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Introduction

Ionic liquids (IL) are compounds with unique properties and have been the subject of intense scientific and technological research in recent decades.1 Their most important property is their liquid state, which makes them appropriate for the substitution of simple organic solvents in various processes, such as organic synthesis,^{2,3} inorganic synthesis,⁴ bio-synthesis,⁵ separations⁶ and energy production/storage.^{7,8} Additional features, such as very low vapour pressure, non-flammability, good thermal stability, and a wide electrochemical window, suggest their use as electrolytes in electrochemical systems,8-10 such as Li-ion batteries,11 dye-sensitised solar cells,12 electrical capacitors,¹³ electrochromic devices,¹⁴ etc.

Most ILs are compounds consisting of organic cations (quaternised nitrogen, phosphorus, tertiarised sulphur, etc.) and relatively large inorganic anions (tetrafluoroborate, perfluoroalkyl-trifluoroborate, triflate, bis(trifluoromethanesulfonyl)amide, bis(fluorosulfonyl)amide, etc.). A significant majority of ILs contain quaternised nitrogen, also in a heterocyclic form (imidazolium).

Existing ionic liquids, however, do not solve all the problems associated with the manufacturing of electrochemical devices,15 especially high power lithium or lithium ion batteries. In lithium batteries, several electrode materials are used; therefore, solvents or electrolytes for use with these materials should



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Another class of ionic liquids was obtained by a combination of bis(perfluoroalkylsulfonyl)amide anions and O-silvlated choline like cations. The protection of the hydrophilic hydroxyl group of hydroxyalkyl substituted quaternary ammonium salts with a trialkylsilyl group changes cations' properties from hydrophilic to hydrophobic; both constituents (cations and anions) of resulting ionic liquids have a hydrophobic character. Their essential physical and chemical properties were investigated. Moderate viscosity and conductivity of ionic liquids follow the Vogel-Tammann-Fulcher model of their dependency on the temperature. All ionic liquids show similar electrochemical stability as anticipated from CV measurements. The cathodic stability for most compounds is below 0 V vs. Li/Li⁺, and anodic decomposition starts typically over more than 5 V vs. Li/Li⁺. These properties suggest that these ionic liquids have potential for the preparation of electrolytes for high voltage lithium batteries.

> exhibit high thermal,¹⁶ electrochemical (typically between 0 and 5 V vs. Li/Li⁺) and chemical stabilities and should wet electrodes properly. The first problem is stability at low potentials (cathodic stability), which is attributed mainly to the cations. Electrochemical intercalation of lithium into graphite anodes in 1-ethyl-3-methylimidazolium (EMI)-based ionic liquids has stimulated interest because these ionic liquids have low viscosities and high conductivities. However, these ionic liquids have narrow electrochemical windows (~4.2 V). Imidazolium cations are prone to being reduced/decomposed at the electrode/electrolyte interface when the (carbon) electrode is polarised to 0.7 V vs. Li/Li⁺. The strong decomposition reaction of the cations prevents the normal operation of the cell. In contrast, tetraalkylammonium salts, including cyclic analogues (i.e. piperidinium, morpholinium, pyrrolidinium and azepanium), have wider electrochemical windows;^{1,10} some are stable well below 0 V vs. Li/Li⁺, so research should focus on ILs containing these fragments. The introduction of oxygen into alkyl chains should improve some properties of such ether-containing ILs; in particular, it should lower their melting point, but it should have deteriorating impact on their electrochemical stability.17,18

> However, electrochemical stability at high potentials is connected with the oxidation of anions,10 so anions with high resistance to oxidation should be used. Most stable are highly fluorinated anions, such as tetrafluoroborates,19 hexafluorophosphates and perfluorinated sulfonylamides.²⁰ ILs formed with pefluorinated sulfonylamides, such as bis(trifluoromethanesulfonyl)amide (TFSI),²¹ bis(fluorosulfonyl)amide (FSI)22 and (fluorosulfonyl)(trifluoromethanesulfonyl)amide (FTFSI),²³ possess the best properties (high stability, wide liquid range, low viscosity, and acceptable conductivity).



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Recently there have been some reports on ionic liquid electrolytes based on bis(fluorosulfonyl)imide (FSI) for rechargeable Li batteries. In particular, FSI-based electrolytes containing Li ions exhibited practical ionic conductivity, and a natural graphite/Li cell with FSI-based electrolytes containing Li bis-(trifluoromethanesulfonyl)imide (LiTFSI) showed cycle performance without any solvent, using 1-ethyl-3-methylimidazolium EMIm FSI and EMIm TFSI,²⁴ and using ILs based on bis-(fluorosulfonyl)imide (FSI)²⁵ as the anion and 1-ethyl-3-methylimidazolium and *N*-methyl-*N*-propylpyrrolidinium as cations. It has also been observed that ILs with a TFSI anion cannot be used alone with graphite electrodes, because only very low capacities could be reached. The performance of such IL based electrolytes was improved by the use of various SEI-layer forming additives.²⁶

However ILs were probed also as solvents in emerging battery technologies revealing great potential for further development.8 Ether functionalised ILs were used to prepare electrolytes showing promising properties (stabilisation of superoxide anions with IL cations) for the manufacture of Li-air batteries.27 Recently, Nohira published electrolytes based on the Na-FSA/Im12-FSA mixture, showing excellent stability and conductivity combined with a reversible plating/dissolving on GC and Al working electrodes. All those desired properties make those mixtures excellent electrolytes for sodium based batteries.28 But this also implicates that the development of sodium batteries is mainly dependent on the manufacture of stable high capacity Na-cathodes. On the other hand magnesium and other polyvalent cation battery technologies are at their beginnings. The manufacture of stable magnesium electrolytes was demonstrated to be difficult already in the molecular solvents,²⁹ the major obstacle being the passivation of Mg and irreversibility of plating/dissolution on/from the working electrode which was not solved yet by the use of ILs,8 but there are still many possibilities to discover new approaches for the preparation of suitable electrolytes which will facilitate the development of Mg batteries.

The hydrophobicity of most ionic liquids is ensured by the use of highly fluorinated anions; there have also been a few reports on the preparation of hydrophobic cations containing perfluorinated alkyl chains.^{30,31}

Choline-like compounds, possessing a 2-hydroxyethyl group, are able to form deep eutectic mixtures,³² but are not suitable for use in electrochemical devices with high operating voltages because of the presence of labile acidic hydroxyl groups. The methylation of hydroxyl groups in choline-like compounds may, however, improve their stability.4,18,19 Another clue for a new class of ILs was the improvement of the stability of various oligoethylene glycols (for use as solvents in batteries), achieved by the protection of the terminal hydroxyl group by various silyl groups, such as the trimethylsilyl group.33 The preparation of silvlated choline compounds has been reported.34 The introduction of siloxy groups onto various surfaces can make those surfaces hydrophobic,35 so the same should also be true for molecules. That concept was proved by Yamazaki, who prepared ionic compounds containing trialkylsilyl moieties and suggested their use as antistatic agents for low surface energy polymers (PTFEs). The prepared antistatic agents were mostly solid at room temperature,³⁶ which suggests that it would be interesting to study the influence of hydrophobicity on the electrochemical behaviour of ILs.

Therefore, we report the systematic synthesis of a series of a new type of ILs, which are composed of tetraalkylammonium cations with increased hydrophobicity (one alkyl chain is the (trialkyl-siloxy)ethyl group) and bis(perfluorosulfonyl)amide anions (TFSI, FSI, and FTFSI). Most of them are liquids at room temperature; they possess moderate viscosity, moderate conductivity and good to excellent electrochemical stability.

Results and discussion

The synthesis of choline-like cations could be realised in three ways, as proposed in Scheme 1. Methods A and B are the most suitable for lab preparation, so these two were used in this study. Method A includes quaternisation of ω-(N,N-dialkylamino)alcohols with an alkylating agent, typically 1-bromoalkane; this yields a bromide salt as a product. It is advantageous to carry out the synthesis at a low temperature (20-40 °C) in a polar solvent, such as acetonitrile or alcohols; the product is isolated by precipitation in ethyl acetate and subsequent filtration. The obtained product is in the form of a colourless hygroscopic solid, which could be recrystallized from an acetone-alcohol mixture. Applying higher temperatures and other solvents during alkylation could result in significant discoloration of the product; this discoloration is very difficult to remove without chromatographic methods. Method B is a reaction between the tertiary amine and w-hydroxy-alkyl halogenide. In most cases only chloro derivatives are available, so higher reaction temperatures are needed to obtain a good yield of the product. In general, amines are highly volatile, so the use of a pressure reactor is advisable. We heated both compounds



Scheme 1 Synthetic possibilities for the preparation of choline-like quaternary ammonium salts.

without a solvent in a Parr pressure reactor (316 SS) equipped with a stirring magnet on a stirring hot plate. The purity of the products obtained by this method was much lower than with Method A. The products were isolated by dissolution in methanol, purification by charcoal, filtration and precipitation in ethyl acetate. In cases of 4-chlorobutanol and 2-chloroethyl-2hydroxyethyl ether, the product was dissolved in water basified with NaOH to remove amine hydrochloride from the product. Method C is only suitable for the preparation of hydroxyethyl compounds. Those compounds are obtained from the reaction between a tertiary amine (or its salt) and ethylene oxide in an appropriate reactor. This method is a major industrial preparation of choline chloride, which is used as a food additive for animals.³⁷

The next two steps in the preparation of the silvlated ILs are presented in Scheme 2. Anion exchange (metathesis) was performed in a water solution,³⁸ because the products are not very water soluble. The starting quaternary ammonium salt 1 was dissolved in MQ water, and a solution of appropriate salt (Li or K) was added in one portion; in less than a minute, separation into a two-phase system occurred. The mixture was further stirred and then the organic phase was diluted with CH₂Cl₂, separated and washed six times with fresh MQ water. Due to the hydrophilic hydroxyethyl group, some compounds were soluble in water to some extent, when the ammonium salt contained longer alkyl substituents on nitrogen, lower solubility of the final product in water was observed and higher yields of the desired product 2 were isolated. Pure ILs 2 were obtained after evaporation of the solvent and subsequent drying in a high vacuum (<30 mTorr) at 60 °C; moreover, it was observed that vigorous stirring and purging with dry Ar (vacuum/refill/vacuum) considerably accelerated the drying. These compounds did not dissolve in CDCl₃ at high concentration, indicating the high polarity of the compounds (for NMR DMSO-d₆ was used). Furthermore, during the extraction process of ILs from water with CH₂Cl₂, it was observed that three layers were formed: a water phase, CH₂Cl₂ saturated with ILs, and an IL layer saturated with CH₂Cl₂. In order to further increase the hydrophobicity of the obtained IL 2 and to ensure the electrochemical stability, silvlation using a silazane reagent (hexamethyldisilazane, dimethylamino-triethylsilane and diethylamino-ethyldimethylsilane) was performed. In this manner, the only by-products are volatile gasses/liquids, which can be easily removed by intense evacuation combined with inert gas purging. Both reactants were mixed without the solvent forming two immiscible layers; vigorous stirring was applied and the fine emulsion was slowly heated under purging with N2. When the temperature reached 50-60 °C, intense evolution of ammonia (amines) was observed,



Scheme 2 Preparation of silylated ionic liquids

and the mixture was homogenised in 30 min. The mixture was stirred and heated for few hours, after which the volatiles were removed by drying in a high vacuum at 70 °C, reaching a final water content of less than 50 ppm in only eight hours. The ease of dewatering of ILs is connected with a hydrophobic character of ILs, *i.e.* more hydrophobic ILs are dried more easily than hydrophilic ones.¹⁹

The newly prepared ILs are listed in Table 1 and consist of four groups of compounds, each of them roughly illustrates the influence of a particular structural feature change. Group 1 (3ae, 3n, 3o and 3p) was obtained by variation of substitution on nitrogen (including heterocycles pyrrolidine and imidazole), Group 2 (3b and 3f-i) by variation of spacers between nitrogen and oxygen (including the chain containing two oxygen atoms), Group 3 by variation of substitution on silicon (3b, 3j and 3k) and Group 4 by variation of anions (3b, 3l and 3m).

Compounds were characterised by ¹H, ¹³C and ¹⁹F NMR. All data are consistent with structures, and data on intermediate compounds could be found in the ESI.[†]

Viscosity

The viscosity of ILs is determined principally by the electrostatic and van der Waals interaction forces between ions and sterical factors, including the size, shape and flexibility of the ions constituting the IL. Sample 3n was solid at RT, so no viscosity measurement was done. Fig. 1 shows a graph showing the dependence of viscosity on the temperature for various ILs prepared in the frame of this work, compared with N1122O1-TFSI, which has the lowest viscosity on the chart; 3k has the lowest viscosity of prepared ILs while 3h has the highest viscosity. It is interesting that the viscosity of 3b and 3h is not much higher compared with N1122O1-TFSI despite the introduction of the much bulkier trimethylsilyl and triethylsilyl groups in place of the methyl group, respectively.

The viscosities vary from 107 mPa s to 430 mPa s at 25 $^{\circ}$ C; the values of absolute viscosities could be calculated using the Vogel-Tammann-Fulcher (VTF) equation (eqn (1) and Table 2).^{39,40}

$$\frac{1}{\eta} = A \frac{e^{\frac{-B}{T-T_0}}}{\sqrt{T}} \tag{1}$$

In eqn (1) η is the viscosity in Pa s, *T* is the temperature in K, and *A*, *B*, and *T*₀ are empirical coefficients. *A* is the pre-exponential factor proportional to $T^{1/2}$; *B* has a dimension of energy and is related to the critical free volume for ion transport, although it is not related to any simple activation process. *T*₀ is the temperature at which the transport function ceases to exist or the liquid structural relaxation becomes zero and may be considered to be the glass transition temperature.

One would expect that increasing the ion size should increase the viscosity of the ionic liquid, but the results suggest that in silylated ionic liquids this is not necessarily true. In our class of ILs, we have three different sites on the cation, where the size could be increased: groups on nitrogen, the length of the linker between the nitrogen-silyl group and substitution on

Table 1 List of prepared silylated ionic liquids

IL no.	Abbreviation	\mathbb{R}^1	\mathbb{R}^2	R ³	R^4	R^5	R^6	R	ANI
3a	N1112OTMS	Ме	Ме	Ме	Ме	Ме	Ме	CH_2	TFSI
3b	N1122OTMS	Ме	Me	Et	Ме	Ме	Me	CH_2	TFSI
3c	N1222OTMS	Ме	Et	Et	Ме	Ме	Me	CH_2	TFSI
3d	N2222OTMS	Et	Et	Et	Ме	Ме	Me	CH_2	TFSI
3e	N1132OTMS	Ме	Me	Pr	Ме	Ме	Me	CH_2	TFSI
3f	N1123OTMS	Me	Me	Et	Ме	Ме	Me	$(CH_2)_2$	TFSI
3g	N1124OTMS	Ме	Me	Et	Ме	Ме	Ме	$(CH_2)_3$	TFSI
3ĥ	N1126OTMS	Ме	Me	Et	Ме	Ме	Me	$(CH_2)_5$	TFSI
3i	N1122O2OTMS	Ме	Me	Et	Ме	Ме	Me	$(CH_2)_2OCH_2$	TFSI
3j	N1122OEDMS	Ме	Me	Et	Et	Ме	Me	CH ₂	TFSI
3k	N1122OTES	Ме	Me	Et	Et	Et	Et	CH_2	TFSI
31	N1122OTMS	Ме	Me	Et	Ме	Ме	Me	CH_2	FSI
3m	N1122OTMS	Me	Me	Et	Ме	Ме	Ме	CH_2	FTFSI
3n ^a	PY12OTMS	Ме	Pyr		Ме	Ме	Ме	CH_2	TFSI
30^b	Im12OTMS	Ме	Im		Ме	Ме	Ме	3-CH ₂	TFSI
3p ^c	MIm12OTMS	Ме	MIm		Ме	Ме	Ме	3-CH ₂	TFSI

^{*a*} *N*-(2-Trimethylsiloxyethyl)-*N*-methylpyrrolidinium TFSI. ^{*b*} 1-(2-Trimethylsiloxyethyl)-3-methylimidazolium TFSI. ^{*c*} 1-(2-Trimethylsiloxyethyl)-2,3-dimethylimidazolium TFSI.



Fig. 1 Viscosity of selected ionic liquids between -20 and 80 °C (3b was measured only above 10 °C, due to solidification around 0 °C).

Table 2Table of coefficients in the Vogel-Tammann-Fulcher equa-
tion for dependence of absolute viscosity of prepared ILs versus
temperature

IL	$A [K^{1/2} Pa^{-1} s^{-1}]$	<i>B</i> [K]	T_0 [K]	η @ 25 °C [Pa s]
3a	$2265 imes 10^3$	2084	82.94	0.122
3b	385.6×10^3	1261	136.8	0.111
3c	208.9×10^3	1014	164.7	0.165
3d	198.8×10^3	984.4	171.2	0.202
3e	416.7×10^3	1230	147.5	0.146
3f	2017×10^3	1768	128.5	0.287
3g	$1046 imes10^3$	1669	130.1	0.340
3h	1264×10^3	1758	128.4	0.430
3i	896.4×10^3	1586	121.4	0.152
3j	1054×10^3	1773	98.00	0.115
3k	$4260 imes 10^3$	1983	103.4	0.107
31	570.2×10^3	1550	112.7	0.129
3m	1251×10^3	1719	108	0.116
3p	745.3×10^3	1453	137.2	0.193

silicon. Different structural features have diverse influences on the viscosity of the corresponding ionic liquids.

The changing size of the ammonium cation does not influence the viscosity as drastically as the elongation of the spacer between silicon and nitrogen. Surprisingly, the IL with the biggest triethylsilyl group has the lowest viscosity; the same rule can be observed in the case of different anions: the FSI IL is the most viscous in this system, while the TFSI IL is the least viscous. This feature may be a consequence of the decreased symmetry of molecules, increased steric hindrance of cations and high dispersion of charge density in anions, which prevent strong inter-ionic bonding.

Conductivity

The ionic conductivity of the ILs is not clearly dependent on their molecular mass but is well in accordance with viscosities.



Fig. 2 Dependence of conductivity of ionic liquids on the temperature between RT and 90 $^\circ\text{C}.$

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On Fig. 2, conductivities of 3a-e *versus* temperature are plotted. The conductivities for 3a-e vary from 1.44 mS cm⁻¹ to 1.10 mS cm⁻¹ at 25 °C, which is significantly lower if compared with data in ref. 19 on ILs containing quaternary ammonium cations and TFSI, BF₄ and RfBF₃ anions. For example, 3b, which differs from N1122O1-TFSI by the size of the OH blocking group (TMS or Me, respectively), has more than two times lower conductivity. The values of conductivities could be calculated using the Vogel-Tammann-Fulcher (VTF) equation (eqn (2) and Table 3).³⁹

$$\kappa = A \frac{\mathrm{e}^{\frac{-B}{T-T_0}}}{\sqrt{T}} \tag{2}$$

In eqn (2), κ is conductivity in S cm⁻¹, *T* is temperature in K, and *A*, *B*, and *T*₀ are empirical coefficients, which resemble the coefficient from eqn (1): *A* is a pre-exponential factor proportional to $T^{1/2}$; *B* has a dimension of energy and is related to the critical free volume for ion transport, although it is not related to any simple activation process. *T*₀ is the temperature at which the transport function ceases to exist or the liquid structural relaxation becomes zero, and may be considered to be the glass transition temperature. However, *A*, *B*, and *T*₀ obtained by fitting conductivity data are different from eqn (1); one would expect that *T*₀ values should be very similar, but actually they differ significantly, which is not yet understood but it has been observed before for the solution of lithium electrolytes.³⁹

Electrochemical stability

The electrochemical stability of ionic liquids is very important for their use in electrochemical applications. We used standard linear sweep voltammetry with platinum wire electrodes versus metallic lithium working and counter electrodes, thus imitating conditions in a typical lithium metal battery. On Fig. 3, linear sweep voltammograms of the representative silvlated ionic liquids in comparison with methylated N1122O1-TFSI are depicted. In general, silvlation improves the cathodic stability of ILs (3b and 3i); in the case of silvlated choline, the stability is not much improved (3a); the imidazolium IL undergoes reduction at 1.21 V vs. Li. On platinum wire electrodes in the first scan at RT; scan rate: 1 mV s^{-1} , reference and counter electrode: a sheet of lithium metal. The anodic and cathode limits for each IL were arbitrarily defined as a current exceeding the value of 0.03 mA. Cathodic (E_{cat}) and anodic (E_{ano}) potential limits versus Li metal and the corresponding electrochemical

Table 3Table of coefficients in the Vogel-Tammann-Fulcher equa-
tion for the dependence of absolute conductivity of selected ILs versus
temperature

IL	$A [{ m mS}~{ m K}^{1/2}~{ m cm}^{-1}]$	<i>B</i> [K]	T_0 [K]	κ (a) 25 °C [mS cm ⁻¹]
3a	4.35	604.0	182.7	1.35
3b	3.71	568.1	184.6	1.44
3c	4.23	576.8	189.6	1.21
3d	3.87	553.7	193.4	1.14
3e	3.66	556.4	192.47	1.10



Fig. 3 Linear sweep voltammograms of various ionic liquids.

windows (ΔE) are summarised in Table 4. In general, the anodic stability of the IL is limited mostly by the decomposition of anions; E_{ano} shows some dependence on the structure of the counter cation. Prepared ILs contain very stable perfluorinated sulphonamides, which exhibit excellent oxidation stability;20 so the obtained results are in accordance with expectations: all ILs are stable over 5 V vs. Li metal, and the majority are around 5.5 V. The cathodic stability of ILs is governed by the decomposition of cations, which are very complex in the present cases. Studies on alkylated choline-like compounds have revealed that alkyl ether chains on small quaternary ammonium compounds are unfavourable for producing stable ILs.19 We imposed the synthesis of silvlated compounds in order to explore the effect of the silicon protection group on electrochemical properties of compounds obtained in that manner. Structurally diverse cations were studied and the influence of substitution on reduction stability was examined. A silvlated choline cation (3a)

Table 4 Cathodic (E_{cat}) and anodic (E_{ano}) potential limits *versus* Li metal and the corresponding electrochemical windows (ΔE) for various ionic liquids determined with a Pt wire electrode

IL^{a}	$E_{\rm cat}$ [V]	$E_{\rm ano}$ [V]	$\Delta E \left[\mathbf{V} \right]$
3a	1.54	5.56	4.02
3b	<0	5.6	>5.6
3c	<0	5.44	>5.44
3d	<0	5.58	>5.58
3e	0.08	5.49	5.41
3f	1.98	5.45	3.47
3g	0.2	5.48	5.28
3h	0.65	5.4	4.75
3i	0.06	5.51	5.45
3ј	0.03	5.26	5.23
3k	0.08	5.04	4.96
31	<0	5.51	>5.51
3m	<0	5.56	>5.56
30	1.21	5.6	4.39
N1122O1-TFSI ^a	0.30	5.52	5.12

^{*a*} *N*-Ethyl-*N*-2-methoxyethyl-*N*,*N*-dimethylammonium bis(trifluoro-methanesulfonyl)amide.

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is not stable due to insufficient steric shading of positive nitrogen and starts to decompose at 1.54 V vs. Li. By changing one methyl group with an ethyl group, a very stable N-ethyl-N-(2trimethylsiloxyethyl)-N,N-dimethylammonium (N1122OTMS, 3b) cation was obtained (stable below 0 V vs. Li). By increasing the substitution on nitrogen, other stable cations were obtained (3c-e); the stability was detrimentally affected by increasing the length of the ethyleneoxy linker between nitrogen and silicon; the propylene group caused the worst effect; 3f is reduced at 1.98 V, while butylene and hexylene show moderate influence increasing with the linkers' length. When a linker resembling a short di(ethyleneoxide) chain is used (3i), the stability is not affected. An N1122O fragment was used to study the influence of various silyl groups on reduction stability; the slight variation of methyl and ethyl groups on silicon does not affect stability, which is in all three compounds nearly the same (3b, j and k). An N1122OTMS cation was also used to study the influence of different anions, but those showed practically no influence on cathodic reactions, so the reduction stability is the same for all three compounds (3b, l and m). When the unsaturated heterocyclic imidazolium cation is used for the construction of the silvlated cation, an intense reduction reaction is observed at 1.21 V vs. Li. By comparing the stabilities of silylated cations, we can conclude that silvlation of the OH group has a beneficial effect on electrochemical stability when compared with methylation.¹⁹ Increased stability may be s consequence of many factors but the most important is definitely the sterically shielding of cations combined with the higher dispersion of charge density. These results suggest that the majority of these ILs could be used as electrolytes in lithium batteries with a high voltage cathodes (LiNiPO₄,⁴¹ LiMnPO₄,⁴² and Li(Mn, Ni, Co)O_x ⁴³) as well as with metallic lithium or graphite anodes. For compounds that are not stable below 1.4 V vs. Li, lithium titanate could be used as the anode.44

The other point is the stability of the passivation film, which is composed of IL molecules and salt, which should occur with these materials. It should be noted that, despite the range of electrochemical stability of ILs, there must be a chemical affinity with the surface of the active material in order to obtain a long cycle life of the battery. This subject will be addressed in further investigations.

Moreover, the prepared ILs are also candidates for the preparation of sodium based electrolytes, but the properties like solubility of appropriate sodium salt in such a system must be checked, because sodium ions need a solvent with stronger solvation power in comparison with lithium. The low polarity of the prepared IL which reflects also in the hydrophobic character may however prevent solubility of sodium salts. Also those features need to be explored in the future.

Experimental section

General

The following reagents were used as received: choline chloride, 2-(dimethylamino)ethanol, 2-(diethylamino)ethanol, *N*-methylpyrrolidine, hexamethyldisilazane, CH_2Cl_2 , bromo-ethane, 1-bromopropane, triethylamine (from Aldrich), methanol, acetone, ethyl acetate (Fischer), 2-bromoethanol, 3-chloropropanol, 3-chlorobutanol, 6-chlorohexanol, 2-chloroethyl-2hydroxyethyl ether, diethyl ether, acetonitrile, diethylamine (Alfa Aesar), (dimethylamino)triethylsilane, ethyldimethylchlorosilane (Gelest), LiTFSI (3 M), and triflic amide (Rhodia). K-FSI,⁴⁵ K-FTFSI²³ and (diethylamino)ethyldimethylsilane⁴⁶ were synthesised according to published methods.

¹H, ¹³C and ¹⁹F NMR spectra were recorded using a 300 MHz Varian Mercury equipped with an SMS-100 sample changer and a 500 MHz Varian VNMRS. D_2O and DMSO-d₆ were used as solvents for halides and DMSO-d₆ for TFSI, FTFSI and FSI hydroxy compounds and CDCl₃ was used for silylated ILs. Chemical shifts are reported relatively to solvents peaks, and for ¹⁹F NMR fluorobenzene was used as the internal reference (-113.10 ppm).

The water content was determined by using a Mettler Toledo V10 Compact Volumetric Karl-Fischer titrator. The water content in all investigated ILs was below 50 ppm.

Viscosity (absolute) was measured using an Anton Paar Physica MCR 301 instrument equipped with a parallel-plate system (PP50-SN5204) with Peltier temperature control, which enabled measuring viscosity *vs.* temperature at constant shear rate of $d\gamma/dt = 500/s$ with a linear temperature increase. Determination of coefficients in the Vogel-Tammann-Fulcher equation has been done using curve fitting (provided by Origin 8.1 programme) on experimental data between -20 and 80 °C.

The conductivity of the neat ILs was measured between room temperature (\sim 23 °C) and 90 °C using a MMulty Conductimeter made by Materials Mates Italia S.r.L in a sealed cell, consisting of two parallel platinised Pt electrodes. The temperature program was very slow; measurement in the complete range was finished in 12 hours. Determination of coefficients in the Vogel-Tammann-Fulcher equation has been done using curve fitting (provided by Origin 8.1 programme) on experimental data.

Electrochemical stability was determined in a 5 ml beaker type three electrode cell having a Pt wire as the working electrode, lithium metal (as a sheet) as the counter electrode and another sheet of lithium metal as the quasi reference electrode (QRE). Measurements were performed in a glovebox with atmosphere containing less than 1 ppm oxygen and water. Linear sweep voltammetry was performed using a VMP3 Modular 16 Channels Potentiostat/Galvanostat/EIS, manufactured by BioLogic Science instruments. The CV curve was measured between 0 and 6 V vs. Li at a scan rate of 1 mV s⁻¹, from an open circuit potential to 6 V and back to 0 V.

Experimental details

For demonstration of the preparation of 3b: *N*-ethyl-*N*-(2-trimethylsiloxyethyl)-*N*,*N*-dimethylammonium bis(trifluoromethanesulfonyl)amide (N1122-OTMS-TFSI, 3b) is given; this compound is prepared in three steps:

N-Ethyl-*N*-2-hydroxyethyl-*N*,*N*-dimethylammonium bromide (1b). In a 500 ml round-bottom flask equipped with a magnetic stirrer were placed 45.3 g (0.508 mol) of 2-dimethylaminoethanol dissolved in 150 ml of MeCN. To this solution, a mixture of 61.5 g (0.550 mol) ethyl bromide and 60 ml of MeCN was added

dropwise over a period of 1.5 h using a water bath (at 20 °C) for cooling during the addition. After half of the EtBr was added, a snow white crystalline product started to precipitate from the solution. The mixture was stirred over a weekend (57 h), and then vacuum filtered, washed with a small amount of acetone, and dried in a vacuum oven at 60 °C. The filtrate was evaporated to dryness and an additional product was isolated. Altogether, 98.13 g (72%) of *N*-ethyl-*N*-2-hydroxyethyl-*N*,*N*-dimethylammonium bromide were obtained.

N-Ethyl-N-2-hydroxyethyl-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (2b). In a 250 ml round-bottom flask, solutions of 52 g (0.263 mol) of N-ethyl-N-2-hydroxyethyl-*N*,*N*-dimethylammonium bromide in 70 ml MQ water and 78 g (0.274 mol) of LiTFSI in 80 ml MQ water were mixed together under vigorous stirring. Phase separation occurred at once, but stirring was continued for another 4 hours at room temperature. Then, 100 ml of CH₂Cl₂ were added and the phases separated. The water phase was extracted with 50 ml of CH₂Cl₂ and the combined organic phases were washed 6 times with 100 ml of MO water. A clear colourless solution was obtained and poured into a round-bottom flask. The solvent was removed using a rotary evaporator and then under high vacuum at 60 °C. In this manner, 70 g (67%) of pure N-ethyl-N-2-hydroxyethyl-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide as a colourless liquid were obtained.

N-Ethyl-N-(2-trimethylsiloxyethyl)-N,N-dimethylammonium bis(trifluoromethanesulfonyl)amide (3b). To a 250 ml roundbottom flask containing 80 g (0.20 mol) of neat N-ethyl-N-2hydroxyethyl-N,N-dimethylammonium TFSI, 31 g (0.20 mol) of hexamethyldisilazane (HMDS) were added at room temperature as a gentle stream of nitrogen was passed through the apparatus to facilitate the removal of forming ammonia. The mixture was slowly heated to 60-70 °C and stirred so that a fine emulsion of HMDS in ILs formed. A vigorous evolution of gaseous ammonia started as the temperature reached 60 °C and ended after a few minutes. The mixture was heated and stirred for an additional four hours after the end of the vigorous reaction. Then, the remaining HMDS, which was in a separate layer on top of the desired product, was evaporated under high vacuum. The round-bottom flask was then refilled six times with argon and again evacuated. The product was heated to 70 °C during this procedure. Finally, the apparatus was cooled down under vacuum and refilled with argon. In this manner, 94 g (quant.) of the title compound in the form of a colourless liquid were obtained.

Conclusion

A new family of low melting ionic liquids with hydrophobic cations and anions were prepared by silylation of choline-like (ω -hydroxyalkyl-trialkylammonium) quaternary ammonium salts possessing hydroxyl groups. The influence of substitution on nitrogen, the length of the spacer between the nitrogen and hydroxyl group and various silyl groups on their physicochemical properties were explored. All but one are liquid at room temperature. These ILs exhibit better cathodic stability than their analogues that have an OH group blocked by a methyl

group, which suggests that silvlation of the OH group makes compounds more cathodically stable. The most stable compounds are stable below 0 V vs. Li. As anions, highly electrochemically stable FSI, TFSI and FTFSI were used, which yielded ILs with anodic stability over 5 V vs. Li metal. Those properties are highly desirable for any liquids that are used for the preparation of electrolytes for electrochemical devices, especially for high energy density Li or Li-ion devices with a high operating voltage, where electrolytes are simultaneously and constantly exposed to low and to high voltages. The majority of the prepared ILs satisfy these demands so we hope that these compounds will contribute to the fabrication of better lithium (and sodium) batteries.

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