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Electrochemistry Communications 8 (2006) 445–449
electrochemistry communications
www.elsevier.com/locate/elecom

# A new Lewis-base ionic liquid comprising a mono-charged diamine structure: A highly stable electrolyte for lithium electrochemistry

Masahiro Yoshizawa-Fujita [a,*], Douglas R. MacFarlane [a],
Patrick C. Howlett [b], Maria Forsyth [b]

[a] School of Chemistry, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
[b] Department of Materials Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia

Received 4 January 2006; accepted 10 January 2006
Available online 8 February 2006

## Abstract

A new Lewis-base ionic liquid (IL) based on mono-charged 1,4-diazabicyclo[2.2.2]octane (dabco) was synthesized and its thermal and electrochemical behaviour was characterized. The dabco-based IL with bis(trifluoromethanesulfonyl)amide (TFSA) anion melts at 76 °C when the *N*-substituted alkyl chain length is 2. The dabco-based IL showed a wide electrochemical window of over 4 V ranging from $-3.5$ to $+1.5$ V vs. Fc/Fc$^+$ and was able to deposit and strip lithium from a nickel substrate at reasonable efficiency.

*Keywords:* Ionic liquid; Lewis base; Lithium electrochemistry; Ionic conductivity

## 1. Introduction

Ionic liquids (ILs), which are generally defined as salts with a melting point below 100 °C, are fascinating materials for a wide range of applications because they are typically non-volatile, non-flammable, and antimicrobial liquids [1–4]. One key area of research is the development of IL-based electrolyte materials for lithium ion rechargeable batteries, fuel cells, capacitors, solar cells, actuators, and so on [5]. Since ILs are composed only of ions, they can realize high ionic conductivity, often over $10^{-2}$ S cm$^{-1}$ at room temperature [6,7]. In most cases, however, such electrolyte applications need target ion transport, for instance, lithium ions in the case of lithium batteries, since the IL component ions are inert to typical electrode processes. Therefore, it is necessary to add these ionic species to the ILs. Unfortunately, the addition of target ions, especially the lithium ion, generally brings about a decrease of ionic conductivity and an increase in viscosity induced by the strong electrostatic interactions of the lithium ion [8–11]. Although there are a few designs such as zwitterions [12,13], anion trapping [14] and liquid crystals [15] for realizing fast target ion transport in ILs, it has been difficult to simultaneously achieve high ionic conductivity and a high target ion transport number in ILs, especially in the case of IL/lithium salt mixtures.

Recently, however, it has been reported that in ILs based on aliphatic and alicyclic ammonium cations, which are very stable electrochemically, dissolved lithium salts can reversibly deposit and strip lithium metal [16–18]. Furthermore, when a zwitterion was added to the IL/lithium salt mixture as a salt dissociator, the coulombic efficiency (calculated from the ratio of the deposition and dissolution charge in the cyclic voltammetry) of the electrolyte system was significantly improved [19]. Furthermore, recent work has reported on the preparation and properties of an IL containing a cyano substituted cation used as a lithium battery electrolyte [20]. Interestingly, the cyano IL showed slightly higher ionic conductivity after the addition of

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[*] Corresponding author. Tel.: +61 3 9905 4535; fax: +61 3 9905 4597.
*E-mail address:* yoshi.fujita@sci.monash.edu.au (M. Yoshizawa-Fujita).

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doi:10.1016/j.elecom.2006.01.008

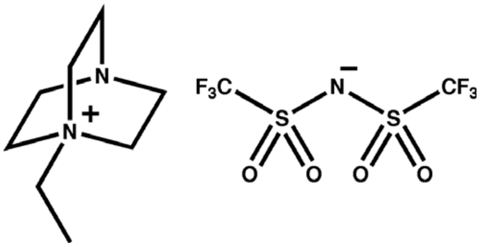

Fig. 1. The structure of [$C_2$dabco]TFSA.

LiTFSA. Thus according to these reports, the incorporation of a functional group that can promote dissociation of the lithium salt seems an attractive way forward in the design of new ILs for lithium batteries.

In this report, we have prepared a new Lewis-base IL based on the 1,4-diazabicyclo[2.2.2]octane (dabco) derivative (hereafter abbreviated as [$C_2$dabco], $C_2$ indicates the *N*-substituted ethyl group) as shown in Fig. 1. This Lewis-base cation was chosen in order to prevent the lithium ion aggregation with the TFSA anions, which is known to induce a decrease in conductivity. We have investigated the possibility that a relatively basic cationic species, [$C_2$dabco] can interact with lithium ions through a tertiary amine group thereby avoiding the expected Li-TFSA aggregation. Thermal and electrochemical behaviour will be reported. In addition, we will discuss the interaction between the lithium cation and the dabco cation by means of $^7$Li NMR.

## 2. Experimental

Synthesis of 1-ethyl-4-aza-1-azoniabicyclo[2.2.2]octane iodide ([$C_2$dabco]I): 1,4-Diazabicyclo[2.2.2]octane (dabco) (98%, Aldrich) was reacted with less than equimolar amount of iodoethane (99%, Aldrich) in ethyl acetate for 2 h at room temperature. The white precipitate was collected by filtration, and was then dried in vacuo. The filtrate was recrystallized from isopropanol to give the compound as a brilliant white powder (yield 91%). m.p. 189 °C; $^1$H NMR (300 MHz, $D_2O$): $\delta$ [ppm] 1.25–1.32 (m, 3H), 3.15 (t, 6H), 3.26–3.35 (m, 8H); MS (ES+): *m*/*z*: 141.0 [$M^+$], (ES−): *m*/*z*: 126.9 [$X^-$].

Synthesis of 1-ethyl-4-aza-1-azoniabicyclo[2.2.2]octane bis(trifluoromethanesulfonyl)amide ([$C_2$dabco]TFSA): The iodide derivative was dissolved in distilled water and slightly excess LiTFSA (donated by 3M Specialty Chemicals Division, USA) aqueous solution was added. Since the TFSA derivative is water soluble, the desired material was extracted from aqueous solution by means of dichloromethane and the solvent was evaporated in vacuo. Acetone and activated charcoal were added to the residue and the solution was stirred with charcoal at room temperature for 2 h. The mixture was filtered through an activated alumina column. The solvent was removed by rotary evaporator and the residue was dried in vacuo for 2 days at 90 °C (yield 29%). m.p. 76 °C; $^1$H NMR (300 MHz, $D_2O$): $\delta$ [ppm] 1.25–1.32 (m, 3H), 3.14 (t, 6H), 3.24–3.34 (m, 8H); MS (ES+): *m*/*z*: 140.9 [$M^+$], (ES−): *m*/*z*: 280.0 [$X^-$].

A chosen amount of LiTFSA was mixed with [$C_2$dabco]TFSA to prepare a series of Li-doped systems. The mixtures were stirred at 100 °C for several hours and then were dried in vacuo at 90 °C overnight and then stored in a dry box prior to further characterisation.

Thermal behaviour was studied from −50 °C to 150 °C at heating/cooling rate of 10 °C min$^{-1}$ by means of TA Q100. Ionic conductivity measurements were carried out in a locally designed cell, made from two platinum electrodes. Cell constants were calculated with 0.01 mol l$^{-1}$ KCl aqueous solution and were about 2.8. Ionic conductivity was obtained by measuring the complex impedance of the cell between 0.1 Hz and 1 MHz using a Solatron 1260. A PAR VMP2/Z multi-potentiostat (ECLab v9.01) was used for the electrochemical measurements, all of which were performed in an argon glovebox. Electrochemical measurements were made using a three-electrode electrochemical cell. For the electrochemical window determination a platinum working-electrode was used with platinum counter electrode. Alternatively, for the lithium deposition/dissolution measurements a nickel working electrode and a lithium counter electrode were used. The surface area of the platinum working electrode (polished 0.05 μm $Al_2O_3$) was determined by applying the Randles–Sevcik equation to the peak currents determined for a 5 mM ferrocene/0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile solution ($D = 2.3 \times 10^{-5}$ cm$^2$s$^{-1}$) at scanning rates of 50, 100 and 200 mV s$^{-1}$. The nickel working electrode (polished 0.05 μm $Al_2O_3$) was prepared by press fitting a nickel rod (Aldrich, 99.999%) into a polyethylene sleeve and the geometric surface area was determined using optical microscopy. The Ag/Ag$^+$ reference electrode has been employed previously by Katayama in ionic liquid electrochemistry and it was shown to provide stable and reproducible potentials [21]. Thus a silver reference electrode was prepared by immersing a silver wire in a 0.01 mol kg$^{-1}$ solution of $AgCF_3SO_3$ in [$C_2$dabco]TFSA. The reference solution was placed in a glass tube with a Vycor frit. The reference electrode was calibrated using a 0.01 mol kg$^{-1}$ solution of ferrocene in [$C_2$dabco]TFSA. All potentials are reported versus the ferrocene/ferrocenium half potential. All of the voltammetry was performed at 80 °C and all of the samples were dried in a vacuum oven for 24 h at 90 °C prior to use. NMR measurements were conducted using a Bruker Avance 300 spectrometer at 21 °C.

## 3. Results and discussion

Interestingly, the IL based on the ethyl derivative coupled with the TFSA anion, [$C_2$dabco]TFSA, is water-soluble and is soluble up to about 0.18 mol l$^{-1}$ in water. This somewhat hydrophilic behaviour most likely results from the hydrogen bonding between the tertiary amine nitrogen and the water molecule. It is, therefore, expected that such