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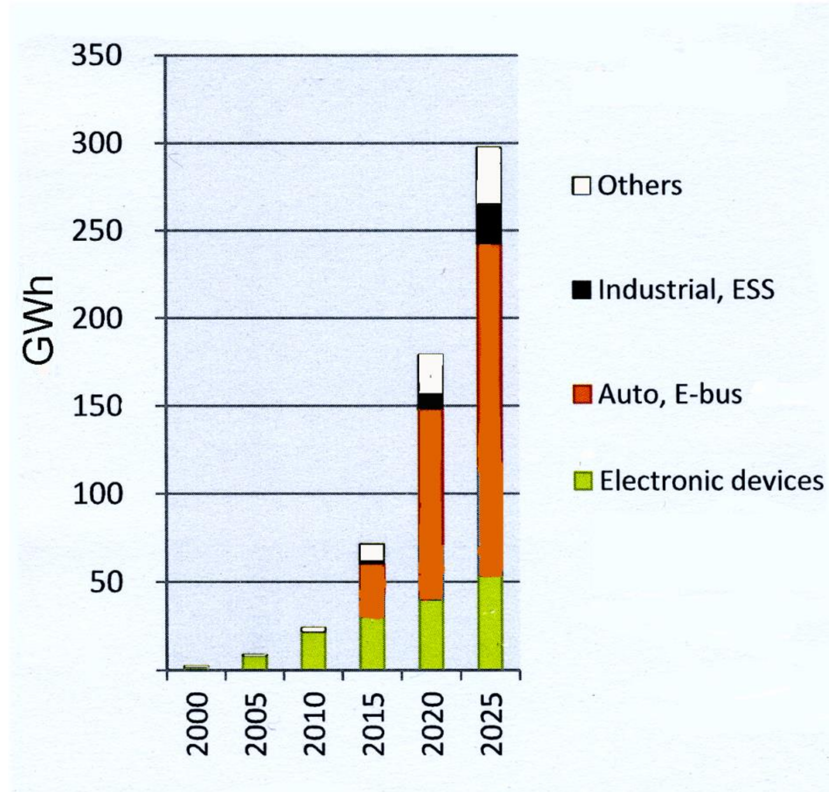
THE NOVELTIES IN THE DEVELOPMENT OF Na-ION BATTERIES

Slavko Mentus
University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12, 11000 Belgrade ,Serbia
Serbian Academy of Sciences and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia

I. Introduction

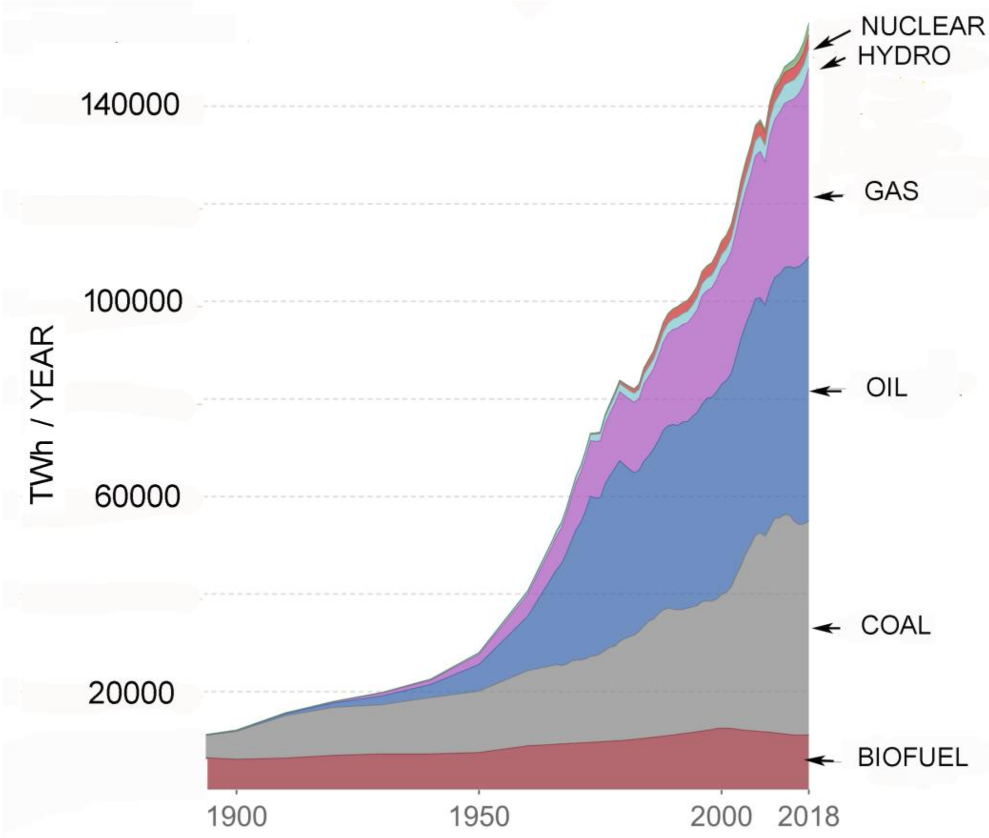
After roughly three decades from their first commercialization (in 1990), the Li-ion batteries overran the market of portable electronic devices, thanks to their high practical energy density (actually ~200 -285 Wh kg^{-1}) and relatively low price, which during time descended from initial ~1500 US $ per one kWh, to actual ~ 150 US $ per one KWh of energy.
Nowadays, within a global trend of decarbonisation of industry, a rapid development of electric cars and energy storage systems (ESS) for urban grid voltage stabilization caused an exponentially growing demand for batteries.



The increase of energy (GWh / year) stored in Li-ion batteries, for various usage areas (portable electronics, electric cars and buses, energy storage systems etc.):

- 180 GWh in 2020
- predicted to rise to~300 GWh in 2025

How large is this scale in comparison to the scale of global energy consumption? –see next slide



The trend of global energy consumption along decades of industrialization age:

~ 150 000 000 GWh (150000 TWh) in 2018.

Fossil fuels: coal, oil and gas are responsible for huge CO_2 emission in atmosphere and climate changes.

Thus in next few decades a considerable part of the consumption of coal and oil (tenths thousends of TWh's) will be replaced by energty of renewable sources (solar, wind), or nuclear one.

Having in mind that the power of renevable sources shows periodical scatter, a rising role of grid stabilisation systems is indispensable. This will cause fast rising demands for batteries for grid energy storage, from actual tens GWh's toward thowsends TWh's in near future.

Can Li-ion batteries satisfy such a fast growing demand? Let us see their chemical composition in the next slide!.

The cathode (NMC, NCA) and the anode materials of contemporary commercial Li-ion batteries enabling practical energy density of ~ 200 Wh kg^{-1}

Electrode material	Specific capacity (mAh g^{-1}) (theoretical / practical)	Volumetric capacity (mAh cm^{-3}) (theoretical / practical)	Average voltage (V vs Li/Li^+)
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC , NCM)	280/170	**1333/600**	**3.7**
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	279/200	1284/700	**3.7**
Graphite	**372 /330**	**837/330–430**	**0.15**

[1] NMC, NCM - F. Lin, *et al.* Nat. Commun. (2014), p. 5

[2] NCA. - S.K. Martha, *et al.* J. Electrochem. Soc., 158 (10) (2011), p. A1115

The defficiency of cobalt and nickel in earths crust makes the production of Li-ion batteries non-sustainable.

The consumption of Co and Ni by battery producers is expected to overrate their total supply from all mining resources alrady in the decades 2020-2040.

Thus, the development of batteries with more abundant raw materials is indispensable

II. The development of electrode materials of Na-ion batteries

Accounting with the limitations in sustainability of Li-ion batteries, during the last decade, the researchers focused the care to the development of sodium-ion batteries, as an real alternative to Li-ion ones. Majority of electrode materials suitable for Na-ion batteries does not require defficient elements, and sodium itself is much more abundant than lithium in natural resources.

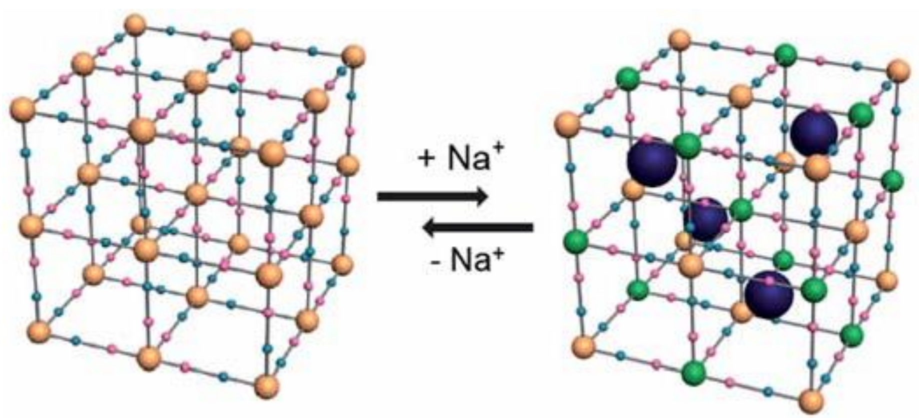
Actually, lower capacity of cathode and anode materials, and lower average potential difference between them, resulting in lower specific energy of ~ 150 mAh g^{-1} make sodium-ion batteries still non-competitive to Li-ion batteries.

Theoretically, sodium-ion battery might become competitive to actual Li-ion batteries (i.e., attain practical gravimetric energy density over 200 Wh kg^{-1}) if cathode specific capacity of 200 mAh g^{-1} and anode specific capacity of 500 mAh g^{-1}, with average potential difference of 3.3 V, may be discovered.

In continuation of this presentation, the survey of recent progress in the development of cathode and anode materials of Na-ion batteries witnesses that this goal is soon attainable.

II.1 Cathode materials

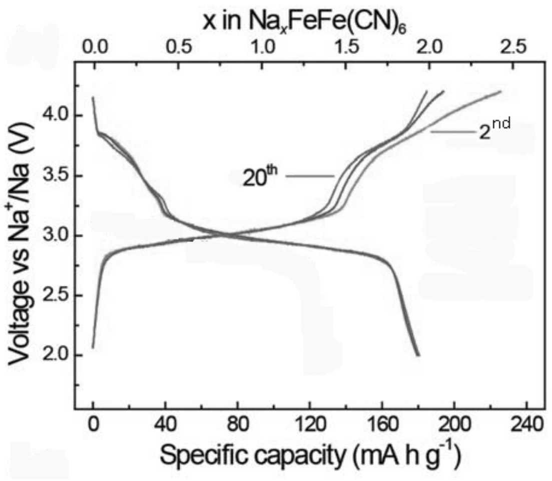
Prussian Blue Analogs (PBA's)



PBA's may be easily synthesized by precipitation, adding solutions of Mn, Fe, Co, Ni or Cu salts to aqueous solution of $Na_4Fe(CN)_6$. They enable intercalation of Na^+ ions on account of $Fe^{3+} \rightarrow Fe^{2+}$ reduction. The solid crystal network enables three-dimensional diffusion of Na^+ ions. PBAs with Mn and Fe are particularly Interesting.

- Prussian Blue crystals and its sodiated form, $Na_xFe[Fe(CN)_6]$

$Na_xFe[Fe(CN)_6]$



Galvanostatic charing/discharging curve (2nd - 20th cycle) of $Na_xFe[Fe(CN)_6]$ in 1 M $NaPF_6$ in EC and DEC (1:1 volume ratio) [3].Y. H. Lu, L. Wang, J. G. Cheng and J. B. Goodenough, Prussian blue: a new framework of electrode materials for sodium batteries, Chem. Commun., 48 (2012) 6544–6546

Attained characteristics:

Voltage ~ 3 V vs Na/Na^+ , capacity 170 mAh g^{-1}, sustainable at least 140 cycles

$Na_xMnFe(CN)_6$.

Characteristics:

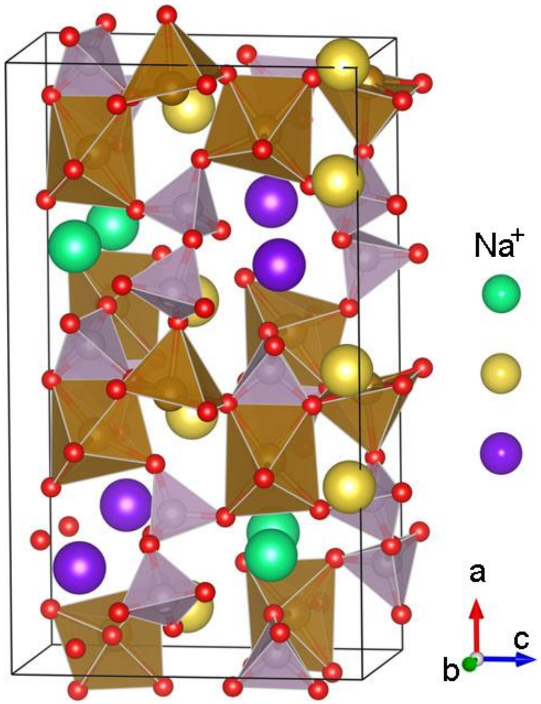
- almost flat galvanostatic charging/discharging plateau at mean voltage 3.6 V vs sodium metal.

-coulombic capacity of 144 mAh g^{-1} under a 0.1 C rate, (115.6 mAh g^{-1} under a 1 C rate, 86.6 mAh g^{-1} under a 10 C rate,

-73.4% retention after 780 cycles under a 0.5 C rate, and 72.7% retention after 2100 cycles under a 1 C rate (Shen et al 2016)

. [4] Z.Shen, S. Guo, C. Liu, Y. Sun,.Z. Chen, J.Tu et al. *Na-rich Prussian white cathodes for long-life sodium-ion batteries*. ACS Sustain. Chem. Eng. 6 (2018) 16121–16129

Mixed phosphate polyanion materials, $Na_4M_3(PO_4)_2P_2O_7$ (M: Mn, Co, Ni)



Crystal structure of $Na_4Fe_3(PO_4)_2P_2O_7$

Different sites of Na ions are

Presented by different colors

$Na_4Fe_3(PO_4)_2P_2O_7$

May be synthesized by usual solid-state reaction

[5] H. Kim, I. Park, D.-H. Seo, S. Lee, S.-W. Kim, W. J. Kwon, Y.-U. Park, C. S. Kim, S. Jeon and K. Kang, New iron-based mixed-polyanion cathodes for lithium and sodium rechargeable batteries: combined first principles calculations and experimental study, J. Am. Chem. Soc., 134 (2012) 10369–10372.

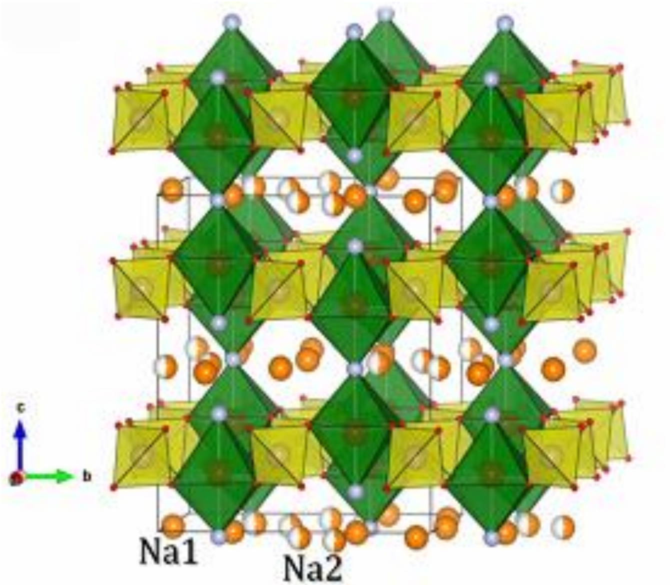
Characteristics:

-activation barrier for Na^+ diffusion in all directions less than 0.8 eV,

-specific capacity of 105 mAh g^{-1} at operating voltage of 3.2 V.

- enables energy density of 380 Wh kg^{-1}.

Fluorinated vanadium phosphate $Na_3V_2(PO_4)_2F_3$ (NVPF)



Crystal structure composed of VO_4F_2 octahedral units forming $[V_2O_8F_3]$ bi-octahedral units and is alternatively bridged by $[PO_4]$ tetrahedral units that form a threedimensional network with large voids in the [110] and [110] directions. In that structure easy Na^+ migration is provided. Two Na(1) sites are fully occupied while the other two Na(2) sites are half occupied by Na ions

[6].M. Bianchini, N. Brisset, F. Fauth, F. Weill, E. Elkaim, E. Suard, C. Masquelier and L. Croguennec, Chem. Mater., 2014, 26(14), 4238-4247.

Electrochmical characteristics:
-High average working voltage (~3.9 V vs. Na/Na+), higher than with any other fluorophosphates
-high theoretical capacity :128 mAh g^{-1}
-practical specific capacity 101 mAh g^{-1} at very high current rate 30 C after even 3500 cycles, and 75 mAh g^{-1} at still higher current rate of 70 C.

[7\ W. Song, X. Cao, Z. Wu, J. Chen, Y. Zhu, H. Hou, Q. Lan and X. Ji, Langmuir, 2014, 30(41), 12438-12446. Copyright © 2014 American Chemical Society.

[8] J. Zhao, X. Yang, Y. Yao, Y. Gao, Y. Sui, B. Zou, H. Ehrenberg, G. Chen and F. Du, Moving to Aqueous Binder: A Valid Approach to Achieving High-Rate Capability and Long-Term Durability for Sodium-Ion Battery, Adv. Sci., 5(4) (2018) 1700768.

II.2 Anode materials

Hard carbon

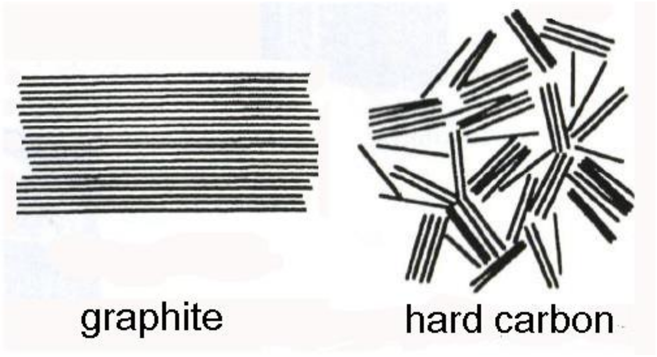


Fig 1. Structure difference between graphite and hard carbon: long -range versus short-range ordering of graphene layers.

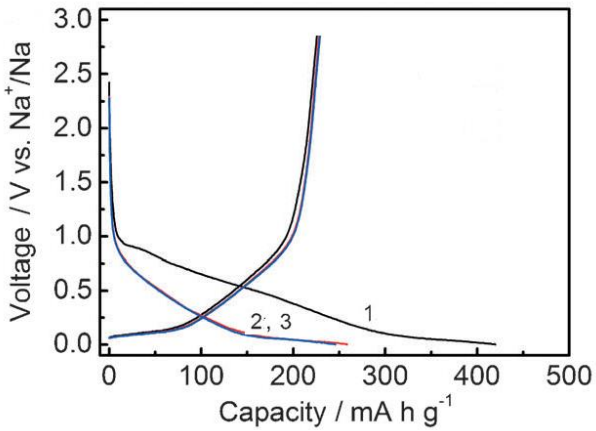


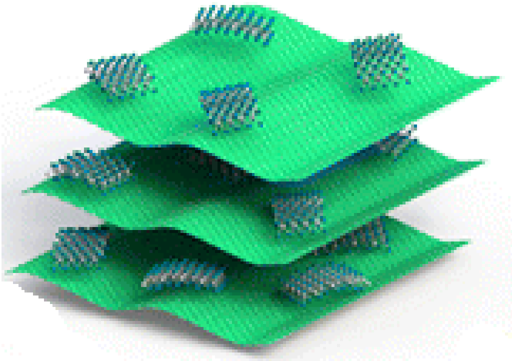
Fig 2. Galvanostatic sodiation (descending V) and desodiation (ascending V) curves of hard carbon electrode in organic solution of sodium salt

N-doped hard carbon (carbonized soyabeans pulp):
Characteristics: capacity of 212 mA h g^{-1} (at 5 A g-1) capacity retention 99% after 7000 charging/discharging cycles [9] S.Wang, L.Xia, L.Yu, L.Zhang, H.Wang, X.W.D. Lou, Free-Standing Nnitrogen-Doped Carbon Nanofiber Films: Integrated Electrodes for Sodium-Ion Batteries with Ultralong Cycle Life and Superior Rate Capability, Adv.EnergyMater. 6 (2016) Art No 1502217

S-doped hard carbon (by annealing at 500 °C the mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and sulphur :
Characteristiccs: 516 mAh g-1 at a current density of 0.02 A g-1. 271 mAh g^{-1} at 1 A g^{-1} retained after 1000 cycles ()

[10] W. Li, M. Zhou, H. Li, K. Wang, S. Cheng and K. Jiang, A high performance sulfur-doped disordered carbon anode for sodium ion batteries, Energy Environ. Sci., 8 (2015) 2916–2921.

Graphene/MoS_2 composite



Synthesis: The composite was synthesized by a hydrothermal method: graphene oxide was suspended in ethanol, $SnCl_4 \cdot 5H_2O$ was added dropwise. Thereafter, CH_3CSNH_2 and glacial acetic acid (HAc) were added, and transferred to an autoclave and heated at 180 °C. The resulting composite was washed with water and ethanol and freeze-dried.

Electrochemical characteristics:

An excellent specific capacity of 765 mAh g^{-1} for sodiation/desodiation reactions at high rate of even 10 A g^{-1} was evidenced. No morphology changes were evidenced after 200 cycles. The authors, (Jang et al 2019) stated they found and excellent anode material for sodium batteries.

[11] Y. Jiang, D. Song, J. Wu, Z. Wang, S. Huang, Y. Xu, Z. Chen, B. Zhao, and J. Zhang, Sandwich-like SnS2/Graphene/SnS2 with Expanded Interlayer Distance as High-Rate Lithium/Sodium-Ion Battery Anode Materials, *ACS Nano* 13(8) (2019) 9100–9111, https://doi.org/10.1021/acsnano.9b03330

Graphene-/phosphorene composite

Layered structure of black phosphorus (phosphorene layers)

Sun et al. [12] synthesized phosphorene–graphene hybrid composite, consisting of few phosphorene layers sandwiched between graphene layers. This nanocomposite material displayed following advantages: The graphene layers acted as buffer mitigating volume expansion to which phosphorene layers are prone on sodiation, and provide high electronic conductivity of this electrode material as well. The large capacity was explained through a dual mechanism of intercalation of sodium ions along the *x* axis of the phosphorene layers, followed by the formation of a Na_3P alloy

[12] J. Sun, H. W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li and Y. Cui, A phosphorene-graphene hybrid material as a high-capacity anode for sodium-ion batteries, Nat. Nanotechnol., 10 (2015) 980–985

Electrochemical characteristics:

This composite material provided a huge specific capacity of 2440 mAh g^{-1} at charging rate 0.05 A g^{-1}. Upon 100 cycles within the voltage range of 0–1.5 V vs. Na/Na^+., a capacity retention of 83% was observed,

- This is a very promising result from the aspect of development of Na-ion batteries.

Table: the survey of promissing cathode and anode materials of Na-ion batteries

Compound	Specific capacity (mAh g^{-1}) (theoretical/practical)		Average voltage (V
$Na_2FeMn(CN)_6$ [13]	170/144(0.1C)115.6(1C)86.6(10C)		3.6
Na4Fe3(PO4)2P2O7 [14]	129/86		3
$Na_3V_2(PO_4)_2F_3$ [15,16]	128/101(30C)		3.9
Hard carbon (HC) Faradion)	/280		1.2
N-doped HC [17]	/212 (5 A g^{-1}) (7000 cycles)		1.2
S-doped HC [18]	516(0.02 A g^{-1}) 271(1 A g^{-1} , 1000 cycles)		1.2
graphene/SnS_2 [19]	765(10 A g^{-1})		1.2
graphene/MoS_2 [20]	563.5 (0.2 mAh g-1)(401 at 10 C)		

[13] Z. Shen, S. Guo, C. Liu, Y. Sun,.Z. Chen, J.Tu et al. *Na-rich Prussian white cathodes for long-life sodium-ion batteries*. ACS Sustain. Chem. Eng. 6 (2018) 16121–16129

[14] H. Kim, I. Park, D.-H. Seo, S. Lee, S.-W. Kim, W. J. Kwon, Y.-U. Park, C. S. Kim, S. Jeon and K. Kang, New iron-based mixed-polyanion cathodes for lithium and sodium rechargeable batteries: combined first principles calculations and experimental study, J. Am. Chem. Soc., 134 (2012) 10369–10372.

[15] S. Yuvaraj, W. Oh, W.-S. Yoon, Recent progress on sodium vanadium fluorophosphates for high voltage sodium io battery, J.Electrochem.Sci.Technol., 10 (2019) 1-13

[16] J. Zhao, X. Yang, Y. Yao, Y. Gao, Y. Sui, B. Zou, H. Ehrenberg, G. Chen and F. Du, Moving to Aqueous Binder: A Valid Approach to Achieving High-Rate Capability and Long-Term Durability for Sodium-Ion Battery, Adv. Sci., 5(4) (2018) 1700768.

[17] S.Wang, L.Xia, L.Yu, L.Zhang, H.Wang, X.W.D. Lou, Free-Standing Nitrogen-Doped Carbon Nanofiber Films: Integrated Electrodes for Sodium-Ion Batteries with Ultralong Cycle Life and Superior Rate Capability, Adv. Energy Mater. 6 (2016) Art No 1502217

[18] W. Li, M. Zhou, H. Li, K. Wang, S. Cheng and K. Jiang, A high performance sulfur-doped disordered carbon anode for sodium ion batteries, Energy Environ. Sci., 8 (2015) 2916–2921.

[19]Y. Jiang, D. Song, J. Wu, Z. Wang, S. Huang, Y. Xu, Z. Chen, B. Zhao, and J. Zhang, Sandwich-like SnS_2/Graphene/SnS_2 with Expanded Interlayer Distance as High-Rate Lithium/Sodium-Ion Battery Anode Materials**,** *ACS Nano* 13(8) (2019) 9100–9111, https://doi.org/10.1021/acsnano.9b03330

[20] J. Sun, H. W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li and Y. Cui, A phosphorene-graphene hybrid material as a high-capacity anode for sodium-ion batteries, Nat. Nanotechnol., 10 (2015) 980–985.

III. Incumbent providers of Na-ion batteries

- Natron Energy in Santa Clara, California, produces both the cathode and anode from Prussian Blue, (transition metal hexacyanoferrates). The battery can be charged and discharge in minutes and can withstand more than 50,000 charging cycles. Nowadays, Natron's customers are data centers and telecom companies. the batteries are now in low-volume production, but intensification is planned [21].
- Faradion is the leading UK sodium-ion battery company [22,23], that uses their own type of hard carbon anode, and several types of cathodes – layered, polyphosphate etc. They announced cooperation with investment group ICM Australia, where grows the demand for residential, commercial and grid scale applications of batteries. They also develop the batteries for commercial vehicles in India. Prototype cells can deliver energy density over 140 Wh kg^{-1}. The company announced cooperation with the energy company Phillips 66 from Houston in the development of lower-cost and higher-performing anode materials, and plans the cooperation with Pacific Northwest National Laboratory (PNNL), in USA, the French National Center for Scientific Research (CNRS), and the French research network on electrochemical energy storage, with the aim to attain practical energy of Na-ion batteries of nearly 200 Wh kg-1. [23]
- CATL is famous Chinese battery supplier, which declared the production of sodium-ion batteries [59] with porous hard carbon anode and Prussian White cathode, modified to avoid rapid capacity fading during cycling. The battery may be charged to 80% in 15 minutes at room temperature. It is also less sensitive to temperature changes than conventional Li-ion battery. The initial version displays energy density of 160 Wh kg-1, however, next generation which is currently under development.is expected to offer energy density of 200 Wh kg-1 . [24]
- Among others, one may still mention AGM Batteries Ltd established in 1997 in Thurso, Caithness, NGK Insulators Ltd, established 1919 in Nagoya, Japan, HiNa Battery Technology Co. Ltd,, established in 2007 in Zhongguancun, Liyang, Jiangsu Province, Tiamat Energy, established in 2017 (founder Laurent Hubard) and Altris , established in 2017 in Uppsala, Sweden
- In the Table that follows at the next slide the comparison is made of main (available) characteristics of contemporary Li-ion batteries to commercial Na-ion batteries of first generation, produced by some battery providers.

[21] https://natron.energy/news-and-events/
[22] K.M. Abraham, How Comparable Are Sodium-Ion Batteries to Lithium-Ion Counterparts? ACS Energy Lett. 5 (2020) 3544−3547
[23] Phillips 66 and Faradion Developing Sodium-ion Battery Materials | Business Wire
https://investor.phillips66.com/financial-information/news-releases/news-release-details/2021/Phillips-66-and-Faradion-Developing-Sodium-ion-Battery-Materials/default.aspx
[24] https://www.greencarreports.com/news/1133059_first-catl-sodium-ion-batteries-revealed-can-charge-to-80-in-15-minutes

Comparison of available characteristics of commercial Li-ion and first generation Na-ion cels

18650 cell	voltage	Wh kg^{-1}	Wh L^{-1}	Cycle life
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	
FARRADION, hard carbon/unknown cathode, (Na-ion)		140		
CNRS CEA - (Na-ion) (ref 25)		90	250	2000
PNNL-WSU hard carbon/ $NaNi_{0.68}Mn_{0.22}Co_{0.10}O_2$(Na-ion)(ref. 26)	2.7	150	375	
ALISTORE hard carbon//$Na_3V_2(PO_4)_2F_3$) (ref. 27)	3.5	75		4000 cycles (1 C rate)
CATL hard carbon/Prussian White (ref 28)		160		

[25] https://news.cnrs.fr/articles/a-battery-revolution-in-motion
[26] J. Song, K Wang,. J. Zheng,. M. H. Engelhard,. B. Xiao, E. Hu,. Z. Zhu, C. Wang,. M. Sui,. Y. Lin, D. Reed,. V. L. Sprenkle, P. Yan, X. Li,. Controlling Surface Phase Transition and Chemical Reactivity of O3-Layered Metal Oxide Cathodes for High-Performance Na-Ion Batteries. ACS Energy Lett. 2020, 5 (6), 1718−1725.
[27] T. Broux, F. Fauth, N. Hall, Y. Chatillon, M. Bianchini, T. Bamine, J.B. Leriche, E. Suard, D. Carlier, Y. Reynier, L. Simonin, C. Masquelier, C.L Croguennec, High Rate Performance for Carbon-coated $Na_3V_2(PO_4)_2F_3$ in Na-ion Batteries. Small Methods 2019, 3, 1800215−1800237.
[28] https://www.greencarreports.com/news/1133059_first-catl-sodium-ion-batteries-revealed-can-charge-to-80-in-15-minutes

IV. CONCLUSIONS

- During the last decade several companies developed first generation of sodium-ion batteries for commercial purposes. The advantage of their production is consumption of environmentally friendly elements very abundant in earths crust.

- Actually, practical energy density of first generation of commercial Na-ion batteries of 70-160 Wh kg^{-1} is attainable. They, as such, may already be used for low-demanding purposes, such as grid voltage stabilization.

- A rapid progress in the development of electrode materials of Na-ion batteries, reviewed in this article, shows: the anode materials approaching in capacity 500 -2500 Ah kg^{-1} and cathode materials approaching in capacity 200 Ah kg^{-1}, fulfill criteria and offer promise that Na-ion batteries of second generation may attain a high level of competitiveness to the Li-ion batteries. This hope is additionally supported by the fact that the duration of the development of Na-ion batteries (since 2010) is only one third of the duration of development of Li-ion batteries.