Readiness Level of Sodium-Ion Battery Technology: A Materials Review

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Since the breakthrough achieved in the research around material intercalating lithium, almost a decade has passed before the commercialization of the first lithium-ion battery (LIB). On the brink of an energy voracious future, convergence of scientific efforts over efficient and low-cost energy production and storage would be advantageous and beneficial. The research hovering around sodium-ion rechargeable batteries (SIBs), a more sustainable alternative to LIBs, has been observing a positive momentum for ten years now, and chemically stable and electrochemically performing anode and cathode materials represent important milestones on the path toward a commercial full-cell. Material science breakthroughs achieved in carbon and graphite based matrices, layered and open framework structures, and sodium storing alloys, disclose new full-cell set up opportunities going beyond traditional “rocking chair” configuration. In this contribution an in-depth analysis of chemical and physical principles lying beyond the energy storage provided by SIBs most recently investigated active materials is given. In the second half of the review, challenges, opportunities, and state-of-the art description of full-cell SIBs lab scale prototypes are discussed. The latter, indeed, stands for a technological validation of a low-cost alternative to lithium-ion batteries guaranteeing energy densities close to 150 Wh kg⁻¹.

1. Introduction

As renewable energy sources are taking a wider share of world-wide energy production,[1] grids reliability and utilization efficiency are plummeting.[2,3] This is mainly due to intermittency and discontinuity of power sources, such as wind and solar, which determine uncertainties in energy production capability and in fulfilling the instantaneous energy demand. This aspect, in turn, sensibly increases the unpredictability of energy prices spikes and marginal and maintenance costs of traditional fossil fuel plants, which are demanded discontinuously to provide for power unbalances between demand and supply. In general, resilience to these drawbacks would be higher providing an incremented flexibility from demand response resources, interregional energy transmission, and energy storage. Plenty of energy storage systems (ESS) are being utilized to curb renewable energy sources intermittency. Among them, worth to be listed are hydroelectric (pumped hydro), mechanical (flywheels and compressed air), and electrochemical (lead-acid, Na-S, Na-NiCl₂, and Li-ion batteries).[4] Nevertheless not all the previously cited energy storage technologies are comparable one with another in terms of scalability, environmental impact, investment costs, maintenance, and moreover, responsibility to energy needs. Batteries energy storage, directly supplying electric energy without requiring any mechanical-to-electrical energy transducer, surely represents the most versatile appliance. In particular, intrinsic flexibility of modern Li-ion batteries coupled to renewable power plants, ensures the proper response not only to grid on-peak condition but also to short term distribution overload situations. Energy storage systems exploiting secondary battery technology revealed to be versatile, scalable, and cost-effective solutions in many stationary applications. Apart from the so called front-of-the-meter storage, namely ESS coupled to centralized energy source plants (i.e., solar or wind, with a nominal power above 1–2 MWₜₜ), an increasing relevance is being gained by the smaller behind-the-meter storage, or in other words on the customer side of the meter (private houses and small enterprises).[5] This aspect is communicating the

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high readiness level of battery technologies in effectively hitting the mass market of private energy storage. Such a fragmented electric energy storage, intended as an extended energy network made of thousands of small-scale storage nodes, could be further extended in its flexibility by integrating the energy storage capabilities of the expanding hybrid electric vehicles (HEVs) and full electric vehicles (EVs) fleet. Some countries started experimenting vehicle-to-grid energy dispatching in order to take advantage of fast energy supply coming from electric vehicles connected to the grid.[8] In this case the benefit is mutual, since a small amount of energy (1–2% of the vehicle battery capacity) is collected by the grid during on-peak periods, avoiding fossil fuel based power plants to be started, while it is returned during off-peak moments, restoring the original capacity. In such way, electric vehicle owners would derive an indirect advantage buying electricity from the grid when its price is lower (low demand and high production from renewables) and sell it back to the grid when its price inflates due to the higher demand (on-peak moments) deriving an overall trade benefit. From the energy supplier’s point of view, intrinsic advantages connected to plant’s maintenance, start-and-stop moments, and production inefficiencies avoidance have to be considered. Such performing albeit complex infrastructure will require its main actor, namely the battery, to be reliable, safe, sufficiently cheap, and environmentally friendly. Lithium-ion battery since its first launch in the market by Sony in 1990 in the LiCoO2 cathode–graphite anode configuration,[7,8] has been observing a booming development in terms of active materials involved and increased performances, which progressively disclosed new applications.[9] In more or less two decades, lithium-ion based batteries’ volumetric energy density has indeed increased from 250 to 570 Wh L−1, thanks to materials and cell design optimization,[10] in the face of a more general energy density and power density of 186 Wh kg−1 (for LiCoO2-based lithium-ion batteries (LIBs))[11] and 1000 W kg−1,[12] respectively. Lithium-ion batteries’ pricing has continuously been dropping since their first commercialization. This effect is ascribable to multiple factors such as expansion of worldwide production capacity, increased by 11% between 2015 and 2016,[13] accompanied with momentary oversupply, since only 40% of available 53 GWh worth lithium-ion cell produced in 2015 was utilized.[14] Significant improvements in materials supply chain evolution, battery manufacturing, and materials handling and processing are contributing in further reducing battery pack cost, which might be hitting values well below 300 US$ kW h−1 within the year 2020.[15] Apart from portable electronics, HEVs plug-in hybrid electric vehicles (PHEVs) and EVs, lithium-ion battery penetration in the on-grid storage market fostered the lithium rush as well. In this landscape, lithium price, and its commercially equivalent Li2CO3, started to rise significantly from the beginning of 2010s. Simultaneously, concerns related to lithium elemental abundance and thus the sustainability of a lithium-economy made their appearance all over the scientific community.[16–18] Calculations revealed that at the average 5% yearly growth rate in lithium mining necessary to pace up the demand steady increase, lithium reserves (esteemed to be around 14 million metric tons[13,19]) will encounter a severe shortage in less than 65 years.[8,20] Together with a possible raw material shortage, also the political sensitivity of countries within whom borders are included the most readily available lithium sources, is casting shadows on future sustainability of lithium market.[21,22] Although these forecasts are affected by uncertainties and conclusions about new lithium reserves depletion might appear premature, the scientific community, embracing a proactive attitude, started investigating alternative energy storage technologies based on more naturally abundant...
alkaline metals, such as sodium, potassium, magnesium, and calcium. Among the cited, sodium chemistry, thanks to chemical–physical similarities with lithium, is the one that ideally would require less technological efforts in operating such a transition. In terms of raw materials supply costs, moreover, sodium outpaces lithium as one of the cheapest element to be extracted and processed to high purity (about $135–165$ per ton against $5000$ per ton for lithium). Together with the supply cost reduced, a further advantage in exploiting a sodium-based energy storage technology would derive from the possible replacement of copper current collector with the lighter and less costly aluminum. This very last element, contrarily to what happens with lithium, does not alloy sodium, and thus can be safely employed as both the anode and cathode material substrate. At the dawn of lithium-ion based energy storage at the end of 70s and beginning of 80s, sodium was being considered as a candidate equally promising as lithium for rechargeable battery applications, and sodium intercalating compounds started to draw research efforts especially involving disulfides and diselenides compounds. Well-known are the exploratory works by Wittingham and Abraham, in which thorough descriptions of mechanistic and structural alkaline cations intercalation in chalcopyrite hosts are provided. It was the ground-breaking discovery of LiCoO$_2$ as a high energy density lithium intercalating cathode made in 1980 by Goodenough and co-workers, and other ancillary studies which paved the way for a high voltage full lithium-ion cell, and that momentarily sank the enthusiasm for sodium and other alkaline metals battery. Thanks to recent renaissance of the matter, encouraged by, as previously stated, sustainability and battery market speciation and expansion, sodium-ion based rechargeable battery research is knowing a positive momentum. Efforts put across last decade in sodium-ion rechargeable batteries (SIBs) chemistries optimization, contributed in reducing the technological gap with lithium counterpart. Commercial SIBs started to appear on the market as well, with chemistries based on aqueous as well as nonaqueous electrolytes.

Among the most puzzling difficulties that sodium-ion rechargeable batteries present, the vast majority are related to physical discrepancies between sodium and lithium ion. The fact that sodium naked ion is 34% larger than lithium one (1.02 Å vs 0.76 Å) entails limitation of intercalation capabilities in host crystalline structures, affects transport properties in solid and liquid phase and mines interphase formation and stability. Nevertheless, in the recent times several classes of crystalline host structures tailored on sodium ionic radius made their appearance. Provided the plethora of promising anode and cathode materials so far proposed for nonaqueous sodium-ion rechargeable batteries, many research groups started investigating whole sodium-ion cell (full-cell). Due to the higher reactivity of sodium, its tendency in forming dendrites and its low melting point (97 °C), several safety issues are connected to the development of a metallic sodium-based full battery. On the contrary fully ion-dependent cells, inspired by lithium-ion “rocking chair” set up, are preferred. In this configuration anodic materials whose electrochemical activity is based on intercalative or pseudocapacitive behavior, are employed in place of metallic sodium. Very recently a large number of both cathode and anode materials has been thoroughly examined and characterized. Among the compounds suitable as cathodes, layered O3 and P2-type transition metal oxides and transition metals polyanion obtained remarkable attention, and so far efforts have been focusing on crystalline phases stability, achieved via doping or selecting the most suitable final crystalline phase by finely tuning the synthetic conditions. On the anode side, instead, more than one single chemistry became appealing and worth to be investigated. The direct transfer of graphitic anode of lithium batteries to sodium one revealed, in fact, as a poor choice. The insufficient interlayer spacing (≈0.34 nm) of standard commercially employed graphite for sodium intercalation, which has been demonstrated to require at least a 0.37 nm gap of a chemically expanded graphite revealed indeed as the most important limitation. Other carbonaceous materials with remarkable sodium storage capabilities include soft carbons, hard carbons, hydrogen and nitrogen-doped carbons and carbon nanostructures, such as nanotubes and nanowires, reduced graphene oxide (rGO). While for carbon-based anode materials applied to sodium environment the achievable specific capacities hardly exceed 300 mAh g$^{-1}$, alloying and conversion types of materials, would represent surprisingly more advantageous alternatives thanks to their theoretical specific capacities abundantly exceeding 600 mAh g$^{-1}$. Among the elements effectively alloying sodium, recent studies focused on 14 group elements ($\text{Ge}$, $\text{Sn}$ and 15 group elements ($\text{Sb}$, $\text{Bi}$)). Their most prominent drawback, namely the dramatic volume expansion during sodium alloying and consecutive mechanical disruption, has been tackled by proposing hybrid structures with carbon matrices able to buffer volume changes. The material classes here only introduced, will be thoroughly and widely analyzed in the following paragraphs.

### 2. Full-Cell Preparation Challenges

The present work is intended to give an in-depth review over the most significant progresses, in terms of practical performances, reached by SIBs in full-cell configuration. Indeed while plenty of review articles have been published in the last years providing a comprehensive view over functional materials for sodium rechargeable batteries, full-cell configurations have been often neglected. The final aim would be that of providing a comprehensive tool to refer to in order to systematically evaluate and critically assess each new sodium-ion full-cell chemistry proposed in the literature, in order to probe its technological readiness level. This is indeed a compulsory process to validate sodium ion technology capability in replacing lithium technology in various energy storage applications, and primarilly large-scale stationary energy storage, which requires considerable manufacturing investments. Not all the applications field would work for a sodium-ion technology. For electric mobility applications, indeed, (i.e., EV, HEV, and PHEV) important figures of merit are both volumetric (kWh dm$^{-3}$) and gravimetric energy density (kWh kg$^{-1}$) since hindrance and weight of the whole battery pack would heavily influence car overall performances. On the other hand for stationary energy storage systems (i.e., power plant backup systems, domestic storage and
new renewable energy sources continuity units), cell final requisites in terms of volumetric and gravimetric energy density are less stringent. Portable electronics, eventually, demand improved capabilities mainly in terms of amount of capacity constrained in a sufficiently small volume and reliability during charge/discharge cycles. When the assembling of a prototype full-cell is considered on a laboratory scale, critical factors ought to be carefully weighted in order to accurately mimic practical cell conditions and thus produce sensible results. Criticalities are (i) the greater sensitivity of cell performance to the coulombic efficiencies of the electrodes, (ii) the irreversible capacity connected to solid electrolyte interphase (SEI) formation (both initially and ongoing during cycling), and (iii) any side reactions occurring within the cell. The latter aspect, in particular, potentially can lead to sensible modification in charge/discharge electrode profiles. This, in turn, will result in an unrealizable full-cell potential output. SEI layer is defined as the polymeric film forming during the very first charge cycle at anode-electrolyte interface. It directly derives from the electrochemical decomposition of electrolyte solvents and salts producing different species. This process entails the irreversible segregation, inside the polymer matrix, of a varying quantity of lithium ions (either complexed or strongly bonded to polymer branches and functionalities). In full-cell configuration this amount of lithium ions it is no more available for further reactivity and thus will set an irreversible contribute to the capacity of the first cycle. This contribute can range from 5 to 15% of the total capacity of the cell and it needs to be properly balanced with an excess of cathode material. Coulombic efficiency (CE), defined as the ratio between the charge supplied during charge and charge obtained during discharge, is moreover an important indicator of the irreversible contributes influencing each charge/discharge loop. A CE of 99.95% (0.05% irreversible capacity per cycle), although might seem contained and not particularly significant, would determine an overall 10% capacity loss in 200 charge/discharge cycles. Such value is incompatible with commercial products which are supposed to last, according to the utilization, between 500 and 10000 cycles. Porosity of the electrodes, intrinsic volume changes during charge/discharge can affect both the volume of the cell and the capacity or rate performances of the electrodes, and therefore careful optimization of the components is required for optimum cell performance. Delicate aspects also include the accurate balancing between anode and cathode materials, in order to pair up capacities Practical specific capacities of anode and cathode species have to be taken into careful consideration. This values often differs from theoretical specific capacity due to limitations in exploiting completely the RedOx and capacitive mechanism involved in the material energy storage. For instance, P2–O2 phase transition of certain layered cathode materials, P2-Na0.1[(Fe0.5Mn0.5)_0.75Co0.25]O2 is an example, determines a progressive capacity reduction during cycling connected to mechanical stresses related to considerable unit cell volume change (±15%). For this reason, in order to achieve a prolonged operation life of the full-cell, excluding such phase transition by reducing operational voltage window and thus the capacity practical achievable, would be appropriate. Differently from half-cell set-ups, in which metallic sodium counter electrode behaves as an almost infinite sodium reservoir, for full-cell configurations irreversible sodium consumption connected to SEI formation at the anode, or electrode activation processes, need to be properly addressed. A selected excess of cathode material has thus to be loaded, but its precise quantification is not an easy task. In research field, where the main focus of the investigation is most of the time the gravimetric energy density of either cathode or anode material, a counter electrode material excess is considered. In reporting the latest results achieved in this field, consequently, it will be always indicated if energy density and specific capacity refer to a cathode or anode limited full-cell. Recently the research around high capacity anodes for SIBs (based on 14th and 15th group elements alloys or oxide based conversion materials) has been knowing a positive momentum, thanks to the hype also deriving from lithium-rich full battery counterpart (silicon[67,68] and sulfur[69] based LIBs). The issue represented by balancing a full cell based on these classes of materials is even more severe. Due to the high gravimetric energy densities of the above mentioned elements and compounds, concerns related to the capacity balancing using a low gravimetric energy densities cathode arise. The required amount of cathode material might result unseemly and eventually can create a dramatic kinetic bottleneck due to resistivity imposed by electrode thickness. The attention will be directed to the description of the most promising full-cell architectures and chemistries proposed so far on a laboratory scale. Full-cell characteristics and electrochemical performances will be eventually collected in capitulatory tables and graphs, in order to facilitate the comparison with lithium chemistries as well, and highlight valuable patterning and clustering of full-cell SIBs architectures on a Ragone-like plot.[70] To better report the recent literature findings, it has been chosen to differentiate the sodium full-cell architectures in two main families: nonsymmetric and symmetric full-cells. In the first category, the adopted configuration resembles the one utilized nowadays by lithium-ion technology in which anode and cathode materials belong to two distinct families. For symmetric devices, the same material will be addressed both as the anode as well as the cathode inside the cell, exploiting its extended electrochemical stability and wide potential window operation and multiredox centers. This last class of device surely represent an interesting and costly efficient configuration albeit often affected by lower energy and power density content.

3. Sodium-Ion Battery Materials

Before diving in the thorough description of full-cell SIBs chemistries and configurations an overlook of the most studied classes of active anode and cathode materials is provided. Specific attention will be addressed to energy storage principia description, and fundamental notions will be accompanied by state-of-the-art research examples. Active materials for SIBs are being continuatively and extensively studied for more than a decade now and many of them are proven as promising cathode and anode compounds ensuring stability and reliability at high currents.[63,64,71–74] The recent discovery and optimization of high-voltage cathode materials for SIBs,[75–79] indeed contributed in reviving the interests for a full sodium ion battery, contrarily to the downing of sodium ion rechargeable batteries in the 1980s.
3.1. Anode Materials for SIBs

Research about anode material of a sodium-ion cell has recently drawn the attention of the scientific community. Despite this, a net numerical discrepancy between published works on cathode material and anode ones has been registered in favor of the former. Among the difficulties experienced by people approaching the negative-side topic worth to be mentioned are the operational potential of the material in a sodium environment, often too high to guarantee an appreciable final energy density, overall stability and frequent disruption of the material throughout cycling and low coulombic efficiencies. A worldwide accepted criterion in investigating this type of species has been so far, mimicking the modern research trend in LIBs research, the proposal of negative material with exceptionally high gravimetric capacities, well above the average values of commercial devices (=300 mAh g\(^{-1}\)).\(^{[80]}\) This approach, albeit source of extraordinary results often limited to first cycles, is short-sighted toward a possible coupling with a cathode material, in a full cell assembly. It must be in fact considered that nowadays research on cathode materials for SIBs, and it will become clear in following sections, is limited to insertion compounds with gravimetric capacities limited to only few hundreds of mAh g\(^{-1}\). Managing materials quantity balance inside the cell and thicknesses of active deposits will then become a critical aspect when full-cell SIB is put under study. The overwhelming number of compounds proposed in literature will be, to facilitate navigation through the present review, organized in four categories, namely (i) carbon-based materials, (ii) oxides based on conversion reaction, (iii) p-block alloying elements (metals, alloys, and phosphorous) showing reversible sodiation/desodiation reaction, and (iv) oxides as Na-insertion topotactic materials.

3.1.1. Carbon-Based Materials

Carbonaceous materials were the most immediate and trivial answers to the need of an anode material for sodium ion batteries. Many aspects can be listed among motivations beyond this, such as lithium-ion batteries heritage connected to graphite, low costs, environmental friendliness, and electro-chemical stability. Most likely, studies of graphite-based anode material intercalating sodium started together with those about lithium and potassium, and confirmed their reversibility, forming Li\(_n\)C\(_6\) and K\(_n\)C\(_6\) graphite intercalation compound (GIC) respectively. Despite Na having a ionic radius (\(\approx 1.05\) Å) situated in the middle between that of Li (\(\approx 0.76\) Å) and K (\(\approx 1.5\) Å), and thus a higher chance to trigger staging into layered material, only 12 mAh g\(^{-1}\) are delivered by its insertion. Difficulties in sodium intercalation refers to incompatibility of the small interlayer distance of graphite (\(d(002) = 0.334\) nm)\(^{[81-85]}\) with ionic radius of solvated sodium. Furthermore, Stage-1 Na-GIC formation (occupation of every interlayer space in graphite layered structure) has been demonstrated to be thermodynamically unfavorable, due to excessively high sodium RedOx potential which makes the sodium plating upon graphite, rather than intercalation in it, more likely.\(^{[86]}\) Other factors that undermine the proper staging are the large elongation of C–C bond length and the scarce binding energy between carbon and sodium atoms. Recently it has been demonstrated how expanding along c axis the single layers stacking of graphite, is possible to achieve reversible capacities hovering around 284 mAh g\(^{-1}\) at 20 mA g\(^{-1}\), with the superior capacity retention of 73% after 2000 cycles if cycled at 100 mA g\(^{-1}\). In the work of Wen et al., indeed, the importance of maintaining a long-range vertical ordering is stressed, and moreover, concentration of oxidized carbon sites, namely surface oxygen concentration, is considered a fundamental aspect.\(^{[41]}\) Jache and Adelhelm claimed that also the electrolyte solution plays a relevant role in allowing sodium intercalation, and they have been able to obtain a reversible insertion of sodium ions using an diglyme-based electrolyte solution.\(^{[87]}\) In their work, the co-intercalation of solvent molecules chelating sodium ions, according to the reported equation, is emphasized

\[
\text{C}_n + e^- + \text{Na}^+ + y \text{solv} \leftrightarrow \text{Na}^+ (\text{solv})_y \text{C}_n
\]  

Low potential intercalation occurs, in this case, with a modest potential extending for \(\approx 100\) mA g\(^{-1}\). Structural X-ray diffraction (XRD) analysis confirms graphite layers expansion along c axis, leading to a total volume expansion of 15%. Theoretical study hypothesized an ether co-intercalation of —one to two molecules of diglyme, considering that alkaline atoms are preferentially coordinated by six oxygen atoms.\(^{[88]}\) Furthermore, Kim et al.\(^{[89]}\) reported unusual Na storage behavior in natural graphite through Na-solvent co-intercalation combined with pseudocapacitive behavior using ether-based electrolyte. Wen et al.\(^{[41]}\) proposed chemically modified graphite\(^{[41,87]}\) as anode for SIBs with an enlarged interlayer lattice distance. The expanded graphite is a graphite-derived material formed by a two-step oxidation–reduction process that retains the long-range-ordered layered structure of graphite, yielding a generally larger interlayer distance (>0.34 nm) as schematized in image (a) in Figure 1. These features provide favorable conditions for electrochemical intercalation of Na ions.

As the utilization of pure graphite has been discouraged, other carbonaceous material, like hard-carbon, soft-carbon, and amorphous carbon started being extensively investigated as alternatives. A large number of nongraphitic carbons have demonstrated to reversibly interact with sodium with mechanisms other than pure intercalation. This class of material includes partially crystalline hard carbons and soft carbons. These two materials differ not only for the synthetic methods and precursors involved but also upon crystalline structure and stability to thermal treatments. Hard-carbons, defined as nongraphitic nongraphitizable carbons, are obtained from solid-phase pyrolysis of phenol-formaldehyde resins, cellulose, charcoal, coconut and sugar,\(^{[90]}\) and other biomass wastes.\(^{[91,92]}\) Soft-carbons, termed as nongraphitic graphitizable carbons, are obtained from liquid or gas-phase pyrolysis. The term nongraphitic refers to the absence, in the carbon structure, of crystalline graphic domains with long-range periodicity. The graphitizable concept, instead, involves the possibility of obtaining such long-range periodicity upon high-temperature (>1000 °C) thermal treatment of the carbon. As hard-carbons appear more stable if subjected to high temperature thermal treatments and oxidative environments, soft-carbons have the advantageous property of graphene sheets interlayer spacing tunability upon appropriate heat treatment.
As thoroughly reported by Luo et al., increasing heat treatment temperatures induces a denser stacking of graphene layers inside micrometric graphitic domains, as confirmed by shift toward higher angles of (002) XRD diffraction peak. Nevertheless, compared to reversible capacity extracted from hard-carbons, soft-carbons deliver lower capacities (≈120 mAh g\(^{-1}\)) at slightly higher potential (0.6 V vs Na/Na\(^{+}\)). As previously quoted, for nongraphitic carbon and hard-carbon in particular, multiple processes contribute to sodium storage and they are inevitably connected to carbon microstructure. Hard-carbons show the higher heterogeneity in structure, namely micrometric-size graphitic domains whose long-range continuity is interrupted by randomly arranged single and few-layer graphene sheets as well as amorphous areas. This casual arrangement, intuitively simplified by depicting it as a "falling cards model," confers a porous structure whose degree depends on pyrolysis conditions such as temperature and gas fluxes. As an explicative case, using sugar as carbon precursor, a steep decrease in micropore surface has been observed if pyrolysis temperature is raised from 900 to 1000 °C, while a smoother decrease occurs above 1200 °C. The specific surface area (SSA) changes accordingly from hundreds to <10 m\(^2\) g\(^{-1}\) if pyrolysis takes place above 1000 °C due to micropores closure. Worth to be noted is that porosity and surface area extension can be also tuned by precursor pretreatments as well as by postpyrolysis heat treatment in particular flowing atmospheres. Analyzing in more details the involved mechanisms in sodium uptake, two main processes are found to be responsible for the majority of the stored capacity. They can be easily spotted by looking at the potential versus capacity curves of a galvanostatic cycling (right side of image (a) in Figure 2), and consist in a sloping potential region extending to ≈0.2 V and a low potential plateau that gently glides toward 0.0 V versus Na/Na\(^{+}\). The former of the two is widely recognized to be due to alkaline ion insertion between layers in pseudographitic domains. These process is not limited and does not coincide with a single potential plateau, as in the case of lithium insertion into graphite, since the pseudographitic domain disorder produces sites with different chemical environments and thus different insertion energies. The process occurring at lower potentials is instead related to ions adsorption in micropores as backed up by recent density functional theory (DFT) calculation. These two processes, also active for lithium, can be practically monitored by ex situ XRD and small-angle X-ray scattering (SAXS) analysis. During the first step an expansion of the interlayer distance between graphene sheets from 3.8 to ≈4.15 Å can be detected, while in connection with the second step, a reduction of the scattering intensity around 0.03–0.07 Å\(^{-1}\) in the SAXS spectra well agrees with the filling of micropores via adsorption mechanism. A common drawback shared, in different extents, by nearly all hard-carbons investigated as anode for sodium batteries, is the non-negligible irreversible capacity correlated with the first sodiation. This is mostly due to SEI formation and only partially to irreversible
sodium trapping inside carbon structure. In general massive capacity losses related to first cycle are deleterious and highly problematic, since they are hardly quantifiable sodium-consuming mechanisms overcomplicating anode to cathode mass balance in full-cell assembly. An overestimation of cathode excess required to counterbalance the irreversible capacity might also lead to hazardous consequences such as sodium plating upon overcharging or at low temperature operation condition. Irreversible capacity is unfortunately a common feature for anode materials, and the highest coulombic efficiency upon the first cycle reported to date is 85% for hard-carbon samples with low SSA (<10 m² g⁻¹). A detailed review of carbon materials, so far the most cost effective and easy to synthesize candidates, as suitable anode for SIBs has been recently provided by Balogun et al.⁴²⃣ Together with concentration of surface functional groups, surface area extension has been demonstrated to be a crucial parameter in defining the SEI layer formation and thus irreversible capacity build up, and a direct linear relation between Brunauer–Emmett–Teller (BET) specific surface area (SSA_{BET}) and irreversible capacity is often observed. Some studies conducted with lithium suggested that more than the SSA_{BET} accessible to the electrolyte, a more indicative parameter of the surface reactivity with alkaline atoms and salts would be the active surface area.⁹⁸⃣ It can be effectively determined via oxygen chemisorption to form oxygenated complexes and the following quantification of oxygen outgassing by mass spectrometry. Direct truthfulness of this aspect for SIBs is still to be confirmed. Anyway, as a general rule of thumb, low surface specific area hard-carbons have to be preferred to higher area ones in consuming less material during SEI formation. Since SEI layer composition strongly depends on sodium salt and solvent employed in electrolyte formulation, many efforts have been addressed to find an optimum electrolyte formulation. Komaba et al. successfully achieved a stable capacity of 230 mAh g⁻¹ for more than 100 cycles with 1 M NaClO₄ in propylene carbonate (PC) or ethylene carbonate (EC):diethylene carbonate based electrolytes.⁹⁷⃣ Under a structural point of view, a progressive reduction in reversible capacity connected to Na⁺ insertion in hard-carbon graphitic layers is observed if the layers spacing is reduced upon increased pyrolysis.

**Figure 2.** a) Cartoons depicting different types of carbonaceous material according to their microstructure; hard-carbon non-graphitizable carbons in the “falling cards” model possess a hierarchical structure in which insertion domain and adsorption microporous and mesoporous sites are both present (left); on the right the two sodium storage mechanisms are illustrated paired up with observed charge/discharge curves. Reproduced with permission. Copyright 2015, Electrochemical Society. b) Evolution of Raman signals for a hard-carbon obtained from PAN pyrolized at different temperatures. Reproduced with permission. Copyright 2014, Elsevier. c) Sodiation profile evolution with cycles of a O-doped carbon obtained from pyrolysis of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA). Reproduced with permission. Copyright 2016, Wiley-VCH.
Table 1. Summary of the most relevant carbonaceous matrices and microstructures proposed as anode materials for sodium ion batteries.

<table>
<thead>
<tr>
<th>Precursor and synthesis</th>
<th>Pyrolysis conditions</th>
<th>(I_D/I_G) or carbon type</th>
<th>SSA(_{\text{BET}}) [(\text{m}^2\ \text{g}^{-1})]</th>
<th>Coulombic efficiency (1st cycle)</th>
<th>Reversible capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped carbon sheet</td>
<td>800 °C, 2 h</td>
<td>0.93</td>
<td>76, mesoporous</td>
<td>26.4%</td>
<td>165 mAh g(^{-1}) at 200 mA g(^{-1})</td>
</tr>
<tr>
<td>Templated carbon([102])</td>
<td>700 °C</td>
<td>Mostly nongraphitic</td>
<td>346 mesoporous  and macroporous</td>
<td>≈17%</td>
<td>110 mAh g(^{-1}) at 372 mA g(^{-1}) decreasing</td>
</tr>
<tr>
<td>Nanospheres([103])</td>
<td>700 °C, 5 min</td>
<td>1.1</td>
<td>4 mesoporous</td>
<td>≈60%</td>
<td>92 mAh g(^{-1}) at 150 mA g(^{-1}) stable</td>
</tr>
<tr>
<td>Hollow nanospheres([104])</td>
<td>1000 °C</td>
<td>Weakly ordered turbostratic carbon structuring</td>
<td>410 microporous</td>
<td>41.53%</td>
<td>150 mAh g(^{-1}) at 100 mA g(^{-1}) stable</td>
</tr>
<tr>
<td>Highly disordered carbon([105])</td>
<td>800 °C, 2 h</td>
<td>1.0</td>
<td>2.5 m(^2) g(^{-1}) macroporous</td>
<td>57.61%</td>
<td>225 mAh g(^{-1}) at 100 mA g(^{-1}) after 180 cycles</td>
</tr>
<tr>
<td>Hollow nanowires([45])</td>
<td>1150 °C, 6 h</td>
<td>Disordered graphite nanocrystals</td>
<td>50.5%</td>
<td>206 mAh g(^{-1}) at 50 mA g(^{-1}) after 400 cycles</td>
<td></td>
</tr>
<tr>
<td>Electrospun nanofiber([46,99])</td>
<td>1250 °C, 30 min, (N_2)</td>
<td>0.97</td>
<td>14.6 mesoporous</td>
<td>72.0%</td>
<td>271 mAh g(^{-1}) at 100 mA g(^{-1}) stable after 100 cycles</td>
</tr>
<tr>
<td>(\text{H}_3\text{PO}_4)-activated porous carbon([45])</td>
<td>700 °C, 2 h, (N_2)</td>
<td>&gt;1.0</td>
<td>1272 mesoporous</td>
<td>27%</td>
<td>181 mAh g(^{-1}) at 50 mA g(^{-1}) after 200 cycles</td>
</tr>
<tr>
<td>Microspheres([45])</td>
<td>500 °C, 2 h</td>
<td>Disordered carbon</td>
<td>393.1 microporous</td>
<td>≈40%</td>
<td>183 mAh g(^{-1}) at 30 mA g(^{-1}) after 50 cycles</td>
</tr>
<tr>
<td>Expanded graphite([51])</td>
<td>600 °C, 1 h, (Ar)</td>
<td>Graphitic</td>
<td>49.5%</td>
<td>280 mAh g(^{-1}) at 100 mA g(^{-1}) after 2000 cycles</td>
<td></td>
</tr>
<tr>
<td>Rape seed shuck hard carbon([50])</td>
<td>700 °C, 2 h, (Ar)</td>
<td>0.53 ((I_D/I_G)) amorphous</td>
<td>11.93 mesoporous</td>
<td>≈80%</td>
<td>143 mAh g(^{-1}) at 0.1 A g(^{-1}) after 200 cycles</td>
</tr>
<tr>
<td>O-doped 3D interdigital carbon([51])</td>
<td>500 °C, 4 h, (Ar)</td>
<td>Disordered carbon</td>
<td>63.1%</td>
<td>223 mAh g(^{-1}) at 1000 mA g(^{-1}) after 1200 cycles</td>
<td></td>
</tr>
</tbody>
</table>

In other words, by increasing heat treatment temperature, an ordering process is induced and eventually a more graphitic structure is obtained as showed by \(I_D/I_G\) bands intensity in Raman spectra (image b in Figure 2). The latter has been recognized as a further diagnostic parameter of the ordering level of carbon structure, being D-band and G-band in Raman spectra defect-induced and \(E_{2g}\) graphitic induced modes, respectively. D-band typically falling at \(-1350\ \text{cm}^{-1}\) is associated with defects of disordered structures. G-band instead, peaking at \(-1580\) corresponds to ordered graphitic domains.\([100]\) \(I_D/I_G\) values thus give a qualitative representation of carbon microstructure, and as they drop below 1, more ordered structure and graphitic-like structures are achieved. Typical values range from 1.05 to 0.94 as the heat treatment temperature is increased from 800 to 1500 °C. On the other hand, reversible capacity associated to low potential plateau, is found to increase with temperature. This means that even if micropores close as the temperature is raised, they are still accessible for Na\(^+\) adsorption and the only parameter controlling low potential capacity is the average pore size. A mounting attention has also been directed to O-rich carbons. Their oxygen containing functionalities, such as C=O and C=O, actively participate to Na\(^+\) storage mechanism by reversible O reduction.\([101]\) In these cases a completely new RedOx process taking place at 1.5 V versus Na\(^+\)/Na progressively appears in the charge/discharge profile as C=O and C=O undergo activation. Previously described carbonaceous materials for SIBs and many other are collected in Table 1. Important parameters are included in the table: synthesis conditions, state of graphitization by reporting \(I_D/I_G\) ratio (when Raman data are available), SSA\(_{\text{BET}}\), and Coulombic efficiency related to the first cycle.

An effective strategy to improve the electrochemical properties of carbonaceous materials has been so far heteroatom (such as N, B, S, and P) doping. Doping hard-carbon or graphene-like structures creates a defect sites to absorb sodium ions and improves the electrode-electrolyte interaction.\([20]\) Hwang et al. recently proposed a 3D interconnected structure of free-standing flexible films composed of nitrogen-doped porous nanofibers that exhibited 212 mAh g\(^{-1}\) at 5 A g\(^{-1}\) with a capacity retention of 99% after 7000 cycles.\([107]\) In another work, nitrogen rich hard carbon derived from biomass with improved capacitance exhibited stable 204 mAh g\(^{-1}\) for over 1000 cycles at 1 A g\(^{-1}\) but a Coulombic efficiency of 34% in the first cycle.\([108]\) Biomass derived carbons, which have been widely investigated due to their low production cost and low energy consumption during the synthesis procedure, indeed often exhibit very low Coulombic efficiency.\([109]\) Dealing with such problem requires properly selecting the biomass resource and optimizing synthesis procedure.\([110]\) Zhang et al., for example, successfully obtained higher Coulombic efficiency in the first cycle (85%) and stable capacity of 334 mAh g\(^{-1}\) after 120 cycles at 0.1 C, optimizing the preparation method of hard-carbon derived by pinecone.\([111]\)
3.1.2. Conversion Materials

**Conversion Transition Metal Oxides**: Conversion transition metal oxides are materials worth of interest as anode for SIBs due to their high theoretical specific capacity (=900 mAh g\(^{-1}\)). They are also thermodynamically favored among other transition metal halides and chalcogenides, thanks to the surpassingly advantageous potential gain in sodium environment if compared with lithium.\(^{[50,113]}\) Considering a full conversion reaction leading to metallic transition metal and sodium oxide, the theoretical specific capacity increases with the initial oxidation state of the transition metal (715 mAh g\(^{-1}\) for CoO where Co\(^{II}\) and 891 mAh g\(^{-1}\) for Co\(_3\)O\(_4\) where Co\(^{III}\)) and decreases with its atomic number. One of the major challenges that conversion oxides materials carry with themselves is the important volume expansion occurring during conversion mechanism, reported below\(^{[50]}\)

\[
\text{M}_x\text{X}_y + (\text{bc})\text{Na} \leftrightarrow \text{aM} + \text{bNa}_x\text{X} \Delta G = \Delta H - T\Delta S
\]

It accounts for 150–250% volume change for oxides and is second only to transition metal phosphide for which it can reach the extraordinary value of 400%. The induced structural strain connected to expansion and contraction is thus considerable especially at the interface between metal and Na\(_2\)O due to lattice mismatch. Using material engineering, many solutions have been proposed in order to minimize this drawback and endless efforts have been addressed to investigating mechanism in order to provide a more detailed analysis of the tricky conversion process. A list of the most emblematic conversion oxides investigated as anode for SIBs is provided below, together with an in-depth discussion of their mechanisms and chemistries.

Iron oxide, in its multiple crystalline phases and allotropes, represents a well investigated conversion material for both lithium and sodium batteries. Hematite \(\alpha\text{-Fe}_2\text{O}_3\), as well as magnetite \(\text{Fe}_3\text{O}_4\) peaks appear in the diffractogram. All the diffraction peaks from its XRD analysis indexed to Co\(_3\)O\(_4\) spinel phase progressively disappear, as can be spotted in image (b) in Figure 3, as potential reaches the first voltage plateaus. Only when no further downward bending of potential curve occurs, close to 0.0 versus Na/Na\(^+\), Na\(_2\)O peaks appear in the diffractogram. Co\(_3\)O\(_4\) is partially recovered upon desodiation. Impurities formation or other Co\(_3\)O\(_4\) phases evolution cannot be excluded since weaker diffraction peak can be clearly distinguished at the end of the first cycle. A distinct modification of charge/discharge profile occurs after the very first cycle and recent XRD ex situ investigation of bulk porous Co\(_3\)O\(_4\) electrodes, successfully confirmed the recovery, after first sodiation, of an intermediate oxidized CoO phase.\(^{[117,118]}\) Under the electrochemical performances point of view, nanoporous Co\(_3\)O\(_4\) shows upon
long cycling a specific capacity of nearly 500 mAh g\(^{-1}\), if compared to bulk Co\(_3\)O\(_4\) particles. If 5% fluoroethylene carbonate (FEC) is added to the electrolyte solution, a net increment of the capacity stability can be achieved (image (c) in Figure 3). FEC is recognized to be a forming agent of particularly stable SEI layers, and its use, in low gravimetric concentrations (2–5 wt%), is often encouraged in investigating anode materials for SIBs.\(^{63,72,119}\) Practical specific capacity is considerably lower than the theoretical value (891 mAh g\(^{-1}\)) but still an interesting value if compared to carbonaceous anode materials. The almost halving of the theoretical value has to be attributed to high irreversible capacity involved in first cycle as well as to the large size and thus poor mobility of Na\(^+\) inside the oxide lattice. In comparison Li, giving a pure conversion mechanism with Co\(_3\)O\(_4\), is a lot more performing giving capacity closer to or higher than 800 mAh g\(^{-1}\) at 1 C.\(^{120,121}\) Other solution have been proposed to accommodate electrode expansion such as homogeneous dispersion of cobalt oxide particles on graphene oxides sheets using a wet method\(^{[122]}\) as well as on a carbon nanotubes network via pulsed plasma technique.\(^{[123]}\) In the latter case ex situ SAED analysis taken after the tenth charge to 0.01 V versus Na/Na\(^+\) revealed how only Na\(_2\)O and metallic Co are present, symptom of a complete conversion reaction. On the other hand, after each discharge back to 3.0 V only one component is identified, whose SAED pattern well matches with crystallographic parameters of Co\(_3\)O\(_4\). These results seem to be backed up by TEM and ex situ XRD analysis of cycled electrodes. Same way as iron oxide, tin oxides, SnO and SnO\(_2\), have been also proposed as safer anodes for SIBs instead of cobalt-based compounds. Flower-like SnO particles and nanometric sized SnO\(_2\) (carbon coated) particles have been hydrothermally synthesized by Lu et al., and their electrochemical properties in
sodium environment thoroughly tested in the potential window with different sodiation cut-off values.\textsuperscript{[124]} SnO particles show, at a first galvanostatic screening analysis, the best electrochemical behavior, guaranteeing a stable specific capacity of 330 mAh g\(^{-1}\) after 50 cycles. On the other hand a decreasing trend is obtained from carbon coated SnO\(_2\), with a capacity retention of 58\% after 50 cycles. From galvanostatic cycling tests adopting different sodiation cut-off potentials (0.3 and 0.05 V vs Na/Na\(^+\)) progressively increasing Coulombic efficiencies, 49.4\% to 61.7\% for SnO and 38.5 to 52.5\% for SnO2/C, are recorded. The even lower Coulombic efficiencies recorder for a higher cut-off (0.5 V) has to be than related to irreversible SEI formation mechanisms taking place at relatively higher potentials during the first sodiation, as observed for other oxide materials. By following reaction mechanism using ex situ XRD analysis, metallic Sn phase starts being detected from 0.5 V for SnO and is not fully reoxidized when electrode potential jumps back to 2.0 V. It is worth noting that by looking at SAED patterns, SnO\(_2\) rather SnO is spotted when the electrode is desodiated, this is presumably due to the higher thermodynamic stability of SnO\(_2\) phase compared to SnO. If this would be completely true, relative performances of the two materials, in term of charge/discharge profiles and specific capacities, should tend to uniform upon cycling resulting in an overlap, which is not achieved. The discrepancies in material morphologies, which are remarkable, must thus have a role. In the case of SnO\(_2\), theoretical specific capacity coinciding with two Na ions per mole of SnO is 398 mAh g\(^{-1}\), nearly half of the capacity extracted during first sodiation (720 mAh g\(^{-1}\)). Authors claimed that this is a demonstration of the reaction mechanism occurring for 55\% via conversion reaction and for 45\% through the alloying reaction of sodium in metallic Sn. Added to this a lower reversibility in the reaction region is also called since Coulombic efficiencies are low for high cut-off potentials. The theoretical conversion capacity for SnO\(_2\) is instead considerably higher (711 mAh g\(^{-1}\)) and therefore in compliance with the practical capacity value extracted from first sodiation. The conversion/alloying balance for SnO\(_2\) has been thus calculated to be 95 to 5. Having the conversion mechanism, affected by a large irreversibility, a major role in contributing to capacity harvesting, SnO\(_2\) performances progressively degrade. The authors then concluded that the outstanding SnO energy storage capabilities must be attributed to various degree of alloying reactions in the sodiation. Partial reoxidation of metallic Sn finds also a counter-check in the work by Su et al.,\textsuperscript{[125]} where tetragonal metallic Sn is detected when the electrode is discharged to 3.0 V. Contrarily to what Lu et al., here SnO is not entirely converted to SnO\(_2\) upon following oxidations, on the other hand, SnO is restored with a change in its crystallographic phase that passes from a tetragonal symmetry to an orthorhombic one. Despite the widespread disagreements still present in literature concerning the reversible mechanism involved in SnO energy storage, two main processes can be undoubtedly cited. The first one is the complete conversion reaction leading to metallic Sn, possibly (but not completely excluded) bypassing a potential sodium intercalation in SnO structure according to the equation

\[
\text{SnO} + 2 \text{Na} \rightarrow \text{Na}_2\text{O} + \text{Sn} \quad (\text{theoretical capacity: 398 mAh g}^{-1})
\]

The second process is sodium alloying in Sn at low potentials leading to NaSn\(_2\), as elucidated by more accurate XRD analysis

\[
2\text{Sn} + \text{Na} \rightarrow \text{NaSn}_2 \quad (\text{theoretical capacity: 112.8 mAh g}^{-1})
\]

The total amount of theoretical specific charge would thus amount to 511 mAh g\(^{-1}\), that well agrees with experimental reversible capacity values (403 mAh g\(^{-1}\) at 20 mA g\(^{-1}\)). Formation of a Na\(_x\)Sn phase has been also recently confirmed by theoretical calculation by Wang and co-workers.\textsuperscript{[126]}

Conversion Transition Metal Chalcogenides: Similar to transition metal oxides, transition metal chalcogenide materials may also undergo two different types of reaction, such as intercalation followed by conversion reaction\textsuperscript{[127]} or conversion followed by alloying reaction.\textsuperscript{[128-129]} Transition metal chalcogenides of general formula TMX (X = S, Se and TM = Fe, Co, Ni, Sn, Mo, W, Sb, Mn, Zn, Cu, Ti, Ta, V, Bi, Nb, or a mixture of them), albeit bearing the advantage of improved specific capacities, introduced new technological challenges. Sulfur-based TMX, for instance, required the shuttling of soluble lithium and sodium polysulfides, intermediate reaction products, to be carefully addressed, while more in general, volume variations remained as a major limit.\textsuperscript{[130-132]}

Transition metal chalcogenides such as SnS and SnS\(_2\), which are subjected both to conversion-alloying mechanism, exhibit high theoretical capacity but bear with themselves the disadvantage of low intrinsic diffusion kinetics and a large volume change. Various approaches have been adapted in order to overcome these drawbacks. Kim\textsuperscript{[128]} successfully prepared via hydrothermal synthesis and sequential carbothermal reduction, SnS/rGO hybrid nanocomposites with SnS crystalline size of 2 nm. Excellent reversible electronic capacity of 1230 mAh g\(^{-1}\) and long cycle stability were achieved, confirming that the low intrinsic electronic conductivity and large volume expansion limits can be successfully overcome by integration with rGO matrix. The rGO matrix was employed for the ad hoc synthesis of acid-exfoliated MoS\(_2\)-graphene self-standing electrode.\textsuperscript{[133]} Despite the interesting mechanical properties, in terms of tensile strength and failure strain, of the MoS\(_2\)/graphene-based paper, its specific capacity when assembled in a sodium half-cell, was limited to only 240 mA h g\(^{-1}\) obtained at 25 mA g\(^{-1}\). Recently, Jung and co-workers collected in a theoretical work the calculated electrochemical data of a large number of transition metal chalcogenides, such as TiS\(_2\), VS\(_2\), CrS\(_2\), CoTe\(_2\), NiTe\(_2\), ZrS\(_2\), NbS\(_2\), and MoS\(_2\).\textsuperscript{[134]} In their theoretical approach, worth to be noted are the efforts put in taking into account also phase transition information, often neglected. TiS\(_2\) and NbS\(_2\) were found to be the chalcogenides with the lowest energetic barrier to sodium diffusion (0.22 and 0.07 eV, respectively). These findings on NbS\(_2\) received recently an experimental confirmation thanks to the work by Yan and co-workers.\textsuperscript{[135]} In this work also metal and Se-doped NbS\(_2\) nanosheets were found to be an excellent high-rate anode compound for SIBs, delivering a capacity of 260 mAh g\(^{-1}\) at 1 A g\(^{-1}\) during the 750th cycle.

In general, three different approaches were successful in tackling the most puzzling limitations of transition metal chalcogenides. Nanostructuration and morphology engineering is one of the most relevant. As an example, chemically exfoliated
SnS$_2$–graphene sheets hybrid with extraordinary power capability. Earlier work by Kang and co-workers, for example, prepared a series of Co-doped FeTe$_2$ nanodisks$_{139}$ have also been reported. Recently, Shen and co-workers$_{140}$ proposed a novel strategy to successfully synthesize SnS$_2$ nanosheets assembled hierarchical tubular structures, by using cobalt–nitrioltriacetic acid chelate nanowires as soluble template. Owing to the hollow core and well separated nanosheets with maximally exposed edges, the SnS$_2$ tubular structures exhibited excellent electrochemical performance. When evaluated as anode material for SIBs, they delivered a high discharge capacity of 708 mAh g$^{-1}$ at 50 mA g$^{-1}$ preserving up to 414 mAh g$^{-1}$ after 50 cycles. Chemical stability can be improved by TMX hybridization with a conductive matrix, e.g., carbonaceous coating, conductive polymers, such as the case of FeTe$_2$–rGO hybrid powders.$^{[141]}$ NiSe$_2$/rGO$^{[142]}$ and SnS$_2$/C.$^{[143]}$ CoS$_2$ nanoparticles anchoring onto multichannel carbon nanofiber (MCNF) have been recently obtained by Zhang and co-workers via a simple solvothermal method.$^{[144]}$ Benefiting from the innovative structure, Co$_2$S$_4$@MCNF electrode delivered high capacity (537.5 mAh g$^{-1}$ at 0.1 A g$^{-1}$), superior rate capacity (537.5 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and 201.9 mAh g$^{-1}$ at 10 A g$^{-1}$), and long cycle life (315.7 mAh g$^{-1}$ at 1 A g$^{-1}$ after 1000 cycles). Very recently, sponge-like composite assembled by cobalt sulfides quantum dots (Co$_{9}$S$_8$ QD), mesoporous hollow carbon polyhedral matrix, and a rGO wrapping sheets were synthesized by Sun and co-workers via a simultaneous conversion material, the uptake of more than a single sodium atom guaranteeing capacity of 205 mAh g$^{-1}$ after 2700 cycles. Chemical stability can be addressed. Contrarily to lithium, for which silicon is overwhelmingly severe for sodium, due to the larger ionic radius, and leads to irreparable consequences if not properly addressed. Contrarily to lithium, for which silicon is a strong game-changer for what concern achievable energy densities,$^{[160]–[162]}$ sodium does not form intermetallic compounds, being the formation of the amorphous compound Na–Si energetically unlikely starting from crystalline silicon.$^{[163]–[164]}$ Nevertheless recent theoretical atomic-level assessment$^{[164]}$ revealed how pure amorphous silicon would allow the uptake of 0.76 Na per Si atom guaranteeing capacity of 725 mAh g$^{-1}$ comparable with other Group 14 elements. Such interesting property is supposed to derive from the relatively strong ionic bond between Si and Na atoms, connected to a modest decrease in Na charge state with x increase, before clustering of Na in Si bulk phase leading to neutral Na atoms. A very recent work aimed at finding an experimental confirmation failed at obtaining the forecasted theoretical capacities, and only a stable capacity of almost 150 mAh g$^{-1}$ has been achieved at 0.05 C, after a poor first cycle Coulombic efficiency of 17%.$^{[165]}$ Baggetto et al. took a basic but thorough electrochemical analysis of sodium alloying in a germanium thin film sputtered on roughened copper foil.$^{[158]}$ Throughout galvanostatic intermittent titration technique measurement at low current (C/60), calculated thermodynamic potential values could be closely approached during sodiation. A larger gap is instead observed when the desodiation is ongoing due to a high polarization connected to sodium removal. Capacity retention, despite promising values extracted during first cycles (=300 mAh g$^{-1}$) quickly drops, within 15 cycles, to few tens of mAh g$^{-1}$. Recent in situ

3.1.3. Alloying Materials

Vast computational efforts have been recently dedicated to predicting electrode potentials and stoichiometry for binary Na–Me intermetallic compounds formed with Group 14 (Si, Ge, Sn, and Pb) and Group 15 (P, As, Sb, and Bi) metallic and non-metallic elements. Differently from intercalation compounds, for which sodium uptake is limited by constraint induced by rigid frameworks, usually metals and metalloids can withstand multiple sodium atoms per single atom, resulting in capacities ranging from 300 to 2000 mAh g$^{-1}$ with operational voltages sufficiently low (below 1.0 V vs Na/Na$^+$) to be appealing for usage on SIBs anode side. Starting from the exploratory theoretical investigation of sodium alloys with group 14, 15, and 16 elements (Si, Ge,$^{[152]}$ Sn,$^{[153,154]}$ Pb,$^{[154]}$ as well as P,$^{[155,156]}$ As and Sb$^{[157,158]}$) conducted by Chevrier and Ceder$^{[159]}$ in 2011, the research activity has flourished. As already highlighted for conversion material, the uptake of more than a sodium atom has dramatic consequences on structural stability of the host material. If this aspect is mild for lithium compounds, it is overwhelmingly severe for sodium, due to the larger ionic radius, and leads to irreparable consequences if not properly addressed. Contrarily to lithium, for which silicon is representing a true game-changer for what concern achievable energy densities,$^{[160]–[162]}$ sodium does not form intermetallic compounds, being the formation of the amorphous compound Na–Si energetically unlikely starting from crystalline silicon.$^{[163]–[164]}$ Nevertheless recent theoretical atomic-level assessment$^{[164]}$ revealed how pure amorphous silicon would allow the uptake of 0.76 Na per Si atom guaranteeing capacity of 725 mAh g$^{-1}$ comparable with other Group 14 elements. Such interesting property is supposed to derive from the relatively strong ionic bond between Si and Na atoms, connected to a modest decrease in Na charge state with x increase, before clustering of Na in Si bulk phase leading to neutral Na atoms. A very recent work aimed at finding an experimental confirmation failed at obtaining the forecasted theoretical capacities, and only a stable capacity of almost 150 mAh g$^{-1}$ has been achieved at 0.05 C, after a poor first cycle Coulombic efficiency of 17%.$^{[165]}$ Baggetto et al. took a basic but thorough electrochemical analysis of sodium alloying in a germanium thin film sputtered on roughened copper foil.$^{[158]}$ Throughout galvanostatic intermittent titration technique measurement at low current (C/60), calculated thermodynamic potential values could be closely approached during sodiation. A larger gap is instead observed when the desodiation is ongoing due to a high polarization connected to sodium removal. Capacity retention, despite promising values extracted during first cycles (=300 mAh g$^{-1}$) quickly drops, within 15 cycles, to few tens of mAh g$^{-1}$. Recent in situ
TEM analysis of amorphous germanium nanowires revealed fast sodiation/desodiation kinetics associated to sodium richer stoichiometry with \( x = 1.56 \). Experimental studies conducted on metallic tin have showed a general inconsistency with DFT calculation aimed at finding the stable intermediate phases in Na–Sn system. Despite calculation would predict a sodiation proceeding through the steps NaSn5, NaSn, Na3Sn4, and Na3Sn4,\textsuperscript{16}\textsuperscript{6} ex situ characterization attempted by Ellis et al. on an experimentally sodiated tin electrode, identified four alloying steps with different composition and phases, namely amorphous NaSn3, α-NaSn, Na3Sn4, and crystalline Na12Sn4. The conclusion of the authors has been that the correspondence between experimental and calculated plateaus is only apparent.

Steps with different composition and phases, namely amorphous NaSn3, α-NaSn, Na3Sn4, and crystalline Na12Sn4 are suitable for sodium storage: NaSb and Na3Sb. Qian et al. first demonstrated a Sb–carbon nanocomposite with the initial capacity of 610 mAh g\textsuperscript{−1}.\textsuperscript{58} Both rate capabilities and cyclability were astonishingly impressive, since 300 mAh g\textsuperscript{−1} could be achieved at 2000 mA g\textsuperscript{−1} and capacity fade was limited to few percent within the first 100 cycles. Nonetheless, the latter feature was achieved only if FEC was employed as electrolyte additive and SEI-forming agent. This aspect strongly bonds the reversibility of sodium alloying mechanism to the stability and mechanical robustness of solid electrolyte interface, and can be reasonably extended to other intermetallic compounds. As for other metals also for antimony information on charge storage mechanism is nowadays limited. XRD patterns of the ongoing alloying process are rather featureless, symptom of intermediate amorphous phases between Sb and Na3Sb.\textsuperscript{54} Sb particles with different morphologies and dimension are investigated. An insight derived from in situ synchrotron XRD measurements taken on Sb/C composite (7:3), Ramireddy et al. failed in the recovery of crystallinity of Sb after first desodiation.

While binary systems involving Sn–Sb,\textsuperscript{168} Sn–Cu,\textsuperscript{169} and Al–Sb\textsuperscript{53} have been studied as potential SIBs anode, a recent trend is to inspect ternary Sn–Sb–Ge phases. Addition of a third element to a binary system further complicates phases stability and equilibria, marking the appearance of amorphous phases or modified lattice parameters due to substitutional solid solubility of Sn into Ge, for example. Many ternary phases have been investigated, and among them Sn60Ge20Sb20, Sn50Ge25Sb2, and Sn33Ge33Sb33 demonstrated to be valid candidates as anode material for SIBs with reversible capacities of 728, 829, 833, and 669 mAh g\textsuperscript{−1} respectively. The highest stability is achieved by Sn50Ge25Sb25 composition, which guarantees 662 mAh g\textsuperscript{−1} after 50 cycles. Interestingly all the experimental values, except for Sn80Ge10Sb10, are well above the weighted average combination of the theoretical capacities of a single element, 800, 743, 714, and 664 mAh g\textsuperscript{−1}. A possible explanation for this advantageous behavior has been put forth thanks to TEM and high-resolution transmission electron microscopy (HRTEM) microstructural analysis and concerns the optimum system constituted by 10–15 nm Sn and Ge(Sn) crystalline nanoparticles dispersed in an amorphous matrix. The enhanced capacity would be a consequence of a unique ability of Ge nanocrystallites, that are heavily alloyed with Sn, to sodiate beyond 1:1 Ge:Na (369 mAh g\textsuperscript{−1}) ratio.\textsuperscript{167} An hybrid conversion–alloying mechanism has been recently proposed to explain SnSe/rGO composite electrochemical behavior.\textsuperscript{59} Overlapping potential profiles and CV scans have been obtained in this case, symptom of highly reversible processes. Sorting all the ongoing process out is however a tough task that requires further investigation. Composites made of nanostructured alloying elements deposited on suitable carbonaceous substrates, positively contributed in extending cycle life of alloying materials in sodium cells. Sn@C-nanosphere,\textsuperscript{[71]} Sb/C,\textsuperscript{[50]} Se/C,\textsuperscript{[72]} Sb/C-nanofibers\textsuperscript{[73]} allowed to achieve promising reversible capacities of 200, 575, 485, 446, and 435 mAh g\textsuperscript{−1}, respectively.

3.1.4. Phosphorus

Phosphorus, belonging to the 15th group of the periodic table, has three widely known allotropes commonly named red, black, and white phosphorus. The latter, whose fundamental forming unit is the P\textsubscript{4} tetrahedron, is highly reactive and toxic. Red phosphorus electrochemical reactivity with sodium has been investigated before but its poor electronic properties make it only a modest and not reliable anode material for SIBs. Black phosphorus, with its unique crystalline structure, is the element currently addressed as the “holy Grail” in many fields, including energy storage one. It is a layered material resembling graphite with an unusual puckered structure made of covalently bonded P atoms.\textsuperscript{174} It has an interestingly high electronic conductivity (≈300 S m\textsuperscript{−1}) and its cycling performances are known to be promising with lithium,\textsuperscript{176} but sluggish with sodium. Cui and co-workers overcame the limitation imposed by the conversion mechanism by preparing a sandwiched graphene–black phosphorus hybrid material with impressive capacity retention and rate capabilities.\textsuperscript{156} As claimed by the authors the graphene sheets provide an elastic buffer accommodating the expansion of exfoliated black phosphorous (phosphorene) layers along y and z axes during alloying to Na\textsubscript{3}P. This guarantees capacities abundantly above 2000 mAh g\textsuperscript{−1}, stable over 100 cycles, at 0.02 C. The sandwiched structure has been obtained by a relatively simple self-assembly approach conducted in N-methyl-2-pirrolydone media. Recently, Komaba and co-workers tried to investigate the mechanism taking place during the three-electron reduction of P to Na\textsubscript{3}P, and a complete
conversion from orthorhombic black P to hexagonal red P was found.\textsuperscript{[175]} Crystalline black P is not obtained upon reoxidation and this has been addressed to the metastable nature of the allotrope. In the same research, the electrolyte solutions and additives have been recognized to have a fundamental role in stabilizing conversion reaction. Amorphous phosphorus has been recognized to be favorable under the volume change point of view and in recent studies this route is encouraged rather than the crystalline phosphorus one. Amorphous red P/carbon composites in which the P–C bonds formation is intentionally sought to firmly anchor P to graphene layers are nowadays able to ensure ultrastable efficiencies (0.002% decay per cycle within 400 cycles) and excellent rate capabilities (809 mAh g\textsuperscript{-1} at 1500 mA g\textsuperscript{-1}).

### 3.1.5. Insertion Materials: Titanate and MXenes

Some inorganic compounds are known to be active toward sodium ions intercalation at low potentials. This feature makes them attractive to be used as anodes in SIBs. The study of such compounds have been focusing in the recent years on TiO\textsubscript{2}-based materials and layered transition metal carbides or as generally called MXenes layered compounds. Titanium oxide in all its polymorphs (anatase, rutile, brookite, and TiO\textsubscript{2}-B\textsuperscript{[177]}) has repeatedly fascinated the scientific community thanks to its interesting physical properties that worthed it the honor to be studied in many different technological fields such as photocatalysis applied to pollutant degradation and water splitting, sensors technology, medicine, and ultimately energy storage facilities. Added to this a further drive to its fortune has been the natural abundance, environmental friendliness, tunable synthesis, and nontoxicity for human beings. Ti\textsuperscript{IV}/Ti\textsuperscript{IV} couple exhibits the relatively high RedOx potential around 1.5 V if cycled against lithium as widely demonstrated in literature.\textsuperscript{[176]} This aspect makes it unsuitable to be used both as high energy anode and cathode for LIBs. In a sodium environment, Ti-based compounds show an electrochemical activity centered at lower potential values, from 0.5 to 1.0 V versus Na/Na\textsuperscript{+}, interesting for a possible development of anodes not shadowed by sodium plating danger. Both amorphous and crystalline TiO\textsubscript{2} have been tested against sodium. The former, shaped in nanotubes directly grown on a Ti substrate, manifests a slow and undesirable activation process that progressively sets the capacity up to ~100 mAh g\textsuperscript{-1}. In this case, the energy storage mechanism seems to occur almost exclusively via double layer capacitance instauration.\textsuperscript{[179]} Mechanism involved in sodium interaction with crystalline TiO\textsubscript{2} is controversial still today. Some studies revealed that the crystalline structures of nanosized anatase TiO\textsubscript{2} are well retained upon sodiation, conversely, other research groups claim that a conversion-like process that in the end leads to metallic Ti is involved.\textsuperscript{[180]} A carbon coating sensibly increases electrochemical performances of anatase nanocrystals (NCs).\textsuperscript{[181]} In a recent investigation, different crystalline facets exposition of ad hoc synthesized TiO\textsubscript{2} anatase nanocrystals confirmed as a fundamental factor in extending capacity and stability.\textsuperscript{[182]}

Sodium titanate with the unit formula Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}, prepared using a ball milling procedure, has been recently investigated.\textsuperscript{[183]} It has been found to be active toward insertion of two sodium ions per unit formula (Na\textsubscript{2}Ti\textsubscript{3}O\textsubscript{7}) at an incredibly low potential (<0.5 V vs Na/Na\textsuperscript{+}) through a two-phase process to which correspond stable plateaus with low charge/discharge hysteresis. Structural analysis of intercalated titanate disclosed interesting properties of crystalline lattice in varying Na site through variation of joint angles between Ti–O block, demonstrating an overall structural flexibility never observed in TMOs. Nevertheless, few days storage of the sodiated compounds in an inert environment gradually makes it reverting back to the Na-poor phase, unveiling a self-discharge mechanism potentially bottlenecking the use of this material as an anode in a full-cell assembly.

MXenes is a class of 2D transition metal carbides and carbonitrides first proposed by Barsoum and co-workers.\textsuperscript{[184]} They are obtained by chemical etching in a hydrogen fluoride (HF)-containing environment, of the A layers from MX\textsubscript{n+1}AX\textsubscript{n} (n = 1,2,3), being M an early transition metal, A a 13 or 14 group element, and X carbon or nitrogen. Since when they were proposed for the first time as anode materials for LIBs the debate focused on the type of mechanism involved in the energy storage process, possibly capacitive/pseudocapacitive involving material surface\textsuperscript{[185]} or more based on a pure intercalation of desolvated Na\textsuperscript{+} ions.\textsuperscript{[186]} In both cases, in which the investigation of Ti\textsubscript{3}CT\textsubscript{x} was perpetrated (where T\textsubscript{r} represents the different surface terminations introduced by the HF treatment\textsuperscript{[187]}), high energy performances resembling supercapacitor ones could be achieved. Wang et al. shed light onto the surface and intercalation processes using DFT and scanning transmission electron microscopy (STEM) and they emphasized the topotactic localization of functional groups (e.g., OH\textsuperscript{−}, F\textsuperscript{−}, O\textsuperscript{2−}) and intercalated Na\textsuperscript{+} ions on the top site of the central Ti atoms and C atoms on the Ti\textsubscript{3}CT\textsubscript{x} monolayer.\textsuperscript{[188]}

To explore their unique properties, single/few-layer MXenes have been prepared by intercalation of water or organic molecules in aqueous medium followed by sonication.\textsuperscript{[189]} In particular, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}/CNT free standing composite electrodes were realized, thanks to the negatively charged nanosheets and the positively charged CNT, which partially prevented the restack of the MXene layers and revealed high volumetric capacity of 420 mAh cm\textsuperscript{-2} at 20 mA g\textsuperscript{-1} and good cycling stability.\textsuperscript{[190]} The importance of MXene electrode architecture in energy storage applications has been further confirmed by Zhao et al. The free standing electrode made of hollow MXene spheres with a 3D macroporous structure prepared via polymethacrylate spherical templates exhibited indeed improved performances compared to the multilayer MXene in terms of capacity and rate capability.\textsuperscript{[191]} Recently Wu et al. reported another delamination method for Ti\textsubscript{3}C\textsubscript{x}T\textsubscript{x} by organic solvent assisted high energy ball milling, which may prevent the partial spontaneous oxidation of the MXenes sheets in the aqueous medium. The as prepared few-layer nanosheets structure shows improved rate performance compared to the pristine MXene when tested as anode in sodium ion batteries. Thanks to their layered structure, hydrophilic terminal groups and excellent electrical conductivity hybrid nanomaterials with MXenes can be easily prepared and show improved reversible capacity in SIB. Sb\textsubscript{2}O\textsubscript{3}/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and MoS\textsubscript{2}/Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} composites have been reported.\textsuperscript{[192,193]} The former in particular inspires possible
further development of novel MXene materials, showing high rate performance and good reversibility as well (470 mAh g\(^{-1}\)) almost constant during 50 cycles at 50 mA g\(^{-1}\) compared to a capacity retention of only 43% in the case of the bare Sb\(_2\)O\(_3\)), suggesting that the MXenes can provide fast electron pathways and help buffering the volume variation during cycling.

3.2. Cathode Materials for SIBs

In this section, an overview of the electrochemical and physical principles lying beyond cathode materials so far synthesized and characterized will be provided. Going through the materials, layered transition metal oxides, whose study has recently regained enthusiasm, will be described at first place. Additionally most recently proposed advancements, such as polyanionic and Na superionic conductor (NASICON)-type compounds, will be discussed as they tried to enhance the cycle stability, environmental friendliness, reliability, and energy densities. Switching from lithium to sodium intrinsically bares with itself the drawback represented by a lower standard reduction potential of Na/Na\(^{+}\). RedOx couple, this is the reason why efforts have to be put in extending reversible capacity in order to reach comparable energy densities. It can be calculated that, in order to overcome the ≈0.5 V discrepancy between lithium and sodium based systems, a 12.5% specific capacity excess should be kept in mind in designing an innovative active material. As previously stated, studies of sodium intercalation in inorganic layered material started at the end of the 1980s, in conjunction with lithiation ones. They were both referred to cathode materials, TiS\(_2\)\(^{196}\) and P2-Na\(_2\)CoO\(_2\)\(^{197,198}\) for which sodium intercalation was confirmed and quantified, as well as anode sodium–lead alloys. Prototypes of full sodium-ion cells were also assembled demonstrating surprisingly high cyclability for more than 300 cycles at an operational potential slightly lower than 3.0 V. Precisely this latter feature, did not particularly draw the attention if compared to high voltage LiCoO\(_2\)/graphite systems. After the sodium renaissance started due to mounting efforts have been put in extending reversible capacity in order to achieve pure P2 phase coupled to an anomalous initial capacity of 107 mAh g\(^{-1}\) at 0.1 C, over a potential range spanning from 2.0 to 3.8 V.

P2-Na\(_2\)MnO\(_2\), despite the electrochemical activity comparable to those of cobalt analogue in the 0.45–0.85 composition range, showed low sodium diffusion and poor structural reversibility due to a strong Jahn–Teller effect of Mn\(^{3+}\).\(^{208}\) In recent investigations, the cations substitution revealed as an efficient method to enhance structural stability of Na\(_2\)MnO\(_2\), Ni/Mn, Fe/Mn, and Co/Mn substitutions have been considered and some research groups succeeded in suppressing the multiple phase transitions improving reversibility. For example, P2-Na\(_{0.75}\)CoO\(_2\) synthesized by solid-state route exhibits a reversible discharge capacity of 107 mAh g\(^{-1}\) at 0.1 C, over a potential range spanning from 2.0 to 3.8 V.

3.2.1. Layered Transition Metal Oxides (TMO)

P2-type TMOs: Na\(_2\)CoO\(_2\) and Na\(_2\)MnO\(_2\) stand as the most widely investigated P2-type layered material in sodium environment. Na\(_2\)CoO\(_2\) can be prepared relatively easily in almost every layered configuration according to synthetic temperature and sodium precursor content.\(^{194}\) P2 phase Na\(_2\)CoO\(_2\) has a well-defined stability window related to a sodium composition (x) falling in the range 0.46 < x < 0.83, while for higher content of Na (0.83 < x < 1.00) a conversion to O3-Na\(_2\)CoO\(_2\) occurs. All the above and other equilibrium phases can be appreciated in the phase diagram reported in Figure 4 (image (a)). P2-Na\(_2\)CoO\(_2\) phase potential profile shows a substantially different trend if compared to lithium analogue one. While in the latter case a single and stable plateau at moderately high potential (4.0 V) with low polarization is observed; the former compounds show a stepwise potential change, spread over a wider window of potential values. As a consequence, energy densities of connected full-cell will be considerably lower. In sodium analogue the potential profile originates from both single-phase, referred to solid solution like mechanism and two-phase processes. In the second case, a two-phase like behavior might manifest inside the same stability range of a P or O, namely the same phase, due to sodium sub-lattice pattern formation. Interestingly, together with phase transformation also a sensible variation in sodium diffusion is obtained. O3-Na\(_2\)CoO\(_2\) outperforms P2-Na\(_2\)CoO\(_2\) at high sodium content, while the trend is reversed for lower sodium concentration in the lattice due to fast Na diffusion in a honeycomb-like sub-lattice. In general, for Na\(_2\)CoO\(_2\), diffusion coefficients are higher by an order of magnitude\(^{207}\) (≈0.5–1.5 × 10\(^{-10}\) cm\(^2\) s\(^{-1}\) vs 1 × 10\(^{-11}\) cm\(^2\) s\(^{-1}\)) than Li\(_2\)CoO\(_2\), and this will result also true for other insertion materials. A plausible explanation to this effect might be related to the weaker nature of Na\(^{+}\) as a Lewis acid compared to Li\(^{+}\) that would allow a faster diffusion between layers. Speaking about electrochemical performances, P2-Na\(_{0.75}\)CoO\(_2\) synthesized by a solid-state route exhibits a reversible discharge capacity of 107 mAh g\(^{-1}\) at 0.1 C, over a potential range spanning from 2.0 to 3.8 V.

P2-Na\(_2\)MnO\(_2\), despite the electrochemical activity comparable to those of cobalt analogue in the 0.45–0.85 composition range, showed low sodium diffusion and poor structural reversibility due to a strong Jahn–Teller effect of Mn\(^{3+}\).\(^{208}\) In recent investigations, the cations substitution revealed as an efficient method to enhance structural stability of Na\(_2\)MnO\(_2\), Ni/Mn, Fe/Mn, and Co/Mn substitutions have been considered and some research groups succeeded in suppressing the multiple phase transitions improving reversibility. For example, P2-Na\(_{0.75}\)CoO\(_2\) synthesized by Lu and Dahn to provide 170.7 mAh g\(^{-1}\) by the reversible extraction of 0.67 of sodium. Further XRD analysis revealed how P2 phase is maintained until 0.33 stoichiometry is reached whereas a coexistence of P2 phase, O2-type stacking faults, and O2 phase is achieved below x = 0.33.\(^{209}\) 20 at% Mg cation substitution in Na\(_2\)Mn\(_{0.75}\)Mg\(_{0.25}\)O\(_2\)\(^{210}\) coupled to a slow cooling step during solid state synthesis, allowed Komaba and co-workers to achieve pure P2 phase coupled to an anomalous initial capacity of 200 mAh g\(^{-1}\), quickly fading toward lower values.\(^{211}\) Further doping of Na–Ni–Mn–O phases, disclosed as a valuable strategy in improving electrochemical performances, and in particular, in suppressing deleterious P2–O2 phase transition occurring at potentials above 4.1 V versus Na\(^+/Na\). In P2-Na\(_{0.83}\)Li\(_{0.07}\)Ni\(_{0.1}\)Mn\(_{0.6}\)O\(_2\)\(^{212}\) substitutional Li\(^+\) into TM sites is accountable for the residual persistence of sodium atoms in the structure even in deep charge conditions, thus stabilizing the layered stacking in the P2 configuration. P2-Na\(_{2/3}\)Ni\(_{1/3}\)Mn\(_{2/3}\)Ti\(_{5/3}\)O\(_4\), with an optimum composition of
Figure 4. a) Temperature/composition phase diagram of layered CoO₂ compound in which single phase stability zones and equilibrium lines of different structures are indicated. Reproduced with permission. Copyright 2014, American Chemical Society. b) Lattice parameters evolution of P2-Na₉₋ₓFeₓMn₀.₄Co₀.₂O₂ electrode from in situ synchrotron analysis, potential profile of capillary cell is also reported at the top of the image. Reproduced with permission. Copyright 2015, Wiley-VCH. c) Schematic illustration of the cell experimental set-up used in synchrotron analysis and in situ XRD patterns evolution for P2-Na₉₋ₓFeₓMn₀.₄Co₀.₂O₂. Reproduced with permission. Copyright 2015, Wiley-VCH. d) Material design of spherical particles with a radially aligned gradient composition and connected charge/discharge profile (left) and GCPL electrochemical characterization at different temperature (right) of the radially aligned particle and a control bulk sample. The core of the particles is mainly composed by Na[Ni₀.₇₅Co₀.₀₂Mn₀.₂₅]O₂ while outer shell gets progressively poorer in Ni concentration, transitioning to Na[Ni₀.₅₈Co₀.₀₆Mn₀.₃₆]O₂. Reproduced with permission. Copyright 2015, Macmillan Publishers Limited.
\( x = 1/3 \), has been investigated by Komaba and co-workers.\(^{[213]}\) It delivered a specific capacity higher than 100 mAh g\(^{-1}\) with a good capacity retention, thanks to the stabilizing effect of Ti atoms which sensibly reduces, by nearly 50\%, the crystalline cell volume shrinkage (23\% of undoped sample versus 12–13\% of the doped one). \( \text{Na}_{0.67}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{Mg}_{0.06}\text{O}_{2} \)\(^{[214]}\) with \( x = 0.05 \) represents, among the stoichiometries investigated (0 <\( x < 0.15 \)), a sensible tradeoff between good specific capacity (≈120 mAh g\(^{-1}\)) and improved capacity retention. The coexistence of P2 and O2 phase was confirmed, for the undoped sample, on the microscale by STEM analysis. This implies stacking faults formation which negatively influences stability and reversibility. Together with P2–O2 transition suppression, different levels of TM substitutions revealed to be effective in containing Mn leaching with cycling. Passerini and co-workers\(^{[215]}\) systematically studied the Ni-to-Fe ratio effect in \( \text{Na}_{0.67}\text{Mn}_{0.67}\text{O}_{2} \) (with \( M = \text{Ni}, \text{Fe}, \text{and Mn} \)) in suppressing Mn dissolution and improving material stability. Worth noticing is that the Ni-rich phase \( \text{Na}_{0.85}\text{Ni}_{0.22}\text{Fe}_{0.11}\text{Mn}_{0.66}\text{O}_{2} \) shows significantly improved electrochemical characteristics.

Apparently the only efficient way to increase reversibility excluding deleterious phase transitions is to narrow the operative potential window. An important contribution to the understanding of phase transition mechanisms was given by Jung et al.\(^{[66]}\) by in situ synchrotron X-ray diffraction of the compound P2-Na\(_{2/3}\left(\text{Fe}_{2/3}\text{Mn}_{1/3}\right)_{1/3}\text{Co}_{2/3}\text{O}_{2} \) \( (x = 0, 0.05, 0.10, \text{and} 0.20) \). Lattice parameters have been observed varying according to multiple effects occurring during charging and discharging (images (b) and (c) in Figure 4). During desodiation (charging), a general contraction on the \( ab \) plane (aligned TMO 2 slabs) is observed due to a decrease in transition metal atoms radii connected to oxidation. Along \( c \) direction, instead an expansion is observed due to a mounting electrostatic repulsion between oxygen atoms, left unsheilded by Na\(^{+} \) cations. Since no phase transitions are so far involved, at least below 4.1 V versus Na/Na\(^{+} \), the general behavior of the material is the one of a solid-solution, with a slight cell volume change (2.1\%) and a sloping operational potential. Above 4.1, a phase transition from P2 (P6\(_{3}/mmc \)) to a O2 (P6\(_{3}mc \)) structure occurs and it is underpinned by two-phase plateau region in potential profile and P2 phase XRD diffraction peaks progressively fading, as clearly visible in associated XRD pattern evolution in image (c) in Figure 4. The phase transition finds its explanation in the gliding of TMO 2 sheets, that modifies the sodium coordination sites; this structural modification induces a severe volume contraction of ≈15\%, accompanied by mechanical stresses that progressively lead to a capacity loss with cycling. Reduction in lattice cell volume has to be specifically connected to shrinking of sheets spacing along \( c \) axis due to deep desodiation, process already observed for P2-Na\(_{2/3}\left(\text{Fe}_{2/3}\text{Mn}_{1/3}\right)_{1/3}\text{Co}_{2/3}\text{O}_{2}.\)\(^{[216]}\)

Nevertheless, this mechanism shows an interesting reversibility even if accompanied with a conspicuous hysteresis due to dramatic cell parameters change. This aspect finds its explanation in the fact that no covalent bonds breaking or forming is involved during P2–O2 phase rearrangement, as would be the case of a P2–O3 transition. In this latter case, together with a lattice plane gliding, a 60° rotation of all the MO 6 octahedra would be involved with an inevitable braking of M–O bonds. Electrochemical performances account for a starting specific capacity of 170 mAh g\(^{-1}\), averagely equal for all the Co level of doping. Starting capacity moderately decreases during the first 60 cycles reaching 100 mAh g\(^{-1}\). It has recently thoroughly examined the coexistence of different crystalline phases in Na\(_{x}\)Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_{2}\) and their interplay mechanism in stabilizing the layered structure.\(^{[36]}\) Na\(_{x}\)Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_{2}\) with intergrowth P2/P3/O3 structures showed a better stability and a suppression of interfacial microstrain during high voltage charging. This eventually allowed to achieve a high initial reversible capacity of 142 mAh g\(^{-1}\) and an outstanding capacity retention of 93\% after 50 cycles.

O3-Type TMOs: As an excess of sodium precursor is employed during layered oxide preparation, O3 phase is more likely to be obtained over a wide range of synthesis temperatures. O3-TMOs \( (M = \text{Mn, Cr, Fe, and Ni}) \) are thus intrinsically provided with a higher starting content of sodium and could potentially deliver stable capacities suitable for commercial rechargeable cells. O3- NaCrO\(_{2}\) has been widely investigated and the most promising results line up on capacities between 113 and 120 mAh g\(^{-1}\), stable for 50 cycles\(^{[217]}\) or more, depending on the application of a carbon coating.\(^{[218]}\) The carbon coating in the latter and other cases has proven to be extremely beneficial, apart from increasing electrode rate capabilities, also in preventing the transition metal ions leaching from the structure during cycling, a drawback responsible for capacity fading. Komaba et al., working on O3-NaNiO\(_{2}\) pure and Mn-doped compounds, highlighted how as in P3-TMOs, likewise in O3-TMOs, the potential window amplitude has a crucial role in limiting deleterious phase transitions. By Mn doping of the structure can be obtained better performance in terms of rate capabilities and stability: stable specific capacities between 105 and 125 mAh g\(^{-1}\) cannot be obtained over a large range of current densities (240–4.8 mA g\(^{-1}\)) in the 2.2–3.8 V versus Na/Na\(^{+} \) window. Capacities drastically improve if the desodiation is pushed further up to 4.5 V, inevitably involving additional phase transition that for O3-NaNi\(_{x}\)O\(_{3}\) to amount to 4: O3→O3′→P3′→P3″.\(^{[35]}\) Despite these multiple steps involved, the material ensures a good reversibility, symptom of the high tolerance to phase transition of a layered structure in which covalent bonds are not involved in vertical ordering. The equilibria Ni\(^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}\) are responsible for the charge compensation inside the structure during desodiation while Mn ions behave as an electrochemically inactive species. A benefit of Ni-rich layered phases resides also in the great difference in the ionic radii of Na\(^{+} \) (1.02 Å) and Ni\(^{2+} \) (0.69 Å), which likely avoids ion exchange between Na\(^{+} \) and Ni\(^{2+} \) in the layers, extending stability and the high-capacity delivery. An outstanding contribution to this topic has been given by Hwang et al.\(^{[195]}\) which in 2015 proposed a O3 cathode constituted by spheres made of radially aligned columnar structures with a gradient composition transition from an inner part richer in Na\(_{x}\)Ni\(_{0.75}\)Co\(_{0.02}\)Mn\(_{0.23}\)O\(_{2}\) to an outer one where Na\(_{x}\)Ni\(_{0.56}\)Co\(_{0.05}\)Mn\(_{0.39}\)O\(_{2}\) was the major phase (image (d) in Figure 4). By scanning electron microscopy (SEM) probe analysis, the Ni concentration reduction, from 80 to 58\% by weight, has been verified to occur along all the 6 μm long columnar structures. In a sodium half-cell configuration, this material delivered reversible specific capacity of 157 mAh g\(^{-1}\) at 15 mA g\(^{-1}\), while in a whole-cell set up,
coupled with a hard-carbon anode, it demonstrated a high capacity retention of 80% after 300 cycle. The improved stability has been addressed to the higher resistance of a Ni poorer phase to electrolyte corrosion compared to a richer phase, which, by many others, has been demonstrated to be a more electrochemically active toward sodium intercalation. Among O3 phases, even Li-doped compounds such as Na$_{0.95}$Li$_{0.05}$Ni$_{0.55}$Mn$_{0.45}$O$_2$[219] Na$_{0.78}$Li$_{0.18}$Ni$_{0.25}$Mn$_{0.58}$O$_2$[220] as well as quaternary phases Na$_2$Mn$_{0.25}$Fe$_{0.25}$Co$_{0.25}$Ni$_{0.25}$O$_{2}$[221] have been recently prepared and suggested as high energy cathodes, delivering ≈200 mAh g$^{-1}$ and improved reversibility compared to NaNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$. Despite being highly promising for what concerns their electrochemical behavior, they heavily suffer stability issues connected to moisture and CO$_2$ sensitiveness. As synthesized O3- NaNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ indeed progressively converts into O1-phase to end up to P3 phase if aged in air for 300 d.[222] Intercalation of water, similarly, competes with Na insertion and progressively excludes the latter and reduces Na uptake capabilities below 0.33 per formula unit upon cycling as demonstrated for Na$_{0.78}$Ni$_{0.22}$Co$_{0.11}$Mn$_{0.66}$O$_2$. Also carbonated insertion, aided by water, has been discussed as a relevant factor that oxidizes Mn$^{3+}$ to Mn$^{4+}$ and decreases reversibility and increases overpotential. Further improvements are thus required to make them not sensitive toward air for their mass production, effort recently put in developing a water-proof cathode material O3-Na$_{0.5}$Li$_{0.5}$Co$_{0.4}$Mn$_{0.4}$O$_{2}$[223] cathode. This class of compounds derives its name from the tetrahedral XO$_4$ and trigonal XO$_3$ groups that partially replace MO$_6$ octahedral metal clusters. A considerable quantity of transition metal phosphates[225,226] fluorophosphates[39] sulfate,[38] and pyrophosphates[37,227,228] just to cite a few, offers the opportunity to exploit their peculiar 3D open-framework structure created by edge or corner sharing polyhedrons, to host alkaline ions. Instead of vertically aligned slabs of covalently bonded atoms, as in layered transition metal oxides, the structure of polyanionic compounds is permeated by straight or tangled channels with relatively low Na$^+$ diffusion energies. Due to the extensively higher rigidity of a covalent 3D network, polyanionic compounds show thermal stability and impressive resistance to oxidation without phase transitioning connected to sodium uptake.[37,229–232] Added to this an overall higher operational voltage has been observed for polyanionic compounds either for lithium and sodium batteries. Since the introduction of olivine LiFePO$_4$ compound by Goodenough and co-workers in 1997 as a high energy cathode for lithium batteries,[233] it appeared clear that large PO$_4^{3-}$ anion, thanks to its strong inductive effect and high electronegativity, has the power of sensibly increasing the operational potential. Nevertheless NaFePO$_4$, in its most thermodynamically stable maricite phase, does not show any activity due to the absence of a sufficiently wide pathway for sodium insertion. Interestingly, an electrochemically active triphylite-type phase obtained from alkaline cation exchange in olivine LiFePO$_4$ delivered 125 mAh g$^{-1}$ with capacity retention of 88% after 50 cycles.[234] Interestingly, NaFePO$_4$ charge/discharge mechanism occurs with different potential profiles. If during discharge two plateaus are observed, during charge only one is present, indicating that sodiation and desodiation might occur through different electrochemical routes. The keystone has been demonstrated to be the intermediate phase Na$_{0.7}$FePO$_4$ and the difference in volumetric mismatch between sodium-free phase FePO$_4$ and Na$_{0.4}$FePO$_4$ (13.48%) compared to Na$_{0.6}$FePO$_4$ and Na$_{0.7}$FePO$_4$ one (3.62%). This means that during charging, before FePO$_4$ starts to form, a complete conversion of NaFePO$_4$ to Na$_{0.7}$FePO$_4$ must occur. The two-step process is clearly visible in potential curve even at high current rates. During discharge, instead, due to the low energetic barrier between sodium-containing phases, once the lattice mismatch between FePO$_4$ and Na$_{0.7}$FePO$_4$ is overcome, sodiation of FePO$_4$ and Na$_{0.7}$FePO$_4$ can happen concurrently and a one-step curve is achieved.[235]

An interesting and handy way to induce sensible lattice modification and create new sodium pathways in a phosphate structure is to insert another anion as a charge-balancing species. It has been done including fluorine atom in the new fluoro- phosphates class of material, recently investigated as cathode for both lithium and sodium-ion batteries. Na$_2$FePO$_4$F[236] and its isostructural Na$_2$CoPO$_4$F[237] have been recently proposed thanks to their interesting electrochemical properties as layered insertion materials in which intercalation mechanism proceeds with a solid-solution RedOx process rather than with a two-phase mechanism. The positive effect induced by F$^-$ ion emerges from its pronounced electronegativity, which further enhances the inductive effect and thus the potential. Added to this, the higher ionicity of Na$-$F bond substantially modifies the coordination geometry of sodium as pseudoocathedral. The exclusive layered structure of fluorine-enriched phosphates results in the uncommon coordination of transition metal ion (Fe, Co, or Mn) which for Na$_2$FePO$_4$F consists in octahedrons whose vertex positions are occupied by four O and two F atoms. The octahedrons are then arranged in face-sharing pairs (Fe$_2$O$_6$F$_3$). These units are corner-sharing connected (via fluorine atoms) to other pairs, forming chains along $c$ direction. Corner-sharing PO$_4^{3-}$ tetrahedra complete the stacking along $c$ direction. Further improvements were achieved by carbon-coating Na$_2$CoPO$_4$F[238] Carbon coating inorganic particles is a procedure that, carried out by pyrolysis of a previously adsorbed organic molecule onto electrochemically active material surface, improves its electronic conduction and then the kinetic properties. In the latter case, Na$_2$CoPO$_4$F/C nanoparticles showed interesting properties for what concerns specific capacity of the first cycle, around 120 mAh g$^{-1}$, and a flat plateau at high potential, namely 4.5 V versus Na$_x$Na$^+$, although further effort should be put in extending its electrochemical stability. Among fluorosulfates, NaFeSO$_4$F had been found, thanks to theoretical calculation, to be potentially active toward sodium intercalation thanks to Fe$^{2+}$/Fe$^{3+}$ couple.[239] Experimental data, however, are...
lacking and no limitations to material synthesis have to be overcome yet.

Silicates: Transition metals orthosilicates, Na2MSiO4 (M = Fe, Mn, Co), have attracted a lot of attention due to their superior environmental sustainability and the possibility of exchanging more than one sodium atom per unit formula. This aspect significantly extends their theoretical capacity to value higher than 250 mAh g\(^{-1}\). Clear electrochemical performances have recently reported for Na2CoSiO4.\(^{240}\) Corner-sharing SiO\(_4\) and CO\(_4\) tetrahedra constitute the backbone of the crystalline structure, while sodium ions occupy the tetrahedral empty spaces created consequently. Specific capacity is however limited to 100 mAh g\(^{-1}\), with an average practical voltage of 3.3 V versus Na/Na\(^+\). Better results were obtained for Na2FeSiO4/C almost phase-pure composite.\(^{241}\) Thanks to Na-rich phase, 181 mAh g\(^{-1}\) could be reversibly extracted from the structure, at a current density of 27.6 mA g\(^{-1}\). Capacity retention was however limited to 80% after 100 cycles, symptom of a progressive degeneration of the structure. Energy density of such compound is not supposed to be exceptionally high, owing the relatively low operational voltage plateau of 2.3 V versus Na/Na\(^+\). Notably, silicates demonstrate an outstanding thermal stability up to several hundreds degrees celsius (>800 °C for Na2FeSiO4). Finally, Na2MnSiO4/C/graphene has been recently synthesized, via a facile assisted sol–gel method, by Zhu et al.\(^{242}\) Due to the electronic insulation nature of silicates, heavy addition of carbon matrices is required. Despite the effective graphene wrapping of Na2MnSiO4/C particles, the interesting initial capacity of 182.4 mAh g\(^{-1}\) is hardly retained during the following tens of cycles. Sodium silicates are extremely interesting compounds, but their sluggish stability still requires research efforts.

NASICON Materials: NASICON (Na\(^+\) superionic conductor)-type materials have been largely studied as solid electrolytes in recent years. The most representative compound of the class, Na3V2(PO4)3, acquires a structure, while sodium ions occupy the tetrahedral empty spaces created consequently. Specific capacity is however limited to 100 mAh g\(^{-1}\), with an average practical voltage of 3.3 V versus Na/Na\(^+\). Despite the effectiveness employed to extend NASICON performances by means of electrospun carbon fiber embedding Na3V4(PO4)3 nanoparticles. The extremely simple preparation was made of two steps: (i) electrospinning of an aqueous formulation containing both the carbon fiber precursor and NASICON precursors (NaH2PO4 and NH4VO3), and (ii) an annealing step in Ar atmosphere.\(^{226}\) The outcome has been a homogeneous dispersion of nanometric particles confined in the central axis of structurally stable carbon fibers. Outstanding cycling performances at relatively high currents (2C), guaranteed more than 70 mAh g\(^{-1}\), provided at a stable potential of 3.4 V versus Na/Na\(^+\). As for general phosphate compounds, also NASICON-type materials can be subjected to fluorination with some beneficial effects. An example is NASICON analogue Na3V4(PO4)3F\(_3\), interesting for its high average voltage of 3.9 V and single-phase behavior with modest volume change (2%). Other examples include Na2FePO4F and Na1.5VPO4.8F0.7.\(^{62}\) The latter revealed excellent cycling performances, with capacities retention of 95% and 84% after 100 and 500 cycles, respectively, at 1 C. Such a promising feature has been recognized to be related to small volume change, fast Na diffusion (\(E_a = 0.35\) eV) in \(ab\) plane and lack of ordered compositions within the RedOx window.\(^{244}\) Other NASICON-type materials include Na1.5Ti2(PO4)3. Unlike previously cited NASICON materials, and however similarly to Ti based compounds, Na1.5Ti2(PO4)3 has been proposed as an high performing anode for SIBs, due to its low operational voltage plateau (<1.0 V vs Na/Na\(^+\)). The clear Faradaic process occurring at such low potential is attributed to Ti\(^{4+}/Ti^{3+}\) RedOx couple, made available by the strong inductive effect of PO\(_4\).\(^{245}\) Recently, transition metal pyrophosphate arose as promising material proposed by Barpanda et al. Na3FeP2O7 was the first of its kind, exhibiting a modest reversible capacity of 82 mAh g\(^{-1}\) at C/20 in the potential window between 2.0 and 4.0 V versus Na/Na\(^+\). In Na2FePO4F lattice Fe\(^{3+}\) ions reside in two different sites and subsequently undergo oxidation to Fe\(^{4+}\) upon charge.\(^{229}\) Particularly, Na2FePO4F supports quasi-3D sodium diffusion network with activation energy that slightly varies according to sites accessibility and transition metal substitution. Energy barriers are indeed lower for Na4Fe2P2O7 (<0.49 eV) and higher for Na4MnP2O7 (0.58 eV).\(^{246}\) Other polymorphs and analogues have been prepared, including \(\beta\)-Na4MnP2O7\(^{247}\) and \(\alpha\)-Na4CoP2O7\(^{240}\) but they all showed similar modest capacities (<80 mAh g\(^{-1}\)), poor cyclability, stability, and rate capabilities. The unique structure of pyrophosphate, despite some of them show a layered structure,\(^{210}\) arises from large tunnels formed by alternate stacking of layers of FeO\(_6\) octahedra and layers containing P2O\(_7\) units. Interestingly, together with a promising thermal stability up to 600 °C, they show also a polymorphic transition happening at 560 °C with no oxygen evolution nor structural rupture, but with a phase change from a triclinic (P-1) to a monoclinic (P2\(_1\)/c) spatial group.\(^{212}\) This stability by far exceeds that of layered oxides and is comparable to other polyanionic compounds. Intrinsically stability of pyrophosphate building block is responsible for its inertness and represents an added value to safety. More exotic polyanion compounds are those based on nitridophosphate group such as Na3TiP3O9N\(^{248}\) Na3TiP3O9N was the first member of cubic ionic conductor (CUBICON) family of materials that showed reversible Na\(^+\) insertion at room temperature. Despite the sodium diffusivity inside CUBICON...
framework is considerably lower if compared to lithium analogues, the ionic conductivity is good, as well as thermal stability. Inside CUBICON structure different sites and sodium paths are possible, and substitution of Ti with other aliovalent transition metals with more than one RedOx pair achievable might extend the practical capacities, limited for Na$_2$TiP$_2$O$_7$N to 80 mAh g$^{-1}$. As previously reported, P2-Na$_2$[Fe$_{0.5}$Mn$_{0.5}$]O$_2$[249] and O3-NaFeO$_2$[250] layered transition metal oxides suffer from low operating voltage, usually around 3.0 V. Yamada and co-workers recently reported an alluduate-type structure cathode compound based on (SO$_4$)$_2$$^{-}$ anion, Na$_2$Fe$_x$(SO$_4$)$_3$.[253] The stable 3D structure made of Fe$_2$O$_{10}$ dimers interconnected via (SO$_4$)$_2$$^{-}$ groups ensures relatively fast sodium diffusion happening at potential of 3.8 V versus Na/Na$^+$. Extraordinarily high for Fe$^{3+}$/Fe$^{2+}$ RedOx couple. Theoretic calculation suggested that a partial Co doping of the above mentioned compound could further raise the operational potential to 4.76 V, when a partial desodiation would occur. Full desodiation would have been predicted to happen at 5.76 V. Experimental details are still lacking due to the difficulties in finding electrolyte solutions stable enough at such high potential values.[38]

4. Sodium-Ion Full-Cell

In the light of what previously introduced, we propose in the following chapters, a comprehensive depiction of the most representative sodium-ion full-cell architectures. The reader will be guided through the most recent advancements in the field. They have been here organized according to the overall symmetric or nonsymmetric assembly first, and subsequently, according to the material classes meaningful for the SIB full-cell architecture.

4.1. Nonsymmetric Full Battery

4.1.1. Graphite-Based SIB Full-Cells

The most widely studied anodes for SIBs are carbon-based materials. This is directly related to electrochemical peculiarities of carbonaceous matrix, as previously stated, in terms of operational intercalation and pseudocapacitance potentials. Added to this, natural abundance, low preparation cost and environmental friendliness add value to this class of materials. Despite solvent co-intercalation mechanism is not fully understood, yet it acquires a foremost importance since it is associated with a complete recovery of the intercalated solvent molecules during discharge, as proven by the stability tests conducted on the full-cell. The practical validity of the graphite in SIBs full cells was examined by combing the graphite anode with different cathode materials. A Na$_{1.5}$VPO$_4$.8F$_{0.7}$/graphite full cell[253] with the NaPF$_6$ in diethylene glycol dimethylether electrolyte is reported and exhibits an average discharge voltage of 2.9 V versus Na$/$/Na. The energy density obtained from this system was about 120 Wh kg$^{-1}$, based on the total electroactive materials, with a retention of the 70% of the initial discharge capacity after 250 cycles. By using laser drilling technique, Han et al.[253] explored a novel porous graphite film for an integrated SIBs anode. When it is assembled with Na$_2$V$_2$(PO$_4$)$_3$ cathode, the full-cell showed an energy density of 130.7 Wh kg$^{-1}$ with a capacity retention as high as 92% after 500 cycles. The possibility of practical use of graphite in SIBs has also been evidenced by Chen and co-workers,[253] by constructing a carbon coated Na$_2$V$_2$(PO$_4$)$_3$ cathode paired full cell with operational voltage above 2.2 V and capacity retention over 80% for 400 cycles. Solvent molecules co-intercalation mechanism leading to a stage-1 GIC formation is considered the key step guaranteeing fast intercalation kinetics and reversibility. Scrosati and co-workers[254] reported a novel high power SIB based on layered P2-Na$_2$S$_x$CoO$_2$ cathode and the graphite anode in an optimized ether-based electrolyte. In this work significant is the graphite electrochemical presodiation process performed in a sodium half-cell, in order to precondition graphite and reduce the irreversible contribution deriving from activation of both anode and cathode material in the full-cell. Following a sodium rocking chair process, this system delivers an overall stable capacity of 80 mAh g$^{-1}$ over more than 100 cycles, maintaining, at 10 C (i.e., 1750 mA g$^{-1}$), 45% of its maximum capacity. The low specific capacity of the graphite is still an issue even though the cycling stability and rate capability of the graphite have been significantly improved over the years.[255]

4.1.2. Hard Carbon-Based SIBs Full-Cells

Exploring alternative anode materials for SIBs, more attention is payed to hard-carbon, which has a highly distorted structure and large interlayer distance.[83] Intercalation mechanism, as we know it at the basis of the mass-market lithium rechargeable batteries, is not the only process contributing to sodium energy storage. Sodium was found to be able to favorably interact with noncrystalline or partially crystalline carbonaceous materials. As previously stated, disordered layers of hard-carbon are accompanied by large specific surface areas. Sodium storage in such structures takes place via different mechanism. They are: (i) direct intercalation in expanded-graphite domains,[96,256] at potential above 1 V versus Na$^+$/Na, the (ii) adsorption on the surface and in correspondence of defects (i.e., surface defects as well as carbon flakes edges), and the (iii) mesopores filling by solvated Na atoms, forming a capacitive double layer, occurring at potentials below 1 V. This last process has been demonstrated to eventually lead to a mild volume expansion.[159] With all these mechanisms concuring in increasing material specific capacity, it becomes important the tracking of possible source of irreversible capacity as well as potential profile evolution with cycling. Despite the numerous studies directed to the disclosure of mechanism of sodium storage in hard-carbons, great discrepancies between results appear. Tarascon and co-workers[256] synthesized carbon nanofibers (CNFs) via electroporus polyacrylonitrile (PAN) fibers carbonization and showed that their electrochemical performances toward Na$^+$ intercalation strongly depend on their structural and morphological characteristics induced by different carbonization temperature (Figure 5, image (a)). Low temperature (stage I) made CNFs contain copious amounts of O and N heteroatoms, a highly disordered structure and high amounts of ultramicropores and surface defects. Carbonization
at $T > 1000 \, ^\circ \text{C}$ (stage II) gradually removes the heteroatoms and increases crystallinity as well as a mesoporous volume. For temperature higher than 2000 $^\circ \text{C}$ (stage III), a massive removal of the pores takes place together with a further ordering of carbon crystalline planes (pairing of graphene sheets and progressive reduction of $d$-spacing). Komaba et al.[97,82] first reported a high capacity and excellent reversibility sodium ion full battery based on a hard-carbon anode and a layered NaNi$_{0.5}$Mn$_{0.5}$O$_2$ cathode (Figure 5, image (b)) in propylene carbonate electrolyte solutions containing different sodium salts in concentration 1 mol dm$^{-3}$: NaClO$_4$, NaPF$_6$, and NaN(SO$_2$CF$_3$)$_2$ (sodium bis(trifluoromethanesulfonyl)amide, NaTFSA). The NaNi$_{0.5}$Mn$_{0.5}$O$_2$/ hard-carbon with 1 mol dm$^{-3}$ NaTFSA propylene carbonate electrolyte exhibited a capacity higher than 200 mAh g$^{-1}$, based on anode mass, and an average operating voltage of 2.8 V. Furthermore, no significant decrease in capacity was observed when the full-cell was tested at the high rate of 300 mA g$^{-1}$. Carbonate-based electrolytes coupled with hard-carbon anodes introduce low first-cycle Coulombic efficiency (FCCE). In recent times, a lot of efforts have been directed to the synthesis of high SSA hard-carbons nanostructures (>400 m$^2$ g$^{-1}$)[104] as the external high surface area demonstrated to positively affect stored capacity, being directly connected to double-layer storage, kinetics properties of the materials, and electrode electronic connectivity. Nevertheless, a large surface area underpins also a prominent SEI formation which massively irreversible segregates sodium atoms. This effect ultimately will decrease the total reversible capacity of the full-cell as the sodium atoms stored in SEI layer will systematically derive from the cathode material.[94,95] Luo et al.[258] employed GO as a 2D dehydration agent to prevent foaming process during caramelization of sucrose used for hard-carbon synthesis. The specific surface area of the resulting carbons reduces from 137.2 to 5.4 m$^2$ g$^{-1}$, and the FCCE result...
improved from 74% to 83%. By pretreating cellulose fiber with 2,2,6,6-tetramethylpiperidine-1-oxyl, before thermal carbonization, Hu and co-workers\textsuperscript{[259]} were able to reduce the as-synthesized hard-carbon surface area from 586 to 126 m² g⁻¹ with even in that case a net curtailing on the irreversible capacity related to the very first cycle. Electrochemical\textsuperscript{[260]} as well as chemical\textsuperscript{[261]} presodiation processes, i.e., sodium enrichment of anode material before full-cell assembling, confirmed to be another effective way to enhance the hard-carbon FCCE, as reported by Ai and co-workers\textsuperscript{[260]} The authors fabricated a full-cell with a layered NaNiTiO₂ cathode and a presodiated hard-carbon anode, via a facile approach in a three-electrode battery. The FCCE of this cell, with respect to a control cell, was enhanced from 64.7% to 73%, with a specific capacity of 93 mAh g⁻¹. Passerini and co-workers\textsuperscript{[257]} recently assembled an optimized Na full battery by combining starch-derived hard-carbon anode with a mixed layered oxide cathode, having the overall composition P₂/2P₃/2O₂Na₇₆Mn₁₀Sn₇Ni₁₂F₉₀₂,Mg₈O₃. The full Na-ion cell exhibited a high operating discharge voltages of 3.3 V, high energy density of 240 Wh kg⁻¹ normalized on both cathode and anode materials, and a capacity retention extended to 200 cycles. In this particular case, carbon anode electrochemical activation, by means of a sodium metal sacrificial electrode, was investigated as well. Notably, the Coulombic efficiencies were found to be close to 100% after the first few cycles. Huang and co-workers,\textsuperscript{[262]} finally, investigated how a composite system made of monodispersed hard-carbon spherules coated with soft-carbon layer can lead to a sensible improvement in first cycle Coulombic efficiency from 54% to 83%. Correct mass balancing of carbon anode and cathode recently arose as one of the trickiest point in sodium full-cell preparation. The main reason is that carbon is fully desodiated while the cathode is often far from being fully sodiated, as Tarascon and co-workers wisely pointed out.\textsuperscript{[263]} A sodium reservoir, namely a cathode material enriched in sodium, would be thus required to overcome this limitation.\textsuperscript{[264]}

4.1.3. Transition Metal Oxides-Based SIBs Full-Cells

Ti and V-Containing Oxides: That of transition metal oxide represents a wide material class worth of interest as anode for SIBs due to their high theoretical specific capacity and sodium insertion reversibility. This class includes conversion species, insertion/intercalation compounds, and pseudocapacitive materials. The former, in particular, is thermodynamically appealing among other transition metal halides and chlorogenides, thanks to the surpassingly advantageous operational potential in sodium environment if compared to lithium.\textsuperscript{[260]}

Among metal oxides, Ti-based electrodes are widely recognized as potential anode materials for SIBs thanks to the low cost, low toxicity, negligible strain, and excellent structural stability during the insertion/extraction of sodium ions. Huang and co-workers\textsuperscript{[260]} demonstrated that the spinel Li₂TiO₃·₂ is a widely investigated “zero-strain” anode for LIBs,\textsuperscript{[260]} is able to withstand sodium insertion, exhibiting an average voltage of 0.91 V with distinguished cycling stability. The same group introduced another layered material, P₂Na₆[Li₂0.22Ti₀.78]O₃,\textsuperscript{[270]} as the negative electrode, which shows a negligible volume change, attested around 0.77%, during sodium insertion/extraction. Both compounds have been tested as anodes in a full-cell configuration, while Na₃V₂(PO₄)₃ was used as cathode. The Na₃V₂(PO₄)₃//Li₂TiO₃·₂ and Na₃V₂(PO₄)₃//Na₀.66[Li₀.22Ti₀.78]O₃ full cells give rise to a 2.4 V plateau at moderate rate and good cyclic performance. Na₂Ti₆O₁₃ has been reported to be another promising anode material with a plateau around 0.8 V. However, the specific capacity of the Na₂Ti₆O₁₃-based full-cell was proved by Balaya and co-workers\textsuperscript{[271]} to be very low, thus seriously limiting its further development. Since the high theoretical capacity of 310 mAh g⁻¹ and the reversible insertion of two sodium ions in Na₂Ti₆O₁₃ were demonstrated to occur at a voltage as low as 0.3 V versus Na⁺/Na, there are several attempts to use this material as anode for the sodium ion full batteries. Li\textsuperscript{[265]} reported a Na₂Ti₅O₁₂ anode with high electrochemical Na-storage activity by growing a surface engineered Na₂Ti₅O₁₇ nanotubes arrays directly on a Ti substrates, as shown in Figure 6, image (a). The assembled Na₂Ti₅O₁₂//Na/Na₁/₃[Ni₁/₃Mn₂/₃]O₂ full cell is capable to work at an average voltage of 2.7 V, delivering a reversible capacity of 210 mAh g⁻¹, and thus a high specific energy of 110 Wh kg⁻¹ (based on the mass of both electrodes). Moreover, the layered Na₂Ti₅O₁₇ nanotubes and VOPO₄ nanosheets have been systematically investigated as anode and cathode materials, respectively, to build high performance sodium ion full-cells by Yu and co-workers,\textsuperscript{[267]} as shown in image (c) in Figure 6. A stable reversible capacity of 76 mAh g⁻¹ at 0.1 C is obtained by normalizing the capacity value over the mass of both anode and cathode materials, with a maximum energy density of 220 Wh kg⁻¹.

As a versatile and cost-effective material, used in numerous important technological areas, TiO₂ has also been investigated in sodium ion full batteries. Xiong et al.\textsuperscript{[272]} proposed an all-oxide sodium-ion full battery with amorphous TiO₂ nanotubes anode coupled with Na₃Li[Ni₀.25Mn₀.75]O₂ cathode. Amorphous TiO₂ high specific surface nanostructures are here investigated as a low cost anode material providing a sodium storage which is predominantly capacitive or pseudocapacitive.\textsuperscript{[273]} The reported battery showed an operation voltage of 1.8 V and good rate capabilities with 70% of the original capacity retained at 11 C. Moreover, Yang and co-workers built a double-wall Sb@TiO₂-x structure\textsuperscript{[274]} by the calcination of Sb₂S₃@TiO₂ nanorods, in a Ar/H₂ atmosphere, produced by the hydrolysis of tetrabutyl titanate on Sb₂S₃ nanorods. The schematic representation of the synthetic procedure is shown in image (b) in Figure 6. In this compound the excellent electrochemical stability of TiO₂-x is combined with the high theoretical capacity of Sb as an alloying material. Such structure accommodates the volume variation upon cycling and then keeps the structure stable. In Sb@TiO₂-x//Na₃V₂(PO₄)₃-C full battery set up, the energy density turned out to be 151 Wh kg⁻¹ with a delivered overall power of 21 W kg⁻¹. The possibility of using V₂O₅ as host structure for Na⁺ was initially explored in the 1980s and continues to raise interest.\textsuperscript{[275]} The amorphous V₂O₅ aerogel as anode material for sodium ion full batteries was explored by Passerini and co-workers\textsuperscript{[276]} When evaluated as Na₃V₂(PO₄)₃//V₂O₅, the full-cell displays the capacities of 113 and 60 mAh g⁻¹ based on the anode and cathode materials, respectively. The cell capacity retention after 150 cycles was about 52% with respect to the maximum value obtained in the 28th cycle. Although
oxide-based anode materials have been extensively investigated in sodium half-cell with good chemical performance, their performances in full-cell still remain insufficient and unsatisfactory.

**Iron Based Conversion Oxides:** Metal oxides undergoing conversion reaction in presence of sodium have been thoroughly explored in full-cell set-ups. Despite their appealing theoretical capacity connected to the many-electrons conversion reaction $(\text{M}_x\text{O}_y + 2y\text{Na}^+ + 2y\text{e}^- \leftrightarrow x\text{M} + y\text{Na}_2\text{O}, \text{M} = \text{transition metal})$, they suffer from poor cycle ability due to difficulties in withstanding volume expansion and SEI disruption. Molybdenum oxide ($\text{MoO}_3$) has attracted great interest as anode material, due to a superior theoretical specific capacity of nearly 1111 mAh g$^{-1}$, which is about three times of that for graphite.$^{[277]}$ The reversible sodium storage in orthorhombic $\alpha$-MoO$_3$ via conversion mechanism was confirmed for the first time by Balaya and co-workers.$^{[278]}$ Despite the poor Coulombic efficiency of 53%$^{[279]}$ associated to the first cycle, the performance of a half-cell set up at 240 mAh g$^{-1}$ at 0.1 C, manifesting a capacity retention of 55% of the initial capacity after 500 cycles at 0.2 C. A MoO$_3$/Na$_3$V$_2$(PO$_4$)$_3$ full-cell$^{[278]}$ operating at 1.4 V in nonaqueous environment was further assembled, and an initial discharge capacity of 164 mAh g$^{-1}$, based on anode mass, achieved.

![Figure 6.](image_url)
low-cost nanostructured Fe$_3$O$_4$, synthesized in round-shaped nanoparticles\cite{280} with an average size of less than 10 nm, has been proposed as an attractive candidate as negative electrode material for SIBs, delivering 130 mAh g$^{-1}$\cite{283}. Nevertheless, Fe$_3$O$_4$-based anodes are affected by poor overall stability\cite{282} and among the conversion materials so far investigated are the less performing if not properly engineered. Full battery made of Na$_3$V$_2$(PO$_4$)$_3$/graphene cathode and precycled (i.e., presodiated) Fe$_3$O$_4$ anode, indeed, quickly loses one third of its original capacity (92 mAh g$^{-1}$) in the first 20 cycles. The precycling step, performed against a Na metal electrode, has been demonstrated to positively affect further cycling in full-cell system by overcoming the large irreversible capacity of Fe$_3$O$_4$. Mechanistic principles lying beyond this effect are however obscure still today and require more studies. The full-cell delivers an initial discharge capacity of 92 mAh g$^{-1}$, calculated in respect to the cathode mass, at 0.2 C. Hydrothermally prepared carbon-coated Fe$_3$O$_4$ particles\cite{283} have demonstrated to have better retain capacity, thanks to the conversion reaction occurring only partially (22% of the total mass of the material). The sodium full-cell prepared assembling C-Fe$_3$O$_4$ anode and O$_3$-type layered Na[Ni$_{0.25}$Fe$_{0.75}$Mn$_{0.25}$O$_2$] as cathode material operates reversibly around 2.4 V, delivering a capacity of about 130 mAh g$^{-1}$ (based on cathode mass), and offers a good capacity retention for extensive cycling: 82.8% at 100th cycle and 76.1% at 150th cycle with a Coulombic efficiency approaching 100%. NaClO$_4$ salt in a mixture of ethyl methanesulfonate electrolyte and 2 vol% FEC additive moreover increased the stability and conductivity of the system. Recently, bearing in mind that conversion processes are accompanied by chemical bond breaking and radical structural rearrangement, Ye et al. prepared ultrasmall, poorly crystalline Fe$_3$O$_4$ nanoparticles supported on carbon nanotubes, to reduce the activation barriers toward the conversion reaction. When combined with Prussian blue cathode materials, it leads to iron-based full batteries with a working voltage of about 2 V and energy density of around 136 Wh k$^{-1}$ g and outstanding cycle life.

4.1.4. Alloy-Based SIBs Full-Cells

A major limitation to sodium–metal alloys implementation resides in the tremendous molar volume increase achieved as higher sodium contents that are reached inside the alloys.\cite{63} This aspect, together with the technological challenge represented by pairing up materials, in a full-cell assembly, with considerably different theoretical specific capacities, contributed in discouraging the investigation of alloy-based sodium full-cells. A successful attempt in doing so has been conducted by Chen and co-workers.\cite{153} They successfully obtained tin nanodots (average size between 1 and 2 nm) simultaneously achieving a homogeneous dispersion on an electrospun N-doped porous carbon matrix (PNC). The absolute strain generated during sodiation/desodiation resulted mitigated, and fracture and decrination of electrode active materials delayed. The as-prepared Sn NDs@PNC free-standing anode has been conveniently paired with NaVPO$_4$F/C cathode, with the full-cell exhibiting an initial capacity of 540 mAh g$^{-1}$, based on the mass of the anode material. After 100 cycles, the reversible residual capacity was 460 mAh g$^{-1}$, proving a good capacity retention (85.2%) with Columbic efficiency hovering around 99%. Xie et al.\cite{284} developed a facile soaking-chemical vapour deposition method to grow core–sheath structured Sn@CNT nanopillars on carbon paper, with a unique 3D hierarchical architecture as free-standing electrodes. Coupled with Na$_9$Co$_{2}$Li$_{2}$Mn$_{13}$O$_{22}$ cathode, the Na-ion full cell was assembled, providing sufficient energy to power a light-emitting diode (LED) light. Moreover, after the homogeneous embedding of Sb and Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles in an interconnected framework of rGO nanosheets, which acts as a structurally stable and electronically conductive housing, Zhang et al.\cite{158} tested the Na$_3$V$_2$(PO$_4$)$_3$/rGO//Sb/rGO full-cell set up. This configuration delivered highly reversible capacity of 400 mAh g$^{-1}$ at a current of 100 mA g$^{-1}$ after 100 charge/discharge cycles. Similarly, Hassoun and co-workers\cite{285} assembled a rechargeable sodium-ion full-cell based on nanostructured Sb–C anode and P2-layered Na$_{0.6}$Ni$_{0.22}$Fe$_{0.11}$Mn$_{0.66}$O$_2$ cathode. The full-cell showed an average working voltage of about 2.7 V and delivered a reversible capacity around 120 mAh g$^{-1}$.

Construction of a hybrid–alloy phase is also a valid method to improve the structural stability of the anode material, since two different metal phases can operate as mutual buffers with each other to reduce the volume changes.\cite{129,170,286–288} Walter et al.\cite{289} reported a simple and inexpensive colloidal synthesis of SnSb NCs notably without involving surfactants molecules, and demonstrated their utility as lithium-ion and sodium-ion anode materials. Full-cells were constructed as well, with Na$_3$VPO$_4$F as cathodes, achieving anodic capacity of 400 mAh g$^{-1}$ with an average discharge voltage of 2.7 V for sodium-ion cell. Interestingly, the cycle life and energy density of the alloy-based sodium-ion full batteries exhibit competitiveness in regard to carbon-based full-cells. However, it is a major challenge to develop the alloy-based sodium ion full cells with promoted operating voltage and extended cycle-life in a cheap way.\cite{255}

4.1.5. Other Nonsymmetric Assemblies

Metal sulfides (Sb$_2$S$_3$\cite{280}, SnS$_2$\cite{291,292}, FeS$_2$\cite{293}, WS$_2$\cite{294}, MoS$_2$\cite{295}, Bi$_2$S$_3$\cite{55}, CoS\cite{296}) have been recently drawing attention among the scientific community as anode material for lithium and sodium energy storage. Potentially, in some of the cases cited above like Sb$_2$S$_3$, SnS$_2$, and SnO$_2$\cite{57} to the conversion reaction previously described, also the alloying in the reduced metal contributes in further extending available theoretical capacity. For such materials have been thus proposed the following tandem mechanisms.\cite{290}

Conversion reaction: Sb$_2$S$_3$ + 6 Na$^+$ + 6 e$^-$ → 2 Sb + 3 Na$_2$S \[ (5) \]

Alloying reaction: 2 Sb + 6 Na$^+$ + 6 e$^-$ → 2 Na$_3$S \[ (6) \]

Theoretical capacity involved in the 12 electrons charge transfer would be in this way increased to 946 mAh g$^{-1}$. Yu et al.\cite{290} reported a uniform coating of antimony sulphide (stibnite) on graphene. The composite preparation was entirely conducted in aqueous environment, starting from graphene oxide stable suspension and Sb hydroxide as antimony sulfide
precursor. $\text{Na}_2\text{Ni}_1/3\text{Mn}_{2/3}\text{O}_2$ was employed as cathode material to form a SIB full-cell. The latter demonstrates an energy density of 80 Wh kg$^{-1}$ and shows good cycle performance. Similarly to oxide-based anode materials, sulfides usually suffer from severe volume expansion during sodiation and sluggish kinetics for related Na$^+$ diffusion. SnS$_2$ possesses a CdI$_2$-like crystalline layered structure (lattice parameters: $a = 0.3648$ nm, $c = 0.5899$ nm, space group P3m1) consisting of alternating layers of tin atoms sandwiched between two layers of hexagonally closed-packed sulfur atoms. A SnS$_2$-rGO hybrid structure was designed for reversible storage of Na$^+$ by Qu et al.$^{[297]}$ The electrons can be fast collected and conducted through the highly conductive rGO network. The SnS$_2$-rGO anode was paired up with P2-Na$_{0.8}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2$ cathode, which holds a theoretical capacity of 118 mAh g$^{-1}$. The full-cell displayed relatively good stability, with a capacity retention of 74% after 50 cycles. Recently, Peng et al.$^{[298]}$ employed a simple solvothermal method for in situ decoration of rGO nanosheets with 2D CoS nanoplatelets. Based on CoS@rGO hybrid anode and electrospun Na$_2\text{V}_2\text{O}_5\text{(PO}_4)_2@$carbon cathode, a full cell has been additionally assembled and its electrochemical characterization manifested high capacity and promising cycle stability, displaying an initial charge and discharge capacities of 498 and 381 mAh g$^{-1}$ respectively (based on the mass of anode) with 75% capacity retention after 100 cycles.

4.1.6. Aqueous Nonsymmetric Sodium Full Battery

Some full-cell configurations have shown exceptional performance with aqueous electrolytes instead of nonaqueous aprotic organic electrolytes. Sodium-ion battery with aqueous electrolyte has the advantage in perspective of lower cost, faster ion transportation, and nonflammability, and therefore it has received much attention for large-scale energy storage application. Full-cell commercial products, directly exploiting aqueous-based sodium storage batteries, recently made their appearance on the market. Low cost, low toxicity, and versatility for stationary storage are among the most notable strengths of manufacturer such as AQUION energy (USA)$^{[34]}$ and FARADION (UK)$^{[20]}$ companies. The former, which recently considered to move manufacturing facilities to foreign countries, made a spinel MnO$_2$/Activated carbon full-cell the core of its business. The excellent cycling performance ensuring more than 10 000 cycles coupled with $\approx20$ Wh kg$^{-1}$ of specific cell capacity, thanks to a sulfate-based aqueous electrolyte and pseudocapacitive sodium storage. The most renown drawbacks of SIBs aqueous technologies are however the limited performance, due to narrow voltage window available, and the limited number of candidate materials. The Prussian blue analogues, i.e., TM hexacyanoferrates and TM hexacyanomanganates, have been studied as aqueous sodium-ion battery cathode materials. Many of them have demonstrated as valuable materials in terms of facile synthesis and stable electrochemical performances$^{[299,300]}$ and some others promising for full-cell aqueous assemblies.$^{[301,302]}$ The rigid metal–organic framework of this class of materials characterized by a large nanometric-sized voids provides a stable scaffold in which a large variety of alkaline cations can be easily and reversibly housed.$^{[304,305]}$ Charge neutrality is ensured by RedOx active couples constituting the metal–organic framework itself. Kim et al.$^{[302]}$ reported an aqueous SIB hybrid full-cell with Prussian blue analogue, namely $\text{KCu}_0.5\text{Cu}_0.5\text{Fe(CN)}_6$, and a novel carbonyl-based organic salt, disodium naphthalenediimide (SDNI), which had high operational voltage of 1.1 V and excellent cycle performance. Polyaniion compounds have also been considered as electrode materials for aqueous sodium-ion battery. Kumar et al.$^{[304]}$ demonstrated a high energy density sodium-ion battery full-cell with aqueous electrolyte with Na$_2\text{V}_2\text{O}_5\text{(PO}_4)_2@$multi-walled carbon nanotubes (MWCNT) composite as cathode material and Na$_2\text{Ti}_3\text{(PO}_4)_4$-C composite or Zn metal as anode material. The as obtained full-cell achieved good cycle stability even under high current density of 10 C and reached the outstanding energy of 84 Wh kg$^{-1}$. Ultimately, vanadium-based compounds are of particular interest as well due to the different oxidation states accessible realizing multielectrons RedOx reactions. 1D nanostructured sodium vanadium oxide Na$_2\text{V}_6\text{O}_{16}\cdot$nH$_2$O was introduced as a novel anode material for aqueous Na-ion batteries by Shang and co-workers.$^{[305]}$ A full aqueous Na-ion battery was built using Na$_9\text{Na}_{0.6}\text{MnO}_2$ as cathode and Na$_2\text{V}_6\text{O}_{16}\cdot$nH$_2$O as anode. However, the charge capacity of the full-cell fades quickly in the initial few cycles, which is in agreement with the fast fading of the sodium-ion intercalation capacity of Na$_2\text{V}_6\text{O}_{16}\cdot$nH$_2$O.

4.2. Symmetric Full Battery

It has been already extensively discussed in literature how partial metal substitution (Li, Mg, Zn, and Ti) proved to be surprisingly effective in incrementing structure stability of layered transition metal oxides when used as SIBs cathode materials. For example, Li doping of P2-type $\beta$-Na$_8\text{M}_{1-x}\text{Li}_x\text{Ni}_{3/4}\text{Mn}_{1/4}\text{O}_2$ ($x = 0.07$) effectively and considerably suppresses Jahn–Teller distortion connected to Mn high oxidation states.$^{[348]}$ Similarly, Mg substitution revealed to be a promising strategy to suppress irreversible P2–O2 transition in Na$_9\text{Na}_{0.6}\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$. Exploration of diverse stoichiometry of mixed transition metal oxides recently led to meaningful results concerning dual-RedOx materials. With this term are addressed compounds in which two red-ox processes can occur at significantly different potential values, this being related to thermodynamics of involved transition metal atoms and their chemical surroundings.$^{[306]}$ This feature, coupled with a crystalline structure capable of sodium hosting, discloses a full-cell set up in which the same material can be used as both anode and cathode. Nonsymmetric sodium ion full batteries, previously described, bear with themselves potential safety concerns related to possible thermal runaway connected to operational potentials close to sodium plating when certain anode materials, especially carbon-based materials, are employed.$^{[20]}$ This kind of SIBs full-cell design unlikely meets long-life, low cost, and safety requirements for large-scale energy storage applications. Safer and easy-to-assemble configuration are thus urgently needed. For this reason, symmetric SIBs became very recently an attractive and promising alternative from a commercial standpoint. The same active material, exploiting different red-ox sites and acting as both cathode and anode, can enable cells overcharging to some extent, buffer the large volume expansion (cathode expanding accompanied by anode shrinking, and vice versa), and greatly
reduce the manufacturing costs and simplify the fabrication process.[255,307–310] Up to now, the full symmetric vanadium and titanium-based SIBs in terms of two TM\textsuperscript{3+}/TM\textsuperscript{4+} and TM\textsuperscript{3+}/TM\textsuperscript{5+} (TM = Ti or V) RedOx couples in the active materials have been proposed.

4.2.1. Sodium-Ion Full-Cells Based on NASICON Structures

NASICON-type phosphates Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (NVP) possesses two RedOx active centers, coinciding with vanadium anions occupying different crystalline sites. Standard potentials, connected to RedOx couples V\textsuperscript{4+}/V\textsuperscript{3+} and V\textsuperscript{3+}/V\textsuperscript{2+}, are 3.4 and 1.6 V versus Na\textsuperscript{+}/Na, respectively. Such properties allow NVP to be used not only as cathode but also as anode. The cell reactions in the considered symmetric cells can be described as follows[311]

\[
\text{(Anode)} A_1 V^{4+}_1 (PO_4)_3 + x A^- + x e^- \leftrightarrow A_{3-x} V^{2+}_{3-x} V^{4+}_x (PO_4)_3 \quad (7)
\]

\[
\text{(Cathode)} A_1 V^{4+}_1 (PO_4)_3 \leftrightarrow A_{1-x} V^{2+}_{1-x} V^{4+}_x (PO_4)_3 + x A^- + x e^- \quad (8)
\]

\[
\text{(Overall cell reaction)} 2A_1 V^{4+}_1 (PO_4)_3 \leftrightarrow A_{3-x} V^{2+}_{3-x} V^{4+}_x (PO_4)_3 + A_{1-x} V^{2+}_{1-x} V^{4+}_x (PO_4)_3 \quad (9)
\]

Where A stands for either Li or Na centers. The NVP/NaVP symmetric cells were first fabricated and examined by Plashnitsa et al.[311] and a moderate dependence of rate capabilities and cycle abilities with temperature was highlighted. Based on the quasi-open-circuit voltage measurements, full-cell charge cut-off voltage was optimized at 1.85 V. To improve the thermal stability of sodium-ion batteries, the room-temperature ionic liquid (RTIL) NaBF\textsubscript{4}/1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF\textsubscript{4}) was used as electrolyte instead of electrolyte solution based on flammable carbonate organic solvents (EC and dimethylcarbonate). The charge and discharge capacities of the NVP symmetric full battery were found to be 102 and 64 mAh g\textsuperscript{-1}, respectively, during the first cycle. The substitution of the organic electrolytes with the safer RTIL resulted in the decrease of the first discharge capacity. However, RTIL-based cells revealed better cyclability and a more stable behavior at elevated temperatures.

Noguchi et al.[307] assembled an all solid-state NVP/NASICON(Na\textsubscript{3}Zr\textsubscript{2}Si\textsubscript{2}PO\textsubscript{12})/NVP symmetric cell.[307] In this case, a NASICON-type material, Zr-based, was employed as solid-state electrolyte. The typical solid-state half-cell was cycled at 2.0–3.6 V and 1.5–2.0 V versus Na. The voltage of the sodium extraction from the cathode falling at about 3.4 V was associated with the V\textsuperscript{4+}/V\textsuperscript{3+} RedOx couple, while the plateau registered at 1.6 V was associated with the V\textsuperscript{3+}/V\textsuperscript{2+} RedOx couple and indicated electrochemical insertion of Na\textsuperscript{+} into the NVP anode (see left side of image (a) in Figure 7). Considering the absolute capacity (mAh of each electrode) balance of the negative/positive electrodes,[316] it was suggested that a cathode-to-anode mass ratio of 1:3 is appropriate for the construction of symmetric-type cells. Parasitic reactions leading to NVP and Zr-NASICON phase decomposition have been detected at NVP/Zr-NASICON interface, and inevitably worsen the capacity extracted from active materials.

4.2.2. Sodium-Ion Full Battery Based on Layered Oxides

Apart from the NASICON structure-type based symmetric full battery, the bipolar materials with layered structure and the general formula A\textsubscript{M}O\textsubscript{2} (A = alkali and M = transition metal), containing two electrochemically active transition metals with RedOx couples such as Ni\textsuperscript{4+}/Ni\textsuperscript{2+} and Ti\textsuperscript{4+}/Ti\textsuperscript{2+}, are also attractive and promising alternatives for the implementation in Na-ion symmetric batteries. Typical Na layered oxides can be defined as P2 and O3 according to the geometry of Na\textsuperscript{+} surroundings (P: prismatic and O: octahedral) and the number of unique oxide layer forming the vertically aligned repetitive unit, as extensively discussed.[255] Guo et al.[309] designed and synthesized the O3-type Na\textsubscript{0.8}Ni\textsubscript{0.4}Ti\textsubscript{0.6}O\textsubscript{2} material, the stoichiometry between
nickel and titanium, defined here as a “golden pair,” not only greatly stabilizes electrochemical sodiation/desodiation process but also exhibits the unique double RedOx couples of Ni$^{4+}$/Ni$^{2+}$ (3.5 V vs Na$^+$/Na) and Ti$^{4+}$/Ti$^{3+}$ (0.7 V Na$^+$/Na).

The proposed symmetric SIB, as shown in Figure 8, exhibits a reversible discharge capacity of 85 mAh g$^{-1}$ with the average voltage of 2.8 V and presents a superior long life exceeding 150 cycles with capacity retention of 75%. Two distinct RedOx peaks set at 3.6/3.5 V (Ni$^{4+}$/Ni$^{2+}$) and 0.95/0.7 V (Ti$^{4+}$/Ti$^{3+}$) can be observed in the cyclic voltammetry reported in image (a) (right-hand side) in Figure 8, and they appear separated by a large potential difference.

In case of the P2-type structure, Wang et al. realized that because of the strong Na$^+$/Na$^+$ interaction in the alkali metal layer and charge ordering in the transition metal layer, most P2-type layered oxides exhibit Na$^+$/vacancy-ordered superstructures, which are supposed to lead to rapid capacity fading during cycling. They found the transition metal ordering is mainly controlled by the difference in the ionic radii of M1 and M2 in P2-Na$_x$[M1,M2]O$_2$-layered oxide. Through selecting transition metals as Cr$^{3+}$ and Ti$^{4+}$ which show similar ionic radii (0.615 and 0.605 Å, respectively) but a substantial difference in RedOx potentials, they designed a P2-Na$_{0.6}$[Cr$_{0.6}$Ti$_{0.4}$]O$_2$-layered oxide, which is highly Cr/Ti and Na$^+$/vacancy-disordered at any sodium content and over a wide range of temperature. The full-cell delivers an average operating voltage plateau at 2.53 V and extraordinary rate and superior cycling performance. Even at a very high rate of 12 C, the capacity retention is 75% if compared to capacity extracted at 1 C, as shown in image (b) in Figure 8. It was demonstrated that this cation-disordered material can function as both positive and negative electrodes with average operation voltages of 3.5 and 0.8 V, corresponding to the RedOx couples Cr$^{4+}$/Cr$^{3+}$ and Ti$^{4+}$/Ti$^{3+}$, respectively. Titanium substitution with manganese in layered oxide chemical formula leads to the compound P2-Na$_{0.5}$Ni$_{0.25}$Mn$_{0.75}$O$_2$ with dual-electrode characteristics.

Contrarily to what has been observed for other manganese containing layered structures, Na$_{0.67}$Mn$_{0.67}$Ni$_{0.33}$O$_2$[317] and Na$_{0.78}$Ni$_{0.23}$Mn$_{0.69}$O$_2$[318] in which Mn remains substantially inert due to potential values above 2.5 V versus Na$^+$/Na, Mn changes its oxidation state when P2-Na$_{0.5}$Ni$_{0.25}$Mn$_{0.75}$O$_2$ is cycled between 1.5 and 2.6 V versus Na$^+$/Na. The dual-electrode behavior is here imputable to Ni$^{2+/4+}$ RedOx couple (operating at 3.72/3.51 V versus sodium) and Mn$^{3+/4+}$...
oxidation taking place at much lower potentials values (2.15/1.76 V versus Na+/Na). Despite the discrepancies between reversible capacities extracted from half-cell configuration (75 vs 100 mAh g⁻¹), mass ratio between anode and cathode for full-cell fabrication was kept equal to 1. Based on this configuration the cell ensured a long cycle ability extended over 100 cycles with a capacity retention of 90% after 50 cycles and an output voltage of 2.0 V.

5. Conclusions and Outlook

This review comprehensively collected the most recent advancements in sodium-ion aprotic full-cell research. Motivation behind this effort can be summarized in a readiness level first assessment of the sodium full-cell technology by reporting the most useful physical quantities to compare battery technology such as energy and power densities and cell stability through cycling. Provided these information, comparison with the affirmed lithium technology performances will be more agile. The final aim, however, is not the encouragement in identifying a sodium chemistry paralleling lithium counterpart performances, a hard task considering physical limitation of Na as stated in the introduction. Instead, the evaluation of suitability of sodium cells for energy storage applications differentiation and speciation would be more appropriate. There are several aspects that might contribute in making sodium technology competitive, in particular for stationary energy storage applications and other low-power utilizations with low-to-null restriction in terms of volumetric occupancy. Among these the most relevant are: (i) the advantages connected to more abundant raw materials, (ii) Co-free active electrode materials, (iii) manufacturing cost reduction deriving from aluminum utilization as anode current collector, and (iv) symmetric configuration. A considerable number of recent works proposing full-cell set-ups have been thoroughly revised and the most significant contributions have been specifically sorted so to highlight unique correspondences between
chemistries and electrochemical features, namely cell voltage and specific capacities. In image (a) in Figure 9, a 3D plot collecting these findings is reported. Particularly, the collected specific capacities normalization has been made over both anode and cathode mass. This operation has often revealed as a challenging task, since electrode mass loadings and/or anode to cathode ratio are not always discussed in the scrutinized papers. The sorting of the sodium chemistries, at the same time, purposely focused, in a first instance, on highlighting anode chemistry over cathode one. The former, indeed, has, at current knowledge, the more severe limitation in terms of stability and capacity retention. The classes of sodium full-cells have been thus organized in carbon-based, conversion/alloying material-based, insertion materials and organic based cells. To these groups, the symmetric cells have been set, fully based on insertion chemistry, and aqueous chemistries have been added. It appears immediately evident the clustering of particular sodium full-cell chemistries within potential and capacity ranges. Interestingly, contrarily to what common sense and half-cell experiments would suggest, conversion or alloying based full-cell (red symbols in Figure 9) seems not to derive surpassing benefits from the superior theoretical capacity of the anode material. This is presumably due to the large excess of cathode compound required to overcome irreversible capacities connected to first cycle and kinetics bottlenecks connected to augmented cathode thickness. Cell potentials, for the above mentioned chemistries, are not surprisingly high as well, being conversion and alloying anode charge/discharge profiles shifted toward high potential values and affected by not negligible overpotential limitations. Contrarily, full-cells based on carbon anodes, either expanded graphite, hard-carbon, and soft-carbon or rGO ensure overall more intriguing performances, especially in terms of cell potentials and capacity retention (z-axis of 3D plot). The involved sodium storage mechanisms (double layer capacitance and expanded graphitic layer intercalation) indeed constitute less damaging and compromising processes, even if occurring at high cell potential values. Data plotting in image (a) in Figure 9 allows also to appreciate the effect of sodium cell chemistries over capacity retention after several cycles. Once again, carbon-based sodium batteries ensure better performances, with capacity retention averagely higher than competing chemistries. Worth noticing are values above 100% for some chemistries, connected to a progressive activation of the full-cell with charge discharge cycles. In image (b) in Figure 9, the XY plane of the 3D plot is reported separately, with references numbers inserted in each data point, in order to facilitate the tracking of the correspondent full-cell chemistry listed in Table 2. Ultimately, in Figure 10, the energy density versus power density plot of investigated full-cell SIBs chemistries is reported. By comparing the listed examples so far explored with lithium technology (amber shaded area), emerges how the formers, despite the nonoptimized performances, overlap with lithium technology in many cases. Notably, in one case among the ones taken in consideration in this review, both power and energy densities of a full-cell SIB chemistry are considerably higher than those of the average

Figure 9. a) 3D plotting of full-cell potential versus specific capacity (normalized over the mass of both the anode and cathode materials) and, when reported by the authors, capacity retention after several cycles (at least 10). b) Cell potential versus specific capacity plot, inside each data circle the bibliographic number referred to the specific sodium-ion assembly is provided.
<table>
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<th>Anode</th>
<th>Cathode</th>
<th>Cell potential [V]</th>
<th>Specific capacity [mAh g(^{-1})]</th>
<th>Energy density [Wh kg(^{-1})]</th>
<th>Power density [W kg(^{-1})]</th>
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<tr>
<td></td>
<td>Na[Fe(<em>{0.7})Mn(</em>{0.3})O(_2)][^{[264]}]</td>
<td>1.2</td>
<td>70</td>
<td>84</td>
<td>59</td>
</tr>
</tbody>
</table>
lithium battery. In this case, the outstanding high-power capability was guaranteed by pseudocapacitive behavior of the composite. Ought to be noted is that in order to make comparable a technology which is already available on the market with a not commercialized and an early-stage one, some assumptions had to be considered. Rather than providing what might have resulted in an unreliable esteem of the mass composition of a marketable sodium-ion battery cell, the resizing of energy and power density of commercial lithium technology, according to electrode mass composition alone, has been preferred. The emerging overall picture well agrees with originally hypothesized limitations of sodium based rechargeable battery, namely the lower energy density connected to discrepancy in standard electrochemical potentials between sodium and lithium. Nevertheless, sodium-ion technology is revealing as a technology capable of replacing lithium one in several applications. Once again, the patterning of SIBs chemistries, even in the Ragone plot-like graph, is evident. A further clustering of the reported data is overlapped in this very last graph in order to provide a classification based also on the cathode materials. This clever plotting provides a quick tool that efficiently and rapidly allows the identification of carbon-based anode/TM-oxides cathode architectures as the most promising in terms of energy density, while the alloying-conversion anode/NASICON cathode geometry as the most performing in terms of power density.

Sodium ion battery technology is demonstrating as a valuable alternative to the increasingly penetrating lithium-ion one. Differentiation of battery pack chemistries, according to application, will be a strategic asset of industrial manufacturers, extremely useful in curbing the deleterious effect deriving from raw materials depletion. A gargantuan effort has nevertheless to be made in SIBs materials optimization and, most of all SIBs electrolytes formulation, topic intentionally neglected here in this review. Among the most delicate material science challenges that has to be faced in the optimization process, is recalled in this closing remarks the tackling of the still limiting irreversible capacity registered during the very first charge/discharge cycle, particularly severe for some anode material classes (alloying and high-surface carbon based materials). Stability of crystalline phases, to thousands of charge/discharge cycles, is
still a major concern on the cathode side, as revealed by the not-so-exceptional capacity retentions of the explored chemistries. Nevertheless in the very last years, SIBs commercial prototypes manufactured in standard formats (18 650 cylindrical cell and prismatic cell) made their appearance on the market. Claims of cyclability above 4000 cycles and improved power and energy densities, similar to lithium counterpart, are comforting and cast silver linings on future energy storage.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

alloying materials, conversion materials, full-cells, layered materials, sodium-ion batteries
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