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Na-ion vs. Li-ion batteries: complementarity rather than competitiveness

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Rechargeable electrochemical batteries, as one of the most versatile energy storage technologies, play a central role in the ongoing transition from fossil fuels to renewable energy for achieving a greener planet. They are the key tools to lower the CO_2 footprint of both vehicle transportation and power grid sectors and are essential in a broad range of strategic industries. Our increasing dependence to batteries that are becoming the heart of our society raised several questions about materials abundance, so that sustainability is becoming an overriding factor. This has led to a booming diversification of the battery research on new chemistries such as Li(Na/Al)-air, Li-S, Mg(Ca)-ion, Na(K)-ion or aqueous Zn-MnO_2 systems. Interestingly, none of these technologies are truly new but solely brought back to the scene by key papers published in high impact journals stating their capabilities for solving the planet's energy storage issues. Oftentimes the media creates a hype, few scientists keep excitements, programs are launched at the national level, new start-up companies relying on private funding are launched, but too frequently promises turn into disillusion as recently demonstrated by the Li-air technology. Distinguishing between hype and reality within the outgrowing literature on a societal and business-driven research topic such as batteries is becoming a real burden for both young scientists and industrial entities seeking to access the market. Therefore, pressure is on specialists with decades of knowledge on batteries to clarify certain facts.

None of the aforementioned "beyond Li-ion" battery technologies have reached the maturation stage yet, but Na-ion is the closest to this goal having given birth to a few companies: **F**aradion (UK), **N**ovosis (USA), HiNa (China) and **T**iamat (France) to name a few. Herein, based on tangible experimental results and facts I will discuss the benefits and weakness of this technology with the hope to simplify researchers and investors' minds to make decisions.

The Na-ion technology enjoyed a speedy development in the past 8 years, simply by learning from the Li-ion chemistry that it mimics. We must recall that, back to 1980's, fundamental research on insertion compounds was parted between Li and Na-based ones. It is only because of the outstanding performance provided by Li-based materials owing to a greater redox potential of Li^+ while being less heavy, that Na^+ research nearly fell into oblivion. Because of increasing societal demands towards sustainability in the 2010's, scientists have reconsidered Na-ion batteries with the eagerness to identify the best positive and negative electrode materials together with the most suitable electrolyte for achieving stable solid electrolyte interface (SEI) while minimizing parasitic reactions; it is a recurrent problematic that has been driving the Li-ion research for last 30 years. This research driven by sustainability has also caught the eyes of industry, as the raw material Na_2CO_3 is much cheaper and less price-volatile than Li raw materials like Li_2CO_3.

A wide survey of electrode materials inspired from studies on Li-ion materials was launched and numerous Na-based insertion compounds were identified having similar structural types as their Li-ion counterparts. These belonged to similar families of layered oxides or polyanionic compounds for the positive electrode and of carbonaceous materials or intermetallic alloys for and negative electrode, respectively.[1, 2] Such findings combined with the feasibility to use Na-based electrolytes alike those of Li-ions in terms of solvents has been a gift to rapidly assemble full Na-ion cells based either of the polyanionic/C or layered/C chemistries and identify the potential of Na-ion technology. In both systems, carbonaceous negative electrode with capacities of ~300mAh/g were preferred over alloying (Na_xM) or conversion electrodes which suffer from large volume expansion, poor reversibility and large voltage hysteresis. The choice was not as straightforward to select the Na-ion positive electrodes but in light of the established supremacy of the layered oxides over polyanionic ones in

today's commercial Li-ion batteries, many scientists hastily decided to pursue the development of the former (Figure 1).

The Na-based layered oxides show an even richer crystal chemistry than the Li-ion ones owing to the ability of sodium to reside in both octahedral (O) and prismatic (P) environment as opposed to a single octahedral environment for Li.[2] However, such a structural difference not only accounts for changes in Na-stoichiometry and therefore in capacity, but it also equally explains why layered oxides are more prone to Na-driven structural phase transitions that reduce their lifetime and limit the power density (charging time). In practice, to alleviate the capacity limitation of the P-type layered oxides associated to its non-stoichiometry in sodium (~0.7-0.8 per formula unit), research has been shifted towards the stabilization of stoichiometric O3- Na_1MO_2 phases via the modification of the nature and content of the transition metals.[3] **F**aradion conceived Na-ion pouch cells with O3-$NaNi_{(1-x-y-z)}Mn_xMg_yTi_zO_2$ phases where more than 0.8 Na can be used and they claimed to reach a specific energy of 150 Wh/kg for the total cell weight at C/3 rate with an average voltage of 3.2 V.[4] For comparison, today's commercial Li-ion batteries based on layered oxides offer a much higher cell-level specific energy, i.e. in excess of 250 Wh/kg. Though the usage of abundant earth elements and the absence of Co is attractive, power performance of layered oxides is not spectacular and also in-depth analyses of high temperature performance and thermal stability are still to be realized.

Deviating from layered structures, the three-dimensional Na-based polyanionic phases such as phosphates ($NaFePO_4$), sulfates $Na_2Fe_2(SO_4)_3$, and flurophosphates ($NaVPO_4F$) were also heavily studied. By exploring the huge parameter space enlisting the material elemental composition and its crystal-electronic structure that determines the cathode's electrochemical performances, $Na_3V_2(PO_4)_2F_3$ (denoted NVPF) compound with its specific crystal structure consisting of open channels for fast Na^+ ions diffusion turns out to be the most attractive electrode from a practical point of view. It can reversibly release 2 Na^+ per formula unit (i.e.,128 mAh/g) at an average potential of 3.9V hence offering a material-level specific energy of ~507 Wh/kg comparable to ~580Wh/kg for $LiFePO_4$ (LFP), widely used as a positive electrode in Li-ion batteries. This gap between NVPF and LFP has almost been filled by harnessing the electrochemical activity of the third sodium of NVPF, via the formation of a disordered $Na_xV_2(PO_4)_2F_3$.[5] The NVPF/C chemistry has been successfully implemented in **T**iamat's 18650 prototype cells delivering 122 Wh/kg at 1C rate. The cells exhibit high power rate capability (90% at 1C) with long cycling life (>4000 cycles), however the inherent drawback being rooted in the use of toxic vanadium that scientists are trying to alleviate by replacing with less toxic and other abundant 3d metals (Mn).

Lastly, the Prussian blue phases, that are known for decades and long considered as electrodes for electrochromic devices that were never commercialized, are regarded as a reversible host positive electrode for Na-ion batteries. They adopt a three-dimensional structural framework whose compositions $Na_{2-\delta}MnFe(CN)_6.yH_2O$ has been the most attractive for Na-ion batteries as demonstrated by **N**ovosis.[4] The positive attributes of Prussian blue phases lies in their non-toxicity, high rate capability and easy synthesis provided we can reproducibly master their particle morphologies and water content that raises difficulties for achieving long lifetime in non-aqueous electrolytes. To curb this difficulty, a water free Prussian blue electrode was recently reported with capacity of 140 mAh/g at 1C rate with an average voltage of 3.4 V with still a modest energy density (volumetric) owing to the low material density (< 1.8 g/cm^3 as compared to 5.1 and 3.5 g/cm^3 for $LiCoO_2$ and $LiFePO_4$, respectively).[4,6]

Besides electrodes, another key to battery technologies is the electrolyte, which mainly governs their performances and lifetime. Initially, scientists blindly transposed the commonly used electrolytes for Li-ion to Na-ion by simply replacing $LiPF_6$ with $NaPF_6$. This strategy offered a rapid way to screen paired positive and negative electrodes in coin cells, but it fell short in achieving the figures of merits required for commercial applications.[7] We experienced this scenario with our first assembled 18650 prototypes based on NVPF//1M $NaPF_6$ in EC-DMC//C chemistry that show excellent electrochemical performance at 25°C, but mediocre performances at 55°C in terms of self-discharge and capacity retention. We identified the linear carbonate component of the electrolyte

(DMC), that is well used in Li-ion batteries, as the troublemaker. This could have been anticipated bearing in mind the milder Lewis acidity of Na^+ as compared to Li^+, that renders the Na-based carbonates more soluble that their Li counterparts, therefore leading to a poor stability of the protecting SEI layer on the C electrode. This backtrack was rapidly overcome via a trial-error approach relying on empirical synergy rules between various additives established for Li-ion electrodes, hence the discovery of an optimized electrolyte enabling to perform over a wide range of temperature with limited parasitic reactions.[8]

In light of such improvements dealing with either positive-negative electrodes and electrolytes, Na-ion batteries has been assembled either as 18650 or Pouch cells and companies such as **Ti**amat, **F**aradion and **N**ovasis hosting the NVPF, layered oxide and Prussian blue chemistry were respectively, created.[4,9] They are offering to users, via prototyping, several opportunities of applications/markets and therefore are providing momentum for the Na-ion technology acceptance. However, some skepticism prevails whose most frequent questions are: What are the chances of success and more so in which market sector this technology could be the winning one? To answer, we next highlight some of the identified advantages that this technology has against the Li-ion that is invading most of the energy storage related markets.

We should reiterate here that, though Na-ion technology mimics the Li-ion with similar types of electrodes and electrolytes, Na is 3 times heavier than Li and has redox potential 300 mV lower which inherently reduces the energy density of Na-ion technology at least by ~30% compared to Li-ion with such volumetric numbers be out of question for Prussian blue. We should also realize that this gap will prevail forever because progress that could be made at the materials level for Na will always be mirrored with progresses on Li since we are dealing with the same family of materials. So straightforwardly, the usage of Na-ion technology in applications requiring high energy density such as vehicle transportation sector is partly eliminated.

Besides energy density, another point of paramount importance is the power applications within the transportation sector for fast charging, breaking recovery and start-stop functions as well as within the grid sector for frequency adjustment. Within this context, Na-ion chemistries relying on the use of open 3-dimensional structures perform extremely well, (Figure 2) as demonstrated for NVPF, and outperform their Li counterparts. This can be illustrated by benchmarking **T**iamat's NVPF/C 18650 batteries against the Super-fast Charging lithium Ion Battery (SCIB) from **T**oshiba (Figure 2). Note that **T**iamat's cells compares favorably with SCIB's ones in terms of power rate while having a higher voltage (3.7 V vs. 2.7V). Thus, the Na-ion technology has definitively a key role to play in the automotive industry where power hungry functions (48 V, regenerative breaking) are needed. In such a case, such Na-ion cells compete favorably as well with high power $LiFePO_4$/C cells and a lower cost.

Another great asset of Na-ion against Li-ion is rooted in their ability to be discharged or maintained at zero volt without any risks of altering their subsequent performances.[4,10] Such advantage is simply rooted in the feasibility of using aluminum current collectors that do not alloy with Na as contrast to Li which forms an alloy (LixAl). Such alloying reaction has forced the use of a more expensive Cu negative current collector for Li-ion cells, which present risks of oxidation ($Cu \rightarrow Cu^{n+}$) when cells stand at zero volt. This difference offers a serious advantage to Na-ion cells that can be transported in their discharge state and therefore are free of legislative transportation rules. Further dealing with safety aspects, both systems are comparable with however the likelihood of having sodium dendrites at high charging rates being lower than for Li owing to the chemically softer nature of Na.

When dealing with sustainability, the Na-ion technology hosts environmentally friendly electrodes made of Mn, Fe, Ni, etc. (Prussian blue and layered oxides) and are Co-free. Bearing in mind that the abundance of chemical elements resonates with lower prizes and the use of cheaper Al than Cu current collectors, a 10% cost reduction of the stored kWh is foreseen with the Na-ion technology over the years if volume production is made possible.[10] Such a target should be feasible as manufacturing of Na-ion cells can utilize the Li-ion assembly lines without the need for further investment. Such sustainability and cost advantage represents a serious asset for

grid applications where space is not limited hence volumetric energy density is not any longer an overriding prerequisite.

In short, we hope that this commentary, based on real and trackable facts will raise the awareness of the battery community about the state of performance that the Na-ion technology can achieve while bearing in mind that only solely seven years of research has been devoted to it as compared to 30 years for Li-ion. Cells can be made for either power applications (**T**iamat) or autonomy (**F**aradion). Achievements were spectacular but further progresses are still needed, in particular at the electrolyte level to reach the perfection of Li-ion in terms of lifetime, durability at various temperatures. We are confident that this objective will be rapidly reached based on the numerous research groups worldwide entering this research field and numerous institutions that have integrated the Na-ion technology in their future road maps.

To conclude, the Na-ion technology is becoming a reality, but please do not take this as a revolutionary new idea. It is not and here is a proof. Remember that in 1869 our French visionary writer Jules Verne has already identified the benefit of this battery technology in his novel "20000 leagues under the sea" who was quoting "Sir, sodium alone is consumed and the sea provides it itself. I will also tell you that sodium batteries should be considered as the most energetic". By highlighting the strength and weakness of the various Na-ion battery chemistries against Li-ion ones, we hope that users will now easily identify the benefits that such a technology could bring to their business not as replacement of Li-ion but for providing added values to Li-ion for specific applications requiring power. It could also complement Li-ion for massive storage applications where specific energy is an overriding factor, hence minimizing the fears of Li shortage. We are at the early stage of the Li-ion age and we must act now not to repeat the polymer history, which was in its booming age in the 1900's and is now becoming the 2000's major global planet problem with the plastic pollution. To avoid repeating such mistake, the Na-ion technology, long predicted but not realized yet, stands as an attractive option towards greener and more sustainable batteries, which is the only way to electrify the world without creating a new environmental burden for the coming generations."

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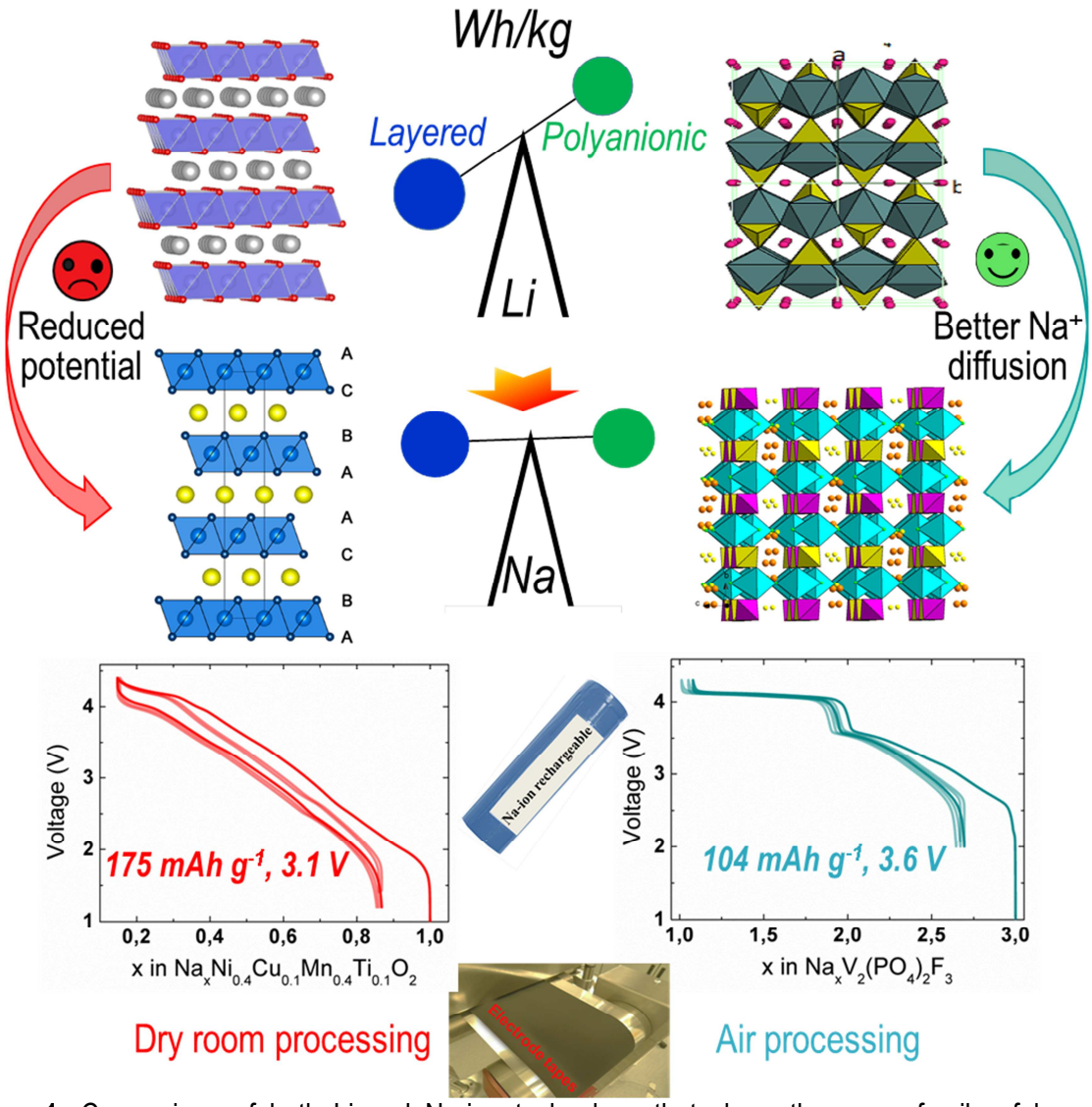


Figure 1: Comparison of both Li and Na-ion technology that share the same family of layered and polyanionic compounds. Power-wise, the supremacy of the latter over the former is enhanced by switching from the Li to Na-ion technology, while the large gain in energy density provided by layered skeletons over polyanionic ones is strongly reduced owing to a diminution of the Na-redox potential in layered oxide. This leads to a lower output cell voltage but also implies the need of handling-processing of the electrode in a moisture-free environment. Some issues can be mitigated by realizing O3-P2 composites or by proper substitution of O3 skeletons to the expense of a lower capacity performance (with the courtesy of S. Mariyappan).

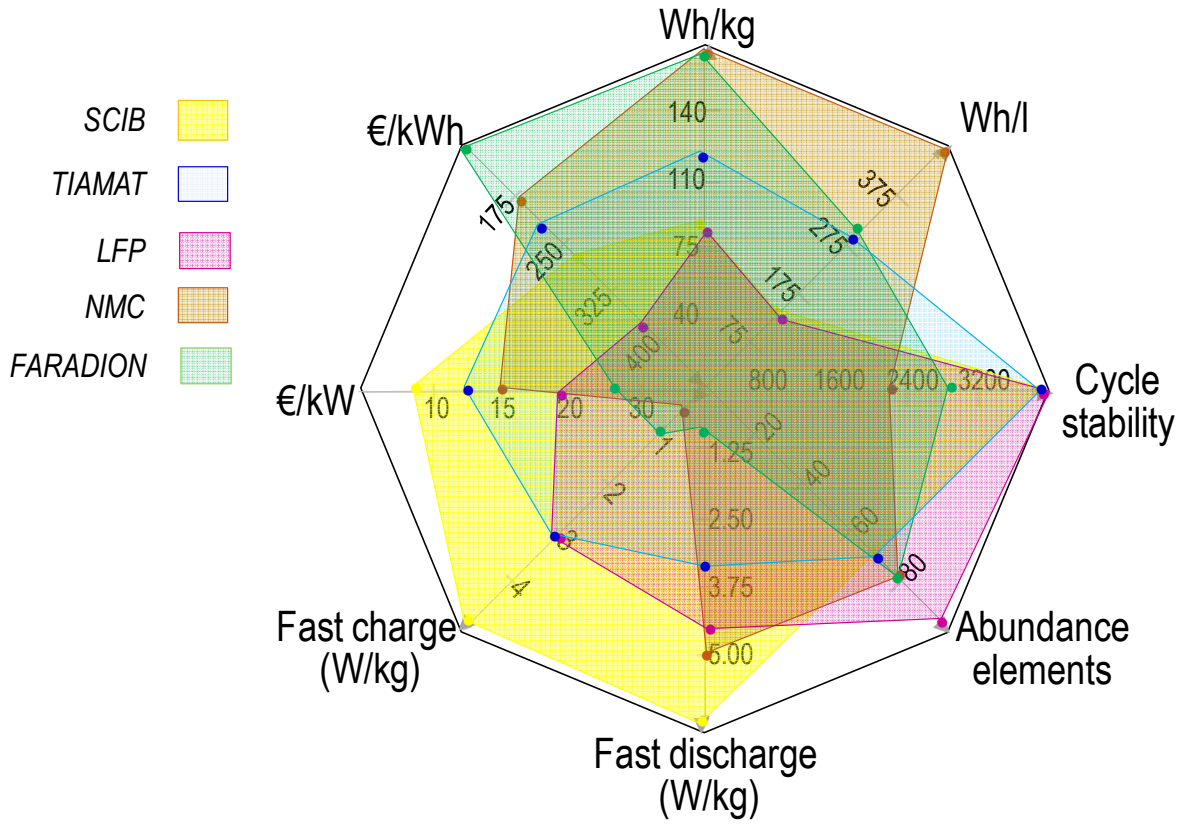


Figure 2: Tentative comparison between high power cells relying on either Na-ion technology NVPF/C 18650 or Na_xMO_2/C pouch cells) or on the Li-ion technology LFP/C (18650) , NMC/C and SCIB pouch cells. Several trends are conveyed from the reported figures of merit deduced from open reports.. The NVPF/C Na-ion system overrides the Na_xMO_2/C in terms power rate with this ranking be reversed when autonomy is considered. Moreover, NVPF/C compares favorably to LFP for nearly all the figures of merit, but it falls short against SCIB in terms of power while less costly in €/kWh and more performing in Wh/kg and Wh/l. Lastly, turning to the importance of qualifying the W/kg_{charge} and $W/kg_{discharge}$ for power application, note that the largest difference is for the Li-NMC chemistry. Obviously, not a single technology meet all the figures of merit at one, but NVPF/C is performing the bests for applications conjugating high power with a correct degree of autonomy. (With the courtesy of M; Morcrette).