

The Comparison of Ion Interactions in Sodium and Magnesium based Ionic Liquid Electrolytes with Al₂O₃ Nano-particles

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Abstract

Ionic liquid (ILs) based electrolytes are novel and considered as safer electrolytes for future rechargeable batteries due to their non-volatility and non-flammability. Lithium salts doped ILs have been studied up to a great extent. However, studies on incorporation of other salts based on sodium (Na) or magnesium (Mg) into ILs are lacking. Since ion transport properties such as ionic conductivity of these IL-salt mixtures are directly depended on the molecular structure and interactions, spectroscopic studies will be helped to develop these materials. In this work, we explore the ionic interactions of sodium triflate (NaTf) and magnesium triflate (MgTf) doped IL systems based on 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) IL and alumina (Al₂O₃) nano-particles by Fourier Transform Infrared (FTIR) spectroscopy. The 10 wt.% of Al₂O₃ nano-particles was added to each IL-salt mixture to investigate the change of solvation structure. Results clearly showed that, the addition of Al₂O₃ nano-particles indicates clear influence in the Na electrolyte system but weak in the Mg electrolyte system. This indicates that the Al₂O₃ nano-particles is more favoured to interact with monovalent cation (Na⁺) rather than divalent cation (Mg²⁺). These findings will help to understand the behaviour of IL based liquid electrolytes with nano-particles and guide experimentalists in optimizing IL-based electrolyte materials.

Keywords: Electrolytes, Ionic Liquids, Sodium, Magnesium, nano-particles, FTIR Spectroscopy

1. Introduction

Recently, research on sodium and magnesium rechargeable batteries has shown steady growth, driven by a communal goal to bring the rechargeable battery to market as an alternative option to the widely used Li-ion batteries (LIBs). The initial motivation originated from the fact that Na and Li ions both belong to the alkali metal family, and thus share many similar chemical properties. More attractive aspects of sodium ion batteries (SIBs) are the abundance of Na, ensuring a more sustainable supply, probably at a cheaper cost, for battery production. Moreover, the magnesium based rechargeable battery systems also have attracted attention due to its performance capabilities, which are expected to be close to those of Li-based rechargeable batteries. Magnesium is one of the ideal materials for the negative electrode for practical batteries because it has low electrochemical equivalence, considerably negative electrode potential, low cost due to natural abundance, and high safety than lithium [1,2,3].

For any successful battery technology, it is of uttermost importance to choose the right combination of electrodes and electrolytes in order to obtain the best performance, also with respect to cost and life-time, but a lot can be gained also by optimizing each component individually. The properties of sodium and magnesium-based electrolytes can be expected to be similar to those of lithium-based electrolytes, however,

there will likely also be differences due to their different cation sizes affecting ion solvation structure and ion transport mechanisms. The rechargeable battery electrolytes can be based on solutions of salts with mixtures of organic solvents, polymers or ionic liquids (ILs), however, among them room temperature ionic liquids (RTILs) have many properties of interest for safer and in some cases environmentally friendly batteries [4]. In particular, ILs are tailorable since they usually contain an irregular shape large organic cation and inorganic anion with high charge delocalization which keeps them liquid even at low temperatures. Also they attracted more attention due to their direct application in energy storage devices as ionically conductive materials, which have shown many advantages over normal organic solvents, including low volatility and better thermal and chemical stabilities. Therefore, they have attracted extensive interest as potential safer electrolyte materials for developing new Na or Mg based rechargeable batteries but there exist only a few scattered studies on Na⁺ and Mg²⁺ ion solvation in ILs [4]. The exploration on the underlying mechanism in super concentrated ILs is still in an initial stage, and it is expected to be different from the transport mechanism in dilute systems. In contrast, Li⁺ ion solvation in ILs in general, and IL-based-lithium-ion battery electrolytes in particular, have been studied extensively using many different approaches during the last decade [5,6,7].

In order to further enhance the physical properties of IL based electrolytes, dispersion of micro or nanosized ceramic particles has been attempted previously [8]. In this work, first we have carried out an analysis of the microscopic organization of concentrated IL systems of 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) IL with sodium triflate (NaTf) and magnesium triflate (MgTf) doped IL/salt mixtures. This will help to determine the solvation/coordination structure of the sodium/magnesium ions in IL and to reveal the structure-dynamics relationships and possible underlying mechanism for Na^+ and Mg^{2+} ion transport. Further, novel nanocomposite liquid electrolytes (CLEs) based on same ionic liquid (IL) and same salts and alumina (Al_2O_3) nano-particles were prepared and analysed the effect of nano-particle addition in two different systems using FTIR vibrational spectroscopy.

2. Materials & methods

Ionic liquid (IL), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf), sodium triflate (NaTf), magnesium triflate (MgTf) and alumina (Al_2O_3) nano particles (<50 nm particle size) were procured from Sigma Aldrich. The NaTf, MgTf and alumina were vacuum dried at 90 °C for about 12 h prior to use.

Initially, sodium and magnesium salts were added to the ionic liquid with compositions mentioned in Table 1 and the solution stirred at room temperature until the salt was fully dissolved. As a next step, alumina nanoparticles were added to the (NaTf/MgTf + BMIMTf) liquid electrolytes prepared as mentioned above and the solution stirred at room temperature until the homogeneous solution obtained. The electrolytes were heated in a vacuum oven at 90 °C for one day, to remove the residual water content. Finally, FTIR spectroscopy was used to determine the IL-salt interactions and the effect of nano-particle addition in two different electrolyte systems.

Table 1: Salt, IL and Al_2O_3 content of prepared samples. (where, molar fraction $x = 0.1$)

LE1	$x \text{ NaTf} + (1-x) \text{ BMIMTf}$
LE2	$x \text{ NaTf} + (1-x) \text{ BMIMTf}$ + 10% wt. Al_2O_3 nanoparticles
LE3	$x \text{ MgTf} + (1-x) \text{ BMIMTf}$
LE4	$x \text{ MgTf} + (1-x) \text{ BMIMTf}$ + 10% wt. Al_2O_3 nanoparticles

3. Results and discussions

The different regions of FTIR spectra of ionic liquid-based electrolytes without nano-particles and with nano-particles in both Na and Mg electrolyte systems are shown in Fig.1 (a-e). The closer inspection of those regions can be observed clear or slightly changed of vibrational bands that are directly connected to IL-salt, IL-nano particle or salt-nano particle interactions. However, changes are more significant for sodium system. The detail description on main changes found in different vibrational modes are discussed below in more details.

The CN deformation vibration of BMIM^+ cation of IL can be found in the region of 800-900 cm^{-1} [9] and shown in Fig. 1-(a). It is evidenced that in the LE1, there is a clear shoulder between wave number 865-885 cm^{-1} and it has disappeared after addition of Al_2O_3 nano-particles. This indicates the lowering of cation-anion interactions of IL after addition of nano-particles. However, formation of such shoulder in LE3 is not very clear and similar shape can be found in even LE4. The CF_3 vibrations of IL can be seen in the position at 1154 cm^{-1} [10] [Fig. 1-(b)]. In the Na electrolyte system (LE1), this band has moved to lower wave number showing increase of intensity after addition of Al_2O_3 nano-particles, however, such change cannot see in Mg based electrolyte system. The change in CF_3 vibrational band indicate that interaction between triflate anion and Al^{3+} in the alumina nano-particles are more significant in IL/NaTf mixture. It may be a result of changing solvation structure of IL and salt with alumina nano-particles and make availability of more free Na^+ ions. Thus, physical properties such as ionic conductivity can be increased.

These interactions could be cause to increase the dipole moment in the C-F bonds in the triflate anion in Na system. In the Mg electrolyte system CF_3 vibrational band appear slightly higher wavenumber compared to Na system showing different solvation structure of IL and salt having divalent cation. After addition of Al_2O_3 intensity of the peak has slightly dropped but peak position does not change. In this case F could be weakly bonded with Al^{3+} in the alumina and solvation structure of IL and salt is not affect with addition of nano-particles. These interactions clearly indicate the contrast in intensity and peak position changers at region 1140-1180 cm^{-1} of both Na and Mg electrolyte systems due to addition of nanofiller.

The big hump of spectra found at around 1220 cm^{-1} is representing the SO_3 anion vibrations from triflate anion [11] [Fig. 1(c)]. It is clear that shoulder appears in two different regions for two electrolyte systems although we used same IL. This difference is again noticeable that influence of different dipole moments of MgTf and NaTf affecting the coordination structure of IL/salt mixtures [12]. In the wavenumber region 1200-1300, intensity differences of spectrums between Mg and Na electrolyte systems indicate that triflate anion from MgTf vibrational mode have not changed after addition of Al_2O_3 . In addition to that, changes in the Na electrolyte system further confirms that CF_3 symmetric/asymmetric vibrations have changed as we discussed above in the wavenumber region 1140-1180 cm^{-1} . Fig. 1(d) indicates triflate anion vibrational intensity drop due to addition of Al_2O_3 in both electrolyte systems. Number of free triflate anion decline could be a reason for this vibrational intensity downshift. That may be the interaction between Al^{3+} and Tf^- when there is alumina in the system. On the other hand, in pure alumina spectrum broader vibrational band at 839 cm^{-1} correspond to Al-O vibrational peak [13] have not appear in the both electrolyte systems that could be another indicator for Al^{3+} interaction with triflate and O^{2-} interaction with BMIM^+ in electrolyte system. From

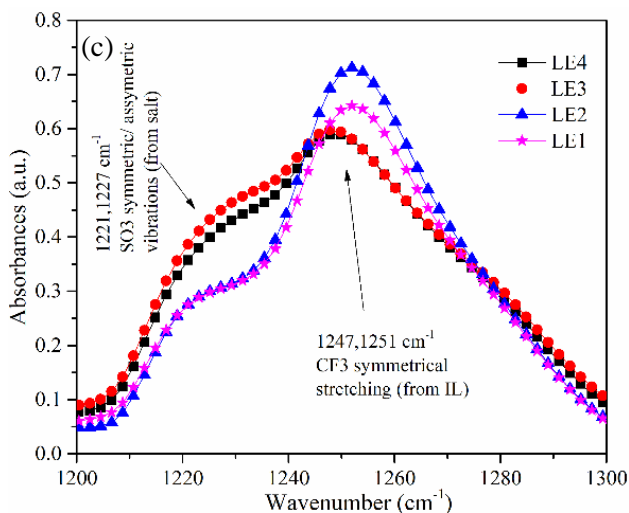
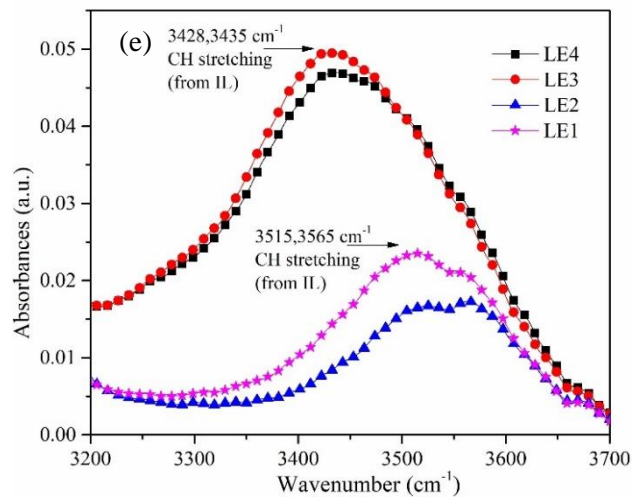
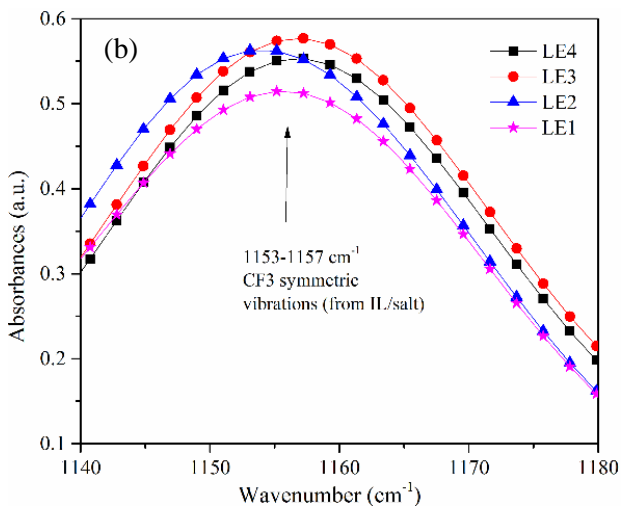
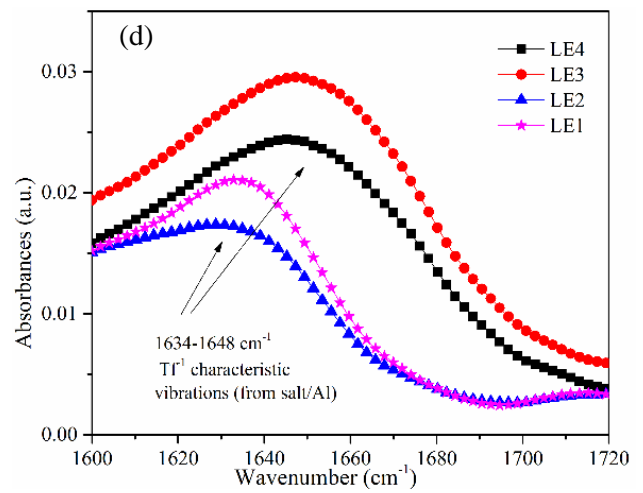
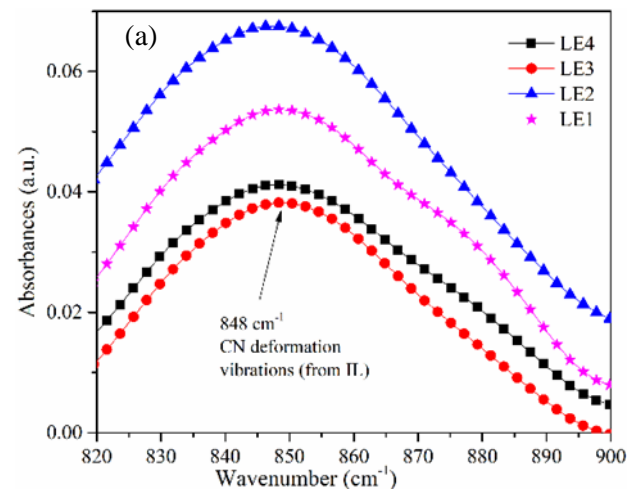


Fig.1 FTIR spectra of ionic liquid-based electrolytes without nano-particles and with nano-particles in both Na and Mg electrolyte systems.

these spectral changes can conclude there are more free Na^+ and Mg^{2+} ions in the electrolyte systems. Because of that we can expect ionic conductivity increment in both electrolyte systems after addition of Al_2O_3 nano particles. C-H stretching vibrations represent at 3565 cm^{-1} in the Na electrolyte system [Fig. 1(e)]. CH vibrational intensity decline can be seen in the spectrum of Na electrolyte system. According to the Fig. 1(e), H in the BMIM^+ could be interact with O^{2-} from Al_2O_3 . Because of these interactions, CH vibrational intensity may have decreased in the spectrum here. However, we cannot explain significant spectral changes in the Mg electrolyte system in this region. We can see that Al_2O_3 filler suggests active engagement in the Na electrolyte system, but Al_2O_3 filler implies poor interaction with the Mg electrolyte system [14].

4. Conclusion

Novel nanocomposite liquid electrolytes (NCLEs) were prepared based on NaTf and MgTf and dispersion of alumina (Al_2O_3) nanoparticle into IL. FTIR spectroscopic analysis was conducted in order to investigate the ion/nano-particle interactions and possible conformational changes in the NaTf/BMIMTf and MgTf/BMIMTf electrolyte systems due to the dispersion of Al_2O_3 nanoparticles. According to the vibrational spectroscopy analysis, the addition of Al_2O_3 nano-filler in to BMIMTf/NaTf mixture has strong influence on ion interaction reducing ion-IL coordination. However, solvation structure of BMIMTf/MgTf system does not change significantly with the addition of nano-filler. Na electrolyte system could be produced more free ions due to addition of Al_2O_3 and that could lead to a high ionic conductivity in the Na electrolyte system.

Conflicts of interest

There are no conflicts to declare

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