ESRF	**Experiment title:** "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"	**Experiment number**: CH-3634
Beamline: BM 20	**Date of experiment**: from: 29.11.2011 to: 04.12.2012	**Date of report**: 13.03.2013
Shifts: 15	**Local contact(s)**: Dr. Carsten Baehtz	*Received at ESRF:*

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Report:

Subtle structural changes occuring during electrochemical insertion of lithium and sodium, respectively, into $Na_2Ti_6O_{13}$ have been studied for the first time using SXRD under operating *in situ* conditions in commercial CR2032 coin cells. A decision in favour of the coin cell approach was made because it presents several advantages over other technologies: high cell stability, reproducibility and durability. Leaking out of electrolyte was not detected after several weeks and would enable future long time cycling studies, which provide valuable information about structural degradation of electrodes up $Na_2Ti_6O_{13}$on extended cycling..The accuracy of electrochemical lithium insertion in $Na_2Ti_6O_{13}$, $Li_2Ti_6O_{13}$ and $H_2Ti_6O_{13}$ performed with *in situ* cells (blue line) is demostrated in Figure 1, data being in excellent concordance with those obtained using standard coin cell technique (red line) [1-3].

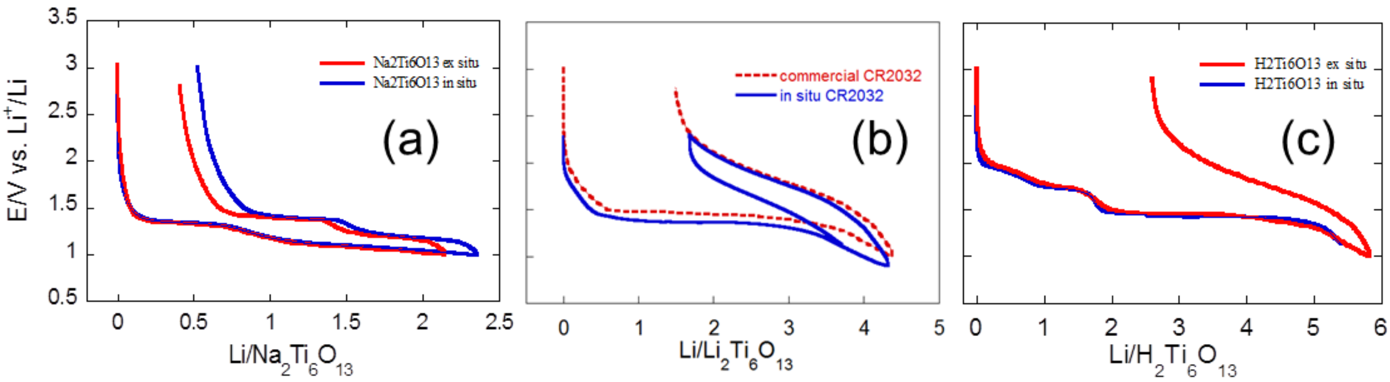

Figure 1: First discharge-charge cycle of Li cells using $Na_2Ti_6O_{13}$ (a) $Li_2Ti_6O_{13}$ (b) and $H_2Ti_6O_{13}$ (c) as the positive electrode with in situ (blue) and commercial coin cells (red).

A house-made sample changer allowed for testing up to five electrochemical cells simultaneously. Cells were successively exposed to the synchrotron beam for approx. 7 min., and diffraction data were collected by using an image plate detector. After completing collection of diffraction data on positions 1-5, measurements continued in the following loop on position 1 etc. For SXRD experiments a constant wavelength λ=0.495638 Å was selected. The *in situ* patterns corresponding to the Li insertion into $Na_2Ti_6O_{13}$, collected at beamline ROBL BM20, show displacement of the cathode material's reflections while the Al reflection, used as current collector and SXR window, does not move (see Figure 2). During the first discharge two two-phase regions are discerned, read by a broadening of the (200), (-201) and (020) reflections and splitting of some of them. This finding is in complete agreement with the electochemical curve in which two plateaus (= biphasic regions) are observed.

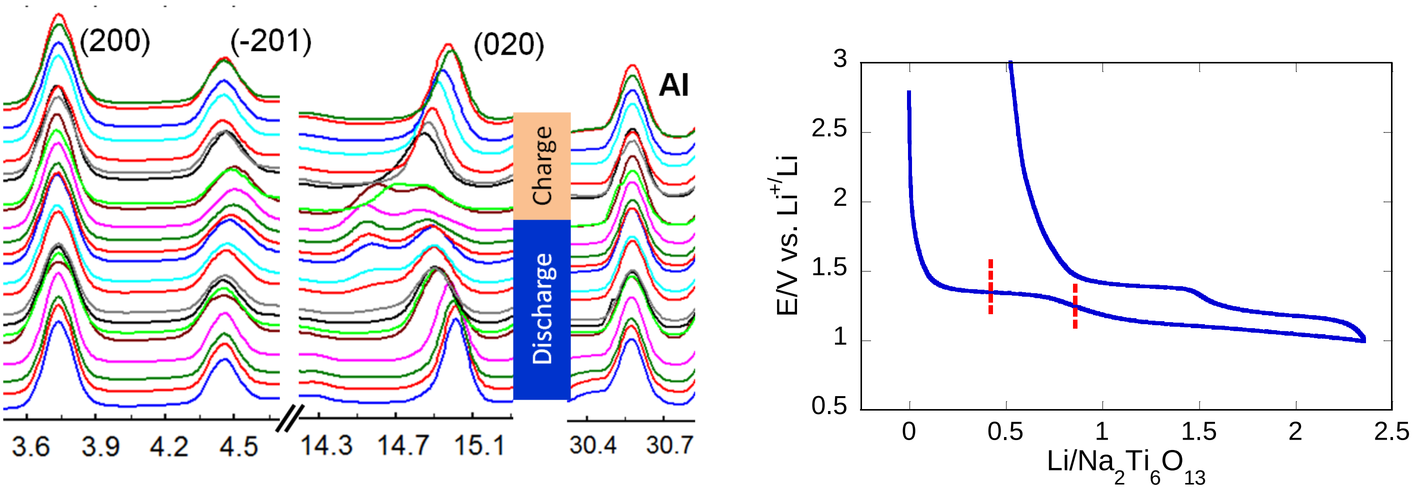

Figure 2: Typical *in situ* patterns collected during electrochemical Li insertion/de-insertion into $Na_2Ti_6O_{13}$ together with the corresponding Li insertion curve.

Na insertion into $Na_2Ti_6O_{13}$ proceeds through a single-phase solid solution regime, perceptible from a continous little displacement of the reflections depicted in Figure 3. $Na_2Ti_6O_{13}$ shows then *zero-strain* behaviour for both Li [1] and Na [4] insertion, producing only slight changes in the cell volume (~1%). This is one of the key factor to develop new long cycle life batterie electrodes.

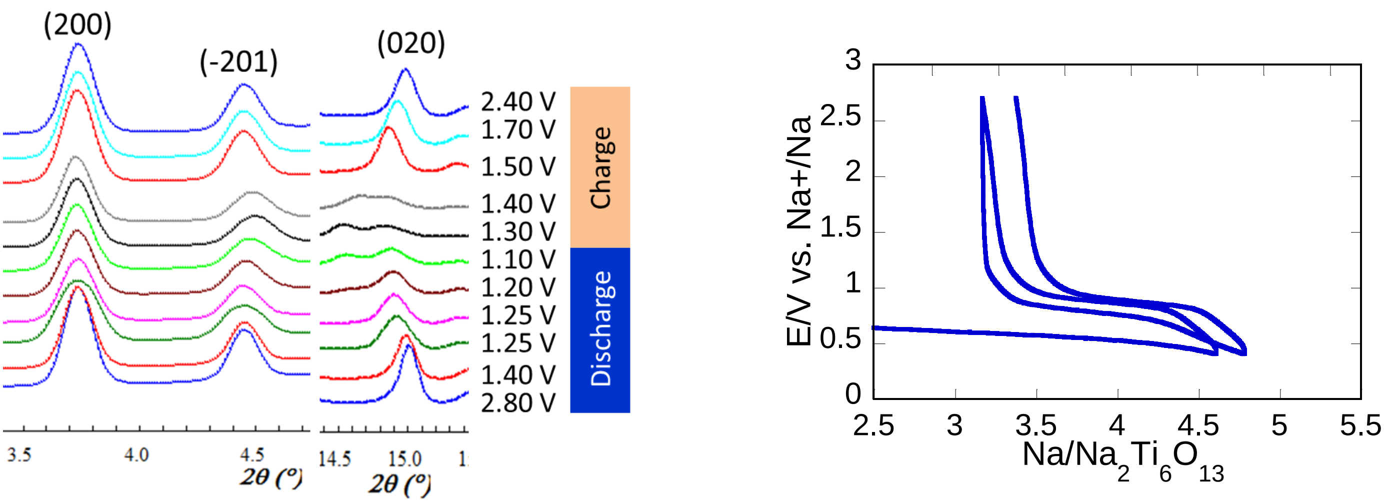

Figure 3: Typical *in situ* patterns collected during electrochemical Na insertion/de-insertion into $Na_2Ti_6O_{13}$ together with the corresponding Na insertion curve.

References:

[1] R. Dominko, E. Baudrin, P. Umek, D. Arcon, M. Gaberscek, J. Jamnik, Electrochem. Commun., 8 (2006) 673–677.
[2] J. C. Pérez-Flores, A. Kuhn, F. García-Alvarado, J. Power Sources 196 (2011) 1378–1385.
[3] J. C. Perez-Flores, C. Baehtz, M. Hoelzel, A. Kuhn, F. Garcia-Alvarado, RSC Advances 2 (2012) 3530–3540.
[4] A. Kuhn et al. (manuscript in preparation)