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Solid-State Post Li Metal Ion Batteries: A Sustainable Forthcoming Reality?

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In the quest for a sustainable society, energy storage technology is destined to play a central role in the future energy landscape. Breakthroughs in materials and methods involving sustainable resources are crucial to protect humankind from the most serious consequences of climate change. Rechargeable batteries of all forms will be required to follow the path. Elements that are eligible to harmonically contribute to the development of a sustainable ecosystem and fulfil the demands of high energy density batteries include Na, K, Ca, Mg, Zn, and Al. Numerous research efforts are underway to explore new battery chemistries based on these elements and, depending on the field of application, different elements inherit different advantages and challenges. Full sustainability implies that the environmental friendliness of these systems must be characterized by a "cradle-to-grave" approach. In this context, the pursuit of global environmental and economical sustainability from mass production, raw materials, and technical challenges is discussed herein for the most recent battery concepts based on monovalent and multivalent metal anodes. A perspective on strategies and opportunities particularly around the development of all-solid-state system configurations is provided, and the most important obstacles to overcome in search of a more sustainable future for electrochemical energy storage are addressed.

1. Introduction

Sustainable energy storage and production are essential for the survival and advancement of humankind, especially, due to the concerns over global warming and related issues arising from the overdependence of environmentally hazardous approaches for energy production and use by industries and society. Present worldwide electricity consumption is estimated to be about 25 000 TWh and is expected to be around 40 500 TWh by 2040.[1] This energy is mainly produced from combustible (coal, gas, oil, biofuel, and waste) fuels (66.3%), nuclear and hydropower (26.3%), and only the remaining 7.4% by solar, wind and geothermal sources.[2] The recent year witnessed a constant increase in electricity production from renewables. This trend is expected to increase drastically in the coming years so that a net-zero CO_2 emissions-based energy production is realized by the end of the

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century using clean energy technologies. An estimate of $ 31 trillion is expected to be invested by 2070 for achieving this target using clean energy technologies and pursuing sustainable development.[3] Thus, worldwide installation of renewable energy production units will increase many folds, which will mandate economical, safe, ethically produced, and efficient energy storage systems. Indeed, batteries must be integrated with renewable energy production units to guarantee continuous and steady energy production and supply, which is also important in stabilizing electricity pricing. Therefore, the extension of batteries to large-scale storage, in addition to electric vehicles (EVs), is crucial. Hence, the application of current energy storage technologies to the renewable energy sector will become critical in achieving sustainable energy production and net-zero CO_2 emissions.[3]

The last three decades witnessed an unprecedented advancement of electronics and related technologies and their influence in human life, chiefly catalyzed by the implementation of Li-ion batteries (LIBs).[4] Performance and cost of batteries have been the focus of battery development in the last decades. LIBs have seen their energy density triple at the cell level since their first commercialization with cost of battery packs decreasing from $1100/kWh in 2010 to $156/kWh in 2020.[5] Energy density and cost are interconnected; less materials are needed for higher energy densities for the same storage capacity, meaning a lower cost. The steep decline in battery costs has not been matched by a similar attention to sustainability of the LIBs over the whole life cycle including mining, material production, battery manufacturing and distribution (**Figure 1**a). Battery manufacturers ingest more than 30% of the world's production of lithium precursors, and the global adoption of EVs will increase it to many folds. Among the battery manufacturers, the largest lithium consumers (77%) are from China (39%), South Korea (20%), and Japan (18%), and the rest of the world consumes only 23%.[6] EVs along with large-scale grid storage will imbalance the demand and supply of lithium precursors, consequently, the price, in addition to concerns regarding the reserves of lithium that are located at geographically constrained locations, so that the availability of lithium precursors will be a big challenge. Indeed, exploring

new resources and establishing efficient recycling technologies might not be sufficient to accommodate the expected huge demand of lithium precursors globally. Sustainability-wise, LIBs may become a future concern both due to the presence of lithium, the natural abundance of which is relatively low in Earth Crust (0.0017%),[7] and due to the elements employed in electrode material fabrication. In comparison, the Li^+ reserve in seawater is estimated to be almost 57 000 times higher than its land abundance. However, Li^+-seawater processing is complicated due to the low concentration of Li^+ (0.026 mmol L^{-1}) and the copresence of chemically analogous ions (Na^+ and K^+). Supply risk score (SRS) is a valuable metric used to summarize a selection of risks connected to the exploitation of a material, ranging from reserves and resources risk to recycling, from substitutability to country, without neglecting socio-political involvements.[8] Mn, Ni, V, P and especially Co have supply risk scores higher than 50 (data from 2017), selected as a critical threshold;[8] noteworthy, as a rule of thumb, the higher the SRS of a material, the more problematic its exploitation. In general, the processing of huge amounts of raw materials have a substantial impact on the environment. A well-known case is that of the water depletion, which is being caused in Chile's "Salar de Atacama" region where one of the biggest world productions of Li from brine is located. In fact, 1900 tons of water are necessary for the extraction of 1 ton of Li, water which is diverted from agriculture thus jeopardizing farmers survival in the region.[9] Enhancing the recovery of raw materials from spent batteries would help alleviating the impact of LIBs production although recycling alone is not enough to replenish supplies of minerals. In addition, at present, second-use applications of end-of-life batteries have been considered preferable to recycling by looking at the economics aspect and for the waste management hierarchy concept.[10]

Achieving a high grade of sustainability is a challenge that brings new opportunities to pursue similar, yet diverse, battery technologies based on sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), zinc (Zn), and aluminum (Al). Most of these elements are available globally and considered by many researchers as technologically promising to effectively support LIB technology in commercial EVs, electronics, and grid
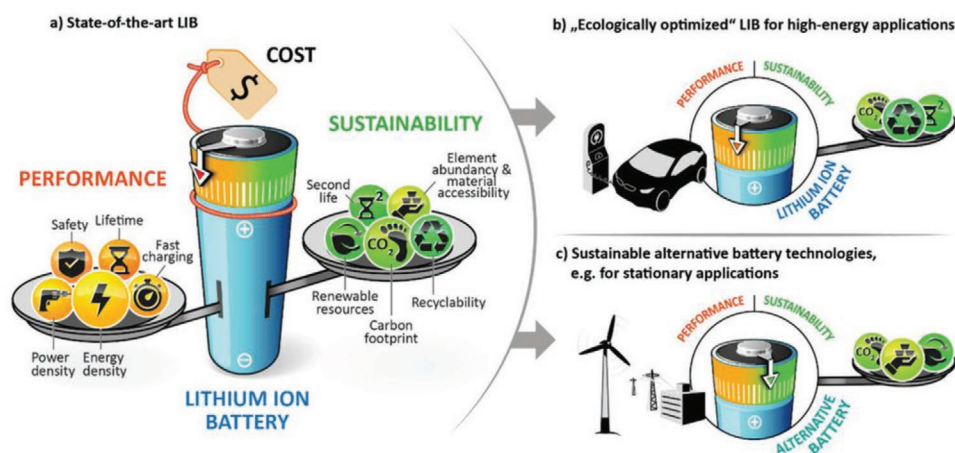
Figure 1. a) Key performance factors versus sustainability of current LIBs; b) ecologically optimized and sustainable alternative technologies. Reproduced with permission.[1] Copyright 2020, Wiley-VCH.

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Table 1. Comparison of basic characteristics of most promising post-lithium battery technology metals that have been proposed in various types of rechargeable batteries.[7,11]

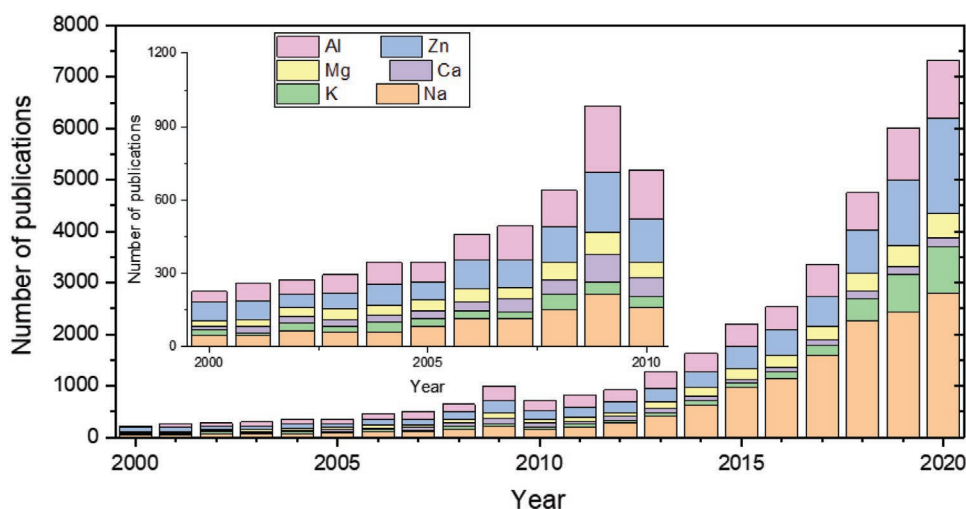|	Li	Na	K	Ca	Mg	Zn	Al
Atomic mass	6.941	22.99	39.09	40.07	24.31	65.38	26.98
Valence electron	1	1	1	2	2	2	3
Ionic radius (Å)	1.45	1.80	2.20	1.80	1.50	1.35	1.25
Density (g cm^{-3})	0.534	0.968	0.89	1.55	1.738	7.14	2.70
Std reduction potential (V) versus SHE	−3.04	−2.71	−2.93	−2.76	−2.37	−0.76	−1.66
Gravimetric capacity (mAh g^{-1})	3829	1165	685	1337	2205	820	2980
Volumetric capacity (mAh cm^{-3})	2062	1131	591	2073	3833	5855	8046
Abundance in Earth crust (%)	0.0017	2.36	2.09	4.15	2.1	0.0078	8.23
Equivalent mass abundance in Earth crust (mol kg^{-1})[11]	0.00288	1.0265	0.5345	2.0708	1.9169	0.00214	9.1512
Price ($ kg^{-1})[11]	17.00	0.15	0.74	0.12	0.28	3.02	0.56

storage (Figure 1b). The use of multivalent ion chemistry in batteries increases the number of electrons taking part in the electrochemical process, which leads in principle to higher capacity values. Magnesium has a volumetric capacity nearly double that of lithium. On the other hand, highly abundant aluminum has the highest volumetric capacity (8040 mAh cm^{-3}), which is nearly four times higher than lithium and a high gravimetric capacity (**Table 1**), which could favor the production of a low-cost and lightweight energy storage device. Whichever the battery chemistries that are intended to be developed, safety, low-cost, and energy storage capacity are the most demanding characteristics of the market and the end-user.

The trend is clear from the research and development point of view where the last five years witnessed several fold increases in the knowledge development in the form of research publications (**Figure 2**) and patents. Among these non-lithium-based technologies, sodium ion batteries (Na-ion batteries, NIBs) are flourishing, and significant improvements are seen in the number of publications and patents. Intriguingly, several battery companies are founded in the recent years, which focuses

on NIBs production and development; two examples are Faradion (www.faradion.co.uk) and Tiamat (www.tiamat-energy.com). NIB is also promising due to the availability of low-cost precursors and abundant Na in the Earth's crust; thus, efforts are made to commercially develop NIBs for EVs[7] along with targeted application in grid storage which is assumed to be the first-hand place for this technology to penetrate soon. Along with NIB, other so called "post-lithium technologies" are expected to flourish in the coming years, however challenges for their success and the hurdles to overcome are immense.

Even though large number of publications are out, post-lithium battery technologies are still young, and many findings are not even pilot-scaled or transferred to industries. Presently studied electrodes and electrolytes are in low technology readiness level (TRL, 1 to 3) and intense research and involvement of industries are necessary to mass-produce the raw materials in a cost-effective manner.

However, the R&D on such systems are encouraging, since many approaches that have been used in LIB research are useful for future development on the post-lithium battery

Figure 2. Shows the number of publications in literatures between 2000 and 2020 for batteries based on Na, K, Ca, Mg, Zn, and Al. (The small increase in number of publications in 2009 for all these technologies and following decrease in interest may be due to the announcement in 2009 by "President Obama, announces $2.4 Billion to Accelerate the Manufacturing and Deployment of the Next Generation of U.S. Batteries and Electric Vehicles").

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technologies. However, the motto of such an approach should be the development of electrochemical systems that are easy to synthesize, safe, non-toxic, ethically conceived, durable, and economic, hence the overall sustainability in energy production, storage and distribution can be realized.

The most recent development of multivalent metal batteries is summarized and discussed in the subsequent sections. An overview is provided of the most significant approaches recently adopted by the scientific community to develop high-performing post-lithium secondary batteries with a clear focus on the sustainability of materials and production processes thereof, which are critically discussed for their environmental impact and cost. After introducing some background, answers to some specific questions, including the opportunities which are related to an all-solid-state metallic technology, are sought through the exploration of some of the most recent and, to our opinion, impactful research works. Specific perspectives on the future paths to be undertaken toward a more focused sustainable development through computational aid and advanced investigation tools are presented. The aim is to stimulate curiosity in the non-specialists and fruitful discussion in the research community for identifying actions that will build a deeper understanding and consensus around the principles of these emerging battery chemistries.

2. Post Li-Ion Cell Technologies

2.1. Why Metal and Solid State?

Distinct products need separate purpose-designed batteries and emergent, new applications require the diversification of battery technologies to meet different performance needs. This huge surge in demand implies that a significant deviation from the classical Li-ion format is necessary, which include the research of new chemistries, materials, and architectures. Now the focus is primarily on safety, increasing lifespan, reducing cost, high energy density at fast charging rate, and the debate is around which battery technology could cheaply deliver more energy per kg with the least environmental impact while addressing the specific energy storage needs. High expected energy density is possible by implementation of lithium metal, which was viewed for many years with skepticism due to its intrinsic issues related to safety.[12] Based on present achievements and trends, and to favor the birth of a European battery industry, the European Union (EU) is promoting and supporting research and development of new (2025) and future (2030) so-called Generations (Gen) 3 and 4, respectively.[13] Gen4, in particular, will exploit the Li-metal anode and high-V conversion cathodes, overcoming the intrinsic limitation of insertion chemistries, in combination with safe, solid-state electrolytes.[14] Solid state battery technology has recently gathered considerable attention from leading companies (e.g., Toyota, BMW, Dyson, etc.)[15] with successful demonstration of lithium metal polymer-based Li/PEO/LFP batteries by Blue Solutions (Bollore group). With the advancement on all-solid-state electrolytes, lithium metal as anode has regained increasing interest.[16] Commercial approaches to enabling Li metal batteries include inorganic, polymerics and hybrid separators.

Toyota recently filed several patents on single crystal garnet LLTO/LLZO prepared in a novel way. They claimed to introduce all solid battery-powered EVs with sulfide-based solid electrolytes by 2022.[17] Medtronic uses inorganic LiPON glass as the protective layer on lithium metal anodes with polymer. As just remarked, Blue Solutions, European car company, is using lithium-metal-polymer batteries in their "blue cars" (30 kWh, 100 Wh kg^{-1}). The operating temperature is ≈80 °C. SEEO (partner of Bosch) claims 220 Wh kg^{-1} for cells built with a block copolymer electrolyte (DryLyte technology), operating at 80 °C. Packs of 10 kWh were claimed in 2015, but very little news was reported after that.[18]

Higher performance requires the gradual introduction of post-Li batteries based on new ions systems. Some of the materials advances now in the research phase hold the promise of significant improvements as drop-in replacements with similar design and manufacturing processes of traditional LIB technology. When higher manufacturing costs are predicted, they still might be counterbalanced by lower materials cost and by a supply chain that is more sustainable and less difficult than for LIBs. The natural abundance of an element on Earth can be used initially to understand the availability of raw materials, although for the application in batteries the molal equivalent mass abundance, that considers the transferable numbers of electrons, might be more meaningful (Table 1).[11] Looking at this latter parameter, K and Na are respectively 190 and 350 times more abundant than Li, with costs remarkably low.

Innovation in non-Li-ion battery systems deals with the creation and advancement of new storage solutions compared to the current systems. There is a huge potential for the development of batteries for a variety of power ranges and energy storage capacities. To boost energy efficiency and decarbonisation of transport, traction batteries are considered a KET (Key Enabling Technology) in electric vehicles. For e-mobility, the specific focus has to be placed on the development of high voltage 4.5–5 V LIBs and all-solid systems with a differentiation made for energy orientated (passenger cars, buses, trains, etc.) and power orientated (heavy duty vehicles, maritime, (P)HEVs, etc.) applications. Driving range, safety, and cost remain the biggest hurdles in the way of mass EVs adoption. Innovative approaches to EV battery manufacturing present the opportunity to maximize stored energy relative to the weight of EVs, allowing for up to three times the driving range. New battery chemistries and designs prevent overheating, are immune to catastrophic failure, and could be incorporated into the structure of a vehicle to improve strength in some cases. For example, in the case of Mg-based batteries, many kinds of solid-state electrolytes have been developed to serve as protective coating materials that allow migration of Mg^{2+} and prevent any side reaction.[19] Much of this can be accomplished at a lower cost compared to conventional batteries, thus bolstering widespread adoption of EVs. Batteries for grid connected stationary applications have somewhat different requirements than those for the automotive sector, so that specific needs drive both the optimization of LIBs and the innovation and development of non-LIB technologies specifically designed to provide high cycle life, long calendar life, optimized safety, and low cost. Aqueous Zn/Al-ion are among those systems that can offer a promising solution to many safety concerns and economic challenges.
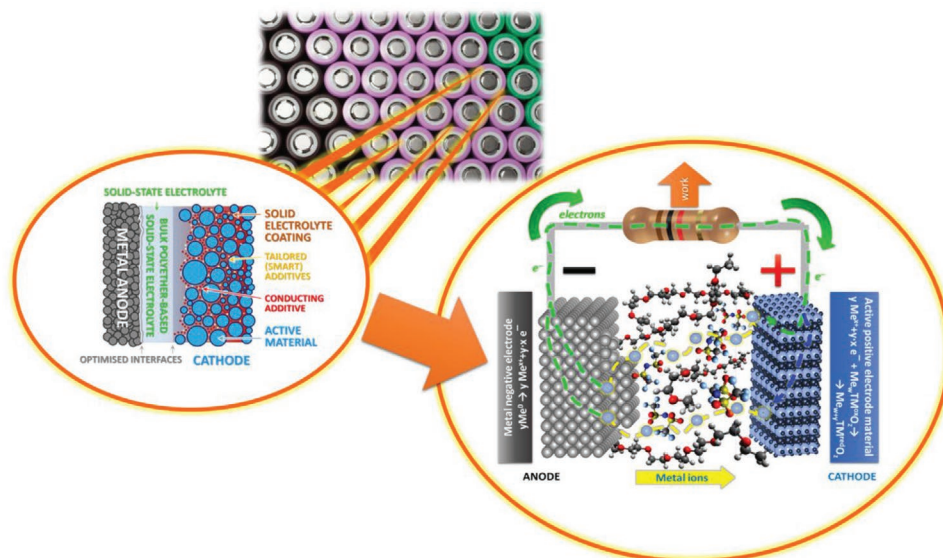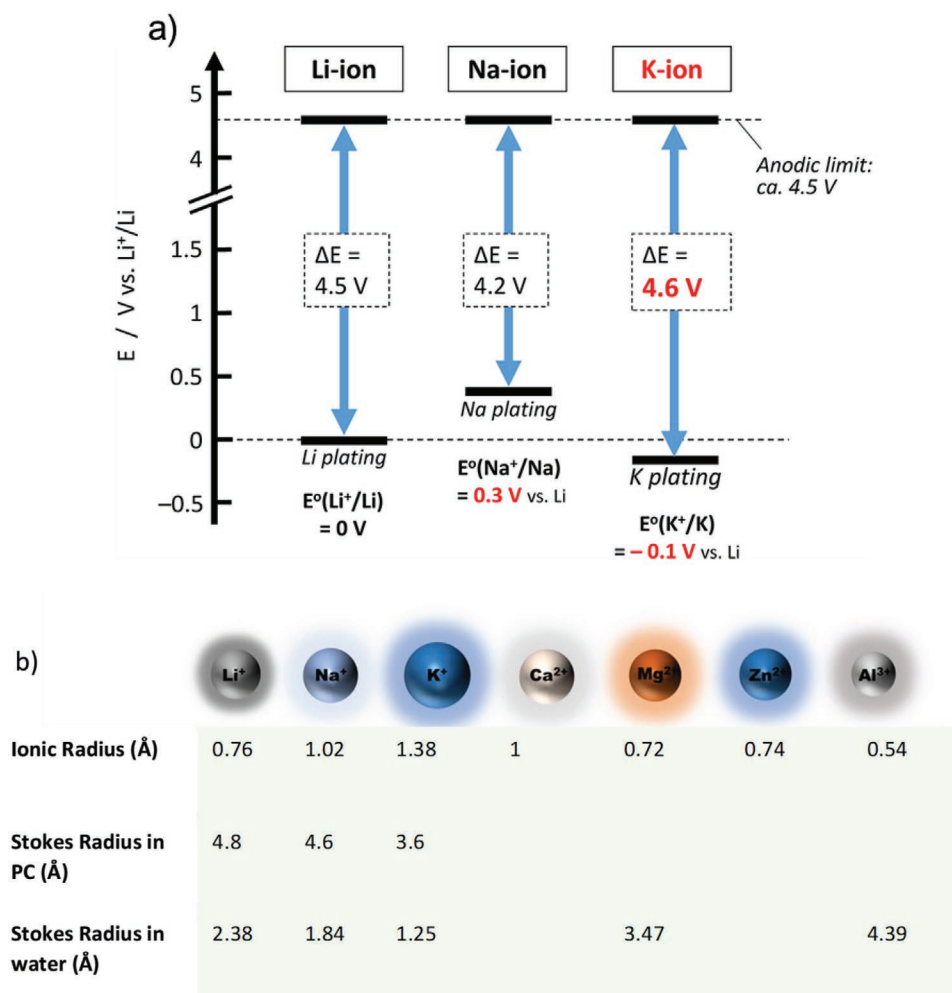
Figure 3. Generic sketched description of full metal solid-state batteries.

Also, solid-state designs based on solid (polymer, ceramic, and hybrid) electrolytes may lead to higher safety levels and would be a more sustainable solution for powering many applications. In the solid-state configuration (**Figure 3**) the porous separator, which is usually impregnated with the liquid electrolyte, is replaced by a solid electrolyte layer that functions as both the separator and the electrolyte.

On one hand, the contact between the composite electrode and the solid electrolyte has to be optimized to obtain a high contact area and good ionic conductivity while liquid electrolytes have the advantage of penetrating in the porous structure of the cathode. On the other hand, for certain chemistry a solid electrolyte can decrease the charging time and facilitate higher power density, also enabling different cell designs. In a conventional liquid-state battery the repeating units are connected in parallel; conversely, the so-called bipolar design where repeating units are connected in series is possible when solid-state electrolytes are used (additional information can be found in Falco et al.[16]). This allows the stacking of many electric cells in a single package, boosting voltage and power.[16,20]

Materials such as alkali metal anodes and solid-state electrolytes in pairing can significantly increase the specific energy (Wh kg^{-1}) of a cell due to the high gravimetric capacity of the metals (see Table 1) compared to 339 mAh g^{-1} for the lithiated graphite anode. For lithium, this fact has been clearly demonstrated by assessing the energy of a model all-solid-state battery (ASSB) cell stack with Li metal anode and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC-811) active cathode material.[21] A viable complementary technology to LIBs can be Na ion batteries (NIB), especially considering the abundance of Na, (see Table 1). Other advantages are related to the overall cost and the possibility of reaching high power performance due to the fast diffusion of Na$^+$ ions compared to Li$^+$ ions in liquid electrolytes. However, the theoretical energy density is estimated to be lower for NIBs than the practical specific energies for LIBs (152 Wh kg^{-1} vs 262 Wh kg^{-1} for a model cell discharged at 0.25C).[22] This difference was also recently debated based on some reports, using

the 18650 type cell (Na-ion) as a model.[23] According to the published Viewpoint,[23] the rough estimation of the possible specific energy of a commercial Na-ion 18650 CNRS-CEA cell is of 90 Wh kg^{-1} with missing information on the cathode and other components. Then, a hypothetical 18 650 cell using an $O3-NaNi_{0.68}Mn_{0.22}Co_{0.10}O_2$[24] advanced cathode was estimated to deliver around 150 Wh g^{-1} which is close to the energy density of an 18650 cell based on $LiFePO_4$ (LFP).[23] This means that when fully developed, NIBs could be well suited for less-demanding applications (short range EVs, energy storage systems for alternative energies like solar and wind, etc.), where normally LIBs based on LFP can be used efficiently. Matching the practical capacity of NIBs with LIBs is still a tough challenge to crack. This difference, which is quite significant, could be only partially alleviated by replacing Cu current collectors at the anode with Al which is a cost saving strategy that also allows lowering the mass of an electrochemical cell. Studies and analyses that assess the cost and performance of various elements are often not comparable and even contradictory, thus have to be interpreted and compared with caution. A recent cost analysis of materials for Na and Li-ion cells including raw materials production and Li and Co supply risk, has highlighted that in case of Li shortage, the use of Na has a substantial cost advantage, also considering that replacing Cu with Al reduces the battery cost.[25] Anyway, other researchers identified a strong inverse correlation between the practical specific energy and the manufacturing costs for NIBs, showing that the cost savings obtained by using Na raw materials play a minor role so that NIBs can be considered as viable alternatives to LIBs only if they can deliver similar practical specific energies.[22] Another possible cost-effective system option recently at the center of noticeable research work is K-metal (and K-ion) batteries owing to some unique characteristics of K: i) elemental abundance; ii) possible lower plating potential than Li under some experimental conditions (**Figure 4**a); iii) no formation of Al-K intermetallic compounds.[26] The operating voltage is an important parameter that determines the energy density of a cell, and in

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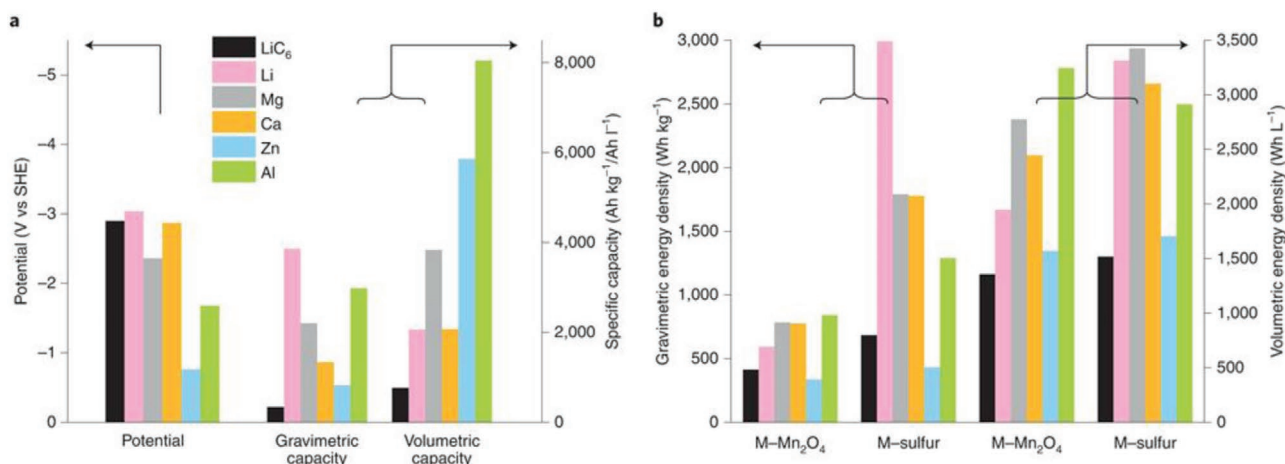
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Figure 4. a) Potential window of Li, Na, and K in carbonate ester solvents; Reproduced with permission;[26] Copyright 2020, American Chemical Society; b) Ionic radii and Stokes radii in water and PC for some ions used in new battery technologies.

metal batteries the potential of the negative electrode is established by the electrode potential of the metal that not always coincides with the standard electrode potential. The solvation state of the metal ions influences the electrode potential and when carbonate ester solvents (propylene carbonate – PC and mixed ethylene carbonate:diethyl carbonate – EC:DEC) are used it was observed that potassium plating/stripping currents begin to flow at −0.15 V versus Li+/Li.[26] Therefore, in these experimental conditions, the voltage window is wider for K than for Li and Na (Figure 4a). Another promising feature that motivates so much research on K batteries is the small Stoke radii of K+ (Figure 4b) which could lead to a higher ionic conductivity and transference number, essential for high-power battery operation.[25] However, the violent chemical reactivity of K is a strong concern toward its practical use.

Multivalent metal/ion batteries for which the metal anode can access to higher oxidation states, M^{2+} and M^{3+}, have also been characterized for their volumetric and gravimetric specific capacity, however, verifying their claimed higher energy densities is challenging as the values are often reported based on the specific or volumetric capacities of the metal anode only (for multivalent metal battery).[19] To get more realistic projections,

the estimations should not be made simply by comparing the energy density data of the materials, but at the cell level, since both the anode and cathode govern the energy density of a battery. In addition, the inactive materials including the separator and the electrolyte, especially when this latter is solid, need to be included in the calculation for reliable results.[9,27] A model cell that is designed to compare the effect of different metal anodes on the total energy should comprise always an identical cathode. For new technologies like multivalent metal batteries this is rather difficult because an optimal and realistically universal cathode material for all the suitable metals (Mg, Ca, Al, and Zn) has not been found yet. Very recently an attempt was made to calculate the theoretical gravimetric and volumetric specific energies of batteries having graphite or metallic, Li, Mg, Ca, Zn, and Al at the anode side and spinel Mn_2O_4 (with a hypothetical $M_1Mn_2O_4$ discharge product) or sulfur as cathodes.[19] Lithium metal has the lower redox potential among these metals therefore E_{cell} can be maximized (**Figure 5**a). In general, all the metal-Mn_2O_4 batteries Zn excluded, showed higher gravimetric and volumetric energy density than the graphite-Mn_2O_4 one. However, the metallic Mg, Ca, and Al cells reached even higher gravimetric energy density values

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Figure 5. a) Redox potential and specific capacity of different anodes and b) theoretical gravimetric and volumetric specific energy densities of batteries against different anodes and Mn_2O_4 or sulfur cathodes. Reproduced with permission.[19] Copyright 2020, Springer Nature.

than metallic Li, being the metallic aluminum cell to show the best volumetric energy density, well above that of Lithium, in this particular cell set-up (Figure 5b). The cell with sulfur as cathode and lithium metal as anode showed higher gravimetric energy density than all other multivalent metals (Figure 5b). It is worth noting that Zn metal batteries (ZMBs) are penalized by their redox potential, which is quite high compared to the other, thus Zn could not compete neither in gravimetric nor in volumetric energy density despite its very high theoretical volumetric capacity of 5854 mAh cm^{-3}.[19]

Other relevant advantages of a technology beyond Li-ion including metal anodes and solid electrolytes are undoubtedly related to safety reasons. Mostly two important electrochemical features are responsible for the failure of cells comprising a pure metal anode: the plating of the metal that is being deposited on the anode and the electrolyte decomposition. These two modes of failure are strongly interconnected.[28]

Lithium metal batteries with organic electrolyte solutions suffer from detrimental high surface area lithium (HSAL) growth, with unfavorable morphologies (e.g., needle like). Indeed, high surface area metal (HSAM) growth during the plating/deposition on Na and K metal anodes is also uncontrollable, which could seriously hamper their practical application. Besides, the formation of a stable protective passivation layer on the metal anode is possible on metallic Li and to an extent on K (an insoluble SEI has been observed), however, such layer is often not obtainable on metallic Na using common carbonate ester electrolytes.[29] In general, multivalent metals except Ca and Mg[30–32] are not largely affected by this issue, since favorable SEI formation have been reported in literature, but rather they suffer from a slow diffusion of the bivalent or trivalent cations through the passivating layer which has ion-blocking properties.[19] Moreover, it has been reported that HSAM free plating is possible on multivalent metal anodes.[28]

Solid-state electrolytes (SSEs), in particular polymer electrolytes (PEs) are beneficial in suppressing the formation of HSAM growth thanks to their mechanical properties. Therefore SSEs/PEs could be the ideal choice to develop safer and high energy density metal batteries for those metals that are prone to HSAM formation. Anyway, many unresolved issues concerning

the degradation of cathode interfaces in inorganic solid-state batteries are still to be solved to enable the integration of solid inorganic electrolytes in full battery cells.

Regarding the cost of SSEs and processing technologies, some analyses have been recently proposed concerning the manufacturing of all-solid-state batteries compared to conventional LIBs.[29,33] Among others, a solid-state metal battery with a sulfide based electrolyte designed for a production output of 6 GWh/year, showed the lowest manufacturing cost, and required investments.[29] The main contribution to the cell manufacturing cost was materials (>75%), but the processing cost was lower for the solid-state system. This economic model has been found sensitive mostly to cathodes and cell designs parameters, while the inert gas housing parameters (inert gas is necessary for the sulfide electrolyte) where almost irrelevant in the processing cost of the sulfide-based solid cell. This is an example that could help in making future considerations for new cells technologies that, in principle, should be setting the cost threshold at a lower level from the beginning compared to lithium technology. If this is true, an all-solid design could be optimal if materials are processed easily, for example by circumventing the use of sensitive inorganic solid replaced with more robust oxides or polymer-based electrolytes. Other factors that have been identified as pivotal for the manufacturing scalability of inorganic solid-state cells are: i) the materials availability and price, ii) the required manufacturing processes due to materials selected, and iii) the expected performances of those materials.[34] The higher the cell energy density, the lower the production cost for each kWh, identifying the cell design as a crucial trade-off. The examined examples of solid-state cells including common solid electrolytes such as $Li_7La_3Zr_2O_{12}$ (LLZO), $Li_{10}GeP_2S_{12}$ (LGPS), and Li_6PS_5Cl, and the analyses carried out on cost and performances have highlighted that the scaling of low-cost, high performance cells can fail if the materials supply chain is strongly constrained. Moreover, in the hypothesis that materials are readily available, the scaling might fail if those materials require costly and cumbersome manufacturing procedures during cell integration.[34] Large-scale production of polymer-based cells has been proven similar to conventional LIBs[20] therefore mostly compatible in

terms of cell production infrastructure. On the other hand, the industrialization of solid-state batteries containing sulfides or moisture sensitive oxides as electrolytes may present technical challenges requiring new manufacturing machinery.[33] In addition, the metal anode processing will require completely new steps in protected atmosphere compared to conventional Li-ion fabrication. Li metal could be extruded or liquefied to make foils[33] but concerning the other alkaline metals, their higher reactivity should not be overlooked, so that to the best of our knowledge, possible methods of preparation and related costing have not been discussed, yet. From a manufacturing perspective, passivation of the metal surface can be a necessary step to control the reactivity, not only during fabrication but also to suppress reaction with the electrolyte and possible HSAM growth. In case of multivalent metals, different systems might be designed in which for example alloys are used at the anode side.[28] These latter could require different processing techniques.

A scalable battery recycling process to recover and regenerate solid electrolytes and cathode materials would represent a further step toward a complete sustainable life cycle for such systems. A model method was proposed based on the principles of direct recycling, which was then verified by experiment on a $Li/Li_6PS_5Cl/LiCoO_2$ cell.[35] The SSE was recovered easily with limited energy consumption and green-house gas emissions and showed ionic conductivity of the same order of its pristine form (1.5 mS cm^{-1}). A new cell was fabricated by using the recovered SSE and cathode, while the Li metal anode was consumed. Achieving sustainability should include the recovery of the metallic anode as well as the other components, if materials are produced in large scale, so that they could effectively be incorporated again to the production system.

2.2. Sustainability: Impact Analysis

The overambitious claim for sustainability is a growing issue to be considered and discussed when new technologies are proposed. Notwithstanding the importance of the topic, as proved by the growing attention of national and supranational institutions,[36] and the targets from the United Nations (that developed 17 main sustainable development goals, SDGs, for a more sustainable future), only a few works have tackled this in the battery field. A thorough comparison between different technologies (including metal batteries) is far to be straightforward due to the lack of data available from a single source. Having these cornerstones in mind, the reader should consider our analyses as an appeal to move toward a pragmatic approach for validating the sustainability rather than a determination of the most sustainable Li "substitute".

If LIBs are compared with alternative (and already developed) technologies (Li-S and Li-air, as well as Na-based batteries with transition metal layered oxide (NNMO) and sodium metal phosphates (NFPF, NTP, and NVP) as cathodes),[8] the former showed worse SRS, exceeding the threshold limit of 50 and presenting a marked increasing trend in the last decade. Milder (and remarkably stable over time) scores are obtained when Na-batteries are investigated, albeit one should consider that a growing demand could seriously affect the SRS. Similar information is not yet available for other post-LIB technologies (based on K, Al, Ca, and Mg) preventing us to provide a complete overview; indeed, the latter technologies are still in their infancy and possible SRS would not be reliable.

As shown in **Figure 6**, when the supply risk for both LIB and post-LIBs is split into singular metal contributions, it appears clear that the highest impact is related to electrode materials,
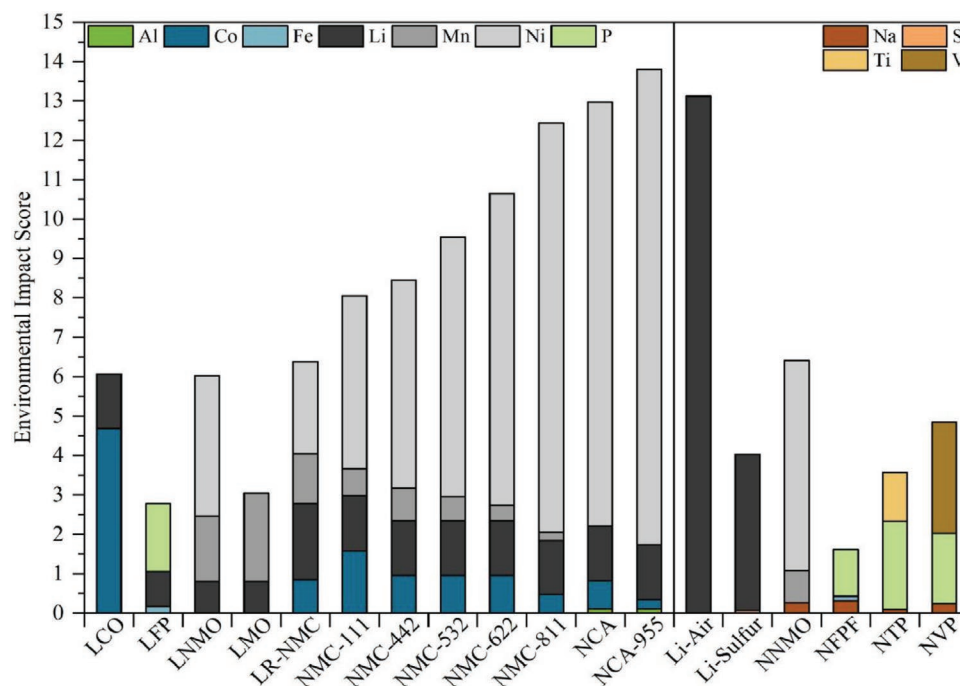
Figure 6. Environmental impact score of 18 technologies with separated individual element contribution on their resulting single score. Reproduced with permission.[8] Copyright 2019, Elsevier.

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whereas Li (and even less sodium) could be considered as a moderately limited factor, being employed in relatively low amount. On one hand, the SRS is reduced when metals with lower risk are employed in the electrodes; on the other, in both Li-air and Li-sulphur batteries the impact of the lithium became meaningful. Therefore, the increased sustainability of the investigated technologies should follow two parallel tracks: i) to develop alternative technologies and ii) to improve the sustainability of the material employed in LIBs.

To minimize the impact of the TRL of a given technology on its sustainability, the SRS, the Environmental Impact Score (EIS) and the cost of raw materials are simultaneously examined.[8] Results well correlated with the ones discussed above, where Na-based energy storage systems are characterized by the lower EIS and SRS but also affordable costs (ranging from 0.1 to 3.4 \$ kg^{-1} for raw materials). Interestingly, the EIS and SRS values of Li-sulphur batteries are comparable to Na-based batteries, but their costs are remarkably higher (7 \$ kg^{-1}), mainly due to the presence of Lithium. All LIBs investigated in that study overcome the critical SRS threshold (placed at 50), but the ones in which the cathode is based on pure manganese oxide (e.g., LiMn$_2$O$_4$) or iron phosphate (e.g., LFP) showed remarkably low environmental impact (even lower than Na-based batteries) still being cost-effective (1.5 and 0.4 \$ kg^{-1}, respectively). With respect to other technologies, NIBs/NMBs (but also K-based systems) have the advantage of being based on a monovalent cation and the knowledge accumulated on LIBs could be transferred, except for intercalation issues. On the other hand, the (electro)chemistry of high-valent species is more complex. Nevertheless, aiming at increasing the volumetric capacity, it is valuable to exploit multivalent ions, such as Mg and Al that coupled with a lower cost and superior safety. However, since their first prototype,[37] Mg-based batteries witnessed a relatively slow development mainly related to the research on different cell components, making it difficult to compare with well-established LIBs. Indeed, in the last five years, scientists have investigated aluminum-ion batteries (AIB). As already discussed above, a thorough and sustainability-driven comparison of AIBs with LIBs is hardly achievable due to infancy of the technology. Nevertheless, some research works report them as a valid alternative in terms of both efficiency and sustainability. For example, some algorithms are used to calculate the best trade-off between the usefulness of the applied electrochemistry and the environmental impact, proving that Al is the best candidate for the battery chemistry.[38] Indeed, the real advantage of Al is still debated, and definitive results are not yet available.

Forced by the lack of data on the sustainability of complete post-Li-ion- (including Al, K, Mg, Ca, and Zn) technologies, establishing the sustainability of materials that are proposed to replace Lithium is not possible, however, a partial comparison among these different metals can be made by overlooking the cell components (anode, cathode, and electrolyte) that seriously impact the green metrics. So, by limiting the sustainability analysis to metals, Lithium has dramatically high SRS, comparable to Cobalt that is worldwide known as a Critical Raw Material (CRM).[39] The factors that negatively impact on the SRS score of Lithium are the recycling, the global supply concentration, and the substitutability, being the latter identified as a major bottleneck also for other metals. With respect

of recycling issues, a literature survey offered very different scenarios,[40] pointing out the importance of a critical Life Cycle Assessment (LCA) analysis of lithium (and related technologies) before drawing any definitive conclusion. The only critical score for sodium is the recycling that, however, could not be considered as a real hotspot due to its large availability (2.36% in the Earth Crust); on the other hand, Al has negative scores only with respect to substitutability.[41]

The environmental impact of different metals was thoroughly investigated recently by means of different metrics such as Cumulative Energy Demand (CED), Global Warming Potential (GWP), and Yearly Global CO$_2$ Emission (YGCE).[42] On one hand, CED measures the total energy usage during the whole life cycle of a given material and it includes both the direct and indirect energy usage (also associated with material consumption);[43] on the other, GWP is the heat absorbed as CO$_2$ equivalent by any greenhouse gas generated throughout the production process (from mining to end-of-life/recycling) and delivered in the atmosphere. Of course, when dealing with metals, these indicators strongly depend on the final utilization of the materials and they are expected to change if large scale use is proposed. Having Lithium as a reference (CED = 125 MJ kg^{-1}, GWP = 7.1 kg CO$_2$-eq/kg and IGCE = 3.07 kg CO$_2$-eq/kg), the other metals under scrutiny for new batteries, generally have milder values: Mg, Zn, and Ca have very low CED (18, 52.9, and 5.8 MJ kg^{-1}, respectively) GWP (5.4, 3.1, and 1.0 kg CO$_2$-eq/kg, respectively) and YGCE (1.05 and 0.98 kg CO$_2$-eq/kg, for Mg and Ca respectively). Zinc, on the other hand, has comparable YGCE values to Li. Quite unexpectedly, Al has slightly higher values for all the metrics, CED = 131 MJ kg^{-1}, GWP = 8.2 kg CO$_2$-eq/kg and IGCE = 9.47 kg CO$_2$-eq/kg). Of course, these values are referred to the production of pure metals starting from naturally available sources and they could be meaningfully downsized by considering appropriate recycling and end-of-life use. Based on these, the most promising candidate to replace Li is Ca. Similar data on alkaline metals (such as Na and K) are still missing, thus the comparison is incomplete. This lack of available data is further pointing toward the necessity of a comprehensive analyses of different materials in the coming future.

Some complementary information could be extracted from the Mineral Commodities Summary (2021),[44] in which the mining and production of different metals (and metal sources) are analyzed even related to social and economic events (e.g., COVID-19 outbreak). Indeed, the cost of a material as well the number of reserves and resources are mandatory input to be considered when analyzing the sustainability and feasibility of a given technology. As already briefly discussed above, lithium demand has rapidly increased also related to its exploitation in batteries and its averaged costs is 13 000 \$ ton^{-1} (carbonate sources, 2019) much higher than for its sodium and potassium homologues (200 and 1000 \$ ton^{-1}, respectively);[45] lithium resources are 86 Mtons and they are relatively equally distributed throughout the planet. Albeit this number could appear huge with respect to the 2020's mine production (i.e., 82 Ktons), one should consider that the exponential growth of Li demand could lead to a relatively fast depletion of these resources. Aiming at a fair comparison, i) Mg resources (even not specifically quantified) are practically infinite, accounting

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only magnesite and brucite for more than 12 Btons without considering the Magnesium that could be produced from seawater and natural brines; ii) Bauxite, the primary source for Al, resources are roughly 65 Btons; iii) estimated world resources for potash (K_2O) are more than 250 Btons whereas its yearly production does not exceed 50 Ktons; iv) Fluorspar (CaF_2) and Lime (mixed calcium oxides and hydroxides) are the main Ca sources with global resources which are practically inexhaustible; v) the same is valid for salt (NaCl) having resources equally distributed throughout the world; vi) Zinc is slightly more problematic being its resources smaller (2 Btons), but this will be mitigated by sizeable zinc recycling (roughly one third of the refined Zn originates from recovered sources).

Of course, beyond availability, some other issues could be considered. For example, the Al industry is responsible for more than 1% of mankind CO_2 emission, being more than 40 kg of CO_2 produced (both by direct and indirect emissions) for each kg of produced Al.

3. Structure and Mechanism of Metal Batteries

The working principle of metal batteries resembles that of Li-ion/metal, the main difference being the replacement of monovalent Li with monovalent Na-K or divalent or trivalent metals. Similar to Li-ion, the multivalent ions shuttle back and forth from the cathode to the anode during the cycling of a cell in an ideally stable electrolyte. However, metal plating/stripping at the anode of multivalent batteries is not as reversible as lithium because of the lack of suitable electrolytes. A system based on intercalation where the metal anode is paired with an insertion cathode material is chasing a dream of yielding a high specific energy at a reasonably high cell voltage and a good rate performance. The concept of a Mg-ion based secondary battery was proposed in 1990[46] and then practically demonstrated in 2000 by Aurbach and co-workers.[37] Since then the research in this field has been very active with several experimental and theoretical demonstrations of fully functional Mg-based cells.[47–48] Although numerous issues are yet to be solved, Mg is the most matured among the multivalent technologies, while Al and Ca are the youngest. In any case, for these chemistries, a very few cathode active materials are available (if none) that could meet the minimum required energy density by considering a techno-economic analysis under the assumption of some of the battery technologies that are targeted for electric vehicles. In this regard, the practical limits of energy density achievable by a Mg battery have been modelled[47] trying to ascertain the main characteristics of a possible cathode, keeping as reference the United States Advanced Battery Consortium (USABC) and Department of Energy's battery technology targets for EV vehicles: 750 Wh L^{-1} at the cell level (and 100 \$ KW h^{-1}). This analysis used only the weight of anode and cathode active materials to calculate the specific energy, assuming an oxide type cathode. The results showed that to meet the 750 Wh L^{-1} target a Mg metal anode (2205 mAh g^{-1}) must be coupled with a cathode that yields a specific energy at cell level (active material only) greater than 800 Wh kg^{-1} (2700 Wh L^{-1}) and voltage higher than 3.1 V. This means that the cathode active material should have a gravimetric capacity of about 298 mAh g^{-1}

(or 1192 Ah L^{-1} volumetric capacity for a 4 g cm^{-3} dense oxide). If the density of the oxide used as cathode is fixed at 4 g cm^{-3} then the active material should have an energy content of 908 Wh kg^{-1} and 3632 Wh L^{-1} to achieve the 750 Wh L^{-1} USABC target. As a comparison, a state-of-the-art Li-ion intercalation system can deliver 200 Wh kg^{-1} at the cell level with energy density of the cathode (for example NMC333) of about 565 Wh kg^{-1} (2600 Wh L^{-1}).[47] It appears obvious that challenges toward the development of suitable cathodes for new technologies are massive.

Anode passivation is also very common for Ca, Mg, and Al, so that oxygen, water, and other contaminants may lead to a cell failure due to the electrochemically inert reaction products that could block almost completely the ions mobility. Thus, Zn-ion batteries may offer a solution since they have been successfully operated both in aqueous and non-aqueous solvents. It should be noted that unlike Li and Na chemistries that use standardized procedures and conventional cell set-ups for electrochemical characterization, the electrochemical data reported for multivalent metals are majorly affected by the difficulties in finding suitable baseline materials and standardized test protocols.[49] Indeed, in multivalent metal battery systems, the electrochemical results could be easily misinterpreted due to the complex reactions arising from the multiple interactions between the electrolyte, electrodes, current collectors, and other components. Thus, the risk is quite high to report overestimated gravimetric capacity and rate performance due to the lack of knowledge of the true mechanisms acting behind the intercalation process. Some recent investigations have pointed out that neither Ca nor Mg has the necessary stability in a non-aqueous electrolyte to be employed as pseudo reference electrodes differently from what normally happens for Li. Alternatives to classical half cells, three electrode cell configurations or hybrid cells with appropriate reference electrodes should be encouraged for more rigorous electrochemical studies of new electrolytes and cathodes.

The cathode choice is driven essentially by the oxidative stability of the electrolyte so that those systems for which a suitable electrolyte is missing also see the development of new cathodes going on at a terribly slow pace. At the same time, other important issues must be addressed concerning the mobility of multivalent ions in host electrodes. The reversible intercalation of one multivalent ion per transition metal center could double or even triple the capacity achievable by the current state-of-the-art lithium cathodes. However, the chemical hardness of the mobile cation and the host anion plays a fundamental role in determining the solid-state ion diffusivity as the charge number of the migrating ions increases. The crystal structure of the host also has a profound impact on the migration of ions since the coordination environment is determined by some structural features, namely the crystal system, framework flexibility and cavity sizes, which dictate the energy barrier to migration.[50] Cathode materials for Mg-batteries have been known since some Chevrel phases with stoichiometries Mo_6T_6 and $Mo_{15}T_{19}$ (T = S, Se or their combination) were found to allow reversible Mg^{2+} intercalation. The crystal structure of those compounds presents many vacant sites at relatively short distances, and Mo clusters with delocalized electrons allowing fast redistribution of charges, that could explain
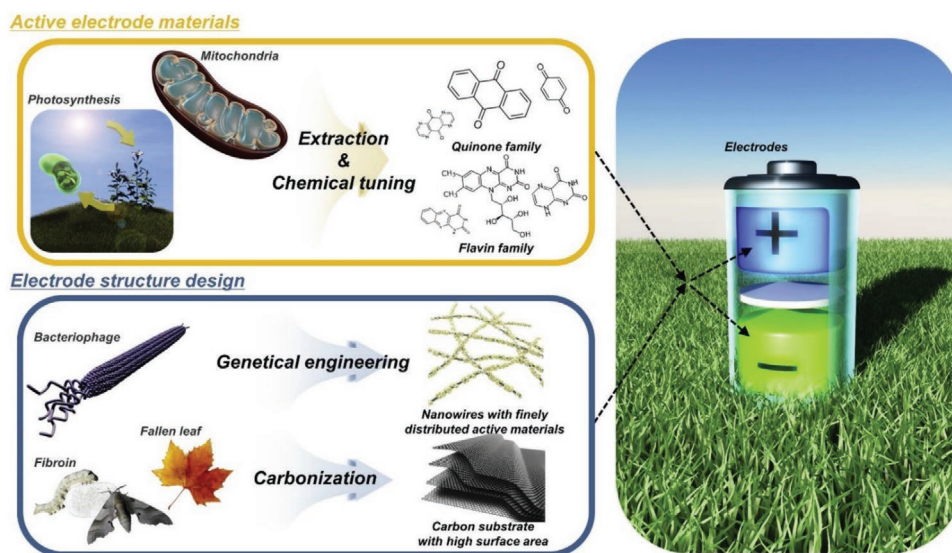
their good Mg^{2+} diffusivity. Although cells containing Mo_6S_8 showed a cycle life comparable to that of many Li-ion materials, the energy density of this Chevrel phases is too poor to be considered for commercialization. A step forward to higher energy densities is now offered by other chalcogenide hosts such as the Ti_2S_4 spinel phase[51] but further studies are needed to fully understand its stability and achieve an efficient use at ambient temperature. Chalcogenides in any case have the disadvantage of low operating voltages so that transition metal oxides appear as a viable alternative, provided that a suitable electrolyte is developed. Some controversial, open questions surround the application of metal oxides in new multivalent (MV) batteries such as, is there any solvent cointercalation that can disguise the real mobility of the cations in the host structure and, is there any boosting effect of water as contaminant in the electrolyte on the performance of the cells? Promising electrochemical performances were reported in water cointercalated hosts such as V_2O_5 and some MnO_2 polymorphs. It was suggested that V_2O_5 could reversibly intercalate both Mg^{2+} and Ca^{2+} ions but conflicting results were published, and the characterization of the inserted phases was inadequate. Recently, through some carefully designed experiments, it was elucidated that diffusion of Mg^{2+} and Ca^{2+} in α-V_2O_5 is indeed very poor which clearly demonstrates that no significant intercalation of multivalent ions occurs in the α-V_2O_5 phase.[52] A protonated phase $H_xV_4O_6$ was identified instead of the expected MgV_2O_5 and CaV_2O_5 suggesting that some decomposition of the electrolyte provided protons that intercalated into the cathode material. Indeed, it became obvious that some previously published results might have witnessed not just multivalent ion intercalation. This is quite important to draw successive paths toward more reliable experiments to discern underlying different possible complex mechanisms. As stated in the introduction, many elements important for the cathode materials have a high SRS; in particular, the widespread use of costly and toxic transition metals oxides such as those including Co and V does not seem consistent with the underlying context of post-Li technologies. Whereas the development of new chemistries may require the investigation of "impractical" materials to gain more knowledge at the research stage, as a line of tendency, those elements which are toxic should be discarded, while studies on alternatives or strategies to reduce their use should increase.

The same classes of materials have also been studied for other MV concepts, for example, for reversible electrochemical intercalation of Al^{3+} in AIBs/AMBs.[53] Scarce reports are presented to the scientific community about research in this field until a couple of years ago, when a significant interest arose around finding proper materials capable of Al^{3+} insertion.[38] Even in this case, Chevrel phases and TiS_2 have been considered, together with V_2O_5, manganese oxides and Prussian blue analogues. These latter have been applied practically in all the emerging technologies and have also been known as host materials for Li^+, Na^+ and K^+. However, their low energy density makes them interesting cathodes mainly as a proof of concept. In any case, it has been proven that a good mobility is plausible for a multivalent ion with high charge even when Coulomb interactions may be extraordinarily strong with the host lattice. A comprehensive study has shown that to achieve fast ion transport for multivalent ions such as Al^{3+}, ternary compounds

containing ions in the lattice with similar charge as the mobile ion under screening is an important feature.[46] Also, crystalline materials with high symmetry should be considered including channels with sites for migration of similar anion coordination and energy, where 3-dimensional paths are possible for fast diffusion.[54] So far, the reversible intercalation of Al^{3+} has been truly proved only for the Mo_3S_8 Chevrel phase. However, when compared with a completely similar Mg battery, the Al battery containing this cathode can only operate at half of the potential offered by the Mg system, at values as low as 0.5 V. Among the other technologies, Zn-based storage benefits from enhanced kinetics compared to harder divalent cations such Mg^{2+} despite the increased concentration of contact-ion pairs raising from the interaction between the solvated ion and its surrounding solvent shell and implying a large charge transfer resistance at the interfaces in organic solvents compared to aqueous media. In the aqueous version of these batteries, MnO_2 has been indicated as a viable candidate as a positive electrode, however, the charge storage mechanism is based on conversion reaction. When organic electrolytes are used, intercalation is possible by using the manganese oxide cathode material; in addition, many different oxides have been tested including the $ZnCo_2O_4$ spinel, doped with Al, Ni and/or Mn to stabilize the Co_2O_4 crystal structure.[55]

Ab initio computing can offer much valid help to identify the thermodynamics and kinetics of many distinct physical phenomena in order to assess specific structural and chemical features of suitable materials. In the Materials Project[56] MV batteries including Mg, Ca, and Zn have been explored through massive materials simulation to build up a map of possible multivalent working ions and corresponding electrodes structure. The examined positive electrodes included sulfides, fluorides, oxides and phosphates that were all modelled to get information on possible voltage, capacity, energy density and ion migration. This expanding work has been proven fundamental to establish an initial set of promising electrodes that were synthesized and tested, especially for Mg batteries. At the same time this approach based on calculation was effective in demonstrating the possible mechanism of Ca^{2+} plating and stripping, thus driving the experimental work toward new achievements.[57]

It is worth mentioning that redox active organic polymers have also been shown to meet the requirements for being cathode materials in both monovalent and multivalent batteries, especially considering their higher sustainability, in terms of a lower carbon footprint, when compared to conventional inorganic cathode materials.[48] Radical polymer-based batteries have shown interesting power capabilities (10–80 C rate) as well as tuneable redox potentials, but lower capacities.[58] Currently similar to supercapacitors, organic radical batteries suffer from low energy density. Anyways, for frequency regulation where the time scale is in seconds, stationary batteries for grid modernization based on polymer-based electrodes that behave like pseudocapacitors are very attractive. In addition, the prospects of a low-cost "green" synthesis of polymers from renewable sources might provide long-lasting commercial solutions at a cost that disrupts the market. It is still not very clear what could be the impact on the environment if polymers are produced from renewables instead of using petrochemicals and

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Figure 7. Some examples of biologically motivated materials for energy storage. Reproduced with permission.[60] Copyright 2018, Elsevier.

fossil fuels as the feedstock. Indeed, it is not simple to understand exactly how much energy is needed for the overall production process.[11] Nevertheless, interesting opportunities are offered by carbonyl compounds and quinone derivatives that are extensively studied in sustainable energy storage technologies (**Figure 7**).[59,60] Besides LiBs, nature-derived and inspired compounds are also advancing as electrode materials in novel systems such as Na batteries.

What is relevant with respect to MV batteries, is that polymer-based redox active materials do not require ions to intercalate into a solid crystal lattice. Such approach could be a great advantage for example for those metal ions that do not have high performance intercalation-type cathode materials. For Mg this is true, since even the most successful cathodes have shown moderate energy and power at high temperature. Recently, research focus has been devoted to redox active organic polymers for Mg technology and dimethoxybenzoquinone (DMBQ), poly(anthraquinonyl sulfide) (PAQS), 1,4-polyanthraquinone (PAQ), polymerized benzoquinone PHBQS, are some of those that have been investigated.[60]
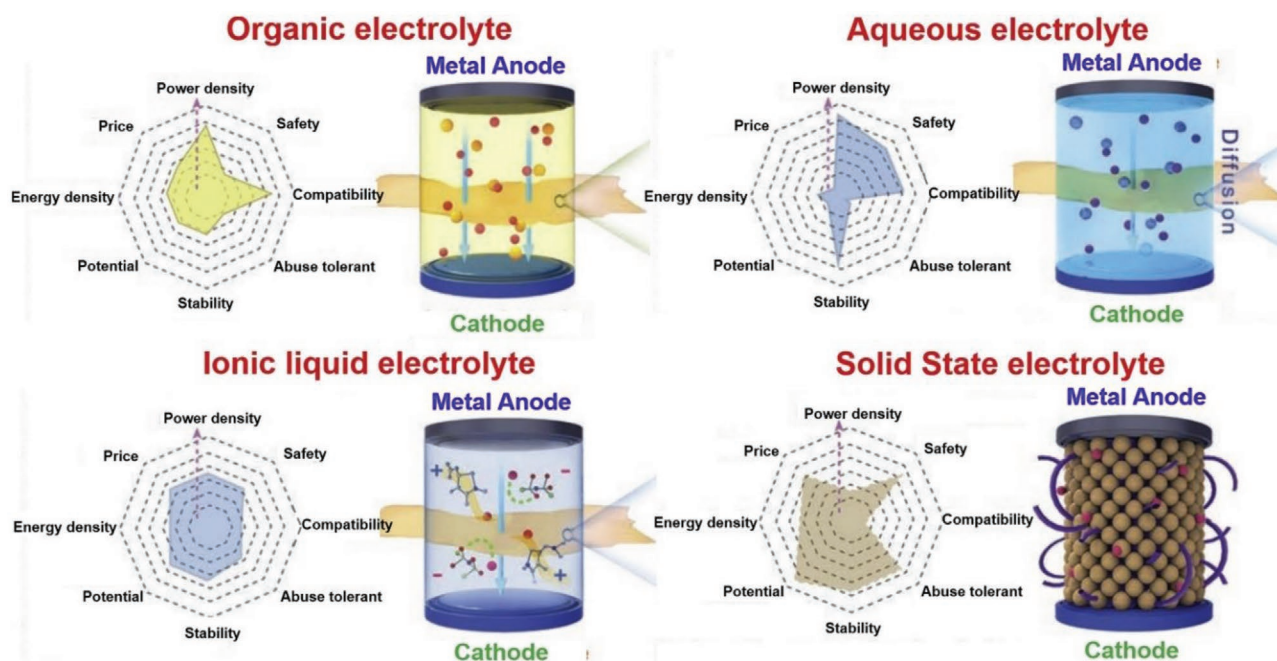
With all these systems the electrolytes have to be carefully selected to positively affect the activation period and the Coulombic efficiency. A chloride-free Mg-based chemistry has been recently proposed showing that with the right combination of organic cathodes (carbonyl compounds) and chloride-free electrolytes, storage of Mg^{2+} in organic electrodes is possible without compromising the reversibility of Mg plating and stripping. This method avoided the storage of $MgCl^+$ instead of Mg^{2+} which could be detrimental for achieving high energy.[61]

3.1. Electrolytes

The practical application of metal anodes is mainly related to the electrolyte. Targeted electrolyte systems must meet important requirements to be useful for future batteries: high ionic conductivity, chemical stability toward the electrodes and the other components, wide electrochemical window, low flammability, environmental friendliness, and low cost. Different possible electrolytes have been proposed for metal batteries namely organic, ionic liquids, water based and solid, as depicted in **Figure 8**.[62]

From an environmental point of view, the classical organic carbonate solvents that are widely used in LIBs would offer some good prospects if utilized also in new battery systems, especially because they show a low ecotoxicity, easy availability in large quantities and possibility of being obtained from renewable resources such as alcohols and urea.[11] On the other hand, they pose some risks regarding safety and low recyclability. Especially, aging of the batteries is accompanied by decomposed fluorinated compounds derived from the salts (such as $LIPF_6$, $NaPF_6$), which can start transesterification of organic carbonate solvents with the formation of organic fluorophosphates, some of which are well known hazardous substances with classified toxicity. Besides the dangers related to the handling of spent batteries, those compounds can interfere with industrial scale recycling processes and this requires the implementation of specific recovery methods.[63] It is quite difficult to make prevision on the aging effect in case of new batteries since aging mechanisms are multiple, and those technologies are not established yet, with many components still under development. In any case, a systemic thinking on recyclability of spent batteries of every kind is mandatory for a more sustainable future. Room temperature ionic liquids (RTILs) could be used as an alternative to make carbonate-free electrolytes. They are often classified as "green" solvents and could have higher recyclability than organic carbonates thus improving the recovery rate of spent batteries. However, certain RTILs can be toxic depending on the combination of cations and anions. Biodegradable RTILs which would be desirable have not been used in the battery field making generalization on their lower impact, risky. In addition, their cost is still fluctuating depending on the availability and the application technology. High manufacturing costs because of their small-scale production are a primary

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Figure 8. Electrolytes for various types of metal batteries and their main properties. Reproduced with permission.[62] Copyright 2020, Elsevier.
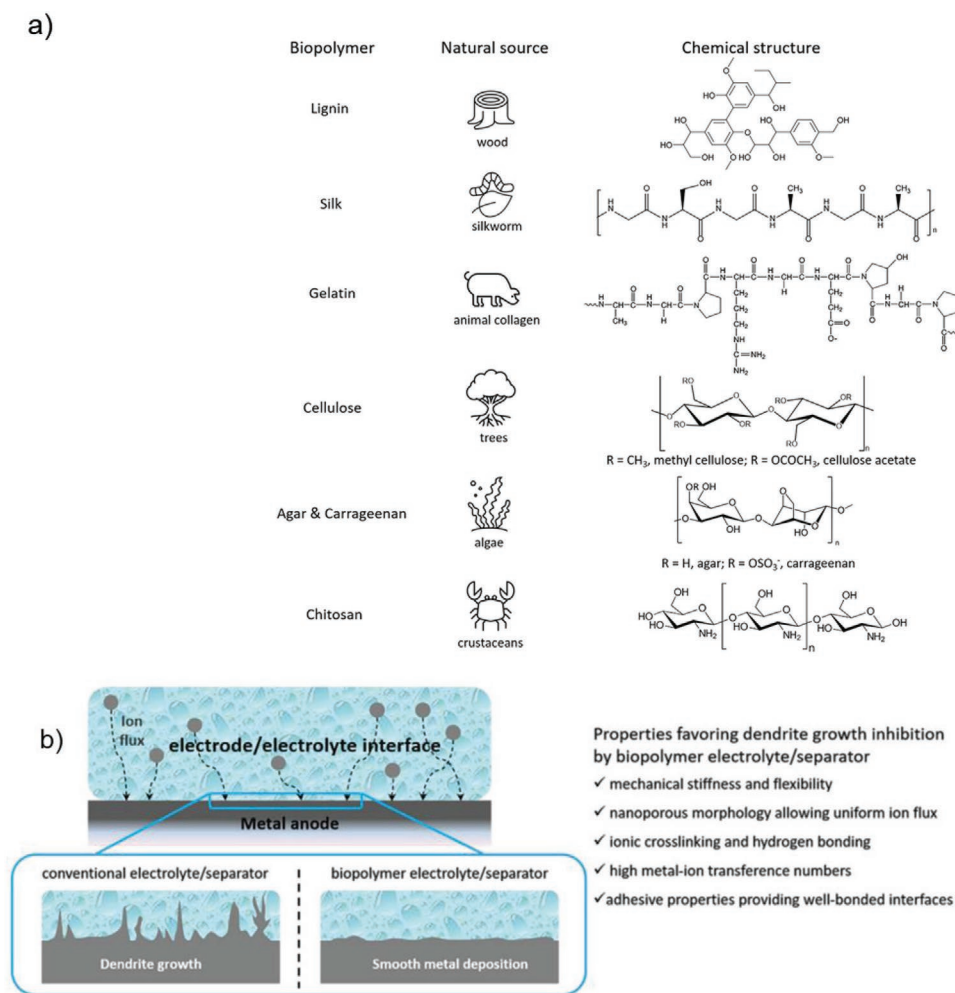
barrier for the penetration of materials in end use applications. Additionally, achieving a higher purity for electrochemical application is another challenge to address. Anyway, even if not prohibitive the cost of RTILs is hoped to drop thanks to the development of continuous synthesis processes. Large-scale ionic liquids supply is expected in the next couple of years, along with at least a 70% decline in price. An example of the economy of scale for the aprotic RTIL 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI), electronic grade, has shown that is sold for 840 $ kg^{-1} on a 1 kg scale, dropping to 490 $ kg^{-1} for 150 kg.[64] Some low cost or less expensive possibilities have been indicated in Al-based batteries with prices around 70 $ kg^{-1}.[65] A very economic and environmentally friendly alternative to imidazolium-based RTILs, is a new class of RTILs called deep eutectic solvents (about 10 $ kg^{-1} for AlCl$_3$:urea).[65] These are very attractive but need optimization in ionic conductivity and stability to be employed for application in the energy storage field. The initial cost of the RTILs is not the only important factor and can be offset since their use is often accompanied by enhanced safety from the replacement of toxic and volatile solvents.

Compared to liquid electrolytes, solid electrolytes could offer advantages due to their reduced flammability and prevention of solvent leakage. If polymeric electrolytes are considered, then other benefits could be related to their production from renewable resources such as bioethanol. For example, poly(ethylene oxide) is one of those polymers that could be produced starting from ethylene obtained from sugar cane instead of fossil fuel, as usually done today.[11] To fully ascertain whether this method is truly beneficial, the impact on the environment of intensive agriculture for sugar cane production, and the overall ethylene processing, which is energy demanding, should be considered. Thus, simple assumptions of lower impact are not possible without a complete analysis. Recently, natural biopolymers

have attracted a great deal of interest to design solid and gel polymer electrolytes (SPE and GPEs) in a more sustainable and eco-friendly way. In addition, they can be applied as separators instead of polyolefin materials.[58] The most studied in this context are reported in **Figure 9**a with the corresponding chemical structures. These macromolecules are biocompatible, biodegradable, nontoxic, obtained from natural resources, easily processable, highly recyclable, and inexpensive.[66] Many of the recent research works on these biopolymers are not limited to ionic conductivity and porosity studies, rather they have revealed their great potentiality in preventing some of the main issues related to metal anodes, like HSAL/HSAM growth (Figure 9b).

For example, a cellulosic separator was used in a Na-based cell that showed a reversible voltage response during galvanostatic cycling, indicating a very stable plating/stripping with considerable dendrite suppression.[67] While for Na-batteries there are still no reports on bio-derived polymeric or gel electrolytes, some work has been done for K, Mg, and Zn. Again, in the case of Zn the use of a gel polymer electrolyte based on xanthan gum was effective in limiting dendrite growth and decreasing the self-corrosion of Zn. Moreover, the mechanical flexibility of Zn cells containing biopolymers as the matrix in GPEs is also explored to obtain flexible batteries for wearable devices.[66] In general, the possibilities offered by these natural biopolymers are huge, especially if chemical functionalization or blending with other components are considered. Anyway, processing of these natural derivatives into functional electrolytes or separators by cost effective and scalable routes might be a challenge.

Starting from the raw materials the transformation involves many steps that can make the final product quite expensive. A separator like the Celgard costs about 1–1.5 $ m^{-2}, while nanocelluloses can be purchased from 2 to 50 $ g^{-1} but then the overall process to make separators comparable to Celgard is

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a)

b)

Figure 9. a) Most common biopolymers for battery applications; b) scheme showing the dendrite suppressing ability of natural biopolymers separators/electrolytes Reproduced with permission.[66] Copyright 2021, Wiley-VCH.

complex and drives up considerably the price.[66] Those transformation processes not only should be economical but also eco-friendly from production to recycling to assure a fully sustainable life cycle.

3.2. Liquid and Ionic Liquid Electrolytes

Initially, the carbonate ester based electrolytes that were successfully implemented in LIBs such as dimethyl carbonate (DMC), EC, DEC, and PC were analyzed also in Na-based batteries, but the results were very poor.[56] The morphological aspects of Na and K metals are similar to that of Li-metal, with the same problems of HSAM formation that can lead to the premature failure of the battery. For alkali-earth metals (Ca and Mg) and Al more pressing problems to solve are the difficult plating/stripping and the formation of an insulating passivation layer, which blocks the ion transport. The design of suitable electrolytes is then undoubtedly essential to find solutions to those problems. Using organic carbonate solvents would be very desirable in any battery system from the industry

perspective due to their widespread production for LIBs at an acceptable cost. It is worth mentioning here that Grignard electrolytes, dichloro-complex (DCC) and all phenyl complex (APC) have been originally used as electrolytes in Mg-batteries. Anyway, alternative solutions are being experimented, to address the complex synthesis of APC, the corrosive nature of halides in both APC and DCC (particularly chloride), and the incompatibility of Grignard electrolytes with S-cathodes.[68,69] Still, halides can play a significant role enabling cycling, even as additives, e.g., in $MgTFSI_2$/DME electrolytes.[70] Carbonates decompose at the Mg-metal surface and the resulting SEI layer does not allow Mg^{2+} ions to pass through. A method to circumvent this issue was proposed recently based on engineering the Mg anode surface by means of a conductive thin layer of thermally cycled poly(acrylonitrile) – PAN.[30] This artificial interphase enabled the reversible cycling of a Mg/V_2O_5 full-cell in water-containing, PC electrolyte. However, this result would need to be rationalized under the observations previously discussed of the doubtful intercalation of Mg^{2+} in vanadium pentoxide, also considering the presence of water.[52] Ether solvents (di- or tetra- ethylene glycol dimethyl ether, i.e., G2 (diglyme) or

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G4) with $Mg(BH_4)_2$ or $Mg(TFSI)_2$ salts have been found to be a simple salt/solvent combination that could assure a good Mg plating efficiency.[71]

Regarding Ca, deposition/dissolution was first demonstrated with $Ca(BF)_4$ in EC/PC at 100 °C.[72] Mixtures of PC and EC or acetonitrile as solvents, with various salts like $Ca(ClO_4)_2$, $Ca(BF_4)_2$, $Ca(PF_6)_2$, have also been used to obtain Ca plating, in most cases at elevated temperature.[30,73] Aprotic solvents that withstand a low potential at the metallic anode are necessary, and recently, a family of ethereal solvents has been shown experimentally to meet the requirements for transferring Ca^{2+}-ions to the electrode surface with minimal parasitic reactions. The salt is also very important, since in early studies, some incompatibility was shown with classical salts due to the formation of surface passivation films on Ca metal, which prevents ion transport. Recently anion oxidation stability of fluorinated alkoxyborate has been predicted from theoretical calculations, then the calcium tetrakis(hexafluoroisopropyloxy)borate, or $Ca[B(hfip)_4]_2$ salt was synthesized for the first time[74] and tested in 1,2-dimethoxyethane (DME), G2 and triethylene glycol trimethyl ether (G3) and tetrahydrofuran (THF)[75 and reference therein]. This salt in ethereal solvents achieved a high oxidative stability up to 4.5 V and a high ionic conductivity thus showing some promise for the realization of room-temperature Ca batteries. Elucidations were also given on the relationship between the solvation structure of Ca^{2+}-ethereal complexes and the electrochemical behavior, evidencing that weaker coordinating solvents enable efficient and reversible Ca plating/stripping.[75] Compared to other MV cations, especially Mg that undergoes chemical disproportionation prior the electron transfer, Zn follows a simple two electron reduction mechanism[76] so that there is no formation of highly reactive intermediates, and sufficiently good ambient temperature kinetics, which are considered as great advantages of Zn-based battery technologies over other post-Li storage systems. Although aqueous cells are inexpensive and safe, and less harmful to the environment, organic electrolytes offering higher oxidative stabilities could enable high voltage batteries. In addition, there are still many urgent problems that require special attention in aqueous Zn-based batteries, such as cathode dissolution, low electrochemical stability of the electrolyte, narrow temperature window, and the growth of anode dendrites.[77] Nevertheless, the larger issues in non- aqueous Zn-based batteries are sluggish kinetics in organic media and strong cation–anion association so that charge transfer between the bulk electrolyte and the electrode is particularly difficult.[55,78] The choice of a proper salt is also a concern; $Zn(TFSI)_2$ and $Zn(OTf)_2$ were tested in ACN with this latter showing better oxidative stability, but the high cost of salts with fluorinated anions should always be considered as potentially compromising the economic advantage of less expensive systems that are needed for renewable and grid scale storage. The use of RTILs in the form of low-cost and environmentally friendly deep eutectic solvents (DES) may effectively address the problems related to the narrow ESW of aqueous electrolytes and mitigate the risk of leakage and evaporation, due to their high viscosity and low vapor pressure. Choline chloride/ urea DES added with $ZnCl_2$ (0.3 м) has been proposed for application in Zn-based batteries,[79] even though the electrochemical performance must be improved.

Besides the performance, safety concerns are particularly pressing in large-scale battery applications storing a high amount of energy. Ionic liquid (RTIL)-based electrolytes are viable alternative to conventional liquid electrolytes, due to their remarkable thermal stability (e.g., 250 and ≈400 °C for $Pyr_{13}FSI$ and $Pyr_{13}TFSI$, respectively), negligible volatility, and flame retarding ability.[80] Besides conventional RTILs, solvate ionic liquids (SILs) are a particular class of ionic liquids consisting of solvate ions and their counter ions. Indeed, binary mixtures of Li, Na, K, and Mg salts and glymes, i.e., $CH_3O(CH_2CH_2O)_nCH_3$ form solvates at stoichiometric ratios 1:1 (1:2 complexes are also known). Complexation of metal ions with glymes inhibits evaporation, thus improving the thermal stability compared to diluted solutions. Moreover, glyme molecules strongly coordinated to the metal ions have lower HOMO energy levels, which imparts higher oxidative stability.[81] Recently, Na-based batteries including RTILs and SILs and have been extensively reviewed.[81–83] Some data on the cycling performances are shown in **Table 2**, with priority for electrode materials devoid of toxic and expensive elements such as V, Co, and Cr.

The use of RTILs in K-based batteries is relatively new, and the first proof of concept reporting of full cell using a graphite anode and a Prussian blue (potassium manganese hexacyanoferrate, KMF) cathode was published in 2020, demonstrating 119 mA h g^{-1} at 4 V versus K^+/K and a Coulombic efficiency of >99.3%.[91] Notably, in another report, potentially corrosive chlorine-containing ILs (carbon fiber paper was used as the current collector for the cathode) were shown to boost the ionic conductivity and improve the passivation layers.[90]

RTILs-based electrolytes devoid of halide-containing compounds were recently exploited for multivalent batteries. RTILs including the alkoxy ammonium cation $[N_{4(20201)3}]^+$ and $[CB_{11}H_{12}]^-$ as the anion show an electrochemical stability window suitable for Mg plating/stripping, owing to the compatibility of the anion with Mg metal, coupled with the good reductive stability of the cation. The anodic stability was limited by the alkoxy chain of the ammonium cation to 1.25 V versus Ag^+/Ag, since $[CB_{11}H_{12}]^-$ has a good anodic stability. After the addition of a small quantity of G4, the electrolyte enabled reversible Mg plating/stripping, with a coulombic efficiency of 70% sustained over 50 cycles.[103]

TiS_2 has been experimented as cathode material with Ca^{2+} in the presence of $Pyr_{14}TFSI$, but the concurrent intercalation of $[Pyr_{14}]^+$ led to the formation of significant interlayer distances and amorphization, accounting for a non-selective process.[104]

Electrolytes based on $Ca(BH_4)_2$ salt in an alkoxy-functionalized IL were found to induce the formation of an organic rich, but inorganic-poor SEI layer, enabling Ca^{2+} plating/stripping. The oxidation stability of the $[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$ electrolyte was found to be ≈ 2.4 V versus Ca metal pseudo-reference. Finally, as a proof-of-concept, a prototype Ca/V_2O_5 cell using the IL-based electrolyte ($[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$) was tested which showed a coulombic efficiency always higher than 100%, pointing at side reactions delivering additional capacity during the discharge step.[96]

The first example of Ca^{2+}-based dual-carbon battery that undergoes simultaneous accommodations of Ca^{2+} in a graphite anode (mesocarbon microbeads MCMB) and of bis(trifluoromethanesulfonyl)- imide (TFSI–) in a graphite

Table 2. Selected cells containing solid and RTIL-based electrolytes and corresponding cycling results.
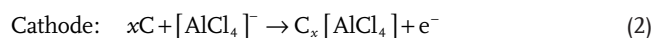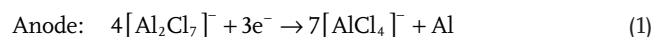
Cell configuration (loading)[a]	Electrolyte	T [°C]	Specific capacity, C.E., Cycles (cyc), Capacity retention, Rate	Ref
Na/α-Na$_{0.44}$MnO$_2$ (5.4 mg cm^{-2})	[Na(G5)][FSI] + HFE	30	≈100 mAh g^{-1} at 12.7 mA g^{-1} for 50 cyc, C.E. 99.7%	[84]
Na/HC (1.9 mg cm^{-2})	[Na(G5)][FSI] + HFE	30	240 mAh g^{-1} at 25 mA g^{-1} for 300 cyc, C.E. 99.9%	[84]
Na/Graphite (3.5–4.4 mg cm^{-2})	Na(G2)][OTf]	25	≈100 mAh g^{-1} at 37.2 mA g^{-1} for 1000 cyc, C.E. >99.87%	[85]
Na/α-Na$_{0.44}$MnO$_2$ (1.5 mg$_{A.M.}$ cm^{-2}, 1:1, presodiated HC)	NaFSI 1 м in Pyr$_{13}$FSI	25	≈100 mAh g$^{-1}_{NMO}$ at 100 mA g^{-1}, 100 cyc, capacity retention 97%	[86]
Na/HC (1.5 mg$_{A.M.}$ cm^{-2})	NaFSI 1 м in Pyr$_{13}$FSI	25	280 mAh g^{-1} at 30 mA g^{-1}, 200 cyc, capacity retention 90%	[86]
Na/calix[4]quinone (1.5 mg$_{A.M.}$ cm^{-2})	NaTFSI 0.3 м in Pyr$_{13}$TFSI	25	≈225 mAh g^{-1} at 130 mA g^{-1}, capacity retention 99.7% after 300 cyc	[87]
HC/ PB (3.04 mg$_{PB}$ cm^{-2})	NaFSI (25 wt%) in PCL$_{80}$PTMC$_{20}$	40	155 mAh g$^{-1}_{PB}$ at 10 µA cm^{-2}, ≈70 mAh g$^{-1}_{PB}$ after 25 cyc	[88]
HC/ PB (1.61 mg$_{PB}$ cm^{-2})	NaFSI (25 wt%) in PCL$_{80}$PTMC$_{20}$	≈ 22	140 mAh g$^{-1}_{PB}$ at 10 µA cm^{-2}, ≈60 mAh g$^{-1}_{PB}$ after ≈ 25 cyc	[88]
Na/NVPF (1.1 mg cm^{-2})	Na$_4$(CB$_{11}$H$_{12}$)$_2$(B$_{12}$H$_{12}$)	25	104 mAh g^{-1} at C/10, 99 mAh g^{-1} at C/5, capacity retention 76% after 800 cyc at C/5	[89]
Na/NVPF (8 mg cm^{-2})	Na$_4$(CB$_{11}$H$_{12}$)$_2$(B$_{12}$H$_{12}$)	25	117 mAh g^{-1} at C/10, 40 mAh g^{-1} at 2C, >100 mAh g^{-1} after 100 at C/5	[89]
K/K$_{1.90}$Mn$_{0.92}$Co$_{0.08}$[Fe(CN)$_6$]$_{0.96}$@rGO (3 mg cm^{-2})	KFSI in KCl/AlCl$_3$/EMImCl + EtAlCl$_2$	25	107 mAh g^{-1} at 50 mA g^{-1}, capacity retention ≈89% after 820 cyc at 100 mA g^{-1}, C.E. ≈99.9%	[90]
K/KMF (1.5–2 mg$_{A.M.}$ cm^{-2})	KFSI 1 m in Pyr$_{13}$FSI	25	1st cycle 119 mAh g^{-1} at 7.75 mA g^{-1} (C/20) (C.E. 80%), capacity retention 88% at 310 mA g^{-1} (2C), 87.4% after 100 cyc at 15.5 mA g^{-1} (C/10), C.E. 99.3%	[91]
K/graphite (1.5–2 mg$_{A.M.}$ cm^{-2})	KFSI 1 m in Pyr$_{13}$FSI	25	235 mAh g^{-1} at 13.95 mA g^{-1} (C/20), capacity retention 99% after 400 cycles, C.E. 99.9%	[91]
Graphite/KMF (0.75/2.6 mg$_{A.M.}$ cm^{-2})	KFSI 1 m in Pyr$_{13}$FSI	25	198 mAh g$^{-1}_{graphite}$ at C/10 (C.E. 67.7%)	[91]
K/PANI (3 mg cm^{-2})	PMMA- KPF$_6$ 0.8 м in EC:DEC:FEC (45:45:10 v:v:v)	25	138 mAh g^{-1} at 10 mA g^{-1}, capacity retention 98% after 100 cycles at 50 mA g^{-1}	[92]
K/PTCDA (1.2–1.4 mg cm^{-2})	KFSI in PPC/Cnw	20	118, 109, 88, and 79 mAh g^{-1} at 10, 20, 50, and 100 mA g^{-1}. Capacity retention 84.3% after 40 cycles at 20 mA g^{-1}	[93]
K/ KFe[Fe(CN)$_6$]	K$_2$Fe$_4$O$_7$		63 mAh g^{-1} at 10C, capacity retention 78% after 50 cycles	[94]
Mg/Mo$_6$S$_8$	Mg(BH$_4$)$_2$-PEO-MgO	100	≈ 90 mAh g^{-1}, 150 cycles	[95]
Ca/V$_2$O$_5$	[Ca(BH$_4$)$_2$]$_{0.05}$[N$_{07}$TFSI]$_{0.95}$		1st discharge 332 mAh g^{-1}, following cycles 250 mAh g^{-1}, C.E. > 100% (side reactions)	[96]
Ca/MCMB	[Ca(G4)]TFSI$_2$ 0.5 м in Pyr$_{14}$TFSI		1st discharge 98 mAh g^{-1} at 20 mA g^{-1} (C.E. 68%). 67 mAh g^{-1} at 200 mA g^{-1}, 91% after 10 cyc	[97]
Ca/KS6L	[Ca(G4)]TFSI$_2$ 0.5 м in Pyr$_{14}$TFSI		1st discharge 71 mAh g^{-1} at 20 mA g^{-1} (C.E. 67%), capacity retention 83% after 100 cyc at 20 mA g^{-1}	[98]
MCMB/KS6L (mg$_{KS6L}$/mg$_{MCMB}$ = 1.2)	[Ca(G4)]TFSI$_2$ 0.5 м in Pyr14TFSI		54 mAh g^{-1} at 200 mA g^{-1}, capacity retention 88% after 300 cycles	[97]
Zn/δMnO$_2$	ZnCl$_2$ 0.3 м in ChCl/Urea DES	25	170 mAh g^{-1} at 50 mA g^{-1}, ≈50 mAh g^{-1} at 200 mA g^{-1} (40th cyc), ≈40 mAh g^{-1} at 50 mA g^{-1} (150th cyc)	[98]
Al/Graphitic foam	AlCl$_3$-EMICl	25	60 mAh g^{-1}, capacity retention 100% after 7500 cyc (C.E. 97±2.3%)	[99]
Al/Graphite	AlCl$_3$/urea	25	≈50 mAh g^{-1} at 600 mA g^{-1} (≈12 C) for 1000 cyc (C.E.; 96%).	[100]
Al/Graphite flakes	AlCl$_3$-EMICl	25	154 mAh g^{-1} at 100 mA g^{-1} for 100 cyc	[101]
Al/Graphite	PAM- AlCl$_3$-EMICl	25	103 mAh g^{-1} at 100 mA g^{-1}, 92 mAh g^{-1} at 200 mA g^{-1}, 84 mAh g^{-1} at 300 mA g^{-1} ≈120 mAh g^{-1} at 60 mA g^{-1}, capacity retention 88.6% after 100 cyc (C.E. 93%) Capacity retention 65% (0 °C) and 60% (−10 °C) at 60 mA g^{-1}	[102]

[a]A.M.: active material; ChCl: Choline cloride; Cnw: cellulose nonwoven membrane; FSI: bis(fluoro sulfanyl)imide; HFE: hydrofluoroether; MCMB: mesocarbon microbeads – graphite; LFP: LiFePO$_4$; Otf: triflate; PAM: poly(acrylamide); PB: Na$_{2-x}$Fe[Fe(CN)$_6$]; Pyr$_{13}$: N-Propyl-N-methylpyrrolidinium; rGO: reduced graphene oxide; tep: triethyl phosphate. C.E.: Coulombic Efficiency.

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cathode (KS6L) was recently demonstrated.[97] The optimum ternary electrolytes consisted in equimolar amounts of Ca^{2+} from $Ca(TFSI)_2$ and G4 dissolved (0.5 M) in $Pyr_{14}TFSI$, which minimized the amount of free-G4, thus enhancing the oxidation stability and maximizing the amount of intercalating $TFSI^-$ in KS6L.[97]

Great efforts have been devoted to developing suitable organic aprotic electrolytes for Al batteries as very few Al salts are able to dissociate completely in aprotic solvents. The reversibility of Al metal electrode was first enabled by RTILs as Al is prone to both corrosion/dissolution and ion/electron-blocking passivation. Indeed, the native surface oxide film has to be removed to enable Al metal redox activity, but the intense removal has been found to induce poor stability.[105] At present, most Al cells rely on the anionic $[AlCl_4]^-$ complex as electrolyte and anion intercalation based cathodes, which results in electrolyte consumption (up to 6 g for each gram of graphite) and consequent limited energy density coupled with possible corrosion arising from chlorides.[48] So far, electrochemically stable current collectors in such batteries are limited to tungsten, molybdenum, chromium, glassy carbon and titanium nitride.
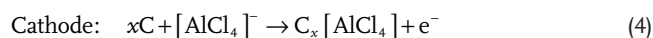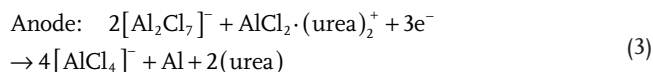
In these cells, the operation mechanism is based on the following redox processes upon charging:

Anode: $\quad 4[Al_2Cl_7]^- + 3e^- \rightarrow 7[AlCl_4]^- + Al \qquad (1)$

Cathode: $\quad xC + [AlCl_4]^- \rightarrow C_x[AlCl_4] + e^- \qquad (2)$

For Al to be reduced at the anode, $[Al_2Cl_7]^-$ complex must be formed. This arises from the combination of $AlCl_3$ and a chloride source, e.g., EMImCl, due to the Lewis acid-base reaction yielding $EMIm^+$ and $[AlCl_4]^-$. For each electrodeposited Al atom, three $[AlCl_4]^-$ anions simultaneously intercalate into graphite. The charge ends when there is only $AlCl_4^-$, corresponding to the neutral form with an $AlCl_3$:EMIMCl molar ratio = 1 (unless the capacity of graphite is reached), therefore balancing the electrolyte components affects the overall energy density (**Figure 10**).[65]

In these systems, graphite is deemed "SEI-free", based on common high initial C.E. > 90% and X-ray photoelectron spectroscopy results.[97] Besides on EMImCl/$AlCl_3$, other ILs have been experimented (Figure 10a),[65] including DES[100] and GPEs[102] electrolytes that have also been demonstrated for this system.

In the case $AlCl_3$-urea DES, a different charging mechanism has been proposed, i.e.,

Anode: $\quad 2[Al_2Cl_7]^- + AlCl_2 \cdot (urea)_2^+ + 3e^-$
$\rightarrow 4[AlCl_4]^- + Al + 2(urea) \qquad (3)$

Cathode: $\quad xC + [AlCl_4]^- \rightarrow C_x[AlCl_4] + e^- \qquad (4)$

3.3. Solid State Electrolytes

As already highlighted in previous sections, the widespread implementation of the solid-state technology is foreseen to significantly enhance the energy density, while lowering the volume of 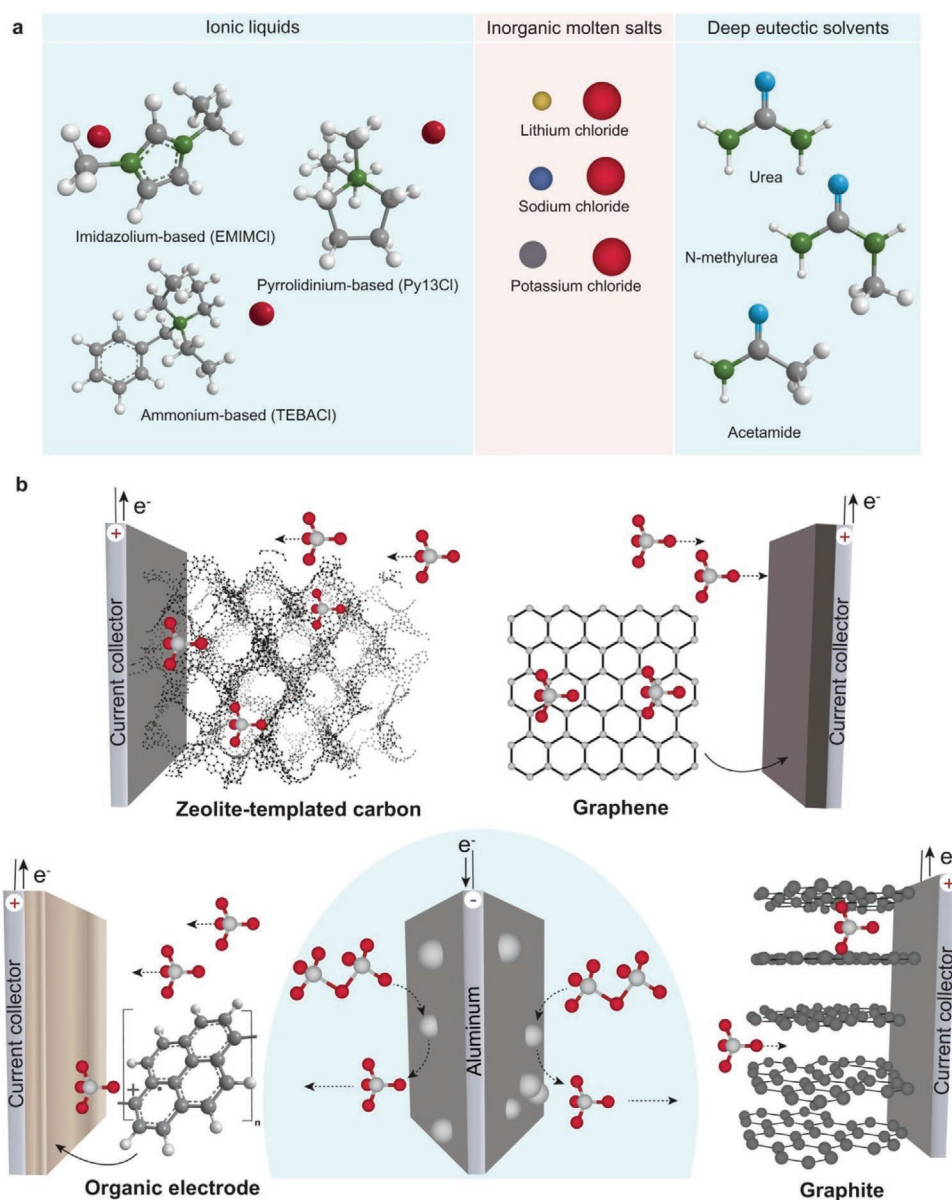device packaging. Indeed, solid-state processing enables bipolar stacking (**Figure 11**) of several cells in a single package.[20] Moreover, the counter measurements necessary to prevent the risk of leakage or fire due to flammable solvents would not be necessary, further reducing the pack weight. The use of advanced, optimized solid-state electrolytes might allow continuous battery operation under extreme (low and high) temperature conditions, in which conventional liquid electrolytes would fail (e.g., by freezing, boiling or decomposition.[106–108]

The difficulties to transition from lab-scale to large-scale solid-state cells, together with the advantages, issues and challenges of solid-state design are addressed in several specific reviews.[20,109–111] At present the focus is mainly on Li- and Na-based battery technologies, but most concepts generally might apply to any all-solid batteries, despite the small number of reports on solid electrolytes for many post-Li chemistries, which are in some case relatively new (e.g., the Ca-plating/stripping was first demonstrated in 2016[72]).

As a general consideration, solid-state electrolytes (SSEs) may be categorized in the three main classes: solid polymer electrolytes (SPEs), solid inorganic electrolytes (SIEs) and composite polymer electrolyte (CPEs), in which the CPEs comprising a polymer matrix encompassing an inorganic phase. System including liquid plasticizers entrapped in a polymer matrix are named GPEs. In an attempt to translate the knowledge achieved in the Li metal battery field to MV systems, according to the pioneering work by Monroe and Newman[112] it is possible to prevent dendrites from shorting the battery by using a solid electrolyte with shear modulus two times larger than metallic lithium. Similar requirements might be needed when dendritic multivalent metal deposits are observed (for example for Ca, Zn, and Al). The development of high shear modulus (G) polymer electrolytes requires nano structuring of soft-ions conducting polymers, such as poly(ethylene oxide) (PEO), with hard, glassy matrixes, as polystyrene (PS), by designing multi-block copolymers. Multivariate architectures with specific transport and mechanical features then will govern the temperature range of cell operation, rate capabilities and the extent of the dendrite-blocking ability. It is worth mentioning here that despite the high shear modulus of SIEs, dendrite formation can occur due to impurities, dopants, grain boundaries, particularly at relatively high current density depending on the electrolyte. The propagation of metal filaments within the electrolyte is also observed in solid-state Na-batteries.[106,107,113,114]

Polymer electrolytes are also characterized by their interaction with ions that, when referring to post-Li chemistries, have not been sufficiently clarified yet. Thus, once a better understanding of the foundations of those interactions will be reached, new polymers in terms of composition and architecture to access faster ion dynamics may be developed to meet the demands for low cost, cycle life, power, etc. for various devices.

Despite several polymer, gel and composite polymer electrolytes have been experimented in Na-based cells, cycling in full cell configuration and operation at RT has been rarely demonstrated in the absence of liquid carbonate ester based electrolytes.[115,116] Promising results with respect to SPE for NIBs were reported by Sångeland et al.[88] using an amorphous poly-caprolactone-polycarbonate (PCL/poly(trimethylene carbonate) (PTMC) with 80% mol of CL) copolymer combined with NaFSI (25 wt%), exhibiting sufficient mechanical stability and ionic

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Figure 10. a) Different classes of Al electrolytes; b) working principle of Al dual-ion batteries. Differently from the "rocking-chair" concept, in this battery the directional motion of ions is not from the positive to the negative electrode. Both electrodes at the same time consume the Al species. This ADIB is composed of aluminum foil at the negative electrode, graphite/graphene/zeolite-templated carbon/polypyrene at the positive electrode, and a chloroaluminate ionic liquid electrolyte. Reproduced with permission.[65] Copyright 2020, Springer Nature.

conductivity (3.9×10^{-3} and 2.2×10^{-2} mS cm^{-1} at 25 and 40 °C, respectively). The SPE enabled proof-of-concept cycling at 40 °C and ambient temperature, showing a capacity fading similar to liquid electrolyte.[88] Based on these promising results, advances may be envisaged investigating the polymer/electrode compatibility (particularly on the anode side), working on increasing the ionic conductivity together with the cell optimization in terms of electrode balancing and formulation. SPEs are a good option in combination with organic cathodes, because the active material is often soluble in organic liquid electrolytes.[107] In this respect, crosslinked poly-(methyl methacrylate) (PMMA) GPE containing KPF$_6$ was tested in a potassium cell with polyaniline (PANi) as the organic anion-insertion cathode

and a K-metal anode. In this system, the anion from KPF$_6$ is inserted into a polyaniline cathode while K$^+$ ion is plated on the potassium-metal anode upon charging. Anion deinsertion from polyaniline and K$^+$ stripping occurs during the discharge process.[92] An all-solid-state potassium cell based on the organic cathode (3,4,9,10-perylene-tetracarboxylicacid-dianhydride, PTCDA) and SPE has also been demonstrated. The SPE consisted in poly(propylene carbonate) (PPC) supported by a nonwoven cellulose membrane with KFSI as the K$^+$ source, which was obtained by a conventional solution-casting technique. The discharging and charging process are both due to the multistep redox of PTCDA, which is distinct from that of the LIBs or the NIBs.[93] Notably, these aforementioned cells with the GPE and

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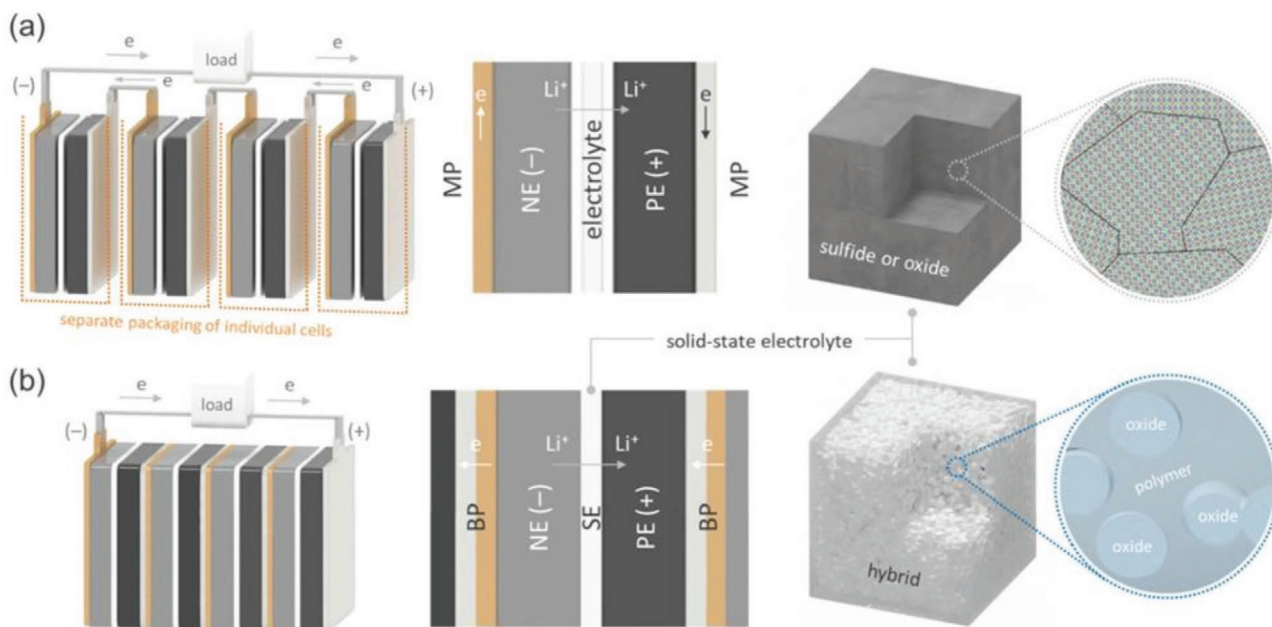
Figure 11. a) Schematics of monopolar design of current LIBs with liquid electrolytes and b) bipolar design of SSLBs equipped with SEs. The Li+ and electron pathways during discharge are also indicated. Reproduced with permission.[109] Copyright 2019, Wiley-VCH.

the SPE outperformed their counterparts with liquid electrolytes in term of prolonged cycling (GPE and SPE) and rate capability (GPE), possibly due to the solubility of the active material in the organic solvent. It is worth underlying that despite the electrolyte is immobilized in the crosslinked polymer matrix, safety issues still affect GPEs due to the presence of flammable solvents, which would require flame-retardant agents,[117] formation/degassing steps, and counter measurements at the package level, increasing the overall battery weight. In the case of the SPE, solvent casting technique poses problems from the scalability perspective, due to the solvent evaporation step (energy demanding, disposal of the solvent, etc.), not forgetting that trace amounts of solvents left in the system may be detrimental for the cell performance.

Several Na^+ ion-conducting SIEs have been reported over the years, and yet despite their great potential, demonstration of stable cycling with cost-effective, safe materials and process are rare.[100] Indeed, there are several problems related SIEs application notwithstanding their excellent properties. Some concerns address the manufacturing difficulties on large areas, related to the fragility of SIEs.[118] On the other hand, there are issues related to the chemical and electrochemical properties of SIEs. For instance, some sulfides and glass-ceramic sulfides containing P have excellent Na^+ conductivities but are unstable when exposed to oxygen or moisture, mainly owing to the high oxygen affinity of phosphorus. Substituting phosphorus with arsenic enhances the air stability, but arsenides are toxic.[119] On the other hand, NASICON-type oxide electrolytes are stable in contact with air moisture, but the presence of Zr^{4+}, Si^{4+} leads to poor electrochemical stability at low voltage.[120] To work around these problems, interlayers and coatings can be adopted, which is also a common strategy to improve the physical contact with the active electrode materials. This latter

aspect not only is dependent on the manufacturing process, but also accounts for the formation of interphases and the volumetric variation occurring upon cycling.[107,108,113,114]

An excellent cycling performance has been recently reported for a class of inorganic hydroborate solid electrolytes, which are commonly affected by a low oxidative stability.[121] In particular, the system $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})$ was obtained combining $[B_{12}H_{12}]^{2-}$ anions, which passivate the electrolyte/cathode interface, and stable $[CB_{11}H_{12}]^-$ anions, which allows Na^+ ion conduction. This SIE enabled RT operation in a Na/electrolyte/$Na_3(VOPO_4)_2F$ (NVPF) all solid cells, with high average discharge cell voltage of 3.8 V and excellent capacity retention (**Figure 12**). Notably, the cells were cycled by increasing the pressure to 3.2 MPa to inhibit dendrite formation, consequently, the cathode loading could be increased.[89] These results are enforced by the high ionic conductivity (≥ 1 mS cm^{-1} at RT), thermal (>350 °C) and chemical stability, combined with favorable mechanical properties which allow obtaining dense pellets by cold pressing. Expensive and complicated synthesis remains a major drawback for these systems.[89]

Despite relatively recent intensive research efforts on K-ion batteries, the first demonstration of a solid-state K-metal cell containing potassium ferrite $K_2Fe_4O_7$ super K-ion conductor has already been published. $K_2Fe_4O_7$ obtained by hydrothermal synthesis shows high room temperature conductivity (5.0×10^{-2} S cm^{-1}), and negligible electronic conductivity. An all-solid-state K metal cell with K Prussian blue as the cathode operating at ≈ 2 V versus K^+/K and $K_2Fe_4O_7$ could deliver a discharge capacity of ≈ 63 mAh g^{-1} ($\approx 72\%$ of the theoretical specific capacity of KPB) at 10C, with a capacity retention of 78% after 50 cycles.[88]

Inorganic solid Mg^{2+} conductors are afflicted by poor RT ionic conductivities. Better ionic conductivities could be achieved by metal organic frameworks (MOFs). In general, demonstration
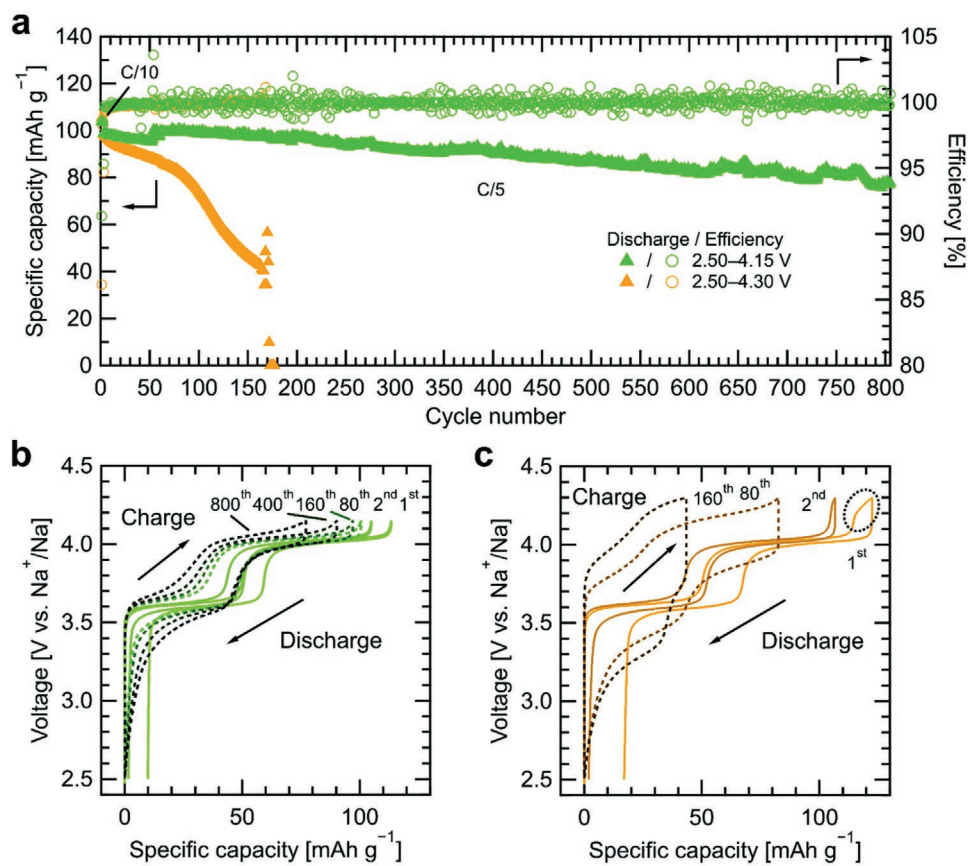
Figure 12. a) Long-term cycling performance of $Na_3(VOPO_4)_2F|$ $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})|Na$ all-solid-state cells cycled between 2.50 and 4.15 V (green) or 4.30 V (yellow) versus Na^+/Na at C/5 following two formation cycles at C/10 at room temperature. Corresponding galvanostatic charge–discharge curves at C/10 (solid) and at C/5 (dashed) with the upper cut-off voltage of b) 4.15 V and c) 4.30 V versus Na^+/Na. Reproduced with permission.[89] Copyright 2020, The Royal Society of Chemistry.

of Mg plating/stripping and cycling in cell configuration are rare.[68,69,122] Solid inorganic Mg^{2+} electrolytes based on ammine magnesium borohydride $Mg(BH_4)_2 \cdot 1.6NH_3$ in combination with 75 wt% MgO nanoparticles forming a nanocomposite with improved ionic conductivity has recently demonstrated a Mg^{2+} conductivity $\approx 10^{-5}$ and 10^{-3} S cm^{-1} at RT and 70 °C, respectively. Anyway, the material undergoes thermal decomposition at 120 °C, and an irreversible oxidation process at 1.2 V in a Mg/electrolyte/Au cell at 60 °C. The electrolyte also enabled continuous Mg plating/stripping in a Mg‖Mg symmetric cell.[123]

Some attempts to address Ca^{2+} conduction in SIEs have been made, e.g., in β-Al_2O_3 and $MZr_4(PO_4)_6$ but unequivocal reports on cycling are anyway missing at present.[107,31]

Polymer electrolytes for Mg batteries have also been experimented, and the cycling ability is demonstrated mostly with gel electrolytes encompassing flammable ethers or organic carbonate solvents.[123] In this respect, a potentially viable hybrid GPE comprising commercially available $Pyr_{14}TFSI$, $Mg(ClO_4)_2$, PVdF-HFP (Poly(vinylidene fluoride-co-hexafluoropropylene) and TiO_2 ceramic nanoparticle fillers has been recently demonstrated to enable reversible Mg plating/stripping. Galvanostatic cycling of Mg‖Mg symmetric cells revealed smooth plating/stripping profiles with overpotentials of 0.08 (80 cycles at 0.05 mA cm^{-2}) and 0.30 V (400 cycles at 0.10 mA cm^{-2}).[69]

This system represents an interesting alternative to flammable solvents enabling room temperature cycling. Direct casting of the metal anode also is an excellent way to achieve a conformal interface, which would benefit from a solvent-free deposition in terms of process scalability and would also avoid the risk of contaminating the metal surface. The use of costly PVdF-HFP represents a drawback, and alternative polymer matrixes should be sought. A dry composite polymer electrolyte based on PEO, $Mg(BH_4)_2$ and MgO enabled stable cycling in $Mg/electrolyte/Mo_6S_8$ for 150 cycles, delivering a specific capacity of $\approx$ 90 mAh g^{-1} at high operating temperature (100 °C), which is an aspect that needs improvement.[124] In addition to the aforementioned electrolytes, a novel polytetrahydrofuran-borate- based GPE coupled with glass fiber was synthesized via an in situ crosslinking reaction of magnesium borohydride [$Mg(BH_4)_2$] and hydroxyl-terminated poly(tetrahydrofuran) (PTHF). Mo_6S_8/Mg batteries were assembled and worked well in the temperature range −20 to 60 °C displaying improvements in safety since no internal short-circuit failure was observed even after a cutting test.[125] This approach offers some initial hints for the development of flexible and large-format Mg batteries notwithstanding all the previous considerations about GPEs encompassing flammable organic solvents with low vapor pressure such as THF.

In the case of Ca, a few photocrosslinked SPEs based on PTHF (epoxy crosslinker/cationic polymerization)[124] and poly(ethylene glycol) (PEG) (diacrylate crosslinker/free radical polymerization) with highly soluble $Ca(NO_3)_2$ were reported.[126] PTHF was selected due to its lower oxygen content per unit and high chain mobility, in a bid to compensate for the strong oxygen-calcium ion interactions. For the PTHF-based system, the O:Ca molar ratio of 1.9 yielded the highest conductivity of 0.114 mS cm^{-1} at room temperature. Dry PEO-based SPEs have also been recently investigated as possible Ca^{2+} conducting medium.[127] Anyway, in neither case Ca^{2+} plating/stripping or cycling ability was demonstrated, and the ether-based matrixes are well known to suffer from relatively low oxidation stability.[128]

Aqueous GPEs have been proposed to reduce the growth of Zn dendrites and the issues related to leakage and electrolyte evaporation. Bio-derived gelling agents such as Xanthan gum, Gelatin, Sodium CMC, Kappa-carrageenan have been proposed and recently reviewed.[129] Synthetic polyacrilammide, sodium polyacrylate, polyvinyl alcohol etc. have been experimented as well. Many systems can undergo stable plating/stripping for thousands of cycles, but the energy and power density appear to be low. On a general note, hydrogel electrolytes may be easily affected by environmental conditions, therefore water evaporation and leakage would still have to be addressed.

4. Materials Optimization and Characterization

4.1. Modelling, Computational Analysis

Design and optimization of functional materials for battery applications are usually time and resource consuming. Often, major changes do not translate into improved performance because, similar to other energy conversion technologies, the device is made by several intertwined components. Besides optimizing single components, the grand challenge concerns the electrode/electrolyte interfaces. For example, scarce chemical compatibility and hindered ion transport at such interface can result in high interfacial resistance, poor storage efficiency, and, overall, unstable devices. Thus, an in-depth understanding of the battery working mechanisms is crucial for deploying new and advanced batteries to the market, but it requires further knowledge of the chemical and electrochemical features of electrodes, electrolytes and their interfaces/interphases at the atomic level, which is challenging to investigate experimentally using the existing analysis techniques. Computational approaches can fill this knowledge gap by offering an atomistic perspective of structure, stability and ion transport. Especially when paired with advanced experimental characterization techniques, theoretical tools are able to identify novel materials with desired properties, and to outline rational design strategies that can significantly accelerate the R&D of new materials. Density functional theory (DFT)[130] has become the workhorse method for simulating the structure and activities of solid-state electrodes in energy storage devices.[131] Among all DFT exchange correlation functionals, the ones belonging to the generalized gradient approximation (GGA) family are the most suited for this kind of systems since they depend on the density and its gradient and can represent properly a wide variety of solids and

their surfaces. GGA functionals (e.g., PBE,[132] PW91[133]) deliver good approximations on lattice constants, thermodynamics properties and voltage trends, but can over-delocalize the electronic structure[134] and neglect noncovalent interactions.[135] For electrode materials featuring transition metals with localized unpaired d electrons (e.g., Co, Mn), the DFT well known self-interaction error must be corrected either adding a Hubbard-like potential to the Hamiltonian in the so-called DFT+U approaches[136] or applying the expensive hybrid HF-DFT functionals (e.g., HSE,[137] PBE0[138]). Weak forces, relevant for the description of 2D electrode materials and adhesion properties at interfaces, are usually efficiently described by adding a semi-empirical term as a-posteriori correction to the electronic energy after each self-consistent cycle, the most common approach is the one developed by Grimme that can also be included during structure optimization.[139] Activation energies and ionic minimum energy diffusion paths at atomic scale, which play a pivotal role in battery applications, can be accurately described by the Climbing Image Nudged Elastic Band (CI-NEB) approach.[140] In ionic conductors with highly disordered mobile cation sublattices, it is convenient to run previous classical or ab initio molecular dynamics so as to individuate the most likely migration paths, which are provided as input for the NEB.[141] This kinetic information can be combined to the calculated phonon spectra to obtain tracer diffusion coefficients directly comparable to the experimental ones.[142] The success of this calculations strongly relies on the correct choice of the structural model. Often in electrode materials, multiple transition metals occupy a given crystallographic position, randomly distributed due to their similar ionic radius. In these cases, the so-called special quasi-random structures (SQS) are the best possible approximations since their cluster vectors closely match those of truly random solid solutions.[143] Since TM mixing tend to suppress Na ordering,[144] the Na sublattice in multi-TM materials can be considered as a solid solution of Na occupied and vacancy sites for each sodiation state as well and, thus, can be well represented with an SQS.

4.2. Na-Based Batteries

This computational machinery has been widely applied for NIB constituent materials. On the cathode side, entire families of inorganic oxides such O3 and P2-type $NaMO_2$, $NaMPO_4$ olivines and their fluoro derivatives, Na_2MPO_4F, have been investigated, as well as some organic compounds and significant computational-derived design insights have been extracted.[145] Calculations have found that, for $NaMO_2$ (M = Co, Mn), Na sublattice disorder induced by TM mixing decreases Na migration barriers, especially with Fe or V co-doping.[146] In Fe or Mn olivines, besides identifying the lowest migration barrier along the [010] channels,[147] the easy formation of TM-Na anti-site defects has been identified as a main source of Na diffusion blockade.[148] Na_2MPO_4F would present more advantageous two dimensional migration paths with lower migration barriers than the 1-D paths in regular phosphates[123] and smaller volume expansion during sodiation.[149] NVPF is object of recent theoretical studies aimed at elucidating the origin of improved properties when doped, for example with Ti[150](due to its best electronic

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conductivity) or with K[151] (due to an enlargement of the migration channels that lowers Na migration barrier). On the anode side, several studies have addressed the capability of TiO_2 polymorphs to reversibly intercalate the Na^+;[152] recent studies were also able to dissect the most convenient facets of titania anatase for effective use as NIB anode.[153] Intercalation and diffusion of Na in composite materials with Graphene such as prototypical anodes TiO_2/G[154] and MoS_2/G[155] have been addressed as well with first principles calculations. Decomposition of polymer electrolytes at the metallic anode surface such EC[156] and FEC/DFEC[157] has been object of few studies using molecular-type non periodic DFT models. Although these studies offer a first valuable indication of the initial steps during SEI formation, they rely on the interaction of the polymer monomers with single Na^+ cations and do not fully seize the complexity of the bulk Na metal in contact with the extended polymer. Regarding electrolytes, several works have addressed sodium ion transport in solid, liquid and composite materials. Methods based on molecular dynamics (MD) with forces computed at the DFT level of theory (AIMD) or with classical force fields have provided many insights on the mechanism of solvation and diffusion of Na^+ in different chemical environments, as recently reviewed.[158] Combination of different methods is mandatory for complex systems and for exotic environment such as for example ionic liquids where standard force fields fails and fully polarizable models should be applied in MD simulations.[159] Overall, the results and the current understanding of NIB electrolyte is mostly related to ideal systems including only the cation and the main electrolyte components. Thus, there is wide room for improving the current theoretical models for electrolyte by including additives, side reactant, and impurities to evaluate the long-term stability of the NIB device.

4.3. K-Based Batteries

Although the methodology does not differ from that applied to Li-ion and Na-ion battery materials, the K-ion (electro)chemistry has not been extensively addressed from a computational point of view. Early articles have proposed two dimensional materials such as CN or B-doped graphene as potential anodes for K-ion batteries, due to their computed storage capacity ($\approx$1000 mA h g^{-1}) and low diffusion barriers (<0.1 eV).[160] Regarding anodes, periodic DFT calculations have been performed to complement in situ X-ray diffraction to unravel the phase transitions of Bi anodes during potassiation.[161] An example of theoretically guided cathode design can be found in the perovskite-like $KMnF_3$, where calculations have shown that O-doping increases the electrical conductivity and lowers K migration barriers: synthesized $KMnO_{0.125}F_{2.875}$ presented actually high capacities and its structure and electrochemical properties as well as its stability with respect to Mn dissolving in the electrolyte were enhanced through carbon coating.[162] DFT has been used to shed light also on K ion diffusion barriers and migration pathways in $KVOPO_4$[163] and $K_xV_2O_5$,[164] and on their electronic and structural changes during potassiation. As for KIBs electrolytes, first-principles MDs have been applied to reveal the solvation structure and dynamic properties of K in EC electrolytes, and the stability window for electrolyte oxidation/reduction by computing the HOMO/LUMO energies.[165]

4.4. Mg-Based Batteries

When it comes to battery materials with multivalent mobile cations, the computational literature is even more narrow and sparse, although recent cutting-edge studies are addressing complex problems such as the SEI formation in MIBs,[166] considering even the potential dependence of the interface electrolyte degradation.[167] We must note that this aspect is virtually neglected in the vast majority of calculations in the battery framework. Also, some Mg binary and ternary compounds have been screened with DFT in order to identify potential coating materials for Mg batteries that could separate the distinct chemistries of the metal-anode and the cathode materials from the electrolyte for the sake of stability.[168] The properties of some alternative anodes for emerging MIB has been studied with DFT, e.g., $FePS_3$,[169] and Mg_3Bi_2,[170] where has been revealed that relativistic spin-orbit coupling effects are linked to low Mg migration barriers. Due to the difficulties in finding suitable compatible cathodes with Mg anode, most reports have focused on computing the redox reaction mechanism, electrochemical and thermodynamic properties of potential suitable materials such as $MnSiO_4$ olivines,[171] tavorite-$FeSO_4F$,[172] VPO_4F[173] or V_2O_5[174] and on how to fine-tune the composition (e.g., by hydrogenation) to improve their electrochemical performances.

4.5. Ca-Based Batteries

The very few computational papers addressing SSEs for CIBs have failed in identifying effective conductive materials,[175] but more fruitful work has been done on the electrode side. DFT and ab initio MD calculations have been used to understand how EC decomposes on a Ca metal anode, with and without the presence of a $Ca(ClO_4)_2$ salt, identifying $CaCO_3$, CaO, and $Ca(OH)_2$ as major SEI inorganic components.[176] Searching for alternatives to Ca metal anode, many metalloids (Si, Sb, and Ge) and (post-)transition metals (Al, Pb, Cu, Cd, and $CdCu_2$) have been identified as promising anodes for CIBs via a four-step high-throughput screening strategy using the DFT-based voltage information obtained from Sn electrochemical calciation.[177] Since only a few Ca battery cathodes have been successfully tested electrochemically, calculations on potential cathode materials on 3D (spinel, perovskites), 2D (V_2O_5), Chevrel phases and Prussian Blue analogues have been useful to identify a low ionicity, low stability of Ca in the crystallographic sites and co-intercalation of solvents to shield the coulombic interactions as desired descriptors of potential cathode materials for CIBs.[178]

4.6. Zn-Based Batteries

When it comes to Zn batteries the very few works available address Zn insertion and migration in cathodes for aqueous batteries (e.g., a and d- MnO_2, VO_2, V_2O_5, $MFe(CN)_6$ (M = Fe, Co, Ni, Cu, Mn)[179] or computation of overpotentials for the ORR reaction at the air electrode for Zn-air batteries (e.g., P and N- co doped C or $(Ni, Co)_3O_4$).[180]

4.7. Computational Perspectives

Overall, we can conclude that, besides the already launched NIBs, computational perspectives on beyond-Li batteries are still in their infancy, especially for all solid-state devices. State-of-the art computational methodologies, assessed and validated in LIBs and NIBs, have enabled a deeper understanding on intrinsic properties of battery materials and the underlying electrochemical mechanisms. Current studies focus on either linking such information with experimental outcomes or suggesting new functional materials.

Following the success cases for LIBs, new materials for advanced battery technologies have been identified by means of high-throughput calculations on thousands of solids from computational materials databases, in particular the Materials Genome Project.[56] Similarly, computationally guided materials genomics screening seeking to identify polymer membranes can provide access to new kind of polymers tailored to the intrinsic chemistry of the battery. The Electrolyte Genome project[181] has tried to develop an open-source infrastructure for screening on a large scale of many chemical components which constitute the electrolytes, and their interactions, including solvents, salts, additives, and redox active molecules. Thousands of organic molecules are catalogued for their characteristics such as electron affinity, ionization potential, redox potentials and others, obtained through first principle and molecular dynamics calculations in order to better understand and predict solvation structure, chemical reactions of monovalent and MV ions in the electrolytes and their behavior at the electrode interfaces. This design strategy based on a computational approach is now essential to accelerate progress in the discovery of new materials for post lithium-ion batteries. Many unpromising candidates can be discarded while the suitable ones can be selected based on successive properties evaluation using computational screening techniques.[182] The experimental synthesis and testing can be then focused only on the promising electrolyte components obtained after multiple tiers of selection. This approach has recently led to significant improvement in the electrochemical window of Mg salts through the design of a weakly coordinated Mg^{2+} by an electron poor anion, perfluoroalkoxyaluminate anion $TFPA^-$ ($TPFA^- = [Al\{OC(CF_3)_3\}_4]^-$) that enabled Mg plating without decomposition. The electron-withdrawing CF_3 groups made possible to mitigate the cathodic decomposition and enhance the anodic stability as revealed by computational and electrochemical analyses on $Mg[TPFA]_2$ ($[TPFA]^- = [Al\{OC(CF_3)_3\}_4]^-$).[183] This study has demonstrated that the weak coordination to Mg^{2+} in solution is important for obtaining a wide electrochemical window of Mg salts, thus suggesting a more general design strategy toward new salts.

Due to the multiple requirements expected for electrodes and electrolytes, such screenings are very useful for narrowing the many possibilities and for triggering the discovery of new chemical formula. However, those approaches rely on bulk-phase energetics and approximate interfaces that may not fully reflect the actual atomic structure, stoichiometry, chemistry, defects or microstructures responsible for the electrochemical behavior of a given material within the battery. Moreover, these studies do not provide new chemical insights at the atomistic level that can help explaining the performances of newly tested materials.

Thus, new proposals are often unsuitable for real applications since calculations are normally made on single components in quite ideal conditions, without taking into account temperature, current and interface effects. Fortunately, this is the perfect time to go beyond routine calculations thanks to current advancements in both computing power and computational codes and to the possibility of building up multiscale models to achieve knowledge of a given systems across different time and length scales (**Figure 13**).[184] The challenges to face span atomistic-scale diffusion in amorphous SEs, grain boundaries, solid state interfaces, degradation and SIE formation, voltage-dependent processes and electrolyte-electrode compatibility. Such level of information would be not only extremely valuable by itself but could also enable data-driven, machine learning-based approaches that could help battery researchers from meet the demand for continuous innovation and improvement.[185]

### 4.8. Advanced Investigation Protocols

The selection and optimization of Li-ion battery materials typically exploits advanced characterization protocols like synchrotron radiation techniques or electron microscopy coupled with electrochemical measurements (the so-called operando studies).[188] Similar approaches have been demonstrated also for post-Li battery components to draw detailed analysis of solid-state reactions as well as interphase transformations.

Na-ion electrodes are by large the most studied among materials for post-Li batteries. The most recent and complex investigation protocols adopt massive data treatment algorithms based on chemometrics to shed light in the phase transformations in batteries upon cycling.[189] The sodiation of TiO_2 electrodes[190] was recently investigated via X-ray absorption spectroscopy under operando conditions by analyzing the 4D data set matrix (cycled capacity, cell voltage, X-ray energy, absorbed intensity) via an innovative and smart approach based on chemometric tools. This approach allows the unbiased and reliable extraction of the maximum amount of meaningful information without the need of any preliminary assumption of the reaction mechanism. The resulting data analysis reveals that the electrochemical sodiation mechanism is mainly based on the reduction of Ti^{4+} to Ti^{3+}, going along with the irreversible amorphisation of the pristine anatase structure. More classical experimental operando protocols have been reported[191] to investigate the performance and mechanism of carbon nanofibers as negative electrodes in K-ion batteries using operando Raman spectroscopy. Similar to the case of graphite electrodes,[192] the K-ion incorporation into amorphous carbon nanofibers occurs though a complex combination of absorption and intercalation processes, like in the electrochemical sodiation of hard carbons.[193]

The capabilities of operando X-ray diffraction have been challenged in multivalent battery systems by Berthelot et al.[194] that demonstrated the reversible cycling of Mg^{2+} ions in a Mg_3Bi_2/S full cell using a facile electrolyte formulation based on a dimethoxy-ethane solution of $Mg(TFSI)_2$. The remarkable substitution of chlorine-based electrolytes allowed a straightforward investigation of the Mg_3Bi_2 de-alloying/alloying and sulfur-magnesiation reactions.
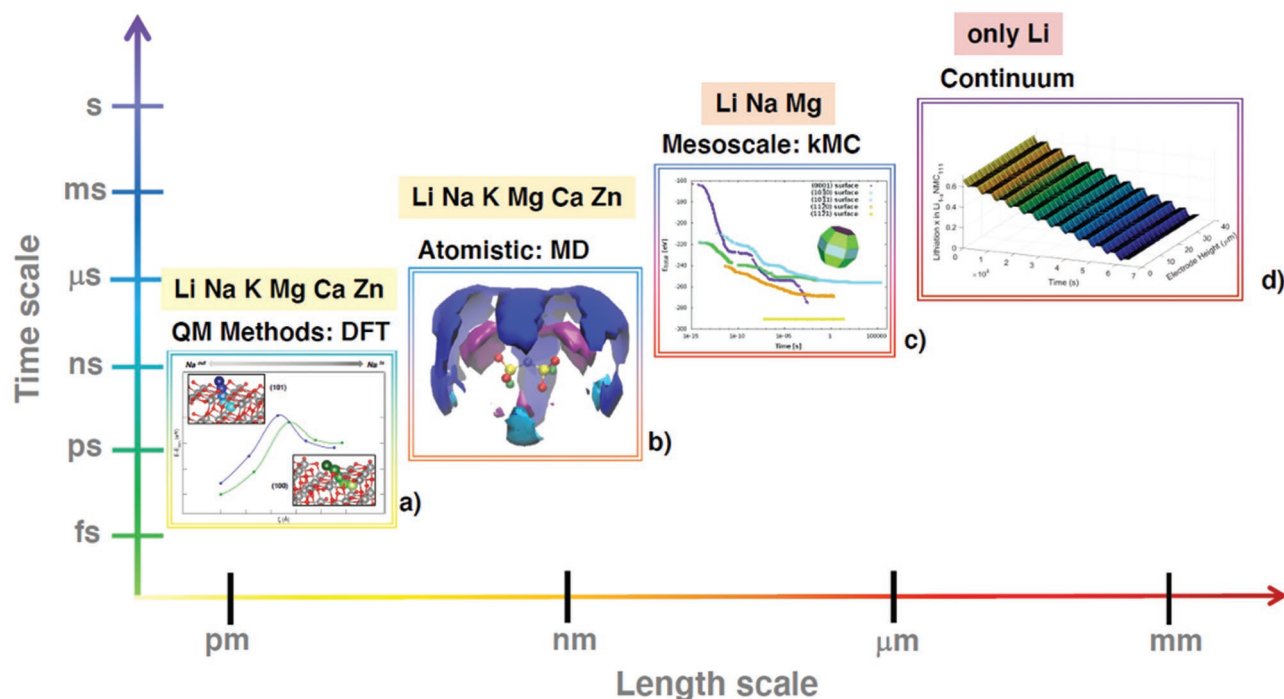
Figure 13. Space and time scales of different modelling methods applied to the battery field. Main chemistries where these methods are applied are indicated. Insets enclose examples of each kind: a) Minimum energy paths and corresponding energy profiles for Na insertion in TiO_2 anatase surfaces calculated at the DFT(PBE)+U level of theory. Adapted with permission.[153] Copyright 2020, The Royal Society of Chemistry. b) Spatial distribution functions of FSI^- (blue), $C_3C_1pyr^+$ (cyan) and Na^+ (purple) around central FSI^- at in an equimolar $[C_3C_1pyr][FSI]/Na[FSI]$ ionic liquid mixture calculated from MD with a polarizable force field. Reproduced with permission.[159] Copyright 2020, The Royal Society of Chemistry. c) Surface energy versus time during kMC simulation on metallic Mg and shape of Mg crystals. Adapted with permission from ref. [186]. d) Mean Li- state along the electrode thickness in terms of computationally performed GITT experiment time on a $35.3\times35.3\times38.8$ μm^3 half-electrode model. Reproduced with permission.[187] Copyright 2020, American Chemical Society.

Operando techniques on multiple elements have been also demonstrated in the case of Ca/S batteries by means of double-edge X-ray absorption spectroscopy: this original approach discloses direct evidence of the redox states as well as the coordination shells surrounding S and Ca ions, upon discharging/charging in cell.[195] The obtained electrochemical solid-state reaction mechanism occurs through the formation of different types of soluble polysulfide species during both charge and discharge at room temperature, and the formation of solid CaS at the end of discharge. Furthermore, the reversible electrochemical activity is proven by the experimental evidence of reformation of elemental sulfur at the end of re-charge. Multiple simultaneous operando techniques are experimental frontiers of battery materials. This challenging approach has been applied to beyond-lithium batteries in the case of the simultaneous operando investigation of aluminum/graphite cells by X-ray diffraction and tomography.[196] Besides the classical insights into the $AlCl_4^-$/graphite intercalation mechanism obtained by diffraction (i.e., a mixed-staged region in the initial stage of alumination and a two-staged region in a second stage), the simultaneous imaging analysis by tomography, revealed the influence of graphite morphology in the electrode volume expansion upon cycling.

Turning to Zn-battery chemistries, operando techniques, also in this case, are playing a pivotal role in the exploration of intercalation reactions. Examples of the use of operando X-ray

diffraction to evaluate the zincation mechanism in vanadium oxides have been reported recently[197–199] highlighting the complexity of the structural alteration of the host matrix as well as the unexpected role played by the electrode/electrolyte interphase.

Overall, advanced experimental investigation protocols based on synchrotron techniques coupled with electrochemical tests (operando approach) are disclosing unprecedented insights in the electrochemistry of materials and interphases. The extraordinary quality and complexity of these studies are shortcutting the innovation chain for novel battery chemistry beyond lithium. On the other hand, the facile production of large amount of detailed data requires to develop massive data processing algorithms tailored for a full exploitation of all experimental evidence.

5. Conclusions

Nowadays, the energy decision makers are concerned with ensuring that: i) appropriate, affordable and adequate services are accessed, ii) the energy-system can do so in a sustainable manner, and iii) broader interactions between systems do not compromise the planet's sustained development. It is evident that strategic advances in the frontier of battery research to increase the efficiency and effectiveness of transmission and distribution of electricity must be realized in the next few decades. Innovation in the field of energy storage can be brought about

from new knowledge gained by means of modern experimental tools, in situ and operando characterizations, computation and simulation, and implementation of artificial intelligence, all allowing a constructionist approach for new technologies with unique performance for emergent needs.

Energy metrics for applications such as grid-storage, EVs, electronics, and many other needs of modern society have to be matched with costs, supply chain and environmental sustainability. When complete devices are analyzed, NIBs result to be more sustainable, with respect to conventional LIBs if comparable energy densities could be achieved. Other post-LIBs, based on other metals which include Al, Mg, Ca, K, and Zn, are still in their infancy preventing to have reliable data. Investigating the energy impacts of different metals, it was found that Ca has the most promising values of all analyzed metrics (i.e., CED, GWP, YGCE) sensibly lower compared to the ones for Li. On the other hand, Al presents slightly higher values in figures of merits.

The ever-growing demand for safer and denser energy storage systems is motivating an intense pursuit of easily scalable and manufacturable all-solid-state batteries. Scaling-up to large-format solid-state batteries requires to rethink the fabrication steps known from traditional battery manufacturing and also implies research on cheaper materials. It is clear that a majority of the cost of the batteries arises not only from the raw materials, but also from the fabrication process. The critical processing environments for the reactive metal anodes and solid-state electrolytes can be costly and easily outweigh the advantages of the cheap raw materials. However, jointly enhancing the cell capacity and the materials supply may help to lower battery cost. Notwithstanding the growing number of publications on post-LIBs, there is a serious lack in the analyses of the actual sustainability of these technologies. As such, the Ca/Mg/Zn/Al batteries for practical applications still have a very long way to go, and their viabilities require careful assessment by the research community. Of course, a sustainability-driven analysis is not an easy task (especially, if fixed numbers are not available); it requires to deal with different figures of merit, ranging from energy consumption to production processes, from emission to social and economic impacts. In this context, we are convinced that a thorough analysis of post-LIB technologies is a milestone from which the development of sustainable but efficient batteries should begin.

Conflict of Interest

The authors declare no conflict of interest.

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