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Battery electrolytes based on saturated ring ionic liquids: Physical and electrochemical properties

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ABSTRACT

Physical and electrochemical properties of mixtures of ionic liquids based on saturated ring systems with carbonate based solvents were investigated. The conductivity and electrochemical stability of two series of ionic liquids based on piperidinium and pyrrolidinium cations with tetrafluoroborate and bis(trifluorosulfonylimide) anions were evaluated. The effects of the ionic liquid cation, substituent chain length of the cation function group, and the anion type on conductivity and electrochemical stability as determined by cyclic voltammetry were studied. The conductivity was influenced by the substituent chain length of the ionic liquid cation and the solvent carbonate type, where higher conductivities were observed with shorter substituent chains and EC versus PC. The saturated ring ionic liquid–carbonate mixtures may show particular promise for implementation as battery electrolytes due to notable high voltage stabilities, where stability >5.5 V was maintained in the presence of lithium salt. This study should promote development of future safe, high voltage lithium ion battery systems.

1. Introduction

As lithium ion batteries continue to supply power for a larger portion of the portable electronic industry, the electric vehicle market, and back-up grid storage, there is an increased demand to maximize their energy density and minimize their cost and safety hazards. Within the components of a lithium ion battery, the electrolyte plays a vital role in the continued operation of the battery, although it does not contribute to the energy content of the cell [1,2]. One key aspect of electrolyte systems that is under substantial investigation is the potential to increase the operational voltage limits of electrolytes beyond 4.5 V while still maintaining the favorable properties of conductivity, viscosity, and stability. This increased window of stability is essential in order to take advantage of novel high-voltage cathode materials to improve the energy density of the cell. Current electrolyte systems based on mixtures of carbonate solvents and a lithium salt offer relatively conductive solutions at 5–10 mS/cm, but their flammability and voltage stability window restrict the progress of lithium ion battery technology [3–5].

Ionic liquids may be a solution to increase the voltage limits of electrolyte systems, and ultimately the battery, while simultaneously increasing the safety of electrolyte systems. Previous studies of ionic liquids have shown electrochemical stabilities above a 4.5 V limit and superior thermal stabilities over conventional carbonate electrolyte systems [6–8]. Ionic liquids have been investigated as alternatives to conventional electrolyte systems due to the promise of increased electrochemical stability and thermal safety [6–8]. Many ionic liquids have been investigated in neat and mixed solutions to find an optimal balance of viscosity, conductivity, electrochemical stability, and thermal safety [9–15]. Pyrrolidinium-based ionic liquids in mixtures with ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC), acetonitrile, and the salts lithium-bis(trimethylsulfonyl) imide (LiTFSI), and lithium hexafluorophosphate ($LiPF_6$) have been investigated [10,16–19]. For many combinations, pyrrolidinium-carbonate mixtures have comparable conductivities to conventional carbonate systems (between 1 and 10 mS/cm). For example, an electrolyte system with a conductivity of ~2 mS/cm was obtained by the use of N-butyl-N-methylpyrrolidinium-TFSI with 1 M $LiPF_6$ EC:DMC [17]. A conductivity of 5.2 mS/cm was obtained

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Table 1
Full names and abbreviations of ionic liquids studied within this work.

Full name	Abbreviation
1-Methyl-1-propylpiperidinium-bis(trifluoromethylsulfonyl)imide	1M1PPi-TFSI
1-Butyl-1-methylpiperidinium-bis(trifluoromethylsulfonyl)imide	1B1MPi-TFSI
1-Ethyl-1-methylpyrrolidinium-tetrafluoroborate	1E1MPyrr-BF4
1-Methyl-1-propylpyrrolidinium-tetrafluoroborate	1M1PPyrr-BF4
1-Butyl-1-methylpyrrolidinium-tetrafluoroborate	1B1MPyrr-BF4
1-Ethyl-1-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1E1MPyrr-TFSI
1-Methyl-1-propylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1M1PPyrr-TFSI
1-Butyl-1-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	1B1MPyrr-TFSI

when the same ionic liquid was mixed with PC (50:50 v/v) and LiTFSI [16]. Piperidinium and morpholinium based ionic liquids have also been studied to a limited extent in carbonate mixtures. For example, in mixtures with 20% DEC, piperidinium-based ionic liquids showed anodic stability up to 5.5 V vs. Li/Li$^+$[18,20].

Investigating fundamental physical and electrochemical properties in a systematic way is beneficial to direct selection of ionic liquids for electrolyte systems. This work expands upon previous investigations to probe the physical and electrochemical properties of ionic liquids with 5- and 6-membered saturated ringed cations, specifically, pyrrolidinium and piperidinium cations with tetrafluoroborate and bis (trimethylsulfonyl) imide anions. The effects of cation type, anion type, and substituent length effects on conductivity and electrochemical stability will be discussed and compared to previously published results [21]. These results are discussed for neat ionic liquids and mixtures with both propylene and ethylene carbonate.

2. Experimental

The ionic liquids used for these experiments were purchased from Iolitec Inc. and were dried under vacuum prior to use. The water content after drying was measured to be below 100 ppm using Karl Fisher coulometry for all the ionic liquids. After drying, the ionic liquids and electrolytes were handled in an inert atmosphere glove box.

Mixtures of ionic liquid with propylene carbonate (PC), with ethylene carbonate (EC), and with $LiBF_4$ and LiTFSI salts were prepared by incrementally adding the PC, EC, or salt to the ionic liquid from 100% to 0% v/v ionic liquid. Conductivities of the solutions were measured using an Oakton CON 11 series conductivity probe at ambient temperature.

Cyclic voltammetry was performed using a glassy carbon working electrode with lithium metal counter and reference electrodes. Scans were completed using a CH Instruments potentiostat at 100 and 20 mV/s starting at 1.0–4.5 V and incrementally increasing the voltage window to 1.0–6.0 V.

3. Results and discussion

The study of the properties of ionic liquids is essential for progress toward their implementation as electrolyte systems for batteries. In conjunction with a previous report on two ionic liquid families based on unsaturated ringed cations [21], this work expands the investigation to their saturated ring counterparts with 5- and 6-membered rings. The physical properties and electrochemical assessment of different ionic liquid families and mixtures were evaluated to further understand the behavior of ionic liquids as potential electrolyte systems. Abbreviations for all of the ionic liquids used in this work, Table 1 is included to provide an abbreviation linked to the full name of each ionic liquid used.

4. Conductivity

Ionic liquids were mixed with carbonates to determine the conductivity as a function of ionic liquid percentage by volume. The conductivities of the ionic liquid mixtures were measured at 10% increments from 100% to 0% ionic liquid (Fig. 1). Fig. 1 shows the conductivities of (a) piperidinium-bis(trifluoromethylsulfonyl) imide (Pi-TFSI) ionic liquids mixed with EC, (b) Pi-TFSI mixed with PC, and (c) 1 M LiTFSI Pi-TFSI mixed with PC. The mixtures that included EC were measured to the upper solubility limit of EC in that given ionic liquid, which occurred at about 60% EC in ionic liquid for the Pi-TFSI series. Fig. 1a shows the conductivities for the series 1-methyl-1-propylpiperidinium-TFSI (1M1PPi-TFSI), and 1-butyl-1-methylpiperidinium-TFSI (1B1MPi-TFSI) combined with EC. The conductivities display a trend that propyl–methyl chain substitutions are more conductive over butyl–methyl substitutions for mixtures of Pi-TFSI ionic liquids with ethylene carbonate. The combination of 1M1PPi-TFSI with EC gives a maximum conductivity of 11.93 mS/cm at 50% ionic liquid, while the maximum conductivity of the 1B1MPi-TFSI:EC mixture is 10.19 mS/cm at the same concentration. This conductivity dependency on chain length is influenced by the viscosity of the ionic liquids, which increases as chain length increases, and is consistent with other reports for a variety of chain lengths with different ionic liquids [22]. Mixtures with PC demonstrate a similar trend with chain length for the same series of ionic liquids (Fig. 1b). The 1M1PPi-TFSI:PC mixture gives a maximum conductivity of 9.49 mS/cm at 40% ionic liquid in PC. The maximum conductivity for the 1B1MPi-TFSI:PC mixture is lower at 8.77 mS/cm occurring at 40% ionic liquid. While the similar trends are observed, the overall values of conductivity are reduced moving from an EC to a PC based mixture for a given ionic liquid.

As electrolytes for batteries would demand the presence of a lithium salt, the influence of LiTFSI at 1 M concentration was explored. The 1 M LiTFSI 1M1PPi-TFSI:PC solutions show a maximum conductivity of 5.63 mS/cm at 10% ionic liquid and the 1 M LiTFSI 1B1MPi-TFSI:PC solution has a maximum at 10% ionic liquid as well with a value of 5.47 mS/cm. The reduced conductivity with the addition of salt to the IL:PC mixtures is attributed to the increased viscosity with the addition of salt, which reduces the mobility of the ions. For the TFSI$^-$ containing solutions, a possible interaction may occur between Li$^+$ and TFSI$^-$ in stable triplets $[Li(TFSI)_2]^-$, reducing the number of charge carriers and decreasing conductivity even further [23].

A second family of ionic liquids was studied, based on pyrrolidinium-ring cations. The conductivity of pyrrolidinium-TFSI ionic liquids mixed with (a) EC, (b) PC, and (c) 1 M LiTFSI salt + PC was determined (Fig. 2). The upper solubility limit of EC in the Pyrr-TFSI series of ionic liquids occurs at 60% EC in ionic liquid for the two ionic liquids (1M1PPyrr-TFSI and 1B1MPyrr-TFSI) in this family that are liquids at room temperature; 1E1MPyrr-TFSI is a solid at room temperature so an EC mixture was not prepared. Fig. 2a shows the conductivities of 1M1PPyrr-TFSI:EC and 1B1MPyrr-TFSI:EC mixtures with maximum conductivities of