LECTURE SCHEDULE

	Date		Topic
1.	Wed	28.10.	Course Introduction & Short Review of the Elements
2.	Fri	30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed	11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri	13.11.	Redox Chemistry
6.	Mon	16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed	18.11.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri	20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon	23.11.	Cr, Mo, W & 2D materials
10	Wed	25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri	27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon	30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed	02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 12, 9:00-12:00 Ke1

PRESENTATION TOPICS/SCHEDULE

Wed	18.11.	Ti: Ahonen & Ivanoff
Mon	23.11.	Mo: Kittilä & Kattelus
Wed	25.11.	Mn:
		Ru:
Fri	27.11.	In:
		Te: Kuusivaara & Nasim
Mon	30.11.	U: Musikka & Seppänen

QUESTIONS: Lecture 2

Name your file Exe-2-Familyname; Return by 4 pm into MyCourses drop-box

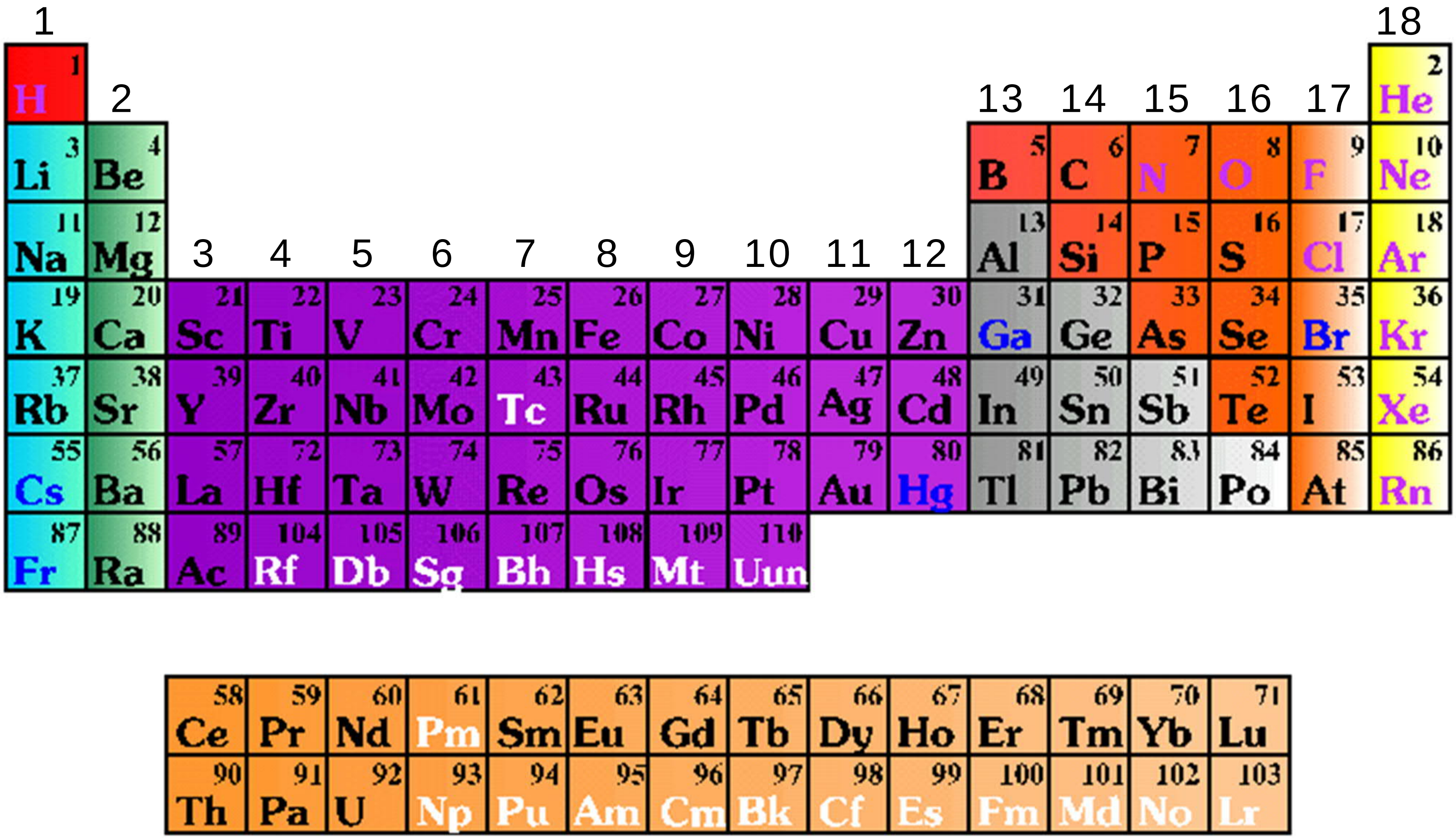
1. Why copper readily exists in the oxidation state +I ? Give the electron configuration for Cu.

2. How many f electrons (in neutral atom) the following elements have: La, Eu, Lu ?

3. How many f electrons the following ions have: La^{3+}, Eu^{3+}, Eu^{2+} ?

4. How many unpaired electrons the following ions have: V^{5+}, Cr^{3+}, Cu^{2+}, Eu^{3+}, Tb^{3+}, Yb^{3+}, Lu^{3+} ?

5. Indicate for each of the following pairs the larger atom/ion, or state that they are of the same size if that is the case: Na–K, K–Ca, Fe^{2+}–Fe^{3+}, Ti^{3+}–Ti^{4+}, Ti^{4+}–Zr^{4+}, Zr^{4+}–Hf^{4+}, La–Lu



Alkali metals
Alkaline earth metals
Halogens
Noble gases
Transition metals
Lanthanides
Actinides

ATOMIC MODEL & ELECTRON CONFIGURATIONS

IMPORTANT HISTORICAL STEPS

- **Thomson 1898-1903:** existence of electrons
- **Rutherford 1911:** small and dense nucleus + electron cloud
- **Einstein 1905:** wave and particle nature of electromagnetic radiation
- **Bohr 1913:** simple atom model (classical physics + some quantum theory features)
- **de Broglie 1924:** wave nature of particles
- **Davisson & Germes 1927:** diffraction of electrons
- **Heisenberg 1926:** uncertainty principle (exact position and momentum of electron)
- **Schrödinger 1926:**
  wave nature of electrons → quantum mechanical atom model
- **Compton 1921 and Goudsmit & Uhlenbeck 1925:** electron spin
- **Pauli 1925:** “exclusion principle”
- **Hund 1925:** minimum energy → maximum number of unpaired electrons

QUANTUM MECHANICAL ATOM MODEL

- **Electrons have simultaneously both wave and particle nature**
- **In an atom electron behaves like standing wave**
- **<u>Schrödinger wave function</u>:**
  - **wavefunction ψ is a solution of Schrödinger equation**
  - **ψ describes the behaviour of electron**
  - **in chemistry: wavefunction → atomic orbital**
  - **Schrödinger equation has several possible solutions (= orbitals)**
  - **each orbital is described with a set of three quantum numbers: n, l and m**
  - **There is a certain energy corresponding to each wave function**
  - **Energy quantization is derived from the Schrödinger equation**

QUANTUM NUMBERS

n	l	m	Orbital	Number
1	0	0	1s	1
2	0	0	2s	1
	1	-1, 0, 1	2p	3
3	0	0	3s	1
	1	-1, 0, 1	3p	3
	2	-2, -1, 0, 1, 2	3d	5
4	0	0	4s	1
	1	-1, 0, 1	4p	3
	2	-2, -1, 0, 1, 2	4d	5
	3	-3, -2, -1, 0, 1, 2, 3	4f	7

Principal quantum number (n): 1, 2, 3, …
- size and energy of the orbital

Angular momentum quantum number (l): 0, 1, … , (n-1)
- shape of the orbital

Magnetic quantum number (m): -l, (-l+1), …, (+l-1), +l
- orientation of the orbital in 3D space

Spin quantum number (s): -½, ½

Pauli's exclusion principle

It is impossible for two electrons in the same atom to have the same set of quantum numbers: n, l, m and s

Aufbau ("building up") principle

Orbitals are filled in the order of increasing energy:
1s–2s–2p–3s–3p–4s–3d–4p–5s–4d–5p–6s–4f–5d–6p–7s–5f–6d–7p

Hund's rule (not necessarily obeyed when the energy levels splitted, ref. crystal field theory)

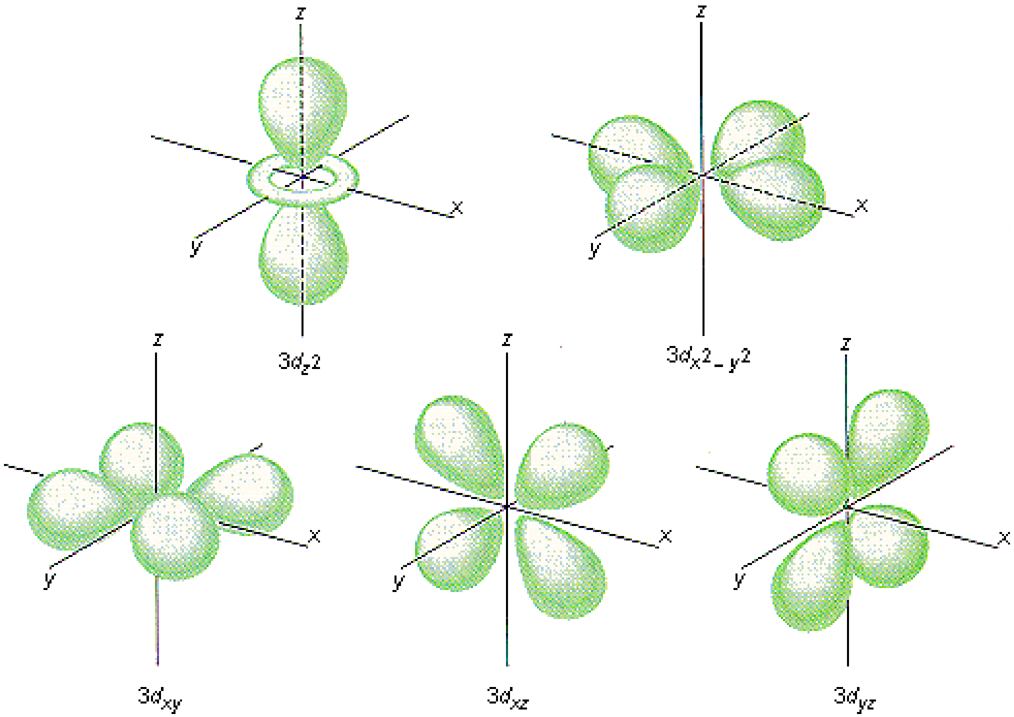
All orbitals in a subshell are first occupied with one electron before two electrons start to occupy the same orbital (to minimize the electron-electron repulsions)

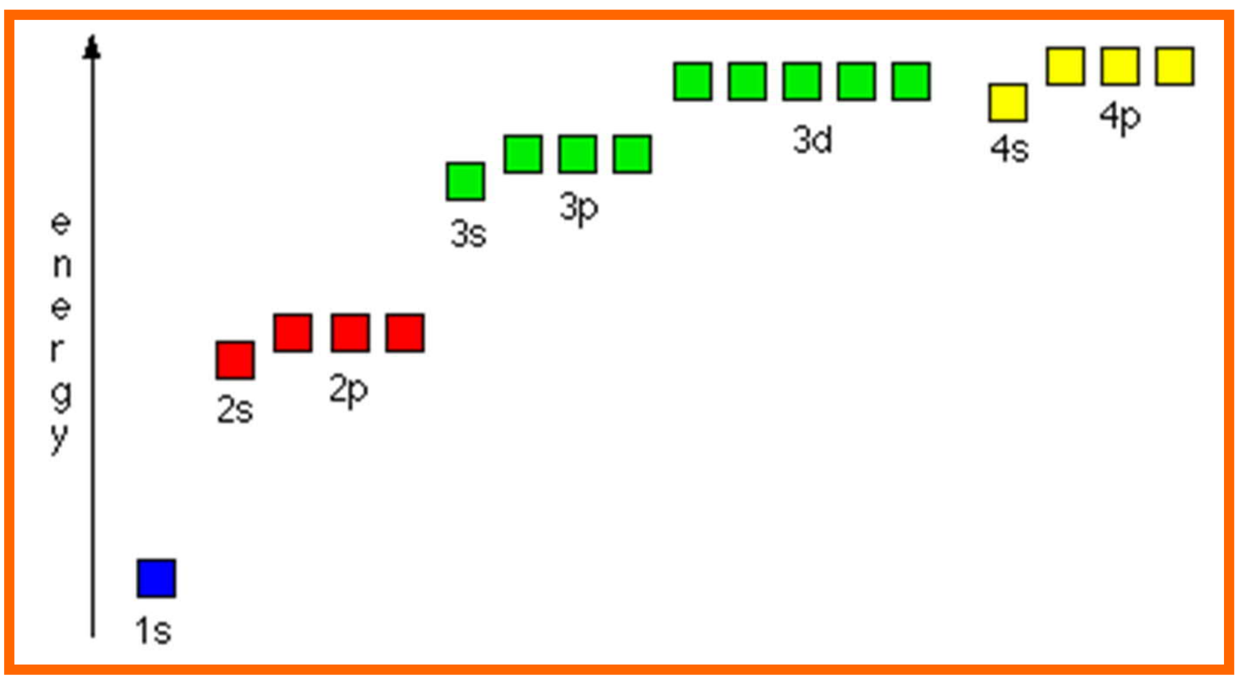
Atom orbitals

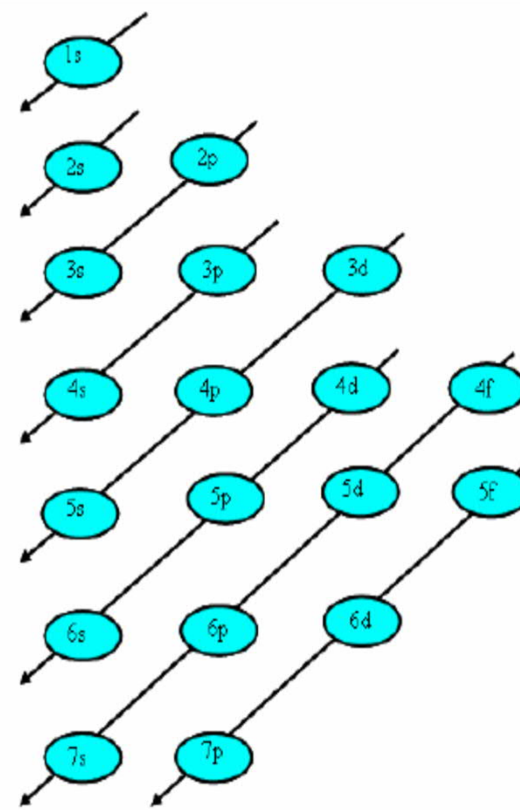
- ψ (wave function):
  does not tell the location or path of electron
  (c.f. Heisenberg uncertainty principle)

- ψ^2 (square of wave function):
  probability of electron to be located in a certain location

  → PROBABILITY DENSITY / ELECTRON DENSITY MAP
  → ”shape” of the orbital


3dz2
3dx2-y2
3dxy
3dxz
3dyz


energy
1s
2s
2p
3s
3p
3d
4s
4p


1s
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
5f
6s
6p
6d
7s
7p

PERIODIC TABLE

s | d | p | f

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIA or 0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

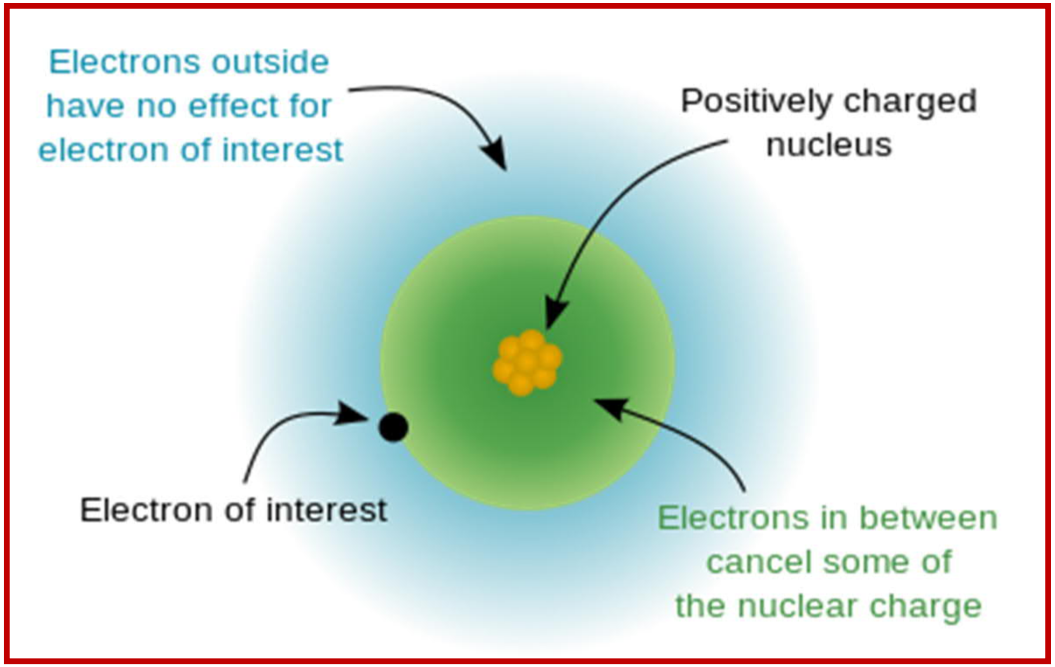
Lanthanide series →	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide series →	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

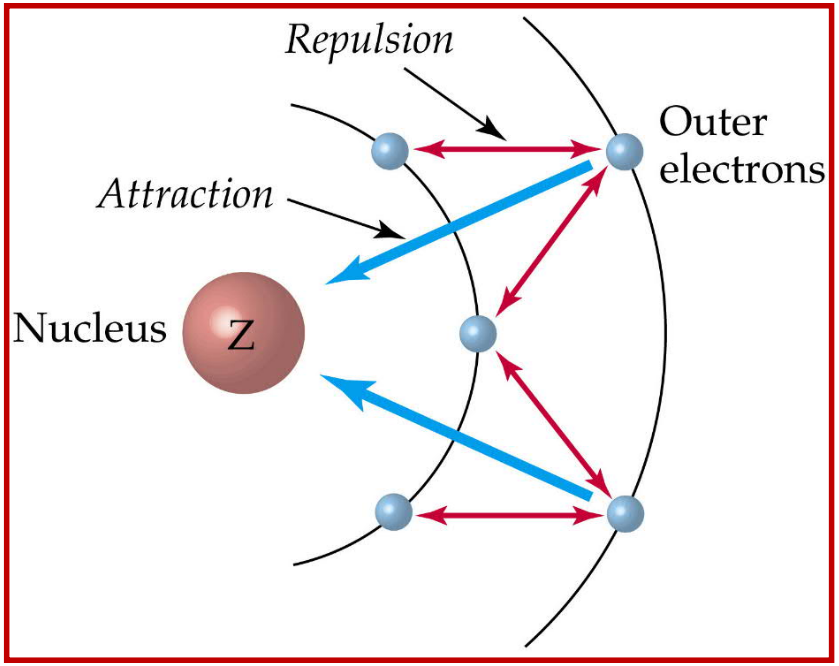
PERIODIC PROPERTIES

- effective nuclear charge
- atomic radius and ionic radius
- ionization energy
- electron affinity
- electronegativity
- oxidation numbers
- density
- melting and boiling points
- reactivity and stoichiometries of compounds
- properties of compounds
- etc.

EFFECTIVE NUCLEAR CHARGE (Z_{eff})

- Atomic number (Z) = number of protons = (true) positive nuclear charge
- Z_{eff}: positive charge experienced by an electron in a multi-electron atom
- Z_{eff} is smaller than Z due to the shielding effect of the other (inner) electrons in the same atom
- Only the electrons that are closer to the nucleus contribute to the shielding effect (not electrons on the same orbitals)
- $+e < Z_{eff} < Z$



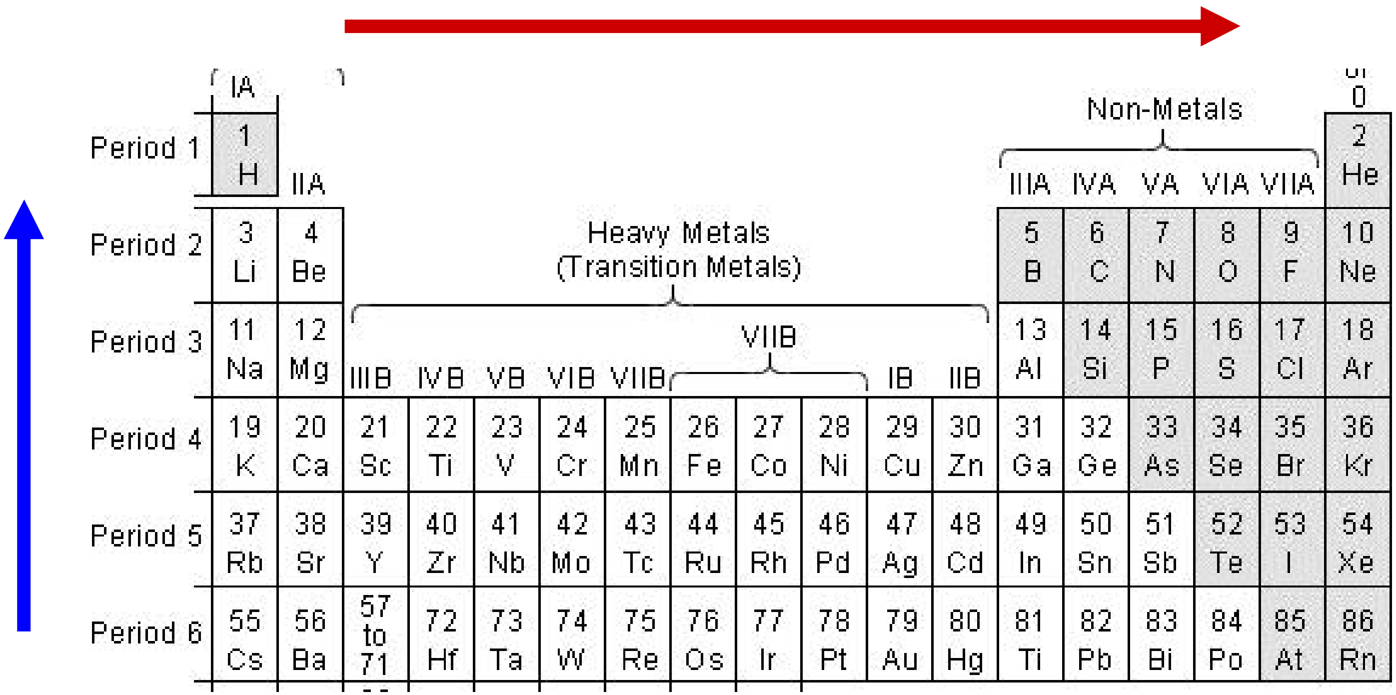


atomic radius (r_{atom})
ionization energy (IE)
electronegativity (EN)

Z_{eff} increases, r_{atom} decreases

$\rightarrow$ IE and EN increase

$Z_{eff} \approx$ constant: IE and EN increase, since r_{atom} decreases

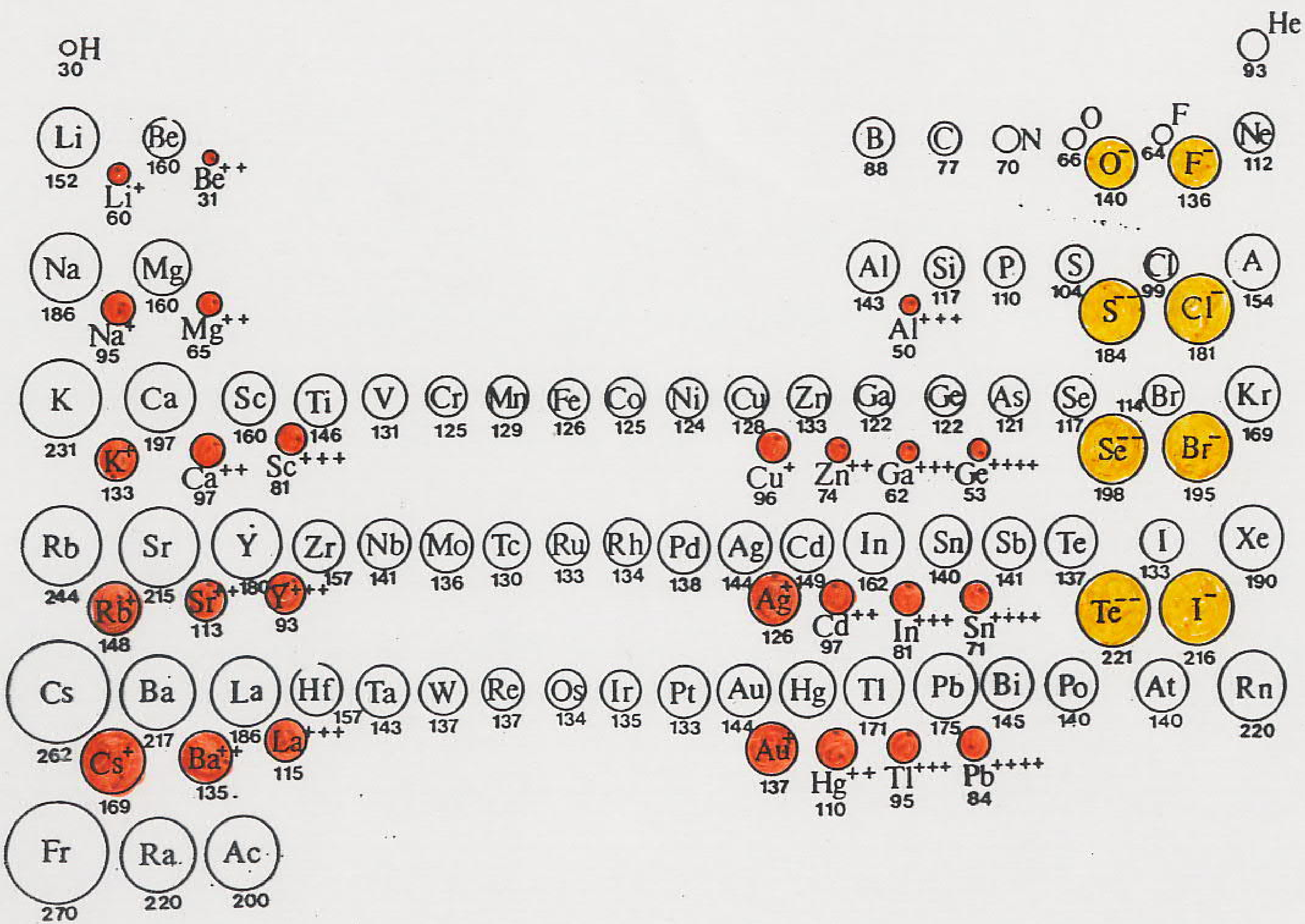


IONIC RADIUS

- **Ionic radius values can not be measured directly**
- **The values are estimated (using statistical techniques) for each ion from a large data set for experimentally determined bond lengths in different ionic compounds**
- **The values are tabulated (originally) in:**

R.D. Shannon, Acta Cryst. A 32, 751 (1976)

You can find ionic radius values at: http://abulafia.mt.ic.ac.uk/shannon/ptable.php



H 30
He 93
Li 152
Li+ 60
Be 160
Be++ 31
B 88
C 77
N 70
O 66
F 64
Ne 112
O- 140
F- 136
Na 186
Na+ 95
Mg 160
Mg++ 65
Al 143
Al+++ 50
Si 117
P 110
S 104
Cl 99
A 154
S-- 184
Cl- 181
K 231
K+ 133
Ca 197
Ca++ 97
Sc 160
Sc+++ 81
Ti 146
V 131
Cr 125
Mn 129
Fe 126
Co 125
Ni 124
Cu 128
Cu+ 96
Zn 133
Zn++ 74
Ga 122
Ga+++ 62
Ge 122
Ge++++ 53
As 121
Se 117
Se-- 198
Br 114
Br- 195
Kr 169
Rb 244
Rb+ 148
Sr 215
Sr++ 113
Y 180
Y+++ 93
Zr 157
Nb 141
Mo 136
Tc 130
Ru 133
Rh 134
Pd 138
Ag 144
Ag+ 126
Cd 149
Cd++ 97
In 162
In+++ 81
Sn 140
Sn++++ 71
Sb 141
Te 137
Te-- 221
I 133
I- 216
Xe 190
Cs 262
Cs+ 169
Ba 217
Ba++ 135
La 186
La+++ 115
Hf 157
Ta 143
W 137
Re 137
Os 134
Ir 135
Pt 133
Au 144
Au+ 137
Hg
Hg++ 110
Tl 171
Tl+++ 95
Pb 175
Pb++++ 84
Bi 145
Po 140
At 140
Rn 220
Fr 270
Ra 220
Ac 200

Ionic radius [Å]

earth-alkaline metals: oxidation state +II

CN	4	6	8	9	10	12
Be	0.27	0.45	-	-	-	-
Mg	0.57	0.72	0.89	-	-	-
Ca	-	1.00	1.12	1.18	1.23	1.34
Sr	-	1.18	1.26	1.31	1.36	1.44
Ba	-	1.35	1.42	1.47	1.52	1.66

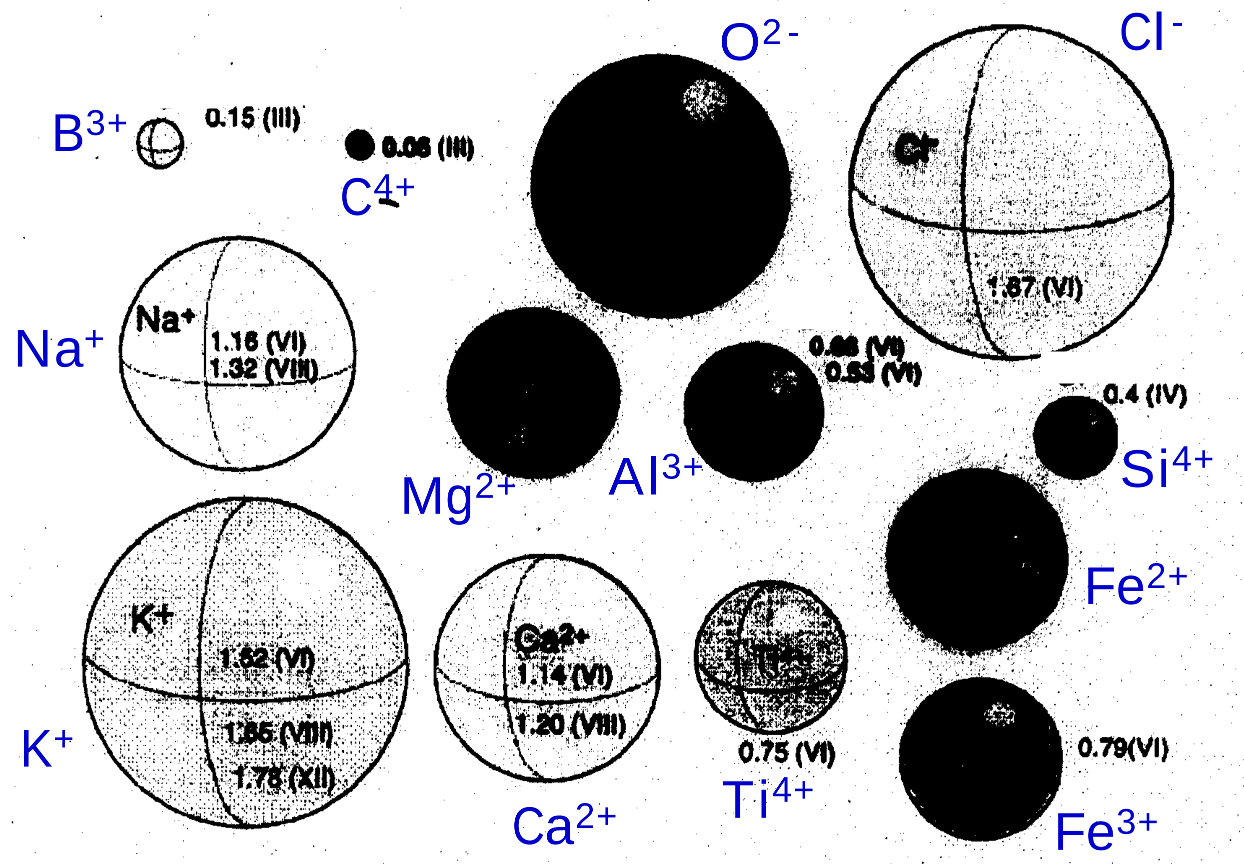
3d cations: CN = 6

Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-

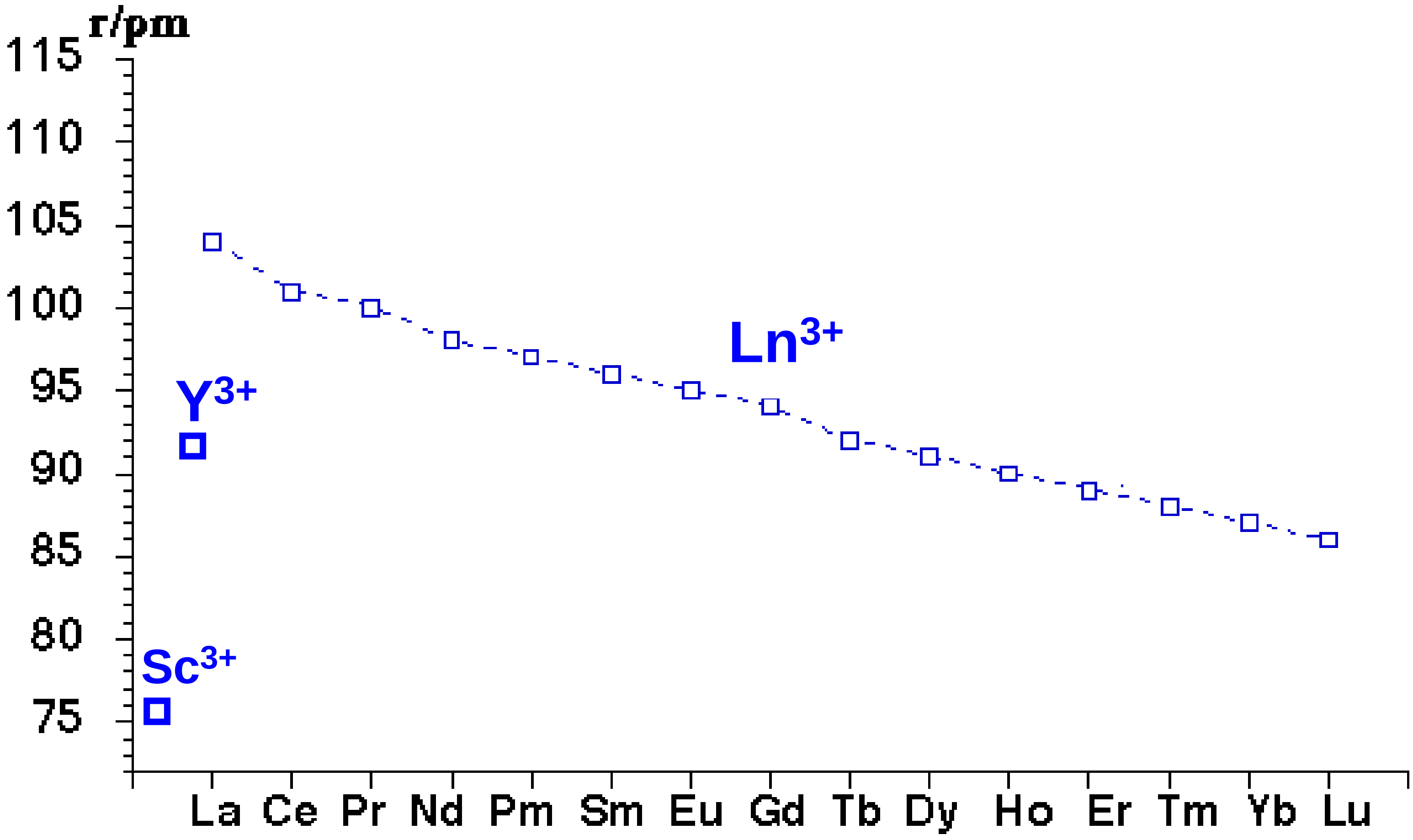
anions: CN = 6

OH^- 1.37	H^- 1.67
O^{2-} 1.40	F^- 1.33
S^{2-} 1.84	Cl^- 1.81
Se^{2-} 1.98	Br^- 1.96
Te^{2-} 2.21	I^- 2.20

Ionic Radii (Shannon, 1976)



LANTHANIDE CONTRACTION



SIMILARITIES BETWEEN THE ELEMENTS

- **Within the groups in the Periodic Table the elements have the same electron configuration for the outer shell**

  → same (possible) oxidation states

  → similar chemical behaviour

- **The group similarity is the clearest for the (main) groups 1, 2, 17 ja 18**

- **In each group the lightest element is clearly much smaller (atomic/ ionic radii) than the others, hence somewhat different from the others in properties**

- **DIAGONAL RELATIONSHIP:**

  The lightest element rather resembles the next lightes element of the next group in the Periodic Table

- **Examples of diagonal relationships:**

  Li-Mg, Be-Al, B-Si, N-S

- **In compounds with OH groups (E-O-H) electronegativity of the cation (E) defines whether the compound is an oxoacid or a base**
- **small electronegativity:** $E\text{-}O\text{-}H \rightarrow E^+ + OH^-$ **(base)**
- **large electronegativity:** $E\text{-}O\text{-}H \rightarrow E\text{-}O^- + H^+$ **(acid)**
- **For example: elements of the third period:**

NaOH	**strong base**
$Mg(OH)_2$	**base**
$Al(OH)_3$	**amfolyte**
$Si(OH)_4$	**weak acid [H_4SiO_4]**
$OP(OH)_3$	**acid [H_3PO_4]**
$O_2S(OH)_2$	**strong acid [H_2SO_4]**
$O_3Cl(OH)$	**strong acid [$HClO_4$]**

↓ Electro-negativity increases

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s, d, p, f

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Electron configurations of 3d metals:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^x$

			3d				4s
Scandium (Sc)	↑						↑↓
Titanium (Ti)	↑	↑					↑↓
Vanadium (V)	↑	↑	↑				↑↓
Chromium (Cr)	↑	↑	↑	↑	↑		↑
Manganese (Mn)	↑	↑	↑	↑	↑		↑↓
Iron (Fe)	↑↓	↑	↑	↑	↑		↑↓
Koboltti (Co)	↑↓	↑↓	↑	↑	↑		↑↓
Nikkeli (Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓
Kupari (Cu)	↑↓	↑↓	↑↓	↑↓	↑↓		↑
[Sinkki (Zn)]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓

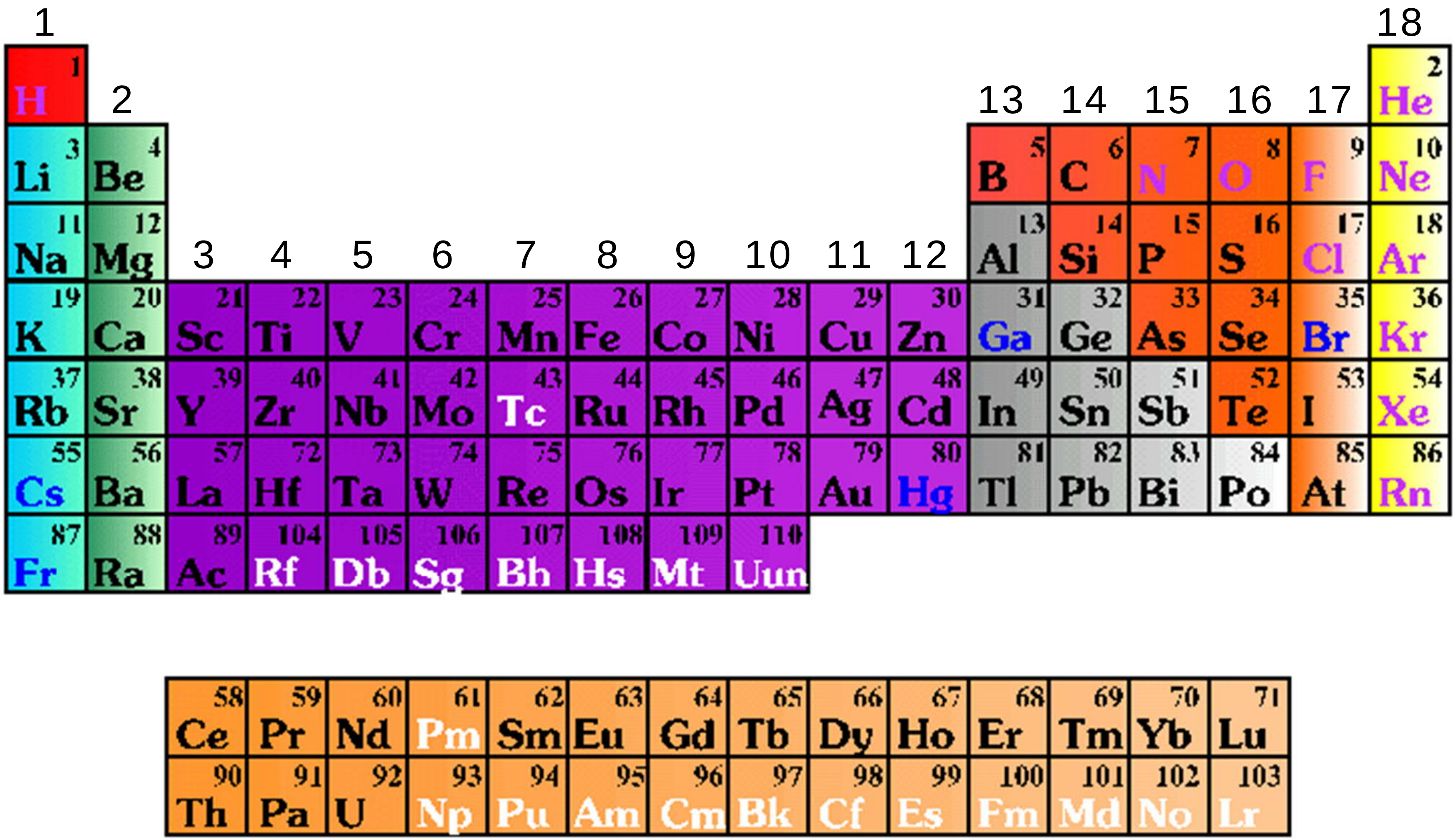
Electronic configurations and oxidation states of lanthanoids

Z	Element	Electronic configuration	Oxidation states
57	Lanthanum (La)	$4f^05d^16s^2$	+III
58	Cerium (Ce)	$4f^15d^16s^2$	+III, +IV
59	Praseodymium (Pr)	$4f^25d^16s^2$	+III
60	Neodymium (Nd)	$4f^35d^16s^2$	+III
61	Promethium (Pm)	$4f^45d^16s^2$	+III
62	Samarium (Sm)	$4f^55d^16s^2$	+III
63	Europium (Eu)	$4f^75d^06s^2$	+II, +III
64	Gadolinium (Gd)	$4f^75d^16s^2$	+III
65	Terbium (Tb)	$4f^75d^26s^2$	+III, +IV
66	Dysprosium (Dy)	$4f^95d^16s^2$	+III
67	Holmium (Ho)	$4f^{10}5d^16s^2$	+III
68	Erbium (Er)	$4f^{11}5d^16s^2$	+III
69	Thulium (Tm)	$4f^{12}5d^16s^2$	+III
70	Ytterbium (Yb)	$4f^{14}5d^06s^2$	+II, +III
71	Lutetium (Lu)	$4f^{14}5d^16s^2$	+III

MAIN GROUP ELEMENTS

- **Hydrogen: position in Periodic Table, isotopes, hydrides, hydrogen storage**
- **Alkali metals: group trends, Li-ion battery**
- **Alkaline earth metals *versus* alkali metals**
- **Boron group: crystal structures & melting points, boranes, borides, BNCT**
- **Isoelectronic: C-C ja B-N**
- **Nitrogen group: metal character and basicity of oxides (N < P < As < Sb < Bi)**
- **Multitude of sulphur compounds**
- **Lightest element *versus* other group members: F – Cl, Br, I**
- **Ionization energies and compounds of noble gases**

Where would you place **hydrogen** in Periodic Table ?



HYDROGEN in the Periodic Table:

Group 1:	**PRO:**	- one s electron - monovalent cation
	CONTRA:	- not a metal - does not react with water
Group 17:	**PRO:**	- one electron to the full shell - non-metal - two-atom molecule
	CONTRA:	- anion not common - relatively inert
Group 14:	**PRO:**	- half-filled electron shell - electronegativity 2.2

Hydrogen, Deuterium & Tritium

- H_2 99.985%, D_2 0.015 %, T_2 10^{-15} %
- Tritium is radioactive (half-life-time 12 years) but found in atmosphere upon cosmic radiation
- Industrial preparation: in nuclear reactors from ^{6}Li; bound into metals, e.g. UT_3
- Uses: medical application as a radioactive tracer, hydrogen bombs, fusion reactors
- H, D & T: all physical properties different, e.g. boiling point
- H, D & T: also chemical properties slightly different, e.g. covalent bond strength
- H-O bond weaker than the D-O bond (gets broken more easily)
  $\rightarrow$ electrolysis of water is utilized for the separation of D_2O from H_2O

$$^{6}_{3}Li + ^{1}_{0}n \dashrightarrow ^{4}_{2}He + ^{3}_{1}H$$

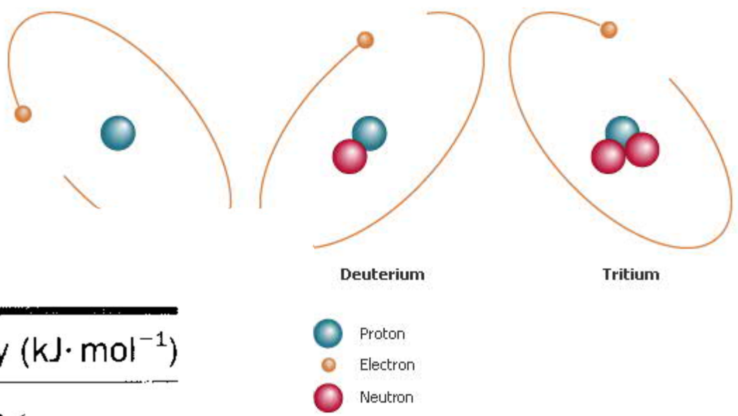


Table 10.1 Physical properties of the isotopes of hydrogen

Isotope	Molar mass ($g \cdot mol^{-1}$)	Boiling point (K)	Bond energy ($kJ \cdot mol^{-1}$)
H_2	2.02	20.6	436
D_2	4.03	23.9	443
T_2	6.03	25.2	447

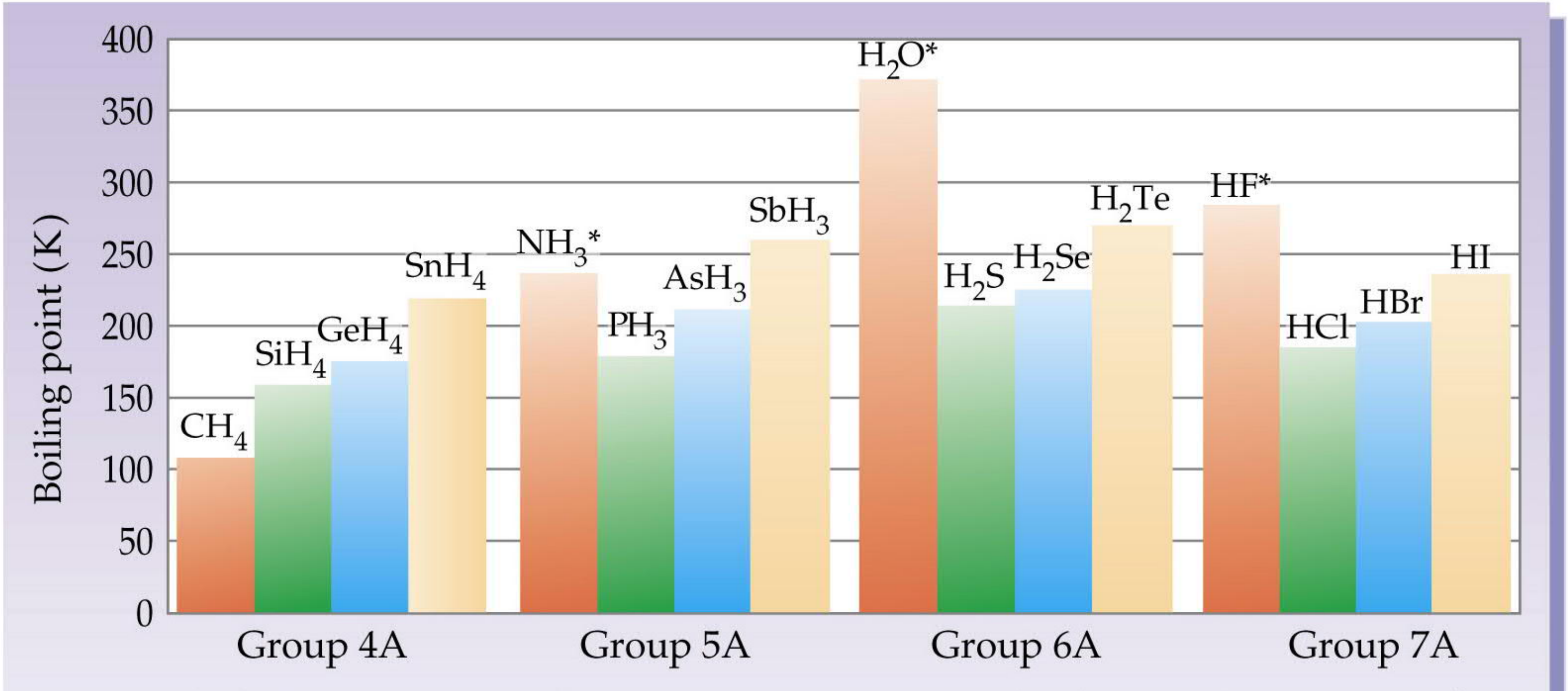
HYDRIDES

- Binary compounds of hydrogen
- Hydrogen forms hydrides with most of the elements
- Electronegativity of hydrogen only little higher than the average electronegativity of elements → many of the "hydrides" do not contain the H^- hydride ion
- Hydrides are categorized according to the type of bonding: ionic, covalent or metallic

- IONIC HYDRIDES

  - with alkali and alkaline earth metals (except Be, Mg)
  - metal cation and H^- ion
  - crystal structures similar to those of halides (Cl replaced by H)
  - very reactive, e.g.: $LiH + H_2O \rightarrow LiOH + H_2$
    (used as reductants)

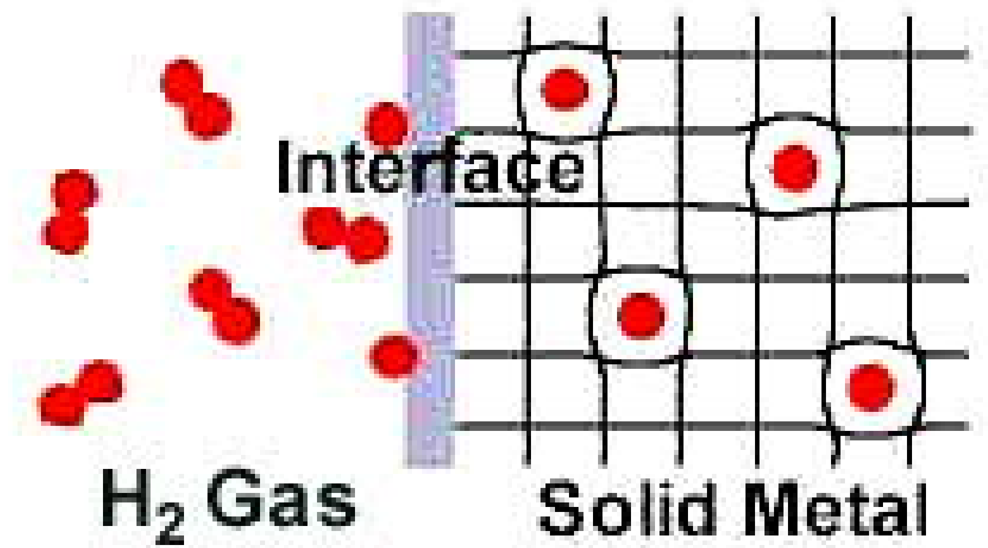
- **COVALENT HYDRIDES (not correct name for all these compounds)**
  - with all nonmetals (except noble gases) and the most electro-negative metals (Sn,Ga)
  - most of these hydrides are gaseous at room temperature

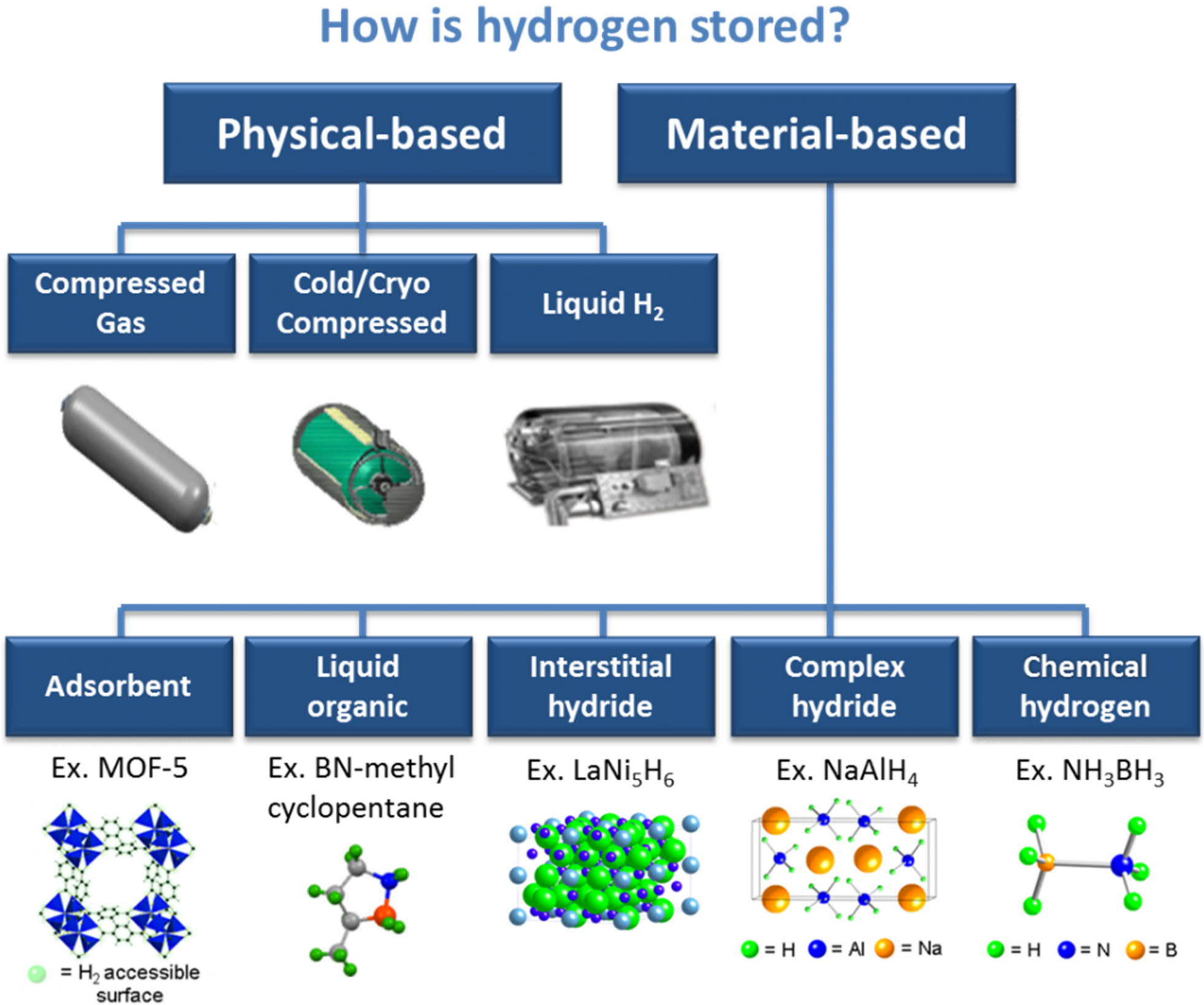


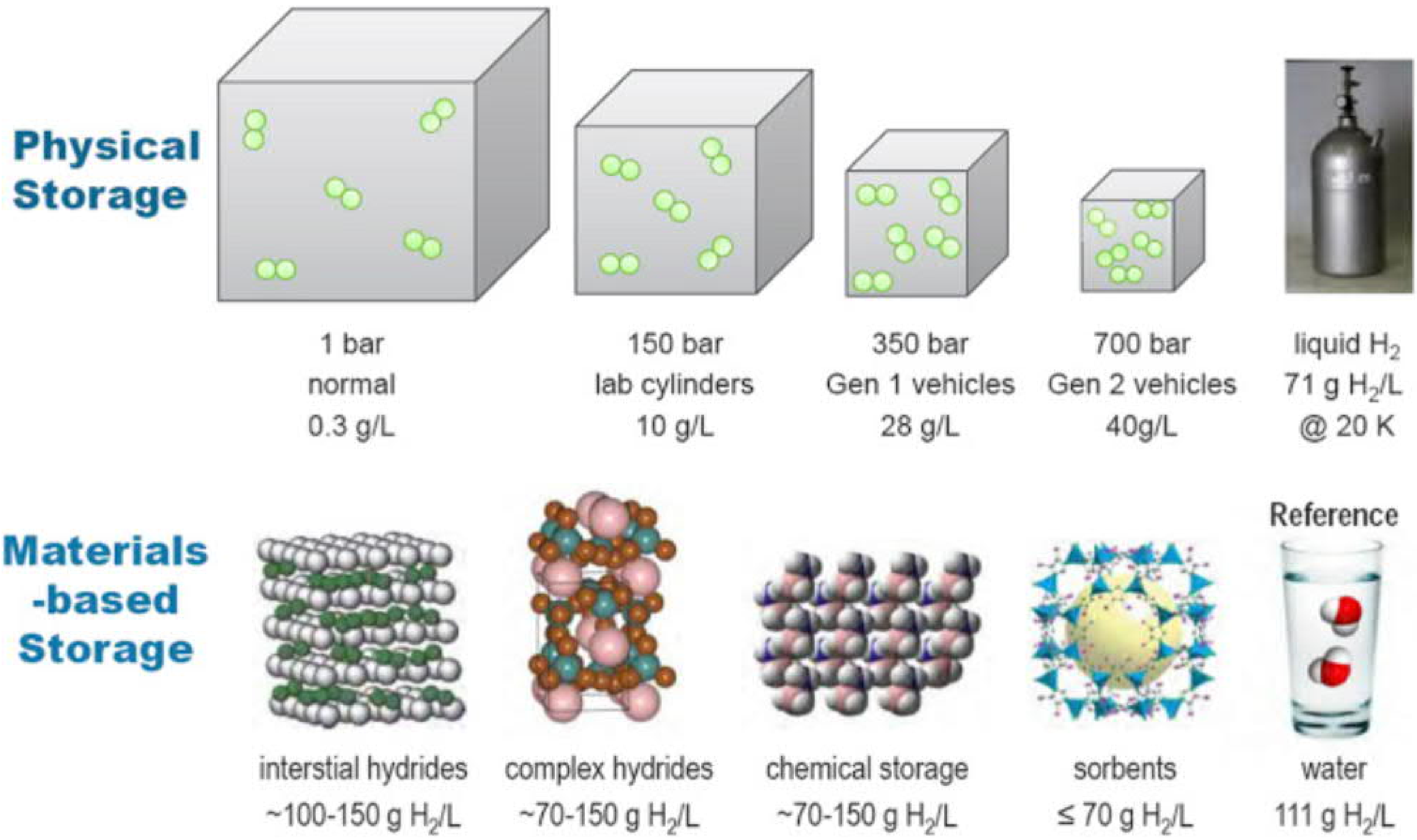
*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH_3), oxygen (H_2O), and fluorine (HF) have abnormally high boiling points because these molecules form hydrogen bonds.

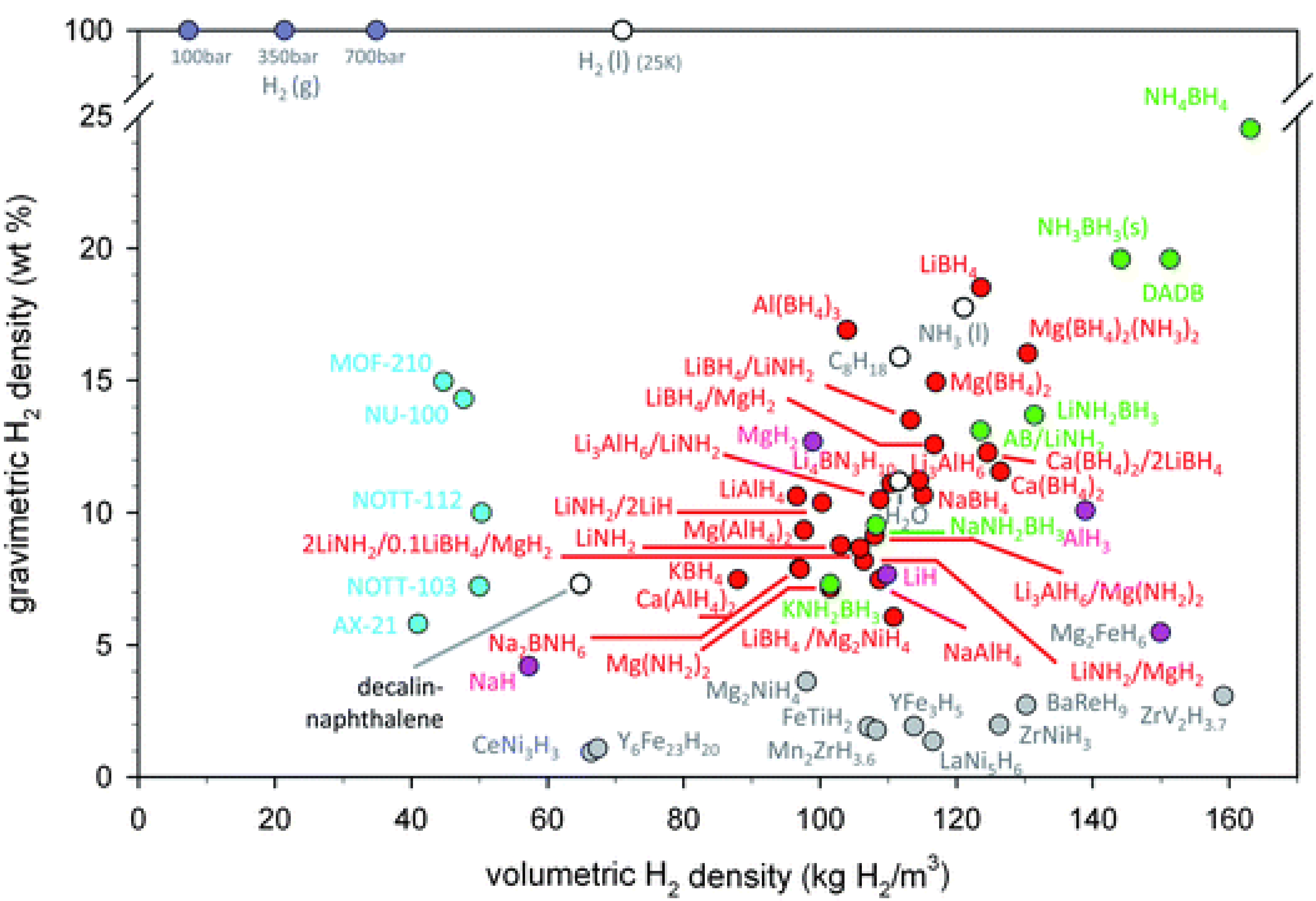
METALLIC (TRANSITION METAL) HYDRIDES

- solid materials
- hydrogen in interstitial positions
- often nontoichiometric, e.g. $TiH_{1.9}$
- volume increases upon hydrogen intercalation
  → no strong bonding (attraction)
- used for HYDROGEN STORAGE
  - $Ti + H_2$ + little heating/pressure → $TiH_{1.9}$
  - $TiH_{1.9}$ + higher temp. → $Ti + H_2$

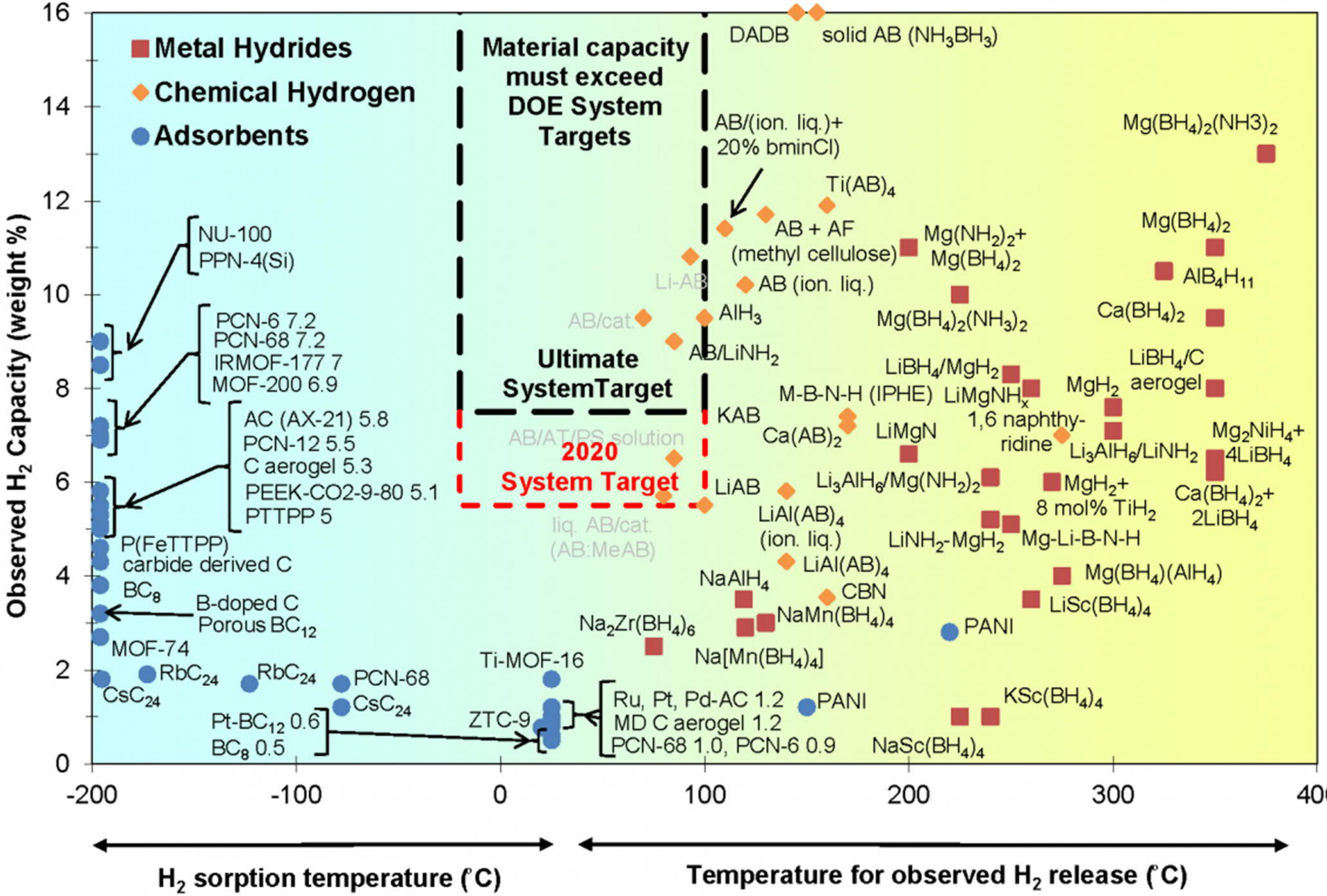



How is hydrogen stored?
Physical-based
Material-based
Compressed Gas
Cold/Cryo Compressed
Liquid H_2
Adsorbent
Liquid organic
Interstitial hydride
Complex hydride
Chemical hydrogen
Ex. MOF-5
Ex. BN-methyl cyclopentane
Ex. $LaNi_5H_6$
Ex. $NaAlH_4$
Ex. NH_3BH_3
= H_2 accessible surface
= H = Al = Na
= H = N = B


Physical Storage
1 bar
normal
0.3 g/L
150 bar
lab cylinders
10 g/L
350 bar
Gen 1 vehicles
28 g/L
700 bar
Gen 2 vehicles
40g/L
liquid H_2
71 g H_2/L
@ 20 K
Materials -based Storage
Reference
interstial hydrides
~100-150 g H_2/L
complex hydrides
~70-150 g H_2/L
chemical storage
~70-150 g H_2/L
sorbents
≤ 70 g H_2/L
water
111 g H_2/L

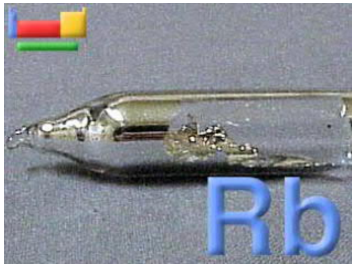


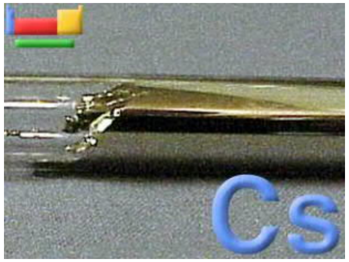
100bar
350bar
700bar
H2 (g)
H2 (l) (25K)
NH4BH4
NH3BH3(s)
DADB
LiBH4
Al(BH4)3
NH3 (l)
Mg(BH4)2(NH3)2
C8H18
LiBH4/LiNH2
Mg(BH4)2
LiBH4/MgH2
LiNH2BH3
MgH2
AB/LiNH2
Li3AlH6/LiNH2
Li4BN3H10
Li3AlH6
Ca(BH4)2/2LiBH4
Ca(BH4)2
LiAlH4
NaBH4
LiNH2/2LiH
H2O
Mg(AlH4)2
NaNH2BH3
AlH3
LiNH2
2LiNH2/0.1LiBH4/MgH2
KBH4
LiH
Li3AlH6/Mg(NH2)2
Ca(AlH4)2
KNH2BH3
Na2BNH6
LiBH4 /Mg2NiH4
Mg2FeH6
Mg(NH2)2
NaAlH4
LiNH2/MgH2
MOF-210
NU-100
NOTT-112
NOTT-103
AX-21
NaH
decalin-
naphthalene
Mg2NiH4
FeTiH2
YFe3H5
BaReH9
ZrV2H3.7
ZrNiH3
CeNi3H3
Y6Fe23H20
Mn2ZrH3.6
LaNi5H6
gravimetric H2 density (wt %)
volumetric H2 density (kg H2/m3)
0
5
10
15
20
25
100
0
20
40
60
80
100
120
140
160


Metal Hydrides
Chemical Hydrogen
Adsorbents
Material capacity must exceed DOE System Targets
Ultimate SystemTarget
2020 System Target
Observed H_2 Capacity (weight %)
H_2 sorption temperature (°C)
Temperature for observed H_2 release (°C)
DADB
solid AB (NH_3BH_3)
AB/(ion. liq.)+ 20% bminCl)
$Ti(AB)_4$
AB + AF (methyl cellulose)
Li-AB
AB (ion. liq.)
AB/cat.
AlH_3
$AB/LiNH_2$
KAB
AB/AT/PS solution
$Ca(AB)_2$
M-B-N-H (IPHE)
LiAB
liq. AB/cat. (AB:MeAB)
$LiAl(AB)_4$ (ion. liq.)
$LiAl(AB)_4$
CBN
$NaAlH_4$
$Na_2Zr(BH_4)_6$
$NaMn(BH_4)_4$
$Na[Mn(BH_4)_4]$
PANI
PANI
$Mg(BH_4)_2(NH3)_2$
$Mg(NH_2)_2$+ $Mg(BH_4)_2$
$Mg(BH_4)_2$
AlB_4H_{11}
$Mg(BH_4)_2(NH_3)_2$
$Ca(BH_4)_2$
$LiBH_4/MgH_2$
$LiMgNH_x$
MgH_2
$LiBH_4$/C aerogel
1,6 naphthy-ridine
LiMgN
$Li_3AlH_6/LiNH_2$
Mg_2NiH_4+ $4LiBH_4$
$Li_3AlH_6/Mg(NH_2)_2$
MgH_2+ 8 mol% TiH_2
$Ca(BH_4)_2$+ $2LiBH_4$
$LiNH_2$-MgH_2
Mg-Li-B-N-H
$Mg(BH_4)(AlH_4)$
$LiSc(BH_4)_4$
$KSc(BH_4)_4$
$NaSc(BH_4)_4$
NU-100
PPN-4(Si)
PCN-6 7.2
PCN-68 7.2
IRMOF-177 7
MOF-200 6.9
AC (AX-21) 5.8
PCN-12 5.5
C aerogel 5.3
PEEK-CO2-9-80 5.1
PTTPP 5
P(FeTTPP)
carbide derived C
BC_8
B-doped C
Porous BC_{12}
MOF-74
CsC_{24}
RbC_{24}
RbC_{24}
PCN-68
CsC_{24}
Ti-MOF-16
ZTC-9
Pt-BC_{12} 0.6
BC_8 0.5
Ru, Pt, Pd-AC 1.2
MD C aerogel 1.2
PCN-68 1.0, PCN-6 0.9

ALKALI METALS

- **Chemically highly coherent group, but lithium somewhat more different (diagonal relationship Li-Mg)**
- **Metal radius (Å):**
  Li 1.52 (Mg 1.60), Na 1.86, K 2.27, Rb 2.48, Cs 2.65
- **Ionic radius (Å):**
  Li 0.76 (Mg 0.72), Na 1.02, K 1.38, Rb 1.52, Cs 1.67
- **Charge/ionic radius:**
  Li 1.40, Na 0.88, K 0.66, Rb 0.60, Cs 0.55
- **Melting point (^{o}C): Li 180, Na 98, K 64, Rb 39, Cs 29**
- **Oxidation product: Li_2O, Na_2O/Na_2O_2, K_2O_2, KO_2, RbO_2, CsO_2**
- **Li compounds more covalent than others**
- **Li compounds dissolve more easily into nonpolar solvents, and less into water**
- **Only Li forms the nitride, Li_3N (ref. Mg_3N_2)**
- **Li salts often contain water of crystallization,**
  e.g. $LiClO_4 \bullet 3H_2O$ (ref. $MgClO_4 \bullet 6H_2O$)





ALKALI *VERSUS* ALKALINE EARTH METALS

- **Alkaline earth metals have larger Z_{eff} than alkali metals**

  → **smaller**
  → **denser**
  → **harder**

- **Alkaline earth metals have two valence electrons per atom**

  → **metal bonds stronger**
  → **better electrical conductivity**
  → **higher melting and boiling points**

	Li/Be	Na/Mg	K/Ca	Rb/Sr	Cs/Ba
Electronegativity	1.0/1.5	0.9/1.2	0.8/1.0	0.8/1.0	0.7/0.9
Metal radius (Å)	1.52/1.12	1.86/1.60	2.27/1.97	2.48/2.15	2.65/2.22
Density (g/cm^3)	0.53/1.85	0.97/1.74	0.86/1.55	1.53/2.63	1.87/3.59
Melting point (^{o}C)	181/1289	98/650	64/842	40/769	28/729
RT-resistivity (μohm cm)	9.47/3.70	4.89/4.48	7.39/3.42	13.1/13.4	

LITHIUM-ION BATTERY

- **WHY Lithium:** the lightest of all metals & the greatest electrochemical potential & the largest energy density per weight & small and easy/fast to move
- Charging: Li-ions from cathode to anode; Discharging: Li-ions from anode to cathode
- Commercialization: Sony 1991
- Used: portable electronics

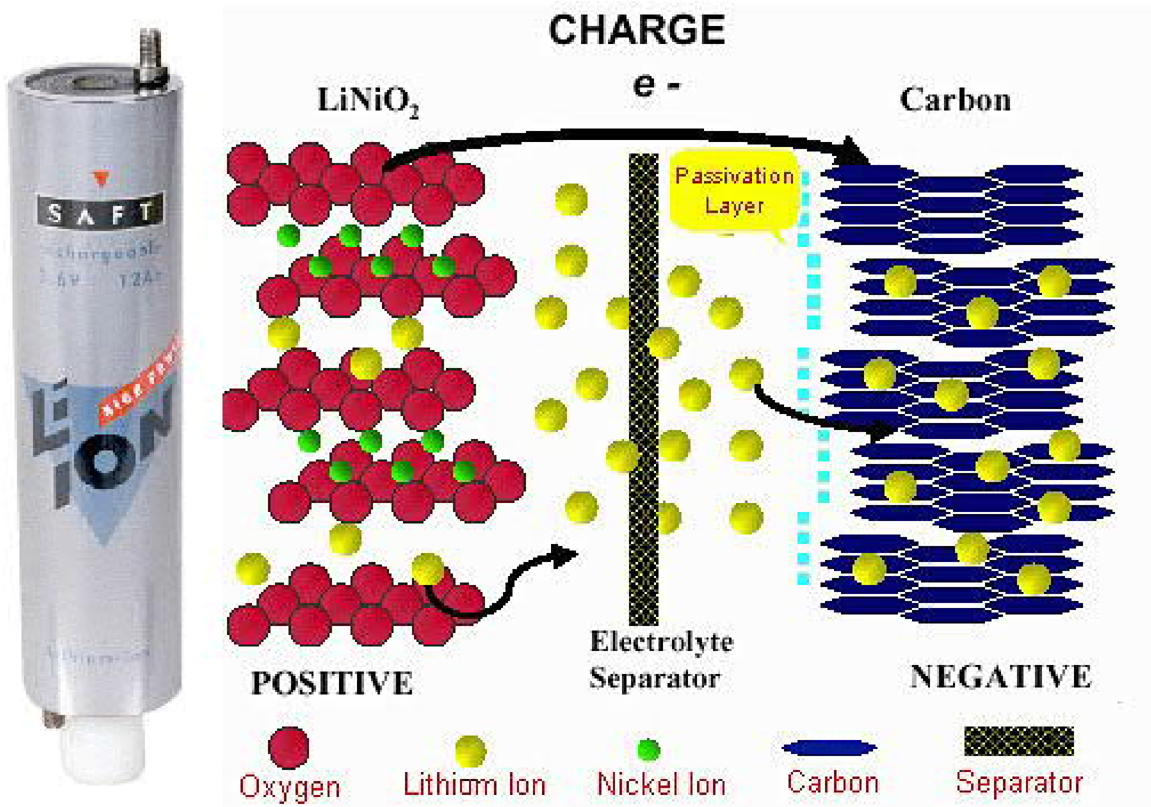
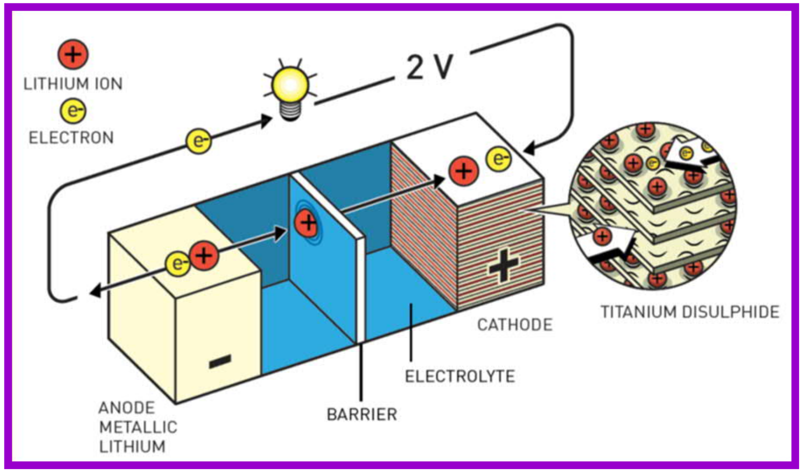
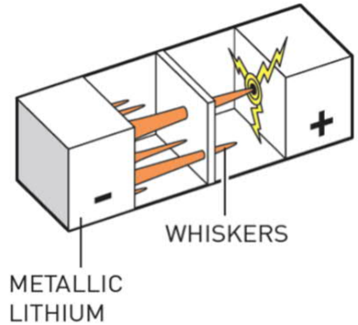
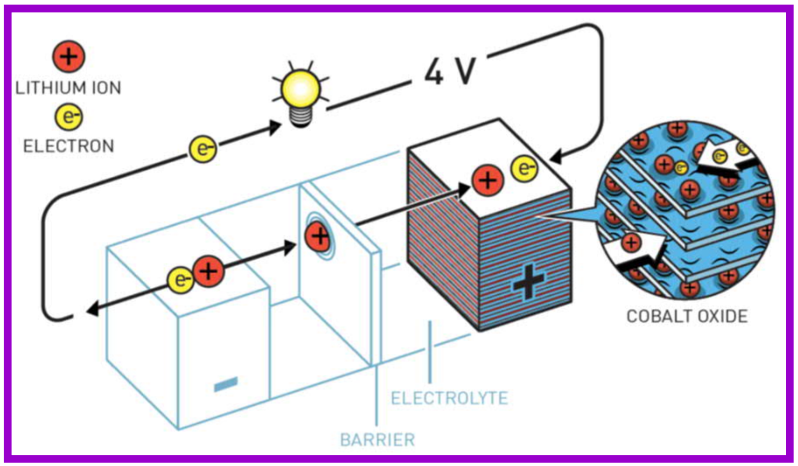


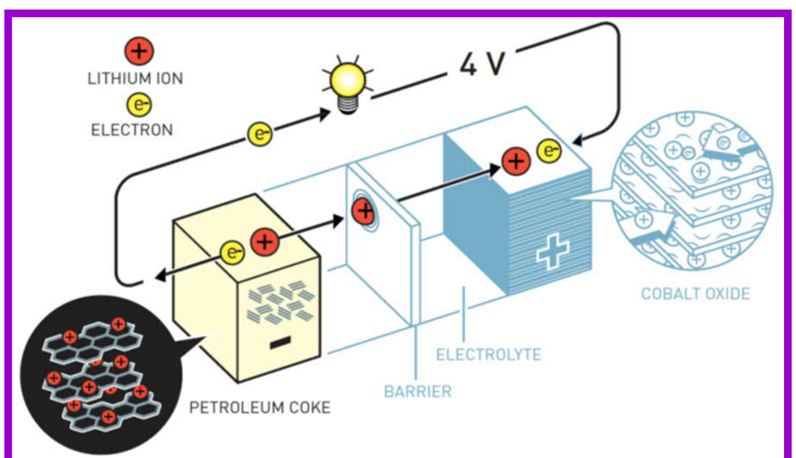
Photo Courtesy of SAFT America





Chemistry Nobel 2019





Stanley Whittingham (born 1941 UK):
- Exxon: TiS_2 cathode 1976

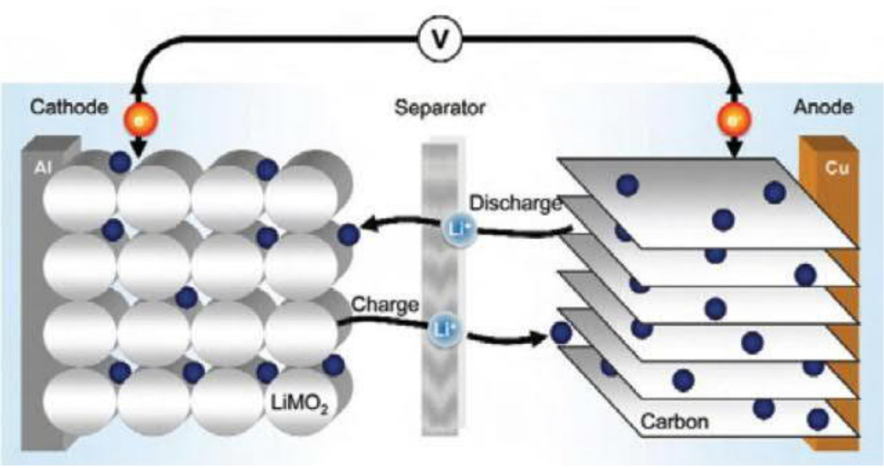
John Goodenough (born 1922 USA/Ger):
- Univ. Oxford: $LiCoO_2$ cathode 1980

Akira Yoshino (born 1948 Jpn):
- Asahi Kasei: carbon-based anode 1985

Commercialization: Sony 1991

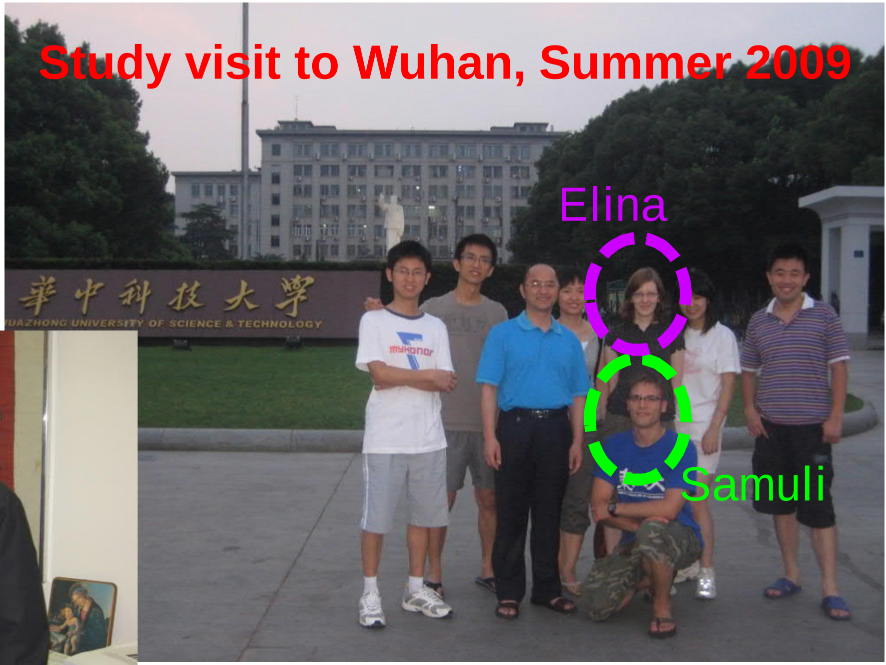
Current Li-ion battery materials

CATHODE:	**$LiCoO_2$**
	$Li(Co_{1/3}Mn_{1/3}Ni_{1/3})O_2$, $LiMn_2O_4$, $LiFePO_4$
ANODE:	**Grafite**
	Si, $Li_4Ti_5O_{12}$
ELECTROLYTE:	**$LiPF_6$ + ethylene carbonate solvent**
	Solid electrolyte materials
BINDERS:	**PVDF (polyvinyldifluoride) + NMP (N-methylpyrrolidone)**
	Vesiliukoiset sidosaineet



Prof. Goodenough, 2005

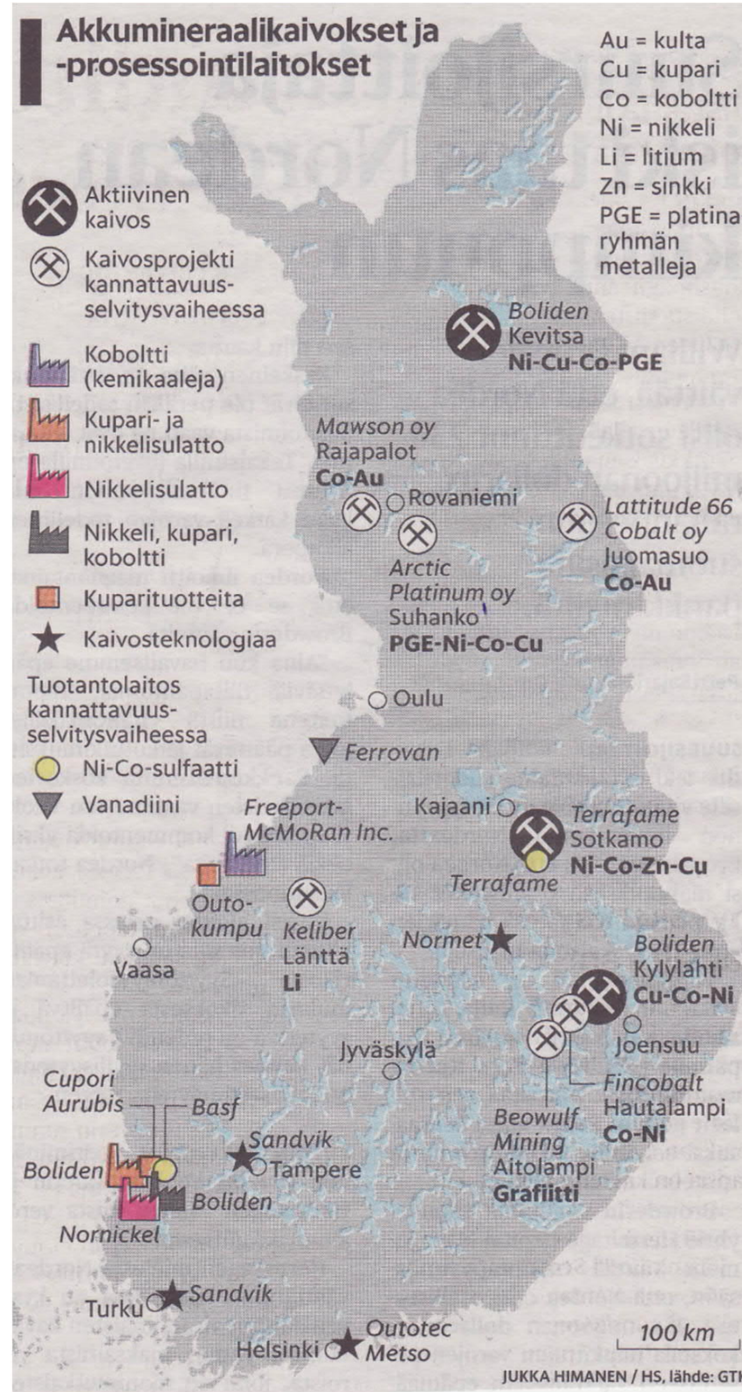
Dr. Huang, Texas 2005



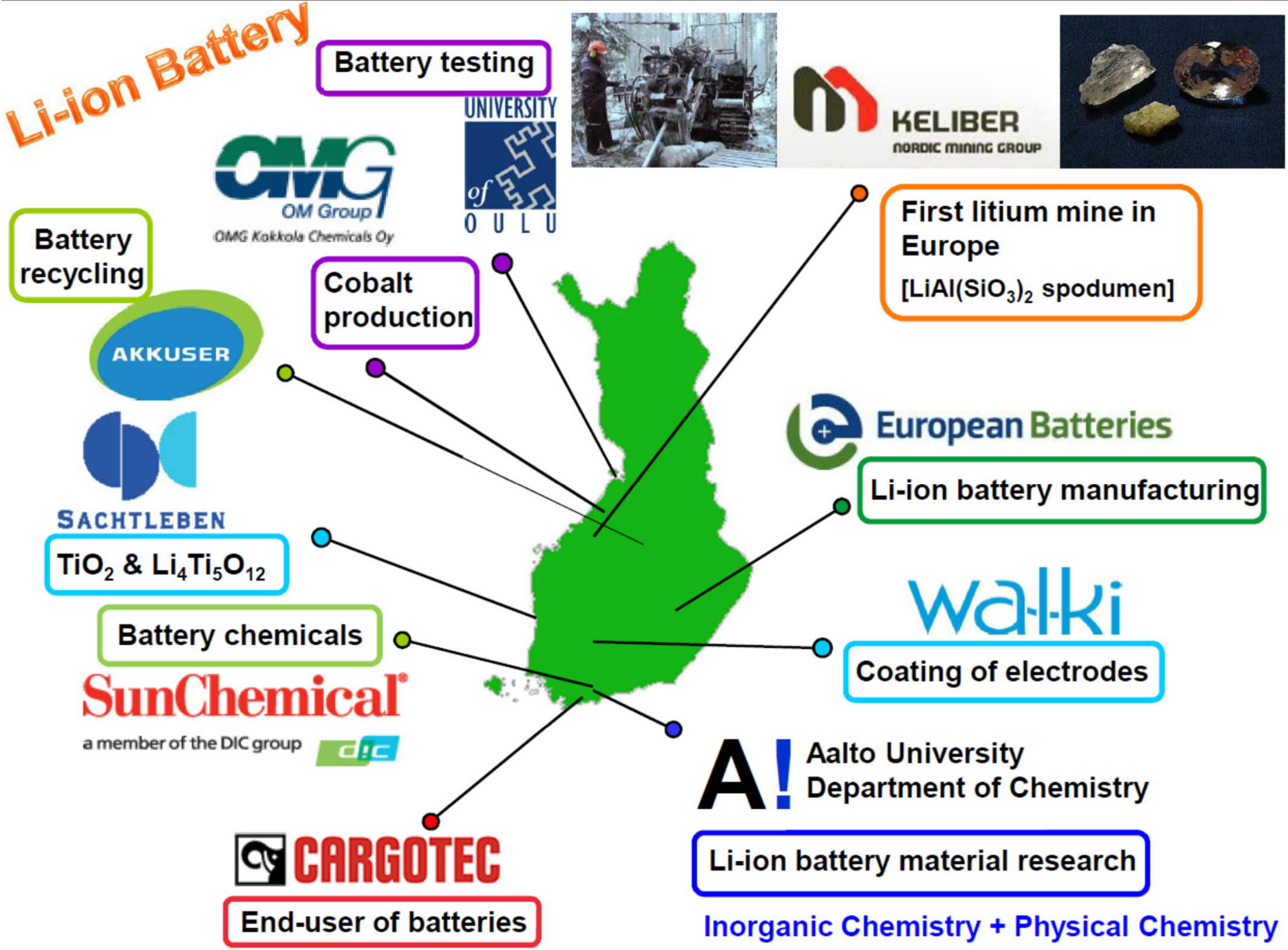
Study visit to Wuhan, Summer 2009

Research group of Prof. Huang, 2010

Visit to Prof. Huang’s company, 2012



Akkumineraalikaivokset ja -prosessointilaitokset
Au = kulta
Cu = kupari
Co = koboltti
Ni = nikkeli
Li = litium
Zn = sinkki
PGE = platinaryhmän metalleja
Aktiivinen kaivos
Kaivosprojekti kannattavuusselvitysvaiheessa
Koboltti (kemikaaleja)
Kupari- ja nikkelisulatto
Nikkelisulatto
Nikkeli, kupari, koboltti
Kuparituotteita
Kaivosteknologiaa
Tuotantolaitos kannattavuusselvitysvaiheessa
Ni-Co-sulfaatti
Vanadiini
Boliden Kevitsa Ni-Cu-Co-PGE
Mawson oy Rajapalot Co-Au
Rovaniemi
Lattitude 66 Cobalt oy Juomasuo Co-Au
Arctic Platinum oy Suhanko PGE-Ni-Co-Cu
Oulu
Ferrovan
Kajaani
Terrafame Sotkamo Ni-Co-Zn-Cu
Terrafame
Freeport-McMoRan Inc.
Outokumpu
Keliber Länttä Li
Normet
Vaasa
Boliden Kylylahti Cu-Co-Ni
Joensuu
Jyväskylä
Fincobalt Hautalampi Co-Ni
Beowulf Mining Aitolampi Grafiitti
Cupori Aurubis
Basf
Sandvik
Tampere
Boliden
Boliden
Nornickel
Sandvik
Turku
Outotec Metso
Helsinki
100 km
JUKKA HIMANEN / HS, lähde: GTK


Li-ion Battery
Battery testing
UNIVERSITY of OULU
OMG
OM Group
OMG Kokkola Chemicals Oy
KELIBER
NORDIC MINING GROUP
First litium mine in Europe
[$LiAl(SiO_3)_2$ spodumen]
Battery recycling
Cobalt production
AKKUSER
European Batteries
Li-ion battery manufacturing
SACHTLEBEN
TiO_2 & $Li_4Ti_5O_{12}$
walki
Coating of electrodes
Battery chemicals
SunChemical
a member of the DIC group
Aalto University
Department of Chemistry
CARGOTEC
Li-ion battery material research
End-user of batteries
Inorganic Chemistry + Physical Chemistry