Functional Inorganic Materials
Fall 2023

Mondays: 10.15 - 12.00
Thursdays: 10.15 - 12.00

Lecture hall locations: U7 in Otakaari 1 / U-wing
Ke1 in Kemistintie 1 (CHEM building)

You can use https://usefulaaltomap.fi/ to see the exact location of U7.

#	Date	Place	Who	Topic
1	Mon 4.9.	U7 (U135a)	Maarit	Introduction + Materials design
2	Thu 7.9.	Ke1 (A305)	Antti	Introduction + Computational materials design
3	Mon 11.9.	U7 (U135a)	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 14.9.	Ke1 (A305)	Maarit	Magnetic oxides
5	Mon 18.9.	U7 (U135a)	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	**Thu 21.9.**	**Ke1 (A305)**	**Maarit**	**Ionic conductivity (Lithium): Li-ion battery**
7	Mon 25.9.	U7 (U135a)	Antti	Thermal conductivity
8	Thu 28.9.	Ke1 (A305)	Antti	Thermoelectricity
9	Mon 2.10.	U7 (U135a)	Antti	Piezoelectricity
10	Thu 5.10.	Ke1 (A305)	Antti	Pyroelectricity and ferroelectricity
11	Mon 9.10.	U7 (U135a)	Antti	Luminescent and optically active materials
12	Thu 12.10.	Ke1 (A305)	Maarit	Hybrid materials

LECTURE 6: Ionic conductivity: Lithium & Proton

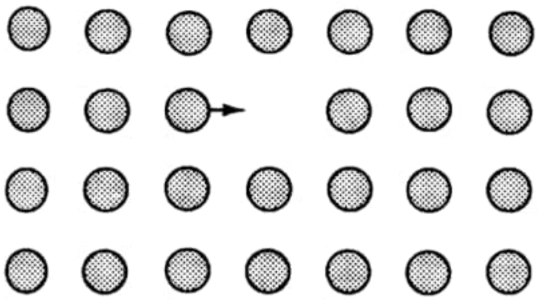
- **Proton conductivity**
- Water/proton absorption & Oxide/hydroxide substitution
- **Lithium ion conductivity**
- Li-ion battery: material issues
- Solid-state electrolytes & Thin-film microbattery

LECTURE EXERCISE 6

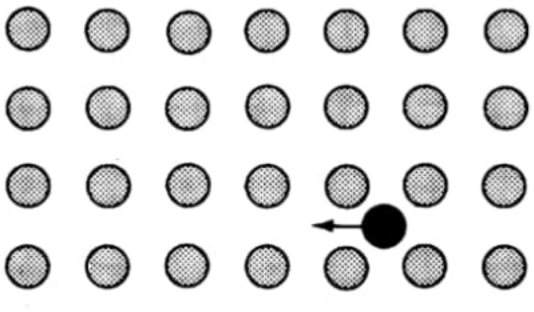
1. **Which useful function could be anticipated for an oxygen-deficient oxide material with a tendency to absorb water? Explain !**
2. **Explain why a layered crystal structure is beneficial for the Li-ion battery electrode material.**
3. **What happens to (a) structure, (b) electrical conductivity, and (c)) Li-ion conductivity of Li_3PO_4 when nitrogen is introduced into it to form LiPON ($Li_xPO_yN_z$) ? Why these are important changes ? What advantages you see in using ALD for the fabrication of LiPON electrolyte films ?**

IONIC CONDUCTIVITY

- Other terminologies:
  Fast ion conductor, Superionic conductor, Solid electrolyte, Solid state ionics
- Highly mobile ions move/hop through an otherwise rigid crystal structure
- Measurement of ionic conductivity: electrochemical impedance spectroscopy (EIS)
- **APPLICATIONS:**
  batteries, fuel cells, supercapacitors, chemical sensors, separation membranes, …



mobile vacancy

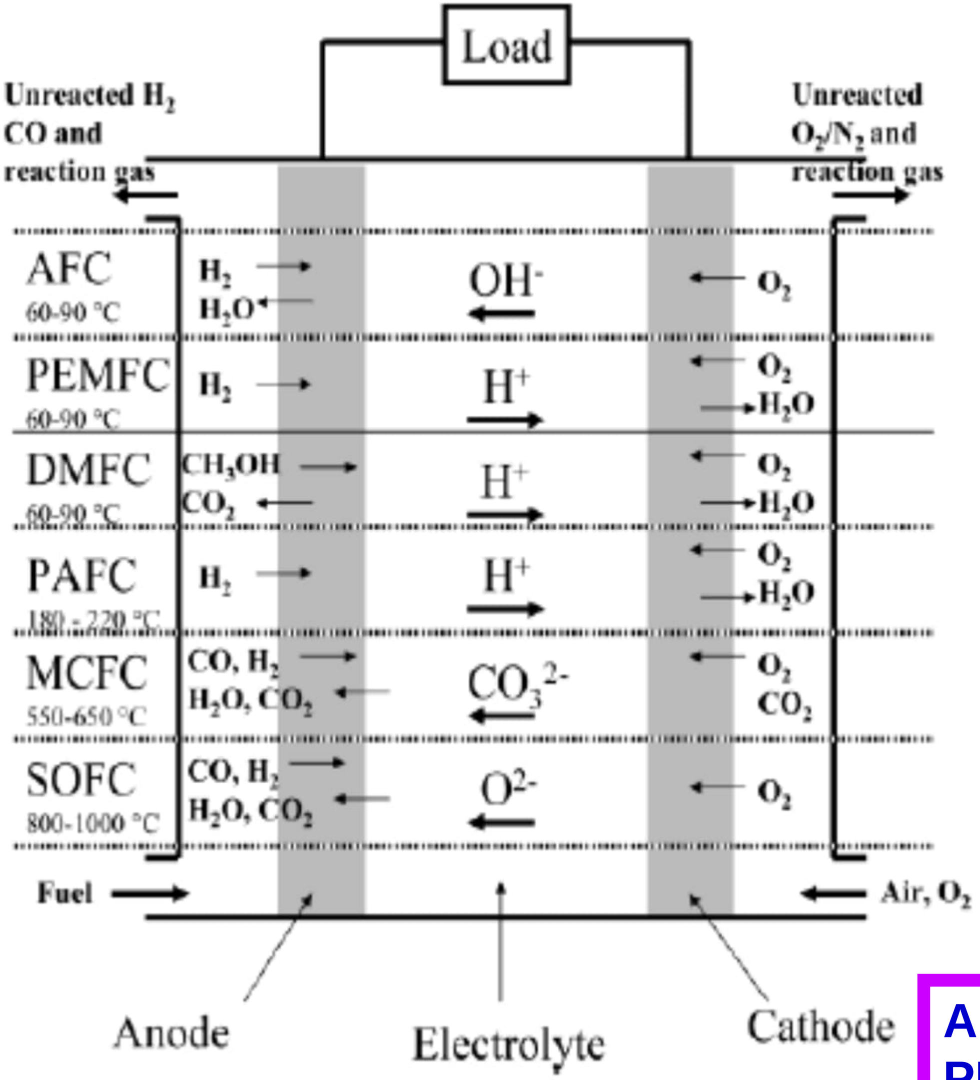


mobile interstitial

EFFECTIVE IONIC RADII

O^{2-}	**140 pm**
OH^-	**137 pm**
Li^+	**60 pm**
H^+	**very small**

FUEL CELLS



Conventional PROTON-CONDUCTING MATERIALS

AFC	Alkaline fuel cell
PEMFC	Proton exchange membrane
DMFC	Methol direct oxidize fuel cell
PAFC	Phosphate fuel cell
MCFC	Molten carbonate fuel cell
SOFC	Solid-oxide fuel cell

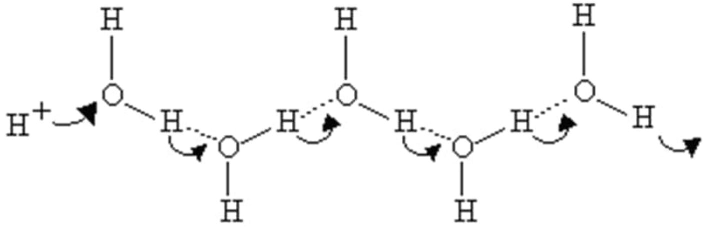
PROTON CONDUCTORS

- **PROTON CONDUCTOR: mobile protons are the primary charge carriers**
- **APPLICATIONS**

  - hydrogen separation

  - sensors

  - fuel cells: PEM, SOFC (intermediate temperature range of 200-500 ºC)
- **MATERIALS**



  - water/ice

  - polymers (e.g. nafion)

  - oxidic materials (oxides, phosphates, sulphates, *etc*.)
- **PROTON-CONDUCTING OXIDES**

  - First proton-conducting perovskites (1980, Iwahara *et al*.): $LaYO_3$, $SrZrO_3$

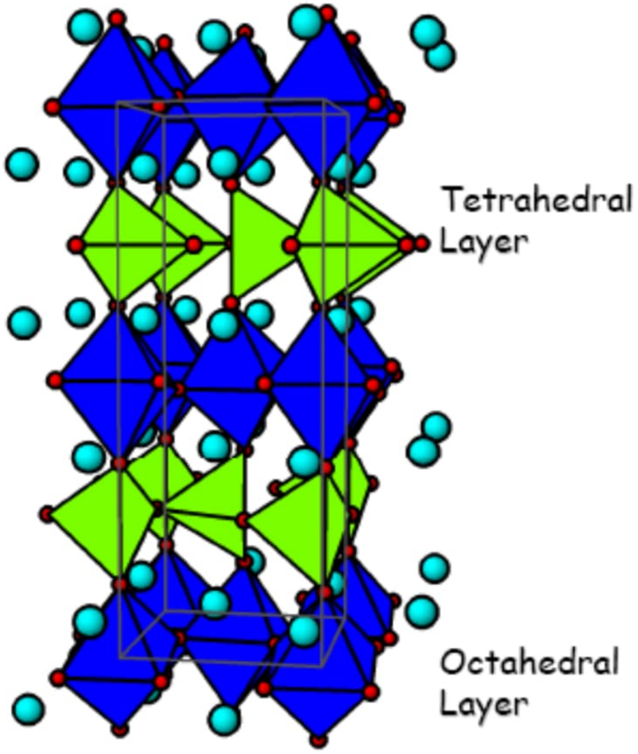
  - Present perovskite prototypes: $SrCeO_3$, $BaCeO_3$

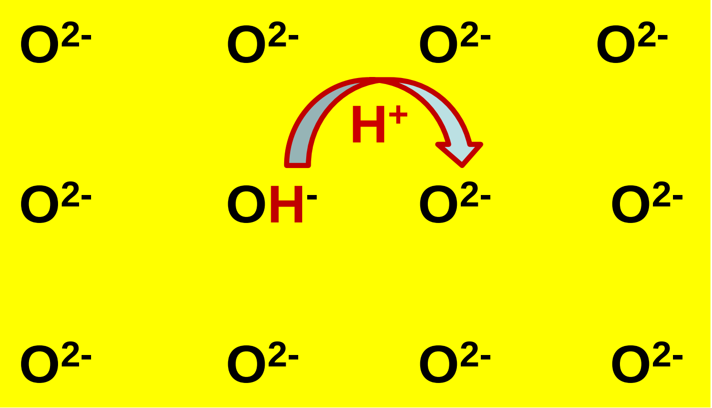
  - Some Ruddlesden-Popper phases

  - Some pyrochlores: $R_2(Zr,Y)_2O_7$, $R_2(Ti,In,Mg)_2O_7$

$Ba_2In_2O_5$ ($BaInO_{2.5}$)

- **Oxide ion conductor**
- **Brownmillerite structure derived from the perovskite structure (oxygen vacancies ordered into layers)**
- **Above 800 °C oxygen vacancies disorder and the oxide ion conductivity jumps from 10^{-3} S/cm to 10^{-1} S/cm**
- **Interesting for PROTON conductivity: $Ba_2(In,Zr)_2O_{5+\delta}$ absorbs water to fill oxygen vacancies and becomes a good proton conductor**





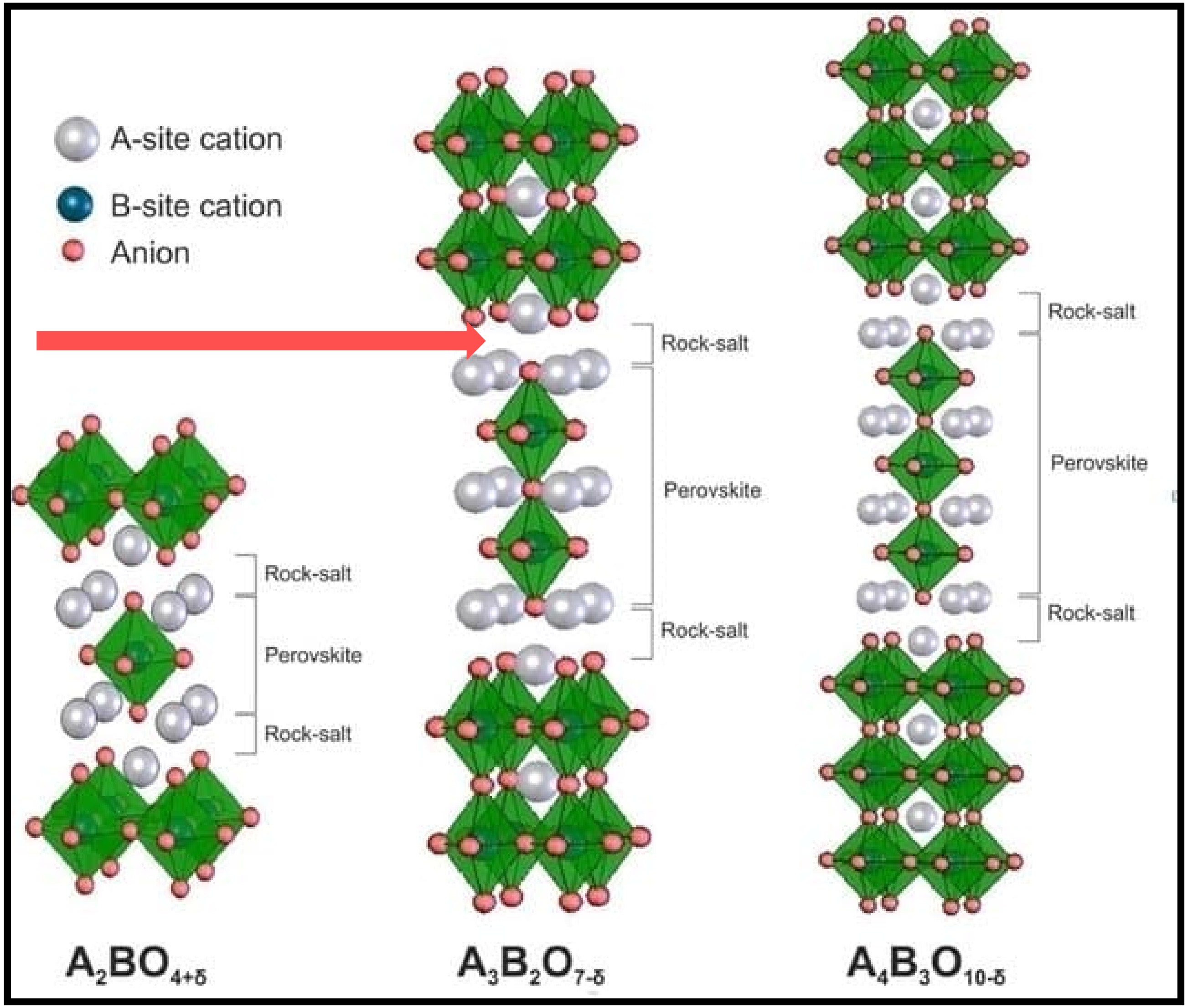
WATER/PROTON ABSORPTION OF OXIDES

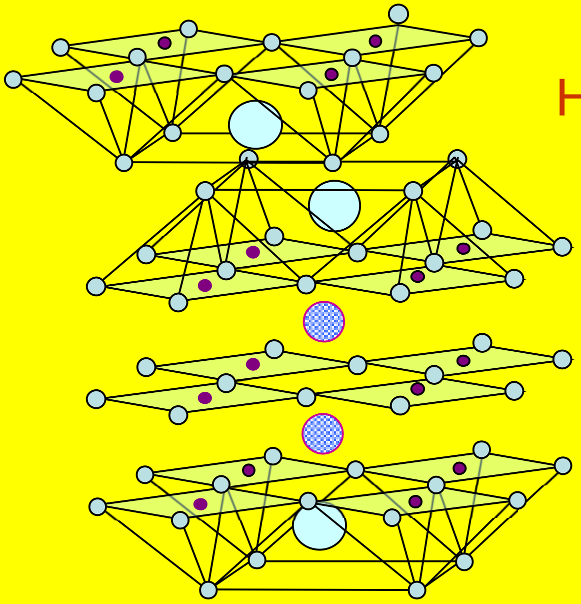
- **Affinity of oxide ion O^{2-} for H^+ is great → in water solutions it immediately captures a proton from the H_2O solvent molecule**
- **Also in solid state O^{2-} ions tend to combine with protons**
- **Proton is very small → when it combines with oxygen the resultant OH^- group is almost identical in size with an O^{2-} ion → the most visible change is seen in the charge balance**
- **Many natural oxide minerals contain OH^- groups, e.g. pyrochlores**
- **Many (nonstoichiometric/highly-oxidized) metal oxides readily absorb water/protons → potential proton conductors**

Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen, water intercalation, excess protons, organic molecules, etc.

O^{2-}, H_2O, H^+





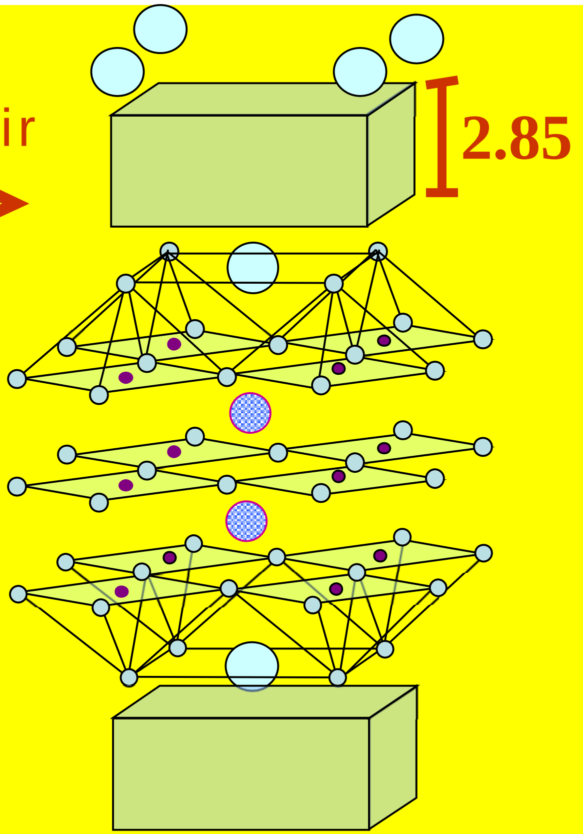
$Ba_2Ca_2Cu_3O_8$

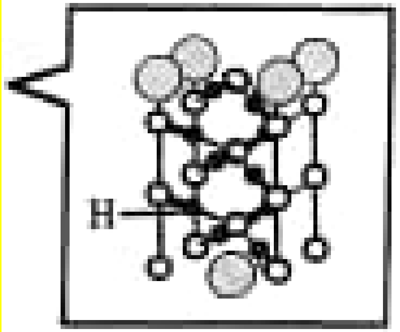
$T_c \approx 126$ K

⇧

High-Pressure Synthesis

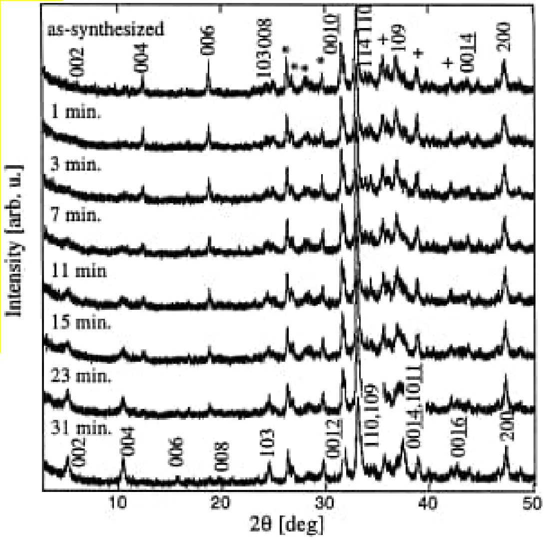
Humid Air ⇨





"Water-Derivative"

T_c = 80～90 K



T. Hosomi, H. Suematsu, H. Fjellvåg, M. Karppinen & H. Yamauchi, *J. Mater. Chem.* 9, 1141 (1999)

Li-ION BATTERY

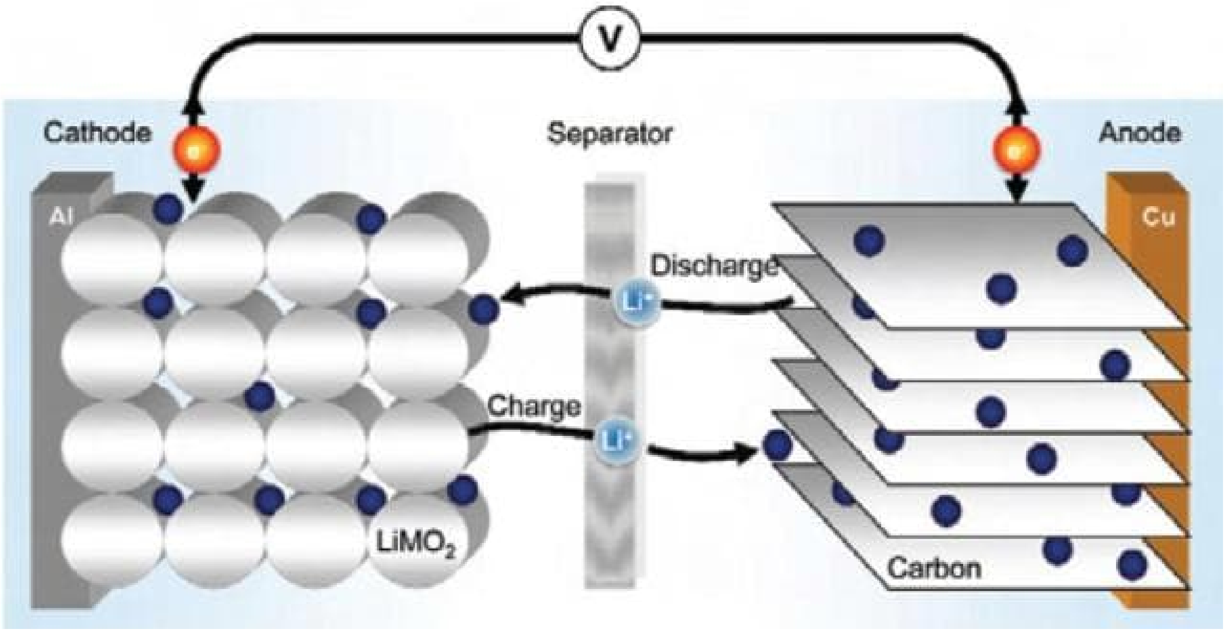
- **Lithium:** lightest of all metals & greatest electrochemical potential & largest energy density per weight & small and easy to move
- **Li-ion battery:** Light-weight, high-voltage & large-energy-density
- **Cell phones, laptops, wearable electronics, electric cars and vehicles, energy storage related to solar cells and wind power, etc.**

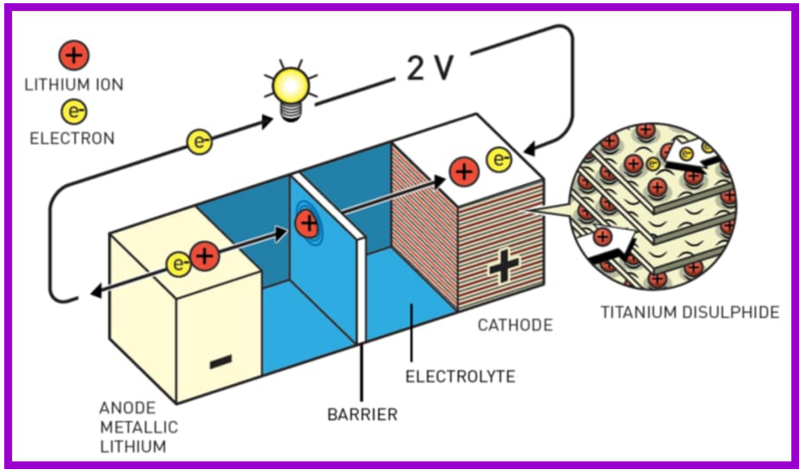
Sony 1991

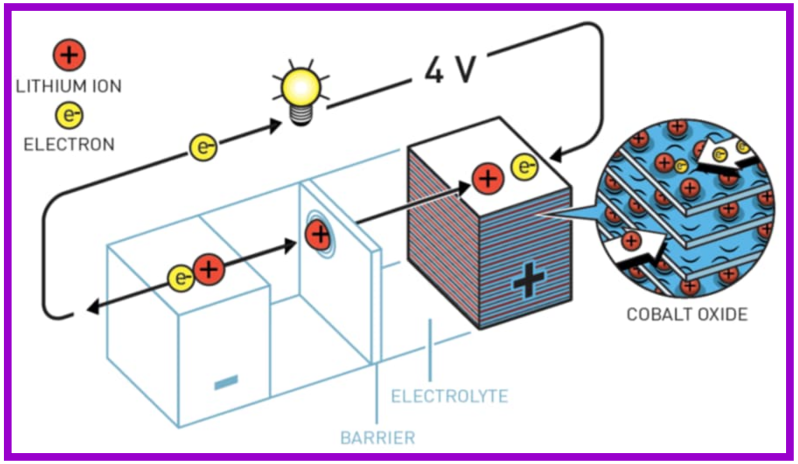
First commercial Li-ion battery

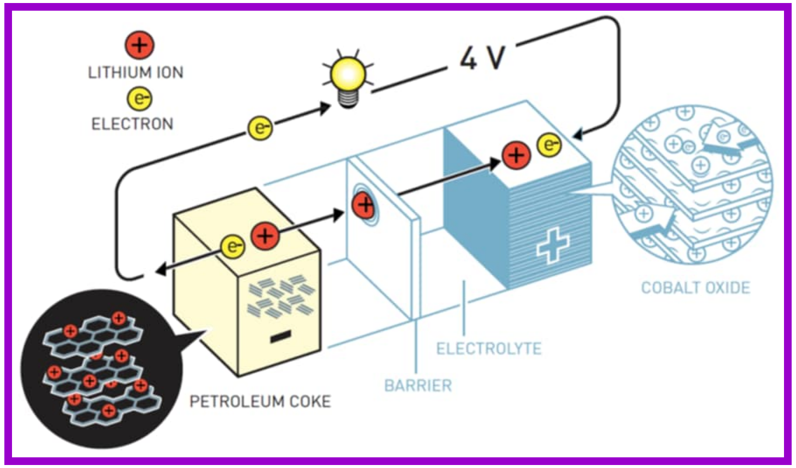
”WET CELL”

- **Anode & Cathode:** **electric & ionic cond.**
- **Liquid electrolyte:** **ionic cond. & elec. insul.**
- **Separator & additives**









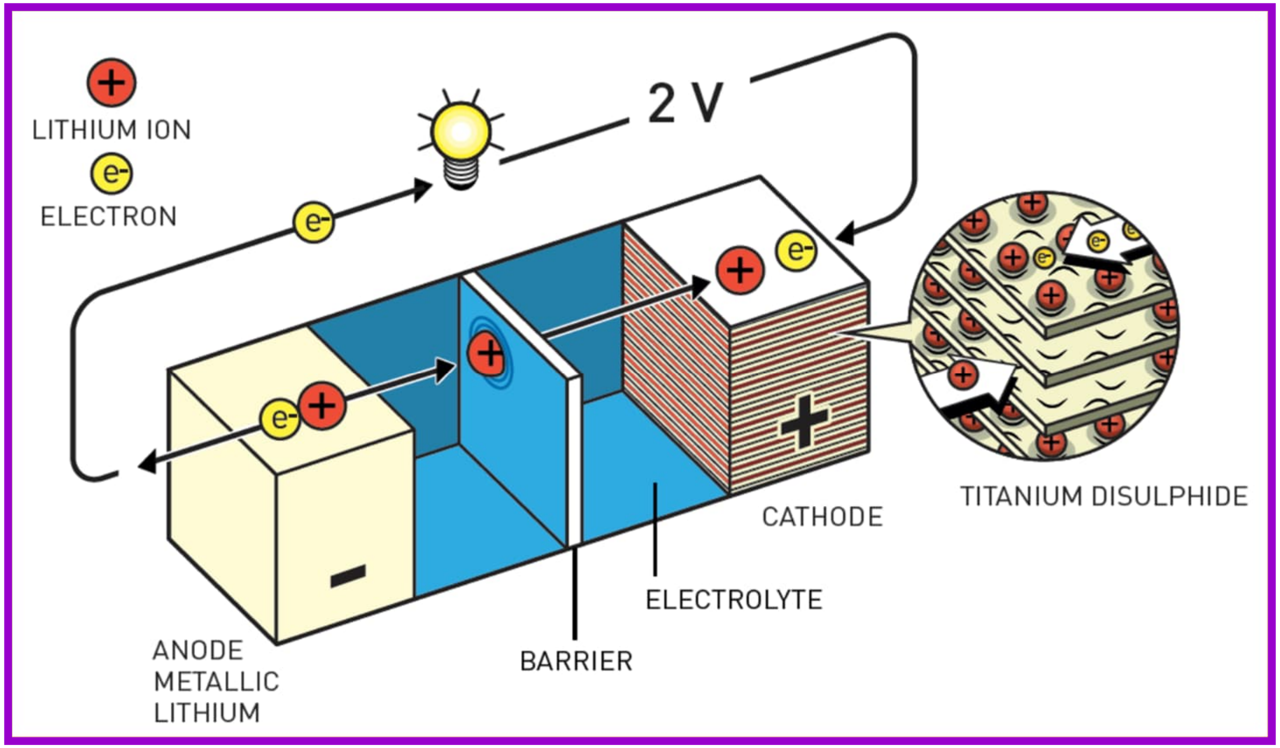
Chemistry Nobel 2019

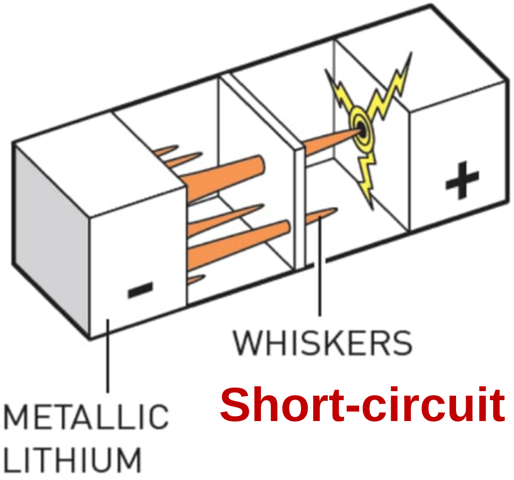
Stanley Whittingham (UK):
- Exxon: TiS_2 cathode 1976

John Goodenough (US):
- Univ. Oxford: $LiCoO_2$ cathode 1980

Akira Yoshino (Jpn):
- Asahi Kasei: carbon-based anode 1985

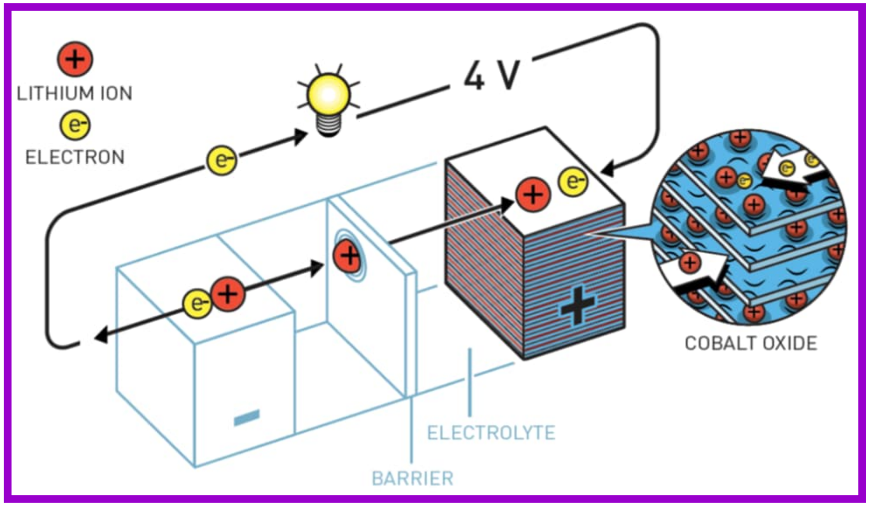
Commercialization: Sony 1991

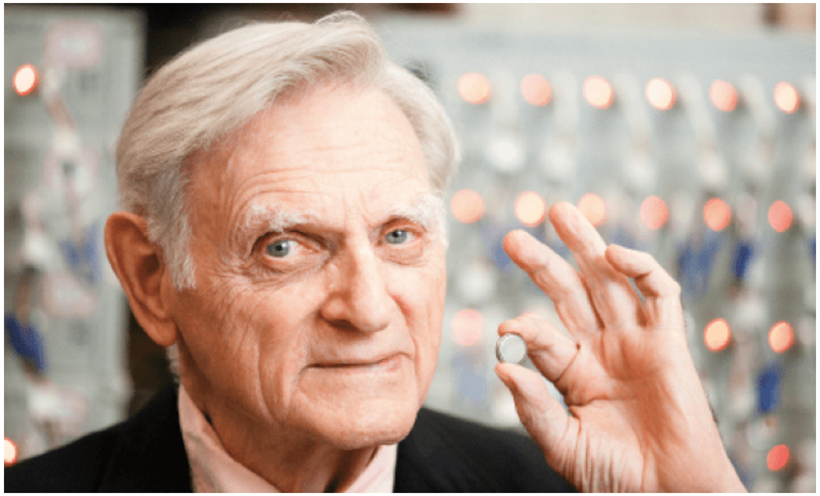




Stanley Whittingham (born 1941 UK)

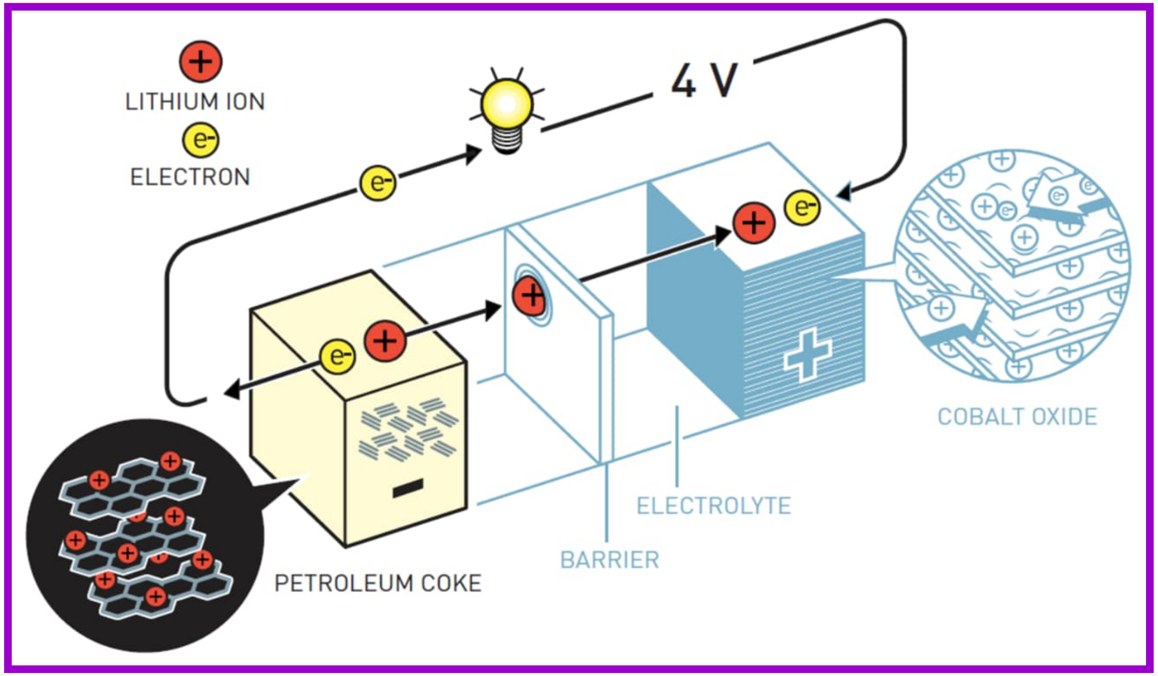
- **PhD 1968 (Oxford University, Chemistry)**
- **Postdoc 1968-1972 (Stanford University)**
- **Exxon 1972-1984:** **- new superconductors → TaS_2**
  - TiS_2 cathode 1976 (Li anode & $LiPF_6$ electrolyte)
- **Prof. 1988 – now (Binghamton University, New York)**





John B. Goodenough (born 1922 Germany/USA)

- BSc 1943 (Yale University, Mathematics)
- PhD 1952 (University of Chicago, Physics)
- Research team leader 1952-1976 (MIT Lincoln Laboratory)
  - Goodenough–Kanamori rules (magnetism)
  - random access memory (computers)
- Prof/Head 1976-1986 (Univ. Oxford, Inorganic Chemistry)
  - Li_xCoO_2 cathode 1980 ($LiMn_2O_4$ cathode 1986)
- Prof. 1986 – 2023 (University of Texas at Austin)
  - $LiFePO_4$ 1996
- e.g. Japan Prize 2001, Enrico Fermi Award 2009, National Medal of Science 2011, Draper Prize 2014, Welch Award 2017, Copley Medal 2019

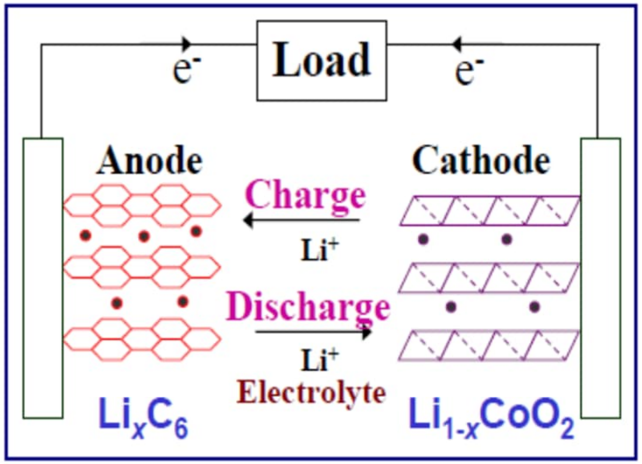


Akira Yoshino (born 1948 Japan)

- **MSc 1972 (Kyoto University)**
- **Asahi Kasei Co. 1972 - now:**
  - **Carbon-based anode 1985** (with $LiCoO_2$ cathode)
  - **Safety tests !**
- **Commercialization: Sony 1991**
- **PhD 2005 (Osaka University)**
- **Prof. 2017 – now (Meijo University, Nagoya)**

Li-ion Battery REACTIONS

- **Rechargable battery: charged (reactions repeated !) thousands times**
- **Reversible intercalation of Li^+ ions within anode & cathode materials (= relatively ”mild” chemical reactions only !)**
- **Graphite & $LiCoO_2$: layered crystal structures**
- **Upon charging: $LiCoO_2 \rightarrow Li_xCoO_2$ (how far reaction can proceed ?)**
- **(Unwanted) reaction between graphite and liquid electrolyte → SEI (Solid-Electrolyte Interphase)**



EC: ethylene carbonate

DEC: dimethyl carbonate

Cell: $(-)\ C\ |\ LiPF_6\text{-}(EC+DEC)\ |\ LiCoO_2\ (+)$

Cathode: $LiCoO_2 \underset{D}{\overset{C}{\rightleftarrows}} Li_{1-x}CoO_2 + xLi^+ + xe^-$

Anode: $6C + xLi^+ + xe^- \underset{D}{\overset{C}{\rightleftarrows}} Li_xC_6$

Total: $LiCoO_2 + 6C \underset{D}{\overset{C}{\rightleftarrows}} Li_{1-x}CoO_2 + Li_xC_6$

PRESENT Li-ion battery MATERIAL VARIETY

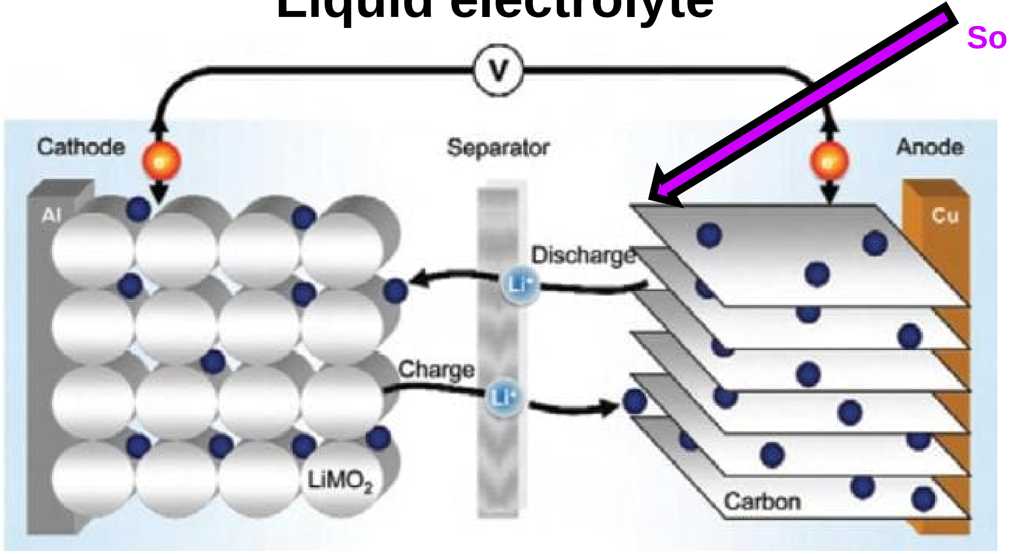
(under intense research)

CATHODE	$LiCoO_2$ $Li(Co,Ni,Mn)O_2$ (raw mat., perfor.), $LiMn_2O_4$, $LiFePO_4$ (safety)
ANODE	Graphite Silicon (energy density), $Li_4Ti_5O_{12}$ (safety)
ELECTROLYTE	$LiPF_6$ + ethylene carbonate solution Solid electrolytes (safety)

Liquid electrolyte

SEI

Solid-Electrolyte-Interphase

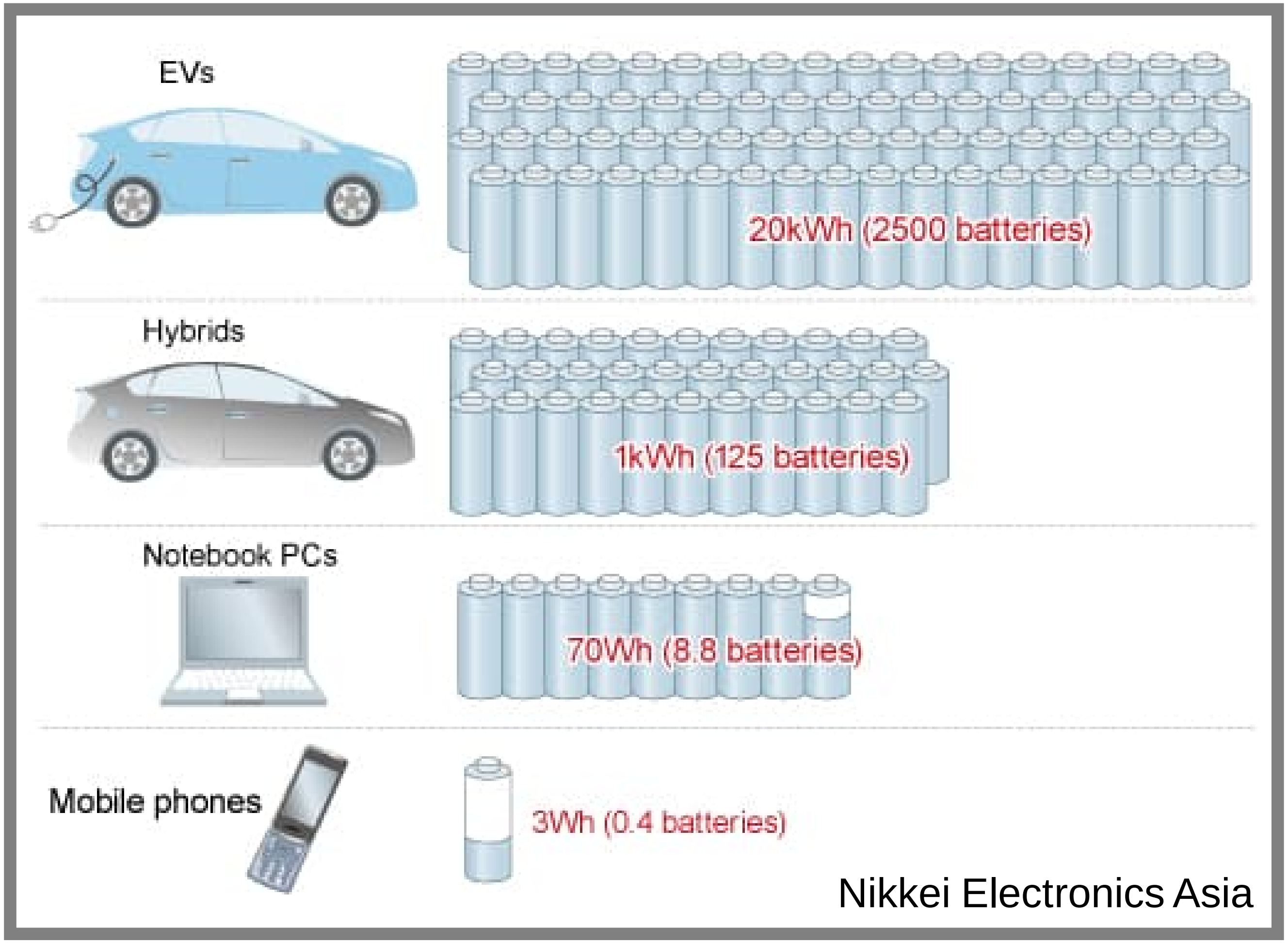


$LiCoO_2$

Graphite

ELECTRIC CAR BATTERY SYSTEM

10 000 times larger energy capacity compared to cell phone



Nikkei Electronics Asia

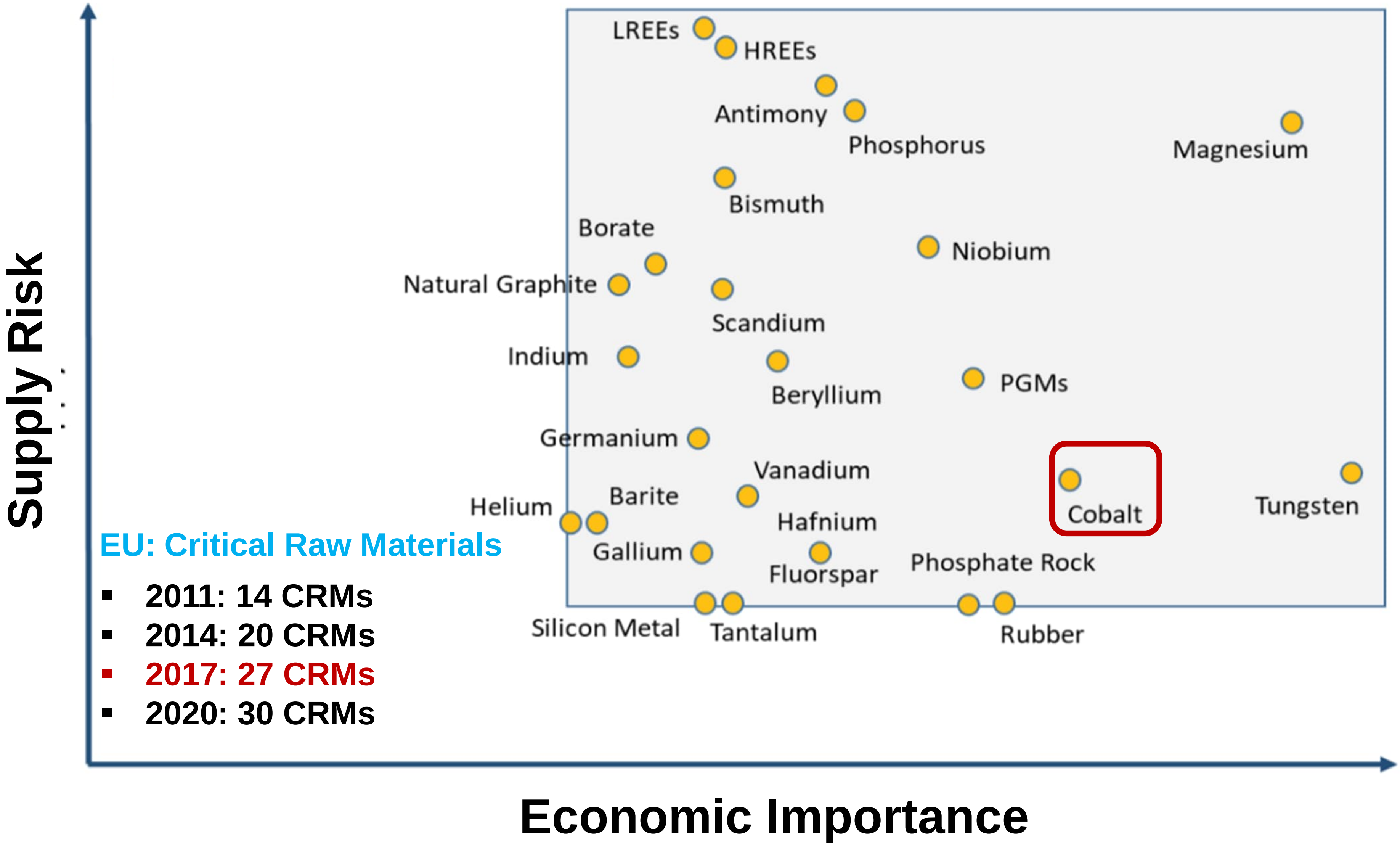
Car battery 600 kg

- 8 kg Li
- 7 kg Co
- 50 kg Ni

Cell phone 130 g

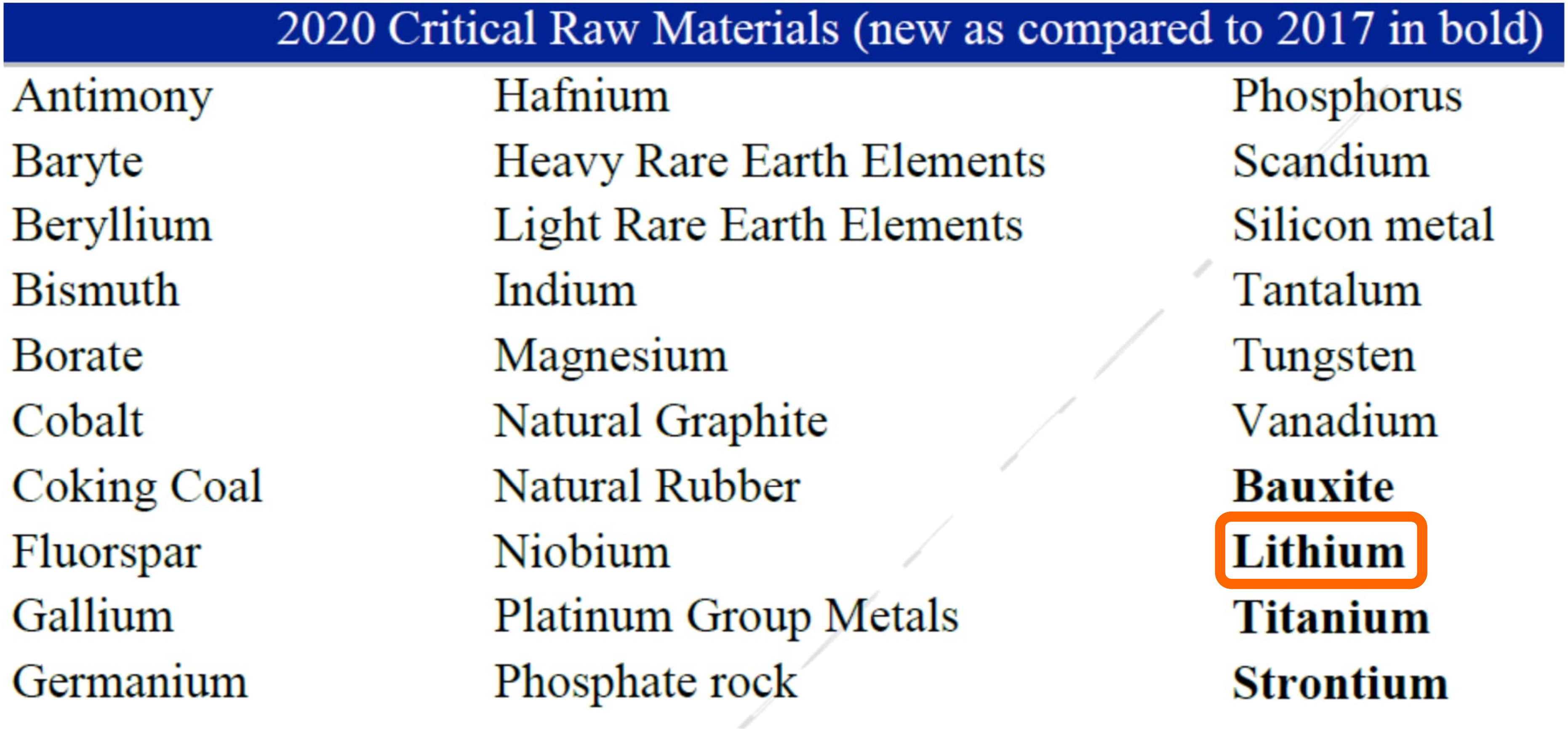
- 3 g Li
- 7 g Co
- 3 g Ni

EU Critical Raw Materials (CRM)



EU: Critical Raw Materials

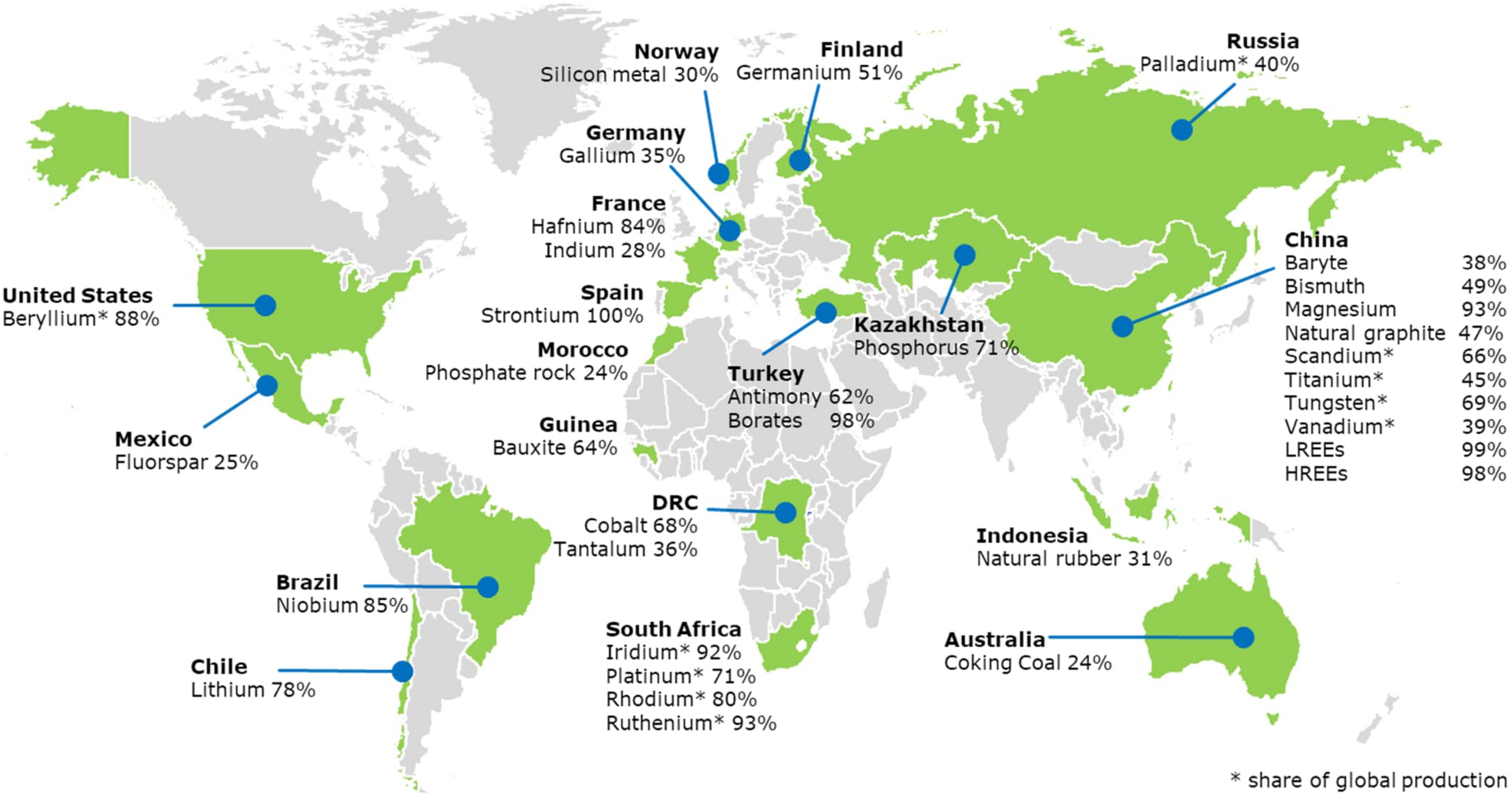
- **2011: 14 CRMs**
- **2014: 20 CRMs**
- **2017: 27 CRMs**
- **2020: 30 CRMs**



2020 Critical Raw Materials (new as compared to 2017 in bold)

- Antimony
- Baryte
- Beryllium
- Bismuth
- Borate
- Cobalt
- Coking Coal
- Fluorspar
- Gallium
- Germanium
- Hafnium
- Heavy Rare Earth Elements
- Light Rare Earth Elements
- Indium
- Magnesium
- Natural Graphite
- Natural Rubber
- Niobium
- Platinum Group Metals
- Phosphate rock
- Phosphorus
- Scandium
- Silicon metal
- Tantalum
- Tungsten
- Vanadium
- **Bauxite**
- **Lithium**
- **Titanium**
- **Strontium**

FROM WHERE the EU CRM materials originate ?



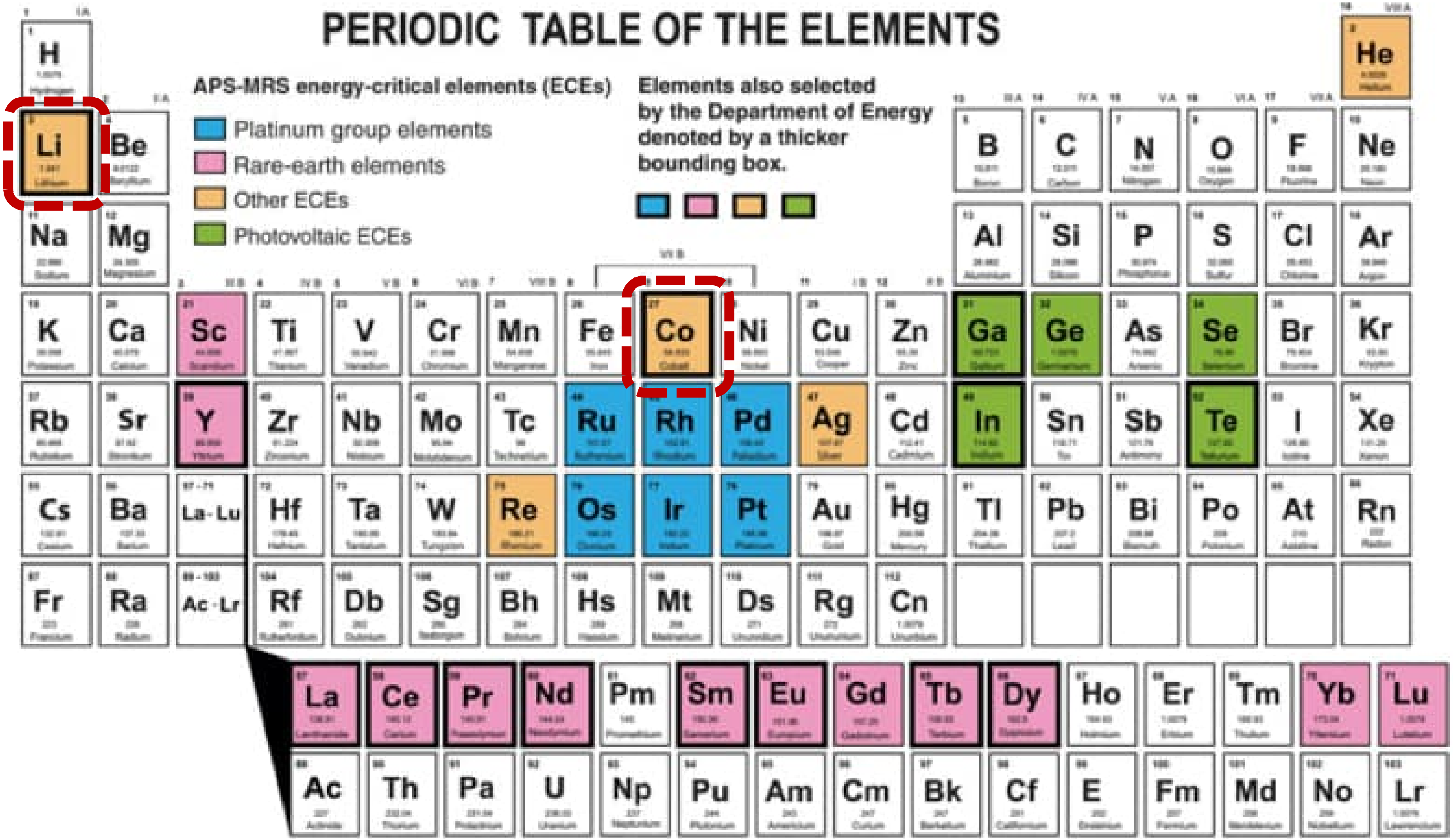
* share of global production

More than 60 % of cobalt in the world is mined in Republic of Congo

(mostly in Chinese ownership)

Cobolt mining place in Congo close
to Kasulo. Valokuvat: Siddharth Kara

ENERGY CRITICAL ELEMENTS



PERIODIC TABLE OF THE ELEMENTS

APS-MRS energy-critical elements (ECEs)

- 🟦 Platinum group elements
- 🟪 Rare-earth elements
- 🟧 Other ECEs
- 🟩 Photovoltaic ECEs

Elements also selected by the Department of Energy denoted by a thicker bounding box.

🟦 🟪 🟧 🟩

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Md	No	Lr

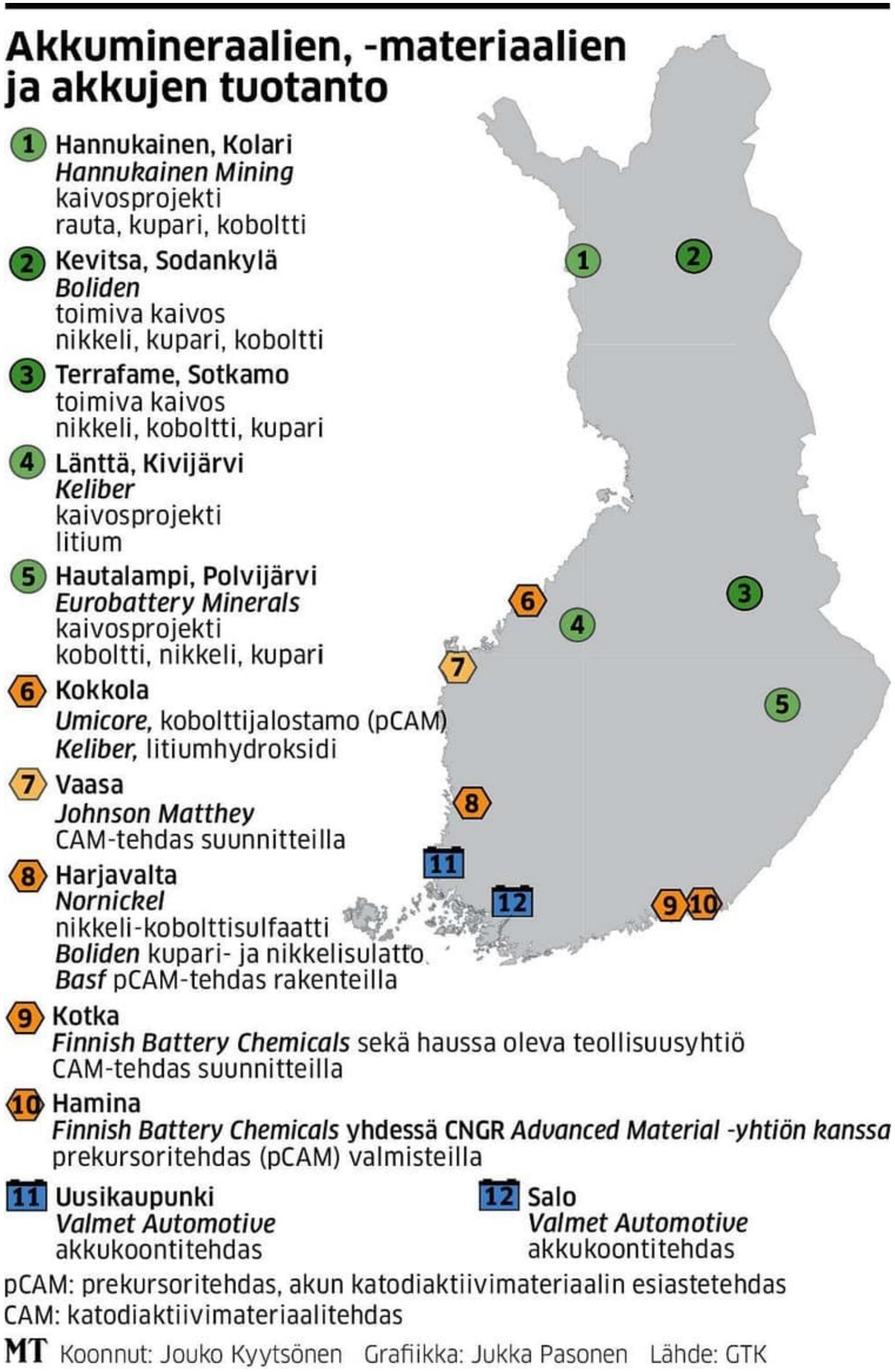
Materials Research Society (MRS), USA

Battery metals in Finland

- **Finland is the only European country to have activities related to all battery metals**
- **Mining: Ni, Cu & Co**
- **Refining: Co (>10%), Ni & Cu**
- **Planned mining/refining: Li**

Battery Chain is already strong in Finland; however, no battery manufacturing (yet).

Cathode material manufacturing is expected in Kotka, precursor manufacturing in Hamina, and in Harjavalta BASF is planning to start the biggest battery material production in European scale.



Akkumineraalien, -materiaalien ja akkujen tuotanto

1 **Hannukainen, Kolari**
Hannukainen Mining
kaivosprojekti
rauta, kupari, koboltti

2 **Kevitsa, Sodankylä**
Boliden
toimiva kaivos
nikkeli, kupari, koboltti

3 **Terrafame, Sotkamo**
toimiva kaivos
nikkeli, koboltti, kupari

4 **Länttä, Kivijärvi**
Keliber
kaivosprojekti
litium

5 **Hautalampi, Polvijärvi**
Eurobattery Minerals
kaivosprojekti
koboltti, nikkeli, kupari

6 **Kokkola**
Umicore, kobolttijalostamo (pCAM)
Keliber, litiumhydroksidi

7 **Vaasa**
Johnson Matthey
CAM-tehdas suunnitteilla

8 **Harjavalta**
Nornickel
nikkeli-kobolttisulfaatti
Boliden kupari- ja nikkelisulatto
Basf pCAM-tehdas rakenteilla

9 **Kotka**
Finnish Battery Chemicals sekä haussa oleva teollisuusyhtiö
CAM-tehdas suunnitteilla

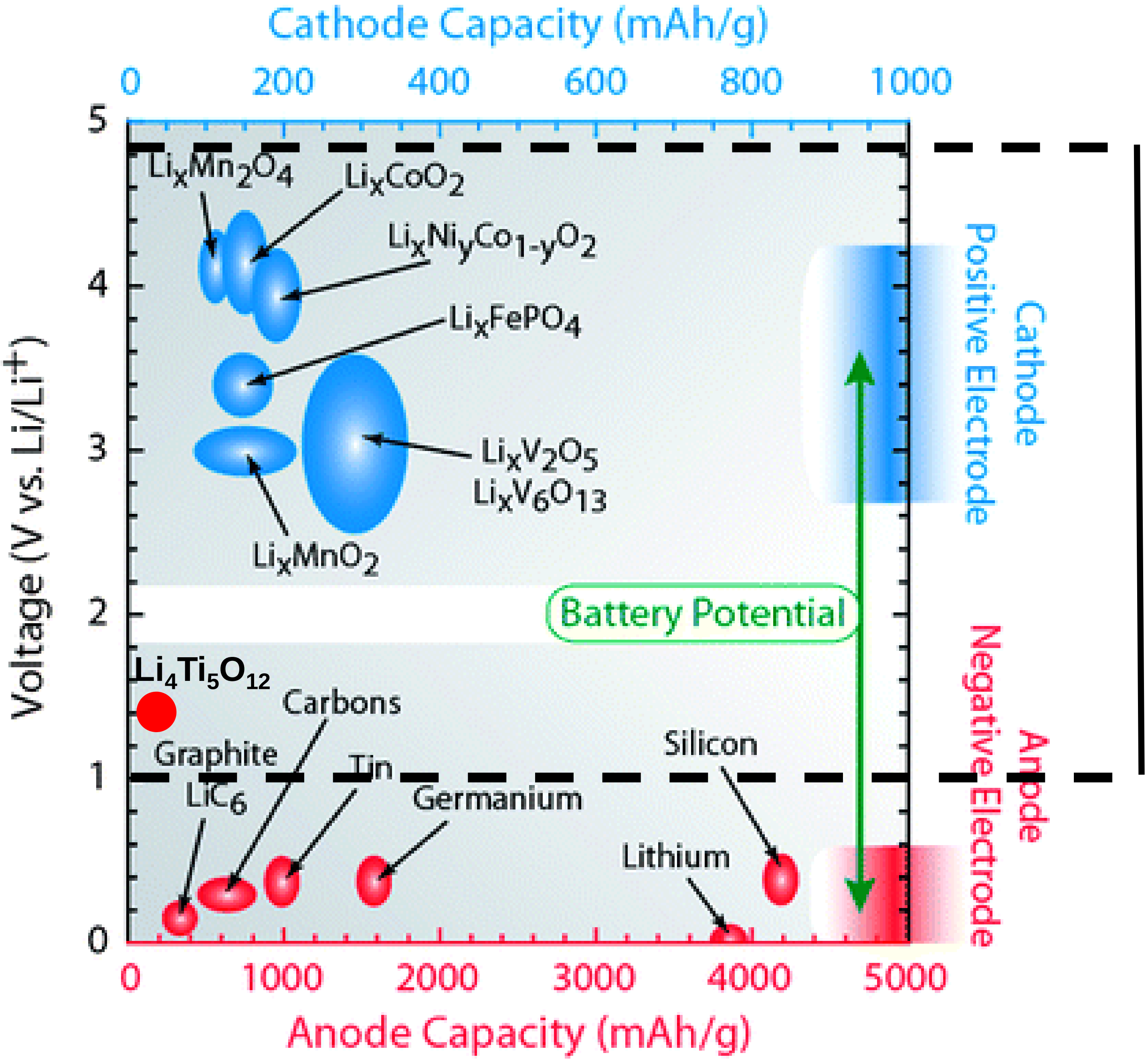
10 **Hamina**
Finnish Battery Chemicals yhdessä CNGR *Advanced Material -yhtiön kanssa*
prekursoritehdas (pCAM) valmisteilla

11 **Uusikaupunki**
Valmet Automotive
akkukoontitehdas

12 **Salo**
Valmet Automotive
akkukoontitehdas

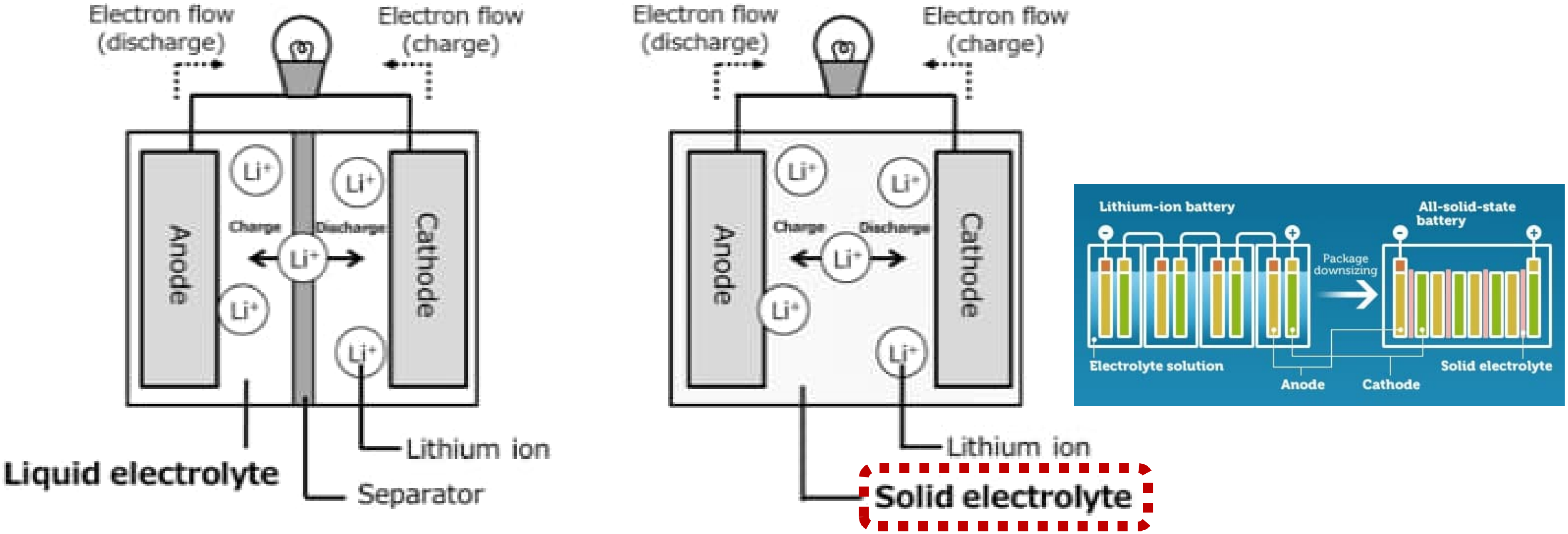
pCAM: prekursoritehdas, akun katodiaktiivimateriaalin esiastetehdas
CAM: katodiaktiivimateriaalitehdas

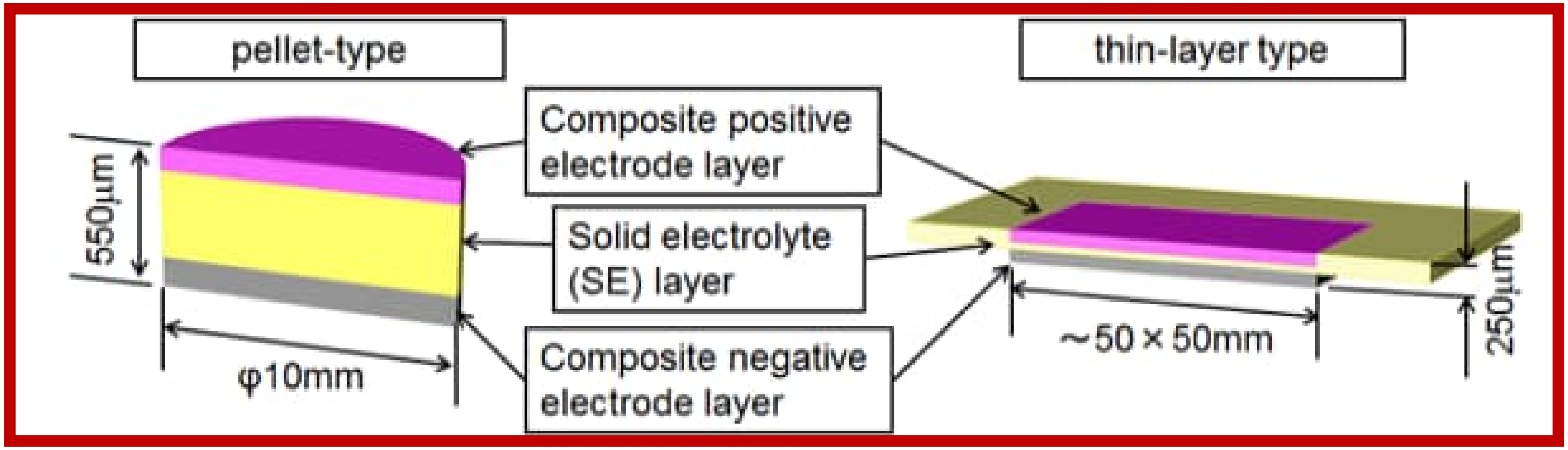
MT Koonnut: Jouko Kyytsönen Grafiikka: Jukka Pasonen Lähde: GTK



Liquid electolyte stability range

SOLID ELECTROLYTES





SOLID ELECTROLYTE

- To address the two major problems of present liquid organic electrolytes: flammability and limited electrochemical stability (reactivity with anode materials)
- **REQUIREMENTS: High ionic conductivity & Low electronic conductivity**
- **Challenge:** Li^+-ion conductivity not yet comparable to liquid electrolytes (~10^{-3} S/cm)

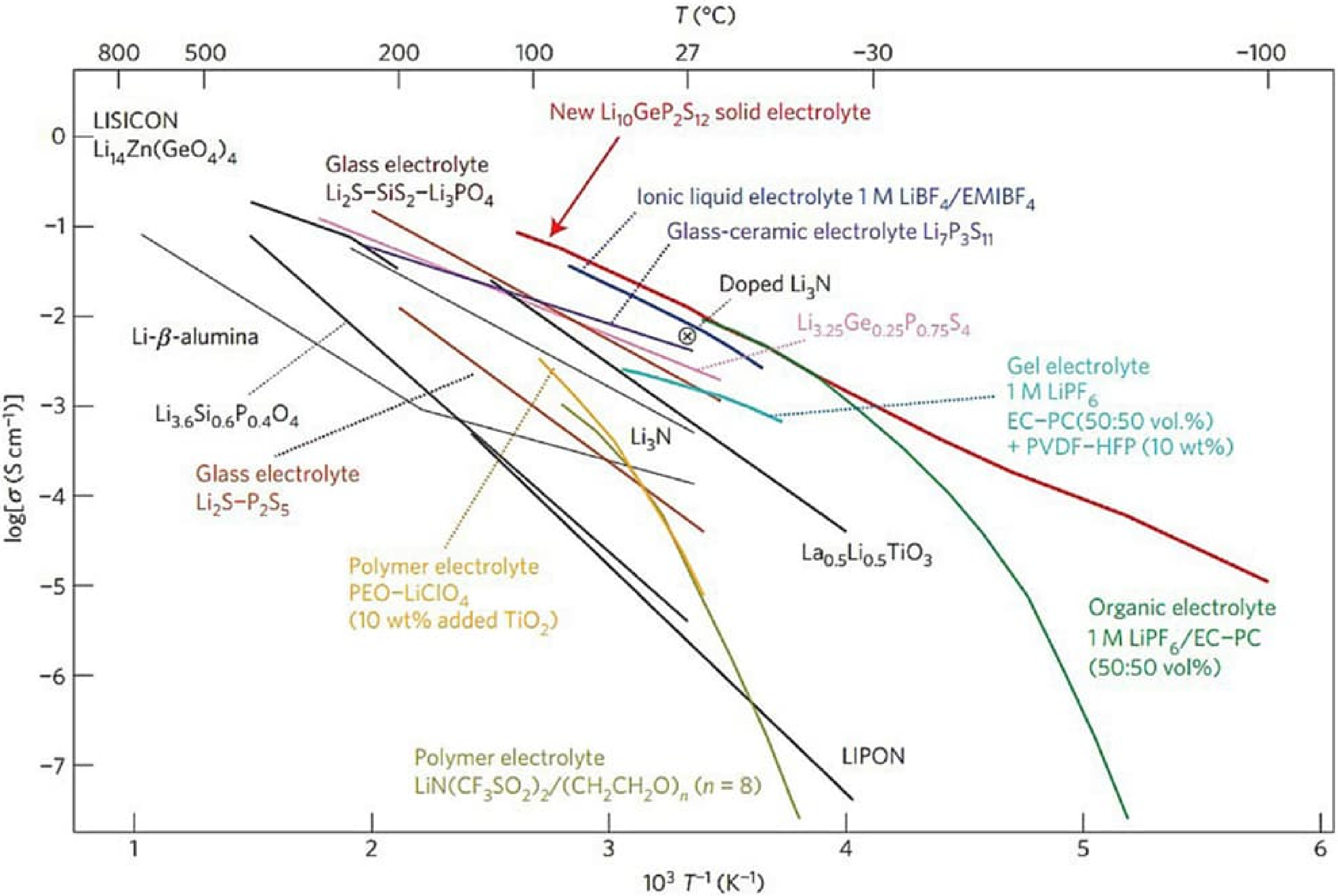
PROS

- Non-flammable → Safety
- Non-reactive with electrode materials (no SEI layers)
- Possibility to use Li metal anode
- Possibility to use >5 V cathode materials → Higher energy density
- Wider operation temperature range
- Simpler cell structure, no need e.g. for an expensive separator
- No risk for electrolyte leakage
- Simpler manufacturing process (in air) → Lower cost

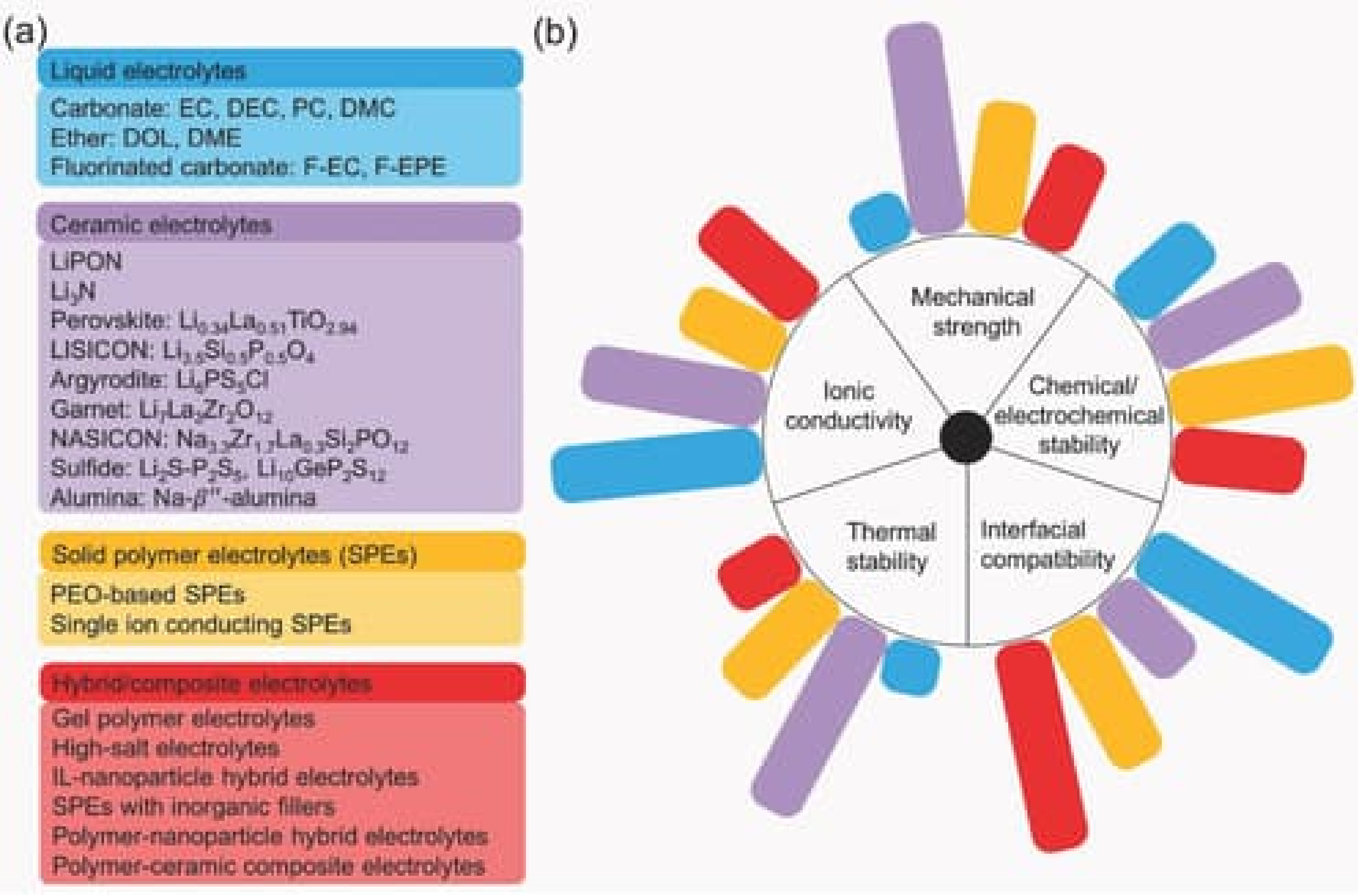
CONS

- Heavier
- Integration (interface contacts) with the electrodes

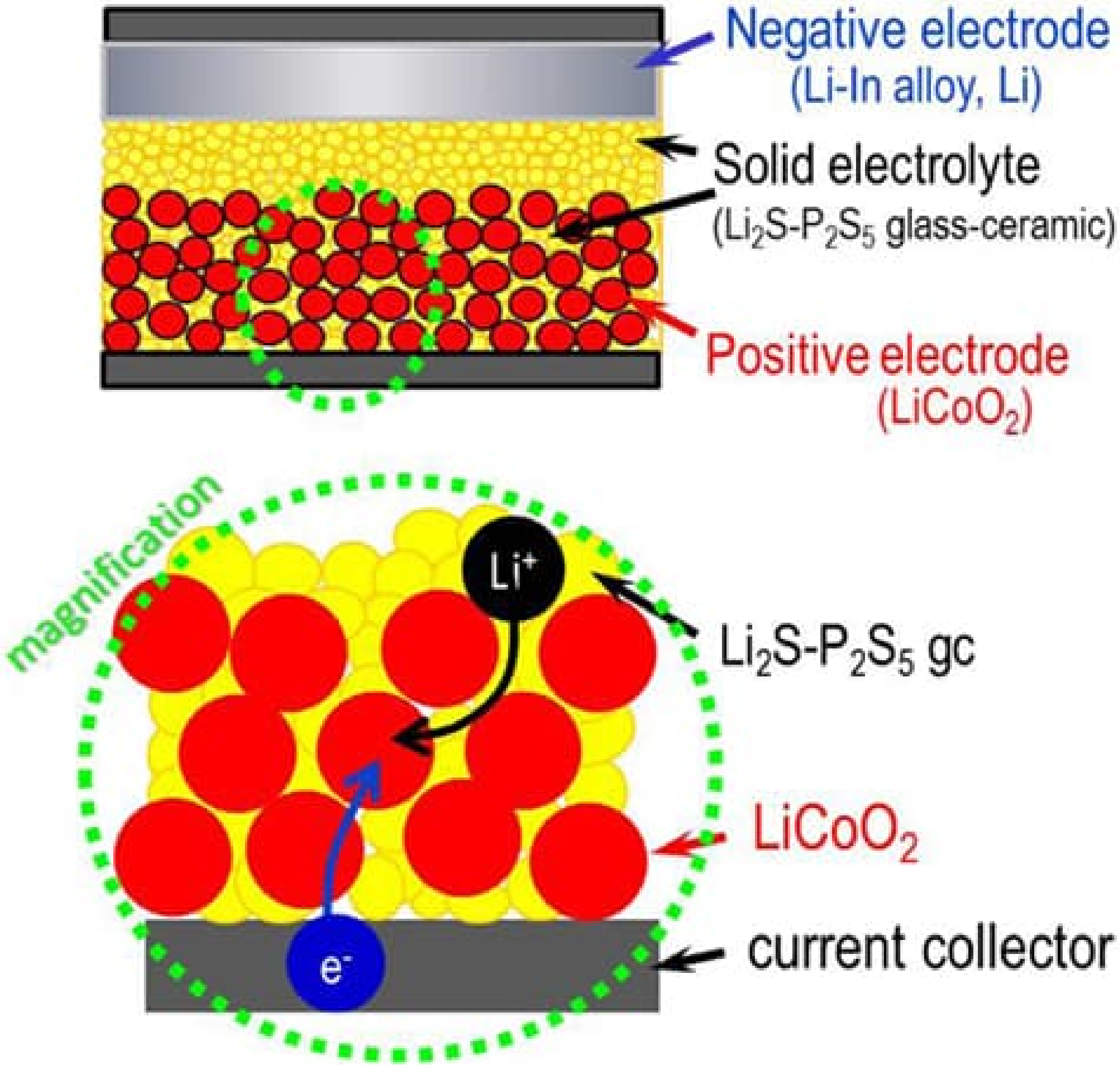
Design principles for solid-state lithium superionic conductors, *Nat. Mater.* 14, 1026 (2015).



LaCoste, J.D., Zakutayev, A., and Fei, L., A review on lithium phosphorus oxynitride, *J. Phys. Chem. C* **125** (2021) 3651–3667.


(a)
Liquid electrolytes
Carbonate: EC, DEC, PC, DMC
Ether: DOL, DME
Fluorinated carbonate: F-EC, F-EPE
Ceramic electrolytes
LiPON
Li_3N
Perovskite: $Li_{0.34}La_{0.51}TiO_{2.94}$
LISICON: $Li_{3.5}Si_{0.5}P_{0.5}O_4$
Argyrodite: Li_6PS_5Cl
Garnet: $Li_7La_3Zr_2O_{12}$
NASICON: $Na_{3.3}Zr_{1.7}La_{0.3}Si_2PO_{12}$
Sulfide: Li_2S-P_2S_5, $Li_{10}GeP_2S_{12}$
Alumina: Na-β''-alumina
Solid polymer electrolytes (SPEs)
PEO-based SPEs
Single ion conducting SPEs
Hybrid/composite electrolytes
Gel polymer electrolytes
High-salt electrolytes
IL-nanoparticle hybrid electrolytes
SPEs with inorganic fillers
Polymer-nanoparticle hybrid electrolytes
Polymer-ceramic composite electrolytes
(b)
Mechanical strength
Chemical/ electrochemical stability
Interfacial compatibility
Thermal stability
Ionic conductivity

Bulk-type battery



Negative electrode
(Li-In alloy, Li)

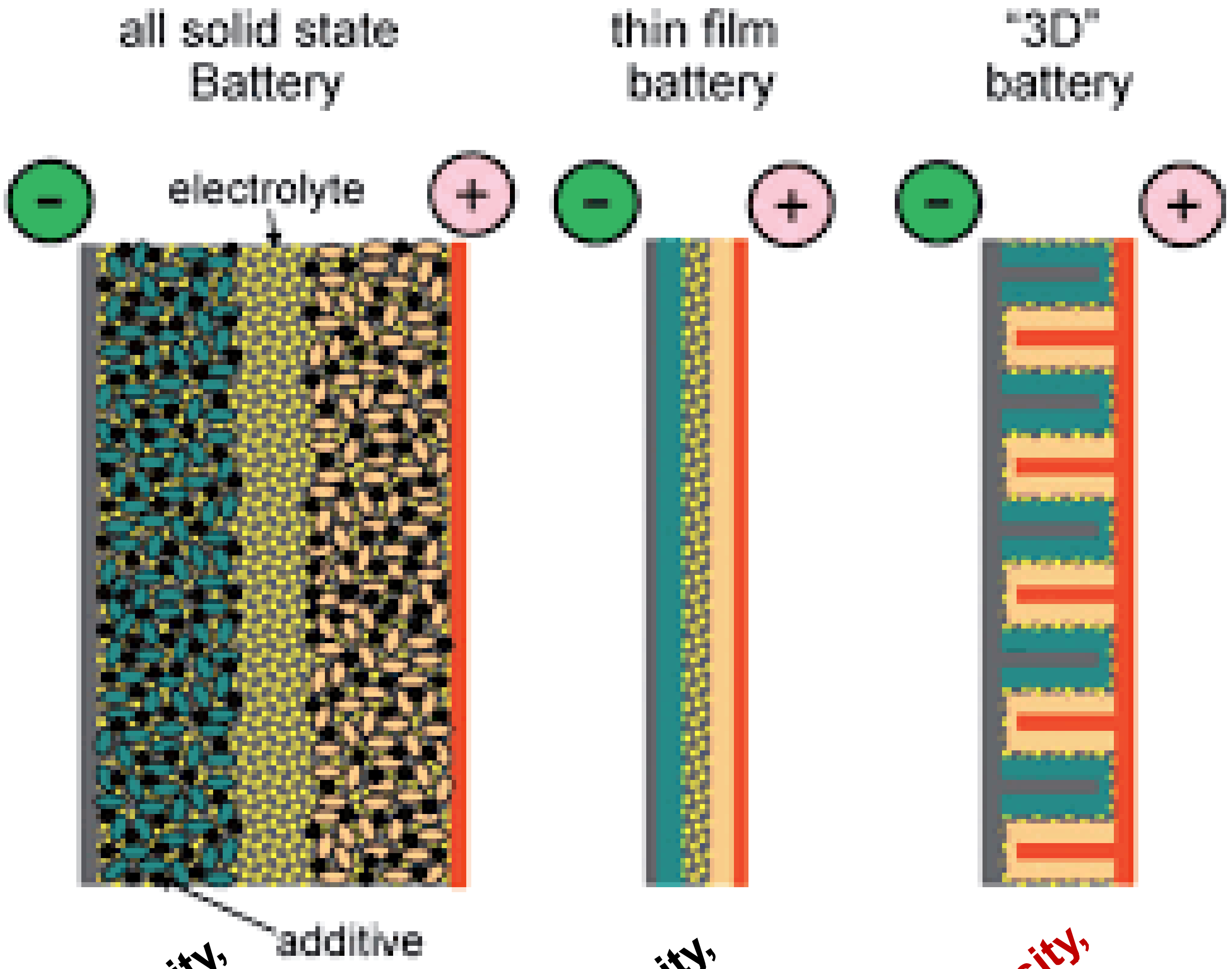
Solid electrolyte
(Li_2S-P_2S_5 glass-ceramic)

Positive electrode
($LiCoO_2$)

Li_2S-P_2S_5 gc

$LiCoO_2$

current collector



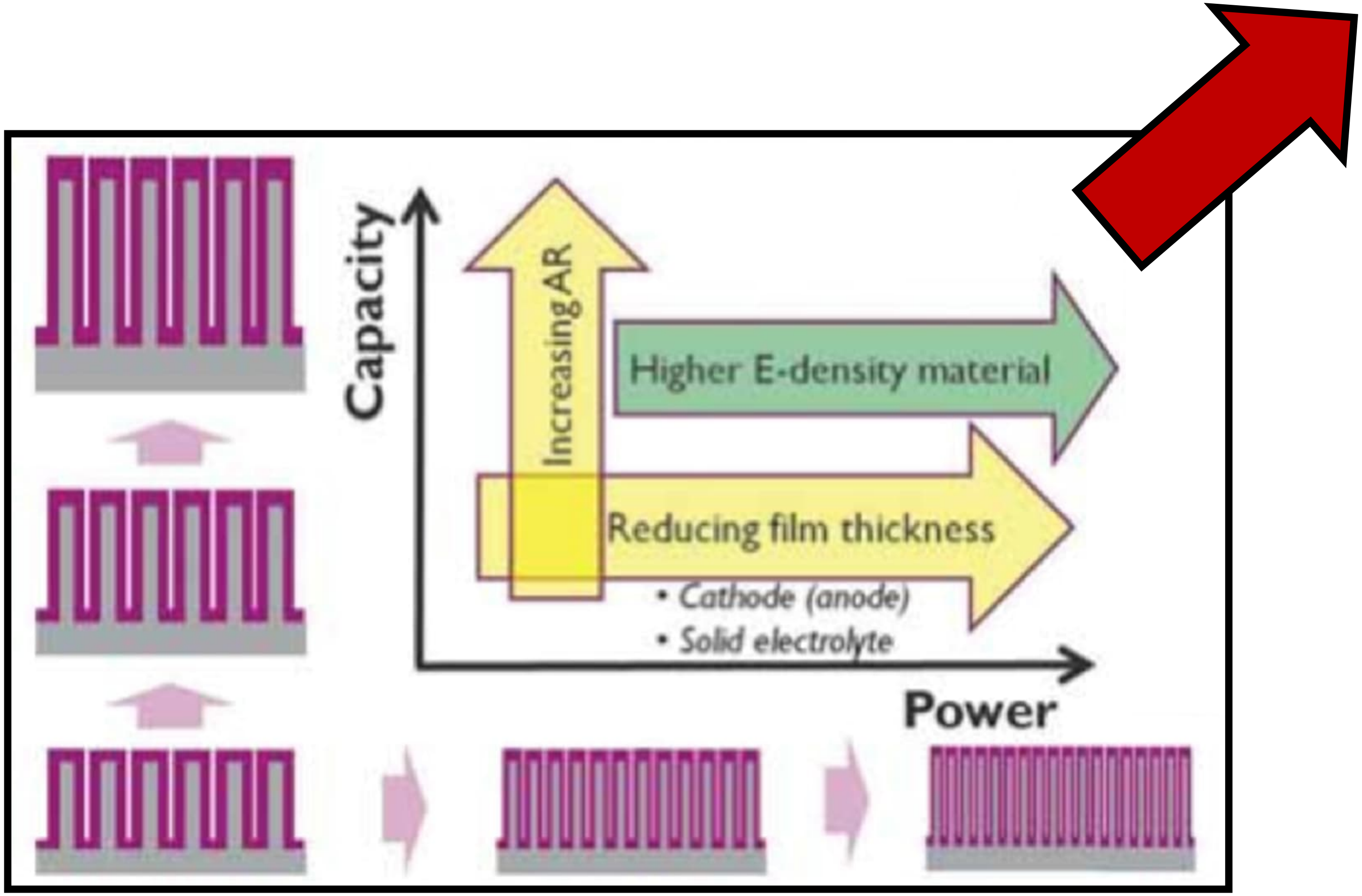
High energy density, Low power density

Low energy density, High power density

High energy density, High power density

ALD

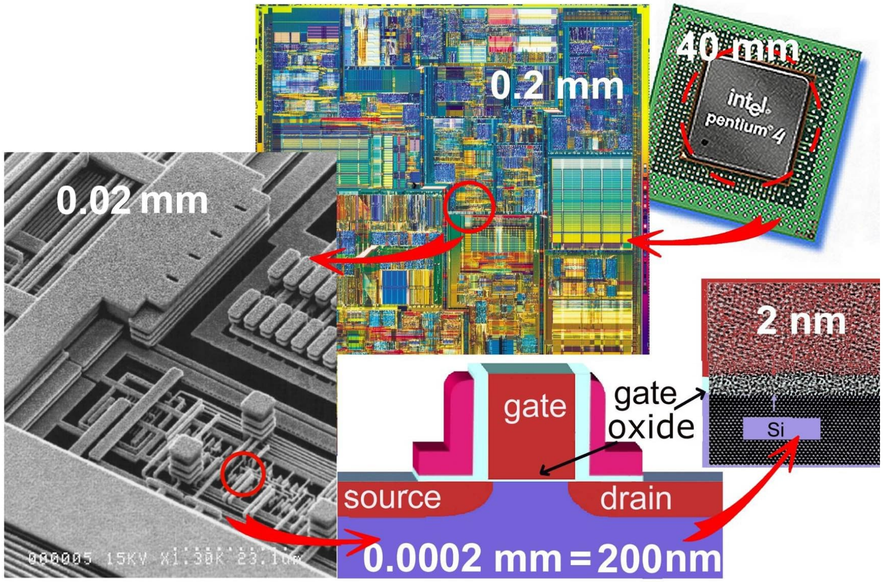
Atomic Layer Deposition



Atomic Layer Deposition (ALD)

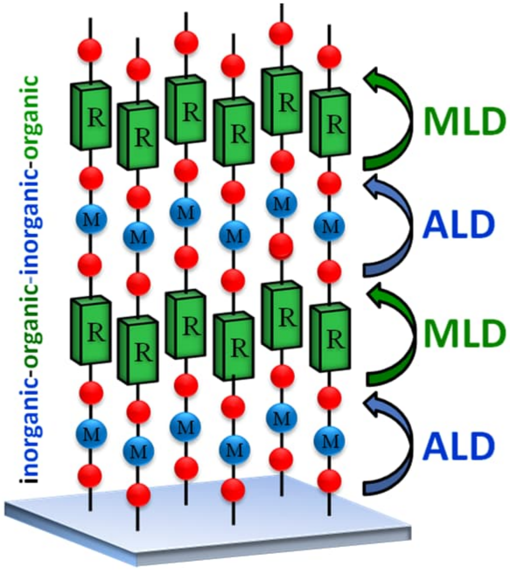
- Advanced gas-phase thin-film technology
- ALD cycle: two (or more) precursors pulsed separately and sequently
- Pin-hole free, conformal & large-area homogeneous thin films with atomic-layer level thickness control for microelectronics and beyond

MOSFET transistor

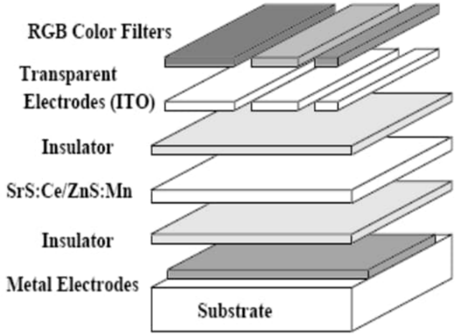


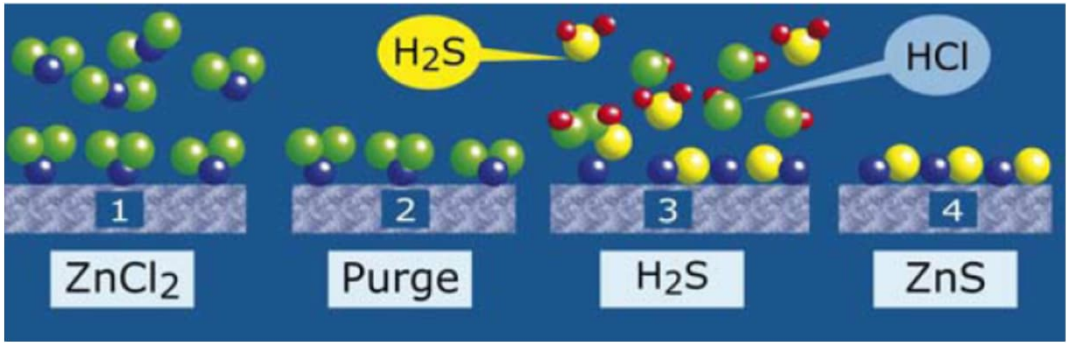
ALD/MLD

- Inorganic-organic thin films
- MLD: molecular layer deposition



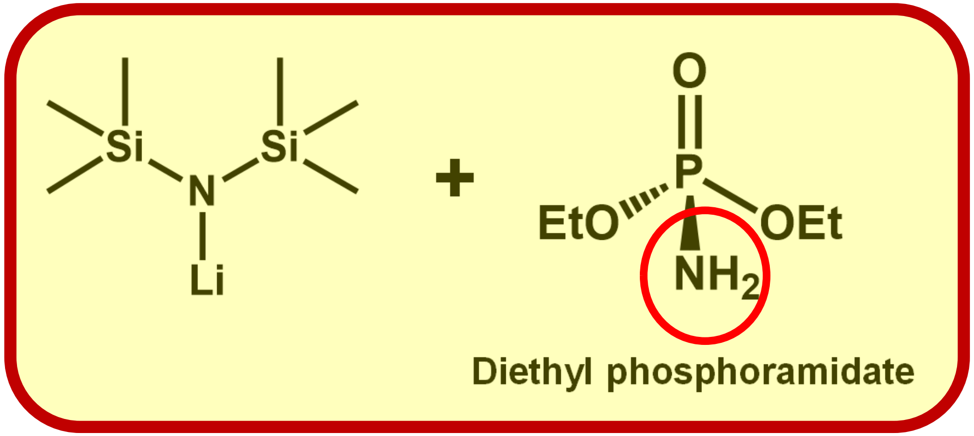
Electro-luminescent display



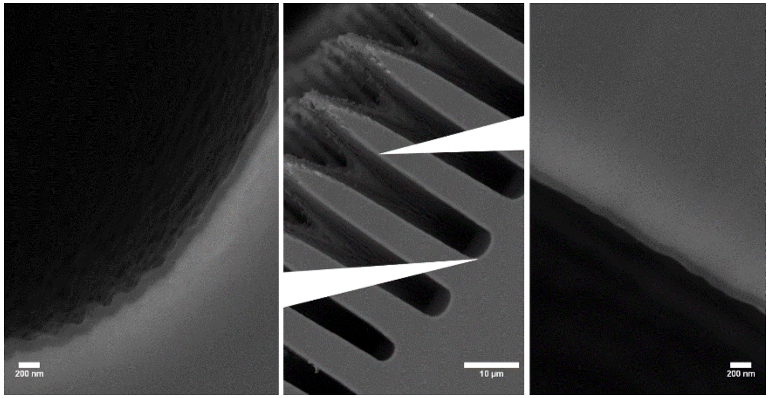


ALD OF LIPON

- LiPON: Lithium phosphorus oxynitride $Li_xPO_{3-y}N_z$
- Oak Ridge National Laboratory: sputtering of Li_3PO_4 target in N_2 plasma
- Stable in air and also in connection with Li anode
- Most promising solid-state electrolyte for thin-film Li-ion microbattery
- **Amorhous** intermediate between crystalline Li_3PO_3 and Li_2PO_2N
- Ionic conductivity greatly enhanced by N doping (up to 10^{-6} S cm^{-1})
- ALD films: RT ionic conductivity 6.6 x 10^{-7} S cm^{-1}



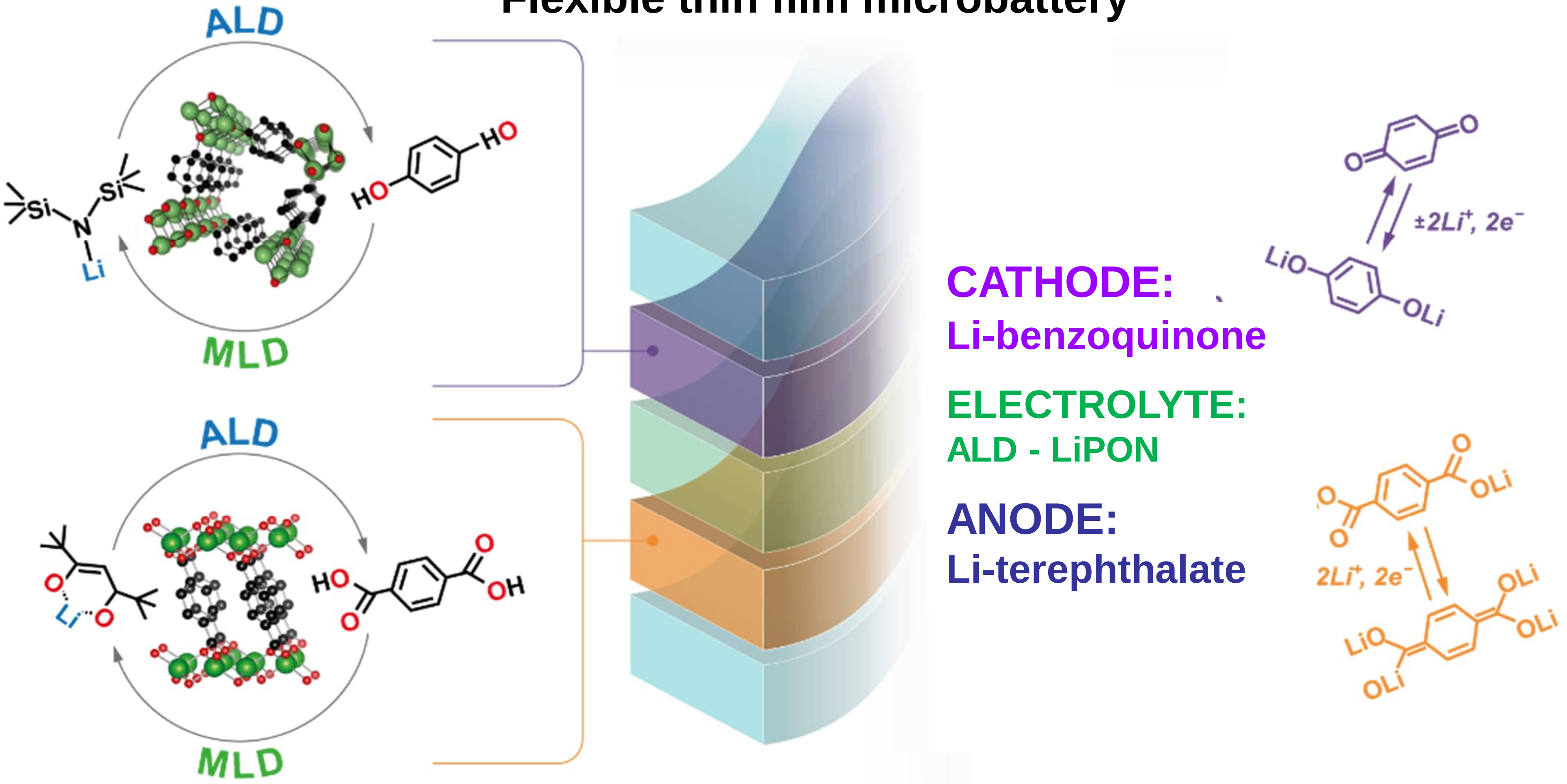
Diethyl phosphoramidate



M. Nisula, Y. Shindo, H. Koga & M. Karppinen,
Chem. Mater. **27**, 6987 (2015).

ALD + MLD: Metal-saving Li-organic microbattery

Flexible thin film microbattery



CATHODE:
Li-benzoquinone

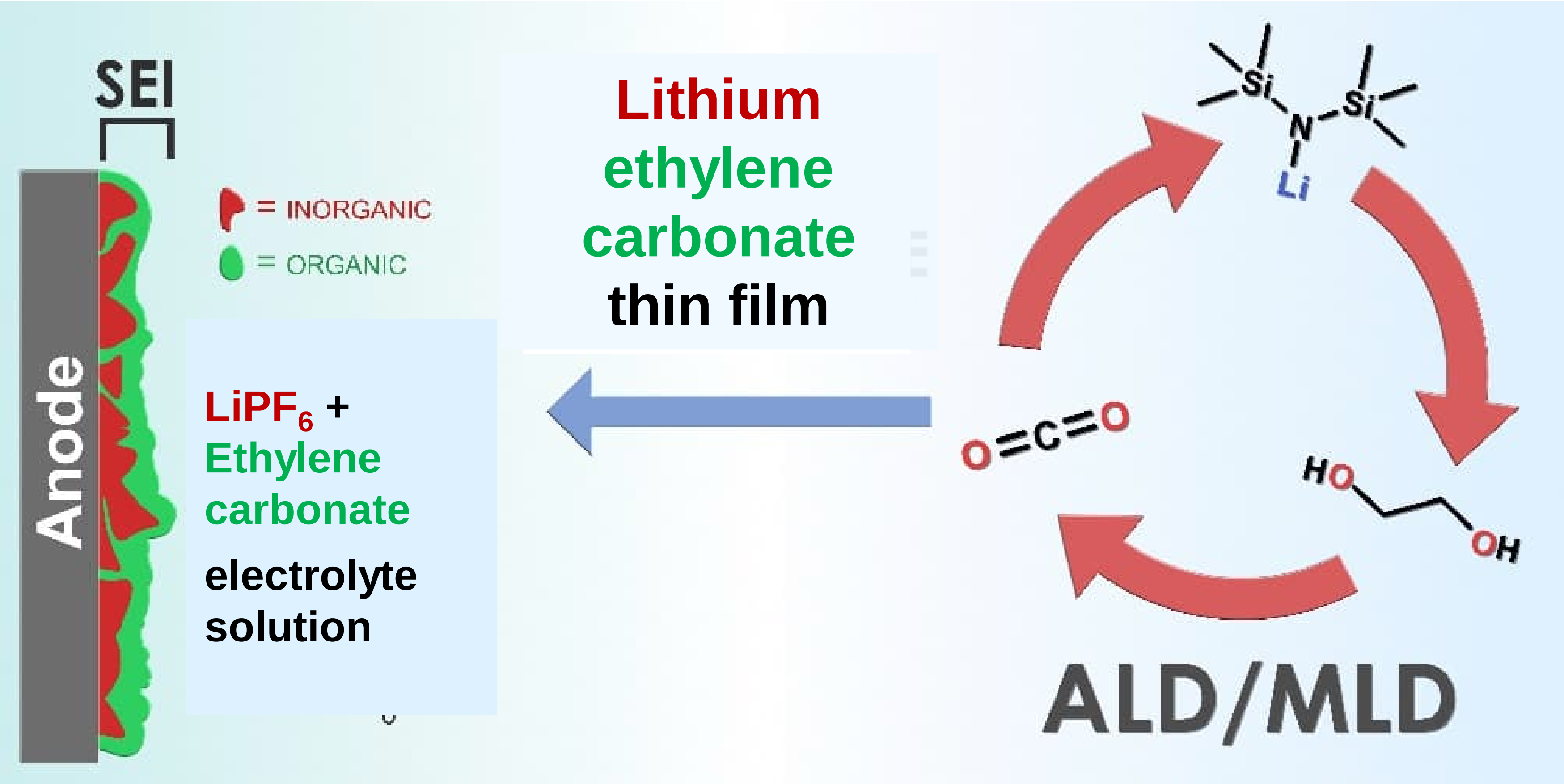
ELECTROLYTE:
ALD - LiPON

ANODE:
Li-terephthalate

ALD/MLD-made Li-organic microbattery is flexible and cobalt-free, ultrafast to charge, but the problem is the low energy capacity. Whole battery structure can be deposited in a same reactor, without additives.

Nisula & Karppinen, In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *J. Mater. Chem. A* 6, 7027 (2018).

ALD + MLD: Artificial SEI-layer for Li-ion battery



Lithium ethylene carbonate thin film

$LiPF_6$ +
Ethylene carbonate
electrolyte solution

SEI: Solid Electrolyte Interphase **(forms naturally in Li-ion battery)**

J. Heiska, M. Madadi & M. Karppinen, CO_2-based atomic/molecular layer deposition of lithium ethylene carbonate thin films, ***Nanoscale Advances*** 2, 2441 (**2020**).