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Introduction to Sodium-Ion Batteries

1.1 Brief Outline

The global energy demand calls for a major transformation in energy sector, driven in large measure by the rapid expansion of power generation from renewables as well as by the increasing focus on electric vehicles. For the former concern, people are looking for possible solutions to shift away from the traditional fossil energy centralized system toward renewable-energy-based power generation. Though renewable resources, such as solar and wind power, are now replacing the roles previously reserved by fossil fuels, fossil fuels are still needed for times when the sun is down or the wind is idle. The intermittency of the electricity generation from renewable energy sources has necessitated the development of energy storage technology that enables the electricity to be delivered and on demand and be able to reach remote rural areas. On the other hand, a profound change in operating norms can be expected with electric vehicles gaining ground as a more environmentally friendly option in the last decade. Therefore, the development of frontier technologies in energy storage is the key that enables them to come into more widespread adoption in the commercial world.

In the past decades, traditional pumped hydrotechnology is once the only commercially viable energy storage that can potentially reshape the energy sector by addressing the limited penetration of renewable energy. However, this technology is eventually losing market share to emerging technologies mainly due to its geographical constraint. Disruptive technologies that come in a combination of flexibility in design, step-change improvement in performance, and good reliability are considered to be critical enabling the transformation in transportation. The emphasis has now been placed on the electrochemical storage that fits in squarely with this focus. As the state of the art in electrochemical energy storage, rechargeable lithium-ion batteries (LIBs) play a significant role in ushering in a swift transition from a fuel-based society to an exclusively all-electric dimension, a fact reflected in the Nobel Prize in Chemistry 2019. They have widely penetrated into the markets owing to the highly sought-after features, including high energy density, good reliability, and lightweight. In fact, LIBs were first commercialized in 1900s by Sony and started out as the power sources of portable electronics and

computers. A few decades later, they are increasingly displacing oil and gas to power our vehicles and buildings, thanks to the scientific breakthrough achieved by researchers along the way. Tesla, the pioneering electric car company, stays at the forefront of this change, where the Tesla's first Gigafactory has been a major cornerstone that pushes the development of LIBs to power energy revolution. The company has also announced its intention to unveil LIBs pack for residential storage that will help in the recent move to decentralized energy. Despite the technology's growing prevalence, a year-long focus on the use of the rare and expensive metal lithium has impeded the widespread adoption of this technology in large-scale applications. In addition, the production of lithium is mainly derived from brine or mined from minerals, but they are geographically restricted to Chile, Bolivia, Argentina, and Australia.

Scientific community started to realize that such scarcity makes the price of lithium fluctuates with demand, which is a fatal flaw inherent to LIBs. A question that researchers trying to answer is whether the incumbent LIB technology can be substituted with a more abundant resources without losing its benefits? Sodium-ion batteries (SIBs) could be the answer. In fact, the concept of SIBs was first brought up in 1980s, but its development is unlike that of LIBs that accept wide market adoption mainly because SIBs are not quite up to par with LIBs in all-round performance. Until the last decade, the topic of SIBs has been revisited to look for possible solution over the safety and cost issues posed by LIBs. Moving beyond lithium to sodium is an advantageous step that offers cost-effectiveness and better safety characteristics without a compromise on the incumbent manufacturing setting based on their chemical similarity and components. This is to say, the manufacturers of LIBs will be fully adaptable toward SIB technology, given that the materials being tested from LIBs can also be potentially transplanted to SIBs without major modification on top of their similar manufacturing processes. The working principle of SIBs is highly similar to LIBs, except the use of sodium as anode instead of lithium. Given that sodium resources can be found in sea water and sodium carbonates (the price of sodium carbonate is estimated to be \$135–165 ton^{-1}, while lithium carbonate costs about \$5000 ton^{-1}) that are vastly available on earth, SIBs are recognized as a cost-effective power solution compared to LIBs [1]. Furthermore, Al current collector that are less expensive and lighter can be used in SIBs due to the chemical inertness between sodium and Al in the formation of alloying compounds. With such a replacement with Cu, the battery cost can be reduced by approximately 3%, based on the price of Al (\$0.3 m^{-2}) and Cu (\$1.2 m^{-2}) foils [2]. On top of the cost reduction, safety is another potential benefit after the possible replacement of Cu with Al current collector on the cathode as well as the anode. The sodium-based cells can be stored at zero state of charge without carrying the risk of thermal runaway. Contrarily to the high reactivity between lithium and Cu at low voltage, the chemical stability of SIBs at zero volts is essential for circumventing the increasingly stringent transportation regulations covering LIBs. Furthermore, the use of Al as current collector not only enhances the safety feature of SIBs but also improves the energy density of SIBs with a lighter element.

Being one of the group I neighbors, sodium shares many chemical characteristics with lithium, and hence, the adoption of existing LIB analogs for SIBs has become the logical strategies. While SIBs can be produced on the same manufacturing lines as their lithium counterparts, numerous studies have not proved it to be a straightforward endeavor. Engineering efforts to the process are still needed to tweak the material morphologies and other properties for more seamless adoption in manufacturing. Alongside the obstacle in real practice, sodium technology also comes with specific challenges related to the chemistries of its components. For example, graphite as a commercial anode in LIBs is not energetically favorable for the intercalation of sodium. This anomalous behavior could be due to the larger size of sodium that imposes greater strain to the lattice of the host materials, which leads structural collapse after several cycles of reaction. In addition, SIBs are less powerful in terms of energy density compared to LIBs due to a 0.3-volt lower cell voltage (-2.71 V vs. standard hydrogen electrode (SHE) for sodium and -3.04 V vs. SHE for lithium). In a theoretical study reported by Ceder and coworkers, the lower output voltage of sodium cell can be due to the cathode effect [3]. It is believed that the weaker Na—O bond compared to the Li—O bond is responsible for the significant lower energy gain upon ion insertion into the host structure. This can be further validated by a distinctly lower the formation energy of Na_2O (-417.98 kJ mol^{-1}) compared to Li_2O (-598.73 kJ mol^{-1}), giving rise to a 1 V difference between Na–O batteries forming Na_2O and Li–O batteries. This study also ruled out the anodic effect to be the predominant factor as Na voltage is supposed to be higher than Li in 0.53 V with the lower cohesive energy of Na.

Despite the drawbacks mentioned earlier, their low cost and abundant nature compared to LIBs may outweigh this concern, which may dictate their wide application in stationary grid storage. The sluggish movement of larger sodium has been recognized as the origin of its slower reaction kinetics. Researcher started to flip their perspective when they found that desolvation energy of ion is likely to play a role as important as the size of ion. Compared to lithium, sodium is a weaker Lewis acid that makes it less stable in organic solvents. The lower desolvation energy exhibited by sodium is indeed beneficial for facile charge transfer at the interface of electrolyte. For ease of comparison, the characteristics of lithium and sodium are summarized in Table 1.1.

The appealing features of SIBs have made their return to the spotlight and achieved astonishing progress in the past decades. For example, the first commercial SIB company, Faradion, announced that its sodium-ion technology that can achieve similar performance to rechargeable batteries powered by conventional chemistries and show exceptional thermal stability and safety. Furthermore, a start-up company, Aquion Energy, has currently experienced commercial success in the development of SIB prototypes that work well at reduced operating temperature and with extended lifespan. If SIBs live up to the promise made by the companies, it could one day accept wider market adoption other than just stationary grid storage.

Table 1.1 Comparison of lithium and sodium properties.

Characteristics	Li^+	Na^+	Reference
Specific capacity ($mAh\,g^{-1}$)	1165	3829	[4]
Ionic radius (Å)	0.76	1.02	[5]
Stokes radius in PC (Å)	4.8	4.6	[6]
E^o (vs. SHE) (V)	−3.04	−2.71	[5]
E^o (A^+_{aq}/A) (vs. Li^+_{aq}/Li) (V)	0	0.326	[7]
Melting point (°C)	97.7	180.5	[4]
E° (A^+_{PC}/A) (vs. Li^+_{PC}/Li) (V)	0	0.23	[7]
Desolvation energy in PC ($kJ\,mol^{-1}$)	215.8	158.2	[5]
Cohesive energy of pure metal @ 298 K ($kJ\,mol^{-1}$)	−598.73	−417.98	[8]
Formation energy of M—X bond (eV)	−1.55	−1.05	[9]

1.2 Key Materials

On the journey to push the envelope of SIBs performance, researchers are consistently working on the optimization of the main components of SIBs, including electrode materials (anode and cathode), electrolytes, binders, and full cell configuration. Based on our current understanding on the fundamental mechanism of charge storage, the engineering of electrode materials has been successfully achieved through nanostructuring, structural modification, design of hybrid composite, and surface engineering. In short, academic research focus is moving from micron-sized to nano-sized materials to buffer the severe volume change for longer cycle life and shorten the ion diffusion distance for improved reaction kinetics. Current trend dealing with a combination of morphological and architectural controls allows the nanostructuring effect to be preserved in addition to the morphological merits. For example, the construction of three-dimensional (3D) secondary structure enables the advantages derived from the primary and secondary morphology to be maintained. In parallel, structural modification can potentially "repair" the intrinsic properties of electrode materials from the aspect of electronic and ionic conductivity, which leads to an improvement in ion diffusion and electron transfer process. The effect of structural engineering is much more significant in cathode materials where intercalation chemistry is kinetically dependent on the lattice structure. Apart from that, hybrid composite design and surface coating are the strategies putting forward to address the disadvantages of electrode materials by leveraging the synergies between different components (usually highly conductive materials) to improve the electronic conductivity and ion transport rate. At the electrode level, the development of binders and additives has great impact on the performance of SIBs, which is a research direction that worth exploring.

With cathode being the limiting factor in the electrochemical performance of SIBs, the emphasis has now been placed on the development of promising cathode materials as they are usually inferior in specific capacity and rate performance compared to most anodes. Current research on cathode materials for SIBs focuses on modifying existing or direct adoption of LIBs analogs, primarily layered- and tunnel-structured transition metal oxides, polyanion cathodes, Prussian blue analogs (PBAs), and organic compounds. In general, transition metal oxides, including metal-free and Na-based structures, show high specific capacity in working potential of about 2.7–3.0 V vs. Na/Na^+. The research of Na-based transition metal oxides, $NaMO_2$ (M = Ni, Co, Mn, Fe, Cr, V, etc.), was inspired by their lithium counterparts that work well as intercalative cathode for LIBs. The fatal flaw inherent to those transition metal oxides lies in the huge lattice expansion and irreversible multiphase transitions, which leads to a poorer cycling stability and rate capability. Aside from the layered Na-based oxides, the Na-free transition metal oxides MO_x (M = V, Mn, Mo) that can adopt sodium ion in an intercalative manner have also been widely studied for their sodium storage properties. Compared to the Na-based transition metal oxides, the Na-free counterparts are able to deliver higher specific capacity based on their lower molecular weight. At stark different from monoanion compounds, polyanionic compounds, including phosphates, pyrophosphates, and fluorophosphates, are more diverse in structure. Despite their low electronic conductivity, the highly covalent 3D framework of polyanionic compounds allows fast ion diffusion within the structure, in addition to the high structural stability. With these excellent charge storage properties, polyanionic phosphates especially $NaMPO_4$ (Fe, Mn) and sodium super ionic conductor (NASICON)-structured $Na_xM_2(PO_4)_3$ (M = V, Ti) are being researched for SIBs. The great success of $LiFePO_4$ in LIBs has encouraged the investigation of its sodium analogs $NaFePO_4$ that has high theoretical capacity of 154 mAh g^{-1} in the voltage range of 2.9 V (vs. Na^+/Na). As compared to low-dimensional sodium ion transport pathways in $NaFePO_4$, the 3D open framework of NASICON-type $Na_3V_2(PO_4)_3$ seems to allow faster sodium diffusion channels. In a two-phase transition that extracts two sodium ions from the lattice of $Na_3V_2(PO_4)_3$ at 3.4 V vs. Na^+/Na as the result of a V^{3+}/V^{4+} redox reaction, a theoretical capacity of 117 mAh g^{-1} can be obtained. Similarly, the study of pyrophosphates $Na_2MP_2O_7$ (M = Fe, Mn, Co) was inspired by its ultrahigh potential (can reach up to 4.9 V) and the high structural stability of $[P_2O_7]^{4-}$ framework upon accommodation of sodium ion. In another subgroup of phosphate family, the inductive effect of fluoride allows fluorophosphates to operate at higher operating potential when coupled with other transition metals M^{3+}/M^{4+} (M = Ti, Fe, V). For example, the working voltage of vanadium-based fluorophosphates can reach 4.0 V (vs. Na/Na^+) with redox couple V^{3+}/V^{4+}, which reflects that a decent energy density could be potentially obtained in full cell operation. PBAs are a group of cyano-coordination polymers with a generic formula of $AM[M'(CN)_6] \cdot xH_2O$ (A = Li, Na, K; M, M' = transition metals of Cr, Mn, Fe, Co, Ni, Cu, Zn, etc.; typically M' = Fe). The metalorganic framework consists of Fe^{II}—C≡N—Fe^{3+} units all along the three directions of the space, leaving a large zeolitic site at the center that allows the accommodation of guest species (e.g. alkali

metals, small organic molecules, water molecules, etc.). With the two different electrochemical active sides in PBAs (M^{2+}/M^{3+} and Fe^{2+}/Fe^{3+} couples), PBAs generally undergo a two-electron transition without breaking their lattice structure apart. What's more is that the partial/complete substitution of Fe^{2+} and Fe^{3+} ions in the cubic lattice of PBAs by other redox-active transition metals (e.g. Co, Ni, and Mn) is kinetically favorable. With such an enhanced flexibility in composition, the charge storage properties can be tuned accordingly to suit certain specifications. For examples, substitution of Fe with Mn and Co pushes the charge/discharge plateaus from around 3.2 V $Na_2Fe[Fe(CN)_6)]$ to higher values of 3.6 V ($Na_2Mn[Fe(CN)_6)]$ [10] and 3.8 V ($Na_2Co[Fe(CN)_6]$) [11], respectively. These features, in addition to their easy preparation through simple and low-cost co-precipitation method, make them highly suitable to be applied in stationary energy storage where cycle life and cost are far more important than energy density. Organic materials are known for their low cost, high tunability, good safety features, and recyclability. With a flexible framework, organic polymers, such as disodium rhodizonate ($Na_2C_6O_6$) and quinone-based tetra-sodium salt, are cathodes that can accommodate large guest ions reversibly with high spatial tolerance. Despite the great progress made in the past decades, the development of SIBs with organic electrode is still very limited. This lies in the fact that conventional polymerization synthesis frequently introduces a large fraction of electrochemical inert residues for the intramolecular linking, which inevitably results in a decrease of the active mass and the gravimetric capacity.

In parallel to the development of cathode, scientists are also working on a number of anode materials to realize high-performance SIBs. The ongoing investigation can be classified into several categories based on their reaction mechanism, including intercalation compounds (carbon-based materials, Ti-based materials), conversion-type compounds (oxides, sulfides, selenides, carbides, etc.), and alloying-type compounds (Si, Ge, Sb, Sn, etc.), as illustrated in Figures 1.1 and 1.2.

Intercalation reactions work exclusively for mostly carbon-based and layered titanium-based materials with large interlayer spacing for the accommodation of guest ions. Typically, the structure of these materials is sufficiently robust to host the occupancy of sodium, but the capacity is limited by the amount of reaction sites. This is to say, the capacities of intercalation compounds are limited by structural stability of the host and stoichiometry. Therefore, it is challenging to achieve specific capacities greater than 200–400 mAh g^{-1} for intercalation compounds.

Carbon-based materials with layered structure are widely used as anode for SIBs, including hard and soft carbons as well as graphene-related carbons. These polymorphs are made of sp^2 carbons arranged in 2D hexagonal covalent form and stacked together via weak Van der Waals interaction. The first anode material that scientists settled on was graphite, but it turned out that its excellent performance in LIBs cannot be duplicated. The Na anomaly has its roots in a general phenomenon: (i) larger size of sodium has made the intercalation reaction kinetically unfavorable; (ii) sodium is intrinsically weaker in binding to carbon (among alkali metals and alkaline earth metals) due to the competition between the ionization of the metal atom and the ion-substrate coupling [14]; (iii) the intercalated carbons, such as NaC_6
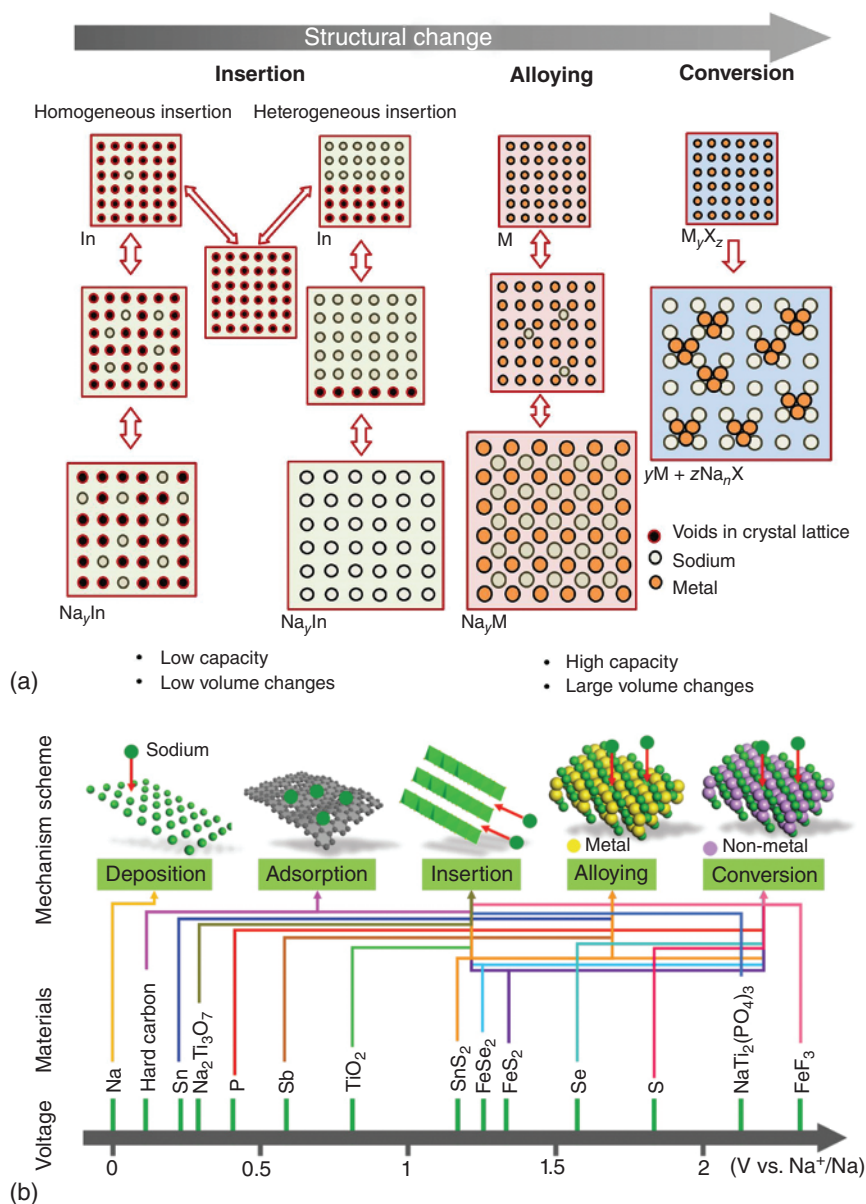
Figure 1.1 (a) Schematic illustration of the generally accepted charge storage mechanism of SIBs. Source: Perveen et al. [4]. Reproduced with permission, 2019, Elsevier. (b) Sodiation voltage and the representative electrode materials for each storage mechanism. Source: Yang and Rogach [12]. Reproduced with permission, 2020, Wiley-VCH.
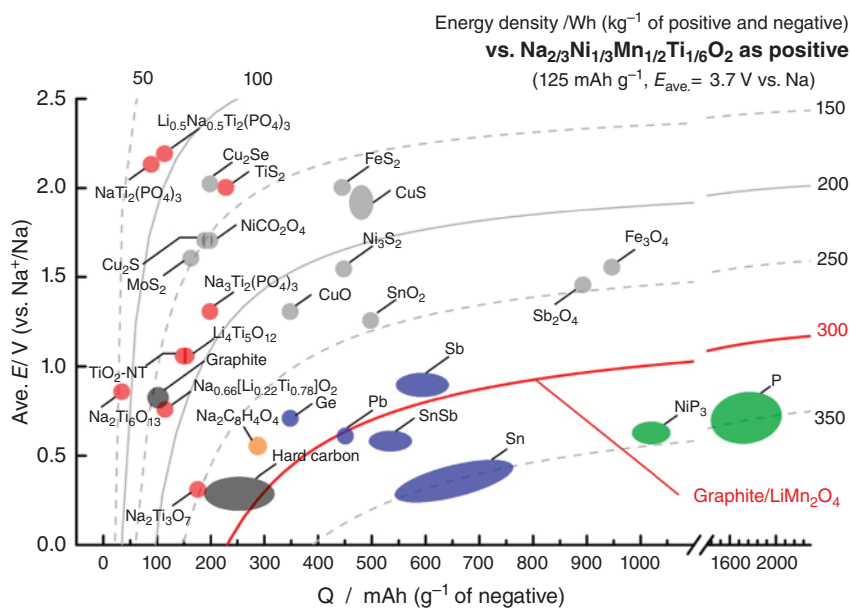
Figure 1.2 Average voltage (V) and energy density (Wh kg^{-1}) vs. gravimetric capacity (mAh g^{-1}) for negative electrode materials for NIBs: (black circles) carbonaceous materials, (red circles) oxides and phosphates as sodium insertion materials, (blue circles) alloy, (green) phosphide/phosphorus, and (gray circles) oxides and sulfides with conversion reaction. Source: Yabuuchi et al. [13]. Reproduced with permission, 2014, American Chemical Society.

and NaC_8, are structurally unstable according to the calculated formation energy [15]. There are several approaches put forward to realize better performance of graphite. The construction of enlarged interlayer spacing in graphite is one of them. Yang and coworkers reported that the lattice distance of graphite was expanded to 4.3 Å through swelling effect of oxygen-containing groups, while the analogous long-range-ordered layered structure of graphite was perfectly retained [16]. Aside from graphite, many other hard carbons have been investigated, especially those that are derived from glucose, cellulose, phenolic resin, etc. [17] Most of these carbons can reach capacity in the range of 250–350 mAh g^{-1}, along with a relatively low oxidation voltages at about 0.3 V. In summary, hard carbons used in SIBs are mostly derived from carbohydrates, while those derived from phenolic resins result in larger energy density. On the other hand, nongraphitizable carbons produced from polymers such as polyaniline (PANI) or polyacrylonitrile (PAN) have also been demonstrated though they usually show relatively low capacities and Coulombic efficiencies. Different from hard carbon, soft carbons usually go on discharge without displaying any voltage plateau at low voltage range, which leads to a lower specific capacity and higher oxidation voltage. Soft carbons can be produced from intrinsic hydrogen-rich precursors, such as polyvinyl chloride (PVC), pitch, petroleum coke, etc. [18] Despite the fact that they have lower energy densities due to aforementioned issues, they outperform hard carbons in rate capability [19].

Overall, the capacities of soft carbons fall in the range of 200–250 mAh g^{-1}, but a slightly higher average oxidation voltages of 0.5 V compared to hard carbons.

As part of the effort to optimize the electrochemical performance of carbonaceous anodes for SIBs, doping strategies have been intensively used to modulate the structure of carbons. Elemental doping, including nitrogen (N), sulfur (S), phosphorus (P), and boron (B), into the lattice of carbons can be easily achieved through the pyrolysis of a heteroatom-containing organic precursors or by mixing the precursor with heteroatom-donor substances. Several improvements can be expected from the incorporation of heteroatoms: (i) larger capacities could be the result of higher fraction of pseudocapacitive contribution from the additional functional groups [20]; (ii) higher ion diffusion rate due to the change in electronic structure of the carbon atoms in the vicinity of heteroatoms [21]; (iii) creates additional reaction sites for sodium [22]; and (iv) induces larger interspacing layers for better reaction kinetics [23]. Different from the N that is electrochemically inert, S itself can serve as the reaction site. In addition, the introduction of larger S atom into the carbon backbone results in significant enlargement in interlayer distance, which further enhances the electrode kinetics. Compared to N- and S-doping, P-doping can be difficult to achieve. Despite the difficulty in synthesis, P-doped carbon has been proven to be excellent in cycling stability and rate capability by Hou et al. [24] For example, a specific capacity of 108 mAh g^{-1} can be achieved at a high current density of 20 A g^{-1}. The long-term cycling investigation shows that the electrode can retain a capacity of 149 mAh g^{-1} after 5000 cycles at a current density of 5 A g^{-1}.

Apart from the intercalation chemistry, reaction mechanism based on redox chemistry is also highly favored due to several reasons: (i) higher specific capacity and energy density arise from the capability to accommodate relatively high stoichiometric ratio of sodium in alloy form; (ii) sodiation takes place at a relatively low voltage range; and (iii) alloy anodes are metallic or metalloid that usually exhibit excellent electrical conductivity. In general, the generic reaction formula of the alloying reaction can be represented as follows:

$$x\mathrm{Na}^+ + x\mathrm{e}^- + \mathrm{M} \leftrightarrow \mathrm{Na}_x\mathrm{M}$$
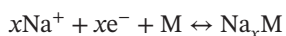
For alloying reaction, the storage of sodium can be achieved through the formation of binary alloy with different stoichiometry in a stepwise manner, where group IVA and VA elements such as tin (Sn), antimony (Sb), bismuth (Bi), silicon (Si), germanium (Ge), and phosphorus (P) are the materials that fit into this category. The main difference to the conventional intercalation reaction lies in the structural evolution upon alloying reaction. It is believed that continuous increase in the amount sodium induces massive volume change to the alloy compounds, which causes the crumbling and breakdown of alloy-type anodes. As the result of the large volume variation, a series of side effects can be triggered. For example, the solid electrode interface (SEI) could become unstable under large stress and strain, impeding the charge transfer at the interface. On the other hand, the structural integrity of the alloy anodes could be affected or even destroyed, which may lead to the loss of active surface. Over the past decades, researchers have been looking for strategies to overcome the bottlenecks of alloy anodes, mainly through understanding their failure

mechanism and identification of the transient intermediate under working states. In general, Sn, Sb, Ge, and Bi exhibit better rate capability thanks to their higher electronic conductivity. As mentioned earlier, their electrochemical performances are limited by mechanical instability due to the large volume variation upon alloying reaction especially in their crystalline state. On the other hand, P and Si are known for their relatively high specific capacity. However, the sluggish reaction kinetics caused by low electronic conductivity has been the major hindrance to their wide adoption in SIBs. Table 1.2 summarizes some of the electrochemical properties of alloying-type anodes that are commonly used in SIBs.

With current alloy anodes reaching almost their performance limits, researchers are scrutinizing every possible strategy to modulate their electrochemical properties for better performance. Therefore, fundamental understanding on how these materials behave in response to sodium (de)insertion from thermodynamic point of view, especially activation energy of sodium ion diffusion, bond breaking, and nucleation energy, is essentially helpful to device effective ways to achieve that goal.

Conversion-type anodes include a diverse group of transition metal oxides, sulfides, and phosphides that are endowed with redox properties. The accommodation sodium in conversion-type anodes involves a series of phase transformation through a change in the valence state of the redox-active centers. The generic equation that represents conversion reactions can be expressed as follows:

$$(b \cdot x)\,Na^+ + (b \cdot x)\,e^- + M_aX_b \leftrightarrow bNa_x X + aM$$
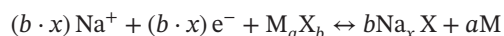
For typical conversion-type anodes, M is a transition metal element (Fe, Co, Ni, Cu, Mn, etc.), X is a nonmetal (O, N, F, S, Se, P, F, H, etc.), and x is the formal oxidation state of X. Upon sodiation, conversion-type anodes generally convert into metallic M before it nucleates in the form of amorphous or crystalline nanoparticles. Na_xX is the final nucleation product that forms a matrix around the M nanoparticles. It is found that the nonmetal species of X affects the cell potential. As compared to the oxide counterparts (M–O), the conversion reaction of chalcogenides is expected to be more kinetically favorable as the result of weaker M—X bond arising from their larger atomic radius [37]. On top of that, the higher electronic conductivity of the

Table 1.2 Electrochemical properties of alloying-type anodes.

Alloy system	Fully alloyed phase	Theoretical capacity (mAh g^{-1})	Volume expansion (%)	Average voltage (vs. Na$^+$/Na) (V)
Sn	$Na_{15}Sn_4$	847	420 [25]	~0.20 [26]
Sb	Na_3Sb	660	390 [27]	~0.60 [28]
Si	$NaSi/Na_{0.75}Si$	954/725	114 [29]	~0.50 [30]
Ge	NaGe	576	205 [31]	~0.30 [32]
P	Na_3P	2596	>300 [33]	~0.40 [34]
Bi	Na_3Bi	385	250 [35]	~0.55 [36]

discharge products M_2S/M_2Se compared to M_2O in the matrix is also responsible for the better reaction kinetics of the chalcogenides. In the family of transition metal sulfides, they exhibit lower theoretical capacity than the oxides due to the higher molecular weight of sulfur element but higher reaction potential. Compared to the rest, transition metal phosphides have rarely been reported due to the difficulty in material synthesis as well as the low stability. In fact, phosphorus is highly abundant that gives it a relatively low cost. Furthermore, the high theoretical capacity of metal phosphides is their most appealing feature in SIBs, which is arisen from a dual-charge storage mechanism. The transformation from metal phosphides to phosphorus via conversion reaction enables them to proceed with alloying reaction in a lower voltage range. Unfortunately, their SIBs performances are still not up to par with their counterparts in LIBs. Despite the great promise of conversion-type anodes, their feasibility for practical use is still being questioned. For example, oxidation of transition metal sulfides and phosphides under ambient condition has been an obstacle for them to be practically used. As a result, additional measures are required to maintain the material consistency, which might increase the cost for material storage and transportation. In addition, the viability of conversion-type anodes is also challenged by a couple of issues, especially the low electronic conductivity of active materials, dissolution and shuttle effect of chalcogens, irreversibility of conversion reaction, etc.

Sodium metal is the simplest form of anode but is an essential component for room-temperature SIBs. In fact, the early development of SIBs was based on the sodium metal-sulfur molten batteries operating at $300\,°C$. These systems required an external energy source to maintain the high operating temperature, causing them less promising compared to room-temperature SIBs when the sophisticated system design, high manufacturing costs, and safety issues are taken into consideration as well [38]. In fact, sodium metal has once been regarded incapable as anode because of the safety concern over the dendrite formation, high reactivity against electrolyte, and low melting point (sodium = $97.7\,°C$ and lithium = $180.5\,°C$). The instability of SEI layer is perhaps the key driver to the remaining associated problems mentioned earlier. For example, the existing explanation of dendrite growth in sodium anode based on sequential growth mechanism is related to the formation of uneven SEI, where dendrite preferentially forms at those protruded spots with concentrated ion flux [39]. On the contrary, researchers might think that SEI is intrinsically heterogeneous concerning its organic–inorganic matrix, which tends to promote the preferential growth of sodium metal at localized region even if it is originally fully isotropic. If dendrites pierce through the separator and short the cell, highly exothermic reaction that can lead to catastrophic thermal runaway such as fire and explosion may result. On the other hand, the preferential dissolution at the base of sodium dendrite causes their delamination from the current collector, which creates so-called "dead" sodium that is no longer electrochemically active but still contributes to the growth of SEI. Hence, a sharp drop in Coulombic efficiency is usually observed accompanied by a rise in impedance [40].

The solutions may be subdivided into the following interrelated taxonomy: (i) tune the compositions of electrolyte and additives; (ii) improve the interfacial

reaction between sodium metal and electrolyte; (iii) rational design of the electrode architecture to reduce the current density during plating-stripping and protect the sodium surface from undesired side reactions; and (iv) optimize the properties of sodium metal through alloy design. The power of sodium lies in its energy density compared to other anodes; however, its successful deployment of metal sodium in real practice might take years of research. It is not quite there yet, but this is definitely more than a "pipe dream."

At the electrode level, the overall SIBs performance is contingent upon the choice of electrolytes (e.g. organic liquids, ionic liquids, gel polymers, and solid electrolytes) but is often overlooked in research. Electrolyte generally consists of sodium salt with matching solvents, along with a tiny amount of additives as booster. The electrochemical properties, in particular voltage window, polarity, and wettability, can be optimized through careful tuning the constituents and ratios of the components. The choice of anions in sodium salt affects electrochemical stability window as it is always the first component to be oxidized that set the upper voltage limit for the electrochemical stability window, while the lower limit is more often dictated by solvent reduction. On the other hand, the ionic conductivity of electrolyte is determined by interaction strength between a sodium cation and a number of anions, which affects the amount of available charge carrier. For organic liquid electrolytes, commonly used anions are ClO_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ (Tf), and $[N(CF_3SO_2)_2]^-$ bis(trifluoromethylsulfonyl)imide (TFSI). The choice of solvent that changes viscosity of electrolyte has great impact on the ion conductivity. In general, the low viscosity organic solvents give higher ionic conductivity. However, the evaporation of flammable vapors at elevated temperature due to their high vapor pressure pose safety issue for SIBs. The use of polymers or ionic liquids with almost no vapor pressure can bypass this problem. However, the downside of both the latter electrolytes are their high viscosities that impede their widespread adoption in room-temperature applications. The poor interfacial contact has long been a critical issue for polymer electrolytes, which counteracts their safety advantage. Apart from the aforementioned categories, ionic liquid is a promising alternative to organic liquid electrolyte but at the expense of cost. They have intrinsically high ionic conductivities, accompanied by a couple of good safety features such as a large liquidus range, thermal and electrochemical stability, and very low vapor pressure. Solid-state batteries with enhanced safety characteristics but is accessible to high energy and power densities could be answered to addressing the concerns over the organic liquid electrolytes that have limited operating voltage window, flammable nature, and safety hazards caused by leakage.

The research on the optimization of binders has always been overlooked. In fact, binder works complementary with other battery components to ensure good mechanical and electrical integrity of the entire electrode [41]. The binder formula containing polyvinylidene difluoride (PVDF) that has gained great success in LIBs was first explored in SIBs. However, this kind of chain polymeric network fails to provide good cycling stability to the electrode [42]. This has prompted the recent investigation in to the low-cost water-soluble binders such as sodium carboxymethyl cellulose (CMC), poly(acrylic acid) (PAA), and sodium

alginate (Na-Alg). The use of these binders with polar functional groups is motivated by the discovery on the unique material–binder interaction that forms a thermally cross-linked 3D interconnection. The formation of this 3D network greatly improves the cycling stability of the electrode by stabilizing the SEI layer and enhancing the adhesion between the active materials and the current collector. As the result, the structural integrity of the active materials can be maintained, along with the intact electrical contact of the electrode. This also works well for electrode materials that undergo high stress and strain upon charge/discharge. Apart from the aforementioned advantages, water-soluble binders (CMC, PAA, and Na-Alg) also show their negligible swellability in organic electrolytes [43]. The promising results of CMC and PAA also prompted the study of their derivatives that contain carboxyl groups or other cross-linked polymers (e.g. chitosan, poly(9,9-dioctylfluorene-*co*-fluorenone-*co*-methylbenzoic ester) [PFM]) [44]. As a rule of thumb, the presence of high density of hydroxyl, carboxyl, or carbonyl groups is responsible for the favorable formation of 3D gel-like structure through hydrogen bonding. Such interaction leads to better mechanical stability and enhanced reaction kinetics of the electrode.

On the other hand, the addition of functional molecules, or so-called additives, is an effective way to stabilize SEI formation process. For example, the use of 1-fluoroethylene carbonate (FEC) and vinylene carbonate (VC) as additives in the PVDF binder formula has successfully suppressed the decomposition of organic electrolytes [44b, 45]. These additives passivate the surface through the decomposition and polymerization of FEC and VC prior to the formation of SEI layer [46]. There are different "sacrificing mechanisms" being reported in the previous studies. In the case of FEC, the protective layer is formed by a reaction associated with the opening of a five-membered ring. On the other hand, the reductive decomposition of VC gives rise to radical anion fragments that are responsible for the suppression of SEI dissolution.

1.3 Toward Future Development

It is recognized that the electrochemical performances examined in a full cell is more conducive to the advancement of SIBs in real setting. There are several ongoing research directions in this field, which can be briefly categorized into nonaqueous liquid sodium-ion full cell, quasi-solid-state sodium-ion full cell, and all-solid-state sodium-ion full cell. Among them, nonaqueous liquid sodium-ion full cell represents the most mature technology that can reach an energy density as high as $300\,Wh\,kg^{-1}$ by considering the mass of both cathode and anode, despite its inferior cycling stability. Quasi-solid-state sodium-ion full cell that is composed of quasi-solid-state electrolyte composed of a mixture of inorganic ceramics, polymer, and a small amount of solvent exhibits better performance than nonaqueous liquid sodium-ion full cell in terms of safety characteristic, interface stability, wider electrochemical window, and flexibility. Although the liquid content is greatly reduced in the quasi-solid-state electrolytes, the formation of the interface film is

still likely to happen, leading to the irreversible consumption of limited sodium supply in the full cell. Therefore, understanding on the pre-sodiation chemistry that can be deployed to offset the irreversible consumption of sodium would be helpful in devising reliable and scalable pre-sodiation strategies. Compared with the above two types of electrolytes, the all-solid-state electrolyte with high voltage stability and safety enables the full redox potential of high-voltage materials to be claimed, which significantly enhances the energy density and power density. Despite these advantages, the full potential of all-solid-state sodium-ion full cell has not been unleashed due to the larger interfacial impedance that gives rise to greater polarization. In general, what is still lack in the research of sodium-ion full cell is the in-depth analysis of the interfacial chemistry of different electrolytes and electrolyte optimization, on top of the development of incumbent strategies to improve the performance of sodium-ion full cells in the aspect of matching capacity and choice of electrode materials.

In recent years, a significant amount of research has been undertaken to develop new battery concept beyond LIBs. SIBs are one of the reliable alternatives that can provide cost-effective solution for future energy storage system. With the development of effective strategies to further optimize different components of SIBs, it is hoped to move this technology past broad commitments toward a durable solution in solving the global energy woes. Before that, there are still a couple of questions need to be answered before SIBs can be deployed on a commercial scale: what are challenges ahead and what are the paths to follow to realize their full potential? Swapping lithium for sodium needs more than just setting sight on tweaking the chemical compositions and lattice structure of the lithium analogs. It requires close partnership between experiment, theory, and simulation to advance fundamental scientific understanding on the charge storage mechanism of those promising electrode materials and to quantify the uncertainty inherent in our assumption. In addition to that, it also requires long-term investment to expedite and facilitate the transformation of scientific research to design tools suitable for the industrial laboratory setting and manufacturing floor. In this book, we aim to provide a comprehensive view on the current development of SIBs by systematically analyzing various important components of SIBs, including anodes, cathodes, electrolytes, binders, and SIBs in full cell configuration. In addition, the design principle is elaborated to provide some guidelines for future development of high-performance SIBs based on those insights gained from the previous studies.

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