



## Functionalized ionic liquids as electrolytes for lithium-ion batteries



Shanthi Pandian <sup>a,\*</sup>, S.G. Raju <sup>a</sup>, Krishnan S. Hariharan <sup>a</sup>, Subramanya M. Kolake <sup>a</sup>,  
Da-Hye Park <sup>b</sup>, Myung-Jin Lee <sup>b</sup>

<sup>a</sup> Computational Simulations Group, SAIT-India Lab, Samsung R&D Institute, Bangalore 560037, India

<sup>b</sup> Energy Material Lab, Samsung Advanced Institute of Technology, 449-712, Republic of Korea

### HIGHLIGHTS

- Accurate and fast screening methodology for evaluation of electrochemical window.
- Enhanced electrochemical stability of phenyl functionalized ionic liquids.
- Phosphonium based ionic liquids with phenyl substitution shows EW of  $-4.4$  V.
- Thermodynamic stability of radical formed due to decomposition a critical factor.

### ARTICLE INFO

#### Article history:

Received 29 September 2014

Received in revised form

12 February 2015

Accepted 20 March 2015

Available online 27 March 2015

#### Keywords:

Lithium ion battery electrolytes

Room-temperature ionic liquids

Electrochemical window

Phenyl substitution

Density functional calculations

### ABSTRACT

The design of potential and new electrochemically stable electrolytes for Li-ion batteries is an important task in the field of energy. Room temperature ionic liquids (RTILs) characterized by a wide electrochemical window (EW) are the commonly used electrolytes for Li battery applications. In this work, a novel quantum computational method is proposed to estimate the electrochemical stability of RTILs that accurately predicts the trends in EWs of ammonium based ILs and is computationally faster than the state-of-the-art methods. Subsequently, the EW of ILs with phosphonium and sulfonium cations are computed and compared against the well-established ammonium congeners. Based on the criterion of electrochemical stability defined with respect to Li, the increasing order of stability is found to be: sulfonium < ammonium < phosphonium based ILs. The effect of various substituents like butyl, phenyl and benzyl on the phosphonium and sulfonium based ILs is examined and a greater stability for the phenyl over other substituents is observed. The key factor influencing the reduction potential of the cations is inferred as the thermodynamic stability of the radical formed during decomposition. Based on the results, design guidelines to identify stable IL systems as electrolytes in high voltage Li-ion battery applications are provided.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Due to desirable physical properties like vanishing vapor pressure, high thermal stability, good ionic conductivity, favorable solvation behavior and high electrochemical stability, characterized by the electrochemical window (EW), room temperature ionic liquids (RTILs) are widely used as electrolytes in Li-ion battery applications [1–4].

RTILs have the advantage that task-specific solvents can be

developed by varying the functional groups to suit the application [5]. Among the commonly used RTILs, ammonium based systems, such as imidazolium (IM), pyrrolidinium (Py) and quaternary ammonium (QA) (referred as acyclic) are extensively studied experimentally and theoretically. The effect of various substituents on IM based ILs have resulted in improved physical properties. The comparison of physicochemical properties on cycloalkyl and n-alkyl substituted IM have revealed that cycloalkyl substituted IM ILs are superior to n-alkyl substituted ILs [6]. Similarly, alkoxy functionalized IM and Py based ILs have shown promising characteristics than their alkyl counterparts [7–10].

An equally important class of ILs are the phosphonium based, which are shown to have superior properties than the nitrogen based congeners [11–14]. Studies on ILs containing cyclic

\* Corresponding author. Samsung R&D Institute, #2870 Phoenix Building, Bagmane Constellation Business Park, Outer Ring Road, Doddanekundi Circle, Marathahalli Post, Bangalore 560037, India.

E-mail address: [shanthi.p@samsung.com](mailto:shanthi.p@samsung.com) (S. Pandian).

phosphonium or sulfonium cations however are scarce. Cyclic phosphonium with benzyl and alkyl substitution, allyl functionalized trialkyl sulfonium, and alkylated cyclic sulfonium are a few promising candidates in this family [15–17]. It is reported that benzyl substituted phosphonium ILs show higher thermal stability and conductivities compared to alkyl-substituted phosphonium and the corresponding ammonium compounds [18]. This phenomenon is attributed to the presence of empty d-orbitals on phosphorous (which is absent in ammonium) and the interaction with  $\pi$ -electrons in the benzyl group, leading to greater bond strength. In terms of electrochemical stability, the alkyl substituted phosphonium with the dicyanamide (DCA) anion is shown to be superior to the ammonium cations [19]. Recently, the new group of ILs based on symmetric and asymmetric sulfonium cations have received interest due to their low viscosity, high conductivity and better physicochemical and electrochemical properties [20,21]. Although improved transport properties are well established, the electrochemical stability of such substituted sulfonium or phosphonium cations have not been examined from a theoretical standpoint in detail.

Quantum chemical studies on the computation of EW for organic or ionic liquid electrolytes for Li batteries are an active area of research [22–26]. Notable contributions in calculation of EW of ILs emphasize the importance of polarizable continuum model (PCM) and an improved way of estimating the EW [23,24]. The experimental values are reproduced accurately [22] using an ion pair model embedded in a polarizable continuum and recently [25], an improved method considering the redox potential of the solvent is proposed.

To the best of our knowledge, quantum chemical studies involve either the Hartree-Fock (HF) theory or density functional approach with significant HF contributions to evaluate the electrochemical stability of ILs. In a recent study [27], various Kohn-Sham density functionals are employed for the study of interaction energies between the cation and anion of ionic liquids. The study concluded that M06-L with a specific basis showed improved agreement with coupled cluster single double (CCSD) results. Recently a novel method [26] based on combined molecular dynamics (MD) and density functional theory (DFT) is shown to be successful in reproducing the EWs of RTILs. Given the maturity of the computational methods, the applicability of non HF based methods with established computational advantages [28] for EW computation of RTILs are not attempted.

The promising experimental results [23,24] on substituted phosphonium and sulfonium cations require sound theoretical models to support the improved performance, and to the best of our knowledge are not reported in literature. Additionally, the applicability of computationally faster non HF based methods for EW computations also needs a detailed analysis. To address both these issues, in this work, a novel quantum computational technique is developed and electrochemical stability of substituted phosphonium and sulfonium cations is estimated. The stability of an IL for Li-ion battery applications is reported principally relative to the Li metal electrode. When IL is used as the electrolyte however, it is the interaction with the Li salt in the electrolyte that decides the stability. Hence a novel stability criterion is defined relative to the Li salt in the electrolyte in terms of the reduction potential, and is analyzed in the present study. In addition the stability against Li electrode is also analyzed. In this work, established state-of-the-art methods and the proposed method are used for EW computation of ammonium based ILs and compared with reported experimental results. In subsequent sections, the proposed method is further used for the prediction of EW for substituted cyclic and acyclic phosphonium and sulfonium RTILs. For most of these molecules, the electrochemical range is not clearly established, and the simulation can provide insights into

their potential applications as electrolytes. In order to rigorously establish the utility of these RTILs, the effect of various functional groups (butyl, benzyl and phenyl) on phosphonium and sulfonium cations and comparison with their ammonium congeners is addressed in section 3.3 of the manuscript.

## 2. Computational details

### 2.1. Methodologies and EW evaluation

The computational approaches used the M06-L [29] and the B3LYP [30] functionals for the calculation of EW for ionic liquids. The performance of these functionals are well acclaimed for reaction mechanistic studies and also their accuracy in predicting electron affinity and ionization energy is well established and the results have been shown to be consistent with the experimental findings [31–35]. Calculations were performed in vacuum and in the implicit solvent phase in conjunction with the triple-zeta basis, 6-311 + G(2d,p) [24] and the SMD implicit solvent model is used [36]. A summary of the methodologies used, along with the procedure for the calculation of EW and the percentage error is provided in Table 1. The present study makes a comparison of two procedures for the evaluation of EW: i)  $\Delta$ SCF – Self Consistent Field method [23] and ii) one electron reduction method [24]. A brief explanation of both the methods as outlined in Refs. [23,24] is provided in the supplementary information. Accordingly, in the present study, methods M1, M2 and M3 involve the evaluation of EW using the  $\Delta$ SCF method and M4 and M5 involves the one-electron transfer accompanied by reduction decomposition of the cations. Amongst these methods, M5 will be of specific interest, as the performance has not been assessed before for EW computations. The EW values reported for the phosphonium and the sulfonium cations are derived from the reduction ( $V_{red}$ ) and oxidation potentials ( $V_{ox}$ ) of the cations and anions respectively, which are calculated as  $V_{red} = G_{cation+e} - G_{cation}$  and  $V_{ox} = G_{anion} - G_{anion-e}$  where  $G_{cation+e}$  and  $G_{cation}$  are the Gibbs free energies of the cation plus an electron and that of the cation respectively. Similarly  $G_{anion}$  and  $G_{anion-e}$  are the free energies for the anion and anion minus an electron respectively. The EW is then evaluated as the difference between  $V_{red}$  and  $V_{ox}$ . All the initial structures for the cations and anion were built using Avogadro [37] and imported as xyz-coordinates for optimization using Gaussian 09 [38].

The criteria considered to characterize the stability of an ionic liquid towards reduction and against the Li are stated as: i) For an IL with less affinity towards an electron have lower reduction potential and in turn higher resistance towards reduction [39] ii) Stability towards Li is evaluated by comparing the reduction potentials between the IL and that of Li/Li<sup>+</sup> reduction potential. Those with reduction potential values lower to that of Li/Li<sup>+</sup> reduction potential are considered to be stable compared to that of the Li in the electrolyte [40].

### 2.2. RTILs analyzed

A schematic representation of the ILs considered for the present investigation is given in Fig. 1. The present list spans the entire family of cations commonly used in RTILs. The bis(trifluoromethane) sulfonimide, (TFSI) anion is chosen as the common anion for the entire range of cations considered. The higher oxidation potential of the TFSI anion accounts for the choice of this anion in the present study [41]. The cations are classified according to the arrangement of the alkyl chains-as cyclic and acyclic structures. Thus, the imidazolium and pyrrolidinium of the ammonium group along with cyclic phosphonium and sulfonium cations forms the cyclic group of cations. The quaternary ammonium along with tetraalkyl

Download English Version:

<https://daneshyari.com/en/article/7732261>

Download Persian Version:

<https://daneshyari.com/article/7732261>

[Daneshyari.com](https://daneshyari.com)