

# Rational design of electrolyte components by ab initio calculations

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## Abstract

This paper is a small review of the use of computer simulations and especially the use of standard quantum-mechanical ab initio electronic structure calculations to rationally design and investigate different choices of chemicals/systems for lithium battery electrolytes. Covered systems and strategies to enhance the performance of electrolytes will range from assisting the interpretation of vibrational spectroscopy experiments over development of potentials for molecular dynamics simulations, to the design of new lithium salts and the lithium ion coordination in liquid, polymer, and gel polymer electrolytes. Examples of studied properties include the vibrational spectra of anions and ion pairs to characterize the nature and extent of the interactions present, the lithium ion affinities of anions, important for the salt solvation and the ability to provide a high concentration of charge carriers, the HOMO energies of the anions to estimate the stability versus oxidation, the anion volumes that correlate to the anion mobility, the lithium ion coordination and dynamics to reveal the limiting steps of lithium ion transport, etc.

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## 1. Introduction

The lithium ion containing electrolyte, whether liquid, polymer, or gel polymer based, is perhaps the part of the lithium batteries of today where there is most room for improvement. Properties of the bulk electrolyte may limit the battery performance (e.g. degradation, flammability, and voltage window), as may the properties of the electrolyte/electrode interfaces. Especially, the nature of the solid electrolyte interfaces (SEIs), both at anodes and cathodes, are strongly dependent on the electrolyte composition. Therefore, there is a strong interest to develop better battery electrolytes and preferably through a fundamental understanding of the factors finally limiting battery performance.

However, direct structure–property relations are troublesome to get about for electrolytes. This is due both to the range of possible interactions within the materials and in the electrode/electrolyte interfaces as well as the disordered structure, which limits the applicability of experimental structure characterization techniques severely compared to those

available for studying electrode materials. Simultaneously there is a driving force to use more complex and specialized electrolytes, which further complicates analysis of the interactions present and the linkage between each component and the resulting electrolyte/battery performance.

There are also high costs associated with the development of new electrolytes. It is thus highly essential to develop a cost-effective and systematic method for selection of appropriate electrolyte components. Ideally, such a method should be used as a tool for rational design of new components prior to usage or synthesis efforts, thereby serving as an effective and reliable screening device. It should also be advantageous with an as general and easily accessible method as possible to make comparisons using data from different sources, e.g. research groups and equipments, unambiguous. With the advent of many academic as well as commercial software packages, efficient and diversely tailored computational algorithms, and the everywhere abundant computational resources it is perhaps natural to seek the answer within publicly available standard ab initio computational chemistry methods.

Computer simulations can in many cases be successfully applied to electrolyte materials. The purpose and outcome

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of the simulations differ with the method applied: molecular dynamics (MD) and Monte-Carlo (MC) simulations model properties accessible using large ensembles. MD simulations have been applied by many different research groups to a wide range of non-aqueous liquid electrolytes [1–5] and to the more complex and intriguing solid polymer electrolytes (SPEs) [6–25], with a strong emphasis on poly(ethylene oxide) (PEO)-based lithium ion containing ones [6–11], but also SPEs based on other polymers than simple linear PEO [10,12,13], as well as SPEs based on other cations than lithium ions [8,14–25], especially sodium ions [14–17,20–22,24,25]. Recently also crystalline SPEs [26] have been subject to MD simulations [27] and also polymer electrolytes containing nano-particles [28–30]. MC simulations have been less frequently used, but have revealed the limiting step in ion conduction in polymer matrices by the development and testing of the dynamic bond percolation theory [31], have been used to model the  $\text{Li}^+$  adsorption on a metal electrode from a liquid electrolyte [32], and explained the difference between the conduction mechanisms in polymer electrolytes and polyelectrolytes [33,34].

On the other hand, ab initio calculations can only be applied to much smaller systems and are thus directed to probe properties dependent on local phenomena. The major benefit of ab initio calculations compared to MD or MC, apart from the inclusion of electrons and thereby electronic properties directly, is that the results are independent of any previously developed force-field and that local phenomena are treated undisturbed. In this paper, we will review the development of the usage of ab initio calculations with respect to lithium battery electrolytes. We have identified four different areas/systems where ab initio calculations have been applied to study properties of battery electrolytes either alone, in conjunction with experimental techniques, or to serve further simulations with necessary input data. The areas: (1) anions and ion pairs calculating the lithium ion affinities of the anions and the effect of formation of ion pairs in vibrational spectra used for characterization of electrolytes. For the anions also the volume and oxidative stability, important for the diffusion and the electrochemical stability window, respectively, can be calculated, (2) polymer conformation and flexibility—in polymer electrolytes the local structures and changes within the polymer chains and the associated energies and energy barriers are very important for the ion conduction mechanism, (3) the lithium ion coordination—the nature of the first solvation shell of solvent molecules, polymer chains, or combinations of these around a cation core, crucial to gain a molecular level insight to the cation conduction mechanism. This also includes the lithium ion environment in the new crystalline polymer electrolytes,  $\text{LiYF}_6\text{P(EO)}_6$  ( $Y = \text{P, As, and Sb}$ ) made by the St. Andrews group [26], and (4) additives to electrolytes to enhance the safety and/or the life-time of the batteries, often by promoting/prohibiting reactions at the electrolyte/electrode interfaces.

In general, the use of ab initio methods also allows the collection of different basic physical properties: local and global minima on potential energy surfaces, bond strengths, interaction strengths, charge distributions, etc. Below we summarize the data and interpretations collected over the years, together with an outlook on future possibilities in the area of applying ab initio methods to battery electrolytes.

## 2. Case studies

### 2.1. Anions and lithium ion–anion pairs

Ions and ion pairs were early studied using ab initio methods, mainly for simple ions like the halogens, but in the 1990s work on larger polyatomic anions and their lithium ion pairs started to appear, among the first being a study on  $\text{LiBF}_4$  [35]. In 1993, the first paper using ab initio calculations with the outspoken purpose of assisting in studies of lithium battery electrolytes was published on the triflate (Tf),  $(\text{CF}_3\text{SO}_3^-)$ , anion [36], quickly followed by two other papers on the triflic acid [37], and the lithium ion pairs [38]. The following year another study on the triflate anion also including lithium ion pairs and higher aggregates appeared [39].

These studies, on the at the time very popular electrolyte anion Tf, all focused on assisting in interpretation of vibrational spectra (IR and Raman). Thus, Gejji et al. calculated the vibrational spectra for Tf, for its corresponding acid HTf, as well as for mono- and bi-dentate 1:1  $\text{LiTf}$  ion pairs. In the work by Huang et al., the coordination environment of the lithium cation was altered to mimic a solvent by including OH-groups, for a more realistic interaction with the anion. One controversy among experimentalist was the order of the S–O and C–F asymmetric stretching vibrations. Together with the experimental and computational work on  $^{18}\text{O}$  substituted anions by Johnston and Shriver [40], the assignment of the vibrational spectra of the “free” Tf anion and the ion pairs was clarified, making future spectroscopic measurements on ionic interactions in electrolytes straight-forward for this anion/lithium salt.

Similar controversies, this time concerning the nature of the lithium ion pairs: mono-, bi-, or tridentate, existed for the  $\text{ClO}_4^-$  anion. In 1996, Klassen et al. [41] presented a paper clearly directed to the electrolyte community showing that the preferred coordination is bi-dentate. However, Ramondo et al. had made the same conclusion earlier, albeit using lower level calculations [42].

Due to the increasing amount of computational resources available, also larger anions become possible to study, following the experimental development of anions with more delocalized charges. Also a more elaborate study on Tf was made possible [43]. In 1995, a comparative study on the Tf, TFSI,  $[\text{N}(\text{CF}_3\text{SO}_2)_2^-]$  (a.k.a. the “imide” anion), and TFSM,  $[\text{CH}(\text{CF}_3\text{SO}_2)_2^-]$  (a.k.a. the “methide” anion), common being the electron withdrawing  $\text{CF}_3\text{SO}_2$  group, was published [44]. This study was directed towards the charge

distribution, analysis of the binding within the anions in detail, and to reveal stabilities by computing the chemical hardness from the HOMO and LUMO energies.

Later, a potential energy surface (PES) investigation revealed two possible stable conformers of the TFSI and its large internal flexibility, providing an additional explanation for the observed plasticizing effect apart from its delocalized charge [45]. Also, the vibrational spectra for the TFSI anion and the HTFSI acid was computed, revealing earlier errors in the assignment of bands used for observation of ion pairing in the electrolytes [46]. Finally also the ion pairs of LiTFSI and LiTFSM have been computed [47,48], revealing the common nature of the binding to two SO<sub>2</sub>-groups for TFSI and TFSM, but showing also that TFSI can complex the lithium cation by the central nitrogen atom [48]. A PES study, very similar to the TFSI one, was also made for the PFSI (or “beti”) anion [49]. In the late 1990s and early 2000s, it was possible to compute a wealth of properties for almost any anion/ion pair of interest at a reasonable computational level. Example of such studies using large anions are the TFSM and CTFSM [C(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub><sup>−</sup>] anions and their ion pairs [50], aromatic lithium salts [51], and the series of salts with the formula LiPF<sub>6−n</sub>(CF<sub>3</sub>)<sub>n</sub> [52].

We identify today two development lines of applying ab initio methods to anions and ion pairs: re-calculating earlier systems with much higher accuracy or extending the systems to include also solvents by explicit molecules or by using continuum models. Examples of the former are the high accuracy calculations, using very large and accurate basis sets, to develop better Li<sup>+</sup>–PF<sub>6</sub><sup>−</sup> potentials for MD simulations [53], studies of higher aggregates of [Li<sub>x</sub><sup>+</sup>(AsF<sub>6</sub><sup>−</sup>)<sub>y</sub>] [54], a new PES study on TFSI (and TFSM) [55] and using DFT methods to correlate dissociation and lattice energies [56]. Examples of the latter are the study on LiBF<sub>4</sub> in acetonitrile using explicit solvent molecules [57], the work by Wang and Balbuena on LiTf in polyphosphazene and water [12], the study on crystalline solvates using LiPF<sub>6</sub> and LiClO<sub>4</sub> and ethers by Grondin et al. [58], the of different ion pairs together with a solvent molecule by us [59], and studies on ion pairs using self-consistent reaction field continuum methods [2,60]. Also, calculations to support interpretation of vibrational spectra as before continues, but now applied to, e.g. the new salts LiTADC [Li<sup>+</sup>(N<sub>5</sub>C<sub>4</sub><sup>−</sup>)] and LiPATC [Li<sup>+</sup>(N<sub>5</sub>C<sub>6</sub><sup>−</sup>)] based on heterocyclic anions [61–63].

However, we find the most exciting development of using ab initio methods the possibility to predict not only stable structures and their vibrational spectra to assist in the characterization of electrolytes, but rather to assist in the development of new salts by assessing the (relative) interaction strengths. This strategy is inspired by Kim et al., showing the excellent correlation between salt lattice energies and interaction energies for 1:1 cation–anion systems [56]. Hereby, anions with low lithium ion affinities can be developed “in silico” (by use of computations prior to synthesis work) in a reliable manner, saving time and money. In Fig. 1, the obtained electronic energy differences for the reaction:

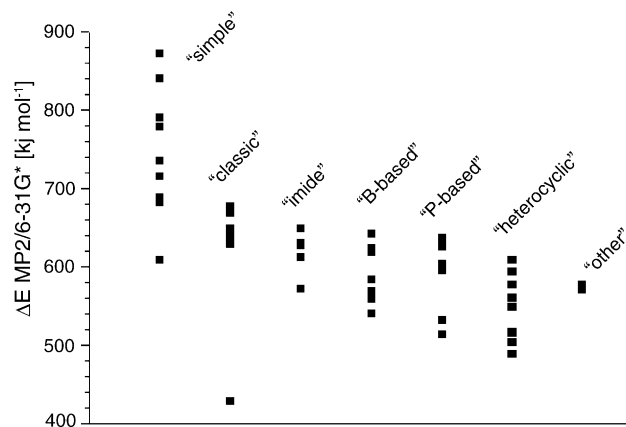


Fig. 1. Electronic energy differences between free anions and cations vs. ion pairs for families of lithium salts.

LiAn ⇌ Li<sup>+</sup> + An<sup>−</sup>, for different classes of anions are plotted. The anions are divided into seven families, albeit somewhat ambiguously: “simple” anions are, e.g. mono-atomic and OCN<sup>−</sup>, HCO<sub>2</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SCN<sup>−</sup>, CH<sub>3</sub>COO<sup>−</sup>, etc., “classic” weakly coordinating anions are, e.g. BF<sub>4</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup>, Tf, etc., “imides” are TFSI, TFSM, PFSI, etc., “B-based” anions those with a boron atom center, e.g. bis-(oxalato)-borate (BOB), malonato-oxalato-borate (MOB), etc., “P-based” anions those with a phosphorous atom center, e.g. PF<sub>6−n</sub>(CF<sub>3</sub>)<sub>n</sub><sup>−</sup>, PF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> (“FAP”), etc., “heterocyclic”, e.g. TADC, PATC, etc., and “other”, e.g. the N(CN)<sub>2</sub><sup>−</sup> anion. These are original data based on new calculations, details of which are to be presented elsewhere [64], though using starting geometries from the literature to a large extent. On the basis of these data, there are possibilities to focus on the types of anion chemistries most promising with respect to reducing the lithium ion affinity, eventually resulting in electrolytes with higher charge carrier concentrations.

The calculations can also be used to evaluate the stability versus oxidation for each anion using the HOMO energy (Fig. 2) as previously described [65,66]. The volume of the anion is another important attainable parameter as the anion diffusion in the electrolyte matrix should be inversely pro-

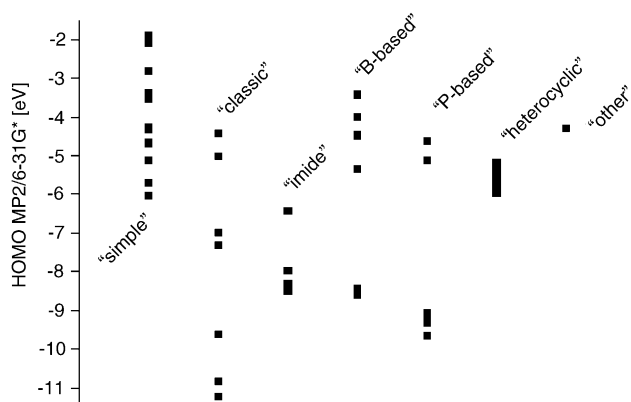


Fig. 2. HOMO energies for families of anions.

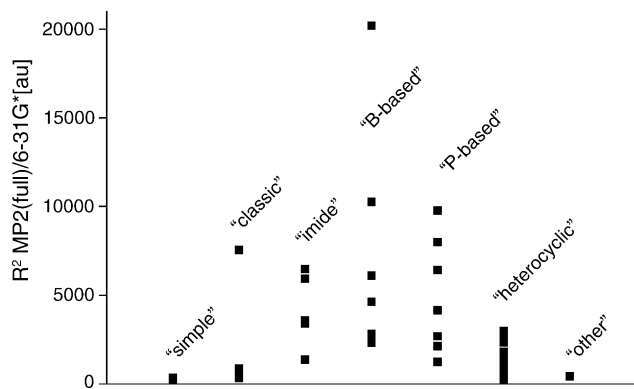


Fig. 3. Volumes for families of anions.

portional to the radius of the anion. A slow diffusion due to a large anion should decrease the total ion conductivity, but increase the cation transference number—one of the most crucial goals to resolve for lithium battery electrolytes. The extreme is the anion tethered or incorporated into the matrix as in single cation conducting polyelectrolytes. In Fig. 3, the volumes of the different families of anions are plotted using the electronic spatial extent as volume measure. The wide range of volumes available for most anion families should allow to specifically target the balance total ion conductivity and cation transference numbers a priori.

By studying the data further, we find the naïve notion of a correlation between a large anion and a highly dissociative salt (Fig. 4), to even qualitatively only be approximate for very small anions/large electronic energy differences.

Together these data provide information to justify choices of anions/lithium salts depending on preferences for the battery electrolyte, e.g. voltage and temperature working range, cation/anion transport number etc, hence showing the power of ab initio calculations on anions and ion pairs to assist in rational design of electrolytes.

One practical way is to apply quantitative structure–property relationships (QSPR) to the data. The choices of

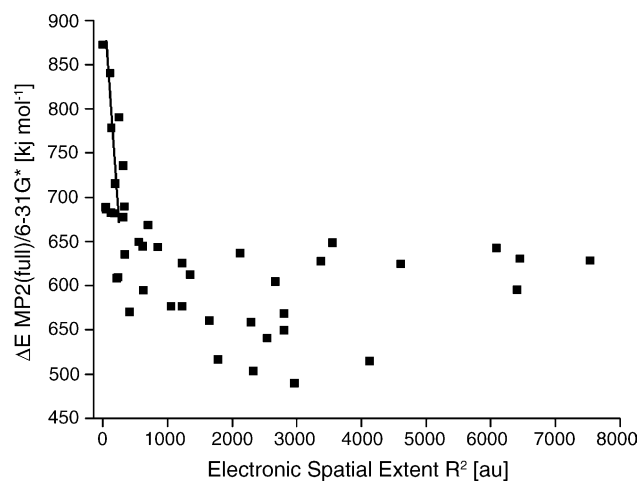


Fig. 4. Volumes of anions vs. electronic energy differences.

independent targets are, e.g. small electronic energy differences (as defined above for Fig. 1), low HOMO energies (large negative values); hence aiming at highly dissociative lithium salts that are electrochemically stable. Anion descriptors can be based both on primary chemical structure (#atoms, #halogens, #O, #N, etc.) and on computed properties (anion size, HOMO, LUMO, maximum atomic charge, etc.). Examples of ion pair descriptors are: electronic energy differences,  $\text{Li}^+$  coordination number, etc. A tentative QSPR analysis shows highly dissociative salts to be products of a large anion, a low LUMO energy for the anion, and preferably a  $\text{Li}^+$ –N coordination site. Low HOMO energies, characterizing electrochemically stable anions, are by the QSPR analysis found to be products of high LUMO energies and many halogen atoms in the structure.

However, the limited range of anions heavily affects the results and thus these conclusions should be used with care. Though, it is re-assuring that the QSPR results, e.g. that heavily fluorinated anions are electrochemically more stable versus oxidation and large anions in general provide dissociative salts, agree with knowledge from experimental data.

## 2.2. Polymer conformation and dynamics

While organic solvents for liquid electrolytes easily can be studied by ab initio calculations, polymers for solid polymer electrolytes are special and have properties difficult to grasp experimentally and thus merit an ab initio treatment. Simultaneously, polymers are difficult to attack by ab initio methods, making the scientific challenge greater. Amongst the polymers used poly(ethylene oxide), PEO ( $-\text{CH}_2\text{CH}_2\text{O}-$ ) $_n$ , has been the archetype ever since the first paper on alkali metal polymeric electrolytes [67] appeared in 1973. Therefore, the dominant model systems used in ab initio calculations to model SPE polymer conformation have been oligomers of PEO and often the so-called glycol dimethyl ethers (“glymes”),  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ . The use of a methyl end-capped oligomer is a very good approximation to high  $M_w$  PEO ( $n \sim 10^5$ ) with two OH-endgroups. Although oligomer models cannot be expected to reveal the ion conduction behaviour of a polymeric system, they can still be used to investigate the local dynamics and energies related to conformational changes.

Monoglyme ( $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_1\text{CH}_3$ ) has been extensively used by several groups for studies of PEO conformations [68–80]. Its small size allowed for treatment with high accuracy models (MP2 and higher) and large basis sets already in the 1980s, and use of continuum environments in the 1990s [68]. The main drawback of monoglyme is the short length making no part of the oligomer truly “non-end”. Several studies have specifically been aimed at calculating preferred conformations and internal torsion barriers between these [68–73,75,79–81]. The agreement between the size of the energy barriers in PEO with internal rotations in TFSI [45], revealed the specific plasticizing effect of the latter in  $\text{LiTFSIPEO}_n$  electrolytes.

Only one similar investigation for the popular experimental model polymer system poly(propylene oxide) (PPO) exists to the best of our knowledge [82]. This may be due to the fact that the “PPO–monoglyme” has a higher computational cost and an increased amount of conformers due to the tactic/atactic possibilities. The work by Sasanuma, however, is an extensive and clear account with most aspects of “PPO–monoglyme”.

One topic of interest from the polymer electrolyte community, as it may also effect the salt solvation capacity, has been the question if ab initio methods can explain the so-called gauche effect of O–C–O-based polymers, i.e. why the gauche conformation about a C–C bond is as or even more stable than an anti conformation [68,74,77,80,82]. The effect has been verified both by using infrared measurements in argon-matrices [69] and electron diffraction [83], and one suggestion made is the presence of a non-bonded C–H···O preferential contact, but there is still no consensus as to the origin of the effect nor to the resulting properties.

The next oligomer in length – the diglyme, CH<sub>3</sub>O(CH<sub>2</sub>–CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub> – has also found extensive use, although its larger size for a long time prohibited use of more sophisticated methods than Hartree-Fock. In 1994, Gejji et al. showed the effect of end-group versus non-end-group to be crucial when generating torsion potentials [84]. Diglyme, having both O–C–O and C–O–C/C–C–O–C dihedral angles that do not involve atoms inherently being from the methyl end-groups, was found to be a much better PEO model than monoglyme. In 1997, a thorough investigation with large basis sets and MP2 level calculations was performed, which revealed a large number of possible stable conformations [85]. The barriers for conformational changes were re-calculated and the authors suggested the gauche effect to become more pronounced for longer oligomer chains. Torsion potentials, for MD simulations, have in many cases been obtained by fitting analytical expressions to values from single-point ab initio calculations [15–17]. This is one way to get high accuracy MD potentials for a specific system, which for polymers-like PEO might be crucial as the intermolecular conversions, i.e. conformational changes, have low energy barriers.

Following a decreased interest in PEO-based electrolytes and other SPEs, together with the wealth of data already accessible, the activity within ab initio calculations to reveal polymer flexibility has declined, though new MD potentials still are published [86].

### 2.3. Lithium ion coordination

Whether the environment is liquid, polymeric, gel-like, or solid, understanding the nature of the lithium ion coordination is crucial to understanding the conductivity mechanism. All the above situations have to different extents been attacked by ab initio calculations.

For lithium ion batteries and liquid electrolytes, cyclic organic solvents like tetrahydrofuran (THF), ethylene carbonate (EC), propylene carbonate (PC),  $\gamma$ -butyrolactone

(GBL), and their mixtures have been proven to be efficient, especially with respect to cyclability. A mixture of two or more solvents allows the design of different electrolyte properties in a wider range and thus to enhance performance. The application of ab initio calculations to liquid electrolytes for lithium batteries was pioneered by Blint and his calculations on different ether and carbonyl oxygen containing species and their mixtures and the coordination of lithium ions [87,88]. His results on EC/PC coordination of Li<sup>+</sup>, always preferentially by the carbonyl oxygen atoms, have later been both verified and further refined by several authors [2,4,89–91]. Blint extrapolated, using data on three EC ligands around Li<sup>+</sup> that a four-coordinated complex would be dominant. Klassen et al. computed exothermal  $\Delta H$  for complexes with up to four EC ligands and recent higher levels of calculations by Wang et al. showed the Gibbs free energy to support the [Li(EC)<sub>4</sub>]<sup>+</sup> complex, with  $\sim S_4$  symmetry, to be the prevailing component. The data are in excellent agreement with MD simulations [1,2] and spectroscopic investigations [92,93], which further showed no preferential solvation in EC/PC mixtures, making the ab initio results using only EC ligands valid also for EC/PC mixtures. Apart from the studies by Blint, which considered also di-methyl ether, di-ethyl ether, acetone and water [87], and acetaldehyde [88], some recent studies have used acetonitrile [57] and  $\gamma$ -butyrolactone [5] as solvents. The latter solvent has gained interest due to its wide liquid-phase temperature range (–42 to 206 °C).

For modeling the lithium ion coordination in polymer solvents the preference for PEO model compounds is clear. Several ab initio studies on 1:1 complexes of monoglyme and a lithium ion were made in the mid 1990s [6,94–98]. The results were correlated with experimental studies on lithium salts both in PEO and in monoglyme [99,100]. Following the computer development larger model compounds for PEO have been used: diglyme (in both 1:1 and 1:2 complexes with a lithium ion) [101–105], triglyme [106], and longer glymes [107,108]. First with the use of longer glyme models a maximum coordination number of six for the lithium cation could be obtained. On the other hand, the di- and tri-glyme modeling efforts were successful in discerning whether the lithium ion transport mechanism in a polymeric matrix involves the anion or not [104], whether ion conduction is due to S<sub>N</sub>1- or S<sub>N</sub>2-type mechanisms [102–104], and located transition states of lithium ion movement along polymer chains and the associated barriers along the dominant internal reaction coordinate paths [102–104]. It seems as if higher Li<sup>+</sup> coordination numbers reduces the migration barriers regardless whether or not an anion is present [104].

Recently, other polymer matrices have been studied, among them the PEO-like polyalkyl oxides, PPO and PTMO, poly(trimethylene oxide) [109,110], and polyphosphazene (PP) [12]. The two former studies revealed steric hindrances to cause the stronger complexation by PEO compared to the other polymers for a six-coordinated lithium cation, while the latter showed the importance on the PP backbone nitrogen in the cation complexation. If other polymers are exploited as

matrices, there are today no obstacles from the computational side to study the local coordination of the cation, regardless of the size of the monomer unit.

A totally different polymeric environment for the lithium cation is found in the crystalline polymer electrolyte  $\text{LiYF}_6\text{P}(\text{EO})_6$  ( $Y = \text{P}, \text{As}, \text{and Sb}$ ) [26]. Recently, we investigated the lithium ion coordination and path of migration within  $\text{LiPF}_6\text{P}(\text{EO})_6$  by using single-point energy calculations on an oligomer model [111]. The obtained energy barrier, 1 eV, compares favorably with the Arrhenius activation energy obtained from ion conductivity data ( $\sim 1$  eV).

Gel electrolytes have been commercially used since 1999 and are today the dominating lithium battery concept [112]. In gels, the macroscopic properties of a polymer is combined with the liquid-like solvent properties, and this may affect also the lithium ion coordination environment. Examples of polymers often used are poly(acrylonitrile) (PAN) and poly(methyl methacrylate) (PMMA). Examples of solvents used are ethylene carbonate, propylene carbonate, or mixtures thereof. Whether the PAN or PMMA polymers take an active part in coordinating the lithium cation can be studied by computing binding energies using different combinations or polymer and solvent molecules [91]. For a PMMA-based gel, the pure solvent complex,  $[\text{Li}(\text{EC})_4]^+$ , seems totally dominant, in excellent agreement with discussions based on spectroscopic data where the interaction with PMMA is suggested to be very weak [91–93]. For a PAN-based gel a significant  $\text{Li}^+$ –polymer interaction, which increases with temperature, was found both computationally and spectroscopically (Fig. 5) [91].

A comparison not made before is that of cation coordination across liquid (e.g. EC/PC) to gel (e.g. PAN/EC/PC) to polymer (e.g. PEO) systems. We find that all three systems provide about equal binding energies for the lithium cation, despite the different maximum coordination numbers of  $\text{Li}^+$

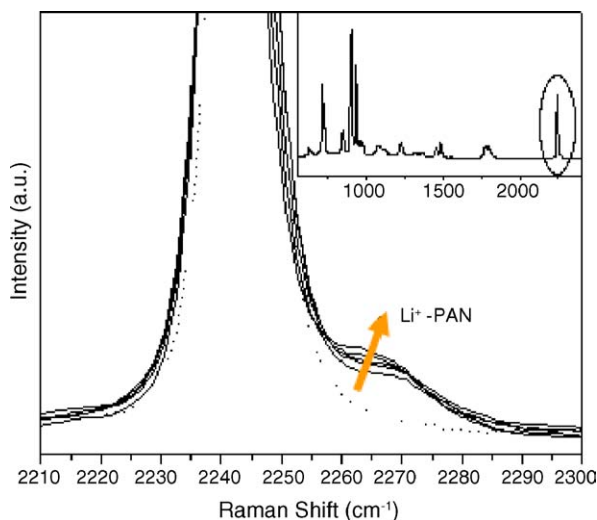


Fig. 5. Raman spectra of the  $\text{LiClO}_4/\text{EC}/\text{PC}/\text{PAN}$  gel polymer electrolyte in the C–N stretching region. The arrow indicates change upon heating (22–90 °C).

(six for the polymer system and four for the gel and liquid). This observation warrants further investigation, e.g. if true also for other polymers, gels, and liquid systems.

However, mixed liquid and polymeric environments of a lithium cation are not restricted to systems forming gels. Recently, Wang and Balbuena performed a study of  $\text{LiTf}$  dissolved in a mixed polymer (PP) and liquid (water) system [12]. The polymer acts as a hydrophobic membrane allowing  $\text{Li}^+$  transport to the anode, with application in Li/sea water batteries.

Mixed coordination can also result from interactions with solids dissolved in polymer or liquid phases, e.g. nano-composite polymer electrolytes. Nano-sized  $\text{TiO}_2$  has been reported to enhance ion conductivity, at least for poorly conducting (semi-crystalline) SPEs, and especially the cation transference numbers [113], while simultaneously increase the cyclability. However, the interactions between the electrolyte species and the nano-particles are not known. Recently, we found a lithium cation to coordinate strongly to a model rutile (1 1 0)  $\text{TiO}_2$  surface [114]. However, the  $\text{BF}_4^-$  anion was the species preferably adsorbed (Fig. 6), as compared to within a PEO matrix. This is in agreement with NMR data showing slower anion dynamics [115], and should result in increased cation transference numbers, as observed.

As new materials and species are used as electrolyte matrices/solvents the lithium ion coordination can easily be modeled using ab initio calculations to assist in the interpretation of the effects on the ion conductivity.

#### 2.4. Additives

Organic solvents used in liquid electrolytes are to some extent decomposed during the first charge/discharge cycle of a battery and a solid electrolyte interface (SEI) is formed. Subsequently, the SEI layer largely determines the performance of the electrode/electrolyte. If a small amount (a few percent) of a suitable additive is used, one which is broken down before the other electrolyte components, a better SEI layer can be formed and thereby reducing further side-reactions or exfoliation of graphite electrodes. Numerous experimental studies on both SEIs and additives exist, but only a few theoretical studies are to be found, most likely due to the more complex and demanding computational levels needed to accurately model reaction paths and systems with unpaired electrons present (as for radical reactions). To the best of our knowledge the first study was made by Scanlon et al. [116] using ab initio calculations in an attempt to correlate the stability of unsaturated cyclic ethers with their reported success to enhance cycle life by an order of magnitude in non-aqueous electrolytes [117]. However, the authors failed to find such a relationship, possibly due to other factors determining the experimental outcome.

More recently, experimental activity has focused on different unsaturated carbonates, e.g. vinylene carbonate (VC) and vinyl ethylene carbonate (VEC). The computational studies, by DFT and using continuum methods to implicitly include

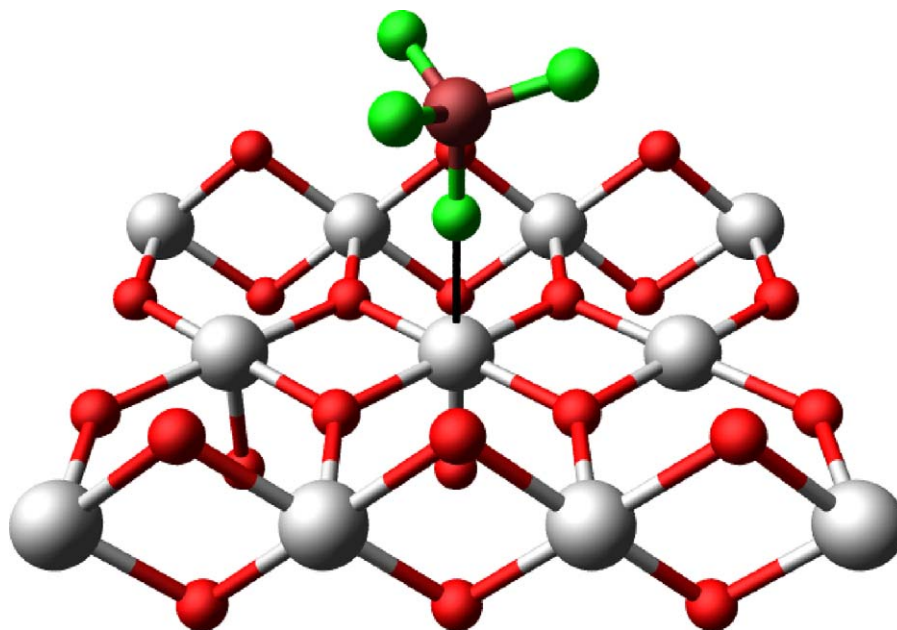


Fig. 6. Coordination of  $\text{BF}_4^-$  to rutile (110).

a solvent, on VC and VEC has focused on if the reduction mechanism is one- or two-electron based [118,119], shown that VEC has no barrier to overcome in its path to forming passivating lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) [119], and suggested how the polymerization of VC products may take place, forming the SEI layer [118].

However, in order to assess the relative stability of the additives versus the main solvents used, also the decomposition of the solvents must be modeled. Endo et al. modeled many different battery solvents using MNDO and HF level calculations [120,121], while later studies have primarily studied EC and PC using different DFT methods and also included solvent effects via SCRF methods [90,118,119,122]. We foresee this area of applying ab initio calculations to problems of battery electrolytes to prosper, as there are many outstanding issues with respect to electrolyte decomposition in general and the formation and stability of the SEI layer in particular.

### 3. Summary and conclusions

The application of ab initio calculations to various aspects of battery electrolytes and how these can assist in the design of new electrolytes has been reviewed. The strategy of by using ion pairs and anions to compute the salt dissociation and the stability versus oxidation form a basis to with confidence suggest new and better lithium salts, perhaps based on QSPR analysis. The calculations can reveal the barriers of conformational changes for polymers used to make polymer electrolytes and to construct new potentials for MD simulations. Furthermore, the calculations can assist in interpreting spectroscopic data, for both liquid, gel, and polymeric elec-

trolytes, and this way reveal the solvation of the lithium ion. Also lithium ion coordination within crystalline and nanocomposite polymer electrolytes has been modeled. The role and use of additives to liquid electrolytes is an important present and future area. The use of modeling techniques can now follow almost any new experimentally launched concept and contribute with accurate and cost-effective data to assist interpretation.

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