Ionic Liquids

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Design, Synthesis, and Electrochemistry of Room-Temperature Ionic Liquids Functionalized with Propylene Carbonate**

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Alkyl carbonates are often employed as solvents for the study of energy-storage devices (ESD), such as lithium secondary batteries (LSB) and electric double-layer capacitors. Some of these solvents, including propylene carbonate (PC) and diethyl carbonate, have already been put to practical use in modern electronics technology, such as in mobile phones and laptop computers. However, all of these organic solvents have potential safety drawbacks related to their flammable and volatile nature that can lead to explosions and/or fire accidents. Furthermore, lithium anodes with a high theoretical discharge capacity (3860 $\mathrm{mAh\,g^{-1}}$) cannot be utilized in such solvents owing to dendritic lithium deposition during the charging cycle. However, room-temperature ionic liquids (RTILs)[1–3] and RTIL-like solvents[3–6] are expected to be a new class of solvents for next-generation rechargeable high-energy-density batteries because RTILs possess unique salt-like properties. Some of these properties, such as high electrochemical stability, negligible vapor pressure, and resistance to combustion, are highly advantageous in electrochemical applications.[1–3,7,8] Thus, we anticipated that chemically combining an appropriate carbonate and organic salt may remove some of the undesirable properties of alkyl carbonates and provide uniquely functionalized RTILs for ESDs, and particularly LSB systems (Figure 1).

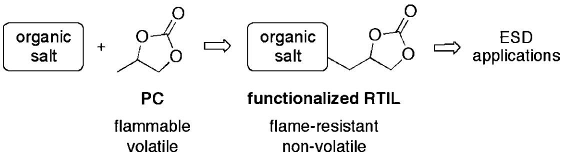

Figure 1. An organic salt (room-temperature ionic liquid; RTIL) attached to propylene carbonate (PC).

Many of common cations of organic salts (for example, imidazolium, pyridinium, ammonium, and phosphonium species) could be used for this ESD-oriented study; however, full-scale electrochemical and physicochemical measurement analysis often requires ten- to hundred-gram quantities of impurity-free samples, and a large-scale preparation of structurally complex organic salts is still synthetically challenging. Therefore, a readily accessible and generally inexpensive tetraalkylammonium salt ($R_4N^+X^-$), more specifically piperidinium salt **1**, seems to be a reasonable substructure to combine with a carbonate functionality (Figure 2).[9]

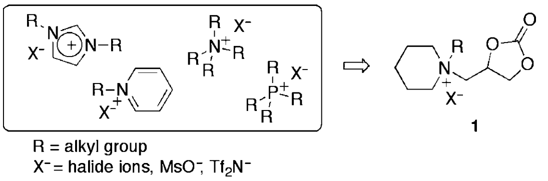

Figure 2. Common organic salts and piperidinium salt attached to PC (**1**).

Herein, we describe a novel RTIL containing a piperidinium cation with a PC moiety, which can form a solid electrolyte interphase (SEI) layer on the lithium deposit.[10] A facile synthetic approach to **1** and the electrochemical properties of **1** as a solvent in a LSB system are also discussed.

The synthesis (Scheme 1) started from inexpensive, commercially available reagents, piperidine and epichlorohydrin, which afforded epoxypropylpiperidine **2** by using a modified Heywood–Phillips procedure.[11] The TBAI-catalyzed cyclic

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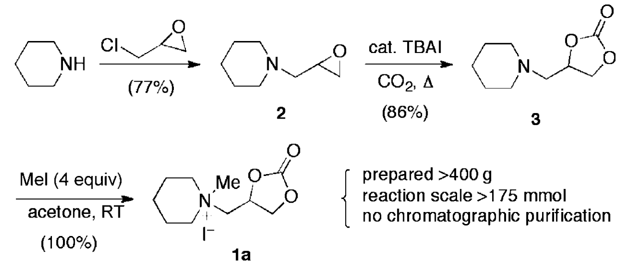
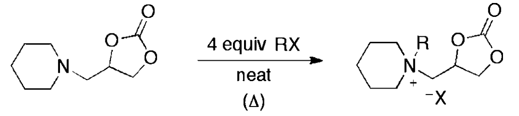


Scheme 1. Large-scale synthesis of salt **1a**. TBAI = tetrabutylammonium iodide.

carbonation of **2** then provided the desired carbonate **3** in 86% yield.[12] Both reactions were successfully operated under solvent-free, large-scale conditions (ca. 250 mmol). Subsequently, exposing carbonate **3** (ca. 175 mmol) with four equivalents of methyl iodide in acetone gave the analytically pure salt **1a** in quantitative yield. This simple three-step approach did not require any chromatographic purification and enabled the large-scale synthesis of the functionalized salt **1a**. Indeed, more than 400 g of the salt was easily prepared; however, subsequent anion exchange of **1a** did not give the desired RTIL (see the Supporting Information, Figure S1).

To test the generality of this route and to explore a low-melting/room-temperature ionic liquid, the other piperidinium salt analogues of **1** were prepared from carbonate **3** (Table 1). For practical reasons, all syntheses were carried out under neat conditions. As expected, methyl iodide (entry 1) rapidly formed the desired salt **1a** in 96% yield. Other primary alkyl halides (entries 2–5) also provided the corresponding products **1b–e** in good yields, although higher reaction temperatures (65-85 °C) and longer reaction times (2–3 days) were required. The use of activated halides, namely benzyl bromide (entry 6) and bromoacetonitrile (entry 7), afforded **1f** and **1g**, respectively in nearly quantitative yields and with short reaction times. The impacts of different counteranions (iodide versus mesylate) and reagent stoichiometry (1.2 versus 4.0 equiv) were also assessed. Methyl methanesulfonate (MeOMs) reacted smoothly at room temperature (entry 8). The resulting mesylate salt **1h** (m.p. 134–136 °C) showed a lower melting point than the iodide salt **1a** (m.p. 171–172 °C). Delocalized charge on the mesylate strongly affected the decrease in melting point of the salt.[13] The near-stoichiometric conditions (entry 9) still worked highly efficiently and gave a 91% yield of **1h**.

Table 1: Synthesis of a series of piperidinium salts **1**.

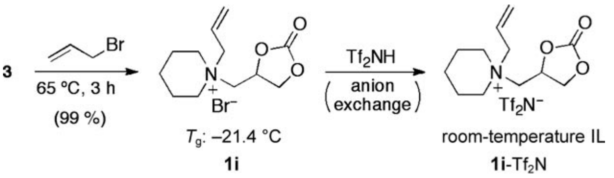


3 **1**

Entry	RX	**1**	T [°C]	t [h]	Yield [%]	m.p. [°C]
1	MeI	**1a**	RT	2.5	96	171–172
2	EtI	**1b**	70	2 days	84[a]	187–188
3	*n*-PrI	**1c**	65	3 days	82	100–102
4	*n*BuI	**1d**	85	3 days	84	129–131
5	*n*HexI	**1e**	85	3 days	92	132–133
6	BnBr	**1f**	65	1	98	140–142
7	BrCH$_2$CN	**1g**	RT	3.5	98	n.a.[b]
8	MeOMs	**1h**	RT	3.5	99	134–136
9	MeOMs	**1h**	RT	3.5	91[c]	134–136

[a] Used 8 equiv of EtI. [b] Not measured owing to product impurities (**1g**/BrCH$_2$CN = 5:1). [c] Used 1.2 equiv of MeOMs.

Interestingly, among these examples, the salt **1c** (entry 3) displayed the lowest melting point (100–102 °C) and, compared to the other alkyl groups (entries 1–5), a three-carbon propyl chain is obviously a critical length to yield a low-temperature melt in this salt system. This is a common behavior of organic salts; for example, 1-alkyl-3-methylimidazolium tetrafluoroborate;[1] that is, the propyl group creates a sterically hindered environment around the cation leading to the appropriate ion–ion separation, which eventually lowers the melting point of **1c**.[14] Although anion exchange of **1c** may help to lower the melting point further, owing to the lack of reactivity of the propyl halide, a more reactive three-carbon-chain reactant, allyl halide, was then employed (Scheme 2). Treatment of **3** with allyl bromide instantly afforded salt **1i** in excellent yield, even under large-scale neat conditions (ca. 120 mmol). Furthermore, **1i** has a glass transition temperature of only −21.4 °C without a true melting point. It should be noted that allyl iodide also worked well (65 °C, 2 hours, near quantitative yield), but minor organic impurities (< 10%) could not be separated from the salt, at least by standard trituration techniques, owing to the high viscosity of the product. Anion exchange of **1i** with bis(trifluoromethanesulfonyl)amine (HTf$_2$N) finally provided the RTIL **1i**-Tf$_2$N.



Scheme 2. Preparation of room-temperature ionic liquids **1i** and **1i**-Tf$_2$N.

Although we have successfully prepared several ILs, **1a**-Tf$_2$N (m.p. 92.0 °C), **1c**, **1i**, and **1i**-Tf$_2$N with melting points of below 100 °C, only **1i**-Tf$_2$N was a true room-temperature ionic liquid. Physical properties of **1i**-Tf$_2$N are summarized in Table S1 in the Supporting Information. The viscosity exceeded 30000 cP at 35 °C and the conductivity was considerably low. The thermal stability and electrochemical stability were also assessed in this investigation. Figure 3 shows thermoanalytical data of **1i** and **1i**-Tf$_2$N estimated by means of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The decomposition temperature T_d was found at 76.4 °C for **1i** and 286.9 °C for **1i**-Tf$_2$N, with the assumption that the decomposition begins at the temperature at which 1 wt% loss was detected. The higher decomposition temperature, that is, higher thermal stability, of **1i**-Tf$_2$N can

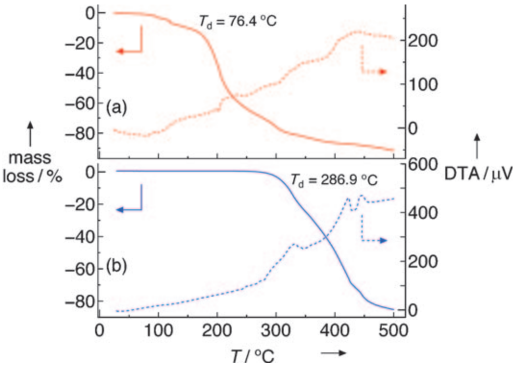


Figure 3. Results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). a) **1i** and b) **1i**-Tf_2N. Rate of temperature increase: 10 °C min^{-1}.

be reasonably explained by the lower nucleophilicity of the Tf_2N^- anion. It should be noted that **1a** and **1a**-Tf_2N showed the same tendency (see Figure S1 in the Supporting Information). Similar observations were also reported by several research groups.[15–17] Differential scanning calorimetry (DSC) confirmed that these salts do not have melting points, but rather have glass transition temperatures at −21.4 °C (**1i**) and −24.3 °C (**1i**-Tf_2N; see Figure S2 in the Supporting Information). The former salt had almost no fluidity at 25 °C owing to the strong cation–anion interactions compared to **1i**-Tf_2N, but the latter was a barely fluidic salt. Thus, we concluded that **1i**-Tf_2N has a wide liquid temperature range exceeding 300 °C.

The electrochemical stability of **1i**-Tf_2N was studied by using linear sweep voltammetry, which was carried out at 45 °C to avoid unfavorable voltammograms resulting from the large IR drops that appeared below this temperature. The potential scan was initiated from the rest potential, which is indicated by the origin of the directional arrows in Figure 4. The electrochemical window at a glassy carbon (GC) and a Pt electrode were about 4.5 V and 5.0 V, respectively. The window was estimated by measuring the cathodic and anodic limiting potentials at which a current density of ± 0.05 mA cm^{-2} was observed. The electrochemical stability is comparable to the other piperidinium-based RTILs that have been reported.[18] There is no obvious redox peaks except the reactions at limiting potentials, suggesting a high-purity grade of this salt.

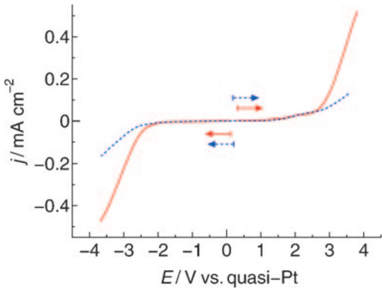


Figure 4. Linear sweep voltammograms recorded at (——) a glassy carbon and (‐‐‐) a platinum disk electrode in **1i**-Tf_2N at 45 °C. Sweep rate: 10 mV sec^{-1}.

Figure 5a shows a cyclic voltammogram recorded at a copper wire electrode in 91.0–9.0 mol % [**1i**-Tf_2N][$LiTf_2N$] binary RTIL system (thermal stability data are given in Figure S3 in the Supporting Information). A very sharp deposition wave with an associated stripping wave appeared at about −3.0 V. Further to this, a very small redox couple, which may be related to the formation of SEI layer, also appeared at about −2.0 V. As shown in Figure 5b, controlled-current electrolysis at −100 µA for 600 s yielded a light gray electrodeposit of lithium metal deposited on the copper substrate; no additives were used. This result implies that the [**1i**-Tf_2N][$LiTf_2N$] binary RTIL system is a promising solvent for next-generation LSB systems.

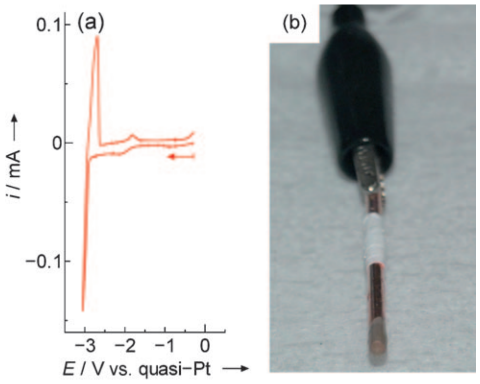


Figure 5. a) A cyclic voltammogram recorded at a copper wire electrode in 91.0–9.0 mol % [**1i**-Tf_2N][$LiTf_2N$]. T = 85 °C. Sweep rate: 10 mV s^{-1}. b) A photograph of the copper wire electrode after the electrodeposition experiment at −100 µA. T = 85 °C. Electrodeposition time: 600 s.

In summary, a highly practical and scalable approach for a series of piperidinium salts **1** has been established. All three-step reactions were carried out under solvent-free/neat conditions and no chromatographic purification was required. Controlling the length of alkyl chain as well as the type of counteranion successfully afforded a room-temperature ionic liquid (**1i**-Tf_2N). This novel RTIL possesses wide thermal stability and lithium metal deposition ability. Thus, the positive aspects of the melt in both synthesis and electrochemistry hold great promise as a candidate solvent for next-generation ESD.

Experimental Section

Piperidinium salts **1a** and **1i** were purified by precipitation from dry ethanol with dry ethyl acetate. Bis(trifluoromethylsulfonyl)amine (HTf_2N, Morita Chemical Industries Co.) was used as received. The ionic liquids were prepared by mixing exactly equal molar amounts of **1a** or **1i** and HTf_2N in ultrapure water. This solution was stirred at room temperature for 24 h. The resulting IL was then extracted with anhydrous dichloromethane (Wako Pure Chemical Industries, dehydrated). The solution was washed repeatedly with reverse-osmosed (RO) water until the aqueous phase was found to contain no chloride as determined by the addition of a few drops of a silver nitrate solution. Finally the dichloromethane solvent was removed by stirring the extraction solution under vacuum (1×10^{-4} torr) at 100 °C for 24 h. The composition of the final products was confirmed by quantitative elemental analysis and FAB-MS (for data, see the Supporting Information). A binary 91.0–9.0 mol% [**1i**-Tf_2N][$LiTf_2N$] IL system was prepared by adding lithium bis(trifluoromethylsulfonyl)amide ($LiTf_2N$, Aldrich, > 99.95 %) to **1i**-Tf_2N.

Thermoanalytical investigations were carried out by the use of a Bruker TG-DTA2000SA and DSC3100SA. This instrument was controlled with a Bruker MTC1000SA workstation utilizing Bruker WS003 software. The analytical data were obtained in aluminum pans; the standard sample was α-alumina. If the sample was hygroscopic, the aluminum pan was sealed in an argon-gas-filled glove box. The analysis was conducted at 10 °C min^{-1} under dry air.

Electrochemical experiments were conducted with a computer-controlled Hokuto Denko HZ-5000 potentiostat/galvanostat. All electrochemical experiments were carried out in three-electrode cells. The working electrodes were a Pt disk electrode (0.020 cm^2), a glassy carbon (GC) disk electrode (0.00785 cm^2), and a copper-wire electrode. A 0.05 cm diameter platinum wire and a large surface-area coiled platinum wire were used as a quasi reference electrode and a counter electrode, respectively. The platinum quasi reference and counter electrodes were immersed in the RTIL. All electrochemical experiments were carried out in an argon gas-filled glove box (VAC Atmospheres NEXUS system) with O_2 and $H_2O < 1$ ppm.

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