



On the role of cyclic unsaturated additives on the behaviour of lithium metal electrodes in ionic liquid electrolytes

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ABSTRACT

Three cyclic vinyl based additives, based respectively on oxygen, sulphur and fluorine, are tested for their ability to improve the cycling of lithium in a hostile ionic liquid medium. Oxygen based vinylene carbonate is found to offer the best protection of the lithium metal whilst allowing very consistent lithium cycling to occur. The vinylene carbonate based system under study is, however, imperfect. Lithium metal is deposited in a dendritic morphology, and vinylene carbonate is rapidly consumed during lithium cycling if it is present in a small quantity. Our results suggest that ionic liquid systems critically relying on a small amount of additive to protect a lithium electrode are not viable for long cycle life secondary batteries. It is suggested that an ionic liquid which itself is lithium metal compatible be used instead.

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1. Introduction

In the development of lithium metal batteries, ionic liquid (IL) based electrolytes are attracting much attention from researchers [1–15]. Currently, there are no commercial rechargeable lithium metal batteries, however, it is envisioned that such batteries may consist of a low viscosity aprotic ionic liquid, a dissolved lithium salt, and perhaps an additive which enables the goal of better lithium cycling to be achieved [2,5,12,16,17]. The ILs typically investigated for battery applications have important properties that are advantageous for the development of safe lithium battery technology: non-flammability and negligible vapour pressure.

Reversible electrochemical plating and stripping (cycling) of lithium has been previously demonstrated in numerous ILs [4,7,10,12,14,16–21], however, this is frequently complicated by the electrochemical instability of the IL moieties at Li⁺ reduction potentials. All the systems reported rely on the formation of a solid electrolyte interphase (SEI) to protect the IL from the reactive lithium metal surface. Hence additives are of interest as they can potentially form quality SEIs in ILs which on their own may form inadequate SEIs. Additionally, electrolyte additives allow the

formation and assessment of SEIs without the need for synthesising a vast range of ILs.

Addition of a lithium salt, LiBF₄, to 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) allows the charging of a lithium metal electrode to Li⁺ reducing potentials, as first shown by Fuller et al. [16]. Addition of an appropriate additive to IL electrolytes has been shown to facilitate or improve lithium cycling while protecting the IL from reduction at the electrode [2,5,12,15,16]. Through the use of appropriate additives a relatively cheap, highly fluid IL, such as EMImBF₄, could potentially find use as an electrolyte in lithium metal batteries.

Since EMImBF₄ is known to be reductively unstable at the potentials required for Li⁺ reduction [16], this system is an excellent choice to study the role of additives on SEI formation for lithium cycling in ILs. SEI formation at a graphite anode, such as those used in lithium ion batteries, has previously been studied in systems where vinylene carbonate (VC) was present as an additive [16,24], and a battery incorporating a conducting polymer type cathode has been cycled using an EMImBF₄-VC electrolyte [17].

This paper reports on our studies of lithium cycling and SEI formation in EMImBF₄ using VC and the similarly vinyl based structures vinylene trithiocarbonate (VTTC) and 3,3,4,4,5,5-hexafluorocyclopent-1-ene (HFCp) as shown in Fig. 1. The three additives each have a C=C bond, potentially allowing for polymerisation, whilst having differing elemental composition throughout the rest of the molecule. They can also potentially indicate whether O, S or F based functional groups are desirable in the SEI layer. We

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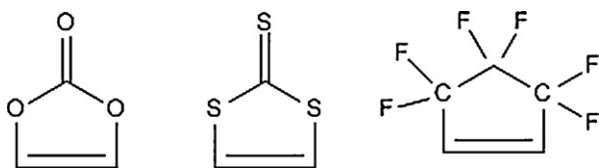


Fig. 1. Additives studied in this work. Left: VC; middle: VTTC; right: HFCp.

also present results of coin cell testing of the Li/EMImBF₄/VC system and report on the cycling behaviour and possible causes of cell failure.

2. Experimental

VC (Aldrich, 99%) was purified by distillation at 165 °C at atmospheric pressure prior to use. VTTC (Fluka, 99%), HFCp (Apollo Scientific, 97%), and EMIm BF₄ (Solvent Innovation GmbH, 98%) were used as received. Water content was measured by a Karl Fischer auto-titration (Metrohm). LiBF₄ (Stella Corp) was dried at 120 °C under vacuum for 24 h prior to use.

For cyclic voltammetric (50 mV s⁻¹) studies, a 500 μm Pt working electrode (electrochemical surface area determined to be 0.0025 cm²), Pt wire counter electrode, and Ag|Ag⁺ reference electrode were employed. The reference electrode consisted of a silver wire immersed in a solution of 10 mM silver triflate in N-methyl, N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide and separated from the main solution by a glass frit as reported by Snook et al. [18]. Potentiostatic control was provided by an Autolab pgstat302 (Eco Chimie, Netherlands) controlled with GPES (Version 4.9.005) software. Lithium metal symmetrical coin cells (CR2032) were assembled in an Argon filled glove box with each electrode being a 10 mm diameter lithium metal disk, the separator was Separion[®] (Evonik Industries AG, 30 μm thick, dried at 100 °C

for 24 h), standard internal stainless steel spacers and springs provided internal pressure. A series 4000 Maccor battery tester was used to cycle symmetrical cells at a current density of 0.16 mA/cm², the cycling time was 32 min per cycle (16 min “charge” and 16 min “discharge”), approximately equal to plating and stripping 0.15 C of lithium. Impedance spectroscopy analysis was performed using a Solartron 1255B frequency response analyser over a frequency range of 1 MHz to 0.1 Hz. All measurements were performed at room temperature, and all potentials are reported referenced to the Ag|Ag⁺ couple.

3. Results and discussion

3.1. Cyclic voltammetry

The characteristics of lithium cycling were investigated by cyclic voltammetry for each of the three additives. Cyclic voltammograms of the Pt electrode in EMImBF₄ with and without additives are shown in Fig. 2. In the absence of additives (including LiBF₄), the reductive limit of EMImBF₄ is -2.6 V vs. Ag/Ag⁺, as shown in Fig. 2(a), which also shows that in the presence of LiBF₄ (0.5 mol/kg) the limit is extended to approximately -3.7 V vs. Ag/Ag⁺. The reductive process however is not mirrored by a subsequent stripping process on the reverse scan. It appears that the dominant reductive process therefore is breakdown of the IL, consistent with the observations of Egashira et al. [2].

Fig. 2(b) shows that on the addition of VTTC to the lithium-doped electrolyte, a new reduction process is observed at -2.2 V. This process was found to be dependent on the concentration of VTTC (not shown), suggesting that it is due to the reduction of VTTC within the electrolyte. Possible lithium reduction is observed at -3.7 V vs. Ag/Ag⁺, however no corresponding Li stripping peak is noted and reduction currents diminish over the course of five cycles (not

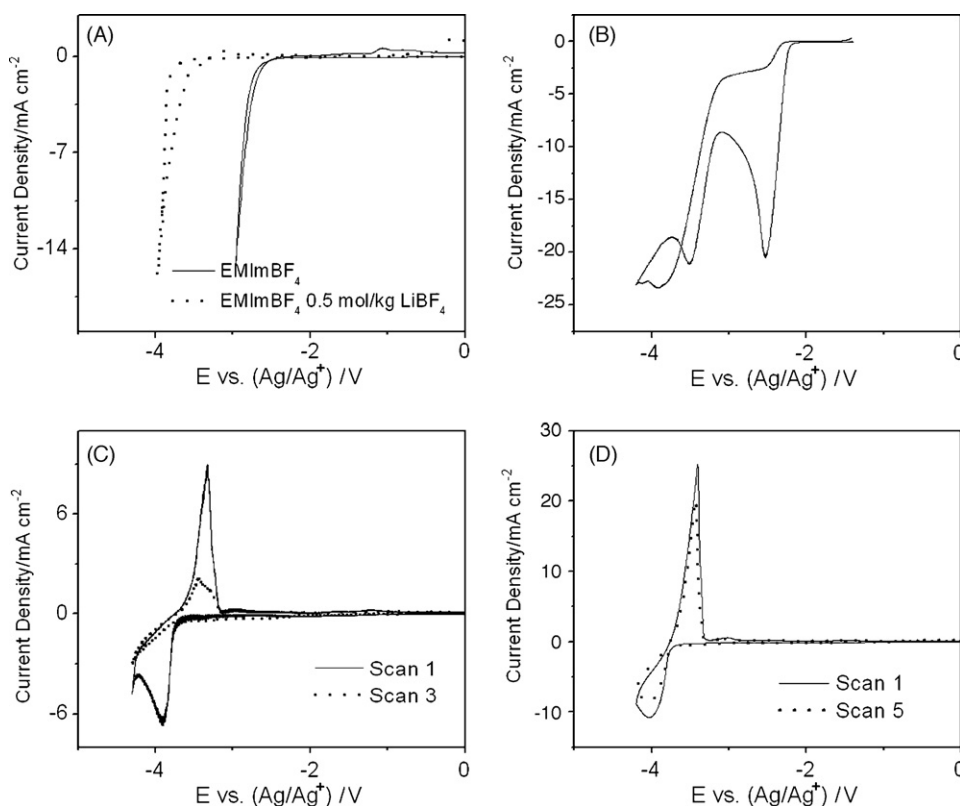


Fig. 2. Cyclic voltammograms of (a) neat EMImBF₄ and EMImBF₄ 0.5 mol/kg LiBF₄, (b) EMImBF₄ 0.5 mol/kg LiBF₄ 5 wt% VTTC, (c) EMImBF₄ 0.5 mol/kg LiBF₄ 10 wt% HFCp and (d) EMImBF₄ 0.5 mol/kg LiBF₄ 10 wt% VC.

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