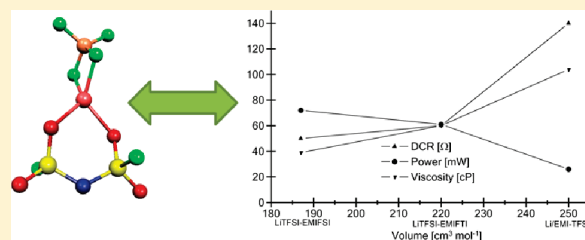


# Ionic Liquid Based Lithium Battery Electrolytes: Charge Carriers and Interactions Derived by Density Functional Theory Calculations

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**ABSTRACT:** The solvation of lithium salts in ionic liquids (ILs) leads to the creation of a lithium ion carrying species quite different from those found in traditional nonaqueous lithium battery electrolytes. The most striking differences are that these species are composed only of ions and in general negatively charged. In many IL-based electrolytes, the dominant species are triplets, and the charge, stability, and size of the triplets have a large impact on the total ion conductivity, the lithium ion mobility, and also the lithium ion delivery at the electrode. As an inherent advantage, the triplets can be altered by selecting lithium salts and ionic liquids with different anions. Thus, within certain limits, the lithium ion carrying species can even be tailored toward distinct important properties for battery application. Here, we show by DFT calculations that the resulting charge carrying species from combinations of ionic liquids and lithium salts and also some resulting electrolyte properties can be predicted.



## 1. INTRODUCTION

Electrolytes based on ionic liquids (ILs) are a promising path toward safer lithium ion battery concepts overall due to the promises of ILs, e.g., wide electrochemical stability windows, nonvolatility, and thermal stability.<sup>1–3</sup> This has been demonstrated in practical tests using various battery electrode chemistries for different IL/lithium salt liquid electrolytes<sup>2–5</sup> or incorporated in a matrix to comprise a gel or within a solid polymer electrolyte.<sup>6–8</sup> While there still are many question marks and doubts about the performance and cost of IL-based electrolytes, the mode of lithium ion solvation in ILs is intriguing from a fundamental scientific point of view and also of the utmost importance practically.

Indeed, in electrolytes based on a lithium salt dissolved in an IL matrix, the nature of the dominant lithium carrying species becomes dramatically different from the situation in traditional nonaqueous liquid electrolytes. In a traditional electrolyte, the lithium ion (Li<sup>+</sup>) is solvated by overall neutral solvent molecules (S) with electron-donating groups to fulfill its first solvation shell, resulting in [Li(S)<sub>n</sub>]<sup>+</sup> complexes. For a lithium ion, the preferred coordination number often is four, and even at rather high lithium salt concentrations, both in liquids and gels, the two dominant charged species are [Li(S)<sub>4</sub>]<sup>+</sup> and “free” solvated anions, proven for, e.g., EC/PC as the solvent.<sup>9</sup> As the anion typically is smaller than the lithium ion carrying species, the cation transference numbers, *t*<sub>+</sub>, are often much less than 0.5<sup>10,11</sup> and thus in practice prohibit the most efficient usage of the electrolyte within a lithium battery.

For IL-based electrolytes, there are no neutral solvent molecules present, and thus the situation is quite different. However, the preferred coordination number is still four for the lithium ion, and the anions from the ionic liquid together with those originating from the lithium salt must fulfill the solvation shell. As many anions (An) of practical interest (BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, TFSI, FSI, etc.)

prefer to coordinate lithium ions in a bidentate manner, triplet formation, [Li(An)<sub>2</sub>]<sup>−</sup>, can be expected to be dominant for the concentration ranges of practical interest. This has indeed been observed primarily by infrared (IR) and Raman spectroscopy for TFSI-based IL/Li salt electrolytes, both in liquids and gels.<sup>12–17</sup> The coordination number of four can of course be fulfilled also in other ways and in the literature molecular dynamics (MD) simulations,<sup>18,19</sup> and other techniques such as ion conductivity measurements and diffusion NMR spectroscopy<sup>20–24</sup> point to a more general picture of different [Li<sub>x</sub>An<sub>y</sub>]<sup>(x−y)</sup> lithium carrying species including large aggregates. However, the dominance of triplets from IR and Raman data is strongly supported both by ab initio and density functional theory (DFT) calculations<sup>13,16,17</sup> as well as by thoroughly analyzed diffusion data from NMR spectroscopy.<sup>14,20,22–24</sup> Some results support also higher-order complexes.<sup>20–22</sup> However, we find no spectroscopy results supporting higher-order complexes, apart from preliminary results obtained for very low lithium salt/IL ratios.<sup>25</sup> Therefore, especially the triplet formation and stability in the electrolytes call for further investigation.

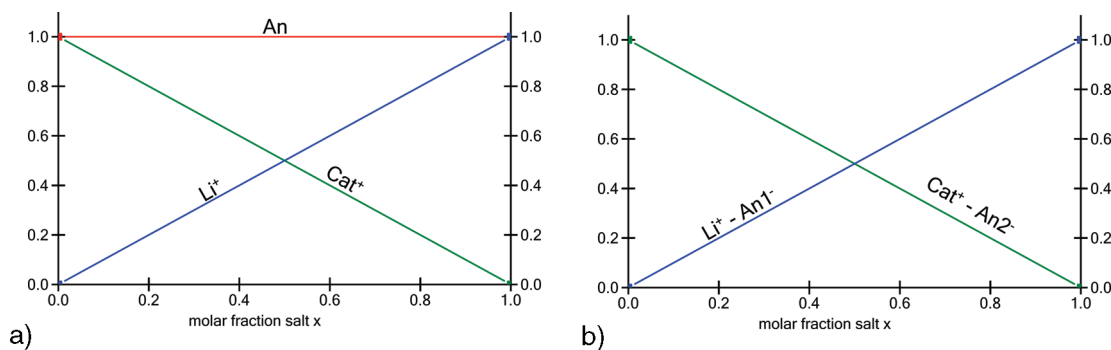
In addition to the lithium ion carrying species, there is a large excess of “bystander” ions that also contribute to the total ion conductivities: “free” anions and “free” IL cations due to the IL matrix. Ion-pair formation is the exception for properly chosen lithium salts, just as for traditional electrolytes, and is only to be found for rather high lithium salt/IL ratios.<sup>16,25</sup>

While it is an important observation in itself that the triplets dominate for the most interesting ratios, it is even more

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Scheme 1. Compositions of (a) Binary and (b) Ternary Systems<sup>a</sup>

<sup>a</sup> Triplets are found to dominate in the approx. range  $0.05 < x < 0.3$ .<sup>14,16,25</sup>

important that the nature of these triplets can be tailored. The two constituent anions in each triplet are determined by both the choice of lithium salt and the choice of IL. There are basically two major categories of systems depending on if the lithium salt and the IL has a common anion or not, i.e., binary  $[(\text{Li}_x\text{Cat}_{1-x})\text{An}]$  or ternary  $[\text{Li}_x\text{An}_{1-x}\text{Cat}_{1-x}\text{An}_{2(1-x)}]$  systems (Scheme 1). For the former concept, only one basic type of triplet can be obtained,  $[\text{Li}(\text{An})_2]^-$ , but for the latter concept both the properties and concentrations of the two different anions will determine the type of dominant triplet,  $[\text{Li}(\text{An}_2)_2]^-$  or  $[\text{Li}(\text{An}_1)(\text{An}_2)]^-$ .

Using the Ansatz above, we here for the first time apply DFT calculations to compare several triplets from different anions with respect to the lithium ion interaction strength, stability, and size of the species to propose paths to tailoring the  $\text{Li}^+$  carrying species in IL-based electrolytes for lithium batteries.

## 2. COMPUTATIONAL

To cover the most important range of IL-based electrolytes and furthermore to allow for some special comparisons, triplets composed of the following five anions were studied: tetrafluoroborate ( $\text{BF}_4^-$ ), hexafluorophosphate ( $\text{PF}_6^-$ ), tetracyanoborate (Bison ( $[\text{B}(\text{CN})_4]^-$ )), bis(trifluoromethanesulfonyl)imide (TFSI ( $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ )), and bis(fluorosulfonyl)imide (FSI ( $[\text{N}(\text{FSO}_2)_2]^-$ )). In addition, some studies also include the less common “half-FSI/half-TFSI”, (fluorosulfonyl)(trifluoromethanesulfonyl)imide: FTI,  $[\text{N}(\text{FSO}_2)(\text{CF}_3\text{SO}_2)]^-$ . For the imide family of anions, only the  $\text{C}_2$  conformer<sup>26,27</sup> was used.

Triplets of two anions and a central Li cation were constructed manually with all the possibilities of mono-, bi-, and tridentate coordination from the anions individually considered. Several different starting configurations were used for each combination. Subsequently, all triplet starting geometries were fully relaxed, and energy minima structures were verified by computing second derivatives of the energies with respect to nuclei displacements giving us normal modes of vibration and corresponding frequencies. Due to the numerical procedure and the finite DFT grid, imaginary frequencies ( $<15 \text{ cm}^{-1}$ ) were obtained for a few cases, but all structures found were considered proper energy minima. For all triplets, double bidentate coordination by the anions to the lithium cation was found to be energetically preferred; thus only this type of triplet will be treated henceforth. For the imide-based anions, the coordination to the lithium central cation is via one oxygen atom from each sulfonyl group, in agreement with previous lithium salt ion-pair data.<sup>28</sup> A typical molecular structure example of a triplet,  $[\text{Li}(\text{BF}_4)(\text{FSI})]^-$ , is shown in Figure 1.

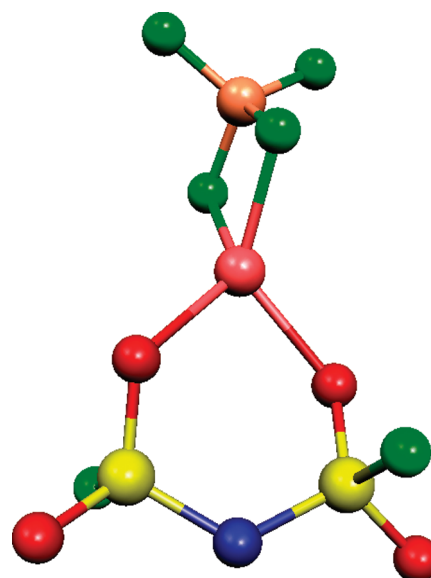


Figure 1. Molecular structure of a typical triplet:  $[\text{Li}(\text{BF}_4)(\text{FSI})]^-$ .

The binding energy,  $\Delta E_{\text{bind}}$ , is defined as the electronic energy difference with respect to the sum of the energies of the ions separately. No BSSE correction was applied to  $\Delta E_{\text{bind}}$  but has previously been shown to be of the order of a few kilojoules/mole for lithium salt ion-pairs<sup>28</sup> and thus of minor importance in light of the large Coulombic interactions presented here:  $>600 \text{ kJ mol}^{-1}$ . The stabilities of the triplets are also estimated by comparing with the corresponding ion-pairs.<sup>28,33</sup>

Volumes, both for anions and triplets, were obtained using a Monte Carlo (MC) based algorithm defining the space occupied with more than  $0.001 \text{ e/bohr}^3$  as the volume. Averages of at least 10 separate MC calculations were used, resulting in final errors of the order of 5–10%.

Preoptimizations were made using the ab initio Hartree–Fock algorithm and the 6-31G\* basis set, while all final calculations and evaluations were performed using DFT: B3LYP/6-311+G\*,<sup>29–31</sup> as implemented in the Gaussian03 program.<sup>32</sup>

## 3. RESULTS AND DISCUSSION

The computed properties of the possible lithium ion carrying triplets are first characterized in terms of binding energies. Second, the sizes of the triplets are commented on, and finally

we correlate both these computed properties with literature data on mobility and conductivity, etc.

**3.1. Triplet Binding Energies.** By using different lithium salts and ILs, we can in theory create many different triplets. The choice(s) of anion(s) will ultimately affect the charge carrying species of the corresponding battery electrolyte(s). To predict which triplets will dominate in each electrolyte, Figure 2 and Table 1 provide some answers from a purely energetic point of view.

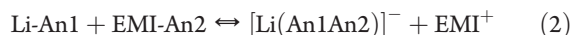
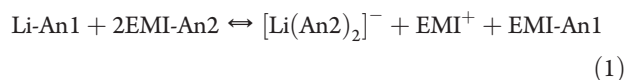
First, some obvious general observations can be made. The  $[\text{Li}(\text{BF}_4)_2]^-$  triplet is the most stable one overall, but not by far. All the  $[\text{B}(\text{CN})_4]^-$  based triplets are much less stable than all other triplets, and most of the  $[\text{Li}([\text{B}(\text{CN})_4])_2]^-$  triplets have a strikingly smaller binding energy. In more detail, the binding energy trend, without exception across the different triplets, is  $\text{BF}_4^- > \text{TFSI} > \text{FSI} > \text{PF}_6^- \gg [\text{B}(\text{CN})_4]^-$ , and this trend is the same as the binding energy trend from the corresponding  $\text{Li}^+$  ion-pairs.<sup>28,33</sup> In addition, across the triplets the binding energies are approximately additive. The differences between the corresponding  $\text{BF}_4^-$  and  $\text{PF}_6^-$  based triplets are all very close, and this behavior is true for all anions and triplets (Figure 2).

From a practical point of view, for the binary systems the trend above is valid and much more pronounced: the  $[\text{Li}([\text{B}(\text{CN})_4])_2]^-$  triplet has a binding energy ca.  $140 \text{ kJ mol}^{-1}$  smaller than the next in line,  $[\text{Li}(\text{PF}_6)_2]^-$  (diagonal of Table 1). These binding energies are interesting when comparing the absolute strength of the lithium ion complexes, but furthermore these triplets will in each binary system be in equilibrium with a single type of  $\text{Li}^+$  ion-pair. The binding energies of these ion-pairs are thus of importance to validate the relative effect. Using literature data, the trend is the same as stated above, but in percentages of the total triplet binding energies the step from ion-pair to triplet is strikingly similar, in the range 21–26% of the total (Table 1<sup>28,33</sup>). Depending on if the electrolyte is a pure lithium salt/IL-based one or a more complex gel- or polymer-based one, the relevance of absolute or relative

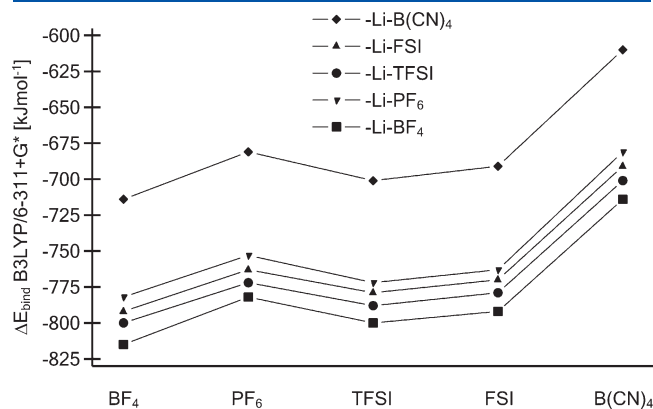
measures will shift. For pure electrolytes, the percentages will allow an estimate of the amounts of triplets vs ion-pairs for each system, while for more complex electrolytes the absolute numbers should be used to compare also with the binding energies of lithium ion complexation by the solvent molecules or by the polymer matrix, as previously outlined for traditional electrolytes.<sup>9,28</sup>

For the ternary systems, the situation is more delicate with quite a number of triplets (8/15) found in a very narrow energy interval of ca.  $30 \text{ kJ mol}^{-1}$  (Table 1 and Figure 2), and thus it is difficult to choose the lithium salt and IL to construct the lithium charge carrier wanted:  $[\text{Li}(\text{An}2)_2]^-$  or  $[\text{Li}(\text{An}1)(\text{An}2)]^-$ . However, by using the binding energies as guidelines an indicative effort can be made. If we restrict ourselves to concentration ranges where the molar ratio of IL to lithium salt is high but still with enough lithium salt doping to be interesting as an electrolyte, ca.  $0.05 < x < 0.3$  (Scheme 1b), we can, based on the stabilities of the triplets, create a summary of the most probable lithium charge carriers (Table 2). Notable is that the sources of the different anions do play an important role, e.g., the ratio of salt-anion/ $\text{Li}^+$  can never exceed unity, and this distinctly affects the triplets it is possible to obtain; i.e.,  $[\text{Li}(\text{An}1)_2]^-$  is impossible on average.

The energy picture of triplets from the DFT calculations, with some caveats from surrounding ions and the IL ion–ion interactions being neglected, becomes a first attempt to predict the charge carriers in lithium salt/IL systems. To further advance the modeling, the IL ion–ion interactions can be taken into account and of course depend on the IL cation used. To exemplify the importance, for 1-ethyl-3-methylimidazolium,  $\text{EMI}^+$ , the interaction with the  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , and TFSI anions have been modeled using ion-pair models and the same DFT method as implemented here, resulting in  $-351$ ,  $-326$ , and  $-320 \text{ kJ mol}^{-1}$ , respectively.<sup>34</sup> For Bison, the corresponding value is  $-284 \text{ kJ mol}^{-1}$ .<sup>35</sup> This enables us to set up balanced equations between ion-pairs and triplets taking also the IL ion–ion interactions into account according to



All triplet forming reactions are endoergic (Table 2); however, this can be explained from the separation of charges in a vacuum, while a real system is embedded and stabilized by an ionic matrix. The changes compared to the picture that emerged from the triplet binding energies in Table 1 are due to the  $\text{BF}_4^-$  anion properties. The strong interaction of this anion with the ionic liquid cation,  $\text{EMI}^+$ , results in the most stable triplets now being less  $\text{BF}_4^-$  containing (Table 2). However, for the main part, the picture from the triplet binding energies is confirmed. We would also like to stress that the rather small relative energy differences obtained for



**Figure 2.** Binding energies,  $\Delta E_{\text{bind}}$ , for  $[\text{Li}(\text{An})_2]^-$  or  $[\text{Li}(\text{An}1)(\text{An}2)]^-$  triplets vs separate ions.

**Table 1.** Computed Binding Energies and Volumes for the Triplet Structures

$\Delta E_{\text{bind}} [\text{kJ mol}^{-1}]$ /volume $[\text{cm}^3 \text{mol}^{-1}]$	$\text{BF}_4^-$	$\text{PF}_6^-$	TFSI	FSI	$[\text{B}(\text{CN})_4]^-$
$\text{BF}_4^-$	−815/82.7	−782/103.6	−800/166.5	−792/127.6	−714/134.3
$\text{PF}_6^-$		−753/115.6	−772/183.6	−763/143.1	−681/150.9
TFSI			−788/249.6	−779/204.9	−701/217.3
FSI				−770/169.4	−691/172.2
$[\text{B}(\text{CN})_4]^-$					−610/184.2

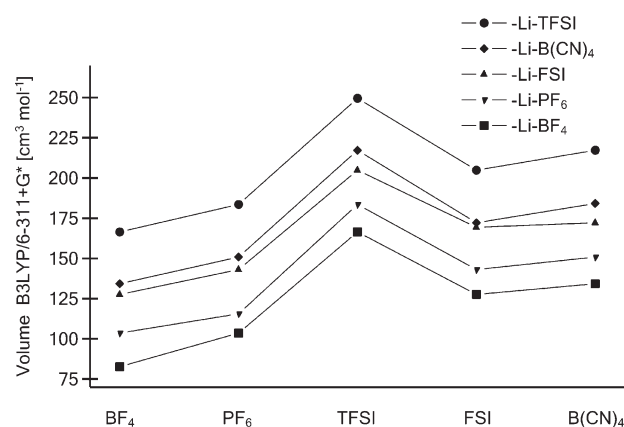
**Table 2.** Probable Charge Carriers in Ternary Systems Based on Lithium Salt and IL Combinations, Triplet Binding Energies, and the Equilibrium Equations

Li-salt	IL	probable charge carrier	eqs 1 and 2 [ $\text{kJ mol}^{-1}$ ] <sup>a</sup>	probable charge carrier <sup>b</sup>
(Li-An1)	(Cat-An2)	(Figure 2)	$[\text{Li}(\text{An}2)_2]^- / [\text{Li}(\text{An}1)(\text{An}2)]^-$	(eqs 1 and 2)
Li-PF <sub>6</sub>	Cat-BF <sub>4</sub>	$[\text{Li}(\text{BF}_4)_2]^-$	+128/+136	$[\text{Li}(\text{BF}_4)_2]^-$
Li-TFSI	Cat-BF <sub>4</sub>	$[\text{Li}(\text{BF}_4)_2]^-$	+159/+143	$[\text{Li}(\text{TFSI})(\text{BF}_4)]^-$
Li-FSI	Cat-BF <sub>4</sub>	$[\text{Li}(\text{BF}_4)_2]^-$	+148/+140	$[\text{Li}(\text{FSI})(\text{BF}_4)]^-$
Li-B(CN) <sub>4</sub>	Cat-BF <sub>4</sub>	$[\text{Li}(\text{BF}_4)_2]^-$	+82/+116	$[\text{Li}(\text{BF}_4)_2]^-$
Li-BF <sub>4</sub>	Cat-PF <sub>6</sub>	$[\text{Li}(\text{BF}_4)(\text{PF}_6)]^-$	+150/+146	$[\text{Li}(\text{BF}_4)(\text{PF}_6)]^-$
Li-TFSI	Cat-PF <sub>6</sub>	$[\text{Li}(\text{TFSI})(\text{PF}_6)]^-$	+171/+146	$[\text{Li}(\text{TFSI})(\text{PF}_6)]^-$
Li-FSI	Cat-PF <sub>6</sub>	$[\text{Li}(\text{FSI})(\text{PF}_6)]^-$	+160/+144	$[\text{Li}(\text{FSI})(\text{PF}_6)]^-$
Li-B(CN) <sub>4</sub>	Cat-PF <sub>6</sub>	$[\text{Li}(\text{PF}_6)_2]^-$	+94/+124	$[\text{Li}(\text{PF}_6)_2]^-$
Li-BF <sub>4</sub>	Cat-TFSI	$[\text{Li}(\text{BF}_4)(\text{TFSI})]^-$	+103/+122	$[\text{Li}(\text{TFSI})_2]^-$
Li-PF <sub>6</sub>	Cat-TFSI	$[\text{Li}(\text{TFSI})_2]^-$	+93/+115	$[\text{Li}(\text{TFSI})_2]^-$
Li-FSI	Cat-TFSI	$[\text{Li}(\text{TFSI})_2]^-$	+113/+122	$[\text{Li}(\text{TFSI})_2]^-$
Li-B(CN) <sub>4</sub>	Cat-TFSI	$[\text{Li}(\text{TFSI})_2]^-$	+47/+98	$[\text{Li}(\text{TFSI})_2]^-$
Li-BF <sub>4</sub>	Cat-FSI <sup>c</sup>	$[\text{Li}(\text{BF}_4)(\text{FSI})]^-$	+121/+130	$[\text{Li}(\text{FSI})_2]^-$
Li-PF <sub>6</sub>	Cat-FSI <sup>c</sup>	$[\text{Li}(\text{FSI})_2]^-$	+111/+124	$[\text{Li}(\text{FSI})_2]^-$
Li-TFSI	Cat-FSI <sup>c</sup>	$[\text{Li}(\text{TFSI})(\text{FSI})]^-$	+142/+133	$[\text{Li}(\text{TFSI})(\text{FSI})]^-$
Li-B(CN) <sub>4</sub>	Cat-FSI <sup>c</sup>	$[\text{Li}(\text{FSI})_2]^-$	+65/+108	$[\text{Li}(\text{FSI})_2]^-$
Li-BF <sub>4</sub>	Cat-B(CN) <sub>4</sub>	$[\text{Li}(\text{BF}_4)(\text{B}(\text{CN})_4)]^-$	+209/+172	$[\text{Li}(\text{BF}_4)(\text{B}(\text{CN})_4)]^-$
Li-PF <sub>6</sub>	Cat-B(CN) <sub>4</sub>	$[\text{Li}(\text{PF}_6)(\text{B}(\text{CN})_4)]^-$	+199/+170	$[\text{Li}(\text{PF}_6)(\text{B}(\text{CN})_4)]^-$
Li-TFSI	Cat-B(CN) <sub>4</sub>	$[\text{Li}(\text{TFSI})(\text{B}(\text{CN})_4)]^-$	+230/+175	$[\text{Li}(\text{TFSI})(\text{B}(\text{CN})_4)]^-$
Li-FSI	Cat-B(CN) <sub>4</sub>	$[\text{Li}(\text{FSI})(\text{B}(\text{CN})_4)]^-$	+219/+174	$[\text{Li}(\text{FSI})(\text{B}(\text{CN})_4)]^-$

<sup>a</sup> Least endoergic reaction values in bold. <sup>b</sup> Changes relative to results from Figure 2 in italic. <sup>c</sup> The interaction being set equal to that of Cat-TFSI.

the two types of triplets in Table 2 and their unknown behavior in an ionic matrix do not allow any unambiguous conclusions to be made concerning the speciation without further experimental confirmation. The similarity of the TFSI and FSI anions is built into the analysis, but furthermore also the weakness of the triplets based on Bison is confirmed. Interesting, the largest separation in energy between eqs 1 and 2, and thus between the  $[\text{Li}(\text{An}2)_2]^-$  and  $[\text{Li}(\text{An}1)(\text{An}2)]^-$  types of triplets, occurs for the mixes of the TFSI and Bison anions, 51 and 55  $\text{kJ mol}^{-1}$ , respectively, depending on the anion origins. To summarize, using all available ion–ion interaction information from lithium salts and ILs as well as triplets, the unique stability of species information is available also for the more difficult ternary systems.

**3.2. Triplet Sizes.** The hydrodynamic radius is a concept fundamentally laden with problems in ILs, and this is true also for lithium-doped systems; for binary as well as ternary systems there are no independent solvent molecules. Yet, the effective radii in particular and the sizes in general of the diffusing species in both pure ILs as well as in lithium-doped IL systems are often needed and used for interpretation of the experimental observations of ion/IL dynamics.<sup>14,20,22,23,36</sup> The sizes of the species can be calculated by simple vdW addition, but here a volume envelope based on the electronic structure extent in space is chosen. For a more stringent approach also the shape of the species and the volume excluded in the resulting electrolyte should be considered, akin to different factors  $c$  in the Stokes–Einstein equation,<sup>23</sup> but as a starting point the size of the volume envelopes will suffice. The triplet volumes are found to vary quite substantially, with the triplets involving the TFSI anion being by far the largest and those with the BF<sub>4</sub><sup>−</sup> anion the smallest, with a maximum factor of 3 between the triplets arising from the binary systems:  $[\text{Li}(\text{BF}_4)_2]^-$  and  $[\text{Li}(\text{TFSI})_2]^-$  (Table 1, Figure 3). The FSI and Bison based

**Figure 3.** Volumes of triplets based on electronic structure extent.

triplets have approximately the same sizes. In terms of designing triplets with respect to their properties, the FSI and TFSI anion based triplets are approximately equally stable but differ by ca. 25% in volume.

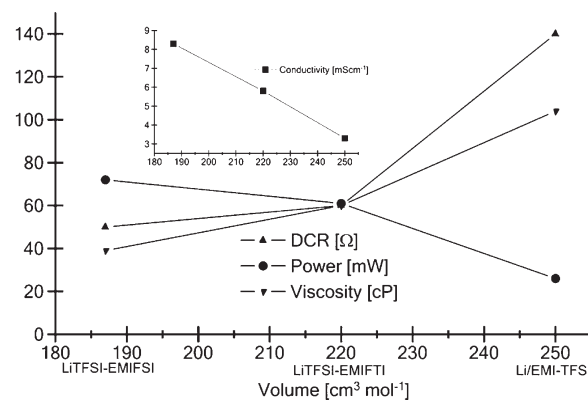
Overall, the obtained triplet volumes are slightly smaller, a few percent, than the sum of the two ingoing anions independently, even without taking into account the small volume contribution of the lithium cation. A comparison with the lithium cation transporting species in traditional EC/PC-based electrolytes, i.e.  $[\text{Li}(\text{EC})_4]^+$ , which has a volume of 232  $\text{cm}^3 \text{mol}^{-1}$ ,<sup>9,35</sup> renders all triplets smaller, except  $[\text{Li}(\text{TFSI})_2]^-$ . This should in principle allow for faster dynamics, but as IL-based electrolytes are more viscous than traditional liquid electrolytes, the diffusion is often found to be significantly slower.



**3.3. Comparison with Experimental Mobilities and Conductivities.** The mobilities of the species in binary electrolytes have predominantly been determined via the diffusion coefficients of the  $^1\text{H}$ ,  $^7\text{Li}$ , and  $^{19}\text{F}$  nuclei by NMR.<sup>10,14,23</sup> From ref 23 it is clear that the diffusing lithium carrying species move slower than both the BMP cation and the TFSI anions. However, it is unclear, due to the high salt concentration,  $x = 0.377$ , if ion-pairs are more significant than triplets in this particular system, which surprisingly also only shows a single peak in the  $^{19}\text{F}$  spectra. Turning to the binary  $[(\text{Li}_x\text{EMI}_{(1-x)})\text{BF}_4]$  system in ref 10, the order of diffusion speed is:  $D_{\text{EMI}} > D_{\text{BF}_4} > D_{\text{Li}}$ . The authors contribute this to the formation of stable complexes being formed between  $\text{Li}^+$  and  $\text{BF}_4^-$ , mentioning triple and/or ion-pairs and “hyperstructures” but with no specific compositions argued for. Very small  $t_{\text{Li}}$  transference numbers,  $<0.05$ , are obtained. Duluard et al. are quite clear in their analysis on the type of charge carrier in the binary  $[(\text{Li}_x\text{BMI}_{(1-x)})\text{TFSI}]$  for  $0 < x < 0.23$ , resulting in negatively charged triplets,  $[\text{Li}(\text{TFSI})_2]^-$ .<sup>14</sup> Furthermore, these authors derive separate diffusion constants for coordinated TFSI, in  $[\text{Li}(\text{TFSI})_2]^-$  triplets and “free” TFSI, with the former mapping perfectly with the diffusion constants for  $\text{Li}^+$  over the entire concentration range. Using calculated volumes for all their three species (BMI:  $119.9 \text{ cm}^3 \text{ mol}^{-1}$  and TFSI:  $128.1 \text{ cm}^3 \text{ mol}^{-1}$ )<sup>35</sup> we qualitatively obtain the inverse sequence to their diffusion speeds ( $D_{\text{BMI}} > D_{\text{TFSI}} > D_{\text{Li}(\text{TFSI})_2}$ ). Notable is that using the vdW radii of BMI and TFSI results in a slightly smaller radius for TFSI than BMI.<sup>14</sup> However, quantitatively both methods result in very similar volumes for the BMI cation and the TFSI anion, and this is not reflected in the rather different diffusion coefficients obtained. Arguably the large conformational flexibilities of both TFSI<sup>26,27</sup> and BMI<sup>37</sup> may affect the effective radius,<sup>14</sup> and/or the shape differences between the two species could lead to different factors  $c$  in the Stokes–Einstein equation.<sup>23</sup>

Apart from direct comparisons with diffusion data, the calculated volumes should also be indirectly connectable to ion conductivities, but quite often conductivities are primarily connected with viscosity. A striking example is found in a direct comparison of the two binary systems  $[(\text{Li}_x\text{EMI}_{(1-x)})\text{BF}_4]$  and  $[(\text{Li}_x\text{EMI}_{(1-x)})\text{TFSI}]$  where a  $\sim 3$ -fold higher conductivity for the former is rather straightforwardly connected with a  $\sim 3$ -fold lower viscosity.<sup>3</sup> However, it is also possible to argue that the viscosity is a secondary effect, caused by the volumes of the species present in the electrolyte. Indeed, for these systems the volume ratio of the two lithium carrying triplets  $[\text{Li}(\text{BF}_4)_2]^-$  and  $[\text{Li}(\text{TFSI})_2]^-$  is  $\sim 3$  (Table 1), as well as the volume ratio of the “free” anions.

To exemplify how our computed data can be further used together with experimental observations, a special set of imide anion family IL-based electrolytes are used.<sup>38</sup> By using a particular set of anions, FSI, FTI, and TFSI, with similar interaction strengths with the lithium cation in their respective triplets, observed changes should primarily be related to the dynamics of the triplets and thus the volumes. In Figure 4 various experimentally observed data from real battery electrolytes, using electrolytes with 22–25% of Li-TFSI salt in EMI-FSI, EMI-FTI, and EMI-TFSI,<sup>37</sup> are correlated with calculated triplet volumes. For the binary system the volume used is simply that for  $[\text{Li}(\text{TFSI})_2]^-$ , while for the two ternary systems it corresponds to 50% of the charge carriers being  $[\text{Li}(\text{An})_2]^-$  type and 50%  $[\text{Li}(\text{An}1)(\text{An}2)]^-$  type, resulting in 187 and  $220 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. (The volumes for the FTI containing triplets are for  $[\text{Li}(\text{FTI})_2]^-$ ,  $212.3 \text{ cm}^3 \text{ mol}^{-1}$ , and for  $[\text{Li}(\text{FTI})(\text{TSFI})_2]^-$ ,  $227.6 \text{ cm}^3 \text{ mol}^{-1}$ .) From Figure 4 the expected correlations with ion conductivity, viscosity, and power



**Figure 4.** Various real battery electrolyte data as a function of charge carrier volumes.

are evident; especially the inverse behavior of power and viscosity, but also the conductivity, decreasing by a factor of 2.52 from left to right, connects excellently to the viscosity increase by a factor 1.66. More surprising is perhaps the strong dependence of the direct-current interfacial resistance (DCR). To speculate, the DCR should at least partly depend on the distance of  $\text{Li}^+$ –surface experienced at the electrolyte/electrode interface, and for  $[\text{Li}(\text{TFSI})_2]^-$ , the sole cation charge carrier in the binary IL, the minimum distance possible is longer than for the other triplets due to the presence of  $-\text{CF}_3$  groups at both ends of both the ingoing anions. However, while more experimental data, with binary as well as ternary lithium salt/IL systems, would be needed to confirm this hypothesis, it is striking how many experimental properties can be mapped onto our simple volume measure.

## 4. CONCLUSIONS

By using DFT to compute the properties of triplets,  $[\text{Li}(\text{An})_2]^-$ , there are several connections made possible between the choice of lithium salt and IL on one hand and the resulting electrolyte properties on the other. The stability of bidentate coordination by the anions to the central lithium ion has been confirmed for all anions, and the possibility to vary the dominant triplet has been obtained both from the stability itself and by including the properties of the IL matrix. Computed volumes show a large variation and have been connected with macroscopic properties such as conductivity and viscosity for lithium salt/IL systems with impact on the final electrolyte performance in batteries. A fine-tuning of electrolyte properties via only varying the triplet volume is suggested based on a correlation with several experimental properties derived from real battery studies.

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