Ion jelly: a tailor-made conducting material for smart electrochemical devices†

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Received (in Cambridge, UK) 8th July 2008, Accepted 21st August 2008
First published as an Advance Article on the web 3rd October 2008
DOI: 10.1039/b811647d

We present a new concept for the design of a polymeric conducting material that combines the chemical versatility of an organic salt (ionic liquid) with the morphological versatility of a biopolymer (gelatin); the resulting 'ion jelly' can be applied in electrochemical devices, such as batteries, fuel cells, electrochromic windows or photovoltaic cells.

A common feature of electrochemical devices, such as batteries, capacitors, fuel cells, actuators, photovoltaic cells, electrochromic windows and light emitting cells, is the presence of an electrolyte whose properties have a pronounced effect on the device performance.[1–4] A reasonable conductivity (above 10^{-4} S cm^{-1}), and a large electrochemical window (above 1 V) are some of the criteria that an electrolyte must meet to be suitable for utilization in an electrochemical device.[1] Room-temperature ionic liquids (RTILs) fit these requirements,[1] with conductivities usually within the range 10^{-4} to 8×10^{-2} S cm^{-1}, and electrochemical windows of 4–5.7 V, respectively.[1] Near nonvolatility, nonflammability and excellent chemical and thermal stability have made ILs an environmentally attractive alternative to conventional organic solvents.[2] The adjustability of IL properties, such as polarity and solvation ability, through changes in the type of chemical moieties present on both cation and anion has led to the designation "designer solvents".[1,2] From the standpoint of device conception, solid electrolytes are preferable to liquid ones since the former allow the building of thin film devices using layer-by-layer techniques. Thus in electrochemical applications ILs are usually coupled to supporting materials, organic polymers such as polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), polyethylene oxide (PEO), polyvinylidene fluoride (PVdF) and Nafion®.[1,3] The synthesis of ILs containing groups that can be further polymerized to produce polymeric conducting materials (PCMs) is also worth attention.[4] Although combined IL–organic polymer materials have successfully replaced traditional electrolytes in some applications, there are still some problems to overcome. These are mainly related to the complexity of processing techniques, which in some cases, such as that of Nafion®, have prohibitive costs.

Gelatin is a widely available, inexpensive and well studied gelling agent. It is prepared by the thermal denaturation, after acid or alkaline pre-treatment, of collagen. The triple helix of type I collagen extracted from skin and bones, as a source of gelatin, is composed of two α1(I) and one α2(I) chains, each with *ca.* 95 kDa molecular mass, 1.5 nm width and 0.3 μm length. Dissolution of gelatin in water occurs at 30–35 °C, where these polypeptide strands undergo a coil–helix transition. Upon cooling, these helices go through an aggregation process similar to that experienced by collagen, with right-handed triple-helical proline/hydroxyproline junctions.[5]

Here we report a very simple way to obtain a PCM by making use of the ability of ILs to dissolve gelatin. The resulting viscous solution jellifies upon cooling below 35 °C, yielding an 'ion jelly' that combines conductivity, which is a characteristic of ILs, with the mechanical flexibility of a polymer (Fig. 1).

The formation of an ion jelly should occur in much the same way as the formation of a water-based gelatin gel. Both gelatin and ILs have ionic character and this leads to strong interactions between the two species, and the high solubility of gelatin. During the renaturing or annealing process, the polypeptide strands will have a tendency to rearrange into the most thermodynamically favourable structure. XRD experiments have been performed with water-based gelatin and ion jelly

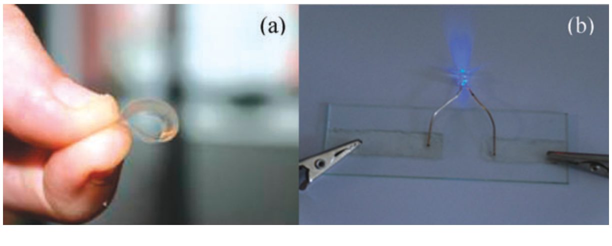

Fig. 1 Ion jelly. (a) Flexible, transparent film. (b) The ion jelly conducting material mediates electron transfer onto a LED.

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† Electronic supplementary information (ESI) available: Materials and methods, pictures of ion jelly materials, ion jelly synthesis table, XRD patterns, DSC analysis, conductivity of ion jelly films, *in situ* spectroelectrochemical cycling data for glass-ITO/PEDOT/ion jelly/PB/ITO-glass, ion jelly wire. See DOI: 10.1039/b811647d

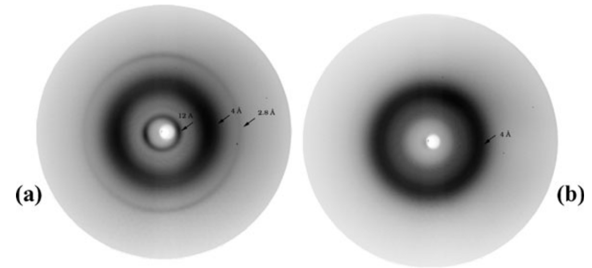

Fig. 2 XRD patterns. (a) Water-based gelatin gel; (b) ion jelly with $[emim][EtSO_4]$ ($R_{IL/gelatin} = 3$).

films (Fig. 2), and significant differences have been observed. Water-based gelatin films (Fig. 2a) exhibit three main diffracting rings at approximately 12 Å, 4 Å and 2.8 Å resolution when exposed to X-radiation. It has been suggested that the high resolution ring arises from the residue periodicity of each helix turn. The rise per residue along the helical axis is 2.9 Å.[6] The low resolution ring corresponds to the diameter of the superhelix aggregate of the film. In the diffraction images of an ion jelly film (Fig. 2b) these rings can no longer be found. This feature indicates pronounced modifications in the conformation of the gelatin left-hand helix, as well as the right-handed superhelix.

Several authors have shown that the structure and properties of water-based gelatin gels can be changed by adding different types of polyelectrolyte compounds during the jellification process, acting *via* ionic and hydrophobic interactions.[7] In the case of the ion jelly, ionic interactions are the most likely, since with the exception of $[C_{10}mim][Cl]$, the ILs used have a low content of hydrophobic chains. Such interactions would occur with side chain charged atoms, namely hydroxyproline, hence interfering with the hydrogen bonding network of the gelatin triple helix. Furthermore, the presence of these large ions bound to the gelatin strands would also prevent the formation of the triple superhelix, and the macro-assemblies typically seen in these molecules could no longer arise. DSC presents additional evidence for the impact of the IL on the structure of the gelatin gel.

Hydrogen bonding must be an important mechanism of interaction between the IL and gelatin. Table 1 shows a selection of cation/anion combinations that provided the formation of either ion jelly or solid structures, which includes the cations imidazolium [Him], 1-methylimidazolium [Hmim], 1-ethyl-3-methylimidazolium [emim], 1-*n*-butyl-3-methylimidazolium [bmim], 1-*n*-octyl-3-methylimidazolium [omim], 1-*n*-decyl-3-methylimidazolium $[C_{10}mim]$, 1-butyl-2,3-dimethylimidazolium [bdmim] and tri-*n*-octylmethylammonium (Aliquat336®) (also see ESI, Table S1†). The hydrophilicity of the IL correlates broadly with its ability to form ion jelly structures. This is well illustrated by the results obtained with the [bmim] series. The result for $[bmim]BF_4$, which is water miscible but still does not form an ion jelly structure, may be due to the weak coordination ability of the BF_4 ion. All the imidazolium cations listed are weak hydrogen-bond donors. Although this alone does not ensure ion jelly formation, it does favour that type of material, unlike quaternary ammonium salts. In this regard, the negative impact of higher IL/gelatin ratios, as shown in Table 1 for one selected case (6 : 1), may be related to the limited availability of sites on the gelatin molecules for hydrogen bonding with the IL, higher proportions of the latter decreasing the internal cohesion of the material formed.

Table 1 Selected cation and anion combinations that led to the formation of an ion jelly

Cation	Anion	IL : gelatin ratio (w/w)	Water miscible?	Type of material formed
[bmim]	Cl	1 : 1	Yes	Solid transparent films
[bmim]	$[N(CN)_2]$	1 : 1		Solid transparent films
		3 : 1	Yes	Solid transparent films
		6 : 1		Liquid gel
[bmim]	$[NTf_2]$	1 : 1	No	No ion jelly formation
[bmim]	$[PF_6]$	1 : 1	No	No ion jelly formation
[emim]	$[EtSO_4]$	1 : 1	Yes	Solid transparent films
		1 : 3		Solid transparent films
[bmim]	$[BF_4]$	1 : 1	Yes	Compact rigid solids
$[C_{10}mim]$	[Cl]	1 : 1	Yes	Solid transparent films
[bdmim]	[Cl]	1 : 1	Yes	Solid transparent films
Aliquat[a]	$[N(CN)_2]$	1 : 1	No	No ion jelly formation

[a] Aliquat336®.

Water itself plays an important role in ion jelly formation. Gelatin is very hydrophilic and it structure is stabilized by water molecules, especially in the denatured form (above 35 °C). Although ILs may also contribute to this, they cannot entirely replace water, as indicated by the absence of jellification of formulations prepared without added water (*i.e.* with just the water carried by the chemicals as supplied, quantified by Karl-Fischer titration), possibly due to inadequate conditions for the stabilization of the unfolded triple helix structure. On the other hand, and similarly to what was observed for high IL : gelatin ratios, large amounts of added water prevent the formation of ion jelly structures, possibly because the amount of water molecules that are able to form hydrogen bonds with sites on the gelatin molecules is exceeded. Water may even be a mediator of the interactions between gelatin and the IL.

The conductivity of the ion jelly materials is strongly affected by the IL used. To quantify the conductivity response of the ion jelly films, frequency dependent ionic conductivity was measured at 25 °C, as shown in Fig. 3. Several systems exhibit, over a wide frequency range, very reasonable conductivity values that are of the order of 10^{-5}–10^{-4} S cm^{-1}. In general, the conductivity pattern observed in disordered conductive systems shows a plateau at the lowest frequencies where the conductivity is identical to dc conductivity (σ_{DC}), bending off at higher frequencies into a dispersive regime, with a strong increase of the conductivity with increasing frequency (σ_{AC}).[8] By analyzing the frequency dependence of the conductivity in Fig. 3, it is obvious that the ion jelly materials conform only partially to the usual profile.[8] Instead of an extended plateau in the conductivity plot in the low frequency region, a decrease is observed, due to sample/electrode interfacial impedance. This means that ionic conduction becomes blocked, *i.e.* ions accumulate in the sample/electrode interface without discharging. The absence of a frequency independent conductivity region impairs the determination of σ_{DC}, and thus a comparison between the different ion jelly materials, at room temperature, can be made *via* conductivity values at 3 different frequencies. The conductivity values exhibited by ion jelly films are *ca.* two orders of magnitude lower than those of

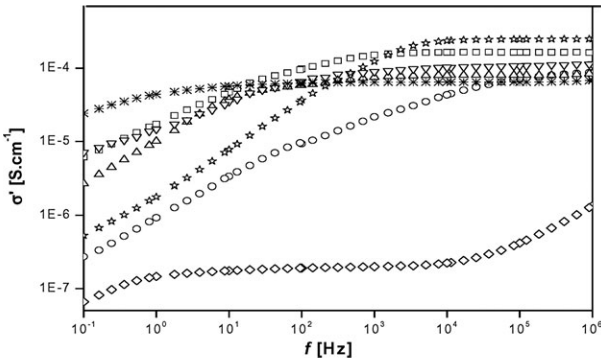

Fig. 3 Conductivity spectra of ion jelly films at 25 °C. □ [bmim][N(CN)$_2$] (R = 3); ○ [bmim][N(CN)$_2$] (R = 1); △ [bmim][Cl] (R = 1); * [Him][Cl] (R = 1); ◇ [C$_{10}$mim][Cl] (R = 1); ▽ [Hmim][Cl] (R = 1); ☆ [emim][EtSO$_4$] (R = 1); $R = m_{\text{IL}}/m_{\text{gelatin}}$.

the ILs used, which agrees with a lower ion mobility in the films than in the ILs. As expected, an increase in the alkyl chain length of the imidazolium cation brings about a decrease in ion jelly conductivity.[9]

There are many applications described in the literature of ILs as electrolytes,[10] usually with solubilized ionic conducting species, such as lithium salts. The very reasonable conductivity values of the ion jelly over a large frequency range led us to explore its utilization in electrochemical devices. For that purpose, we built an electrochromic window based on Prussian blue (PB) and poly(3,4-ethylenedioxythiophene) (PEDOT) as electrochromic layers (Fig. 4). Although this type of electrochromic window was designed to work with a highly concentrated electrolyte solution, electrochromic windows built with an ion jelly performed reasonably well in terms of contrast and stability. This suggests that the ion jelly network has a charge transport mechanism with sufficient degree of freedom. The lower switching velocity observed can be explained by the absence of an electrolyte salt, but can be partly circumvented by incorporating ionic species in the ion jelly *via* their solubilization in the RTIL.

To elucidate the type of electrical conduction in ion jelly materials, we set up the experiment shown in Fig. 1b, where two ion jelly films were placed on a glass surface and connected to a power supply. Upon connecting the two films *via* a LED, the LED lit up. While conductivity frequency dependent measurements probed ionic conductivity (Fig. 3), which in disordered systems takes place due to hopping movements of mobile charge carriers between different positions in a matrix, the result shown in Fig. 1b is consistent with electronic conduction. Thus, these materials exhibit mixed electronic and ionic conductivity.

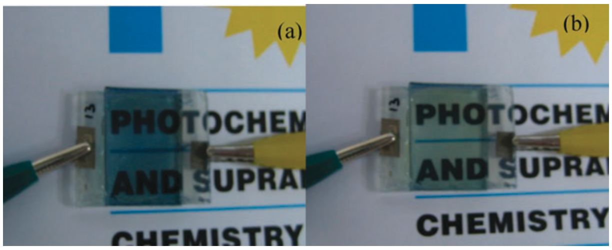

Fig. 4 Ion jelly smart window. glass-ITO/PEDOT/ion jelly/PB/ITO-glass. (a) Colored state; (b) bleached state.

We have presented a very simple way to obtain a PCM through the combination of gelatin with an IL. Gelatin is a natural polymer that can be easily modified *via* functionalization by chemical or biological agents.[11] ILs themselves can be custom made. This and their ability to solubilize both organic and inorganic compounds lends even greater versatility to ion jelly materials, and makes possible the tailoring of the ion jelly properties to meet desired applications, from those that require different degrees of conductivity, to several bio-applications.

This work has been supported by Fundação para a Ciência e Tecnologia (FCT, Portugal) through research contracts PPCDT/BIO/57193/2004, POCI/QUI/57735/2004 and the grants SFRH/BD/18487/2004 (N. L.) and SFRH/BD/2003 (P. V.), and by FEDER. We thank Dr Carla Rodrigues for DSC measurements. We thank Solchemar for the gift of ILs.

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