

Le stockage électrochimique : Les batteries à ions multivalents

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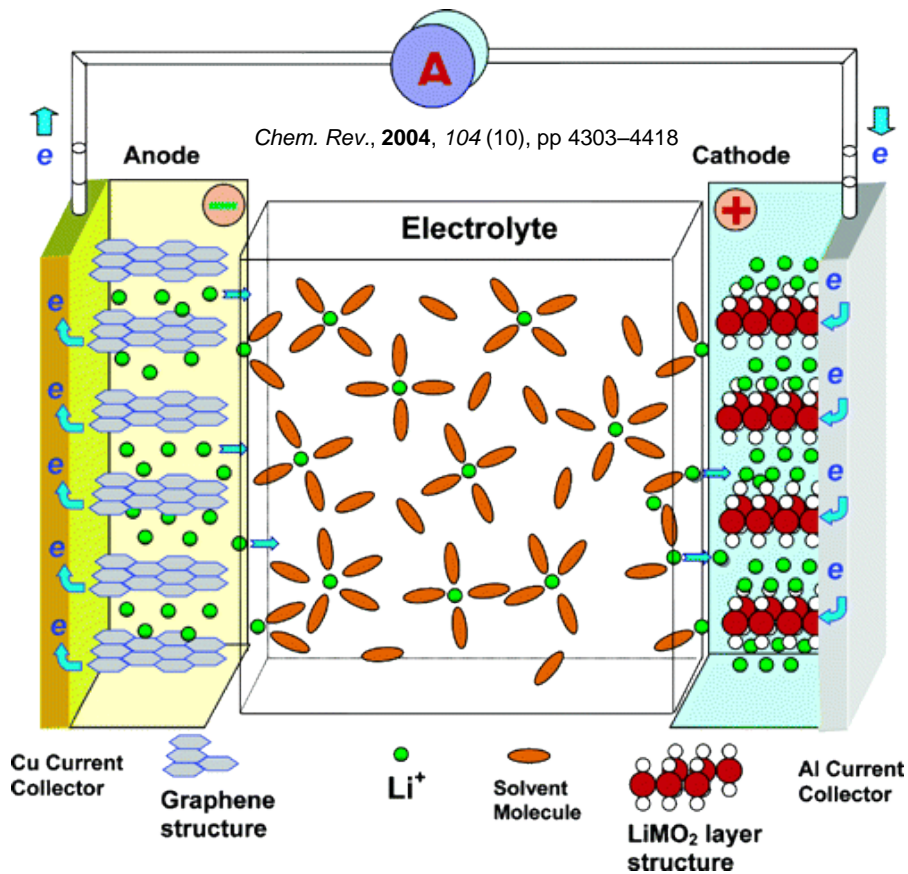
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^g *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens, France.*

Les batteries lithium-ion

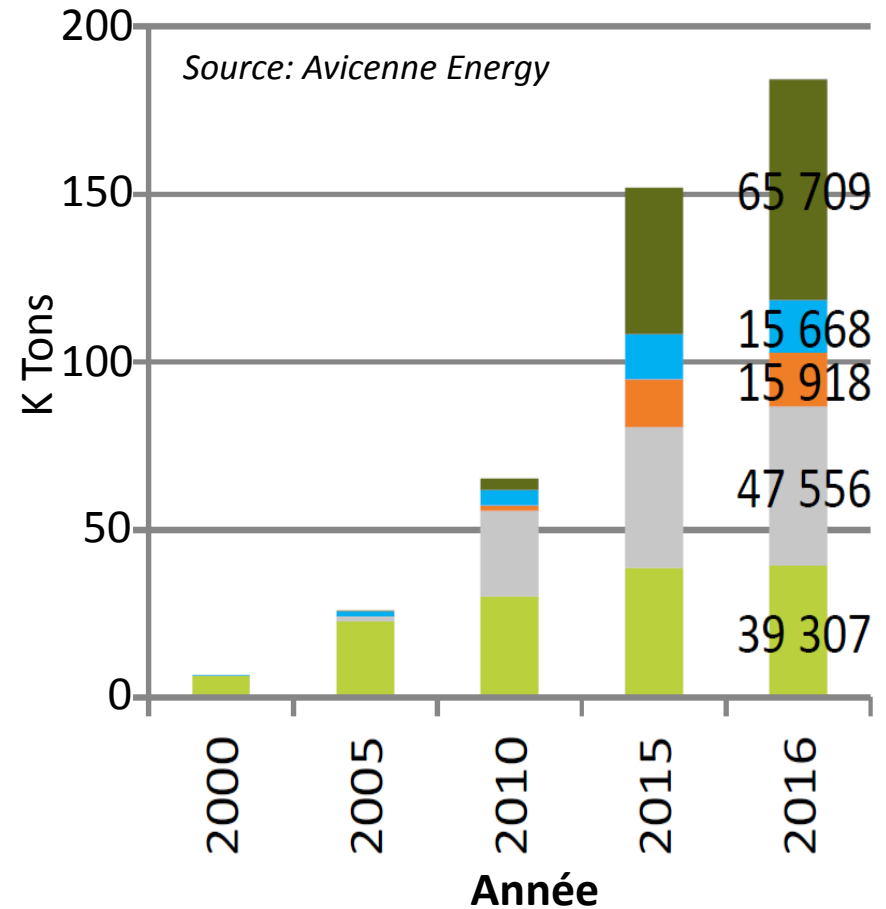
Le principe



Les applications :

- Dispositifs électroniques (tablettes, portables, objets connectés), etc.
- Transports (vélos, véhicules électriques)
- Le stockage stationnaire

La production des matériaux cathodes



LiFePO₄

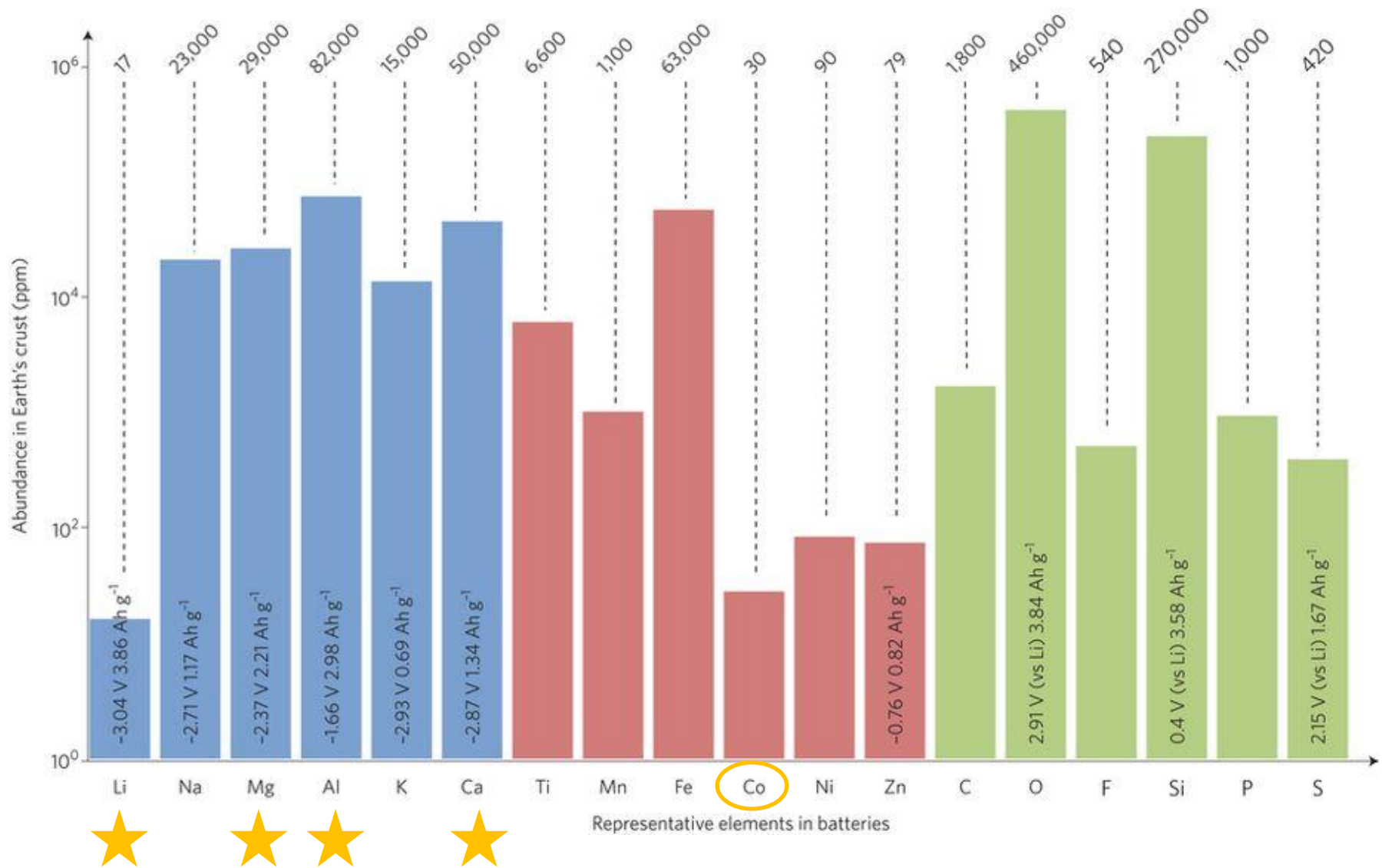
LiMn₂O₄

LiNi_{0.8}Co_{0.15}Al_{0.05}O₂

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂

LiCoO₂

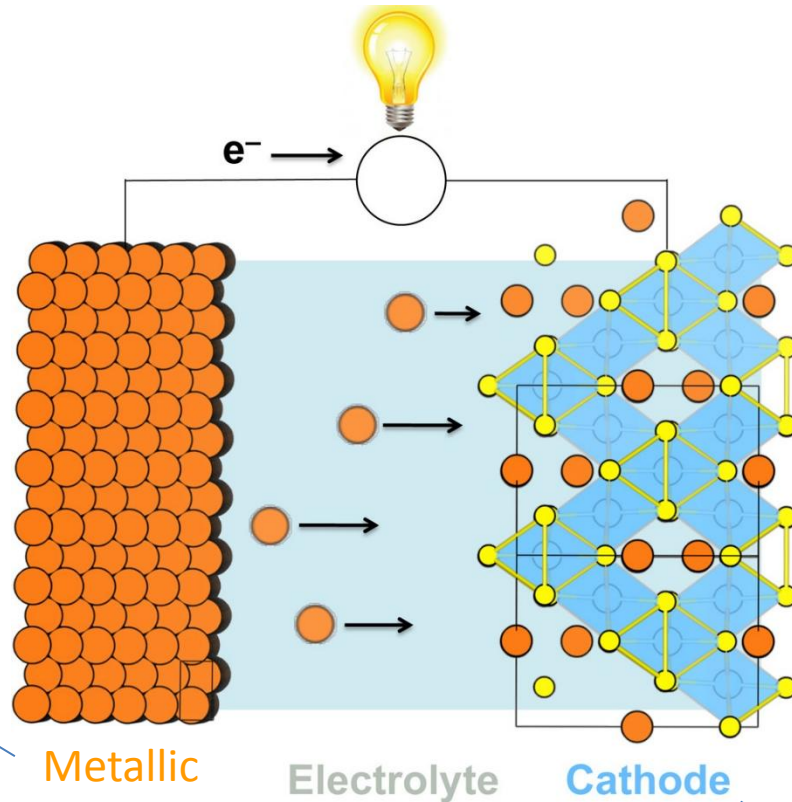
Au-delà du lithium-ion



Les batteries à ions multivalents



Mg, Al, Ca, Zn
✓ Abondants



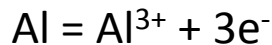
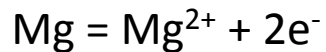
Metallic
anode

Electrolyte

Cathode

✓ Pas de formation de dendrites

✓ Densité d'énergie par *Volume*

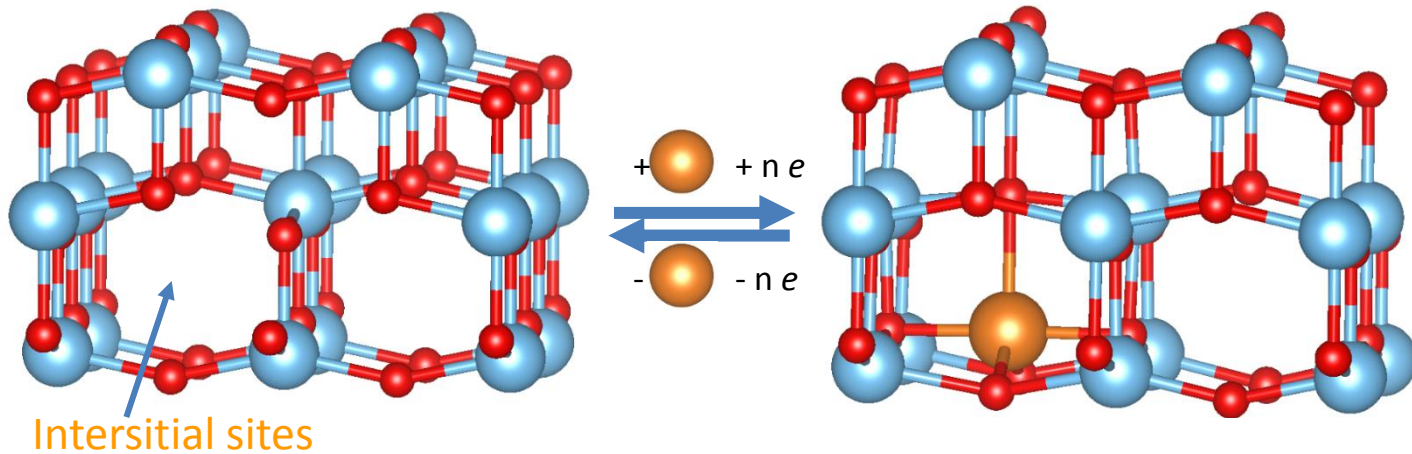


✗ Conductivité ionique
Dépôt/dissolution
Stabilité électrochimique

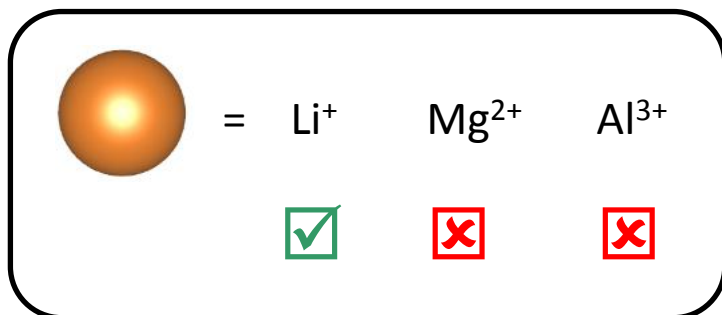
✗ Peu de matériaux électrochimiquement actifs vis-à-vis des ions MVs

La chimie d'intercalation des ions multivalents

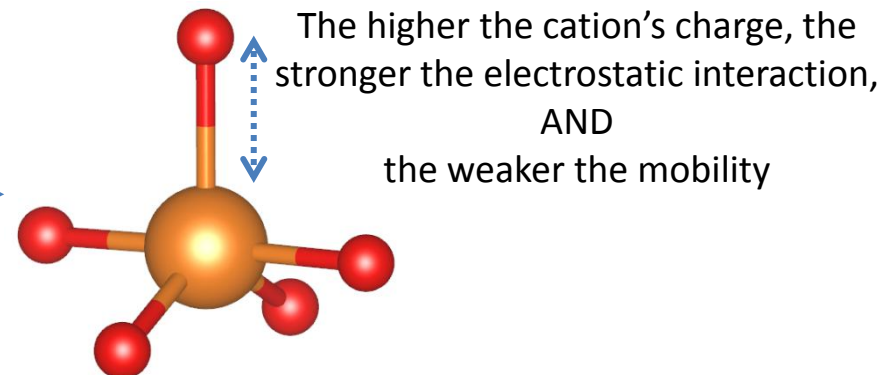
TiO₂



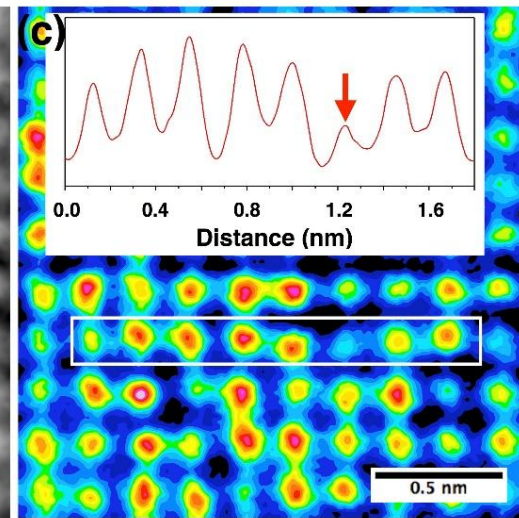
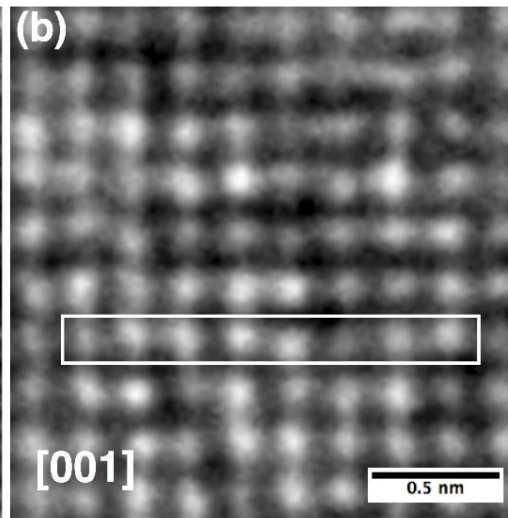
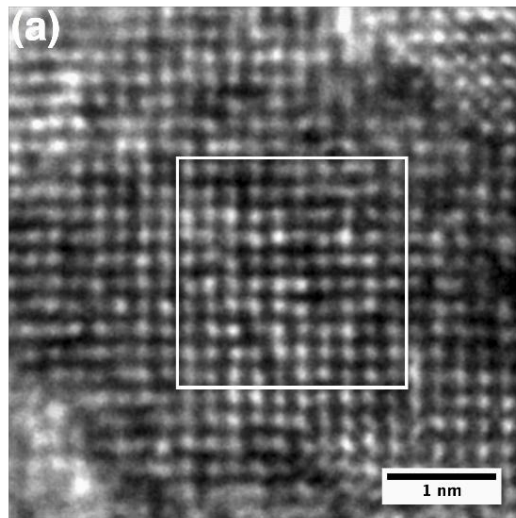
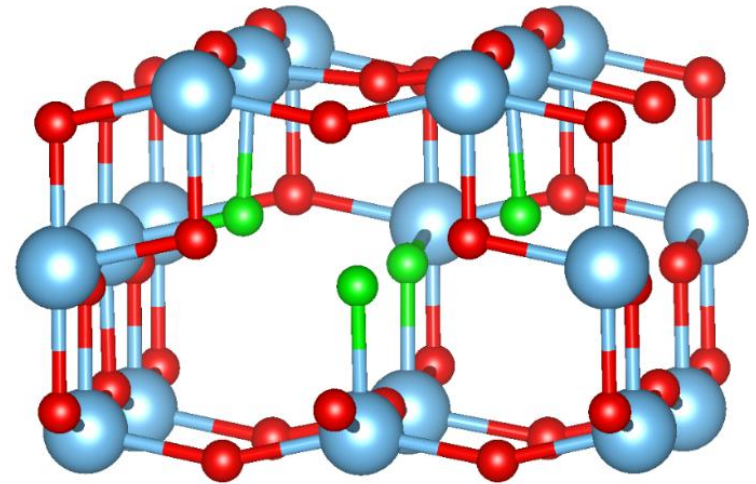
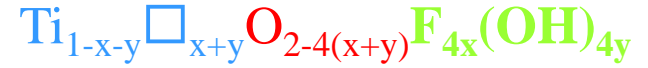
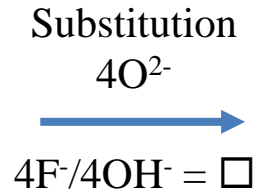
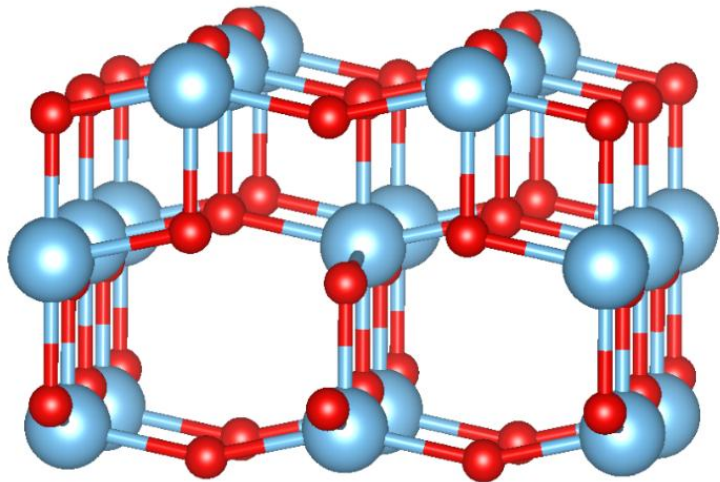
	Li ⁺	Na ⁺	Mg ²⁺	Al ³⁺
Shannon's ionic radii (Å) (CN=VI)	0.76	1.02	0.72	0.53
Polarizing power (Z/r ²)	1.73	0.96	3.85	10.68



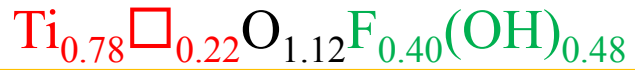
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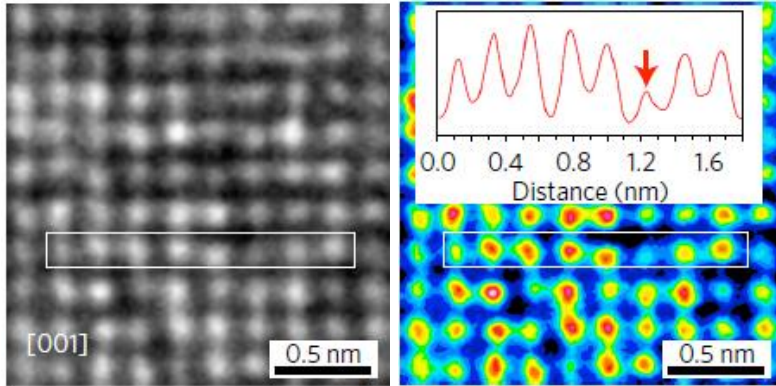
La chimie des défauts



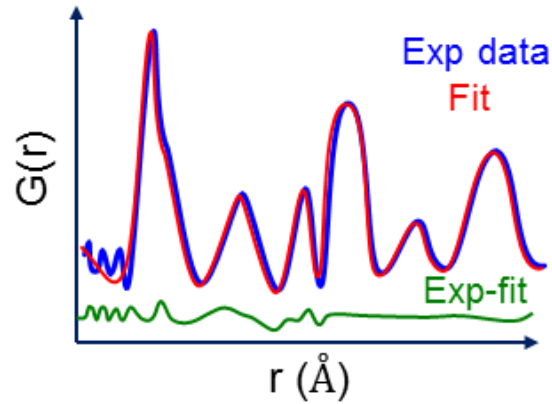
Des matériaux complexes



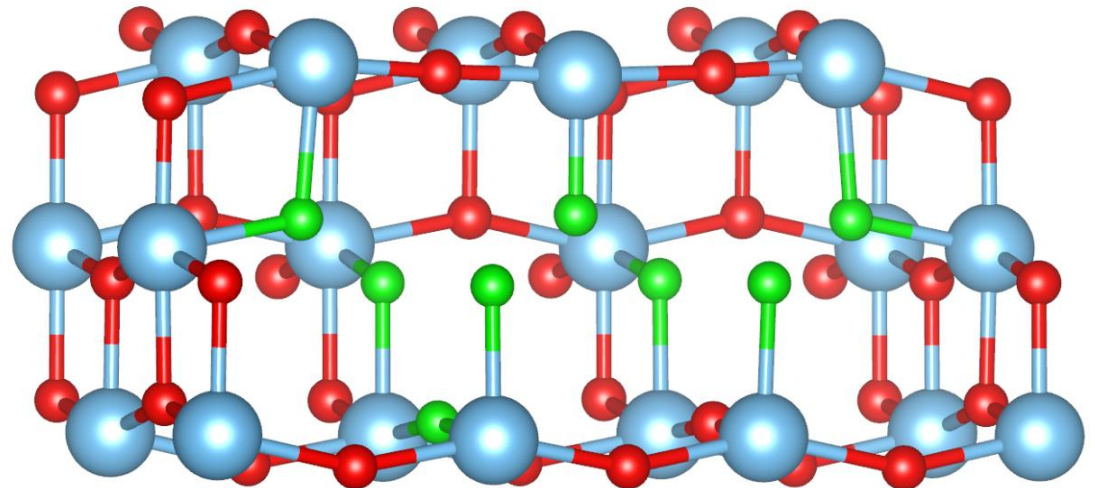
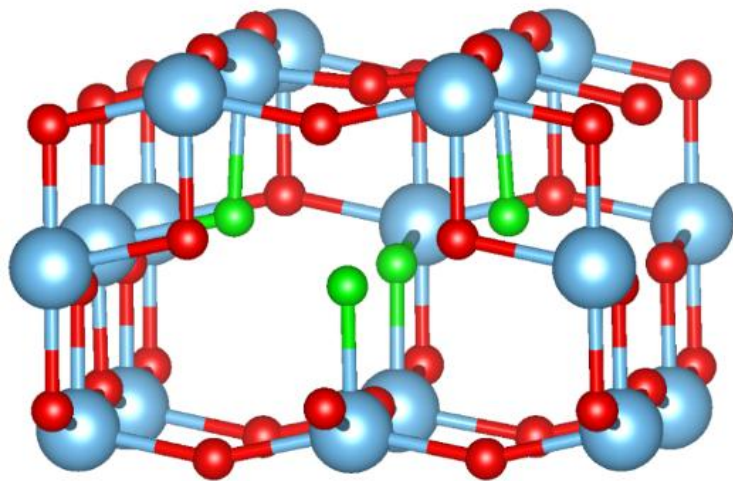
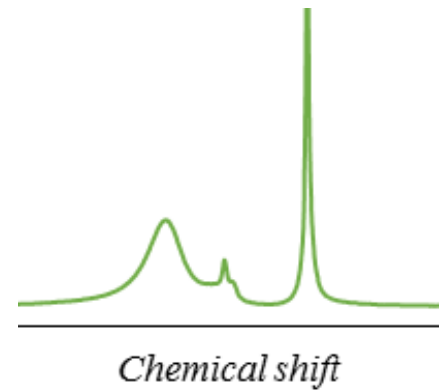
High-resolution TEM



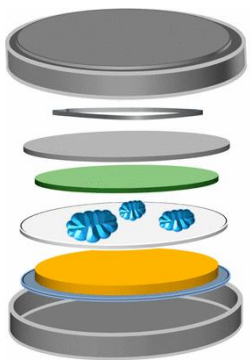
X-ray Pair Distribution Function



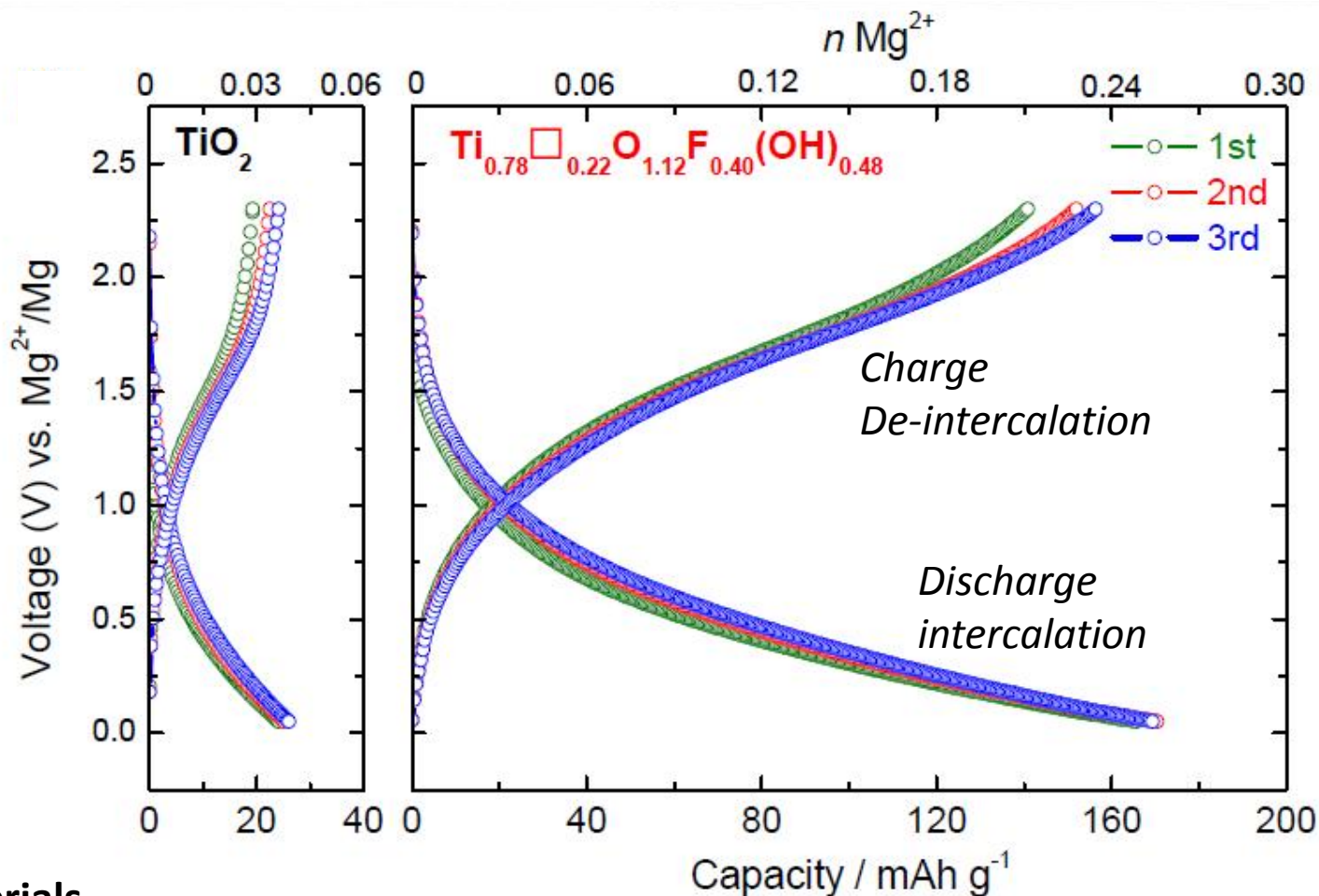
^{19}F , ^1H Solid-state NMR



Activité électrochimique vs. Mg^{2+}/Mg



(-) Mg || 0.2 mol L⁻¹ MgPhCl₂/AlCl₃ in THF electrolyte || F-TiO₂ (+)



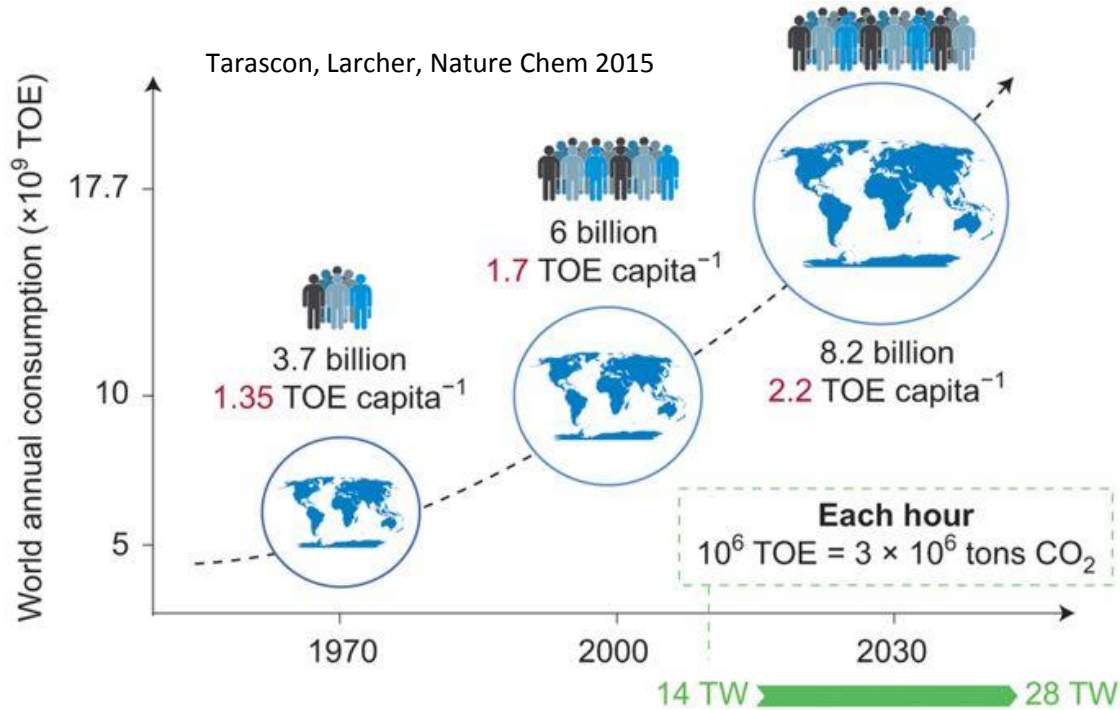
Nature Materials
16 (11), 1142, 2017

Effet des lacunes sur l'activité électrochimique

Conclusion

- **Les enjeux du stockage électrochimique :**

(i) Développement de systèmes capables la demande croissante,



(ii) Développement de nouveaux matériaux (à forts taux de recyclabilité)

Remerciements

Jiwei Ma, Mathieu Salanne, Toshinari Koketsu, Peter Strasser, Benjamin Morgan, Monique Body, Christophe Legein, Franck Fayon, Olaf Borkiewicz



FRENCH FLUORINE NETWORK



French research network on
electrochemical energy storage



Société Chimique de France

References

High Substitution Rate in TiO₂ Anatase Nanoparticles with Cationic Vacancies for Fast Lithium Storage

Wei Li, Dario Corradini, Monique Body, Christophe Legein, Mathieu Salanne, Karena W. Chapman, Peter J. Chupas, Anne-Laure Rollet, Christian Julien, Karim Zhagib, Mathieu Duttine, Alain Demourgues, Henri Groult, and Damien Dambournet
Chemistry of materials, 27 (14), p 5014, **2015**.

Reversible Magnesium and Aluminium-ions Insertion in Cation-Deficient Anatase TiO₂

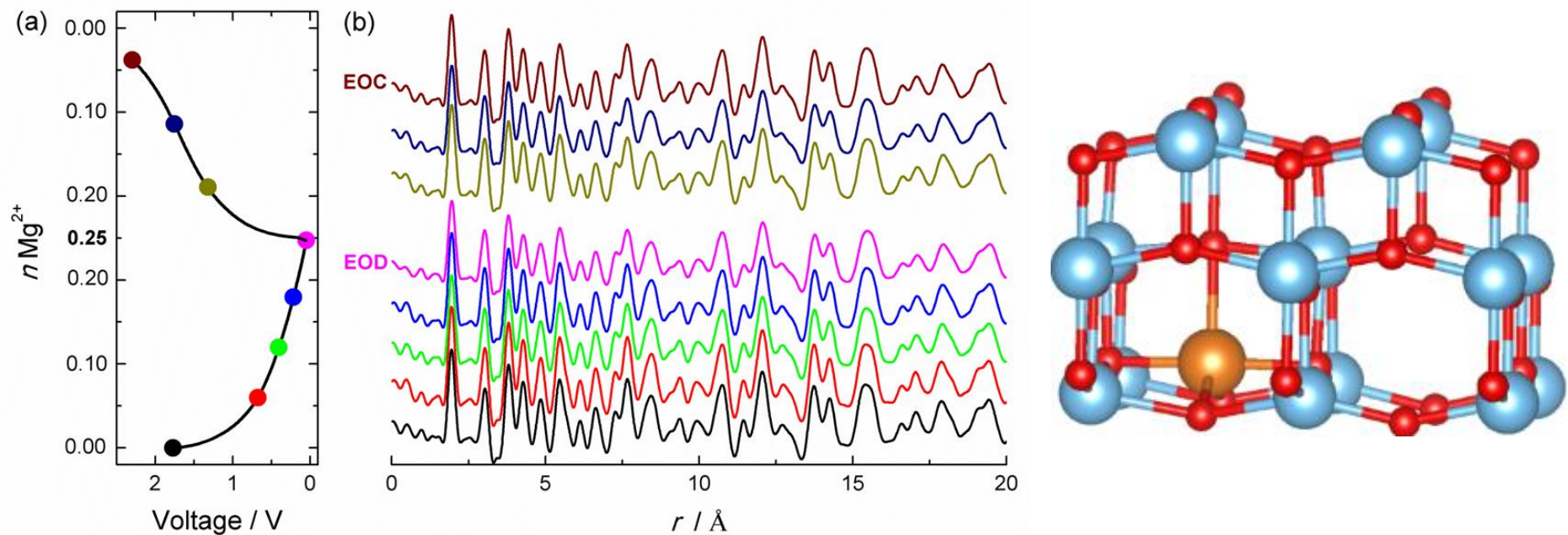
Toshinari Koketsu, Jiwei Ma, Benjamin J. Morgan, Monique Body, Christophe Legein, Walid Dachraoui, Mattia Giannini, Arnaud Demortiere, Mathieu Salanne, François Dardoize, Henri Groult, Olaf J. Borkiewicz, Karena W. Chapman, Peter Strasser, and Damien Dambournet
Nature Materials, 16, p 1142, **2017**.

La Chimie des défauts, un outil pour le stockage de l'énergie

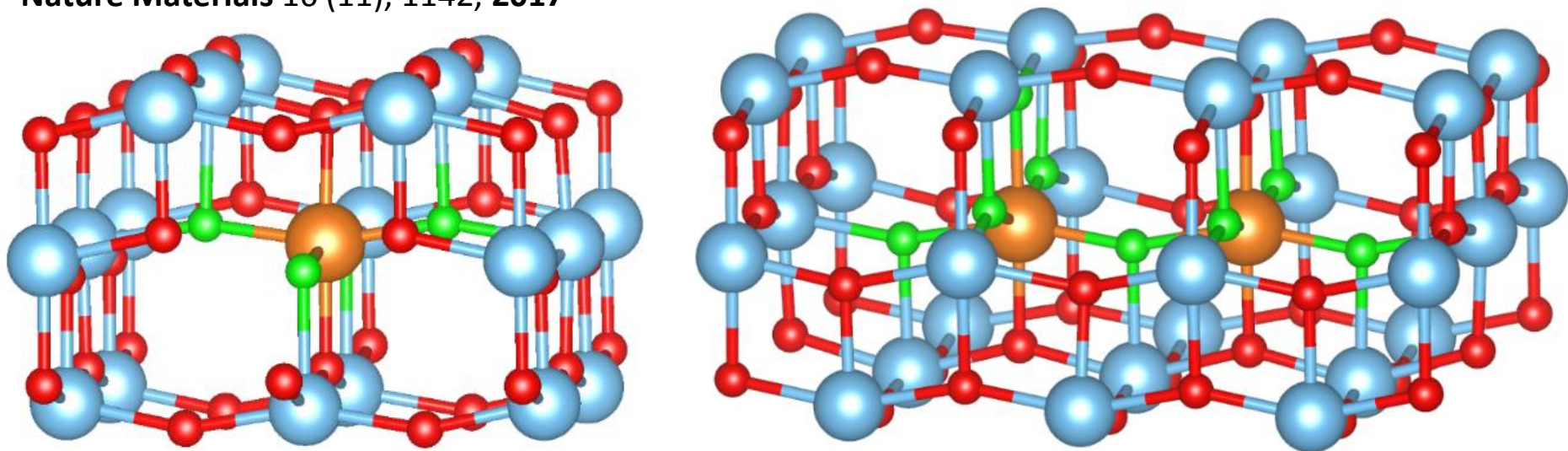
D. Dambournet

L'actualité chimique, 2018.

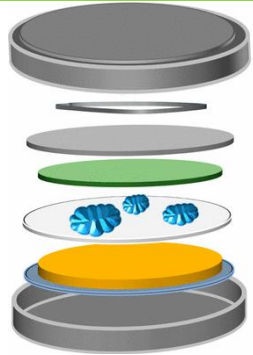
Etude des mécanismes d'intercalation



Nature Materials 16 (11), 1142, 2017

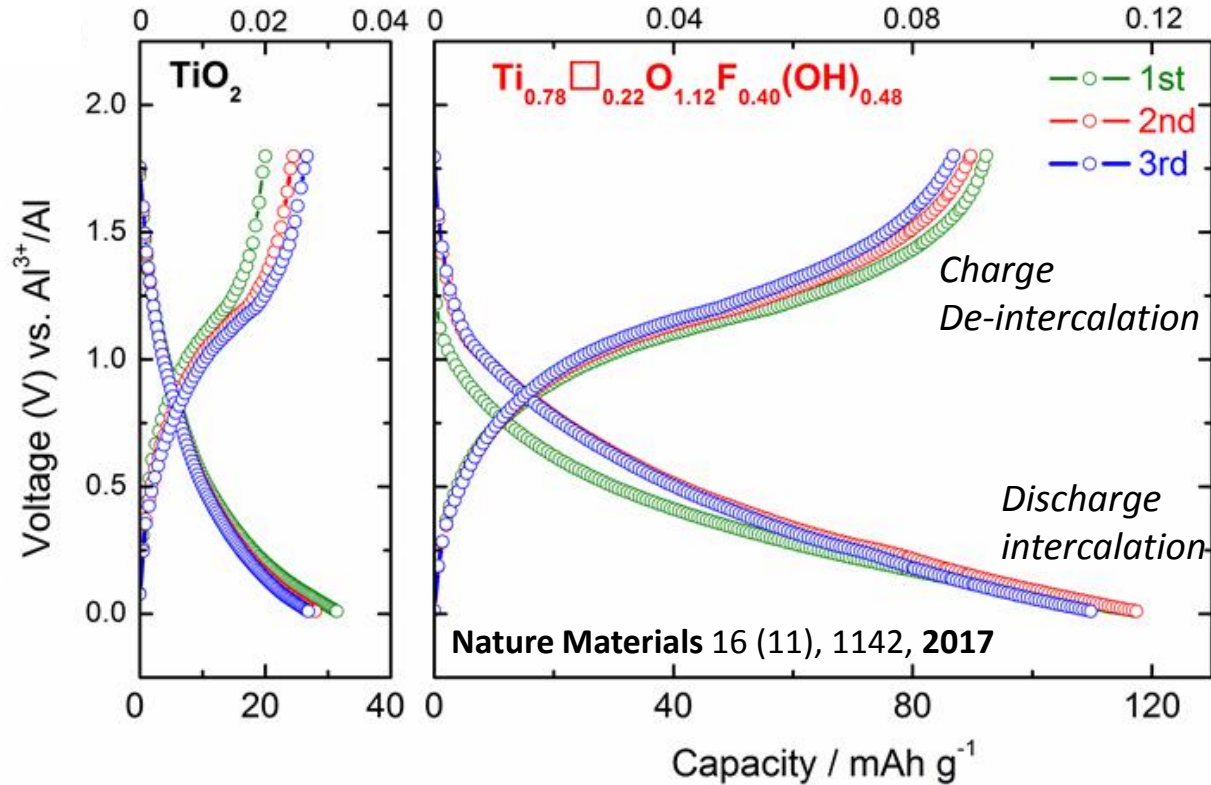


Electrochemical properties vs. Al^{3+}/Al



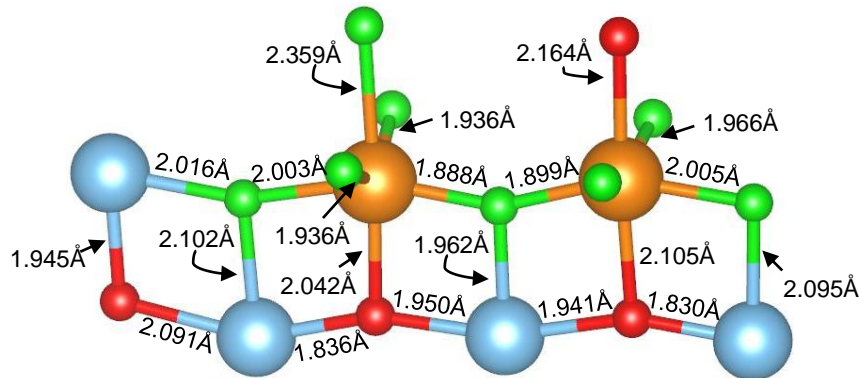
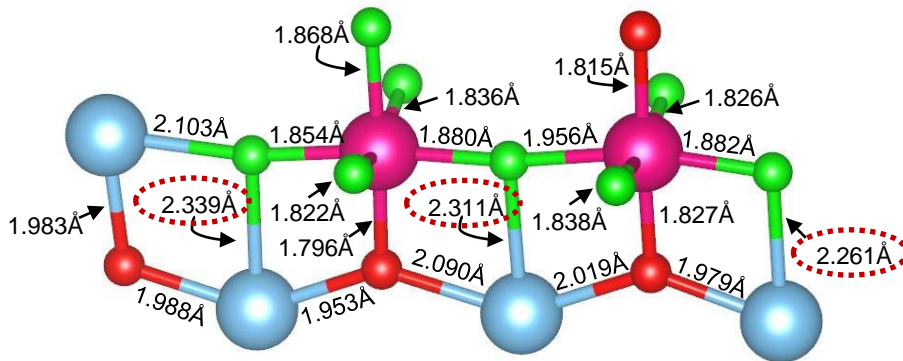
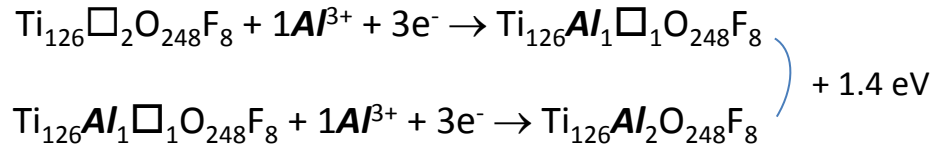
(-) Al || ([EMIm]Cl-AlCl₃) 1 : 1 || F-TiO₂ (+)

$n \text{Al}^{3+}$

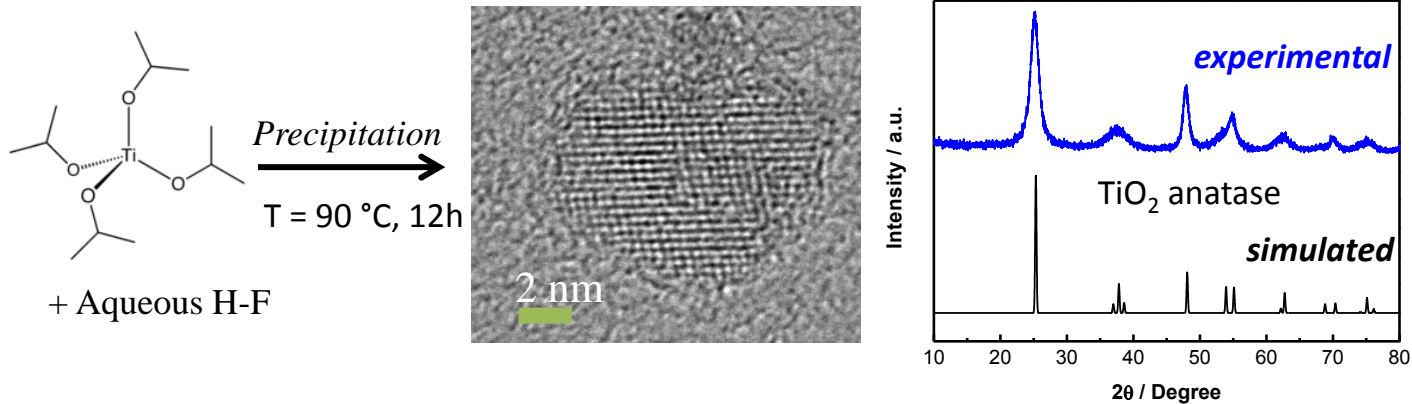


Capacity improvement – Empty vacancies ?

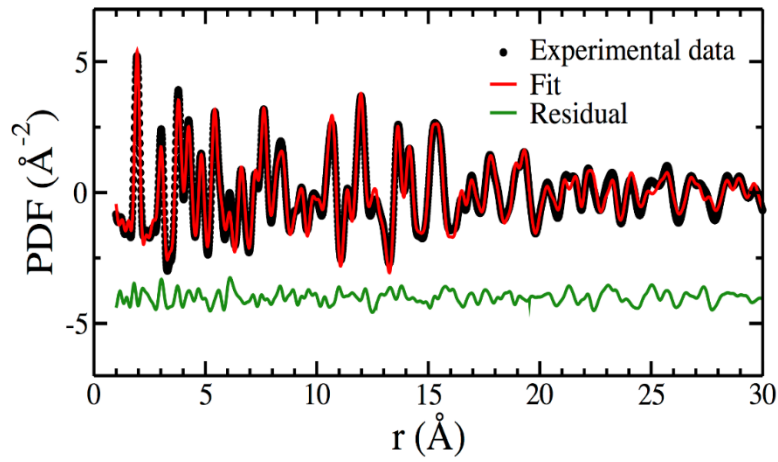
DFT calculations



Introduction of titanium vacancies by Hydroxy/fluorination



Pair Distribution Function, $G(r)$

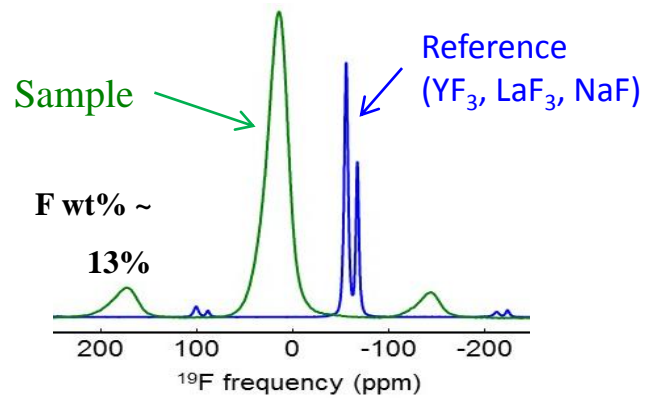


⇒ Structural analysis

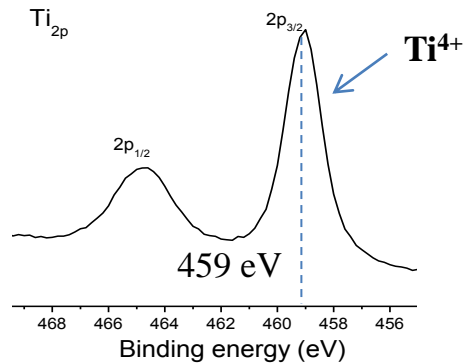
	TiO_2	F- TiO_2
a (\AA)	3.7695(5)	3.784(1)
c (\AA)	9.454(2)	9.448(6)
V (\AA^3)	134.33(4)	135.28(10)
$d_{\text{Ti-O}}$ (\AA)	2*1.972(3) 4*1.925(1)	2*1.984(6) 4*1.929(1)
Ti (4a) occupancy	1.00(1)	0.74(4)

Determination of the chemical composition

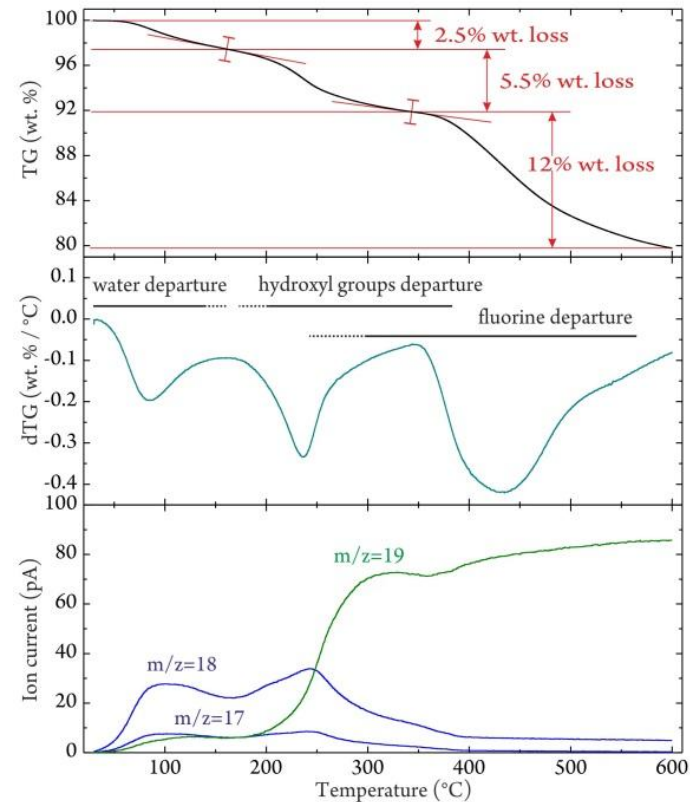
Solid state ^{19}F NMR spectroscopy



X-ray Photoelectron Spectroscopy

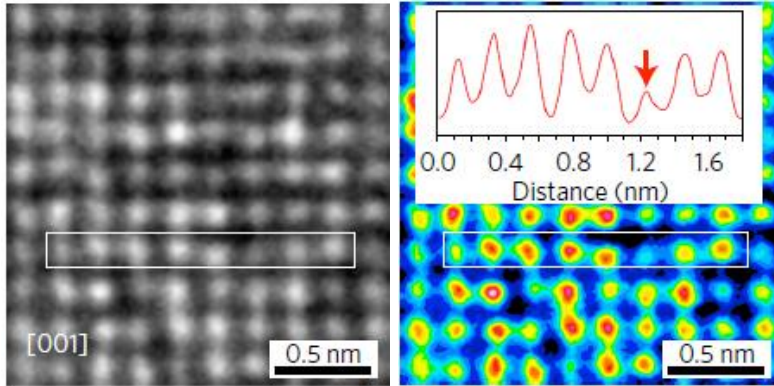


ThermoGravimetric Analysis with MS

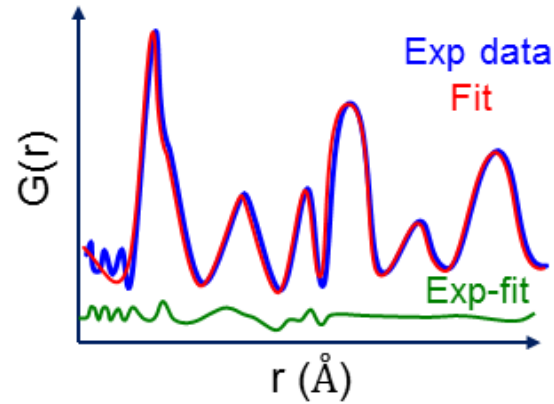


Des matériaux complexes

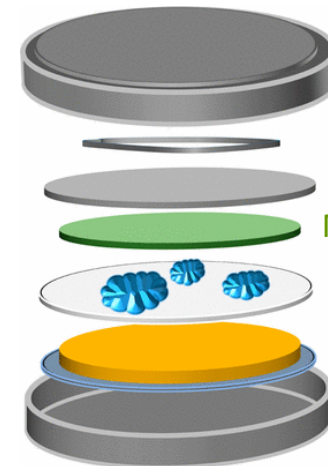
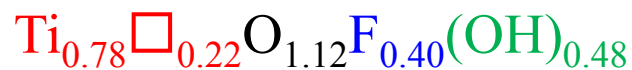
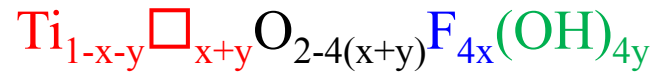
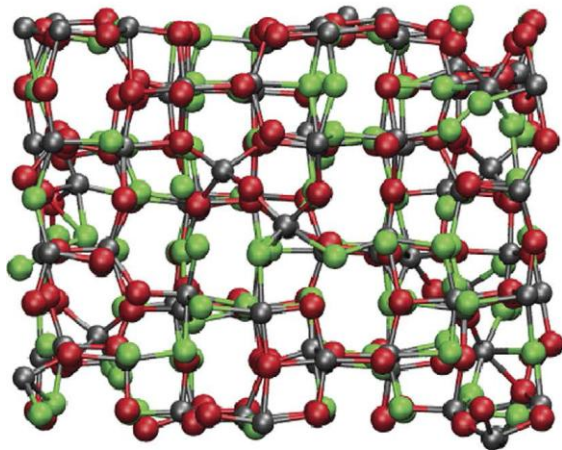
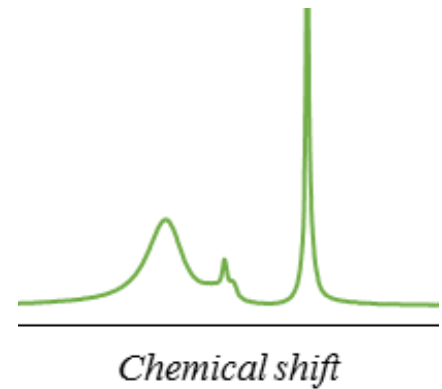
High-resolution TEM



X-ray Pair Distribution Function



^{19}F , ^1H Solid-state NMR



Top cap

Spring

Spacer

Anode

Mg, Al

Electrolyte

Separator

Cathode

Bottom cap

Nazar et al, Chem mater