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Ionic Liquid-based Electrolytes for Li Metal/Air Batteries: A Review of Materials and the New 'LABOHR' Flow Cell Concept

Dominic Bresser, Elie Paillard, and Stefano Passerini*

Institute of Physical Chemistry & MEET Battery Research Center, University of Muenster, Corrensstrasse 28/30 & 46, 48149 Muenster, Germany

ABSTRACT

The Li-O$_2$ battery has been attracting much attention recently, due to its very high theoretical capacity compared with Li-ion chemistries. Nevertheless, several studies within the last few years revealed that Li-ion derived electrolytes based on alkyl carbonate solvents, which have been commonly used in the last 27 years, are irreversibly consumed at the O$_2$ electrode. Accordingly, more stable electrolytes are required capable to operate with both the Li metal anode and the O$_2$ cathode. Thus, due to their favorable properties such as non volatility, chemical inertia, and favorable behavior toward the Li metal electrode, ionic liquid-based electrolytes have gathered increasing attention from the scientific community for its application in Li-O$_2$ batteries. However, the scale-up of Li-O$_2$ technology to real application requires solving the mass transport limitation, especially for supplying oxygen to the cathode. Hence, the 'LABOHR' project proposes the introduction of a flooded cathode configuration and the circulation of the electrolyte, which is then used as an oxygen carrier from an external O$_2$ harvesting device to the cathode for freeing the system from diffusion limitation.

1. Introduction

Lithium-oxygen (Li-O$_2$) batteries, commonly called lithium-air batteries, are presently considered as the "holy grail" of battery research, offering a theoretical specific energy and energy density of 3582 Wh kg^{-1} (including the weight of oxygen) and 3436 Wh L^{-1}, respectively [1-3]. However, despite remarkable advances within the last few years [4], some issues need to be addressed before bringing these batteries to the market. Among these, the stabilization of the Li metal anode, the stability of the electrolyte towards O$_2^{\bullet-}$, the conditions of use of a Li-O$_2$ battery in general, the recharge efficiency, and the O$_2$ access to the reaction sites at the cathode are likely the most relevant ones.

Here, we give a short overview on the challenges related to the identification and development of a suitable electrolyte for Li-air batteries, focusing particularly on ionic liquid-based electrolytes. Indeed, the utilization of ionic liquids (ILs) in Li-O$_2$ batteries has recently gathered an increasing interest due to their stability towards the superoxide anion radical, their enhanced safety, as well as their negligible vapor pressure. However, some issues remain, among which the O$_2$ mass transport to the cathode will be specifically addressed herein. In the same context, we will present the EU-funded 'LABOHR' project, which is targeting a new approach to overcome this mass transport limitation by proposing a flow-cell concept and an external oxygen harvesting device.

2. The electrolyte challenge for Li-O₂ batteries

Initially, most studies focused on the use of organic carbonate-based electrolytes, commonly used in state-of-the-art lithium-ion batteries [5], by this following the early work of Abraham and Jiang on a secondary Li-air battery [6].

However, it was shown that alkyl carbonates are not stable towards oxidation in a lithium-oxygen cell configuration [7-9]. In fact, the inclusion of nanostructured inorganic catalysts is likely even further accelerating this electrolyte decomposition, while evidences of true electrocatalysis for the reversible formation of Li_2O_2 are lacking [10]. Recently, Bruce and co-workers [11] reported the utilization of dimethyl sulfoxide (DMSO) as electrolyte solvent, showing that electrolytes based on this solvent are stable enough for the operation of a lithium-oxygen battery. Nevertheless, DMSO is hygroscopic, which prevents its utilization in a final device open to atmosphere, while the Li electrode stabilization, obtained in this case by dipping it into propylene carbonate (PC), requires further investigation. Another class of solvent has then been proposed showing an interesting performance: the oligo (ethylene glycol) dimethyl ethers, commonly referred to as glymes [4]. Among these, tetraethylene glycol dimethyl ether (tetraglyme or TEGDME) appears as the most promising candidate, presenting a rather low volatility and a good compatibility versus lithium metal, similarly to PEO-based electrolytes. However, there exist conflicting reports in scientific literature concerning the stability of TEGDME versus the $O_2^{\bullet-}$ superoxide anion radical and in general its stability in Li-O₂ cells. Indeed, some reports conclude on the instability of $O_2^{\bullet-}$ in TEGDME [12] when used 'as received', while carefully purified TEGDME [13,14] appears to be stable versus $O_2^{\bullet-}$-similarly to DME [15]. Nevertheless, although Li_2O_2 is found as the main product during the first discharge in a Li-O₂ configuration, the formation of other discharge products after a few cycles was reported [8,14]. Indeed, if carbon and its surface defects are likely to be involved in the formation of byproducts [11,16], the electrochemical oxidation of the solvent does not appear totally unlikely over time, particularly if rather high cut-off voltages are used [4,14,17]. As a matter of fact, in case of repetitive cycling, the reported studies commonly show an evolution of the voltage profile towards higher potentials [4,14,18], which origin is not fully clear, yet. Besides, however, the nature of the Li salt might also have a significant influence on the reactions taking place at the oxygen cathode upon operation of the cell [19,4] and, indeed, the previously cited studies are not fully consistent regarding this point.

3. Ionic liquid-based electrolytes in Li-ion and Li metal batteries

In addition to their enhanced thermal, chemical, and electrochemical stability, ionic liquids offer an attractive alternative to molecular solvents due to their hydrophobic nature and negligible vapor pressure when composed of appropriate ions [20,21]. The molecular formulas of the most commonly used IL cations and their abbreviations are shown in Fig. 1.

In fact, the suitability of ionic liquid-based electrolytes for lithium-ion batteries has already been reported in literature. Passerini and co-workers [22-24], for instance, investigated the use of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in *N*-butyl-*N*-methyl pyrrolidinium bis(fluorosulfonyl)imide (PYR₁₄FSI) as electrolyte for $Li_4Ti_5O_{12}$-LiFePO₄ (LTO-LFP) lithium-ion full-cells, showing not only an improved safety compared to common organic carbonate-based electrolytes but also a very steady electrochemical performance. Hassoun *et al.* [25] reported a slightly modified ionic liquid by exchanging the methyl substituent of the pyrrolidinium cation by an ethyl group, *i.e.*, *N*-butyl-*N*-ethyl pyrrolidinium, and FSI by TFSI (PYR₂₄TFSI). This electrolyte including the salt LiTFSI appeared to be able to form a stable solid electrolyte interphase (SEI) on a nanostructured Sn-C anode. Focusing on a different cation, *N*-methyl-*N*-propyl
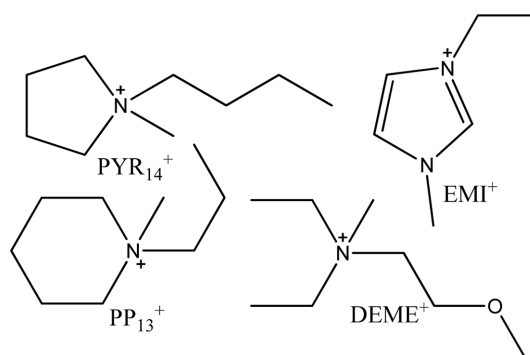

Fig. 1. Molecular formulas of some cations commonly incorporated in ionic liquids.

piperidinium (PP$_{13}$), Reiter *et al.* [26] confirmed that an electrolyte including the ionic liquid PP$_{13}$TFSI and LiFSI is compatible with both graphite-based anodes and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$-based cathodes, suggesting that such a full-cell might also show a stable electrochemical performance. A different ionic liquid was used by Sato *et al.* [27] who reported an electrolyte based on *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulf-onyl)imide (D EME-TFSI) for graphite-LiCoO$_2$ lithium-ion cells, obtaining a stable cycling performance for more than 350 cycles, with the addition of a small percentage of ethylene or vinylene carbonate (EC or VC) as SEI-forming agent in the electrolyte. In fact, an almost unlimited variety of ionic liquids, having different - or in other words tailorable - physical, chemical, and electrochemical properties, can be conceived, allowing the design of suitable compounds for almost any purpose [20,28].

With respect to the utilization of lithium metal, IL-based electrolytes offer an additional major advantage, since they show a significantly improved cycling performance of the lithium electrode as compared with conventional Li-ion electrolytes, especially when incorporating PYR$_{14}^+$ paired with TFSI$^-$ and incorporated [29,30] or not [31] in solid polymer electrolytes (SPEs) or paired with FSI$^-$ for lower temperature applications [32,33]. Fig. 2 shows a typical voltage profile of a Li/0.9 PYR$_{14}$FSI − 0.1 LiFSI/LFP cell, which operates close to the theoretical capacity of LFP with very high reversibility.

However, literature on the use of ionic liquid-based electrolytes for lithium-oxygen batteries is still rather scarce and only little work has been published. Addi-
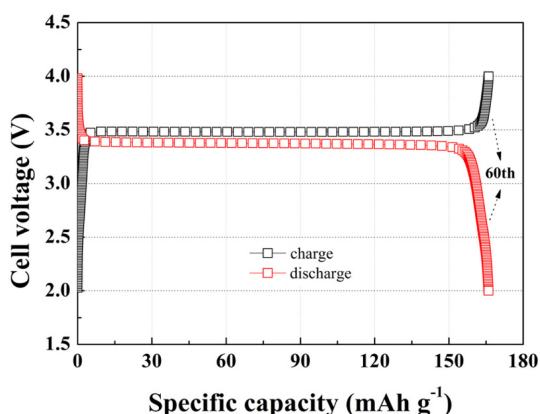

Fig. 2. Potential profile of the 60th cycle of a Li/0.9 PYR$_{14}$FSI − 0.1 LiFSI/LFP half-cell at 20°C and C/10.

tionally, the wide family of ILs is generally considered as all behaving similarly, which is certainly a wrong approach, especially in a system in which both SEI forming properties at the anode side and high chemical and electrochemical stability versus oxidation is required.

4. Ionic liquid-based electrolytes for Li-O$_2$ batteries

Kuboki *et al.* [21] reported the use of ionic liquids-based electrolytes for lithium-oxygen batteries for the first time using of EMITFSI (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide), EMI-BETI (EMI bis(pentafluoroethylsulfonyl)imide), MOITFSI (1-methyl-3-octylimidazolium TFSI), BMINf (1-butyl-3-methylimidazolium nonafluorobutyl sulfonate), and BMIPF$_6$ (BMI hexafluorophosphate) in primary lithium-air cells. In case such hydrophobic ionic liquids are used as electrolyte solvent, the electrolyte evaporation and lithium hydrolysis are prevented, rendering such electrolytes suitable for lithium-air batteries open to the environment. If the best results were obtained for EMITFSI, only primary lithium-oxygen and lithium-air cells were investigated within their study. More recently, Ye and Xu [34] reported in 2008 the utilization of a PVdF-HFP-based polymeric membrane saturated with a mixture of PYR$_{13}$TFSI-LiTFSI as solid electrolyte and a cobalt phthalocyanine-carbon composite as air electrode. This membrane showed a wide electrochemical stability window and allowed reversible lithium plating/stripping but the rechargeability of a lithium-oxygen cell comprising this membrane as solid electrolyte was rather poor and the voltage hysteresis was relatively high. These drawbacks were attributed to the diffusion of oxygen through the electrolyte to the lithium metal anode, passivating the anode surface by a thick Li$_2$O film.

If the reduction of oxygen and the formation of the superoxide O$_2^{\bullet-}$ is electrochemically quasi-reversible in several imidazolium-, ammonium-, piperidinium-, and pyrrolidinium-based ionic liquids, *inter alia* PYR$_{14}$TFSI, as illustrated in Fig. 3, for PYR$_{14}$TFSI saturated with O$_2$ [35-43] - due to the complexation of the superoxide anion by the relatively large cation of the ionic liquid [22] - the presence of Li$^+$ results in the formation of insoluble lithium oxide species, thus turning the oxygen redox reaction (O$_2$ + e$^-$ $\leftrightarrow$ O$_2^{\bullet-}$)
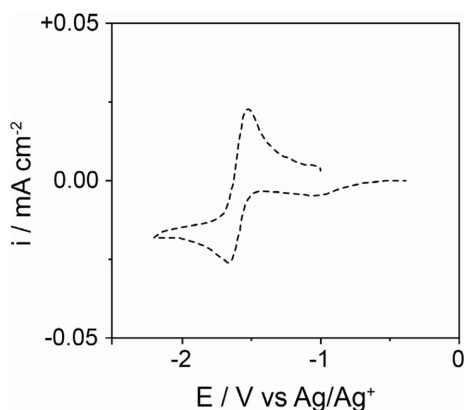
Fig. 3. Voltamperometry of $PYR_{14}TFSI$ saturated with O_2, at $10\ mV\ s^{-1}$, WE: Pt (Ø ≈ 0.5 cm), CE: Pt, RE: Ag/ $0.01\ M\ AgCF_3SO_3$ in $PYR_{14}TFSI$.

electrochemically irreversible [35].

The influence of the lithium cation on the oxygen redox reaction (oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)) was also investigated by Abraham and co-workers using the ionic liquid EMITFSI [44]. Their results show that the LiO_2 initially formed disproportionates to O_2 and Li_2O_2, which can then be further reduced to Li_2O. In a later study [45] they correlated the ORR to the charge density of the conducting cations. While the current response decreased rather rapidly for a glassy carbon electrode, very promising results regarding the stability of the current response were obtained for a gold electrode [44].

Mizuno *et al.,* [46] studied the use of *N*-methyl-*N*-propyl piperidinium bis(trifluoromethanesulfonyl)imide ($PP_{13}TFSI$) as electrolyte solvent for lithium-oxygen batteries. $PP_{13}TFSI$ is considered to be stable towards the superoxide anion radical initially formed. In fact, no decomposition of the ionic liquid was observed in absence of lithium. However, the reversible capacity in presence of lithium using a carbonaceous oxygen electrode employing MnO_2 as catalyst was rather limited ($< 150\ mAh\ g^{-1}$) and about 60% of the initial capacity was retained after 30 cycles. Interestingly, the onset of the charge step was significantly reduced to about 3.2 V *vs.* Li/Li^+. Nevertheless, both potential profiles - charge and discharge - appeared rather slopy, increasing the hysteresis of the system, which the authors related to the slow oxygen and superoxide diffusion in $PP_{13}TFSI$ and the kinetics of the reaction at the cathode. However, the perfor-

mance was significantly improved in a flowing study, thanks to an optimized cell design, in which the distance between the anode and cathode was reduced. [47] The average charge potential was around 3.4 V, while the reversible capacity was dramatically increased to about $1800\ mAh\ g^{-1}$. However, the authors did not report a continuous cycling of this cell. Replacing $PP_{13}TFSI$ by DEMETFSI, led to further improvement yielding higher specific discharge capacities ($> 4500\ mAh\ g^{-1}$) as well as an enhanced rate capability attributed to lower viscosity and improved oxygen diffusion [48]. A later study confirmed these results by comparing four ionic liquids, namely DEMETFSI, $PP_{13}TFSI$, *N*-methoxyethyl-*N*-methylpiperidinium ($PP_{12O1}TFSI$), and $PYR_{14}TFSI$, regarding their stability versus the oxygen superoxide. Among these, $PP_{12O1}TFSI$ exhibited the lowest stability towards the superoxide radical anion, while $PYR_{14}TFSI$ and DEMETFSI were shown to have the highest oxygen diffusion coefficients [49]. However, for the study of such ionic liquids in lithium-oxygen cells, they compared electrolytes made of $PP_{13}TFSI$ and DEMETFSI comprising $0.32\ mol\ kg^{-1}$ of LiTFSI and no continuous (dis-)charge cycles of the studied cells were presented. Repetitive cycling was done by Cui *et al.* [50] with $PP_{13}TFSI$-$LiClO_4$ (0.4 M) as electrolyte and an oxygen electrode made of vertically aligned carbon nanotubes. The values for the first (dis-)charge capacity and the observed (dis-)charge potentials were comparable to those reported by Mizuno *et al.,* [47] Higashi *et al.,* [48] and Nakamoto *et al.,* [49] indicating that the cation of the employed ionic liquid is of major importance. However, the specific capacity dropped rather rapidly upon 20 cycles (20% to 56% capacity retention, depending on the cycling protocol).

In a more recent study, Mastragostino and co-workers reported the use of $PYR_{14}TFSI$-LiTFSI (9:1 molar ratio) as electrolyte and a catalyst-free, porous, carbonaceous oxygen electrode for a lithium-oxygen cell [51]. Interestingly, they observed a reduced charge potential of around 3.4 V *vs.* Li/Li^+, up to now one of the lowest values reported in scientific literature as well as a discharge voltage around 2.7 V. The capacity delivered was around $2500\ mAh\ g^{-1}$ at 60°C and limiting the discharge capacities to about $550\ mAh\ g^{-1}$ led to a 90% recharge efficiency, while continuous cycling with a discharge limited to $200\ mAh\ g^{-1}$ led to stable cycling for 15 cycles with recharge efficiencies around 80% using 3.8 V as the highest cut-off voltage. The

utilization of LiTFSI-PYR$_{14}$TFSI as electrolyte was also reported by Piana *et al.* [52]. However, in this study, the obtained reversible specific capacity was rather low (< 300 mAh g^{-1}) and the potential increased from around 3.3 V to around 4.8 V *vs.* Li/Li$^+$ upon charge. Interestingly, nevertheless, Garsuch *et al.* [53] observed only very poor performance for lithium-oxygen cell employing 10% LiTFSI in PYR$_{14}$TFSI as electrolyte and MnO$_2$ supported carbon cathode. The specific capacity was limited to about 60 mAh g^{-1} and the voltage hysteresis was very high with round-trip efficiency of only 58%.

Another report by Cecchetto *et al.* [54], presented an electrolyte mixture based on LiCF$_3$SO$_3$ (LiTf) in TEGDME (0.91 M) and PYR$_{14}$TFSI, the latter two mixed in a volume ratio of 1:1. This mixture showed an improved conductivity compared to a solution of LiTf in TEGDME only. Most importantly, however, a Li-O$_2$ cell using this electrolyte composition presented a reduced overvoltage for the charge reaction, which has been assigned to the increased conductivity as well as a modified film formation on the air electrode, thus improving the overall kinetics of the oxygen reduction and oxidation.

5. The oxygen mass transport issue and the LABOHR approach

Whatever the type of electrolyte used, mass transport of the electro-active species at the cathode is considered as one of the major challenges [55-57], as the reaction, in a (partially) flooded system is clearly related to the diffusion of electro-active species and O$_2$ in particular, as its diffusion coefficients and concentration are rather low, even if the fluorine content within the IL has a positive influence [57]. Thus, new approaches are needed to address a system, which presents some similarities with PEMFC. In fact, both systems require a steady supply of O$_2$ as a reactant, but there are also differences with respect to the organic nature of the electrolyte and the formation of solid reaction products within the cathode in case of aprotic Li-O$_2$ batteries.

Indeed, the best performances in terms of rate capability reported so far were obtained using rather thin electrodes [4,11], operating at the interface of an O$_2$ atmosphere in a flooded or semi-flooded configuration, which minimize the limitations of O$_2$ transfer to the active sites. However, the demand for power

would *in fine* require a considerable O$_2$ flow into the cell. Thus, it is not clear yet whether a wetted configuration, maximizing the O$_2$ direct transport to three phase interfaces, similarly to fuel cells, might be reached, given the deposition of the reaction products onto the reactive site. Moreover, it is worth pointing out the lower flexibility as compared to a system using water as a solvent in regards to tuning the 'solvent content' of the inflowing gas and by this, the wetting of the electrode.

Moreover, a flooded system, using O$_2$ dissolved in solution could possibly lead to a more homogeneous distribution of the reaction products, which is proposed to lead to less pore clogging and thus to a better O$_2$ access.[58] The slow diffusion of O$_2$ and the need for optimizing the wetting of electrodes was recently highlighted with mass loadings of c.a. 2 mg cm^{-2}, showing dramatic losses in terms of discharge capacity with the full flooding of the electrode by the electrolyte, while tuned wetting allowed faster O$_2$ transfer [59]. If the possibility of maintaining wetted three phase configuration in carbon cathodes of Li-air system is still an open question, the transport limitation can be addressed in a different way. This is why the EU funded 'LABOHR' project ('Li-air Battery with Split Oxygen Harvesting and Redox Processes') proposes the use of a O$_2$ saturated electrolyte circulation to feed oxygen to the cathode, as illustrated in Fig. 4. In this case, the oxygen is harvested and transported by an O$_2$-saturated IL-based electrolyte, acting like an artificial "blood system", while the circulation of the electrolyte within the cathode is expected to minimize the diffusion mass transport limitation for O$_2$ by decreasing the typical diffusion dis-
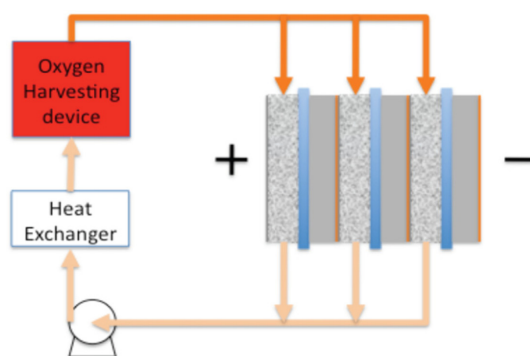

Fig. 4. Schematic illustration of the LABOHR concept based on flowing O$_2$-saturated ionic liquid-based electrolyte through the cell.

tances. A concept of flow Li-air battery was actually also proposed recently by Chen *et al.* [60] for the semi-aqueous version of a Li-air battery, in which the discharge products are soluble and need to be stored within the electrolyte. In the case of an aprotic Li-O_2 cell, however, the reaction products would either be included in the cathode's pores or, alternatively, be precipitated in a reservoir, providing that the reaction can be displaced.

The electrolyte circulation approach and the limitation by diffusion was verified using a templated meso-/microporous carbon, by utilizing a rotating disk electrode, showing a first set-up of such a flow cell [61]. This proof of principle allowed clear improvement in terms of O_2 transport, although the reported device was still far from being optimized in terms of Li protection, as the O_2-saturated electrolyte was circulated directly in the separator rather than in the back of the cathode. Nevertheless, a specific capacity of 600 mAh g^{-1} was obtained with a recharge efficiency close to 92%.

Another advantage of the fluid circulation system, in view of the electric car market, would be the possibility of using this circulating fluid as part of the temperature regulation system as recently shown by AVL [62]. In this regard, the use of ILs enables the operation of the cell at higher temperature, which would also simplify the heat dissipation compared to common Li-ion cells.

At the same time, circulating the electrolyte opens new possibilities: Owen and co-workers [63,64], for instance, proposed the use of a redox shuttle, which, if correctly chosen, allows accelerating the O_2 transfer at the O_2/IL interface, by displacing the site of the Li_2O_2 formation to the O_2/electrolyte interface. In addition to accelerating the kinetics of O_2 dissolution and suppressing the need of its transport, this approach enables the possibility of storing the reaction product apart from the cathode pores. By this, the pore clogging issue might be overcome. Although the use of such shuttle raises the question of their influence on the whole system as well as the possibility to re-oxidize Li_2O_2, the recent proposition of Bruce and co-workers of a mediator for the charge reaction [65], theoretically opens a route for new Li-O_2 flow battery concepts.

Conclusion

Among the many challenges to be addressed for realizing the commercialization of the Li-O_2 battery, IL-based electrolytes appear highly promising due to their non-volatility as well as their electrochemical and chemical inertia, especially towards the superoxide anion radical. In addition, they offer favorable interfacial properties with Li metal, leading to a growing interest in the field of Li-O_2 batteries. Nevertheless, in case flooded cathodes are used, the mass transport of O_2 is of primary concern and, in general, the feasibility of a semi-wetted cathode as it is the case in PEMFCs is unclear. Thus, the LABOHR project proposes the use of a circulating electrolyte, acting as an artificial "blood system" for the cell and allowing fast transport of O_2 from an external O_2 harvesting device to the reactive sites at the cathode.

Acknowledgements

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