

## Sodium-Ion Battery Technologies

Sodium-ion batteries are a type of reusable battery that uses sodium ions as charge carriers. The battery-grade salts of sodium are cheap and abundant, much more so than those of lithium. This makes them a cost-effective alternative especially for applications where weight and energy density are of minor importance such as grid energy storage for renewable energy sources such as wind- and solar power.<sup>[1][2]</sup>

## Applications

As of 2014 Aquion Energy offered a commercially available sodium-ion battery with cost/kWh capacity similar to a lead acid battery for use as a backup power source for electricity micro-grids.<sup>[3]</sup>

Another company, Faradion, offered for license a range of low-cost sodium-ion materials, which are a drop-in replacement for established lithium-ion technology.<sup>[4]</sup> Unlike sodium-sulfur batteries,<sup>[5]</sup> sodium ion batteries can be made portable and can function at room temperature (approx. 25°C). Sodium-ion also offers enhanced safety and transportation features, particularly over lithium-ion.

## Energy Storage

Like all batteries, the sodium ion battery stores energy in chemical bonds of its anode. When the battery is charging Na<sup>+</sup> ions de-intercalate and migrate towards the anode. Meanwhile charge balancing electrons pass from the cathode through the external circuit containing the charger and into the anode. During discharge the process reverses. Once a circuit is completed electrons pass back from the anode to the cathode and the Na<sup>+</sup> ions travel back to the cathode.<sup>[6]</sup>

Sodium ion cells have been reported with a voltage of 3.6 volts, able to maintain 115 Ah/kg after 50 cycles, equating to a cathode-specific energy of approximately 400 Wh/kg.<sup>[7]</sup> Inferior cycling performance limits the ability of non-aqueous Na-ion batteries to compete with commercial Li-ion cells. Faradion claimed to have improved cycling in full Na-ion pouch cells using a layered oxide cathode.<sup>[8]</sup>

## Anode

Using Na<sub>x</sub>C<sub>6</sub> as the anode, the average voltage on the low potential plateau was higher on Na cells compared to Li cells. Unlike traditional Li cells, which make use of an intercalated graphite anode with a fully lithiated stoichiometry of LiC<sub>6</sub>, Na cells do not reversibly bind graphite. This is in part due to the larger ionic radius of the Na<sup>+</sup> ion compared to the Li<sup>+</sup> ion, which causes the graphite to expand. For this reason, carbon-based anodes rely on amorphous carbon consisting of spatially disoriented graphene sheets, defect and interstitial pores. These amorphous carbon allotropes can be categorized into a dichotomy of hard and soft. Hard carbons cannot be transformed into graphite through annealing at high temperatures, while soft carbons can be. The hard carbon materials can be derived from a variety of feed stocks such as: sugar, starch, fiber and certain polymers.<sup>[9]</sup>

In addition to carbon anodes, alloying different types of anode with additives such as Antimony (Sb), Tin (Sn), Phosphorus (P), Germanium (Ge) and Lead (Pb) can also yield results. As opposed to carbon anodes, which merely provide organic complexes for the storage of Na<sup>+</sup> ions, alloyed anodes form inorganic complexes with the Na<sup>+</sup> ions such as Na<sub>3</sub>Sb, Na<sub>3</sub>Sn and Na<sub>3</sub>P. This capability gives alloy anodes a greater theoretical capacity than carbon. Whereas amorphous carbon based carbon anodes have shown capacity between 300-400 mAh g<sup>-1</sup>, a Na<sub>3</sub>P anode has a theoretical capacity of 2596 mAh g<sup>-1</sup>. However, the alloying process causes an extremely large volume change, sometimes nearing 400%, in the anode. This large volume change results in the fractures and displaces the alloying material, which causes it to passivate and become 'dead weight', unable to accept sodium ions. Unchecked, these

large volume changes reduce cycle life. For this reason, much of the research conducted in the area of anode alloys focuses on mitigating the volume changes that happen upon sodiation, as well as reducing their negative effects.

## Cellulose

In one study, tin-coated wood anodes replaced stiff anode bases that are too brittle to withstand the swelling and shrinking that happens as ions come and go. Wood fibers proved supple enough withstand more than 400 charging cycles. After hundreds of cycles, the wood ended up wrinkled but intact. Computer models indicated that the wrinkles effectively reduce stress during charging and recharging. Na ions move via the fibrous cell walls and diffuse at the tin (Sn) film surface.<sup>[10][11]</sup>

Another researcher published a way to use MoS<sub>2</sub>/graphene composite paper as an electrode, yielding 230 Ah/kg with Coulombic efficiency reaching approximately 99%..<sup>[12][13][14]</sup>

## Cathode

Tests of Na<sub>2</sub>FePO<sub>4</sub>F and Li<sub>2</sub>FePO<sub>4</sub>F cathode materials indicated that the sodium iron phosphate cathode can replace a lithium iron phosphate cathode in a Li cell.<sup>[7]</sup> The lithium-ion and sodium-ion combination would lower manufacturing costs.<sup>[7]</sup>

P2-Na<sub>2/3</sub>[Fe<sub>1/2</sub>Mn<sub>1/2</sub>]O<sub>2</sub> delivered 190 Ah/kg of reversible capacity in sodium cells using electrochemically active Fe<sup>3+</sup>/Fe<sup>4+</sup> redox at room temperature.<sup>[15]</sup> Triclinic Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> was examined as rechargeable sodium ion batteries by a glass-ceramics method. The precursor glass, also made of Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub>, was prepared by melt-quenching. Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> exhibits 2.9 V, 88 Ah/kg.<sup>[16]</sup>

Separately, chromium cathodes employed the reaction:



The effects of Cr doping on cathode performance materials was analyzed in terms of crystal structure, charge/discharge curves and cycle performance and indicated that the Cr-doped materials expressed better cycle stability. The initial reversible capacity was 83.3 Ah/kg and the first charge/discharge efficiency was about 90.3%. The reversible capacity retention of the material was 91.4% after the 20th cycle.<sup>[7][17]</sup>

Cathode materials	First charge capacity (Ah/kg)	First discharge capacity (Ah/kg)	Capacity loss in the first cycle (Ah/kg)	Reversible efficiency in the first cycle (%)	Discharge capacity after 20 cycles (Ah/kg)	Capacity retention ratio after 20 (%)
NaV <sub>0.92</sub> Cr <sub>0.08</sub> PO <sub>4</sub> F	83.3	75.2	8.1	90.3	68.8	91.4
NaV <sub>0.96</sub> Cr <sub>0.04</sub> PO <sub>4</sub> F	93.3	82.6	10.7	88.5	67.9	82.2
NaVPO <sub>4</sub> F	106.9	87.7	19.2	82.0	64.5	73.5

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