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The re-emergence of sodium ion batteries: testing, processing, and manufacturability

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Abstract: With the re-emergence of sodium ion batteries (NIBs), we discuss the reasons for the recent interests in this technology and discuss the synergies between lithium ion battery (LIB) and NIB technologies and the potential for NIB as a "drop-in" technology for LIB manufacturing. The electrochemical testing of sodium materials in sodium metal anode arrangements is reviewed. The performance, stability, and polarization of the sodium in these test cells lead to alternative testing in three-electrode and alternative anode cell configurations. NIB manufacturability is also discussed, together with the impact that the material stability has upon the electrodes and coating. Finally, full-cell NIB technologies are reviewed, and literature proof-of-concept cells give an idea of some of the key differences in the testing protocols of these batteries. For more commercially relevant formats, safety, passive voltage control through cell balancing and cell formation aspects are discussed.

Keywords: sodium ion battery, NIB, cell manufacturing, electrode processing, Na ion, cell testing, anode, cathode, full cells

Introduction and background

Sodium ion batteries (NIBs) have been studied for many years, and sodium intercalating materials, in particular, were studied in the 1970s and 1980s. However, as the interest in lithium intercalation materials grew, until recently, the attention toward NIBs subsided.[1–6] Lithium ion batteries (LIBs) were commercialized by Sony (Japan) in the 1990s, utilizing a material that was invented by Prof John Goodenough (LiCoO$_2$, LCO) from the University of Oxford.[6–8] The patent was held in the UK by UKAEA and licensed to Sony. The material first utilized a hard carbon anode and subsequently a high-performance graphite anode.[9,10] Although initially optimized for consumer electronics, this technology is now used for a wide variety of applications – the automotive industry being the largest market (Table 1). LIBs currently dominate across many different industries (Table 1), with future growth predicted; the LIB market is predicted to grow from 350 GWh (USD 61 billion) in 2015 to 610 GWh (>USD 95 billion) in 2025.[11] Despite this, there is still a large market for lead acid batteries (PbAs), for applications where LIBs are not suitable – the PbA market is reported to have a value of ~USD 20 billion in 2016.[11] PbA is a low-energy, low-cost one and will not be displaced until a lower-cost alternative to LIB is established. The replacement of PbAs with low-toxicity batteries, and the growth in emerging markets such as stationary energy storage open up opportunities for alternative battery technologies such as NIBs.

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Table 1 Summary of current major sector use, requirements, and drivers

Cell properties	Automotive	Personal electronics	Stationary storage	PbA
Market size 2016	45K MWh	31.5K MWh	4.5K MWh	350 GWh
2025	190K MWh	55K MWh	22K MWh	550 GWh
Energy (Wh/L)	~500	~550	~300	~110
C rate: charge/discharge	~2/~2	~0.5/0.5C	~0.5/~2	
Cycle life	>8–10 years	>1–2 years	(10 years)	5 years
Main properties	High energy density/power	High energy density	Low cost, long life	Power, cost

Abbreviations: PbA, lead acid battery; Wh, watt-hour.

There are many similarities between LIBs and NIBs, especially in terms of the material components, and the manufacturing methodologies of the materials and cells. These similarities make NIBs a "drop-in" technology for LIBs, with the main difference being the charge carrier ion, Na^+ rather than Li^+. Hwang et al[12] have compared the main characteristic differences of lithium vs. sodium electrochemical energy devices. Sodium ions (Na^+) are heavier and have a larger ionic radii than lithium ions (Li^+), 23 g/mol, 1.02 Å and 6.9 g/mol, 0.76 Å, respectively. This difference in ionic size and atomic weight is important in terms of the maximum specific capacities of the materials, as the difference sizes affect the stability of the host crystal structures upon desodiation and delithiation. For example, it has been well documented that safety implications arise if too much lithium is removed from the $Li_{1-x}CoO_2$ crystal structure (> ca. 0.5 mol Li) because of irreversible changes in the crystal structure.[13,14] In comparison, sodium-layered oxides can show a greater stability window for $Na_{1-x}MO_2$.[15–17] Furthermore, sodium has an electrode potential of higher standard compared to lithium (-2.71 V vs. SHE cf. -3.02 V vs. SHE), which typically results in lower cell voltages for sodium materials.

In recent years, there has been a huge resurgence in materials research for new sodium ion anode and cathode materials.[18–28] One of these driving forces is involved in the cost of LIBs. Up to 80% of the cost of a cell manufactured by the larger producers (Giga factories) is the material, and so in order to reduce the cost of the cells further, lower-cost materials are required. Sodium is the sixth most abundant element on the planet, it is found both in sea water and in mineral form, and is, therefore, not geographically limited unlike lithium reserves. Furthermore, the low cost of NIBs is achieved by simply substituting specific parts of an LIB with sodium-containing materials, specifically a cathode, and electrolyte salt replacement. On average, the cathode, anode, and electrolyte contribute to 21%, 7%, and 8%, respectively, of the total cost of a cell. A simple comparison

of one of the brine sources (carbonate salts) of lithium and sodium compounds demonstrates a vast difference in prices; the cost of Li_2CO_3 is USD 6600/Mt and Na_2CO_3 USD 60/Mt (LME). This results in a cell design and process that can be produced on the same manufacturing lines as LIB, and in similar conditions but at a fraction of the cost.

In addition to cost, NIBs offer a potential safety benefit over LIBs. Aluminum alloys with lithium below 0.1 V vs. Li/Li^+ but does not alloy with sodium, therefore, can be used as an anodic current collector for NIB (as opposed to copper, a widely used anodic current collector for LIBs). However, aluminum is less dense than copper and thicker current collectors may be required, negatively affecting the volumetric energy density of the cell. Copper current collectors also dissolve into the electrolyte at low voltage and, upon recharge, copper can precipitate out forming dendrites and internal short circuits. As a result, LIBs are typically transported at 5%–30% state of charge, which prevents the dissolving of copper and subsequent precipitation.[29,30] For NIBs, where aluminum can be used as a current collector for both the anode and cathode, safe transportation can be achieved at 0 V (external short circuited) with no energy, and as chemicals with significant benefits to both safety and transport costs.[31]

In summary, NIB has two main benefits: cost and safety, with the potential to approach the performance characteristics of LIB, with the lower cost associated with PbA technologies. We can compare the cost and performance parameters of NIB technologies with current and future lithium ion technologies. Table 2 shows the comparison data calculated using Batpac[32] with material costs estimated using a materials market report.[11] Estimates were based upon standard cell constructions with electrodes of ~30% porosity, 20 μm aluminum, and 10 μm copper, and anode-to-cathode ratio was 1.1. NIB is the performance of the state-of-the-art NIB reported in the literature,[33] NIB-1 is the demonstrated and calculated energy density,[16] NIB-2 shows the future targets for NIB with novel tin alloy anodes, and NIBSLI is a low-cost

Table 2 Summary of costs and energy densities of different cell chemistries as estimated by BatPac©

Cathode		NIB	NIB-1	NIB-2	NIBSLI	PbA	LCO	NCA	NMC	NMC442	NMC
Anode		HC	HC	Sn	HC		Gr	Gr	Gr	Gr	Si
Cost	US$/Wh	131	123	106	116	110	158	159	168	136	130
Energy density	Wh/L	306	340	488	278	90	435	513	444	504	800
	(demo)	180	250								
	Wh/kg	162	191	227	137		206	238	204	241	400

Abbreviations: Gr, graphite; HC, hard carbon; LCO, LiCoO$_2$; LFP, LiFePO$_4$; NCA, LiNi$_x$Co$_y$Al$_z$O$_2$; NIB, sodium ion battery; SLI, Na$_2$Fe$_2$(SO$_4$)$_3$; NIB-1, Ni$_{1/3}$Mn$_{1/3}$Mg$_{1/6}$Ti$_{1/6}$O$_2$; NIB-2, Ni$_{1/2}$Mn$_{1/4}$Ti$_{1/8}$Sn$_{1/8}$O$_2$; NMC, Li$_{1-xyz}$Ni$_x$Mn$_y$Co$_z$O$_2$; PbA, lead acid battery; Wh, watt-hour.
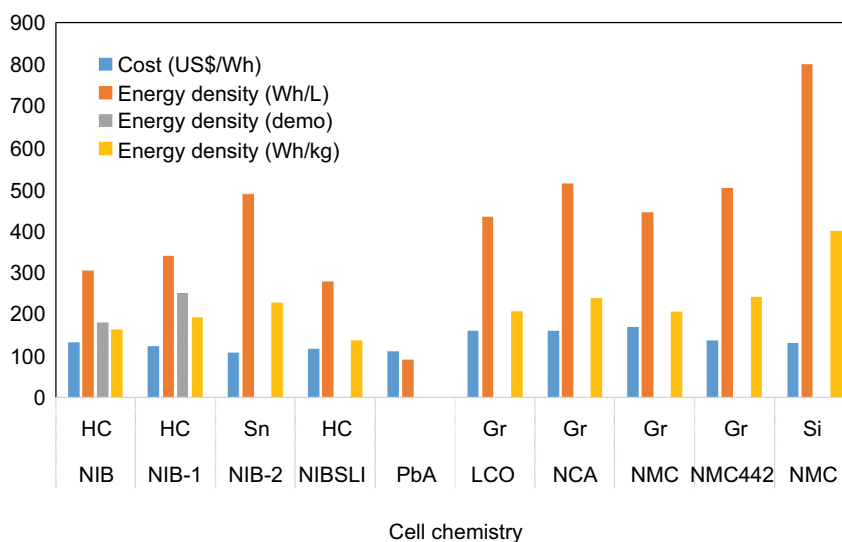
Figure 1 Summary of the energy densities and costs of different cell chemistries and batteries.
Abbreviations: Gr, graphite; HC, hard carbon; LCO, LiCoO$_2$; NCA, LiNixCoyAlzO2; NIB, sodium ion battery; NMC, Li1-xyzNixMnyCozO2; PbA, lead acid battery; Si, Silicon; Sn, Tin; Wh, watt-hour.

replacement suggestion for PbA. Although NIB technologies currently offer lower-cost solutions than lithium ion technologies, the energy density is still significantly lower than that of lithium. However, with a potential PbA replacement technology, the costs are slightly higher than PbA but improved energy densities are observed, and a comparison of the technologies can be observed in Figure 1.

NIB is a reemerging technology that is in its infancy, and because of the higher atomic weight of sodium and higher standard electrode potential vs. SHE, it is unlikely to reach the energy densities of LIB. However, due to its "drop-in" nature, lower cost, and potential transport benefits, it may offer alternatives to the lower-energy density and low-cost, already-established, PbA technology. This paper looks at the similarities in the manufacturability of NIBs compared with LIBs and summarizes some of the advancements made in full-cell devices and cell commercialization.

Manufacturing

NIBs are being marketed as a "drop-in" technology for LIBs; therefore, the reduction in cost is due solely from the

materials' contribution rather than the manufacturing methods. Here, we compare the LIB manufacturing processes with those required for sodium ion and discuss whether it is truly a "drop-in" technology.

The application of the electrode to the current collectors is typically performed using a tape casting type method; however, other coating methods have been used and developed. The electrodes are formed through a multistep process that begins with the manufacture of an electrode ink (or electrode slurry), as seen in Figure 2.

Many of the fundamental processing techniques utilized for LIB manufacturing are expected to be directly transferable to NIBs and hence a "drop-in" technology. However, material properties can mean additional process and control measures are required for NIB processing, compared to LIB processing. The sodium-layered oxides are more prone to water absorption than the lithium analogs. This is because the spacing between the transition metal layers is larger, and water can more easily intercalate.[34,35] In particular, this is observed for the O3-type layered oxides, and this can lead to difficulty in producing stable inks for electrode coatings
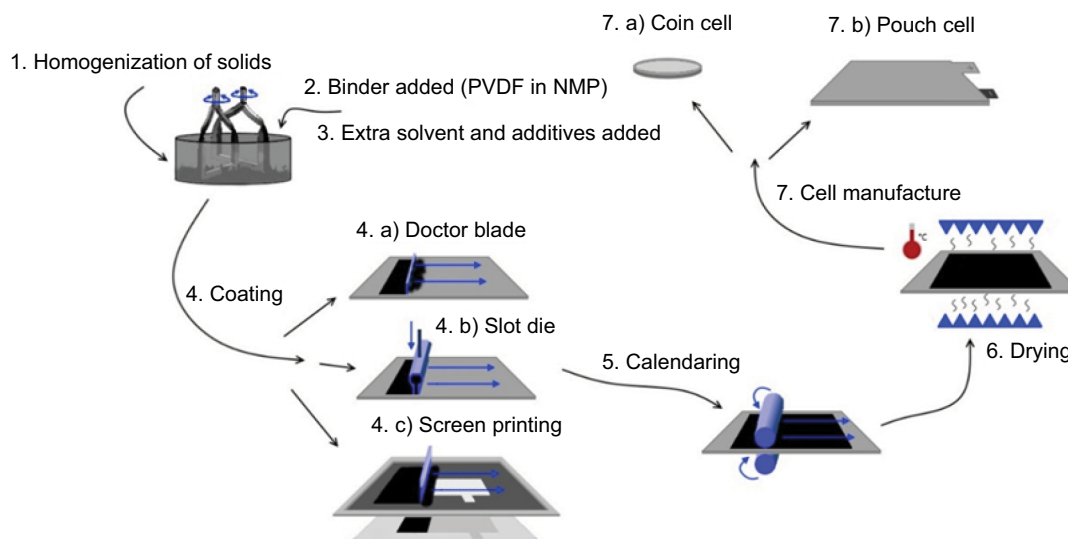
Figure 2 Standard process of LIB/NIB manufacture.
Abbreviations: LIB, lithium ion battery; NIB, sodium ion battery; NMP, N-methyl 2-pyrrolidone; PVDF, polyvinylidene fluoride.

and has been observed previously.[36] Basic components in an N-methyl 2-pyrrolidone–polyvinylidene fluoride ink will cause an instability in the ink, which will thicken and eventually gel over time. One method in overcoming small levels of basicity is by adding an acid into the formulation.[37] Other methods to reduce water intercalation are by selective substitutions into the crystal structure, and Mu et al[38] have developed cathode materials using iron and copper substitutions to stabilize the material to air. In other examples sodium-deficient materials have been synthesized, which can also further stabilize the materials to air. However, the sodium-deficient materials have less sodium content, and, therefore, in a non-pre-sodiated full cell, much lower energy densities are observed (Table 2). Sodium materials are generally more basic than the lithium counterparts, and, therefore, careful temperature and humidity control during the mixing and coating is required to ensure a stable ink to ensure coating homogeneity. With the stability of the powders in air being such an issue, we must consider also the shelf life of the electrodes. An electrode shelf-life study by Jung et al[39] on electrode coatings for NMC811 and NMC111 compared the degradation of the two electrodes in air over a period of time. The NMC111 material showed very little change; however, significant deterioration of the NMC811 material was observed, with a combination of hydroxides and carbonates forming on the surface of the particles. With the issues observed in ink stabilities for the O_3-layered oxides and the difference in the quality of the coatings when performed in a dry room rather than in the laboratory, the

shelf life of these electrodes after manufacturing process and before assembling into a cell should be assessed. There is a high likelihood that even in a dry room atmosphere the shelf life of these sodium-based electrodes are limited. More knowledge about the material and electrode stabilities at varying humidity and temperature is required to gain an understanding of the ink stability over time, and the shelf life of these highly moisture-sensitive components.

One aspect of cell manufacturing that determines the lifetime and performance of the cell is the anode-to-cathode balance and the formation method. In LIBs, typically a 10% excess capacity is utilized for the anode, and this is in part a safety attribute; by increasing the anode capacity it means that lithium dendrites are less likely to form. There is ample capacity for utilizing the lithium from the cathode, and a "margin" to compensate for small inhomogeneities in electrode coatings. In addition, typically the first cycle loss on the graphite is <10% and on the cathode typically <1%.[40,41]

For the sodium systems, the irreversible capacity on first cycle for the hard carbon anode is typically 20%, and similar irreversible capacities are observed on the layered oxide materials (Figure 3). Surprisingly, when partnered in a cell configuration, the losses are not additive but are complementary, this means that the irreversible sodium loss from the cathode on the first cycle is used to form the SEI layer upon the anode, and is consumed within the first cycle loss upon the anode. Therefore, the precise mass balance of the anode and cathode and the reversible voltage windows can be extremely important for internal cathode- and

anode-specific voltage control within a full cell. When balanced such that the two losses on each electrode are complementary, improved capacity fade during cycling
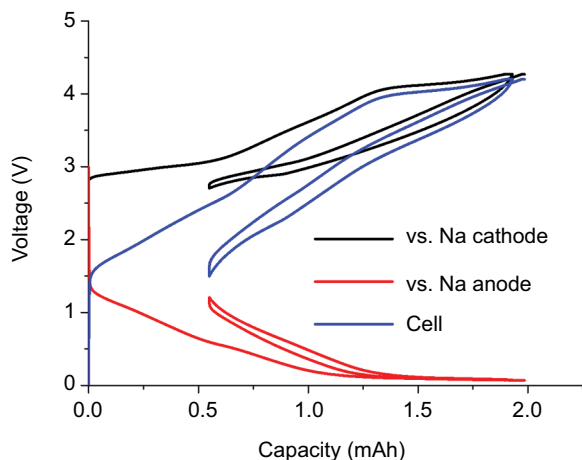
and improved safety characteristics such as reduced sodium dendrite growth are observed. Controlling the mass ratio between the active charge storage materials of the positive and negative electrodes within the NIB cell stack can also lead to a method of passive control over the maximum and minimum voltages reached by these electrodes during repeated cycling.[42] In addition, the formation cycles can be chosen such that the first loss is maximized for a higher voltage capacity, and the cell is then subsequently cycled at a lower voltage, which also prolongs the life time of the cell.[43] Figure 4 shows the differential capacity plots for a sodium ion full cell utilizing a layered oxide cathode and hard carbon anode. The cells that are formed at 4.2 V utilize the cathode loss to form the SEI on the hard carbon and a good cycle life is observed over 80 cycles (Figure 4A, B). On the other hand, the cell that is cycled at 4.2 V maximum shows a degradation in the differential capacity indicating an irreversible structure change in the cathode upon cycling (Figure 4C, D).

Figure 3 Voltage profile for a three-electrode full sodium ion cell, showing the cathode, anode, and full-cell voltage, taken from work done at SHARP Laboratories of Europe.
Notes: Data from Smith et al[16] and Treacher et al.[42]
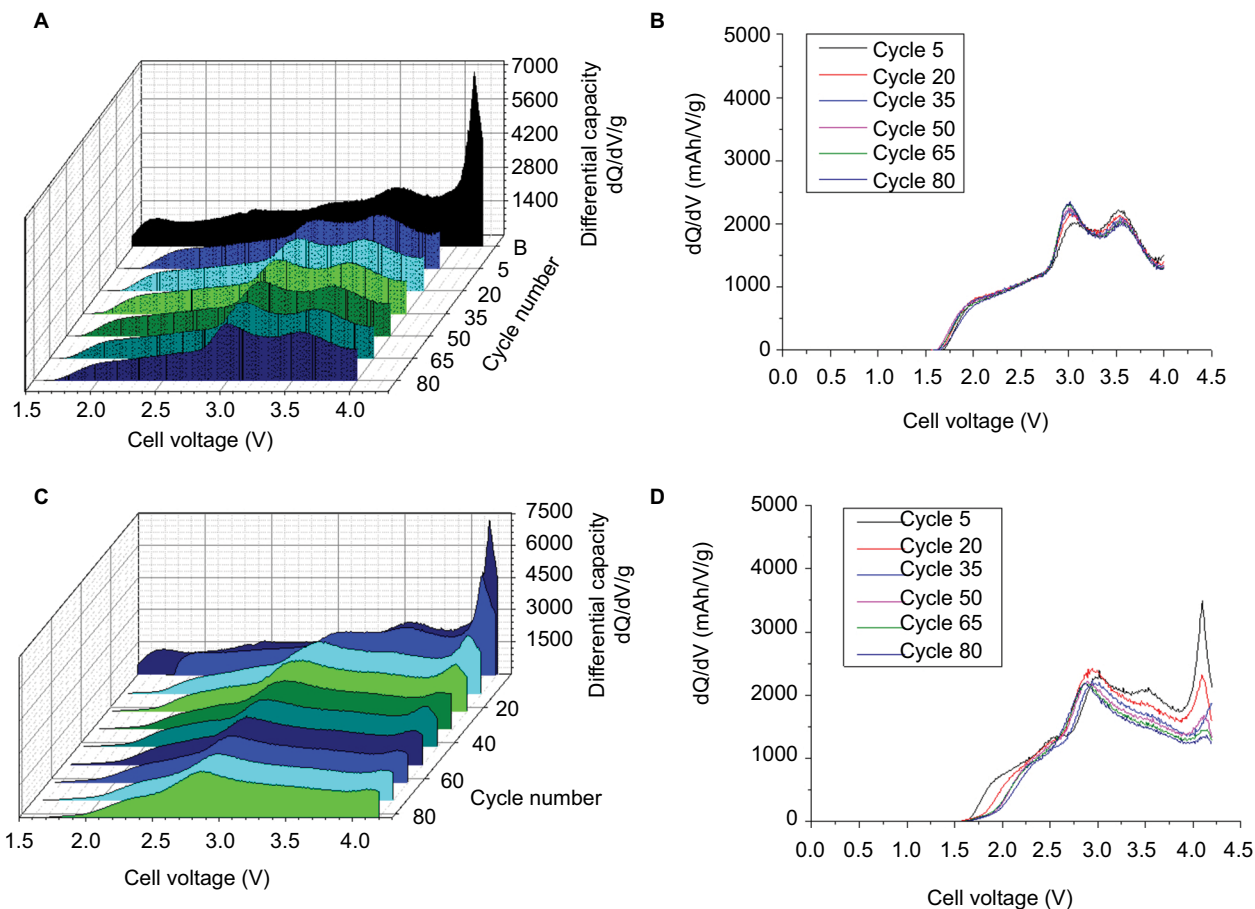

Figure 4 Differential capacities for cells that have undergone a formation cycle to 4.2 V and cycling at 4.0 V (**A, B**), compared to 4.3 V cycling (**C, D**) taken from work done at SHARP Laboratories of Europe.
Notes: Data from Smith et al[16] and Kendrick et al.[43]

Electrochemical testing and characterization methods

There has been a wealth of new publications regarding materials for NIBs, anodes, electrolytes, and cathodes. In addition, materials that have been investigated for LIBs are also now being revisited for NIB applications. Many articles have summarized these advancements.[12,18,20,21,23,24,27,28,44–52] However, the testing and electrochemical characterization methodologies have typically been adopted from lithium ion testing; here, we discuss the merits of this, and highlight some of the different observations for sodium ion testing compared with lithium ion. Electrochemical testing of materials is often performed in two-electrode arrangements, with a metallic lithium or sodium counter electrode, commonly referred to as half-cells. For lithium ion materials, half-cell testing gives good material characterization data, and cells can be made in a dry room atmosphere with limited water content. For sodium half-cells, issues can arise in half-cell testing, larger impedances that occur at the metal–electrolyte interfaces are observed, and the cells need to be made in glove boxes where water or oxygen content is limited.

Iermakova et al[53] show the differences between sodium and lithium metal symmetrical cells, highlighting the increased interfacial resistances on sodium compared to lithium in standard electrolyte systems during stripping and plating. At all current densities sodium exhibited significantly larger polarizations. At higher current densities of 5 mA cm^{-2}, thermofusible voltage spikes were observed for sodium, which is indicative of dendrite growth. Similar observations were noted by Ledwoch et al[54] in sodium metal counter and reference three-electrode cells during the testing of hard carbon. When controlling the cell voltage between the working and counter electrode, the lower voltage limit (0.01 V vs. Na/Na$^+$) was reached almost 30 mAh/g before complete sodiation of the hard carbon, even at low rates of charge and discharge, 0.1 C. At higher rates of charge and discharge, the polarization was shown to reach 0.1 V at 5 C. Both groups also observed variable voltages and polarizations during the stripping and plating process.

These observations indicate that two-electrode half-cell-testing, particularly for negative electrode materials where low-voltage cutoff could be problematic, premature arrival at low voltages can mean that full sodiation may not be observed.

In addition to the high polarizations observed in sodium half-cells, the sodium metal reacts with some electrolyte systems. This leads to electrolyte depletion over time, and inefficiencies in charge and discharge profiles. To combat the electrolyte depletion, a diverse portfolio of salts, solvents, and additives can be used.[55,56] However, stabilities of the sodium metal are generally poor in carbonate-based electrolytes.[57,58] Other solvent systems have been investigated and good reversibility of sodium stripping and plating has been observed with NaPF$_6$ in glyme[59] and in fluorinated ethylene carbonate (FEC).[57,60] In these systems, the formation of a stable Na$_2$O and NaF surface interface coating was observed. Similar improvements to the sodium metal cycling were observed with NaBr coatings.[61] What is not yet fully understood is the effect of different electrolyte additives upon the stabilization of a low-resistance interface layer on the sodium ion anodes, improving the cycling performance. Che et al have discussed the addition of rubidium and caesium ions for hard carbons to improve this interface.[62] A standard additive for LIB, vinyl carbonate, has proved to be ineffectual for sodium ion,[63] whereas FEC shows more promise and improves the cycling performance.[64]

To overcome some of the issues around testing with a sodium metal anode, different testing procedures are utilized. Three-electrode cells can eliminate the observation of the polarization on the sodium metal so long as the operating voltage is controlled between the reference and the working electrode, rather than the counter electrode.

In some cases, testing is performed using a pre-sodiated hard carbon counter electrode, and this method is still often used to overcome the first-cycle losses associated with hard carbon in full cells. It is a workable practice on a small local level, but does not translate through to manufacturing.[65–67] In the early sodium ion full-cell configurations, lead and tin were used as alloy anode materials for sodium,[68] and interestingly work is still continuing to investigate and stabilize tin-based anodes to increase the possible energy density of NIB.[69–72]

While it is important to understand the potential loss in coulombic efficiencies and poor cycle life in a sodium half-cell, we must remember that these materials and electrodes are to be cycled in full cells. This means that the cells do not contain metallic sodium, and, therefore, the issues that arise because of electrolyte decomposition in half-cell testing do not translate into full cells unless dendrite growth is observed. Therefore, carbonate solvents are utilized in full-cell configurations with fewer observed side reactions and inefficiencies. As a result, fewer electrolyte studies have been performed in full cells than in half-cells. However, some interesting phenomena have been observed. It has been shown that the performance of the electrolytes is not solely related to maximizing the ionic conductivities and minimizing the viscosity, but also relates to forming low-resistance interfaces. In

particular, when DME is used as a cosolvent, high polarizations are observed, and hence incomplete sodiation occurs at the low voltages. Additionally, DME has been shown, by use of electrochemical impedance spectroscopy and Bode diagrams, to gradually hinder – more than other cosolvents – cation diffusion through the electrode. In comparison, DMC as a cosolvent has been shown to reduce the resistances of these interfaces resulting in good rate capability.[73]

For the main organic electrolyte solvent, such as DC and EC, solvation and transport properties of Li^+ and Na^+ have been compared computationally,[74] resulting in differences between the two intercalating ions. It was observed that lithium ions form a tetrahedral solvation sphere in EC, whereas sodium ions exhibit more disordered and flexible coordinations. These more flexible coordinations are beneficial to ion diffusion; the difference in the strength of the coordination and weaker solvation energies leads to fast ionic diffusion for sodium ions, with diffusion coefficients three times that of lithium.[74]

Alternatives to carbonate-based liquid electrolytes such as the polymeric sodium ion conducting electrolytes may also offer advantages in terms of safety, voltage stability, and thermal runaway. In particular, PVDF and poly(ethylene oxide) (PEO) have been shown to offer interesting properties, with high voltage stabilities (4.7 V vs. Na/Na+) and conductivities of 1 mS/cm at 25°C observed for PEO-based electroyltes.[75–77]

Ultimately, it is important to understand the electrochemical testing methods and their limitations. The best practices for lithium ion electrochemical testing does not translate to sodium ion electrochemical testing in metal anode or half-cell test configurations. In a sodium ion test the performance of a material in a half-cell is very dependent upon the electrolyte types and is affected by the polarization occurring at the sodium metal and electrolyte interface. Due to coulombic inefficiencies observed because of the side reactions of the electrolyte with the sodium metal, higher specific capacities may be observed upon charge in a half-cell compared to that in a full-cell configuration. In addition, many electrolytes not stable in a half-cell are fine for use in a full-cell configuration; however, care must be taken to ensure that the anodes and cathodes in the cells are well balanced and to prevent sodium dendrites forming on the surfaces of the anodes, as this would cause gassing, as well as coulombic inefficiencies.

Commercial prospects of NIB technologies

As with LIBs, different NIB chemistries are being developed; materials for anodes, cathodes, and electrolytes are all being

investigated in great detail. This section summarizes the work in developing full-cell technologies rather than specific materials. Most cathode and anode materials for NIBs can be characterized into four groups. For cathodes: layered O3, layered P2, polyanionic compounds, and Prussian blue analogs; for anodes: carbonaceous, alloy, phosphoric, and metal oxide/sulfide.[12,78] A comparison table of the full-cell parings is shown in Table 3. The quoted reversible capacities are typically with respect to the cathode, but when calculated with respect to the anode this is noted in Table 3. It should also be highlighted that the loadings of the respective anodes and cathodes nor the balance between the anode and cathode mass are always recorded, both of which are important for further understanding and optimizing these NIB technologies. The layered oxide cathode cells in general exhibited higher reversible capacities than the polyanion systems. What is noticeable is that the cells for which the anode was pre-sodiated showed higher reversible specific capacities, as expected with extra sodium inserted into the system. If we consider, however, the translation to manufacture, the question remains unanswered to whether pre-sodiation is viable. Whereas for pre-lithiation, a third electrode, or lithiated alloys, may be inserted into the cell under dry conditions,[79,80] and for sodium this must be performed in a glove box because of sodium reactivity in air.[67]

Since 2014, several key NIB commercial advancements have been shown by several companies globally. Sumitomo demonstrated a prototype pouch cell using O_3-type $NaNi_{0.3}Fe_{0.4}Mn_{0.3}O_2$ and hard carbon anode, 650 mAh.[81] In 2015, SHARP labs of America demonstrated a 3 V Prussian white cathode vs. a hard carbon battery, and this exhibited a 30% first-cycle loss and the rate capability was limited by the hard carbon anode.[82] In 2015, Faradion demonstrated a 126 watt-hour (Wh)/kg cell based upon a nickel-based layered oxide cathode and a hard carbon anode, with 300 cycles. The first cylindrical prototype was demonstrated by CNRS and RS2E and now being commercialized by Tiamat.[83] This exhibited over 2000 cycles at 90 Wh/kg. In 2016, SHARP labs of Europe demonstrated a 3.4 and a 4.2 Ah pouch cell with energy densities of 211 and 250 Wh/L currently the highest reported volumetric energy density in a NIB to date.[16] This utilized a tin-doped sodium nickelate oxide material with a hard carbon anode.

Summary and future opportunities

In summary, NIB offers a wealth of new opportunities in terms of new battery technology development. With the advancements of the materials and the improvement in testing techniques, the true properties of these materials can

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Table 3 The composition, performance, and testing parameters of sodium-ion full-cell pairings as reported in the literature

Material pairing	Cathode/anode active materials	Electrode composition, A:B:C[a,b]	Electrode properties Coat weight (gsm)[b]	Electrochemical performance Potential (V)	Current density (mA/g)	Reversible capacity (mAh/g)	Pre-sodiation	References
LO3-O	$Na_{0.75}Mn_{0.7}Ni_{0.23}O_2$/$Na_2BDC$	80:10:10/60:30:10	13–25	2.0–4.2	20 (–C/13)	238 (anode) 50 (cathode)	N	84
LO3-PH	$Na[Cu_{0.1}(Fe_{1/3}Mn_{2/3})_{0.9}]C_2O_4$/P-$TiP_2$-C	85:7.5:7.5/–	C: 20/A: 5	1.2–3.4	12 (C/10)	130	Y	85
LO3-C	$NaNi_{0.5}Ti_{0.2}Mn_{0.3}O_2$/hard carbon	80:10/94:1:5	–	1.5–4.0	12	131	Y	66
LO3-MOS	$NaCrO_2$-C/SnO_2-rGO	85:3.75:3.75:7.5^c /94.5:0.5:5	–	1.5–3.4	55 (C/2)	87	N	86
LO3-C	$NaCrO_2$/hard carbon	80:15:5/96:0:4	–	1.5–3.5	–	260	Y	87
LO3-MOS	Zr-$NH_4V_4O_{10}$/H-$Na_2Ti_3O_7$	–	–	0.1–3.5	100	228	Y	88
LO3-C	$Na[Li_{0.05}(Ni_{0.25}Fe_{0.25}Mn_{0.5})_{0.95}]O_2$/hard carbon	85:7.5:7.5/–	–	1.75–4.3	17 (C/10)	134	Y	89
LO3-A	$NaMnO_2$/FeSb alloy ribbons	60:20/60:20:20	–	1.1–3.5	50	300	N	90
LO3-C	$NaCrO_2$/–	85:3.75:3.75:7.5^d/–	–	1.8–3.4	150C	99	N	91
LO3-C	Al_2O_3–$Na[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$/hard carbon	85:10:5/80:0:20	–	1.0–4.1	C/2	~155	N	92
LO3-C	$Na(Ni_{1/3}Fe_{1/3}Mn_{1/3})O_2$/carbon	–	–	1.5–4.1	C/2	100	N	93
LP2-A	$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$/Sb-C	80:10:10/80:10:10	–	0.7–4.1	30	180	Y	94
LP2-C	$Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2$/hard carbon	85:10:5/80:10:10	C: 25.9/A: 12.1	0.5–3.95	1C	220	Y	95
LP2-A	$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$/Sb-C	80:10:10/80:10:10	–	0.5–4.5	10	120	N	96
LP2-C	$Na_xNi_{0.2}Mn_{0.6}Co_{0.2}O_2$/hard carbon	85:15:0/85:15:0	A: 55	0.5–4.0	C/50	150	N	97
LP2-C	$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$–$NaN_3$/hard carbon	55:20:15:10^d/95:0:5	C: 82.5/A: 80.9	1–4.1	15	76	N	98
LP2-C	$Na_{2/3}Fe_{1/3}Mn_{2/3}O_2$/hard carbon	80:10/90:55:5	–	1.5–4.1	C/20	79	N	99
P-A	$Na_3V_2(PO_4)_3$/FeSe@FeS	67.5:22.5:10/80:10:10	–	0.3–2.9	1C	100	N	100
P-A	$Na_3V_2(PO_4)_3$/$SnSe_2$	67.5:22.5:10/75:15:10	A: 18	0.3–2.9	C/2	100	N	101
P-MOS	$Na_3V_2(PO_4)_3F_3$/SnS/G+C	70:25:5/–	–	1.1–3.6	257	248	N	102
P-C	$Na_3V_2(PO_4)_3F_3$/hard carbon	–	–	1.5–4.2	C/5	75	Y	103
P-A	$Na_3V_2(PO_4)_3$-based nanocomposite/LS-Sb@G	80:10:10/80:10:10	–	2–3.5	C/5	105	Y	104
P-MOS	$Na_3V_2(PO_4)_3$-based nanocomposite@C–$Li_4Ti_5O_{12}$	80:10:10/80:10:10	–	1.5–3.0	C/5	100	N	105
PBA-PBA	$FeFe(CN)_6$–$FeFe(CN)_6$ (symmetric)	80:10:10/80:10:10	–	0.2–1.5	2C	42	N	106
PBA-PBA	$(Cu^{II}—N\_C—Fe^{III/II})/(Mn^{II}—N\_C—Mn^{III/II})$	80:9:2:9^c/80:9:2:9^c	C: 100/A: 100	0.65–1.35	10C	26	N	107
PBA-C	$Na_xFeFe(CN)_6$/CNT-FeO_x	70:20:10/60:20:20	C: 20/A: 10	0.5–3.0	25	115	Y	108
PBA-C	$Na_2MnFe(CN)_6zH_2O$/Kureha hard carbon	70:20:10/95:0:5	–	1.5–3.8	100	140	N	109
PBA-C	$Fe_4[Fe(CN)_6]_3·xH_2O$/N-doped carbon	80:10:10/80:10:10	–	1.6–3.6	100	76	N	110
PBA-C	$Fe_4[Fe(CN)_6]_3·xH_2O$/hard carbon	70:20:10/80:10:10	–	2–4.2	100	70	N	111

Notes: [a]A:B:C – active ingredient:conductive additive:binder; [b]Cathode/anode; [c]A:B1:B2:C – active ingredient:conductive additive 1:conductive additive 2:binder; [d]A1:A2:B:C – active ingredient 1:active ingredient 1:active ingredient 2:conductive additive:binder. "–" indicates data not available.
Abbreviations: A, alloy; C, carbonaceous; LO_3, layered O_3; MOS, metal oxide/sulfide; O, organic, P, polyanionic, PBA, Prussian blue analog; PH, phosphoric; LP2, layered P2.

be realized; however, more knowledge and know-how are required in the testing and characterization of these materials and the composite electrodes. Although NIB is labeled a "drop-in" technology, we have highlighted that often direct methodology transfer from a lithium ion test to a sodium ion test is not necessarily the best way. The manufacturability of NIB is also a key question, and the ability to utilize the existing LIB manufacturing lines for NIB production runs is still unproved.

Although NIB materials are similar, there are key differences in the stability of some of the materials in air, particularly the high-energy density O_3-type layered oxides. This may lead to differences in mixing and coating procedures to improve the shelf life of the components. In addition, little is yet known about the safety aspects of NIB compared with LIB, although fundamentally substitution of the copper current collector for aluminum will eliminate one of the failure mechanisms, and initial results look promising.[17] Significantly more information is required upon the SEI stability and thermal stability to ascertain a more complete benefit. NIBs offer a low-cost solution to alternative battery technologies, and while they may never rival the energy densities observed for LIBs, they may offer alternative advantages in safety, which needs more investigation.

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Disclosure

The authors report no conflicts of interest in this work.

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