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The roles of ionic liquids as new electrolytes in redox flow batteries

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Abstract

Redox flow batteries (RFBs) have emerged as a prominent option for the storage of intermittent renewable energy in large and medium-scale applications. In comparison to conventional batteries, these systems offer the unique advantage of decoupling energy and power densities, which can be separately scaled. Flowing liquid electrolytes, stored in external adjacent tanks to the cell stack, allow the reversible conversion of chemical energy into electricity by exploiting the difference in oxidation states between electroactive species. RFBs are at an early stage of commercialization, but the energy density is still low for the widespread use and full implementation. The attractive physicochemical properties of ionic liquids (ILs), with adventurous electrochemical features over aqueous and organic electrolytes, have drawn growing interest for their use in energy devices. Due to their versatility, ILs can be applied in the main components of RFBs, showing great potential for the further development of the technology. For the first time, this work reviews the recent progress on the application of IL materials in RFBs, discussing their roles as i) supportive electrolytes and additives, ii) redox reaction media, iii) redox-active species and iv) electrolyte membranes. The advantages and limitations of the multiple functionalities of ILs in RFBs are detailed, underlining the promising prospects and future research trends in the field.

Keywords: Redox flow batteries; ionic liquids; electrolyte; energy efficiency; redox couples; renewable energy; ion exchange membrane

Table of contents

1. Introduction

In the current global energy scenario, energy demands primarily rely on fossil fuels, which have a finite nature and pose major environmental problems associated with their burning, while energy consumption rates continue increasing [1]. Sustainable growth requires the promotion of renewable energy sources for industrial and household uses in portable or stationary applications with desirable zero or low emissions, from small to large-scale implementation. In the last case, several sources of renewable energy such as wind and solar power are intrinsically fluctuant and thus, they must be supported by suitable energy storage systems. As the contribution of fluctuating renewable energy to electrical production is rising, energy storage is becoming more important to ensure continuous supply to end-users. For this reason, a new industry of advanced energy devices is being currently deployed. Especially, the study of redox flow batteries (RFBs) has been intensified in the last years as they are realistic candidates for storing intermittent renewable energy at medium and large scales, with the possibility of decoupling energy and power [2,3].

Flow batteries are electrochemical devices that exploit the energy differences from the oxidation states of certain species (often, but not only, ion metals) to store and discharge energy. RFBs are usually formed by two half-cells or compartments separated by an ion-exchange membrane equipped with additional and separate tanks in which electrolytes are stored and recirculated through the system during charge and discharge stages. In these rechargeable batteries, electrolytes contain dissolved electroactive elements reversibly transforming chemical energy into electricity. Available charge in flow batteries is stored total or partially in the electrolytes being recirculated, while in conventional systems such as Li-ion batteries the charge is stored entirely inside the cell, specifically in the electrodes (active materials), with no electrolyte recirculation. Such a method of charge storage facilitates the scaling of RFBs, with additional advantages in terms of costs and safety. Moreover, flow batteries can be swiftly recharged by electrolyte replacement with simultaneous recovery of the consumed materials for re-energization [4,5].

The most general classification of flow batteries is based on the occurrence of the phase transition distinguishing two main categories, 'true' RFBs, the most studied option, and hybrid systems (HFBs). [6]. Flow batteries are named after the liquid electrolyte flowing through the battery system, each category utilizing a different mechanism. A ‘true’ RFB uses a liquid phase reduction-oxidation reaction and the total electricity generation capacity depends on the storage tank size. In contrast, hybrid RFBs have a liquid-solid transition and store at least some energy in a solid layer during charge, implying that one of the active species is stored inside the stack, while the other remains in the liquid electrolyte and is stored in the external coupled tanks. More recently, membrane-free flow batteries (MLFB) have been developed, with no physical electrolyte separation, representing an innovative design in the field [7]. With regards to both economic and safety considerations, flow batteries are deemed among the most promising electrochemical technologies for storing energy in the range from several kWh to tens of MWh [4]. The stability of RFBs are facilitated by their advantage of decoupling energy density, depending on tank size, electrolyte concentration and cell voltage, and power generation capability, controlled by electrode size and reaction kinetics [8].

Despite the great advantages of RFBs, further studies are required to overcome the remaining technological constraints. As mentioned, the low levels of energy density achieved are among the main drawbacks, mostly caused by the restricted solubility of active species in electrolytes and the relatively high cost of components, which critically limits widespread implementation [9]. In order to use the technology in medium-scale and large-scale applications, higher energy densities are required to reduce battery size and cost. Another important aspect is the performance and resources limitations in using conventional electrolytes based on oxidation/reduction of inorganic species. Thus, the development of flow-battery technologies has mostly focused on low-cost and highly soluble redox materials and robust battery chemistries [9]. Strategies to enhance energy density can go through the exploration of new electroactive species (redox couples) in the anolyte and the catholyte, and their combination, the search for new electrolytes as well as the optimization of operating and design parameters. Among the new materials being explored in RFBs are ionic liquids (ILs). The research of these compounds in different electrochemical applications has gained growing attention in the last few years, but their incorporation in RFBs is more recent. In this sense, these solvents could open new opportunities to reduce the material cost, to create flexibility with tunable redox potential, solubility and ionic conductivity, and to overcome other bottlenecks present in RFBs, although their use in these systems is still at a very early stage [10].

ILs can be defined as salts consisting entirely of ions. These compounds usually remain in the liquid state below 100 ºC due to the weak coordination between ions, even at ambient temperature, in which case they are known as room temperature ionic liquids or RTILs. In IL molecular structures, at least one ion presents a delocalized charge or some degree of charge shielding, which prevents the formation of a stable crystal lattice; besides, one component is typical of organic nature [11,12]. The growing interest in ILs largely stems from their distinctive properties, namely high ion conductivity, chemical and thermal stability, extremely low volatility, non-flammability and low toxicity, which can be efficiently exploited in electrochemical systems for energy generation and storage [13–15].

As electrolytes in energy devices, ILs have shown to be prominent candidates in fuel cells [16], batteries (e.g. lithium-ion and lithium-sulfur batteries) [17–20], supercapacitors [21–23], dye-sensitized solar cells [24,25]. Because of the almost limitless tunability of ILs through anion and cation combinations and the changes in their chemical nature by substitution of functional groups, there is still a broad scope to be explored in terms of structure-property relationships to optimize their performance in energy devices. Due to their electrochemical stability and conductivity, ILs can replace conventional organic-solvent based electrolytes, contributing to the long-term durability of the systems. Also, ILs can be used to manufacture electrolyte membranes to act as ion exchange separators in those devices and can be designed to display redox-active behavior [26,27].

In line with the trends to incorporate ILs as electrolytes in energy electrochemical devices, these compounds are being researched in RFB systems. This work reviews and discusses the recent advances in the application of ILs in RFBs as functional materials for the main components of such systems, namely as: i) supporting electrolytes and additives, ii) reaction media, iii) electroactive species and iv) electrolyte membranes. While most of the studies focus on the use of ILs as supporting electrolytes, recent works showing their potential use as electroactive species and electrolyte membranes have opened up new research pathways for further RFB development. On the other hand, and as complementary information, the application of organic compounds based on imidazolium, ammonium and pyridinium are commented as a related approach of application in RFBs since they present similar nature to several cations found in ILs. In this case, representative works are selected since non-complete IL structured are used.

2. Key aspects and typology of redox flow batteries

RFB systems are formed by three main components, a stacked cell, external energy storage tanks and a flow system. The reversible conversion of chemical energy into electrical energy takes place while the liquid electrolytes flow through the battery. In ‘true’

RFBs, the reaction occurs between the two electrolyte phases rather between the electrodes and the electrolytes, with the advantages of no electrodeposition nor electroactive species losses when the cell is cycled [28]. Additionally, electrolyte flow is usually driven by pumping units but, recently, gravity-induced flow options have been developed [29]. The singular set-up of RFB distinguishes from the rest of battery systems and enables the decoupling of energy storage and power generation, which in turn serves as a means of adapting capacity and power output to the final application requirements [28]. This may be the most relevant advantage of RFB systems over conventional batteries. This feature is not fully given in hybrid RFBs, in which at least one of the active species remains as a solid.

There is a broad typology of RFBs according to the nature of the components and materials used. In order to describe the working principle of RFBs, an all-vanadium battery, which is one of the most studied types, can be taken as a representative case (Figure 1) [30]. In the system, the vanadium ion displays different oxidation numbers from bivalent to pentavalent states, which are effectively exploited for energy storage and generation. The electrolytes flow to the adjacent half-cells physically separated by an ion-exchange membrane, in which vanadium species are chemically oxidized and reduced. A complete cycle in RFBs includes charge and discharge stages, respectively. During discharge, electrons are removed from the anolyte (negative side) and transferred to the catholyte (positive side) through an external circuit [31]. The electron flow is reversed during the charge stage; when external power is supplied, the reduction process takes place now in the anolyte and the oxidation in the catholyte. Redox couples V^{3+}/V^{2+} and V^{4+}/V^{5+} (in the form of oxovanadium cations VO_2^+/VO^{2+}) are used in the anolyte and the catholyte, respectively. RFBs can provide an electrical current until the electrolytes are completely discharged. The main role of the membrane is the prevention of short circuit between electrodes and allowing the transfer of ions such as protons or sulfate ions present in electrolyte media to balance the charge [32].

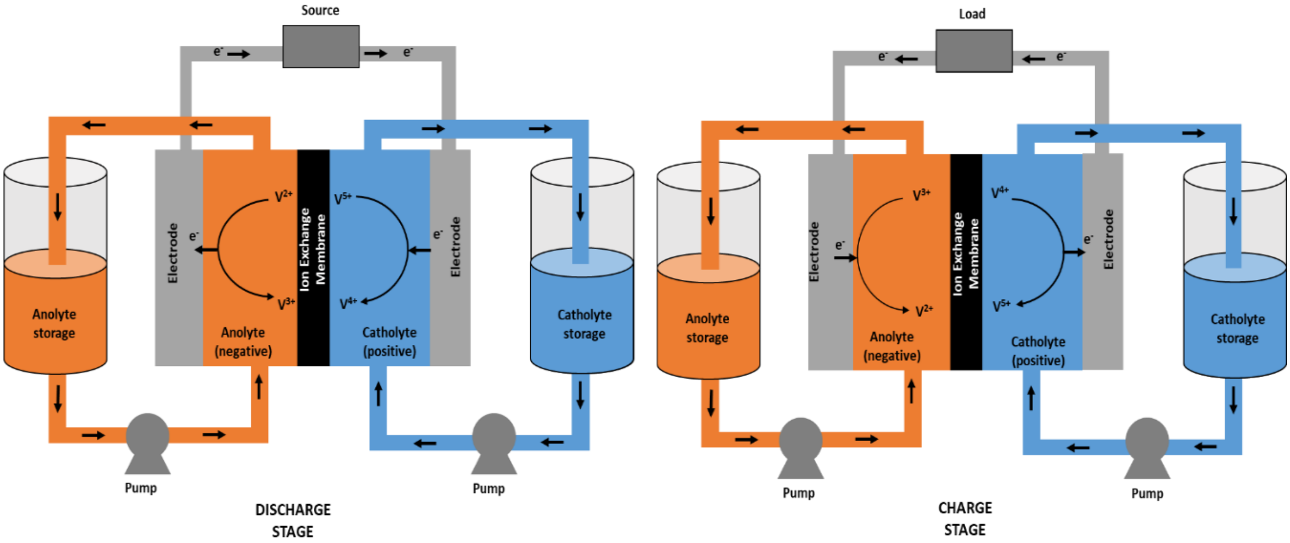

Figure 1. Schematic representation of an all-vanadium redox flow battery (RFB) and redox reactions during discharge and charge stages, respectively (adapted from [30]).

The redox-active species or charge carriers are the primary key elements of RFBs in determining performance efficiency. The energy density is given by both the redox potentials and the solubility of the electroactive species present in the electrolytes. First, the voltage output of the stack is dependent on the equilibrium potentials of the redox couples in the half-cells. On its part, the effective concentration in the electrolytes represents the capacity of the system, defined as the solubility of the species multiplied by the transferred charges in the redox reactions [28,33]. The first type of flow battery was designed by NASA in the 1980s and was based on iron-chromium, using Cr(III)/Cr(II) and Fe(III)/Fe(II) as redox-active species (in negative and positive active sides, respectively) [34]. Since then, RFBs have greatly evolved and the range of redox couples investigated has been significantly widened. Among them, all-vanadium and sulfur-bromine batteries developed by the University of New South Wales (UNSW, Australia) [35] and the Innogy company (UK) [36], respectively, have arisen great interested and have been fully researched for operation optimization. It is also worth mentioning that vanadium RFBs have already reached the commercialization stage. Apart from all-metal RFBs, the electroactive species that have been used in these systems also include halogen ions, metal complexes, metal-free organic compounds, sulfur species and Li-based materials (see Table 1).

In addition to the electroactive redox species, the nature of the solvent electrolyte and supporting species (such as salts) are other important factors in half-cells. Depending on whether water is employed as a solvent in the electrolytes, RFBs can be classified as aqueous and non-aqueous batteries. In all cases, the operational potential is restricted by the electrochemical stability window of the solvents. Aqueous systems are cheaper and safer in comparison to organic solvent-based batteries, and common RFBs such as all-vanadium, polysulfide-bromide or zinc-bromine systems usually contain aqueous media [2]. However, the electrochemical window of water is lower than 2.0 V (depending on pH) [4]. As energy and power densities are given by the cell potential, these parameters are limited by the electrochemical stability of water in aqueous batteries. Organic solvents display higher electrochemical window than water and thus, they have been explored as electrolyte media to enhance the levels of power and energy density, with the possibilities of operation at higher voltages (above the water breakdown voltage) and in a wider working temperature range, which include low temperatures (below 0 °C, the freezing point of water) [37]. For example, the performance of non-aqueous RFBs using metal complex active species (e.g. based on V, Cr or Mn) in acetonitrile has been frequently explored [38–40]. By contrast, the use of organic solvents poses the drawbacks of flammability risks in RFBs with possible evaporative losses. Electrolytes with low volatility and non-flammability properties together with wide electrochemical potential windows are then ideal options. These key properties are precisely found in ILs, and thus, they could play a significant role in the progress of the technology. Despite the increasing interest raised by non-aqueous $\mathrm{RFB_S}$, they are still at an early research stage and further advancement is necessary for their practical implementation.

In fact, in conventional aqueous RFBs, redox species are mostly limited to transition metal ions and halogen ions species, and non-aqueous systems have gained growing attention. Besides, metal-free organic compounds have been effectively used as redox species, representing a lower-cost option with higher chemical diversity and possibilities in terms of redox combinations in comparison to metal species [41]. The use of organic solvent electrolytes cannot be confused with the role of organic compounds as charge redox electroactive species (charge carriers), in which case the systems are regarded as organic RFBs, but still can be based on aqueous electrolytes. In comparison to metal active species, electron transfer in organic redox pairs involves the formation of stable radicals. Neutral organic molecules can provide radical cations or anions, depending on whether they lose or gain electrons, respectively [42]. Also, the electron transfer between radical ions from neutral molecules entails certain redox potential. For instance, quinones are considered attractive redox species since they display fast reversible proton-coupled electron transfer [28].

Other redox species such as sulfur have been incorporated in RFBs because of their high theoretical capacity to design unexpansive batteries. In this case, polysulfide is usually employed in the anolyte in aqueous electrolytes [43]. Moreover, in comparison to ion metals such as vanadium and chromium, they offer less toxicity. On the other hand, hybrid systems such as semi-flow RFBs, have been developed to benefit from the advantage of lithium-based materials. In this respect, Li metal can be used as anode electrode submerged in an alkali solution coupled to a flow aqueous catholyte (half flow cell), with Li^+ being released in the process. As metallic Li^0 is characterized by displaying the highest anodic specific capacity (3860 mA·h/g) while providing low anodic potential, it can enhance the energy density achieved in RFBs, although it also presents low cycle stability, which represents a handicap [44]. Other recent approaches for the enhancement of RFB performance consist of providing the external tanks with suspended solid or semi-solid active species. In this strategy, the constraints posed by the solubility limitations of active species are avoided. Solid storage materials often include lithium-metal oxides (e.g. $LiCoO_2$) [45]. This new concept shows that new configuration and hybrid concept designs of RFBs are constantly being explored.

Table 1 includes several representative types of RFBs according to the redox species exploited for energy storage and power generation, including the reactions involved in normal charge-discharge stages, and associated electrical parameters for specific configurations reported in the literature.

Table 1. Representative types of RFBs

RFB type	**Main half-cell redox reactions or redox species**	**OCV and efficiencies (at the specified current)**	**Separator**	**Electrolytes**	**Ref.**
Iron-Chromium	*Anolyte* : $Cr^{3+} + e^- \xrightleftharpoons[\text{discharge}]{\text{charge}} Cr^{2+}$	1.18 V 97 % (coulombic) 77 % (voltage) 73 % (energy) (40 mA·cm^{-2})	Nafion®-117	Iron and chromium chlorides in aqueous hydrochloric acid solution	[46]
	Catholyte: $Fe^{2+} \xrightleftharpoons[\text{discharge}]{\text{charge}} Fe^{3+} + e^-$				
All-vanadium	*Anolyte*: $V^{3+} + e^- \xrightleftharpoons[\text{discharge}]{\text{charge}} V^{2+}$	1.5 V >99 % (coulombic) >95 (voltaic) ≈95 % (energy) (20 mA·cm^{-2})	Sulfonated fluorinated poly(arylene ether) (SFPAE)	Vanadium sulfates in aqueous sulfuric acid solution	[47]
	Catholyte: $VO^{2+} + H_2O \xrightleftharpoons[\text{discharge}]{\text{charge}} VO_2^+ + e^- + 2H^+$				

Vanadium-Bromine	*Anolyte*: $2VBr_3 + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 2VBr_2 + 2Br^-$	1.3 V 86 % (coulombic) 62 % (voltaic) 53 % (energy) (20 mA·cm^{-2})	Gore® L01854	Vanadium bromide in an aqueous solution of hydrogen bromide and hydrochloric acid	[48]
	Catholyte: $2Br^- + Cl^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} ClBr_2^- + 2e^-$				
Zinc-Bromine	*Anolyte: $Zn^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Zn$*	1.8 V 96 % (coulombic) 83 % (voltaic) 79 % (energy) (20 mA·cm^{-2})	Daramic® microporous polyethylene membrane	Zinc bromide, zince chloride and bromine species in aqueous solutions	[49]
	Catholyte: $2Br^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Br_2 + 2e^-$				
Zinc-Cerium	*Anolyte*: $Zn(CH_3SO_3)_2 + 2H^+ + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Zn + 2CH_3SO_3H$	2.4 V >92 % (coulombic) >68 % (voltaic) 63 % (energy) 50 mA·cm^{-2}	Nafion®-117	Zinc and Cerium methylsulfonates in Methanesulfonic acid	[50,51]
	Catholyte: $2Ce(CH_3SO_3)_3 + 2CH_3SO_3H \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 2Ce(CH_3SO_3)_3 + 2H^+ + 2e^-$				
Chromium acetylacetonate complex	*Anolyte*: $Cr(acac)_3 + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} [Cr(acac)_3]^-$	3.4 V 58 % (coulombic) 22 % (energy) (0.014 mA·cm^{-2}) *(evaluation in H-cell)*	Neosepta® AHA anion-exchange membrane	Active species in acetonitrile (CH_3CN) and tetraethylammonium tetrafluoroborate ($TEABF_4$)	[38]
	Catholyte: $Cr(acac)_3 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} [Cr(acac)_3]^+ + e^-$				
Chromium-EDTA complex	*Anolyte*: $2[Cr(EDTA)(H_2O)]^- + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} 2[Cr(EDTA(H_2O)]_2$ *(EDTA: Ethylenediaminetetraacetic acid)*	2.12 V < 7% (energy) 41 % (voltage) (2.5 mA·cm^{-2})	-	Chromium-EDTA complex in water	[52]
	Catholyte: $[Cr(EDTA(H_2O)]_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} [Cr(EDTA)(H_2O)]^+ + 2e^-$				
Polysulfide–Polyiodide	Anolyte: $2S_2^{2-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} S_4^{2-} + 2e^-$	1 V 98 % coulombic 50 % (voltaic) 50 % (energy) (65 mW·cm^{-2})	Nafion® membrane	NaI_3 in aqueous acid and Na_2SO_4 and Na_2S_4 and Na_2S_2 in NaOH	[43]
	Catholyte: $3I^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} I_3^- + 2e^-$				
Organic (methyl viologen/ OH-TEMPO)	*Anolyte*: $(C_5H_4NR)^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} (C_5H_4NR)^{2+}$	1.25 V >99 % (coulombic) 83 % (voltaic) 82 % (energy) (20 mA ·cm^{-2}))	Selemin® anion exchange membrane	Active materials in aqueous sodium chloride solution	[53]
	Catholyte: $[4\text{-}OH\text{-}TEMPO] \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} [4\text{-}OH\text{-}TEMPO]^+ + e^-$ *(TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxyl)*				
Organic (Anthraquinone/ Benzoquinone)	*Anolyte*: $AQS + 2H^+ + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} H_2AQS$ *(AQ: anthraquinone)*	0.76 V > 90% (coulombic) (10 mA·cm^{-2}))	Nafion®-117	Active materials in aqueous sulfuric acid solution	[54]
	Catholyte: $H_2BQDS \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} BQDS + 2H^+ + 2e^-$ *(BQD: benzoquinone)*				
Organic (quinoxaline derivatives / DBMMB)	*Anolyte*: quinoxaline derivatives redox reactions	2.4 V 70 % (coulombic) 37 % (energy) (0.0625 mA·cm^{-2}))	Nafion®-117	$LiBF_4$ in propylene carbonate	[55]
	Catholyte: $DBMMB \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} DBMMB^+ + e^-$ *(DBMMB: 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene)*				

*Lithium - catholyte-flow battery *(half RFB)	Anolyte: $Li^+ + e \underset{discharge}{\overset{charge}{\rightleftharpoons}} Li$	3.4 V 99 % (coulombic) (3.5 mA·h)	Li conductive NASICON® electrolyte	$K_3Fe(CN)_6$ in aqueous solution (catholyte)	[44]
	Catholyte: $Fe(CN)_6^{4-} \underset{discharge}{\overset{charge}{\rightleftharpoons}} Fe(CN)_6^{3-} + e$				

As mentioned before, anolyte and catholyte can include supporting electrolytes, which play an important role. In aqueous systems, common supporting electrolytes consist of inorganic acids and salts (e.g. sulfuric acid [56], sodium chloride [51]). In general, pure water and pure organic solvents display very low ionic conductivities. The ionic conductivity of pure water is around $6 \cdot 10^{-8}$ S·cm^{-1} and, in the case of organic solvents, these values can be several orders of magnitude lower, e.g. $6 \cdot 10^{-10}$ S·cm^{-1} for acetonitrile [42]. Hence, supporting electrolytes are necessary to obtain enough conductivity in the reaction media and also they can influence on the reaction kinetics and help stabilize redox reactive species.

Finally, but not least, the separator is another key component of RFBs that avoids the crossover of half-cell electrolytes while enabling ion transfer during charge-discharge cycle stages. This component usually displays the highest cost in comparison to other materials in RFBs (e.g. electrodes and electrolytes) accounting for 20-40 % of the total system cost [50].. Among other features, suitable membranes should include high ion conductivity (generally, high proton conductivity is sought), high ion selectivity, good chemical and mechanical stabilities, high effectiveness at preventing cross-contamination and excessive water transfer between half-cells, as well as high resistance to redox processes, especially to oxidation [50]. Therefore, the membrane is another important target for the optimization of RFB performance and one of the most limiting factors for the up-scaling of the technology [57].

3. Electrochemical properties of ionic liquids.

In the last few years, energy storage and generation devices have become among the most prominent fields for the research of IL applications. The physicochemical properties of these compounds offer a series of advantageous features over water and organic solvents for their incorporation in energy systems. There is a large number of possible combinations of cations and anions; the nature of the anion and the cation as well as their interaction specifically determine the properties of ILs. Nevertheless, in general, several properties can be deemed characteristic of this group of materials. To date, ILs have attracted attention mostly as functional electrolytes, due to their high ion conductivity, low volatility and flammability, and high electrochemical stability and the possibility of tuning their properties in terms of polarity, solubility or charge distribution. Many of these properties are determined by the directionality between cation and anion interactions, van der Waals forces between ions and electrostatic (coulombic) interactions given, for instance, by the presence of Lewis basicity or acidity in their structure [58]. Figure 2 displays common anions and ions in ILs widely studied in electrochemical applications.

Already in the early 1980s, molten salts containing chloroaluminate anions (i.e. $AlCl_4^-$) in combination with pyridinium and imidazolium cations started to be studied, showing interesting electrochemical properties [59]. However, the applications of ILs based on metal halide anions are limited due to their high moisture sensitivity. For instance, chloroaluminate tends to hydrolyze forming HCl, which has corrosive properties [60]. In the following decade, ILs significantly evolved into air- and water-stable forms when Wilkes and Zaworotko [61] reported, for the first time, species including the cation 1-ethyl-3-methylimidazolium ($EMIm^+$) in combination with non-metallate counter-ions such as nitrate (NO_3^-), nitrite (NO_2^-), tetrafluoroborate (BF_4^-) or acetate ($MeCO_2^-$). Although some of these anions can also undergo hydrolysis processes (e.g. BF_4^-), the new species presented significantly enhanced stability in comparison to halometalle ILs and became a breakthrough for the development of these materials [60]. Since then, the range of new tailor-made compounds, as well as their field of application, has continuously broadened. ILs have already been studied in very different technological areas, from catalysis and separation processes to nanomaterial fabrication and energy generation and storage, playing the role of solvents, functional materials and electrolytes [62–68].

Figure 2. Common IL anions and cations used in electrochemical applications.

Among the most prominent properties of ILs for energy applications are their broad electrochemical stability window. Commonly, the positive limit potential is determined by the resistance of the anion to oxidation, while the negative potential limit is given by the stability of the cation against reductive processes. Thus, this property is inherently influenced by the nature of the cations and anions, but also by the purity of the organic salt. ILs can offer wide electrochemical window values between 2 V and 6 V, but most of ILs present potential stabilities around 4.5 V. As general trends, ILs with single halide anions such as chloride (Cl^-) and bromide (Br^-) display electrochemical stabilities in the lower region of the mentioned range, between 2 V and 3 V, while those based on fluorine-containing anions such as bis(trifluoromethanelsulfonyl)imide, $TFSI^-$, show superior electrochemical window up to 6 V. ILs based on tetraalkylammonium cations also present significant electrochemical stabilities with values above 4 V [69–71]. The combination of imidazolium, pyrrolidinium, piperidinium, quaternary ammonium and sulfonium cations with anions such as tetrafluoroborate (BF_4^-), the already mentioned $TFSI^-$ and bis(fluorosulfonyl)imide (FSI^-) have shown extremely broad electrochemical windows [58,72]. On the other hand, the interaction between the ILs and the electrode materials with which they are in contact is another factor that influences the potential stability. For instance, the electrochemical window of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIm][TFSI], is higher in contact with a Pt working electrode (4.5 V) than with glassy carbon materials (4.1V) [73].

ILs have demonstrated to be excellent media for coupled redox reactions, enabling their use in electrochemical systems for harvesting thermal and solar energy (in dye-sensitized solar cells and thermocells), as conducting electrolytes in rechargeable batteries and for energy storage in RFBs. Specifically, in lithium batteries, the research of lithium salts in ILs has currently gained a prominent place for the development of the technology [72]. In such cases, electroactive species have to display enough solubility, suitable redox potential, adequate reversibility and relatively high diffusion rates in IL media. These entire factors greatly depend on the chemical nature of the ILs and their particular interactions with the charge carriers. For example, the redox chemistry of common metal complexes such as bipyridyl-based compounds (e.g. $[Ru(bpy)_3]^{3+/2+}$) in ILs can greatly vary in terms of electron transfer rates depending on the metal center and the associated re-organization energy [74]. On its part, organic redox reactions in IL media have been increasingly studied and, in this case, the chemical species and their particular behavior in ILs can be very diverse. However, regardless of the type of active species, the high viscosity of ILs is one of the limitations to be addressed for further application in electrochemical systems. High viscosities hinder diffusion rates and redox kinetics. The viscosity of ILs can be significantly higher compared to conventional solvents (from 10 times higher in comparison to water; viscosity of pure ILs can range from 0.41-257000 mPa·s [75]). In summary, the electrochemistry of ILs greatly differs from that of conventional electrolytes, offering higher complexity; one of the reasons being that diffusion in ILs resembles solid-state diffusion, albeit with continuously changing diffusion pathways caused by ion-pair formation [72,76].

On the other hand, the specific conductivities of ILs are lower in comparison to conventional aqueous electrolytes but still, they can provide significant values, in the order of those offered by inorganic electrolytes in aprotic organic solvents. The conductivities of ILs at room temperature can reach values of up to 100 $mS \cdot cm^{-1}$, although the range 0.1-23 $mS \cdot cm^{-1}$ is more frequent [69,77]. ILs containing dialkyl-substituted imidazolium cations present higher average conductivities than those based on the ammonium, pyrrolidinium, piperidinium and pyridinium groups. Similarly, the conductivity of binary mixtures of IL in e.g. water, can vary greatly depending on the IL nature and concentration. For example, the conductivity of imidazolium-based ILs in water at concentrations of 2.8 M has been reported as high as 88 $mS \cdot cm^{-1}$ [78]. As expected, ILs with lower viscosities tend to offer higher conductivities [16]. In contrast, the conductivity of aqueous KOH-based solutions (ca. 30 wt%, used in alkaline batteries) is 540 $mS \cdot cm^{-1}$, while aqueous H_2SO_4 -based electrolytes (ca. 30 wt%, used in lead-acid batteries) offer conductivities in the order of 730 $mS \cdot cm^{-1}$ [69].

ILs can also display redox properties acting as electroactive species by the attachment of functional groups to their anions or cations. This is a potential strategy to achieve high concentrations of redox-active species and to overcome the mass transport issues in IL-based electrolytes arising from their high viscosity and low solubility of certain redox couples. A wide range of inorganic and organic redox-active ILs can be synthesized, including biredox compounds [79,80].

All these properties have greatly risen the interest in the study of ILs in electrochemical applications, such as double-layer capacitors, solar cells, actuators, thermocells, electrolyzers, fuel cells, lithium batteries and more and more increasingly in RFBs. In this last type of system, the properties of ILs have been explored for almost all the relevant functionalities required, namely as supporting electrolytes, redox reaction media, electroactive species and electrolyte membranes. These applications are widely discussed in the following sections.

4. Ionic liquids in RFBs

4.1. Ionic liquids as supporting electrolytes and additives

Supporting electrolytes are primarily employed to guarantee enough conductivity in the half-cell solutions of RFBs, ensuring efficient operation. When it comes to their selection, important factors to be considered include chemical stability, influence on the reaction kinetics, and safety [81]. The use of new redox species can also imply the research of suitable supporting electrolytes for their optimal implementation. Due to the electrochemical properties of ILs, they can offer great advantages as supporting electrolytes in these systems, enhancing system stability and cycling, species diffusion, the solubility of active species and widening the electrochemical window of cell media as discussed below. On the other hand, additives are intended to perform other specific functionalities such as the role of sequestrating agents. In this sense, ILs have shown to be effective as sequestrating agents in zinc-based RFBs (Table 2).

ILs as supporting electrolytes started to be first employed in non-aqueous RFBs. As commented before, organic solvents offer higher electrochemical potential windows in comparison to water (e.g. 5 V for acetonitrile versus values below 2 V for water). As the cell potential determines the level of energy and power densities achievable in RFBs, non-aqueous systems can then provide higher power and energy outputs than aqueous batteries. In the last case, energy densities are limited to around 25 Wh·Kg $^{-1}$ because of the constrained open circuit potential posed by the limits for water oxidation and proton reduction in the half-cells [82]. Additionally, ILs can help to increase system stability and enhance RFB performance in non-aqueous systems as supporting electrolytes [83,84]. Among the ILs investigated as supporting electrolytes are those containing the anions hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and bis(trifluoromethanesulfonyl)imide ($TFSI^-$). As regards common cations, quaternary ammonium, e.g. tetrabutylammonium (TBA^+) and tetraethylammonium (TEA^+), and imidazolium-based cations, e.g. 1-ethyl-3-methylimidazolium ($EMIm^+$), have been employed in non-aqueous flow batteries because of their electrochemical stability. The first types of non-aqueous RFBs included ruthenium complexes as active species, $[Ru(bpy)_{3]}^{2+}$/$[Ru(bpy)_3]^{3+}$ (where bpy is bipyridine) [85] and ruthenium acetylacetonate, $[Ru(acac)_3]$ [86], employing tetraethylammonium tetrafluoroborate ($[TEA][BF_4]$) as supporting salt in acetonitrile. Similarly, acetylacetonate complexes based on vanadium, $V(acac)_3$, manganese, $Mn(acac)_3$ and chromium, $Cr(acac)_3$, have been explored as active species in the same type of electrolyte [38–40]. $[TEA][BF_4]$ is a well-known electrolyte salt in electrochemical systems with good conductive properties and good stability. This salt has a melting point above 300 ºC and thus, it does not present the general properties of ILs. In comparison, ILs can display higher electrochemical potential windows and $[TEA][BF_4]$ still competes in solubility with metal acetylacetonate complexes in organic solvents [42]. Among the first attempts to characterize ILs as supporting electrolytes for potential application in RFBs systems is that of Zhang et al. [83], who studied two ILs based on the hexafluorophosphate anion, PF_6^-, in a characterization work, using $V(acac)_3$ as electroactive species in acetonitrile media (in an H-type glass cell). Specifically 1-ethyl-3-methyl imidazolium hexafluorophosphate ($[EMIm][PF_6]$) and tetrabutylammonium hexafluorophosphate ($[TEA][PF_6]$) were compared to the conventional salt $[TEA][BF_4]$. Both ILs enabled slightly higher cell potential (up to 2.37 V) and resulted in electrochemically inert. The diffusion coefficients for $V(acac)_3$ in IL-based media (at different concentrations) were also reported to be higher than those in $[TEA][BF_4]$, with values of up to $3.79 \cdot 10^{-6}\ cm^2 \cdot s^{-1}$. However, the IL $[TEA][PF_6]$ offered a more positive impact on the kinetics of the electrode reactions due to the higher reversibility of redox reactions in its presence [83]. The coulombic efficiencies were relatively low in all cases (up to 57 %). As mentioned, this was a preliminary characterization research work and the ILs were not studied in a full RFB system.

Table 2. Assessment of Ionic liquids used as supporting electrolytes and additives in redox flow batteries.

Experimental Set-up	Flow	Active species forms	Solvent	IL liquid as supporting electrolyte or additive	Cycles reported	Cell potential	Current	Coulombic efficency	Voltaic efficiency	Energy Efficiency	Ref.
H-type glass cell (characterization study)	Static	Vanadium acetylacetonate (0.01 M)	Acetonitrile	1-ethyl-3-methyl imidazolium hexafluorophosphate or tetrabutylammonium hexafluorophosphate (0.2 M)	6	2.3-2.4 V	0.1 mA	43-57 %	n.a.	n.a	[83]
All-organic RFB Flow	n.a.	9-fluorenone (0.5 M) and DBMMB (0.5 M)	Acetonitrile	tetrabutylammonium bis(trifluoromethanesulfonyl)imide (1 M)	100 (quick drops during the first 10 cycles, afterwards gradual increases. Charge capacity losing 80% of its original value)	2.37 V	15 mA·cm^{-2}	86 %	81 %	71 %	[87]
All-organic RFB	50 mL min^{-1} (Vol. 10 mL)	Benzophenone (0.01 M) and 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB, 0.01 M)	Acetonitrile	tetraethylammonium bis(trifluoromethylsulfonyl)imide (0.1 M)	50 (stable performance)	2.95V	1.0 mA·cm^{-2}	97 %	46 %	44 %	[88]
Hybrid Zn-Ce RFB	20 mL min^{-1} (Vol. 12 mL)	$ZnSO_4$ (0.05 M) and $Ce(SO_4)_2$ (0.1 M)	Water	1-butyl-3-methylimidazolium chloride (0.01 M)	fast capacity loss from the second cycle	2.1 V	0.025 - 0.075 mA·cm^{-2}	n.a.	73%	n.a.	[89]
Hybrid Zn–Fe RFB	30mL min^{-1} (Vol. 10 mL)	$ZnCl_2$ (10 mM) and $FeCl_2$ (50 mM)	Water	1-butyl-3-methylimidazolium chloride (8 mM) (only in catholyte, with 1 M HCl)	150 (capacity loss of 0.13% per cycle)	1.5 V	20 mA·cm^{-2}	94 %	≈ 80 %	75 %	[90]
Zn-Br RFB	300 mL min^{-1} (Vol. 40 mL)	$ZnCl_2$, $ZnBr_2$ and Br_2	Water	1-ethyl-3-methylimidazolium bromide (1 M)	4 h (charge/discharge)	> 2 V	20 mA cm^{-2}	91 %	69 %	63 %	[91]
Zn-Br RFB	300 mL min^{-1} (Vol. 40 mL)	$ZnCl_2$, $ZnBr_2$ and Br_2	Water	1-ethylpyridinium bromide (1 M)	4 h (charge/discharge)	> 2 V	20 mA·cm^{-2}	91 %	61 %	56 %	[91]
Organic RFB	55 mL min^{-1} (Vol: 6 mL)	4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (0.6 M) and methyl viologen dichloride (0.6 M)	Water	1-butyl-3-methylimidazolium chloride (3 mM)	150 cycles (capacity retention of 94.2 %)	≈ 1.2 V	50 mA·cm^{-2}	99.5 %	≈ 80%	≈ 80%	[92]
Organic RFB	55 mL min^{-1} (Vol: 5 mL catholyte, 15 mL anolyte)	4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (0.6 M) and methyl viologen dichloride (0.6 M)	Water	1-ethyl-3-methylimidazolium chloride (3 mM)	250 cycles (capacity retention of 91.2 %)	≈ 1.2 V	80 mA·cm^{-2}	99.7 %	≈ 60%	≈ 60%	[92]

ILs as supporting electrolytes have also been studied for their application in all-organic RFBs. In this case, the interactions between the ILs and the active organic compounds have to be thoroughly taken into consideration since some supporting ions such as tetrafluoroborate and hexafluorophosphate anions offer some reactivity towards organic active species, causing stability issues and chemical degradation [88]. In this sense, Wei et al. [87] reported a nonaqueous all-organic RFB based on fluorenone (FL) and 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB) as active organic compounds in the anolyte and the catholyte, respectively. For this configuration, the IL [TEA][TFSI] was used as supporting electrolyte in acetonitrile media, obtaining coulombic, voltage and energy efficiencies of 86 %, 83 % and 71 %, respectively (at 15 $mA{\cdot}cm^{-2}$), and energy densities of 15 $Wh{\cdot}L^1$ (charge stage) and 11 $Wh{\cdot}L^1$ (discharge stage). However, the system was not capable of producing stable cycling. To analyze the effect of supporting electrolyte and solvent combination on stability, several tetraethylammonium (TEA^+)-based salts were studied (including the conventional salt [TEA][BF_4]) with electron spin resonance in two different solvents, acetonitrile and 1,2-dimethoxyethane (for solvent effect analysis), at 10 $mA{\cdot}cm^{-2}$. The results showed that the IL [TEA][TFSI] in 1,2-dimethoxyethane provided the highest stability primarily due to the high chemical stability of both the IL and 1,2-dimethoxyethane against the active species. The flow cell using such combination maintained 90 % of its original capacity over 50 cycles (although the voltaic and energy efficiencies were lower in comparison to the configuration based on [TEA][TFSI] in acetonitrile). Regarding the influence of the solvent, with the same IL [TEA][TFSI], the fluorenone radical generated in the redox reaction is considerably more chemically stable in 1,2-dimethoxyethane than in acetonitrile. On the other hand, in the specific case of using the conventional [TEA][BF_4] salt, a fast inactivation of the organic redox pairs was observed because of their high reactivity with the anion BF_4^-. Hence, the compatibility of redox species with supporting electrolytes in combination with the solvent is a critical factor to ensure the normal operation of the system over long-term performance.

The advantageous properties of [TEA][TFSI] as supporting electrolyte in all-organic RFBs have been confirmed in other works using different organic redox species. In a similar approach as that of Wei et al. [87], this IL has shown superior performance in comparison to other salts sharing the same anion or cation (specifically the salt [TEA][BF_4] and the ionic liquids [TEA][PF_6] and [EMIm][TFSI]), in an RFB system employing benzophenone (BP) and 1,4-di-tert-butyl-2,5-dimethoxybenzene (DBB) as active species [88]. The configuration based on [TEA][TFSI] could achieve a cell open voltage of 2.95 V, with the highest coulombic and energy efficiencies (97% and 44 %, respectively) among the other salts assessed. The electrolytes containing the anions BF_4^- and PF_6^- and the cation $EMIm^+$ showed low stability, possibly caused by their interaction with the free radicals derived from the organic active compounds ($BP^{\bullet-}$ and $DBB^{\bullet+}$).

The performance of aqueous RFBs can be also enhanced using ILs as supporting electrolytes. They can help to drift the potentials of the undesirable H_2 and O_2 evolution reactions resulting from water decomposition toward more negative and more positive potentials respectively to expand the electrochemical window of the electrolyte, thus, increasing the possibility of obtaining higher power and energy densities. While the adjustment of several parameters such as pH, temperature and acid strength in aqueous solutions can increase water stability under RFB operation, these strategies can compromise redox reaction kinetics and the solubility of the electroactive species; however, the use of ILs has shown the possibility of avoiding these drawback. The IL 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), which is soluble in water, has been used in different all-metal hybrid RFBs. Specifically, the addition of this IL in a hybrid Zn-Ce RFB enhanced the stability of the aqueous electrolytes against hydrolysis [89]. The cell voltage was 2 V while, under normal conditions, aqueous systems are generally stable up to cell potential of around 1.5 V. Besides, the addition of [BMIm]Cl widened the electrochemical window up to 3 V, which is significantly higher than the electrochemical window of water. More recently, the same IL was successfully applied as supporting electrolyte in a Zn–Fe hybrid RFB [90]. Interestingly, the addition of this compound was beneficial when added in the catholyte half-cell (in aqueous 1 M HCl solution) because it can regulate the redox behavior of iron species. However, its application in the anolyte (zinc side) offered no improvement, and in fact, it provided lower efficiency in comparison to a conventional supporting electrolyte consisting of an acidic solution of NH_4Cl and $CaCl_2$. The coulombic and energy efficiencies for the Zn−Fe hybrid RFB using the IL in the catholyte reached 94% and 75%, respectively, and the open-circuit voltage was as high as 1.8 V.

ILs have also shown to be effective at increasing the solubility of organic redox molecules widely studied in aqueous RFBs such as 4-OH-TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl) [92]. The solubility of this compound in pure water is 2.4 M. By the addition of imidazolium ILs the solubility of 4-OH-TEMPO increases up to 4.3 M, which also implies an increase in theoretical volumetric capacity of up to 115 $Ah \cdot L^{-1}$ (8-fold increase in capacity in comparison to the use of NaCl as supporting electrolyte in water, in which the solubility is 0.5 M in a 1.5 M NaCl solution). Also, a high conductivity can be achieved in the IL/water solutions (83.9 $mS \cdot cm^{-1}$ at about 3.5 m of IL) and the use of ILs as supporting electrolytes can offer superior cycling stability and rate performance in comparison to sodium salts. Huang et al. [92] tested the ILs 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium chloride as respective supporting electrolytes in an RFB using methyl viologen dichloride (MV) and 4-OH-TEMPO as anodic and cathodic organic redox species. Aqueous solubility of 3 M for 4-OH-TEMPO was achieved using 3 mmol IL/g of water in the cathode with the IL 1-ethyl-3-methylimidazolium chloride. The coulombic efficiency and energy efficiency were as high as 99.7% and 60% (at 80 $mA{\cdot}cm^{-2}$), respectively, over 250 cycles with an excellent capacity retention of 91.2 %. This energy efficiency was 65 % at 30 $mA{\cdot}cm^{-2}$. When the concentration of 4-OH-TEMPO was adjusted to 0.6 M, the nitroxyl radical also showed remarkable chemical stability and high cycling stability. In this last case, the energy efficiency was 86% (at 30 $mA{\cdot}cm^{-2}$) with 0.6 M of 4-OH-TEMPO in the catholyte. Again, this highlights the need for simultaneous optimization of the active materials and the selection of supporting electrolytes to achieve optimal performance in concentrated electrolytes. The specific mechanisms reported by the authors that are responsible for the increase in the solubility of 4-OH-TEMPO lies on the interaction between the constituent ions of the IL and the organic radicals, which is stronger than the lattice energy of 4-OH-TEMPO. Besides, the imidazolium cations may also contribute to avoiding collision-caused structural decomposition among 4-OH-TEMPO molecules, which in turns affects the cycling behavior and capacity retention when used as active species in RFBs.

In line with this work, several hydrophilic IL in water were studied as ‘water-in-ionic liquid’ supporting electrolytes by Zhang et al. [93]. For this purpose, imidazolium- and ammonium-based ILs were dissolved in water at different concentrations (from 5 to 20 mmol of IL per g of water) and investigated by cyclic voltammetry showing wide electrochemical windows from 3 to 4.4 V. The resulting IL/water mixtures also offered high ionic conductivity with optimal values at 5 mmol IL/g water. The ionic conductivity of the mixture of 1-ethyl-3-methylimidazolium chloride in water offered the maximum conductivity of ~81 $mS{\cdot}cm^{-1}$. When the concentration was increased to 20 mmol IL/g water, the conductivity dropped to 37 $mS{\cdot}cm^{-1}$ because of the interaction between cations and anions in the aqueous solution. One of these mixtures was tested in an aqueous TiO_2/Fe^{2+} hybrid battery, ensuring the feasibility of (de)lithiation reaction of TiO_2 at a low negative potential at the anode, and enhancing the $Fe^{3+/}Fe^{2+}$ redox reaction at a moderate positive potential at the cathode. Although the resulting mixtures were not assessed in a flow system, this work serves as an example of how ILs can help to enhance redox performance when used as electrolytes.

ILs can play another important role as additives in RFBs, specifically as sequestrating agents in aqueous zinc-bromine systems. In this type of battery, during the charge stage, zinc ions (Zn^{2+}) are reduced to zinc metal, which electroplates over the negative electrode surface, while bromide (Br^-) is oxidized to form bromine (Br_2) in the catholyte. This evolved form of bromine combines with Br^- ions to form aqueous polybromide ions that can diffuse to the zinc side and react with the electroplated zinc promoting battery self-discharge and offering operating issues. To avoid this phenomenon, sequestrating agents are required to minimize the amount of bromine in aqueous solution. These agents complex the evolved bromine and retain it in a separate phase from the aqueous electrolyte. On the other hand, sequestrating agents must facilitate the release of bromine from the complex form during discharge to ensure the full discharge capacity of the battery. Quaternary ammonium bromide salts such as 1-ethyl-1-methylpyrrolidinium bromide, [C_2MPyrr]Br (melting point >290 ºC), were already used in early studies as an effective bromine sequestrating agent [94] and have become a common additive in Zn-Br RFBs. In this respect, ILs have attracted interest as alternative sequestration agents, especially those based on the bromine anion in combination with imidazolium and pyridinium cations [95,96]. Schneider et al. [91] demonstrated that the addition of ILs containing the bromine anion in combination with 1-ethyl-3-methylimidazolium and 1-ethylpyridinium cations ($[C_2MIm]^+$ and $[C_2Py]^+$, respectively) enhanced the performance of a Zn-Br system at 1 M concentrations in aqueous media [91]. Interestingly, this work found that high strong bonding between the IL cations and the polybromide species can pose a negative effect on RFB performance. While very strong bonding interactions between polybromide species and the sequestration agent minimize the content of bromine in the aqueous electrolyte, inhibiting the self-discharge effect aforementioned, the transport of bromine to the electrode surface can be greatly hindered, thus causing electrode polarization and preventing full discharge capacity. This effect was shown for the IL 1-ethyl-1-methylpiperidinium bromide, [C_2MPip]Br. It is worth noting that the application of ILs could be extended to other RFB types that employ Br_2/Br^- as active species.

Other analytical works have highlighted the potential application of ILs in Zn-Br RFBs, especially concerning the electrodeposition process of zinc in the negative electrolyte (anolyte). This phenomenon is an important factor in this type of batteries since the grade of compactness of the electroplated zinc have shown to increase their performance. The addition of 1-ethylpyridinium bromine in a zinc half-cell [96] showed a positive contribution by decreasing polarization resistance and increasing exchange currents, and also displayed positive effects on the shape and size of the electrodeposited zinc. Other works have specifically analyzed the electrodeposition of zinc both in pure ILs but from analytical perspectives [97,98]. In such cases, it was shown that the electrodeposition of Zn in pure imidazolium-based ILs containing the trifluoromethanesulfonate anion ([TfO]) enabled the formation of highly compact zinc deposition morphology (at current efficiencies of 99%).

These analytical studies also underline the potential application of ILs for Zn electrodeposition control as reaction media in RFBs, as will be explained in the following section.

4.2. Ionic liquids as reaction media

In conventional aqueous RFBs such as all-vanadium RFB, concentrated sulfuric acid solutions are usually employed as electrolytes. In such cases, both the electrolysis of water and the corrosion of the battery components by the acidic conditions pose operational limitations. Alternatively, organic solvents offer flammability and pollution issues that need to be addressed for further improvement. Due to the special properties of room temperature ILs, their use as redox reaction media in RFBs has begun to be studied to overcome the drawbacks related to organic and water solvent-based electrolytes (Table 3). Several early studies already characterized the kinetics (namely, standard rate constants and diffusion coefficients) of bipyridine complexes based on Fe(II) and Ru(II) in imide- and amide-type ILs, offering interesting features as reaction media for redox processes [99–102].

Later works studied the behavior of several redox species in room temperature IL media for potential application in RFBs, although, as in the previous cases, they were not tested in full battery systems but in electrochemical cells for characterization. These electrochemical studies are useful to determine the preliminary suitability of active species in ILs before being investigated in full RFBs. In this regard, it is essential to find optimal combinations of active redox species and ILs in terms of high solubility, stability and redox reversibility. Tsuda et al. [103] analyzed the electrochemical performance of a Lewis acidic $AlBr_3$-IL (IL: 1-ethyl-3-methylimidazolium bromide), in which $AlBr_3$ would play the role of active species. Although the results were satisfactory, the variation in the anionic species at the vicinity of the electrodes during the charge-discharge cycles offered limitations for the full application. Similarly, electrochemical oxidation and reduction of $V(acac)_3$ has been proven to be quasi-reversible in the IL 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [EMIm][TFSI], in which vanadium species are stable, thus showing its potential application in RFBs [104].

In other cases, the kinetics of redox reactions in room temperature ILs are poor. For example, the evolution of Fe(II) complexes in the form of $[Fe(ML)_x][Tf_2N]_2$, (in which ML stands for multidentate ligands) in ILs sharing the same anion (e.g. 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[BMIm][Tf_2N]$) has been reported very limited due to the low solubility of the active species [105]. Even, similar metal complexes can work differently depending on the IL employed. While $V(acac)_3$ can properly perform as reactive species in [EMIm][Tf_2N] (using carbon electrodes), the redox processes of metal complexes such as $Mn(acac)_3$ and $Cr(acac)_3$ are irreversible. Only $Mn(acac)_3$ could act as effective electroactive species in this IL in the presence of gold electrodes. This approach, however, would greatly increase the cost of RFBs for practical implementation [104].

The above-discussed studies were performed under static conditions; other approaches have undergone the study of common redox couples in IL media under flow conditions, but still not in full RFB systems, trying to simulate more realistic conditions for potential application in flow batteries (e.g. Zr-Br configurations). One case of interest is the utilization of ILs as reaction media for the zinc redox couple to achieve high energy densities and to control the morphology of the deposited zinc generated during the reactions, as previously mentioned. Several IL species formed by the dicyanamide anion can offer suitable reaction media containing significant zinc concentration, which is important to ensure the generation of sufficiently high current density, using water as an additive. The redox couples Zn^{3+}/Zn^0 in 1-ethyl-3-methylimidazolium dicyanamide, [EMIm][dca], and Zn^{2+}/Zn^0 in N-butyl-N-methylpyrrolidinium dicyanamide, [C_4mpyr][dca], with respective water concentrations below 3 %wt have been proposed as suitable systems for the negative half-cells of RFBs [106,107]. In the last case, the concentration of zinc species resulted especially high (up to 46 mol%) accompanied by long stability over 100 cycles. Regarding zinc electrodeposition, high compactness and uniformity were achieved with no dendrite formation observed under flow conditions, which is one of the highest limitations in aqueous Zr-Br RFBs. Although the addition of water above 1 %wt leads to a reduction of efficiency, the addition of water in IL media is needed to enable the deposition of zinc in compact and dendrite-free form and to enhance its adherence to the electrode surface, ensuring the stable cyclability of the system. These results provide promising prospects for the application of ILs as reaction media in zinc-based batteries.

Experimental Set-up	**IL media**	**Active species in IL**	**Observations**	**Ref.**
Electrochemical cell	1-ethyl-3-methylimidazolium bromide	$AlBr_3$	Low stability of anionic species	[103]
Electrochemical cell	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	$V(acac)_3$	Quasi-reversibility of active species using carbon electrodes	[104]
Electrochemical cell	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$Mn(acac)_3$ or $Cr(acac)_3$	Irreversibility of active species using carbon electrodes	[104]
Electrochemical cell	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$[Fe(ML)_x][Tf_2N]_2$ (complexes)	Fairly poor kinetics of active species	[105]
Electrochemical cell	1-ethyl-3-methylimidazolium dicyanamide	Zn^{3+}/Zn^0	Suitable system for the negative half-cell of RFBs. High compactness and uniformity of electrodeposited Zn	[106]
Electrochemical cell	N-butyl-N-methylpyrrolidinium dicyanamide	Zn^{2+}/Zn^0	Suitable system for the negative half-cell of RFBs. High compactness and uniformity of electrodeposited Zn	[107].
Complete Membrane-free	1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)i	Parabenzoquinone	100 % (coulombic efficiency)	[108]

RFB	mide (in anolyte; wather phase in catholyte).	(pBQ)	70 % (energy efficiency) Migration of the species through the interphase	

Table 3. Potential application of ILs as reaction media in RFBs.

Although the potentiality of ILs as reaction media (solvents of electrolyte species) has been demonstrated mostly through characterization studies, the assessment of RTILs in complete RFB systems has very recently been shown. One interesting feature of ILs is the application in membrane-free configurations. This type of design is based on the immiscible electrolytes to form a biphasic system lacking a proper separator between the negative and the positive half-cells, in which the interphase creates a natural barrier. As a proof of concept, the research group lead by R. Marcilla (IMDEA Energy, [108]) has recently proved the viability of this configuration based on the use of an IL and an acidic solution as respective immiscible half-cell electrolytes, with dissolved quinoyl species as organic redox couples (parabenzoquinone dissolved in the IL side or anolyte, and hydroquinone in the aqueous acid side or catholyte). The IL employed, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [bmpyr][TFSI], is insoluble in water and therefore allows its combination with an aqueous phase in the absence of a physical separator (Figure 3). The RFB yielded an open circuit voltage of 1.4 V with an energy density of over 22 Wh·L^{-1}. In discharge mode, it was capable of delivering 90% out of the total capacity, achieving high efficiencies (coulombic efficiency of 100% and energy efficiency of 70%) with good long-term performance. Although not fully examined, the authors observed the migration of the species through the interphase, specifically that of hydroquinone from the aqueous phase to the IL. Nevertheless, no irreversible electrolyte contamination occurred, and only a loss of capacity occurred during electrolyte imbalance.

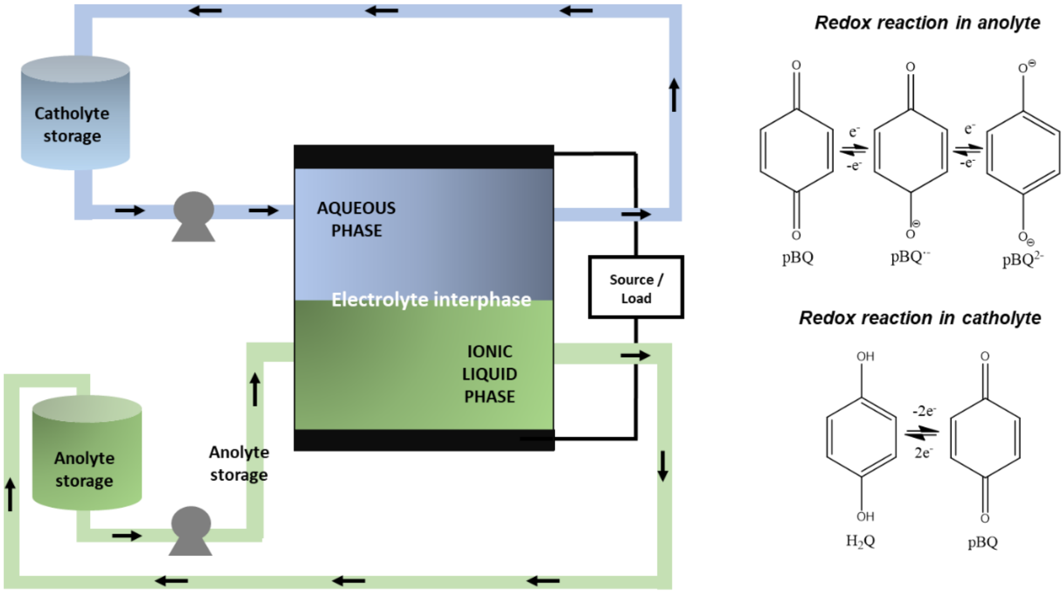

Figure 3. All-organic RFB based on a membrane-free configuration using aqueous and IL electrolytes as redox reaction media [108].

The use of IL as electrolytes in a membrane-free configuration opens a new pathway to follow, with multiple combinations of ILs and active species yet to be explored. At the same time, membrane-free RFBs are expected to receive more attention since the separator is considered the major obstacle for wide implementation and large scale.

There is another group of works that report the use of mixed solvents (non-pure ionic liquid media) including high molality of IL in water o the mixture of IL with a minimum amount of a co-solvent. Takechi et al. [109] designed a highly-concentrated catholyte based on a solvate ionic liquid for a lithium RFB. In this case, a new type of catholyte was synthesized in the form of a stabilized supercooled liquid through the combination of a redox compound (4-methoxy-2,2,6,6-tetramethylpiperidine 1-oxyl or MeO–TEMPO) and a plasticizing lithium salt (LiTFSI). The resulting media can be classified as a solvated IL. A minimum amount of water was added to the mixture improving some properties needed for practical application, such as viscosity and conductivity, but without modifying the substantial nature of the catholyte. The battery tests were conducted using LiTFSI in propylene carbonate in the anode and a Li ion-conducting glass-ceramic separator. Battery performance provided high charged and discharged capacities (93% and 92% of the theoretical capacity 1.21 mA·h, at 0.1 mA·cm^{-2}), with a high coulombic of 99% and energy density of 200 W·h·L^{-1}. Thus, this work offers a strategy to increase the levels of energy density with organic redox compounds, using a suitable combination of active species with supporting salts, to crease a solvated IL as means of reaction media (although it required some added water to increase conductivity and viscosity as already mentioned).

4.3. Ionic liquids as redox-active species.

ILs can act as redox compounds in the negative and positive half-cells of RFBs. Several configurations relying on the use of ILs as active species have been proposed, whether in combination with other compounds in one of the half-cells or in both compartments. In the first case, according to the general principles of RFBs, voltage generation is due to the difference in redox potentials between the IL species. Besides, these ILs could act both as electroactive species and reaction media, offering the opportunity of reaching high energy density. Mainly, two main groups of ILs have been studied as redox-active species in RFBs, metal-containing ILs and polymeric ILs, also known as poly-ILs. It is worth noting that in metal-containing ILs, metal ions are ultimately responsible for the redox reactions. On the other hand, salts containing typical cation groups found in ILs such as ammonium, imidazolium and pyridinium derivative compounds are commented.

Metal-containing ILs constitute a relevant sub-class with emerging applications in diverse research fields, from organic synthesis to separation processes. More recently, these compounds have been investigated as new materials in RFBs systems. Although there is still no standard classification, metal-based ILs can be divided into (i) ILs with a metal ion in the cation and/or the anion, (ii) ILs in which the cation or the anion is coordinated to a metal ion or metal complex and, (iii) ILs with dissolved metal salts or complexes [110]. Different ILs and metal nanoparticle composites are also possible. In this section, the metal-based ILs used in different works as redox-active species belong to the first two groups (i) and (ii). When redox metal ions are integrated in the anions and/or the cations of ILs, the resulting metal ion concentrations can be very high, favoring large charge and energy densities [111].

Different metal-containing ILs were initially proposed for potential application in RFB systems. Staiger et al. [112] characterized a wide range of room temperature ILs, consisting of metal coordination cations and weakly coordinating anions in combination with a ligand (alkanolamines) for possible application in these batteries. One of the advantages of such materials consisted of the simplicity of the synthesis route, through a single-stage process in which metal salts are heated in the presence of a ligand containing multiple polarizable functional groups. A representative example of this type of materials is $Fe(DEA)_6(TfO)_3$, which can be synthesized in pure viscous liquid form through the mixing of the salt iron(III) triflate, $[Fe(OTf)_3]$, with the ligand diethanolamine (DEA). Among the species developed, the most promising electrochemical properties were given by cerium-based ILs such as $Ce(EA)_8(TfO)_3$ (in which ethanolamine or EA is used as a ligand instead of DEA) because of its high conductivity. Also, copper-containing species like $Cu(DEA)_6(TfO)_2$ offered positive results due to its good electrochemical reversibility and conductivity. One important issue posed by these compounds, however, is their high viscosity, which can offset their advantageous electrochemical properties, for real implementation in RFBs as simultaneous active species and electrolyte media, in the absence of other solvents. Nevertheless, the simplicity of the synthesis offers great possibilities in terms of cation, anion and ligand combinations to overcome such limitations, and the addition of other solvents at minimum possible amounts could be considered to reduce the viscosity of ILs.

The viability of a flow battery based on an all-metal containing ILs was proved with the copper-based species $[Cu(MeCN)_4][Tf_2N]$. This IL can act both as the solvent and redox couples due to the copper ion incorporated in its structure. As pointed out before, these types of compounds are characterized by high metal concentrations. The high concentration of Cu enabled to obtain charge and energy densities of 300 kC L^{-1} and 75 W·h L^{-1}, respectively, with coulombic efficiencies of up to 80%. It is worth noting that such energy density is higher than the typical values achievable in commercial RFBs.

Higher coulombic efficiencies have been achieved with advanced approaches based on the design of ionic liquid-metal/sulfur clusters as active species. Modrzynski et al. [113] designed new active species including iron/sulfur cluster anions ($[Fe_4S_4(SR)_4]^{n-}$ (in which SR represents a thiolato ligand) with IL imidazolium cations to be employed in the anodic electrolyte (negative side) (Figure 4). The resulting materials were room temperature metal-based ILs offering interesting electrochemical properties. Moreover, the viscosity of the materials significantly decreases at temperatures higher than 50 ºC. These active species provided significant performance when assessed in an RFB in combination with the well-known bromide/bromine redox couple in the positive half-cell (in IL solution). Specifically, when the cation 1-ethyl-3-methyl imidazolium was combined with the iron-sulfur clusters, high coulombic and relatively high energy efficiencies were obtained (95 % and 96 %, respectively) with a theoretical energy density of 88 WhL^{-1}.

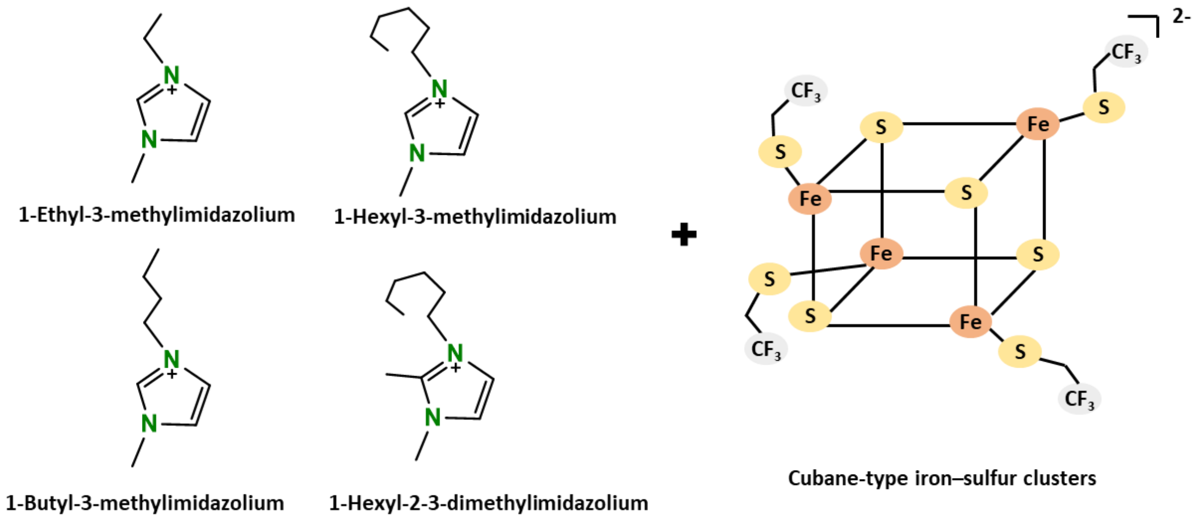

Figure 4. Novel room temperature ILs based on anionic iron-sulfur anionic clusters (right) in combination with imidazolium cations (left) for application in the negative side of RFBs [113].

More recently, poly-ILs have been proposed as potential active species in flow batteries. These compounds have been already widely investigated in catalysis, polymer synthesis and modification separation processes. In general, polymer species with electroactive redox groups are interesting materials as potential redox-active compounds and are gaining growing attention in RFBs, but also in other electrochemical systems such as conventional batteries. Frequently, the functional groups with redox properties are attached to the polymer backbone through covalent bonds, which is achieved through different synthesis methods. One advantage of poly-ILs is that their functionalization can be attained by relatively simple methods. In this sense, Hernández et al. [27] studied the incorporation of counter-anions (acting as redox-active groups) into a polymer backbone based on a cationic poly(IL), specifically poly(diallyldimethylammonium), as potential electroactive species to be employed in RFB systems. The counter-anions can be organic redox moieties that react with the cationic polymer. In such work, anthraquinone (AQ) was used for the application in the anolyte and TEMPO for the catholyte. These two organic species have been already used in organic RFBs, but their incorporation in poly-ILs offers further advantages. For example, these functionalized poly-ILs can be used in different states, whether in solid form or in solution. The benefits of this type of poly-ILs are underlined by its commercial availability and non-corrosive properties. Although these species were not tested in full RFBs, their characterization in an electrochemical cell, dissolved in another non-polymer IL (N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide or $PYR_{14}TFSI$) as electrolyte media, showed wide electrochemical stability window, with the possibility of obtaining OCV values of almost 2 V. Yet, their performance in terms of efficiency and energy density needs to be fully explored.

Together with the above-mentioned IL classes, quaternary ammonium-based functional groups have been proposed as effective redox-active organic materials in aqueous RFBs [114–117]. For example, Hu et al. [115] reported the good performance provided by (ferrocenylmethyl)trimethylammonium chloride as catholyte material in NaCl-based aqueous electrolytes. Specifically, when this catholyte was paired with methyl viologen as a redox-active anolyte, the RFB systems offered excellent long-cycling performance (700 cycles at 60 $mA\cdot cm^{-2}$ with 99.99% capacity retention per cycle) with power densities of up to 125 $mW\cdot cm^{-2}$. Also, to overcome the limitations posed by the redox compound TEMPO, a redox-active nitroxyl radical widely explored as redox catholyte, Janoschka et al. [116] employed the ionic trimethylammonium chloride group as a substituent in this molecule. The aqueous RFB system with the designed active catholyte material, and with the viologen derivative N,N'-dimethyl-4,4-bipyridinium dichloride in the anolyte, offered energy densities of 38 $Wh\cdot L^{-1}$ at a cell voltage of 1.4 V. In a similar approach, Chang et al. [117] synthesized the cationic grafting of 4-hydroxy-TEMPO through its reaction with the glycidyltrimethylammonium cation. The so synthesized cation-grafted TEMPO offered better performance in comparison to the commercial 4-hydroxy-TEMPO, increasing coulombic, voltage and energy efficiencies and cycling stability over 140 cycles in comparison to the commercial 4-hydroxy-TEMPO when used as active catholyte material.

On the other hand, TEMPO has been successfully modified with imidazolium substituents. This strategy was showed by Chang et al. [118], which functionalized TEMPO with 1-methyl-imidazolium and was tested in an aqueous RFB using the redox couple Zn^{2+}/Zn^{0} in the anolyte. Again, compared to 4-hydroxy-TEMPO an increase in voltage was observed (1.64 V in discharge mode) due to a shift in the redox potential to more positive values. In this case, the coulombic efficiency was 99.8% with long performance stability over 400 charge/discharge cycles at 50 $mA\cdot cm^{-2}$.

Similarly, salts based on pyridinium – a frequent cation found in ILs- have also been proposed as novel redox species. Specifically, Sanford et al. [119] synthesized the salt N-methyl 4-acetylpyridinium tetrafluoroborate as a new organic redox species to be used Li-ion anolyte in RFBs. This compound provides two reversible redox couples in acetonitrile/$LiBF_4$ media. First, the authors aimed to design new organic anolyte materials compatible with Li-on electrolytes and that are commonly limited to insoluble lithium salts of arylcarboxylates. On the other hand, this work serves as a representative case of iterative design processes to tailor the electrochemical properties of anolyte materials, showing the complexity and multi-faceted posed by non-aqueous redox flow chemistries [120].

4.4. Ionic liquid as electrolyte membranes.

ILs have been already recognized as attractive materials for membrane doping and preparation in fuel cells and anhydrous battery systems due to their high conductivity, wide electrochemical window, good chemical and thermal stabilities [16,121]. Surprisingly, the study of ILs as electrolyte membranes in RFBs remains scarce, but the already demonstrated application of ILs as electrolyte membranes in other energy and storage systems set a new research pathway to overcome some of the limitations related to membrane operation in RFBs.

Separators directly influence the efficiency in RFBs, and thus, this component represents a key to improve their performance. Generally, the primary function of separators in RFBs is to enable the transport of ions from supporting electrolytes between the negative and positive compartments while avoiding the transference of the respective half-cell redox-active species. Ion exchange membranes are usually used in RFBs, but porous separators can also be employed. Also, the separator should prevent the excessive transfer of solvent between the anolyte and catholyte. On the other hand, this is a truly cost relevant component and plays a critical role in determining the economic feasibility of RFBs, particularly when considering large-scale applications [57,122]. Hence, ideal membranes should present high ionic conductivity and selectivity, low permeabilities towards active species and good chemical, thermal and mechanical stabilities, while offering low costs.

Ion-exchange membranes (IEMs) are the most common option employed (both anion and cation exchange membranes) [56,123], but other types of separators such as non-ionic nanofiltration [124] and ultrafiltration [125] membranes have also been explored. However, depending on the active species, electrolyte nature and ion species present in RFBs, the specificity of membrane property requirements and related operating issues can greatly vary. For example, in aqueous Fe-Cr RFBs, anion-selective membranes can be subjected to fouling as a consequence of the formation of ferric chloride complexes. Meanwhile, cation exchange membranes such as Nafion® have provided effective performance. In the S-Br batteries, electrolyte solutions are separated by cation exchange membranes preventing the diffusion of sulfide anions from the negative to the positive half-cells, which would cause the reaction between sulfide and bromine shortening the lifetime of the battery [126]. In all-vanadium aqueous RFBs, separators should display high proton conductivity, low vanadium permeability, low water permeability and oxidative resistance. Fluorinated and non-fluorinated cation exchange membranes are commonly used, including bare and doped Nafion®, which offers excellent resistance to oxidation, polymers blended with polyvinylidene fluoride (PVDF) or functionalized materials based on thermoplastic polymers, e.g. polyether ether ketone (PEEK), polyether sulfones (PES) and polybenzimidazoles (PBI). However, while cation exchange membranes can offer high proton conductivity, they often present vanadium crossover issues. Other types of materials such as Daramic® microporous polyethylene separators have been extensively explored [126,127], but they have shown to be susceptible to chemical attack by vanadium species [128]. On its part, polymer anion exchange membranes can also be employed in aqueous RFBs with acid-base electrolytes. In this case, supporting acids are embedded into the hydrophilic nanochannels of the membrane, simultaneously enabling the transportation of protons and anions. One of the major features of anion exchange membranes is their low vanadium permeability. However, their poor chemical stability in RFBs still poses a serious limitation for their practical implementation [129].

The aforementioned membrane materials can be extended to aqueous RFBs using organic compounds as active species, with particular issues arising again depending on the diversity of species present in the system [4]. It is worth noting that a large number of materials being currently researched are bowered from other technologies, such as fuel cells [53].

In non-aqueous RFBs, the separators offer higher challenges due to a lack of suitable options. Most of the ion exchange membranes available for aqueous RFBs are relatively ineffective in non-aqueous systems. For example, Nafion® presents an ionic conductivity of five orders of magnitude lower in acetonitrile electrolytes in comparison to aqueous media [130]. Largely, nonporous materials such as nanoporous silica, polyacrylonitrile and specially nanoporous aramid nanofibre separators have been seen as plausible alternatives in non-aqueous batteries [124,131,132].

ILs have been widely studied to synthesize ion exchange membranes through different strategies including the incorporation of ILs into a polymer network, typically by casting techniques, the preparation of composites containing ILs and other filling materials (e.g. metal oxides and nanoparticles) and the synthesis of solid membranes through the polymerization of IL monomers [133]. Especially, protic ionic liquids, which display a mobile proton on the cation, can be used to prepare ion exchange membranes in devices that require high proton conductivity both under hydrous and anhydrous conditions [134,135]. However, their full applications in RFBs are yet to be explored.

Very recently, Song et al. [136] studied the performance of a membrane based on poly(oxyphenylene benzimidazole) (OPBI) polymer modified with the IL [BMIm][BF_4], 1-butyl-3-methylimidazolium tetrafluoroborate, as a novel separator in an aqueous vanadium RFB with sulfuric acid as supporting electrolyte. This configuration offered very interesting features for RFB applications. On one hand, stable membranes with a thickness of 30 μm were obtained (the thickness of commercial Nafion®-115 is 150 μm). Thanks to the formation of hydrogen bonds between the polymer backbone and the IL [BMIm][BF_4], the typical problems related to the leakage of IL phases from modified polymer membranes were overcome, and the synthesized membranes could offer stable behavior during RFB performance. On the other hand, the resulting proton conductivity of the membrane was higher in comparison to that of the commercial Nafion®-115 ($1.4\cdot10^{6}$ S min·cm^{-3} versus $1.6\cdot10^{4}$ S min·cm^{-3}). Moreover, the incorporation of the IL into the OPBI polymer lowered the vanadium ion permeability, due to the Donnan exclusion effect that takes place between vanadium ions and the cations in the IL, which is a common problem in commercial cation exchange membranes, as seen before. Vanadium permeability of the polymer composites at 20 %wt of IL was as low as $5.2\cdot10^{-9}$ cm^{2} min^{-1}, three orders of magnitude below that of Nafion®-115. This optimal configuration translated into high coulombic and energy efficiencies (>99 and 92 %, respectively), with maintained stability over 1000 cell charge-discharge cycles.

The extrapolation of the suitability of IL membranes from other systems such as fuel cells to RFBs cannot be directly done since RFBs present a wide range of redox-active and solvent possibilities, whose interaction with IL membranes should be specifically addressed. Hence, there is still a vast field of research for the study of IL polymer membranes in RFBs.

On the other hand, and as a related approach, several works have addressed the modification and functionalization of polymers with organic groups such as ammonium, pyridinium and imidazolium ones, especially for their application in vanadium RFBs. Although complete IL structures are not used in this case, this group of works can be representative of the advantages of including moieties of similar nature to the organic cations found in ILs. The incorporation of these functionalizing groups can effectively help to reduce vanadium ion permeability due to Donnan exclusion (repulsion of vanadium cation by the introduced groups) as well as to improve chemical stability, and thus to enhance the coulombic efficiency and cycle stability of vanadium RFBs [137].

In this sense, several works have reported quaternary ammonium-based polymers with immobilized cations as ion-exchange membranes. Chen et al. [138] functionalized poly(arylene ether sulfone)s -Radel®- membranes with quaternary ammonium moieties, showing that, for optimal conditions, the conductivity of the membrane can be of the same order than that display by the commercial Nafion®-212 membrane (44 $mS \cdot cm^{-1}$), but with noticeably lower VO^{2+} permeability. In RFBs, the coulombic efficiency was higher than 97% within an intensity range from 20 to 80 $mA \cdot cm^{-2}$, and always superior to that displayed by the Nafion®-212 membrane in the same range. Still, the application of this strategy is not restricted to vanadium RFBs. Li et al. [139] reported anion exchange membranes prepared from poly(phenylene oxide) for application in a non-aqueous all-copper RFB. The membranes presented a cross-linked structure containing quaternary ammonium groups, which help to reduce the crossover of the active copper species. In terms of cell performance, the RFB system with this crosslinked membrane yielded a coulombic efficiency of 89%, a voltage efficiency of 61%, and an energy efficiency of 54% at 7.5 $mA \cdot cm^{-2}$. Nevertheless, quaternary ammonium functionalized membranes present several disadvantages over other groups: (i) they present lower conductivity in comparsiton to, for example, imidazolium, limiting RFB performance and large-scale application [137], (ii) ammonium groups can be readily degraded when a high concentration of acid supporting electrolyte is used (H_2SO_4) or by high-oxidative reactive species as the own VO^{2+} cation [140].

As an alternative to quaternary ammonium-based membranes, anion exchange membranes containing pyridinium groups have been also studied in vanadium RFBs [140–142]. Through these works, it has been shown that pyridinium groups can promote proton transport due to acid-base interactions. A representative case is that of Zhang et al. [141], who reported poly(phenyl sulfone) anion exchange membranes functionalized with pyridinium groups, providing higher performance when compared to the results obtained with Nafion®-117 in a vanadium RFB system. Specifically, the reported membrane displayed lower vanadium ion permeability while exhibiting higher battery efficiency with coulombic efficiency of ~98% and energy efficiency of ~80 % (versus 96 % and 77%, respectively, for the Nafion®-based system) at high current density (100 $mA \cdot cm^{-2}$). Another interesting configuration was reported in the work by Maurya et al. [142], in which a single-step synthesis method consisting of simultaneous polymerization and quaternization was used to prepare crosslinked anion exchange membranes. They consisted of an inter-polymer of poly(vinyl chloride)/poly(4-vinyl pyridine) with 1,4-dibromobutane to tune the crosslinking density of the membrane. This configuration also offered better results in comparison to another commercial membrane, Neosepta-AHA, with reduced vanadium ion permeability and higher efficiencies (~93%, ~97% and ~88 % for coulombic, voltage and energy efficiencies, respectively).

Despite these promising results, other research works have also demonstrated that the pyridinium groups can still be subjected to degradation processes due to the introduction of hydrophilic carbon in the benzene ring during membrane synthesis. Thus, further strategies have been developed to increase the stability of pyridinium functionalized membranes. In this sense, Zeng et al. [140] presented highly stable cross-linked pyridinium-functionalized anion exchange membranes based on bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BrPPO), which was selected as the starting polymer to graft the pyridinium functional groups. Under optimal conditions in terms of membrane composition, this separator was capable of providing higher coulombic and energy efficiencies in comparison to the use of Nafion®-212 in a vanadium RFB system. Above all, this membrane offered outstanding stability properties. In terms of cycling stability in RFBs, the high chemical stability of the membrane led to a decrease in 80% of the initial value of specific discharge capacity after 537 cycles (at 200 $mA\cdot cm^{-2}$). In the case of the Nafion®-212, the specific discharge capacity decreased to 80% of the initial value after only 302 cycles.

The utilization of functionalized polymers with imidazolium has also offered promising results for application in RFBs. Reported configuration includes membranes based on imidazolium grafted poly(arylene ether ketone) [143], amphoteric membranes using imidazolium-functionalized polysulfone [144] or polyphenylene oxide [137] with sulfonated poly(ether ether ketone) (SPEEK), copolymers based on N-vinylimidazole [145] and fluorinated poly(aryl ether oxadiazole) membranes derivatized with imidazolium groups [146]. This type of membranes can offer high chemical stability and higher cell performance in comparison to commercial membranes. As a representative and recent case, Chu et al. [137] included the synthesis of amphoteric membranes functionalized with imidazolium groups. Such membranes were synthesized through the combination of imidazolium functionalized polyphenylene oxide (ImPPO) together with SPEEK, a polymer widely used for the preparation of ion-exchange membranes. This configuration contains sulfonate groups that provide the membrane with high proton conductivity, while the imidazolium groups allow the achievement of low vanadium ion permeability due to the Donnan exclusion effect. Moreover, the presence of imidazolium groups enhanced the swelling ration in comparison to bare SPEEK membrane because of the ionic bonds formed by them and the sulfonate groups of the SPEEK backbone. When testing in a vanadium RFB system, high efficiencies were obtained (from 97 % at 60 $mA\cdot cm^{-1}$ to over 99 % at 140 $mA\cdot cm^{-1}$), significantly higher in comparison to the values provided by the commercial Naffion®-212 membrane, with also superior cycle stability after 30 cycles, with respective capacity retention of 75% for the reported membraned and 57% for the Nafion®-212 membrane.

Although the reported configurations are not based on the use of complete IL structures, the commented works create a research framework that exemplifies the benefits of functionalizing polymers with organic groups of the same nature that can be found in ILs to create ion-exchange membranes.

OUTLOOK

RFBs offer promising prospects as energy storage systems due to their economy and scalability, especially for large-scale stationary applications. At the same time, ILs provide new pathways to overcome some of the limitations found in aqueous and organic systems, in which the levels of energy density are still relatively low for full implementation. Together with their excellent electrochemical features, the high tailoring possibilities to create new chemical species are greatly rising the interest in ILs for their exploration in flow batteries. The versatility of ILs has been already demonstrated in various energy storage technologies and, more recently, their application in RFBs has intensified showing multifunctional and advantageous performance benefits. The current trends in this research field have been detailed, discussing the different roles that ILs can play in RFBs and the associated benefits and drawbacks. Accordingly, the following general conclusions and perspective on the use of ILs for the further development of RFB technology can be drawn:

(i) As supporting electrolytes, ILs can help to increase energy efficiency in aqueous and non-aqueous RFBs, widening the electrochemical stability windows and increasing the ionic conductivity of the media. This allows obtaining higher cell potentials in RFBs in comparison to conventional salts. Moreover, ILs offer high chemical stability towards redox active species such as electroactive organic compounds, ensuring long-term performance. ILs based on quaternary ammonium cations and the bis(trifluoromethanesulfonyl)imide ($TFSI^-$) anion, among others, have shown promising options. To date, the role of ILs as supporting electrolytes is the most studied functionality.

(ii) ILs can be effectively employed as sequestrating agents in aqueous zinc-bromine RFBs to control the electroplating process of zinc occurring in this type of batteries. Specifically, the use of ILs as additives in such systems enables the enhancement of compactness in the deposited metal, increasing the efficiency of the system.

(iii) The primary advantages of room temperature ILs as reaction media in RFBs lie on the safety (non-volatility) and broad electrochemical potential window. The kinetics of redox reactions in ILs can greatly vary depending on the nature of the active species and the interaction between them and the IL media. However, ILs typically have higher viscosities than conventional solvents and the sluggish mass transport of active species in IL electrolytes remains an issue. In line with the previous point, ILs as media in zinc-bromine systems can be also used as a way to control zinc electrodeposition. Most of the works on this role have been performed through analytical studies rather than in full RFB set-ups.

(iv) One of the most interesting features of ILs as reaction media consists of the possibility of being used to create membrane-free configurations, an option that has been recently demonstrated for organic active species. The application of ILs as electrolytes for this purpose opens a new pathway to be explored.

(v) IL structures can display redox properties and thus they can be exploited as active species in RFBs. Two groups of ILs have been specifically targeted as active species, metal-containing ILs and polymeric ILs or poly-ILs. This last option offers the advantage of polymer functionalization through relatively simple methods. Potentially, ILs could act both as electroactive species and reaction media to obtain high energy densities.

(vi) The use of polymer IL-based ion exchange membranes in RFBs remains virtually unexplored. The studies performed until now, however, offer very positive results since they have demonstrated that IL separators can greatly reduce, for example, vanadium ion permeability, which is an important limitation in systems employing commercial cation exchange membranes, while offering high proton conductivity. As this class of membranes has gained growing attention in other energy systems such as fuel cells, it is expected that they become increasingly popular in RFBs. In contrast, quaternary ammonium, pyridinium and imidazolinium functionalized polymers have been studied in vanadium RFB systems that the resulting configurations can greatly reduce vanadium ion mobility and increase battery performance in comparison to commercial membranes.

To sum up, the incorporation of ILs in RFBs can be considered a very recent and emerging research field, and their study in such systems is likely to greatly expand in the coming years for the main components of these batteries. Some of the functionalities have been very scarcely investigated and plenty of future research possibilities with new IL structured being developed are to arise.

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