



Comparative study of imide-based Li salts as electrolyte additives for Li-ion batteries

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HIGHLIGHTS

- Imide-based salts (LiTFSI, LiFSI, and LiFTFSI) as additives in carbonate-based electrolyte.
- Effect of imide salts on the SEI formed on graphite.
- Incorporation of imide salts in the graphite's SEI.
- Effect of imide salts on the 1st cycle coulombic efficiency in graphite/LFP cells.
- Addition of LiTFSI results in the capacity retention above 98% even after 600 cycles.

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ABSTRACT

Herein, we report the results of a detailed study on the use of different Li imide salts (LiTFSI, LiFSI, and LiFTFSI) as electrolyte additives for lithium-ion batteries. The introduction of lithium imide salts in the electrolyte is shown to considerably improve the first cycle coulombic efficiency and the long-term cycling stability of graphite/LiFePO₄ cells. Using LiTFSI, a capacity fading of only ~2% occurred over 600 cycles while the control cell with the state-of-the-art additive (VC) lost ~20% of the initial capacity at 20 °C. The results of the XPS and impedance spectroscopy measurements of graphite electrodes show that, after the formation cycle, the SEI obtained in the presence of imide salts is thinner, contains more LiF and is less resistive than that obtained using VC. Despite the beneficial effect of the imide salts on the lithium-ion cell performance, a slightly reduced thermal stability of the SEI is observed.

1. Introduction

Lithium-ion batteries (LIBs) are nowadays largely used in portable electronics and are quickly penetrating the automotive and stationary energy storage sectors. Indeed, LIBs offer higher specific energies (150–200 Wh/kg) and energy efficiencies with respect to other rechargeable batteries, e.g., Ni-MH or lead-acid batteries [1,2].

The graphite anode used in commercial LIBs can reversibly deliver about 370 mAh g⁻¹ at an operating voltage close to that of metallic lithium. One of the key factors ensuring the prolonged cycle life of the anode is the formation of the solid electrolyte interphase (SEI) as a consequence of the electrolyte reduction reaction during the first

lithiation (charge of the Li-ion cell) [3]. Ideally, being electronically insulating, the SEI prevents further electrolyte decomposition, while allowing fast Li⁺ ion conduction [4,5]. However, the anode's volume change during Li⁺ insertion and de-insertion process causes the exposure of fresh graphite surface to the electrolyte. This generates a continuous growth of the SEI, which implies Li⁺ consumption and increase of cell resistance leading to capacity fading upon cycling. Therefore, it is crucial to obtain an SEI with appropriate mechanical, chemical and thermal stabilities, electronic resistance, ionic conductivity and thickness during the formation cycle. These characteristics are determined principally by the electrolyte composition. The “state-of-the-art” electrolytes are mixtures of cyclic and linear organic

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carbonates dissolving lithium hexafluorophosphate (LiPF₆). Although this salt suffers from poor thermal and chemical stabilities, it grants SEI formation, high ionic conductivity, relatively wide electrochemical stability window (ESW) and Al current collector passivation [6,7].

Many efforts have been devoted to link the SEI characteristics to its composition. It is generally agreed that the SEI consists of two different layers. The inner layer, in contact with the graphite surface, is dominated by insoluble inorganic components, e.g., LiF, Li₂CO₃ and Li₂O [8,9], i.e., purely ionic conductors, which prevent further electrolyte decomposition. The outer layer instead is more porous and composed of organic species, e.g., ROLi and ROCO₂Li [5], which may be partly soluble in the electrolyte leading to continuous modification of the layer composition and morphology [4].

The SEI composition can be further tuned by introducing additives (usually less than 10% either in weight or in volume) in the electrolyte [6]. Reductive-type additives are decomposed at potentials higher than that of the electrolyte solvent(s) and salt(s). The widely used vinylene carbonate (VC) belongs to this category, forming a polymeric surface layer upon reduction at about 1.0 V, which enhances the cycling stability and the safety of the cell [10,11]. On the other hand, reaction-type additives are not always electrochemically reduced. Instead, they can react with electrolyte decomposition products such as radical anions, thus, stabilizing the SEI [6,12].

Lithium imide salts, e.g., lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium bis(fluorosulfonyl)imide (LiFSI), have been proposed as alternatives to LiPF₆ due to their lower sensitivity to hydrolysis and their increased thermal and electrochemical stabilities [7,13–17]. However, being anodically more stable than LiPF₆, their use requires the presence of fluorinated electrolytes [18] or LiPF₆ as a co-salt [19] to avoid the anodic dissolution of aluminum current collector.

Dahn et al. [20] investigated the use of LiTFSI and VC as additives in different Li-ion cells by careful and precise measurement of the coulombic efficiency and end-point slippage rate. They found that the addition of LiTFSI (2–4 wt%) does not have any impact on the cycle life, but rather on the reduction of the cell impedance (especially in combination with VC), and thus, on improving the cells rate capability and capacity retention at high rates. These authors suggested LiTFSI to change the electrode surface film composition, leading to a thinner but more protective film [15]. The same group reported that the combination of LiFSI with VC can reduce the gas formation and the voltage drop at 60 °C [21]. However, presently it is not fully understood how low concentrations of Li-imide salts in the electrolyte affect the SEI composition.

Herein, we elucidate the impact of Li-imide salt addition (2 wt%) on the electrochemical performance of graphite electrodes. Three salts with different anions have been selected, namely LiTFSI, LiFSI and lithium fluorosulfonyl(trifluoromethanesulfonyl)imide (LiFTFSI), whose chemical structures are shown in Fig. S1 of the Supporting Information. The electrochemical characteristics of half and full cells, as well as the surface composition of the graphite electrodes, are compared with those of electrodes cycled using the pure and VC-added electrolytes.

2. Experimental

2.1. Electrodes and electrolytes

The calendered graphite and LiFePO₄ (LFP) electrodes were kindly provided by CEA-LITEN. The graphite electrodes, comprising 95% of active material and calendered to a porosity of 39%, had an average loading of 8 mg cm⁻² (~2.75 mAh cm⁻²). The LFP electrodes with 90% of active material and 35% porosity had an average loading of 17.5 mg cm⁻² (~2.5 mAh cm⁻²), determining an anode/cathode capacity ratio of 1.1 for the graphite/LFP Li-ion cells. The electrodes for the electrochemical stability window test comprised 80% of CMC binder and 20% of Super C45 conductive carbon, with an average loading of 5 mg cm⁻².

1 M LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC) 1:1 (LP30, UBE), and VC (Solvionic) were used as received. LiTFSI (> 99% battery grade, 3M), LiFSI and LiFTFSI (both from Provisco CS Ltd.) were pre-dried under rotary vane pump vacuum for 12 h and subsequently dried under the turbomolecular pump (< 10⁻⁷ mbar) for at least 20 h. All electrolytes formulations were prepared by adding 2 wt% of each additive into the pristine electrolyte in an argon-filled glove-box (O₂ and H₂O levels below 0.1 ppm), followed by mixing prior to use.

2.2. Electrochemical tests

Coin cells (type 2032) were assembled in an argon filled glove-box by sandwiching a glass fiber separator (Whatman GF/D) soaked with 100 µL of electrolyte between graphite or LFP electrodes (1.13 cm²) and Li electrode (1.54 cm², Rockwood Lithium). Coin cells were used also for the assembly of the graphite/LFP Li-ion cells.

All cycling tests were conducted by storing the cells inside a climatic chamber (Binder) at 20 ± 1 °C. The cells were left at open circuit voltage (OCV) for 16 h (half-cells) or 24 h (Li-ion cells) prior to the measurements, which were conducted using a Maccor Series 4300 Battery Tester. The applied cycling protocol for half-cells is illustrated in Table S1 of the Supporting Information. The cycling rate of 1C corresponded to specific currents of 372 mA g⁻¹ and 170 mA g⁻¹ for graphite and LFP electrodes, respectively.

The Li-ion cells were initially charged/discharged at 20 ± 1 °C at C/20, then C/2, and, finally, at 1C rates (cathode-limited cells, i.e., 1C equals 170 mAh g⁻¹). After 10 cycles at 1C rate some cells were placed at 40 ± 1 °C and thermally equilibrated for 6 h. Then these cells were cycled at C/2 for 3 cycles, followed by long-term cycling at 1C.

The electrolytes' electrochemical stability window (ESW) was measured using three-electrode Swagelok cells with Pt (0.0078 cm²) or carbon (1.13 cm²) as working electrodes and Li metal as counter and reference electrode. The cells were characterized by linear sweep voltammetry using the VMP-3 potentiostat (BioLogic) from OCV to either -1.0 V or 6.0 V (using a fresh cell for each cathodic or anodic scan) with a scanning rate of 0.1 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) measurements were conducted using specially designed cells (ECC-PAT-Core, EL-CELL). The cell assembly procedure and scheme are described in detail in Fig. S2 of the Supporting Information. The cells were subjected to a rest period (12 h at 20 °C) prior to cycling of the graphite electrode at a rate of C/20 (using a Modulab, Solartron). The cycle was interrupted at different cell potentials (0.7, 0.5, and 0.01 V vs Li/Li⁺ upon lithiation) and the cell was let to rest for 2 h at open circuit potential (OCP) prior to impedance measurements made using an AC amplitude of 5 mV in the frequency range of 10 kHz–0.1 Hz.

2.3. Differential scanning calorimetry (DSC) measurements

Electrodes from Li/graphite coin cells (type 2032) were used in this study. The graphite electrodes were subjected to a single lithiation at C/20 down to 0.01 V. The cells were then carefully disassembled in a glove-box. The lithiated graphite (Li_xC₆) powders, obtained by scratching the active material from the current collectors, were directly placed in closed, high-pressure DSC pans. The experiments were performed with a Discovery DSC (TA Instruments) and conducted by heating the sample at 5 K min⁻¹ up to 300 °C under constant helium flow.

2.4. X-ray photoelectron spectroscopy (XPS) conditions

To analyze the SEI composition, Li/graphite half-cells were subjected to one lithiation-delithiation cycle as described in Table S1. To investigate the SEI evolution upon cycling, some cells were exposed to additional 50 cycles at C/2, also including the constant voltage step

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