

On the Challenging Quest for Positive Electrode Materials for Mg Batteries



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2018 Early Career Scientist Summit

WMRIF
World Materials Research Institute Forum

NPL
National Physical Laboratory

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CHALMERS



Massachusetts Institute of Technology



SAPIENZA
UNIVERSITÀ DI ROMA

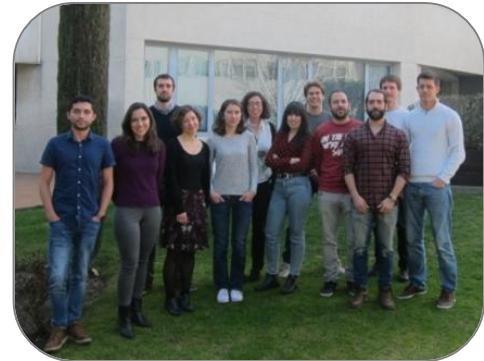
PhD in **Chemical Sciences** (2015)

Bachelor (2010) and Master (2012)

Degree in **Chemistry**



Barcelona (Spain)



**Solid State Chemistry Department
Inorganic Battery Group
Prof. R. Palacín**



Bachelor (2010) and Master (2012)

Degree in Chemistry

Materials Science

Solid State Chemistry

Multivalent Metal Batteries

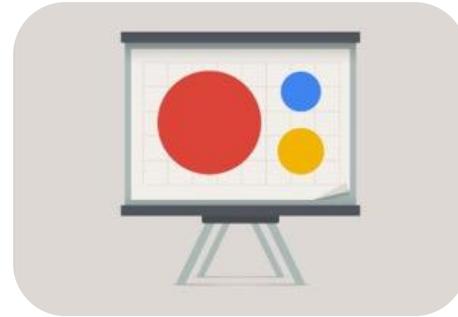


Outline

- General Introduction to Post Lithium Ion Batteries
- Magnesium Batteries : State of the Art and Open Challenges
- The quest for Mg Battery Cathodes : a Chemist's Approach
- Study of Mg²⁺ ions (de)Intercalation Process through Combined Techniques

MgMoN₂ and TiS₂ as Case Studies

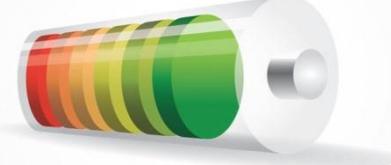
- Conclusions and Future Perspectives



Introduction



Electrochemical Energy Storage



Rechargeable Batteries

Performance



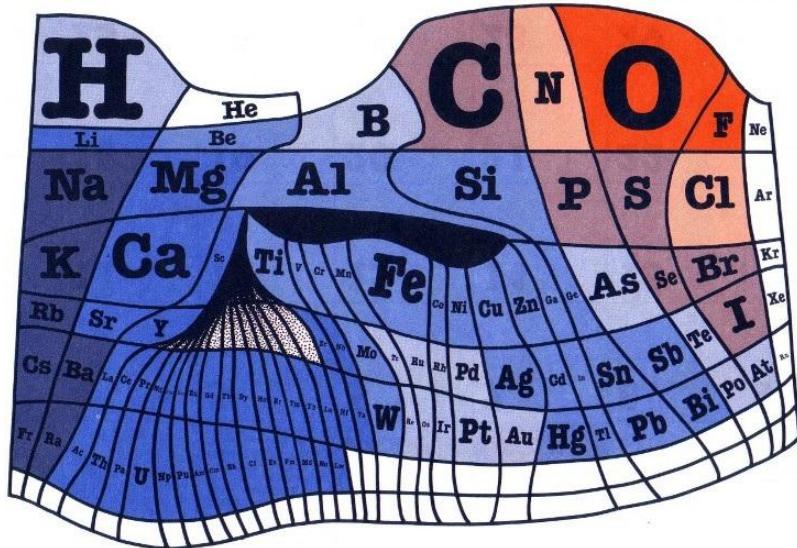
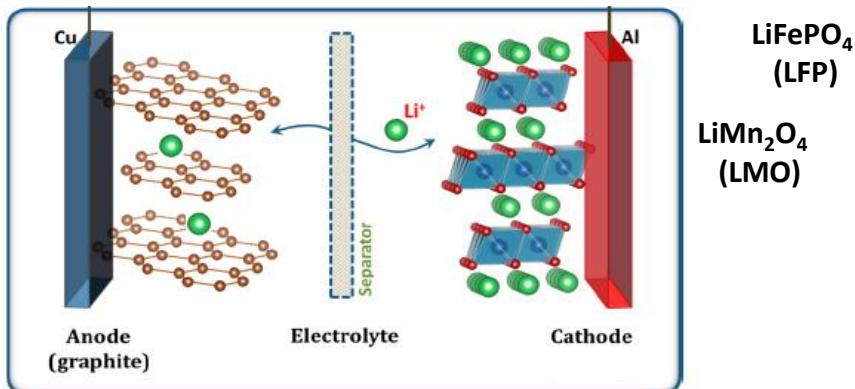
Application



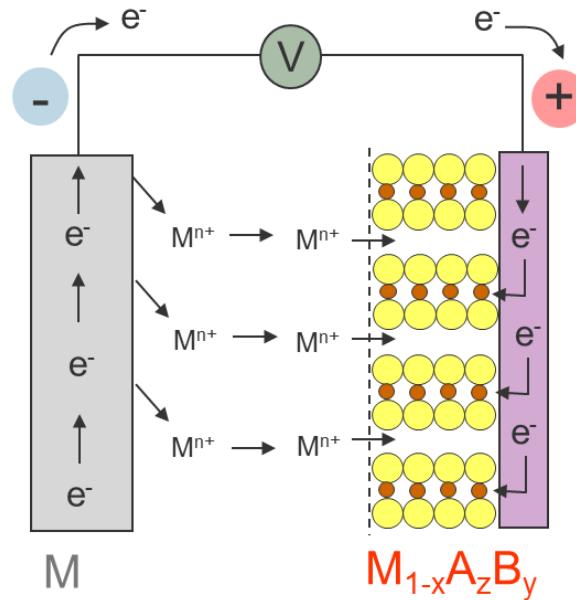
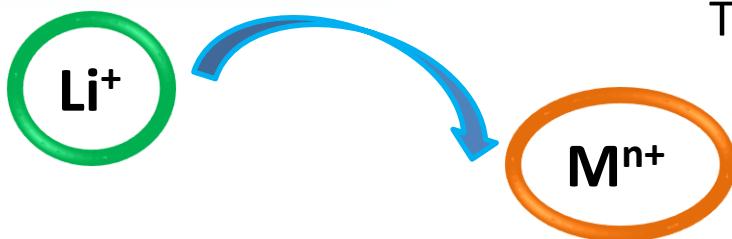
Sustainability



Beyond Li-ion Batteries



Towards more **abundant** elements

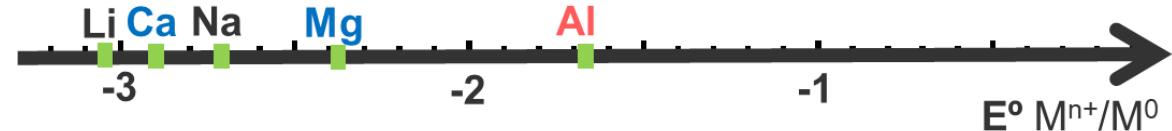
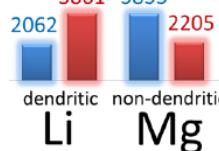


Towards multivalent metal batteries

Mg Batteries

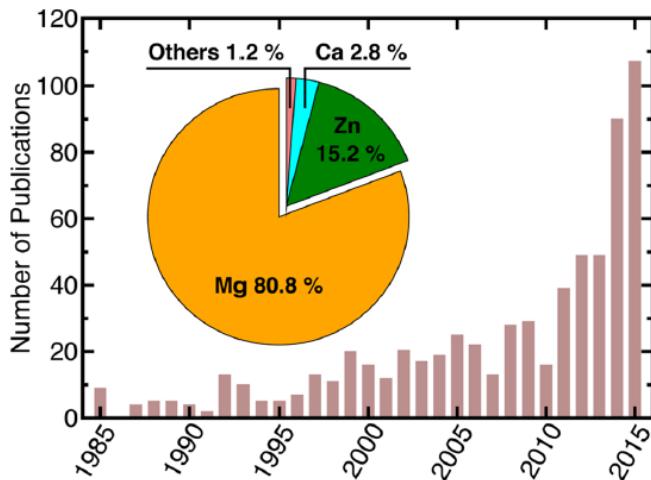


Mg is the 8th most abundant element
on the Earth's crust (Li is the 33rd)



Possible use of metallic anode

- Volumetric Capacity, mAh/ml
- Specific Capacity, mAh/g

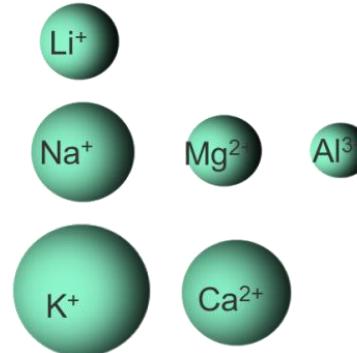


Proof-of-concept Mg battery

$Mg / 0.25M Mg(AlCl_2BuEt)_2, THF / Mo_6T_8 (T: S, Se)$



BUT



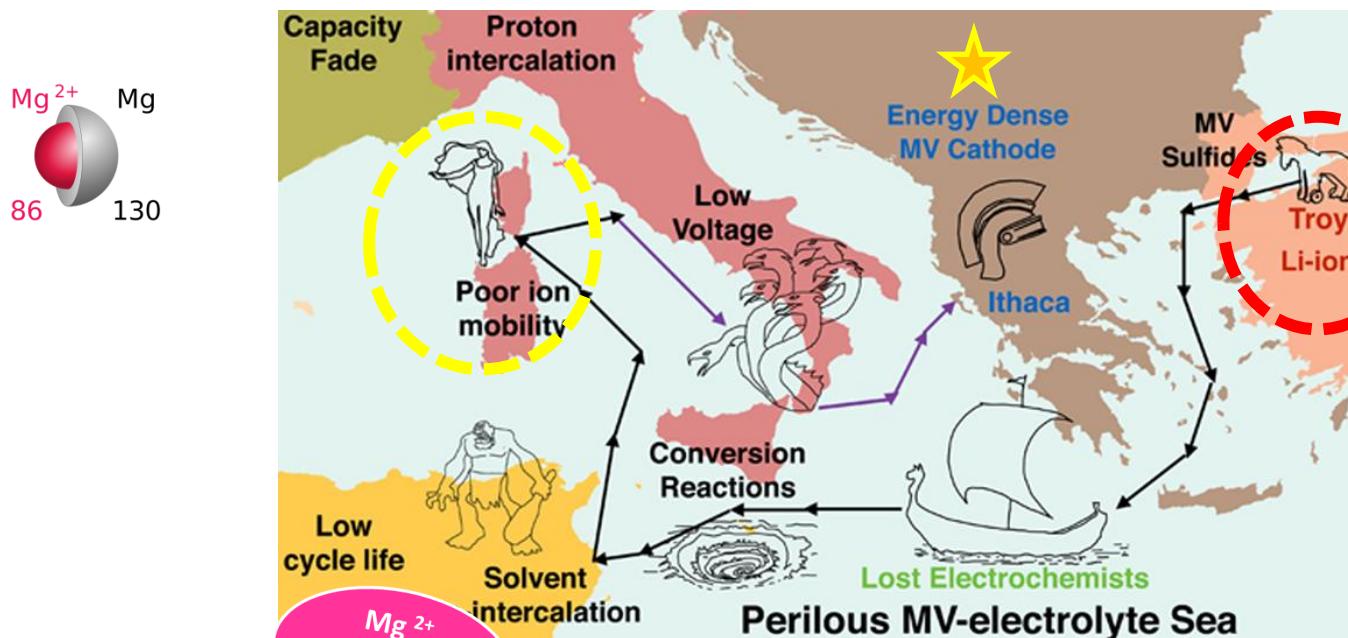
Charge/radius $Mg^{2+} \gg Li^+$



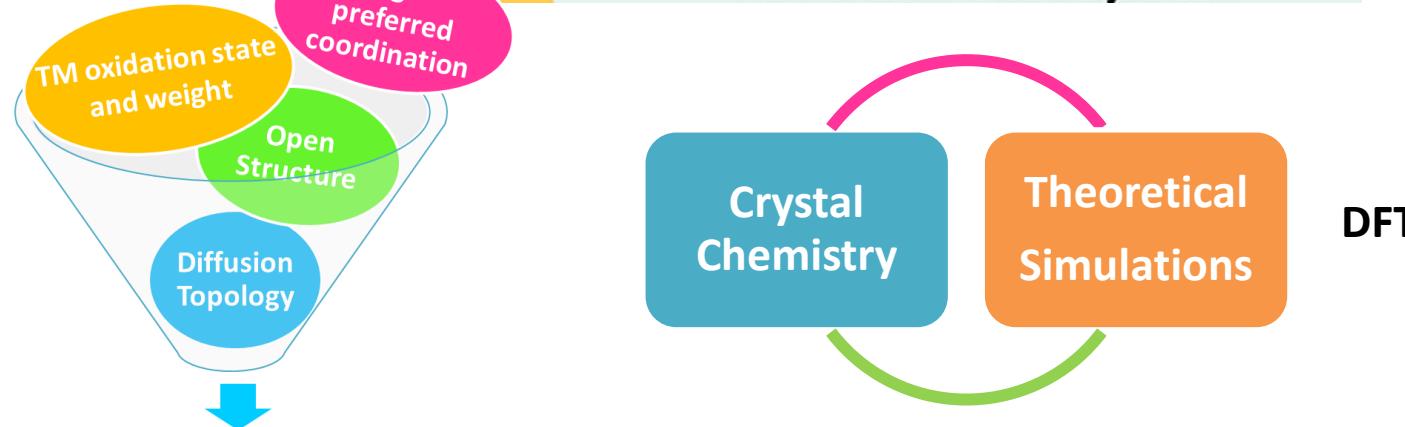
Slower Diffusion Kinetics

The quest for Mg Battery Cathodes

The Odyssey of Multivalent Cathodes



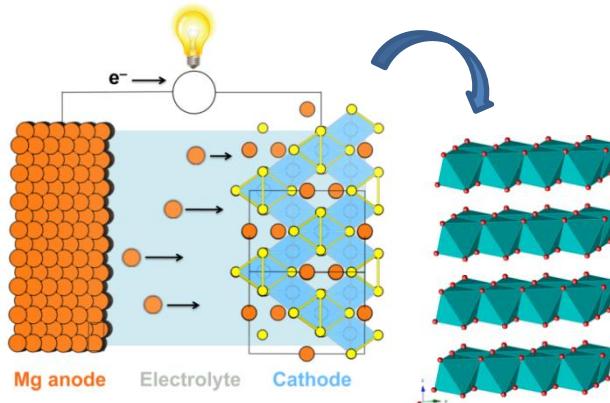
Li-ion battery expertise is not directly transferable to Mg systems



Design and Synthesis of Optimal Phases

P. Canepa et al., *Chem. Rev.*, 2017, **117**, 4287–4341.
A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, *APL Materials*, 2013, **1**(1), 011002.

Study of novel and traditional layered materials



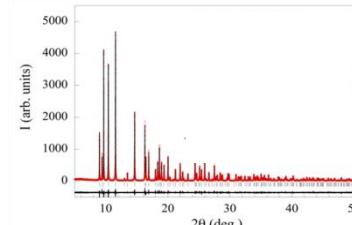
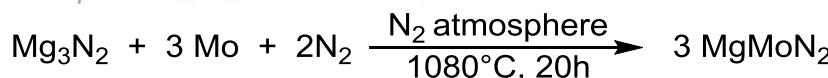
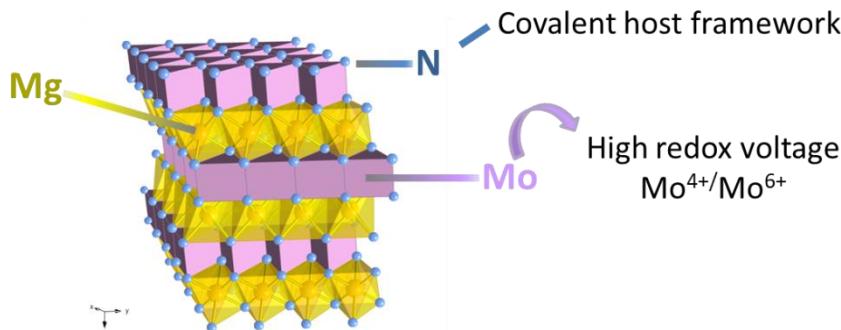
- **Open Layered Structure**

Enhance the Mg²⁺ mobility

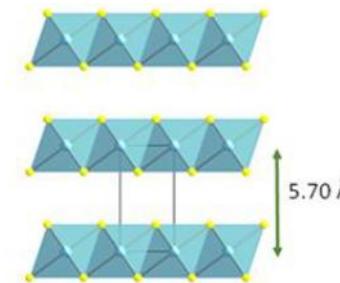
- **Soft Anionic Host Framework**

Mitigate the high Mg²⁺ polarizing effect

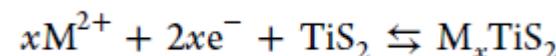
MgMoN₂



TiS₂



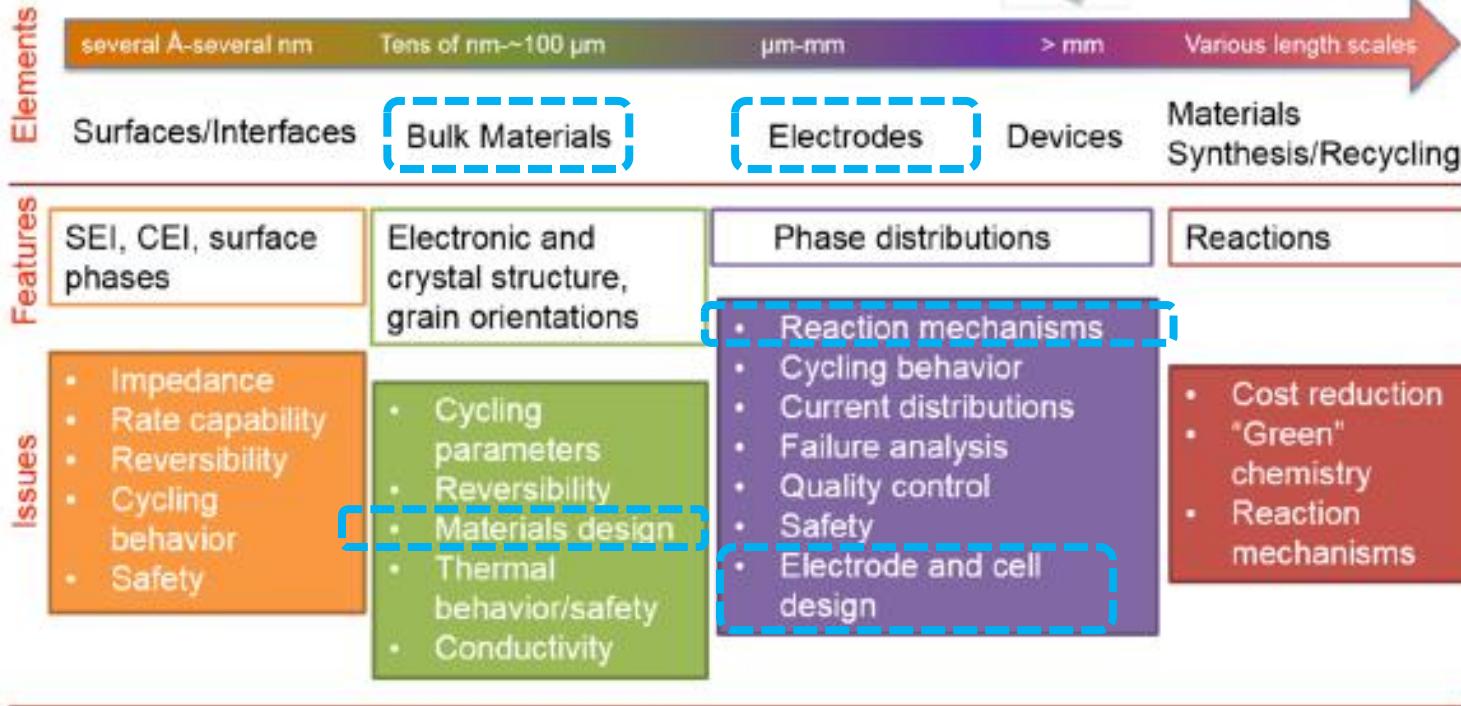
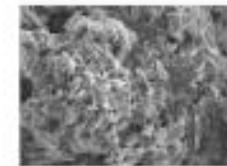
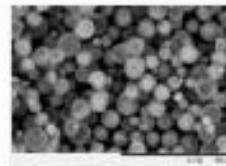
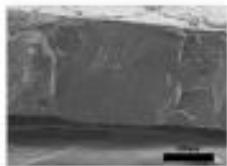
Theoretical Specific Capacity = **479 mAh g⁻¹**



M. S. Whittingham, C. Siu, J. Ding *Acc. Chem. Res.* (2018), 51 (2), 258.

D. Tchitchevka, A. Ponrouche, R. Verrelli, T. Broux, C. Frontera, A. Sorrentino, F. Barde, N. Biskup, M.E. Arroyo-de Dom Pablo, M.R. Palacín, *Chem. of Mat.* (2018), 30, 847.

Study of battery electrode materials



Ex-situ and In-situ Experiments

Imaging and mapping

Surface sensitive and bulk techniques

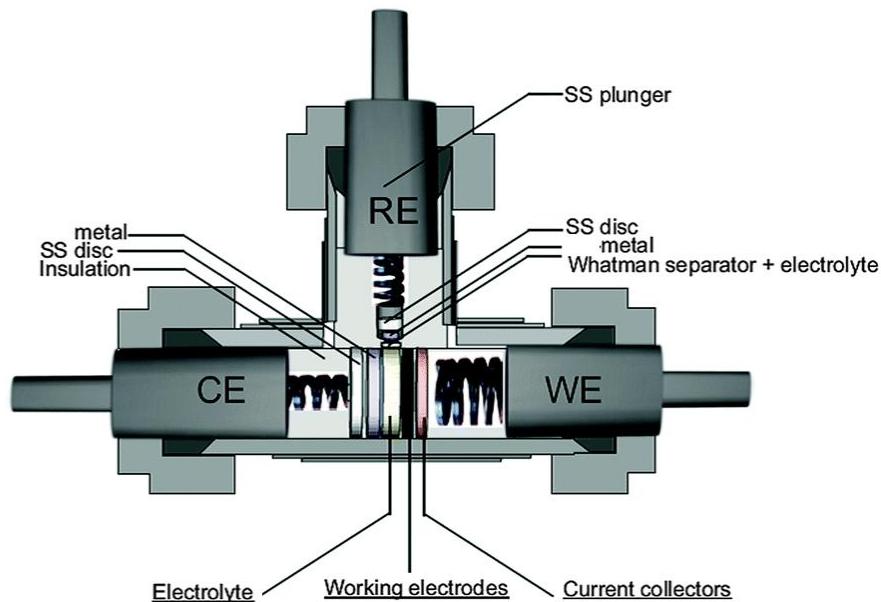
Our Approach

Galvanostatic cycling with Potential Limitations (GCPL)

Extended Potentiostatic Steps (EPS) tests

(Various Cycling rates, T)

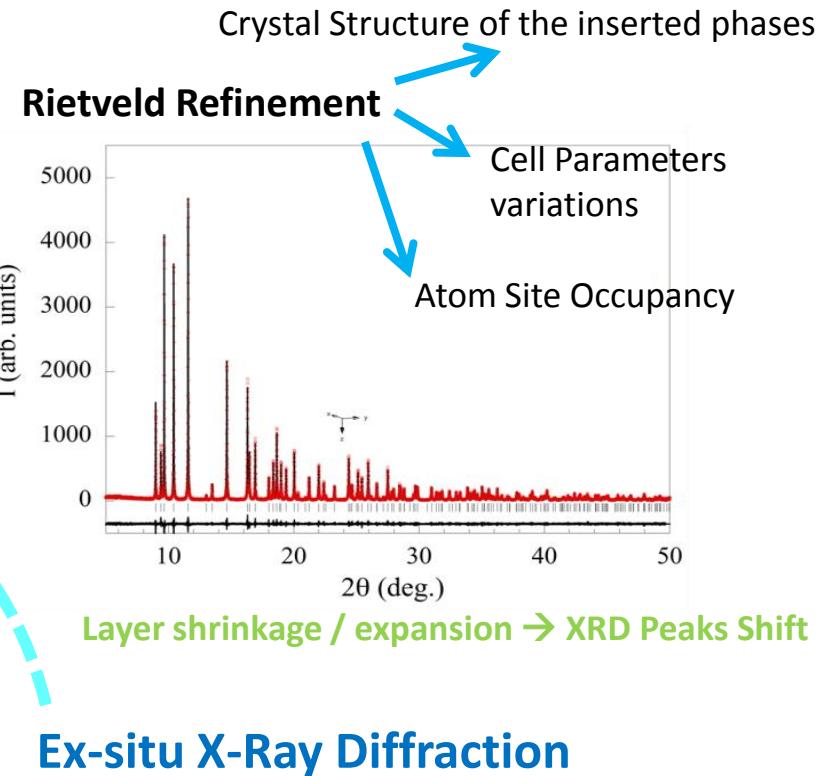
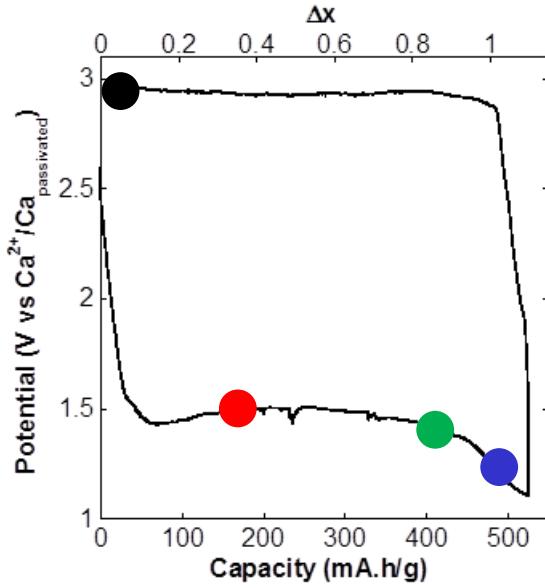
Electrochemical Tests



Our Approach

Galvanostatic cycling with Potential Limitations (GCPL)
Extended Potentiostatic Steps (EPS) tests
(Various Cycling rates, T)

Electrochemical Tests



Ex-situ X-Ray Diffraction

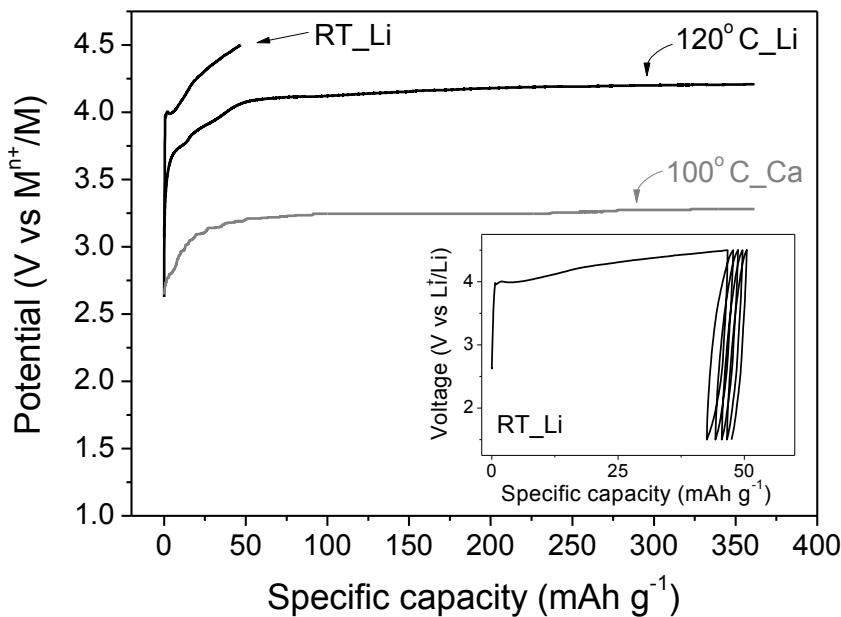


Is exchanged capacity
a conclusive evidence for MV ion insertion?

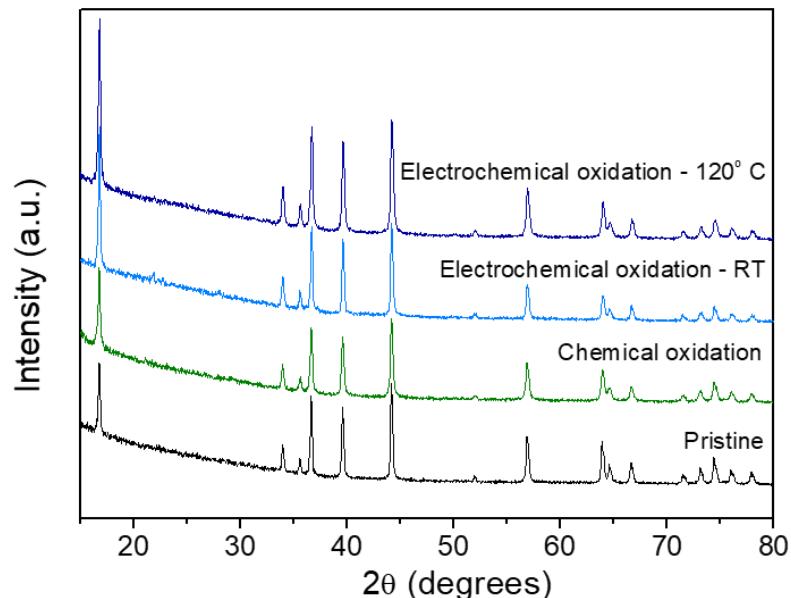
Insertion driven structural changes
of the active phase upon cycling

MgMoN₂

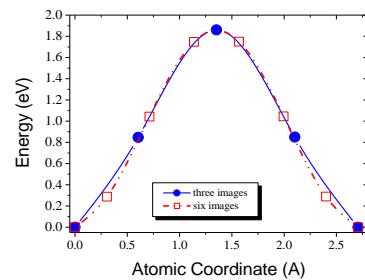
Galvanostatic Cycling



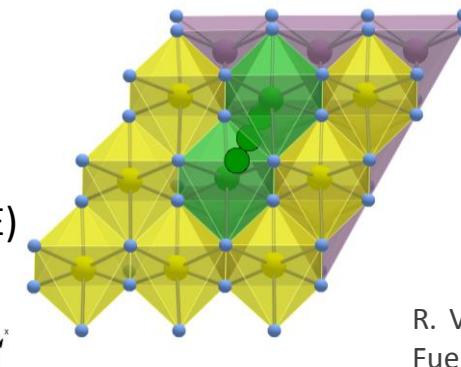
Ex-situ XRD



No evidence for electrochemical Mg²⁺ de-intercalation



DFT

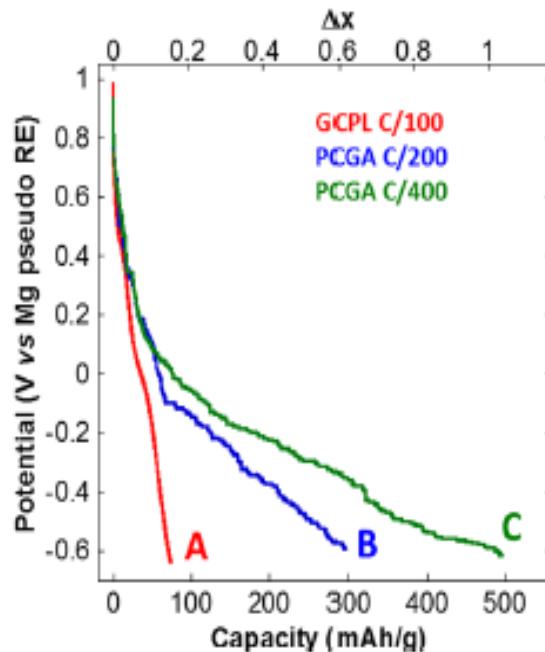


Calculated barrier (PBE)
1.8 eV

Direct Mg²⁺ migration between octahedral sites
→ Strong Mo⁴⁺ - Mg²⁺ Columbic repulsion
→ High migration barrier

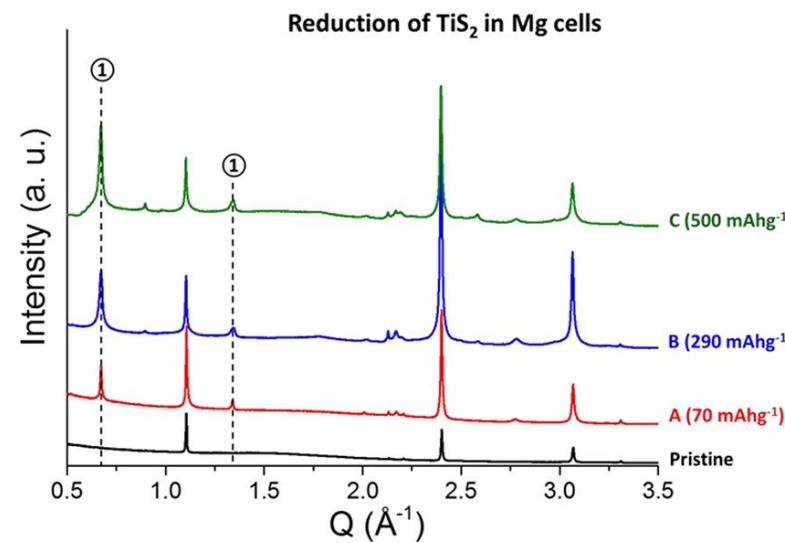
TiS₂

Extended Potentiostatic Steps

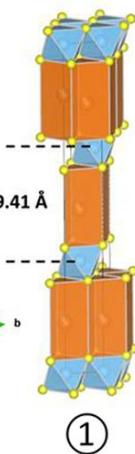


Mg / 0,3 M Mg(TFSI)₂, EC:PC 1:1v / TiS₂

Ex-situ SXRD



SG: R̄3m
 $a=3.418(1)$ Å
 $c=28.236(1)$ Å



Unreacted TiS₂

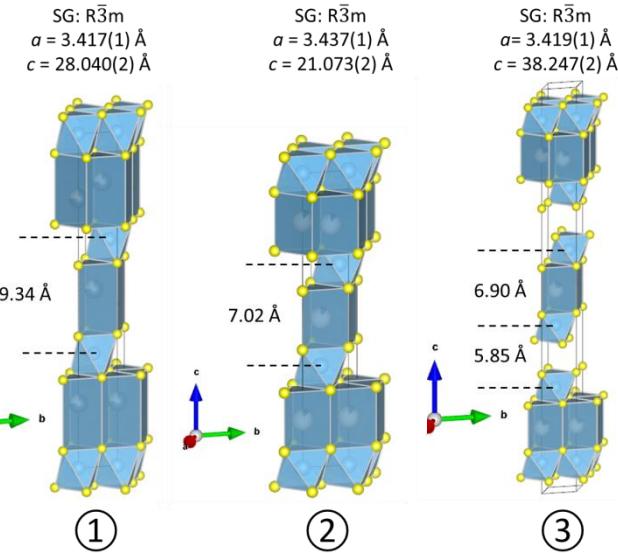
1 phase with changed d spacing

- 1 Co-intercalated solvent (EC/PC)

Further studies are needed....



Ca^{2+} Intercalation into TiS_2



Unreacted TiS_2

Different phases with \neq interlayer spacing

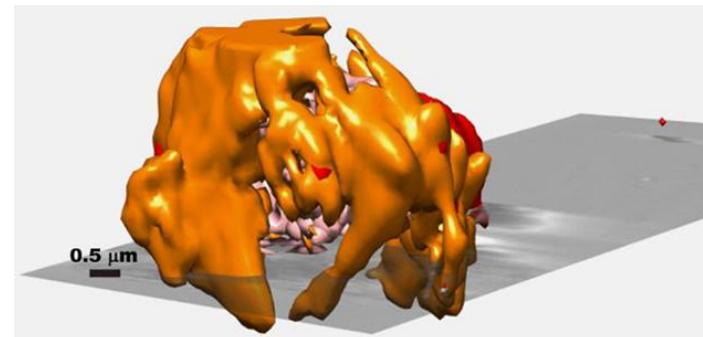
- 1 Co-intercalated solvent (EC/PC)
- 2 $\text{Ca}_{0.5}\text{TiS}_2$
- 3 Non solvated Stage 2 phase

Full Reversibility

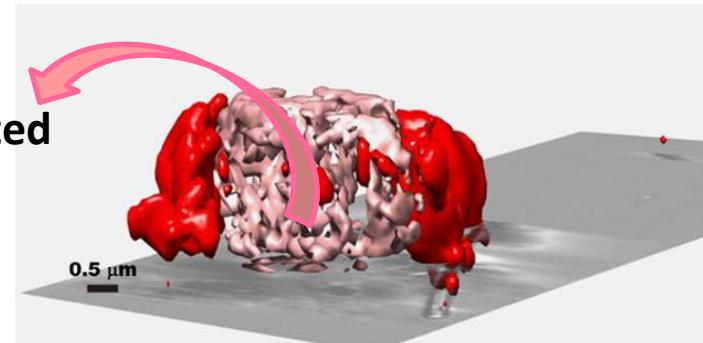
3D reconstruction of the $\text{Ca } \Delta\mu$ distribution

Differential Absorption X-Ray Tomography Ca L_2 edge

ALBA



Intercalated
Ca



Conclusions

- Highly covalent anionic framework may not represent a viable strategy to overcome the Mg^{2+} mobility issue if not coupled with **low energy Mg^{2+} diffusion pathway**, i.e. with low energy intermediate state as well as with migration sites well matching with the preferred Mg^{2+} coordination
- Structural changes observed upon Mg intercalation into TiS_2 , most probably related to **solvent co-intercalation**
- **Need of complementary techniques for the unambiguous assessment of MV ions intercalation** (Absorption X-ray Tomography proved to be viable to demonstrate Ca^{2+} insertion into TiS_2)



Future Perspectives

- Solvent-assisted expansion of the interlayer distance as a strategy to increase the MV ion mobility within solid hosts

Thanks for your kind attention



