Insight into the channel ion distribution and role on the lithium insertion properties of hexatitanates $A_2Ti_6O_{13}$ (A=Na, Li, H) as candidates for anode materials in lithium-ion batteries

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Detailed Rietveld Refinement

The A (A= Na, Li, H) position sites have been located using Difference Fourier Synthesis maps starting from the basic $Ti_6O_{13}^{2-}$ skeleton framework. Rietveld refinement of every $A_2Ti_6O_{13}$ hexatitanate was first performed using the corresponding previously reported structural model[1] , monoclinic space group *C2/m* (Z=2), but in which A tunnel atoms were not included. The discrepancies between the observed and calculated intensities provided information on the extra scattering density, which was not considered in the starting model. A difference Fourier synthesis based on the difference between observed and calculated structure factors, F_{obs}-F_{cal}, gave information on the location of the missing alkaline atom.

In all cases, the A^+ tunnel cation was found at 4*i* (x,0,z) sites in the y = 0 section. The refined occupation factor of the A atom after its introduction into the structural refinement was in good agreement with the expected A content (2 A atoms/formula unit) for all cases.

Crystal structure refinement of $Na_2Ti_6O_{13}$

A first Rietveld refinement of $Na_2Ti_6O_{13}$ was performed using the previously reported structural model[1] , but in which Na atoms were not included. The starting parameters used were those of $Na_2Ti_6O_{13}$ with the monoclinic space group *C2/m* (Z=2) [1]. The Rietveld refinement of the structural model, in which Na atoms were omitted, yielded the following agreement factors: R*p* = 4.49%, R*wp* = 5.90%, χ^2 = 15.3, R*Bragg* = 6.31%, R*F* = 3.62%. It was observed that independent refinement of thermal displacement factor of Ti2 lead to negative values, while oxygen B factors were nearly zero for O2 and too large for O1 and O5 (B~1). To overcome this problem, B factors of all three Ti atoms were constrained refined to the same value. This procedure resulted in a satisfactory stable B value (0.301(1)). An accurate refinement of thermal displacement factors of oxygen atoms was obtained by a constrained refinement of groups, which consisted of grouping oxygen atoms into a) skeleton atoms (i.e. oxygen atoms O2,O4 and O6 linking ribbons of edge-sharing TiO_6 octahedra) and b) channel atoms (i.e. oxygen atoms O1, O3, O5 and O7 building the channel walls). This constrained refinement in groups gave satisfactory B values of 0.429(1) and 0.645(1) for skeleton and channel wall oxygen atoms, respectively. Finally, constraint extended to all oxygen atoms (O1-O7) yielded an intermediate B value of 0.545(1). However, R values did not improve significantly.

Crystal structure refinement of $Li_2Ti_6O_{13}$

Initial Rietveld refinement of $Li_2Ti_6O_{13}$ was done using the previously reported structural model[2, 3] , but in which Li atoms were not included. Starting parameters for Ti and O atoms were taken from our previous report on $Li_2Ti_6O_{13}$ with the monoclinic space group *C2/m* (Z=2).[2] The following agreement factors: R*p* = 3.26%, R*wp* = 4.32%, χ^2 = 10.4, R*Bragg* = 4.41%, R*F* = 2.99% were obtained with this structural model, in which Li atoms were not included.

Similar problems to those observed for $Na_2Ti_6O_{13}$ arose during Rietveld refinement when thermal displacement B factors of Ti atoms were refined independently. For this reason B factors of all three Ti atoms were constrained refined to the same value, resulting in a reasonable B value of 0.537(7). Thermal displacement factors of oxygen atoms were satisfactorily refined using a constraint of groups, analogous to that followed for $Na_2Ti_6O_{13}$ yielding B values of 0.523(2) and 0.704(2) for skeleton (O2,O4,O6) and channel wall (O1,O3,O5,O7) oxygen atoms, respectively.

$H_2Ti_6O_{13}$

For an initial Rietveld refinement of $H_2Ti_6O_{13}$ structural parameters were taken from the structure of herein reported $Li_2Ti_6O_{13}$ with the monoclinic space group *C2/m* (Z=2),[2-4] but in which protons were omitted. The Rietveld refinement of this structural model, omitting the channel atom, yielded the following agreement factors: R*p* = 2.62%, R*wp* = 3.27%, χ^2 = 2.34, R*Bragg* = 7.69%, R*F* = 7.29%.

Similar to the Rietveld refinement followed for $Na_2Ti_6O_{13}$ and $Li_2Ti_6O_{13}$, Ti atoms were constrained refined to the same value, yielding a reasonable B value of 0.409(74). Thermal displacement factors of oxygen atoms were satisfactorily refined using a constraint of groups, analogous to that followed for sodium and lithium hexatitanate, yielding B values of 0.349(3) and 0.653(2) for skeleton (O2,O4,O6) and channel wall (O1,O3,O5,O7) oxygen atoms, respectively.

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2. J. C. Pérez-Flores, A. Kuhn and F. García-Alvarado, *Journal of Power Sources*, 2011, **196**, 1378-1385.
3. K. Kataoka, J. Awaka, N. Kijima, H. Hayakawa, K.-i. Ohshima and J. Akimoto, *Chemistry of Materials*, 2011, **23**, 2344-2352.
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Table 2 Atomic coordinates, isotropic thermal factors (B_{iso}), selected bond distances (Å) and angles (º) for $Na_2Ti_6O_{13}$ at 300 K using powder neutron diffraction data

Atom	Site	*x*	*y*	*z*	s.o.f.	B_{iso} (Å^2)
Na1	4i	0.46156(16)	0	0.26726(23)	1.0	2.996(8)*
Ti1	4i	0.11498(20)	0	0.09868(38)	1.0	0.305(1)
Ti2	4i	0.16547(21)	0	0.43519(44)	1.0	0.305(1)
Ti3	4i	0.22747(21)	0	0.76951(40)	1.0	0.305(1)
O1	2a	0	0	0	0.5	0.666(1)
O2	4i	0.24117(7)	0	0.24459(13)	1.0	0.411(1)
O3	4i	0.07012(7)	0	0.29212(12)	1.0	0.666(1)
O4	4i	0.29655(7)	0	0.57209(13)	1.0	0.411(1)
O5	4i	0.12768(7)	0	0.61357(13)	1.0	0.666(1)
O6	4i	0.35641(7)	0	0.88307(11)	1.0	0.411(1)
O7	4i	0.16374(6)	0	0.91532(10)	1.0	0.666(1)

* anisotropic betas for Na (x10^4): β11=26.7, β22=404.6, β33=130.8 , β13=15.0, β12=β23= 0

Na-O distances		Angles (edges of prism)			
Na1-O1 x 2	3.2092(16)	O1-Na1-O3 (x2)	55.41(5)	O1-Na1-O1	71.36(4)
Na1-O3 x 2	2.4752(17)	O1-Na1-O7 (x2)	51.78(7)	O3-Na1-O3	98.27(6)
Na1-O5 x 2	2.6416(19)	O3-Na1-O5 (x2)	78.45(7)	O5-Na1-O5	90.25(6)
Na1-O7 x 2	2.9820(17)	O5-Na1-O7 (x2)	57.70(7)	O7-Na1-O7	77.76(5)
Mean Na-O	2.823				

Ti-O distances					
Ti1-O1	1.833(3)	Ti2-O2	2.225(3)	Ti3-O2 x 2	1.9456(9)
Ti1-O2	2.150(3)	Ti2-O3	1.787(3)	Ti3-O4	2.242(3)
Ti1-O3	2.009(3)	Ti2-O4 x 2	1.9629(10)	Ti3-O5	1.909(3)
Ti1-O6 x 2	1.9207(7)	Ti2-O4	2.155(3)	Ti3-O6	2.071(3)
Ti1-O7	1.931(3)	Ti2-O5	1.817(3)	Ti3-O7	1.754(3)
Mean Ti1-O	1.961	Mean Ti2-O	1.985	Mean Ti3-O	1.978

Table 3 Atomic coordinates, isotropic thermal factors (B_{iso}), selected bond distances (Å) and angles (º) for $Li_2Ti_6O_{13}$ at 300 K using powder neutron diffraction data

Atom	Site	*x*	*y*	*z*	s.o.f.	B_{iso} (Å^2)
Li1	4i	0.06192(36)	0	0.76274(70)	1.0	1.355(89)*
Ti1	4i	0.11190(19)	0	0.10075(42)	1.0	0.537(7)
Ti2	4i	0.16508(19)	0	0.42933(45)	1.0	0.492(10)
Ti3	4i	0.23004(19)	0	0.77145(33)	1.0	0.537(7)
O1	4i	0	0	0	1.0	0.704(2)
O2	2a	0.24035(12)	0	0.24218(21)	0.5	0.523(2)
O3	4i	0.07156(13)	0	0.28968(21)	1.0	0.704(2)
O4	4i	0.29359(12)	0	0.57101(23)	1.0	0.523(2)
O5	4i	0.13456(14)	0	0.61118(24)	1.0	0.704(2)
O6	4i	0.35441(13)	0	0.88616(23)	1.0	0.523(2)
O7	4i	0.15934(12)	0	0.91027(19)	1.0	0.704(2)

* anisotropic betas for Li (x10^4): β11=19.8, β22=181.6, β33=60.4 , β13=-8.9, β12=β23= 0

Li-O distances		Angles			
Li1-O1	2.508(5)	O1-Li1-O3	72.07(14)	O1-Li-O5	166.9(2)
Li1-O3	2.026(6)	O1-Li1-O7	75.2(2)	O3-Li-O7	147.2(3)
Li1-O5	1.916(5)	O3-Li1-O5	121.0(2)		
Li1-O7	1.842(5)	O5-Li1-O7	91.8(2)		
Mean Li-O	2.073				

Ti-O distances					
Ti1-O1	1.869(7)	Ti2-O2	2.185(8)	Ti3-O2 x 2	1.942(2)
Ti1-O2	2.113(8)	Ti2-O3	1.760(7)	Ti3-O4	2.193(7)
Ti1-O3	1.929(10)	Ti2-O4 x 2	1.964(2)	Ti3-O5	1.952(7)
Ti1-O6 x 2	1.931(2)	Ti2-O4	2.159(7)	Ti3-O6	2.014(7)
Ti1-O7	1.945(9)	Ti2-O5	1.825(9)	Ti3-O7	1.845(7)
Mean Ti1-O	1.953	Mean Ti2-O	1.976	Mean Ti3-O	1.981

Table 4 Atomic coordinates, isotropic thermal factors (B_{iso}), selected bond distances (Å) and angles (°) for $H_2Ti_6O_{13}$ at 300 K using powder neutron diffraction data

Atom	Site	*x*	*y*	*z*	s.o.f.	B_{iso} (Å^2)
H1	4i	0.00151(25)	0	0.31196(37)	1.0	1.304(11)*
Ti1	4i	0.11311(24)	0	0.10068(37)	1.0	0.454(7)
Ti2	4i	0.16861(30)	0	0.44881(49)	1.0	0.454(7)
Ti3	4i	0.22471(30)	0	0.77044(844)	1.0	0.454(7)
O1	4i	0	0	0	1.0	0.823(3)
O2	2a	0.2384(2)	0	0.2470(3)	0.5	0.360(3)
O3	4i	0.0666(2)	0	0.3051(3)	1.0	0.823(3)
O4	4i	0.2956(2)	0	0.5669(3)	1.0	0.360(3)
O5	4i	0.1211(2)	0	0.6187(3)	1.0	0.823(3)
O6	4i	0.3573(2)	0	0.8716(2)	1.0	0.360(3)
O7	4i	0.1690(2)	0	0.9298(3)	1.0	0.823(3)

* anisotropic betas for H (x10^4): β11=13.0, β22=325.3, β33=29.5 , β13=-13.8, β12=β23=0

H-O distance		Angle	
H1-O3	0.971(5)	O3-H1-O5	164.4(5)
H1-O5	1.981(6)		

Ti-O distance					
Ti1-O1	1.808(6)	Ti2-O2	2.234(9)	Ti3-O2 x 2	1.959(2)
Ti1-O2	2.144(7)	Ti2-O3	1.867(9)	Ti3-O4	2.262(7)
Ti1-O3	2.102(7)	Ti2-O4 x 2	1.956(3)	Ti3-O5	1.955(7)
Ti1-O6 x 2	1.931(2)	Ti2-O4	2.055(9)	Ti3-O6	2.041(7)
Ti1-O7	1.854(7)	Ti2-O5	1.799(9)	Ti3-O7	1.769(7)
Mean Ti1-O	1.962	Mean Ti2-O	1.978	Mean Ti3-O	1.991