



New battery technologies demand new electrolyte concepts?!

hydrogen	1	H	boron	4	Be
helium	2	He	nitrogen	7	N
lithium	3	Li	oxygen	8	O
beryllium	4	Be	fluorine	9	F
magnesium	12	Mg	neon	10	Ne
potassium	19	K	silicon	14	Si
calcium	20	Ca	carbon	6	C
rubidium	37	Rb	nitrogen	7	N
sodium	11	Na	manganese	25	Mn
magnesium	12	Mg	iron	26	Fe
aluminum	13	Al	cobalt	27	Co
chromium	24	Cr	copper	29	Cu
manganese	25	Mn	zinc	30	Zn
nickel	26	Ni	gallium	31	Ga
cobalt	27	Co	germanium	32	Ge
nickel	28	Ni	arsenic	33	As
copper	29	Cu	se	34	Se
zinc	30	Zn	bromine	35	Br
gallium	31	Ga	kr	36	Kr
germanium	32	Ge	tin	32	Ti
arsenic	33	As	lead	34	Pb
se	34	Se	tin	35	Tl
bromine	35	Br	antimony	32	Sb
kr	36	Kr	tin	33	Sn
tin	32	Ti	lead	34	Po
lead	34	Pb	tin	35	At
tin	35	Tl	lead	36	Rn
lead	36	Rn	tin	37	Uuo
tin	37	Uuo	lead	38	Uuq

* Lanthanide series	57	La	cerium	58	Ce	praseodymium	59	Pr	neodymium	60	Nd	promethium	61	Pm	samarium	62	Sm	europium	63	Eu	gadolinium	64	Gd	thulium	65	Tb	dysprosium	66	Dy	holmium	67	Ho	erbium	68	Er	thulium	69	Tm	ytterbium	70	Yb																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
** Actinide series	90	Ac	thorium	91	Th	protactinium	92	Pa	uranium	93	U	neptunium	94	Np	plutonium	95	Pu	americium	96	Am	curium	97	Cm	berkelium	98	Bk	californium	99	Cf	einsteinium	100	Es	fermium	101	Md	mendelevium	102	No	nobelium	103	Rf	rutherfordium	104	Lr	lawrencium	105	Db	dubnium	106	Sg	seaborgium	107	Bh	bohrium	108	Hs	hahnium	109	Mt	moscovium	110	Uuu	ununtrium	111	Uub	ununbium	112	Uuq	ununquadium	113	Uuo	ununoctium	114	Uuo	ununoctium	115	Uuq	ununoctium	116	Uuo	ununoctium	117	Uuo	ununoctium	118	Uuo	ununoctium	119	Uuo	ununoctium	120	Uuo	ununoctium	121	Uuo	ununoctium	122	Uuo	ununoctium	123	Uuo	ununoctium	124	Uuo	ununoctium	125	Uuo	ununoctium	126	Uuo	ununoctium	127	Uuo	ununoctium	128	Uuo	ununoctium	129	Uuo	ununoctium	130	Uuo	ununoctium	131	Uuo	ununoctium	132	Uuo	ununoctium	133	Uuo	ununoctium	134	Uuo	ununoctium	135	Uuo	ununoctium	136	Uuo	ununoctium	137	Uuo	ununoctium	138	Uuo	ununoctium	139	Uuo	ununoctium	140	Uuo	ununoctium	141	Uuo	ununoctium	142	Uuo	ununoctium	143	Uuo	ununoctium	144	Uuo	ununoctium	145	Uuo	ununoctium	146	Uuo	ununoctium	147	Uuo	ununoctium	148	Uuo	ununoctium	149	Uuo	ununoctium	150	Uuo	ununoctium	151	Uuo	ununoctium	152	Uuo	ununoctium	153	Uuo	ununoctium	154	Uuo	ununoctium	155	Uuo	ununoctium	156	Uuo	ununoctium	157	Uuo	ununoctium	158	Uuo	ununoctium	159	Uuo	ununoctium	160	Uuo	ununoctium	161	Uuo	ununoctium	162	Uuo	ununoctium	163	Uuo	ununoctium	164	Uuo	ununoctium	165	Uuo	ununoctium	166	Uuo	ununoctium	167	Uuo	ununoctium	168	Uuo	ununoctium	169	Uuo	ununoctium	170	Uuo	ununoctium	171	Uuo	ununoctium	172	Uuo	ununoctium	173	Uuo	ununoctium	174	Uuo	ununoctium	175	Uuo	ununoctium	176	Uuo	ununoctium	177	Uuo	ununoctium	178	Uuo	ununoctium	179	Uuo	ununoctium	180	Uuo	ununoctium	181	Uuo	ununoctium	182	Uuo	ununoctium	183	Uuo	ununoctium	184	Uuo	ununoctium	185	Uuo	ununoctium	186	Uuo	ununoctium	187	Uuo	ununoctium	188	Uuo	ununoctium	189	Uuo	ununoctium	190	Uuo	ununoctium	191	Uuo	ununoctium	192	Uuo	ununoctium	193	Uuo	ununoctium	194	Uuo	ununoctium	195	Uuo	ununoctium	196	Uuo	ununoctium	197	Uuo	ununoctium	198	Uuo	ununoctium	199	Uuo	ununoctium	200	Uuo	ununoctium	201	Uuo	ununoctium	202	Uuo	ununoctium	203	Uuo	ununoctium	204	Uuo	ununoctium	205	Uuo	ununoctium	206	Uuo	ununoctium	207	Uuo	ununoctium	208	Uuo	ununoctium	209	Uuo	ununoctium	210	Uuo	ununoctium	211	Uuo	ununoctium	212	Uuo	ununoctium	213	Uuo	ununoctium	214	Uuo	ununoctium	215	Uuo	ununoctium	216	Uuo	ununoctium	217	Uuo	ununoctium	218	Uuo	ununoctium	219	Uuo	ununoctium	220	Uuo	ununoctium	221	Uuo	ununoctium	222	Uuo	ununoctium	223	Uuo	ununoctium	224	Uuo	ununoctium	225	Uuo	ununoctium	226	Uuo	ununoctium	227	Uuo	ununoctium	228	Uuo	ununoctium	229	Uuo	ununoctium	230	Uuo	ununoctium	231	Uuo	ununoctium	232	Uuo	ununoctium	233	Uuo	ununoctium	234	Uuo	ununoctium	235	Uuo	ununoctium	236	Uuo	ununoctium	237	Uuo	ununoctium	238	Uuo	ununoctium	239	Uuo	ununoctium	240	Uuo	ununoctium	241	Uuo	ununoctium	242	Uuo	ununoctium	243	Uuo	ununoctium	244	Uuo	ununoctium	245	Uuo	ununoctium	246	Uuo	ununoctium	247	Uuo	ununoctium	248	Uuo	ununoctium	249	Uuo	ununoctium	250	Uuo	ununoctium	251	Uuo	ununoctium	252	Uuo	ununoctium	253	Uuo	ununoctium	254	Uuo	ununoctium	255	Uuo	ununoctium	256	Uuo	ununoctium	257	Uuo	ununoctium	258	Uuo	ununoctium	259	Uuo	ununoctium	260	Uuo	ununoctium	261	Uuo	ununoctium	262	Uuo	ununoctium	263	Uuo	ununoctium	264	Uuo	ununoctium	265	Uuo	ununoctium	266	Uuo	ununoctium	267	Uuo	ununoctium	268	Uuo	ununoctium	269	Uuo	ununoctium	270	Uuo	ununoctium	271	Uuo	ununoctium	272	Uuo	ununoctium	273	Uuo	ununoctium	274	Uuo	ununoctium	275	Uuo	ununoctium	276	Uuo	ununoctium	277	Uuo	ununoctium	278	Uuo	ununoctium	279	Uuo	ununoctium	280	Uuo	ununoctium	281	Uuo	ununoctium	282	Uuo	ununoctium	283	Uuo	ununoctium	284	Uuo	ununoctium	285	Uuo	ununoctium	286	Uuo	ununoctium	287	Uuo	ununoctium	288	Uuo	ununoctium	289	Uuo	ununoctium	290	Uuo	ununoctium	291	Uuo	ununoctium	292	Uuo	ununoctium	293	Uuo	ununoctium	294	Uuo	ununoctium	295	Uuo	ununoctium	296	Uuo	ununoctium	297	Uuo	ununoctium	298	Uuo	ununoctium	299	Uuo	ununoctium	300	Uuo	ununoctium	301	Uuo	ununoctium	302	Uuo	ununoctium	303	Uuo	ununoctium	304	Uuo	ununoctium	305	Uuo	ununoctium	306	Uuo	ununoctium	307	Uuo	ununoctium	308	Uuo	ununoctium	309	Uuo	ununoctium	310	Uuo	ununoctium	311	Uuo	ununoctium	312	Uuo	ununoctium	313	Uuo	ununoctium	314	Uuo	ununoctium	315	Uuo	ununoctium	316	Uuo	ununoctium	317	Uuo	ununoctium	318	Uuo	ununoctium	319	Uuo	ununoctium	320	Uuo	ununoctium	321	Uuo	ununoctium	322	Uuo	ununoctium	323	Uuo	ununoctium	324	Uuo	ununoctium	325	Uuo	ununoctium	326	Uuo	ununoctium	327	Uuo	ununoctium	328	Uuo	ununoctium	329	Uuo	ununoctium	330	Uuo	ununoctium	331	Uuo	ununoctium	332	Uuo	ununoctium	333	Uuo	ununoctium	334	Uuo	ununoctium	335	Uuo	ununoctium	336	Uuo	ununoctium	337	Uuo	ununoctium	338	Uuo	ununoctium	339	Uuo	ununoctium	340	Uuo	ununoctium	341	Uuo	ununoctium	342	Uuo	ununoctium	343	Uuo	ununoctium	344	Uuo	ununoctium	345	Uuo	ununoctium	346	Uuo	ununoctium	347	Uuo	ununoctium	348	Uuo	ununoctium	349	Uuo	ununoctium	350	Uuo	ununoctium	351	Uuo	ununoctium	352	Uuo	ununoctium	353	Uuo	ununoctium	354	Uuo	ununoctium	355	Uuo	ununoctium	356	Uuo	ununoctium	357	Uuo	ununoctium	358	Uuo	ununoctium	359	Uuo	ununoctium	360	Uuo	ununoctium	361	Uuo	ununoctium	362	Uuo	ununoctium	363	Uuo	ununoctium	364	Uuo	ununoctium	365	Uuo	ununoctium	366	Uuo	ununoctium	367	Uuo	ununoctium	368	Uuo	ununoctium	369	Uuo	ununoctium	370	Uuo	ununoctium	371	Uuo	ununoctium	372	Uuo	ununoctium	373	Uuo	ununoctium	374	Uuo	ununoctium	375	Uuo	ununoctium	376	Uuo	ununoctium	377	Uuo	ununoctium	378	Uuo	ununoctium	379	Uuo	ununoctium	380	Uuo	ununoctium	381	Uuo	ununoctium	382	Uuo	ununoctium	383	Uuo	ununoctium	384	Uuo	ununoctium	385	Uuo	ununoctium	386	Uuo	ununoctium	387	Uuo	ununoctium	388	Uuo	ununoctium	389	Uuo	ununoctium	390	Uuo	ununoctium	391	Uuo	ununoctium	392	Uuo	ununoctium	393	Uuo	ununoctium	394	Uuo	ununoctium	395	Uuo	ununoctium	396	Uuo	ununoctium	397	Uuo	ununoctium	398	Uuo	ununoctium	399	Uuo	ununoctium	400	Uuo	ununoctium	401	Uuo	ununoctium	402	Uuo	ununoctium	403	Uuo	ununoctium	404	Uuo	ununoctium	405	Uuo	ununoctium	406	Uuo	ununoctium	407	Uuo	ununoctium	408	Uuo	ununoctium	409	Uuo	ununoctium	410	Uuo	ununoctium	411	Uuo	ununoctium	412	Uuo	ununoctium	413	Uuo	ununoctium	414	Uuo	ununoctium	415	Uuo	ununoctium	416	Uuo	ununoctium	417	Uuo	ununoctium	418	Uuo	ununoctium	419	Uuo	ununoctium	420	Uuo	ununoctium	421	Uuo	ununoctium	422	Uuo	ununoctium	423	Uuo	ununoctium	424	Uuo	ununoctium	425	Uuo	ununoctium	426	Uuo	ununoctium	427	Uuo	ununoctium	428	Uuo	ununoctium	429	Uuo	ununoctium	430	Uuo	ununoctium	431	Uuo	ununoctium	432	Uuo	ununoctium	433	Uuo	ununoctium	434	Uuo	ununoctium	435	Uuo	ununoctium	436	Uuo	ununoctium	437	Uuo	ununoctium	438	Uuo	ununoctium	439	Uuo	ununoctium	440	Uuo	ununoctium	441	Uuo	ununoctium	442	Uuo	ununoctium	443	Uuo	ununoctium	444	Uuo	ununoctium	445	Uuo	ununoctium	446	Uuo	ununoctium	447	Uuo	ununoctium	448	Uuo	ununoctium	449	Uuo	ununoctium	450	Uuo	ununoctium	451	Uuo	ununoctium	452	Uuo	ununoctium	453	Uuo	ununoctium	454	Uuo	ununoctium	455	Uuo	ununoctium	456	Uuo	ununoctium	457	Uuo	ununoctium	458	Uuo	ununoctium	459	Uuo	ununoctium	460	Uuo	ununoctium	461	Uuo	ununoctium	462	Uuo	ununoctium	463	Uuo	ununoctium	464	Uuo	ununoctium	465	Uuo	ununoctium	466	Uuo	ununoctium	467	Uuo	ununoctium	468	Uuo	ununoctium	469	Uuo	ununoctium	470	Uuo	ununoctium	471	Uuo	ununoctium	472	Uuo	ununoctium	473	Uuo	ununoctium	474	Uuo	ununoctium	475	Uuo	ununoctium	476	Uuo	ununoctium	477	Uuo	ununoctium	478	Uuo	ununoctium	479	Uuo	ununoctium	480	Uuo	ununoctium	481	Uuo	ununoctium	482	Uuo	ununoctium	483	Uuo	ununoctium	484	Uuo	ununoctium	485	Uuo	ununoctium	486	Uuo	ununoctium	487	Uuo	ununoctium	488	Uuo	ununoctium	489	Uuo	ununoctium	490	Uuo	ununoctium	491	Uuo	ununoctium	492	Uuo	ununoctium	493	Uuo	ununoctium	494	Uuo	ununoctium	495	Uuo	ununoctium	496	Uuo	ununoctium	497	Uuo	ununoctium	498	Uuo	ununoctium	499	Uuo	ununoctium	500	Uuo

Acknowledgements



HONDA



J. Scheers



S. Jeschke



R. Arvidsson T. Mandai



N. Lindahl



M. Kerner



N. Plylahan



R. Palacín



R. Dominko



Patrik Johansson



Layout & Learning Outcomes

Next Generation Batteries (NGBs) – a crash-course

- Why? Who cares?
- 3 Perspectives
- Examples



What are NGBs and why should we care?

=> Motivation, basics, examples, critical properties,...

NGB Electrolytes – from fundamentals to application

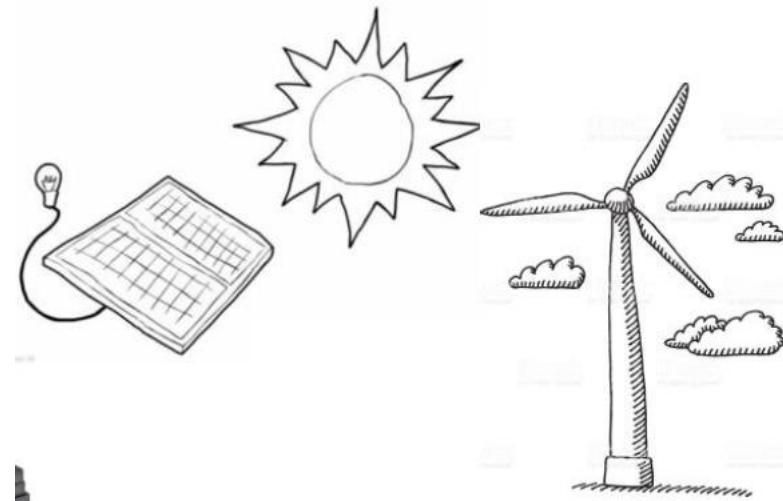
- General functionalities
- Special NGB demands & limits
- Common measures
- Examples



How are NGB electrolytes composed and why?

=> Material choices and motivations, differences, problems,...





1. Nanosensors and the Internet of Nanothings – With the Internet of Things expected to comprise 30 billion connected devices by 2020, one of the most exciting areas of focus today is now on nanosensors capable of circulating in the human body or being embedded in construction materials. Once connected, this Internet of Nanothings could have a huge impact on the future of medicine, architecture, agriculture and drug manufacture.



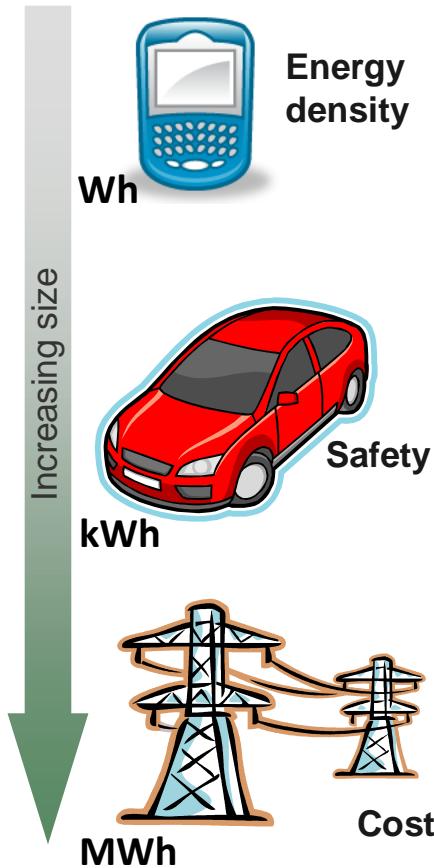
2. Next Generation Batteries – One of the greatest obstacles holding renewable energy back is matching supply with demand, but recent advances in energy storage using sodium, aluminium and zinc based batteries makes mini-grids feasible that can provide clean, reliable, round the clock energy sources to entire villages.





Performance

Energy
Power
Life-length
Safety
Cost
...
Driving range
Charging time



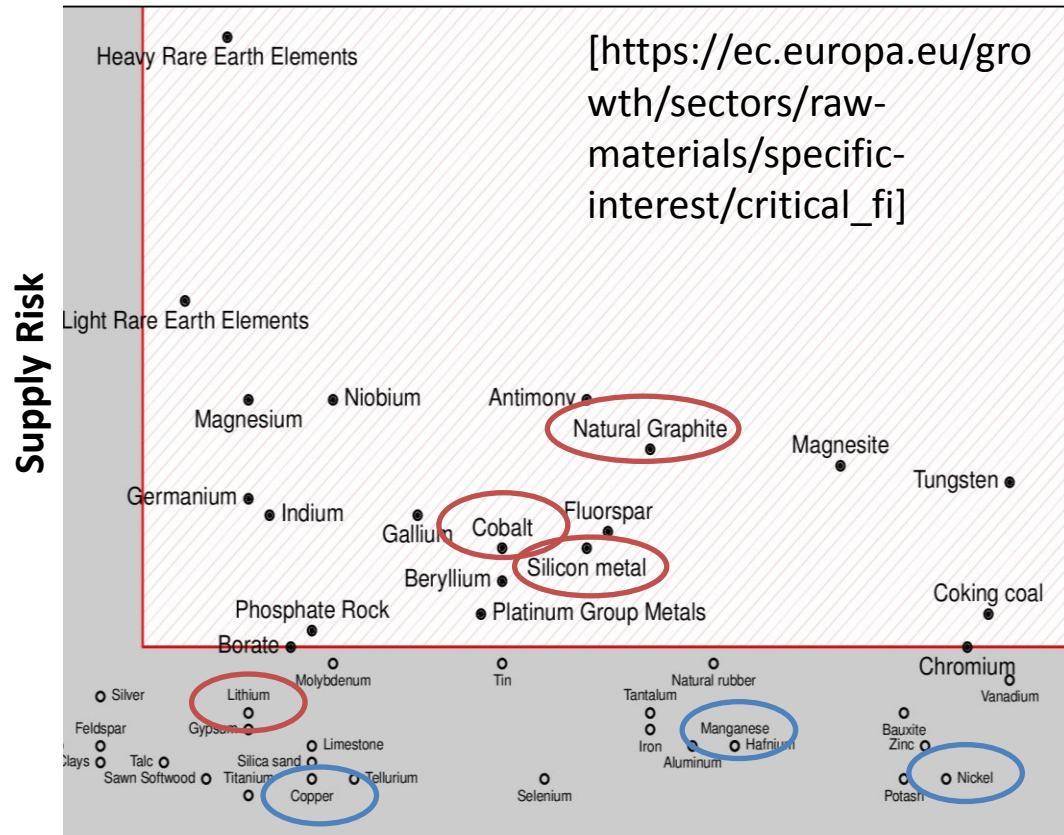
"New" Applications
=>
New demands





Sustainability

- Resources**
- Production**
- Efficiency**
- 2nd use**
- Recycling**
- ...

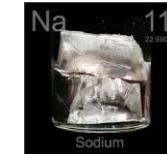


Economic importance



**Abundance
in Earth's crust:**

20 ppm



22700 ppm





Curiosity

"Technology is always limited by the materials available"
- DARPA 1960's

What if...?

How can...?

Can we...?

...

hydrogen 1 H 1.0079	beryllium 4 Be	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 16.000	fluorine 9 F 18.998	neon 10 Ne 20.190
lithium 3 Li 6.941	magnesium 12 Mg 24.320	silicon 14 Si 28.096	sulfur 16 S 32.065	phosphorus 15 P 30.974	arsenic 33 As 74.922	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vandium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.905	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc 98.001	ruthenium 44 Ru 101.07
cesium 55 Cs 132.91	boron 56 Ba 137.33	lutetium 71 Lu 174.97	zirconium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23
francium 87 Fr 223.0	radium 88 Ra 226.0	lawrencium 103 Lr 262.0	rutherfordium 104 Rf 261.0	dubnium 105 Db 262.0	seaborgium 106 Sg 269.0	bohrium 107 Bh 264.0	hassium 108 Hs 269.0
*	*	57-70	*	106-121	107-122	108-123	109-124
francium 87 Fr 223.0	radium 88 Ra 226.0	lawrencium 103 Lr 262.0	rutherfordium 104 Rf 261.0	dubnium 105 Db 262.0	seaborgium 106 Sg 269.0	bohrium 107 Bh 264.0	hassium 108 Hs 269.0
francium 87 Fr 223.0	radium 88 Ra 226.0	lawrencium 103 Lr 262.0	rutherfordium 104 Rf 261.0	dubnium 105 Db 262.0	seaborgium 106 Sg 269.0	bohrium 107 Bh 264.0	hassium 108 Hs 269.0

* Lanthanide series

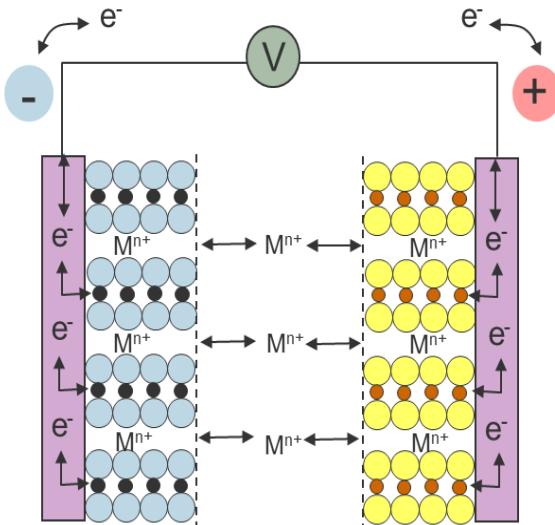
** Actinide series

lanthanum 57 La 139.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	proneodymium 61 Pm 149.04	samarium 62 Sm 150.36	europeium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 169.93	yterbium 70 Yb 173.04
actinium 89 Ac 227.0	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np 237.01	plutonium 94 Pu 244.0	americium 95 Am 243.0	curium 96 Cm 247.0	berkelium 97 Bk 247.0	californium 98 Cf 251.0	einsteinium 99 Es 252.0	fermium 100 Fm 257.0	mendelevium 101 Md 258.0	nobelium 102 No 259.0





Metal-ion batteries: Na-ion (SIB/NIB)



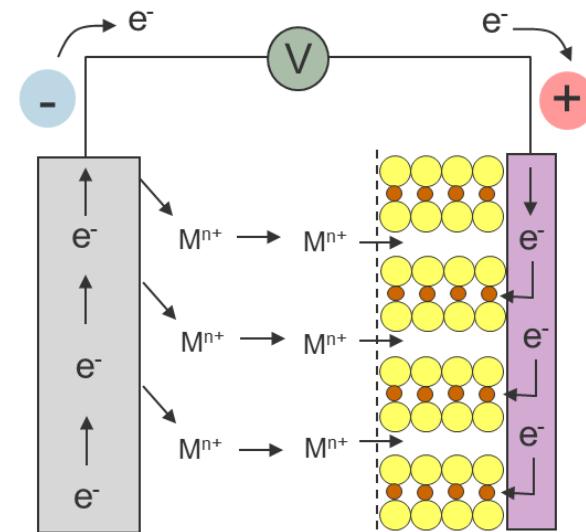
Intercalation of M^+ into electrodes

No pure metal inside the battery (= LIBs)

Capacity not intrinsically = $f(\text{metal})$

Metal batteries:

- Li, Li-S, Li-O₂
- Na (Na-S)
- Mg, Ca, Al



Stripping/plating of metal

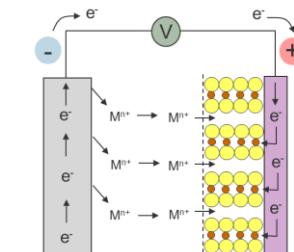
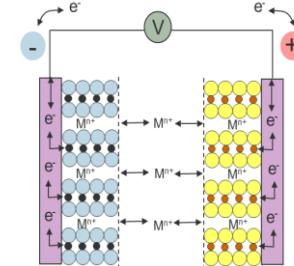
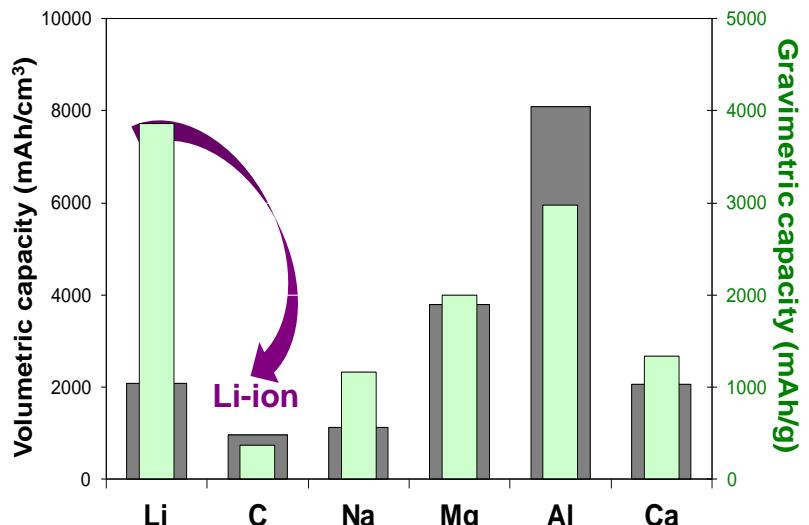
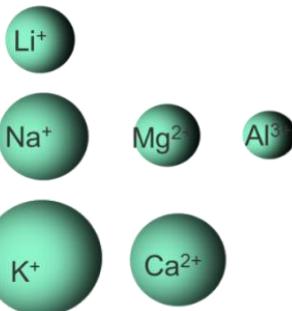
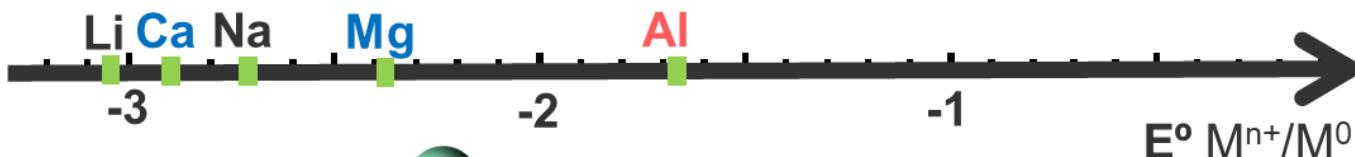
Pure metal inside battery

Capacity intrinsically = $f(\text{metal})$





Energy \approx Potential x Capacity



M Problems/Issues

- Li** Unsafe? TMO_x , S or O_2 cathodes?
- Na** Low melting/unsafe?! Na-S $T_{op} \approx 200^\circ$
- Mg** Stable electrolytes, migration
- Ca** Reversible plating/stripping, migration(?)
- Al** Reversible plating/stripping, migration

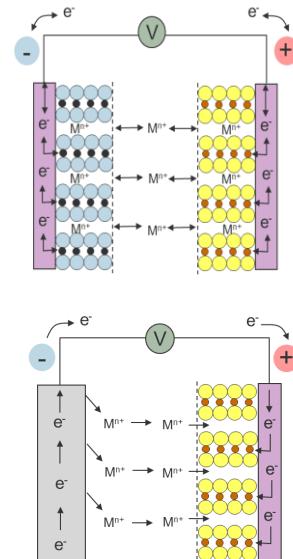
SIBs? Na in C host – as for LIB (graphite => HC)





=> **Electrolyte = Salt(s) + Solvent(s) + Additive(s)** <=

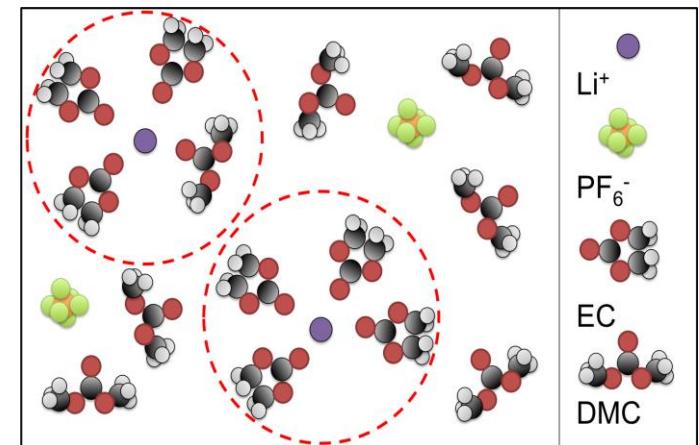
- Mechanically stable – separate electrodes
- No e^- transport
- Rapid M^+ transport – ion conductivity
- Low viscosity – ion conductivity & cell-making
- Electrochemically (meta-)stable - ESW
- Acceptable T working range



Conventional LIB Electrolytes

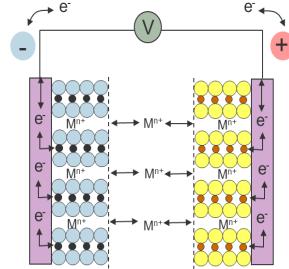
- Sustainable
- Non-toxic
- Safe
- Low-cost

...



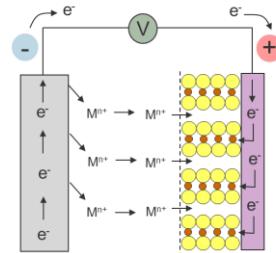
“Standard”: 1 M $LiPF_6$ in EC:DMC





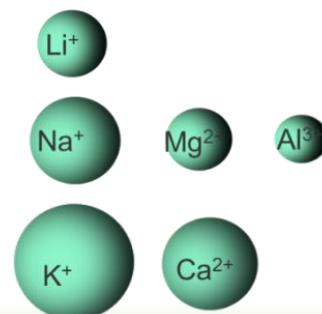
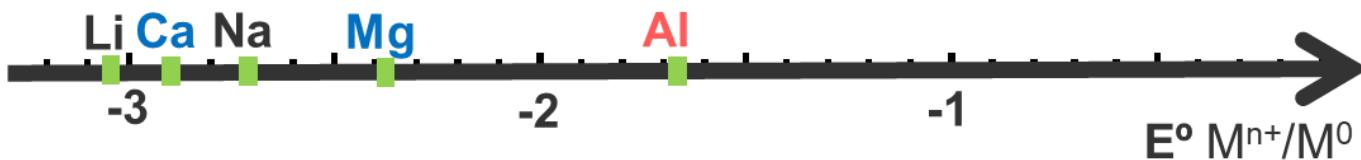
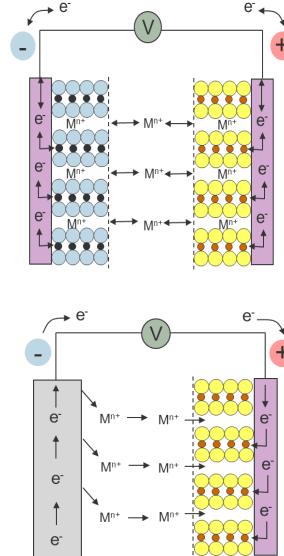
Discuss in groups of 3 persons for ca. 5 minutes

1. What do you know about electrolytes in general?
2. Do you think 1 M LiPF₆ in EC:DMC sounds OK?
3. What alternatives can you think of?





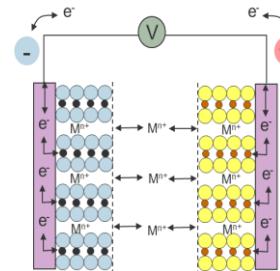
NGB	ESW	Solubility	Other
Li	≈LIB	≈LIB	Stable vs. Li (SEI)
Li-S	ca. 2 V	Not S, PS	Stable vs. Li (SEI)
Li-O ₂	ca. 3 V	Yes O ₂	Stable vs. Li ₂ O ₂ , Li (SEI)
Na-ion	≈LIB-0.3 V	≈LIB	
Na	≈LIB-0.3 V	≈LIB	Stable vs. Na, high T _{op} ?
Mg	ca. 3-4 V	salt 0.5 M	Stable vs. Mg
Ca	≈LIB(?)	salt 0.5 M	
Al	reduced, shifted	salt 0.5 M	[AlCl ₄] ⁻ transport?





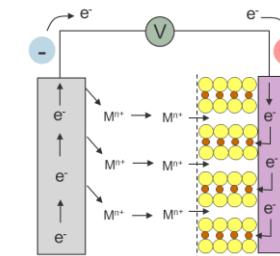
Ion conductivity

“1 mS/cm” AC imp., dielectric spectroscopy



Thermal stability

“-30 - +50 °C mS/cm” TGA (iso-thermal), DSC



ESW

LSV, CV

Solubility

UV-VIS/cycling for S & PS, microelectrodes & DEMS for O₂

Density, Viscosity

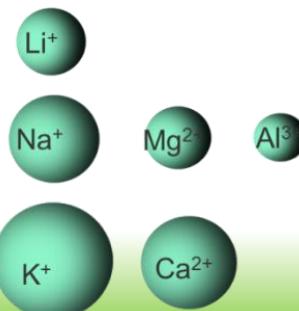
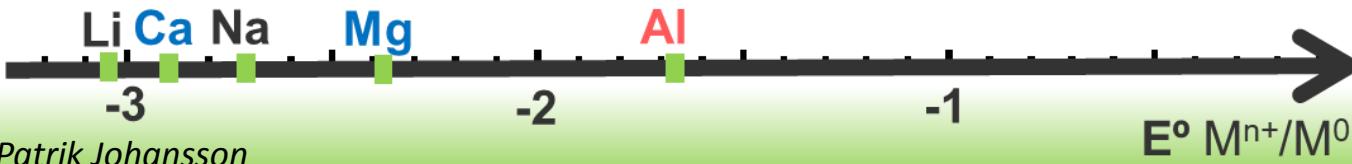
limitations in Wh/kg, transport

NMR, IR, Raman

ion transference/mobility, speciation

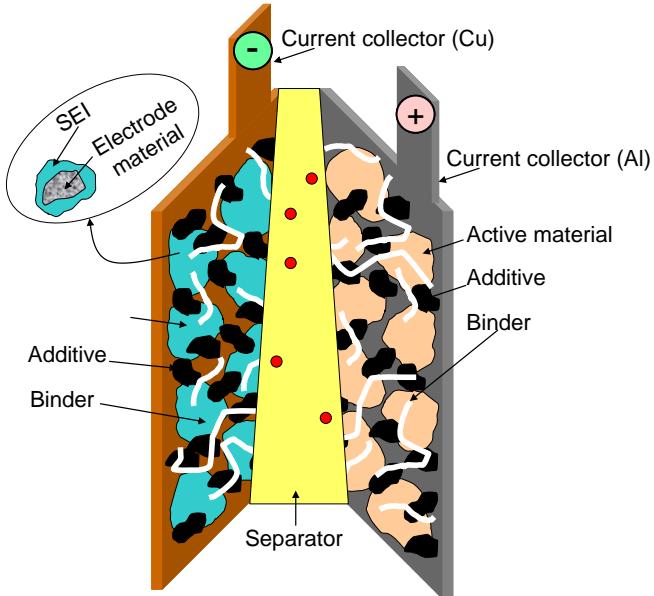
Cell cycling

...





LIB



Cu-graphite

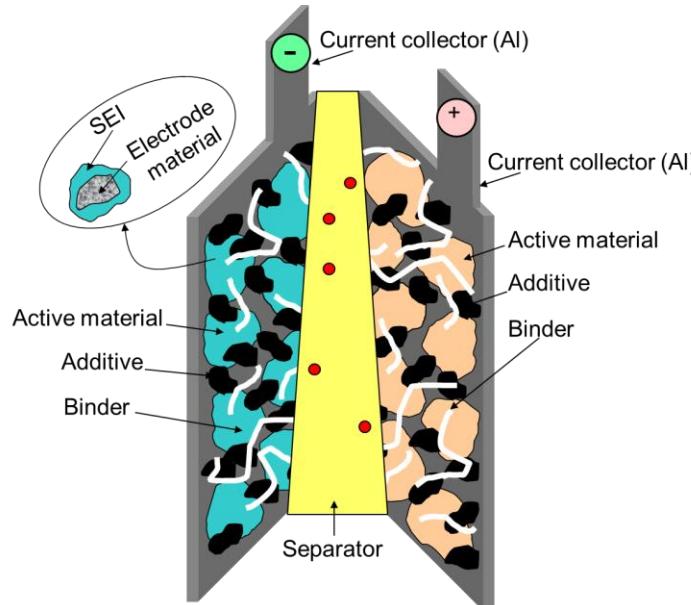
Same

1 M LiPF₆ in EC:DMC

Different

PC exfoliates graphite

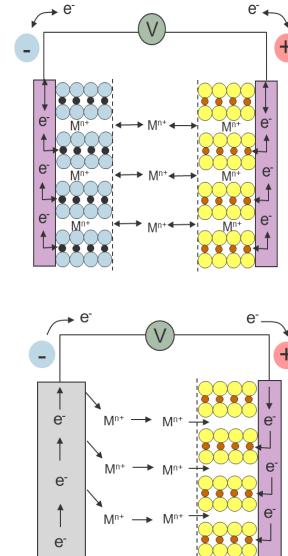
SIB



Al-HC

1 M NaPF₆ in EC:DMC

PC can be (and is) used



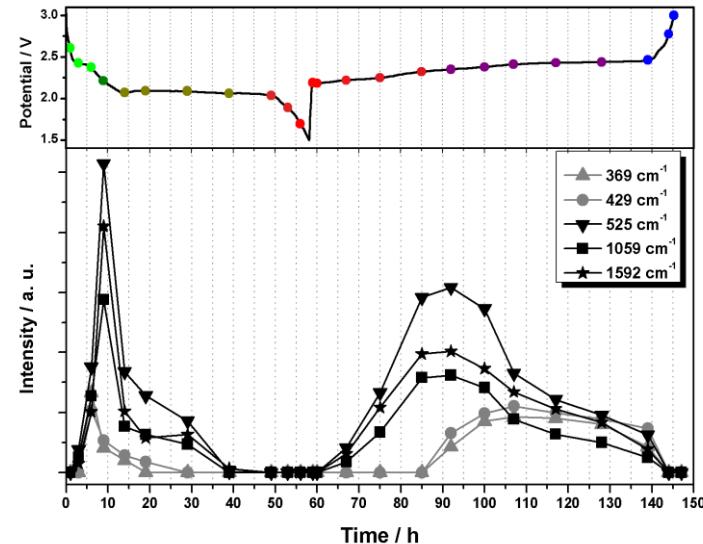
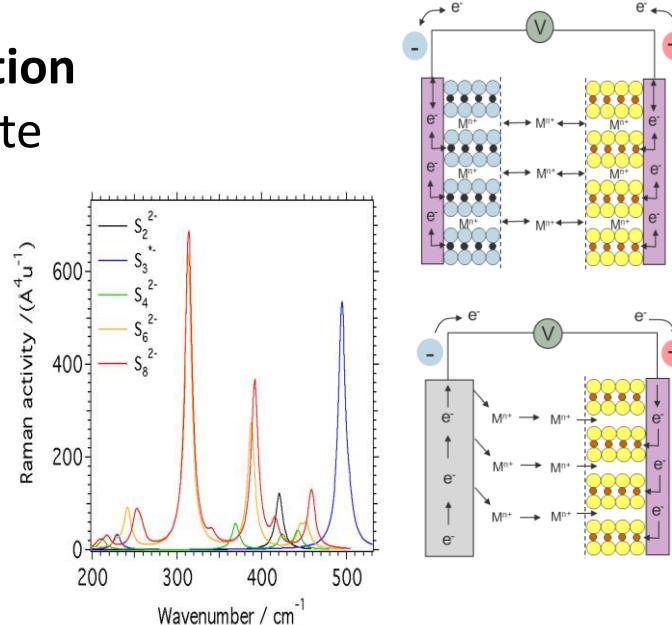
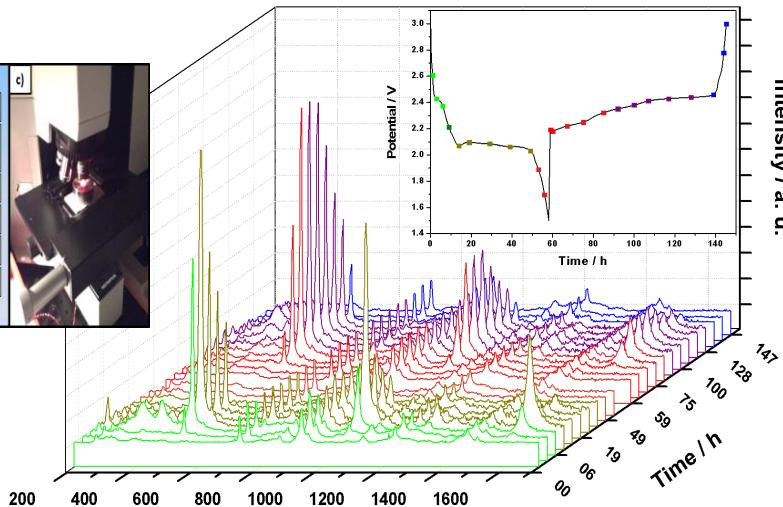
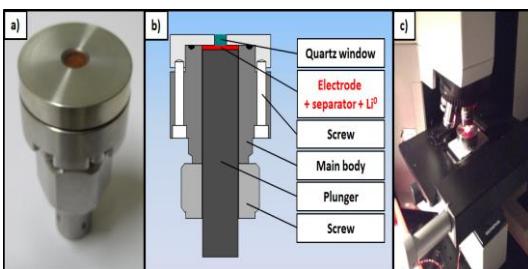
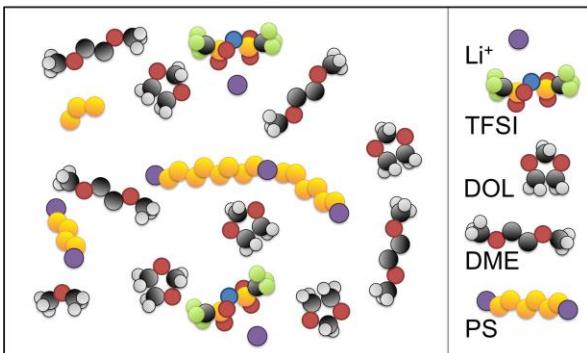


Solubility of S and PS = f(SOC) & cell composition

Cell: Li | 1 M LiTFSI in DOL:DME | C/S composite

Here: *Operando* confocal Raman + DFT comp.

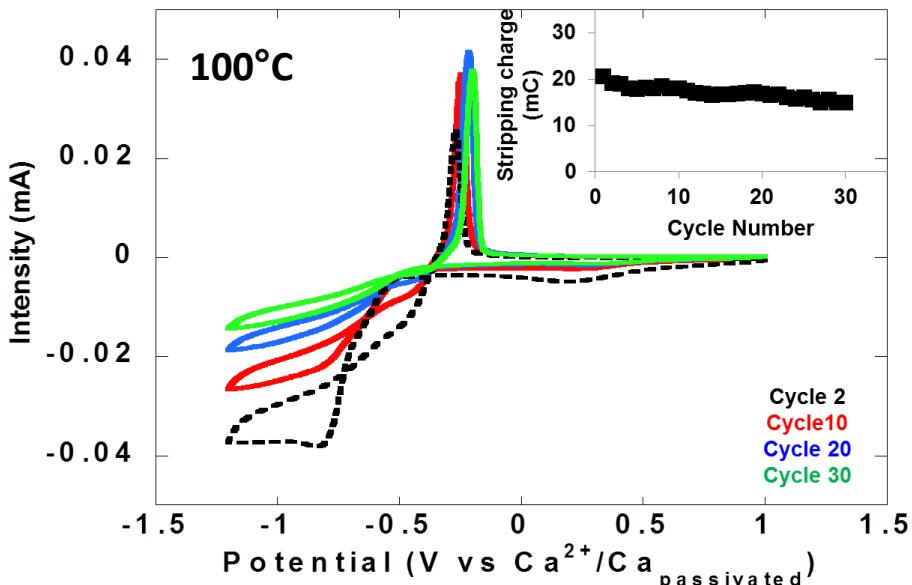
Li-S Battery Electrolytes





Stripping/plating of Ca difficult

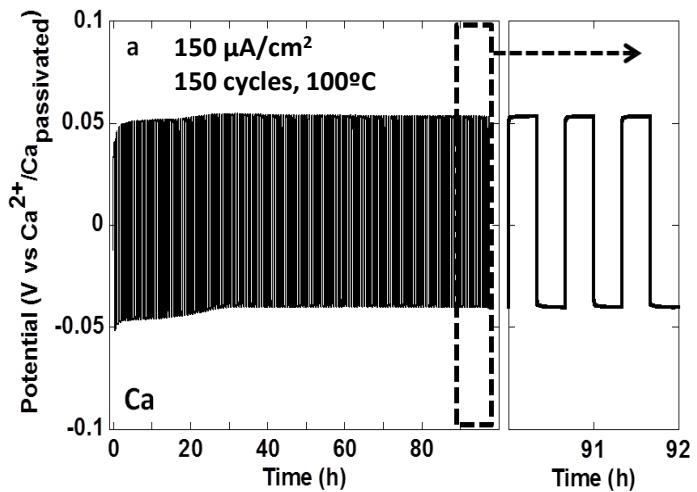
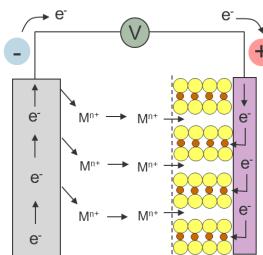
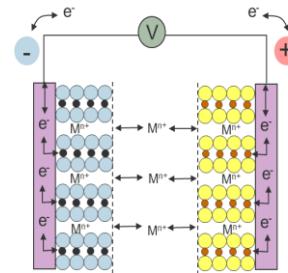
Half-cell: Ca | 0.45 M Ca(BF₄)₂ in EC:PC, T_{op} = 100°C



😊 Capacity stable

😢 Large polarisation

😢 Electrolyte decomposes



A. Ponrouch, C. Frontera, F. Barde, M.R. Palacin *Nature Materials* 15, 2016, 169



**NGB electrolytes:**

- are often rather similar – also to LIB electrolytes
- have a few or more unique demands, esp. Li-O₂, Li-S
- stability is “always” an issue – esp. vs. metal electrode
- solubility is tricky to handle/measure *realistically*
- progress is in need for many tools and techniques

Concepts/Things I have not (yet) talked about:

- Ionic liquid based electrolytes
- Aqueous electrolytes
- Solid-state electrolytes (ceramics, glasses, polymers)
- ...





Thanks!

What questions do you have now?



patrik.johansson@chalmers.se



Patrik Johansson