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Sodium-Ion Batteries Paving the Way for Grid Energy Storage

*Hayley S. Hirsh, Yixuan Li, Darren H. S. Tan, Minghao Zhang, Enyue Zhao, and Y. Shirley Meng**

Dedicated to the pioneering scientists whose work have made sodium-ion batteries possible

The recent proliferation of renewable energy generation offers mankind hope, with regard to combatting global climate change. However, reaping the full benefits of these renewable energy sources requires the ability to store and distribute any renewable energy generated in a cost-effective, safe, and sustainable manner. As such, sodium-ion batteries (NIBs) have been touted as an attractive storage technology due to their elemental abundance, promising electrochemical performance and environmentally benign nature. Moreover, new developments in sodium battery materials have enabled the adoption of high-voltage and high-capacity cathodes free of rare earth elements such as Li, Co, Ni, offering pathways for low-cost NIBs that match their lithium counterparts in energy density while serving the needs for large-scale grid energy storage. In this essay, a range of battery chemistries are discussed alongside their respective battery properties while keeping metrics for grid storage in mind. Matters regarding materials and full cell cost, supply chain and environmental sustainability are discussed, with emphasis on the need to eliminate several elements (Li, Ni, Co) from NIBs. Future directions for research are also discussed, along with potential strategies to overcome obstacles in battery safety and sustainable recyclability.

1. Introduction

The past decade has seen dramatic reductions in levelized cost of energy (LCOE) for renewables such as wind and solar. This has allowed us to achieve grid parity against traditional fossil fuels in the United States and many other parts of the world.[1] However, the widespread adoption of renewables has been consistently plagued by challenges of intermittency in supply and the inability to meet peak demand fluctuations especially when deployed in urban grids. As such, energy storage is vital to bridge the disconnect between renewables generation and distribution for consumption. While stationary storage such as pumped hydroelectric and compressed air exist, their lack of flexible form factors and lower energy efficiencies limit their scalable adoption for urban communities.[2] Thus, batteries are believed to be more practical for large-scale energy storage capable of deployment in homes, cities, and locations far from the grid where the traditional electrical infrastructure does not reach.

Today's battery technologies are dominated by lithium ion batteries (LIBs) and lead acid batteries. While LIBs do well to serve emerging markets in electric vehicle and portable electronic devices, its deployment for large-scale grid storage is still inhibited by high cost, low safety, and sustainability concerns.[3] Other alternatives that meets the combined properties of low cost, high performance, and safety are urgently needed. In addition, methods of handling large volumes of spent batteries at their end-of-life have not been fully developed till date, resulting in the accumulation of battery waste that can potentially undo the environmental benefits it rightfully seeks to achieve. In terms of cost, decades of industrial commercialization have enabled prices of LIBs to tumble by more than an order of magnitude compared to when it first entered the market. This was achieved through improvements in active (such as better electrode and electrolyte materials) and inactive components of LIBs (such as current collector, separator, packaging, etc.) combined with streamlining of manufacturing protocols to achieve economies of scale. However, production level optimization of LIBs today are approaching its saturation limit, where it is becomes increasingly clear that eliminating use of expensive elements such as Li, Co and Ni are vital to realize further reductions in cost per kWh ($/kWh).[4] Concerns of energy security and geopolitical considerations in supply chain also drive nations without local access to such materials to seek alternative chemistries to meet energy storage demands. As such, sodium-ion batteries (NIBs) and its commercialization is slated to serve as one of the alternatives to LIBs for grid energy storage applications.

NIBs offer a host of benefits that include elemental abundance, low costs per kWh, and its environmentally benign nature. While NIBs are commonly perceived to exhibit inferior electrochemical performance compared to conventional LIBs,

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recent developments in high-voltage sodium-based cathodes with high capacity and high power capability are starting to challenge such notions. State of the art NIBs today can achieve volumetric energy densities close to conventional LIBs, making them competitive in the grid storage markets. Moreover, environmentally friendly NIBs can alleviate the growing battery waste problems exacerbated by accumulation of spent LIBs retrieved from end-of-life electric vehicles and portable devices, which could only worsen if conventional toxic LIBs are deployed at large scales to serve the grid. In the subsequent sections, we discuss the role of NIBs and how their features of low cost, good performance, and environmental sustainability can overcome obstacles faced in electrochemical grid energy storage and offer perspectives on future directions for research and development.

2. Discussion

While it might be intuitive to imagine grid storage as massive deployments of large container-like battery units sprawled across large open areas, current market trends in stationary storage reflect a different reality. Customer demands in stationary storage are starting to skew toward behind-the-meter type installations which typically cover households (kWh) to communal microgrids (MWh), compared with traditional utility scale installations of (GWh).[5] This has been driven by international pressure to reduce reliance on traditional energy sources such as nuclear and fossil fuels, incentivizing cities to install standalone renewables generation coupled with storage units within compact urban areas.[6] Such configurations allow businesses and consumers to utilize the existing electrical infrastructure for energy redistribution and avoid long range transmission losses from traditional generation plants. As a result, it would be naive to assume that energy density of battery installations is inconsequential when stationary storage in urban environments are considered. In fact, volumetric energy density (Wh L^{-1}) at the system level, is a key evaluation parameter to assess electrochemical grid storage technologies. **Figure 1**a compares the gravimetric energy density (Wh kg^{-1}) versus volumetric energy density (Wh L^{-1}) of various battery chemistries, with additional details provided in Table S1, Supporting Information.[7] Comparisons on relative costs and lifetime are also displayed for reference. For the same unit of energy, higher volumetric energy density indicates smaller devices, while higher gravimetric energy density represents lighter systems. Depending on their typical market applications, batteries are divided into four major regions in the figure. The upper right region (light and small batteries) is commonly used in electrical vehicles and personal devices, where portability is essential. On the opposite end, the left bottom region (heavier and larger batteries) is used for power tools or starters that do not require continuous operation. Batteries for drones and flight need to be light, but not necessarily very small; while batteries for stationary storage should take up as little space as possible, with less regard for its weight. To address safety concerns of batteries that pose fire hazards, electrolyte types used in each system is also included in Figure 1a.[8] All solid-state batteries that utilize solid-state electrolytes in place of conventional flammable organic liquid electrolytes are believed to be a potential solution to address these safety concerns since they are intrinsically not flammable.[9] As such, sodium-ion batteries stand out as a competitive candidate for grid storage applications because of its suitable energy density, relatively low cost, and its potential to offer improved safety and long cycle life especially when solid state electrolytes are used.

Most battery materials today are synthesized from precursors using lithium carbonate (Li_2CO_3) and sodium carbonate (Na_2CO_3). Thus, price fluctuations in these raw materials can result in significant implications on the cell level costs of batteries per kWh. Figure 1b compares the price trend of Li_2CO_3 and Na_2CO_3 over the past 15 years.[10] It is clearly shown that the prices of Na_2CO_3 are approximately two orders of magnitude

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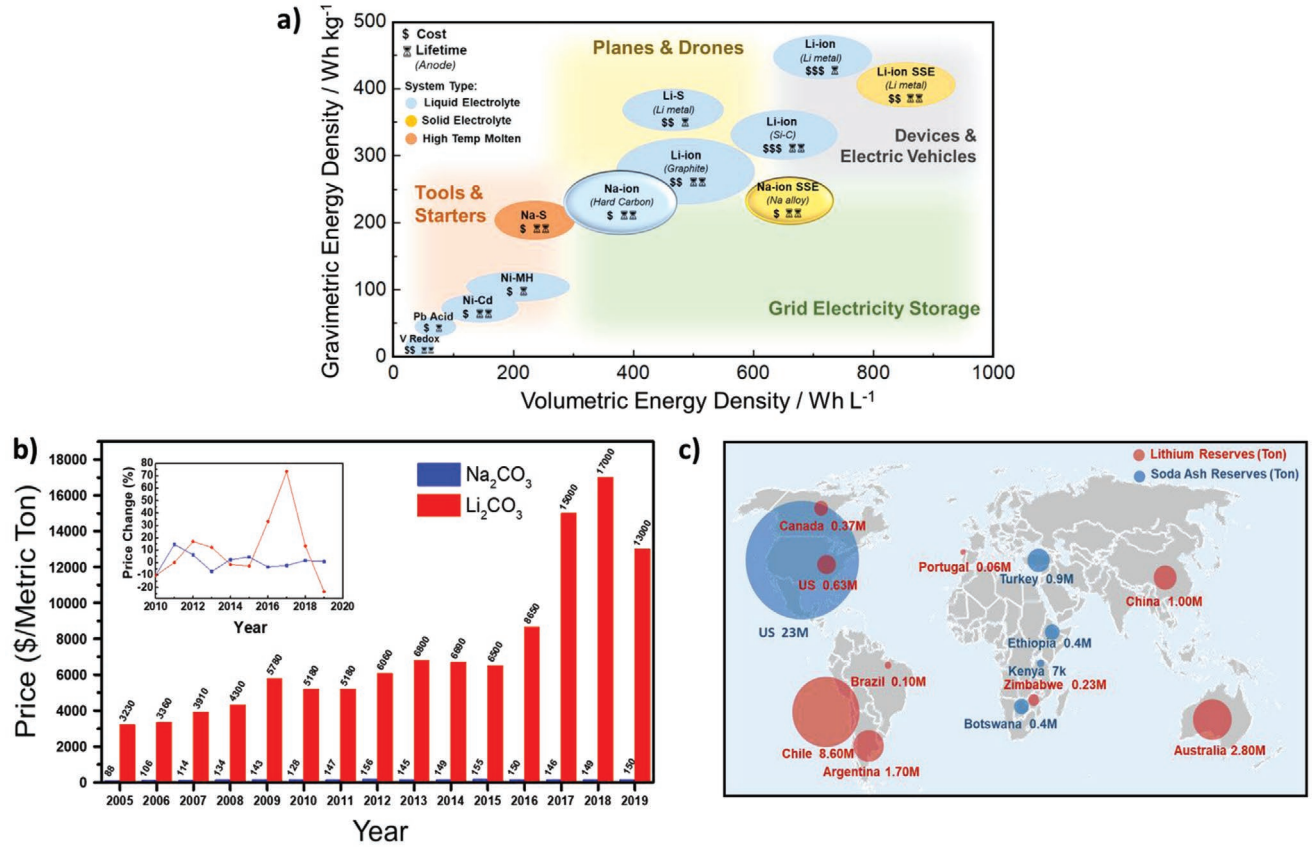

Figure 1. a) Current electrochemical storage technologies gravimetric energy density versus volumetric energy density compared. b) The price trend of sodium carbonate and lithium carbonate from 2005–2019. The inset is the percentage of price changes of both materials over the past 10 years. c) A map of the Li reserves and Soda Ash (Na reserves) in the world reported in 2020. Li reserves are depicted by red circles and soda ash reserves are depicted by blue circles. The size of the circle represents the amount of reserves in metric tons. Brine is also a source of sodium and this is illustrated by the light blue color of the ocean.

lower than its lithium counterparts, with Li_2CO_3 at \$13 000 per metric ton compared to Na_2CO_3 at \$150 per metric ton in 2019. Additionally, the trend in prices also differ across both materials. Since 2010, the price of lithium carbonate has increased from \$5180 to \$13 000 per metric ton (a 151% increase); while the price of sodium carbonate only increased from \$128 to \$150 per metric ton (a 17% increase). This has been largely attributed to the limited geographical availabilities in lithium mining sources that drive up prices as demand for batteries grow. By contrast, ubiquitous availability of sodium along with the mature soda ash mining industry keeps prices of Na_2CO_3 relatively stable for the foreseeable future. Economically, this makes NIBs a better choice over LIBs for applications in grid storage where market stability is crucial for both manufacturers and customers alike to make long-term projections of profitability and utility.

Besides pricing and market considerations, the geopolitical concerns for lithium and sodium material sources should also be analyzed as well. Figure 1c depicts the global reserves of lithium and soda ash (a major sodium source) illustrated as circles (on a square root scale) corresponding to their actual reserve quantities.[11] Chile (8.6 million tons) and Australia (2.8 million tons) represents the top holders of lithium reserves and are the largest exporters by a significant margin. These are followed by Argentina and China, rounding out the top four, with no other countries coming close in lithium reserves around the world. The past century saw the political influence of key natural resources such as fossil fuels around the world, demonstrating the importance of energy security for growing economies. It is natural for lithium and other vital energy resources to play an equivalent or more significant role in future economic and geopolitical considerations. As a result, developing lithium alternatives such as NIBs are of great interest to certain countries such as the United States, who holds the largest natural soda ash reserves in the world and is a major international supplier of soda ash as well. The current estimated natural soda ash reserve in the United States is 23 million tons, allowing the United States to benefit from reduced uncertainties in production and supply chain compared to other regions. Moreover, sodium is one of the most abundant elements in the world, making up 2.36% in the continental crust and 2.7% sodium salt salinity in seawater.[12] This availability potentially opens up alternative mining sources for sodium raw materials, and provide stable production supply to meet rapidly growing demands for energy storage.

Cathodes for NIBs are generally categorized in the following classifications: layered oxides, polyanion, and Prussian blue analogs (PBAs). The gravimetric and volumetric energy densities for these three types of cathode materials are shown in

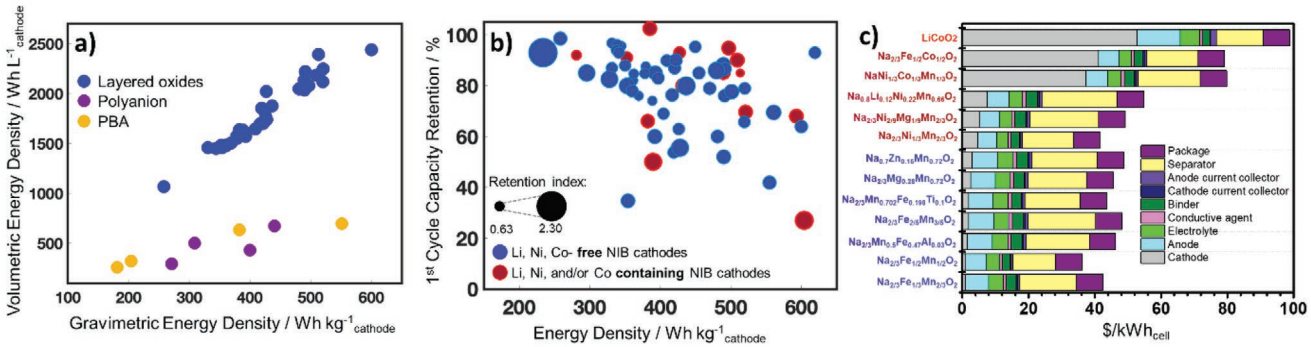

Figure 2. a) Volumetric energy density (Wh L^{-1}) versus the gravimetric energy density (Wh kg^{-1}) are compared for differed types of sodium cathode materials. The blue circles are layered oxides, the purple circles are polyanion, and the yellow circles are PBA. b) Capacity retention of the capacity versus first discharge energy density (Wh kg^{-1}) for layered cathode materials in NIBs. Blue circles are Li, Ni, Co-free sodium cathode materials and red circle are Li, Ni, and/or Co containing sodium cathode materials. The size of the circle represents the severity of the testing conditions using the calculated retention index (Equation (1)). c) Price of energy ($/kWh) at full cell level for selected sodium cathodes and a representative lithium cathode. The Li, Ni, Co-free sodium cathodes are labeled in blue and the ones that contain Li, Ni, and/or Co are labeled in red. Price of energy ($/kWh) for selected sodium cathodes that are Li, Ni, Co-free (blue) and contain Li, Ni, and/or Co (red). (Inset) A pie chart that contains the average cost percentage of lithium-ion battery components, with cathodes representing 44% of the total battery cost (CC = current collector). The price of each element is sourced from metallary.com

Figure 2a and Table S2, Supporting Information.[13–15] Polyanion and PBAs inherently have low volumetric energy densities due to low atomic packing density which makes them better suited for application in tools and starters. Layered oxide cathode materials have higher volumetric and gravimetric energy densities, making them more suitable for grid storage applications. Strategies to enhance the energy density of polyanions and PBA type cathodes include incorporating elements such as Ni, Co, and V to increase both the reversible capacities and nominal voltages delivered.[16] However, use of such rare elements would inadvertently diminish the cost advantages of NIBs. Additionally, the PBA synthesis process can be difficult to scale due to potential safety hazards involved, such as the release of cyanide containing fumes under heat and generation of toxic waste.[16] Among these major classes of cathodes, some layered oxides have been shown to exhibit some anionic redox behavior, serving as an additional source of reversible capacity from the same cathode material. During anionic redox, a reversible O^{2-} to O_2^{n-} transformation occurs during electrochemical charge and discharge.[13] Such oxygen activity have been reported in a variety of layered oxides such as Li/Mg substituted layered oxides (e.g., $Na_{0.6}Li_{0.2}Mn_{0.8}O_2$, $Na_{2/3}Mg_{0.28}Mn_{0.72}O_2$), Na deficient oxides (e.g., $Na_{4/7}Mn_{6/7}O_2$, $Na_{0.653}Mn_{0.929}O_2$), and 4d/5d transition metal containing oxides (e.g., Na_2RuO_3).[13] For these reasons, layered oxides are more commonly studied as cathode materials for NIBs and will be further evaluated in the next section.

The costs and performance of layered oxide materials in both LIBs and NIBs are highly sensitive to chemistries chosen that make up its chemical structure. Most battery cathode materials today contain Li, Ni, and Co, collectively making up 44% of total LIB costs.[17] Unfortunately, expensive elements of Ni and Co are unavoidable to increase the performance (energy density and capacity utilization) of the lithium-based cathode materials and are difficult to replace. However, this is not necessarily the case for sodium ion batteries. Sodium cathode materials free of these less-abundant earth elements can achieve equal or better performance than those using such elements in the transition metal oxides. These comparisons are shown in Figure 2b.[14,15] Due to the lack of standardized evaluation criterion for NIBs, it is difficult to assess different sodium cathode performances across the literature. Conventionally, cathodes are evaluated by their reported rate capabilities, number of cycles, and voltage ranges. Though equally important, electrolyte excess, cathode mass loading and testing temperatures are seldom reported. To this end, we defined a "retention index" (Equation (1)) that normalizes the reported number of cycles, voltage range, and C-rate (1 C = discharge in 1 h) in order to evaluate various sodium cathode electrodes reported in the literature thus far.

$$\text{Retention index} = \frac{\text{No. of cycles}}{500} + \frac{(V_{max} - V_{min})}{3.5} + \left(\frac{\text{C-rate}}{5}\right)^{0.5} \quad (1)$$

In Figure 2b, the retention index is represented by the size of the circles; a larger circle represents more aggressive testing conditions. Using this retention index, cathode capacity retention as a function of percentage (%) is plotted against the first cell discharge energy density for layered sodium cathodes reported in the literature (Figure S1 and Tables S3 and S4, Supporting Information). Only layered sodium cathode materials are included in this analysis, conversion or organic-based cathodes are excluded from the analysis because there are fewer comparative studies on them.[18] Shown by the blue circles, sodium cathode materials free of Li, Co, and Ni exhibit performances equal to or even exceeding those that contain Li, Ni, and/or Co with respect to energy density and retention. In terms of cost, Li, Ni, and Co-free sodium cathode materials exhibit significant advantages over other materials. As shown in Figure S3, Supporting Information, the costs per kWh for $Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$, a cathode material free of expensive earth elements is reported to be under 1 USD whereas Li and Ni containing cathode cost upwards of $5/kWh (materials cost only). Prices can reach up to ≈$40/kWh when significant fractions of Co are used. When considering the differences in material performance and their influence in the needed amount of

electrolyte/anode and other cell components, a detailed full cell level cost breakdown is presented in Figure 2c with the supporting information presented in Table S5, Supporting Information. In this figure, we estimated the cost to construct a full cell at 1 kWh energy level with different cathode materials. The analysis shows that the relative costs from other components carbon, binder, current collector, anode materials, and electrolytes in different cells are not significantly different. By contrast, the cathode price is the main determining factor influencing total cost. This analysis shows that sodium cathodes can achieve good electrochemical performance while keeping costs of materials low by avoiding the use of Li, Ni, and Co.

While layered oxides free of Co and Ni are ideal for grid storage, they still face challenges such as air sensitivity and sodium deficiencies, which limit their potential commercialization. Layered oxides containing Fe and Mn tend to form impurities on the surface and risk water intercalation when stored in air, which can irreparably harm its electrochemical performance.[19] While moisture sensitivity can be avoided through use of dry environments during production, this would also result in increased manufacturing costs. Alternative strategies include use of productive coatings, TM substitution, and/or ethanol washing can be used to reduce the materials' air sensitivity.[19] With regards to sodium deficiency, cathodes with robust electrochemical performances (often layered oxides with P2 phases) tend to be 25–40% sodium deficient in their stoichiometry. This brings about challenges in full cell capacity matching especially under lean electrolyte conditions with a limited sodium reservoir. To mitigate such deficiencies, use of sacrificial salts such as NaN_3, $NaNO_2$, and EDTA-4Na have been studied and found to be promising in compensating sodium deficiencies in the cathode.[20] However, improved selection of salt chemistries are still required to mitigate continuous side reaction against the cathodes over cell cycling.[20]

Despite the prospects of low-cost and high-performance sodium cathode materials, there are still fundamental obstacles to overcome at the cell level before NIBs can be commercialized for the grid. These are summarized as five root challenges in **Figure 3**; electrolyte robustness, anode material selection, interfacial stability (between electrodes and electrolytes), safety concerns, and battery recyclability at its end of life.

First, while organic liquid electrolytes are commonly used in commercialized LIBs, its specific formulations along with optimized solvent, salt, and additives selection still has much room for improvement. As applications in grid storage require NIBs to perform well under a wide range of climatic and intermittent conditions, liquid electrolytes used would require wider operating temperature ranges in order to reduce costly thermal management requirements at the pack and system level. Likewise, cell level engineering and design needs to mitigate the possibility for potential liquid electrolyte leakage and gas evolution over much longer operating lifetimes in stationary storage compared to LIBs used in portable devices. Investigating new systems of electrolytes that have the potential to increase lifetime, such as ionic liquids and solid state electrolyte have led to promising results.[21]

Second, as graphite-based anode materials in LIBs cannot be used in NIBs, alternative carbon-based materials such as hard carbon are often used in NIBs due to its relatively high sodium

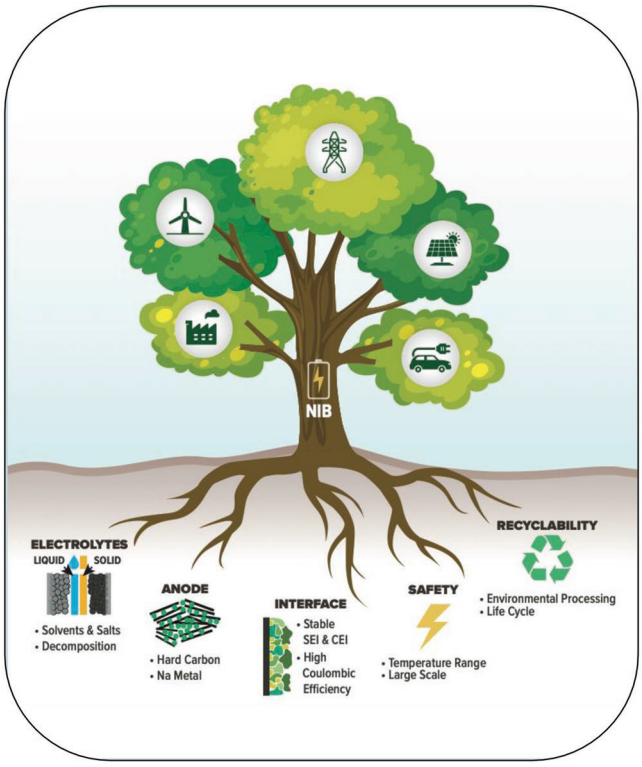

Figure 3. The root scientific challenges (bottom) of sodium-ion batteries that need to be overcome to support sustainable, safe, large-scale energy storage applications (top).

capacity and chemical potentials close to sodium metal.[22] Moreover, hard carbon is commonly produced from various biomass materials (e.g., mangosteen shells,[23] sugar,[24] pomelo peels,[25] shaddock peels,[26] peanut shells,[27] cellulose,[28] corn cobs,[29] cotton,[29] macadamia shells,[31] and wood[32]), offering environmental benefits through its secondary usage in NIBs. However, hard carbon still exhibits low first cycle columbic efficiencies resulting from sodium consumption to form the solid electrolyte interface, keeping reversible capacities low. While the use of sacrificial salts have been shown to mitigate columbic efficiency losses,[33] resolving the performance challenges of hard carbon is still impeded by a poor understanding of its sodium storage and degradation mechanisms.[34] Alternative anode materials for NIBs can be explored instead, such as the use of metallic sodium or metallic sodium alloys (Sn, Sb) that possess higher storage capacities and chemical potentials compared to hard carbon.[35] Although metallic anodes have issues with stability and large volume changes, they also have the potential to drastically increase volumetric energy densities of NIBs due to their dense packing and high mass density. To utilize the benefits of both systems, composites of carbon-based storage together with high capacity metallic anodes may serve as a promising compromise in future NIB anode electrode materials.

Third, designing and optimizing stable interfaces between the electrolyte and anode/cathodes respectively are vital for NIBs to serve grid storage over decades of operation. Interfacial degradation and continuous SEI/CEI growth can result in

increased cell impedance overtime, which can detrimentally affect the battery's rate capability. Additionally, continuous interface reactions can cause low columbic efficiencies that will severely limit a battery's lifetime. Strategies to address this include selecting electrolyte formulations with improve thermodynamic stabilities against the anode/cathode or by controlling the kinetics of degradation by incorporating a highly stable coating on the electrodes.[36]

Fourth, certain battery safety hazards reported in portable devices can bring about some inconveniences and potential minor injury to individual users. However, the dangers of battery fires and explosions would be more catastrophic at the grid scale, with potential for costly property damage and loss of lives.[37] Safety should be highly considered in battery grid storage design with considerations made for its components and geometry. It is encouraging that some reports on NIBs show that they can be safer than conventional LIBs due to its material's superior thermal stabilities.[38] Nonetheless, ideal battery systems deployed at the large scale near densely populated urban grids still need to completely eliminate fire and explosions risks. A promising pathway to achieve this is through the adoption of nonflammable solid-state electrolytes to replace the flammable organic liquid electrolytes, forming sodium based all solid-state batteries. All solid-state batteries are also stable and can operate over a wide range of temperatures, potentially enabling their operation under extreme weather conditions without the need for sophisticated thermal management.[21] Such configurations also allow the adoption of high voltage cathodes without risk of liquid electrolyte leakage or gas evolution over extended cell cycling.

Fifth, it would be hypocritical for proponents of NIB adoption to combat climate change, to not consider how to deal with NIBs at its end of life. LIBs today are facing a rapidly growing battery waste problem, with most batteries not designed for recycling. While it might be too late for incumbent LIB manufacturers to change their manufacturing protocols, potential battery recycling strategies for future NIBs manufacturers should be developed to achieve safe and sustainable disposal of large volumes of spent batteries. Fortunately, new recycling processes are currently being researched based on the principles of direct recycling, allowing battery materials to be processed with reduced energy costs and limited waste generation.[39] However, any effective sustainable strategies would require the co-operation of both manufacturers and policy makers alike, and be regulated to include labeling of their chemical classifications that allow ease of sorting based on their core materials for recycling. This is especially crucial in grid storage batteries due to their large variations in battery chemistries compared to LIBs and longer intended lifespans that potentially forces companies to handle decade old battery packs.

3. Conclusion

Sodium ion batteries (NIBs) and its development shows great promise for grid energy storage applications as an alternative to conventional lithium ion batteries (LIBs). Metrics of energy density, cost, and lifetime are compared across various battery chemistries, where NIBs are surmised as front runners to meet the needs of the grid storage market. Its relative material abundance and ability to deliver good electrochemical performance without use of expensive earth elements are the main drivers of low costs per kWh. Concerns for supply chain reliability and energy security are also discussed where materials availability are considered. Fundamental obstacles toward commercialization include electrolyte composition, anode performance, electrode-electrolyte interfacial stability, safety hazards, and sustainable recyclability are analyzed, along with discussions for potential solutions to tackle them. However, to truly enable NIBs for grid storage, it would require the scientific community to shift development efforts beyond the academic level toward applied research, supported by investments and inputs from the industry to enable a concerted push toward practical cell/pack level testing and evaluation similar to what LIBs have achieved over the past four decades. Ultimately, today's NIBs may or may not be the perfect solution for every challenge faced by grid-scale energy storage, but it will certainly have far-reaching impacts in enabling renewable energy storage and distribution to improve our electrical grid's resilience and reduce humankind's reliance on traditional fossil fuels.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

grid energy storage, intercalation compounds, sodium-ion batteries, sustainability

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