

Research Highlight

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# Recent commentaries on the expected performance, advantages and applications of sodium-ion batteries

Alexey M. Glushenkov<sup>1,2,\*</sup>

<sup>1</sup>Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia.

<sup>2</sup>Battery Storage and Grid Integration Program, The Australian National University, Canberra, ACT 2601, Australia.

\*Correspondence to: Prof. Alexey M. Glushenkov, Research School of Chemistry, The Australian National University, Building 137, Sullivans Creek Rd, Canberra, ACT 2601, Australia. E-mail: alexey.glushenkov@anu.edu.au

**How to cite this article:** Glushenkov AM. Recent commentaries on the expected performance, advantages and applications of sodium-ion batteries. *Energy Mater* 2023;3:300010. <https://dx.doi.org/10.20517/energymater.2022.70>

**Received:** 31 Oct 2022 **First Decision:** 5 Dec 2022 **Revised:** 23 Jan 2023 **Accepted:** 3 Feb 2023 **Published:** 3 Mar 2023

**Academic Editors:** Wei Tang, Jiazhao Wang, Yuping Wu **Copy Editor:** Fangling Lan **Production Editor:** Fangling Lan

**Keywords:** Sodium-ion batteries, lithium-ion batteries, performance, industrial developments

Sodium-ion (Na-ion) batteries represent an interesting and emerging alternative to the currently prominent lithium-ion (Li-ion) batteries. They operate on the same “rocking chair” principle, in which shuttle ions (sodium ions, in this instance) move reversibly between the positive and negative electrodes, inserting themselves into one of these and de-inserting themselves from the counter electrode. Historically, Na-ion and Li-ion batteries emerged in parallel in the 1970s; however, the spotlight shifted to lithium considerably in the 1980s, leading to the commercialization of Li-ion batteries by Sony in 1991 and the subsequent emergence of a number of Li-ion battery subclasses [including the lithium cobalt oxide (LCO), lithium manganese oxide (LMO), nickel cobalt aluminum (NCA), nickel manganese cobalt (NMC) and lithium iron phosphate (LFP) battery chemistries]. Sodium-ion batteries returned to the research community’s attention in the 2000s and 2010s decades due to concerns about the limited reserves of lithium and, subsequently, cobalt precursors. The research in this area flourished and a significant number of papers (hundreds) were published per year<sup>[1,2]</sup>. The research in this area generated significant excitement, with some contributors expecting sodium-ion batteries to be an equal or even superior alternative to Li-ion technology.



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A significant body of research and a degree of excitement is often followed by commercial efforts. Indeed, a number of emerging industry players can be identified at the moment in the sodium-ion battery space, including Faradion, Tiamat and Novosis, to name a few. Practical prototypes of the batteries appear, and their metrics and the expected performance may be quantified with reasonable certainty levels. Experts in the field can then analyze the available information and provide analytical commentaries able to define the expected performance envelopes, strengths and limitations of the emerging technology. Two such contributions have been recently published in the peer-reviewed literature, in the form of a viewpoint from Prof. Abraham<sup>[3]</sup> and a commentary from Prof. Tarascon<sup>[4]</sup>. Both contributors are well-known expert researchers in the field. Prof. Abraham has contributed to the development of lithium, Li-ion and Li-air batteries, and served on the editorial board of *Journal of Power Sources* and as a Chair of the Battery Division of the Electrochemical Society. Prof. Tarascon<sup>[4]</sup> is a creator of the European Network of Excellence ALISTORE-ERI and the French Network on Electrochemical Energy Storage (RS2E), and a strong research participant in the field of Li-ion and Na-ion batteries. It is interesting to compare and discuss their two opinions in the context of Na-ion batteries, as one of the expert commentators (Prof. Abraham) can be regarded as an outsider in the field, while the second expert commentator (Prof. Tarascon) is a clear insider, who significantly contributed to the sodium-based technology research and is also a shareholder and development committee member in one of the emerging Na-ion battery companies, Faradion.

Both commentators comment on the choice of materials that enable Na-ion batteries. Hard carbon is highlighted as the preferred material for negative electrodes (anodes) of these batteries. This type of carbon is made up of disordered graphene layers and nanopores and has a typical sloping voltage region followed by a plateau. Usually, optimal samples of hard carbon have reversible capacities of ~250 mAh/g, which corresponds to the formation of  $\text{Na}_{0.67}\text{C}_6$ <sup>[3]</sup>. The incorporation of sodium into hard carbon is usually described in terms of a combination of its insertion between the disordered carbon layers and the filling of nanopores present in the carbon host. Other negative electrode materials, such as  $\text{Na}_2\text{Ti}_3\text{O}_7$ ,  $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$  and materials that alloy with Na, have also been described; however, hard carbon remains the truly dominant negative electrode material and is used in the vast majority of practical prototypes<sup>[3,4]</sup>.

The choice of cathode materials is less singular and well defined. During the research activities on Na-ion batteries, three main cathode material types have emerged, including layered sodium transition metal oxides, typical for batteries produced by one of the industry pioneers Faradion, sodium vanadium fluorophosphate  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  used in practical battery prototypes by Tiamat and Prussian blue analogues such as  $\text{Na}_{2-6}\text{MnFe}(\text{CN})_6 \cdot \gamma\text{H}_2\text{O}$ , adopted in batteries developed by Novosis<sup>[3,4]</sup>. These positive electrode materials have distinctly different capacities and average voltages (up to 150 mAh/g with varied average voltages, depending on the materials, for sodium layered oxides; 128-135 mAh/g and 3.8-3.9 V for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ; 80-160 mAh/g and 3-3.5 V for Prussian blue analogues) and enable three main types of commercial cells adopted by the industry.

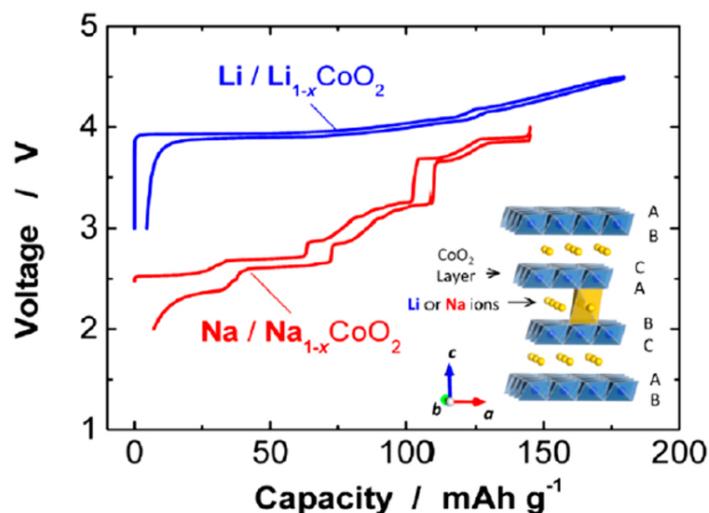
Electrolytes in Na-ion batteries are a variation of an appropriate salt [ $\text{NaPF}_6$ ,  $\text{NaN}(\text{SO}_2\text{CF}_3)_2$  or  $\text{NaClO}_4$ ] and mixed organic carbonate solvents chosen from ethylene carbonate (EC), ethyl methyl carbonate (EMC), propylene carbonate (PC), diethyl carbonate (DEC) and dimethyl carbonate (DMC). In order to enable better stability in the cell, electrolyte additives may be used, which include, most commonly, fluoroethylene carbonate (FEC) and sometimes other additives such as bis(2,2,2-trifluoroethyl) ether (BTFE). An important point is that an electrolyte formulation cannot be simply copied from somewhat analogous Li-ion batteries and need to be tailored for a particular combination of electrodes in a Na-ion cell<sup>[3,4]</sup>.

An important consideration in Na-ion batteries is the possibility of avoiding the use of copper current collectors in the negative electrodes and aluminium can be used instead as a cheaper alternative. This is related to the lack of parasitic alloying of sodium with aluminum, which is, unfortunately, a problem that exists for lithium in Li-ion cells.

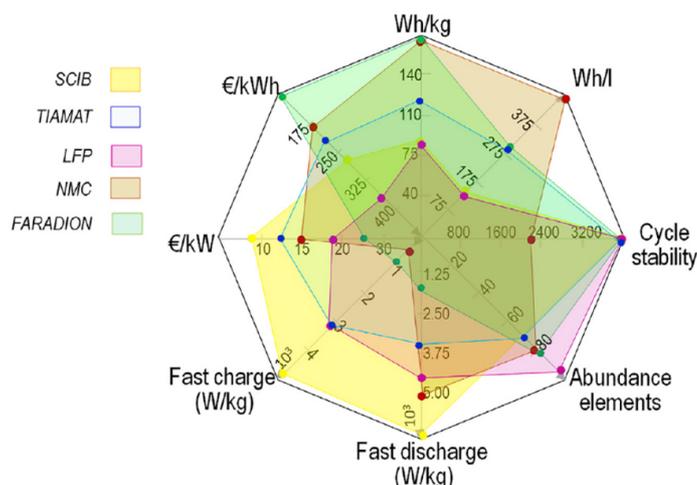
In his viewpoint published in ACS Energy Letters, Abraham raises a question on how comparable Na-ion batteries are to their Li-ion counterparts<sup>[3]</sup>. This is discussed through the consideration of actual and hypothetical batteries assembled in the format of 18650 cells and the analysis of their specific energies (Wh/kg) and energy densities (Wh/L). Li-ion batteries [graphite - LiCoO<sub>2</sub> (3.7 V, 206 Wh/kg, 530 Wh/L), graphite - LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub> (3.6 V, 210 Wh/kg, 530 Wh/L), graphite - LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (3.6 V, 285 Wh/kg, 785 Wh/L), graphite - LiFePO<sub>4</sub> (3.4 V, 126 Wh/kg, 325 Wh/L) and graphite - LiMn<sub>2</sub>O<sub>4</sub> (3.8 V, 132 Wh/kg, 340 Wh/L)] are used as established benchmarks. In turn, three Na-ion battery prototypes are considered - a commercial Na-ion battery prototype from CNRS CEA (90 Wh/kg and estimated 250 Wh/L), a Na-ion battery prototype from the joint work of Washington State University and Pacific Northwest National Laboratory utilising an O3-type layered oxide NaNi<sub>0.68</sub>Mn<sub>0.22</sub>Co<sub>0.10</sub>O<sub>2</sub> (2.7 V, 150 Wh/kg, 375 Wh/L) and a Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>-based Na-ion cell built by European research centre ALISTORE (3.5 V, 75 Wh/kg). It should be noted that the specific energy of the latter cell is likely underestimated in Abraham's consideration, as a value of energy at a high 1C rate is taken into account.

Considering the above values, it is concluded in Abraham's viewpoint that Na-ion cells are not comparable to high-energy Li-ion batteries such as those with LiCoO<sub>2</sub> (LCO), LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub> (NMC) or LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) cathode chemistries<sup>[3]</sup>. However, some of the emerging Na-ion batteries may have specific energies and energy densities close to those of Li-ion cells with LiFePO<sub>4</sub> (LFP) cathode chemistry. It may be therefore expected that similar applications (e.g., electric vehicles with short range, power backup or energy storage systems used with localised renewable energy generators) may be envisaged for Na-ion batteries. Moderate energy contents per mass or volume in Na-ion batteries may be traced to the behaviour of many cathode materials; it is commonly observed that Na-containing cathode candidates have a reduced capacity and a smaller average operating voltage than their lithium counterparts. As an example, the voltage - capacity profiles for Na<sub>1-x</sub>CoO<sub>2</sub> and Li<sub>1-x</sub>CoO<sub>2</sub> may be compared [Figure 1]<sup>[1]</sup>. Concluding his assessment, Abraham also envisages that some cost reduction may be possible in Na-ion batteries (10%-20% cheaper than their Li-ion counterparts) in the long term and cites the sustainability (Li- and Co-free nature) as the major advantage of these new batteries. He also emphasises that their energy densities are much superior to those offered by old-school battery types in the form of lead-acid, nickel-cadmium and nickel - metal hydride cells<sup>[3]</sup>.

Similarly, the commentary by Tarascon is concerned with distinguishing between the hype associated with the earlier development of Na-ion batteries and reality<sup>[4]</sup>. His discussion is based on the cells publicized by three start-up companies in this space, Faradion (layered oxide cathode chemistry) Tiamat (Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> cathode chemistry) and Novosis (using Prussian blue analogue as a cathode). These cells are compared with graphite - LiFePO<sub>4</sub> batteries and, importantly, with Toshiba's Super Charge Ion Battery (SCIB) cells. The latter benchmark is new in our discussion (not considered previously in Abraham's viewpoint<sup>[3]</sup>) and is very interesting as these batteries represent another category of Li-ion cells - specialised low energy, high power batteries. A spider diagram [Figure 2] represents a comparison of various parameters of the cells under consideration<sup>[4]</sup>. One minor criticism addressed to Figure 2 may be the specific energy and energy density of LFP cells, which seems lower than the usually publicized data. In the opinion of the author of this Research Highlight, higher values should have been used for the LFP cells in the benchmarking exercise.



**Figure 1.** Comparison of charge-discharge curves of Li/LiCoO<sub>2</sub> and Na/NaCoO<sub>2</sub> half-cells. Schematic illustration of Li(Na)CoO<sub>2</sub> crystal is also shown. Reprinted with permission from<sup>[1]</sup>. Copyright 2014 American Chemical Society.



**Figure 2.** Tentative comparison between high power cells relying on Na-ion technology either in 18650 format from TIAMAT [Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> (NVPF)/Hard Carbon] or pouch cells [Na<sub>x</sub>M<sub>1-y-z</sub>M'<sub>y</sub>M''<sub>z</sub>O<sub>2</sub>/Hard Carbon] from FARADION and on Li-ion technology in 18650 format (LiFePO<sub>4</sub>(LFP)/Graphite and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>/Graphite) and pouch cells (SCIB [NMC/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>]). Reprinted with permission from<sup>[4]</sup>. Copyright 2020 Cell Press.

It is highlighted that polyanionic materials may have a higher importance in Na-ion batteries<sup>[4]</sup>. In Li-ion batteries, the layered oxides are usually dominant, except for the specific cases of LiFePO<sub>4</sub> or spinel LiMn<sub>2</sub>O<sub>4</sub>. Despite a high abundance of sodium layered oxides, their advantages are less pronounced due to the typically reduced (lower) potentials of their electrochemical reactivity (an observation similar to that by Abraham<sup>[3]</sup>) with respect to those of similar compounds in lithium-based cells. At the same time, a better diffusion of a shuttle ion (Na<sup>+</sup> instead of Li<sup>+</sup>) is expected in polyanionic materials in Na-ion batteries, and air processing (instead of dry room processing) may be applied to these materials<sup>[4]</sup>. Tarascon highlights that Tiamat's 18650 cells (Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>-based) can deliver a specific energy of 122 Wh/kg at 1C (a higher value that quoted by Abraham) vs. 150 Wh/kg for the Faradion's pouch cells employing an O3 or O3-P2 intermixed (inter-grown) NaNi<sub>(1-x-y-z)</sub>Mn<sub>x</sub>Mg<sub>y</sub>Ti<sub>z</sub>O<sub>2</sub> layered phases at C/3 (much slower) rate. The quoted specific energies of these cells are clearly much lower than those of comparable Li-ion cells with layered

oxide cathodes (higher than 250 Wh/kg). Thus, Tarascon reaches the same conclusion as in the previous viewpoint: Na-ion batteries are clearly inferior in terms of their energy densities (or specific power) to some of the more energy-dense Li-ion batteries but may be comparable to some of the more specialised long stability or high power Li-ion battery cells such as graphite -  $\text{LiFePO}_4$  or Toshiba's SCIB cells<sup>[4]</sup>.

Another possible Na-ion battery chemistry based on the use of Prussian blue analogues (technology trialed commercially, for example, by Novosis) is also mentioned briefly in the assessment by Tarascon<sup>[4]</sup>. However, the cell-level metrics are not provided, and the discussion is brief. It is mentioned that the morphology and moisture content control may represent challenges for this cathode chemistry, and the energy density (in Wh/L) may be on the lower side for such cells due to the low density of the cathode material.

As a researcher with first-hand knowledge of the commercialisation effort in Na-ion batteries, Tarascon provides extra remarks on the specific advantages of these new cells not directly considered in the viewpoint by Abraham<sup>[4]</sup>. One of such remarks concerns the extra safety of Na-ion batteries. This characteristic originates from the fact that, unlike Li-ion batteries, their sodium counterparts can be shorted by connecting the opposite battery terminals without an irreversible consequence for the battery performance. As a result of this very practical property, the transportation and storage of Na-ion batteries is much easier. In the case of Li-ion batteries, they need to be treated as dangerous goods, with special safety measures linked to their inherent flammability and ability to explode. In contrast, for the batteries that can be temporarily shorted, the requirements for transportation and storage in the discharged state are much softer, favouring the adaptation of Na-ion cells in practice<sup>[4]</sup>.

One of the considerably advantageous attributes of Na-ion cells that Tarascon envisages in his commentary is their capability of fast charge and performing as high power cells, particularly in the Tiamat's cells with vanadium fluorophosphate chemistry. Their specific power compares favourably with LFP-type Li-ion batteries while offering, according to the author, better cost in terms of €/kWh or €/kW. The fast charge ability is also not dissimilar to Toshiba's SCIB cells. While this property is somewhat inferior in Tiamat's Na-ion cells, they offer an advantage of a higher voltage (3.7 V vs. 2.7 V) and better specific energy and energy density parameters than those of SCIB batteries. The commentator envisages that sodium-based cells may find applications in "power-hungry functions", including regenerative braking and fast-charging public transport<sup>[4]</sup>.

In conclusion, both expert commentators assessed the expected performance, advantages and applications of Na-ion batteries. It is highlighted that Na-ion cells are unlikely to be a true replacement for Li-ion batteries in all applications. This is linked to their relatively limited energy density with respect to that achievable by Li-ion batteries with layered cathodes (in LCO, NMC and NCA chemistries). Instead, Na-ion batteries (pioneered commercially by Faradion and Tiamat and also those assessed by the researchers from Washington State University and Pacific Northwest National Laboratory) with specific energies at the level of 120-150 Wh/kg are more comparable to LFP Li-ion batteries or specialised fast-charge SCIB batteries marketed by Toshiba. Specific advantages of Na-ion batteries include their excellent sustainability (the lack of critical elements such as lithium and cobalt), increased safety (an ability to be shorted during storage and transportation) and excellent fast charge capabilities and power densities for the  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ -based cells. Possible applications for Na-ion batteries include regenerative braking and other "power-hungry functions" such as fast-charging e-buses, and the uses where LFP Li-ion batteries could have been otherwise considered (electric vehicles with short range, power backup or energy storage systems used with localised renewable energy generators).

This Research Highlight lags behind the two original commentaries by approximately two years. Therefore, it is interesting to reflect on what has changed since those were published. The notable developments include a larger number of start-ups and established commercial companies venturing in the space of Na-ion batteries. In addition to Faradion<sup>[5]</sup>, Tiamat<sup>[6]</sup> and Novosis already discussed, Na-ion cells are being worked on by HiNa Battery (layered oxide chemistry)<sup>[7]</sup>, Altris and Natron Energy (Prussian blue analogues)<sup>[8,9]</sup>. It is interesting to note that the realisation that Na-ion cells can be subdivided into different classes, for example, “higher energy content” cells and “high power cells”, firms up. In particular, Tiamat aims to add “higher energy content cells” as a separate product to their more established fast-charge batteries under development. Finally, it is newsworthy to highlight the direct participation of a major battery company in this space; China-based Contemporary Amperex Technology Co. Limited (CATL) has joined the ranks of emerging Na-ion battery manufacturers in 2021<sup>[10]</sup>. The commercialisation of Na-ion batteries is clearly in full swing, and it will be very interesting to follow up with further developments.

## DECLARATIONS

### Author' contributions

The author contributed solely to the article.

### Availability of data and materials

Not applicable.

### Financial support and sponsorship

None.

### Conflicts of interest

The author declared that there were no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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