Na-Ion Batteries—Approaching Old and New Challenges

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The last 10 years established the beginning of a post-lithium era in the field of energy storage, with the renaissance of Na-ion batteries (NIBs) as alternative for Li-based systems. The development of this technology has required intense work in materials research in order to produce and optimize anodes, cathodes, and electrolytes for NIBs. The strong and weak points of the main families of compounds for each battery component are analyzed in this progress report. Taking into account the achievements made in materials for NIBs, the industrial scene is analyzed through the existing prototypes and commercial cells and also from an economical viewpoint. In this scenario, where Na-ion technology seems to be ready for a coming second generation, the use of Na can be extended to almost the whole spectrum of electrochemical energy storage systems: the new room temperature Na–S systems, high-energy Na–air technology, or high-power Na-based hybrid supercapacitors. Thus, the degree of development of NIBs, together with the promising performance of newer Na-based energy storage systems, makes Na the key to the coming commercial post-lithium systems.

1. Introduction

Joint efforts are required toward the achievement of a sustainable and low-emission energy model to cope with the important challenges of the climate change, resource wastage, and increased urbanization in coming years. This energy transformation will hinge on the extensive use of renewable and green sources, which in most cases are intermittent and weather/season dependent. Therefore, to ensure affordable and continuous energy for consumers as well as to increase the security of the energy supply, the development of energy storage solutions is critical. Batteries are an inseparable part of this transition, and as society continues to grow and evolve, so must too battery technologies. Sodium-ion batteries (NIBs) in particular

are proving to be an emergent technology with potentially very attractive properties. They are potentially low cost and environmentally friendly with reduced supply risk. However, the development of NIBs faces various challenges such as low gravimetric and volumetric energy densities and difficulty in achieving broader voltage windows.

Although early studies in NIBs date back to the 1970s, just like Li-ion battery (LIB) research, the commercialization of the former systems in 1991 by the team formed by Sony and Asahi Kasei marked a milestone not only in the field of energy storage technology but also in the evolution of the modern society. This technological breakthrough had been possible thanks to several preceding contributions, particularly the works by M. S Whittingham,[1] J. Goodenough,[2,3] and A. Yoshino[4] on the discovery of Li-ion intercalation materials (Nobel Laureates in Chemistry 2019). This important historical event polarized material science research toward Li-ion technology and slowed down considerably the advances in the field of sodium. However, at the end of the 2000s, mainly driven by the concerns about future lithium supply and the uneven worldwide distribution of its reserves and resources, the research on Na-ion re-emerged and so did the number of articles published (**Figure 1**). The intercalation chemistry of both metal ions is very alike, and thus, the materials tested for NIBs could be similar to those used in Li-ion systems. Both systems share the same working principle, and therefore, in terms of manufacturing, the industry producing LIBs can be easily tuned towards NIB fabrication, which is an important asset to invest in and support this technology. NIBs started to reach the market in the early 2010s, about two decades after their Li counterparts. Nevertheless, the progress has been relatively fast due to the straightforward LIB equipment and facility transfer just mentioned.

In the search of high performance, low cost, abundance, low environmental impact, long-term cyclability and safety, layered metal oxides, polyanionic compounds and Prussian blue analogues (PBAs) are among the most studied families of Na-ion cathode materials. On the anode side, metallic sodium exhibits the same operation and safety problems as lithium, and therefore, it cannot be considered an option in conventional NIBs. Thus, in this scenario, most of the research has been dominated by the use of disordered carbons, mainly hard carbons (HCs). Other prospective anodes

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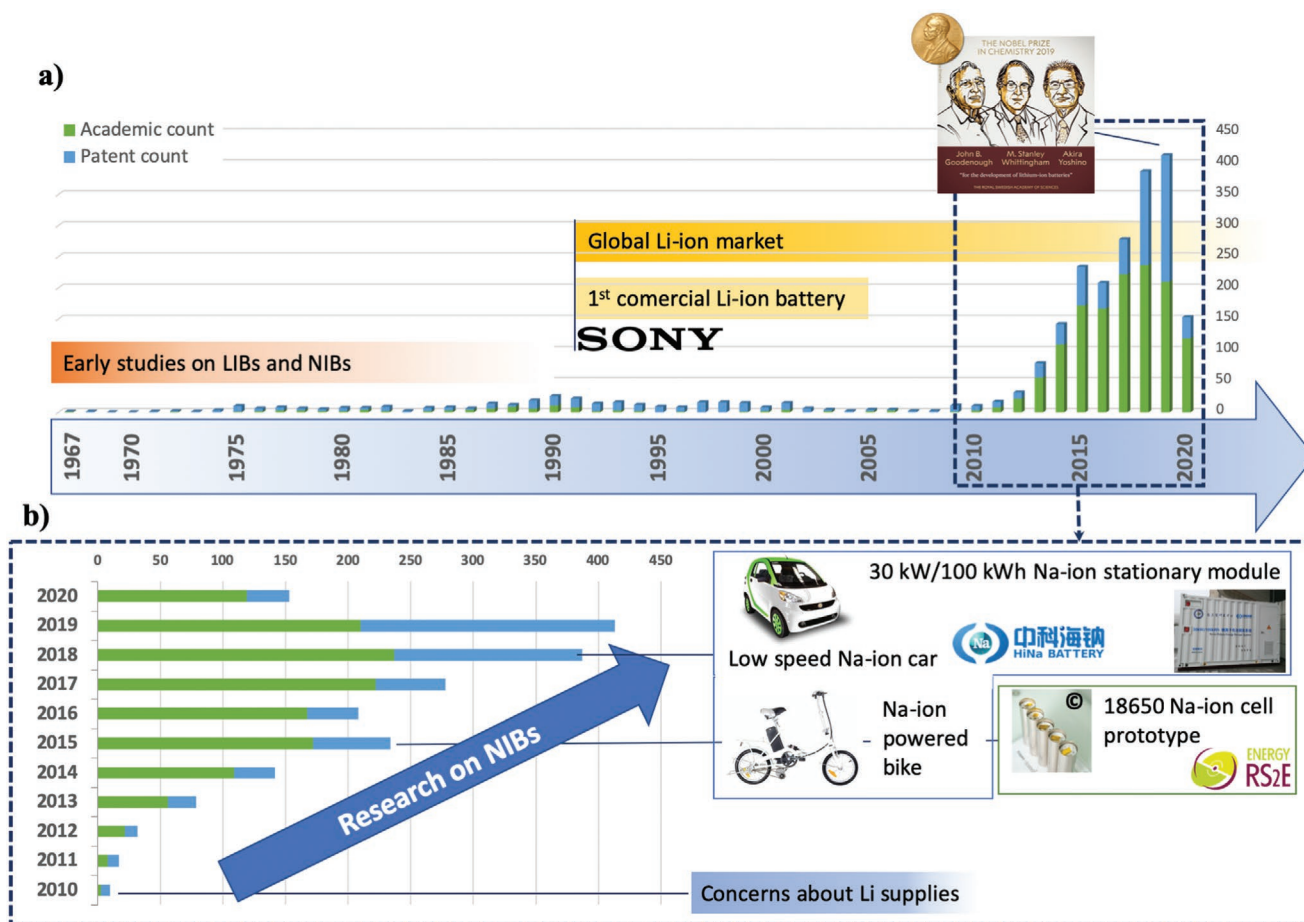ADVANCED
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Figure 1. a) Number of academic publications and patents regarding "sodium ion battery" and "Na ion battery" concepts and chronology of battery development last updated on 22nd May 2020); b) detail of the enormous increase on NIBs in the last 10 years, together with the main achievements in the field. Image of 18650 cells, Reproduced with permission. Copyright Cyril FRESILLON, Tiamat, CNRS Photothèque. Image of Car and bicycle reproduced with permission. Copyright HiNa battery company.

that are also discussed in this work include alloying and conversion materials.

In NIBs, most of the research efforts have been directed toward the improvement or finding of electrode active materials. Nevertheless, for this technology to succeed, all other components also need to be considered. Among all, of foremost importance are electrolytes, which have to be highly stable in the electrochemical window defined by the very low reduction potential of the anode and the high potential of the cathode material. However, considering the battery chemistry, one of the future trends is all-solid-sate-batteries. Thus, this will be one of the main topics discussed herein and, consequently, solid-state or quasi-solid-state electrolytes will also be carefully considered. After analyzing the most important advances in terms of materials, with a careful analysis of the different pros and cons, the full-cell combinations that have reached the market are analyzed in terms of performance and cost. NIBs have generally been directed toward stationary applications where size is not an issue. However, their niche is yet to be defined and mobility applications cannot be discarded as already shown by various companies. The commercialization and production of these systems is still at a very infant stage as compared to LIBs. However, recent news on the Australian market have shed some light on the near future of this technology. In this regard, a special issue covering recent advances in electrode and electrolyte materials, characterization techniques, and modeling together with the scaling up and commercialization was recently published in this journal.[5] Finally, after summarizing prospective directions on NIBs, future perspectives of the closely related Na-ion hybrid capacitors, room temperature Na–S batteries, and Na-air batteries are discussed.

2. Sodium Ion Batteries: Retrospective and Advances

2.1. Anodes

The search of appropriate anodes for NIBs has been an issue difficult to solve due to the limited capacity of the conventional anode materials for LIBs, such as graphite and silicon, to store Na. Even metallic sodium itself is not eligible as anode for a Na metal system because of its trend to form dendrites and its low melting point, (97.7 °C) that would lead to security issues. The scope of materials that have been proposed as possible anodes for
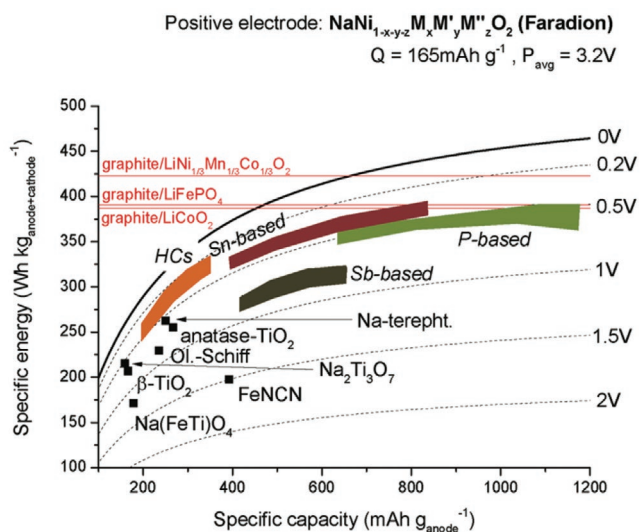
Figure 2. Energy density versus specific capacity range for various negative electrodes materials used in NIBs, namely hard carbons (orange), Sn-based (red) and Sb-based (dark green) alloys, and P-based compounds (light green). Oxides and organic electrodes are also represented by black squares. Full cells are considered where gravimetric energy density (Wh kg⁻¹), based on the weight of active materials in optimally balanced positive and negative electrodes, is calculated by the difference of average potential and reversible capacity of active materials examined in Na half cells according to previous reports. The positive electrode chosen for these full cells is a commercial layered oxide $NaNi_{1-x-y-z}M_xM'_yM''_zO_2$ from Faradion Company. Reproduced with permission.[8] Copyright 2017, John Wiley & Sons, Inc.

Na-ion systems is wide and covers compounds that store sodium through insertion, conversion, and alloying mechanisms.[6] These possible anode materials comprise organic compounds as carbonyls, Schiff bases,[7] or quinone derivatives; inorganic oxides such as TiO_2, $Na_2Ti_3O_7$ (intercalation), Fe_2O_3, Co_3O_4, or CuO (conversion); elements of group 14 and 15 (Sn, P, Sb, Bi, and Ge) that alloy with sodium; and disordered carbons. The performance of these materials can be compared by estimating the specific energy of theoretical full cells with a commercial layered oxide as cathode counterpart and plotting it versus the specific capacity (C_{sp}) of the anode materials (**Figure 2**). The analysis of these parameters indicates that these anode materials can be classified into two groups. First, those that achieve energy density values of ≈250 Wh kg⁻¹(anode+cathode) and those that surpass the 300 Wh kg⁻¹(anode+cathode) threshold. Organic electrodes and oxide materials can be classified into the first group, whereas alloy materials and carbon based anodes can provide specific energies close to the ones registered for commercial graphite/$LiCoO_2$ cells.[8]

2.1.1. Metal Oxides

A close look at the first group of materials shows that oxide-based materials, for example, $Na(Fe,Ti)O_4$ or $Na_2Ti_3O_7$ possess limited specific capacity due to their relatively high molar mass, but their inorganic scaffold confers these materials superior stability that leads to good cycling performance.[9] Diverse forms of titanium dioxide, such as anatase,[10] rutile,[11] or β-TiO_2[12] have also been explored as anodes. Each of these polymorphs

shows a different degree of reversible Na insertion by going through distinct structural changes during electrochemical reaction.[13–15] Although the mechanisms involved in the Na reversible insertion processes of these phases are compelling from the in situ and ex situ characterization perspective, they also present relatively low specific capacity to belong to commercial Na-ion batteries.

2.1.2. Organic Materials

In the case of organic anodes, these materials present undeniable advantages such as their low cost, abundant resources, high C_{sp}, and a huge structural versatility, but also the disadvantage of a low first cycle coulombic efficiency (FCCE), pulverization during cycling, low electrical conductivity, and dissolution of organic molecules in the electrolyte.[16] The use of additives such as graphene can mitigate these drawbacks by enhancing the conductivity of the composite electrode while anchoring the organic molecules.[17] Other strategies to overcome the dissolution of organic compounds beyond the use of additives, can be the encapsulation, polymerization, surface modification, salt formation, and the electrolyte choice. The development of organic NIBs is still in an initial state with promising results. A more detailed description of the organic anode materials under research and their electrochemical mechanisms can be found in refs. [8,16,18] and herein.

2.1.3. Conversion and Alloy-Based Materials

Conversion and alloying materials deliver high specific capacities but the large volume changes during the reversible electrochemical process leads to pulverization of the active materials and loss of electrical contact within the electrode, which heads to rapid capacity fade. The wide variety of possible alloy and conversion anodes covers elements such as Sn, Sb, or P transition metal oxides and chalcogenides (M_xO_y or M_xS_y where M = Fe, Co, Cu, Mn, Ni, Mo) and transition metal nitrides and phosphides (Cu_3N, Fe_2N, Mo_2N, etc.). The strong and weak points of all these materials can be found in these references and herein.[19,20] A possible approach to mitigate the limitations shown by all these anode materials consists on the use of additives such as graphene. Optimal use of graphene as additive should entail increasing the low FCCE caused by its high surface area.[17] The preparation of bimetal sulfides such as the Ni@$NiCo_2S_4$ composite with enhanced electrochemical performance, recently published by Shen et al., opens a new path to obtain conversion anodes with improved properties.[21]

2.1.4. Carbon-Based Materials

The use of carbon-based materials, such as amorphous carbons or graphene is currently under research in order to mitigate the capacity decay with cycling. Given the prevalence of carbon-based anodes in the early commercial systems that will be presented in Section 3, the discussion will focus on disordered carbon anodes. Among the wide variety of carbon-based

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materials, graphite does not play a principal role because it shows negligible sodium uptake when conventional electrolytes are used; only glyme-based electrolytes allow reversible cointercalation of Na^+ ions into graphite material.[22] Although graphite presents stable performances and low irreversibility in the first cycle, it presents lower specific capacity and large volume change. For these reasons, disordered carbons that combine amorphous regions with crystalline ones, such as hard and soft carbons (HCs and SCs, respectively), are the main materials under research. The electrochemical behavior of SCs and HCs is closely related to the precursor and the synthesis conditions.[23] In addition to these materials, reduced graphene oxide (rGO), 3D porous carbon frameworks, and the N, B, or P-doped counterparts of HCs, SCs, and rGO present promising features as carbon-based anodes. A detailed description of these doped carbon materials and the structural changes leading to increased specific capacity can be found in refs. [24–27] and herein. **Figure 3** presents the reversible specific capacity of the mentioned carbons versus their average oxidation voltage.

As it can be observed, among carbons identified as group A (low voltage carbons), HCs present relatively high specific capacity values with the lowest oxidation voltages, and SCs show slightly lower C_{sp} with higher oxidation voltage. In the case of HC, theoretical calculations indicate that a specific capacity higher than 530 mAh g^{-1} could be obtained from this type of materials by combining Na^+ insertion and absorption into HCs.[26] Recently, Komaba's group has reported a 480 mAh g^{-1} specific capacity value for a hard carbon prepared by using a MgO template.[28,29] In any case, for both HCs and SCs, improving the FCCE is still a challenge related to specific surface area and the choice/formulation of the electrolyte.
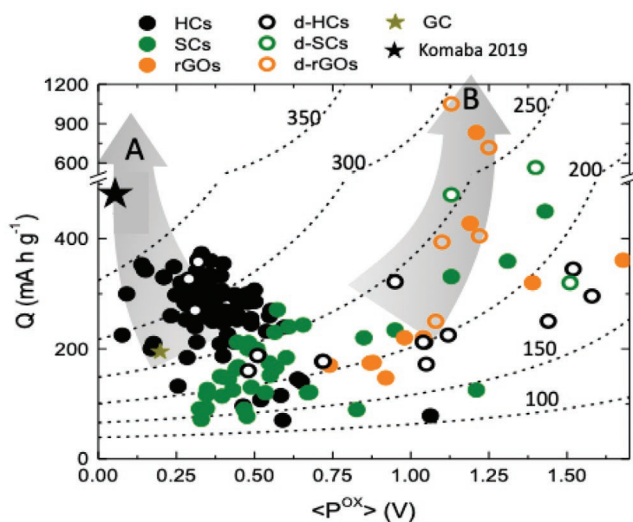
On the other hand, the key challenge in the short term for carbon materials represented as group B (high specific charge carbons) is to moderate the low coulombic efficiency and to diminish the operating voltage in order to obtain higher specific energy anode materials.

In any case, it can be said that both precursors (raw biomass or synthetic polymers) and synthetic conditions (the use or not of a pretreatment) are determining parameters to achieve a final carbon with a unique microstructure/microporosity/surface area set of properties that will control the electrochemical performance of the material.[30] Optimization of all these aspects would represent great benefit in terms of sustainability and economics for a global-scale market as grid-energy storage.

2.2. Cathodes

The set of materials that can be used as cathodes for Na-ion systems is characterized by a rich chemistry that covers a wide variety of chemical families. This ample range of materials derives from the size difference between Na^+ ions and the transition metal ions that stabilizes a great diversity of functional structures that allow reversible Na^+ extraction/insertion.[31] The main families studied as cathode materials for Na-ion comprise layered transition metal oxides, polyanionic compounds (phosphates, fluorophosphates, mixed phosphates...), Prussian Blue derivatives, conversion materials (transition metal fluorides or oxyfluorides, sulfides, selenides...), and organic compounds (conjugated carbonyls or redox active polymers). **Figure 4** gathers these families of compounds together with their strong and weak points.

Among the mentioned cathode materials, layered transition metal oxides and polyanionic compounds are the most

Figure 3. Specific capacity versus average oxidation voltage of hard carbons (HCs, black circle and black star, the one reported by Komaba in 2019 with outstanding specific capacity), glassy carbon (GC, green star), soft carbons (SCs, green circle), reduced graphite oxides (rGOs, orange circle), doped hard carbons (d-HCs, black open circles), doped soft carbons (d-SCs, green open circles), and doped rGOs (d-rGOs, open orange circles). The discontinuous lines correspond to the specific energy at full cell level. The gray arrows identify the two main groups distinguished among carbon materials as anodes for NIBs, A) low voltage carbons, B) high specific charge carbons. Reproduced with permission.[23] Copyright 2018, John Wiley & Sons, Inc.
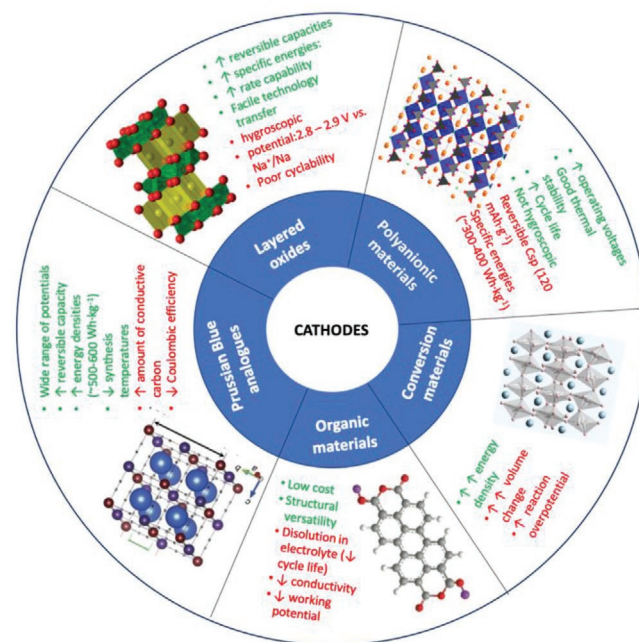

Figure 4. Chemistry families explored as cathodes for Na-ion batteries with their strong and weak points (green and red, respectively).

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promising options. Each type of material possesses different features and limitations that can be appropriated for different applications.

2.2.1. Sodium Layered Oxides

These types of cathodes are popular in NIBs for multiple reasons such as their excellent electrochemical performance, having been derived from earth abundant precursors, being inexpensive, and feature scalable synthesis. Several recent review papers are available which contain excellent discussions on the state of knowledge of sodium layered oxide cathodes and shed light on the development of these materials.[32–37] Among the different possible structures of the Na_xMO_2 compounds, the most interesting from an electrochemical point of view are P2- and O3-phases, which differ from each other by the different stacking sequence of the sodium ions and the transition metal layer (**Figure 5**).

The P2-type phases show higher rate performance and capacity retention than the O3-type, although they are only stable with sodium contents ≤0.67, which translates into lower capacities. In the O3-type phases, it is possible to achieve the fully sodiated phase, delivering higher capacities, but this structure is less reversible due to the O3-P3 phase transitions that alter the diffusion mechanism of the Na^+ ions giving rise to large energy barrier that Na^+ ions must overcome. In fact, one of the main intrinsic drawbacks of sodium layered oxides is due to these phase transitions that cause large volume changes in the material (≈23%) and lead to poor capacity retention and cycling performance.[37] This structural instability is specially critical in Mn-based sodium layered oxides, where the presence of Mn^{3+} cations causes a distortion in the structure due to the Jahn Teller effect leading to degradation on cycling. By doping/substitution with different elements, it is possible to stabilize the structure limiting the amount of Mn^{3+} ions. Following this strategy, introducing Ni into the structure, greater stability of the P2 phase and better cyclability are obtained since Mn acts as an inactive redox structural element, while Ni^{2+}/Ni^{4+} couple participates in the redox reaction.[38] A higher Na content (>2/3) in the structure allows a reduction of the average oxidation state of Ni, promoting the oxidation of Ni^{2+} to Ni^{4+} at lower charge voltages, leading to higher structural stability of the P2

phase, as observed in P2-type $Na_{45/54}Li_{4/54}Ni_{16/54}Mn_{34/54}O_2$.[39] The use of Ni as an active redox element results in higher working average voltage, although the charging voltage must be limited to avoid detrimental phase transitions (≈3.5 V). In addition, the presence of Ni reduces sensitivity to air making it difficult to insert harmful species such as CO_3^{2-} in the transition metal layer.[40] Rational choice of doping/substitution elements leads to dramatic performance improvements. Thus, the introduction into the structure of other inactive elements of similar ionic radii (such as Li, Mg, Cu, or Zn) allows the structure to be stabilized without damaging the electrochemical performance.[34] Furthermore, a correct composition optimization can further increase the Na content (from 0.67 to 0.85) in P2-type materials, delivering superior performance (improved reversible capacity and enhanced cycling stability), achieving air-stable materials as in the case of the P2-type $Na_{7/9}Cu_{2/9}Fe_{1/9}Mn_{2/3}O_2$ and $Na_{0.85}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$ phases.[41–44] Binary Mn/Fe layered oxides are another promising family of materials that combine high operating voltages (due to Fe^{3+}/Fe^{4+} couple) and excellent specific capacity. An increase in Mn content in the P2-$Na_{2/3}Mn_{1-y}Fe_yO_2$ phase has been determined to result in increased capacity retention, but also worse electrochemical capacity.[45,46] Specifically, an 80% Mn content has been determined to provide the best balance between specific energy and cycling stability. Doping this phase with Ti (P2-$Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$), it is possible to obtain a Co and Ni free cathode that exhibits an extraordinary capacity retention (>95% after 50 cycles) and reaches reversible capacities of more than 130 and 80 mAh g^{-1} for C/10 and 1C, respectively.[47,48] Recently, the addition of sacrificial salts in the P2 phases (e.g., NaN_3, Na_3P or $Na_2C_4O_4$) as additional sources of sodium has been explored, decreasing the irreversible capacity of the first cycle and increasing significantly the capacity and the capacity retention.[49–52] The O3-type phases, due to the higher sodium content, provide higher capacities, such as the O3-$NaNi_{0.5}Mn_{0.5}O_2$ phase that can deliver ≈105 and 125 mAh g^{-1} at rates of 24 and 4.8 mA g^{-1}, respectively, in the voltage range of 2.2–3.8 V.[53] The presence of other co-dopant elements in the appropriate amounts such as Fe, Co, or Ti can improve long-term cycling ability in addition to excellent specific energy density.[37] A clear proof of the positive synergistic effect of the introduction of co-dopants is the $Na_aNi_{(1-x-y-z)}Mn_xMg_yTi_zO_2$ material, selected by Faradion
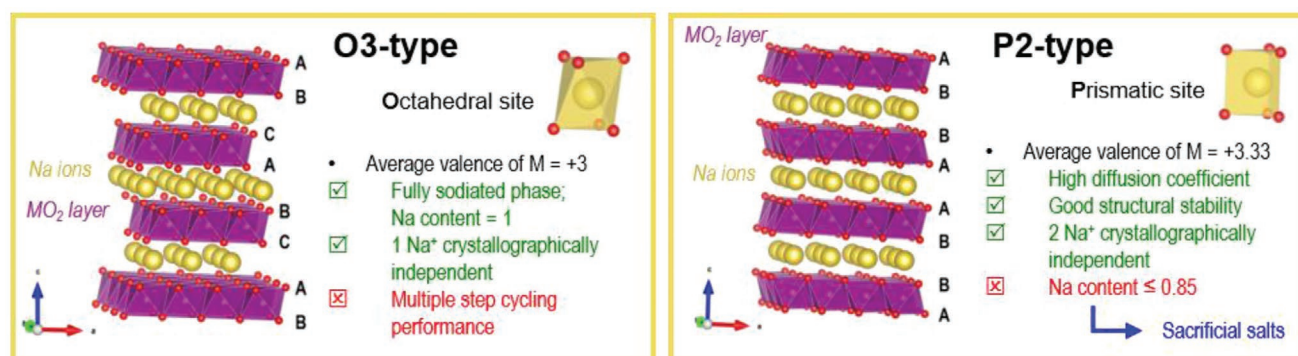

Figure 5. Representation of the O3- and P2-type structures of $NaMO_2$-layered oxides and their main characteristics. The MO_6 octahedra and Na-sites are shown in purple and yellow, respectively.

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Limited as cathode in its prototype of commercial NIB.[54] Small amounts of doping can influence the structure evolution of the materials upon cycling, improving electrochemistry. Surface coating (carbon, TiO_2, Al_2O_3, polymeric coating,…) can mitigate the capacity fading and increase cycle life, protecting from harmful side reactions between the cathode and the electrolyte, in addition to facilitating better contact in the case of using solid electrolytes.[55] This approach has been successfully applied in the Al_2O_3-modified P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ system, forming a more flexible cathode electrolyte interphase (CEI) that protects layered oxide cathode from exfoliation processes, which results in higher coulombic efficiency and superior cycling performance between 2.3 and 4.5 V.[56] Morphology and particle size are also critical factors in the design of the cathode with optimized electrochemical performance, for which it is of vital importance to control the synthesis method.[57] Combining the individual properties of each phase by synthesizing P2/O3 composites leads to materials that exhibit high specific capacity (O3 acts as Na reservoir and avoids the gliding of the main phase upon cycling) and improved rate performance and structural stability (P2 provides a lower barrier to Na^+ diffusion), as has been demonstrated in manganese-rich P2/O3-phase $Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$ material.[58]

It also worth highlighting the anomalous excess capacity observed in some alkali-rich transition metal oxides (TM). The most widely accepted interpretation is the reversible O^{2-}/O^- oxygen redox hypothesis,[59–62] which is a radical departure from the materials chemistry point of view. However, there are some important controversies regarding this interpretation. This way, A. Van der Ven´s group, analyzing some Li-rich manganese cathode materials, strongly criticizes this hypothesis and attributes the origin of the anomalous capacity to the Mn oxidation processes (from Mn^{4+} to Mn^{7+}) together with the migration of these cations from octahedral to tetrahedral sites.[63] This hypothesis can explain the activation step, the voltage hysteresis, and voltage fade observed in some alkali-rich Li and Na layered oxides.

For the commercialization of this type of sodium layered oxide cathodes, it is important to be aware that, in the literature, studies generally focus on half cells obtaining energy densities of 500–550 Wh kg^{-1}, but when transferring the materials to studies in full cell, this value falls dramatically to ≈300 Wh kg^{-1}.[64] The exploration of full cells has been discussed in depth in a recently published review.[65] It is essential to carry out full cell studies in order to promote the development of practical NIBs for energy storage systems in the near future.

2.2.2. Polyanionic Materials

These materials present higher redox potentials than that of layered oxides due to the inductive effect of polyanionic groups (up to 4 V vs Na^+/Na) and stable and robust structural framework, which confers long cycle life; high thermal stability and safety.[66,67] Limitations of polyanionic materials comprise their low ionic and electronic conductivity and the lower specific capacity of these compounds due to their elevated molar mass. Different strategies have been used to mitigate the effects of these limitations, such as the control of particle size, the use of carbon coatings, and the introduction of dopant elements in order to enhance Na^+ diffusion and to increase intrinsic and extrinsic conductivity of the material.

Two family of materials, Nasicon-type $Na_3V_2(PO_4)_3$ and $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ stand out among the vast scene of polyanionic compounds, that gathers chemical species containing polyanion units such as $(SO_4)^{2-}$, $(PO_4)^{3-}$, $(BO_3)^{3-}$, $(SiO_4)^{4-}$, $(P_2O_7)^{2-}$, or their combination with F^- or even between them (mixed phosphates).

NASICON (Na SuperIonic CONductor) family of compounds can accept a great number of transition metals to form $Na_3M_2(XO_4)_3$, where M = V, Fe, Ni, Mn, Ti Cr, Zr, etc., and X = P, S, Si, Se, Mo, etc., and presents open 3D Na^+ transport channels in the scaffold that allow Na^+ high diffusion rates during the electrochemical reaction.[68,69] This configures a robust structure that can be tuned by combining different transition metals and anions, although the Nasicon-structured materials studied as cathodes are in general phosphates with different combinations of transition metals, such as V, Fe, Mn, or even combinations between them. In particular, Nasicon-structured $Na_3V_2(PO_4)_3$ is one of the most extensively studied positive electrode materials. The different operating voltages that can be displayed according to the redox couple of V that is reacting with sodium ions, 3.4 and 1.5 V versus Na^+/Na (with theoretical C_{sp} of 117 mAh g^{-1} for each reaction voltage) make possible the preparation of symmetrical full cells by using this same compound as anode and cathode.[70] The control of particle size and the use of different carbon coatings have promoted excellent rate capabilities for this compound, with 115 mAh g^{-1} at C/10 low rate[71] and reaching 44 mAh g^{-1} at 200C.[72] Moreover, a $Na_3V_2(PO_4)_3$/C@RGO composite material has achieved an ultralong cycle life of 10 000 cycles at 100C.[73] These two parameters, outstanding rate capability and extended cyclability, make this material a great candidate to be used in high power systems, such as hybrid supercapacitors. A detailed revision of the main works on Nasicon based cathodes can be found in ref. [70] and herein.

Sodium vanadium fluorophosphate family, $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$, where x goes from 0 to 1, is a group of V^{3+} ($x = 0$), V^{4+} ($x = 1$), or $V^{3+/4+}$ mixed valent compounds that display high operation voltage in two pseudoplateaux at 3.6 and 4.1 V versus Na^+/Na.[74,75] As in the case of $Na_3V_2(PO_4)_3$, this family of materials has been thoroughly studied in the last years, providing a theoretical specific capacity of 130 mAh g^{-1} and excellent cyclability of even 1200 cycles with 90% of specific capacity retention.[76]

It must be said that both groups of compounds are based in V transition metal, which is considered a drawback due to its toxicity and cost when compared to environmentally friendly Mn-based layered oxides.

There are two Fe-based polyanionic compounds that also deserve to be mentioned. The first one, $Na_2FeP_2O_7$, provides excellent power capability, safety, and cycle stability but presents a low operating voltage (3.0 V vs Na^+/Na) that limits its energy density. The second is alluaudite structure $Na_2Fe_2(SO_4)_3$ that presents high operation voltage and is made of environmentally friendly elements.[77] In this case, the practical use of this material is hindered by its strong hygroscopic nature.

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2.2.3. Prussian Blue

A third option to be used as cathode in NIBs are the Prussian Blue and its analogues (PBAs), of formula $Na_2M[Fe(CN)_6]$ (where M = Fe, Co, Mn, Ni, Cu, etc.). These hexacyanoferrates present an open framework structure with abundant redox active sites and strong structural stability. Prussian Blue can reach a high capacity of ≈160 mAh g^{-1} at a 3.1 V versus Na^+/Na, whereas the double Mn analogue can reach 209 mAh g^{-1} at 3.5 V. The great variability of available transition metals to be incorporated into the structure leads to a wide range of potentials. Moreover, these materials present high reversible capacity, high energy densities (about 500–600 Wh kg^{-1}), and can be synthesized by low temperature methods. As disadvantages, they need high amounts of conductive carbon that leads to lower volumetric capacities, coulombic efficiency still needs to be optimized, and they present potential toxicity if free cyanide ions are liberated, so additives would be needed in the battery to prevent it. In addition, as the synthesis process for these compounds is usually in aqueous medium (hydrothermal or precipitation), these materials contain a certain amount of coordinated or interstitial water. This fact is considered a drawback for PBAs in non-aqueous batteries due to the reactivity of water inside the system. On the contrary, the use of PBAs with aqueous electrolytes is an advantage, where outstanding cyclabilities can be achieved with no security issues. A more thorough description of PBAs and their application as cathode materials for NIBs can be found in ref. [78] and herein.

2.2.4. Conversion-Based Cathode Materials

There are also possible cathode materials that react with sodium via conversion reactions, such as transition metal fluorides (MF_x, where M = Fe, Ti, V, Co, Ni and Cu; and x = 2 or 3), oxyfluorides, sulfides (Fe_xS_y, Co_xS_y), selenides, or CuCl and $CuCl_2$. These materials present theoretically much higher specific capacities and, thus, energy densities than the ones based on intercalation reactions, so they would allow configuring high-performance NIBs. For example, FeF_3 and FeS_2 possess a theoretical specific capacity of 731 and 892 mAh g^{-1}, respectively, much higher than the C_{sp} values calculated for insertion compounds. However, up to date, they present strong limitations related to their large volume change and overpotential during the electrochemical reaction and slow Na^+ diffusion. Several strategies are under investigation to overcome these drawbacks, but the progress in conversion-based cathodes or NIBs is still in its first stages, so there is a long way to go through in order to optimize these materials for their practical use. Features of conversion materials are displayed in ref. [79] and herein.

2.2.5. Organic Materials

Organic positive electrodes for NIBs have been considered promising alternative cathode materials due to the absence of a transition metal, their low cost and molar mass, abundant resources, structural versatility, safety, and mechanical flexibility. All these features can lead to flexible, bendable, lightweight, and portable NIBs. More specifically, the research carried out on organic NIBs has been mainly focused on the development of renewable and environmentally responsible organic batteries.[16] For this purpose, a wide catalog of materials are under research, such as conducting polymers, organosulfur compounds, organic radical compounds, carbonyl compounds (PTCDA and disodium rhodizonate).[18,80–82] These latter, carbonyl compounds, are the most studied family of organic electrodes in the last years, but they are still concerns that must be resolved. The main drawbacks of these systems are the dissolution of the cathode in the electrolyte that leads to rapid capacity fade, their low electronic conductivity that causes poor rate performance, and the increase of working potentials and tap density of the electrodes that would lead to high energy density cathodes.[83] Nevertheless, the possibility of fabricating a whole organic battery, with the mentioned advantages of low price, bendability, and even the possibility of making "green" batteries can provide organic electrodes a prominent place among battery materials if the mentioned limitations are controlled and minimized.

Figure 6 shows the relationship between the composition of different cathodic materials from each of these families and the theoretical and experimental capacities obtained in half-cell systems.

As it can be seen in the figure, layered oxides present the highest theoretical specific capacities among the three cathode families. In fact, TM^{3+} transition metal-based cathodes (Mn^{3+} or Co^{3+}) are generally capable of delivering high capacities (>100 mAh g^{-1}) below 4.0 V, while TM^{2+}-based cathodes (Ni^{2+} or Cu^{2+}) tend to show high voltages, higher than 3.2 V.[39] However, there is still room for improvement in order to get closer to the theoretical values in almost all the depicted materials. Polyanionic materials show lower theoretical specific capacities due to their larger specific mass but their experimental specific capacities are very close to their theoretical values. In the case of PBAs, the theoretical and experimental specific capacity values show great variability depending on the transition metals involved. Some of the PBAs show higher specific capacity than the one initially calculated as theoretical because these materials could insert more Na^+ ions than expected. The three analyzed families (layered oxides, polyanionic materials, and PBAs), show experimental specific capacity values in the 100–200 mAh g^{-1} range, which is adequate for their practical use as cathodes in commercial NIBs.

2.3. Electrolytes

Electrolyte development for NIBs follows, in general, that of LIBs with common solvents and salts. However, Na-Salts have higher cohesive energy, thereby more thermal stability and safety.[84] Based on the type of solvent selected,[85] the electrolytes can be classified as aqueous, organic (or non-aqueous), and solid-state electrolytes. **Figure 7** provides an overview of the ionic conductivities of the most representative electrolytes in NIB systems.
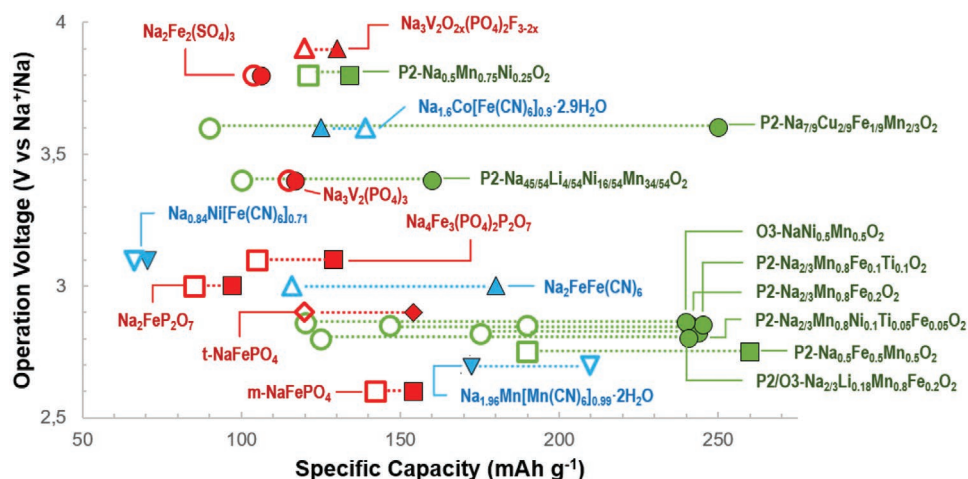
Figure 6. Overview of the most representative cathodic materials in NIB systems: sodium-layered oxides (green), polyanionic materials (red), and PBAs (blue). The filled symbols show the theoretical capacity, while the empty ones refer to the experimental capacity. The type of symbol is related to the C-rate at which the capacity has been obtained: ▲ 1C; ▼ C/5; ● C/10; ■ C/20; ◆ C/50.

2.3.1. Aqueous Liquid Electrolytes

The interest in this type of electrolytes lies in their low cost, high security, and lower environmental toxicity. Different formulations have been studied based on the use of several sodium salts, with 2 M Na_2SO_4 being the best candidate.[86] By using other types of salts such as NaTFSI or $NaCF_3SO_3$, it is possible to extend the electrochemical window up to 2.5 V.[87] On the other hand, the concept of "water-in-salt" electrolyte, in which high salt concentrations are used, has been studied leading to higher rate capabilities.[87,88] The main drawback of aqueous electrolytes is the lower electrochemical stability window that is dictated by the electrochemical decomposition of H_2O limited by the O_2 and H_2 evolution reactions. This point is especially critical when selecting the most suitable electrodes, which must also be protected against corrosion processes. Furthermore, if
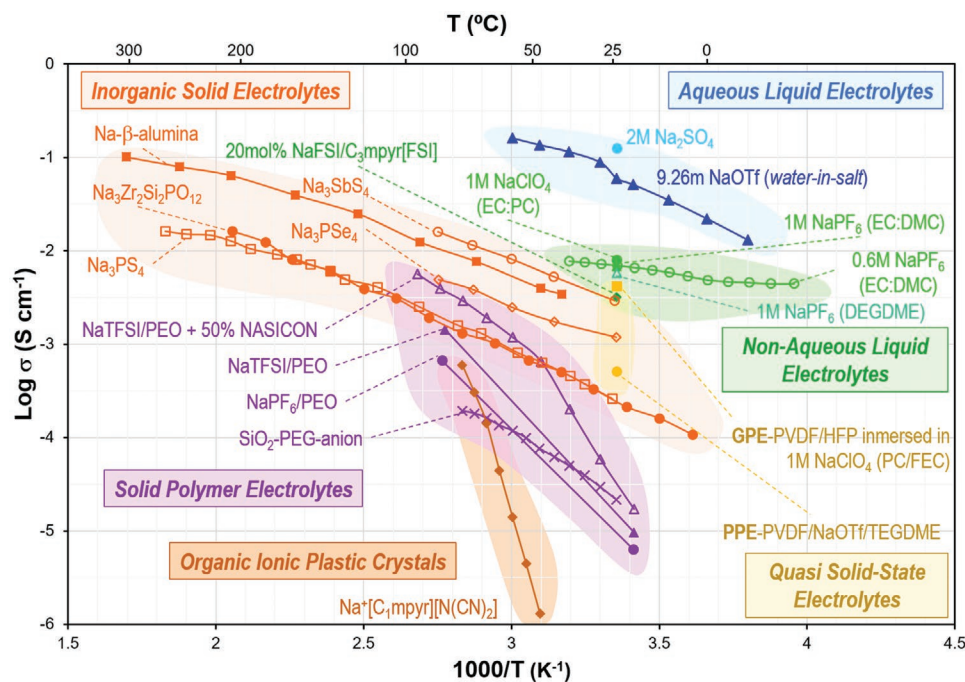

Figure 7. Summary of temperature-dependent ionic conductivities of representative sodium based electrolytes. The abbreviations are listed as below: $C_1mpyr[N(CN)_2]$ (*N*-methyl-*N*-methyl-pyrrolidinium dicyanamide), $C_3mpyr[FSI]$ (*N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide), DEGDME (diethylene glycol dimethyl ether), DMC (dimethyl carbonate), EC (ethylene carbonate), FEC (fluorinated ethylene carbonate), NaFSI (sodium bis(fluorosulfonyl)imide), NaOTf (sodium trifluoromethanesulfonate), NASICON (Na super ionic conductor structure), NaTFSI ($NaN(SO_2CF_3)_2$), PC (propylene carbonate), PEG (polyethylene glycol), PEO (poly(ethylene oxide)), PVDF (polyvinylidene fluoride), PVDF/HFP (poly-(vinylidene fluoride-hexafluoropropylene)), and TEGDME (tetraethylene glycol dimethyl ether).

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intercalation-based electrodes are used, it is necessary to avoid intercalation of the protons at the electrode. Detailed studies on aqueous electrolytes are described in different reviews.[85,89,90]

2.3.2. Non-Aqueous Liquid Electrolytes

The most studied systems are the non-aqueous liquid electrolytes, among which carbonate ester and ether based- electrolytes stand out. Concerning the former, cyclic carbonates allow much better cycle capabilities to be achieved, since the linear ones are not stable at low potentials, forming soluble decomposition products; therefore, an efficient SEI layer is not possible to form.[91] Unlike LIB, in which the EC:DMC solvent mixtures are used, in the case of NIB, the most common solvent mixtures are EC:PC and EC:DEC. Single solvent formulations are very rare, except a few using PC.[85] For sodium salts, the most used salt is $NaClO_4$, with good electrochemical behavior and low price, but exhibits explosion hazards. The PF_6^- anion in organic carbonate solvents (EC:PC) and TFSI-based ionic liquid (IL) solvents are the best electrolyte choices in NIB. On the other hand, NIB electrolytes react with the electrodes the electrodes giving rise to the formation of passivation layers (SEI). The study of SEI properties in sodium-based systems is in its early stage. To create a protective SEI on alkali-metal anodes, it is essential that the equivalent volumes of the SEI materials be greater than that of the metal anode. In carbon derivative anodes, the carbon matrix has a more marked effect on the composition and thickness of the SEI than does the nature of the electrolyte.[92] The use of additives such as fluoroethylene carbonate (FEC) favors the formation of very thin films that protect the negative electrode.[93] Tris(trimethylsilyl)phosphite is an additive commonly used as flame retardant and also as SEI-building and phase transition inhibitor in NIBs.[94]

The ester based electrolytes (glyme-type solvents) have received attention because they allow Na^+-solvent co-intercalation in graphite electrodes building stable SEIs.[22,95–97] In the intercalation mechanism, the solvent plays a critical role, determining that glymes with higher molecular weights have a greater intercalation potential, although as a consequence of their higher viscosity, a decrease in the rate capability is produced.[98] At the same time, very good reversibility has been obtained in Na metal plating/stripping processes when glymes are used, since the formation of an inorganic rich SEI is favored, which makes the appearance of dendrites difficult.[99] Furthermore, glymes present an interesting electrochemical stability window (up to 4.5 V) due to the absence of side reactions.

Zhang and co-workers compared the SEI compositions in 1 M NaOTf in carbonate ester (EC:DEC) and ether (diglyme)-based electrolytes on the surface of reduced graphite oxide.[100] As can be seen in **Figure 8**, the SEI formed in the ether-based electrolyte consists of a more compact, highly stable, thinner and conductive organic layer at the exterior, which can significantly decrease the diffusion length of Na ions and prevent extra decomposition of the electrolyte on rGO surfaces.

By constructing the ether-based SEI, a large reversible specific capacity of 509 mAh g^{-1} after 100 cycles at a current density of 0.1 A g^{-1} (196 mAh g^{-1} at 5 A g^{-1}) was achieved in the rGO anode. The initial coulombic efficiency (ICE) in carbonate-based
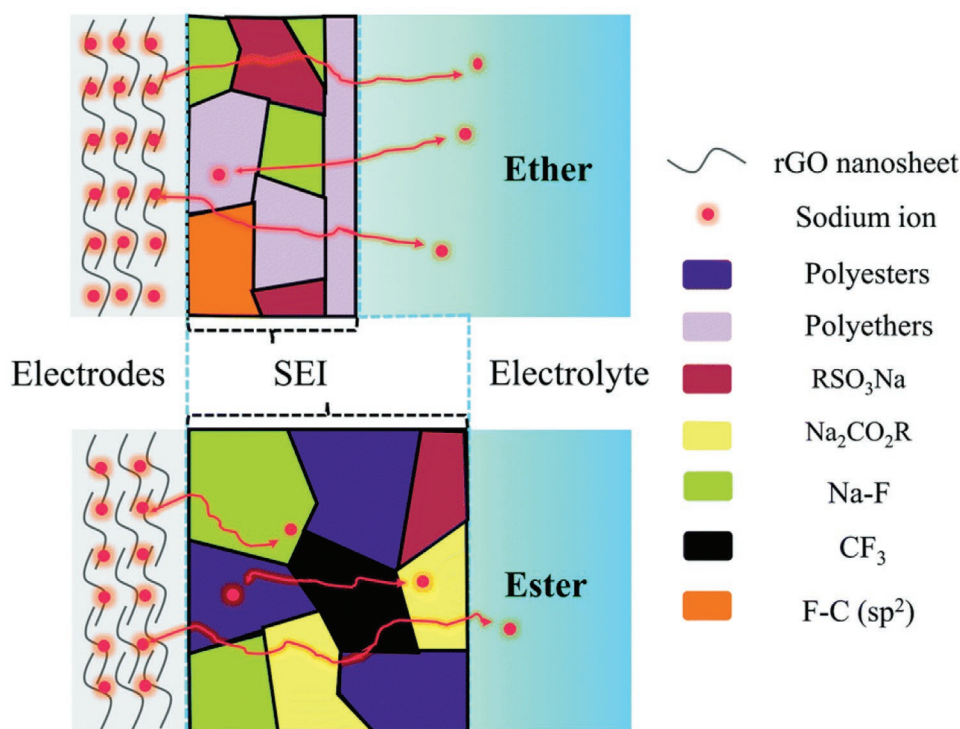

Figure 8. Illustration of different components of the SEI in different electrolytes as well as its correlation with sodium storage. Reproduced with permission.[100] Copyright 2017, The Royal Society of Chemistry.

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electrolyte (EC:DEC) is very low (40%) in comparison with that obtained using diglyme as solvent with ≈75% of ICE.

Ionic Liquids: The last major family of non-aqueous electrolytes are those based on the use of ionic liquids (ILs), which present their best operation at temperatures around 60–80 °C, but at room temperature their performance is much more limited mainly due to their low ionic conductivity and higher viscosity compared to carbonate-type electrolytes. The most studied organic molecules in ILs are the imidazolium and pyrrolidinium.[85] The concentration of the sodium salt is a critical factor in improving organic electrolytes in general. High Na^+ content electrolytes have a greater stability in cycling as well as withstanding higher current densities due to a faster charge transfer at the interface..[101] A variety of electrode materials have been tested using IL electrolytes. Solutions of NaFSI with IL incorporating alkyl phosphonium cations have been used in polyanionic phases ($NaFePO_4$, $NaVOPO_4$,...) and layered oxides such as P2 and O3-$Na_{2/3}Mn_{1/3}Fe_{2/3}O_2$.[102,103] A comparative study of the P2-$Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$ layered oxide phase with 1 M $NaPF_6$ EC:PC + 2 wt% FEC as organic electrolyte and 1:9 mol% (0.35 M) NaFSI in $Pyr_{14}FSI$, as IL electrolyte showed higher capacity retention for the IL at low and high C rates and better specific capacity at high C rates than those of the organic electrolyte.[47,104] IL electrolytes can be postulated as next generation of Na-based electrolytes. However, despite the advances in the development of this type of systems, they have different drawbacks such as cost and low ionic conductivity at room temperature, this being the critical parameter to improve the performance of ILs in future NIBs.

2.3.3. Solid-State Electrolytes

The development of all-solid-state batteries for the next generation of NIBs is crucial in order to avoid or diminish the safety problems associated with the use of volatile and flammable solvents. The main advantages of the solid-state electrolytes (SSEs) are the high thermal stability, wider electrochemical stability window, and excellent mechanical properties. However, an important drawback is the low ionic conductivity at RT compared to the liquid ones.[85,105,106] The SSEs used for sodium batteries can be classified into three main categories: i) solid polymer electrolytes (SPEs), ii) composite solid polymer electrolytes (CSPEs), and iii) inorganic solid electrolytes (ISEs)

SPEs: SPEs contain sodium salts and flexible polymer matrices with good versatility, flexibility, and thermodynamic stability but the ionic conductivity at RT is very poor. The improvement of the ionic conductivity in these systems can be reached by the regulation of both the electrolyte salts ($NaPF_6$, NaTFSI, NaFSI...) and polymer matrices. Polyethylenoxide (PEO) is the most common polymer capable of dissolving a wide variety of sodium salts. This way, good high conductivity and thermal, electrochemical, and interfacial stability have been obtained with different sodium salts.[106] The physicochemical and electrochemical properties of other polymer matrices have been described in different reviews and references herein.[85,105,106]

CSPEs: The CSPEs consist of inorganic fillers (SiO_2, Al_2O_3, TiO_2,...) on solid polymer electrolytes (polymer crosslinking, blending,...), which improve the ionic conductivity due to the decrease of the crystallinity and glass transition temperature (T_g) together with the possible interactions of the surface groups of the inorganic fillers with the polymer chains and salts. Hu et al. used Nasicon materials as active inorganic fillers obtaining excellent ionic conductivities of 2.4×10^{-3} S cm^{-1}.[107,108] It is also worth noting the new type of inorganic-organic hybrid consisting of SiO_2 nanoparticles grafted with a sodium salt, 2-[(trifluoromethane-sulfonylimido)-N-4 sulfonyl-phenil]ethyl, with or without polyethylene glycol (PEG) strands, leading to new solid electrolytes when the particles are dispersed in plasticized PEO. This inorganic–organic hybrid material exhibit conductivities of >10^{-5} S cm^{-1} at RT meeting the requirements for electrochemical devices.[109] The proper optimization of the nanoparticle and polymer can lead to a new class of CPEs with high ionic conductivities at RT and good mechanical properties.

ISEs: ISEs involve ceramic systems, thus, hard and inflexible materials such as oxides, phosphates, sulfites, or hydrides. Among these families of compounds, β''-Al_2O_3 (beta alumina) and NASICON $Na_3Zr_2Si_2PO_{12}$ are the most used Na^+ conducting solid ceramic electrolytes up till now, specially in high or intermediate temperature electrochemical energy storage systems, such as Na–S.

Beta alumina presents two different crystal structures, named β-Al_2O_3 and β''-Al_2O_3, where the β'' form presents the highest ionic conductivity value. Dopants as Li^+ and Mg^{2+} are used to stabilize β''-Al_2O_3 phase, enhancing conductivity, whereas ZrO_2 is added to reduce material fragility but decreases ionic conductivity.[85]

NASICON compounds (already described in the cathode section) present high Na^+ conductivity so they can be used as solid electrolytes in NIBs with $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \le x \le 3$) composition. Conductivity of these compounds is about 0.15–0.2 S cm^{-1} at 200 °C and can reach 3.5×10^{-3} S cm^{-1} at room temperature by using Na excess of formula $Na_{3.1}Zr_{1.95}Mg_{0.05}Si_2PO_{12}$. Although these materials are usually employed as electrolytes in high temperature batteries, $Na_3Zr_2Si_2PO_{12}$ has also been explored as ceramic solid electrolyte in room temperature NIBs together with $Na_3V_2(PO_4)_3$ electrode material.[108] The challenges shown by these all-solid systems lie in the interfacial contact of the battery components. Regarding this point, it has been demonstrated that the combination of a NASICON electrolyte with a small amount of ionic liquid provides outstanding cyclability with 90 mAh g^{-1} specific capacity and 95% capacity retention at 10C for 10 000 cycles. This can be ascribed to the ionic liquid that enhances ionic transport and provides a "soft" buffer space to compensate the cathode volume expansion during cycling.[110] Besides, NASICON compounds have also been prepared in the form of glasses by using different additives such as Na_3BO_3 and decreasing heating temperature from 1200 °C (sintering process) to 700–900 °C temperatures. This strategy has also been successful to produce room temperature conductive ceramic solid electrolytes.[111,112]

The use of glassy materials is an important approach in the area of inorganic solid electrolytes. Glasses can offer varied compositions, show reduced issues related to grain boundaries,

and they can provide good contact to the electrodes because they are easy to mold or to form films. In this regard, sulfide-based chemistry is one of the most promising ones. Accumulated experience on glassy sulfides for LIBs motivated the interest in Na-conducting sulfides as $Na_{10}GeP_2S_{12}$, $Na_{10}SnP_2S_{12}$, or Na_3PS_4. This latter is one of the most widely studied material as Na-conducting solid electrolyte. The cubic β-Na_3PS_4 presents a 2×10^{-4} S cm^{-1} conductivity at room temperature and its electrochemical window goes up to 5 V versus Na^+/Na. In addition to this sulfide, other related compounds as Na_3PSe_4 or Na_3SbS_4 have been explored with favorable conductivity values at room temperature, of about 10^{-3} S cm^{-1} in both cases.[113,114] Moreover, there have been studies that combine these materials to form binary or ternary systems, such as $94Na_3PS_4 \cdot 6Na_4SiS_4$ or substitutions on P, as, for example, $Na_3P_{1-x}As_xS_4$.

Other Solid Electrolytes: Organic ionic plastic crystals (OIPCs) are novel electrolytes which significantly improve the safety and performance of NIBs.[115] They consist of an organic cation–anion pair like those with IL but they have regular crystal structures in the solid state. There are few studies for NIBs but the results obtained with OIPCs mixed with sodium salts exhibit high ionic conductivity, and with a favorable economy of scale, they could be good candidates for intermediate temperature technologies.

2.3.4. Quasi Solid-State Electrolytes

The limited ionic conductivity at room temperature of the solid polymer electrolytes can be solved by using liquid components as plasticized polymer electrolytes (PPEs)[116] and gel polymer electrolytes (GPEs) with less and more than 50 wt% amount of liquid plasticizers, respectively. Ether and carbonate solvents, and less volatile and non-flammable ionic liquids (ILs) have been used as plasticizers for NIBs. A detailed study on these systems has been carried out describing the physicochemical and electrochemical properties, including the cell performances of the systems.[106] Other interesting systems are the Semi-Solid electrolytes based on Deep Eutectic Solvents (SeSE_DES). An extensive study of these systems has been carried out for LIBs using different lithium salts. This study can be extended to sodium salts with the same anions for sodium batteries with promising results.[117]

In summary, both aqueous and non-aqueous systems exhibit the highest ionic conductivity values, although the former show a low electrochemical stability window and the latter have problems related to the SEI stabilization and flammability. These drawbacks can be overcome through the design of functional solid-state electrolytes. In **Figure 9**, the main pros and cons of the previously discussed solid and quasi solid electrolytes are gathered.

Finally, for all kind of electrolytes, it is worth mentioning the use of advanced theoretical simulation tools in the development of high-performance NIB electrolytes. Currently, there is a vast toolbox to determine the significance of the solvation shell and the desolvation kinetics at the electrode/electrolyte interface, the strength of the cation-anion interactions in the Na salts, or the effect of the additives.[118–121] Simulation and modeling studies are not only limited to elucidation of conduction mechanisms, but also provide fundamental information on the ability of different Na^+-conducting materials to create a stable SEI. The combination of experimental studies with theoretical calculations is essential for the development of the next generation of high-performance battery systems, reducing time-to-market.
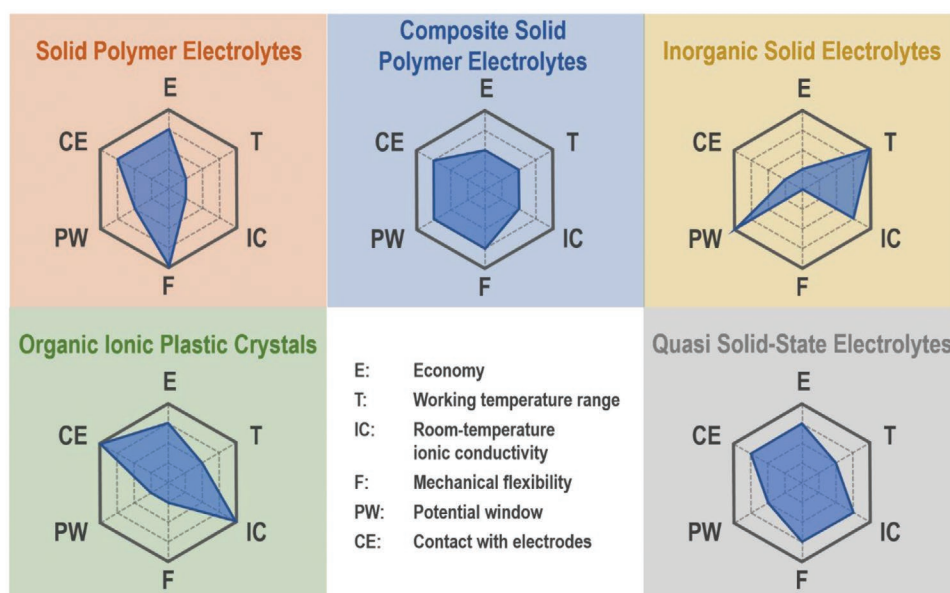

Figure 9. Qualitative description of the main solid (polymer, composite polymer, inorganic and organic ionic plastic crystals) and quasi solid-state Na-ion battery electrolytes on the basis of six important criteria for electrochemical energy storage devices: economy, working temperature range, RT ionic conductivity, mechanical flexibility, potential window, and contact with electrodes.

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3. Industrial Developments

3.1. Prototype and Commercial Cells

Despite all the challenges to overcome, first-generation NIBs are already attracting commercial interest for a wide variety of energy storage applications. In all of these nonaqueous prototypes or marketable cells, the anode is a disordered carbon, predominantly an HC. Earlier, Sumitomo demonstrated a 600 mAh prototype pouch cell using O3-type $NaNi_{0.3}Fe_{0.4}Mn_{0.3}O_2$ cathode. At the time, Toyota also was working on room-temperature Na-ion prototype cells, but it was the UK-based company Faradion which fabricated the first nonaqueous commercial NIB for an electric bike in 2015.[122] The e-bike operated with a 400 Wh battery pack based on a pouch cell construction. In this case, the cells were built using a sodium nickel layered oxide, $Na_aNi_{(1-x-y-z)}Mn_xMg_yTi_zO_2$, as the positive electrode.[123] Currently the company claims to be able to produce 12 Ah prototype cells of 150–160 Wh kg^{-1} (or 270–290 Wh L^{-1}), with a cycle life of more than 3000 cycles at 1C rate (to 80% DOD) and able to operate between −20 and 60 °C. Concurrently, in 2015, the first 18 650 Na-ion cell was launched by the French research network on electrochemical energy storage, the so-called RS2E.[124] These cells, using $Na_3V_2(PO_4)_2F_3$ as the positive electrode material, exhibited a specify energy of 90 Wh kg^{-1}.[125] Later, using this same technology, an upgraded cell was developed by the Tiamat spin-off able to reach a power density of 2 to 5 kW kg^{-1} (a fivefold increase with respect to LIBs) and able to charge in just 5 min.[126] More recently, based on a O3 phase multicomposite layered cathode, the Chinese HiNa is producing both 10 Ah pouch and 18 650 cylindrical cells with a gravimetric energy density reaching 135 Wh kg^{-1}, with 90% capacity retention by varying the discharge rate from C up to 5C rate and a cycle life of over 3000 cycles at 3C rate.[127] Moreover, batteries can be discharged at −30 °C at 0.3C rate still preserving 80% of the room temperature capacity and stored at temperatures as high as 85 °C for 3 days with full recovery of capacity in the following cycles.

A different type of materials that have also entered the market are PBAs. As already mentioned, these materials are lower cost and they show better cycling as well as rate performance at the expense of reduced gravimetric and volumetric energy density values. While the use of polyanionic compounds and layered oxides has been the choice of European/Asian companies, the usage of PBAs is an American technological and commercial bet. In 2015, Sharp Laboratories of America in close collaboration with J. B. Goodenough demonstrated that a Prussian white cathode ($Na_{1.92}Fe[Fe(CN)_6]$) could be successfully scaled to get a 3 V battery.[128] With all this background, Novasis Energies recently built a cell using $Na_xMnFe(CN)_6$, and through improved cell formation and engineering, they have been able to get 100–130 Wh kg^{-1} (or 150–210 Wh L^{-1}).[54] Natron Energy, a spin-off from Stanford University, is another newly founded company that uses PBAs for both the cathode and anode but in this case utilizing an aqueous electrolyte. At the expense of lower energy density values than those of organic-based batteries, this cell configuration allows run times as short as 30 s achieving power values of 775 W kg^{-1} (or 1550 W L^{-1}). The cells are able to run over 25 000 cycles at 12C rate accessing
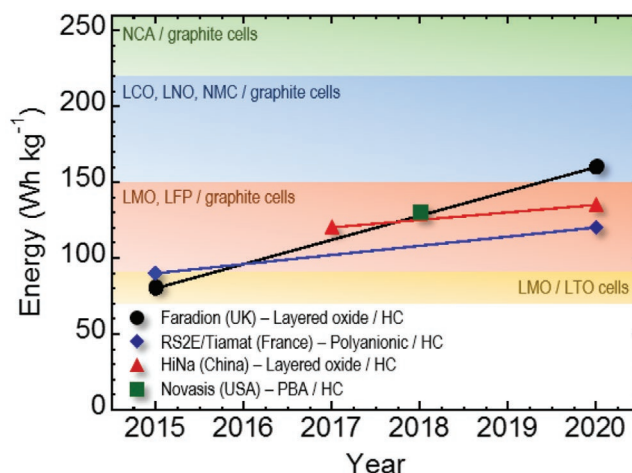

Figure 10. Summary of commercially available nonaqueous NIBs in terms of specific energy and announcement year. For a better comparison, the energy densities achieved by the different LIB cell configurations are depicted in the background. Abbreviations: HC, hard carbon; LCO, $LiCoO_2$; LFP, $LiFePO_4$; LMO, $LiMn_2O_4$; LNO, $LiNiO_2$; LTO, $Li_4Ti_5O_{12}$; NCA, $LiNi_xCo_yAl_zO_2$; NMC, $Li_{1-xyz}Ni_xMn_yCo_zO_2$; PBA, Prussian blue analogues.

about 70% of the total capacity and with only 6% degradation measured over the duration of the test (6 months). For more detailed information on the electrochemical performances and commercialization potential of both layered Na_xMO_2 and PBAs, the reader is hereby referred to previously published review articles.[64,129]

In terms of performance, room-temperature non-aqueous NIBs offer by now a real alternative to Li-ion systems (**Figure 10**). Moreover, considering they are still at their commercial inception and that most of the research efforts have been focused on electrode active materials, further improvements on electrolytes, binders, current collectors, and other cell components promise a prosperous future for this technology.

Nevertheless, the commercial success of a technology is not just based on performance indicators such as gravimetric and volumetric energy densities (Wh kg^{-1} and Wh L^{-1}), gravimetric and volumetric power densities (W kg^{-1} and W L^{-1}), cycle and calendar life, and charge time but safety, sustainability, and cost are equally or even more critical parameters.

3.2. Cost Projection

Directly linked to the enriched distribution of sodium across the world (sixth most abundant element Earth), cost aspects are pointed out as one of the most important strengths of NIBs. In fact, according to cost analyses using industry standard methods (Argonne National Laboratory BatPac), the contribution of battery materials to the final cell costs are generally lower in NIBs than in LIBs.[54,130–132] On the one hand, significant cost benefits are obtained for NIB cathode active materials due to the use of less expensive precursors. NIBs also offer the great advantage of working with Al current collectors not only in the cathode side but also in the anode because Al does not alloy with Na at

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low potentials. Currently, Al is about three times less expensive than Cu, \$1.611 kg^{-1} versus \$5.183 kg^{-1}, respectively as of March 2020, which has a significant impact in the price. Nevertheless, to improve the cell performance, carbon-coated aluminum collectors are the choice of some companies, which at the end increases the cost and, consequently, in terms of price, there is no difference when switching from Cu to Al. Still, Al does not undergo oxidation during overdischarge (external short circuited), which makes it at least a safer option. On the other hand, in NIBs, there is a significant increase of the anode contribution to the total price. In fact, HCs have a lower specific density than graphite, and thus, thicker laminates are needed, and as the irreversible capacity is also larger, more active material is required. However, there is a great range of raw materials that can be used as HC (or SC) precursors, including natural waste materials,[26] which can greatly reduce the anode cost in the near future. Fluctuations in raw material prices do occur, and this is a major concern for battery manufacturers, but even if metal prices would change in the years to come, based on the abundancy data, Na precursors will be more affordable than Li equivalents.

When the energy density of the cells is considered, back with the numbers from 2017, Faradion, for instance, claimed that at a manufacturing scale the material cost could be below \$150 per kWh (≈140 € per kWh).[54] This number agreed well with other studies that also predicted a price of \$140 per kWh for layered oxide NIBs with material prices available as of September 2015.[133] The lower energy density of NIBs remains a challenge to overcome, and thus, the cost for the energy stored is still higher than, for example, by lithium-nickel-manganese-cobalt-oxide (NMC) batteries.[130,133] However, these numbers are significantly below those of lithium-iron-phosphate (LFP) batteries, which highlights the potential of Na-ion systems.[130] Moreover, provided that new NIB materials exhibit increased voltage and specific capacity values similar to those of LIB materials, NIBs could become preferred to LIBs, both in terms of performance and cost, especially for high-power applications.[134] Also, as the portfolio of HCs grows, a further decrease in NIB price is very likely to occur. Even lower prices could be achieved by NIBs working with PBAs, which are based on abundant and low-cost elements. Thus, although there are only few studies that delve into NIB cost analyses and still material, processing, and manufacturing requirements are highly speculative, this new technology has the potential to become cost-competitive and find a niche in the market not only for stationary applications but also in the mobility sector. For instance, in 2018, HiNa developed both a NIB powered low-speed mini electric vehicle and a home storage, and as of April 2020, Faradion company announced a first order from ICM Australia for its high-energy NIBs for use in the Australian market.[135]

4. Concluding Remarks and Future Perspectives of Na-Ion Batteries

NIB is a relatively nascent technology but has demonstrated attractive properties due to the rapid advances and discoveries in the last years. Throughout the first part of this work, the most recent studies and current understanding of NIBs have

been discussed. Taking into account the state of the art of this technology, it is possible to establish the direction to be followed in the development of the next generation of NIBs. In this sense, there are some critical problems in the materials design that must be solved, in addition to a series of scientific topics that must be studied in depth:

Anodes:

- Hard carbon materials with low-voltage electrochemical profile are suitable candidates for the first generation of commercial Na-ion batteries. Up to date, hard carbons with ≈500 mAh g^{-1} have been obtained, which accomplishes the limits established for the satisfactory performance of a Na-ion full cell. However, the improvements needed for these materials are related to maximize the first cycle coulombic efficiency by manipulating the surface/electrolyte interphase.

Cathodes:

- Polyanionic compounds, layered oxides, and Prussian Blue analogues stand out among the broad scope of available chemistries as cathode materials for Na-ion batteries. These families of materials are well positioned in order to be the cathodes of the near-future commercial NIBs, each one focused on different applications.
- The low toxicity in Mn-based layered oxides, together with their adequate operation voltage and high specific capacity, make this family of compounds strategical for NIBs aimed for light transportation (e-bikes, short-range electric cars, etc.) apart from stationary storage as main application. Small doping/substitution of carefully selected elements for optimized stoichiometries will improve significantly the performance of these materials. A detailed experimental study on several Li/Na-excess cathode materials at high voltages should be carried out in order to corroborate the reversible O^{2-}/O^- oxygen redox hypothesis as the origin of the anomalous excess capacity. In addition, considering that the intercalation compounds are metastable and highly susceptible to decomposition reactions, detailed analyses of the possible presence of different Mn species and in situ experimental probes should be performed.
- Polyanionic materials, specially, sodium vanadium fluorophosphates and Nasicon structure sodium vanadium phosphate, are adequate for applications where higher voltages and long cycle life are needed, such as stationary electrical storage for electrical grid buffering. The high operation voltage of these compounds makes them also suitable for high-power applications. The main polyanionic compounds are based in V transition metal, which is a weak point due to its toxicity and cost when compared to environment friendly Mn- or Fe-based compounds.
- Prussian Blue analogues are satisfactory cathodes for aqueous NIBs because they present outstanding cyclabilities with no security issues. Despite their low gravimetric energies, these compounds can be suitable for high-power applications. Manganese- and iron-based compounds not only comprise environment friendly metals in their composition, but also display the best performance in terms of specific capacity and cyclability.

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Electrolytes:

- Sodium salt is a component of the electrolyte that needs to be further studied, being necessary to discover new salts that are compatible with different solvents, and show good electrochemical performance while being safe and non-cost-prohibitive.
- The electrode/electrolyte interface issues should be analyzed in depth and rigorously, combining multidisciplinary studies using advanced characterization techniques in order to clarify the internal action mechanism.
- Combination of theoretical calculations with experimental studies and advanced characterization techniques will aid in the design of new and optimized electrolytes, in addition to being able to decipher the behavior of the electrode/electrolyte interfaces.
- Solid-state batteries are the most suitable design for large-scale energy storage, mainly due to their stability and lower risk of explosion. However, for this new generation of batteries to become a reality, it is critical to decrease the resistance at the electrode/electrolyte interfaces due to contact failure. In this sense, there are several strategies to explore, such as the use of interlayers that favor ionic transport at the interface, design of polymer/ceramic composites that prevent the growth of Na dendrites, or the use of inorganic solid electrolytes with a lower elastic modulus.

Industrial developments:

- The lower cost per cell as well as the improved safety properties make NIBs an appealing energy storage technology not only for large-scale stationary applications but also for mobility.
- First-generation commercial NIBs have already hit the market; however, second-generation cells need to decrease the cost per kWh to become real competitors for LIBs. Based on modeling calculations, this target will be achieved when developing NIB cells reaching 210 Wh kg^{-1} operating with a cathode of 200 mAh g^{-1} coupled with a 500 mAh g^{-1} hard carbon and with an average cell voltage of 3.3 V.
- Individual cell components practically meet sub-targets, that is, polyanionic compounds and Prussian Blue analogues exhibit the desired cyclability (>5000 cycles) with almost no capacity degradation, whereas layered oxides and hard carbons have a Na storage capacity of 180 and 480 mAh g^{-1}, respectively. Further development of materials is required (e.g., second generation) to fully meet the targets

In conclusion, the commercialization of first generation systems and the development of next generation materials by tailoring first-generation ones will make this technology more attractive from a commercial perspective. Na-ion technology is already well-placed in the sea of emerging technologies, and via oriented material research and technology innovation, NIBs will reach their full potential in the near-term. For the next steps, future Na-based technologies must be developed.

5. Perspectives and Future Trends on Other Sodium-Based Technologies

Today the applications powered by energy storage systems are very diverse and keep increasing continuously. A single technology cannot fulfill the technical requirements of all the applications, and thus, it is important to research in different system configurations and chemistries. **Figure 11** summarizes the energy to power characteristics of several Na-based electrochemical energy storage technologies on the so-called Ragone plot. The very infant Na-ion capacitors (NICs), like Li-ion capacitors (LICs), are designed to cover the gap between NIBs (or LIBs) and supercapacitors and, thus, provide enough power in applications where batteries are not suitable. LICs, for instance, are already used in hybrid buses, trams, elevators, and power quality equipment among others.

Na-air or Na-oxygen (Na–O$_2$) and room-temperature Na-sulfur (Na–S) batteries, on the other hand, are promising high energy density storage technologies that can meet the performance requirements for stationary applications. In the following sections, the perspective of each of the above-mentioned technologies will be discussed in more detail.

5.1. From Energy to Power Density

Electrochemical capacitors (ECs) or supercapacitors are energy storage systems that can complement or substitute batteries in certain applications.[136] The most common type of ECs are electric double-layer capacitors or EDLCs, where
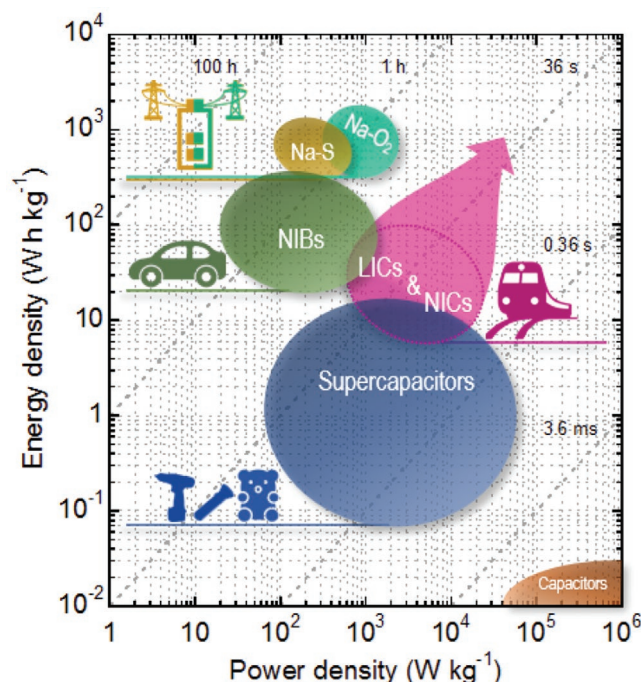
Figure 11. Typical specific power to energy regions of Na-ion batteries (NIBs), supercapacitors, Li-ion capacitors (LICs), and Na-based emerging technologies: Na-ion capacitors (NICs), Na–S batteries, and Na–O$_2$ batteries. In diagonal, the time constants of the systems are shown.

the ions from the electrolyte are adsorbed on the surface of the oppositely polarized electrode material. Because of this capacitive charge storage mechanism, EDLCs are characterized by fast charge and discharge rates in the order of few seconds, high cycle life (>10 00 000 charge/discharge cycles), and power density values exceeding 10 kW kg^{-1}.[137] In some way, ECs stand out in the indicators where batteries are less attractive, and vice versa. So, in order to get the best of both technologies and meet the energy and power demand of an increasing number of new applications, hybrid systems were conceived. Just like in battery chemistries, first LICs were proposed in 2001,[138] and as NIBs acquired enough maturity, NICs were studied almost a decade later.[139,140] The essence of this hybridization is to inherit the advantages of ECs and batteries by combining in the same cell an EC-type electrode (typically the anode) with a battery-type electrode (typically the cathode) while using a metal-ion containing non-aqueous electrolyte (**Figure 12**). Hybrid systems have the potential to offer a serious alternative to high-power batteries and will find their niche in those applications where ECs are too expensive in terms of $ per kWh and batteries too slow to charge (typically <30 s).

In LICs, the most successful configuration is the all-carbon-based system where the EC type electrode is an activated carbon (AC) or a high-surface microporous carbon and the negative electrode is a pre-lithiated graphite. In fact, in 2011, JM Energy (Japan) launched both first laminate-type and prismatic LIC cell and modules based on the just mentioned cell configuration and almost 10 years later, the products continue being on the market[141] and even have competitors from other companies

such as Yunasko (Ukraine), Aowei (China), and Taiyo Yuden (Japan). On the contrary, NICs are still an emerging technology waiting for the deployment, which should be relatively smooth as the industrial framework for LIC and NIB fabrication is ready and can be easily adapted. Taking into consideration performance indicators, the most promising NICs are all-carbon-based systems with a pre-sodiated disordered carbon as the anode.[46] Indeed, in 2015, the best all-carbon-based NIC developed to date was reported, which showed superior energy and power density values compared to LICs and demonstrated the potential of these Na-ion-based devices.[142] Other anode materials tested in NICs include TiO_2 and sodium titanates, metal oxides, alloys, and organic materials, and the results have been summarized in various extensive review works.[143–148]

NIC marketability would also benefit from the custom design of electrolytes. Most of the electrolytes used in NICs are just like the ones used in NIBs, even though the operation conditions of hybrid systems are different from battery requirements. Therefore, the specific formulation of NIC electrolytes has the potential to improve the performance of these devices while ensuring a safe operation. Another important research and commercial interest for both LICs and NICs is the unavoidable pre-lithiation or -sodiation step, respectively. As the AC positive electrode is not a metal-ion source, it hinders the pre-sodiation (or pre-lithiation) process of the carbonaceous anode. This issue can be circumvent using a sacrificial metallic sodium electrode, loading metal powder or stripes onto the surface of negative electrodes,[149,150] or using a sodiated (or lithiated) sacrificial.[151] The use of an additional metal electrode is the most typical and convenient approach in the lab as well as the
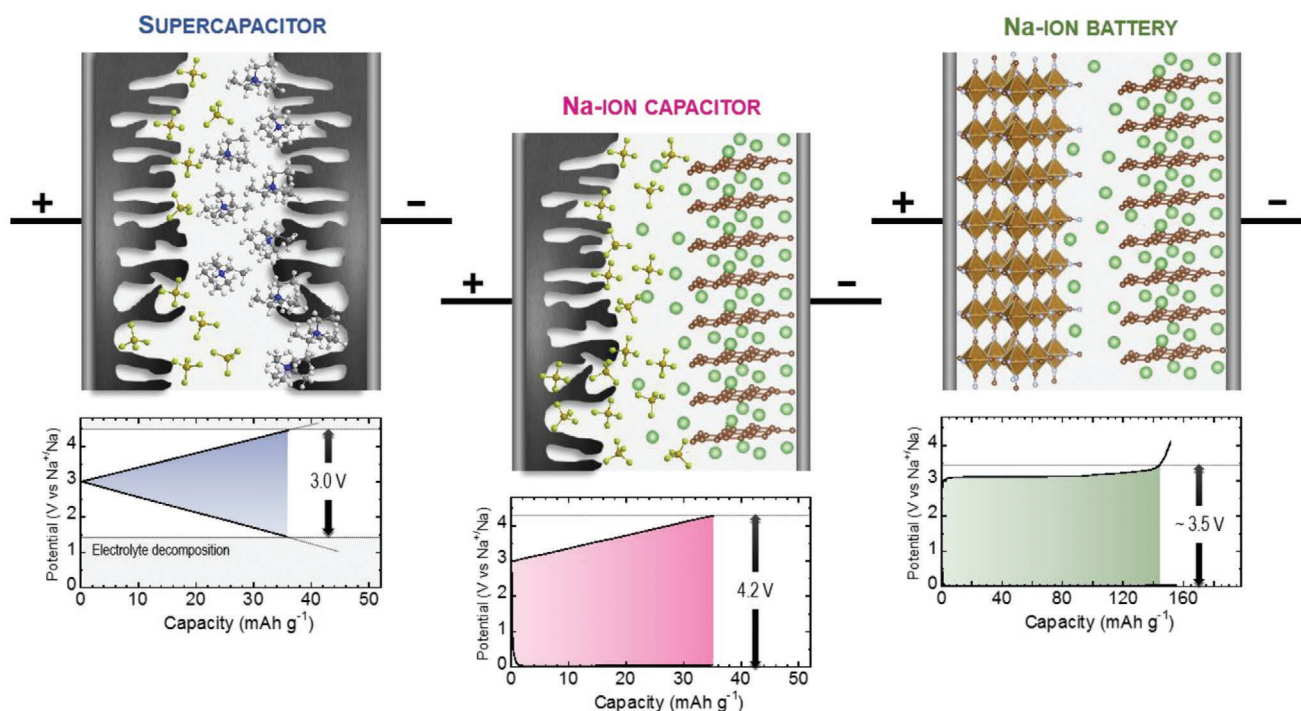

Figure 12. Scheme of a supercapacitor, a Na-ion battery, and a Na-ion capacitor built with a supercapacitor-type positive electrode and a battery-type negative electrode. Below the schemes, the typical galvanostatic charge profiles are shown.

procedure followed by JM Energy for their commercial system. However, this process can take several days and requires porous current collectors for the metal-ion to travel across the cell laminates, so its impact in manufacturing costs are not negligible. Therefore, of all the pre-metalation methods, the use of sacrificial additives or salts is acquiring now increased attention due to its simplicity, scalability, and the use of non-toxic and low-cost compounds. As already mentioned, for a technology to leave the laboratory and enter the market cost is a parameter as important as performance indicators. Thus, for prospective commercial NICs, it will be important to keep the cost as low as possible, and thus, the pre-sodiation step should be a key research focus. So, although several challenges need yet to be overcome, the future of NICs remains very promising.

5.2. Ambient Temperature Na–S Batteries

Na–S batteries based on the conversion chemistry have higher theoretical energy density (1274 Wh kg^{-1}) and lower cost compared to NIBs (**Figure 13**). Based on the operating temperature, Na–S batteries can be classified into high-temperature (HT), intermediate-temperature (IT), and room-temperature (RT) Na–S batteries. Typically, HT and IT Na–S batteries work at relatively high temperatures of about 300 and 150 °C, respectively.[152,153] In those circumstances, both the sodium anodes and sulfur cathodes are in a molten state with high chemical reactivity and corrosivity, which causes a severe safety hazard. Besides, the overall costs of HT and IT Na–S batteries are inevitably increased by employing stringent sealing technology, stable solid-state electrolytes, and inert current collectors.[154] These two drawbacks prohibit the widespread applications of HT and IT Na–S batteries. For instance, the NGK Insulators NAS battery units (Figure 13) were commercialized for large-scale energy storage with an energy density of about 222 Wh kg^{-1}, which is less than the one-third theoretical value

of Na–S system. On the contrary, RT Na–S batteries with sodium metal anode, sulfur cathode, and organic-based electrolytes are much safer, more cost-efficient, and have higher energy density, compared with their HT and IT counterparts, making them promising for grid-scale energy storage and transportation applications.[155]

RT Na–S batteries are very similar to Li-sulfur (Li-S) batteries in terms of the composition of system and reaction mechanism. On discharge, electrons transfer from anode to cathode to reduce sulfur (S_8), and the reduced S species react with Na$^+$ ions to form sodium polysulfides (Na_2S_x, $1 \leq x \leq 8$), which are reversibly converted back to sulfur after desodiation.[156,157] Further unraveling of the detailed underpinning reaction mechanism is of significance to guide the future research on RT Na–S batteries, through theoretical simulations and cutting-edge characterization technologies, such as cryo-TEM, in situ synchrotron-based X-ray, and enhanced Raman spectroscopy.

RT Na–S batteries have some inherent problems that widely exist in metal-sulfur batteries, including low electronic conductivity and sluggish electroactivity of sulfur, and the "shuttle effect" of polysulfide species.[158] To address these issues, many validated strategies in Li-S batteries have been adapted to RT Na–S. These include physical confinement of sulfur in porous carbonaceous materials,[159] chemical fixation of sulfur molecules with polymers,[160] construction of functional interlayers or separators,[161] and optimization of electrolytes.[162] Although some progress has been achieved, it still remains a great challenge to realize the practical deployment of RT Na–S batteries. For example, the practical discharge capacity of RT Na–S cells is far below the theoretical capacity (1672 mAh g^{-1}, corresponding to the final discharge product of Na_2S), and the sluggish conversion reaction kinetics exacerbates the "shuttle effect", resulting in poor reversibility of Na_2S. Those problems accelerate the exploration of electrocatalytic effects on the full conversion of sodium polysulfides and the novel design of cathode hosts.[163] Furthermore, it is imperative to realize highly
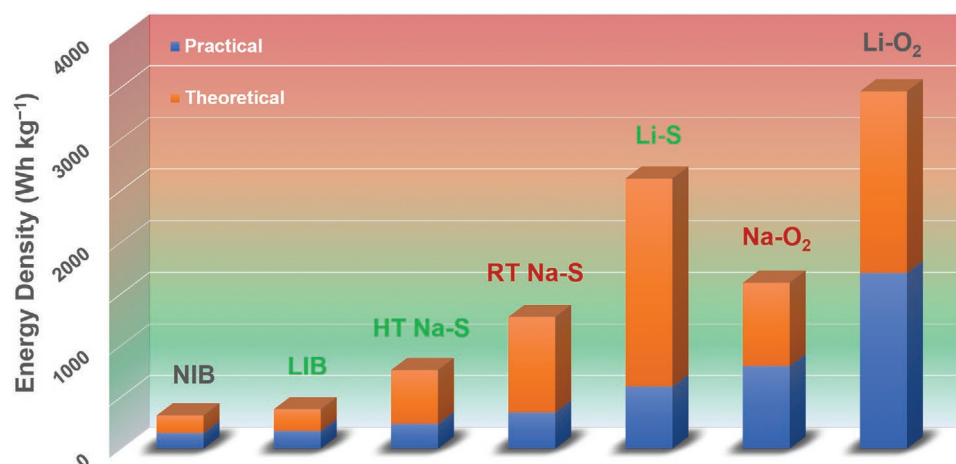

Figure 13. Theoretical and practical energy densities of select rechargeable batteries, including NIB-sodium-ion battery, LIB-lithium-ion battery, HT Na–S-high-temperature sodium-sulfur battery, RT Na–S-room-temperature sodium-sulfur battery, Li-S-lithium-sulfur battery, Na–O₂-sodium-oxygen battery, and Li-O₂-lithium-oxygen battery. The theoretical values of RT Na–S and Na–O₂ are based on the discharge product of Na₂S and Na₂O₂, respectively. The battery systems labelled in green have been commercialized, those in grey have been widely investigated in research communities, and those in red need to be further developed.

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reversible and non-dendritic striping and plating of sodium metal for achieving long-term cycling stability and addressing safety concerns. Besides, building pouch-type, large size full-cells is still at an embryonic stage.[164] Therefore, comprehensive research and development are required to commercialize RT Na–S batteries.

5.3. From Na-Ion to Na-Air

As a novel high-energy-density energy storage system developed in recent years, Na–O_2 batteries have the highest theoretical energy density (1605 Wh kg^{-1}, over ten times higher than NIBs as shown in Figure 13) among all sodium-based batteries and three times higher than LIBs.[165] A typical Na–O_2 battery consists of a Na metal anode, a porous oxygen cathode, and a separator soaked in organic electrolyte. On discharge, oxygen is reduced and reacted with Na$^+$ migrated from the Na metal to form insoluble sodium oxides at the cathode side. The discharge products are reversibly decomposed to oxygen, while sodium ions are reduced to sodium metal and plated on the anode in the subsequent charge process.[166] It is noteworthy that there are some controversies regarding the reaction pathways for the formation of Na$_2$O$_2$ (E^0 = 2.27 V) or Na$_2$O (E^0 = 2.33 V) as the final discharge product.[167] In order to promote the development of Na–O_2 batteries, this issue needs to be addressed in priority via a variety of advanced in situ/ex situ characterization techniques.[168,169]

Although research progress on Na–O_2 batteries has taken a leap forward in the past few years, many challenges such as sluggish oxygen reaction kinetics, electrolyte decomposition, and sodium metal corrosion are main hurdles for practical applications. Among the factors influencing the performance of Na–O_2 batteries, porous oxygen cathodes are of greatest importance since oxygen passes through cathodes back and forth, on which the discharge products deposit and decompose.[170] An ideal cathode must possess high electrical conductivity, large surface area with a hierarchical porous structure not only for oxygen diffusion and electrolyte penetration but also for accommodating the insoluble discharge products, and preeminent catalytic activity to promote the oxygen reduction and evolution reaction. Among various candidates, carbonaceous materials are the best choice for fabricating oxygen cathodes because they are capable of meeting those requirements except for high catalytic activity. Heteroatom doping or combining porous carbon matrixes and catalytic metal particles or metal-based compounds can overcome the shortcomings and further improve the performance.[171,172]

Meanwhile, a stable electrolyte with high oxygen solubility with resistance to the highly oxidizing environment in Na–O_2 batteries is desired for achieving excellent cycling performance. Additionally, apart from the common requirements for batteries such as low viscosity and high ionic conductivity, the electrolyte for Na–O_2 battery should also have low volatility since the system is open to the gas phase at cathode compartment. Currently, ether-based electrolytes are more widely used than carbonate-based electrolytes owing to their better stability toward oxygen species. Many strategies have been adopted to mitigate the parasitic reactions of electrolytes. These include adding additives like redox mediators to reduce charge over-potentials,[173,174] applying high-concentration salts to broaden voltage windows of organic electrolytes,[175] and using solid-state electrolyte alternatives. Even so, it is necessary to gain further insight into the decomposition mechanism of organic electrolytes (both carbonate and ether-based) and identify a new, completely stable electrolyte.[176] Recently, the presence of singlet oxygen in aprotic metal-O_2 batteries is recognized as one of the major reason for the degradation of the electrolyte.[177–179] The study of the mechanisms involved in its generation is unequivocal in order to mitigate its harmful influence on the performance of this type of batteries.

Similar to Na–S batteries, the corrosion and poor reversibility of sodium stripping and plating is another obstacle hindering the practical application of Na–O_2 batteries. The construction of artificial protective layers or surface passivation films on Na metal anodes is very crucial for the development of high-performance Na–O_2 batteries.[180] On the other hand, replacing Na metal anodes with pre-sodiated composites is also under consideration because this approach can avoid most of the aforementioned problems. However, it will partially sacrifice the energy density of Na–O_2 batteries, whereas the development of Na–O_2 batteries is still at the early stage and far from being practically applicable. Therefore, fundamental breakthroughs must be achieved through both theoretical studies and experimental investigations.

In conclusion, while Na-ion batteries already occupy high technology readiness levels or TRLs (6–7), which means that they are at a development stage, Na-ion capacitors and Na–S and Na–O_2 batteries are still in a research and validation phase (TRLs 1–3). Nevertheless, despite these systems still having a long way to go, with the required research and technological support, they are expected to play an important role in future scenarios.

Conflict of Interest

The authors declare no conflict of interest.

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