

Review

Beyond Lithium: Future Battery Technologies for Sustainable Energy Storage

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Abstract: Known for their high energy density, lithium-ion batteries have become ubiquitous in today's technology landscape. However, they face critical challenges in terms of safety, availability, and sustainability. With the increasing global demand for energy, there is a growing need for alternative, efficient, and sustainable energy storage solutions. This is driving research into non-lithium battery systems. This paper presents a comprehensive literature review on recent advancements in non-lithium battery technologies, specifically sodium-ion, potassium-ion, magnesium-ion, aluminium-ion, zinc-ion, and calcium-ion batteries. By consulting recent peer-reviewed articles and reviews, we examine the key electrochemical properties and underlying chemistry of each battery system. Additionally, we evaluate their safety considerations, environmental sustainability, and recyclability. The reviewed literature highlights the promising potential of non-lithium batteries to address the limitations of lithium-ion batteries, likely to facilitate sustainable and scalable energy storage solutions across diverse applications.

Keywords: battery materials; energy storage; sodium-ion batteries; potassium-ion batteries; magnesium-ion batteries; aluminium-ion batteries; zinc-ion batteries; calcium-ion batteries; sustainable energy; recyclability; battery safety; electrochemical energy storage



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1. Introduction

Lithium-ion batteries power our world. Handheld devices, electric vehicles (EVs) and aerospace applications have widely adopted lithium-ion technology [1–3]. With the shift towards renewable energy, lithium-ion energy storage technology is also being integrated into our electrical grid. Although battery energy storage accounts for only 1% of total energy storage, lithium-ion batteries account for 78% of the world's battery energy storage system as of 2021 [4]. Lauded for their high energy density, lithium-ion batteries dominate the battery market.

The field of lithium-based batteries is continually developing. In the 1980s, Goodenough's laboratory predicted that transition metal oxides could reversibly intercalate lithium ions and provide higher operating voltages (~4 V) [5]. In 1991, Sony Corporation commercialised the first lithium-ion battery using LiCoO₂ (LCO) as the cathode material [6]. Since then, the recurrent safety issues related to thermal runaway and fires spurred the development of the lithium iron phosphate (LiFePO₄ or LFP) cathode, which compromised some energy density for added thermal stability [7]. Today, industry continually demands batteries with further reductions in cost and increments in energy density.

Despite this, the supply of lithium, cobalt and nickel—crucial materials for lithium-ion batteries—is becoming increasingly scarce or difficult to obtain. Furthermore, global electricity demands are predicted to rise by 57.1% from the year 2020 (22,536 Tw) to 2040 (35,407 Tw) [8]. Coupled with the push for renewable energy, which tends to be intermittent (e.g., solar and wind energy) [9], there will be a surge in demand for battery energy storage systems [10],

placing unprecedented strain on the availability of critical resources. This would considerably drive up the cost of a lithium-ion battery in the future. Moreover, material improvements are inevitably approaching saturation in lithium-ion batteries [11]. Thus, the future of energy storage may not lie in lithium-ion batteries—alternative battery chemistries need to be explored. Importantly, raw materials used must be more abundant and easier to recycle. Consequently, research efforts have shifted towards developing non-lithium-based alternatives that not only offer comparable energy densities but also address issues of safety and environmental sustainability. Figure 1 illustrates the increasing research efforts into non-lithium metal-ion batteries.

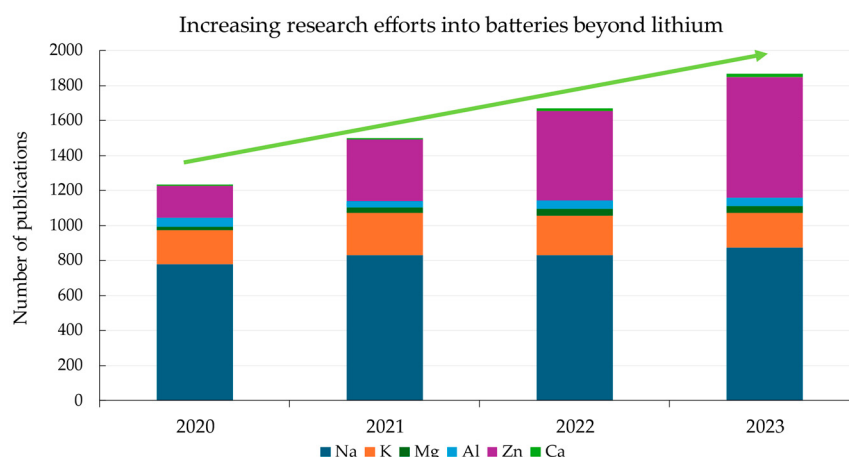


Figure 1. Chart showing the number of papers highlighting non-lithium-ion batteries across the years. Search results were obtained from Web of Science, searching titles with the keywords “X-ion AND batteries”, where X = Na, K, Mg, Al, Zn, Ca.

For a summary of the electrochemical properties of non-lithium batteries as of 2020, the reader is directed to the review article cited here [12]. Since then, there have been developments in this fast-moving field. Beyond electrochemical properties, there is a need to simultaneously consider the safety, sustainability, and recyclability of batteries. Herein, we aim to provide a comprehensive overview of the latest advancements in non-lithium battery technologies, elucidate their strengths and weaknesses, and assess their technological readiness level in different applications. By evaluating these factors, we aim to determine the potential of these alternatives to meet the future demands of energy storage.

2. Approach and Method

This literature review synthesises relevant research articles and reviews on non-lithium batteries for future energy storage. The search focused on recent publications from 2020 onwards to ensure the inclusion of the latest advancements in the field. The academic database “Web of Science” was used with keywords related to non-lithium battery technologies, namely sodium-ion batteries, potassium-ion batteries, magnesium-ion batteries, aluminium-ion batteries, zinc-ion batteries, and calcium-ion batteries. The selected articles were critically evaluated to extract key findings and insights regarding the performance, challenges, and potential applications of non-lithium battery systems. Only peer-reviewed articles that highlighted the electrochemical performance, safety features, environmental sustainability, and recyclability of non-lithium batteries were shortlisted.

Figure 2 provides an overview of the procedure used to gather relevant research articles for review. The procedure to narrow down the pool of shortlisted articles from 2020 onwards is as follows: for each battery system, the most cited papers were included to understand the general research directions in the literature. An equal number of the most recently published papers were included to elucidate how the field has evolved over the years. Noting that sodium-ion batteries have always been a research focus and that zinc-ion batteries are an emerging field based on the number of search results (Figure 1), we decided

to place more emphasis on these fields, dedicating a total of 40 articles to each of these fields. Other more nascent battery systems, namely the potassium-ion, magnesium-ion, aluminium-ion, and calcium-ion batteries, were dedicated the 20 most relevant articles each.

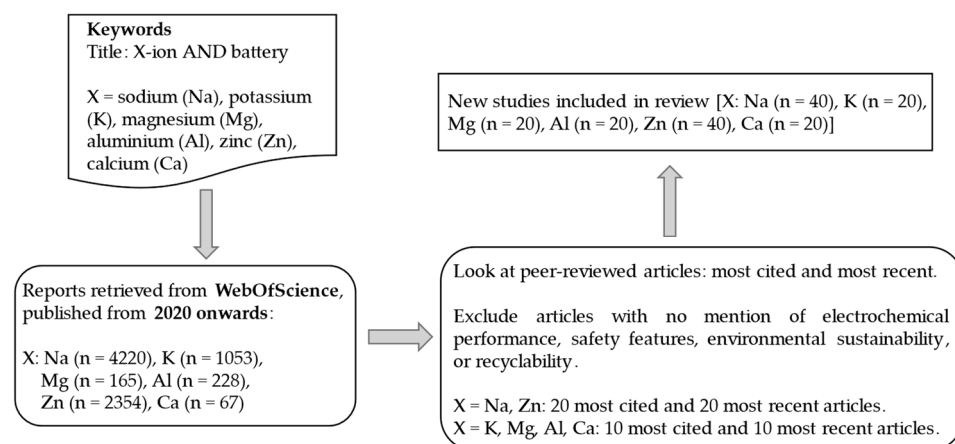


Figure 2. Flowchart outlining the methodology employed in this literature review. Search results are accurate as of September 2024.

Section 3 briefly discusses the principles of the operation of secondary batteries and the key material challenges impacting their rechargeability and cycle life. It also highlights the key strengths and limitations of the most promising lithium-ion batteries available today. Section 4 summarises the key electrochemical properties of the non-lithium battery technologies. Emphasis was placed on the long-term cycling behaviour of the battery, a crucial aspect of secondary batteries. In doing so, we hope to highlight the various promising research directions in the field. Section 5 critically evaluates the current technology readiness levels of the alternative technologies, manufacturing costs, availability of raw materials, environmental impact, and potential safety issues. Comparisons are drawn between the technologies and with the state-of-the-art lithium-ion battery where relevant. Section 6 summarises key takeaways and provides an outlook for the future of non-lithium batteries.

3. Theoretical Considerations of Secondary (Rechargeable) Batteries

3.1. Principles of Operation

During the discharging process into a resistive load, the battery acts as an electrochemical cell with a spontaneous overall reaction, characterised by a positive standard cell potential (E_{cell}):

$$E_{cell} = E_{cathode} - E_{anode} \quad (1)$$

where $E_{cathode}$ and E_{anode} are the standard electrode potentials (with respect to the Standard Hydrogen Electrode) of the cathodic and anodic reactions, respectively.

To recharge the battery, a current in the opposite direction is applied. The battery then acts like an electrolytic cell, eventually recovering the starting materials at both the anode and cathode. Thereafter, another discharge–recharge cycle can commence.

Two technologies are being actively explored. The first is the metal-ion battery (Figure 3a). A metal ion is shuttled from the anode to the cathode during discharge through the electrolyte. In this spontaneous process, electrons are produced, which flow through an external circuit from the anode to the cathode. This electrical energy can be harnessed to do useful work. The reverse process occurs during charging, where an external current is applied. Commonly, a carbon-based anode is employed with different materials incorporating the active metal species as the cathode [13,14].

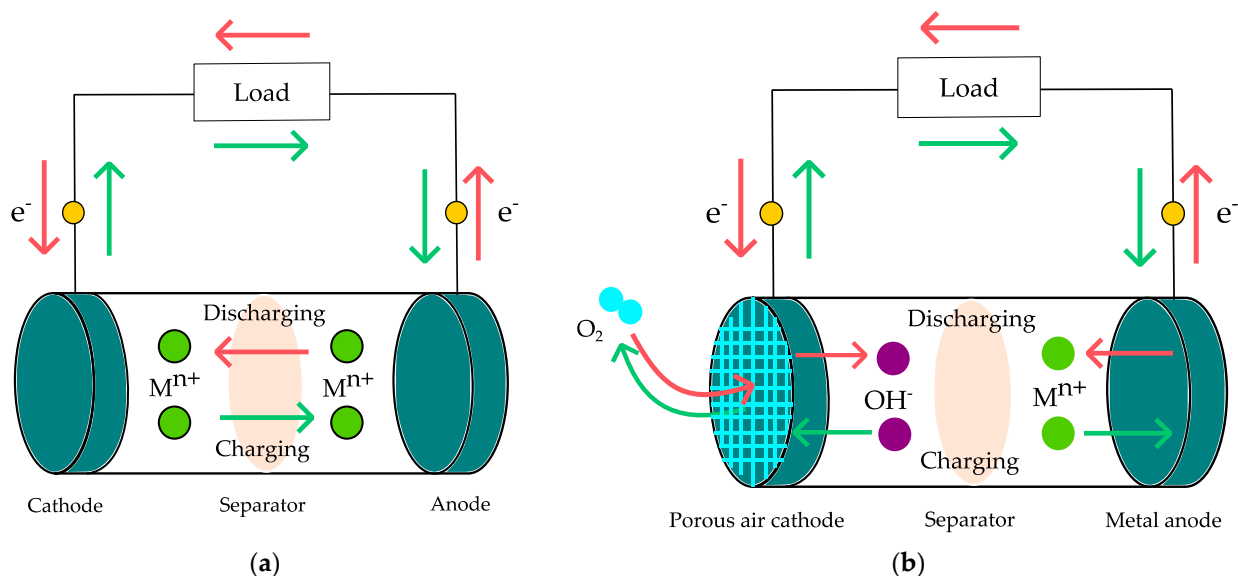


Figure 3. Schematics showcasing the working principle behind the different types of batteries: (a) the metal-ion battery; (b) the metal-air battery (MAB) in an aqueous, alkaline electrolyte.

Metal-air batteries (MABs) have also been explored (Figure 3b). Instead of shuttling ions between electrodes, a porous cathode is used, which allows ambient oxygen to diffuse into the air electrode catalyst, where it is reduced. The pure metal species is commonly used as the anode. To protect the metal from excessive/unwanted corrosion, an alkaline electrolyte is commonly used; however, some research has shown that aluminium-air batteries display a higher activity and lower corrosion rate when a neutral electrolyte is used [15]. This is not entirely surprising as the oxide of Al is amphoteric. Research efforts have been directed towards MABs given the promise of a lighter, greener battery with air as an Earth-abundant active ingredient and a theoretical energy density 3 to 30 times greater than traditional LIBs [16]. Despite this, MABs face significant limitations that prevent their full potential from being harnessed, with their main limiting factor revolving around the air cathode and sluggish oxygen reduction reaction (ORR), together with poor cycling stability of the bifunctional catalyst [16]. We consider metal-air batteries as an emerging field and encourage readers to refer to the review article cited here for more details [17]. Therefore, this review focuses on metal-ion batteries beyond lithium.

While it is chemically possible to construct a reversible electrochemical cell, it is impossible to obtain an infinitely rechargeable battery due to a multitude of material challenges of the different components. A secondary battery typically comprises many components, namely the anode, cathode, electrolyte, separator, and current collector. These components are prone to degradation over time. To obtain an energy capacity of 80% after 1000 cycles, a minimum Coulombic efficiency of 99.98% per cycle is required [18]. As such, research efforts have been directed towards end-of-life solutions for when the battery inevitably fails; for example, the recovery of precious metals from cathodic and anodic black mass [19].

For a battery to be rechargeable and have a sufficiently long cycle life, it is necessary to overcome the practical challenges faced by each component of the battery. The overarching challenges to overcome for an efficient secondary battery are listed in Table 1.

To choose appropriate active elements to construct a secondary battery with, there are a few criteria that should be met. Firstly, the element must not be inherently dangerous, such as a radioactive element. Thereafter, the requirements would depend on the specific application. For everyday applications, like in electric vehicles (EVs) and electronics, the element should generally be lightweight (nearer to the top of the Periodic Table) and have a sufficiently negative standard electrode potential, so that its energy and power density are sufficiently high for the use case. Lithium is theoretically the best element out of those

considered, with the most negative standard electrode potential (Figure 4) and having the lowest density, producing the highest theoretical energy density.

Table 1. Summary of the main problems affecting the rechargeability of secondary batteries.

Challenge	Affected Battery Component(s)	Mechanism of Failure of Battery
Overcharging or discharging below optimal level	Anode, cathode	- Layered structure collapses upon de-intercalation of metal ion - Reduction in capacity upon recharging due to lack of sufficient intercalation sites - Possible side reactions resulting in decreased capacity
Dendritic growth on electrodes	Anode, cathode, separator	- Short circuit of battery if dendrite contacts the opposite electrode - Puncture of separator - Irreversible loss in capacity if dendrites drop off into electrolyte
Passivation	Anode, cathode	- Formation of an insulating oxide layer, decreasing capacity, as the inner metal layer cannot be oxidised during discharging - Decrease in Coulombic efficiency as internal resistance increases
Parasitic side reactions	Anode, cathode, electrolyte	- Production of unknown substances that may be toxic and unsafe - Electrolyte depletion - Irreversible loss of capacity
Phase change of electrode material	Anode, cathode	- Volume change causing structural instability - Change in diffusion mechanism, potentially increasing energy barrier and slowing diffusion - If phase transition is irreversible, capacity decreases
Decomposition of electrolyte	Electrolyte	Change in chemistry of electrochemical cell; the electrochemical reaction becomes no longer spontaneous

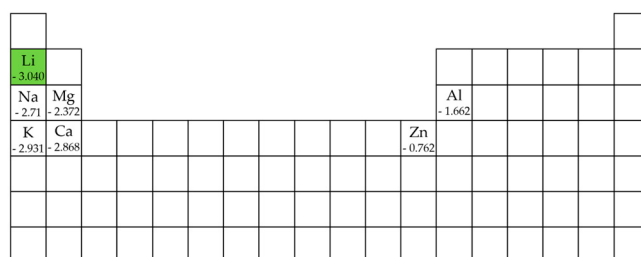


Figure 4. The periodic table with elements of interest as the active species shown. Lithium, the current state-of-the-art, is highlighted in green. Values of the standard electrode potential for the reaction $M^{n+} + ne^- \rightarrow M$, with reference to the standard hydrogen electrode (SHE), are shown below each element and obtained from [20].

3.2. Key Battery Performance Indicators

Before we proceed further, it is important to define the key indicators of battery performance. The virtue of secondary batteries lies in their rechargeability and long-term use; we have thus placed emphasis on indicators highlighting the battery’s long-term cycling behaviour (Table 2).

Table 2. Summary of the key battery performance indicators emphasised in this review.

Performance Indicator	Definition
Initial reversible capacity (mAh g ^{−1})	Charge per unit mass stored by the battery or electrode, after accounting for irreversible losses caused by the formation of the solid–electrolyte interface (SEI).
Capacity retention (%/number of cycles/rate)	Percentage of the initial reversible capacity obtained after a certain number of cycles at a given cycling rate.
Cycle life	Number of charge/discharge cycles for the reversible capacity to fade to 80% of the initial value.
Initial Coulombic efficiency (%)	For cells manufactured in the discharged state, this is the percentage of Coulombic charge produced during discharge ($Q_{discharge}$) to that required to charge the battery (Q_{charge}) in the first cycle. $ICE = 100 \times \frac{Q_{discharge}}{Q_{charge}}$ For cells manufactured in the charged state: $ICE = 100 \times \frac{Q_{charge}}{Q_{discharge}}$

In a battery's lifetime, its first charge/discharge cycle tends to incur the greatest capacity loss, due to the consumption of some active ions to form a stable solid–electrolyte interface (SEI). Therefore, ICE is an important parameter as it determines how many of the active ions are consumed in forming this layer. An ICE close to 100% is ideal, as few active ions are consumed by the SEI. Meanwhile, a low ICE indicates that little charge will be left over for reversible storage. An ICE above 100% is a sign of an unknown parasitic reaction and thus is not desirable. Thereafter, the initial reversible capacity contains the maximum amount of charge that could be reversibly stored and released. Ideally, an infinitely rechargeable battery with no losses would have a capacity retention of 100%. However, the practical challenges mentioned in Table 1 mean that the maximum amount of ions stored at the electrodes would gradually decrease, which decreases the maximum amount of charge released per cycle. Overall, a comparison of the initial reversible capacity and cycle life affords a practical way of comparing the electrochemical performance of two batteries.

3.3. State-of-the-Art: Lithium-Ion Batteries

Lithium is considered the best available chemistry for a battery due to its highly negative electrochemical potential with respect to the standard hydrogen electrode (SHE) of -3.040 V [21]. Furthermore, the low density of lithium as compared with other contenders means that lithium-ion batteries (LIB) have very high energy and power density. As such, the LIB is currently state-of-the-art. Together with its long cycle life, the LIB is a strong candidate in portable applications where a low storage weight is desired, thus being ubiquitous in today's world.

In a typical lithium-ion battery, graphite is used as the anode. It demonstrates the reversible intercalation of the lithium ion, forming LiC_6 , has excellent electronic conductivity, and is inexpensive and lightweight. These properties make graphite an excellent material of choice. Meanwhile, the cathode is often a lithium-containing salt with a layered structure, allowing for the reversible (de-)intercalation into the electrodes. Of these, lithium nickel manganese cobalt oxide (NMC) is projected to have the highest market share of 35% in 2030, followed by lithium iron phosphate (LFP) and lithium nickel cobalt aluminium oxide (NCA), with a combined market share of 40% [22]. Organic carbonates are often used as the electrolyte—they form a stable solid–electrolyte interface for effective long-term cycling. Together, the cost of a lithium-ion battery is about US\$150 kWh^{−1} [23], with high energy densities of more than 250 Wh kg^{−1} [24].

However, there are limitations with regard to the safety of available LIBs. Thermal runaway through excessive overcharge or short-circuiting from dendritic growth on the electrodes results in a dangerous exothermic reaction and the possibility of fire and explo-

sion. Over the years, safety has been improved through the development of the LFP battery with a considerably higher exothermic onset temperature (T_{onset}) of 194 °C to replace the lithium cobalt oxide (LCO) chemistry ($T_{\text{onset}} = 130.9$ °C); a significantly lower maximum temperature T_{max} from thermal runaway was also observed in LFP battery (259.1 °C) as opposed to the LCO battery (714.5 °C) [25]. However, the use of iron in the LFP technology substantially increases battery mass and thus decreases energy density, rendering it inferior in portable applications to other technologies. Moreover, there persists an inherent safety concern in the underlying battery technology, requiring a robust battery management system (BMS) to prevent overcharging.

There are also geopolitical concerns regarding the availability of crucial components for the manufacturing of LIBs. Cobalt supply is scarce and hard to access; over 70% of the global production of cobalt was located in the Democratic Republic of Congo in 2023 [26]. Lithium supply is projected to become scarce with demand growth of 390% from 2013 levels, projected to the year 2035 [27]. This is not to mention that there have historically been ethical issues surrounding the mining of cobalt. These factors drive present-day research efforts to find suitable lithium- and cobalt-free alternatives.

4. Non-Lithium Batteries

4.1. Sodium-Ion Batteries

Sodium-ion batteries (SIBs) have emerged as promising alternatives to LIBs due to the abundance of sodium resources (such as seawater) and their similar chemical properties, being in the same group in the periodic table as lithium. However, sodium is denser than lithium with a larger ionic radius. Together with its less negative standard electrode potential of -2.71 V versus the -3.040 V of lithium (Figure 4), SIBs typically display lower energy density and power density compared to their lithium counterparts, making them less ideal for portable applications.

However, recent research has focused on optimising electrode materials and electrolytes to enhance performance. Studies have shown that SIBs can achieve high energy densities comparable to LIBs while being more environmentally sustainable [28]. Moreover, sodium-based materials are more cost-effective, making them attractive for large-scale energy storage applications. For a recent review of the latest SIB technologies and their technical intricacies, the reader is directed to the 2023 review paper by Singh et al. [29]. However, this review will focus on the electrochemical data regarding capacity, capacity retention, and cycle life, as well as the discussion regarding the recyclability and safety of the technology. Table 3 summarises the electrochemical properties of the full-cell SIBs analysed herein.

Table 3. Summary of the performance indicators of the full-cell SIBs analysed in this review. All values were measured at room temperature.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Na _{1.73} Fe[Fe(CN) ₆]·3.8H ₂ O	Hard carbon (HC)	1 M NaClO ₄ in ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PC)/fluoroethylene carbonate (FEC)	—	78/1000/1C	820 *	99.3 *	[30]
Amorphous FePO ₄ yolk-shell nanospheres	Hierarchical porous carbon fibres	1 M NaClO ₄ in EC/DEC/FEC	146.9/20	81/300/20	>300	85	[31]
P2-Na _{2/3} Ni _{1/3} Mn _{1/3} O ₂	WS _{2-x} /ZnS @ C	1 M NaPF ₆ in diglyme	200 */1000	44.7/500/1000	40 *	88 *	[32]
Na _{0.612} K _{0.056} MnO ₂	Pre-sodiated HC	1 M NaPF ₆ in PC/FEC	230.6/50	80/60/50	60 *	50 *	[33]

Table 3. Cont.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ^{−1} /mA g ^{−1} or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
High-entropy Na ₃ V _{1.9} (Ca,Mg,Al,Cr,Mn) _{0.1} (PO ₄) ₂ F ₃	HC	3.04 M NaPF ₆ in DEG/DME/1,3-dioxolane	111 */1C	90.7/300/1C	>300	96.2 *	[34]
P2-Na _{0.85} Li _{0.12} Ni _{0.22} Mn _{0.66} O ₂	HC	1M NaClO ₄ in EC/PC/FEC	286 */0.2C	85.6/100/0.2C	>100	86.5 *	[35]
NaNMC	HC	1.5 M sodium bis(fluorosulfonyl)imide in dimethyl carbonate (DMC) and tris (2,2,2-trifluoroethyl) Phosphate	153 */0.2C	94.8/300/0.2C	>300	84.49	[36]
Na ₃ V ₂ (PO ₄) ₃	Dual-phase MoS ₂	1 M NaCF ₃ SO ₃ in diglyme	210/500	77.1 */100/500	89 *	84.5 *	[37]
Na ₃ V ₂ (PO ₄) ₃	FeSe ₂ @ NC (nitrogen-doped carbon) microrods	1 M NaCF ₃ SO ₃ in diglyme	292 */500	87.7 */150/500	>500	—	[38]
Na ₃ V ₂ (PO ₄) ₃	Fe _{x−1} Se _x /MXene/FCR hybrid aerogel	1 M NaClO ₄ in EC/DMC	315/100	82.1 */400/100	>400	96.5 *	[39]
Cubic Na _x MnFe(CN) ₆	TiO ₂	1 M NaPF ₆ in PC/FEC	95.8 */100	67.1 */100/200	17 *	76.3	[40]
Na ₂ MnFe(CN) ₆	NaTi ₂ (PO ₄) ₃	2 mol kg ^{−1} sodium tri-fluoromethanesulfonate (aq)	25.4 */1C	94.9/200/1C	>200	83.4 *	[41]
O3-Na _{0.95} Li _{0.06} Ni _{0.25} Cu _{0.05} Fe _{0.15} Mn _{0.49} O ₂	Na metal	Polyvinylidene fluoride hexafluoropropylene-based gel as polymer solid electrolyte	92.1/5C	96/400/5C	>400	98.8	[42]
Na ₃ V ₂ (PO ₄) ₃ /C	Manganese-doped copper sulfide three-dimensional (3D) hollow flower-like sphere	1 M NaPF ₆ in diglyme	457/100	78.3/100/100	89 *	92.5	[43]
Na ₃ V ₂ (PO ₄) ₃	Sb/Sb ₂ O ₃ nanoparticles embedded in N-doped porous carbon	1 M NaPF ₆ in DMC/EC/FEC	113 */1C	86.8/100/1C	>100	87.1	[44]
Na ₃ V ₂ (PO ₄) ₃	Carbon-encapsulated MnSe-FeSe nanorods	NaPF ₆ in dimethyl ether (DME)	226 */1000	110 */900/1000	>900	—	[45]
Na ₃ V _{1.7} (GaCrAlFeIn) _{0.06} (PO ₄) ₃	HC	1 M NaClO ₄ in EC/diethyl carbonate (DEC)/FEC	114 */1C	94.2 */300/1C	>300	98.1 *	[46]
Na ₃ V _{1.83} Co _{0.15} Mo _{0.02} (PO ₄) ₃	HC	1M NaClO ₄ in EC/DEC/FEC	163/0.1C	69.8 */50/0.1C	10 *	99.3	[47]
NaNi _{1/3} Fe _{1/3} Mn _{1/3} O ₂	MoO ₂ /MoS ₂ @NC-15	1M NaClO ₄ in EC/DEC/FEC	427 */100	77.5/20/100	11 *	70.1 *	[48]
O3-Na[FeCoNiTi] _{1/6} Mn _{1/4} Zn _{1/12} O ₂	HC	1M NaClO ₄ in DME	112 */30	79/50/30	45 *	76.3 *	[49]
Na ₃ V ₂ (PO ₄) ₃	Na _{0.23} TiO ₂ particles coated on a nitrogen-doped carbon sphere with resorcinol	1M NaClO ₄ in EC/PC	229 */100	72.4 */100/100	57 *	57.4 *	[50]
Na ₃ V _{1.8} (CrMnFeZnAl) _{0.2} (PO ₄) ₃	HC	1M NaPF ₆ in PC/FEC	99.5 */5C	88.9 */550/5C	>550	98.5 *	[51]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

It is common practice for batteries to be pre-cycled to achieve stable cycling. In a rocking-chair battery (Figure 3a), there is typically an irreversible loss in capacity due to the initial formation of the solid–electrolyte interface (SEI). Where an abnormally large drop has been observed in the first few cycles, the initial reversible capacity was taken to be the first stable capacity, usually after one to three cycles.

Most recent research efforts emphasise the development of new electrode materials for SIBs. Although it is tempting to borrow the same electrode materials from their LIB counterpart, SIBs are, in fact, not analogous to LIBs; the main difference between the two systems is the larger ionic diameter of sodium (1.06 Å) versus lithium (0.67 Å). This not only reduces its ionic diffusivity [53] but also causes structural distortion to the active electrode material during intercalation through phase changes or structural pulverisation [54,55]. This effect is more pronounced for a larger number of charge/discharge cycles, which is detrimental to the recyclability of SIBs. Therefore, great emphasis is placed on developing new electrode materials that could provide good specific capacities and rapid ion diffusion kinetics.

To combat such structural instability of the electrode materials upon battery cycling, electrode materials involving heterostructures have been explored. Generally, these hierarchical materials facilitate better electron transfer and ionic diffusion, improving the rate capability of SIBs. Some also incorporate a porous structure with sufficient space to accommodate the larger sodium ions, alleviating the problems surrounding significant volume expansion upon sodium-ion intercalation. For example, nanomaterials such as yolk-shell nanospheres, hollow nanorods, and nanosheets were explored with generally improved cycling stability and rate capability [31,39,45,48,50,56–58]. However, the presence of pores within the structure increases the volume of the battery, thereby decreasing its volumetric energy density. To counteract this issue, Yang et al. have developed a method to tune the void volume within the Bi-C yolk-shell nanosphere, maximising its volumetric energy density and power density; this allows for a very fast rate of charge and discharge of 6.2 s [59].

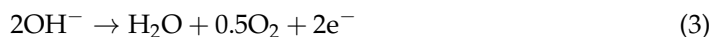
To improve the safety and environmental sustainability of SIBs, Liu et al. explored the use of an aqueous electrolyte for SIBs [41]. Unlike traditional organic electrolytes, aqueous electrolytes are non-flammable and are less likely to cause fires or explosions—pertinent problems surrounding LIBs today. However, for the aqueous electrolyte to be practically feasible with competitive electrochemical properties, practical issues must first be addressed. Electrochemically, water molecules decompose to form oxygen at the anode and hydrogen at the cathode. The uncontrolled evolution of these gases, especially hydrogen, could pose safety risks like the possibility of explosion due to pressure build-up. Usually, this means a smaller electrochemical window for aqueous electrolytes (1.23 V for H₂O) [60]. However, by engineering a composite of NaX zeolite (general formula (NaAlO₂)_x(SiO₂)_y·mH₂O [61]) and NaOH-neutralised Nafion to act as a molecular sieve, Liu et al. expanded the electrochemical window to 2.70 V by selectively allowing the dehydrated sodium ion to be in contact with the electrodes.

Below are the relevant reactions involving the reduction and oxidation of water at the anode and cathode, respectively, all occurring in an alkaline medium.

Hydrogen evolution reaction (HER):



Oxygen evolution reaction (OER):



Looking to further improve the inherent safety of SIBs, solid-state SIBs have been explored by Cai et al. [42]. Improving upon the use of aqueous electrolytes, the risk of electrolyte leakage causing short circuits and fires is mostly eliminated. Furthermore, dendritic growth on the electrodes is suppressed, minimising the risk of internal short-circuiting and thermal runaway. However, there seems to be a compromise between the

safety and electrochemical performance of the battery, since a comparatively low initial reversible capacity of 92.1 mAh g^{-1} was achieved at a 5C rate. This trade-off between battery safety and energy density has been empirically observed in LIBs, where a lower proportion of battery-related accidents was caused by the safer and less energy-dense LFP cathode (compared to NMC) [62]. To achieve a safe yet high-energy-density battery is a fundamental challenge to be tackled.

4.1.1. Cathode Materials

Cathodes free of expensive and scarce cobalt have been developed. Unlike LIBs, the SIB cathode does not rely solely on cobalt to improve its structural and electrochemical properties [63]. Instead, the role of cobalt can be replaced by non-critical metals like Mg, Al, and Ti.

Like in LIBs, SIBs usually employ layered oxides incorporating the active sodium ions, which undergo repeated intercalation and de-intercalation upon discharging and recharging. Among these are O3-phase and P2-phase layered oxides, corresponding to the octahedral and prismatic interstitial sites in which the sodium ion sits (Figure 5).

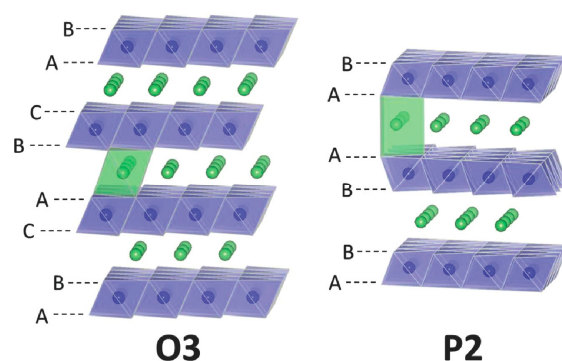


Figure 5. Structural model for the O3- and P2-type layered transition metal oxides. The blue and green spheres represent, respectively, the transition metals and sodium ions. The different oxygen stacking sequences (each distinct layer is denoted by a letter “A”, “B”, or “C”) generate either octahedral or trigonal prismatic Na coordination, accordingly. Reproduced from Ref. [64] with permission from the Wiley Online Library.

While potentially similar in terms of their composition, these two phases offer different electrochemical properties as cathode materials. The larger interlayer distance of P2-type oxides as compared to O3-type oxides suggests that the corresponding transition state of P2-type sodium-ion diffusion is slightly more stable. Katcho et al. [65] investigated using density functional theory (DFT) calculations that for a material with the same composition, O3-type diffusion involves a higher activation energy (monovacancy: 866 meV, divacancy: 201 meV) than P2-type diffusion (127 meV). In return, O3-type materials can store more sodium due to the higher number of octahedral sites, potentially meaning a higher capacity [66]. These two competing effects make the choice between O3 and P2-phase cathode materials not easy to make (Table 4).

Table 4. Summary of the performance indicators of cathode materials in analysed SIBs; only half cells with sodium metal as the counter electrode were included. The measured values are with respect to Na^+/Na at room temperature.

Cathode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Rhombohedral $\text{Na}_{1.73}\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 3.8\text{H}_2\text{O}$	1 M NaClO_4 in EC/DEC/PC/FEC	97.3 */100	71/500/100	240 *	97.4	[30]
Cubic $\text{Na}_{1.53}\text{Fe}[\text{Fe}(\text{CN})_6] \cdot 4.2\text{H}_2\text{O}$	1 M NaClO_4 in EC/DEC/PC/FEC	104 */100	66/200/100	110 *	120	
Amorphous $\text{Na}_{0.9}\text{FePO}_4$ yolk-shell nanospheres	1 M NaClO_4 in EC/DEC/FEC	145.1/20	91.3/1000/100	>1000	86.1 *	[31]
$\text{Na}_{0.612}\text{K}_{0.056}\text{MnO}_2$	1 M NaPF_6 in PC/FEC	240.5/50	98.2/100/50	>100	54.8 *	[33]
$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3\text{@C}$	1 M NaClO_4 in PC/FEC	108 */0.5C	86.5 */200/0.5C	>200	—	[67]
Pristine $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$	1 M NaClO_4 in PC/FEC	86.1 */0.5C	85.2 */200/0.5C	>200	—	
High-entropy $\text{Na}_3\text{V}_{1.9}(\text{Ca,Mg,Al,Cr,Mn})_{0.1}(\text{PO}_4)_2\text{F}_3$	1 M NaClO_4 in PC/FEC	113 */0.5C	90.2/400/0.5C	>400	91.2 *	[34]
		94.6 */20C	80.4/2000/20C	>2000	85.8 *	
P2- $\text{Na}_{0.85}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$	1 M NaClO_4 in EC/PC/FEC	94.7/5C	85.4/500/5C	>500	99.6 *	[35]
(NASICON)-type $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$	1 M NaClO_4 in PC/FEC	54.6 */5C	86.5/600/5C	>600	80.9 *	[68]
Cubic $\text{Na}_x\text{MnFe}(\text{CN})_6$	1 M NaPF_6 in PC/FEC	120/200	70/500/200	110 *	97.8 *	[40]
O_3 - $\text{Na}_{0.95}\text{Li}_{0.06}\text{Ni}_{0.25}\text{Cu}_{0.05}\text{Fe}_{0.15}\text{Mn}_{0.49}\text{O}_2$	1 M NaClO_4 in PC/FEC	111.4/8C	83.2/500/8C	>500	87.6 *	[42]
		85.8/20C	85.1/1000/20C	>1000	74.5 *	
$\text{Na}(\text{Ni}_{2/9}\text{Fe}_{1/3}\text{Cu}_{1/9}\text{Mn}_{1/3})_{0.98}\text{Mn}_{0.02}\text{O}_2$	1 M NaPF_6 in PC/FEC	133.3/1C	71.4/300/1C	134 *	—	[69]
High-entropy $\text{Na}_3\text{V}_{1.7}(\text{GaCrAlFeIn})_{0.06}(\text{PO}_4)_3$	1 M NaClO_4 in EC/DEC/FEC	109/30C	90.97/5000/30C	>5000	98.2 *	[46]
P2- $\text{Na}_{0.55}\text{Ni}_{0.1}\text{Co}_{0.1}\text{Mn}_{0.8}\text{O}_2$	1 M NaClO_4 in EC/DEC/FEC	120 */100	78.4/200/100	183 *	~ 100 *	[70]
$\text{Na}_3\text{V}_{1.83}\text{Co}_{0.15}\text{Mo}_{0.02}(\text{PO}_4)_3$	1 M NaClO_4 in EC/DEC/FEC	96.3/5C	77.2 */1200/5C	889 *	99.6 *	[47]
		93.8/10C	68.1 */1500/10C	752 *	94.7 *	
		90.7/50C	75.5/2000/50C	592 *	99.2 *	
$\text{Na}_{3.4}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{Cr}(\text{PO}_4)_3/\text{C}$	1 M NaPF_6 in PC/FEC	81.0/10C	91.0/500/10C	>500	—	[71]
$\text{Na}_2\text{FePO}_4\text{F}$ (15% PEG-coated)	1 M NaPF_6 in PC/FEC	85/ $\frac{\text{C}}{15}$	81.1/50/ $\frac{\text{C}}{15}$	>50	—	[72]
$\text{Na}_4\text{P}_2\text{O}_7$ decorated $\text{Na}_4\text{MnV}(\text{PO}_4)_3/\text{C}$ composite	1 M NaClO_4 in EC/DMC/ethyl methyl carbonate (EMC)/FEC	105.4/0.1C	89.4/50/0.1C	>50	—	[73]
		93/5C	93.2/100/5C	>100	—	
High-entropy O_3 - $\text{Na}[\text{FeCoNiTi}]_{1/6}\text{Mn}_{1/4}\text{Zn}_{1/12}\text{O}_2$	1 M NaClO_4 in DME	127.3/0.1C	80/100/0.1C	100	83.0	[49]
$\text{Na}_3\text{V}_{1.8}(\text{CrMnFeZnAl})_{0.2}(\text{PO}_4)_3$	1 M NaPF_6 in PC/FEC	119.8/1C	86.8 */450/1C	>450	92.4 *	[51]
		102 */10C	78.5 */3000/10C	1770 *	90.2 *	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

It is noted that the tested cathode in a half cell (Table 4) usually performs better than its corresponding full cell (Table 3), both in terms of its initial capacity and cycle life. This is due to the limited sodium reserve in the full cell, which is consumed irreversibly at the anode to form the SEI during the first few cycles, whereas there is an infinite supply of sodium in the half cell using the Na^+/Na counter electrode [74]. Additionally, it is beneficial that the same reference electrode is used (sodium metal), because it provides a basis for direct comparison across different works. However, sodium metal cannot be used as the anode for real applications due to safety concerns. Not only is sodium metal extremely reactive to moisture, but it also supports dendritic growth upon repeated charge/discharge cycles, potentially leading to internal short circuits and thermal runaway.

It is also observed that cycling the battery at a higher C-rate, or current density, leads to poorer long-term performance. The initial discharge capacity is lowered, which indicates a decreased energy density, all else kept equal. This phenomenon is due to an increased

charge-transfer resistance at higher rates, leading to a higher overpotential and decreasing the amount of metal ions transferred to the anode in the initial charge cycle [75]. Electronic conductivity in the external metal wire is much greater than the ionic mobility within the electrolyte; the rate of transfer of ions becomes diffusion-limited at a higher current density, causing a reversible loss in capacity [1].

Despite this, a higher rate of charge enables fast charging, and a higher rate of discharge is essential in high-power applications. As such, efforts have been made to increase the rate capability of SIBs. To this end, sodium (Na) super ionic conductor (NASICON)-type cathodes have been explored. This class of materials can facilitate fast sodium-ion transport, owing to the low activation energy for sodium-ion diffusion through the interstitial sites, importantly in all three dimensions (Figure 6) (0.0904 eV, 0.11774 eV, 2.438 eV) [76]. $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) is a promising NASICON-type cathode candidate with a high theoretical specific energy due to the three-electron redox reaction ($\text{V}^{2+} \rightleftharpoons \text{V}^{5+}$). However, NVP still suffers from poor electronic conductivity and structural stability. Several approaches have been taken to improve NVP as a cathode material. Gu et al. [34], and later Zeng et al. [49], Zhou et al. [51], and Ding et al. [46], have synthesised high-entropy NVP (HE-NVP) analogues incorporating five or more transition and non-transition metals. The high configurational entropy serves to stabilise the crystal structure, allowing for reversible phase transitions upon cycling and thus better cycling stability [77]. Moreover, doping NVP with multiple metallic elements has been shown to decrease its bandgap, facilitating easier electron excitation from the valence to the conduction band [78]. Indeed, it is observed that the cycle life of HE-NVP analogues is in the thousands and rate capability is generally excellent (Table 4), highlighting the benefits of the high-entropy approach.

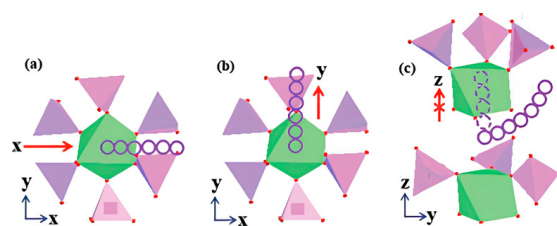


Figure 6. Schematic showing the three-dimensional (3D) sodium-ion transport channels in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, along the (a) x, (b) y, and (c) curved z directions. The purple tetrahedron represents a PO_4 unit while the green octahedron represents a VO_6 interlink. In the middle of each octahedron is one Na^+ ion. Reproduced from Ref. [79] with permission from the Royal Society of Chemistry.

Other strategies were adopted to optimise NASICON-type cathodes. Zhang et al. [68] first reported a new NASICON-type $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ cathode with a promising energy density of 566.5 Wh kg^{-1} but faced a problem regarding the moderate volume change of 7.7% during cycling. Later, Chen et al. [71] improved upon the electrochemical properties of this cathode by substituting a fraction (30%) of the Mn^{2+} with Ti^{4+} , suppressing structural changes and improving charge transfer at the electrode–electrolyte interface. Notably, they found that the modified cathode displayed a significantly higher capacity retention than the unmodified cathode for the same C-rate (91.0% vs. 54.8% at 10C). This is not to mention that a higher initial discharge capacity was obtained after the modification (81.0 mAh g^{-1} vs. $\sim 50 \text{ mAh g}^{-1}$). Ti^{4+} ions are known to withstand the local distortion caused by the Jahn–Teller effect (Figure 7), a disadvantage of cathodes incorporating Mn^{3+} ions (with the high-spin d^4 electronic configuration) [80], allowing the modified electrode to display superior cycling stability. Meanwhile, Zhang et al. [47] co-doped NVP with Co^{2+} and Mo^{6+} . They work synergistically—the Co^{2+} ions provide structural support and increase interplanar spacing to facilitate better ionic diffusivity, while Mo^{6+} ions maintain charge balance and provide n-type doping effects, boosting electronic conductivity.

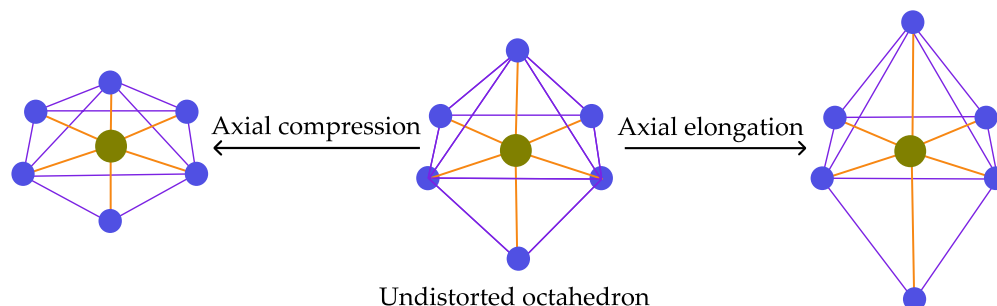


Figure 7. Schematic showing the Jahn–Teller distortion for high-spin d^4 species in octahedral sites. The green spheres represent high-spin Mn^{3+} or Cr^{2+} (with the d^4 electronic configuration) in a six-fold octahedral coordination with O^{2-} ions in blue.

Prussian Blue Analogues (PBAs) form another family of candidates for SIB cathode material. Both Tang et al. [40] and Wang et al. [30] have reported PBAs that show repeated cycling stability, albeit by different mechanisms; Tang et al. managed to stabilise the cubic phase of the PBA, $Na_xMnFe(CN)_6$, throughout the charge and discharge, while Wang et al. showed that $Na_{2-x}FeFe(CN)_6$ could undergo highly reversible phase transformations.

4.1.2. Anode Materials

In LIBs, graphite is the default material used for the anode. It is affordable and lithium shows good intercalative affinity with it. However, graphite is not effective at intercalating sodium ions. This is because the interplanar spacing of graphite (3.35 Å) is lower than that required for effective Na^+ intercalation (3.7 Å), as evidenced by theoretical calculations and experimental observations [81]. The larger ionic radius of sodium is unable to intercalate into the smaller interstitial sites in graphite. Meanwhile, hard carbon (HC) has a larger interplanar spacing of 3.7 Å to 4 Å and facilitates multiple ion storage mechanisms. Based on intercalation and pore-filling mechanisms, HC delivers an excellent theoretical capacity of $>530 \text{ mAh g}^{-1}$ [82]. As a result, HC has become a default anode material, replacing the usual graphite anode used in LIBs.

However, HC has its drawbacks. Due to its complex structure, there is still dispute over the mechanism of sodium-ion storage in HC [83]. This renders rational material design difficult, although recent experimental efforts have confirmed a few ion storage mechanisms and improved the initial Coulombic efficiency (ICE) of HC [84]. The intrinsic structure of HC plays a pivotal role in determining the electrochemical performance of the battery. Nonetheless, practical applications have capacities rather far from the theoretical limit (Table 3).

Heteroatom doping into carbon frameworks is a well-known strategy to improve the rate capability and performance of the battery. In particular, covalent heteroatoms (N, S, P) can enhance the electrical conductivity and porosity of the electrode, as well as introduce defects that increase electrode capacity [85]. With reference to Table 5, Zhao et al. [86] synthesised S-doped carbon nanosheets, which afforded excellent capacity retention of 94% at a current density of 5 A g^{-1} after 2000 cycles. However, the initial reversible capacity seems to be below average for the same current density, at 228 mAh g^{-1} . Jin et al. [87] used a N and S co-doping strategy, which was shown to synergistically improve battery performance. Again, capacity retention was excellent at 110% after 2000 cycles at 1 A g^{-1} . It is difficult to make a fair comparison between the two systems at different current densities.

Table 5. Summary of the performance indicators of anode materials in analysed SIBs; only half cells with sodium metal as the counter electrode were included. The measured values are with respect to Na^+/Na at room temperature.

Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Sb ₂ S@FeS ₂ /N-doped graphene	1 M NaCF ₃ SO ₃ in diethylene glycol (DEG)/DME	534.8/5000	85.7/1000/5000	>1000	82.4	[57]
WS _{2-x} /ZnS @ C	1 M NaPF ₆ in diglyme	303 */5000	57.1 */5000/5000	100 *	65.4 *	[32]
Nb ₂ CT _x @MoS ₂ @C	1 M NaClO ₄ in EC/DEC/FEC	600 */100	78.1 */200/100	125 *	53.8 *	[88]
		510 */1000	74.1 */2000/1000	920 *	97.3 *	
		349 */20,000	55.6 */1000/20,000	495 *	92.7 *	
Carbon particles doped with N and S	1 M NaClO ₄ in EC/DEC/FEC	203 */1000	110 */2000/1000	>2000	—	[87]
Dual-phase MoS ₂	1 M NaCF ₃ SO ₃ in diglyme	279 */500	109 */200/500	>200	~100 *	[37]
		181 */2000	140 */500/2000	>500	77.0 *	
MoSe ₂ /MXene	1 M NaClO ₄ in PC/EC/FEC	493 */1000	87.6 */200/1000	>200	70.3 *	[89]
		398 */2000	69.5 */400/2000	170 *	81.2 *	
3D scaffolding framework of carbon nanosheets heavily doped with sulphur	1 M NaClO ₄ in EC/DEC/FEC	228 */5000	94/2000/5000	>2000	58	[86]
FeSe ₂ @NC microrods	1 M NaCF ₃ SO ₃ in diglyme	443 */5000	91.4 */2000/5000	>2000	~100 *	[38]
MoS ₂ /SnS hollow superassembly	NaClO ₄ in PC/FEC	600 */500	85.8 */150/500	>150	—	[56]
Fe _{x-1} Se _x /MXene/FCR hybrid aerogels	1 M NaClO ₄ in EC/DMC	781 */100	77.5 */100/100	65 *	52.4	[39]
		436 */10,000	79.6 */2000/10,000	1920 *	—	
Bi@Void@C-2 nanosphere	1 M NaPF ₆ in DME	252 */1000	~100 */500/1000	>500	46	[59]
		236 */20,000	95.3 */10,000/20,000	>10,000	75.8 *	
Manganese-doped copper sulfide 3D hollow flower-like sphere	1 M NaPF ₆ in DME	673 */100	~100 */100/100	>100	~100 *	[43]
		605 */2000	99.2 */1000/2000	>1000	80.9 *	
		600 */10,000	83.8 */10,000/10,000	>10,000	88.4 *	
Sb/Sb ₂ O ₃ nanoparticles embedded in N-doped porous carbon	1 M NaPF ₆ in DMC/EC/FEC	340.3/1000	86.7/1000/1000	>1000	97.3 *	[44]
MnSe-FeSe@C nanorods	NaPF ₆ in DME	550 */1000	81.4 */700/1000	>700	77.3 *	[45]
CoSe ₂ /Sb ₂ Se ₃ @C@CNF	1 M NaClO ₄ in EC/DEC/FEC	310 */1000	97/2000/1000	>2000	47.9 *	[58]
		223 */5000	103/12,000/5000	>12,000	50.2 *	
MoO ₂ /MoS ₂ @NC-15	1 M NaClO ₄ in EC/DEC/FEC	550 */100	63.6 */50/100	11 *	—	[48]
3D vertical graphene composite (from waste tyres)	1 M NaClO ₄ in EC/DMC/EMC/FEC	320 */200	78.9 */100/200	18 *	32.3 *	[90]
		130 */1000	103 */1900/1000	>1900	85.5 *	
OHC-1400 (pre-treated bamboo waste)	1 M NaPF ₆ in EC/DMC	280/0.1C	101 */100/0.1C	>100	68.9 *	[91]
Na _{0.23} TiO ₂ particles coated on a nitrogen-doped carbon sphere with resorcinol	1 M NaClO ₄ in EC/PC	213 */100	91.4 */300/100	>300	40.9 *	[50]
		132 */1000	86.3 */2000/1000	>2000	—	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Most recent articles try to improve upon covalent atom doping by introducing metallic atoms. Cao et al. [43] encapsulated Mn-doped CuS spheres with the N and S co-doped carbon. The doping of Mn was shown to increase the electronic state density at the Fermi level through DFT, which explains why battery performance is improved with Mn doping. Importantly, the hollow structure developed through Ostwald ripening promotes sodium-ion diffusion while simultaneously mitigating volume changes during cycling. The introduction of this Mn-doped framework produced similarly excellent capacity retention, but capacity was noticeably higher ($\sim 600 \text{ mAh g}^{-1}$ vs. 203 mAh g^{-1}) (Table 5).

Transition metal chalcogenides (TMCs) are a promising class of materials for the anodes of SIBs. These are ionic compounds where the anion is a chalcogen anion (e.g., S^{2-} , Se^{2-}), which is paired with a transition metal cation. Specifically, transition metal dichalcogenides (TMDs) with large interplanar spacings, which could account for volume fluctuation during cycling, were identified as an area of research interest [92]. Indeed, numerous such works were identified in this review. Of these, $\text{FeSe}_2@\text{C}$ microrods by Pan et al. [38] showed promise, as high cycling stability was demonstrated with 91.4% capacity retention after 2000 cycles at 5 A g^{-1} . It must be noted that the dual-phase (1T trigonal + 2H hexagonal) MoS_2 synthesised by Wu et al. [37] showed a gradual capacity increase after 200 and 500 cycles at 0.5 A g^{-1} and 2 A g^{-1} , respectively, although longer cycling performance was not determined. Recently, Li et al. [58] demonstrated that an ultra-long cycle life was possible with $\text{CoSe}_2/\text{Sb}_2\text{Se}_3$ nanocrystals embedded into a nanocage-in-nanofiber carbon framework. Admittedly, synthesising such an intricate heterostructure is complicated. Nonetheless, 12,000 charge/discharge cycles were carried out at 5 A g^{-1} with no capacity attenuation. This work shows the promise of bi-metal selenide heterostructures for use as an SIB anode material.

To promote environmental sustainability, Leng et al. [91] and Zhou et al. [90] have upcycled waste materials (bamboo waste and waste tyres, respectively) to produce hard carbon anodes. As a proof of concept, they have demonstrated their use as anodes in half-cell SIBs. Interestingly, at a current density of 1 A g^{-1} , the waste tyre-derived anode showed an initial decrease in reversible capacity to $\sim 68\%$ of its initial reversible capacity after about 30 cycles, followed by a steady increase. As such, it has a cycle life of >1900 cycles. However, to obtain satisfactory electrochemical performance, a combination of chemical treatments and high-temperature pyrolysis ($>1000^\circ\text{C}$) were used, suggesting that the eco-friendliness of the resulting anode may be overstated. While the upcycling of waste material to valuable electrode material is an emerging field, this nonetheless shows the promising potential of non-lithium batteries to be more environmentally friendly than LIBs in future.

4.1.3. Electrolyte

The role of the electrolyte is crucial in facilitating ion transport and intercalation, preventing undesirable side reactions, and producing a stable solid–electrolyte interface (SEI). An unstable SEI is detrimental to long-term cycling stability; the SEI commonly incorporates the active metal ion in salt form, so the repeated formation of the SEI will result in capacity fade [93].

In this review, most SIBs either employed organic carbonate-based electrolytes commonly with fluoroethyl carbonate (FEC) as an additive or ether-based electrolytes. The chemistry of the formation of the SEI with FEC is rather complex; we encourage readers to read this article for more information [94]. FEC addition is crucial in forming a stable SEI in carbonate systems. Meanwhile, in cells with HC as an anode, research has shown that ether-based electrolytes were shown to exhibit better long-term cycling stability compared to traditional carbonate-based electrolytes [82]. Zeng et al. [49] showed that both 1,2-dimethoxyethane and carbonate-based EC: PC mixture showed similar long-term cycling performance at 25°C , but the ether-based electrolyte was significantly better at -20°C .

Out of the extracted data, little innovation of the electrolyte was observed. Possibly, the existing carbonate and ether electrolytes were sufficiently good choices and more room

for improvement could be derived from electrode development. Notably, Jin et al. [36] developed an electrolyte system that displays low solubility towards the SEI, thus exhibiting >90% capacity retention over 300 cycles using the classic HC | NaNMC full cell at high voltage (4.2 V). Through rationally choosing a solvent with an adequately low dielectric constant, there was minimal dissolution of the SEI, while sodium ions still exhibited good ionic conductivity.

4.2. Potassium-Ion Batteries

Although less popular than the LIB and SIB, potassium-ion batteries (PIBs) are another class of beyond-lithium batteries currently being researched. Potassium is inexpensive and widely abundant, being the 7th most abundant element in the Earth's crust [95]. With the standard electrode potential (Figure 3) of potassium (−2.931 V) being more negative than sodium (−2.71 V), PIBs tend to have higher theoretical operating voltages than SIBs, potentially translating to higher-energy-density batteries.

As K belongs in the same group as Na and Li, the same class of materials can potentially be borrowed from the more mature LIBs and SIBs to be used in PIBs. Despite this, the markedly bigger ionic radius of potassium (138 pm) compared to sodium (102 pm) means that the extent of volume expansion upon the intercalation of K^+ ions into electrodes is more severe [96] and will require more attention. However, the larger radius of K^+ also implies a smaller charge density compared to Na^+ , indicative of a weaker solvent shell. The result of ab initio molecular dynamics simulations is consistent with this theory. In ethylene carbonate, a common electrolyte used in monovalent metal-ion batteries, solvation energies of 4.12, 4.76, and 5.85 eV for K^+ , Na^+ , and Li^+ , respectively, were obtained [97]. Since the de-solvation of ions is a crucial step in their intercalation into electrodes, PIBs have great potential to display excellent rate capability.

Aqueous electrolytes are not commonly employed in PIBs. The limited electrochemical stability window (ESW) of water produces flammable hydrogen gas through the hydrogen evolution reaction (HER). Further, parasitic side reactions tend to occur, causing structural degradation of the electrode and poorer cycling stability [98]. Instead, carbonate or ether-based electrolytes are commonly employed in PIBs. Therefore, research efforts are commonly geared towards developing improved electrode materials to accommodate the larger K^+ ions (Table 6).

Table 6. Summary of the performance indicators of the full-cell PIBs analysed in this review. Unless otherwise stated, glass fibres were used as separators. All values were measured at room temperature.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g^{-1} /mA g^{-1} or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
$K_{1.82}Mn[Fe(CN)_6]_{0.96} \cdot 0.47H_2O$	3,4,9,10-perylenetetracarboxylic diimide (PTCDI)	0.2 M $Fe(CF_3SO_3)_3$ in 21 M KCF_3SO_3 (aq)	68.8 */1500	82.5/6500/1500	>6500	~100	[99]
Potassium Prussian blue (KPB)	N/O dual-doped hard carbon	0.8 M KPF_6 in EC/DEC	255.8/100	52.3/100/100	15 *	53.2 *	[100]
Perylenetetracarboxylic Dianhydride (PTCDA)	3D N-doped turbostratic carbon	0.8 M KPF_6 in EC/DEC	316 */200	76.4 */100/200	77 *	97.8 *	[101]
$KFeC_2O_4F$	Soft carbon (SC)	1 M KPF_6 in PC/EC	77.7 */100	~100/200/100	>200	100 *	[102]
PTCDA	Graphite	3:8 potassium bis(fluorosulfonyl)imide: trimethyl phosphate (KFSI:TMP)	111.3 */20	72.6 */200/20	9 *	72.2 *	[103]
KMgHCF nanoplates	Dipotassium terephthalate	3 M KFSI in TEP	73.4/100	86.1/1000/100	>1000	93.1 *	[104]
KMgHCF nanoplates	Graphite	3 M KFSI in TEP	65.6/100	90.1/1000/100	>1000	95 *	

Table 6. Cont.

Cathode	Anode	Electrolyte	Initial Reversible Capacity ($\text{mAh g}^{-1}/\text{mA g}^{-1}$ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
PTCDA	Amorphous iron oxide/ $(\text{BiO})_2\text{CO}_3$ composite on reduced graphene oxide (rGO)	5 M KFSI in DEG/DME	203 */80	56.2 */115/80	42 *	99.8 *	[105]
PTCDA	Acid-treated graphite	3 M KFSI in EC/DEC	99.7/0.5C	82.6/25/0.5C	>25 *	79.8 *	[106]
PTCDA	FeSe_2 nanorods within a ketjenblack carbon matrix	1 M KFSI in EC/DEC	120 */100	89.2 */200/100	>200	36.5 *	[107]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Two novel electrolyte systems were designed to tackle the problems plaguing carbonate-based electrolytes: (1) the poor cycling stability of PIB electrodes and (2) the inherent safety risk regarding their volatility and flammability. Ge et al. [99] enhanced the viability of Mn-based Prussian Blue Analogues (PBAs) as long-term stable cathode materials by inhibiting capacity fade due to the dissolution of Mn compounds by electrolyte corrosion and the Jahn–Teller effect [108]. An outstanding cycle life of >6500 was obtained. The proposed mechanism is as follows: Mn primarily dissolves into the electrolyte during charging; the $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ additive allows for Fe^{3+} substitution into Mn vacancies during discharge, restoring active sites for K^+ intercalation (Figure 8a). Meanwhile, Liu et al. [103] achieved a stable cycling performance for a graphite anode using a KFSI/TMP electrolyte. Although the full-cell performance was not ideal, the graphite half-cell could run for 2 years with a capacity retention of 74%, owing to the stable F-rich SEI formed on the graphite (Figure 8b). Moreover, TMP is known to reduce the risk of thermal runaway, further contributing to safety [109].

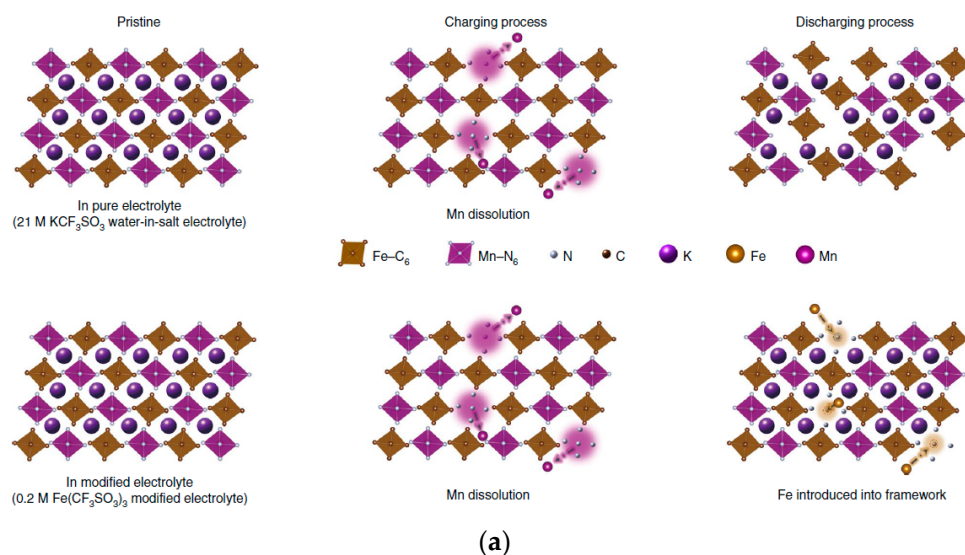


Figure 8. Cont.

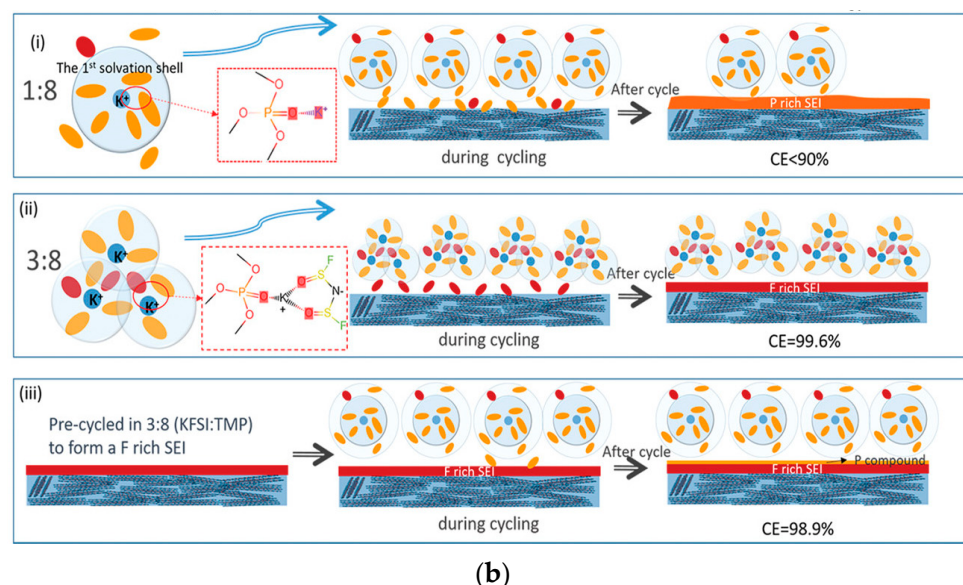


Figure 8. Two innovative electrolytes to improve the electrochemical performance of PIBs: (a) schematic of the surface-modification strategy for mitigating structural instability due to Mn dissolution in the KMnF electrode. Reproduced from Ref. [99] with permission from Springer Nature. (b) Schematic illustrations of the solvation structure and SEI formation on graphite in 1:8 (KFSI:TMP) electrolyte (i) and 3:8 (KFSI:TMP) electrolyte (ii), respectively. (iii) the schematic illustration shows a pre-cycled graphite electrode with an F-rich interface cycling in 1:8 (KFSI:TMP) electrolyte. (The orange and red symbols represent the TMP solvent molecule and the FSI[−] anion, respectively). Reproduced from Ref. [103] with permission from the Wiley Online Library.

Across the full-cell PIBs, perylenetetracarboxylic dianhydride (PTCDA) is commonly used as the cathode material, which is compatible with common organic electrolytes. PTCDA is an organic molecule that can accommodate two K^+ ions in the voltage range of 1.5–3.5 V versus K/K^+ , exhibiting a high capacity of 131 mAh g^{-1} at a current density of 50 mA g^{-1} and a capacity retention of 66% after 200 cycles [110]. When discharged to even lower potentials, a maximum of 11 K^+ ions per PTCDA molecule was obtained, allowing it to display a very high capacity (Figure 9).

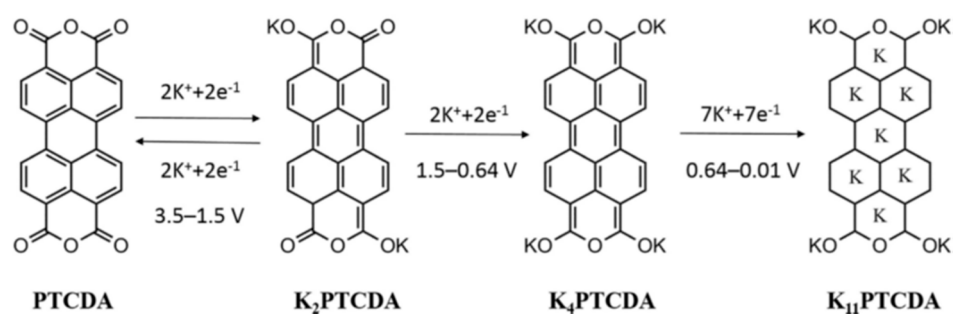


Figure 9. Schematic for the proposed electrochemical reaction mechanism of PTCDA in KIBs during the discharge/charge process. Reprinted from Ref. [110], copyright (2024) Elsevier, with permission from Elsevier.

When PTCDA was paired with 3D nitrogen-doped turbostratic carbon as the anode, Zhang et al. [101] achieved a high full-cell capacity of $>300 \text{ mAh g}^{-1}$ at a current density of 200 mA g^{-1} . Both edge-nitrogen doping and carbon vacancies produce larger interstitial sites to accommodate more K^+ ions, enhancing capacity. Meanwhile, when PTCDA was paired with $FeSe_2$ nanorods in a ketjenblack (KB) matrix, Chen et al. [107] noted that the resulting full cell displayed great stability, with a capacity retention of $\sim 90\%$ after 200 cycles

at 100 mA g^{−1}. Not only did the KB carbon improve electrical conductivity, but it also provided a structural framework to alleviate the volume expansion of FeSe₂ nanorods during K⁺ insertion, maintaining stability over many cycles.

4.2.1. Anode Materials

Interestingly, although the graphite anode used in LIBs cannot support the intercalation of Na⁺ ions, K⁺ has been shown to intercalate into graphite [111–113]. Considering that K⁺ is larger than Na⁺, the intuitive concept of interlayer spacing is insufficient to explain the underlying intercalation mechanism. Through theoretical calculations, it was found that for Group 1 alkali metals, only NaC₆ has a positive enthalpy of formation [111]. However, it is LiC₆ that is the exception—the ionic character of the metal–carbon bond increases down the group as the difference in electronegativity increases, resulting in more exothermic enthalpies of formation For LiC₆, and there is a non-negligible covalent bond character which allows it to exist stably. Due to the wide abundance, low cost, and chemical inertness of carbon, carbonaceous materials are the focus of PIB anode research, including graphitic carbon, soft carbon, and hard carbon (Table 7).

Table 7. Summary of the performance indicators of anode materials in analysed PIBs; only half cells with potassium metal as the counter electrode were included. The measured values are with respect to K⁺/K, at room temperature.

Anode	Electrolyte	Initial Reversible Capacity (mAh g ^{−1} /mA g ^{−1} or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
N-doped 3D mesoporous carbon nanosheet	0.7 M KPF ₆ in EC/DEC	449 */2000	79.7 */700/2000	~700	63.4 *	[114]
		329 */5000	109 */5500/5000	>5500	72.2 *	
Pitch-derived soft carbon	0.8 M KPF ₆ in EC/DEC	296 */0.1C	93.2/50/0.1C	>50	—	[115]
		92.9 */1C	93.1/1000/1C	>1000	65	
PDDA-NPCN (N-rich porous carbon nanosheets)/Ti ₃ C ₂	0.8 M KPF ₆ in EC/DEC	584/100	61.4/300/100	19 *	73 *	[116]
		487 */1000	51.7 */2000/1000	22 *	66 *	
		389 */2000	40.3 */2000/2000	22 *	—	
S-doped N-rich carbon	0.8 M KPF ₆ in EC/DEC	188/2000	75/3000/2000	198 *	94.3 *	[117]
N/O dual-doped hard carbon	0.8 M KPF ₆ in EC/DEC	398.2/100	76.1 */100/100	24 *	40.8	[100]
		335 */1000	56.4 */5000/1000	226 *	73.6 *	
3D N-doped turbostratic carbon	0.8 M KPF ₆ in EC/DEC	288 */1000	93.1/500/1000	>500	83.6 *	[101]
N/S dual-doped graphitic hollow architectures (NSG)	0.8 M KPF ₆ in EC/DEC	111 */5000	90.2/5000/5000	>5000	56 *	[118]
Graphite	3:8 KFSI:TMP	274 */0.2C	74/2000/0.2C	894 *	57.8 *	[103]
Layered KTiNbO ₅ /rGO nanocomposite	1 M KFSI in EC/DEC	128.1/20	76.1/500/20	58 *	53.4 *	[119]
SnP ₃ —CNT/KB (ketjenblack)	1 M KFSI in EC/DEC	223 */1000	87.8 */200/1000	>200 *	64.05	[120]
As ₂ S ₃ @CNT	2 M KFSI in TEP	253/500	94/1000/500	>1000	—	[121]
Ca _{0.5} Ti ₂ (PO ₄) ₃ submicron cubes embedded in carbon nanofibers	1 M KFSI in EC/PC	148 */1000	83 */1000/1000	>1000 *	87.2 *	[122]
Amorphous iron oxide/(BiO) ₂ CO ₃ composite on rGO	5 M KFSI in DEG/DME	388 */100	~100 */1550/100	>1550	67.1 *	[105] ¹
Acid-treated graphite	3 M KFSI in EC/DEC	193 */200	114 */100/200	>100	61.9 *	[106]
FeSe ₂ nanorods within a ketjenblack carbon matrix	1 M KFSI in EC/DEC	501 */100	96.9 */100/100	>100	88.8 *	[107]
		357 */1000	80.7 */3500/1000	>3500 *	—	
MoS ₂ /rGO	1 M KFSI in EMC	272.49/500	98.9/100/500	>100	—	[123]
		128 */1000	85.5 */500/1000	>500 *	—	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52]. ¹ The anode was left to rest for 3 weeks on the ~716th cycle before resuming normal cycling.

Jeong et al. [106] used acid and alkali treatments to functionalise the surface of graphite, as well as to introduce some defects to promote K^+ intercalation. When used in a half cell, the acid-treated graphite showed higher capacity than the alkali-treated and pristine analogues, with great cycling stability (negligible capacity fade over 100 cycles at 200 mA g^{-1}). Cyclic voltammetry (CV) tests revealed a primarily diffusion-controlled process—this is consistent with the surface $-C=O$ functionalisation of the acid-treated graphite, which attracts the positively-charged K^+ ion and facilitates fast ion transport.

Reduced graphene oxide (rGO) is another prominent anode material for PIBs, which is often used in composites with non-carbon-based materials. Often, ceramics with open channels and interstitial sites can accommodate K^+ ions well but are limited by their electrical conductivity. rGO synergises with these compounds to improve the electrical conductivity of the anode, improving rate performance [124]. An outstanding electrochemical performance was observed by Wang et al. [105], who synthesised $(\text{BiO})_2\text{CO}_3$ nanocrystals crystallographically aligned with amorphous Fe_2O_3 supported on rGO. Even upon resting for 3 weeks in the middle of charge/discharge cycling, the half cell maintained an impressive capacity of $>350 \text{ mAh g}^{-1}$ at 100 mA g^{-1} with negligible capacity fade. Although the synthesis of nanocomposites often involves multiple intricate steps, this research paves the way for future developments of related materials for PIB anodes.

Nitrogen-doping is a method to introduce appropriately sized pores within the graphene layer to host the larger K^+ ions. This is believed to improve the capacity of the carbonaceous material. Huang et al. [114] introduced a very high level of pyridinic and pyrrolic N into carbon nanosheets, accommodating the volume changes during potassiation and de-potassiation (Figure 10a). This allowed for an extremely stable cycling performance with no capacity fade for 5500 cycles at a high current density of 5 A g^{-1} . Moreover, a high initial capacity of $\sim 330 \text{ mAh g}^{-1}$ was also obtained. Doping carbonaceous materials with two heteroatoms have also been explored, where Lu et al. [118] synthesised nitrogen/sulphur dual-doped graphitic hollow architectures (NSG) in a single step, which maintained excellent capacity retention of $\sim 90\%$ after 5000 cycles at 5 A g^{-1} (Figure 10b).

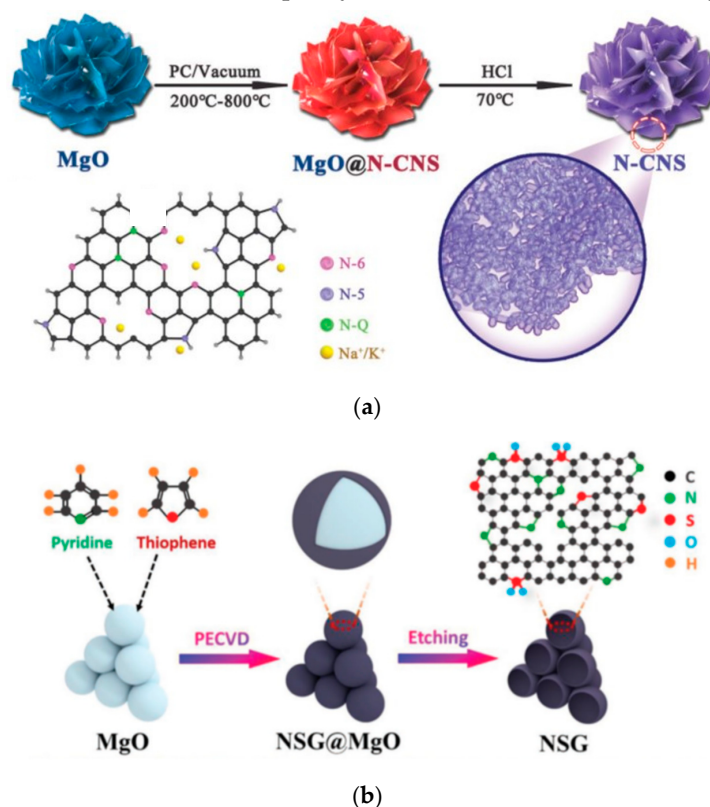


Figure 10. Heteroatom doping of graphene layers to promote long-term cycling stability of graphitic materials: (a) the structure of N-doped carbon nanosheets with pyridinic N (N-5), pyrrolic N (N-6),

and graphitic N (N-Q) defects. Reproduced from Ref. [114] with permission from the Wiley Online Library. (b) The structure of N/S dual-doped carbon. Reproduced from Ref. [118] with permission from the Wiley Online Library.

In an effort to develop scalable and sustainable manufacturing methods for anode materials, Cui et al. [100] proposed carbonising the piths of sorghum stalks to produce N/O dual-doped hard carbon with relatively high capacity. Besides being environmentally friendly, the low cost of raw materials and relatively easy synthesis also make such methods attractive.

4.2.2. Cathode Materials

Like in SIBs, the cathode material of PIBs contains the active metal ion; the corresponding full cell is assembled in the discharged state. Besides the organic compound PTCDA, other classes of materials were synthesised as cathode materials—layered oxide, polyanionic compound, and PBAs (Table 8).

Table 8. Summary of the performance indicators of cathode materials in analysed PIBs; only half cells with potassium metal as the counter electrode were included. The measured values are with respect to K^+/K , at room temperature.

Cathode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
K _{1.82} Mn[Fe(CN) ₆] _{0.96} ·0.47H ₂ O	0.2M Fe(CF ₃ SO ₃) ₃ in 21M KCF ₃ SO ₃ (aq)	114 */2500	107 */130,000/2500	>130,000	89.2 *	[99]
KFeC ₂ O ₄ F	1M KPF ₆ in PC/EC	97.3 */200	107 */2000/200	>2000	70.9 *	[102]
KMgHCF/C nanoplates	3M KFSI in TEP	61.3 */500	84.0/15,000/500	>15,000	98.5 *	[104]
LiF/Li _x PF _y O _z -coated K _{0.27} MnO ₂ ·0.54H ₂ O microspheres	0.8M KPF ₆ in EC/DEC	100.2/50	66.3/100/50	28 *	—	[125]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

PBAs (general formula A_xM[Fe(CN)₆]_{1-y}·nH₂O, where y represents the number of [Fe(CN)₆] vacancies per formula unit) show great promise as PIB cathode materials due to their open ionic channels and large interstitial sites [126]. However, a 2020 review of PIBs [127] evaluated one major challenge of PBAs to be the presence of interstitial water content, which could be released, resulting in unwanted side reactions, worse electrochemical properties, and possible safety concerns. To this end, Liao et al. [104] synthesised (100) face-oriented potassium magnesium hexacyanoferrate (KMgHCF) nanoplates, which had fewer such vacancies where the water of crystallisation tends to reside, through a combination of a low precipitation rate and annealing at 550 °C. As such, KMgHCF displayed an excellent capacity retention of 84.0% after 15,000 cycles at 500 mA g⁻¹. PBAs incorporating M = Mn also show great promise as PIB cathode materials. Synergistically combining them with an Fe-based electrolyte additive, Ge et al. [99] obtained an ultralong cycling life of >130,000 at a relatively high current density of 2500 mA g⁻¹. These studies highlight the promise of rationally designed PBAs.

Being inspired by PBAs, a fluoroxalate compound KFeC₂O₄F was synthesised by Ji et al. [102]. This compound has similarly open channels for K⁺ ionic transport, facilitating good rate performance. The stable cycling performance (~100% after 2000 cycles at 200 mA g⁻¹) suggests that such fluoroxalate compounds show promise as cathode materials. Moreover, the optimisation of the electrolyte and anode in the full cell remains to be explored and can bring about further improvements in capacity.

4.3. Zinc-Ion Batteries

Zinc-ion batteries (ZIBs) have gained attention as promising candidates for future energy storage (Figure 1). Despite its markedly less negative standard electrode potential of -0.762 V compared to lithium (Figure 4), zinc is abundant, relatively inexpensive, and inherently safer than alkali metals. Moreover, ZIBs offer the advantage of utilising environmentally friendly and recyclable materials, apt for next-generation sustainable energy storage solutions.

While lithium is a monovalent alkali metal, zinc is a divalent metal exhibiting an oxidation state of +2. Thus, the oxidation of one Zn atom at the anode produces two electrons which are driven around the external circuit to do work, as opposed to only one electron per Li atom:



This suggests that ZIBs may be more suitable for high-power applications. With these advantages, current research efforts have focused on developing high-performance electrode materials and stable electrolytes to overcome critical challenges related to zinc dendrite formation and poor electrochemical performance (Table 9).

Table 9. Summary of the performance indicators of full-cell ZIBs analysed in this review. Unless otherwise stated, glass fibres were used as separators and an aqueous electrolyte was used. All values were measured at room temperature.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
α -MnO ₂	MXene-coated Zn foil	2 M ZnSO ₄ /0.2M MnSO ₄	252.8/1000	81/500/1000	>500	100 *	[128]
α -MnO ₂	3D porous Zn	2 M ZnSO ₄ /0.1M MnSO ₄ /0.05 mM TBA ₂ SO ₄	223 */1000	94/300/1000	>300	99.0 *	[129]
δ -MnO ₂	Ultrathin, fluorinated two-dimensional porous covalent organic framework (FCOF) film @Zn	2 M ZnSO ₄	133 */3C	73.1 */3C	800 *	97.5 *	[130]
MnO ₂ nanowire	Metal–organic framework (MOF)-modified Zn	2 M ZnSO ₄ /0.1 M MnSO ₄	237 */0.1C	81.2 */100/0.1C	>100 *	94.2 *	[131]
			60 */1C	83.3 */5000/1C	>5000 *	87.7 *	
LiMn ₂ O ₄ (LMO)	Zn-metal anode with ultrathin N-doped graphene oxide (NGO@Zn)	1 M ZnSO ₄ + 2 M Li ₂ SO ₄	124 */1C	78.3 */180/1C	63 *	92 *	[132]
δ -MnO ₂	Al ₂ O ₃ @Zn	3 M Zn(SO ₃ CF ₃) ₂ /0.1 M Mn(SO ₃ CF ₃) ₂	177/3.33C	89.4/1000/3.33C	>1000	—	[133]
			304.9 */0.33C	74.3 */200/0.33C	140 *	99.5 *	
Montmorillonite (MMT)-MnO ₂	MMT-coated Zn foil	2 M ZnSO ₄ /0.1 M MnSO ₄	210/2C	91.2/1100/2C	>1100	98.1 *	[134]
I ₂ /activated carbon (AC)	Zn@ZnS	2 M ZnSO ₄ /0.1 M MnSO ₄	106 */1000	62.3 */900/1000	270 *	92.3 *	[135]
α -MnO ₂	Zn@ZnS	2 M ZnSO ₄ /0.1 M MnSO ₄	172 */500	75.2 */1200/500	893 *	100 *	
NH ₄ V ₄ O ₁₀	ZnSiO ₃ nanosheet @Zn	2 M ZnSO ₄	253/1000	38.7/1000/1000	312 *	99.9 *	[136]
α -MnO ₂	Zn coated with MOF-74	Weakly acidic ZnSO ₄	202 */200	79.5 */1000/200	871 *	97.9 *	[137]
α -MnO ₂	Zn foil coated with activated peanut red skin-derived carbon	2 M ZnSO ₄ /0.1 M MnSO ₄	108 */1000	56.7/1000/1000	377 *	96.5 *	[138]
Na-doped VO ₂	Zn coated with sodium carboxymethyl cellulose in hydrogel	1 M ZnSO ₄	145 */500	82.3 */1500/500	>1500 *	105 *	[139]

Table 9. Cont.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Amorphous V ₂ O ₅ in carbon framework	Zn foil	3 M Zn(CF ₃ SO ₃) ₂	271 */40,000	91.4/20,000/40,000	>20,000	96.8 *	[140]
Mn _{0.15} V ₂ O ₅ ·nH ₂ O	Zn	1 M Zn(ClO ₄) ₂ in PC	98.6 */10,000	155 */8000/10,000	>8000 *	92.2 *	[141]
CaVO nanoribbons	Zn foil	4 M Zn(CF ₃ SO ₃) ₂	107 */10,000	161 */10,000/10,000	>10,000 *	90.1 *	[142]
MoS ₂ /graphene nanocomposite	Zn foil	3 M Zn(CF ₃ SO ₃) ₂	224 */1000	88.2/1800/1000	>1800 *	91.4 *	[143]
Poly(3,4-ethylenedioxythiophene) (PEDOT) intercalated into NH ₄ V ₄ O ₁₀	Zn foil	3 M Zn(CF ₃ SO ₃) ₂	104 */10,000	154 */5000/10,000	>5000 *	92.8 *	[144]
Carbon-coated MnO	Zn foil	2 M ZnSO ₄ /0.1M MnSO ₄	117.2/1000	99.3/1500/1000	>1500	66.7 *	[145]
Sulphur heterocyclic quinone dibenzo[b,i]thianthrene-5,7,12,14-tetraone (DTT)	Zn foil	2 M ZnSO ₄	94.3 */2000	83.8/23,000/2000	>23,000	82.8 *	[146]
Proton-intercalated MnO ₂ (H-MnO _{2-x})	Zn foil	2 M ZnSO ₄ /0.1M MnSO ₄	281 */1000	86.6 */160/1000	>160 *	—	[147]
			127.5/3000	73.2 */960/3000	547 *	—	
[C ₆ H ₆ N(CH ₃) ₃] _{1.08} V ₈ O ₂₀ ·0.06H ₂ O	Zn	3 M Zn(CF ₃ SO ₃) ₂	329/4000	87/2000/4000	>2000	100 *	[148]
δ-K _{0.25} MnO ₂ nanospheres	Zn foil	2 M ZnSO ₄ /0.1 M MnSO ₄	258 */1000	69.4 */500/1000	242 *	94.2 *	[149]
			194 */3000	64.8 */1000/3000	488 *	99.5 *	
Cu _{0.05} K _{0.11} Mn _{0.84} O ₂ ·0.54H ₂ O	Zn foil	2 M Zn(CF ₃ SO ₃) ₂ /0.2 M MnSO ₄	113.4/1000	75.1/1000/1000	807 *	111 *	[150]
			270 */100	207 */100/100	>100 *	95.4 *	
Cu@Cu ₃₁ S ₁₆	Zn foil	2 M ZnSO ₄	288 */500	97/2000/500	>2000	99.5 *	[151]
BiOI@MWCNTs (N-doped multi-walled CNTs)	Zn foil	2 M Zn(CF ₃ SO ₃) ₂	231 */2000	68.1 */600/2000	22 *	88.5 *	[152]
Na ⁺ and PO ₄ ³⁻ co-embedded layered V ₂ O ₅	Zn foil	2 M Zn(CF ₃ SO ₃) ₂	255.3/4000	100/2000/4000	>2000	100 *	[153]
V ₂ O ₃ /VO ₂ @NC@GO nanosheets	Zn	2 M Zn(CF ₃ SO ₃) ₂	429 */5000	87.9 */1000/5000	>1000 *	100 *	[154]
V ₂ O ₅ with CNTs	Zn powder	Polyacrylamide hydrogel containing EG	0.53 * mAh cm ⁻² /0.4 mA	77.4 */500/0.4 mA	440 *	100 *	[155]
PEDOT-MnO ₂	Zn foil	0.3 M Zn(CF ₃ SO ₃) ₂ in DMSO/10% H ₂ O	177.57/100	94.0/50/100	>50	98.93	[156]
V ₂ O ₅ with poly(acrylic acid) (PAA) binder	Zn	3 M Zn(CF ₃ SO ₃) ₂	250/1000	80.8/2500/1000	>2500	101 *	[157]
Laser-modified MnO ₂	Zn sheet	2 M ZnSO ₄ /0.1 M MnSO ₄	233/1000	71.6/1000/1000	740 *	107 *	[158]
V ₂ O ₅	Zn	0.5 M Zn(CF ₃ SO ₃) ₂ /triethyl phosphate (TEP):H ₂ O (1:1)	250/5000	~100/1000/5000	>1000	87.4 *	[159]
Polyaniline/carbon cloth	Zn/carbon cloth	Dual network hydrogel	105 */5000	76.8 */2000/5000	31 *	94.5 *	[160]
Na ₂ V ₆ O ₁₆ ·nH ₂ O	Zn	0.5 m Zn(ClO ₄) ₂ with 18 m NaClO ₄	70 */4000	126 */2000/4000	>2000 *	84.2 *	[161]
NH ₄ V ₄ O ₁₀	Zn	Eutectic Zn(ClO ₄) ₂ ·6H ₂ O-N-methylacetamide	295 */500	51.5 */1000/500	137 *	101 *	[162]
			227 */1000	61.8 */1000/1000	380 *	93 *	

Table 9. Cont.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
NH ₄ V ₄ O ₁₀	Zn	2 M ZnSO ₄ + penta-sodium diethylene-triaminepentaacetic acid salt (1.5 wt% DTPA-Na)	292 */1000	79.4 */600/1000	570 *	103 *	[163]
			200 */3000	64.1 */1200/3000	467 *	93.5 *	
KVOH	Zn	2 M ZnSO ₄ /γ-Valerolactone-3%	304.98/3000	78.7/90/3000	74 *	102 *	[164]
			242 */5000	74.7/1000/5000	900 *	98.2 *	
V ₂ O ₅	Zn	2 M Zn(CF ₃ SO ₃) ₂	88.1 */1000	95.3/800/1000	>800	97.8 *	[165] ¹
MnO ₂ /graphite	Zn	2 M ZnSO ₄ /0.5 M MnSO ₄	80.2 */1000	87.5/1000/1000	>1000	100 *	
α-MnO ₂	Zn foil	2 M ZnSO ₄ /0.1 M MnSO ₄	219 */1000	85/1000/1000	>1000	100 *	[166] ²
Lignin-derived porous carbon/α-MnO ₂	Zn	2 M ZnSO ₄ /0.2 M MnSO ₄	197 */1000	89.2 */1000/1000	>1000 *	—	[167] ³
Activated carbon	Zn	2 M ZnSO ₄	88 */1000	125 */5000/1000	>5000 *	89.8 *	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52]. ¹ Separator: cellulose nanofibers and graphene oxide. ² Separator: glass fibre modified by Zr-based MOF (UiO-66-GF). ³ Separator: cellulose film.

4.3.1. Aqueous Zinc-Ion Batteries

Aqueous zinc-ion batteries (AZIBs) are a prominent research focus in the literature. Unlike reactive Group 1 metals (Li, Na, K) which give a dangerously exothermic reaction with water, zinc metal is stable in water. This allows for metallic zinc to be used as the anode in AZIBs with a high theoretical capacity of 820 mAh g⁻¹ [168]. Furthermore, aqueous systems tend to have lower flammability than the organic electrolytes used in LIBs, promoting better safety.

To prevent the passivation of the zinc anode through the formation of Zn(OH)₂, slightly acidic conditions are favoured (Figure 11). However, there are concerns regarding the corrosion of Zn metal in acidic media. Besides this, dendritic growth onto the Zn metal and the parasitic hydrogen evolution reaction (HER) hampers electrochemical performance [169]. Although excess zinc could be used to compensate for the continuous loss of useable Zn during cycling, the excess weight would result in a suboptimal energy density [168]. Thus, research efforts are commonly geared towards developing a Zn metal coating that serves these vital purposes: (1) to prevent dendritic growth upon cycling and (2) to maximise the Coulombic efficiency, indicating fewer undesirable side reactions like the HER and corrosion of Zn metal.

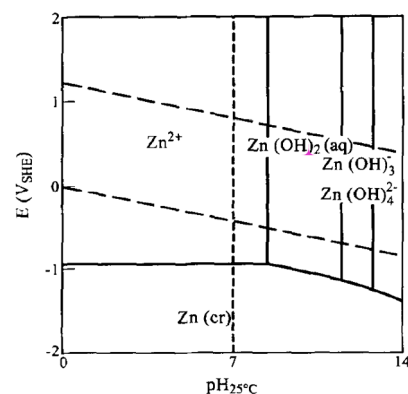


Figure 11. Pourbaix diagram of a Zn/H₂O system at 25 °C. Reprinted from Ref. [170], copyright (2024) Elsevier, with permission from Elsevier.

Yuksel et al. [131] used a wet chemistry method to construct a MOF-based coating directly on the surface of Zn metal. The unique porous structure of the MOF allowed for easy electrolyte infiltration and Zn^{2+} diffusion, suppressing dendritic growth. While a long cycle life (>5000) was indeed observed, the initial reversible discharge capacity was modest, at only 60 mAh g^{-1} at a rate of 1C. The initial Coulombic efficiency was suboptimal at 87.7%, which still suggests that undesirable side reactions may be taking place. Yan et al. [134] engineered a zinc-based montmorillonite (MMT) to be used as both an anode and cathode coating. Its unique negatively charged lamellae serve as a “freeway” for Zn^{2+} transport, ensuring good Zn^{2+} transport even at higher current densities. This is indicated by the superior electrochemical performance of the constructed AZIB even at a higher C-rate of 2C. The enhanced capacity (210 mAh g^{-1} at 2C) of the AZIB was attributed to the greater degree of hydrophobicity of the coated Zn metal, facilitating the de-solvation of Zn^{2+} ions during deposition.

Recently, Liu et al. [139] used sodium carboxymethyl cellulose (CMC) hydrogel as a surface coating for the Zn anode and achieved great long-term cycling stability (cycle life > 1500 at 0.5 A g^{-1}). Interestingly, they suggested that the increased hydrophilicity was instead the reason for the rapid and uniform distribution of Zn^{2+} , reducing the impedance of interfacial electron transfer. These two studies suggest that a balance exists between the hydrophobicity and hydrophilicity of an electrode material (Figure 12). Indeed, experiments and DFT calculations suggest that some degree of hydrophobicity forces the de-solvation of Zn^{2+} at the electrode–electrolyte interface, facilitating bare- Zn^{2+} deposition or intercalation into host lattices, but too hydrophobic a material would lead to sluggish kinetics [171]. These studies show promise that an appropriate optimisation of electrode wettability could show further electrochemical improvements.

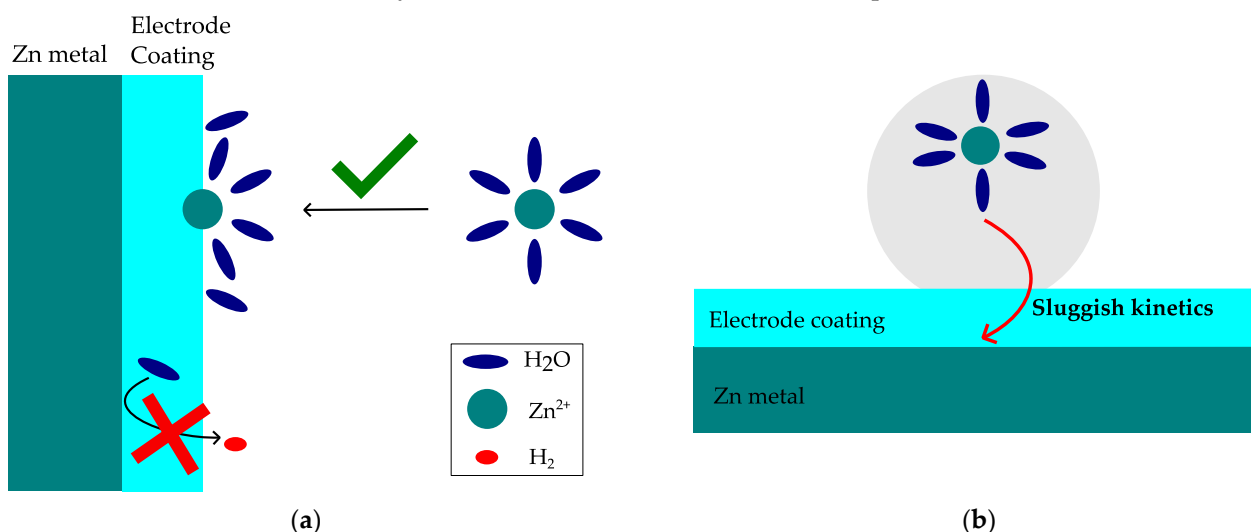


Figure 12. Schematics highlighting the intricate balance needed in the degree of hydrophilicity of an electrode material: (a) some degree of hydrophobicity aids in the de-solvation of Zn^{2+} ions, facilitating the deposition of zinc metal without side reactions, while (b) too much hydrophobicity would lead to sluggish electrochemical kinetics.

The problem of zinc dendrites can also be tackled by improving the separator material. AZIBs commonly use glass fibres as the default separator material. Glass fibre has an innately porous structure, good wettability, excellent ionic conductivity and poor electrical conductivity, while being chemically inert [172]. However, its poor mechanical strength means that puncture by Zn dendrites is a common mode of failure; this is not to mention that the electric field in such AZIBs is likely non-uniform, further encouraging Zn dendrite formation [173]. Thus, research efforts have been put into improving the separator.

To this end, Cao et al. [165] developed a composite of cellulose nanofibers and graphene oxide. Although the long cycle life (>800) is indicative of the stability of the

separator, the initial discharge capacity is rather limited ($\sim 80 \text{ mAh g}^{-1}$ at 1 A g^{-1}). Song et al. [166] improved upon glass-fibre separators by functionalising them with highly tunable MOFs. These separators control the crystallographic orientation of Zn deposits onto the Zn anode upon charging, favouring the formation of horizontal (002) platelets rather than dendrites (Figure 13a). Zhou et al. [167] developed a cotton-derived cellulose film with dense and uniform nanopores, enabling a uniform deposition of zinc. Furthermore, the functionalised hydroxyl (-OH) groups can aid in the de-solvation of Zn^{2+} ions through hydrogen bonding to the water solvent shell, improving capacity and minimising side reactions (Figure 13b). Figure 14 shows the AFM and SEM images of the Zn anode with the standard glass fibre (GF) as compared to the improved cellulose film (CF) separator by Zhou et al. [167], highlighting the important role of the separator in determining plating morphology.

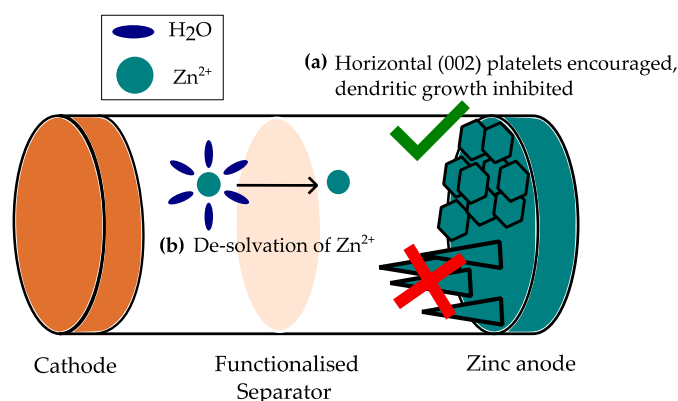


Figure 13. Schematic showing the benefits of functionalised separators in AZIBs: (a) control of the crystallographic orientation of the Zn deposits to prevent dendrite formation, and (b) the de-solvation of Zn^{2+} ions when passing through the separator.

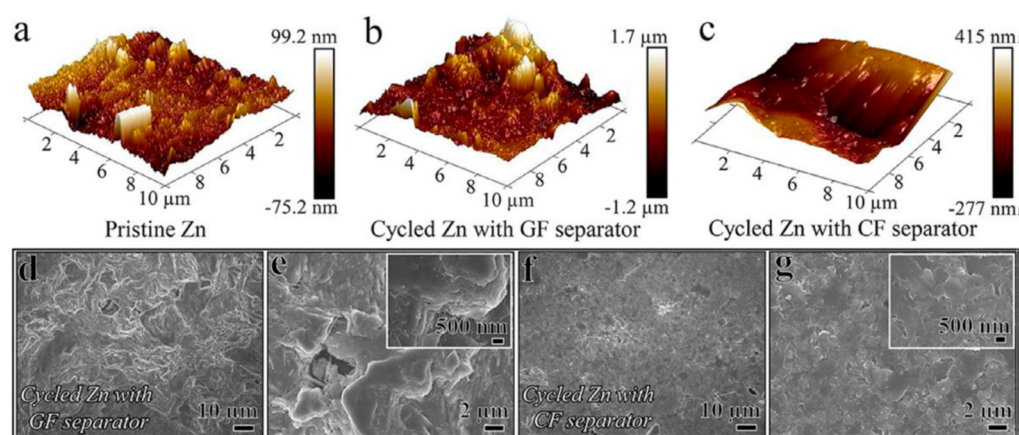


Figure 14. AFM images of (a) the pristine Zn electrode and the Zn electrodes after electrochemical cycling (b) with the GF separator and (c) with the CF separator. Top-view SEM images of the cycled Zn electrodes after electrochemical cycling (d,e) with the GF separator and (f,g) with the CF separator. Adapted from Ref. [167], copyright (2024) Elsevier, with permission from Elsevier.

Considerable research attention is being placed into the development of suitable cathode materials for AZIBs. AZIBs are commonly manufactured in the charged state, where the cathode is a layered material with vacancies to be filled up by the Zn^{2+} cations, and the anode is metallic zinc, which is oxidised to produce Zn^{2+} . Multivalent cations like Zn^{2+} tend to exhibit significantly stronger ionic interactions with the host cathodic lattice due to their greater Coulombic attraction, as opposed to monovalent cations like Li^+ and Na^+ . As a result, a lattice contraction is commonly observed upon the intercalation of Zn^{2+} due to the screening of interlayer electrostatic repulsion and the expulsion of water from

the interlayers [174]. This can cause structural instability and an irreversible reduction in capacity.

Another issue with current AZIB cathode materials is the dissolution of the cathode over time. MnO_2 is commonly used as a cathode material, but it faces problems of Mn dissolution. Adding MnSO_4 into the electrolyte limits cathode dissolution, but some extent of cathode dissolution is still detrimental to long-term cycling stability [175]. To overcome some of the challenges, Deng et al. [140] and Wang et al. [146] proposed different cathode materials, which exhibited ultra-long cycle life ($>20,000$). Crucially, the cathode materials used (amorphous V_2O_5 incorporated into a carbon framework, and DTT) are insoluble in water. The long cycle life shows promise in the application of AZIBs in grid-scale applications in future. Both works highlighted the use of AZIBs as flexible batteries for more niche applications, such as flexible wearable electronics.

To enhance the structural stability of cathode materials, strategies to increase the interlayer spacing were adopted. Bin et al. [144] pre-intercalated PEDOT polymer between layers of $\text{NH}_4\text{V}_3\text{O}_8$, while Hu et al. [150] doped MnO_2 with copper. By expanding the interlayer distance, Zn^{2+} ions can move freely in the host lattice without damaging the electrode, allowing for stable long-term cycling. Intriguingly, the specific capacity of the AZIB increased after cycling in both cases, with capacity retention greater than 100%. The same phenomenon was observed for the first 5000 cycles by Wang et al. [176] using a hierarchically porous structure of a $\text{Zn}_{0.3}\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ cathode with an ultralong cycle life of $>20,000$ at 10 A g^{-1} . They ascribed the initial increase in capacity to the gradual activation of the electrode as more active sites are accessible. Besides this, defect engineering is another strategy to boost the long-term stability of cathode materials in AZIBs. Zhu et al. [145] deliberately induced Mn defects into MnO by encouraging Mn dissolution, which allowed Zn^{2+} to occupy the vacancies rather than interstitial sites. This increased the structural stability of the cathode material, allowing it to display a great cycle life of >1500 cycles at 1 A g^{-1} with little capacity fade.

4.3.2. Non-Aqueous Zinc-Ion Batteries

Although rare, some ZIBs have used organic electrolytes in place of aqueous electrolytes. Notably, Geng et al. [141] opted for $1\text{M Zn}(\text{ClO}_4)_2$ in PC and achieved excellent long-term electrochemical performance with an increased capacity after 8000 cycles, even at a high current density of 10 A g^{-1} . Whilst zinc and the other electrode materials used are indeed less scarce than lithium and its counterparts, the specific capacity and energy density the ZIB provides cannot match typical LIBs. It thus remains to be seen if similar systems in future can improve on the electrochemical properties of non-aqueous ZIBs to make them worthwhile.

4.4. Aluminium-Ion Batteries

Aluminium-ion batteries (AIBs) are emerging in the field of multivalent metal-ion batteries. The motivation behind research into AIBs can be attributed to a few key factors: aluminium is the most abundant metal in the Earth's crust [95], inexpensive, inherently safe, and its redox reaction involves three electrons, which enables a high theoretical volumetric capacity of 8046 mAh cm^{-3} , which is slightly less than four times that of lithium (2062 mAh cm^{-3}) [177]. Although the atomic mass of aluminium is significantly greater than lithium, the three-electron redox reaction of Al allows their theoretical gravimetric capacities to be comparable (Al: 2980 mAh g^{-1} , Li: 3870 mAh g^{-1}) [178]. Such a promising electrochemical property is only effectively utilised when aluminium metal is used as the anode. Therefore, research into AIBs commonly emphasises the cathode and electrolyte.

The promise of a three-electron redox reaction with just one aluminium atom is alluring. However, realising such a system requires overcoming the critical material challenges listed in Table 10.

Table 10. Summary of the key challenges plaguing rechargeable AIBs [179].

Challenge	Explanation
Passivation of Al anode	- Nano-scale thickness Al_2O_3 forms on pristine Al in ambient air - Worsens or completely impedes the electrochemical activity of Al anode
Difficulty in electrodeposition/electro-stripping of Al onto anode	- Possible dendritic growth onto Al anode, potential short-circuiting - Uncontrolled dissolution of Al anode when idling
Unstable cathode material	Dissolution of cathode material leading to self-discharge, poor shelf life
Poor electrochemical properties of cathode materials relative to Al anode	- Difficulty de-intercalating high charge density Al^{3+} ions while avoiding structural collapse - Difficulty intercalating large AlCl_4^- ions into the cathode

4.4.1. Non-Aqueous Aluminium-Ion Batteries

Aluminium is known for forming a passivation layer of aluminium oxide (Al_2O_3), which, when open pore-free, is non-permeable to water and thus is widely used in applications where non-rusting behaviour is important, like in food packaging and in the construction and marine industries [180]. While this property confers aluminium its stability under ambient conditions, it is precisely the reason for its often-disappointing electrochemical performance when aqueous electrolytes are used without the pre-treatment of the aluminium anode, as the oxide layer insulates aluminium-ion transport [177]. As such, researchers have developed room-temperature ionic liquids (RTILs) as promising electrolytes for AIBs (Table 11).

Table 11. Summary of the performance indicators of full-cell non-aqueous AIBs analysed in this review. All values were measured at room temperature.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh $\text{g}^{-1}/\text{mA g}^{-1}$ or C Rate)	Capacity Retention(%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Protonated polyaniline (PANI)/single-walled CNTs	Al	$[\text{EmIm}]\text{Al}_x\text{Cl}_y$	107*/10,000	87.6/8000/10,000	>8000	90.6 *	[181]
2D WS_2 microsheets	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	232*/1000	51.3*/500/1000	72 *	99.4 *	[182]
Tetradiketone macrocycle	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.5:1)	213*/100	79.5*/300/100	293 *	—	[183]
			91.4*/1000	78/8000/1000	7643 *	94.5 *	
Anthracene	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	157/100	82.8/800/100	>800	75.8 *	[184]
SnSe nanoparticles	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	584/300	18.4/100/300	9 *	83.27	[185]
VS_4 nanowire clusters	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	45.8*/400	283*/120/400	>120	58.7 *	[186]
3D graphene	Al with Galinstan	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$	147*/—	101*/50/—	>50	96.4 *	[187]
FeSe_2/GO (graphene oxide)	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	168*/1000	66*/500/1000	253 *	85.9 *	[188]
B-doped expanded graphite	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.1:1)	78.2*/500	112*/300/500	>300	—	[189]
Emeraldine-based PANI on multi-walled CNTs	Al	$[\text{EmIm}]\text{Al}_x\text{Cl}_y$	284/1000	91.19/5000/1000	>5000	97.3 *	[190]
N-doped carbon xerogel	Al	$\text{AlCl}_3/\text{urea}$ (1.5:1)	455*/100	73.5*/300/100	30 *	90.8 *	[191]
Mo_6S_8	AlSn@Cu	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ (1.3:1)	60.5*/100	85*/1400/100	>1400	—	[192]
Fluorinated graphene	Al	$\text{AlCl}_3/[\text{EmIm}]\text{Cl}$	97.8*/200	105*/300/200	>300	72.8 *	[193]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

The RTIL of $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ forms the overwhelming majority of the analysed non-aqueous AIBs. Unlike monovalent ion batteries, non-aqueous AIBs based on the RTIL do not follow the typical rocking-chair mechanism (Figure 3a). Instead, depending on the molar proportions of each component, varying mixtures of Cl^- (Lewis basic), AlCl_4^- (neutral), and Al_2Cl_7^- (Lewis acidic) are formed in situ. It has been shown that only the Lewis acidic species is able to support aluminium deposition and extraction at the anode without the decomposition of the RTIL (Equation (6)). Schoetz et al. [194] investigated the effect of the degree of acidity on the morphology of Al deposits on cleaned and polished aluminium. While they found the average grain size to increase with the degree of acidity, no dendrite plating behaviour was observed for all cases. Therefore, Lewis acidic AlCl_3 is used in greater proportions in all cases (Table 11). Figure 15 gives a brief overview of the charging/discharging mechanism of the $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ system at the anode.

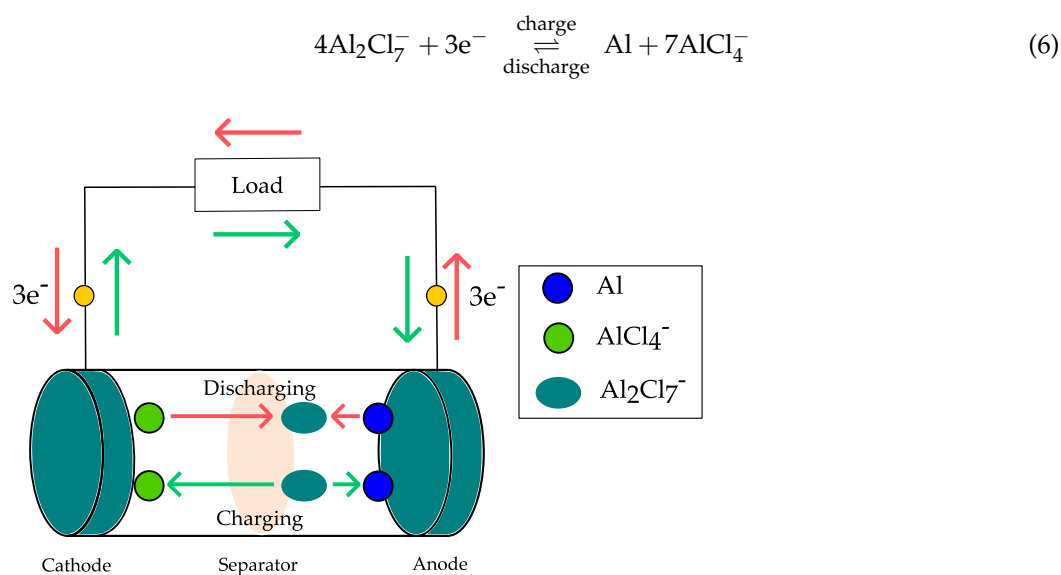


Figure 15. Overview of the charging and discharging mechanisms of aluminium-ion batteries using the $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ electrolyte system. Instead of the usual rocking-chair mechanism where Al^{3+} is shuttled between the cathode and anode, the active species Al_2Cl_7^- is reduced to Al (deposited at the anode) and AlCl_4^- (deposited at the cathode) during charging.

Interestingly, the active species containing aluminium are anionic and not cationic; this is unlike previously mentioned battery systems. Thus, AlCl_4^- is stored in the cathode during charge and released during discharge; the $[\text{EmIm}]^+$ ion is a spectator ion and does not partake in electrochemical processes. It also must be noted that the active species are monovalent and rather heavy, not to mention that four Al_2Cl_7^- ions are required to drive three electrons around the circuit. This results in a practically obtained capacity which is far from the ideal theoretical capacity involving Al^{3+} ions with high charge density.

An advantage of the $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ electrolyte is the dendrite-free plating at sufficiently low current densities. Jiang et al. [195] found that when aluminium was used as the anode at current densities of $10\text{--}100\text{ mA cm}^{-2}$, the resulting deposits were dense and well-adhered to the anode surface; meanwhile, dendritic growth was observed at higher current densities. This is likely because the deposition process becomes diffusion-limited, causing Al to preferentially deposit on the outermost edges of the substrate. Using the $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ electrolyte, one promising class of cathode materials is polyaniline (PANI). PANI is a conducting organic polymer thanks to its extended π -conjugation, with the basic nitrogen atoms enabling the incorporation of metal ions into the polymer backbone [196]. Two groups, Wang et al. [181] and Wei et al. [190], used different types of PANI embedded in a carbon nanotube (CNT) framework to further enhance electrical conductivity. Instead of the usual AlCl_4^- intercalation into the cathode, PANI systems utilise smaller AlCl_2^+ ions produced through the asymmetric cleavage of aluminium chlorides, allowing for easier

intercalation. Wang's group synthesised protonated PANI, where the protonated active sites improved electrochemical kinetics, while Wei's group found emeraldine-based PANI to exhibit the highest capacity. Excellent long-term cycling stability was achieved with both versions of PANI (Table 11).

The theoretically obtainable energy density could be further improved with a multivalent charge carrier. To this end, Yoo et al. [183] designed a tetradiketone macrocycle, which preferentially reacts with the divalent AlCl_2^{2+} species rather than the monovalent AlCl_2^+ (Figure 16). An energy density of 189 Wh kg^{-1} and power density of 2600 W kg^{-1} was achieved using this system, outperforming the monovalent counterparts. However, the rate performance of the divalent system was worse, which is likely due to the more sluggish diffusion of the higher charge density AlCl_2^{2+} .

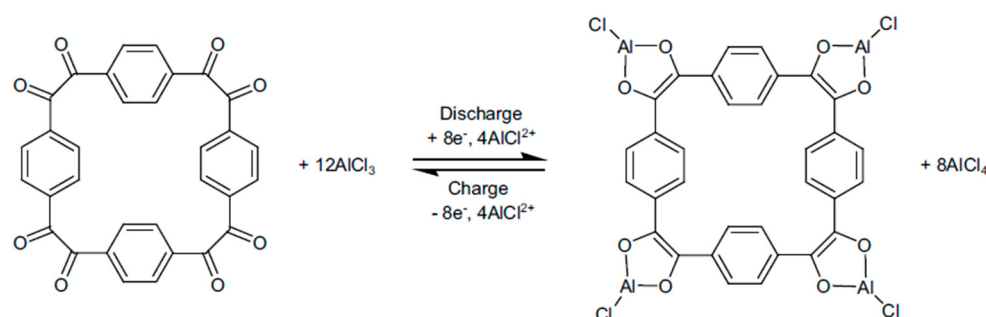


Figure 16. The electrochemical storage of the divalent AlCl_2^{2+} ion with the synthesised tetradiketone macrocycle. Adapted and reproduced from Ref. [183] under the CC-BY-4.0 license (<https://creativecommons.org/licenses/by/4.0/>).

Aluminium foil is often used as an anode material due to its innate stability and good plating morphology. Chen et al. [197] elucidated experimentally that the aluminium oxide film serves as a protective layer to contain the aluminium dendrites. Wang et al. [192] observed short-circuiting when polished aluminium foil without the oxide layer was used. Meanwhile, the artificial SEI layer gave a uniform deposition of Al, potentially because Sn provided more active sites evenly distributed across the surface. Consequently, the battery could be cycled stably for 1400 cycles at a current density of 100 mA g^{-1} . Interestingly, dendritic growth was encouraged by Shen et al. [187] to obtain ultra-fast charging behaviour. Sluggish kinetics during charging were observed with pure Al, owing to (1) the electrostatic repulsion due to the reaction of species with like charges (Equation (6)) and (2) the formation of an electric double layer (EDL) requiring additional energy for Al deposition. Experimentally, Al deposition was found to be predominant at defect sites. Pre-treatment with Galinstan, a eutectic liquid metal, fills the defects and provides amorphous active sites, which promote fast Al plating. Crucially, the adequately interspersed active sites allow for the Al dendrites to be wide and not sharp. As a result, a full charge of the battery only requires an impressive 0.35 s.

Another RTIL has been explored by Almodóvar et al. [191], who used urea in place of $[\text{EmIm}]\text{Cl}$. Compared to the $\text{AlCl}_3/[\text{EmIm}]\text{Cl}$ system, the $\text{AlCl}_3/\text{urea}$ eutectic is much cheaper, less corrosive, and more environmentally friendly [198,199]. A compatible carbon xerogel doped with nitrogen was developed for this eutectic, which attained an impressive initial discharge capacity of 455 mAh g^{-1} at 100 mA g^{-1} , but the cycling performance was relatively unstable.

4.4.2. Aqueous Aluminium-Ion Batteries

Aqueous AIBs (AAIBs) are relatively less popular compared to RTIL systems. To devise an effective AAIB, one must prevent the passivation of the Al anode and employ a cathode material that can withstand the high charge density of the Al^{3+} ion without pulverisation. Despite this, successfully overcoming these practical challenges would mean a higher energy density battery, as the promise of a trivalent active ion is realised.

Commonly, aqueous salts of either $\text{Al}(\text{CF}_3\text{SO}_3)_3$ or $\text{Al}_2(\text{SO}_4)_3$ are used, with different modifications of the anode or cathode (Table 12).

Table 12. Summary of the performance indicators of the full-cell aqueous AIBs analysed in this review. All values were measured at room temperature.

Cathode	Anode	Electrolyte	Initial Reversible Capacity ($\text{mAh g}^{-1}/\text{mA g}^{-1}$ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Potassium nickel hexacyanoferrate (KNHCF)	Al	5 M $\text{Al}(\text{CF}_3\text{SO}_3)_3$	46.5/20	51.6 */500/20	33 *	97.2 *	[200]
$\text{V}_2\text{O}_5/\text{MXene}$	Al	5 M $\text{Al}(\text{CF}_3\text{SO}_3)_3$	336 */400	23.3 */100/400	6 *	74 *	[201]
KNHCF	Sn single-atom catalyst on Al	0.5 M $\text{Al}_2(\text{SO}_4)_3$	90.1 */100	67.3 */300/100	42 *	91.3 *	[202]
Al_xMnO_2	Sn single-atom catalyst on Al	0.5 M $\text{Al}_2(\text{SO}_4)_3$ /0.15M MnSO_4 additive	344 */100	34.9 */120/100	7 *	79.9 *	
High-entropy PBA-Cu	Al pre-treated with ionic liquid	2 M $\text{Al}(\text{CF}_3\text{SO}_3)_3$ /0.2M $\text{Mn}(\text{CF}_3\text{SO}_3)_2$	139 */200	84.4 */500/200	>500	—	[203]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Developing a suitable electrolyte is a key challenge for AAIBs. During the initial charging phase, a stable SEI that is conductive to Al^{3+} must be formed. Traditional salt-in-water electrolytes contain a large excess of free water molecules, resulting in a propensity for water decomposition, as the driving force for HER is higher than that of Al deposition [177]. Instead, water-in-salt electrolytes use a high concentration of salt in water. By promoting the formation of ion pairs, water molecules are intimately bound in solvation shells, expanding the electrochemical window by reducing the availability and hence the electrochemical activity of water [204,205]. As such, concentrated $\text{Al}(\text{CF}_3\text{SO}_3)_3$ is a common electrolyte choice in AAIBs.

PBAs are a class of promising cathode materials for AAIBs. One major pain point regarding AAIBs is the lack of sufficiently stable cathode materials that can withstand the high charge density of Al^{3+} . The structure of PBA confers naturally large interstitial voids and diffusion pathways, which can withstand the higher strain fields induced by the Al^{3+} ions [206]. To this end, some groups [200,202,207] have synthesised potassium nickel hexacyanoferrate (KNHCF) with different morphologies, including at the nanoscale. Of these, Ru et al. [207] only evaluated the performance of KNHCF with a three-electrode system. Although the repetitive cycling of Al^{3+} was possible, capacity fade tended to be quite significant even at a low current density of $\leq 100 \text{ mA g}^{-1}$. Gao et al. [200] suggested this to be because of the unstable SEI at the Al anode due to Ni dissolution at the cathode. PBAs are also lauded for their high tunability. To further improve on the long-term performance of PBAs, Du et al. [203] recently developed a high-entropy PBA incorporating five metallic elements (Fe, Ni, Mn, Cu, Co; not too dissimilar to Cantor alloys such as CrMnFeCoNi) with different charges and ionic radii. In theory, this confers a large anisotropic strain field, which withstands pulverisation upon repeated cycling. In fact, a “respiration effect” was observed via in situ X-ray diffraction (XRD), where the underlying lattice expanded reversibly to accommodate the intercalation of Al^{3+} ions (Figure 17). Alongside pre-treatment with an ionic liquid to obtain a good SEI layer, Du et al. achieved a markedly improved cycling behaviour, with 84.4% capacity retention after 500 cycles at a higher current density of 200 mA g^{-1} .

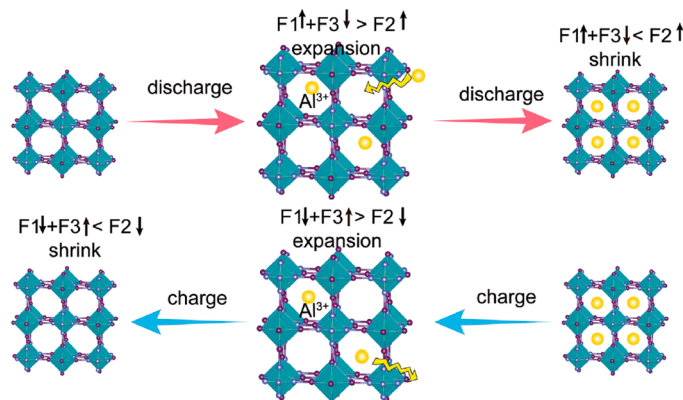


Figure 17. Schematic of the proposed lattice change during cycling. Three forces were identified by the authors during the intercalation process: electrostatic repulsion between Al^{3+} and the PBA (F1), bond cooperation between metal ions and $-\text{CN}-$ groups (F2), and homo-ionic repulsion between M^{2+} and M^{2+} ions (F3). Reproduced from Ref. [203] with permission from the Wiley Online Library.

Transition metal oxides incorporating Mn or V were also explored [201,202], obtaining impressive initial capacities of $>300 \text{ mAh g}^{-1}$. However, capacity fade is a major problem, with low initial Coulombic efficiencies of $<80\%$ indicating a possible significant loss of active material through SEI formation.

4.4.3. Other Aluminium-Ion Battery Systems

Ramakrishnan et al. [208] synthesised a starch gel electrolyte which incorporated AlCl_3 via the salting-in effect. An ionic conductivity of 1.59 mS cm^{-1} was reported, which is comparable to liquid electrolytes (10^{-3} to $10^{-2} \text{ S cm}^{-1}$) [209]. Consequently, the assembled $\text{Al}|\text{MoO}_3$ cell gave an initial discharge capacity of 193 mAh g^{-1} at 100 mA g^{-1} , with 59.1% capacity retention after 100 cycles (ICE = 73.5%). With future improvements in electrochemical performance, related solid-state batteries could potentially eliminate the issues of electrolyte leakage and moisture sensitivity plaguing liquid-based AIBs [210].

An anode-free AIB was assembled by Lu et al. [211], where a Cu current collector was placed at the anode position. To replenish the Al loss upon cycling, the PANI-coated graphene cathode was supplemented with Al_2TiO_5 . The main selling point of such an anode-free design is the dendrite-free plating thanks to the lack of excess Al sites, allowing a very stable cycling performance for 4000 cycles at 1.3 A g^{-1} , with an initial discharge capacity of 148 mAh g^{-1} and a capacity retention of 60.3% after 4000 cycles.

4.5. Magnesium-Ion Batteries

Research into rechargeable magnesium-ion batteries (MIBs) is still in its infancy. However, merits pertaining to better safety, greater abundance of raw materials (Mg is the 8th most abundant element in the Earth's crust [95]), and higher volumetric capacity compared to LIBs underscore the potential of this beyond-lithium technology [212]. A unique advantage of MIBs compared to other battery types is the dendrite-free plating of Mg onto Mg metal, instead forming ideal compact crystals [213]; this reduces the risk of internal short-circuiting and thermal runaway. Nonetheless, there are significant material challenges to overcome before a practical MIB with satisfactory electrochemical properties can be achieved. These challenges are detailed in Table 13.

Table 13. Summary of the key challenges plaguing rechargeable MIBs [212,214].

Challenge	Explanation
Sluggish kinetics due to a lack of suitable cathode materials	• Mg^{2+} has a smaller ionic radius than Li^+ and a much higher charge density • Consequently, high energy barrier to de-solvation of hydrated Mg^{2+} • Difficult reversible intercalation of Mg^{2+}
Incompatibility of electrolyte with electrodes	• Difficult to find an electrolyte compatible with both electrodes • Possible passivation of Mg anode or dissolution of cathode material
Passivation of Mg anode	• Formation of an SEI which is impermeable to Mg^{2+} • High charge transfer resistance

Despite facing challenges related to sluggish kinetics and limited electrolyte compatibility, recent advancements in electrode design and electrolyte formulation have shown promising results. Research efforts have focused on developing high-capacity electrode materials and novel electrolyte systems to improve cycling stability and charge/discharge rates (Table 14).

Table 14. Summary of the performance indicators of full-cell MIBs analysed in this review. All values were measured at room temperature and glass-fibre separators were used.

Cathode	Anode	Electrolyte	Initial reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Expanded graphite	PTCDI	0.4 M Mg(TFSI) ₂ in Pyr ₁₄ TFSI ionic liquid	51.3 */5C	95.7/500/5C	>500	90.9 *	[215]
NiSe ₂ -CoSe ₂ @TiVCT _x	Mg	0.4 M APC (2PhMgCl-AlCl ₃ in THF)	25.2 */500	288 */500/500	>500	79.8 *	[216]
V ₂ O ₅ intercalated with PANI	AC	0.3 M Mg(TFSI) ₂ in acetonitrile (AN)	249 */100 94.4 */4000	119 */50/100 87.5 */500/4000	>50 >500	92.9 * 98.4 *	[217]
V ₂ O ₅ intercalated with PANI	Mg	0.2 M Mg(CF ₃ SO ₃) ₂ -MgCl ₂ -AlCl ₃ in DME	91.5 */100	70.4 */50/100	44 *	99.3 *	
Mg(Mg _{0.5} V _{1.5})O ₄	AC	0.3 M Mg(TFSI) ₂ in AN	250/100 141 */1000	92.1/100/100 68.9 */500/1000	>100 372 *	93.6 * 100 *	[218]
Mg(Mg _{0.5} V _{1.5})O ₄	Na ₂ Ti ₃ O ₇	0.3 M Mg(TFSI) ₂ in AN	113 */50	90.2 */100/50	>100	71.3 *	
VS ₄ @Ti ₃ C ₂ /C	Mg	0.25 M methylpyrrolidinium chloride in 0.25 M APC	184/500	80/900/500	900	80.6 *	[219]
NaV ₂ O ₂ (PO ₄) ₂ F/rGO	Mg _{0.79} NaTi ₂ (PO ₄) ₃	0.3 M Mg(TFSI) ₂ in AN	48.3 */100	85/200/100	>200	91.1 *	[220]
NaV ₂ O ₂ (PO ₄) ₂ F/rGO	AC	0.3 M Mg(TFSI) ₂ in AN	83.8 */100 60.2 */500	97.5/1000/100 76/9500/500	>1000 6783 *	98.0 * 96.7 *	
Te @ carbon spheres	Mg	0.4 M APC	298/500	77.1/500/500	237 *	91.7 *	
NiS ₂ /Ni-based CNTs	Polished Mg	APC	164.3/200	58/2000/200	431 *	80.4 *	[222]
PANI/carbon cloth	AC cloth	0.3 M Mg(TFSI) ₂ in AN	197 */200 111 */1000	80 */300/200 93.6 */1500/1000	~300 * >1500	108 * 100 *	[223]
PANI/carbon cloth	MgNaTi ₃ O ₇	0.3 M Mg(TFSI) ₂ in AN	75/50	66.7/30/50	13 *	45.8 *	
VOPO ₄ ·2H ₂ O pre-intercalated with triethylene glycol	Mg	0.5 M Mg(TFSI) ₂ in DME	215 */100	89.8 */1000/100	>1000	100 *	[224]

Table 14. Cont.

Cathode	Anode	Electrolyte	Initial reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Mo ₆ S ₈	Mg–Sn@Mg	0.4 M APC	92.2/1C	85.9/1000/1C	>1000	102 *	[225]
			56.1 */10C	87.0 */5000/10C	>5000	100 *	
Mo ₆ S ₈	Mg–Bi@Mg	0.4 M APC	85.7/1C	87.0/1000/1C	>1000	103 *	
			54.7 */10C	83.4 */5000/10C	>5000	100 *	
CuHCF	Mn-doped NaVO ₃	1:1:7 MgCl ₂ ·6H ₂ O: acetamide: urea	39.0 */1000	99.2 */800/1000	>800	70.0 *	[226]
V ₂ O ₅ ·xH ₂ O/MoS ₂ quantum dots/multi-walled CNTs	AC	0.5 M Mg(TFSI) ₂ in DME	146/1000	77.1/1000/1000	14 *	91.7 *	[227]
			135 */2000	35.2 */15,000/2000	27 *	84.3 *	
NiCoMg-layered double hydroxide	AC	3 M MgSO ₄ (aq)	80 */1000	78.8 */2000/1000	1935 *	94.2 *	[228]
NiCoMg-layered double hydroxide	PTCDI	3 M MgSO ₄ (aq)	55.4 */2000	82/1500/2000	>1500	88.9 *	
Mg _{0.75} V ₁₀ O ₂₄ ·nH ₂ O	PTCDA	2 M Mg(CF ₃ SO ₃) ₂ (aq) in PEG/H ₂ O	58/4000	62/5000/4000	1804 *	100 *	[229]
MnO ₂ /GO	PTCDA	20 M LiTFSI + 2 M Mg(TFSI) ₂ (aq)	150/1000	85/2000/1000	>2000	78.9 *	[230]

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Uncommon electrolyte systems are used in MIBs. Polar aprotic solvents are not suitable due to their tendency to passivate the Mg anode, increasing interfacial charge transfer resistance and shortening cycle life [212,231]. Notably, when Mg(PF₆)₂ in polar aprotic solvents are used in MIBs, the salt decomposes to form an impermeable MgF₂ layer on the Mg anode [232]; this indicates that electrolytic systems common for LIBs are not transferrable to MIBs. Meanwhile, typical aqueous solvents are also not suitable due to the difficulty in de-solvating high-charge density Mg²⁺ ions for reversible intercalation and the tendency for water decomposition at the electrodes (standard electrode potential of Mg²⁺/Mg is −2.372 V vs. SHE, Figure 4). Therefore, the main electrolyte systems used are all-phenyl complex (APC), Mg(TFSI)₂ in acetonitrile, and, less commonly, aqueous electrolytes.

The APC electrolyte was developed by Mizrahi et al. [233] and consists of a Grignard reagent PhMgCl and a Lewis acid AlCl₃, where active Mg-containing species are formed in situ through an acid–base reaction. They tuned the ratio of these components and found the optimal ratio of PhMgCl to AlCl₃ to be 2:1, with the active species in the resulting solution being Ph₂AlCl₂[−], AlPh₄[−], MgCl⁺, and Mg₂Cl₃⁺. The improvement in electrochemical stability over previously developed analogous systems using alkyl ligands was attributed to the stronger Al–C bond in aromatic ligands.

The Mg(TFSI)₂ in acetonitrile electrolyte is commonly employed, where the large and diffuse TFSI[−] anion displays weak ionic interactions with Mg²⁺, allowing Mg²⁺ to be relatively unhindered in solution. However, acetonitrile may cause Mg passivation at low voltages [231]; for this reason, other anode materials must be developed to allow for stable long-term cycling performance (Table 14).

4.5.1. Cathode Materials

When the APC electrolyte was developed, its creators suggested Mo₆S₈ as a possible cathode material for reversible Mg-ion intercalation, although no detailed study of long-term battery performance was conducted. Mo₆S₈ adopts the Chevrel phase, which has an open structure suitable for intercalating the large MgCl⁺ and/or Mg₂Cl₃⁺ ions (Figure 18a).

Besides Chevrel-phase cathodes, spinel-phase cathodes (general formula AB₂×₄) have also been developed (Figure 18b), where the battery is manufactured in the discharged

state with Mg^{2+} intercalated into the cathodic lattice. Such compounds have the advantage that Mg-free anodes can be used, bypassing the problem of Mg passivation in common electrolytes. Zuo et al. [218] synthesised $\text{Mg}(\text{Mg}_{0.5}\text{V}_{1.5})\text{O}_4$, where the change in valency of V accommodates the reversible intercalation of Mg^{2+} . When used with AC as the anode, a commendable initial discharge capacity of $\sim 140 \text{ mAh g}^{-1}$ at a high current density of 1 A g^{-1} was achieved. Zhang et al. [234] developed $\text{MgFe}_{1.33}\text{Mn}_{0.67}\text{O}_4$, where Fe doping was targeted at improving the electrical and ionic conductivity of the material. Notably, when tested in a three-electrode system, the specific capacity increased with cycling and stabilised at 88.3 mAh g^{-1} at a current density of 1 A g^{-1} . The authors attributed this phenomenon to the gradual activation of the electrode over time.

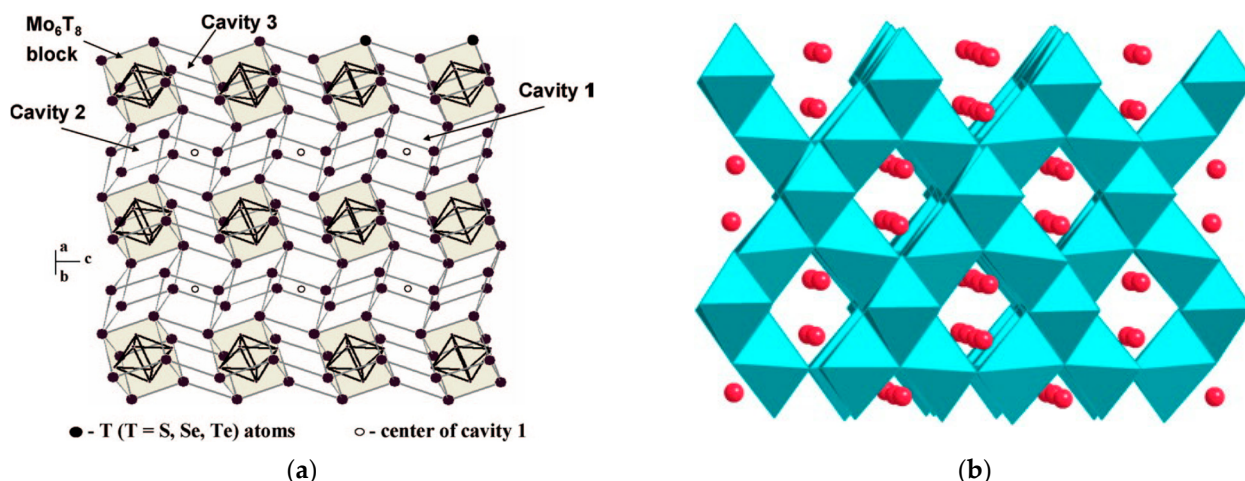


Figure 18. (a) Crystal structure of the Chevrel phase with cavities for 3-dimensional ion transport. Reprinted with permission from Ref. [235]. Copyright 2019 American Chemical Society. (b) Crystal structure of the spinel phase of general formula AB_2X_4 (red: A ions; centre of blue octahedra: B ions; corners of blue octahedra: X ions). Adapted from Ref. [236], copyright (2024) Elsevier, with permission from Elsevier.

The pre-intercalation of layered cathode materials was attempted by Zuo et al. [217] and Zhang et al. [224]. By increasing the interlayer spacing, one could reduce the activation energy for Mg^{2+} diffusion, thereby improving diffusion kinetics and rate capability while reducing the likelihood of cathode pulverisation. Zuo et al. intercalated PANI into V_2O_5 which conferred additional advantages of enhanced electronic conductivity, additional Mg^{2+} storage sites, and better flexibility due to the conjugated π -system of PANI. Consequently, significantly better cycling performance was achieved compared to pristine V_2O_5 . Later, Zhang et al. elucidated the relationship between interlayer spacing and battery performance by synthesising a series of pre-intercalated VOPO_4 compounds with varying interlayer spacing. Notably, they found that some degree of interlayer expansion promoted Mg^{2+} diffusion kinetics, whilst a material with excessive interlayer spacing could be more prone to structural collapse, as evidenced by the poor capacity retention of 70.1% after 100 cycles at 100 mA g^{-1} .

4.5.2. Anode Materials

A crucial drawback of using an Mg anode is its tendency to be passivated in aqueous and common organic electrolytes, creating an electronically and ionically insulating SEI [237]. As such, pure Mg is not commonly used in practical MIBs. To this end, three main strategies have been employed to increase the electrochemical performance of the anode, namely alloying-type, intercalation-type, and conversion-type compounds.

Chai et al. [225] improved upon the initial work of Mizrahi et al. [233] by designing an alloy-type artificial protective layer on the Mg anode (Figure 19a). Using the same Mo_6S_8 cathode, Chai et al. demonstrated that the alloyed anodes had higher discharge capacities

and more stable cycling behaviour for 5000 cycles at a 10C rate and 1000 cycles at a 1C rate. They attributed this to the more uniform plating of Mg onto the anode, where no “dead” Mg layer was formed during cycling, unlike in pure Mg. Porous Bi anodes with the same alloying mechanism were developed by Zheng et al. [238]. They determined the first discharge-specific capacity with the Mo_6S_8 in both 0.5M $\text{Mg}(\text{TFSI})_2$ in diglyme and 0.4M APC to be about 120 mAh g^{-1} at 10 mA g^{-1} , although Mg cycling stability is poor.

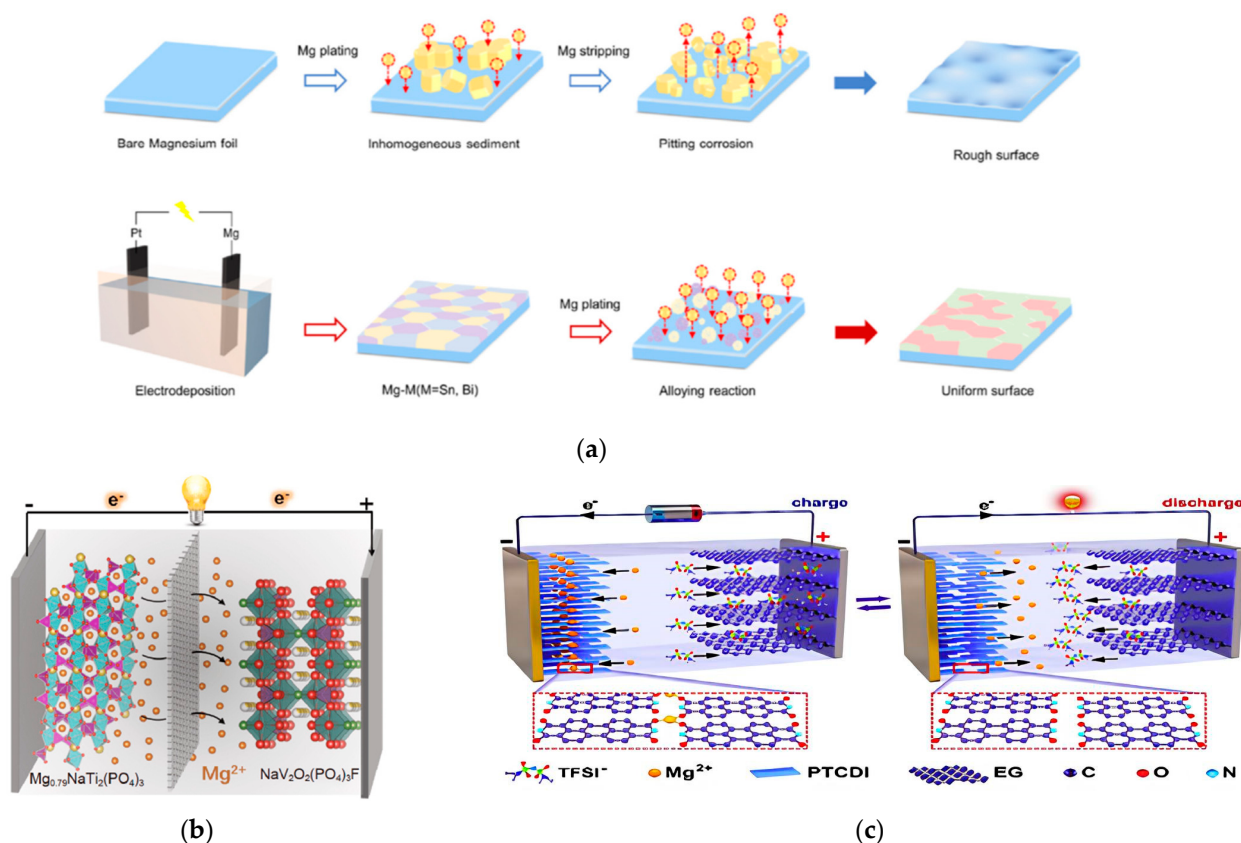


Figure 19. Summary of MIB anodes displaying different Mg-ion storage mechanisms. (a) Schematics of the electrochemical behaviour of bare Mg and Mg-M@Mg (M = tin and bismuth) anodes. Reproduced from Ref. [225] with permission from the Royal Society of Chemistry. (b) Schematic illustration of the Mg-ion full-cell using an intercalation-type anode. Reproduced from Ref. [220] with permission from Springer Nature. (c) Schematic illustration of the working mechanism of the magnesium dual-ion battery (Mg-DIB) based on the PTCDI anode and EG cathode. Reprinted from Ref. [215], copyright (2024) Elsevier, with permission from Elsevier.

Mg passivation is an issue that has attracted attention. Intercalation-type anodes were also explored to avoid the problem of Mg passivation. Wang et al. [220] used $\text{Mg}_{0.79}\text{NaTi}_2(\text{PO}_4)_3$ as the anode coupled with $\text{NaV}_2\text{O}_2(\text{PO}_4)_3\text{F}$ as the cathode, which are both phosphate intercalation-type compounds (Figure 19b). Although a stable cycle life of >200 cycles at a current density of 100 mA g^{-1} was obtained, the initial discharge capacity is rather limited at less than 50 mAh g^{-1} .

Small organic molecules rely on conversion reactions between their functional groups and the active ionic species. To this end, Lei et al. [215] developed a magnesium-ion-based dual-ion battery using PTCDI as the anode, where both Mg^{2+} and TFSI^- ions contribute to the overall specific capacity of the cell (Figure 19c). They found that PTCDI was insoluble in the organic electrolyte, $\text{Mg}(\text{TFSI})_2/\text{Pyr}_{14}\text{TFSI}$, unlike PTCDI, which dissolved quickly, leading to a decay in specific capacity. At a high C-rate of 5C, a cycle life of more than 500 cycles was achieved.

4.5.3. Electrolytes

Although aqueous electrolytes pose a lower fire and explosion risk compared to organic electrolytes, they are often limited by the HER and OER of water. To address this problem, a water-in-salt electrolyte, 20 M LiTFSI + 2 M Mg(TFSI)₂, was developed by Yang et al. [230]. Compared to the 1M Mg(NO₃)₂ dilute electrolyte which has an electrochemical stability window (ESW) of 1.7 V, the ESW of the water-in-salt electrolyte was extended to 2.1 V, resulting in a higher specific capacity. Furthermore, the water-in-salt electrolyte inhibits the dissolution of MnO₂, enhancing long-term cycling stability. Several other systems have been explored to overcome the issue associated with the limited stability window. A ternary eutectic electrolyte comprising MgCl₂·6H₂O: acetamide: urea in a 1:1:7 molar ratio was developed by Song et al. [226] as an attempt to broaden the ESW. A small proportion of acetamide was introduced to compete with urea in coordinating with the Mg²⁺ ions, thereby allowing the liberated urea molecules to form a more extensive hydrogen-bonding network with the water of crystallisation and broaden the ESW (Figure 20a). The determined ESW of the optimised electrolyte was 3.5 V. Interestingly, they demonstrated that the anodic SEI exhibited a “breathing effect”, curbing unwanted dissolution and side reactions (Figure 20b).

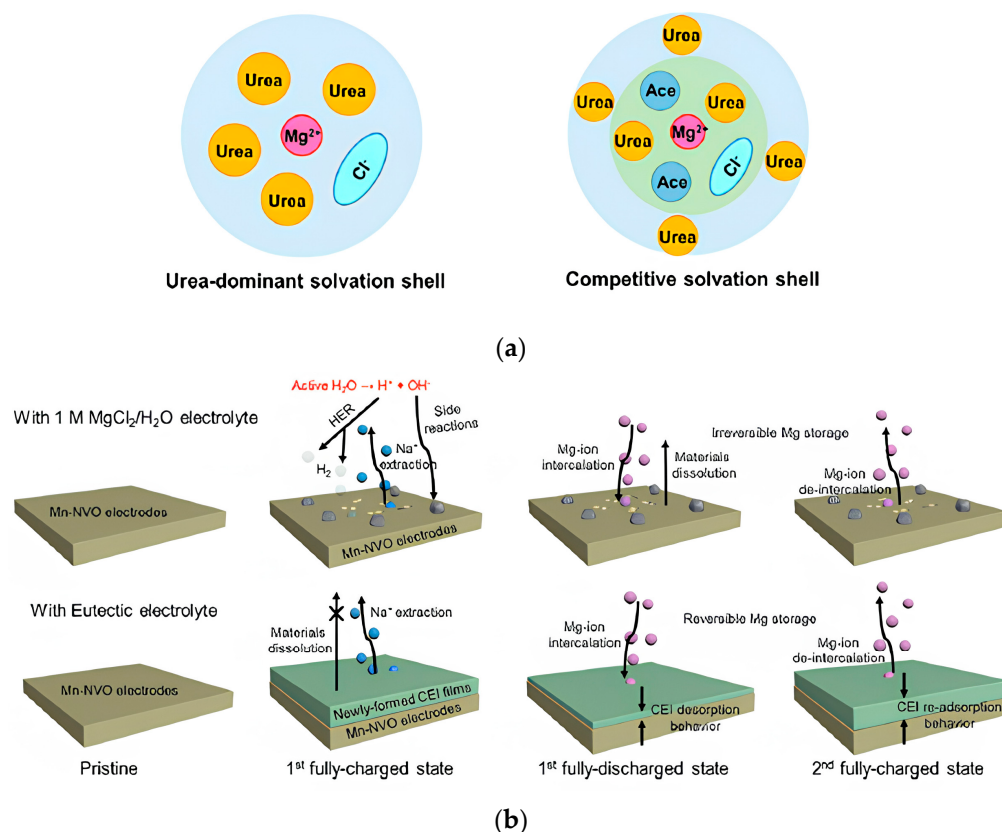


Figure 20. (a) Schematic illustration of the urea-dominant solvation shell in the absence of acetamide (left) and the competitive solvation shell with acetamide (right). Adapted with permission from Ref. [226]. Copyright 2024 American Chemical Society. (b) Schematic illustrations of the reactions occurring on the interface of the Mn-NVO electrode when assembled with the 1M MgCl₂/H₂O and optimised MgCl₂·6H₂O: acetamide: urea electrolyte (1:1:7). Adapted with permission from Ref. [226]. Copyright 2024 American Chemical Society.

4.6. Calcium-Ion Batteries

The calcium-ion battery (CIB) is a relatively new technology, but it is beginning to gain traction as a promising beyond-lithium technology [239,240]. The first primary room-temperature CIB using Ca/SOCl₂ was assembled in the 1980s by Staniewicz [241], but

it was not until 2015 that the first rechargeable CIB using the Sn/MnHCF system was developed [242]. Shortly thereafter, reversible calcium stripping and plating were observed with CaSi_2 in an alkyl carbonate electrolyte [243].

Calcium is abundant (Ca is the 5th most abundant element in the Earth's crust [95]) and cost-effective, being directly below magnesium in the periodic table. Although this means that their chemical reactivity is similar, there are still intrinsic differences driven by their differences in property. The divalent nature of the Mg^{2+} ion allows two electrons per ion to be driven around the circuit, but it is a challenge to find suitable electrode materials to accommodate these higher charge density ions without structural collapse. Meanwhile, Ca^{2+} has a larger ionic radius and thus lower charge density, alleviating this issue to an extent. Notably, Ca has a more negative standard electrode potential than Mg relative to SHE (-2.868 V vs. -2.372 V, Figure 4), indicating a possibly higher voltage battery provided that a suitable high-potential cathodic reaction can be realised.

However, CIBs have their unique set of challenges. Firstly, the interplanar spacing of intercalation-type electrodes needs to be sufficiently large to accommodate the larger Ca^{2+} ions. Also, the more diffuse valent shell of Ca means that electrons are lost more easily, making Ca metal more reactive compared to Mg metal. This causes the formation of a passivating SEI layer when in contact with conventional organic electrolytes like AN, THF, and PC, making calcium deposition extremely difficult without high overpotentials [244]. As such, much of the focus has been on developing suitable electrode materials and alternatives to the highly reactive Ca metal for the anode, with a balance of aqueous and non-aqueous systems (Table 15).

Table 15. Summary of the performance indicators of the full-cell CIBs analysed in this review. All values were measured at room temperature and glass-fibre separators were used.

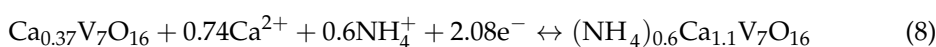
Cathode	Anode	Electrolyte	Initial Reversible Capacity ($\text{mAh g}^{-1}/\text{mA g}^{-1}$ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
1,4-polyanthraquinone	Ca_xSn	0.2 M $\text{Ca}[\text{B}(\text{hfp})_4]_2$ in DME	269 */0.5C 234 */1C	54.3 */1200/0.5C 33.8 */5000/1C	22 * 39 *	102 * 101 *	[245]
Prussian blue	$\text{Ni}(\text{OH})\text{-}[\text{C}_6\text{H}_4(\text{COOH})(\text{COO})]$ (Nidbc)	1 M $\text{Ca}(\text{ClO}_4)_2$ in AN	82/100	62/100/100	39 *	~100	[246]
Prussian blue	$\text{Ni}[\text{C}_6\text{H}_4(\text{NH}_2)(\text{COO})_2]$ (NidbcNH ₂)	1 M $\text{Ca}(\text{ClO}_4)_2$ in AN	86/100	77/100/100	72 *	—	
$\text{Ca}_3\text{Co}_4\text{O}_9$	V_2O_5	$\text{Ca}(\text{TFSI})_2$ in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, polymerised with PEGDA	137 */C/14	14.6 */25/C/14	3 *	—	[247]
$\text{H}_2\text{V}_3\text{O}_8$ with Zn^{2+} pre-insertion	PTCDA	1 M $\text{Ca}(\text{ClO}_4)_2$ in tetraethylene glycol dimethyl ether (TEGDME: $\text{H}_2\text{O} = 4:1$)	65.7/1000	82.5 */730/1000	>730 *	99.5 *	[248]
$(\text{NH}_4)_2\text{V}_7\text{O}_{16}$	Ca	0.5 M $\text{Ca}(\text{ClO}_4)_2$ in AN	74.0 */20	78.5/20/20	18 *	133 *	[249]
2D-Prussian green	NidbcNH ₂	$\text{Ca}(\text{ClO}_4)_2/(\text{H}_2\text{O})_{4.0}(\text{AN})_{4.8}$	59.5 */100	92.3 */350/100	>350 *	68.3 *	[250]
CuHCF	PANI/carbon cloth	2.5 M $\text{Ca}(\text{NO}_3)_2$ (aq)	125/800	95/200/800	>200	97.1 *	[251]
Ca_2MnO_4	Mesoporous silica @ poly-PTCDI	1 M $\text{Ca}(\text{NO}_3)_2$ (aq)	139 */100	81.9 */800/100	>800	85.0 *	[252]
$\text{Ca}_{0.3}\text{CuHCF}$	Se/mesoporous carbon (CMK-3)	6.25 M $\text{Ca}(\text{TFSI})_2$ (aq)	31.2 */100	97.2 */50/100	>50 *	50.9 *	[253]
Ca_xCuHCF	Nitrogen-rich covalent organic framework with multiple carbonyls (TB-COF)	3.4 M CaCl_2 (aq)	174 */5000	73.5/3000/5000	1710 *	92.5 *	[254]
$\text{K}_{0.11}\text{Co}_{0.02}\text{Mn}_{0.98}\text{O}_2 \cdot 1.4\text{H}_2\text{O}$ @ carbon cloth	Polyimide	2 M $\text{Ca}(\text{NO}_3)_2$ (aq)	32.9 */1000	114 */1000/1000	>1000	99.7 *	[255]

Table 15. Cont.

Cathode	Anode	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
MnHCF	Covalent organic framework with repeated pyrazine and pyridinamine units (PTHAT-COF)	6.67 M CaCl ₂ (aq)	60.1 */20,000	85.1 */10,000/20,000	>10,000	99.8 *	[256]
CuHCF	PTCDI	5 M Ca(OTF) ₂ (aq)	73.5 */1000	89.7 */30,000/1000	>30,000	100 *	[257]
K ₃ V ₂ (PO ₄) ₃ /C	PTCDI	5 M Ca(OTF) ₂ (aq)	80.7 */100	75.3/100/100	62 *	1.2 *	[258]
			62.0 */500	86.2/200/500	>200	0.2 *	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Of the full-cell CIBs, it is noted that only one of them explored the use of Ca metal as the anode [249]. Even at a low current density of 20 mA g⁻¹, cycling stability was poor. The authors attributed this to the electrolyte instability with the Ca metal anode, which created continual side reactions during charging. A telltale sign was the abnormally high coulombic efficiencies, which were consistently maintained well above 100%. Nonetheless, Bu et al. demonstrated a unique reaction mechanism, where the first step involved an irreversible structural change involving the exchange of all NH₄⁺ with some Ca²⁺ ions (Equation (7)), followed by the reversible co-insertion and extraction of both NH₄⁺ and Ca²⁺ (Equation (8)).



Notably, Qiao and co-workers developed two similar systems using the same organic anode (PTCDI) and a water-in-salt electrolyte of 5 M Ca(OTF)₂ [257,258]. One system used the PBA of CuHCF, while another used a NASICON-type K₃V₂(PO₄)₃/C material. Under these conditions, CuHCF outperformed K₃V₂(PO₄)₃/C, with a higher discharge capacity at a higher current density and a capacity retention of nearly 90% even after 30,000 cycles. This is possibly due to the larger interstitial sites within the PBA, allowing for long-term structural stability and a lower degree of degradation of active sites over time.

4.6.1. Cathode Materials

Among the half-cell CIBs, all the cathode materials were layered and used an intercalation-based mechanism, although different electrolytic systems were explored (Table 16).

Table 16. Summary of the performance indicators of cathode materials in analysed CIBs; only half cells were included. All values are measured at room temperature.

Cathode	Counter//Reference	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
Ca _{0.13} MoO ₃ ·(H ₂ O) _{0.41}	AC	0.5 M Ca(ClO ₄) ₂ in AN	90.7/2C	94/50/2C	>50	108 *	[259]
BaV ₆ O ₁₆ ·3H ₂ O@GO	AC cloth	0.8 M Ca(TFSI) ₂ in EC/DMC/PC/EMC	151 */300	20.3 */1000/300	36 *	89.6 *	[260]
H ₂ V ₃ O ₈ with Zn ²⁺ pre-insertion	Pt//Ag/AgCl	1 M Ca(ClO ₄) ₂ in TEGDME: H ₂ O = 4:1	76.4/5000	78.3/1000/5000	877 *	100 *	[248]
V ₂ O ₅ pre-intercalated with Ni ²⁺	Pt//Ag/AgCl	1 M Ca(ClO ₄) ₂ in TEGDME: H ₂ O = 4:1	147 */1000	64.7 */600/1000	144 *	94.6 *	[261]
(NH ₄) ₂ V ₇ O ₁₆	AC//Ag/Ag ⁺	0.5 M Ca(ClO ₄) in AN	116 */20	49.7 */50/20	7 *	103 *	[249]
V ₂ O ₅ ·0.63H ₂ O	AC//Ag/AgCl	1 M Ca(NO ₃) ₂ ·4H ₂ O (aq)	115 */5C	80.1 */350/5C	~350 *	99.5 *	[262]

Table 16. Cont.

Cathode	Counter/Reference	Electrolyte	Initial Reversible Capacity (mAh g ⁻¹ /mA g ⁻¹ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
K ₂ V ₆ O ₁₆ ·2.7H ₂ O	Pt//Ag/AgCl	5 M Ca(NO ₃) ₂ (aq)	94.0/50	78.3/100/50	94 *	104 *	[263]
			60.0/100	66.5/200/100	106 *	104 *	
K _{0.11} Co _{0.02} Mn _{0.98} O ₂ ·1.4H ₂ O @ carbon cloth	Pt//Ag/AgCl	2 M Ca(NO ₃) ₂ (aq)	103 */2000	93.5 */1000/2000	>1000	103 *	[255]
K ₃ V ₂ (PO ₄) ₃ /C	AC cloth	5 M Ca(OTF) ₂ (aq)	102 */100	91.6/500/100	>500	49.7	[258]
			89.1/500	71/6000/500	668 *	55.7 *	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Many vanadium-based layered cathodes were developed (Table 16). Vanadium exhibits multiple possible valence states from V⁵⁺ to V²⁺, so incorporating it into the host material can facilitate the reversible intercalation of Ca²⁺ ions. Not only that, reversible intercalation in MIBs has also been demonstrated with vanadium-based oxides [264], underscoring their potential in CIBs. Moreover, it was found that the presence of water of crystallisation helped to shield the strong charge density of Mg²⁺, reducing the diffusion barrier and improving electrochemical storage performance (Figure 21) [265]. This result highlights the potential of better Ca²⁺ intercalation due to its bulkier nature with lower charge density than Mg²⁺.

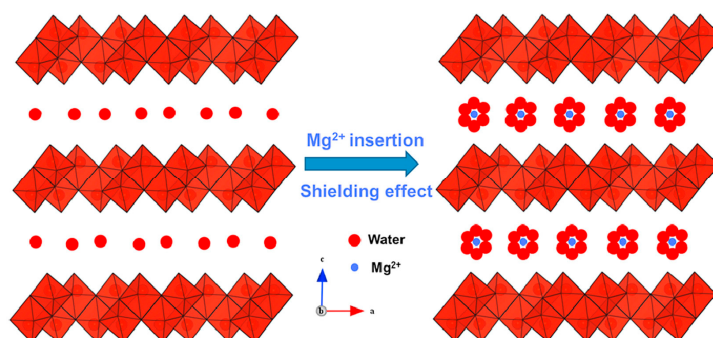


Figure 21. Shielding effect of Mg²⁺ in the hydrated V₂O₅·*n*H₂O. The strong polarisation of the divalent Mg²⁺ could be significantly reduced by solvating with water of crystallisation. Reprinted from Ref. [265], copyright (2024) Elsevier, with permission from Elsevier.

Double-sheet vanadium oxide, V₂O₅·0.63H₂O has been probed as a cathode material for CIBs by Chae et al. [262]. Its large interlayer spacing of >8 Å means that the water of crystallisation can be intercalated together with Ca²⁺, possibly further reducing the polarisation of the underlying lattice structure, along with the associated stresses and strains, as depicted in Figure 21. An illustration of the cathode material upon cycling is given in Figure 22. Consequently, good cycling stability was achieved even at a high rate of 5C (i.e., charging or discharging takes 1/5 h, or 12 min).

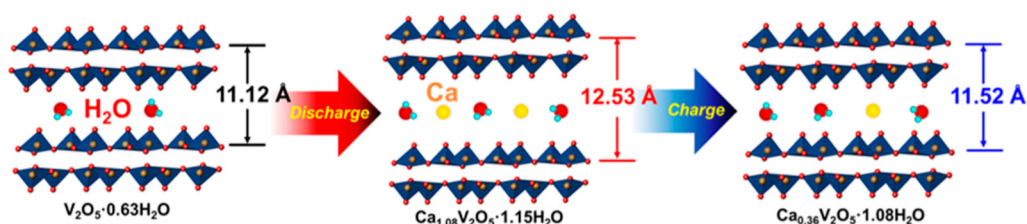


Figure 22. A conceptual illustration of the evolution of the DS-V₂O₅ structure upon cycling. Reproduced from Ref. [262] with permission from the Wiley Online Library.

The pre-intercalation of vanadium oxides is a promising strategy to improve their performance. Wang et al. [248] pre-intercalated Zn^{2+} ions into the interlayers of $\text{H}_2\text{V}_3\text{O}_8$, which acted as “pillar” ions, expanding the interlayer spacing to 1.8 nm to facilitate the easier intercalation of the Ca^{2+} ions (ionic radius = 0.099 nm). Furthermore, DFT calculations revealed that the intercalation of Zn^{2+} had improved the electrical conductivity of the cathode material, improving rate performance. Meanwhile, Zhao et al. [261] synthesised V_2O_5 pre-intercalated with various transition metal ions ($\text{M} = \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}$). Notably, they elucidated the effect of both the interlayer spacing and the physicochemical properties of the intercalants on the performance of the resultant cell. Interestingly, they found that pre-intercalating with Ni^{2+} , which resulted in the smallest M-O and M-V interatomic distances, performed the best. This suggests that beyond interplanar spacing, the role of the intercalant as an electrical bridge and stabiliser of the lattice structure must also be considered.

Manganese-based oxides are also a well-known electrochemical storage material but commonly face problems of unstable cycling due to Mn dissolution from the Jahn–Teller effect. To this end, Xu et al. [255] developed a 2% cobalt-doped cathode material, $\text{K}_{0.11}\text{Co}_{0.02}\text{Mn}_{0.98}\text{O}_2 \cdot 1.4\text{H}_2\text{O}$, on carbon cloth. It was found that cobalt-doping effectively inhibited the Jahn–Teller effect by strengthening the Mn–O bond, allowing for excellent long-term cycling stability with only ~6.5% capacity fade in 1000 cycles at 2 A g^{-1} . Interestingly, this cathode performed poorly in the analogous magnesium electrolyte $\text{Mg}(\text{NO}_3)_2$ due to the irreversible phase transition from layered to spinel and an accompanied reduction in active sites. Meanwhile, the larger Ca^{2+} prefers to occupy the octahedral site of the layered structure, thus inhibiting the unwanted phase transition.

4.6.2. Anode Materials

Due to the reactivity of the Ca metal in typical electrolytes and the tendency to form an electrically and ionically insulating SEI on the Ca metal surface, the Ca metal anode is not usually used in practical CIBs. Therefore, unlike other multivalent ion battery technologies like the ZIB, MIB, and AIB, alternatives to the pure metal anode must be further probed. Intercalation and conversion-type anodes have been explored (Table 17).

Table 17. Summary of the performance indicators of anode materials in the analysed CIBs; only half cells were included. All values are measured at room temperature.

Anode	Counter/Reference	Electrolyte	Initial Reversible Capacity ($\text{mAh g}^{-1}/\text{mA g}^{-1}$ or C Rate)	Capacity Retention (%/Number of Cycles/Rate)	Cycle Life	Initial Coulombic Efficiency (%)	Source
$\text{Na}_2\text{Ti}_3\text{O}_7$	AC	0.5 M $\text{Ca}(\text{TFSI})_2$ in DME	165/100	80.1 */300/100	~300 *	96.3 *	[266]
			74.7 */500	77.2 */2000/500	267 *	92.4 *	
Se/CMK-3	AC	0.25 M $\text{Ca}(\text{TFSI})_2$ in EC/DMC	265 */500	56 */300/500	12 *	89.6 *	[253]
Se/CMK-3	AC	6.25 M $\text{Ca}(\text{TFSI})_2$ (aq)	354 */300	53.6 */50/100	9 *	47.9 *	
Nitrogen-rich covalent organic framework with multiple carbonyls (TB-COF)	AC//Ag/AgCl	1 M CaCl_2 (aq)	183/5000	69.9/3000/5000	1543 *	99.6 *	[254]
Covalent organic framework with repeated pyrazine and pyridinamine units (PTHAT-COF)	AC//Ag/AgCl	6.67 M CaCl_2 (aq)	82.2/20,000	89.9/10,000/20,000	>10,000	100 *	[256]
PTCDI	AC cloth	5 M $\text{Ca}(\text{OTF})_2$ (aq)	131 */100	95.8/4500/100	>4500	99.5 *	[257]
			106 */1000	72.7/68,000/1000	29763 *	31.6 *	

* Data from figures were extracted to obtain these values using the PlotDigitizer online tool (Version 3.1.5.) [52].

Covalent–organic frameworks (COFs) are emerging in the field of electrochemical storage materials [267–269]. While both MOFs and COFs are porous materials built from basic building blocks, COFs use only lightweight organic elements to make up the overall polymer. This confers the advantage of a less dense material which can potentially translate to a higher energy density. Specifically, two-dimensional (2D)-COFs are widely praised for having extended π - π stacking for better electrical conductivity [270] and an aligned one-dimensional channel for effective ionic transport.

COFs allow the intricate and rational design of the electrode material, both microscopically and macroscopically: (1) it is easy to tune the functional groups of the individual molecules to incorporate redox-active sites, which would then be periodically repeating in the assembled COF, and (2) the resulting pore size is well-defined and tunable. To this end, Zhang et al. [254] and Wang et al. [256] rationally designed different COFs for use in aqueous CIBs. Zhang et al. synthesised a nitrogen-rich COF incorporating multiple carbonyls, where the C=C, C=N, and C=O functional groups served as active sites for Ca^{2+} intercalation (Figure 23a). A stable cycling performance was obtained at a high current density of 5 A g^{-1} . Wang et al. synthesised another COF based on repeating pyrazine and pyridinamine units, where C=N active sites were harnessed for Ca^{2+} storage (Figure 23b). At a high current density of 20 A g^{-1} , the COF displayed extremely stable cycling stability for 10,000 cycles, indicating the high reversibility of the Ca^{2+} binding process. Both groups have also demonstrated the effectiveness of their COF in full-cell aqueous CIBs with PBA cathodes (Table 15), underscoring their potential as next-generation CIB anode materials with high energy density and ultralong cycle life.

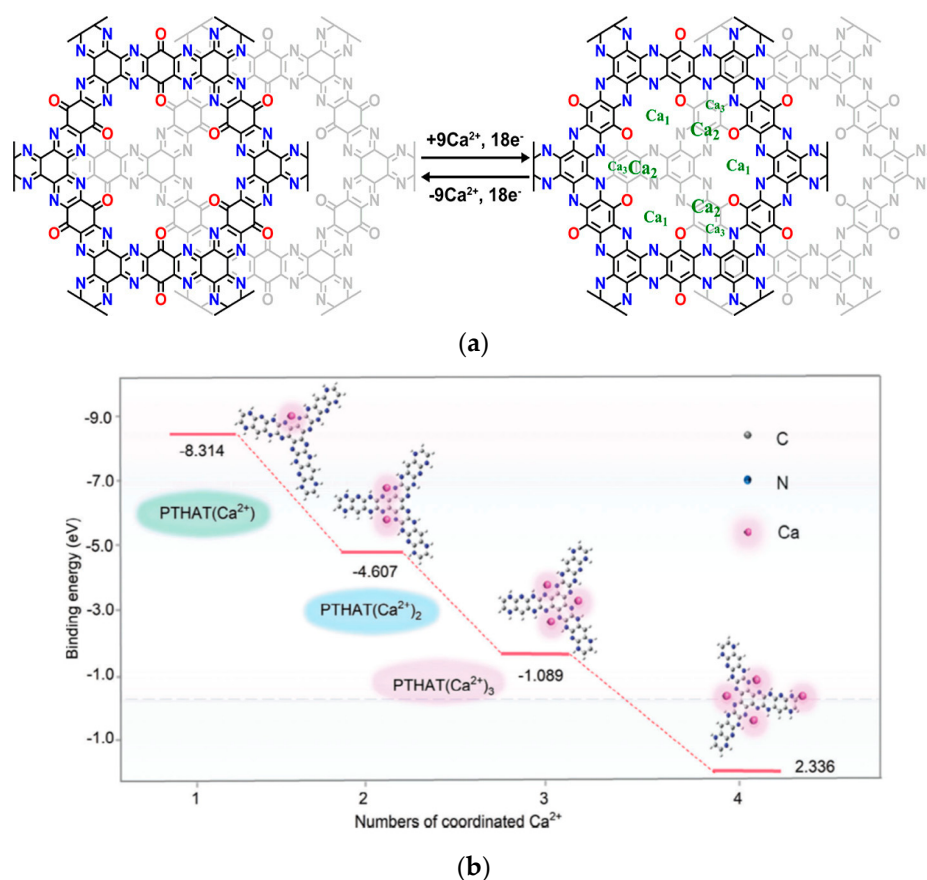


Figure 23. (a) The mechanism diagram of one-layer 2COF-18Ca₁. Reprinted with permission from Ref. [254]. Copyright 2023 American Chemical Society. (b) Structural evolution of PTHAT-COF repeat unit during the discharge process. Reproduced from Ref. [256] with permission from the Wiley Online Library.

Zhou et al. [253] explored the use of Se/CMK-3 as a conversion-type anode. Inspired by other metal–selenium batteries, this cathode utilises an ordered mesoporous carbon CMK-3 to trap the polyselenides and reduce the interface contact resistance. It operates based on a conversion-type reaction to reversibly incorporate Ca (Figure 24). Notably, they demonstrated the versatility of this anode in both aqueous and non-aqueous electrolytes, as both obtained an impressive initial capacity of above 250 mAh g^{−1}. However, their cycling stability should be further improved to realise a high-capacity anode material for CIBs.

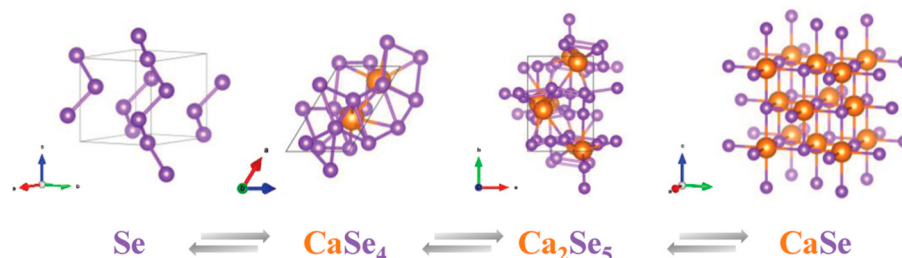


Figure 24. Computed electrochemical conversion path of Se electrode for CIBs. Reproduced from Ref. [253] with permission from the Wiley Online Library.

4.6.3. Electrolyte

Water-in-salt electrolytes are often used to expand the ESW by limiting free water content and suppressing the OER and HER side reactions, but the high salt concentrations potentially lead to low ionic conductivity and high viscosity, causing sluggish diffusion. To maintain a wide ESW while using a low salt concentration, Anh et al. [250] developed a hybrid electrolyte which uses a salt, $\text{Ca}(\text{ClO}_4)^-$, dissolved in a mixture of organic (acetonitrile) and aqueous solvents. Upon optimising the electrolyte system, the hybrid electrolyte displayed an ESW of ~3 V. Interestingly, the discharge capacity increased over the first 70 cycles, which the authors ascribed to the decomposition of the electrolyte or active material to form a stable SEI. Although a lower maximum reversible capacity was observed as compared to a similar system employing a purely organic electrolyte [246] (Table 15), this hybrid electrolyte showed a more stable cycling behaviour.

Solid-state electrolytes alleviate concerns regarding electrolyte leakage and thermal runaway but often come with limited ionic conductivity, which leads to poor performance. To this end, an ionic liquid gel electrolyte was developed by Biria et al. [247]. It is promising that an ionic conductivity of 10^{-4} to 10^{-3} S cm^{−1} was obtained at room temperature. However, the cycling performance of the reported full cell was unsatisfactory at a low rate of C/14. The authors ascribed this phenomenon to electrode degradation. Nonetheless, compatible electrodes must be developed before a practical battery of this type can be realised.

5. Discussion

5.1. Electrochemical Performance

A common basis had to be established for a fair comparison across the battery types. Thus, only full-cell data analysed in this review were compared. Ideally, battery C-rate is a gold standard for establishing common ground, as batteries subjected to the same C-rate would require the same time to charge and discharge fully. However, based on the data from the articles analysed in this review, only 25 full cells were tested based on C-rates, while other journals tested the cells based on a constant current density. Even among these 25 full cells, varying C-rates were used for testing, making comparison between these data points difficult. To overcome these limitations, we compared all full cells tested at current densities of 100 mA g^{−1} (30 data points) and 1000 mA g^{−1} (34 data points). For each current density, the initial capacities and cycle lives of the full-cell batteries were plotted in the form of a box-and-whisker plot (Figure 25).

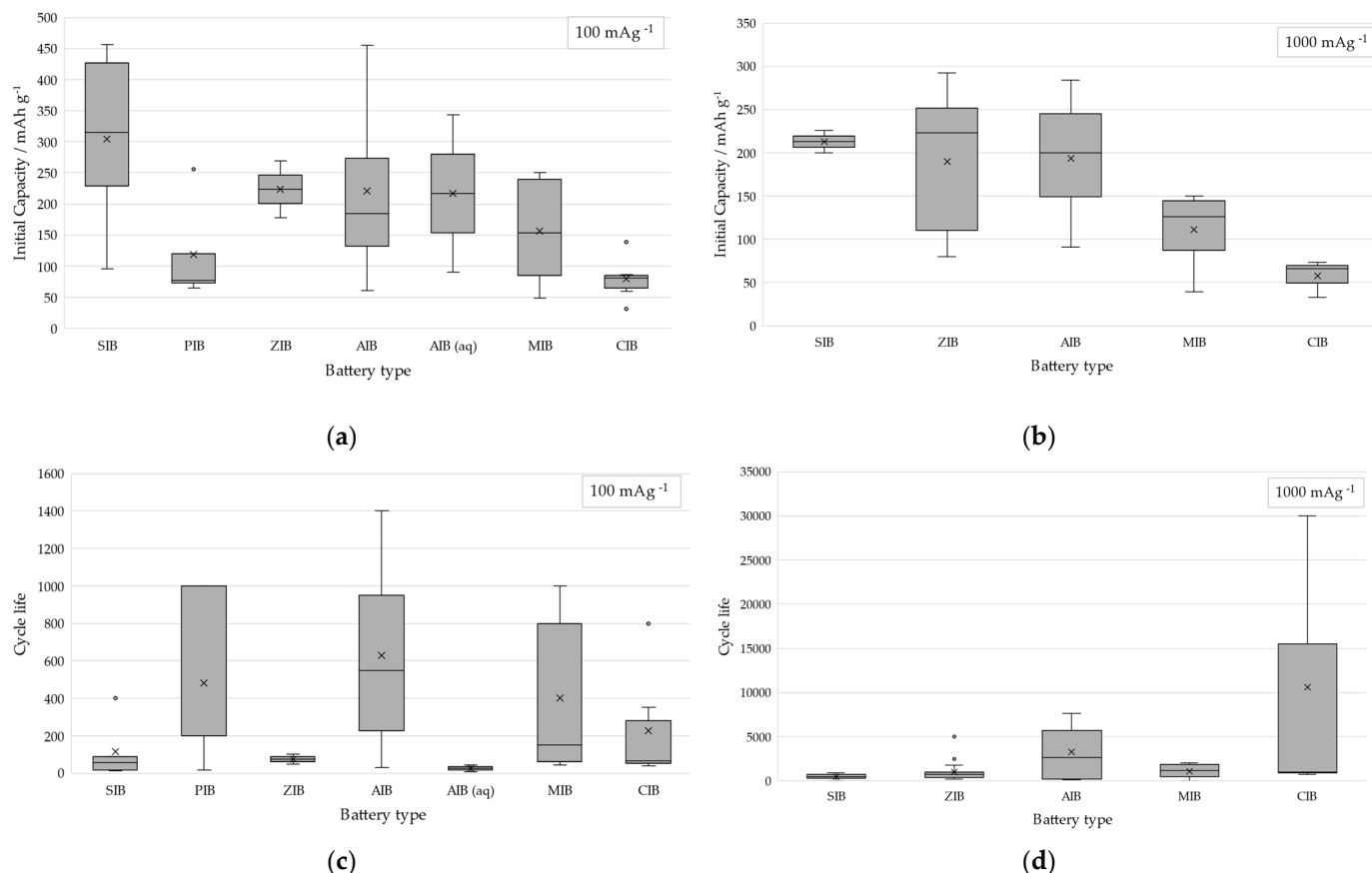


Figure 25. Box-and-whisker plots of initial capacity for full cells in this review at a current density of (a) 100 mA g⁻¹; (b) 1000 mA g⁻¹. Box-and-whisker plots of cycle life for full cells in this review at a current density of (c) 100 mA g⁻¹; (d) 1000 mA g⁻¹. All plots were generated using an inclusive median.

Before interpreting the data, it is important to acknowledge the limitations of this approach. Unfortunately, limited literature data were available for each battery system at each current density, specifically for the current density of 1000 mA g⁻¹, which is missing data from PIBs and aqueous AIBs. More importantly, in most instances, the initial capacity was normalised to the mass of the active material and not the entire battery mass, which affects how interpretable the data are. Some batteries have specific capacities still above 80% of their initial value at the end of electrochemical testing, which makes it difficult to extrapolate their actual cycle lives. For these cases, we have taken a conservative approach and used a cycle life which is equal to the number of cycles reported. Bearing these considerations in mind, one should not take these plots at face value, but rather analyse the underlying trends.

In the box-and-whisker plots, the line inside the box represents the median and the cross (x) represents the mean. The use of the median is more resistant to any outliers present in the dataset. The lower and upper edges of the box represent the 25th and 75th percentiles, respectively. Thus, the degree of spread of the data can be represented by the length of the box, called the interquartile range (IQR). The whiskers on each end of a box extend to the smallest and largest data points within 1.5 times the IQR. Any outliers outside of this range would be shown as a point on the graph.

Firstly, comparing the initial capacity of the different types of batteries (Figure 25a), SIBs show the most potential to deliver the highest energy densities. Notably, there is an observable decrease in the initial capacity of PIBs in the IQR. Two factors may contribute to this overall observation: (1) the greater atomic mass of potassium, which could translate to higher mass batteries for analogous systems, and (2) the more sluggish intercalation kinetics

of the bulkier K^+ ions as opposed to Na^+ due to more pronounced lattice interactions. In this review, Cao et al. [39] used the same MXene-based anode for both SIB and PIB systems, employing $Na_3V_2(PO_4)_3$ and $K_3V_2(PO_4)_3$ as the cathode material, respectively. They observed a similar trend consistent with our findings: the initial capacity of the SIB was higher than that of the analogous PIB. After 400 cycles at a current density of 100 mA g^{-1} , a specific capacity of 261.3 mAh g^{-1} was measured for the SIB compared to 138.7 mAh g^{-1} for the PIB.

The multivalent metal-ion batteries generally display comparable performance. Although each multivalent ion can transfer multiple electrons per ion, this is balanced by the potentially denser materials used and the more sluggish diffusion kinetics associated with a higher charge density ion. At a higher current density, initial capacities for each system generally decrease (Figure 25b). This is to be expected, as an increased charge-transfer resistance can lead to a higher overpotential and the rate of transfer of ions becomes diffusion-limited at higher current densities. At both current densities, CIBs perform worst among the beyond-lithium batteries. This points to the more nascent CIB landscape; more research would be needed to develop suitable systems to reduce overpotentials and allow the accommodation of Ca^{2+} ions into more active sites without undesirable side reactions. It is difficult to infer clear-cut trends from the cycle life box plots (Figure 25c,d). This is partly because the batteries were subjected to different numbers of testing cycles. However, when comparing the median, AIBs seem to show the best cycle life at both current densities. The spread of data in general is large, indicating that the general long-term performance of a battery is very specific to the system in question.

A few works in this review directly compare the performance of analogous LIB and SIB systems. Ru et al. [56] compared the half-cell performance of the MoS_2/SnS hollow super-assembly in an organic carbonate electrolyte with lithium and sodium foil as the counter electrodes. Although the current densities used are not equal, the initial capacity of the LIB half-cell ($\sim 1000\text{ mAh g}^{-1}$) is greater than its SIB counterpart ($\sim 600\text{ mAh g}^{-1}$). Sun et al. [48] observed the same trend with the LIB half-cell having an initial capacity of $\sim 1030\text{ mAh g}^{-1}$, compared to $\sim 580\text{ mAh g}^{-1}$ for the SIB half-cell at a current density of 100 mA g^{-1} . Such findings highlight the difficulty of achieving energy densities competitive with the state-of-the-art LIBs.

This is no reason to avoid pursuing beyond-lithium batteries. Granted, lithium is ideal for energy storage, being a lightweight element with excellent intercalative ability due to its small ionic radius. However, it is important to recognise that the priorities of the battery properties will depend heavily on the type of application. In grid applications, factors like low cost and excellent long-term stability might take precedence; in EVs, their mileage and hence the energy density and rate performance of the battery might be higher on the priority list. To be pragmatic, we should strive for the adoption of beyond-lithium batteries in applications not requiring very high energy or power output. We must recognise that it is unlikely for applications strictly requiring high energy densities (such as EVs) to switch away from LIBs in the near future. Meanwhile, we can leverage the long-term cycling stability of beyond-lithium batteries, which can be comparable to LIBs. Throughout this review, some reports have demonstrated excellent cycling stability in different battery systems [99,146,203,257]. Furthermore, multivalent ion batteries allow the direct use of a metal anode, which drastically improves volumetric energy density. These advantages could potentially allow the specialised application of beyond-lithium batteries.

5.2. Sustainable Growth

In the grand scheme of things, improving the energy density and rate performance (measured by C-rate) of batteries helps battery energy storage systems (BESS) become increasingly viable. In the event of a large mismatch between the supply and demand of electricity, the batteries may need to (dis)charge at a high rate to accommodate for the difference. Incorporating BESS into the electrical grid makes renewable energy more efficient through peak-shaving or load shedding (i.e., storing the excess energy first and

releasing it later when demand increases, Figure 26) [271]. This idea is intimately linked to our long-term ambition of using clean energy to power our world [272,273], which means that there is also a need for sustainable development of our battery technology.

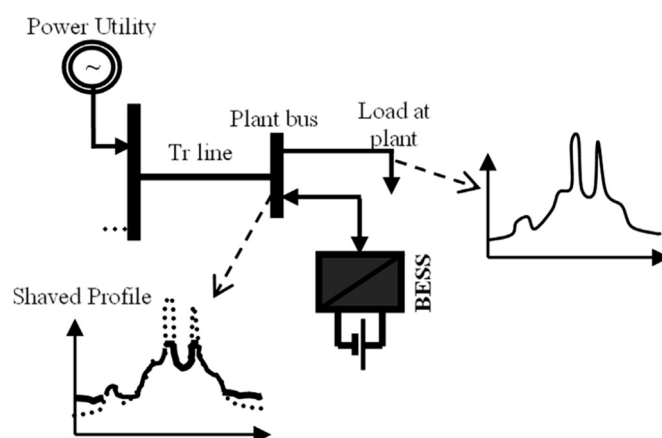


Figure 26. Load peak shaving by battery energy storage system. Reproduced from Ref. [274], copyright (2014) Elsevier, with permission from Elsevier.

A key factor motivating the push towards beyond-lithium batteries is the scarcity of crucial metals used in state-of-the-art LIBs today, such as lithium and cobalt. Using the European Union as a case study, the first list of critical raw materials (CRMs) was introduced by the European Commission (EC) in 2011, which aimed to identify the raw materials that carry high economic impact but also a relatively high supply risk in Europe [275]. Notably, lithium was first identified to be a CRM in the 2020 report. Recently, manganese and nickel were added to the 2023 list as strategic raw materials (SRMs), as the EU recognises their crucial role in battery production but has concerns regarding their domestic supply chains. It can thus be seen that the raw materials used for LIB manufacturing are becoming increasingly scarce, partly driven by their ever-increasing demand, and efforts to develop beyond-lithium batteries should moderate the use of these CRMs if practically feasible. However, it was observed throughout the review that some beyond-lithium batteries incorporated lithium, cobalt, and nickel. In some chemistries, this was carried out to achieve acceptable battery performance and long-term cycling stability. For instance, manganese-based oxides are a common class of intercalation-type electrode materials which commonly show relatively good specific capacities. Among the promising SIB batteries, 13 out of 22 full cells in this review contain the CRMs of Li, Co, Mn, and Ni (Table 3). There is hence a difficult balance to strike between the goals of sustainability and practical battery performance.

In evaluating the sustainability of beyond-lithium technologies, beyond the criticality of the raw materials used, the whole battery's life must be considered. This ranges from the extraction of raw materials and battery manufacturing to its daily operation and recycling. Figure 27 shows the carbon dioxide emissions from a typical LIB, which we should strive to improve upon in beyond-lithium batteries. Notably, half of the total emissions come from raw material extraction and refining; lithium and cobalt mining practices also have the potential to cause social injustices and destruction to local habitats [276]. Fortunately, the shift away from LIBs has the potential to bring about a greener battery market. For instance, sodium and SIB electrodes can be more easily extracted from sea salt (seawater has significant quantities of Na, Mg, and Ca) [277], potentially leaving a lower carbon footprint, and Li/Co-free electrode materials can be developed.

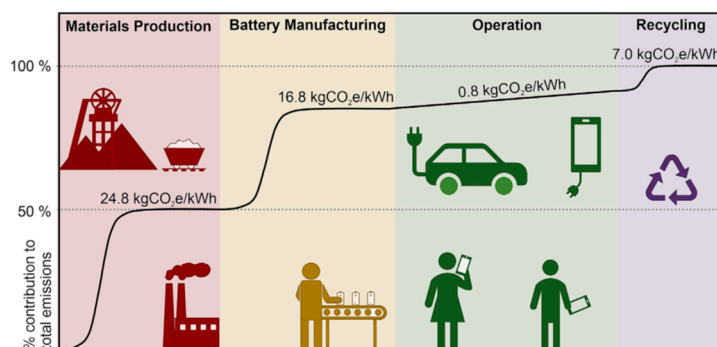


Figure 27. CO₂ emissions of LIB production, manufacturing, operation, and recycling. Emissions for the operation (or charging) were estimated using the Greenhouse Gas Emissions from Electric and Plug-In Hybrid Vehicles—Results from the US Department of Energy and converted assuming a 40 kWh battery has a range of 226 miles. Reprinted from Ref. [278], copyright (2024) Elsevier, with permission from Elsevier.

First, the manufacturing process of a next-generation battery should be scalable and sustainable for it to be congruent with clean energy. AZIBs not only use materials that are relatively abundant (aqueous electrolyte, zinc), but they are oxygen- and moisture-stable, which means that they can be reliably assembled in air. This is unlike other battery types, such as the Group 1 metal-ion batteries, which require an argon-filled or inert environment to be assembled, potentially adversely impacting their scalability and increasing manufacturing costs.

Second, to keep the next-generation batteries sustainable, end-of-life solutions must also be explored. To this end, it is important to take into consideration the waste management hierarchy. Before recycling, reusing is higher on the priority list as it reduces the energy costs incurred from material sorting and processing. An end-of-life battery can be repurposed for another application with a lower energy requirement provided it has a sufficiently good state of health, for example from retired EV batteries to BESS in Germany, the Netherlands, and Japan [279,280]. After repurposing, recycling completes the circular flow of materials, allowing the recovered materials to be used to produce more batteries. Recycling methods are being actively explored for LIBs using various techniques like pyrometallurgy and hydrometallurgy [281]. However, only 44.6 wt% of portable batteries sold in the EU were collected for recycling in 2021 [282]. Gaines et al. [283] estimated the global LIB recycling rate to be 59% in 2019. Such a dismal figure exacerbates the scarcity of CRMs as many new batteries will need to be manufactured. Ideally, a recycling rate as close to 100% as possible will mean a greatly reduced reliance on new raw materials. Fortunately, there are signs that efforts to make electrodes from recycled materials that display good electrochemical performance could be practically achievable [284,285], although more research has to be done in this area to ascertain these findings. In essence, upon the eventual widespread adoption of beyond-lithium batteries, we must be equipped with the know-how and awareness of recycling these batteries to close the “sustainability” loop for a greener battery economy. Figure 28 shows a schematic illustrating the methods we can use to achieve a circular battery economy.

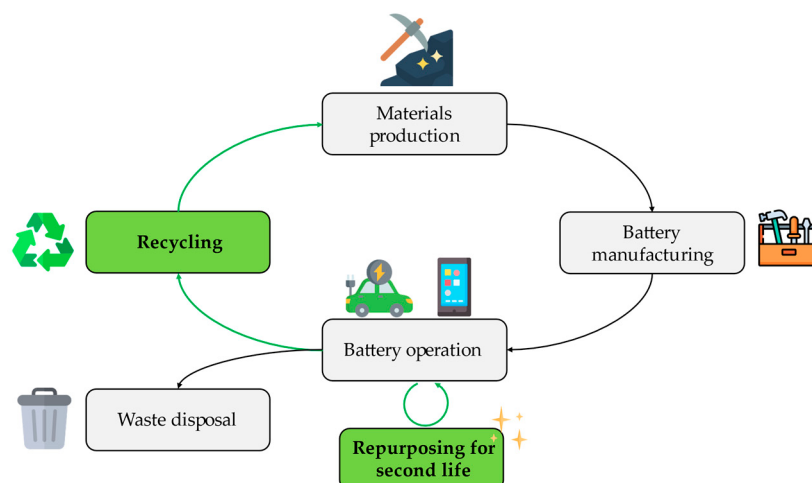


Figure 28. A schematic highlighting the potential solutions (in green) for a circular battery economy. Free-for-use icons made by Freepik, Konkapp, Smashicons from www.flaticon.com, accessed on 12 September 2024.

The technical aspect of battery recycling comes with many challenges. Upon reaching the end of its life, each battery needs to be first discharged, then separated and sorted into its various components, which brings about an inherent safety risk. Current research is largely focused on improving the recovery of critical metals like Li, Co, Ni, and Mn from cathodic black mass using a combination of hydrometallurgy, pyrometallurgy, and, more recently, bio-leaching [286,287]. Leaching agents like deep eutectic solvents (DES) are capable of displaying great recyclability and leaching efficiencies of typically >90% [288,289]. However, as highlighted by Neumann et al. [290], most of these recycling methods have only been tried in lab-scale experiments. The scale-up to industrial processes will be tricky with various chemical leaching agents due to cost and safety considerations. For similar battery systems employing intercalation-type electrodes, similar methods can eventually be adopted for beyond-lithium batteries, but scaling up will likewise be an issue. It should be noted that most ZIBs, AIBs, and some MIBs and CIBs use the metal directly as the anode. Although commercial LIBs do not use a metal anode, a more efficient recycling process is possible, as metals are more homogeneous than layered ionic compounds, which tend to incorporate many elements. In fact, the zinc metal has been demonstrated to be upcycled from spent ZIBs through thermal treatment, exhibiting favourable properties like a lower overpotential, lesser extent of dendrite formation, and higher reversibility than the commercial Zn foil [291]. This shows the promise of a more efficient recycling process for future beyond-lithium batteries, although more work needs to be carried out in scaling up to the industrial level.

5.3. Safety Considerations

Since the commercialisation of LIBs, they have attained a reputation for being prone to thermal runaway caused by overcharging, overheating, and mechanical puncture, leading to fires and explosions, which compromise safety [292,293]. Therefore, the prospect of safer and more durable batteries was one of the key motivations behind the development of beyond-lithium batteries. However, changing the active metal ion does not automatically make the system safer—Group 1 metals like sodium and potassium are unstable in ambient air and react violently with water; zinc metal is prone to dendritic growth, which could lead to separator puncture and internal short-circuiting; certain alternative battery systems also employ an organic electrolyte which is inherently flammable. It is thus crucial to investigate the thermal runaway hazards of beyond-lithium batteries.

Yue et al. [294] recently published their work detailing the comparison of thermal runaway hazards between LIBs and SIBs using accelerating rate calorimetry (ARC). They found that the safety of the NTM battery (cathode: Na_xTMO_2) was worse than the LFP

battery but better than the NCM battery (cathode: $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$) (Figure 29). However, as far as we are aware, no other reports detailing similar investigations for other beyond-lithium battery systems are present in the literature. This is an area for future research, as the knowledge of this information is vital for the complete characterisation of the different battery systems and can guide future research into safer and promising technologies (e.g., solid-state electrolytes or aqueous systems).

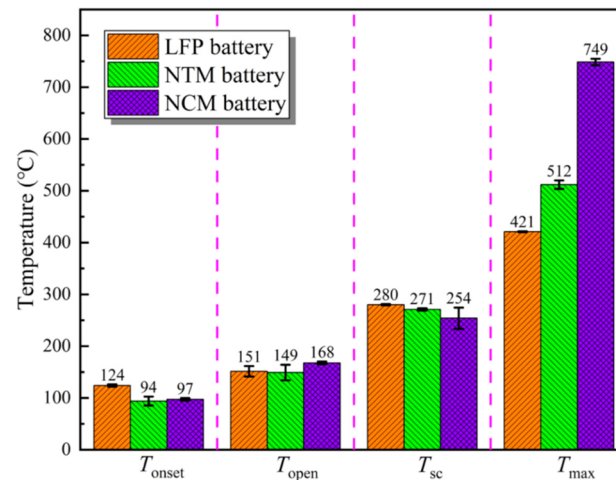


Figure 29. Comparison of the characteristic temperatures of the three types of batteries. T_{onset} represents the temperature where self-heating occurs; T_{open} represents the temperature at which the battery's safety valve is opened to release pressure; T_{sc} represents the temperature at which the separator collapses, resulting in internal short-circuiting; T_{max} represents the maximum temperature during thermal runaway. Reprinted from Ref. [294], copyright (2024) Elsevier, with permission from Elsevier.

Some battery chemistries are inherently safer than others. Although all components have a role to play in contributing to overall battery safety, the electrolyte often exacerbates the consequence of a thermal runaway event. The last stage of thermal runaway involves electrolyte combustion, which is facilitated by the high temperature and the presence of oxygen due to SEI decomposition, cathode decomposition, and other exothermic chemical reactions. The heat produced increases the combustion rate, further increasing the temperature and continuing the feedback loop [295]. The large amount of gases produced leads to pressure build-up in the containment system that eventually results in an explosion. The degree of flammability of the liquid electrolyte is determined by its flash point; a lower flash point indicates a lower temperature requirement for the ignition of electrolyte vapour due to exothermic combustion reactions. Therefore, one important parameter of battery safety is the flash point of the electrolyte used. Figure 30 shows the flash points of the most used liquid electrolytes of the analysed papers in this review, in ascending order.

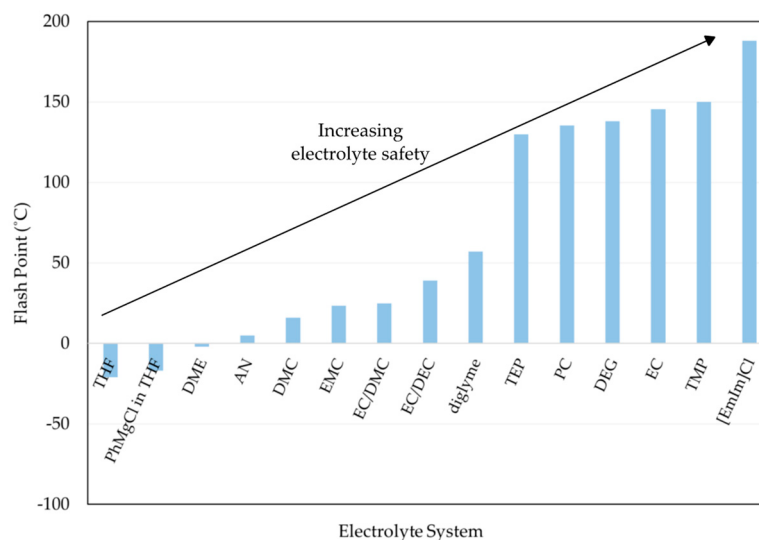


Figure 30. The flash points of commonly used liquid electrolytes in this review, sorted in ascending order; the electrolytes are thus sorted in terms of increasing safety. Note that water and solid-state electrolytes do not have flash points. The data were obtained from Refs. [296–298].

Out of the liquid electrolytes, [EmIm]Cl has the highest flash point. The AlCl_3 /[EmIm]Cl electrolyte commonly used by AIBs is thus relatively safer than other liquid electrolytes. Trimethyl phosphate (TMP), with the second-highest flash point, is a known fire-retardant and is sometimes added into the electrolyte as an additive to lower the overall flammability of the composite electrolyte [299]. Although it is true that THF (used in the APC electrolyte) and AN have very low flash points, making these electrolytes used in MIBs the most combustible, this risk may be mitigated by the fact that Mg exhibits excellent dendrite-free plating morphology. Organic carbonates and ethers commonly used in SIBs and PIBs have flash points somewhere in between.

Aqueous and solid-state electrolytes are comparatively safer in terms of a substantially lower risk of combustion. For aqueous electrolytes, the AZIB battery technology shows promise with good cycle life—recent research has also demonstrated that non-dendritic growth onto Zn metal is possible with the right choice of separator material, reducing the probability of a thermal runaway event. In a review on LIB safety, Liu et al. [295] suggested the development of solid-state electrolytes as the ultimate solution for the safety issues of LIBs. Not only would the risk of internal short-circuiting be greatly reduced, but the resulting impact of a thermal runaway incident would also be less serious given the absence of a flammable electrolyte. However, from this review, only a small fraction of articles (5 out of 160, i.e., ~3%) report on the development of solid-state electrolytes. This is indicative that the technological readiness level of liquid-based electrolytes far exceeds that of their solid-state counterparts, suggesting that further research and development is required before solid-state batteries become a viable alternative.

The electrochemical cell merely represents the barebones chemistry and materials engineering required to achieve reliable and reversible charge production. In practical, large-scale applications, batteries could comprise several cells connected in series and/or parallel to meet voltage requirements. Having a real-time readout of battery indicators like the state-of-charge (SOC) and state-of-health (SOH) would be extremely helpful and contribute to overall battery and user safety. The battery management system (BMS) tracks the real-time voltage, current, and temperature of the battery, thereby preventing overcharging/discharging and providing appropriate warnings of failures based on the data trends. There is an entire research area dedicated towards the integration of batteries with reliable and accurate BMS and the intricacies of hardware and software integration [300,301], which is especially paramount for the large batteries used in EVs [302]. For example, determining the placement of temperature sensors and communication between different modules (e.g.,

temperature sensor, voltage and current acquisition units), as well as with the overall system (e.g., the vehicle control unit in EVs) [303].

Beyond ageing-related safety concerns, sudden and unpredictable battery failures must also be mitigated. Upon the detection of an abnormally high current indicative of a short-circuit, or a dangerously high temperature which points to a possible thermal runaway incident, the design of the battery pack must incorporate multiple safety features to prevent escalation. Multiple cell-level and battery package-level safety mechanisms have been developed [304] and multiple levels of safety mechanisms should be incorporated to minimise safety risks. For instance, current-interrupting devices like fuses as well as safety vents to alleviate pressure build-up due to electrolyte decomposition are useful as a last resort to prevent catastrophes should thermal runaway occur.

6. Conclusions and Future Outlook

While LIBs indeed have their drawbacks, the need to develop beyond-lithium batteries goes beyond the issues of sustainability and safety. With the push for renewable energy sources, EVs, and the increasingly digitalised world we live in, the demand for batteries will increase. Yet, the supply of the critical raw materials required to produce LIBs is ever-declining. It is not a question of *if* but *when* the cost of LIBs will rise to the point of commercial infeasibility. Therefore, in this review, we have evaluated the promising chemistries and electrode/electrolyte materials for sodium-ion, potassium-ion, magnesium-ion, aluminium-ion, zinc-ion, and calcium-ion batteries. Among these, sodium-ion batteries seem to show the most promise in terms of initial capacity. Meanwhile, aqueous zinc-ion batteries are inherently safer and have been demonstrated to exhibit stable cycling performance with commendable specific capacity, thus receiving increasing research attention.

Nevertheless, batteries represent only one jigsaw piece of the energy puzzle. Both sustainable energy generation and sustainable energy storage are crucial for sustainable growth. A seamless integration of these next-generation technologies is required to maximise our energy efficiency. The progress in non-lithium battery technology underscores their potential to revolutionise the energy storage landscape and contribute to a sustainable future. However, being burgeoning fields relative to LIBs, these beyond-lithium technologies have not reached the level of sophistication for commercial adoption. As such, we have listed a few prospects and suggestions for future research into beyond-lithium battery systems:

1. *Standardise electrochemical testing procedures and reporting.* To aid the interpretability of the results, authors should report their electrochemical testing in terms of C-rate. Reporting based on current density can be inconsistent across publications as the mass used can vary from the mass of an active material (anode/cathode) to the mass of the entire battery.
2. *Increase focus on full cell fabrication.* While half cells are excellent tools to optimise conditions with respect to one electrode, full cells need to be tested to push the development of practical, real-world batteries.
3. *Test batteries under real-world conditions.* To translate the most promising batteries from laboratory to commercialisation, testing them in real applications entails varying charging and discharging rates, which is a good gauge in determining the suitability of the battery.
4. *Decrease reliance on critical raw materials.* Future beyond-lithium batteries must at least reduce our reliance on CRMs like cobalt to avoid the recurrence of resource scarcity in the short to medium term.
5. *Develop scalable battery recycling procedures.* To ensure the sustainability of our battery needs, we should reduce first-life battery waste by recovering the precious materials in a battery. The recovered materials could then be used to reproduce new battery electrodes, reducing strain on resource production.
6. *Explore aqueous and solid-state electrolytes.* These systems show promise to be safer and thus could promote easier adoption into real-world applications.

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Nomenclature

Abbreviations	Definition
AAIB	Aqueous aluminium-ion battery
AC	Activated carbon
AFM	Atomic force microscopy
AIB	Aluminium-ion battery
AN	Acetonitrile
APC	All-phenyl complex solvent
AZIB	Aqueous zinc-ion battery
BMS	Battery management system
CIB	Calcium-ion battery
COF	Covalent–organic framework
CV	Cyclic voltammetry
DEC	Diethyl carbonate
DEG	Diethylene glycol
DFT	Density functional theory
DMC	Dimethyl carbonate
DME	Dimethyl ether
EC	Ethylene carbonate
EDL	Electric double layer
EG	Ethylene glycol
EMC	Ethyl methyl carbonate
[EmIm]Cl	1-ethyl-3-methylimidazolium chloride
ESW	Electrochemical stability window
EV	Electric vehicle
FEC	Fluoroethylene carbonate
HC	Hard carbon
HCF	Hexacyanoferrate
HER	Hydrogen evolution reaction
ICE	Initial coulombic efficiency
KFSI	Potassium bis(fluorosulfonyl)imide
KPB	Potassium Prussian blue
KNHCF	Potassium nickel hexacyanoferrate
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
MAB	Metal–air battery
MIB	Magnesium-ion battery
MOF	Metal–organic framework
NASICON	Sodium (Na) super ionic conductor
NC	Nitrogen-doped carbon
NCA	Nickel cobalt aluminium oxide
NMC	Nickel manganese cobalt oxide
NSG	N/S dual-doped graphitic hollow architectures

OER	Oxygen evolution reaction
PANI	Polyaniline
PBA	Prussian Blue analogue
PC	Propylene carbonate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEG	Poly(ethylene glycol)
PEGDA	Poly(ethylene glycol) diacrylate
PIB	Potassium-ion battery
PTCDA	Perylenetetracarboxylic dianhydride
PTCDI	3,4,9,10-perylenetetracarboxylic diimide
rGO	Reduced graphene oxide
RTIL	Room-temperature ionic liquid
SC	Soft carbon
SEI	Solid–electrolyte interface
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SIB	Sodium-ion battery
TEGDME	Tetraethylene glycol dimethyl ether
TEP	Triethyl phosphate
TFSI	Bis(trifluoromethanesulfonimide)
THF	Tetrahydrofuran
TMD	Transition metal dichalcogenides
TMP	Trimethyl phosphate
XRD	X-ray diffraction
ZIB	Zinc-ion battery

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