



Towards practical sulfolane based electrolytes: Choice of Li salt for graphite electrode operation



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HIGHLIGHTS

- Sulfolane/dimethylcarbonate electrolytes have been prepared and characterized.
- LiPF₆, LiTFSI, LiBF₄, LiFSI, LiTDI and LiDFOB have been used at 1 M.
- Most electrolyte are stable above 5 V on particulate carbon black electrodes.
- Graphite electrode operation is possible with all salts but LiTDI and LiFSI.
- LiDFOB allows efficient graphite cycling in graphite/LiFePO₄ cells.

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ABSTRACT

Sulfolane (tetramethylene sulfone, SL) is known for leading to Li-ion electrolytes with high anodic stability. However, the operation of graphite electrodes in alternative electrolytes is usually challenging, especially when ethylene carbonate (EC) is not used as co-solvent. Thus, we study here the influence of the lithium salt on the physico-chemical and electrochemical properties of EC-free SL-based electrolytes and on the performance of graphite electrodes based on carboxymethyl cellulose (CMC). SL mixed with dimethyl carbonate (DMC) leads to electrolytes as conductive as state-of-the-art alkyl carbonate-based electrolytes with wide electrochemical stability windows. The compatibility with graphite electrodes depends on the Li salt used and, even though cycling is possible with most salts, lithium difluoro-oxalato borate (LiDFOB) is especially interesting for graphite operation. LiDFOB electrolytes are conductive at room temperature (*ca.* 6 mS cm⁻¹) with an anodic stability slightly below 5 V vs. Li/Li⁺ on particulate carbon black electrodes. In addition, it allows cycling graphite electrodes with steady capacity and high coulombic efficiency without any additive. The testing of graphite electrodes in half-cells is, however, problematic with SL:DMC mixtures and, by switching the Li metal counter electrode for LiFePO₄, the graphite electrode achieves better practical performance in terms of rate capability.

1. Introduction

Current lithium-ion batteries (LIBs) electrolytes are mostly made of lithium hexafluorophosphate (LiPF₆) dissolved in mixtures of ethylene carbonate (EC) and linear alkyl carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethylmethyl carbonate (EMC) [1–3]. The use of EC was once dictated by the use of graphite electrodes, for which EC possesses excellent Solid Electrolyte Interphase (SEI) [4,5] forming ability. More recently, SEI additives, such as vinylene carbonate (VC) or fluoroethylene carbonate (FEC) have allowed the operation of graphite anodes even when mixed with electrolytes with poor SEI forming ability such as propylene carbonate (PC) [6], alkyl nitriles

[7], linear sulfones [8] or TFSI-based ionic liquids [9]. However, for best graphite performance, mixtures of EC and linear alkyl carbonates are still mainly used, in combination with additives.

In the last years, many attempts have been made to increase further the energy density of LIBs and cathode materials operating above 4.5 V versus Li/Li⁺ have been proposed in the late 90's, such as LiNi_{0.5}Mn_{1.5}O₄ [10,11], LiCoPO₄ [12,13] or, more recently, LiCoPO₄F [14,15]. However, the so-called '5 V' LIB is still not a reality, due to the failure of EC/linear alkyl carbonate mixtures to operate above 4.3 V. Indeed, if the electronic structure (HOMO) of each single electrolyte components plays a role in the anodic stability of electrolyte mixtures [16], the presence of Li salt [17] often leads to inferior anodic stabilities

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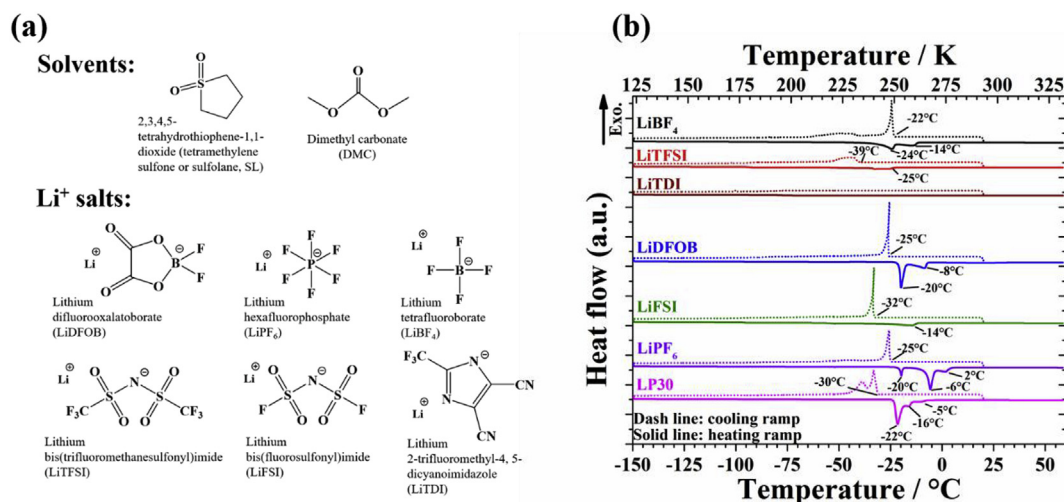


Fig. 1. (a) Structural formulae and acronyms of solvents and lithium salts used, (b) DSC traces of the 1 M SL:DMC (1:1, wt.) electrolytes and LP30. First cooling ($10\text{ }^{\circ}\text{C min}^{-1}$) and last heating ($5\text{ }^{\circ}\text{C min}^{-1}$) ramps shown.

than those derived from HOMO calculation for the solvent alone. In particular, it explains why EC, despite having among the lowest calculated HOMO energy of all alkyl carbonate solvents, leads to electrolytes with lower practical anodic stabilities as compared to its intrinsic stability. In fact, Borodin et al. noted the detrimental effects of BF_4 , PF_6 and $\text{B}(\text{CN})_4$ on alkyl carbonate solvents, while, on the other hand, they have less influence of sulfone-based solvents such as sulfolane (SL) (Fig. 1a), which explains their better performance at high voltage [18,19]. According to these studies, however, DMC anodic stability was found to be also significantly lowered by the presence of Li salts, whereas mixtures of SL and other solvents, such as EMC [20] or ethyl acetate [21] are reported having similar anodic stability as SL alone. The reason would be linked to the double layer structure where the electro-oxidation occurs [22], which also explains the stronger decomposition of EC vs. DMC in EC/DMC mixtures [23].

SL is a by-product of the oil industry, thus cheap and produced by tons [24]. Its high potential of oxidation, as well as those of linear sulfones [25], above 5 V vs. Li/Li^+ has recently attracted interest as a high voltage electrolyte solvent [26]. Moreover, concerning the practical stability in reduction (linked to the ability to form an effective SEI onto graphite and Li metal electrodes), SL was used as early as 1985 in Li metal studies [27] and a first report of a ‘high EMF’ electrochemical cell based on Li metal electrodeposited onto graphite from SL electrolytes was issued in 1971 [28]. More recently, SL has shown promising SEI forming ability on graphite at $90\text{ }^{\circ}\text{C}$ [29], which makes it a good candidate for Li-ion application, while linear alkyl sulfones necessitate SEI forming additives for graphite operation [8].

Despite these interesting properties and studies focusing on cathodes performance [30,31], only few reports deal with carbon-based electrodes [32] and even less [33] with EC-free electrolytes able to operate a full Li-ion cell including graphite. Recently, Dahn’s group reported on full Li-ion using VC and other additives in SL-based electrolytes [34] and we reported that, by use of carboxymethyl cellulose (CMC)/styrene-butadiene rubber (SBR)-based graphite anodes, efficient cycling of graphite is possible in a 1 M LiPF_6 SL:DMC (1:1, wt.) electrolyte without any SEI forming additives [35]. As it is known that the Li salt can have a strong influence on the SEI formation on graphite [36–38], we examine here the effect of various lithium salts, (shown in Fig. 1a), on the physico-chemical properties of SL:DMC-based electrolytes and assess their suitability for graphite electrode operation.

2. Experimental

Electrolytes: The commercial electrolytes LP30 (1 M LiPF_6 EC:DMC

(1:1, wt.)) and LP47 (1 M LiPF_6 EC:DEC (3:7, wt.)) were purchased from BASF (Selectilyte™), stored in a Mbraun glove box under argon atmosphere with O_2 and H_2O content below 1 ppm and used as received. The lithium salts were used either as received (LiBF_4 (Sigma-Aldrich, 99.99%) and LiPF_6 (Sigma-Aldrich, 99.99%)) or after drying under vacuum at $80\text{ }^{\circ}\text{C}$ for 48 h (lithium difluoro(oxalato)borate (LiDFOB) (Sigma-Aldrich) or at $90\text{ }^{\circ}\text{C}$ for 48 h (lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (3M, 99.99%), lithium bis (fluorosulfonyl)imide (LiFSI) (99%, Provisco CZ), lithium 2-trifluoromethyl-4,5-dicyanoimidazole (LiTfDI) (Solvionic, 99%)). DMC (BASF, Selectilyte™) was used as received and SL (Sigma-Aldrich, 99%) was distilled under vacuum and dried with molecular sieves (3A) until the water content decreased below 20 ppm as determined by coulometric Karl-Fischer titration on a KF 851 Titrand (Mettler Toledo) located in a dry room (RH < 0.2% at $20\text{ }^{\circ}\text{C}$). All electrolytes were prepared by mixing the lithium salt with pre-mixed SL:DMC (1:1, wt.) in a Mbraun glove box under argon atmosphere with O_2 and H_2O content below 1 ppm. The final electrolytes all had water content below 40 ppm as determined by Karl-Fischer titration.

Electrodes: Graphite electrode composition: 96/2/2 (graphite (SLP30, Timcal)/CMC/SBR), total mass loading: 7.5 mg cm^{-2} . LFP electrode: 90.5/4.5/5 (LFP/PVdF/Carbon black), total mass loading: 17 mg cm^{-2} . Carbon black electrodes composition: 90/10 (Super C65 (IMERYS)/PVdF (Solef 5130, Solvay)). The active mass loading of the electrodes was ca. 1 mg cm^{-2} . Graphite, LFP and carbon black electrodes (12 mm \varnothing) were punched and dried in vacuum at $110\text{ }^{\circ}\text{C}$ for 48 h. Ni foil (99.99%, Schlenk), previously washed with ethanol, was punched into electrodes (12 mm \varnothing) and dried in vacuum at $80\text{ }^{\circ}\text{C}$ for 24 h before the electrochemical stability window test. Pt electrodes (1 mm \varnothing , eDAQ) were polished and washed with acetone and dried under vacuum for 1 h before each voltamperometry scan.

Thermal analysis: Differential scanning calorimetry (DSC) was performed on a Q2000 DSC (TA Instrument) under helium flow. Aluminum hermetic (TZERO™) pans were sealed in a glove box with H_2O and O_2 below 1 ppm. The samples were annealed at low temperature to favor crystallization: At $10\text{ }^{\circ}\text{C min}^{-1}$, a cooling ramp from $20\text{ }^{\circ}\text{C}$ to $-150\text{ }^{\circ}\text{C}$ was followed by a heating ramp to $-30\text{ }^{\circ}\text{C}$ with a 15 min isotherm and by a ramp down to $-150\text{ }^{\circ}\text{C}$. The final heating ramp to $60\text{ }^{\circ}\text{C}$ was then done at $5\text{ }^{\circ}\text{C min}^{-1}$.

Viscosity and density: Viscosity and density were measured using a Stabinger Viscometer™ (Anton Paar, SVM™ 3001) located in a dry room (RH < 0.2% at $20\text{ }^{\circ}\text{C}$).

Electrochemical tests: Linear sweep voltammetries were performed with a VMP3 potentiostat (BioLogic) in three electrode

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