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Electrochemical storage systems: Safer and more sustainable batteries

Maria Assunta Navarra, Matteo Palluzzi, Akiko Tsurumaki and Sergio Brutti

Department of Chemistry, Sapienza University of Rome
Piazzale Aldo Moro 5, 00185 Rome, Italy

Summary. — Lithium-ion batteries (LIBs) are the predominant power source for portable electronic devices, and in recent years their use has extended to higher-energy and larger devices. However, to satisfy the stringent requirements of safety and energy density, further material advancements are required. Due to the inherent flammability of organic solvent-based liquid electrolytes and their instability against materials utilized in high-energy systems, a transition to alternative ion-conductive media becomes urgent. In this paper, some possible solutions, shifting from molecular liquids to a class of materials based on ions, such as ionic liquids (ILs), and polymers, such as gel polymer electrolytes (GPEs), will be briefly discussed. Moreover, innovative technologies, the so-called beyond-lithium batteries, will be presented, considering a more sustainable anode material based on calcium.

1. – Introduction

Lithium-ion batteries (LIBs), launched by Sony in 1991, have quickly outperformed their rivals and become the standard choice for electronic devices. After more than 30 years, LIBs remain a vital part of our everyday life, and their use is spreading to new sectors, such as hybrid/electric vehicles (H/EVs) and stationary energy storage

from renewable sources [1]. However, to develop batteries suitable for such applications, advancements are necessary to improve their energy density and cycle life, in addition to their safety and sustainability.

The internal failure of a LIB is mainly caused by intrinsic flammability of organic carbonate-based liquid electrolytes (LEs), such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) and volume expansion of electrodes during cycling.

The energy density can be enhanced by replacing graphite anodes, currently adopted in commercial LIBs, with lithium metal anodes (theoretical specific capacities of $372\,\mathrm{mAh\,g^{-1}}$ and $3860\,\mathrm{mAh\,g^{-1}}$, respectively), *i.e.*, shifting from LIBs to lithium-metal batteries (LMBs) [2]. Nonetheless, such attempts have been hampered by the incompatibility of lithium metal with commonly used LEs, which cause formation of dead lithium and growth of dendrites, inducing battery short-circuits and a consequential risk of fire or explosion.

A replacement of conventional LEs with ionic liquids (ILs) and gel polymer electrolytes (GPEs) may offer improved performance and safety of the battery cell [3].

The electrolyte should possess a series of properties: i) high ionic conductivity and low viscosity to ensure a fast Li^+ diffusion, ii) high electrochemical stability and a wide electrochemical stability window (ESW) to avoid its degradation, iii) thermal stability to guarantee the safety of devices, iv) chemical inertness against other components of the battery, including separators, current collectors, and the electrodes, to avoid their corrosion, and v) an ability to form a protective, Li^+-conductive, and electron-insulating layer on the surface of anode materials, so-called a solid electrolyte interphase (SEI) [4].

Ionic liquids are expected to play an important role in the progress of modern electrolytes because of their well-balanced ionic interactions and dissociation, resulting in both high thermal stability and high ionic conductivity. On the other hand, the introduction of a polymeric matrix into the electrolyte prevents liquid electrolyte from leakage and also improves safety of the device by contemporary reducing flammability and suppressing the formation of lithium dendrites.

Looking to the future, due to limited lithium availability as a critical raw material, calcium (Ca) batteries are emerging as a promising next-generation electro-chemical energy storage system, due to the abundant reservation of calcium and the competitive redox potential of Ca^{2+}/Ca. However, the practical realization of rechargeable Ca and Ca-ion batteries (CIBs) still relies on the identification of suitable electrodes and electrolytes [5].

2. – Ionic liquids for lithium batteries

ILs are generally defined as molten salts at room temperature. They are usually composed of a large and asymmetric organic cation and an organic/inorganic anion with a charge delocalization to reduce the Coulombic interactions. Being composed only of ions, ILs possess unique physicochemical properties that cannot be attained by molecular solvents, such as exceptional thermal stability, low vapor pressure and flammability, good ionic conductivity, and an ability to dissolve inorganic salts. However, ILs still suffer from

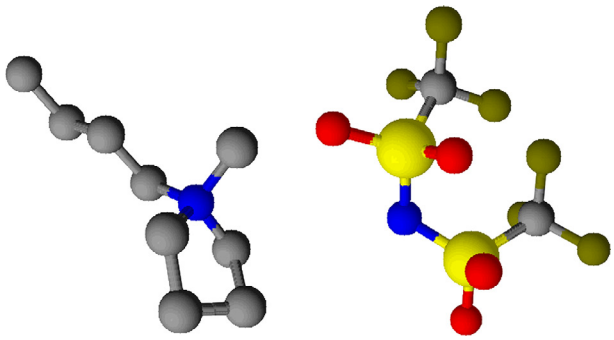


Fig. 1. – Structure formula of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [Py_{14}]TFSI, ionic liquid (in blue: nitrogen; in gray: carbon/methyl/methylene; in red: oxygen; in yellow: sulfur; in dark green: fluorine).

several disadvantages compared to organic solvents, which limits their use. First, ILs are highly viscous owing to their Coulombic interactions and the steric hindrance caused by the large ions [6], and their Li^+ transference number (t_{Li^+}) is lower than that of the conventional LEs because ions composing ILs also migrate according to a gradient potential, comparatively reducing Li^+ conductivity. Second, the synthesis procedures of ILs present an obstacle to their industrial use since these involve the utilization of environmentally unfriendly organic solvents, expensive precursors and energy- and time-consuming steps generally consisting of quaternization, anion exchange reaction, and purifications. Many efforts have been devoted to the development of economical, greener, and faster synthesis methods [7].

Although several issues remain, ILs are recognized as potential materials for battery applications because of their design flexibility.

They have been used i) as electrolyte itself (IL-Li salt system), ii) as main component in electrolytes (soln.-in-IL), or iii) as additive for electrolytes (IL-in-soln.) [8-10]. Pyrrolidinium-based ILs, such as 1-butyl-1-methylpyrrolidinium hexafluorophosphate ([Py_{14}]PF_6) or 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([Py_{14}]TFSI) (fig. 1), are widely used for battery applications and have been employed as an additive for carbonate-based electrolytes such as 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (1 : 1 in vol%), so called LP30, or even as a main component in the mixture [11, 12].

By increasing the concentration of the IL, both the thermal stability and electrochemical stability are improved [13]. With respect to thermal stability at high temperature, the mixture with a flash point higher than 35 °C and without a tendency of combustion, which is one of the definitions for non-flammable solution according to the UN regulation, can be realized by increasing the IL concentration to 50 wt.%. In addition, interactions between the IL and organic solvents can also guarantee the suppression of crystallization, enhancing transport property at low temperatures. With respect to electrochemical properties, ionic conductivity tends to decrease slightly with increase in the IL concen-

tration due to increased viscosity. However, the presence of IL contributes to prolonged battery cycle life because of their stability [14, 15].

A thorough understanding of structure-property relationships revealed that even a small change in the structure of ions, such as the alkyl chain length of cations or the presence of functional groups, leads to a great change in their physical and chemical properties. For instance, in the case of 1-alkyl-3-methylimidazolium tetrafluoroborate, by changing the alkyl side chain from methyl to butyl, its T_{m} decreases from 100 to $-71\,^{\circ}\mathrm{C}$ [16]. Also, the choice and modification of the anion influence the properties of the resulting IL, enabling the possibility of "fine-tuning" for desired applications [17]. As an example, ILs containing bis(oxalato)borate (BOB) and difluoro(oxalato)borate (DFOB) anions enable the formation of protective layers on both negative and positive electrodes.

Recently, two novel ionic liquids (ILs), which contain BOB or DFOB as the anion, have been synthesized and applied as additives to the commercial LP71 electrolyte (*i.e.*, 1 M $LiPF_6$ in ethylene carbonate:diethyl carbonate:dimethyl carbonate, EC:DEC:DMC) for high-voltage battery applications [11]. When 0.3 M IL was added, reduction and oxidation currents were observed during cyclic voltammetry for cathodic and anodic sides, respectively, due to the formation of a solid electrolyte interface (SEI). The high voltage $Li||LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cell, employing these electrolytes, exhibited high discharge capacity around $120\,\mathrm{mAh\,g^{-1}}$. The highest stabilizing effect was obtained with the BOB-IL electrolyte, allowing a retention of discharge capacity equal to 99.5% after 100 cycles, much higher than the one achieved with pristine LP71 (fig. 2).

By means of impedance analysis during the galvanostatic cycling, the growth of SEI was confirmed when BOB-IL was used as an additive. In this case, in the infrared spectra of cycled LNMO electrodes, peaks related to borate compounds and polycarbonate were observed. This confirms that the BOB-IL promotes the formation of a stable interface between the electrolyte and LNMO, positively affecting the cycling performance and extending the battery life.

3. – Gel polymer electrolytes for lithium batteries

Polymeric electrolytes can be divided in two main families: solid polymer electrolytes (SPE) and gel polymer electrolytes (GPE) [18-20]. The former is solvent-free and consists of lithium salts and solid polymer matrices, while the latter includes liquid components in the SPE structure. In the case of GPE based on polyethylene oxide (PEO), lithium ion conduction simultaneously occurs along both the segmental motion of polymer chains and the diffusion of liquid components. When fluorinated polymers such as poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) are used as a matrix, the polymer matrices reinforce the mechanical stability, and liquid electrolytes mainly control the ion conduction, *i.e.* functions are allocated to each component.

In general, problems delaying the development of polymer electrolytes include low conductivity of most SPEs at ambient temperature and reactivity with the lithium metal electrode in solvent-plasticized polymer systems. In this view, the combination of a

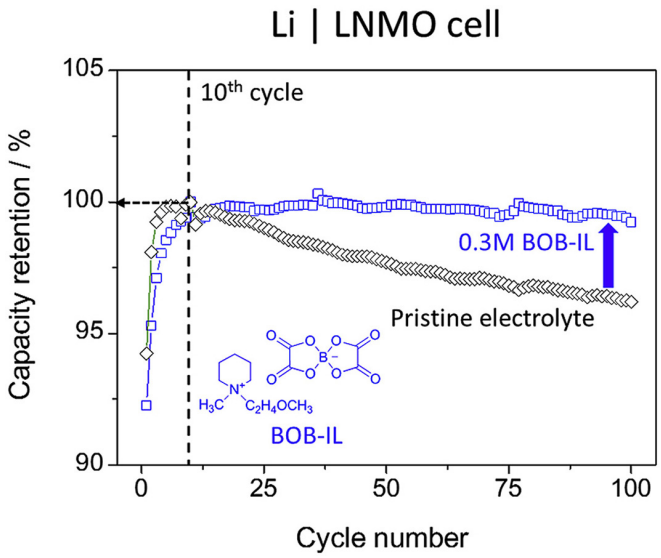


Fig. 2. – Discharge capacity retention during galvanostatic cycling at 1 C (= 130 mA g^{-1}) of the Li‖LNMO cells containing either BOB-IL or pristine LP71 electrolyte. Reprinted from [11], © 2019 with permission from Elsevier.

polymer matrix together with an ionic liquid solution, represents an attractive strategy since it joins the mechanical and chemical stability of the polymer component with the intrinsic good conductivity, non-flammable nature and high thermal stability of the ionic liquid component. Few examples of this class of materials for application in lithium batteries have been reported in literature. Shin *et al.* reported on a lithium-metal battery formed by a $LiFePO_4$ cathode and a polymer electrolyte consisting of poly(ethylene oxide), LiTFSI and a room temperature ionic liquid, having high and stable performance at 40 °C [21]. Improved cycling performances were shown by Chew *et al.* by replacing conventional liquid electrolytes with an ionic liquid polymer composite, in a lithium-metal cell using a polypyrrole coated lithium vanadium oxide cathode at room temperature [22]. J.-K. Kim *et al.* developed two PVdF-based polymer membranes based on room temperature ionic liquid and organic carbonate electrolytes and successfully tested them in a lithium battery having a carbon coated $LiMn_{0.4}Fe_{0.6}PO_4$ cathode [23]. Our group proposed gel-type polymer electrolytes formed by immobilizing a solution of lithium N,N-bis(trifluoromethanesulfonyl)imide (LiTFSI) in N-butyl-N-ethylpyrrolidinium N,N-bis(trifluoromethanesulfonyl)imide (Py_{24}TFSI) IL with the addition of organic solvent mixtures, such as ethylene-, propylene-, and dimethylcarbonates (EC-PC-DMC), into a PVdF-HFP matrix [24]. We demonstrated that the addition of the organic solvent mixtures to the IL solution results in an improvement of the ionic conductivity and in the stabilization of the interface with the lithium electrode. Conductivity values in the order of 10^{-3}–10^{-2} S/cm were obtained in a wide temperature range. These unique properties allowed the effective use of the proposed membranes as electrolytes for the development of

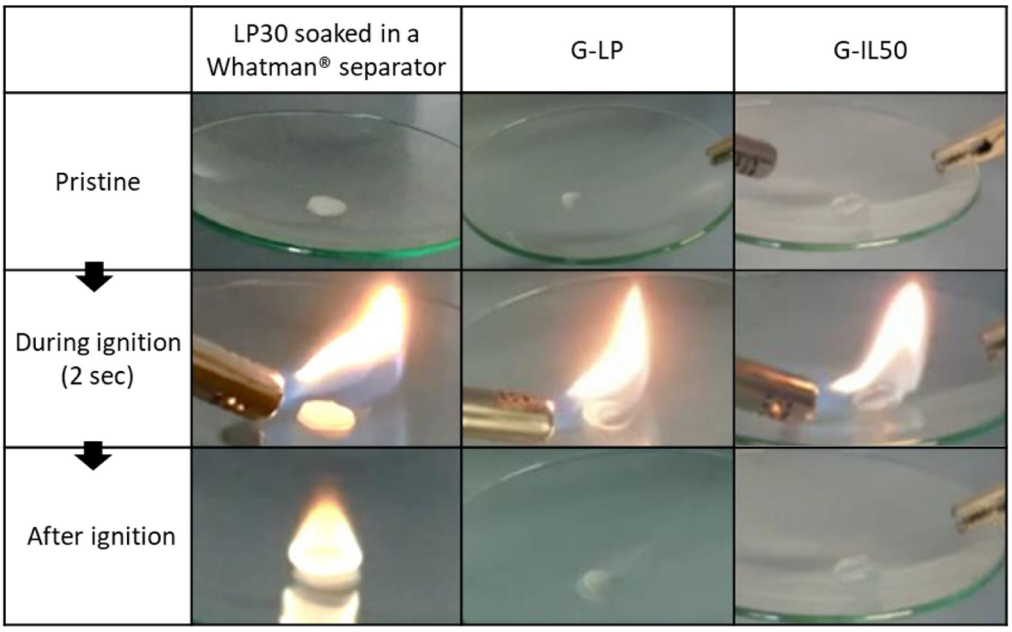


Fig. 3. – Images during flammability tests of LP30 soaked in a Whatman® glass fiber separator, GPE containing LP30 (center), and GPE containing LP30+50 wt.% IL (right). Reprinted from [25], © 2022 with permission from Elsevier.

advanced polymer batteries based on a lithium metal anode and an olivine-type lithium iron phosphate cathode.

When looking to high-voltage batteries, for high-density applications, stabilization of the cathode-electrolyte interface must be provided. In this case, the choice of both polymers and liquid components becomes even more severe for suitable GPEs. As an example, the widely used PEO-based electrolytes, due to limited oxidative stability, cannot be adopted with LNMO cathode, operating up to 4.8 V *vs.* Li^+/Li. In this context, we recently reported gel polymer electrolytes, based on PVdF-HFP, 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate EC/DMC, so called LP30, and 1-butyl-1-methylpyrrolidinium hexafluorophosphate ($[Py_{14}]PF_6$), having improved inherent safety for high voltage lithium batteries [25]. Dry PVdF-HFP membranes, prepared with EC/DMC, were soaked in LP30 and in its mixtures with 30 wt.% and 50 wt.% [Py14]PF_6 to obtain GPEs. Safety and thermal stability of the proposed GPEs were assesed by means of flammability tests. As shown in fig. 3, the GPEs are non-flammable under flame ignition. On the contrary, a Whatman® glass fiber separator soaked in pure LP30 combusts continuously even after the igniting flame is removed, while G-LP and G-IL50 (*i.e.*, the GPE containing LP30 and LP30+50 wt.% $[Py_{14}]PF_6$, respectively) form a small amount of fume but do not catch a fire. The flammability test proved that the GPEs based on PVdF-HFP and $[Py_{14}]PF_6$ are highly thermally stable even when they contain flammable components.

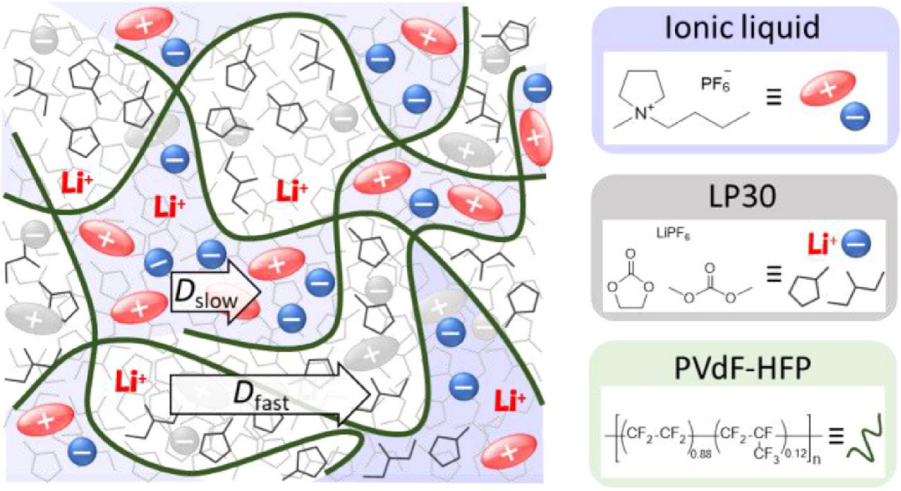


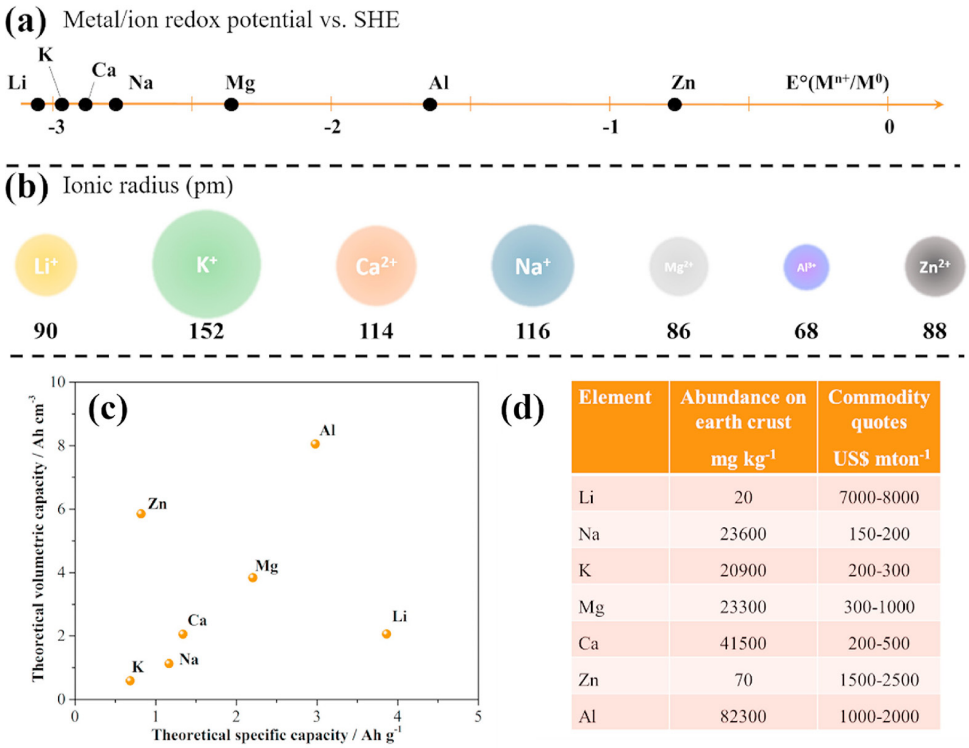
Fig. 4. – Schematic illustration of micro-segregation within the GPE, containing IL-rich domain with slower self-diffusion coefficients of mobile species (D_{slow}) and EC/DMC-rich domains with faster self-diffusion coefficients of mobile species (D_{fast}). Reprinted from [25], © 2022 with permission from Elsevier.

The proposed GPEs were also characterized in terms of mechanical and transport properties. An interesting finding arose on the microscopic properties, as well as the gel formation mechanism. Our hypothesis was that a micro-segregation within the gel occurs, in which micro-domains of IL-rich and EC/DMC-rich phases are created, as designated in fig. 4. The former should have a micro-viscosity greater than the latter, which slows down the mobility of the species contained in it. This molecular segregation between the IL and the carbonate molecules is somehow induced by the polymer during the formation of the gel. In terms of lithium-ion mobility, G-IL30 (GPE containing LP30+30 wt.% IL), where the lithium diffusion coefficients are approximately superimposed on those of the G-LP (GPE containing pure LP30), guaranteed the best response. Most likely, this IL concentration produced a proper microstructure of the gel which favors the lithium transport.

G-IL30 also demonstrated the most promising performances in the Li‖LNMO cell configurations especially in terms of battery cycling life. The overvoltage was smaller for G-IL30 than G-LP suggesting that $[Py_{14}]PF_6$ is a suitable additive to improve oxidation stability of the electrolyte and enable the stable cycle of high-voltage LMBs with LNMO cathodes.

4. – Next-generation calcium batteries

Despite reversible calcium plating-stripping being recently demonstrated [26], efforts are still needed to improve kinetics and efficiency and to allow a wider range of electrolyte formulations. In the very last years the spectrum of searched electrolytes and cathodes expanded to achieve proof-of-concept full Ca batteries.



Element	Abundance on earth crust mg kg^{-1}	Commodity quotes US$ mton^{-1}
Li	20	7000-8000
Na	23600	150-200
K	20900	200-300
Mg	23300	300-1000
Ca	41500	200-500
Zn	70	1500-2500
Al	82300	1000-2000

Fig. 5. – (a) Metal/ion redox potential *vs.* SHE (standard hydrogen electrode), (b) mean size of the ionic species (Shannon ionic radium for 6-fold coordinated cations), (c) theoretical capacities in electrochemical cells and (d) abundance on Earth's crust and mean commodity costs of mono- and multi-valent atomic species used in beyond-lithium batteries. Reprinted from [5], © 2021 with permission from Elsevier.

Calcium is a divalent alkaline earth metal with an extraordinarily strong oxidative ability in consideration of the −2.87 V *vs.* SHE (standard hydrogen electrode) redox potential for the Ca^{2+}/Ca couple, to be compared to the −3.04 V *vs.* SHE of the lithium metal electrode. In comparison to other elements under study for battery applications, calcium is the multivalent metal with the most negative redox potential (fig. 5a) and an ionic radium very similar to Na^+ (fig. 5b), a cation easily intercalated/deintercalated in/from a variety of materials [27].

The theoretical properties of calcium metal electrodes, in terms of gravimetric and volumetric specific capacities (fig. 5c), overcome those of potassium, sodium (both gravimetric and volumetric) and zinc (gravimetric), and is similar to that of lithium (volumetric), thanks to the favorable combination of intermediate atomic weight and density. Compared to aluminum and magnesium, calcium has a larger ionic radius and a smaller electronegativity, thus suggesting on the one hand a lower coordination binding in the liquid phase thanks to the smaller charge density, and on the other hand a less covalent bonding in solid lattices. Furthermore, it is highly abundant on Earth's crust, much

more than Li, Na, K, Mg and Zn, and industrially inexpensive (fig. 5d) [28].

Overall, aprotic calcium-based battery chemistries can theoretically achieve performance of interest, not far to those of lithium-based ones. The research in the field is still in its infancy. Ca-based batteries may disclose remarkable innovations and technological breakthrough, either from a fundamental science point of view or from an application perspective.

While Ca metal is by far the most promising anodic material, its electrochemistry is rather complex (*e.g.*, a very stable calcium oxide is formed) and, due to low Coulombic efficiency, it is still far from meeting the expectations for commercial applications. As a possible alternative to calcium metal, tin has attracted interest and Ca-Sn alloy anodes are considered a viable strategy towards the new family of Ca-ion batteries [29].

Room-temperature electrolytes, stable against high-voltage cathodes, are currently looked for as a necessary requirement for high-energy density Ca batteries. Size and charge of the Ca^{2+} cation complicate the realization of classical intercalation cathodes with electrochemical performance similar to the state-of-the-art Li-based positive electrodes.

Among the limited practical studies on positive active materials, based on calcium intercalation chemistry, layered oxides, in particular V_2O_5 and MoO_3, proved to be promising [30]. Also, calcium cobaltite materials have shown exciting results, due to the 1D crystal structure, which may facilitate cation migration along with the inter-chain spaces. However, the use of cobalt-based materials is not recommended and will challenge the recycling process beyond them.

Intercalation limitations can be circumvented through alternate electrochemical mechanisms such as conversion or coordination. Among other possible positive materials, O_2 is certainly an intriguing solution to achieve low-cost, safe and environmentally friendly calcium batteries, even though important issues associated with its chemistry are still a challenge for sodium and lithium systems. As demonstrated by the calculation model reported by Stievano *et al.* [5], applied to hypothetical Ca-O_2 and Li-O_2 cells, the former may not compete in energy density. Ca-O_2 batteries could only be advantageous for large-scale stationary applications, due to lower cost and abundance of calcium. The same model applied to many other calcium- and lithium-based cell configurations, revealed in the quoted study that the estimated energy densities for calcium batteries could surpass the state-of-the-art LIBs, while most likely having lower cost. Particular voltage/capacity combinations, associable to realistic Ca-cell materials, would provide both gravimetric and volumetric energy densities higher than targeted values at cell level for the year 2030 [31]. Given a 2 C current rate, not easy to achieve, due to the sluggish diffusion of the bivalent calcium ion, but already demonstrated by few examples in literature, also power density performances, expected by 2030 at cell level, would be surpassed.

5. – Conclusions and outlook

Safety and energy density of LIBs remain focal issues to be solved. The utilization of ILs as electrolyte component will be at the forefront of the transition from LIB to LMB

technology, whereby the lithium metal anode is fundamental to realizing high energy density batteries. Toward the advancement of ILs, it is necessary to carry out molecular engineering to create "IL-based composite materials". IL mixtures with organic LEs or polymers, deserve to be developed. In addition to molecular design, future focus is necessary on the conformational design between ILs and other materials to control ion segregation and allocate special functions to the segregated phases, *e.g.*, a highly concentrated electrolyte systems [32]. The composite materials of ILs and inorganic solid-state electrolytes (SSEs) to yield quasi-SSEs are another class of prospective materials to be investigated [33].

With respect to rechargeable calcium batteries, despite technical aspects concerning the implementation and upscaling of this technology, as discussed in sect. **5** of the review by Stievano *et al.* [5], calcium batteries are considered a research avenue worth pursuing. By mainly addressing the cycle life issue, it is a future emerging technology particularly advantageous from a techno-economic point of view for large scale stationary applications.

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