Metal electrodes for next-generation rechargeable batteries

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Abstract

The electrification of transport and the transition to renewable energy sources are driving demand for versatile and efficient storage of electrical energy − principally batteries, which can store energy with high efficiency, in a variety of designs and sizes. Compared to conventional batteries that contain insertion anodes, next generation rechargeable batteries with metal anodes can yield more favourable energy densities, thanks to their high specific capacities and low electrode potentials. In this review, we provide an overview of the recent progress in metal anodes for rechargeable batteries. We examine design concepts and application opportunities, and highlight the differences between metal and insertion-type electrodes in interfacial (two-dimensional) and interphasial (three-dimensional) chemistries. Finally, we analyze available cell chemistries and architectures focusing on the design strategies for sustainability, as well as existing roadmaps for next generation batteries.

[H1] Introduction

Electrochemical energy storage is essential for meeting the increasing demands of electrified transport and transition to renewable energy sources. A rechargeable battery is an electrochemical energy storage device that, after being discharged, can be charged again by applying direct current to its terminals[1]. The core of the battery consists of redox-active electrodes separated by an ionically conductive electrolyte (for a general introduction to batteries please refer to **Box 1**). The electrodes are critical elements of the battery: they store charges as well as electrical energy by (mostly) reversibly converting it to chemical energy.

Any electronically conductive material can act as an electrode when placed in an ionically conductive medium that provides suitable reaction partners for the charge and discharge reactions. Early-prototypes of primary (non-rechargeable) and secondary (rechargeable) batteries contained metal electrodes, as these have high specific capacity (charges per unit mass) and good material availability. Metals are typically employed as anodes rather than cathodes because of their low standard reduction potentials (that is the tendency of ions to be reduced to the respective metals). In this manner, the cell voltage can be enhanced by maximizing the difference between the anode and cathode potential.

Reversible reactions are key to ensure a long cycle life (>1,000 charge/discharge cycles), but present a major challenge for rechargeable metal batteries due to a fundamentally different charging/discharging process compared to ion-based batteries. In conventional ion-based batteries (for example, Li-ion batteries), ions are intercalated into graphitic carbons upon charge and deintercalated upon discharge; whereas in a metal-based battery, metal is deposited and dissolved at the anode. These deposition and dissolution processes are often inhomogeneous and not fully reversible because of the continuous side reactions with the electrolyte constituents that eventually lower the Coulombic efficiency (discharge/charge balance) and the lifetime of the cells[2].

Among all metal anodes, Li metal is highly promising owing to its low standard reduction potential and high specific capacity, both of which influence the amount of energy actually storable in a cell[3]. Examples of already commercialized or promising rechargeable metal batteries are Bolloré's polymer-based Li metal battery (LMP technology) and Quantumscape's 'anode-less' battery (**Fig. 1a**).

Rechargeable Na metal batteries have been developed, for example, by the start-up company LiNa Energy since 2020. Other metals such as Ca, Mg or Zn have also been considered, although undesired side reactions and associated loss of active metal reservoirs limit their effective applications so far[4]. Through alloying, Mg and Al metals could potentially be utilized as metal anode in future batteries[5,6]. Intercalation of Zn into the cathode material α-manganese dioxide (α-MnO_2) and of Ca into titanium disulfide (TiS_2) have also marked important milestones on the way to rechargeable metal batteries containing multivalent metals as anodes[7,8]. Soon, advanced cell constituents (such as functional coatings, tailored additives and artificial interphases) may further promote the development of these batteries.

In this review, we present an overview of state-of-the-art rechargeable metal batteries and highlight potential applications. We first consider the natural abundance and the suitability of the different metals for rechargeable batteries and underline the key properties relevant for cell operation. Next, we elaborate on the importance of the electrode–electrolyte interfaces and interphases, where interfaces are the intimate two-dimensional contact areas between the electrode and electrolyte surfaces, and interphases are the three-dimensional interlayers that inevitably form between electrodes and electrolytes[9]. The development steps from single cells to batteries are discussed, ranging from electrolyte and cathode chemistries to manufacturing challenges. Finally, we outline examples and highlight some aspects of recycling and circular economy with respect to rechargeable metal batteries.

[H1] Anode raw materials

Precursor materials for metal electrodes are harvested from deposits in mines around the globe. Evaluating the natural abundance of the resources and their applicability as electrodes in commercial rechargeable batteries is fundamental.

[H2] Natural abundance

Natural resources can be defined as the amount of naturally occurring materials for which larger-scale extraction is potentially feasible, whereas reserves denote available resources that can be exploited economically[10]. Natural resources and reserves of metal elements vary considerably depending on the element type (**Fig. 1b**). Al, Ca and Mg are among the most abundant elements in the Earth's crust, while Na is readily available from both the crust and seawater. With estimated global reserves of more than 5 billion tons each, Na, Mg and K are one to two orders of magnitude more abundant than natural graphite, which amounts to 330 million tons in reserves and is frequently used in conventional Li-ion batteries as an anode material[11]. Today Li metal reserves and resources (26 and 98 million tons, respectively) are roughly three orders of magnitude lower than those of Na and K. Being the material of first choice in modern battery technology, Li is the most important reserve, but it is also the least abundant. Global Li demand is expected to grow rapidly within the next two years from 176 kt in 2023 to 254 kt in 2025 (**Fig. 1c**), driven by the accelerated production of batteries for electric vehicles[12]. Fortunately, the gap between supply and demand − that was particularly noticeable in 2022 − is expected to narrow and completely vanish in 2023, as production gathers pace worldwide to accommodate the increasing demand[12].

Owing to natural geographic distribution as well as mining capacity, annual production of metals and precursors varies unevenly around the globe (**Box 2**). China remains the leading supplier of most metals (except Li, Al and K). Independent multilateral commercial or materials exchange agreements with (and without) China, as well as recycling efforts, are necessary for those countries with lower primary-production capacity.

[H2] Metals as anodes

Besides natural abundance, the chemical and electrochemical properties of the metals are important parameters to evaluate their applicability in rechargeable batteries. Therefore, we focus on those key parameters and properties that are relevant for battery operation. Standard reduction potentials (or electrode potentials, in volts versus standard hydrogen electrode, or SHE; see **Box 1**) and available specific capacities (measured in mAh g^{-1}) of metal anodes are key baseline indicators for both the achievable operating voltage and specific energy (Wh kg^{-1}) of cells (**Fig. 2a**). Metallic Li provides the lowest standard reduction potential (−3.04 V versus SHE) and highest specific capacity (3,861 mAh g^{-1}) of the materials considered here. Other metals with low standard reduction potentials (< -2.7 V versus

SHE) are Na, K, and Ca, all of which can store substantially fewer charges per unit mass than Li. For example, Ca has a specific capacity of 1,337 mAh g^{-1}, which is almost three times lower than that of Li. Mg and Al provide moderate standard reduction potentials (−2.4 V and −1.7 V versus SHE, respectively) and comparably high specific capacities (2,205 mAh g^{-1} and 2,980 mAh g^{-1}, respectively). The lowest specific energy and operating voltage is expected from Zn, Cd and Pb, which show both high reduction potentials (> −1.0 V versus SHE) and low specific capacities (< 1,000 mAh g^{-1}).

Batteries should be not only lightweight but also compact, hence the storable charge per unit volume, or charge density, is another parameter that must be considered. Here, based on the charge density (mAh cm^{-3}) of different materials, we present the metal layer thickness that corresponds to a capacity of 1 mAh cm^{-2} (**Fig. 2b**). For example, depositing metallic Li with a current density of 1 mA cm^{-2} for a duration of 1 h results in a metal layer thickness of 5 µm, assuming an estimated density of deposited metallic Li of 0.54 g cm^{-3}. Note that realistic charge capacities of more than 4 mAh cm^{-2} are needed in electric vehicle applications[13] and, as anode volume expands upon cell operation, this must be accounted for in cell designs.

Na and K require the largest thicknesses to store 1 mAh cm^{-2} of charge (9 µm and 17 µm, respectively). Mg could be an attractive alternative, at only 2.6 µm per 1 mAh cm^{-2}. However, the formation of passivation layers and/or interphases at the Mg surface hinders the Mg^{2+} ions from passing through and requires adjustment of interphase chemistries or electrolyte formulations. Formation of a non-cation-conducting passivation layer is also a challenge for Ca metal electrodes. Although this type of electrode is associated with fast corrosion[14], alloying Ca with tin (Sn) results in prototype coin cells (coin-shaped batteries consisting of a single cathode|electrolyte|anode layer) that operate at room temperature[15]. Reversible Zn metal anodes are another example of multivalent metal electrodes that exhibit a high specific capacity (of 820 mAh g^{-1}) and can potentially store a large amount of charge per unit volume (1.7 µm for 1 mAh cm^{-2}). They also have the advantage of stability against aqueous electrolytes[16,17], which are often more environmentally friendly and less costly compared to non-aqueous electrolytes, thus preferable[18]. Owing to its trivalent nature, Al metal provides the highest charge density (1.2 µm for 1 mAh cm^{-2}), but similar to other multivalent metals, the formation of a passivating layer (such as Al_2O_3) constitutes a major challenge, although it can be mitigated by using aqueous electrolytes under alkaline conditions[19] or alloying aluminium with copper[6].

Other metal properties also come into play. Alkali metals have much lower melting points (180 °C, 98 °C, 64 °C for Li, Na, and K, respectively) compared with alkaline earth metals (649 °C and 842 °C for Mg and Ca), which can lead to operational safety issues for alkali metal electrodes. Also, the electrochemical reactivity of metals — as indicated, for example, by electronegativity following the Pauling scale — renders alkali metals (Li, Na, K: electronegativity < 1) more reactive than metals such as Mg, Al and Zn (electronegativity > 1). But the formation of passivation layers on Ca and Mg, as mentioned above, present a particular challenge: these interphases, formed at electrode–electrolyte interfaces, are a bottleneck for industrial application of these metal anodes. In the following section, we will therefore discuss how to control the formation of interphases based on both the electrodes and the electrolyte compositions.

[H1] Interfaces and interphases

Technical applications of metal-based batteries such as in electric vehicles require the cells to withstand elevated current densities. For example, charging at a rate of 2 C (that is, charged to full capacity in 30 min) would require a current density of 8 mA cm^{-2} when utilizing a cathode with areal capacity of 4 mAh cm^{-2} (which is the common cathode loading in Li-based cells[13]). When operating with such high currents, optimizing the charge transfer dynamics at the electrodes is essential — in particular, minimizing the charge transfer resistances while maximizing the ionic conductivity across the corresponding electrode–electrolyte interphases. Explicit control of the redox processes at the electrodes (for example, by incorporating functional polymeric layers or patterned surfaces[20]) may limit continuous interfacial and interphasial reactions, thereby boosting metal reversibility and longevity of the metal-based cells.

[H2] The solid electrolyte interphase

Complex (electro-)chemical interfacial and interphasial processes at metal electrodes typically result in the formation of decomposition layers. These processes ideally occur during the first cycles of battery operation (often referred to as formation cycles), thereby stabilizing and governing the subsequent interfacial redox reactions. These transiently changing, ionically conductive — and as yet, not well understood — layers are known as solid electrolyte interphases (SEIs; **Fig. 2c**). SEI layer formation starts when a metal electrode is immersed in or brought into contact with an electrolyte, and dynamically changes upon applying a bias or a current, thus forcing electrochemical reactions. The ionic components of the electrolyte mainly yield insoluble inorganic compounds that are deposited in the vicinity of the metal surface, whereas the solvent molecules mainly contribute to the formation of organic compound layers closer to the electrolyte[9,21].

For applications, metal electrodes require the presence of a robust and sufficiently cation conductive SEI layer that facilitates the reversible deposition and dissolution of the metal upon repeated cell charging and discharging cycles. The reversible metal deposition and dissolution cycle (ideally more than 1,000 cycles) is typically described using two parameters: the capacity retention (percentage of initial capacity after a given number of cycles) and the Coulombic efficiency (ratio of discharge capacity over charge capacity). A robust SEI constitutes the precondition for reversible deposition and dissolution cycling (high Coulombic efficiency) and is ideally characterized by low resistances ($< 100\ \Omega\ \mathrm{cm}^{-2}$) [22].

The presence of SEI layers was first observed in the case of alkali and alkaline earth metals in contact with non-aqueous electrolytes[23]. SEI layers occur on metal anodes in aqueous batteries as well, comprising compounds such as lead(II) sulfate ($PbSO_4$) on Pb, zinc hydroxide ($Zn(OH)_2$) on Zn or cadmium hydroxide ($Cd(OH)_2$) on Cd anodes. However, they are not as protective as the SEI constituents − for example, lithium oxide (Li_2O), lithium fluoride (LiF) and lithium carbonate (Li_2CO_3) − on metallic Li[24]. In contrast to SEIs on most insertion electrodes (such as graphite), SEI layers on metals have to compensate for the substantial volume changes during operation while mitigating metal corrosion or dissolution or other degradation reactions involving the electrolyte constituents. Note that SEI thicknesses of 10–100 nm are typically observed on Li and Na metal electrodes[21], whereas multivalent metals (Mg, Ca, Zn, Al, and others) may form thicker electronically and ionically passivating layers (non-SEI-like layers formed by decomposition products from the electrolytes[9]), thereby blocking or limiting further metal deposition reactions[4]. Introducing specific electrolyte constituents, such as additives, or electrode alloys can enhance the electrochemical properties of the interphases on multivalent metals, making these interphases behave like SEIs[4].

The formation of interphases at cathodes (often referred to as cathode electrolyte interphase, CEI[25]) can also be very relevant for the overall Coulombic efficiency and energy efficiency[26] of the electrochemical cells. In the case of metallic anodes, especially, cross-talk between SEI and CEI layers is often not negligible, as components may travel from one electrode (usually transition metals from the cathodes) to the opposite one[27,28].

[H2] Understanding SEI layers

Reliable models that describe SEI layer requirements and composition are needed for a tailored design of the electrode–electrolyte interfaces and related interphases. Although the importance of SEI layers was already recognized in the 1970s[23], and despite substantial research efforts[2,29,30] since then, knowledge of how to control SEI composition and formation is still limited[31].

An ideal SEI should exhibit several properties, including: excellent cation conductivity σ_{SEI}, (at least larger than the bulk ionic conductivity[32]); very poor electronic conductivity; mechanical flexibility, but also sufficient robustness to withstand any metal deposit protrusion and large volume changes without cracking; insolubility of SEI constituents in the electrolyte to prevent the occurrence of cross-talk between the anode and the cathode. Tailoring the formation and the composition of the SEI layers can significantly enhance the reversibility of metal anodes and thus the capacity retention and Coulombic efficiency of metal-anode based batteries, enabling long battery lives and fast charge capabilities. Note that rational designs of artificial interphases require advanced understanding of metal deposition and dissolution phenomena.

Although the key performance indicators (reversibility, charge capability and cycling stability) are rather similar for all metal electrodes, there are specific properties of different metals and ‘native’ SEI layers that necessitate tailored solutions. For example, Na metal deposits are mechanically softer and more plastically deformable compared with more rigid Li metal species and thus behave differently upon exposure to mechanical stress during cell operation[33]. Better understanding of interfacial reactions and SEI formation processes including structural aspects is needed, as thin layers are experimentally demanding to characterize, especially in a non-destructive way. But there are techniques that have great promise for resolving SEI structures at the nanometer scale. Cryogenic electron microscopy (cryo-EM)[34] and cryogenic scanning transmission electron microscopy (cryo-STEM[35]) have recently demonstrated, for Li metal anodes, that fluorine-rich domains comprising the SEI can be resolved and differentiated from dendritic metal structures containing potentially detrimental lithium hydride[35]. Also, technological advances in dynamic nuclear polarization enhanced nuclear magnetic resonance spectroscopy (DNP-NMR) enable unambiguous resolution of SEI constituents in situ. For example, fluorine-rich SEI domains have been identified near the Li metal surface by utilizing free electrons (Fermi electrons) within the Li metal to enhance the signal intensity in layers close to the metal surface[36]. Note that, in principle, such DNP-NMR studies should also be feasible for Al- and Na-based metal electrodes (as they have reasonably sensitive NMR nuclei).

[H1] From electrodes to cells to batteries

Metal anodes can only work if paired with appropriate cathodes and electrolyte formulations, combined in a suitable cell design with scalable electrodes and cell fabrication processes that are compatible with large-scale battery production. Various electrolyte and cathode chemistries can be found in the literature, reflecting the fact that there is no universal electrolyte and cathode chemistry suitable for all metal anodes. **Table 1** reports examples of prototypes and model cells comprising different metal anodes. The large differences in operating voltage (0.7 V to 3.8 V) and in stages of development (from lab-scale 3-electrode cells to industrial multilayer pouch cells) are a clear indication that the required cell chemistries vary (for example, in regard to high-voltage stability). But there are also notable commonalities, such as the borate-based salts dissolved in ether-based electrolytes used in cells that contain Ca or Mg anodes (these salts have high ionic conductivity, 8–11 mS cm^{-1} at room temperature)[15,37]. In the following sections, we explore recent achievements in electrolyte and cathode chemistries, as well as progress in cell design and the challenges of larger-cell manufacturing.

[H2] Electrolytes

The electrolyte plays a central role in achieving cell longevity and highly reversible redox chemistry. It not only constitutes the core of all batteries, but also determines bulk charge transfer dynamics (related to the conductivity and the diffusivity of the ions in the electrolytes) and interfacial redox processes at the electrodes. Tailoring the electrolyte composition enables the interfacial reactivity to be controlled. Even a small addition (< 5 wt%) of supporting functional components in the electrolyte can have a large impact on the battery life time (for example, an increase in capacity retention after 150 cycles of more than 50 %)[38].

Key performance requirements of electrolytes comprise sufficiently high ionic conductivity (ideally $> 10^{-3}$ S cm^{-1})[39], low electronic conductivity ($< 10^{-10}$ S cm^{-1})[40], electrochemical stability (within the potential window of the electrodes), and interfacial compatibility with the electrodes (that is, no undesired side reactions). For rechargeable metal batteries, electrolytes should be able to mitigate or suppress the formation of inhomogeneous metal deposits. Liquid electrolytes are often employed because of their high ionic conductivity (> 1 mS cm^{-1}) and excellent electrode contacts[41,42].

In case of Li metal batteries, electrolytes containing ether-based solvents[43] and functional additives such as lithium nitrate ($LiNO_3$) and fluoroethylene carbonate (FEC) may yield Li_2O- and LiF-rich SEI layers on Li metal anodes, thereby stabilizing the electrode–electrolyte interfaces[44]. Polymers and inorganic ceramic materials are viable alternatives to liquid electrolytes, attractive for their lower flammability (for battery safety) and greater mechanical robustness (to withstand metal protrusion and rupture)[45,46]. Indeed, a combination of different types of electrolyte — or 'hybrid electrolyte' — is among the most promising strategies, with the drawbacks of individual materials (such as insufficient conductivity or mechanical stability) ideally overcome in hybrid systems. As such, a combination of inorganic $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) particles and poly(ethylene glycol methacrylate) (PEGMA) polymerized in situ on Li metal has enabled thin electrolyte layers (8.5 µm) with impressive charging rates of > 1C at elevated temperatures[47]. Another example of a hybrid electrolyte comprises two polymers (crosslinked polycaprolactone and polyethylene oxide) in a sandwich-like set-up with flowable oligomer catholytes: high cathode mass-loadings (11 mg cm^{-2}) and cell energy densities (356 Wh L^{-1}) are achieved, compared with other solvent-free polymer-based Li batteries[48]. Also, with a view to enhancing cell safety by reducing flammability, liquefied gas electrolytes have been introduced. They not only act as recyclable fire-extinguishing agents but also operate across a wide temperature range, from −60°C to 55 °C. Although still at an early stage of development, this approach could lead to safer next-generation Li metal batteries[49].

The high reactivity of Na metal with ether-based solvents requires alternative electrolytes and, for example, stabilized SEI layers containing Na_2O and NaF have been achieved in glyme-based solvents[33]. Solid-type Na superionic conducting electrolyte (NASICON) presents a conductivity of 4 mS cm^{-2} at room temperature and is an attractive alternative electrolyte for the operation of Na metal batteries, also because of its excellent selectivity for Na^+ ions (no other species can pass through) and robustness against mechanical deformation[50].

Efforts to develop electrolytes for multivalent metal electrodes face the challenge of strong Coulombic interactions among the solvated cations and their surrounding solvent shell[16]. Ether-based electrolytes have been identified as appropriate candidates for operating Mg-based rechargeable metal batteries, due to their stability against cathodes and, if properly functionalized, also against the Mg anode[51]. Other possibilities include magnesiated Nafion-based gel-type electrolytes[52] and borate-based anions like tetrakis(hexafluoro-iso-propoxyl)borate ($[B(HFIP)_4]^-$) as weakly coordinating anions[53]. Ca-based electrolytes are often highly concentrated. For example, Calcium(II) Bis(trifluoromethanesulfonyl)imide ($Ca(TFSI)_2$) salt in propylene carbonate with a fluorinated diluent creates a wide electrochemical stability window (> 4.5 V) and enhanced ion transfer at electrode–electrolyte interfaces[54,55]. Zn-based electrolytes have great potential in terms of resource consumption and sustainability, because Zn metal is operable in aqueous-based electrolytes with inexpensive salts[16,17]. In case of Al metal batteries, the strong Coulombic interactions among Al-cations and their anionic counterparts require a high level of solvation of Al^{3+}-ions in organic solvents[19]. Room-temperature-applicable chloroaluminate ionic liquids have been proposed as non-aqueous electrolytes but are compromised for applications by high costs and limited scalability[56].

[H2] Cathodes

Excellent anode reversibility and electrolyte formulations are, however, practically irrelevant in cells for which there are no appropriate cathode chemistries. Fortunately, various cathode active materials have been developed. In the case of Li-based chemistry, decades of research have provided various cathode materials, among which layered oxides[57], iron phosphates[58] and sulfur-based cathodes[59] are the most promising candidates for future battery applications. In particular, high-capacity Ni-rich layered oxides, including Al/Zr-doped single-crystalline lithium nickel manganese oxide $LiNi_{0.88}Co_{0.09}Mn_{0.03}O_2$, show great promise for high-energy and high-power-density cell systems[60]. Appropriate cathode chemistries for Na batteries comprise P2-type layered metal oxides, sodium vanadium phosphate $Na_3V_2(PO_4)_3$ and Prussian blue analogues[61]. Development of cathodes suitable for multivalent metal batteries is challenging, as the strong electrostatic interactions among the multivalent cations and cathode host lattices, as well as solvent molecules, cause comparatively sluggish (unfavourably slow) reaction kinetics[62], eventually inhibiting fast charging. Potential cathode materials for Mg-based batteries were proposed more than 20 years ago, involving sulfur-based structures[63]; recent high-voltage cathodes include transition metals to afford cell voltages of around 3 V [64]. An impressive 0.7 Ah prototype pouch cell based on an alloyed Mg metal foil and vanadium sulfide cathode was demonstrated this year (2023) — an important step towards practical cell applications[37]. Regarding reversible Ca chemistries, several cathodes have been proposed, including a copper sulfide (CuS) cathode[65], Se-based cathode[66], and vanadium oxide-based cathode[67,68]. A highly stable cathode based on 1,4,-polyanthraquinone (14PAQ) has been operated with Ca_xSn alloy anodes for more than 5,000 cycles at 1 C (ref. [15]). Suitable cathodes for aqueous Zn-based batteries are typically manganese or vanadium oxide-based, and Prussian blue analogues, although challenges of active material dissolution, proton co-intercalation and oxygen evolution at higher cell voltages remain[16]. Cathodes utilized in Al-based cell chemistries comprise graphitic materials[19], transition metal oxides – such as, manganese dioxide (MnO_2)[6] –, as well as sulfur-based cathodes – for example, molybdenum sulfide (Mo_6S_8)[56].

[H2] Cell design strategies

In most cell systems, metal anodes provide an excess metal reservoir to partially accommodate the capacity losses caused by the irreversible redox processes upon cell operation. Functional coatings or structured current collectors can be employed to increase the reversibility of the available metal inventory (that is, the redox active metal or metal ions) and to mitigate irreversible metal losses that contribute to the overall battery capacity fading[20]. This may result from inhomogeneous metal deposition, including 'dead' metal fractions (electrochemically isolated) or high surface area metal deposits, and/or corrosion reactions in the presence of electrolyte constituents. To achieve energy densities >500 Wh L^{-1}, this excess metal volume should be kept to a minimum. For example, based on a projection for next generation Li metal batteries[22], a reduction from 100 µm to 20 µm of Li excess foil thickness would increase the multilayer cell energy density from 460 Wh L^{-1} to 670 Wh L^{-1}.

Note that thin metal films can be produced by extrusion (lamination), melt processing, vapour deposition or electrodeposition[11], which may imply prohibitive costs[69]. Metals that are less ductile than alkali metals (such as Mg) render production of thin metal films challenging[37]. Alloying Mg with other metals (such as AZ31, containing 3 % Al and 1 % Zn) can yield thin films of 25 µm (ref. [5]). Another strategy comprises 'warm' roll-pressing of Mg at 300 °C to achieve thin films (< 45 µm) required for higher energy densities[70]. From an economic point of view, in the ideal case, anodes should not contain initial excess metal other than a (structured or coated) current collector foil (for example, copper foil[71]). — this is the 'zero-excess' or 'anode-free' concept. Here, the major challenge comprises reversible (high Coulombic efficiency) metal deposition and dissolution on the employed current collectors. The introduction of functional artificial interphases may enhance the achievable Coulombic efficiencies of the cells, as demonstrated, for example, by modifying porous Li scaffolds with barium titanate ($BaTiO_3$)[72] or strontium fluoride (SrF_2) nanoparticles[73]. Instead of omitting the extra active metal layers, some cells employ free-standing metal anodes, in which the metal serves as both the anode and the current collector[74]. The advantage of having a lighter cell, owing to the absence of the current collector (copper foil, for example, has a density of 8.96 g cm^{-3}), is countered by the higher electric resistivity of the active metal (five-fold higher for Li metal compared with copper), eventually resulting in increased heat development upon cell operation at higher current densities or even increased losses of the metal reservoir (as reflected by battery capacity fading).

[H2] Towards larger batteries

One of the major challenges in the development and implementation of new battery technologies is that cell chemistries need to be scalable for the assembly of multilayered cells and eventual packaging of battery modules (that is, stacks of multiple cells within a compartment)[75]. Prototype cells with capacities of 0.1–10 Ah are necessary to demonstrate realistic performance of the metal-based cell chemistries[76]. Stacking or folding is required of cathode–electrolyte–anode cell units with electrode areas larger than a few cm^2 (which is the size typically employed in laboratory-scale cells). Scalable manufacturing of cell stacks (using, for example, a roll-to-roll technique[11]) is critical and can be demanding in the case of metal electrodes, considering that a controlled atmosphere is necessary to avoid degrading reactions caused by moisture, residual solvent vapours or other atmospheric components. Furthermore, thin metal foils (< 50 µm) are beneficial to increase the energy density, but may be either mechanically too brittle (as in the case of Mg, Ca) or too soft (Li, Na) for continuous roll-to-roll manufacturing[11].

Volumetric expansion upon charging of the cells is another critical phenomenon that is pronounced in larger metal-based batteries, as each individual layer contributes to the overall expansion. In the case of metal anodes, the expansion depends on the metal itself and on the reversibility of the metal inventory, as continuous degrading reactions at the interfaces between the metal and the electrolyte may cause substantial accumulation of passivated metal deposits that further increase the volumetric expansion of the battery[77]. Implementing elastic materials, such as polyurethane foams, might compensate the volumetric expansion while enhancing the operational safety of the individual battery packs[78].

In contrast to conventional Li-ion batteries, the low melting point of some relevant metal anodes (98 °C in the case of Na) requires further safety considerations. For example, it might be necessary to employ robust cylindrical casings (often used in electric vehicles[79]) instead of pouch bags (light-weight, but less robust), that could not withstand the presence of molten metal anodes in the accidental case of thermal runaway of the cells.

[H1] Applications and sustainability

The current stage of development of the different metal-based cell systems varies from early proof-of-concept studies to actual demonstrator cell designs, to larger-scale applications. Technology readiness level (TRL), first introduced by NASA in 1989, is a practical metric used to describe and assess the technological maturity of a product. It was adopted, for example, in 2022 to develop the Battery 2030 roadmap for battery research in Europe[75]. The 'Battery Component Readiness Level', a related metric, describes battery technological developments specifically, ranging from basic research and lab-scale prototypes to upscaled systems and the final stage of commercialization[80]. The path towards application and commercialization comprises multiple steps (**Fig. 3a**), ranging from materials research to the demonstration of cell chemistries in prototype applications. Once suitable materials have been developed, appropriate cell designs that focus on thin and dense layers will be required to gain advantages in energy density. Also, cell systems need to be scalable in terms of both materials synthesis and manufacturing. In the case of cell chemistries based on metal electrodes, further developments of suitable cathode and electrolyte materials or functional coatings are required, including consideration of electrochemical and thermal stability windows, as well as reversible electrochemical reactions.

[H2] Scenarios for metal batteries

Electric vehicles and stationary storage systems are among the most relevant applications for metal-based batteries. Batteries for the electric mobility sector necessitate high energy densities (500 to 800 Wh L^{-1}) and fast charge applicability (1 to 5 C, as suggested by the United States Advanced Battery Consortium), but specifications for local storage batteries are less demanding. Here, cost-effectiveness (typically < 100 US\$ kWh^{-1})[75], sustainability and longevity are decisive. **Table 1** reports examples of metal-anode-based cell chemistries and their current stage of development.

Among the considered chemistries, rechargeable Li metal batteries are the most advanced solution and are already commercialized or close to commercialization by various cell manufacturers, such as Bolloré and SES. Current research and development efforts are dedicated to reducing the amount of excess Li, enhancing the energy density and cycle life, and increasing operational safety. Introducing advanced liquid-based or gel-type electrolytes or switching to mechanically more robust electrolytes, such as polymers[22,81,82] or inorganic ceramics[39] are among the potential solutions. Despite the fact that

Li metal batteries have been utilized in electric vehicles for more than 15 years (Bluecar), what role they might have in future applications is unclear, owing to emerging and already partially commercialized systems for alternative anodes (such as silicon-based anodes[83]). As for most metal-based cells, it is crucial to keep the size of the Li reservoir (its thickness) at the anode side as small as possible to achieve optimal energy densities of the cells.

Only a few Na metal batteries are commercially available, for example, the solid-state Na metal battery introduced by the British company LiNa Energy. Na-sulfur batteries with liquid Na are also commercially available and distributed by BASF (NAS Battery). Intercalation-type Na-ion batteries offered by the French company Tiamat afford fast charging (5 min, or rates of 12 C) and lifetimes of more than 5,000 cycles. Another innovative example involving Na-ion or Na metal anode materials is the 'seawater battery' that exploits natural Na sources within seawater as a cathodic electrolyte[84–86]. In this case, the anode (Na metal) is separated from the catholyte by a solid electrolyte membrane and is immersed in a non-aqueous anodic electrolyte (anolyte). Cost-advantages over Li-based batteries render the Na-based cell chemistry also attractive for the setup of larger-scale stationary energy storage systems[86].

Due to their expected low costs at moderate energy densities (< 300 Wh L^{-1}), Zn, Mg and Ca-based batteries may also be relevant for large-scale energy storage. However, they are still at an early stage of technological development and seem to be limited by low specific discharge capacities or lower operating voltages (**Fig. 3b**). Zn and Al-based metal batteries have the advantage of being compatible with environmentally friendly aqueous electrolytes and can be fabricated in atmospheric environments, thereby reducing production costs[16].

[H2] Circular economy and recycling

The rapidly increasing demand for metal-based batteries together with the associated material consumption and waste production require implementation of a circular economy and recycling efforts already at the single-cell level (**Fig. 3c**). Analogous to the established recycling processes for conventional Li-ion batteries, a mixture of leaching as well as pyro- and hydrometallurgical techniques can be considered for the extraction of materials from used batteries, with a major focus on hydrometallurgy to extract metal ions[87]. In contrast to the recycling of batteries containing conventional intercalation electrodes, residual active metal likely remains in metal-based batteries even after full discharge. Alkali metals are chemically more reactive than conventional graphite, for example, and hydrogen gas may form during the recovering of metal elements in form of salts (such as LiOH), thus necessitating additional safety precautions during recycling steps[88].

Considering that next-generation electrolytes (polymers, ceramics, or hybrids) may be required to enable metal anodes, their impact on recycling cannot be neglected. Here, one major challenge is the separation of the electrolyte components from the active materials[88], as these are often pressed together or even mixed if catholytes or anolytes are used. Recycling companies such as Umicore and Lithion specialize in Li-ion technologies and consequently, at later stages of metal-based battery commercialization, they may adapt the corresponding recycling routines for rechargeable metal batteries, if economically feasible.

By design, active materials and implemented cell designs should be suitable for at least partial recycling and extraction of the active materials. However, as of 2023, this is not the case. The targeted Li-ion recovery rate of 70 % for 2030, as stated in the European Green Deal initiative[89], demonstrates the high ambitions of policy makers, but also reflects the limitations of current recycling efforts. Utilization of abundant, low-cost materials such as Na or Ca means that the 'natural' recycling incentives that exist for more precious materials often do not exist, hence necessitating legislative regulation. As such, an 'extended producer responsibility' may be effective, by making battery producers responsible for end-of-life treatments of energy storage products[87] — although this would likely lead to higher prices for consumers.

Battery lifetime is also crucial and may be extended by introducing next-generation metal batteries and realizing second-life scenarios. For example, batteries used in electric vehicles that cannot fulfil the high requirements of e-mobility (fast charge and long range) any longer can be repurposed for less demanding home storage (coupled with photo voltaic) or industrial load-levelling storage systems[90]. The lifetime of electric-vehicle batteries may be 8 years or more, but it can be extended in second-life applications to 15–25 years[87].

A further example is Co, which is a critical resource used in some cathodes in Li-ion and Li metal batteries as its production frequently raises environmental and social concern[91]. Here, circular economy strategies should aim to reduce the reliance on primary materials by either switching to Co-less chemistries, implementing appropriate second-life applications or improving recycling rates[92]. An analogous strategy for metal-based batteries could be the reduction of the amounts of critical elements (that is, limiting the degree of excess metal reservoirs within the cells) and simultaneously increasing recycling efforts (**Box 3**).

[H1] Conclusion and Outlook

Rechargeable metal batteries are an attractive class of next-generation batteries thanks to the high abundance of most of the metals involved, and to their high capacity and energy density compared to insertion-type anodes. The formation and eventual tailoring of interphases, to enable highly reversible redox-reactions and maintain reversible metal inventory, constitute a major challenge for all metal-based batteries. In particular, the demanding requirements for electromobility applications — such as fast charge (high limiting current densities), high power applications (high voltage) and cell longevity (reversible metal inventory) — are difficult to accommodate in currently available Li or Na metal-based cell concepts (for example, NMC||Li; $NaVPO_4$||Na (ref. [76,93])). Here, achieving control of the interfacial and interphasial reactions at the electrodes, for example, by tailored design of structured surfaces or artificial SEI layers, as well as implementing high-performance electrolytes (especially solid-state concepts) are keys to enable the development of next generation batteries suitable for use in electric vehicles.

In contrast, for stationary storage applications, batteries made from rather low-cost and abundant materials (Al, Mg or Ca) implemented in MnO_2||Al, VS_4||Mg, or CuS/C||Ca cell concepts offer reasonable capacities and operational voltages[6,37,65]. However, despite the material abundance, application of these batteries is limited by the tendency of these metals to form non-cation conductive and highly resistive interphases. In this respect, future milestones could include the development of suitable functional coating layers and modified electrolytes, ideally harvested from renewable resources.

In summary, future directions for research and the development of metal-based batteries should focus on transferring fundamental understanding of relevant redox-processes, charge carrier transport at electrolyte–electrode interfaces and their interphases to the design of novel electrolytes. It will also be essential to exploit computer-simulation-supported engineering for the development of application-oriented materials and appropriate cell systems that foster recycling by design. However, because there is currently no single technological solution in sight, it is important to define general benchmarks that will serve various applications. Notably, cost-efficiency (< 100 US$ kWh^{-1}) is central for stationary storage systems, whereas the energy density (500–800 Wh L^{-1}) and charging rates (1–5 C) are most relevant for enabling premium or moderate electromobility cells.

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G.B. and P.L. equally contributed to this paper. All the authors contributed substantially to discussion of the content. G.B. and P.L. wrote the article. All the authors reviewed and/or edited the manuscript before submission.

Competing interests

The authors have no competing interests to declare.

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Key points

- Metal electrodes, which have large specific and volumetric capacities, can potentially enable next-generation rechargeable batteries with high energy densities.
- The charge and discharge processes for metal anodes (involving deposition and dissolution of metals) require reversible chemical reactions that constitute a major challenge.
- Controlling the formation of interphases between the metal electrode and the electrolyte is key to achieving high reversibility and long cycle life, as well as fast charging rates.

- There is no universal concept for the design of advanced electrolytes or single strategy for the control of interfacial chemistry, meaning that advanced understanding of occurring redox processes is needed.
- The transition from developing cell chemistries to designing the complete metal-anode battery is critical, as the manufacture of thin metal foils and the assembly of prototype cells are not straightforward.
- For real applications, the fast-charge requirements (related to electron and ion transport) currently do not favour alternatives to Li or Na anode systems; batteries with anodes made using rather low-cost and abundant materials (Al, Mg, Ca, Na) are suitable for stationary storage systems.

Table 1| Available exemplary metal anode-based cell chemistries and their current stage of development. Abbreviations are as following: 1,2-dimethoxyethane (DME), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), poly(ethylene oxide) (PEO), poly(ethylene glycol) (PEG), poly(acrylonitrile) (PAN), tetrahydrofuran (THF), 1,4-polyanthraquinone (14PAQ), N,N-dimethylformamidium trifluoromethanesulfonate (DOTf).

Cell chemistry	Anode (excess thickness)	Cathode (capacity)	Electrolyte	Operating voltage (average)	Discharge capacity	Stage of development/cell type
$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ || Lithium (ref. [76])	Li metal (20 µm, 4 mAh cm^{-2})	Layered oxide, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (4 mAh cm^{-2})	Ether-based, 1.5 M LiFSI in DME/TTE	3.8 V	160 mAh g^{-1}	Pouch cell prototypes (≈ 2 Ah), 600 cycles
$LiFePO_4$ || Lithium (ref. [74])	Li metal (50 µm, 10 mAh cm^{-2})	Lithium iron phosphate, $LiFePO_4$ (0.6 mAh cm^{-2})	Hybrid, Al-*co*-PEG in PEO	3.3 V	145 mAh g^{-1}	Pouch cell prototypes (≈ 0.5 Ah), 2000 cycles
Sulfur cathode || Lithium alloy (ref. [94])	Li-In alloy	Carbon-Sulfur-Composite cathode, S-C-LPB	Inorganic ceramic Li_3PS_4-2$LiBH_4$ (LPB)	1.6 V	1070 mAh g^{-1}	Moderate stage, 3-electrode cells, 800 cycles
$NaVPO_4$-F || Sodium (ref. [93])	Na metal	Sodium vanadium fluorophosphate, $NaVPO_4$-F (1 mAh cm^{-2})	Composite polymer electrolyte, $Na_3Zr_2Si_2PO_{12}$ in PAN/PEO	3.4 V	100 mAh g^{-1}	Moderate stage, coin cells, 200 cycles
CuS/C ||Calcium (ref. [65])	Ca metal	Copper sulfide composite, CuS/C	$Ca(CB_{11}H_{12})_2$ in DME/THF	1.8 V	140 mAh g^{-1}	Early stage, 3-electrode set-up, 500 cycles
14PAQ || Calcium alloy (ref. [15])	Ca_2Sn (100 µm)	1,4-polyanthraquinone, 14PAQ (1.5 mg cm^{-2})	Borate-based $Ca[B(hfip)_4]_2$ in DME	1.8 V	150 mAh g^{-1}	Early stage, coin cell set-up, 5000 cycles at 1C
VS_4 || Magnesium (ref. [37])	AZ31 Alloy (96 % Mg, 3 % Al, 1 % Zn, 25 µm)	Vanadium sulfide, VS_4 (11.8 mg cm^{-2}, 3.5 mAh g^{-1})	Borate-based $Mg[B(hfip)_4]_2$ in DME	1.1 V	300 mAh g^{-1}	Pouch cell prototypes (≈ 0.7 Ah), 200 cycles
Vanadium oxide || Zinc (ref. [95])	Zn on Cu (3 mAh cm^{-2}, 5 µm)	Zn Vanadium oxide, $Zn_{0.25}V_2O_5 \cdot n\ H_2O$, (1.2 mAh cm^{-2})	$ZnSO_4$ in water + 50 mM DOTf	0.7 V	238 mAh g^{-1}	Early stage, 3-electrode set-up, 1000 cycles
Al_xMnO_2 || Aluminum-Copper alloy (ref. [6])	$Al_{82}Cu_{18}$ alloy (400 µm)	Aluminum manganese oxide, $Al_xMnO_2 \cdot nH_2O$ (1 mg cm^{-2})	2M $Al(OTF)_3$ in water	1.6 V	380 mAh g^{-1}	Early stage, coin cells, 400 cycles

Fig. 1 | Timeline of relevant milestones and steps towards commercial application of rechargeable metal batteries and natural abundance of selected metals. a, Overview of important milestones in the development of rechargeable metal batteries. From left to right: Bolloré Blue Solutions, Zinc intercalation in α-MnO_2[7], Ca intercalation in TiS_2[8,14], QuantumScape’s anode-less battery, Na metal battery start-up LiNa Energy, , AZ31 Mg alloying foils[5], Al-Cu alloy anode for aqueous Al metal batteries[6]. **b**, Natural abundance in million metric tons, based on estimated world reserves and resources of the year 2023. The arrows indicate an inexhaustible amount of reserves and resources for Na, Mg and Ca. The terms in brackets denote the raw materials that the values refer to in the original reference[10]. **c**, Annual world Li production and demand, given in kt of contained Li equivalents (derived from lithium carbonate equivalent, as set out in ref.[12]).

Fig. 2 | Electrochemical characteristics of metal electrodes and interphases in metal batteries. a, Standard reduction potentials (vs. Standard-Hydrogen-Electrode, SHE) of selected metals and their corresponding specific charge capacities (amount of charge storable per unit mass). **b**, The layer thickness combines density and specific capacity to demonstrate spatial (volume) expansion upon deposition of metals with areal charge capacity of 1 mAh cm^{-2}. For example: Electroplating of Li metal at a current density of 1 mA cm^{-2} for 1 h results in a minimum metal layer thickness of 5 µm, assuming a Li density of 0.54 g cm^{-3}. **c**, Visualization of the interfaces and interphases in a metal-based battery (left) and their development before and after continuous charging and discharging cycles (right). The different colors of the solid electrolyte interphase (SEI) constituents represent different inorganic and organic components. Size, shape, and elemental composition depend on individual electrolyte formulations and are kept general here. CEI, cathode electrolyte interphase; CE the Coulombic efficiency; σ_{SEI} the ionic conductivity of the SEI. M, metal; z is an integer (either 1, 2, or 3).

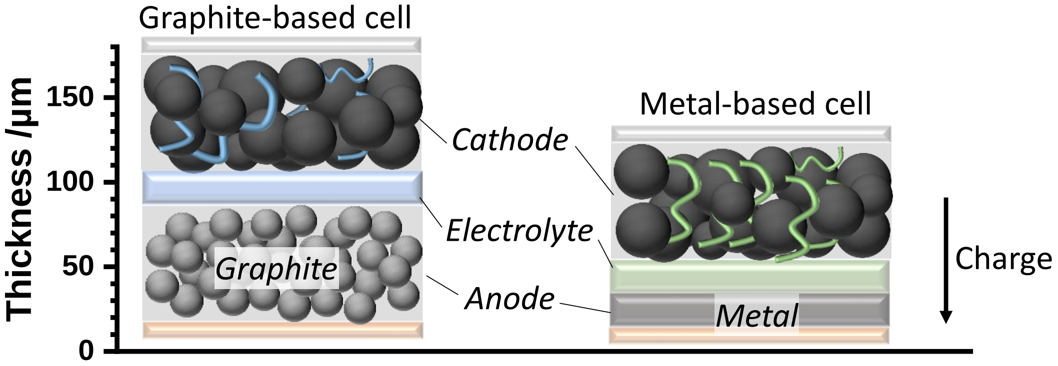
Fig. 3 | Development, performance parameters and ideal life cycle of metal-based batteries. a, Stages for the development of metal-based batteries, with associated technology readiness level (TRL) indicated. An estimated time frame from stage 1 (materials research, TRL1) to stage 5 (application, TRL 8-9) is 7-12 years. **b**, Average operating voltage vs. average specific discharge capacity reported for recently developed cell chemistries (for details see Table 1). **c**, Aspects of circular economy, including research & development, application and recycling.

Box 1: What are batteries?

An electrochemical cell is a device that generates electrical energy from chemical reactions. It consists of two active electrodes separated by an ion-conducting membrane, the electrolyte. The electrode at which electrons are accepted or consumed is the cathode, whilst the electrode at which electrons are liberated or released is the anode (by convention the positive and negative electrode upon discharging, respectively). When the electrolyte is a liquid, an additional porous separator is required between the two electrodes.

A rechargeable battery comprises one or multiple electrochemical cells. It can store and release energy — that is, transform chemical energy into electrical energy (and vice versa) through electrochemical reactions. The amount of storable energy per kilogramme or per litre in an electrochemical cell depends on the difference between the cathode's and the anode's electrode potentials (their tendency to lose or gain electrons) and on their charge capacity, which is expressed per mass or volume unit (in mAh g^{-1} or mAh cm^{-3}). The standard hydrogen electrode (SHE) serves as point of reference (defined redox potential of 0 V) and reflects the reaction of H_2 to H^+ at 298 K, 1 atm and a concentration of 1 M.

With regard to applications and high energy density, electrode materials with high specific and volumetric capacities and large redox potentials, such as metal electrodes (for example, Li metal with 3861 mAh g^{-1} and −3.04 V versus SHE), are favourable compared to conventional graphite-based electrodes (see the figure**,** values for cell thicknesses are motivated from ref. [11]). As metals typically have negative redox potentials versus SHE, they are utilized as anode rather than cathode materials. In practice, high-voltage and high-capacity anodes often lack electrochemical reversibility (that is, the discharge reaction comes with a lower energy than the charge reaction, resulting in limited cell lifetime because of capacity fading) and the ability for fast charge, owing to substantial interfacial changes upon operation and ongoing side reactions with the electrolyte. A robust solid electrolyte interphase should be formed upon the first few cycles (including so-called formation procedures), thus protecting electrodes from side reactions, enabling reversible electrode–electrolyte charge transfer dynamics and pronounced longevity of the cells.



Box 2: Metal production around the globe

Metal resources relevant for rechargeable metal batteries are not evenly distributed across the planet. Central Asia (particularly China), Australia and South America are the regions with the most metal resources and consequently present the highest production of metals and precursors (see the table, graphite is listed for comparison; data calculated from ref. [10]).

As of the end of 2023, China is the leading producer of Na, Mg, Ca, Zn, Pb, Cd and graphite, whereas Australia currently leads production of both Al and Li. Although the distribution of abundant metals (Na, Al, Ca, K, Mg) means that there is not a single global player, the situation is different for production of Li and graphite. With 65 % of the global annual graphite production, China is by far the largest producer of graphite, with implications for dependencies in global manufacturing of batteries. Similarly, Australia and Chile produce 77 % of all Li and thus are immensely relevant for worldwide supplies for the manufacturing of Li-based batteries.

Metal element	Global annual mine production in million metric tons	Main producing countries (Percentage of annual mine production to global mine production)
Na (rock salt)	290	**China** (22 %), India (16 %), USA (15 %)
Al (bauxite)	380	**Australia** (26 %), China (24 %), Guinea (23 %)
K (potash)	40	**Canada** (40 %), China (15 %), Russia (13 %)
Mg (MgO)	27	**China** (63 %), Australia (10%), Turkey (7 %)
Ca (lime)	430	**China** (72 %), USA (4 %), India (4 %)
Zn	13	**China** (32 %), Peru (11 %), Australia (10 %)
Pb	4.5	**China** (44 %), Australia (10 %)
Li	0.13	**Australia** (47 %), Chile (30 %), China (15 %)
Cd	0.024	**China** (42 %), Korea (17 %), Japan (8 %)
Graphite	1.3	**China** (65 %), Mozambique (13 %), Madagascar (8 %)

Box 3: Low-resource considerations

Laboratory-scale cell chemistries can be expensive in both cost and material availability, but low-resource considerations can be brought into materials development. There are three major aspects that should be considered for materials selection: affordability, toxicity and recyclability. Lack of affordability of materials and equipment is an immediate barrier to product development or market entry as well as to economies of scale. In case of accidents or the failure of utilized cells, the environmental impact can be limited if battery components have no, or only negligible, toxicity, including those products released from unintended side reactions due to thermal runaway of the cells. Limited recyclability will have impact on the long-term availability of active materials. Recycling potential and incentives should be considered as early as possible, as material abundance for some parts of a battery is typically limited and production of new materials may be resource-intensive. It will be highly beneficial to utilize abundant precursor materials and to reduce the complexity of material and cell production steps without overly compromising the intended features that govern battery applications.

Online ToC

Efficient storage of electrical energy is mandatory for the effective transition to electric transport. Metal electrodes − characterized by large specific and volumetric capacities − can enable the next generation of high energy density rechargeable batteries. This Review highlights advances and challenges in the field and evaluates future application scenarios.