

LECTURE 3: Li-ion (& proton) conductors

Functional Inorganic Materials Fall 2020

Tuesdays: 10.15 - 12.00
Thursdays: 10.15 - 12.00
Remote Zoom lectures

#	Date	Who	Topic
1	Tue 27.10.	Maarit	Introduction + Superconductivity: High- T_c superconducting Cu oxides
2	Thu 29.10.	Maarit	Ionic conductivity (Oxygen): SOFC & Oxygen storage
3	Tue 03.11.	Maarit	Ionic conductivity (Lithium & Proton): Li-ion battery
4	Thu 05.11.	Maarit	Hybrid materials
5	Tue 10.11.	Antti	Thermal conductivity
6	Thu 12.11.	Antti	Thermoelectricity
7	Tue 17.11.	Antti	Ferro-, pyro-, and piezoelectricity
8	Thu 19.11.	Antti	Magnetic and multiferroic oxides
9	Tue 24.11.	Mady	Metal-based energy-saving applications
10	Thu 26.11.	Mady	Metal-based energy-efficient windows and solar absorbers
11	Tue 01.12.	Mady	Metal oxides for energy-saving applications: Past and new trends
12	Thu 03.12.	Mady	Materials design and new perspectives

#	DATE	TOPIC & KEYWORDS
1	27.10.	(High-T_c) Superconductivity New-material design, Multi-layered crystal structure, Mixed-valency, Oxygen nonstoichiometry
2	29.11.	Ionic conductivity: Oxygen Oxygen vacancies, Redox-active cations, Mixed valency, Cation substitutions (isovalent/aliovalent), Crystal symmetry, Oxygen storage, SOFC
3	03.11.	Ionic conductivity: Hydrogen & Lithium Water absorption & Oxide/hydroxide, Li-ion battery, Solid-state electrolytes
4	05.11.	Hybrid materials Inorganic-organic materials, MOF, ALD/MLD, Layer-engineering

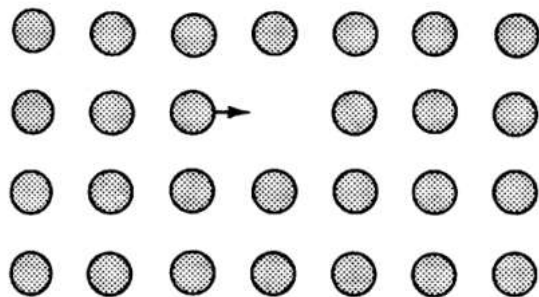
LECTURE EXERCISE 3

1. Which useful function could be anticipated for an oxygen-deficient oxide material that can absorb water? Explain !
2. Explain why a layered crystal structure is useful for Li-ion battery electrode materials.
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 ($\text{Li}_x\text{PO}_y\text{N}_z$) ? Why these are important changes ?

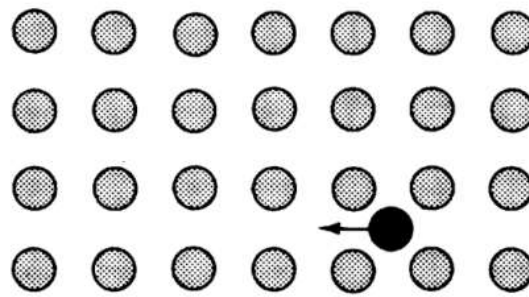
NOTE: There will be an additional question in the Exercise 4 which is partly related to the topics covered in Lecture 3.

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
- Fast ion conductors are intermediate between **regular crystalline solids with immobile ions** & **liquid electrolytes** (without a regular structure) **with fully mobile ions**
- Measurement of ionic conductivity: electrochemical impedance spectroscopy (EIS)
- APPLICATIONS:
batteries, fuel cells, supercapacitors, chemical sensors, separation membranes, ...



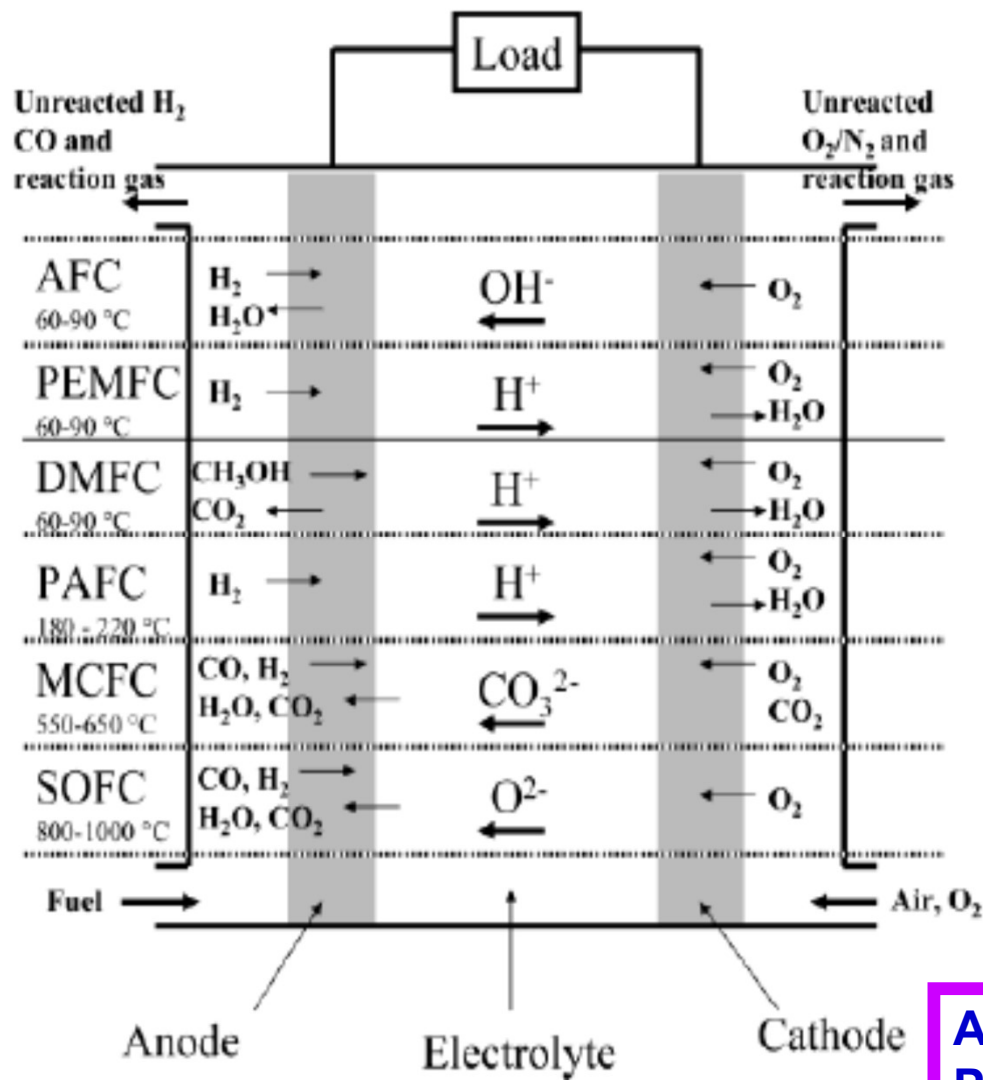
mobile vacancy



mobile interstitial

EFFECTIVE IONIC RADII

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



FUEL CELLS

PROTON-CONDUCTING MATERIALS

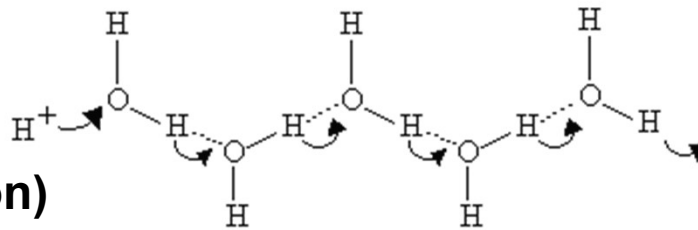
- AFC** Alkaline fuel cell
- PEMFC** Proton exchange membrane
- DMFC** Methol direct oxidize fuel cell
- PAFC** Phosphate fuel cell
- MCFC** Molten carbonate fuel cell
- SOFC** Solid-oxide fuel cell

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.)

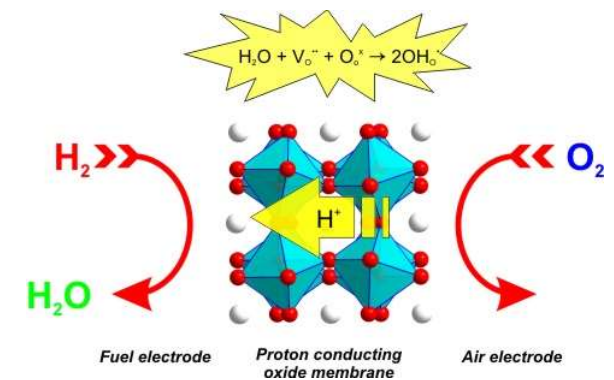


- **PROTON-CONDUCTING OXIDES:**

- Historically important perovskites (1980, Iwahara *et al.*): LaYO_3 , SrZrO_3
- Present perovskite prototypes: SrCeO_3 , BaCeO_3

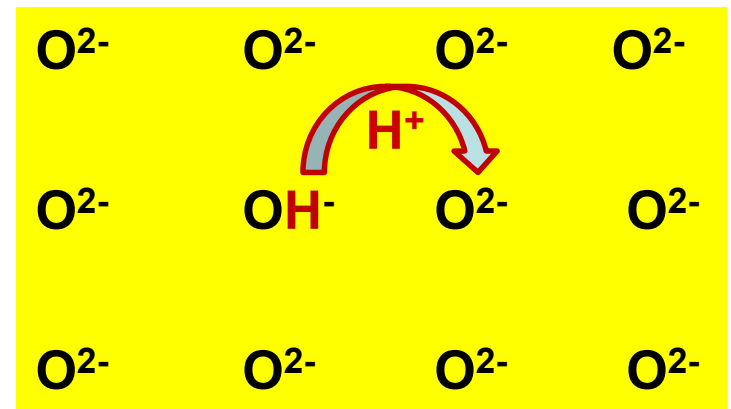
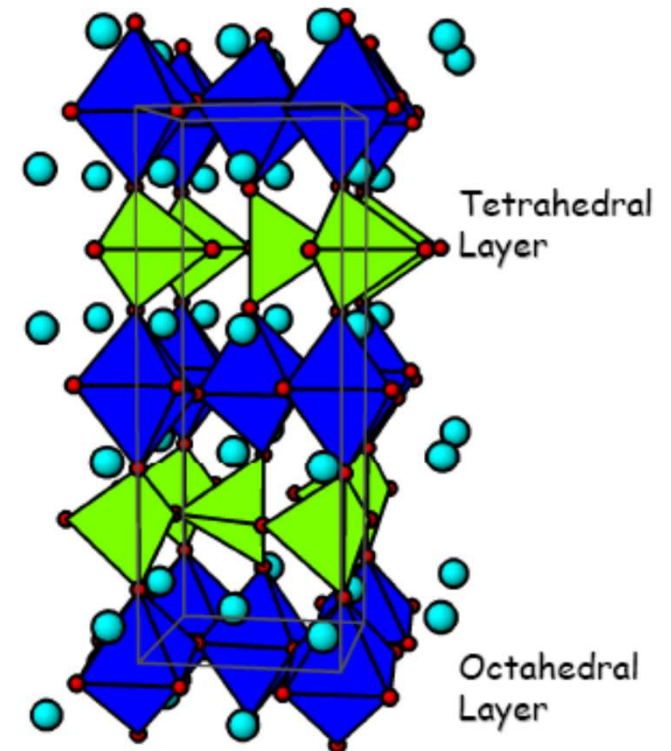
- **NEW OXIDE CANDIDATES:**

- Ruddlesden-Popper phases
- Pyrochlores $\text{R}_2(\text{Zr}, \text{Y})_2\text{O}_7$, $\text{R}_2(\text{Ti}, \text{In}, \text{Mg})_2\text{O}_7$



$\text{Ba}_2\text{In}_2\text{O}_5$ ($\text{BaInO}_{2.5}$)

- 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
- **ADDITIONAL INTERESTING FEATURE:** BaZrO_3 - $\text{Ba}_2\text{In}_2\text{O}_5$ solid solution absorbs water to fill oxygen vacancies and becomes a good proton conductor



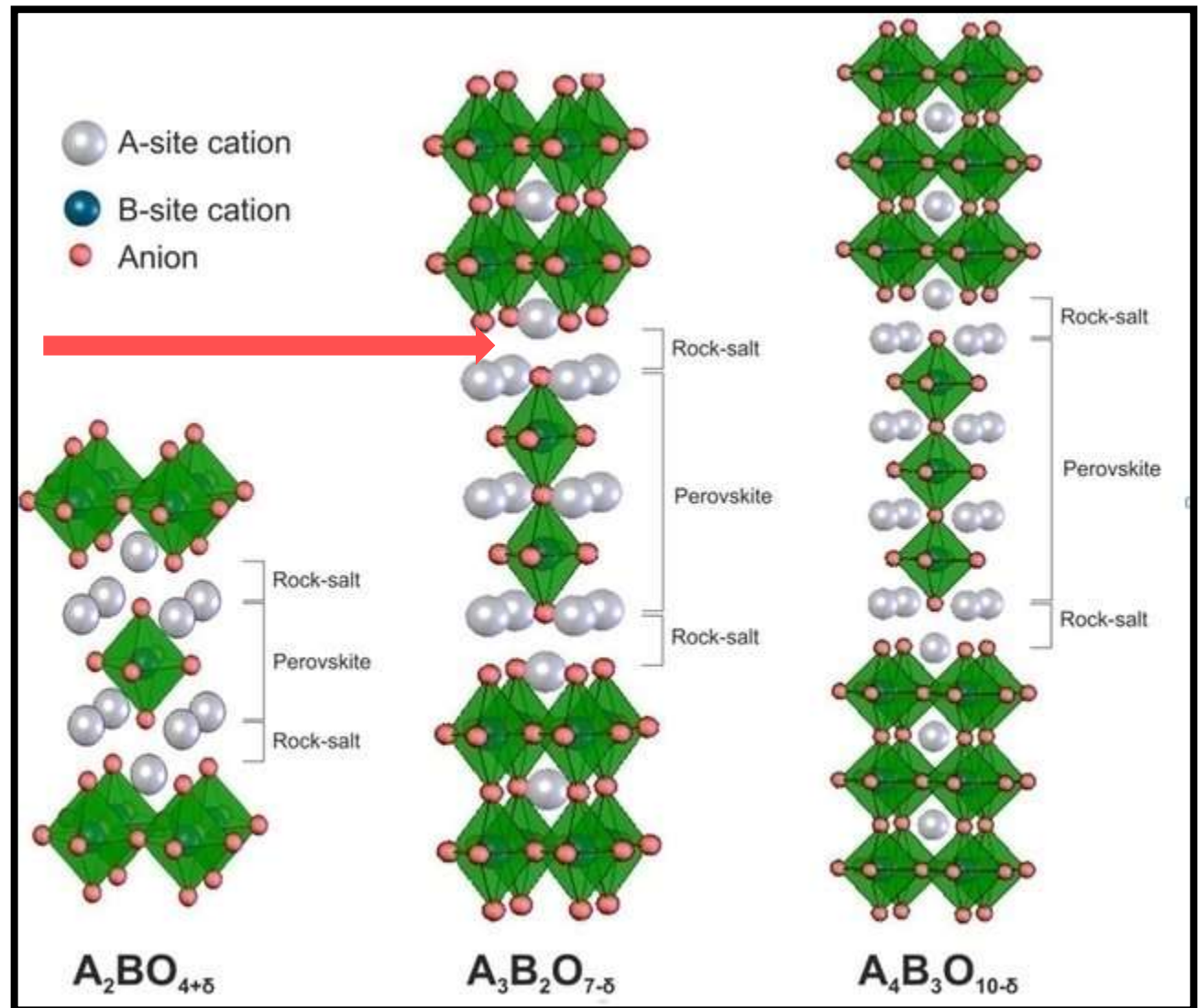
WATER/PROTON ABSORPTION OF OXIDES

- **Affinity of oxide ion O^{2-} for H^+ is great \rightarrow 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 \rightarrow when it combines with oxygen the resultant OH^- group is almost identical in size with an O^{2-} ion \rightarrow the most visible change is seen in the charge balance**
- **Many natural oxide minerals contain OH^- groups, e.g. pyrochlores**
- **Many (nonstoichiometric/mixed-valence/highly-oxidized) metal oxides readily absorb water/protons \rightarrow potential proton conductors**

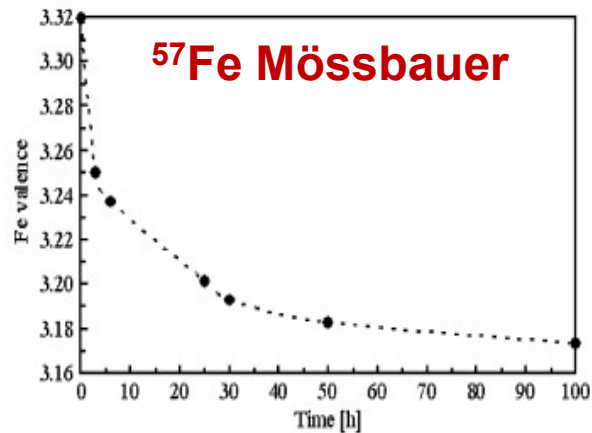
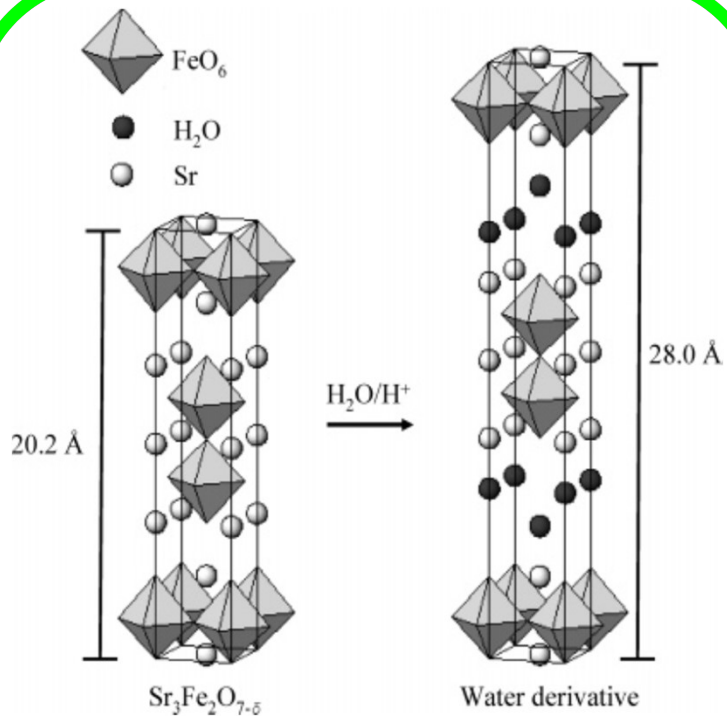
Ruddlesden-Popper $A_{n+1}B_nO_{1+3n}$

- Enough space for interstitial oxygen, water intercalation, etc.

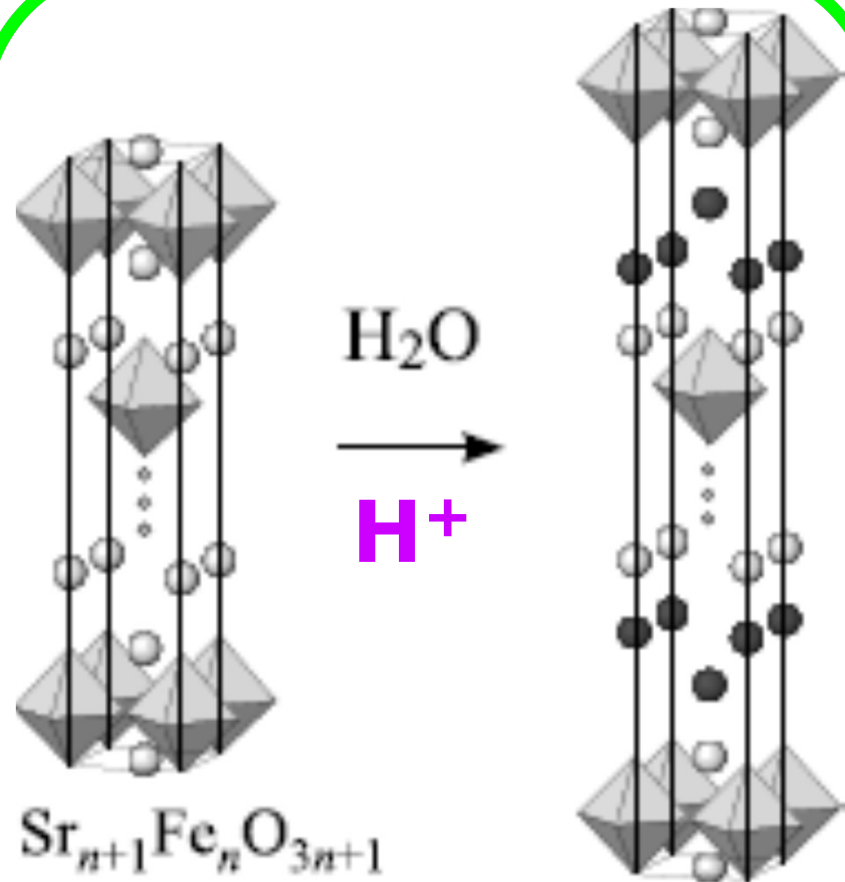
O^{2-} , H_2O , H^+



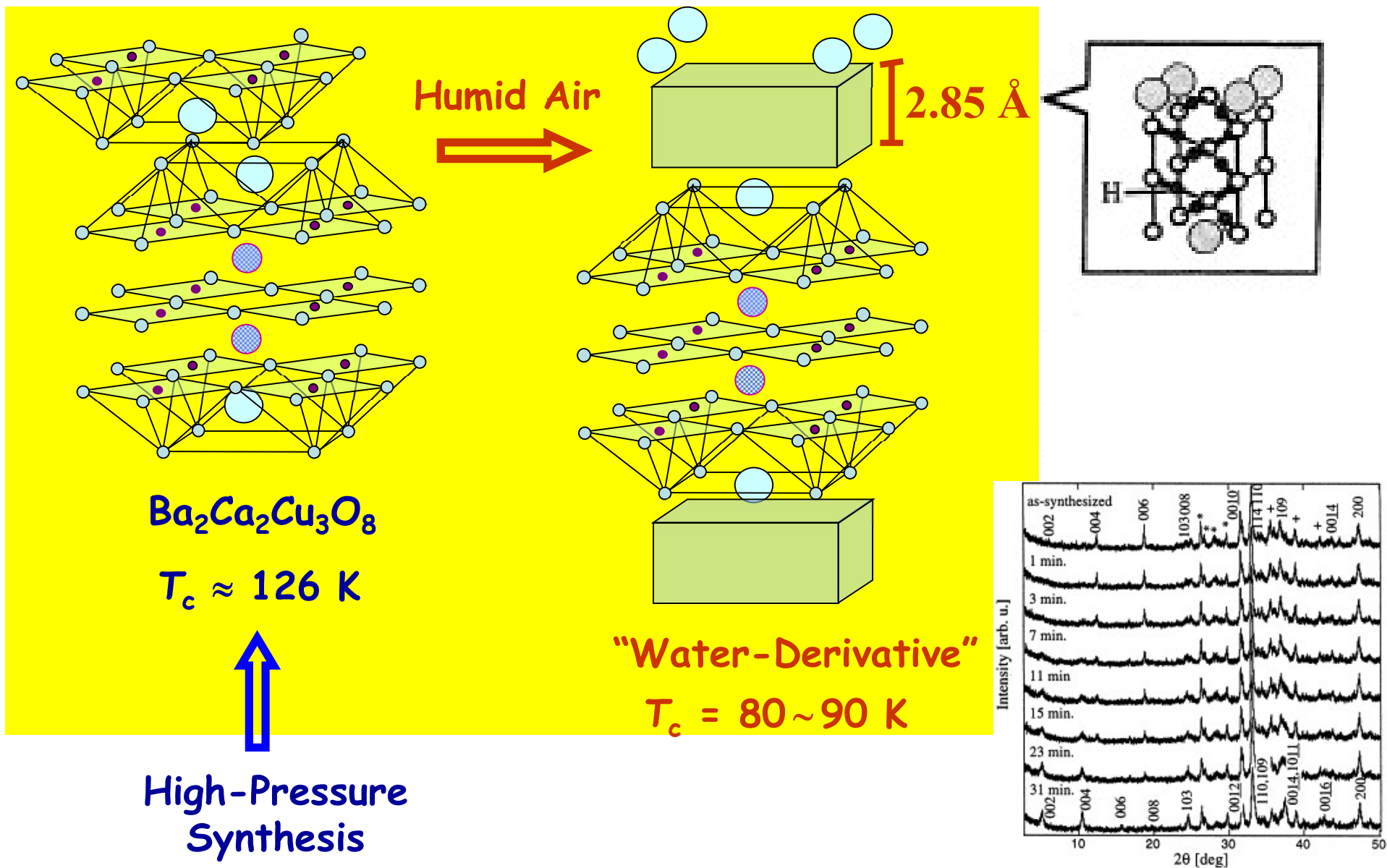
Water-derivatives of $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$



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



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

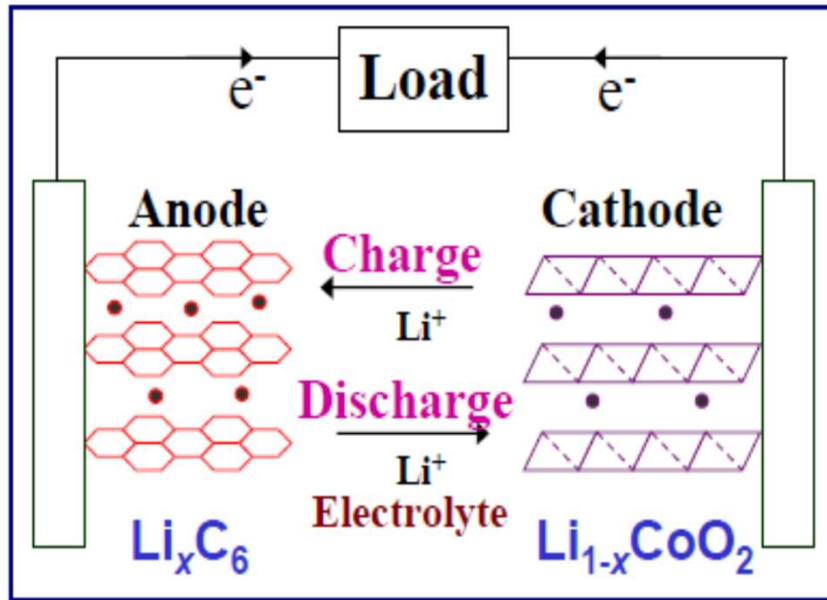


T. Hosomi, H. Suematsu, H. Fjellvåg, M. Karppinen & H. Yamauchi, *J. Mater. Chem.* 9, 1141 (1999)

Li-ION BATTERY

LITHIUM

- lightest of all metals
- largest electrochem. potential
- largest energy density per mass
- small and easy/fast to move



EC: ethylene carbonate

DEC: dimethyl carbonate

1991
First commercial
Li-ion battery
by Sony

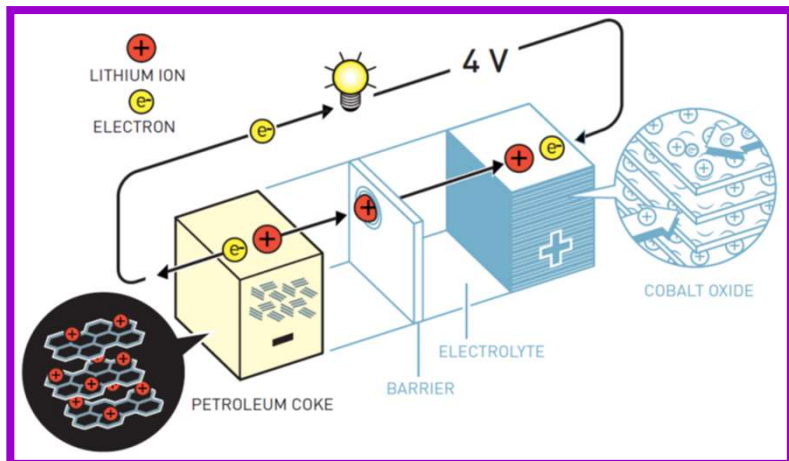
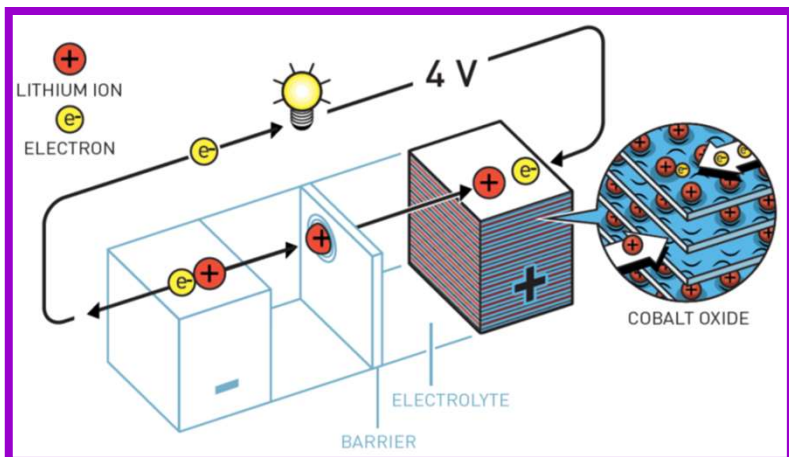
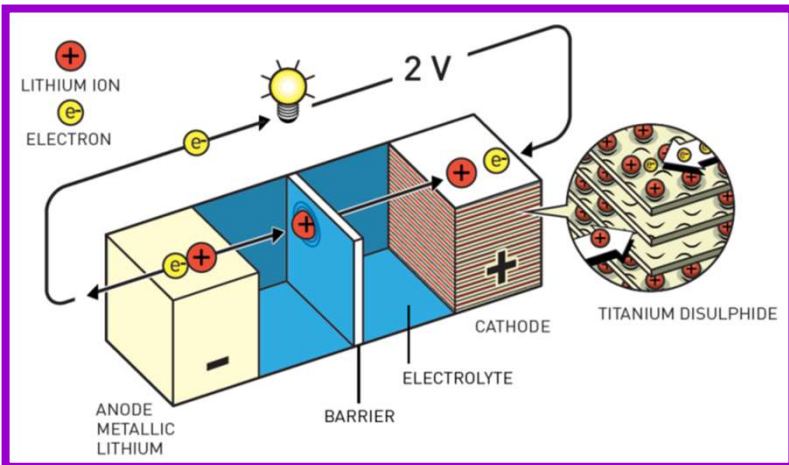
Cell: (-) C | LiPF_6 -(EC+DEC) | LiCoO_2 (+)

Cathode: $\text{LiCoO}_2 \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$

Anode: $6\text{C} + x\text{Li}^+ + xe^- \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_x\text{C}_6$

Total: $\text{LiCoO}_2 + 6\text{C} \xrightleftharpoons[\text{D}]{\text{C}} \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6$





Chemistry Nobel 2019



Stanley Whittingham (UK):

- Exxon: TiS_2 cathode 1976

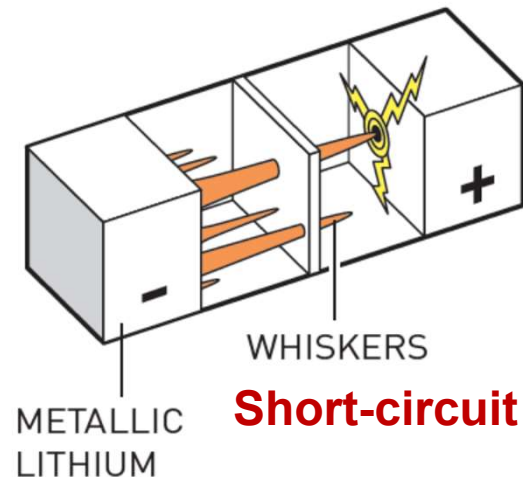
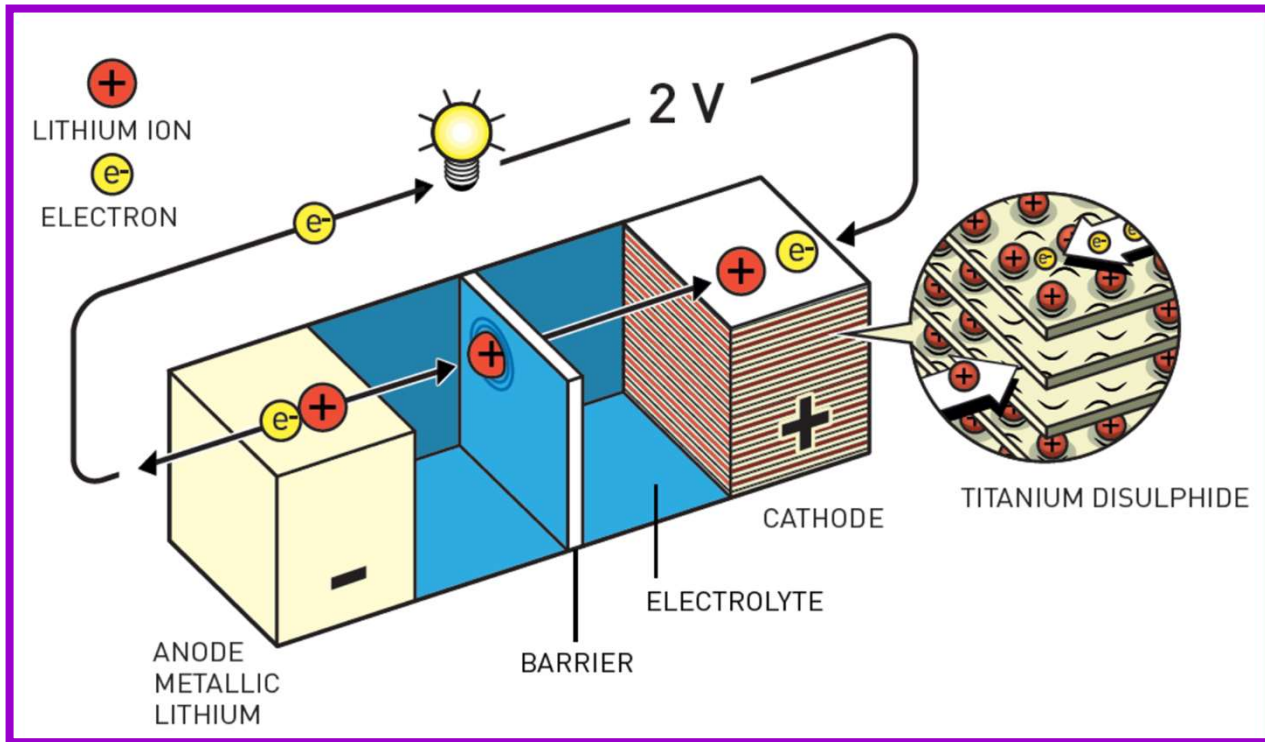
John Goodenough (US):

- Univ. Oxford: LiCoO_2 cathode 1980

Akira Yoshino (Jpn):

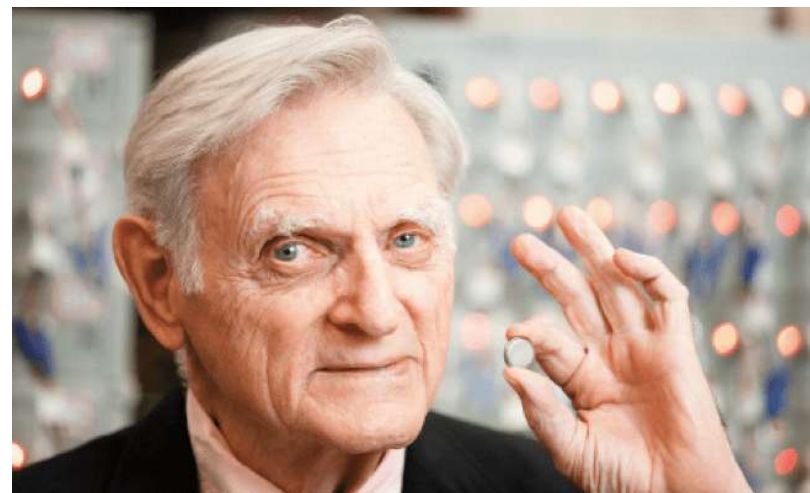
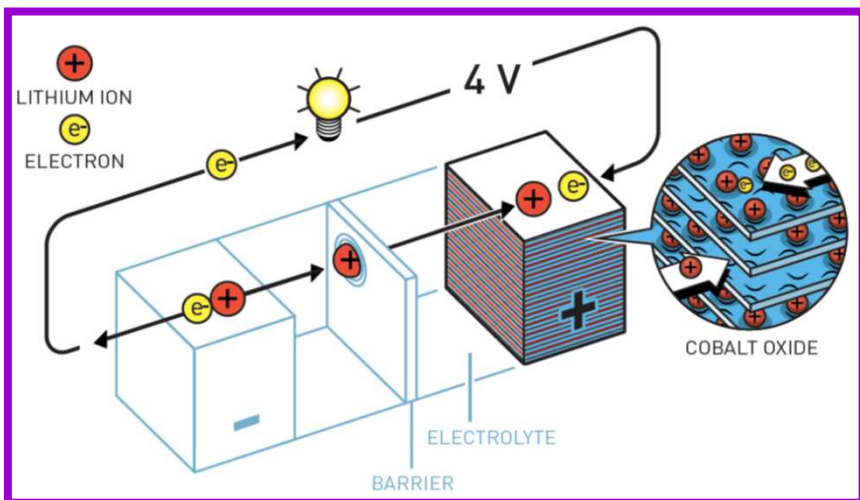
- Asahi Kasei: carbon-based anode 1985

Commercialization: Sony 1991



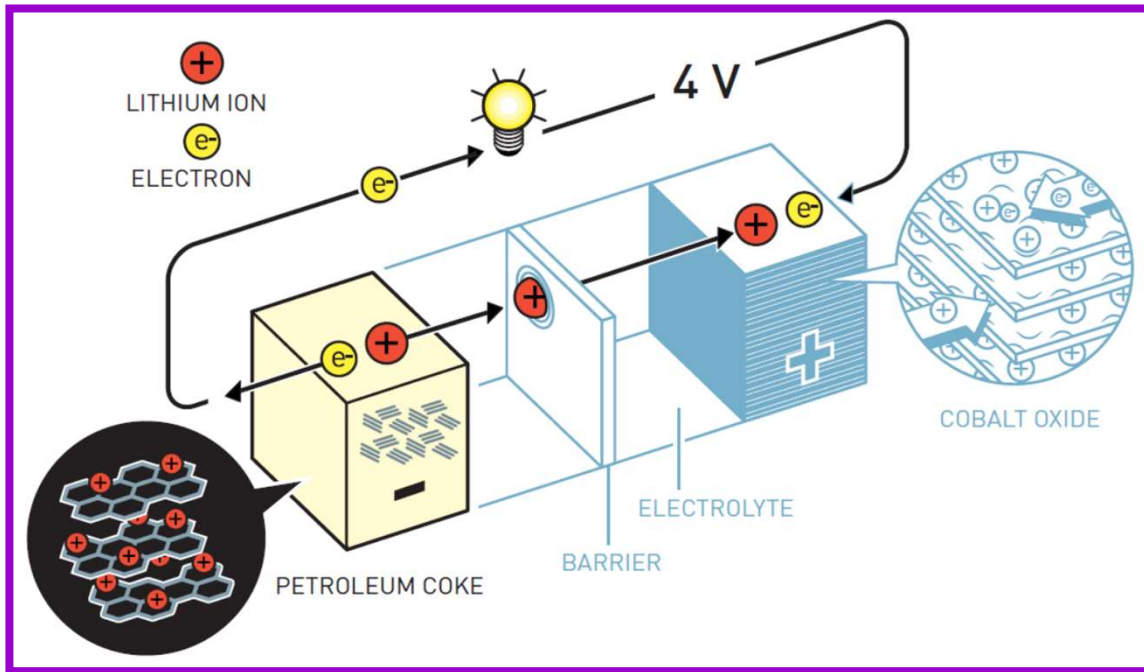
Stanley Whittingham (born 1941 UK)

- 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)
- 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_xCoO₂ cathode 1980** (LiMn₂O₄ cathode 1986)
- Prof. 1986 – now (University of Texas at Austin)
 - LiFePO₄ 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)

LITHIUM-ION BATTERY

- **Secondary (= rechargeable) battery:**
 - **charged/recharged hundreds/thousands times**
- **Li-ion battery does not involve extensive chemical reactions (which would soon destroy the battery) but is based on movement/intercalation of Li^+ ions between/within the anode and cathode materials**
- **Electrode materials (graphite and LiCoO_2) have layered crystal structures capable of accommodating large amounts of Li^+ ions**
- **Light-weight, high voltage, large energy density**
- **No "memory effect", small self discharge**
- **Cell phones, laptops, wearable electronics, electric cars and other vehicles, energy storage related to solar cells and wind power, etc.**

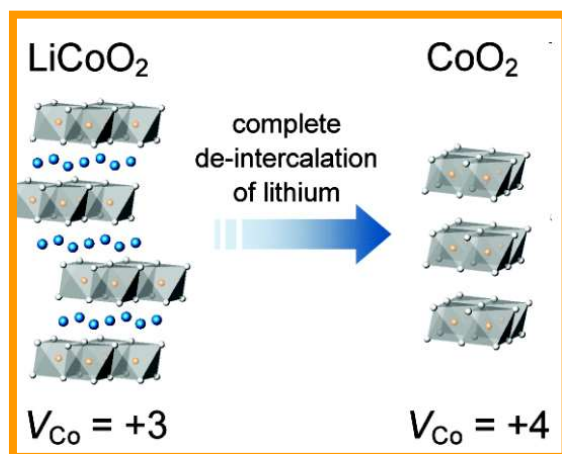
PRESENT MATERIAL VARIETY

Cathode: LiCoO_2 , $\text{Li}(\text{Co}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3})\text{O}_2$, LiMn_2O_4 , LiFePO_4

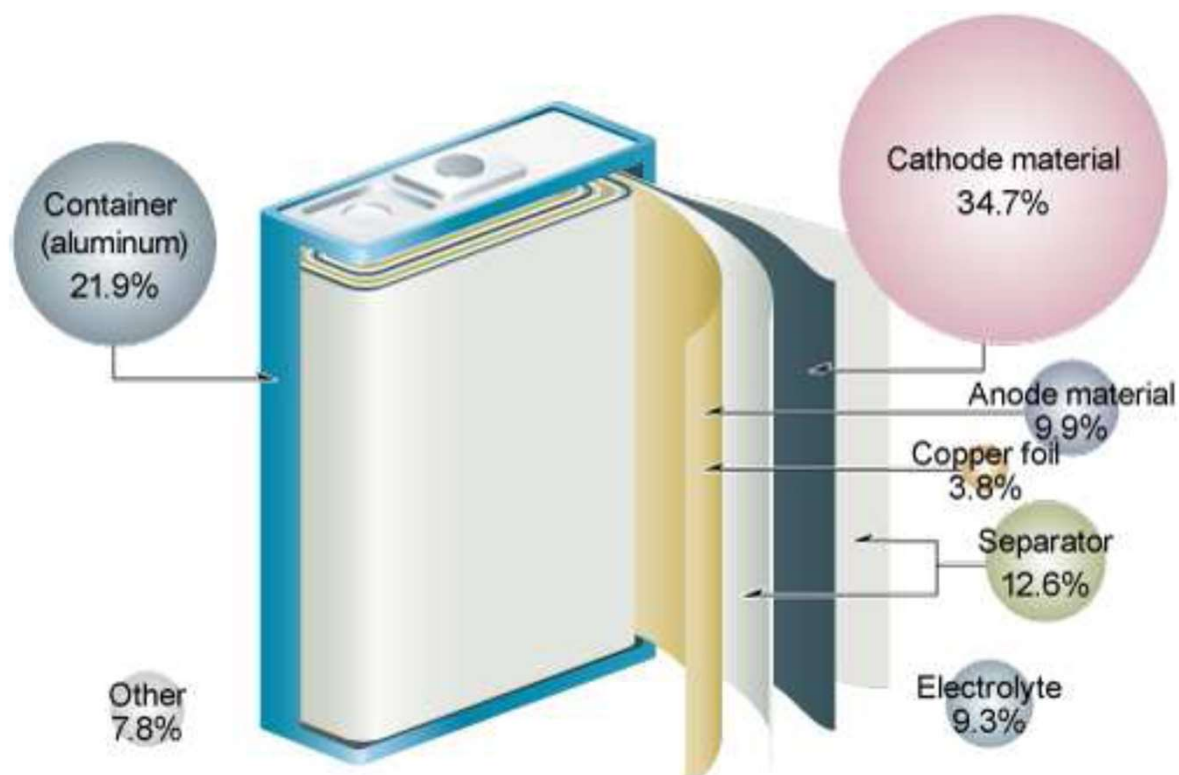
Anode: Graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Electrolyte: LiPF_6 (in ethylene carbonate)

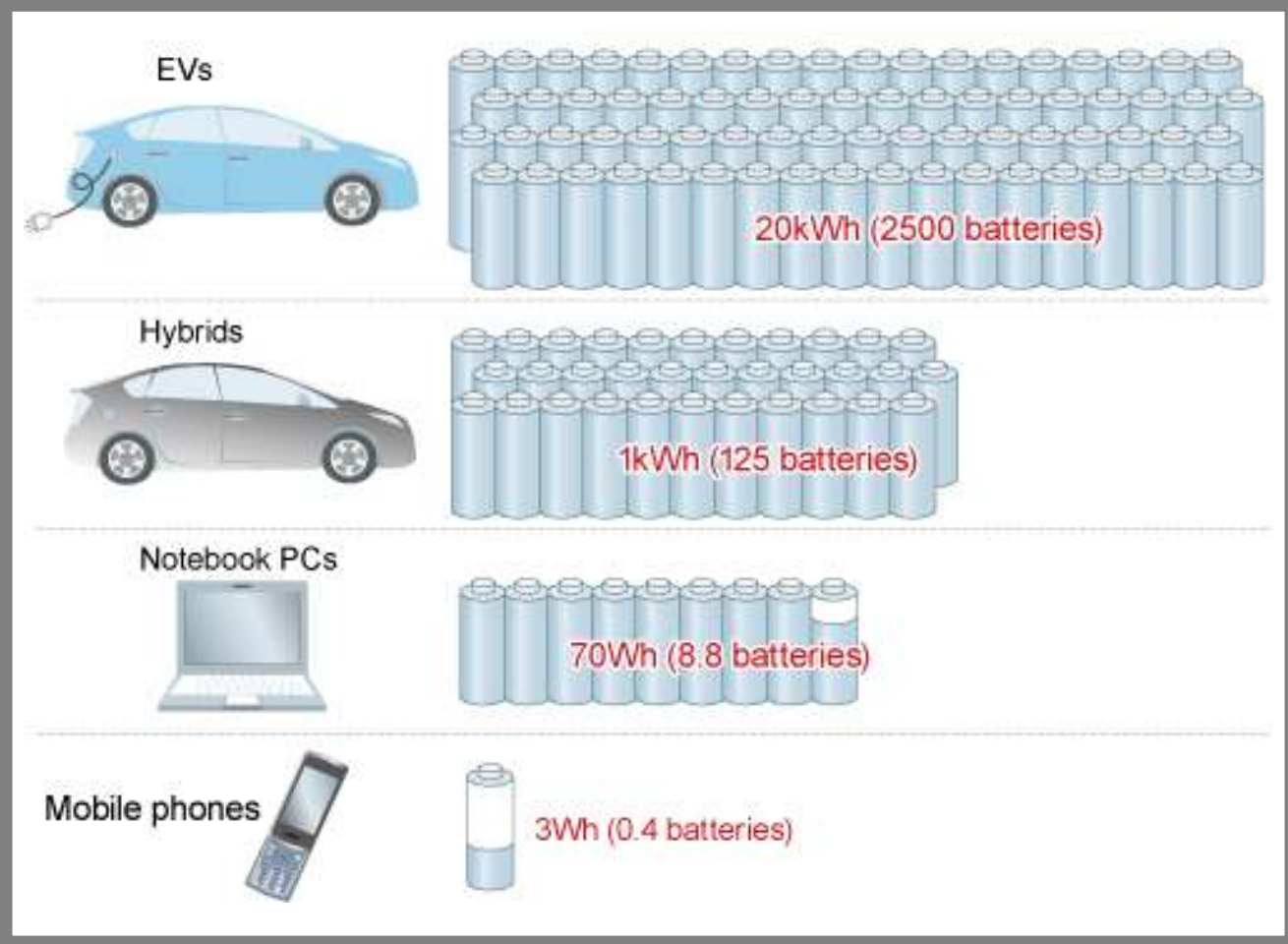
Binder: PVDF (polyvinyl difluoride) + NMP (N-methylpyrrolidone)



T. Motohashi, et al.,
Chemistry of Materials **19**, 5063 (2007).



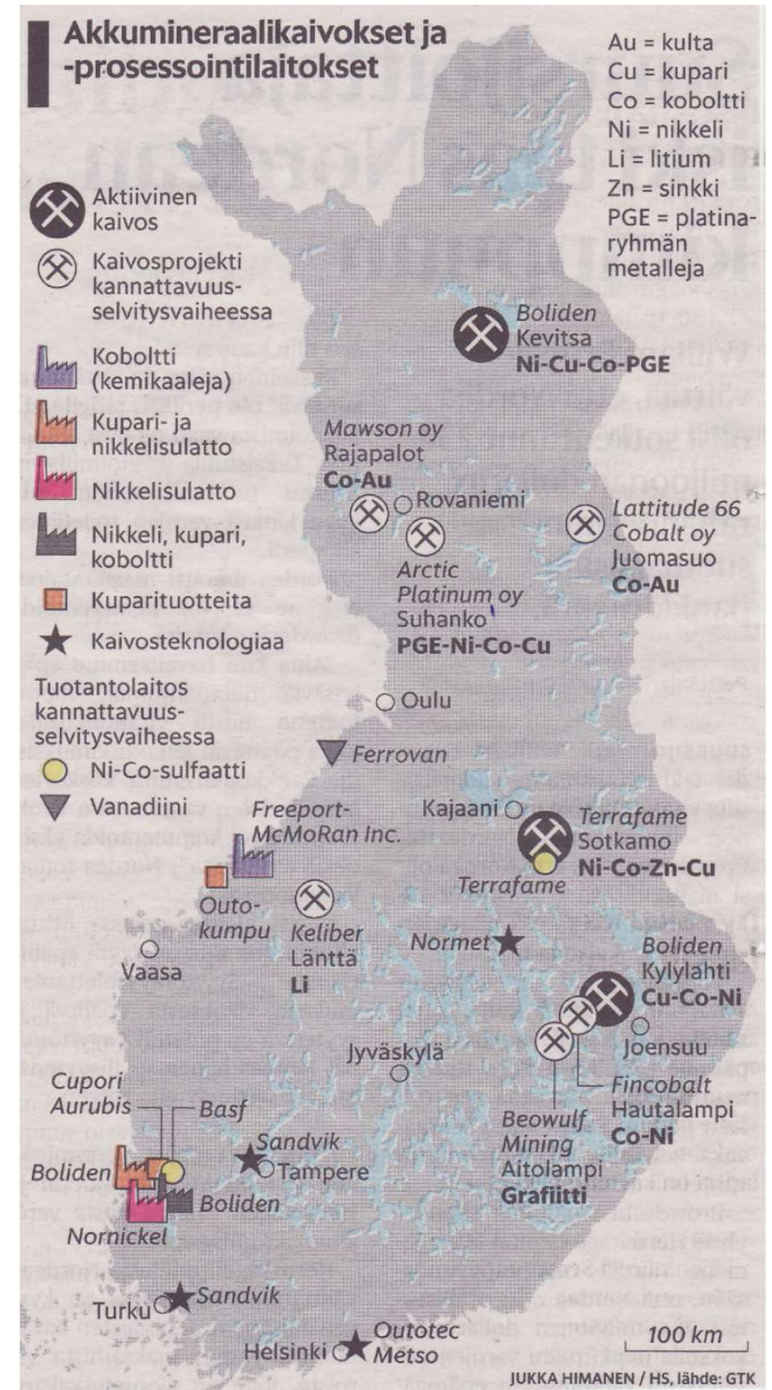
**Capacity of a battery needed for an electric car
is 10 000 times larger than that
of a mobile phone**

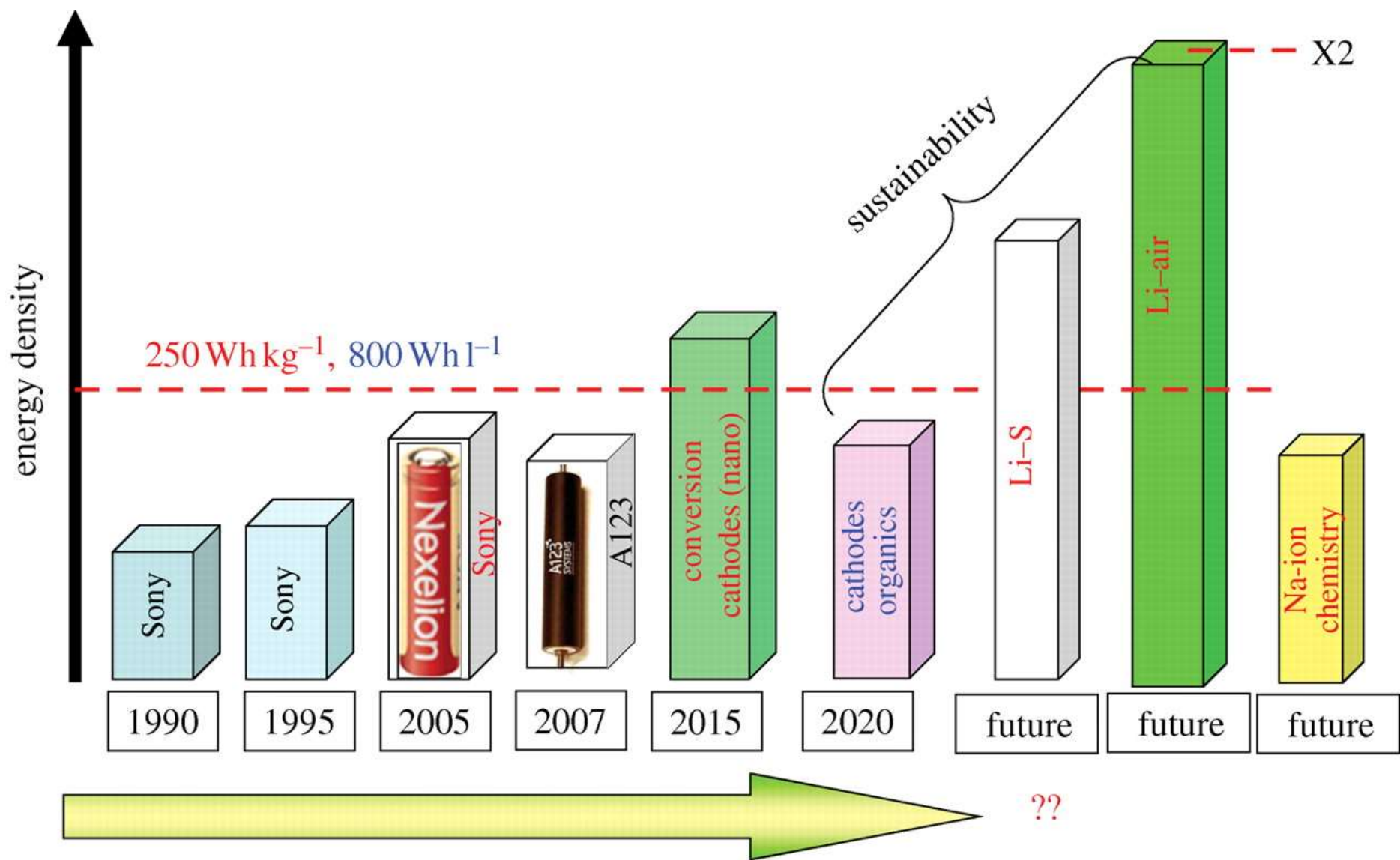


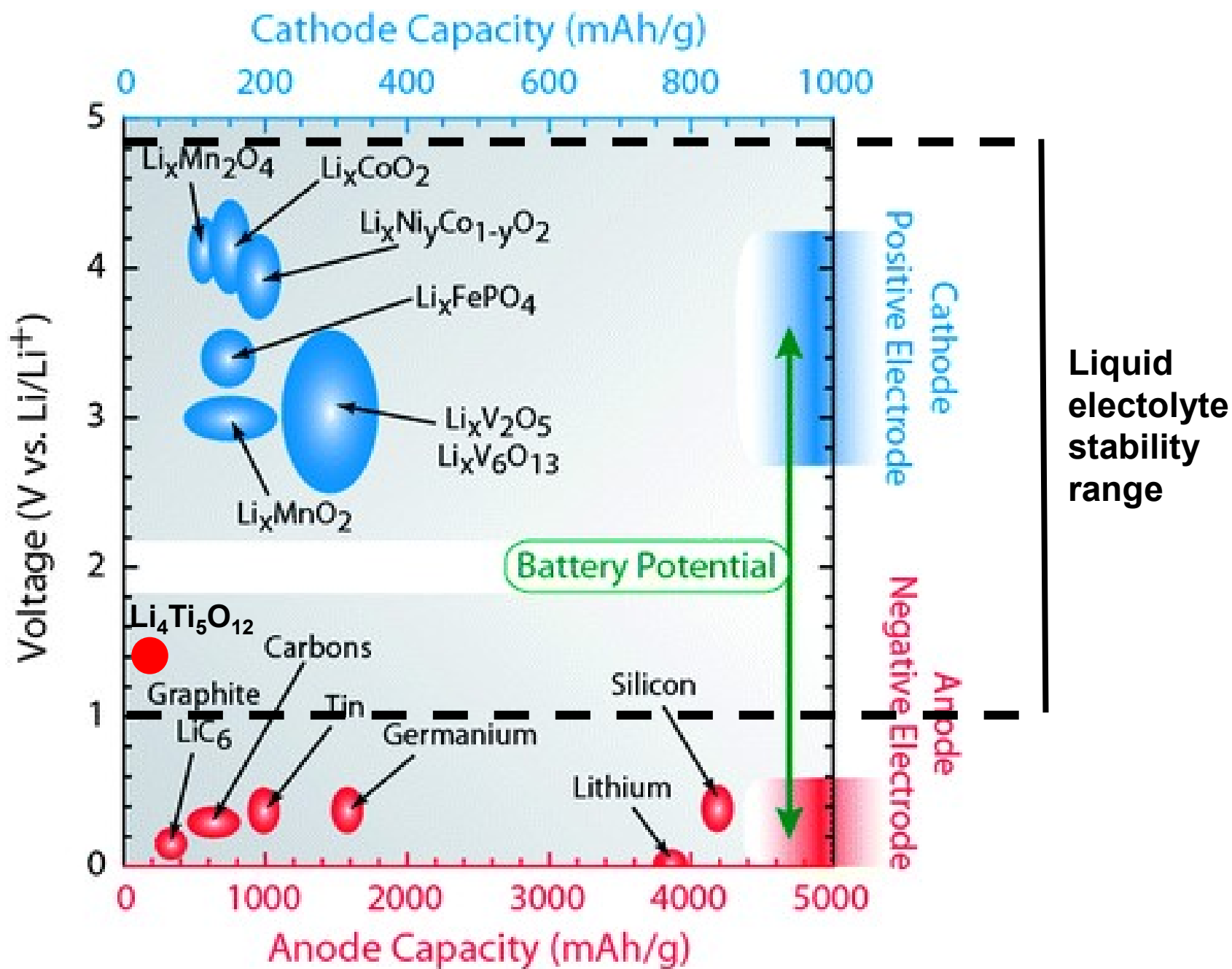
A!

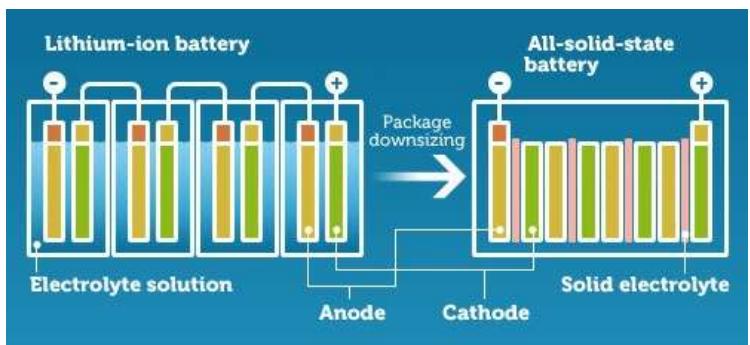
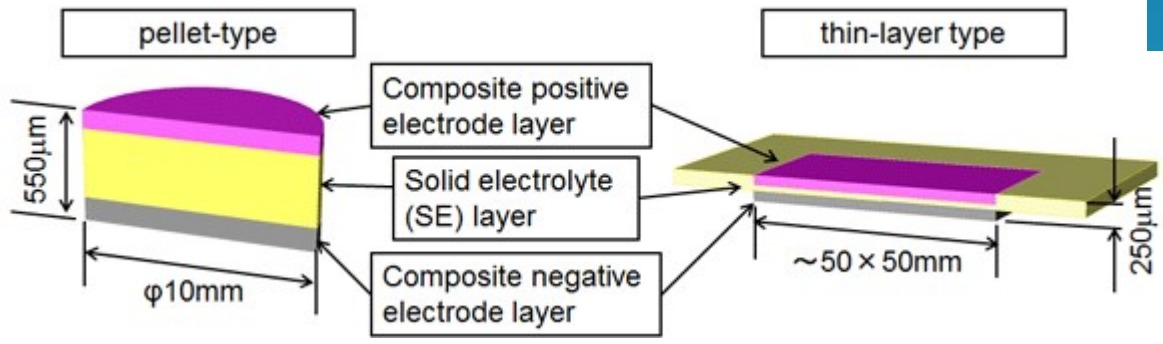
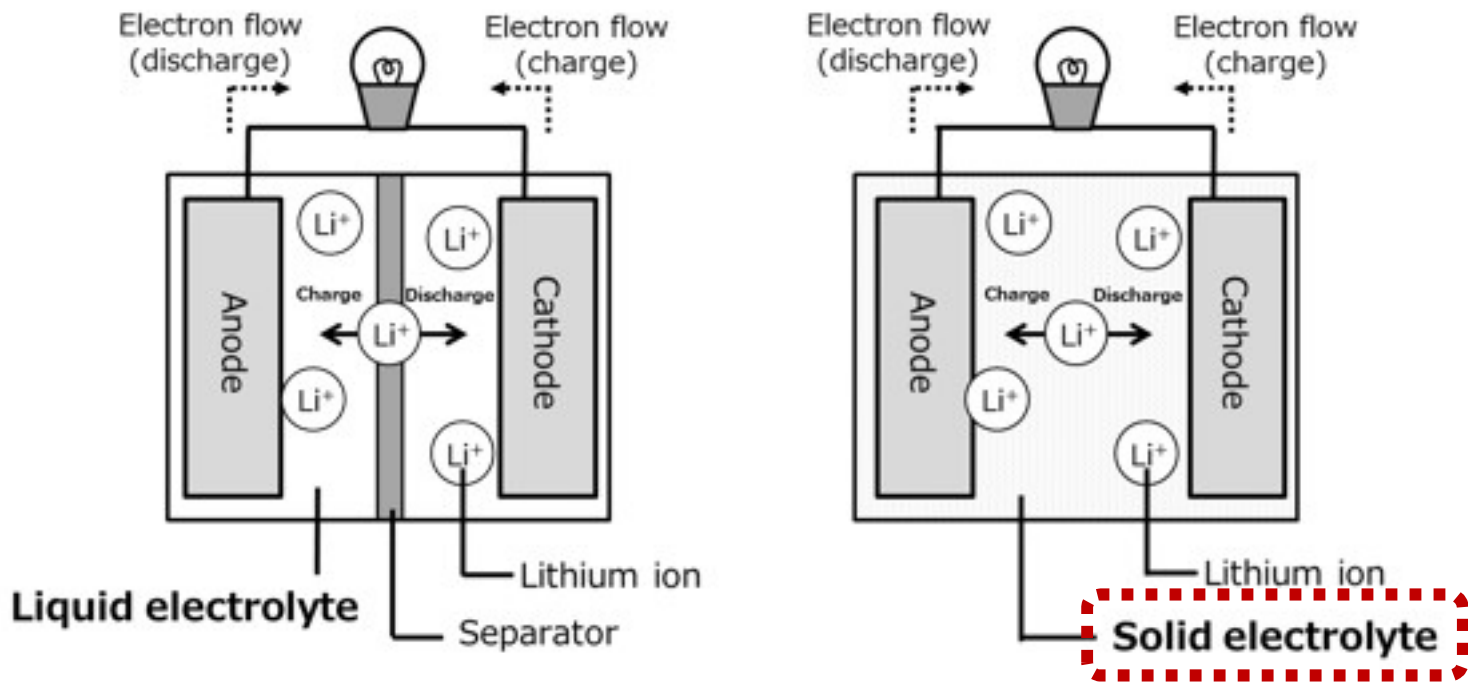
Helsingin Sanomat
23.10.2018

AKKUALA SAA UUTTA PUHTIA Saksalainen yhtiö Basf rakentaa Suomeen akkukemikaalitehtaan









Design principles for solid-state lithium superionic conductors

Nature Materials 14, 1026 (2015).

wet-cell

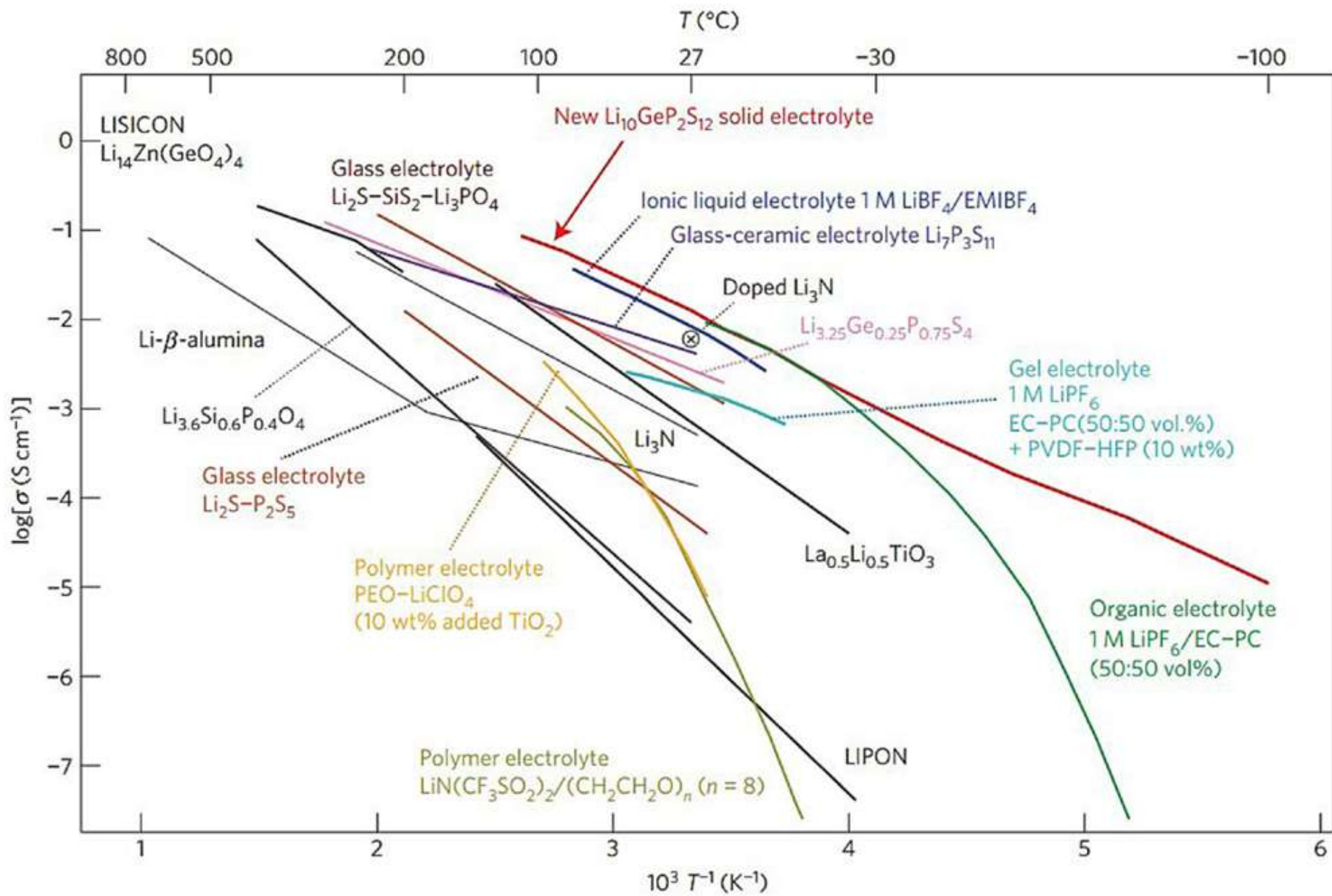
liquid

Lithium solid electrolytes can potentially address two key limitations of the organic electrolytes used in today's lithium-ion batteries, namely, their flammability and limited electrochemical stability. However, achieving a Li⁺ conductivity in the solid state comparable to existing liquid electrolytes ($> 1 \times 10^{-3} \text{ S cm}^{-1}$) is particularly challenging.

In this work, we reveal a fundamental relationship between anion packing and ionic transport in fast Li-conducting materials and expose the **desirable structural attributes of good Li-ion conductors**: We find that an underlying body-centred cubic-like anion framework, which allows direct **Li hops between adjacent tetrahedral sites is most desirable for achieving high ionic conductivity**, and that indeed this anion arrangement is present in several known fast Li-conducting materials and other fast ion conductors.

SOLID ELECTROLYTE:

ionically highly conducting but electronically insulating !



USE of SOLID ELECTROLYTE

PROS

- Simpler cell structure, no need for expensive separator
- Possibility to use Li metal anode
- High decomposition voltage
 - Possibility to use >5 V cathodes → Higher energy density
- Non-flammable → Safety
- Wider operation temperature range
- No risk for electrolyte leakage
- Simpler manufacturing process → Lower cost
- Components can be manufactured in air

CONS

- Higher density
- **Interface** between the solid electrolyte-electrode

(a)

Liquid electrolytes

Carbonate: EC, DEC, PC, DMC

Ether: DOL, DME

Fluorinated carbonate: F-EC, F-EPE

Ceramic electrolytes

LIPON

Li_3N

Perovskite: $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$

LISICON: $\text{Li}_{1.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$

Argyrodite: $\text{Li}_6\text{PS}_5\text{Cl}$

Garnet: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

NASICON: $\text{Na}_{2.7}\text{Zr}_{1.7}\text{La}_{0.3}\text{Si}_2\text{PO}_{12}$

Sulfide: $\text{Li}_2\text{S-P}_2\text{S}_5$, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$

Alumina: Na- β'' -alumina

Solid polymer electrolytes (SPEs)

PEO-based SPEs

Single ion conducting SPEs

Hybrid/composite electrolytes

Gel polymer electrolytes

High-salt electrolytes

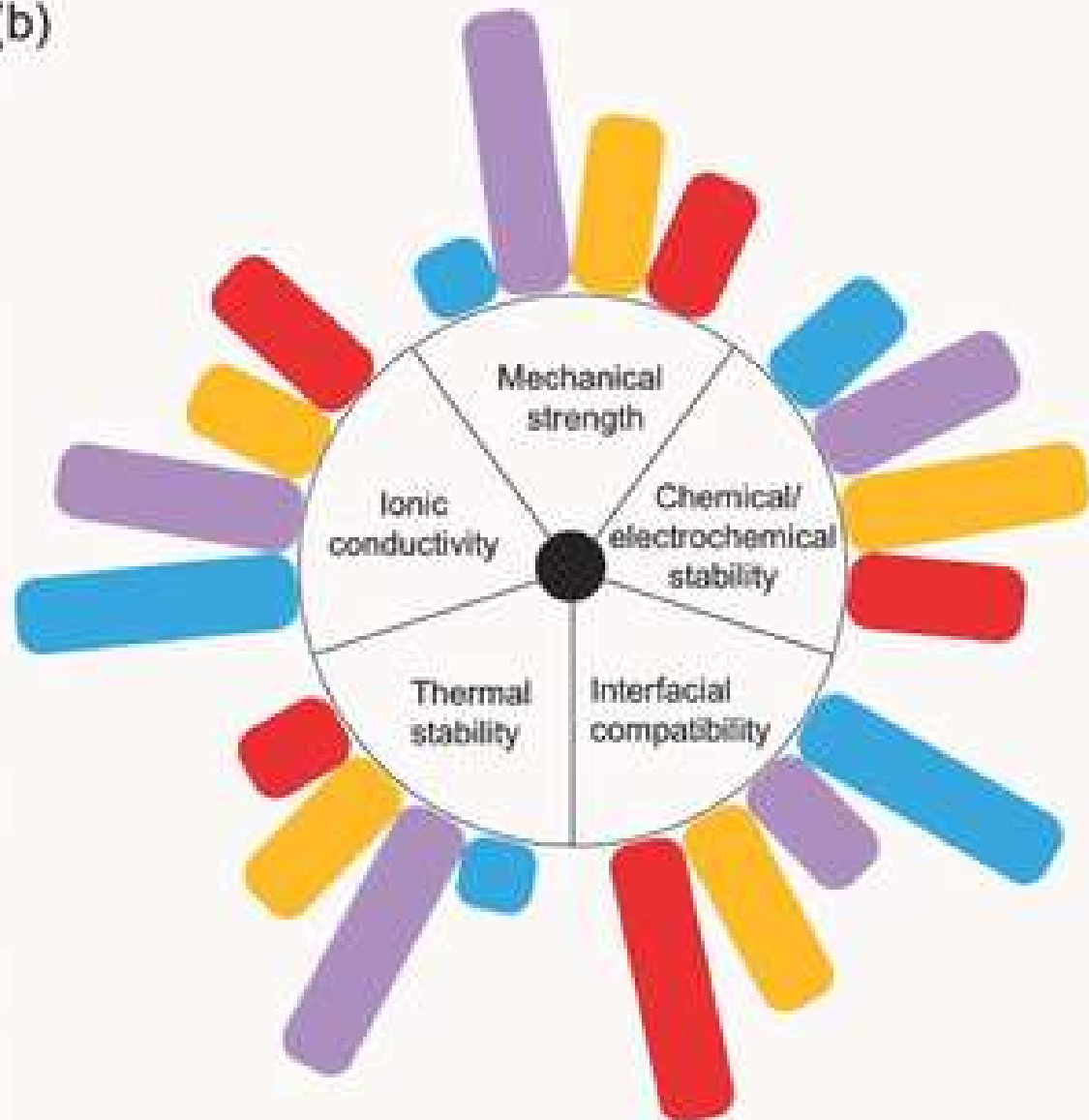
IL-nanoparticle hybrid electrolytes

SPEs with inorganic fillers

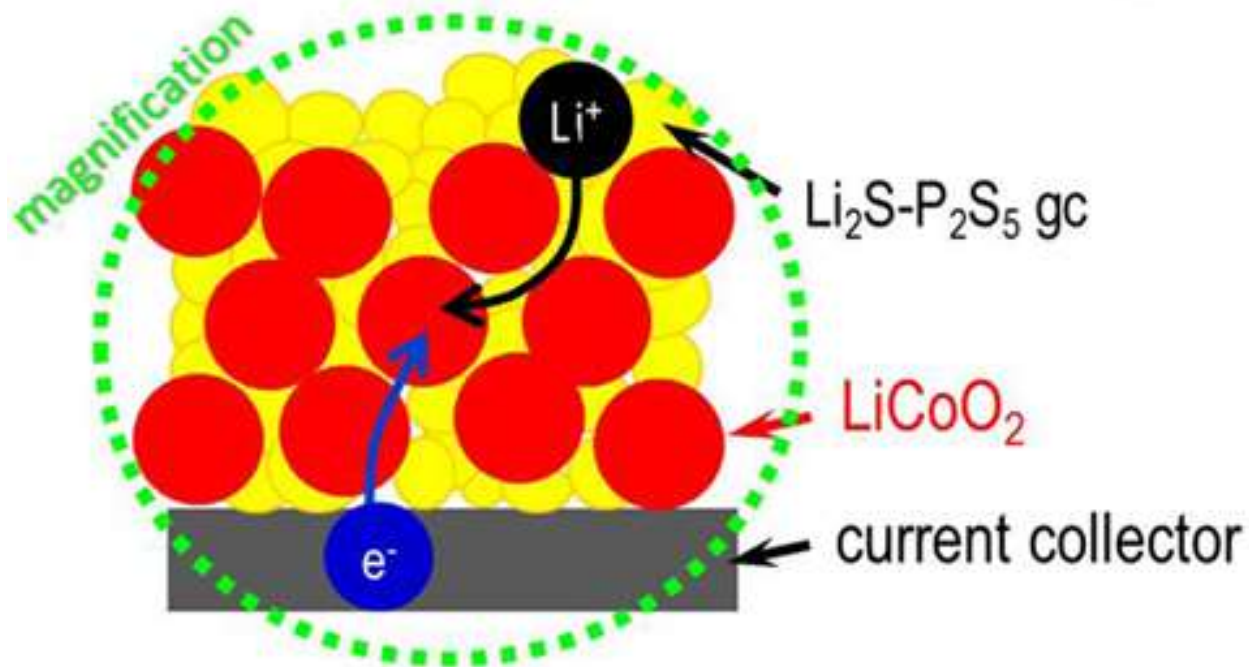
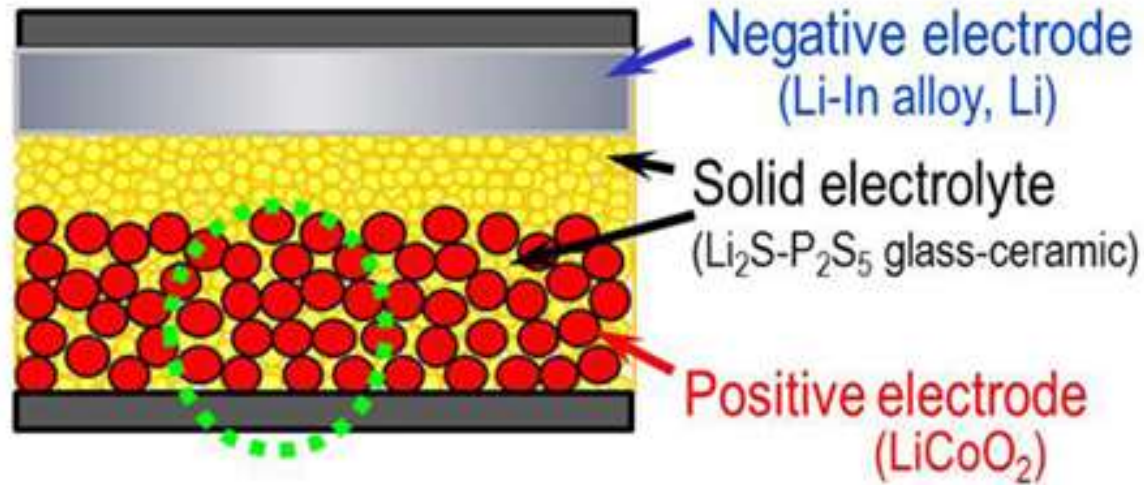
Polymer-nanoparticle hybrid electrolytes

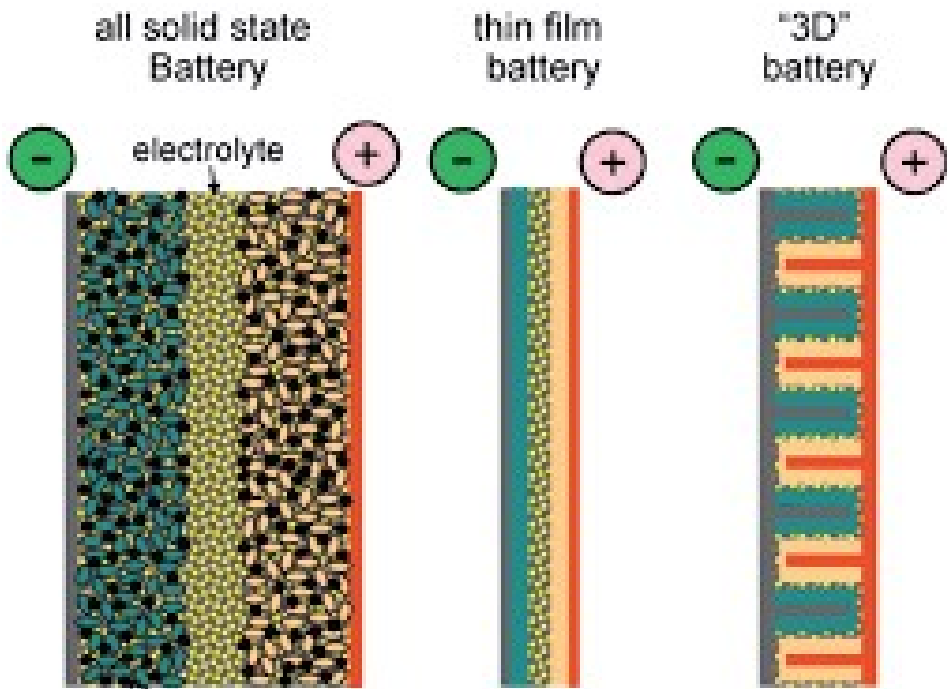
Polymer-ceramic composite electrolytes

(b)



Bulk-type battery

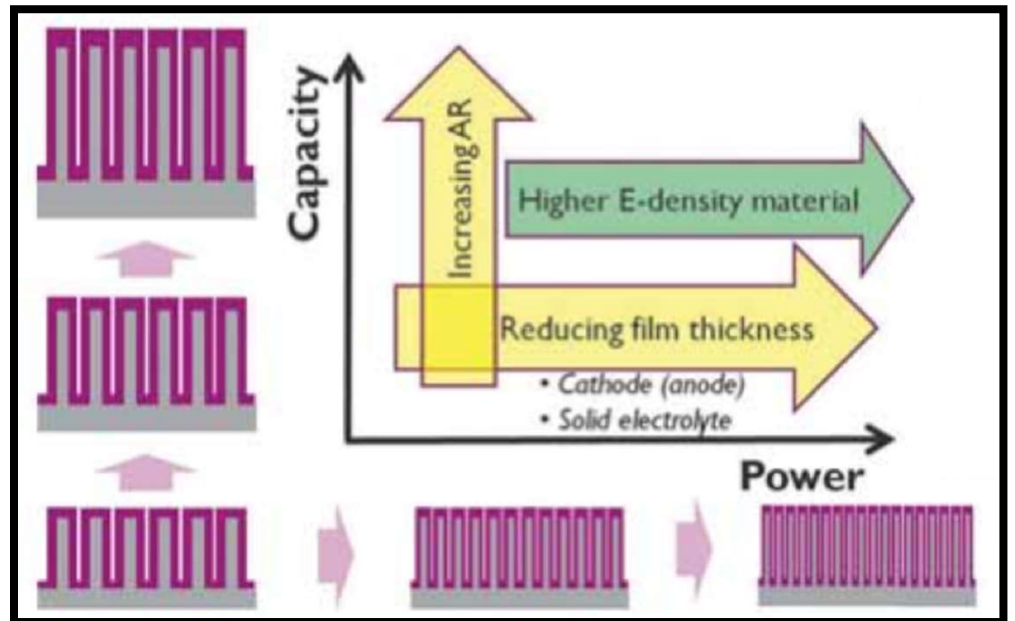




High energy density,
Low power density

Low energy density,
High power density

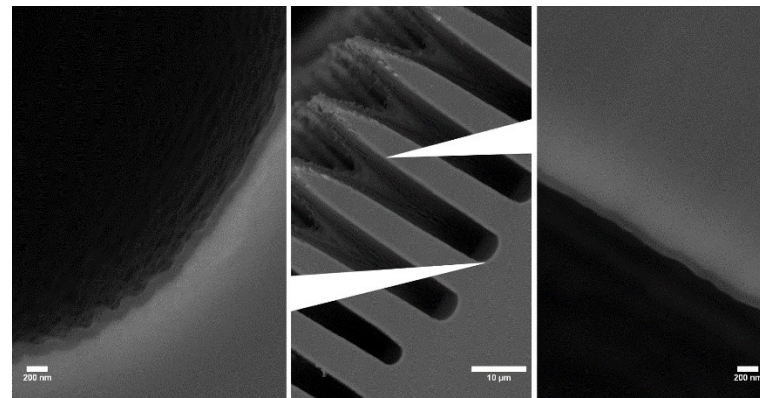
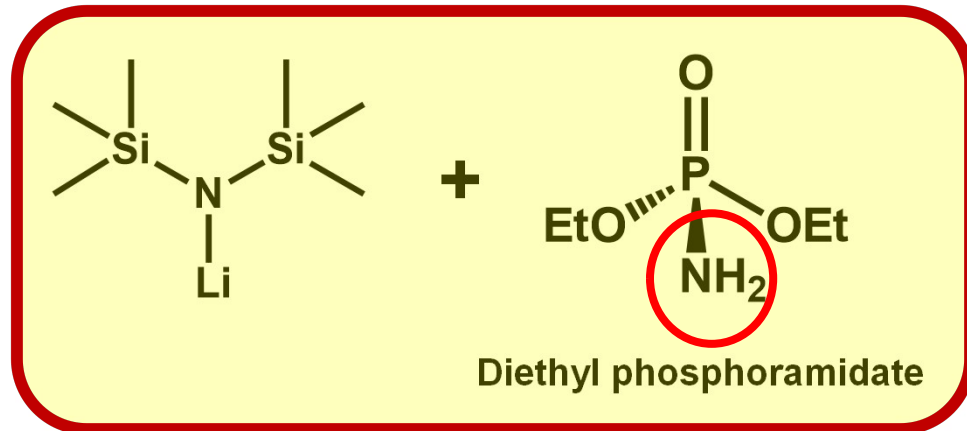
High energy density,
High power density



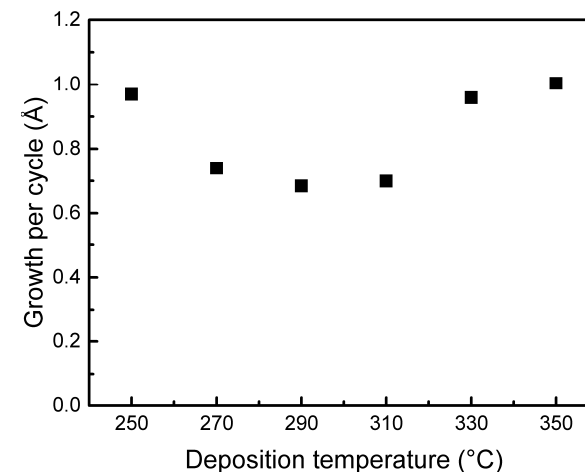
ALD OF LIPON



- LiPON: Lithium phosphorous oxynitride $\text{Li}_x\text{PO}_{3-y}\text{N}_z$
- **Amorphous** intermediate between crystalline $\text{LiPO}_3 \rightarrow \text{Li}_2\text{PO}_2\text{N}$
- (Most) promising solid-state electrolyte for thin-film Li-ion microbattery
- Ionic conductivity greatly enhanced by N doping (up to $10^{-6} \text{ S cm}^{-1}$)



	RBS-NRA	RT ionic cond.
290 °C	$\text{Li}_{0.90}\text{PO}_{3-y}\text{N}_{0.55}$	$0.9 \times 10^{-7} \text{ S cm}^{-1}$
330 °C	$\text{Li}_{0.94}\text{PO}_{3-y}\text{N}_{0.60}$	$6.6 \times 10^{-7} \text{ S cm}^{-1}$

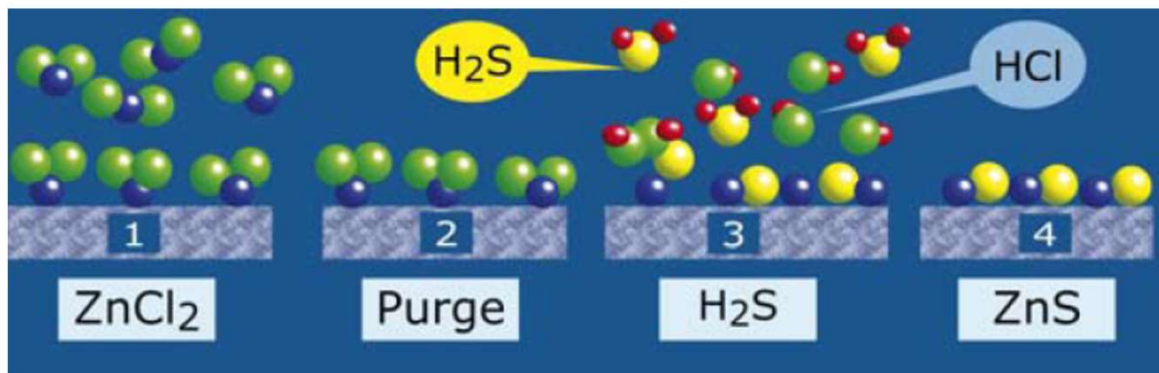
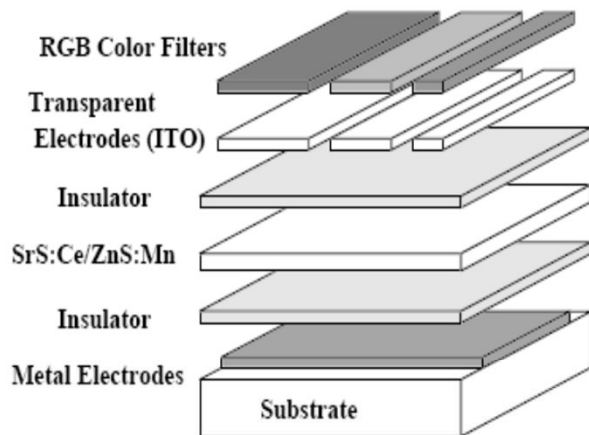


M. Nisula, Y. Shindo, H. Koga & M. Karppinen, *Chem. Mater.* **27**, 6987 (2015).

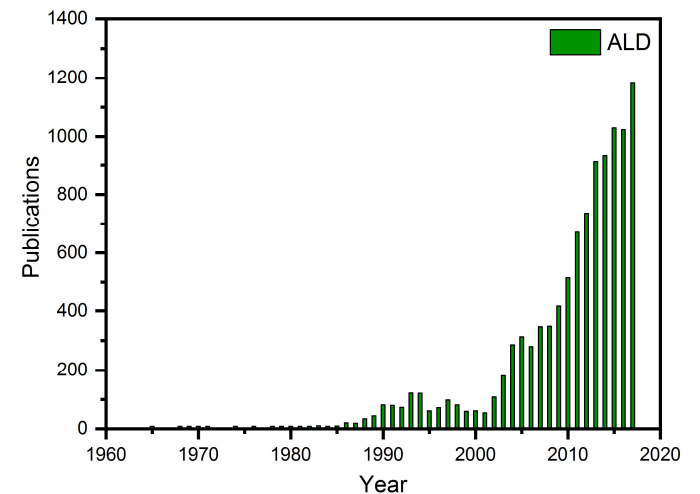
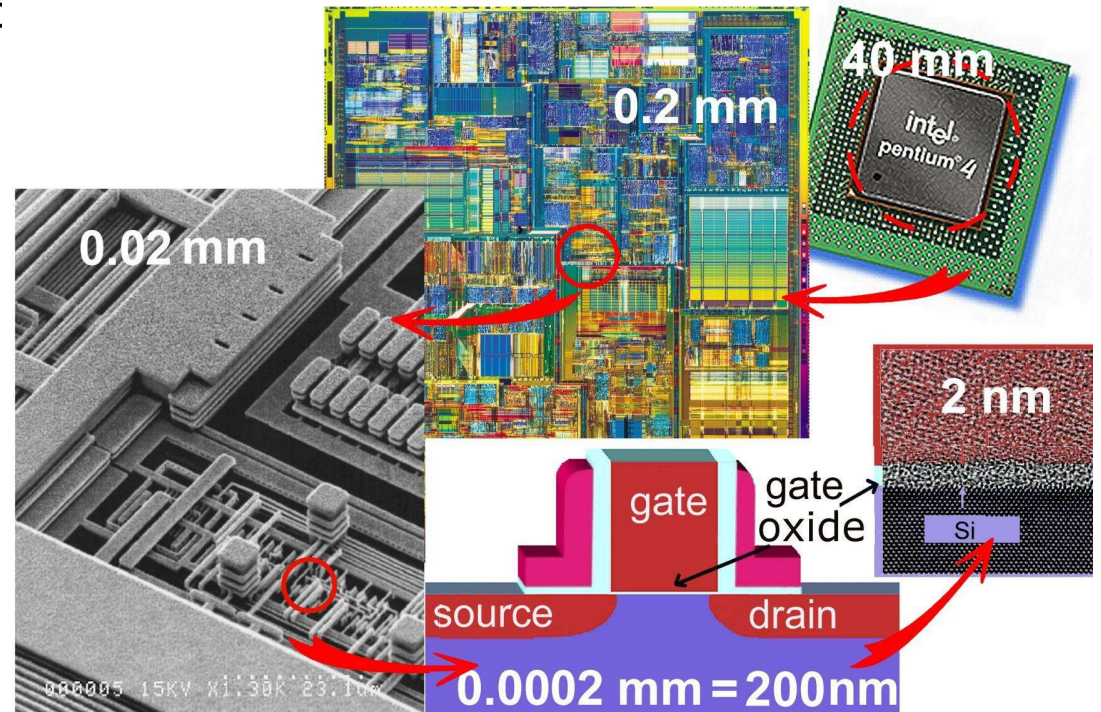
Atomic Layer Deposition (ALD)

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

Electroluminescent display



MOSFET transistor



**Kalevala Koru
(Finland):**

**- traditional
silver
jewelry**



**Beneq (Finland):
- Al₂O₃ coating by ALD**



BEFORE

uncoated



AFTER TARNISHING TEST

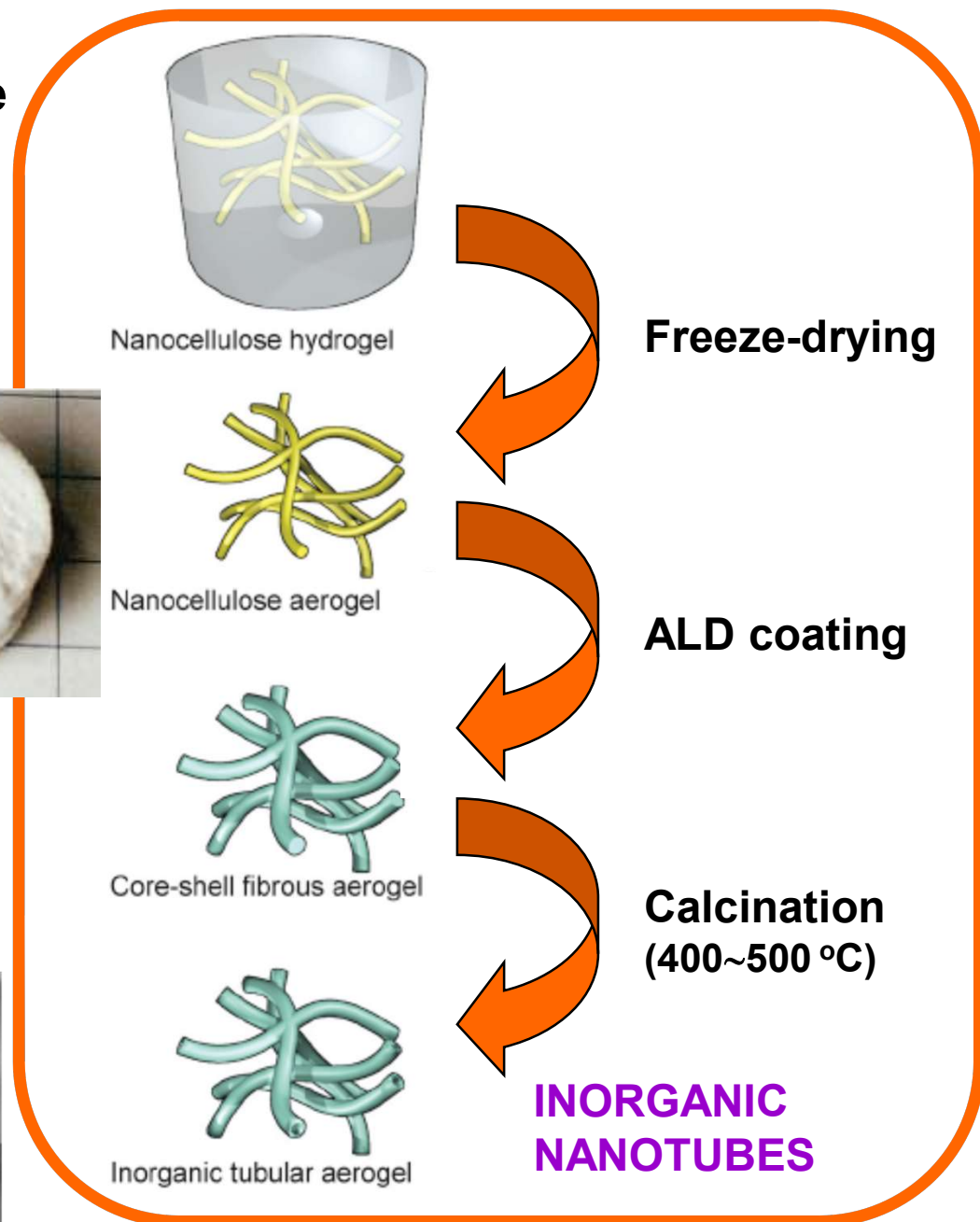
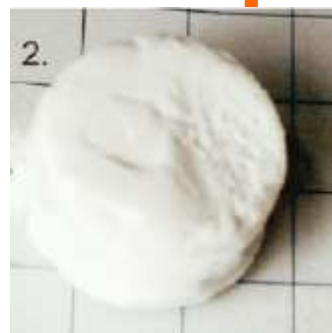
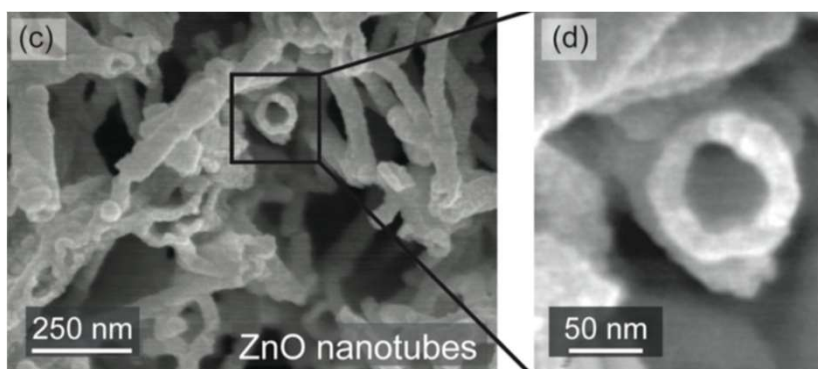
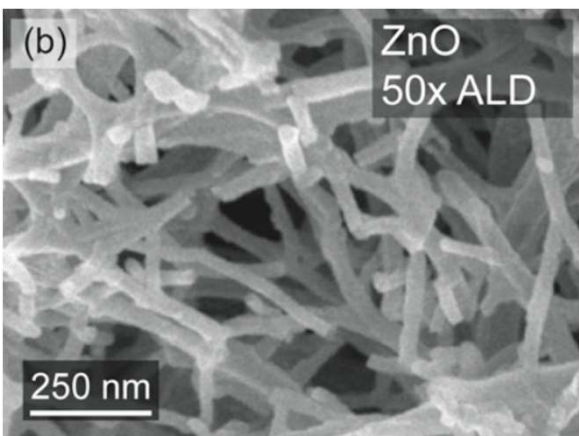
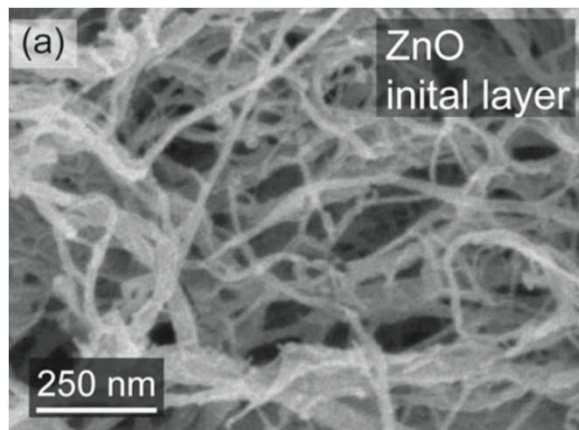
Al₂O₃-coated



**Dense, pinhole-free
& highly **conformal**
ALD-Al₂O₃-nanocoating
efficiently protects
silver jewelries
from tarnishing**

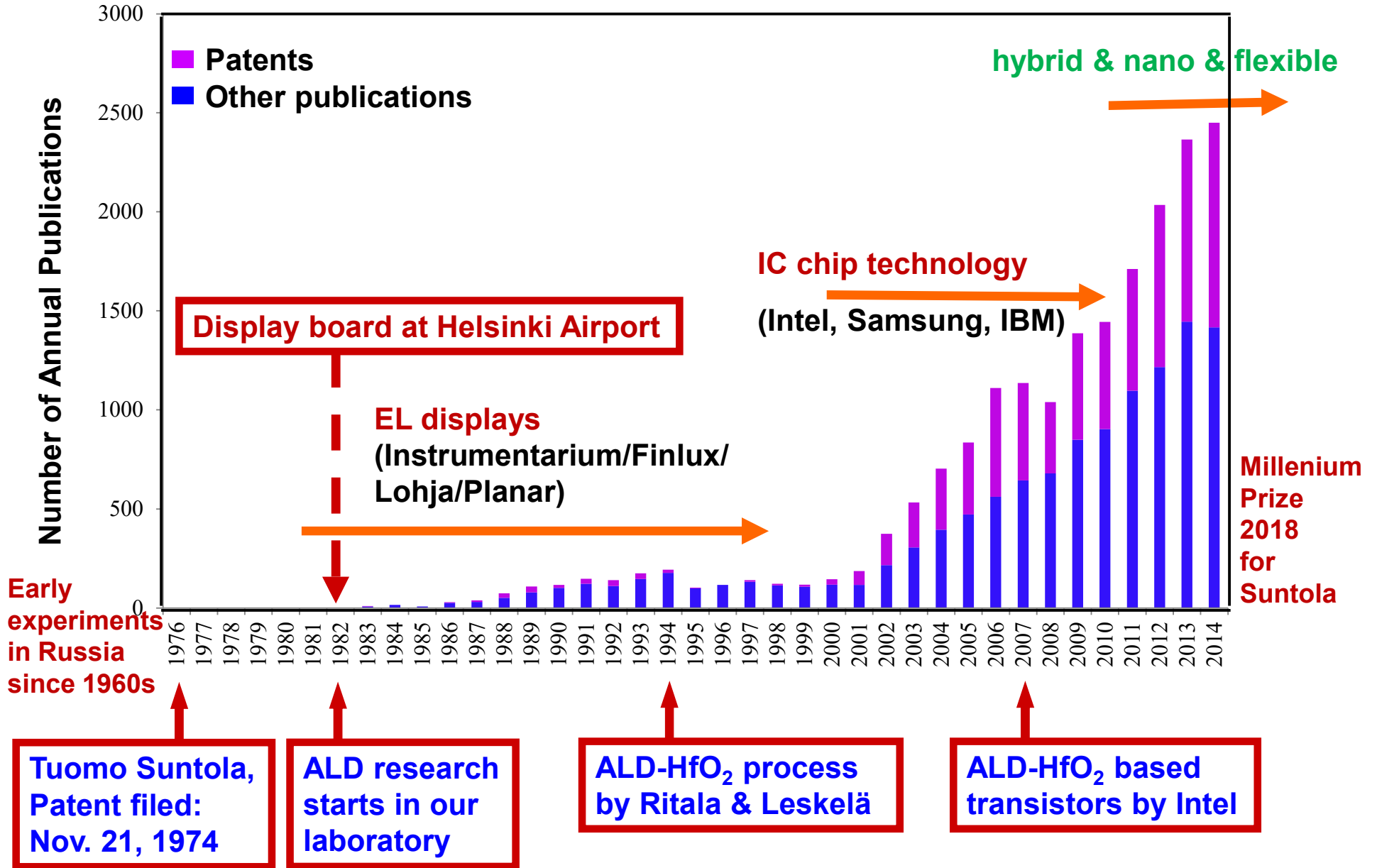
NANOSTRUCTURING by ALD

- nanocellulose aerogel template



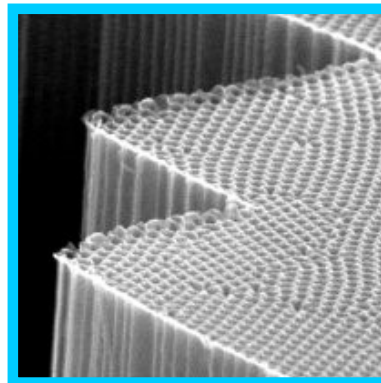
J.T. Korhonen, J. Malm, M. Karppinen,
O. Ikkala & R.H.A. Ras, *ACS Nano* 5, 1967 (2011).

Some historical steps of ALD Technology



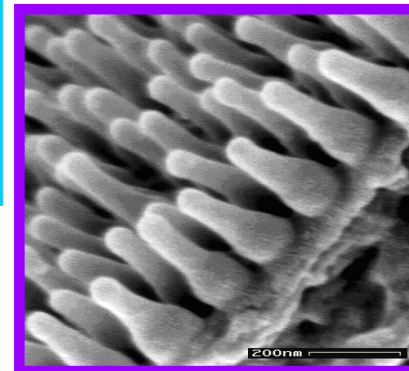
ADVANTAGES of ALD

- Relatively inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Large area uniformity
- Easy doping
- Excellent conformality



ELECTRONICS

NANO



BIO

- Low deposition temperature
- Gentle deposition process
- Organic/polymer films
- Inorganic/organic hybrid materials

NEW



Allen Hill, Tony Cass and Graham Davis made the crucial discovery which led to the development of a unique electronic blood glucose sensor now used by millions of diabetics worldwide.

16 July 2012



National Chemical Landmark

Dorothy Crowfoot Hodgkin
OM, FRS
(1910-1994)

Led pioneering work in this building from 1956-1972 and elsewhere in Oxford on the structures of antibiotics, vitamins and proteins including penicillin, vitamin B12 and insulin, using X-ray diffraction techniques for which she received the Nobel Prize in Chemistry in 1964.

6 May 2014

RSC
Advancing the
Chemical Sciences

National Chemical Landmark

**Inorganic Chemistry
Laboratory**

where in 1980, John B. Goodenough with Koichi Mizushima, Philip C. Jones and Philip J. Wiseman identified the cathode material that enabled development of the rechargeable lithium-ion battery. This breakthrough ushered in the age of portable electronic devices.

30 November 2010