Ionic Liquid Electrolytes as a Platform for Rechargeable Metal-Air Batteries: A Perspective

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Complete List of Authors:	Kar, Mega; Monash University, Simons, Tristan; Deakin University, MacFarlane, Doug; Monash University, Australia, Forsyth, Maria; Deakin University, Institute for frontier Materials; Deakin University,

Ionic Liquid Electrolytes as a Platform for Rechargeable Metal-Air Batteries: A Perspective

Authors: Mega Kar [a,c], Tristan J. Simons [a,b], Maria Forsyth [a,b], Douglas R. MacFarlane [a,c]

Affiliations:

[a] ARC Centre of Excellence for Electromaterials Science

[b] Institute for Frontier Materials (IFM), Deakin University Burwood Campus, Burwood, 3125, Victoria, Australia

[c] School of Chemistry, Monash University, Clayton, 3800, Victoria, Australia

Abstract

Metal air batteries are a well-established technology that can offer high energy densities, low cost and environmental responsibility. Despite these favourable characteristics and utilisation of oxygen as the cathode reactant, these devices have been limited to primary applications, due to a number of problems that occur when the cell is recharged, including electrolyte loss and poor efficiency. Overcoming these obstacles is essential to creating a rechargeable metal-air battery that can be utilised in efficiently capturing renewable energy. Despite the first metal-air battery being created over 100 years ago, the emergence of reactive metals such as lithium has reinvigorated interest in this field. However the reactivity of some of these metals has generated a number of different philosophies regarding the electrolyte of the metal-air battery. Whilst much is already known about the anode and cathode processes in aqueous and organic electrolytes, the shortcomings of these electrolytes (i.e. volatility, instability, flammability etc.) has led some of the metal-air battery community to study room temperature ionic liquids (RTILs) as a non-volatile, highly stable electrolyte that has the potential to support rechargeable metal-air battery processes. In this perspective, we discuss how some of these initial studies have demonstrated the capabilities of RTILs as metal-air battery electrolytes. We will also show that much of the long-held mechanistic knowledge of the oxygen electrode processes might not be applicable in RTIL based electrolytes, allowing for creative new solutions to the traditional irreversibility of the oxygen reduction reaction. Our understanding of key factors such as the effect of catalyst chemistry and surface structure, proton activity and interfacial reactions is still in its infancy in these novel electrolytes. In this perspective we highlight the key areas that need the attention of electrochemists and battery engineers, in order to progress the understanding of the physical and electrochemical processes in RTILs as electrolytes for the various forms of rechargeable metal-air battery.

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1.0 - Introduction:

As the world population grows and innovative technology requires significantly more energy to function, the requirements placed upon the dwindling fossil fuel reserves are accelerating. If we are to continue using energy for industrial processes, transport, electronics and domestic comforts at the current expanding rate, it is generally accepted that renewable energy sources such as wind and solar power will be needed to supply some of the demand.

However, the variability of the electrical supply that renewables provide has inhibited wider uptake into global markets. Cost effective, reliable energy storage mechanisms that can compensate for power supply fluctuations are desperately needed to overcome this issue.

Metal-air batteries are a class of battery that have received much attention of late due to the enormous theoretical capacities (several times current Li-ion technology) that are possible using materials which are a fraction of the price. These batteries use a metallic anode (made of pure metals such as lithium or zinc) whose oxidation into metal cations drives the reduction of dioxygen from the atmosphere at the cathode. Due to the fact that this device uses an abundant and free cathode oxidant (O_2), it is envisaged that successful secondary devices would be extremely cost efficient, have high energy densities and would be environmentally friendly.[1] Such devices are currently in a developmental phase with fundamental research attempting to overcome the many obstacles that confront large-scale rechargeable metal-air batteries. In some cases such as Zn-air, the recharge process is the current focus of attention. In others, such as lithium-air and magnesium-air even the discharge process for use as a primary device has been challenging.[2] But such are the rewards in a successful commercial metal-air device that research into overcoming these issues is being performed in many research laboratories around the world.

Metal-air batteries are unique among other electrochemical devices in that they are deliberately open to the atmosphere in order to allow dioxygen into the cell. One obvious complication from this fact is that, whilst it allows entry of air *into* the cell, it also allows the electrolyte to evaporate *out* of the cell through the porous cathode. Zn-air battery technology (currently the only established commercial metal-air device), which use aqueous electrolytes has struggled with this drying-out issue for over 100 years.[3]

Drying out is the principle reason that researchers have begun to focus on Room Temperature Ionic Liquids (RTILs) as metal-air battery electrolytes, since they can be extremely non-volatile, highly conductive and have been shown to support the electrochemistry of a number of metals.[4] RTILs are low temperature molten salts, composed entirely of organic cations and anions. The ions often have a delocalized or shielded charge configuration and this is responsible for the low melting point of the salt. They have been used in electrochemical devices such as lithium-ion batteries[5], fuel cells[6] and capacitors[7] – but due to high cost and their relatively short history of investigation, RTILs are not currently used in commercial devices.

The application of RTILs as metal-air battery electrolytes is a relatively new area of study that is steadily gaining traction in the electrochemical and engineering communities. Traditional metal-air battery electrolytes, such as those based on aqueous and organic liquids[8], are still considered to be the mainstream approach to addressing the shortcomings of this technology. Thus, if RTIL electrolytes are going to be successfully applied in rechargeable metal-air batteries, a fundamental understanding (such as there is for aqueous electrolytes) of battery processes needs to be developed. The aim of this perspective is to highlight the recent advances in understanding how RTIL electrolytes can support redox processes of metals at the anode[9], the oxygen reduction and evolution processes at the cathode[10] and showcase the relatively few examples of half and full cells operating with an RTIL electrolyte. With many key aspects of their physical, chemical and electrochemical behaviour not yet understood in the context of metal-air batteries, it is critical to combine the knowledge and skills of electrochemists, materials engineers and electrical engineers in order to advance this technology that could enable the more widespread adoption of renewable energy sources. Our goal here is to provide a perspective on the current state of knowledge in this field and highlight important areas for future study.

A Note on RTIL Nomenclature

Because RTILs have only relatively recently been promoted to widespread attention in the scientific literature, variation in abbreviations for both cations and anions has occurred. For simplicity and posterity, a single convention of naming RTILs and their acronyms has been used for this review, regardless of what was used in the original publication.

2.0 - The Oxygen Electrode Processes

The Oxygen Reduction Reaction (ORR) – that is the reduction of dioxygen gas to either hydrogen peroxide or water (Equation 1 and 2) – has been extensively studied in aqueous electrolytes of varying pH, such that the potentials, thermodynamics and mechanisms of the reactions are well understood when conventional catalysts (e.g. MnO_2) are used. As aqueous electrolytes are so cost efficient they continue to feature heavily in the scientific literature concerning the ORR, with many excellent reviews on the subject.[1, 11]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \text{Equation 1}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{Equation 2}$$

In spite of these benefits, it is apparent that if more reactive metals are to be utilized in a rechargeable metal-air cell, non-aqueous electrolytes that can support both ORR and Oxygen Evolution Reaction (OER) need to be investigated. The volatility of organic electrolytes and the low solubility of reaction products has caused several safety concerns to be raised, which is why the following explores the recent fundamental research investigating the ORR in non-volatile RTIL based electrolytes. Even though this reaction has been investigated extensively in aqueous and organic based systems, the mechanisms of ORR in RTIL electrolytes have only recently begun to be explored.

2.1 –The Oxygen Reduction Reaction (ORR)

During many of the initial studies of the ORR in various aprotic RTILs – that is RTILs that do not contain free or chemically available protons - it was observed that the reaction proceeded via a 1-electron quasi-reversible reduction of dioxygen to form superoxide ($O_2^{\bullet-}$), as shown in Equation 3 (See below and Scheme 1).[12-26]

$$O_2 + e^- \rightarrow O_2^{\cdot -} \qquad \text{Equation 3}$$

However this reaction has been found to be irreversible in some IL electrolytes - such as N-(3-Hydroxypropyl)pyridinium *bis*(trifluoromethanesulfony)imide ([NTf$_2$]).[27]

This quasi-reversibility has been demonstrated many times through cyclic voltammetry (CV) using glassy carbon (GC) or platinum (Pt) working electrodes in dioxygen saturated RTIL samples.[12] It has been determined that the nature of the working electrode – in this experiment the working electrode is also playing the role of the ORR catalyst – affects the mechanism by which the ORR proceeds. By changing the substrate or catalyst materials used, the observed over-potentials (η) and current densities of the reaction, which are key indicators of the potential performance and kinetics of the reaction in an electrochemical device can vary significantly.[12, 14, 20, 22-24, 26, 28-30]

These studies also raise the question as to how the seemingly reactive superoxide species can be stable enough to be re-oxidized back to dioxygen during the operation of a cell. Several studies, for example those of Barnes *et al.*[31] and Islam *et al.*[32], found evidence for ion-pairing between the superoxide generated via the ORR and imidazolium[26], ammonium[33] or phosphonium[34] cations of the RTIL. They proposed that this quasi-reversibility of the 1-electron ORR, was in fact due to this ion-pairing interaction which stabilizes the generated superoxide radical, allowing it to be re-oxidized during the reverse potential scan, rather than reacting with the surrounding molecules. Longer term experiments by Islam *et al.*[21] investigating the stability of superoxide in DMSO containing imidazolium chloride have found that superoxide is observable by UV-Visible spectroscopy for up to two weeks after the addition of KO$_2$, suggesting that an imidazolium cation may indeed be able to stabilize the superoxide species on a much longer time scale. It should be noted that the effect of DMSO on this interaction, as opposed to the RTIL electrolyte, was not explored.

While it is possible that these interactions may indeed stabilize the superoxide in some RTILs, the reality is that superoxide is not a particularly reactive radical species.[35] It is however, a strong nucleophile, meaning that it will react with any available protons in the electrolyte in a chemical reaction, as shown in Equation 4 (See below and Scheme 1).

$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot}$ Equation 4

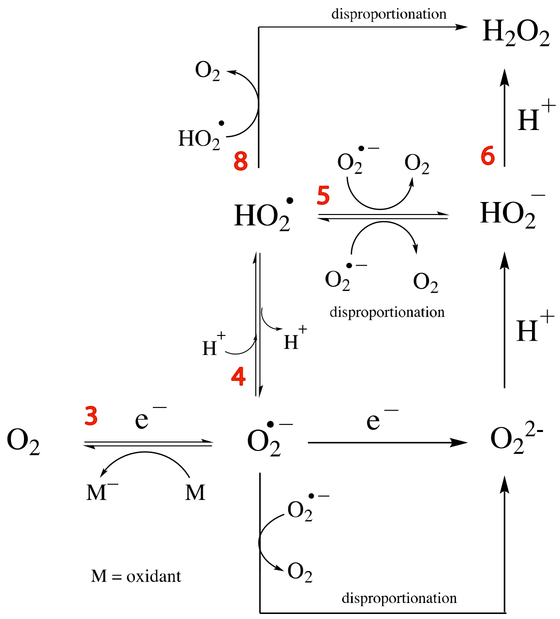
The origin and importance of this free proton has been the subject of many excellent papers in recent years,[10, 36, 37] as this chemical step also allows the second 1-electron reduction step to occur between the generated per-hydroxy radical ($HO_2^{\bullet}$) and an existing superoxide (Equation 5 below and Scheme 1):

$HO_2^{\cdot} + O_2^{\cdot -} \rightarrow HO_2^- + O_2$ Equation 5

This can undergo a final protonation step (Equation 6 below and Scheme 1) to form hydrogen peroxide (H_2O_2), completing the 2-electron reduction process of dioxygen.

$HO_2^- + H^+ \rightarrow H_2O_2$ Equation 6

For clarity, a summary of the chemical, electrochemical and disproportionation reactions of the 2- electron reduction of dioxygen to peroxide can be found in Scheme 1.



Scheme 1: Summary of the possible chemical, electrochemical and disproportionation reactions involved in the 2- electron reduction of dioxygen to hydrogen peroxide. Note - Numbers (red) indicate corresponding Equations in the text.

From Scheme 1, it is evident that in order to arrive at hydrogen peroxide, protons must be chemically available. Despite its relatively low acidity (pK_a = 15.7)[38], water has been used as a proton source in non-aqueous systems, but was found to impede 1-electron ORR reversibility due to a competing disproportionation reaction with the generated superoxide species (Equation 7).[34]

$$2O_2^{\cdot-} + H_2O \rightarrow O_2 + HO_2^- + OH^- \qquad \text{Equation 7}$$

Pozo-Gonzalo *et al.*[10] demonstrated that highly alkylated, hydrophobic phosphonium chloride RTILs do not support this disproportionation reaction, thereby allowing reversible 1-electron ORR even in the presence of up to 4.5 wt.% H_2O. It should be noted that this particular RTIL appears to be unique in this property and the exact mechanisms are as yet unexplored.

In a bid to probe the role of the proton in the ORR and its reversibility, researchers have investigated various proton sources other than water. Protic Ionic Liquids (PILs) have been investigated with respect to the ORR as they contain chemically available protons as part of the electrolyte structure.[39] Whilst PILs have shown great promise in both fundamental and applied studies in fuel cells[33, 40-42] the exact activity of protons is harder to quantify in this context than in traditional aqueous solutions.[43] For example, benzoic acid displays a pK_a of 4.2 in H_2O, 11.1 in DMSO and 21.5 in acetonitrile,[38] due to the varying dielectric constants of the media and the chemical properties of the acid. For this reason, researchers have been studying as wide a pK_a range as possible when investigating the effects of acidic additives on the ORR in RTILs.[37]

Another factor that will play a significant role in the ORR is the electrode material used and its catalytic ability towards dioxygen. Pt catalysts have been to shown to support the full 4-electron reduction of oxygen in PIL containing fuel cells[33], while electrodes based on GC and Au have shown a more modest ORR performance of either 1 or 2-electrons[12, 14, 28-30]. Despite this, pure Pt metal is prone to poisoning by carbon monoxide (CO). Johnson *et. al.*[33] have shown that residual H_2O present in the PIL facilitates the formation of Pt-O layers on the surface of the Pt metal which hinders the ORR and increases the overpotential required, even at higher temperatures (100 ˚C). For this reason, catalysts that bind oxide species more weakly than pure Pt metal will likely show more efficient ORR performance.

Rene *et al.*[25] have shown that the addition of a very weakly acidic molecule such as phenol (pK_a = 25 in H_2O)[38] is sufficient to progress the ORR from a 1-electron process to a 2-electron process in 1-ethyl-3-methylimidazolium ($[C_2mim]$)$[NTf_2]$, via the chemical protonation step (Equation 4, Scheme 1). The fact that superoxide and phenol behave as a weak base and acid respectively is overcome by the fast kinetics of the following disproportionation step. Following this, the usual disproportionation (Equation 5, Scheme 1) and protonation (Equation 6, Scheme 1) steps occur to complete the 2-electron reduction to hydrogen peroxide.

In order to probe this chemical protonation step in more detail, Switzer *et al.*[37] investigated a range of acidic additives spanning 30 pK_a units. Using the aprotic RTIL 1-butyl-2,3 dimethylimidazolium trifluoromethanesulfonate ([C_4dmim][OTf]) in conjunction with both Pt and GC working electrodes, a relationship was found between pK_a and the onset of ORR in the RTIL under study (Figure 1), despite the limitation of aqueous pK_a as an indicator of the actual proton activity in non-aqueous solutions.

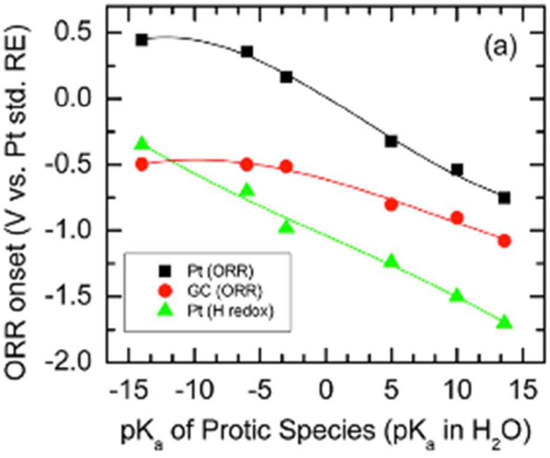


Figure 1: ORR reaction onset potentials vs pK_a (aqueous) in O_2 saturated 1-butyl-2,3-dimethylimidazolium Triflate ([C_4dmim][OTf]) containing 100 mM of various protic additives. Scan Rate 10 mV.s^{-1}, 1600 rpm. Reprinted with permission from (E. E. Switzer, R. Zeller, Q. Chen, K. Sieradzki, D. A. Buttry and C. Friesen, *Journal of Physical Chemistry C*, 2013, 117, 8683-8690.) Copyright (2013) American Chemical Society.

In particular, it was highlighted that, once the generated superoxide species had undergone protonation, it could suffer one of two possible fates, both shown in Scheme 1. Either the hydroperoxyl radical could combine to form hydrogen peroxide and dioxygen (Equation 8 below and Scheme 1), or it could undergo a further 1 electron reduction at the electrode to generate peroxide (Equation 9). From this point, the peroxide anion can undergo further protonation to complete the 2-electron reduction of dioxygen to hydrogen peroxide.

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad \text{Equation 8}$$

$$HO_2^{\cdot} + e^{-} \rightarrow HO_2^{-} \qquad \text{Equation 9}$$

This study by Switzer *et al.*[37] also produced the first confirmation of a 4-electron process in an aprotic RTIL containing protic additives – that is, the full reduction of dioxygen to water. Whilst the 2-electron reduction has been investigated in detail by several groups,[26, 34, 37, 39] the full 4-electron process has yet to be fully elucidated in RTILs. Several studies have cited the well established 2-electron reduction of hydrogen peroxide to water (Equation 10) as the mechanism of the second 2 electron reduction.[26, 34, 37, 39]

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \text{Equation 10}$$

The reaction proceeds to 4 electrons with relative ease on Pt electrodes, due the ability of Pt to catalytically decompose hydrogen peroxide into oxygen and water (Equation 11). The oxygen generated in this reaction can return to be reduced once again at the electrode. On GC WEs the second 2-electron step (Equation 10) was found to only be available at potentials more negative than -1.7 V vs Pt reference indicating that, while it was less efficient to complete the full reduction of dioxygen to water on GC than Pt, it was certainly possible.[37]

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \qquad \text{Equation 11}$$

Pozo-Gonzalo *et al.*[10] have also recently observed the full 4 electron reduction – in two 2-electron steps - on glassy carbon in a phosphonium chloride RTIL (tetradecyl-trihexylphosphonium chloride ($[P_{6,6,6,14}]Cl$) containing ethylene glycol (EG). Despite the relatively poor proton donating ability of EG (pK_a = 14.2 in H_2O[38]), it was proposed that self-stabilization of the EG after deprotonation allowed this reaction to proceed without the need for a highly acidic proton donor. Once again, the onset potential of the second 2-electron process was significantly more negative that the first 2-electron step, but became more positive with the addition of higher concentrations of EG (4.44 mmol), as shown in Figure 2.

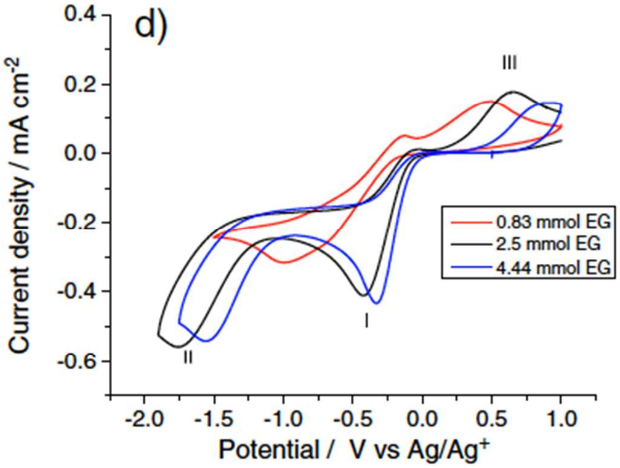


Figure 2: CVs of O_2 saturated $[P_{6,6,6,14}][Cl]$ containing various concentrations of EG (mM.g^{-1} of RTL) on GC working electrode, where the peak labelled I includes the reduction of oxygen to peroxide (defined by Equations 1,2 and 3, also in Scheme 1). The peak labelled II involves the reduction of peroxide to water (defined by Equation 9) and the peak labelled III includes the oxidation of peroxide back to oxygen. Reprinted from *Electrochem. Comm,* Volume 38, C. Pozo-Gonzalo, C. Virgilio, Y. Yan, P. C. Howlett, N. Byrne, D. R. MacFarlane and M. Forsyth, Enhanced performance of Phosphonium based Ionic Liquids towards 4 Electrons Oxygen Reduction Reaction upon Addition of a Weak Proton Source, Pages 24-27, Copyright (2014), with permission from Elselvier.

2.2 – The Oxygen Evolution Reaction (OER)

One key characteristic of the ORR in RTILs that has not been given a great deal of attention is the issue of reversibility. Whilst it has been shown that the first electron process in the ORR is quasi reversible – the difference in diffusivity between dioxygen and superoxide reduces the coulombic efficiency – subsequent protonation and reduction steps appear to be only sparingly reversible if it all.[39]

The OER has been extensively studied from the perspective of water splitting, which is the production of oxygen from water by oxidation, shown in Equation 10.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{Equation 12}$$

The defining challenge to the efficient oxidation of water to oxygen is the prohibitive over-potential required, which is why catalysts have been the primary focus for researchers in this field,[44-46] however an understanding of how these reactions proceed in RTIL media containing ORR products is largely unexplored.

Recent work by Izgoradin *et al.*[47] have explored the use of a hydrated PIL tetrabutylammonium bisulfate ($[N_{4,4,4,4}][HSO_4]$) in aiding the oxidation of water using MnO_2 as a catalyst. It was found that currents in the order of 1 $mA.cm^{-2}$ could be achieved at an overpotential of ~150 mV when the composition of IL/H_2O was 50/50 at a pH of 10, due to the ability of the cation to associate with the water molecules being oxidized (Shown in Figure 3). It was found that this hydrated IL composition performed far better than the traditional alkaline electrolyte.

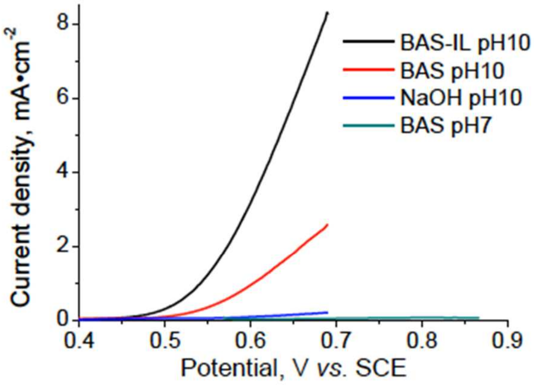


Figure 3: Linear Scan Voltammograms of MnO_x electrode the $[N_{4,4,4,4}][HSO_4]/H_2O$ electrolytes at low ionic strength (BAS), high ionic strength (BAS-IL) and NaOH electrolyte. Scan Rate: 1 $mV.s^{-1}$. Reproduced with permission from Reference 44 with permission from The Royal Society of Chemistry.

This study highlights the promise of using RTILs and various mixtures to support the OER in a rechargeable metal-air battery. This idea has been further developed by Pozo-Gonzalo *et al.*[10] who have shown that in the pure $[P_{6,6,6,14}][Cl]$ IL containing EG, full reversibility of the 2-electron process is possible, as the protonation and disproportionation reactions (Equations 4 & 5) do not exhibit a large enough free energy change to render them irreversible in this system. At this stage, reversibility of the 4-electron reduction of dioxygen to water has not yet been demonstrated in IL media and it is an area in which the focus of the electrochemical community should remain.

But it may also transpire that the 4-electron reduction of oxygen is not required to make metal-air rechargeable batteries viable for the consumer market. If the energy required to regenerate O_2 from H_2O is too great, the demonstrated reversibility in the 1- and 2-electron reductions discussed above may prove to be sufficient. This concept is demonstrated in Figure 4, where each step in the mechanism is represented. As the final 2-electron step from hydrogen peroxide to water happens in one large energy step, it may prove to be difficult to reverse efficiently. The possibility of stabilizing the peroxide product and using its proven reversibility may be the most effective path forward for the OER in RTILs.

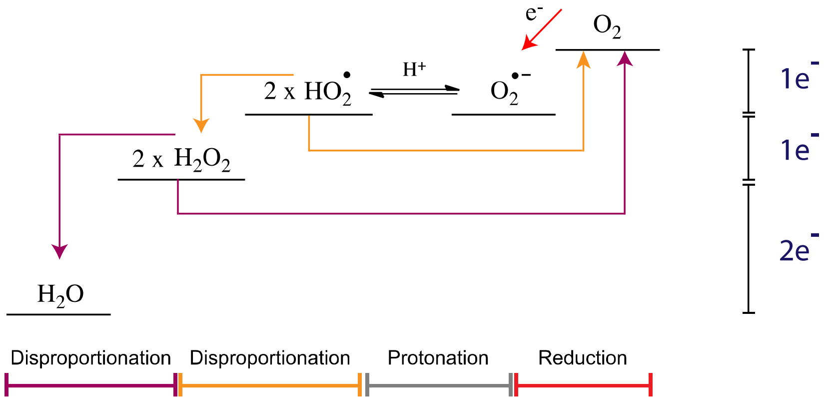


Figure 4: Representation of the steps for the ORR/OER in RTILs.

2.3 – Oxygen Solubility and Mass Transport

Another factor relevant to the development of secondary metal-air batteries is the mass transport characteristics of the active species in the electrolyte. As the rate at which the battery can be charged and discharged is often determined by the ability of the electrolyte to transport these species to the electrode, it is not surprising that the rates of diffusion of both dioxygen and superoxide in RTILs has been extensively studied.[28, 31, 39, 48] Many of these studies investigate the values of the diffusion and concentration of both dioxygen and the generated superoxide species (Table 1), concluding that oxygen is extremely soluble in IL electrolytes (usually in the range of a 1-10 mM)[22, 49], compared to distilled water (0.46 mM at 25 ˚C[50]). From Table 1 it can be seen that there is a wide range of solubilities and diffusivities for different RTIL species, however even the most modest are significantly greater than H_2O. Due to the limited understanding of ORR in RTILs and the fact that most studies concentrate on only one or two different electrolyte solutions, very few conclusions about appropriate anion or cation families can be drawn.

Table 1: Solubility of oxygen in various RTIL media, H_2O and DMSO + 0.1 M $[N_{4,4,4,4}][PF_6]$ at saturated oxygen levels.

RTIL	*C /(mM)*	*x 10^{-10} D_{O2} /$m^2.s^{-1}$*	*x 10^{-11} $D_{O2^{\bullet}}$ /$m^2.s^{-1}$*	*T/ ˚C*	*Ref*
$[C_2mim][NTf_2]$	3.9	8.3	2.7	20	27
$[N_{6,2,2,2}][NTf_2]$	11.6	1.5	0.5	20	27
$[C_4mim][PF_6]$	3.6	2.2	-	30	48[51]
$[C_4mpyr][NTf_2]$	6.1	5.2	3.5	35	29
$[P_{6,6,6,14}][NTf_2]$	6.0	7.5	-	35	29
$[P_{6,6,6,14}][FAP]$	7.8	6.1	-	35	29
$[C_2mim][BF_4]$	1.1	17	-	25	26
$[C_4mim][BF_4]$	1.1	12	-	25	26
$[C_4dmim][NTf_2]$	5.3	1.8	-	25	22
[MOPMMPip][a]$[NTf_2]$	14.3	1.0	-	25	34
$[C_6mpyr][NTf_2]$	14.5	2.5	-	25	34
$[dema][NTf_2]$	1.79	11	-	25	32
$[C_4mpyr]$[beti][b]	10.7	3.0	-	30	45
$[C_4mpyr][IM_{14}]$[c]	14.3	2.0	-	30	45

H_2O dist.	0.46	19.7	-	20	38
DMSO + 0.1M $[N_{4,4,4,4}][PF_6]$	2.1	9.7		22	49[52]

[a] 1-3methoxypropyl-1-methylpiperidinium
[b] *bis*(pentafluoroethanesulfonyl)imide
[c] (nonafluorobutylsulfonyl)(trifluoromethanesulfonyl)imide

Monaco *et al.*[48] have studied the diffusion of both dioxygen and superoxide in RTIL electrolytes, determining that the diffusion of oxygen was in the region of 10 x 10^{-6} $cm^2.s^{-1}$ depending on the RTIL under study. It should be noted that due to the range of techniques and temperatures used to determine diffusion coefficients in ILs, the values that have been reported span several orders of magnitude.[34, 37, 39] Monaco *et al.*[48] have also observed that the diffusion of superoxide was much slower (by a factor of 30) than dioxygen, causing an imbalance that can change the reduction onset and shape of observed CVs.

The inequality of diffusion coefficients of dioxygen and superoxide has been discussed in several studies.[28, 48] Zigah *et al.*[53] have shown that by adding dimethylformamide, the diffusion coefficient of superoxide can be increased through disrupting coordination to other components of the electrolyte. This interaction of superoxide with RTIL ions has been interpreted as a stabilizing factor[32], but it also appears to retard the motion of superoxide, thus, making its oxidation an inefficient, quasi-reversible process.

2.4 – Catalysts

Apart from considering the relevant discharge products and oxygen solubility, work also needs to be done in order to decrease the over-potentials required and the kinetics of the ORR/OER, which can be optimised by investigating the relationship between the electrolyte and the catalyst.

When considering a metal-air rechargeable battery the air cathode must be able to perform both the ORR and OER efficiently. Electrodes that contain separate catalysts for the ORR and OER reactions (dual electrodes) as well as the rare examples of catalysts that can perform both the ORR and OER efficiently (bifunctional electrodes) have both been extensively investigated in aqueous[54-56] and organic electrolytes.[54, 57-59]Many groups of catalysts such as metals[60, 61], transition metal oxides[1, 62] and functional carbon materials[63] have been investigated for their potential to provide catalytic behaviour for ORR. Whilst metals such as platinum have shown high catalytic activity in respect of the ORR in alkaline media, however the metal is expensive and limited in supply. There is ongoing work in trying to overcome some of these challenges by mixing Pt with other metal alloys[61, 64-66] or replacing Pt altogether with cheaper metals such as silver[66]. Alternatives such as metal oxides, i.e. MnO_2 have also been shown to facilitate both ORR and OER reactions, raising significant interest in their role as bi-functional catalysts.[54, 62, 67]

Much of the work on the use of MnO_2 and other single and mixed metal-oxides that have been applied in aqueous and non-aqueous electrolytes shows that information such as the crystallographic structure, porosity and the addition of additives can yield insights into the mechanism of action of these catalysts. The excellent performance of MnO_2 in aqueous systems has encouraged investigators to begin to study this catalyst family for ORR in RTILs, For example, recently it has been shown[68] that RTILs blended with MnO_2 can further increase the performance of the MnO_2 catalyst. *N*-ethyl-*N*′-(3-dimethyl aminopropyl) carbodiimide methiodide incorporated into graphene nanosheets showed high ORR catalytic activity in Zn-air batteries, "with a maximum peak power density of 120 mW cm^{-2}; a higher performance than that from commercial cathode catalysts". Although the use of this RTIL played a key role in the increased catalytic activity of MnO_2, the reduction pathway (2 x 2-electron or 4-electron) was dominated by the quantity of MnO_2 loaded on the graphene sheets. Highly concentrated manganese oxide may result in poor ORR and force the process into the 4-electron pathway.

2.5 – The Effect of Metal Ions

A further consideration of researchers investigating the ORR in ILs for secondary metal-air batteries, is the presence of a metal anode that will invariably release metal cations (Li^+, Mg^{2+} etc.) into the electrolyte as the battery is discharged. The phenomenon of insoluble by-products being formed at the anode and/or cathode has been observed previously in both aqueous and non-aqueous electrolytes.[69] Several studies[36, 37, 70] have revisited the formation of such metal salts in RTILs in a bid to understand how the presence of metal cations can play a role on the ORR products formed. De Giorgio *et al.*[70] have investigated several additives on the ORR reaction in 1-propyl-1-methylpyrrolidinium ([C_3mpyr]) [NTf_2]. The addition of Li^+ cations in the form of $LiNTf_2$ was found to have a detrimental effect on the ORR, rendering it irreversible and reducing the observed currents, as had been observed previously by Monaco *et. al.*[48] It was proposed that the Li^+ caused the generated superoxide species to become unstable and form a lithium/oxygen salt, which was insoluble in the electrolyte and coated the electrodes, which in turn reduced the catalytic performance. The removal of the superoxide also prevented the reaction from being electrochemically reversible. When tetrafluoroborate ([BF_4]) anions were added to the system, the reaction currents were improved while the ORR remained irreversible which suggests that this additive increases the solubility of the lithium/oxygen by-products, but does not prevent the degradation of the superoxide species.

This ability for certain additives to control the nature of the ORR products was the topic of an excellent study by Allen *et al.*[36] who used NMR spin-lattice relaxation measurements to evaluate the Lewis acidity of various additives in both [C_2mim][NTf_2] and 1-butyl-1-methylpyrrolidinium ([C_4mpyr])[NTf_2] electrolytes. Superoxide is by nature a soft Lewis base and found to be stabilized by soft Lewis acids such as tetraalkylammonium or imidazolium cations – explained previously as “ion-pairing”. Upon addition of low concentrations of hard Lewis acids (such as Li^+, H^+ or K^+), superoxide was found to disproportionate into hard Lewis bases such as O_2^{2-} or O^{2-}, which then formed very stable metal salts that displayed low solubility in the RTIL (Equation 13). This also had the effect of increasing the potential required to re-oxidize that same species back to dioxygen (the OER) as the hardness of the Lewis acid increased (Figure 5).

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \qquad \text{Equation 13}$$

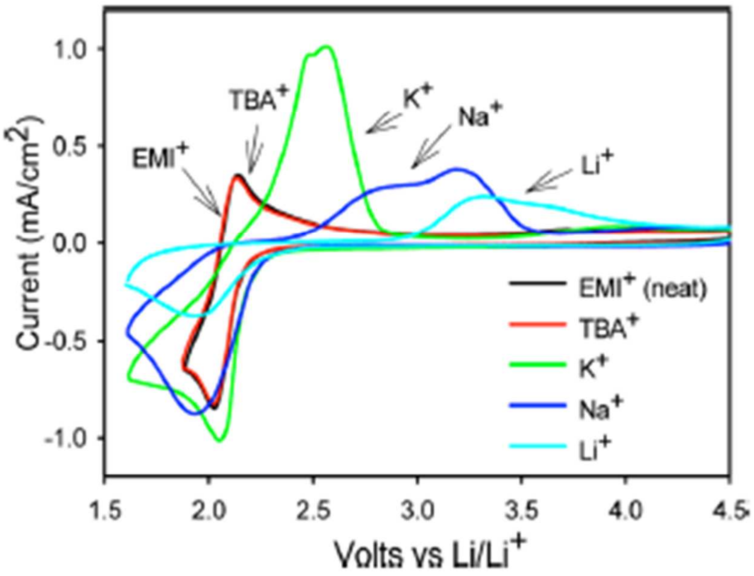


Figure 5: CVs of neat [C_2mim][NTf_2] with various salts (C = 25 mM) of a GC electrode at 100 mV.s^{-1}. Reprinted with permission from C. J. Allen, J. Hwang, R. Kautz, S. Mukerjee, E. J. Plichta, M. A. Hendrickson and K. M. Abraham, *Journal of Physical Chemistry C*, 2012, 116, 20755-20764. Copyright 2012 American Chemical Society.

Using the Hard/Soft theory for acids and bases, it also becomes evident why addition of acidic species promotes the 4-electron reduction of oxygen in ILs as shown by Switzer *et al.*.[37] As the concentration of the hard acid H^+ is increased, superoxide disproportionates to form a higher proportion of the hard base product– in this case peroxide (O_2^{2-}), shown in Scheme 1. The peroxide formed undergoes a final disproportionation to oxide (O^{2-}), generating the stable H_2O and dioxygen (Equation 11). This pathway involves several intermediates that are include but are not limited to those numbered in Scheme 1.

As well as providing a clear model to predict the ORR mechanism, this study also provided methods by which RTIL electrolytes could be "tuned" to more desirable reduction pathways. For example, the addition of organic solvents (such as DMSO) was shown to coordinate to certain hard acids and have the effect of making them softer, reducing the extent to which they promoted disproportionation of superoxide.

It is in this concept that the paradox currently facing metal-air battery researchers resides. The ultimate energy storage capacity offered by rechargeable metal-air technologies lies in the ability to reversibly reduce and oxidize all 4 electrons in the dioxygen/water couple. However, as hard Lewis acid additives are added to drive that reduction process to its full extent, the ability to easily recover those electrons from the now lost superoxide species has been sacrificed.

This problem may be better understood through an understanding of the thermodynamics of the disproportionation couples, or by providing a way for the hardness of the Lewis acids present to be altered depending on the state of charge. This obstacle to secondary metal-air batteries is one that can only be overcome through elegant scientific solutions, driven by the combined efforts of the electrochemical and battery communities.

2.6 - ORR in Practical Metal-Air Batteries

Zinc

While it is important to understand the fundamental science involved in the ORR/OER reactions alone, it is just as vital to understand how these processes combine with a metal anode to make a working electrochemical device. One example is the commercial primary zinc-air battery, which is widely used in hearing aids. The device uses an aqueous potassium hydroxide [KOH] electrolyte and MnO_2 is used as an electro-catalyst for the reduction of dioxygen.[71] The reversibility of these batteries is hindered due to the over-potential required to re-oxidize the $Zn(OH)_4^{2-}$ complex in the presence of the alkaline electrolyte (See Scheme 2 below), and the inefficiency of replating Zn metal onto the electrode caused by side reactions such as the production of hydrogen gas.

Anode: $$Zn_{(s)} + 4OH^{-}_{(aq)} \longrightarrow Zn(OH)_4{}^{2-}_{(aq)} + 2e^{-} \qquad E^0 = -1.26\text{ V} \qquad \text{(i)}$$

Electrolyte: $$Zn(OH)_4{}^{2-}_{(aq)} \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2OH^{-}_{(aq)} \qquad \text{(ii)}$$

Cathode: $$O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \longrightarrow 4OH^{-}_{(aq)} \qquad E^0 = +0.40\text{ V} \qquad \text{(iii)}$$

Overall: $$\boxed{Zn_{(s)} + 1/2O_{2(g)} \longrightarrow ZnO_{(s)} \qquad E = 1.66\text{ V} \qquad \text{(iv)}}$$

Scheme 2: Main chemical reactions occurring in a zinc-air cell in an aqueous alkaline electrolyte.

In the presence of air, reactions apart from the ORR and OER also need to be considered in a zinc-air battery. Since these_cells require atmospheric oxygen, a major obstacle to long cycle-life is that of carbon dioxide (CO_2) entering from the atmosphere. CO_2 then reacts with the hydroxide ions present in the alkaline electrolyte to form potassium carbonate (K_2CO_3) precipitates, which can clog the pores of the cathode, reducing battery life. Although attempts to use anion exchange membranes to prevent the formation of the carbonate precipitate have been reported,[72] it is also important to consider moving away from alkaline electrolytes.

Lithium

In lithium-air batteries, the choice of electrolyte is limited to those that are stable to lithium metal. The formation of lithium peroxide (Li_2O_2) is desired in order to facilitate the reversible overall reaction $2Li + O_2 <-> Li_2O_2$[73-75] via the reactions in Scheme 3. Although it is evident from Scheme 3 that lithium superoxide (LiO_2) is an alternate discharge product that can be formed via a 1-electron pathway (3i), it almost immediately undergoes a disproportionation reaction (3ii), or a further reduction (3iii), to produce the Li_2O_2. Although reduction of O_2 can also produce lithium oxide [Li_2O] (3iv), this intermediate also readily reacts to form Li_2O_2.[1, 76-78]

$$Li^+ + O_2 + e^- \longrightarrow LiO_2 \qquad \text{(i)}$$

$$2LiO_2 \longrightarrow Li_2O_2 + O_2 \qquad \text{(ii)}$$

$$LiO_2 + Li^+ + e^- \longrightarrow Li_2O_2 \qquad \text{(iii)}$$

$$Li_2O_2 + 2Li^+ + 2e^- \longrightarrow 2Li_2O \qquad \text{(iv)}$$

Scheme 3: Reactions in a lithium-air cell.

Many authors have studied a range of non-aqueous solvents[76, 79-86] such as organic carbonates,[78] ethers,[81] acetonitrile[86] and dimethoxyethane,[85] for this battery however, concerns were raised on solvent volatility, decomposition and the formation of insoluble lithium carbonate (Li_2CO_3) which is produced by the reaction between the organic carbonate electrolyte and lithium metal.[75, 85] Interestingly, Bruce *et. al.*[87] have also shown that Li_2CO_3 can also be formed at ORR electrode, which decreases shelf-life due to the decomposition of the organic electrolyte. The use of RTILs as electrolytes in these batteries is currently being widely researched. Some RTILs, such as [C_3mpyr][NTf_2], have already been shown to produce O_2 during charge, indicating the reversible formation of the discharge product Li_2O_2.[88, 89]

However, further work is required to quantify the Faradaic efficiencies in this electrolyte. In their work, Cecchetto and co-workers have emphasised the importance of electrolyte composition, which can affect oxygen reaction kinetics.[90] By adding [C_4mpyr][NTf_2] to lithium trifluoromethanesulfonate (LiOTf) in tetraglyme [TG], reversible oxidation of Li_2O_2 was observed via XRD analysis, while reduced bulk resistance and charge transfer resistance were demonstrated through electrochemical impedance spectroscopy (EIS) measurements. This work suggests that the kinetics of oxygen reactions are faster in [C_4mpyr][NTf_2]/ [LiOTf]/TG mixtures compared to other electrolytes. Nevertheless highly reversible cycling must be achieved and the concentration of the electrolyte components is yet to be optimised.

Much work has also been directed towards utilizing hydrophobic RTILs (such as [C_2mim] [BF_4] and [C_2mim][NTf_2][91]) in the Li-air context, the goal being to minimise water uptake in the electrolyte. It was hypothesised that the use of hydrophobic RTILs would prevent corrosion reactions at the anode and thus increase the performance of the battery. Moreover, when cobalt phthalocyanine was the ORR catalyst, the use of these RTILs produced discharge capacities as high as 5360 mAh.g^{-1} at a current density of 0.01 mA.cm^{-2}. Nonetheless the long-term efficiency of the battery was still compromised due to atmospheric moisture entering the cell and corroding the lithium metal anode; the presence of moisture can also disrupt the formation of Li_2O_2 (Scheme 3) and create H_2O_2 in the cell.

In order to overcome the challenges of using expensive catalysts such as cobalt phthalocyanine and preventing traces of water entering from the atmosphere, Zhang *et al.* investigated $LiNTf_2$ in the hydrophobic RTIL $[C_4dmim][NTf_2]$ mixed with silica in a PVdF-HFP polymer composite.[80] It was proposed that the gel type electrolyte would mitigate the penetration of the moisture to the lithium anode. Although this resulted in long time operation of the cell, the discharge capacities in this system were much lower (2800 mAh.g^{-1} at current density of 0.02 mA.cm^{-2}) than that reported by Kuboki *et. al*.[91]

3.0 - Anode Reactions

While it would be accurate to say that the over-potential associated with reversing the ORR at the cathode is the most fundamental obstacle that needs to be overcome in the development of rechargeable metal-air batteries, the importance of the electrochemical processes occurring at the anode cannot be underestimated. As the name "metal-air battery" suggests, the anode is usually a metal in its zero oxidation state, which is one of the reasons for the high specific energy of this class of batteries. Zinc, with its stability to air and water, has been used in such devices for over 100 years,[92] largely due to its excellent performance in simple aqueous electrolytes. More recently, reactive metals such as lithium[93] have come to the fore, enabled by organic electrolytes that are more stable at the very large potentials involved. These advances have also generated renewed interest in the more challenging metals such as aluminium[94] and magnesium[9], in the hope that these abundant materials can be harnessed for energy storage applications.

Regardless of the metal under study, all metal anodes will undergo oxidation to their cationic species during discharge, according to Equation 14.

$$M_{(s)} \rightarrow M^{n+}_{(electrolyte)} + ne^{-} \qquad \text{Equation 14}$$

Where ne^{-} is the number of electrons produced per atom of metal ($M_{(s)}$) oxidized and $M^{n+}_{(electrolyte)}$ is the metal cation, which can either be solvated by the electrolyte, or form a solid precipitate.

Table 2 outlines the charge density and the energy density (vs O_2) of several metals commonly investigated for metal-air batteries.

Table 2: Reduction potential and specific capacities of several metals.

Metal	ρ (g.cm^{-3})	n electrons	Theoretical Capacity		E^0 (V) vs. SHE	Theoretical Energy Density (excl. O_2)	
			mA.h.cm^{-3}	mA.h.g^{-1}		W.h.dm^{-3}	W.h.kg^{-1}
Li	0.53	1	2060	3860	-3.04	7050	13200
Zn	7.14	2	5850	820	-0.76	6800	950
Mg	1.74	2	3830	2210	-2.37	10500	6050
Na	0.97	1	1120	1170	-2.71	3510	3630
Al	2.70	3	8040	3820	-1.66	16600	6150

It can be seen in Table 2 that different metals can provide vastly different amounts of capacity, derived from the varying ability to donate electrons at different redox potentials. Of the elements listed, only zinc has a reduction potential more positive that water at pH = 7, meaning it alone can utilize aqueous electrolytes without reducing water to hydrogen gas during battery operation.[92] In some cases where the metal has a reduction potential more negative than water, organic electrolytes (such as carbonates) have been utilized with varying success, however, safety issues such as flammability and volatility have been demonstrated.[95]

There are several problems that are common to most metal anodes in metal-air rechargeable batteries:-

- The oxidation product of the metal can form insoluble salts that may passivate either the anode or cathode, preventing the battery from functioning
- The metal may not undergo efficient reduction from the electrolyte back to the anode during recharging
- If it can support recharging, it may not produce the smooth metal surface that is required to prevent short circuits
- It may be unstable to products formed at the ORR cathode
- It may react with the electrolyte and create breakdown products detrimental to battery operation

In the past, these issues have been overcome in several ways. As mentioned above, organic electrolytes have been used to overcome the issue of electrolyte breakdown of reactive metals.[95] Additives have often been used in electrolytes – similar to brighteners in electroplating – to ensure smooth metal surfaces during recharge.[96] Mechanical recharge – that is physically replacing a depleted anode and electrolyte at the end of a discharge – has been proposed as a method for systems that simply cannot re-oxidize the ORR products.[97]

These issues can be overcome through innovative electrolyte design. Electrolytes that are stable to the metal (high electrochemical stability), can solvate large concentrations of metal cations, facilitate efficient metal cation reduction and can also support the ORR/OER are difficult to find. RTILs, with their unique physical properties, have been proposed as a possible candidate for metal-air battery electrolytes. [98] The wide variety of physical properties generated from the sheer number of different anions and cations available results in a class of truly “tunable” electrolytes.

Despite the obvious benefits of applying such a versatile electrolyte class to full cells, the lack of fundamental understanding of battery processes in RTIL electrolytes has meant that most studies in this area are fundamental investigations using traditional electrochemical techniques such as a 3-electrode cell using cyclic voltammetry (CV),[99] chronoamperometry (CA)[100] and symmetrical cells.[98]

3.1 - Zn-air

As the standard reduction potential of zinc is more negative than the hydrogen evolution reaction (HER) at pH = 13, (E^0 (Zn/Zn^{2+})= -1.25 V SHE; E^0 (H_2O/H_2) = -1.18 V vs. SHE at pH = 13)[38] even the most promising attempts to electrodeposit zinc from aqueous electrolytes during recharge have only managed around 60-70% efficiency.[29, 101] This is due to the HER, which in the past has been suppressed by additives such as mercury in the zinc electrode. Even if the environmental issues of mercury are ignored, additives such as these are effective only for one or two cycles before being consumed.[29, 101] RTILs have been extensively studied as electrolytes for electrodeposition of metals, and the authors suggest the following reviews as an excellent resource for a more in depth discussion of that topic.[4, 102] Yamamoto *et al.*[103] were one of the first groups to investigate RTILs for Zn deposition processes, achieving smooth deposits from trimethylpropylammonium ($[N_{1,1,1,3}]$)[NTf_2] with EG as an additive. Several groups since have been investigating RTILs specifically for Zn based battery applications. Deng *et al.*[104] found that many metals could be both deposited and stripped from [C_2mim] dicyanamide ([dca]), later investigating Zn electrochemistry in [C_4mpyr][dca][105]. It was concluded that the RTIL could support favourable deposition onto Mg substrates due to the formation of a $Zn(dca)_3^-$ complex anion, which resulted in smooth morphologies of deposited Zn. It is possible that the nitrile groups contained in the dca anion perform a role analogous to the cyanide anion (CN^-) with regard to Zn^{2+} complexation, as cyanide has been a particularly successful brightener in the Zn electroplating industry for many years.[106]

From this work, Simons *et al.*[99] refined the conditions under which [C_2mim][dca] could support reversible Zn electrochemistry. It was found that [C_2mim][dca] + 3 wt% H_2O + 10 mol % $Zn(dca)_2$ displayed high current densities on both deposition and stripping (40 mA.cm^{-2} and 70 mA.cm^{-2} respectively), as well as reduced Zn over-potentials for deposition onto GC substrates. It was also found that the presence of the minor component of water facilitated smoother Zn surfaces (Figure 6). The coordination of Zn in the electrolyte was never fully identified, however, strong evidence for a complex ion of the type $Zn(dca)_x^{(2-x)}$ was found using FT-IR techniques, complementing the work done previously by Deng *et al.* in [C_4mpyr][dca].[105, 107]

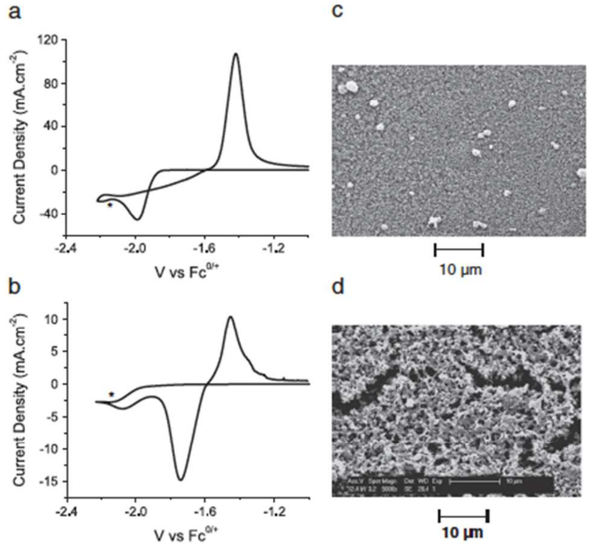


Figure 6: CVs and SEMs of 10 mol% $Zn(dca)_2$ in [C_2mim][dca] on GC WE held at -2.15 V vs Fc$^{0/+}$ for 10 mins at different H_2O concentrations a) CV of 3 wt% H_2O b) CV of 0.05 wt% H_2O c) SEM of 3 wt% H_2O d) SEM of 0.05 wt% H_2O. Reprinted from *Electrochemistry Communications, Vol* 18, High current density, efficient cycling of Zn2+ in 1-ethyl-3-methylimidazolium dicyanamide ionic liquid: The effect of Zn2+ salt and water concentration, T. J. Simons, A. A. J. Torriero, P. C. Howlett, D. R. MacFarlane and M. Forsyth, 119-122, Copyright (2012), with permission from Elselvier.

Further fundamental studies of Zn electrochemistry have also been performed in RTILs based on [C_2mim], [C_4mpyr], [NTf_2] and [dca] containing $Zn(NTf_2)_2$.[3, 108] Zinc electrochemistry was found to be quasi-reversible and cycleable in all of the NTf_2 and dca RTILs under study, however, the addition of water was found to increase current densities at the expense of electrochemical stability.[3] In a separate study of [C$_2$mim][dca] containing Zn(NTf$_2$)$_2$, DMSO was added to the water-containing RTIL.[108] At a mole ratio of [C$_2$mim][dca] : H$_2$O : DMSO of 1:1:2.3, the electrolyte showed very stable and reversible zinc electrochemistry, albeit at a modest current density (less than 5 mA.cm^{-2}). When the concentration of water was increased (such that the ratio was 1:6.6:2.3), the current densities and zinc deposition currents increased to 15 mA.cm^{-2}. Unfortunately, this increase came at the cost of cycling stability as the reoxidation of zinc was nearly eliminated completely by the 100th cycle (Figure 7). It was shown that this was due in part to passivating deposits of ZnO at the electrode surface.

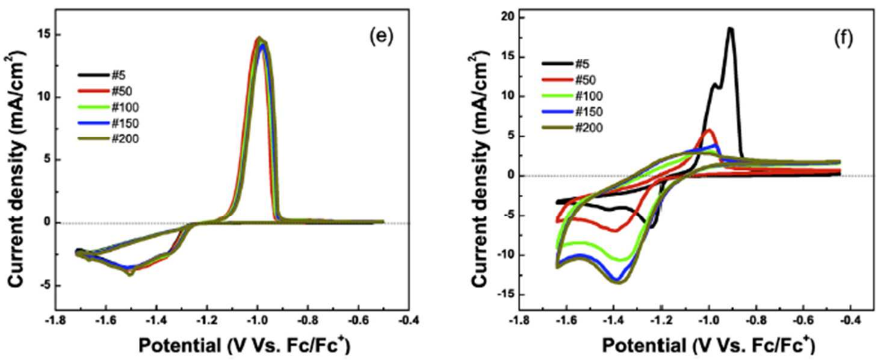


Figure 7: Cyclability of Zn$^{0/2+}$ in [C$_2$mim][dca] based electrolytes e) [C$_2$mim][dca] : H$_2$O : DMSO = 1:1.1:2.3 f) [C$_2$mim][dca] : H$_2$O : DMSO = 1:6.6:2.3 Reprinted from *Journal of Power Sources*, 252, Improved Zn/Zn(II) redox kinetics, reversibility and cyclability in 1-ethyl-3-methylimmidazolium dicyanamide with water and dimethyl sulfoxide added, M. Xu, D. G. Ivey, W. Qu and Z. Xie, 327-332, Copyright (2014), with permission from Elselvier.

Previously electrodeposition processes have been optimized by using either charged (eg oxalate) or chelating species (eg tetraglyme) to coordinate the metal cation prior to electroreduction.[109, 110] Kar *et al.*[111] have attempted to combine these properties into novel RTILs based on ether-containing ammonium cations and NTf$_2$ anions. The motivation of this work was to chelate the Zn^{2+} species with the ether oxygens of the cation, allowing it to be reduced from this species more favourably than from complex species involving the NTf_2 anion.

These results show excellent promise in using RTILs as media for reversible zinc electrochemistry, however combining the RTILs with effective additives – such as DMSO or EG offers further potential for improvement. Recent results have shown excellent progress in this regard, although the quest to find a RTIL electrolyte to support highly reversible zinc electrochemistry capable of long cycle life is a challenge that remains for the metal-air battery community.

3.2 Lithium Cycling with Regard to Lithium-Air

With its extremely high specific energy (3860 $mA.h.g^{-1}$) and negative reduction potential (-3.04 V vs SHE), lithium metal enables lithium-air batteries to have one of the highest specific energy densities (5200 $Wh.kg^{-1}$ including oxygen), however its extreme reactivity with atmospheric components such as O_2 and H_2O make utilizing lithium metal anode in non-hermetic environments a key challenge to this technology[29, 75, 95, 112]. The metal is also highly reactive to protic solvents as well as many organic solvents. This high reactivity towards most electrolytes has led to challenges when trying to replate lithium metal during the recharging process. In many liquid electrolytes, a non-uniform multilayer structure may be formed on the metal known as a solid-electrolyte interphase (SEI), which can result in uneven current distribution resulting in dendritic growth of the metal. [89, 113, 114] On the other hand, the SEI is designed to prevent reaction between the lithium metal and the electrolyte while still allowing the passage of lithium cations.[115] Despite this, these multilevel SEI layers can still break down, eventually causing degradation of the lithium anode. For this reason, electrolytes have traditionally been successful when they can form stable SEI layers that are selectively permeable only to Li^+, thereby preventing further breakdown of the electrolyte and lithium metal corrosion.

As Rahman and Wang [75] have summarised in their review on lithium-air batteries, certain elements (eg F) and atmospheric components (CO_2) can lead to successful SEI layers. The ability to control the atomic composition of RTILs creates an exciting opportunity to design electrolytes that have favourable physical properties as well as optimal SEI forming ability. Many authors, such as Ye *et al.* have shown promising electrochemical cycling efficiencies in their early investigations of Li/O_2 battery processes in the presence of RTILs[116] incorporated in a polymer gel, by controlling the SEI and preventing undesirable reactants reaching the cell surface. However it was suggested that crossover from the cathode to the lithium anode needs to be prevented in order to prevent further degradation of the battery. Altering the type of RTIL cation or anion may aid in preventing this crossover.

In their work, Zhang *et al.*[80] used an electrolyte based on a hydrophobic RTIL $[C_3dmim][NTf_2]$ mixed with a silica-PVdF-HFP polymer composite to supress lithium corrosion, by reducing even trace amounts of moisture from entering their lithium-air cell. At a current density of 0.02 $mA.cm^{-2}$ in ambient atmosphere, discharge capacities up to 2800 $mA.g^{-1}$ (excluding the O_2 catalyst) were observed owing to a “stable interface resistance and better waterproof conditions ” (Figure 8).

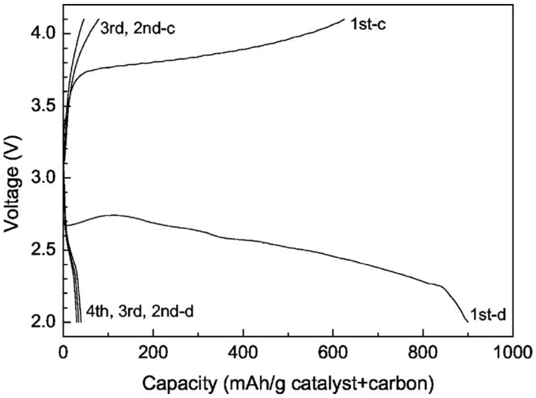


Figure 8: Discharge/charge curves of a preliminary Li/O_2 cell based on the 1 M $LiNTf_2/[C_3dmim][NTf_2]$/PVDF-HFP polymer gel electrolyte membrane. Current density is 0.05 $mA.cm^{-2}$ of cathode. Reprinted from Journal of Power Sources, 195, D. Zhang, R. Li, T. Huang and A. Yu, Novel composite polymer electrolyte for lithium air batteries, 1202-1206, Copyright (2010), with permission from Elselvier.

3.3 - Magnesium-Air

In recent years, magnesium has received increasing attention in energy storage applications. Due to the high abundance and low cost of magnesium metal, magnesium-based devices (such as Magnesium-Air batteries) have been a key focus of the automotive industry, where high capacity and low cost batteries could see a wider adoption of Electric Vehicles (EVs).

Magnesium metal offers many of the same challenges as lithium and sodium; it is a reactive metal that is unstable to water, oxygen and most organic compounds. It forms a porous corrosion layer which allows further corrosion and it is reduced at relatively negative reduction potentials (-2.36 V vs SHE)[38] where many electrolytes are reactive. Many studies have investigated magnesium intercalation electrodes (similar to lithium-ion electrodes) for both the anode and cathode, further details of which can be found in several review papers.[29, 117, 118]

Early work developing electrolytes for reversible magnesium processes were centred on Grignard type chemicals of the formula RMgX (where R = alkyl, aryl group and X = halide) or similar, dissolved in an organic solvent such as tetrahydrofuran (THF) or diethyl ether.[118, 119] Instability and low conductivity led to the development of pseudo Grignard type electrolytes, composed of charged acidic and basic components in ethereal solutions.[120] While these novel organic magnesium-stable electrolytes are adequately conductive and have high electrochemical stability, they remain volatile. For this reason, several studies have investigated the combination of Grignard type electrolytes with RTILs in the hope that conductivity can be increased and volatility decreased by the introduction of non-volatile charged species.[121-125]

Unlike the previously discussed ethereal solutions, many RTILs are reactive to the magnesium metal surface and form a layer of breakdown products.[126] These layers that form on the surface are generally not permeable to magnesium ions, so rather than creating permeable SEI layers as is the case with Lithium SEI layers, magnesium surfaces tend to passivate.[126] In fact, the ability to form protective films under potential bias has been the motivation of many studies investigating RTILs as protective agents against magnesium alloy corrosion.[127]

Nonetheless, a number of studies have shown electrochemical experiments that support the idea that magnesium can be both deposited and stripped from certain RTILs (including Phosphonium) on the timescale of CV experiments (in the range of a few minutes).[128-132] However, several of these experiments were not easily reproduced,[126] which has prompted the investigation of the reactivity of common cations (such as imidazolium and pyrrolidinium) with magnesium metal in order to understand whether this could prevent reversible magnesium electrochemistry in an electrochemical device.[122, 133]

Despite the fact that most neat RTILs are unsuitable for magnesium electrochemistry, their role as additives to increase conductivity and reduce volatility of electrolytes has not been fully explored. Yoshimoto *et al.*[125] have found that the addition of N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium [$N_{1,2,2,102}$][NTf_2] to ethereal Grignard solutions (EtMgBr/THF) showed improved cyclability, decreased volatility and a coulombic efficiency of 93%. Kakibe *et al.*[122] had similar success using the *bis*(fluorosulfonyl)imide [FSI] anion and the same cation in a Grignard solution (MeMgBr/THF), finding that the FSI anion was most effective at improving cycling efficiency to above 90% when combined with the NTf_2 anion explored previously. Similar results were also published earlier the same year in a study by Yoshimoto *et al.*[124] who studied the effect of the alkyl chain on the Grignard molecule. Like Kakibe *et al.*[122], it was found that MeMgBr/THF with [$N_{1,2,2,102}$][NTf_2] yielded conductive solutions that supported efficient cycling of magnesium metal.

Whilst many of the commercial RTILs available have been unstable to magnesium metal, the “tunability” of the chemistry is an area that has not been explored in any detail. With an appropriate understanding of the chemistry desired, it is not unreasonable to suppose that a suitable RTIL could be synthesized that could alone sustain reversible magnesium electrochemistry and hence be plausible in an electrochemical device based on magnesium. Such an IL would either be directly stable at Mg potentials or form a Mg ion permeable SEI on reaction at the metal surface.

One step toward this goal has come from the work of Khoo *et al.*[134], who studied magnesium dissolution in the form of a primary magnesium-air cell discharged in a [$P_{6,6,6,14}$] Cl RTIL containing a small amount of H_2O as an additive. The reactivity of magnesium would lead one to consider water an inappropriate additive, however, it has been found that it is a necessary ingredient for this RTIL electrolyte system (as shown in Figure 9).

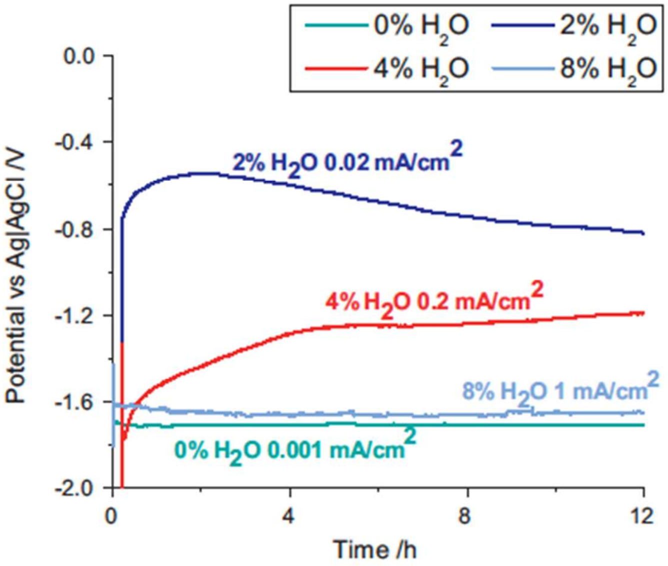


Figure 9: Discharge curves of a magnesium electrode in a [$P_{6,6,6,14}$][Cl] electrolyte containing 0, 2,4 and 8 wt% H_2O. Reprinted from *Electrochimica Acta, 87,* Khoo, T.; Somers, A.; Torriero, A. A. J.; MacFarlane, D. R.; Howlett, P. C.; Forsyth, M., Discharge Behaviour and Interfacial Properties of a Magnesium Battery Incorporating Trihexyl(Tetradecyl)Phosphonium Based Ionic Liquid Electrolytes, 701-708, Copyright (2013), with permission from Elselvier.

Khoo *et al.*[9] investigated this behaviour further and discovered that the H_2O present, in combination with the discharge of Mg^{2+} cations into solution, facilitates the generation of a gel-type interfacial layer that is both conductive to Mg^{2+} and stable to ORR electrode products – mainly hydroxide. It was found that when magnesium metal electrodes were immersed in [$P_{6,6,6,14}$][Cl] under a potential bias, a white gel was formed on the electrode surface, which dried out upon extraction from the cell. Through elemental analysis and spectroscopic studies, this gel was found to have a stoichiometry of

$[P_{6,6,6,14}][Cl]\bullet 2(MgCl_2)\bullet 37H_2O$ and when such a gel was prepared ex-situ and then used as the electrolyte, it was able to sustain a magnesium discharge reaction at 0.05 $mA.cm^{-2}$ for over 48 hours against an ORR electrode (Titanium mesh). Currently this electrolyte has only demonstrated ability as a primary magnesium-Air electrolyte, but it highlights the possibility of stabilizing magnesium cycling for secondary magnesium-air cells when an Mg^{2+} cation permeable electrode/electrolyte interphase can be generated.

3.4 - Sodium-Air

The theoretical energy density of a sodium-air battery is 1980 $Wh.kg^{-1}$ including oxygen.[135] Generally in this metal-air battery two competing discharge products, sodium peroxide (Na_2O_2) and sodium superoxide (NaO_2) are often observed where the open circuit potential for the former is 2.3 V and for the latter is 1.95 V.[136] Unlike lithium, the formation of NaO_2 in sodium electrolytes is quite stable and thus is likely to form as readily as the Na_2O_2.[137, 138]

The high reactivity of sodium with water from the atmosphere again calls for a protective, and more importantly a stable, SEI layer to form at the anode-electrolyte interface. Efficiencies as high as 85% were achieved upon cycling of molten sodium (105 ˚C) from electrolytes such as polyethylene oxide and $[C_4mpyr][NTf_2]$ (Figure 10).[139]

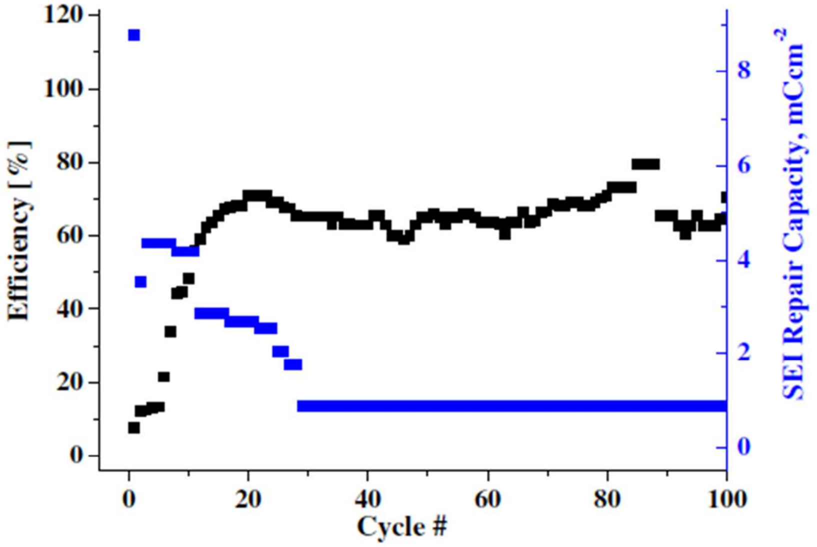


Figure 10: Faradaic efficiency (black) as a function of cycle number of Na-Air cell with 0.5 M NaOTf + 0.1M Na_2SO_4 in [C_4mpyr][NTf_2] based electrolyte. Reprinted from *Journal of Power Sources,* 195, Challenges and Obstacles in the Development of Sodium-Air Batteries, Peled, E.; Golodnitsky, D., Hadar, R., Mazor, H., Goor, M., Burstein, L., 1202-1206, Copyright (2013) with permission from Elselvier.

Although the use of molten sodium lowers the surface tension and thus prevents the formation of dendritic growth, the SEI repair time have been found to be too high for an efficient rechargeable sodium-air battery to be achieved. Furthermore, the discharge products in these electrolytes are unknown.

Similarly, Das *et al.*[140] have also compared [C_2mim][NTf_2] to an organic electrolyte based on tetraglyme, using a mixture of CO_2 and O_2 (40 : 60). Even though similar discharge capacities of sodium were observed for both electrolytes, XRD and FTIR Spectroscopy results indicate that using RTIL only sodium oxalate ($Na_2C_2O_4$) discharge product is formed, while both sodium carbonate (Na_2CO_3) and $Na_2C_2O_4$ are observed in tetraglyme. Not only does the addition of CO_2 increase the capacity of the cell (Figure 11), it also utilizes ORR intermediates to sequester CO_2 into carbonates and oxalates.

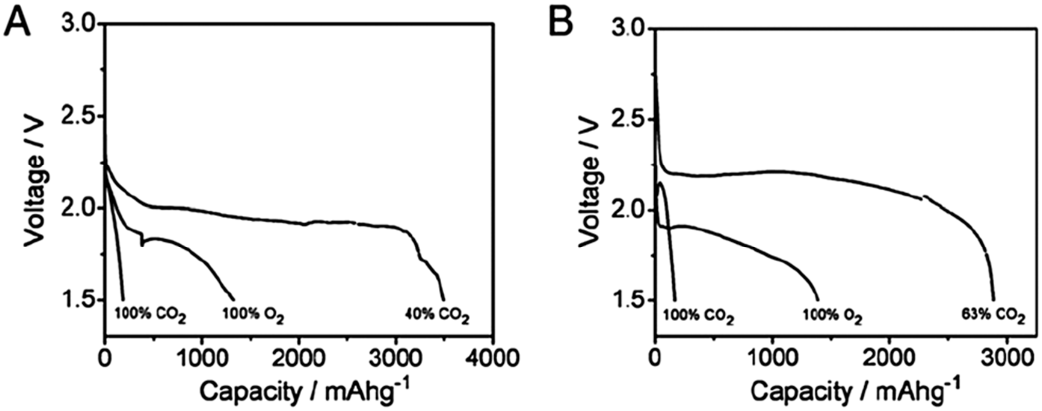


Figure 11: Discharge profiles for Na–CO_2/O_2 cells operated with different O_2/CO_2 feeds by using (a) 0.75 M $NaNTf_2$ in [C_2mim][OTf] electrolyte and (b) 1 M $NaClO_4$ in TG based electrolyte. Reprinted from Electrochemistry Communications, 27, S. K. Das, S. Xu and L. A. Archer, Carbon dioxide assist for non-aqueous sodium–oxygen batteries, 59-62, Copyright (2013) with permission from Elselvier.

Although the mixture of CO_2 and O_2 shows high discharge capacities, CO_2 would not be suitable for a rechargeable device due to the formation of sodium carbonate and oxalate over time in the cathode, as also suggested by Palamores and co-authors.[135]

Overall, very little is currently known about sodium-air batteries, let alone sodium-air batteries with RTILs. Significant work needs to be done to better understand and characterize the SEI layer as well as the discharge products in the presence of RTILs. Moreover, the use of RTILs in a practical sodium-air device is yet to be investigated in any depth.

3.5 Aluminium-Air

Similar to sodium-air, aluminium-air batteries have received much less attention from researchers. Nevertheless these metals would be just as advantageous in a commercial rechargeable battery since aluminium is abundant and much cheaper than metals such as lithium. The theoretical energy density and potential of an aluminium-air battery is approximately 400 $Wh.kg^{-1}$ and 2.06 V respectively for a full primary device. In alkaline aqueous electrolytes, Aluminium hydroxide ($Al(OH)_3$) is generated along with competing products such as Al_2O_3.[141] While the former discharge product is recyclable, the latter is not. Moreover, the layer of Al_2O_3 formed on the anode passivates the electrode and prevents long-term cell operation. Although the use of highly conductive alkaline electrolytes are able to dissolve large amounts of $Al(OH)_3$ yielding energy densities as high as $175 Wh.kg^{-1}$, the evolution of hydrogen occurs before the deposition of aluminium. [94] Thus, it is essential to explore non-aqueous electrolytes for aluminium-air cells if rechargeable Al-air cells are to be achieved.

In their work, Abedin *et al.* [142] were able to show current densities of aluminium oxidation being as high as 12 $mA.cm^{-2}$ in RTILs such as $[C_2mim][NTf_2]$ (Figure 12). The authors also concluded that the role of the cation in this electrolyte played a key role in the high current densities, since the RTILs $[C_4mpyr][NTf_2]$ and $[P_{6,6,6,14}][NTf_2]$ produced current densities only as high as 0.1

mA.cm^{-2} and 0.4 mA.cm^{-2} respectively, possibly due to fact they are much more viscous than [C$_2$mim][NTf$_2$].

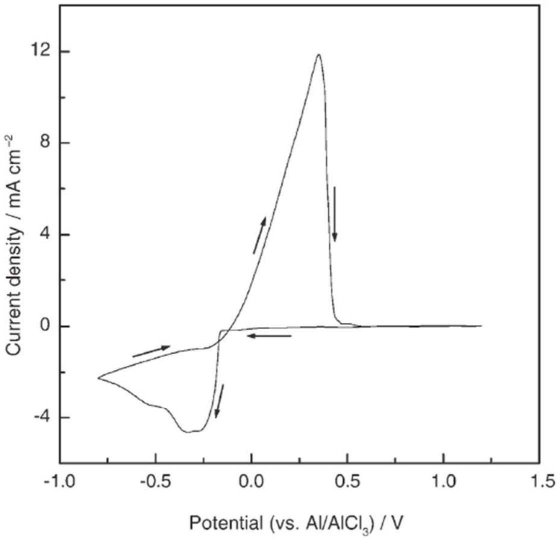


Figure 12: Cyclic voltammetry of 5 M AlCl$_3$ in [C$_2$mim] [NTf$_2$] at 20 ˚C using Au WE (Scan rate 10mV/s). Reproduced from Reference 142 with permission from Wiley.

4.0 Conclusions and Challenges

It is evident from the literature that significant steps in both fundamental and applied research in this important field of metal-air batteries have taken place in recent years. An understanding of the key processes that determine the reversibility of the electrochemical reactions that will lead to the development of an efficient and stable rechargeable metal-air battery is evolving. Several examples of such prototype devices have been discussed in this perspective, but it is important to note that large companies such as Toyota, Korean Institute of Science and Technology (KIST) and start-up companies i.e. EOS Systems, Fluidic Energy & ZAF Energy are emerging as key stakeholders in the intellectual property of metal-air rechargeable technology.[91, 143-147] Many patents are centred on the design of these batteries[148, 149] and some mention RTILs being possible candidates as battery electrolytes. To our knowledge, it is only a very small percentage that have demonstrated electrochemistry in RTILs, such as the Zn-air rechargeable batteries produced by Fluidic Energy.[144, 147]

Summary

Due to the ideal properties of RTILs (including the low volatility, high conductivity, high thermal stability and wide electrochemical window) they are uniquely placed to address many of the long-standing obstacles to rechargeable metal-air batteries.

The low volatility of RTILs can essentially eliminate the continuing problem of “drying out” of the electrolyte from the cell. The high thermal stability allows the battery to operate at a range of temperatures, whilst the high conductivity and wide electrochemical window allow for electrochemistry of reactive metals, which have previously been beyond the capabilities of conventional electrolytes.

We have shown that the body of literature available to date has encompassed at a vast number of different RTILs with varying properties, which have demonstrated:

- the ability to support the ORR and to a limited degree, the OER.
- successful deposition and stripping of the metal ions (Zn^{2+}, Li^{+}, Mg^{2+}, Na^{+}, Al^{3+}.)
- that in some cases (e.g. Zn^{2+} species), high solubility of the discharge products are formed from both the cathodic and anodic reactions. However this was not observed in all cases (e.g. Li_2O_2)

RTILs have in addition also shown that they can act cooperatively with additives (i.e. H_2O) to achieve a desired electrochemical outcome. Conservative estimates of the number of possible ILs are in the millions, and the unique ability to design desirable properties into RTILs surely has the potential to contribute to the development of the energy storage devices discussed above.

Certainly there are a few challenges to overcome with RTILs. For example:

- Many RTILs are expensive to synthesise, however if a specific IL is found to be useful for a commercial rechargeable metal-air battery then large volumes of this IL at a time will be required, which will reduce the synthesis costs. In addition, as evident in this paper, many ILs still require the aid of additives and therefore a mixture of RTILs with additives will be cheaper to use than the neat ILs themselves.
- Although electrochemical deposition of the metal from most of the RTILs discussed in this paper is certainly possible, currents obtained are still rather low, which affect the charging and discharging rates of the battery. For this reason, many more family of RTILs must be investigated and the use of additives, such as water, is predicted to enhance the electrochemical properties. Investigating further working electrodes, catalysts and other experimental conditions may also enhance the electrochemical properties.

Whilst an investigation of the large family of RTILs that may be likely candidates will be time consuming, the RTILs presented in this paper have already provided an insight of some of the cations and anions that have been found to be advantageous in the field of metal-air batteries. Thus this should allow researchers in this field to work collaboratively and focus on the more promising candidate ions and potential functional groups that are likely to show good performance in metal-air batteries.

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