

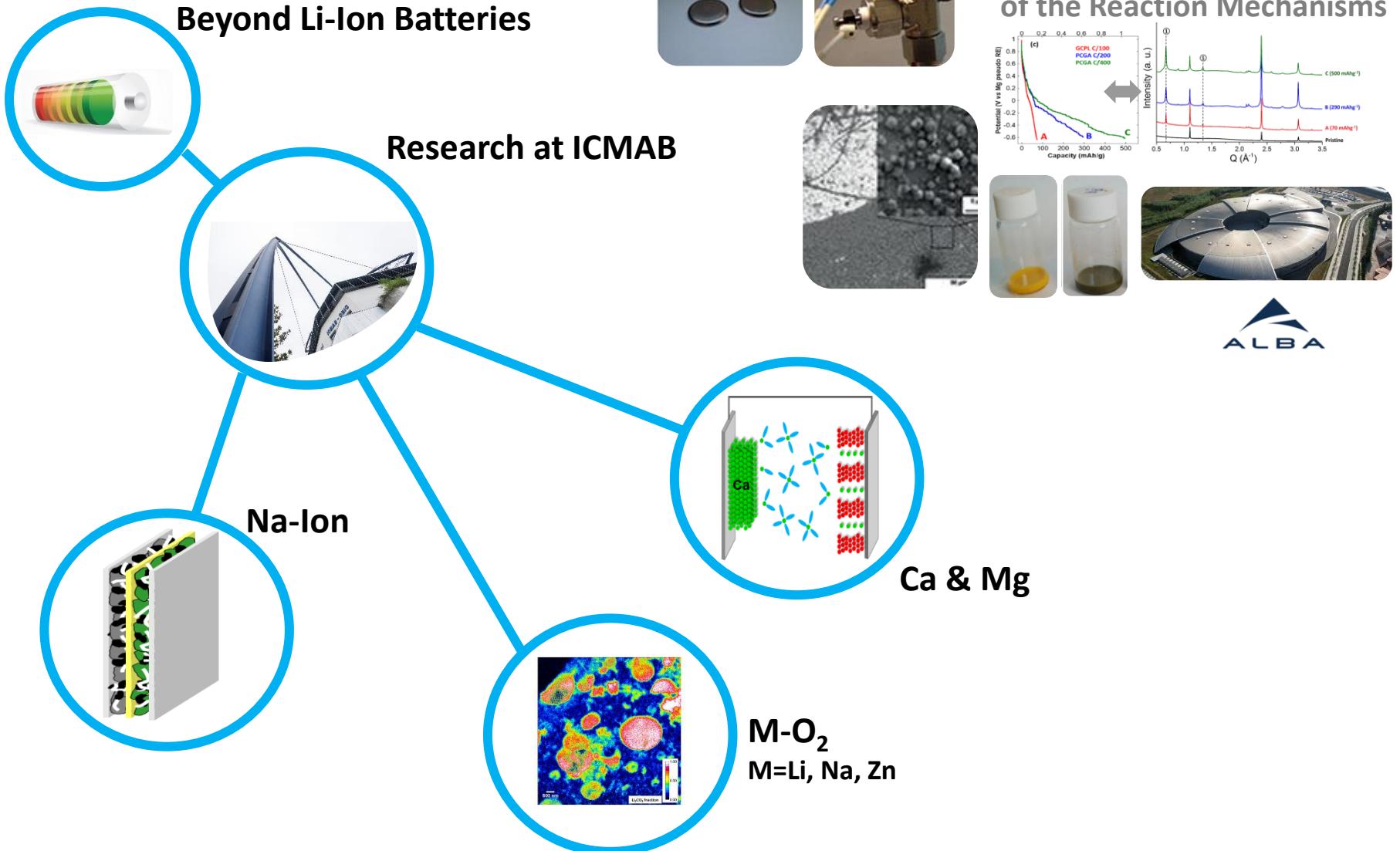


# Towards Post-Lithium Ion Batteries: Improving Sustainability / Energy Density

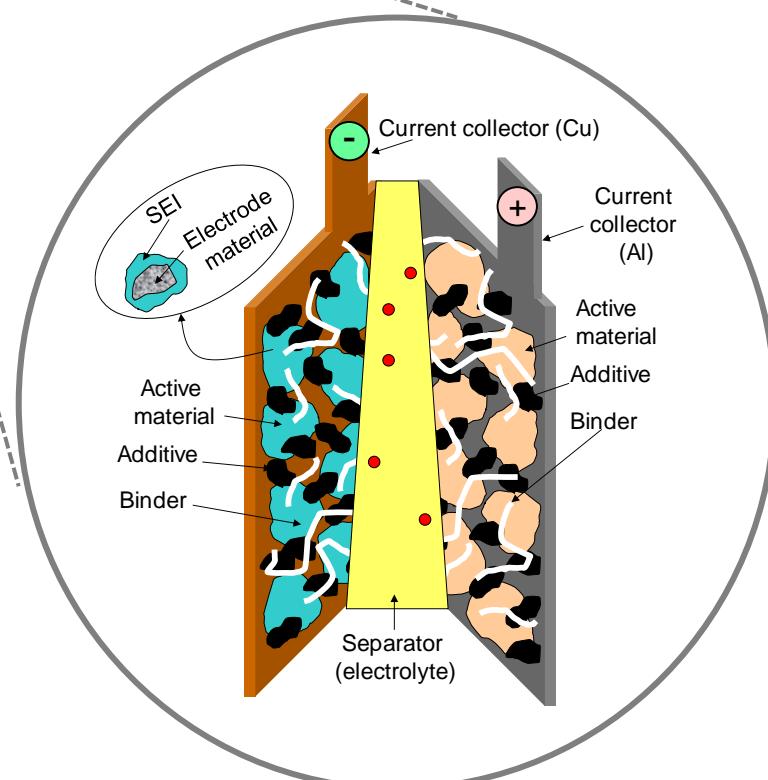
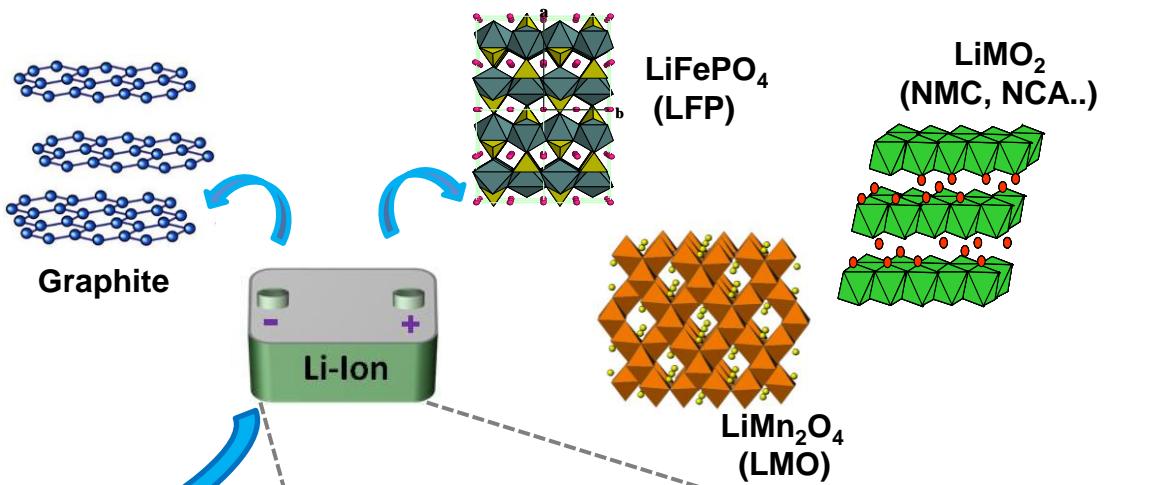
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Roberta Verrelli

# Outline



# Introduction



# Introduction

## Performance



## Application



## Sustainability



# Introduction

## Performance



## Application



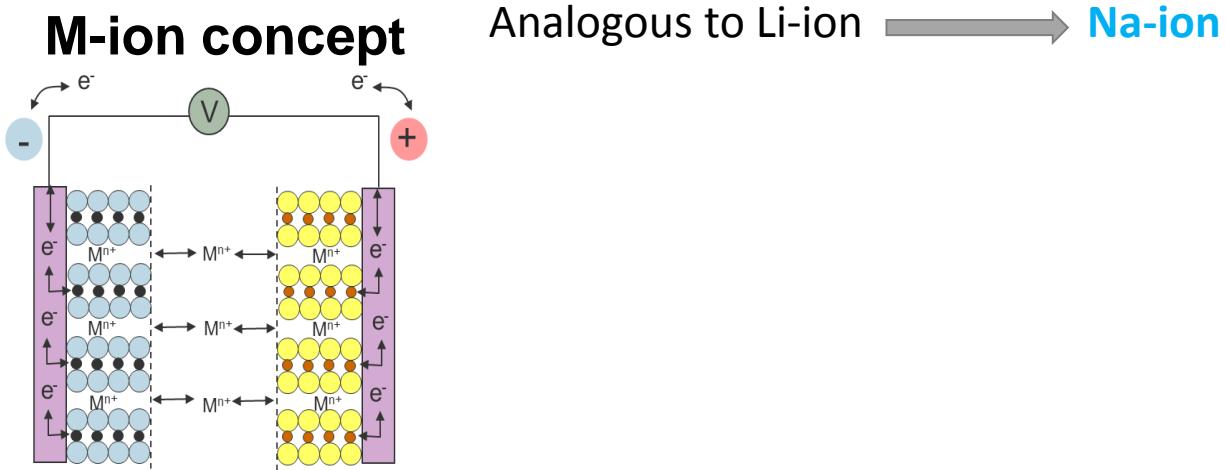
## Sustainability



Towards more abundant elements

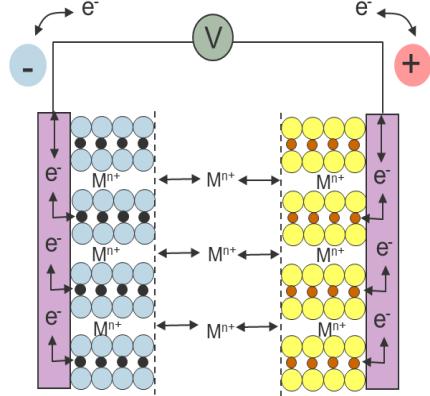


# Beyond Li-Ion Batteries



# Beyond Li-Ion Batteries

## M-ion concept



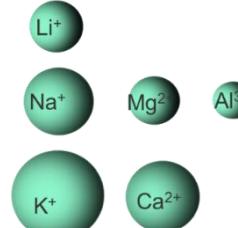
Analogous to Li-ion Na-ion

$M^{n+}$  as charge carriers instead of  $Li^+$

Increased Capacity



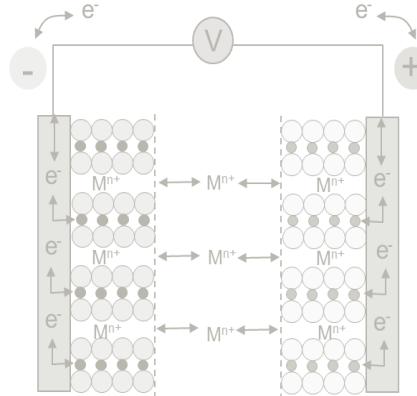
BUT



Poor Kinetics  
High de-solvation Barriers

# Beyond Li-Ion Batteries

## M-ion concept

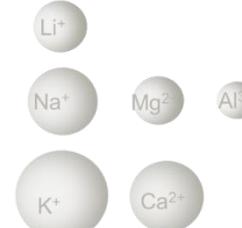


Analogous to Li-ion → Na-ion

$M^{n+}$  as charge carriers instead of  $Li^+$

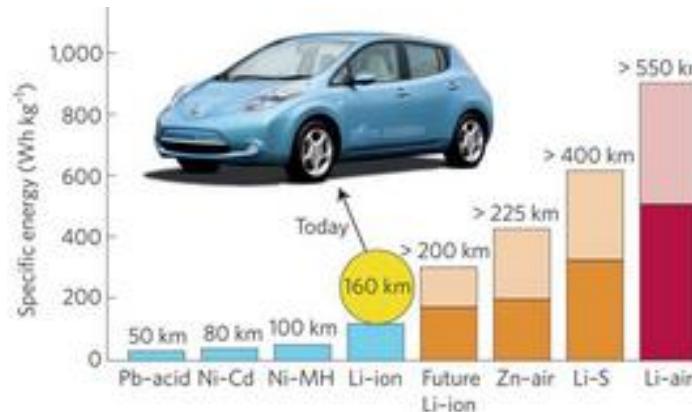
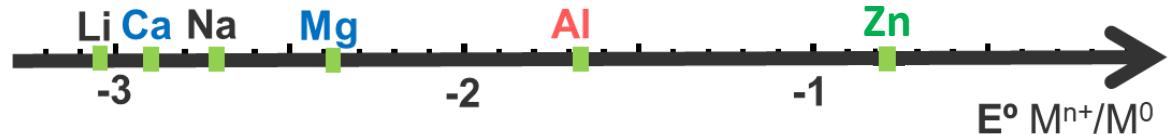
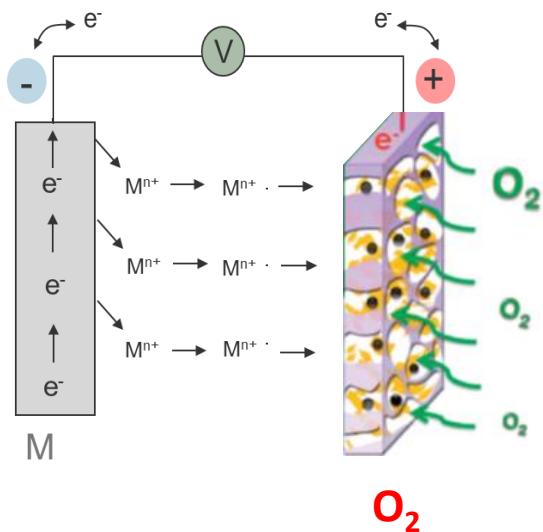


Increased Capacity



Poor Kinetics  
High de-solvation Barriers

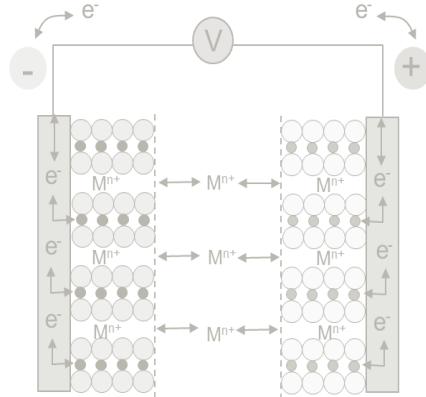
## M-anode concept



M/Air

# Beyond Li-Ion Batteries

## M-ion concept

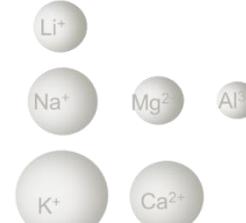


Analogous to Li-ion  $\longrightarrow$  Na-ion

$M^{n+}$  as charge carriers instead of  $Li^+$

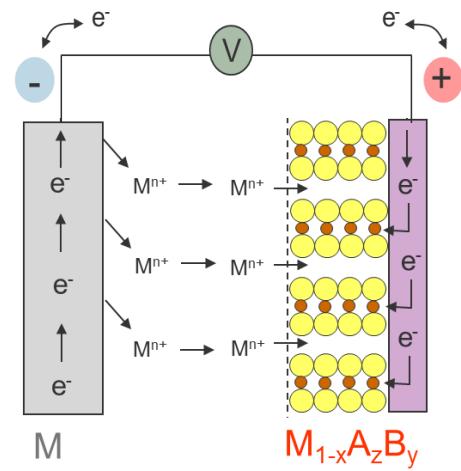


Increased Capacity

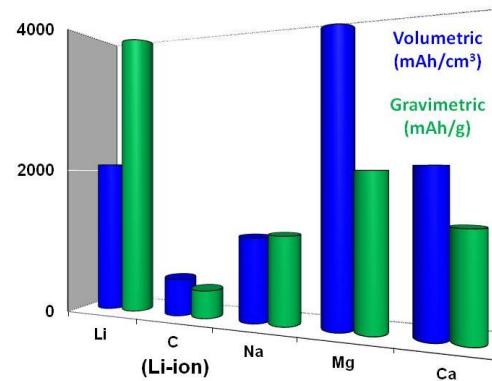


Poor Kinetics  
High de-solvation Barriers

## M-anode + M-ion concept



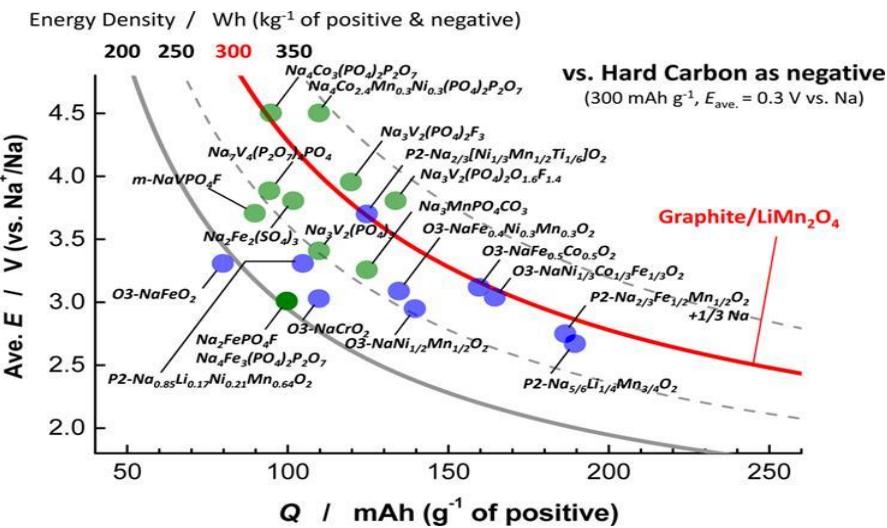
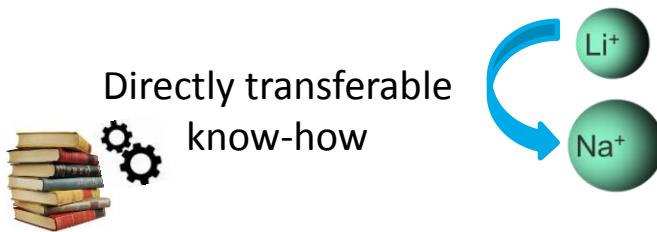
20 ppm      46600 ppm      27640 ppm



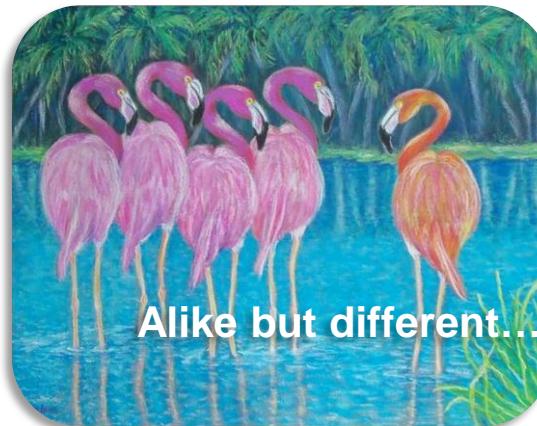
Ca & Mg

# Na-Ion Batteries

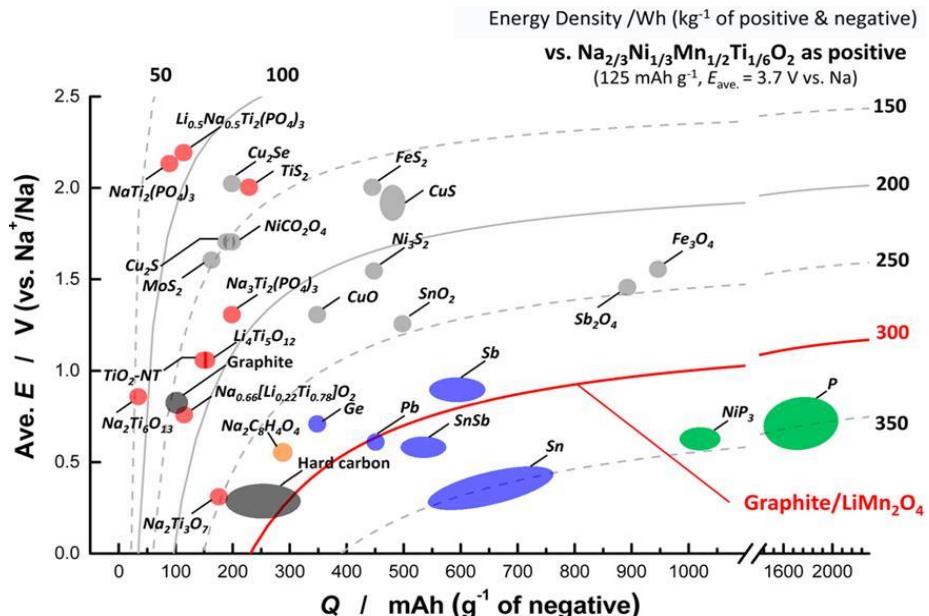
- Natural Abundance, Low Cost
- High standard reduction potential (-2.71 V vs. NHE)
- No alloy formation with Al



PI: M.R. Palacín

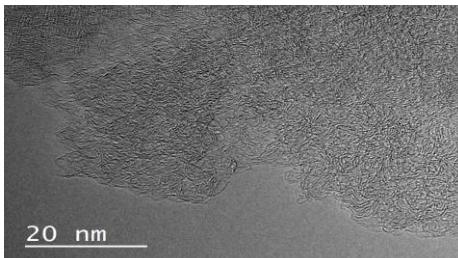


- Ionic radius
- Coordination/Crystal Chemistry
- Polarizing character, Kinetics
- Solvation energy, Solubilities, SEI

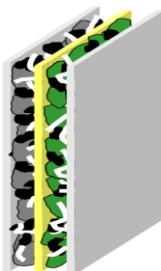


# Na-Ion Batteries

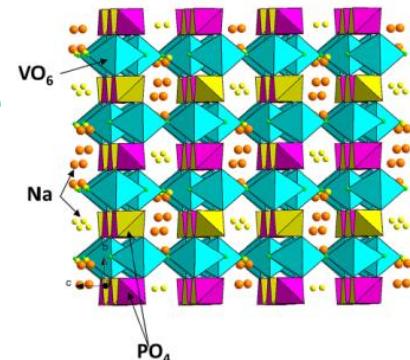
Hard C // 1 M NaPF<sub>6</sub>, EC<sub>0.45</sub>:PC<sub>0.45</sub>:DMC<sub>0.1</sub> // Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub>



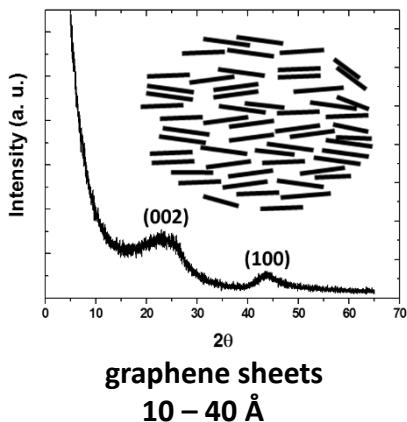
Non-graphitizable  
Anode  
(sp<sup>3</sup> cross-linking)



Polyanionic Cathode

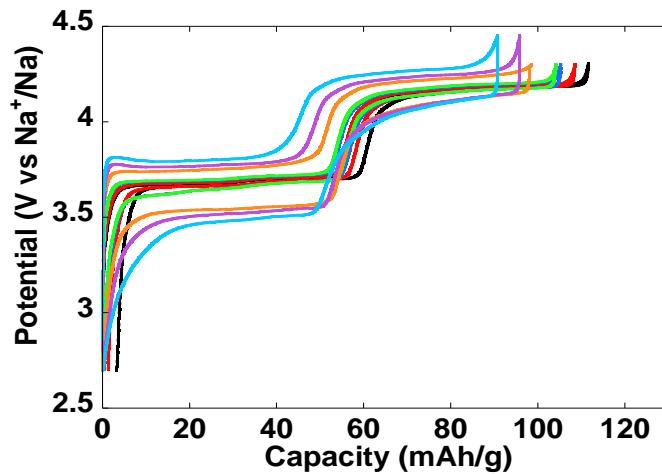
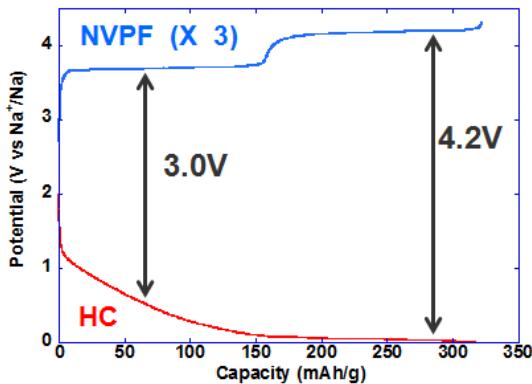


Theoretical energy density : 78 Wh/kg



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

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



A. Ponrouch, R. Dedryvère, D. Monti, A. E. Demet, J. M. Ateba Mba, L. Croguennec, C. Masquelier, P. Johansson, M. R. Palacín, Energy & Environ. Sci. 6 (2013) 2361.

E. Irisarri, A. Ponrouch, M. R. Palacín. J. Electrochem. Soc. 162 (2015) A2476

# Lab Upscaling



E

RÉSEAU SUR LE STOCKAGE  
ÉLECTROCHIMIQUE DE L'ÉNERGIE



**NAIADES**

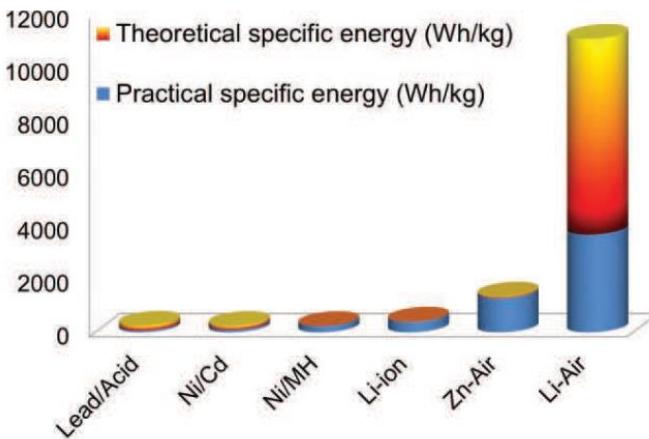
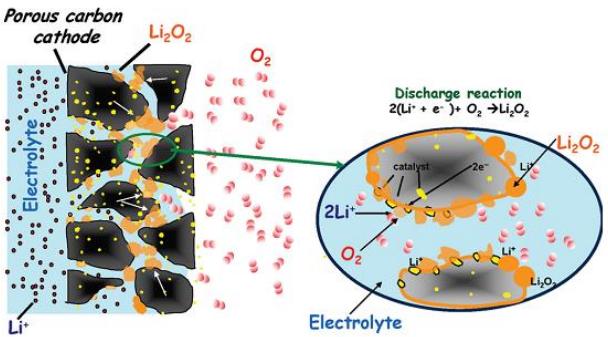


**1000 Wh**

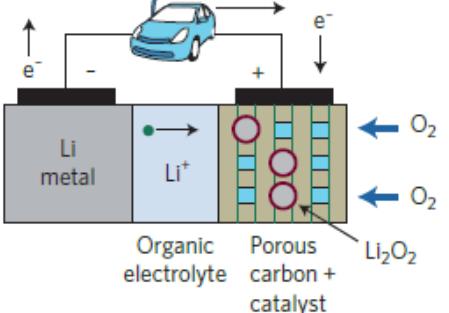
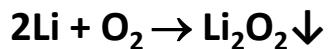


**PI: M.R. Palacín**

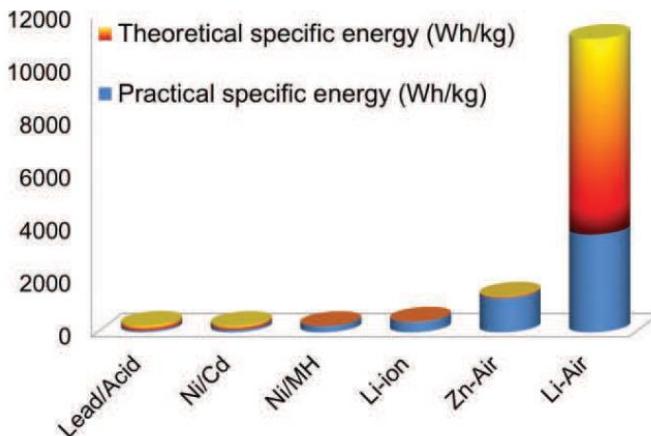
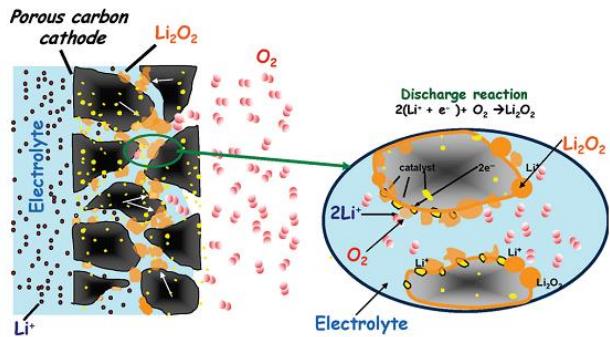
# Metal-O<sub>2</sub> Batteries



## Aprotic Li-O<sub>2</sub>

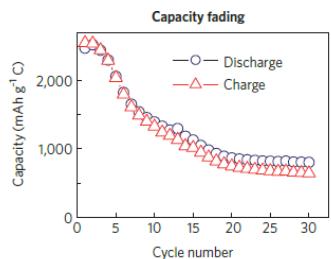
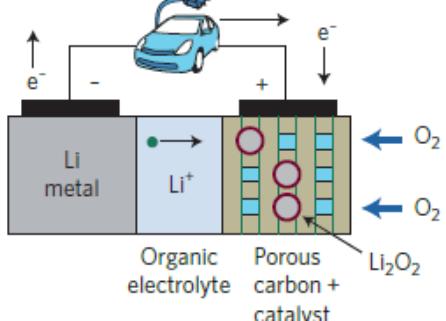


# Metal-O<sub>2</sub> Batteries



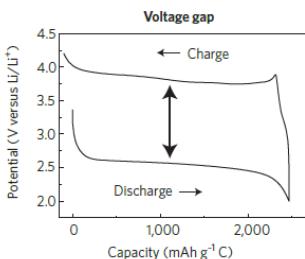
## Problems of Li metal

- Dendrite formation
- Cycling efficiency
- Requires stable solid-electrolyte interphase
- Safety issues



## Electrolyte

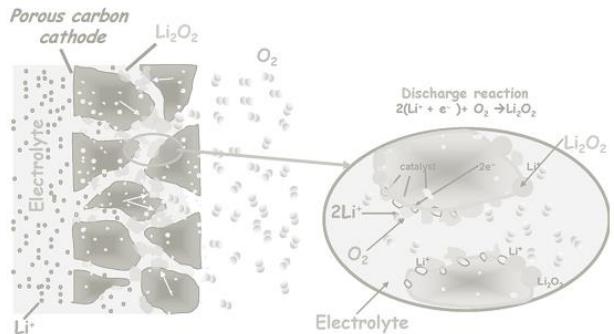
- Stability
- Conductivity
- Volatility
- O<sub>2</sub> solubility, diffusivity



## Porous cathode design

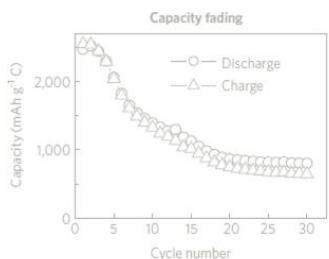
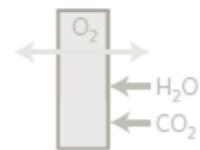
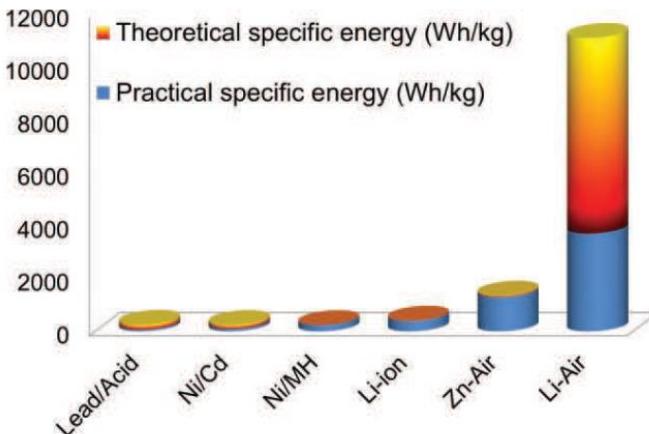
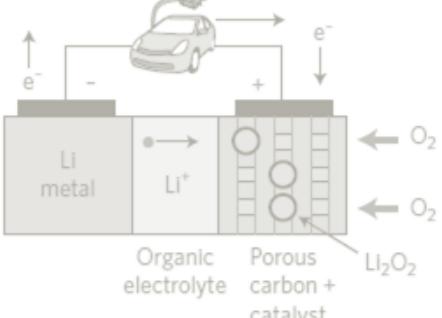
- Pore size, distribution
- Catalyst — type, distribution, loading

# Metal-O<sub>2</sub> Batteries

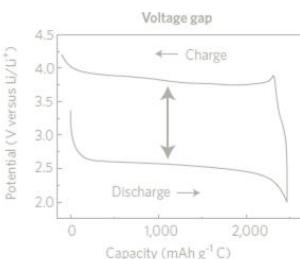


Anode

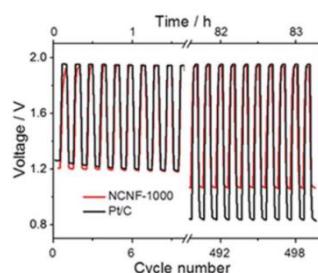
- Problems of Li metal**
- Dendrite formation
  - Cycling efficiency
  - Requires stable solid-electrolyte interphase
  - Safety issues



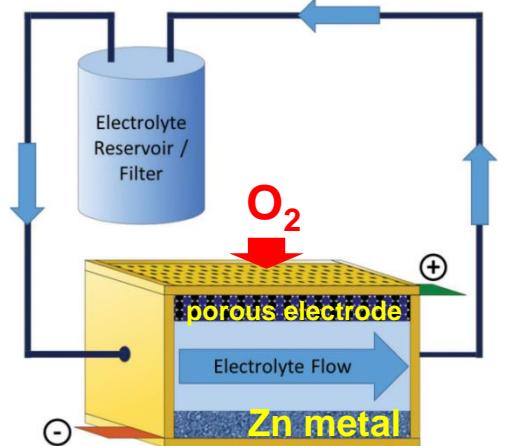
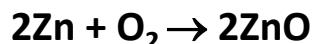
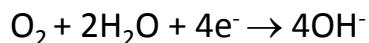
- Electrolyte**
- Stability
  - Conductivity
  - Volatility
  - O<sub>2</sub> solubility, diffusivity



- Porous cathode design**
- Pore size, distribution
  - Catalyst — type, distribution, loading



## Aqueous Zn-O<sub>2</sub>



- Soluble discharge intermediate: no passivation/clogging
- Less severe dendrite formation and stability issues
- Longer cycle life

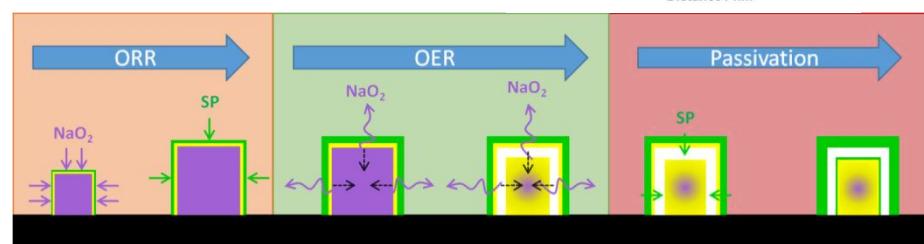
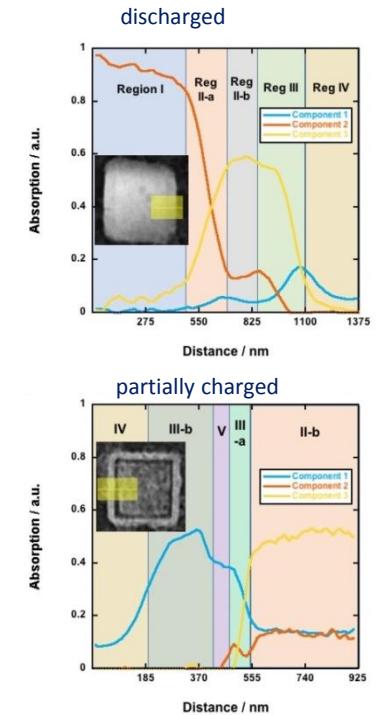
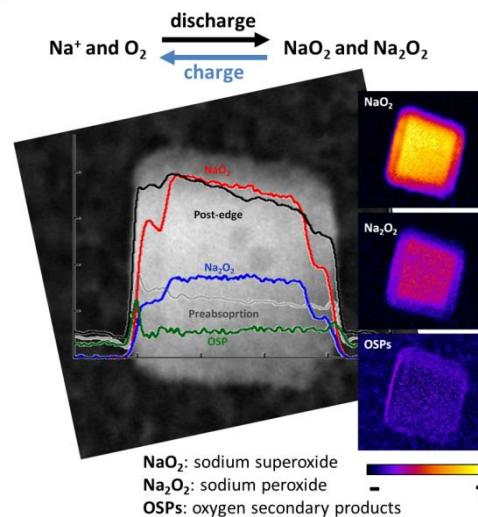
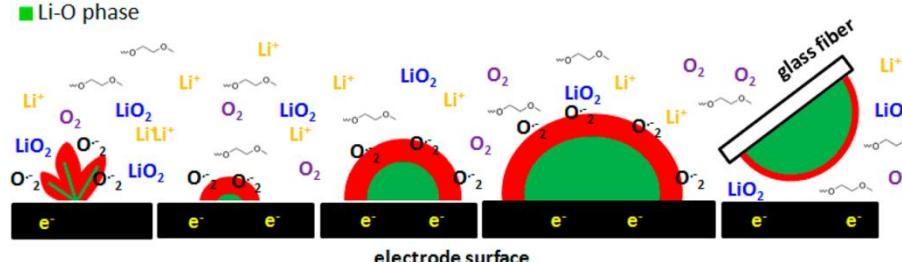
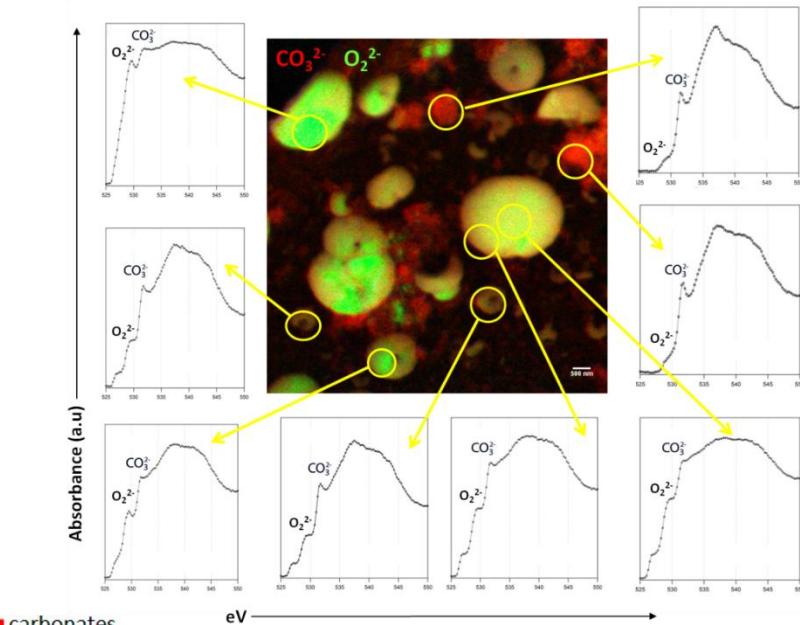
PI: D. Tonti

# Soft X-Ray Transmission Microscopy on Li- and Na-O<sub>2</sub> Batteries



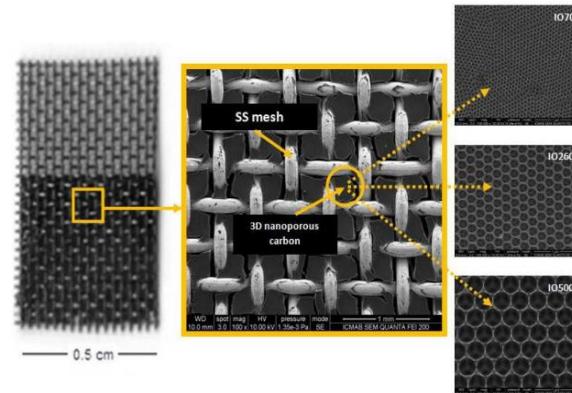
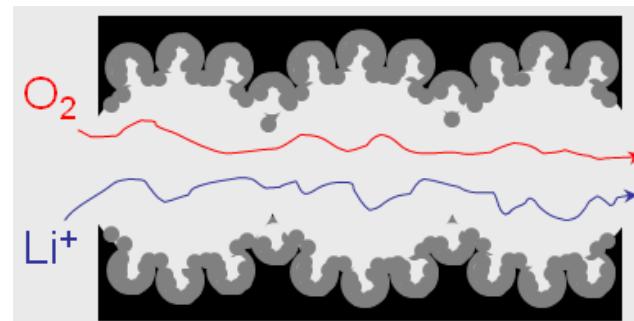
PI: D. Tonti

- Spectroscopic access to the oxygen chemical state
- Distribution of oxygen discharge products elucidated
- LiO<sub>2</sub> observed on large Li<sub>2</sub>O<sub>2</sub> toroidal particles (not on smaller deposits)
- Presence of Na<sub>2</sub>O<sub>2</sub> in NaO<sub>2</sub> cubic particles
- Carbonates irregularly distributed and covering Li<sub>2</sub>O<sub>2</sub> and NaO<sub>2</sub> particles



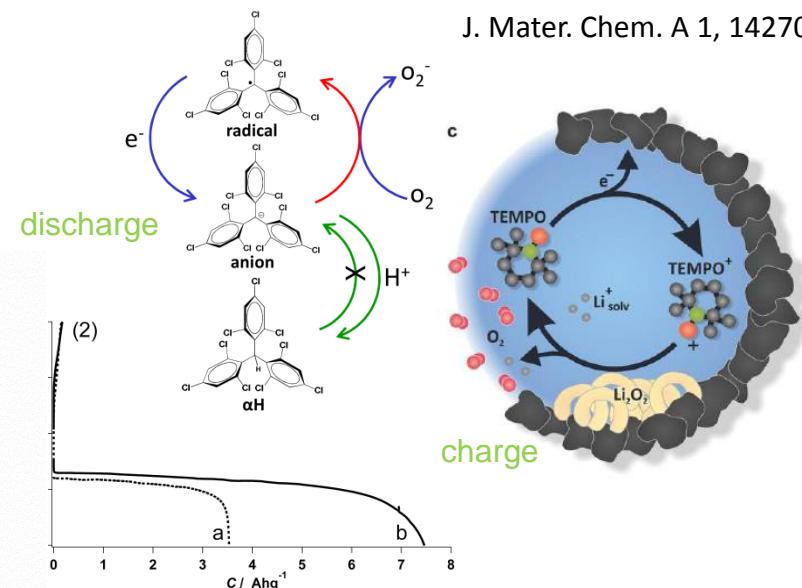
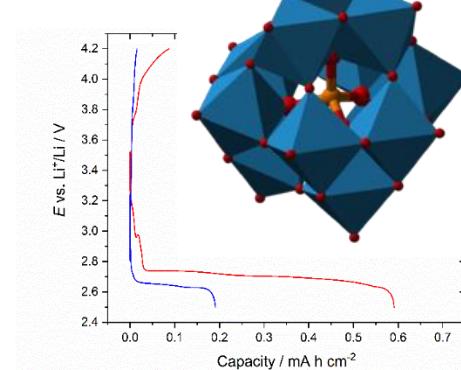
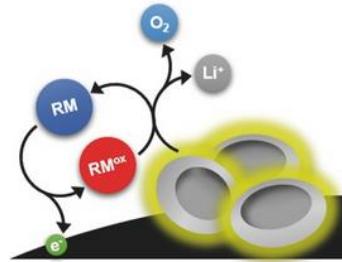
# Li-O<sub>2</sub> Batteries

## Cathode architectures



Hierarchic porosity to preserve electrolyte access to active interface

## Redox Mediators



Electron transport to and from the bulk: enhancing discharge and enabling full charge

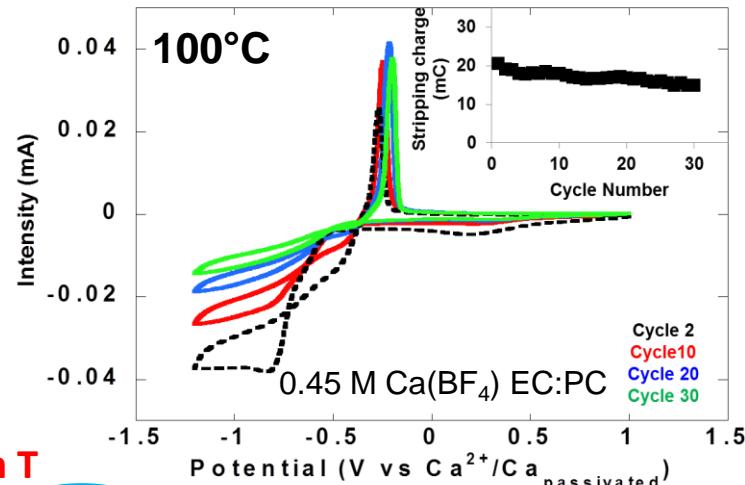
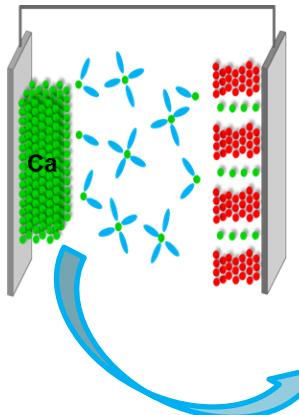
Y. Tesio et al., Chem. Commun. 51, 17623 (2015)

I. Landa-Medrano et al., Electrochim. Commun. 59, 24 (2015)

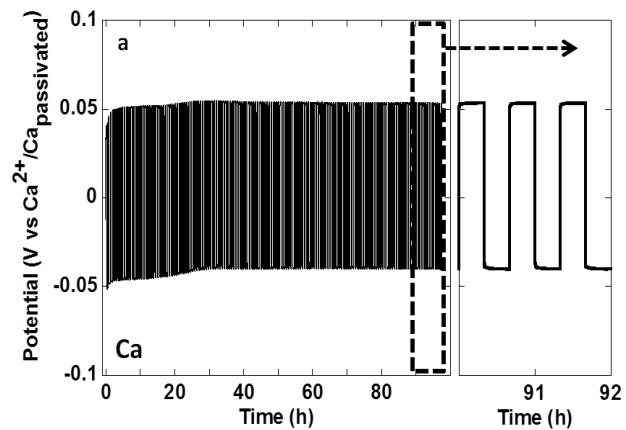
T. Homewood et al. Chem Commun 54 (2018) 9599

PI: D. Tonti, N. Casañ

# Multivalent Batteries: Ca Metal Anode



High T

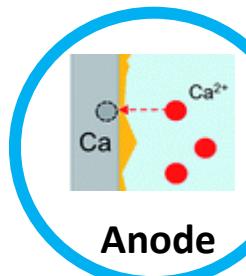


- Feasibility of Ca electrodeposition
- First step towards Ca-Battery proof of concept

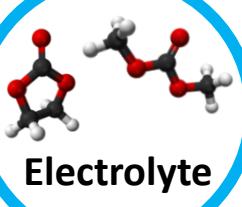
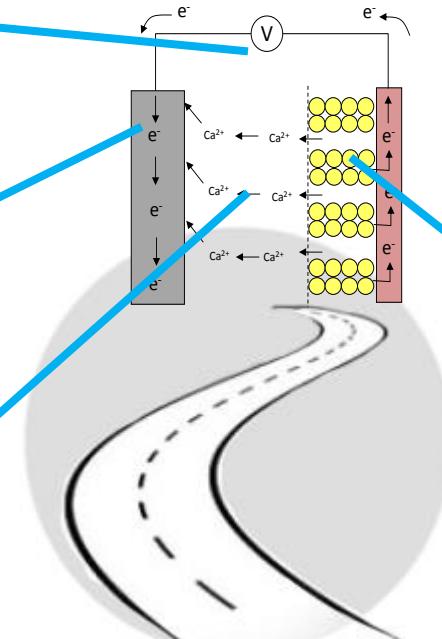


European Research Council

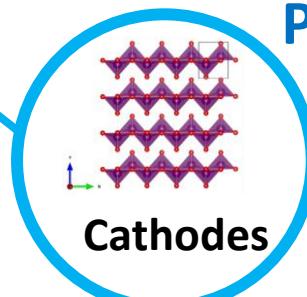
PI: A. Ponrouch



Cell Set-Up



Anode



PI: M.R. Palacín

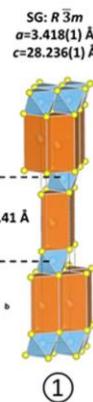
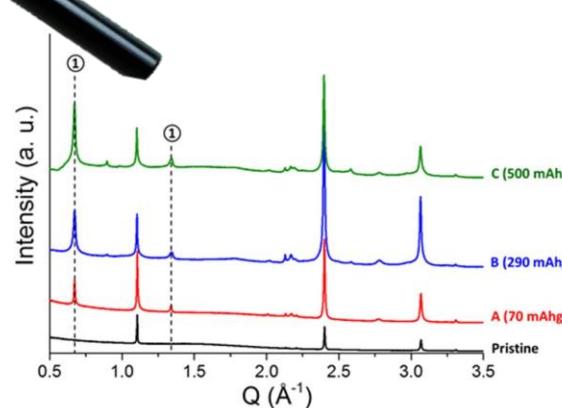
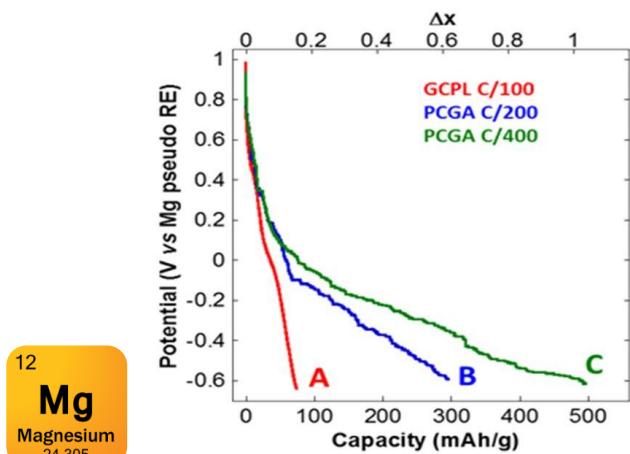
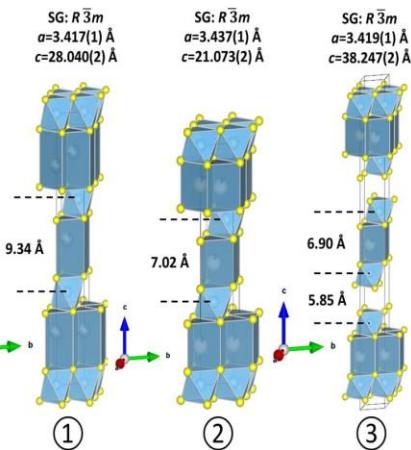
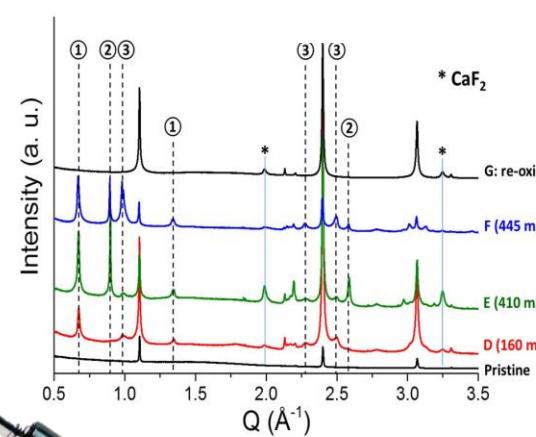
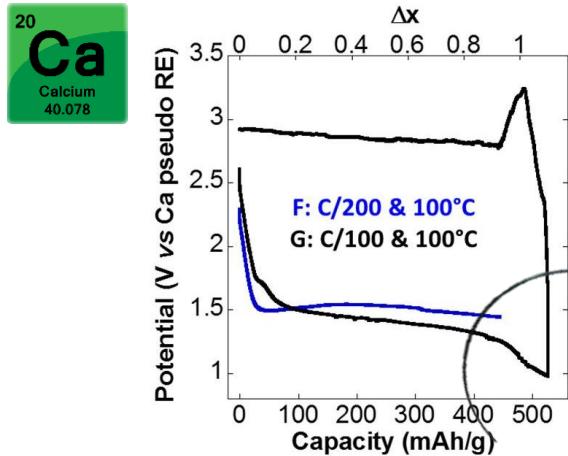
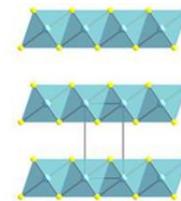
CARBAT



# Multivalent Batteries: The Quest for Cathode Materials



Revisting Traditional Intercalation Hosts  $\rightarrow \text{TiS}_2$



PI: A. Ponrouch & M.R. Palacín

# Multivalent Batteries: The Quest for Cathode Materials

Differential Absorption  
X-Ray Tomography  
Ca L<sub>2</sub> edge

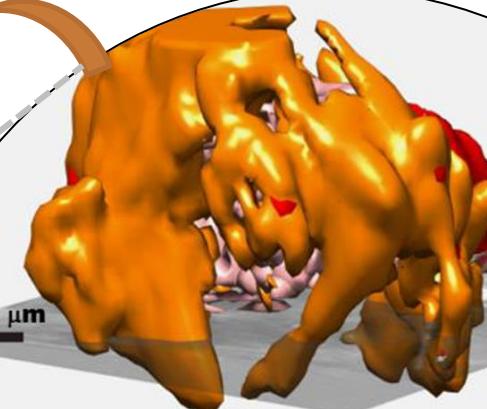


Dr. A. Sorrentino

Low absorption external Ca  
**Polymeric surface layer**

$$\Delta\mu = 1.0 \pm 0.3 \text{ } \mu\text{m}^{-1}$$

0.5  $\mu\text{m}$



High absorption external Ca



$$\Delta\mu = 3.2 \pm 0.9 \text{ } \mu\text{m}^{-1}$$

Intercalated Ca



PI: A. Ponrouch & M.R. Palacín

# 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 development
<b>Timing</b>	One to three years	One to three years	Three to four years	Three to five years
<b>Staffing</b>	One	Two to four	Four to ten	Eight to sixteen
<b>Materials Batch</b>	Grams	10 to 50 g	100 g to 1 kg	1 kg to 10 kg
				<b>10-19 years!!</b>

# Acknowledgements

## Solid State Chemistry Department (SSCH)



**Thanks for your kind attention**

