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LiFSI *vs.* $LiPF_6$ electrolytes in contact with lithiated graphite: Comparing thermal stabilities and identification of specific SEI-reinforcing additives

Gebrekidan Gebresilassie Eshetu[a,c], Sylvie Grugeon[a,c], Grégory Gachot[a,c], David Mathiron[b], Michel Armand[a], Stephane Laruelle[a,c,*]

[a] *Laboratoire de Réactivité et de Chimie des Solides, UMR CNRS 7314, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens, France*
[b] *Plate-Forme Analytique, Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens, France*
[c] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*

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ABSTRACT

Lithium bis(fluorosulfonyl) imide (LiFSI) is regarded as an alternative to the classical $LiPF_6$ salt in today's $LiFePO_4$/graphite-based Li-ion batteries electrolyte owing to its slightly higher conductivity and lower fluorine content. In an attempt to better evaluate the safety issues, here we report the comparative study of the LiFSI and $LiPF_6$ based electrolyte/lithiated graphite interface thermal behavior. DSC measurements with LiFSI-based electrolyte reveal a sharp exotherm with large heat release though at higher onset and peak temperatures compared to $LiPF_6$-based electrolyte. With the help of GC/MS, ^{19}F NMR and ESI-HRMS analyses, we assume that this highly energetic peak around 200 °C, which is dependant upon the lithium content, is mainly related to electrochemical reduction of FSI^- anion. In a strategy to limit the probability and damage of thermal runaway event, electrolyte additives such as vinylene carbonate (VC), fluoro ethylene carbonate (FEC), di-isocyanato hexane (DIH) and toluene di-isocyanate (TDI) have been investigated and shown to significantly lower the energy associated with the exothermic phenomenon.

1. Introduction

The quest for the use of green energies for large-scale applications such as in the electro mobility, renewable or dispersed energy storage, makes high energy density lithium–ion technology of choice. Though it has conquered the portable electronics market successfully, for most large conventional Li-ion cells use, safety has been found to be the most critical barrier for its emergence into this market [1–4]. Hence, the success of this technology will rely on a careful evaluation of its safety and an *ad hoc* choice of battery components such as electrolyte salts and solvents, which play a crucial role with respect to safety and proper functioning, stabilizing interfacial reactions.

The classical electrolyte consists of $LiPF_6$ salt dissolved in carbonates solvents. Thermal instability, moisture sensitivity, and release of HF *via* hydrolysis of PF_6^- with protic species suggest a priority for the replacement of $LiPF_6$ with new solutes with improved thermal, chemical and/or electrochemical properties [5–19,27]. Thereby, over the past two decades, great efforts have been made in hunting for such compounds and lithium imide salts have been found to be first-rate alternatives [20–23]. $Li[(CF_3SO_2)_2N]$ (LiTFSI) has been known for its conductivity and stability, but forms a stable soluble Al salt and thus does not protect the aluminum current collector above 3.5V. LiTFSI is used in Li-metal polymer batteries where corrosion is not a problem; with liquid solvents as an additive to $LiPF_6$, or the only solute when the current collector is not Al^0 but graphite foil [24]. Within the imide family, there is now a rapidly growing interest for bis(fluorosulfonyl) imide, $Li[(FSO_2)_2N]$ (LiFSI) to be used in liquid electrolyte owing to well-balanced properties such as absence of release of HF, low viscosity and high conductivity, high-rate and excellent low temperature performances [22,25], storage characteristics at both high temperature and fully charged states. However, despite all these intrinsic worthy features, there have been concerns regarding first, its tendency to allow aluminum current collector corrosion beyond 3.8 V *vs.* Li^+/Li^0 [21], though less pronounced than LiTFSI; hence this property limits the choice of positive active material, $LiFePO_4$ (-LFP-) being a suitable candidate. The other critical concern regards its thermal stability [22,26,28,29]; Zaghib et al. [29] studied the thermal response of lithiated graphite in the presence of different salts such as $LiPF_6$, $LiBF_4$, LiTFSI, LiBETI and LiFSI using accelerated rate calorimetry (ARC). In this study, although the onset temperature of LiFSI based electrolyte (~130 °C) was found to be higher than those of other salts, the self-heating rate of LiFSI was found

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[*] Corresponding author. Tel.: +33 122827585; fax: +33 122827585.
E-mail address: stephane.laruelle@u-picardie.fr (S. Laruelle).

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to be the highest thus this calls for more detailed studies on the thermal behavior of the salt.

There is yet little information published about LiFSI-based carbonate electrolytes, and there is virtually no comprehensive research work available on the thermal stability of these electrolytes in contact with lithiated (charged) negative electrode materials. Hence in the present study, we wish to report a comparative study of the thermal stability of $LiPF_6$ and LiFSI based electrolytes co-existing with lithiated graphite electrode and on some selected additives aiming at lowering the energy generated at high temperature.

2. Experimental

2.1. Materials investigated

Ethylene carbonate (EC) and dimethyl carbonate (DMC) (50/50 w/w)-based electrolytes with $LiPF_6$ and LiFSI 1 M lithium salt were investigated (named as $LiPF_6$-electrolyte and LiFSI-electrolyte respectively). Four molecules were studied as additive in LiFSI based electrolyte namely, Vinylene Carbonate (VC) from Sigma–Aldrich, Fluoro-Ethylene Carbonate (FEC) from Solvay Fluor GMBH, Toluene Diisocyanate (TDI) from Aldrich and Diisocyanato Hexane (DICH) from Alfa Aesar. Except for $LiPF_6$-electrolyte (LP30), the electrolytes were prepared inside a dry box from a high quality of lithium bis(fluorosulfonyl) imide (LiFSI) salt (Suzhou Fluolyte®) Co. Ltd. and DMC and EC Selectilyte® electrolyte solvents. LP30 and solvents were purchased from Merck. SFG6 graphite (of particle size 6.5 μm (d_{90}) and BET surface area of 17 m^2/g) and Super P carbon black, both from TIMCAL Corporation were used as anode electrode and conductivity additive materials respectively.

2.2. Cells assembling and cycling

Swagelok-type half cells composed of 90 wt.% SFG6 graphite and 10 wt.% Super P carbon black as working composite electrode (10 mg), 0.1 mL of $LiPF_6$-electrolyte and LiFSI-electrolyte (with or without additive) as electrolytes, an electrolyte-impregnated Whatman GF/D borosilicate glass fiber as separator and a lithium metal foil as counter electrode were used and assembled inside an argon-filled glove box. Once assembled, the cells were subjected to C/20 galvanostatic discharge (resulting in LiC_6) or a discharge/charge (delithiation forming Li_0C_6) at room temperature and were cycled between their OCV to 0.01 V (lower limit) and 1.5 V (upper limit) *vs.* Li^+/Li^0 respectively.

2.3. Differential scanning calorimetry (DSC) conditions

Once the cells were in discharged or charged state, they were carefully dismantled inside a dry glove box (O_2 and H_2O <0.1 ppm) and the samples recovered (studied material with its electrolyte) were directly used for DSC analysis. All the DSC experiments were conducted using a Netzsch DSC 204F1 heat flux differential calorimeter at a heating rate of 10 K/min in a temperature range of 25–500 °C under a constant argon flow of 200 mL/min. To ensure reproducibility, two DSC measurements were conducted on each sample.

2.4. GC/MS and GC/FTIR conditions

GC conditions: The loaded DSC crucibles were pierced inside the glove box before being immediately placed into a laboratory-designed stainless steel cell. This cell was introduced in a furnace heated from room temperature to final experimental temperature (80, 140 or 200 °C) at 10 °C/min then maintained at this temperature for 3 h. Then, the evolved gases were transferred to a trace GC ultra gas chromatograph (Thermo Scientific) equipped with a six-port, 2 positions valve (Valco®) and a 0.5 mL injection loop. The total duration of GC analysis was 52 min. The transfer line was maintained at 250 °C.

MS conditions: The GC was connected to an ITQ 1100 mass spectrometer. Calibrating of the mass spectrometer was done using perfluorotributylamine ionization fragments. The mass spectrometer was operated with a filament current of 250 μA and electron energy of 70 eV in the electron ionization (EI) mode and the ion source was set at 200 °C. The mass range was 10–300 u and data acquisition processed with the Xcalibur 2.0.7 software. Compounds identification and corresponding structural formulae were assigned using the National Institutes of Standards and Technology (NIST) library.

IR conditions: The GC was interfaced with a FTIR system Nicolet 6700 through a light-pipe GC/FTIR system (Thermo) equipped with a medium band liquid nitrogen cooled mercury/cadmium telluride (MCT) detector. The transfer line and light-pipe temperatures were maintained constant at 200 °C during the analyses. Real time spectra were recorded from 4000 to 650 cm^{-1} with a spectral resolution of 4 cm^{-1}. Compounds identification was assigned using the Aldrich vapour phase FTIR library.

2.5. ^{19}F NMR conditions

^{19}F NMR experiments were performed at 300 MHz using Bruker Avance-300 SB spectrometer, with trichloro-fluoro-methane $CFCl_3$ (^{19}F) as reference and Dimethyl Sulfoxide-(DMSO-d_6) as solvent. For the salt, the sample was directly dissolved in (DMSO-d_6) in argon filled dry box and then subjected to direct NMR analysis. For lithiated samples, powders from electrochemically cycled cells were recovered inside glove box and directly transferred to heating cell heated up to the specified temperatures (140 °C and 200 °C) for 3 h. Then, the powders were dissolved in DMSO, filtered before being analyzed.

2.6. IR conditions

Once the cells were in delithiated state, then opened in the Ar filled dry-box, the recovered powders were rinsed three times with DMC to eliminate residual traces of solvents and salts then dried. Fourier transform infrared (FTIR) spectra were recorded on KBr pellets using a Nicolet Avatar 370DTGS spectrometer.

3. Results and discussion

3.1. Thermal stability of LiFSI-electrolyte and $LiPF_6$-electrolyte co-existing with lithiated graphite

3.1.1. DSC measurements

While exploiting the DSC traces from the safety evaluation point of view, three parameters have been taken into consideration. The first two parameters deal with the exotherm onset and peak temperatures, which both relate to the probability for thermal runaway. The third parameter is the total heat generated which enables the comparison of electrolytes and/or electrodes in terms of their reactivity, with lower enthalpies of reaction being the safest.

Fig. 1 displays the DSC profile up to 400 °C for lithiated (LiC_6) and de-lithiated (Li_0C_6) graphite materials in presence of $LiPF_6$-electrolyte and LiFSI-electrolyte. Lithiated graphite DSC traces behave quite differently; as already found [30], LiC_6 in presence of $LiPF_6$-electrolyte (Fig. 1b) results in broad phenomena in the 130–250 °C temperature range with two predominant peaks around 145 °C and 200 °C. On the other hand, LiC_6 in LiFSI-electrolyte (Fig. 1a) presents one significant sharp exothermic peak around 200 °C preceded by a broad exotherm of weak intensity