POLITECNICO DI TORINO

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Solventi eutettici profondi per batterie ricaricabili

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Infine, un ringraziamento va anche agli amici che mi hanno sostenuto sia nei momenti difficili che in quelli felici.

1. List of acronyms

ASR = area specific resistance

ChCl = choline chloride

CNF = carbon nanofiber

CP = carbon paper

DCE = dichloroethane

DEC = deep eutectic catholyte

DES = deep eutectic solvent

DMC = dimethyl carbonate

DSP = DES-based self-healing polymer

EA = ethyl acetate

EC = ethylene carbonate

EG = ethylene glycol

ETG = eutectogel

HBD = hydrogen bond donor

HCl = hydrochloric acid

HFB = hybrid flow battery

IL = ionic liquid

LBM = lattice Boltzmann method/model

LCO = lithium cobalt oxide

LFP = lithium iron phosphate

LIB = lithium ion battery

LiTFSI = lithium bis[(trifluoromethyl)sulfonyl]imide

LMO = lithium manganese oxide

LMP = lithium manganese phosphate ($LiMnPO_4$)

LTO = lithium titanate oxide

MAc = N-methylacetamide

NCA = nickel cobalt aluminium

N-G = nitrogen-doped graphene

NMC = nickel manganese cobalt

NTO = sodium titanate oxide

NTP = $NaTi_2(PO_4)_3$

OA = oxalic acid

OCV = open circuit voltage

PE = pristine electrode

PEG200 = polyethylene glycol

PNZ = phenazine

PVDF = polyvinylidene fluoride

RES = renewable energy source

RFB = redox flow battery

SDA = structure directing agent

SE = segmented electrode

SIB = sodium ion battery

SOC = state of charge

SXM = soft X-ray microscope

TEA = triethanolamine

ZES = zinc eutectic solvent

ZIB = zinc ion battery

2. Introduction

The utilization of renewable energy sources (RESs) is growing all over the world with the aim of reducing the dependence on fossil fuels of our civilization. Such dependence is problematic for two main reasons: the well-known climate change issue and the limitation of the natural resources which, at the current utilization pace, cannot sustain our society for a very long time, only few decades according to the BP estimation [1]. On the other hand, RESs are unlimited by definition and the negative impact of their usage on the climate change is, in general, negligible. Wind and solar power are the green technologies that were developed the most in the last decades; furthermore, the installation of new solar and wind plants is in the order of hundreds of GW every year and is still showing a growing trend [2]. However, RESs exploitation usually presents a huge drawback: the discontinuity of the power generation, which depends on the climate conditions and the hour of the day, while availability is one of the best quality of the fossil fuels, we can burn them when we need. Therefore, it is crucial to couple the renewables with storage systems that can be charged when the renewables power output is larger than the demand and, vice versa, can be used to power the grid when the power plants are not capable of sustain the demand. Storage systems are already used in the current electrical grid; pumped hydroelectric storage is by far the most common storage technology available due to its simplicity and low operational costs. However, pumped hydro requires huge spaces and volumes with massive impacts on the landscape of the selected regions. Moreover, in general, it is difficult to find places where new dams could be located, especially in the developed countries.

2.1. Batteries

Electrochemical storage systems are rising as an interesting solution not only for grid storage but also for the transport sector, at least in the light vehicles, because of the great size modularity, efficiency and flexibility that such systems can ensure. Lithium ion (Li-ion) is actually the dominant technology, despite the safety concerns, due to its reliability, cost, which is constantly declining, and the good energy and power density [3]. However, the research in this field is massive and not only focused on improving performance and safety of Li-ion but also on the development of cells based on different materials in order to find feasible alternatives. In any case, electrochemical storage systems have been used by common people since a very long time and are commonly defined as batteries, although such name indicates a group of two or more cells connected together to provide electrical power. Nowadays, almost any portable electronic device (smartphones, laptops, etc.) is powered by a rechargeable "battery" or secondary cell; however, there are still some devices such as remote controls that are usually powered by primary cells, which are non-rechargeable and need to be replaced when they are depleted.

2.1.1. Battery categories

The electrochemical storage systems are divided in two main macro categories: closed systems and semi-closed systems; obviously, inside each category there are many technologies based on different chemistry and working conditions.

The closed systems denomination indicates that there are no mass transfer phenomena between the cell and the external environment. The electrodes composing materials represent the chemistry of the cell; therefore, the electrodes materials define the characteristics and the performance of the cell. The number of technologies enclosed in this category is huge but only few are available on the market, such as lead-acid batteries or the previously mentioned Li-ion; however, the research in this field is very active and many technologies are finally showing comparable or even better performance than the Li-ion. In any case, the general structure of a closed cell, as shown in Figure 1, is composed of two electrodes, an anode and a cathode made of different materials; the electrodes are attached to two current collectors, made of aluminium or copper; the separator divides the two side of the cell, preventing the contact between the electrodes and the consequent short circuit; the electrolyte, between the electrodes, is usually liquid but it can be solid, it has the function to let the active ions move between the electrodes; in the end, the housing which separate the cell from the external environment [4].

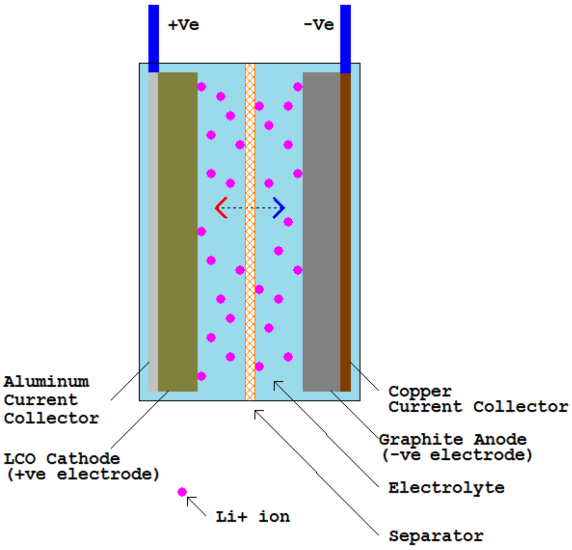

Figure 1. Schematic representation of a lithium-ion cell. Adapted and reprinted with permission from [4].

The shape of the cell can be different depending on the applications. In general, the coin shape is the most used during the laboratory experimentations due to its simple production, while the cylindrical shape is probably the most famous commercially; however, there are also prismatic shapes, in particular hard-case and pouch, which present interesting advantages in term of cost and volume usage, especially important for the automotive and electronics sectors; Figure 2 shows the most commercially used cell shapes [5].

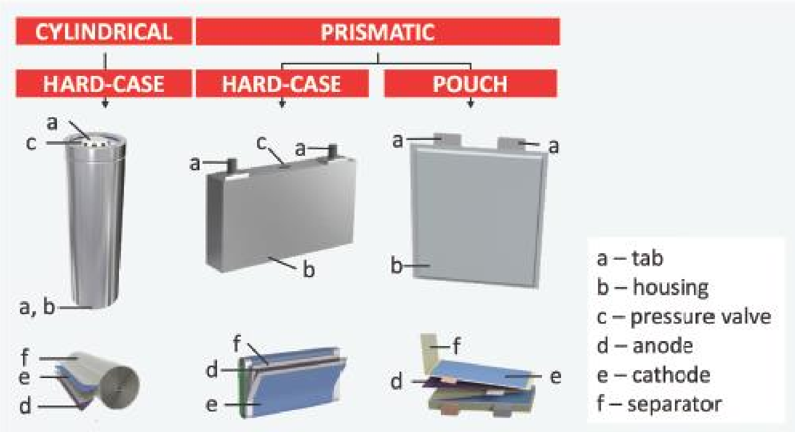

Figure 2. Industrially relevant cell shapes for closed system.
Adapted and reprinted with permission from [5].

The partially closed systems, on the contrary, could present mass transfer phenomena between the cell and the external environment. The two families of such category are Redox Flow Batteries (RFBs) and metal-air cells.

As regards the RFBs, these cells are made of separated components. The cell core seems to be similar to the closed cells with two electrodes, the separator and the electrolyte; however, the differences are substantial. First of all, the electrodes are usually the same carbon material in both sides, which indicates that the characteristics of the cell are not strictly dependent on them; on the other hand, there are two liquid electrolytes, one for each side of the cell, in which are dissolved redox active species; therefore, the electrolytes define all the parameters of the cell. The two electrolytes are separately stored in tanks and pumped to the cell core during the charge and discharge processes. The tanks are obviously part of the system but they can be considered as external components of the cell. The redox reactions occur in the cell core between the two electrolytes [6]. Such configuration presents one important benefit which is the separation of power from energy; in other words, the power depends on the redox reactions occurring in the cell core, while the energy depends on the tanks volume. Therefore, RFBs could represent a feasible and low cost solution even for long term energy storage because the amount of the stored energy only depends on the tanks dimensions.

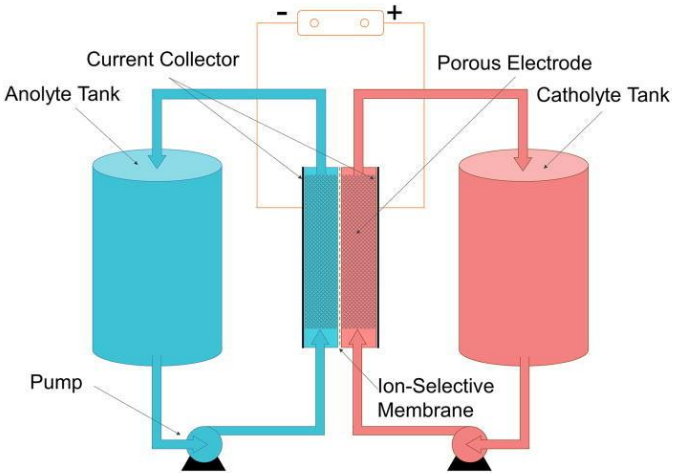

Figure 3. General representation of a RFB.
Adapted and reprinted with permission from [6].

As regards the metal-air batteries, the structure of such cell is defined half open and it is composed of a metal anode, an electrolyte and a porous cathode. There is a huge variety of metals that can be used for the anode, such as lithium, sodium, zinc, iron, etc. As shown in Figure 4, the electrolyte can be based on different substances such as aqueous, aprotic, a combination of the two or even solid-state. The cathode is made of a porous material and it is exposed to ambient air in order to collect the oxygen, which is the cathode active material. Such technology is really interesting because of its huge theoretical energy density, at least an order of magnitude above the commercial Li-ion cells. However, these systems are still far from the market due to some practical challenges such as rechargeability, safety and high costs [7].

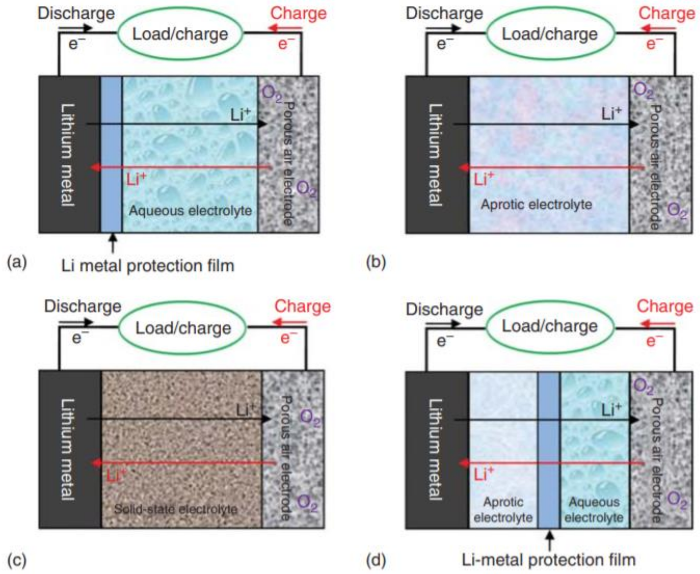

Figure 4. illustration of a lithium air cell with different electrolytes; (a) aqueous electrolyte, (b) aprotic electrolyte, (c) solid-state electrolyte and (d) hybrid solution of aqueous and non-aqueous electrolyte.
Adapted and reprinted with permission from [7].

2.1.2. Cell main parameters

Regardless of the considered technology or structure, the performance of each cell can be evaluated considering few crucial parameters: nominal capacity, nominal voltage and energy content. The nominal capacity of a cell can be defined as the amount of charge that can be stored in a cell and is generally measured in Ampere hours (Ah). Such parameter depends on the cell active materials and on the geometrical dimension of the cell. Furthermore, the charging and discharging cycles usually lead to a decrease of the cell capacity. The cell nominal voltage is obviously measured in Volt (V) and depends on the active materials; in particular, it depends on the thermodynamic of the reaction and, therefore, it is directly proportional to the variation of the Gibbs free energy of reaction. However, the cell voltage is not constant but, instead, is a function of the state of charge (SOC), which is the ratio between the actual cell capacity and the nominal one, and the charge/discharge current density, which is the ratio between the current and the conductive surface, or the C-rate, which can be define as the ratio between the current and the nominal capacity, i.e. 1C indicates the current that can completely charge/discharge the cell in one hour. Figure 5 shows an example of a cell polarization curve, voltage trend, as a function of C-rate and SOC. At last, the energy content is the product of the nominal voltage and capacity and is measured in Wh or kWh. Such parameter can even be used considering a battery made of a certain number of cells put in series or parallel; it is enough to multiply the nominal voltage and capacity by the number of connected cells [8][9].

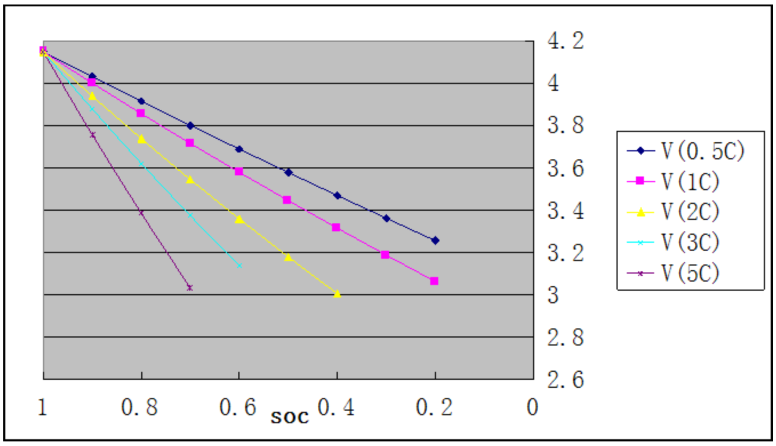

Figure 5. Polarization curve as a function of the SOC and C-rate. Adapted and reprinted with permission from [9].

2.2. Deep eutectic solvents

The deep eutectic solvents (DESs) are generally considered as ionic liquid (IL) analogues due to the numerous similarities in terms of physical and electrochemical characteristics, in particular the liquid phase at a temperature below 150 °C. However, it important to affirm that DESs and ILs are two different type of solvents; as a matter of fact, DESs are not completely made of anionic species and they can be obtained from non-ionic species. In general, DESs are made of two or three inexpensive components, Lewis or Bronsted acids and bases, which could contain anionic and cationic species; such components are able to form a eutectic mixture, usually through hydrogen bond interactions, with a melting temperature lower than that of each specific component [10][11].

ILs have been highly investigated in scientific literature especially due to the versatility, which allows their use in many technical applications, as an alternative to the aqueous solvents. However, the ILs high cost and toxicity limited their industrial applications. DESs, on the other hand, have emerged as a new generation of solvents because of their general low cost, easy preparation, safety and low environmental impact.

DESs can be described using the general formula:

$$Cat^{+}X^{-}zY$$

Where Cat^+ can be any ammonium, phosphonium or sulfonium cation; X indicates a Lewis base, usually a halide anion, while Y is a Lewis or Bronsted acid (z indicates the number of Y molecules that react with the anion) [10].

DESs are generally classified in four groups depending on the Y nature, as indicated in Table 1. It is important to notice that the DESs fourth group shows a particular composition based on metal chlorides and different hydrogen bond donors (HBDs) such as ethylene glycol or urea.

Table 1. General formula for the classification of DESs [10].

Type	General formula	Terms
Type I	$Cat^+X^-zMCl_x$	M = Zn, Sn, Fe, Al, Ga, In
Type II	$Cat^+X^-zMCl_xyH_2O$	M = Cr, Co, Cu, Ni, Fe
Type III	Cat^+X^-zRZ	Z = $CONH_2$, COOH, OH
Type IV	$MCl_x + RZ = MCl_{x-1}{}^+RZ + MCl_{x+1}{}^-$	M = Al, Zn & Z = $CONH_2$, OH

Most of the studies have investigated DESs based on different quaternary ammonium salts, especially choline chloride, in combination with HBDs due to the general low cost and safety of these components, Figure 6 shows the most used halide salts and HBDs.

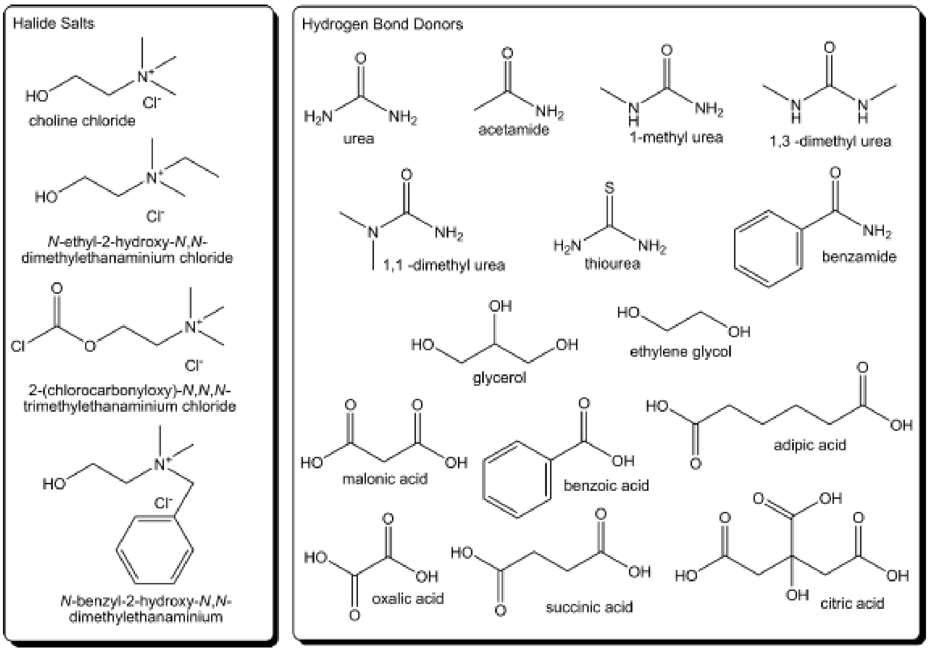

Figure 6. Some halide salts structure, on the left, and hydrogen bond donors, on the right, which are used to form DES
Adapted and reprinted with permission from [10].

2.2.1. DESs physicochemical properties

DESs properties are easy tailorable, similarly to ILs, given that they can be produced through the combination of a huge variety of chemicals reactants; furthermore, after the selection of the chemicals, it is possible to choose the components molar ratio, which lead to an even larger possibility for the modification of the solvent properties.

The DES freezing temperature is one of the most considered characteristic. Generally speaking, a DES with a freezing temperature below 50 °C is more industrially interesting because it can be easily used in many applications. The freezing temperature should be dependent on the DES lattice energy, on the way the components interact with each other and on the entropy changes related to the formation of the liquid phase. The density is another important parameter which is highly dependent on the DES molar ratio. DESs viscosity is usually very high at room temperature (>100 cP) which is a problem that have to be addressed. The reason for the high viscosity is often associated to the hydrogen bond network between the components as well as the van deer Waals and electrostatic interactions. The viscosity of most DESs decreases when the temperature rises. The development of room temperature low viscosity DESs is crucial to enhance their potentialities as green solvents. The ionic conductivity is closely related to the viscosity; the general DESs high viscosity is the main reason for their poor ionic conductivity (< 2 mS/cm at room temperature). Therefore, the temperature rise remarkably enhances the DESs conductivity due to the viscosity reduction. Surface tension is another interesting parameter that has to be considered during the development of DES. In general, at room temperature the DESs surface tension value is between 40 and 80 mN/m which is comparable to common ILs, while it is higher than most molecular solvents [11].

2.2.2. DESs green credentials

DESs are often considered as a green alternative to most ILs; however, type I, II and IV DESs are composed using metal salts which are inherently toxic; on the other hand, tyre III DESs can be produced using a variety of amides and polyols which are non-toxic. In any case, the toxicity of the eutectic mixtures is not the same as that of the single components; therefore, even though a DES could be composed of non-toxic components, the non-toxicity of the mixture is not inherently ensured. Furthermore, DESs present a lower vapor pressure compared to other molecular solvent which means a lower emission to the atmosphere; however, DESs are miscible with water and, thus, a solvent leakage could pollute the aqueous environment [10].

2.2.3. DESs applications

Since the first scientific publication in 2001 [12], the interest on DESs possible applications has remarkably grown at both the academic and industrial levels.

2.2.3.1. Metal processing

One of the most important application of DESs is represented by the metal processing. Traditionally, the use of aqueous systems represents the basis of the electrofinishing industry due to the high solubility of metal compounds in water which ensures the good solutions conductivity. However, water presents a relatively narrow potential window which could lead to a low current efficiency; moreover, the solutions toxicity is concerning. The crucial advantages of DES based system, aside from the previously mentioned low cost and simple production, are the wider potential window, the high solubility of metal salts and the absence of water [10].

The metal electrodeposition processes are generally based on aqueous acidic or basic solutions. Such methods are limited by the electrochemical stability of the electrolytes; in particular, the formation of a passivation layer on the electrodes, made of insoluble metal oxide and hydroxide, lead to an inhibition of the desired metal deposition; moreover, the aqueous solvents have to be purified from the toxic additives before the release in the watercourse. On the contrary, DES-based methods do not suffer from the passivation effect because of the high solubility of metal oxides and hydroxides in DESs which lead to an easier deposition of even thicker metal films [10].

The metal electropolishing is the controlled dissolution of a metal surface with the aim to minimize the surface roughness, which lead to an increase of the optical reflectivity and corrosion resistance. The commercially used methods are based on aqueous sulfuric and phosphoric acid mixture; such methods, however, present some issues such as the solvent toxicity and the low current efficiency caused by the massive gas evolution during the process. On the contrary, DES based processes do not require any additives and do not produce relevant gas evolution; therefore, higher current efficiencies are achievable. Besides, DESs are less toxic and more environmentally friendly compared to the aqueous solution [10].

Metal extraction or recovery is another very interesting application. In particular, the selective recovery of metals from depleted batteries is receiving more and more attention, in the circular economy perspective, due to the constant expansion of the demand for electrochemical storage. In this case, the most common industrially used processes are the pyrometallurgical, based on high temperature, and hydrometallurgical, based on hazardous solutions, or a combination of the two. On the contrary, DESs can be used in solvometallurgical processes, which usually require mild operating conditions, ensuring good performance and low toxicity; we are going to analyse some scientific papers later in this work [10].

2.2.3.2. Chemical synthesis

The preparation of new inorganic materials with a crystallin and porous structure is often achieved by hydrothermal synthesis, adding organic templates as Structure Directing Agents (SDAs) to a molecular solvent. However, ionothermal synthesis, in which ILs or DESs could be used as both the solvent and the SDA, shows some interesting benefits compared to the hydrothermal. Such advantages are the possibility to operate at ambient pressure, avoiding the risks associated to the high solvents pressures; the much larger availability of usable DESs, potentially millions, compared to the molecular solvents, around 600, required by the hydrothermal synthesis; the reduction of water tendency to be enclosed in the final structure, even if it is present in small amounts [10].

Another interesting topic, which has been investigated in literature, is CO_2 capture and sequestration using DESs. DESs could be used in ionothermal synthesis to produce a suitable material for the CO_2 adsorption. Furthermore, DESs could be directly utilized as solvent to capture not only CO_2 but also other gases such as sulphur oxides which are another typical products of fossil fuel combustion [11].

DESs could also be used for biodiesel separation from the residual glycerol. Biodiesel is usually produced by the transesterification reaction of vegetal oils with an alcohol, such as ethanol or methanol; the reaction produces glycerol as an unwanted byproduct which can be separated from biodiesel through a liquid to liquid decantation process. However, some glycerol remains in the biodiesel which lead to the need of further separation steps. Some DESs, based on choline chloride, were proved to be capable of extracting all the free glycerol from the biodiesel. Furthermore, the recovered glycerol, considering its saturated market, could be used as the HBD in the preparation of new DESs [10][11].

2.2.3.3. Electrochemical storage

The DESs utilization in electrochemical storage systems is gaining a growing interest due to the DESs high potentialities in terms of safety, performance and low cost; many scientific papers, on these aspects, are going to be analysed, later in this work.

As regards the closed systems, lithium-ion batteries (LIBs) represent the most used technology. The common LIBs electrolytes are generally based on a mixture of carbonates and an inorganic salt such as $LiPF_6$. Such electrolytes ensured good electrochemical performance to the cell; however, they present, in general, high toxicity and can react with water producing hazardous gas emission; moreover, the cell temperature rise could lead to safety issues such as thermal runaway and dangerous electrode-electrolyte interactions. On the other hand, it was proved that the use of DES based electrolytes in LIBs ensured not only comparable performance to the traditional electrolytes but also an improved thermal stability and lower toxicity.

The partially closed electrochemical systems, such as RFBs and metal air batteries, represent another research field for the development of DES based electrolytes. Regarding the RFBs, in particular, the commercially used technology is usually based on the vanadium chemistry with the use of aqueous electrolytes. The use of DES based electrolytes could improve the RFBs performance especially in terms of energy and power density. Furthermore, DES electrolytes enhance the thermal stability and the solubility of the active ions on the electrolyte. The main issue of such systems is the high viscosity, with the related low ionic conductivity, at room temperature; however, a slight increase in the operating temperature, at around 50 °C, or the use of some additives can mitigate such problem.

3. Literature review

3.1. Applications of DESs in lithium-ion batteries

Nowadays, Li-ion cells represent the state of the art technology in the electrochemical storage landscape. However, even though such cells are usually made of a graphite anode, the cathode can be composed of different lithium based metal oxide (MO_x)-type compounds.

Lithium-ion cells are based on the intercalation of the lithium ions (Li^+) with the two electrodes through the electrolyte, which is usually an inorganic liquid based on a lithium salt. Figure 7 shows the scheme of a lithium ion cell. It is interesting to notice the presence on the anode side of a Solid Electrolyte Interphase (SEI) layer which is formed during the first few charging and discharging cycles; it may slowly grow during the cell operation. However, although such layer is able to protect the graphite anode from the direct exposure to the electrolyte, it could cause a capacity loss and an increase in the cell internal resistance [3].

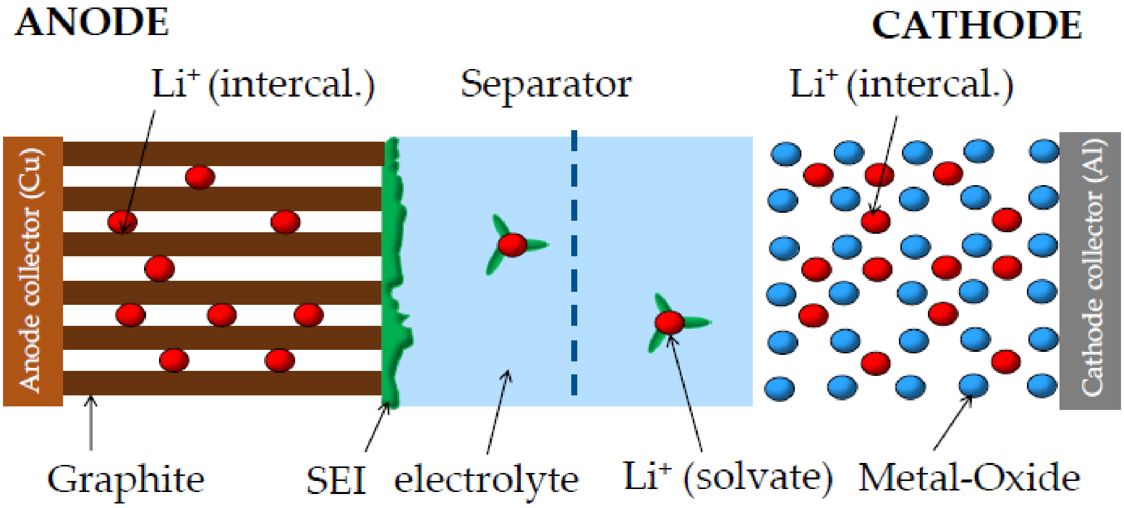

Figure 7. Scheme of a generic lithium ion cell.
Adapted and reprinted with permission from [3].

The most commercially used cathode materials are Nickel-Cobalt-Aluminum-Oxide (NCA), Nickel-Manganese-Cobalt (NMC), Lithium-Iron-Phosphate (LFP) and Lithium-Cobalt-Oxide (LCO). Each cathode material ensures different characteristics to the cell in terms of cycle life, calendar life, nominal voltage, energy and power density, costs and safety. Therefore, the choice of a certain cathode material instead of another one, for a specific application, represents a trade off in which the importance of some of the previous characteristics is elevated because of the application itself. In the automotive sector, for example, NMC cells are generally preferred due to their good energy and power density, while the low cost and the long cycle and calendar life of LFP cells make them interesting for stationary storage applications [3].

The research for this technology is focused on different aspects. The increase of cells safety, in particular against thermal runaway, is one of the most important challenge for the researchers. Furthermore, the cost reduction is another crucial aspect, which is generally faced through the economies of scale but also through the development of cells based on less expensive materials, cobalt utilization trend is a clear example on this behalf; the LCO cathode material was the most commercially used until recently, while nowadays cobalt based cathodes are phasing out due to the cobalt high cost and ethical issues. As regards the energy density, the highest energy density of commercially available cells ,around 250 Wh/kg, is close to the theoretical limit of the current Li-ion technology. Such limitation is primarily imposed by the graphite anode which is the main limiting factor for the Li-ion cells. Therefore, different alternatives such as silicon, lithium metal and lithium titanate oxide (LTO) are currently under development to replace the graphite.

Boisset *et al.* analysed the properties of a DES made of two components, *i.e.* lithium bis[(trifluoromethyl)sulfonyl]imide (LiTFSI) and N-methylacetamide (MAc), in order to understand if it was possible to use it as an electrolyte for lithium-ion batteries and electric double layer capacitors [13]. As regards the application in lithium-ion batteries, the study was focused on coin cells with LFP coated onto aluminium and a Lithium foil as cathode and anode, respectively.

The results of the study were interesting. First of all, the ionic conductivity of the electrolyte was function of the LiTFSI molar concentration at 25 °C. The highest conductivity was equal to 3.05 mS/cm at a LiTFSI concentration of 0.41 M. However, this concentration was too low for any electrochemical application, thus was increased and fixed to 3.2 M (equivalent to a LiTFSI mole fraction of 1/4, or x_{LiTFSI}=0.25) and the new value of ionic conductivity was 1.61 mS/cm. At this concentration, the conductivity was analysed as a function of temperature, from -12 °C to 150 °C, and, as expected, the detected value increased. The ionic conductivity of the electrolyte did not obey to the Arrhenius law. However, it was well fitted to the Vogel-Tamman-Fulcher equation, probably due to the strong interactions between the two components of the DES. The viscosity behaviour of the fluid at $x_{LiTFSI} = 0.25$ was typical of a Newtonian fluid, the shear stress to shear rate ratio was constant, decreasing from 250 mPa (at 2 °C) to 3 mPa (at 80 °C). The Walden's rule, which indicates that the molar conductivity (conductivity per mole of charge) is proportional to the fluidity, the inverse of the viscosity, was used to determine the ionicity of the DES from 2 to 80 °C, *i.e.* the effective fraction of ions available to participate in conduction. Figure 8 shows that the LiTFSI/MAc based DES was constantly above the Walden's plot ideal line, thus it could be considered as a superionic liquid, which means that it could be used as electrolyte for batteries applications. The DES showed good thermal stability with the liquid phase from -72 °C to 240 °C. The vapor pressure, which determines the volatility of the liquid, was equal to 0.2 mbar at 40 °C, a value much higher than the vapor pressure of the generic aprotic ionic liquid, but definitely lower than the value for an organic solvent, about 100 mbar, and even water, 73.8 mbar, at the same temperature, *i.e.* 40 °C. The performance of the DES-based electrolyte was studied in Li-ion cells. The resulting behaviour in terms of specific capacitance, i.e. 150 mAh/g at a 0.26C rate, was comparable to the common values typically observed for standard electrolytes, such as alkyl carbonates with $LiPF_6$. Furthermore, the Coulombic efficiency was around 99% and the cycling performance of the battery showed that the electrolyte did not react with electrode surface, even though only 20 cycles were done at 80 °C, considering that the capacitance remained stable. To sum up, the article by Boisset *et al.* demonstrated that the newly formulated DES was a promising electrolyte, with comparable performance with respect to traditional electrolytes, also showing some relevant characteristics in terms of safety, thermal stability and low cost.

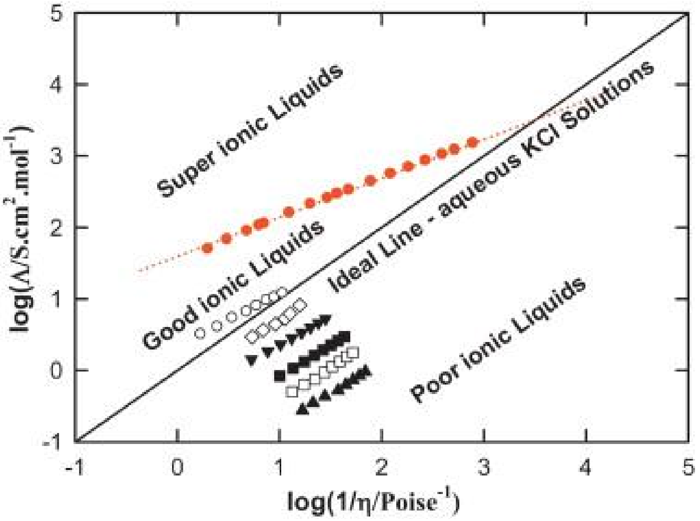

Figure 8: Walden's plot of a LiTSFI/MAc DES at x_{LiTFSI} = 0.25. Adapted and reprinted with permission from [13].

Boisset et al. analysed the properties of three DESs, based on the mixture of N-methylacetamide (MAc) and a lithium salt (LiX, with X = bis[(trifluoromethyl)sulfonyl]imide, TFSI; hexafluorophosphate, PF_6; or nitrate, NO_3), in order to understand if they can be used as the electrolyte in a lithium-ion battery [14]. The lithium salt mole fraction was fixed at 0.2 for the tests. The thermal properties measured from the test were fairly similar; the eutectic temperature of the three DESs were below -50 °C, thus they were liquid at ambient temperature. The ionic conductivity was measured in a range of temperature from 20 to 80 °C. The DESs showed similar performance with ionic conductivity values of 1.2-1.3 mS/cm at 20 °C and 9.2-10.1 mS/cm at 80 °C. Moreover, the results showed that the system behaviour did not follow the Arrhenius law, but the Vogel-Tamman-Fulcher equation. The viscosity, which heavily affects the mass transport phenomena, was similar for the three systems, between 80, for LiTFSI, and 110 mPa s, for $LiNO_3$, at 25 °C, decreasing with the temperature increase.

Cycling tests, at ambient temperature, were performed in order to understand the behaviour of a lithium-ion battery, with LFP positive electrode and aluminium anode, using the MAc/LiTFSI DES as the electrolyte. The results were interesting. First of all, the presence of water inside the cell reduced its specific capacity but did not affect the common voltage plateau trend in the charge and discharge curve. Besides, the capacity of the Two electrodes increased for the first 100 cycles, when the stability was reached, and the Coulombic efficiency was stable at around 99.9%. During these tests, the corrosion of the aluminium electrode, which usually occurs at 3.8 V, was checked; using the MAc-LiTFSI DES, the corrosion observed was negligible which was an important point in favour of the DES. The study also analysed how the temperature affected the cycling stability. The temperature was imposed at 60 °C in the 2.8–4.2 V vs. Li^+/Li voltage window. The measured capacity values of the cell, at 1C, were 160, 150 and 140 mAh/g with $LiNO_3$, LiTFSI and $LiPF_6$, respectively, as shown in the Figure 9(a), comparable with the standard value obtainable with common electrolytes. The Coulombic efficiency was constantly above 99%. Increasing the temperature up to 80 °C (Figure 9(b)), the cell delivered almost its theoretical capacity but the Coulombic efficiency, after 20 cycles, dropped to 90%.One last test was performed using LFP as the cathode, MAc-LiTFSI DES as the electrolyte and lithium titanate (LTO) as the anode; again, the capacity reached the maximum after around 100 cycles, at about 100 mAh/g, which was definitely lower than what it can be achieved with an organic electrolyte or with an ionic liquid, but the efficiency was good and stable during each cycle and - for this reason - the DES can be considered as a possible electrolyte even for this type of cells. To conclude, the study by Boisset *et al.* provided evidence of the fact that this family of DESs can be considered as a good electrolyte, even at high temperature, for lithium-ion batteries in terms of performance, cost, safety and for the environment.

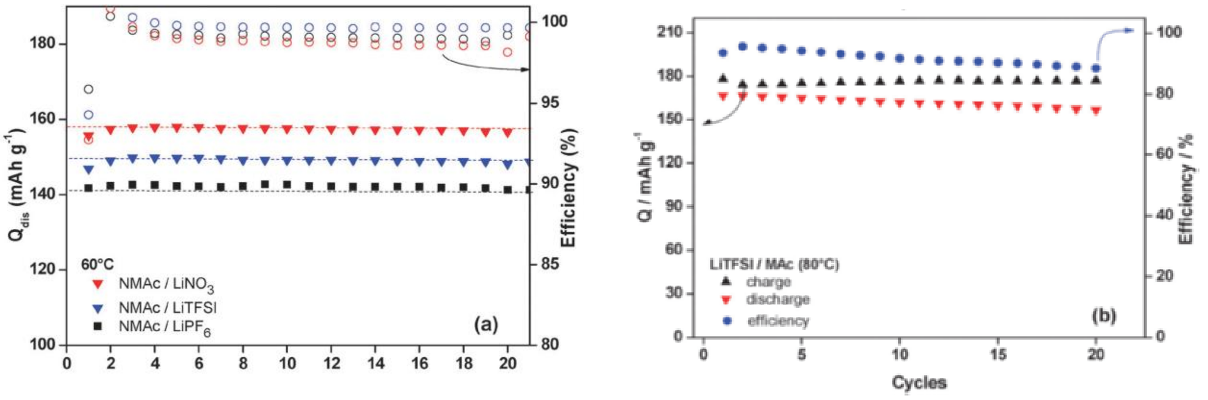

Figure 9. Capacity and Coulombic efficiency cell obtained during tests carried out at a 1 C rate for LFP-based cell containing (a) LiNO$_3$-MAc, LiTSFI-MAc, LiPF$_6$-MAc as electrolyte at 60°. (b) LiTSFI-MAc as electrolyte at 80 °C.
Adapted and reprinted with permission from [14].

The study by Wu *et al.* analysed the chemical synthesis of olivine-type LiMnPO$_4$/C nanorods as cathode material for LIBs, using a DES based on choline chloride and ethylene glycol with a 2:1 molar ratio [15]. In many studies LiMnPO$_4$ (LMP) was investigated due to its promising characteristics for battery applications, such as the optimal redox potential (4.1 V vs Li$^+$/Li) and high energy density, around 20% higher than the commercially available LFP. On the other hand, the LMP chemistry showed some drawbacks such as a slow lithium ions diffusion and a poor electronic conductivity. The formation of a nanostructure and the coating with a conductive layer were some of the possible solutions to overcome those issues. LMP nanorods are conventionally prepared using an EG based solvothermal approach, which ensures an easy morphology control and provides good performance of the final product. However, this method requires high temperature, a massive need of pumping and a long time. A ionothermal method based on ILs was developed by Wu *et al.* in order to avoid the use of autoclaves typical of solvothermal method. Nonetheless, the method did not become the standard due to high cost, toxicity and poor biodegradability of the ILs. To overcome the ILs limitations, *Wu et al.* investigated a new method based on the application of a DES for the preparation of LMP/C nanorods. This method guaranteed many advantages such as low cost, nontoxicity and a good biodegradability.

Figure 10 schematically illustrates the LMP/C nanorods formation process. The raw materials used in solution with the DES were H_3PO_4 (85% P_2O_5), $MnSO_4 \cdot H_2O$ and $LiOH \cdot H_2O$. The LMP were obtained by the precursor suspension heated up at 130 °C, in atmospheric pressure, for 4 hours; then it was centrifuged to collect the LMP powder. The collected LMP powder was then dispersed in a sucrose solution, in order to improve the conductivity and crystallization. The suspension of LMP and sucrose was dried to obtain a mixture powder. Finally, the sucrose/LMP powder was heated up at 300 °C for 1 hour, which created the coating layer, and then the $LiMnPO_4$/C (LMP/C) was obtained after the cooling to ambient temperature. The process above was repeated with only ethylene glycol (EG) as the solvent, instead of chloride and ethylene glycol-based DES, in order to investigate the differences. The LMP/C behaviour, from DES solvent, was tested in various conditions using it in coin cells. Cycling tests were performed at different C-rates, showing consistent results over time, with a decrease in specific discharge capacity from 144 to 106 mAh/g at 0.2C and 5C, respectively. Using a 1C discharge rate the specific capacity value was 127.9 mAh/g in the first cycle, with a Coulombic efficiency of 92%; after 100 cycles the cell preserved the 92.6% of the initial specific capacity, indicating a good cycling stability. The comparison of the LMP/C prepared in EG and in DES was presented in terms of specific capacity. In the first cycle at 1C, the capacity value was 117 mAh/g for the one prepared using the EG, which was lower than the previously indicated 127.9 mAh/g using DES; after 50 cycles the cells preserved the 88% and the 95% of the initial discharge capacity for the one prepared in EG and that in DES, respectively. The results clearly showed the superior performance of the LMP/C prepared in DES. To conclude, the article by Wu *et al.* defined a new method for the synthesis of LMP/C nanorods prepared in a DES which guaranteed not only good and consistent performance of the product but also a significant improvement, with respect to the commonly used methods, in terms of required time, pumping and temperature; moreover, the DES utilization ensured the low cost and nontoxicity of the system.

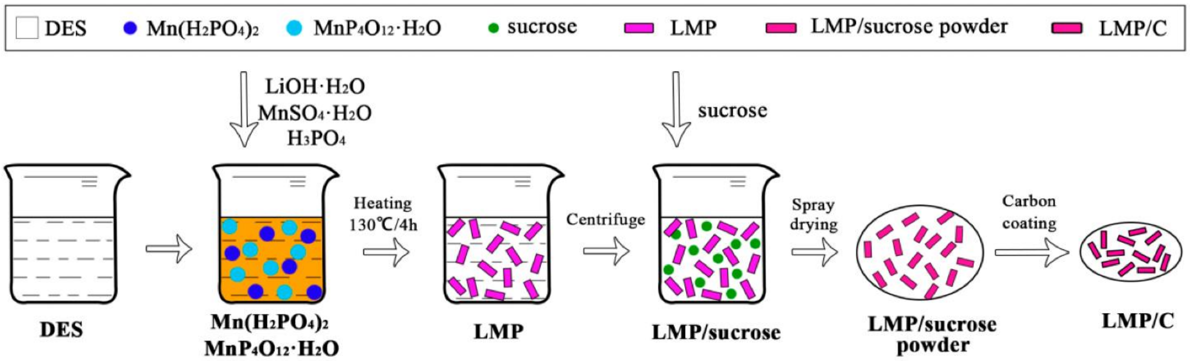

Figure 10. All the steps of the DES-based ionothermal process to obtain the LMP/C nanorods. Firstly, the solution of reactants and DES has to be heated up to 130 °C for 4 hours, then the solution has to be centrifuged to collect the LMP powders which are going to be dispersed in a sucrose solution. The LMP/sucrose suspension is dried to obtain a mixture powder. In the end, the mixture powder is heat up to 300 °C, then sintered at 600 °C and finally cool down to room temperature to obtain the LMP/C nanorods.

Adapted and reprinted with permission from [15].

Albler *et al.* analysed a possible method for the recovery of cobalt and nickel during the battery recycling [16]. The use of a DES based on ChCl and lactic acid was figured out and the main issue was the extraction of the metals from the DES in industrially relevant conditions.

The use of a chloride ionic liquid, Aliquat 336 in this case, for the extraction of cobalt from the DES produced the transformation, over time, of the DES in choline lactate. The changing to lactate of the DES impeded the extraction of cobalt by the Aliquat 336. In order to extent the working life of the DES, it was fundamental to avoid the accumulation of lactate in the DES. It was decided to extract both nickel and cobalt from the DES with a combination of an acidic reagent, DEHPA, and nitrogen donors or a pyridyl pyrazole in solvent 70, a kerosene, and use a further step to separate the two metals. Moreover, it was experienced that the increase of extraction agents concentration from 62.5 to 250 mM enhanced the distribution ratios, which is the measure of the extraction of a species. However, a further increase to a 500 mM concentration did not favourably affect the nickel distribution ratio. Figure 11 shows the distribution ratio trends as a function of the mixture concentration. Furthermore, it was proved that the extraction could be reversed by shaking with aqueous nitric acid. In the end, the previous methods were compared in terms of toxicity. The new method based on organic reagents for the coextraction of cobalt and nickel from the DES was proved to be less harmful, to both environment and human life, than the old method based on a solution of Aliquat 336 in toluene for the extraction of cobalt. To conclude, the study by Albler *et al.* demonstrated the industrial feasibility and the low toxicity of a new method for the coextraction of nickel and cobalt from a liquid made of the shredded battery (black mass) dissolved in a DES, during the battery recycling process.

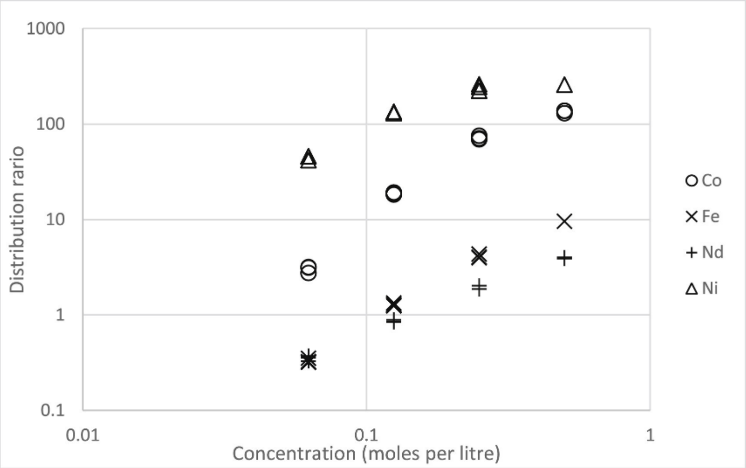

Figure 11. The extraction of cobalt, iron, manganese, neodymium and nickel as function of the concentration of a 1:1 mixture of DEHPA and a pyridyl pyrazole. Adapted and reprinted with permission from [16].

The study by Millia *et al.* analysed two DESs in order to understand their feasibility as electrolytes in LIBs [17]. The first DES was composed of EG and ChCl with a 3:1 molar ratio, while the second DES composed of L-(+)-lactic acid and ChCl with a 2:1 molar ratio. Two lithium salts, LiTSFI and $LiPF_6$, were added to the DESs at a concentration of either 0.5 M or 1.0 M. All the configurations considered were in liquid state in the temperature range -50 °C to 100 °C and did not show any degradation phenomena. The electrolytes based on the EG/ChCl DES showed the best performance in terms of ionic conductivity and viscosity. Moreover, the addition of 0.5 M of $LiPF_6$ increased the conductivity and had the lowest negative effects on the viscosity.

The Walden's plot, which is used to evaluate the ionicity of a solution, indicated as "super ionic" liquid the fluids based on EG/ChCl with the two lithium salts. Therefore, the two liquids based on EG/ChCl and either 0.5 M $LiPF_6$ or 0.5 M LiTSFI were used as the electrolyte in a lithium-ion cell; in preliminary tests, both demonstrated huge potentialities. The stability windows of the EG/ChCl eutectic mixture with the two salts were 3.8 V and 3.5 V using LiTSFI and $LiPF_6$, respectively, as shown in Figure 12. To conclude, the study by Millia *et al.* demonstrated that the EG/ChCl DES with a lithium salt, LiTSFI or $LiPF_6$, could represent an interesting electrolyte for future lithium ion cells because of its good ionic conductivity, at room temperature, and electrochemical stability. Besides, the EG/ChCl DES was inexpensive, nontoxic and eco-friendly.

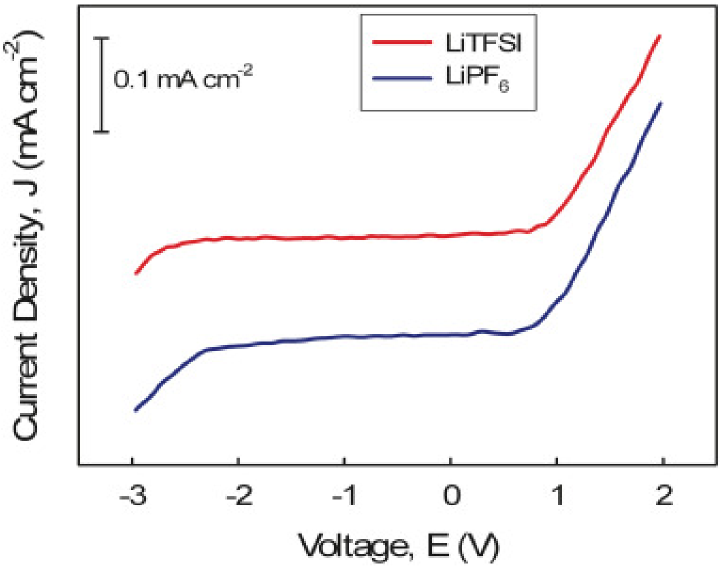

Figure 12. Stability windows of EG/ChCl with LiTFSI and $LiPF_6$ 0.5 M vs. a glassy carbon electrode. Adapted and reprinted with permission from [17].

The commercially used graphite anode material could be considered a limitation for the LIBs energy density because of its low theoretical capacity of 372 mAh/g [18]. The utilization of Sn as anode material could represent an important improvement due to its low cost and the theoretical capacity of 991 mAh/g; however, the tin massive volume change, about 300%, caused by lithium ions during the charge and discharge cycles, compromise the performance of the cell. Therefore, the use of Sn-M (M indicates a metal) intermetallic compounds can mitigate the volume change issue and, especially tin-based ternary alloys, had been highly investigated in literature. The study by Rao *et al.* analysed the preparation of a porous Sn-Ni-Cu alloy film, by the electrodeposition on Ni foam using a DES, to be used as anode material for LIBs. The DES used in the article was based on ChCl and EG with a 1:2 molar ratio (12CE DES).

The cathodic potential influence on the electrodeposition process was demonstrated using three different cathodic potentials: -0.4 V, -0.6 V and -0.8 V, each time at 333 K for 15 min. The surface morphology of the Sn-Ni-Cu alloy film using a cathodic potential of -0.4 V was a uniform structure with letter-shape particles which constructed a porous network. When the cathodic potential was shifted to -0.6 V the surface morphology showed a needle-like grains structure, with an increasing dimension of the grain. Lastly, when the cathodic potential was shifted to -0.8 V the Ni foam substrate was covered by a hollow structure made by dendritic nodules. The three Sn-Ni-Cu alloy films were then assembled into coin cells and tested in order to evaluate their electrochemical performance. The tests were performed with a current density of 100 mA/cm^2, between 0.01 and 2.0 V (vs. Li/Li$^+$). The initial charge and discharge curves were similar for the three cells as well as the initial capacity and the low Coulombic efficiency, approximately 66%. However, after 50 cycles the cycling performance of the three cells were different, as shown in Figure 13. Only the cell, which used the Sn-Ni-Cu alloy films obtained at −0.4 V showed good cycling performance in terms of capacity retention after 50 cycles, with a specific discharge capacity of 614 mAh/g at the second cycle and 533 mAh/g at the 50th cycle; the other cells showed a consistent drop after around 25 cycles. On the other hand, the Coulombic efficiency of the three cells were fairly stable, showing values, for each cell, constantly above 90%. After 50 cycles the morphology of the three Sn-Ni-Cu alloy films showed significant differences compared to their initial conditions. The structure obtained at −0.4 V was damaged; however, it maintained its uniform structure coherently with the cycling performance. The other structures were cracked (as the one obtained at −0.6 V) or pulverised (as the one obtained at −0.8 V) which indicated the effects of the huge volume expansion during the charging and discharging cycles. To summarize, the article by Rao *et al.* proved that the electrodeposition of Sn-Ni-Cu alloy on nickel foam in the inexpensive and environmentally friendly 12CE DES was feasible; moreover, the electrochemical performance of the Sn-Ni-Cu alloy film electrodeposited at −0.4 V were promising for the application as anode material in LIBs.

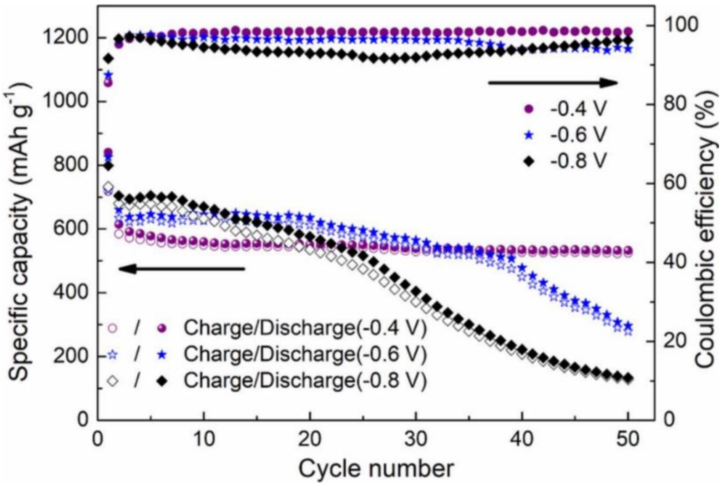

Figure 13. Cycling performance of the Sn-Ni-Cu alloy films obtained using different cathodic potentials at a current density of 100 mA/g.
Adapted and reprinted with permission from [18].

The study by Tran *et al.* analysed a DES-based method for the recycling of LIBs cathode [19]. The development of an efficient and eco-friendly method for the recovery of the precious materials from LIBs is going to become more and more important considering the growing utilization of this storage technology in many applications such as automotive and electronics. The researchers developed a LIBs cathode recycling method based on a ChCl and EG DES which was capable of extracting precious metals from LIBs with different cathode chemistry such as LCO and NCM.

The experiments were usually performed adding 0.1 g of cathode powder to 5 g of DES. Many DES and LCO samples were prepared and heated at different temperatures for 24 h, in order to understand the effect of temperature on the leaching efficiency. As shown in Figure 14, it was clear that, below 120 °C, the concentration of Co in the DES was almost negligible; from 135 °C, instead, the concentration and the leaching efficiency remarkably increased. The highest Co leaching efficiency of 94.1% was reached at 220 °C, the highest temperature tested. Lowering the amount of LCO powder in DES, from 100 mg to 13 mg, it was measured a leaching efficiency of 99.3% at 180 °C. Subsequently, the effect of time on cobalt extraction was investigated at three different temperatures for 24, 48 and 72 h. It was observed that the effect of time in the Co concentration was negligible at 25 °C; at 50 °C the Co concentration doubled from 24 to 48 h and at 105 °C the increase was one order of magnitude from 24 to 72 h. Other experiments were performed in order to recover the metals from the DES as useful products. At first, by precipitating the dissolved ions and calcining the recovered compounds, it was measured that around 74% of cobalt could be recovered from the DES in the form of Co_3O_4. Subsequently, electrodeposition was tested as an alternative method; in this case, it was observed the electrodeposition of $Co(OH)_2$ onto the stainless steel electrode. Moreover, the residual DES could be reused, with the same efficacy, to leach metals from the cathode powder. To sum up, the article by Tran *et al.* demonstrated that, considering the expected growth for the demand of LIBs and, consequently, the importance of their recycling, the use of DESs-based LIBs recycling methods could be considered a green alternative to the conventional methods because of the DESs low toxicity, cost and eco-friendly nature.

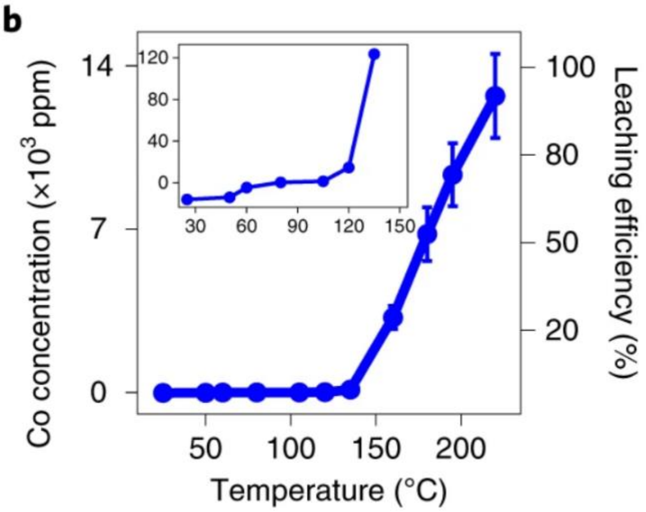

Figure 14. Cobalt concentration (left axis) and leaching efficiency (right axis) as a function of temperature using the DES-based process. The inset is a magnifying view of the Co concentration from 25 to 135 °C.
Adapted and reprinted with permission from [19].

The use of a new electrolyte, based on the mixture of a DES and water, to be used in LIBs, was analysed in the study by Jiang *et al.* [20]. The DES investigated in the article was composed of methylsulfonylmethane (MSM) and $LiClO_4$ with molar ratio of 1.8:1; however, the DES showed a relatively high melting point of 49 °C. Water was added to the mixture in order to decrease the melting point and enhance the physical and chemical characteristics of the DES, in particular Li^+ diffusion coefficient, ionic conductivity and viscosity. The fluid was defined DES-1 and its final molar ratio was 1.8:1:1 (MSM:$LiCLO_4$:H_2O). At room temperature, the DES-1 electrolyte showed an ionic conductivity of 3.71 mS/cm, a Li^+ diffusion coefficient of 2.27×10^{-11} m^2/S and a viscosity of 148 mPas; moreover, the DES-1 melting point decreased to -48 °C, which was important in order to be considered a room-temperature liquid.

Subsequently, the electrochemical performance of the DES-1 was investigated. The electrochemical stability window was fairly large, around 3.3 V, and, for this reason, the DES-1 was tested in a lithium-ion cell. Lithium manganese oxide (LMO) and LTO were used as positive and negative electrodes of a cell, respectively, and DES-1 was used as the electrolyte. At first, the cycling performance of the two electrodes was analysed separately, through a galvanostatic technique. The LMO cathode was tested at 4.5C, showing a high Coulombic efficiency of around 99.6%, an initial capacity of approximately 45 mAh/g and a capacity retention of 91 % after 1000 cycles (Figure 15, top). The anode LTO was tested at 20C, showing a capacity retention after 1000 cycles of 85.2% and high Coulombic efficiency of 99.5% (Figure 15, middle). Considering the promising result obtained from the two separate electrodes, a full cell LTO/DES-1/LMO was assembled and tested. The cell showed a voltage output of 2.4 V, a high good density above 160 Wh/kg and a Coulombic efficiency of 92.4% at 1.5C. Subsequently, the cycling behaviour of the cell was analysed at 4.5C for 1000 cycles showing a Coulombic efficiency of approximately 99% and a capacity retention of 72.2% (Figure 15, bottom). To summarize, the low cost and environmentally friendly water-in-DES based electrolyte, presented in the study by Jiang *et al.*, showed great potentialities in LIBs application and could represent an important step in the development of a new family of green and inexpensive electrolytes.

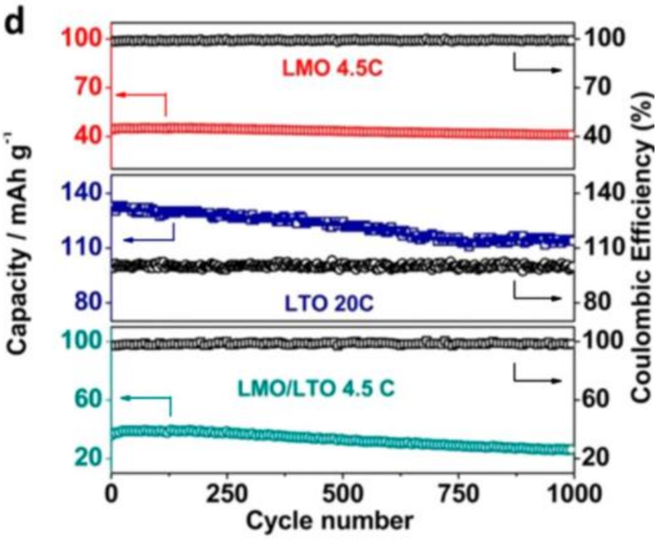

Figure 15. Cycling performance of LMO positive electrode at 4.5C, LTO negative electrode at 20C, and LMO/DES-1/LTO cell at 4.5C
Adapted and reprinted with permission from [20].

The study by Wang *et al.* analysed a low cost and environment friendly method based on a DES for the separation of the cathode materials and the aluminum foil during the recycling process of LIBs [21]. An important purpose for the LIBs recycling was the recovery of the precious metals in the positive electrode. The separation of Al foil and cathode materials was a crucial aspect to obtain an efficient recycling process. In order to obtain the separation, the organic binder polyvinylidene fluoride (PVDF), which represents the 3-4 wt.% of the cathode materials, had to be broken down; however, this was not a simple task due to the high stability of PVDF and its strong bonding capacity.

The method presented in the article was based on the use of an inexpensive DES, which was composed of ChCl and glycerol. In order to maximize the peeling percentage, which is the ratio between the mass of cathode materials recovered and the theoretical cathode mass, three variables were adjusted: operational temperature, heating time and ChCl/glycerol molar ratio. The obtainable theoretical highest peeling percentage was 99.88% with 190 °C of operating temperature, a 2.33:1 molar ratio and 15 min of heating time. In the real experiment, the molar ratio was imposed to 2.3:1 and the other two conditions have been set as the theoretical case; the measured peeling efficiency was 99.86%, close to the theoretical value. Figure 16 shows the main steps of the process. It was observed that the surface morphology of the cathode was damaged after the process; however, its crystal structure was not wrecked. On the other hand, the surface morphology of the separated Al foil was smooth, without the residual presence of cathode materials. Furthermore, the DES physical and chemical characteristics remained stable after the process, which meant it could be recycled. In the end, a short comparison between the considered DES and the [BMIm]BF_4 ionic liquid was presented. The operating temperature and heating time was similar for the two separation processes and both solvents could be reused; however, considering the reagents needed to treat 1 kg of LIBs, the reagent cost for the ionic liquid was 402.30 $, while the DES reagent cost was only 6.80 $; in addition, the DES components, choline chloride and glycerol, were already commercially used and non-toxic. To conclude, the article by Wang *et al.* demonstrated that an inexpensive, non-toxic and eco-friendly DES could be used in a highly effective method to separate the Al foil from the cathode materials during the LIBs recycling process.

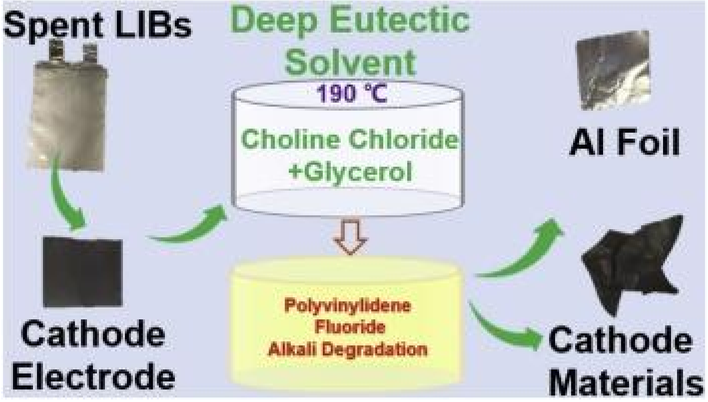

Figure 16. Schematic representation of the aluminium foil and cathode material DES-based separation process.
Adapted and reprinted with permission from [21].

The article by Wang *et al.* analysed the preparation of tin negative electrodes for LIBs by electrodeposition onto nickel foil using a DES at different temperatures [22]. In general, the Sn electrodeposition was obtained using aqueous electrolytes; however, these methods presented some issues, such as hydrogen evolution reaction and equipment corrosion. In order to overcome such common issues, DES-based electrolytes have been considered a feasible alternative due to their low cost and toxicity.

The DES developed for the study was composed of ChCl and EG with a 1:2 molar ratio, then 50 mM $SnCl_2$ was added to the DES as the active material for the electrolyte. All the electrodeposition tests were performed varying the temperature from 313 K to 353 K with a 10 K step for each test; such temperature variation highly influenced the behaviour of the electrodeposition process. Elevating the temperature, from 313 to 353 K led to an increase of Sn(II) diffusivity, from 0.893 $\times10^{-7}$ to 3.189 $\times10^{-7}$ cm^2/s. Moreover, the cell voltage declined at the beginning of the process because the temperature rise and, above 333 K, it suddenly dropped, after around 0.35 h, as shown in Figure 17(a). The variation of temperature halved the viscosity and increased the conductivity. Such changes led to an increase from 13.7% to 87.78% of the current efficiency of the electrodeposited Sn, which is the ratio of the actual mass of the cathode product and the theoretical one, while the energy consumption dropped from 7089.07 to 289.02 kWh/t, as shown in Figure 17(b). Subsequently, the powders morphology was investigated. When the temperature was 313 or 323 K, the Sn powders shape was dendritic and homogeneous; at 333 K, the dendritic shape was gradually substituted with a tower cone shape; at 353 K, the dominant shapes were tower cone and pagoda. In general, raising the temperature increased the dimension of the shapes. In the end, the previously described Sn electrodeposits at different temperatures were assembled in a half cell with $LiPf_6$-based electrolyte to test their electrochemical performance. The specific discharge capacities, using a current density of 0.1

A/g in the voltage range 0.01 and 2.0 V (vs. Li/Li$^+$), were between 1050 mAh/g, with the 313 K deposited electrode, and 340 mAh/g, with the 353 K deposited electrode. The Coulombic efficiency was more stable, between 70 and 83.6%; however, the highest value was associated with the electrode prepared at 313 K. Therefore, the cell with the electrode prepared at 313 K presented the best performance due to its uniform morphology. To summarize, the ChCl:EG DES proved to be a good electrolyte for the tin electrodeposition because of its low cost and good physicochemical characteristics. Moreover, it was determined that the low temperature Sn electrodeposition increased the electrode performance.

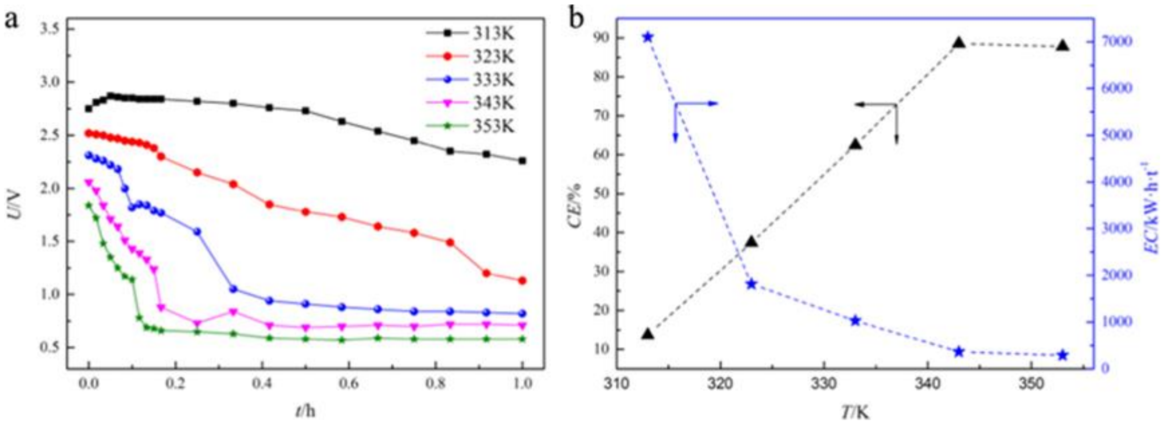

Figure 17. (a) Voltage trend as a function of temperature and time; (b) Current efficiency and energy consumption of the electrodeposited in DES Sn powders as a function of temperature. Adapted and reprinted with permission from [22].

The study by Roldán-Ruiz *et al.* developed a method based on a DES and mild conditions to recover cobalt and lithium from LIBs cathode [23]. The DES used in the article was composed of p-toluenesulfonic acid monohydrate and choline chloride (PTSA:H_2O:ChCl) with a 1:1:1 molar ratio; in addition, the DES was also prepared with stoichiometric dilutions of water producing 1:2:1 and 1:3:1 molar ratio.

The Li-ion cells were manually dismantled to separate the cathode from the other components; subsequently, the cathode was immersed and stirred in a solution of NaOH 5 wt% to separate the aluminum foil and the active materials, in this case LCO with Li and Co content of around 5 and 60 wt%, respectively. In the end, the cathode materials powder was dissolved into the DES. Figure 18 shows the colour of the $LiCoO_2$-DES solution. In order to maximize the leaching efficiency under mild conditions, the DES capabilities were tested adjusting the operating temperature, time and amount of solvent. The best result was obtained with a DES molar ratio of 1:3:1 (PTSA:H2O:ChCl) at 90 °C for 15 min and a 0.05 mass of solute and mass of hydrogen bond donor ratio. Subsequently, the cobalt recovery from the DES was investigated using either Na_2CO_3 or $(NH_4)_2CO_3$ to precipitate a salt that, after a calcination process, was transformed into Co_3O_4, which could be used for the preparation of new Lithium-ion cells. The Co recovery efficiency for the entire process, from the dismantling of the cell to the production of Co_3O_4, was 94%. To sum up, the article by Roldán-Ruiz *et al.* demonstrated the feasibility of a cobalt and lithium recovery method based on a low cost and environmentally friendly DES;

moreover, the considered method was remarkably efficient at low temperature, with a short dissolution time and without the need of additional solvent.

Figure 18. Solution obtained after dissolving $LiCoO_2$ in the PTSA:H2O:ChCl DES Adapted and reprinted with permission from [23].

Peeters *et al.* investigated a solvometallurgical process for the cobalt recovery from LCO, a common cathode material commercially used in LIBs, using a DES as a green, safe and inexpensive solvent [24]. Solvometallurgy processes are based on non-aqueous solvent; the DES used in the study was composed of choline chloride and citric acid with a 2:1 molar ratio and was combined with a water addition of 35 wt% to reduce the viscosity. It was ensured that the added water did not affect the typical DES behaviour; therefore, the obtained solution was still considered as non-aqueous. Interestingly, aluminum and copper have been used in combination as a reducing agent of Co(III), during the leaching process, in order to avoid the use of additional reducing agents.

The leaching mechanism on LCO was tested varying temperature, time and solid to liquid (S:L) ratio. The authors of the study chose an operating time of 1 h at 40 °C and a S:L ratio of 20 g/L; such conditions leached 38% Al(III), 98% Co(II), 94% Cu(I/II) and 93% Li(I). The effect of Al and Cu on the leaching system was investigated. The tests showed that copper was an effective reducing agent for Co(III), while aluminium was not; however, aluminium reduced Cu(I) and Cu(II), which were formed after the reduction of Co(III), to copper metal, making it available again for the reduction of Co(III). Subsequently, a comparison between the DES and the conventionally used hydrochloric acid (HCl) leaching was performed. The results indicated that the DES leaching was enabled by the cobalt(III)/copper redox reactions, while in the HCl leaching the oxidation of chloride anions to chlorine gas reduced Co(III) to Co(II). In general, HCl leaching was better than the DES-based one in terms of velocity, energy consumption and higher possible S:L ratios, but was less selective and more hazardous because of the chlorine gas formation. In the end, the extraction of copper and cobalt from the DES solution was carried out in different steps. At first, Cu(I/II) was quantitatively extracted with the LIX 984 (60 vol%) extracting agent; moreover, such step showed a 5% co-extraction for each of the other three metals. The second step was the extraction of cobalt, which was performed using the A336 extracting agent. 85% of cobalt was extracted from the solution without the co-extractions of other metals. Other steps were required to extract the remaining metals but the authors decided not to go further, leaving approximately the 95% of lithium and aluminium in the DES. The oxalic acid was used to precipitate both copper and cobalt from their loaded organic phases. The resulting recovery yield values were 81% and 94% for cobalt and copper, respectively. Figure 19 shows the scheme of the entire process. To conclude, the report by Peeters *et al.* demonstrated the efficacy of the choline chloride-citric acid DES-based process in the cobalt leaching from LCO with the presence of copper and aluminium as reducing agents.

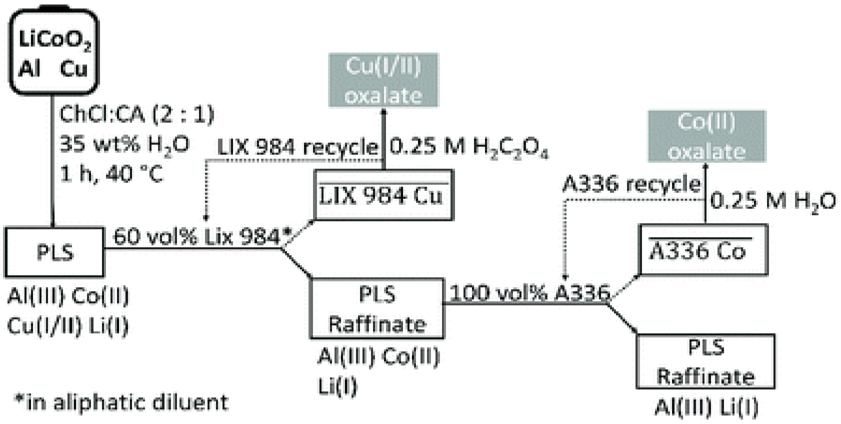

Figure 19. Schematic description of the DES-based solvometallurgical recovery process. Firstly, the LCO with Al and Cu are put in solution with the DES. Subsequently, Cu(I/II) was extracted from the solution, using the LIX 984 extracting agent, and then the A336 extracting agent is used to extract Co(II).
Adapted and reprinted with permission from [24].

Wang *et al.* investigated the effectiveness of a DES based method to recover precious metals from the LIBs cathode material [25]. Pyrometallurgy and hydrometallurgy were the most common methods for the recovery of metals from spent LIBs. However, such methods required high temperature (pyrometallurgy) or harmful chemicals (hydrometallurgy). DES-based methods were considered as an alternative green solution because of the mild operating conditions and the DESs low toxicity, cost and safety. The DES investigated was composed of choline chloride and urea (ChCl:urea) with a 1:2 molar ratio. Furthermore, the ChCl:urea DES was compared with a ChCl:EG DES developed with the same purpose in a previous study.

Cyclic voltammetry tests were performed by the authors in order to determine the reduction potential of the DESs, knowing that a more negative reduction potential accelerates the extraction process. The CV experiments were performed between 140 and 180 °C, showing that the reduction current peak appeared from 0.40 to 0.50 V (vs. Ag) for the ChCl:EG DES, while it appeared between −0.45 and −0.35 V (vs. Ag) for the ChCl:urea DES. Therefore, the reduction potential of the ChCl:urea DES was more negative than that of the ChCl:EG DES, which meant that the metals extraction could be improved using the ChCl:urea DES. Subsequently, the ChCl:urea DES metal extraction performance was investigated. 0.1 g of LCO powders, a common LIBs cathode material, and 5 g of ChCl:urea DES were mixed allowing to react in a range temperature between 140 and 180 °C, in a time range between 1 h and 24 h, as shown in Figure 20. The results indicated that, after 24 h at 140 °C, the extracted Li and Co were just around 10%; the extraction percentages surged to 97.9% for cobalt and 94.7% for lithium, which was equivalent to a concentration of around 14 g/L for cobalt and 1.6 g/L for lithium, after 12 h when the temperature was increased to 180 °C. For comparison, the cobalt extraction using the ChCl:EG DES reached 94.1% at a higher temperature, 220 °C, for 24 h. In the end, the leached cobalt in DES was recovered as spinel cobalt oxide (Co_3O_4) through a dilution–precipitation–calcination process. Ethanol was used for the dilution. For the precipitation, three different precipitants were investigated, *i.e.* $H_2C_2O_4$, NaOH and Na_2CO_3. However, according to the X-ray analysis results on the calcinated powders, the preferred precipitants were $H_2C_2O_4$ and NaOH. To conclude, the study by Wang *et al.* demonstrated that, for the recovery of precious materials from spent LIBs, a DES with a more negative reduction potential could be used efficiently at a lower operating temperature and with a shorter reaction time.

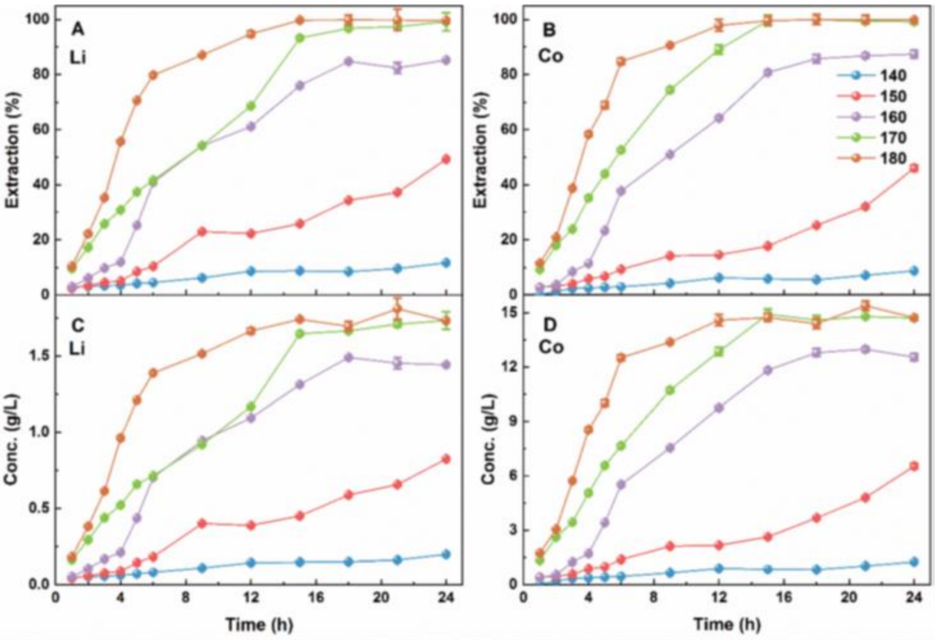

Figure 20. Extraction of Co and Li as a function of temperature and time for the DES-based process. Extraction percentage for Li (a) and Co (b); extraction concentration in g/L for Li (c) and Co (d). Adapted and reprinted with permission from [25].

Chen *et al.* analysed the dissolution process of LCO, a common cathode material commercially used in LIBs, in a DES under mild conditions [26]. The DES developed for the study was composed of polyethylene glycol (PEG200) and thiourea with a 2:1 molar ratio. Moreover, the PEG200/thiourea DES was inexpensive, environmentally friendly and presented a low viscosity at mild temperatures.

The dissolution of 0.1 g of LCO in 5 g of DES was investigated as a function of time and temperature. In general, it was observed that the colour of the solution changed from transparent to dark blue/black when the LCO dissolution increased. After the visible colour change of the solution, the actual concentration of cobalt and $LiCoO_2$ was evaluated as a function of time, at first, considering a fixed temperature of 80 °C. The Co concentration increased remarkably in 24 h, starting at 1.05 ppm after 10 min, 774.60 ppm after 6 h, 1299.25 ppm after 12 h and reached 2121.44 ppm after 24 h, as shown in Figure 21(c). Subsequently, the effect of temperature was investigated, as shown in Figure 21(d). Below 60 °C, the Co concentration was very low even after 24 h because of the DES viscosity which was very high at low temperature but considerably dropped at higher temperature, i.e. 177.2 cP at 25 °C and 13.1 cP at 60 °C; therefore, a minimum operating temperature of 80 °C was required to obtain a decent Co concentration in DES. Furthermore, raising the temperature to 120 and 160 °C for 24 h enhanced the Co concentration to 3480.02 and 8440.14 ppm, respectively. The Co leaching efficiency, which is the ratio between the mass dissolved and the initial mass, was evaluated at 80, 120 and 160 °C for 24 h. The obtained results were 15.1%, 24.8%, and 60.2% at 80, 120 and 160 °C, respectively. A comparison for the Co concentration after 24 h at 80 °C was carried out among the PEG200/thiourea DES and other two DESs, p-toluenesulfonic acid/water/ChCl (1:1:1) and ChCl/EG (1:2). The results indicated that the Co concentration in PEG/thiourea DES was almost 2 times higher than the p-toluenesulfonic acid/water/ChCl DES and around 35 times higher than the ChCl/EG DES. To summarize, the report by Chen *et al.* demonstrated the efficacy of a cheap and green DES developed for the dissolution of LCO under mild conditions. The considered method could represent an interesting alternative to the industrially used methods based on strong acids or high temperature.

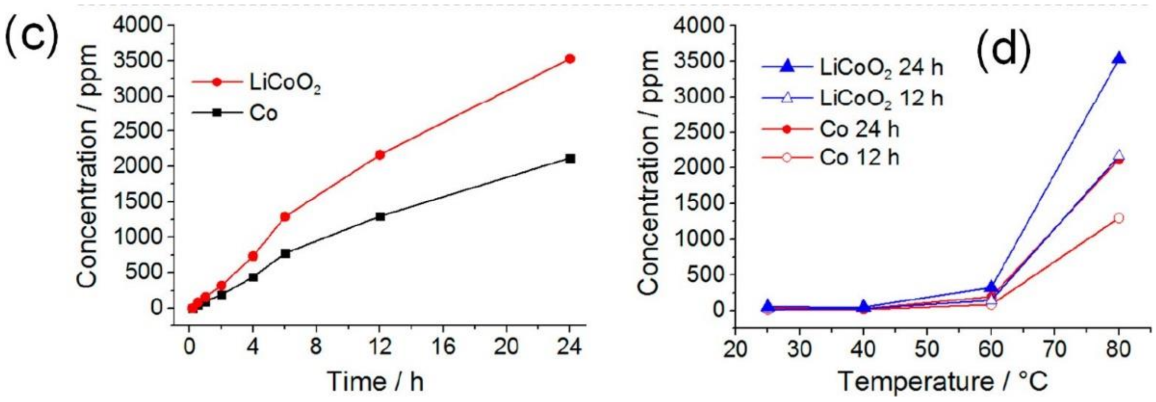

Figure 21. (c) Effect of time on Co and LCO concentration and (d) effect of temperature on Co and LCO concentration using the DES-based method.
Adapted and reprinted with permission from [26].

Dinh *et al.* investigated the performance of a new DES in order to use it as electrolyte in LIBs [27]. In scientific literature, DES-based electrolytes have been increasingly considered interesting due to their low cost, non-flammability, eco-friendliness and non-toxic behaviour. The DES developed by the authors was composed of LiTFSI and 2,2,2-trifluoroacetamide (TFA) with a 1:4 (LiTFSI:TFA) molar ratio, which showed the best ionic conductivity and viscosity among the tested molar ratios. Furthermore, ethylene carbonate (EC) was added, in specific amounts, to the selected DES in order to reduce the viscosity. The two electrolytes tested were a mixture of 1:4 DES with EC 10 wt%, which showed an ionic conductivity of 1.86 mS/cm and a viscosity of 30.5 cP at 30 °C, and 1:4 DES with EC 20 wt%, which showed an ionic conductivity of 2.59 mS/cm and a viscosity of 28.6 cP at 30 °C. Both the electrolytes presented a relatively high electrochemical stability, around 5.0 V vs. Li$^+$/Li, and a good thermal stability up to 150 °C.

Subsequently, the electrolytes electrochemical properties were tested in a Li||LMO half-cell in the potential range 3.2 and 4.5 V (vs. Li^+/Li). The electrolyte with 10 wt% EC showed the best electrochemical performance with an initial discharge specific capacity of 102 mAh/g, around 70% of the theoretical capacity, and a Coulombic efficiency of 70% at 0.1C and room temperature. The specific capacity declined to around 80 mAh/g after 20 cycles, while the Coulombic efficiency initially increased, reaching 84% after 12 cycles, but then dropped below 60% after 20 cycles, as shown in Figure 22. As regards the electrolyte with 20 wt% EC, the initial discharge specific capacity was 50 mAh/g, only 42% of the theoretical value, and the Coulombic efficiency was just below 80% at 0.1C and room temperature. After 20 cycles, the specific capacity almost halved to around 30 mAh/g, while the Coulombic efficiency slightly increased overcoming the 80%. To conclude, the article by Dinh *et al.* demonstrated that the developed DES-based electrolytes were not a feasible alternative to the commercially available electrolytes, due to their higher viscosity which led to a lower ionic conductivity. Therefore, different diluents should be evaluated in order to reduce the viscosity of the electrolyte.

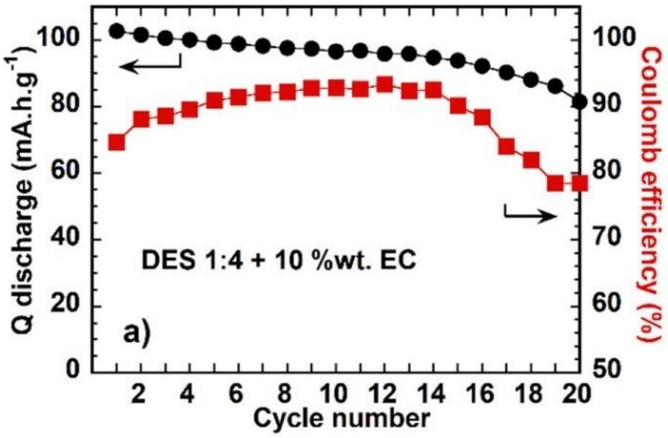

Figure 22. Cycling performance at 0.1C of the Li||LMO cell using the DES 1:4 + 10 %wt EC electrolyte.
Adapted and reprinted with permission from [27].

The study by Schiavi *et al.* developed a method for the recovery of the precious metals, especially cobalt, from the cathode materials of LIBs using a DES as a green, non-toxic and inexpensive solvent [28]. The authors investigated a solvometallurgical method based on a non-aqueous electrolyte and mild conditions. Solvometallurgical methods could be consider as a green alternative to the more common pyrometallurgical and hydrometallurgical methods, which require high temperature or strong acids. The solvent used for the metals recovery was a DES composed of ChCl and EG with a 1:2 molar ratio. The cathode powders were composed of cobalt, which showed the largest concentration, nickel, manganese and lithium; furthermore, copper, aluminium and iron were found in the electrode powders as impurities deriving from the cell current collectors and the steel case.

The metals extraction was investigated at different operating temperatures, from 90 °C to 180 °C, and with reaction times up to 72 h. At 90 °C, the copper extraction yield reached its maximum, around 85%, after 24 h and remained stable in the period 24-72 h, while the extraction of other metals was negligible, except for Li and Mn extraction values, which were around 16% and 9%, respectively, after 72 h. The temperature increase to 180 °C led to an extraction yield, after 24 h, of about 90% and of only 11% for cobalt and nickel, respectively, while the other metals extraction yields were around 60% and 70%, except for the copper extraction which was around 90%. Therefore, the authors decided to use, as one of the initial steps, the selective removal of copper at 90 °C for 24 h; subsequently, the solution was heated up at 180 °C for 20 h, in order to obtain the selective cobalt and manganese leaching. In the end, the extraction of Mn and Co metals from the DES was performed using the D2EHPA solvent, with an optimized concentration. The recovered cobalt, in particular, was obtained in the oxalate form and was, then, used to synthetize LCO, which is a common cathode material used in LIBs. Each step of the process is shown in Figure 23. After the metals extraction, the performance of the residual DES was investigated in order to verify its reusability. The results indicated that the residual DES was comparable to the fresh DES in terms of leaching capacity; interestingly, the Ni extraction yield, at 180 °C for 24 h, increased from 10%, using the fresh DES, to around 40% with the reused DES. In the end, the electrochemical performance of the LCO cathode, produced from the recovered cobalt, was analysed in a half-cell using lithium metal as the anode. The galvanostatic cycling tests, performed at 1C, indicated an initial specific discharge capacity of around 150 mAh/g, while the capacity retention after 100 cycles was around 83%. The Coulombic efficiency was stable at 99% after the first 10 cycles. Therefore, the results demonstrated that the recovered cobalt was equivalent to the virgin metal. To sum up, the article by Schiavi *et al.* proved the feasibility of a DES-based solvometallurgical method for the recovery of the precious materials from the cathode of spent LIBs as a green alternative to the industrially used pyro and hydrometallurgical methods.

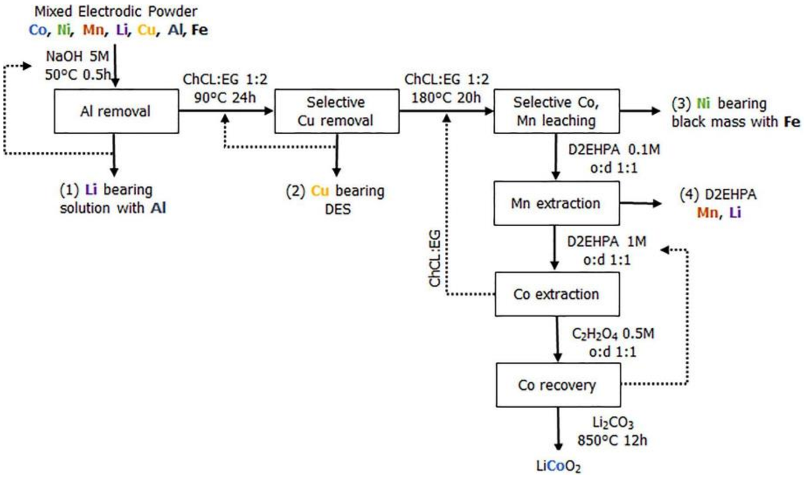

Figure 23. Scheme of the DES-based solvometallurgical process adopted in the report. The first step is the removal of Al impurities from the electrodes powder mixture with a NaOH solution. Subsequently, using the DES solvent, the selective removal of Cu is performed before the selective leaching of Co and Mn. In the end, Mn and Co are separately extracted using the D2EHPA extractant Adapted and reprinted with permission from [28].

The study by Xu *et al.* developed a microwave-assisted method, based on a DES and mild conditions, for the recovery of precious materials from the cathode of spent LIBs [29]. The leaching experiments were performed using commercial LIBs with LMO cathode. First of all, the LMO material was separated from the aluminium current collector before the recovery treatment. Subsequently, the LMO powders were mixed with a DES; the produced mixture was heated up using a microwave oven. In the end, the treated mixture was separated from the residues of LMO, which were not extracted by the DES, through a needle filter. Figure 24 shows a schematic representation of the whole recovery process. The method was based on four parameters: type of DES, temperature, liquid to solid (L/S) ratio and time. In particular, the authors considered three DESs: ChCl and urea (ChCl-U) with a 1:2 molar ratio, choline chloride and oxalic acid (ChCl-OA) with a 1:1 molar ratio, choline chloride and ethylene glycol (ChCl-EG) with a 1:2 molar ratio.

A series of orthogonal experiments were performed in order to understand the importance of each parameters on the leaching rate. The results indicated that the DES type was the most important parameter, followed by the L/S ratio, temperature and time, in this order. However, these experiments did not provide great results in terms of leaching rate. Subsequently, a series of single-factor experiments were performed in order to optimize the four conditions increasing the process leaching performance. The results indicated that, after the optimization of the four parameters, the leaching rate of both lithium and manganese reached 96%. Such optimal conditions were the use of ChCl–OA DES, a L/S ratio of 6 g/0.1 g, at 75 °C for 15 min. To summarize, the article by Xu *et al.* demonstrated that the microwave-assisted DES-based method for the recovery of precious metals from the cathode of spent LIBs was a promising alternative not only to the industrially used pyro and hydrometallurgical methods, but also to the green DES-based methods which, using the traditional heating processes, required higher working temperatures and prolonged operational times, in the order of hours or even days, to obtain the same results.

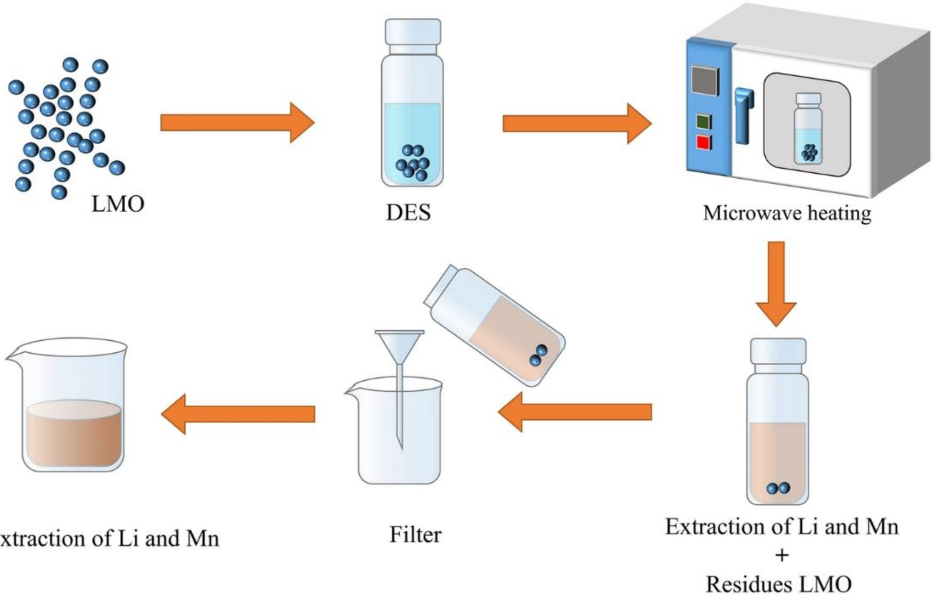

Figure 24. Schematic representation of the microwave-assisted DES-based process. The LMO powders are put in solution with one of the DESs and then heated up using a microwave oven. Subsequently, the solution is separated from the LMO residues, not dissolved in the DES, through a needle filter.
Adapted and reprinted with permission from [29].

3.2. Applications of DESs in lithium-metal batteries

Lithium metal cells are considered a promising candidate for the next generation of rechargeable batteries because of the huge potentialities especially in terms of energy density.

Lithium metal is a great anode material for rechargeable cells because of its high theoretical specific capacity, around 3860 mAh/g, which could lead to very high specific energy density for a complete cell, above 400 Wh/kg is already feasible but the potential is up to 1000 Wh/kg. Obviously, the specific energy density depends on the selected cell technology. The lithium metal anode, in fact, could be used in different systems such as the previously mentioned Li-ion, replacing the graphite electrode, lithium sulphur and lithium air [30].

However, lithium metal anode is not ready for the commercialization due to presence of severe and unsolved issues. The Li dendrites formation is the most important challenges because it is critical for both the performance and the safety of the cell. The lithium deposition and dissolution occurring during cycling leads to a large formation of Li dendrites on the anode surface. Li dendrites cause the reduction of the cell Coulombic efficiency; furthermore, the continuous growth of dendrites could pierce the separator and reach the cathode which would generate a short circuit, inducing the fire or even the explosion of the cell. The "dead lithium", which indicates the separation of lithium particles from the anode surface caused by the repeated electrode volume change, represents another important issue. The formation of "dead Li" causes the loss of the anode active material reducing the cell capacity. Another concern is the high reactivity between lithium and air, containing oxygen and humidity, which could be problematic not only for the lithium air cells but also for other technologies in which, in case of accident, the anode could be directly exposed to the ambient air.

The study by Jaumaux *et al.* analysed the performance of a lithium-metal cell using a new self-healing polymer electrolyte based on a DES [31]. The lithium-metal anode could represent a huge step forward to increase the energy density of the commercially available LIBs; however, Li-metal application was far from the market due to numerous issues associated to the technology, such as the use of flammable and toxic electrolytes and the formation of dendrites, which not only reduced the cell performance and cycle life but could also cause short circuits. DES-based electrolytes were able to solve just few problems, such as the toxicity and the flammability of the electrolyte; however, their use caused low reversibility and low cycling life.

The article presented a quasi-sold-state DES-based self-healing polymer (DSP) electrolyte for Li-metal cell. The DES considered in the study was composed of LiTFSI and N-methylacetamide (MAc) with a 1:4 molar ratio, which ensured the liquid state for a wide temperature range and an ionic conductivity of 8.9 x10-4 S/cm at 25 °C. Subsequently, 10 wt % fluoroethylene carbonate (FEC) was added to the DES in order to increase the ionic conductivity and the electrochemical stability. In the end, the DSP electrolyte was prepared by thermally polymerizing UPyMA and PETEA monomers in the presence of the above DES and the FEC additive. The DSP electrolyte was non-flammable, self-healing and presented a high ionic conductivity of 1.79 mS/cm at 25°C, as well as electrochemical stability up to 4.5 V vs. Li^+/Li^+, and stable interfacial properties. The performance of the DSP electrolyte was tested in a cell composed of Li metal and LMO as the electrodes. It was observed the formation of thin and stable protective layers on both the electrodes, which ensured an excellent cycling stability; the formation of a SEI (solid electrolyte interphase) film on the Li metal anode guaranteed the protection against dendrites formation; the CEI (cathode electrolyte interface) formation avoided the structural deterioration of the cathode. The Li/DSP/LMO cell was investigated at different C-rates; the reversible specific capacity of the cell was stable at each C-rate and decreased from 117.2 mAh/g at 0.1C to 104.3 mAh/g at 2C. Subsequently, the cycling performance was tested at 0.1C for 200 cycles, as shown in Figure 25. At the end of the test, the measured specific capacity was 99.5 mAh/g, with a capacity retention of 86.1%. In addition, the Coulombic efficiency, after the first 10 cycles, was stable above 90%. For comparison, the same tests were carried out using the DES-based electrolyte. It was observed that the cell could not be cycled with a C-rate above 0.5C and the specific capacity remarkably dropped after 80 cycles. The Coulombic efficiency was fairly stable for the first 60 cycles, then it started to decline. To conclude, the report by Jaumaux *et al.* demonstrated that the use of a quasi-solid-state DES-based electrolyte could enhance the safety and the cycling life of lithium metal cells. Moreover, the present approach could be considered for other rechargeable metal cells, such as sodium metal or zinc metal.

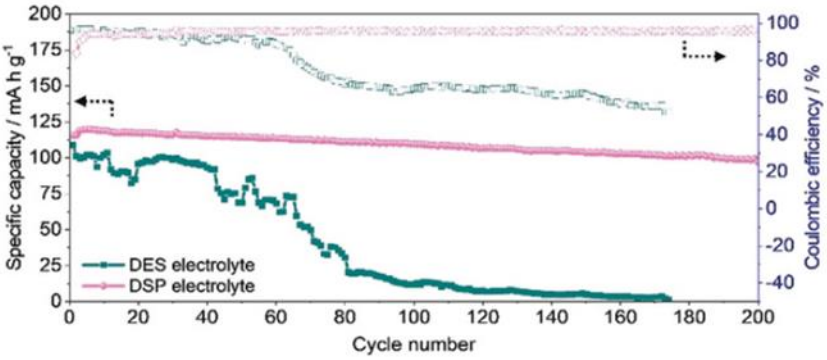

Figure 25. Cycling performance of the cell with the DSP and the DES electrolyte. Adapted and reprinted with permission from [31].

The study by Li *et al.* presented a new solid state electrolyte, to be used in lithium metal cells, based on a DES immobilized in a polymer matrix [32]. The liquid based electrolytes, commercially used in many lithium-based cells, usually present concerning safety issues, such as high toxicity and flammability. The development of solid electrolytes could represent a promising solution not only in terms of safety, but also in the mitigation of the dendritic formations, one of the major problems affecting the cycling performance of lithium metal cells, which is preventing their commercialization. The authors prepared an eutectogel (ETG), a flexible solid state electrolyte based on a MAc-LiTFSI DES, which was immobilized within a poly(vinylidene fluoride-hexafluoro-propylene) (PVDF-HFP) matrix. The ETG was formed by 70 wt% of DES; such percentage ensured great mechanical properties, while larger percentages made the ETG very fragile. Different MAc-LiTFSI DES molar ratios were tested in order to achieve the ETG highest ionic conductivity. The maximum ETG ionic conductivity value at room temperature was obtained with a 4:1 MAc-LiTFSI molar ratio and was equal to 3.05x10-4 S/cm, which was remarkable. Furthermore, it was proved that the ETG electrolyte was non-flammable and safe even under a direct flame. The ETG showed a wide electrochemical stability window, around 5 V, which is another important parameter that defines the ability of the electrolyte to tolerate high voltage. Such parameter affects safety and energy density of the cell.

The electrochemical performance of the ETG electrolyte was investigated assembling a coin cell. The cell was composed of lithium metal as the anode, LFP as the cathode and the ETG electrolyte. At first, a cycling voltammetry test proved the good electrochemical reversibility of the solid electrolyte. Subsequently, the cell capacity and cycling behaviour were investigated, as shown in Figure 26; the cell was charged and discharged in the voltage range of 2.8-4.2 V at 0.1C and 25 °C. The initial cell specific discharge capacity was around 164.4 mAh/g. After 40 cycles, the cell specific capacity was still around 162.8 mAh/g, which indicated an acceptably low capacity fade; however, reaching the 100th cycle, the residual specific capacity decreased to 133.9 mAh/g; the reason of such remarkable decrease was related to the increase of the cell internal resistance. The Coulombic efficiency, on the other side, remained stable just below 100% for the whole 100 cycles. After the cycling test, the cell rate performance was tested at different C-rates. The specific capacities were stable at low C-rates, below 0.5C, while with higher ones (i.e. 1C) the capacity dropped with cycling; however, when the C-rates was reduced from 1C to the starting value of 0.05C, the capacity was immediately recovered. For the last test, a Li|ETG|LFP pouch cell was built to verify the flexibility and the damage resistance ensured by the solid state electrolyte. The cell was connected to a green LED. Even though the cell was twisted, cut and pierced, it remained operational powering the LED in all the conditions. Such tests proved the safety and the flexibility ensured by the ETG electrolyte. To summarize, the article by Li *et al.* demonstrated the huge potentialities in terms of safety, low cost and performance of an ETG membrane for the development of solid state electrolytes to be used in lithium based batteries.

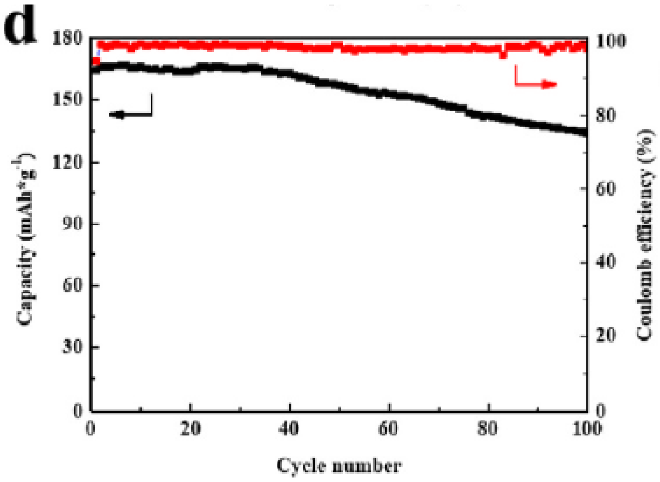

Figure 26. Cycling performance of the Li|ETG|LFP cell at 0.1C and 25 °C. Adapted and reprinted with permission from [32].

3.3. Applications of DESs in sodium-ion batteries

Similarly to lithium, sodium is an alkali metal belonging to group 1. However, sodium is the fourth most abundant element in the earth crust; therefore, it is much less expensive and more well distributed than lithium.

The sodium ion technology is considered one of the most attractive solution to replace or at least to flank Li-ion for the next generation of rechargeable batteries. The reason behind such huge consideration is obviously related to the sodium low cost but also to the fact that the sodium ion technology is fairly similar to the Li-ion technology and, therefore, some of the knowledge learn from Li-ion is applicable to the sodium ion, an example on this behalf is presented by the intercalation chemistry of sodium which is similar to that of lithium [33].

However, the sodium ion cells, usually defined as sodium-ion batteries (SIBs), present some important issues such as low cycling stability and poor rate performance, which is the amount of charge that can be delivered by (and to) the cell at a specific C-rate. The reason for such problems is related to the huge volume variation during the charging and discharging cycles. Therefore, the research on the sodium ion technology is mainly focused on the development of electrodes, for both the anode and the cathode, that can ensure long cycle life and good rate capacity. Another crucial aspect to be considered is the high reactivity of sodium metals with water, even the moisture content of air, which is potentially harmful to the performance of the cell due to the formation of NaOH on the electrodes. Hence, it is essential to prepare sodium ion cells in a moisture free environment.

The study by Wang *et al.* analysed the performance of a SIB using $Na_2Ti_3O_7$ (sodium titanate oxide or NTO) synthesized through a mild process in ChCl/EG-based DES as electrode materials [34]. The commonly used processes to synthesize NTO require high temperature (>800 °C) or long time (> 48 h) and the final product presents two main issues for electrochemical applications: low capacity and poor cycle stability. The article showed that the DES-based method for the production of layered NTO, required lower temperature and lower reaction time. In addition, the electrochemical properties of the NTO were excellent.

The sodium-ion cell was tested at 25 °C in the voltage range of 0.01–2.50 V. The charge and discharge cycles were carried out at different C-rates, from 0.1C to 5C. As shown in the Figure 27 (a) and (b), the measured specific capacity was stable at 155 mAh/g and 127 mAh/g after 50 cycles using 0.1C and 1C, respectively. The cycling performance of the cell was tested at 5C for 2000 cycles and showed that the specific capacity remained stable at around 72 mAh/g. The Coulombic efficiency was stable as well at around 100%, after the first few cycles, regardless of the C-rate used. To summarize, the article by Wang *et al.* demonstrated that the use of a DES in a mild process for the synthesis of $Na_2Ti_3O_7$ was feasible because of the non-toxicity, low cost and ease of production of DES. Moreover, the produced sodium titanate provided excellent electrochemical performance and stability to the sodium-ion cell.

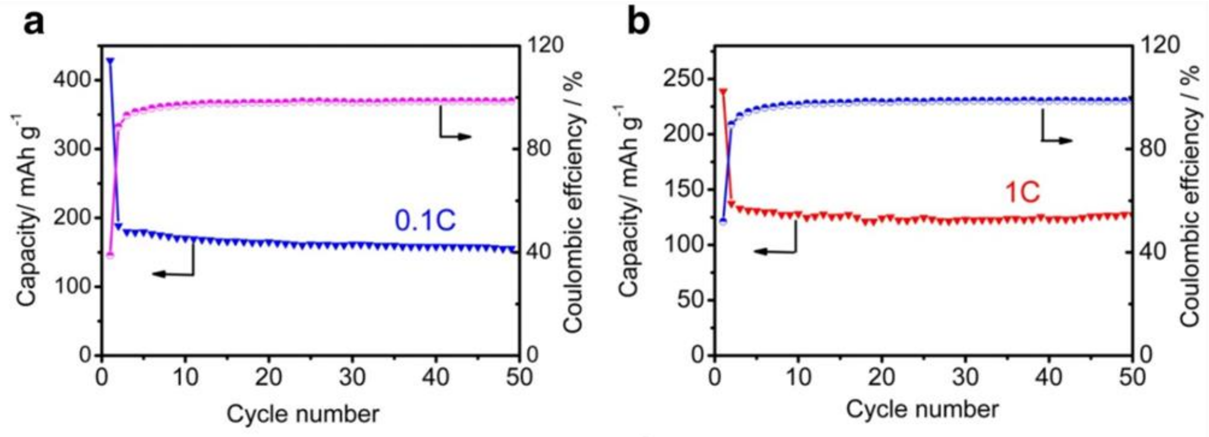

Figure 27. Sodium-ion cell with $Na_2Ti_3O_7$ electrode synthetized using a DES-based process: (a) cycling performance at 0.1C; (b) cycling performance at 1C.
Adapted and reprinted with permission from [34].

The study by Jiang *et al.* investigated the use of a DES for the synthesis of $NaTi_2(PO_4)_3/C$ (NTP/C) with a new porous structure to be used as the anode material for SIBs [35]. SIBs could represent an alternative to LIBs, due to the abundance of sodium and the lower cost of the needed raw materials compared to that for LIBs. However, SIBs suffer of poor rate and cycling performance due to the huge volume variation during the charge and discharge cycles. Therefore, it was crucial to develop a new electrode material which could solve the SIBs common issues. The DES used in the article was composed of ChCl and triethanolamine (TEA) with a 2:1 molar ratio. The carbon-coated NTP electrode, synthesized by the ChCl:TEA DES, presented an abundant mesoporous structure; such structure could facilitate the electrolyte penetration and the intercalation reaction.

A coin cell was assembled with the new electrode in order to test the electrochemical performance. The galvanostatic charge and discharge cycles were performed at different C-rates at 25 °C, between 1.4 V and 3.0 V. The cell provided an excellent specific capacity of 116 mAh/g at 5C and 113 mAh/g at 20C. The cell cycling stability was remarkable, with a capacity retention of 99% after 1000 cycles at 5C and 20C, as shown in Figure 28. Moreover, the Coulombic efficiency was stable above 98% during the cycling tests at 5C and 20C. The C-rate increase, from 5C to 20C, slightly reduced the energy density from 223 to 217 Wh/kg, while the power density showed a huge boost from 1115 to 4346 W/kg. In the end, the electrochemical performance of a cell with a bare NTP electrode, without the carbon coating, was investigated for comparison; the results indicated that the cell reversible capacity was only about 50 mAh/g at 1C, as indicated in the inset of Figure 28, much less compared to the use of the NTP/C electrode. To summarize, the article demonstrated the successful preparation of a 3D hierarchical porous NTP with carbon coating using the ChCl:TEA DES. Furthermore, the as-synthesized NTP/C was proved to be an excellent electrode to be used in SIBs, ensuring impressive rate performance and cycling stability even at high current densities.

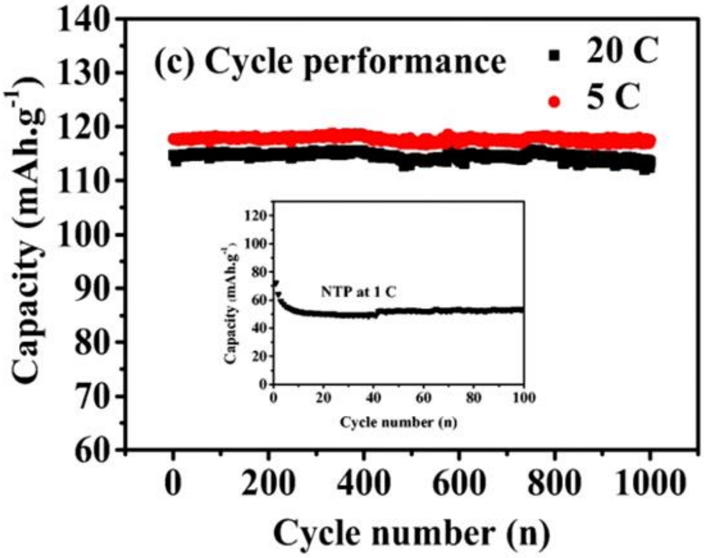

Figure 28. Cycling performance at 5C and 20C with the NTP/C electrode prepared a DES-based method; the inset shows the performance with the NTP electrode at 1C. Adapted and reprinted with permission from [35].

3.4. Applications of DESs in redox flow batteries

Considering the strict requirements for large scale grid storage, such as low cost, long cycle and calendar life, good energy efficiency and rapid response to load variation, RFBs could represent a very interesting technology for such crucial application. In particular, the previously mentioned separation of power, defined by the cell core, and energy, defined by the stored reactants, is probably the most important feature of this technology because it could even allow the simple and inexpensive long term energy storage.

Nowadays, commercially available RFBs are mostly based on vanadium chemistry and aqueous electrolytes. However, the aqueous-based electrolytes represent the major limiting factor to the electrochemical performance of RFBs in terms of narrow electrochemical potential window and low concentration of active species. Therefore, the development of non-aqueous electrolyte is crucial to enhance the RFBs energy and power density [36].

Lloyd *et al.* analysed the behaviour of a RFB, based on a copper and chlorine redox couple, using a DES as the electrolyte in which anhydrous $CuCl_2$ was dissolved, forming a 1 M solution [37]. The DES was based on ChCl and EG, at 1:2 molar ratio, and was called "ethaline". Furthermore, the presence, inside the RFB, of copper in three different states, *i.e.* Cu(s), $Cu(I)Cl_3^{2-}$ and $Cu(II)Cl_4^{2-}$, connected to the redox reactions in the positive and negative electrodes, allowed the development of an all-copper RFB. It is interesting to notice that all the commercially available separators tested were not useful due to their reduction in ionic conductivity when put in contact with the DES. To overcome this problem, the jellification of the electrolyte was carried out, by adding 5 wt.% polyvinyl alcohol to the plain ethaline. It was estimated that the concentration in the electrolyte of the Cu(II) complex was 2/3 of that of the Cu(I) complex, due to the diffusion coefficient of the Cu(I) complex, which was the double with respect to Cu(II). The jellified membrane showed a low permeation only to the Cu(I) complex, over weeks of testing at 50 °C; therefore, the separation between the two electrodes was guaranteed. The conductivity of the jellified and the plain DES was almost identical in a range of temperatures.

The performance analysis of the redox flow battery showed that the transition from charging to discharging occurred at 0.72 V, and the ohmic impedance was four times higher than the expected value and this led to higher ohmic losses. Another performance analysis was carried out for a miniature redox battery, which was built in order to define the performance of the cell with minimal oxygen presence and a uniform temperature. In this case, the ohmic impedance measured - *ex situ* - was close to the expected value. This indicated that the ex situ measurements can provide a good evidence to the behaviour of the complete cell. Moreover, the conductivity of the electrolyte was equivalent to the one of the pure DES. The performance was analysed even on long term. At first, the cell was monitored for 38 cycles, in charge and discharge, at a current density of 10 mA/cm^2. The average Coulombic efficiency measured was 94.3% and the energy efficiency was 52.1%, but the amount of charge passed was equivalent to just a fifth of the theoretical capacity. The open circuit voltage (OCV) values measured were 0.773 V in charge and 0.683 V in discharge, respectively. Another cycling performance analysis was performed at a current density of 7.5 mA/cm^2, as shown in Figure 29. The lower current density remarkably increased the performance, doubling the charge passed, reaching the 40% of the theoretical capacity and increasing the energy efficiency to 62%, due to a slightly larger shift of the OCVs. Other tests were performed applying a further reduction of the current density which led to a higher energy efficiency, but the time required by those tests was too long and so the number of cycles done was not enough to validate the results. To summarize, the study by Lloyd *et al.* demonstrated that the analysed RFB was not feasible due to the small OCV and the high ohmic losses which with a current density not particularly high, 50 mAh/cm^2, hit hard the efficiency. A suggested possible solution was to increase the working temperature above 50 °C. On the other hand, the DES was proved to be a good electrolyte for a RFB as an ionic liquid, but with a lower cost and an easier handling.

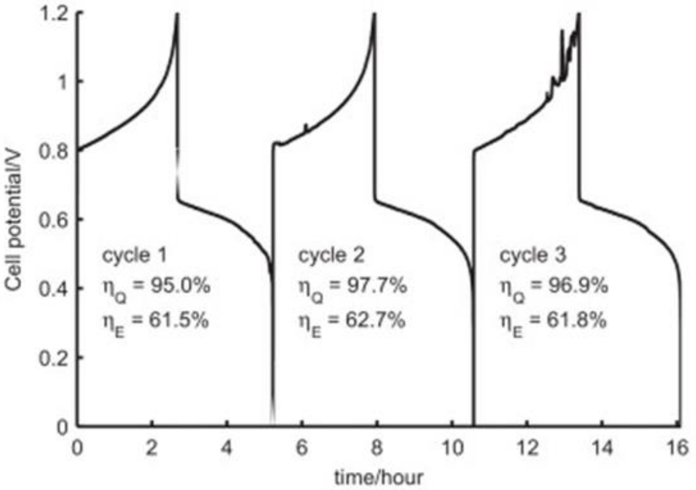

Figure 29. Three charging/discharging cycles of the miniature cell at a current density of 7.5 mA/cm^2 for the all-copper RFB using the DES-based electrolyte. Adapted and reprinted with permission from [37].

The study by Miller *et al.* analysed the behaviour of an iron based RFB. The electrolyte used in this cell was a DES based on ChCl and EG in solution with an elevated concentrations of iron chloride ($FeCl_x$) [38]. The measured OCV of the cell was 1.21 V, which was similar to the expected OCV using an aqueous electrolyte. The DES based electrolytes can be an important step to increase energy and power density of the RFBs compared to the commonly used aqueous electrolytes, without the safety hazards of the organic solvents based electrolytes and at a fraction of the cost of the ILs-based electrolytes.

The first tests were performed with an electrolyte molar ratio of 1:1:4 ($FeCl_x$:ChCl:EG), which seemed promising due to high Coulombic efficiency and fast kinetics, at a current density of 50 mA/cm^2, 80 °C and considering a symmetric cell. However, these results were not repeatable in a full cell due to the fact that the battery could not be discharged. The problem was caused by the change of the $FeCl_3$ to $FeCl_2$, which highly effected many characteristics of the electrolyte, such as the conductivity, varying from 20.9 to just 2.4 mS/cm, with only $FeCl_3$ and only $FeCl_2$, respectively. To overcome such problem, the electrolyte ratio was varied to 0.5:1:4 and the cell was tested again. In this case, the charging and discharging cycles were performed at 5 mA/cm^2 for 1 h, at 80 °C, and the results obtained were definitely better than the previous case. The performance of the cell was stable for the first 14 cycles, then it started to fade, as Figure 30 shows. The ionic conductivity values measured were 25.5 and 19.2 mS/cm with only $FeCl_3$ and only $FeCl_2$, respectively, which were much more consistent than the previous attempt. In order to understand the reason for such different performance, the electrodeposition of iron was analysed through the variation of the concentration ratio. It was observed that a lower concentration of iron chloride led to a faster kinetic of the reactions. Moreover, iron nucleation was studied to understand how it electrodeposited. The result showed the important correlation with the chloride to iron ratio. A high level of chloride concentration was the cause of rough iron deposits, which led to a problematic reversibility of the system and a lower Coulombic efficiency. The study showed that Cl to Fe ratio also strongly impacted the ionic conductivity. Therefore, a ratio of at least 4:1 was fixed in order to obtain a high conductivity; however, it was not useful to further increase the ratio, considering that the conductivity did not significantly increase. Besides, the liquid properties were not affected by the EG concentration. To summarize, the electrolyte with the 0.5:1:4 ratio was proved to be a feasible solution for iron-based RFBs from a performance viewpoint. The Cl to Fe ratio dominated the electrochemical and physical properties. Furthermore, it was important to maintain the Cl to Fe ratio above 4:1 to preserve a high conductivity.

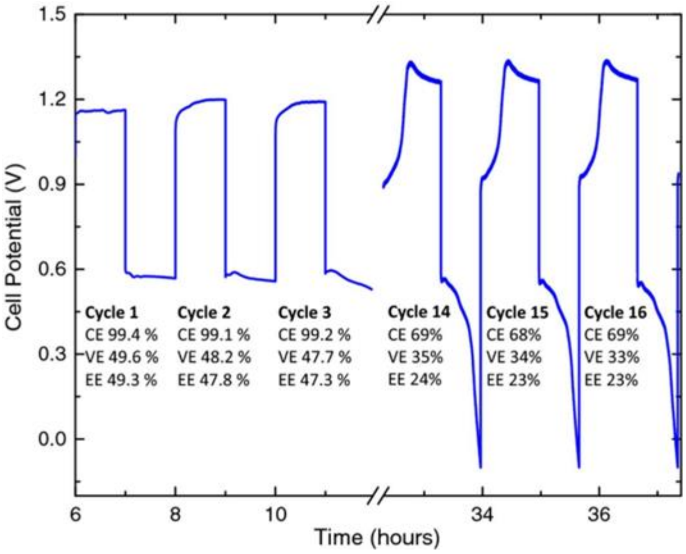

Figure 30. 1 h charging/discharging cycles, at 5 mA/cm^{2}and 80 °C, with 0.5:1:4 (FeCl$_x$:ChCl:EG) composition of the DES-based electrolyte.
Adapted and reprinted with permission from [38].

The study by Zhang *et al.* analysed the feasibility of an aluminium-based RFB using a DES as the anolyte [39]. The article presented a prototype Al-halogen RFB with an Al-based DES, mixed with 1,2-DCE, as anolyte and an aqueous solution of I_2 or Br_2 as catholyte. Regarding the Al-DES anolyte, it was prepared combining urea and $AlCl_3$ at ambient temperature with a molar ratio of 1:1.3. The ionic conductivity of the DES was 0.36 mS/cm, too low for a sufficient mass transport. Thus, the Al-DES was diluted with 1,2-DCE and named Al-DES/DCE; the molar ratio of Al in Al-DES/DCE was around 39.7%. The ionic conductivity value of the diluted anolyte was 1.9 mS/cm, five times higher than that of the non-diluted Al-DES, due to a reduced viscosity.

The performance of the Al-I_2 RFB has been analysed through many tests. The potential plateau values were around 1.34 and 1.69 V in charge and discharge, respectively. The rate performance, which is the amount of energy that can be delivered by the cell at a specific C-rate, was pretty high for low C-rates, at 0.5C the rate performance was 92%; however, it heavily dropped with higher C-rates, *i.e.* 55% at 1C and 44% at 1.5C. A concentration of 4.5 M iodine catholyte provided the highest values of volumetric capacity, *i.e.* 145 Ah/L at 0.1 mA/cm2 and 132 Ah/L at 0.5 mA/cm^2, as shown in the Figure 31. The measured energy density values were 189 Wh/L and 165 Wh/kg. Other tests have been performed using a Br_2 based catholyte. The potential plateau was higher with this configuration, *i.e.* around 2.0 V. The Al–Br_2 RFB theoretical energy capacity could reach 201 Wh/L, using a Br_2 2 M concentration. Cycling tests with a current density of 0.1 mA/cm^2 showed negligible losses in efficiency and capacity after 100 cycles; the Coulombic efficiency remained stable at 99% and the energy and voltage efficiencies were stable at 89.5 % and 90.4 %, respectively. To sum up, the study by Zhang *et al.* demonstrated that the use of DES in RFBs, properly diluted to enhance the ionic conductivity, could lead to a good efficiency and to a higher energy density with respect to the well-known aqueous-based RFBs. Furthermore, the tests showed the great performance of the Al-DES as anolyte, which could represent the basis for the development of cheap, high performance and eco-friendly RFBs.

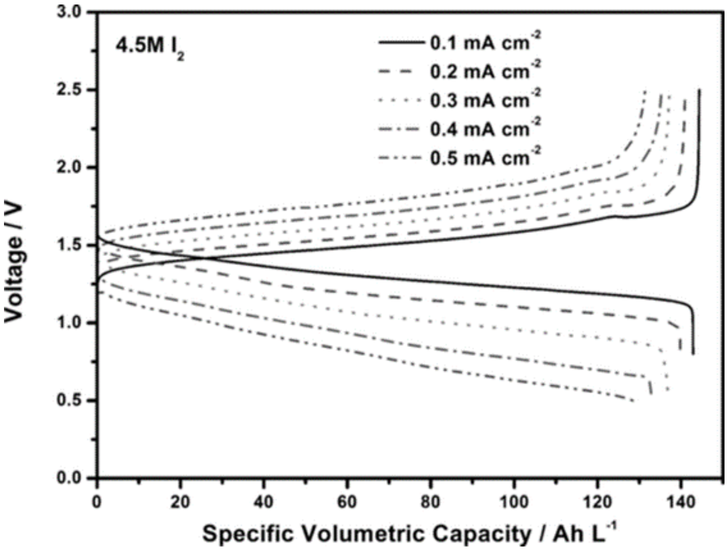

Figure 31. Charge and discharge curves, at different current densities, of the Al–I_2 RFB using the Al-based DES as anolyte and the aqueous based catholyte with 4.5 M of I_2.
Adapted and reprinted with permission from [39].

Kawase *et al.* presented a new deep eutectic catholyte (DEC) based on $FeCl_3 \cdot 6H_2O$/urea (FeU-DEC), which was infused in a self-standing carbon nanofiber (CNF) to be used in RFBs [40]. The FeU-DEC was a non-flammable, biodegradable and inexpensive fluid prepared with $FeCl_3 \cdot 6H_2O$ and urea with a molar ratio of 2:1. For the cathode, different materials were tested and the most promising were the CNF, carbon paper (CP) and carbon pasted Ti mesh (C-Ti), all of which showed an OCV of approximately 3.8 V.

The FeU-DEC based RFBs was tested using the different cathodic materials, in the voltage range from 2.0 to 4.5 V; the rate performance was measured with the current densities from 10 to 300 mA/g at 25 °C. The best performance was shown by the RFB with the CNF cathode soaked in FeU-DEC. Figure 32 shows the power density of the RFB with CNF cathode at different current densities. The highest measured power density was 874 mW/g at a current density of 300 mA/g. The specific capacity was high as well, up to 27.28 mAh/g, because of the high theoretical capacity of FeU-DEC (89.24 mAh/g). Furthermore, the CNF presented a good stability regarding the degradation. Moreover, the study established that the wettability control of the FeU-DEC on the electrode was very important in order to improve the electrochemical performance of the RFB and, for this reason, should be applied to the development of any deep eutectic catholytes and anolytes. To sum up, the study by Kawase *et al.* showed a high performance and environmentally friendly RFB, based on a safe and low cost deep eutectic catholyte, which could represent an important step for the development of green and inexpensive energy storage solution for renewable energy sources.

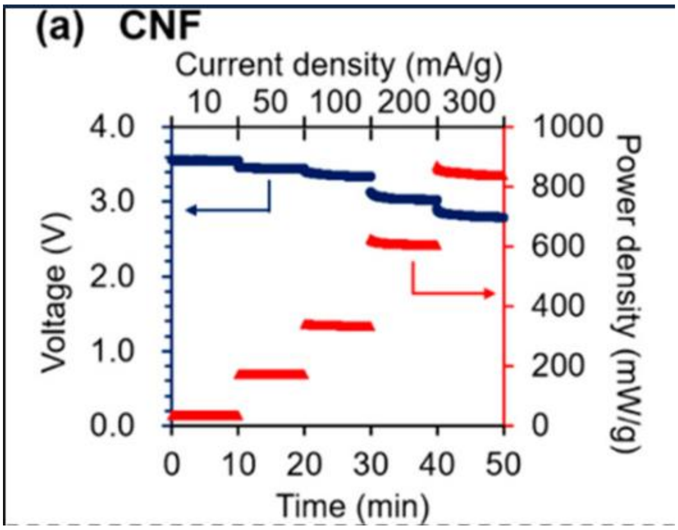

Figure 32. Power densities of the FeU-DEC based RFB with CNF cathode, using different current densities at 25 °C.
Adapted and reprinted with permission from [40].

The article by Xu *et al.* analysed the effect of CO_2 as additive on the physical and electrochemical characteristics of a DES containing Fe(II)/Fe(III) redox couple in order to be used as the electrolyte for a RFB [41]. The use of non-aqueous electrolytes has been highly investigated in the literature with the aim to increase the performance of RFBs. The DESs presented the highest potentialities in terms of safety, cost, environmental impact and ease handling. The study considered a DES based on ChCl and urea with a 1:2 molar ratio with the use of CO_2 as additive towards reducing the common DES issues, low viscosity and small diffusion coefficient.

The performance of the DES was tested with and without the saturated CO_2. The resulting viscosity, at 25 °C, decreased from 690.4 cP to 620 cP (around 10.1%) with the CO_2 addition. Increasing the temperature led to a reduction of CO_2 solubility and, consequently, to a lower percentage reduction of the viscosity, *i.e.* 7.0% at 55 °C. Furthermore, the cyclic voltammograms shown in Figure 33 (A) did not show any particular variation in the redox reaction kinetics with the CO_2 addition. The ohmic resistance, on the other hand, showed a remarkable decline of about 24.5% at 25 °C with saturated CO_2 (Figure 33 (B)). To summarize, the study by Xu *et al.* established that adding CO_2 to the DES-based electrolyte could improve the viscosity and reduce the ohmic resistance of the electrolyte especially at lower temperature, without effecting the redox reactions. Given such premises, a further investigation of the cell performance could be considered.

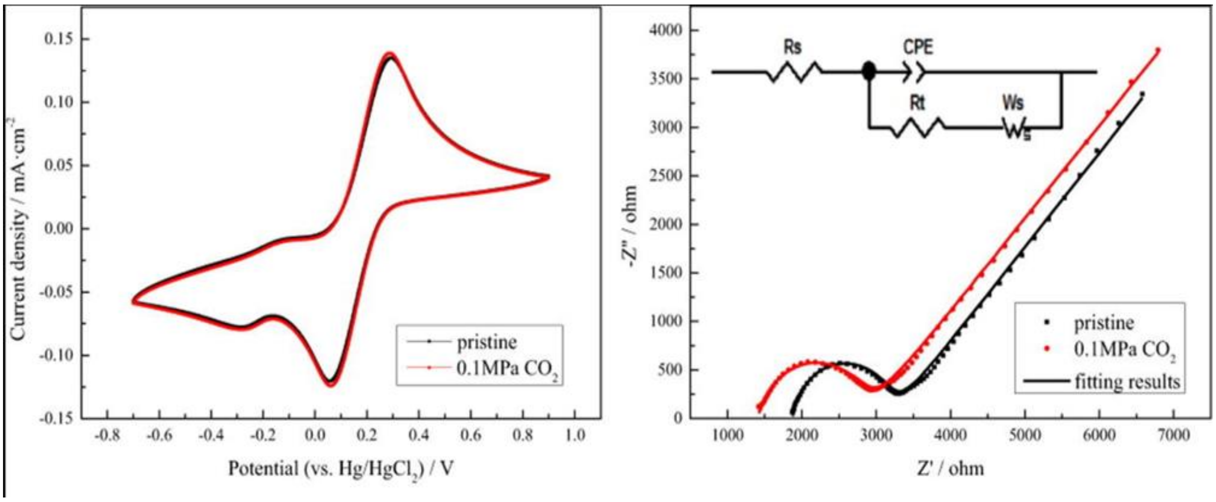

Figure 33. (A) Cyclic voltammograms of 0.1 M $FeCl_3$ in DES with and without 0.1 MPa CO_2 at 25 °C. (B) Nyquist Plots of the electrolyte with and without CO_2 at 25 °C. Adapted and reprinted with permission from [41].

The use of non-aqueous electrolytes in RFB could represent a solution to improve the energy density and to solve some of the aqueous-based RFB issues, such as the poor thermal stability and the low solubility of redox couple ions [42]. DES-based electrolytes could be considered as the best alternative among other non-aqueous electrolyte due to their low cost, biodegradability and thermal stability. The article by Xu *et al.* analysed the performance of a vanadium-iron (V-Fe) RFB using DES-based anolyte and catholyte. A ChCl-urea-based DES, with a 1:2 molar ratio, was used for both the anolyte and the catholyte. At room temperature, 22 °C, the solubility of ferrous ions in the positive side of the cell was 1.59 M and that of the vanadium ions, on the negative side, was 1.44 M; moreover, the temperature raise from 22 °C to 50 °C almost doubled the solubility to 2.81 M and 2.32 M for ferrous and vanadium ions, respectively. In comparison, the maximum solubility in aqueous electrolyte for vanadium ions was less than 1.5 M and it was unstable above 45 °C. Therefore, the specific capacity of the cell increased by 54.6% with respect to the aqueous based cell.

The cell electrochemical performance was tested through various tests and the SOC was maintained between 15% and 85%. First of all, it was measured an OCV, at 85% SOC, of 0.86 V; after 8h, the OCV dropped to 0.81 V, equivalent to a decreasing rate of 0.005 V/h, which is one half of the decreasing rate shown by the aqueous vanadium RFBs. Subsequently, the cell was charged and discharged at 30 °C using different current densities, from 0.5 to 5.0 mA/cm^2, as shown in Figure 34. The Coulombic efficiency slightly increased from 92.1% at 0.5 mA/cm^2 to 97.2% at 5.0 mA/cm^2, while the voltage efficiency dropped from 89.0% to 42.3%, as well as the energy efficiency from 81.9% to 41.1%. The high drops of voltage efficiency and energy efficiency at higher current densities mostly depended on the high viscosity of the electrolytes which caused a high internal resistance of the cell, a slow kinetics of the redox reactions and higher energy consumption for the pumping. Increasing the temperature from 30 °C to 50 °C highly reduced the viscosity; therefore, considering a current density of 2.0 mA/cm^2, the voltage efficiency increased from 68.3% to 79.1% as well as the energy efficiency from 64.7% to 75.0%. To conclude, the study by Xu *et al.* demonstrated that the use of non-aqueous DES-based electrolytes enhanced the performance of the RFB in terms of thermal stability, specific capacity and capacity retention. The high ohmic and parasitic pumping losses, which were the major drawbacks of this system, could be easily solved with a slight increase of the operating temperature to 50 °C.

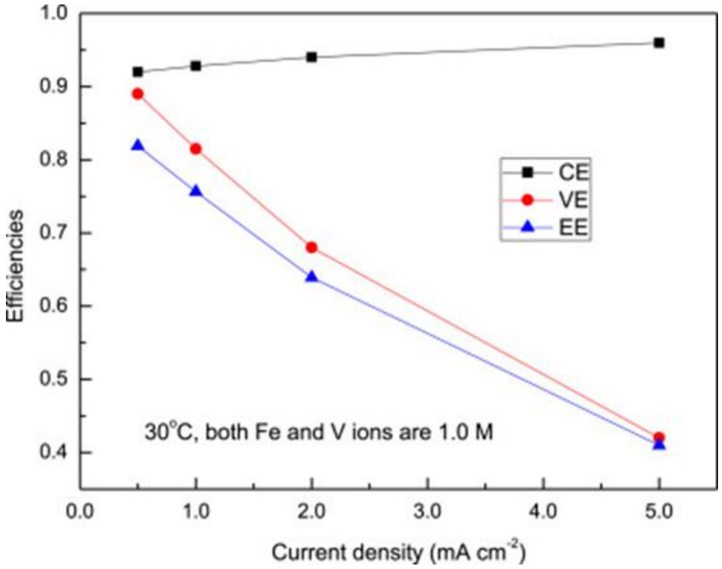

Figure 34. Coulombic efficiency, voltage efficiency and energy efficiency of the cell, with the DES-based electrolytes, at different current densities.
Adapted and reprinted with permission from [42].

The study by Ma *et al.* established a pore scale multiple-relaxation-time (MRT) lattice Boltzmann model (LBM) in order to predict the complex transfer behaviours, such as electrolyte flow and species/charge transfer, and the electrochemical reaction in the positive electrode of an all-copper RFB, which used a non-aqueous DES-based electrolyte, at various operating temperatures [43]. The validity of the model has been certified by comparing the obtained results with that of other studies. The 3D fibrous porous structure of the electrode has been reconstructed with a stochastic method providing the desired values of porosity and fibre diameter.

The numerical results, using a constant current density 600 A/m^2, showed that decreasing the porosity of the electrode extended the depletion time of Cu(I) and improved the concentration gradient of Cu(I) from the inlet value, leading to a higher SOC in the electrolyte and to an improved electrolyte utilization efficiency, which is the ratio between the effective discharge capacity and the theoretical capacity in the DES electrolyte, in the charging cycle. Moreover, considering that the overpotential of the electrode depends on its specific surface area, the average overpotential with an electrode porosity of 0.95 was 2.55 times higher than that of an electrode with a porosity of 0.75. Subsequently, it was observed that the operational temperature had a huge impact on the performance. Increasing the temperature, from 293 K to 333 K with a 0.85 porosity, the viscosity of the DES decreased, leading to 2.64 times increase in flow rate, which reduced the depletion time of Cu(I) and decreased by 23% the overage SOC. Furthermore, the average overpotential declined nonlinearly 4.2 times, with a 0.85 porosity, when the temperature increased from 293 K to 333 K, as shown in Figure 35. On the other hand, the variation of the average transfer current density was negligible. To sum up, the study by Ma *et al.* successfully proposed a LBM to analyse how the structure of an electrode and the variation of temperature effected the characteristics of an all-copper RFB with a DES-based electrolyte.

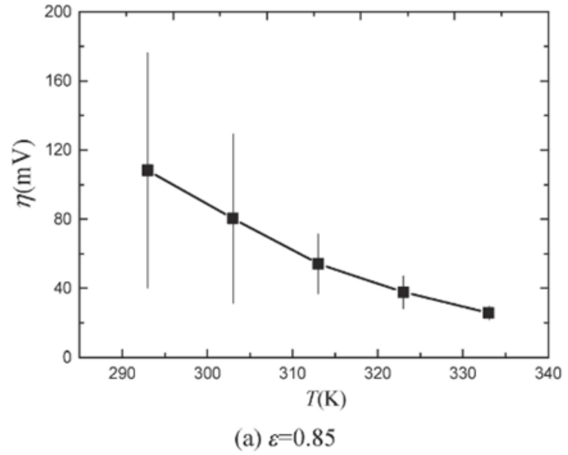

Figure 35. Average overpotential of the RFB, with the DES-based electrolyte, as a function of temperature, with a 0.85 porosity.
Adapted and reprinted with permission from [43].

Xu *et al.* implemented a numerical stationary two-dimensional model to study the effect of temperature on the performance of iron-vanadium RFB based on a DES electrolyte [44]. There were few numerical simulation models, in scientific literature, to study the behaviour of DES systems; therefore, in the present article the most important parameters, such as the diffusion coefficient and reaction rate constant, for DES electrolyte were determined through experimental tests. The DES was based on choline chloride and urea with a 1:2 molar ratio; moreover, 0.1 M VCl_3 was added to the DES in the negative side, while 0.1 M $FeCl_2$ was added in the positive side. The model was validated comparing the simulating and the experimental values of the voltage as a function of the density current; it was observed that the average relative error was below 3%.

First of all, the electrodes overpotential in charge and discharge was observed as a function of the SOC with a fixed current density of 3 mA/cm^2 at 25 °C. The overpotentials reached the minimum values when the SOC was at around 50%. On the contrary, when the SOC was close to 0% or 100%, the electrodes overpotential highly changed, which could cause more side reactions reducing the cycling performance of the cell. Consequently, it was decided to keep the SOC between 10% and 85%. Furthermore, the overpotentials were higher near the membrane, which is the element that separates the two electrodes, due to the higher electrical conductivity of the electrodes than the ionic conductivity of the electrolyte; therefore, the ion conduction determined the current transfer in the electrodes. Subsequently, the effect of temperature was analysed under different aspects. Increasing the temperature from 25 °C to 55 °C led to a lower viscosity, which caused a lower pressure drop on the positive and negative electrolytes flow; it also reduced the pressure drop difference between the two electrolytes. Moreover, the pumping power loss remarkably decreased from 0.138 W at 25 °C to 0.022 W at 55 °C. As regards the negative and positive overpotentials, the viscosity reduction decreased the overpotentials in the whole electrodes region, as shown in Figure 36 for the positive electrode, because of the higher electrolyte ionic conductivity. In the end, the effect of temperature was investigated on the local current density of the negative electrode. It was observed that at 25 °C the local current density was higher near the membrane; however, the temperature rise led to a more uniform distribution of the local current density and, consequently, to a higher reaction rate along the electrode. In general, increasing the temperature highly improved the cell performance. To conclude, the study by Xu *et al.* demonstrated that, in order to investigate the effect of the temperature variation, the use of a stationary two dimensional model could represent an important guideline for the development of DES-based RFBs. In addition, because of its low cost, safety and environment friendly features, the DES-based electrolyte was proved to be an interesting alternative to aqueous solutions when the operating temperature was raised to 55 °C.

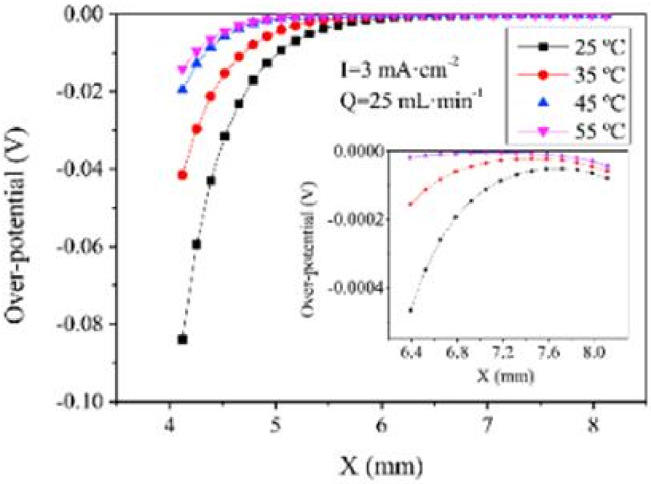

Figure 36. Overpotentials distribution, in the positive electrode of the DES-based redox flow cell, at different temperatures. The inset is a magnified view of the same overpotentials distribution but focused on the separator region.
Adapted and reprinted with permission from [44].

Chakrabarti *et al.* analysed the performance of vanadium RFB using a biodegradable and non-toxic DES based electrolyte and a modified carbon paper (CP) for the electrodes [45]. The use of non-aqueous electrolytes could enhance energy and power density of RFBs. ILs and DESs were largely considered as a feasible solution; however, in order to use such solvents, different factors such as conductivity, viscosity and price had to be considered. The report initially considered two possible electrolytes, one based on a IL, *i.e.* 1-ethyl-methylimidazolium tricyanomethanide, and the other based on a DES, which was named ethaline and was composed of choline chloride and ethylene glycol with a 1:2 molar ratio. A concentration of 0.1 M $V(acac)_3$ was added in the IL, while 0.1 M $V(acac)_3$ in 0.5 M tetraethylammonium tetrafluoroborate ($TEABF_4$) was added in the ethaline.

The cells with the two electrolytes were tested in charge and discharge, from the second cycle, in the SOC range 20-95% using a current density of 10 mA/cm2 at 45 °C, with the OCV of 1.4 V which shifted to the cut-off voltages of 2.2 V in charge and 0.8 V in discharge. The energy and Coulombic efficiencies were very low, only 8% and 47%, respectively, using the IL-based electrolyte and for this reason it was not further tested. On the other hand, the DES-based cell showed an energy efficiency of 63% and a Coulombic efficiency of 98%. Moreover, replacing the commonly used CP electrodes with nitrogen-doped graphene (N-G)-modified CP increased the energy efficiency to around 75%. Subsequently, the effect of the current density on the energy efficiency was investigated, as shown in Figure 37. It was observed that increasing the current density led to a decrease in energy efficiency, regardless of the used electrodes, due to the high viscosity and low conductivity of the DES. However, the use of the N-G/CP electrodes ensured a slightly higher energy efficiency and an improved cycling stability, which was analysed for 20 cycles. The improved performance provided by the N-G/CP electrodes with respect to the traditional CP electrodes was related to a porosity reduction of about 3%, which lowered the cell internal resistance, and to the increase in volume-specific surface area, the ratio between the surface area and the sample volume, of about 24%. In the end, the article highlighted the crucial aspects for the commercialization of DES-based RFBs. Finding the best combination between electrolyte and electrodes was indicated as the most important aspect to investigate, in order to raise the operating current density, without increasing the temperature; furthermore, the cost reduction was the other fundamental condition which could drive the DES-based RFBs commercialization. To summarize, the article by Chakrabarti *et al.* demonstrated the greater electrochemical performance of a vanadium RFB using a DES-based electrolyte with respect to an IL-based electrolyte. Moreover, the use of N-G/CP electrodes enhanced the performance and the cycling stability of the cell. However, in order to commercialize such technology was crucial to cut costs and raise the operating current density without reducing the energy efficiency of the cell.

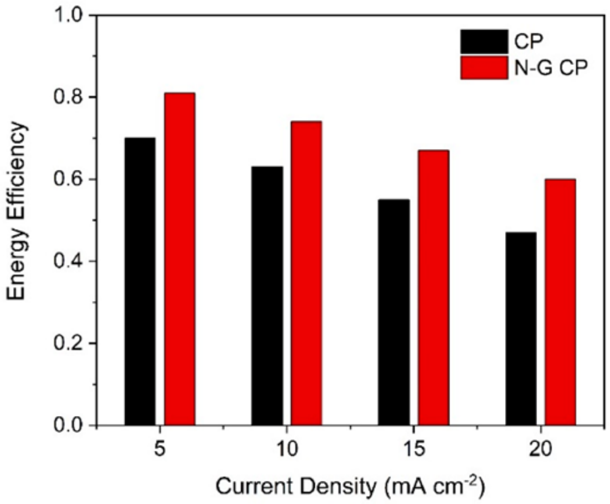

Figure 37. Energy efficiency at different current densities using electrolyte the CP and the N-G/CP electrodes with the ethaline-based electrolyte.
Adapted and reprinted with permission from [45].

The study by Ma *et al.* applied a lattice Boltzmann method (LBM) model for a pore-scale investigation to reveal the reactive transfer mechanism of vanadium-iron RFBs using a DES-based electrolyte, which could enhance the electrochemical performance of RFBs [46]. The DES used in the article was ethaline, which was composed of choline chloride and ethylene glycol with a 1:2 molar ratio. In the positive side, $FeCl_3$ at a concentration of 0.1 M was added to ethaline to form the catholyte, while in the negative side VCl_3 was added to ethaline, at 0.1 M concentration, to form the anolyte. The most important transfer properties of iron and vanadium ions, such as diffusivity, transfer coefficient and reaction constant, were evaluated using a cyclic voltammetry experiment. In the validated LBM, the 3D structure of the porous carbon paper electrodes was randomly reproduced, providing some key parameters such as dimensions, porosity and fibre diameter.

Considering the isotropic porous electrode, the numerical results indicated that, under galvanostatic discharge, considering the same required pumping power, decreasing the electrode porosity and fibre diameter increased its permeability, which led to an increase of the Fe(III) depletion rate and to a lower average electrolyte SOC. On the contrary, increasing the electrode porosity and fibre diameter improved the flow velocity of the electrolyte, leading to a higher average electrolyte SOC and to a reduction of the depletion rate of the reactants. Moreover, increasing the porosity and the fibre diameter increased the overpotential absolute value and reduced the electrolyte utilization efficiency. The effect of anisotropy on the reactive transfer process of the porous electrodes was then investigated. It was observed that, using a fixed porosity and fibre diameter, the electrolyte flow velocity was lower in the cross-plane electrode compared with the isotropic and the in-plane flow velocity, which led to a higher reactants depletion and to a lower average SOC in the electrodes. Subsequently, a comparative investigation between the cathode and the anode was performed. The SOC in the two electrodes was similar, as shown in Figure 38, because of the same flow condition of the positive and negative electrolytes, which was related to the identical electrode structure and viscosity of the two fluids. However, the activation overpotential in the anode was much higher than that in the cathode due to the lower diffusivity, charge transfer coefficient and reaction constant of vanadium ions. In the end, the results of a comparison between vanadium-iron RFB with DES-based electrolyte and vanadium RFB with aqueous electrolyte showed that the average SOC of the vanadium RFB was higher than that of the vanadium-iron RFB; the reason of such result was related to the lower viscosity of the aqueous electrolyte, which led to a higher flow velocity. Furthermore, the activation overpotential of vanadium RFB in the anode was lower with respect to the vanadium-iron RFB, because of the lower diffusivity and transfer coefficient of vanadium ions in DES electrolyte. In the cathode, on the contrary, the activation overpotential of vanadium RFB was higher, in absolute value, than that of vanadium-iron RFB, due to the lower reaction constant of vanadium ions in aqueous electrolyte with respect to the iron ions in DES electrolyte. In summary, the article by Ma *et al.* demonstrated the applicability of an LBM at pore-scale level; moreover, such method could be considered a very useful tool in the development of DES-based RFBs.

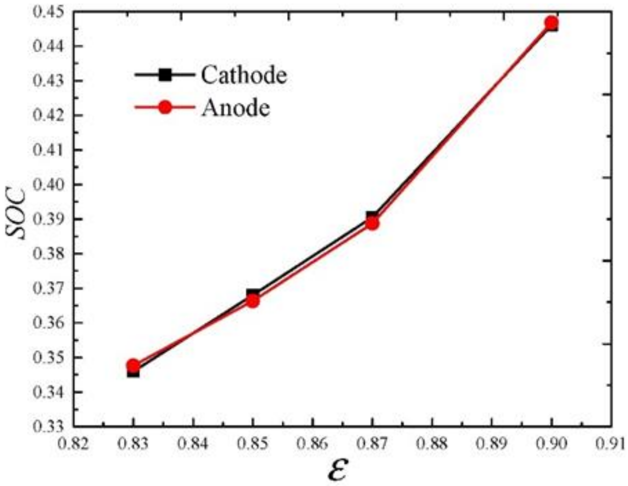

Figure 38. Average DES-based electrolytes SOC as a function of the porosity in cathode and anode. Adapted and reprinted with permission from [46].

Lu *et al.* investigated how two different additives could enhance the physical and electrochemical properties of a DES in order to use it as the electrolyte in non-aqueous RFBs [47]. The use of DES-based electrolytes ensured low cost and high thermal and electrochemical stability. However, pure DESs presented high viscosity and low ionic conductivity. Therefore, the use of additives could improve the conductivity of the DESs, without participate to the reactions. The electrolyte used in the article was based on a DES composed of ChCl and urea, which was define reline, with a 1:2 molar ratio, and the addition of $FeCl_3$, with a concentration of 1.0 M, as the active material. The two additives considered by the authors were EC mixed with dimethyl carbonate (DMC) with a 1:1 volume ratio, and ethyl acetate (EA).

The effect of the DMC+EC addition, with different volume fraction, was investigated. The cyclic voltammetry results indicated that the addition of DMC+EC on the electrolyte enhanced the reversibility of the iron ions and accelerated the chemical reaction rate on the electrode. The best performance was obtained with the highest DMC+EC volume fraction tested, 12.5%. Furthermore, the DMC+EC 12.5% ensured the highest electrolytes impedance reduction, about 24.8%, as well as the higher viscosity reduction from 241.8 mPa s, for the pristine electrolyte, to 172.2 mPa s at 23 °C. The same investigation was performed with the EA additive. In this case, the best performance was obtained with EA volume fraction of 5.0%. In general, the EA addition did not improve the electrochemical performance; on the contrary, the EA volume fraction increase deteriorated the iron ions reversibility. The 5.0% volume fraction ensured an electrolyte impedance reduction of 10.5%, similarly to the 12.5% EA volume fraction. Moreover, the viscosity dropped from 241.8 mPa s, for the pristine electrolyte, to 216.4 mPa s, for the 5.0% EA volume fraction, at 23 °C; however, a further increase to the EA volume fraction only led to a slight viscosity reduction. Therefore, the study proved that the DMC+EC additive enhanced the performance of the DES-based electrolyte much more than the EA additive. Such conclusion was confirmed even by the Raman spectroscopy of the electrolyte, which showed that the peak intensity was enhanced in the DES with DMC+EC additive with respect to that in the DES with EA additive which showed weaker peaks, as shown in Figure 39. To summarize, the study by Lu *et al.* demonstrated that the use of two additives, EA and DMC+EC, could improve the electrochemical performance of RFBs DES-based electrolyte. In particular, the DMC+EC, with a volume fraction of 12.5%, was the best to enhance the electrolyte properties.

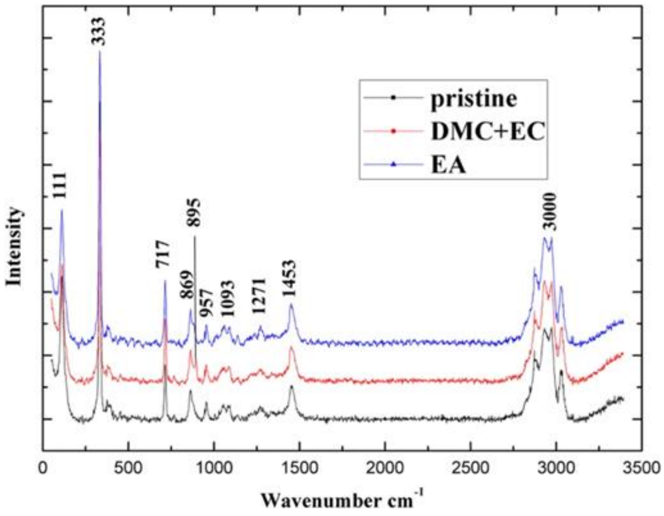

Figure 39. Raman spectroscopy of the DES-based electrolytes with and without the additives. Adapted and reprinted with permission from [47].

The study by Cheng *et al.* investigated the effect of a magnetic field on the performance of an iron-vanadium RFB using a DES-based electrolyte [48]. The DES used for the analysis was composed of ChCl and cholesterol with a 1:2 molar ratio. The redox active materials added to the DES were $FeCl_3$, in the positive side , and VCl_3, in the negative side, both with a concentration of 0.1 M. Moreover, the SOC of the cell was maintained between 15% and 85%.

First of all, the effect of the magnetic field intensity on the anolyte and catholyte was investigated through cyclic voltammetry tests. The results indicated that in both the positive and negative electrolytes the increase of the magnetic field intensity, up to 325 mT, increased the redox current densities, which led to an acceleration of the ions movements improving the electrochemical performance. Subsequently, the authors analysed the effect of magnetic field timeliness. Since the magnetic field was removed, the results of cyclic voltammetry analysis for the catholyte indicated that the oxidation-reduction rate initially increased reaching its maximum after 1 h, then it started to decrease. The same tests on the anolyte indicated that the oxidation-reduction rate only decreased when the magnetic field was withdrawn. Therefore, the timeliness of the magnetic field effect was better for the iron DES electrolyte than the vanadium DES electrolyte. In the end, the cell discharge polarization curves were analysed at different magnetic field intensity. It was observed that the area specific resistance (ASR) of the cell, which is directly proportional to the ohmic overpotential, declined when the magnetic field intensity was raised, as shown in Figure 40; the highest measured ASR reduction was 16.65%, under a magnetic field intensity of 325 mT. Furthermore, the cell energy efficiency rose from 53.2% to 56.37%, under the 325 mT magnetic field intensity, as well as the limiting current density and power density which increased from 11.39 mA/cm^2 and 2.81 mW/cm^2 to 14.97 mA/cm^2 and 3.48 mW/cm^2. To conclude, Cheng *et al.* demonstrated that the use of an external magnetic field could improve the electrochemical performance of non-aqueous iron vanadium RFBs.

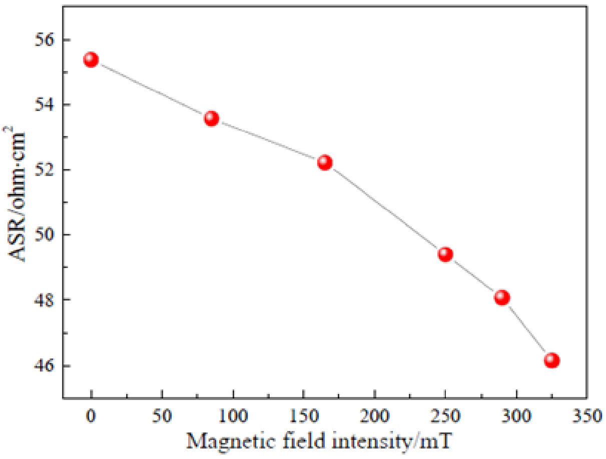

Figure 40. DES-based redox flow cell ASR as a function of magnetic field intensity. Adapted and reprinted with permission from [48].

The study by Cheng *et al.* investigated the performance of a DES-based iron vanadium RFB using modified graphite felt electrodes [49]. The most common RFBs electrode materials were carbon-based, such as graphite felt and carbon felt, because of their low cost, good conductivity and electrochemical stability. However, these materials presented some common drawbacks, such as a small specific surface area and a poor hydrophilicity, which represented a limitation for the RFBs energy efficiency and power density. The authors developed a modified graphite felt using a method based on electrolysis in ammonium sulphate. The electrolysis method improved the carbon felt specific surface area, wettability and increased the number of oxygen-containing functional groups on its surface. The electrode used in the cell was segmented, combining a pristine and a modified graphite felt. The pristine graphite felt was placed in the electrolyte inlet flow region, while the modified graphite felt was placed in the outlet flow region. Such combination was selected in order to uniform the electrochemical reactions along the electrolyte flow; moreover, the ohmic and charge transfer resistance decreased from 6.34 and 6.21 ohm with the pristine graphite felt to 5.42 and 4.2 ohm, respectively, with the segmented graphite felt. The electrolyte used in the iron vanadium RFB was based on ethaline DES, which was composed of choline chloride and ethylene glycol with a 1:2 molar ratio. The redox active materials added to the DES were VCl_3, for the negative electrolyte, and $FeCl_2 \cdot 4H_2O$, for the positive electrolyte, both at a 0.1 M concentration.

The performance of an iron vanadium cell with the segmented electrodes (SE) was compared with that using the pristine electrodes (PE). It was observed that the maximum power density provided by the SE cell was 12.18 mW/cm^2, while for the PE cell it was 11.01 mW/cm^2, a difference of about 10%. Furthermore, the galvanostatic charge and discharge tests, carried out using a current density of 2.0 mA/cm^2, were performed in order to evaluate the energy efficiency of the two electrode configurations. Both configurations showed a high initial energy efficiency, above 90%, which dropped heavily after 5 cycles; however, the SE-based cell presented a slightly higher energy efficiency than the PE-based cell, as indicated in Figure 41. To summarize, the article by Cheng et al. demonstrated that the use of an inexpensive and easy to prepare segmented graphite felt electrode could improve the performance of the DES-based iron vanadium RFBs.

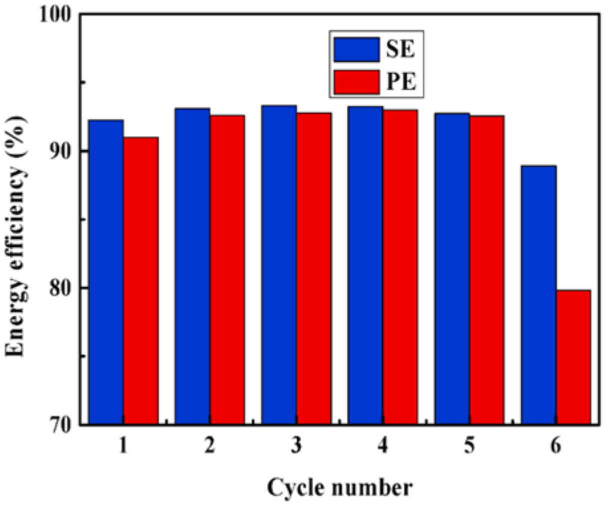

Figure 41. Energy efficiency of the DES-based iron vanadium RFB during different cycles with the pristine and the segmented electrodes.
Adapted and reprinted with permission from [49].

3.5. Applications of DESs in aluminium-chalcogenide batteries

Aluminium is a safe, inexpensive and earth abundant element; such properties are the reason for the massive use of this metal in many industrial sectors. As regard the electrochemical applications, many scientific studies investigated the potentialities of this metal in order to develop a new generation of electrochemical storage, which could represent an improvement to the commercially used LIBs. Aluminium offers many advantages in terms of cost, safety and no dendritic growth upon plating, with respect to other metals such as lithium or sodium. Moreover, the Al volumetric capacity is 8 Ah/cm^3, about four times the Li capacity, and the gravimetric capacity is 3 Ah/g, comparable with that of lithium, *i.e.* 3.86 Ah/g. Therefore, it is crucial to find a feasible cathode material to fulfil such potentialities. In this regards, chalcogenide compounds could represent an excellent electrode material in terms of costs and theoretical capacity.

Among the chalcogenide compounds, sulphur ones are largely considered as an interesting cathode material for the development of a new generation electrochemical energy storage due the low cost and high theoretical energy density; however, it is difficult to obtain a decent capacity retention from sulphur-based cell, even after just few cycles, because of the side reactions occurring in the electrolyte and the sulphur low electronic conductivity, which lead to a slow electrochemical reaction kinetics. Even though selenium is a chemical analogue of sulphur, it presents a much higher electronic conductivity and a lower ionization potential; these characteristics could solve the slow electrochemical reaction kinetics. On the other hand, the development of an electrolyte is still required in order to mitigate the side reactions issue [50].

The study by Chu *et al.* analysed the performance of a rechargeable aluminum-sulphur cell with a DES-based electrolyte [51]. Aluminium has been considered as a promising anode material because of its low cost and high theoretical capacity. Sulphur was used as the cathode material due to its theoretical capacity of 1675 mAh/g. The DES-based electrolyte was composed of $AlCl_3$ and acetamide with a 1.3:1 molar ratio. Observing the charging and discharging curves of the cell, it was noted that the potential plateau values at 25 °C were 1.4 V and 0.55 V in charge and discharge, respectively. Raising the temperature to 40 °C led to a reduction in the potential hysteresis of about 0.2 V. The charge voltage plateau decreased to 1.28 V, while the discharge one increased to 0.63 V.

The electrochemical performance of the cell was tested at 25 °C. The cycling behaviour was investigated using a current density of 100 mA/g (Figure 42). The high initial discharge capacity of 2100 mAh/g immediately dropped, reaching 800 mAh/g after 20 cycles and 500 mAh/g after 60 cycles. The measured Coulombic efficiency dropped from 96% of the second cycle to 78.6% of the fifth cycle; afterwards, it was stabilized with a slightly increase to 84.9% at the 20th cycle. Another test, performed at different current densities, showed the remarkable specific capacity of the cell even at high current density, proving the good rate performance of the cell, *i.e.* 962, 871 and 688 mAh/g at 100, 200 and 300 mA/g, respectively. Moreover, the results indicated that the cycling stability of the cell improved using higher current densities, which was explained by the lower specific capacity which led to a lower volume expansion. To summarize, the study by Chu *et al.* proved that the use of a low cost DES-based electrolyte could represent an important component for the development of a high performance and inexpensive Al-S cell.

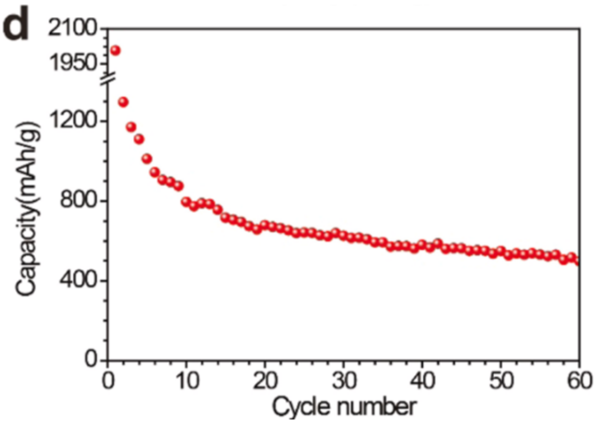

Figure 42. Cycling behaviour at 100 mA/g of the Al-S cell with the DES-based electrolyte at 25 °C. Adapted and reprinted with permission from [51].

Wu *et al.* analysed the performance of a rechargeable aluminium-selenium cell, using a new DES based electrolyte [52]. The DES produced in the report was composed of thiourea (Sur) and $AlCl_3$ with a 1.3:1 molar ratio. The cathode structure was another interesting aspect of the study; Figure 43 shows the process scheme; the cathode was made of selenium nanowires grown directly onto a flexible carbon cloth. The selenium nanowires were synthetized using a low temperature selenization process.

The performance of the Al-Se cell with the Sur-$AlCl_3$ DES electrolyte was tested in the potential ranges of 0.01 to 1.5 V (vs. Al^{3+}/Al) using different current densities. The cell specific capacity, at 50 mA/g, was 260 mAh/g. The cell cycling behaviour was investigated at 100 mA/g for 100 cycles, showing remarkable results. Excluding the first cycle, in which the specific capacity was very high, above 300 mAh/g, the cell specific capacity was stabile just below 200 mAh/g until the end of the test, as well as the Coulombic efficiency, which was nearly 93% after 100 cycles. For comparison, the same cell was tested using the more common EMIC-$AlCl_3$ DES electrolyte; it showed a higher initial specific capacity of 455 mAh/g, due to the lower polarization of the electrolyte; however, after a huge initial drop, the specific capacity was unstable and continued to decline. To summarize, the article by Wu *et al.* demonstrated excellent performance and cycling stability of the Al-Se cell using the Sur-$AlCl_3$ DES electrolyte and the peculiar cathode with the selenium nanowires grown onto a flexible carbon cloth. Furthermore, this approach could be useful in the development of rechargeable Al-chalcogenide (S, Se, Te) batteries.

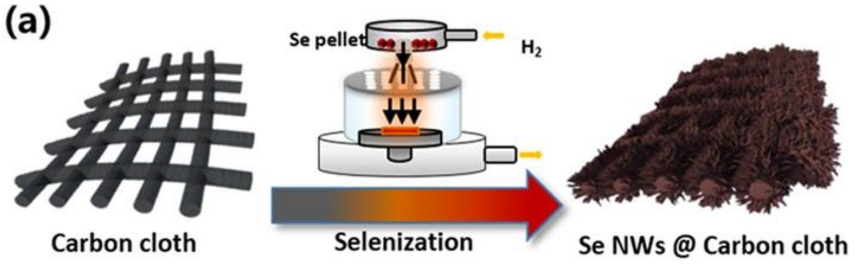

Figure 43. Schematic process of the Se nanowires (NWs) formation onto the flexible carbon cloth, creating the cathode material for the Al-Se cell with the DES-based electrolyte. Adapted and reprinted with permission from [52].

3.6. Applications of DESs in aluminium-air batteries

The aluminium-air batteries combine the previously mentioned advantages of the metal-air batteries with the potentialities of the aluminium. Therefore, Al-air cells could represent a huge improvement compared to the commercially available LIBs in terms of performance, safety and cost; furthermore, Al-air cells present high theoretical nominal voltage and energy density, *i.e.* 2.7 V and 8.1 kWh/kg, second only to the Li-air cell but with much less sensitivity to the air humidity, which represents an important issue for the development of Li-air cells. However, one of the major challenges that the Al-air cells present is the accumulation of byproducts, such as Al_2O_3 and $Al(OH)_3$, at both the electrodes, which suppress electrochemical reactions [53].

The study by Mori analysed the performance of a solid-state rechargeable aluminum–air battery with a DES-based solid electrolyte [54]. The cell considered in the study was built using Al board for the anode and titanium nitride (TiN) and PVDF with a molar ratio of 1:0.3 for the air cathode. The DES electrolyte was based on $AlCl_3$ and urea; however, to obtain a solid-state electrolyte, carboxymethyl cellulose (CMC) and glycerine were added to the basic composition of the DES in order to increase the viscosity and to reduce the volatility, respectively. The final composition of the electrolyte was $AlCl_3$/urea/CMC/glycerine with a molar ratio of 3:2:1:1.

The cell was tested at a current density of 0.1 mA/cm^2 between 0.2–1.5 V. Figure 44 shows the cycling stability of the charging and discharging curves of the cell. The specific capacity value was just 35.8 mAh/g at the first cycle; however, the capacity retention of the cell was remarkable, 97.8% after 50 cycles. It was important to notice that the two byproducts Al_2O_3 and $Al(OH)_3$ were not observed on either the anode or the cathode due to the use of the DES based electrolyte, similarly to what was observed in previous studies using ionic liquids. It was observed the formation of a layer of sedimentation compounds on the surface of the TiN air cathode after the charge and discharge reactions; however, this layer did not impact the performance of the cell. To conclude, the study proved the feasibility of a solid-state rechargeable aluminum–air cell using a DES based electrolyte. The DES electrolyte ensured a comparable level of electrochemical performance with a lower cost compared to ionic liquid based electrolytes.

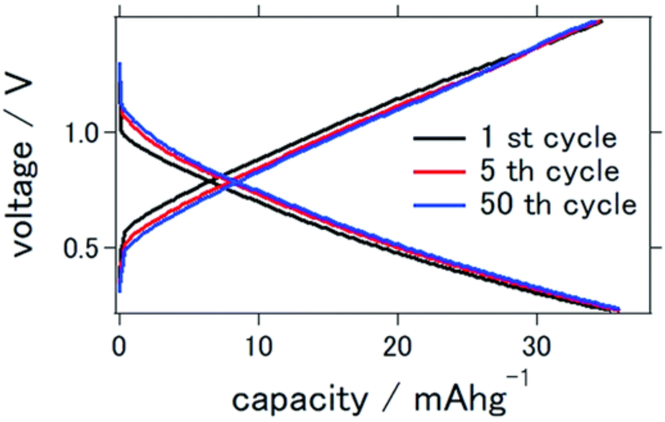

Figure 44. Charge and discharge curves of the solid state Al–air cell with the DES-based electrolyte. Adapted and reprinted with permission from [54].

3.7. Applications of DESs in iron-aluminium batteries

The iron-aluminium rechargeable battery is defined hybrid flow battery (HFB) representing a peculiar form of RFB in which the anode is made of an aluminium strip, typical of a closed battery, while the cathode is soaked in an iron solution, which is contained in an external tank, typical of an RFB. This technology is limited in energy by the surface of the negative electrode, the aluminium strip in this case.

The study by Zhang et al. analysed the feasibility of a Fe-Al HFB based on a Fe DES as catholyte and an Al DES as anolyte [55]. The anolyte was an Al DES, based on aluminium chloride and urea, mixed with a 1.2-dichloroethane (DCE) to reduce the viscosity and enhance the ionic conductivity. The catholyte was a Fe DES. The Fe DES was based on $FeCl_3 \cdot 6H_2O$ and urea; moreover, EG was added to the Fe DES to adjust the physical properties of the fluid in terms of viscosity, freezing temperature and to enhance the reversibility of the redox reactions. Fe(126) and Fe(210) DESs (the numbers indicate the molar ratios of $FeCl_3 \cdot 6H_2O$/urea/EG) were chosen as catholytes for the tests, due to the high reversibility of Fe(126), and the high concentration of Fe(210). A small quantity of EC and DMC was added to the Fe-DESs in order to decrease the viscosity.

The tests on the Fe-Al HFB showed interesting performance. In the case of Fe(126) DES, the discharging capacity measured was 41.4 Ah/L and the energy density was 58.1 Wh/L at a current density of 0.1 mA/cm^2, with an average operating voltage of 1.57 V and 1.41 V in charge and discharge, respectively. Moreover, after 60 cycles at room temperature, with 90% of cell utilization, no capacity fade was observed and the Coulombic efficiency was stable at around 96%, as shown in Figure 45. In the case of Fe(210) DES, a huge rise in discharging capacity was observed (around 120 Ah/L) as well as for the energy density (166.2 Wh/L) at 0.1 mA/cm^2, with an average potential in discharge of 1.41 V. Therefore, the high concentration of the Fe(210) DES favourably impacted the energy density, but could negatively affect the cycling behaviour of the cell. To summarize, this approach demonstrated the great potential of Fe-Al HFB in terms of low cost and performance. Moreover, the anolyte and catholyte DESs could represent the starting point for the development of a new family of inexpensive and environmentally friendly RFB.

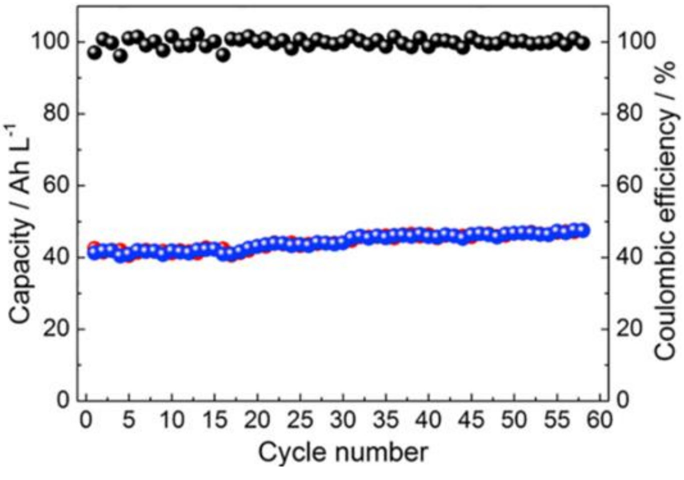

*Figure 45. Charging and discharging capacity and Coulombic efficiency over 60 cycles at 0.1 mA/cm^2 of the Al-Fe cell using the DES-based anolyte and catholyte.
Adapted and reprinted with permission from [55].*

3.8. Applications of DESs in zinc-ion batteries

Zinc is an interesting element for electrochemical applications due to the fact that it is non-toxic, inexpensive and abundant. Therefore, zinc-ion batteries (ZIBs) are considered a feasible alternative to LIBs because they can be assembled using the same LIBs industrial processes but using much cheaper raw materials. Moreover, the theoretical volumetric capacity of ZIBs is higher than that of LIBs, *i.e.* 5855 mAh/cm^3 compared to 2061 mAh/cm^3 of LIBs. Aqueous electrolytes are the most used in ZIBs because they ensure high energy density, safety and cycling stability; however, they present several issues such as hydrogen evolution, electrolyte decomposition and Zn electrode passivation. Such problems reduce the cell electrochemical performance and capacity retention cycle after cycle. Different non-aqueous or even mixture of aqueous/non-aqueous electrolytes are currently under development with the aim to enhance the reversibility of Zn dissolution/deposition and widen the operating voltage window [56].

The article by Kao-Ian *et al.* analysed the performance of a zinc-ion cell using a DES as the electrolyte, in order to understand if it could replace the commonly used aqueous electrolyte [57]. The study considered a coin cell made of metal Zn as the negative electrode, delta-type manganese oxide (δ-MnO_2) as the positive electrode and ChCl/urea based DES, 1:2 molar ratio, with the addition of 0.3 M $ZnCl_2$ as the electrolyte.

First of all, the reversibility of the Zn plating and stripping was positively proved. The cycling behaviour of the Zn electrode was tested at different current densities and the maximum voltages did not increase, which indicated that the passivation layer was not formed onto the Zn electrode. Furthermore, after 150 cycles at 1.0 mA/cm^2 no dendrites formation was observed on the Zn electrode. Subsequently, the cell electrochemical performance was investigated through a galvanostatic (constant-current) cycling test. The two cut off voltages of the cell were 0.4 V and 1.9 V, and the open circuit voltage was 1.5 V. The current densities used for the test were 50, 100, 150 and 200 mA/g, with ten cycles for each current density, as shown in Figure 46(a). The cell showed, at 50 mA/g, an initial discharge capacity of 170 mAh/g, which dropped to 92 mAh/g after five cycles and remained stable for the next five cycles. Increasing the current density led to an obvious discharge capacity drop, *i.e.* 51 mAh/g at 200 mA/g. When the current density was shifted again to 50 mA/g for the next 10 cycles, the discharge capacity increased toward 85 mAh/g. From the 51st to the 150th cycle (Figure 46(b)), the current density was increased to 100 mA/g; such current density led to a constant slight capacity decrease, around 0.7% per cycle. The Coulombic efficiency was above 80% for the entire cycling test, except for the very first cycles. To sum up, the study by Kao-Ian *et al.* demonstrated that the use of a low cost and eco-friendly DES-based electrolyte in ZIBs determined good performance and stability; moreover, the new electrolyte solved the important issue associated with the aqueous electrolytes such as electrolyte decomposition and Zn electrode passivation. For these reasons, the ChCl/urea DES could be considered a promising electrolyte for ZIBs.

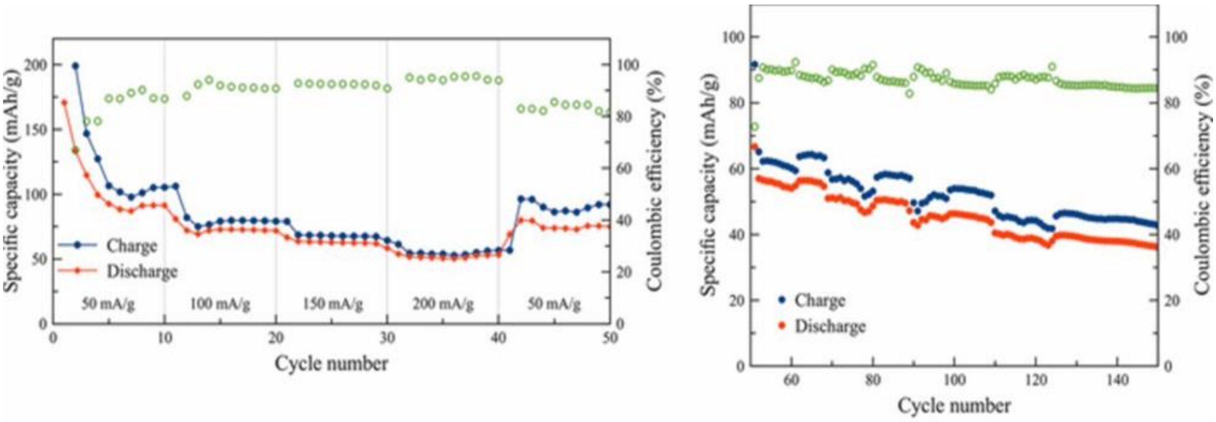

Figure 46. Electrochemical performance of the cell with the DES-based electrolyte: (a) specific capacity using different current densities (50, 100, 150, and 200 mA/g); (b) cycling performance at 100 mA/g from the 51st to the 150th cycle.
Adapted and reprinted with permission from [57].

Zhao *et al.* analysed the performance of a rechargeable zinc metal cell using an electrolyte based on the mixture of water and a DES [58]. In the article, the developed electrolyte was based on a DES made of three components: LiTFSI, $Zn(TFSI)_2$ and urea. Such DES was defined LZ-DES. The LiTFSI/urea molar ratio was fixed at 1:3.8, while the LiTFSI/$Zn(TFSI)_2$ ratio was fixed at 20:1. A small amount of water was added to the LZ-DES in order to preserve the characteristics of the LZ-DES. The presence of water increased the ionic conductivity and reduced the viscosity of the fluid. Moreover, given the low concentration of the water molecules in the DES, they were isolated from each other and the intensified interactions between water and DES suppressed the water reactivity with Zn. The final electrolyte was defined LZ-DES/$2H_2O$.

The experiments were performed using a coin cell and pouch cells. Zn foil was used for the anode and two different materials were used for the cathode: LMO or LFP. First of all, considering the Zn/LMO cell, the charging limit voltage, using the typical aqueous electrolyte, was around 2.0 V for various C-rates, from 0.06C to 0.3C. The use of the LZ-DES/$2H_2O$-based electrolyte increased the voltage limit by 0.3 V using the previous C-rates. Furthermore, the cell delivered a specific discharge capacity of 117 mAh/g at 0.06C rate and the energy density was 224.6 Wh/kg, considering an average cell voltage of 1.92 V. The good cycling behaviour of the cell was proved in terms of capacity retention using three C-rates. At the end of the tests, the remained specific discharge capacity was 90.8% after 300 cycles at 0.1C, 82.7% after 600 cycles at 0.5C and 86.6% after 600 cycles at 2C. On the contrary, using the aqueous electrolyte, the capacity of the cell dropped immediately, as shown in Figure 47. The Coulombic efficiency of the cell was stable and close to 100%, regardless of the C-rate, using the LZ-DES/$2H_2O$ electrolyte. The last tests were performed using a Zn/LMO pouch cell with a capacity of 2000 mAh to demonstrate the potentialities of the developed electrolyte with an industrially relevant format. The measured energy density, at 0.2C and room temperature, was 52 Wh/kg and, after 160 cycles, the cell maintained a Coulombic efficiency above 96% and the capacity retention was 84.8%. To conclude, the article by Zhao *et al.* demonstrated the feasibility of a rechargeable

ZIB using a water-in-DES based electrolyte. Such electrolyte, combining the benefits of DES and water, was non-toxic, inexpensive and provided good performance and stability to the cell.

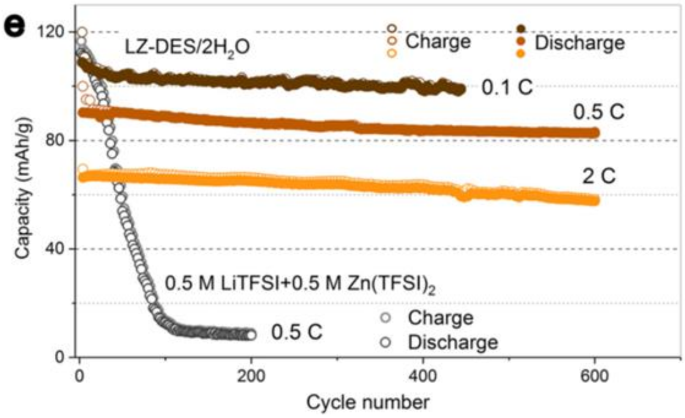

Figure 47. Capacity retention of the cell with the two electrolytes, LZ-DES/2H$_2$O and aqueous, at different C-rates.
Adapted and reprinted with permission from [58].

The study by Shi *et al.* developed a new electrolyte, based on a DES and water, to be used in rechargeable ZIBs [59]. The electrolyte used in the article was based on a DES, or ZES (zinc eutectic solvent), composed of ZnCl2 and acetamide, with a 1:3 molar ratio, and the addition of water. The "water-in-ZES" electrolyte, with a final composition 1:3:1 ($ZnCl_2$:acetamide:water), was defined ZES-1. The ZES-1 electrolyte was highly compatible with the Zn anode, since the water molecules were able to reduce the Zn(II) desolvation energy barrier through the regulation of Zn(II) solvation structure, promoting the uniform nucleation of Zn on the collector instead of on pre-existing sites.

The combination of Zn anode and ZES-1 electrolyte was tested in a Zn/Zn symmetric cell. The result demonstrated the great cycling stability of Zn anode, which could be cycled for 1400 h without any overpotential increase. Furthermore, the performance of ZES-1 electrolyte was further proved using it in a Zn/Ti half-cell. Such configuration remained stable for 1000 cycles, with a current density of 0.1 mA/cm^2, showing an average Coulombic efficiency of 98%. In the end, a full cell was assembled using Zn as the anode, phenazine (PNZ) as the cathode and ZES-1 as the electrolyte. The cell, tested between 0.4 and 1.2 V, showed a specific discharge capacity of 100 mAh/g at 1C and 65 mAh/g at 10C. Moreover, the cell capacity retention was remarkable at 1C, with a 76.1% after 1000 cycles, and outstanding at 10C, as shown in Figure 48, with 85.7% after 10000 cycles. The Coulombic efficiency was stable and close to 100% with both the C-rates. To conclude, the article by Shi *et al.* demonstrated the great potentialities of a "water-in-ZES" electrolyte in terms of performance, safety and low cost for rechargeable ZIBs. In particular, the new electrolyte was able to solve the cell poor cycling stability and the reversibility of the Zn anode, which were the main issues related to the traditional aqueous electrolytes.

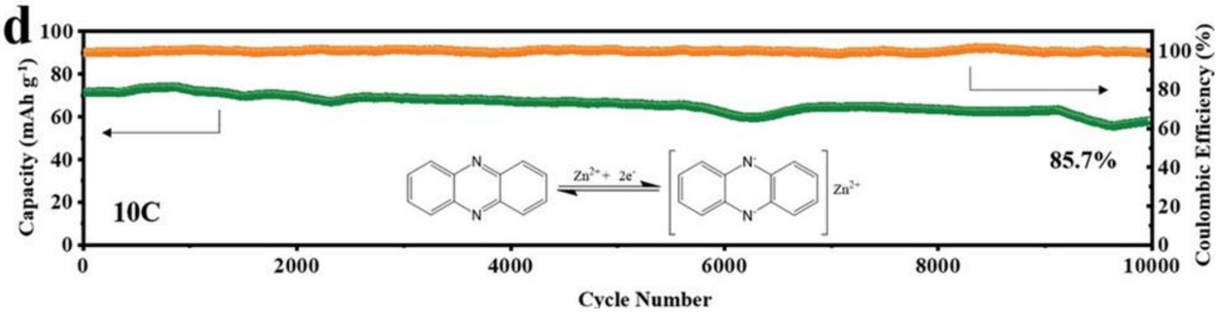

Figure 48. Cycling stability of the Zn| ZES-1|PNZ cell at 10C.
Adapted and reprinted with permission from [59].

3.9 Applications of DESs in zinc-air batteries

Zinc represents another interesting solution to be used in as the anode material for metal-air cells, similarly to the mentioned above aluminium. The reasons for that are related to the good theoretical gravimetric and volumetric energy density, *i.e.* 1218 Wh/kg and 6136 Wh/L, as well as to the zinc low cost and safety. However, Zn-air cells present important challenges that need to be addressed. The dendrites formation on the electrode surface, during the charging process, is one of the most important issues, which highly reduces the cell cycle life. Furthermore, the currently used aqueous alkaline electrolytes are the cause of the reduction in cell performance and cycling life due to the carbonate formation and electrolyte evaporation or absorption of water from the ambient air; therefore, it is crucial to develop new electrolytes in order to improve cells cycling life and efficiency [60].

Bozzini *et al.* investigated an operando scanning soft X-ray microscope (SXM) analysis of a Zn-air cell in order to map the Zn electrode using a lateral resolution of a few tens of nanometre [61]. The article used the SXM to study the cathodic and anodic processes of the Zn phase formation in an electrolyte based on choline chloride and urea DES with a 1:2 molar ratio. The DES negligible reactivity, in the potential range of electrodeposition, was observed using the cyclic voltammetry.

First of all, the results of a steady state experiment, after 1000 s of electrodeposition at -1.0 V, proved the clear formation of dendrites in both the high current density region, around 2.5 mA/cm^2, and the low current density region, around 0.5 mA/cm^2. Subsequently, the influence of time was tested on a new cell, again at -1.0 V, comparing low (0.5 mA/cm^2) and intermediate (1.2 mA/cm^2) current density regions. In both cases, the dendrites formation was similar and increased with time, as shown in Figure 49. To conclude, the report by Bozzini *et al.* proved the feasibility of the SXM, which could represent a fundamental source of information to control the dendrites formation and the modifications on the Zn electrode shape.

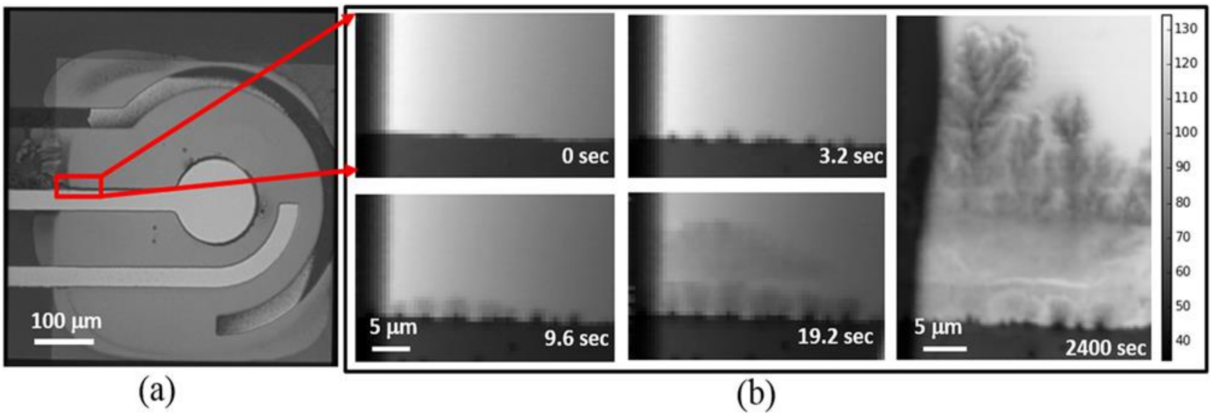

Figure 49. (a) Micro picture of the cell at the end of the experiment; (b) sequence of SXM pictures of a section of the cell at different instants of time. The scale bar for images in panel (b) is in arbitrary units.
Adapted and reprinted with permission from [61].

4. Conclusion

DESs are often considered as green solvents; therefore, a multitude of possible applications have been recently developed and there is still space for a further expansion, considering that they were investigated for the first time in literature just 20 years ago (2001). Interestingly, DESs present similar chemical and physical properties to those of ILs. However, DESs show significant advantages compared to ILs in terms of simple production, low cost, since they could be produced using largely used chemicals, and the general low toxicity, especially for type III DESs. Furthermore, all the DESs properties could be easily modified by choosing different components or changing their molar ratio, thus offering millions of possible properties variations.

Among the DESs possible applications, the metal processing applications are noteworthy, such as electrodeposition and electrofinishing, in which the DESs adoption might substitute the currently used aqueous solutions improving both the efficiency and the safety of the processes, or metal extraction, in which DESs-based solvometallurgical processes under mild operating conditions might replace the currently used processes based on high temperatures or hazardous solvents. Synthesis applications such as ionothermal synthesis, gas adsorption and the separation of biodiesel from glycerol represent other important fields for the application of DES-based processes. Furthermore, one of the main topic of this work, the DESs utilization as electrolyte in rechargeable batteries is another significant area of research.

The huge number of scientific publications on the DESs utilization for electrochemical applications, many of them analysed in this work, tells us that the DESs potentialities on this field are great. The applications were related to a plethora of different technologies: the well-established Li-ion cells, which are the market state of the art, metal-air cells, which are still far from the maturity, RFBs, Zn-based cells, Al-based cells, Na-based cells, etc. The main topics of the researchers investigation were the use of DES-based electrolyte, the synthesis of new electrodes using DES-based processes and the DES-based recovery of precious metal during the cell recycling processes.

As regards the DESs use for LIBs, which was the most investigated technology (in terms of number of articles), the studies analysed were mostly focused on the use of DESs as an alternative to the currently used electrolytes; the DES advantages were mainly the lower cost and higher safety, while the cell performance were generally comparable or inferior to the traditional solutions. Another aspect largely investigated was the recovery of precious metals from the cathode materials during the recycling process. In this case, the DESs allowed the utilization of solvometallurgical methods which ensured high efficacy under mild conditions.

Regarding the DES use for RFBs, the second most investigated technology, the articles main focus was related to the substitution of the currently used aqueous anolyte and catholyte with DES-based one in order to enhance the cells electrochemical performance. However, the use of the novel electrolytes presents important issues related to the high viscosity, which had to be faced increasing the operating temperature or mixing the DESs with additives.

The other technologies previously mentioned are, in general, not ready for the commercialization due to poor performance, short cycling life or both. Therefore, the articles about the use of DESs in those systems were mainly focused on understanding if DESs could represent a feasible solution to solve or, at least, mitigate the issues affecting each specific technology.

Among the previously analysed articles, one of most interesting was that by Xu *et al.* in which it was developed a microwave-assisted method using a ChCl:OA DES for the recovery of precious metals during the recycling of a Li-ion cell [29]. Such method presents a remarkable leaching efficiency, *i.e.* 96%, after just 15 min at 75 °C. Another absorbing articles was that by Jiang *et al.* in which a ChCl:TEA DES was used to synthetize a new porous electrode (NTP/C) that ensured astonishing performance and cycling stability to a sodium ion cell, *i.e.* 116 and 113 mAh/g at 5C and 20C, respectively, with a capacity retention at both C-rates of 99% after 1000 cycles [35]. In any case, one of the DESs most important drawbacks is the general high viscosity at room temperature causing poor ionic conductivity, which is probably the most important parameter for electrochemical applications. Therefore, the development of new DESs with low viscosity at room temperature or the use of additives for such purpose is crucial to expand the DESs fields of application.

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