SFB 595

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Sodium insertion properties of titanates and related materials as negative electrodes for Na-ion batteries

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Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)

HZDR
HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

CEU Universidad San Pablo

Outline

- Introduction
- Li-ion vs. Na-ion batteries
- Hexatitanate $Na_2Ti_6O_{13}$
- Hollandite TiO_2
- Summary

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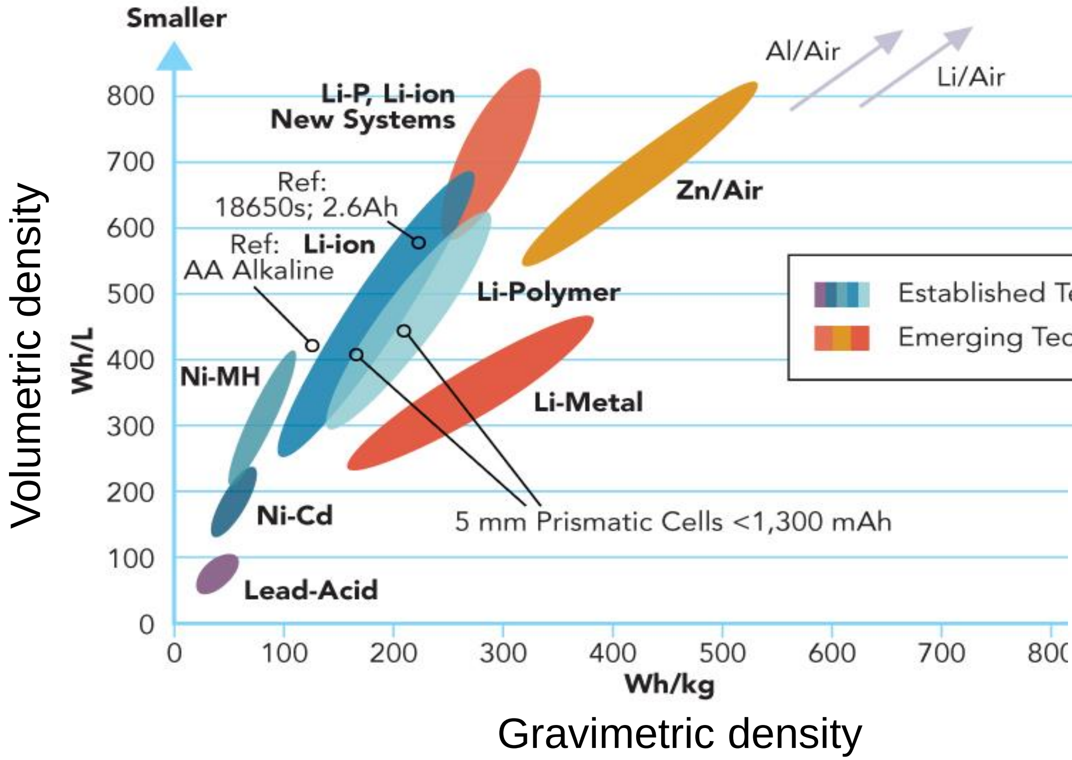
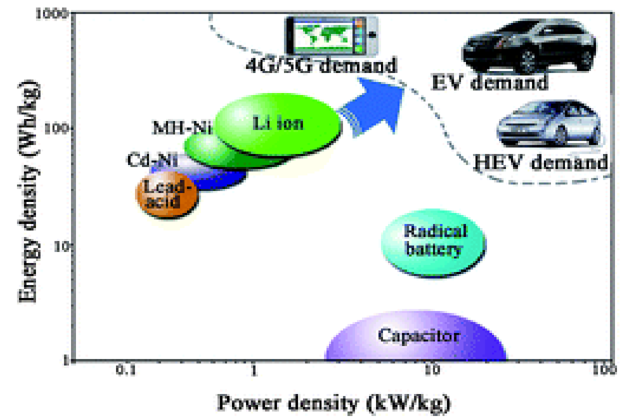
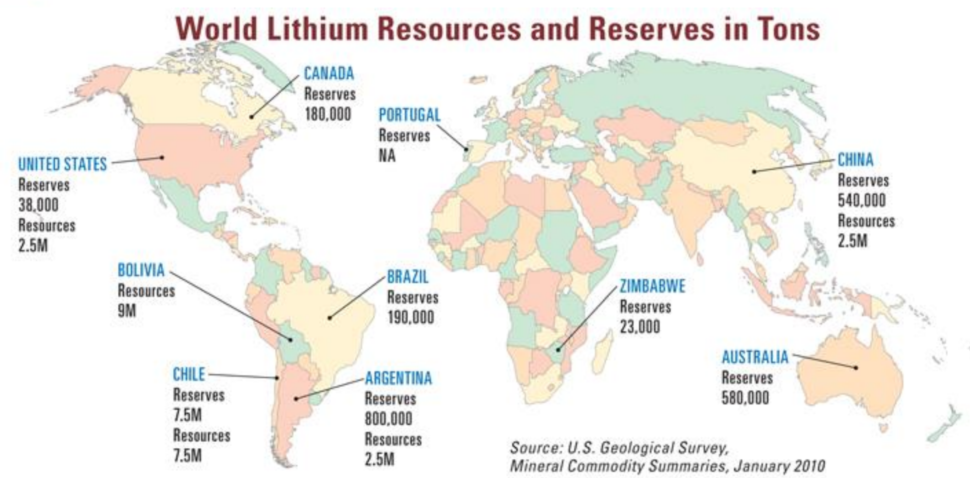
Introduction







Nexergy (www.iccnexergy.com)
See for example: Xue-Ping Gao and Han-Xi Yang, Energy Environ. Sci., 2010,3, 174-189

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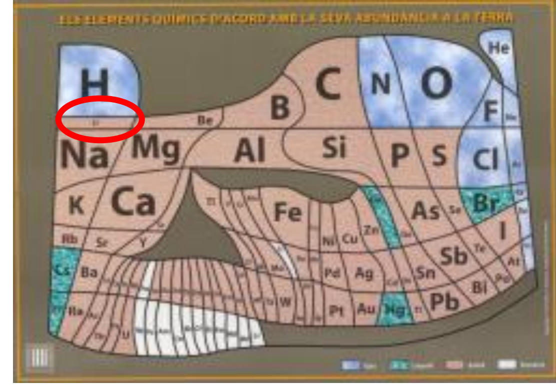
Advantages of sodium



- Inexhaustible resources

Earth crust Na: 23600 ppm – Li: 20 ppm

Sea water Na: 10800 ppm – Li: 0.18 ppm

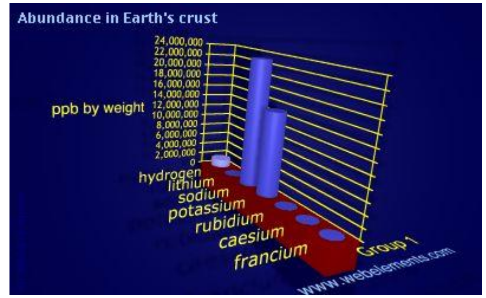
- Low cost

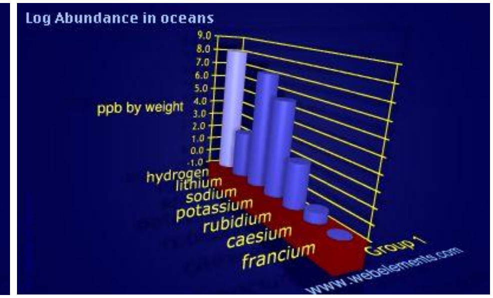
Na_2CO_3 : 0.11 $/kg ; Li_2CO_3 3.45 $/kg

- High standard reduction potential

(–2.7 vs NHE)

- No alloying with Al
- Sodium based technologies already existing
- Intercalation chemistry similar to Li





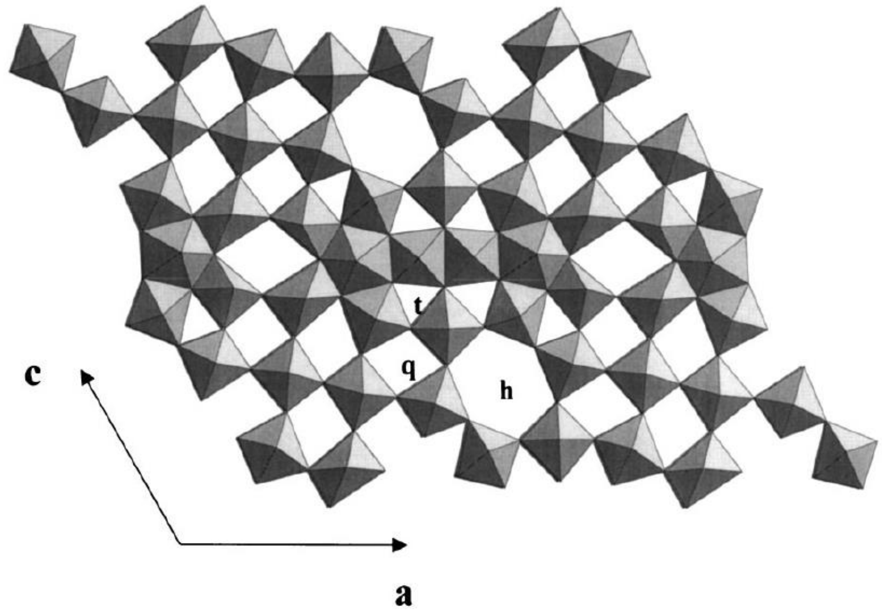
http://www.webelements.com/periodicity/abundance_crust/group_1.html

M.S Whittingham, Prog. Solid State Chem., 1978, 12, 41.
C. Delmas, Solid State Ionics, 1981, 3/4, 165.
K.M. Abraham, Solid State Ionics, 1982, 7, 199.
T.R. Jow, L.W. Shacklette, M. Maxfield, D. Vernick. J. Electrochem. Soc., 1987, 134, 1730.
M.M. Doeff et al. Electrochimica Acta, 1990, 40, 2205.
D.A. Stevens et al. J. Electrochem. Soc. 2000, 147, 1271.
J. Barker et al. US Patent 2002/0192553

But:

- Size +59% (r Li^+ = 73 pm ; r Na^+ = 116 pm)
- Diffusion coefficient
- Solubility of salts …

Electrochemical intercalation into $W_{18}O_{49}$



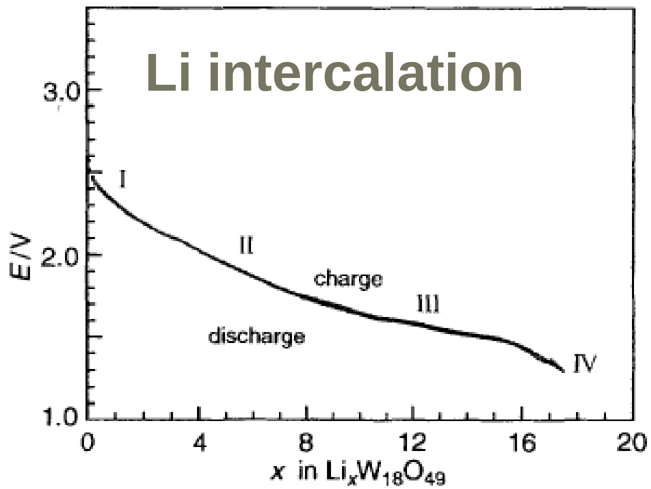


Fig. 3 Open-circuit voltage between 3.3 and 1.3 V of a lithium cell using $W_{18}O_{49}$ as the positive electrode

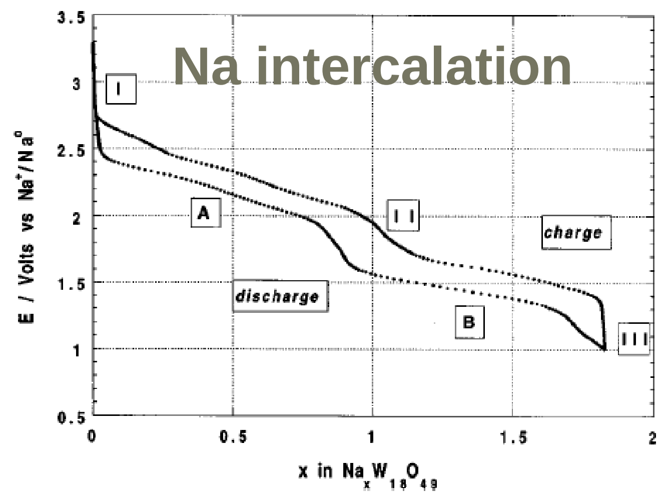
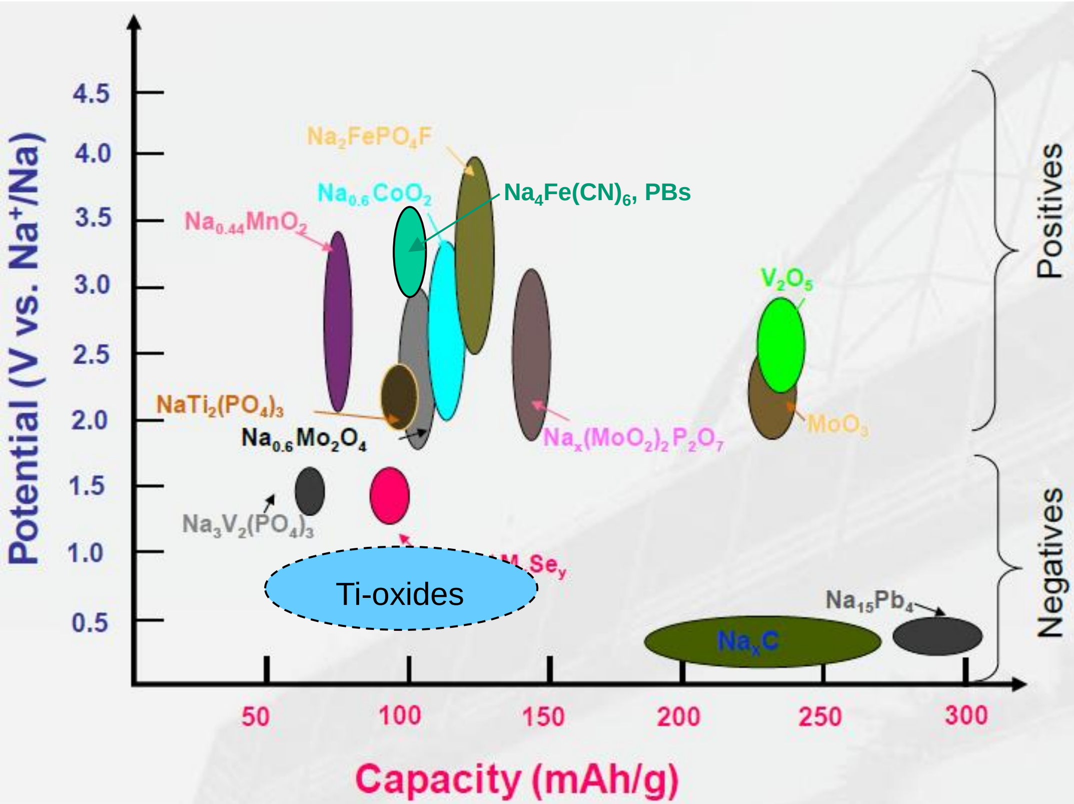


FIG. 2. Voltage–composition plot obtained from potentiostatic cycling of a cell Na//$W_{18}O_{49}$.

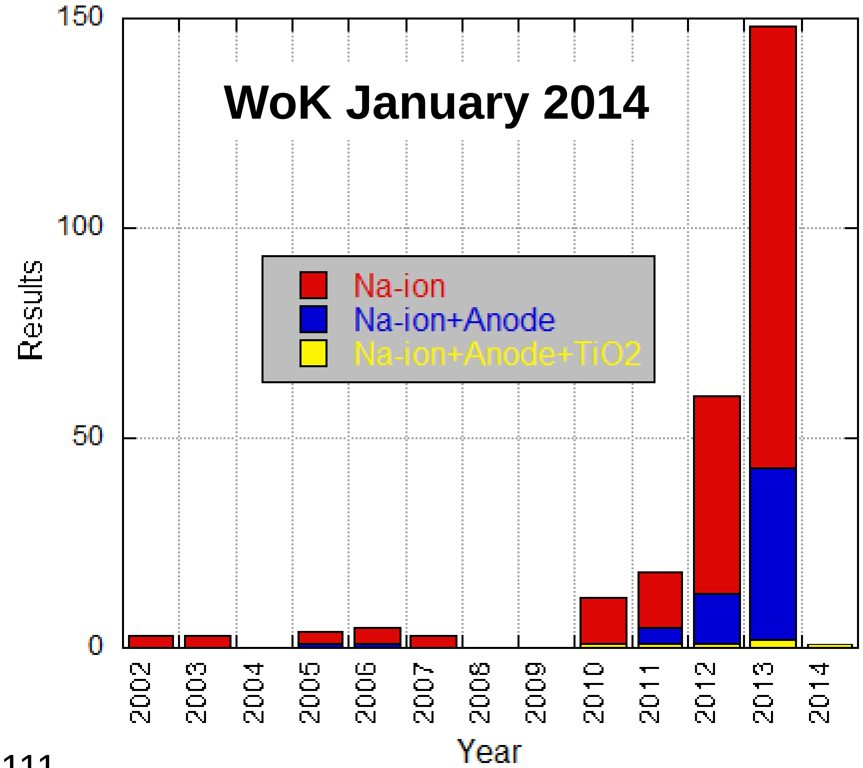
A. Martínez de la Cruz et al, J. Mater Chem. 1995

A. Martínez de la Cruz et al, J. Solid State Chem. 2000

Na-ion battery materials



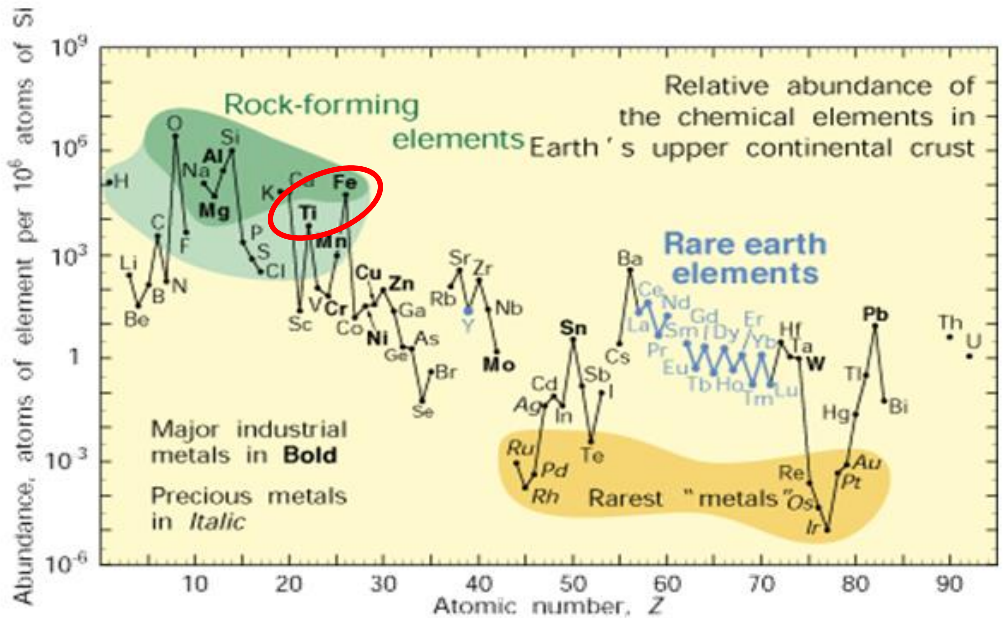
Updated from P. Senguttuvan et al., Chem. Mater. 23, 2011, 4109–4111



Total results “Na-ion battery”: 259 ;
Anode: 84 ; TiO_2: 7

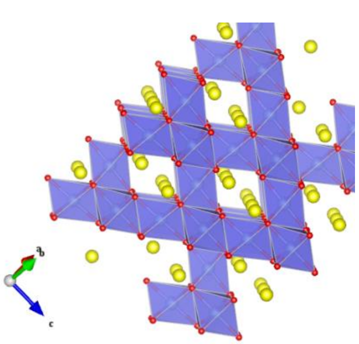
Ti-based oxides: potential new negatives

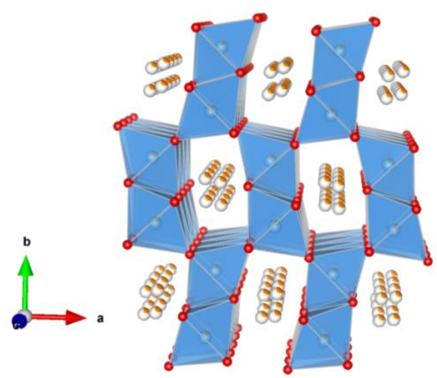
- Abundance
- Low cost of TM
- Non toxic, environmentally benign
- **Safe in LiB** Ti^{4+}/Ti^{3+}: 1.5V
- High capacities in LiB ~170 Ah/kg
- High structural stability (“zero strain”)



Source - U.S. Geological Survey Fact Sheet 087-02

In LIB:

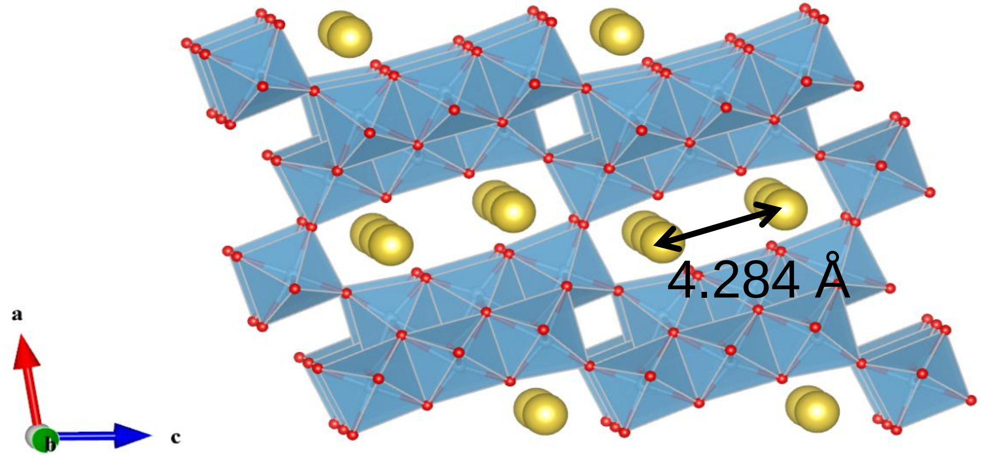




Spinel $Li_4Ti_5O_{12}$ (LTO)
170 mAh/g

Ramsdellite $Li_2Ti_3O_7$
200 mAh/g

New Materials: $Na_2Ti_6O_{13}$



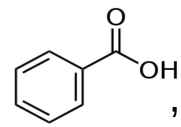
S.G. *C*2/*m*

Na: 4*i* (x,0,z): 100%

pseudocubic NaO_8

S. Andersson, A. D. Wadsley, Acta Cryst. 15 (1962) 194-201

Rich ion-exchange chemistry:

$Na_2Ti_6O_{13}$ —($LiNO_3$, 325°C)→ $Li_2Ti_6O_{13}$ —(, 180°C)→ $H_2Ti_6O_{13}$

W. A. England, et al. J. Solid State Chem 49 (1983) 289-299
J. C. Pérez-Flores et al., RSC Advances *2 (*2012) 3530-3540

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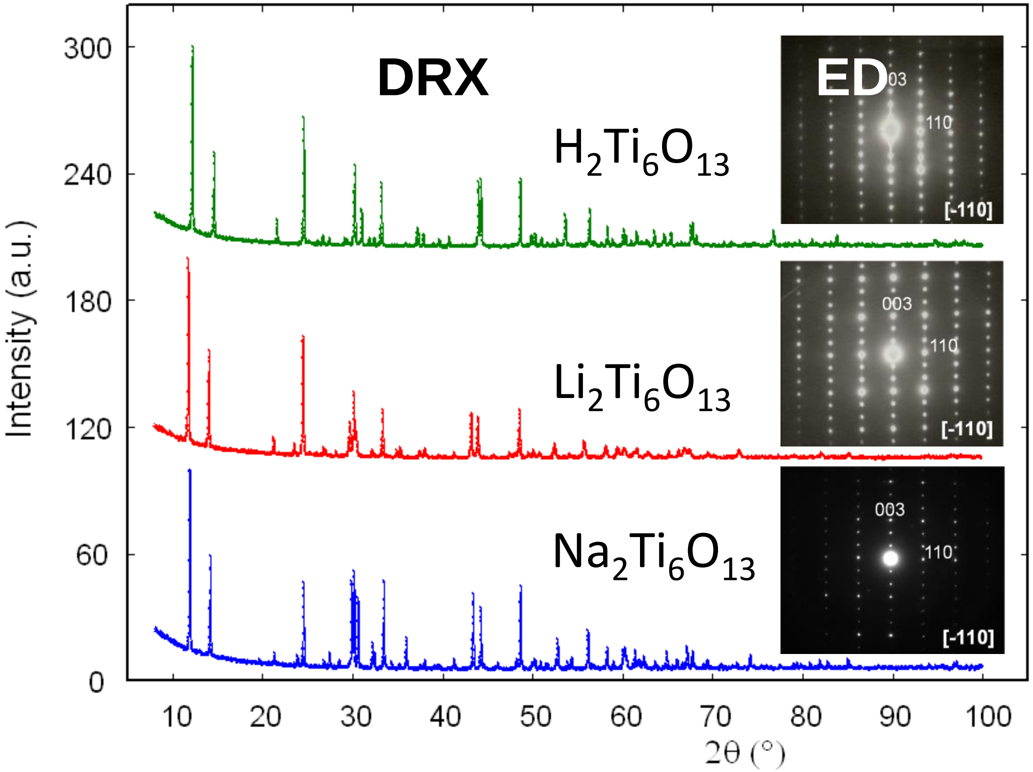
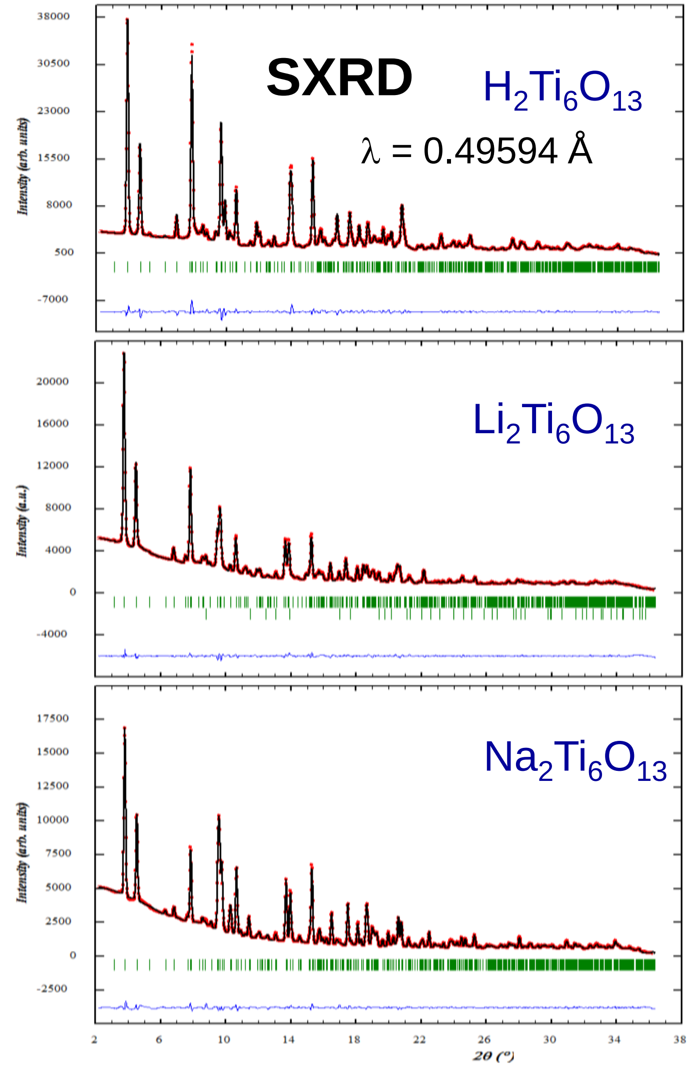
Structural characterization of $A_2Ti_6O_{13}$





C2/m	$Na_2Ti_6O_{13}$	$Li_2Ti_6O_{13}$	$H_2Ti_6O_{13}$
a (Å)	15.1075(4)	15.3457(7)	14.6702(3)
b (Å)	3.74474(8)	3.7527(1)	3.7447(1)
c (Å)	9.1735(2)	9.1528(2)	9.2594(2)
β (°)	99.031(3)	99.466(2)	96.941(2)
V (Å³)	512.54(2)	519.92(3)	504.94(2)

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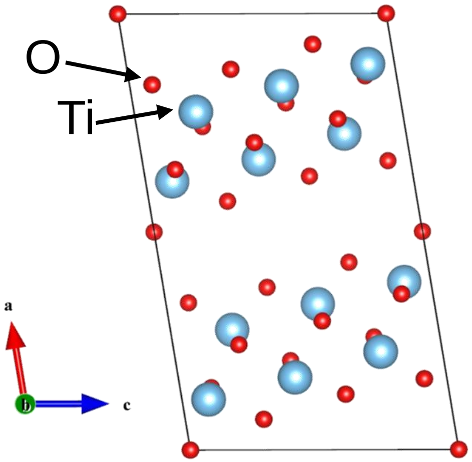
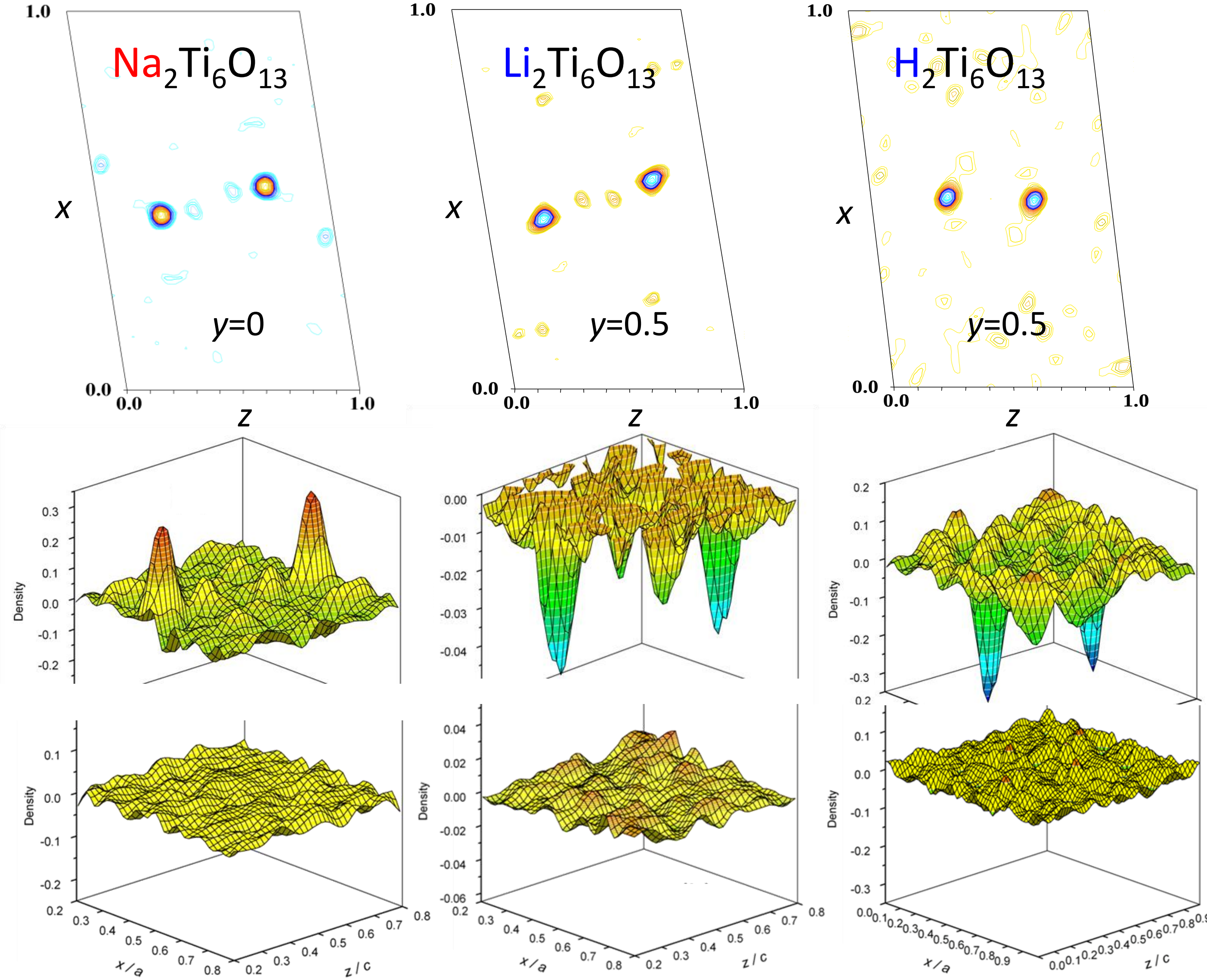
J.C. Pérez-Flores et al., Phys. Chem. Chem. Phys., 2012, **14**, 2892–2899;
J. C. Pérez-Flores et al., RSC Advances 2, 2012, 3530-3540

Locating the channel ions with NPD

Difference Fourier synthesis maps using the $[Ti_6O_{13}^{2-}]$ skeleton





	Na-T	Li-T	H-T
R_{wp} %	5.90	4.32	3.27
	3.45	3.50	2.45
χ^2	15.3	10.4	2.34
	5.21	6.73	1.31
R_B %	6.31	4.41	7.69
	2.90	3.96	3.94

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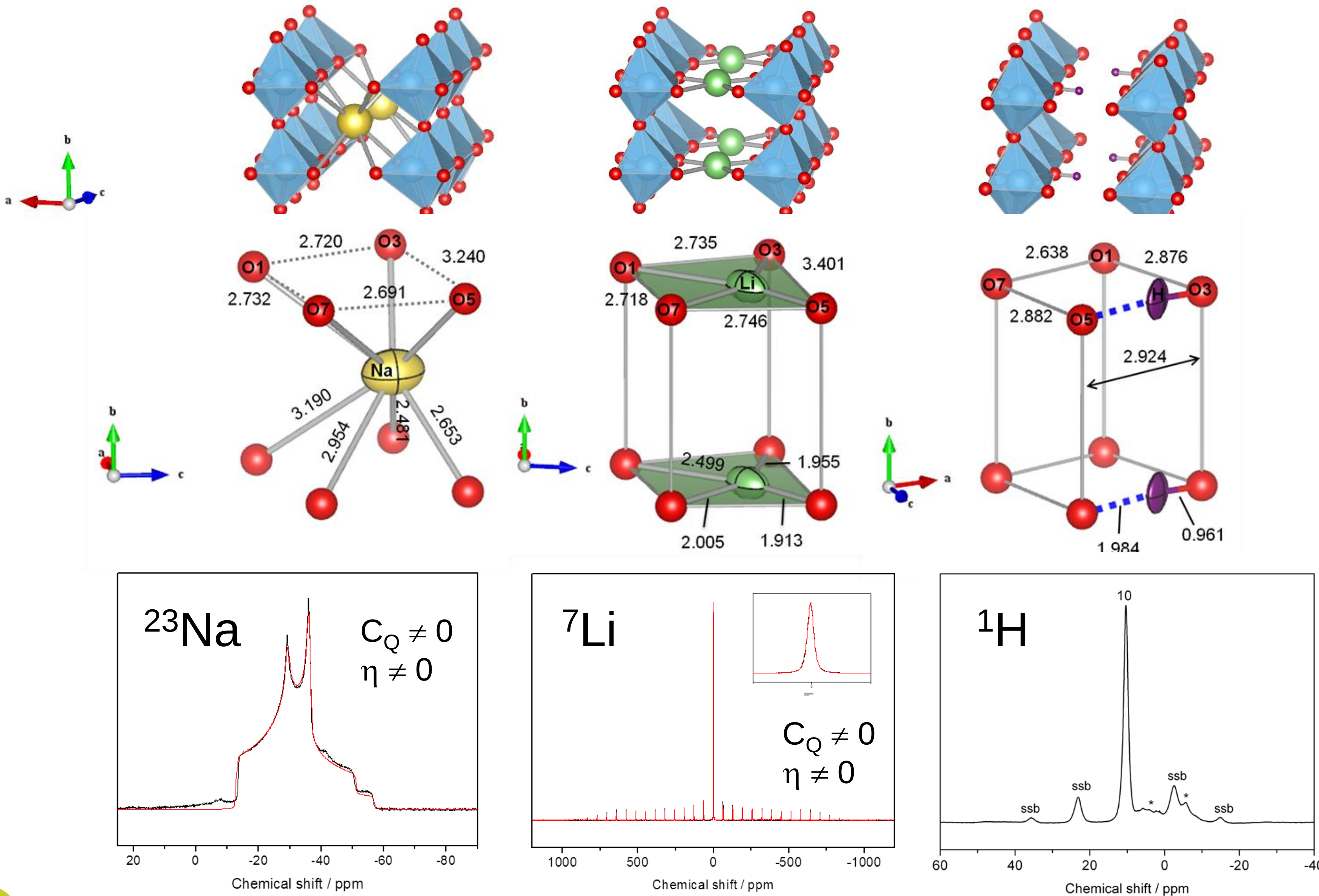
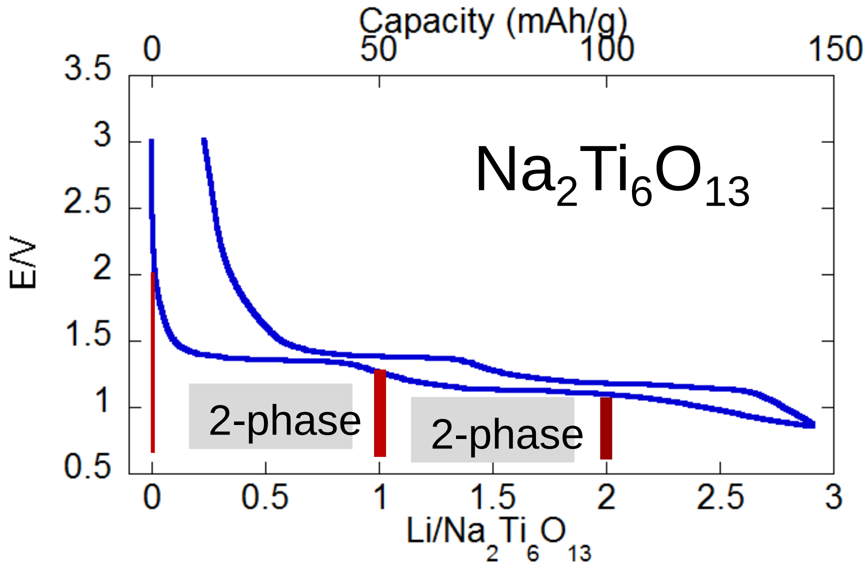
MAS-NMR spectroscopy using ^{23}Na, ^{7}Li y ^{1}H



Lithium insertion in $Na_2Ti_6O_{13}$

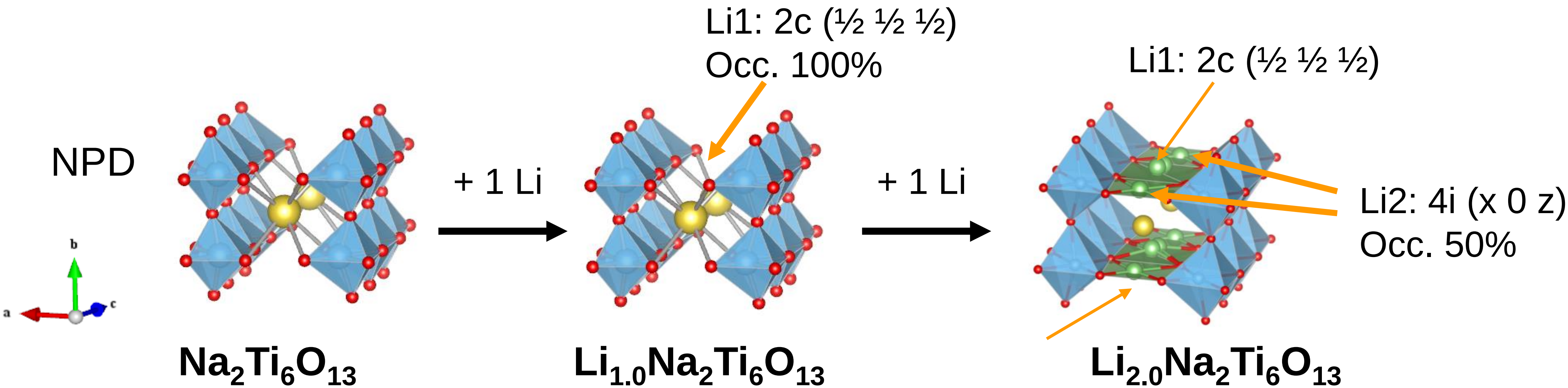


2 reversible Li
Capacity: 100 mAh/g

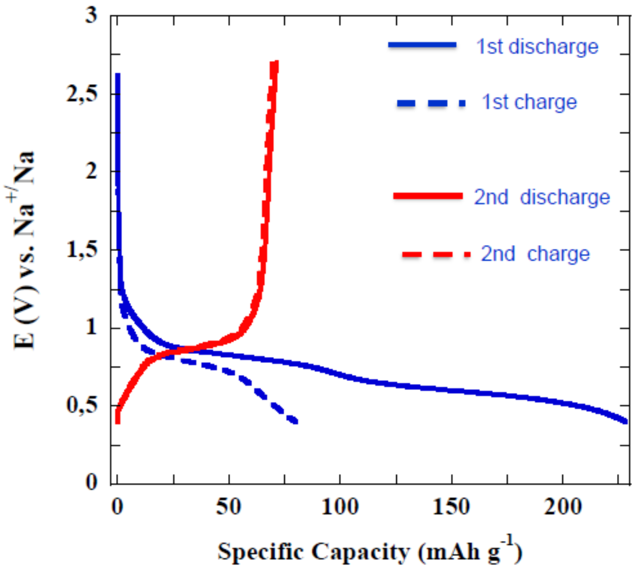
R. Dominko et al. , Electrochem. Comm. 8 (2006) 673-677;
R. Dominko et al. J. Power Sources 174 (2007) 1172-1176;
J. C. Pérez-Flores et al., Phys. Chem. Chem. Phys. (2012)

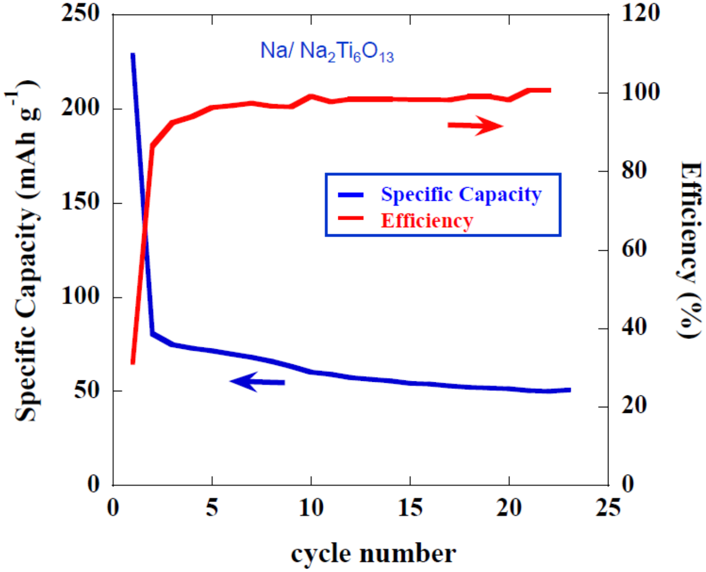
Chemical lithiation: $Na_2Ti_6O_{13} + x\ C_4H_9Li \rightarrow Li_xNa_2Ti_6O_{13} + x/2\ C_8H_{18}$

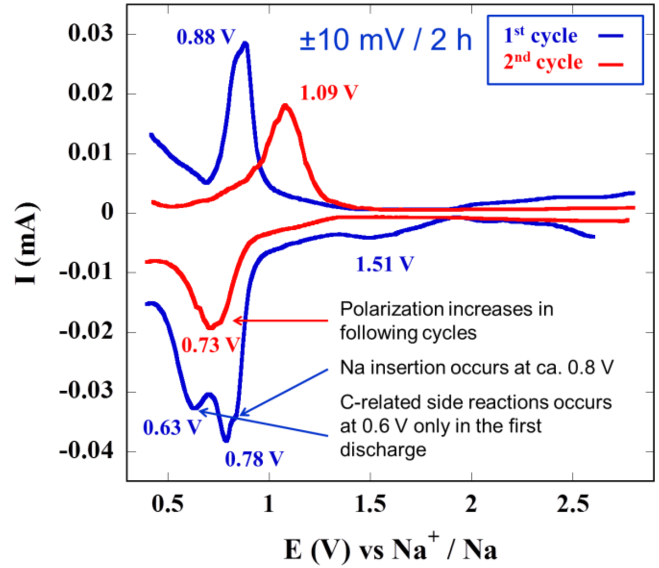
NPD



Sodium insertion in $Na_2Ti_6O_{13}$

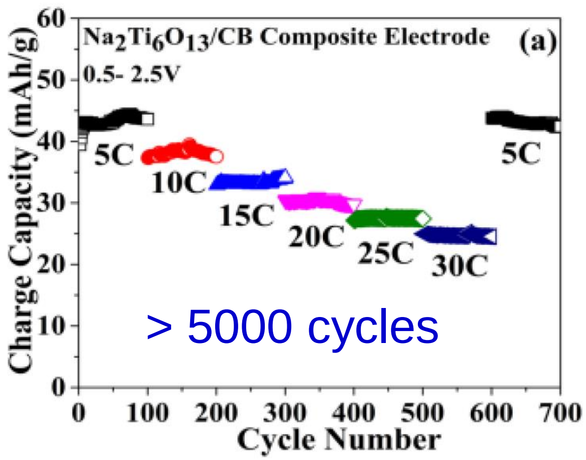






A. Kuhn et al. (to be submitted)

1 reversible Na
Capacity: ~ 50 mAh/g



Proposed as promising negative electrode material for Na-ion battery

A. Rudola et al., Chem. Comm. 49, 2013, 7451-7453

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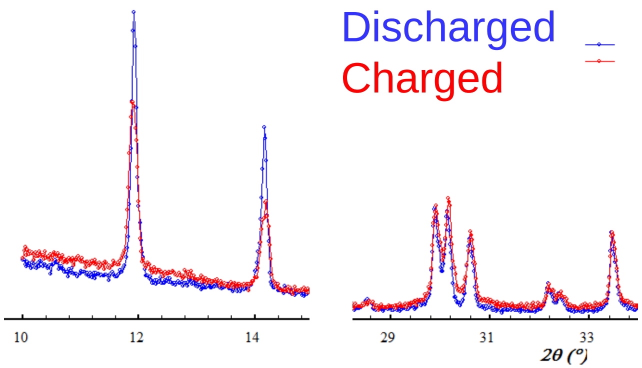
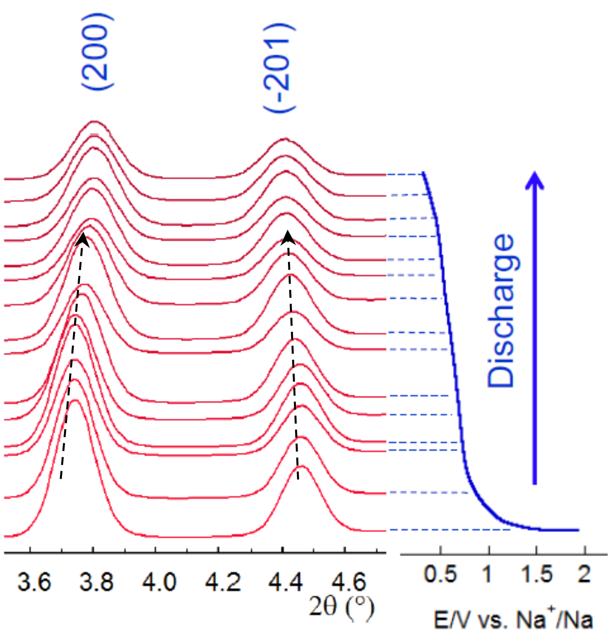
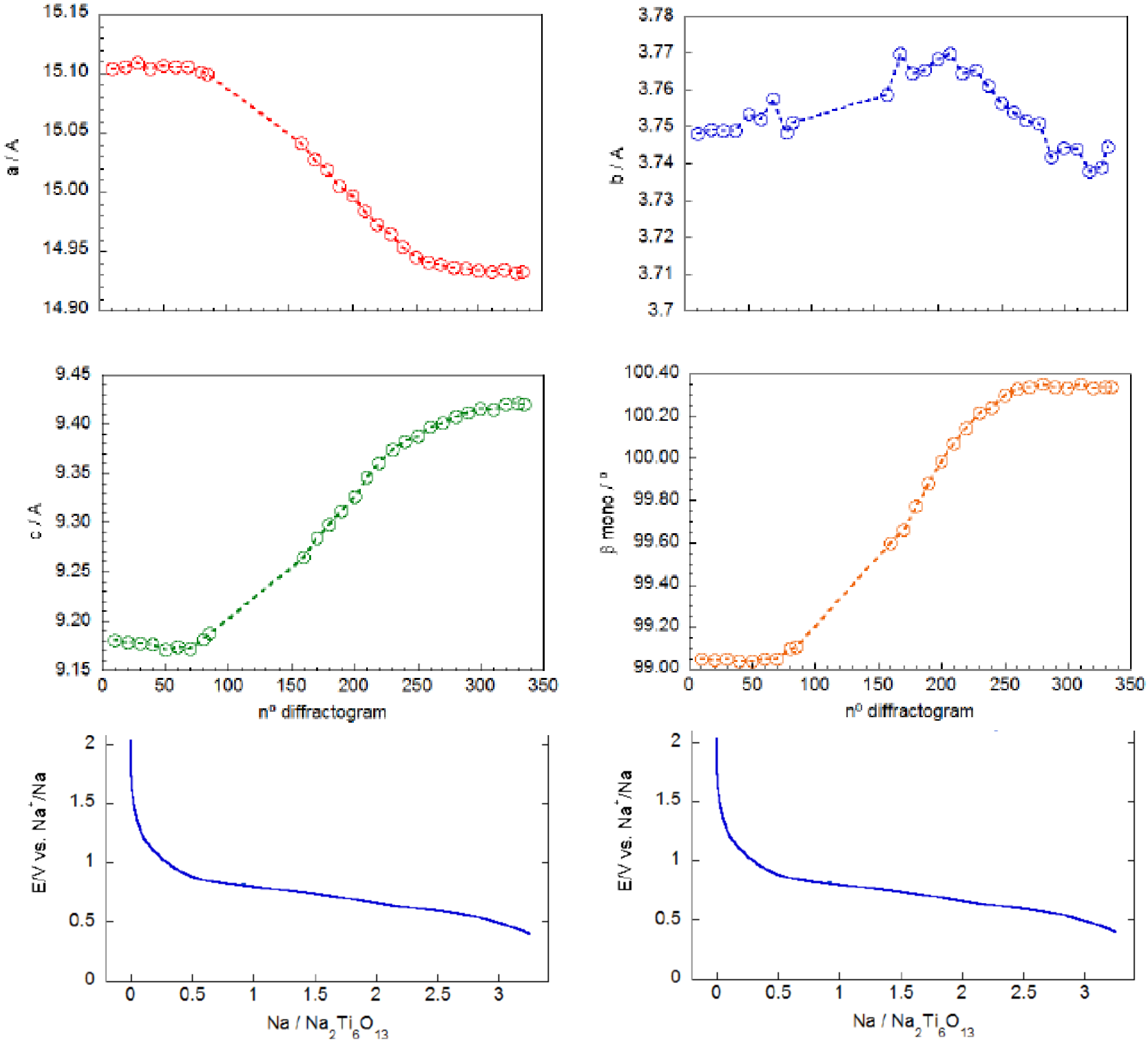
Structural characterization of $Na_{2+x}Ti_6O_{13}$

Ex situ XRD: no significant change



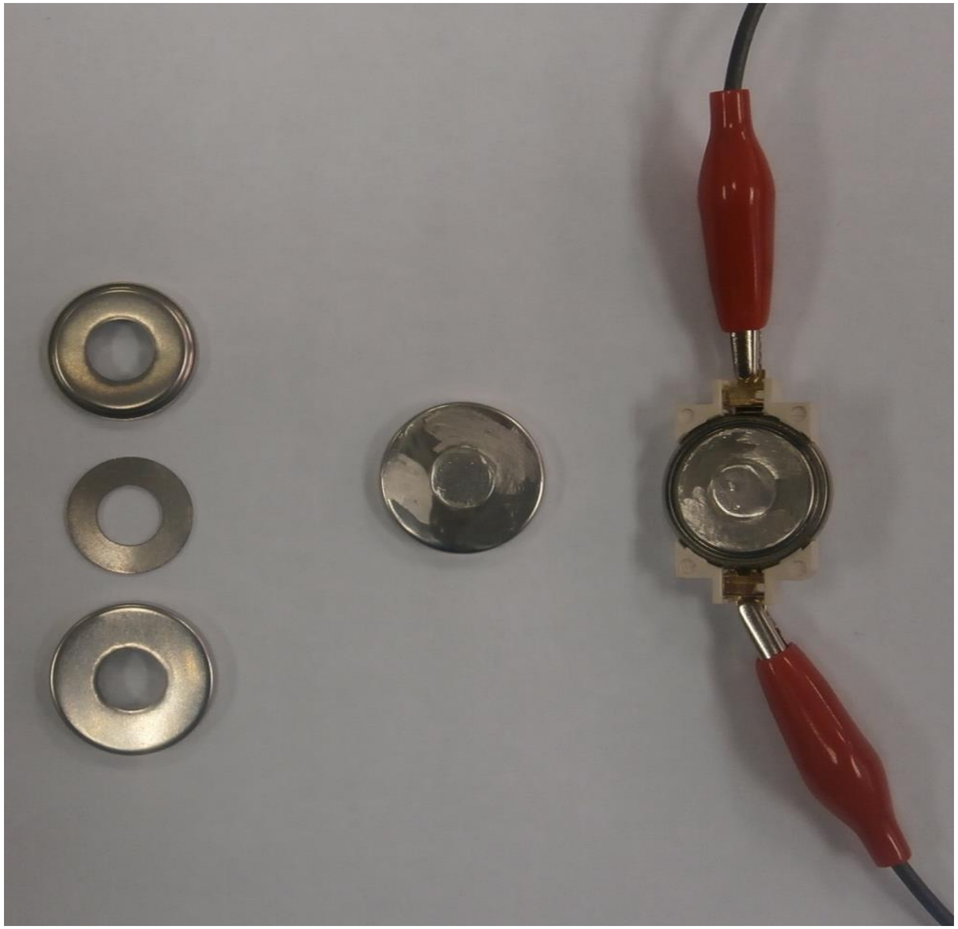


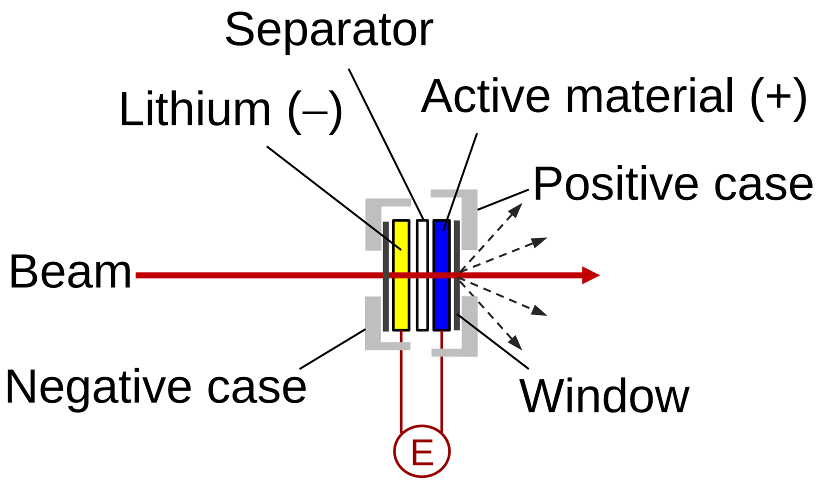


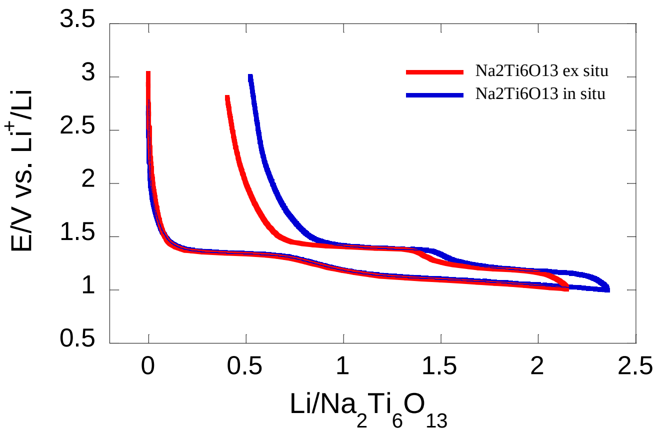
In situ SXRD: little change in lattice parameters

Volume change: little 1.3%

Home-made *in situ* cell for synchrotron facilities

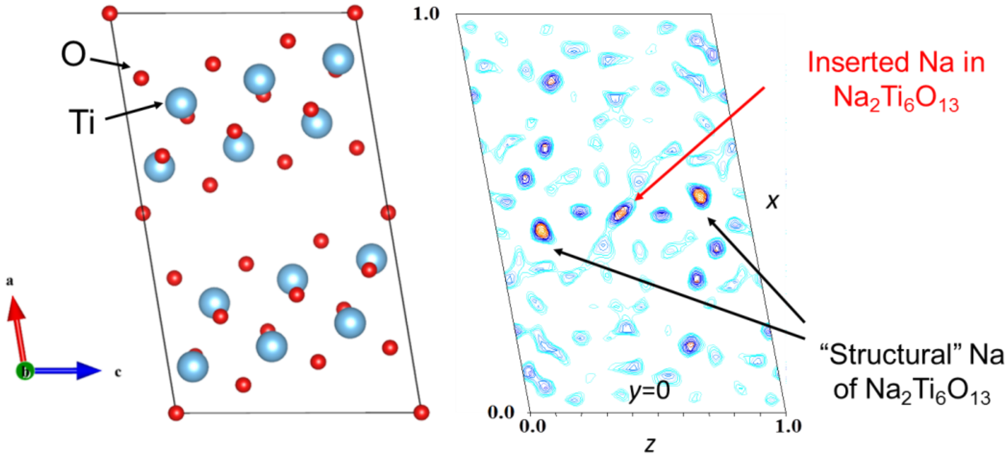




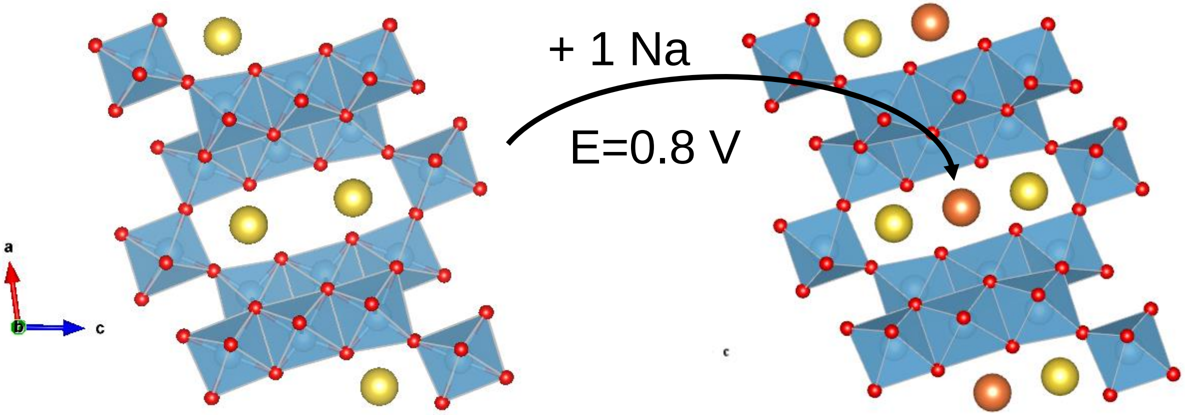


«Shedding light on the lithium insertion mechanism in $A_2Ti_6O_{13}$ electrode materials for Li ion batteries using in situ synchrotron diffraction operated in commercial coin cells»
SPD Beamline BM20 HZDR ESRF, Grenoble (Project CH-3634).

Location of sodium channel atoms in $Na_{2+x}Ti_6O_{13}$ using SXRD



Difference Fourier synthesis maps using the $[Ti_6O_{13}^{2-}]$ skeleton



$Na_2Ti_6O_{13}$ **$Na_3Ti_6O_{13}$**

J. C. Pérez-Flores et al., Dalton Trans., 2012, 41, 14633
A. Kuhn et al., (to be submitted)

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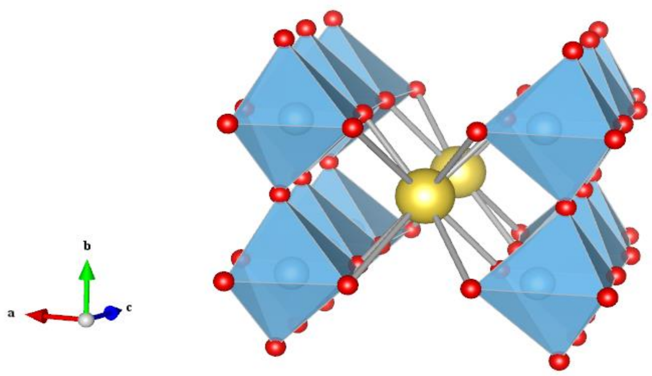
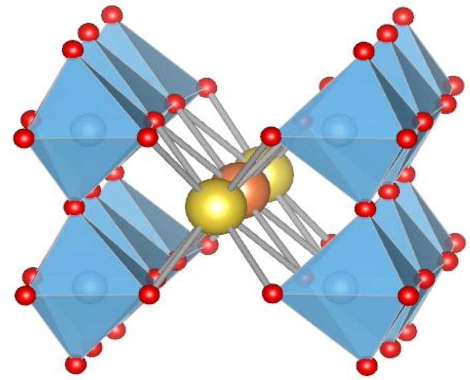


$+ Na^+$
(E=0.8 V)



$Na_2Ti_6O_{13}$

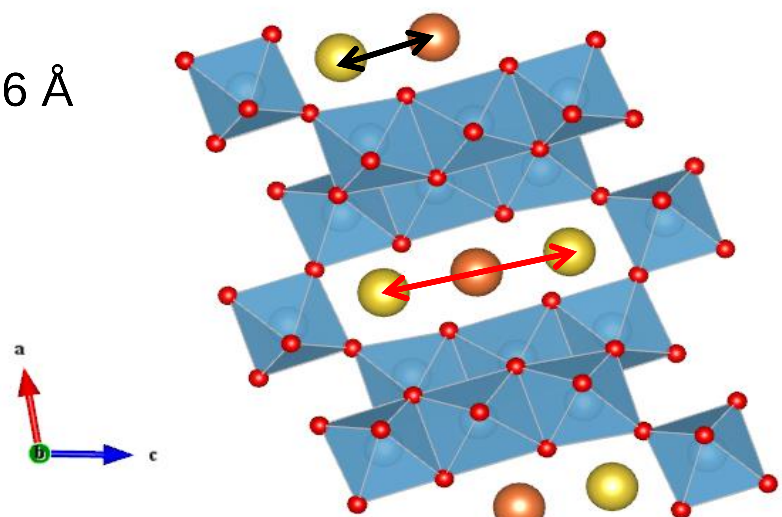
$Na_{2+x}Ti_6O_{13}$

Structural Na:
4i (x,0,z)

Inserted Na:
2d (½ 0 ½) occ 100%

2.721 Å

Na-Na $Na_4Ti_5O_{12}$(h.t.): 2.86 Å



Na-Na 5.443 Å
instead of 4.284 Å

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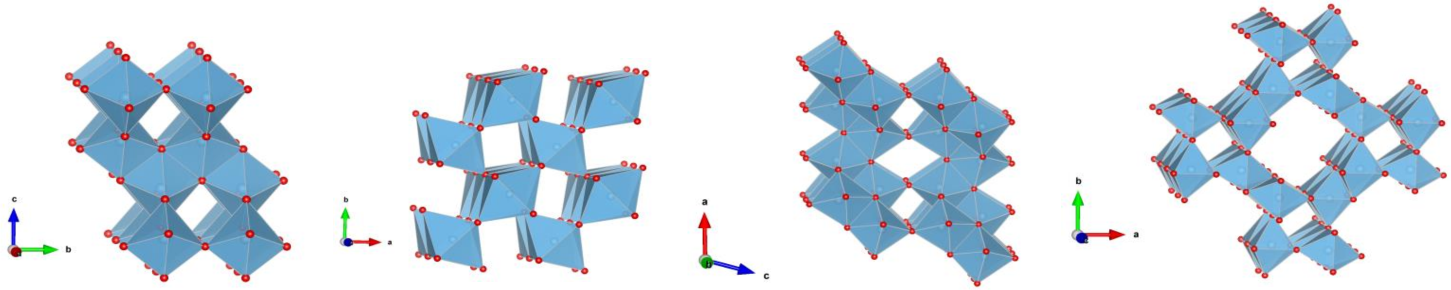
Hollandite TiO_2

Up to 7 known polymorphs of TiO_2



anatase — rutile — TiO_2-B — TiO_2-H

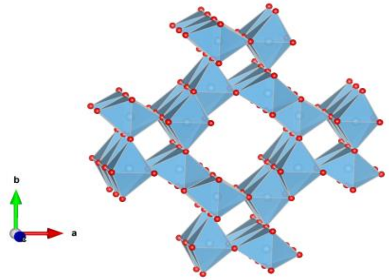
Y. Xu et al., Chem. Commun. 49, 2013, 8973—8975 (A-NC)
J.P. Huang et al., RSC Adv., 2013, 3, 12593–12597 (B-NT)

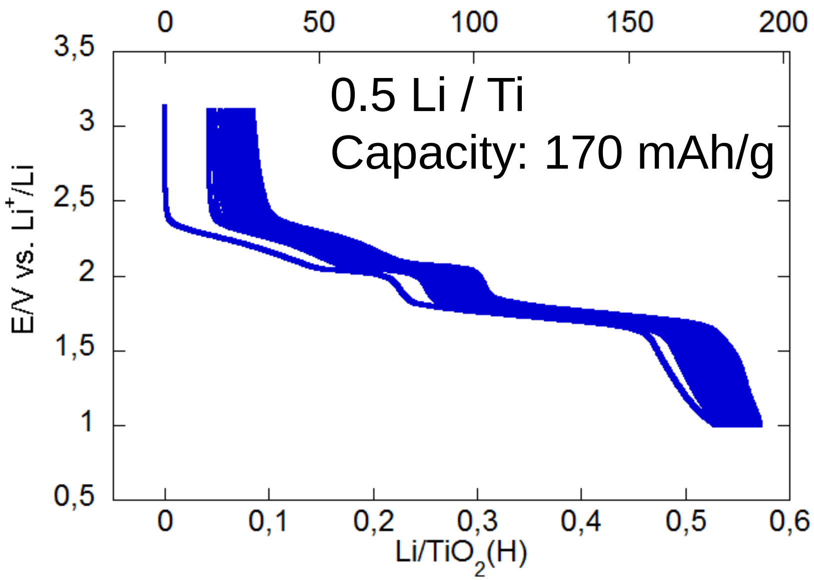
TiO_2(H): topotactic oxidation - K^+-extraction from $K_{0.2}TiO_2$(H) bronze

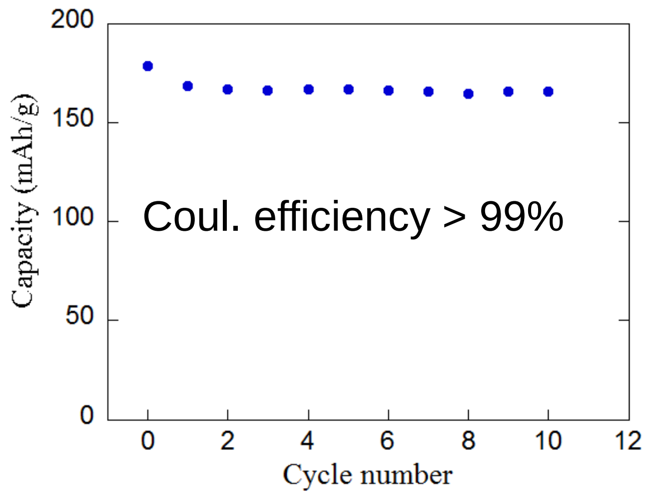
1.) $K_2CO_3 + 10\ TiO_2 + H_2 \rightarrow 10\ K_{0.2}TiO_2(H) + H_2O + CO_2$
2.) $K_{0.2}TiO_2(H) + 0.2\ Ox \rightarrow TiO_2(H) + 0.2\ K^+ + 0.2\ Ox^-$ $\qquad Ox=H_2O_2(H^+)$

M. Latroche et al., J. Solid State Chem. 81, 1989, 78-82

Lithium insertion in TiO_2(H)







A. Kuhn et al., Int. J. Inorg. Mat. 1, 1999, 117-121
A. Kuhn et al., J. Power Sources 81-82, 1999, 85-89
L.D. Noailles, J. Power Sources 81-82, 1999, 259-263

“Theoretical” capacity 1Li (or Na)/f.u. : 335 mAh/g

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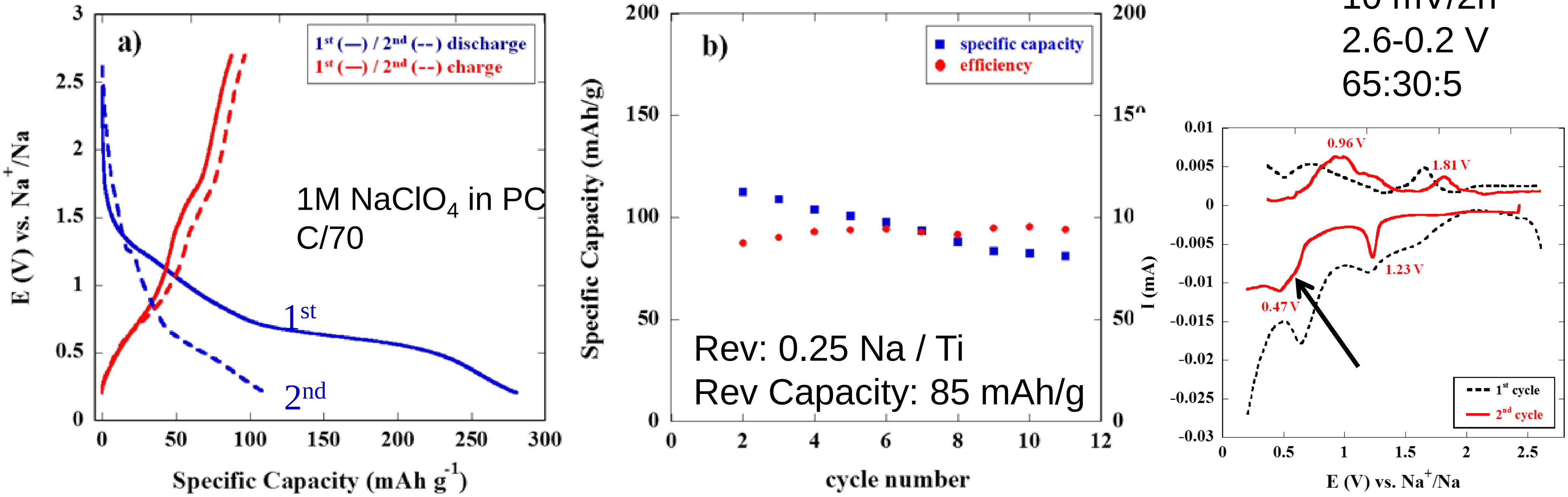
Sodium insertion in TiO_2(H)

10 mV/2h
2.6-0.2 V
65:30:5



J.C. Pérez et al., J. Mater. Chem. A, 2014,2, 1825-1833

- C-related, SEI processes: 0.64 V.… vanishes after second cycle
- Na insertion related processes: 1.23 and 0.47 from second cycle on

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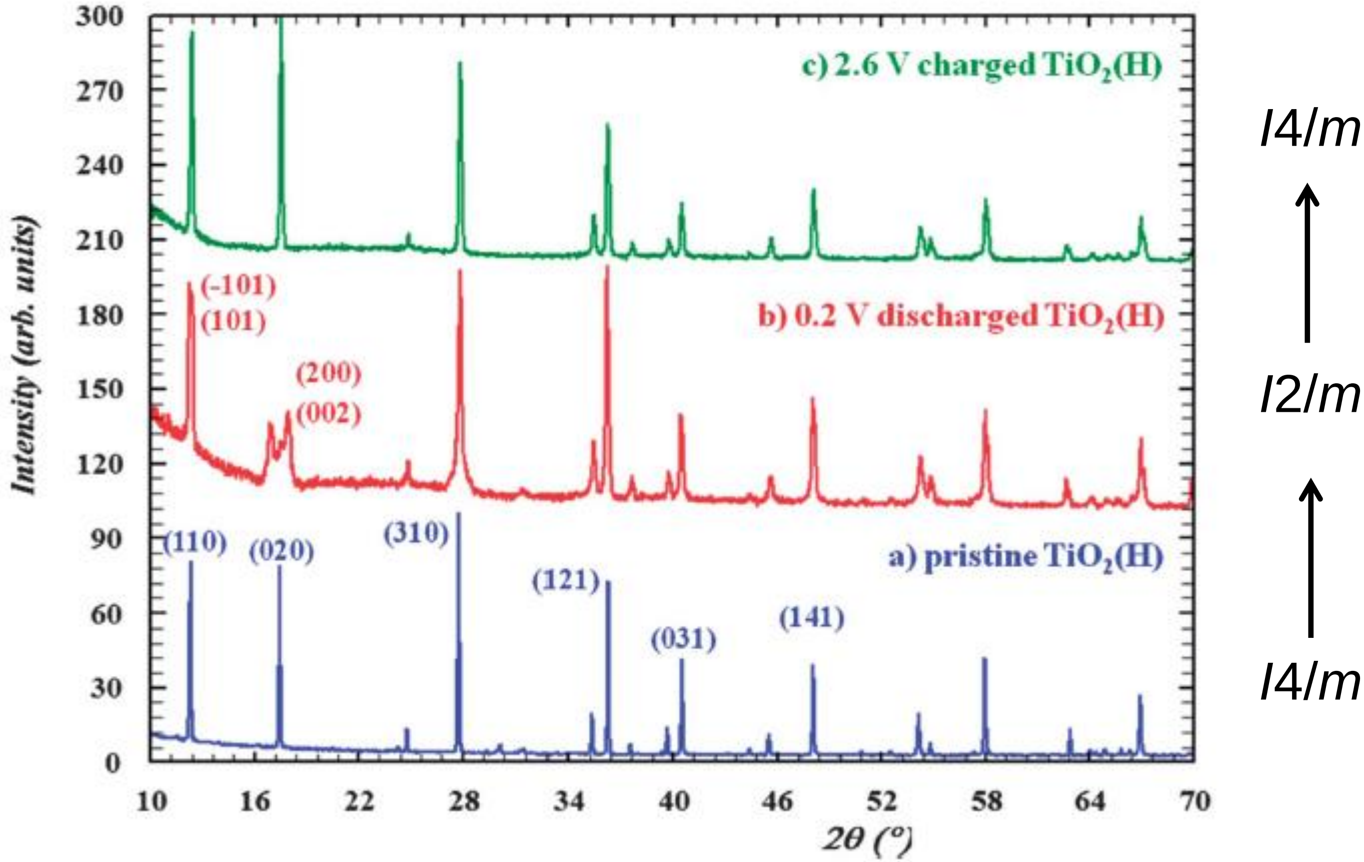
Ex situ XRD study of Na insertion in TiO_2(H)



Discharged state:
- Splitting of (110) and (020)
- Broadening of peaks

J.C. Pérez et al., J. Mater. Chem. A, 2014,2, 1825-1833

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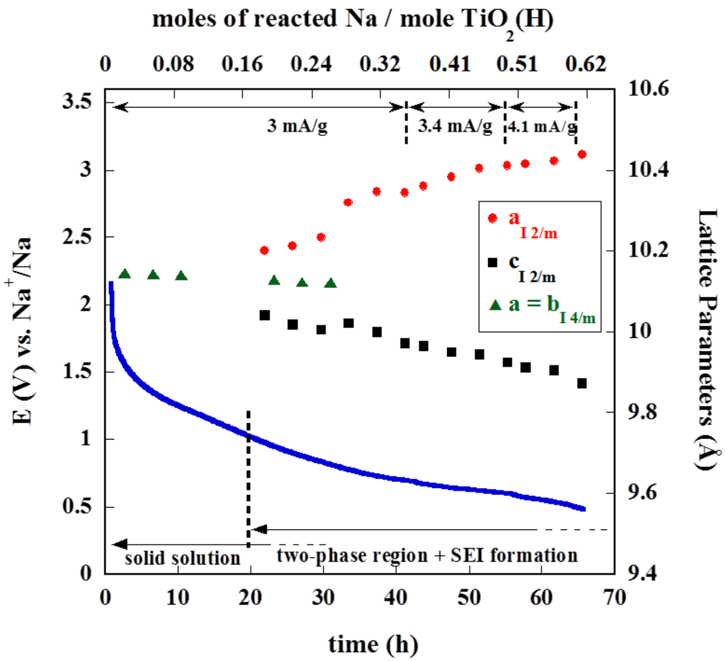
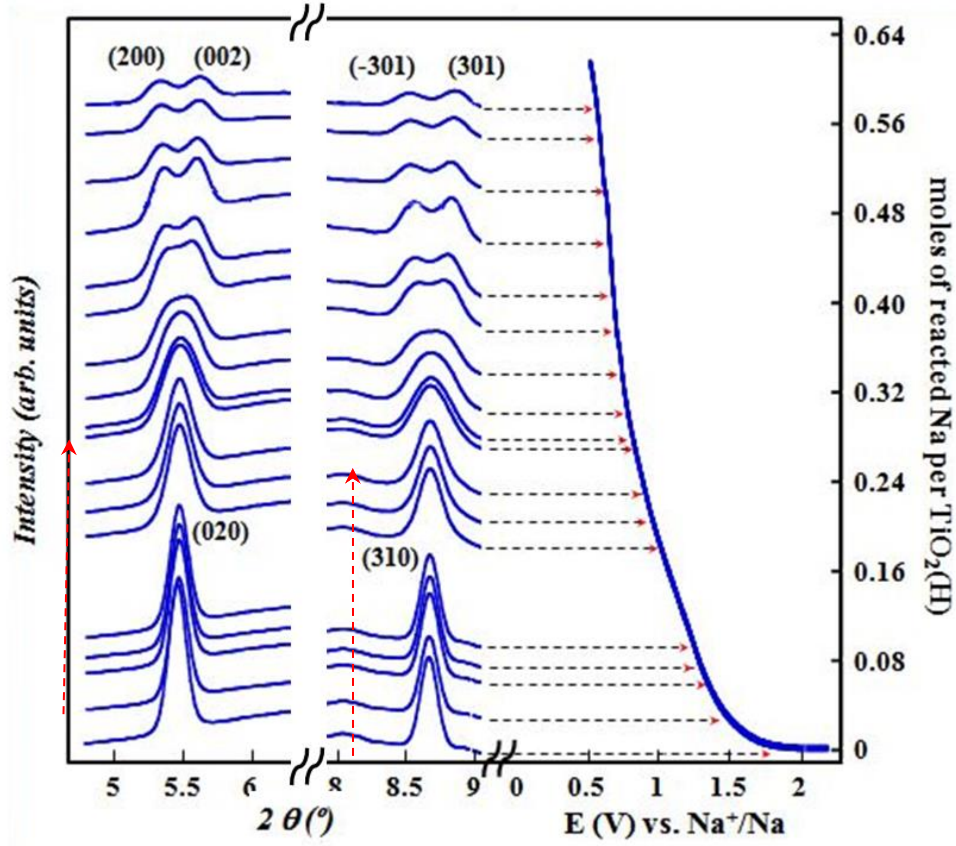
Structural characterization of $Na_xTiO_2(H)$

In situ SXRD





Closely related phases:
Volume change only 1.1%!

1) Little angular shifts from *ocv* to ca. 1 V: single phase region
2) Broadening of peaks from 1 to 0.75 V : two very related phases
3) Below 0.55 V . Solid solution of the monoclinic phase.

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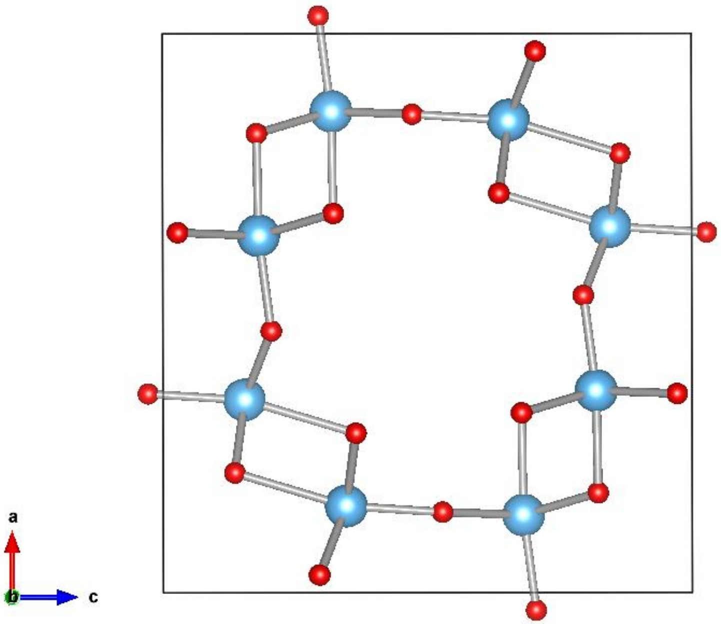
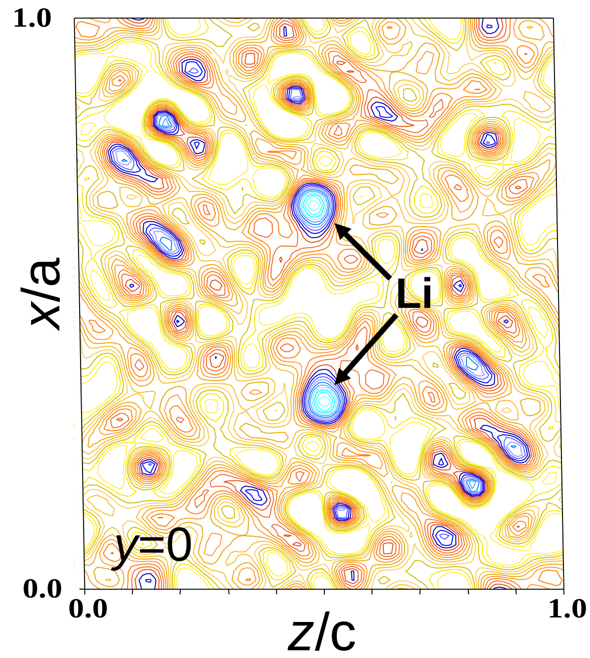
Locating the channel ions in TiO_2(H)

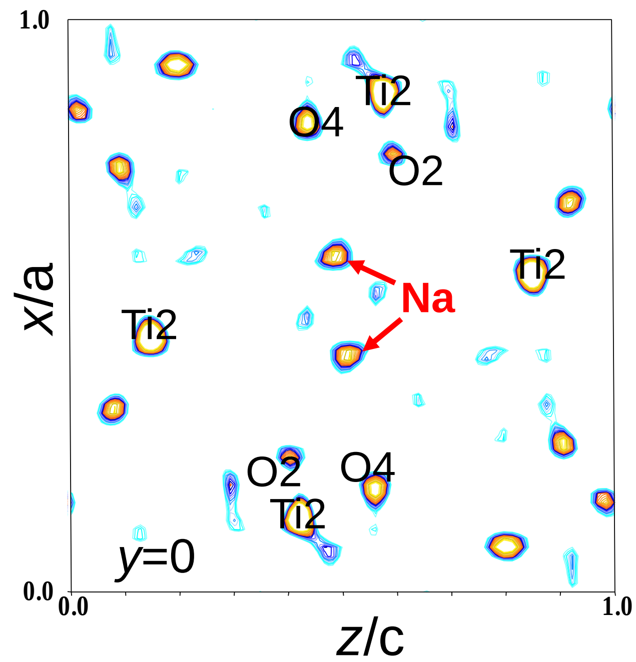


TiO_2(H)
skeleton



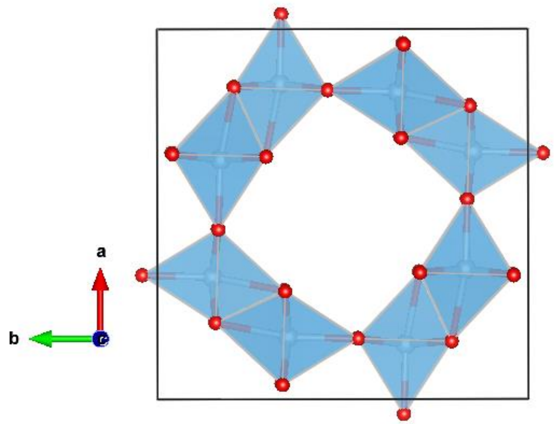
$Li_{0.5}TiO_2$(H)

NPD

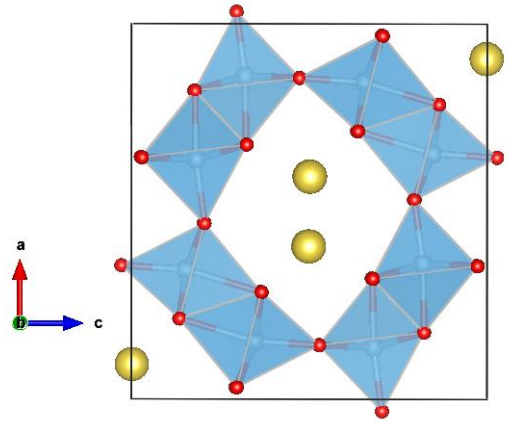


$Na_{0.25}TiO_2$(H)

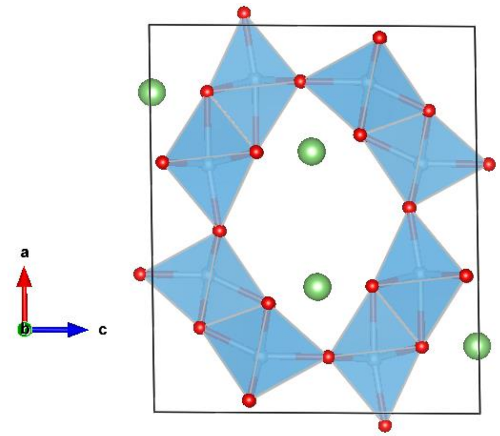
SXRD



$TiO_2(H)$



$Na_{0.25}TiO_2(H)$



$Li_{0.5}TiO_2(H)$

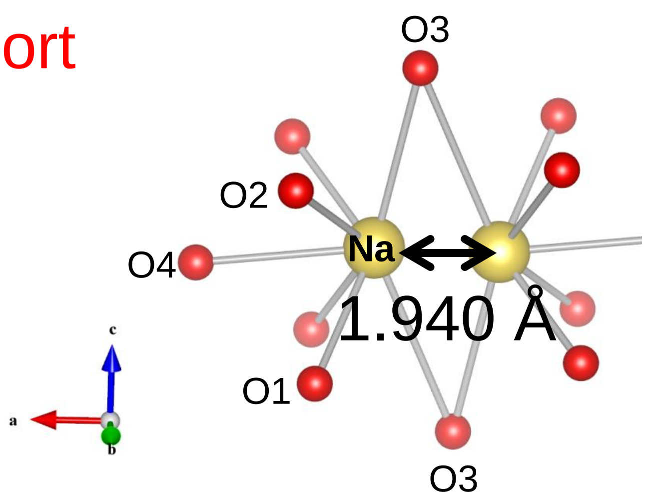
Li occ. :100 %

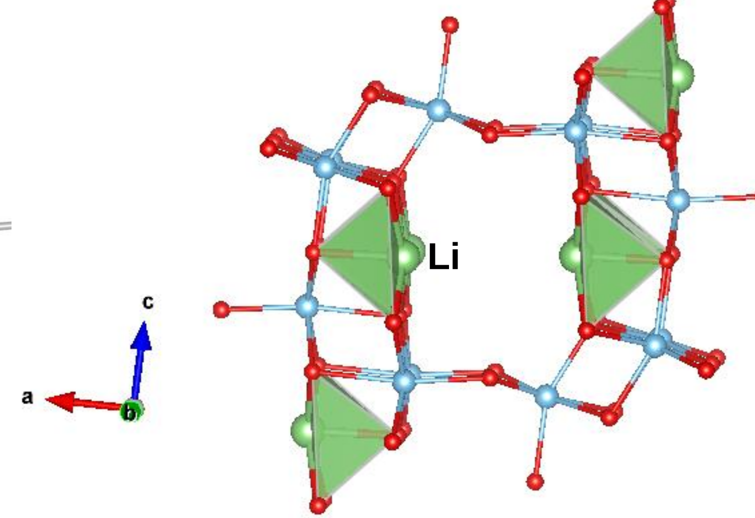
d(Na-Na) is very short

↓

Na occ. 50%

Recall:
2.721Å in $Na_3Ti_6O_{13}$





Summary

	Voltage (V, vs. Na^+/Na)	Capacity (mAh/g)	Coul. Efficiency (%)	Cycling	Safety
Hard carbon [1]	1.2 - 0	200	78 - 99.5	Good	Poor
$Na_2Ti_3O_7$ [2,3]	0.3	175	50 - ?	Moderate	Moderate
$Li_4Ti_5O_{12}$ [4]	0.91	155	81 - 99.5	Good	Good
$Na_2Ti_6O_{13}$ [5,6]	0.8	50	High	Good	Good/moderate
$NaTi_3O_6(OH)\cdot xH_2O$ [7]	1.5 - 0.2	30-40	Low	Moderate	
TiO_2-NT [8]	2.5 - 0.9	70	63 - ?	Moderate	Good
TiO_2-A-NC [9]	1.6 - 0.3	150	42 - ?	Good	
TiO_2-B-NT [10]	2.2 - 0.8	55	-	Moderate	Good
TiO_2-H [11]	2.0 - 0.3	85	50 - 98	Moderate	Good/moderate

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Summary

- $Na_2Ti_6O_{13}$ and TiO_2(H) have interesting structures for dual Li- and Na-insertion chemistry

- $Na_2Ti_6O_{13}$ reversibly inserts 1 Na: 50 mAh/g. Improvement of electrode performance is not expected, because of structural space limitations.

- TiO_2(H) reversibly inserts 0.25 Na: 85 mAh/g. Optimization of electrode (binder, carbon) is important to improve performance.

- General optimization of cell performance is required: fading, rate capability …

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GOBIERNO DE ESPAÑA

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La Suma de Todos

Comunidad de Madrid

Thank you for your attention!!

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