Electrochemical Applications of Room-Temperature Ionic Liquids

by Tetsuya Tsuda and Charles L. Hussey

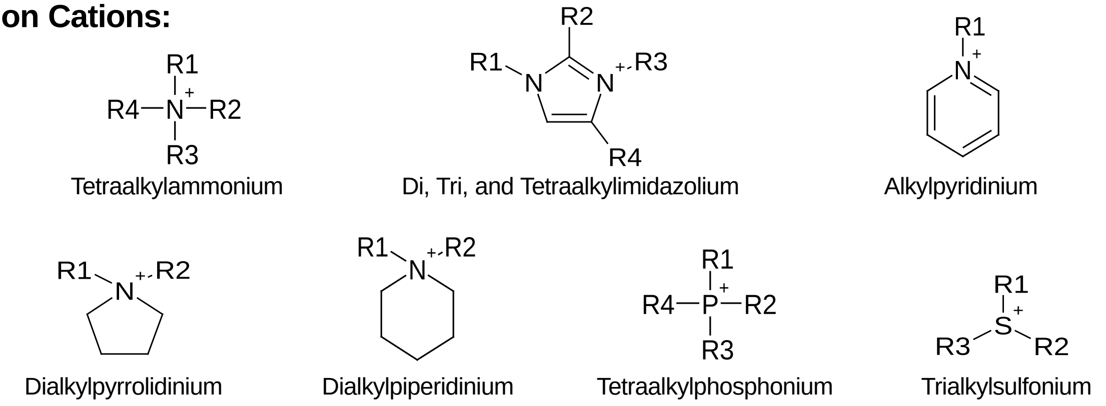
There is good evidence that the first room-temperature ionic liquid or RTIL was identified and characterized by Walden in 1914, who examined the electrical conductivity of ethylammonium nitrate.[1] Thus, it would not be an exaggeration to say that the very beginnings of electrochemistry involved room-temperature ionic liquids! Although once considered to be a curious subset of the general class of substances called "molten salts," RTILs have taken on a life of their own and now occupy the attention of scientists worldwide. In fact, scientific interest in these interesting materials continues to grow exponentially. Today a literature search with SciFinder Scholar (Chemical Abstracts Online) employing the keywords ionic liquid or room-temperature ionic liquid produces hundreds of articles, whereas just ten years ago a search would produce only a handful of papers. From the viewpoint of electrochemistry, RTILs are under investigation as solvents for technological applications such as metal surface finishing, batteries, capacitors, fuel cells, electrosynthesis, and nuclear waste treatment.

The question as to what exactly constitutes an ionic liquid or RTIL is discussed in the preceding article by Keith Johnson and will not be considered further herein. Although a large number of different RTILs have been reported in the literature, most can be classified into one of seven families on the basis of their cationic structures, as depicted in Fig. 1. Some of the common anions on which RTILs are based are also given in this figure. One advantage of having such a diverse selection of anions and cations is that it is possible to "engineer" the physicochemical properties of RTILs by the choice of the ionic constituents. For example, the combination of an imidazolium cation, such as 1-ethyl-3-methylimidazolium ion with BF_4^- results in a hydrophilic RTIL, whereas the combination of this cation and $N(SO_2CF_3)_2^-$ (NTf_2^-) produces a strongly hydrophobic ionic liquid. Although other factors may play a role, the viscosity and conductivity of such ionic liquids is largely a function of the chain length of the alkyl substituents, a factor that also carries over to the other classes of cations in Fig. 1.

Unfortunately for electrochemists and despite these opportunities for structural engineering, there are only a limited number of RTILs that are really suitable for electrochemistry. This is because most exhibit low electrical conductivity (< 5 mS cm^{-1}) and high viscosity (> 50 cP). In some cases, RTILs that do have sufficient conductivity for electrochemical applications exhibit meager electrochemical windows and/or show limited chemical stability toward reactive materials and ions such as Li, H^- or O_2^-. Thus, it is sometimes difficult to identify RTILs having all of the properties necessary to guarantee the success of a specific application. Relatively speaking, the combination of imidazolium- or sulfonium-based cations and complex halide anions such $AlCl_4^-$, BF_4^-, $CF_3CO_2^-$, $CF_3SO_3^-$, NTf_2^-, $N(SO_2F)_2^-$, or $F(HF)_{2.3}^-$ results in RTILs with good working conductivities. From the relationship known as Walden's rule, we know that the conductivity of an electrolyte is approximately correlated with its viscosity. Thus, one cannot expect viscous RTILs prepared from cations with long-chain substituents to show appreciable conductivities, and this is universally the case. With regard to the electrochemical window of RTILs, tertraalkylammonium-, dialkylpyrrolidinium-, and dialkylpiperidinium-based ionic liquids typically exhibit superior electrochemical stability relative to imidazolium-based RTILs, owing to their superior resistance toward reduction compared to cations based on aromatic heterocyclic species. This is true provided that the accompanying anions are not reduced before the cations. But unfortunately, the conductivities of these systems are usually inferior to the imidazolium- and sulfonium-based RTILs, illustrating the trade-off between stability and favorable transport properties. There are several excellent monographs[2] and review articles[3] that describe the synthesis, purification, physicochemical, and electrochemical properties of RTILs. In many cases, they also provide guidance about the applications of various RTILs to specific electrochemical problems.

Although "historical" RTILs, *i.e.*, ionic liquids composed of an anhydrous metal chloride combined with an organic chloride salt, *e.g.*, $AlCl_3$–1-ethyl-3-methylimidazolium

Common Cations:



Common Anions:

BF_4^-, $B(CN)_4^-$, $CH_3BF_3^-$, $CH_2CHBF_3^-$, $CF_3BF_3^-$, $C_2F_5BF_3^-$, n-$C_3F_7BF_3^-$, n-$C_4F_9BF_3^-$, PF_6^-, $CF_3CO_2^-$, $CF_3SO_3^-$, $N(SO_2CF_3)_2^-$, $N(COCF_3)(SO_2CF_3)^-$, $N(SO_2F)_2^-$, $N(CN)_2^-$, $C(CN)_3^-$, SCN^-, $SeCN^-$, $CuCl_2^-$, $AlCl_4^-$, $F(HF)_{2.3}^-$ etc.

Fig. 1. *Common cations and anions for room-temperature ionic liquids.*

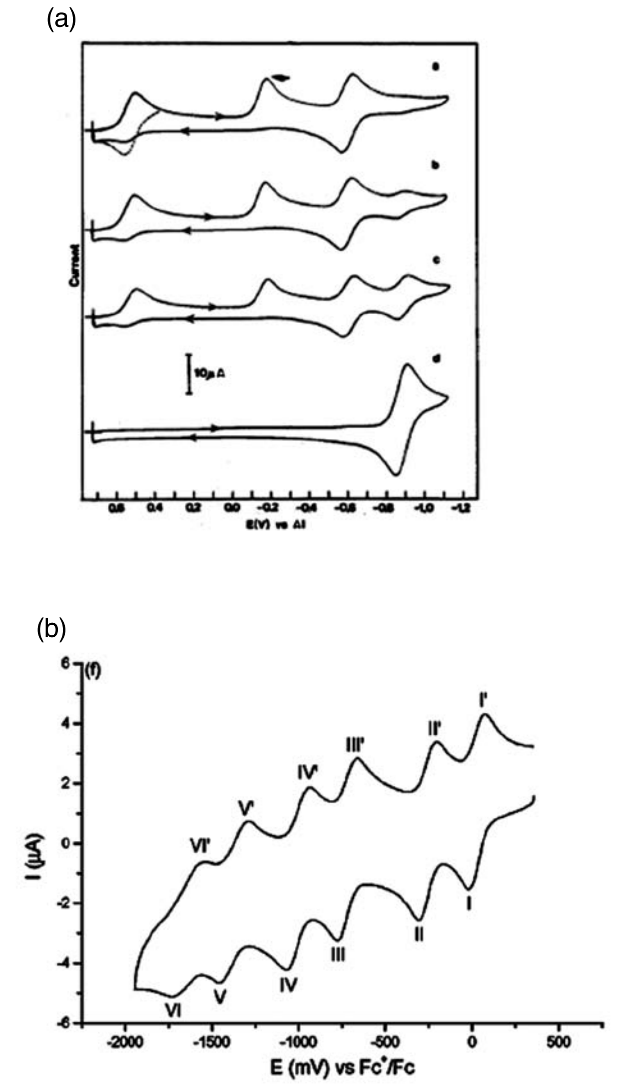


Fig. 2. *(a) Cyclic voltammograms of 5.07 mmol L^{-1} $[n\text{-}Bu_4N][Re_2Cl_9]$ in a Lewis basic 44.4–55.6 mol % $AlCl_3$–EtMeImCl at a GC electrode: (A) fresh solution; (B) after 70 min, (C) after 197 min, (D) solution in C after being heated to 363 K for 60 min and cooled. The sweep rates were 0.050 V s^{-1}, and the temperatures were 301 K. (Reproduced from Ref. 7 with permission from The Electrochemical Society.) (b) Cyclic voltammogram of 5 mmol L^{-1} $[n\text{-}Bu_4N]_4[S_2W_{18}O_{62}]$ in n-BuMeImPF$_6$ at a GC electrode. The sweep rate was 0.10 V s^{-1}, and the temperature was 293 K. (Reproduced from Ref. 8 with permission from the American Chemical Society.)*

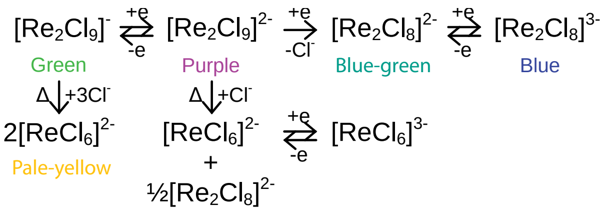
chloride (EtMeImCl), $AlCl_3$–1-(1-butyl)pyridinium chloride (BuPyCl), and CuCl–EtMeImCl, are highly sensitive to moisture, these RTILs are still the preferred choice for applications involving metal surface finishing, *e.g.*, electroplating. This is because it is much easier to dissolve salts of the plating metals in these RTILs compared to the more inert fluoroanion-based systems such as EtMeImBF$_4$, *n*-BuMeImPF$_6$, or EtMeImNTf$_2$. In addition, it has been demonstrated many times that metallic films on the order of μm-thicknesses can be readily electrodeposited from these RTILs.[4,5] On the other hand, there are technologies that can take advantage of the chemical inertness of these fluoroanion-based systems. One example is the use of these liquids as electrolytes for Li batteries and low-temperature fuel cells.

We describe below some selected research highlights involving current electrochemical applications of RTILs. We also provide literature citations to guide the interested reader.

Electrochemical Investigations of Inorganic Complexes

Although they are environmentally unstable and require manipulation in an inert atmosphere glove box or sealed cell, chloroaluminate RTILs have proven to be especially versatile solvents for electrochemical studies of inorganic chloride complexes and low-valent metal species. This is because the Lewis acidity of these RTILs can be adjusted by changing the $AlCl_3$/RCl ratio, where RCl is the organic chloride salt, *e.g.*, EtMeImCl. Ionic liquids containing a molar excess of $AlCl_3$ are Lewis acidic because they contain coordinately unsaturated species such as $Al_2Cl_7^-$ that are strong chloride acceptors. On the other hand, chloroaluminate RTILs containing a molar excess of RCl are Lewis basic because they contain chloride that is not bound to aluminum. Acidic chloroaluminate RTILs readily dissolve and stabilize low oxidation state transition metal species, *e.g.*, polynuclear metal-metal bonded clusters such as $[Nb_6Cl_{12}]^{z+}$ and $[Ta_6Cl_{12}]^{z+}$. They have proven to be excellent, if not unique solvents for probing the electrochemistry of these interesting inorganic species.[6]

Basic chloroaluminate RTILs support the formation of anionic chloride complexes similar to those found when metal ions are introduced into molten mixtures of alkali chlorides such as LiCl–KCl. They have been used as solvents to investigate the room-temperature electrochemistry of a large number of transition metal and main group chloride complexes of the type $[M_pCl_q]^{(q-pn)-}$, where M is the metal with an oxidation state of n. An interesting example is the electrochemistry of $[Re_2Cl_9]^-$ in Lewis basic 44.4–55.6 mol% $AlCl_3$–EtMeImCl.[7] Figure 2a shows a series of cyclic voltammograms for $[Re_2Cl_9]^-$ that were recorded at a glassy carbon electrode in this RTIL. Three reduction waves with approximate peak potentials of 0.52, -0.16, and -0.61 V, respectively, appear on the negative scan in the fresh solution, but only the first and last waves exhibit an associated oxidation current. The first wave corresponds to the one electron reversible reduction of $[Re_2Cl_9]^-$ to $[Re_2Cl_9]^{2-}$. The latter two reduction waves were also present in the RTIL when it contained only $[Re_2Cl_9]^{2-}$ and were found to arise from the chemically irreversible reduction of this species to $[Re_2Cl_8]^{2-}$ and the subsequent one-electron reversible reduction of $[Re_2Cl_8]^{2-}$ to $[Re_2Cl_8]^{3-}$. After a period of a few hours, the original waves for $[Re_2Cl_9]^-$ and its progeny begin to disappear, and a new wave attributed to the reversible one-electron reduction of $[ReCl_6]^{2-}$ to $[ReCl_6]^{3-}$ becomes evident. On the other hand, $[Re_2Cl_9]^{2-}$ disproportionates into a mixture of this monomeric species and dimeric $[Re_2Cl_8]^{2-}$. In both cases, the conversion process can be expedited by heating the solution. Combined with electronic spectroscopic data, these electrochemical investigations reveal a rich and diverse chemistry for $[Re_2Cl_9]^-$ in this chloride-rich RTIL as summarized below:



$$\begin{tikzcd}
\underset{\text{Green}}{[Re_2Cl_9]^-} \arrow[r, shift left, "+e"] \arrow[d, "\Delta"', "+3Cl^-"] & \underset{\text{Purple}}{[Re_2Cl_9]^{2-}} \arrow[l, shift left, "-e"] \arrow[r, "+e", "-Cl^-"'] \arrow[d, "\Delta"', "+Cl^-"] & \underset{\text{Blue-green}}{[Re_2Cl_8]^{2-}} \arrow[r, shift left, "+e"] & \underset{\text{Blue}}{[Re_2Cl_8]^{3-}} \arrow[l, shift left, "-e"] \\
\underset{\text{Pale-yellow}}{2[ReCl_6]^{2-}} & [ReCl_6]^{2-} \arrow[r, shift left, "+e"] & [ReCl_6]^{3-} \arrow[l, shift left, "-e"] & \\
 & + \tfrac{1}{2}[Re_2Cl_8]^{2-} & &
\end{tikzcd}$$

Non-chloroaluminate RTILs have also proven to be valuable for exploring the electrochemistry of novel inorganic species. For example, tetrabutylammonium salts of the polyoxometallate anions $[M_6O_{19}]^{2-}$, $[\alpha\text{-}SiM_{12}O_{40}]^{4-}$, and $[\alpha\text{-}S_2M_{18}O_{62}]^{4-}$, where M = Mo or W, dissolve readily in *n*-BuMeImPF$_6$ with heating.[8] Figure 2b shows a cyclic voltammogram recorded at a glassy carbon electrode for a solution of the latter anionic species in this RTIL. This voltammogram exhibits six well-defined reduction

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waves on the negative scan, labeled I to VI in the original figure reproduced herein, and each reduction wave has an associated oxidation wave. These waves were ascribed to the six reversible one-electron reactions given in the scheme below.

$$[\alpha\text{-}S_2W_{18}O_{62}]^{4-} \underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{5-} \underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{6-} \underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{7-}$$

$$\underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{8-} \underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{9-} \underset{-e}{\overset{+e}{\rightleftarrows}} [\alpha\text{-}S_2W_{18}O_{62}]^{10-}$$

Electrochemical Mechanical Actuator Devices

There is considerable on-going interest in using conjugated polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) to fabricate lightweight, highly efficient electrochemical mechanical actuator devices or artificial muscles. This proposed application is based on the observation that these polymers physically deform when undergoing an oxidation/reduction cycle in an electrolyte solution. This deformation is due to the contraction/expansion resulting from the reversible expulsion/incorporation of electrolyte ions or solvent from the solution (electrochemical doping). However, the construction of an effective mechanical actuator device from these polymers requires an electrolyte solution with certain favorable properties. Foremost, the polymer used in the actuator must be completely stable in the electrolyte solution during the oxidation/reduction cycle, and the solution must exhibit reasonable conductivity and a large electrochemical window. Also, in order to achieve fast switching speeds, the doping ions should have high ionic mobilities in the electrolyte. Clearly, environmentally stable RTILs are ideally suited for this application due to their chemical inertness, high intrinsic conductivities, large electrochemical windows, and negligible vapor pressures. Furthermore, such RTILs should permit the operation of actuators at higher temperatures and larger voltages than is possible with conventional molecular solvent/electrolyte systems.

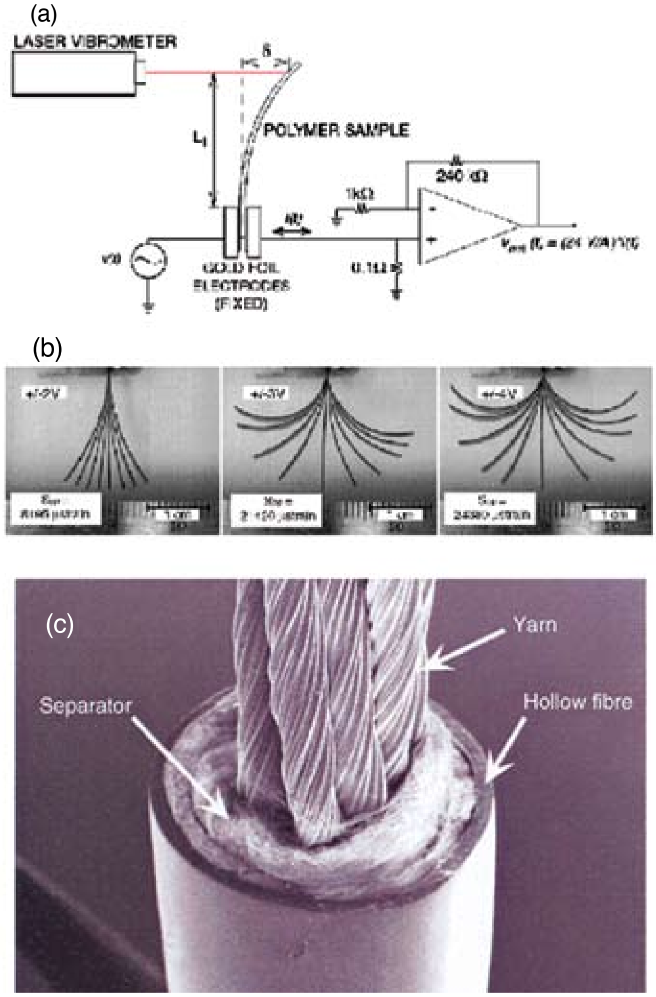

Fig. 3. *(a) Experimental apparatus for free deflection and impedance tests of polymer film electrochemical actuators. (b) Photographs of the deflected shapes as a function of amplitude for a square wave potential input to a polymer film electrochemical actuator. (Reproduced from Ref. 11 with permission from Elsevier B.V.) (c) A SEM image of a yarn-in-fiber electrochemical linear actuator fabricated by threading eight Panion triflate yarns into a Panion triflate hollow fiber. (Reproduced from Ref. 12 with permission from CSIRO Publishing.)*

The application of RTILs as electrolytes for electrochemical mechanical actuator devices has been explored by several groups, with the first report appearing in the journal *Science* in 2002.[9] In this archetypical investigation, PANI and PPy were cycled in n-BuMeImBF$_4$ or n-BuMeImPF$_6$ under ambient conditions and exhibited no failure after 1 million cycles. For PANI, the doping mechanism involves the insertion/expulsion of n-BuMeIm$^+$ cations. However, for PPy, the nature of the doping mechanism was reported by the authors to be potential dependent, involving the insertion of n-BuMeIm$^+$ cations at low potentials and PF$_6^-$ anions at high potentials. Since the appearance of this original publication, several new approaches and different materials have been proposed for electrochemical actuators based on RTILs.[10] But in each case, the basic concept is the same in that the main components are an electrochemically-active polymeric material and a suitably conductive, but inert RTIL.

The instrumentation used to study the deformation of polymer films during electrochemical doping in RTILs is designed to examine both the strain and electrical impedance of the actuator material. A state-of-the-art experimental set-up used for this purpose is shown in Fig. 3a.[11] The experiments used to characterize the polymer films consist of applying a random potential with a RMS magnitude of ~1 V to the sample and measuring the displacement of the sample as a function of frequency with the laser vibrometer. By measuring the induced current as a function of the frequency of the applied potential, the impedance of the sample can also be determined. The deflected shapes of model actuators prepared from Nafion membranes painted with Au and/or RuO$_2$ powder, soaked with EtMeImTfO (TfO$^-$ = CF$_3$SO$_3^-$), and hot pressed between gold foils are shown in Fig. 3b.[11] It can be seen in this figure that the range of motion increases as the amplitude of the square wave input is increased.

Figure 3c illustrates the basic structure of the device proposed by Lu, *et al*.[12] This device is fabricated from PANI that is doped with trifluoromethane sulfonic acid. The polymer has been formed into the shape of a fiber, designated by the authors as a "panion triflate fiber." Several such fibers were wound into a yarn and threaded into a hollow tube also made from PANI; this tube serves as the counter electrode. An electrically insulating layer of non-woven polyacrylonitrile nanofiber serves as the separator and was soaked with a RTIL, in this case, n-BuMeImBF$_4$. With the application of a suitable potential, this actuator generated a stress of 0.42 ~ 0.82 MPa, which exceeds the stress generated by skeletal muscle (0.1 ~ 0.5 MPa). This example illustrates that the practical application of such devices may not be far in the future.

Dye-Sensitized Photoelectrochemical Cells

Dye-sensitized electrochemical photovoltaic or photoelectrochemical solar cells consist of a dye-sensitized film of a mesoporous oxide semiconductor, *e.g.*, TiO$_2$, which has been deposited on a conductive transparent surface and coated with a chemisorbed layer of a photoactive dye such as *cis*-RuL$_2$(SCN)$_2$, where L = 2,2'-bipyridyl-4,4'-dicarboxylate.[13,14] The surface

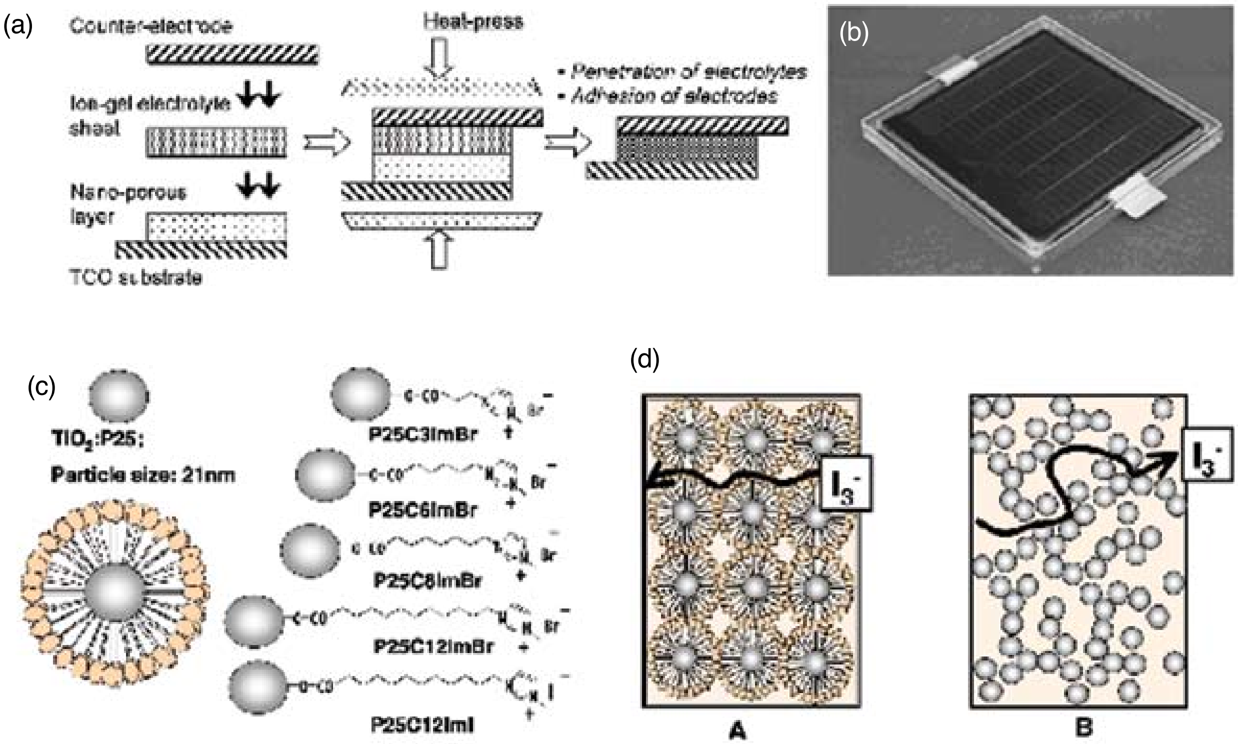

Fig. 4. *(a) Diagram showing the fabrication of an ion-gel sheet-type dye-sensitized solar cell. (b) 100 mm × 100 mm array of the dye-sensitized solar cells. (Reproduced from Ref. 17 with permission from Elsevier B.V.) (c) Modified* TiO_2 *nanoparticles. (d) Diffusion of* I_3^- *through a matrix of (A) modified and (B) unmodified* TiO_2 *nanoparticles. (Reproduced from Ref. 18 with permission from The Electrochemical Society.)*

of the semiconductor, which serves as the photoanode, is in contact with a solution containing a redox mediator, usually I^-/I_3^-. Upon exposure to light of a suitable wavelength, the dye injects electrons into the semiconductor, becoming oxidized. The oxidized dye layer accepts electrons from the mediator in the electrolyte, which is itself regenerated by electrons from the external circuit provided by the cathode.[14]

Typically, volatile organic solvents such as acetonitrile are used to prepare the electrolyte/mediator solution used in dye-sensitized photoelectrochemical cells. However, the high vapor pressure associated with conventional organic solvents, especially under conditions where considerable solar heating may take place, is problematic. As a result, much research has been devoted to identifying and characterizing RTILs that can be used to replace the organic solvents normally used in these photoelectrochemical cells.[15] One of the first RTILs to be investigated was *n*-HexMeImI (Hex = *n*-hexyl),[16] but as research in this area progressed, RTILs such as $EtMeImNTf_2$ have been used successfully.[17] By dissolving $EtMeImNTf_2$ and poly(vinylidenefluoride-*co*-hexafluoropropylene) together in a volatile organic solvent, it is possible to prepare an ion-gel electrolyte that can be surface cast.[17] Figure 4a shows the construction of a typical ion-gel based cell using a cast polymer electrolyte sheet. A 100 mm × 100 mm array of such cells is illustrated in Fig. 4b.

Recently, Hayase, *et al.*[18] have succeeded in preparing RTIL-based gel electrolytes by chemically modifying 21 nm TiO_2 particles with various 1-alkyl-3-methylimidazolium salts via the formation of Ti-O-CO-R bonds, where R = 1-alkyl-3-methyl-imidazolium bromide or iodide. The structures of the modified nanoparticles are illustrated in Fig. 4c. Clay-like gel electrolytes synthesized from regular TiO_2 nanoparticles and RTILs generally lead to a decrease in photoelectrochemical performance, especially at higher nanoparticle content. Fortunately, this problem can be avoided using these modified TiO_2 nanoparticles. The improved performance seen in this case depended on the alkyl chain lengths. For shorter alkyl groups or the regular unmodified nanoparticles, the mediator ions, I_3^- and I^-, likely diffuse randomly as shown in "B" in Fig. 4d. In contrast, ordered structures on the TiO_2 resulting from modification with longer chain alkyl groups provide paths for rapid diffusion by the mediator ions as depicted in "A" in Fig. 4d.

Overall, the conversion efficiency of dye-sensitized photoelectrochemical solar cells is only about 50% of that typically seen for conventional Si-based photovoltaic cells. However, the former are much cheaper to produce. Although the energy conversion efficiency for dye-sensitized photoelectrochemical cells based on RTILs is somewhat inferior to cells prepared with conventional organic solvent-based electrolytes, the benefits of replacing the volatile organic solvent component far outweigh this disadvantage. Do not be surprised to see commercially viable cells of this type that utilize RTILs in some form or another in the near future.

Electrochemical Supercapacitors

Electrochemical supercapacitors are simple energy storage devices with high rate charging-discharging capabilities and high power density. The latter property greatly exceeds that of conventional electrochemical energy storage devices, *e.g.*, batteries and fuel cells. Furthermore, supercapacitors can store a much greater charge per unit volume of mass than conventional dielectric-based capacitors. An electrochemical supercapacitor is based on the electrochemical double layer resulting from the electrostatic adsorption of ionic species at the electrode-solution interface, *i.e.*, no actual redox reaction is supposed to take place during the charging-discharging of these devices. To obtain the maximum possible capacitance, supercapacitor electrodes must have a high surface area; the standard material used in these devices is typically high surface area carbon. Because these devices are based on the electrosorption of ionic species, the region between the electrodes of the capacitor must contain an electrolyte with mobile ions. To obtain the maximum operating voltage without solvent decomposition, it is necessary to use aprotic solvents such as acetonitrile.

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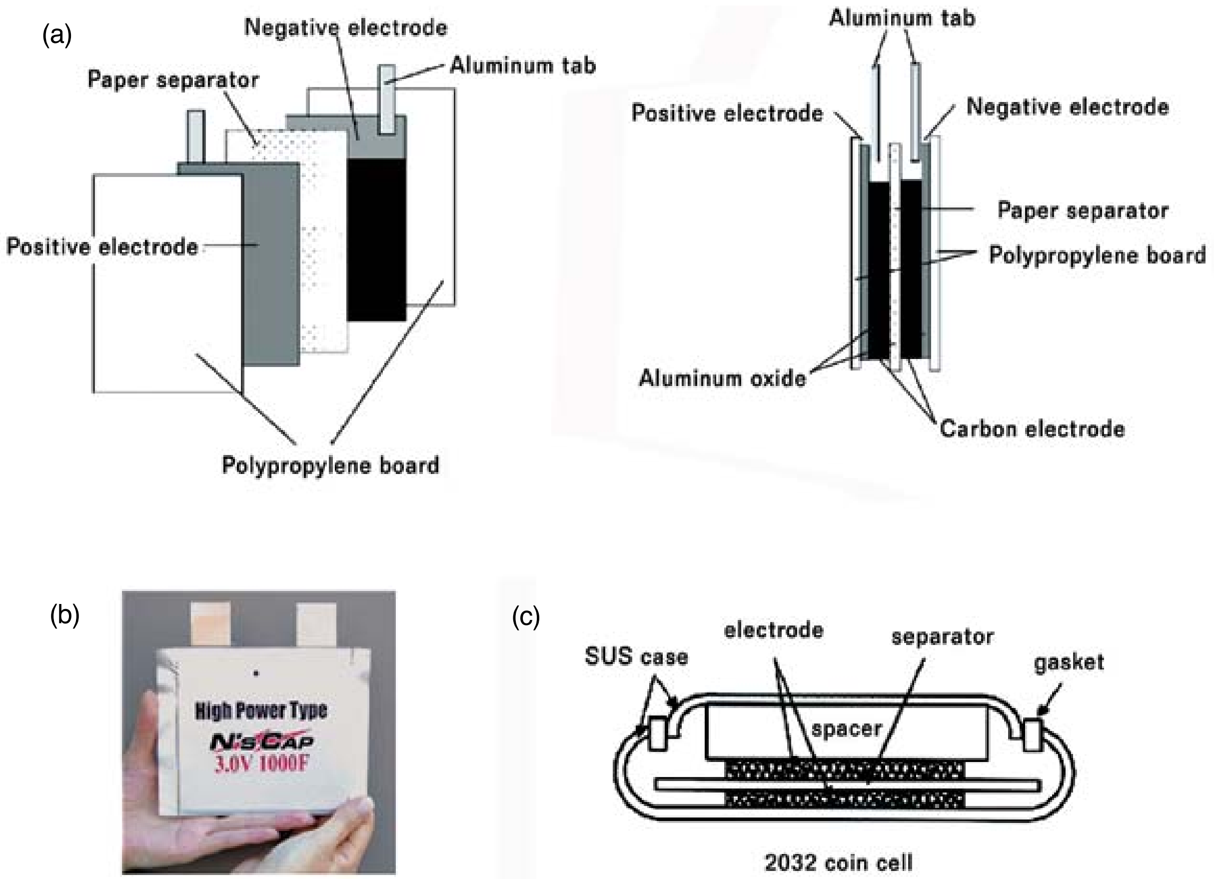

Fig. 5. *(a) Schematic diagram of a pouch-type electrochemical double layer supercapacitor. (Reproduced from Ref. 20 with permission from Elsevier Ltd.) (b) A commercialized pouch-type cell. (Reproduced from Japan Radio Co., Ltd. Website: http://www.jrc.co.jp/jp/whatsnew/20061018/index.html with permission.) (c) A 2032 coin-type electrochemical double layer supercapacitor. (Reproduced from Ref. 21 with permission from The Electrochemical Society.)*

Carbon-based supercapacitors based on conventional aprotic electrolytes are commercially available.

Not surprisingly, because of the numerous favorable properties described above, RTILs are considered to be promising electrolytes for electrochemical supercapacitors. $EtMeImBF_4$ and $EtMeImNTf_2$ dissolved in alkyl carbonate solvents were among the first RTILs to be investigated.[19] More recently, an electrochemical supercapacitor based on *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate was shown to have superior properties compared to supercapacitors based on conventional aprotic electrolytes such as mixtures of Et_4NBF_4 in propylene carbonate.[20] A diagram of a commercial supercapacitor that utilizes this electrolyte is shown in Figs. 5a and 5b. This device is available commercially from Japan Radio Co., Ltd. and has a rated potential of 3 V, a capacity of 1000 F, and a power density of 13.5 kW L^{-1}.

A coin-type supercapacitor fabricated from the very conductive fluoride-based RTIL, $EtMeImF(HF)_{2.3}$, that utilizes carbon cloth electrodes is shown in Fig. 5c.[21] In spite of limitations imposed by the potential stability of this RTIL, this device was found to exhibit better energy storage capabilities than supercapacitors based on aqueous H_2SO_4. A RTIL-based supercapacitor has even been prepared from carbon nanotubes. This device utilizes carbon gel electrodes fabricated by combining $EtMeImNTf_2$ with pulverized single-walled carbon nanotubes.[22]

Hybrid supercapacitors obtain energy storage from the electrostatic double layer capacitance obtained at a high surface area carbon electrode as discussed above and from a rapid, reversible charge-transfer process that occurs at a dopable conjugated polymer, *e.g.*, poly(3-methylthiophene).[23] This charge-transfer process is designated as a pseudocapacitance. Not surprisingly, RTILs have also found their way into hybrid supercapacitors. In fact, a hybrid supercapacitor based on activated carbon, poly(3-methylthiophene) and *n*-$BuMePyrNTf_2$ (Pyr = pyrrolidinium) may be the first viable supercapacitor based on a RTIL, producing 24 Wh kg^{-1} and 14 kW kg^{-1}.[24]

Lithium-Ion Batteries

Lithium-ion batteries are now ubiquitous in society and serve as the power sources in almost all portable electronic devices that are marketed to today's consumer. Articles devoted to or that discuss some aspects of lithium-ion batteries have appeared in *Interface* on several occasions.[25] Therefore, no effort is made herein to discuss either the background or the electrochemistry of these devices. With such widespread use and in view of the safety issue of lithium-ion batteries, there are considerable ongoing efforts by battery manufacturers to improve the performance of these devices. As a result of the many attractive aspects of RTILs, there is a modest, but continuing interest in using them as electrolytes for these cells. Until several years ago, the RTIL electrolyte of choice was some variety of chloroaluminate,[26] but interest in the use of non-chloroaluminate ionic liquids has gradually increased.

It is difficult to pinpoint the first instance where non-chloroaluminate RTILs were used in lithium-ion batteries. An early report describes a successful $Li/LiMn_2O_4$ cell prepared with 1,2-dimethyl-4-fluoropyrazolium tetrafluoroborate + $LiBF_4$ or $LiAsF_6$.[27] $Li/LiCoO_2$ cells utilizing *n*-$PrMePipNTf_2$ (Pip = piperidinium) show good cyclic efficiency,[28,29] and it is clear that RTILs based on those anions that offer good anodic stability, *e.g.*, NTf_2^- or $N(SO_2F)_2^-$, give the best performance.[29,30] At the present time, the main problem is the incompatibility of the anode, *e.g.*, Li metal, and the RTILs. That is, the solid electrolyte interphase film that is produced on the anode during the charge/discharge process is less stable than that obtained in conventional organic solvents. This incompatibility problem limits the cycling efficiency of the cell. MacFarlane, *et al.*[31] have succeeded in elucidating the mechanism of film formation on Li in RTILs based on *N*-alkyl-*N*-methylpyrrolidinium ions and NTf_2^-.[31] Perhaps, future research of this nature will lead to resolution of this problem, enabling the practical use of RTILs as electrolytes in Li batteries.

Treatment of Nuclear Waste

When spent nuclear reactor fuel is reprocessed, large volumes of liquid waste are produced, called "tank waste." This liquid waste, which may be acidic or basic depending on the treatment process, contains many long-lived radioactive products, including the β-emitters ^{137}Cs, ^{129}I, ^{90}Sr, and ^{99}Tc, and a variety of transuranic elements, which are normally α-emitters. The problems associated with this waste have been described previously in *Interface*.[32] The $^{137}Cs^+$ and $^{90}Sr^{2+}$ in tank waste are normally present at low concentrations in a large volume of liquid, and any treatment process for this waste must therefore produce a significant reduction in the volume of this liquid. A number of strategies have been employed to selectively extract $^{137}Cs^+$ and $^{90}Sr^{2+}$ from aqueous tank waste with ionophores specific for $^{137}Cs^+$ and $^{90}Sr^{2+}$, such as calix[4]arene-bis(*t*-octylbenzo-crown-6), BOBCalixC6, and dicyclohexano-18-crown-6, respectively, dissolved in hydrophobic solvents, including hydrophobic RTILs.[33] However, in order to formulate an economically-viable treatment process based on RTILs, a process must be devised to recycle the expensive RTIL/ionophore mixtures. We found in our own work that electrochemistry can play a useful role in this recycling process.

A schematic of the process developed for the extraction of Cs^+ from tank waste utilizing BOBCalixC6 dissolved in *n*-$Bu_3MeNNTf_2$ is shown in Fig. 6.[34] After extraction of Cs^+ into the hydrophobic RTIL, the extraction solvent is dried and the oxygen is removed by sparging with dry N_2 or by heating. The complexed Cs^+ is then selectively removed from the extraction solvent by reduction at a Hg electrode. The Cs(Hg) produced during the last step can be transported to another cell, where the Cs can be chemically or electrochemically stripped from the Hg into a minimum volume of aqueous solution. This proposed electrochemical process for remediation of the extraction solvent preserves both the ionophore and the RTIL.

Lab-on-a-Chip System

Although it is not based on classical electrochemistry, a novel and noteworthy application of RTILs is their use by Dubois, *et al.*[35] as solvents in electrowetting on dielectric (EWOD) microreactors or lab-on-a-chip systems. Microreactors are devices for carrying out microscale synthesis, and as such, are very useful for preparing small quantities of rare, expensive, or dangerous materials. In the case of the microreactor based on a RTIL, EWOD actuation is used as a fluidic motor to move and combine ionic liquid droplets containing the reagents of interest on two-dimensional, addressable chips by the application of a potential. Each segment of the chip is fabricated from gold electrodes coated with a dielectric of Si_3N and a hydrophobic layer of Teflon (Fig. 7). The negligible vapor pressure of the RTIL that was employed by these workers makes the manipulation of small liquid volumes (< 1 μL) of reagents possible in an open system without complications due to the loss of the solvent. The viability of this RTIL-based microreactor was demonstrated by carrying out a synthetic reaction involving multiple components that resulted in the preparation of tetrahydroquinolines, *i.e.*, Grieco's reaction.

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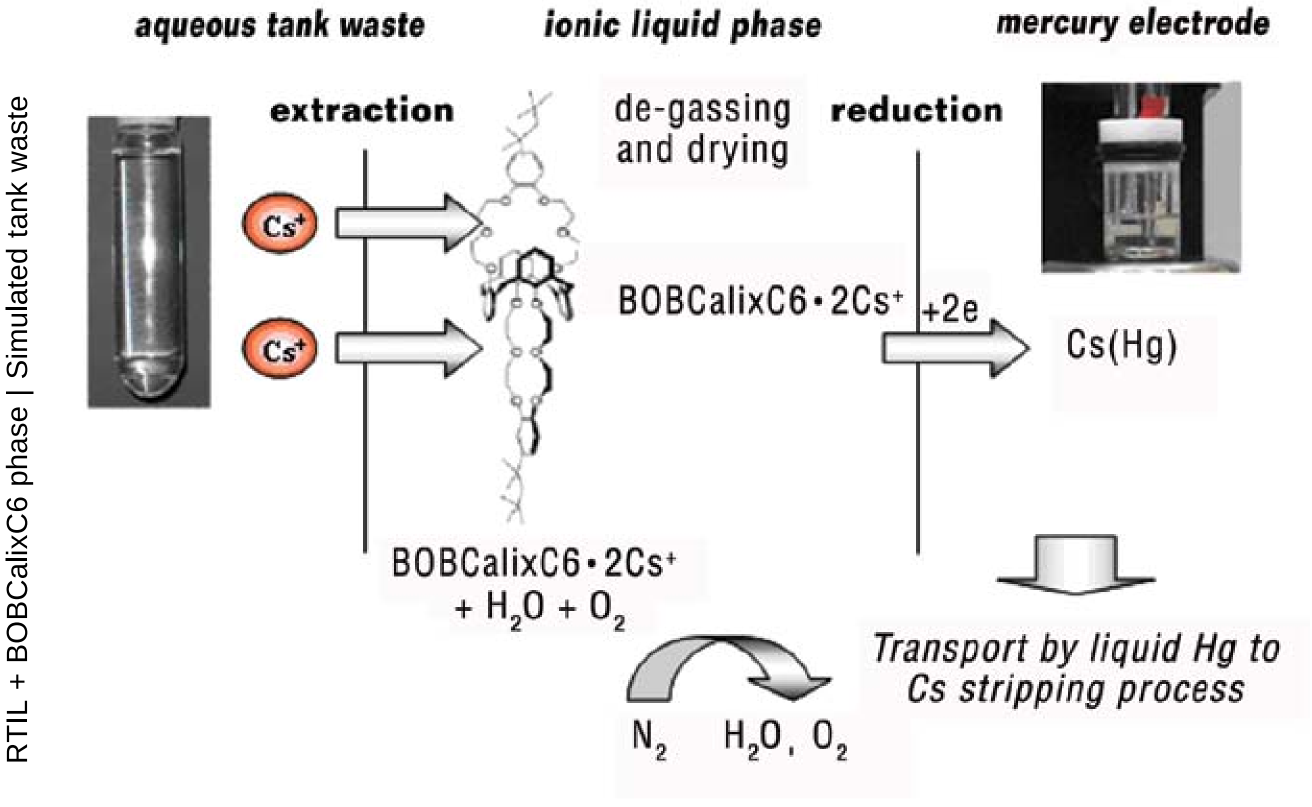

Fig. 6. *Proposed process for the extraction of cesium from aqueous tank waste using n-$Bu_3MeNNTf_2^-$ + BOBCalixC6. (Reproduced from Ref. 34 with permission from The Electrochemical Society.)*

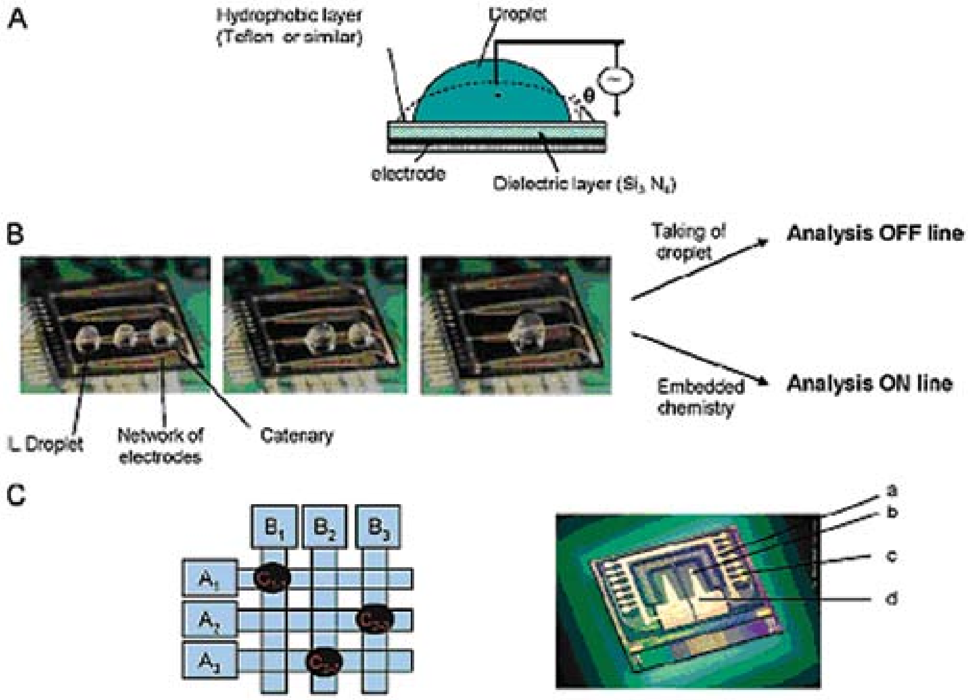

Fig. 7. *(A) Ionic liquid drop on a dielectric electrode. (B) Chemical synthesis by merging ionic liquid droplets on an e-microreactor. (C) Left: multiplexed chip for performing parallel synthesis. Right: fluidic processor for parallel syntheses: (a) electrode bus for communication; (b) reservoir entry; (c) reagent storage and dispensing, and (d) reservoir for dispensing task-specific ionic liquid. (Reproduced from Ref. 35 with permission from the American Chemical Society.)*

Control of Experimental Conditions during Electrochemical Experiments with RTILs

Although RTILs have many attractive features for electrochemistry, they can be exceedingly difficult to purify. The expectation is that RTILs will be clear, colorless liquids with a wide, clean electrochemical window, as assessed with voltammetry. Unlike conventional aprotic organic solvents, the fact that RTILs exhibit virtually no vapor pressure eliminates the most powerful purification technique: distillation. Thus, the real business of purification must begin with the reagents that are used in the preparation of the RTIL of interest. The various procedures that are used to prepare and purify these components are too numerous to list here, and they tend to be specific for the RTIL that is being prepared. See for example the recent paper by Appetecchi, *et al.*[36] Articles appearing in the literature wherein the procedures used to purify the starting materials, to eliminate undesirable reaction byproducts, and to assess the impurity levels of the resulting RTIL are absent or unclear should be viewed with skepticism.

One particularly insidious contaminant is water. It is well established that even small amounts of adventitious water can strongly affect both the physicochemical and electrochemical properties of RTILs. Figure 8 shows photographs of three Pyrex test tubes containing different types of RTILs before and after the intentional addition of water. Included in this figure are a classical moisture-reactive ionic liquid, 60.0–40.0 mol % $AlCl_3$–EtMeImCl; an air stable hydrophilic ionic liquid, EtMeImF$(HF)_{2.3}$; and a hydrophobic ionic liquid, *n*-Bu_3MeNNTf$_2$. The appearance of each RTIL before the addition of water is shown in the top picture. The addition of water to an open test tube of the Lewis acidic $AlCl_3$–EtMeImCl results in a violent reaction with the evolution of heat and HCl gas and an obvious change in the appearance of the RTIL (Fig. 8, bottom picture). **(Please don't try this test without using proper safety precautions!)** In contrast, the addition of water to EtMeImF$(HF)_{2.3}$ and *n*-Bu_3MeNNTf$_2$ results in no obvious chemical change. To the eye, the former remains unchanged, whereas the latter exhibits a simple phase separation as expected due to its strong hydrophobicity. However, in reality the hydrophobic RTIL also dissolves a considerable quantity of water. In fact, the exposure of this supposedly hydrophobic liquid to atmospheric moisture for several days raises the water content from an initial value of ~ 4 ppm to 1000 ppm (= 5.55×10^{-2} mol kg^{-1})[34]! Fortunately, in this case, the water is not strongly bound and can be removed with heating under vacuum, restoring the RTIL to its initial condition. Thus, all RTILs, even those thought to be hydrophobic, should be handled under an inert gas atmosphere or in a glove box if water contamination is to be avoided.

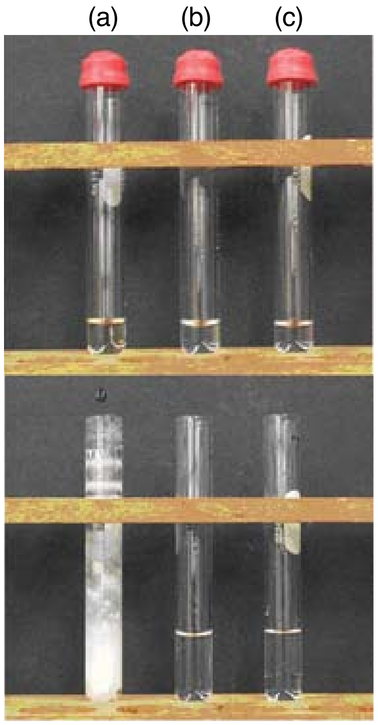

Fig. 8. *Photographs of (a) 60.0–40.0 mol% $AlCl_3$–EtMeImCl; (b) EtMeImF$(HF)_{2.3}$; (c) n-Bu_3MeNNTf$_2$: (top) before the addition of water, and (bottom) 20 s after the addition of water.*

Conclusion

In this article, we have attempted to present a short overview of some of the many ways that RTILs have been applied to electrochemical problems. A comprehensive review devoted to the use of RTILs as electrolytes for supercapacitors would alone occupy the entire space allotted for this article. Obviously, RTILs have great potential for electrochemical applications in science and technology. Some of the readers may hold the opinion that RTILs are "messy, intractable" solvents, *i.e.*, hard to make and hard to purify, and to some extent this is true. But, there is no longer any doubt about the attractiveness of RTILs as solvents for electrochemistry because some have excellent physicochemical properties for this purpose, including ample intrinsic conductivities, wide electrochemical windows, and negligible vapor pressures. Among the various classes of known solvents, only RTILs have this combination of desirable characteristics. ■

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