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# **Redox-active Ionic Liquids for Energy Harvesting and Storage Applications**

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## **Abstract**

Building electrochemical activity into ionic liquids extends their practical potential beyond acting as inert electrolytes or solvents to being multi-functional electro-materials with a myriad of application including in energy harvesting and storage. This review looks back briefly to their origins and goes on to outline and discusses recent important developments in the field. The prospect for these useful new materials is also discussed.

**Key words:** ionic liquids, redox-active, energy, recovery, storage.

## **Introduction**

Since the introduction [1] of stable room temperature ionic liquids (RTILs), there has been an explosion of research activity across disparate scientific and technical disciplines to harness their physical and physio-chemical properties [2–4]. From the outset, their role in electro-technology was implicit although much of the early research concentrated on non-electrochemical applications, in particular in “green chemistry” [2–4] in tuning their unique chemical / physiochemical properties to direct the course of chemical reactions, for example [5]. While the concept of deliberately introducing chemical functionality into RTIL structure to create task specific ionic liquids (TSILs) was formally introduced in 2002 [6], earlier reports of incorporating electro-activity into molten salts exist [7]. Because ILs are inherently ionically conducting, non-volatile, and are usually extremely redox-robust [1,8], incorporating redox functionality was a logical development as it introduces the opportunity to create multi-functional electro-materials not only for a range of important contemporary applications where molecular solvent based electrolytes have predominated, but for potentially entirely new electrochemical applications and strategies.

For simplicity, this review will focus on applications rather than materials' types. This reflects the significant development of thermo-electric cells (ETECs), hybrid super-capacitors, and redox (flow) batteries (R(F)Bs) over the past several years.

**Ionic liquids, “Ionic liquid like”, and redox electrolytes**

For clarity it is necessary to define what is meant by the term “ionic liquid” based on what it is generally understood, or accepted, to be in the literature. It is sometimes stated that there is an almost unlimited number of possible ionic liquids. However, it is more accurately to state that there is an almost unlimited number of salts (i.e. anion/cation combinations) but increasing the molecular mass of either ion, or both, risks solidification, or the creation of materials so viscous they cannot be regarded, or used, as liquids *per se*. So there is a finite number of salts liquidous at temperatures  $\leq 100$  °C. This is exacerbated by redox functionalisation which not only increases mass but contributes new intermolecular forces which are potentially detrimental to the liquidous state. The creation of new charged states upon redox that may, or may not, be compatible with the native IL co-ions must also be considered.

There are many examples of redox-active ionic liquids [7,9,10] that are liquid at ambient temperature (e.g. the ferrocene-appended 1-butyl-3-methyl imidazolium ([C<sub>4</sub>mim]) shown in Figure 1(a) [9]) but there are also many examples of salts identified as ILs that are solids such as the TEMPO- (2,2,6,6-tetramethyl-1-piperidinyloxy) appended [Bmim] shown in Figure 1(b) [10]. Even though these are not ILs, they are frequently referred to as such, or described as “ionic liquid like”, since they possess IL-type ions, and are usually deployed in ILs composed of common co-ions, which generally assures miscibility in all proportions whilst maintaining the desired electro-activity and the physiochemical characteristics of ILs. Strictly speaking, this make these systems IL-based redox electrolytes. Here, no distinction is made between true electro-active ILs and IL-based “redox electrolytes” since the mixtures are still IL in composition.

## Energy applications

### *Electrochemical Thermo-electric cells (ETECs)*

ETEC energy harvesting [11,12] and storage devices are based on the well-known Seebeck effect (coefficient  $S_e$ ) which describes the potential difference ( $\partial E(T)$ ) between two redox couples held at two different temperatures ( $T_2 - T_1 = \partial T$ ), as given in Equation 1 which relates  $S_e$  to the entropy change ( $\Delta S$ ) associated with the redox reaction involving  $n$  electrons

$$S_e = \frac{\partial E(T)}{\partial T} = \frac{\Delta S}{nF} \quad (1)$$

Like all electrochemical energy devices, the ultimate performance is dictated by the sum of total internal resistances therefore to aid comparison between studies TECs are usually described using a figure of merit (ZT) which relates device efficiency to the ionic ( $\sigma$ ) and thermal ( $\kappa$ ) conductivities of the supporting electrolyte (Equation 2).

$$ZT = \frac{S_e^2 T \sigma}{\kappa} \quad (2)$$

Also, since the power output ( $P$ , ( $J s^{-1}$ )) of TECs is approximately a linear function of  $\Delta T^2$  the quotient  $P_{\max} / \Delta T^2$  is a useful measure of performance.

Since traditional semi-conductor and polymer bases TE devices exhibit low  $ZT$  (ca. 0.1) and  $S_e$  ( $\ll 1.0$  mV / K) [12], and aqueous systems are severely restricted due phase changes at 0 and 100 °C whilst useful waste low- grade heat is typically  $> 100^\circ\text{C}$ , the search for more efficient and practical TEC materials is evident; in particular, ETECs deploying redox active ionic liquids, or IL-based redox electrolytes, since many are liquid and stable over very large temperature ranges thus maximising  $P$ . Also, IL-based systems are considered to be potentially easier and less expensive to harness for direct heat-to-electricity energy harvesting than other systems.

Efficient ETE conversion critically relies on appropriate redox couples which exhibit large  $\Delta S$  such as certain Fe or Co complexes that undergo significant local solvent reorganisation upon redox. Efficiency is also a function of other resistances (over-potentials,  $\eta$ ) within the cell including mass transport ( $D$ ,  $\text{cm}^2 / \text{s}$ ) and heterogeneous electron transfer ( $k^\circ$ ,  $\text{cm} / \text{s}$ ), both of which may be significantly altered in IL media [13]. Redox couples are chosen for large  $k^\circ$  but ILs are notorious for low  $D$  which can be 2-3 orders of magnitude lower than in molecular solvents, and  $k^\circ$  is an inverse function of viscosity [13]. For comparative purposes, aqueous 0.4 mol / L ferri/ferrocyanide is considered the benchmark ETE system which exhibits a  $S_e$  of -1.4 mV / K [14].

The most salient work on TECs using redox-active ionic liquids originate from MacFarlane and co-workers who have produced a series [12,15-17] of reports on the topic since 2013. The authors have extensively examined both ferro-/ferri-cyanide (in aqueous) and Co bipyridyl complexes as the ETE material. In terms of “ionic liquid-like” materials, the authors used  $[\text{Co}^{\text{III}}(\text{bipy})_3][\text{NTf}_2]_{2/3}$  (e.g. 0.1 mol / L) as the redox couple (bipy = 2,2-bipyridyl and  $\text{NTf}_2$  = bistrilimide) dissolved in various ionic liquids (i.e. redox electrolytes) including:

- 1-ethyl-3-methylimidazolium bistriflimide ( $[\text{C}_2\text{mim}][\text{NTf}_2]$ ),
- 1-butyl-3-methylpyrrolidinium bistriflimide ( $[\text{C}_4\text{mpyr}][\text{NTf}_2]$ ),
- 1-ethyl-3-methylimidazolium tetracyanoborate ( $[\text{C}_2\text{mim}][\text{B}(\text{CN})_4]$ ),

1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C<sub>2</sub>mim][eFAP]).

The structures of these ILs are shown in Figure 2.

The outcome of early work [12] demonstrated that high Seebeck coefficients (1.5 – 2.2 mV / K) could be achieved in such redox-active ionic liquid media but cell performances were limited by slow mass transfer. This work was followed up by inclusion of 1-methoxypropionitrile (MPN) molecular solvent in order to reduce electrolyte viscosity thus increasing diffusion rates where a vol/vol ratio of 3:1 MPN : [C<sub>2</sub>mim][B(CN)<sub>4</sub>] operating at a  $\Delta T$  of 70 °C delivered **an impressive** maximum power density ( $P_{max}$ ) of 880 mW / m<sup>2</sup> which corresponds to a  $P_{max} / \Delta T^2$  value of 0.180 mW / K<sup>2</sup> / m<sup>2</sup> which was significantly larger than in either MPN or [C<sub>2</sub>mim][B(CN)<sub>4</sub>] alone [15]. This superior performance was attributed to enhanced conductivity and mass transport rates in the solvent / IL redox electrolyte mixture thus reducing ohmic resistances. The most recent and significant results [16] by these authors report massively increased  $P_{max} / \Delta T^2$  values of 0.54 mW / K<sup>2</sup> / m<sup>2</sup> achieved by deploying high surface area “pin electrodes” and replacing [C<sub>2</sub>mim][B(CN)<sub>4</sub>] with [C<sub>2</sub>mim][NTf<sub>2</sub>] which reduces ionic resistance without significantly affecting  $S_e$  values.

It is a moot point to consider if a 3:1 (by volume) mixture of molecular solvent to ionic liquid is really an ionic liquid based redox electrolyte or just a concentrated organic redox electrolyte. From a purely practical perspective the liquid nature of the native IL facilitates miscibility with the solvent in all proportions and, is therefore, not limited by the energetics of dissolution. Hence, ETEC construction and operation is facilitated. **The large  $S_e$  coefficients achieved with the redox-active ionic liquids, and the novel cell arrangements, bodes well for the future development of real energy storage devices based on the ETEC devices.**

#### *Hybrid supercapacitors*

Since the energy stored within capacitors increases with  $V^2$ , the extreme redox robustness of many conventional ILs and their low or non-volatility, makes them ideal containable electrolytes in electrochemical double-layer (ECDL) capacitors [18,19]. In addition to purely capacitive storage, faradaic redox processes of surface-confined functional groups, or redox of bulk electrode materials such as conducting polymers or metal oxides, gives rise to a pseudo-capacitance behavior that greatly enhances the energy density and power of these devices. However, the idea of deliberately including redox functionality into capacitors' electrolytes to enhance energy storage is relatively new [20-21] and effectively results in hybrid devices where energy is accumulated, and delivered, capacitively within/from the ECDL, and

galvanically within/from the redox electrolyte i.e. the function as both capacitor and battery. Such hybrid devices have been termed “supercapattery” and “supercabattery” [22] and have received considerable interest over very recent years.

Early work on these devices in aqueous media with bromate or iodide redox electrolytes reported “strikingly” high energy densities [21], thereafter IL based systems were soon reported. For example, Ishikawa *et al.* [23] examined the behaviour of 1.0 mol / L [C<sub>2</sub>min][Br] in [C<sub>4</sub>min][NTf<sub>2</sub>] at activated carbon cloth electrodes where Br<sub>2</sub> and Br<sub>3</sub><sup>-</sup> were the stable oxidation products. The authors reported 99.7% coulombic efficiency and excellent cyclability over 10000 cycles of the “electrolytic charge storage systems”. In a similar vein, but avoiding halides, Marcilla *et al.* [24] reported the incorporation of p-benzophenone in [C<sub>4</sub>mpyr][NTF<sub>2</sub>] where the specific capacitance (C<sub>s</sub>) and specific real energy (E<sub>real</sub>) at Vulcan and Pica carbons both doubled relative to the performance in pure [C<sub>4</sub>mpyr][NF<sub>2</sub>] IL.

In more ambitious work, Rochefort *et al.* [25] have reported redox-active IL-like salts where both the anion (a triflimide derivative) and cation (an imidazolium) are functionalised with ferrocene moieties, as shown in Figure 3. The authors examined these salts as 80 wt. % in acetonitrile (ACN) solvent (up to 2.4 mol / L) were achieved along with a 2.5 V operational voltage. Overall energy storage and delivery performance was increase by 83% relative to the unfunctionalised [C<sub>4</sub>min][NTf<sub>2</sub>] IL. Interestingly, the authors also report the oxidation of [Fc-mpyr][NTf<sub>2</sub>] to the neutral [Fc<sup>+</sup>-mpyr][NTf<sub>2</sub>], which, in the absence of any other charge-compensation electrolyte, forms an insoluble passivating film on the anode which, fortuitously inhibited self-discharge. This serves as a reminder that electro-generated ions in IL media require charge compensation, and some consideration of their compatibility with the IL to avoid inadvertent ion metathesis.

The most significant recent work is that by Fontaine *et al.* [26,27] who reported “biredox ionic liquids” (liquid at 60 °C) for high-energy super capacitors the structures of which are shown in Figure 4. These redox ILs possess either a functionalised anthraquinone or a TEMPO derivative which provides two couples with well separated redox potentials for battery-like storage capacity within unsymmetrical supercapacitor devices. The authors, using the Marcus-Hush theory, have shown that k<sup>o</sup> is controlled by the radius of the functional electro-active subunit appended to the ion rather than the radius of the ion itself. In terms of energy storage ability the salts were examined in [C<sub>4</sub>mim][NTf<sub>2</sub>] or in the pure state at 60°C where the measured capacitance was twice that of the unfunctionalised IL and performance was sustained for 2000 cycles without deterioration. The authors state rightly, that these developments “open up new opportunities to develop high energy super capacitors and a wide new field in redox materials”.

### *Redox (flow) batteries (R(F)Bs)*

Application of redox-active ILs in RBs and RFBs have received considerable attention because of their potential to increase energy and power density relative to aqueous and conventional solvent-based systems. For battery applications it is important to keep in mind where the stored energy resides i.e. either in a phase on an electrode (i.e. in battery as in Li<sup>+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup> metal batteries), or in the electrolyte using soluble redox couples where regenerative fuel cells are used to harvest and deliver that energy. Since “on electrode” storage scales by area, and interfacial nucleation, deposition and stripping events are inevitable, these systems are considered much harder to control and deploy for large scale (e.g. grid) applications than for device-level applications.

Because of the abundant options for galvanic storage a plethora of approaches deploying redox-active ILs have been reported over very recent years. For example, the work of Passerini *et al.* [28] on the Li/air FB harnessed the non-volatility and O<sub>2</sub> solubility of [C<sub>4</sub>mpyr][NTf<sub>2</sub>] to demonstrate the first non-aqueous Li/O<sub>2</sub> flow cell under semi-ambient conditions. In terms of the “beyond Li” concept (i.e. multi-valent metals) Vassalo *et al.* [29] reported the influence of a range of IL-type ammonium cations for their bromine sequestering ability and their influence on the Zn/Zn<sup>2+</sup> half-cell reaction in Zn/Br batteries. It was found that [C<sub>2</sub>Py] (Py= pyridinium), [C<sub>2</sub>mim] and [C<sub>2</sub>OHPy] improved maximum currents, power and energy densities as well as reducing Zn/Zn<sup>2+</sup> nucleation and stripping over-potentials. Han *et al.* [30] reported the first rechargeable aluminium/iodine redox battery using a polyvinylpyrrolidone – I<sub>2</sub> (PVP-I<sub>2</sub>) complex in a chloroaluminate melt comprising a molar ratio of 1.3 : 1 of AlCl<sub>3</sub> : [C<sub>2</sub>min] [Cl]. The reported capacity was ca. 200 mAh / g which constitutes a significant advance for rechargeable aluminium batteries (RABs.) Unfortunately chloroaluminates are moisture/air sensitive which explains the lack of much activity with these types of ILs. Another significant work presented by Sawinell *et al.* [31] reported deep eutectic melts formed from FeCl<sub>3</sub>, choline chloride and ethylene glycol with the 1:1:4 molar ratio where up to 6.3 mol / L concentrations of energy-storing redox centres could be achieved. These devices exhibited large  $k^0$ , low viscosity, and high  $\sigma$  (7.8 cP and 12.7 mS / cm at 80 °C).

### **Conclusions and outlook**

The potential of incorporating redox functionality into IL structure for energy applications is clear from the rapid developments made over very recent years. Significantly, thinking and practice have moved on from the ideal scenario of deploying pure materials to using them as redox solutes in IL-based redox electrolytes, and deploying benign molecular solvents to optimise mass transport rates and ionic conductive. In this new paradigm, they are seen as

and used as key enabling components in electrochemical devices. This opens up a vast array of potentially useful materials that are “ionic liquid like” but not ILs per se.

### Conflict of interest

None exists for this review.

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## Figures

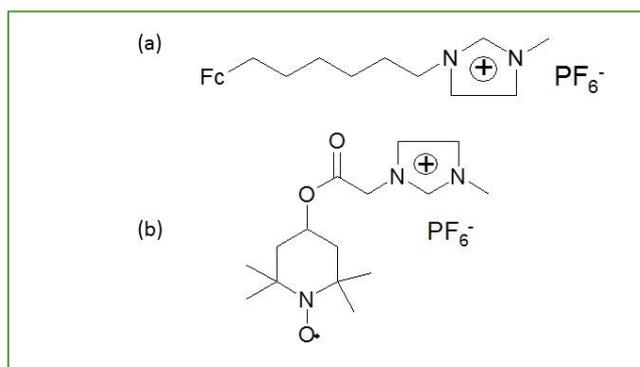


Figure 1. Structure of ferrocene- (a, [9]) and TEMPO- (b) appended 1-butyl-3-methyl imidazolium salts (a, [9]) and TEMPO- (b, [10]) appended [C<sub>4</sub>mim].

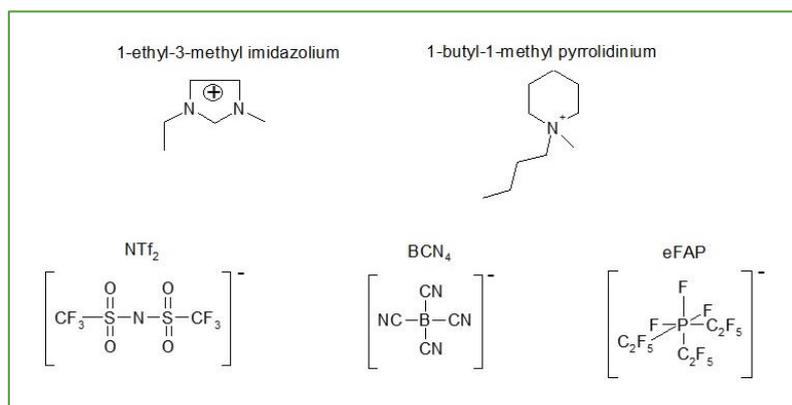


Figure 2. Structure of the ions comprising the following ILs: 1-ethyl-3-methylimidazolium bistriflimide ([C<sub>2</sub>mim][NTf<sub>2</sub>]), 1-butyl-3-methylpyrrolidinium bistriflimide ([C<sub>4</sub>mpyr][NTf<sub>2</sub>]), 1-ethyl-3-methylimidazolium tetracyanoborate ([C<sub>2</sub>mim][B(CN)<sub>4</sub>]) and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C<sub>2</sub>mim][eFAP]).

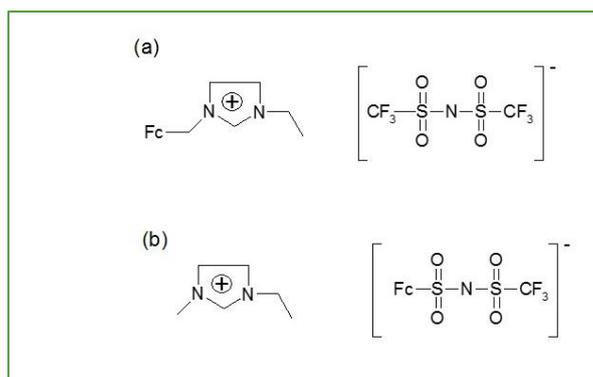


Figure 3. Structures of ferrocene-based redox-active ionic liquid-like salts reported by Rochefort *et al.* [25].

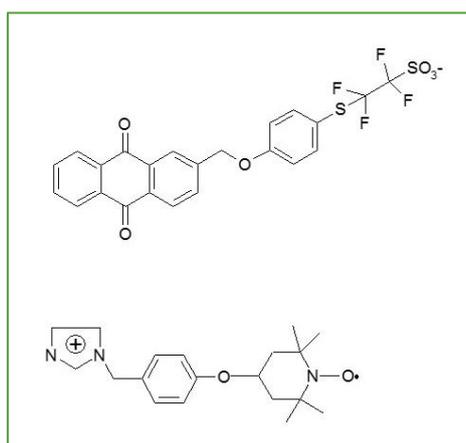


Figure 4. Structures of Fontaine *et al.*'s "biredox ionic liquids" for high-energy super capacitors [26, 27].