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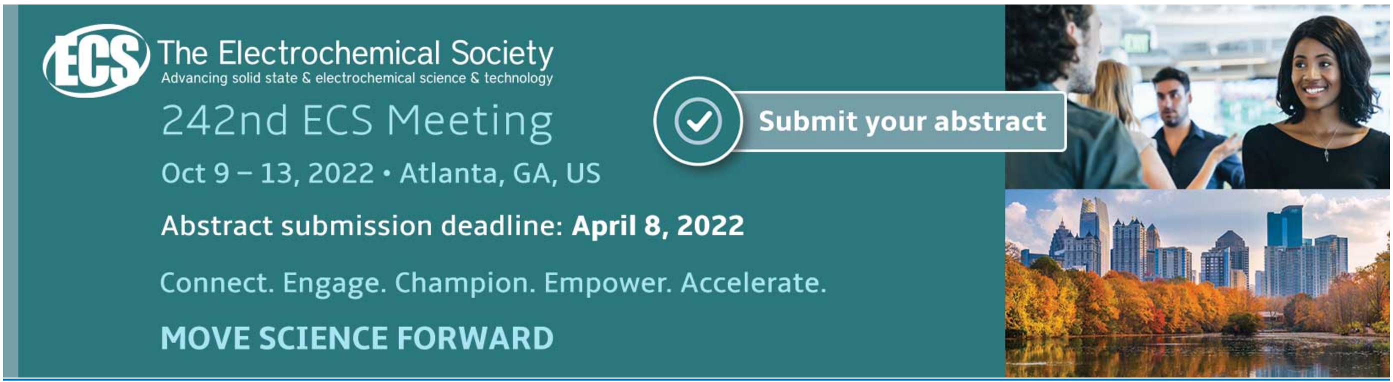
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Perspective—Redox Ionic Liquid Electrolytes for Supercapattery

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Adding redox activity into ionic liquids (ILs) extends their practical roles beyond an inert ionic conductor or electrolyte for applications in electrochemical energy storage. Especially for supercapatteries, redox ILs are desirable because they can contribute to increasing the charge storage capacity by merging the capacitive and Nernstian storage mechanisms without compromising their intrinsic wide potential windows. Several prospects of redox ILs are identified and discussed for optimising performance in supercapatteries.

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Energy storage as an intermediate step for the conversion of renewable energy to a usable form becomes increasingly important for sustainable provision and exploitation of energy. Electrochemical energy storage (EES) devices, such as rechargeable batteries, supercapacitors, and supercapatteries, are a desirable fit because of their modular nature, commercial attractiveness, and potentially fossil-comparable energy capacity.[1] Among them, supercapatteries are innovative hybrid devices that combine the merits of rechargeable battery and supercapacitor.

A supercapattery (= ***supercapa***citor + ba***ttery***) can be made by pairing a supercapacitor electrode with a battery electrode.[2–5] For example, the battery electrode may be the negative electrode (= negatrode) and store charge via the reversible transfer of localised valence electrons that are governed by the Nernst equation, i.e. the Nernstian storage mechanism. In the positive electrode (= positrode), charge storage may be achieved via the electric double layer (EDL) capacitance or pseudocapacitance, or even a combination of both mechanisms. The EDL capacitance is based on the physical adsorption of ions at the electrolyte/electrode interface, and the pseudocapacitance is a capacitive Faradaic process resulting from the transfer of zone-delocalised valence electrons.[6]

It is worth mentioning that the current positrode materials used in commercial lithium ion batteries (LIBs) are kinetically unable to support fast intercalation of Li^+ ions and have relatively low reversible storage capacity in comparison with that of the negatrode. For example, the $LiCoO_2$ positrode in LIBs has a usable capacity of 160 mAh g^{-1} that is much smaller than that of the graphite negatrode of 372 mAh g^{-1}.[7] Cobalt is still an expensive resource with a high human and environmental impact in its supply chain. As a successful alternative, the $LiFePO_4$ positrode exhibits much improved thermal and chemical stability, cell safety, higher discharge rate, and longer cycle life.[8] Unfortunately the moderate potential of $LiFePO_4$ (< 3.5 V vs Li^+/Li) and its high self-discharge rate lead to a low exploitable energy density. Whilst efforts are still ongoing to overcome the shortcomings of existing lithium intercalation based positrodes, it may be worth considering other charge storage mechanisms in place of lithium intercalation in the positrode. An option is to combine capacitive and Nernstian charge storage mechanisms in the positrode without invoking lithium intercalation. This thought can be further developed based on recently reported novel electrode materials and electrolytes for building hybrid EES devices capable of providing higher power capability and energy capacity with longer cycling durability.[9–13]

As a key component in EES devices, electrolytes insulate direct electron flow and conduct ions between, and assist charge transfer reactions on the positrode and negatrode. Therefore, electrolytes can greatly affect the performance of the EES devices in terms of both kinetics and thermodynamics.[14–16] The working or cell voltage of the device largely relies on the electrochemical stability window (ESW) of electrolyte if no decomposition of the electrode materials occurs.[17] In EES devices, aqueous, organic and ionic liquid electrolytes are all used, but ionic liquids (ILs) offer the widest ESW, which is beneficial to increasing the working voltage, U, and hence the energy storage capacity, W, according to Eq. 1a below:

$$W = \int_{0}^{U_{\max}} i(t)\,U(t)\,dt \qquad [1a]$$

For a supercapacitor, Eq. 1a can be simplified as Eq. 1b.

$$W = \frac{1}{2}CU^{2} \qquad [1b]$$

where C is the capacitance of the supercapacitor.

Organic electrolytes are usually formed by dissolving appropriate salts into organic solvents and can offer a wide range of ESW beyond 3.0 V. However, their relatively high cost, moderate ionic conductivity (<50 mS cm^{-1} at room temperature), low specific capacitance (<150 F g^{-1}) in comparison with those of aqueous electrolytes in carbon-based supercapacitors, and safety issues have raised great concerns in their commercial use.[14,18,19] Recent investigations have recognised ILs as good alternatives to aqueous and organic electrolytes for supercapacitors to achieve higher cell voltages, more ionised environments, negligible volatility, and high thermal, chemical and electrochemical stabilities.[18,20,21]

However, against expectations, ILs usually exhibit high viscosity and hence low ionic conductivity less than 15 mS cm^{-1} at room temperature. Also, some electrode materials showed reduced specific capacitance and power capability in ILs,[14] which may be at least partly related to the high viscosity of ILs restricting ion mobility and accessibility in the electrode.

Nevertheless, it has been reported that supercapacitors may perform better with mixed IL electrolytes. For example, in an EDLC with micro-mesoporous carbon electrodes and an 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) electrolyte with 5 wt% 1-ethyl-3-methylimidazolium iodid (EMImI), a specific capacitance value of 245 F g^{-1} at 1.0 V was achieved, which is nearly 50% greater than that obtained in the pure $EMImBF_4$

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electrolyte.[22] Approximately a 30% increase in specific energy and a 60% increase in specific power were also achieved in the EMImI + $EMImBF_4$ mixture due to the I^- adsorption on the electrode surface. A eutectic mixture of N-methyl-N-propylpiperidinium bis(fluorosulfonyl)imide ($PIP_{13}FSI$) and N-butyl-N-methylpyrrolidinium bis (fluorosulfonyl)imide ($PYR_{14}FSI$) was used to extend the operation temperature range of the supercapacitors with different types of carbon electrodes.[23] Such supercapacitors were able to operate from −50 to 100 °C in a wide voltage window (up to 3.7 V) at very high charge/discharge rates of up to $20\ V\ s^{-1}$. Similarly, performance enhancement to supercapacitors was made by mixing ILs with polar organic solvents.[24–26]

Alternatively, to enhance the energy capacity of supercapacitors, redox active species (also called redox additives or redox mediators) can be added into the electrolyte to induce reversible electron transfer reactions inside a porous EDL electrode to gain additional storage capacity.[16,27] Further, ionic redox additives can increase the ionic conductivity of the electrolyte to a certain degree.[28,29] Self-discharge caused by shuttling of redox species between electrodes is of concerns,[30] but it can be mitigated by, for example, electrostatic trapping the anionic redox species inside the pores of an EDL positrode at sufficiently high positive potentials. In this vein, redox ILs are being developed to enhance charge storage capacity at high positive or negative potentials according to the nature of redox reactions, although there are still some technical issues to be addressed.[27]

In this article, we aim to bring attention to redox IL electrolytes with an overview of the recent relevant research progress. It should be emphasised that a supercapacitor employing redox electrolytes stores charge via both the capacitive and Nernstian mechanisms becomes effectively a supercapattery. Therefore, the discussion will be focused on the opportunities and challenges for developing high-performance supercapatteries.

Current Status

The success of redox aqueous electrolytes in enhancing the storage capacity of electrical charges has inspired the expansion of the concept to include redox IL electrolytes in supercapatteries to extend the cell voltage. Redox additives, such as transition metal ions,[31] halides,[32] organic molecules,[33,34] and inorganic and organic complexes,[35,36] have been used in various ILs and investigated to improve the device performance. These redox additives in ILs can contribute to increasing the charge storage capacity of a porous EDL electrode. As schematically illustrated in Fig. 1a, the enhanced charge storage capacity can result from the three main electrochemical processes occurring on a porous electrode, including (i) the redox species in their oxidised or reduced states (either O_{bulk} or R_{bulk}) enter the pores of the electrode via the equilibria of desolvation and solvation of the species and reach the transition states (O* or R*); (ii) the transition states are then converted to adsorbed states (O_{ads} and R_{ads}); and (iii) the electrons transfer between O_{ads} and R_{ads}, leading to the increase of storage capacity.[27]

Moreover, ionic redox additives, either added or formed on the electrode, may also contribute to the primary EDL capacitive storage in the porous electrode.[36] Therefore, due to the combination of capacitive and Nernstian charge storage mechanisms, the cyclic voltammogram (CV) of a porous EDL electrode in a redox electrolyte differs from that of a supercapacitor electrode or a battery electrode. Figure 1b shows an example CV that is a simple addition of a peak-shaped Nernstian CV on a rectangular capacitive CV. However, in reality, the CV of combined Nernstian and capacitive charge storage may not show any current peak,[37] depending on the nature of the redox additive, its interaction with the porous electrode, and the conditions for recording the CV, such as potential scan rate, potential window and experimental temperature.

For a cell with capacitive positrode and negatrode in a redox electrolyte, the CV and galvanostatic charge/discharge profile (GCD) may vary significantly, depending on the relative contributions of the capacitive and Nernstian mechanisms. In many reported cases of redox electrolytes in supercapacitors, the GCDs of the cell featured voltage plateaus, comparable to those of conventional EDL Capacitors (EDLCs), as shown in Fig. 1c.[27] In the same voltage range for charging and discharging, the higher the voltage plateau, the larger the energy capacity of the cell in comparison to that of the supercapacitor counterpart containing no redox additives.[21,38] A high voltage plateau requires the redox reaction at either very negative or very positive potentials, and more importantly an electrolyte with sufficiently wide ESW which is the fundamental reason to develop redox IL-based supercapatteries. It is worth noting that a plateau shaped GCD obtained in redox ILs is more beneficial for generating a stable or constant power output from the cell, whilst external electronic assistance is needed for a supercapacitor to achieve the same output. In addition, the plateau on the GCD also indicates a smaller fraction of unusable energy at voltages lower than the minimum working voltage in some applications. These potential advantages of using redox IL electrolytes deserve more research effort.

In a recent study, para-benzoquinone (p-BQ, 0.4 M) was dissolved in an IL, N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($PYR_{14}TFSI$) to form a redox IL.[33] Two pairs of current peaks appeared on the CV recorded on a glassy carbon working electrode in the redox IL, indicating the occurrence of faradaic reactions of the quinone. This redox IL was then tested in the symmetrical two-electrode cell with commercial activated carbon electrodes. It was observed that CVs and GCDs of the two-electrode cells also indicated the presence of redox processes, but the features were much less obvious. There was only one pair of very broad current peaks on the fairly rectangular CVs (Fig. 1d), but the GCD profile in Fig. 1e showed approximately four regions including a voltage plateau between 1.5 V and 0.8 V during discharging. These features are indicative of the coexistence of EDL capacitive and Nernstian processes. The specific energy of the cell with the redox IL at 2.0, 3.0, and 3.5 V were notably greater than that with pure $PYR_{14}TFSI$. However, the effect of the redox IL was more significant using Vulcan carbon ($240\ m^2\ g^{-1}$ in specific area) in comparison with Pica carbon ($2400\ m^2\ g^{-1}$), with the latter enabling much higher specific energy with or without using the same redox IL. This observation suggests the strong influence of electrode materials and structures on the effectiveness of using redox ILs.

Potassium ferrocyanide ($K_4[Fe(CN)_6]$) was added in 1-butyl-1-methylpyrrolidinium dicyanamide ([BMP][DCA]) and tested in a symmetrical cell with composite electrodes of manganese oxide/N-doped reduced graphene oxide nanoflower (MnO_x/N-rGO).[35] Coulombic efficiency (CE) beyond 98% was achieved in [BMP][DCA] with 1 M $K_4[Fe(CN)_6]$ in a voltage window of 3.0 V. In this study, $K_4[Fe(CN)_6]$ not only offered the redox activity on the electrode surfaces but also served as an additional source for ions that helped reduce the ionic resistance of the electrolyte. A notable increase in surface confined activity was observed during the charge storage contribution analysis, which resulted from the additional reversible Nernstian storage on the active surface of the MnO_x/N-rGO. This was confirmed through the measurement of the oxidation state of Mn via in situ electrochemical X-ray absorption spectroscopy, which showed a wider oxidation state variation range in the presence of $K_4[Fe(CN)_6]$, implying the higher redox activity on the electrode surface.

The addition of 1.0 M 1-ethyl-3-methylimidazolium bromide (EMImBr) in 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIm]BF_4$) resulted in a significantly higher discharge capacity than that of pure $[EMIm]BF_4$ and an excellent cyclability with 98% capacitance retention over 10,000 cycles.[32] Similarly, Cu^{2+} ions were added into $[EMIm]BF_4$ for a comparison of the performance with the pristine IL.[31] Here, the Cu^+ intermediate of the redox reaction of Cu^{2+} during the charge/discharge process contributed to a current peak on the CV, leading to a double increase of the energy capacity than the same test in pristine $[EMIm]BF_4$. However, this

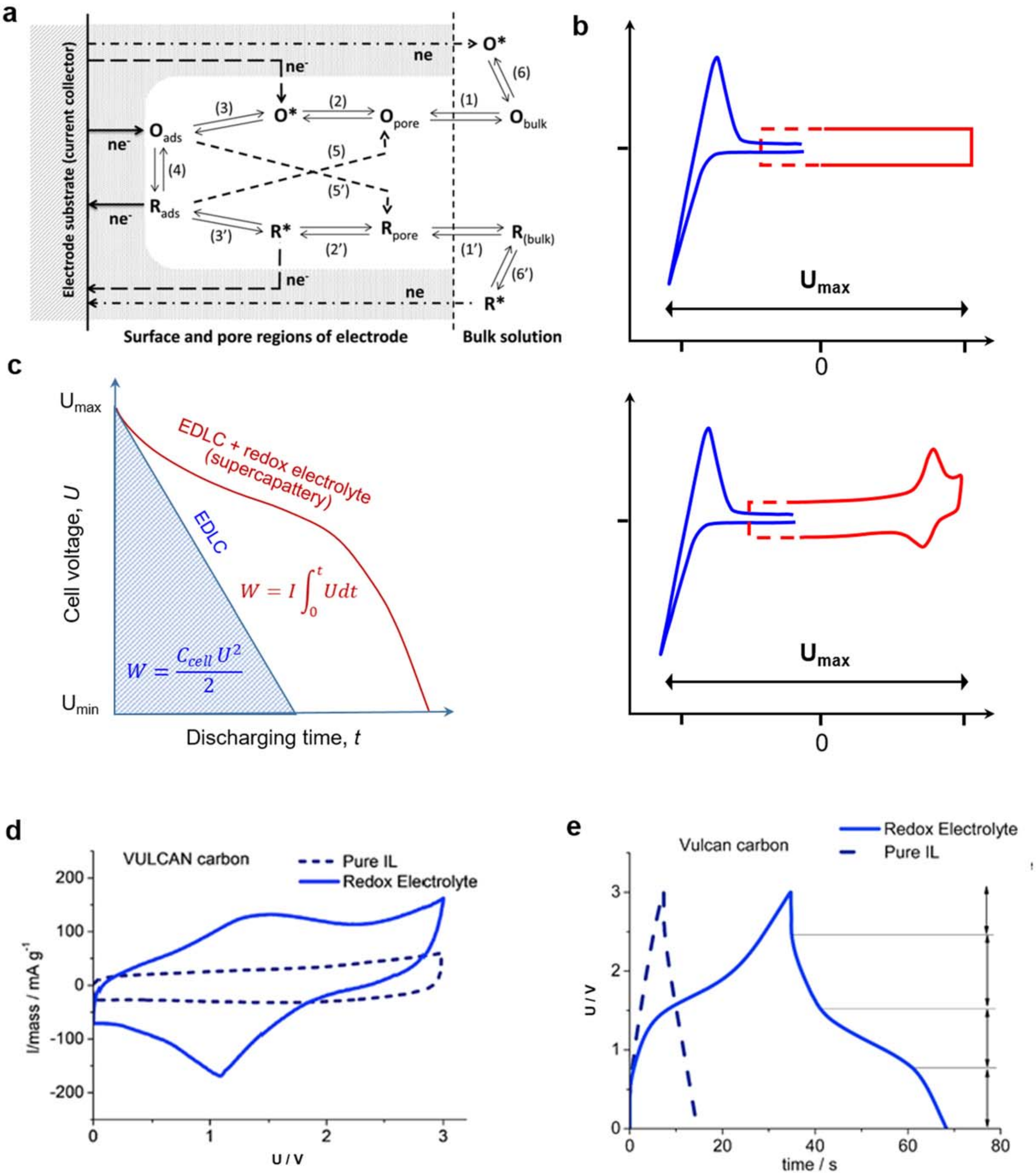

Figure 1. Schematic illustration of (a) charge storage mechanisms in the porous carbon electrode of a supercapacitor with a redox electrolyte,[21] (b) the hypothetic CVs of the capacitive positrode (red lines) and the metal negatrode (blue line) for supercapatteries with (top) inert electrolyte and (bottom) redox electrolyte that is active on the positrode, and (c) discharge profiles of EDLCs with and without a redox electrolyte, which is redrawn from Ref. 29 with permission from Rightslink; (d) CVs of the supercapacitor with Vulcan carbon electrodes in a redox electrolyte of 0.4 M p-BQ in $PYR_{14}TFSI$ compared with the pure IL of $PYR_{14}TFSI$ at a scan rate of 5 mV s^{-1} and 60 °C, and (e) related GCD plots up to 3 V and at a current density of 10 mA cm^{-2} and 60 °C (Reprinted from Ref. 25 with permission from Rightslink).

electrolyte exhibited poor electrochemical stability due to the formation of copper dendrites on the electrode surface. Selected reported redox IL electrolytes and their performance are listed in Table I.

Redox ILs can also be formed by covalent bonding of a redox moiety to either the IL cation or anion, as shown in recent work that succeeded in attaching ferrocene (Fc) to the [EMIm] cation or [NTf2] anion of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIm][NTf2]) to form two redox ILs.[41] An 83% increase in energy density at a working voltage of 2.5 V was achieved vs the unmodified IL and the self-discharge at the positrode was fully suppressed due to the formation of a stable passivation layer on the electrode. Another effort was made to prepare biredox ILs with either a functionalised anthraquinone or a TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) derivative that provided two redox couples with well-separated redox potentials for Nernstian storage in asymmetrical devices.[42,43]

In general, with the introduction of redox electrolytes, the dead weight of the electrochemically inert electrolytes and wasted pore volume in the electrodes of conventional supercapacitors can be explored and used as a reservoir for redox active species to supply extra capacity and enhance the energy density.[44] However, there are essential requirements to be satisfied by the redox species and some hurdles to overcome.[37,38,45] For example, the solubility of redox

Table 1. Redox ILs and carbon-based supercapatteries and their performances.

Electrolyte[a)]	Electrode materials	Specific capacitance (F g^{-1})	Cell voltage (V)	Specific energy (Wh kg^{-1})	Cyclability (Cycles)	References
HQ in TEATFSI	activated charcoal	72 at 0.57 mA cm^{-2}	2.5	31.22	1000	34
p-BQ in PYR_{14}TFSI	Vulcan carbon	70 at 5 mA cm^{-2}, 60 °C	3	10.3	1000	33
	Pica carbon	156 at 5 mA cm^{-2}, 60 °C	3	30	—	
EMImBr in $EMImBF_4$	activated carbon fiber cloths	59.6 at 100 mA g^{-1}	2	—	10000	32
EMImI in $EMImBF_4$	D-glucose derived activated carbon powder	245 at 1 V	2.2	33.4	2500	22
EMI-I in EMITFSI	porous carbon	228.4 at 0.1 A g^{-1}	3.5	175.6 at 1 A g^{-1}	5000	39
$CuCl_2$ in $EMImBF_4$	activated carbon	225 at 1 mA cm^{-2}	2	45	500	31
$K_4[Fe(CN)_6]$ in [BMP][DCA]	MnOx/N-rGO	199.4 at 1 A g^{-1}	3	44.7	20000	35
FM in [BMP][DCA]	N-rGO	112.1 at 0.25 A g^{-1}	3	34.2	5000	36
DmCc in EMImTFSI + ADN	single-walled carbon nanotubes	57.1 at 0.5 A g^{-1}	3.1	75.6	8000	40

a) HQ = hydroquinone; TEATFSI = triethylammonium bis(trifluoromethane)sulfonimide; p-BQ = para-benzoquinone; PYR_{14}TFSI = N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide; EMImBr = 1-ethyl-3-methylimidazolium bromide; $EMImBF_4$ = 1-ethyl-3-methylimidazolium tetrafluoroborate; EMImI = 1-ethyl-3-methylimidazolium iodide; [BMP][DCA] = 1-butyl-1-methylpyrrolidinium dicyanamide; MnO_x/N-GO = composite of manganese oxide/nanoflower of N-doped reduced graphene oxide; FM = ferrocene methanol; NrGO = N-doped reduced graphene oxide aerogel; EMI-I = 1-ethyl-3-methylimidazolium iodide; EMITFSI = 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; DmCc = decamethylcobaltocene; EMImTFSI = 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; AND = adiponitrile.

species in the electrolyte needs to be high to maximise the storage capacity and so does the reversibility of their redox reactions for a high CE. The potential of the redox species should be within the ESW of the electrolyte so that the cell working voltage and hence energy capacity can be maximised. However, if the redox potentials are in the middle of the ESW of the IL, the energy storage capacity of the supercapattery using such redox species may not be significantly increased, although an increased amount of charge can be stored at low cell voltages.[37] The mass of redox species should be particularly considered for scale-up as the omission of the redox additives as active materials could lead to overestimations of the charge and energy storage capacities of the device.[27] Another challenge in the application of redox ILs in supercapatteries is self-discharge due to redox shuttling between the positrode and negatrode, which is well known for aqueous redox electrolytes.[46,47] The consequences also include a low CE and irreversible side reactions. In addition, ILs usually have high viscosity and moderate conductivity, and hence a high equivalent series resistance (ESR) in the supercapattery, which compromises the rate or power performance and energy efficiency.

It should be mentioned that as illustrated in Fig. 1a, the charge storage enhanced by a redox electrolyte is based on the absorption of the redox species into the pores of the electrode and the conversion between the oxidised and reduced states of the absorbed species. Since the electrode materials are not involved in the storage chemistry, they will be stable during the charge/discharge cycling. This has been evidenced in the research listed in Table I, which showed the excellent cyclability of supercapatteries (or hybrids of battery and supercapacitor). Similarly, it is expected that when a chloride salt is used as the redox additive as proposed in this article, the Cl^-/Cl_3^- couple carry negative charges and contribute to the charge storage by their being electrostatically trapped inside the porous positrode at sufficiently positive potentials without chemical interactions with the electrode materials. Thus, the positrode will be stable to accommodate the repeated adsorption of the redox species.

Future Needs and Prospects

Supercapatteries are emerging high-performance EES devices that offer a promising opportunity to complement or even overperform batteries and supercapacitors to meet market needs for reducing CO_2 emissions without compromising energy supply. Recent research progress has demonstrated the ability of the supercapattery to deliver high energy capacity with good cycling retention.[48–51] To further enhance the performance of supercapatteries, it will be wise to employ redox IL electrolytes to increase the charge capacity of the capacitive positrode and hence the energy capacity of the device. In particular, the electrolyte compositions can be optimised or customised to meet certain requirements of the device performance (e.g. ionic conductivity and the working temperature) since the physical and chemical properties of ILs are highly tunable by combining the large variety of cations and anions.[19] Nevertheless, a better fundamental understanding through both laboratory and theoretical studies is certainly needed.

A unique approach is to combine a supercapacitor positrode (either an EDLC carbon-based or pseudocapacitive electrode) with an alkali or alkaline metal negatrode of high theoretical specific capacities in a supercapattery with a redox IL electrolyte. Following the success of lithium based batteries, other alkali or alkaline earth metals (AAEMs) are widely studied as the negatrodes for batteries, mainly because of the concerns regarding the limited lithium resources. However, even after decades of studies, the lack of suitable positrode host materials for the ions of these non-lithium AAEMs remains the bottleneck for future development. In the authors' opinion, this bottleneck may be bypassed by using a supercapacitor positrode and redox ILs that can enhance the charge capacity of the positrode to match that of the AAEM negatrode. Although the aforementioned redox shuttles between the positrode and negatrode could cause self-discharge and energy loss, it is possible to migrate such side reactions using redox additives whose reduced and oxidised forms have the same sign of charge. A good and cheap example is the redox conversion between chloride and trichloride ions, i.e. $Cl^-$and Cl_3^-. Of these two anionic species, Cl_3^- decomposes to Cl_2 and Cl^- spontaneously in aqueous electrolytes, but remains stable in ILs.[52,53] The potential of the Cl^-/Cl_3^- couple is much more positive than many redox species studied in ILs but still remains inside the ESWs of most known ILs. This means that the anionic couple of Cl^-/Cl_3^- can be electrostatically trapped inside the porous positrode at sufficiently positive potentials and hence become unavailable for redox shuttling. Certainly, the contribution of the Cl^-/Cl_3^- based redox ILs to charge capacity will depend on the chloride concentration in the electrolyte and the property of the supercapacitor electrode. Unlike many inorganic or organic redox additives whose solubility in ILs is limited, many chloride salts are readily soluble in ILs, such as tetrabutylammonium chloride (TBACl) or 1-butyl-3-methylimidazolium chloride (BMImCl). There are still many unknowns on using the Cl^-/Cl_3^- couple in supercapatteries with an AAME negatrode, but it can be anticipated that more research in this area can lead to better theoretical understanding, and more advanced and affordable technological strategies. For example, a concern is that the amount of charge from the Cl^-/Cl_3^- couple may exceed the adsorption capacity of the capacitive positrode, leading to redox shuttling. Although this unwanted scenario may be avoided by an appropriate charge balance between the positrode and negatrode via controlling the mass ratio, it needs experimental verification on if it would be more effective to limit the concentration of the redox additive, or both.

In order to truly realise the promise of redox ILs to enhance the supercapattery performance, it is of equal importance to pay attention to and discuss the design principles and device engineering of supercapattery in the following aspects: (i) a better understanding of the combination of capacitive and Nernstian mechanisms; (ii) performance correlations with the electrode structure and electrolyte composition; (iii) matching electrolyte and possibly separator membrane with the electrodes in design and test. More and in-depth research efforts are needed to understand the electron transfer reactions of redox species and kinetics of charge storage processes at the electrode/IL electrolyte interface, particularly inside the porous electrode structure for technological advancement. Both experimental and theoretical studies are required to understand the electrolyte ion dynamics and interactions, and solvation/desolvation in ILs using theoretical modelling at the molecular and electronic levels, and through in situ characterisation techniques such as EIS and NMR.

For a practical application of redox IL electrolytes in supercapatteries, the positrode, for example, must be sufficiently porous to retain the redox species and the products from the charging reaction inside the pores of the electrode for facilitating the Nernstian charge storage.[27] Accommodation of the redox species in the electrode could depend on the surface properties of the electrode material. For example, redox species can be simply retained in a porous carbon electrode by electro-adsorption. More effectively, they can be bonded to the electrode material via the interaction with the reactive edge sites and functional groups on the internal surfaces of carbon materials that are functionalised with carbonyl groups. Additionally, an optimal pore size may be required to ensure effective electro- or chemisorption of some redox species. Furthermore, it is also important to match the concentration of the redox species to the supporting IL electrolyte to achieve fast and reversible electrochemical activity to enable stable charging-discharging cycles.

Since the mechanism of enhancement of redox electrolytes to charge storage capacity varies with the electrode materials used, another design strategy is to match the electrolyte with the electrode to enhance the charge storage of the supercapattery. For a supercapattery with an activated carbon positrode, it may be beneficial to use halide salts-based IL electrolytes because the reactant (halide ion) and the product (polyhalide ion) of the electro-oxidation are both negatively charged and serve as the charge balancing anions in the EDL of the positrode. Thus, the charge capacity can be increased via the electro-sorption of the anionic species inside the porous positrode. When the positrode of a supercapattery is made of pseudocapacitive or battery materials and hence redox active, the redox reactions in the electrolyte will likely help electron transfer in the redox active electrode and contribute to the charge storage capacity. This mechanism is certainly worthy of investigation for future development of the supercapattery with redox IL electrolytes in terms of optimising the match between the electrolyte and electrode materials to improve the overall performance.

Uniquely, multivalence transition metal ions can form negatively charged complex ions with suitable ligands, such as ferro-/ferricyanide anions that should interact with the positrode via electrosorption. It is desirable to develop electron-withdrawing ligands so that the redox potential of the multivalence metal complex anions can be positively shifted. Additional retention of such multivalence metal complex anions may be achieved by functionalising the internal surface of the porous carbon positrode with oxy-groups that can have an affinity to the transition metal ions. It is worth noting that, unlike halide ions which are oxidisable on the positrode but not reducible and hence have no effect on the negatrode, metal complex anions may be oxidised to a higher valence, and also reduced to the metal. Therefore, metal complex anions in the electrolyte may be transported simultaneously to both the positrode and negatrode, undergoing oxidation and reduction, respectively. In such cases, suitable membrane separators may become a necessity in the construction of the whole supercapattery cell.

Summary

The potential of incorporating redox activity into ILs for EES application is clear from the rapid developments of redox electrolytes in recent years. Based on the unique combination of capacitive and Nernstian charge storage mechanisms, the redox IL electrolytes can help enhance storage in supercapatteries by improving the charge capacity of the capacitive positrode via fast electron transfer reactions at the electrode/electrolyte interface. Although various redox additives have been investigated, we propose to use chloride salts to increase the charge capacity of the positrode because the high oxidation potential of Cl^- can be effectively utilised in ILs to achieve a high cell voltage. Such chloride enhanced-IL electrolytes will offer a new, simple, and cost-effective approach to boosting the charge storage of a porous or pseudocapacitive positrode in supercapatteries. There are undoubtedly further improvements in the design principles and device engineering, but, thanks to the knowledge and technology advancements in batteries and supercapacitors, the supercapattery will become more competitive and promising in the near future.

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