Battery energy storage beyond Li-ion

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Introduction

…ter in the same order an…
…nnected by wires that pic…
… in the two differe…
…uids respectively.
…e device was designed …
…tablish the position …
…ercury in the scale …
…ectromotor bodies.

PHILOSOPHICAL

TRANSACTIONS,

OF THE

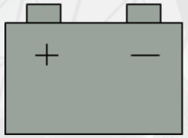
ROYAL SOCIETY

OF

LONDON.

XVII. *On the Electricity excited by the mere Contact of conducting Substances of different kinds. In a Letter from Mr. Alexander Volta, F. R. S. Professor of Natural Philosophy in the University of Pavia, to the Rt. Hon. Sir Joseph Banks, Bart. K. B. P. R. S.*

Read June 26, 1800.



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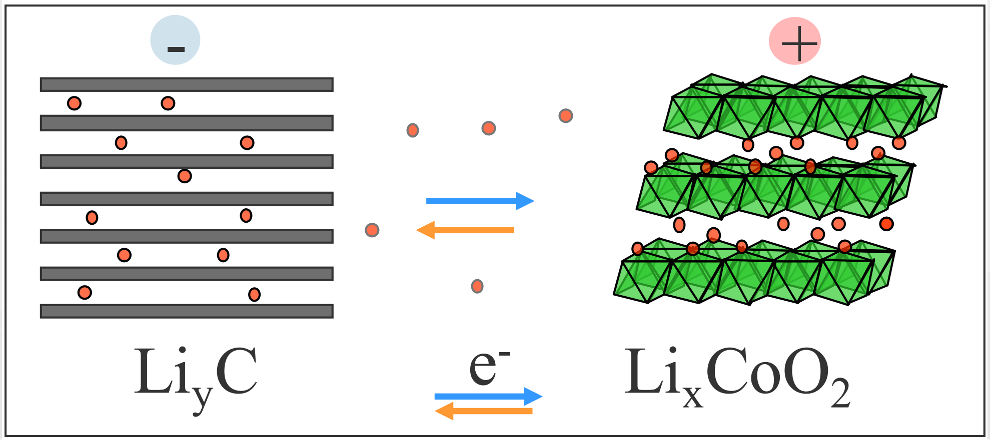


Schematic of the Overall Battery R&D Process from Conception to Production

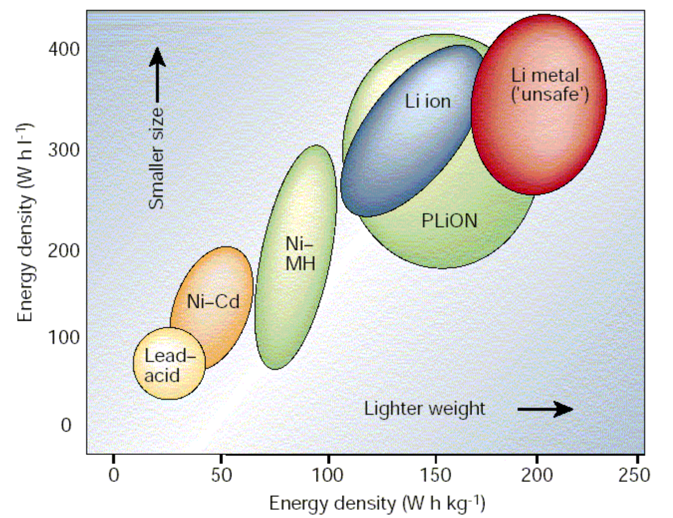
Concept Generation → **Production**

	Concept Validation	Research	Applied Research	Development	Advanced Development
	An idea in a creative mind Limited exploratory laboratory experiments Establish repeatability of performance Is there a market?	Scale-up experiments Characterize fundamental properties of concept, chem. composition, structure, etc. Evaluate size of commercial opportunity	Lab/prototype cells Initial map of performance, rate, cycling, temperature, etc. Scale-up of material preparation Preliminary market scope	Confirm research results Establish initial product format Develop unit assembly operations Make, test, and characterize 5 to 10 cell lots of 100 cells each Construct business plan	Design initial cell product Design and construct unit operations Scale-up prototype cell fabrication Run 3 to 5 sizable pilot line-factory trials Finalize business plan Market development
Timing	One to three years	One to three years	Three to four years	Three to five years	Two to four years
Staffing	One	Two to four	Four to ten	Eight to sixteen	Twelve to thirty
Materials Batch	Grams	10 to 50 g	100 g to 1 kg	1 kg to 10 kg	10 kg to 100 kg

10-19!!!

R. Brodd, ATP Working Paper Series Working Paper 05–01, NIST (US)

Performance



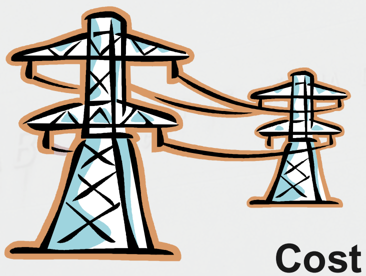
Tarascon & Armand, Nature 414 (2001) 359

Application

Increasing size

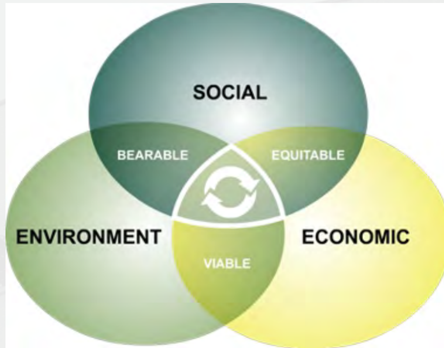
Energy density

Safety



Cost

Sustainability



energy / water footprint

recycling

critical vs. abundant materials

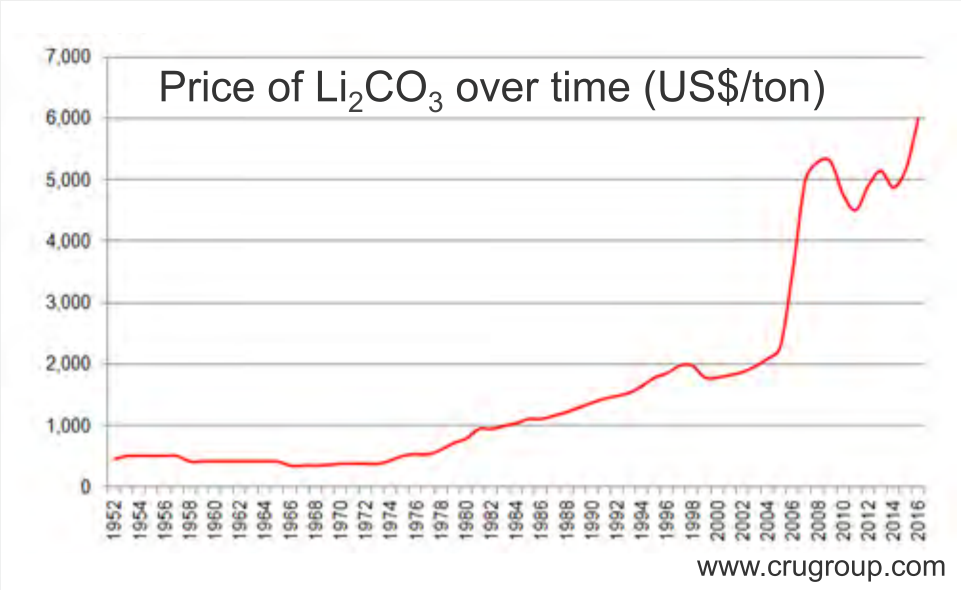
Growing larger….

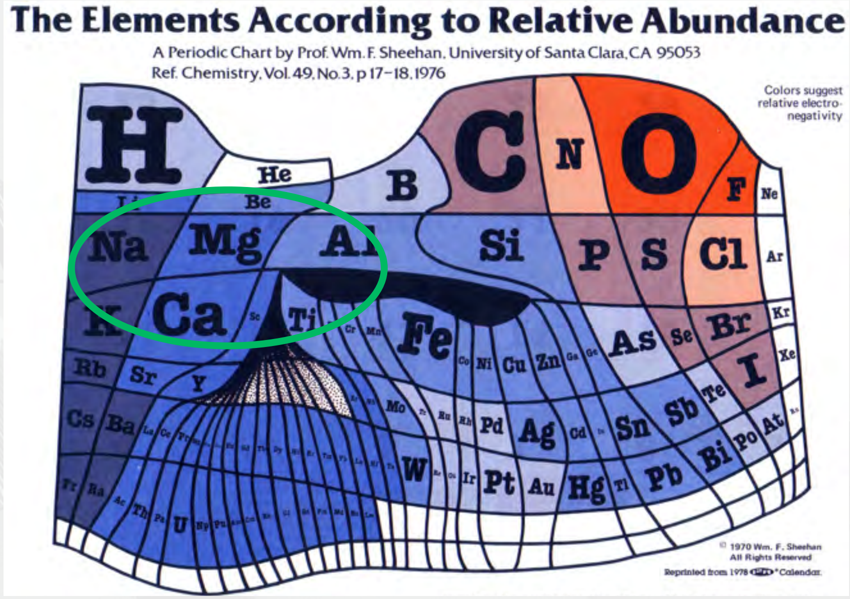
~ x 10

~ x 620

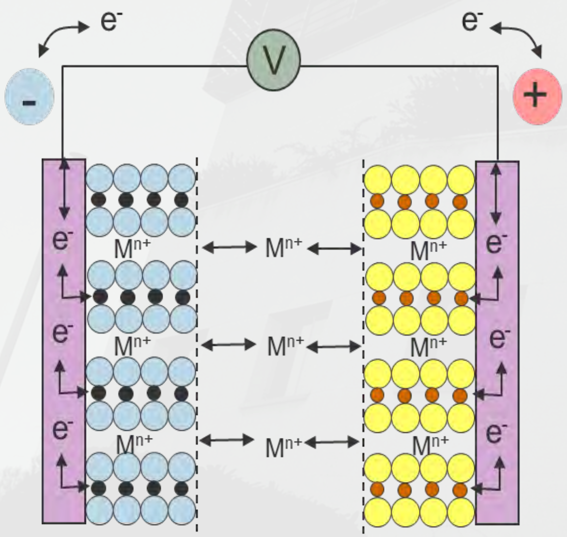
~ x 5900

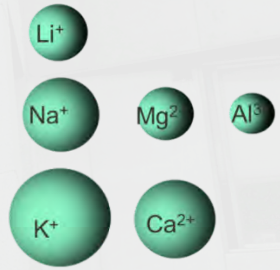
… and larger if grid applications are considered !!!





M-ion concept





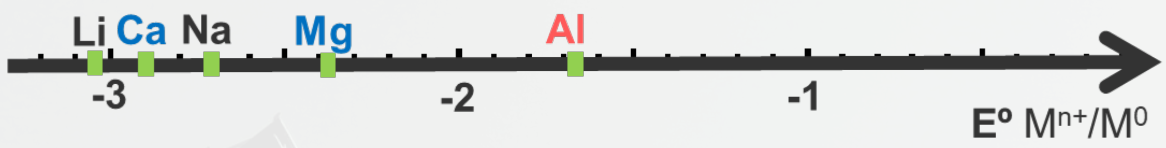
analogous to Li-ion

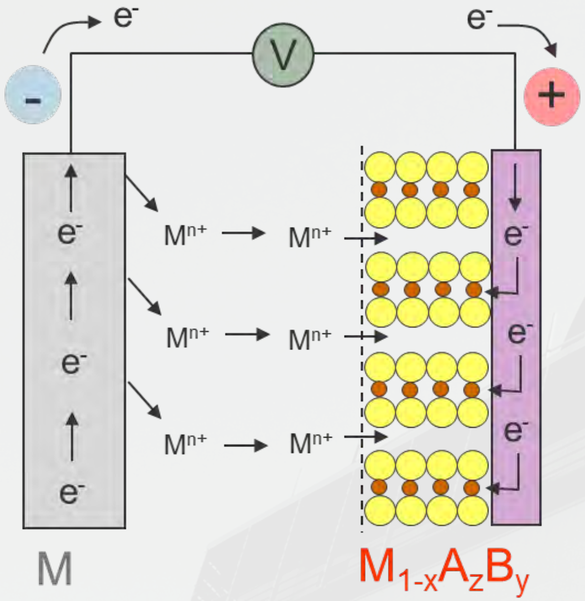
M^{n+} as charge carriers instead of Li^+
(migration may be an issue for n>1, coulombic interactions)

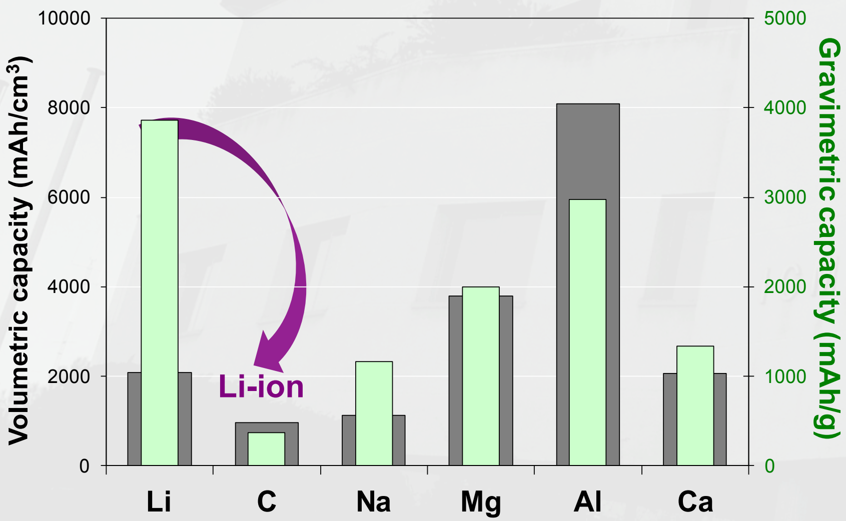
energy density not directly related to M
(but to electrode material capacities & potentials)

→ Na-ion

M-anode concept







Li “unsafe” ? polymer electrolyte ?
air or sulphur cathodes?

Na low melting T, “unsafe” as solid?
Na/S successful (liquid electrodes)

Mg electrolytes with wide V window?
high energy density cathodes?

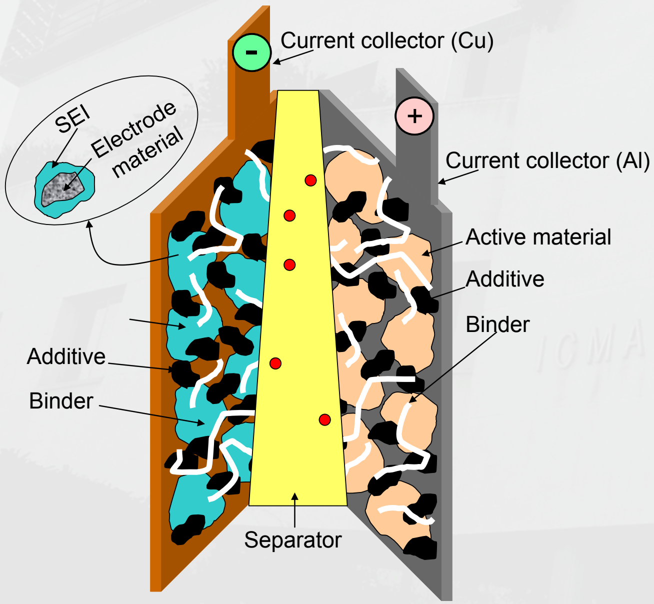
Ca interesting potential
reversible plating/stripping?

Al lower potential
reversible plating/stripping?

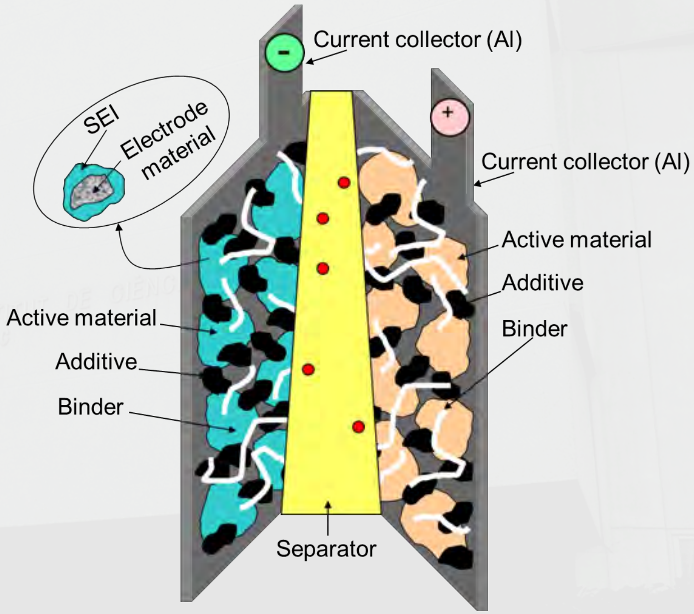
Na-ion batteries

			
→ "unlimited" Na resources	20 ppm	22700 ppm	Earth's crust
→ high standard reduction potential	-3.04	-2.71	vs. NHE
→ alloy formation with Al	yes	no	

Li-ion



Na-ion



→ Similar chemistry

- Faster progress

→ Differences

- Ionic radius – coordination – crystal chemistry
- Polarizing character – diffusion – kinetics
- Solvation energy – solubilities – SEI

Graphite // $LiPF_6$ EC:DMC // $LiFePO_4$

↓

Graphite // $NaPF_6$ EC:DMC // $NaFePO_4$

Practical prospects

$Na_{15}Pb_4$ || Na_xCoO_2

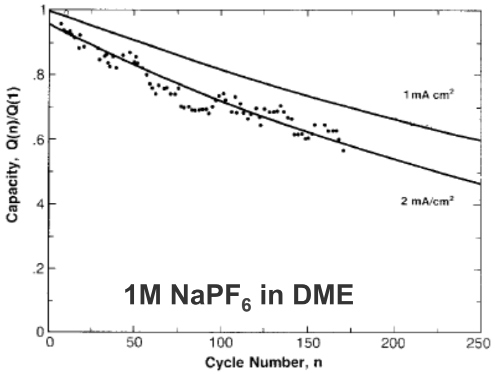
th: 350 Wh/kg, 1470 Wh/l

J. Electrochem. Soc.: ELECTROCHEMICAL SCIENCE AND TECHNOLOGY *November 1988* 2669

Rechargeable Electrodes from Sodium Cobalt Bronzes

L. W. Shacklette,* T. R. Jow,* and L. Townsend

Allied-Signal, Incorporated, Corporate Technology, Morristown, New Jersey 07960

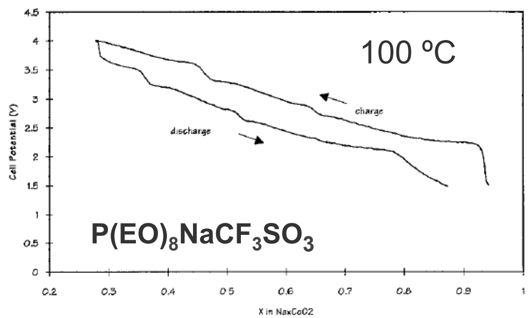


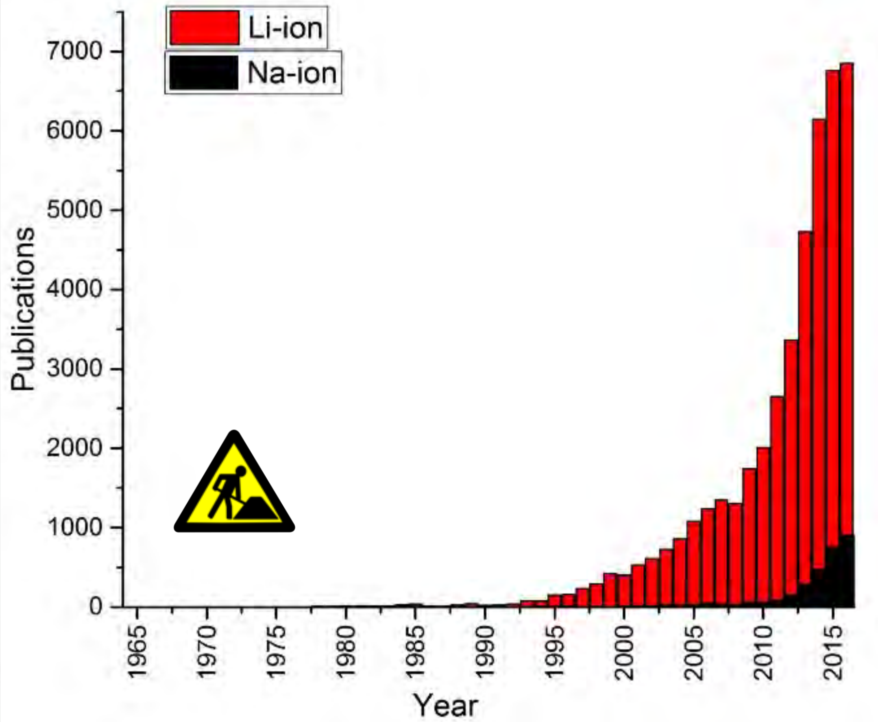
J. Electrochem. Soc., Vol. 140, No. 10, October 1993

Rechargeable Na/Na_xCoO_2 and $Na_{15}Pb_4/Na_xCoO_2$ Polymer Electrolyte Cells

Yanping Ma,* Marca M. Doeff,** Steven J. Visco, and Lutgard C. De Jonghe

Materials Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720





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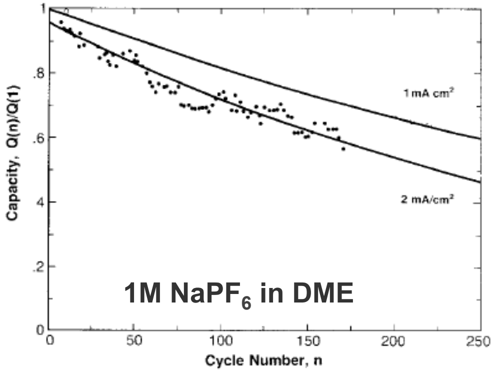

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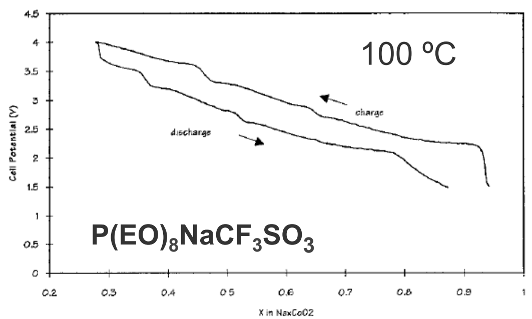
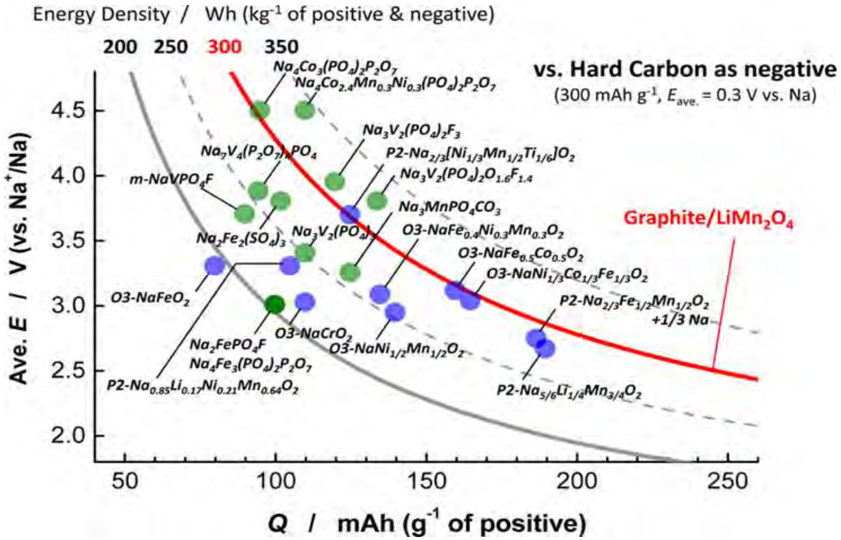
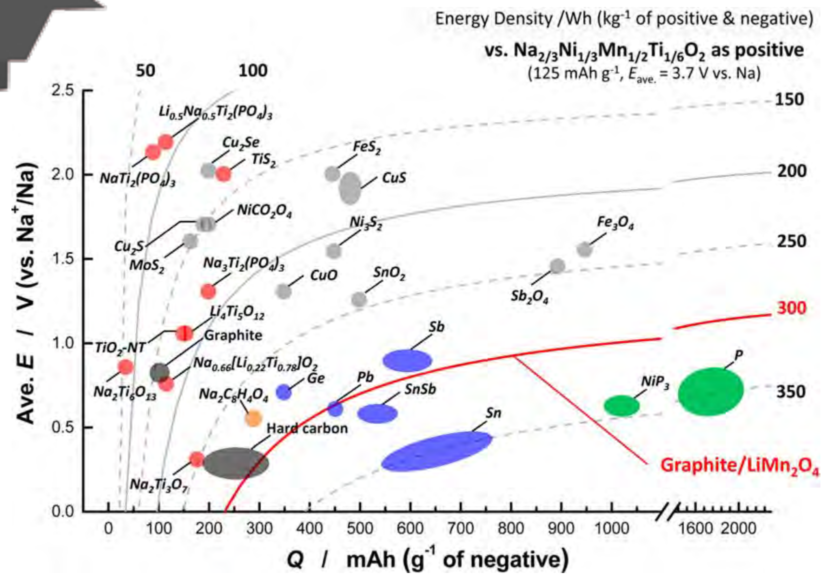
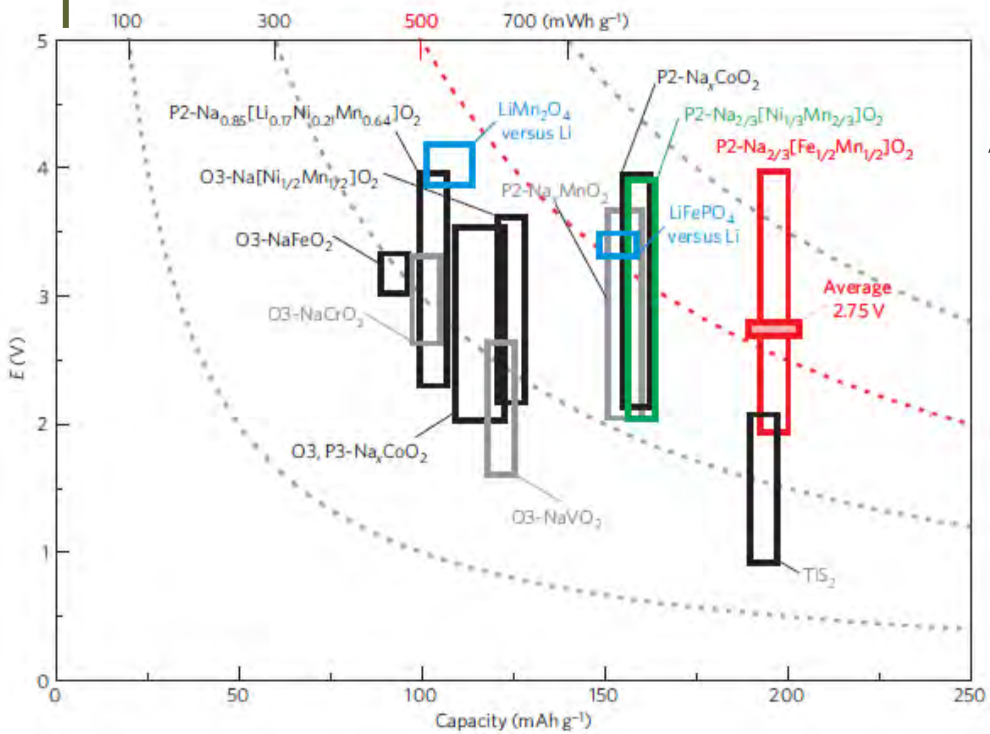






N. Yabuuchi et al. Chem. Rev. 114 (2014) , 11636.

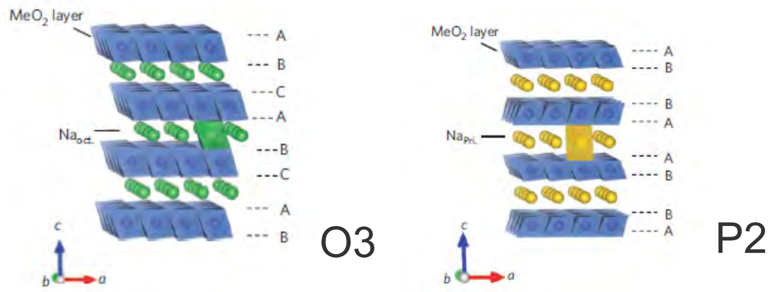
Positive electrode materials



N. Yabuuchi et al. Nature Materials 11(2012) 512

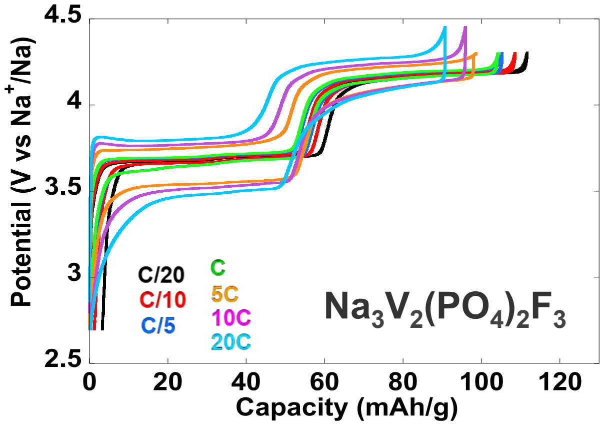
Some V windows too wide to be practical

Air stability can be an issue



O3 higher capacity & P2 higher stability

Layered materials Na_xMO_2



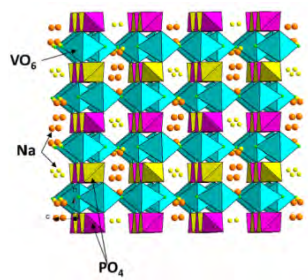
A. Ponrouch et al. Energy & Environ. Sci. 6 (2013) 2361.

Frameworks typically different from Li - based

Lower capacities than layered (« inactive groups »)

Poor conductivity (C coating)

High stability

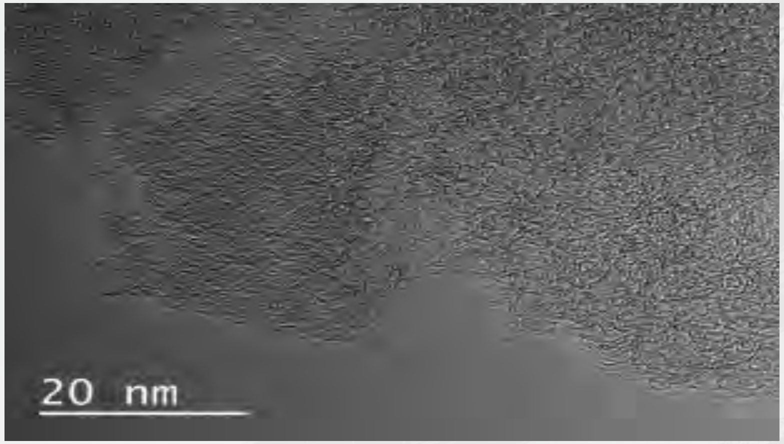


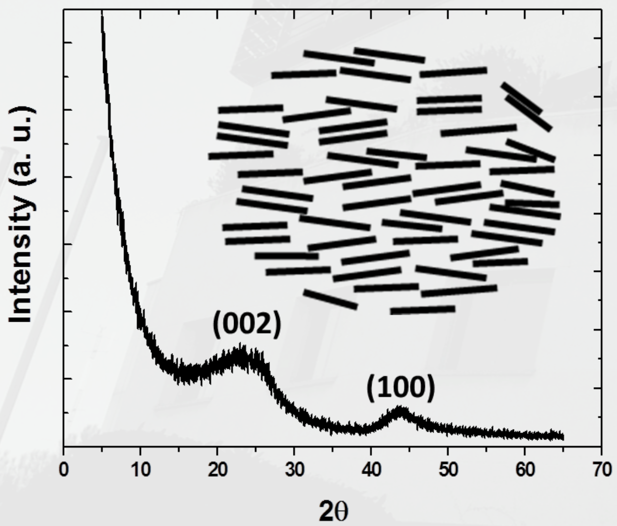
Polyanionic frameworks

Negative electrode materials: hard C

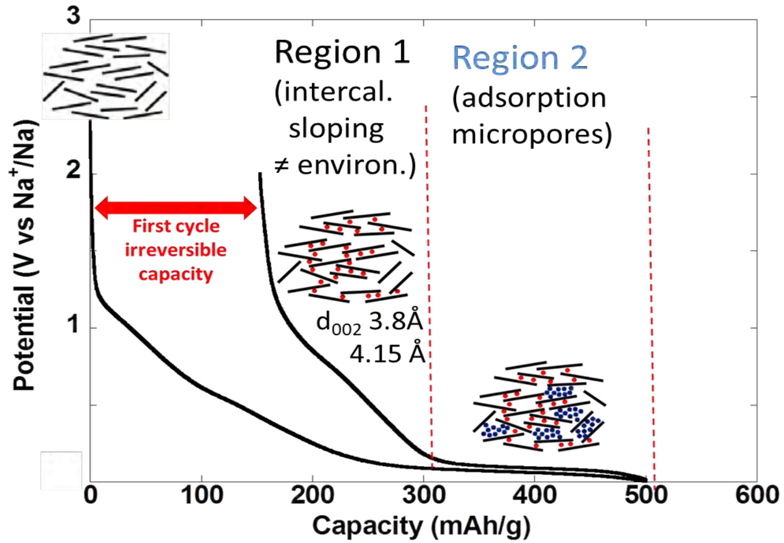
Non-graphitizable (sp^3 cross-linking)

Prepared by pyrolisis of solid precursors (cellulose, charcoal, phenolic resins, sugar…)





graphene sheets
10 – 40 Å
(1-3 layer stacks)



Current *state of the art* material

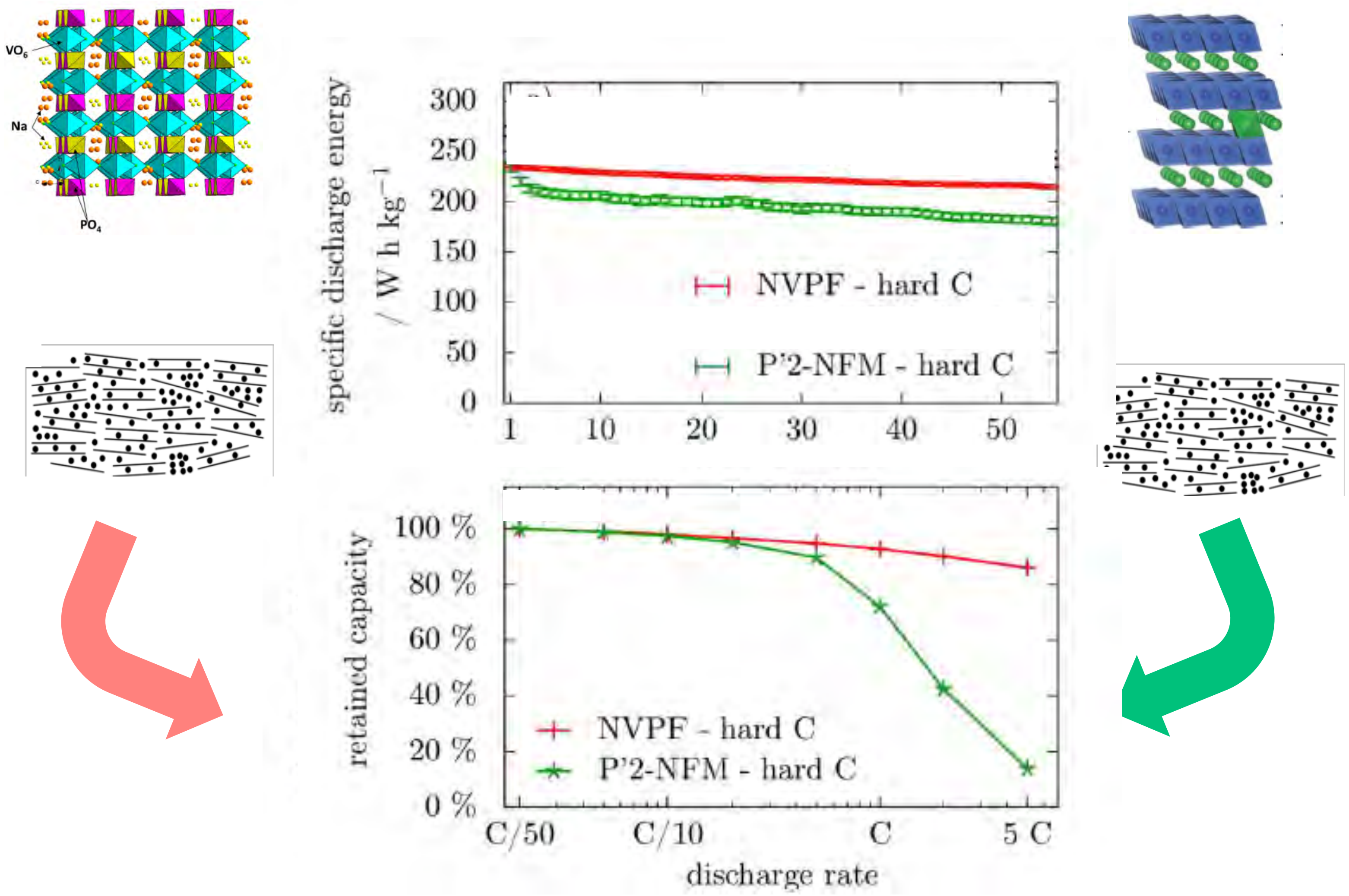
Very low V operation (plating risk?)

1st cycle irreversibility is an issue

capacity ⟺ microstructure, electrolyte

E. Irisarri et al. J. Electrochem. Soc. 162 (2015) A2476

Reported performance: lab cells



R. Dugas et al. *J. Electrochem. Soc.* 2016, 163, A867.

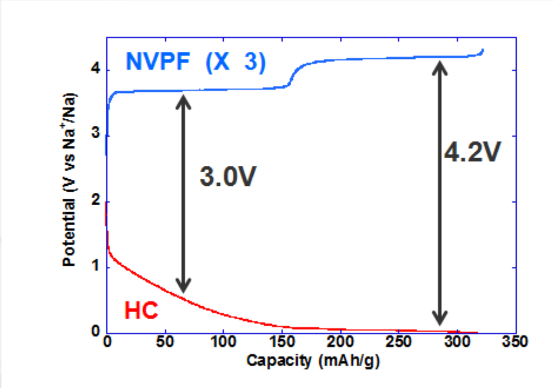
Sustainability

Hard C // $EC_{0.45}$:$PC_{0.45}$:$DMC_{0.1}$ // $Na_3V_2(PO_4)_2F_3$

3.6 V cell
300 mAh/g (HC)
110 mAh/g (NVPF)

Theoretical energy density : 78 Wh/kg
(BatPac v1.0)

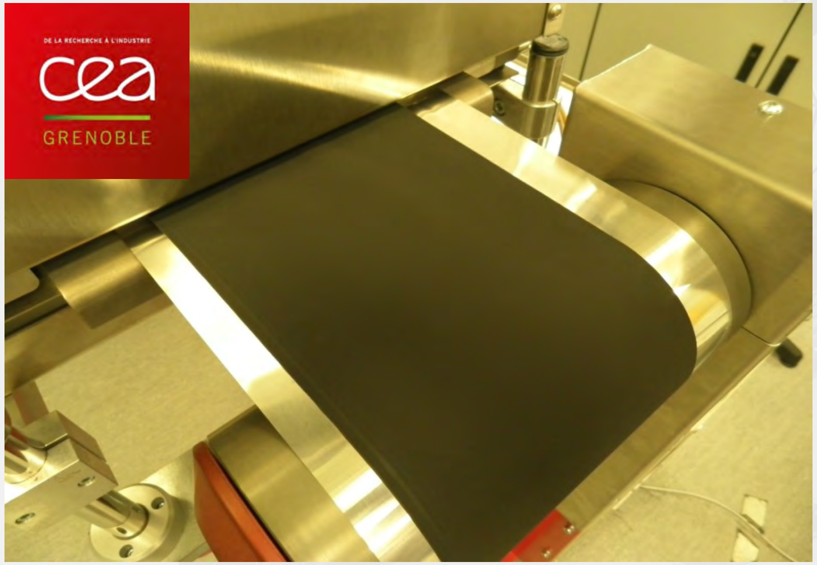
(for comparison Graphite//LP30//$LiFePO_4$ gives 75 Wh/kg)

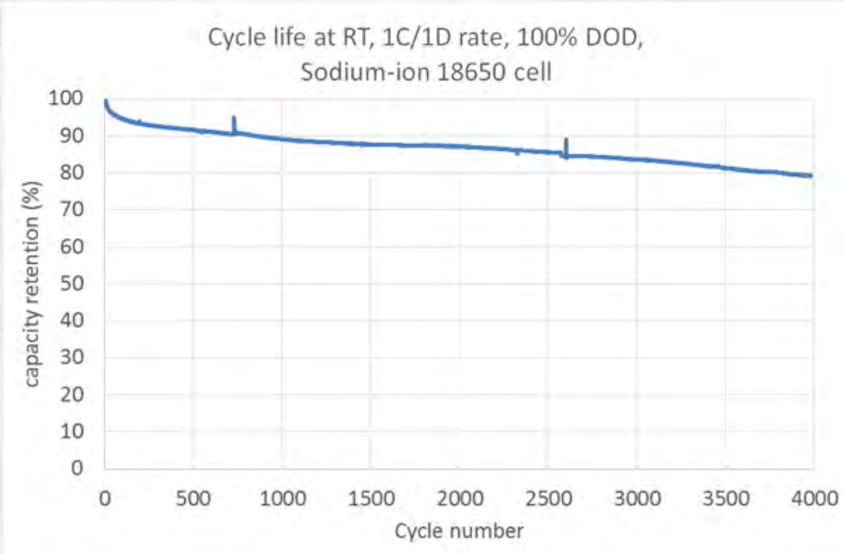


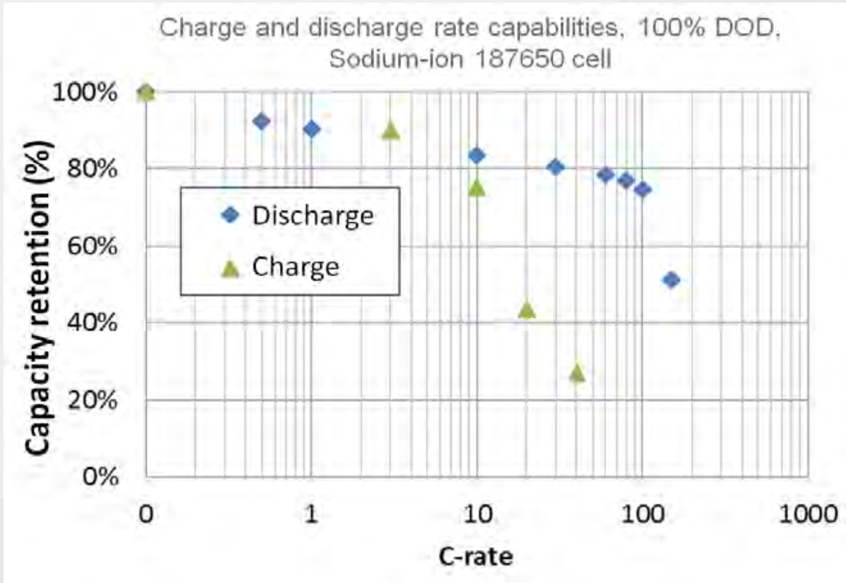
CALCULATED NATURAL CAPITAL COST [€/kWh capacity]				
	Sodium Ion Batteries	Lithium Ion Batteries		
Elem.	HC|elec |NVPF	Graph.|LP30|$LiFePO_4$	Graph.|LP30|$LiMn_2O_4$	$Li_4Ti_5O_{12}$|LP30|$LiMn_2O_4$
Al	0.36	0.18	0.11	0.51
C	0.073	0.08	0.057	0.068
Cu	-	185	110	-
F	2.17	1.09	0.8	2.42
H	0	0	0	0
Fe	-	0.6	-	1.5
Li	-	0.0085	0.0078	0.04
Mn	-	-	6.56	15.1
O	0	0	0	0
P	1.43	0.15	0.081	0.24
Na	0	-	-	-
Ti	-	-	-	1.56
V	27.5	-	-	-
Sum	**31.5**	**187**	**117**	**19.9**

A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, M.R. Palacin *J. Mater. Chem. A* 2015, 3, 22.

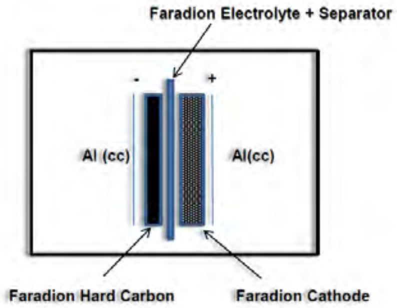
Reported performance: upscaling







Reported performance: industrial cells

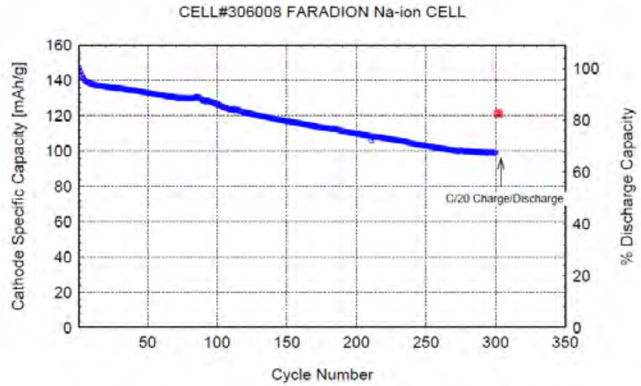


4 cm² or 100 cm²

Typical Faradion Na-ion Pouch Cells

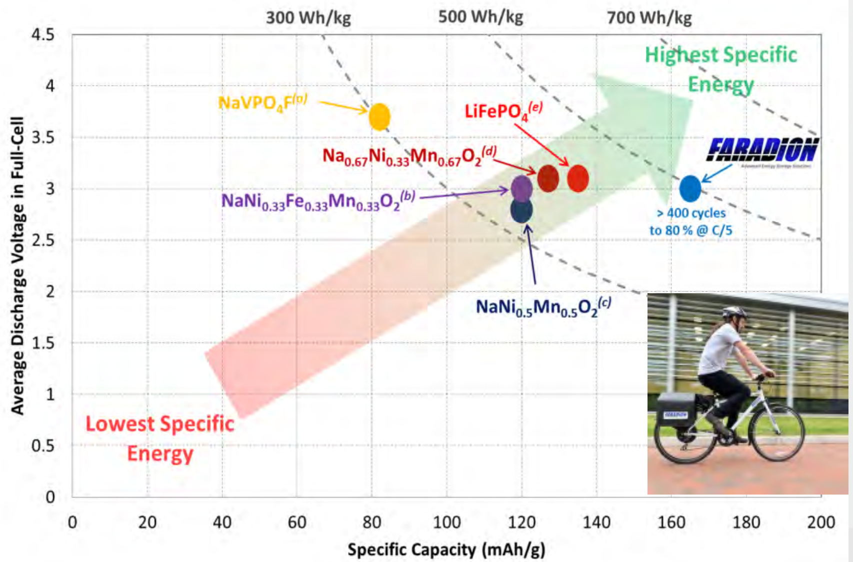
Typical cell capacity = 10-12 mAh (4 cm²) and 250-300 mAh (100 cm²)

Typical Bi-cell capacity = 500-600 mAh (100 cm²)



Hard Carbon//$NaNi_{1-x-y-z}M^1_xM^2_yM^3_zO_2$ Layered Oxide

- **Pouch Cell**
- **1.0 – 4.2 V CC/CV @30°C**
- **C/10 Rate Charge and Discharge**



http://www.faradion.co.uk

Na-ion presentation http://www.faradion.co.uk/technology/354-2/

Reported performance: industrial cells

ALISTORE European research institute · ICMAB · CSIC

18650 - Energy Cell - Prediction Cell Chemistry : Graphite // LiFePO4	Cathode		Anode	
Prescription	Material / Name	Rate / Spec	Material / Name	Rate / Spec
Activity Material	LiFePO4	92.00%	Graphite	92.75%
Residual Carbon	Residual from synthesis	2.00%	Anode Additive	0.25%
Conductivity Carbon	Conductive Carbon	2.00%	Conductive Carbon	3.00%
Binder	PVDF/ (High MW)	4.00%	PVDF/ (High MW)	4.00%
Total Long	664	mm	670	mm
Foil Thickness(mm) Cu and Al	0.02	mm	0.015	mm
1st coat surface long	624	mm	653	mm
2nd coat surface long	607	mm	603	mm
Coat both single surfaces total long	1231	mm	1256	mm
Single side thickness not including foil's thickness	0.0820	mm	0.0500	mm
both side including foil thickness	0.184	mm	0.115	mm
Width of electrode	5.6	cm	5.75	cm
single electrode total coat area	689.36	cm^2	722.2	cm^2
Material Coat Wt (g) /cm2	0.016192	g/cm^2	0.0072	g/cm^2
Total Coat Wt (g)/cm2	0.0176	g/cm^2	0.00780	g/cm^2
Theoetical Capacity / g	140	mAh/g	360	mAh/g
Reversible Capacity / g	125	mAh/g	300	mAh/g
Non reversible Cap.	10		20	mAh/g
Capacity / unit area	2.02	mAh/cm^2	2.06	mAh/cm²
Press Strech Rate	100.3	%	100.1	%
Real Unit Area Capacity	2.02	mAh/cm^2	2.06	mAh/cm²
Unit Area of C/A Weight compare	2.234	Unit Area of A/C Capacity Compare	1.021	
Whole electrode of C/A		Whole Electrode A/C Capacity		

18650 - Energy Cell - Prediction Cell Chemistry : Hard Carbon // Layered Oxide	Cathode		Anode	
Prescription	Material / Name	Rate / Spec	Material / Name	Rate / Spec
Activity Material	Layered Oxide	94.00%	Hard Carbon	92.75%
Residual Carbon	Residual from synthesis	0.00%	Anode Additive	0.25%
Conductivity Carbon	Conductive Carbon	2.00%	Conductive Carbon	3.00%
Binder	PVDF/ (High MW)	4.00%	PVDF/ (High MW)	4.00%
Total Long	472	mm	478	mm
Foil Thickness(mm) Al both sides	0.02	mm	0.02	mm
1st coat surface long	432	mm	461	mm
2nd coat surface long	415	mm	421	mm
Coat both single surfaces total long	847	mm	882	mm
Single side thickness not including foil's thickness	0.0820	mm	0.0500	mm
both side including foil thickness	0.184	mm	0.120	mm
Width of electrode	5.6	cm	5.75	cm
single electrode total coat area	474.32	cm^2	507.15	cm^2
Material Coat Wt (g) /cm2	0.02491	g/cm^2	0.0164	g/cm^2
Total Coat Wt (g)/cm2	0.0265	g/cm^2	0.01770	g/cm^2
Theoetical Capacity / g	200	mAh/g	360	mAh/g
Reversible Capacity / g	150	mAh/g	240	mAh/g
Non reversible Cap.	20		120	mAh/g
Capacity / unit area	3.74	mAh/cm^2	3.74	mAh/cm²
Press Stretch Rate	100.3	%	100.1	%
Real Unit Area Capacity	3.73	mAh/cm^2	3.74	mAh/cm²
Unit Area of C/A Weight compare	1.514	Unit Area of A/C Capacity Compare	1.004	
Whole electrode of C/A		Whole Electrode A/C Capacity		

Will performance equal / beat Li-ion?

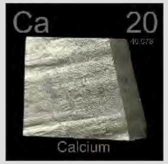
For myself I am an optimist ,

it does not seem to be much use being anything else.

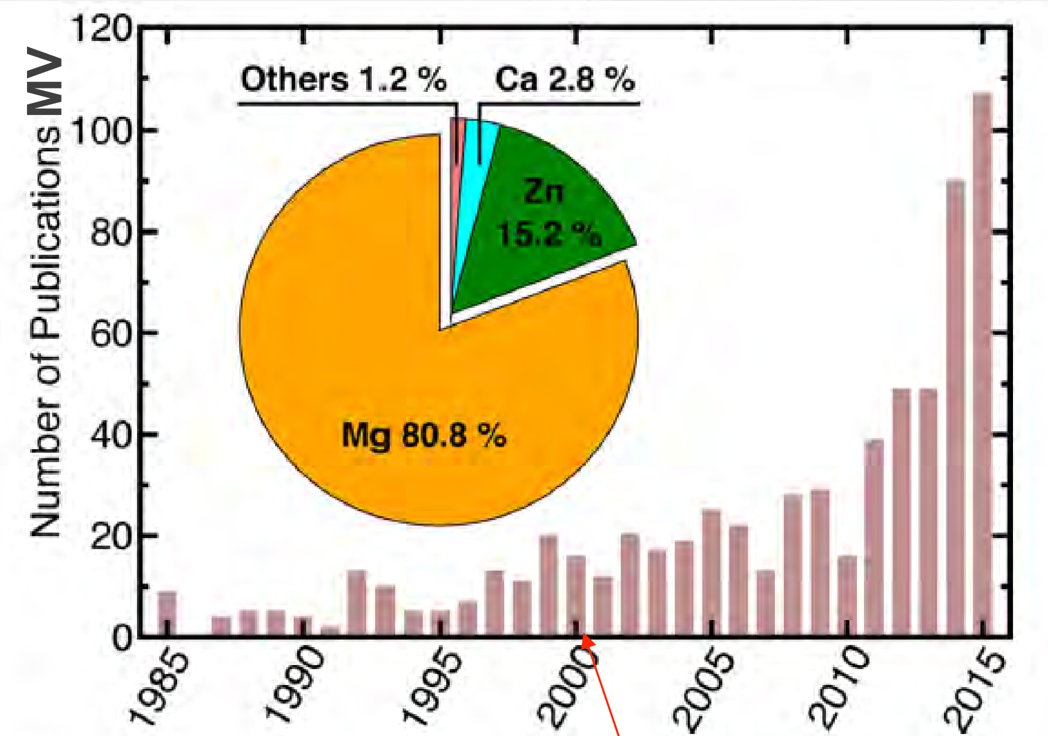
(Sir Winston Churchill, Nov. 9th, 1954)

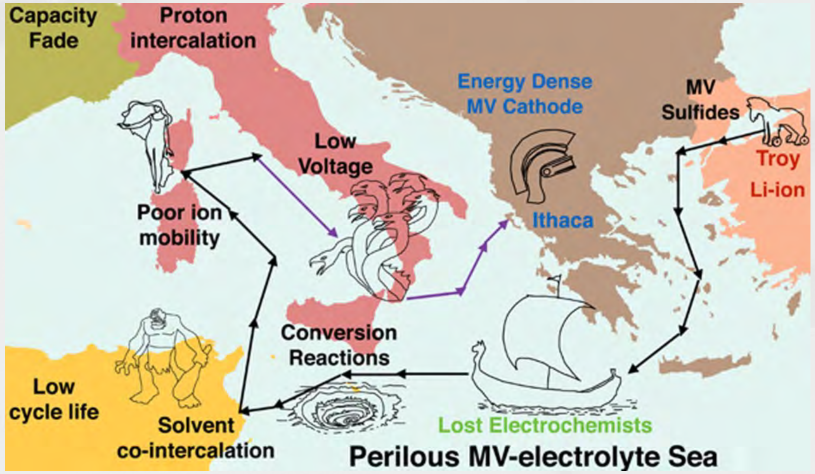
Ca batteries

Why Ca anode?



	Li	Mg	Ca	
→ "unlimited" resources	20 ppm	27640 ppm	46600 ppm	Earth's crust
→ high standard reduction potential	-3.04	-2.37	-2.87	vs. NHE





The Odyssey of Multivalent Cathodes

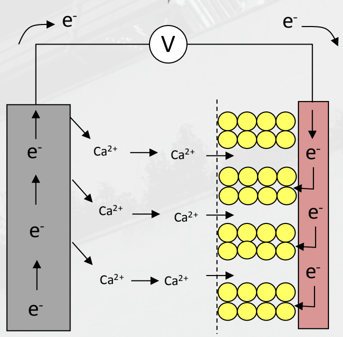
P. Canepa et al. *Chem. Rev.* 2017, 117, 4287.

Proof-of-concept Mg anode (Aurbach et al. Nature)

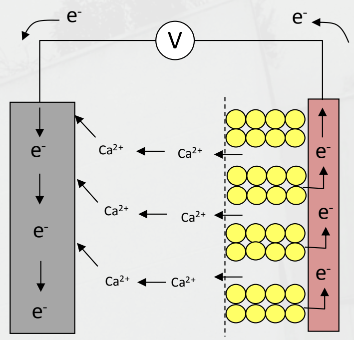
M anodes: the case of Ca…

1991 **Ca deposition not possible in organic solvent electrolytes**
Aurbach et al. (SEI does not conduct Ca^{2+} ions)

Suitable ~~electrolytes~~ (plating) ➡ cathode ~~development~~

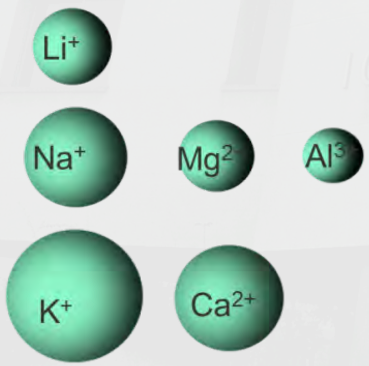


Reduction of the WE:
Ca stripping at the CE



Oxidation of the WE:
Ca deposition ???

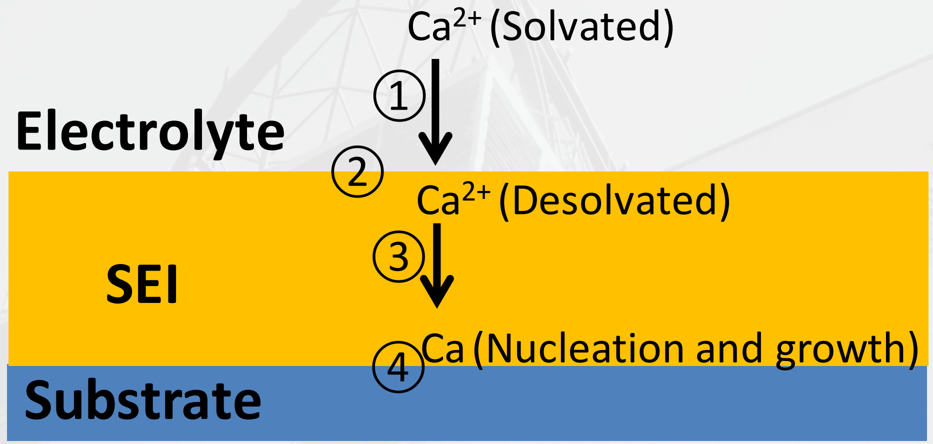
BUT



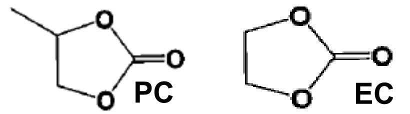
Charge/radius $Ca^{2+} << Mg^{2+}$

Easier migration

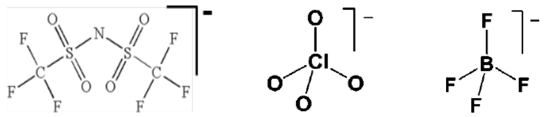
M anodes: the case of Ca…



Alkyl carbonates (high ε, large redox window)

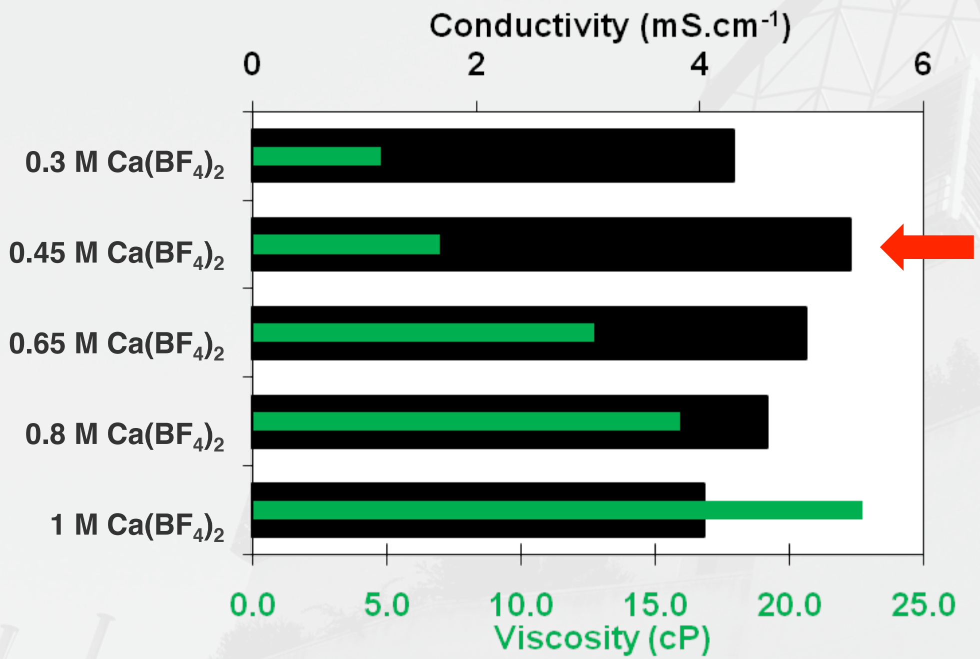


Commercial salts



Is Ca electrodeposition viable?

EC:PC RoomT



Ca^{2+} electrolytes

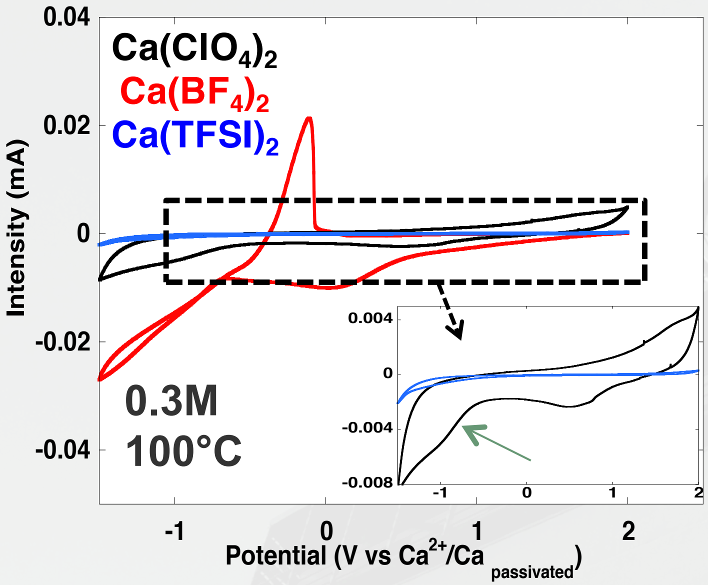
Concentration ↑ ➡ Viscosity ↑

Conductivity ↑, ↓

Low conductivities at RT
Ion pairing

➡ **High T (50-100ºC)**

Is Ca electrodeposition viable?

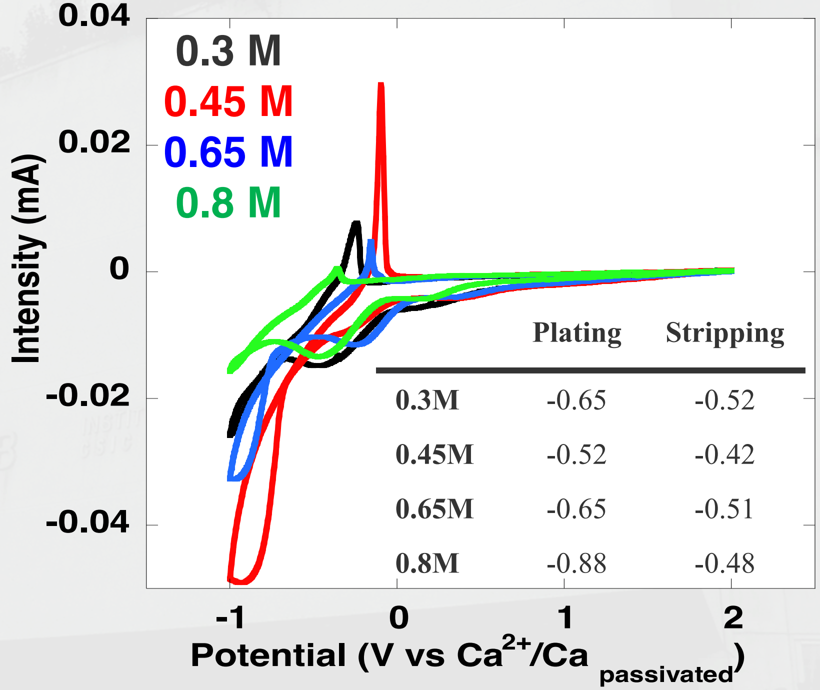


Reversible redox process in $Ca(ClO_4)_2$ & $Ca(BF_4)_2$

Ca plating???

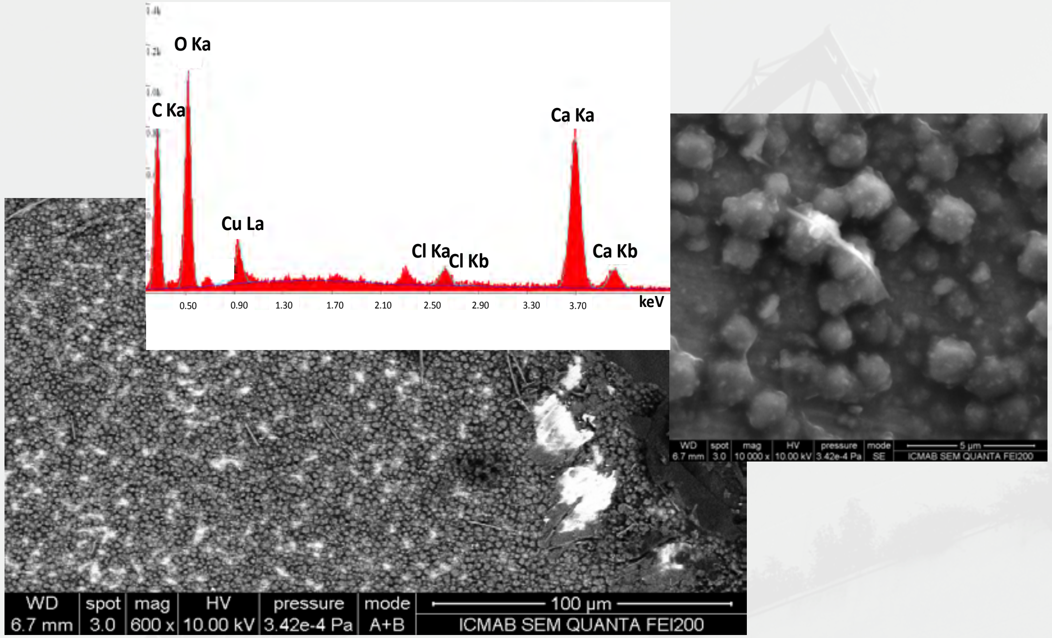
Intensity ↑ with:
$Ca(BF_4)_2$
↑ temperature
↑ ionic conductivity

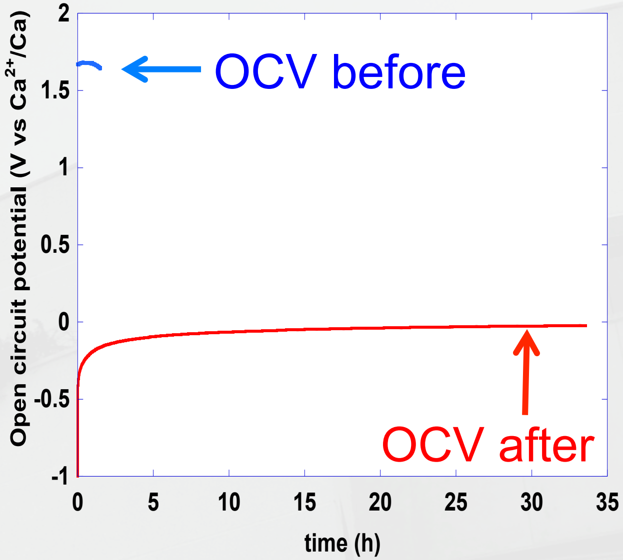
$Ca(BF_4)$ EC:PC 100°C



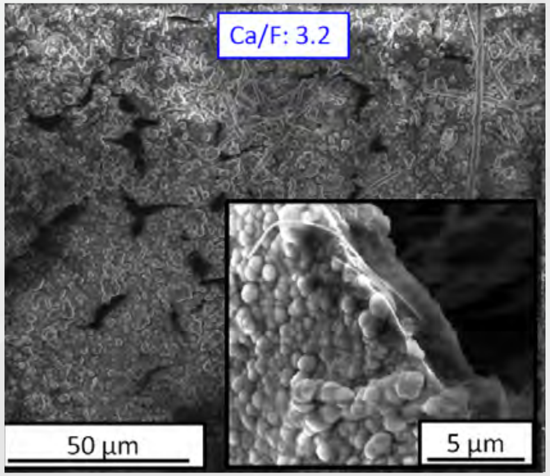
	Plating	Stripping
0.3M	-0.65	-0.52
0.45M	-0.52	-0.42
0.65M	-0.65	-0.51
0.8M	-0.88	-0.48

Is Ca electrodeposition viable?





100ºC, 200h, -1.5V



0.3M $Ca(BF_4)$ EC:PC

Higher T, longer t

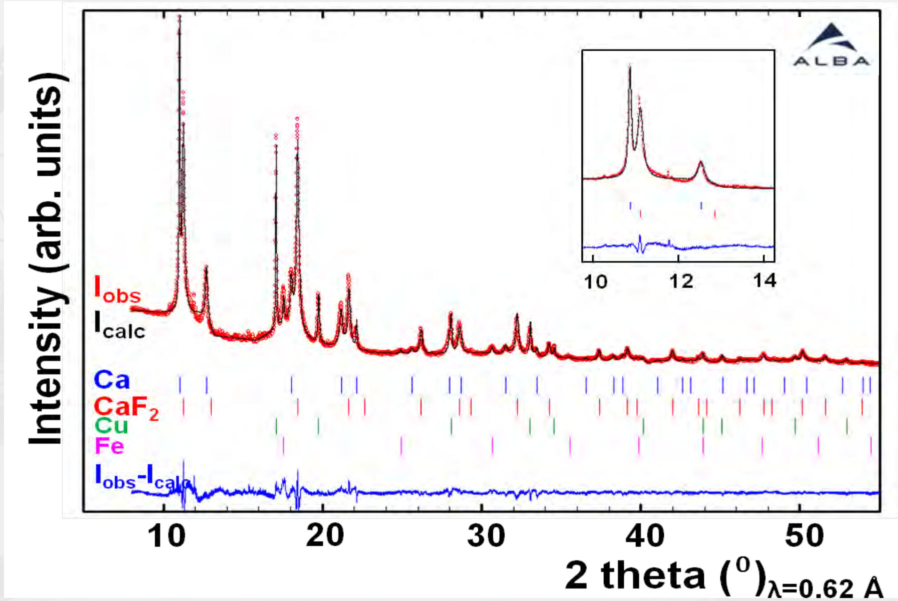
thicker deposits

higher Ca/F ratio

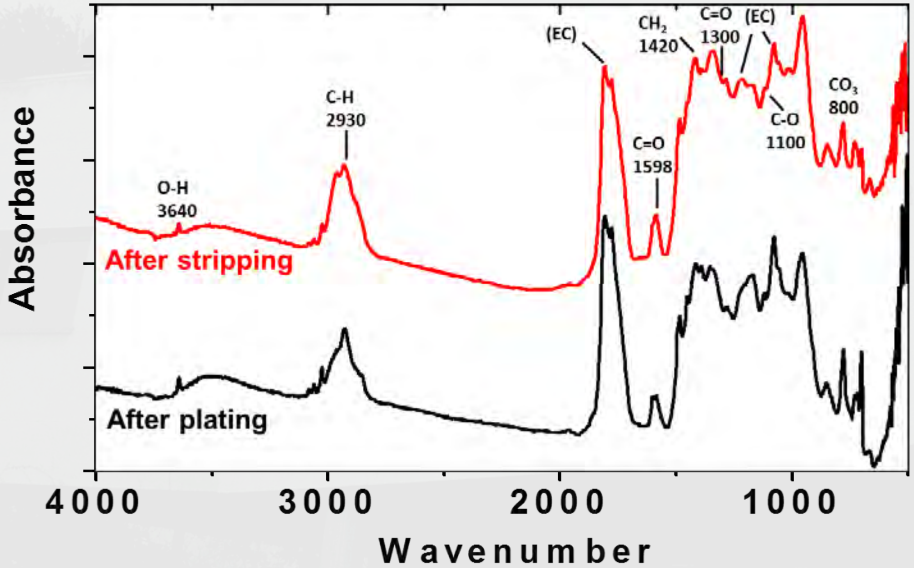
Bubbling in H_2O: H_2?

Ca plating/stripping

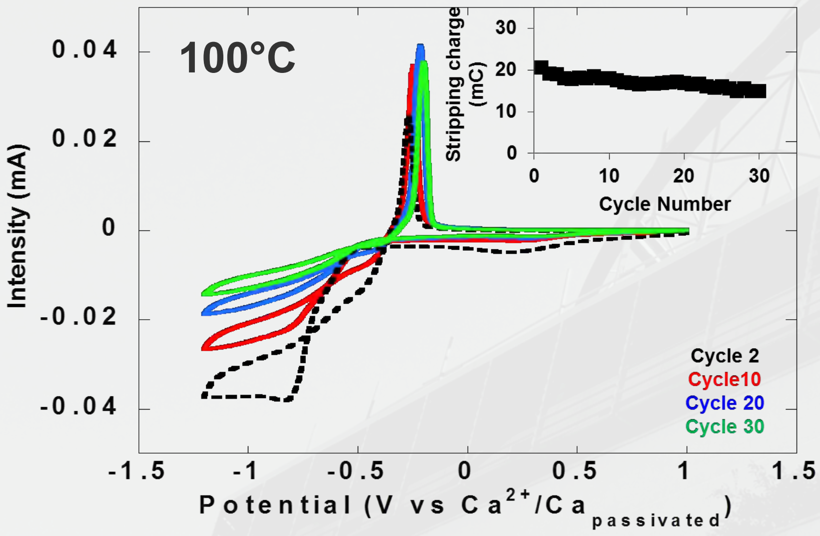
Deposits consist of a mixture of Ca metal and CaF_2 (SEI)



SEI seems stable: permeable to Ca^{2+} ??

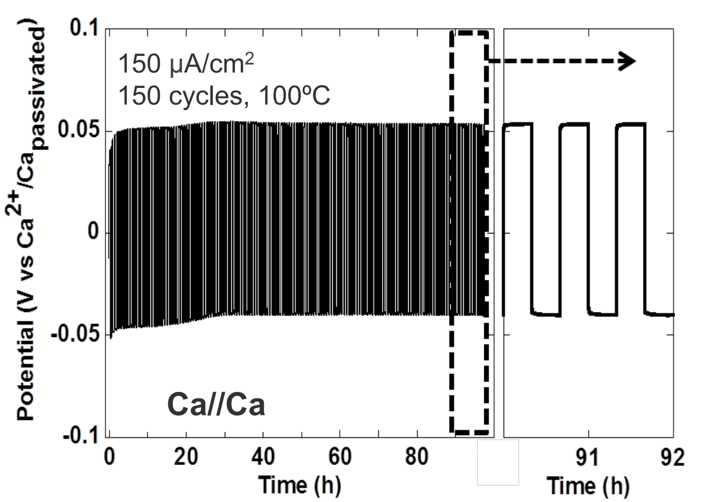


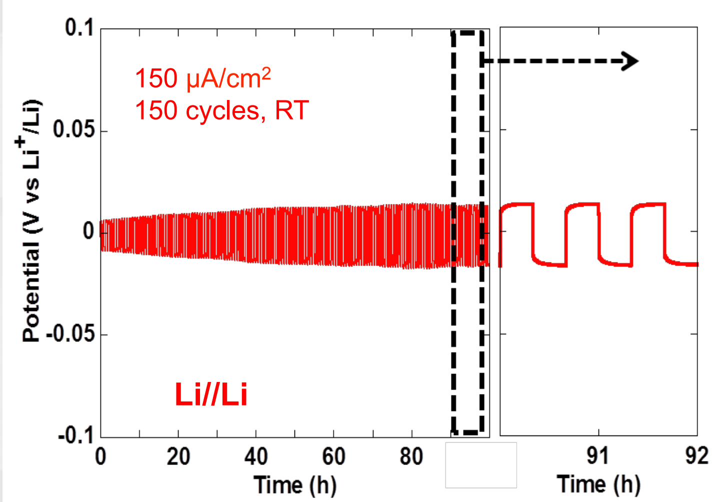
Ca plating/stripping



Capacity stable upon cycling

BUT:
competition with electrolyte decomposition
(efficiency to be improved)

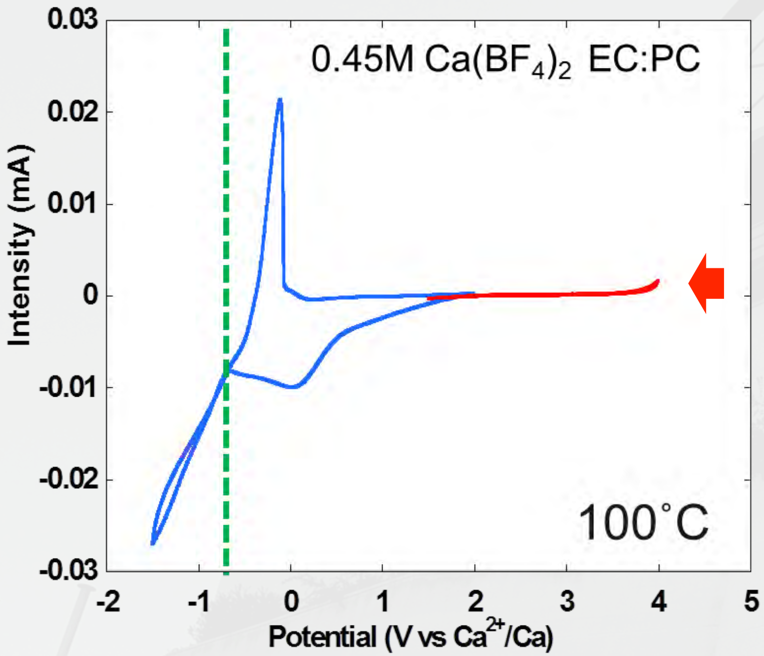


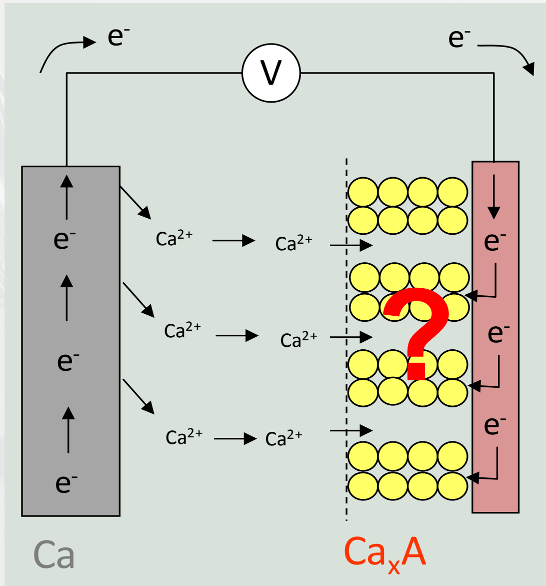


Good cyclability
BUT
high polarisation

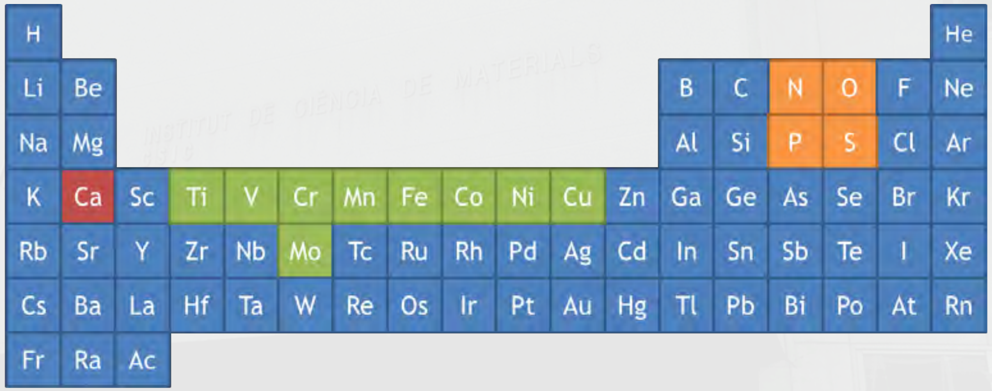
A. Ponrouch, C. Frontera, F. Barde, M.R. Palacin *Nature Materials* 15, 2016, 169

The quest for a cathode





Insertion cathodes?

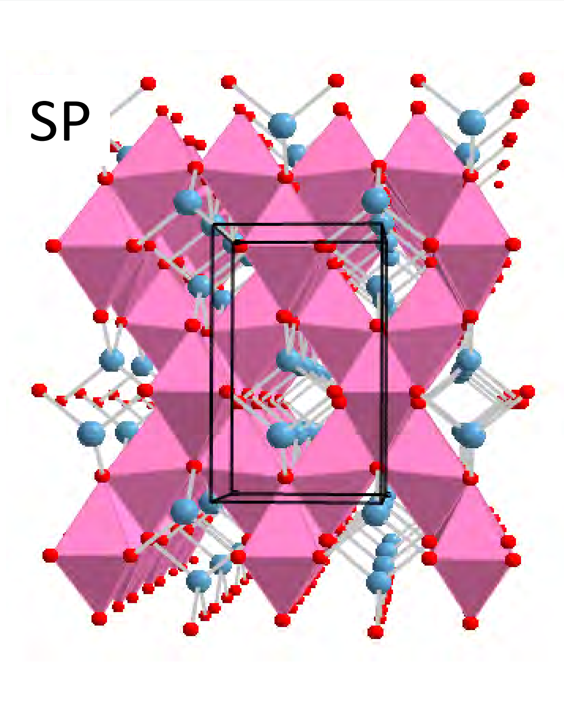


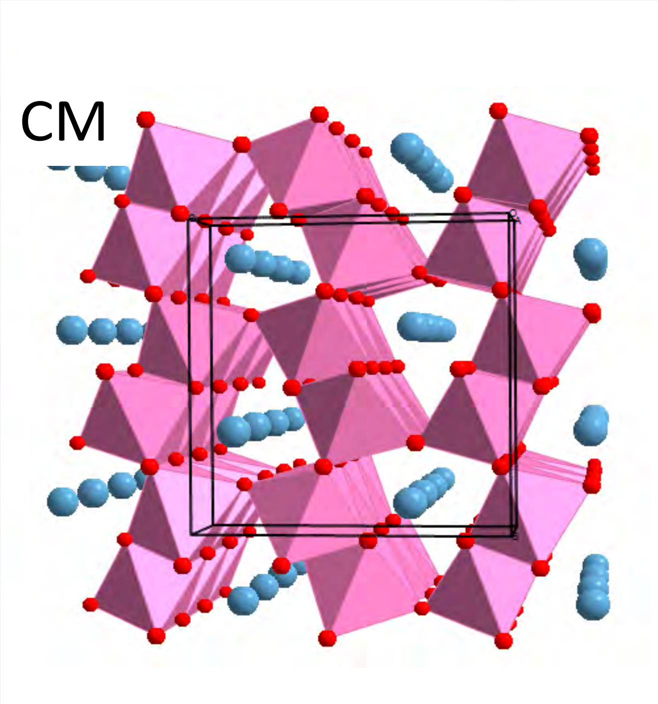
"Technology is always limited by the materials available"

DARPA, US, 1960´s

Is $CaMn_2O_4$ a viable cathode?

Mn^{3+} / Mn^{4+} Th.capacity Δx=1: 250 mAh/g





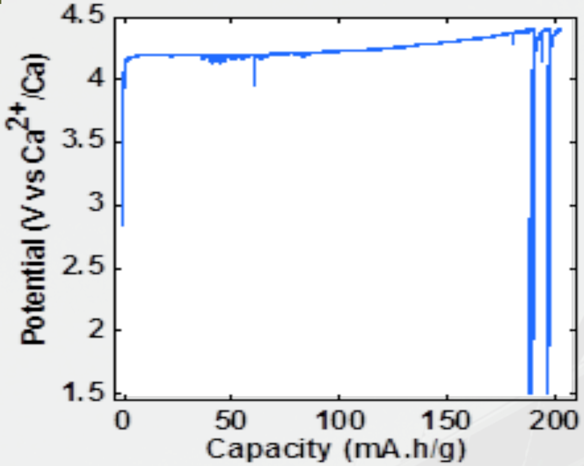
Spinel (not known)

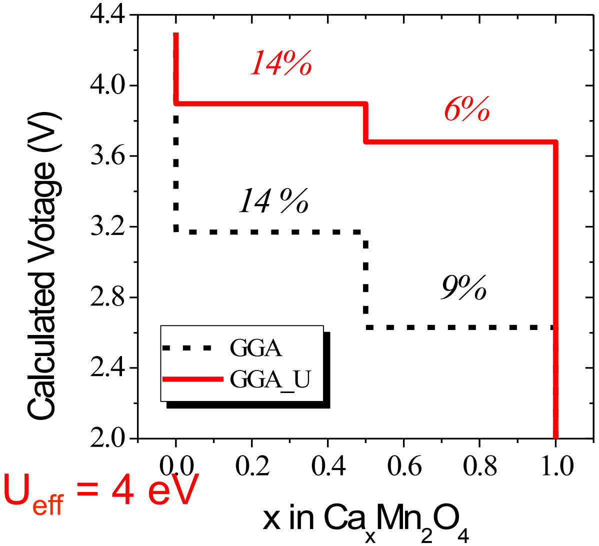
Ca Td
~3V, migration barrier 0.5 eV
Persson et al. 2015

Marokite (1200°C, 72h)

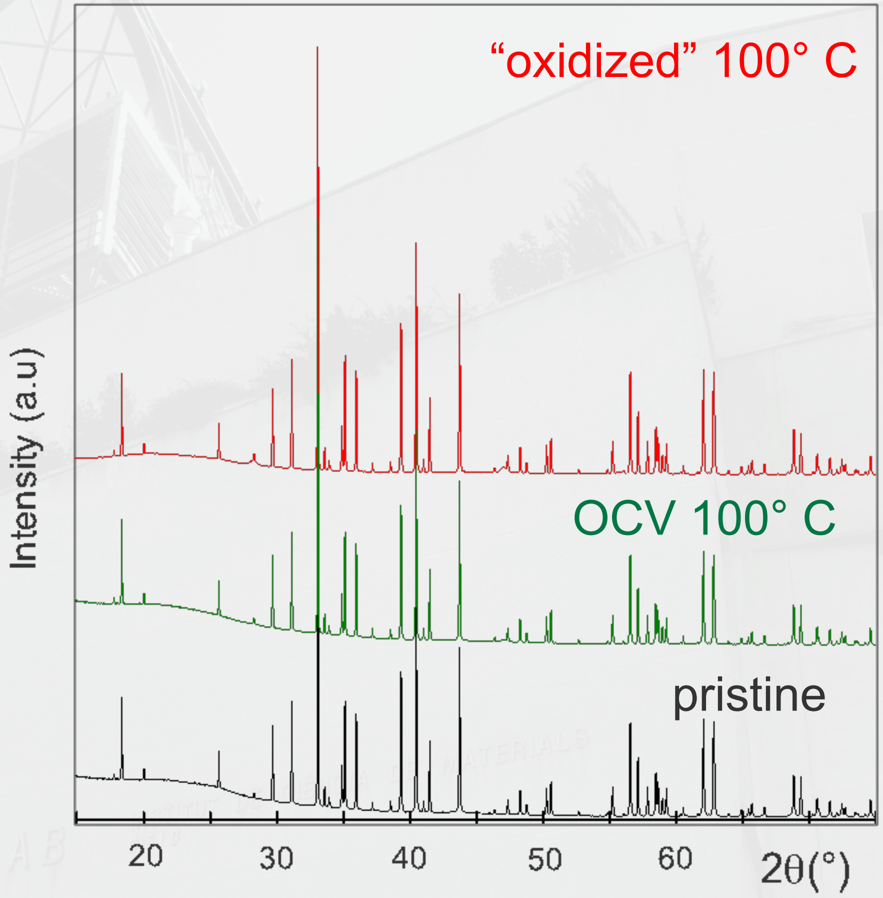
Ca CN=8

What about $CaMn_2O_4$ - Marokite?





U_{eff} = 4 eV



Complementary characterization COMPULSORY!!!

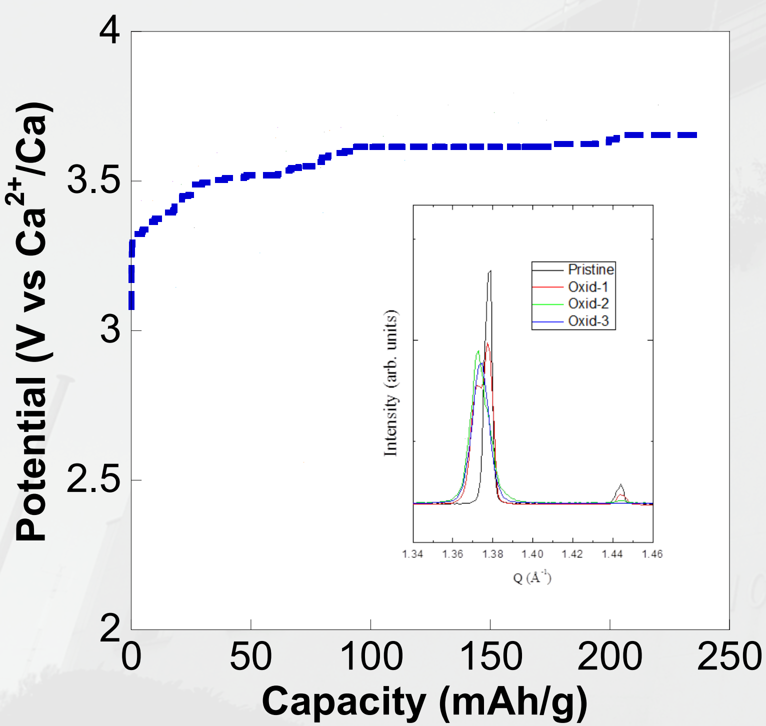
Suitable potential
BUT migration barrier > 1.5 eV

M. E. Arroyo-de Dompablo, C. Krich, J. Nava-Avendaño, M.R. Palacín, F. Bardé *Chemistry of Materials* 28, 2016, 6886.

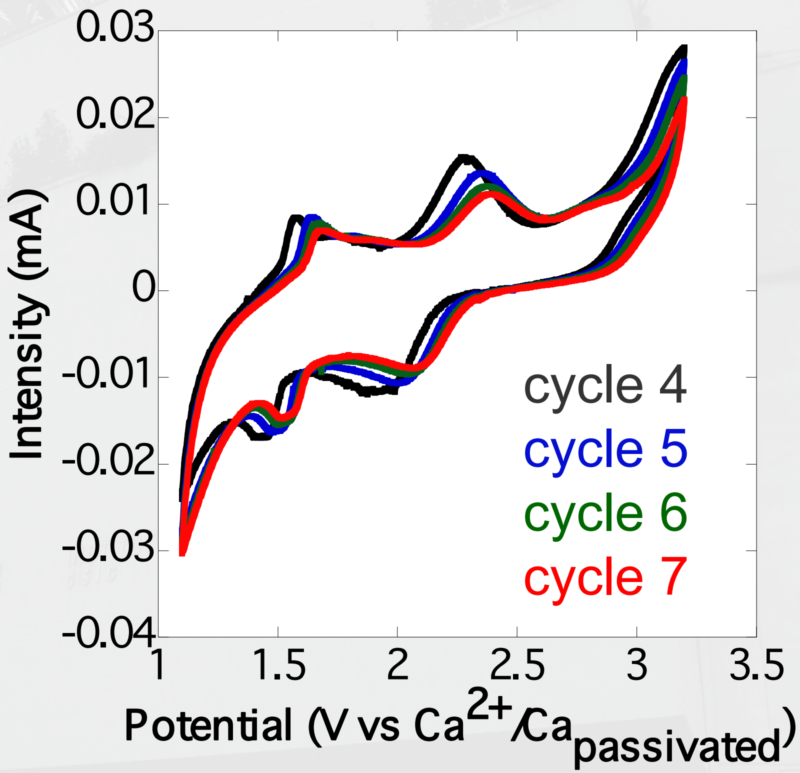
Other alternatives?

Preliminary proof of electrochemical reactivity in some Ca-M-X and M-X phases

Ca-M-X



M-X



D. Tchitchekova et al. (in preparation)

Other alternatives?

ICMAB CSIC

Complementary characterization: XRD may not be enough…

M-X

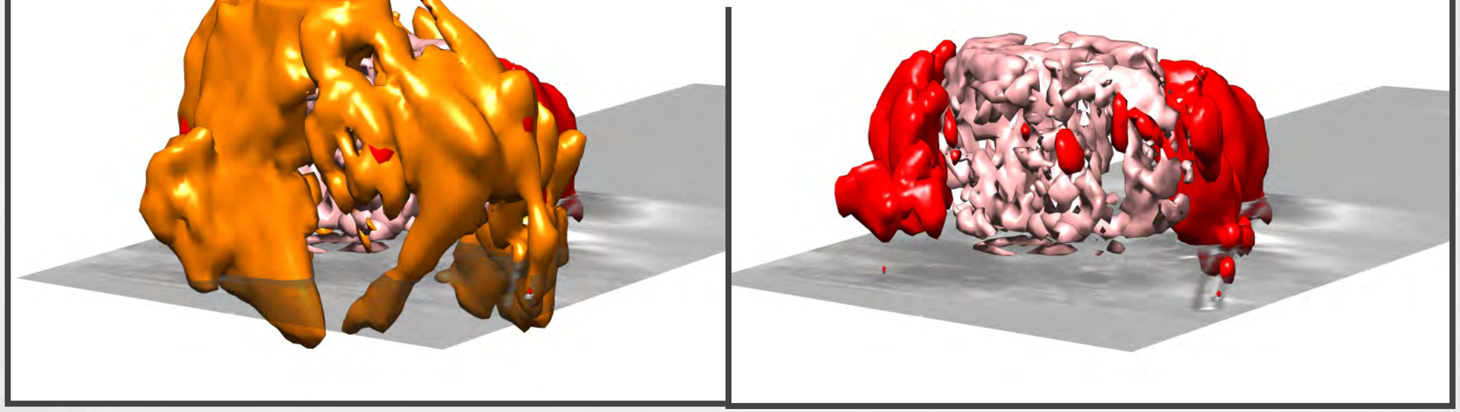
↓

Ca-M-X

Tomographic reconstruction
Transmission X-ray Microscopy
Ca L edge XANES

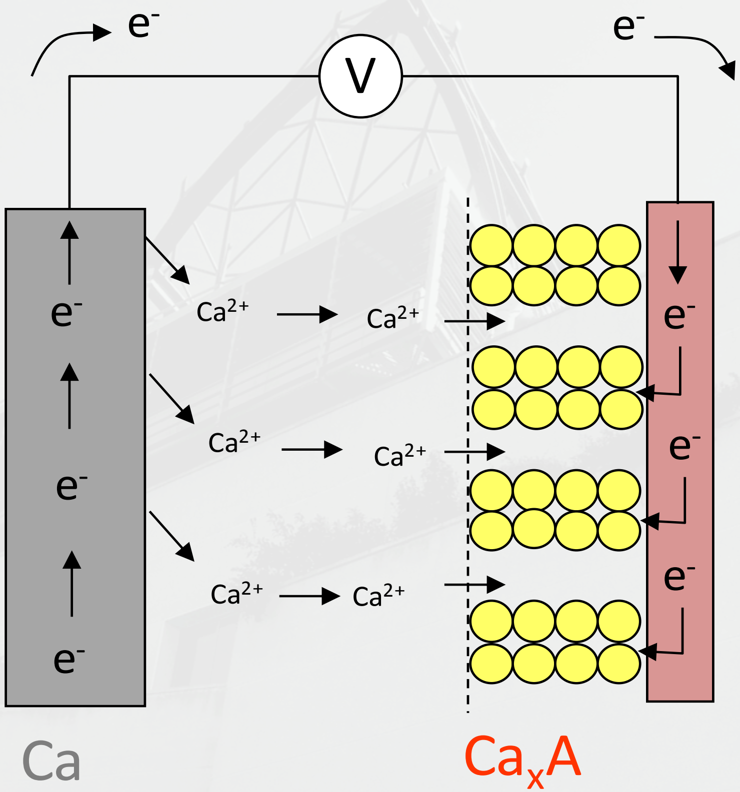
Standards: **M-X**, **$CaCO_3$**, **CaF_2**

Ca-M-X



… to be continued

Towards Ca metal batteries?



Positive

Efficient Ca^{2+} migration
Large specific capacity
High operation potential

Negative

Plating/stripping

Electrolyte

Plating/stripping
Large potential window

Operation T
Efficiency

I always like to look on the optimistic side of life, but I am realistic enough to know that life is a complex matter. **Walt Disney**

Ackowledgements

ICMAB

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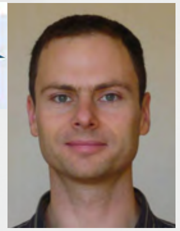
L. Croguennec

LRCS

C. Masquelier

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR



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ALBA

A. Sorrentino

TOYOTA

F. Bardé

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
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