Synthesis and Characterization of Novel Ionic Liquids: N-Substituted Aziridinium Salts

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Ionic liquids based on three-membered ring aziridinium cations have been synthesized for the first time using a straightforward synthetic route. *N*-butyl-*N*-methylaziridinium bis(trifluoromethanesulfonyl)imide, *N*-propyl-*N*-ethylaziridinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylaziridinium dicyanamide, and *N*-butyl-*N*-ethylaziridinium dicyanamide were thus obtained in good yields and satisfactory purity and fully characterized.

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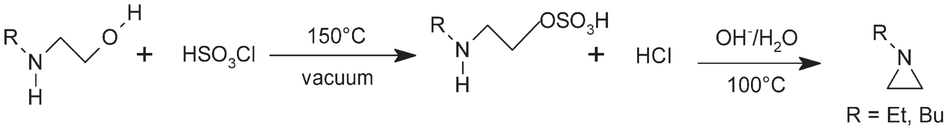
INTRODUCTION

Ionic liquids (ILs) are room temperature fluids constituted of a bulky and asymmetric organic cation associated with a small organic or inorganic anion. Interests in ILs have steadily grown in recent years, because their unique solvent properties provide the possibility for clean manufacturing in chemical industry [1–3]. Regularly, various publications and patents report novel applications of ILs such as catalytic synthesis [4–7], separation [8–11], polymerization [12], nanotechnology [13], biocatalysis [14,15], composite preparation [16], and renewable resource utilization [17,18]. To date, there have been numerous commercial applications since BASF's (Badische Anilin und Soda-Fabrik) first successful use of an IL in 2003 [19]. Because of their unique physicochemical properties [20] ionic liquids have been regarded as promising candidates for lithium battery electrolytes. Conventional nonaqueous organic electrolytes are widely used in commercial Li-ion batteries, however, these organic solvents are volatile and in many cases highly flammable. Li-ion batteries using these electrolytes can become dangerous when subjected to extreme conditions. Furthermore, because of insufficient electrochemical stability electrolyte decomposition may occur, accompanied by an irreversible consumption of electrolyte and lithium, which leads to a decrease of the specific energy of the battery and overall performance [21,22]. Therefore, the search for new electrolyte systems and optimization of conventional electrolytes is an important research area in the Li battery industry. Room temperature ionic liquids (RTILs) have advantages of nonflammability, high electrochemical stability, and negligible vapor pressure [23–25]. Application of RTILs as electrolytes in Li-ion batteries may completely solve the safety problems [26–28] and suppress the strong interfacial reactions. 1-Ethyl-3-methylimidazolium-based IL electrolytes have the virtue of low viscosity and high conductivity. However, practical application of imidazolium RTILs in 4 V Li-ion batteries seems to be difficult because of their narrow electrochemical window (*ca.* 4.2 V) to withstand cathodic reduction and anodic oxidation [29]. ILs with more stable cations such as cyclic tetraalkylammonium show wider electrochemical windows (often more than 5 V) [30–32]. An ionic liquid capable of operating as supporting electrolyte for 4-V-class rechargeable Li batteries must have the following properties: (i) a low melting point to operate over a wide range of temperature, (ii) a weakly coordinating nature for its anion to depress ion pairing, (iii) a low viscosity at room temperature to enhance the mobility of ionic species, and (iv) a large electrochemical window that allows the Li^+/Li redox reaction taking place in both the anode and the cathode sides to be reversible.

Scheme 1. Synthesis of *N*-alkylaziridines.



Concerning the anion, the bis(trifluoromethanesulfonyl) imide ion ($[(CF_3SO_2)_2N)]^-$, TFSI) has been mentioned as a promising candidate because of both its electrochemical stability and its weakly coordinating capability [30]. Concerning the viscosity lowering, the dicyanamide ion ($[(CN)_2N]^-$, DCA) also appears to be promising [33]. The length of the alkyl arms brought by the nitrogen atom of the heterocyclic ring of the cation has also influence on the above properties. As a rule, the alkyl groups should have lengths different enough to avoid cation symmetry, whereas maintaining a small ion size to favor low viscosity [34]. Furthermore, introduction of oxygen atoms in the alkyl side-chains is also known to lower the IL's viscosity in the case of cyclic quaternary ammonium cations [31].

Recent research has also focused on the ILs for electric double-layer capacitors, usually named supercapacitors. Although batteries store energy in chemical reactions, capacitors store it in surface charges, so they can provide rapid bursts of power. Such power storage devices, when involving porous materials with high surface areas serving as electrodes, fill the gap between dielectric capacitors and traditional batteries, and usually require salts dissolved in a solvent having a high dielectric constant. However, the use of solvent-free ILs enables to reach the high cell voltages necessary for increasing energy.

One of the more promising classes of ILs as electrolytes seems to be that containing the *N*-methyl-*N*-alkylpiperidinium and pyrrolidinium cations [31]. Application of these ionic liquids into Li-ion batteries seems to be more practical [35–38]. In this paper, we synthesized several new ILs based on three-membered ring aziridinium cations to compare their electrochemical properties with their five-membered ring pyrrolidinium homologs.

RESULTS AND DISCUSSION

The preparation of *N*-Alkyl-*N*-alkyl′-aziridinium ions has been scarcely reported in the literature [39] because of the lack of general synthetic access to their precursor *N*-alkylaziridine [40]. However, *N*-butylaziridine may conveniently be prepared by cyclization of the corresponding 2-(butylamino)ethanol [41,42]. As large quantities of *N*-alkylaziridines were required in this work, an efficient laboratory procedure was developed from commercially available 2-(alkylamino)ethanols by modification of the Wenker's general method [43]. A 2-(alkylamino)ethanol was treated with concentrated chlorosulfonic acid at high temperature under vacuum to give the inner salt of the sulfate ester. This intermediate was then treated *in situ* with a concentrated solution of sodium hydroxide from which the corresponding *N*-alkylaziridine was collected by steam-distillation as a pure product (Scheme 1). *N*-butyl- and *N*-ethylaziridines were synthesized using this procedure with moderate but reproducible yields.

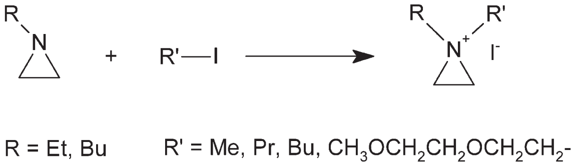
N-alkyl-*N*-alkyl′-aziridinium iodides were synthesized by a modification of the Graetzel's quaternization method [44]. An alkyliodide and a slight excess of *N*-alkylaziridine were mixed and stirred at room temperature without solvent. Evaporation under vacuum of the excess of aziridine gave high yield of the pure expected compounds (Scheme 2). 2-(2-Methoxyethoxy)ethyl iodide was synthesized in two steps from 2-(2-methoxyethoxy)ethanol (Scheme 3).

N-Alkyl-*N*-alkyl′-aziridinium TFSI ILs were synthesized by mixing two equimolar aqueous solutions of *N*-alkyl-*N*-alkyl′-aziridinium iodide and lithium TFSI according to a published method with modification [30]. *N*-Alkyl-*N*-alkyl′-aziridinium DCA ILs were synthesized by mixing an aqueous solution of *N*-alkyl-*N*-alkyl′-aziridinium iodide and silver dicyanamide (AgDCA) according to a published method with modifications (Scheme 4; ref. [41]).

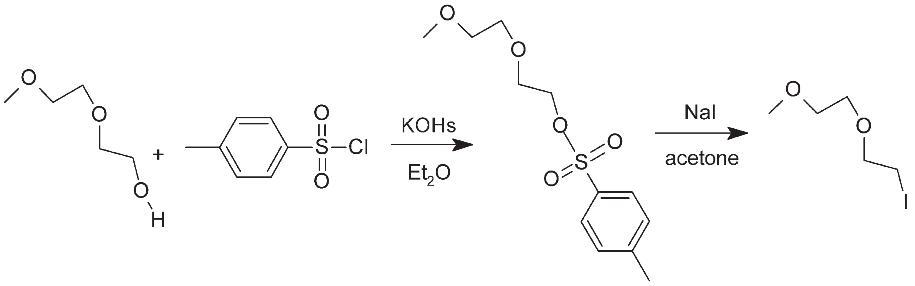
Using this methodology, five ILs have been synthesized: *N*-butyl-*N*-methylaziridinium TFSI, *N*-propyl-*N*-ethylaziridinium TFSI, *N*-butyl-*N*-[2-(2-methoxyethoxy) ethyl]aziridinium TFSI, *N*-butyl-*N*-methylaziridinium DCA, and *N*-butyl-*N*-ethylaziridinium DCA.

The physicochemical data of these compounds are reported in Table 1. The structure and composition of the salts prepared were confirmed by elemental analysis and by NMR spectroscopy. The thermal properties of the salts prepared were characterized by differential scanning calorimetry (mp). For salts that are liquid at room temperature, their dynamic viscosity (η) and ionic conductivity (σ) were measured at 25°C. Electrochemical windows ΔE were also determined.

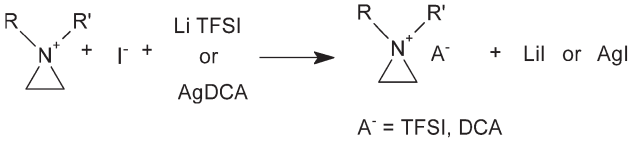
Scheme 2. Synthesis of the *N*-alkyl-*N*-alkyl′-aziridinium iodides.



Scheme 3. Synthesis of 2-(2-methoxyethoxy)ethyl iodide.



Scheme 4. Synthesis of *N*-alkyl-*N*-alkyl′-aziridinium ionic liquids.



The data reported in Table 1 indicate that some of the aziridinium-based ILs synthesized are liquid at room temperature with quite low melting points. However, their viscosities are relative high (on comparison with *N*-butyl-*N*-methylpyrrolidinium TFSI). As a direct consequence, the conductivity is low (this value depends on the ions mobility). Furthermore, the electrochemical windows, situated around 2 V, are too narrow to be useful in battery applications. This quite disappointing behavior may be attributed to the flat nature of the aziridine ring favoring some stacking of the molecules. A molecular modeling such as that conducted on linear quaternary ammonium IL [45] would probably be useful.

Further, to investigate the potentiality of the newly synthesized aziridinium-based ILs, we examined the performances of a double-layer capacitor composed of a pair of activated carbon fabrics as electrodes and *N*-butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium TFSI, which was compared with the commonly used nonaqueous electrolyte *N*-butyl-*N*-methylpyrrolidinium TFSI. A Whatman GF/A separator was plunged in the electrolyte and sandwiched between two identical immersed carbon fabrics (9 mm in diameter; 1700 m^2 g^{-1}) acting as composite electrodes. The cell was assembled in a glove box under argon atmosphere. The assembled cell was charged (discharged) by applying a constant voltage: 2 V (0 V). The capacitance was evaluated from the charge curve. The capacitance of the aziridinium-based cell was estimated at 160 mC cm^{-2}, whereas that of the *N*-butyl-*N*-methylpyrrolidinium TFSI cell was measured at 820mC cm^{-2}.

CONCLUSIONS

In this work, we have synthesized representative compounds of a new family of room temperature ionic liquids built from three-membered ring aziridinium cations. The reactions involved were straightforward and efficient with only a few by-products. The anions used were the weakly coordinating TFSI and DCA. The high viscosities and narrow electrochemical windows of these new ionic liquids restrict their potentials as electrolytes in Li-ion batteries and in supercapacitors. However, applications in catalysis or extraction may be found for this new class of ionic liquids.

Table 1

Physicochemical properties of synthesized aziridinium-based ILs.

	mp[a] (°C)	η[b] (cP)	σ[c] (mS cm^{-1})	E_c (V)	E_a (V)	Δ*E* (V)
N-Butyl-*N*-methylpyrrolidinium TFSI[d]	−19	76	2.6	−3.0	+2.0	5.0
N-Butyl-*N*-methylaziridinium TFSI	53	–	–	–	–	–
N-Propyl-*N*-ethylaziridinium TFSI	129	–	–	–	–	–
N-Butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium TFSI	−60	650	0.21	−1.5	+0.5	2.0
N-Butyl-*N*-methylaziridinium DCA	−25	1050	0.40	–	–	–
N-Butyl-*N*-ethylaziridinium DCA	−49	320	0.60	−1.7	+0.7	2.4

[a] Melting point.

[b] Viscosity at 25°°C.

[c] Specific conductivity at 25°°C.

[d] Data obtained from the literature [31].

EXPERIMENTAL

Reagents and methods All solvent were freshly distilled from the appropriate reagents before use. The alkyl iodides, 2-(butylamino)ethanol, 2-(ethylamino) ethanol, chlorosulfonic acid, 2-(2-methoxyethoxy)ethanol, *p*-toluenesulfonyl chloride, and lithium bis(trifluoromethanesulfonyl)imide were purchased from Sigma–Aldrich Chemical (Lyon, France) and used without further purification. Unless otherwise specified, all manipulations were carried out on a double manifold Schlenk vacuum line under an atmosphere of nitrogen.

^{1}H-NMR (300 MHz, Me_4Si) and ^{13}C-NMR (150 MHz, Me_4Si) spectra were collected using a Bruker ADX-300 spectrometer. *J* values are given in Hz. Infrared spectra were obtained using a Perkin-Elmer Spectrum 100 Spectrometer. Microanalyses were conducted at the CNRS Service Central d'Analyse, France.

Melting points were determined using differential scanning calorimetry in a Perkin-Elmer Pyris 1 DSC equipped with a liquid nitrogen cryostatic cooling. An average sample weight of 5–10 mg was sealed in an aluminum pan and quenched initially to −100°C, and then heated at a rate of 5°C min^{-1}.

Dynamic viscosities (η) were measured with a Brookfield viscosimeter (model DV-III+) using 1 mL sample at 25°C.

Specific ionic conductivities (σ) were measured by a conductivity meter (Radiometer Analytical, model CDM230) in a sealed conductivity cell at 25°C.

The cathodic and anodic limits, E_c and E_a (V), *versus* ferrocene (Fe)/ferrocenium (Fc^+) redox couple were investigated by linear sweep voltammetry on a glassy carbon electrode.

***N*-Butylaziridine.** Chlorosulfonic acid (213 mmol, 25 g) was placed into a round bottomed flask and cooled to 0°C in an ice bath. 2-(Butylamino)ethanol (213 mmol, 25 g) was placed in a dropping funnel and added slowly to the acid while maintaining the temperature at 0°C. After the addition, the mixture was heated to 150°C under vacuum for 2 h. The reaction was cooled, and water (30 mL) was added followed by an aqueous solution of potassium hydroxide (60 g of KOH in 60 mL of water). The alkaline solution was gently heated to ~120°C and the desired product that distilled off was collected as a light yellow mobile oil (12.3 g, 58%). Eb = 100–105°C [41]. δ_H(DMSO): 2.08 (2H, t, *J* = 7.1), 1.52 (2H, m), 1.42 (2H, m), 1.33 (2H, m), 1.00 (2H, m), 0.87 (3H, t, *J* = 7.2). δ_C(DMSO): 62.2, 30.0, 28.1, 21.4, 14.8. Found: C, 72.37; H, 13.35; N, 14.23. Calc. for $C_6H_{13}N$: C, 72.67; H, 13.21; N, 14.12%.

***N*-Ethylaziridine.** *N*-Ethylaziridine was obtained using a similar procedure as described for *N*-butylaziridine (7.2 g, 46%). Eb = 45–50°C. δ_H(DMSO): 2.11 (2H, q, *J* = 7.1), 1.52 (2H, m, *J* = 2.3), 1.03 (3H, t, *J* = 7.1), 0.99 (2H, m, *J* = 2.3); δ_C(DMSO): 57.3, 27.1, 14.5. Found: C, 67.23; H, 12.91; N, 19.51. Calc. for C_4H_9N: C, 67.55; H, 12.75; N, 19.69%.

***N*-Butyl-*N*-methylaziridinium iodide.** *N*-Butylaziridine (20 mmol, 2.0 g) was cooled in an ice bath and iodomethane (18 mmol, 2.5 g) was slowly added while stirring. Following the addition, the reaction was stirred for 24 h at room temperature. After this time the reaction volume was reduced under high vacuum (1 mmHg), leaving the desired product as a white solid (4.1 g, 95%). δ_H(DMSO): 3.66 (4H, m), 3.52 (2H, m), 3.25 (3H, s), 1.63 (2H, m), 1.26 (2H, m), 0.92 (3H, t). Found: C, 34.50; H, 6.23; N, 5.85; I, 52.67. Calc. for $C_7H_{16}NI$: C, 34.87; H, 6.69; N, 5.85; I, 52.63%.

***N*-Propyl-*N*-ethylaziridinium iodide.** *N*-Ethylaziridine (42 mmol, 3.0 g) was mixed with iodopropane (38 mmol, 6.5 g) and stirred for 24 h at room temperature. After this time, the reaction volume was reduced under high vacuum (1 mmHg) leaving the desired product as a white solid (8.7 g, 95%). δ_H(DMSO): 3.75 (4H, s), 3.57 (2H, m), 3.40 (2H, m), 1.63 (2H, m), 1.23 (3H, m), 0.95 (3H, m). Found: C, 34.55; H, 7.01; N, 5.12; I, 52.42. Calc. for $C_7H_{16}NI$: C, 34.87; H, 6.69; N, 5.85; I, 52.63%.

***N*-Butyl-*N*-ethylaziridinium iodide.** *N*-Ethylaziridine (42 mmol, 3.0 g) was mixed with iodobutane (36 mmol, 6.6 g) and stirred for 24 h at room temperature. After this time, the reaction volume was reduced under high vacuum (1 mmHg) leaving the desired product as a white solid (8.7 g, 95%). δ_H(DMSO): 3.71 (4H, m), 3.51 (2H, m), 3.28 (2H, m), 1.63 (2H, m), 1.30 (2H, m), 1.23 (3H, t), 0.97 (3H, t). Found: C, 36.96; H, 6.85; N, 5.72; I, 49.37. Calc. for $C_8H_{16}NI$: C, 37.66; H, 7.11; N, 5.49; I, 49.74%.

2-(2-Methoxyethoxy)ethyl iodide. 2-(2-Methoxyethoxy)ethanol (0.54 mol, 65 g) was dissolved in dry ether (500 mL), and powdered potassium hydroxide (0.5mol, 28 g) and *p*-toluenesulfonyl chloride (0.5 mol, 95.3 g) were added. The suspension was vigorously stirred at room temperature for 10 h under nitrogen. The mixture was then filtered, and the filtrate washed with water (3 × 50 mL) then dried under $MgSO_4$ before concentrating under vacuum to leave raw 2-(2-methoxyethoxy)ethyl-*p*-toluene sulfonate (118 g, 86%). This product (118 g, 0.43 mol) was dissolved in dry acetone (250mL) and sodium iodide (0.5 mol, 75 g) was added. The solution was stirred at room temperature under nitrogen in the dark for 24 h. The solvent was evaporated under vacuum to give a colorless liquid that was distilled (82 g, 77%; Eb = 120°C at 20 mmHg) [40]. δ_H($CDCl_3$): 3.28 (2H, t), 3.42 (3H, s), 3.55 (2H, t), 3.68 (2H, t), 3.75 (2H, t). Found: C, 26.50; H, 4.11; I, 55.42. Calc. for $C_5H_{11}O_2I$: C, 26.10; H, 4.82; O, 13.91; I, 55.16%.

***N*-Butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium iodide.** *N*-Butylaziridine (200 mmol, 19.8 g) was added to 2-(2-methoxyethoxy)ethyl iodide (180 mmol, 41 g), and the reaction was stirred for 24 h at room temperature. After this time, the reaction volume was reduced under high vacuum (1 mmHg) for 24 h resulting in a white solid (57 g, 96%). δ_H($CDCl_3$): 3.73 (4H, m), 3.52 (2H, t), 3.35 (2H, m), 3.29 (2H, t), 3.27 (2H, t), 3.19 (2H, t), 1.63 (2H, m), 1.26 (2H, m), 1.23 (3H, t), 0.95 (3H, t). Found: C, 40.23; H, 7.36; N, 4.50; I, 38.22. Calc. for $C_{11}H_{24}NO_2I$: C, 40.13; H, 7.35; N, 4.25; O, 9.72; I, 38.55%.

***N*-Butyl-*N*-methylaziridinium bis(trifluoromethanesulfonyl) imide.** *N*-Butyl-*N*-methylaziridinium iodide (15.3 mmol, 3.7 g) was dissolved in distilled water (100 mL), and lithium bis (trifluoromethanesulfonyl)imide (15.3 mmol, 4.4 g) dissolved in water (20 mL) was added. The solution was vigorously stirred for 1 h then allowed to stand. A pale yellow phase, which separated from the water layer, was collected and washed three times with distilled water. The ionic liquid product was dissolved in ethanol and passed through a plug of basic alumina and charcoal. The liquid volume was reduced under high vacuum (1 mmHg) for 1 week and the final product stored under dry nitrogen (5.8 g, 96%). δ_H(DMSO): 3.66 (2H, m), 3.52 (2H, m), 3.25 (2H, m), 3.01 (3H, s), 1.63 (2H, m), 1.26 (2H, m), 0.92 (3H, t). Found: C, 27.71; H, 4.23; N, 7.41; S, 15.61; F, 28.53. Calc. for $C_9H_{16}N_2O_4F_6S_2$: C, 27.41; H, 4.09; N, 7.10; O, 16.23; S, 16.26; F, 28.90%.

***N*-Propyl-*N*-ethylaziridinium bis(trifluoromethanesulfonyl) imide.** *N*-Propyl-*N*-ethylaziridinium iodide (8.3 mmol, 2.0 g) was dissolved in water (25 mL) and a solution of lithium bis (trifluoromethanesulfonyl)imide (8.3 mmol, 2.4 g) dissolved in water (20 mL) was added. The reaction was stirred for 4 h, then the water layer was decanted off and the remaining oil was washed three times with water. The remaining product was dissolved in a small amount of acetone and filtered, the filtrate volume was reduced under high vacuum (1 mmHg) for 1 week and the final product stored under dry nitrogen (3.1 g, 94%). δ_H(DMSO): 3.66 (2H, m), 3.52 (2H, m), 3.25 (2H, m), 3.21 (2H, m), 1.62 (2H, m), 1.28 (3H, t), 0.96 (3H, t). Found: C, 27.85; H, 4.34; N, 7.32; S, 15.74; F, 28.62. Calc. for $C_9H_{16}N_2O_4F_6S_2$: C, 27.41; H, 4.09; N, 7.10; O, 16.23; S, 16.26; F, 28.90%.

***N*-Butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium bis(trifluoromethanesulfonyl)imide.** *N*-Butyl-*N*-[2-(2-methoxyethoxy)ethyl]aziridinium iodide (82 mmol, 27 g) was dissolved in distilled water (100 mL), and lithium bis (trifluoromethanesulfonyl)imide (82 mmol, 23.5 g) dissolved in water (20 mL) was added. The solution was vigorously stirred for 1 h, and then allowed to stand. A pale yellow phase, which separated from the water layer, was collected and washed three times with distilled water. The ionic liquid product was dissolved in ethanol and passed through a plug of basic alumina and charcoal. The liquid volume was reduced under high vacuum (1 mmHg) for 1 week and the final product stored under dry nitrogen (36 g, 91%). δ_H($CDCl_3$): 3.66 (4H, m), 3.48 (2H, t), 3.25 (2H, m), 3,21 (2H, t), 3.18 (2H, t), 3,01 (2H, t), 1.55 (2H, m), 1.16 (2H, m), 1.20 (3H, t), 0.91 (3H, t). Found: C, 32.82; H, 5.58; N, 5.38; S, 13.27; F, 23.03. Calc. for $C_{13}H_{24}N_2O_6F_6S_2$: C, 32.36; H, 5.01; N, 5.81; O, 19.90; S, 13.29; F, 23.63%.

***N*-Butyl-*N*-methylaziridinium dicyanamide.** Sodium dicyanamide (4.5 mmol, 0.4 g) dissolved in water (20 mL) was added to a solution of silver nitrate (4.5 mmol, 0.77 g) in water (30 mL). The white precipitate, which immediately formed, was collected *via* filtration and washed with water [42]. The AgDCA precipitate was added to a solution of *N*-butyl-*N*-methylaziridinium iodide (4.1 mmol, 1.0 g) in water (20 mL). The mixture was stirred for 3 h at 40°C, and it gradually turned pale yellow (due to the formation of AgI). The mixture was cooled and filtered, and the volume reduced under high vacuum. Acetone was added to the remaining oil to precipitate any remaining silver iodide or AgDCA (0.7 g, 92%). δ_H(DMSO): 3.66 (2H, m), 3.52 (2H, m), 3.25 (2H, m), 3.01 (3H, s), 1.63 (2H, m), 1.26 (2H, m), 0.92 (3H, t). Found: C, 59.26; H, 8.95; N, 31.15. Calc. for $C_9H_{16}N_4$: C, 59.97; H, 8.95; N, 31.08%.

***N*-butyl-*N*-ethylaziridinium dicyanamide.** Sodium dicyanamide (15.7 mmol, 1.4 g) dissolved in water (30 mL) was added to a solution of silver nitrate (15.7 mmol, 2.7 g) in water (30 mL). The white precipitate, which immediately formed, was collected *via* filtration and washed with water. The AgDCA precipitate was added to a solution of *N*-butyl-*N*-ethylaziridinium iodide (14.5 mmol, 3.7 g) in water (30 mL). The mixture was stirred for 3 h at 40°C, and it gradually turned pale yellow (due to the formation of AgI). The mixture was cooled and filtered and the volume reduced under high vacuum. Acetone was added to the remaining oil to precipitate any remaining silver iodide or AgDCA (2.6 g, 93%). δ_H(DMSO): 3.66 (2H, m), 3.52 (2H, m), 3.25 (2H, m), 3.21 (2H, m), 3.01 (3H, s), 1.63 (2H, m), 1.26 (2H, m), 0.92 (3H, t). Found: C, 61.45; H, 9.77; N, 28.24. Calc. for $C_{10}H_{18}N_4$: C, 61.82; H, 9.34; N, 28.84%.

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REFERENCES AND NOTES

[1] Rogers, R. D.; Seddon, K. R. Ionic Liquids: Industrial Applications to Green Chemistry; ACS Symposium Series, ACS: Washington, DC, 2002; Vol. 818.

[2] Rogers, R. D.; Seddon, K. R. Ionic Liquids as Green Solvents: Progress and Prospects; ACS Symposium Series, ACS: Washington, DC, 2003; Vol. 856.

[3] Rogers, R. D.; Seddon, K. R.; Volkov, S. Green Industrial Applications of Ionic Liquids; Kluwer Academic: Dordrecht, The Netherlands, 2002.

[4] Leveque, J. M.; Cravotto, G. Chimia 2006, 60, 313.

[5] Zhang, Z. C. Adv Catal 2006, 49, 153.

[6] Muzart, J. Adv Synth Catal 2006, 348, 275.

[7] Parvulescu, V. I.; Hardacre, C. Chem Rev 2007, 107, 2615.

[8] Zhao, H.; Xia, S. Q.; Ma, P. S. J Chem Technol Biotechnol 2005, 80, 1089.

[9] Kubota, F.; Goto, M. Solvent Extr Res Dev Jpn 2006, 13, 23.

[10] Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. Acc Chem Res 2007, 40, 1208.

[11] Dietz, M. L. Sep Sci Technol 2006, 41, 2047.

[12] Kubisa, P. Prog. Polym Sci 2004, 29, 3.

[13] Antonietti, M.; Kuang, D. B.; Smarsly, B.; Zhou, Y. Angew Chem Int Ed 2004, 43, 4988.

[14] van Rantwijk, F.; Sheldon, R. A. Chem Rev 2007, 107, 2757.

[15] Swatloski, R. P.; Rogers, R. D.; Holbrey, J. D. WO Patent 029,329, 2003; Chem Abstr 2003, 138, 289216.

[16] Turner, M. B.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Biomacromolecules 2005, 6, 2497.

[17] Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G. Green Chem 2006, 8, 325.

[18] Zhu, S. J Chem Technol Biotechnol 2008, 83, 777.

[19] Freemantle, M. Chem Eng News 2003, 81, 9.

[20] Sakaebe, H.; Matsumoto, H. In Electrochemical Aspects of Ionic Liquids; Ohno, H., Ed.; Wiley: Hoboken, NJ, 2005; Chapter14.

[21] Wang, Y. X.; Nakamura, S.; Tasaki, K.; Balbuena, P. B. J Am Chem Soc 2002, 124, 4408.

[22] Aurbach, D.; Gamolsky, K.; Markovsky, B.; Gofer, Y.; Schmidt, M.; Heider, U. Electrochim Acta 2002, 47, 1423.

[23] Xu, W.; Angell, C.A. Science 2003, 302, 422.

[24] Welton, T. Chem Rev 1999, 99, 2071.

[25] Fuller, J.; Carlin, C. T.; Osteryoung, R. A. J Electrochem Soc 1997, 144, 3881.

[26] Sato, T.; Maruo, T.; Marukane, S.; Takagi, K. J Power Sources 2004, 138, 253.

[27] Shin, J.-H.; Henderson, W. A.; Passerini, S. Electrochem Commun 2003, 5, 1016.

[28] Fung, Y. S.; Zhou, R. Q. J Power Sources 1999, 81–82, 891.

[29] Garcia, B.; Lavallee, S.; Perron, G.; Michot, C.; Armand, M. Electrochim Acta 2004, 49, 4583.

[30] Sakaebe, H.; Matsumoto, H. Electrochem Commun 2003, 5, 594.

[31] Zhou, Z.-B.; Matsumoto, H.; Tatsumi, K. Chem Eur J 2006, 12, 2196.

[32] Li, X.; Zeng, Z.; Garg, S.; Twamley, B.; Shreeve, J. M. Eur J Inorg Chem 2008, 3553.

[33] MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. Chem Commun 2001, 1430.

[34] Zhou, Z.-B.; Matsumoto, H.; Tatsumi, K. Chem Eur J 2005, 11, 752.

[35] Nakagawa, H.; Fujino, Y.; Kozono, S.; Katayama, Y.; Nukuda, T.; Sakaebe, H.; Matsumoto, H.; Tatsumi, K. J Power Sources 2007, 174, 1021.

[36] Egashira, M.; Okada, S.; Yamaki, J.; Dri, D. A.; Bonadies, F.; Scrosati, B. J Power Sources 2004, 138, 240.

[37] Zhou, Z.-B.; Takeda, M.; Ue, M. J Fluorine Chem 2003, 123, 127.

[38] Stefan, C. S.; Lemordant, D.; Biensan, P.; Siret, C.; Claude-Montigny, B. J Therm Anal Calorim 2010, 102, 685.

[39] Kim, Y.; Ha, H.-J.; Yun, S. Y.; Lee, W. K. Chem Commun 2008, 4363.

[40] Sweeney, J. B. Chem Soc Rev 2002, 31, 247.

[41] Darensbourg, D. J.; Phelps, A. L.; Le Gall, N.; Jia, L. J Am Chem Soc 2004, 126, 13808.

[42] Elderfield, R. C.; Hageman, H. A. J Org Chem 1949, 14, 605.

[43] Wenker, H. J Am Chem Soc 1935, 57, 2328.

[44] Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Graetzel, M. Inorg Chem 1996, 35, 1168.

[45] Siqueira, L. J. A.; Ribeiro, M. C. C. J Phys Chem B 2009, 113, 1074.