



Novel binary deep eutectic electrolytes for rechargeable Li-ion batteries based on mixtures of alkyl sulfonamides and lithium perfluoroalkylsulfonimide salts



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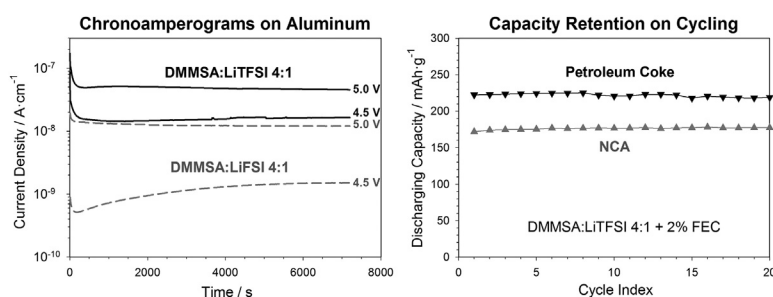
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HIGHLIGHTS

- Alkyl sulfonamide-Li perfluorosulfonimide salt deep eutectic electrolytes (DEEs).
- The viscosity of the DEEs exceeds that of LiPF₆/organic carbonates by factors ≥ 10 .
- A room temperature conductivity akin to that of LiPF₆/linear carbonate is achieved.
- Eutectics with LiTFSI display much higher thermal stability than those with LiFSI.
- Stable cycling with both negative and positive electrodes is demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

Ionic liquids (IL's) were proposed for use in Li-ion batteries (LIBs), in order to mitigate some of the well-known drawbacks of LiPF₆/mixed organic carbonates solutions. However, their large cations seriously decrease lithium transference numbers and block lithium insertion sites at electrode-electrolyte interfaces, leading to poor LIB rate performance. Deep eutectic electrolytes (DEEs) (which share some of the advantages of ILs but possess only one cation, Li⁺), were then proposed, in order to overcome the difficulties associated with ILs. We report herein on the preparation, thermal properties (melting, crystallization, and glass transition temperatures), transport properties (specific conductivity and viscosity) and thermal stability of binary DEEs based on mixtures of lithium bis(trifluoromethane)sulfonimide or lithium bis(fluoro)sulfonimide salts with an alkyl sulfonamide solvent. Promise for LIB applications is demonstrated by chronoamperometry on Al current collectors, and cycling behavior of negative and positive electrodes. Residual current densities of 12 and 45 nA cm⁻² were observed at 5 V vs. Li/Li⁺ on aluminum, 1.5 and 16 nA cm⁻² at 4.5 V vs. Li/Li⁺, respectively for LiFSI and LiTFSI based DEEs. Capacities of 220, 130, and 175 mAh g⁻¹ were observed at low (C/13 or C/10) rates, respectively for petroleum coke, LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ (a.k.a. NMC 111) and LiAl_{0.05}Co_{0.15}Ni_{0.8}O₂ (a.k.a. NCA).

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1. Introduction

At present, battery industry state-of-the-art electrolyte solutions for rechargeable Li-ion batteries (LIBs) are based on solutions of lithium hexafluorophosphate (LiPF_6) in mixtures of organic carbonates. These electrolyte solutions, while being today's best compromise between acceptable cost, desirable properties, and drawbacks, are truly not optimal for Li-ion battery performance due to several shortcomings: poor hydrolytic stability and thermal stability of the LiPF_6 salt; low flash points and high vapor pressures, hence flammability risk of linear carbonates and their reduction at graphitic negative electrode surfaces, with a mixture of gases as decomposition products. Given the drawbacks of carbonate-based LiPF_6 electrolyte solutions, considerable efforts have been expended over the past twenty years on the development of new salts [1–6], partially fluorinated organic carbonate solvents [7–11], as well as novel concepts such as redox shuttle additives [12–14], ionic liquids [15–18], and polymeric ionic liquids [19–22]. However, despite progress in all these areas, there still does not exist a viable electrolyte solution to replace LiPF_6 /carbonates mixtures in high energy or high power rechargeable LIBs.

Ionic liquids (or ILs, for short; a.k.a. room temperature molten salts) were proposed as alternatives to, and also as major components of, LiPF_6 -based LIB electrolytes, due to some very attractive properties: wide liquid range, exceptional thermal stability, nano-Torr vapor pressures, high intrinsic ionic conductivity, very wide electrochemical stability windows (ESWs), and the ability to reversibly cycle metallic lithium electrodes. However, most if not all ILs proposed so far for LIB use have some serious drawbacks. First, the ionic conductivity of the ILs often decreases upon addition of a lithium salt [23–26], which is the only electrolyte of importance for LIBs. Second, while in conventional lithium salt-in-solvent solutions the Li^+ transference number ranges from 0.33 to 0.40, for most IL-based Li electrolytes it has values of only 0.15 to 0.20 [27–30]. Third, the large cations of ILs accumulate at the electrode-electrolyte interface towards which the Li^+ cations are moving, leading to an increased interfacial polarization and a significant decrease in the rate capability of LIBs [25,31]. Fourth, the low temperature conductivity of ILs is significantly lower than that of traditional (liquid) electrolyte solutions, leading to a worsening rate performance with decreasing temperature, which makes ILs impractical for use in batteries that must operate at low temperatures [32]. Some of the drawbacks of ILs could be removed by using a Li^+ cation-only IL having a high lithium cation transference number, improved conductivity across the entire operating temperature range of interest for LIBs, and an electrochemical stability window appropriate for higher voltage LIB electrodes. The existence of Li^+ as sole cation should significantly improve the rate capability of LIBs with such an electrolyte, due to an increase in lithium transference number and the elimination of electrode polarization. However, the formulation of an IL with Li^+ as the only cation remains so far an unsolved challenge. Formulation of such ILs is hindered mainly by the fact that the only experimental variables available for their formulation are the chemical structure and the relative ratios of anions in the IL.

An alternative to pure ILs, which displays similarly desirable properties, are salt-in-solvent systems, i.e., solvent-deficient mixtures in which the solvent-to-salt mole ratio is equal to or even smaller than the solvation number of the respective salt in a dilute solution. Such concentrated solutions are often binary eutectic melts, formed by mixing organic compounds and lithium salts all of which are in solid form at room temperature. Binary eutectic mixtures, also known as binary deep eutectic electrolytes (or DEEs, for short), represent a class of Li^+ cation-only melt electrolytes which has been investigated during the past decade [33–39]. We

would like to point out that DEEs have been erroneously described previously as ionic liquids in the peer-reviewed literature, even though the term “ionic liquid” is reserved strictly for systems consisting solely of anion and cation mixtures, i.e., devoid of any neutral (covalently bound) components. The best-in-class (as far as the specific conductivity concerns) among these types of binary systems so far are mixtures of acetamide with bis(trifluoromethyl)sulfonimide (LiTFSI) and with lithium bis(perfluoroethyl)sulfonimide (LiBETI) salts. The acetamide:LiTFSI system has a specific conductivity of 1.07 mS cm^{-1} at 25°C at 4:1 composition, while oxidation and reduction potentials are 4.4 V and 0.7 V vs. Li/Li^+ , respectively [35]. The acetamide:LiBETI system, while exhibiting a slightly higher specific conductivity of 1.27 mS cm^{-1} at 30°C , has a narrower ESW with oxidation and reduction potentials of 3.8 V and 0.6 V vs. Li/Li^+ , respectively [39]. While a few of these DEEs have properties desirable for LIB electrolytes [35–39], it must be noted that their specific conductivity is still inadequate for automotive LIB applications at room temperature and seriously deficient at low temperatures.

We hereby report on a new class of binary deep eutectic electrolytes consisting of mixtures of alkyl sulfonamides (methanesulfonamide, $\text{CH}_3\text{SO}_2\text{NH}_2$ or MSA, melting point 85°C ; and N,N-dimethylmethanesulfonamide, $\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)_2$ or DMMSA, melting point 49°C) with lithium perfluoroalkylsulfonimide salts (lithium bis(fluoro)sulfonimide, $\text{FSO}_2)_2\text{NLi}$ or LiFSI; and lithium bis(trifluoromethane)sulfonimide, $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ or LiTFSI). Although we prepared and investigated a large number of these binary solutions, the present publication discusses only the materials with the highest specific conductivity in each class, that is, the most promising candidates for LIB applications. Their preparation method is presented herein, together with characterization of their thermal properties by differential scanning calorimetry (DSC); transport properties by specific conductivity and viscosity measurements; and thermal stability by DSC and thermogravimetric analysis (TGA). The density of these DEEs was also measured and was used for determining their molar conductivities. Their promise for LIB applications is demonstrated by chronoamperograms measured on Al working electrodes and by their cycling behavior in half cells with petroleum coke, $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ (a.k.a. NMC 111) and $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$ (a.k.a. NCA) electrodes.

2. Experimental

The following materials were used from commercial sources: methanesulfonamide 98+% ($\text{CH}_3\text{SO}_2\text{NH}_2$ or MSA), N,N-dimethylmethanesulfonamide 98+% ($\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)_2$ or DMMSA), from Alfa Aesar, Ward Hill, MA; LiTFSI salt 98+% (or LiTFSI) known as product HQ-115 from 3 M Company, St. Paul, MN; and potassium bis(fluoro)sulfonimide ($(\text{FSO}_2)_2\text{NK}$ or KFSI) from HUST, Wuhan, China. Lithium LiFSI was synthesized in-house at Clemson University, using KFSI as precursor, as described in the [Supplementary Material](#). Binary mixtures of alkyl sulfonamides and lithium perfluoroalkylsulfonimide salts were prepared at several mole ratios inside an argon-filled glove box by simple mechanical mixing of pre-weighed amounts of the two components.

To elucidate phase behavior, differential scanning calorimetry (DSC) was performed between -120 and 150°C with a temperature change rate of $10^\circ\text{C min}^{-1}$, using a Mettler Toledo 820 calorimeter, to determine the glass transition (T_g), crystallization (T_c), and melting (T_m) temperatures. The test protocol consisted in cooling from room temperature to -120°C , followed by three heating-cooling cycles between -120°C and $+150^\circ\text{C}$ to check for data reproducibility. The data shown in the figures was collected during the second thermal cycle.

The specific conductivity was determined from -40°C to 100°C

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