Contemporary materials 2020
ANURS, Banja Luka,  11-12 September 2020

# The rolle of batteries in near-future energetics

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The lecture is inspired by the Nobel price in chemistry in 2019., awarded to the scinetists mostly meritorius for the discovery of Li-ion battery

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# 1. Introductory definitions: battery and its characteristics

**Battery is a** chemical reactor which transforms energy of a chemical redox reaction directly into electric energy. In so called s**econdary batteries** the chemical precesses are completely reversible, thus this type battery may be recharged upon discharging

## Main characteristics of a battery

Oxidation number

Number of moles of anode or cathode material

Faraday constant

Coulombic capacity = $n_{a(c)}$ x (z x 26,8) Ah

(The meaning: the amount of electricity released by a completely charged battery)

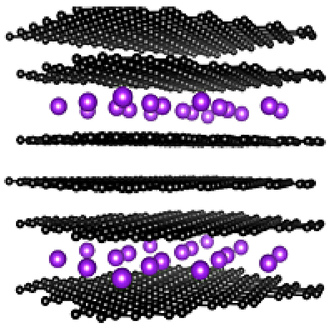
Practical energy density $= \dfrac{n_{a(c)} \times Z \times 26{,}8 \times \varepsilon}{n_a M_a + n_c M_c + \sum M_{constr}}$ Wh/kg

Simply said: Practical energy density is a product of coulombic capacity and voltage ε, divided by the sum of masses of anode and cathode materijals, and all construction materials making battery practically usable

# 2. The discovery of Li-ion batteries: the contributions of the inventors awarded by Nobel price for chemistry in 2019

First oil crisis in early 70-ties incited electrochemists to search for chemical power sources able to replace oil as a power source in trafic.
Classic lead-acid and Ni-Cd batteries displayed insufficient energy density (35 and 50 Wh/kg, respectively)
**Remarkable success was achieved in the decade 1980-1990 through the discovery of Li-ion battery**. **The substantial role in this discovery played a previous discovery of intercalate compounds**

Intercalate compounds include solid of layered structure (with strong ionic or covalent bonds inside layers and weak van der Waals bonds between layers) called host, and layers of foreign atoms or molecules, called guests incorporated between host layers. Usually the difusion of guest constituents into host structure occurs under thermal activation.
During insertion, hosts elemental cell does not suffer remarkable change in cell dimensions.



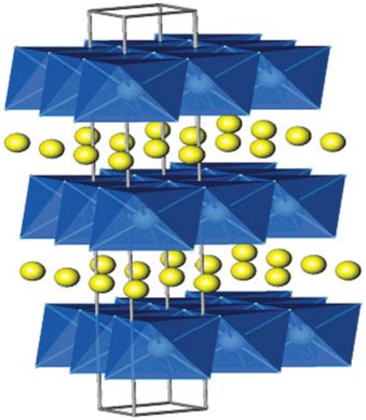
Graphite salt

First reported intercalate compounds are graphite salts $C_x(H_2SO_4)$, $C_x(Br_2)$ (1938)

In 1972, $LiTiS_2$ was synthesized by the thermally assisted reaction of Li with $TiS_2$

$$Li + TiS_2 = LiTiS_2$$

This is a redox reaction: during insertion the Li atoms reduce Ti(IV) to Ti(III) .



$LiTiS_2$

W. Rüdorff, U. Hofmann, Über Graphitsalze, Z.Anorg.Allgem.Chemie, 238 (1938)1

E Bayer, W. Rüdorff, Reaction of Metalldisulfides having layer structures with alkalinaphthalides-solutions, Z. Naturforschung B, 27 (1972) 1336-1339

# Contribution of S. Whittingham

S. Whittingham constructed a battery with Li anode and $TiS_2$ cathode, in the electrolyte $LiClO_4$ in organic solvent dioxolane.

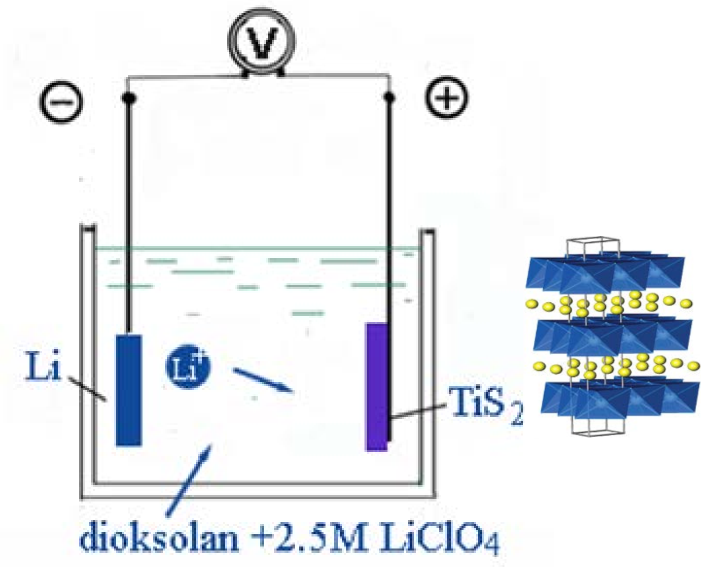
Anode reaction

$$Li = Li^+ + e$$

Cathode reaction ( formation of intercalate compound $LiTiS_2$)

$$TiS_2 + Li^+ + e = LiTiS_2.$$

The voltage was 2,5 V.




This experiment discovered the possibility of electrochemical formation of intercalate compounds and indicated the way to use lithium in the world of secondary batteries, thus Whittingham was selected as one of three of Nobel price winers in 2019.

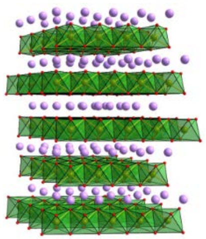
Note: This battery was not commercialized. Its practical appliaction was limited by ability to selfignition and explossion caused by the use of metallic lithium.


M.S.Withingham, The Role of Ternary Phases in Cathode Reactions, J. Electrochem Soc., 123 (1976) 315

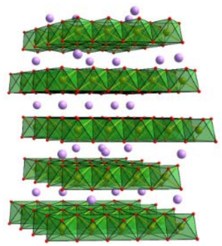
M.S. Whittingham; Chemistry of intercalation compounds: Metal guests in chalcogenide hosts Prog. Solid State Chem. 12 (1978) 41

# Contribution of J.B.Goodenough

The group of prof  Goodenough discovered that some  oxides of transition metals build intercalates with lithium, having high mean potential ~ 4V versus lithium. This enabled to build batteries richer in energy than Whittinghams one.

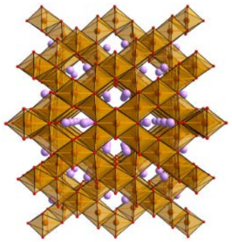


**Lithium Cobalt Oxide**
**$LiCoO_2$**

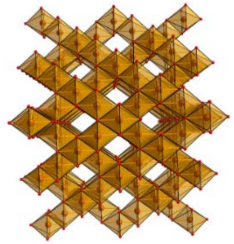


**Lithium-deficient Cobalt Oxide**
**$Li_{0.5}CoO_2$**

*1980-Layered Oxide: Mizushima, Jones, Wiseman, Goodenough — Materials Research Bulletin **15,** 783 (1980)*

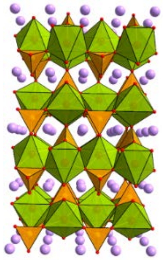


**Lithium Manganese Oxide**
**$LiMn_2O_4$**

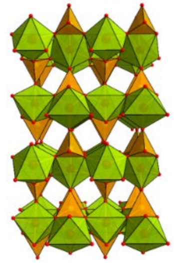


**Manganese Oxide**
**$Mn_2O_4$**

*1983: SPINEL OXIDE*
*M.M.Thackeray, W.I.F.David, P.G.Bruce, J.B.Goodenough — Materials Research Bulletin **18,** 461 (1983)*



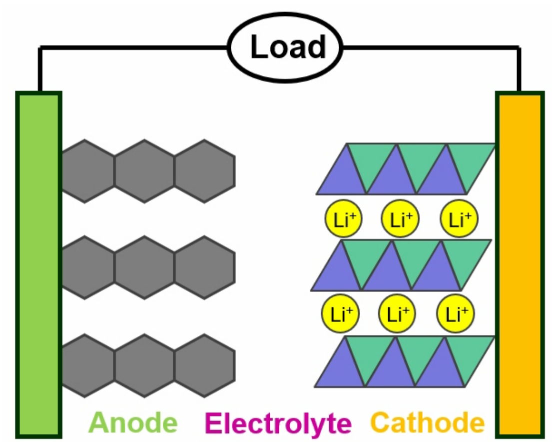
**Lithium Iron Phosphate**
**$LiFePO_4$**



**Iron Phosphate**
**$FePO_4$**

*1997: POLYANION (OLIVINE) OXIDE*
*Citation: Padhi, Nanjundaswamy, Goodenough — Journal of the Electrochemical Society **144,** 1188 (1997)*

# Contribution of A. Yoshino : first practically usable Li-ion battery



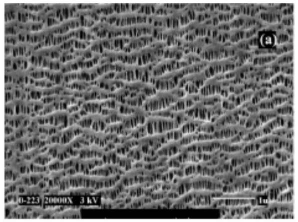

Dr. Yoshino between 1985 and 1989 realized first safe and commercially usable battery, by using graphite-like carbon as anode, instead of too reactive metallic lithium. Cathode was one of Goodenough's discoveries: $LiCoO_2$. and electrolyte was $LiPF_6$ in organic solvents mixture: ethylene carbonate –diethylcarbonate 1:1. Voltage was 3,7 -4 V

A. Yoshino K.Sanechika, T.Nakajima, Secondary Battery USP4,668,595 and JP1989293, filing date (priority) May 10, 1985 (Basic patent of the LIB. Certain crystalline carbon) ],
A. Yoshino, K. K.Sanechika, Nonaqueous secondary battery, JP2128922, filing date May 28, 1984 (Al current collector)
A. Yoshino K. Nakanishi, A. Ono, Explosion-proof secondary battery, JP2642206, filing date December 28, 1989 (Separator)

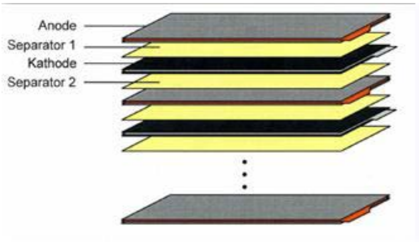
The reactions in the battery:

Charging: $6C + LiCoO_2 = LiC_6 + CoO_2$

Discharging: $LiC_6 + CoO_2 = 6\ C + LiMeO_2$



Separator: thin porous polypropylene foil




Small amount of electrolyte allows stacking of cathode-separator-anode thin layers into compact self-supporting packs of prismatic or cylindric form

In 1991., three big companies started commercial production of batteries: Sony Energytec. Inc., - $C/LiCoO_2$, Moli Energy Ltd., - $C/LiNiO_2$, and Bell Communication Research (Bellcore) - $C/LiMn_2O_4$.

From 1991 up to now, some more suitable cathode materials were discovered, the best being the complex oxides such as $LiNi_{0,33}Mn_{0,33}Co_{0,33}O_2$, (NCM) (abbrev. of Ni-Co-Mn) or nickel rich $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) (abbreviation of Ni-Co-Al).

T. Ohzuku, Y.Makimura, Layered lithium insertion material of LiCo1/3Ni1/3Mn1/3O2 for lithium-ion batteries. Chem. Mater. 2001, 30, 642–643.
M.Guilmard, C. Pouillerie, L. Croguennec, C. Delmas, Structural and electrochemical properties of LiNi0.70Co0.15Al0.15O2. Solid State Ionics 160 (2003) 39–50, DOI: 10.1016/S0167-2738(03)00106-1
K.-J. Park, J.-Y. Hwang, H.-H. Ryu, F. Maglia, S.-J. Kim, P. Lamp, C.S. Yoon and Y.-K. Sun, Degradation Mechanism of Ni-Enriched NCA Cathode for Lithium Batteries: Are Microcracks Really Critical? ACS Energy Lett. 4, 6, (2019), 1394–1400

Table 1. The cathode and anode materials, electrolytes, voltage, theoretical and practical energy density of classical (lead-acid, and alkaline Ni-Cd) and contemporary (Li-ion) battery variances

| Type | anode | cathode | electrolyte | voltage (V) | Wh $kg^{-1}$ Theor. | Wh $kg^{-1}$ Practic. | Wh $l^{-1}$ Practic. |
|---|---|---|---|---|---|---|---|
| $Pb/PbO_2$ | Pb | $PbO_2$ | $H_2SO_4$ | 2.0 | 252 | 35 | 70 |
| Cd-Ni | Cd | NiOOH | KOH | 1.2 | 244 | 50 | 75 |
| Li-ion | $LiC_6$ | $Li_xCoO_2$ 0.6e | EC/DMC + $LiPF_6$ | 3.7 | **420** | 206 | 530 |
| Li-ion | $LiC_6$ | $LiMn_2O_4$ 0.8e | EC/DMC + $LiPF_6$ | 3.8 | 330 | 132 | 340 |
| Li-ion | $LiC_6$ | $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ 0.7e | EC/DMC + $LiPF_6$ | 3.6 | 450 | 210 | 530 |
| Li-ion | $LiC_6$ | $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ 0,75e | EC/DMC + $LiPF_6$ | 3.6 | 470 | 265 | 690 |

This table explains why energy density of Li-ion batteries is much higher from that of classical $Pb/PbO_2$ and Ni-Cd batteries: one deals with lower molar masses of cathode and anode materials (~70 g/mol) and much higher voltage (3.6-3.8 V vs. 2 and 1.2 V)

# 3. How the batteries change everdays life

From 1990 - expansion of portable electronic devices occurs: phone cells, tablets, laptop computers. To 2010 21 GWh, to 2030 100 GWh is predicted to be incorporated in consumer electronics

Since 2010: to prevent danger of climate changes OUN started to replace oil powered cars by electric cars. In 2017 more than million of electric cars was produced. 76 GWh/year in 2020, 245 GWh/year in 2030 is planed to carry by electric automobiles.

Since ~2015: In order to reduce consumption of fossil fuels below 30 % of todays one, which requires rising usage of wind and solar energy, the need rises for grid energy stabilization, based on batteries. 2 GWh/year by 2020 and 30 GWh by 2030 is anticipated

129 MWh stabilisation station within an australian wind-generator field Hornsdale Power Reserve. Tesla 2018

Table 2. The dynamic of consumption of Li-jon batteries from 2010 to 2020 and forecast by 2030, in units GWh/year

| | 2010 | 2015 | 2020 | 2025 | 2030 |
|---|---|---|---|---|---|
| Portable electronics (mobile phones, tablets, cameras, lap-top computers | 21 | 31 | 45 | 66 | 100 |
| Electric vehicles ( all types) | 0 | 13 | 76 | 137 | 245 |
| Grid energy storage stations | 0 | 0 | 2 | 10 | 30 |
| Other applications | 1 | 1 | 2 | 7 | 15 |
| Total | 22 | 45 | 125 | 220 | 390 |

G. Zubi, R. Dufo-Lopez, M. Carvalho and G. Pasaoglu, „The lithium-ion battery: State of the art and future perspectives", *Renewable and Sustainable Energy Reviews*, 89 (2018): 292–308.

# 4. Possible limiting factor for Li-ion battery type: the availability of raw materials

Planned consumption of energy of batteries assumes corresponding consumption of raw materials, some of which are not enough abundant in Earths crust.

1 kWh of contemporary batteries requires ~0.16 kg Li, ~O.4 kg Ni and ~0.10 kg Co

Table 3. Global reserves of Li, Ni and Co, production rate in 2016 and anticipated consumption in 2025 ( for 10-20 millions of electric cars per year) Mt = million of tons

| | Global reserves Mt | Production rate Mt/year in 2016 | Predicted Mt/year for batteries in 2025 |
|---|---|---|---|
| Lithium | 47 (14) | 0.0378 | 0.16-0.32 |
| Nickel | 78 | 2.25 | 0.4-0.8 |
| Cobalt | 7 | 0.123 | 0.1-0.2 |

-In 2016., from 37800 tons of produced lithium metal, ~ 14700 tons (39 %) was used in batteries.
- In 2016., 123000 tons of cobalt was produced in total, 37000 tons was used in batteries
-In 2025., 10 - 20 millions of electric cars per year will be produced. That means 100,000–200,000 tons of cobalt — **similar or more than produced in 2016**. This is also 400,000–800,000 tons of nickel, 20 – 40% of the production in 2016, what means that defficiency of nickel may appear between 2030 and 2040.
Conclusion: Rising global goals anticipated by 2050 may not be achieved by Li-ion batteries, new types will be necessary

G. Zubi, R. Dufo-Lopez, M. Carvalho and G. Pasaoglu, „The lithium-ion battery: State of the art and future perspectives", *Renewable and Sustainable Energy Reviews*, 89 (2018): 292–308.

Possible (not unique) alternative to Li-ion batteries are Na-ion batteries.

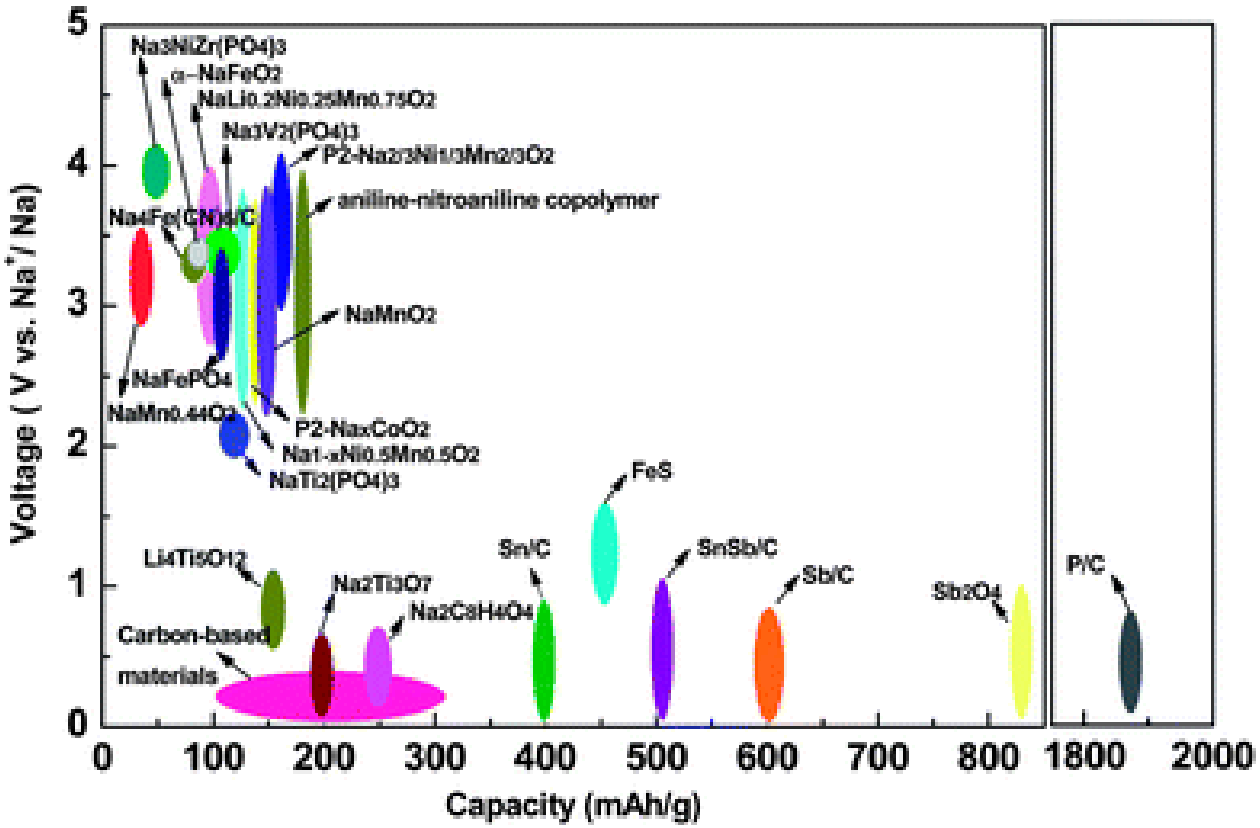



Figure: Potential versus coulombic capacity of some anode (0-1 V) and cathode(2-4V) materials of Na-ion batteries, reported up to 2013.

H.Pan, Y.-S. Hu, L.Chen, *Room-temperature stationary sodium-ion batteries for large-scale electic energy storage*, Energy Environ. Sci., 6 (2013) 2338-2360

This figure shows that suitable choice of cathode and anode materials enables the voltage of ~3V and (cathode limited) capacity of ~150 Ah/g. Presently, this is not competitive to the best Li-ion battery, but may satisfy the demands of stationary users (grid power stabilisators). However, it is not excluded that better competitiveness may be achieved in near future. At least, Na-ion batteries may prolong the usage period of Li-ion batteries of most demanding users.

# 5. Conclusions

Li-ion batteries appeared in 1991. as a commercal products. Their energy density is roughly four times that of their predecessors, $Pb/PbO_2$ and Ni-Cd battery. This is reason why this battery conquer the overal battrey market . The significance of this discovery is recognized by the Nobel committee, which awarded Nobel price for chemistry in 2019 to the scientist most meritorius for this discovery

The batteries really change the everydays life, playing the following roles:

-They are energy suppliers for great deal of portable electronics (mobile phones, tablets lap/top computers), bearing 31 GW/year in 2015, anticipated to extend to 100 GWh/year in 2030

- Starting with 2010., as a part of battle against climate changes, battery powered cars tend to replace those povered by internal combustion engines. For this purpose batteries beared 13 GWh/year of energy in 2015, anticipated to extent to 245 GW/year in 2030

-As a support to use renevable energy sources (wind and solar energy) instead of fossil fuels, battery packs for grid energy stabilizers will be increasingly used, bearing ~0 GWh/year in 2015, anticipated to bear 30 GWh/year in 2030.

The huge demand for batteries arising in the course of expelling of fossil fuels from global uses, will overrate soon the global production of metals used as raw materials of Li-ion batteries. Deficiency of cobalt is anticipated already in 2025. and deficiency of nickel is anticipated in the decade 2030-2040. Thus there is an urgent need for search for other types of batteries, not requiring deficient raw materials.

Presently Na-ion batteries seem to be a real alternative, at least for stationary use.