

# Li-ion solvation in TFSI and FSI -based ionic liquid electrolytes probed by X-ray photoelectron spectroscopy

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**Abstract.** For Li-ion batteries, the Li-ion solvation in liquid electrolytes is a crucial parameter affecting directly the electrochemical cycling performance. X-ray photoelectron spectroscopy (XPS) can play an essential role for investigating the cation and anion electronic structure and monitoring the Li-ion solvation into various solvent and salt environments. In this contribution, we demonstrate the capability of conventional laboratory XPS using Al K $\alpha$  X-ray source to determine the anions solvation shell of Li<sup>+</sup> cation within the low vapour pressure and vacuum compatible ionic liquid electrolytes. 1M of LiTFSI and 1M of LiFSI salts dissolved in (EMIM<sup>+</sup>-FSI<sup>-</sup>) and (EMIM<sup>+</sup>-TFSI<sup>-</sup>) ionic liquids respectively are investigated by acquiring the F1s, N1s, C1s, S2p and Li1s core levels. The binding energy difference between the N1s component originating from the EMIM<sup>+</sup> cation and the N1s component originating from TFSI<sup>-</sup> or FSI<sup>-</sup> anions solvating the Li<sup>+</sup> confirms that both TFSI<sup>-</sup> and FSI<sup>-</sup> contribute simultaneously to the Li<sup>+</sup> solvation. Additionally, the stability of the TFSI and FSI -based ionic liquid electrolytes is carefully discussed for long X-ray exposure times.

## 1 Introduction

The continuous need for increasing the energy density, safety and electrochemical performance of Li-ion batteries (LiBs) requires an incessant development of characterization techniques capable of providing better insights into the physics and chemistry of the various parts in a battery.[1] Upon cycling, both the bulk and the surface of the electrode's components are modified with a direct impact on the battery performance. When explicitly investigating the surface and interface modifications, X-ray photoelectron spectroscopy (XPS) is routinely employed and considered to be one of the suitable characterization techniques for LiBs allowing to study the interface evolution occurring on cycled electrodes. [2, 3] The advantage of the XPS is the surface sensitivity providing direct information of the by-product species related to the electrolyte stability, in both liquid [4] and solid [5],[6],[7] -based electrolytes. Furthermore, by probing the active materials, XPS offers the possibility to identify the potential dependency of their oxidation states and redox reactions. Moreover, by using synchrotron facilities and tuning the X-ray energy source from soft to hard, a non-destructive depth profile analysis can be performed by probing deeper from the surface down to 50 nm.[8], [9] The usage of XPS in LiBs goes beyond the *ex-situ* investigation of cycled electrodes. *Operando* XPS in all-solid-state batteries can probe the electrified solid/solid interface between the active materials and solid electrolyte. This was recently demonstrated to provide valuable information concerning the (electro-)chemical and electronic properties of the interface.[10],[11] In

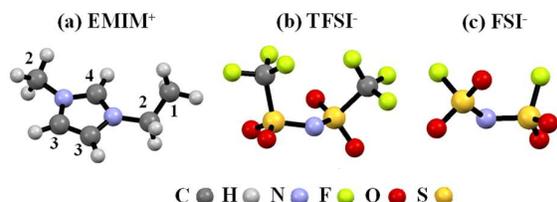
addition, probing the electrified liquid/solid [12] interface have been attempted, for instance between the ionic liquid electrolyte and the Li metal anode.[13, 14] XPS in LiBs is not limited to study the electrolyte/electrode interface, it can also be carried out to probe just the liquid electrolyte and investigate the Li-ion solvation for example in carbonate -based electrolytes as already demonstrated by our group using near ambient pressure photoemission (NAP) combined with a liquid jet.[15] Such experiment and information are very precious, as the Li-ion solvation in the LiBs' electrolyte play an important role in improving the cycling performance, by directly affecting the ionic conductivity, the stability at high or low potential and temperature, as well as the property of the solid electrolyte interphase (SEI).

In this work, conventional XPS using Al K $\alpha$  X-ray source is employed to investigate the cation and anion electronic structure and to monitor the Li-ion solvation within droplets of low vapour pressure and vacuum compatible ionic liquid electrolytes.

Ionic liquid-based electrolytes are considered as promising alternative for next generation high energy density LiBs owing to their low vapour pressure and high thermal as well as electrochemical stability. However, not all ionic liquid-based electrolytes can successfully be deployed in LiBs. For example, stable electrochemical cycling of graphite in ionic liquid electrolytes can be achieved in presence of FSI<sup>-</sup> anion originating either from the LiFSI salt or as an anion from the ionic liquid.[16] On the contrary, graphite cannot be cycled when TFSI<sup>-</sup> anion is used, unless FSI<sup>-</sup> is added in the electrolyte, despite the structural similarity between

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the anions. Intrigued about this phenomenon, we examined in this study the Li-ion solvation when both TFSI<sup>-</sup> and FSI<sup>-</sup> are present simultaneously in the electrolyte, as a salt or as anion in the ionic liquid. 1M of LiTFSI and 1M of LiFSI salts dissolved in (EMIM<sup>+</sup> - FSI<sup>-</sup>) and (EMIM<sup>+</sup> - TFSI<sup>-</sup>) ionic liquids respectively are investigated by acquiring the F1s, N1s, C1s, S2p and Li1s core levels. The abbreviation of EMIM, TFSI and FSI stand for 1-ethyl-3-methylimidazolium, bis(trifluoromethanesulfonyl) imide and bis(fluorosulfonyl) imide respectively (Fig.1).



**Fig. 1.** Structural formula of (a) EMIM<sup>+</sup> cation, (b) TFSI<sup>-</sup> and (c) FSI<sup>-</sup> anions.

## 2 Experiments

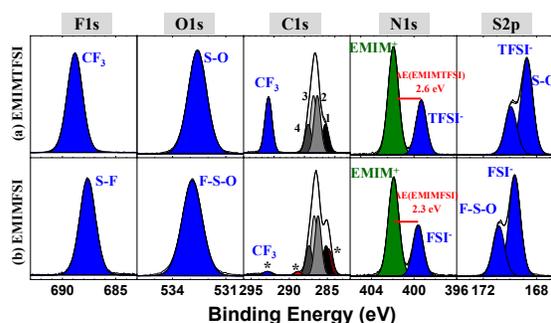
XPS measurements were performed with a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) with a base pressure of  $\sim 2 \times 10^{-9}$  mbar using a focused monochromatized Al K $\alpha$  radiation (1486.6 eV) with a beam size of  $\sim 500 \mu\text{m}^2$ . The spectrometer was pre-calibrated by performing a measurement on a clean silver surface, whereby the Ag 3d<sub>5/2</sub> peak was aligned to a binding energy of 368.25 eV with a full width at half-maximum of 0.78 eV at a pass energy of 30 eV. All the narrow energy span spectra are recorded with a dwell time of 50 ms, using a pass energy of 30 eV in steps of 0.05 eV. Peak deconvolution is performed by applying the sum of Gaussian (70%) and Lorentzian (30%) line shapes after a Shirley-type background subtraction. The peaks binding energy alignment is done on the N1s originating from the EMIM<sup>+</sup> cation component located at 402 eV.

All the ionic liquids and electrolytes are dried at 80 °C under  $10^{-2}$  mbar in a schlenk line for more than 6 hours and transferred under vacuum to the Ar filled glovebox. The XPS measurements are performed on droplets deposited on the electronically conductive active carbon substrate transferred from the glovebox to the XPS load lock using a dedicated transfer chamber sealed under Ar atmosphere. First, the XPS measurements are performed on two reference samples of pure [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and [EMIM<sup>+</sup>-FSI<sup>-</sup>] ionic liquids and then on four ionic liquid electrolytes where 1M of LiTFSI and 1M of LiFSI salts are dissolved in either [EMIM<sup>+</sup> - FSI<sup>-</sup>] or [EMIM<sup>+</sup> - TFSI<sup>-</sup>] ionic liquids.

## 3 Results

### 3.1 [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and [EMIM<sup>+</sup>-FSI<sup>-</sup>] ionic liquids

The XPS core levels acquired on the [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and [EMIM<sup>+</sup>-FSI<sup>-</sup>] ionic liquids presented in Fig. 2 are used as reference spectra to identify the exact binding energy (BE) position and full width half maximum (FWHM) of the peaks originated from both cation and anion. The extracted parameters BE and FWHM will be used to deconvolute precisely the components originating from the Li<sup>+</sup> cation and its solvated shell in the electrolytes.



**Fig. 2.** F1s, O1s, C1s N1s and S2p XPS core levels acquired on (a) [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and (b) [EMIM<sup>+</sup>-FSI<sup>-</sup>] ionic liquid droplets.

In the [EMIM<sup>+</sup>-TFSI<sup>-</sup>] solution (Fig.2.a) we distinctly identify in the N1s core level the components located at 402 eV and 399.4 eV associated with the N atom in the EMIM<sup>+</sup> and TFSI<sup>-</sup> respectively with a BE difference  $\Delta E = N1s_{(EMIM^+)} - N1s_{(TFSI^-)} = 2.6$  eV. The C1s core level is comprehensibly deconvoluted with the components originating from EMIM<sup>+</sup> (Fig.1.a) related to the (1) aliphatic carbon CH<sub>x</sub>, (2) C-N bonds, (3) C-C<sup>\*</sup>-N and (4) N-C<sup>\*</sup>-N located at 285.2 eV, 286.3 eV, 286.8 eV and 287.5 eV respectively. The CF<sub>3</sub> component located at 292.7 eV, which originates from the TFSI<sup>-</sup> (Fig.1.b). As expected both F1s and O1s show a single component located at 688.8 eV and 532.6 eV respectively, while the S2p is deconvoluted with the j=3/2 and j=1/2 spin-orbitals located at 168.7 eV and 169.9 eV respectively. The F1s, O1s and S2p signals originate all from the TFSI<sup>-</sup> (Fig.1.b). No traces of contamination or ionic liquid degradation under the X-ray source is detected in the solution.

In the [EMIM<sup>+</sup>-FSI<sup>-</sup>] solution (Fig.2.b) we can still identify with the same level of distinction both the N1s components located at 402 eV and 399.7 eV from EMIM<sup>+</sup> and FSI<sup>-</sup> respectively but with reduced BE difference  $\Delta E = N1s_{(EMIM^+)} - N1s_{(FSI^-)} = 2.3$  eV. The C1s components associated with the EMIM<sup>+</sup> are deconvoluted in the same way as above. However, additional non expected components located at \*284.9 eV, \*289 eV and \*292.7 eV had to be added in order to satisfy the fit. Those additional components are affiliated with C-H, O=C-O and CF<sub>3</sub> impurities or EMIMFSI degradation. We cannot also exclude signals coming from the active carbon even though the substrate is soaked by the ionic liquid and forming a large droplet

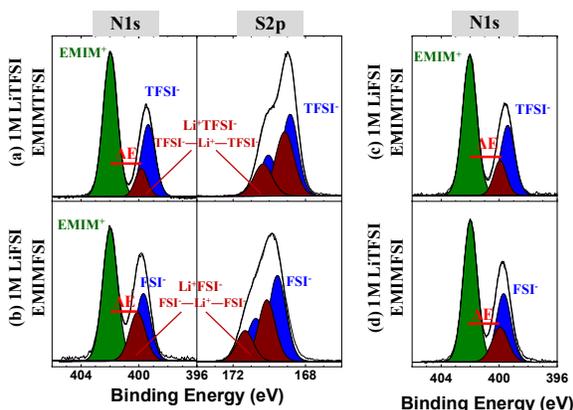
on the surface. The F1s, O1s and S2p still detected as single peaks located at 687.6 eV, 532.9 eV and 169.6 eV respectively, all originating from FSI<sup>-</sup> (Fig.1.c). The atomic percentage of the different elements present in EMIMTFSI and EMIMFSI electrolyte are displayed in Table 1. An error of 2% is expected calculated on a clean Cu foil reference using the Cu2p, Cu3s and Cu3p core levels.

**Table 1.** Estimated atomic percentage (%) of on the elements present in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and [EMIM<sup>+</sup>-FSI<sup>-</sup>] ionic liquids.

N1 <sub>Scation</sub>	N1 <sub>Sanion</sub>	O1s	S2p	F1s	C1s
EMIMTFSI					
11%	6%	21%	11%	39%	12%
EMIMFSI					
16%	9%	35%	19%	21%	-

### 3.2 Li<sup>+</sup> solvation by TFSI<sup>-</sup> and FSI<sup>-</sup> anions

By dissolving 1M of LiTFSI in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] we can be sure that the Li<sup>+</sup> cation is solely solvated by TFSI<sup>-</sup> anions (TFSI<sup>-</sup>-Li<sup>+</sup>-TFSI<sup>-</sup>). Similarly, by dissolving 1 M of LiFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>], Li<sup>+</sup> cation is solely solvated by FSI<sup>-</sup> anions (FSI<sup>-</sup>-Li<sup>+</sup>-FSI<sup>-</sup>). The N1s and S2p core levels acquired on those electrolytes are presented in Fig.3.a and b. Additional components are detected as soon as the salts are added. In the N1s peaks the extra components are located at 399.85 eV/400.1 eV between the EMIM<sup>+</sup> and TFSI<sup>-</sup>/FSI<sup>-</sup> components while in the S2p it is located at high BE from TFSI<sup>-</sup>/FSI<sup>-</sup> components.



**Fig. 3.** N1s and S2p XPS core levels acquired on (a) 1M LiTFSI in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and (b) 1M LiFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>]. N1s acquired on (c) 1M LiFSI in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and (d) 1M LiTFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>].

The signal of those additional components originate from the TFSI<sup>-</sup>/FSI<sup>-</sup> anions solvating the Li<sup>+</sup> cations called hereafter Li<sup>+</sup>TFSI<sup>-</sup> and Li<sup>+</sup>FSI<sup>-</sup>. The BE difference between the EMIM<sup>+</sup> and the Li<sup>+</sup>TFSI<sup>-</sup> [ $\Delta E = N1s_{(EMIM)} - N1s_{(LiTFSI)}$ ] or Li<sup>+</sup>FSI<sup>-</sup> [ $\Delta E = N1s_{(EMIM)} - N1s_{(LiFSI)}$ ] components are calculated to be 2.15 eV and 1.9 eV respectively. As the EMIM<sup>+</sup> cation is present in all the investigated electrolytes, so it is used as reference unchangeable component. Based on the assumption that its electronic structure will not change, as it is not expected to participate in the first solvation shell of the

Li<sup>+</sup>. Thus, the measured  $\Delta E$  can be assumed as characteristic parameter linked directly to the Li<sup>+</sup> solvation in the electrolyte. To summarise, when Li<sup>+</sup> is fully solvated by TFSI<sup>-</sup> the resulting  $\Delta E$  is equal to 2.15 eV while when Li<sup>+</sup> is fully solvated by FSI<sup>-</sup>  $\Delta E$  is reduced to 1.9 eV.

By applying the same methodology, we are interested in understanding the mechanism of the Li<sup>+</sup> solvation when both TFSI<sup>-</sup> and FSI<sup>-</sup> are present simultaneously in the electrolyte as salt or as anion in the ionic liquid. For that, the N1s core level acquired on both 1M LiFSI in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and 1M LiTFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>] electrolytes are presented in Fig.3.c and d. The BE difference  $\Delta E = N1s_{(EMIM)} - N1s_{(solvated Li)}$  is calculated to be 2.07 eV and 2.06 eV for 1M LiFSI in [EMIM<sup>+</sup>-TFSI<sup>-</sup>] and 1M LiTFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>] respectively, which is between the  $\Delta E$  measured above when Li<sup>+</sup> is fully solvated by TFSI<sup>-</sup> and FSI<sup>-</sup>. This result demonstrate that Li<sup>+</sup> is solvated by both TFSI<sup>-</sup> and FSI<sup>-</sup> when both anions are present in the electrolyte as salt or in the ionic liquid. All the calculated  $\Delta E$  are reported the table 2 below.

The same trend is obtained when the BE energy difference is calculated between [ $\Delta E = N1s_{(EMIM)} - S2p_{(solvated Li)}$ ] or [ $\Delta E = N1s_{(solvated Li)} - Li1s_{(solvated Li)}$ ]. However, we do not recommend using the Li1s core level with the risk to introduce error on the measurements caused by the electrolytes instability under the X-ray source and the formation of LiF during the acquisition as discussed in the next paragraph.

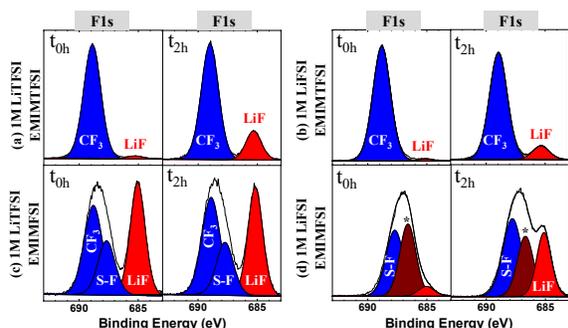
**Table 2.** Calculated  $\Delta E = N1s_{(EMIM)} - N1s_{(solvated Li)}$  for the different prepared ionic liquid electrolytes

N1s	$\Delta E = N1s_{(EMIM)} - N1s_{(solvated Li)}$	
1M LiTFSI EMIM <sup>+</sup> -TFSI <sup>+</sup>	2.15 eV	TFSI <sup>-</sup> ...Li <sup>+</sup> ...TFSI <sup>-</sup>
1M LiFSI EMIM <sup>+</sup> -FSI <sup>+</sup>	1.9 eV	FSI <sup>-</sup> ...Li <sup>+</sup> ...FSI <sup>-</sup>
1M LiFSI EMIM <sup>+</sup> -TFSI <sup>+</sup>	2.07 eV	TFSI <sup>-</sup> ...Li <sup>+</sup> ...FSI <sup>-</sup>
1M LiTFSI EMIM <sup>+</sup> -FSI <sup>+</sup>	2.065 eV	FSI <sup>-</sup> ...Li <sup>+</sup> ...TFSI <sup>-</sup>

### 3.3 Electrolyte stability under the X-ray beam

The stability of the electrolytes under the X-ray source is investigated by acquiring the F1s core level. It is worth mentioning that the measured pure ionic liquids EMIM<sup>+</sup> TFSI<sup>-</sup> or EMIM<sup>+</sup> FSI<sup>-</sup> without the salts show good stability under X-ray. No sign of any ionic liquid degradation is detected and no change in the XPS core levels is observed even after long exposure time beyond 2 hours. However, as soon as the salts are added in the ionic liquid, then LiF component is detected in the F1s core level located at 685 eV (Fig.4.). It is a chemical reaction between the Li-ion and the F from either TFSI or FSI. The amount of LiF increases with the exposure time. Some exception is observed for the 1M LiTFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>] (Fig.4.c), where the amount of LiF was high initially directly after exposure to X-ray and did not evolve after 2 hours. For the 1M LiFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>] an additional, unknown component is detected in the

F1s (fig.4.d) located at 687 eV besides the LiF, which both evolve after 2 hours exposure time to X-ray.



**Fig. 4.** F1s XPS core levels acquired directly after transfer ( $T_{0h}$ ) and after 2 hours ( $T_{2h}$ ) exposure to X-ray Al K $\alpha$  for the electrolytes: (a) 1M LiTFSI in [EMIM<sup>+</sup>-TFSI], (b) 1M LiFSI in [EMIM<sup>+</sup>-TFSI], (c) 1M LiTFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>] and (d) 1M LiFSI in [EMIM<sup>+</sup>-FSI<sup>-</sup>].

## 4 Conclusion

In our study, we show a new approach for investigating the Li-ion solvation in TFSI and FSI-based ionic liquid electrolytes carried out by conventional laboratory XPS using Al K $\alpha$  X-ray source. This is conceivable thanks to the low vapour pressure of the ionic liquid and its stability under ultra-high vacuum. We demonstrate that the Li<sup>+</sup> cation is solvated by both TFSI<sup>-</sup> and FSI<sup>-</sup> when the two anions are present in the electrolyte as salt or in the ionic liquid. This result can partially explain why adding FSI<sup>-</sup> in the electrolyte prevents the EMIM<sup>+</sup> co-intercalation in the graphite by forming a favorable SEI during the first reduction. Moreover, this study sheds light on the stability of the ionic liquid electrolyte under the X-ray source, which can limit our ambition in performing *operando* XPS measurements at the interface of ionic liquid electrolytes versus working electrodes, [16],[14] where alternative solutions need to be invented for such an issue. Finally, to overcome the electrolyte instability when investigating the Li<sup>+</sup> ion solvation, we recommend the use of liquid jet [15] where fresh electrolyte is continuously measured.

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