Ionic Liquids (ILs)-based Electrolytes System for Lithium Ion Batteries

Astrid O. Nandika, Achmad Rochliadi, Aep Patah*

Inorganic and physical Chemistry Research Group, Faculty Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

*Corresponding author: aep@chem.itb.ac.id

Abstract. Electrolyte system plays an important part in Lithium Ion Batteries (LIBs) due to its role in lithium ion (Li⁺) transport between anode and cathode. Commercial LIBs use organic carbonates-based electrolytes system, but these electrolytes are flammable and volatile. For these reasons, replacement with non-flammable, non-volatile and high conductive compounds become recent research focus. Owing to the excellent properties, ILs are expected to cover the limitation of the organic-based electrolytes system in LIBs. The conductivity of electrolytes system which consists of dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1, v/v) as organic solvent (OS) and imidazolium-based ILs is measured at various temperatures. Furthermore, the thermal stability of the electrolytes and the redox properties of lithium ion in IL-based electrolytes system are also investigated. [bmim][BF₄]-based electrolyte yields a conductivity of ~13 mS cm⁻¹ at 20 °C which is 10,000 times higher than DMC/DEC based only. Thermal analysis shows that the IL-based electrolytes decompose at 360 °C, much higher than the organic-based only (~110 °C). Cyclic voltammetry measurement of the ILs-based electrolytes with [bmim][BF₄]: DMC (3:1:1) + LiBF₄ 0.2 M compositions displays reversible redox reaction. The presence of [bmim][BF₄] affects the redox reaction of Li⁺ ion, in both current and potential. Based on these results, a mixture of ILs and organic solvent has a potential as a new electrolytes system in the next LIBs.

Keywords: Conductivity, Electrolyte system, Imidazolium, Ionic Liquids, Lithium ion

1. Introduction
Nowadays, lithium ion batteries (LIBs) are one of the most important rechargeable batteries. LIBs have been applied in various electronic devices due to their high energy density, long life cycle and less toxic compared to other commercial batteries.[1,2] In general, LIBs consist of electrodes (cathode and anode), separator membrane and electrolytes system. Electrolytes system plays an important role in lithium ion transport. Commercial LIBs usually use organic carbonates-based electrolytes system such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or a mixture of EC/DMC. However, their volatile and flammable properties have been a safety issue of LIBs which can initiate into an explosion.[3]

Some researchers proposed to replace the commonly used organic carbonates compound with polymer or ionic liquids (ILs) as the electrolytes system. Wang et al. reported a Li/LiFePO₄ cell with a
mixture of [bmim][BF$_4$]/γ-butyrolactone and vinylene carbonate resulted a high discharge capacity of 123 mAh g$^{-1}$ and stable up to 20 cycles.$^{14}$ Moreover, ILs can be an alternative electrolyte due to their excellent properties such as non-flammable, high thermal stability and conductivity.$^{5,6}$ Electrolytes system with a high conductivity, low viscosity and high thermal stability is needed to develop LIBs. To the best of our knowledge, the study of imidazolium-based ILs, DEC/DMC and LiBF$_4$ mixture in Graphite/LiFePO$_4$ batteries has not been reported. Here, we report the investigation of physical, electrical, thermal stability and electro-chemical properties of ILs-based electrolytes system.

2. Experimental Method

2.1. Materials
All chemicals were commercially purchased. 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$] 99.5% (Io-li-tec), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf$_2$] 99.0% (Io-li-tec), 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$] 99.5% (Io-li-tec), lithium tetrafluoroborate (LiBF$_4$) 98.0% (Sigma-Aldrich), DMC 99.0% (Merck) and DEC 99.0% (Merck).

2.2. Electrolytes System
Electrolytes system consisted of imidazolium-based ILs: DEC: DMC in various ratios of volume/volume. The different ratio between organic solvent and ILs was employed to investigate the optimal condition for the electrolytes system. The ratio between imidazolium-based ILs: DEC: DMC was (4:3:3), (2:1:1), (3:1:1) and (14:3:3) v/v. Lithium salt LiBF$_4$ 0.2 M was used in this electrolytes system.

2.3. Density and viscosity of ILs
The density of electrolytes system was measured using pycnometer, meanwhile the viscosity using Ostwald viscometer 200 at various temperatures of 20, 30, 40, 50, and 60 °C.

2.4. Conductivity of ILs
The conductivity of electrolytes system was determined using Hanna instrument HI 9033. Prior to use, the conductometer was calibrated with KCl solution 0.01 M, 0.1 M and 1 M at room temperature. The conductivity of electrolytes system was measured three times at various temperatures of 20, 30, 40, 50, and 60 °C.

2.5. Conductivity of ILs
Thermal stability of electrolytes system was obtained using Thermal Analyser NETZSCH STA 449F1. Sample (± 3 mg) was heated at temperature range of 20–500 °C under a N$_2$ atmosphere with a flow rate of 20 mL min$^{-1}$ at a heating rate of 10 °C min$^{-1}$.

2.6. Cyclic Voltammetry
Redox reaction of electrolytes system under voltammetric cyclic method was investigated using Gamry reference 3000 potentiostat/Galvanostat/ZRA. Glassy Carbon (GC), Platina (Pt) and Tungsten (W/WO$_3$) were used as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. Range of voltage from -3.5 until 3 V, scan rate of 100 mV s$^{-1}$ and equilibrium time of 600 s were employed in this measurement.

3. Results and discussion
An ideal electrolytes system should have low viscosity, high ionic conductivity, high thermal stability and reversible redox reaction. Those properties are important for LIBs electrolytes system.
3.1. Density and viscosity of ILs

The viscosity of liquid affects the ion mobility between anode and cathode, but on the other hand it depends on the density. Therefore, we measure the density of three types of ILs such as [bmim][BF₄], [bmim][NTf₂] and [bmim][PF₆]. Figure 1 shows the density and viscosity of ILs, [bmim][BF₄] yields the lowest density affected by its molecular mass. Molecular mass of [bmim][BF₄], [bmim][NTf₂] and [bmim][PF₆] is 226.03 g mol⁻¹, 284.18 g mol⁻¹ and 419.37 g mol⁻¹, respectively.

These results show good linear trends as reported by L. E. Barrosse-Antle et al. Furthermore, the increase of temperature measurement leads to the decrease of ILs density. Molecular mobility increases at a higher temperature and enlarges the volume which is inversely proportional to the density. Viscosity of ILs affects the lithium ion (Li⁺) transport between anode and cathode. ILs with a lower viscosity enhance the Li⁺ ion transport to electrode, thus facilitating the redox reaction process on the surface of electrode. Figure 3.1 also shows that the viscosity increases with an increase in temperature. These phenomena are caused by the thermal energy from environment that induce the molecules to move faster than at a low temperature. As a result, ion requires a relatively short time to move and decreases the viscosity of ILs. Moreover, the bulkiness of anion also affects the viscosity of ILs, a bulky anion requires a long time to move and reach the low part of viscometer. [bmim][NTf₂] yields the lowest viscosity compared with [bmim][BF₄] and [bmim][PF₆] because [NTf₂]⁻ anion has a less bulky structure among other ILs.

![Figure 1](image1.png)  
**Figure 1.** Density (black line) and viscosity (red line) of ILs at various temperatures.

![Figure 2](image2.png)  
**Figure 2.** Viscosity (red line) and conductivity (black line) of ILs at various temperatures.

3.2. Conductivity of ILs

The conductivity of ILs at various temperatures shows that [bmim][BF₄] has the highest conductivity compared with [bmim][NTf₂] and [bmim][PF₆]. Besides the viscosity, other factors such as ion pairing (H-bonding) between cation-anion and the environment condition (water or Cl⁻ ion impurities content) also influence the conductivity. Generally, ILs with low viscosity exhibit a higher conductivity due to the faster ion mobility. However, in this measurement [bmim][BF₄] yields the highest conductivity among other ILs because of the ability of ion pairing between [bmim]⁺ and [BF₄]⁻. Kundong et al. reported the order of ion pairing stability (H-bonding in imidazolium ring and anion) as follows: [BF₄]⁻ > [NTf₂]⁻ > [PF₆]⁻ using DFT calculation and molecular dynamic simulation. The more stable H-bonding with anion, the more difficult to dissociate. The conductivity of ILs depends on the cation, anion and also the impurities such as Cl⁻ ion and water content. It is already known that [bmim][BF₄] was a hydrophilic ILs, thus makes a further distance between anion and cation because of the water content in ILs. The presence of low amount of water in [bmim][BF₄] starts to weaken or break down the hydrogen bonding between the proton in imidazolium ring and anion. Therefore, this
property enables [bmim][BF₄] to have a higher conductivity than [bmim][NTf₂] which has the lowest viscosity. The result of conductivity measurement is shown in Figure 2.

Electrolytes system contains two crucial things, there are lithium salt and electrolytes. ILs have been investigated to replace the organic carbonates-based electrolytes system, but on the other hand ILs have a higher viscosity compared with common organic solvent. To overcome the low solubility of lithium salt in ILs, combination of organic solvent and ILs is used. Organic carbonates-based solvent is used to dissolve lithium salt and decrease the viscosity of ILs.

A mixture between [bmim][BF₄] and organic solvents DEC: DMC (1:1, v/v) has the highest conductivity among others, as shown in Figure 3. The conductivity increases proportionally with the number of ions involved in a mixture system. This system yields the highest conductivity due to the effect of organic solvents addition such as DEC and DMC that decreases the viscosity of [bmim][BF₄], therefore the ion mobility and conductivity increase.

Furthermore, in this study we use the ratio of organic solvents DEC: DMC (1:1, v/v) to optimize the electrolytes system. The optimization of electrolytes was conducted at 5 different ratios between ILs and organic solvent. The optimal condition of electrolytes system is [bmim][BF₄]: DEC: DMC (3:1:1, v/v), as shown in Figure 4. When the ILs ratio is higher than the organic solvents, it slows down the ion mobility due to the viscosity of ILs. Therefore, the conductivity decreases proportionally with the less organic solvent ratio.

3.3. Cyclic Voltammetry of Electrolytes system

Cyclic voltammetry (CV) is an electrochemical technique generally used to investigate the reduction and oxidation processes of molecular species. Voltammogram of electrolytes system that consists of [bmim][BF₄]: DEC: DMC (3:1:1, v/v) + LiBF₄ 0.2 M shows three reversible reduction and oxidation peaks. The first and second reduction peaks that reveal at -0.5 V and -1.5 V represent the reduction of [bmim]+ cation. Kroon et al. reported a formation of 1-butyl-3-methylimidazolium radical from [bmim]+ cation. [bmim] radical undergoes several reactions such as radical-radical coupling (dimer) or disproportionation reaction. The most possible mechanism was proposed by Kroon et al.
Figure 5. Voltammogram of [bmim][BF₄] + LiBF₄ 0.2 M (black line), [bmim][BF₄]: DEC: DMC (3:1:1, v/v) + LiBF₄ 0.2 M (red line) and EC: DMC (1:1) + LiBF₄ 0.2 M (blue line).

Radical-radical coupling reaction

Disproportionation reaction of two [bmim] radicals

Radical mechanism proposed by Kroon et al.

Figure 6. Radical mechanism proposed by Kroon et al.
Reduction peak at -2.5 V (Figure 6 (III)) indicates the intercalation of Li⁺ ion, meanwhile oxidation peak at 1.1 V (Figure 6 (III')) belongs to the de-intercalation of Li⁺ ion. Redox reaction of Li⁺ ion is found shifted when dissolved in ILs. The main factor of this result is suggested by the different viscosity of the solvents. In a high viscous solvent like ILs, the diffusion coefficients of Li⁺ are smaller than in organic solvent. Patah et al.[17] reported electro-active species like complex ion have various diffusion coefficients in different medium that depend on their viscosities. Moreover, the disproportionation reaction product (alkene) can be oxidized to form [bmim]⁺, this oxidation occurs at +1.5 V (Figure 6 (II')).

3.4. Thermal stability of ILs

Thermal stability characterization was conducted to investigate the decomposition temperature of electrolyte system. [bmim][BF₄]: DEC: DMC (3:1:1, v/v) + LiBF₄ 0.2 M electrolyte system exhibits a higher thermal stability than DEC: DMC (1:1) + LiBF₄ 0.2 M. TGA profile of this electrolyte system shows two steps of decomposition. The decomposition at 110 °C and 360 °C corresponds to the organic solvent and [bmim][BF₄], respectively. This electrolyte system stability is indicated by there is no significant weight loss at temperature range of 100–300 °C. This result explains that [bmim][BF₄]: DEC: DMC (3:1:1, v/v) + LiBF₄ 0.2 M electrolyte system has a great thermal stability even after heating process above 500 °C, yields residue about 33.9%. Addition of ILs to electrolyte system increases the thermal stability and the similar result has been reported by Wang et al.[8]

4. Conclusion

Electrolyte system of [bmim][BF₄]: DEC: DMC (3:1:1, v/v) has high conductivity, reversible lithium ion redox reaction and high thermal stability. This electrolyte system provides promise as an alternative to replace the organic carbonates-based in lithium ion batteries.

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