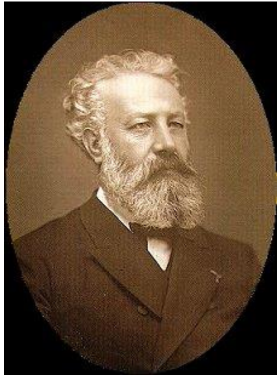
Laboratoire de Réactivité et Chimie des Solides
Université de Picardie Jules Verne, Amiens, FRANCE

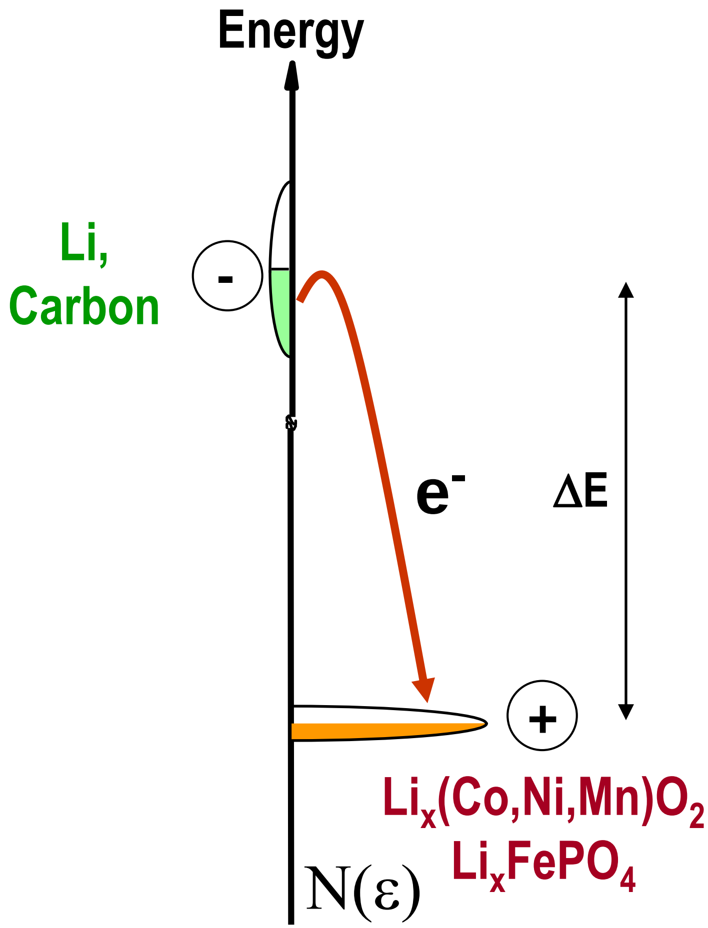


CRYSTAL CHEMISTRY OF IMPORTANT POLYANIONIC MATERIALS USED AS CATHODES IN REAL SODIUM-ION BATTERIES: THE DECISIVE IMPACT OF SYNCHROTRON X-RAY DIFFRACTION

C. Masquelier, L. Nguyen, T. Broux, S. Park, M. Bianchini, A. Iadecola, J.N. Chotard, V. Seznec, P.E. Canepa, F. Fauth, J. Olchowka, D. Carlier, L. Croguennec

AUSE & ALBA User Meeting, Oviedo, September 4th, 2024

Discharge of a battery :
Transformation of chemical energy into electric energy



Oxidation at the negative electrode

$$Li \longrightarrow Li^{+} + e^{-}$$

Reduction at the positive electrode

$$M^{n+} + e^{-} \longrightarrow M^{(n-1)+}$$

The associated structural transformations should be, preferably, <u>REVERSIBLE</u>

The <u>Crystal structure</u> of the positive electrode material plays a <u>MAJOR ROLE</u>

APPROACH

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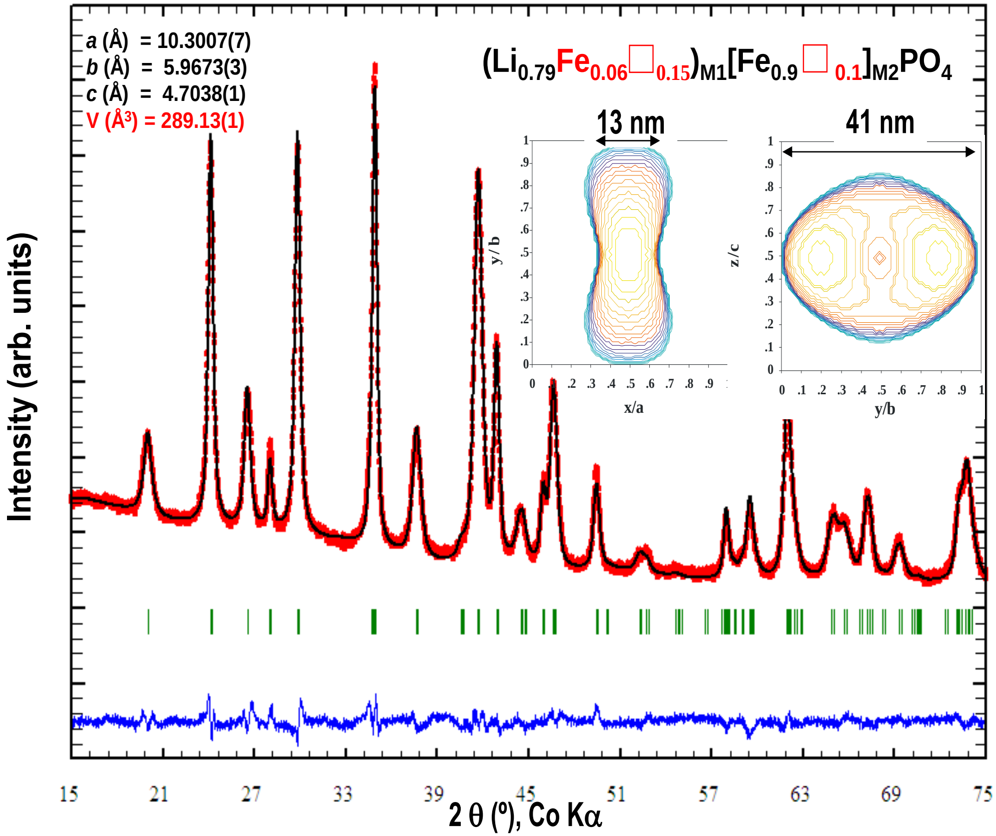
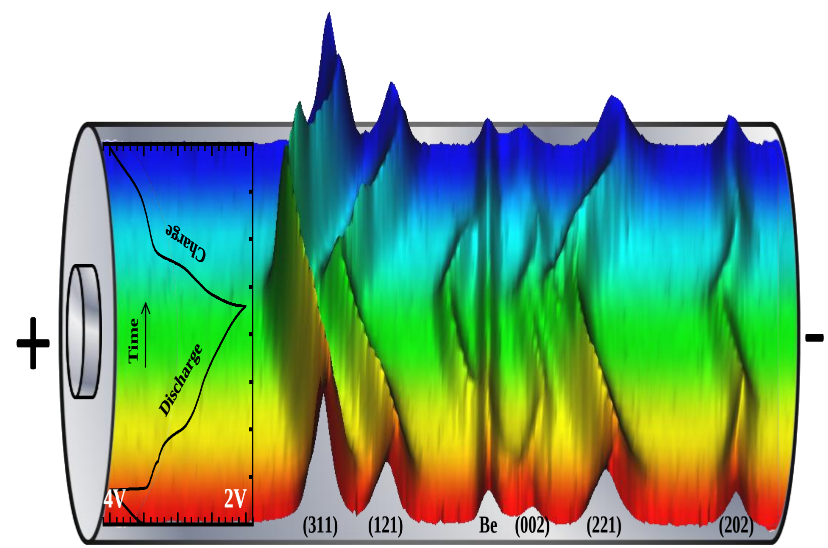
Extensive use of Diffraction (X-Ray and/or Neutrons)

Caracterization of New Phases synthesized and of Phase Transitions

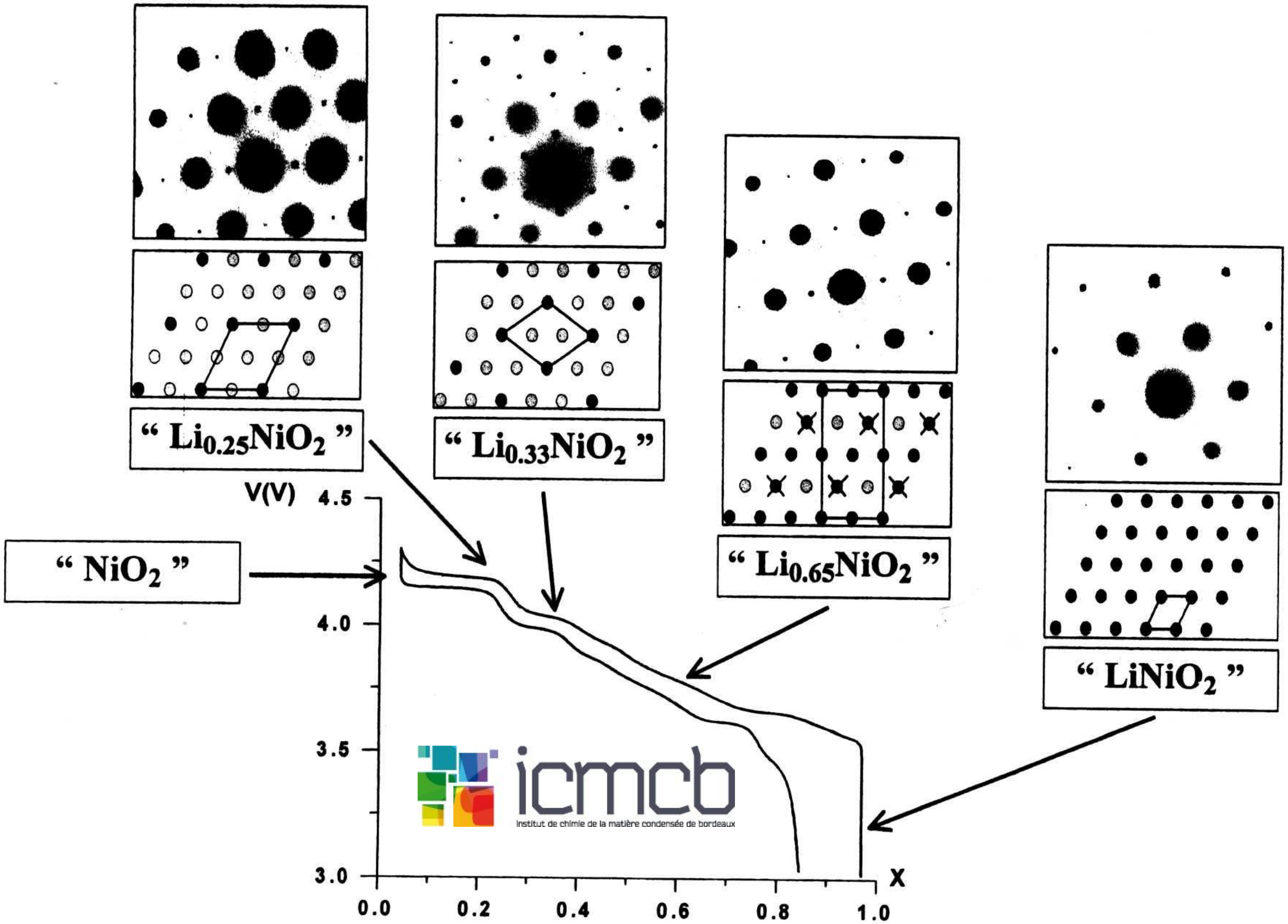
In Situ / Operando techniques for mechanisms of Li^{+} insertion / extraction

Also with : TEM, NMR, Mössbauer, XAS, EELS, DSC, conductivity …



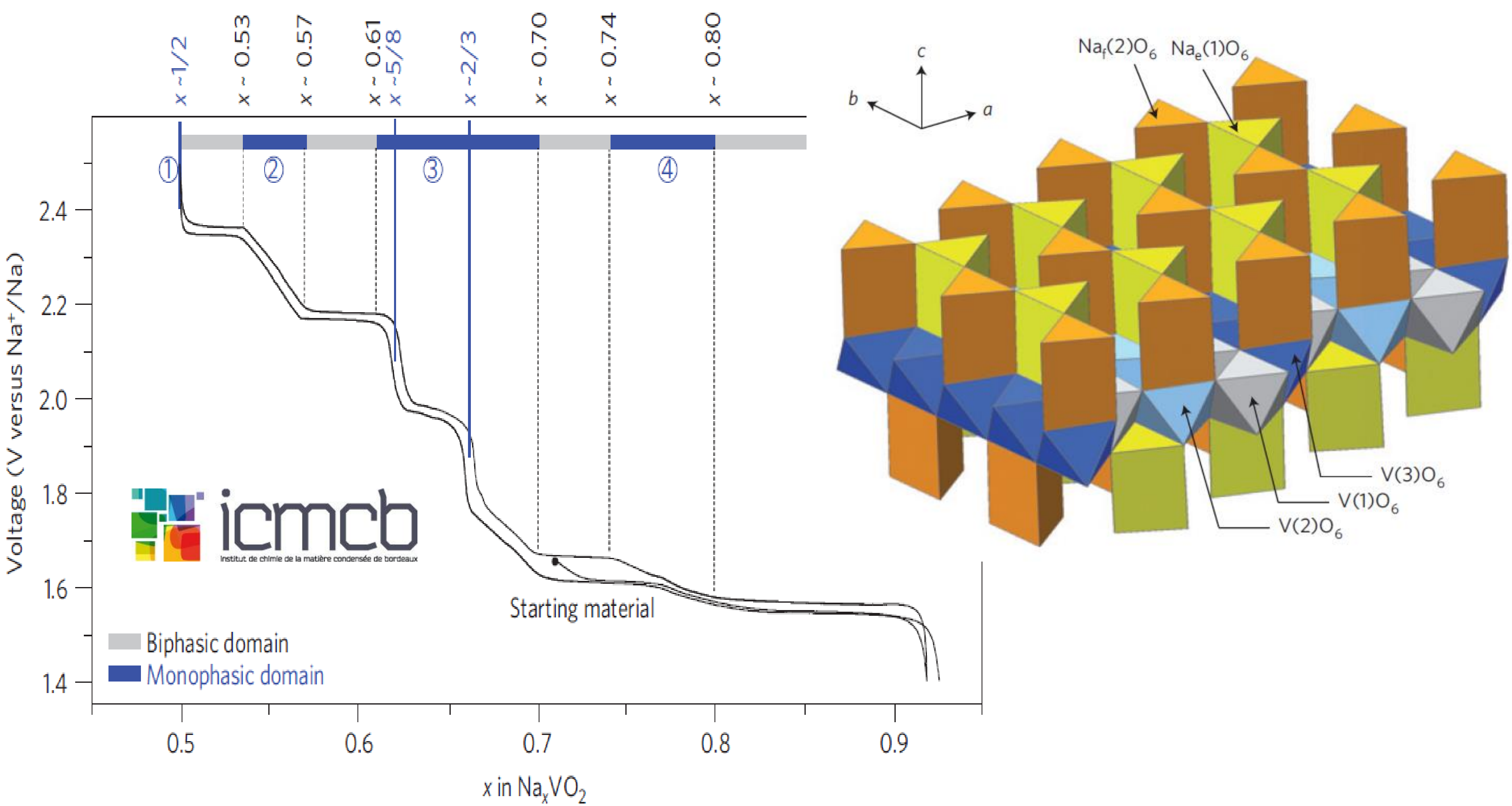


Complex series of phase transitions spotted through electron diffraction In $Li_{1-x}NiO_2$



C. Delmas et al., *Int. J. Inorg. Mater.*, 1 (1999) 11-19

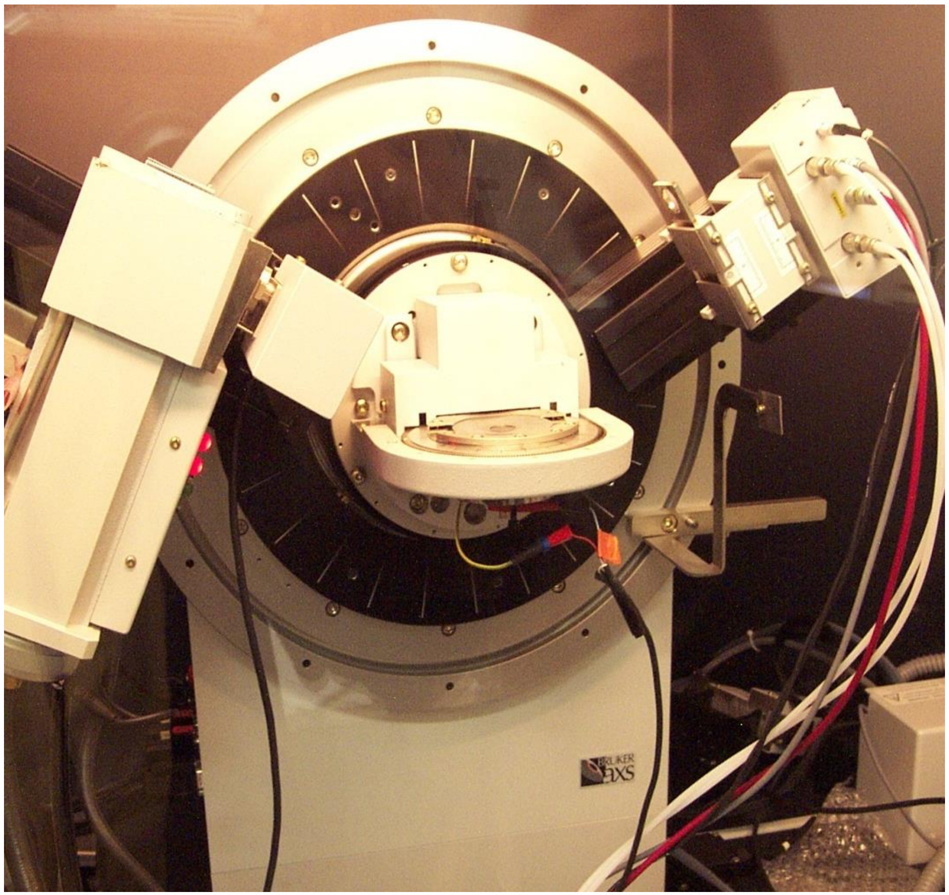
Complex series of phase transitions spotted through in situ diffraction
$Na_{1-x}VO_2$



M. Guignard, C. Didier, J. Darriet, P. Bordet, E. Elkaïm, C. Delmas et al., *Nature Materials, 2012*

In Situ X-Ray Diffraction during battery operation (Reflexion)

Co K_{α} Radiation,
Réflexion θ-θ geometry, PSD counter
Within a Be-capped cell



Invented at LRCS (2005), commercialized worldwide by BRUKER
(new ones (much better !!), designed by Jean-Noël Chotard, are also sold now…..)

LRCS
Amiens

In Situ X-Ray Diffraction during battery operation (Transmission)

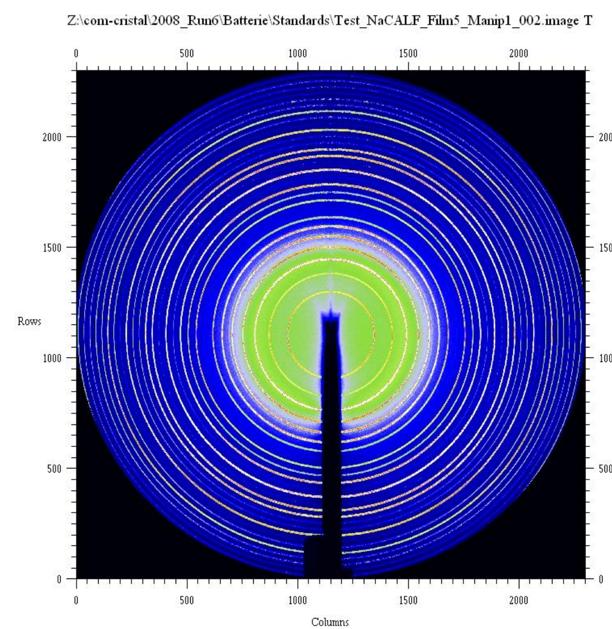
UNIVERSITÉ de Picardie Jules Verne

A606 *Journal of The Electrochemical Society*, **157** (5) A606-A610 (2010)
0013-4651/2010/157(5)/A606/5/$28.00 © The Electrochemical Society

An Electrochemical Cell for *Operando* Study of Lithium Batteries Using Synchrotron Radiation

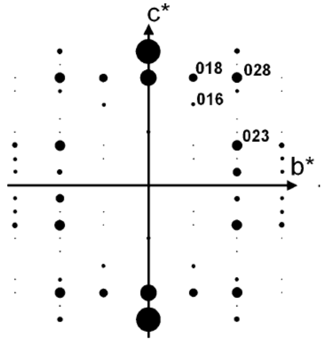
J. B. Leriche,[a] S. Hamelet,[a] J. Shu,[a] M. Morcrette,[a] C. Masquelier,[a,z] G. Ouvrard,[b] M. Zerrouki,[b] P. Soudan,[b] S. Belin,[c] E. Elkaïm,[c] and F. Baudelet[c]

[a]*Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie Jules Verne, CNRS UMR 6007, 80039 Amiens Cedex 9, France*
[b]*Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS UMR 6502, BP 32229, 44322 Nantes Cedex 3, France*
[c]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP 48, 91192 Gif sur Yvette, France*

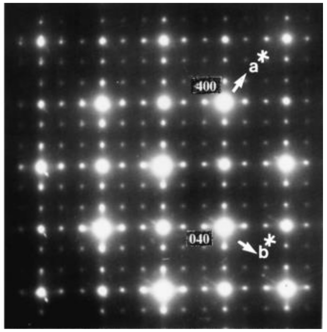


Materials @ a glance

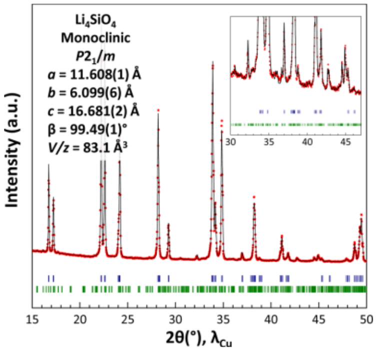
$Ag_7Fe_2(P_2O_7)_4$



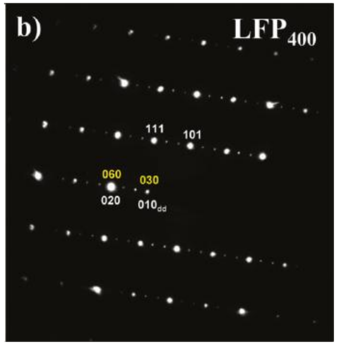
$LiMn_2O_4$



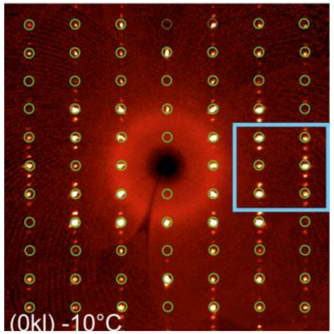
Li_4SiO_4



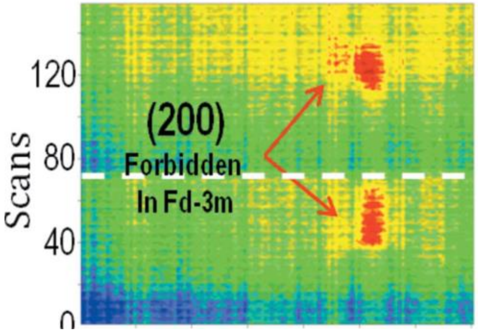
$LiFe_{2/3}PO_4$



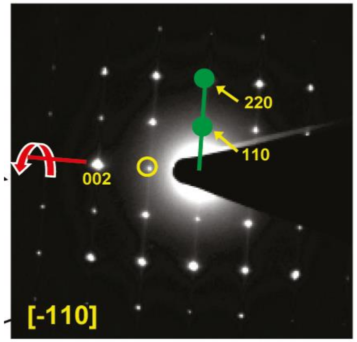
$Na_3V_2(PO_4)_3$



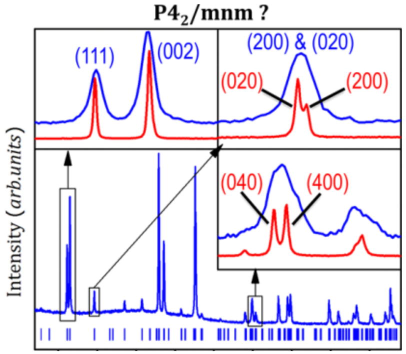
$Li_{0,5}Mn_2O_4$



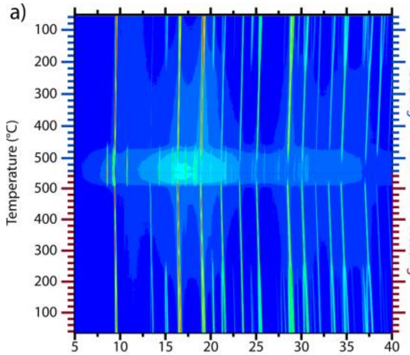
Li_2FeSiO_4



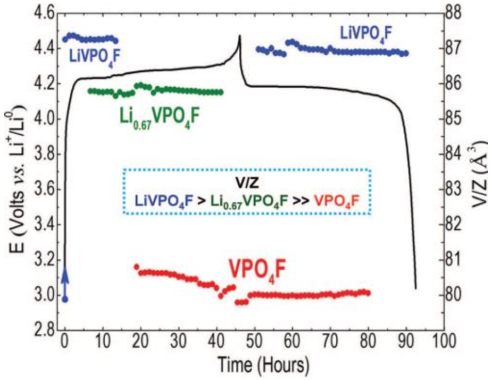
$Na_3V_2(PO_4)_2F_3$



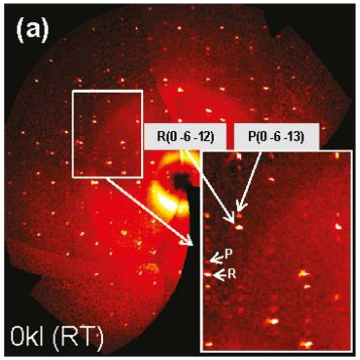
Na_3PS_4



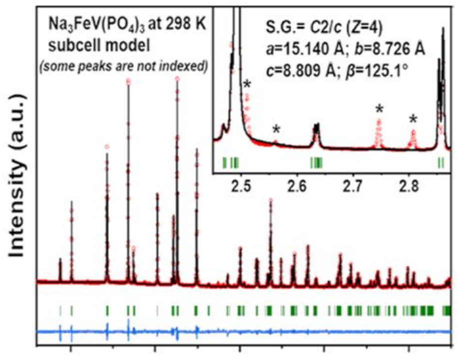
$Li_{0.67}VPO_4F$



$Na_3Ti_2(PO_4)_3$



$Na_3FeV(PO_4)_3$



The growing activity around Na Batteries….

LRCS Amiens

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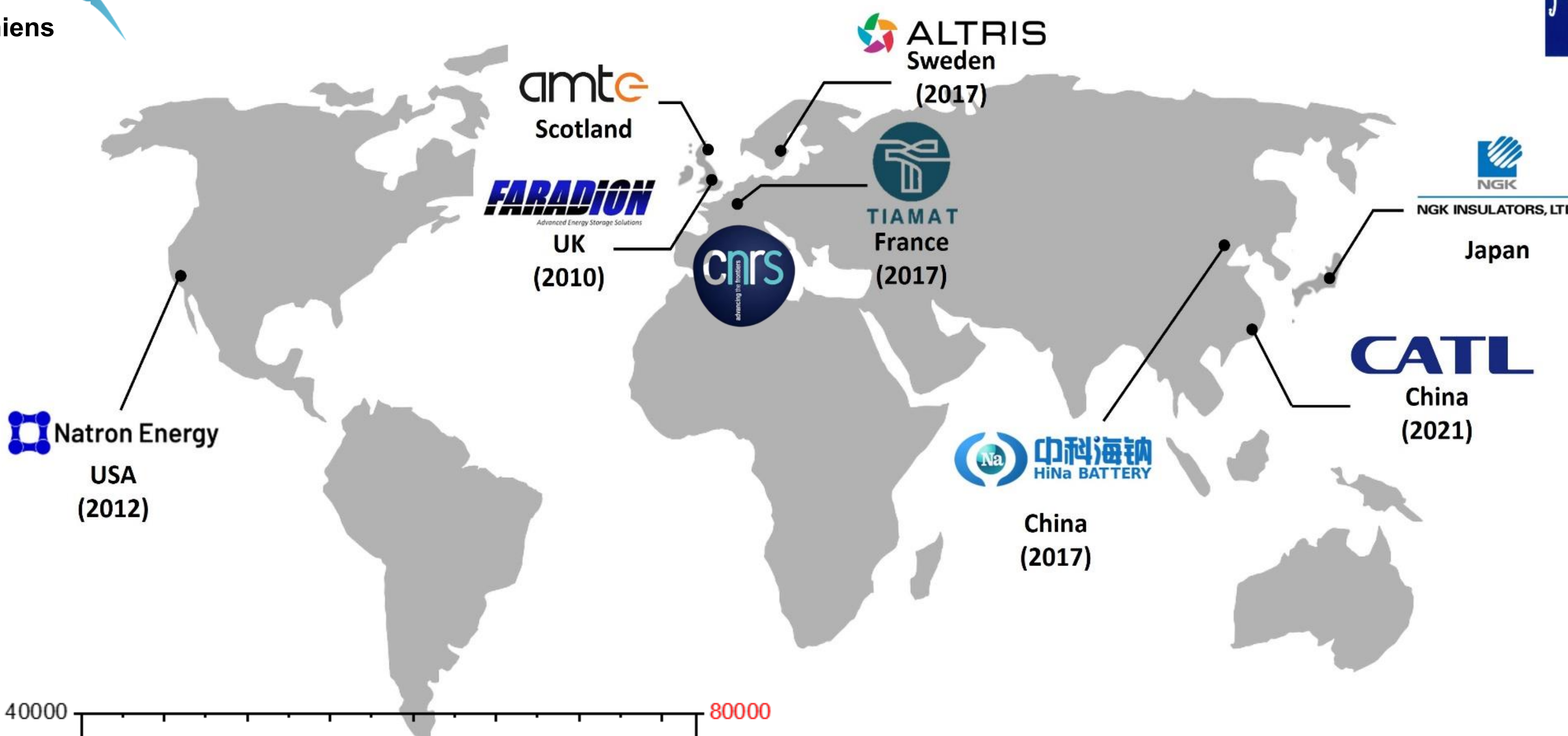
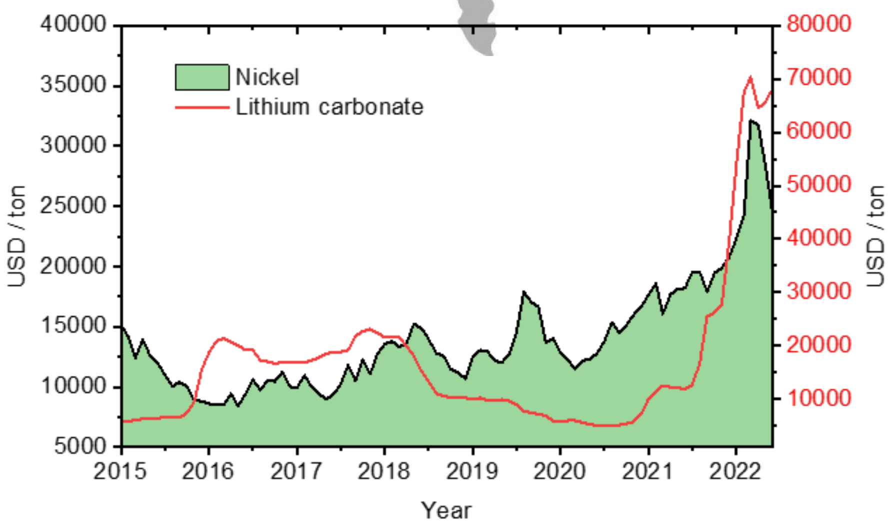




Challenges of today for Na-based batteries of the future

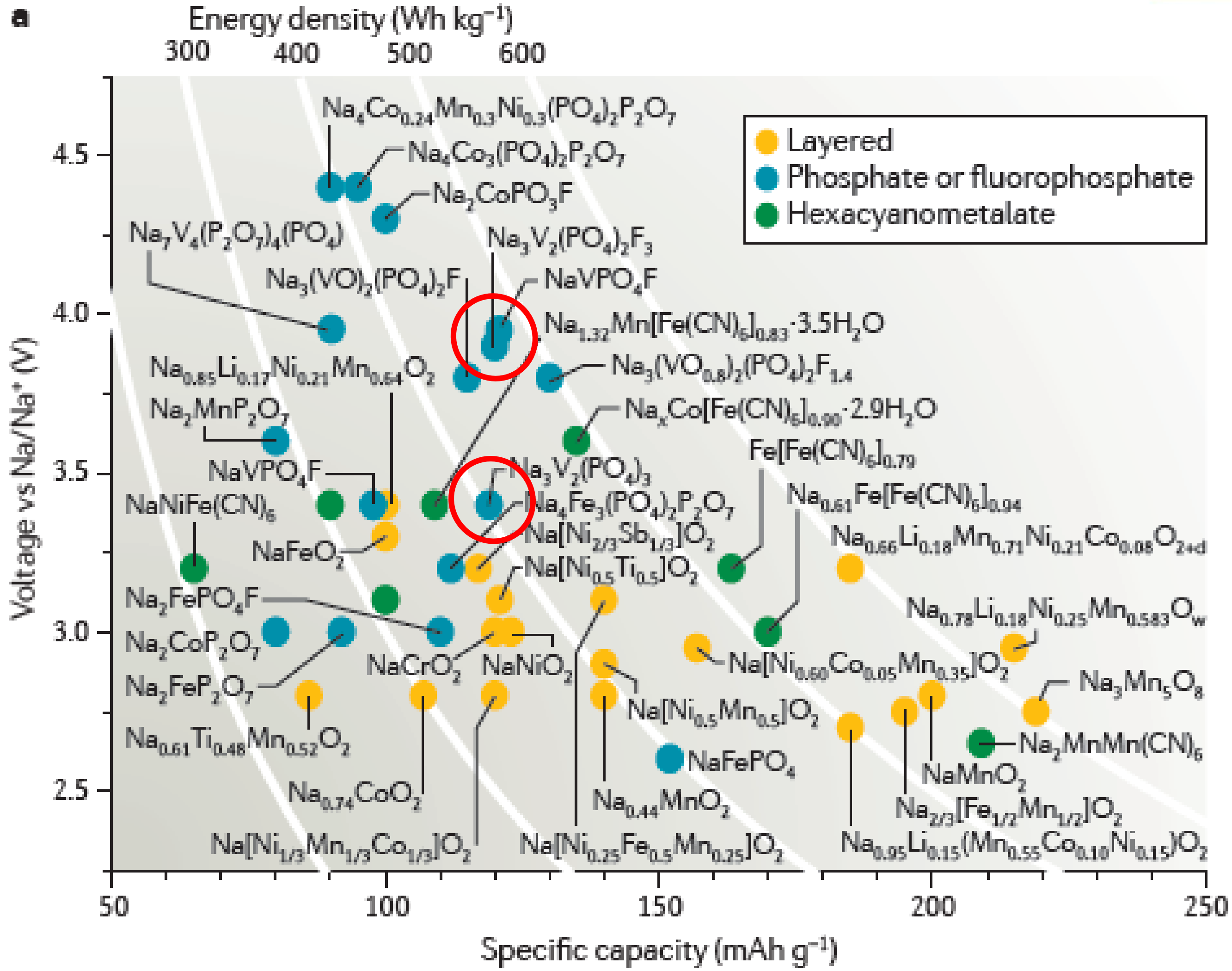
P. Adelhelm, M. Casas-Cabanas, L. Croguennec, I. Hasa, A. Koposov, S. Mariyappan, C. Masquelier, D. Saurel

J. Power Sources, 482, 228872 (2021)

Na-containing Positive electrodes for Na-Ion Batteries

Abundance of Na

Analogous intercalation chemistry to their lithium counterparts



Choi, Aurbach, *Nature Review*, 1, 1, (2016)

P. Adelhelm, M. Casas-Cabanas, L. Croguennec, I. Hasa, A. Koposov, S. Mariyappan, C. Masquelier, D. Saurel, *J. Power Sources*, 482, 228872 (2021)

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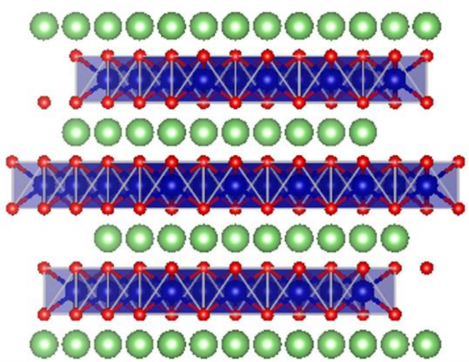
Positive Electrodes for Na Batteries….

UNIVERSITÉ de Picardie Jules Verne

- **Layered oxides**

Na_xMO_2



TIAMAT

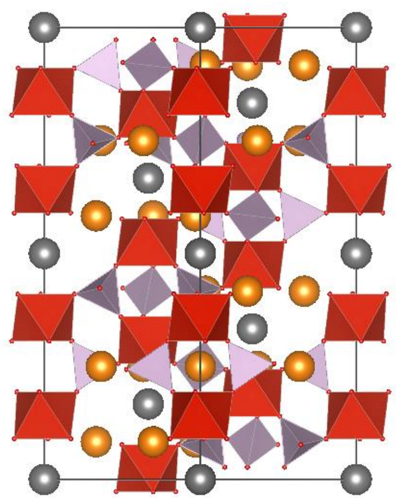
CATL

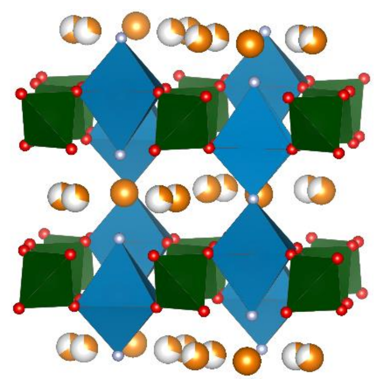
FARADION
Advanced Energy Storage Solutions

中科海钠 HiNa BATTERY

Polyanions

$Na_3V_2(PO_4)_3$ $Na_3V_2(PO_4)_2F_3$

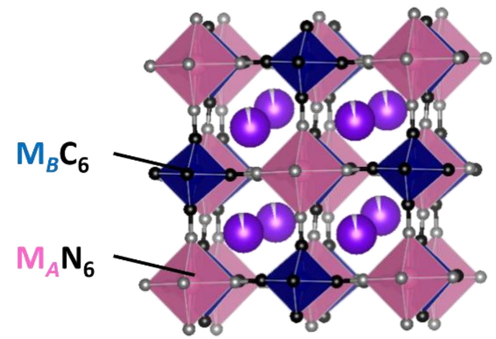




TIAMAT

- **Prussian blue/white**

$Na_xM_A[M_B(CN)_6]_y{\cdot}zH_2O$



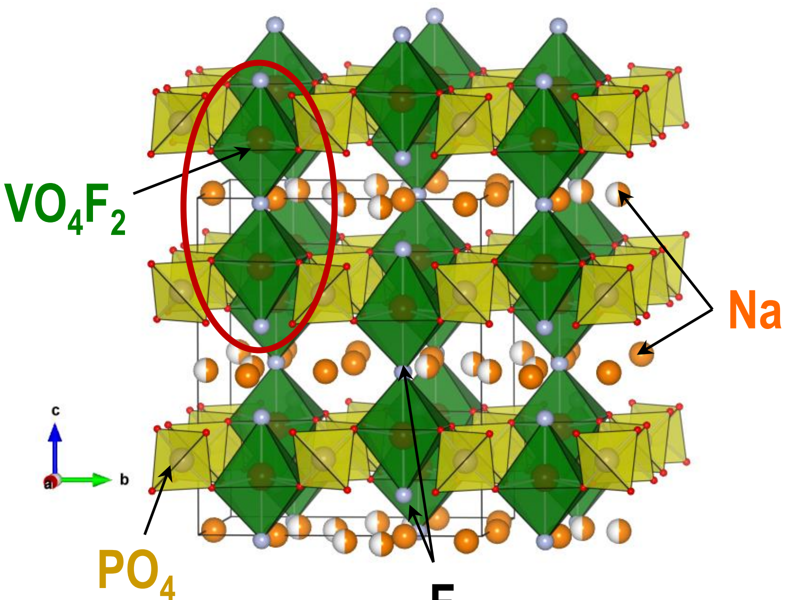
ALTRIS CATL

Natron Energy

Among the 2 best contenders for Na-Ion Batteries

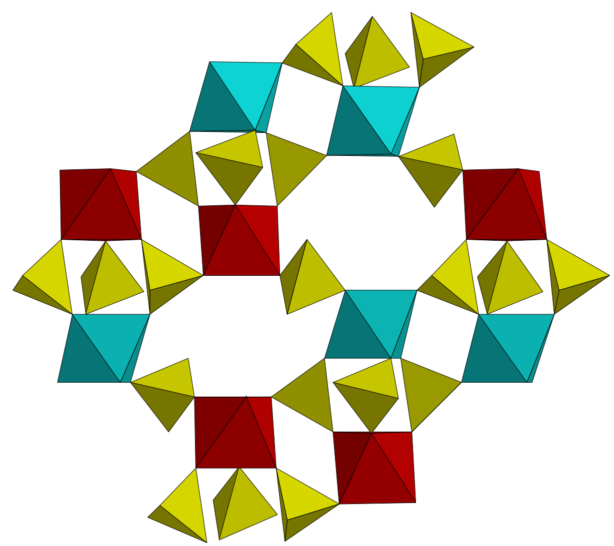
Menu of Today

$Na_3V^{3+}_2(PO_4)_2F_3$



~ 500 Wh/kg

$Na_3V^{3+}_2(PO_4)_3$
NASICON-type

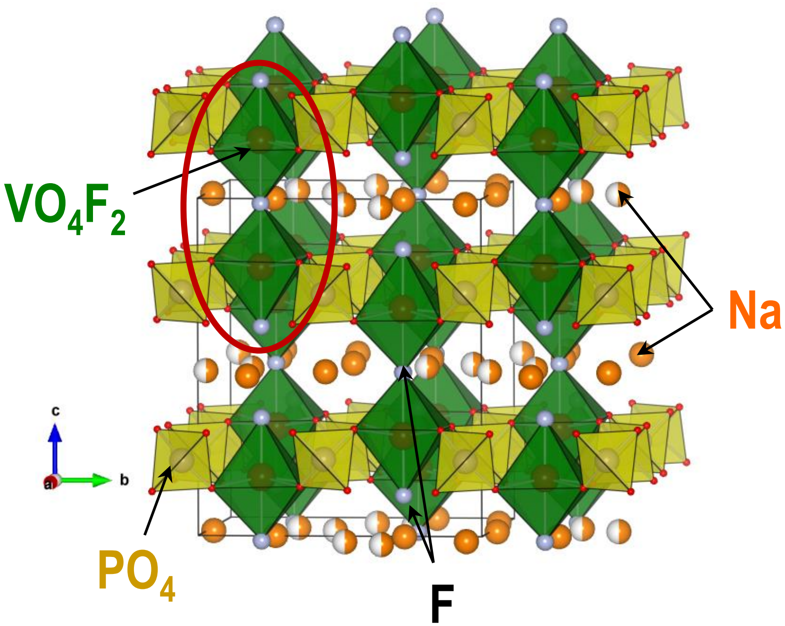


~ 400 Wh/kg

Among the 2 best contenders for Na-Ion Batteries

Menu of Today - 1

$Na_3V^{3+}{}_2(PO_4)_2F_3$



~ 500 Wh/kg

A very high rate material

Subbtle orthorhombic distortion

Fluorine / Oxygen content $V^{3+} \rightarrow (VO)^{2+}$

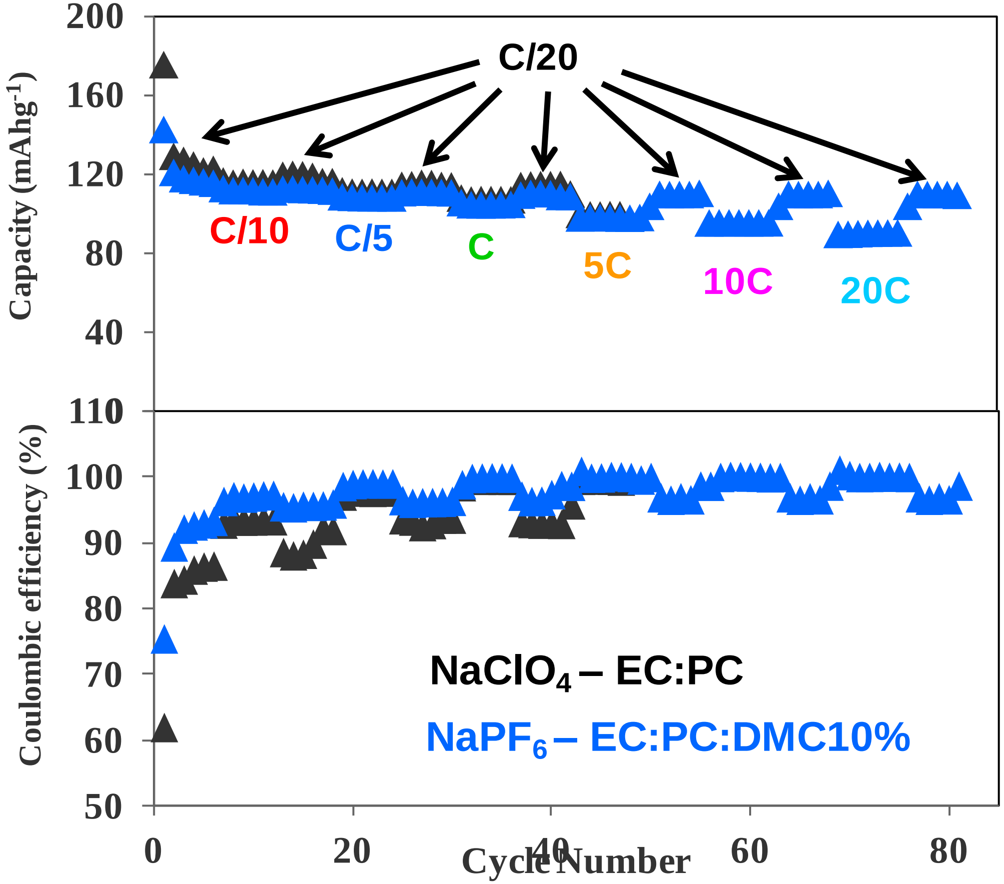
Ionic transport as a function of T

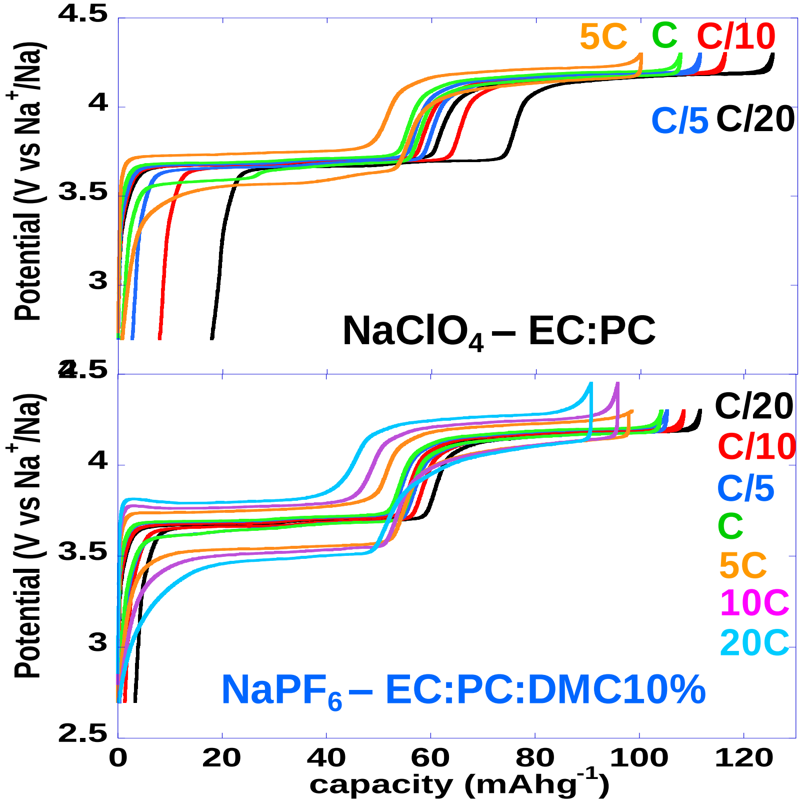
Operando XRD under high rate and at various temperatures

CEA-CNRS Patents Licenced by TIAMAT, a RS2E-funded Start-Up, now a Company, a Gigafactory starting in 2025 !!

$Na_3V_2(PO_4)_2F_3$ identified as a promising electrode

LRCS Amiens — ICMAB — icmcb Bordeaux





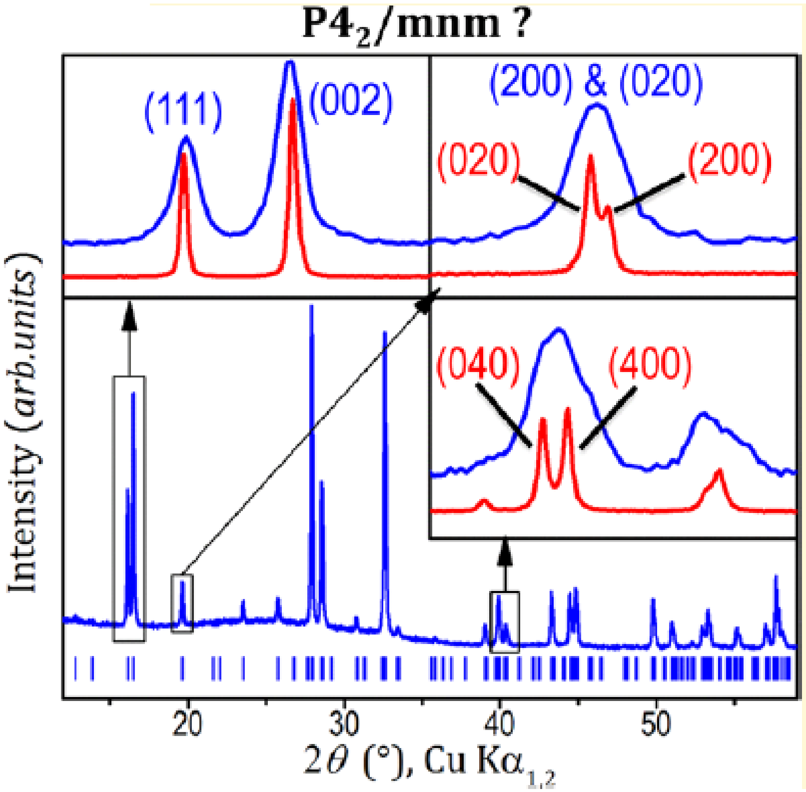
Interesting performance spotted, especially at high rate

A. Ponrouch, R. Dedryvère, J. M. Ateba Mba, L. Croguennec, C. Masquelier, P. Johansson, M. R. Palacín, *Energy Environ. Sci.*, 6, 2361-2369 (2013)
N. Hall, S. Boulineau, L. Croguennec, S. Launois, C. Masquelier & L. Simonin, Patent FR 1559709 13-10-1-2015 – CEA / CNRS / UPJV

$Na_3V_2(PO_4)_2F_3$: Crystal Structure re-determined

LRCS Amiens

icmcb Bordeaux



Amam

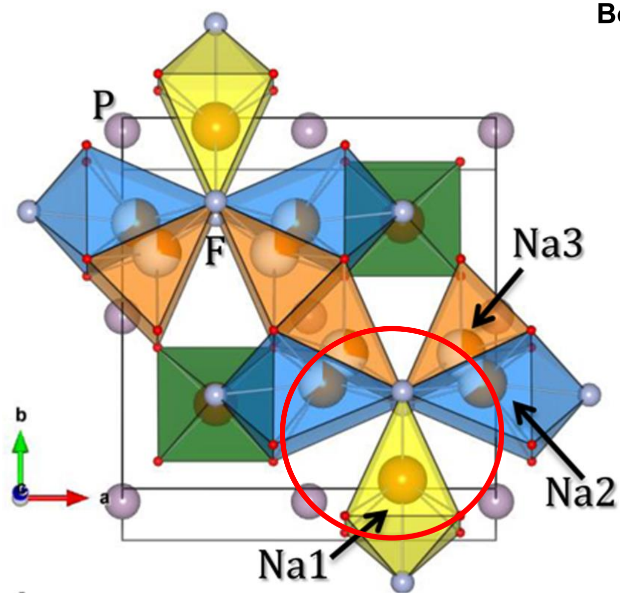
a = 9.0285 Å ; b = 9.0444 Å ; c = 10.7467 Å

a ≠ b (b/a ~ 1.002)

SMALL Orthorhombic distortion

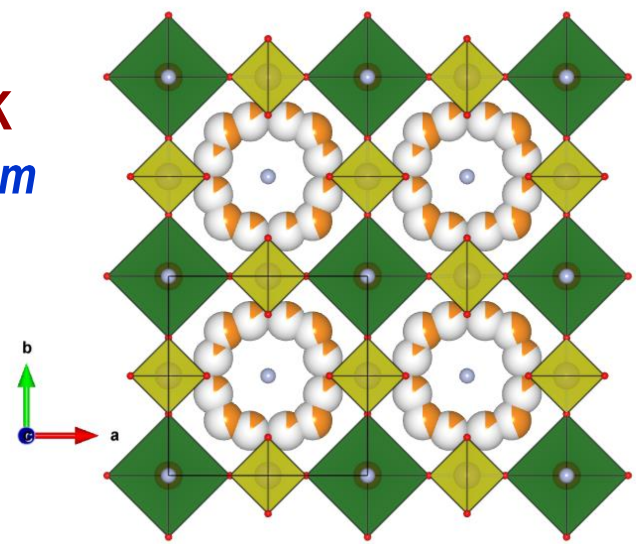
298 K

Amam



400 K

I4/mmm



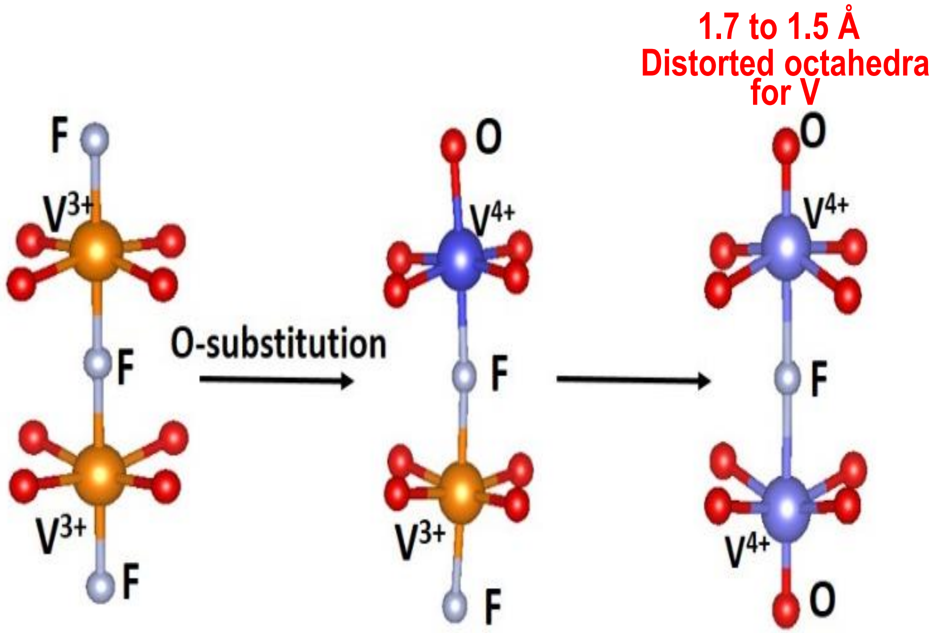
M. Bianchini, N. Brisset, F. Fauth, F. Weill, E. Elkaim, E. Suard, C. Masquelier & L. Croguennec, *Chem. Mater.*, 26(14), 4238-4247 (2014)

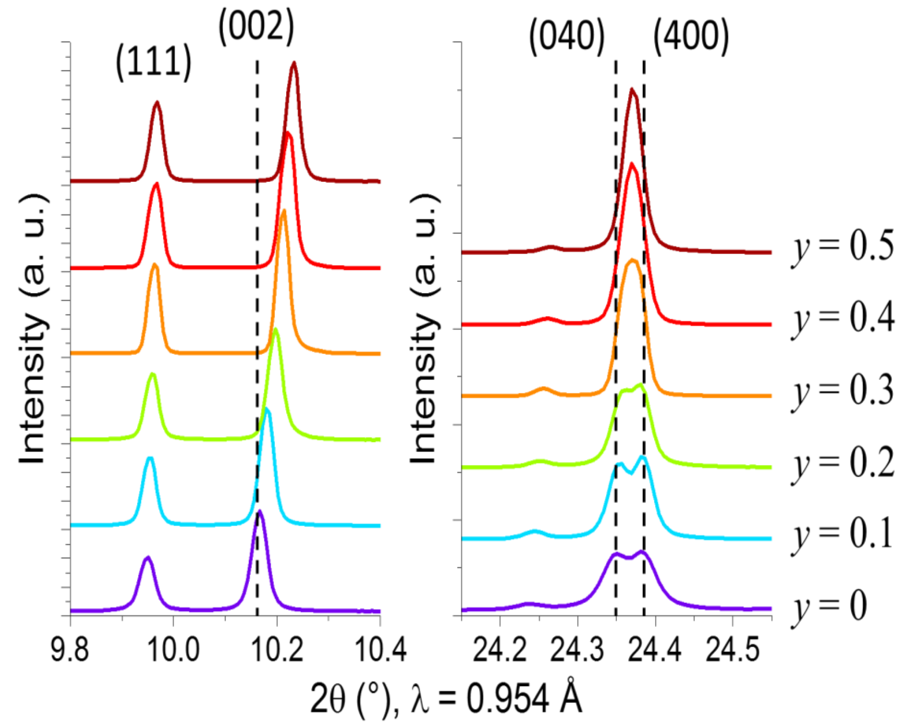
Amiens

$Na_3V_2(PO_4)_2F_3$ – $Na_3V_2(PO_4)_2FO_2$

Bordeaux

$$(3\text{-}y)\ NaF + (2\text{-}y)\ V^{3+}PO_4 + y\ V^{5+}PO_4O + y/2\ Na_2CO_3 \rightarrow Na_3V^{3+}_{2-y}(VO)^{2+}_{y}(PO_4)_2F_{3-y}$$





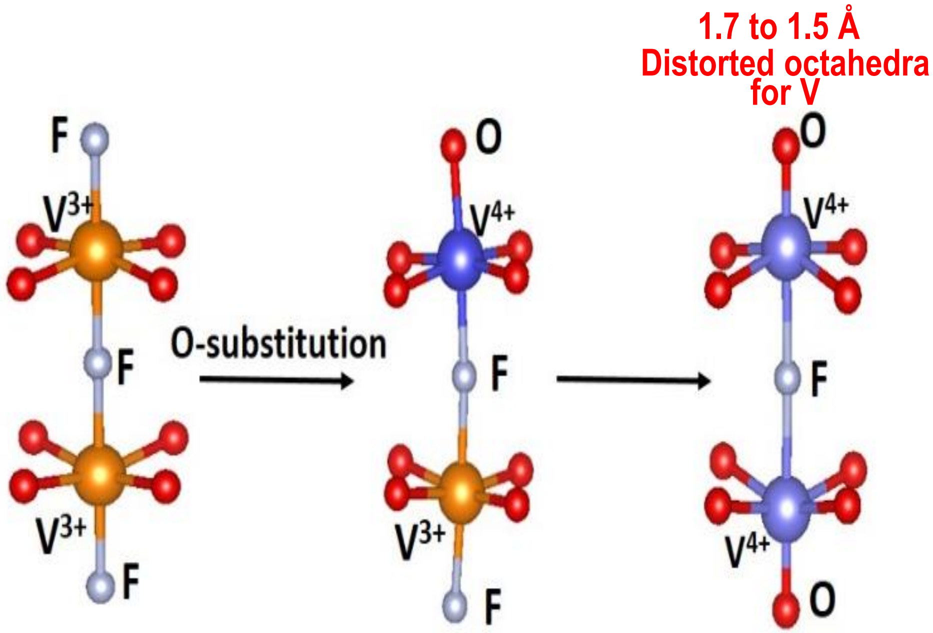
Broux, Bamine, Fauth, Simonelli, Olszewski, Marini, Ménétrier, Carlier, Masquelier & Croguennec, *Chem. Mater*. 28(21), 7683-7692 (2016)
L. H. B. Nguyen, P. Sanz Camacho, T. Broux, J. Olchowka, C. Masquelier, L. Croguennec & D. Carlier, *Chem. Mater*., 31, 9759-9768 (2019)
L. H. B. Nguyen, T. Broux , A. Iadecola, F. Fauth, D. Carlier, J. Olchowka, C. Masquelier & L. Croguennec, *Energy Storage Materials*, 20, 324-334 (2019)

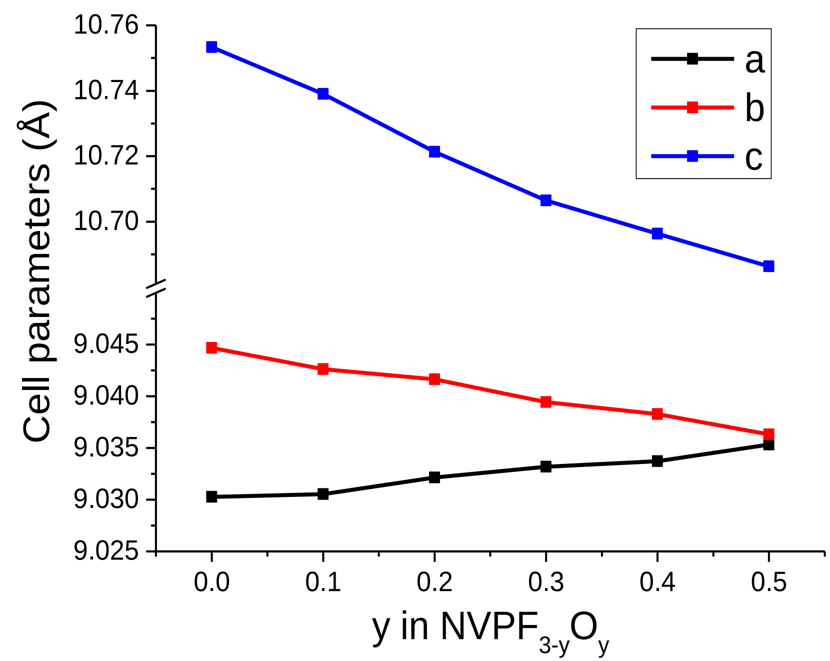
Amiens

Bordeaux

$Na_3V_2(PO_4)_2F_3$ – $Na_3V_2(PO_4)_2FO_2$

$$(3\text{-}y)\ Na\mathbf{F} + (2\text{-}y)\ V^{3+}PO_4 + y\ V^{5+}PO_4\mathbf{O} + y/2\ Na_2CO_3 \rightarrow Na_3V^{3+}_{2\text{-}y}(V\mathbf{O})^{2+}_{y}(PO_4)_2\mathbf{F}_{3\text{-}y}$$





b/a = 1.002 to 1.0002 !!!

Broux, Bamine, Fauth, Simonelli, Olszewski, Marini, Ménétrier, Carlier, Masquelier & Croguennec, *Chem. Mater*. 28(21), 7683-7692 (2016)

L. H. B. Nguyen, P. Sanz Camacho, T. Broux, J. Olchowka, C. Masquelier, L. Croguennec & D. Carlier, *Chem. Mater*., 31, 9759-9768 (2019)

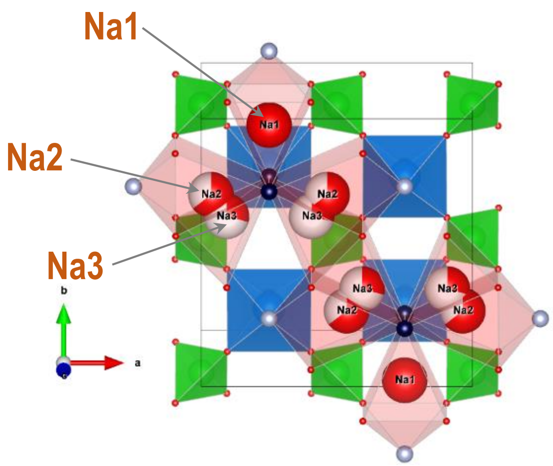
L. H. B. Nguyen, T. Broux , A. Iadecola, F. Fauth, D. Carlier, J. Olchowka, C. Masquelier & L. Croguennec, *Energy Storage Materials*, 20, 324-334 (2019)

LRCS Amiens

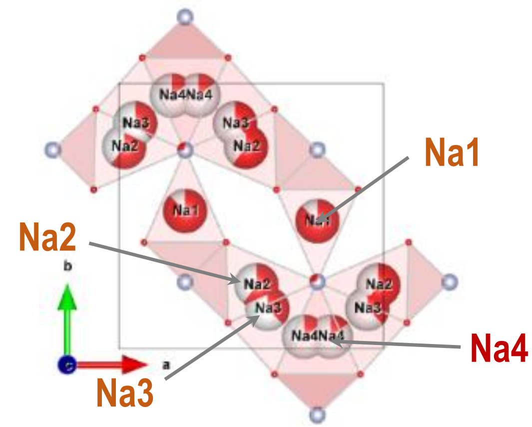
F substituted by O : $Na_3V^{3+}_{2-y}(VO)^{2+}_y(PO_4)_2F_{3-y}$

icmcb Bordeaux

$Na_3V_2(PO_4)_2F_3$



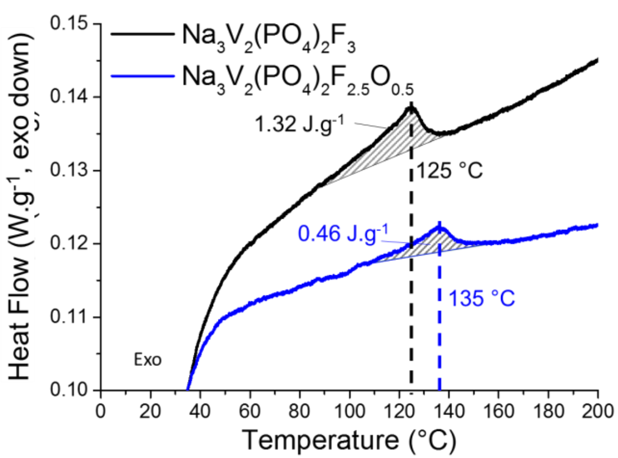
$Na_3V_2(PO_4)_2F_{2.5}O_{0.5}$

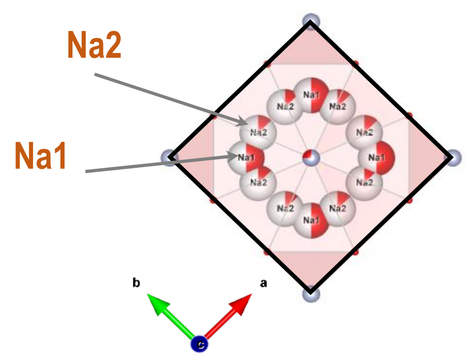


Amam

T ↗

I4/mmm





Orthorhombic to tetragonal phase transition: change in the sodium ions distribution

T. Broux, B. Fleutot, R. David, A. Brüll, P. Veber, F. Fauth, L. Croguennec & C. Masquelier, *Chem. Mater.*, 30(2), 358 (2018)

LRCS
Amiens

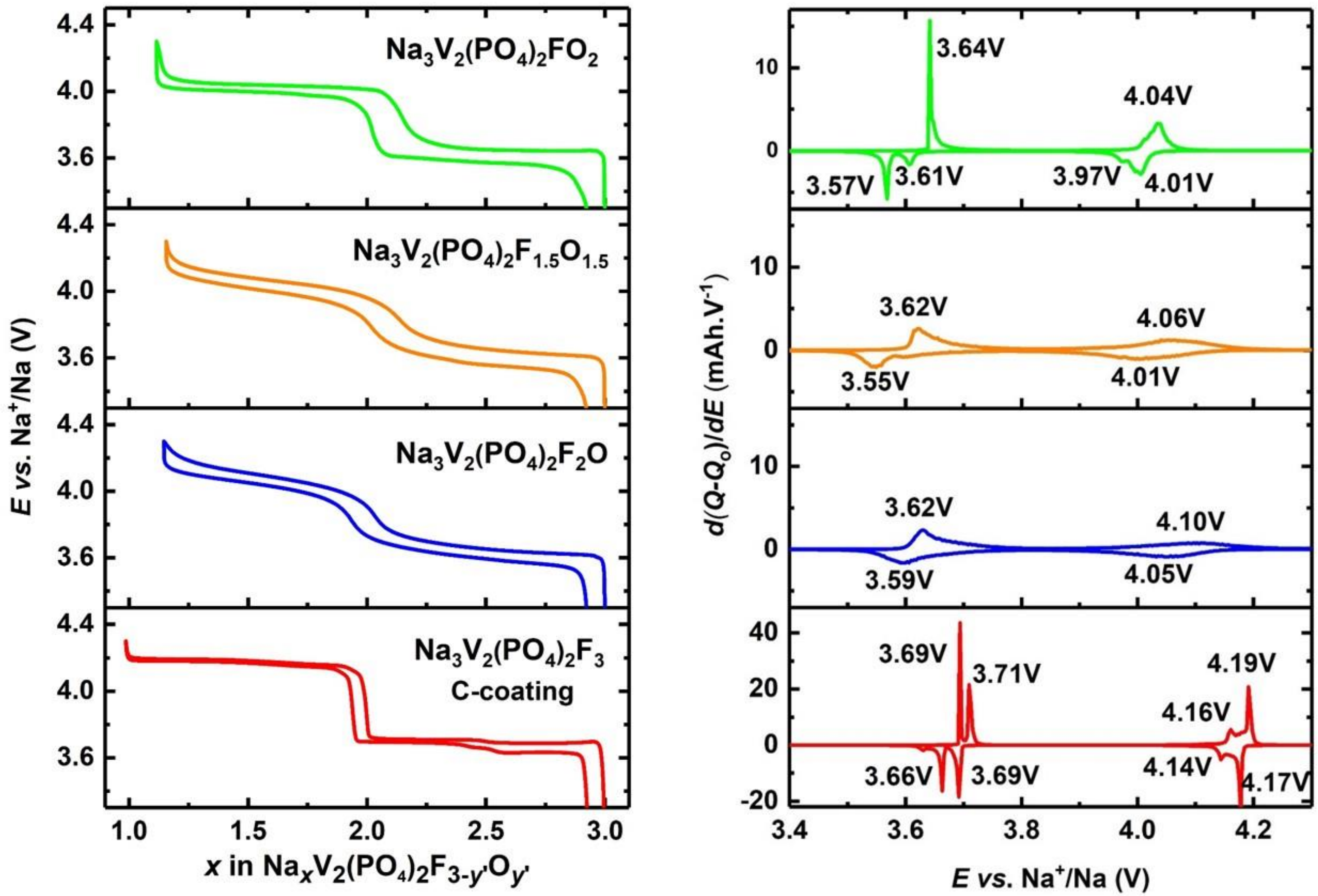
F substituted by O : $Na_3V^{3+}_{2-y}(VO)^{2+}_y(PO_4)_2F_{3-y}$

icmcb
Bordeaux

Increasing fluorine content

=

Increasing operating voltage



V^{5+}=O / V^{4+}=O

V^{4+}-O(F) / V^{3+}-O(F)

T. Broux, B. Fleutot, R. David, A. Brüll, P. Veber, F. Fauth, L. Croguennec & C. Masquelier, *Chem. Mater.*, 30(2), 358 (2018)

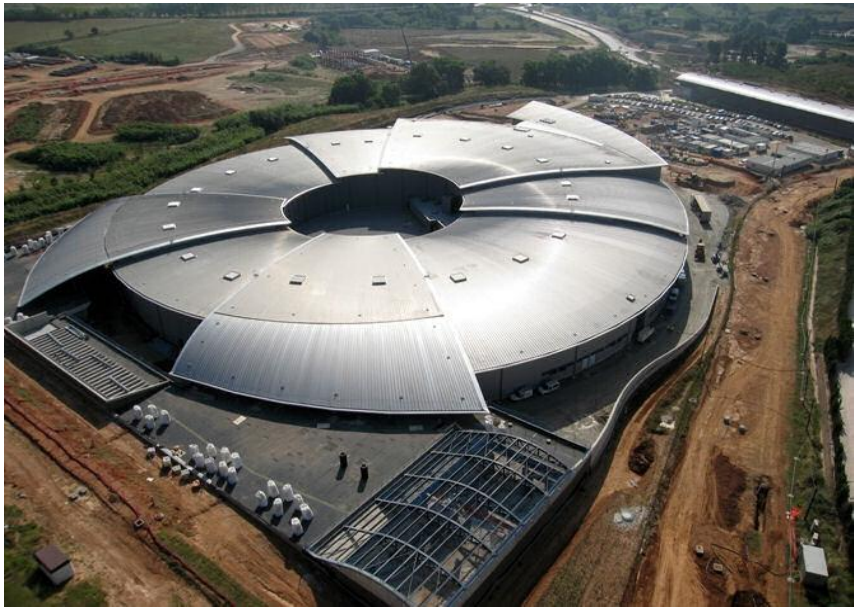
Mechanism of Na^+ extraction

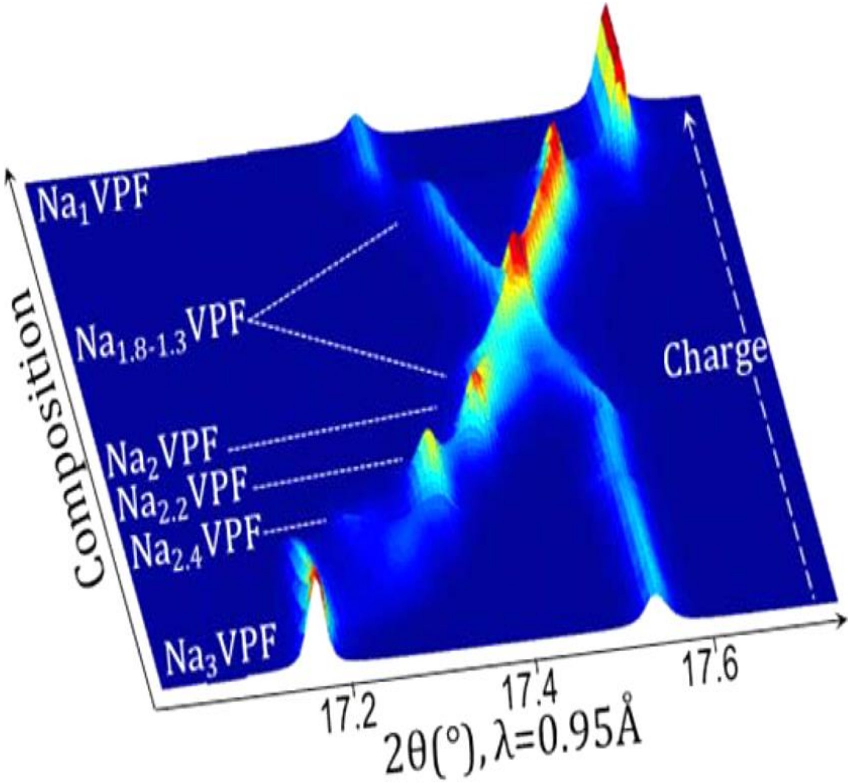
Amiens

Bordeaux

$$NaV^{4+}_2(PO_4)_2F_3 \Leftrightarrow Na_3V^{3+}_2(PO_4)_2F_3$$

ALBA Barcelona





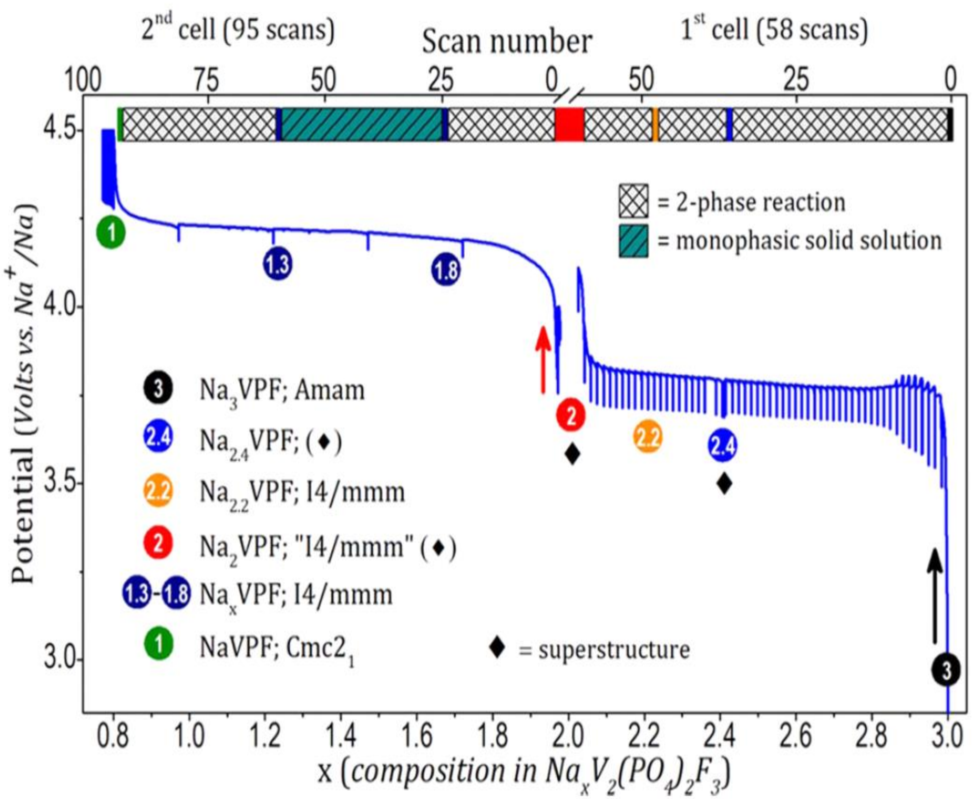
Bianchini et al., *Chem. Mater.*, 26(14), 4238 (2014)
Bianchini et al., *Chem. Mater.*, 27(8), 3009 (2015)
Broux et al., *Chem. Mater.*, 28 (21), 7683 (2016)
Nguyen et al. *Chem. Mater.*, 31, 9759 (2019)
Broux et al., *J. Phys. Chem C*, 121 (8), 4103 (2017)
Nguyen et al., *J. Phys. Chem. C, J. Phys. Chem. C., 124(43)* (2020)

Amiens

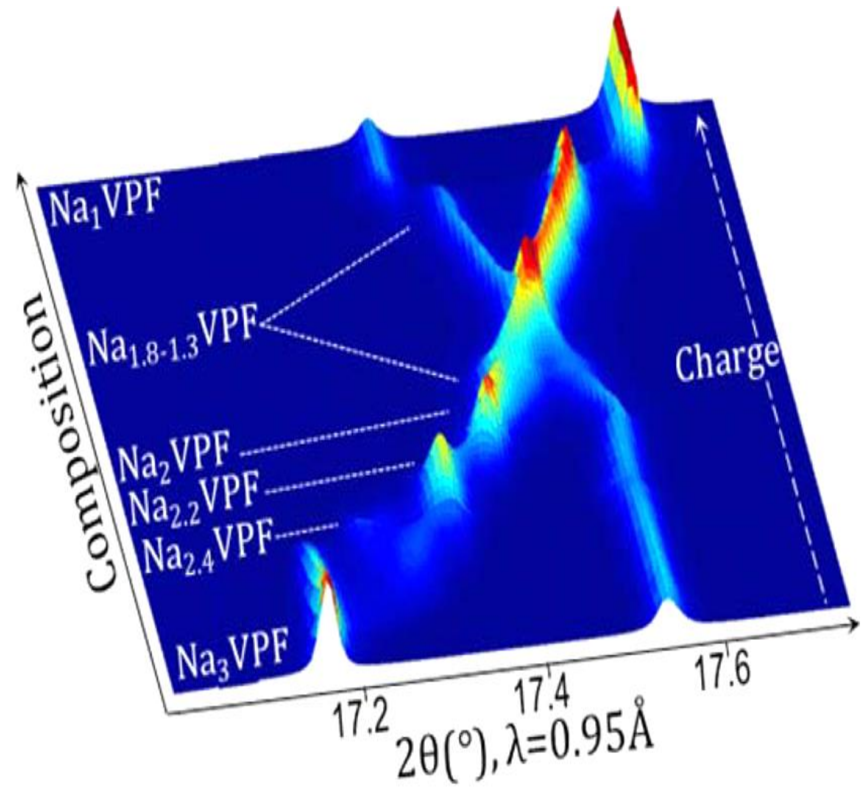
Mechanism of Na^{+} extraction

Bordeaux

$NaV_2(PO_4)_2F_3$



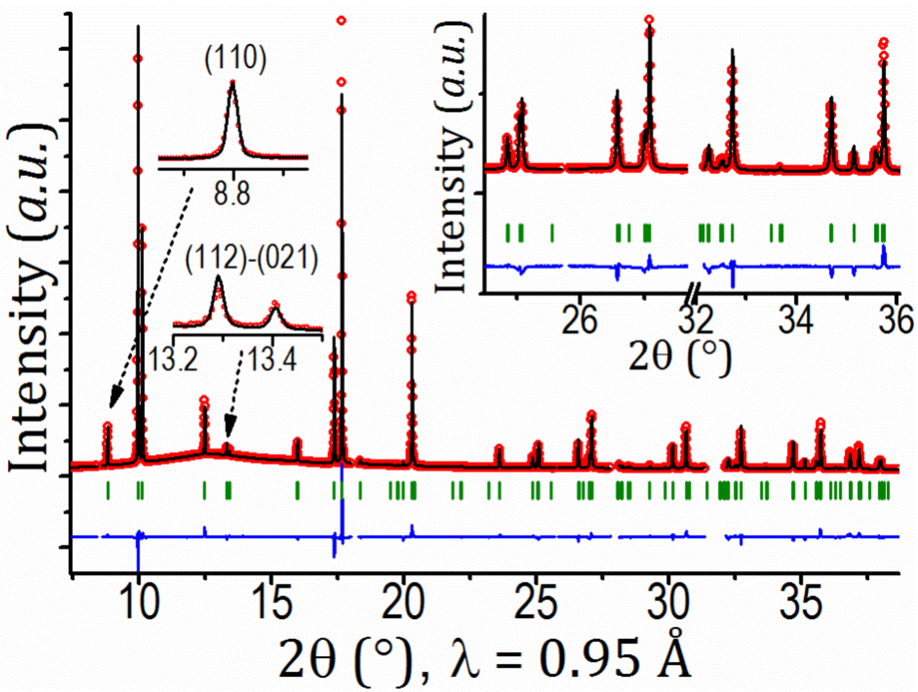
$Na_3V_2(PO_4)_2F_3$

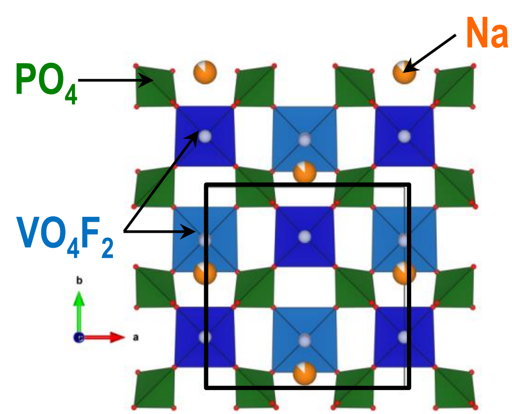


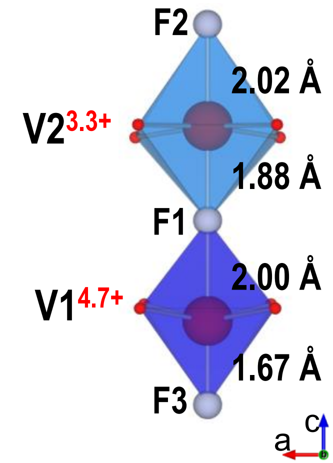
Bianchini et al., *Chem. Mater.*, 26(14), 4238 (2014)
Bianchini et al., *Chem. Mater.*, 27(8), 3009 (2015)
Broux et al., *Chem. Mater.*, 28 (21), 7683 (2016)
Nguyen et al. *Chem. Mater.*, 31, 9759 (2019)
Broux et al., *J. Phys. Chem C*, 121 (8), 4103 (2017)
Nguyen et al., *J. Phys. Chem. C, J. Phys. Chem. C., 124(43)* (2020)

Mechanism of Na^+ extraction

$NaV_2(PO_4)_2F_3$, $Cmc2_1$







Ion and charge ordering

Formation of V^{3+} - V^{5+} pairs

$Na_3V^{III}V^{III}(PO_4)_2F_3 \rightarrow Na_2V^{III}V^{IV}(PO_4)_2F_3$

$\cancel{\nearrow}$ $Na_1V^{IV}V^{IV}(PO_4)_2F_3$

$\searrow$ $Na_1V^{III}V^{V}(PO_4)_2F_3$

V^{4+} disproportionation

T. Broux, T. Bamine, L. Simonelli, L. Stievano, F. Fauth, M. Ménétrier, D. Carlier, C. Masquelier & L. Croguennec, *J. Phys. Chem C*, 121(8), pp. 4103-4111 (2017)

Performances in « tough » conditions

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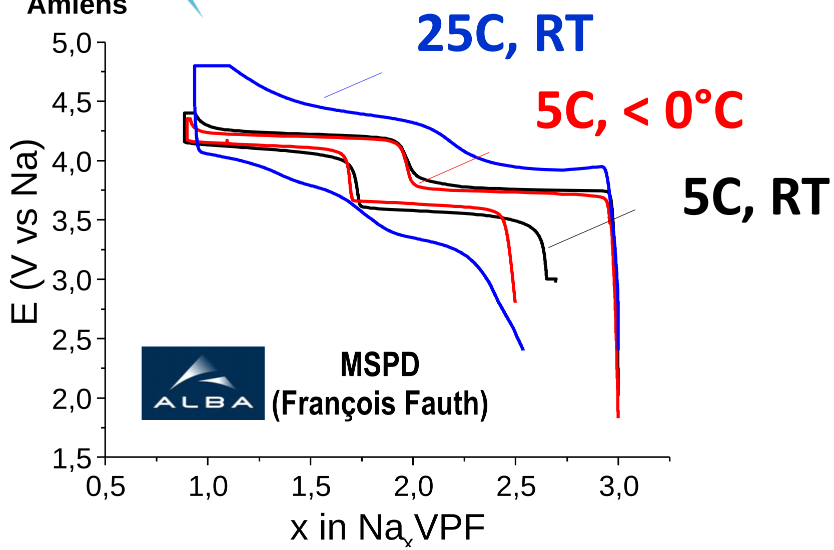
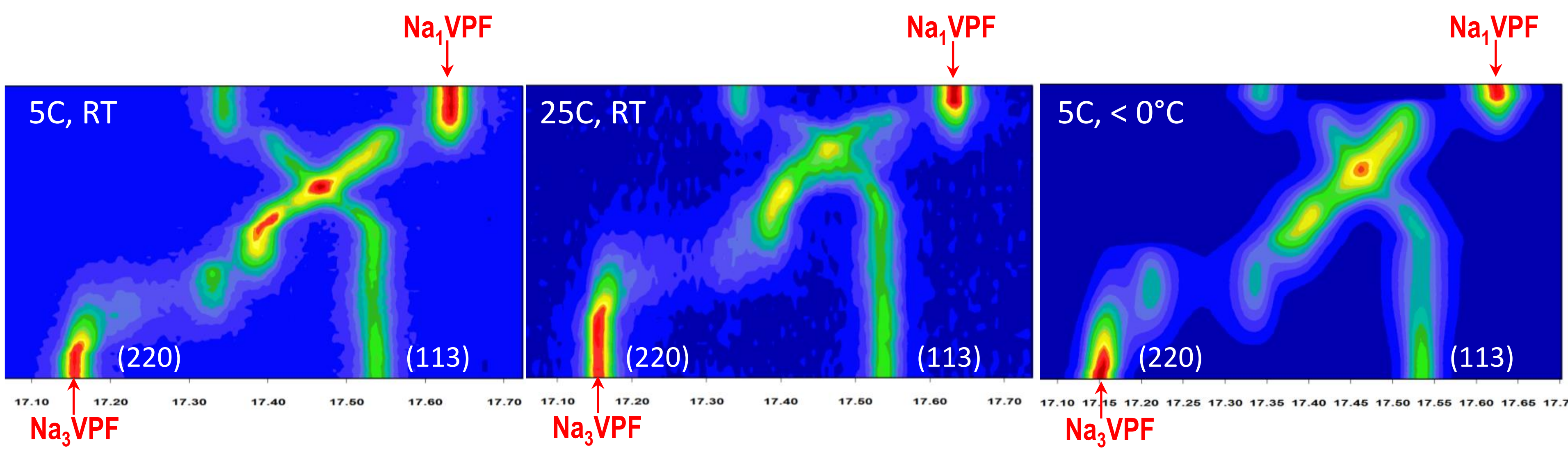


$NaPF_6$ in EC : DMC (1:1)

Active material/Carbon additive/Binder (35/55/10wt.%)

Similar phase diagram whatever the **rate** and/or the **temperature**

2D representation of the SXRD patterns obtained during the charge



T. Broux, F. Fauth, N. Hall, M. Bianchini, T. Bamine, J.-B. Leriche, E. Suard, D. Carlier, L. Simonin, C. Masquelier & L. Croguennec

Small Methods, 3, 1800215 (2019)

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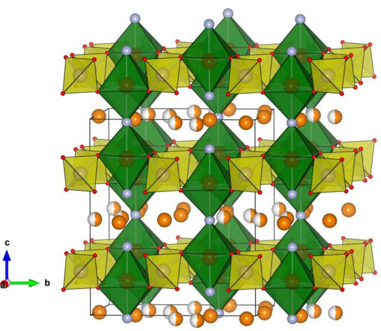
Performances in « tough » conditions

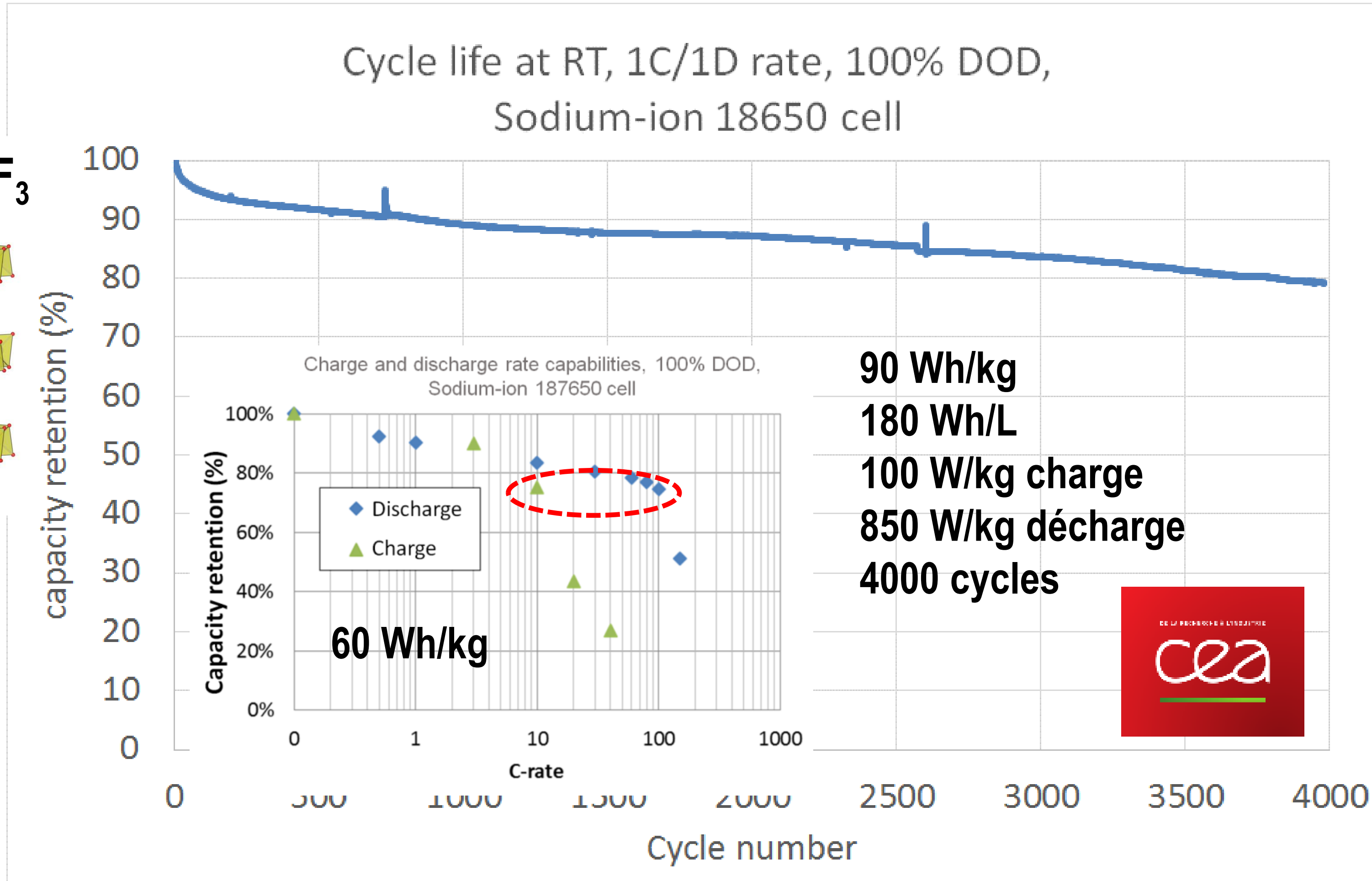
Bordeaux

DEFI DESCARTES

ANR-13-DESC-0003-01

$Na_3V^{3+}_2(PO_4)_2F_3$





N. Hall, S. Boulineau, L. Croguennec, S. Launois, C. Masquelier & L. Simonin

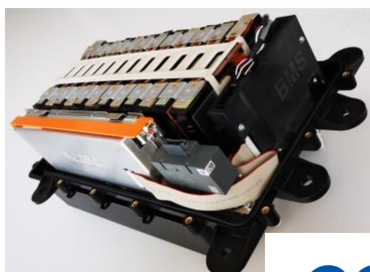
Patent FR 1559709 13-10-12015 - CEA/CNRS/UPJV

T. Broux, F. Fauth, N. Hall, M. Bianchini, T. Bamine, J.-B. Leriche, E. Suard, D. Carlier, L. Simonin, C. Masquelier & L. Croguennec
***Small Methods,* 3, 1800215 (2019)**

The growing activity around Na Batteries….

1st Na-ion 18650 cell in 2015

TIAMAT



ST@RTEC developpement

TIAMAT

PLASTIC OMNIUM

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, 2361-2369 (2013)

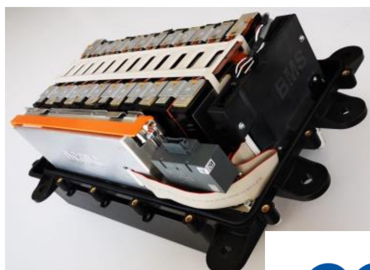
N. Hall, S. Boulineau, L. Croguennec, S. Launois, C. Masquelier & L. Simonin,
Patent FR 1559709 13-10-1-2015 – CEA / CNRS / UPJV

The growing activity around Na Batteries….

1st Na-ion 18650 cell in 2015

TIAMAT

LEROY MERLIN



ST@RTEC developpement

TIAMAT

PLASTIC OMNIUM

JUST RELEASED (October 2023)

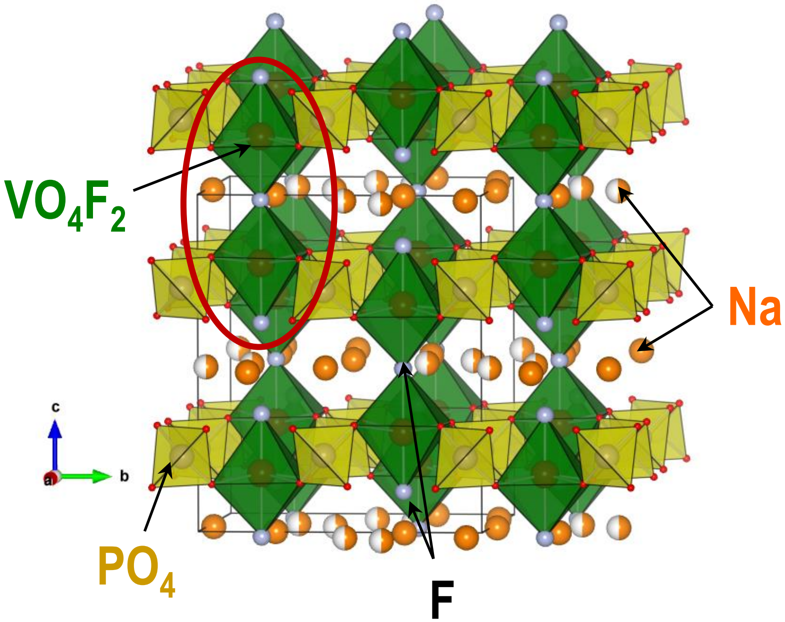
Amiens

Among the 2 best contenders for Na-Ion Batteries

Bordeaux

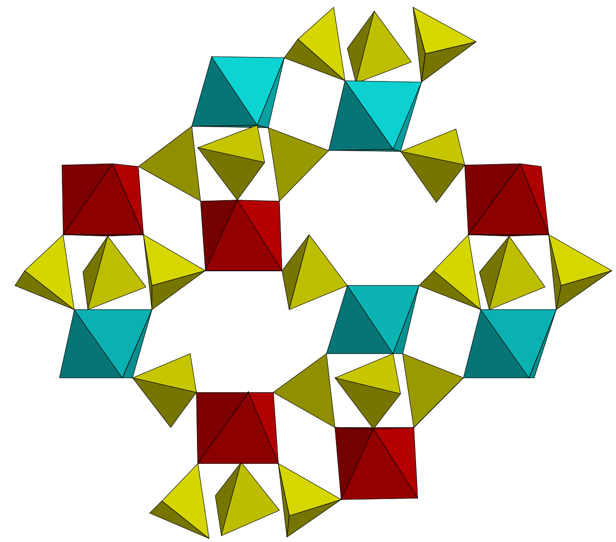
Menu of Today

$Na_3V^{3+}_2(PO_4)_2F_3$



~ 500 Wh/kg

$Na_3V^{3+}_2(PO_4)_3$
NASICON-type



~ 400 Wh/kg

LRCS
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Among the 2 best contenders for Na-Ion Batteries

icmcb
Bordeaux

Menu of Today

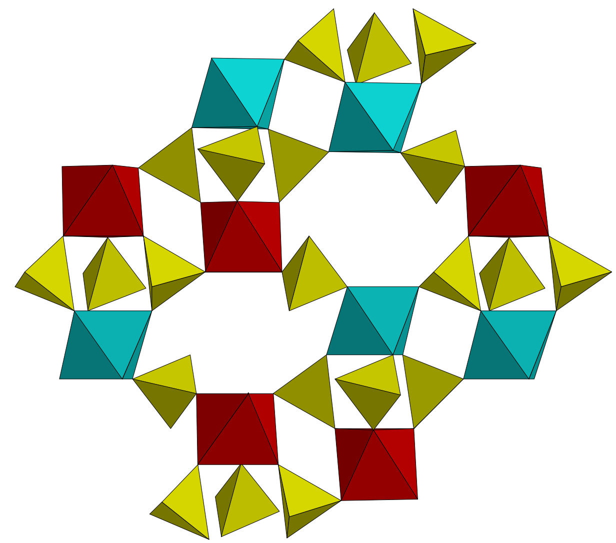
Very high **structural stability**

A great playground for chemical substitutions and **voltage monitoring** through the inductive effect

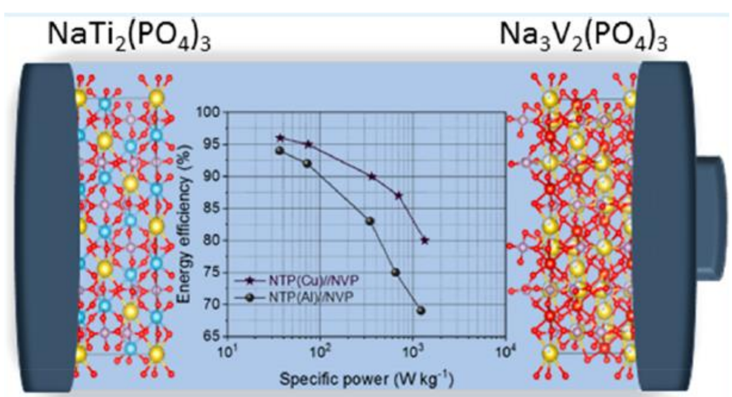
Na^+ **order-disorder phenomena** (as a function of T and depending on Na^+ content) lead to complex distortions and superstructures

Interesting, as well, for all **solid-state batteries** due to the high 3-D ionic conductivity

$Na_3V^{3+}_2(PO_4)_3$
NASICON-type



~ 400 Wh/kg



Zhang, Qin, Bucholz & Passerini, *ACS Applied Materials*, 1, 6425 (2018)

LRCS Amiens

NASICONs Framework on the Spotlight
Ionic conductors and/or Positive/Negative electrodes

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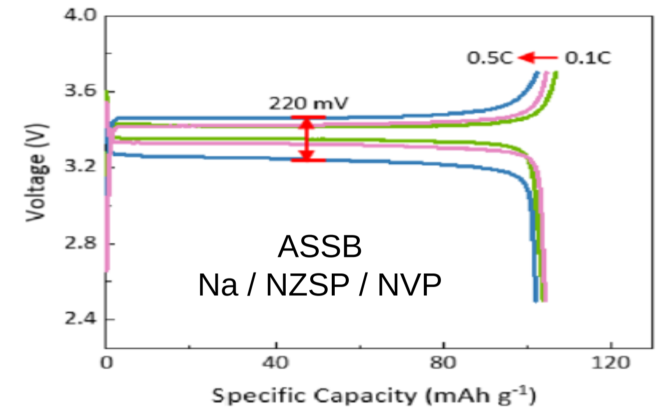
ACS APPLIED ENERGY MATERIALS 2020

www.acsaem.org Article

$Na_3Zr_2Si_2PO_{12}$: A Stable Na^+-Ion Solid Electrolyte for Solid-State Batteries

Zhizhen Zhang,*,# Sebastian Wenzel,# Yizhou Zhu,# Joachim Sann, Lin Shen, Jing Yang, Xiayin Yao, Yong-Sheng Hu,* Christopher Wolverton, Hong Li, Liquan Chen, and Jürgen Janek*

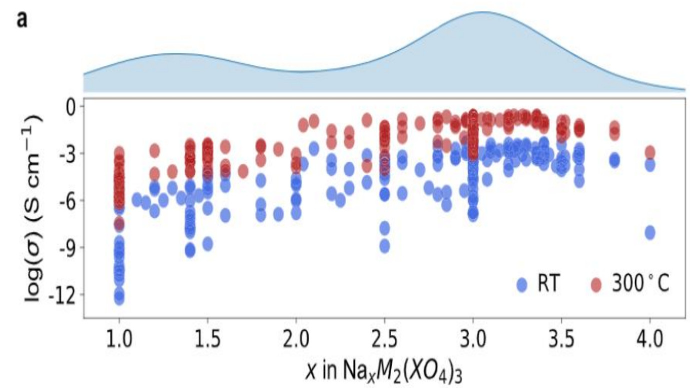


ARTICLE

https://doi.org/10.1038/s41467-021-26006-3 OPEN 2021

Synthetic accessibility and stability rules of NASICONs

Bin Ouyang[1,2,4], Jingyang Wang[1,2,4], Tanjin He[1,2], Christopher J. Bartel[1,2], Haoyan Huo[1,2], Valentina Lacivita[3], Haegyeom Kim[1] & Gerbrand Ceder[1,2]✉



cm CHEMISTRY OF MATERIALS 2020

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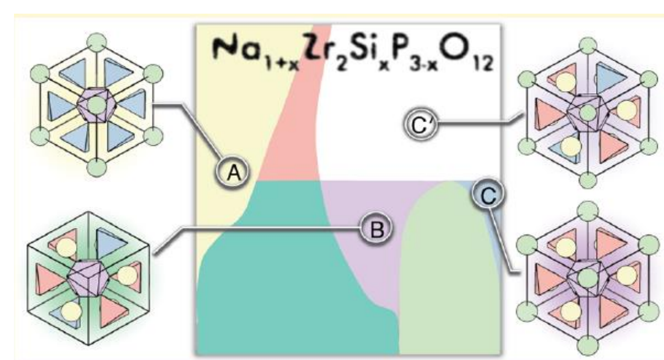
Phase Behavior in Rhombohedral NaSiCON Electrolytes and Electrodes

Zeyu Deng,* Gopalakrishnan Sai Gautam, Sanjeev Krishna Kolli, Jean-Noël Chotard, Anthony K. Cheetham, Christian Masquelier, and Pieremanuele Canepa*



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NASICONs Framework on the Spotlight
Ionic conductors and/or Positive/Negative electrodes

Bordeaux

ACS APPLIED ENERGY MATERIALS 2020

www.acsaem.org Article

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F. Lalère, J.B. Leriche, M. Courty, S. Boulineau, V. Viallet, C. Masquelier & V. Seznec
J. Power Sources, 247(1), 975-980 (2014)

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Rich Crystal Chemistry in the NASICON Framework

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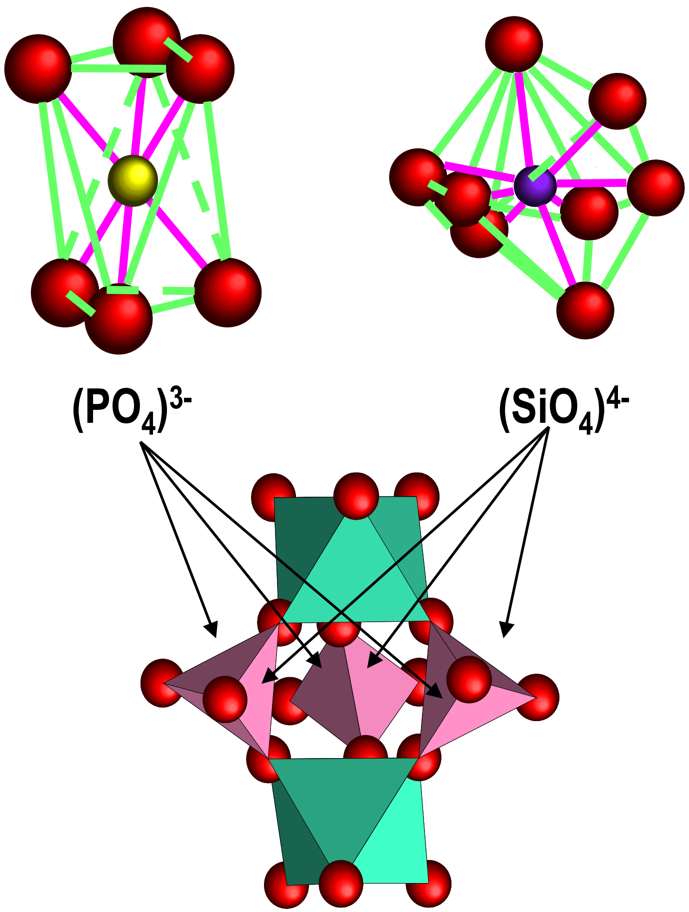
$Na_xMM'(XO_4)_3$

1 site Na(1)   3 sites Na(2)



$Nb^{5+}Ti^{4+}(PO_4)_3$	Quarton, 1991
$NaNb^{5+}Fe^{3+}(PO_4)_3$	Quarton, 1992
$NaTi^{4+}Ti^{4+}(PO_4)_3$	Delmas, 1984
$Na_2Ti^{4+}Fe^{3+}(PO_4)_3$	Patoux, 2003
$Na_3Fe^{3+}Fe^{3+}(PO_4)_3$	Delmas, 1978
$Na_3V^{3+}V^{3+}(PO_4)_3$	Gopalakrishnan, 1978
$Na_3V^{3+}Al^{3+}(PO_4)_3$	Chotard, 2021
$Na_3Ti^{4+}Mn^{2+}(PO_4)_3$	Goodenough, 2016
$Na_3Ti^{3+}V^{3+}(PO_4)_3$	Ehrenberg, 2016
$Na_3Cr^{3+}Cr^{3+}(PO_4)_3$	Delmas, 1978 Yamada, 2018
$Na_4V^{3+}Mn^{2+}(PO_4)_3$	Goodenough, 2016

Rich Crystal Chemistry in the NASICON Framework

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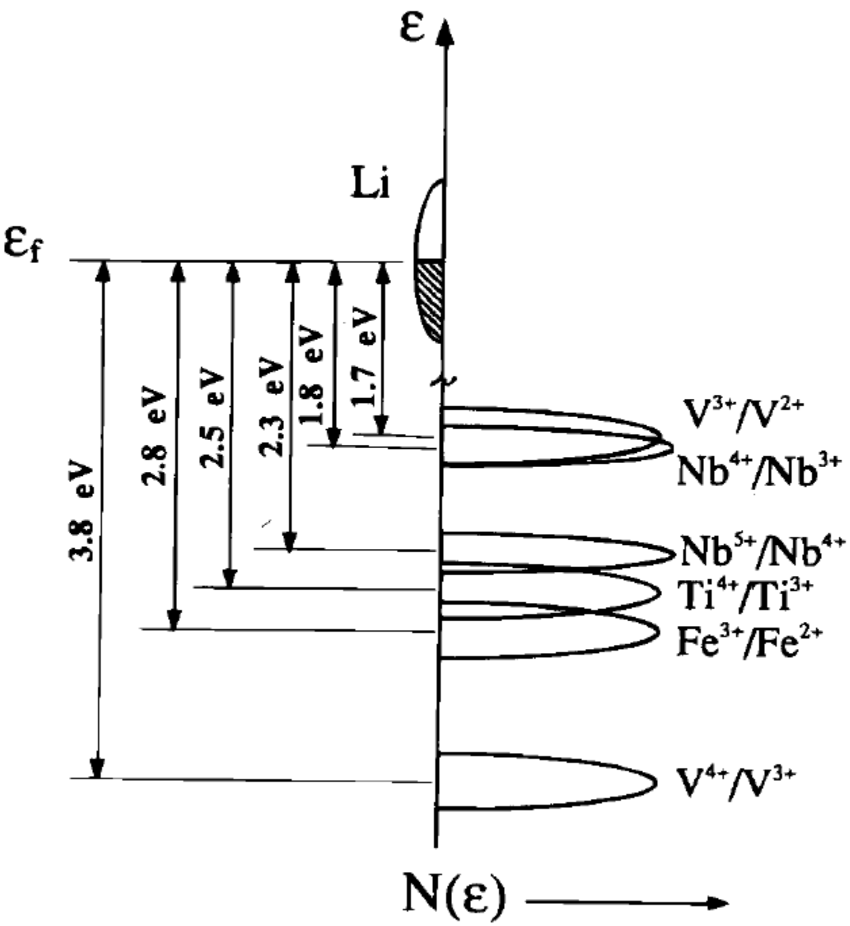
$Na_xMM'(XO_4)_3$



A. K. Padhi, K.Nanjundaswamy, C. Masquelier & J.B. Goodenough, *J. Electrochem. Soc.*, 144(8), 2581 (1997)

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$Na_3Cr^{3+}Cr^{3+}(PO_4)_3$	Delmas, 1978 Yamada, 2018
$Na_4V^{3+}Mn^{2+}(PO_4)_3$	Goodenough, 2016

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$Na_xMM'(PO_4)_3$ vs. Na

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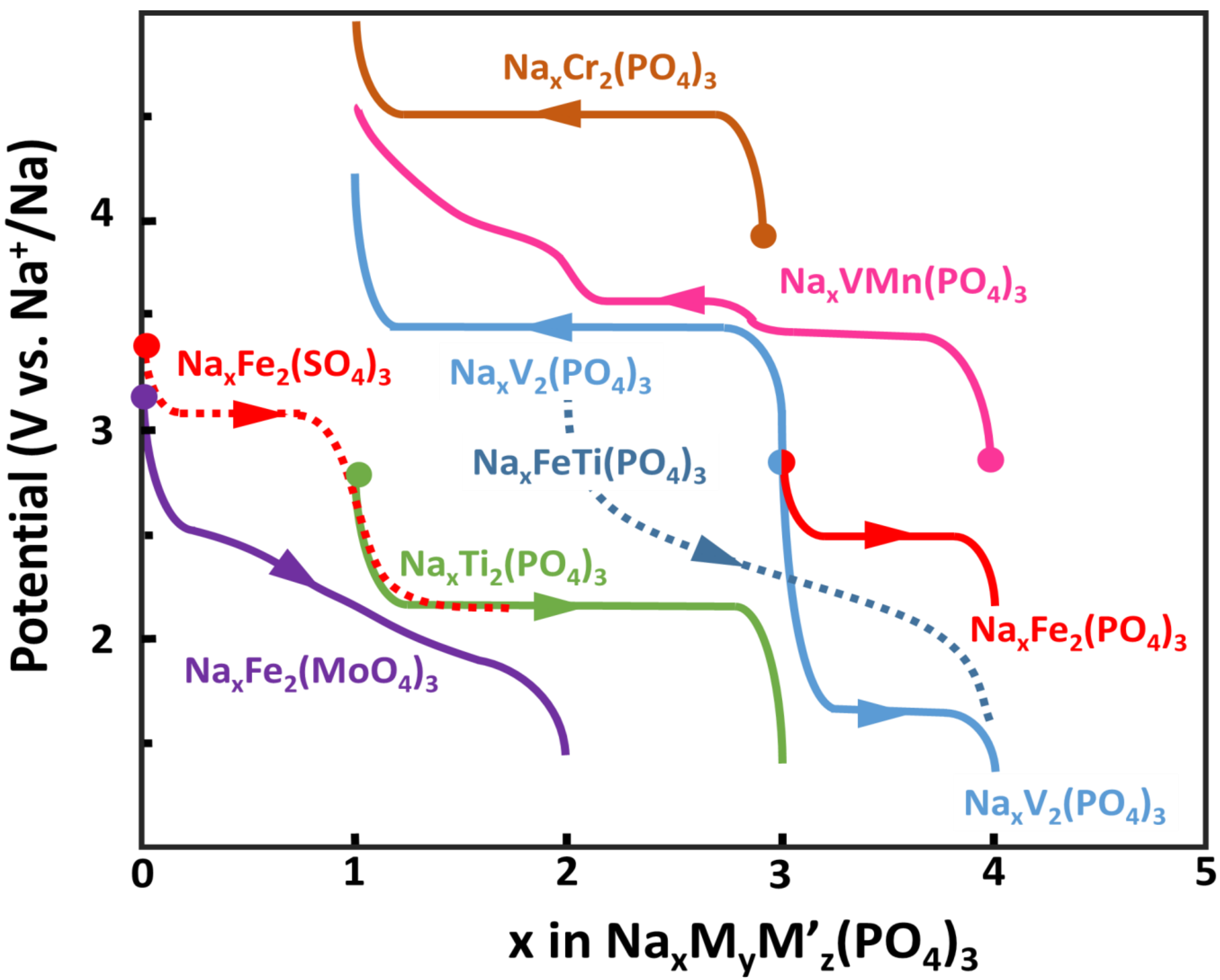

Delmas et al. *C.R. Acad. Sciences*, 287, 169−171 (1978)

Chotard, Carlier, Croguennec, Masquelier, Guignard, Delmas, *l'Actualité Chimique* (2021)

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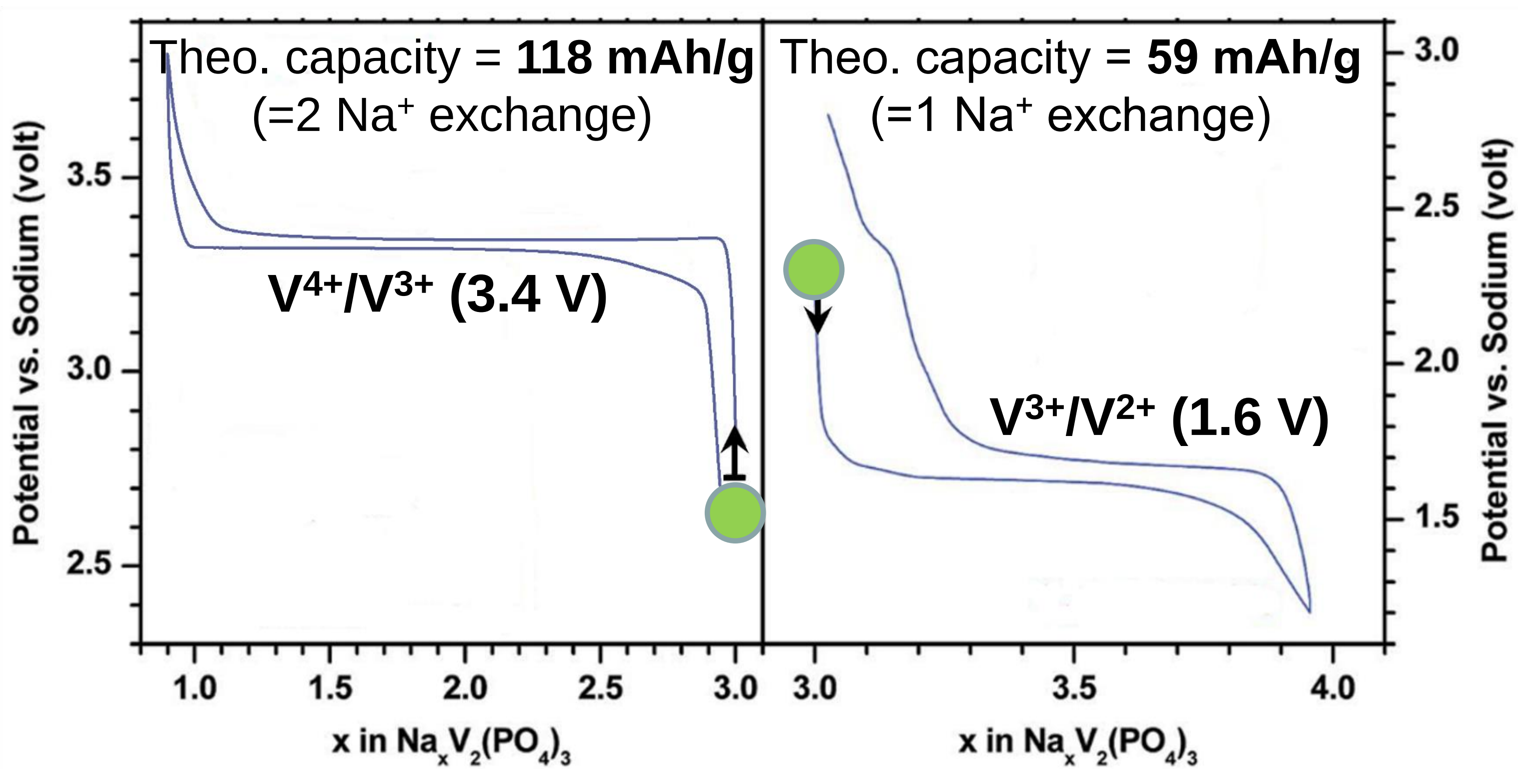
Institut de chimie de la matière condensée de bordeaux
Bordeaux

$Na_1V^{III}V^{III}(PO_4)_3$ – $Na_4V^{IV}V^{IV}(PO_4)_3$

New Na_2 Intermediate Composition spotted and structure determined

$Na_1V^{4+}{}_2(PO_4)_3$ ⬄ $Na_3V^{3+}{}_2(PO_4)_3$ ⬄ $Na_4V^{3+}V^{2+}(PO_4)_3$



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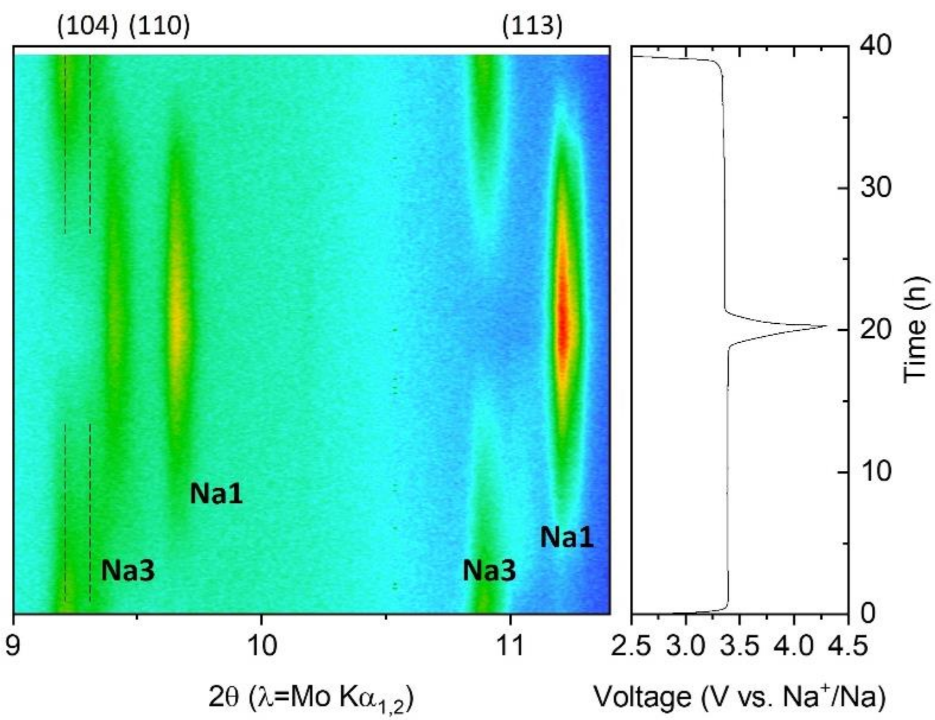
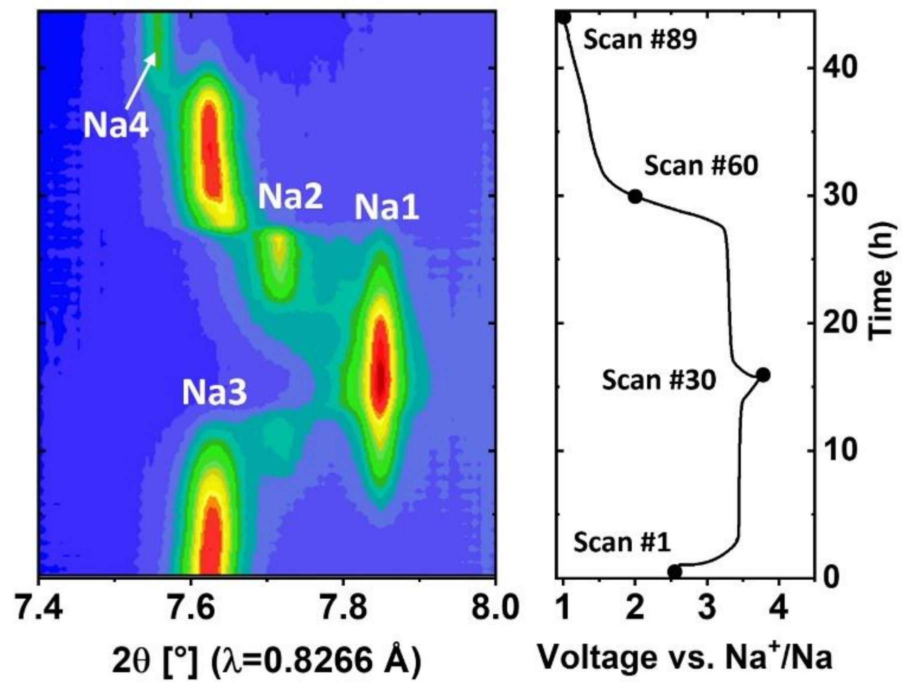
$Na_3V_2(PO_4)_3$: still some surprise to reveal.....

$Na_1V^{4+}_2(PO_4)_3$ ⇔ $Na_3V^{3+}_2(PO_4)_3$

Equilibrium condition



Nonequilibrium condition



S. Park, Z. Wang, Z. Deng, I. Moog, P. Canepa, F. Fauth, D. Carlier, L. Croguennec, C. Masquelier, J. N. Chotard, *Chem. Mater. 34*, 4515355-5367 (2021)

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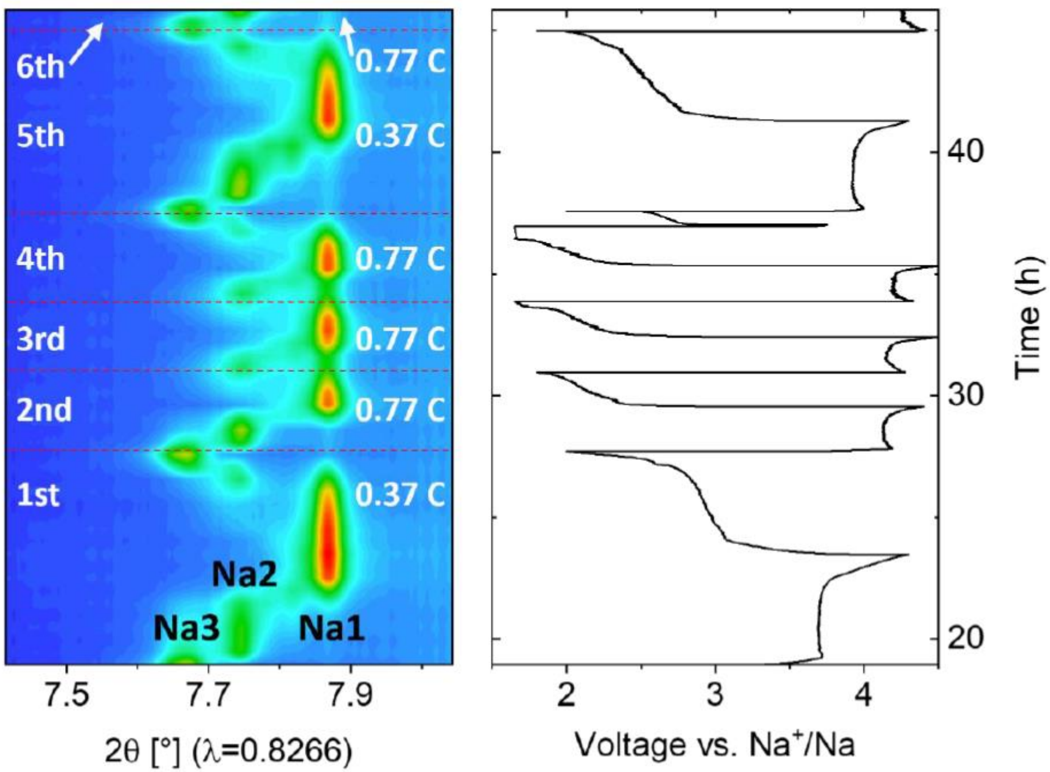
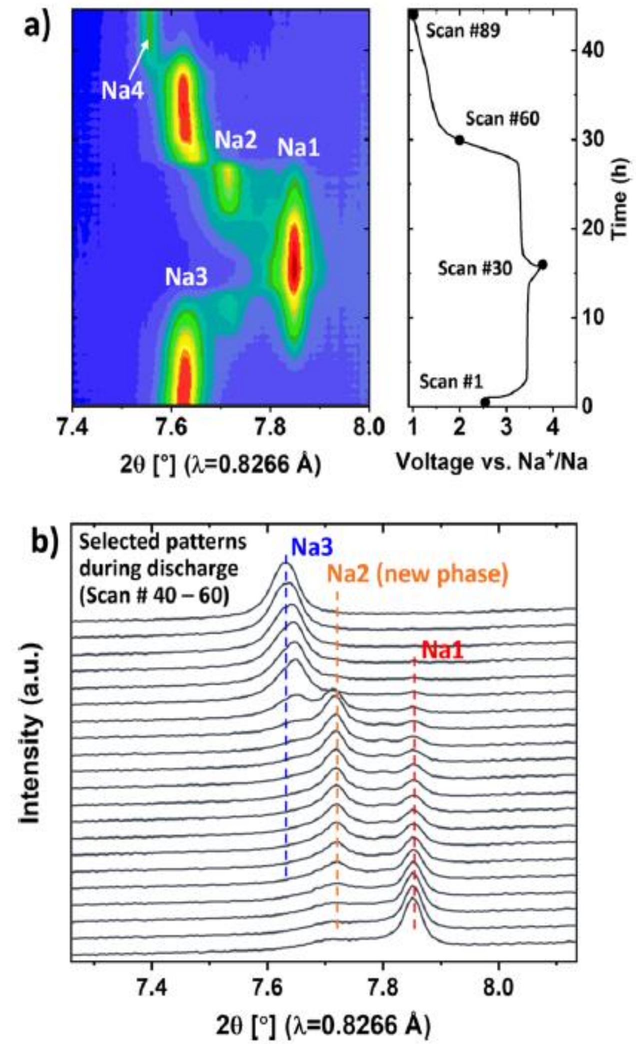
$Na_3V_2(PO_4)_3$: still some surprise to reveal…..

$Na_1V^{4+}_2(PO_4)_3 \Leftrightarrow Na_3V^{3+}_2(PO_4)_3$





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$Na_3V_2(PO_4)_3$: still some surprise to reveal…..

The Crystal Structure of $Na_2V_2(PO_4)_3$

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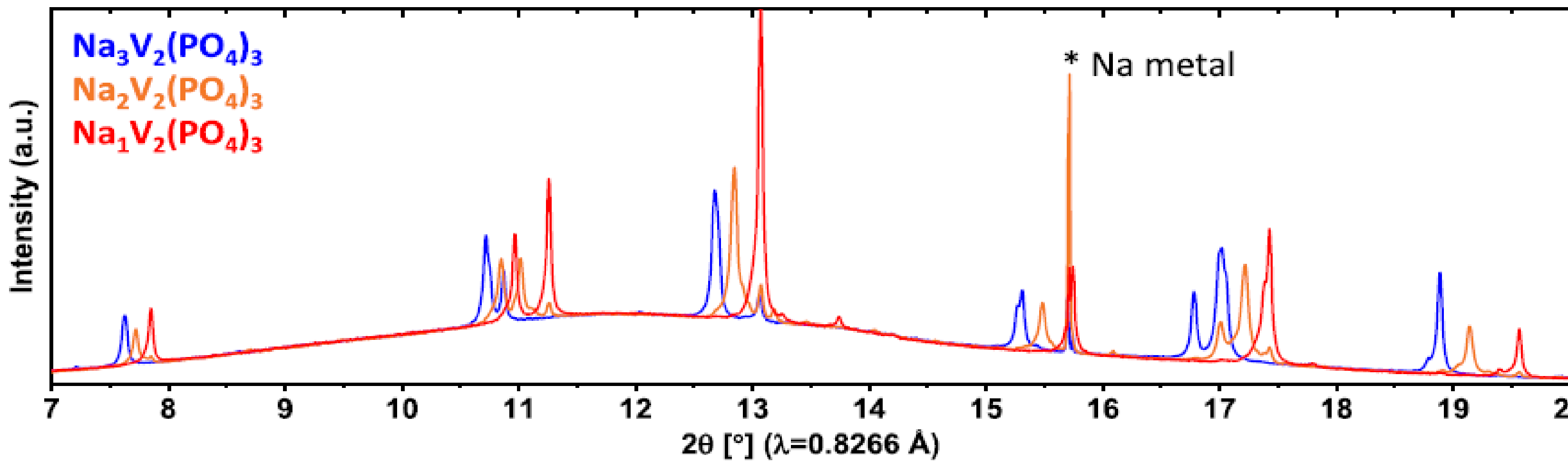

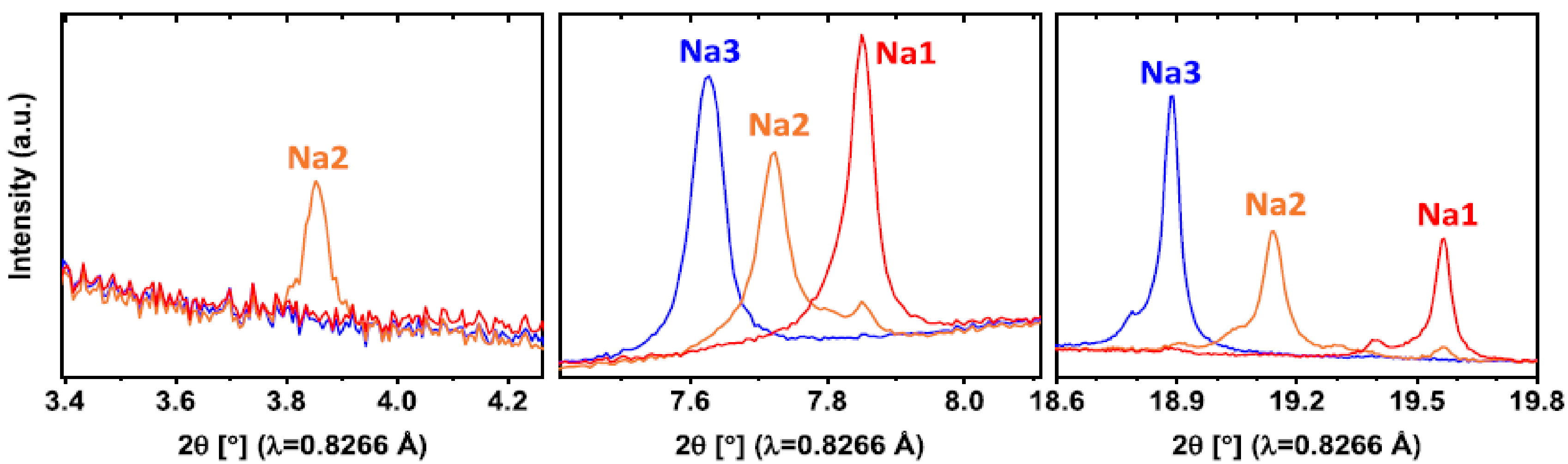

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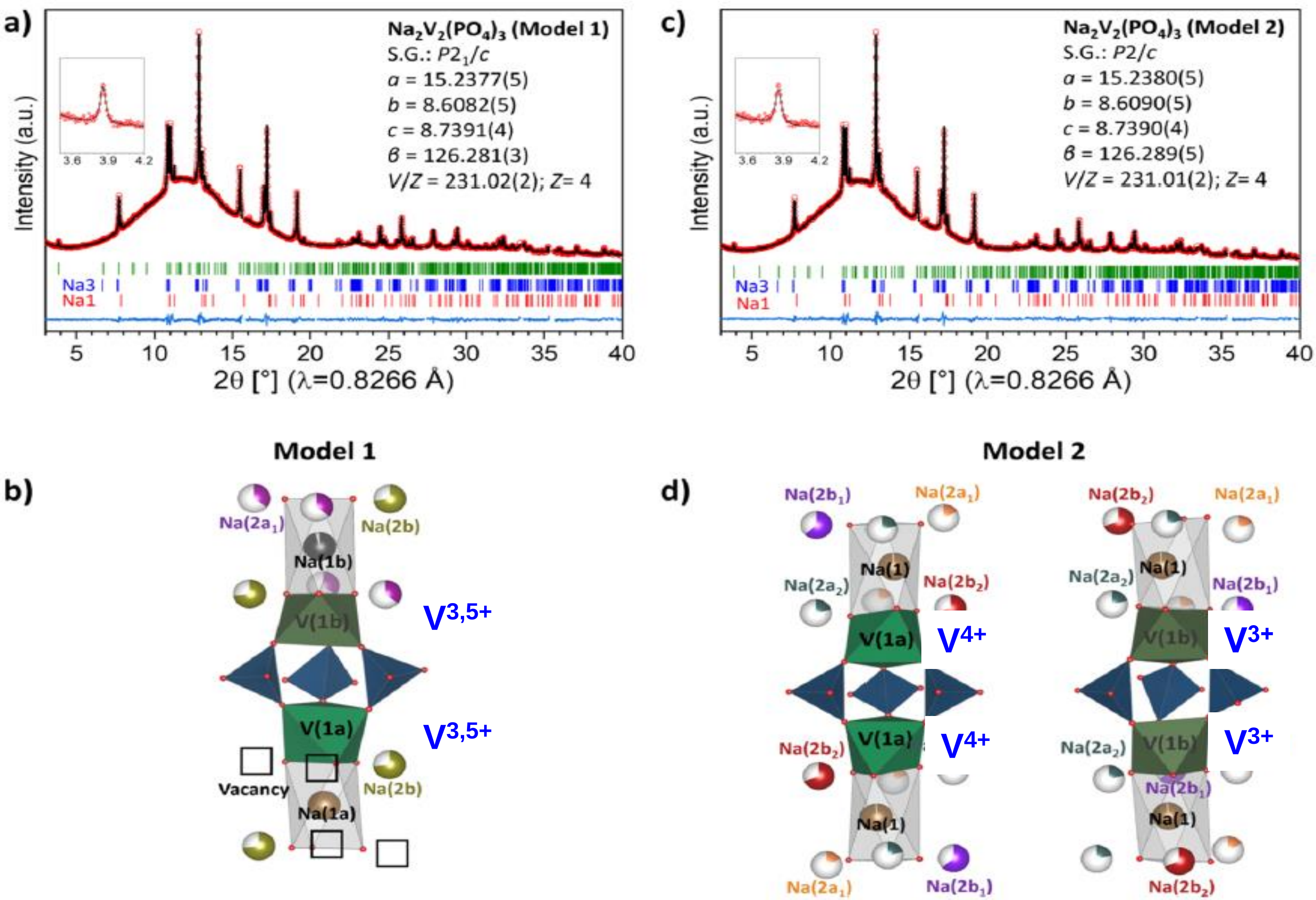

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Is it possible to prepare $Na_2V_2(PO_4)_3$?

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ALBA
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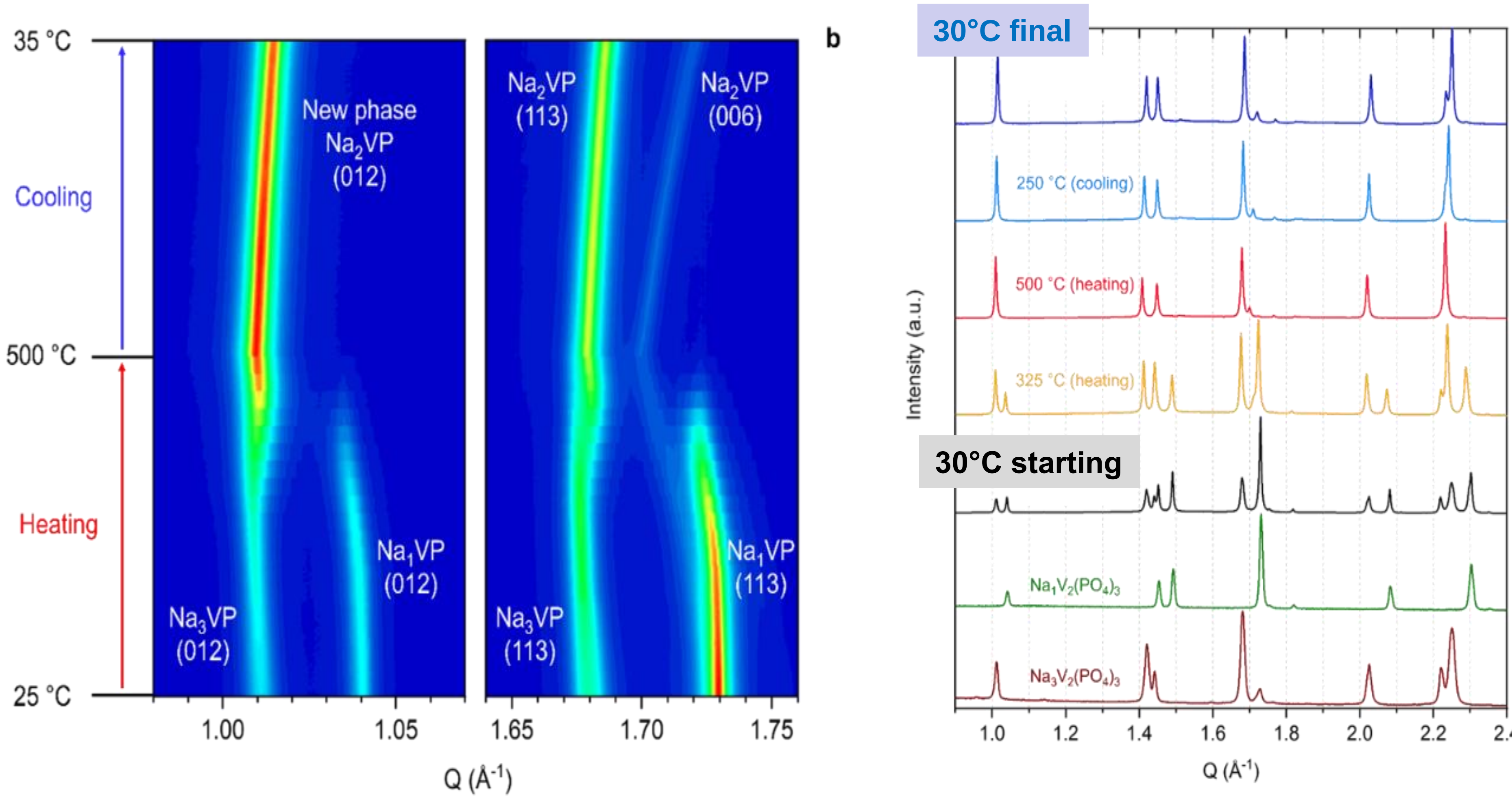
Bordeaux
NUS National University of Singapore

From a 1:1 $Na_3V^{III}_2(PO_4)_3$: $Na_1V^{IV}_2(PO_4)_3$ mixture



Park, Wang, Canepa, Chotard, Carlier, Croguennec, Masquelier, C. *European Patent, filed*, EP22305644, (2022)
Park, Wang, Choudari, Canepa, Chotard, Carlier, Fauth, Croguennec, Masquelier, *Nature Materials*, In Press (2024)

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Is it possible to prepare $Na_2V_2(PO_4)_3$?

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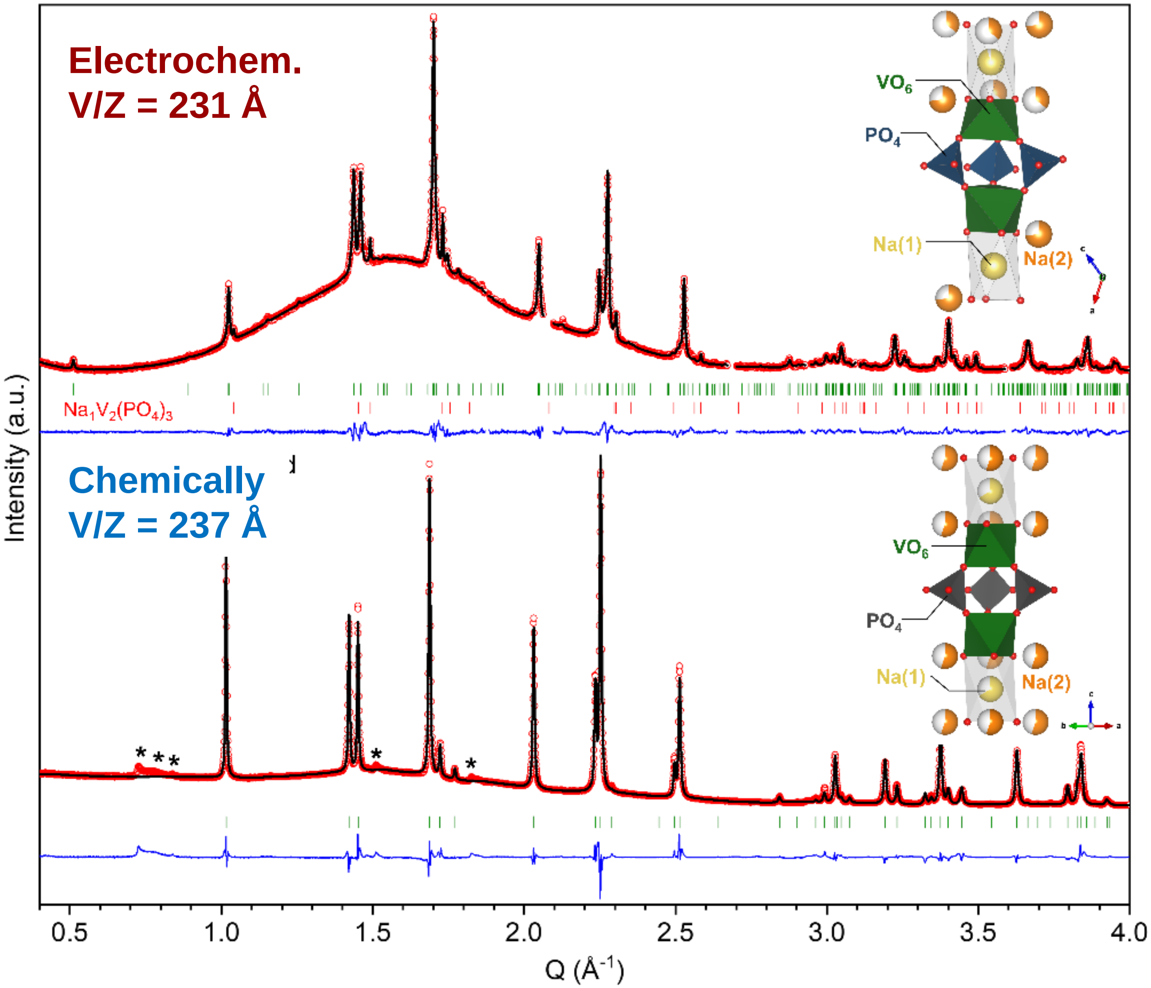

	Na(1) Occ.	Na(2) Occ.
	0.98(4)	0.363(6)
Electrochem.	0.98(5)	0.33(2)
Chemically	0.66(4)	0.55(3)

Park, Wang, Canepa, Chotard, Carlier, Croguennec, Masquelier, C. *European Patent, filed*, EP22305644, (2022)

Park, Wang, Choudari, Canepa, Chotard, Carlier, Fauth, Croguennec, Masquelier, *Nature Materials*, In Press (2024)

Is it possible to prepare $Na_2V_2(PO_4)_3$?

From y $Na_3V_2(PO_4)_3$: (1-y) $Na_1V_2(PO_4)_3$ mixtures

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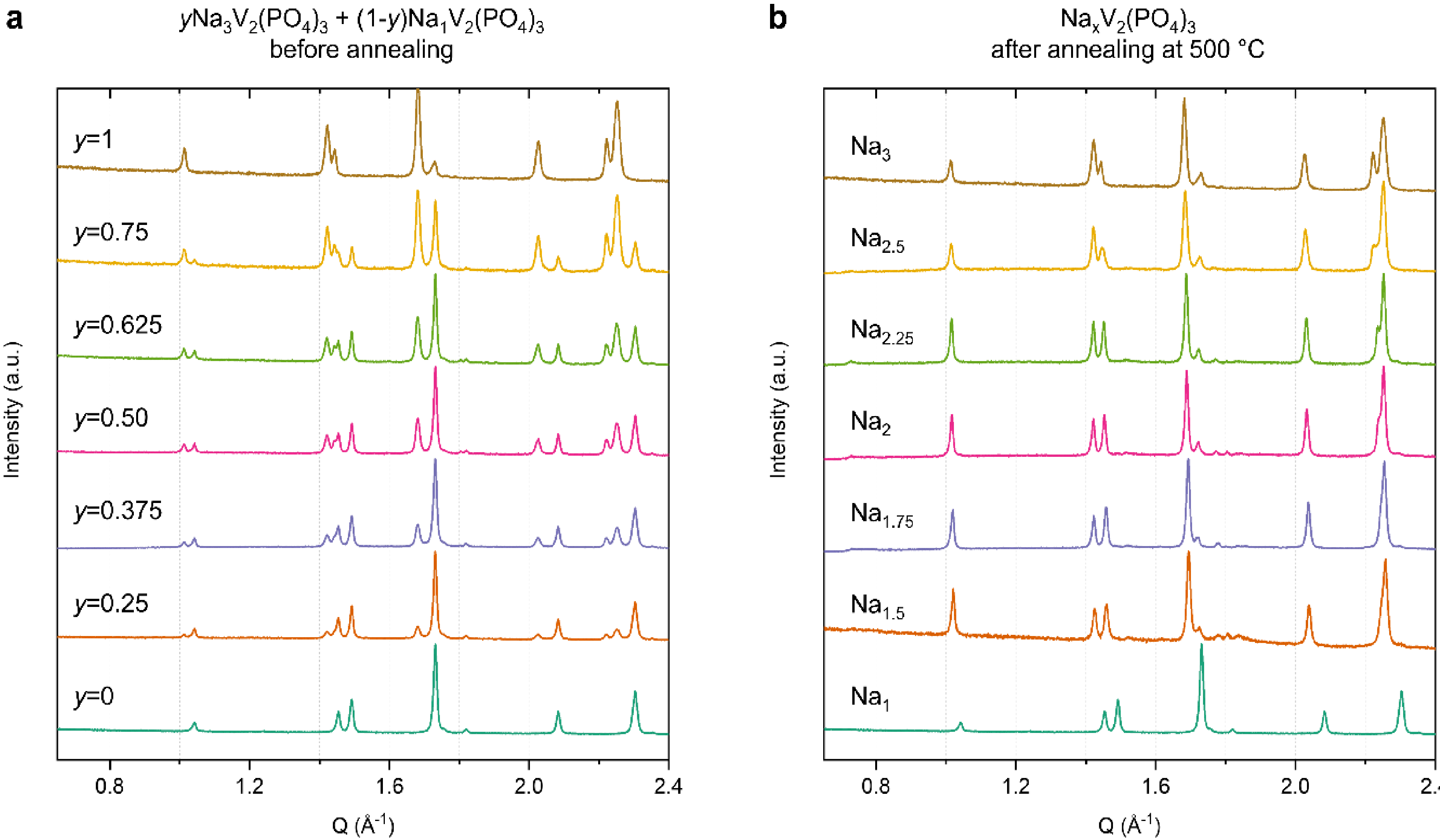
icmcb Bordeaux
NUS National University of Singapore



A new series of $Na_xV_2(PO_4)_3$ compositions has been discovered

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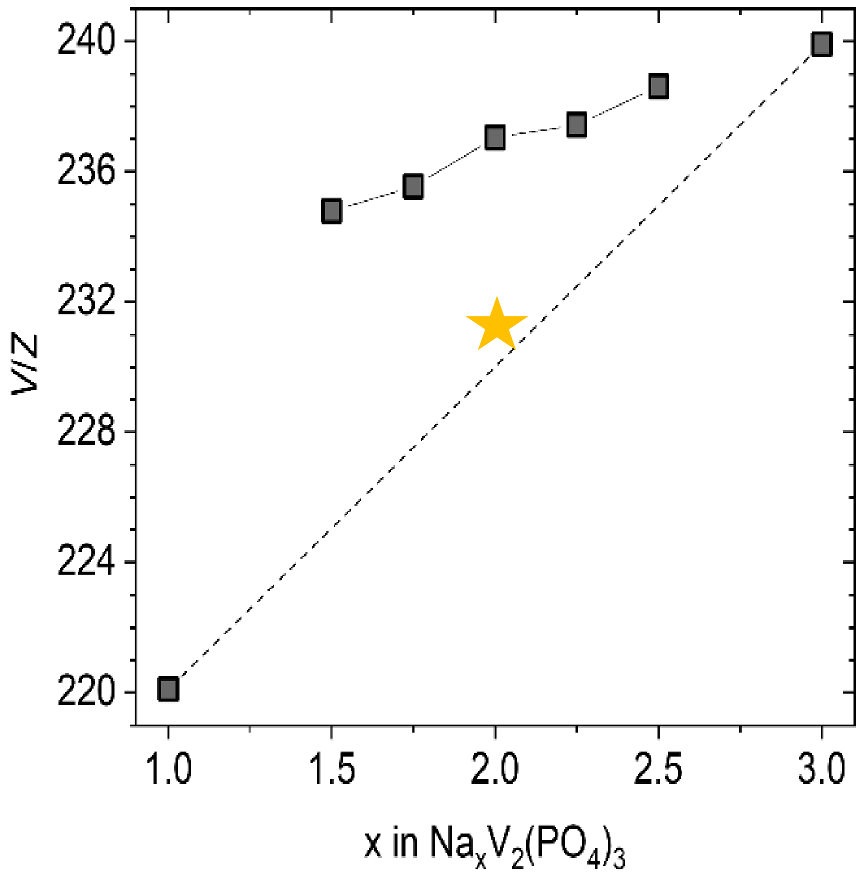
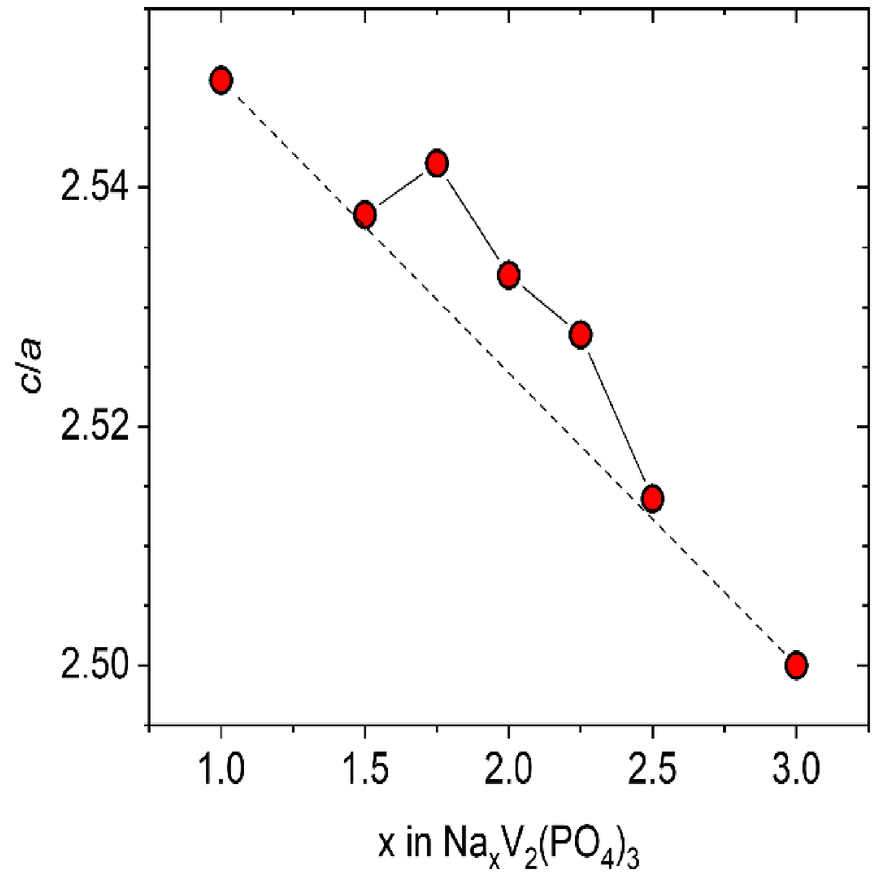
From y $Na_3V^{III}_2(PO_4)_3$: (1-y) $Na_1V^{IV}_2(PO_4)_3$ mixtures





These new materials do not belong to the expected solid solution

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What about the Electrochemistry ?

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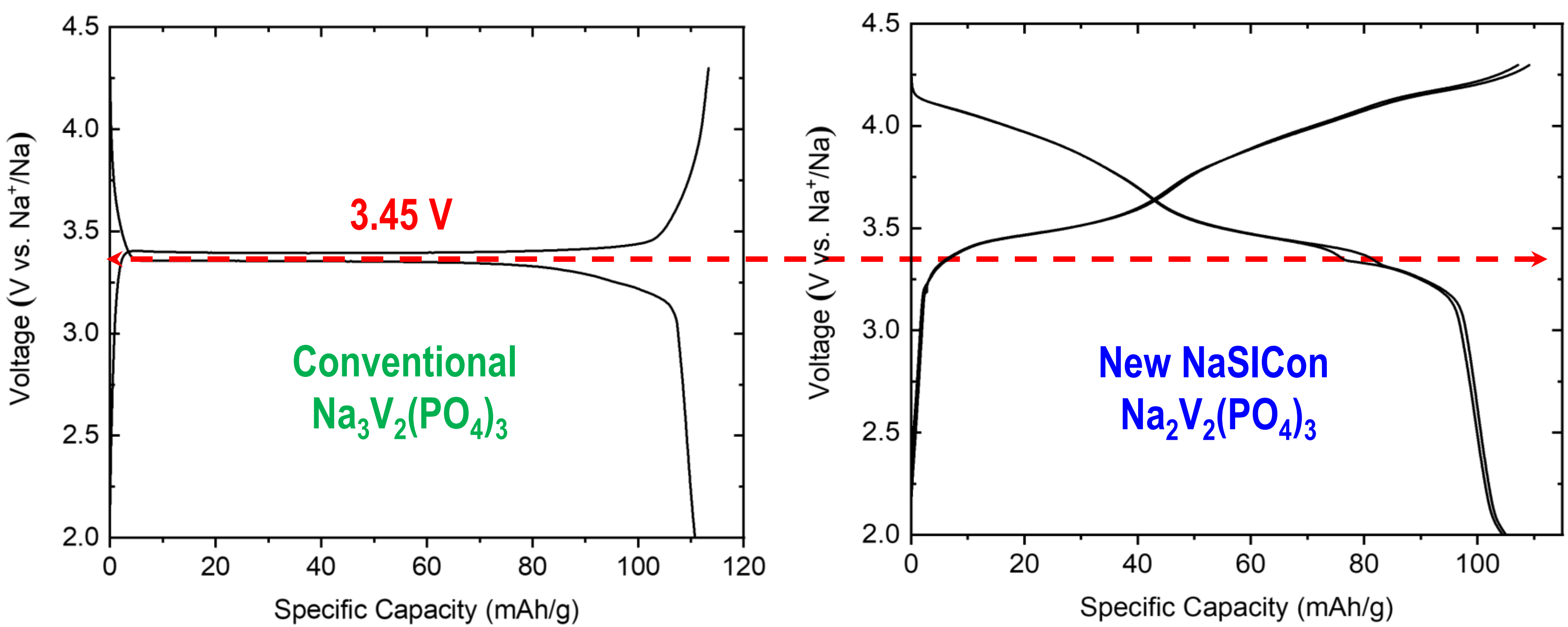

- Working voltage of ca. 3.7 V vs. 3.45 V vs. Na^+/Na
- Solid-solution vs. biphasic reaction
- Less Volume Expansion / Contraction: < 6 % vs. 8.2 %

Park, Wang, Canepa, Chotard, Carlier, Croguennec, Masquelier, C. *European Patent*, *filed*, EP22305644, (2022)
Park, Wang, Choudari, Canepa, Chotard, Carlier, Fauth, Croguennec, Masquelier, *Nature Materials*, In Press (2024)

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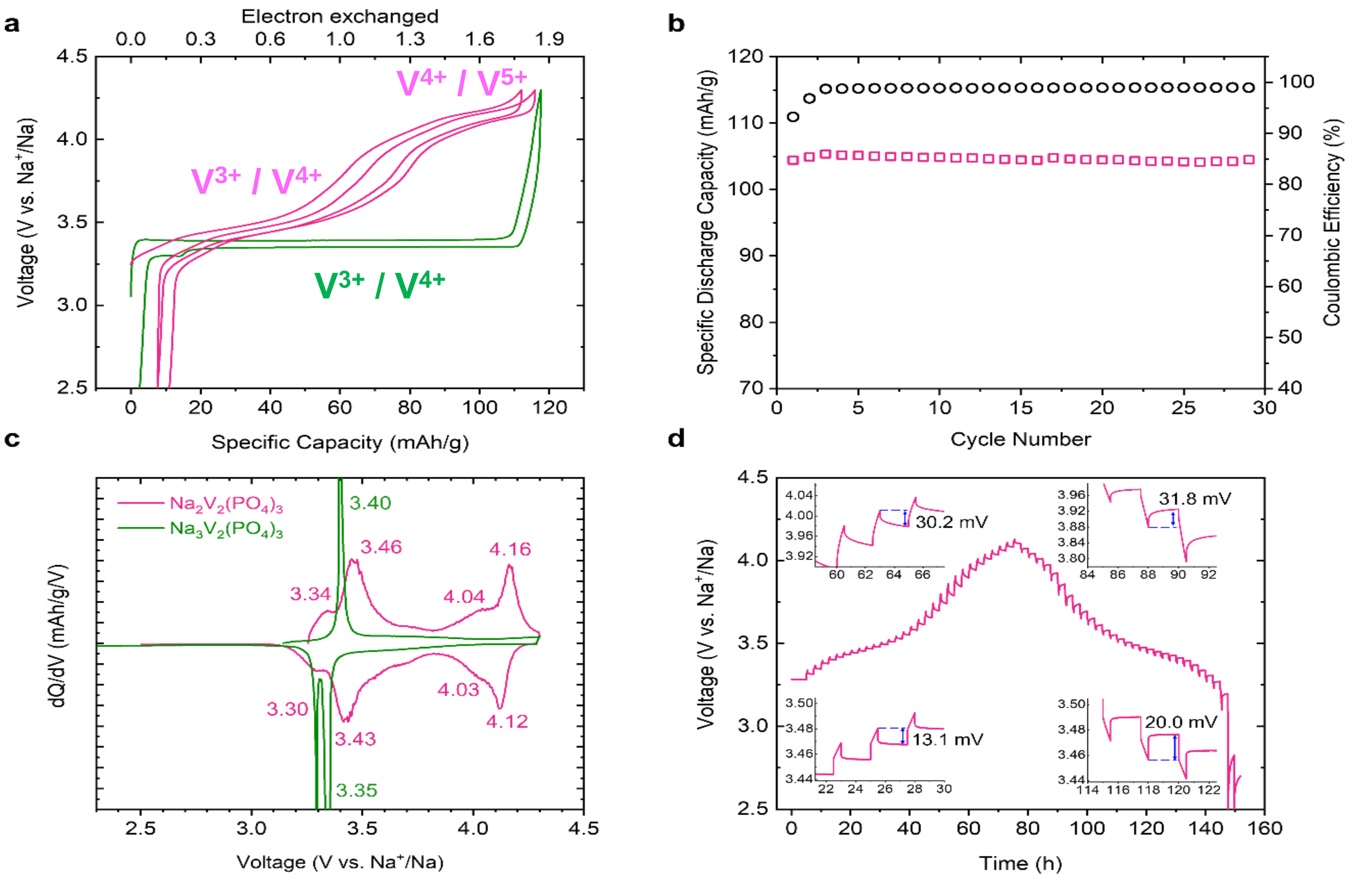
What about the Electrochemistry ?

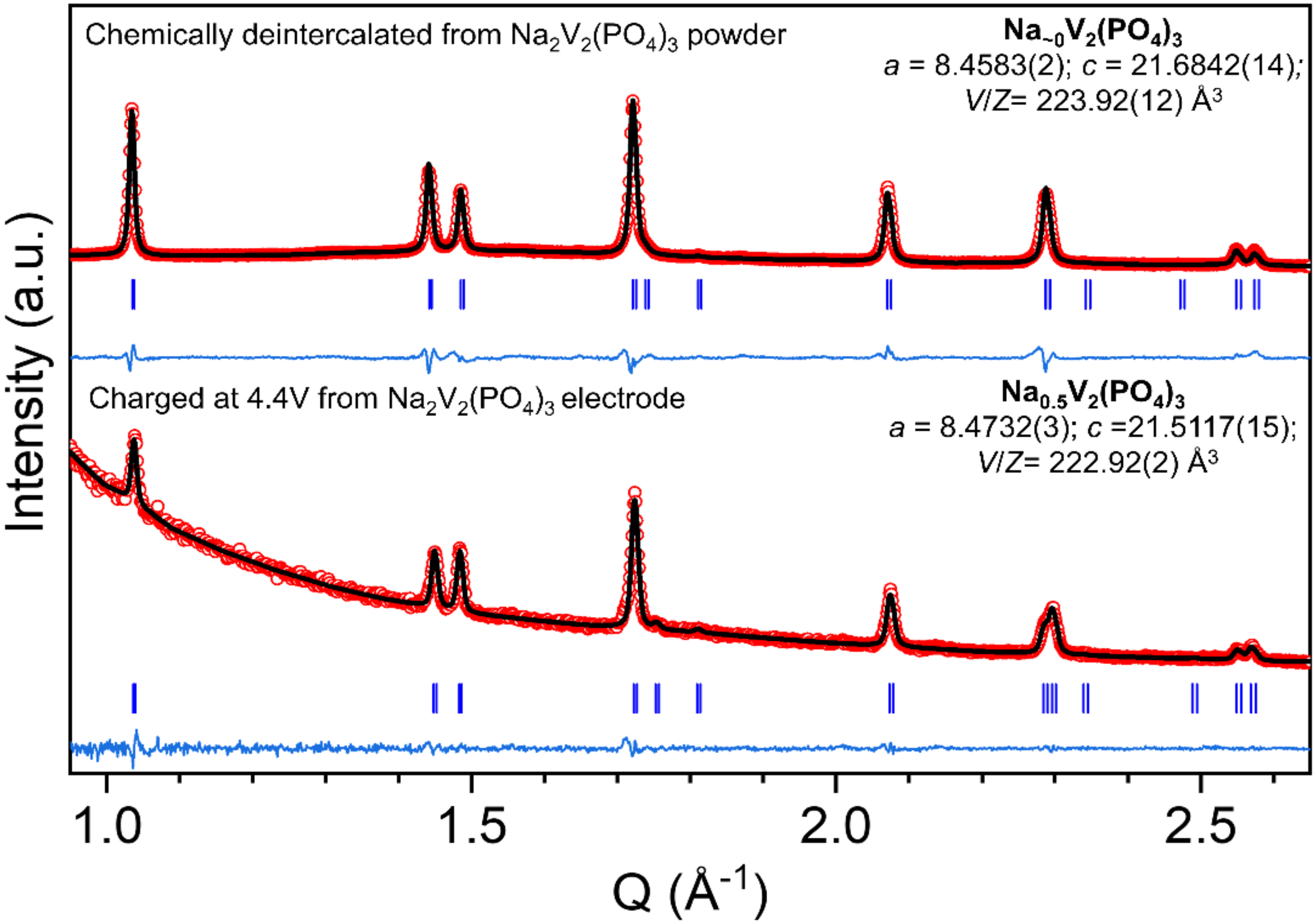
Bordeaux



LRCS
Amie

$V_2(PO_4)_3$ spotted for the first time !!!

icmcb
Bordeaux



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Park, Wang, Choudari, Canepa, Chotard, Carlier, Fauth, Croguennec, Masquelier, *Nature Materials*, In Press (2024)

$Na_xMM'(PO_4)_3$ vs. Na

Issues, approaches, advantages, opportunities

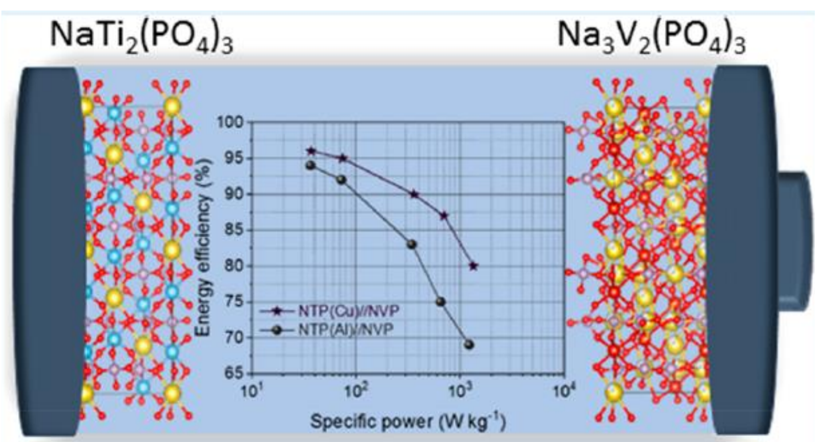
LRCS Amiens

icmcb Bordeaux

Fast Na^+ ion transport within a framework structure → **High rate, long term electrochemical cycling**

Tuning the voltage → **Symmetrical, all NASICON systems, for ASSBs or Aqueous-based batteries. High voltage for Fe**

Mn, V → **Three electron exchange possible (for 2 transition metal elements)**



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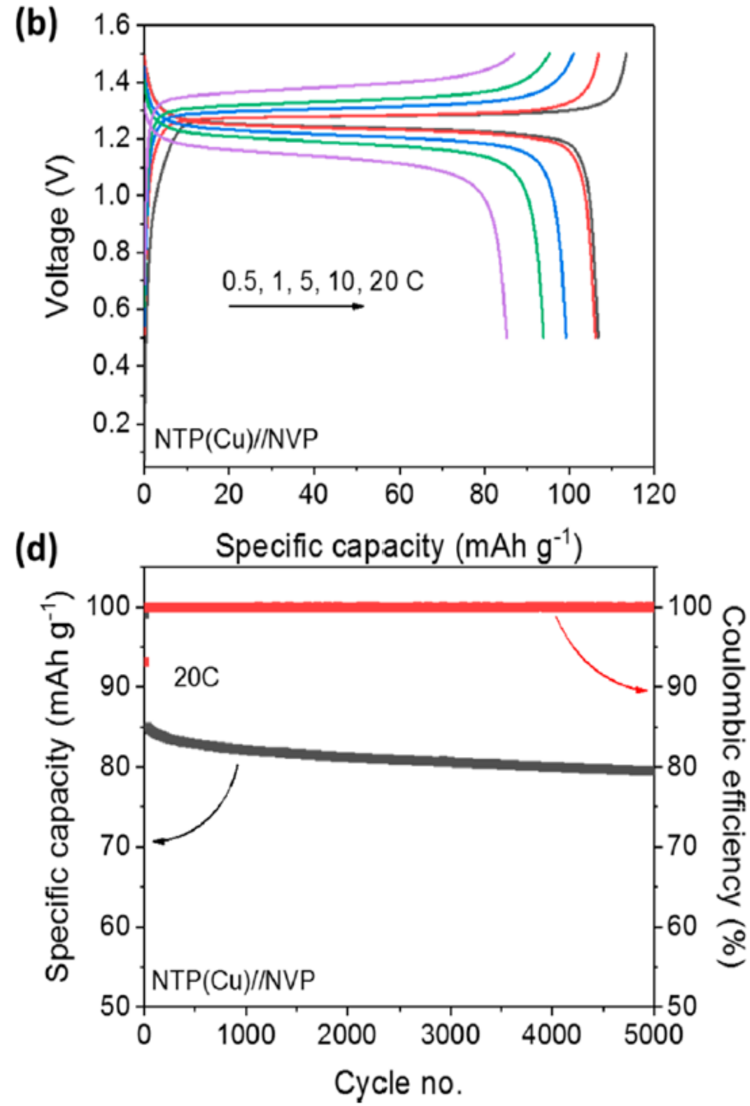

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