

How Comparable Are Sodium-Ion Batteries to Lithium-Ion Counterparts?

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A recent news release from Washington State University (WSU) heralded¹ that “WSU and PNNL (Pacific Northwest National Laboratory) researchers have created a sodium-ion battery that holds as much energy and works as well as some commercial lithium-ion battery chemistries, making for a potentially viable battery technology out of abundant and cheap materials”. Naturally this news created a lot of excitement in the battery community and the general public to the extent that some even suggested that a new sodium (Na)-ion battery would replace the expensive lithium-ion batteries. The excitement encouraged this author to take a deep dive into the original WSU/PNNL reports in *ACS Energy Letters*,^{2,3} examine the state of the art of Na-ion battery technology, and compare it to the mature and ubiquitous lithium (Li)-ion batteries. This Viewpoint, borne out of this enquiry, seeks to answer the question “how comparable are sodium-ion batteries to lithium-ion counterparts”. It is not a comprehensive review of Na-ion batteries as several such reports have appeared elsewhere recently.^{4–6}

The chemistry and electrochemistry of electrode materials for Na-ion batteries are sufficiently different from that of their Li-ion counterparts that candidates suitable for practical batteries have become available only recently. Figure 1 displays the schematic of a Na-ion battery cell. It has a structure similar to that of Li-ion batteries.⁷ Laboratory test cells and

representative prototype cells have been built and evaluated with hard-carbon anodes and cathode materials selected from layered transition metal oxides, transition metal fluorophosphates, and Prussian blue and its analogues.^{4,5,8–10}

Layered transition metal dioxides, NaMO₂, where M = Fe, Ni, Mn, Co etc., exist in O3 and P2 crystallographic versions. In the O3-NaMO₂ phase, Na resides in octahedral sites, while in the P2-phase Na is in prismatic sites.

The electrode reactions in a Na-ion battery utilizing hard-carbon (C₆) anode and a layered transition metal oxide, NaMO₂, cathode are depicted in eq 1. The discharged electrodes are on the right-hand side of eq 1.



The NaCoO₂ cathode, like LiCoO₂, is initially brought into the Na-ion cell in the discharged state, and the cell is activated by charging first to form the Na intercalated anode and Na deintercalated cathode in the fully charged cell. The charge and discharge voltage versus capacity curves of Li/Li_{1-x}CoO₂ and Na/Na_{1-x}CoO₂ half-cells compared in Figure 2⁴ reveals stepwise voltage profiles for the Na cell. They reflect the multiple phase changes of the NaCoO₂ crystals as Na is deintercalated from it to form Na_{1-x}CoO₂ during charge, and vice versa during discharge. Both LiCoO₂ and NaCoO₂ have the same O3 crystal structure consisting of CoO₂ slabs alternately accommodating Li⁺ or Na⁺ ions between the slabs along the *c*-axis of the A_{1-x}CoO₂ crystal (where A = Li or Na). The crystal structure changes of NaCoO₂ in a Na cell begin with the removal of Na during the first charge. Sodium ions in the O3-type phase are originally stabilized at edge-shared octahedral sites within the MO₆ octahedra. When Na⁺ ions are partly extracted from the O3-phase, those Na⁺ present at prismatic sites become energetically stable and transform the crystal to a P3-phase by the sliding of MO₂ slabs without breaking M–O bonds. This conversion between the prismatic and octahedral phases by sliding the MO₆ slabs occurs in just about all the layered transition metal oxides when they are used as cathodes in Na-ion batteries. The result is multiple

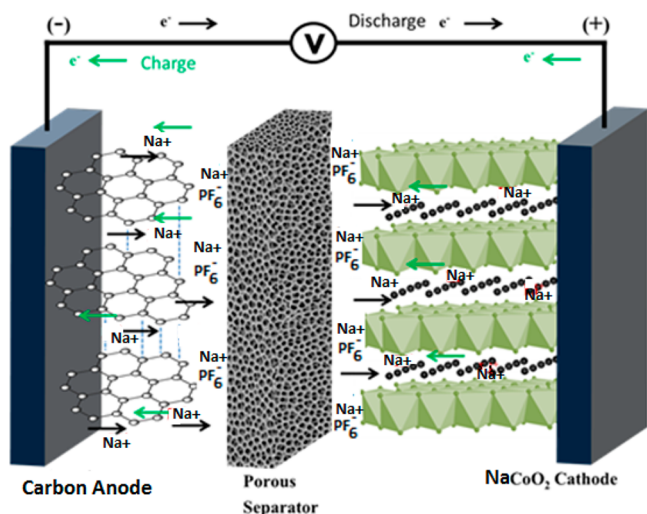


Figure 1. Schematic representation of a Na-ion battery cell.

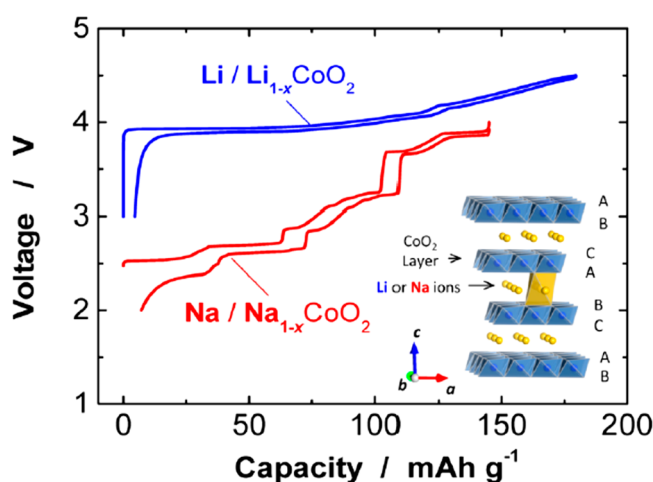


Figure 2. Comparison of charge–discharge curves of Li/LiCoO₂ and Na/NaCoO₂ half-cells. Schematic illustration of Li(Na)CoO₂ crystal is also shown (reprinted from ref 4, copyright 2014 American Chemical Society).

voltage plateaus in the cell's voltage versus capacity curves reflecting the phase changes (Figure 2). Mixed metal oxide cathodes exhibit additional voltage plateaus in Na-ion cells, reflecting the oxidation states of the different metals being reduced and oxidized during cell discharge and charge. The NaCoO₂ electrode has a rechargeable capacity of about 150 mAh/gram at an average voltage of 3 V. Layered transition metal dioxides investigated as Na-ion battery cathodes include NaFeO₂, NaNiO₂, NaCrO₂, NaVO₂, and NaTiO₂ and mixed metal dioxides derived from them such as NaFe_{1/2}Co_{1/2}O₂, NaNi_{1/3}Fe_{1/3}Co_{1/3}O₂, NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂, and NaNi_{1/4}Fe_{1/4}Co_{1/4}Mn_{1/4}O₂.^{4,5,8,9} The WSU/PNNL Na-ion battery which motivated the writing of this Viewpoint utilizes a mixed metal oxide of the composition NaNi_{0.68}Mn_{0.22}Co_{0.10}O₂ with an O3-type layered crystal structure.²

A variety of metal phosphates and fluorophosphates have also been studied as Na intercalation cathodes for Na-ion batteries. Among these are NaFePO₄ (triphylite-type), Na₂Fe(P₂O₇), Na₄Fe₃(PO₄)₂(P₂O₇), Na₂FePO₄F, and Na/Na₂[Fe_{1/2}Mn_{1/2}]PO₄F.^{4,5} Other metal phosphates examined include Na₃V₂(PO₄)₂F₃, Na₃V₂(PO₄)₃, and Na₄Co_{2.4}Mn_{0.3}Ni_{0.3}(PO₄)₂P₂O₇ (see Figure 23 in ref 5). Among these, Na₃V₂(PO₄)₂F₃ showed reasonable performance in Na half-cells at room temperature with a reversible capacity of about 135 mAh/g at an average voltage of 3.8 V.

Miscellaneous cathode materials investigated as Na-ion battery cathodes include Prussian blue and its analogues, KFe₂(CN)₆ and MnFe(CN)₆, and the iron(III) system Fe₂(CN)₆ without alkali metal ions.⁴ They show reversible capacities of 80–120 mAh/g in Na half-cells at voltages of 3–3.5 V. A Prussian blue analogue material, Na_{1.92}Fe₂(CN)₆, described as Prussian white, has shown a discharge capacity of 160 mAh/g at low rates with good rechargeability in a Na half-cell.¹⁰ A drawback of Prussian blue and its analogues is low density. For example, Prussian blue has a density of 1.8 g/cm³, which would provide lower volumetric energy densities for Na-ion batteries, compared to those using transition metal oxide cathodes of the same specific capacity (in mAh/g).

The anode material in most studies has been hard-carbon, although other low-voltage Na intercalating materials such as Na₂Ti₃O₇, Na₃Ti₂(PO₄)₃, and Na alloys have been inves-

tigated.^{4–6,11} A hard-carbon anode has a practically useful reversible capacity of about 250 mAh/g, corresponding to the formation of Na_{0.67}C₆ at an average voltage of 0.25 V versus Na/Na⁺.⁴ Electrode materials useful for anodes in Na-ion batteries should have low Na intercalation and deintercalation voltages, preferably below 0.5 V versus the Na/Na⁺ electrode, and capacities exceeding 250 mAh/g. Note that it is the Na deintercalation voltage of the anode material that is important because Na⁺ ions are deintercalated from the anode and intercalated into the cathode during discharge of a Na-ion cell. The difference between these two electrode voltages is the cell voltage.

The choice of the electrolytes is important for developing practical Na-ion batteries. Organic carbonate solvent-based electrolytes containing sodium salts such as NaPF₆, NaN(SO₂CF₃)₂, and NaClO₄ are used together with small amounts of additives to stabilize the anode and cathode during cycling.⁸ The aforementioned WSU/PNNL cell used the additive bis(2,2,2-trifluoroethyl) ether (BTFE), while other studies have used fluoroethylene carbonate (FEC).¹² Typically, mixed organic carbonate solvents selected from ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC) are used to produce electrolytes that provide optimal discharge and charge over a wide temperature range, thermal stability, high rate capability, and long cycle life and shelf life in Na-ion batteries.⁸

Sodium-Ion Battery Prototypes. An 18650-size cell reported by the French research agency CNRS CEA appears to be the first Na-ion battery commercial product.¹³ Note that the number 18650 comes from the dimensions of a cylindrical cell in a metal container having 18 mm diameter and 65 mm height. In the case of Li-ion batteries, an 18650 cell is the most advanced commercial cell in terms of engineering and chemistry. The CEA Na-ion cell reportedly has a specific energy of 90 Wh/kg and was cycled more than a thousand times. However, no information was provided on electrode and electrolyte materials used, cell capacity, voltage, and cycling parameters. The cell was claimed to be high-power capability. We can estimate a few additional specifications of this cell as follows. First, assume that the cell has a weight of 46 g similar to the weight of a commercial 18650 Li-ion cell.⁷ Then, the energy of the 18650 Na-ion cell is 4.14 Wh. The volume of the 18650 cylindrical metal housing is 16.5 mL. Therefore, the volumetric energy density of this 4.4 Wh Na-ion cell is 250 Wh/l. We can now estimate from the 4.14 Wh energy and an average voltage of 3 V, as found in many Na-ion cathode materials, that the CEA 18650 Na-ion cell has a capacity of 1.38 Ah (4.14 Wh divided by 3 V).

Now let us take a look at the Na-ion battery described in the Washington University/PNNL announcement.^{1,2} It has a hard-carbon anode and utilizes O3-NaNi_{0.68}Mn_{0.22}Co_{0.10}O₂ as the cathode material. At the C/10 rate of 0.25 mA/cm², the cell delivered a capacity of 184 mAh/g based on the hard-carbon anode and 141 mAh/g based on the metal oxide cathode. A pouch cell of 60 mAh capacity exhibited a specific energy of 290 Wh/kg based on the active materials which the authors extrapolate to a practical specific energy of 156 Wh/kg. This estimated value of the WSU/PNNL Na-ion battery is much higher than what was actually found in the aforementioned CEA 18650 cell. It should be noted that the 156 Wh/kg is an extrapolated value from the specific energy of 290 Wh/kg determined for electrodes, using a conversion factor of 55%,

taking into account the masses of the electrolyte, electrode current collectors, separator, metal container, and other inert materials, as found in commercial 18650 Li-ion cells.

We can estimate the practical specific energy for another Na-ion cell, fabricated from the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode mentioned earlier⁵ and hard-carbon anode. This cell has a voltage of 3.5 V, and its specific energy is 295 Wh/kg based on the electrode materials. At 50% laboratory cell to commercial cell conversion efficiency, a practical cell from this chemistry would exhibit about 150 Wh/kg, similar to the estimated value for the WSU/PNNL cell. It is interesting to note that Alistore-European research agency¹⁴ built an 18650 cell using an $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ cathode and a hard-carbon anode, and it demonstrated 75 Wh/kg and 4000 cycles at the 1C rate. Clearly, the specific energy of this 18650 cell is only half of the value estimated above from electrode capacities in lab cells.

Realistically, considering the reversible capacities and voltages of the numerous cathode materials examined and the specific capacity of hard-carbon anode of about 250 mAh/g, a specific energy of 100–150 Wh/kg appears to be the best that can be expected for a fully developed Na-ion battery. From the rate capability information available for the electrode materials in Na battery cells and the reported Na^+ diffusion coefficients in cathode and anode materials,¹⁵ Na-ion batteries can be expected to provide good rate capability comparable to that of Li-ion batteries. An important question to answer for this discussion is “how do Na-ion batteries compare to their Li-ion counterparts” in terms of energy densities, cost, applications, and overall consumer acceptance.

How Do Sodium-Ion Batteries Compare to Their Lithium-Ion Counterparts? In order to answer this question let us first take a look at the specific energies and energy densities of commercial Li-ion batteries. The highly engineered 18650 size cells are the most appropriate for this comparison. Specific energies of 18650 size commercial Li-ion batteries with graphite anode (~ 350 mAh/g capacity) and different types of cathodes are presented in Table 1.⁷ The cells with the layered transition metal cathodes LiCoO_2 (LCO), $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC), and $\text{LiN}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) have capacities of 2.4, 2.4, and 3.6 Ah, respectively, which convert to specific energies of 206, 210, and 285 Wh/kg, respectively, and to volumetric energy densities between 530 and 785 Wh/L. The cells with LiFePO_4 and LiMn_2O_4 cathodes have lower specific

energies of about 130 Wh/kg and volumetric energy densities of around 330 Wh/L. Considering the reversible capacities of the various Na intercalating metal oxide and metal phosphate cathode materials presented in this account, we can project that 18650 size Na-ion cells utilizing these cathodes and hard-carbon anodes will have specific energies around 150 Wh/kg at best, closer to that of Li-ion cells with LiFePO_4 cathode. What that says is that Na-ion batteries, when fully developed, would be suitable for applications similar to those where LiFePO_4 batteries are currently deployed. These include short-range electric vehicles; energy storage systems (ESS) for solar, wind and other alternative energy conversion facilities; power backup in electric utilities; and many other applications where energy density required of the battery is less demanding than that offered by their Li-ion batteries but substantially higher than the energy densities of the traditional rechargeable batteries Pb-acid, Ni/Cd, and Ni/MH.⁷

The foremost advantage of Na-ion batteries comes from the natural abundance and lower cost of sodium compared with lithium. The abundance of Na to Li in the earth's crust is 23600 ppm to 20 ppm, and the overall cost of extraction and purification of Na is less than that of Li. Moreover, Na-containing metal oxide and polyanion cathode materials can be fabricated from naturally abundant transition metals such as iron, manganese, vanadium, and titanium, without using cobalt, making Na-ion batteries sustainable and affordable in rich and poor countries alike.

Sanders from Avicenne, a French battery market forecast company, has reported¹⁶ that the worldwide Li-ion battery market will grow to more than \$150 billion by 2025. The ESS market alone is expected to be >\$50 billion. The higher volume of battery materials production in response to this rising market is expected to reduce the cost of Li-ion batteries at the pack level to about \$100/kWh from the present \$150/kWh.

According to Sanders, the cathode is the costliest component of a Li-ion battery at about 25% of the total cost. An examination of Li-ion and Na-ion battery components reveals that the nature of the cathode material is the main difference between the two batteries. Because the preparation cost of the cathode from raw materials is more or less the same for both Li-ion and Na-ion technologies, the main cost reduction for Na-ion batteries comes from raw materials. On the basis of the information currently available we can project the cost of Na-ion batteries to be about 10–20% less than that of their Li-ion counterparts.

The major advantage of Na-ion batteries is sustainability, which is important for a world striving to be free of carbon-based energy sources. We can foresee Na-ion batteries with hard-carbon anodes and cobalt-free cathodes as sustainable lower-cost alternatives to Li-ion batteries for applications such as short-range electric vehicles and large-scale energy storage (ESS) in a world that is increasingly being transformed to wind, solar, and hydroelectric power, which depend on battery energy storage for uninterrupted, around-the-clock, performance.

Future research should focus on discovering advanced anode and cathode materials for Na-ion batteries with higher specific capacities and voltages so as to produce practical Na-ion batteries with specific energies approaching 200 Wh/kg. Efforts should also be made to develop advanced electrolytes that enable Na-ion battery performance at high charge–discharge rates over a wide temperature range while exhibiting the long

Table 1. Specific Energies and Energy Densities of 18650 Size Li-Ion and Na-Ion Batteries

battery (18650 cell)	voltage (V)	specific energy of 18650 Li-ion cell (Wh/kg)	energy density of 18650 Li-ion cell (Wh/L)
graphite(C)/LiCoO ₂ - (Li-ion)	3.7	206	530
C/LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂ - (Li-ion)	3.6	210	530
C/LiN _{0.8} Co _{0.15} Al _{0.05} O ₂ - (Li-ion)	3.6	285	785
C/LiFePO ₄ - (Li-ion)	3.4	126	325
C/LMn ₂ O ₄ - (Li-ion)	3.8	132	340
CNRS CEA 18650 cell - (Na-ion) (ref 13)		90	250 (estimated; see text)
PNNL-WSU 18650 cell - (Na-ion) (values estimated from ref 2)	2.7	150	375
ALISTORE 18650 cell - (Na-ion) (ref 14)	3.5	75	

cycle-life and shelf life required for large-scale energy storage applications. Research also should focus on gaining a deeper understanding of the crystal structure–ion transport property relationships in Na intercalation electrodes in order to acquire the ability to systematically design and develop high-capacity, reversible electrodes for Na-ion batteries. Research and development efforts should also continue on Na-ion battery prototypes with particular emphasis on evaluating their temperature- and rate-dependent performance and safety hazards.

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Notes

Views expressed in this Viewpoint are those of the author and not necessarily the views of the ACS.

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