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Bio-inspired choline chloride-based deep eutectic solvents as electrolytes for lithium-ion batteries

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ABSTRACT

The safety issues of lithium-ion batteries require the substitution of volatile and flammable organic components of the electrolyte. In this context, deep eutectic solvents (DESs) represent an interesting alternative to conventional ionic liquids as green solvents to dissolve common lithium salts. This paper explores two eutectics: i) ethylene glycol/choline chloride (EG/ChCl, 3:1 mol/mol), and ii) L-(+)-lactic acid/choline chloride (LA/ChCl, 2:1 mol/mol). The lithium salts added in both cases were $LiN(CF_3SO_2)_2$ and $LiPF_6$, both in concentration of either 0.5 M or 1 M. They still retain their liquid properties despite the addition of relatively high molar contents (up to 1.0 M) of lithium salts. The 0.5 M $LiPF_6$/EG:ChCl electrolyte, in particular, displays ionic conductivity of 7.95 mS cm^{-1} at room temperature, and is thus very promising as a green and cheap electrolyte.

1. Introduction

The energy demand of the ever-increasing world population and the issues related to fossil fuel depletion and global warming require concerted efforts to develop sustainable battery systems for electrical energy storage [1]. Lithium-ion batteries are at present the state-of-the-art storage devices. They suffer, however, from several problems including availability and toxicity of active materials, high materials costs, short life cycles, and electrolyte safety at high current rates [2,3]. This last issue requires the replacement of hazardous and volatile organic solvents [4] with safer, cheaper and more sustainable materials. Whereas ionic liquids (ILs) have been a matter of intense research as alternative electrolyte media in recent years [5], deep eutectic solvents (DESs) are opening up new and exciting possibilities as promising next-generation neoteric fluids. DESs are eutectic mixtures easily formed by mixing and gently heating naturally occurring hydrogen-bond donors (e.g., urea, renewable polyols, carbohydrates, carboxylic acids, amines, amides) and hydrogen-bond acceptors (e.g., choline chloride (ChCl), phosphonium salts). Compared with traditional ILs with which they share some physicochemical properties (e.g., negligible vapour pressure, a high thermal stability, nonflammability, recyclability), DESs display attractive advantages such as high biodegradability, low cost (DESs are about ten times cheaper than ILs), and very low toxicity. The solvent properties can be tuned by simply changing the nature and the molar ratio of the components. This last decade has witnessed an exponential increase of the publications on this topic both in academia and industry [6–12]. In particular, recent breakthroughs in applications of DESs in the fields of organo- and biocatalysis [13–16], organometallic chemistry [17–24], and solar technology [25], have been extremely relevant.

Recently, DESs based on *N*-methylacetamide (MAc) with different lithium salts (lithium bis(fluoro)sulfonimide ($LiN(CF_3SO_2)_2$), $LiPF_6$, $LiNO_3$) have been proposed as electrolytes for lithium-ion cells. These systems, however, were liquid at room temperature only for Li molar fraction < 0.35, which limited their ionic conductivity to about 1 mS cm^{-1} [26]. Geiculescu et al. reported on the usefulness of binary DES electrolytes consisting of mixtures of methanesulfonamide ($CH_3SO_2NH_2$) and *N*,*N*-dimethyl methanesulfonamide [$CH_3SO_2N(CH_3)_2$] with $LiN(FSO_2)_2$ and lithium bis(trifluoromethane)sulfonimide [$LiN(CF_3SO_2)_2$] (LiTFSI) [27]. The main limitations of this approach were the high viscosity and a relatively low conductivity with respect to $LiPF_6$ in organic carbonate solvents. The transport properties of some of these mixtures were investigated by means of Pulse Field Gradient (PFG) NMR diffusion experiments coupled with molecular dynamics simulations [28].

In this paper, we report on binary DES systems, which still retain their liquid properties despite the addition of a relatively high molar concentration (1 M) of a lithium salt. In particular, we explore two eutectics: i) ethylene glycol/choline chloride (EG/ChCl, 3:1 mol/mol), and ii) L-(+)-lactic acid/choline chloride (LA/ChCl, 2:1 mol/mol) with LITFSI and $LiPF_6$ as the lithium salts, both in concentrations of either

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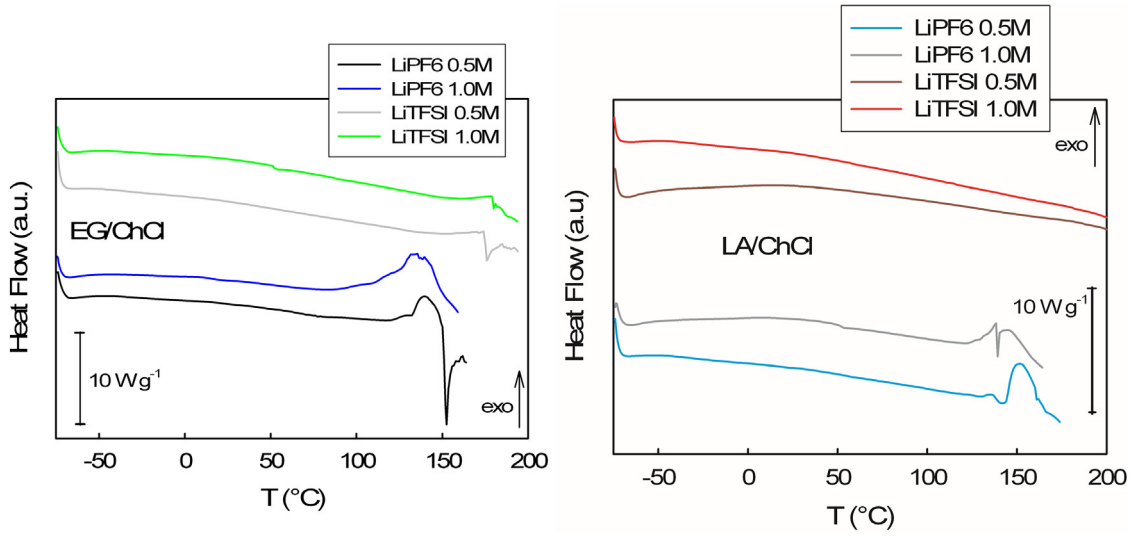

Fig. 1. DSC thermograms of the DESs-based electrolytes under investigation.

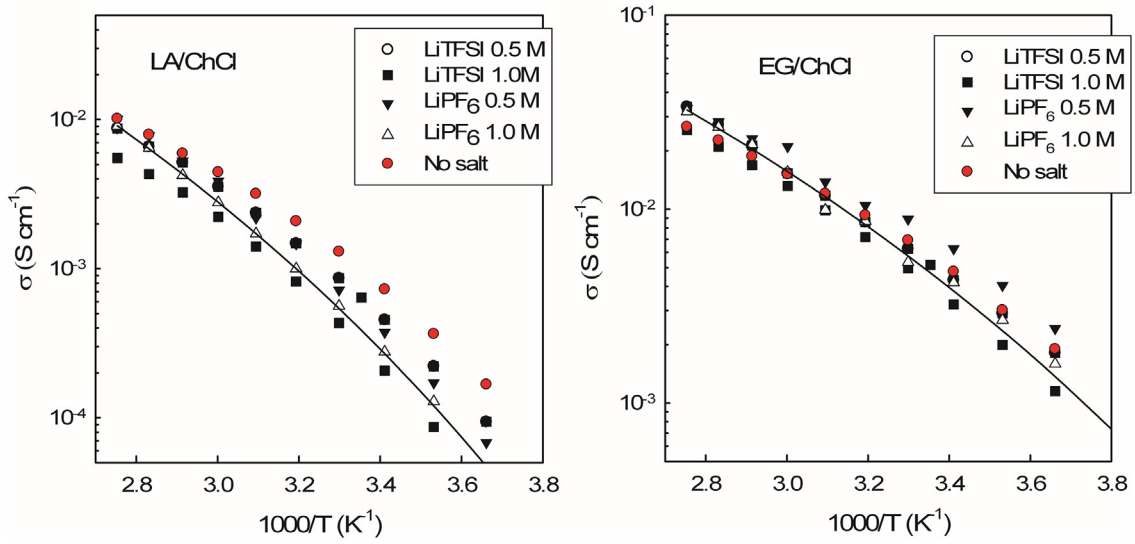

Fig. 2. Arrhenius plots of DESs-based electrolytes under investigation.

Table 1
Parameters of Vogel-Tammann-Fulcher (VTF) fits for each electrolyte together with selected physical properties at $T = 25\,^{\circ}C$. 0, B and T0 are the pre-exponential factors, pseudo-activation energies and "ideal" glass transition temperatures with R2 > 99%, respectively. σ, Λ_m, η and $\Lambda_m.\eta$ are ionic conductivity, molar conductivity, dynamic viscosity, and Walden product, respectively.

Sample	VTF			σ (S cm^{-1})	Λ_m (S cm^2 mol^{-1})	η (cP)	$\Lambda_m.\eta$ (S cm^2 mol^{-1} P)
	σ_0 (S cm^{-1})	B (K^{-1})	T_0 (K)				
LA/ChCl	0.73	791.74	177.92	1.06×10^{-3}	0.29	143.8	0.42
LA/ChCl $LiPF_6$ 0.5 M	0.71	668.20	205.88	5.41×10^{-4}	0.13	298.2	0.39
LA/ChCl $LiPF_6$ 1.0 M	12.21	1536.40	149.88	3.95×10^{-4}	0.08_5	611.1	0.52
LA/ChCl LiTFSI 0.5 M	0.41	623.93	202.14	6.39×10^{-4}	0.15	554.8	0.83
LA/ChCl LiTFSI 1.0 M	0.12	405.75	231.30	2.99×10^{-4}	0.06	668.1	0.40
EG/ChCl	0.57	594.83	168.64	5.27×10^{-3}	1.53	68.5	1.05
EG/ChCl $LiPF_6$ 0.5 M	0.71	593.23	168.43	7.95×10^{-3}	2.02	88.4	1.79
EG/ChCl $LiPF_6$ 1.0 M	4.17	1107.23	135.08	4.76×10^{-3}	1.07	94.3	1.01
EG/ChCl LiTFSI 0.5 M	3.23	1003.34	144.32	5.16×10^{-3}	1.31	121.7	1.60
EG/ChCl LiTFSI 1.0 M	1.04	725.73	167.26	4.03×10^{-3}	0.91	143.8	1.31