



Effects of variation in chain length on ternary polymer electrolyte – Ionic liquid mixture – A molecular dynamics simulation study



S.G. Raju ^{a,*}, Krishnan S. Hariharan ^a, Da-Hye Park ^b, HyoRang Kang ^b, Subramanya Mayya Kolake ^a

^a Computational Simulations Group (SAIT-India), Samsung R&D Institute India-Bangalore, #2870 Phoenix Building, Bagmane Constellation Business Park, Outer Ring Road, Doddanekundi Circle, Marathahalli Post, Bangalore 560 037, India

^b Energy Materials Lab, Samsung Advanced Institute of Technology, Samsung Electronics Corporation, 449-712, Republic of Korea

H I G H L I G H T S

- Structure and dynamics of IL in ternary polymer electrolyte-IL mixture are studied.
- In ternary mixtures, there is larger propensity of ion-pair formation than in pure IL.
- Regions where polymer and TFSI anion interact with the IL cation are identified.
- Diffusion coefficient of C₃MPy is larger than of TFSI unlike C₉MPy and C₆MPy.

A R T I C L E I N F O

Article history:

Received 9 March 2015

Accepted 6 June 2015

Available online 14 June 2015

Keywords:

Lithium-ion battery

Polymer electrolyte

Ionic liquid

Molecular dynamics

A B S T R A C T

Molecular dynamics (MD) simulations of ternary polymer electrolyte – ionic liquid mixtures are conducted using an all-atom model. N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C_nMPy][TFSI], n = 1, 3, 6, 9) and polyethylene oxide (PEO) are used. Microscopic structure, energetics and dynamics of ionic liquid (IL) in these ternary mixtures are studied. Properties of these four pure IL are also calculated and compared to that in ternary mixtures. Interaction between pyrrolidinium cation and TFSI is stronger and there is larger propensity of ion-pair formation in ternary mixtures. Unlike the case in imidazolium IL, near neighbor structural correlation between TFSI reduces with increase in chain length on cation in both pure IL and ternary mixtures. Using spatial density maps, regions where PEO and TFSI interact with pyrrolidinium cation are identified. Oxygens of PEO are above and below the pyrrolidinium ring and away from the bulky alkyl groups whereas TFSI is present close to nitrogen atom of C_nMPy. In pure IL, diffusion coefficient (D) of C₃MPy is larger than of TFSI but D of C₉MPy and C₆MPy are larger than that of TFSI. The reasons for alkyl chain dependent phenomena are explored.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Room temperature ionic liquids (IL) [1–5] are a class of substances containing only ions and are liquid at or below 100 °C. These compounds are generally composed of an organic cation and an organic or inorganic anion. Since the constituents of ionic liquids interact via strong and long ranged Coulombic forces, they exert practically no vapor pressure. They can be used as solvents for a wide range of polar and non-polar solutes. Many reactions have been shown to be influenced when they are used as a solvent

[6–10]. IL are being studied [11–13] as replacements for polar-aprotic electrolyte solutions in lithium ion batteries. Standard organic electrolyte solutions could be problematic in terms of safety, when used with high potential cathodes. IL provide advantages in terms of thermal and electrochemical stability and non-flammability. Since bis(trifluoromethylsulfonyl)imide (TFSI) provides good anodic stability [12,11] to IL, it is the most commonly used anion and its interaction with Li⁺ is extensively studied [14–16].

Solid polymer electrolytes that are being studied for lithium ion batteries contain Li salts (LiX) and high molecular weight polymers like polyethylene oxide (PEO). Replacing the liquid electrolyte with polymers like PEO enables the creation of flexible, compact and powerful energy storage devices without the risk of electrolyte

* Corresponding author.

E-mail address: srini.raju@samsung.com (S.G. Raju).

leakage. These electrolytes however, have relatively low ionic conductivity even at ambient temperatures (10^{-5} S/cm). Addition of plasticizers [17–21] improves the electrical properties of polymer electrolytes by reducing the degree of crystallinity. Incorporation of room temperature ionic liquids, into polymer electrolytes enhances the ionic conductivity without compromising their electrochemical stability window [22–27]. A study on polymer-IL electrolytes made of poly (acrylonitrile), poly (ethyloxide) and poly (vinylalcohol), with imidazolium and pyrrolidinium based ionic liquids, has reported an electrochemical window of 3 V and ionic conductivity as high as 15 mS/cm [28]. Polymer-IL gels made up of N-butyl-N-methylmorpholinium bis(trifluoromethanesulfonyl)imide and poly (vinylidene fluoride)–hexafluoropropylene copolymer (PVdF(HFP)) have been shown to have good thermal stability and these gels with propylene carbonate have high conductivity [29].

In order to enhance the electrolyte applications of polymer – IL mixtures, recent studies have focused on tailoring the IL cations. Modification of the imidazolium cation by using longer alkyl chains [30,31] or by substituting the alpha-hydrogen [32–34] and use of new anion has resulted in reasonably good success [35–37]. Although modification of the IL ions is observed experimentally, there has been few studies to understand this effect from a molecular perspective. In this work, molecular dynamics simulation is used to understanding the effect of changing the chemical structure of pyrrolidinium cation in a ternary electrolyte. Four ternary electrolyte systems containing PEO chains, Li salt and IL with varying chain length are simulated. To assess the enhancement of the properties of IL in ternary electrolytes, pure IL systems are simulated for comparison. Structural and dynamic properties are calculated to provide a molecular level understanding of these ternary Li ion battery electrolytes.

2. Simulation methodology

Four ternary electrolyte systems containing IL, PEO chains and Li salt are simulated. N-alkyl-N-methylpyrrolidinium cation and bis(trifluoromethylsulfonyl)imide (TFSI) anion are used for IL. The alkyl chain on pyrrolidinium cation has one, three, six and nine carbon atoms. TFSI is the common anion for Li^+ and pyrrolidinium cation. Systems containing N,N-dimethyl-pyrrolidinium will be referred to as C1 systems. N-propyl-N-methylpyrrolidinium will be referred to as C3. Similarly systems with six and nine carbon chain on the pyrrolidinium ring will be referred to as C6 and C9. Each PEO chain has 27 monomers and 150 such polymers are used. 488 IL pairs, 195 Li^+ and an equal number of TFSI anions are used in the ternary systems. To compare the structure and dynamics of ionic liquids, simulation cells containing only IL are also generated. Each such simulation cell has 1250 ion pairs and varied in the length of the alkyl chain length on the cation. The starting configurations of all the systems are generated using the PACKMOL [38] package. All the molecules are randomly arranged in a cubic box in such a way that the closest distance between any two atoms is greater than a chosen tolerance value (3 Å). To achieve rapid mixing of all the components of the system, partial charges on all the atoms are halved and isothermal-isobaric (NPT) simulations are performed at 500 K for 5 ns. Average volume at this temperature is used to perform NVT (canonical ensemble) simulations at the same temperature for 5 ns. This process is repeated for 475 K and 450 K. Now all the partial charges are brought back to their original values and NPT and NVT simulations are performed at 425 K. A total equilibration of approximately 50 ns is performed on each system. Nose-Hoover thermostat [39–41] and barostat [42–44] is used. After the equilibration, trajectory of approximately [45] ns is obtained for each system at 425 K. Equations of motion are integrated using velocity Verlet algorithm with a time step of 0.5 fs. MD simulations

are performed using LAMMPS [45] code. The non-bonded potential was truncated at 12 Å and tail corrections to energy and pressure are applied. Coulombic interactions are treated using particle–particle mesh Ewald method using an accuracy of 10^{-4} . OPLS all atom force field [46,47] is used to describe the bonding and non-bonding interactions of PEO. These parameters were used by other researchers [48,49] to study PEO solutions using MD. Parameters developed by Lopes and Padua [50] and OPLS force field [51,52] for IL are used. These parameters were earlier successfully used [53] to describe the structure of pyrrolidinium ionic liquids. Lorentz–Berthelot mixing rules are used to obtain Lennard–Jones parameters for the cross terms.

3. Results and discussion

3.1. Structure

To study the local structure of IL and their interaction with PEO chains and Li^+ , radial distribution functions (RDF) are calculated. Interactions between molecules of IL can be classified as polar–polar (cation–anion, cation–cation and anion–anion), apolar–polar (cation–tail and anion–tail) and apolar–apolar (tail–tail). RDF of pure C3 are in Fig. 1. Center of mass of the cation and anion are used in these $g(r)$. They exhibit correlations identical to earlier molecular dynamics studies [54] of this ionic liquid. Notice the presence of two peaks in the cation–cation $g(r)$, which is typical of this cation family. Pair correlation functions between the center of mass of the pyrrolidinium ring and the center of mass of TFSI anion for the four pure IL systems are in Fig. 2. Since the center of mass of the cation changes when its the chain length increases, center of mass of the ring is used for the calculation fo these $g(r)$. There is an increase in the intensity of the first peak with increase in chain length on the cation. This increase in intensity is earlier observed for imidazolium based ionic liquids as well [55]. Comparison of $g(r)$ between cation and anion in the four ternary systems is in Fig. 3a. With increase in chain length of cation, there is an increase in cation–anion near neighbor correlation. The order of first peak's intensity is identical to that in pure IL systems. Comparison of cation–anion RDF of C3 system between ternary and pure IL is in Fig. 3b. Compared to pure IL, in the ternary system there is an enhancement of local structure between cation and anion. Similar increase in intensity of peaks is observed in C1, C6 and C9 systems (Figure S-1). This indicates an increase in the propensity of ion–pair formation in ternary systems compared to pure IL. This is confirmed

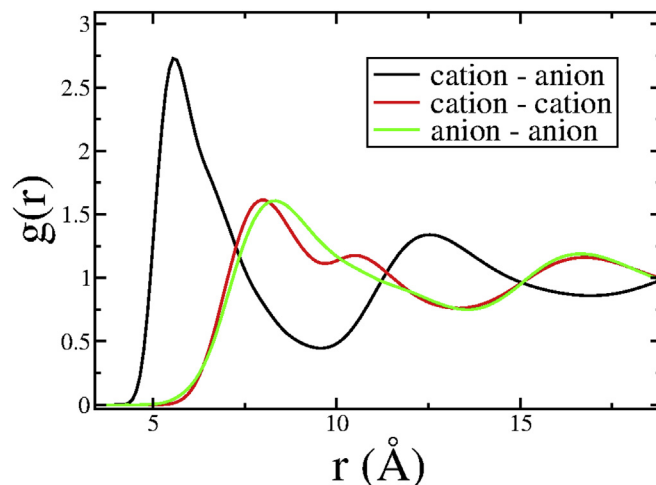


Fig. 1. Radial distribution function between ions in pure C3 IL.

Download English Version:

<https://daneshyari.com/en/article/7731621>

Download Persian Version:

<https://daneshyari.com/article/7731621>

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