Journal of Power Sources 196 (2011) 776–783

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effect of sulfites on the performance of LiBOB/γ-butyrolactone electrolytes

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ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form 23 July 2010
Accepted 26 July 2010
Available online 3 August 2010

Keywords:
Lithium ion battery
sulfite
γ-Butyrolactone
Lithium bis(oxalate)borate

ABSTRACT

γ-Butyrolactone (GBL) increases the irreversible capacity of lithium ion battery when it is employed as the solvent for the lithium bis(oxalate)borate (LiBOB)-based electrolyte. To solve this problem, four sulfites are introduced to the electrolyte. The effects of ethyl sulfite (ES), propylene sulfite (PS), dimethyl sulfite (DMS) and diethyl sulfite (DES) on the LiBOB/GBL-based electrolytes are studied. The ionic conductivity, electrochemical stability, cycle performance and thermal stability of the sulfite containing electrolytes are tested and compared with that of the common electrolyte and the 1 M LiBOB/GBL electrolyte. The results indicate that the cyclic sulfites ES and PS show little benefit to the performance of the electrolyte. However, the linear sulfites DMS and DES could increase the ionic conductivity of the electrolyte and form an effective SEI film on the anode surface. In particular, the 1 M LiBOB/GBL + DMS (3:1 wt.) electrolyte mitigates the irreversible capacity and enhances the first coulomb efficiency and the capacity retention. The thermal stability of the DMS containing electrolyte is also improved and is better than that of the common electrolyte. These beneficial effects make them possibly to be a promising cosolvent for the LiBOB/GBL electrolyte.

1. Introduction

Lithium ion batteries have been a preferred power source because of their high energy density and excellent electrochemical properties, but safety issue is still a concerned problem as lithium ion battery accidents occur frequently. Lithium ion batteries are composed of highly energetic electrode materials and highly active electrolytes which are apt to become fire hazardous substance. The identification of a suitable electrolyte is essential to a safe high-performance lithium ion battery [1].

At present, the commercial electrolyte always consists of fluorine-containing lithium salt and alkyl carbonate solvents, such as the $LiPF_6$/ethylene carbonate (EC) + diethyl carbonate (DEC) electrolyte. However, $LiPF_6$-based electrolyte shows poor thermal stability and may be undergo thermal runway when it is subjected to thermal disturbance [2,3]. The typical carbonate solvents are not fully satisfactory. Dimethyl carbonate (DMC) and DEC have low flash points and highly volatile, which may cause a poor thermal response in the lithium ion batteries. EC has a high melting point which may lead to poor low temperature performance (Table 1). Therefore, many studies have sought new alternatives based on other salts and solvents [4–8].

Lithium bis(oxalate)borate (LiBOB) has been identified as a lithium salt with unique benefits in lithium ion battery use [9,10]. The fluorine free composition and good thermal stability of LiBOB are important for improving the safety of the lithium ion batteries, and its environment-friendly features are attractive. However, the lower solubility and inferior conductivity of LiBOB in alkyl carbonate solvents limit its application in electrolyte.

Xu [11] reported that the lactones-based solvents can effectively dissolve LiBOB to high concentrations and generate low interfacial resistance on graphitic electrode, especially for γ-butyrolactone (GBL). The physical and electrochemical properties of GBL make it an effective lithium ion battery solvent. The melting point, the boiling point and the flash point of GBL are −44 °C, 204 °C and 101 °C, respectively. Thus, GBL has a wider liquid temperature range and better thermal stability than that of the alkyl carbonate solvents. Meanwhile, its high dielectric constant and low viscosity are just sufficient for the demand of lithium ion battery electrolyte. However, GBL aggravates the irreversible capacity associated with the reduction process of the BOB anion on carbonaceous anode surface [11].

Since adding additive is a convenient way to improve the performance of electrolyte, many efforts have been devoted to the study of the chemicals with special features, such as organic sulfites. Organic sulfites have similar structures to organic alky carbonates (Table 1), and some reports show that certain sulfites show promising performances when used as film-forming electrolyte additives [12,13].

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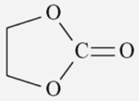
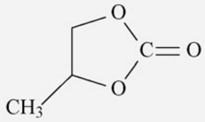
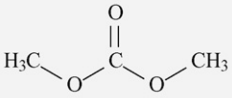
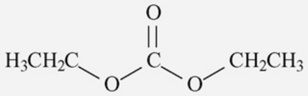
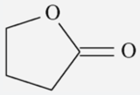
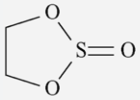
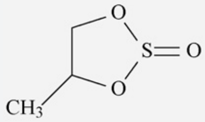
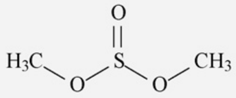
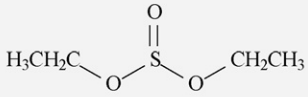
doi:10.1016/j.jpowsour.2010.07.064

Table 1
The basic physical and electrochemical properties of the solvents.

Solvents	Structure	Structural formula	Melting point (°C)	Boiling point (°C)	Flashing point (°C)	Dielectric constant ($CV^{-1}\ m^{-1}$)	Viscosity (mPa S)
Ethylene carbonate (EC)		$C_3H_4O_3$	39	248	160	89.6[a]	1.86[a]
Propylene carbonate (PC)		$C_4H_6O_3$	−49.2	241.7	135	64.4	2.53
Dimethyl carbonate (DMC)		$C_3H_6O_3$	4.6	90	18	3.18	0.5902
Diethyl carbonate (DEC)		$C_5H_{10}O_3$	−43	126.8	31	2.82	0.748
γ-Butyrolactone (GBL)		$C_4H_6O_2$	−43.53	204	98.3	39.1	1.73
Ethyl sulfite (ES)		$C_2H_4O_3S$	−17	172–174	79	NA	NA
Propylene sulfite (PS),		$C_3H_6O_3S$	79	68[b]	NA	NA	NA
Dimethyl sulfite (DMS)		$C_2H_6O_3S$	−141	126	30	22.5	0.8732
Diethyl sulfite (DES)		$C_4H_{10}O_3S$	−112	159	53	15.6	0.889

[a] At 40 °C.
[b] 20 mmHg.

It should be noted that the desirable features reported for these sulfites mainly for cyclic sulfites, such as ethyl sulfite (ES) and propylene sulfite (PS). The linear sulfites, such as dimethyl sulfite (DMS) and diethyl sulfite (DES), have no satisfactory performances like the cyclic sulfites, and they are inferior electrolyte additives for EC comparing with linear alky carbonates [14]. However, the existing studies have focused on adding sulfites to the alky carbonate electrolytes. Little is known about their effects on the electrolyte with GBL as the main solvent. Moreover, in order to ensure fewer negative effects, the additive level has always been kept low, which may limit the benefits of additives. Furthermore, the thermal stability of the electrolytes after the addition of these additives is rarely discussed.

Here, we report the influence of sulfites on LiBOB/GBL electrolytes. The sulfites were used as a cosolvent at a high concentration (50 wt.% and 25 wt.%) to improve the performance of the electrolytes. The ionic conductivity, electrochemical stability, cycle performance and thermal stability of the sulfites electrolytes were tested and discussed.

2. Experimental

EC, DEC and GBL were produced by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. ES and PS were produced by Fujian Chuangxin Science and Technology Develops Co., Ltd. DMS and DES were produced by Shanghai Jieshi Chemical Co., Ltd. $LiPF_6$ and LiBOB were produced by Tianjin Jinniu Power Sources Material Co. and Chemetall Inc., respectively. The electrolytes were prepared in an argon-filled glove box (MBraun Labmaster 130, <1 ppm O_2 and H_2O). All solvent ratios appearing in the paper are in weight ratios.

A negative electrode consisting of mesophase carbon microbeads (MCMB) (92 wt.%) and poly(vinylidene fluoride) (PVDF) (8 wt.%) was made on copper foils. The positive electrode consisting of $LiCoO_2$ (84 wt.%), acetylene black (8 wt.%) and poly(vinylidene fluoride) (PVDF) (8 wt.%) was made on aluminum foils. Then the electrodes were dried for 12 h in a vacuum at 70 °C. For the $LiCoO_2$/MCMB full lithium ion cells and the Li/MCMB half-cells, the negative electrodes were both MCMB, and the counter electrodes were $LiCoO_2$ and lithium metal foil, respectively. The weight of $LiCoO_2$ and MCMB of $LiCoO_2$/MCMB cell is 5.5 mg and 3.1 mg, respectively. The weight of MCMB of Li/MCMB cell is 5.0 mg.

The ionic conductivities of the electrolytes were measured using a Model DDS-307A conductivity meter (Shanghai Precision & Scientific Instrument Co. Ltd., China) over a temperature range of −30 °C to 50 °C. Each measurement of conductivity was conducted after holding the electrolyte at a given temperature for 30 min to reach full thermal equilibrium.

The electrochemical stabilities of the electrolytes on the negative electrodes were measured by cyclic voltammetry (CV), using CHI 604A Electrochemical Workstation with a scan rate at 0.5 mV s^{-1} between 0 V and 3.0 V. AC impedance was measured using the same workstation. The voltage amplitude was set at 5 mV from 10 kHz to 0.01 Hz. The morphology of MCMB was observed under a scanning electron microscope (SEM, HitachiX-650).

Cycling tests for the cells were performed in constant current–constant voltage (CC–CV) charge mode and constant current (CC) discharge mode on a multi-channel battery cycler (Neware BTS2300, Shenzhen). The constant current mode was between 2.5 V and 0.01 V at a current density of 0.20 mA cm^{-2}. The constant voltage (CV) mode ended when the current is less than 0.03 mA cm^{-2}.

The thermal stabilities of the electrolytes were measured by C80 micro-calorimeter in argon atmosphere. The sample mass in all cases was constant. The heating rate was set at 0.2 °C min^{-1} from ambient temperature to 300 °C.

3. Results and discussion

3.1. Ionic conductivity

The dependence of ionic conductivity on temperature for the electrolyte is shown in Fig. 1. It can be found that the ionic conductivities of the electrolytes decrease with temperature dropping. When the temperature is above −10 °C, the conductivity of 1 M LiBOB/GBL electrolyte is lower than that of 1 M $LiPF_6$/EC + DEC electrolyte (Fig. 1). When 50 wt.% of DMS or DES is added into pure GBL, the conductivity is markedly enhanced. The conductivity of 1 M LiBOB/GBL + DMS (1:1 wt.) electrolyte is even greater than that of 1 M $LiPF_6$/EC + DEC (1:1 wt.) electrolyte at the same temperature. The high conductivity is mainly due to the low melting point, low viscosity and higher dielectric constant of linear organic sulfites (Table 1). A low melting point means a wider liquid temperature range, and a low viscosity favors ionic movement, and a high dielectric constant increases the dissociation of ion pairs from the dissolved salt. However, the desirable enhancement of conductivity does not appear with the addition of ES or PS. The decline in conductivity indicates the compatibility of the cyclic organic sulfites with the LiBOB/GBL electrolyte may not be as good as that of the linear organic sulfites.

Trace of solid material emerges from the 1 M $LiPF_6$/EC + DEC (1:1 wt.) electrolyte below −10 °C, and the precipitation becomes clear as the temperature decreases. This phenomenon is believed to be the main reason for the reduction in conductivity of the 1 M $LiPF_6$/EC + DEC (1:1 wt.) electrolyte to below that of other electrolytes [15]. At −30 °C, the conductivity of the carbonates-based electrolyte is merely 0.41 mS cm^{-1}, and that of the pure GBL-based electrolyte is 0.94 mS cm^{-1}, while that of the LiBOB/GBL + sulfite electrolytes is 0.79 mS cm^{-1}(ES), 0.59 mS cm^{-1} (PS), 1.2 mS cm^{-1} (DES) and 1.34 mS cm^{-1} (DMS), respectively. The 1 M LiBOB/GBL + DMS (1:1 wt.) and the 1 M LiBOB/GBL + DES (1:1 wt.) electrolytes have better ionic conductivity, even at lower temperature.

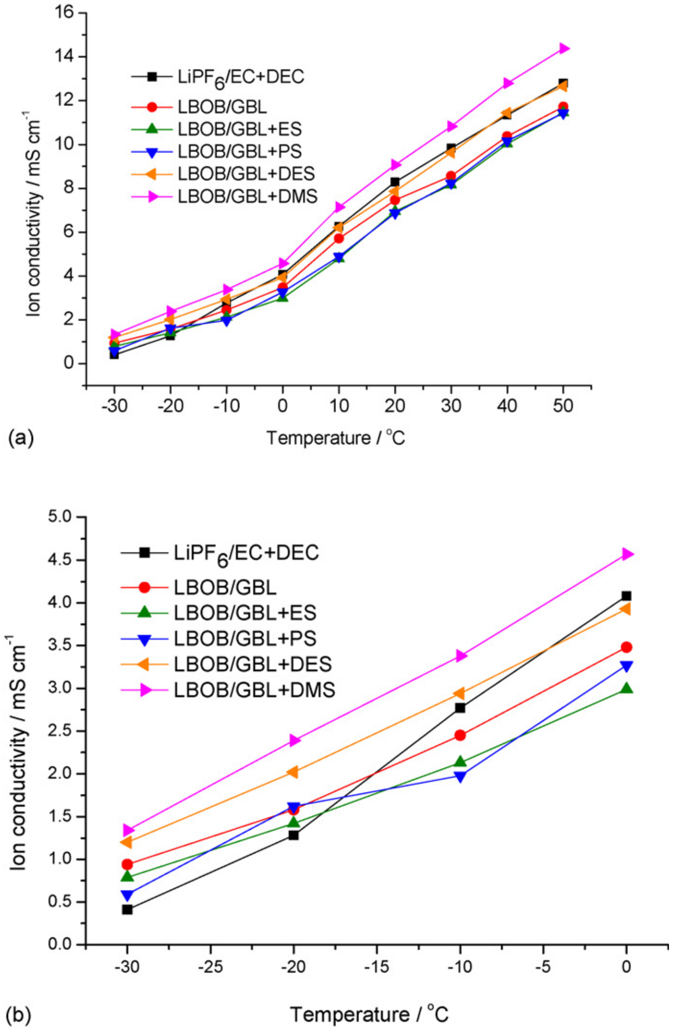


Fig. 1. The dependence of ionic conductivity on temperature for six kinds of electrolytes: (a) the temperature range is from to −30 °C to 50 °C; (b): the temperature range is from to −30 °C to 0 °C.

3.2. Electrochemical stability

Electrochemical stability is necessary for the lithium ion battery, so the electrochemical behaviors of electrolytes were studied by cyclic voltammetry, AC impedance measurement and SEM. Six kinds of electrolytes were used here, with the 1 M $LiPF_6$/EC + DEC (1:1 wt.) electrolyte as a reference.

3.2.1. Cyclic voltammetry

Fig. 2 shows the CV test results for Li/MCMB half-cells containing six kinds of electrolytes separately. The CV curve of the reference is shown in Fig. 2a. While that for the 1 M LiBOB/GBL is given in Fig. 2b. It can be seen that an undesirable phenomenon occurs for the electrolyte. There are two reductive current peaks at around

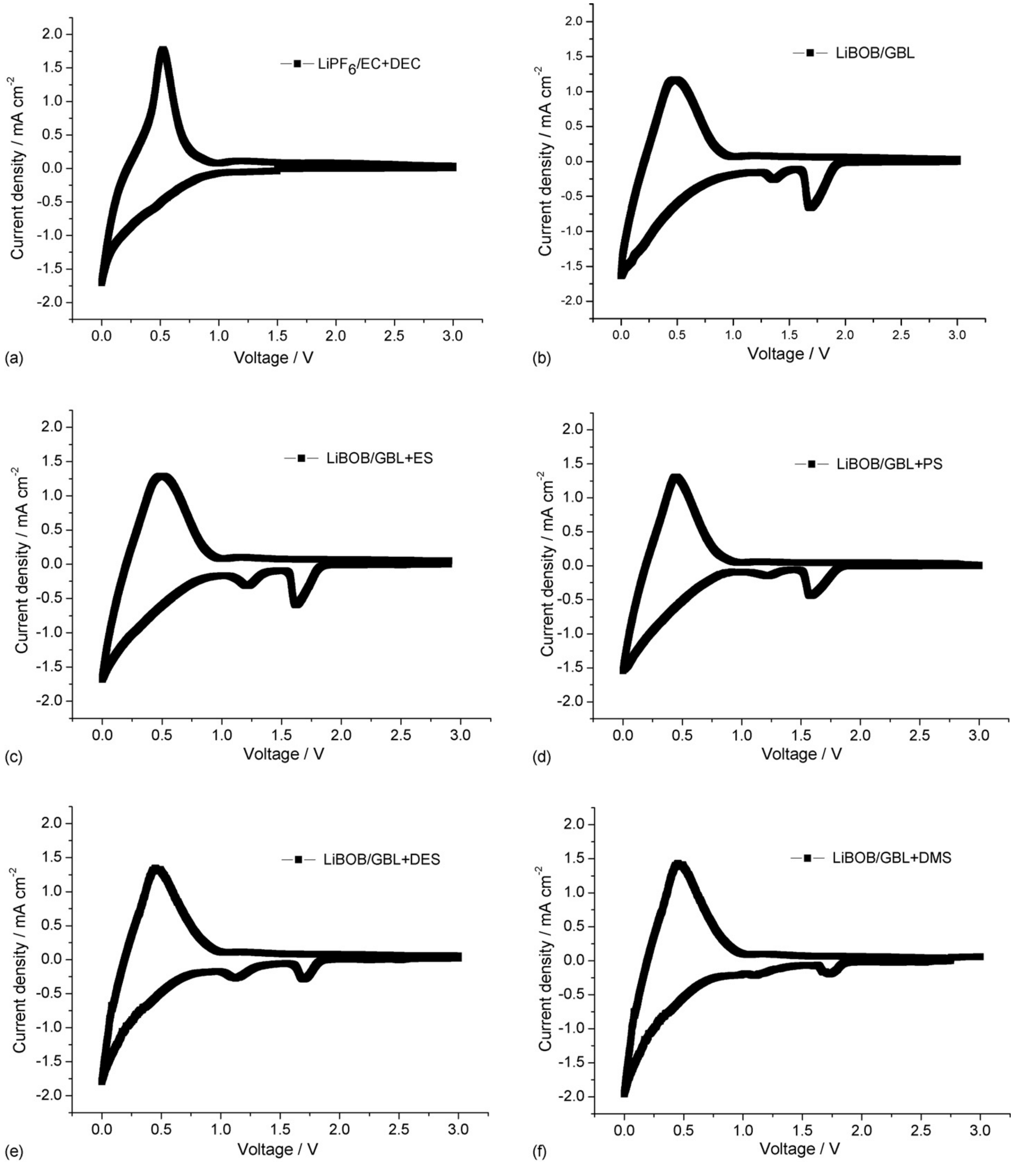


Fig. 2. The CV test results of Li/MCMB half-cells containing six kinds of electrolytes: (a) 1 M $LiPF_6$/EC + DEC (1:1 wt.); (b) 1 M LiBOB/GBL; (c) 1 M LiBOB/GBL + ES (3:1 wt.); (d) 1 M LiBOB/GBL + PS (3:1 wt.); (e) 1 M LiBOB/GBL + DES (3:1 wt.); (f) 1 M LiBOB/GBL + DMS (3:1 wt.).

1.3 V and 1.7 V. The reduction current peak of 1.3 V belongs to GBL [16]. The reduction current peak of 1.7 V arises from BOB anion. Or, to be more accurate, the 1.7 V reduction process is owing to the trace amount of oxalate ester or oxalate anion that existed as impurities in LiBOB [17].

These two reductive current peaks indicate that there is still a difference in electrochemical stability between the pure GBL solution and the reference. Fig. 2c–f shows the CV test results of electrolytes containing sulfites. In comparison with Fig. 2b, the reductive currents of the peaks in these figures decrease to vary-

Table 2
The reductive current peaks appearing in the CV test of Li/MCMB half-cells containing different electrolytes.

Electrolytes	Reductive current density 1 (mA cm^{-2})	Reductive current density 2 (mA cm^{-2})
1 M LiBOB/GBL	0.66 (1.70 V)	0.26 (1.30 V)
1 M LiBOB/GBL + ES (3:1 wt.)	0.59 (1.63 V)	0.32 (1.22 V)
1 M LiBOB/GBL + PS (3:1 wt.)	0.44 (1.58 V)	0.14 (1.22 V)
1 M LiBOB/GBL + DES (3:1 wt.)	0.29 (1.71 V)	0.25 (1.13 V)
1 M LiBOB/GBL + DMS (3:1 wt.)	0.19 (1.73 V)	0.20 (1.10 V)

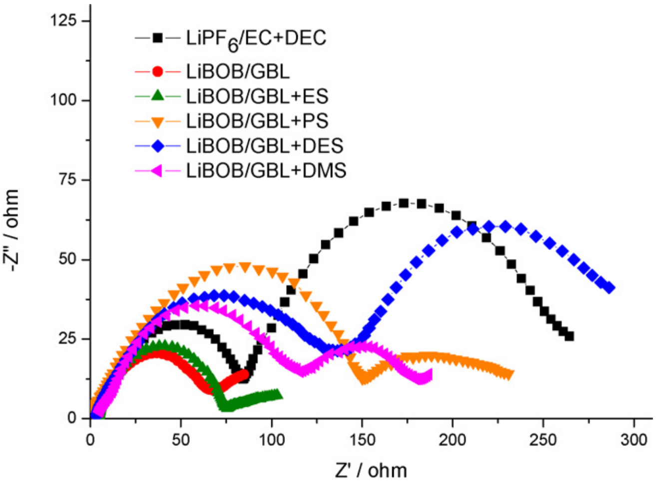


Fig. 3. The AC impendence of Li/MCMB half-cells containing six kinds of electrolytes.

ing extents. The modest decrease in reductive current of the 1 M LiBOB/GBL + ES (3:1 wt.) is thought to be caused by the dilution of GBL. The noticeable decrease for other three electrolytes indicates that the addition of PS, DMS and DES appears to be beneficial to the pure GBL-based electrolyte. Where the reduction appears at around 1.7 V, the 1 M LiBOB/GBL + DMS (3:1 wt.) has the lowest reductive current density, which is almost 3.5 times as small as that of the neat GBL electrolyte (Table 2). The reduction at around 1.3 V is not visibly weakened after the addition of sulfites, and the electrolytes containing PS and DMS experience a decrease in reductive current of 23% and 46%, respectively. In contrast, the CV curve of 1 M LiBOB/GBL + DMS (3:1 wt.) compares well with that of the reference.

3.2.2. *AC impedance measurement*

AC impedance 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, which should not be too high or too low. The higher migration rate would mean the SEI film might not be formed successfully, and the lower rate would hinder the ion transport.

Fig. 3 shows the impedance spectra of the cells. The spectra are composed of a high-medium frequency flat semicircle and straight sloping line at low frequency. The resistance of SEI is corresponding to the semicircle at high frequency [18]. It is evident that the diameter of the semicircle (corresponding to SEI) is much lower for ES and pure GBL solutions compared to other solutions. The main reason is probably that the SEI films are too thin for the resistance to be detected, as is evident from the poor performance of the corresponding Li/MCMB half-cells. The higher surface resistances of the MCMB anode in the DMS, DES and PS solutions may indicate that the SEI films were formed but were thicker than that of the reference. PS corresponds to the largest diameter of the semicircle, and this may have led to the largest resistance for the ion transport and have contributed to the unfavorable performance of the cell.

3.2.3. *SEM measurement*

Using SEM we can observe the surface of the anode MCMB before and after the electrochemical measurement. The SEM images are shown in Fig. 4. The typical SEM image of the MCMB prior to the electrochemical measurement is shown in Fig. 4a. The anode surface in the case of the 1 M LiPF$_6$/EC + DEC (1:1 wt.) electrolyte is shown in Fig. 4b.

Fig. 4c shows an exfoliation for the pure GBL solution-based anode surface. In the case of GBL + ES solution, as shown in Fig. 4d, it can be seen that the exfoliation is inconspicuous but the SEI film is not as stable as the reference film, shown in Fig. 4b. The morphology of the GBL + PS solution-based MCMB in Fig. 4e is close to that of the reference, but it still has some small cracks in the thick film layer which may have been caused by the cointercalation of solvent molecules.

The clear films on the MCMB surfaces seen in Fig. 4f and g indicate that the effective forced formation of a SEI film is accomplished. This film formation corresponds with the smaller reductive current peaks in the CV tests for the GBL-based electrolytes with DES and DMS. The smaller reductive current peaks appear to be closely connected with protection for the MCMB anode and the reduction of the cointercalation of solvent molecules, both benefits of a stable SEI film. When an electrolyte containing DMS is used, the anode is completely covered with a plain layer of SEI film that is much smoother than that in the case of a containing DES electrolyte.

3.3. *Cycle performance*

GBL undergoes reductive decomposition on the anode surface, which worsens the cell performance. The reduction behaviors of the electrolytes were studied by analyzing the first charge-discharge curves of Li/MCMB half-cells, as shown in Fig. 5.

It can be seen that the irreversible capacity appears at 1.7 V and 1.3 V when pure GBL is used as the solvent. The irreversible process limits the lithium ion and leads to a drop of 24% in the first coulomb efficiency. Therefore, GBL is not the practical neat solvent for the electrolyte. Using mixed solvents of GBL and sulfite maybe an effective way to alleviate the irreversible process. The enlarged figure (Fig. 5b) shows that the irreversible capacity at 1.7 V and 1.3 V is reduced to negligible levels using 1 M LiBOB/GBL + DMS (3:1 wt.) electrolyte. Meanwhile, the first coulomb efficiency rises to 95.1% (Table 3).

Table 3
The capacity and the coulomb efficiency of the first charge-discharge cycle of Li/MCMB half-cells containing different electrolytes.

Electrolytes	The first charge capacity density (mAh g^{-1})	The first discharge capacity density (mAh g^{-1})	Coulomb efficiency
1 M LiPF$_6$/EC + DEC (1:1 wt.)	311.17	300.62	96.6%
1 M LiBOB/GBL	290.16	220.61	76.0%
1 M LiBOB/GBL + ES (3:1 wt.)	288.35	248.54	86.2%
1 M LiBOB/GBL + PS (3:1 wt.)	297.92	266.54	89.5%
1 M LiBOB/GBL + DES (3:1 wt.)	304.83	277.28	91.0%
1 M LiBOB/GBL + DMS (3:1 wt.)	312.78	297.4	95.1%

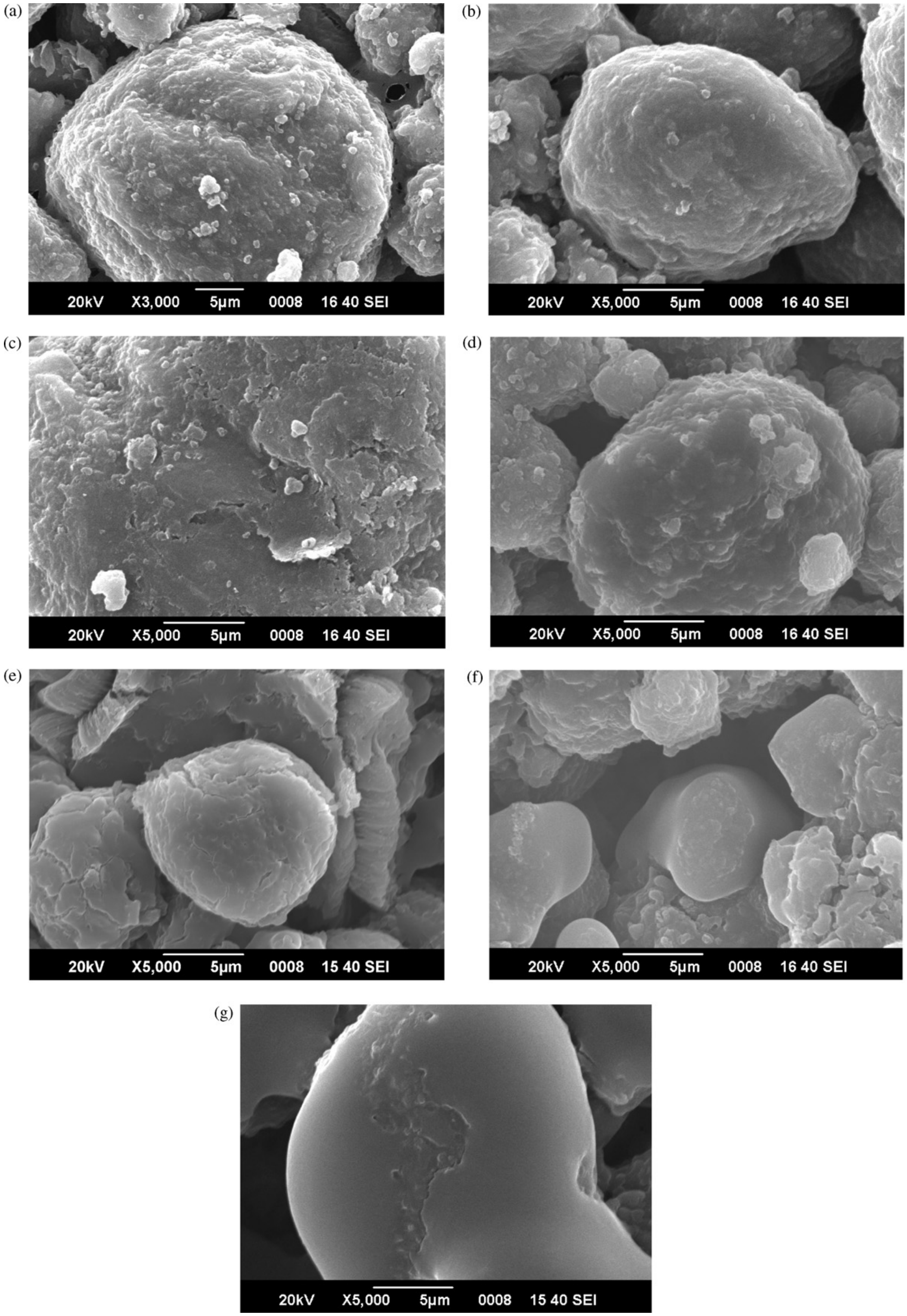


Fig. 4. The SEM images of the surface of anode MCMB prior to the electrochemical measurement and in the case of six kinds of electrolytes: (a) the surface of anode MCMB prior to the electrochemical measurement; (b) 1 M $LiPF_6$/EC + DEC (1:1 wt.); (c) 1 M LiBOB/GBL; (d) 1 M LiBOB/GBL + ES (3:1 wt.); (e) 1 M LiBOB/GBL + PS (3:1 wt.); (f) 1 M LiBOB/GBL + DES (3:1 wt.); (g) 1 M LiBOB/GBL + DMS (3:1 wt.).

Table 4
The cycling performance of $LiCoO_2$/MCMB cells containing different electrolytes.

Electrolytes	1 M LiPF6/EC + DEC (1:1 wt.)	1 M LiBOB/GBL	1 M LiBOB/GBL + ES (3:1 wt.)
The first discharge capacity (mAh)	0.784	0.761	0.770
The 100th discharge capacity (mAh)	0.746	0.533	0.617
Capacity retention (the 100th cycle)	95.15%	70.04%	80.13%
Electrolytes	1 M LiBOB/GBL + PS (3:1 wt.)	1 M LiBOB/GBL + DES (3:1 wt.)	1 M LiBOB/GBL + DMS (3:1 wt.)
The first discharge capacity (mAh)	0.771	0.778	0.783
The 100th discharge capacity (mAh)	0.668	0.703	0.736
Capacity retention (the 100th cycle)	86.64%	90.36%	94.00%

A charge–discharge cycling performances of $LiCoO_2$/MCMB cells using different electrolytes were conducted. The relationship between the capacity retention of cells and the cycle number is shown in Fig. 6. GBL electrolytes containing a linear sulfite demonstrate show better cycle performance than other electrolytes. Their capacity deteriorates more slowly, where with as much as 90% of the original capacity maintained even beyond the 100th cycle (Table 4). This good cycle performance confirms that the film-forming property is improved after adding a linear sulfite to the GBL solution. The stable and efficient SEI film created by DES or DMS can protect the electrode material and prevent the capacity from fading with cycle times increasing.

3.4. Thermal stability (C80)

A comparison of the C80 profiles for six kinds of electrolytes is shown in Fig. 7. The details C80 results are compared in Table 5.

The common electrolyte 1 M $LiPF_6$/EC + DEC (1:1 wt.) begins to react at 127 °C. Then an endothermic process follows at 160 °C, with heat absorption of 35.6 J g^{-1}. With the temperature increasing, a large exothermic phenomenon was detected with heat

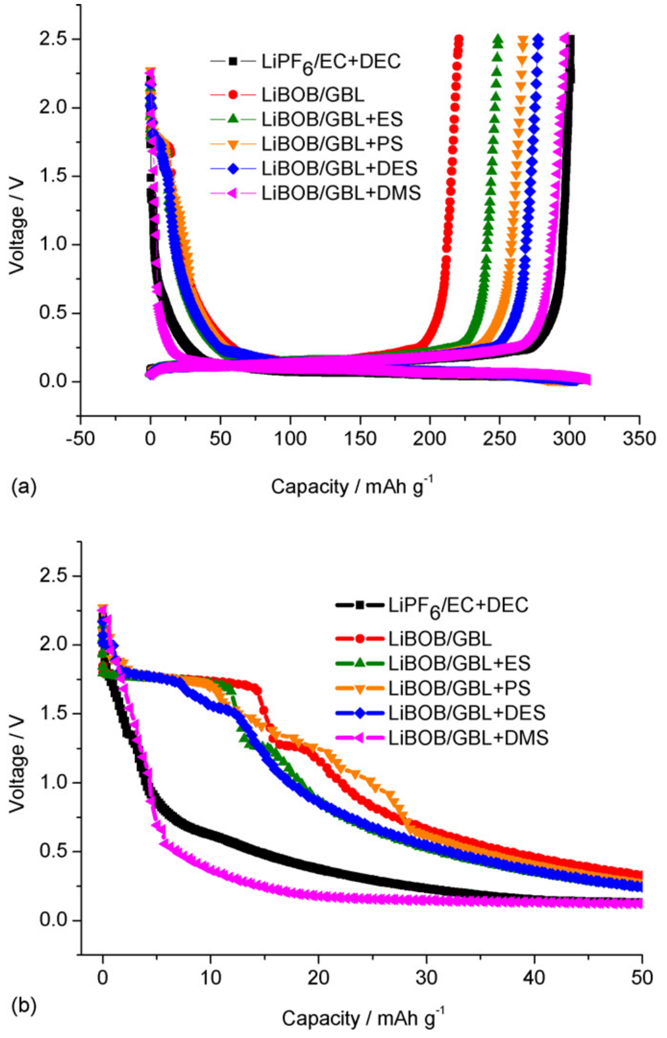


Fig. 5. The first charge-discharge voltage profiles of the Li/MCMB half-cells containing six kinds of electrolytes: (a): the capacity range is from 0 mAh g^{-1} to 350 mAh g^{-1}; (b) the enlarged figure that the capacity range is from 0 mAh g^{-1} to 50 mAh g^{-1}.

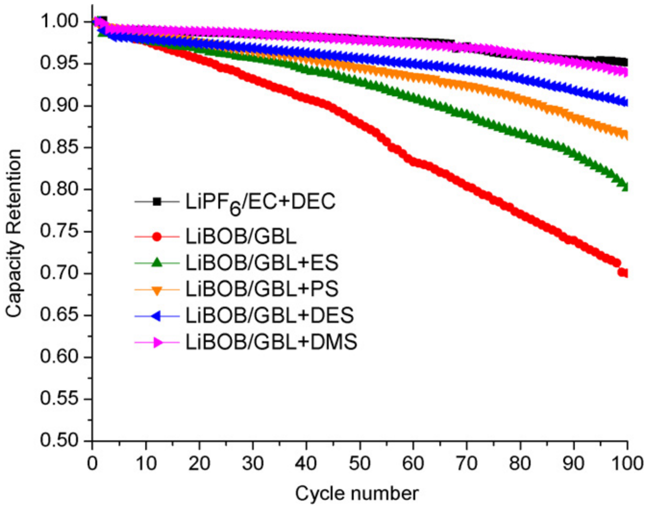


Fig. 6. The cycling performance of $LiCoO_2$/MCMB cells containing six kinds of electrolytes.

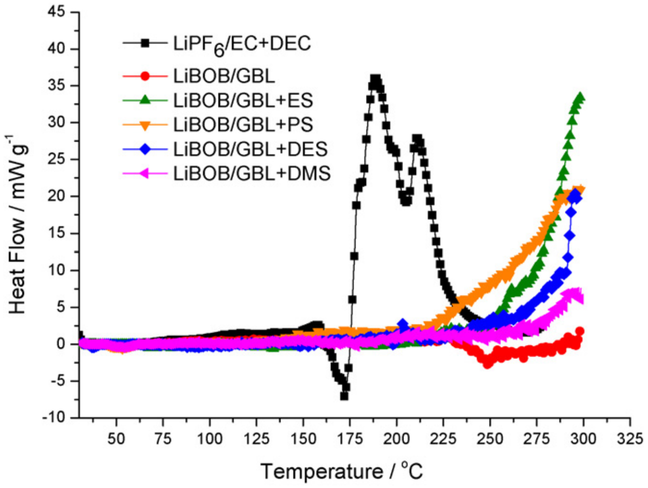


Fig. 7. C80 heat flow curves of six kinds of electrolytes.

Table 5
The C80 results (the onset temperature and the heat generation) of different electrolytes from ambient temperature to 300 °C.

Electrolytes or solvents	Onset temperature (°C)	Heat generation ($J\,g^{-1}$) (ambient temperature to 300 °C)
1 M $LiPF_6$/EC + DEC (1:1 wt.)	127	35.6 −412.60
1 M LiBOB/GBL	227	14.31
1 M LiBOB/GBL + ES (3:1 wt.)	223	−214.19
1 M LiBOB/GBL + PS (3:1 wt.)	196	−304.42
1 M LiBOB/GBL + DES (3:1 wt.)	200	−136.48
1 M LiBOB/GBL + DMS (3:1 wt.)	252	−73.07

generation of $-412.6\,J\,g^{-1}$ till 300 °C. As for LiBOB/GBL-based electrolytes, it is evident that their onset temperatures are almost always higher than 200 °C, which are much higher than that of 1 M $LiPF_6$/EC + DEC (1:1 wt.). As the exothermic process occurs later and intensifies until the end of the C80 measurement, the heat value in Table 5 should only be considered as part of that total heat generation for the electrolyte. The delayed exothermic process nonetheless demonstrates that better thermal stability can be obtained by the new composition of the electrolytes.Furthermore, it should be noted that the thermal stabilities of the LiBOB/GBL electrolytes decline somewhat with the addition of sulfites, which are reflected in the higher heat generation and lower onset temperature of the sulfites containing electrolytes comparing with the 1 M LiBOB/GBL electrolyte. The onset temperature of the GBL + ES electrolyte (223 °C) is close to that of the neat GBL-based electrolyte (227 °C), but its heat generation increases rapidly with an increase in temperature. The GBL + PS electrolyte begins to release heat at 196 °C, which is the lowest onset temperature among the LiBOB/GBL electrolytes. After this temperature, the exothermic process is aggravated with heat generation of $-304.42\,J\,g^{-1}$ till 300 °C, which is higher than that of the other LiBOB/GBL-based electrolytes. The exothermic process of the electrolyte containing DES was detected at 200 °C. Under the influence of high temperature, the releasing heat is $-136.48\,J\,g^{-1}$. The GBL-DMS electrolyte also has an exothermic process that begins at 252 °C, but the heat generation of the process is only $-73.07\,J\,g^{-1}$, which is the lowest one among the GBL-sulfite electrolytes.

Here we can see that the beneficial effects of the new electrolytes are due to the good thermal stability of LiBOB and GBL. The sulfites have some adverse impact on thermal stability, but the effect of the addition of DMS is negligible.

4. Conclusion

The effects of sulfites on the performance of LiBOB/GBL-based lithium ion battery electrolytes were studied in this paper. The linear sulfites DMS and DES improve the ionic conductivity of the LiBOB/GBL electrolyte and form an effective and stable SEI film on the anode surface. The beneficial effect protects the anode surface and reduces the cointercalation of the solvent molecules.

1 M LiBOB/GBL + DMS (3:1 wt.) presents especially good electrochemical stability. In the case of an electrolyte containing DMS, the irreversible capacity associated with the reduction process of a BOB anion on a carbonaceous anode surface is mitigated. The first coulomb efficiency is elevated to 95.1%, and the capacity loss occurring in the charge–discharge cycling measurement is prevented. Moreover, the 1 M LiBOB/GBL + DMS (3:1 wt.) also demonstrates good thermal stability. In comparison with the common alkyl carbonates electrolyte, its heat generation can be neglected.

The cyclic sulfites do not present such desirable features as the linear organic sulfites in the LiBOB/GBL electrolyte, especially ES. The introduction of PS is beneficial in enhancing the performance of the pure GBL-based electrolyte, but the cointercalation of the solvent molecules could not be alleviated effectively and which sometimes may results in a higher resistance of the thick SEI film.

Overall, although the mechanism of the suppression of the irreversible capacity needs further discussion, it is evident that the use of linear sulfites as the main solvents with GBL when the lithium salt is LiBOB should be feasible.

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