



Short communication

Enabling steady graphite anode cycling with high voltage, additive-free, sulfolane-based electrolyte: Role of the binder

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HIGHLIGHTS

- 1 M LiPF₆ SL/DMC is evaluated as electrolyte for Li-ion battery without additive.
- CMC-SBR-based graphite electrodes allows for good electrochemical performance.
- Full Li-ion cells (Graphite/NMC) can be operated at 4.5 V without additive.

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ABSTRACT

We demonstrate here the possibility of operating both high voltage spinel and high mass loading graphite electrodes in a 1 M LiPF₆ in SL/DMC (1/1, wt/wt) electrolyte without the use of additive. A crucial point for practical graphite electrode operation is the use of the cheaper and environmentally friendly carboxymethyl cellulose (CMC)/styrene-butadiene rubber (SBR) combination instead of the PVDF-based electrodes used in most laboratory studies. With this type of anode we also show the operation of a full Li-ion cell operating at 4.5 V without any additive and show that most of the Li⁺ transport limitation observed in half-cells are in fact due to the Li metal counter electrode. The anode binder influence is to be considered for the development of high voltage electrolytes lacking good intrinsic SEI building properties, as the anode binder does not affect cathode performance, contrary to most additives. It opens the route for further improvement by use of SEI forming additives (molecular and salts), keeping in mind the requirement for the cathode.

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1. Introduction

In order to push further the energy density of Li-ion batteries, high voltage cathodes operating above 4.5 V such as LiNi_{0.5}Mn_{1.5}O₄ [1] or LiCoPO₄ [2] have been proposed since the late 90's. However, these materials are still not implemented in commercial Li-ion batteries, due to the lack of electrolyte able to operate both a graphite anode, necessary for high energy density batteries, and a high voltage cathode. This is linked to the need to build an efficient

solid electrolyte interphase (SEI) [3,4] at the surface of graphite for allowing its operation, which has been first achieved by using ethylene carbonate (EC) [5].

In fact, additives such as vinylene carbonate (VC) or fluoroethylene carbonate FEC [6,7] or Li salts, such as lithium bis(oxalate) borate, LiBOB [8], lithium difluoro(oxalate)borate LiDFOB [9] or lithium bis(fluororsulfonyl)imide LiFSI [10,11] can participate in the SEI formation and, in principle, overcome the use of EC. However, it is still a staple for most electrolytes, due to its excellent SEI forming ability and most Li-ion batteries thus use additives combined with EC. Unfortunately, EC is seen as the main weakness for anodic stability and multiple attempts to replace it have been made, in view of operating high voltage cathodes, be it by fluorinated

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molecules [12,13], dinitriles [14] or sulfones [15,16].

Among its potential substitutes, tetramethylene sulfone (sulfolane, SL, see developed formula in Fig. 1), was first reported in 1971 in a 'high EMF' graphite anode cell [17] and later in the 80's for Li metal cells, either as self-standing solvent or in mixtures with ether solvents [18,19], hinting for reasonable SEI formation at low potential. Since then, it has been used, alone or mixed with linear carbonates, for operating high voltage cathodes [2,20]. Furthermore, theoretical studies have recently explained why sulfolane (and alkyl-sulfone in general)-based electrolytes are more stable in oxidation than carbonate-based electrolytes and why this stability would extend to its mixtures with low dielectric solvents such as linear carbonates [21–23], making these electrolytes viable candidates for high voltage Li-ion batteries.

However, only few studies can be found dealing with graphite electrode operation in SL-based electrolytes, and most report only on limited cycling [24–30]. In fact, it is often used in combination with SEI forming agents, such as additives, co-solvents or Li salts and, to the best of our knowledge, no study ever showed practical performance of a graphite electrode in a sulfolane-based electrolyte (namely: high efficiency combined with cycling stability) able, at the same time, to operate up to 4.8 V. This is most likely due to the presence of unsuitable additives or Li salts. In fact, in some cases, graphite and LiFePO_4 are operated in SL-based electrolytes [24,25,27], while electrolytes without additives (or SEI forming salts) seem to allow the operation of $\text{Li}_5\text{Ti}_7\text{O}_{12}$ and high voltage cathodes [20]. Among the studied electrolytes, Dahn and coll. reported VC containing SL/ethyl methyl carbonate (EMC) electrolytes able to operate NMC cathodes at 4.5 V in full Li-ion cells [28,29], but it should be emphasized that VC has an anodic stability around 4.6 V itself and that its use above this potential is questionable [31]. Some sulfonyl isocyanate added in 1 M LiDFOB solution of SL also allowed for decent graphite cycling, but again, cathode operation was only limited to NMC up to 4.5 V [26].

Thus, we report here on a 1 M LiPF_6 SL/DMC (1/1, wt/wt) electrolyte and the operation of both a high voltage spinel and graphite electrode in the same electrolyte without the use of any additive. Instead, we compare the influence of the graphite electrode processing in allowing stable cycling of the electrolyte. Indeed, most commercial anodes are water processed using carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) latex as binders, which is a cheaper and environmentally friendly alternative to N-

methyl-2-pyrrolidone (NMP) processed PVDF-electrodes. However, most studies only use PVDF laboratory-made electrodes. Thus, we compare here the performance of thin PVDF-based electrodes to a more realistic, high mass loading, CMC-SBR electrode and verify the compatibility of the electrolyte in a full Li-ion operated at 4.5 V as well.

2. Experimental

2.1. Electrolyte preparation

SL (Aldrich, 99%) was distilled under vacuum and dried on molecular sieve at 50 °C until its water content decreased below 20 ppm as determined by coulometric Karl-Fischer titration (KF 851 Titrando, Mettler Toledo). Dimethyl carbonate (DMC) and LiPF_6 (BASF, Selectilyte™) were used as received. The electrolyte was prepared and stored in a Mbraun glove box under argon with O_2 and H_2O content below 0.5 ppm.

2.2. Electrode preparation

The $\text{LiNi}_{0.43}\text{Mn}_{1.5}\text{Cr}_{0.07}\text{O}_4$ electrodes were prepared by casting a NMP slurry with a solid weight ratio of 85/10/5 ($\text{LiNi}_{0.43}\text{Mn}_{1.5}\text{Cr}_{0.07}\text{O}_4$ (Primet Precision Material)/SuperP (Cabot)/PVDF (Solef 5130, SOLVAY)). Active material (AM) mass loading: c.a. 2.6 mg cm^{-2} . The CMC/SBR graphite electrodes were casted using an aqueous slurry with a solid weight ratio of 95/1/2/2 (Graphite (SLX30, Imerys)/SuperC45 (Imerys)/CMC (DOW Wolff CRT30000PA)/SBR (TRD102A, JSR micro)). The CMC has a degree of substitution of c.a. 0.85 and a viscosity at 1% in H_2O between 3000 and 4000 mPa s. AM mass loading: c.a. 6.0 mg cm^{-2} , Thickness: c.a. 70 μm . The PVDF-based graphite electrodes were casted using a NMP slurry, with a 93/2/5 mass ratio (graphite (MAGE, Hitachi chemicals)/SuperC45 (Imerys)/PVDF (5130, Solvay)). AM mass loading: c.a. 3.2 mg cm^{-2} . Thickness: c.a. 53 μm . $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ electrodes were bought from Custom Cells, with mass loading c.a. 14.5 mg cm^{-2} and 86% of active material.

2.3. Electrochemical testing

Voltamperometries were done on a VMP potentiostat (BioLogic) in three electrode Swagelok™ cells with Li counter and reference electrodes (Rockwood lithium) at room temperature (c.a. 21–23 °C). Cycling was done on a Maccor 4300 battery cycler in three electrode Swagelok™ cells placed in a temperature-controlled chamber at 20 °C. Conductivity was measured using a Biologic MCS10, impedance-based conductimeter, from 60 °C to –40 °C with 30 min stabilization every 5 °C.

3. Results and discussion

3.1. Physico-chemical properties of the electrolyte

Fig. 1 shows the electrochemical properties of the electrolyte. With a conductivity of 6.1 mS cm^{-1} at 20 °C, the conductivity is in the same range as commercial Li-ion electrolytes such as LP47 (1 M LiPF_6 EC/DEC 3/7, σ (20 °C) = 4.6 mS cm^{-1}). It is lower than that of LP30 (1 M LiPF_6 , EC/DMC 1/1, σ (20 °C) = 10.1 mS cm^{-1}) as an effect of the higher viscosity and lower dielectric constant of SL as compared to EC. In addition, no crystallization was observed down to –20 °C. While the phase behavior is somehow complicated, given the ternary mixture considered, with 3 different phases forming when going down to –140 °C, the electrolyte, in these conditions, starts crystallizing between –20 °C and –25 °C and fully melts below 0 °C, as seen with the hysteresis between cooling

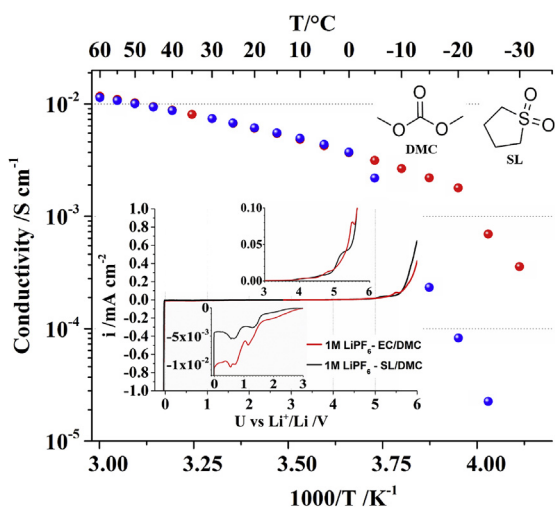


Fig. 1. Arrhenius conductivity plot of the 1 M LiPF_6 SL/DMC 1/1 (wt/wt) electrolyte. (Insert): Voltamperogram at 0.1 mV s^{-1} on Ni (cathodic scan) and Pt (anodic scan) of 1 M LiPF_6 in SL/DMC 1/1 (wt/wt) and EC/DMC 1/1 (wt/wt). RE and CE: Li.

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