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Published paper

Rennie, A.J.R, Hall, P.J, Sanchez-Ramirez, N and Torresi, R.M (2013) *Ether-bond-containing ionic liquids as supercapacitor electrolytes*. Journal of Physical Chemistry Letters, 4 (17). 2970 - 2974.

Ether-Bond-Containing Ionic Liquids as Supercapacitor Electrolytes

Anthony J. R. Rennie,^{*,†} Nédher Sanchez-Ramirez,[§] Roberto M. Torresi,[§] and Peter J. Hall^{*,†}

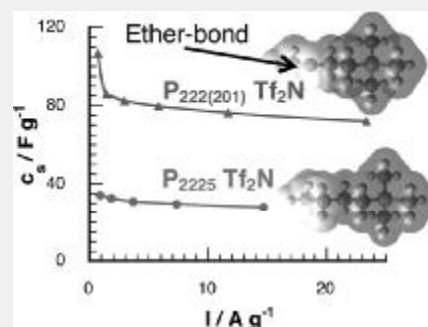
[†]Department of Chemical & Biological Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom

[§]Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo, Brazil

S Supporting Information

ABSTRACT: Electrochemical capacitors (ECs) are electrical energy storage devices that have the potential to be very useful in a wide range of applications, especially where there is a large disparity between peak and average power demands. The use of ionic liquids (ILs) as electrolytes in ECs can increase the energy density of devices; however, the viscosity and conductivity of ILs adversely influence the power density of the device. We present experimental results where several ILs containing different cations have been employed as the electrolyte in cells containing mesoporous carbon electrodes. Specifically, the behavior of ILs containing an ether bond in an alkyl side chain are compared with those of a similar structure and size but containing purely alkyl side chains. Using electrochemical impedance spectroscopy and constant current cycling, we show that the presence of the ether bond can dramatically increase the specific capacitance and reduce device resistance. These results have the important implication that such ILs can be used to tailor the physical properties and electrochemical performance of IL-based electrolytes.

SECTION: Energy Conversion and Storage; Energy and Charge Transport



Electrochemical capacitors (ECs), often referred to as supercapacitors, are electrical energy storage devices that absorb and release charge at relatively high rates when compared with electrochemical cells.¹ In addition to high power densities, they exhibit exceptionally long cycle lives coupled with high efficiency, enabling them to complement batteries and fuel cells in systems where there is a substantial difference between peak and average power demands.^{2–5}

Charge is stored through two different mechanisms in ECs; in electrical double-layer capacitors (EDLCs), energy is stored through the physical separation of charges at the electrode–electrolyte interface, whereas in pseudocapacitors, fast redox reactions result in the transfer of charge between the electrolyte and electrode.¹

ECs have relatively low energy densities when compared with batteries, which severely restricts their range of application. Because the maximum power and quantity of energy stored in an EC varies quadratically with operating voltage, a small increase in operating potential results in a substantial increase in the amount of useful energy stored in the device. For example, a conventional EDLC electrolyte is a solution of tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile and is limited to an operating potential of roughly 2.7 V.

Ionic liquids (ILs) can exhibit remarkably wide electrochemical stability windows^{6–8} and have garnered much interest as electrolytes for ECs.^{9–22} ILs are salts with relatively low melting temperatures (typically < 373K) owing to the weak interactions between their constituent ions, which are usually flexible and/or asymmetrical. The physical properties of ILs depends on their constituent ions, and the nature of the ions and ion size strongly

influence viscosity.²³ Several studies have shown that the physical properties of ILs have a considerable influence over their performance as EC electrolytes, and a substantial body of work has explored the importance of the relationship between ion size and electrode pore size distribution on the performance of ECs.^{15,17,19–21} Mesoporous carbon material with a relatively wide average pore width was chosen for use in this study to reduce the influence of electrode resistance, to minimize the effects of pore blocking, and to maintain good rate capability.²¹

As well as possessing good electrochemical stability, ILs also exhibit high thermal stability, low flammability, and low volatility and can therefore be seen as a safer alternative to organic solvent-based electrolytes for ECs.²⁰ A difficulty with many ILs has been poor electrical conductivity at low temperatures; however, recent work has shown that mixed IL electrolytes can perform well over a substantially wider temperature range than devices using conventional electrolytes or pure ILs.^{24–26}

In this work, we investigate the influence that cation structure has on the behavior of ILs when used as EC electrolytes. The bis(trifluoromethanesulfonyl) imide anion (Tf₂N) was chosen for use here as it is often found in ILs that exhibit low viscosity, relatively high conductivity, and a wide electrochemical stability window. This is in part due to the partially delocalized charge in the Tf₂N anion, which imparts flexibility into the structure and interacts weakly with other charged species.²³

Received: August 5, 2013

Accepted: August 19, 2013

Published: August 19, 2013

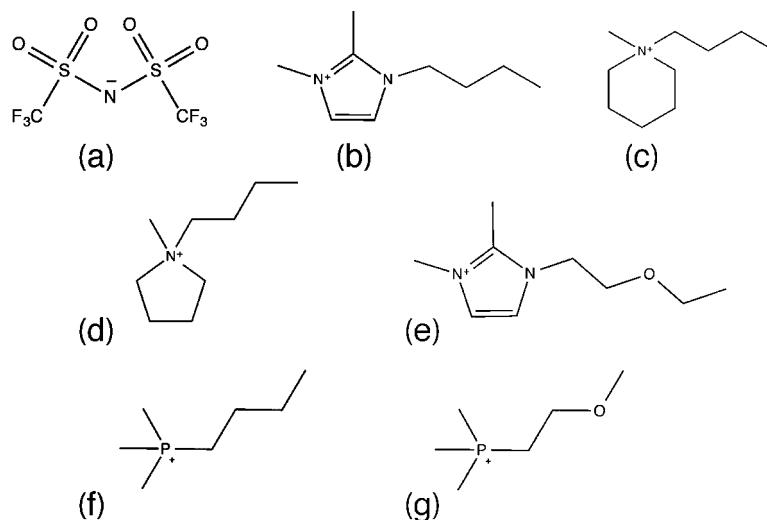


Figure 1. Schematic structure of the constituent ions in the ILs under study, (a) Tf_2N , (b) 1-*n*-butyl-2,3-dimethylimidazolium (BMMIm), (c) *N*-*n*-butyl-*N*-methylpiperidinium (BMPi), (d) *N*-*n*-butyl-*N*-methylpyrrolidinium (BMPy), (e) 1-(2-ethoxyethyl)-2,3-dimethyl-1*H*-imidazol-3-ium ($\text{EtO}(\text{CH}_2)_2\text{MMIm}$), (f) butyltrimethylphosphonium (P_{2225}), and (g) (2-methoxyethyl)trimethylphosphonium ($\text{P}_{222(201)}$).

The viscosity of ILs has been found to have considerable influence over their performance as EC electrolytes²² as it partly defines the conductivity of the IL. Higher electrolyte conductivities reduce the internal resistance of ECs, maximizing the power output. The limited conductivity of ILs remains a challenge as values tend to be at least an order of magnitude lower than that of conventional electrolytes based on organic solvents.

It has been proposed that a degree of flexibility can be introduced into a cation through the inclusion of an ether bond into the alkyl side chain, which can dramatically alter the physical properties of an IL.²⁷ Of particular relevance to the application of ILs as electrolytes, the presence of the ether bond can reduce the viscosity and increase the conductivity markedly. It has been reported that this type of IL can result in higher specific capacitances than a conventional EDLC electrolyte,²⁸ and in this study, we compare the behavior of ether-bond-containing ILs with the performance of ILs that have similar structure and ion size but that contain purely alkyl side chains. This Letter reports that when using ILs containing ether linkages as an EC electrolyte, profound differences in their electrochemical performance characteristics are observed and moreover that this behavior is observed when using two different classes of cation.

Schematic chemical structures of the ions present in the ILs studied are given in Figure 1, and a summary of their physical properties is given in Table 1.^{27,29} Cation volumes were calculated using the Molinspiration Property Calculation Service.³⁰ (For comparison, a widely used organic-based EC electrolyte, 1 mol L⁻¹ TEABF₄ in propylene carbonate, has a viscosity of 4 mPa s and a conductivity of approximately 13 mS cm⁻¹ at 25 °C.)

Table 1 shows that the viscosity of $[\text{EtO}(\text{CH}_2)_2\text{MMIm}][\text{Tf}_2\text{N}]$ (which contains an ether bond in a side chain) is significantly lower than that of $[\text{BMMIm}][\text{Tf}_2\text{N}]$, which is structurally similar but contains purely alkyl side chains. This difference is even more pronounced when comparing the viscosities of $[\text{P}_{2225}][\text{Tf}_2\text{N}]$ (which is purely alkyl) and $[\text{P}_{222(201)}][\text{Tf}_2\text{N}]$ (which contains an ether bond). As a result of their lower viscosities, the ILs

Table 1. Physical Properties^a of ILs Used in This Work at 25 °C^{27,29}

IL	$T_d/^\circ\text{C}$	$T_m/^\circ\text{C}$	$\delta/\text{g cm}^{-3}$	$\eta/\text{mPa s}$	$\sigma/\text{mS cm}^{-1}$	$V_c/\text{\AA}^3$
$[\text{BMMIm}][\text{Tf}_2\text{N}]$	430	-13	1.42	93	1.6	169
$[\text{BMPi}][\text{Tf}_2\text{N}]$	400	-25	1.38	183	1.2	186
$[\text{BMPy}][\text{Tf}_2\text{N}]$	426	-6	1.41	76	2.2	169
$[\text{EtO}(\text{CH}_2)_2\text{MMIm}][\text{Tf}_2\text{N}]^b$	405	-31	1.42	67	2.3	178
$[\text{P}_{2225}][\text{Tf}_2\text{N}]$	457	16	1.30	85	2.3	152
$[\text{P}_{222(201)}][\text{Tf}_2\text{N}]^b$	467	10	1.38	48	3.8	145

^a T_d is the thermal decomposition temperature, T_m is the melting temperature, δ is the density, η is the viscosity, σ is the conductivity, and V_c is the volume of the cation³⁰ (volume of $[\text{Tf}_2\text{N}]$ anion = 148 Å³).

^bBold type denotes ILs containing an ether bond on an alkyl side chain.

containing ether bonds exhibit significantly higher conductivities than their purely alkyl counterparts.

ILs containing cations with cyclic structures were employed as electrolytes in ECs, and the spectra obtained using EIS are given in Figure 2. (ILs were synthesized at the Inst. de Química, Universidade de São Paulo; experimental methods are contained in the Supporting Information (SI).) Electrode preparation is described elsewhere.^{21,22,31} The electrode material used in the ECs was a mesoporous carbon with a BET surface area of 1270 m² g⁻¹, average pore size of roughly 7 nm (using the BJH adsorption method), and an average particle size of 10 μm (MAST Carbon, U.K.).

Figure 2 shows a significant deviation from ideally capacitive behavior for each of the ILs as a constant phase angle is present at low frequencies. When 1 mol L⁻¹ TEABF₄ in PC was used as an electrolyte, almost vertical behavior was observed at low frequencies. The presence of this deviation can be associated with inhomogeneity in the double layer, but in this case, it is a result of the IL's low conductivity. This can be inferred from the fact that the deviation from the vertical at low frequencies increases as the conductivity of the IL decreases and can be attributed to the occurrence of slow processes such as the

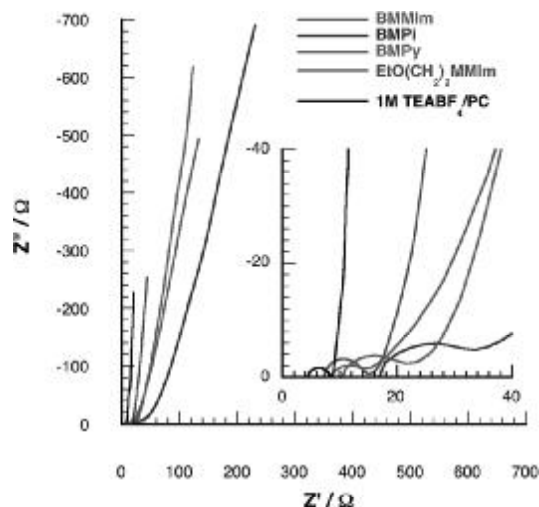


Figure 2. Nyquist plots obtained using electrochemical impedance spectroscopy (EIS) for ILs containing ring structures, with a magnified high-frequency region (inset). The spectrum for a cell using a conventional EDLC electrolyte (1 mol L⁻¹ TEABF₄ in PC) is provided for comparison purposes.

adsorption of ions or the rearrangement of ions at the electrode/electrolyte interface due to self-discharge/charge redistribution phenomena.^{32–34} The influence of electrolyte conductivity is also evident in the inset of Figure 2, which shows a magnified portion of the Nyquist plots at higher frequencies. It is clear that greater resistances are associated with more viscous/less conductive ILs. Cell characteristics calculated from the EIS data are given in Table 2. For comparison purposes, cells using 1 mol L⁻¹

Table 2. Cell Characteristics^a from Spectra Obtained through EIS

IL	c_s /F g ⁻¹	R_s /Ω	R_i /Ω	ESR/Ω
[BMMIm][Tf ₂ N]	64.9	9.7	9.9	15.2
[BMPi][Tf ₂ N]	47.8	16.7	21.7	27.6
[BMPy][Tf ₂ N]	69.3	8.9	11.2	15.9
[EtO(CH ₂) ₂ MMIm][Tf ₂ N]	80.9	7.2	9.0	15.8
[P ₂₂₂₅][Tf ₂ N]	30.5	13.6	7.3	20.4
[P ₂₂₂₍₂₀₁₎][Tf ₂ N]	82.7	5.9	6.0	11.6

^a c_s is the specific capacitance (determined at 10 mHz), R_s is the series resistance (see the SI), R_i is the ionic resistance (see the SI), and ESR is the equivalent series resistance (determined at 1 kHz)

TEABF₄ in PC yielded an average specific capacitance (c_s) of roughly 70 F g⁻¹, an R_s of 2 Ω, and R_i of 5 Ω, and equivalent series resistance (ESR) of 6 Ω (at 1 kHz).

[BMPi][Tf₂N] has a noticeably lower specific capacitance and higher resistances than both [BMMIm][Tf₂N] and [BMPy][Tf₂N]. This can be attributed to the increased cation size of [BMPi][Tf₂N], which results in a reduced concentration of ions in the double-layer region and therefore reduced displacement of charge. The trend in capacitance values determined using EIS is confirmed by the results of constant current cycling, the results of which are illustrated in Figure 3. At all rates studied, [BMPi][Tf₂N] has a substantially lower specific capacitance than the other two, with [BMPy][Tf₂N] performing slightly better than [BMMIm][Tf₂N]. It is possible that the more localized charge on the [BMPy] cation results in a more favorable

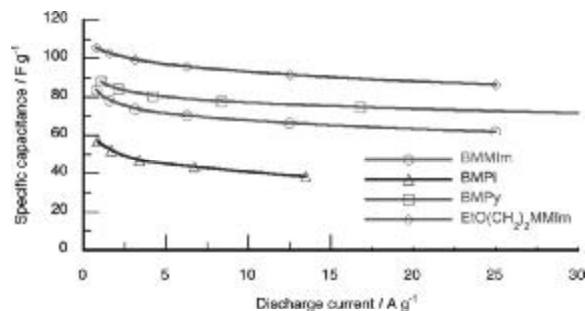


Figure 3. Specific capacitance determined at different rates of constant current discharge between 0 and 3.0 V for cells using ILs containing ring structures.

molecular orientation and greater concentration of adsorbed ions on the electrode surface when compared with the relatively delocalized charge on the [BMMIm] cation.

As discussed previously, the presence of the ether bond has benefits in both the viscosity and conductivity of the IL, and the influence of this is evident in the characteristics determined from EIS. Cells constructed using [EtO(CH₂)₂MMIm][Tf₂N] have slightly lower solution and ionic resistances and significantly greater specific capacitances than those using [BMMIm][Tf₂N] (which can be thought of as a purely alkyl analogue for comparison purposes). This is corroborated by the behavior illustrated in Figure 3 where cells using [EtO(CH₂)₂MMIm][Tf₂N] display a specific capacitance of roughly 20 F g⁻¹ greater than those using [BMMIm][Tf₂N] over the entire range of rates studied.

The presence of an ether bond has an even more marked effect on the performance of phosphonium-based ILs ([P₂₂₂₅][Tf₂N] and [P₂₂₂₍₂₀₁₎][Tf₂N]), as is evident in Figures 4 and 5.

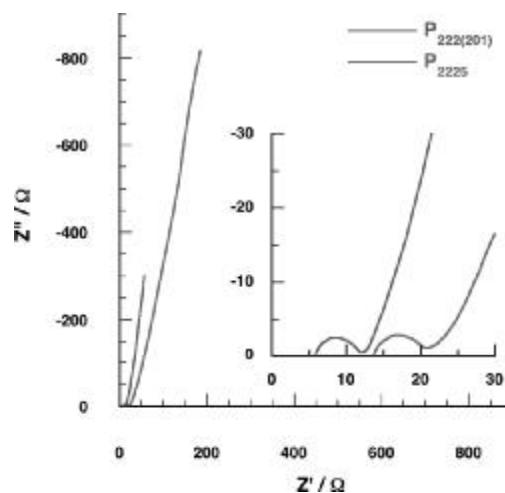


Figure 4. Nyquist plots obtained using EIS for phosphonium-based ILs, with a magnified high-frequency region (inset).

In this case, the structural difference between the two cations is that the penultimate carbon atom in the longer alkyl chain has been substituted with an oxygen atom. This results in a smaller ion size as well as introducing an ether bond to the ion, which drastically reduces the viscosity and increases the conductivity.

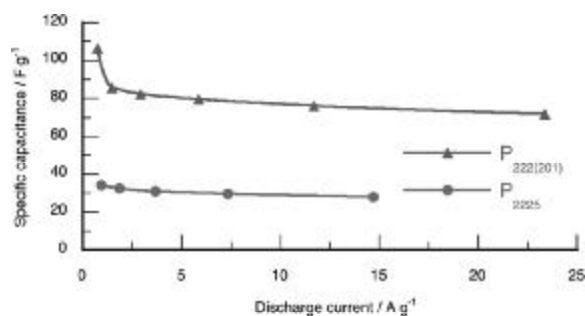


Figure 5. Specific capacitance determined at different rates of constant current discharge between 0 and 2.5 V for cells using phosphonium-based ILs.

Figure 5 shows clearly that cells using $[P_{222(201)}][Tf_2N]$ have a substantially higher specific capacitance than $[P_{2225}][Tf_2N]$ cells, at least by 50 F g^{-1} , over the range of current densities studied. In addition, the associated resistances of $[P_{222(201)}][Tf_2N]$ are substantially reduced, with values of R_s and ESR being roughly half that of those determined from cells using $[P_{2225}][Tf_2N]$.

The additional flexibility added to the cation through the presence of the ether bond may result in the difference in performance observed. A further possibility is that the ether bond introduces a small electronegative region to the cation structure that facilitates a denser packing of ions at the electrode surface, thereby resulting in a greater amount of charge being displaced in the electrode.

These results show that despite ILs being more viscous and less conductive than conventional electrolytes, their physical properties can be manipulated through the inclusion of an ether bond into an alkyl side chain of the cation. This provides much scope for future research as the performance of ECs will be improved by the production of more conductive IL electrolytes alongside the development of electrode materials with suitable pore characteristics, tailored to the ILs in question. This will extend the energy density of ECs, expanding the range of applications where they can be utilized and guaranteeing their place as an important technology in the future of energy storage.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures are supplied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: a.rennie@sheffield.ac.uk (A.J.R.R.); peter.hall@sheffield.ac.uk (P.J.H.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

P.J.H. and A.J.R.R. would like to acknowledge the U.K. Engineering and Physical Sciences Research Council for supporting this work (EP/K000292/1; SPECIFIC Tranche 1: Buildings as Power Stations). R.M.T and N.S.R thank FAPESP (09/53199-3 and 10/08646-9) and CNPq for financial support.

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