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Cyclic and acyclic sulfites: new solvents and electrolyte additives for lithium ion batteries with graphitic anodes?

Gerhard H. Wrodnigg, Jürgen O. Besenhard, Martin Winter*

Institute for Chemical Technology of Inorganic Materials, Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria

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Abstract

The low viscosities of the linear sulfites dimethyl sulfite and diethyl sulfite are suggesting an investigation of their suitability as low viscosity co-solvents for ethylene carbonate based electrolytes. In this study, electrochemical performances at graphitic anodes and conductivities in the temperature range -60 to $+60^{\circ}\text{C}$ are presented. Comparisons with the linear carbonates dimethyl carbonate and diethyl carbonate, which have been currently used as low viscosity solvents in lithium ion batteries, are made. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion battery; Graphite anode; Solid electrolyte interphase; Electrolyte additive; Conductivity

1. Introduction

In previous studies, we have reported on the use of the cyclic organic sulfites ethylene sulfite (ES) [1] and propylene sulfite (PS) [2] as film forming electrolyte additives for lithium ion batteries with graphitic anodes (also see Fig. 1). Small amounts of the cyclic sulfites (typically 5 vol.%) added to propylene carbonate (PC) based electrolytes improve the anode behavior significantly as PC co-intercalation into graphite is suppressed or even avoided. Recently, we extended our study on further sulfur-containing organic compounds, such as the linear sulfites, dimethyl sulfite (DMS) and diethyl sulfite (DES), and others [3]. Comparing the electrochemical performance of the cyclic sulfites with that of the linear sulfites, we found that the filming strength (capability for the formation of an effective solid electrolyte interphase (SEI) film, which prevents the graphite from PC co-intercalation and thus keeps the irreversible charge losses low) decreases in the order: $\text{ES} > \text{PS} \gg \text{DMS} > \text{DES}$. In short, the linear sulfites DMS and DES are not suitable as electrolyte additives in PC-based electrolytes.

Here, we will show that the linear sulfites can be used as electrolyte co-solvents in combination with ethylene carbonate (EC). The idea is that the (highly viscous) EC takes over

the filming task and the low viscosity solvents DMS and DES assure a good low temperature conductivity (cf. Table 1). In order to judge the data properly, we will compare the conductivity data and the constant current charge/discharge cycling data of EC/DMS and EC/DES electrolytes with those of correspondingly composed EC/dimethyl carbonate (DMC) and EC/diethyl carbonate (DEC) electrolytes. Thereby, it might be interesting to notice that the organic sulfites ES, PS, DMS and DES can be formally considered as structurally familiar to the commonly used organic carbonates, EC, PC, DMC and DEC (cf. Fig. 1).

2. Experimental

DMS (Fluka, 97%) and DES (Fluka, 98%) were distilled under vacuum, DMC (Merck, >99%) and DEC (Merck, >99%) under Ar atmosphere. The solvents were stored over 4 Å molecular sieves under high purity argon for several days. EC and LiClO_4 (Merck, Selectipur, battery grade) were used as received. Graphite based anodes were made from TIMREX[®] SFG 44 synthetic graphites (Timcal group). For electrode preparation, a slurry of the graphite suspended in a solution of poly(vinylidene) fluoride (PVDF, Aldrich) in 1-methyl-2-pyrrolidinone (Aldrich) was spread on a stainless steel mesh current collector, dried at 120°C overnight, then pressed at 100 kg cm^{-2} , and finally dried under vacuum at 120°C for 4 h again. The electrodes contained 5 w/o PVDF binder. Electrolyte preparation and cell

* Corresponding author. Tel.: +43-316-873-8268;

fax: +43-316-873-8272.

E-mail address: winter@ictas.tu-graz.ac.at (M. Winter).

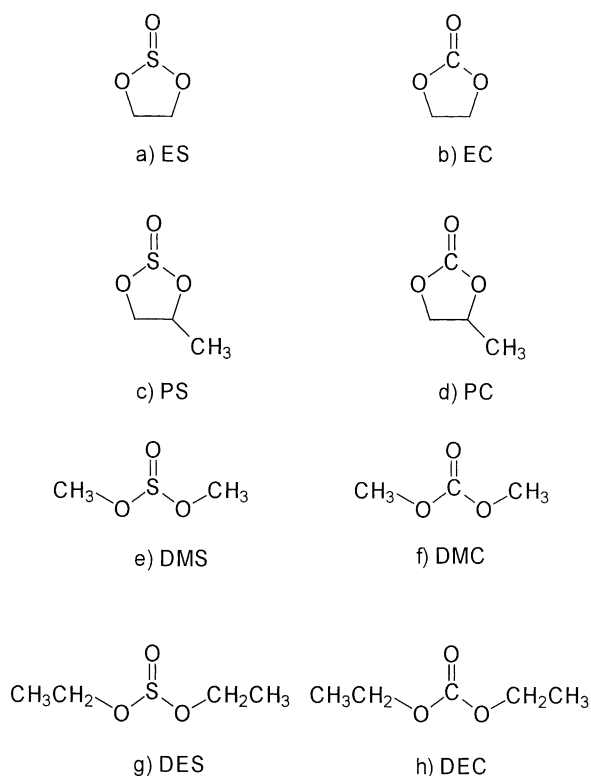


Fig. 1. Structural formulae and abbreviations of (a) ethylene sulfite; (b) ethylene carbonate; (c) propylene sulfite; (d) propylene carbonate; (e) dimethyl sulfite; (f) dimethyl carbonate; (g) diethyl sulfite; (h) diethyl carbonate.

assembly were accomplished under dry argon atmosphere in a glove box. The water content of the electrolytes determined by Karl Fischer titration was less than 15 ppm. Electrochemical experiments were carried out in laboratory type glass cells with bulk lithium counter and reference electrodes and an excess of electrolyte. The electrodes were not closely packed in separator materials, but placed in the electrolyte without any further support or protection.

3. Results and discussion

The constant current charge/discharge cycling data of EC/DMS (1/1 by volume) and EC/DES (1/1 by volume) in

Table 1

Melting points (mp), boiling points (bp), flash points (fp), viscosities (at 25°C) (η) and dielectric constants (ϵ) of cyclic carbonates, linear carbonates, and linear sulfites investigated in this study

Solvent	mp (°C)	bp (°C)	fp (°C)	η (cP)	ϵ
EC	36.5	238	160	1.9 ^a	90.36 ^a
DMC	4.6	90	18	0.5902	3.18
DEC	-43	126.8	31	0.748	2.82
DMS	-141	126	30	0.8732	22.5
DES	NA	159	53	0.839 ^b	15.6 ^b

^a At 40°C.

^b At 20°C.

Table 2

Reversible (C_{rev}) and irreversible (C_{irr}) specific charges as well as discharge/charge efficiencies (Eff) of synthetic graphite TIMREX[®] SFG 44^a

Cycle	C_{rev} (Ah kg ⁻¹)	C_{irr} (Ah kg ⁻¹)	Eff (%)
1 M LiClO ₄ in EC/DMS (1/1 by volume)			
1	349.8	98.0	78.1
2	348.2	5.7	98.4
3	346.9	6.0	98.3
4	351.8	5.4	98.5
5	349.0	4.0	98.9
6	354.6	3.6	99.0
7	352.7	3.3	99.1
8	353.2	3.9	98.9
9	350.2	2.4	99.3
1 M LiClO ₄ in EC/DES (1/1 by volume)			
1	355.6	72.0	83.2
2	355.8	18.1	95.2
3	356.3	12.0	96.8
4	350.7	9.5	97.4
5	352.1	8.7	97.6
6	350.3	9.8	97.3
7	348.2	8.8	97.5
8	342.0	6.9	98.0
9	336.8	6.9	98.0

^a $i = \pm 20$ mA g⁻¹, cut-off = 1.80/0.025 V vs. Li/Li⁺.

comparison to the corresponding EC/DMC and EC/DEC mixtures are displayed in Tables 2 and 3. In short, constant current charge/discharge cycling is possible in ES/DMS and EC/DES electrolytes with quite reasonable efficiencies and reversible specific charges. However, even regarding the preliminary character of this study, the irreversible specific charge losses in the EC/DMS and EC/DES electrolytes seem to be higher than those obtained in the EC/DMC and EC/DEC electrolytes.

Electrolyte conductivity measurements (Fig. 2) disclose that the addition of the low viscosity solvents DMS, DMC, DES, and DEC enlarges the usable liquidity range at low temperatures as was expected. Though the viscosities of the

Table 3

Reversible (C_{rev}) and irreversible (C_{irr}) specific charges as well as discharge/charge efficiencies (Eff) of synthetic graphite TIMREX[®] SFG 44^a

Cycle	C_{rev} (Ah kg ⁻¹)	C_{irr} (Ah kg ⁻¹)	Eff (%)
1 M LiClO ₄ in EC/DMC (1/1 by volume)			
1	326.5	42.2	88.6
2	328.5	7.0	97.9
3	326.7	6.1	98.2
4	325.3	6.5	98.0
5	327.9	5.8	98.3
1 M LiClO ₄ in EC/DEC (1/1 by volume)			
1	344.7	32.3	91.4
2	338.2	4.0	98.8
3	338.7	2.5	99.3
4	336.9	1.8	99.5
5	336.9	1.6	99.5

^a $i = \pm 20$ mA g⁻¹, cut-off = 1.80/0.025 V vs. Li/Li⁺.

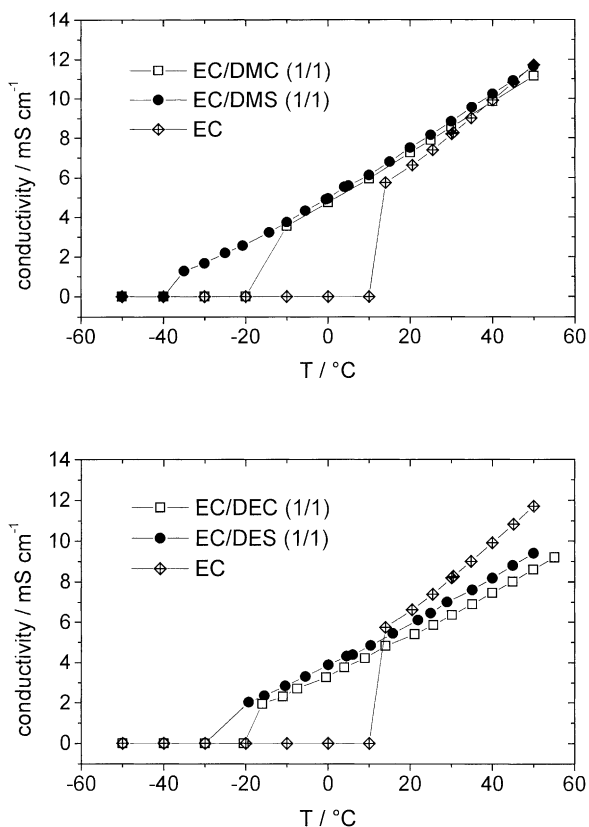


Fig. 2. Conductivity vs. temperature diagrams (top) of 1 M LiClO_4 in EC/DMC (1/1 by volume), in EC/DMS (1/1 by volume) and in EC, respectively, and (below) of 1 M LiClO_4 in EC/DEC (1/1 by volume), EC/DES (1/1 by volume) and in EC, respectively.

linear sulfites and linear carbonates are comparable, the electrolyte conductivities of the ES/DMS and EC/DES electrolyte mixtures are notably better than those of the corresponding EC/DMC and EC/DEC electrolytes, in particular at low temperatures, which might be attributed to their much higher dielectric constants. Finally, DMS and

DES might be also interesting electrolyte co-solvents from the viewpoint of safety, as their flash points¹ are higher than those of the presently used co-solvents DMC and DEC.

4. Conclusions

Judging from the constant current charge/discharge cycling data, the linear sulfites DMS and DES are inferior electrolyte co-solvents for EC, if a comparison with the commonly used low-viscosity solvents, the linear organic carbonates DMC and DEC is made. However, electrolyte mixtures of DMS or DES with EC (1/1 by volume) exhibit much better electrolyte conductivities, in particular at lower temperatures, than the correspondingly composed EC electrolytes with DMC and DEC. This suggests further studies on DMS and DES as low-viscosity co-solvents in electrolyte mixtures with EC. Investigations on the oxidation stability of these electrolytes are in progress.

Acknowledgements

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¹The flash point is defined as the temperature at which an external ignition inflames a solvent vapor/air mixture.