



# Solvation structure in dilute to highly concentrated electrolytes for lithium-ion and sodium-ion batteries



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## ARTICLE INFO

### Article history:

Received 7 January 2017

Received in revised form 3 March 2017

Accepted 4 March 2017

Available online 7 March 2017

### Keywords:

Highly concentrated electrolytes

Solvation structure

Lithium ion batteries

Sodium ion batteries

## ABSTRACT

The solvation structure of several lithium and sodium based electrolytes are explored as a function of salt concentration over a wide range via a detailed PM7 computational study. The cation coordination shells are found to be well-defined and solvent rich for dilute electrolytes, while disordered and anion rich for the more concentrated electrolytes. The Na-based electrolytes display larger cation coordination shells with a more pronounced presence of fluorine as compared to the Li-based electrolytes. The origins of the structural differences are discussed as well as their consequences for properties of battery electrolytes and battery usage—especially targeting the current large interest in highly concentrated electrolytes.

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## 1. Introduction

In a world with a growing urge for electrical energy storage, advances in battery technology are needed to improve the attractiveness for large-scale storage and electrical vehicles (EVs). The limitations with respect to stability, energy and power density needs to be addressed in order to better meet the safety, autonomy, and power standards and improvements required [1,2]. Lithium-ion batteries (LIBs) represent one of the most promising technologies, readily used already today, but recently also the prospect of sodium-ion batteries (SIBs) has re-emerged and grown into an active research topic. The cost of sodium is more than an order of magnitude lower than lithium and sodium is more than three orders of magnitude more abundant, while at the same time SIBs promise a similar level of performance as LIBs [3–7], rendering them future candidates for grid storage [8]. Moreover, the possibility to replace the Cu current collector in LIBs for Al current collectors at both sides in SIBs could push the energy densities further and again lower cost [6,9]. However, the similarities are more plentiful than the differences as for LIBs vs. SIBs.

For both LIBs and SIBs the electrolyte is a key component; e.g. the charge carrier concentration and the ion mobility are both crucial for the power rates as well as overall functionality. The standard LIB electrolyte is today based on 1.0 M LiPF<sub>6</sub> in mixtures of organic carbonates (propylene carbonate (PC), ethylene carbonate

(EC) and dimethyl carbonate (DMC)) with similar salts and solvents being investigated for SIBs [1,10]. Future LIBs/SIBs, however, will require novel electrolytes displaying *i*) wider electrochemical stability windows to allow cycling of high energy capacity cathodes and especially at higher voltages e.g. up to 5 V vs. Li<sup>+</sup>/Li<sup>0</sup> [11], *ii*) compatibility with these and other new electrode chemistries [5], *iii*) better thermal stability to withstand wider operational temperatures [12], and *iv*) surface and bulk structures and dynamics that allow for faster charge/discharge, i.e., cation desolvation and solvation [13].

Another important aspect is safety, which is mostly addressed by using polymer electrolytes to reduce/eliminate the risk of leakage of flammable liquids. However, polymer electrolytes still suffer from rather poor room-temperature conductivity [14,15]. Recently another concept has emerged; non-aqueous electrolytes with salt concentrations significantly above 1.0 M have been reported to exhibit remarkable properties including non-volatility, raising the concept of *super-concentration* (up to ca. 5 M or even above) as an interesting strategy [16]. Reversible LIB operation using both graphite and lithium metal anodes, and with enhanced kinetics have been demonstrated for a number of salts and solvents [17,18]. These improvements are attributed to a unique electrolyte structure that promotes an effective electrode passivation [13,18], prevents solvent co-intercalation into graphite [13,17,19], and facilitates (de)lithiation via a different lithium de-solvation mechanism as compared to “conventional” electrolytes [19–21]. The extensive ion-ion interactions are also inferred to be the reason for reduced volatility and hence increased thermal stability and also prevent polysulfide dissolution in the case of Li-S batteries

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[18,22]. Furthermore, a sharp increase in alkali cation transference number have been observed in ionic liquid based electrolytes, indicating that the transport mechanism is altered at elevated concentrations [23–25], and indeed an increase in lithium transference number was also observed in [18].

As solvents, both acetonitrile (ACN) and PC have recently been shown to allow for a reversible lithium intercalation in graphite only at high salt concentrations [13,26]. ACN possesses a dielectric constant of  $\epsilon_r = 37$ , a high oxidation stability [21], and is a rather small and well-studied molecule with respect to both liquid structure and ion solvation [27–29]. As for PC, it remains liquid over a much larger temperature range than the often used co-solvent EC and has a higher dielectric constant compared to ACN ( $\epsilon_r = 65$ ), allowing for a larger degree of salt dissociation enabling higher concentrations. Altogether this makes PC a solvent of interest for highly concentrated electrolytes [9,26].

An understanding of how these solvents and resulting electrolytes behave at the molecular level is needed for any rational improvement. Locally the electrolyte structure can be described in terms of *i*) the various solvates formed upon salt dissolution, *i.e.*, solvent separated ion pairs (SSIPs), contact ion pairs (CIPs), aggregates (AGG) [27], and *ii*) the cation coordination, primarily characterized by the cation-solvent and cation-anion distances and angles. This can either be done experimentally or computationally, and we will here advance the latter approach.

Indeed, the molecular level details of highly concentrated electrolytes have been addressed by several computational studies. Molecular dynamics (MD) simulations have been used to generate a large amount of configurations, thus allowing statistics on solvates as functions of salt concentration and anion type and linking these to phase behaviour [27,28] and transport properties [30]. However, the (classical) force fields used may fail in providing a proper description of highly concentrated electrolytes as the interactions become very non-standard. Density functional theory (DFT) in principle allows for an accurate description of the (electronic) structure, but as the computational cost scales rapidly with system size, this severely limits the possibilities of modelling any large ensembles and restricts the number of configurations. Therefore, DFT has so far been applied to optimize and validate MD force fields [22] and only recently to reveal the shift of the location of the electrolytes' LUMO - from solvent to anion - at high salt concentrations, the latter connected to the improved salt-based SEI with better passivation properties [31]. While combining MD with DFT allows for moderate ensemble sizes, the reduced number of configurations will *e.g.* produce radial distribution functions (RDFs) with a limited spatial resolution [31], and thus the fine structure information of the coordination environment is lost.

As a remedy, we here study the equilibrium configurations from a significant sampling of large ensembles obtained using semi-empirical quantum mechanical calculations. The Parametrized Method 7 (PM7) [32] is a Hartree-Fock based method with significantly improved descriptions of non-covalent interactions such as dispersion, hydrogen bonds and halogen bonds as compared to *e.g.* PM3 and PM6 [32,33]. By analysing descriptors such as radial distribution functions (RDFs), geometry, and topology, the methodological drawbacks of PM7 tend to vanish, giving results of similar quality as much more expensive DFT methods [34–36], why it also has been used for computations of  $\text{Li}^+$ -solvent cluster dynamics [37,38]. In this study we present PM7 calculations on lithium and sodium hexafluorophosphate ( $\text{LiPF}_6$  and  $\text{NaPF}_6$ ) in PC and ACN at different salt-to-solvent ratios covering dilute, concentrated, and highly concentrated electrolytes.

## 2. Computational

A set of systems of  $\text{LiPF}_6/\text{NaPF}_6$  in ACN with different salt-to-solvent ratios; 1:20, 1:16, 1:12, 1:6, 1:4, 2:5, and 4:7, were all built using the software Avogadro [39]. The ratios/concentrations were chosen to span the range from “dilute” via concentrated to highly concentrated electrolytes as addressed and classified by Seo *et al.* [18,28]. Similar molecular ensembles were created for  $\text{LiPF}_6/\text{NaPF}_6$  in PC; 1:12, 1:11, 1:10, 1:8, 1:7, 1:6, 1:5, 1:4, and 2:5. These ensembles were made with a racemic mixture of *R*-PC and *S*-PC. The explored molar ratios approximately correspond to 1.0–5.0 M for ACN [30], and for PC *ca.* 1.0–3.0 M.

The ensembles were subsequently divided into three categories; dilute, concentrated, and highly concentrated. For ACN, the ensembles with molar ratios 1:20, 1:16 and 1:12 were designated as dilute, 1:6 and 1:4 as concentrated, and 2:5 and 4:7 as highly concentrated systems, respectively, and for PC the molar ratios 1:12 and 1:11 as dilute, 1:10, 1:8, 1:7, 1:6 and 1:5 as concentrated, and 1:4 and 2:5 as highly concentrated systems, respectively. These three concentration systems/ranges were analysed for the influence of the cation, solvent, and salt concentration on the electrolyte structure.

Geometry optimizations were performed in MOPAC2012 [40,41] using PM7 with an implicit solvent applied via Andreas Klamt's COSMO solvation model with  $\epsilon_r = 36.64$  for ACN and  $\epsilon_r = 64.92$  for PC, using a radius of 0.18 nm [10]. Furthermore, frequency calculations were performed and only configurations corresponding to local minima were kept. For the dilute electrolytes 30 cations (extracted from 11 stable configurations) were studied in the ACN based electrolytes and 16 (16 configurations) in the PC, for the concentrated 43 (15 configurations) in ACN and 62 (54 configurations) in PC, and for the highly concentrated 50 (11 configurations) in ACN and 48 (20 configurations) in PC. For the smaller clusters (31 atoms, excluding the hydrogen atoms) stable structures were obtained in less than a minute, while for the larger (272 atoms, excluding the hydrogen atoms) a few hours were needed using an Intel® CORE™ i7 processor with 16 GB of RAM.

The RDFs  $g(r)$  were explored to obtain the interatomic distances between the electrolyte species. The RDFs are defined as the number  $n(r)$  of B atoms located at a distance  $r$  from a central atom A within a shell of volume  $4\pi r^2 \Delta r$ :

$$g(r) = n(r)/4\pi r^2 \Delta r.$$

RDFs were calculated for all geometries and then combined to form a single RDF for each of the categories and choice of cation. The first peak in the RDFs was integrated to yield the coordination number (CN). As several ensembles were used to create the RDF the variance

$$\text{Var}(\text{CN}) = \sum_i (\text{CN}_i - \mu)^2 / N,$$

and the standard error

$$\bar{\sigma} = \sigma / \sqrt{N},$$

were both calculated, where  $\text{CN}_i$  is the coordination number of cation  $i$ ,  $N$  the total number of cations present in all the ensembles belonging to the category,  $\mu$  is the mean CN, and  $\sigma$  is the standard deviation.

The solvation structures were further analysed by the angles; N–cation–N and O–cation–O for all nitrogen and oxygen atoms within a distance of 0.32 nm of a cation and their distributions were fractionated in six regions: I–VI, 0–30°, 30–60°, 60–90°, 90–120°, 120–150°, and 150–180°.

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