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LOMONOSOV MOSCOW STATE UNIVERSITY

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Russian Science Foundation

Crystallography and Crystal Chemistry
VIII International School-Conference of Young Scientists 2023

NASICON-type materials for Na-ion batteries: crystal structure and electrochemical properties

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PhD in **Materials Science, Research Scientist**

Chemistry Department

Lomonosov Moscow State University

November 12th, 2023

Plan

- History of NaSICon development
- $Na_3V_2(PO_4)_3$
- $Na_3VCr(PO_4)_3$
- $Na_3MnTi(PO_4)_3$
- $Na_4MnV(PO_4)_3$
- $NaNbV(PO_4)_3$

NASICON

Na^+ Super Ionic CONductor

Who showed fast Na ionic conductivity? Part I

1967 – reported high ionic conductivity in Na-β alumina

J. inorg. nucl. Chem., 1967, Vol. 29, pp. 2453 to 2475. Pergamon Press Ltd. Printed in Northern Ireland

ION EXCHANGE PROPERTIES OF AND RATES OF IONIC DIFFUSION IN BETA-ALUMINA

YUNG-FANG YU YAO and J. T. KUMMER
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

(*Received* 30 *January* 1967)

Abstract—The sodium ion in beta-alumina has been exchanged in molten salts with a number of univalent and divalent ions. The sodium and potassium concentrations in the solid beta-alumina in contact with various binary Na–K nitrate compositions have been carefully determined and the free energy difference between K^+ and Na^+ beta-alumina calculated. The self diffusion coefficients of Na^+, Ag^+, K^+, Rb^+, and Li^+ in single crystals of beta-alumina have been determined as a function of temperature. Sodium ion has the largest self diffusion coefficient (1×10^{-5} cm²/sec at 300°C and $4{\cdot}0 \times 10^{-7}$ cm²/sec at 25°C) followed by Ag^+, K^+, Li^+, and Rb^+. Data are also presented for interdiffusion coefficients and dielectric loss measurements, and some speculations are made as to the mechanism of the diffusion.

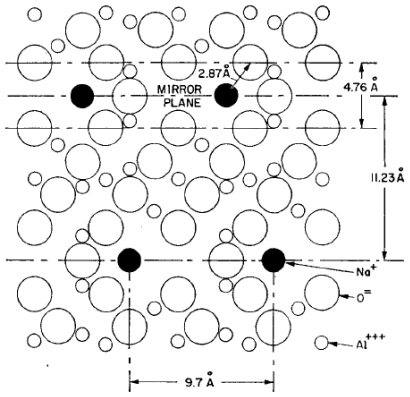
INTRODUCTION

BETA-ALUMINA, which has the empirical formula $Na_2O{\cdot}11Al_2O_3$, can be made by fusing Al_2O_3 and Na_2CO_3 together in the correct proportions.[1] The crystalline structure has been determined.[1–3] This hexagonal layer structure has the lattice

A Sodium-Sulfur Secondary Battery

Joseph T. Kummer and Neill Weber
Scientific Laboratory, Ford Motor Co.

BETA ALUMINA



J. T. KUMMER AND NEILL WEBER

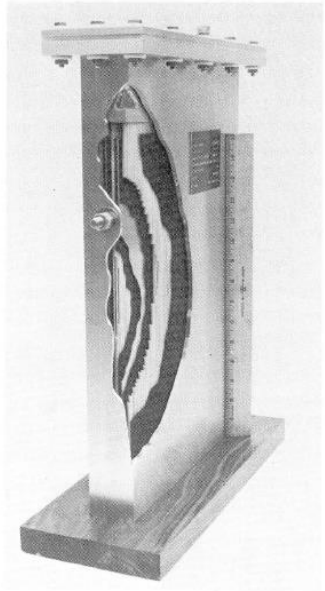


Fig. 8 - Mock-up of a proposed 2 kW cell, showing planar array of sodium filled ceramic tubes

Ford Motor Co., 1966:

the battery breakthrough

using a Na/S chemistry instead of lead-acid

would mean a car about the size of a Ford Falcon could go 82 miles on a single charge

$$Na_xO{\cdot}11Al_2O_3$$

Yao and Kummer,
J. Inorg. Nucl. Chem. 29 (1967) p. 2453

1967 Automotive Engineering Congress and Exposition

Mat. Res. Bull. Vol. 11, pp. 203-220, 1976. Pergamon Press, Inc.
Printed in the United States.

Who showed fast Na ionic conductivity? Part II

FAST Na^+ - ION TRANSPORT IN SKELETON STRUCTURES*

J. B. Goodenough, H. Y-P. Hong, and J. A. Kafalas
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, Massachusetts 02173

(Received December 17, 1975; Communicated by J. B. Goodenough)

ABSTRACT

Skeleton structures have been explored experimentally for fast Na^+ - ion transport. A skeleton structure consists of a rigid skeletal array of atoms stabilized by electrons donated by alkali ions partially occupying sites in a three dimensionally linked interstitial space. Fast Na^+ - ion transport was demonstrated in several structures, and the system $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ has a Na^+ - ion resistivity at 300°C of $\rho_{300} \leq 5\Omega$-cm for $x \approx 2$, which is competitive with the best β" - alumina. An activation energy $\mathcal{E}_a \approx 0.29$ eV is about 0.1 eV larger than that of β" -alumina.

Introduction

The discovery[1] of fast Na^+ - ion transport in β - and β"-alumina has stimulated interest in the use of solid electrolytes in cells and thermoelectric generators.[2] The best compositions have resistivities for fast Na^+ - ion transport at 300°C of $\rho_{300} = 4\Omega$-cm with an activation energy for the mobility $\mathcal{E}_a = 0.16$ eV[3]. The volatility of sodium together with the refractory character of Al_2O_3 has made awkward economic fabrication of ceramic membranes, but this problem appears to be solved.[4] Nevertheless, β-and β"-alumina are layer compounds in which the Na^+ ions are constrained

$$Na_{1+3x}Zr_2(P_{1-x}Si_xO_4)_3$$

What is known today as

NASICON

Na^+ Super Ionic CONductor

Was there anyone working on this structure too?

$NaU_2(PO_4)_3$

CROATICA CHEMICA ACTA 37 (1965) 115

CCA-369 548.7:549.752:546.33-841-79

Preliminary Note

Synthesis and Crystallographic Data of Sodium Thorium Triphosphate, $NaTh_2(PO_4)_3$, and Sodium Uranium(IV) Triphosphate, $NaU_2(PO_4)_3$

B. Matković

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

and

M. Šljukić

Department of Analytical Chemitry, Faculty of Science, University of Sarajevo, Bosnia and Herzegovina, Yugoslavia

Received February 2, 1965

Sodium thorium triphosphate was first prepared by K. A. Wallroth[1] and sodium uranium(IV) triphosphate by M. A. Colani[2]. Both compounds are very stable and practically insoluble in acids. Single crystals of these compounds were prepared by methods which slightly differ from the above mentioned.

REFERENCES

1. K. A. Wallroth, *Bull. Soc. Chim.* **39** (1883) 316.
2. M. A. Colani, *Ann. Chim. Phys.* **12** (1907) 107.

Was there anyone working on this structure too?

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ACTA CHEMICA SCANDINAVICA 22 (1968) 1822–1832

The Crystal Structure of $NaMe_2^{IV}(PO_4)_3$; Me^{IV} = Ge, Ti, Zr

LARS-OVE HAGMAN and PEDER KIERKEGAARD

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

REFERENCES

1. K. A. Wallroth, *Bull. Soc. Chim.* **39** (1883) 316.
2. M. A. Colani, *Ann. Chim. Phys.* **12** (1907) 107.

Who is making NASICON electrolytes?

$Na_3Zr_2Si_2PO_{12}$

https://www.msesupplies.com

$750

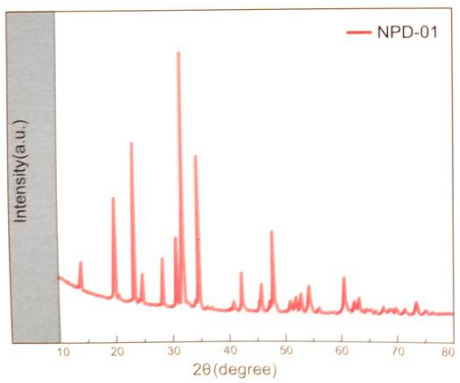
$Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$

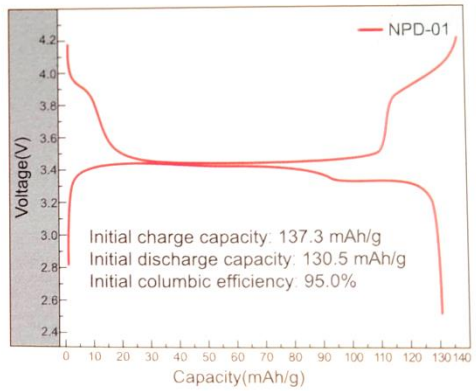
Who is making NASICON cathodes?

NASICON

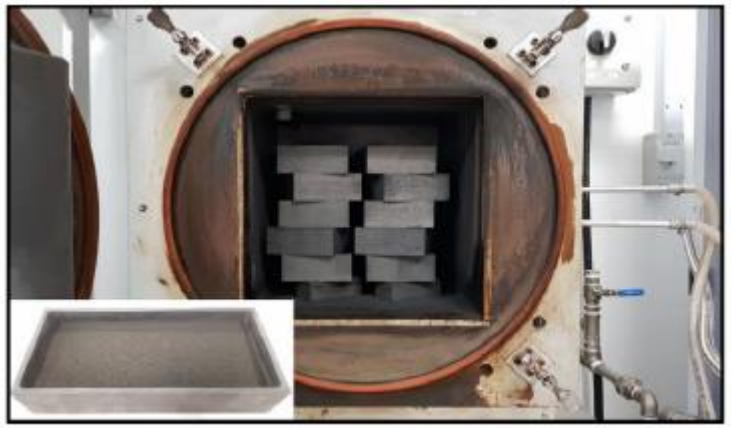
钠思科

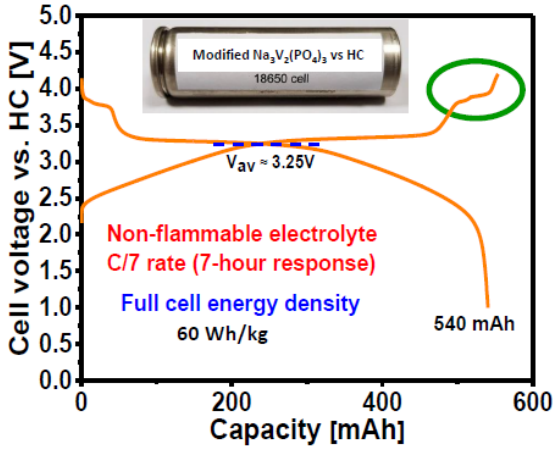
★ VOLTAGE: ~3.45 V
★ INITIAL COLUMBIC EFFICIENCY: >92%
★ PARTICLE SIZE DISTRIBUTION: D50=5±1 μm
★ COMPACTION DENSITY: 1.8-2.0 g/cm³
★ TAP DENSITY: >0.8 g/cm³



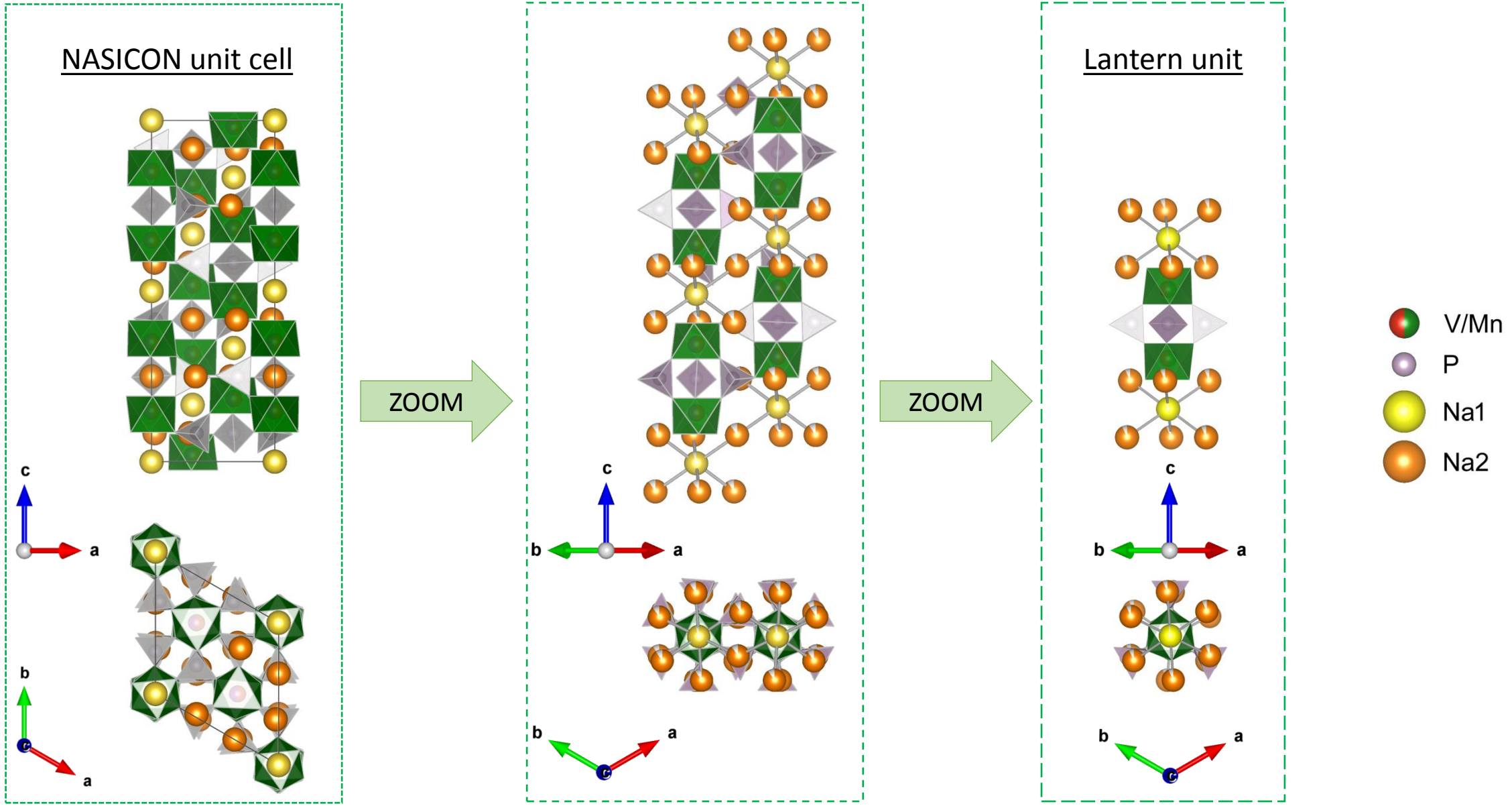


SgNaPlus

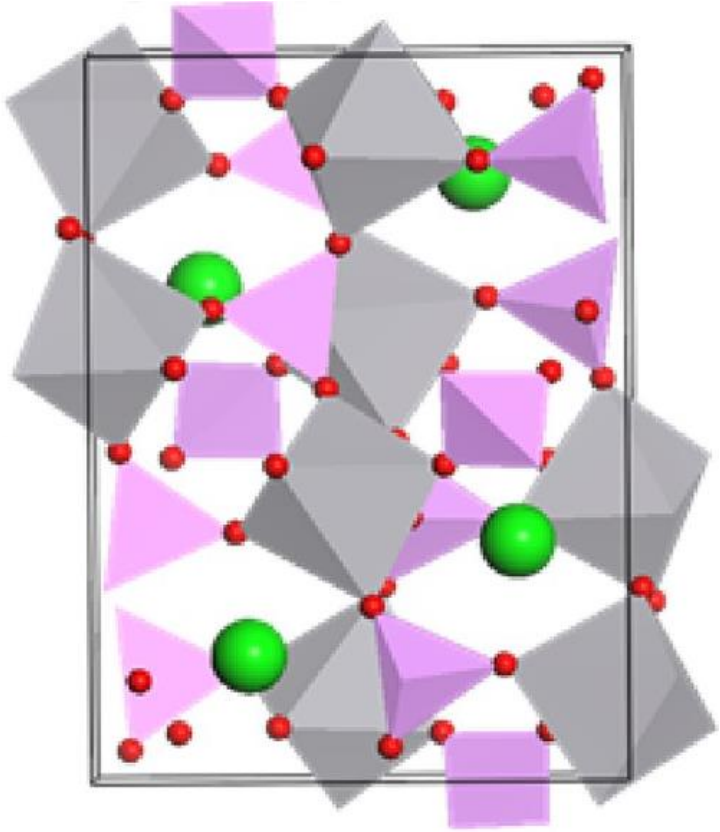


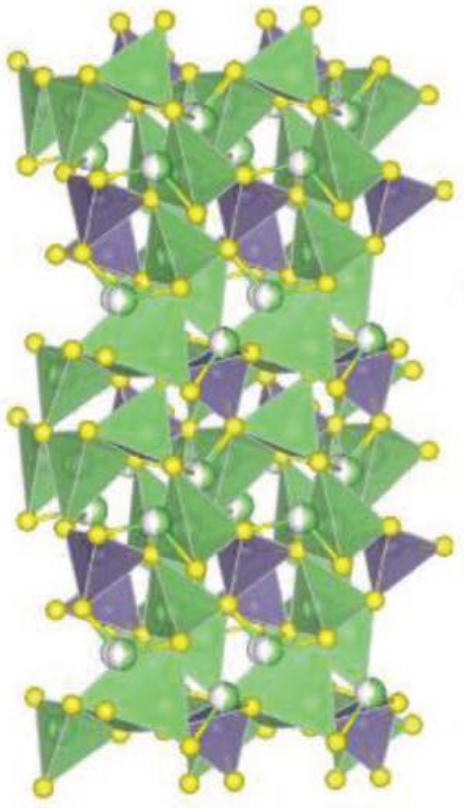


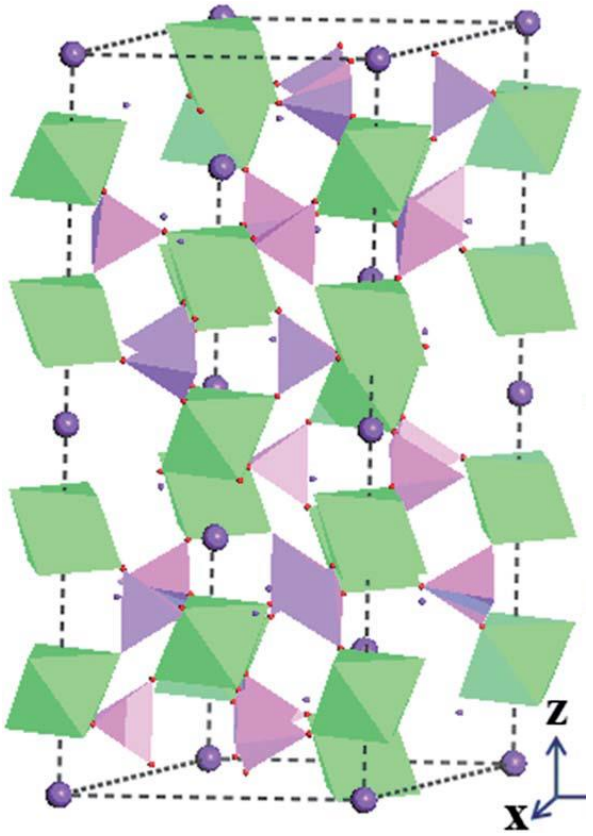
NASICON crystal structure



Which one is NASICON?





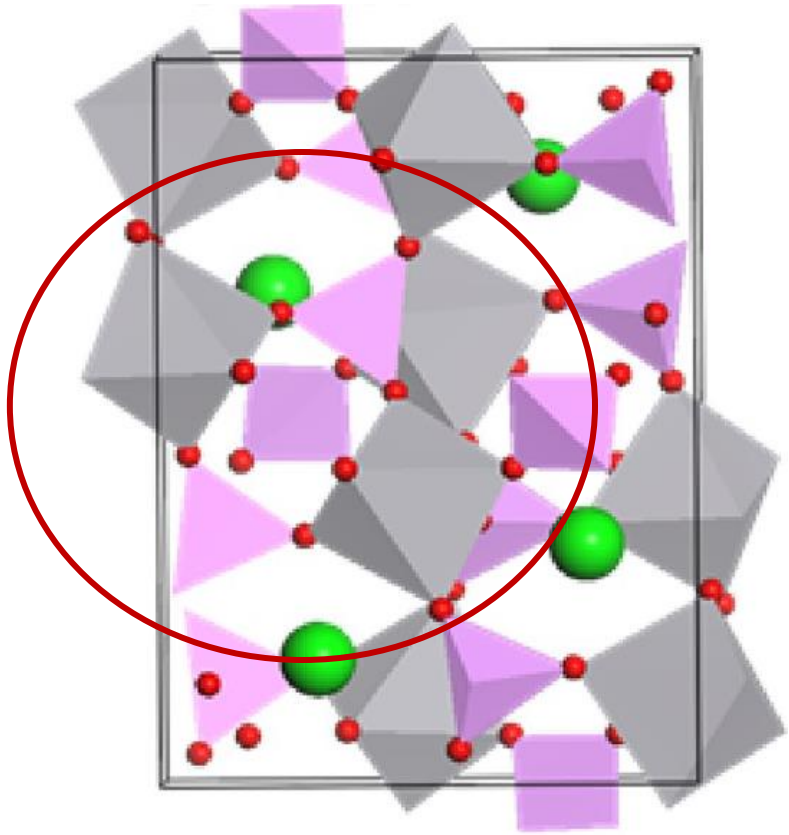


Lee et al // J. Phys. Chem. C 2012, 116, 48, 25190–25197

Zhang et al // Adv. Mater. **2019**, 1901131

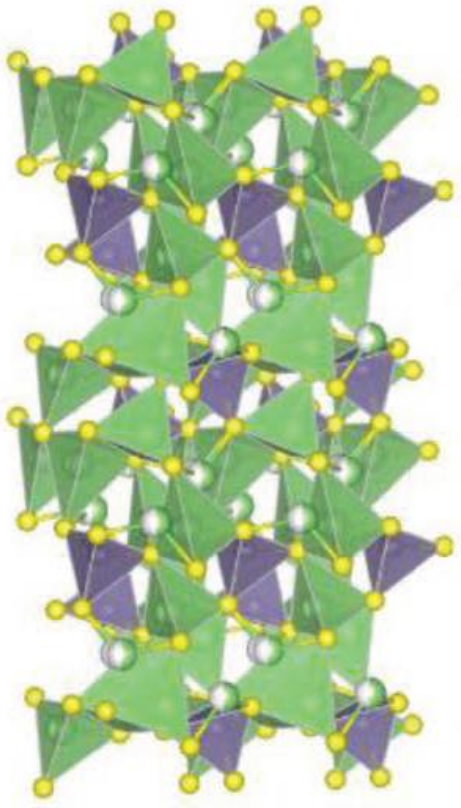
Song et al // J. Mater. Chem. A, 2014, 2, 5358–5362

Lantern unit is a feature of NASICON



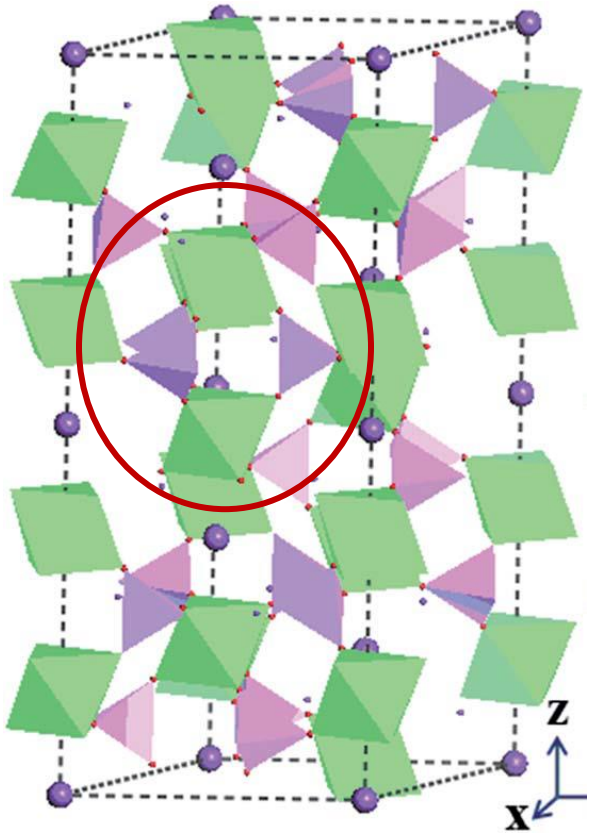
Anti-NASICON

Lee et al // J. Phys. Chem. C 2012, 116, 48, 25190–25197



LISICON

Zhang et al // Adv. Mater. **2019**, 1901131



NASICON

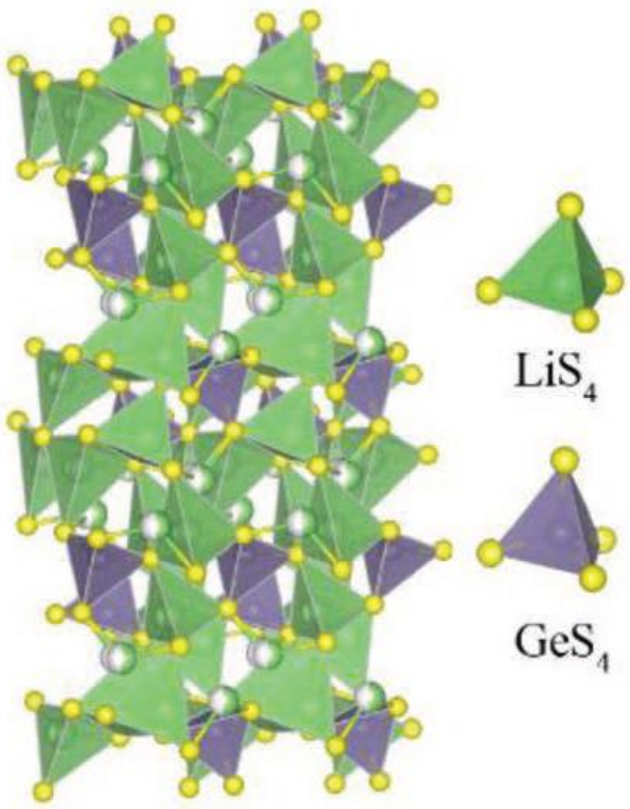
Song et al // J. Mater. Chem. A, 2014, 2, 5358–5362

LISICON's framework differs from NASICON

Mat. Res. Bul. Vol. 13, pp. 117-124, 1978. Pergamon Press, Inc. Printed in the United States.

CRYSTAL STRUCTURE AND IONIC CONDUCTIVITY OF $Li_{14}Zn(GeO_4)_4$ AND OTHER NEW Li^+ SUPERIONIC CONDUCTORS*

H. Y-P. Hong
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, Massachusetts 02173



$Li_{14}Zn(GeO_4)_4$

LISICON

Li_4GeS_4

Thio-LISICON

Zhang et al // Adv. Mater. **2019**, 1901131

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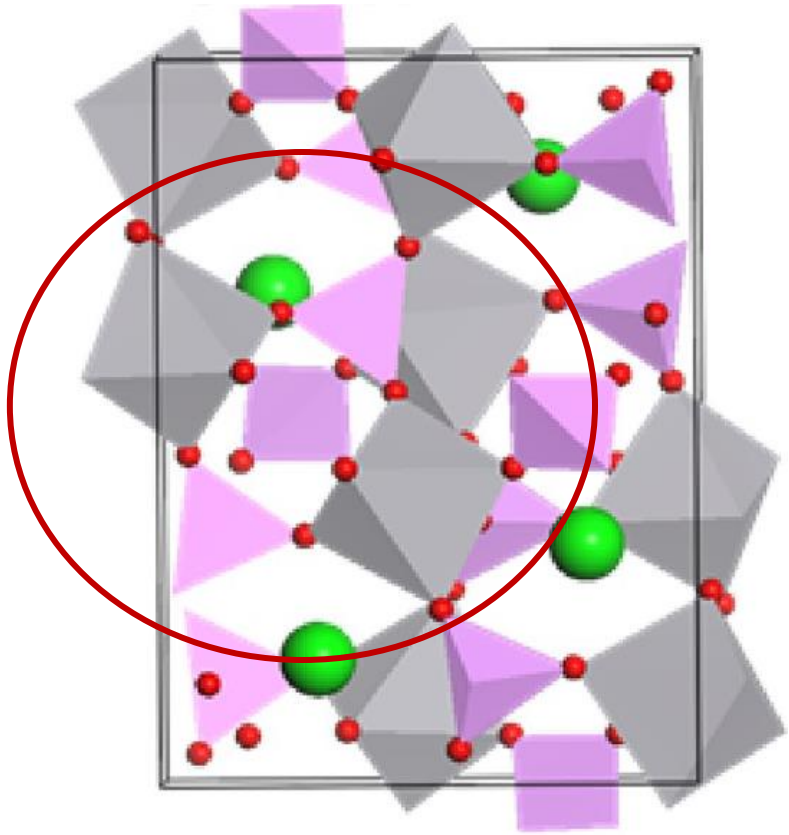

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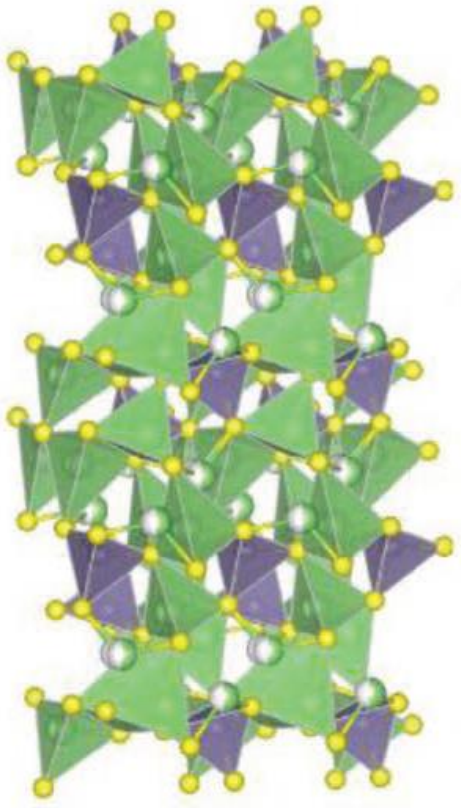

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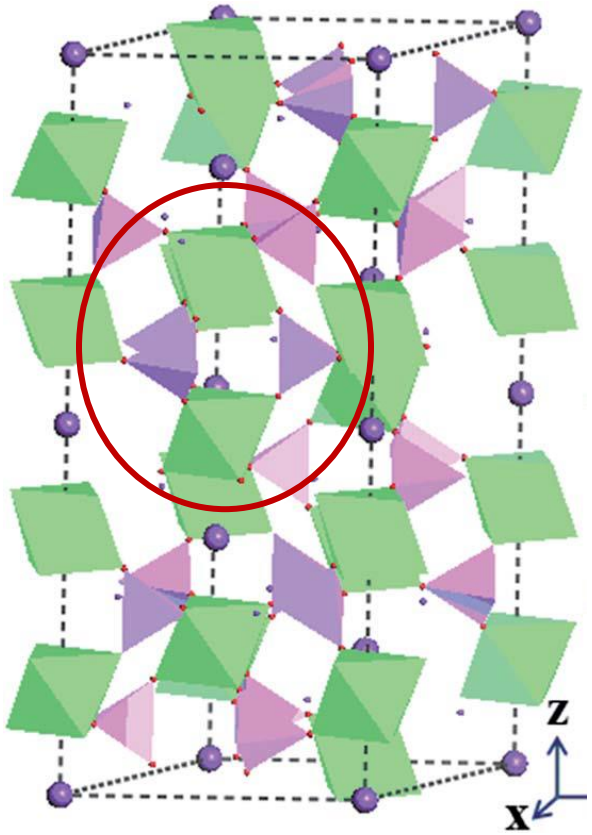

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NASICON framework

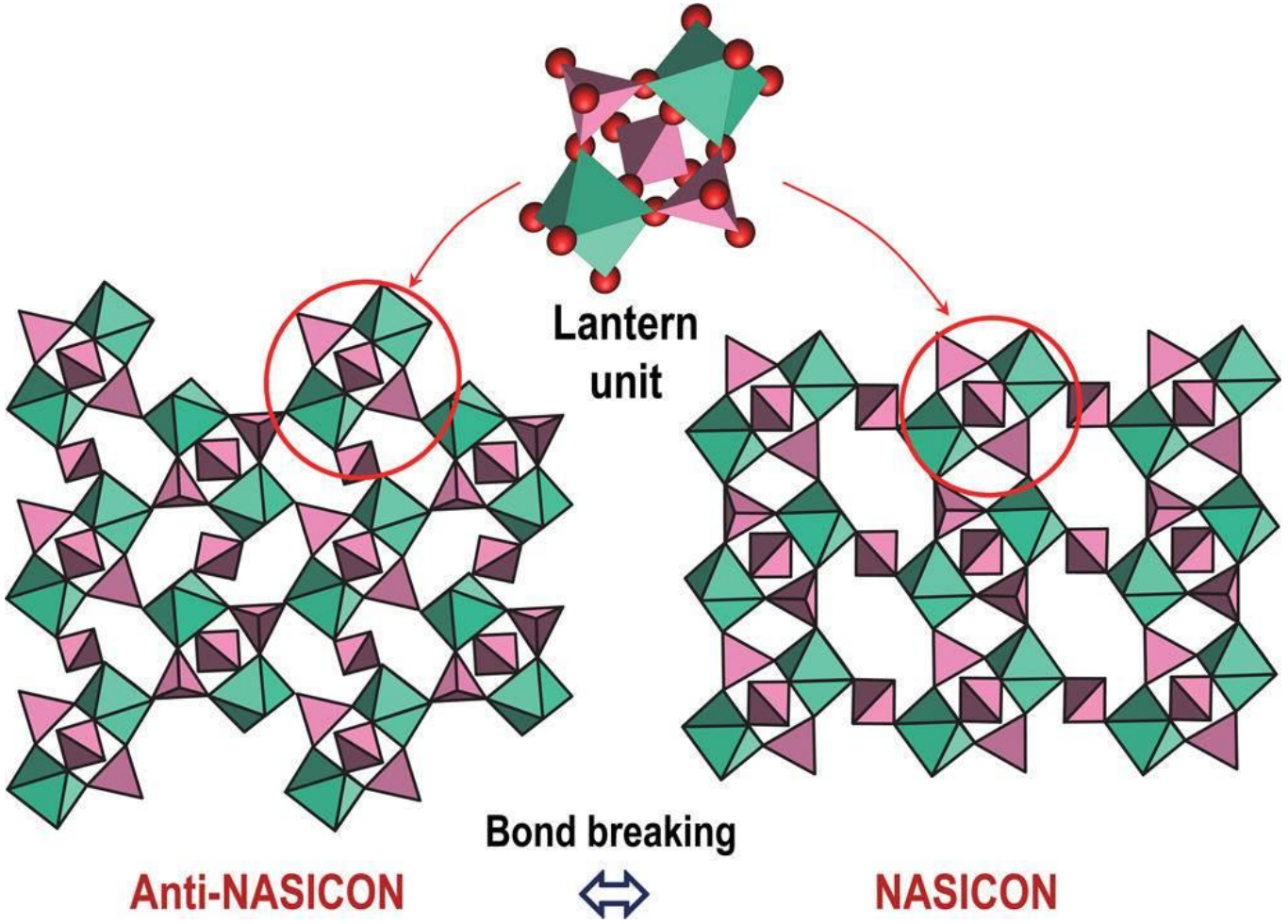
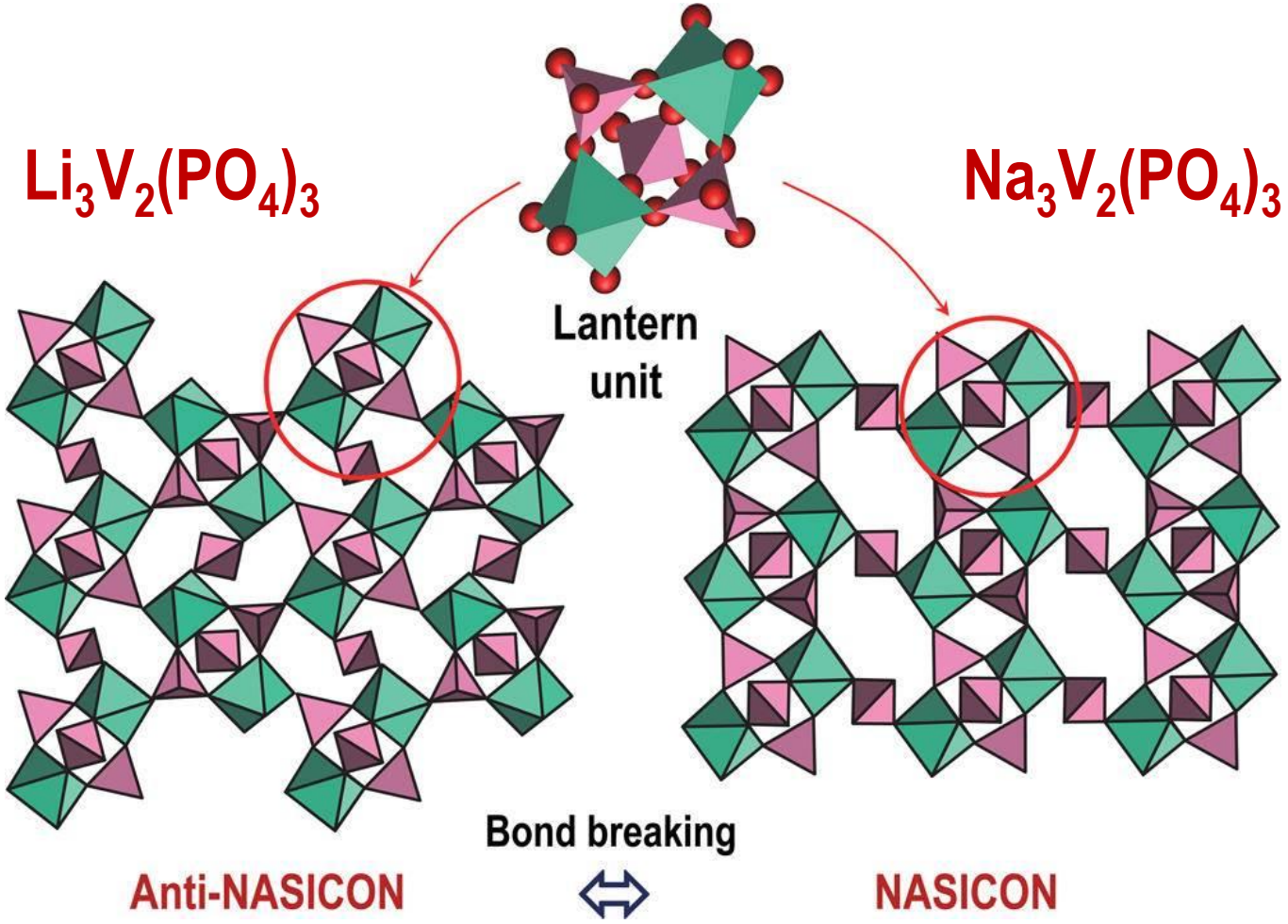


Figure 2. NASICON (generally rhombohedral) and anti-NASICON (generally monoclinic) frameworks of general formula $A_xMM'(XO_4)_3$.

Chinese Lantern

C. Masquelier et al // *Chem. Rev.*, 2013, 113 (8), pp 6552–6591

NASICON framework



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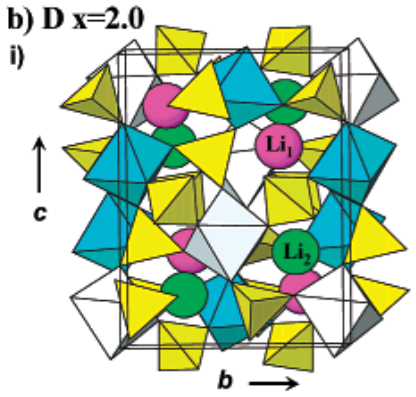
$Li_3V_2(PO_4)_3$: Electrochemical properties



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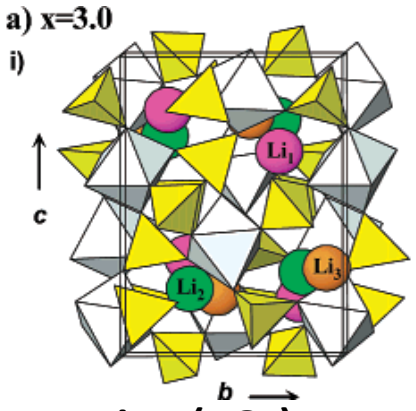

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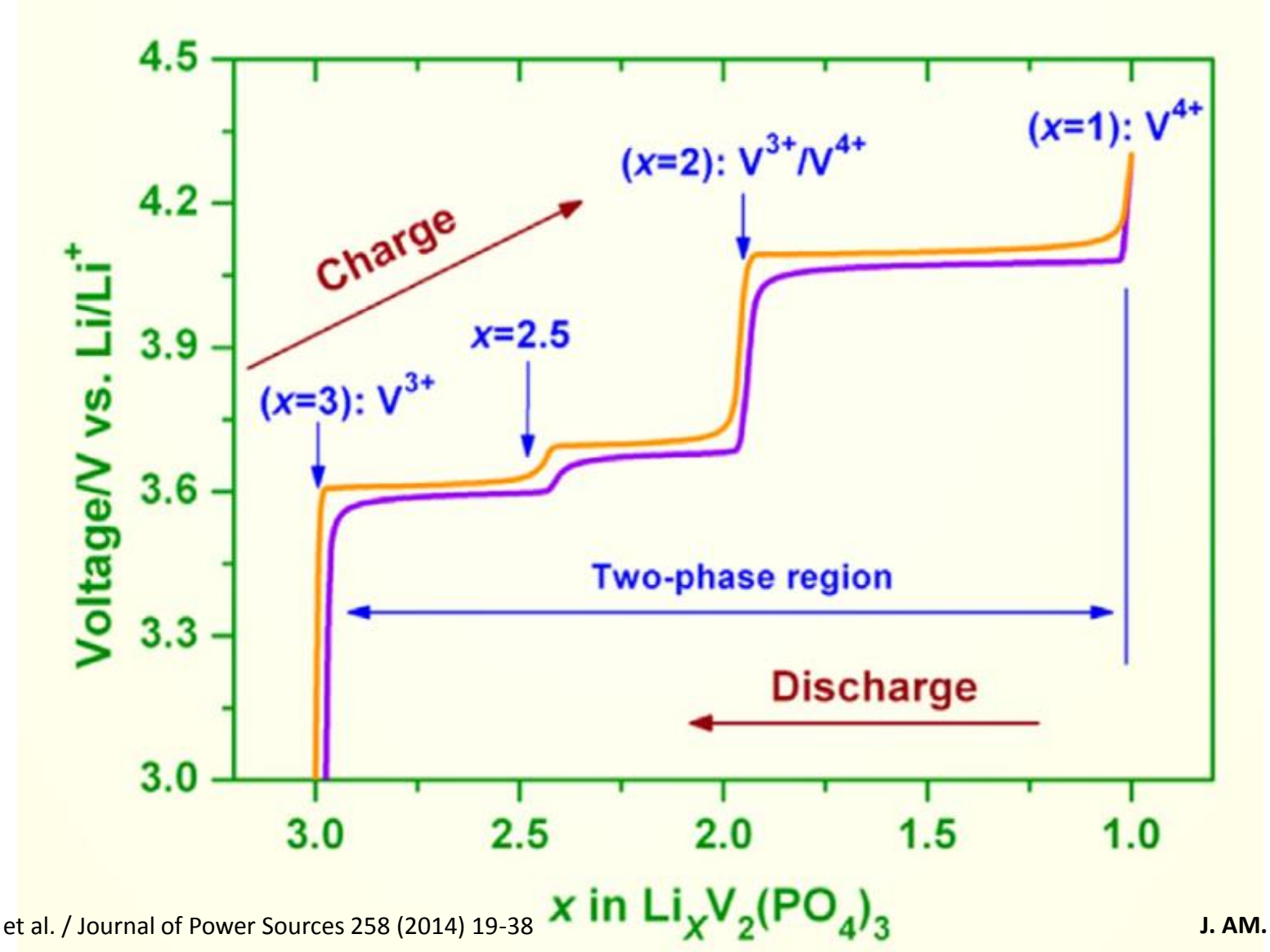
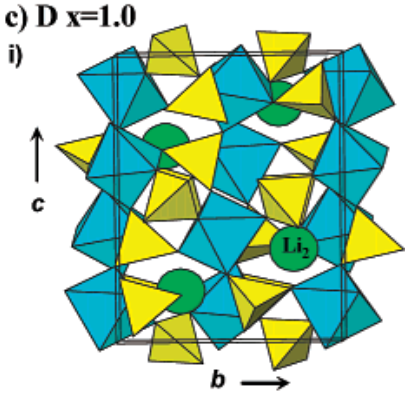


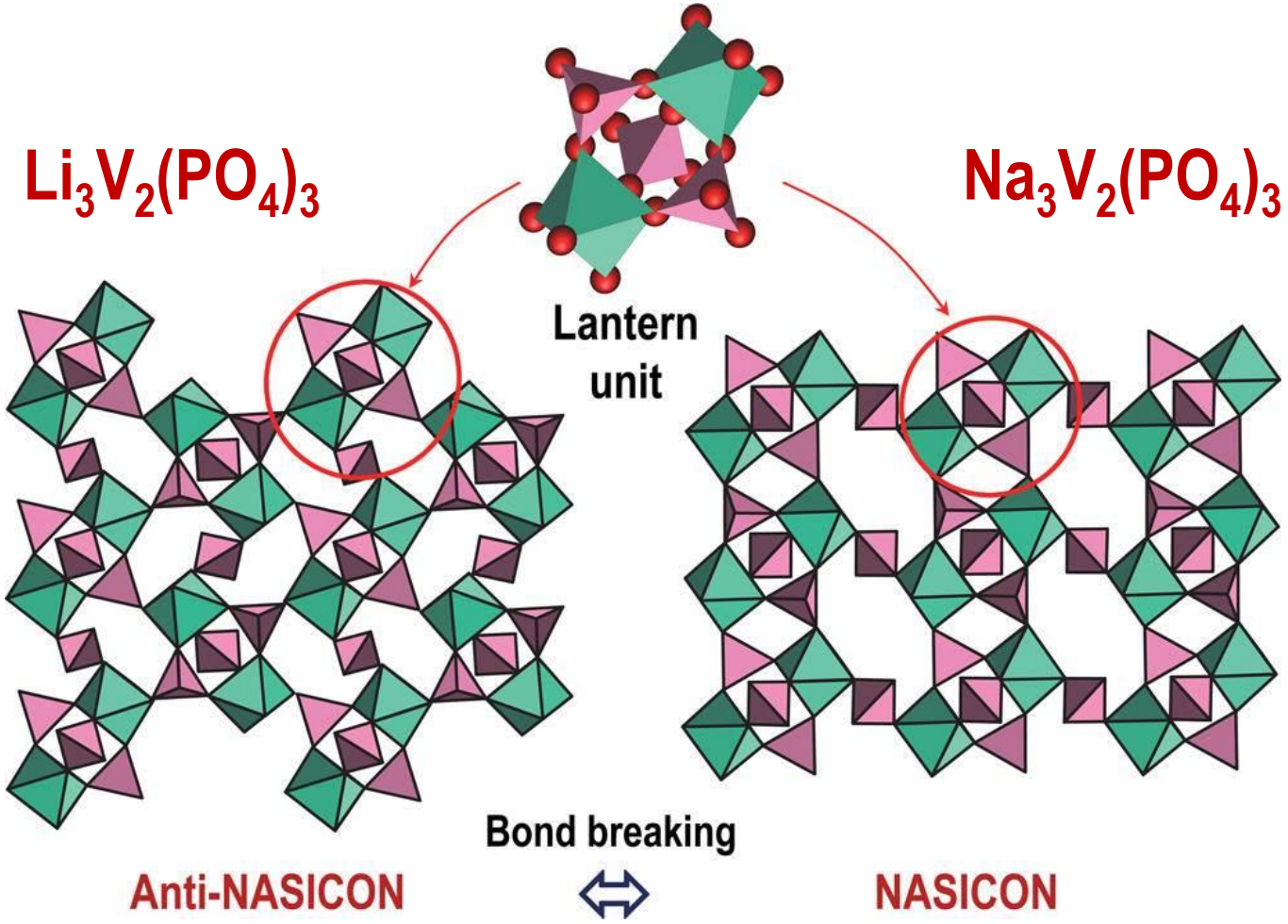


$LiV_2(PO_4)_3$

X. Rui et al. / Journal of Power Sources 258 (2014) 19-38

J. AM. CHEM. SOC. 2003, 125, 10402-10411

NASICON framework



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Chinese Lantern

C. Masquelier et al // *Chem. Rev.*, 2013, 113 (8), pp 6552–6591

$Na_3V_2(PO_4)_3$

Eisen

I 7100

7902 – 0 4 1

Neue Familie von Phosphaten mit der Formel $Na_3M_2(PO_4)_3$ (M = Ti, V, Cr, Fe). – Entsprechend den Gleichungen A und B wurden durch thermische Reaktionen die Verbindungen (I) und (II) dargestellt. (I) und (II) kristallisieren hexagonal und lassen aufgrund ihrer Isotypie mit $NaZr_2(PO_4)_3$ interessante Ionenleitereigenschaften erwar-

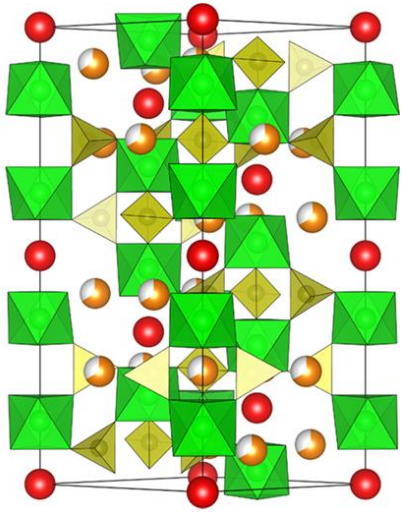
Physikalische Eigenschaften **1979**

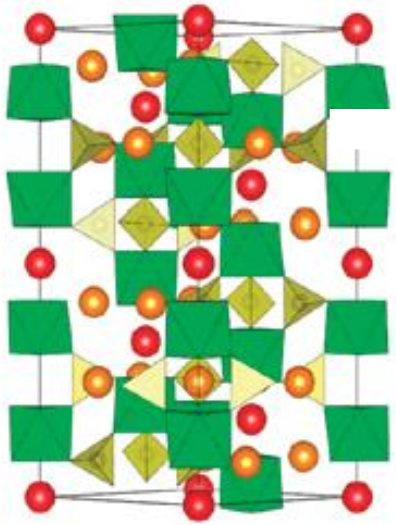
D 2000

ten. – (DELMAS, C., OLAZCUAGA, R., CHERKAOUI, F., BROCHU, R. und LE FLEM, G.; C. R. Acad. Sci., Sér. C 287 (1978) 5, 169–71; Lab. Chim. du Solide du C.N.R.S., Univ. de Bordeaux-I, 33405 Talence; franz.) – Betcke

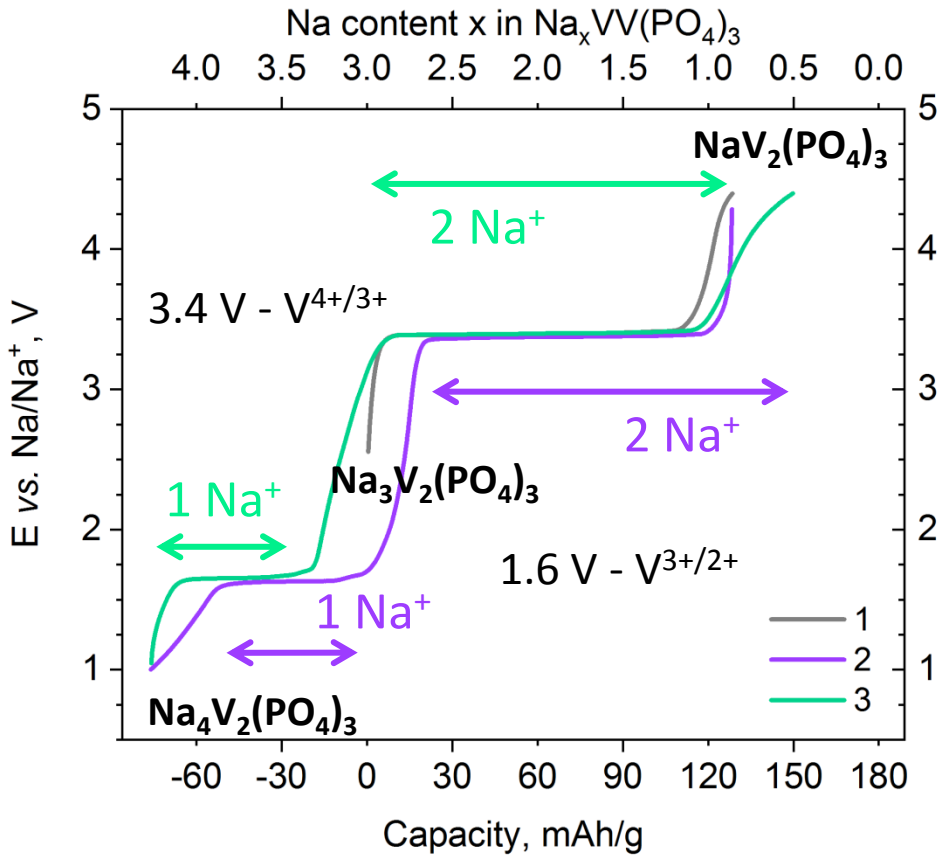
$Na_3V_2(PO_4)_3$: Electrochemical properties

$Na_3V_2(PO_4)_3$

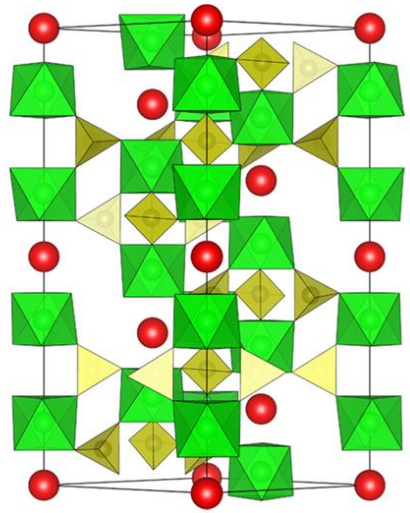


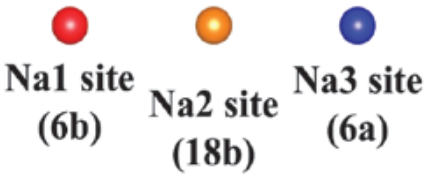


$Na_4V_2(PO_4)_3$



$NaV_2(PO_4)_3$

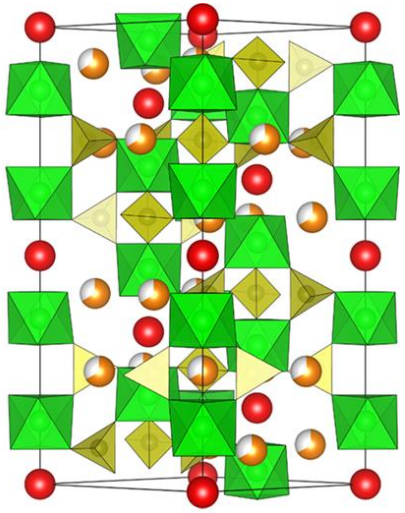


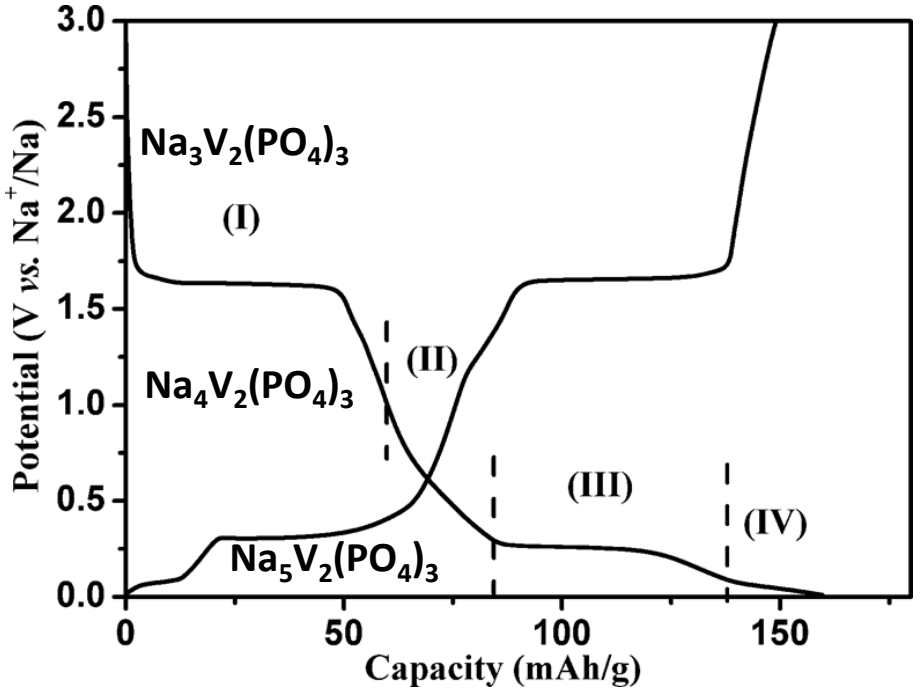


Z. Jian et al. / ***Chem. Commun.***, 2015,**51**, 6381-6383

$Na_3V_2(PO_4)_3$: Electrochemical properties

$Na_3V_2(PO_4)_3$





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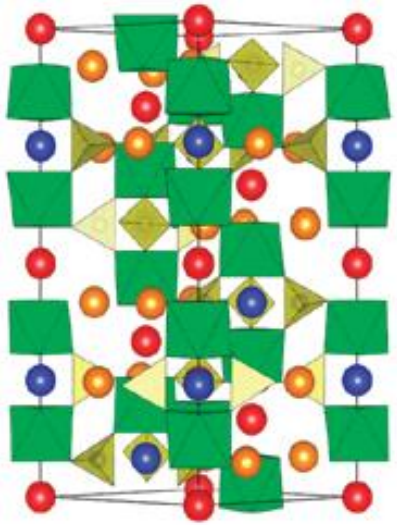
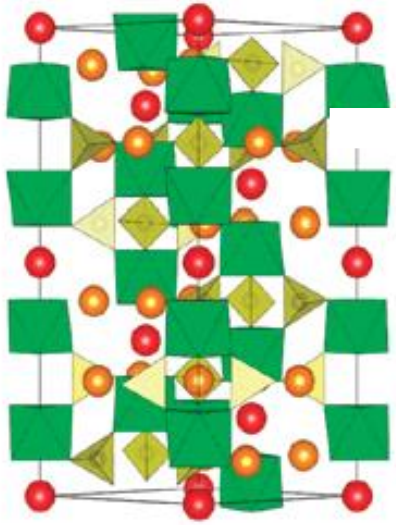
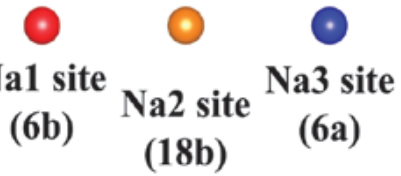




$Na_4V_2(PO_4)_3$

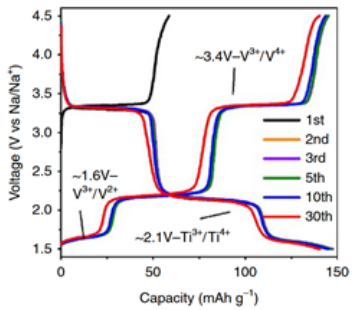


Z. Jian et al. / ***Chem. Commun.***, 2015,**51**, 6381-6383

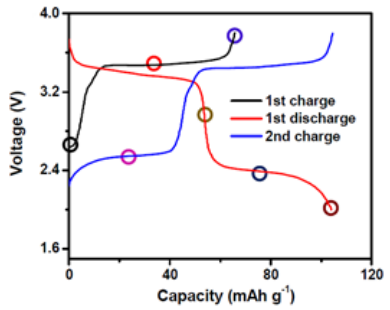
Z. Jian et al. / ***Chem. Commun.***, 2015,**51**, 6381-6383

NASICON-type electrode materials for sodium-ion batteries

$Na_2TiV(PO_4)_3$



$Na_3FeV(PO_4)_3$



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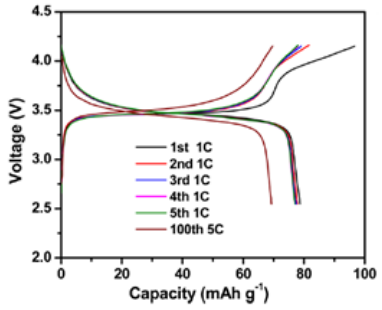
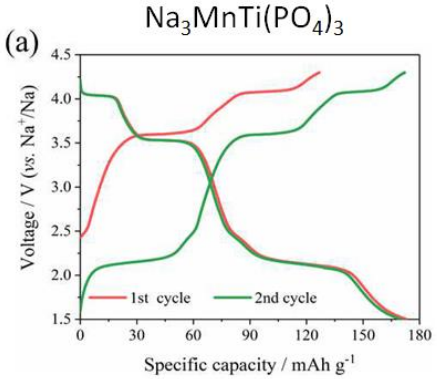
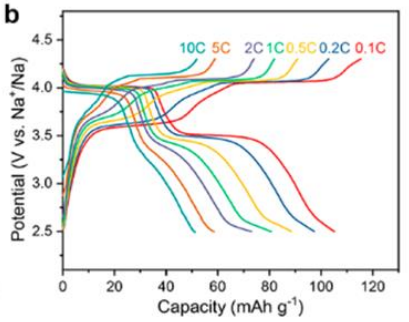


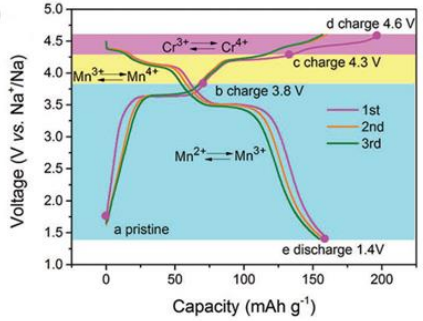
$Na_3MnTi(PO_4)_3$



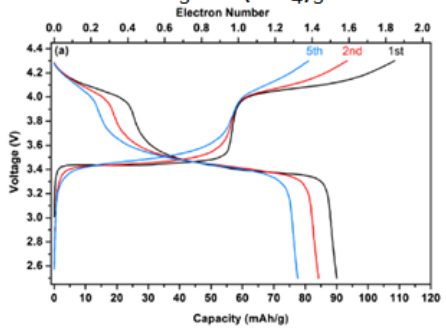
$Na_3MnZr(PO_4)_3$



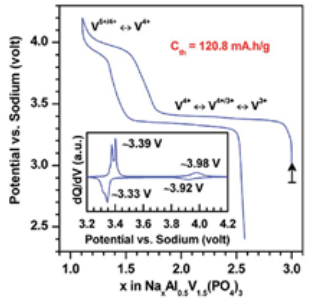
$Na_4MnCr(PO_4)_3$



$Na_3CrV(PO_4)_3$



$Na_3Al_{0.5}V_{1.5}(PO_4)_3$



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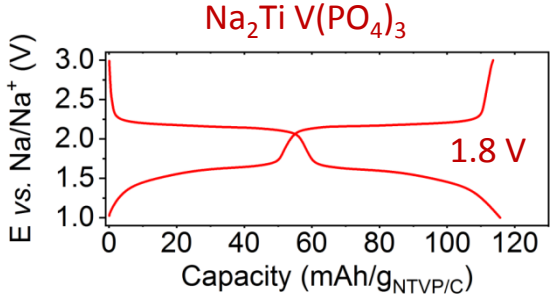
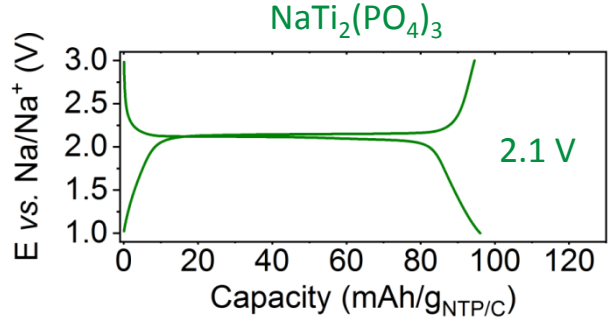


$NaTi_2(PO_4)_3$



D. Wang, Nat. Commun. 8 (2017) 1–7.

R. Liu, ACS Appl. Mater. Interfaces. 9 (2017) 43632–43639

F. Lalère, J. Mater. Chem. A. 3 (2015) 16198–16205

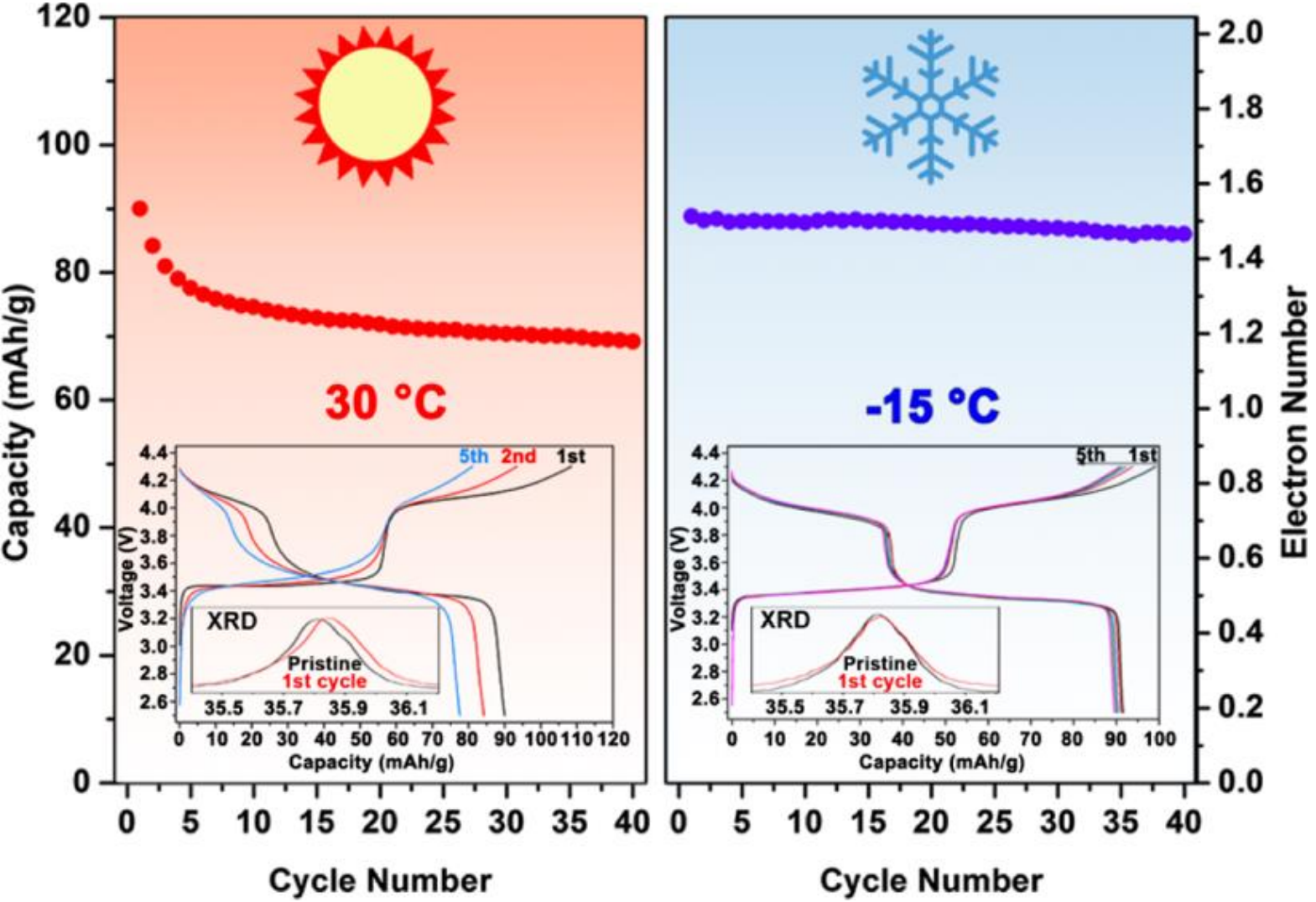
W. Zhou, Nano Lett. 16 (2016) 7836–7841.

H. Li, Energy Storage Mater. 26 (2020) 325–333

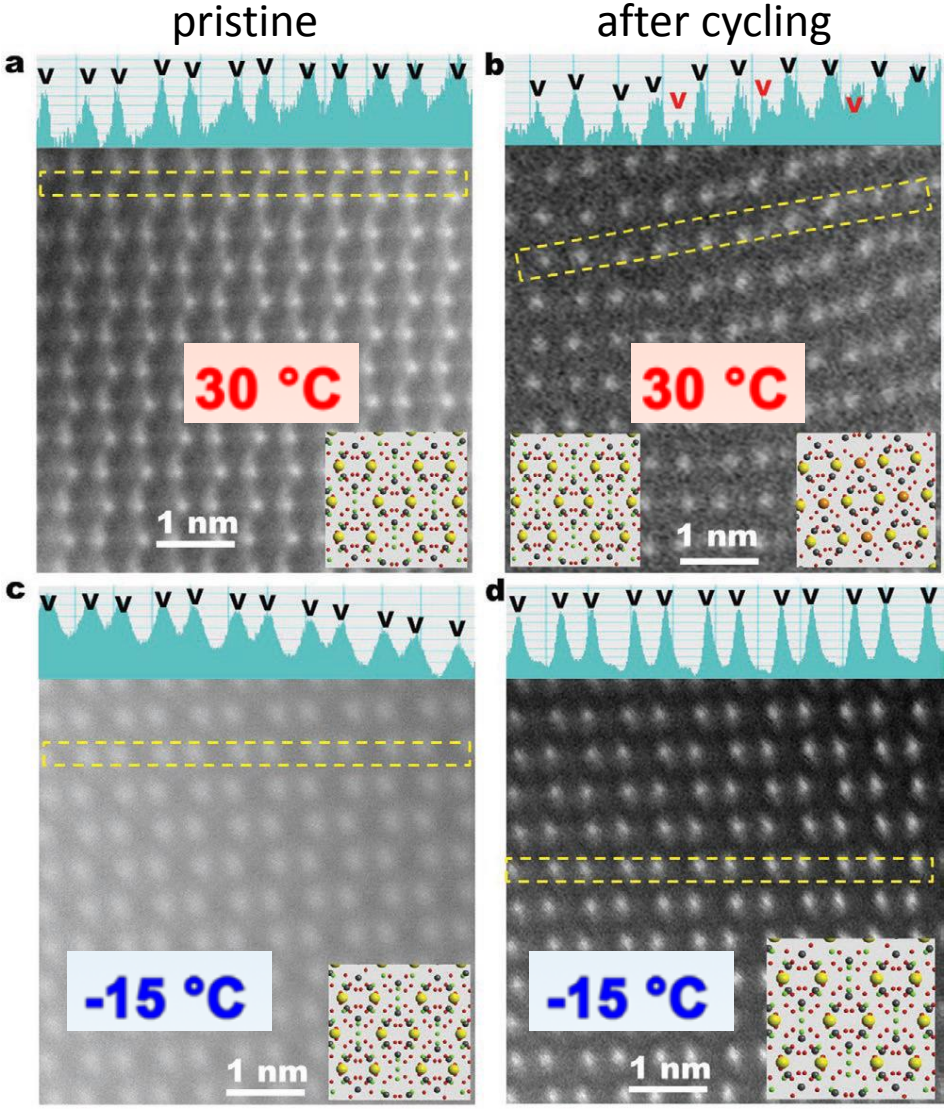
H. Gao, J. Am. Chem. Soc. 140 (2018) 18192–18199.

J. Zhang, Adv. Mater. 32 (2020) 1–8.

$Na_3VCr(PO_4)_3$: V–to–Na1 site migration

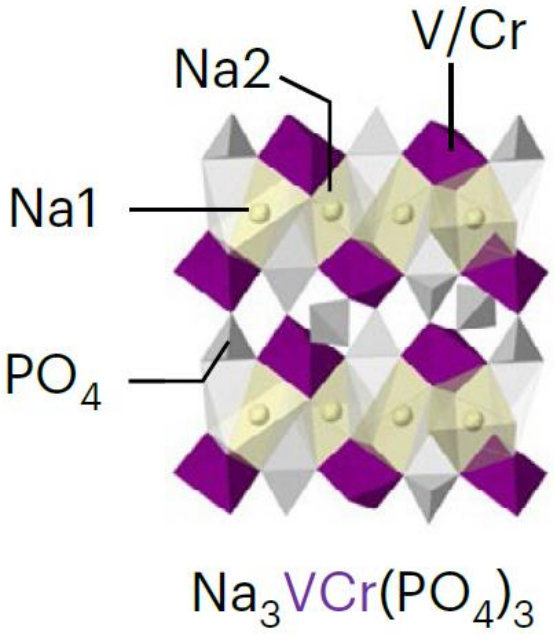


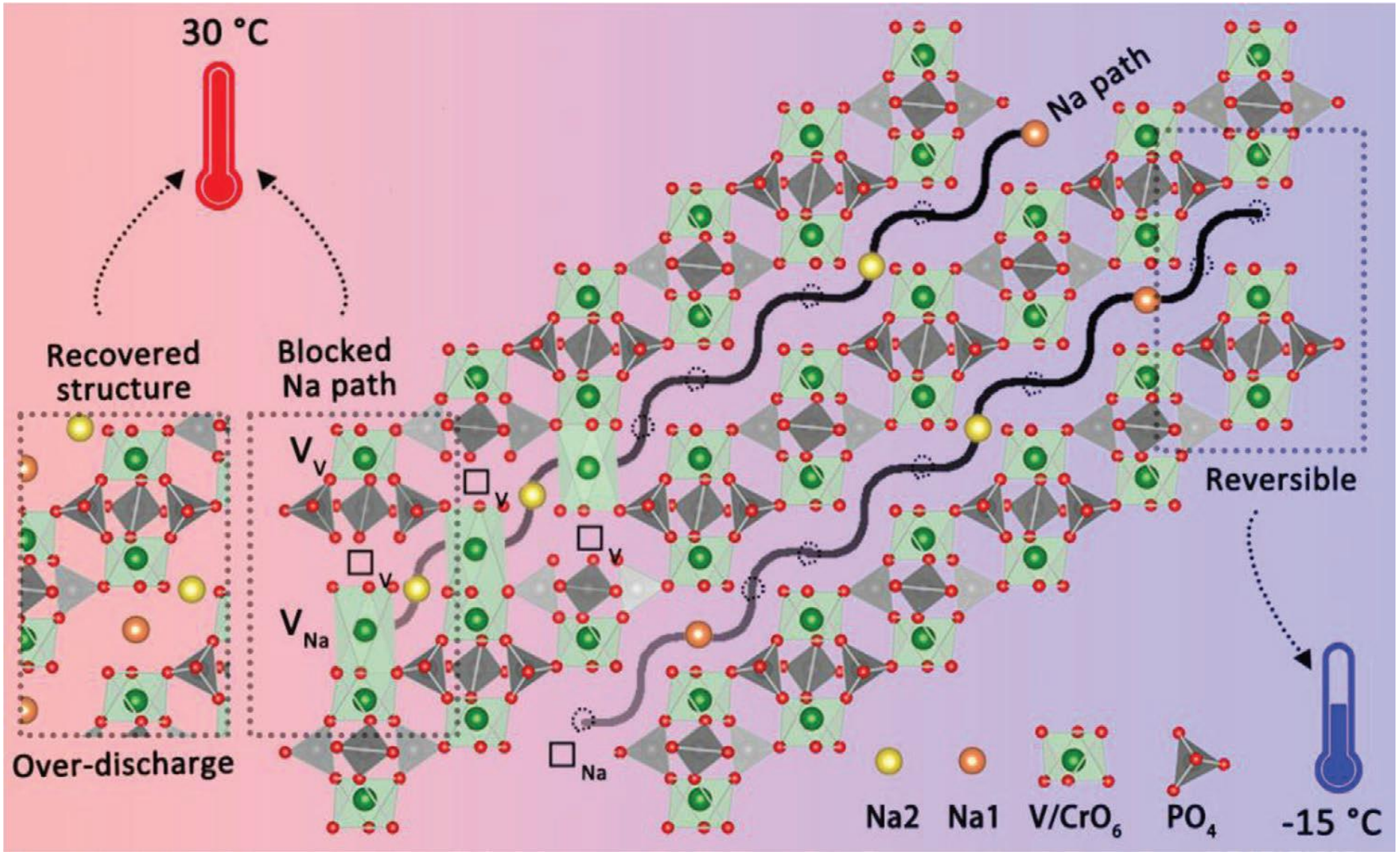
R. Liu // ACS Appl. Mater. Interfaces. 9 (2017) 43632–43639



R. Liu // *Adv. Energy Mater.* **2021**, *11*, 2003256

$Na_3VCr(PO_4)_3$: V–to–Na1 site migration

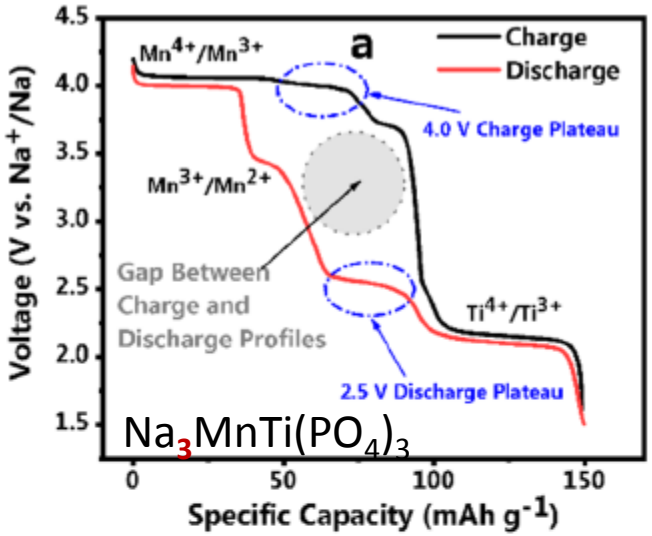


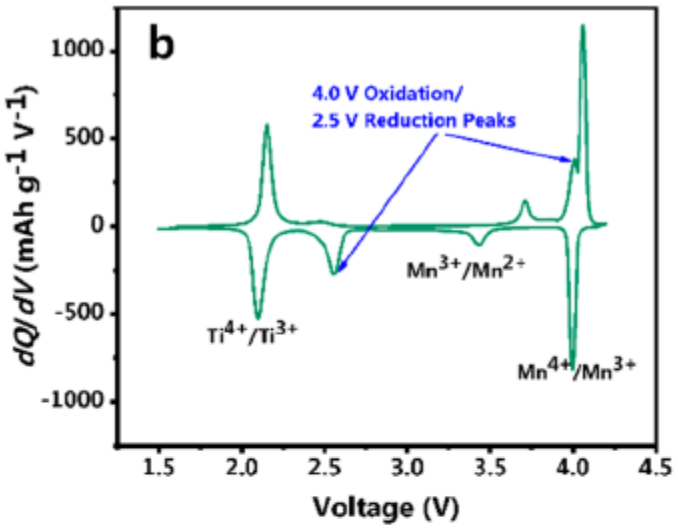


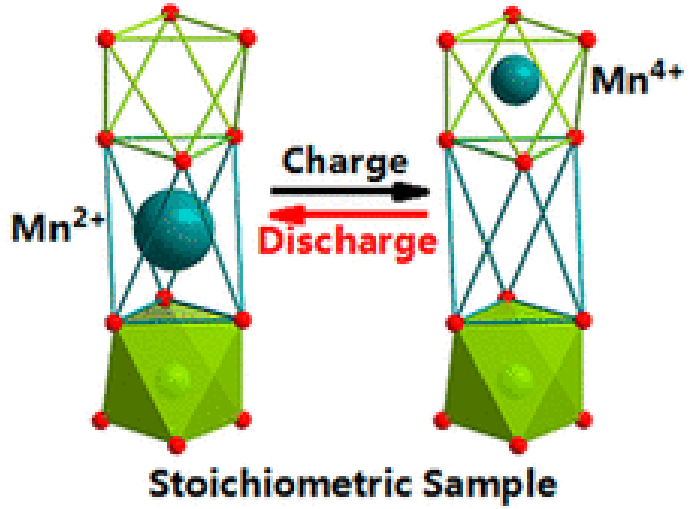
Y. Liu et al // *Nat Energy* **8**, 1088–1096 (2023)

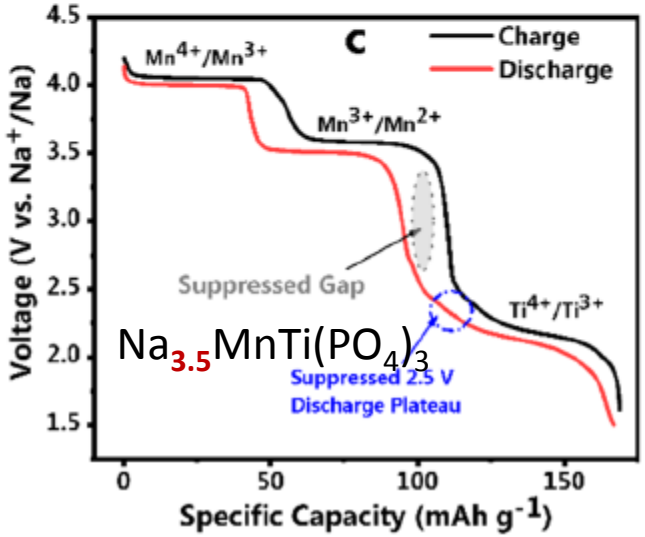
R. Liu // *Adv. Energy Mater.* **2021**, *11*, 2003256

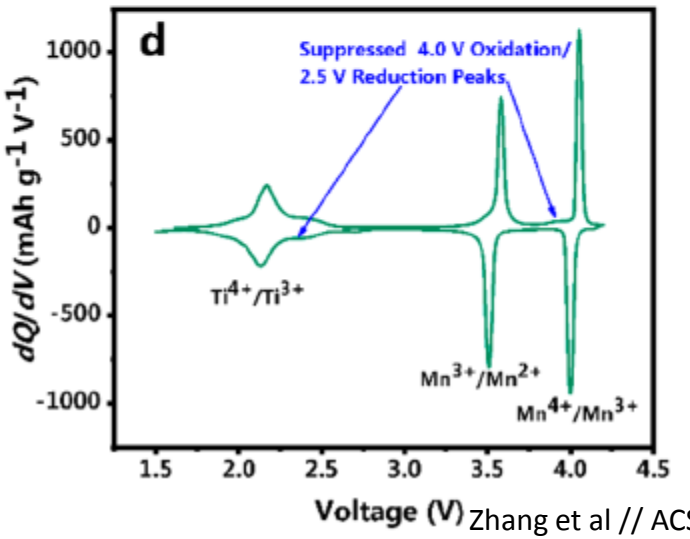
$Na_3MnTi(PO_4)_3$: Mn–to–Na site migration

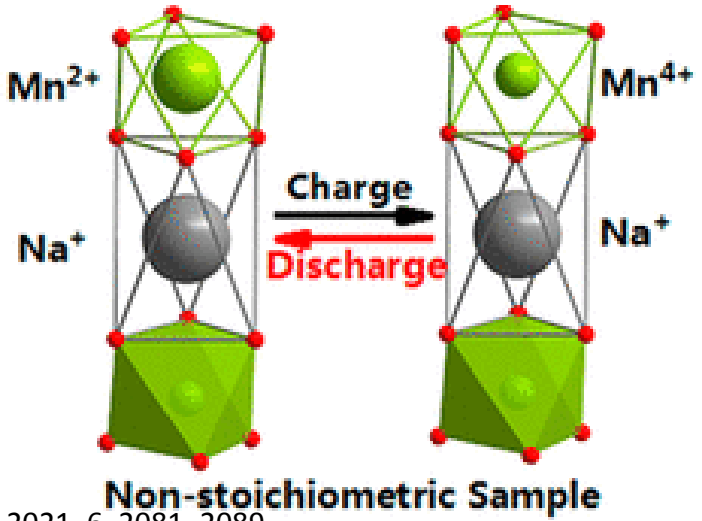






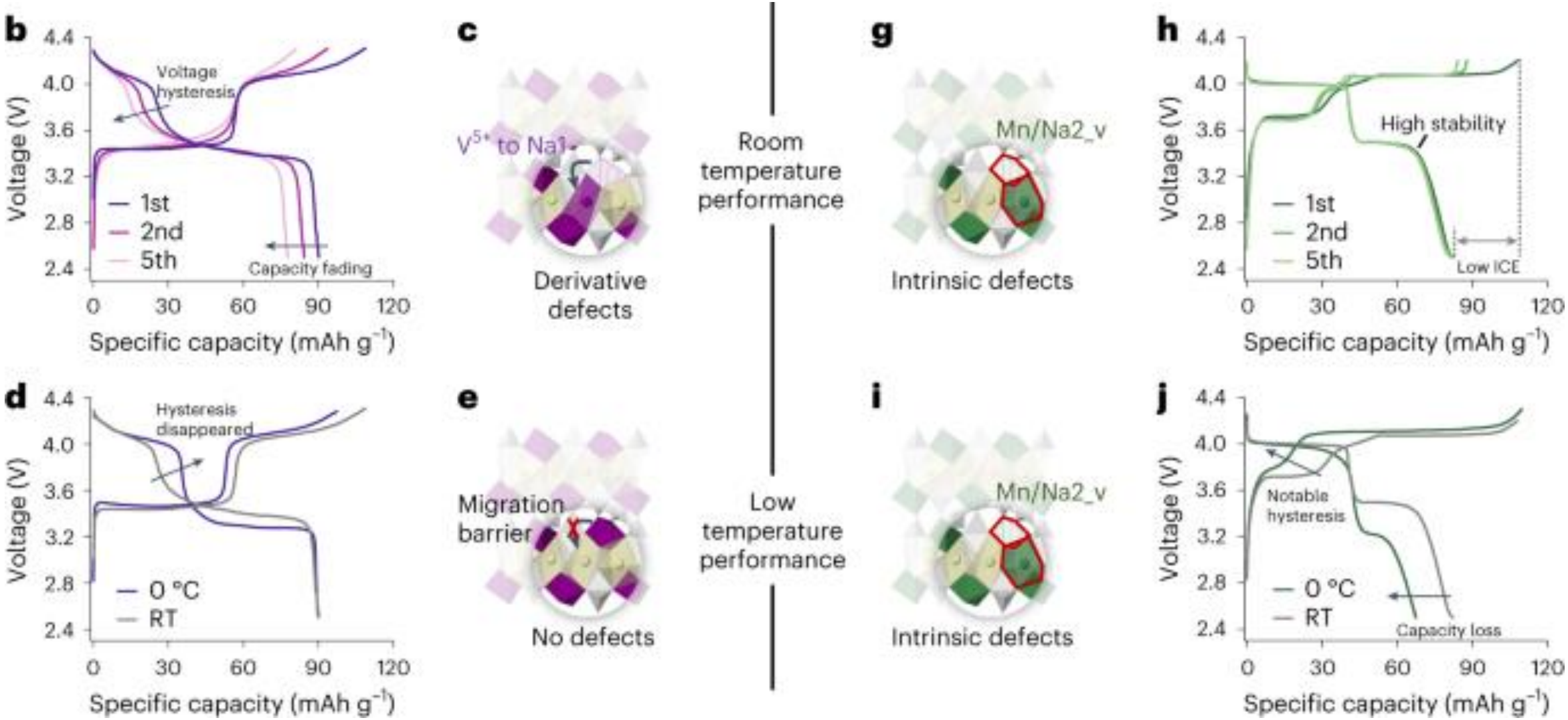






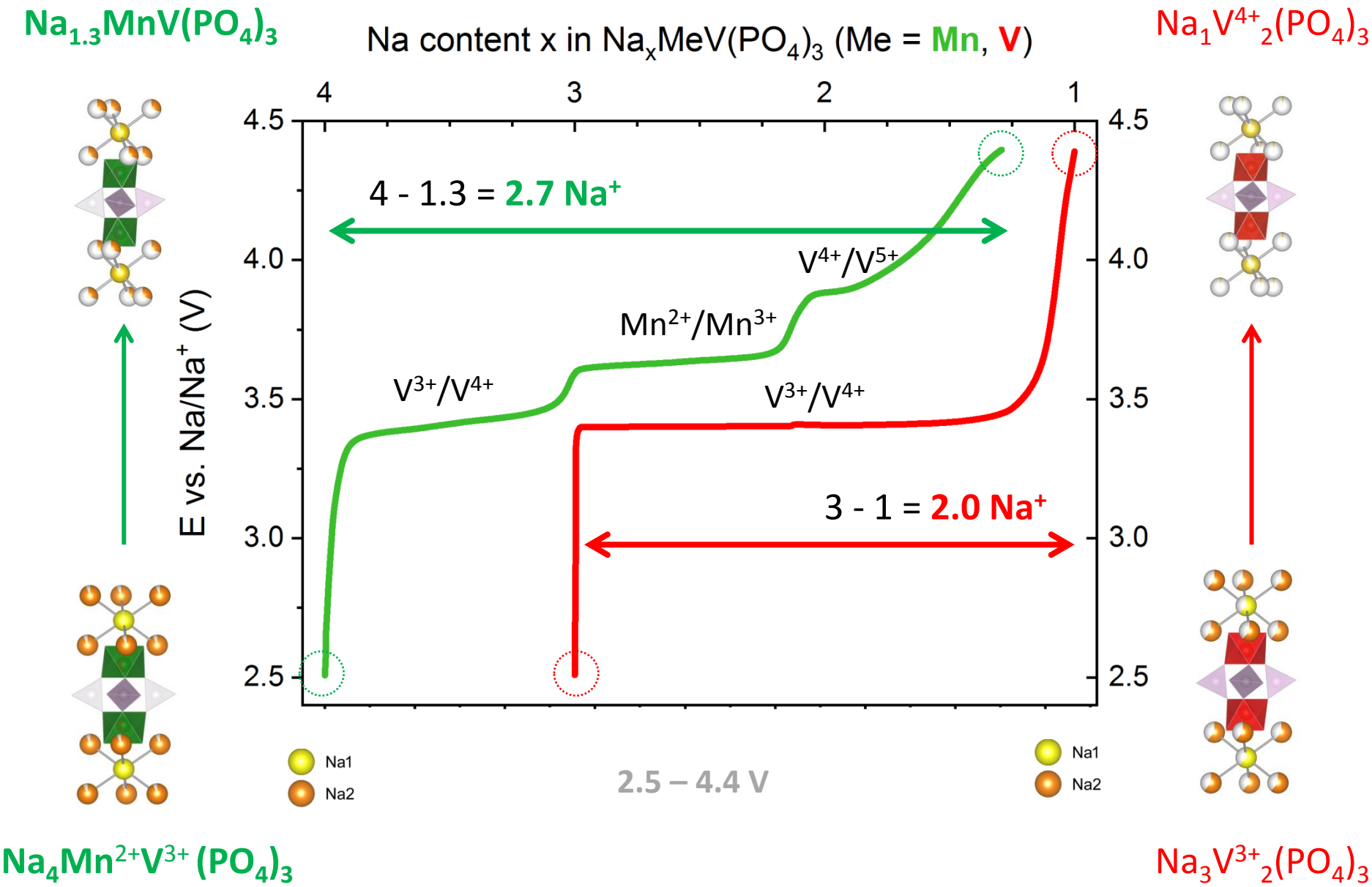
Zhang et al // ACS Energy Lett. 2021, 6, 2081−2089

$Na_3MnTi(PO_4)_3$: Mn–to–Na site migration

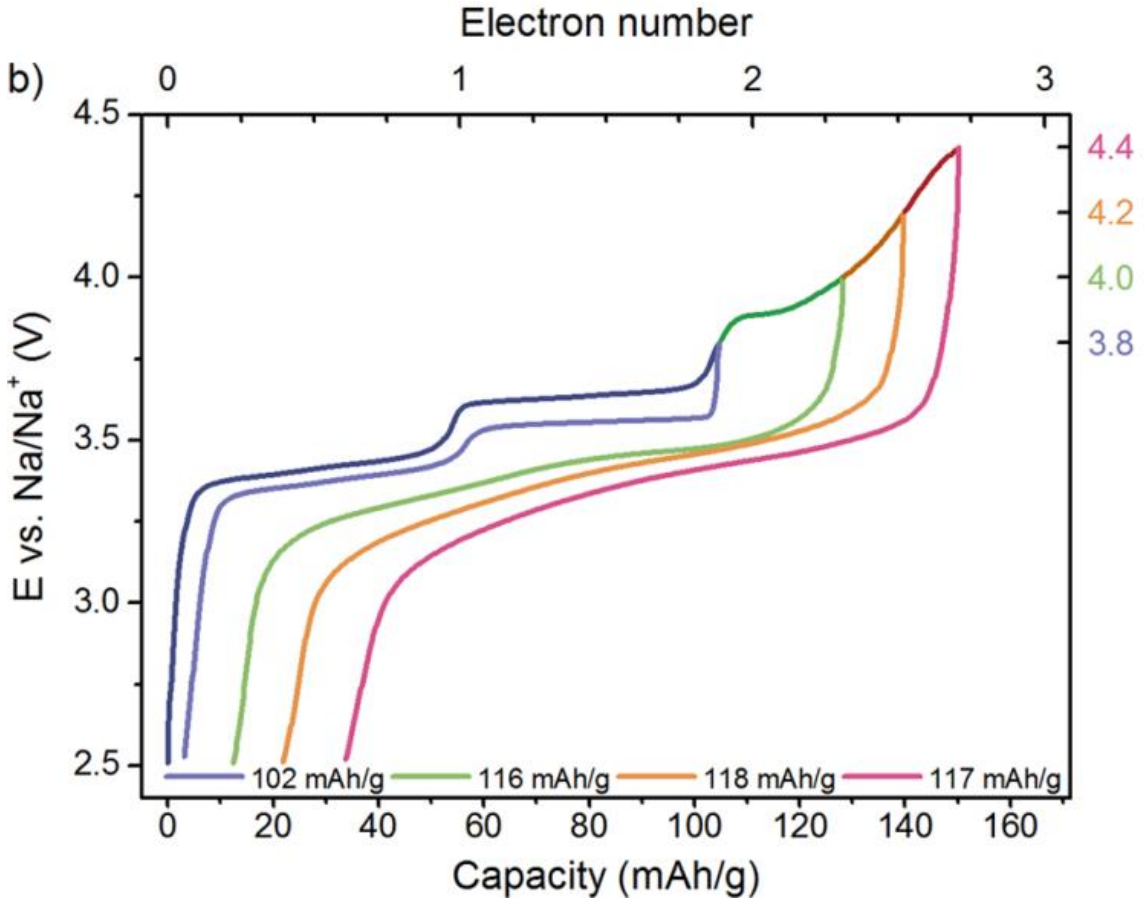


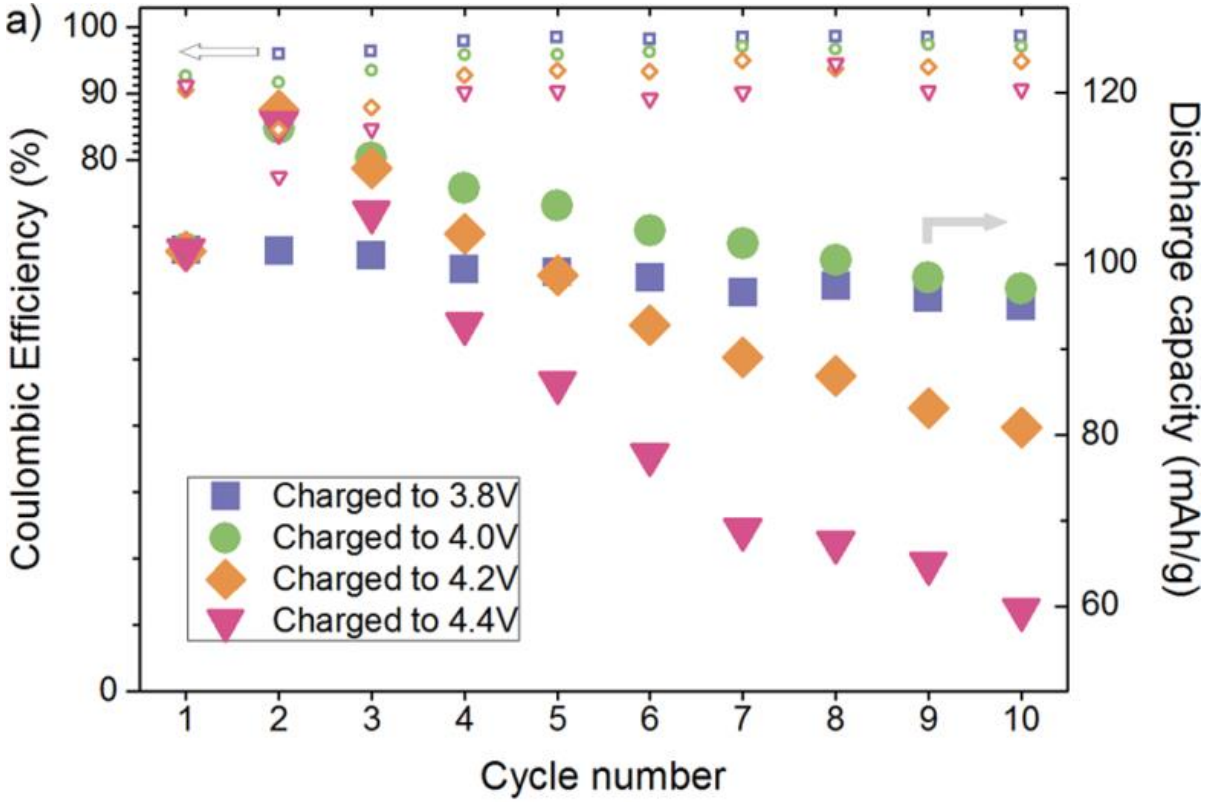
Liu et al // *Nat Energy* **8**, 1088–1096 (2023)

$Na_4MnV(PO_4)_3$ has higher average potential



$Na_4MnV(PO_4)_3$: cut-off voltage dependence





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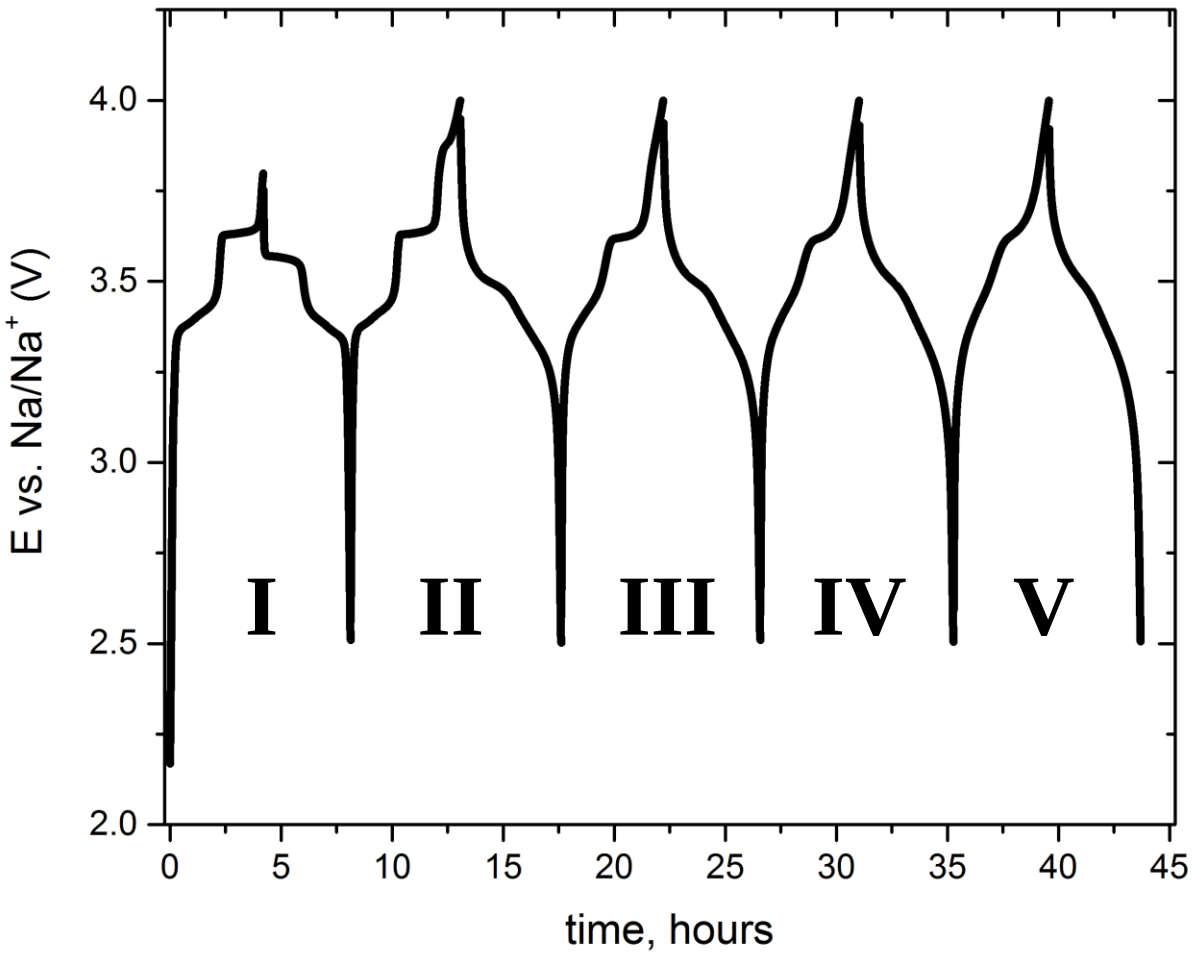
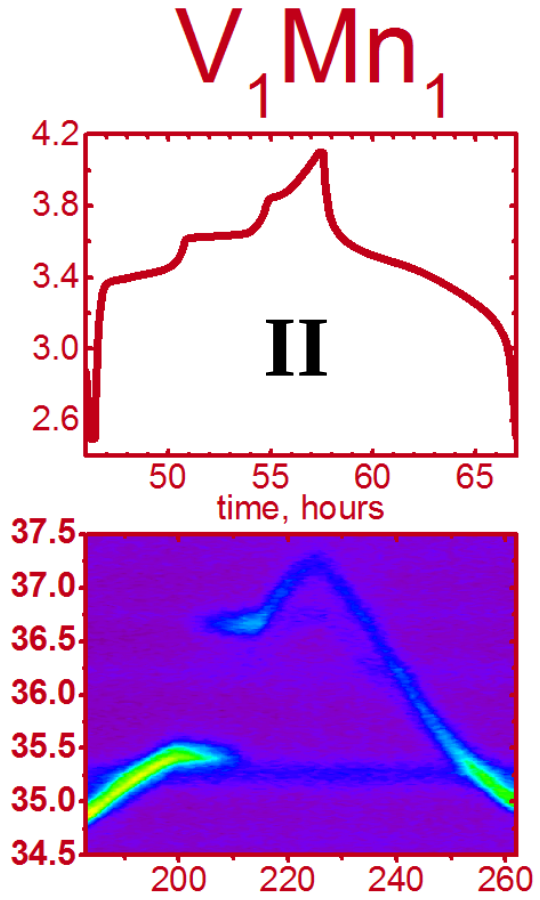
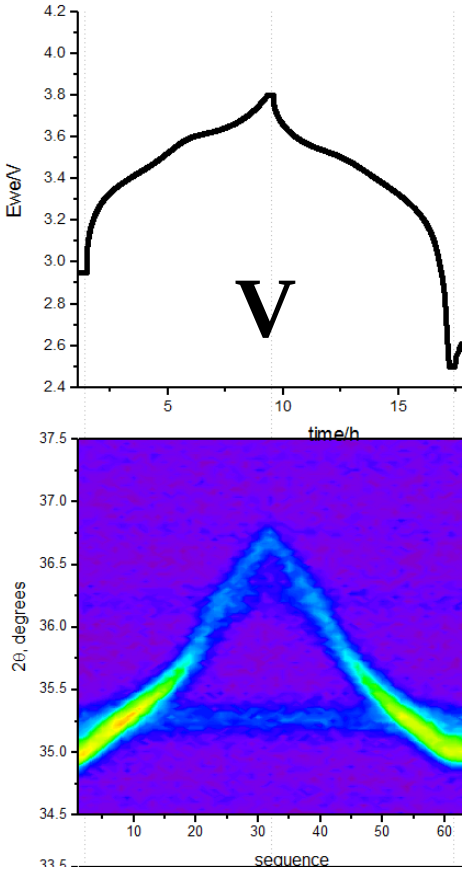
$Na_4MnV(PO_4)_3$: transformations during cycling



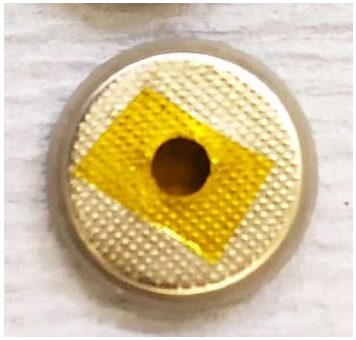


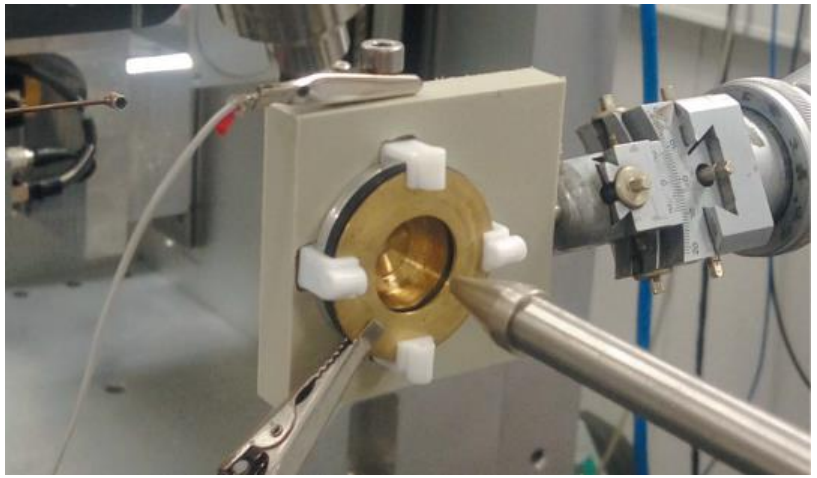


Zakharkin et al // ACS Applied Energy Materials, 2018, 11 (1), p 5842-5846

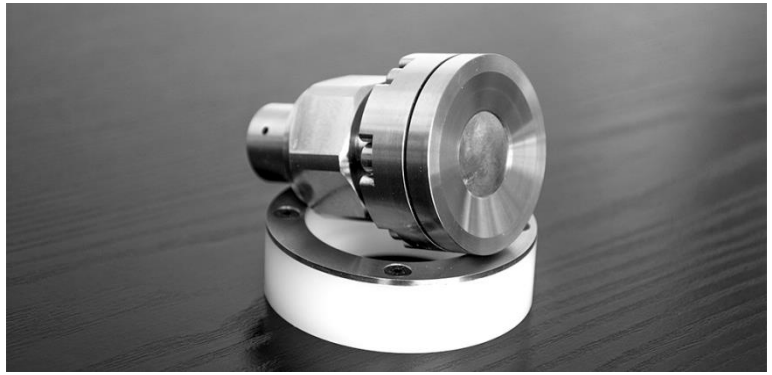
$Na_4MnV(PO_4)_3$: operando cells

V.V. Shapovalov, et al. //
Radiation Physics and Chemistry
175 (2018) 108065





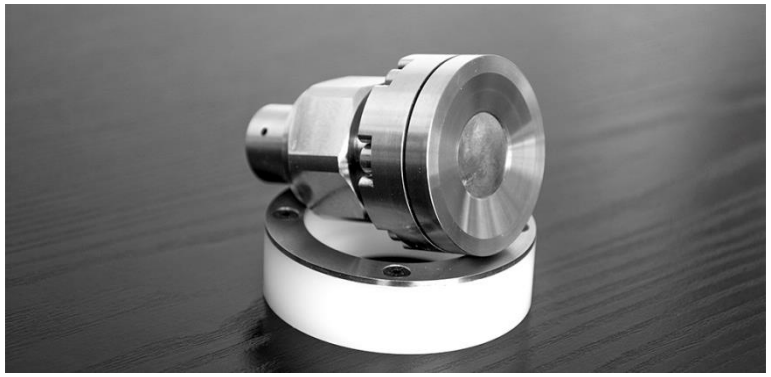
Drozhzhin et. al. // J. Synchrotron Rad. (2018) 25, 468–472

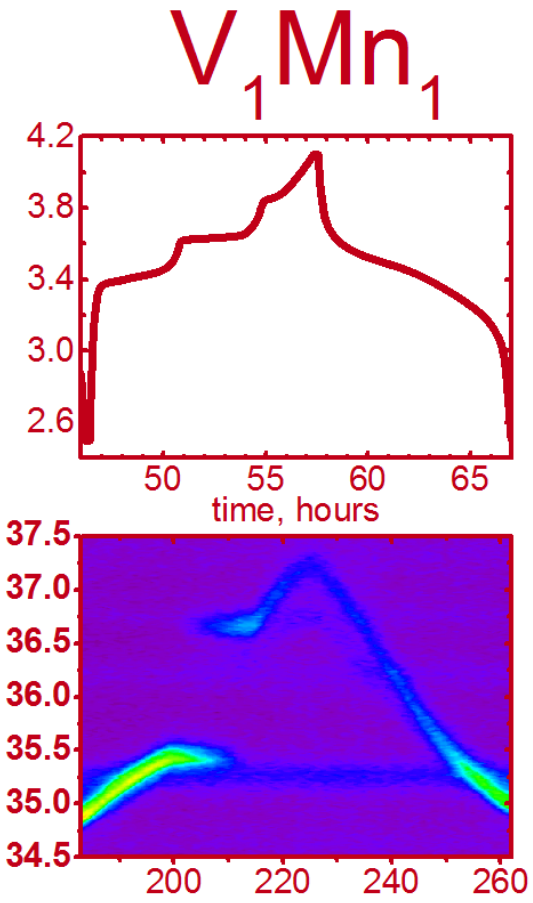


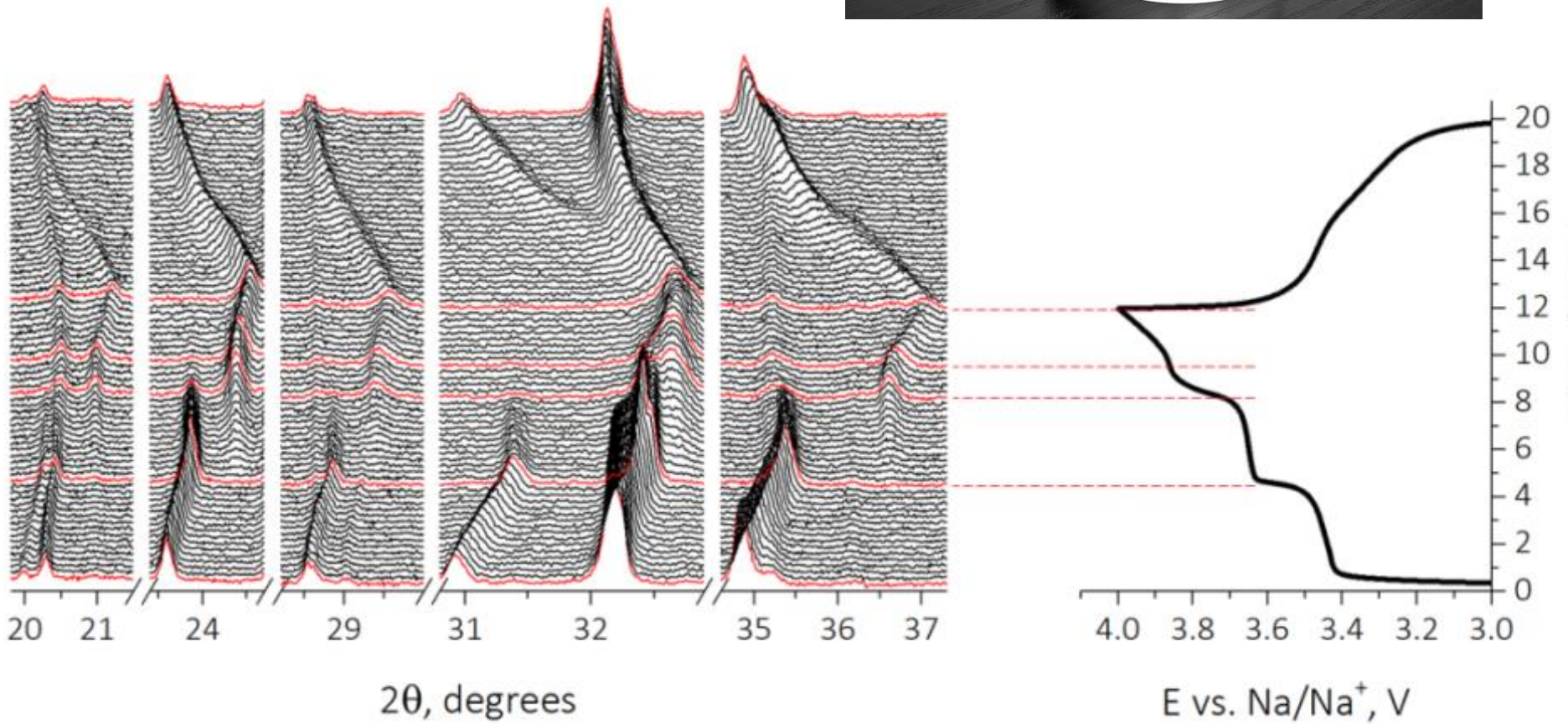
J.B. Leriche et al //
J. Electrochem. Soc. 157
(2010) A606

$Na_4MnV(PO_4)_3$: stack vs map

J.B. Leriche et al //
J. Electrochem. Soc. 157
(2010) A606

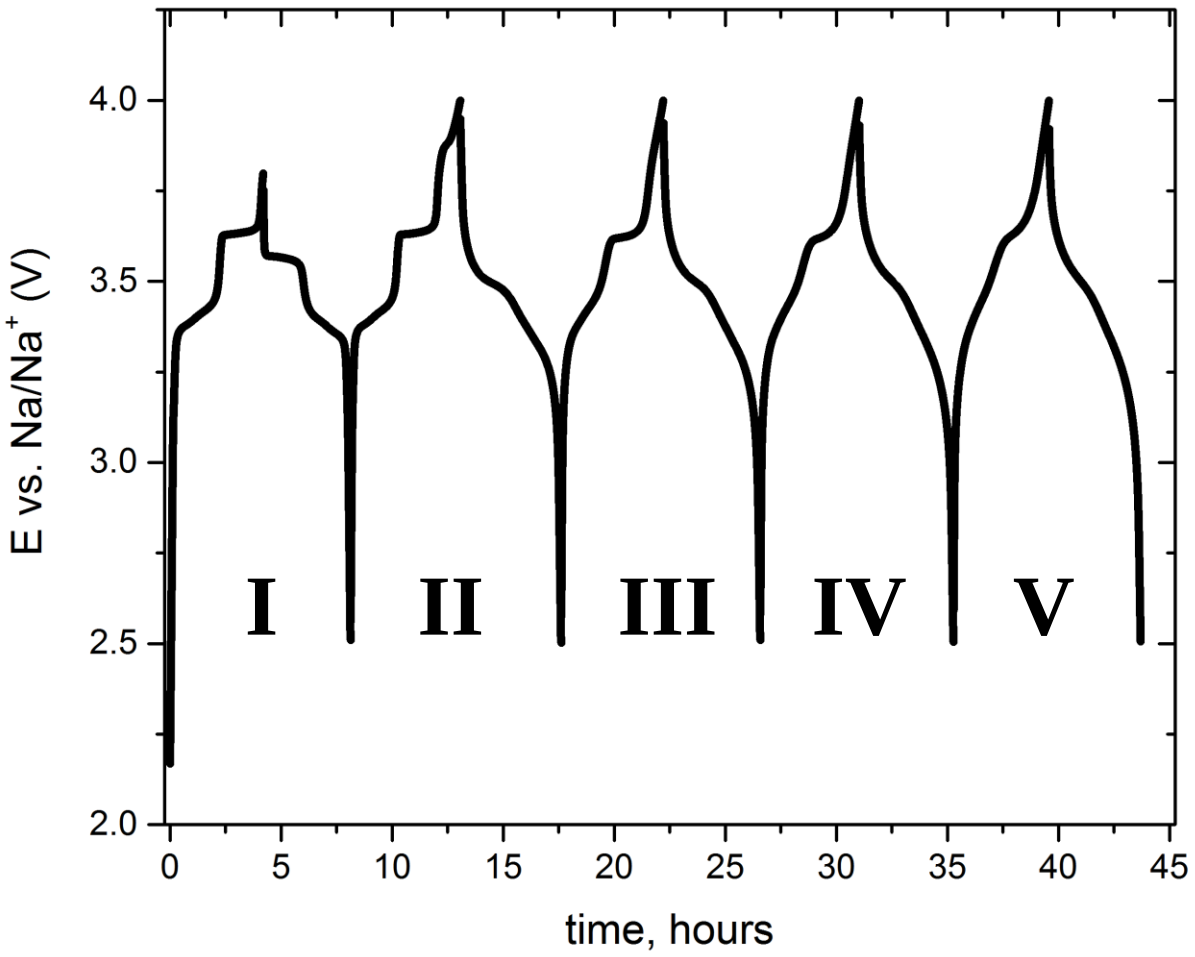


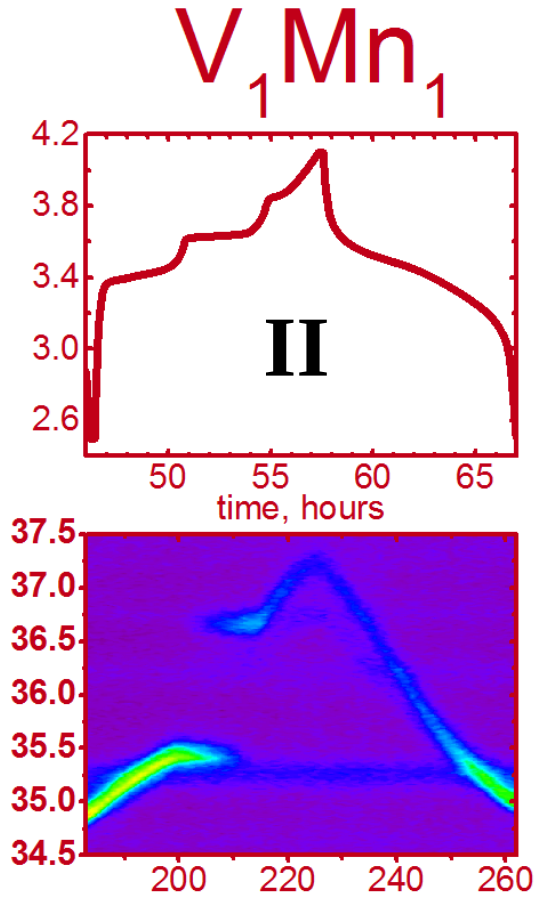


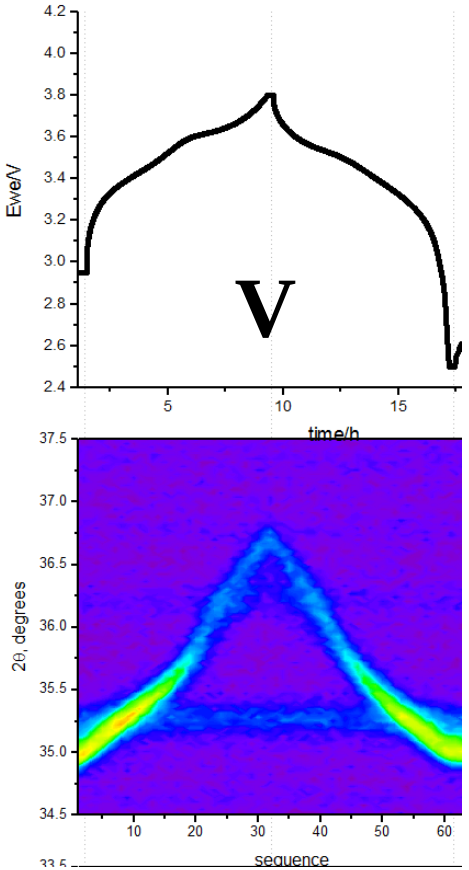


Zakharkin et al // Journal of Power Sources 470 (2020) 228231

$Na_4MnV(PO_4)_3$: transformations during cycling

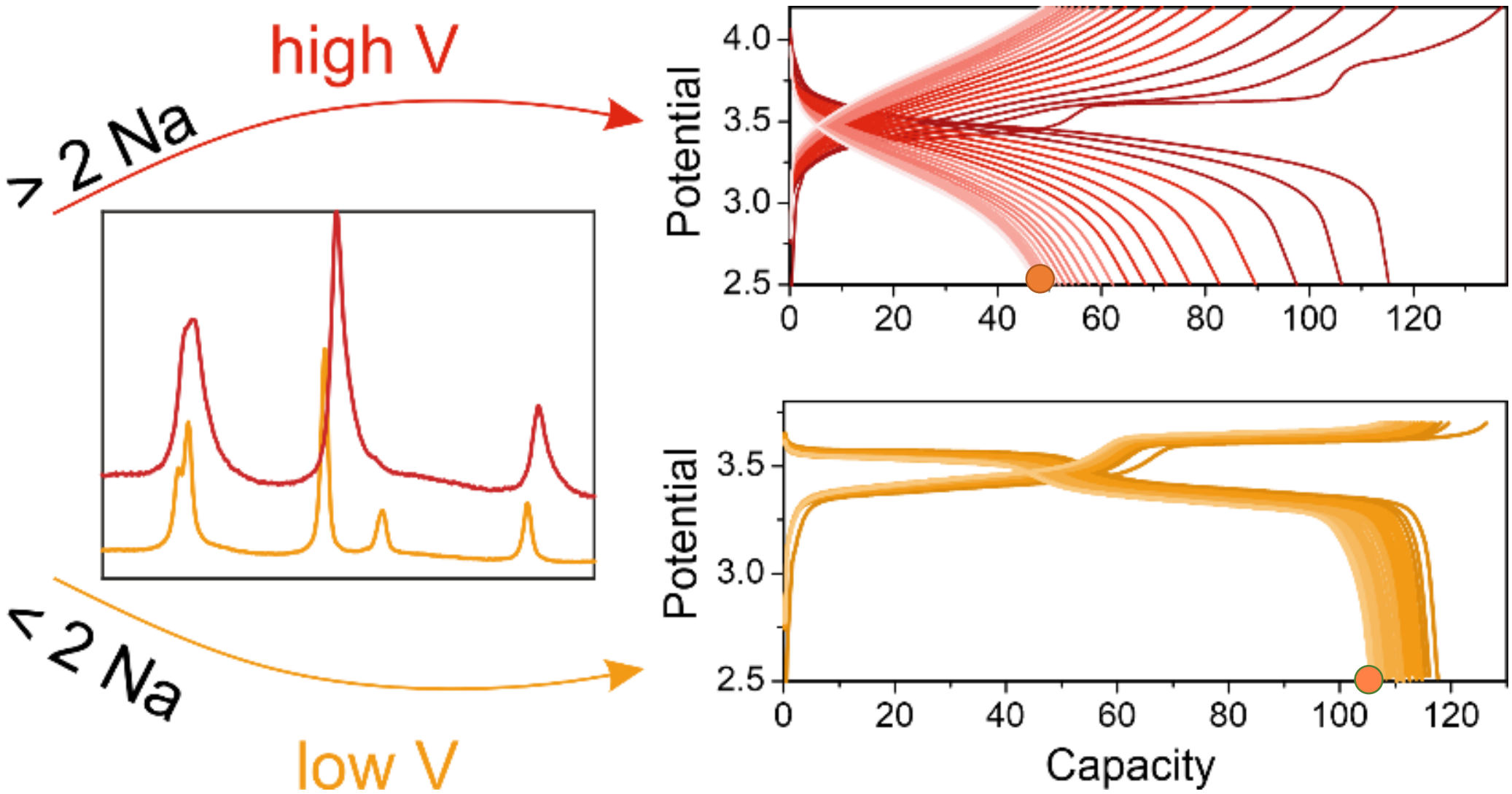






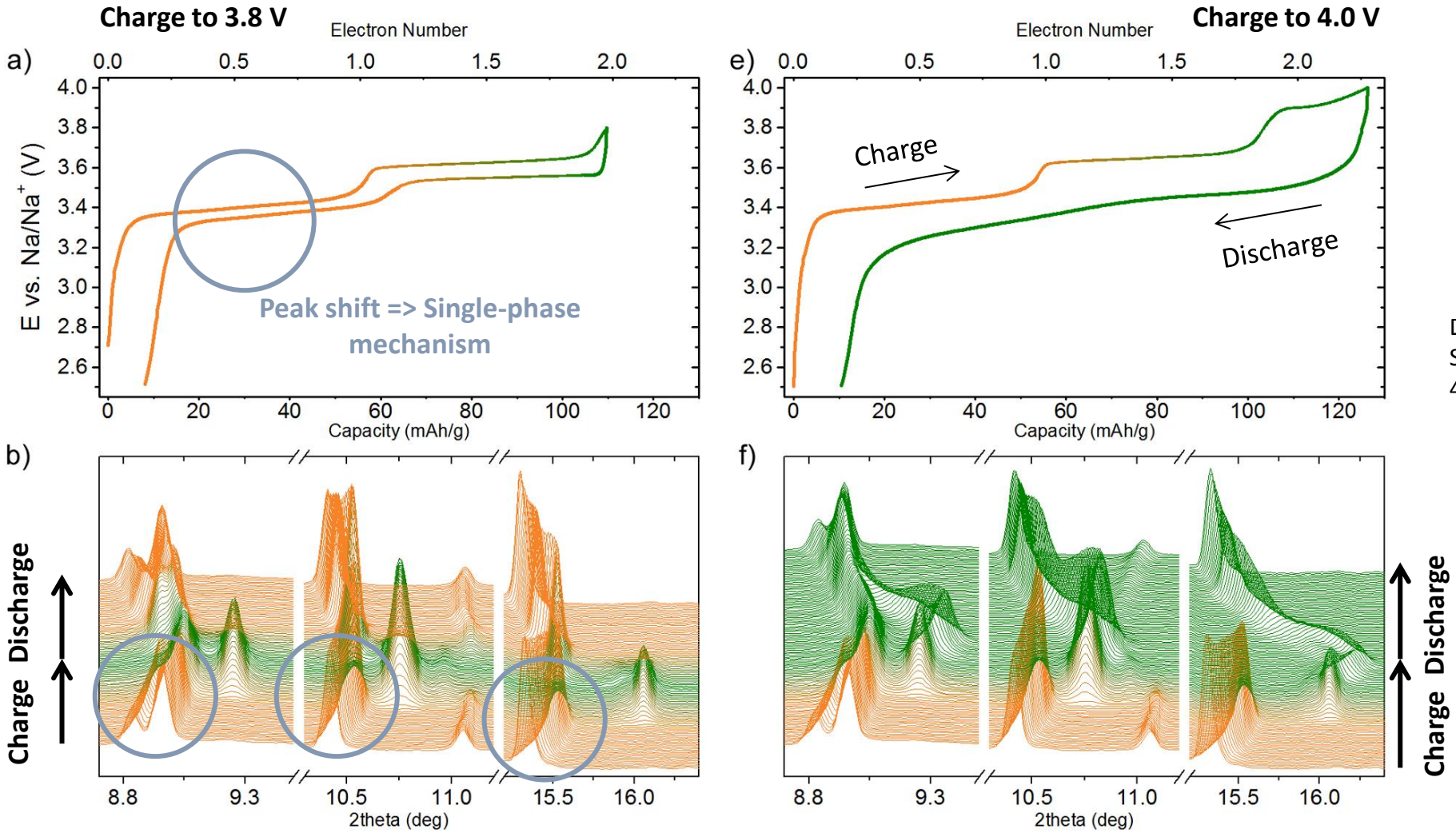
Zakharkin et al // ACS Applied Energy Materials, 2018, 11 (1), p 5842-5846

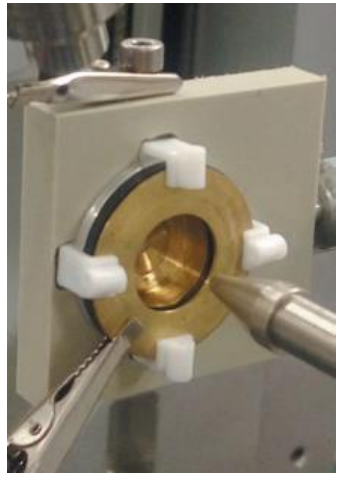
$Na_4MnV(PO_4)_3$: transformations during cycling



Buryak et al // Journal of Power Sources 518 (2022) 230769

$Na_4MnV(PO_4)_3$: transformations during cycling





Drozhzhin et. al. // J. Synchrotron Rad. (2018) 25, 468–472

Zakharkin et al // ACS Applied Energy Materials, 2018, 11 (1), p 5842-5846

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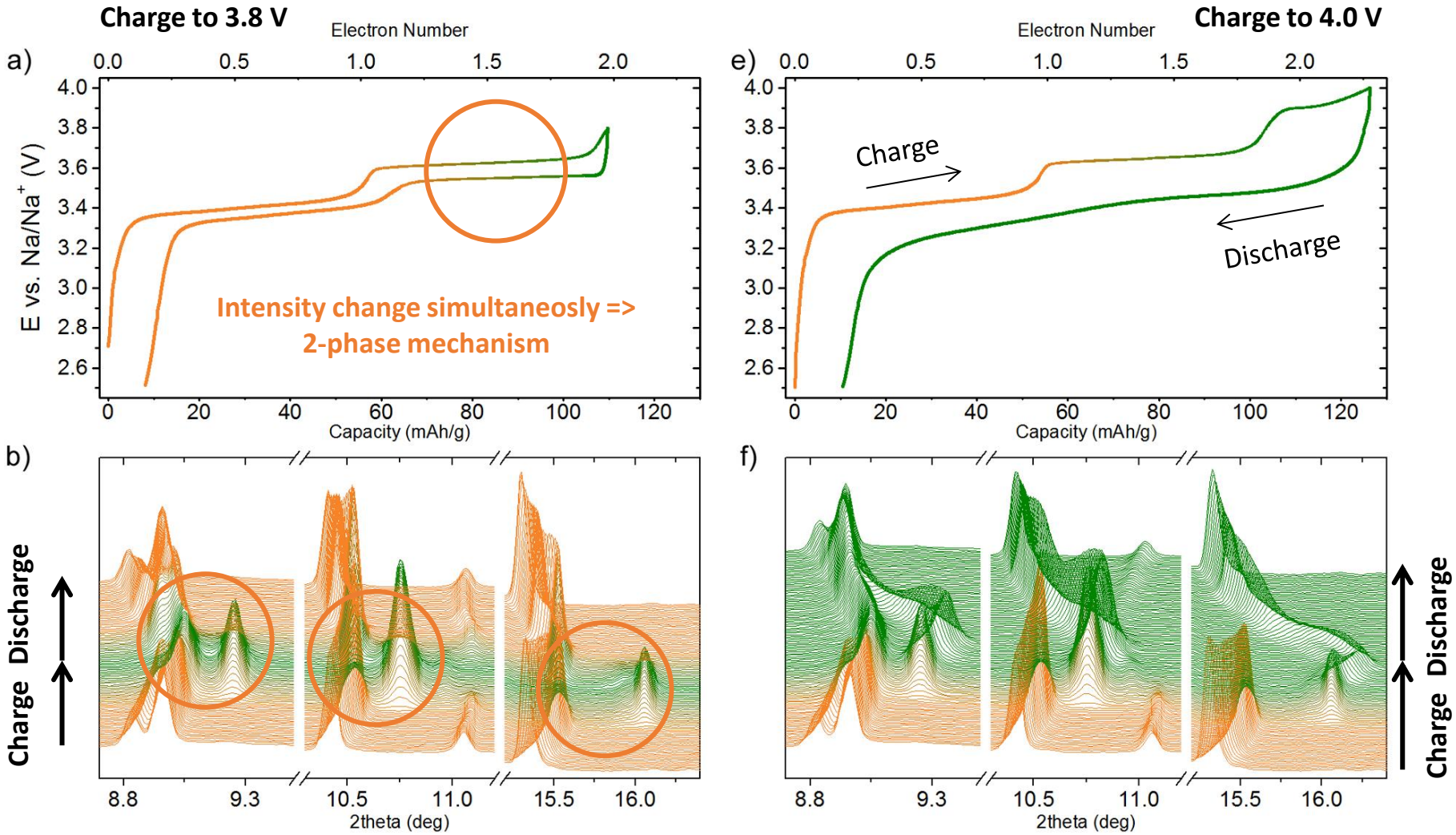

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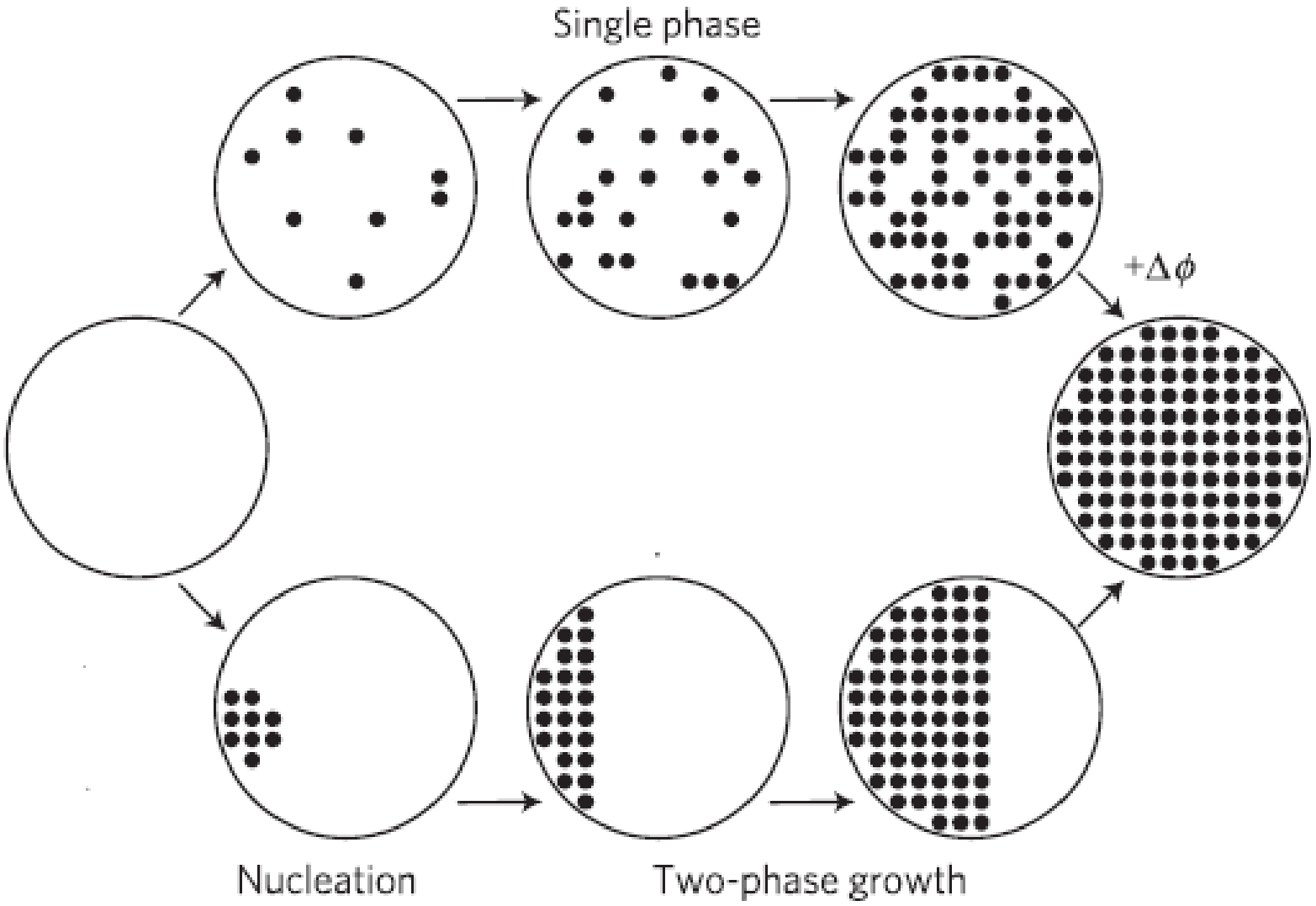
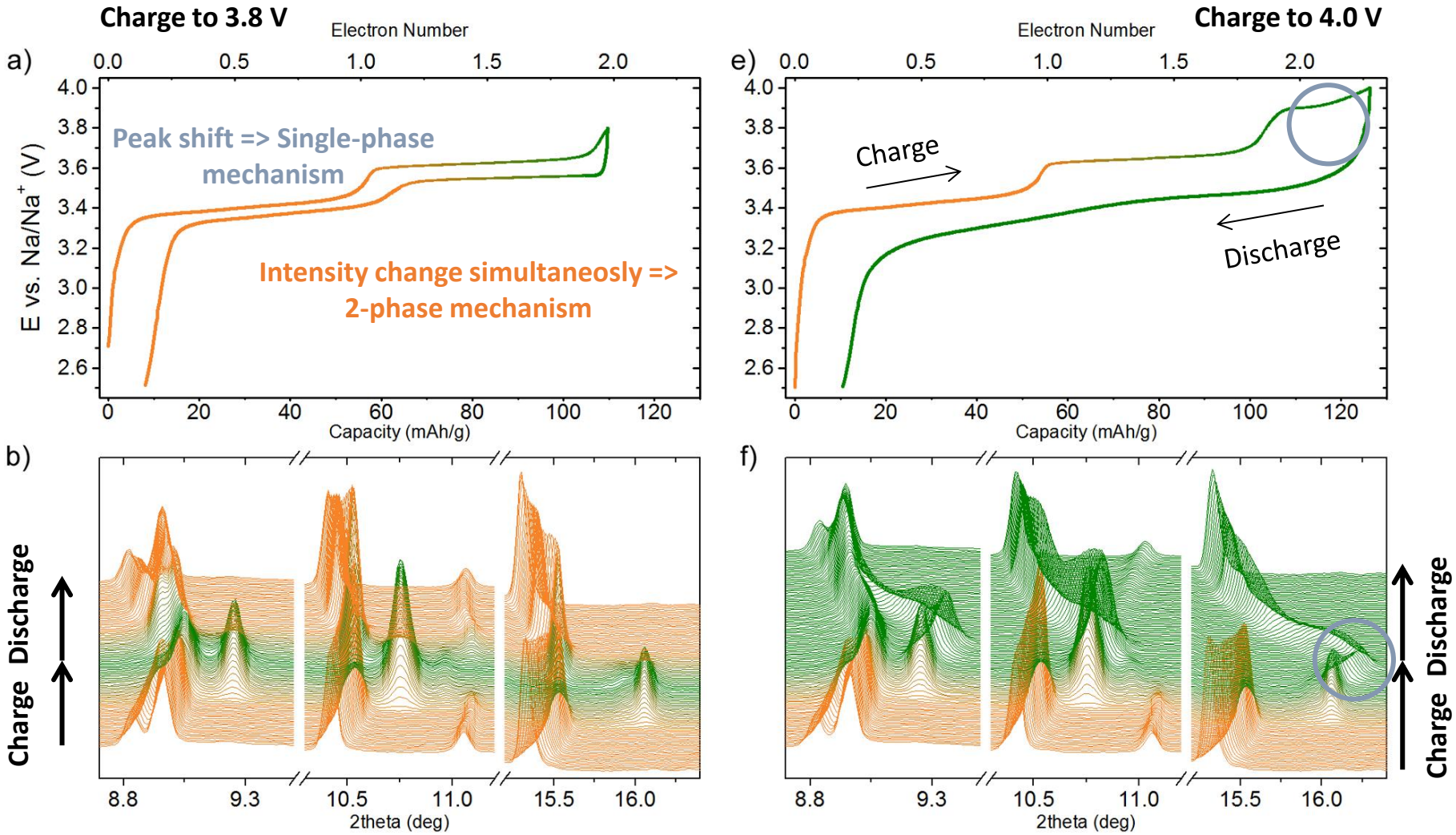
Insertion mechanisms



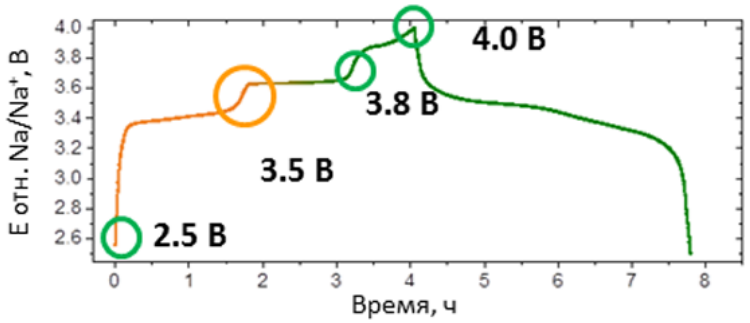
Malik, Ceder // Journal of The Electrochemical Society, 160 (5) A3179-A3197 (2013)

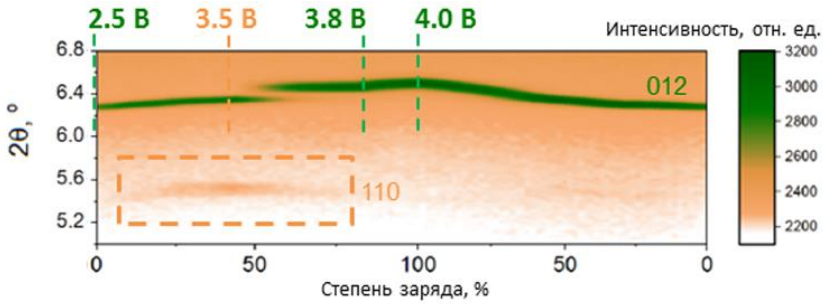
$Na_4MnV(PO_4)_3$: transformations during cycling

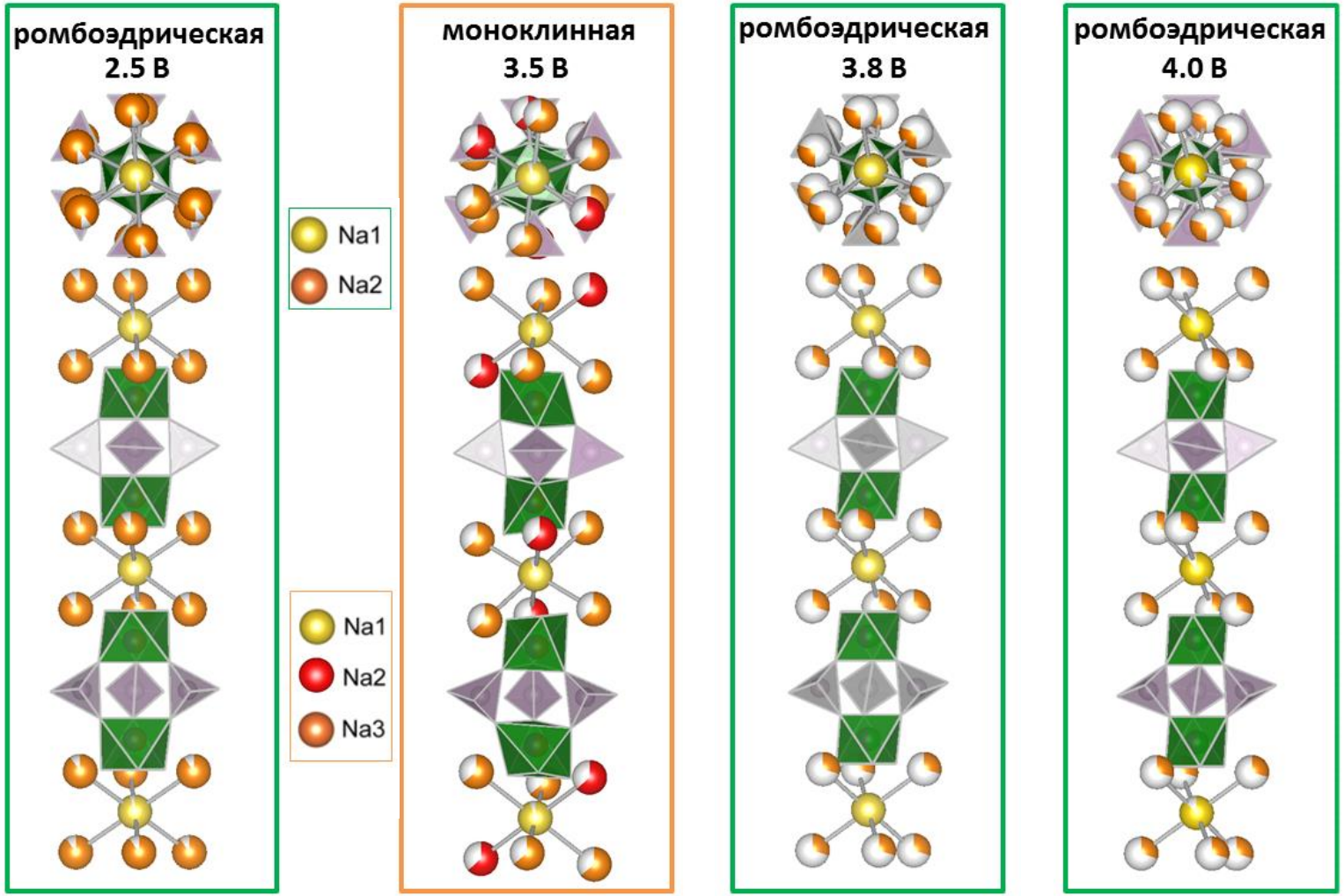


Zakharkin et al // ACS Applied Energy Materials, 2018, 11 (1), p 5842-5846

$Na_4MnV(PO_4)_3$: transformations during cycling







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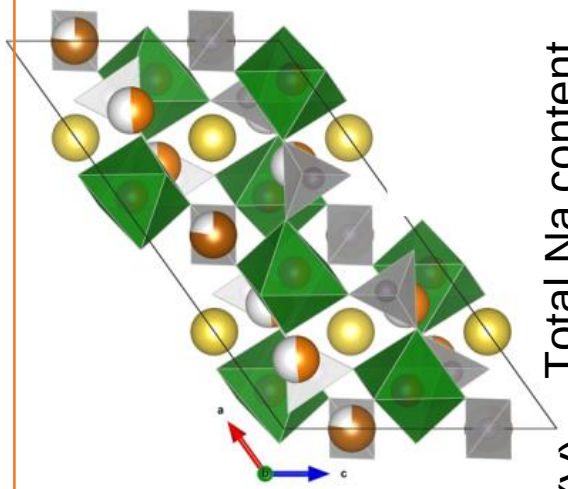
$Na_4MnV(PO_4)_3$: transformations during cycling

monoclinic phase



Na1
Na2
Na3

Site occupation

Na1 m (*4d*)
Na2 m (*4e*)
Na3 m (*8f*)
Na1 rh (*6b*)
Na2 rh (*18e*)
Na sites occupation

Total Na content

Monoclinic
Rhombohedral
Na content x in $Na_xMnV(PO_4)_3$

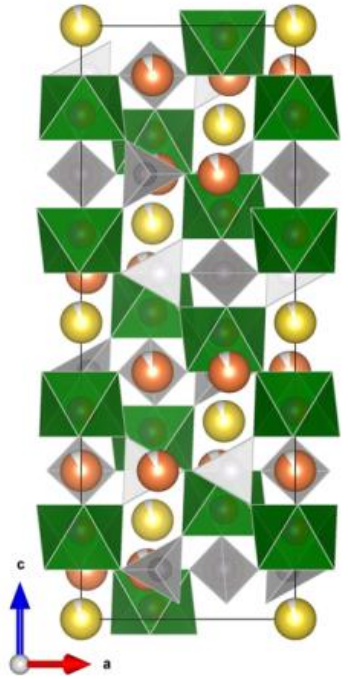
E vs. Na/Na^+ (V)

Na^+ deintercalation
Na^+ intercalation

Time, hours

Charge to 4.0 V

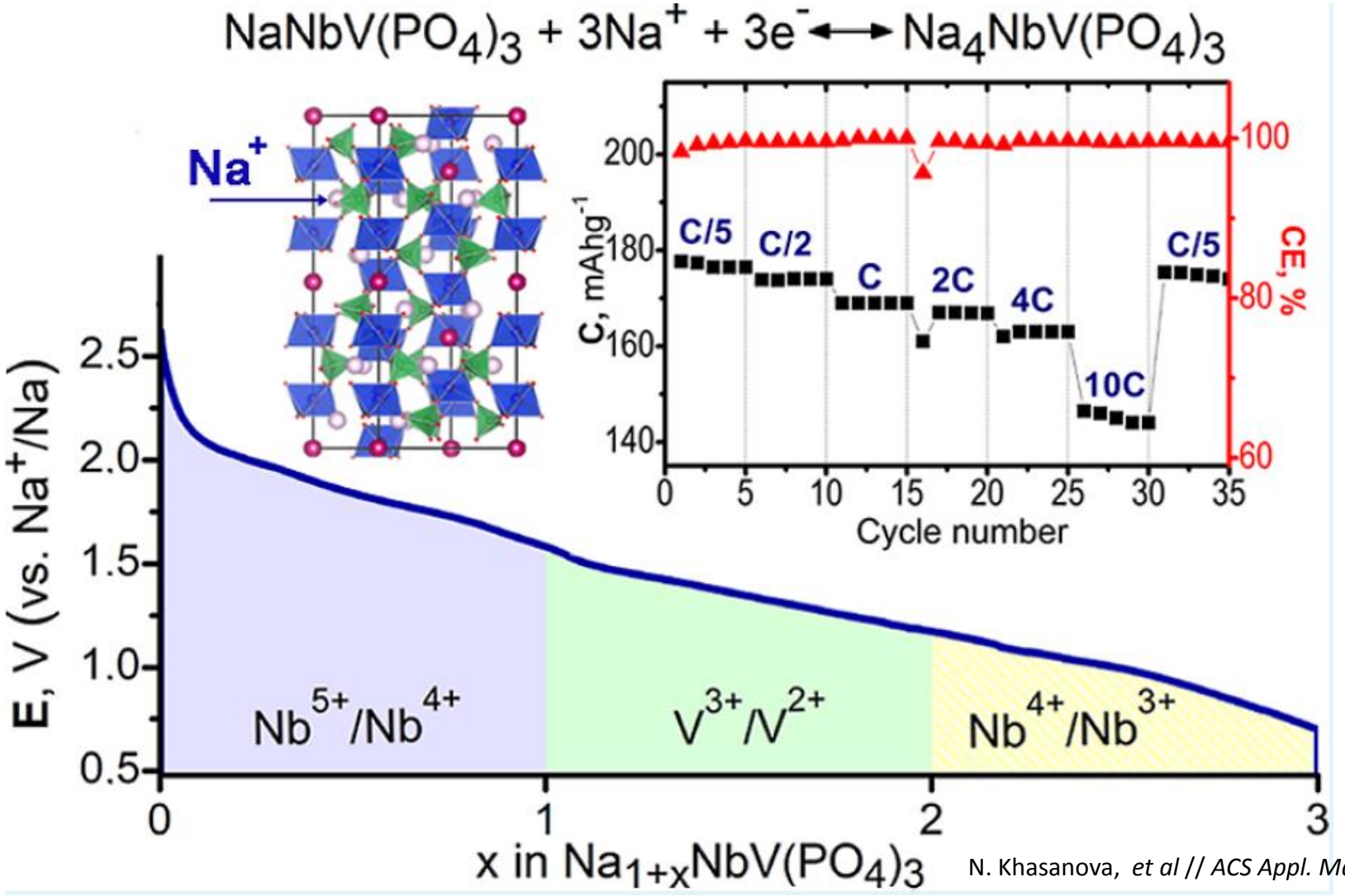
rhombohedral phase



Na1
Na2

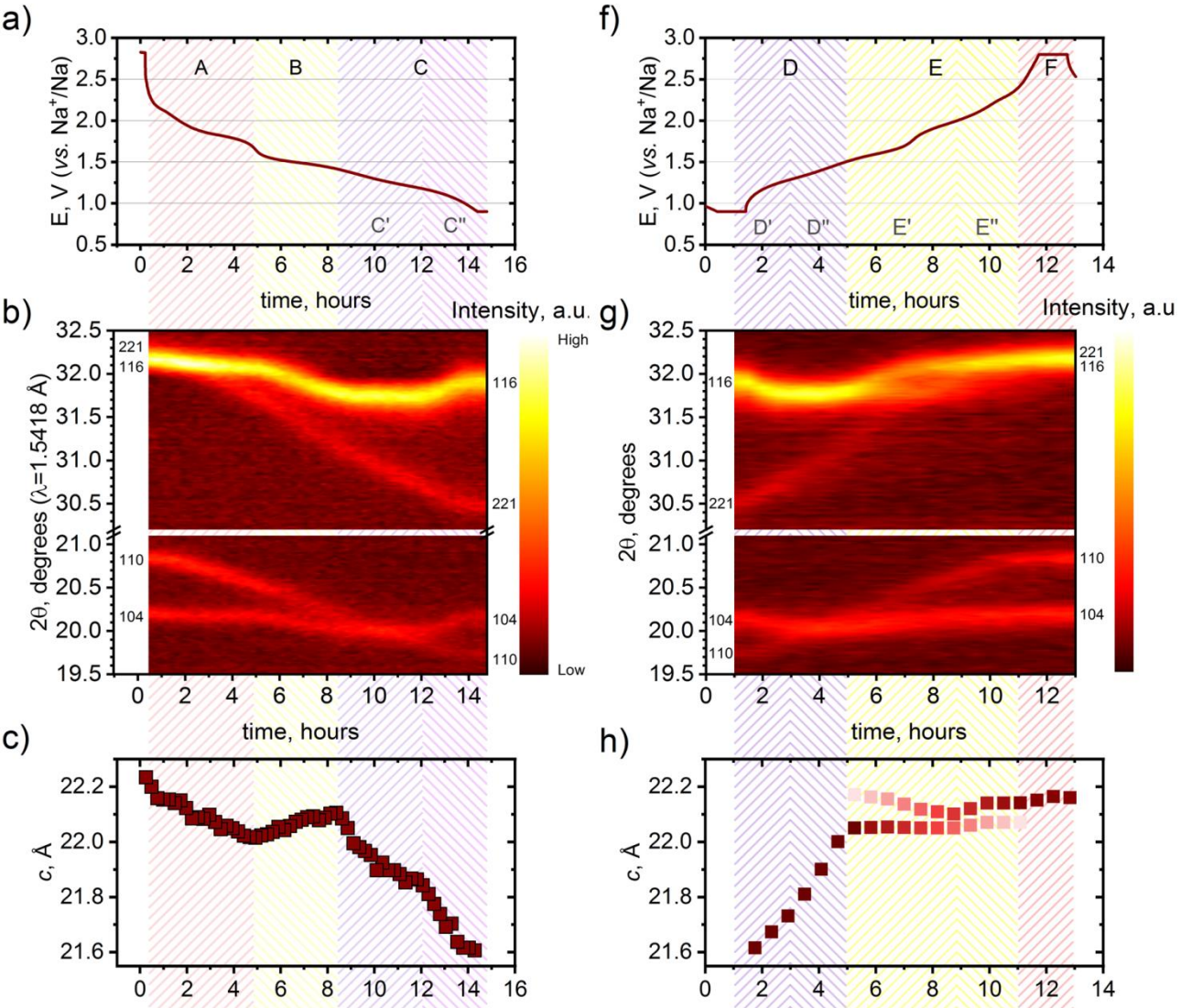
ACS Applied Energy Materials, 2018, 11 (1), p 5842-5846

$NaNbV(PO_4)_3$: 3 electron NASICON-type Anode

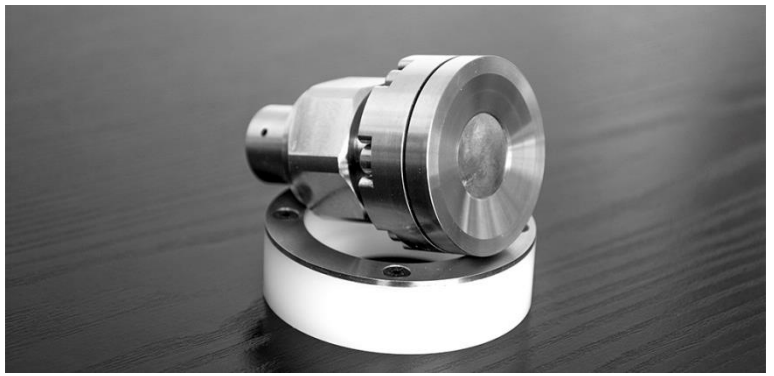


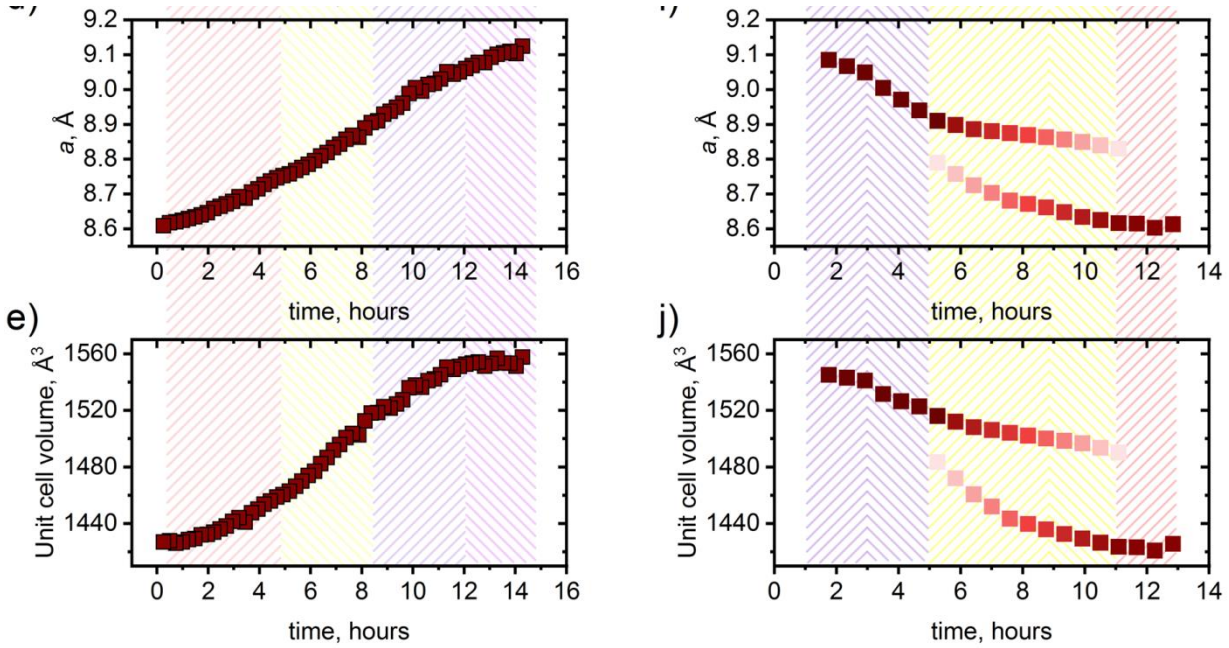
N. Khasanova, *et al* // *ACS Appl. Mater. Interfaces* **2023**, 15, 25, 30272–30280.

$NaNbV(PO_4)_3$:transformations during cycling



J.B. Leriche et al // J. Electrochem. Soc. 157 (2010) A606





N. Khasanova, *et al // ACS Appl. Mater. Interfaces* **2023**, 15, 25, 30272–30280.

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- Export structure to ▸
- CIF utilities ▸
- Structure ▸
- Import model from ▸
- Reflection file ▸
- Cyclic refinement ▸ (New / Open)
- Exit

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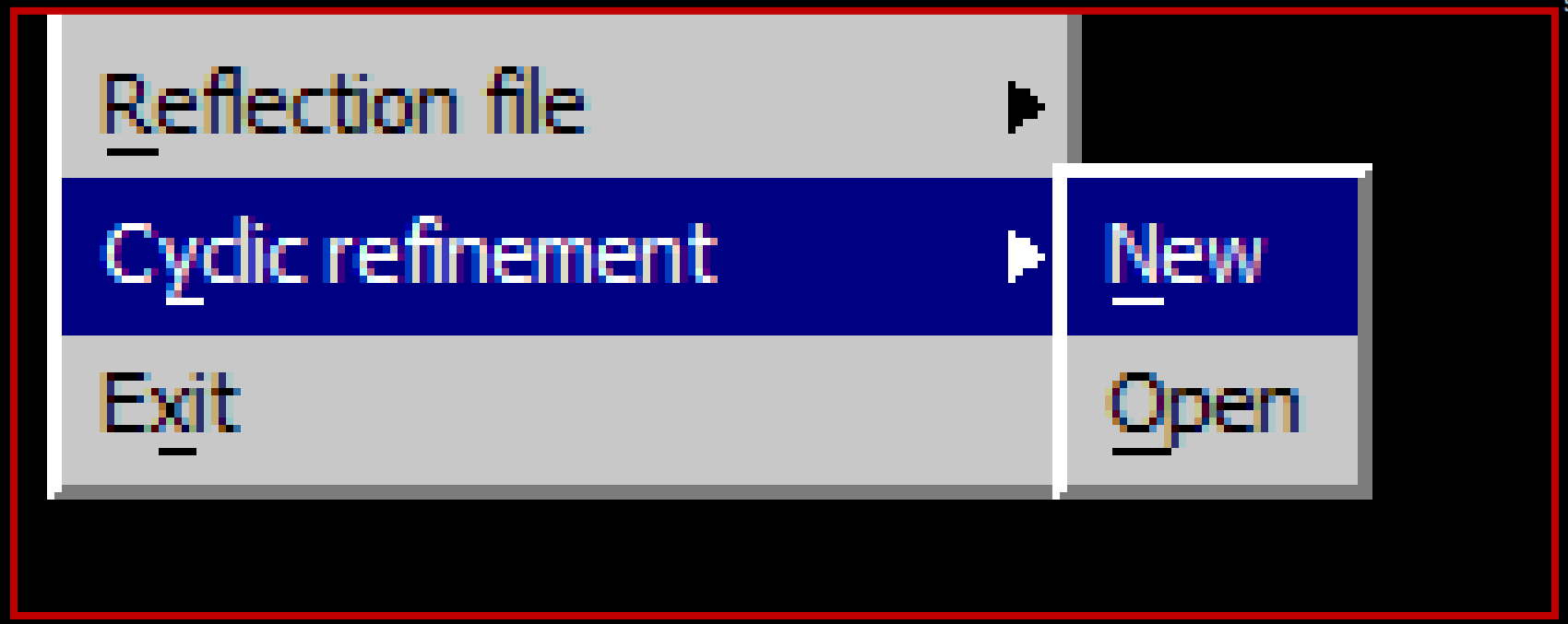
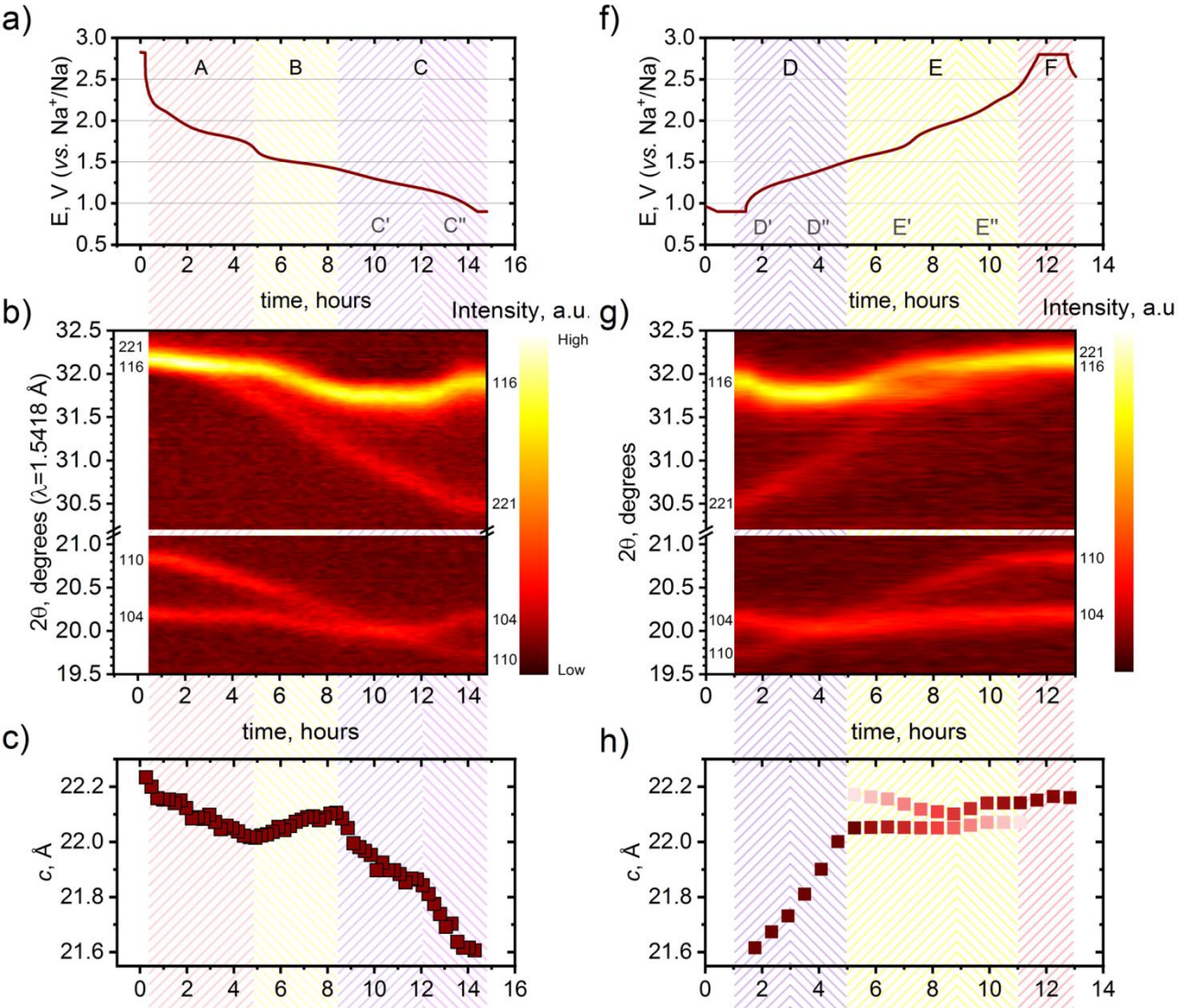
Plot structure Profile viewer Gra

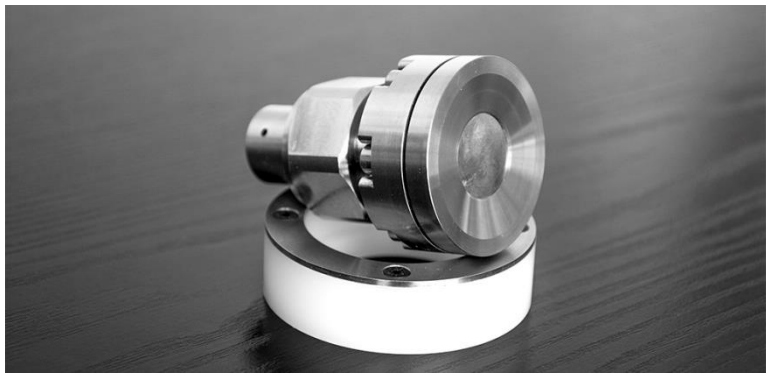
SetCommands

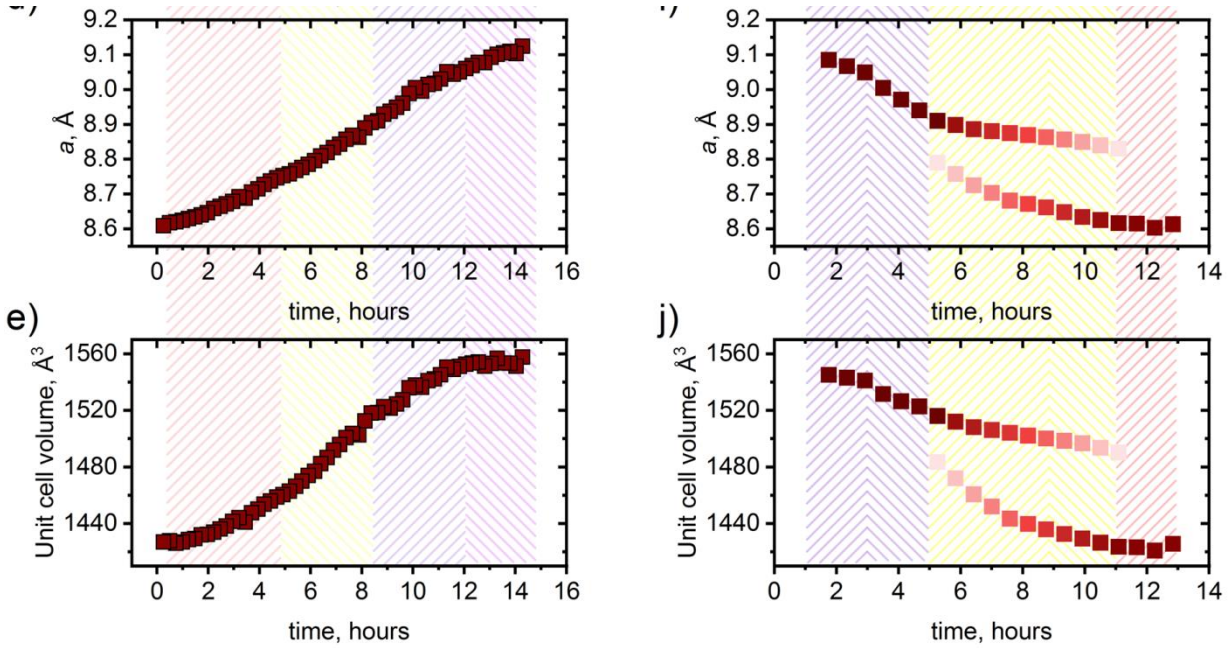


$NaNbV(PO_4)_3$:transformations during cycling



J.B. Leriche et al // J. Electrochem. Soc. 157 (2010) A606





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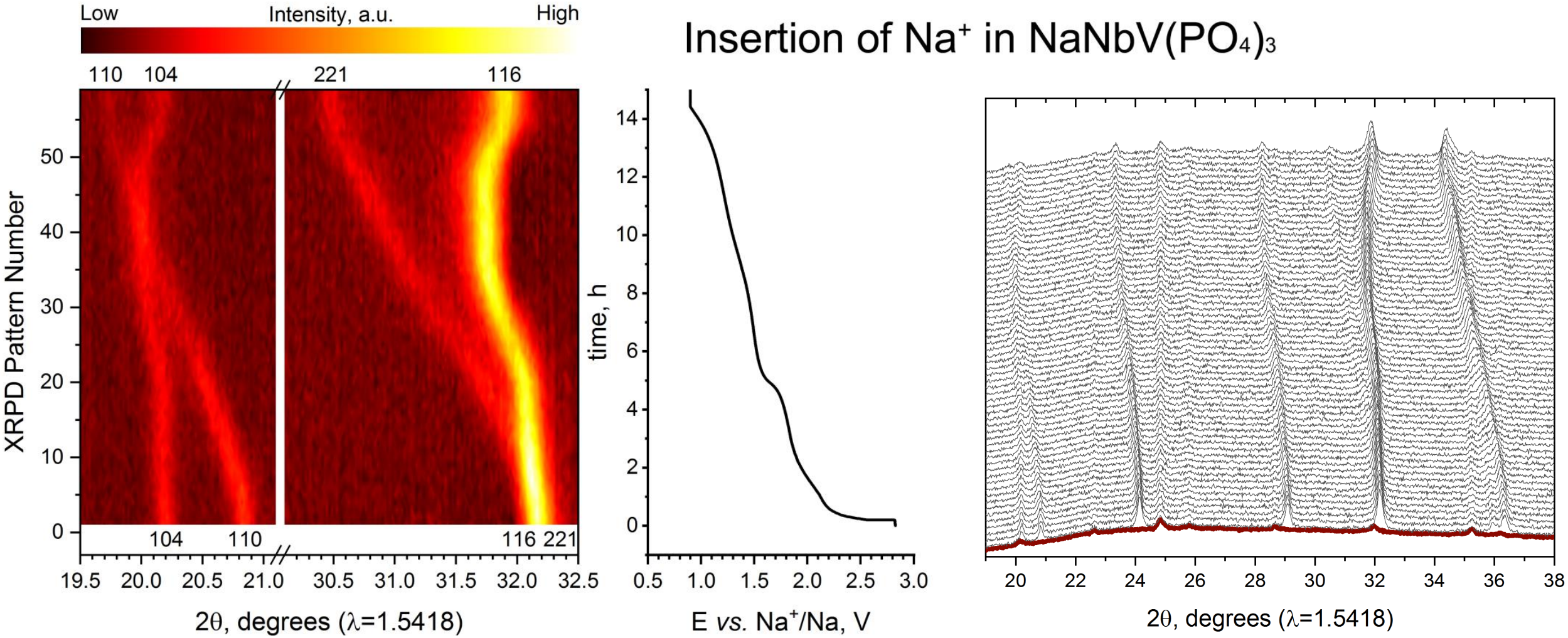
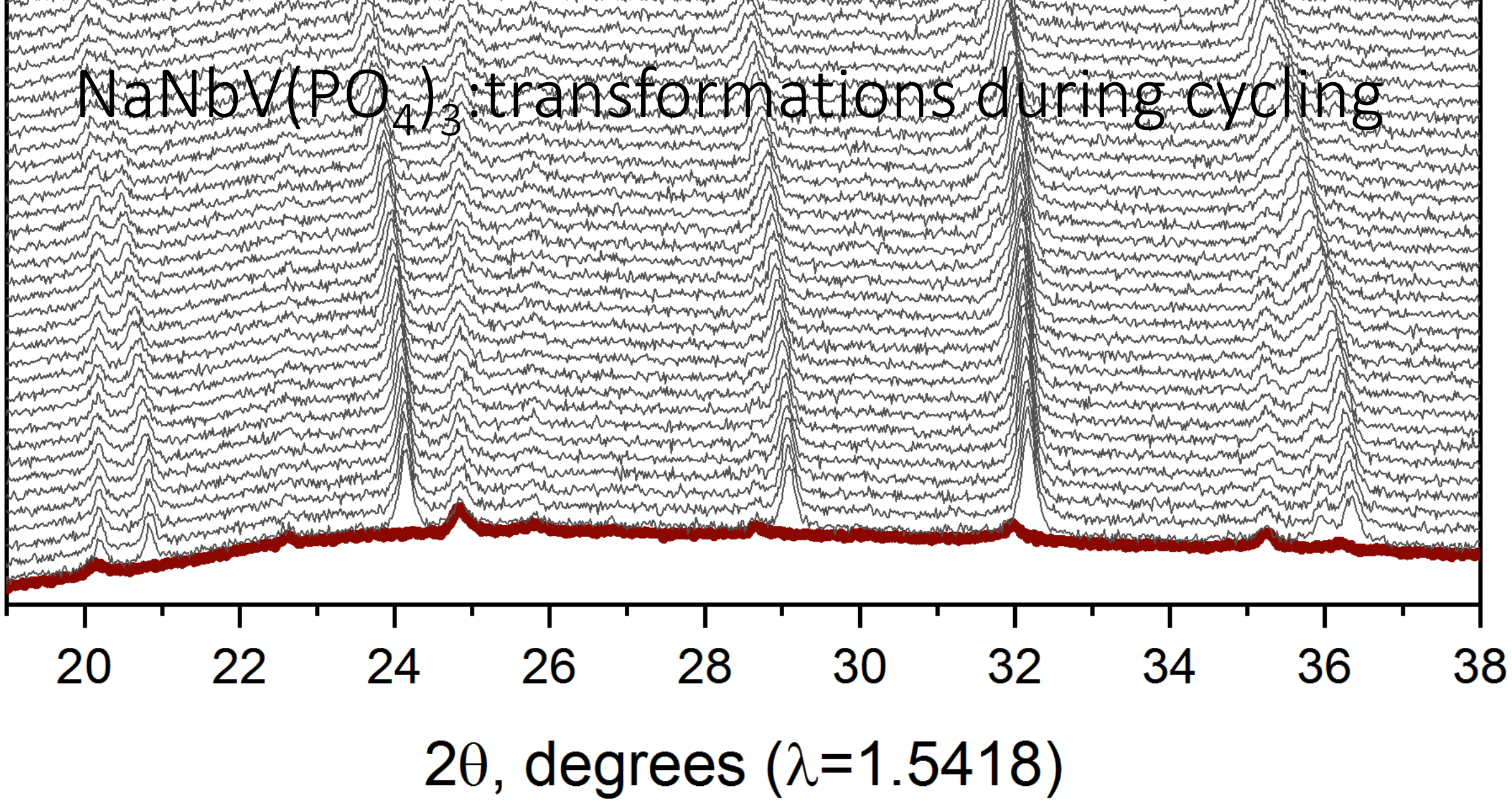
$NaNbV(PO_4)_3$:transformations during cycling



N. Khasanova, *et al // ACS Appl. Mater. Interfaces* **2023**, 15, 25, 30272–30280.

$NaNbV(PO_4)_3$:transformations during cycling



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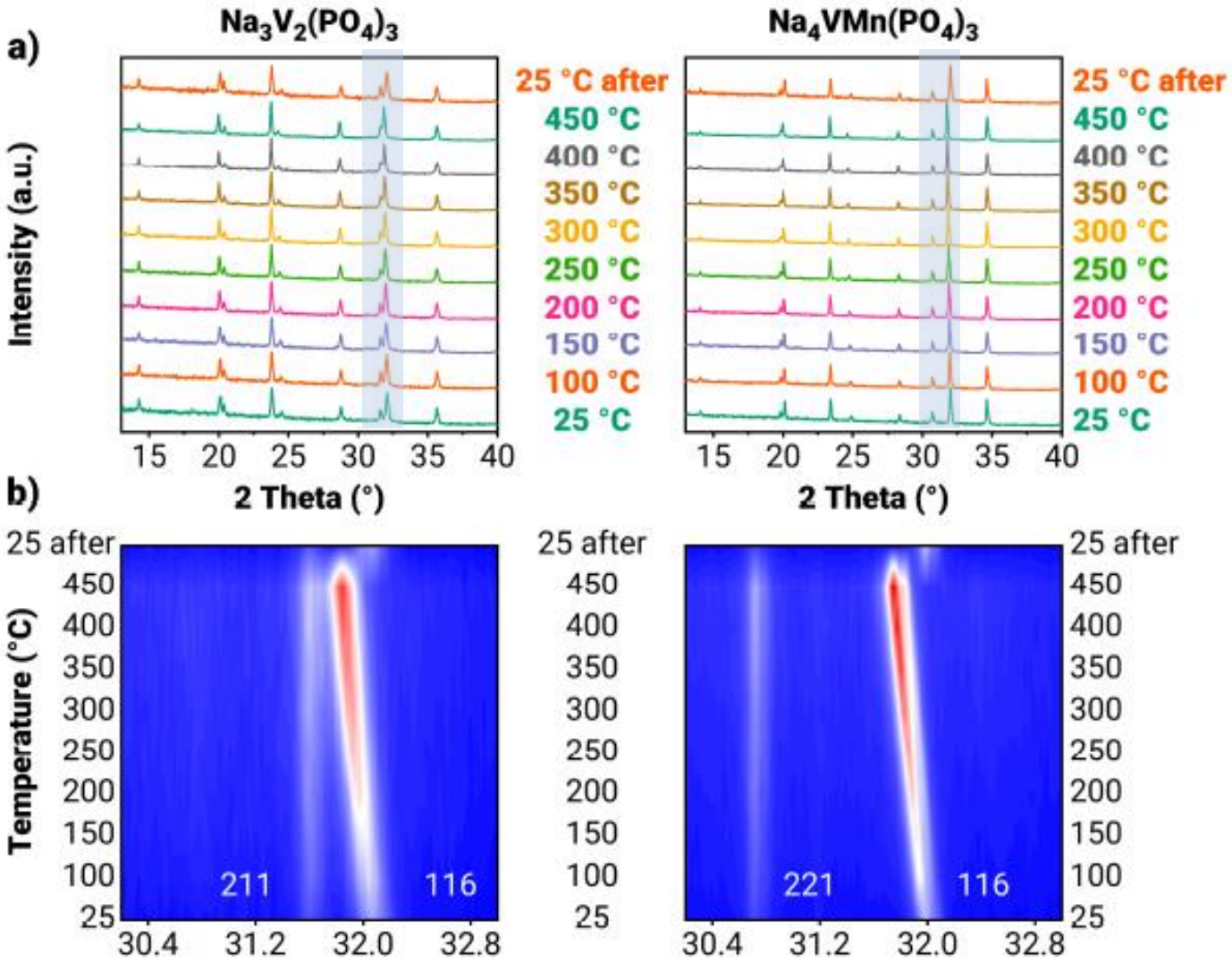
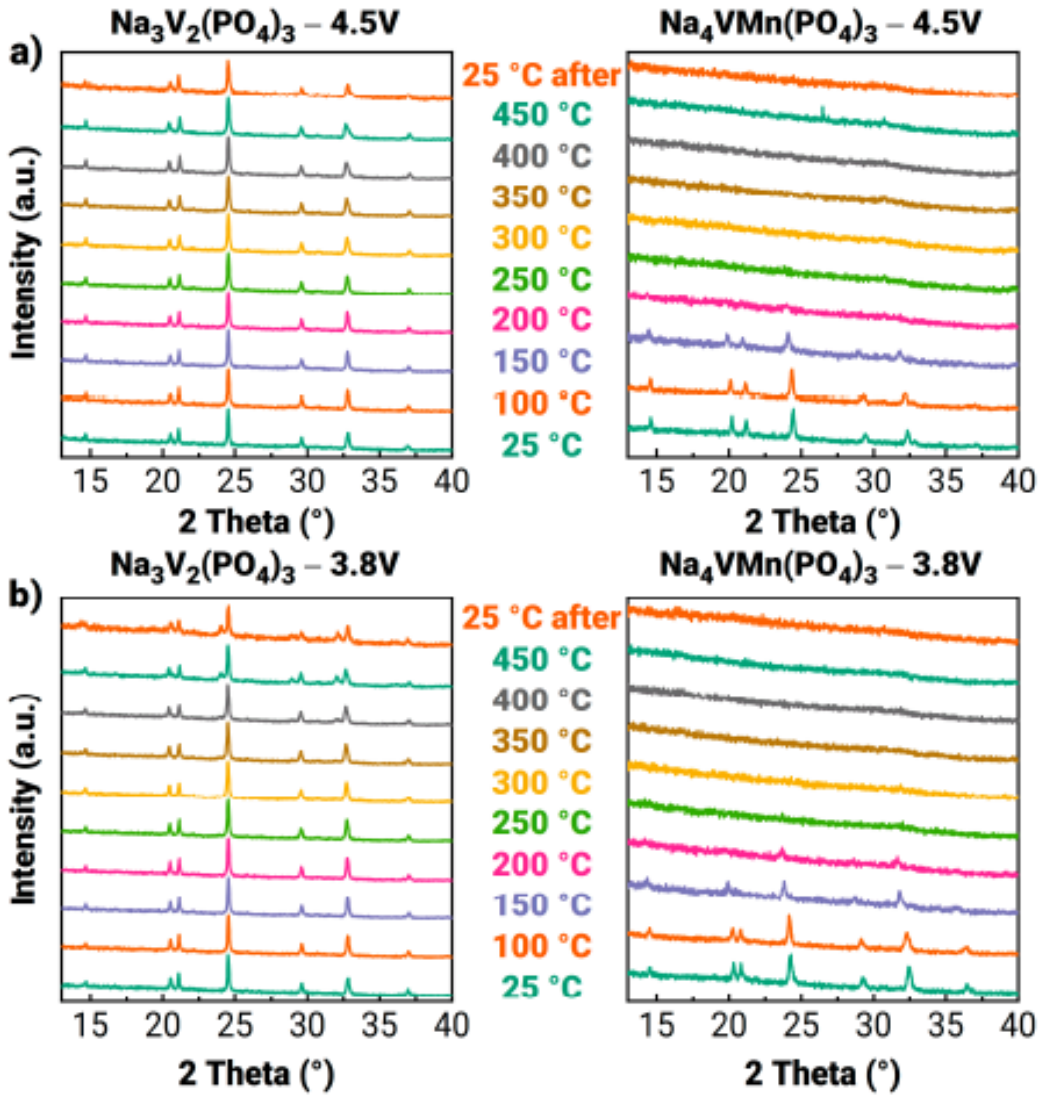
$Na_4MnV(PO_4)_3$ transformations





Samigullin et al // *Energies* **2023**, *16*, 3051

Conclusion

NASICONs still show lots of intriguing features!

Thx!