

# Batteries for Future: A New Alternative of Li-ion Battery

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## **Abstract.**

The rapid evolution of energy storage technology has necessitated the exploration of alternatives to conventional Li-ion batteries. It is driven by the limitations of resource scarcity, safety concerns, and sustainability challenges. This chapter critically discusses the technical, economic, and environmental aspects of emerging battery technologies. While Li-ion batteries are instrumental in powering electronics, electric vehicles, and renewable energy systems, their reliance on limited lithium and cobalt deposits, flammability risks, and recycling hurdles necessitate the development of next-generation solutions. A compelling alternative is solid-state batteries based on non-flammable ceramic, polymer, and glasses. These batteries feature enhanced safety, higher energy density, and improved thermal stability. These parameters satisfy applications in vehicles. Yet, challenges related to manufacturing scalability, interfacial resistance, and cheap production persist. Na-ion batteries gain researchers' attention due to the low cost of sodium. Despite their lower energy density compared to Li-ion, recent advancements in cathode and anode materials can decrease the performance gap. Another promising avenue is lithium-oxygen and zinc-air systems. The latter offer theoretical energy densities surpassing the ones of Li-ion systems. Oxygen management, electrolyte degradation, and limited cycle life remain limiting barriers. Redox flow batteries, particularly vanadium and organic redox flow systems, provide scalable solutions for long-duration performance, though their bulkiness and lower energy density eliminate their compatibility with tablets and smartphones. Mg-, Ca-, and Al-ions are cheap and offer high theoretical capacities. A slow-ion kinetics must be dealt with in the future. Organic and biodegradable batteries leverage eco-friendly materials and designs, while their current

performance limitations restrict them to niche applications. Presently, Li-ion remains the dominant player due to its established infrastructure and cost-effectiveness. Therefore, recycling and sustainability efforts, such as closed-loop recovery systems and ethical sourcing initiatives, are critical in minimizing the ecological footprint of Li. Technological optimizations and machine-learning optimizations are essential for the future of energy storage and portable devices.

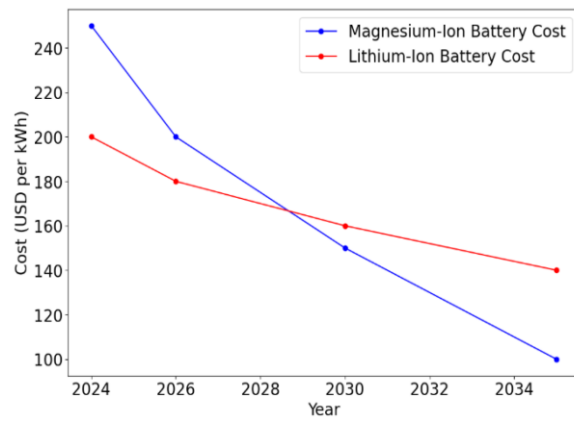
## **Demand for Alternatives to Li-ion Batteries**

The global demand for energy storage and portable energy sources is undergoing unprecedented growth. It is driven by the rapid expansion of electric vehicles, renewable energy integration, and miniaturized electronic devices. Li-ion batteries have been at the forefront for three decades. Li-ion batteries offer high energy density, relatively long cycle life, and acceptably low self-discharge rates. These characteristics make these batteries a preferred choice for a wide range of applications. Despite their dominance in the market, several critical limitations of Li-ion batteries become increasingly apparent. These shortcomings necessitate the exploration of alternative chemistries that address persisting challenges yet maintain competitive performance according to, at least, a few categories of requirements.

One of the primary concerns mentioned continuously in the context of Li-ion batteries is the scarcity and ethical sourcing of key raw materials. This criticism relates particularly to lithium, cobalt, and nickel. The extraction of these metals involves environmentally damaging mining practices. Brine evaporation for lithium is used, It consumes vast amounts of water in arid regions. Artisanal cobalt mining raises essential ethical concerns regarding labor conditions and human rights. The concentration of raw material supplies in specific locations implies a significant amount of uncertainty. Democratic Republic of the Congo accounts for over seventy percent of global cobalt production. In turn, the "Lithium Triangle" (Argentina, Bolivia, and Chile) holds a significant fraction of the world's lithium reserves. This situation creates supply chain

vulnerabilities. It threatens long-term battery production stability and unfavorably affects the market costs of resulting Li-ion batteries. As global demand for rechargeable energy storage devices continues to surge, the need for elaborating alternative chemistries becomes more and more urgent. The development of a more sustainable global economy would prefer the reliance on more abundant, ethically sourced, and environmentally sustainable materials. Other alkali and alkali earth metals can potentially take the place of lithium. e.g., sodium, potassium, magnesium, calcium, and even aluminum. Yet, the sizes of the corresponding cations are larger than that of lithium, undermining the energy densities of the resulting batteries (Ahn et al., 2017a).

Beyond resource concerns, safety, and thermal management remain persistent challenges in Li-ion technology (Figure 1). The use of flammable organic liquid electrolytes in conventional Li-ion batteries introduces a danger of thermal runaway. The latter represents a self-sustaining exothermic reaction that leads to catastrophic failure in extreme conditions. Thermal runaway is linked to battery fires in electric vehicles, laptops, and aerospace applications. The questionable safety of Li-ion batteries prompts systematic research into non-flammable electrolyte alternatives. Therefore, solid-state batteries replace liquid electrolytes with ceramic, polymer, or glass-based materials. Solid-state batteries offer enhanced safety and a certain potential for attaining higher energy densities. However, interfacial resistance, manufacturing complexity, and cost represent the challenges to be addressed before solid-state batteries can boast of widespread commercial adoption (Ahn et al., 2017b).



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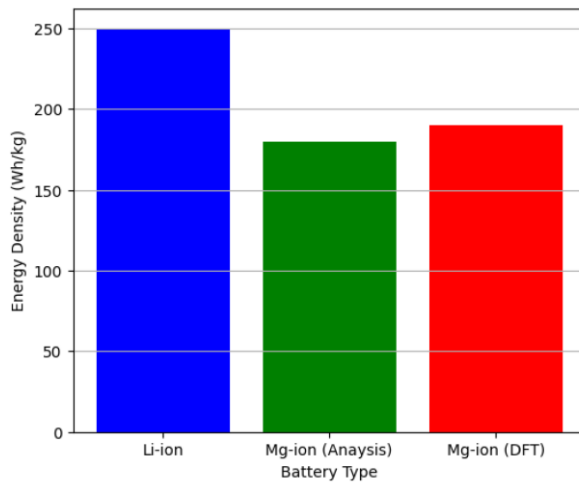


Figure 1. (Top) The forecast of the production cost evolutions of Li-ion and Mg-ion batteries during the next decade. (Bottom) Comparison of stored energy density in Li-ion batteries and Mg-ion batteries. Reproduced from (Malachi et al., 2025). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Another pressing issue is battery degradation and longevity, which directly impact the economic viability and sustainability of energy storage systems. Li-ion batteries, particularly those using high-nickel cathodes and silicon-based anodes, experience accelerated capacity fading under high-power applications and fast charging scenarios. Degradation mechanisms including (1) lithium plating, (2) dendritic growth, and (3) electrolyte decomposition reduce battery lifespan. Furthermore, they contribute to waste generation and sophisticated recycling challenges. Despite obvious progress in the field during the last decades, currently marketed Li-ion recycling rates remain to be fairly low. According to the estimates, less than 5% of Li-ion batteries are effectively

recycled. Traditional recycling methods, such as pyrometallurgy and hydrometallurgy, are energy-intensive. Economically viable direct recycling and closed-loop recovery strategies are urgent. These solutions preserve valuable materials for reuse and minimize waste (Alfaruqi et al., 2017). As the world energetics transitions toward decentralized energy systems and electrified transportation, the limitations of Li-ion batteries are increasingly troublesome. These are resource constraints, safety concerns, recycling inefficiencies, and price volatility as discussed in the above paragraphs. In this chapter, we highlight the most promising alternatives to the current state of the Li-ion technology. We examine their technical feasibility, economic potential, and environmental impact. We strive to provide a comprehensive overview of the future landscape of energy storage and critically forecast the most viable pathways for next-generation batteries. The emerging societal demands of building a carbon-neutral future are accounted for in the proposed discussion.

### **Context of Li-ion Battery Development**

The development of modern battery technology represents a continuous pursuit of higher energy density, improved safety, and sustainable energy storage. While Li-ion batteries have become the dominant energy storage solution in the 21st century, their evolution originated from a long history of electrochemical discoveries and technological breakthroughs. The origins of rechargeable Li-ion battery technology as a learning technology are traced back to the 1850s when the development of lead-acid batteries took place. Those were among the first practical rechargeable battery systems. Although lead-acid batteries offered a reliable means of energy storage, they exhibited a low energy density, a heavy mass, and limited cycle life. These drawbacks make them unsuitable for modern portable applications. The next major advancement came already in the second half of the 20<sup>th</sup> century with the commercialization of nickel-metal hydride batteries. The latter found widespread use in early consumer electronics, such as digital cameras and mobile phones. Nickel-metal hydride batteries offered higher energy density and reduced toxicity compared to lead-acid batteries. Yet, they suffered from memory effects and relatively short lifespans, which limited their scalability for high-performance applications. It was the

introduction of Li-ion batteries in the early 1990s that marked a turning point in energy storage technology. Li-ion batteries leveraged the lightweight and high electrochemical potential of lithium. Compact and high-energy-density power sources revolutionized portable electronics, electric vehicles, and renewable energy storage (Figure 2).

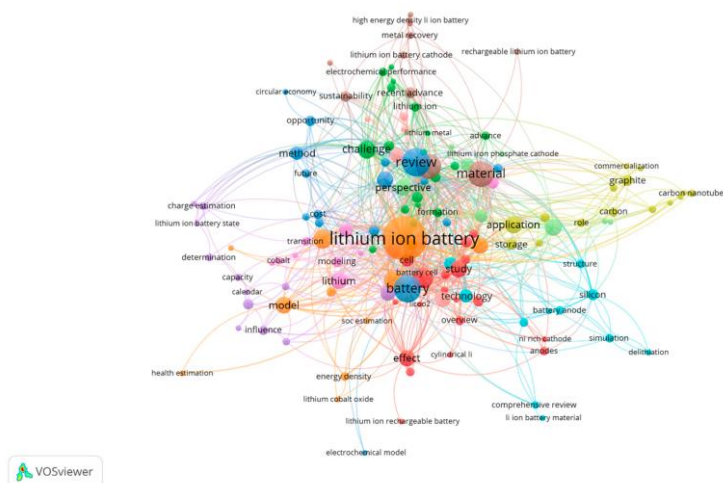


Figure 2. The clustered network visualization map depicting regularly proposed keywords related to Li-ion batteries. Reproduced from (Kumar et al., 2020). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Despite the success of Li-ion batteries, their limitations spurred ongoing research into alternative chemistries and novel materials in the 21st century. The scarcity of lithium and cobalt, coupled with safety concerns associated with flammable liquid organic carbonates, led one to explore solid-state batteries, Na-ion batteries, K-ion batteries, Mg-ion batteries, Ca-ion batteries, Al-ion batteries, metal-air batteries, and flow batteries as potential successors. These emergent technologies aim to address the technical, economic, and environmental challenges of Li-ion batteries and maintain their performance metrics. While solid-state batteries and Na-ion batteries have been the focus of research in physical chemistry and electrochemistry for over a decade, their large-scale commercialization does not look to be a ready process shortly. Other technologies are even less developed to exhibit commercial competitiveness. Understanding the historical trajectory of battery development provides crucial insights into the innovations that have shaped

modern energy storage and the persisting need for next-generation, more sustainable alternatives (Attidekou et al., 2017).

## Alternative Battery Chemistries

Given the highlighted limitations of Li-ion batteries, the search for alternative chemistries intensified recently (Figure 3). The ideal alternative to lithium must address resource scarcity, safety concerns, cost volatility, and environmental impact. In turn, energy density, cycle life, and charging efficiency must remain comparable or superior performance. A few promising candidate setups emerged. Each candidate exhibits distinct advantages and challenges. These must be carefully evaluated to determine their potential for large-scale deployment.

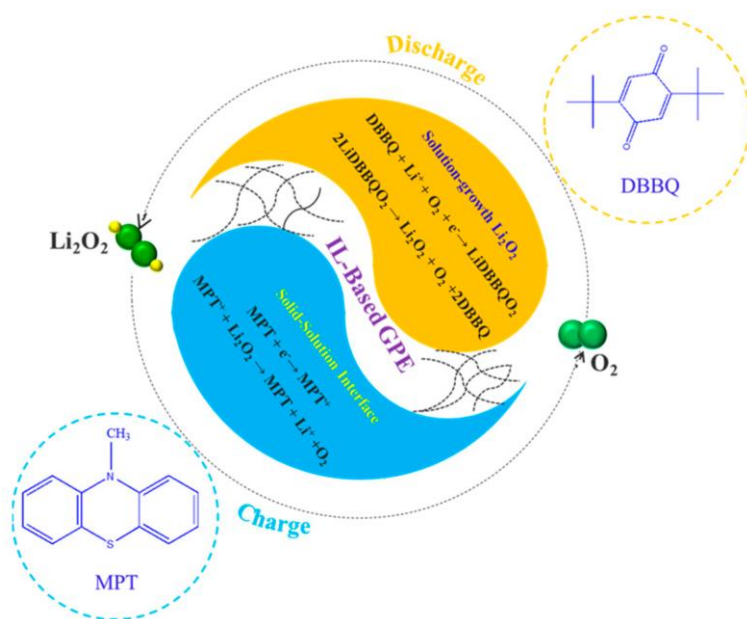


Figure 3. Schematic of cathodic reactions on discharging and recharging with DBBQ and MPT. See in-plot designations for more details. Reproduced from (Feng et al., 2023). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

One of the most promising alternatives is solid-state batteries. They replace the flammable liquid electrolytes – lower organic carbonates, as well as their mixtures of finely tuned chemical compositions – with a principally non-flammable solid electrolyte (Auvergniot et al., 2017). Solid

electrolytes offer enhanced safety, potentially higher energy densities, and improved thermal stabilities. Solid-state electrolytes, such as ceramic-based materials and polymer-based electrolytes, enable the use of lithium metal anodes. The latter offer theoretical capacities significantly higher than those of graphite. Companies such as Toyota, QuantumScape, and Samsung SDI made notable progress in solid-state battery development. The commercialization of solid batteries in the next decade is mentioned in this context. However, interfacial resistance between the electrolyte and electrodes, manufacturing scalability, and cost-effectiveness must be addressed before solid-state batteries manage to replace liquid Li-ion technology.

Another compelling and rather deeply explored alternative is Na-ion batteries. It leverages the abundance of sodium in the Earth's crust and seawater to provide a sustainable, low-cost energy storage solution. Unlike lithium, sodium is widely available. The obtaining of sodium does not require energy-intensive extraction processes. This feature makes Na-ion batteries an attractive option for large-scale energy storage systems. Na-ion batteries look to fully satisfy the needs of stationary applications, such as grid-scale renewable energy storage. Na-ion batteries currently exhibit lower energy density compared to Li-ion. Yet, recent advancements in cathode materials and anode designs significantly improve their performance. Companies CATL and Faradion introduced Na-ion battery prototypes. This event signals a growing interest in sodium-based chemistry. Cycle life limitations and electrolyte stability issues remain key hurdles that must be overcome for Na-ion batteries to compete with Li-ion in high-performance applications (Björklund et al., 2017).

Metal-air batteries – mainly lithium-air ( $\text{Li-O}_2$ ) and zinc-air ( $\text{Zn-O}_2$ ) systems – represent another frontier in energy storage, as of 2025. These batteries operate by reacting metal anodes with oxygen from the ambient air. Employing such a principle eliminates the need for heavy internal oxidizers and offers theoretical energy densities far exceeding those of Li-ion batteries. For instance, Li-air batteries, have a theoretical energy density of over 3,000 Wh/kg. Optimized  $\text{Li-O}_2$  batteries are a potential game-changer for long-range electric cars and aerospace

applications. Practical implementation is hindered by oxygen management challenges and electrolyte degradation. Furthermore, the formation of insulating discharge products, such as lithium peroxide  $\text{Li}_2\text{O}_2$ , reduces cycle life and efficiency. Zinc- $\text{O}_2$  batteries are naturally more stable and cost-effective. Yet, they also face reversibility issues and limited cycle life. Their current usage is acceptable primarily in low-power applications. Ongoing research into catalytic materials and advanced electrolytes, as well as oxygen management systems, continues to steadily push the boundaries of metal-air battery technologies. Zinc- $\text{O}_2$  batteries seem to exhibit more potential for commercialization thanks to their lower cost and higher sustainability.

Redox flow batteries represent a fundamentally different approach to energy storage. These rely on liquid electrolyte solutions as opposed to solid-state intercalation mechanisms. These batteries store energy in external tanks. Such a setup allows one to achieve scalable, long-duration energy storage by simply increasing the volume of electrolytes. Vanadium redox flow batteries were swiftly commercialized soon after development for grid-scale storage. They exhibit long cycle life and deep discharge capabilities. The high production costs of redox flow batteries and low energy density limit their utility in portable and high-power applications. Organic redox flow batteries aim to address these limitations by replacing expensive vanadium-based electrolytes with cheap organic compounds. While organic flow batteries offer renewable feedstocks and tunable redox properties, challenges related to chemical stability, solubility, and undesirable degradation must be resolved before large-scale commercialization (Casals and García, 2017).

Multivalent metal batteries include magnesium, calcium, and even aluminum. They are in the nascent state of research. Theoretically, these chemistries are high-capacity alternatives to lithium. Multivalent metals offer higher theoretical volumetric capacities compared to lithium. This feature potentially enables denser and more efficient energy storage. For example, magnesium batteries could theoretically store twice as much energy per unit volume as lithium. In turn, aluminum batteries offer high theoretical capacity combined with even lower production costs due to the abundance of aluminum. However, the development of these technologies is still in its early

stages. An omnipresent issue linked to electrolyte compatibility and slow ion kinetics applies. Significant obstacles must be overcome to consider multivalent cations instead of lithium as charge carriers. Novel electrolyte formulations and interfacial engineering techniques are intensively pursued to overcome these barriers and unlock the full potential of multivalent metal batteries for future breakthrough technologies. Organic and biodegradable batteries are even more exotic options for sustainable energy storage. These batteries utilize organic redox-active compounds. These are derived from renewable sources and offer the potential for biodegradability. Biodegradable batteries reduce the environmental footprint of energy storage systems (Flynn et al., 2017). Organic batteries exploit the features of quinone-based redox reactions. They demonstrate promising charge-discharge characteristics, although their limited cycle life and lower energy density, as compared to Li-ion batteries necessitate, further developments.

Biodegradable batteries incorporate naturally occurring or synthetic polymers. They are attractive for short-lived electronic devices, medical implants, and disposable sensors. In these low-energy applications, environmental impact and end-of-life disposal are critical considerations. Fully organic battery technologies are still in the early research phase. Their potential for green energy storage nowadays positions them as a compelling alternative in sustainable battery development. The exploration of alternative battery chemistries reflects a broader industry shift toward diverse, scalable, and environmentally responsible energy storage solutions. The development of these emerging technologies plays a crucial role in shaping the future of energy storage. It ensures that the transition to renewable energy, electric motors, and portable electronics is both technologically feasible and economically viable (Gélinas et al., 2017). Progress in batteries must take place in parallel with the optimization of energy demands from practical applications.

### **Solid-State Batteries**

One of the most significant advantages of solid-state batteries over present Li-ion batteries is their superior safety profile. The elimination of liquid organic electrolytes removes the primary

fuel source for battery fires. Solid-state batteries represent inherently more stable energy storage devices under extreme conditions. Lithium lanthanum zirconium oxide and lithium phosphorus sulfide exhibit exceptional thermal stability. Many solid electrolytes of similar compositions remain intact at temperatures exceeding 300 °C. Solid-state batteries are particularly attractive for high-risk environments. Such applications unite electric cars, helicopters, and aerospace, wherein fire safety is a critical concern. The absence of a separator in many solid-state configurations simplifies battery design and enhances its mechanical robustness. The likelihood of internal short circuits caused by dendritic lithium growth is decreased heavily (Guignard and Delmas, 2017).

Solid-state batteries exhibit the potential for higher energy density as soon as they are paired with lithium metal anodes. Conventional graphite anodes in Li-ion batteries exhibit a theoretical capacity of 0.4 Amper-hour per gram, whereas lithium metal anodes possess a theoretical capacity of nearly four Amper-hour per gram. Therefore, lithium anodes are ten times more attractive for high-energy applications than graphite anodes. In traditional Li-ion batteries, lithium metal is prone to dendritic growth. The latter routinely causes internal short circuits and thermal runaway. Solid-state electrolytes robustly mitigate this risk by physically blocking dendrite propagation over the battery. This capability allows for the development of high-capacity, lightweight batteries that significantly extend device runtime.

Several technical challenges prevent the commercialization of solid-state batteries. These are material compatibility, interfacial resistance, and manufacturing scalability. The high interfacial resistance between the solid electrolyte and the electrode represents a primary obstacle. It impedes ion transport and reduces overall efficiency. In Li-ion batteries, liquid electrolytes provide uniform wetting of electrodes. Uniformity is essential for an efficient charge transfer. In contrast, solid electrolytes must maintain excellent mechanical contact between the electrolyte and electrodes. In practice, this is often challenging to preserve over extended cycling. Nanoscale coatings, composite electrolyte designs, and pressure-assisted manufacturing techniques mitigate

interfacial resistance. Thus far, however, achieving industrial-scale improvement remains to represent a significant hurdle (Yamagishi et al., 2021).

Manufacturing complexity is another critical barrier to the widespread adoption of solid-state batteries (Imagawa and Itahara, 2017). Unlike established technologies to manufacture conventional Li-ion batteries, solid-state batteries require specialized fabrication techniques to form uniform electrolyte layers and high-quality electrode integration. Ceramic-based solid electrolytes require high-temperature sintering before they can be actually applied. Sintering is routinely regarded as an expensive method of processing. It increases production energy consumption and, thus, introduces additional production costs. Polymer-based electrolytes are easier to process. Yet, these materials suffer from low ionic conductivity. Polymer-based Li-ion batteries can provide due performance at elevated operating temperatures. Contrariwise, they are not competitive at room and lower temperatures. The integration of solid-state electrolytes with existing battery manufacturing infrastructure presents logistical challenges. This is because all existing production lines are optimized for liquid electrolyte filling and solvent-based electrode processing. A capital investment in new equipment and the adaptation of processes is demanded. As of 2025, solid-state batteries are much more expensive than their liquid-electrolyte Li-ion competitors (Kato et al., 2023).

Economically, the cost of materials and production scalability remains a key challenge for solid-state batteries. The high cost of ceramic electrolytes and lithium metal anodes currently offsets enhanced safety savings. The lack of established supply chains for solid electrolyte materials contributes to even higher production costs. As research progresses and mass production techniques improve, economies of scale may eventually drive the adoption of solid electrolytes. We must, nevertheless, keep in mind that safer and more benign technologies always come to humanity at a cost.

## **Present State of Na-Ion Batteries**

Na-ion batteries emerged as a compelling alternative to Li-ion batteries, even though it was understood well that Na-ion is unable to offer competitive stored energy densities. Na-ion batteries offer a sustainable, low-cost energy storage solution thanks to the abundance and accessibility of sodium. Sodium is widely available and easily extracted from seawater and known salt deposits. This fact eliminates many of the supply chain constraints and ethical sourcing issues associated with Li-ion batteries. This abundance positions Na-ion batteries as a viable candidate for large-scale energy storage systems in grid-scale renewable energy storage. Therein, energy density represents a less critical consideration than cost and sustainability. Na-ion batteries operate on similar intercalation chemistry as Li-ion batteries. Sodium ions shuttle between the anode and cathode during charge and discharge cycles. The larger size of Na-ions compared to lithium ions results in slower diffusion kinetics and, consequently, lower voltage output. Li-ion batteries deliver energy densities of, at least, 250 Wh/kg, whereas Na-ion batteries offer somewhat more than 100 Wh/kg. One of the most active areas of research in Na-ion batteries is the development of high-capacity cathode materials that deliver stable voltage profiles and extended cycle life. Li-ion cathodes, such as layered oxides like  $\text{LiCoO}_2$  are less effective in Na-ion systems due to greater structural instability. This is because larger Na-ions must be accommodated. Layered transition metal oxides, such as  $\text{NaFeO}_2$ , and polyanionic compounds are viable cathode materials to deal with the size of Na-ion. For instance,  $\text{NaNiMnO}_2$  cathodes hold promise for maintaining voltage stability and cycle life in commercial prototypes. Structural degradation and phase transition of the cathode lead to capacity fading over repeated charge-discharge cycles. Efforts to stabilize cathode structures through doping and surface modifications are ongoing. Among recent breakthroughs, sodium manganese oxide  $\text{NaMnO}_2$  and sodium iron phosphate  $\text{NaFePO}_4$  deserve to be mentioned. On the anode side, hard carbon emerged as the most viable option for Na-ion batteries. It offers reasonable capacity and stability in a cost-effective and scalable form. Unlike the limited intercalation capacity of graphite, hard carbon exhibits a higher Na-ion storage

capability. Titanium-based oxides, alloying materials, and conversion reaction-based anodes to further enhance anode performance are under active research (Lan et al., 2023).

Suitable electrolyte development is an essential area of Na-ion battery research. Liquid, gel, and solid-state electrolytes were explored to optimize ionic conductivity and electrochemical stability. Recent advancements focus on ether-based electrolytes. These electrolytes demonstrate superior stability and solubility for sodium salts. The development of solid-state Na-ion electrolytes, such as sodium superionic conductors and polymeric electrolytes fosters safety and enables the use of sodium metal anodes.

From an economic perspective, the lower material costs of Na-ion batteries present a significant advantage over Li-ion technology. The abundance of sodium eliminates the need for resource-intensive mining operations. The elimination of cobalt and nickel in Na-ion chemistries boosts cost-effectiveness and sustainability. The current lack of established manufacturing infrastructure for Na-ion batteries limits their commercial potential. Na-ion batteries are expected to play an increasingly important role and complement Li-ion technology.

### **Metal-Air Batteries: Energy Density versus Instability**

Metal-air batteries represent a class of energy storage systems that leverage oxygen from the ambient environment as a reactant, eliminating the need for heavy internal oxidizers and enabling exceptional theoretical energy densities. Among the most studied metal-air chemistries are lithium-air ( $\text{Li-O}_2$ ), zinc-air ( $\text{Zn-O}_2$ ), and aluminum-air ( $\text{Al-O}_2$ ) batteries, each offering unique advantages and limitations. While these systems hold extraordinary energy density potential, significant technical, electrochemical, and practical barriers must be overcome before they can achieve widespread commercialization.

One of the most promising metal-air technologies is lithium-air ( $\text{Li-O}_2$ ) batteries, which have a theoretical energy density of over 3,400 Wh/kg, surpassing that of conventional Li-ion batteries by a significant margin. This high energy density stems from the lightweight nature of lithium

metal anodes and the elimination of dense cathode materials in favor of oxygen reduction and evolution reactions at the air cathode. However, the practical implementation of Li-air batteries has been hindered by several critical challenges, including electrolyte decomposition, oxygen management, and the formation of insulating discharge products. During discharge, lithium metal reacts with oxygen to form lithium peroxide  $\text{Li}_2\text{O}_2$  or lithium oxide  $\text{Li}_2\text{O}$ , both of which are insoluble in most electrolytes, leading to rapid cathode clogging and capacity deterioration. The high reactivity of lithium metal with moisture and carbon dioxide necessitates strict environmental controls. Despite these challenges, research into protective anode coatings, stable electrolyte formulations, and advanced catalysts for oxygen evolution continues to push the boundaries of Li-air technology.

Zn- $\text{O}_2$  batteries, another well-established metal-air system, offer a more mature platform with proven applications in hearing aids, electric buses, and grid-scale energy storage. Unlike Li- $\text{O}_2$  batteries, Zn-air systems operate in aqueous electrolytes, which reduces safety concerns and facilitates oxygen transport at the cathode. The high theoretical capacity of zinc,  $5,200 \text{ mAh/cm}^3$ , and its low cost and abundance make Zn-air batteries an attractive option for low-voltage, high-capacity applications. However, their limited rechargeability remains a significant drawback, as zinc dendrite formation and pH imbalances in aqueous electrolytes contribute to capacity degradation and shortened cycle life. Non-aqueous Zn-air systems, zinc anode protection layers, and catalytic oxygen evolution materials improve reversibility and longevity.

Al- $\text{O}_2$  batteries represent another high-energy-density alternative. Its theoretical energy density is over  $8,000 \text{ Wh/kg}$ . Al-air batteries utilize aluminum as the anode and oxygen as the cathode reactant. Aqueous or ionic liquid electrolytes facilitate the electrochemical reactions. The high abundance and low cost of aluminum position Al-air batteries as a viable alternative to Li-ion in specific niche applications. Practical deployment is hindered by well-known aluminum

passivation. Oxidation layers of  $\text{Al}_2\text{O}_3$  on the anode surface impede reversible operation, and corrosion issues in aqueous electrolytes, which limit cycle life and efficiency. Recent advancements in alloyed aluminum anodes, corrosion-resistant coatings, and non-aqueous electrolyte formulations mitigate these challenges to a certain extent. Nonetheless, full commercialization remains distant.

Beyond  $\text{Li-O}_2$ ,  $\text{Zn-O}_2$ , and  $\text{Al-O}_2$  batteries characterized above, other metal-air chemistries, such as potassium-air  $\text{K-O}_2$  and calcium-air  $\text{Ca-O}_2$  systems garnered research interest due to their theoretical energy density advantages and material abundance.  $\text{K-air}$  batteries, for example, offer high theoretical capacity and favorable redox potentials, though their poor reversibility and electrolyte degradation remain significant obstacles. Calcium- $\text{O}_2$  batteries are promising in terms of energy density and material availability. However, they face even greater challenges in reversibility and electrolyte stability. The potential of metal-air batteries to deliver unprecedented energy density continues to drive fundamental and applied research of novel materials, electrochemical mechanisms, and system designs.

Metal-air batteries offer exceptional theoretical energy density. Yet, their practical implementation is hindered by intrinsic electrochemical limitations. Material degradation and system complexity have to be attended to yet. One of the primary challenges across all metal-air chemistries is the reversibility of the oxygen reduction and evolution reactions at the air cathode. The oxygen evolution reaction during charging suffers from high overpotential. This leads to significant energy losses and reduced round-trip efficiency. This inefficiency diminishes the practical energy density and accelerates catalyst degradation. The undesirable reactions limit the cycle life of metal-air batteries. Noble metal catalysts and their non-precious metal alternatives are known to enhance the reaction kinetics. These materials often suffer from instability in aqueous or corrosive environments. Long-term operation is challenging.

Another critical issue is the management of discharge products in non-aqueous systems. In Li-air batteries, the formations of insulating lithium peroxide  $\text{Li}_2\text{O}_2$  and lithium oxide  $\text{Li}_2\text{O}$  during discharge block oxygen diffusion pathways. As a result, capacity fades and the cell fails prematurely. Porous carbon cathodes and nanostructured catalyst supports mitigate clogging. Yet, achieving consistent performance over multiple cycles remains elusive. Zn-air batteries face pH imbalance in aqueous electrolytes. Herewith, alkaline conditions lead to zinc dendrite formation and electrolyte degradation. Bifunctional catalysts, ion-selective membranes, and non-aqueous electrolyte formulations may address some of these challenges, even though they introduce additional complexity and expenses.

The environmental and operational constraints of metal-air batteries decrease their real-world applicability. Note that metal-air cells must continuously interact with ambient air. This requirement necessitates advanced gas diffusion layers, moisture control mechanisms, and even  $\text{CO}_2$  scrubbing systems.  $\text{CO}_2$  contaminates electrolytes and boosts anode corrosion. Metal-air batteries are considered to be less suitable for compact, sealed applications such as smartphones and laptops. Contrariwise, they are more viable for open-system configurations, such as electric vehicle range extenders and long-duration energy storage, wherein air exposure is manageable. Even in these setups, the need for active oxygen management and anode protection layers presents engineering and cost challenges. Despite these obstacles, metal-air batteries remain a compelling area of research, particularly for long-range electric vehicles and aerospace applications. Advancements in protective anode coatings, such as lithium nitride  $\text{Li}_3\text{N}$ , and polymer electrolyte interfaces, show promise in mitigating dendrite formation and suppressing side reactions. Hybrid metal-air systems, such as rechargeable Zn- $\text{O}_2$  batteries with aqueous gel electrolytes, demonstrate improved cycle life and reduced dendritic growth. This suggests a certain potential for low-cost, moderate-power applications.

### **Long-Duration Energy Storage in Redox Flow Batteries**

Redox flow batteries represent a fundamentally different approach to energy storage compared to conventional intercalation-based Li-ion batteries. Redox flow batteries store energy in liquid electrolyte solutions, which are pumped through electrochemical cells to generate power. This unique architecture decouples energy capacity from power output. Thus, independent scaling of storage volume and power delivery is possible. This technology is well-suited for grid-scale energy storage, in which long-duration discharge, deep cycling, and long operational lifespans are critical. Vanadium redox flow batteries achieved commercial deployment in utility-scale applications. Organic redox flow batteries reduce costs and improve sustainability by replacing expensive transition metals with carbon-based redox-active compounds.

Vanadium redox flow batteries are considered to be the most successful redox flow technology to date. It offers 10,000 cycle life, deep discharge capability, and moderate energy density. Vanadium-based cations in multiple oxidation states are employed, e.g.,  $V^{2+}/V^{3+}$  at the cathode and  $VO^{2+}/VO_2^+$  at the anode. This chemical stability contributes to long operational lifetimes. Vanadium cost represents a bottleneck, combined with a relatively low energy density. It limits their applicability in compact or high-power scenarios. Hydrogen evolution and vanadium crossover are parasitic reactions across the ion exchange membrane. They contribute to capacity fade.

To address the cost and sustainability limitations of vanadium-ion batteries, the focus was shifted to organic redox flow batteries (Giagloglou et al., 2018). These batteries employ carbon-based redox-active molecules – quinones, viologens, and TEMPO-based derivatives – as charge carriers. The absence of the transition metal in this technology contributes to ecological friendliness. For instance, aqueous organic redox flow batteries utilize anthraquinone disulfonic acid at the cathode and methyl viologen at the anode. It demonstrates promising cycling stability and solubility. Challenges related to degradation mechanisms, limited voltage windows, and lower energy density persist. Recent advancements in non-aqueous organic analogs, which use aprotic solvents to expand the electrochemical stability window, showed improved energy density and

efficiency. Still, higher electrolyte costs and relatively low ionic conductivity currently restrict their commercial viability. A key advantage of redox fuel batteries is their scalability. The energy storage capacity can be increased simply by enlarging the electrolyte tanks. Power output is adjusted by modifying the stack size and electrode surface area. This modularity makes this sort of battery attractive for long-duration energy storage. The absence of dendrite formation and lower thermal risks, compared to Li-ion batteries, enhance the safety profile of redox flow batteries. These systems are bulky and require pumps, tanks, and complex fluid management. Portable applications are challenging.

### **Multivalent Metal Batteries**

Multivalent metal batteries, including magnesium, calcium, and aluminum, represent a promising class of energy storage systems. They surpass the performance of Li-ion batteries in terms of theoretical energy density and resource abundance.  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$  transport multiple electrons per ion. Multivalent metal batteries are attractive for high-energy applications, in which weight and space constraints are critical. Multivalent metal batteries face significant technical challenges, such as electrolyte instability, slow ion kinetics, and interfacial compatibility issues.

One of the most extensively studied multivalent metal batteries is the magnesium (Mg) battery. It offers a theoretical capacity of almost 4 mAh/cm<sup>3</sup>. This is significantly higher than that of lithium metal, 2 mAh/cm<sup>3</sup>. Magnesium also exhibits lower chemical reactivity compared to lithium. Thus,  $\text{Mg}^{2+}$  decreases safety concerns in Li-ion batteries.  $\text{Mg}^{2+}$  is abundant and cost-effective. Its global reserves far exceed those of lithium. The development of Mg-ion batteries is hindered by the lack of suitable electrolytes to support reversible Mg deposition and dissolution. Most conventional electrolytes form passivating films on the Mg-metal anode. This prevents efficient ion transport and limits battery cycle life. Deliberately developed complex organoboron-based electrolytes –  $\text{Mg}(\text{TFSI})_2$  with boronate ester additives – enable reversible Mg plating/stripping. Yet, the limited ionic conductivity and narrow

electrochemical stability window of Mg-ion electrolytes remain significant barriers to the practical implementation of Mg-ion batteries.

Ca-ion batteries exemplify a multivalent metal system with high theoretical energy density, 2 Ah/cm<sup>3</sup>, and widespread elemental availability. A low redox potential of Ca, -2.87 V vs. SHE, makes it a promising candidate for high-voltage batteries. Its abundance in the Earth's crust reduces dependency on geopolitically sensitive materials. However, the development of Ca-ion batteries is slower than that of Mg batteries. It is challenging to pick up a correct electrolyte supporting a reversible deposition of calcium. Calcium bis(trifluoromethanesulfonyl)imide Ca(TFSI)<sub>2</sub> and calcium borohydride Ca(BH<sub>4</sub>)<sub>2</sub> suffer from high overpotential, poor reversibility, and interfacial instability. The large ionic radius of Ca<sup>2+</sup> leads to slower diffusion kinetics, reducing rate capability, and charging efficiency.

Al-ion batteries present a unique opportunity for high-capacity energy storage. Its theoretical capacity amounts to 8 h/cm<sup>3</sup>. This is the highest computed value. Aluminum is extremely abundant, non-toxic, and cost-effective. The problem lies in electrolyte formulation and electrode compatibility. Traditional aprotic organic electrolytes used in Li-ion batteries are incompatible with Al due to severe corrosion. Ionic liquid electrolytes, e.g., AlCl<sub>3</sub>-urea and AlCl<sub>3</sub>-1-ethyl-3-methylimidazolium chloride, foster reversible Al deposition but increase shear viscosity. These ionic liquids enable reversible Al deposition, but their high viscosity, corrosive nature, and limited compatibility with high-voltage cathodes restrict progress. Recent advancements in aluminum-graphite dual-ion batteries and aluminum-sulfur chemistries demonstrated improved energy density and cycle life. Low Coulombic efficiency and poor rate capability remain critical obstacles.

The compatibility of multivalent metals with cathode materials presents another major hurdle. Successful batteries require entirely new cathode chemistries that can accommodate multivalent ion insertion and extraction without structural degradation. Sulfides and polysulfides exhibit promise due to their high theoretical capacity. Yet, they suffer from shuttle effects,

solubility issues, and limited reversibility. Transition metal sulfides, such as MoS<sub>2</sub> and FeS<sub>2</sub>, were investigated as potential host materials for Mg<sup>2+</sup> and Ca<sup>2+</sup>. Slow kinetics and phase transitions impede the corresponding battery performance. Organic and conductive polymer cathodes are explored as alternatives to inorganic materials. However, these organic materials normally exhibit poor cycling stability and require chemical modifications to enhance durability and ionic conductivity.

Multivalent metal batteries hold significant potential due to high-density energy, safety, resource sustainability, and energy density. The ongoing development of novel electrolytes, protective anode coatings, and high-capacity cathode materials gradually addresses the existing issues. If these advancements reach industrial maturity, Mg, Ca, and Al batteries would play a complementary role in stationary energy storage and long-duration grid storage, where material abundance and safety outweigh current performance limitations.

### **Sustainable Energy Storage in Organic and Biodegradable Batteries**

As the demand for sustainable energy storage grows, organic and biodegradable battery chemistries are investigated. Unlike inorganic batteries, organic and biodegradable batteries utilize carbon-based redox-active compounds. They are sustainably sourced, chemically tailored, and decomposed naturally at end-of-life. These attributes position organic and biodegradable batteries as promising candidates for low-power electronics, disposable sensors, and eco-conscious energy storage solutions. One of the most extensively studied organic battery technologies is the organic redox flow battery. This technology employs soluble organic molecules as charge carriers in liquid electrolyte solutions. Quinones, viologens, and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) derivatives undergo reversible oxidation and reduction. This feature allows one to develop customizable molecular structures, exhibiting highly tunable redox potentials. Compared to conventional vanadium redox flow batteries, organic analogs eliminate the need for heavy metal-based electrolytes. Organic redox species are derived from biomass and synthetic precursors. A

renewable alternative must be preferred to finite inorganic resources. However, organic flow batteries face challenges, e.g., molecular degradation, limited solubility, and lower energy density compared to Li-ion and solid-state batteries. Radical-stabilizing functional groups, cross-linked polymers, and non-aqueous electrolyte systems are developed (Figure 4).

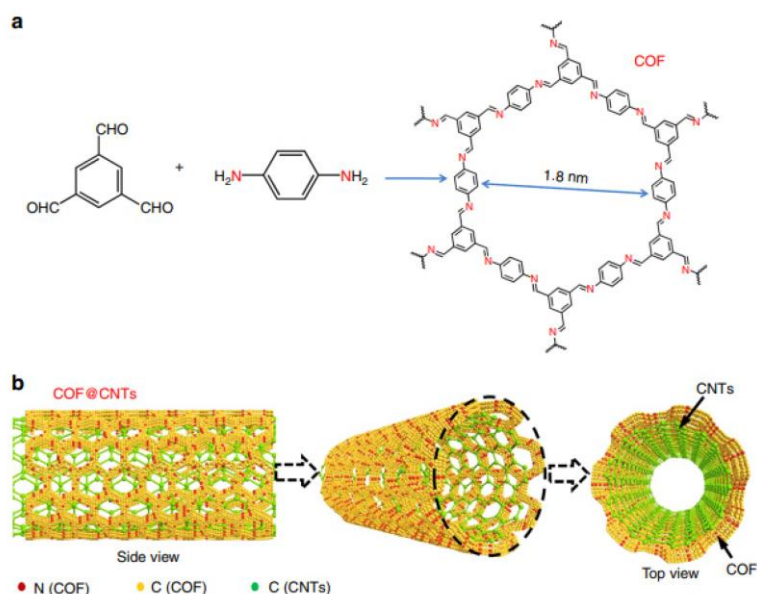


Figure 4. (a) Scheme illustrating the preparation of covalent organic framework with an average pore size of 1.8 nm; (b) graphical representation of the COF@CNTs anode material with few covalent organic framework layers covered the surface of carbon nanotubes. Reproduced from (Lei et al., 2018). The image is licensed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Beyond flow batteries, organic solid-state and aqueous batteries gained attention for their low environmental footprint and potential for corroborating flexible, lightweight designs. Organic batteries typically utilize carbonyl-based polymers, conductive polymers, or molecular redox species as active materials. These are synthesized from renewable sources and designed for biodegradability. For instance, polyimide-based cathodes and quinone-based anodes demonstrated promising charge-discharge descriptors. Yet, their capacity retention and cycle stability remain much below those of conventional Li-ion chemistries. A major limitation of organic batteries is their susceptibility to hydrolysis and oxidation in aqueous environments. To address this, researchers are exploring non-aqueous electrolytes, protective coatings, and covalent organic

frameworks (COFs) that enhance chemical stability and conductivity while maintaining sustainability.

Biodegradable batteries represent a growing segment of organic battery research. Their niche is seen to be biomedical implants, disposable sensors, and short-lived electronic devices. These batteries leverage naturally occurring redox-active compounds, such as flavins, quinones, and conjugated polymers. Some prototypes demonstrated functional operation for several hours to days. They are suitable for low-power, transient electronics that do not require extended cycle life. Modern biodegradable batteries suffer from limited energy density, low efficiency, and restricted operating conditions. Large-scale deployment of organic batteries is not likely. Ongoing research is focused on improving molecular stability, enhancing charge transport, and integrating biodegradable components. Integration of biodegradable elements into hybrid energy storage devices aims to balance sustainability with performance.

We presently see organic and biodegradable batteries as complementary technologies in the evolving rechargeable energy storage landscape. Their environmental benefits, renewable material sources, and potential for closed-loop recycling align with global trends of reducing electronic waste and carbon emissions. As advancements in molecular engineering, electrolyte formulation, and device integration develop, organic and biodegradable batteries may find niche applications in green electronics, wearables, and low-impact energy storage.

### **Economic and Environmental Considerations**

The transition from Li-ion batteries to alternative energy storage technologies is not solely determined by technical performance but also by economic benefits and environmental sustainability (Zubieta López and Chigo-Anota, 2024). While emerging battery chemistries offer enhanced safety, higher energy density, and reduced reliance on scarce resources, their economic feasibility and environmental impact must be duly evaluated to guarantee long-term adoption. The

costs of raw materials, manufacturing, recycling, and supply chain play a crucial role in shaping the future landscape of energy storage.

One of the key economic considerations is the cost of raw materials. These significantly impact the affordability and scalability of alternative battery technologies. Li-ion batteries rely on lithium, cobalt, and nickel. These materials are resource-constrained and subject to price volatility due to geopolitical dependencies. Contrariwise, Na-ion batteries benefit from the abundance and low cost of sodium. Na-ion batteries represent a promising alternative for large-scale stationary energy storage. Solid-state batteries eliminate the need for flammable liquid electrolytes and enable the use of lithium metal anodes. Yet, the production of ceramic or polymer-based solid electrolytes is energy-intensive and expensive. Metal-air batteries offer low material costs due to the widespread availability of zinc and aluminum. However, the complexity of oxygen management and electrolyte stability introduces additional manufacturing and maintenance expenses. Organic and biodegradable batteries are environmentally favorable, assuming expenses for material synthesis and its scalability. Many redox-active organic compounds are more expensive to synthesize compared to other materials used in electrochemistry.

Manufacturing scalability represents a critical factor in battery production. It influences the economic feasibility of alternative battery technologies. Li-ion batteries benefit from established production infrastructure. Global supply chains are optimized for mass production. Whereas, emerging chemistries need new fabrication techniques, specialized equipment, and modified assembly lines. All these factors contribute to higher capital expenditures for novel battery technologies. For example, solid-state batteries require high-precision layer deposition and controlled atmosphere processing. That is why manufacturing complexity and cost are much higher than that of Li-ion batteries. Organic redox flow batteries demand fine electrochemical engineering to ensure the long-term stability of organic molecules. Metal-air systems necessitate gas diffusion layers and active oxygen management. Some alternative battery technologies, such as Na-ion batteries and zinc-air batteries, leverage existing Li-ion manufacturing facilities with

minor modifications. Others require entirely new production paradigms. The latter are not likely to join the electrochemical market soon.

Recyclability expenses are paramount. Current Li-ion recycling rates remain alarmingly low, below five percent. Required techniques must preserve electrode materials for reuse. In this context, alternative battery chemistries offer some opportunities, yet combined with some challenges. Na-ion batteries may avoid recycling thanks to the ecological friendliness of sodium and its abundance in seawater. Solid batteries pose recycling challenges due to the integration of ceramic and polymer electrolytes. The latter materials require specialized recovery techniques to separate electrode materials from solid electrolytes. Organic and biodegradable batteries may be disposed of without recycling.

The economic and environmental considerations of alternative battery technologies underscore the need for a holistic evaluation of future technological solutions. While some alternatives offer significant advantages in material sustainability, their production costs and recycling challenges must be addressed through innovation and policy support. The integration of economic and environmental factors into battery design is essential for accelerating the transition to sustainable, scalable energy storage systems. The development of alternative battery chemistries is driven by a wave of technological innovations. They range from advanced materials engineering to battery optimization based on machine learning, and novel manufacturing techniques. These advancements must address performance limitations, expenditure constraints, and environmental concerns.

Materials engineering drives the design of high-capacity electrodes, stable electrolytes, and novel interfacial coatings that enhance ion transport and electrochemical stability. In solid-state batteries, the focus is on ceramic electrolytes. Lithium lanthanum zirconium oxide and lithium phosphorus sulfide propose exceptional ionic conductivity and thermal stability. Nanoscale material engineering, such as composite electrolyte designs, combines ceramic particles with

polymer matrices to improve flexibility and manufacturability (Zhang et al., 2024). Atomic layer deposition and sputtering techniques create ultra-thin protective layers and block desirable side reactions.

Advances in electrode materials play a role in improving the energy density and cycling stability of Na-ion batteries. Layered transition metal oxides, Prussian blue analogs, and polyanionic compounds promote sodium storage capacity and structural integrity. Hard carbon anodes are optimized through surface functionalization and pore-structure engineering to reinforce ion intercalation pace.

Organic and biodegradable batteries are benefiting from innovations in molecular design and electrochemical stability. Organic redox molecules with enhanced solubility in water, redox reversibility, and chemical durability are pursued to decrease production costs. Quinone-based polymers and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) derivatives are modified to improve charge retention and resist degradation under prolonged cycling. The integration of covalent organic frameworks and metal-organic frameworks enables higher energy density and improved charge transport in organic batteries. Biodegradable battery materials are advanced thanks to natural flavins and quinones. The latter materials are integrated into transient electronics and biomedical implants. These exemplify environmentally responsible alternatives to modern battery systems.

Additive manufacturing and 3D printing are utilized to create customized battery architectures. This shall enhance ion transport and reduce material waste. In solid-state batteries, roll-to-roll processing and thin-film deposition techniques are optimized to achieve uniform electrolyte layers at industrial scales. Modular battery designs are being proposed for Na-ion and organic batteries. As a result, easy disassembly and component recovery in closed-loop recycling is enabled.

## **Final Remarks**

To recapitulate, we herein discussed alternative battery chemistries beyond conventional Li-ion technology with liquid electrolytes. As the interest in electrically powered cars and helicopters increases and portable electronics emerge, the limitations of Li-ion batteries inspire a global effort to develop next-generation rechargeable energy storage devices. Solid-state batteries, Na-ion systems, metal-air chemistries, redox flow batteries, and biodegradable alternatives present unique advantages. In particular, they offer pathways to higher energy density, improved safety, reduced cost, and enhanced sustainability. However, the successful commercialization of these technologies assumes advancements in materials science, as well as scalable and low-cost production. As of 2025, solid-state batteries stand out for their inherent safety benefits as they eliminate thermal runaway and flammability concerns. By canceling the need for liquid electrolytes and fostering the integration of lithium metal anodes, solid-state systems have the potential to substitute Li-ion batteries in numerous applications. High production costs, interfacial resistance, and problematic production of solid electrolytes have not been attended to yet. In turn, Na-ion batteries offer a trustworthy sustainable alternative to Li-ion technology, thanks to the abundance of sodium, acceptable longevity, and reasonable performance. Metal-air batteries surpass current Li-ion technology according to their energy densities. Challenges of reversibility, oxygen management, and electrolyte stability have not been overcome yet. Organic redox flow batteries exhibit much lower energy density. They are scalable solutions for long-duration energy storage in grid-scale renewable energy integration. Their modular design allows one to achieve independent scaling of energy capacity and power output. Organic redox flow batteries are ideal for load balancing and peak shaving as long as the compact form is not the cornerstone. The chemical instability of organic redox molecules and their limited solubility necessitates further molecular design to warrant long-term operational viability.

Multivalent metal batteries are based on relatively simple chemistry. This makes Mg-, Ca-, and Al-ion batteries similar to rather established Li-ion and Na-ion technologies. Volumetric energy density and resource sustainability are key advantages. Mg-ion batteries benefit from low

dendrite risk and abundant raw materials. In turn, Al-ion batteries do not raise environmental issues and possess exceptional theoretical stored energy capacities. Advanced electrolytes are urged to boost ionic kinetics in such batteries.

The transition to a diversified ecosystem of versatile and finely tuned batteries anticipates interdisciplinary collaboration, policy-driven incentives, and industry-led innovation. Regulatory bodies must prioritize sustainable resource management and promote closed-loop recycling systems. This policy ensures the long-term viability of alternative chemistries. Industry leaders are to invest in scaling production, optimizing manufacturing processes, and developing standardized recycling protocols. Advances in materials science, electrochemical engineering, and machine learning battery optimization are to circumvent the technical barriers that currently limit performance.

The future of energy storage is not a single replacement for Li-ion batteries. It is rather a complementary suite of technologies tailored to specific low-energy and high-energy applications. Nowadays, the utilization of Li-ion remains dominant in high-performance and portable applications. In the next decades, solid-state, Na-ion, metal-air, and organic batteries will play pivotal roles in stationary storage, long-range mobility, and sustainable electronics. In a broad context, the energy storage industry iteratively pushes a paradigm shift toward cleaner, safer, and more resilient energy consumption.

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