# Functional Inorganic Materials
# Fall 2022

Tuesdays: 12.15 - 14.00 (U8)
Thursdays: 10.15 - 12.00 (Ke1)

| # | Date | Who | Topic |
|---|---|---|---|
| 1 | Mon 5.9. | Maarit | Introduction + Materials design consepts |
| 2 | Thu 8.9. | Antti | Introduction + Computational materials design |
| 3 | Tue 13.9. | Maarit | Superconductivity: High-$T_c$ superconducting Cu oxides |
| 4 | Thu 15.9. | Maarit | Magnetic (oxide) materials |
| 5 | Tue 20.9. | Maarit | Ionic conductivity (Oxygen): SOFC & Oxygen storage |
| **6** | **Thu 22.9.** | **Maarit** | **Ionic conductivity (Lithium & Proton): Li-ion battery** |
| 7 | Tue 27.9. | Antti | Thermal conductivity |
| 8 | Thu 29.9. | Antti | Thermoelectricity |
| 9 | Tue 4.10. | Antti | Piezoelectricity |
| 10 | Thu 6.10. | Antti | Pyroelectricity and ferroelectricity |
| 11 | Tue 11.10. | Maarit | Hybrid materials |
| 12 | Thu 13.10. | Antti | Luminescent and optically active materials |

# LECTURE 6: Ionic conductivity: Lithium & Proton

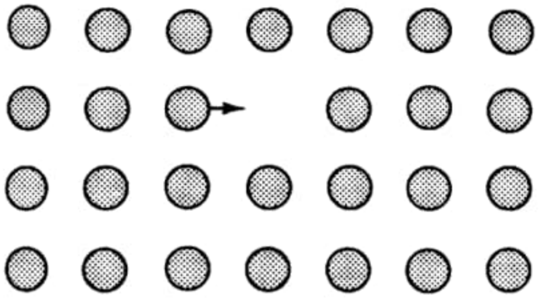
- **Proton conductivity**
- Water/proton absorption & Oxide/hydroxide substitution
- **Lithium ion conductivity**
- Li-ion battery: material issues
- Solid-state electrolytes & Thin-film microbattery

# LECTURE EXERCISE 6

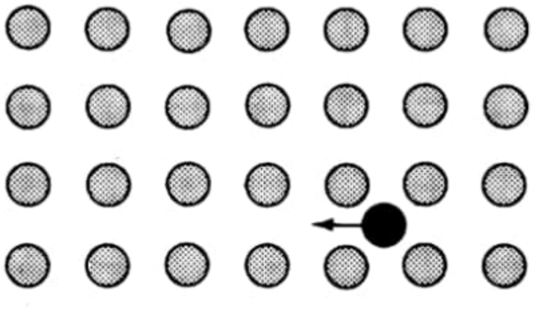
1. Which useful function could be anticipated for an oxygen-deficient oxide material with a tendency to absorb water? Explain !
2. Explain why a layered crystal structure is beneficial for the Li-ion battery electrode material.
3. What happens to (a) structure, (b) electrical conductivity, and (c) ) 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

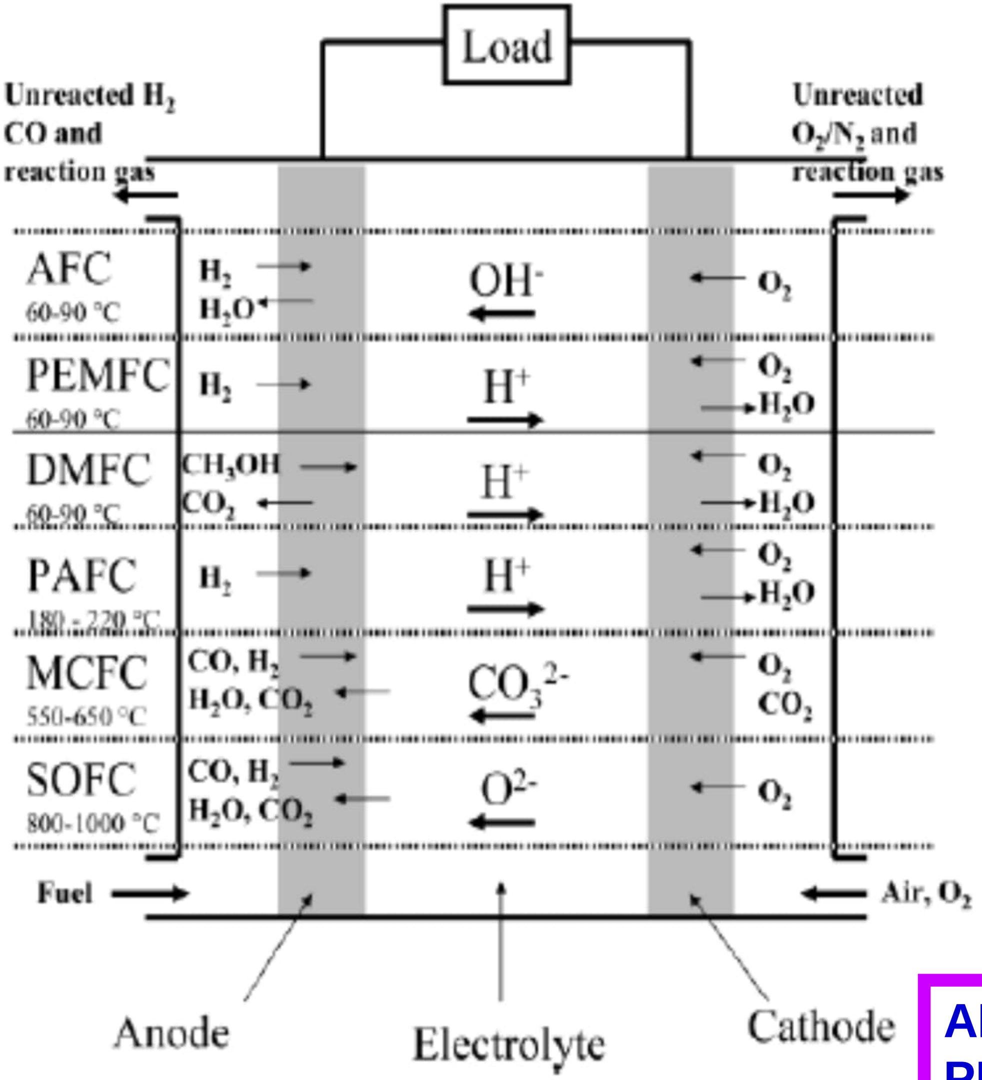


mobile interstitial

**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**

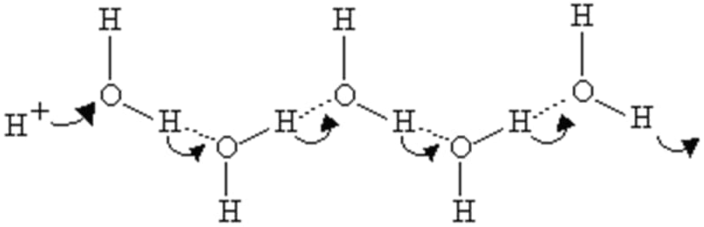
  **- sensors**

  **- 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*.): $LaYO_3$, $SrZrO_3$**

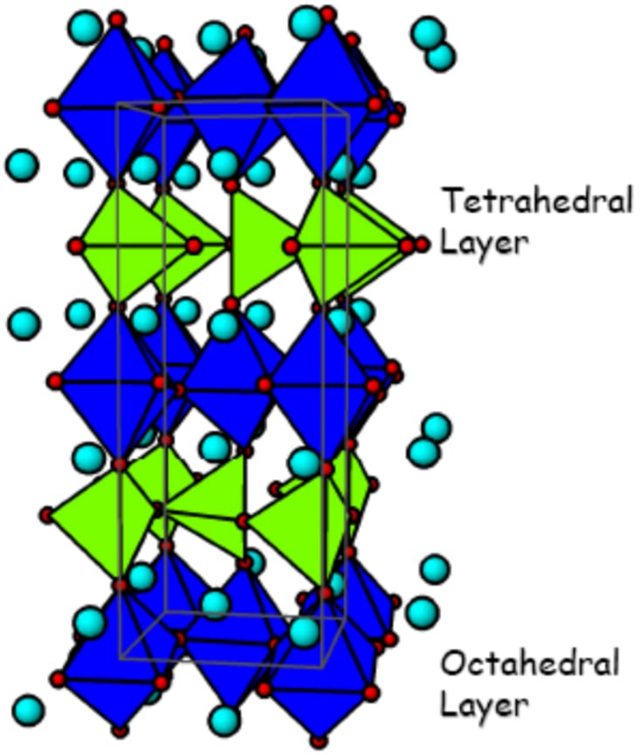
  **- Present perovskite prototypes: $SrCeO_3$, $BaCeO_3$**

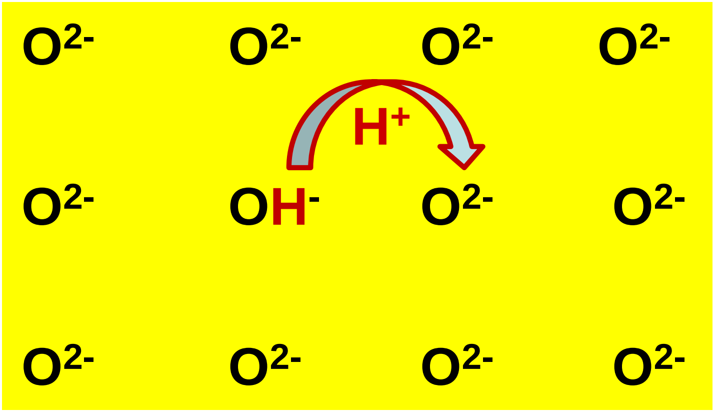
  **- Some Ruddlesden-Popper phases**

  **- 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 $^{o}$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**





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

$H^{+}$

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

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

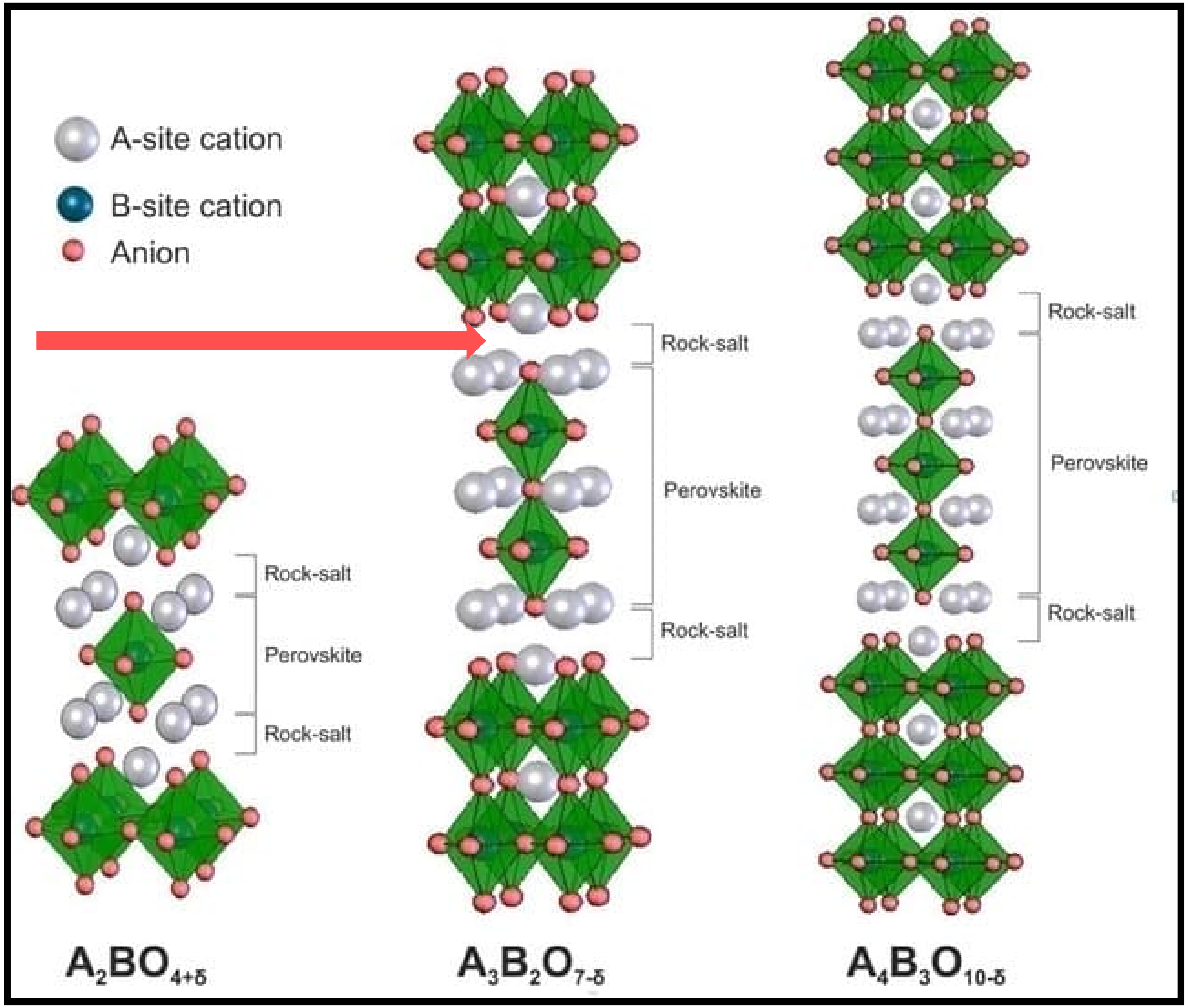
# WATER/PROTON ABSORPTION OF OXIDES

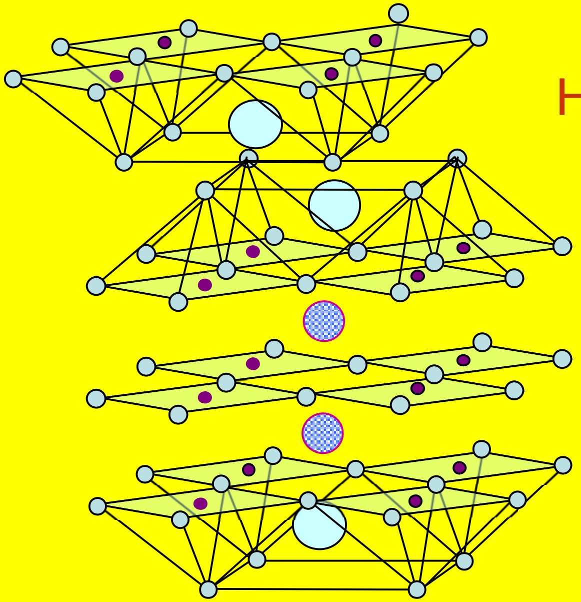
- **Affinity of oxide ion $O^{2-}$ for $H^+$ is great → in water solutions it immediately captures a proton from the $H_2O$ solvent molecule**
- **Also in solid state $O^{2-}$ ions tend to combine with protons**
- **Proton is very small → when it combines with oxygen the resultant $OH^-$ group is almost 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.

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





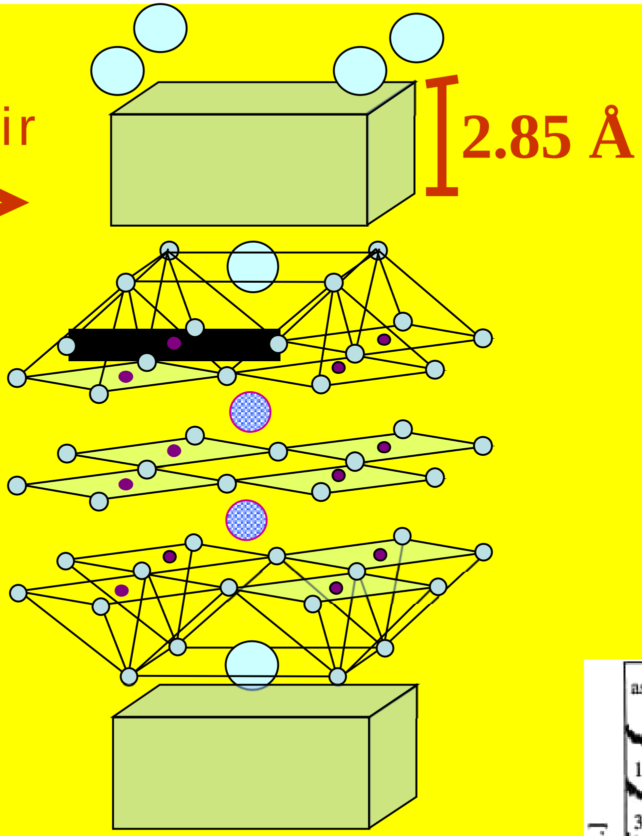
$Ba_2Ca_2Cu_3O_8$

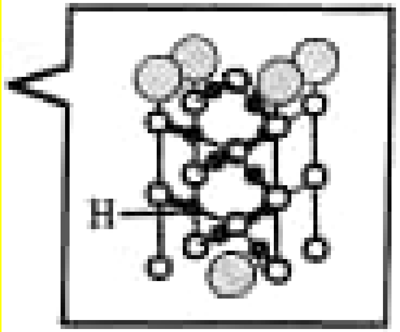
$T_c \approx 126$ K

⇧

High-Pressure Synthesis

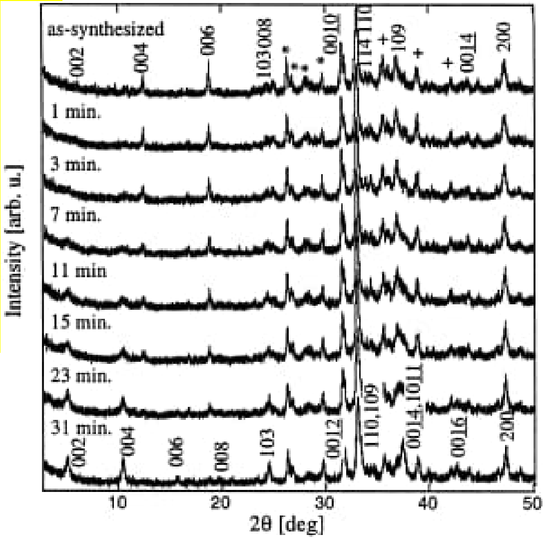
Humid Air ⇨





“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

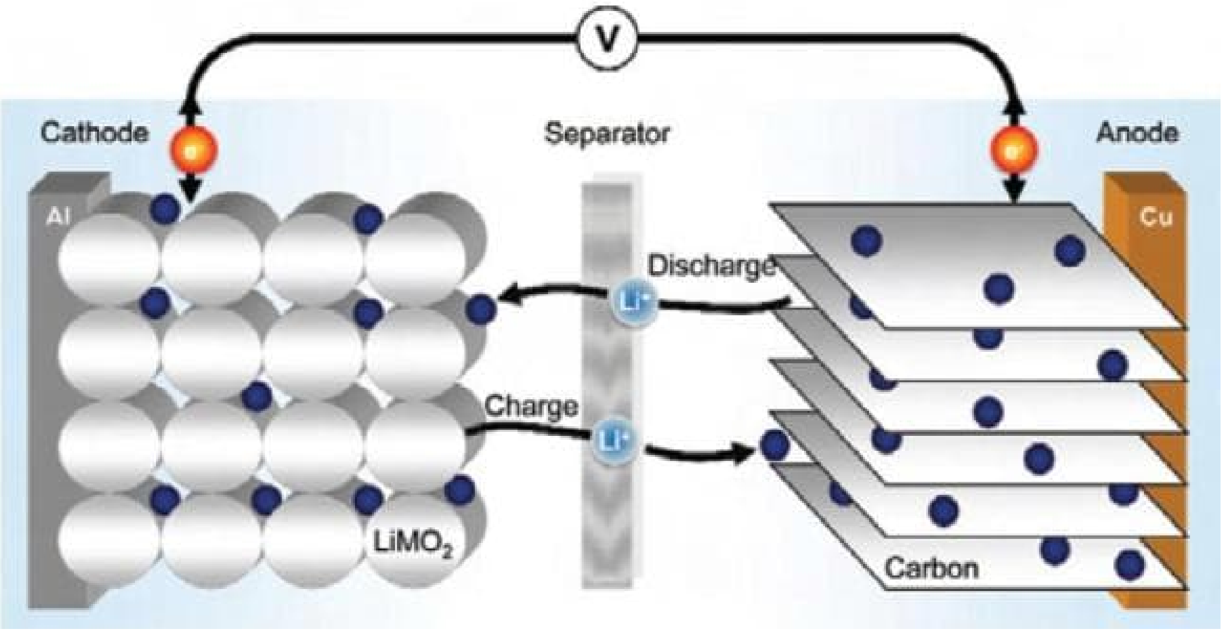
- **Lithium: lightest, smallest and largest electrochemical**
- **Li-ion battery: Light-weight, high-voltage, and large-energy-density**
- **Cell phones, laptops, wearable electronics, electric cars and vehicles, energy storage related to solar cells and wind power, etc.**

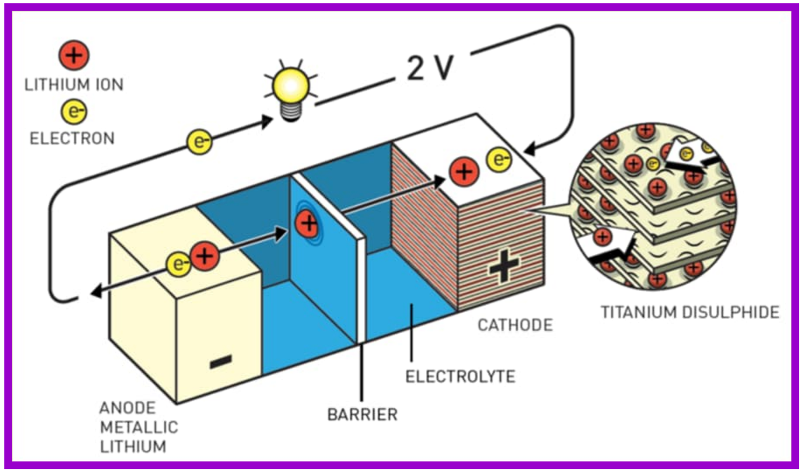
**Sony 1991**

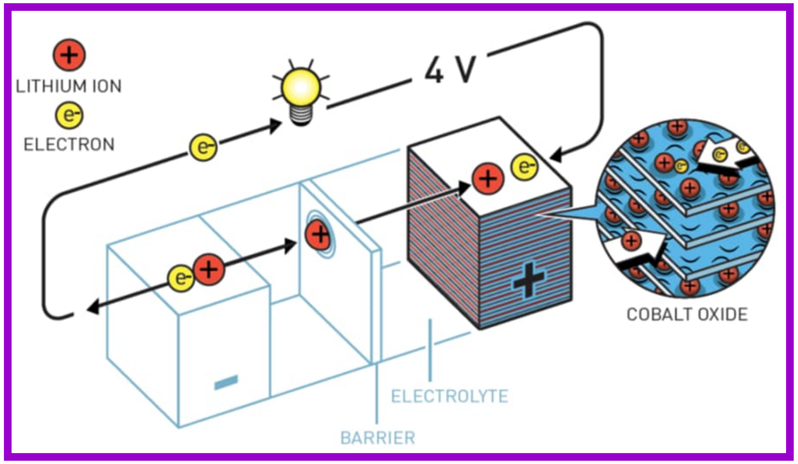
**First commercial Li-ion battery**

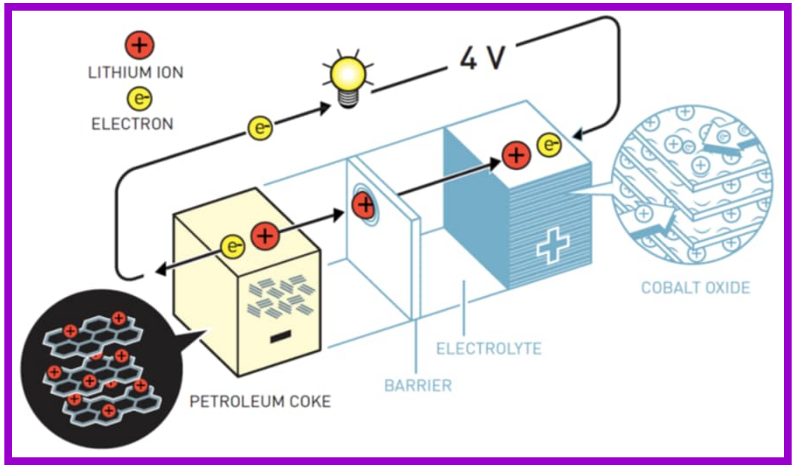
## ”WET CELL”

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









# Chemistry Nobel 2019

Stanley Whittingham (UK):

- Exxon: $TiS_2$ cathode 1976

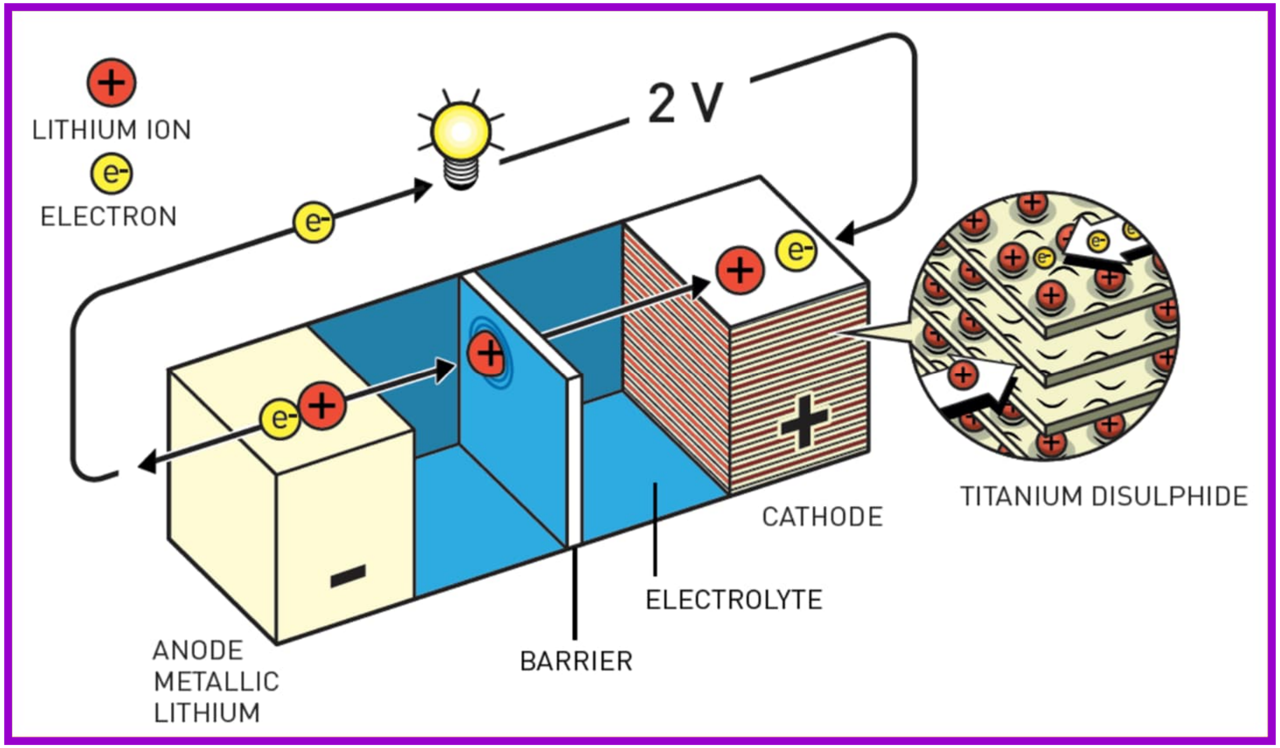
John Goodenough (US):

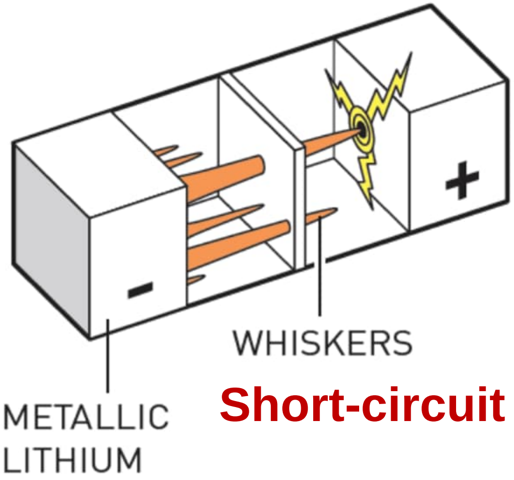
- Univ. Oxford: $LiCoO_2$ cathode 1980

Akira Yoshino (Jpn):

- Asahi Kasei: carbon-based anode 1985

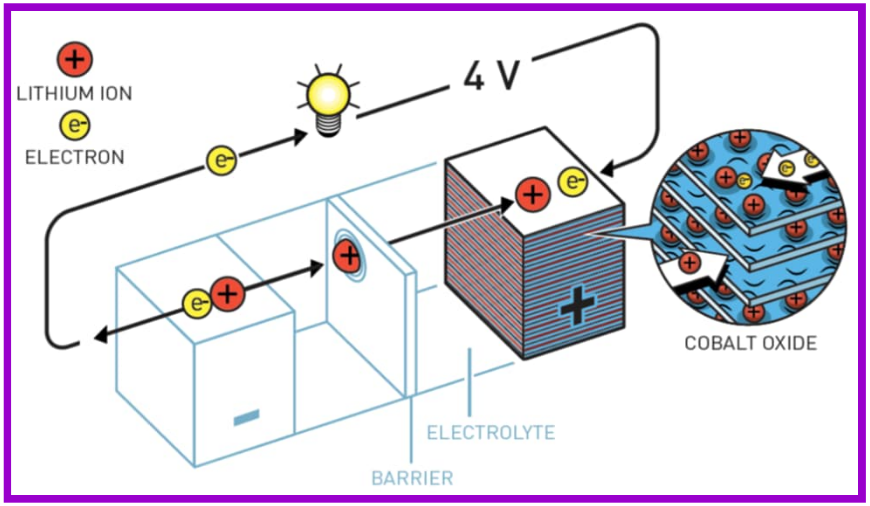
Commercialization: Sony 1991

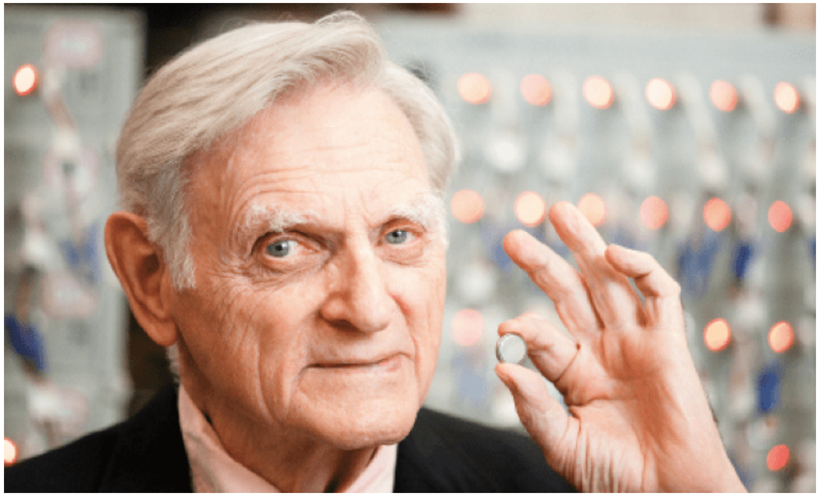




# Stanley Whittingham (born 1941 UK)

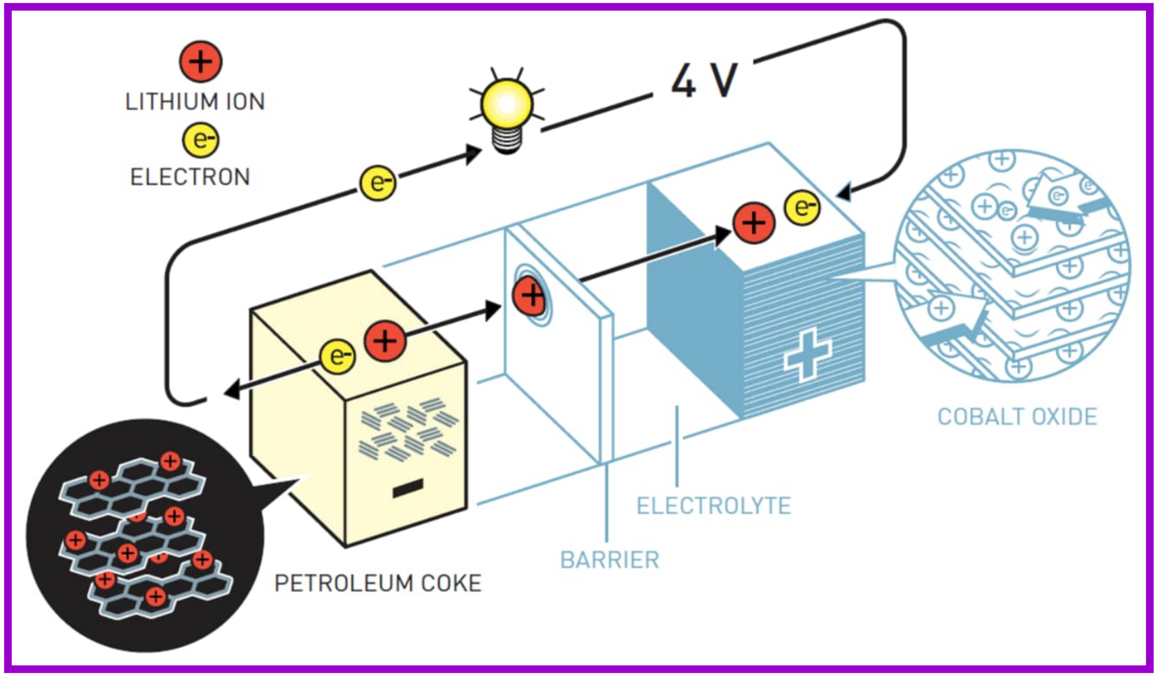
- **PhD 1968 (Oxford University, Chemistry)**
- **Postdoc 1968-1972 (Stanford University)**
- **Exxon 1972-1984:** **- new superconductors → $TaS_2$**
  - **- $TiS_2$ cathode 1976** (Li anode & $LiPF_6$ electrolyte)
- **Prof. 1988 – now (Binghamton University, New York)**
- **Scopus (337 publ; 21 000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

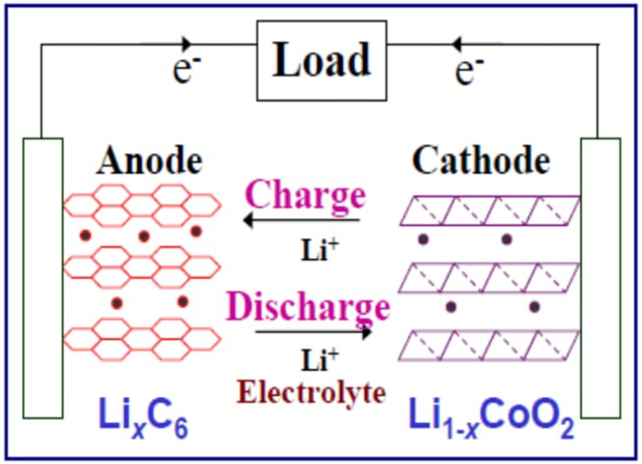


# Akira Yoshino (born 1948 Japan)

- **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)**

# 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:** $(-)\ C \mid LiPF_6\text{-}(EC+DEC) \mid LiCoO_2\ (+)$

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

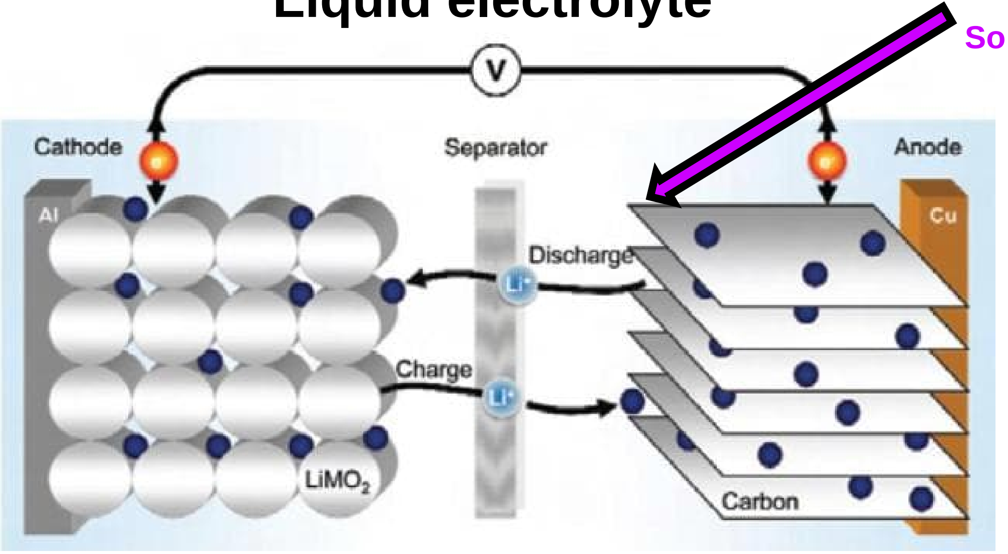
**Anode:** $6C + xLi^+ + xe^- \underset{D}{\overset{C}{\rightleftarrows}} Li_xC_6$

**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**

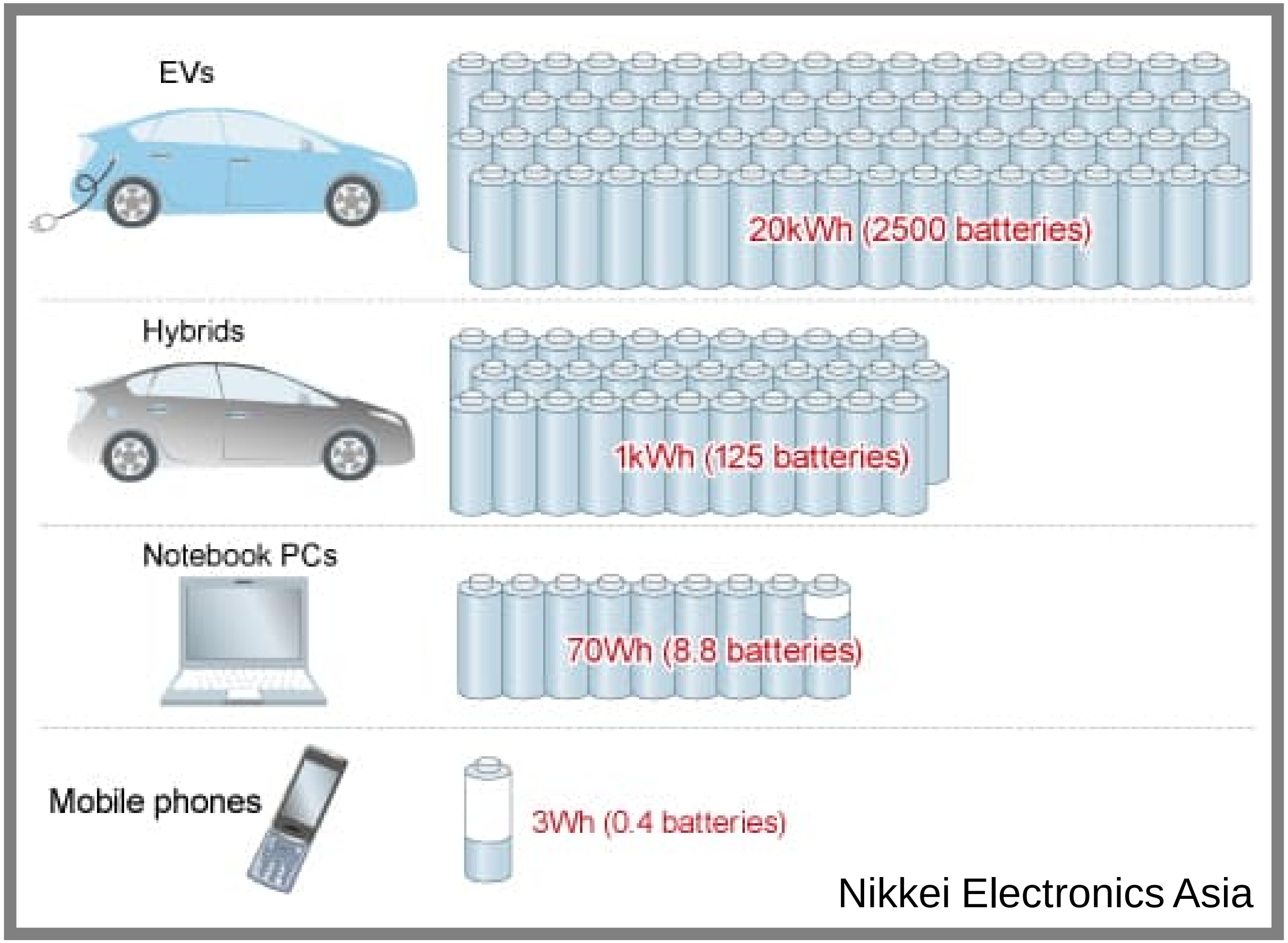
Solid-Electrolyte-Interphase

$LiCoO_2$

Graphite

# ELECTRIC CAR BATTERY SYSTEM

## 10 000 times larger energy capacity compared to cell phone



Nikkei Electronics Asia

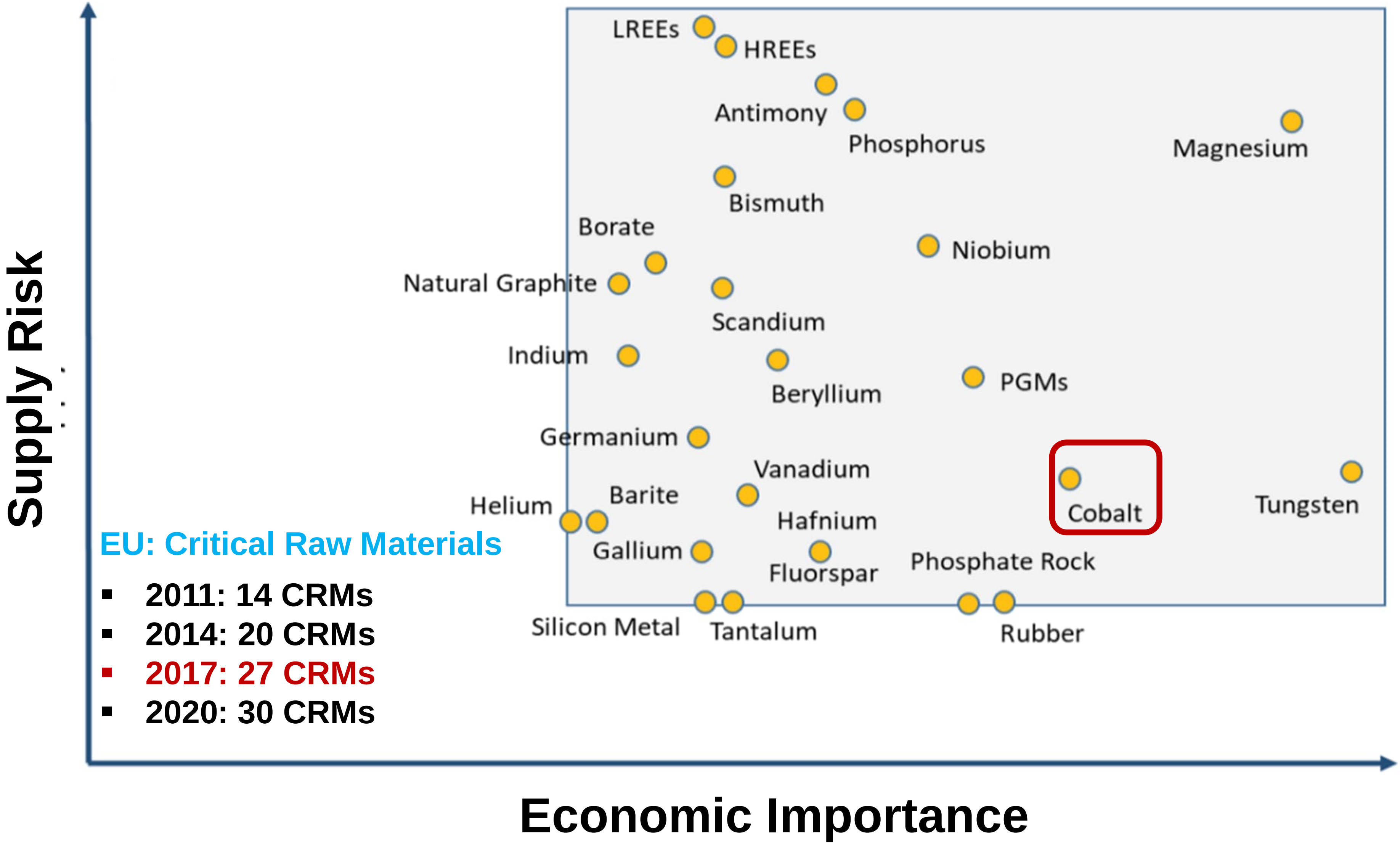
**Car battery 600 kg**

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

**Cell phone 130 g**

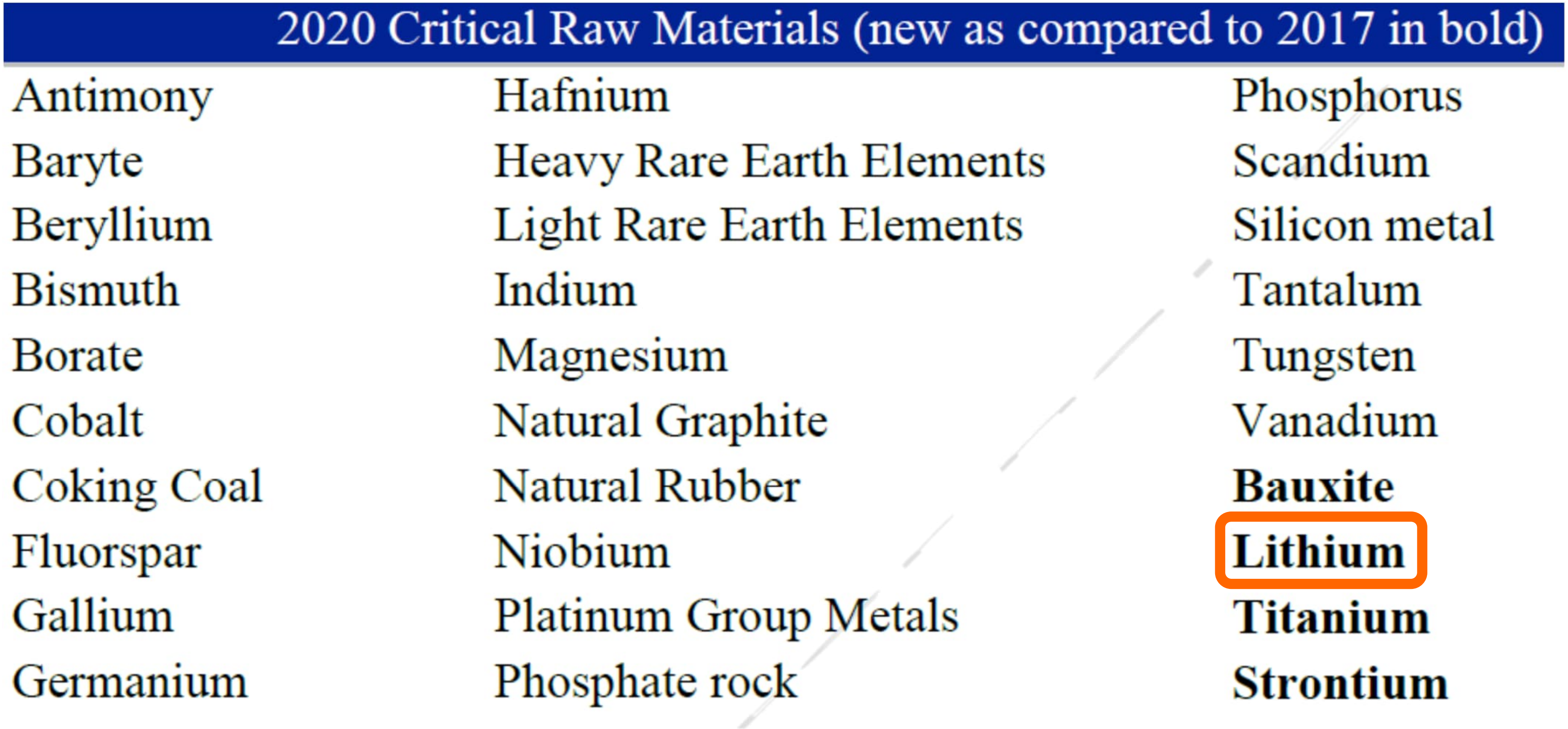
- 3 g Li
- 7 g Co
- 3 g Ni

# EU Critical Raw Materials (CRM)



**EU: Critical Raw Materials**

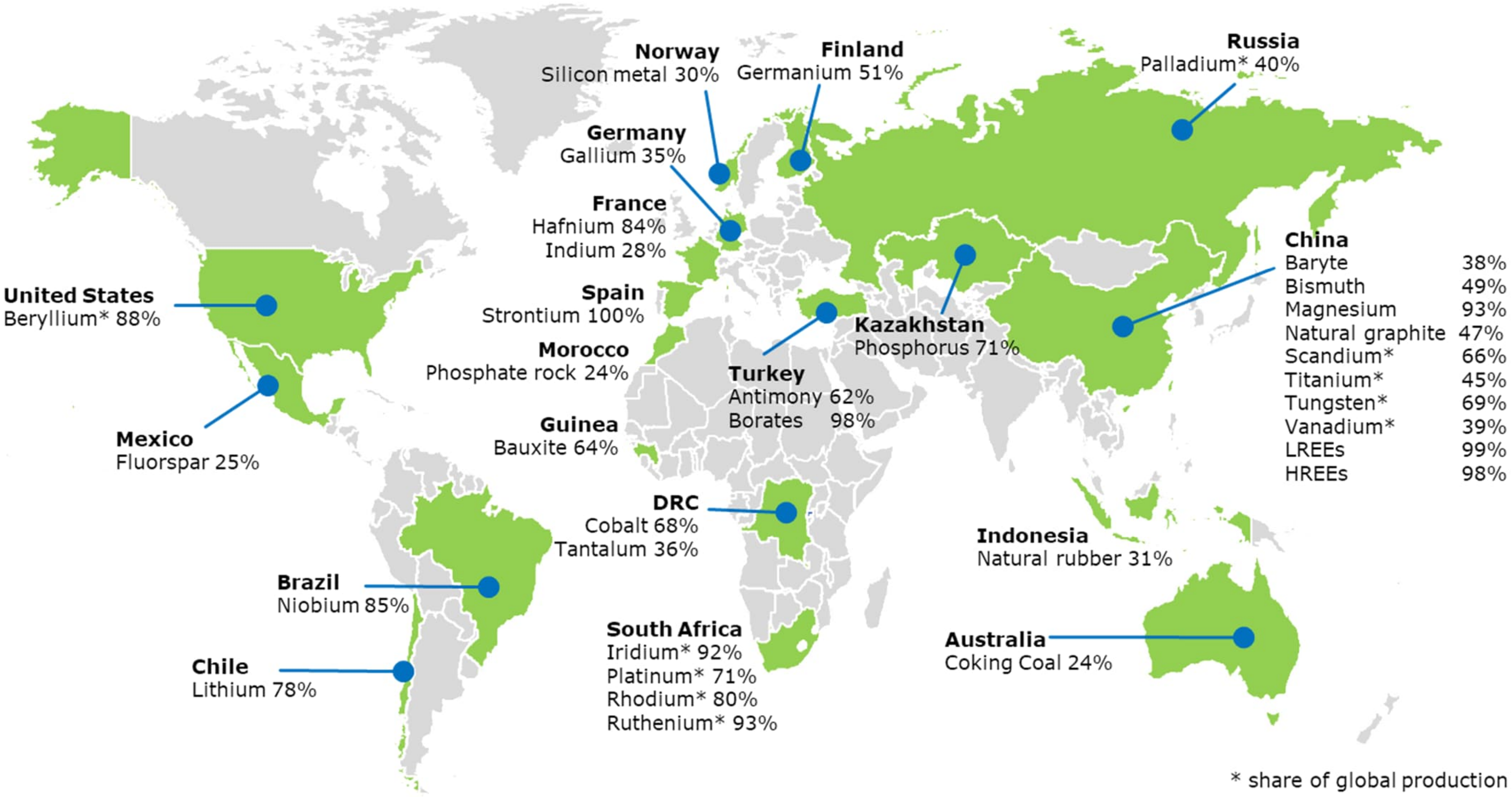
- **2011: 14 CRMs**
- **2014: 20 CRMs**
- **2017: 27 CRMs**
- **2020: 30 CRMs**



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 ?



**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

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

**(mostly in Chinese ownership)**

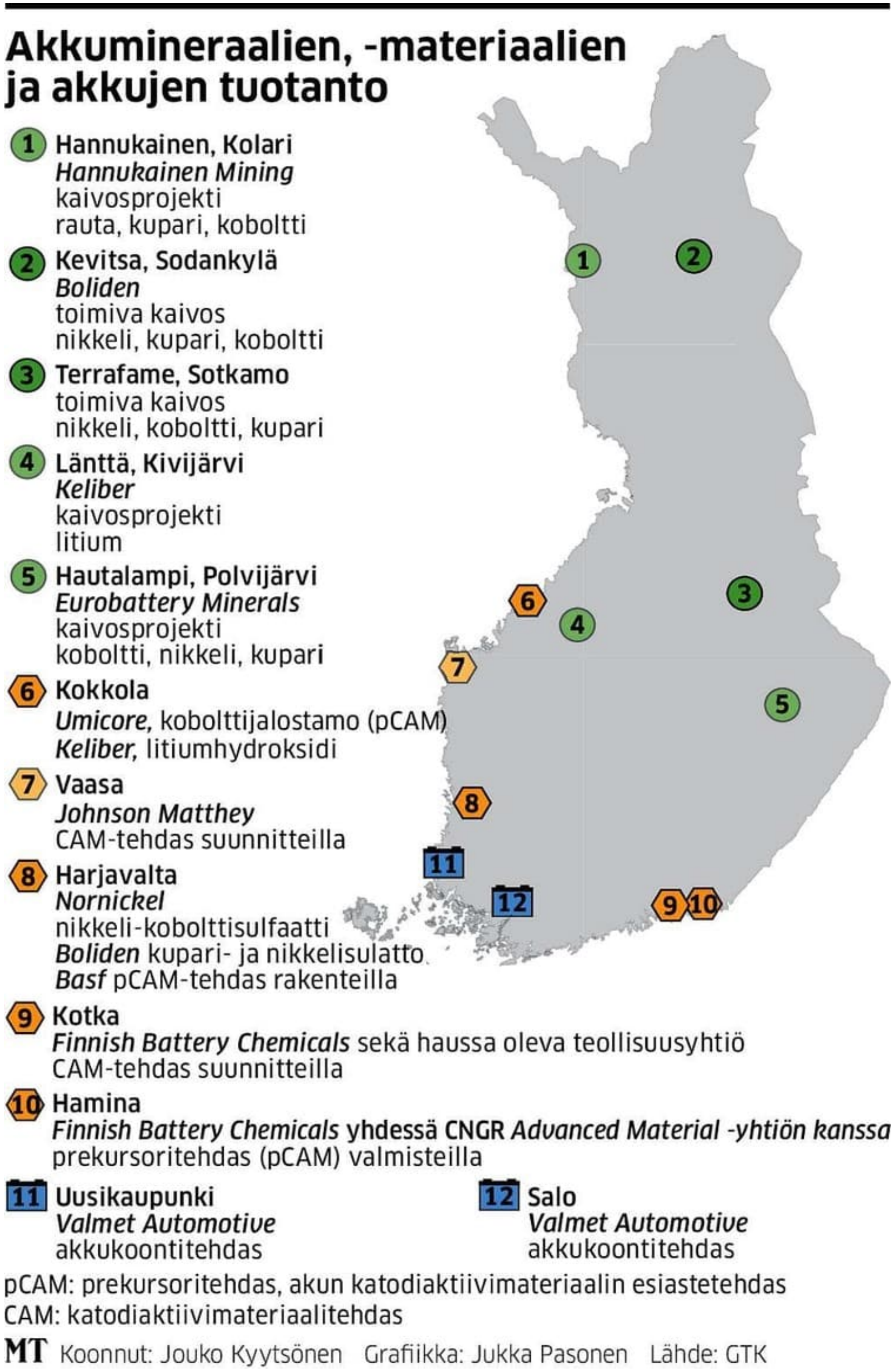
Cobolt mining place in Congo close
to Kasulo. Valokuvat: Siddharth Kara

# 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

**Prof. Mari Lundström**
**Hydrometallurgy**

Battery metals from recycled batteries

**Prof. Maarit Karppinen**
**Material chemistry**

# RESEARCH COLLA-BORATION

New active materials from recycled metals

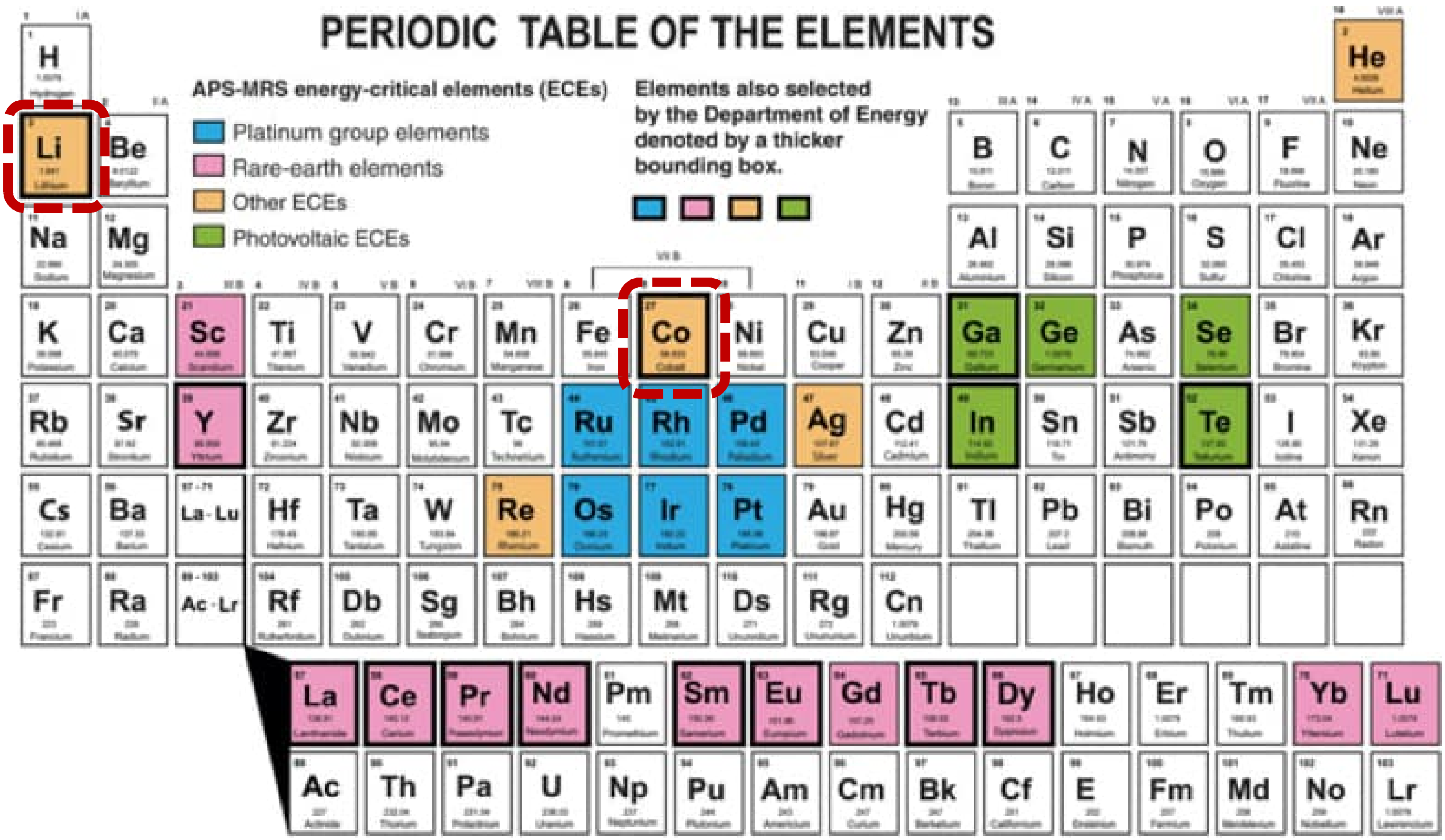
**Prof. Tanja Kallio**
**Electrochemistry**

Batteries from new materials

## Aalto CHEM School Battery Research Groups

C. Peng, K. Lahtinen, E. Medina, P. Kauranen, M. Karppinen, T. Kallio, B.P. Wilson and M. Lundström, Role of impurity copper in Li-ion battery recycling to LiCoO$_2$ cathode materials, *Journal of Power Sources* **450**, 227630 (2020).

# ENERGY CRITICAL ELEMENTS



PERIODIC TABLE OF THE ELEMENTS

APS-MRS energy-critical elements (ECEs)

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

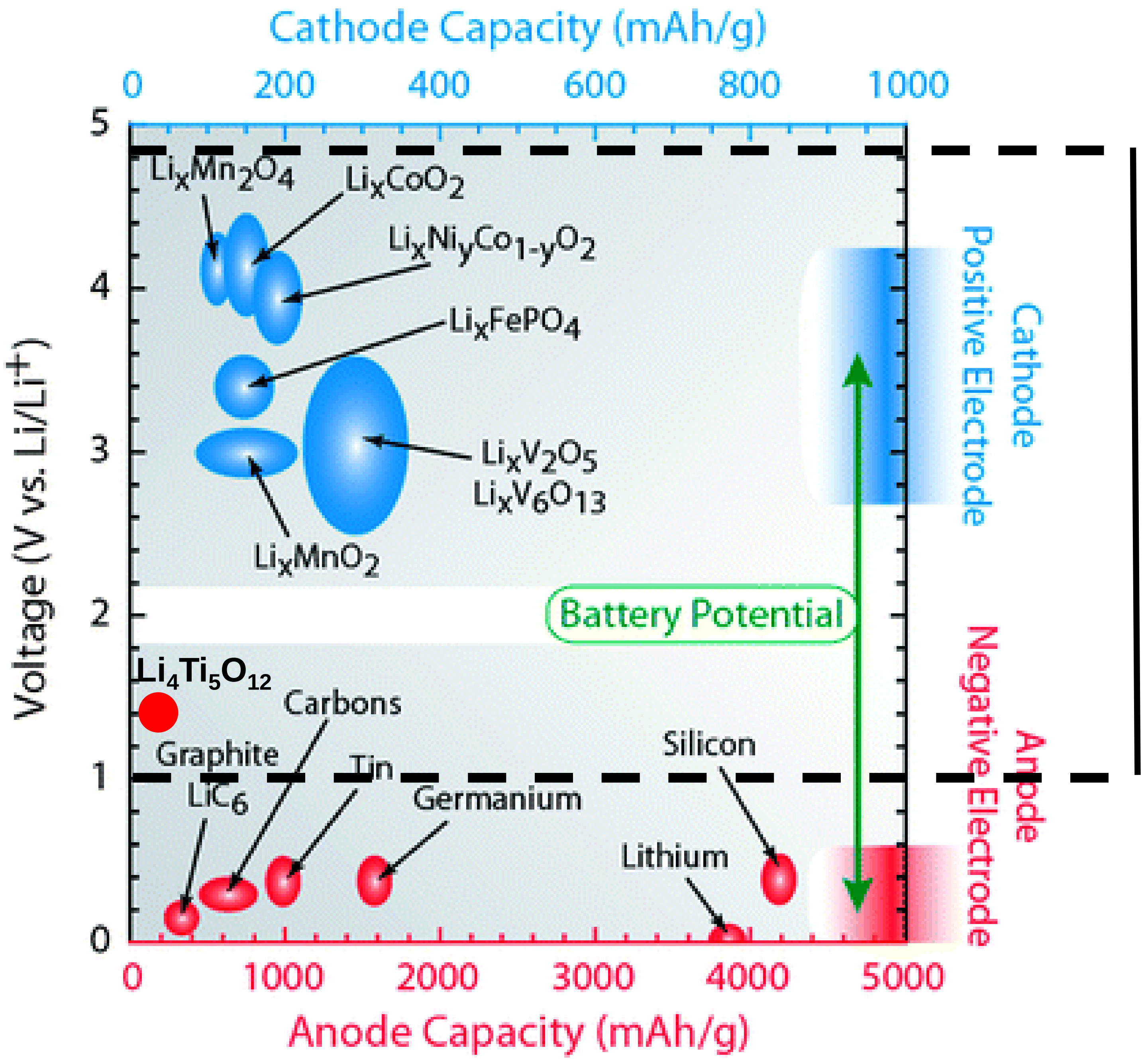
Elements also selected by the Department of Energy denoted by a thicker bounding box.

🟦 🟪 🟧 🟩

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 | | | | | | |

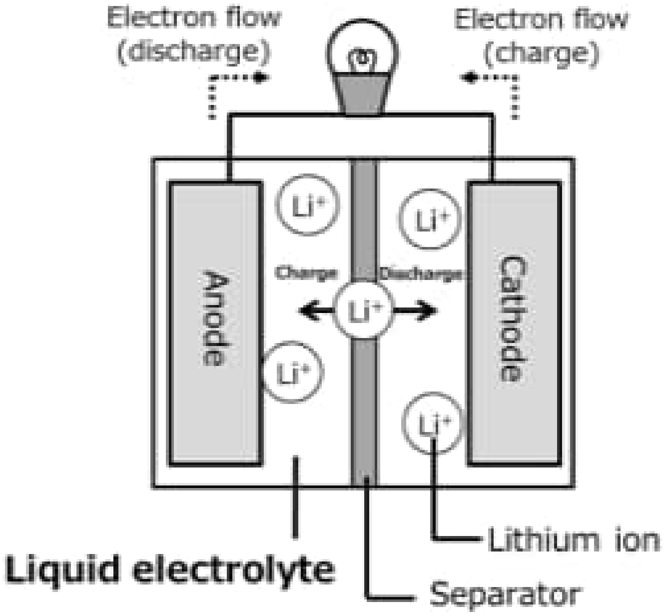
| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | E | Fm | Md | No | Lr |

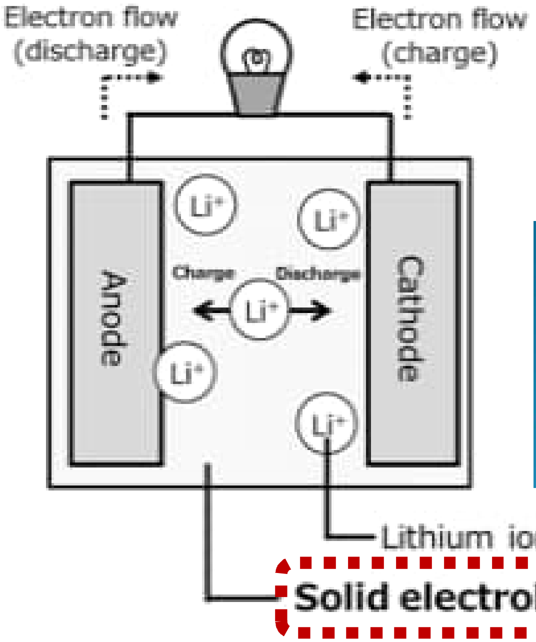
***Materials Research Society*** **(MRS), USA**

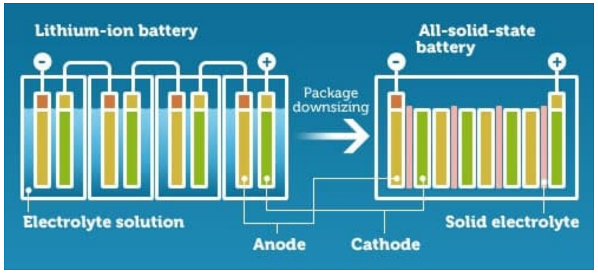


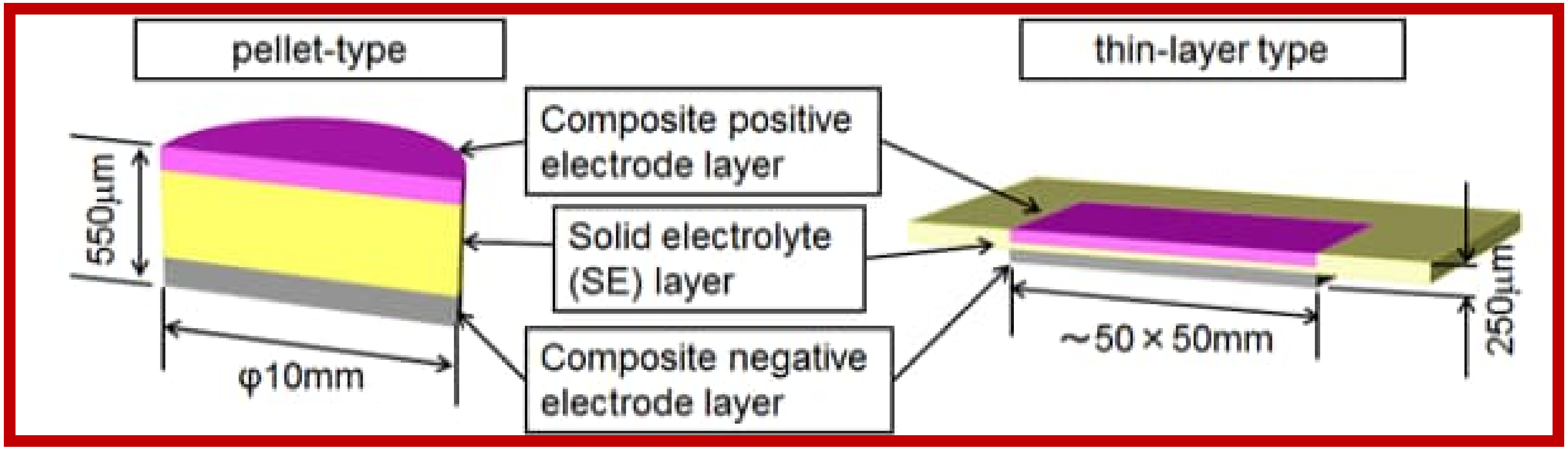
**Liquid electolyte stability range**

# 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 not yet comparable to liquid electrolytes (~$10^{-3}$ S/cm)

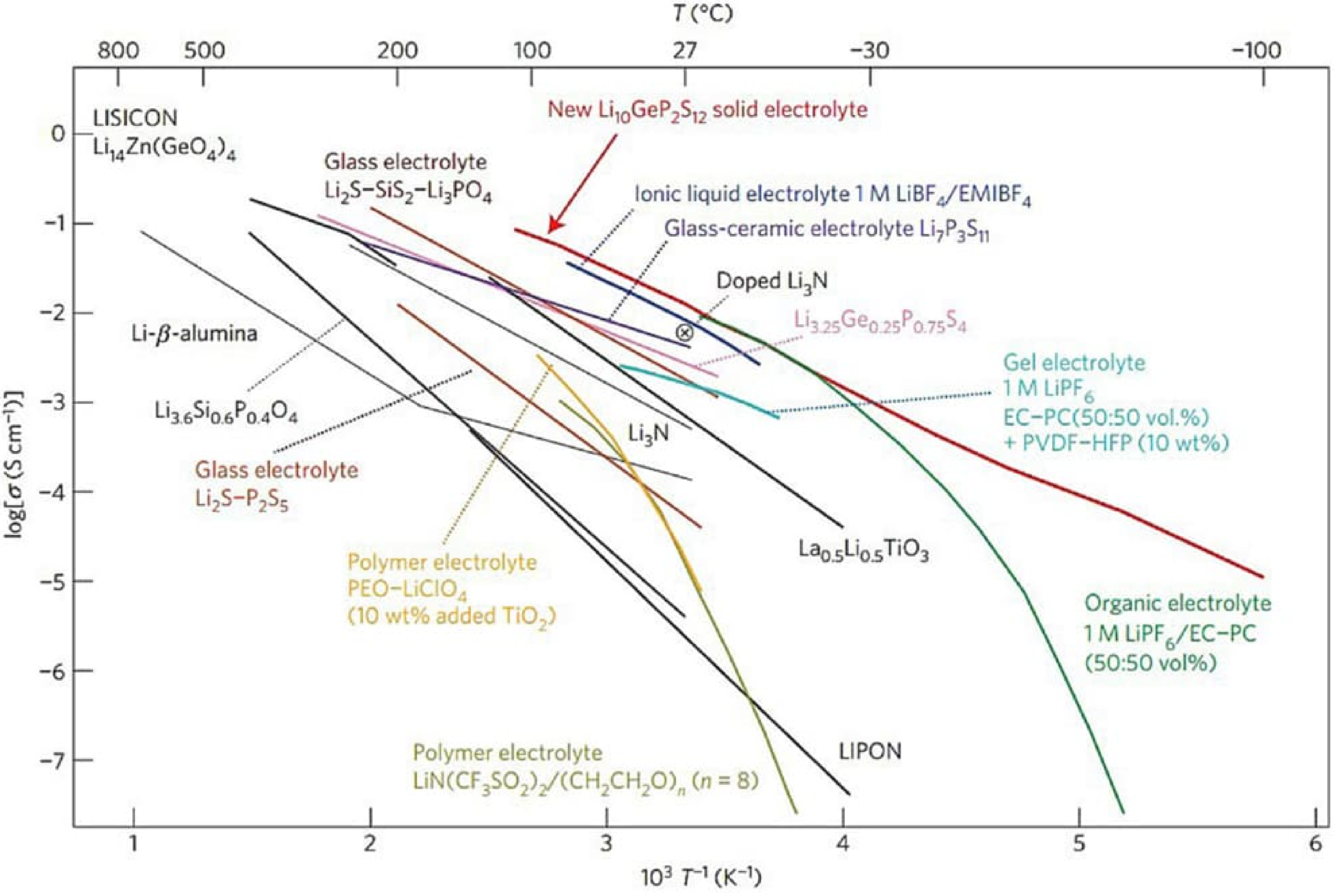
## PROS

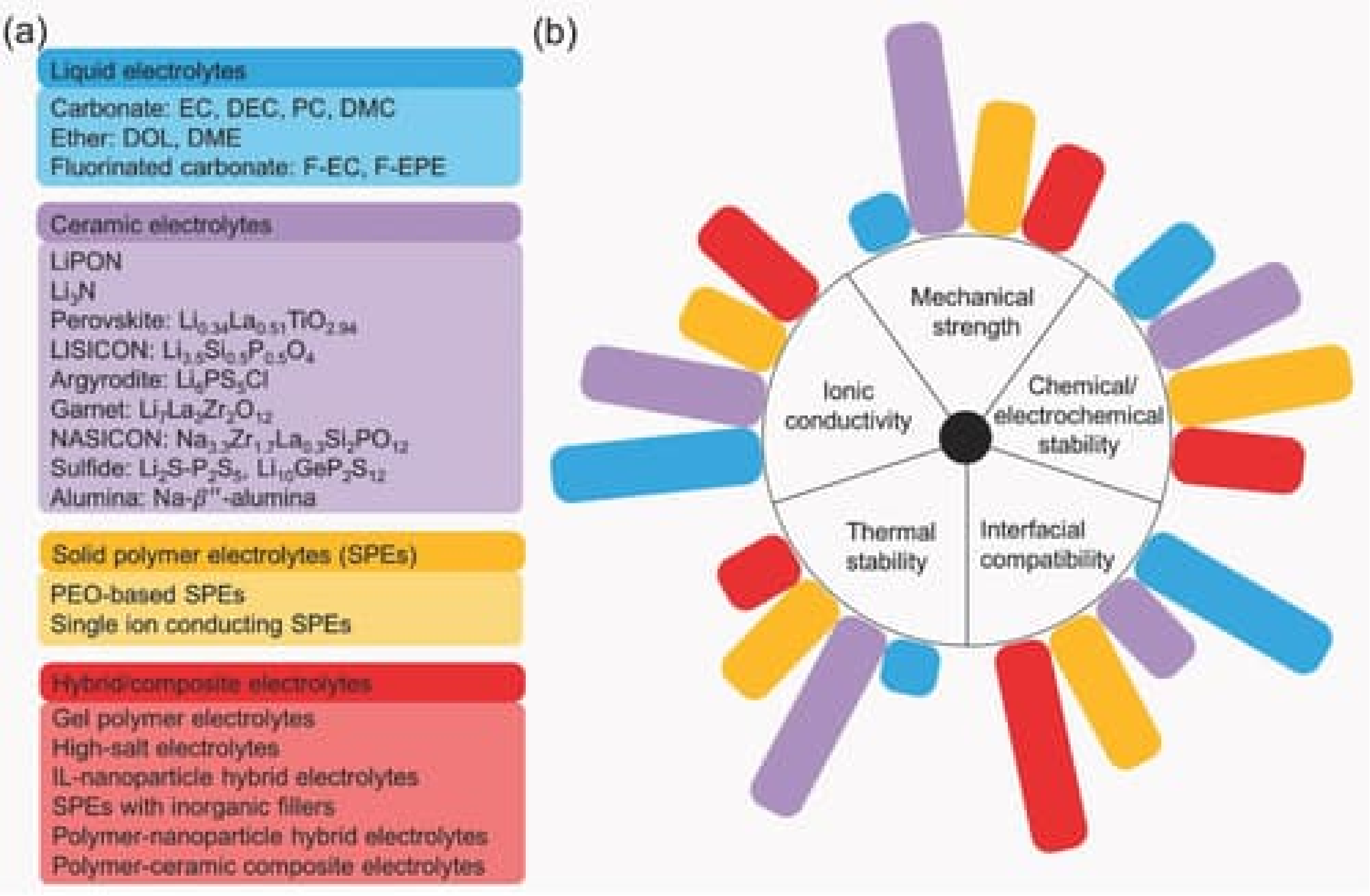
- Non-flammable → Safety
- Non-reactive with electrode materials (no SEI layers)
- Possibility to use Li metal anode
- Possibility to use >5 V cathode materials → Higher energy density
- Wider operation temperature range
- Simpler cell structure, no need e.g. for an expensive separator
- No risk for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


$T$ (°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 $Li_3N$
$Li_{3.25}Ge_{0.25}P_{0.75}S_4$
Li-β-alumina
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%)
LIPON
Polymer electrolyte
$LiN(CF_3SO_2)_2/(CH_2CH_2O)_n$ ($n$ = 8)
$\log[\sigma\ (S\ cm^{-1})]$
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: $Li_2S\text{-}P_2S_5$, $Li_{10}GeP_2S_{12}$
Alumina: Na-$\beta''$-alumina

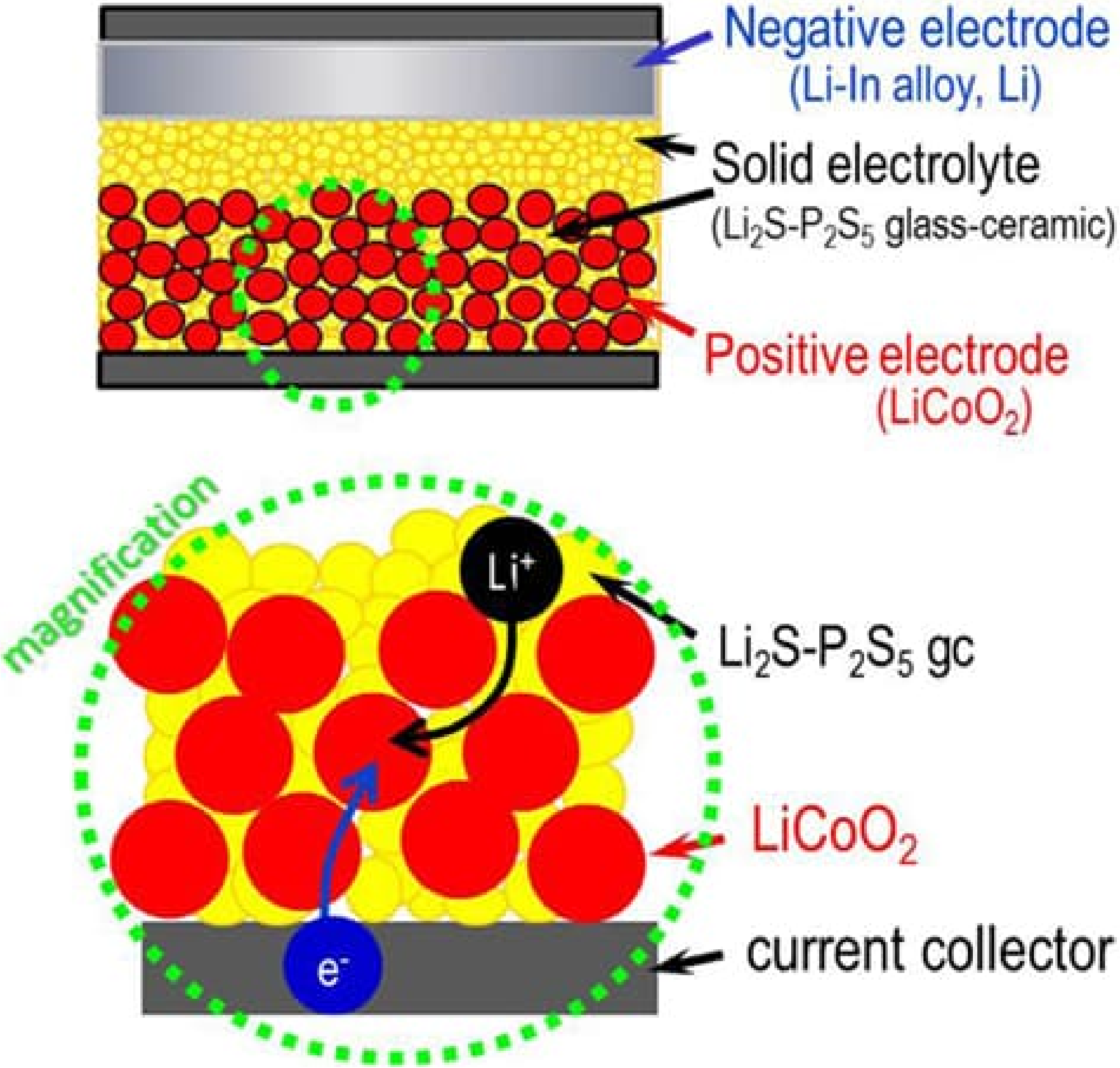
**Solid polymer electrolytes (SPEs)**

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

# Bulk-type battery



Negative electrode
(Li-In alloy, Li)

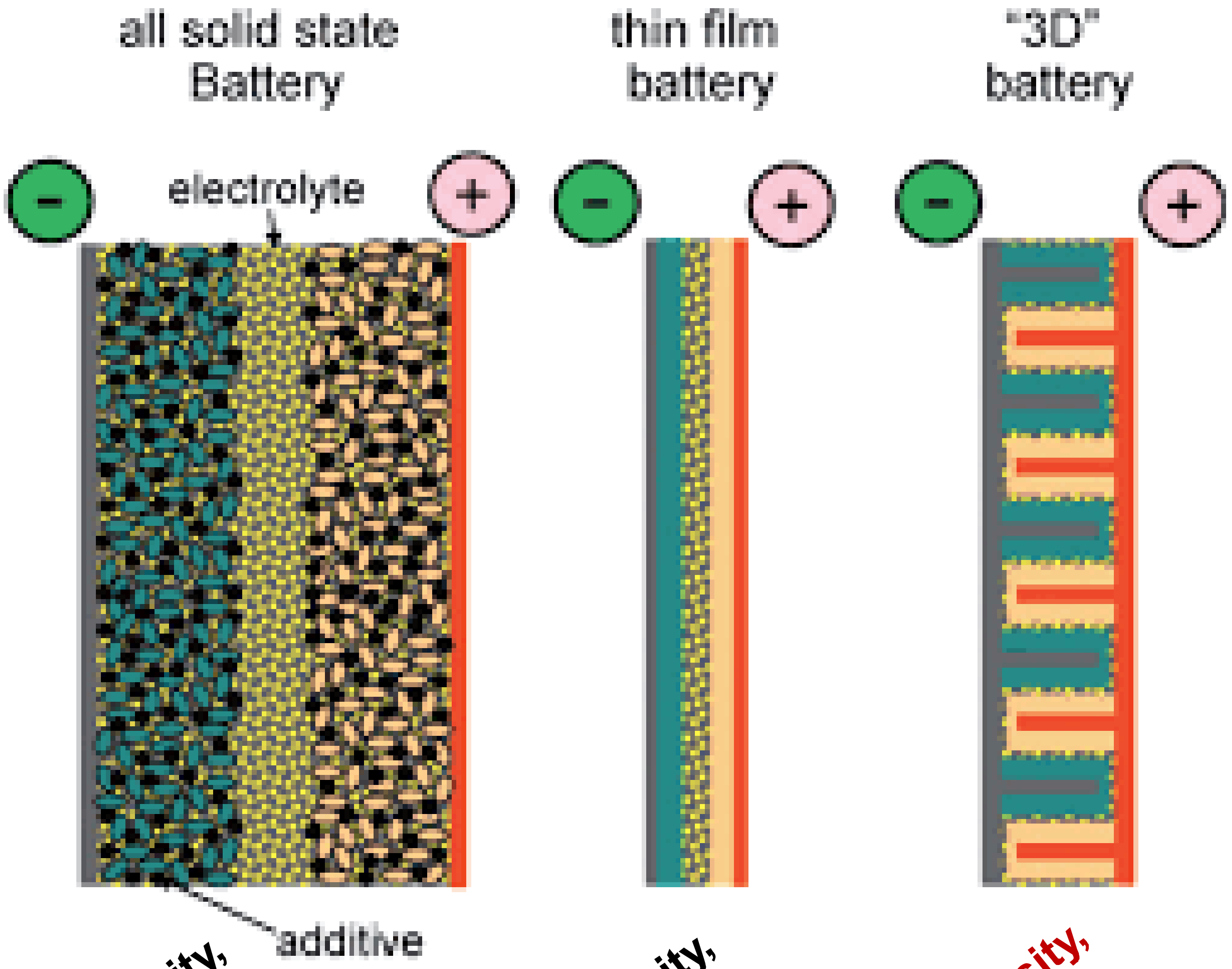
Solid electrolyte
($Li_2S$-$P_2S_5$ glass-ceramic)

Positive electrode
($LiCoO_2$)

$Li_2S$-$P_2S_5$ gc

$LiCoO_2$

current collector



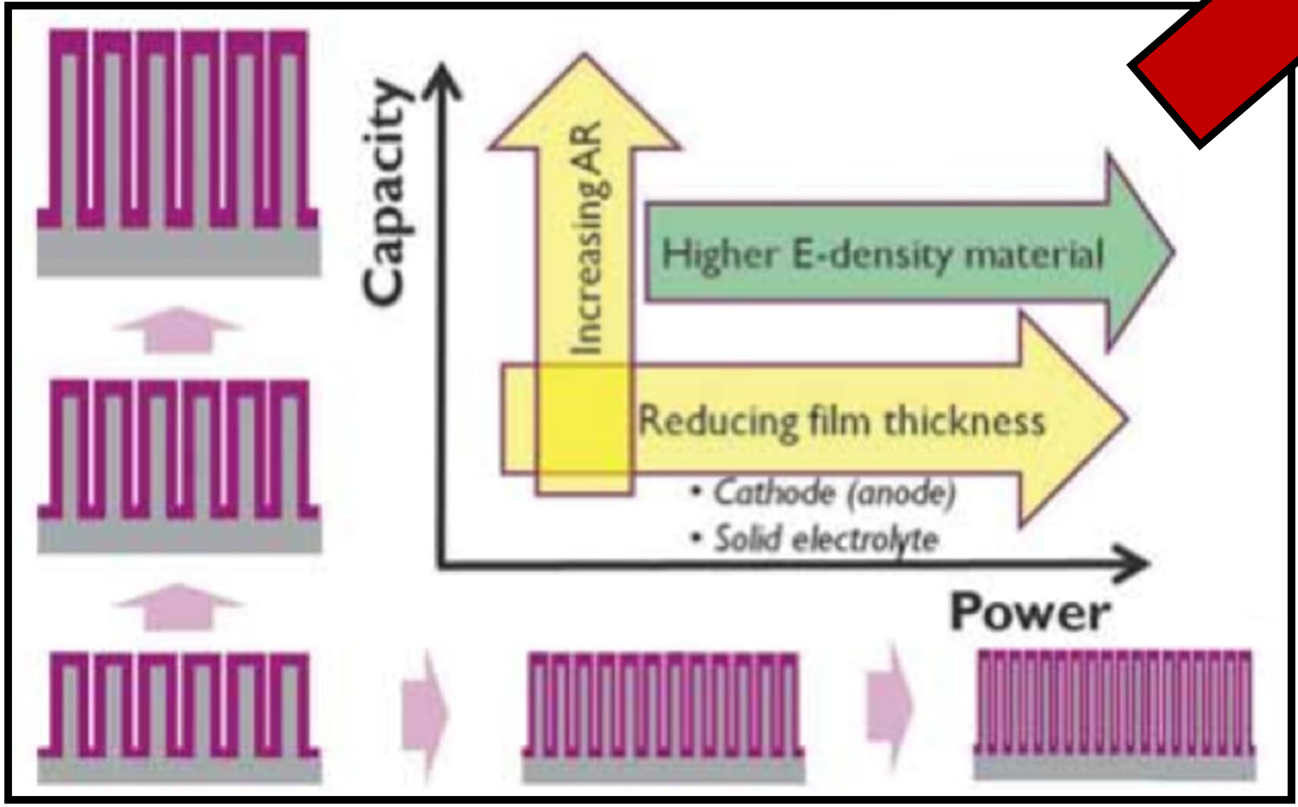
High energy density,
Low power density

Low energy density,
High power density

High energy density,
High power density

# ALD

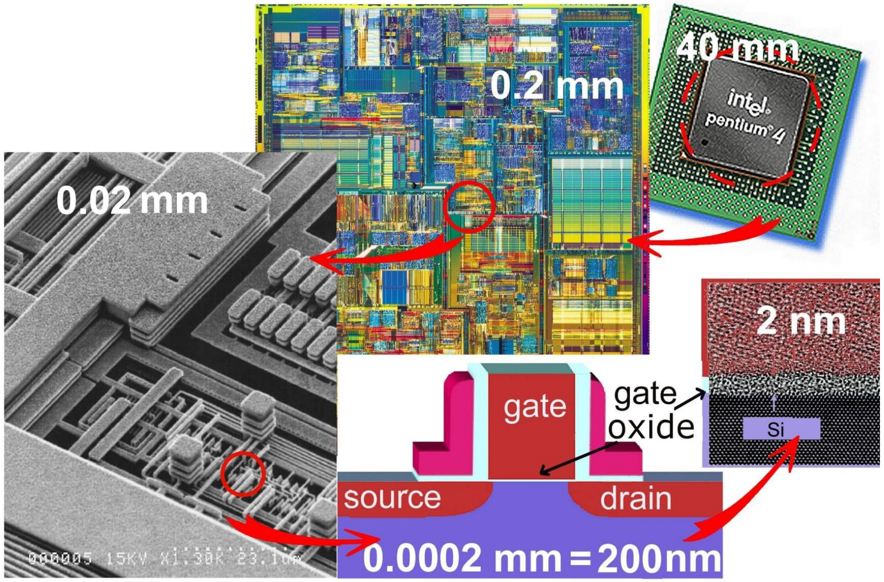
## Atomic Layer Deposition



# Atomic Layer Deposition (ALD)

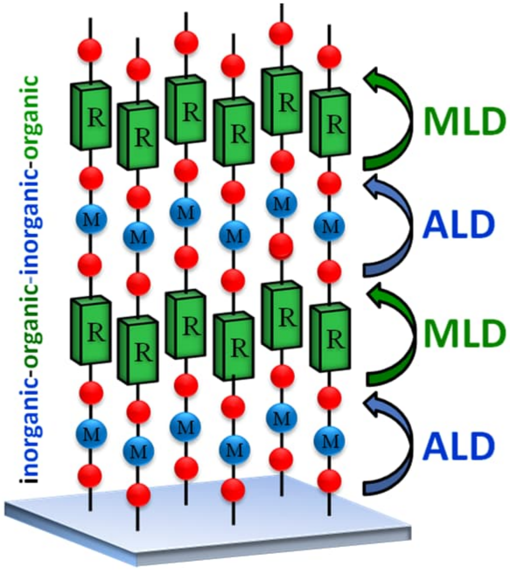
- Advanced gas-phase thin-film technology
- ALD cycle: two (or more) precursors pulsed separately and sequently
- Pin-hole free, conformal & large-area homogeneous thin films with atomic-layer level thickness control for microelectronics and beyond

## MOSFET transistor

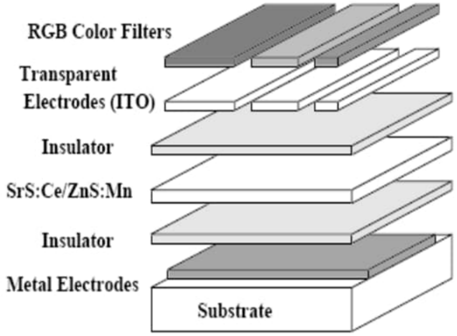


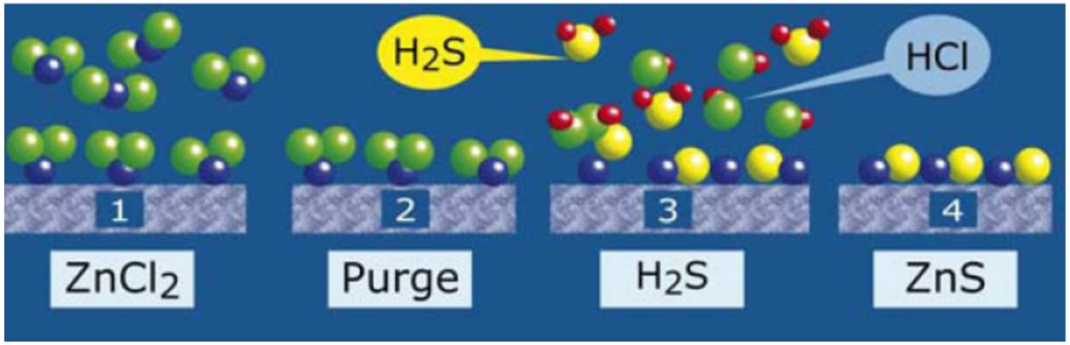
## ALD/MLD

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



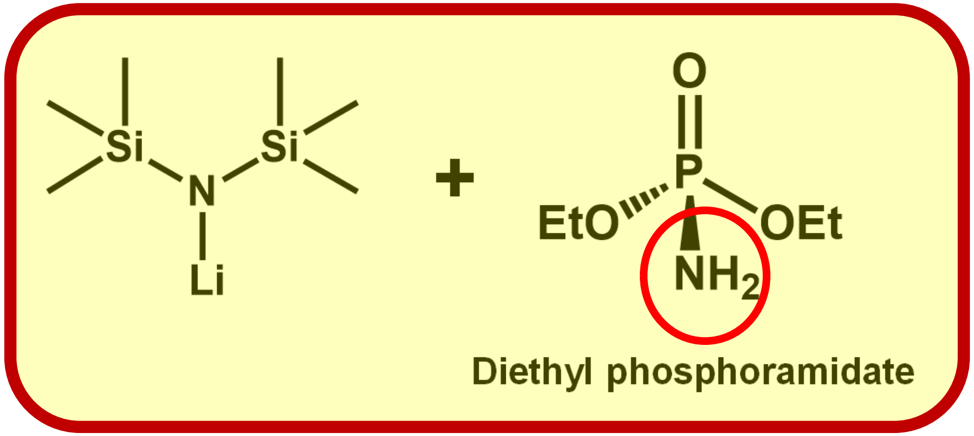
## Electro-luminescent display



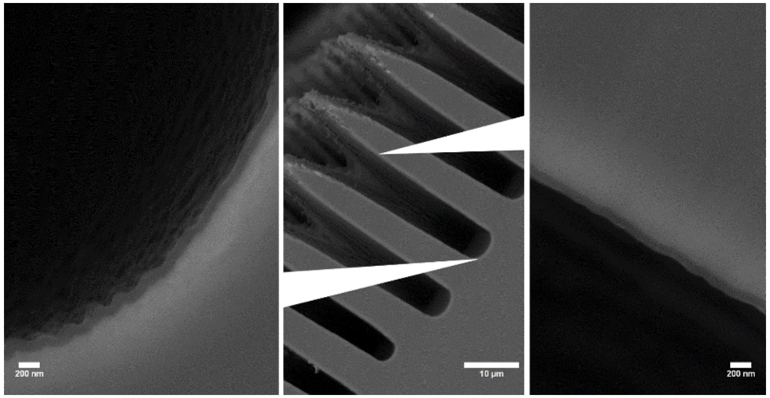


# ALD OF LIPON

- 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

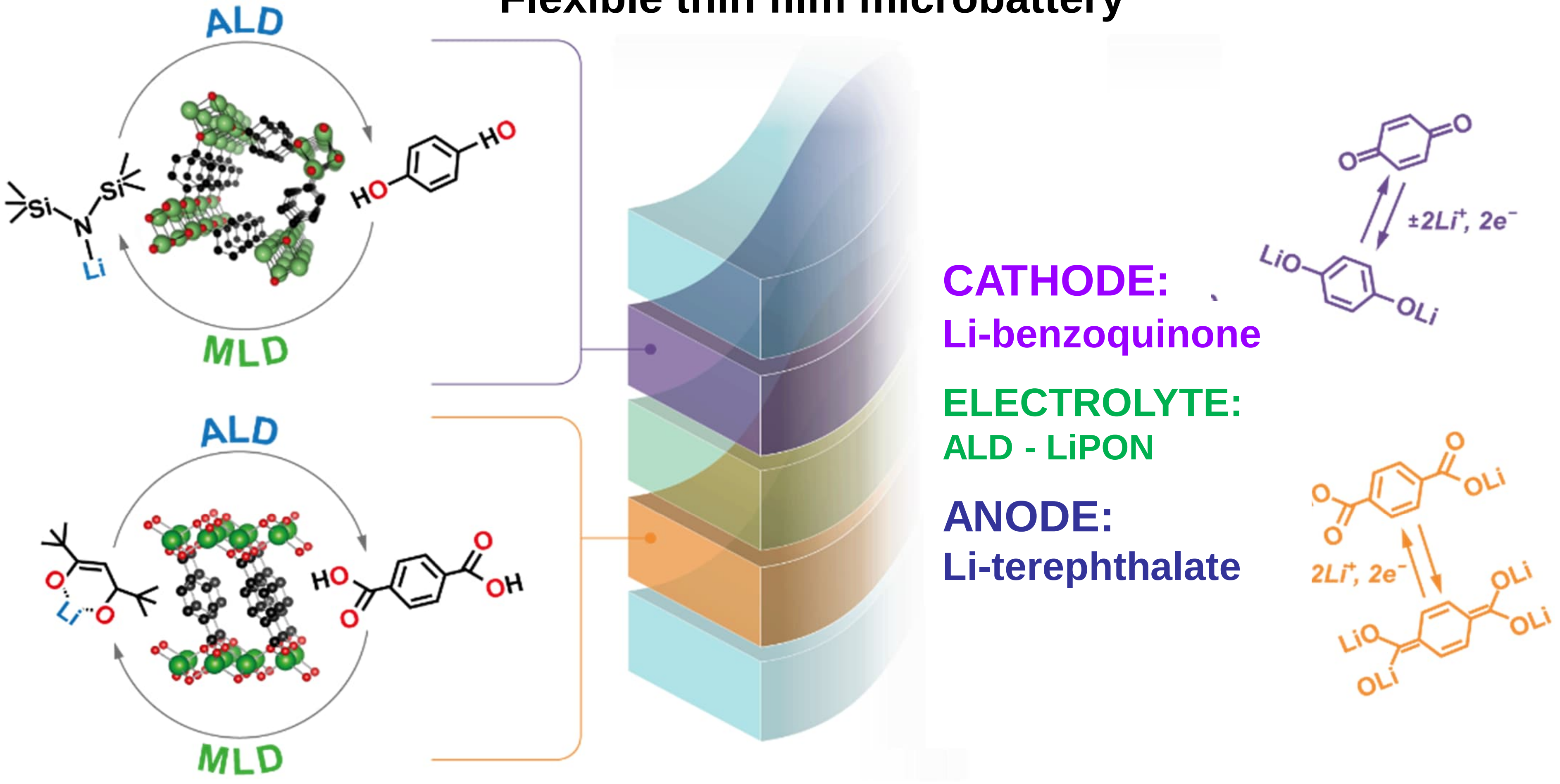


M. Nisula, Y. Shindo, H. Koga & M. Karppinen,
*Chem. Mater*. **27**, 6987 (2015).

TOYOTA

# ALD + MLD: Metal-saving Li-organic microbattery

## Flexible thin film microbattery



**CATHODE:**
**Li-benzoquinone**

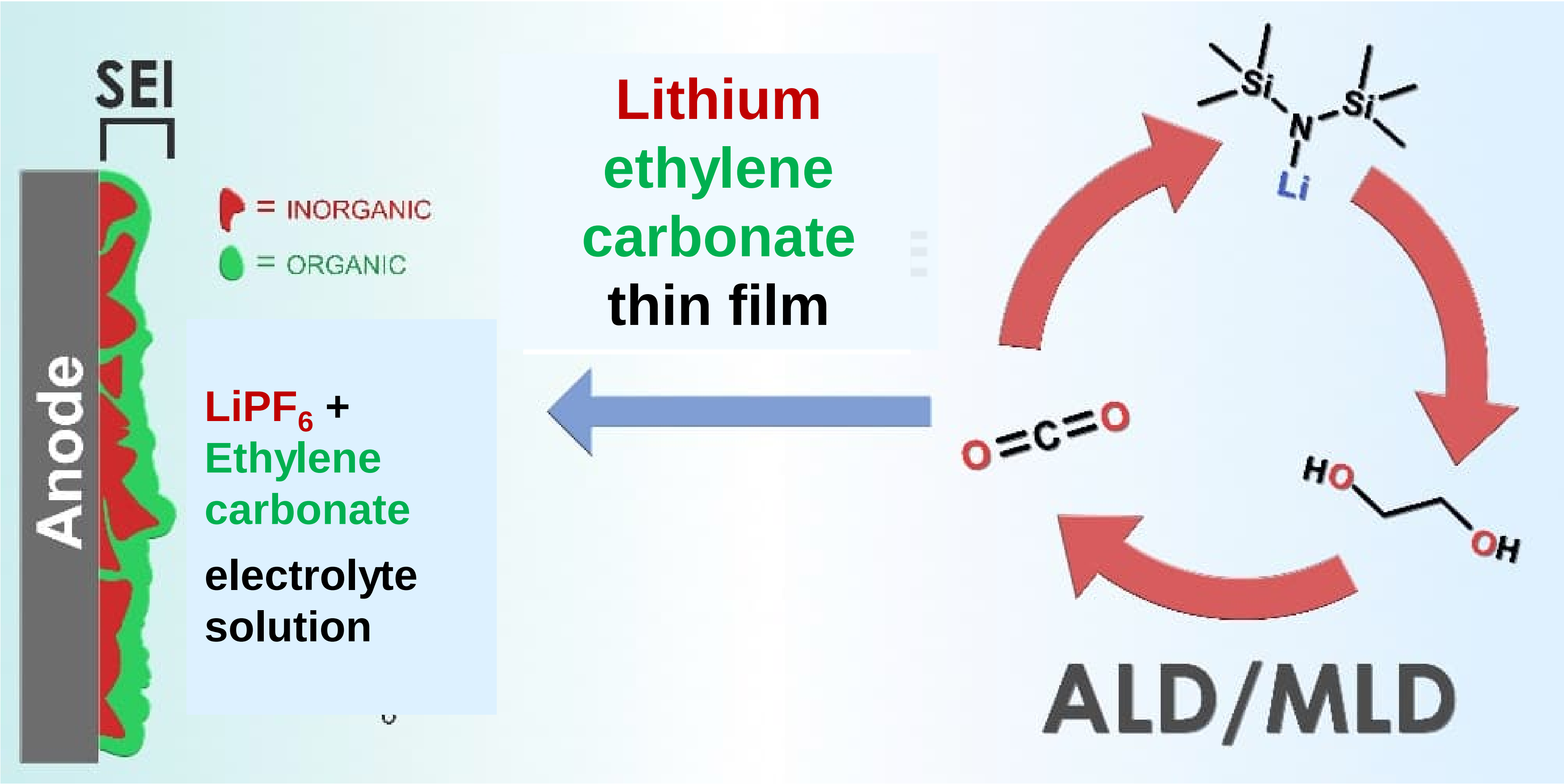
**ELECTROLYTE:**
**ALD - LiPON**

**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**).