A study on sulfites for lithium-ion battery electrolytes

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Abstract

Because of the similarity in the structures of organic sulfites with those of organic carbonates, the applications of organic sulfites for lithium-ion battery electrolytes were studied. The main differences in the bond lengths and the bond angles, which are resulted from the difference between carbon atom diameter and sulfur atom diameter, are analyzed. The physical properties of organic carbonates and organic sulfites are compared. The results of cyclic voltammetry (CV) test show that the decomposition potentials of propylene sulfite (PS) and dimethyl sulfite (DMS) are much higher than 4.5 V, it is satisfied with the requirements as the solvents for lithium ion batteries. But the decomposition potentials of ethylene sulfite (ES) and diethyl sulfite (DES) are lower than 3.5 V, they can only be used as additives for lithium ion battery electrolytes. The results of charge–discharge tests show that both ES and PS have excellent film-forming properties; the performance of $LiCoO_2$/graphite cell was improved evidently even with the ES addition as little as 0.3 wt.% in $1\,mol\,L^{-1}$ $LiPF_6$ EC/DMC/DEC (1:2:2) electrolyte. DMS can improve both the conductivities of electrolytes and the capacities of batteries, therefore it is a good electrolyte co-solvent.
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1. Introduction

Lithium-ion batteries are now considered as the most competitive power sources because of their high energy density and superior power capability. With increasing development of commercial lithium-ion batteries, the majority of research work is focused on improving cycling life and safety of the battery. Currently, commercial lithium-ion batteries use mixed solvent electrolytes containing high viscous ethylene carbonate (EC) and low viscosity diluents, such as dimethyl carbonate (DMC) or diethyl carbonate (DEC) as main solvents. However, the cell performance at low temperature is not satisfied due to the high melting point (36 °C) of EC. In addition, DMC and DEC have high volatile and their flash points are relatively low (DMC 18 °C, DEC 31 °C), which may have a considerable impact on battery safety. Therefore, it is important to seek more suitable solvents and additives to further improve the performance of the lithium ion battery. During recent years, organic sulfites such as ES, PS, DMS and DES have received much

attention because of their similar structures with organic carbonates. G.H. Wrodnigg et al. reported that both ES and PS could improve the electrochemical stability of the $LiMn_2O_4$ cathode [1,2]. The electrochemical performances at the graphite anodes of the lithium-ion batteries with $1\,mol\,L^{-1}$ $LiClO_4$ EC/DMS and $1\,mol\,L^{-1}$ $LiClO_4$ EC/DES were studied [3]. In this article, the physical, chemical and especially the electrochemical properties of sulfites and their applications on Li ion cells were studied in order to investigate thoroughly the possibilities of organic sulfites used in lithium-ion battery electrolytes.

2. Experimental

2.1. Materials and reagents

The cathode and anode active materials are lithium cobalt oxide ($LiCoO_2$) and modified natural graphite. Organic sulfites ES, PS, DMS and DES were synthesized according to the methods available in the literature [4] and purified up to the point where their water content was less than 100 ppm determined by the coulombic Karl Fischer titration. $LiPF_6$ was purchased from Merck. The separator was used a Celgard 2400 microporous membrane.

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2.2. Electrochemical measurements

Test cells were cycled on a Land BT-10 tester (Wuhan, China). A CH Instrumental electrochemical workstation (CHI660A) was used for the cyclic voltammetry (CV). An IR spectrum was recorded by FT-IR-8400 Fourier Transform Infrared Spectrophotometer (SHIMADZU).

3. Results and discussion

3.1. Structures and physical and electrochemical properties of organic sulfites

ES, PS, DMS and DES are structurally similar to the commonly used organic carbonates EC, PC, DMC and DEC. Fig. 1

shows the structural formulae and the three-dimensional structures of organic carbonates and organic sulfites.

The carbon atom is replaced by sulfur atom in the structures of organic sulfites. The main differences in the bond lengths and the bond angles, which are resulted from the difference between carbon atom diameter and sulfur atom diameter, are displayed in Table 1. The distances of S1–O2 (3, 4) are longer than those of C1–O2 (3,4), and the O–S–O angles are smaller than the O–C–O angles. This difference distinguishes the physical properties of organic carbonates and organic sulfites.

The physical properties of organic carbonates and organic sulfites are displayed in Table 2. Table 2 reveals that organic sulfites have a wider liquid temperature range and higher flash points compared with organic carbonates, and linear sulfites
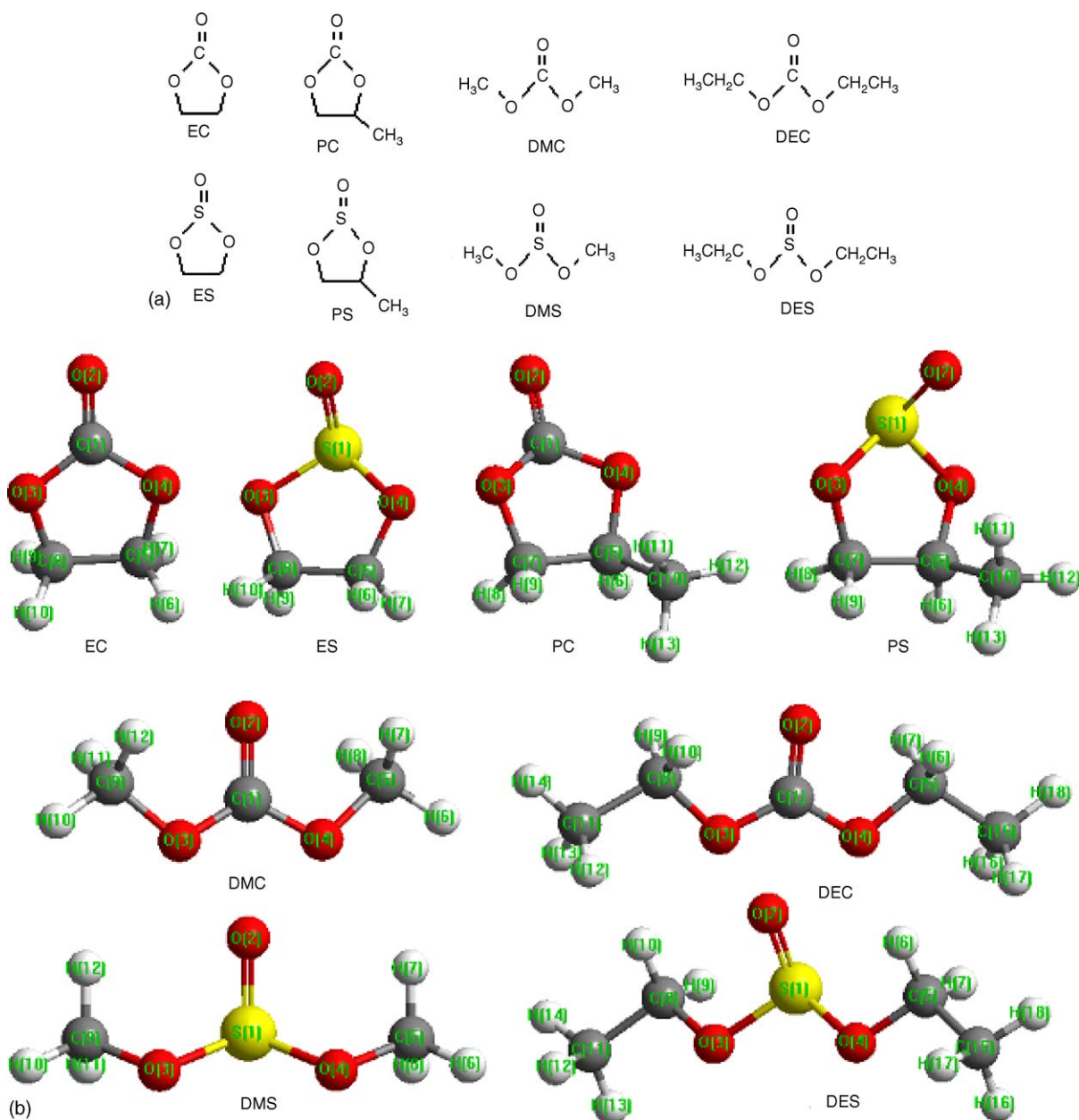

Fig. 1. Structural formulae and the three-dimensional structures of organic carbonates and organic sulfites.

Table 1
The parameters of bond lengths and bond angles of organic carbonates and organic sulfites

Organic carbonates				Organic sulfites			
Atoms	Bond lengths (nm)	Atoms	Bond angles (°)	Atoms	Bond Lengths (nm)	Atoms	Bond angles (°)
C(1)—O(2)	0.1208	O(2)—C(1)—O(3)	122	S(1)—O(2)	0.1480	O(2)—S(1)—O(3)	109.5
C(1)—O(3)	0.1338	O(2)—C(1)—O(4)	122	S(1)—O(3)	0.1660	O(2)—S(1)—O(4)	109.5
C(1)—O(4)	0.1338	O(3)—C(1)—O(4)	111	S(1)—O(4)	0.1660	O(3)—S(1)—O(4)	104.0

Table 2
The physical properties of organic carbonates and organic sulfites (25 °C)

Solvent	mp (°C)	bp (°C)	fp (°C)	η (cP)	ε	Solvent	mp (°C)	bp (°C)	fp (°C)	η (cP)	ε
DMC	4.6	90	18	0.5902	3.18	DMS	−141	126	30	0.8732	22.5
DEC	−43	126.8	31	0.748	2.82	DES	NA	159	53	0.889	15.6
EC	39	248	160	1.86[a]	89.6[a]	ES	NA	68 (20 mmHg)	79	NA	NA
PC	−49.2	241.7	135	2.53	64.4	PS	NA	NA	NA	NA	NA

[a] At 40 °C.

(DES, DMS) have a higher dielectric constant than linear carbonates. Therefore, using organic sulfites as solvents for lithium ion battery electrolyte will provide better low temperature conductivity and safety.

The solvents for lithium ion batteries must exhibit good electrochemical stability. The decomposition potential must exceed 4.2 V. The oxidation decomposition potential of organic sulfites is measured by the cyclic voltammetry method. Fig. 2 shows the current–potential curves of organic sulfites containing LiPF₆. According to the literature the current density of $0.5 \, \text{mA cm}^{-2}$ can act as an indicator of decomposing of electrolytes at this scan rate [5], it can be confirmed that the decomposition potentials of PS and DMS are much higher than 4.5 V. Both PS and DMS satisfied the requirements as the solvents for lithium ion batteries. However, due to the insufficient decomposition potentials of ES and DES, which are less than 3.5 V, they will only be used as additives for lithium-ion battery electrolytes.
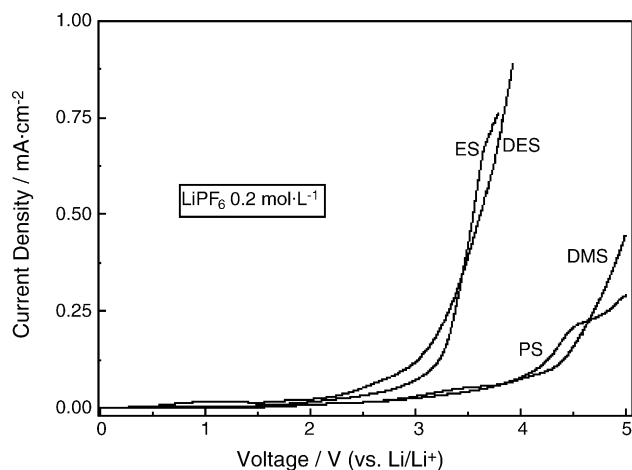

Fig. 2. The current–potential curves of organic sulfites at a scan rate of $5 \, \text{mV s}^{-1}$ at 18 °C.

3.2. The applications of ES and PS as additives in lithium-ion battery electrolytes

It is well known that EC is indispensable because it takes on the filming task in common lithium-ion battery electrolytes. Although PC possesses a lower melting point compared with EC, it cannot be widely used in batteries with a graphite anode because PC would co-intercalate into graphite [6,7]. There is a steady plateau about 0.8 V, but it does not reach the lithium-ion intercalation potential (below 0.3 V) in the first discharge curves of Li/graphite half cells using $1 \, \text{mol L}^{-1}$ LiPF₆ /PC electrolytes (Fig. 3), and no charge–discharge capacity of cells was found. Because PC cannot form efficient SEI film on the surface of graphite, it leads to the continual decomposition of battery electrolyte. This decomposition can be suppressed by adding additives with good film-forming properties into the electrolyte [8–12]. Both ES and PS have excellent film-forming properties. When Only 5 wt.% of ES or PS is added into pure PC electrolytes, the co-intercalation into graphite is definitely suppressed. Fig. 3a and b shows the charge–discharge curves of Li/graphite half-cells using $1 \, \text{mol L}^{-1}$ LiPF₆ /PC electrolytes containing ES or PS. With a little addition of either ES or PS in $1 \, \text{mol L}^{-1}$ LiPF₆ /PC electrolytes, a good cycle performance of Li/graphite was observed. The first coulomb efficiency of batteries containing ES and PS were 88% and 73%. After five cycles, the charge capacity retention efficiencies of cells containing ES and PS were 82.7% and 99.4%. It should be pointed out that there is a brief reduction process around 1.7 V at the first discharge curve of batteries containing ES or PS, but it does not occur for additive-free electrolytes. This process is irreversible and it does not appear in the following delithiation or lithiation cycles. It could be concluded from such comparison that this reduction process was associated with the peculiar properties of SEI film formed in electrolytes containing ES or PS additives. This result is consistent with the temperature programmed desorption or decomposition-gas chromatography/mass spectrometry (TPD-
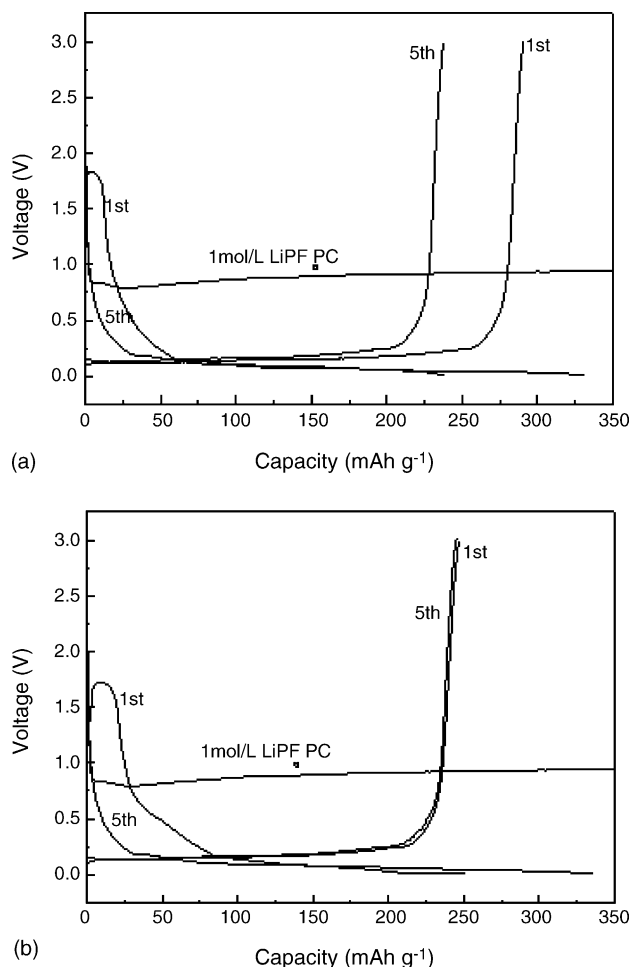
Fig. 3. The charge–discharge curves of Li/graphite half batteries used $1\,\mathrm{mol}\,L^{-1}$ $LiPF_6/PC$ electrolytes (a) containing 5% ES (b) containing 5% PS.

Fig. 4. (a) Discharge capacity maintenance efficiency of $LiCoO_2$/graphite cell containing $1\,\mathrm{mol}\,L^{-1}$ $LiPF_6$ EC/DMC/DEC (1:2:2). (b) Charge–discharge efficiency of $LiCoO_2$/graphite cell containing $1\,\mathrm{mol}\,L^{-1}$ $LiPF_6$ EC/DMC/DEC (1:2:2).

GC/MS) analysis of the SEI on the graphite anode in the PC/ES electrolyte system [13].

In addition, the performance of the cell was studied by adding ES to the standard electrolyte. Fig. 4a and b shows the comparison of discharge capacity retention efficiency and charge–discharge coulomb efficiency of $LiCoO_2$/graphite cell using electrolytes of both with 0.3 wt.% ES and without ES. Fig. 4a shows that from the first cycle, the discharge capacity retention efficiency of the lithium-ion cell containing ES was higher than that of ES-free cell. After 100 cycles, the discharge capacity retention efficiency of the lithium-ion cell containing ES was 90%, better than 83% of ES-free cell. Fig. 4b shows that the charge–discharge coulomb efficiency of the lithium-ion cell containing ES was about 99.5%, but that of ES-free cell was 99% or lower due to the efficient SEI could not be formed on the poor surface morphology of modified natural graphite. After adding ES to the electrolyte, the cell performance was improved due to the strong film-forming property brought by ES.

In order to further identify the formation potential of SEI of the standard electrolyte containing ES, the CV curves of lithium-ion cells were investigated. Fig. 5a shows the first and second CV curves of Li/graphite half-cells containing a 0.3 wt.% ES. Fig. 5a reveals that two reductive current peaks appeared separately at
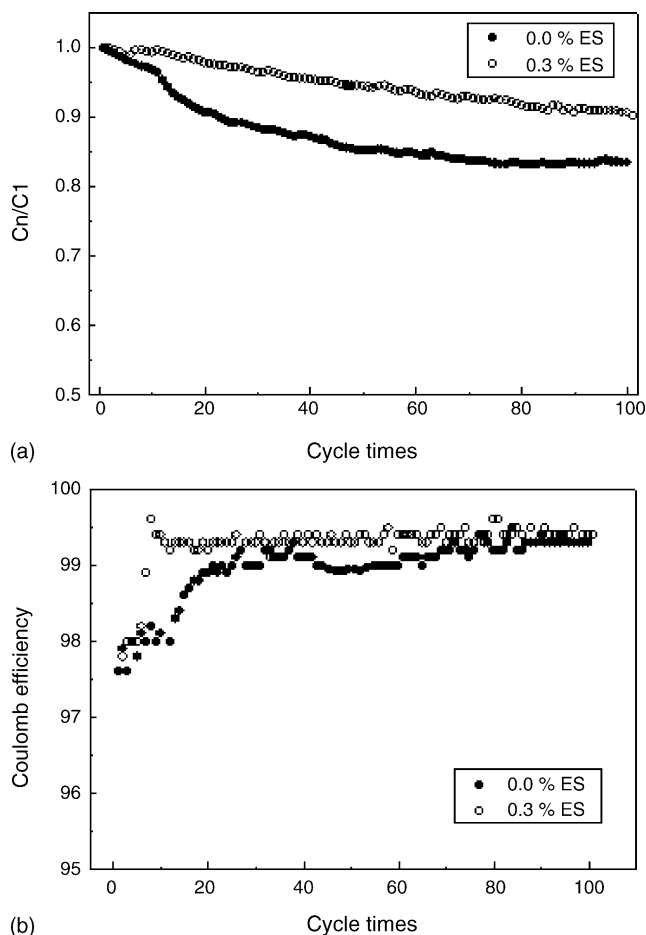
around 1.5 and 0.6 V during the first discharge of the cell, then they disappeared during the second discharge. This behavior was different from that of the standard electrolyte without ES, as shown in Fig. 5b. There was only one irreversible current peak at 0.6 V which was the formation potential of the SEI film. From this comparison, it can be concluded that the peaks at 1.5 and 0.6 V in Fig. 5a were aroused by the irreversible reaction of ES and electrolyte components reduction. It indicates that there are two steps in the SEI formation of the Li/graphite half-cells containing ES. The first step was the decomposition of ES, and the second step was electrolyte component reduction.

An infrared test was carried out in order to analyze the components of SEI formed on the graphite surface. Fig. 6 shows the infrared spectrum of SEI formed in a standard electrolyte containing ES. Table 3 shows the main IR peaks of SEI and their assignments. In Fig. 6, three tiny peaks were separately observed at 1321, 903 and $667\,cm^{-1}$ corresponding with the existence of RSO_2Li and SO_3^{-2}.

Combining the results from the CV test and the infrared test, it can be concluded that the structure of SEI formed on the graphite surface in a standard electrolyte containing ES includes both inorganic components Li_2SO_3 and Li_2CO_3 and organic compo-
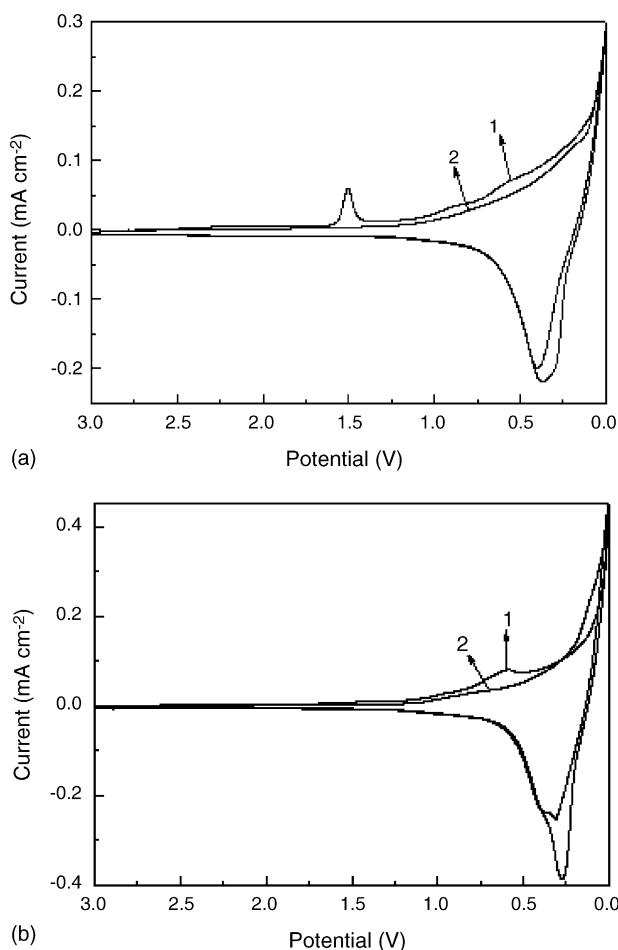
Fig. 5. (a) CV curves of Li/graphite cell in $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMC/DEC (1:2:2) containing 0.3% ES cycled between 0 and 3 V at 0.05 mV/s. (b) CV curves of Li/graphite cell in $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMC/DEC (1:2:2) cycled between 0 and 3 V at 0.05 mV/s.

nents, such as $ROCO_2Li$, $RSO_2Li(R=CH(CH)-CH_3)$ and so on. This unique inorganic–organic structure of SEI was more stable during later cycles.

3.3. The applications of DMS and DES as co-solvents in lithium-ion battery electrolytes

DMS and DES could not form stable, effective SEI on graphite like ES and PS. But compared with DMC or DEC, using DMS in combination with EC as the electrolyte co-solvent would create electrolytes with higher conductivity in a wider
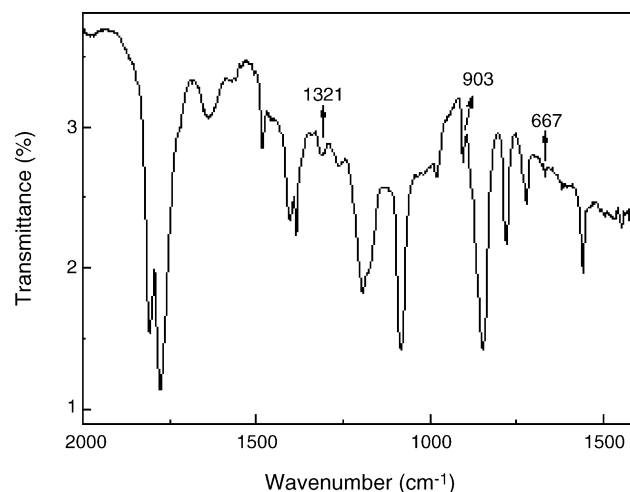

Fig. 6. The infrared spectrum of SEI formed on the graphite surface in $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMC/DEC (1:2:2) containing 0.3% ES.

Table 3
Main IR peaks of SEI and their assignments

Wavenumber (cm^{-1})	Possible assignment
1816 and 1778	C=O oscillating in phase and out of phase
1635	CO$_2$ (carboxyl) stretch; C=C double bonding stretch
1474	LiCO$_3$
1404 and 1391	EC + ROCO$_2$Li; R—CH$_2$—(P), CH$_3$ asym. bend and/or CH$_2$ scissors deform.; CO$_3{}^{2-}$
1321	RSO$_2$Li
1261	CH$_3$ asym. bend
1191	C—O stretch; C—O—C stretch in formate esters
1084	C—O stretch in primary (RCH$_2$OH) or secondary (RR$'$CHOH) alcohols
979	P—O—C, vinyl compounds
903	SO$_3{}^{2-}$
846	Vinyl compounds
779	P—F trivalent, P—C bonding
721	CO$_2$ asym. of R in R—CO$_2$Li
667	SO$_3{}^{2-}$
559	LiPF$_6$

temperature range due to its properties of low melting point, low viscosity and higher dielectric constant. The room temperature (25 °C) conductivity of $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMS (1:1 by vol.) was $16.8 \, \text{mS} \, \text{cm}^{-1}$, which was higher than $11.2 \, \text{mS} \, \text{cm}^{-1}$ of $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMC (1:1 by vol.). The cycle performances of Li/graphite cells with $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMS (1:1) electrolyte and $1 \, \text{mol} \, L^{-1}$ LiPF$_6$ EC/DMC (1:1) electrolyte were

Table 4
The comparison of the performances of cells containing EC/DMS (1:1) electrolyte and EC/DMC (1:1) electrolyte

Cycle numbers	$1 \, \text{mol} \, L^{-1}$ LiPF$_6$/EC -DMC		$1 \, \text{mol} \, L^{-1}$ LiPF$_6$/EC-DMS	
	Charge capacities (mAh g^{-1})	Cycle efficiency (%)	Charge capacities (mAh g^{-1})	Cycle efficiency (%)
1	325.5	88.4	348.8	77.0
2	327.5	96.9	348.4	92.9
3	323.7	97.9	346.8	100.0
4	327.3	98.1	351.1	99.5
5	325.9	98.5	350.0	99.8

compared. Table 4 shows the comparison of the performances of cells containing EC/DMS (1:1) electrolyte and EC/DMC (1:1) electrolyte. The batteries containing the $LiPF_6$ EC/DMS (1:1) electrolyte exhibited much higher charge capacities than those containing the $LiPF_6$ EC/DMC (1:1) electrolyte. Although the first cycle efficiency of the cells containing DMS was somewhat lower than that of the cells containing DMC, the later cycle efficiencies of the cells containing DMS was higher than those of the cells containing DMC. This result is similar to that reported by Wrodnigg [3].

4. Conclusions

Organic sulfites are promising solvents to be developed as electrolytes component in lithium ion batteries. Both ES and PS have excellent film-forming properties. When Only 5 wt.% of ES or PS is added into pure PC electrolytes, the co-intercalation into graphite is definitely suppressed. The performance of $LiCoO_2$/graphite cell was improved with only the 0.3 wt.% addition of ES to $1 \, mol \, L^{-1}$ $LiPF_6$ EC/DMC/DEC (1:2:2) electrolyte. DMS has good oxidation stability, low melting, moderate viscosity and high dielectric constant, and is an excellent candidate of co-solvent for lithium ion batteries to improve low temperature performance.

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