

Post Li-ion batteries: promises and challenges

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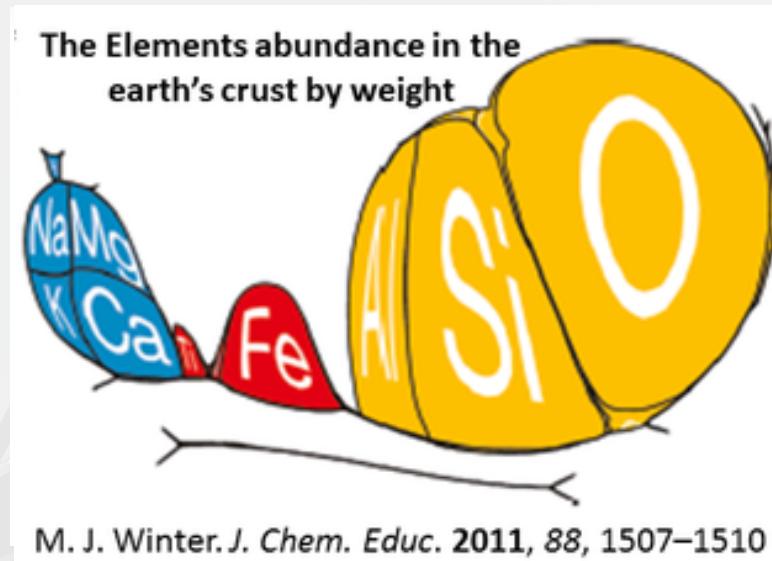


Top 10 Emerging Technologies of 2016

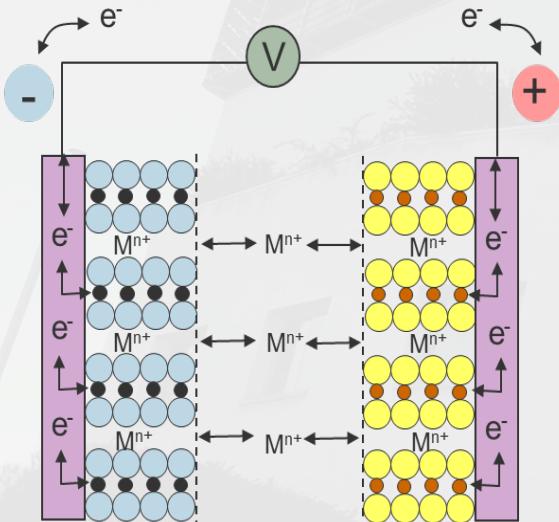
1. Nanosensors and the Internet of Nanothings – With the Internet of Things expected to comprise 30 billion connected devices by 2020, one of the most exciting areas of focus today is now on nanosensors capable of circulating in the human body or being embedded in construction materials. Once connected, 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.





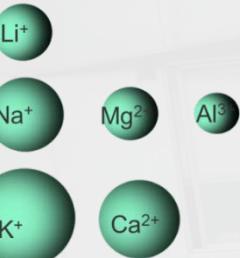
M-ion concept



analogous to Li-ion

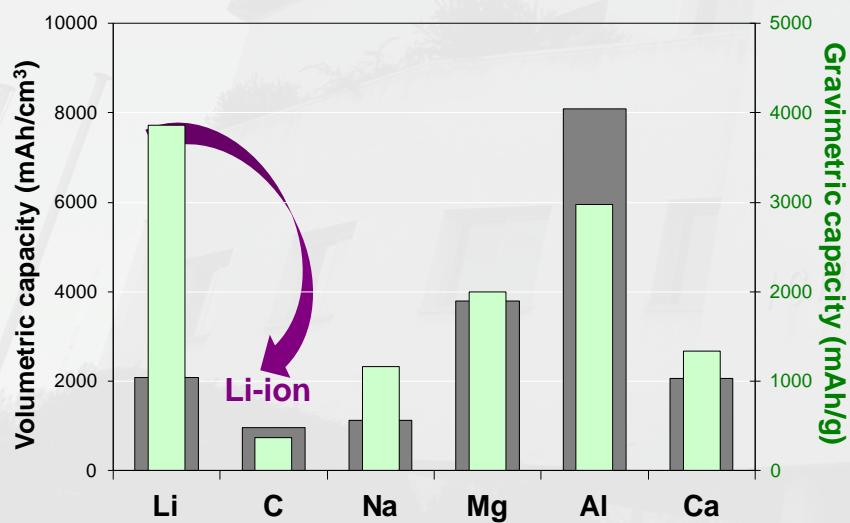
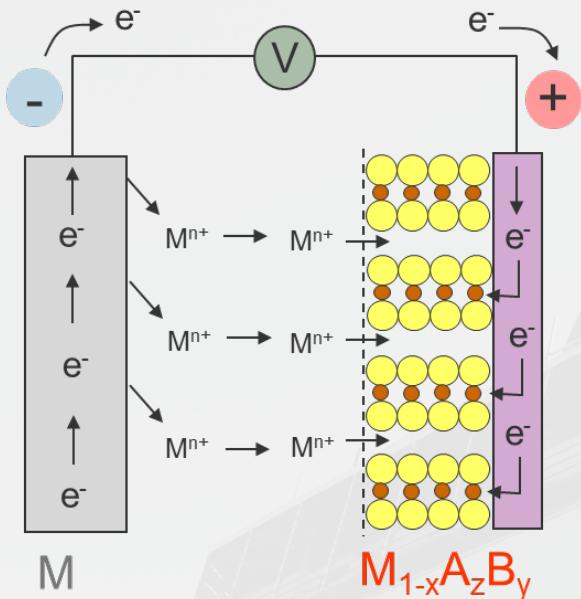
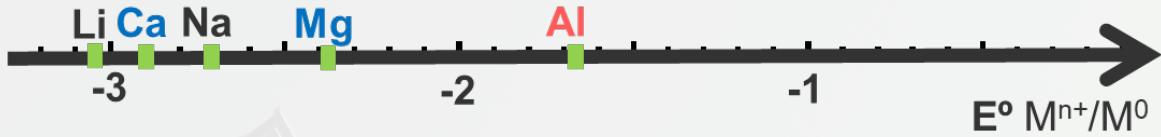
M^{n+} as charge carriers instead of Li^+
(migration may be an issue for $n > 1$, coulombic interactions)

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

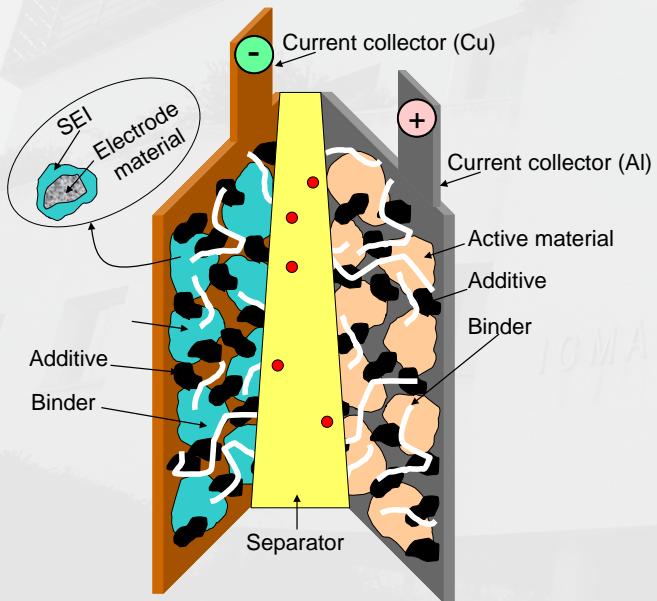
lower potential
reversible plating/stripping?

Why Na-ion?

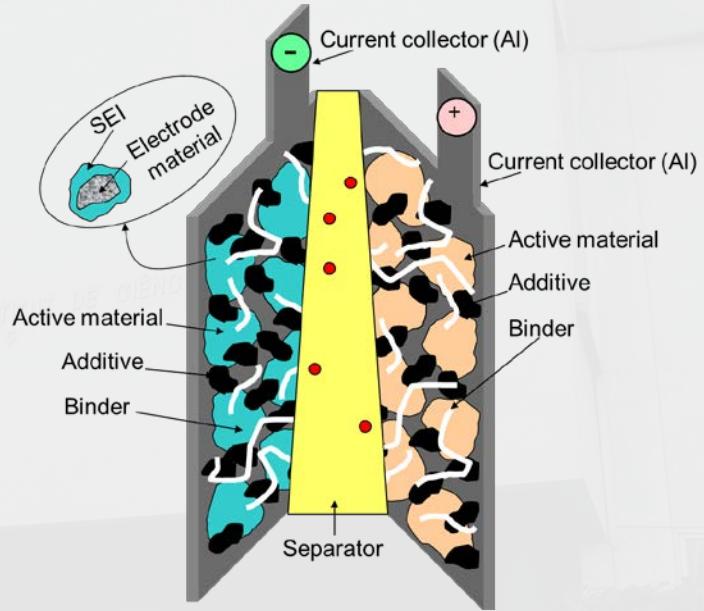


→ “unlimited” Na resources	20 ppm	22700 ppm	Earth’s crust
→ high standard reduction potential	-3.04	-2.71	vs. NHE
→ alloy formation with Al	yes	no	

Li-ion



Na-ion



Why 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



ALISTORE
European research institute

ICMAB



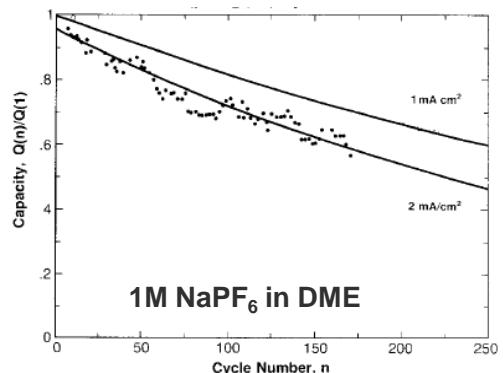
th: 350 Wh/kg, 1470 Wh/l

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

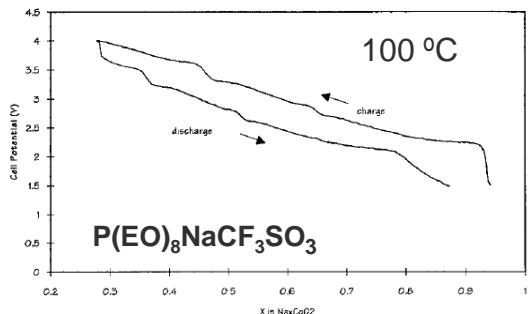


J. Electrochem. Soc., Vol. 140, No. 10, October 1993

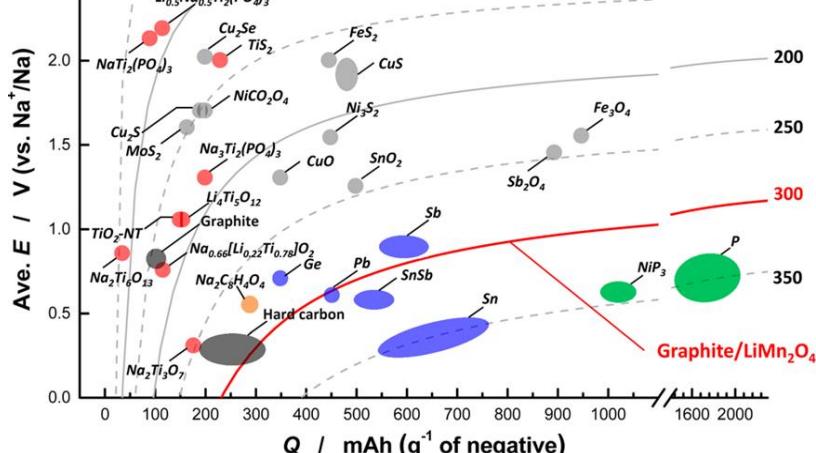
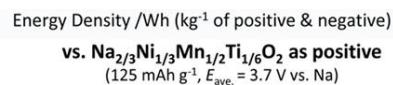
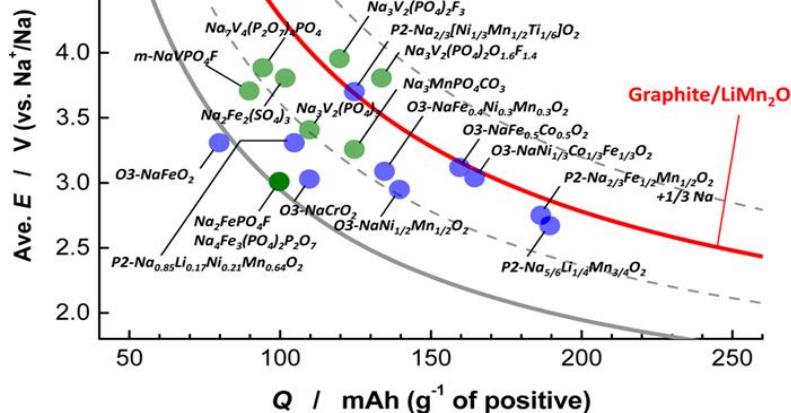
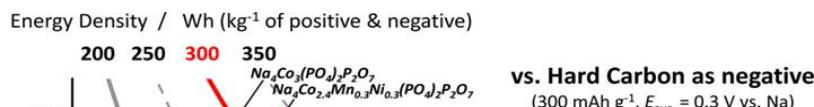
Rechargeable $\text{Na}/\text{Na}_x\text{CoO}_2$ and $\text{Na}_{15}\text{Pb}_4/\text{Na}_x\text{CoO}_2$ Polymer Electrolyte Cells

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

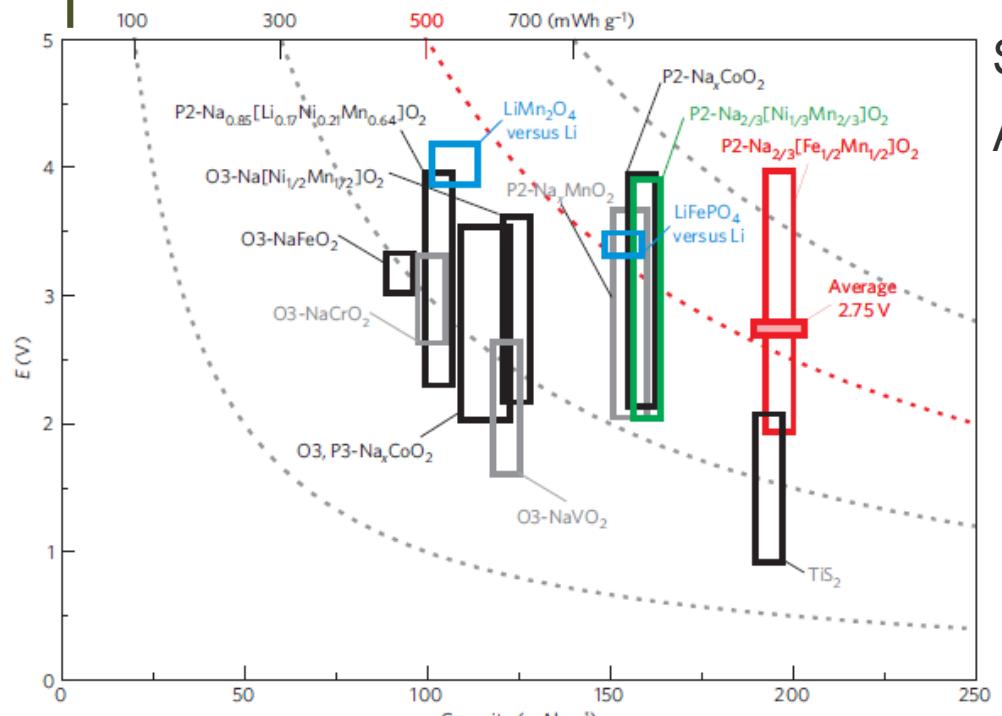


~1990



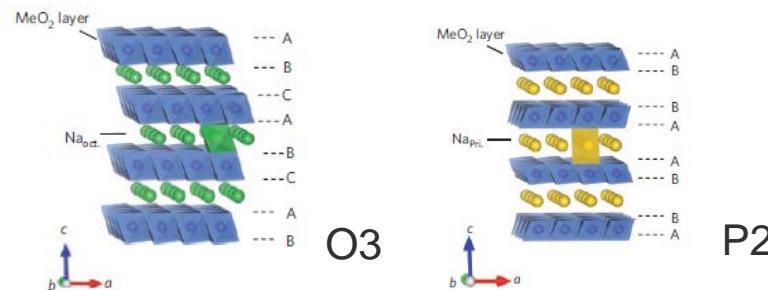
N. Yabuuchi et al. Chem. Rev. 114 (2014), 11636.

Positive electrode materials



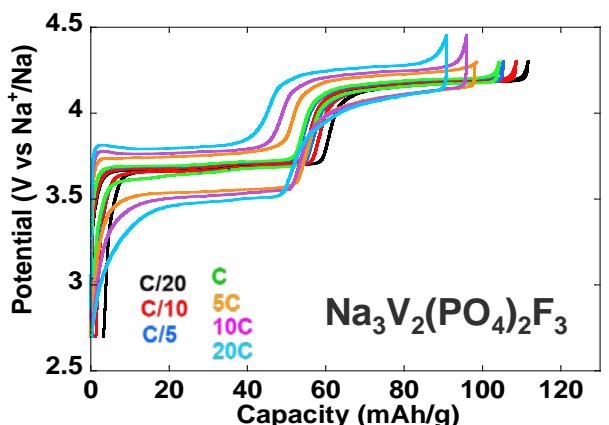
N. Yabuuchi et al. Nature Materials 11(2012) 512

Some V windows too wide to be practical
Air stability can be an issue



O3 higher capacity & P2 higher stability

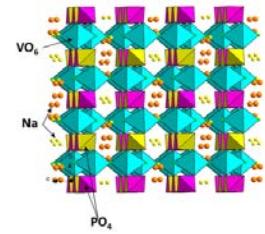
Layered materials Na_xMO_2



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

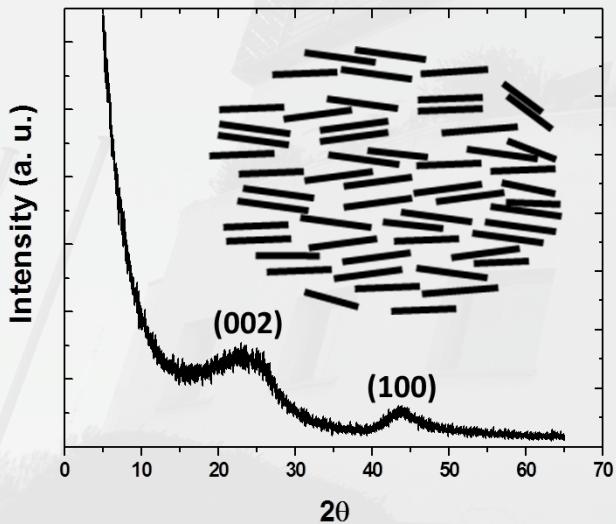
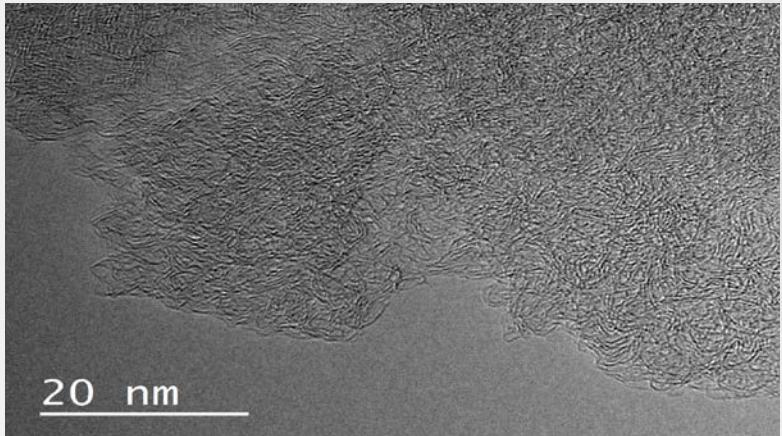
Frameworks typically different from Li - based
Lower capacities than layered (« inactive groups »)
Poor conductivity (C coating)
High stability

Polyanionic frameworks

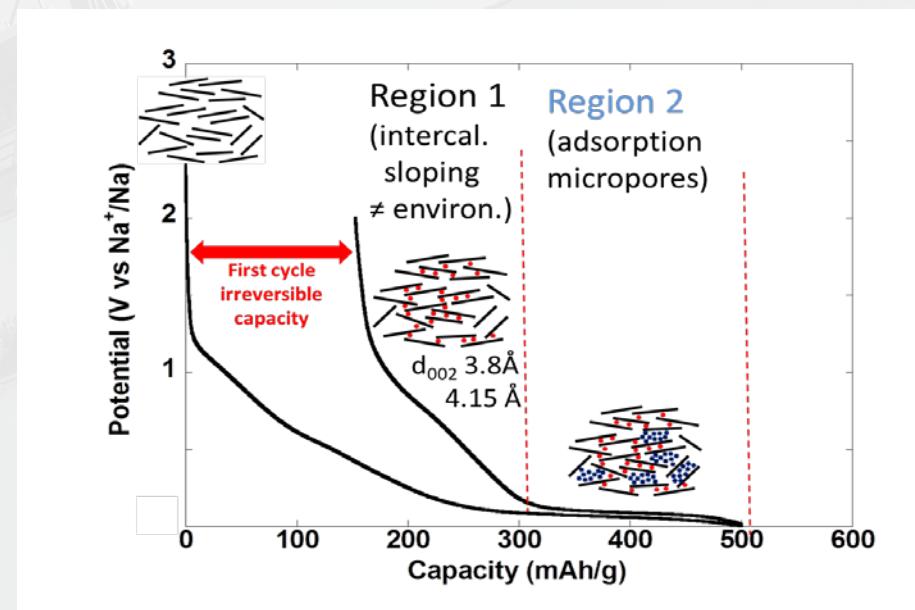


Negative electrode materials: hard C

Non-graphitizable (sp^3 cross-linking)



Prepared by pyrolysis of solid precursors
(cellulose, charcoal, phenolic resins, sugar...)



Current state of the art material

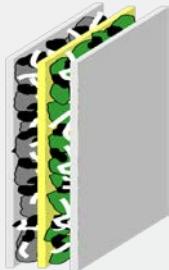
Very low V operation (plating risk?)

1st cycle irreversibility is an issue

capacity  microstructure, electrolyte

Sustainability

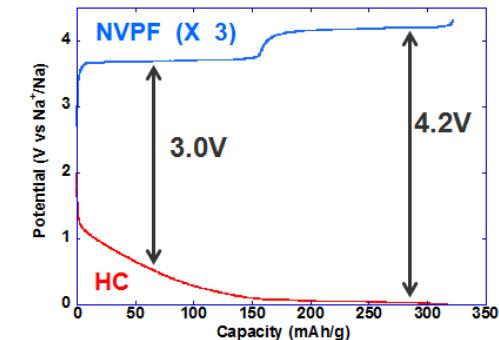
Hard C // EC_{0.45}:PC_{0.45}:DMC_{0.1} // Na₃V₂(PO₄)₂F₃



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

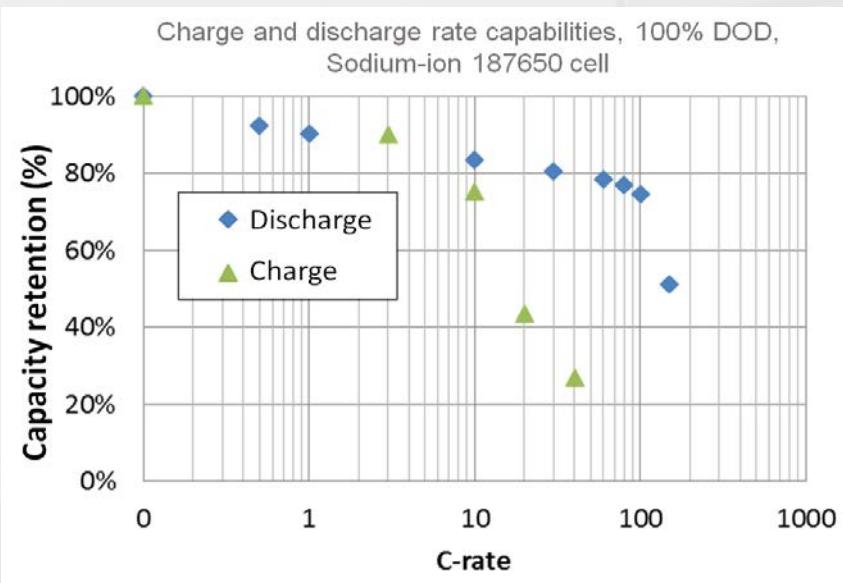
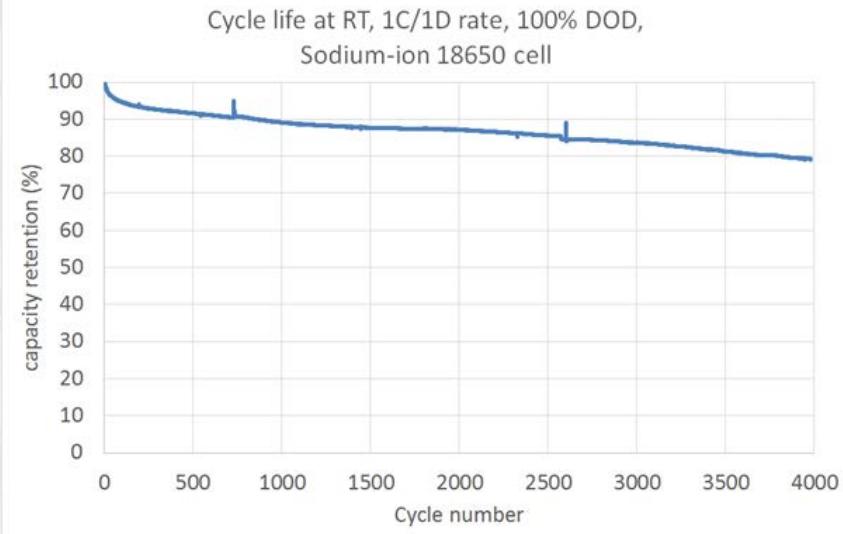
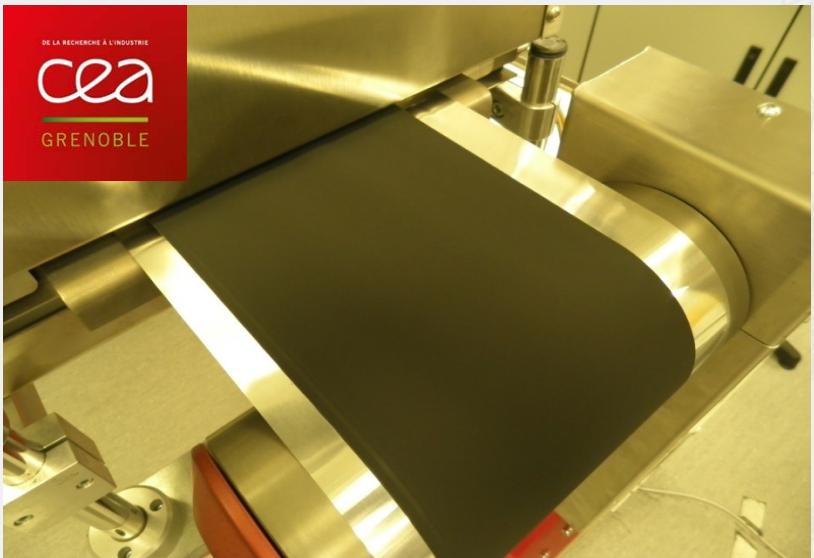
Theoretical energy density : 78 Wh/kg
 (BatPac v1.0)

(for comparison Graphite//LP30//LiFePO₄ gives 75 Wh/kg)



CALCULATED NATURAL CAPITAL COST [€/kWh capacity]				
Elem.	Sodium Ion Batteries		Lithium Ion Batteries	
	HC elec NVPF	Graph. LP30 LiFePO ₄	Graph. LP30 LiMn ₂ O ₄	Li ₄ Ti ₅ O ₁₂ LP30 LiMn ₂ O 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

Reported performance: upscaling



Na-ion: lab upscaling





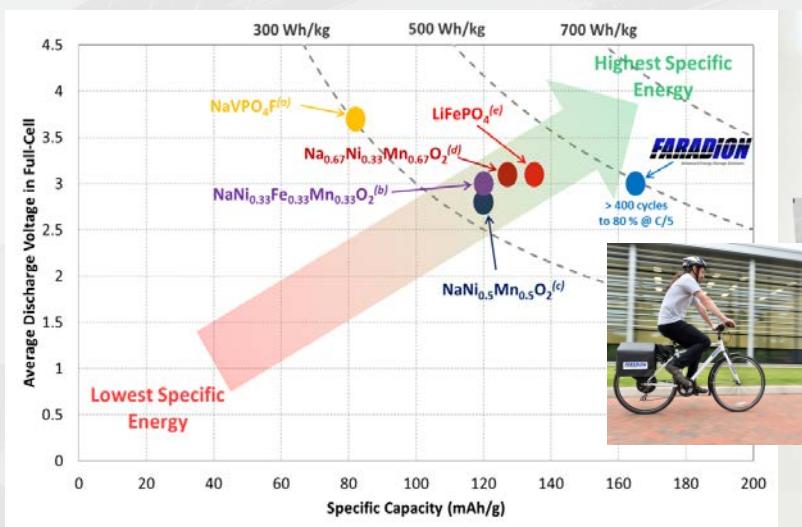
COMMUNIQUÉ DE PRESSE NATIONAL | PARIS | 23 NOVEMBRE 2017

Une start-up pour des batteries de plus en plus rapides

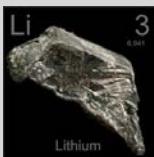
6 partenariats en R&D

Et une équipe de recherche coordonnée par Jean-Marie Tarascon (Collège de France)

<http://www.tiamat-energy.com>



Why Ca metal?



→ “unlimited” resources

20 ppm

27640 ppm

46600 ppm

Earth's crust

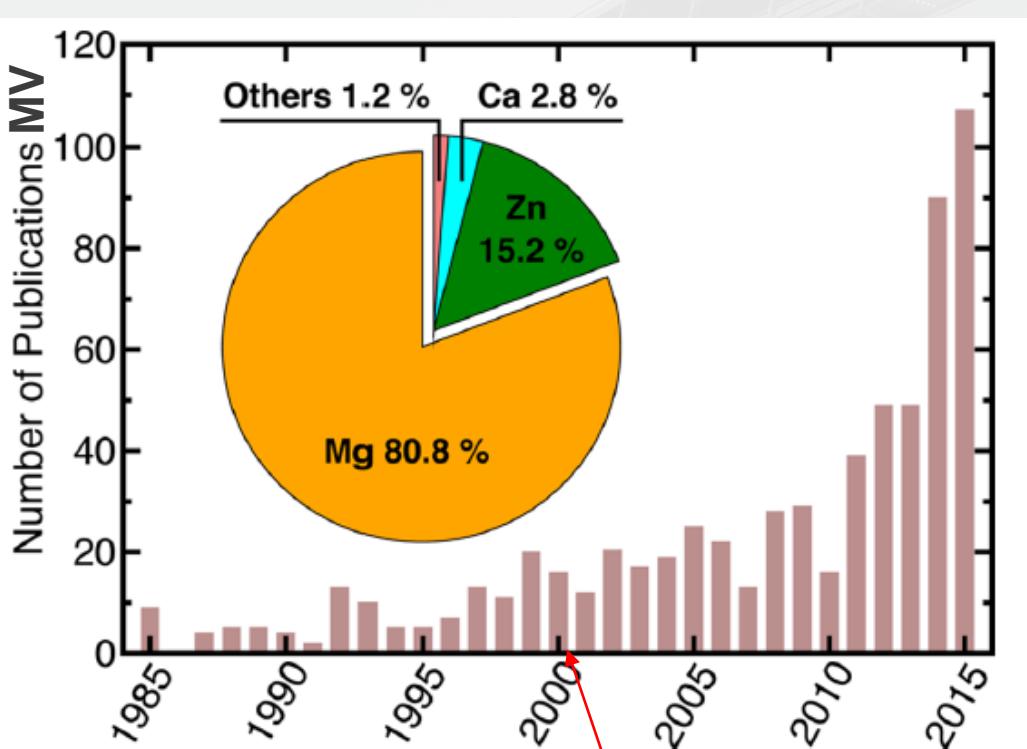
→ high standard reduction potential

-3.04

-2.37

-2.87

vs. NHE



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

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

Charge/radius $\text{Ca}^{2+} \ll \text{Mg}^{2+}$



Easier migration

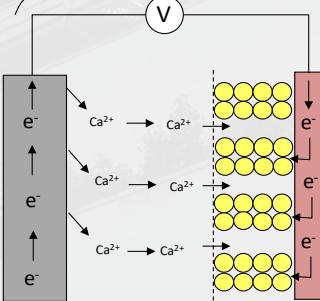
1991

Aurbach et al.

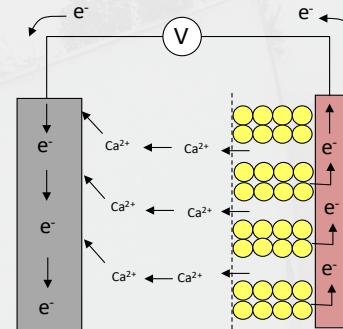
Ca deposition not possible in organic solvent electrolytes
(SEI does not conduct Ca^{2+} ions)

~~Suitable electrolytes (plating)~~

~~cathode development~~



Reduction of the WE:
Ca stripping at the CE



Oxidation of the WE:
Ca deposition ???

2003 Hayashi et al.

2005 Amatucci et al.

2013 Seshadri et al.

2014 Sadoway et al.

2015 Ingram et al.

V_2O_5 (primary)

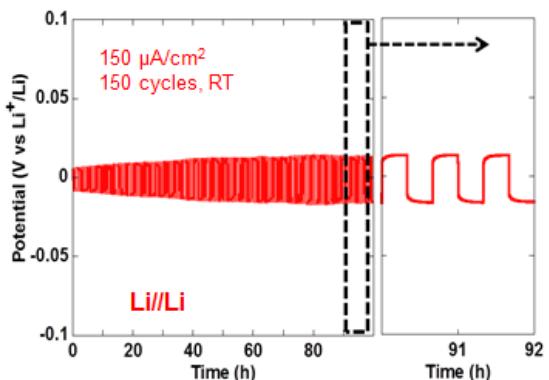
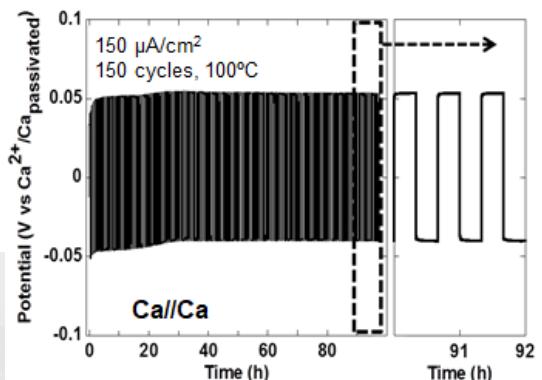
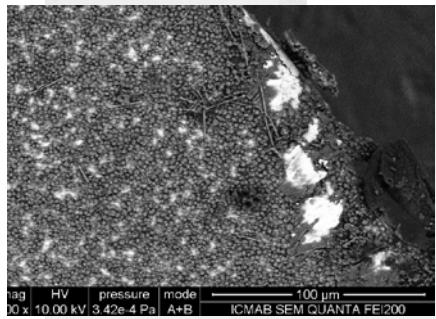
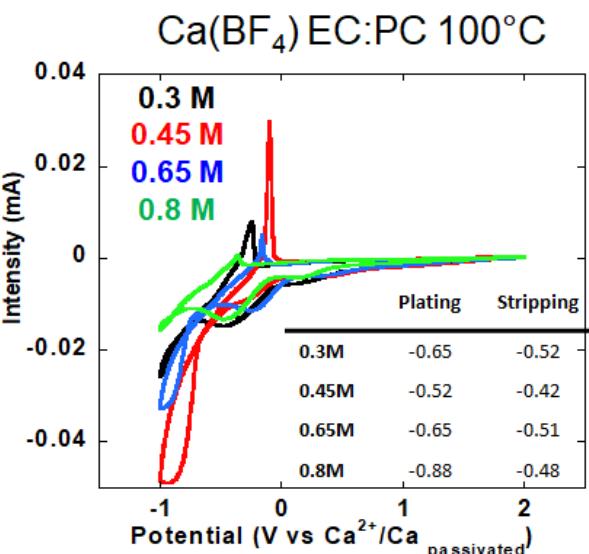
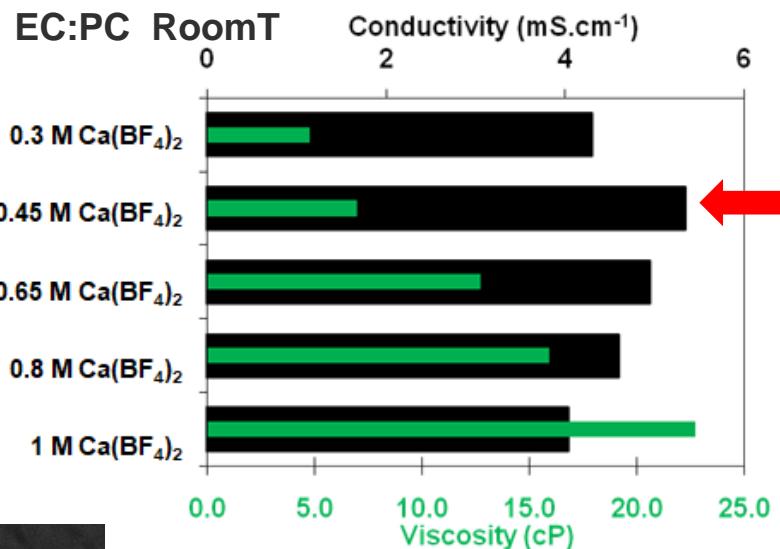
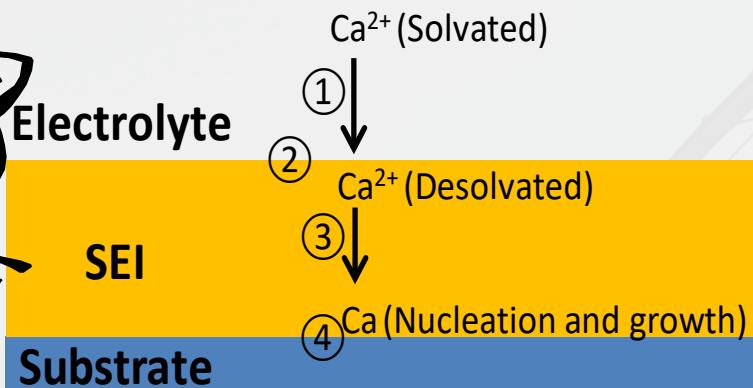
V_2O_5 (high surface carbon CE)

S (primary)

Mo_6Se_8 (Ca-Hg CE)

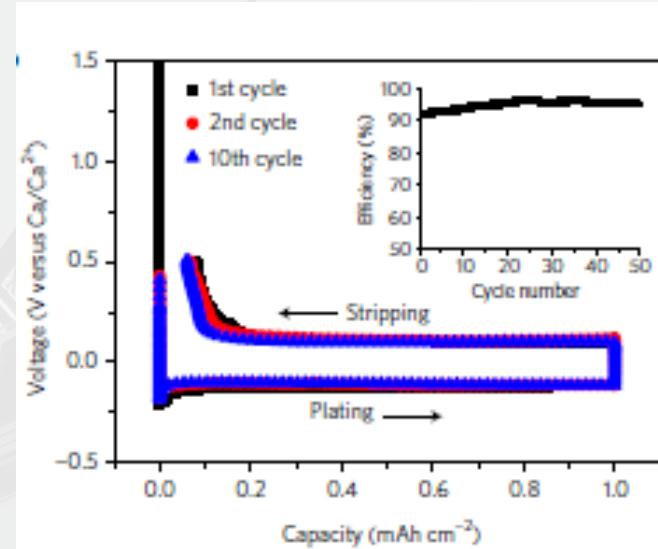
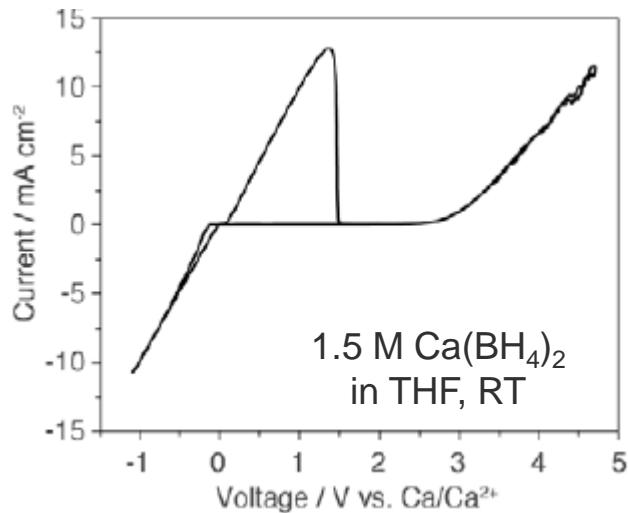
$\text{Ca}_x\text{MnFe}(\text{CN})_6$ (Ca-Sn CE)

M anodes: the case of Ca...



Good cyclability
BUT
high polarisation

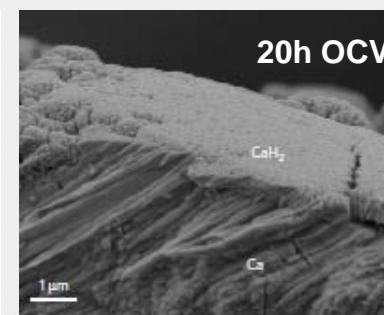
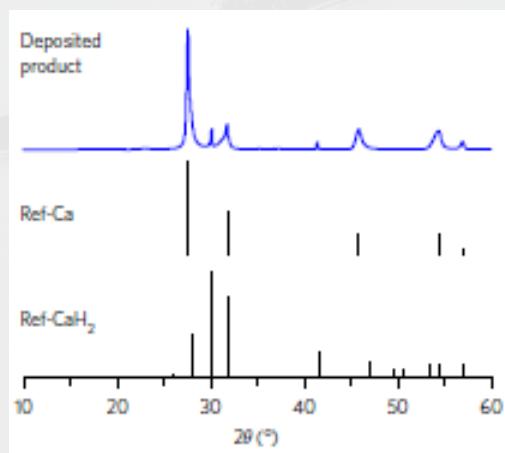
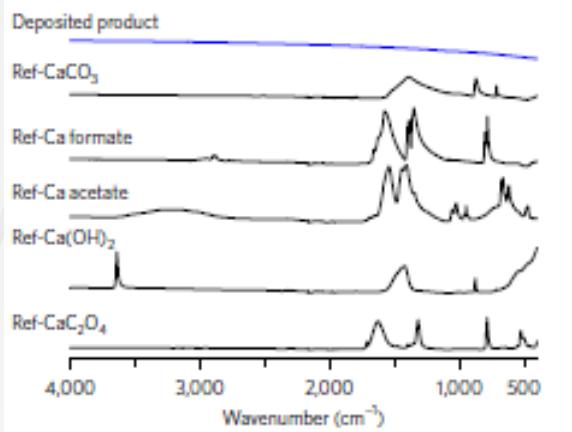
M anodes: the case of Ca...



Efficiency ~ 95%

BUT

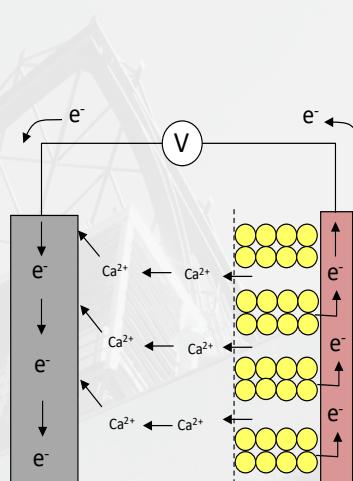
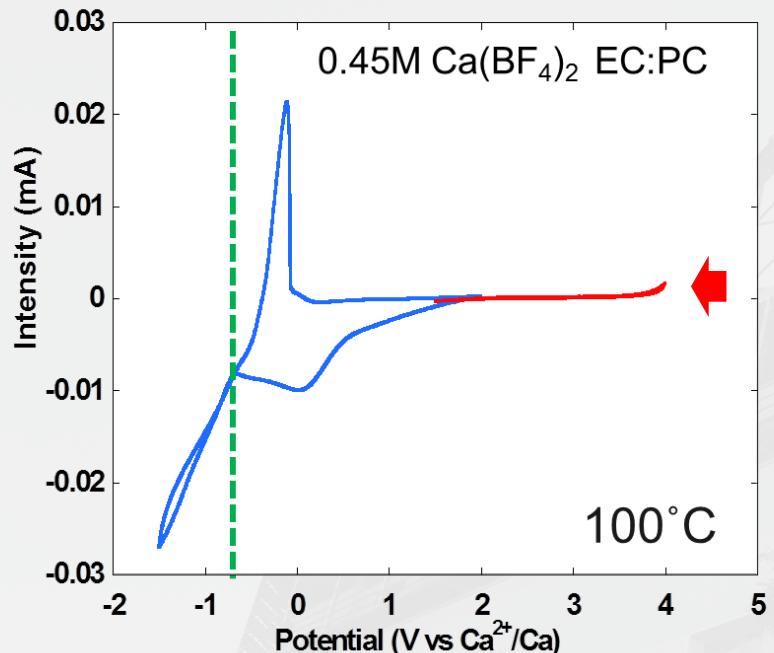
limited V window



No electrolyte decomposition

BUT deposited Ca reacts to form CaH₂

On the quest for cathodes: setup



Ca anode “half cells” ?

CE overpotential
may mislead results

CV (Fc⁺/Fc internal standard)

3 electrode cells ?



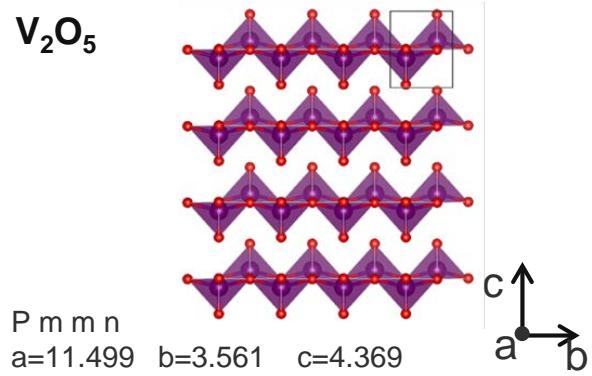
reliable RE needed!



Traditional hosts: V_2O_5 , TiS_2 ...
“new hosts”: Ca-M-O

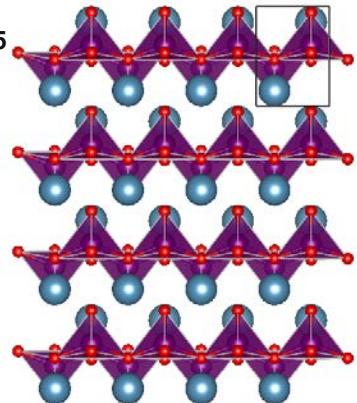
Revisiting V_2O_5

V_2O_5



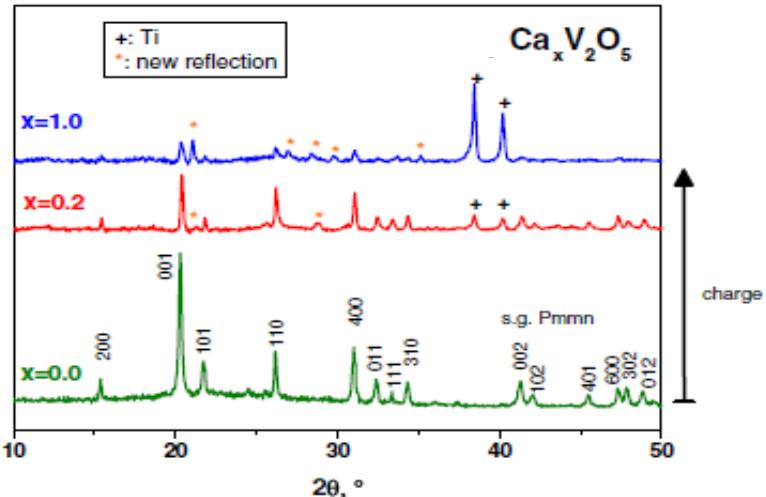
Theoretical Capacity:
 V_2O_5 (CaV_2O_5)
~ 295 mA.h/g

CaV_2O_5

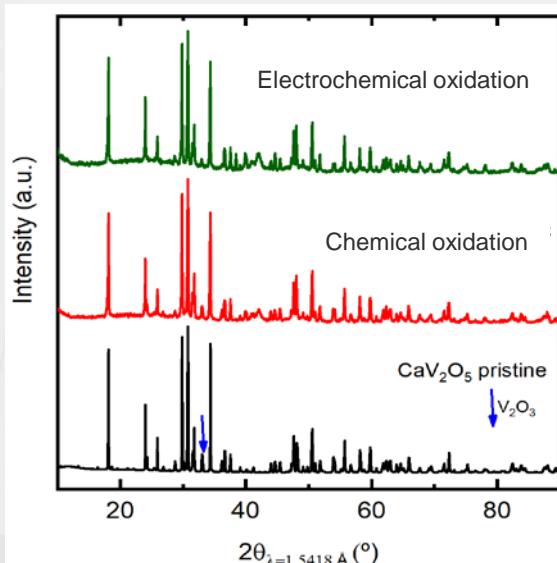


M. Boloux et al. J. Solid State Chem. 1976, 16, 385
M. Onoda et al. J. Solid State Chem. 1996, 127, 359

R. Verrelli et al. J. Power Sources 407, 162 (2018)



M. Cabello et al. Electrochim. Comm. 2016, 67, 59



Oxidation not feasible
(large migration barrier!!)

no proof of Ca^{2+} intercalation in V_2O_5



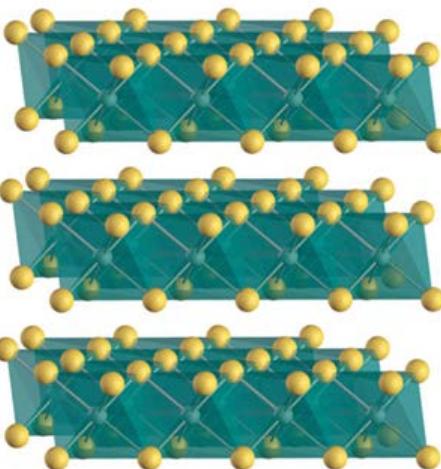
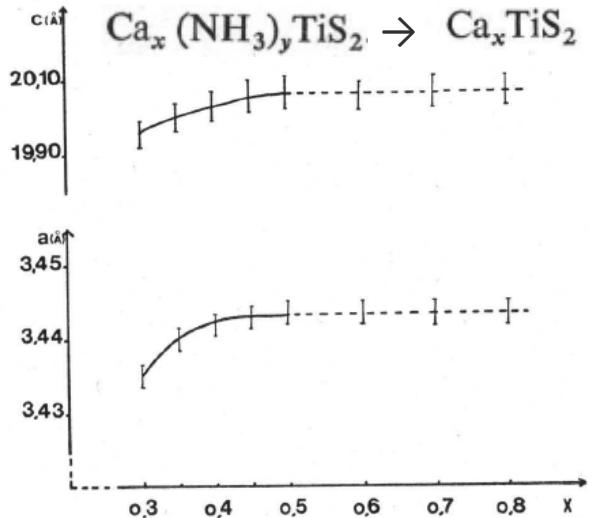
Revisiting TiS_2

C. R. Acad. Sc. Paris, t. 279 (19 août 1974)

Série C — 303

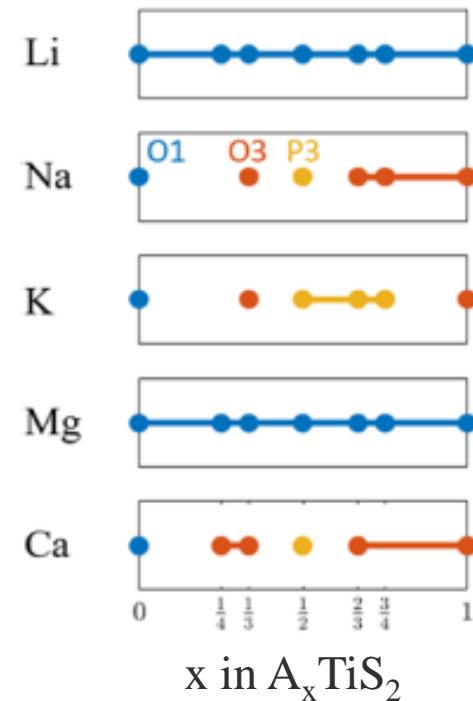
CHIMIE MINÉRALE. — *Facteurs physiques et structuraux dans les systèmes d'intercalaires : systèmes $\text{A}_x^{++}\text{TiS}_2$, cas du calcium.* Note (*) de M^{me} Annie Le Blanc-Soreau et M. Jean Rouxel, présentée par M. Georges Champetier.

Le calcium en solution dans l'ammoniac liquide réagit avec le disulfure de titane. Deux phases Ca_xTiS_2 ont été identifiées : elles correspondent respectivement à $0,13 < x \leq 0,25$ et $0,30 \leq x \leq 0,50$. La limite supérieure $x = 0,50$ comparée à $x = 1$ pour Na_xTiS_2 , alors que le paramètres géométriques sont analogues, met en relief le rôle du facteur électronique. Une discussion générale des divers facteurs physiques intervenant pour fixer les structures, ou les limites de phases, est donnée.



M.D. Radin & A. Van der Ven

DOI: [10.1021/acs.chemmater.6b03454](https://doi.org/10.1021/acs.chemmater.6b03454)
Chem. Mater. 2016, 28, 7898–7904



Complementary characterization: XRD may not be enough...

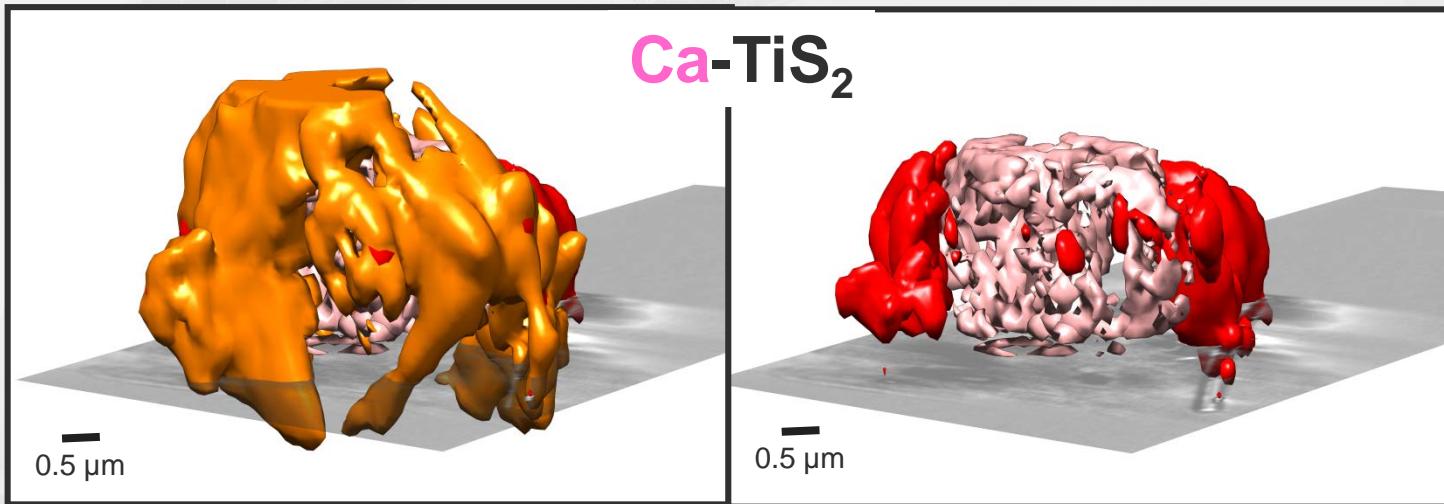
M-X



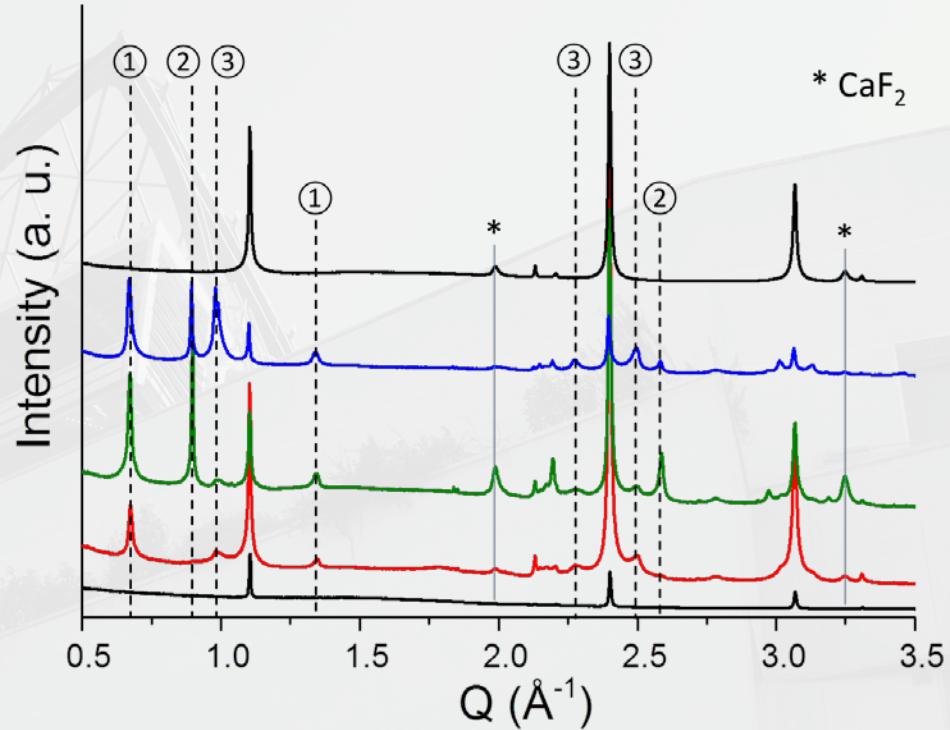
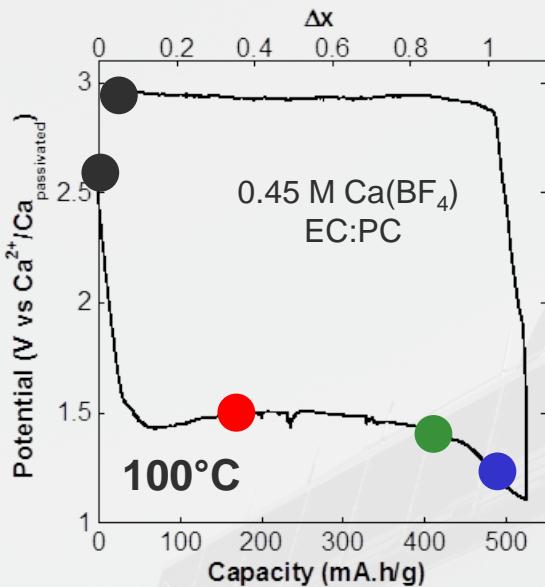
Ca-M-X

Tomographic reconstruction
Transmission X-ray Microscopy
Ca L edge XANES

Standards: **M-X**, **CaCO₃**, **CaF₂**



Revisiting TiS_2

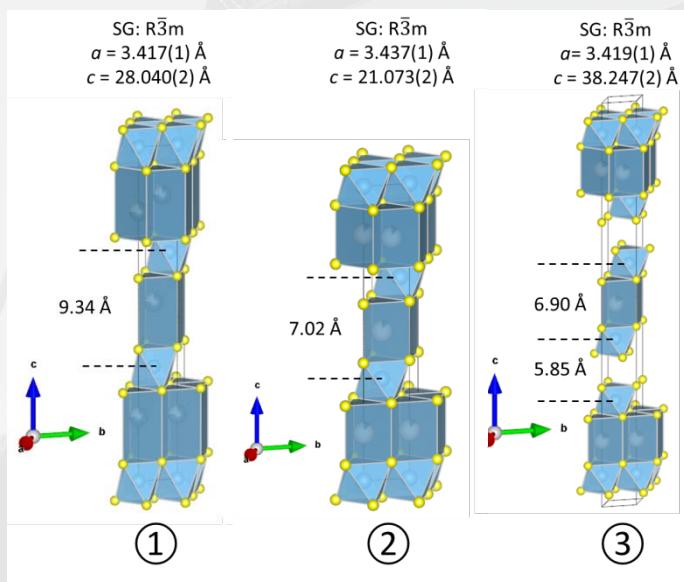


Unreacted TiS_2

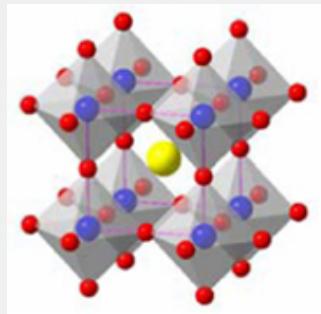
Different phases with \neq interlayer spacing

- ① Co-intercalated solvent (EC/PC) ?
- ② $\text{Ca}_{0.5}\text{TiS}_2$?
- ③ Stage 2 phase ?

Fully reversible BUT huge overpotential !!!

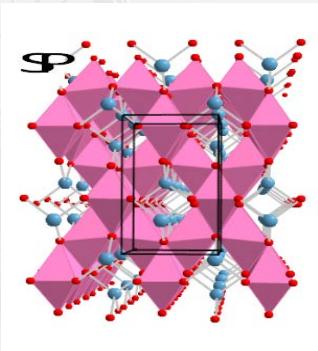


CaMoO_3

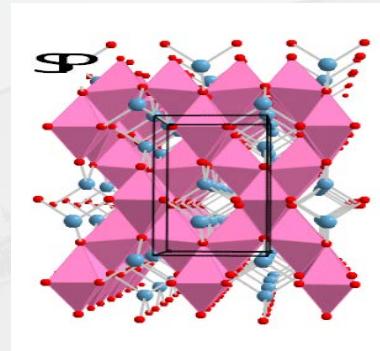


$\text{Mo}^{6+} / \text{Mo}^{4+}$ $\Delta x=1$
Th.capacity: 291 mAh/g

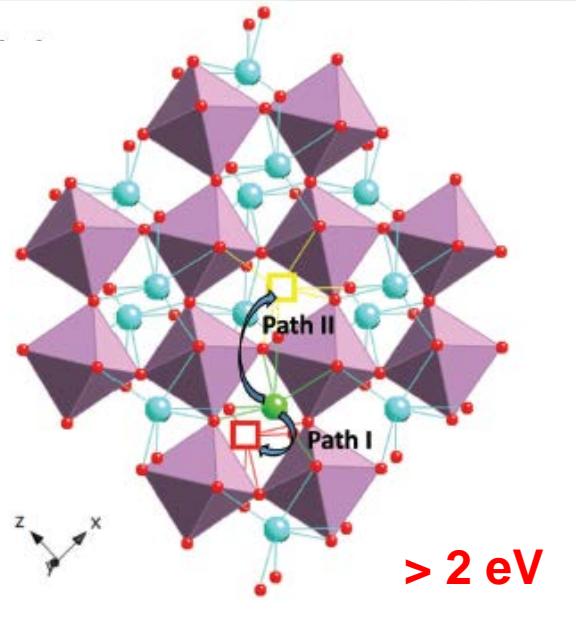
CaMn_2O_4 $\text{Mn}^{3+} / \text{Mn}^{4+}$ Th.capacity $\Delta x=1$: 250 mAh/g



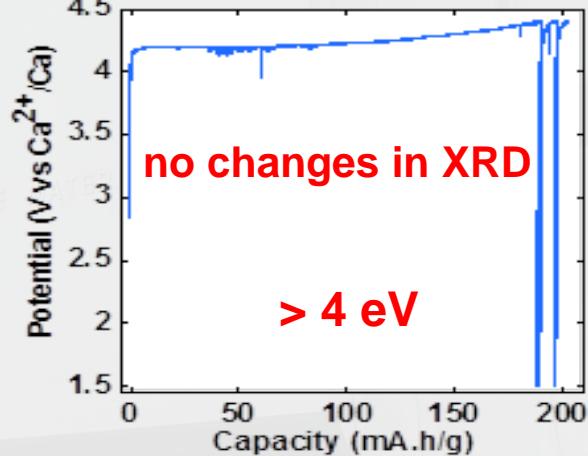
Spinel (not known)



Marokite (1200°C, 72h)

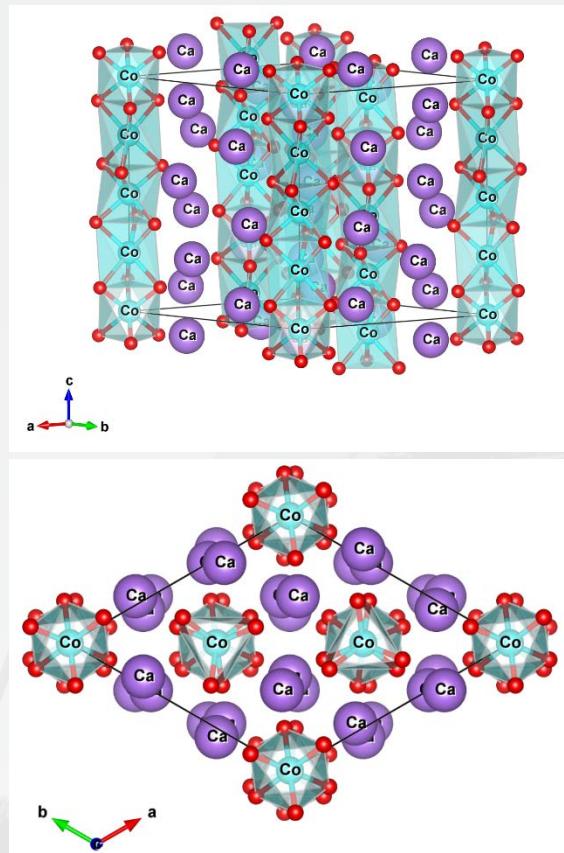


Ca Td
~3V, migration barrier 0.5 eV
Persson et al. 2015



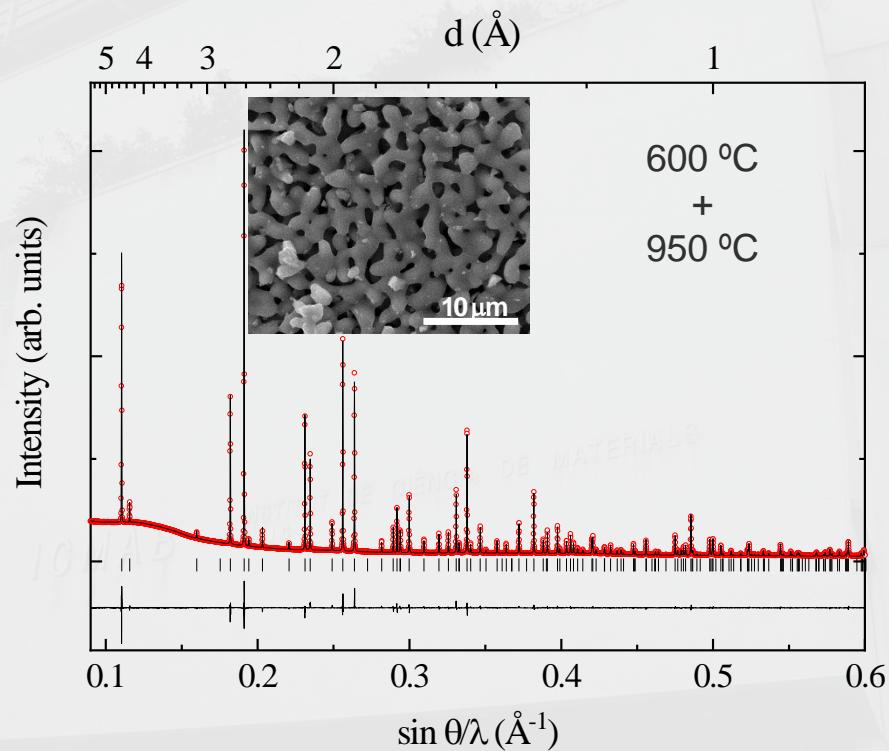
$\text{A}_{1+x}(\text{A}'_x\text{B}_{1-x})\text{O}_3$ ($\text{A} = \text{Ca, Sr, Ba....}$) 1D framework

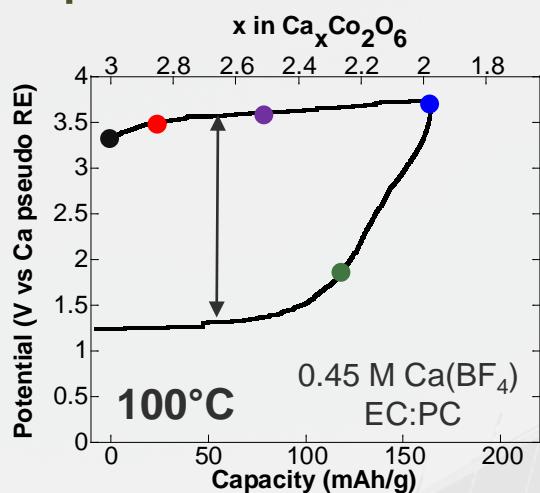
$\text{Ca}_3\text{Co}_2\text{O}_6$ $\text{A}=\text{Ca}$, $x=0.5$, $\text{A}' = \text{B} = \text{Co}$



$\text{Co}^{3+} / \text{Co}^{4+}$
Th.capacity
 $\Delta x = 1: 250 \text{ mAh/g}$

Pechini synthesis
(nitrates, citric acid, EG)

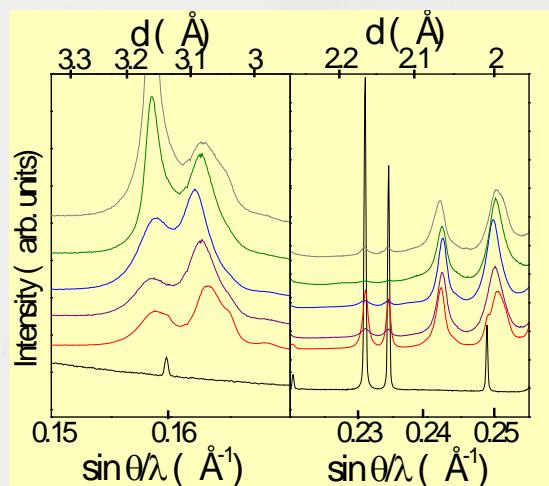
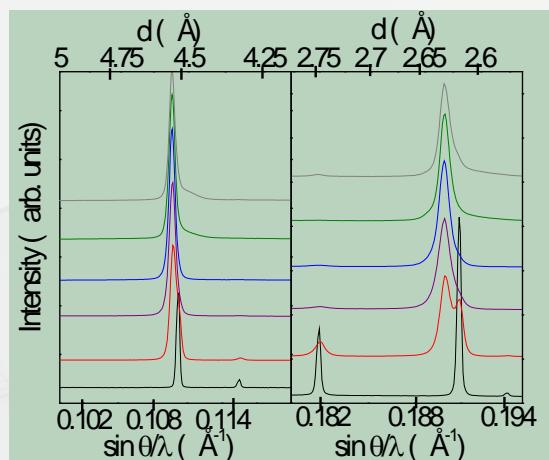
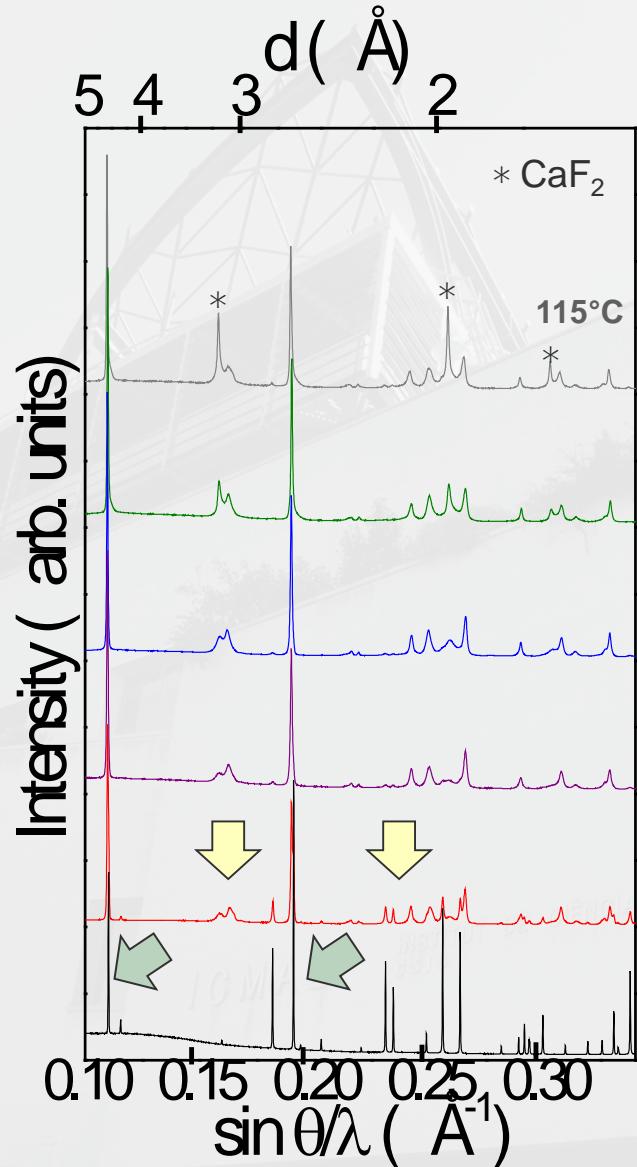




Large hysteresis

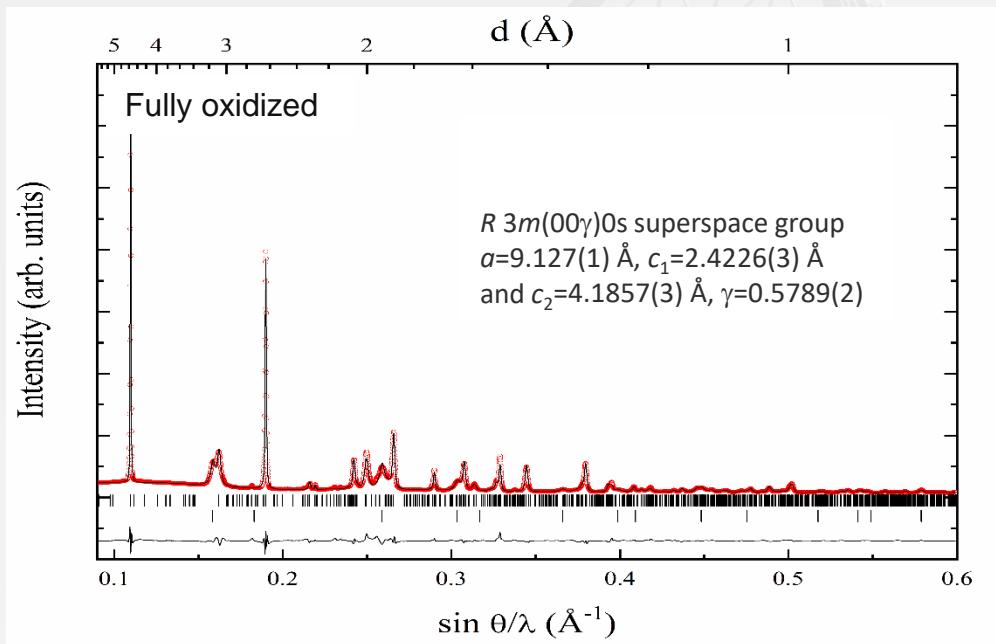
Changes in XRD
partially reversible?

Electrolyte decomp.
at $V < 1.5$ V
especially if $T > 100^\circ\text{C}$



Are structural changes
related to Ca^{2+} extraction???

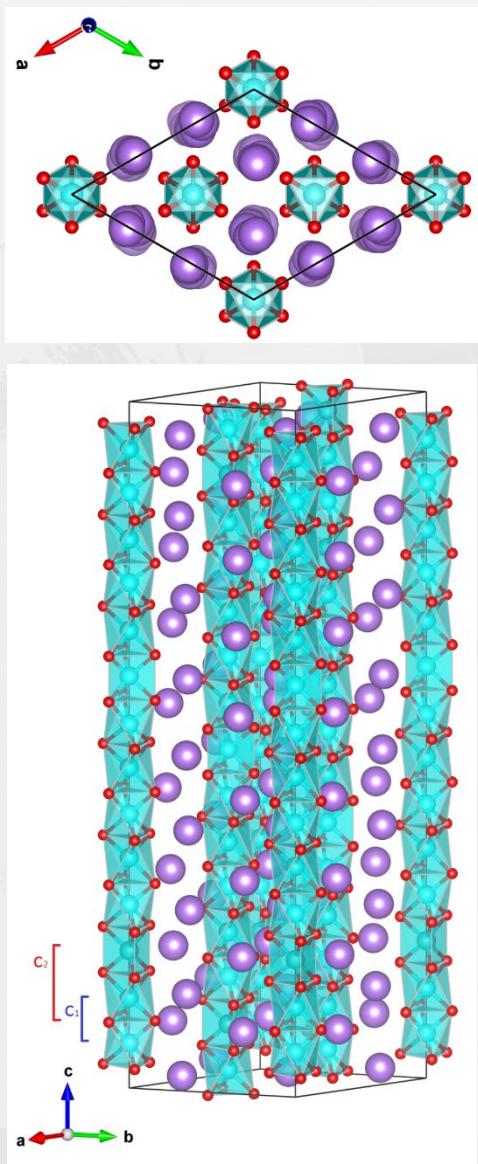
Efforts to develop a structural model basing on other $\text{A}_{1+x}(\text{A}'_{x}\text{B}_{1-x})\text{O}_3$ members with lower x values (end member BaCoO_3 , hexagonal perovskite, only Oh)



c_1 (Co-O) & c_2 (Ca)

changes in peak positions slight for Co-O subcell BUT large for Ca subcell (c_2/c_1 not rational, incommensurate)

Ca_xCoO_3 with ($x=2*c_2/c_1$) → $\text{Ca}_{2.3}\text{Co}_2\text{O}_6$



Towards Ca metal batteries?

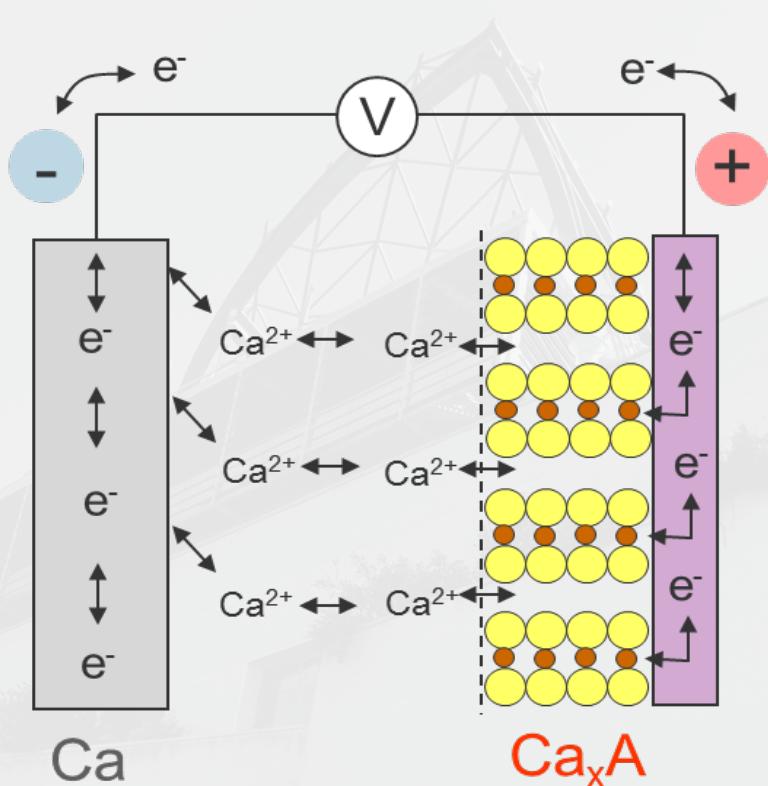


Negative

Plating/stripping



Operation T Efficiency



Electrolyte

Plating/stripping
Large potential window



Positive

Efficient Ca²⁺ migration
Large specific capacity
High operation potential



... to be continued

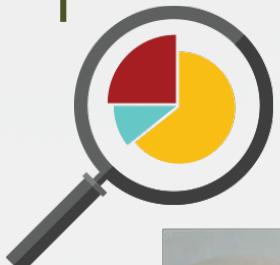
CARBAT

Fraunhofer
ISIT



ICMAB
UNIVERSIDAD
COMPLUTENSE
MADRID

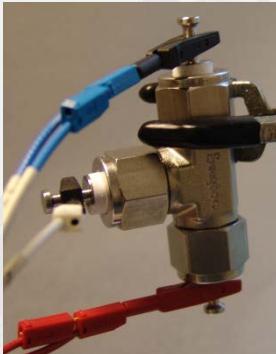
Conclusions



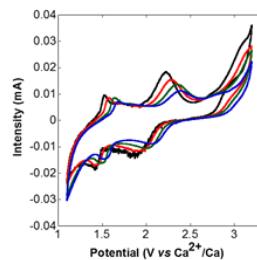
Methodology for multivalent battery chemistry research



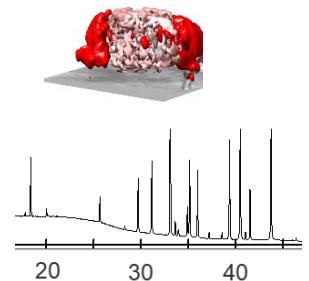
Blank experiments



3 electrodes



Complementary characterization
(lack of standards, side reactions!)



(Ca)-M-X

TiS_2 Reversible intercalation of (solvated) Ca^{2+} 😊

V_2O_5 😕

CaMn_2O_4 😕

$\text{Ca}_3\text{Co}_2\text{O}_6$ Electrochemical extraction of Ca^{2+} proved 😊

- Ca^{2+} interaction with solvents? new electrolytes?



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	Scale-up experiments	Lab/prototype cells	Confirm research results	Design initial cell product
Limited exploratory laboratory experiments	Characterize fundamental properties of concept, chem. composition, structure, etc.	Initial map of performance, rate, cycling, temperature, etc.	Establish initial product format	Design and construct unit operations
Establish repeatability of performance	Evaluate size of commercial opportunity	Scale-up of material preparation	Develop unit assembly operations	Scale-up prototype cell fabrication
Is there a market?		Preliminary market scope	Make, test, and characterize 5 to 10 cell lots of 100 cells each	Run 3 to 5 sizable pilot line-factory trials
			Construct business plan	Finalize business plan
				Market



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

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TOYOTA



