Functional Inorganic Materials
Fall 2021

Tuesdays: 14.15 - 16.00
Thursdays: 12.15 - 14.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 02.11.	Maarit	Introduction + Materials design
2	Thu 04.11.	Antti	Computational materials design
3	Tue 09.11.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	Thu 11.11.	Maarit	Ionic conductivity (Oxygen): SOFC and Oxygen storage
5	**Tue 16.11.**	**Maarit**	**Ionic conductivity (Lithium & Proton): Li-ion battery**
6	Thu 18.11.	Antti	Thermal conductivity
7	Tue 23.11.	Antti	Thermoelectricity
8	Thu 25.11.	Maarit	Hybrid materials
9	Tue 30.11.	Maarit	Luminescence and optically active materials
10	Thu 02.12.	Antti	Piezoelectricity
11	Tue 07.12.	Antti	Pyroelectricity and ferroelectricity
12	Thu 09.12.	Antti	Magnetic and multiferroic oxides

LECTURE 5: Ionic conductivity: Lithium & Proton

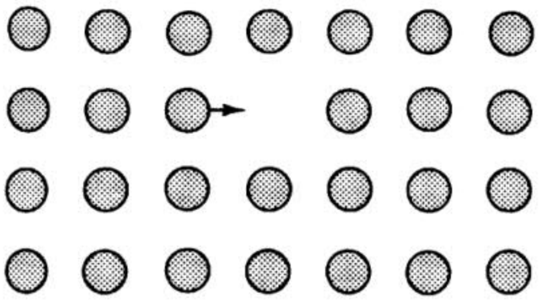
- **Proton conductivity**
- Water/proton absorption & Oxide/hydroxide substitution
- **Lithium ion conductivity**
- Li-ion battery: material issues
- Solid-state electrolytes & Thin-film microbattery

LECTURE EXERCISE 5

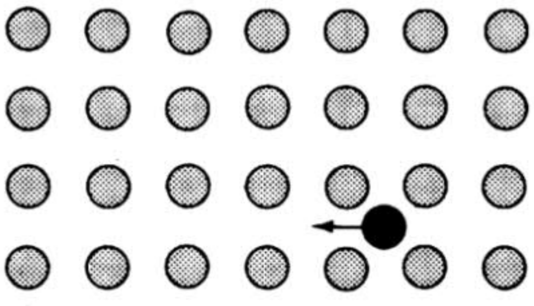
1. Which useful function could be anticipated for an oxygen-deficient oxide material with a tendency to absorb water? Explain !
2. Explain why the best Li-ion battery electrode materials have layered crystal structures.
3. What happens to (a) structure, (b) electrical conductivity, and (c)) Li-ion conductivity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

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

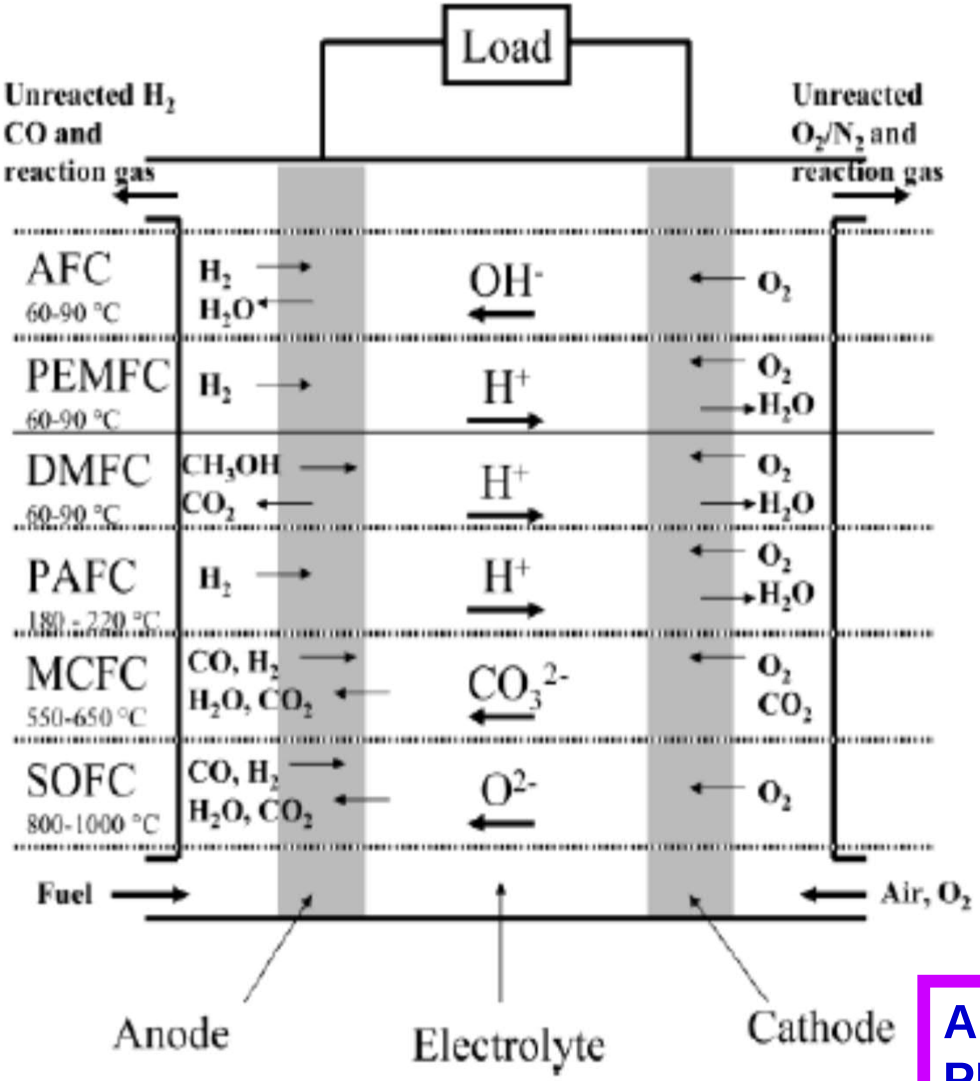


mobile interstitial

EFFECTIVE IONIC RADII

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

FUEL CELLS

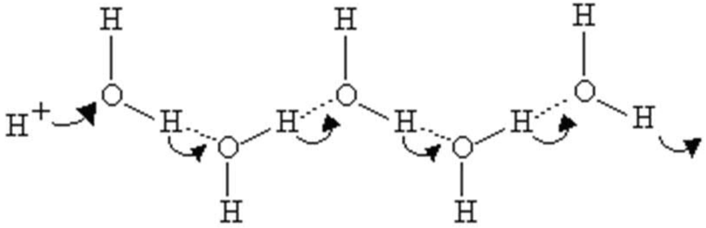


Conventional PROTON-CONDUCTING MATERIALS

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

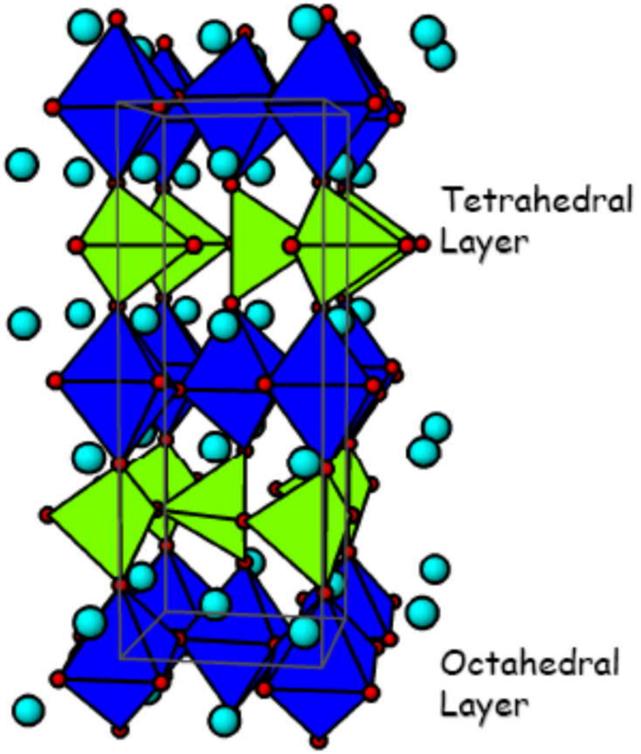
- **PROTON CONDUCTOR:** (solid) electrolyte in which movable hydrogen ions are the primary charge carriers
- **APPLICATIONS:**
  - hydrogen separation
  - sensors
  - fuel cells: PEM, SOFC (intermediate temperature range of 200-500 °C)
- **MATERIALS:**
  - water/ice
  - polymers (e.g. nafion)
  - oxidic materials (oxides, phosphates, sulphates, *etc*.)

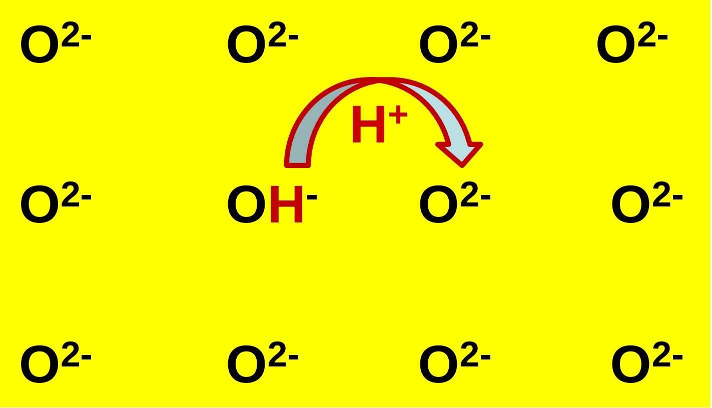


- **PROTON-CONDUCTING OXIDES:**
  - First proton-conducting perovskites (1980, Iwahara *et al*.): $LaYO_3$, $SrZrO_3$
  - Present perovskite prototypes: $SrCeO_3$, $BaCeO_3$
  - Some Ruddlesden-Popper phases
  - Some pyrochlores: $R_2(Zr,Y)_2O_7$, $R_2(Ti,In,Mg)_2O_7$

$Ba_2In_2O_5$ $(BaInO_{2.5})$

- **Oxide ion conductor**
- **Brownmillerite structure**
  derived from the perovskite structure (oxygen vacancies ordered into layers)
- **At 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




O^{2-} O^{2-} O^{2-} O^{2-}

H^+

O^{2-} OH^- O^{2-} O^{2-}

O^{2-} O^{2-} O^{2-} O^{2-}

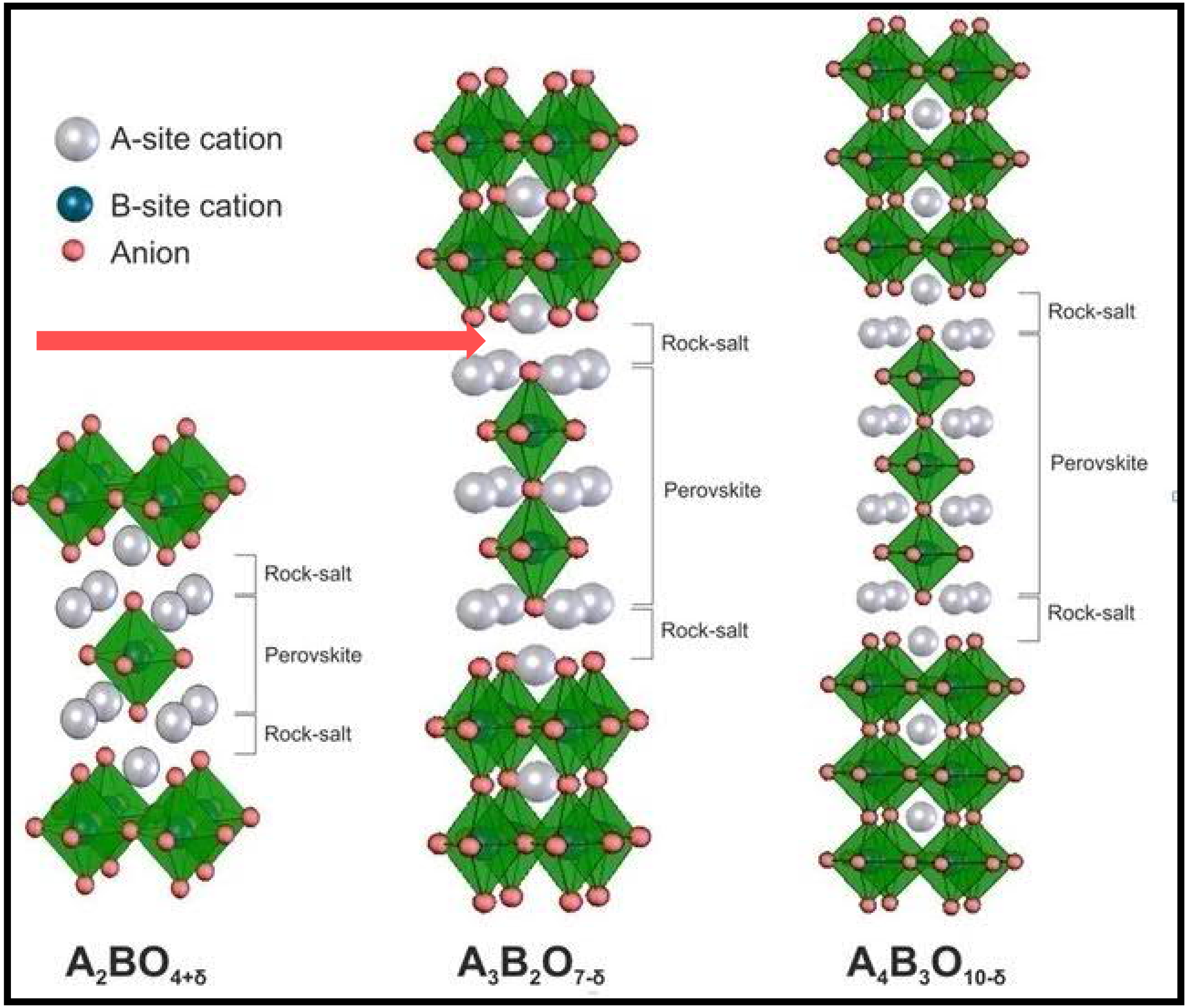
WATER/PROTON ABSORPTION OF OXIDES

- **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**

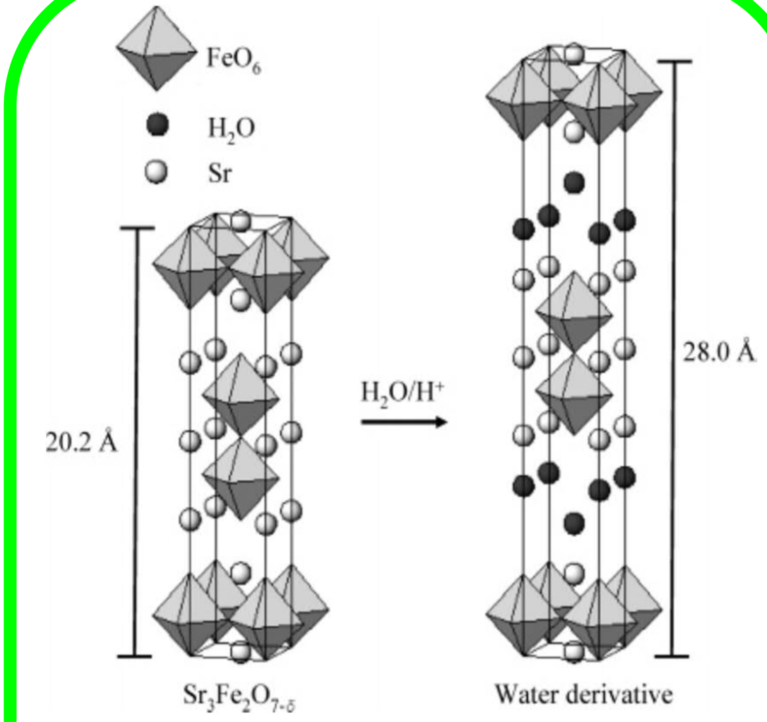
Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

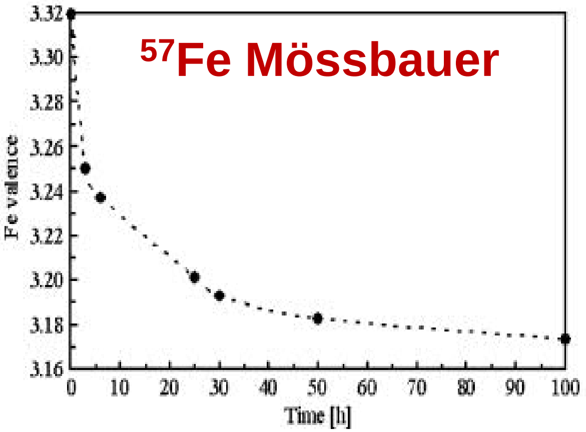
- Enough space for interstitial oxygen, water intercalation, excess protons, organic molecules, etc.

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



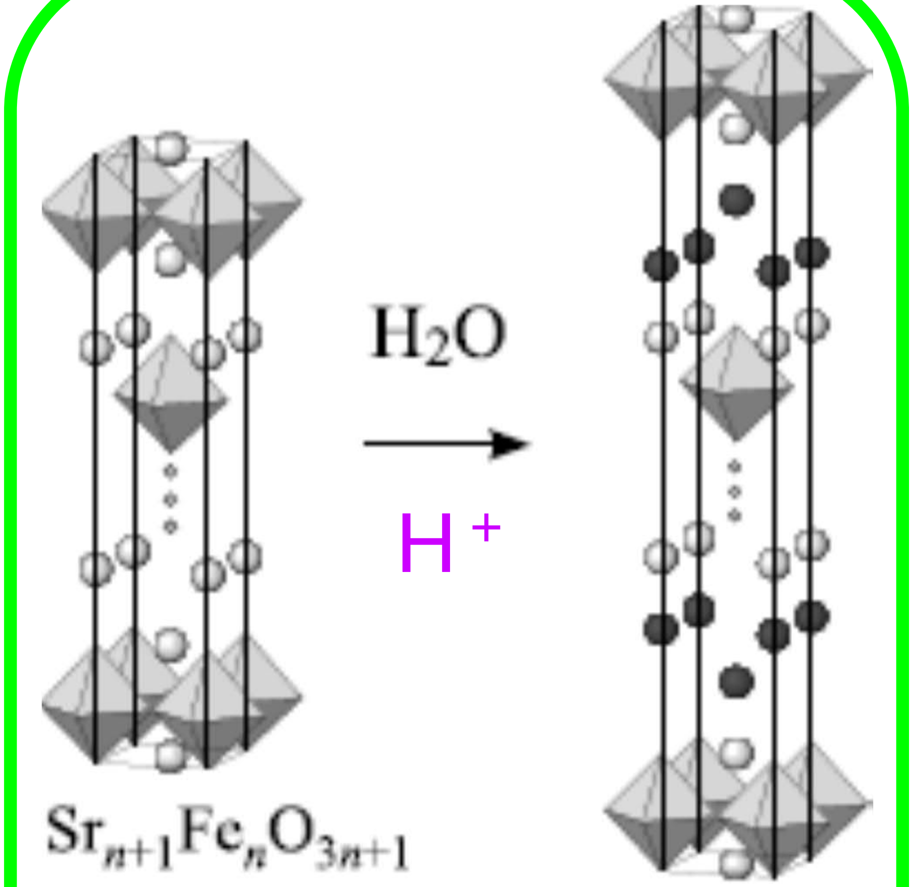
Water-derivatives of $Sr_{n+1}Fe_nO_{3n+1}$



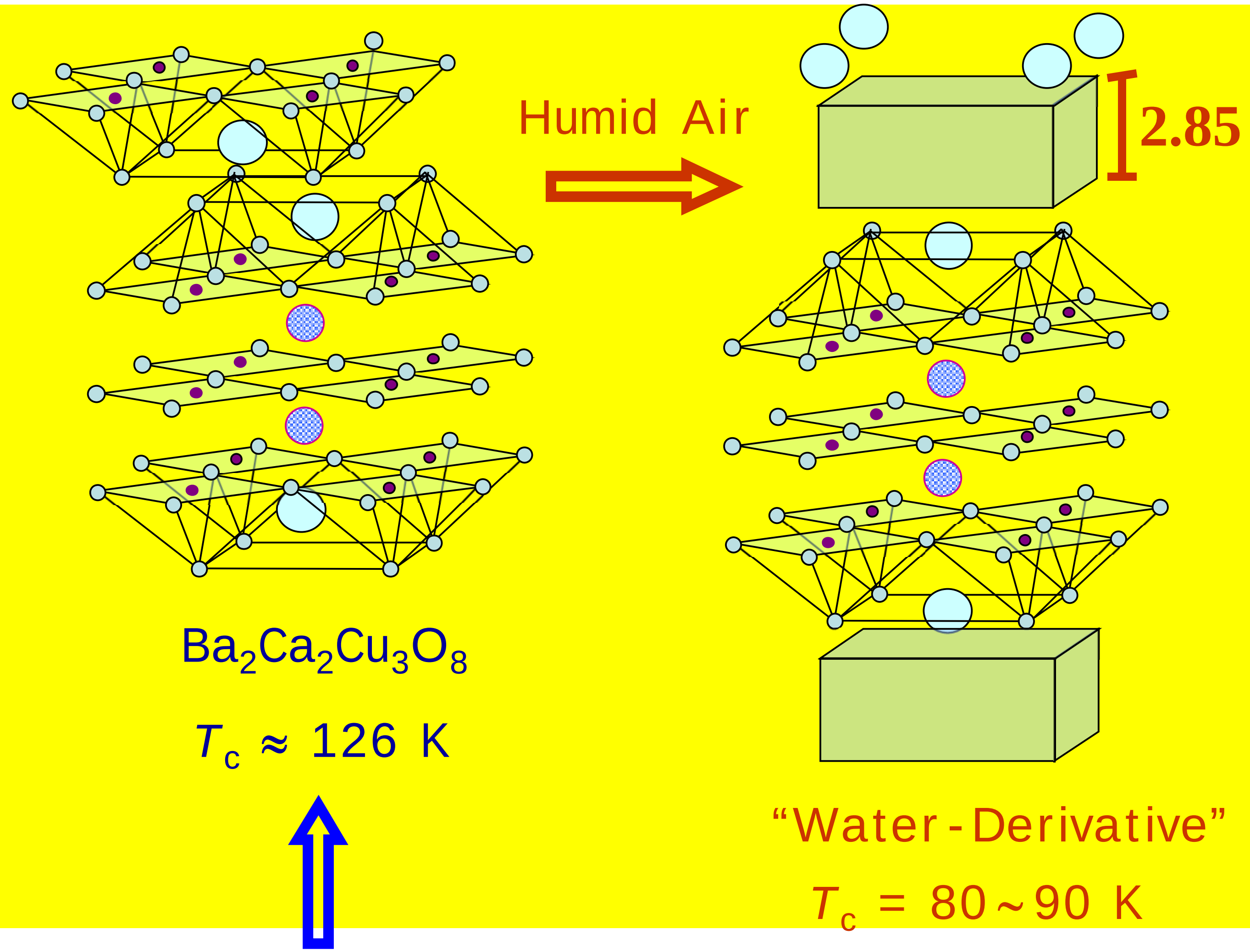


^{57}Fe Mössbauer

Matvejeff, Lehtimäki, Hirasa,
Huang, Yamauchi & Karppinen,
Chem. Mater. **17**, 2775 (2005).



Lehtimäki, Hirasa, Matvejeff,
Yamauchi & Karppinen,
J. Solid State Chem. **180**, 3247 (2007).



Humid Air

2.85 Å

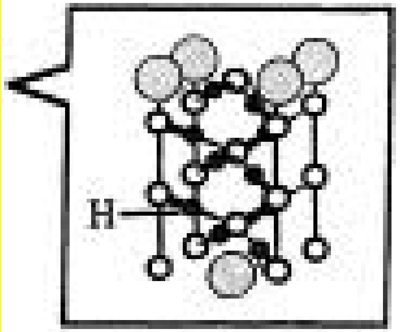
$Ba_2Ca_2Cu_3O_8$

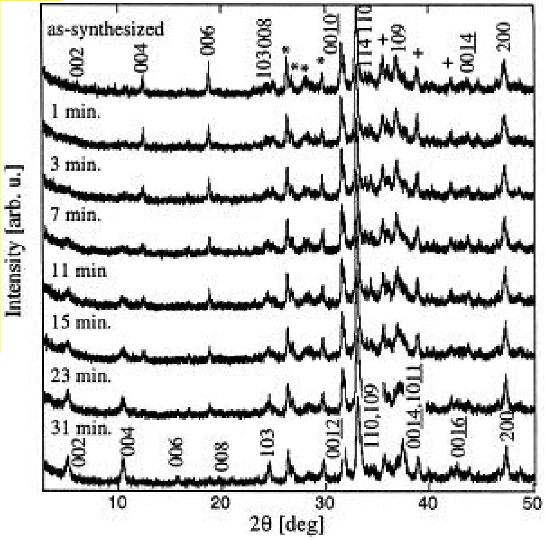
$T_c \approx 126$ K

"Water-Derivative"

$T_c = 80 \sim 90$ K

High-Pressure Synthesis





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

Li-ION BATTERY

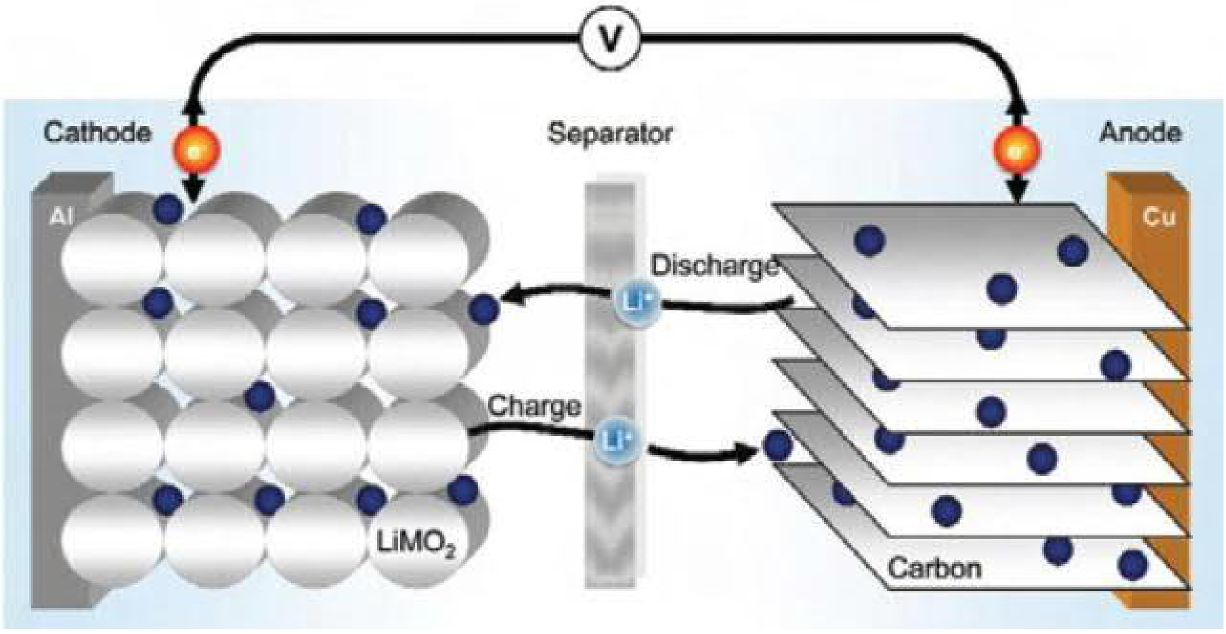
- Li is lightest and smallest of all metals
- Li has largest electrochemical potential
- Light-weight, high voltage, large energy density battery
- No ”memory effect”, small self discharge
- Cell phones, laptops, wearable electronics, electric cars and vehicles, energy storage related to solar cells and wind power, etc.

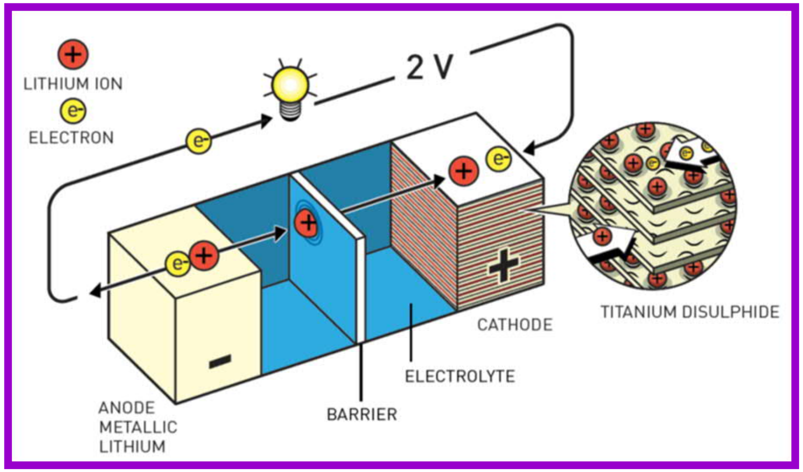
Sony 1991

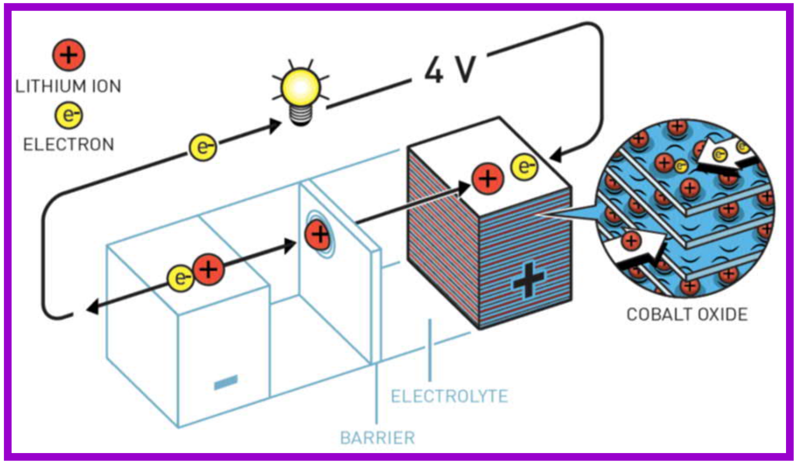
First commercial Li-ion battery

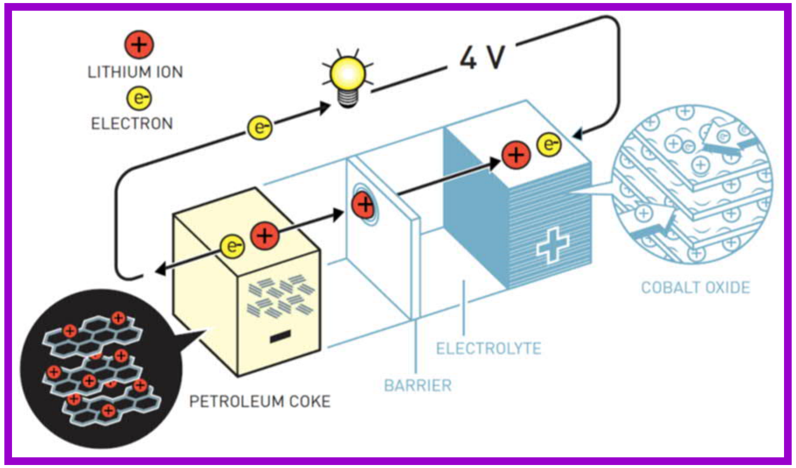
”WET CELL”

- **Anode & Cathode:** electric and ionic cond.
- **Liquid electrolyte:** ionic conductivity
- **Separator & additives**









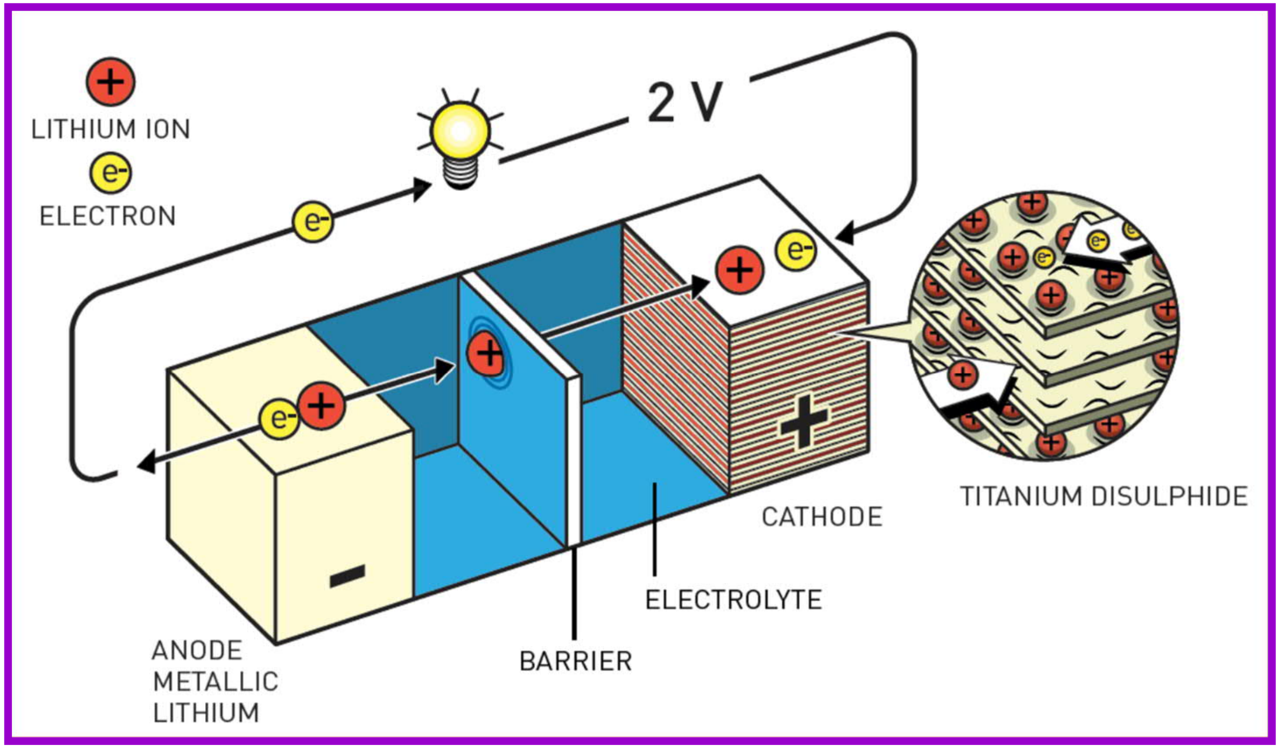
Chemistry Nobel 2019

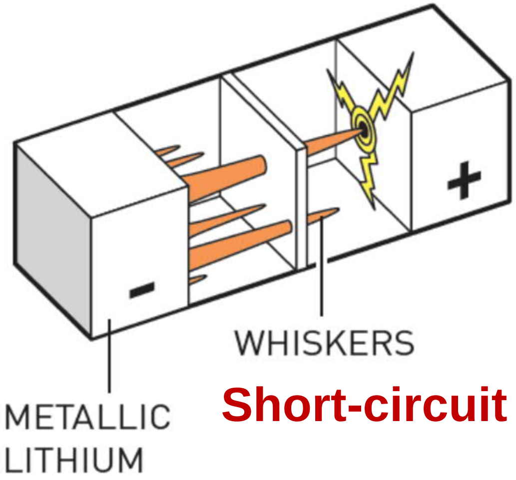
Stanley Whittingham (UK):
- Exxon: TiS_2 cathode 1976

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

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

Commercialization: Sony 1991

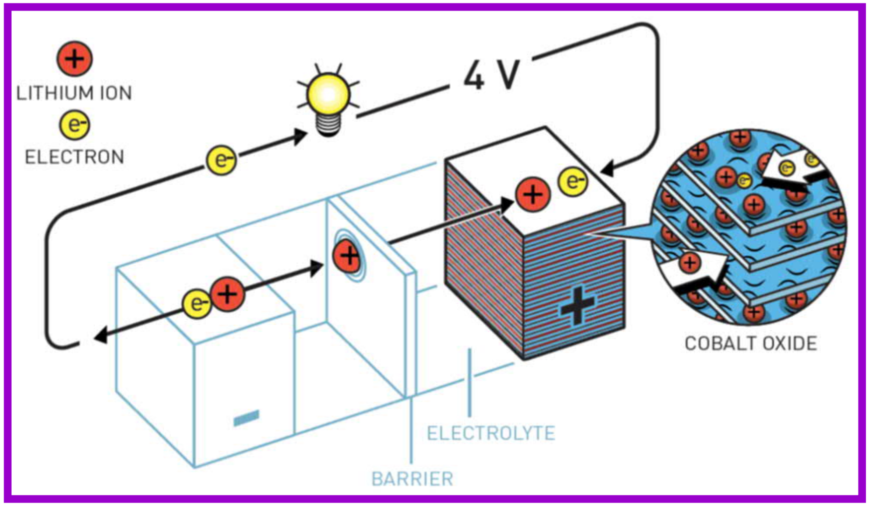


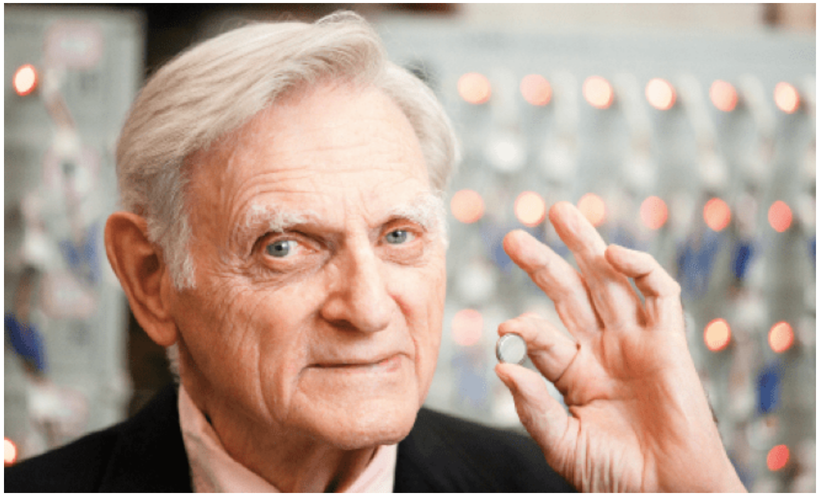


Short-circuit

Stanley Whittingham (born 1941 UK)

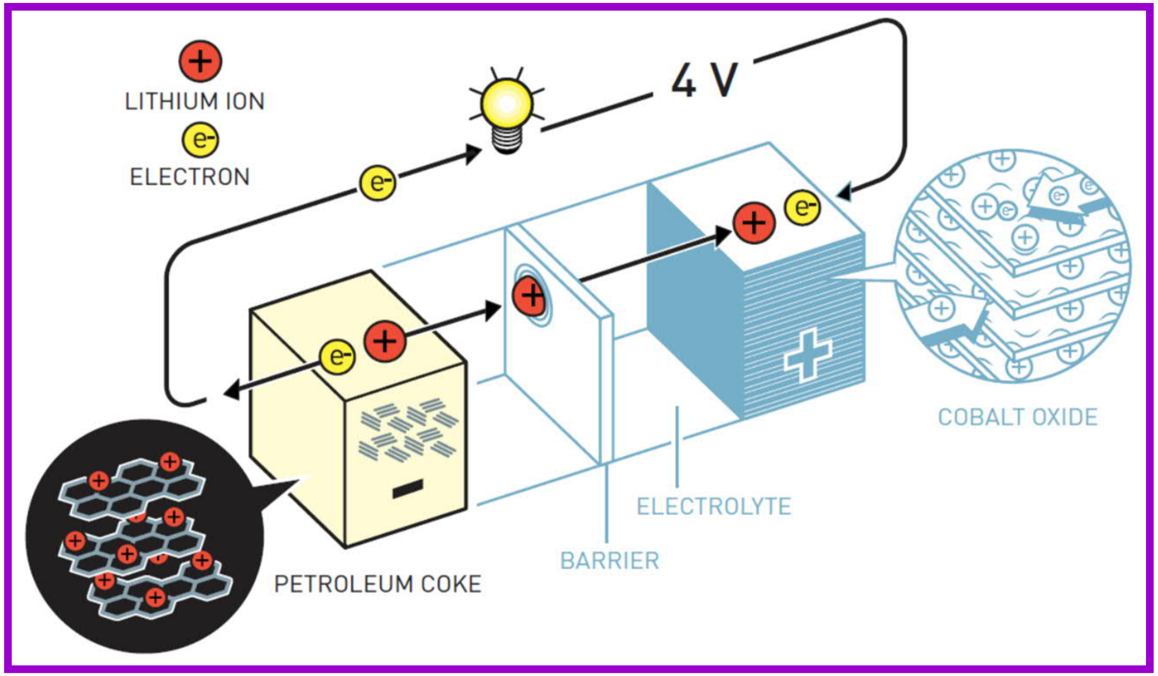
- **PhD 1968 (Oxford University, Chemistry)**
- **Postdoc 1968-1972 (Stanford University)**
- **Exxon 1972-1984:** **- new superconductors → TaS_2**
  - TiS_2 cathode 1976 (Li anode & $LiPF_6$ electrolyte)
- **Prof. 1988 – now (Binghamton University, New York)**
- **Scopus (337 publ; 21 000 citations)**





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 – now (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
- Scopus (887 publ.; 85 000 citations)

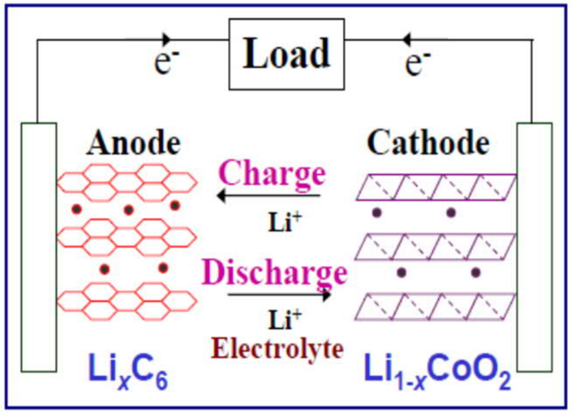


Akira Yoshino (born 1948 Japan)

- **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)**
- **Scopus (17 publ; 750 citations)**

ACTIVE MATERIALS & REACTIONS in Li-ion Battery

- **Rechargable (= secondary) battery: charged hundreds/thousands times**
- **No extensive chemical reactions (which would quickly destroy the battery)**
- **Reversible intercalation of Li^+ ions within anode & cathode materials**
- **Graphite anode & $LiCoO_2$ cathode: layered crystal structures**
- **Upon charging: $LiCoO_2 \rightarrow Li_xCoO_2$ (how far reaction can occur ?)**
- **Unwanted reaction between graphite and liquid electrolyte**
  → SEI (Solid-Electrolyte Interphase)



EC: ethylene carbonate

DEC: dimethyl carbonate

Cell: (-) C | $LiPF_6$-(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

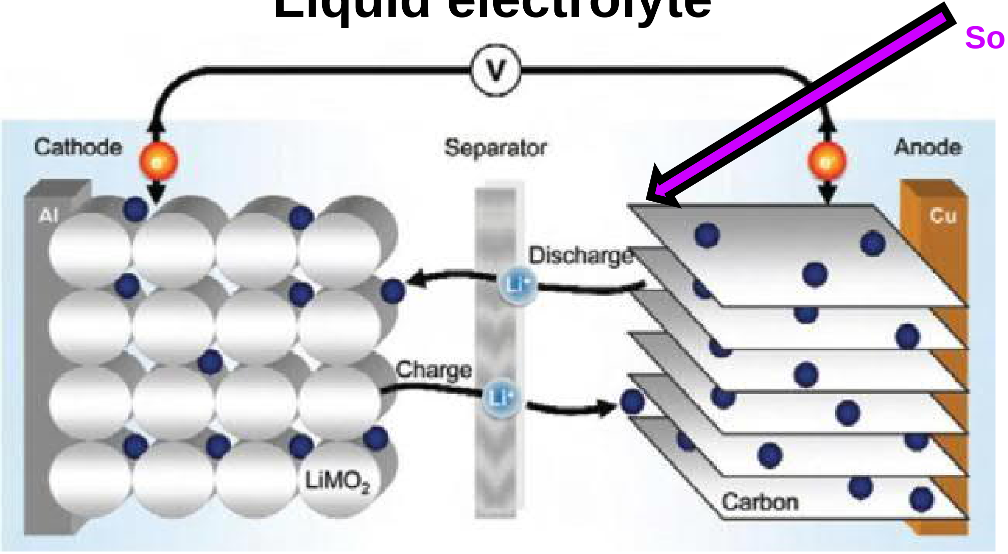
(under intense research)

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)**
ELECTRO-LYTE	**$LiPF_6$ + ethylene carbonate solution** **Solid electrolytes (safety)**

Liquid electrolyte

SEI

Solid-Electrolyte-Interphase



$LiCoO_2$

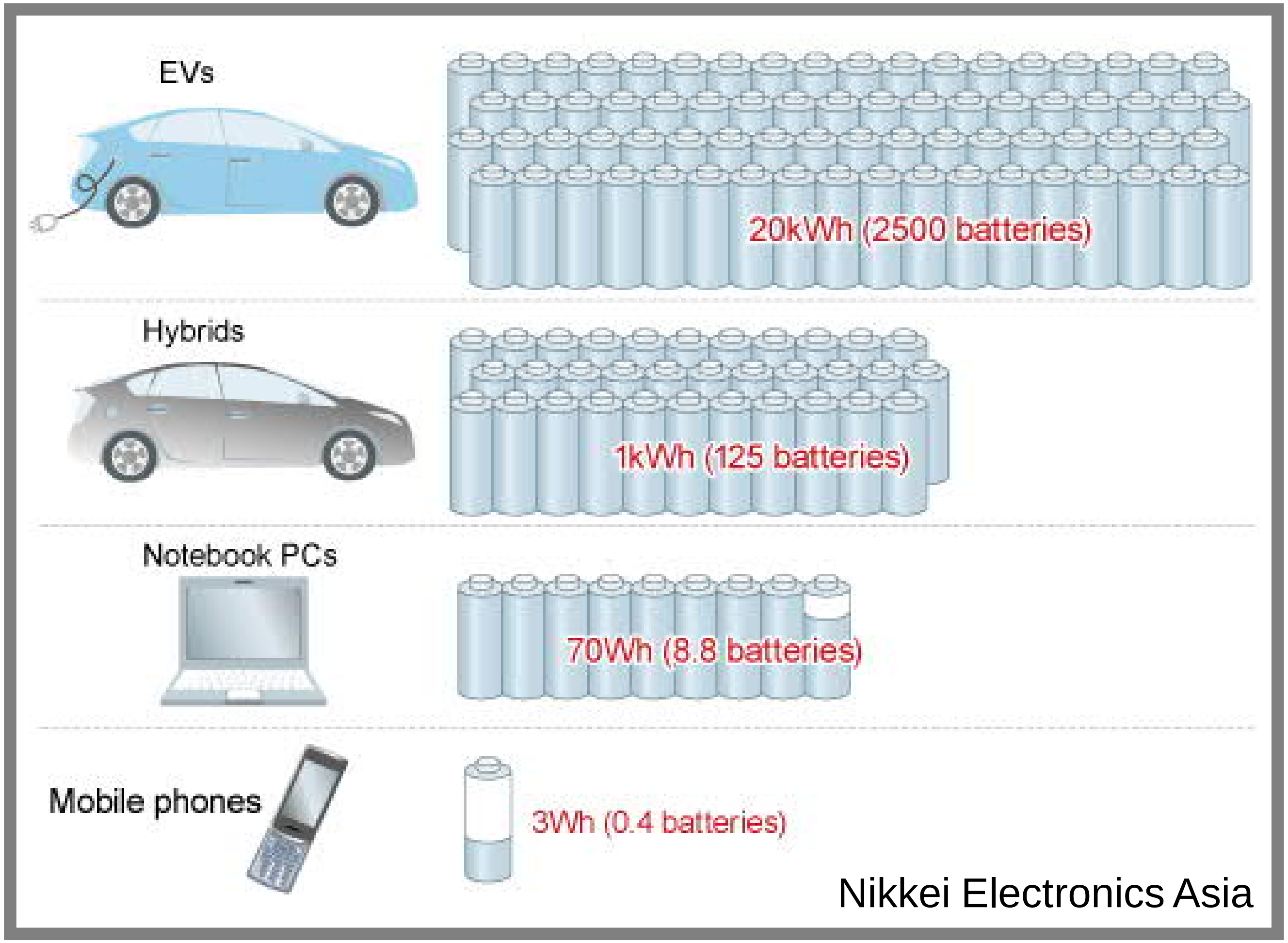
Graphite

SOME MATERIAL ISSUES (to be solved/understood)

- Current state-of-the-art Li-ion battery was developed already 40 years ago and was commercialized 30 years ago
- Materials/performance already mostly finetuned/optimized, without major changes compared to the original material components (despite the unprecedented research & development investments world-wide)
- CRITICAL RAW MATERIALS for Li and Co (NOT to forget graphite !)
- SAFETY: charged hundreds/thousands times
- No extensive chemical reactions (which would quickly destroy the battery)
- Reversible intercalation of Li^+ ions within anode & cathode materials
- Graphite anode & $LiCoO_2$ cathode: layered crystal structures
- Upon charging: $LiCoO_2 \rightarrow Li_xCoO_2$ (how far reaction can occur ?)
- Unwanted reaction between graphite and liquid electrolyte → SEI layer
- Possible future directions: Co → Ni (Mn, Al); Li → Na, Mg, Al; Liquid electrolyte → Solid electrolyte; Protecting/barrier layers; Li-S; Li-air; Organic materials; Structural battery, …
- Current recycling level: Lithium ca. 1 %, Cobalt some tens of %

ELECTRIC CAR BATTERY SYSTEM

10 000 times larger energy capacity compared to cell phone



Nikkei Electronics Asia

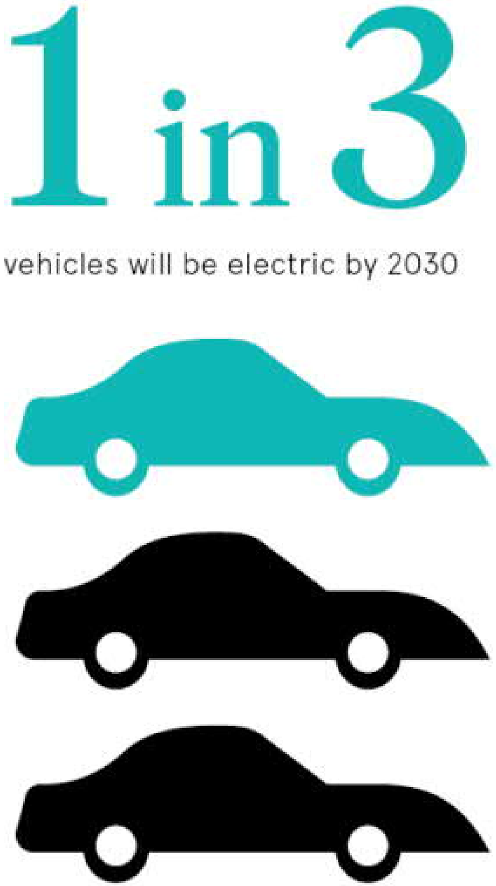
Car battery 600 kg

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

Cell phone 130 g

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

One vehicle out of three electric car by 2030 ?



Bloomberg New Energy Finance 2017

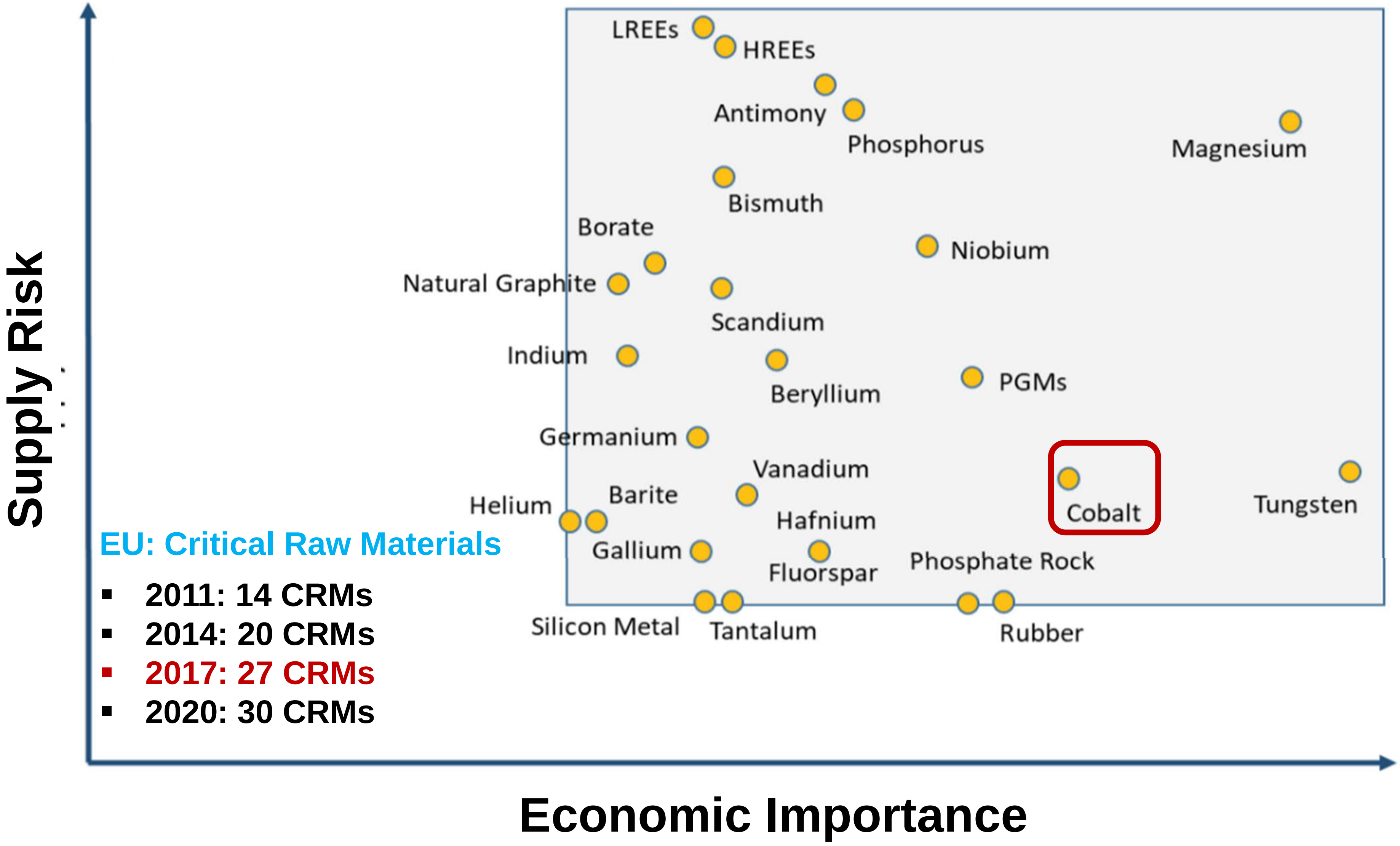
Lithium & cobalt needed tens if not hundreds time more to fulfill the European carbon neutrality targets

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

(mostly in Chinese ownership)

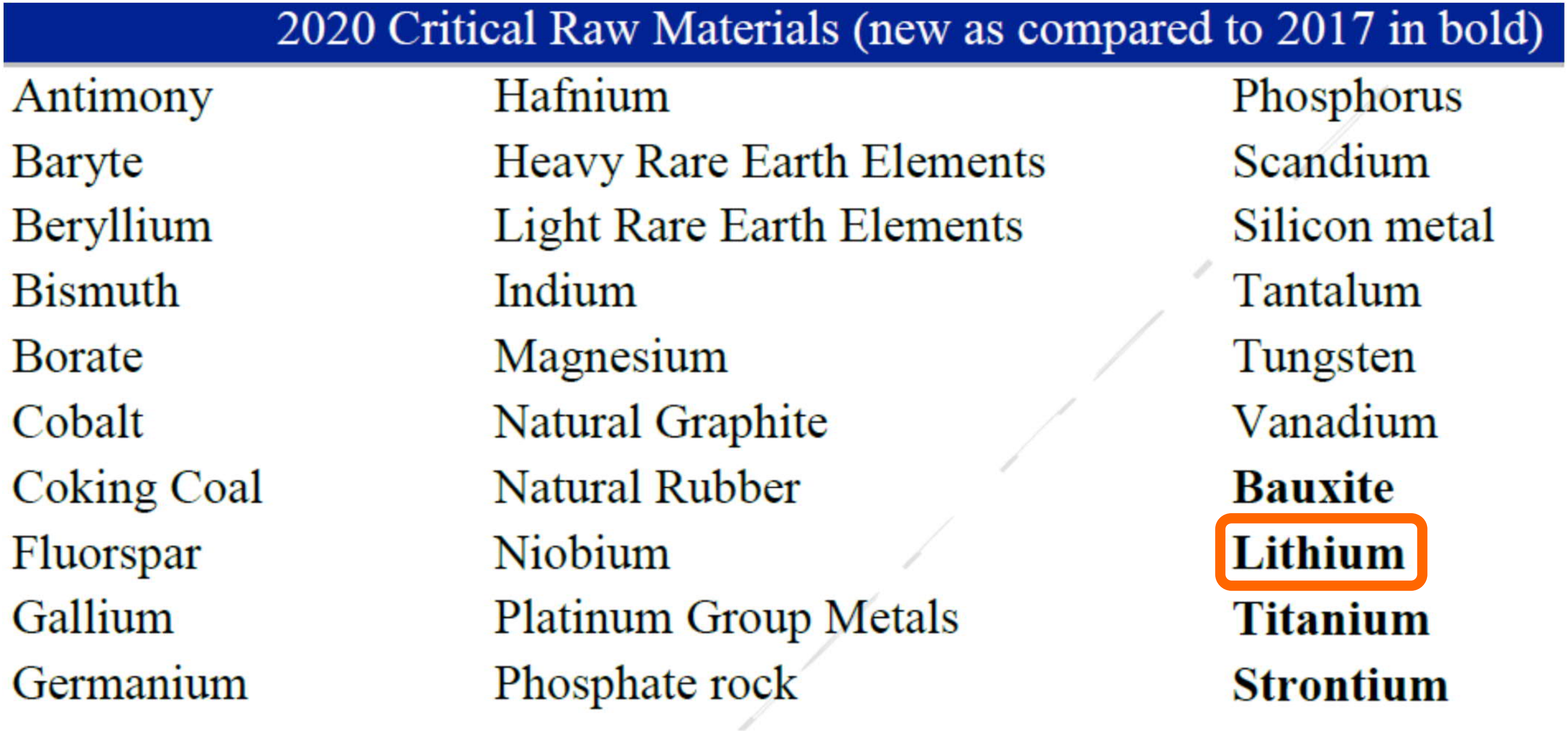
Cobolt mining place in Congo close
to Kasulo. Valokuvat: Siddharth Kara

EU Critical Raw Materials (CRM)



EU: Critical Raw Materials

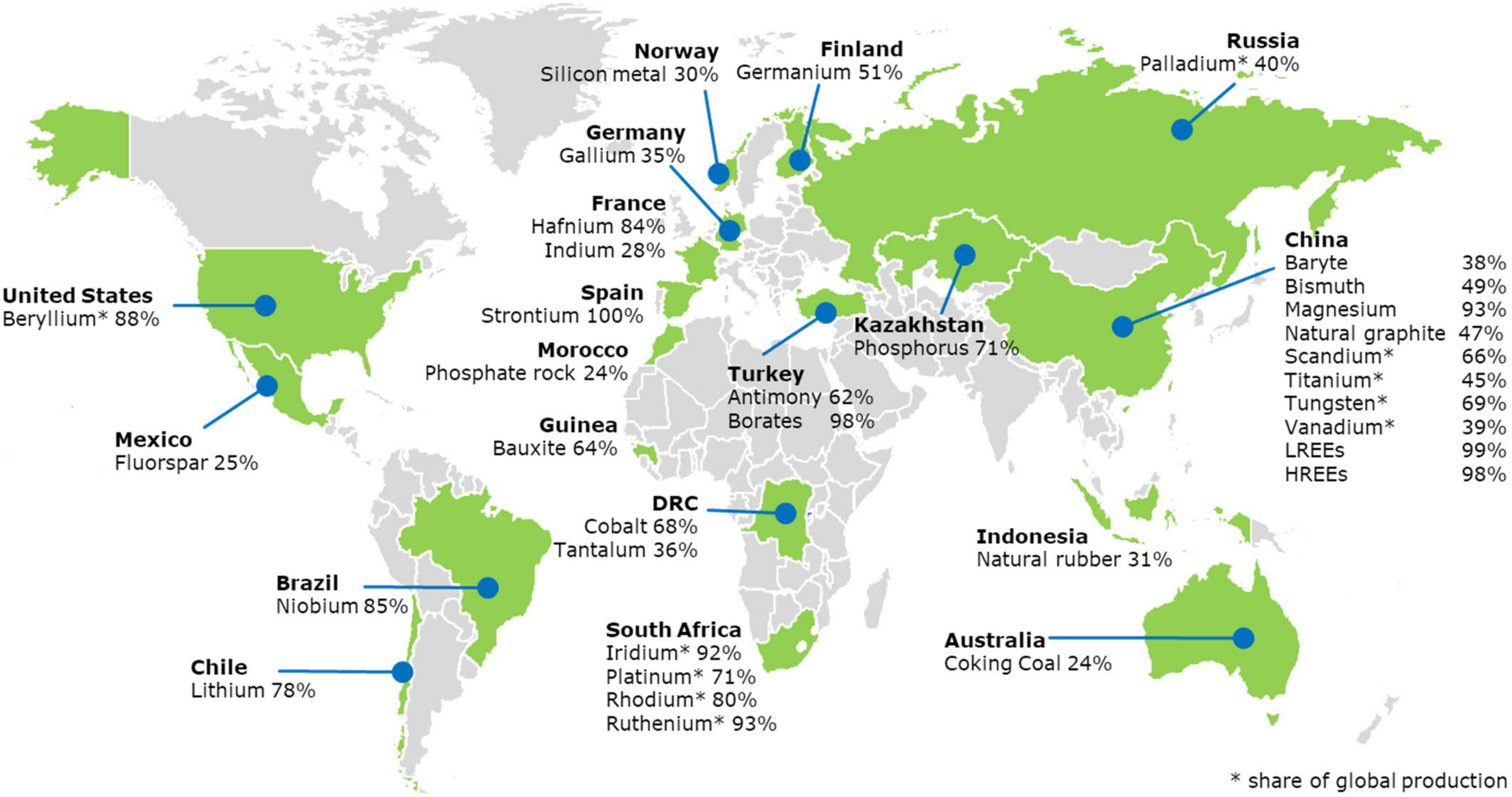
- **2011: 14 CRMs**
- **2014: 20 CRMs**
- **2017: 27 CRMs**
- **2020: 30 CRMs**



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 ?



Norway
Silicon metal 30%

Finland
Germanium 51%

Russia
Palladium* 40%

Germany
Gallium 35%

France
Hafnium 84%
Indium 28%

United States
Beryllium* 88%

Spain
Strontium 100%

Morocco
Phosphate rock 24%

Kazakhstan
Phosphorus 71%

Turkey
Antimony 62%
Borates 98%

Mexico
Fluorspar 25%

Guinea
Bauxite 64%

China

Baryte	38%
Bismuth	49%
Magnesium	93%
Natural graphite	47%
Scandium*	66%
Titanium*	45%
Tungsten*	69%
Vanadium*	39%
LREEs	99%
HREEs	98%

DRC
Cobalt 68%
Tantalum 36%

Indonesia
Natural rubber 31%

Brazil
Niobium 85%

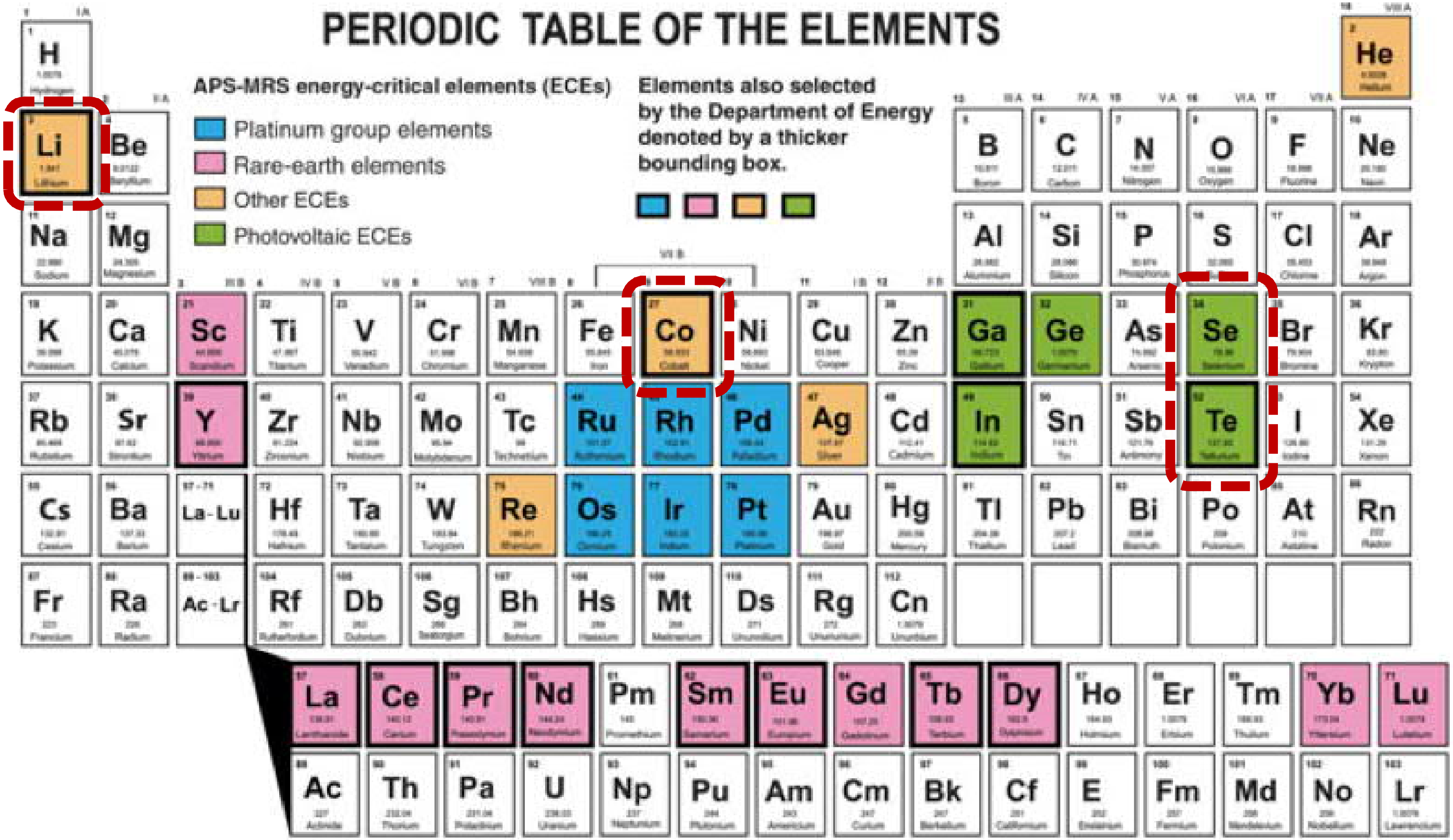
South Africa
Iridium* 92%
Platinum* 71%
Rhodium* 80%
Ruthenium* 93%

Australia
Coking Coal 24%

Chile
Lithium 78%

* share of global production

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.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII B	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
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

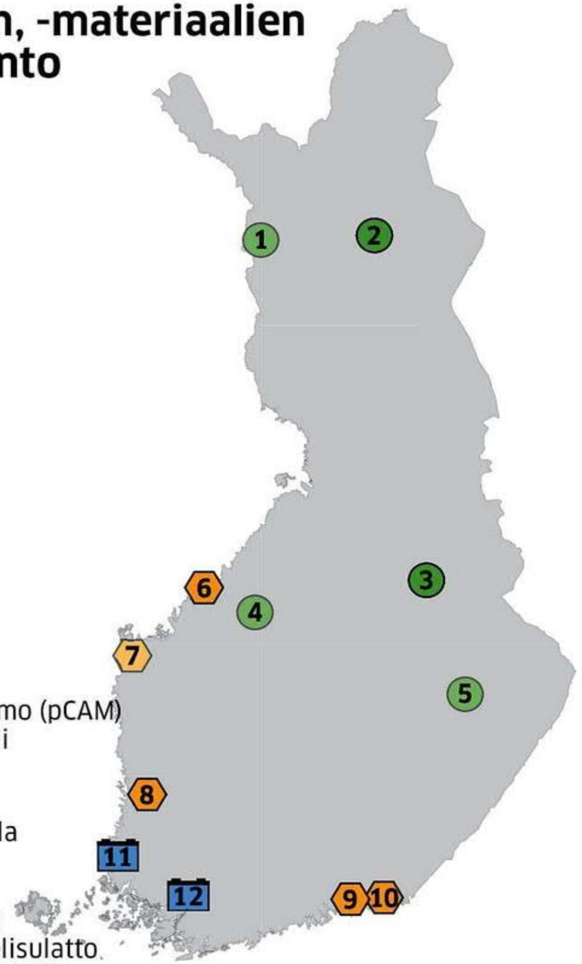
Materials Research Society (MRS), USA

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

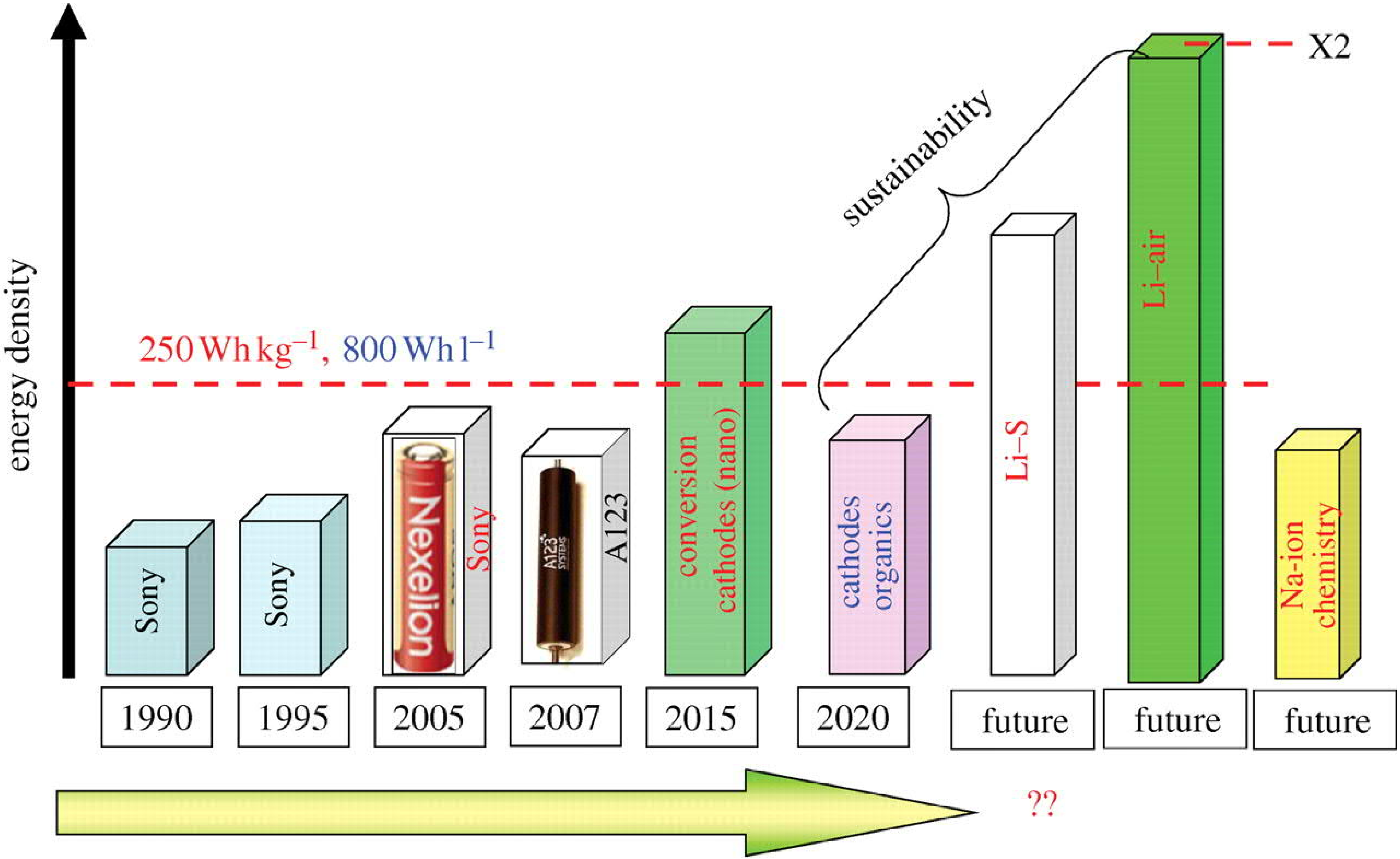
⑩ **Hamina**
Finnish Battery Chemicals yhdessä CNGR ***Advanced Material -yhtiön kanssa***
prekursoritehdas (pCAM) valmisteilla

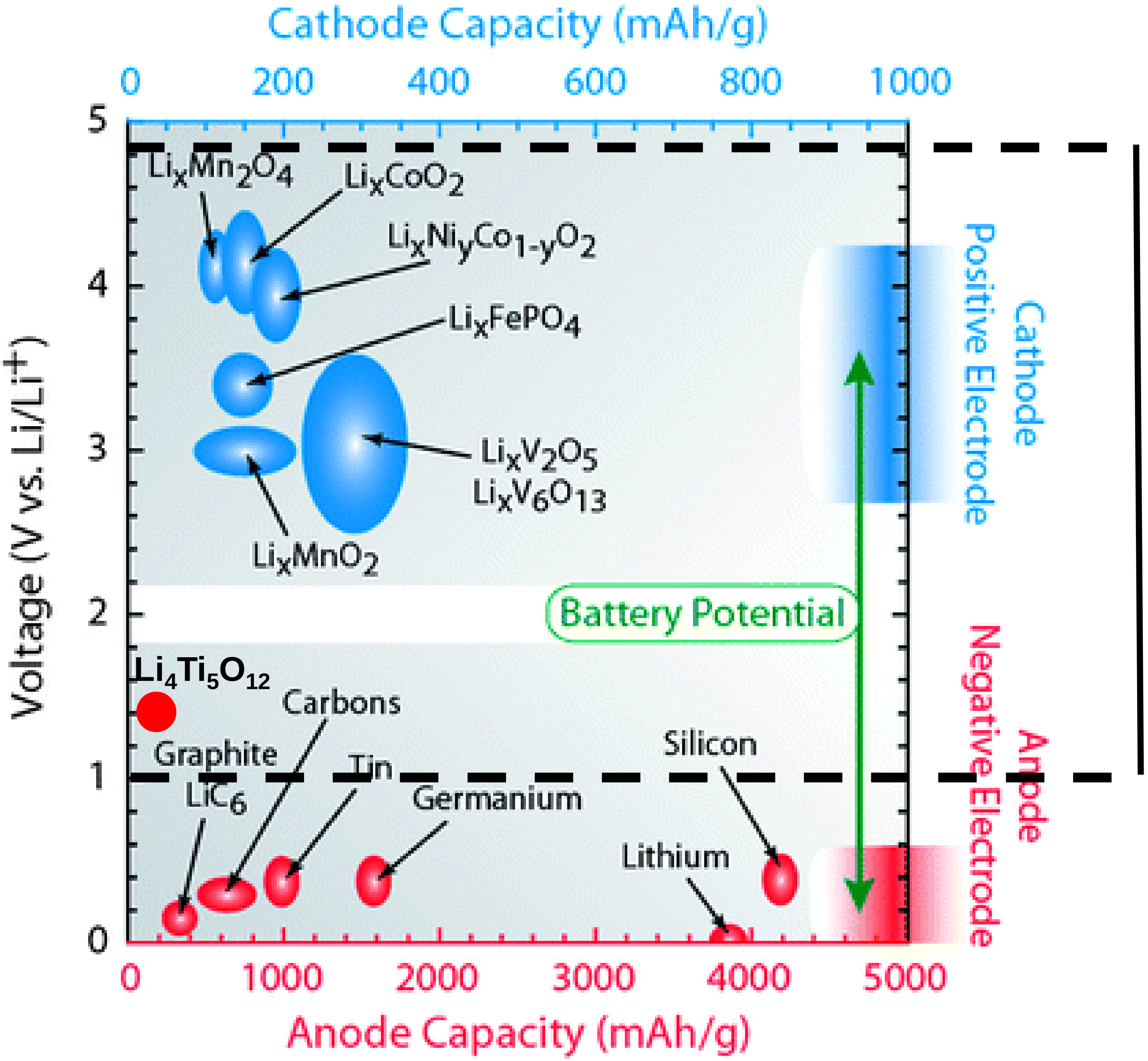
11 **Uusikaupunki**
Valmet Automotive
akkukoontitehdas

12 **Salo**
Valmet Automotive
akkukoontitehdas

pCAM: prekursoritehdas, akun katodiaktiivimateriaalin esiastetehdas
CAM: katodiaktiivimateriaalitehdas

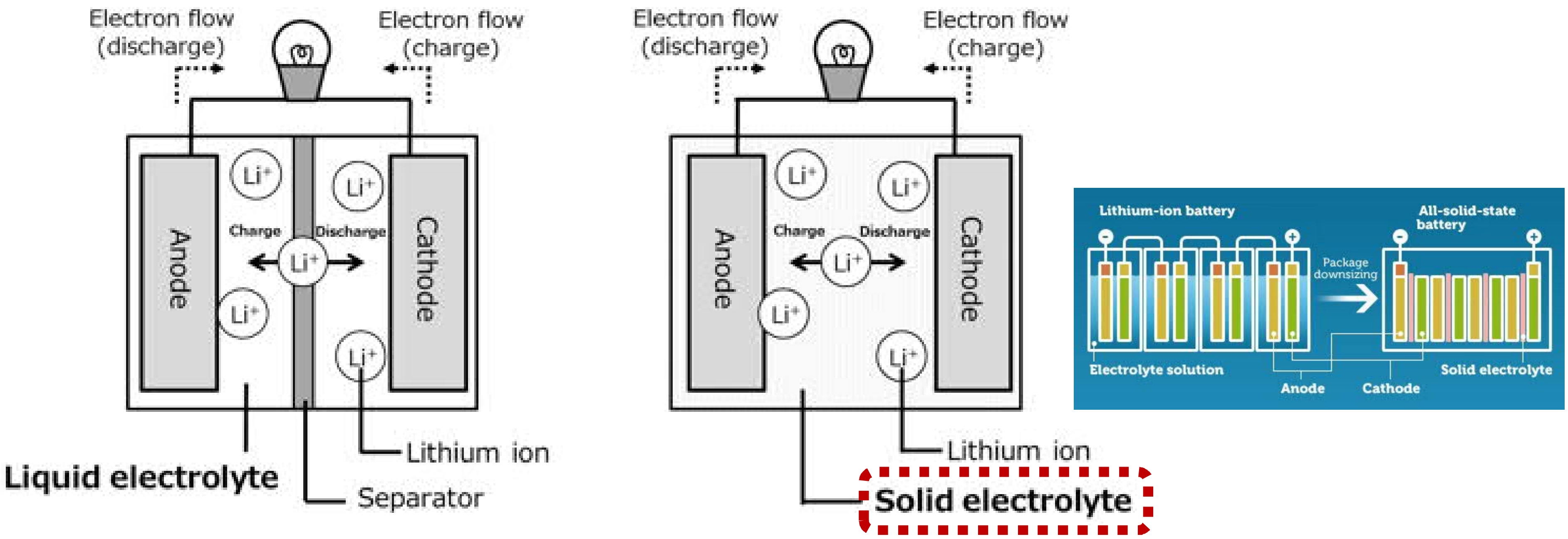
MT Koonnut: Jouko Kyytsönen Grafiikka: Jukka Pasonen Lähde: GTK

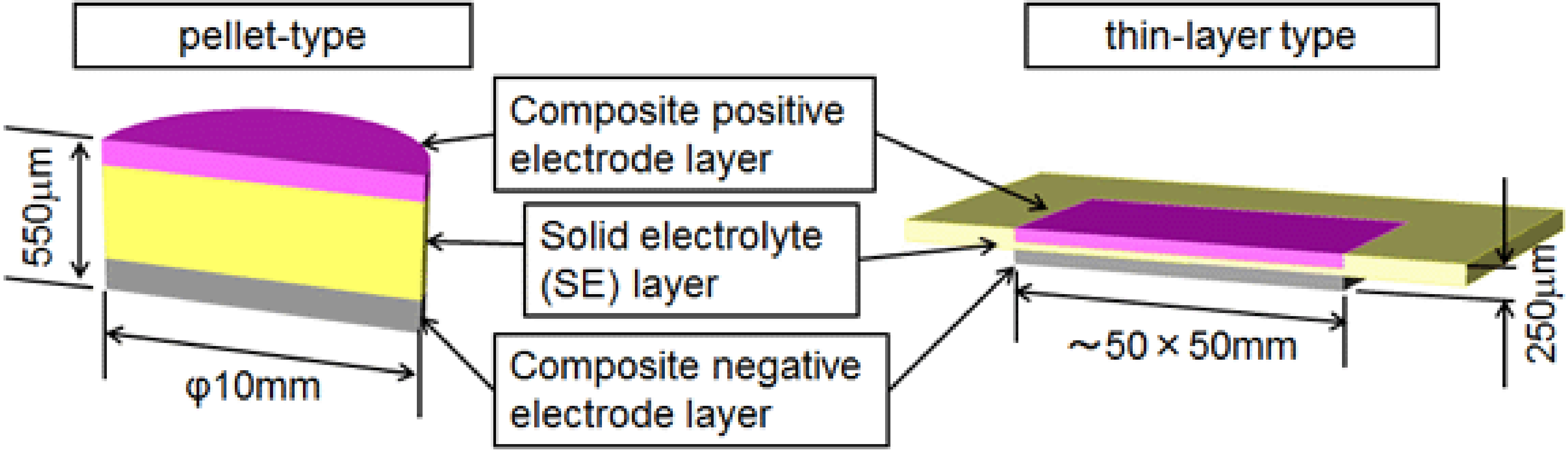

energy density
250 Wh kg⁻¹, 800 Wh l⁻¹
X2
sustainability
Sony
Sony
Nexelion
Sony
A123
conversion cathodes (nano)
cathodes organics
Li–S
Li–air
Na-ion chemistry
1990
1995
2005
2007
2015
2020
future
future
future
??



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)
- **High ionic conductivity & Low electronic conductivity**
- **Challenge:** Li^{+}-ion conductivity comparable to present liquid electrolytes (10^{-3} S/cm)

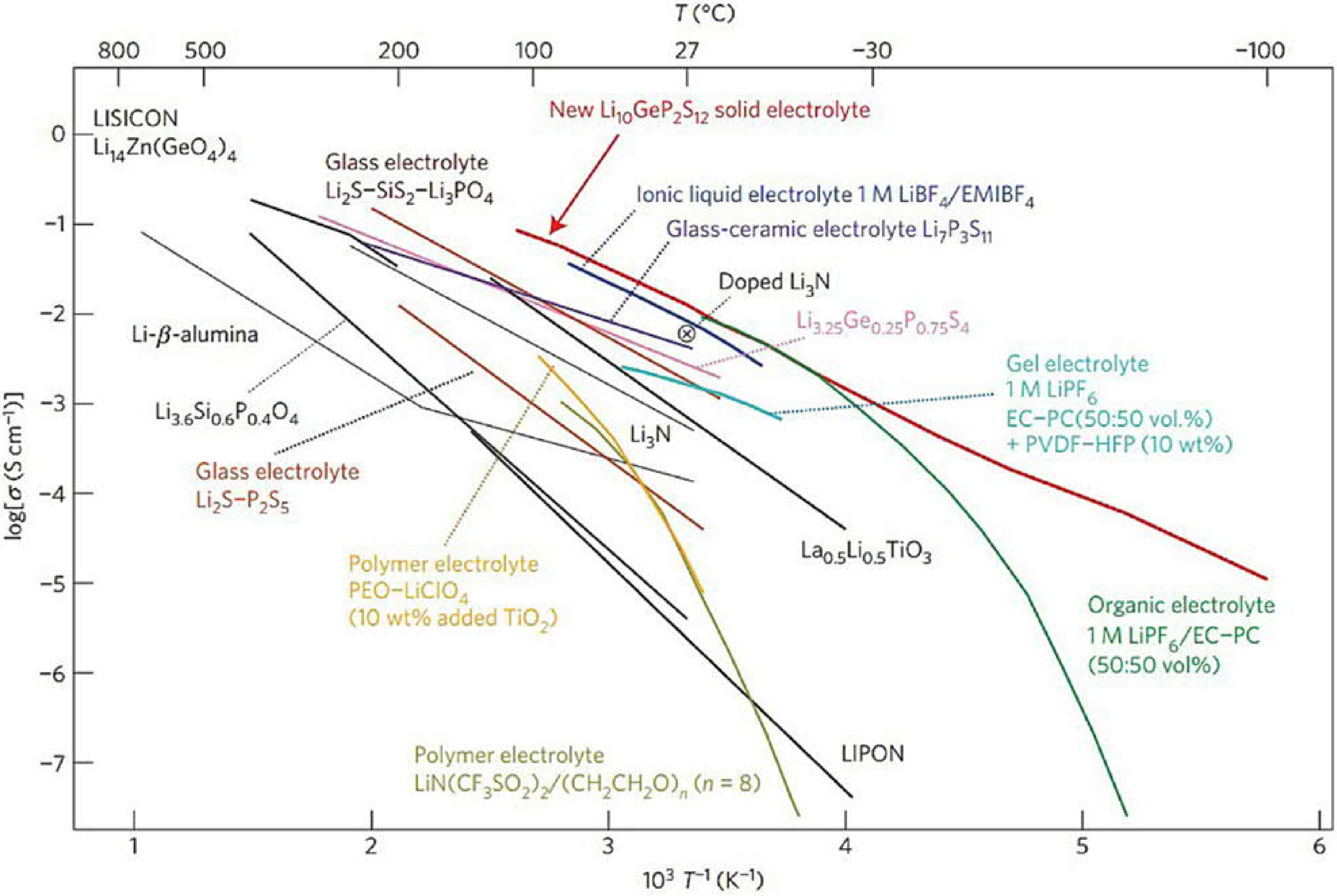
PROS

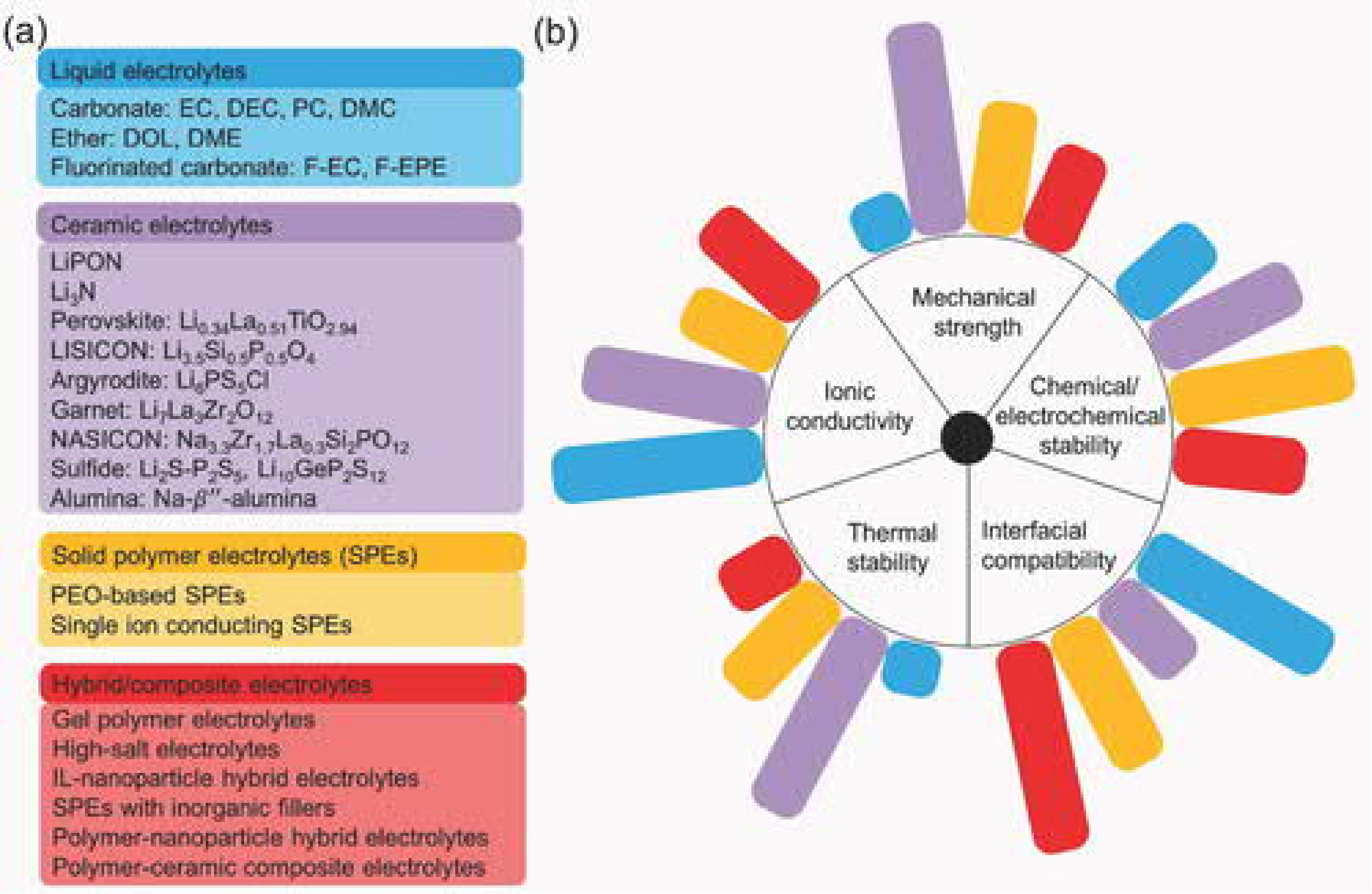
- Non-flammable → Safety
- Non-reactive with electrode materials (no SEI layers)
- Possibility to use Li metal anode
- Possibility to use >5 V cathode materials → Higher energy density
- Wider operation temperature range
- Simpler cell structure, no need e.g. for an expensive separator
- No risk for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

CONS

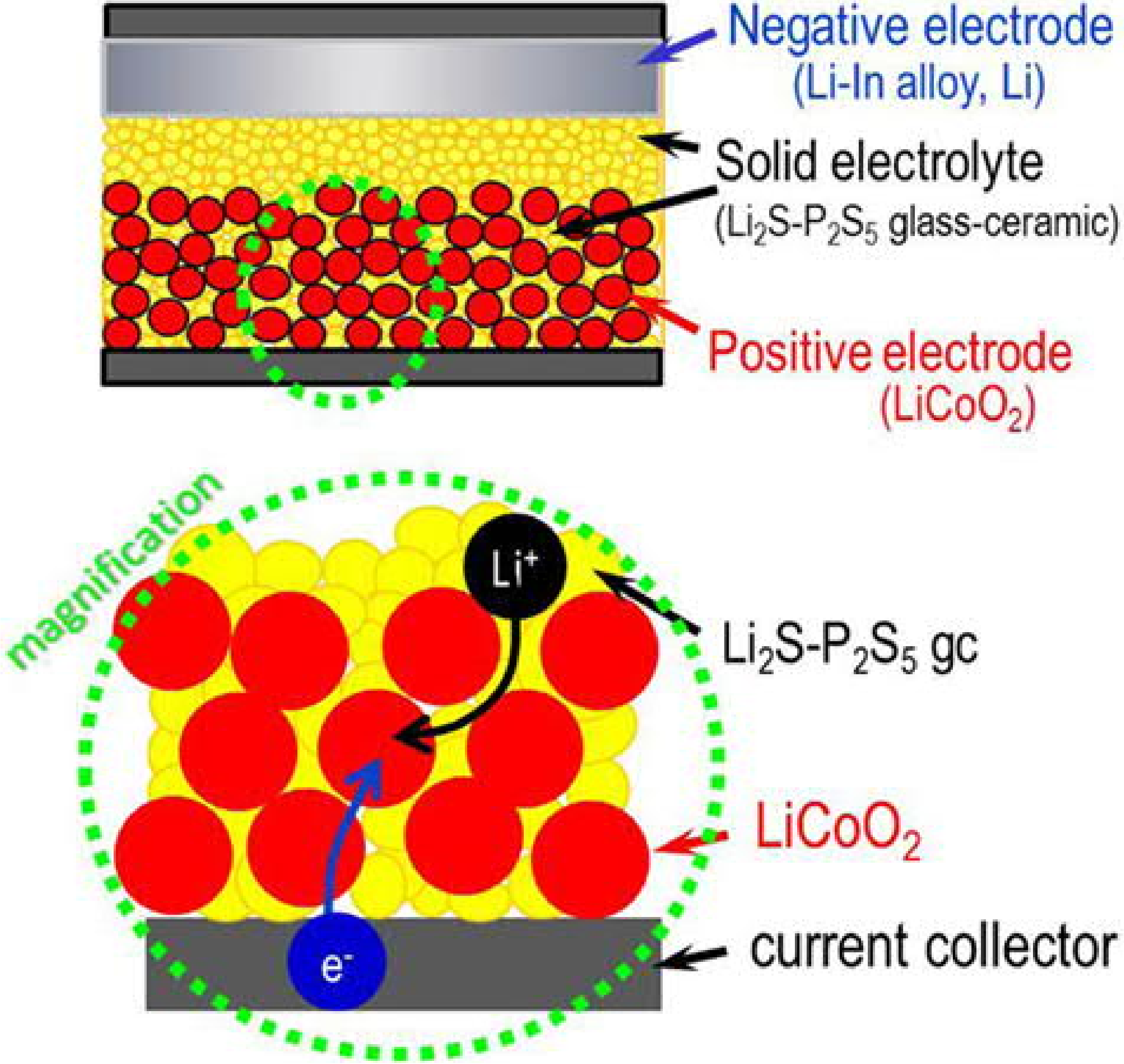
- Heavier
- Integration (interface contacts) with the electrodes

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


T (°C)
800
500
200
100
27
−30
−100
LISICON
$Li_{14}Zn(GeO_4)_4$
New $Li_{10}GeP_2S_{12}$ solid electrolyte
Glass electrolyte
$Li_2S-SiS_2-Li_3PO_4$
Ionic liquid electrolyte 1 M $LiBF_4$/EMIBF$_4$
Glass-ceramic electrolyte $Li_7P_3S_{11}$
Doped Li_3N
Li-β-alumina
$Li_{3.25}Ge_{0.25}P_{0.75}S_4$
Gel electrolyte
1 M $LiPF_6$
EC−PC(50:50 vol.%)
+ PVDF−HFP (10 wt%)
$Li_{3.6}Si_{0.6}P_{0.4}O_4$
Li_3N
Glass electrolyte
$Li_2S-P_2S_5$
$La_{0.5}Li_{0.5}TiO_3$
Polymer electrolyte
PEO−$LiClO_4$
(10 wt% added TiO_2)
Organic electrolyte
1 M $LiPF_6$/EC−PC
(50:50 vol%)
Polymer electrolyte
$LiN(CF_3SO_2)_2/(CH_2CH_2O)_n$ (n = 8)
LIPON
$\log[\sigma$ (S cm^{-1})]
0
−1
−2
−3
−4
−5
−6
−7
1
2
3
4
5
6
10^3 T^{-1} (K^{-1})


(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)

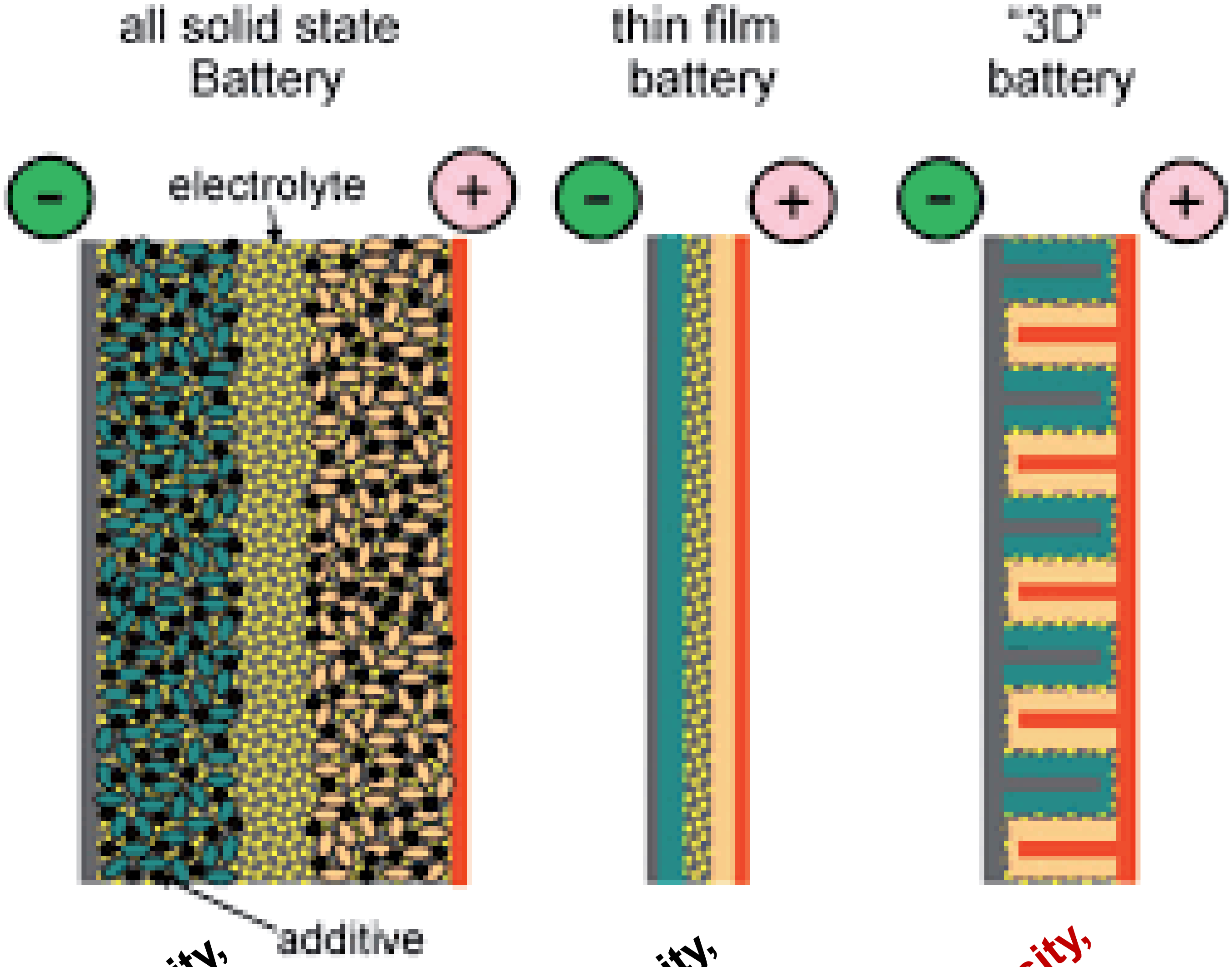
Positive electrode

($LiCoO_2$)

Li_2S-P_2S_5 gc

$LiCoO_2$

current collector



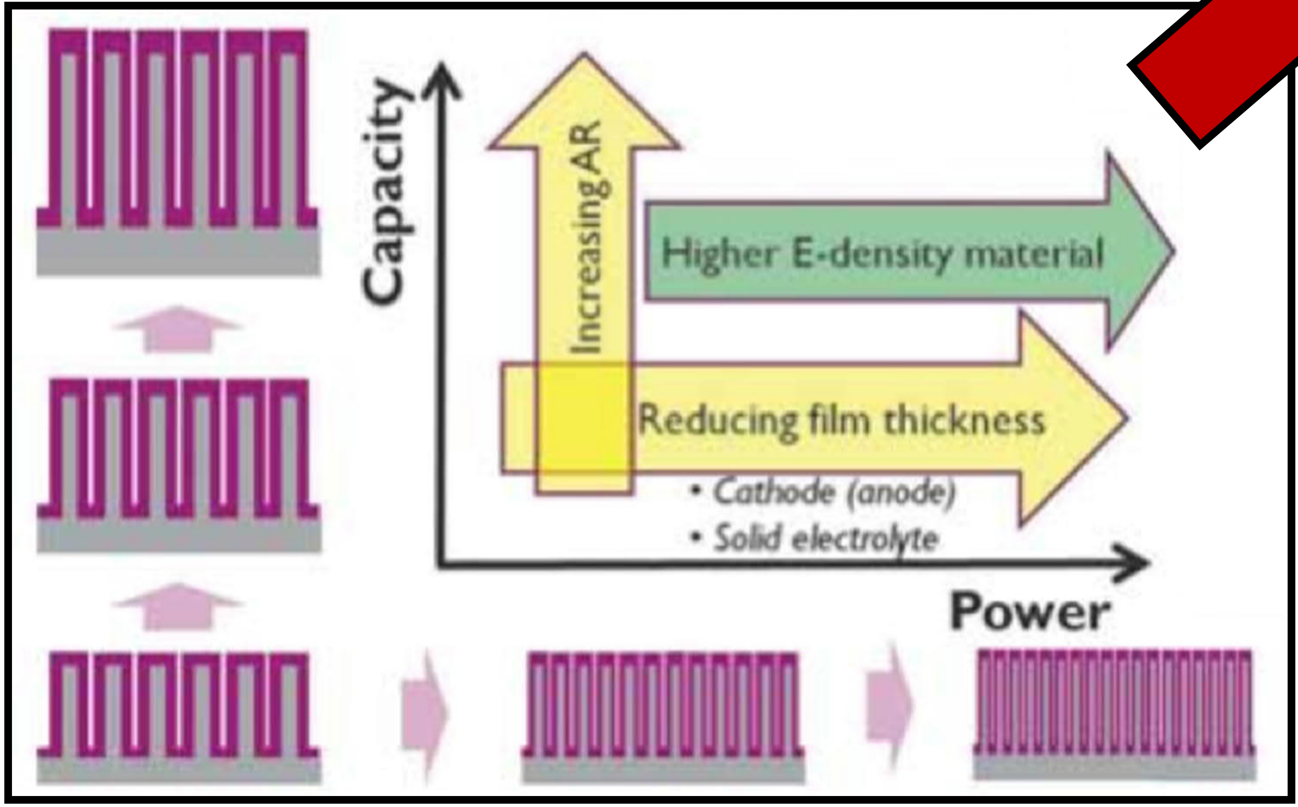
High energy density,
Low power density

Low energy density,
High power density

High energy density,
High power density

ALD

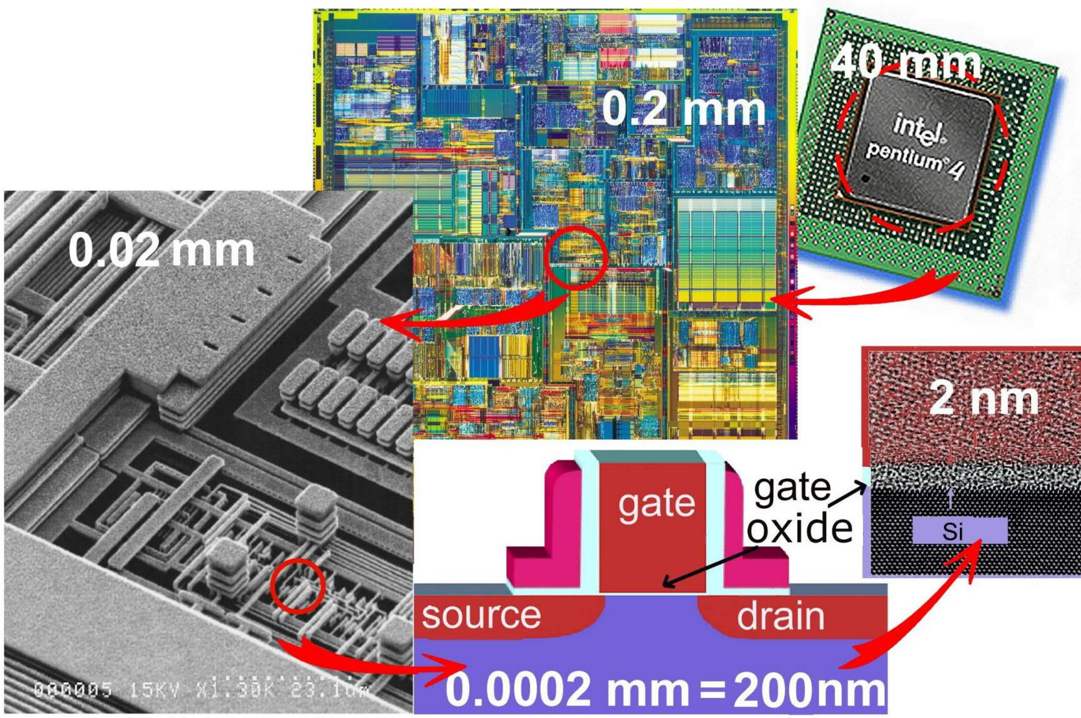
Atomic Layer Deposition



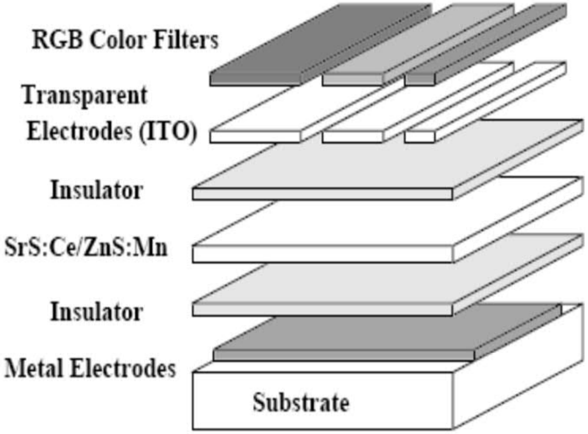
Atomic Layer Deposition (ALD)

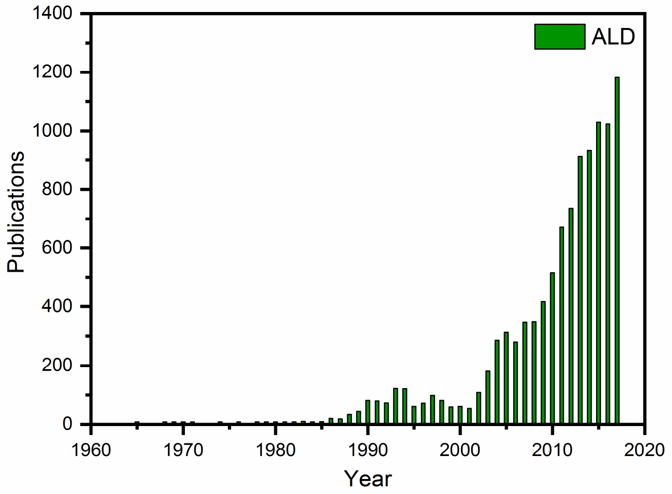
- Advanced gas-phase thin-film tec
- Self-limiting surface reactions
- Pin-hole free
- Large-area homogeneous
- Conformal

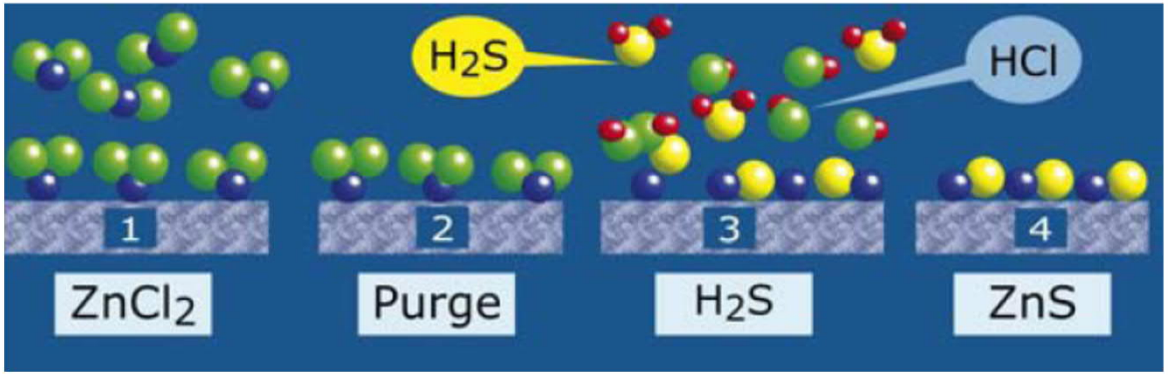
MOSFET transistor



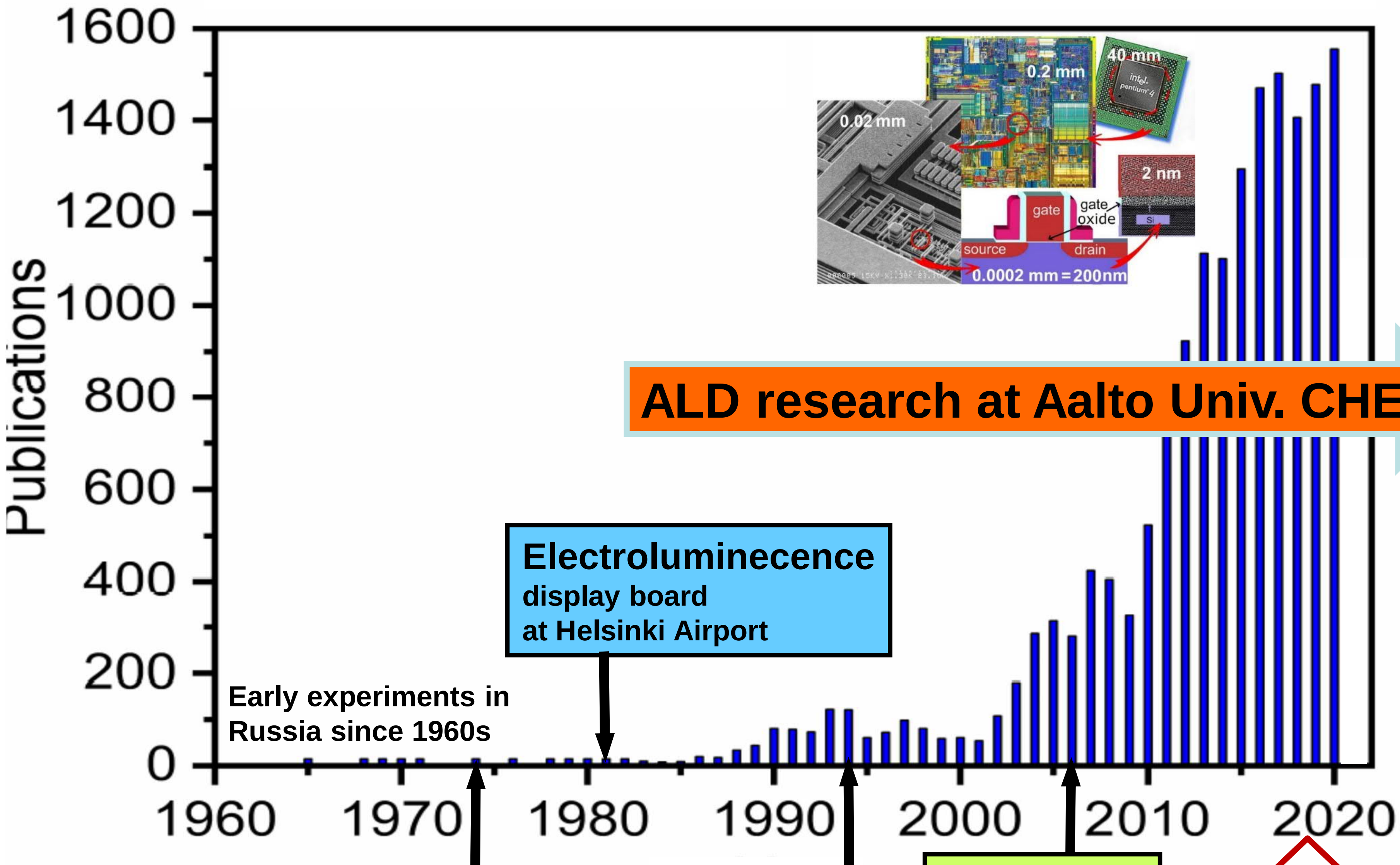
Electroluminescent display







ALD publications annually



ALD research at Aalto Univ. CHEM

Electroluminecence
display board
at Helsinki Airport

Early experiments in
Russia since 1960s

Tuomo Suntola:
Patent filed 1974

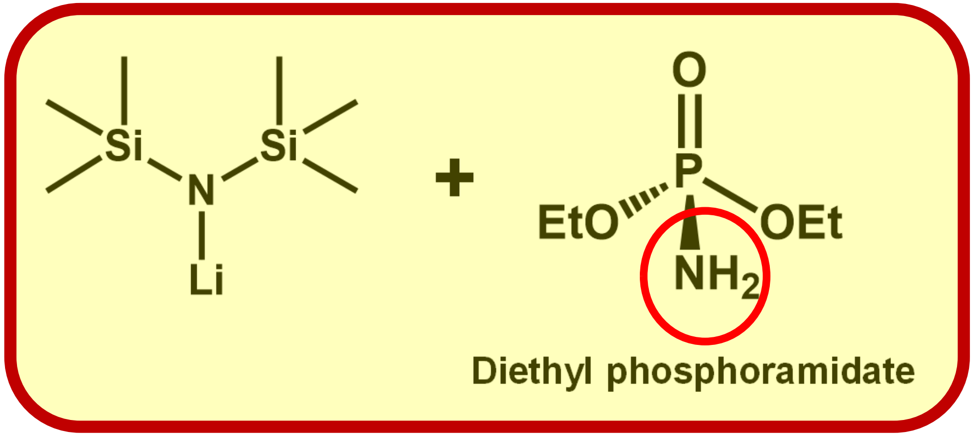
ALD-HfO$_2$ process
by Ritala & Leskelä

ALD-HfO$_2$
by Intel for
transistors

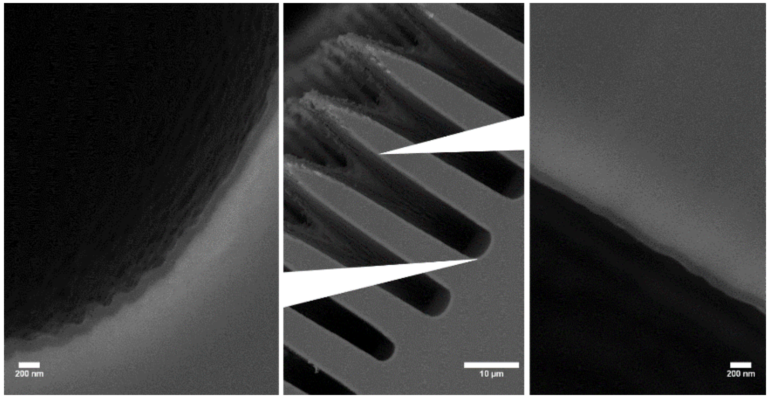
Millenium
2018 Prize
for Suntola

ALD OF LIPON

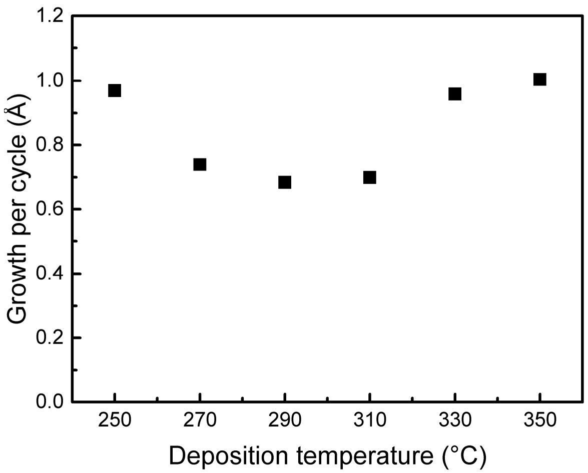
- LiPON: Lithium phosphorus oxynitride $Li_xPO_{3-y}N_z$
- **Amorhous** intermediate between crystalline $LiPO_3$ and Li_2PO_2N
- (Most) promising solid-state electrolyte for thin-film Li-ion microbattery
- Ionic conductivity greatly enhanced by N doping (up to 10^{-6} S cm^{-1})



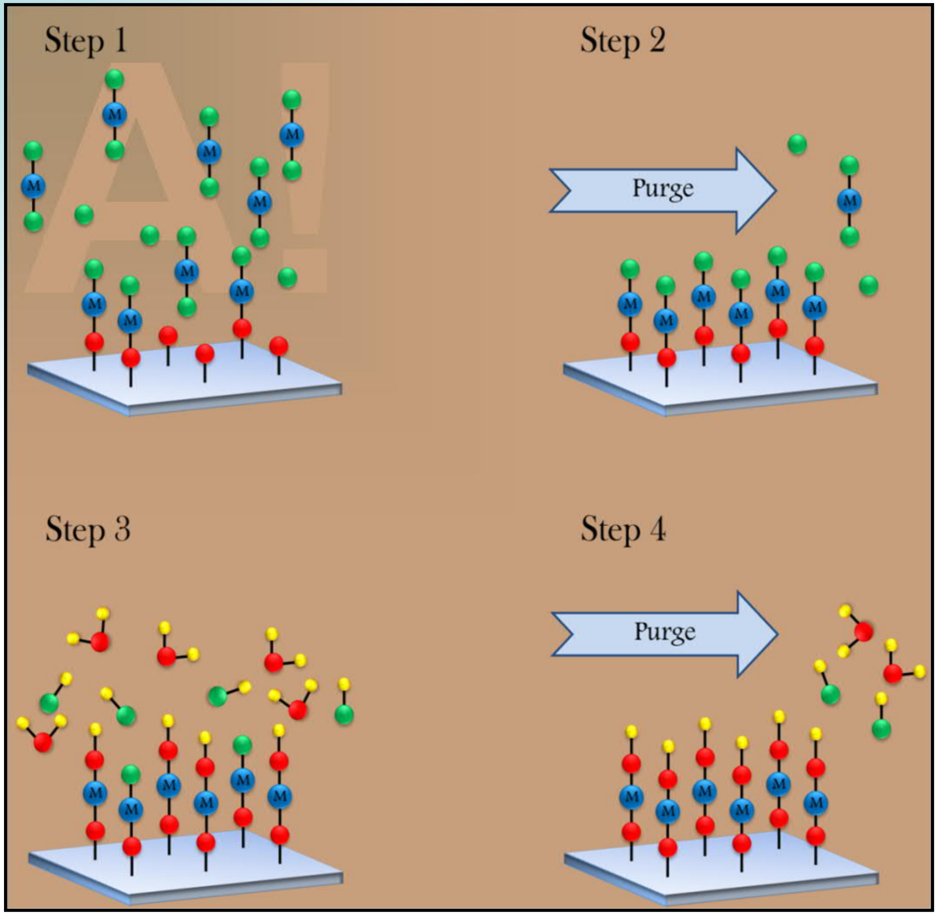
Diethyl phosphoramidate



	RBS-NRA	RT ionic cond.
290 °C	$Li_{0.90}PO_{3-y}N_{0.55}$	0.9×10^{-7} S cm^{-1}
330 °C	$Li_{0.94}PO_{3-y}N_{0.60}$	6.6×10^{-7} S cm^{-1}

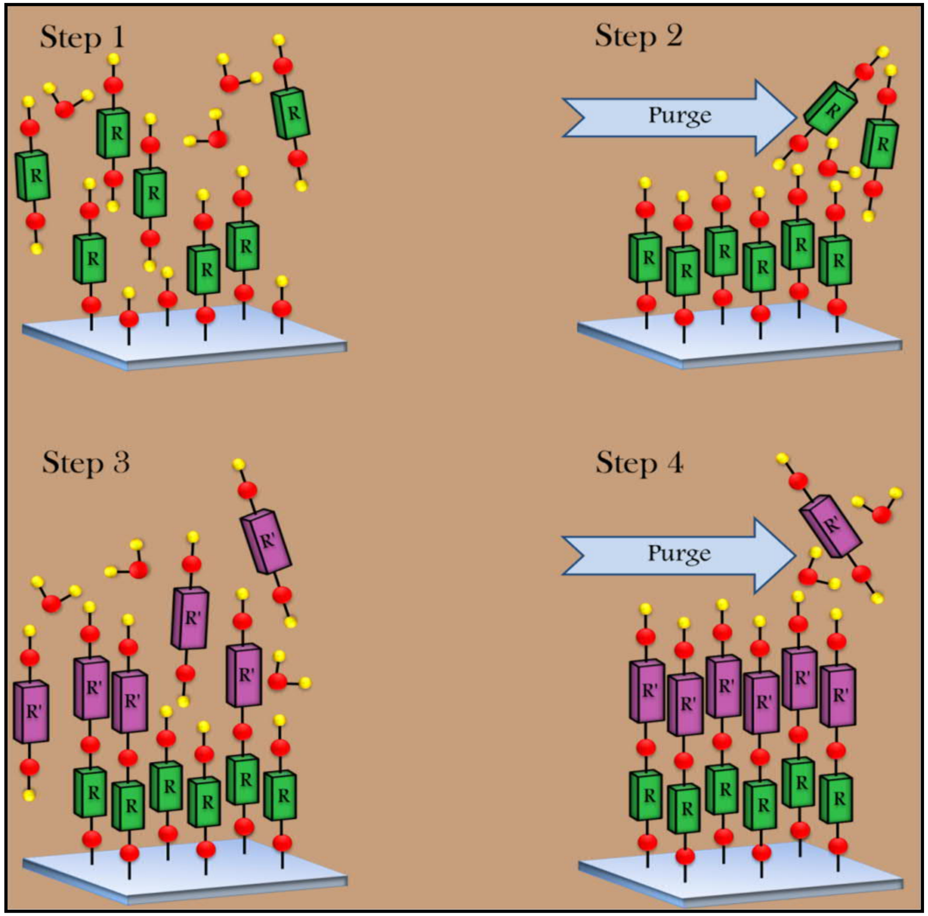


M. Nisula, Y. Shindo, H. Koga & M. Karppinen,
Chem. Mater. **27**, 6987 (2015).



ALD (Atomic Layer Deposition)

EPÄORGAANISET OHUTKALVOT



MLD (Molecular Layer Deposition)

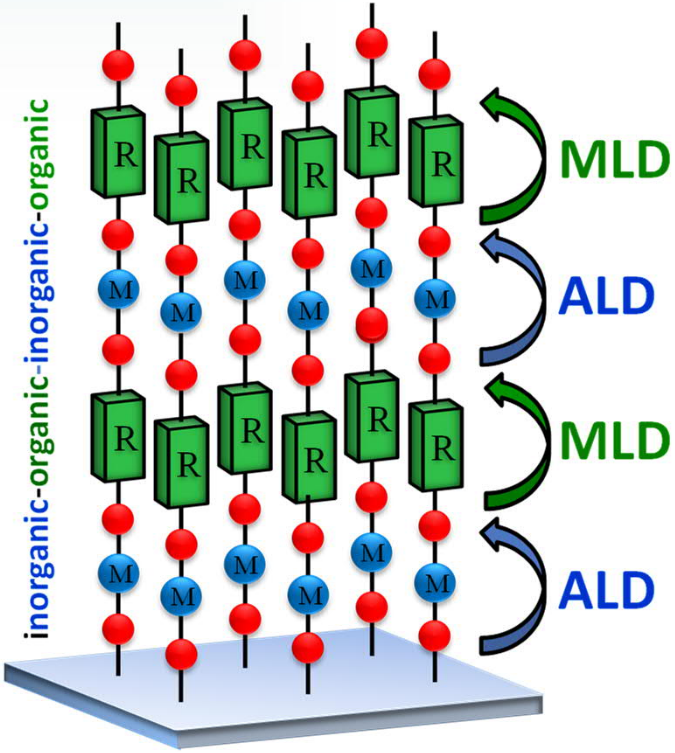
ORGAANISET OHUTKALVOT

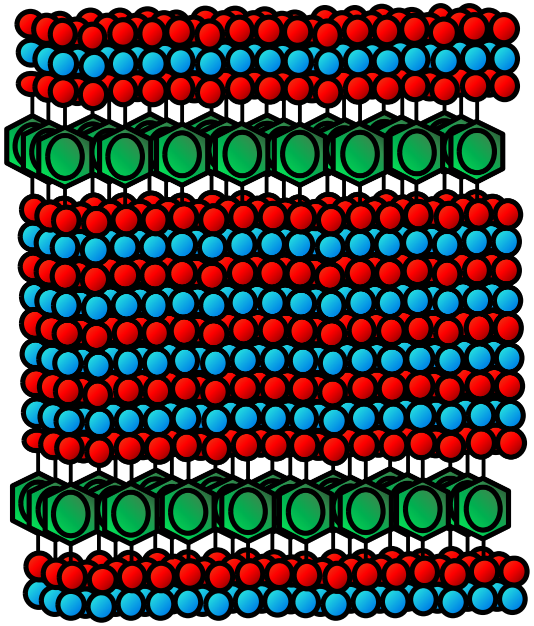
Aalto University
School of Chemical
Engineering

MLD: younger sister of ALD

Inorganic-Organic thin films

with combined ALD / MLD technique

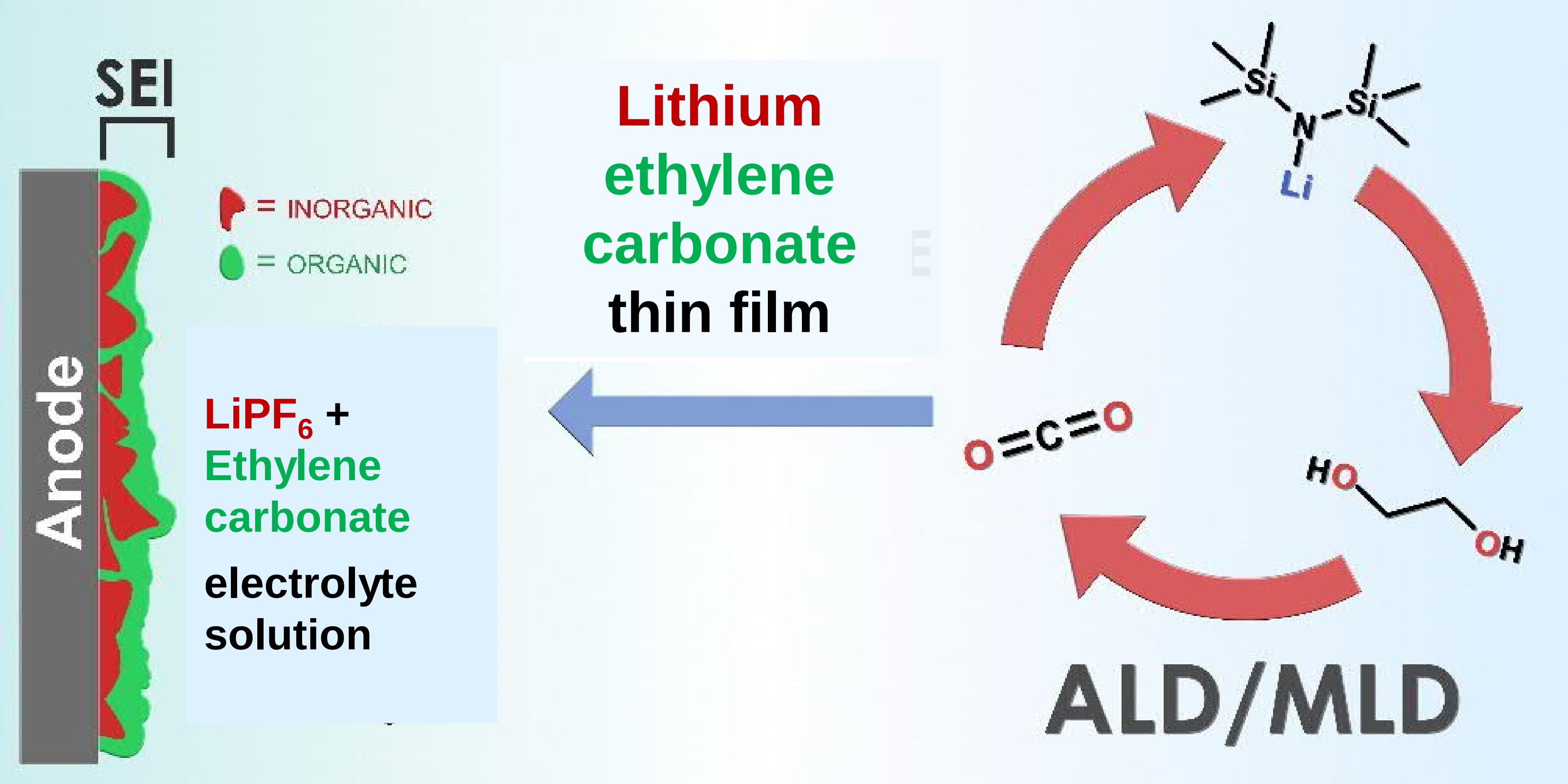




Superhila

ALD + MLD → HYBRID THIN FILMS

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



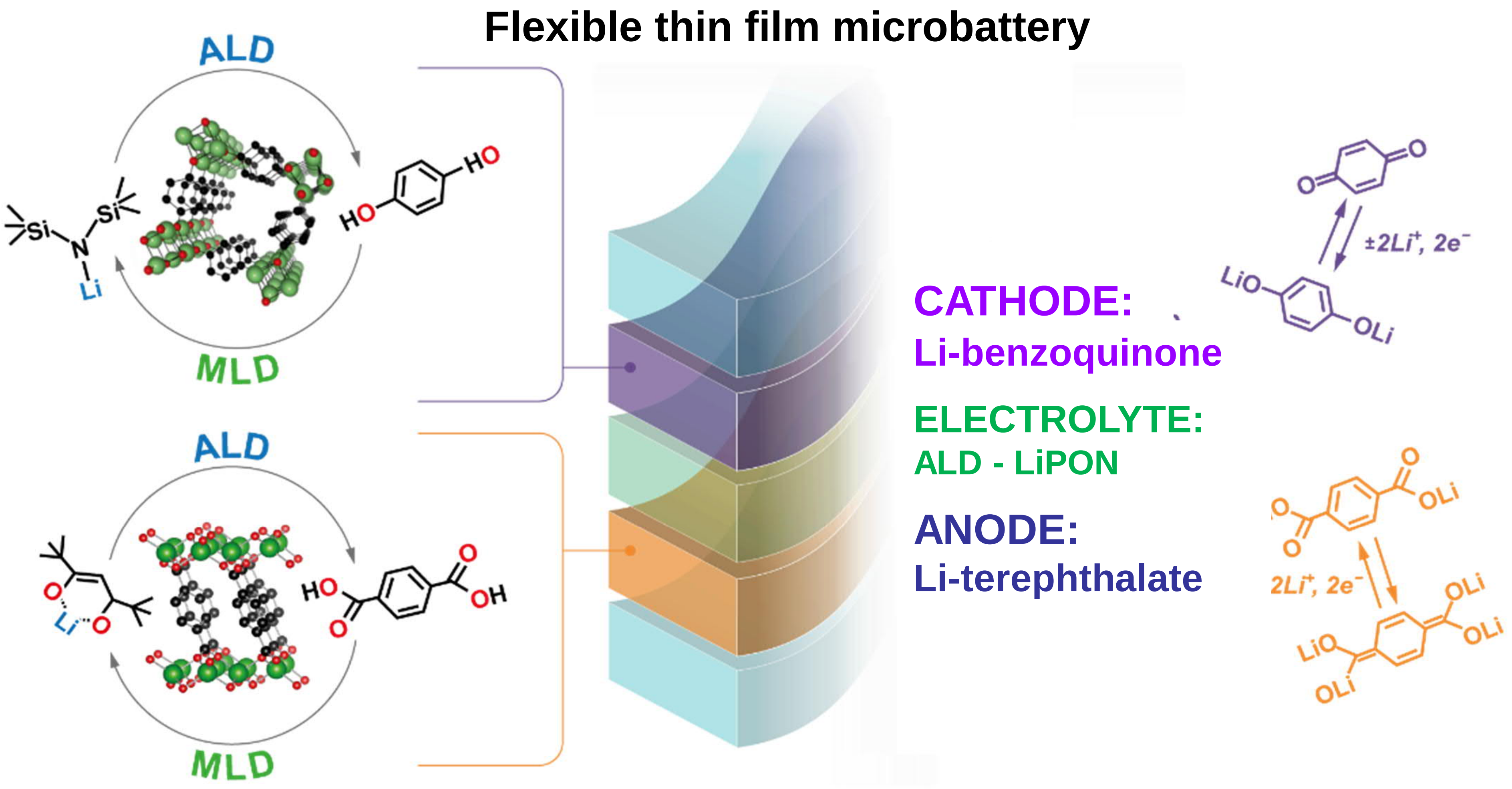
Lithium ethylene carbonate thin film

$LiPF_6$ + Ethylene carbonate electrolyte solution

SEI (Solid Electrolyte Interphase)

- SEI-layer forms naturally/unavoidably upon charging/discharging on top of the anode surface due to the unwanted reactions between anode and liquid electrolyte
- SEI protects the anode from further reactions (requirement: homogeneous and pinhole-free), but it consumes Li-ions when it forms
- ALD/MLD: high-quality artificial barrier coating which esembles the natural SEI layer

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. It is ultrafast to charge, but the problem is the low energy capacity. Whole battery structure can be deposited active-layer by active-layer in a same reactor, without additives.

Prof. Mari Lundström
Hydrometallurgy

Battery metals
from recycled
batteries

Prof. Maarit Karppinen
Material chemistry

RESEARCH COLLA-BORATION

New active
materials from
recycled metals

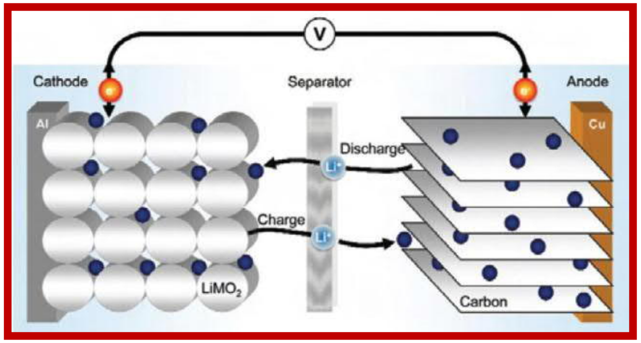
Prof. Tanja Kallio
Electrochemistry

Batteries from
new materials

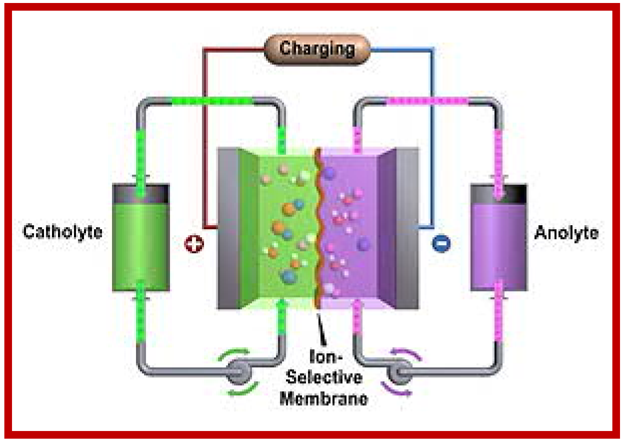
A!
Aalto University
School of Chemical
Engineering

Aalto CHEM School Battery Research Groups

LITHIUM-ION BATTERY



FLOW BATTERY



HYDROGEN FUEL CELL

ENERGY STORAGE

ENERGY HARVESTING

SOLAR CELL

WIND POWER

THERMOELECTRICS