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Innovative Ionic Liquids: Electrolytes for Ion Power Sources

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Introduction: As technologies evolve from fixed-site equipment to warfighter-portable devices, the need for safe, compact, rechargeable power sources continues to grow. In spite of the emphasis on high energy density lithium ion (Li-ion) power sources, the fire and/or explosive hazards of these severely limit their utility to the warfighter. Logistical concerns further compound these difficulties, and are reflected in numerous federal and international regulations that limit how, and how many, lithium ion batteries can be shipped together. Thus, a twofold problem exists: increasing the energy density of batteries, while at the same time improving the safety of these devices to enhance their utility to the U.S. Navy and the Joint Services.

The key component responsible for the hazards associated with lithium ion batteries is the electrolyte. Typically, these electrolytes, even in gel form, are more flammable than jet fuels. Therefore, enhancing the safety of these systems is dependent on being able to replace these common electrolytes with a safer system. An ideal replacement choice is ionic liquids (ILs).

ILs are organic-based molten salts that are liquid at ambient temperatures. In general, the composition of these ILs incorporates a thermally and electrochemically stable, positively charged ring system, and an anion, such as a perfluorinated imide. It is this thermal and electrochemical stability and the stability of the organic components that have made ILs attractive alternatives to the more common organic solvents. As salts, the ILs are highly ionically conductive, have nearly no vapor pressure, and as such are non-volatile. Thermal analysis indicates that not only are they stable to over 350 °C, but also they do not explosively ignite as most other common organic solvents do, but instead thermally degrade by charring. Additionally, their dual salt and organic nature tends to make them useful as universal solvents. All of these factors combine to make them the ideal replacement for the more common, volatile electrolytes used in today's state-of-the-art Li-ion batteries.

Technical Approach: Our research demonstrates that tri-substituted imidazolium imide-based ILs can function not only as the electrolyte in a conventional lithium ion battery, but also as a solid nanocomposite separator when combined with an electrochemically stable polymer, such as PVdF-HFP (defined below), and ceramic nanoparticles, such as TiO₂ or BaTiO₃.¹ These components combine to form different types of either solid polymer ionic liquid (SPIL) separators

when only the ionic liquid and the polymer are present, or c-SPIL separators when nanoparticulate ceramics are present. Additionally, through the use of laser direct-write (LDW) techniques, we explore the process of forming LDW lithium ion microbatteries for direct incorporation into micro-circuitry.^{2,3}

Our research focuses on the ionic liquids composed of one of the two cations shown in Figs. 4(a) and (b), and one of the two imide-based anions, shown in Figs. 4(c) and (d), for a total of four different types of ionic liquids. All of the ionic liquids used in this work are prepared and purified at NRL. Two different types of polymers are used to prepare the SPIL nanocomposite separators: poly(ethylene oxide), PEO, which is a hydrophilic type of polymer, and poly(vinylidene fluoride-co-hexafluoropropene), PVdF-HFP, a hydrophobic polymer type.⁴

Results: Figure 5(a) shows a drop-cast PVdF-HFP SPIL separator, without nanoparticles. These flexible films exhibit nearly 90 percent of the ionic conductivity of the pure ionic liquid. Figure 5(b) is a high-resolution SEM image of the nanocomposite SPIL separator used for Li-ion microbatteries, deposited by the LDW process. As shown, these c-SPIL separators can be laser transferred as solid continuous membranes into a variety of configurations, forming a solid, electrolytic separator. Thus, these SPIL separators can not only be used as separators for batteries, but also as micro-electrochemical cells for a variety of sensing and/or energy harvesting technologies.

Our results also show that SPIL separators prepared using the hydrophilic polymer PEO exhibit much poorer mechanical and electrochemical characteristics when compared to SPIL separators prepared using the hydrophobic polymer PVdF-HFP. Experimental evidence indicates that in the PVdF-HFP gel the mobility of the Li ion is not limited by secondary interactions with the polymer backbone, which occur in the hydrophilic PEO-based SPIL separators. Analysis indicates that the hydrophobic tail of the imidazolium ring is strongly associated with the non-polar backbone of the PVdF-HFP, while the anion and the lithium salt are located in nanochannels within the mesoporous SPIL separator. Thus, the PVdF-HFP gels exhibit ionic conductivity comparable to the pure ionic liquid.

Figure 6 shows the charge-discharge behavior of the micro lithium ion battery created entirely by the LDW process (inset figure shows a sealed Li-ion micro-battery). The capacity, charge-discharge performance, and lifetime are all comparable to typical lithium ion batteries.

Conclusions: Our research has shown that these ionic liquids are not only suitable to replace the more flammable and dangerous types of electrolytes in

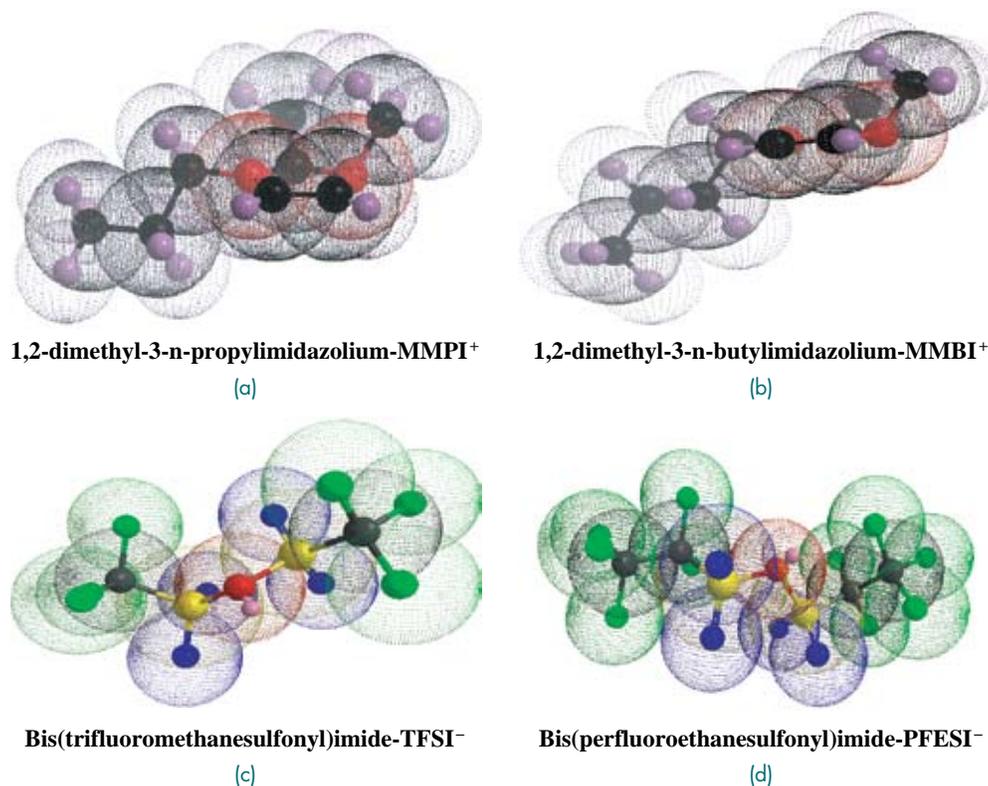


FIGURE 4

Molecular structure of cations (a,b) and anions (c,d) of the ionic liquids. Black spheres=carbon; red spheres=nitrogen; blue spheres=oxygen; yellow spheres=sulfur; green spheres=fluorine; purple spheres=hydrogen; small pink spheres=lone pair of electrons on the nitrogen of the imide. These four ions combine to form the following four ionic liquids: MMPI⁺TFSI⁻, MMPI⁺PFESI⁻, MMBI⁺TFSI⁻, and MMBI⁺PFESI⁻.

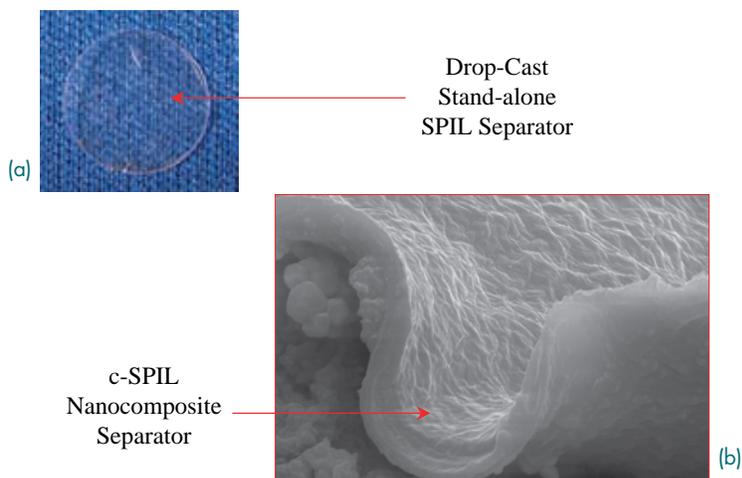


FIGURE 5

(a) Stand-alone SPIL separator composed of 80% MMPITFSI and 20% PVdF-HFP. (b) High-resolution SEM of a LDW-written c-SPIL separator. The LDW process creates a solid, continuous, flexible separator.

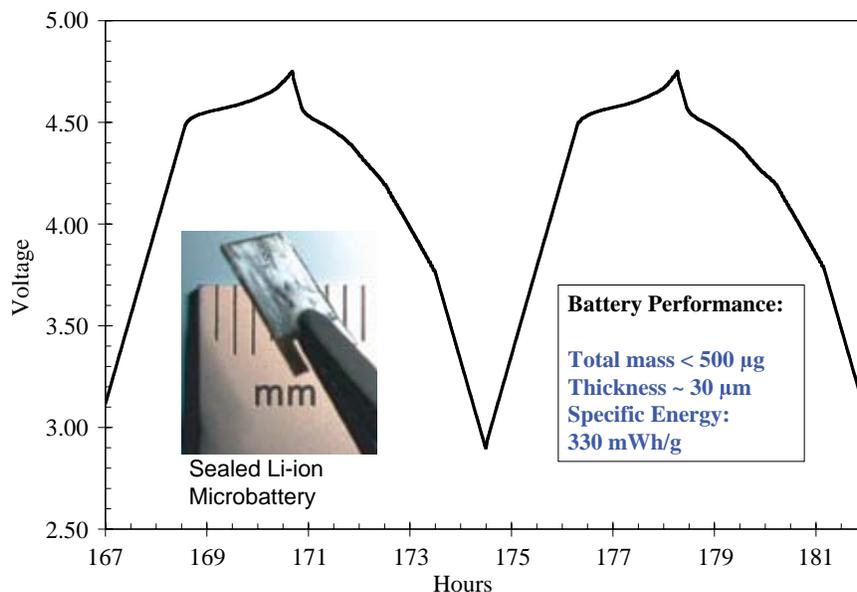


FIGURE 6 Charge-discharge behavior of the IL-based lithium ion microbattery. Inset on the left shows a sealed lithium ion microbattery. Inset on the right lists the battery performance.

lithium ion power sources, but that they can also be directly incorporated into micro-devices. As such, the enhanced safety should significantly increase the types of applications for these ionic liquids, and the ability to field safe, high energy density systems for the war-fighter.

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