LARGE-SCALE ENERGY STORAGE — PERSPECTIVE

Perspective: Design of cathode materials for sustainable sodium-ion batteries

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ABSTRACT

Manufacturing sustainable sodium ion batteries with high energy density and cyclability requires a uniquely tailored technology and a close attention to the economical and environmental factors. In this work, we summarized the most important design metrics in sodium ion batteries with the emphasis on cathode materials and outlined a transparent data reporting approach based on common metrics for performance evaluation of future technologies.

Sodium-ion batteries are considered as one of the most promising alternatives to lithium-based battery technologies. Despite the growing research in this field, the implementation of this technology has been practically hindered due to a lack of high energy density cathode materials with a long cycle-life. In this perspective, we first provide an overview of the milestones in the development of Na-ion battery (NIB) systems over time. Next, we discuss critical metrics in extraction of key elements used in NIB cathode materials which may impact the supply chain in near future. Finally, in the quest of most promising cathode materials for the next generation of NIBs, we overlay an extensive perspective on the main findings in design and test of more than 295 reports in the past 10 years, exhibiting that layered oxides, Prussian blue analogs (PBAs) and polyanions are leading candidates for cathode materials. An in-depth comparison of energy density and capacity retention of all the currently available cathode materials is also provided. In this perspective, we also highlight the importance of large data analysis for sustainable material design based on available datasets. The insights provided in this perspective, along with a more transparent data reporting approach and an implementation of common metrics for performance evaluation of NIBs can help accelerate future cathode materials design in the NIB field.

Discussion

— Sustainable Developments—Will sodium-ion batteries be the future solution for energy storage challenges?

— Prospective Environmental Effects—Should we consider life-time as an important factor in battery design and production to mitigate the overusing of natural resources?

— Battery Recycling—Is it necessary to evaluate the recyclability factors in parallel with new battery chemistry developments?

Introduction

The world's ever-growing energy demand has highlighted the role of energy storage systems more than ever. During the past few decades, lithium-ion batteries (LIBs) has been the gold standard technology both for mobile and grid level storage. Lithium-containing resources, e.g. mineral ore spodumene or mineral rich brine, are centered in three main countries: Australia, Chile, and Argentina.[1–3] Such localized distribution of lithium (Li) accounts for more than 80% of the global reserves[4] and creates an imbalance in supply and demand for growing large-scale applications. Prior to 2010, the cost of lithium metal accounted only for a very small fraction (< 2%) of total cost of LIBs. Emerging new technologies, such as electric vehicles and exponential production rise in small electronics, has disrupted the lithium metal market and led to a continuous increase on the market price of lithium metal. For instance, the price of Li_2CO_3, a well-known extraction resource for lithium metal, has tripled over the past 10 years.[5] The high demand of Li resources and its increasing cost have triggered the exploration of alternatives or complementarities to Li-based battery technologies.[6]

Low cost per energy density, high safety, reliability, and sustainability are the key requirements for alternatives of lithium-ion batteries. Among different candidates, Na-ion batteries (NIBs) hold a great promise mainly due to the fact that, unlike Li, sodium (Na) is an earth abundant and cost-effective element. Moreover, Na^+/Na redox couple possesses a reduction potential of − 2.73 V vs. standard hydrogen electrode (SHE) (compared to − 3.02 V vs. SHE for Li^+/Li) making it a promising candidate by enabling a similar operating voltage in NIBs compared to LIBs.[5,7] Sodium has a higher molar mass (23 g mol^{-1} vs. 6.9 g mol^{-1} for Li^+) and larger ionic radius (1.02 Å vs. 0.76 Å for Li^+), leading to great differences in its chemical and electrochemical properties, compared to lithium.[8] Higher chemical reactivity of sodium can cause faster solid electrolyte interphase (SEI) formation and a rapid electrolyte consumption.[9–11] On the other hand, since sodium does not form an alloy with aluminum, even at reduced potentials, aluminum (Al) instead of copper (Cu) can be used as the current collector in NIBs. Al is more favorable due to its higher earth's abundance and lower price compared to Cu (abundance in earth's crust: 8.23% for Al and 0.0068% for Cu).[12] Moreover, the charge density (q/r ratio) of Na^+ is lower than Li^+ in solid materials and in certain cases the diffusion of Na^+ in solid phases is much faster than Li^+, thus allowing a fast-charging up to 500 °C current rate (58.5 A.g^{-1}) as recorded by Yang et al.[13] Despite the higher molar mass of Na, Na-containing materials exhibit a great diversity in their structures, especially in polyanions, where Na^+-extracting voltages can be tuned easily through the so-called "inductive effect", which can be used to design high-voltage materials and compensate the energy density loss due to the weight penalty.[14–16]

The attempt of employing the Na^+ as the intercalating guest ion was first introduced in 1980 by G. Newman and L. Klemann from Exxon Research and Engineering Company.[17] A reversible Na^+ insertion/extraction using titanium sulfides (TiS_2) as the host structure at ambient temperature was demonstrated with the cycling up to 16 cycles using sodium triethyl (N-pyrrolyl) borate in 1,3-dioxolane as the electrolyte. Nevertheless, the (de)-sodiation of TiS_2 occurred at rather low voltages (below 2.0 vs. Na^+/Na)[17] that it is not an ideal cathode for NIBs. In the same year, Delmas et al.[18] published a summary study on the structural classification and properties of A_xMO_2 layered oxides (where A stands for alkali metal and M stands for transition metals). In this study, the authors carefully investigated the crystal structures of several A_xMO_2 compositions, including A = Na, and classified them as O3, P2, and P3 types, depending on the Na crystallographic site and stacking sequence of MO_2 slabs. This nomenclature is still widely used up to the present time. The transport properties such as the ionic mobility of the alkali ions based on the crystal chemistry were studied in continuation of their previous works on sodium oxides.[19,20] Soon, the same team reported the electrochemical performance of Na_xCoO_2 ($0.5 \leq x \leq 1$) layered oxide with a promising performance and this was also considered as the first layered oxide for the cathode in NIBs.[21,22] Based on this pioneering work, several generations of layered oxides[23] were developed including those with anionic redox activity.[24–26]

Besides layered oxides, polyanions are an important class of cathode materials for NIBs. Depending on the structure of the crystallized materials, polyanions can be classified as olivine,[27] alluaudite,[28,29] tavorite,[30] $Na_3V_2(PO_4)_2F_3$,[31–33] or NA-Super-Ionic-CONductors[34,35] (NASICON)-like structures. Among them, NASICON-type materials have been widely developed as prospective cathodes for NIBs. This class of materials was discovered in 1976 by Goodenough et al.[34,35] and its general chemical formula can be written as $A_nM_2(XO_4)_3$ (where A stands for alkali metal ions or vacancies, M stands for transition or main-group metals, and X stands for sulfur (S), phosphor (P), silicon (Si), or arsenic (As)). The structure possesses a robust tridimensional network due to the strong covalent bonds between XO_4 tetrahedra and MO_6 octahedra. Despite its early discovery, the electrochemical activity of NASICON in Na-based batteries had not been demonstrated till the mid-1980s with the pioneering work of Delmas et al.[36] on $NaTi_2(PO_4)_3$. Later, PBAs as another type of NIB cathode materials with the general formula of $A_xM_y[M'(CN)_6]_z\ nG$ (where A stands for an alkali metal, M and M' stands for transition metals, and G stands for neutral molecules such as H_2O) were developed.[37–44] They were first introduced in the 1980s and 1990s, but their applications as cathode materials for NIBs using a non-aqueous electrolyte were demonstrated by Goodenough et al. in 2012.[45,46] As this perspective discusses the future development of cathode materials for NIBs, they will be focused in more detail in later sections.

The discoveries and developments in anode structures also catalyzed the improved performance of NIBs. Graphite has been historically known as a prevailing anode in LIBs and many early works in the field of NIBs attempted to employ graphite to this new technology.[47–49] However, Na^+ ions cannot be intercalated

into graphite due to the instability of the Na^+ – graphite intercalation (Na-GIC) and the low potentials of the reaction, which hinder the application of graphite in NIBs.[50-54] Na^+ can only be inserted into graphite as a solvated form in diglyme (or bis(2-methoxyethyl) ether) solvent, but the capacity of the reaction is too low, which is not suitable for practical applications.[55,56] Hard carbon, also known as non-graphitizable carbon, was initially introduced by Dahn et al.[57] as anodes for NIBs in 2000. Hard carbon (with a gravimetric theoretical capacity of 300 mAh g^{-1} and volumetric theoretical capacity of 420 mAh cm^{-3})[58] can be synthesized by a wide range of methods such as chemical, thermal, or biomass-derived processes from various organic compounds at elevated temperatures (700–2000 °C).[58] Low-cost precursors and easy synthesis procedures have made hard carbon a promising anode material for NIBs. However, there are still some fundamental challenges for the implantation of hard carbon in NIBs: (i) its limited practical storage capacity (around 300 mAh g^{-1}), (ii) the electrochemical performance of hard carbon depends strongly on the nature of the precursors as well as processing temperature, which requires a careful optimization, and (iii) the Na^+ storage mechanism needs to be better understood by employing advanced characterization techniques.[59-61]

Besides hard carbon, non-carbonaceous anodes for NIBs were also developed in the last few years.[62] Depending on the reaction mechanism with Na^+, they can be classified as conversion (metal oxides,[63,64] sulfides,[65,66] and selenides[67,68]), alloying [tin (Sn),[69-71] bismuth (Bi),[72] phosphorus (P),[73,74] and antimony (Sb)[75,76]], or insertion materials (titanium-based oxides,[77-79] transition metal chalcogenides,[80,81] and MXenes[82]). Among them, Sn and Sb have shown the greatest promises[83-87] due to their high theoretical capacities (with a theoretical gravimetric capacity of 847 mAh g^{-1} for Sn and 660 mAh g^{-1} for Sb),[88,89] good electrical conductivity (8.7×10^6 S m^{-1} for Sn and 2.55×10^6 S m^{-1} for Sb at 20 °C), low reaction potentials vs. Na^+/Na (0.2–0.4 V for Sn and 0.4–0.8 V for Sb),[89] and less safety concerns associated with them. However, both Sn and Sb suffer significant volume expansions during sodiation process (~ 420% for Sn and ~ 390% for Sb),[7,72] which might lead to contact loss and substantial irreversible capacities upon long-term cycling. Furthermore, the high price and the low abundance in the earth's crust of these two elements (0.00023% for Sn and 0.00002% for Sb)[12] have prevented their wide implementation in NIBs.

Beyond research level prototypes, the advances in this field have enabled some commercialized energy storage systems based on NIB technology in the past few decades. In the 1980s, prior to the commercialization of LIBs, Elsenbaumer et al.[90-92] from Allied Corp. (USA) and Takeuchi et al.[93,94] from Hitachi Ltd. (Japan) have introduced the first full-cell model for NIBs with P2-Na_xCoO_2 as cathode and sodium-lead alloy as anode. The cell could operate up to 300 cycles with no failure. However, the low energy density due to the low operational voltage (< 3 V) did not help these systems compete with the relatively high energy density LIBs available at that time (3.7 V for a Graphite||$LiCoO_2$ cell).

Many years later, the first non-aqueous NIB system was introduced by Faradion Limited in 2015. The company, established in 2011 in the United Kingdom (UK), showcased their first product as an e-bike, powered by NIBs with an energy greater 400Wh per pack. Faradion batteries utilized O3/P2-type $Na_aNi_{1-x-y-z}Mn_xMg_yTi_zO_2$ layered oxides (130 mAh g^{-1}) as the cathode and hard carbon anode (230 mAh g^{-1}). The cells utilized non-aqueous electrolyte and could operate from – 20 to 60 °C.[95-97] In the next few years, several start-ups and companies aiming at commercializing NIBs were created all around the world with a great diversity in the choice of chemistry in the commercialized products. In 2017, the start-up Tiamat[98-100] (France) introduced their first Hard carbon||$Na_3V_2(PO_4)_2F_3$ cylindrical 18,650 cells, which could deliver an energy density of 100–120 Wh kg^{-1}. At the same time, HiNa company[101] (China) developed power banks (120 Wh kg^{-1}) using O3-type $Na_x[Cu,Fe,Mn]O_2$ layered oxide cathode. Altris AB (Sweden) and Natron Energy[102,103] (USA) have also developed prototypes using PBA cathode materials. Recently, Contemporary Amperex Technology Co., Ltd. (CATL)[104] (China) announced a NIB prototype (160 Wh kg^{-1}) for electric vehicles (EVs) with a plan for supply chain (target to 200 Wh kg^{-1}) with a cost $40 per kWh in 2023.

So far, we provided a historical timeline on the advances in the field of NIBs with examples on efforts on both cathode and anode materials as well as some commercialization attempts. A roadmap of NIBs over the years is shown in Fig. 1. While all these efforts have pushed the performance boundaries of NIBs and highlighted their promise as a complement to LIBs, most of the current reports in the literature are rather scattered on different electrode materials with different cycling conditions. Therefore, there remains the need to a clearer roadmap on the design and required performance metrics for NIBs to meet the current market goals. Amongst various components of NIBs, cathode materials are widely considered as the primary limiting factor in part because of their restraint energy density and substantial structural complexity; leading to challenging stability over long cycle life.[7] Given the critical role of cathode material in the cost efficacy and performance of NIB systems,[5,105] we first discuss the important metrics in the key metals in cathode materials that will impact the supply risk and market price in near future. Next, we provide a perspective on design metrics of cathode materials based on an extensive survey on 295 reports in the past 10 years with the focus on the implemented chemistry and composition, and its correlation to battery performance. An outlook on supply risk factor for NIB technology along with performance insights based on a large experimental data set as shown in this work, can set clear directions for future research efforts and pave the path for design of next generations of NIB cathode materials from sustainable and abundance resources.
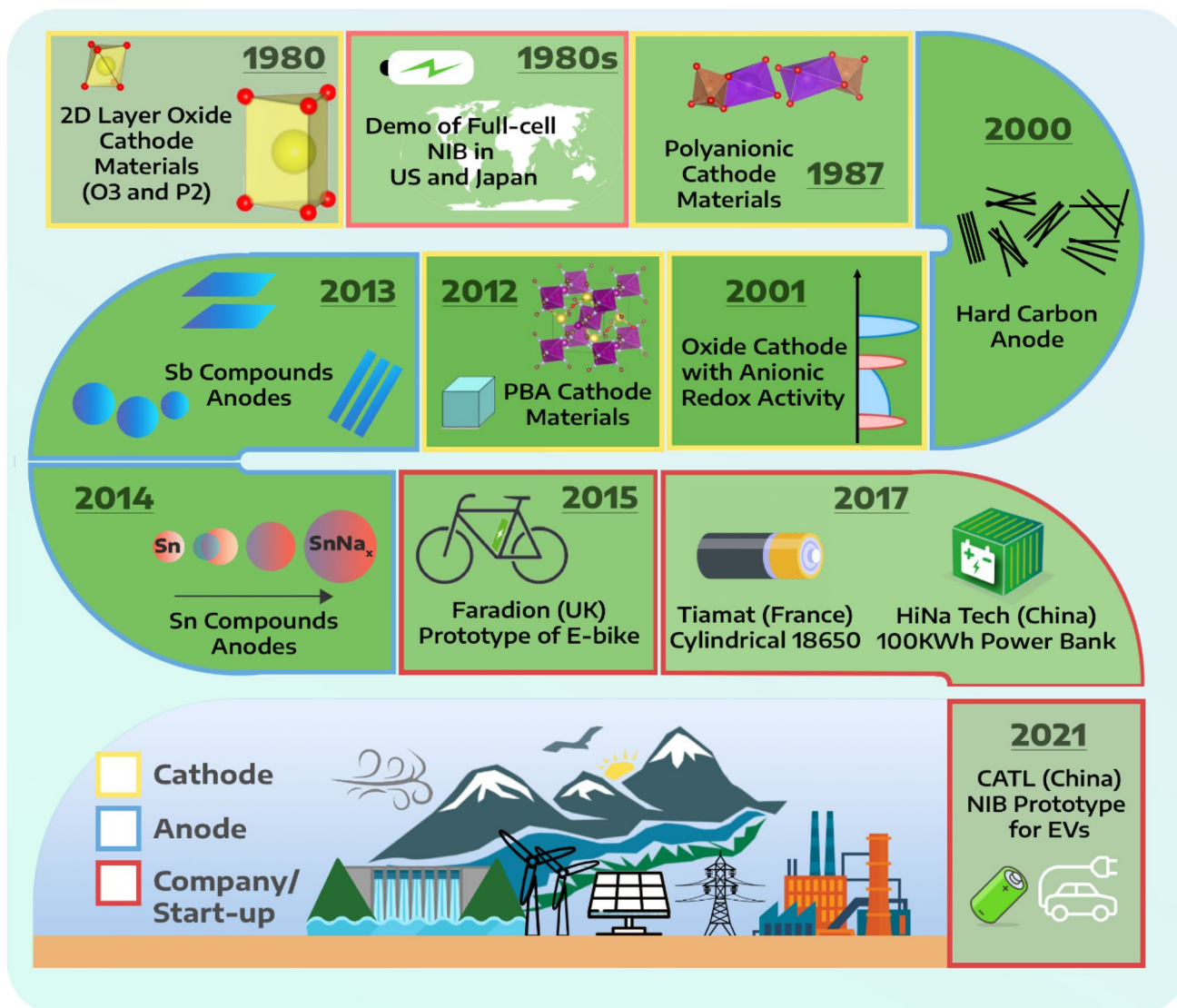
Figure 1. The schematic roadmap of sodium-ion batteries over years, highlighting the discovery of key materials and the relevant prototypes.

Elements applied in cathode materials for NIBs

The research on NIBs has been on the rise since 2010, mainly due to their high-power density and cost-effectiveness. Even though there have been several studies on cathode materials with different structures and elemental compositions,[16,106–108] no benchmark NIB cathode is considered in the battery community. Designing new cathode materials with high energy density, sustainability, and long cycle-life is crucial for NIBs to compete with current LIBs. Habib et al. reported[109] a study on the resource assessment for passenger EVs based on the baseline, moderate, and stringent scenarios. They estimated an increase to a total number of 2.25–2.6 billion passenger vehicles in 2050 compared to 1.13 billion in 2011 and EVs will take over from 24 up to 73% of these passenger vehicles. The authors also pointed out that the use of critical elements in batteries might be the possible limiting factor, impeding the transition to EVs in the near future.[110] In this context, a sustainable design of cathode materials is crucial as all cathodes contain transition metal ions[111–113] and many of which are considered as "critical" due to natural or geopolitical constraints.

The main transition metals used in sodium cathode materials are manganese (Mn), Iron (Fe), Aluminum (Al), Titanium (Ti), Nickel (Ni), Vanadium (V), and Cobalt (Co). The metals are
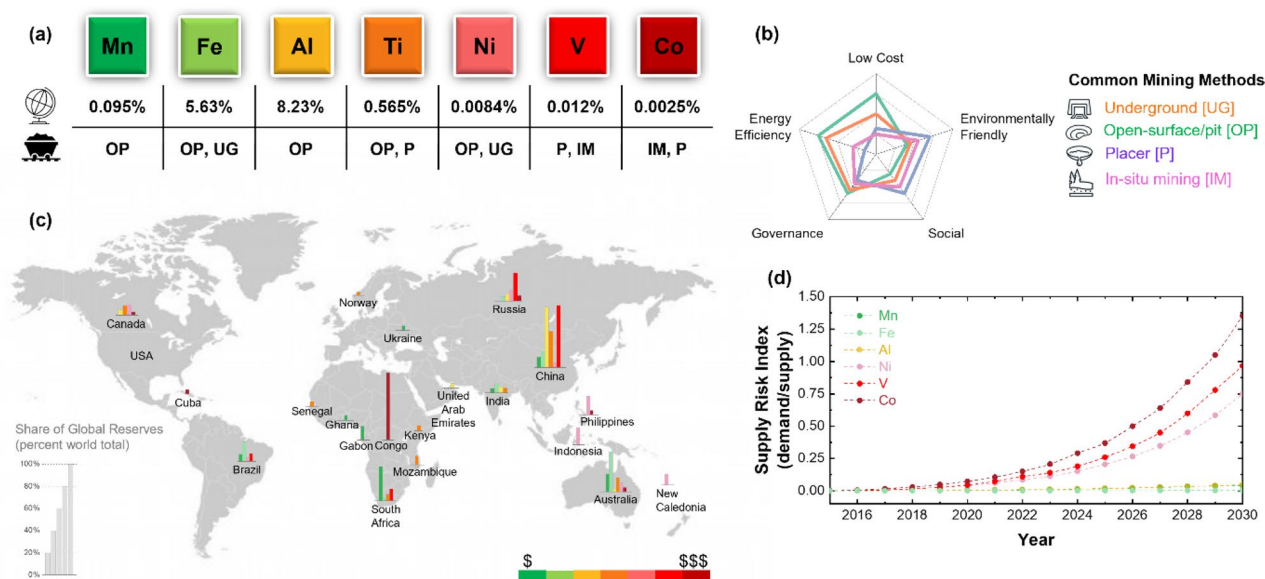
Figure 2. Main metal elements used in cathode materials for NIBs. (a) The abundance of elements in the earth's crust and the main methods of their mining. (b) Spider plot comparing various desirable parameters for the main four mining methods. (c) Share of global reserves for the main metal elements presented on the world's map as in percent world total. (d) Supply risk for the main metal elements from 2015 to 2030.

sorted in order of their price per ton and are shown in Fig. 2a. The overall abundance of the elements in the earth's crust[12] is shown in Fig. 2a. Among these elements, Al and Fe are the most abundant, while Ni and Co have the lowest abundance in the earth's crust.

Metals can be extracted from ores and rocks as the naturally formed compounds in the Earth's crust. The minerals with high enough concentrations of desired metals can be considered as a source of metals. There are four common mining methods for the extraction of metals: underground mining, open surface (pit) mining, placer mining, and in-situ mining.[114] Underground mining requires to dig down (varied between 300 and 3000 m) into the earth with horizontal tunnels and vertical and diagonally sloped shafts to reach the ore deposits. It is considered as a suitable method for minerals located deep under the surface of the earth. The open surface or pit method requires removal of the plant life, soil, and potentially bedrock to access the deposits of ore, which is suitable for minerals located closer to the earth's surface. Many minerals can be accessed by both underground and open surface mining, and the choice of the method depends on the depth of depositions and their economic value. However, these two methods pose several environmental and social concerns, such as physical disturbance to landscapes, degradation of the surface (soil) and groundwater quality, and increase of air-borne dust and emissions like sulfur dioxide and nitrogen oxides.[115] Open surface method is known as a more cost-effective method compared to the underground method. Furthermore, it should be noted that the modern mining tries to mitigate these undesirable environmental impacts by the implementation of advanced scientific and technological approaches.[116,117]

Placer and in-situ mining are expensive techniques, but they cause minimal disturbance to the surface and minimal waste rock generation. The placer method separates metals from sediments through sifting.[118] In-situ method or solution mining is an in-place extraction approach by injecting a chemical solution to dissolve the minerals in their original location and pumping back the solution including the minerals (known as the pregnant solution) to the surface. There is no extraction of rocks and ore to the surface for any process.[118]

From the scientific point of view, the choice of mining method[114] is usually determined based on four main factors: (i) the location of the mineral, (ii) the financial value of the deposit, (iii) environmental considerations, and (iv) the chemical composition of the mineral. However, other external parameters can also have a great impact, such as (i) energy efficiency, (ii) governance (characterizing the adequacy of national political and regulatory institutions), (iii) cost (including logistic, production, and labor), (iv) social impacts (reflecting the national and regional socioeconomic factors of vulnerability such as poverty, inequalities, and demographic imbalance), and (v) environmental effects (impacting waste containment including climatic and topographic factors, water resources and availability, biodiversity).[119,120] The impacts of these external factors on the four mining methods are compared in a spider plot in Fig. 2b. Open surface and underground mining methods possess higher energy efficiency, lower cost, and better governance compared to placer and in-situ mining methods and are mainly used for Mn, Fe, Al, and Ni. On the other hands, placer and in-situ mining methods are considered as better social and environmentally friendly methods used for V and Co, although exhibiting lower energy efficiency and higher cost.

Global reserves and supply risk for critical elements

The share of global reserves for main metal elements in the world is shown in Fig. 2c.[4] These values are presented in percent of the world total and are reported for the countries with above 3% global shares. The unbalanced geographical distribution of some critical metals highlights the limitation of the supply chain around the world. For example, the Democratic Republic of Congo solely retains more than 60% of global reserves for cobalt while Russia, Australia, and Cuba are the following countries with less than 5% of the global share in each country. Another critical element is vanadium, which is distributed mainly in China, Russia, and South Africa with about 56%, 25%, and 11% of the global share, respectively, leading to above 92% of the total global share. On the other hand, manganese is distributed in Australia, Asia, Africa, and South America, yet there is a lack of resources in North America. Overall, the unequal geographical distribution of critical elements leads to long-term economic, ecological, and political challenges over the world especially for countries with no sufficient share reserves.

The limited share of global reserves and the increasing demand for critical metals have a great impact on their economic values around the world.[121-123] Therefore, ensuring a sustainable supply of these metals is the essential key for industrial and large-scale manufacturing. The supply risk index, defined as the ratio between demand over supply, for some critical metals from 2015 to the forecast of 2030 is presented in Fig. 2d. Co, V, and Ni are predicted to suffer high supply risks with a rapid demand in the coming years. This risk will be substantial by 2030 and the demand can hit the supply need. In order to ensure a sustainable supply of critical metals for future applications, recycling could be an essential solution. Direct, pyrometallurgy, and hydrometallurgy recycling methods have been extensively developed for LIBs,[3,124,125] which can thus be translated to Na-ion technology. Even though several encouraging achievements have been obtained in the field of NIBs,[126-129] further studies are required to develop more sustainable recycling methods that can be applied to different types of materials.[130] Furthermore, battery recyclability and planning for batteries' end of life (EOL) must be considered in the design step to minimize environmental and economic effects.[131,132]

Main sodium cathode categories: Oxides, polyanions, and PBAs

Over the past 20 years, research for positive electrode materials in NIBs has been mainly centered around layered oxides, polyanions, and PBAs. The representative crystal structure of these materials and their general formulae are given in Fig. 3a. In this figure, M is representative of the transition metals (TMs) in these structures and the most common TMs for each category are listed as well. In LIBs, there is a great interest focusing on high-Ni NMC-based layered oxides ($LiNi_xMn_yCo_{1-x-y}O_2$); nevertheless, there is no clear trend on which class of sodium cathode materials should be the main target for successful commercialization.

To gain insight on the most promising candidates for the next generation of sustainable NIBs cathode structures, one needs to hold a full picture of the current experimental results in the literature. Here, we summarized the performance of the 295 Na-ion half-cells using oxide, PBA, or polyanion as cathode materials. The upper cut-off voltage (V) versus the 1st discharge specific capacity (mAh g^{-1}) and the capacity retention (%) versus energy density (Wh kg^{-1}) are shown in Fig. 3b and c, respectively. The size of the circle diameter represents the number of cycles. Overall, we can observe that high energy densities do not lead to high capacity-retentions and long-term cycling. On average, layered oxides exhibit a higher specific capacity and energy density compared to polyanions and PBAs, owing in part to their lower molar mass, but they usually suffer from shorter lifetimes. It should be noted that most layered oxides possess a high electronic conductivity in the pristine or desodiated states, allowing them to exhibit excellent electrochemical performance even without any coatings. On the other hand, polyanions are usually electronic insulator due to the strong covalent bonds in the structure and thus carbon coating is widely used to help them achieving good electrochemical behaviors, especially at high current rates. In layered oxides, the layer exfoliation and high-volume expansion occur during cycling, leading to capacity loss and short lifetime. The strong covalent bonds in polyanions and PBAs result in a robust network that can support long-term cycling (Fig. 3c). It is important to note that the operating voltage, stability, and energy density of the oxides strongly depend on the structure, Na-content, and the nature of the transition metals present in the composition. Furthermore, most electrolytes reported in the literature utilize organic carbonate- or ether-based solvents, exhibiting an upper stable voltage at ~ 4.2 to 4.5 V vs. Na$^+$/Na, which also limits the performance of cathode materials.

To achieve a compositional design of a sustainable cathode material, implementation of advanced tools such as machine learning on predictive models with descriptors such as crystal structure of materials, their surface characteristics, and their electrochemical performance is vital.[133-137] Figure 4 summarizes the energy density and capacity retention of different sodium cathode materials depending on their crystal type, space group, and TM-content in the composition.

Layered oxides (Na_xMO_2) are generally classified by the Na crystallographic site and the number of the metal oxide sheets (MO_2) in the stacking sequence. In layered oxides, Na$^+$ can reside in the prismatic (P) or octahedral (O) sites between MO_2 sheets, and Delmas et al.[18] suggested that the resulted structure should be called as P- or O-type. These characters are followed by an index indicating the number of MO_2 slabs required to generate a repeating unit. While O-type structure is exclusively encountered in Li_xMO_2, the large ionic radius of Na$^+$ allows the stability of both O- and P-types in Na_xMO_2 with P2 and O3 are the two common ones.

In P2-Na_xMO_2 layered oxides, Mn, Fe, Ti, Ni, and Co are the most used TMs. Mn is the most frequent TM used in P2 oxides in the range of (0.5–1) thanks to its low cost, high abundance,
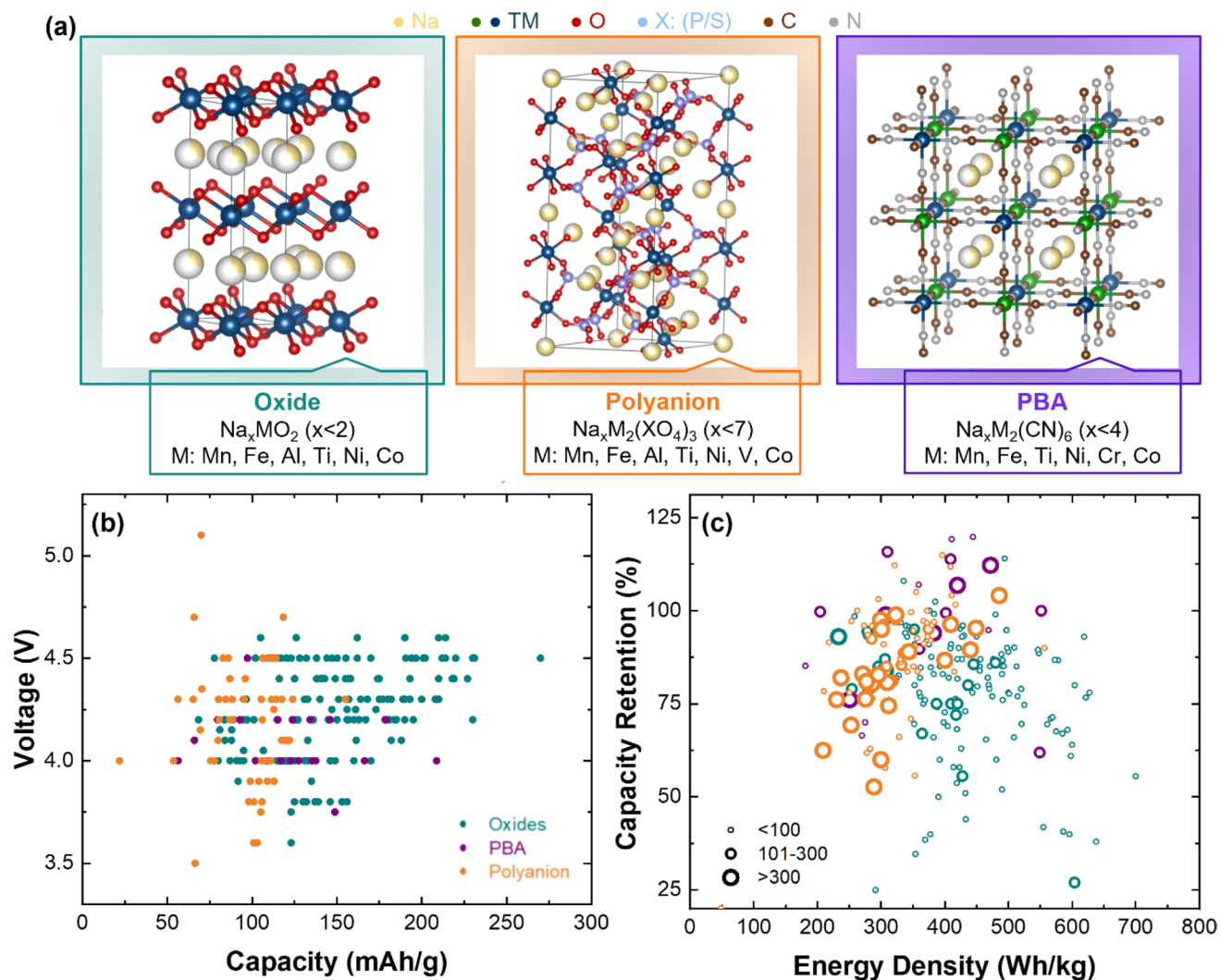
Figure 3. The three main types of cathode materials for sodium-ion batteries: oxide, polyanions with NASICON as a representative, and PBAs. (a) A representative crystal structure of oxide, polyanion (NASICON), and PBA as the three main types of cathode materials for sodium-ion batteries. The general formula for each type of material is listed below the schematic. M is the representative of TM. The performance of the 295 NIB system using oxide, polyanion, and PBA cathodes is presented as (b) Upper cut off voltage versus capacity, and (c) Capacity retention versus energy density. The circle diameter is representative of cycle numbers.

and good electrochemical performance that can ensure high energy densities. Many Mn-rich layered oxides (Mn-content of 0.7–0.8) show high capacity-retention and high cycle life as the electroactivity of Mn can be activated in the average potential range with minimal degradation of the active material. Therefore, Mn-containing layered oxides are usually considered as the main cathode material[138,139] for NIBs while other substitutions can be implemented to further enhance their performance. The presence of Ni can increase the operating voltage and thus the energy density; however, high voltages always lead to severe degradation processes. This leads to a limited Ni usage in the layer oxides (usually in the range of 0.1–0.3).[140-149] Co can increase the intrinsic electronic conductivity of the materials and its usage in a higher amount is desired to optimize the cycling rate and

capacity retention. However, our dataset shows that it will be at the cost of energy density.[150-152] Ti- and Fe-substitutions are also widely used. The presence of Ti usually lowers the voltage and energy density of the active materials,[153,154] but its usage at low concentration helps to shift down the operating voltage to the electrochemical window of most currently available electrolytes and to lead to higher energy density and capacity retention.[155-158] Fe-substitution in Na_xMO_2 usually increases the material's theoretical capacity thanks to the reversible activity of Fe^{4+}/Fe^{3+} redox couple at high voltages in sodium layered oxides.[159,160] Furthermore, a recent study has shown that the presence of Fe^{3+} also helps to obtain reversible anionic activity.[140] However, a closer look showed us that higher Fe content can lead to lower capacity retention in a wide range of energy
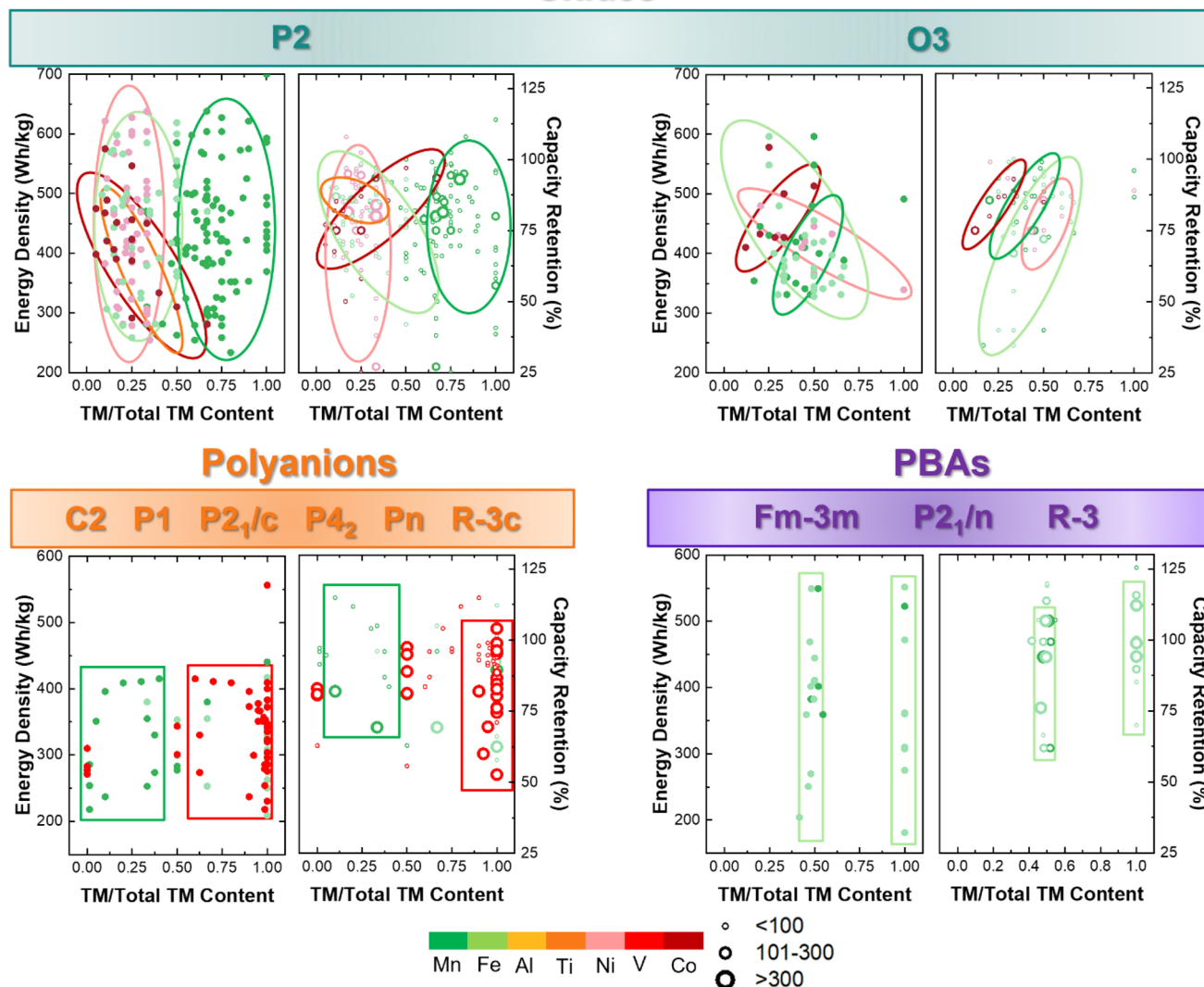
Figure 4. Energy density (Wh kg^{-1}) and capacity retention (%) for the three main types of cathode materials for the most common phases used in NIBs. The size of the dot represents number of cycles while the color indicates the type of metal.

densities.[161,162] It should be noted that the electrochemical performance of a material does not depend solely on one kind of ion substitution, it depends greatly on the presence of other cations in the structure and the mutual interaction between them. In general, P2-Na$_x$MO$_2$ can potentially enable higher rate capability due to the facile sodium ion mobility through the adjacent trigonal prismatic environment.[24,25,163–165] This feature is unique to P2 sodium materials as a superior advantage compared to LIB cathodes.

Similar analysis on O3-type oxide cathode materials shows that most materials reported in the literature contained an Mn-, Co-, or Ni- content with less than 0.5 ratios while Fe-content was usually in the range of 0.25–0.75. High Mn- and Co-content usually leads to higher energy density and capacity retention[166,167] while high Fe- and Ni-content tends to result in lower energy density but higher capacity retention.[168–173] In order to achieve

a sustainable supply, Mn-based compositions should be the main focus for layered oxides, where their physical/electrochemical properties can be modulated through the incorporation of other metal ions. The choice of the metal substitution depends on the requirement of the applications, such as voltage, specific capacity, or cycle life.

The second category of the cathodes is polyanions. The crystal structure of polyanions is quite rich and depends strongly on the nature and the interconnection between the polyhedral constituting the framework. The main space groups encountered in this class of materials are $C2$, $P1$, $P2_1/c$, $P4_2$, Pn, and $R\text{-}3c$ (Fig. 4). For NASICON-based materials, $R\text{-}3c$ is the dominant space group; nevertheless, Na$^+$ ordering can also occur with a symmetry reduction to monoclinic systems.[174] Strong covalent bonds between polyhedral units enable this type of material to support long-term cycling with minimal

structural degradation.[175] Figure 4 presents that V, Mn, and Fe are the widely used TMs in Na polyanions cathode materials. Fe/V-content is mainly used in the range of 0.5–1 thanks to their great feasibility to reside in the different polyanionic frameworks. Among them, V-based polyanions can enable high capacity and long-term cycling. While Mn, Ni, and Co dominate layered oxides research, their presence in polyanions is quite modest. This could be explained by their specific chemical and crystallochemical properties where Mn, Ni, and Co can hardly be incorporated in the polyanionic framework. Except few structures such as olivine ($LiMPO_4$), Mn, Ni, and Co can only exist in polyanionic frameworks at a minor portion (less than 0.5) thanks to the presence of other structural stabilizers. Some important examples of these compounds are $Na_xMV(PO_4)_3$ (M = Mn, Ni,).[176,177] The energy density of polyanions can be engineered by modulating the operating voltage by varying the nature of the electroactive ions or the counterpart anions. For example, incorporating fluorine (the most electronegative element) into some polyanion structures[178,179] allowed an operating voltage up to 4 V vs Na^+/Na with high energy densities. Despite this feature, the development of polyanion materials with low-cost and earth-abundant elements is necessary and is still an ongoing research challenge.[180-183]

The third category of sodium cathodes is PBAs with the general formula of $A_xM_y[M'(CN)_6]_z$ nG. PBAs structures include one or more transition metal ions (in M and M' sites) coordinated by CN^- ions to form hexacyano complex. The connection between $[M'(CN)_6]^{n-}$ units results in opened channels allowing a fast ionic diffusion process inside the structure. Their crystal structure can be indexed in the Fm-$3m$, R-3, or $P2_1/n$ space group depending on the degree of distortion induced by the amount of Na^+, water molecules, and the nature of the electroactive center. Most PBAs utilize abundant elements such as Mn and Fe, making this class of cathode materials one of the best price-to-performance ratios reported to data.[103,184] Mn- and Fe-based PBAs can provide a wide range of energy densities (200–600 Wh kg^{-1}) and capacity retentions over relatively high number of cycles in non-aqueous electrolytes (Fig. 4). The accessible specific capacity strongly depends on the stoichiometry of the structure and the initial Na^+ concentration. Generally, the electrochemical cycling of the PBAs is categorized into two main classes: (i) only hexacyanometallate active group, and (ii) active M site TM as well as the hexacyanometallate active group.[103] The class (ii) with higher electron transfer reactions is more favorable in practical batteries by enabling higher specific capacity. Manganese hexacyanoferrate is the most well-known and commonly used PBA cathode material with two active sites of transition metals offering two electron transfers. Recently, cobalt hexacyanoferrate is also introduced as another type of the PBA cathode material with this property,[185,186] yet low yield of synthesis considering the high cost of cobalt suppresses the large-scale applications. The number of the electrochemical active TM also affects the operating potentials. For example, an active polarized M site TM can tune the inductive effect on $M'(CN)_6$ leading to higher operating potentials. These cathodes with two electron transfers are considered among the highest energy density cathode materials with more than 150 mAh g^{-1} specific capacities in above 3 V operating voltages in NIBs.

One of the limiting factors in TM selection in PBAs is originated from the synthesis procedure to obtain a stable and insoluble PBA material. Most common bulk synthesis methods are from the reaction of a transition metal salt (M^{m+}) with a simple cyanide (CN^-) or with a hexacyanometallate salt ($[M'(CN)_6]^{n-}$). Although using the simple cyanide results in high yield production, but it limits the material to only one type of the transition metal resulting in lower specific capacity. On the other hand, utilization of hexacyanometallate salt is considered as a flexible and high yield method and is the main method used in the most patent documents using PBA cathode materials. One of the well-studied materials with this method is manganese hexacyanoferrate with sodium-rich initial composition enabling full two electron transfers.[187] Another synthesis method for PBAs is through the decomposition products of a hexacynometallate salt.[188,189] This method leads to a highly crystalline and fine primary crystal grain size; however, it is not a suitable method for large batch production and scalability due to the required high temperature or pH and large quantity of HCN as the by-product.[190,191] Moreover, the long cycle-life of PBA materials is mainly limited by the electronic conductivity in the bulk of the active materials due to the limited reversible sodium intercalation into the bulk structure.[192] This point highlights the importance of the size and morphology control in this type of materials. Many ongoing researches have focused on the employment of multi-electroactive centers to enhance the stability and the electrochemical performance of this class of materials. For example, Moritomo et al.[193] showed lower capacity loss by partial substitution of the Mn with Fe or Ni in manganese hexacyanoferrate.

In general, the energy density of polyanions and PBAs are not as high as those of layered oxides, which is a penalty of the high weight of the anionic part. However, the cyclability of polyanions and PBAs are greatly higher than oxides with the average number of cycles for oxides, PBA, and polyanions are 93, 257, and 686, respectively. The robustness of polyanions and PBAs helps them to find their place in applications where energy density is not the critical criterion, such as large-scale applications in grid storage or aqueous batteries.

Yet, the cyclability of NIBs is inferior to LIBs at the moment. This can be due to several factors such as (i) less advancement in design and structure of the sodium cathode materials, (ii) more sensitivity of the cathode materials to moisture and carbonates which results in more limitations in preparing and handling of the cathode materials, and (iii) limited electrolyte study and development in NIBs. Majority of the studies in NIBs are still in discovery stage with the focus on the synthesis and development of materials with different compositions and their electrochemical performance in limited time and conditions. Moreover, there is a very limited attention to the long cycling performance and the mitigation of the degradation mechanisms. In overall, as suggested, development of next generation of NIBs for large-scale production, require a comprehensive investigation with more than thousands of cycles.

It is important to note that to reach a sustainable design for NIBs, one needs to hold a full picture of all battery components including anode and electrolyte. As such, while the current work provides a practical framework to screen and design of the cathode structures, it is crucial to develop similar datasets with a focus on the anode and on the electrolyte.

Data reporting standard for NIBs

In the literature, P2- and O3-layered oxides have generally shown comparable energy densities and capacity retention, however, it is noteworthy that P2 materials have often been tested under more rigorous conditions compared with O3 (higher applied current densities, longer cycle numbers, and deep discharge). On the other hand, PBAs and polyanions have shown noticeably longer cyclability than layered oxides. Unfortunately, due to large variations in these testing conditions, it is difficult to accurately evaluate the overall performance across all materials.

As outlined in this manuscript, the sustainable design of the cathode materials is crucial for feasibility studies of next generation of sodium ion batteries. Our in-depth review demonstrated that there several topics that are not well explored in current NIB studies such as, (i) cathode degradation mechanism, (ii) cathode-electrolyte interphase (CEI) design, and (iii) SEI engineering. Despite their vital importance, there has been very limited studies on these topics that requires more in-deep fundamental investigations using advanced characterization techniques. Future studies on these can provide a better outlook on the next generation NIBs.

Commercialization and manufacturing of batteries are mostly not considered at laboratory-level research. Investigations at cell-level are necessary for the materials level evaluations, however, scale-up needs investigation for optimal parameters and conditions at large-scale formats.[194] Academia with laboratory-scale studies needs to be linked to the industry with large-scale applications. This approach saves the extra costs in research and facilities and helps to facilitate the path towards manufacturing.

The statistical summary of reported data from 295 sodium-ion half-cells published in the literature is shown in Fig. 5. The data shows that only about 37% of the studies reported the cathode loading (data varies between less than 1 mg/cm^2 (0.8 mg/
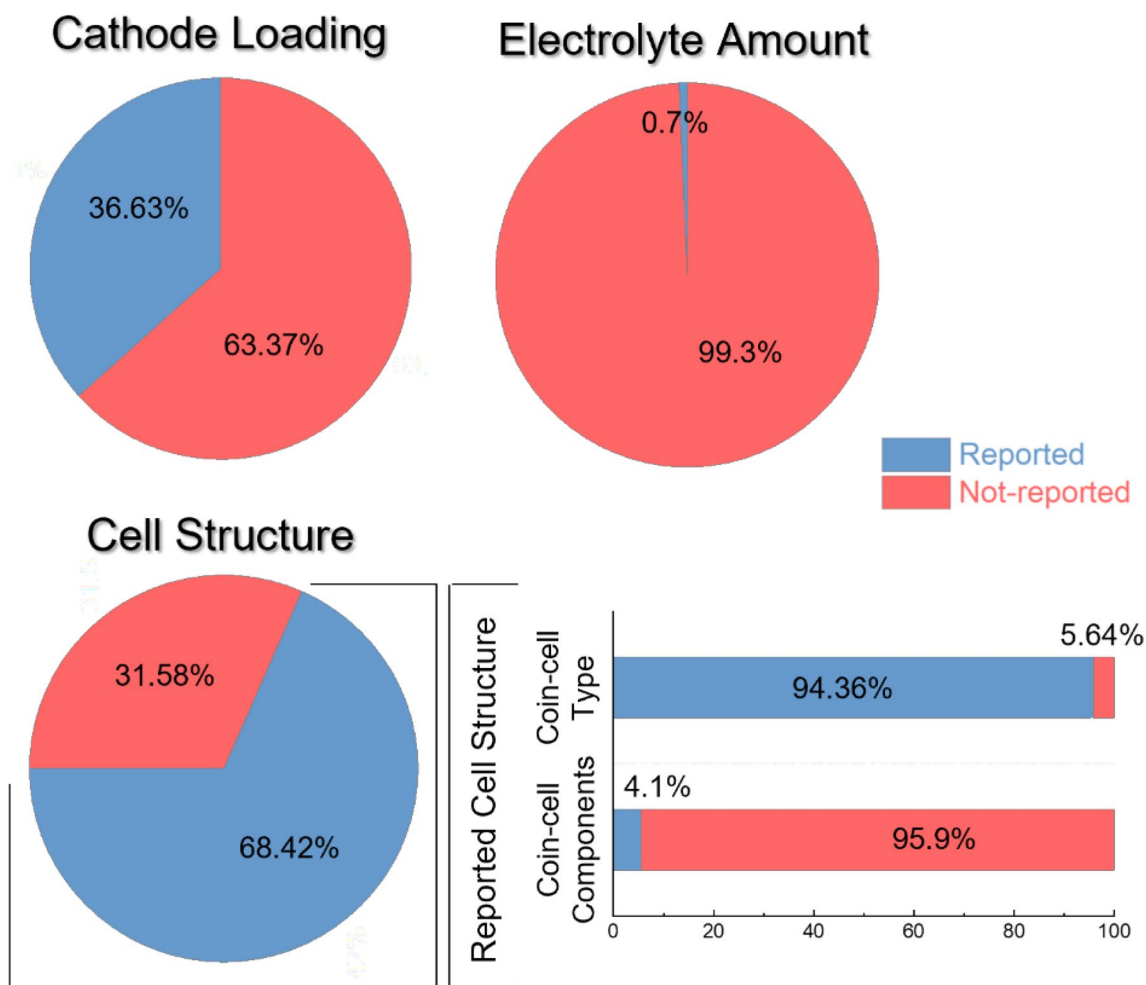

Figure 5. Statistical summary of reported data from 295 sodium-ion half-cells reported in the literature.

cm^2) to 10 mg/cm^2) and only less than 1% of them reported the electrolyte amount. It is also observed that about 69% of the studies reported the cell structure. Among these, the coin-cell type (CR2016 or CR2032) is the main information stated while the coin-cell components are not commonly mentioned. Only about 2.8% of the total systems have reported details about coin-cell components.

To this end, it is necessary to have a standardized and transparent data reporting in the battery community. It is also important to develop a common set of testing protocols among NIB battery researchers and developers to regulate common testing parameters. The following information is vital in battery data reporting: areal capacity, cathode loading and composition, conductive agent and binder types and contents, electrolyte amount, cathode to anode ratio, separator type, cycle number, applied current density, operating temperature, and cell configuration. Similar sets of protocols have already been laid out by the Battery500 Consortium led by the US Office of Energy Efficiency & Renewable Energy for LIBs as it was followed in the work of Niu et al.[195] These protocols mandate participating researchers c in order to facilitate the evaluation of LIBs. If applied to NIB research, it can serve to both create transparency across reports in the literature, as well as streamline resources toward the most urgent challenges faced by NIBs.

Conclusions

Manufacturing sustainable green and low-cost NIBs with high energy density based on earth-abundant elements can play a significant role in the next generation of energy storage systems. In order to establish a material design outlook for this goal, here we critically evaluated 295 research articles based on various cathode structures for NIBs, published in the past 10 years. Given the importance of future material supply in such perspective, we evaluated main metal elements (Mn, Fe, Al, Ti, Ni, V, and Co) used in sodium cathode materials using the following metric: abundance in the earth's crust, global share reserves, side-effects of their mining methods, and their supply risk. Our perspective shows that Mn and Fe satisfy most promising criteria for sustainable designs.

While the recent studies show encouraging results of enhanced energy density and overall cycle performance in oxides, polyanions, and PBA cathode materials, cross analyzing all reported results suggest that higher energy density does not lead to higher capacity retention and cycle life in all cases. Considering this broad outlook suggests that a cathode metal needs to be tailored in detail for optimum capacity and electrochemical cell performance.

We acknowledge that this data set still has some limitations including the lack of data scalability from the half-cell to full-cell or consistent and coherent reporting of testing parameters. Thus, the analysis conducted here is not a universal standard for adoption but rather an example of a common database for NIBs which may be used to accelerate research efforts on this front. We believe such an effort would promote a more collaborative research environment, avoid unnecessary repetition of work, and benefit the entire battery community to advance the next generation of NIBs.

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Declarations

Conflict of interest

The authors declare no competing financial interest.

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