

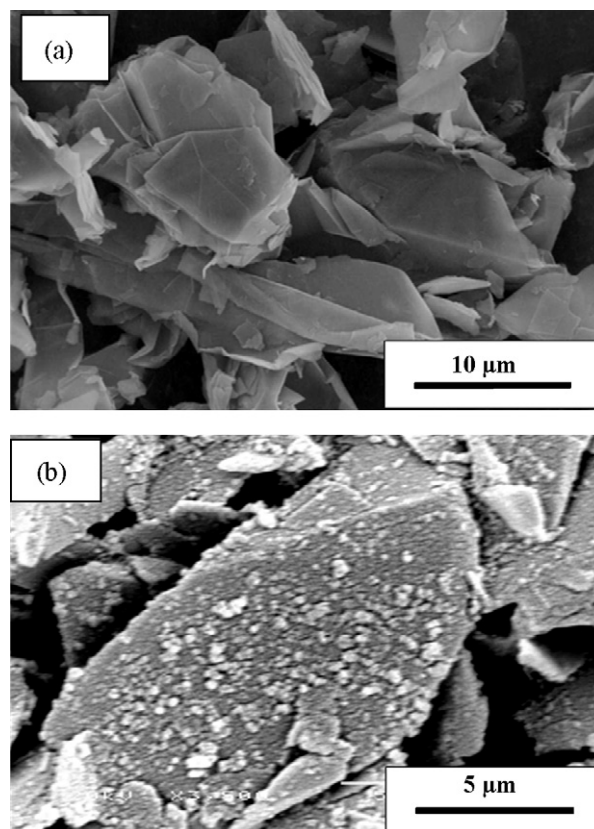
**Fig. 2(a)** shows the charge/discharge profile of the Li/graphite cells in  $\text{LiPF}_6\text{-PC/DEC}$  (1:1 vol.) electrolyte alone. PC-based electrolytes were a convenient and effective means of evaluation of additives and are widely used as fingerprint electrolytes. For the cell without an additive, only a long discharge plateau is observed, due to decomposition of the PC from 0.7 to 0.8 V, without any lithium intercalation process. The decomposition of PC molecules takes place at a capacity near  $3300 \text{ mAh g}^{-1}$ . Charging of this cell was impossible, suggesting that decomposition of the PC prevented formation of an effective surface layer on the graphite surface. This consequently results in the exfoliation of the graphite electrode. Conversely, in the case of the addition of 0.5 wt% PS (**Fig. 2(b)**), there is no long and obvious plateau between 0.7 and 0.8 V in the discharge curve. Moreover, it clearly shows the effect of the PS additive suppressing decomposition of the PC. The capacity during the first discharge process was  $390.9 \text{ mAh g}^{-1}$ . When the cell is charged to 2.5 V, lithium de-intercalation occurs, corresponding to a capacity of  $357.2 \text{ mAh g}^{-1}$  and an irreversible capacity of  $33.7 \text{ mAh g}^{-1}$  which mainly occurs to decompose electrolyte and form a passivation layer film. The coulombic efficiencies of first and second cycle are only 91.3 and 99.8%, respectively. At the second and subsequent cycles, graphite electrode shows good reversibility with coulombic efficiency of nearly 100%. The intercalation and de-intercalation of Li ions into graphite seems to be very smooth in the presence of the PS additive and seems to form a protective layer on the graphite during the first charging process, with Li ion intercalation occurring even in PC-based electrolytes. The PS additive was effective at forming the protective layer with appropriate properties on the surface of the graphite anode.



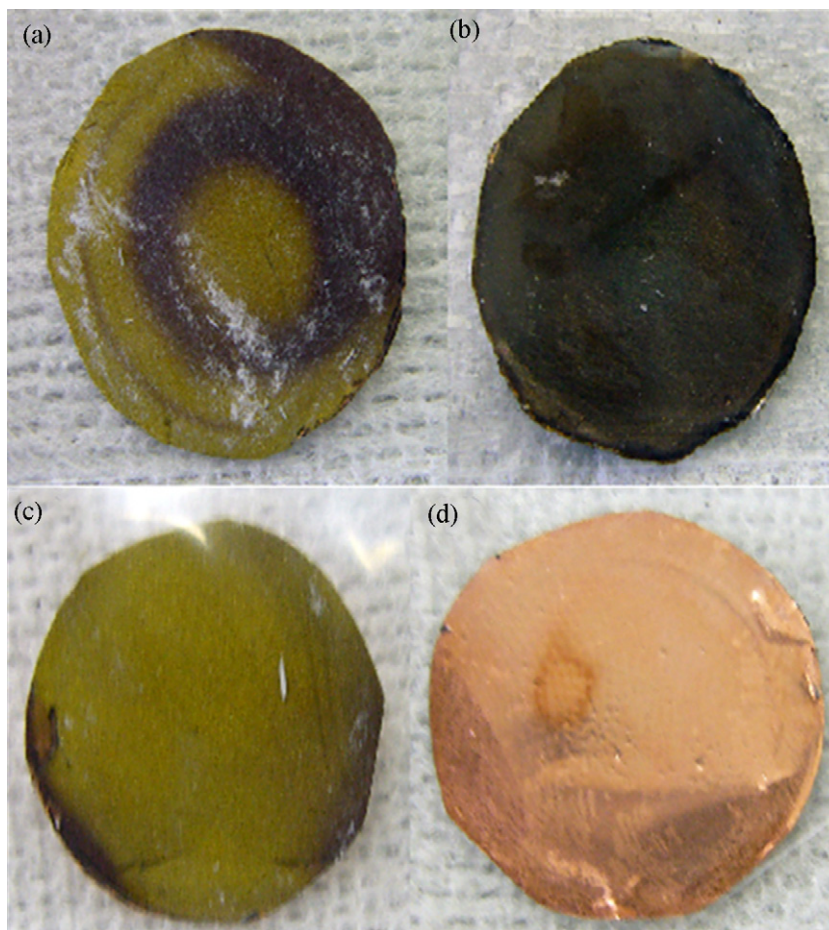
**Fig. 3.** Capacity vs. cycle number of graphite electrode cycled in 1 M  $\text{LiPF}_6\text{-PC/DEC}$  (1:1 vol.) containing 0.5 wt% 1,3-propane sultone.

A cycle performance of a Li/graphite cell containing 1.0 M  $\text{LiPF}_6\text{-PC/DEC}$  (1:1 vol.) with 0.5 wt% PS is presented in **Fig. 3**. The test conditions were a current density of  $0.4 \text{ mA cm}^{-2}$  for a cut-off voltage from 2.5 to 0.005 V at room temperature. The initial discharge capacity was  $357.2 \text{ mAh g}^{-1}$  which is close to the theoretical value of  $372 \text{ mAh g}^{-1}$  based on  $\text{LiC}_6$  and exhibited no capacity loss after 45th cycle. On the other hand, graphite electrode without PS is very difficult to obtain the result of cycle property due to suffer exfoliation of the graphite electrode during first charge process.

**Fig. 4(a)** shows a typical SEM image of the natural graphite anode prior to the electrochemical experiments. In previous reports, we observed that the PC-based electrolytes caused natural graphite



**Fig. 4.** SEM images of the natural graphite surface: (a) original; (b) after the third charge-discharge cycling in the electrolyte of 1.0 M  $\text{LiPF}_6\text{-PC/DEC}$  (1:1 vol.).



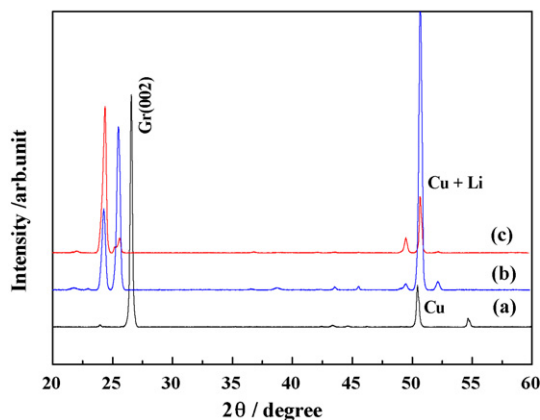
**Fig. 5.** Appearance of: (a) front side; (b) backside for the natural graphite electrode cycled in the absence of the electrolyte additive, at  $-5^{\circ}\text{C}$ ; and (c) front side; (d) backside for the natural graphite electrode cycled in the presence of the electrolyte additive with the third cycle at room temperature, followed by one discharge process at  $-5^{\circ}\text{C}$ .

exfoliation [5]. The surface of natural graphite before cycling is of a homogenous formation, but, it is clearly seen that the SEI film formed on the graphite surface is not a homogeneous formation (Fig. 4(b)). A large number of minute spots are observed instead and form due to PS addition to the electrolyte. The adequately formed SEI film plays a crucial role in the safety of the LIB while in operation.

We found another important and interesting result revealing the effects of the PS additive. Fig. 5(a) and (b) shows appearances on the natural graphite anode after the first discharge process, with a current density of  $0.1\text{ mA cm}^{-2}$  for a cut-off voltage of  $0.005\text{ V}$  at  $-5^{\circ}\text{C}$  with the cell being equilibrated at  $0.005\text{ V}$  for 10 h. The electrolyte was  $1.0\text{ M LiPF}_6\text{-EC/DEC (3:7 vol.)}$ . In general, Li deposition occurred at temperatures below  $0^{\circ}\text{C}$  and high current. We conducted severe conditions below  $0^{\circ}\text{C}$  to easily form lithium deposits on the surface of the graphite. The color of the front side was golden and dark brown. We speculate that the golden color is the first stage color of lithiated graphite ( $\text{LiC}_6$ ) [16] and the dark brown is formation of lithium deposits on graphite or another stage of the lithium–graphite intercalation compound (Li–GICs). The color of backside changed to black, indicating that the graphite electrode, in the absence of the PS additive, may undergo lithium deposition only during the first discharge process. Conversely, Fig. 5(c) and (d) shows appearances of the front and backside of the natural graphite electrode using the PS additive electrolyte. The test conditions were a current density of  $0.1\text{ mA cm}^{-2}$  for a cut-off voltage to  $0.005\text{ V}$  at room temperature in three cycles to decompose the PS additive and deposit it at the active sites of the graphite electrode,

followed by low temperature test as above low temperature test condition with absence of PS additive. Unlike the appearance of the graphite electrode in the absence of the PS additive, the color of the electrode in the presence of the PS additive was nearly all golden with a little dark brown about the edges. Its backside did not change and maintained the original color of copper. The above results indicate that the PS additive decomposed during the first discharge process and deposited at active sites of the graphite, thereby preventing metallic Li deposition on the surface of the graphite.

To verify the above results of suppression of lithium deposition on the graphite by the PS additive in the electrolyte, we used *ex situ* XRD measurements. Fig. 6 shows *ex situ* XRD results of: (a) pristine natural graphite; (b) in the absence of the PS additive after cycling; (c) in the presence of the PS additive after cycling. The natural graphite used in this study had an interlayer distance value,  $d_{(002)}$ , of  $3.353\text{ \AA}$ . The lithium ion is intercalated within the graphite to form lithium–graphite intercalation compounds [17,18]. The stage phenomenon characterized by the intercalate layer is the most important and characteristic property of GICs. The mechanism of lithium intercalation into graphite is well known and has been studied using X-ray diffraction. The stage structure changes from a higher to a lower stage during electrochemical lithium intercalation. The graphite allows lithium intercalation up to a composition of  $\text{LiC}_6$  at stage 1. The graphite cycled in the absence of the PS additive shows a Li peak at  $51^{\circ}$  with a mixture of  $\text{C}_6\text{Li}$  at  $24.3^{\circ}$  and  $\text{C}_{12}\text{Li}$  at  $25.4^{\circ}$ , corresponding to stages 1 and 2, respectively. It also shows that formation of  $\text{C}_{12}\text{Li}$  is greater than  $\text{C}_6\text{Li}$ , indicating a certain level of difficulty for intercalation of the lithium ion within the graphite



**Fig. 6.** *Ex situ* XRD results of natural graphite: (a) pristine natural graphite sheet; (b) natural graphite electrode cycled in the absence of the electrolyte additive at  $-5^{\circ}\text{C}$  and (c) natural graphite electrode cycled in the presence of the electrolyte additive with the third cycle at room temperature, followed by one discharge process at  $-5^{\circ}\text{C}$ .

layer as it was cycled at a low temperature enough to slow mobility of the lithium ions. However, graphite cycled in the presence of the PS additive clearly shows a smaller Li-metal peak with much improved formation of  $\text{C}_6\text{Li}$  compared with graphite cycled in the absence of the PS additive, in spite of the test conditions at a low temperature. The films formed by reduction of the PS can improve the effectiveness of the overall films compared to in the absence of the PS additive.

We suggest that the 1,3-propane sultone can improve the safety of lithium ion batteries because it can easily decompose at active sites of the graphite and make a new SEI film, potentially constituting a different component in comparison with cycling in the absence of a PS additive. PS additives are good for suppressing metal deposition on the surface of the graphite and accelerate intercalation into graphite-formed  $\text{C}_6\text{Li}$ .

#### 4. Conclusion

1,3-Propane sultone has been investigated as an additive for the electrolytes in lithium-ion batteries and was found effective for suppressing PC decomposition and Li metal deposition on the surface of the natural graphite electrode through covering of the active sites of the graphite by the reduced compounds of the additive, protecting the graphite surface and maintaining a homogenous potential profile of the surface of the electrode. PS additives and their formation processes of their protective layers on graphite are a very effective tool for improving safety of lithium ion batteries.

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