ESRF	**Experiment title:** "Investigation of electrochemical lithium insertion/de-insertion reactions in new promising cathode materials for lithium batteries using *in situ* synchrotron diffraction techniques"	**Experiment number**: CH-3207
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Report:

A Swagelok-type electrochemical *in situ* cell was charged among others with pellets containing Li_3FeF_6 and $Na_2Ti_6O_{13}$, respectively, as the active cathode material (65%). The corresponding X-ray patterns obtained with synchrotron radiation together with the graphical results of Rietveld refinement are given in Fig. 1. The refined cell parameters of Li_3FeF_6 : a =14.281(2) Å; b=8.626(1) Å; c=9.945(1) Å ; β = 95.532(9)º , space group C2/c, are in good agreement with earlier reports [1], though systematically lower than those reported. The same was found for $Na_2Ti_6O_{13}$ (space group C2/m) with the following refined lattice parameters: a=15.0101(4) Å; b=3.7205(1) Å; c=9.1132(3) Å; β=99.060(1)º [2]. Detailed results of the structural refinements will be published elsewhere [3].

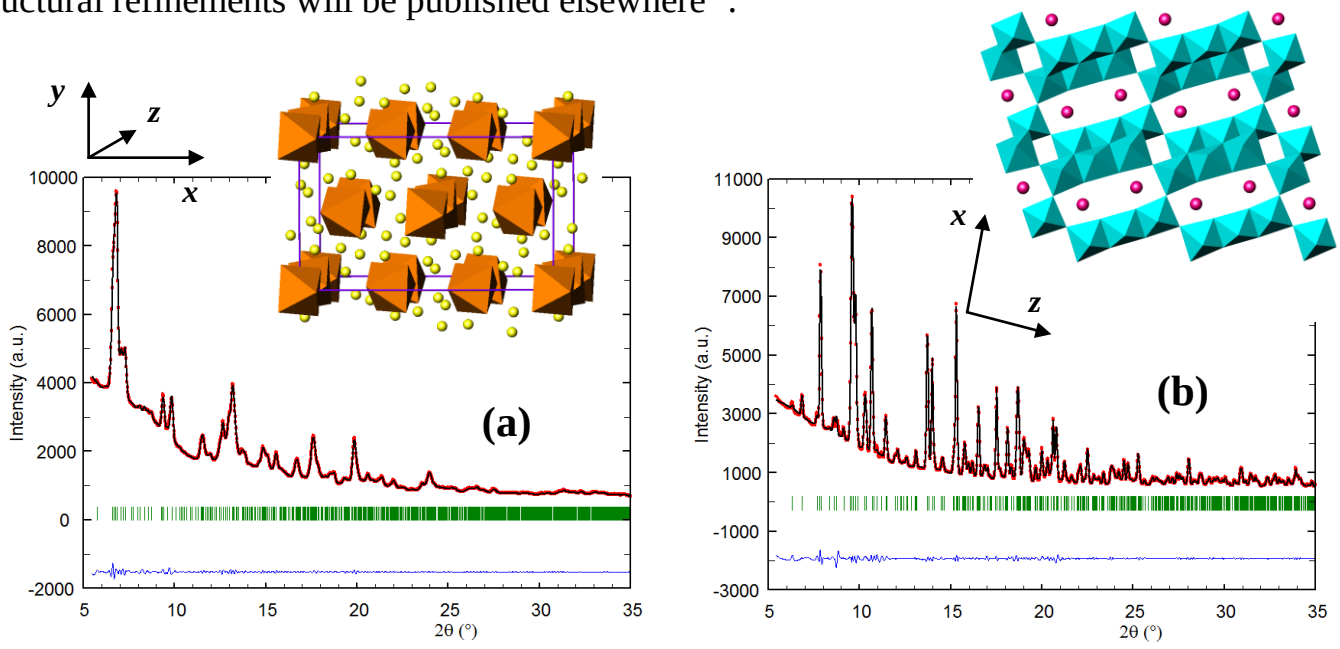

Figure 1: Graphical result of the Rietveld refinement using the Swagelok-type cell used for the intended Li insertion experiments under *in situ* conditions of (a) monoclinic Li_3FeF_6 (S.G. C2/c) and (b) monoclinic $Na_2Ti_6O_{13}$ (S.G. C2/m). The respective refined structural models are shown as inset to the corresponding Rietveld plot. (1a) left: isolated FeF_6 octahedra (ocre) and Li atoms (filled circles); (1b) right: corner and edge-sharingTiO_6 octahedra (pink) and Na atoms (filled circles) are highlighted.

Unfortunately, the discharge-charge cycles peformed with this electrochemical in situ cell did not produce reliable experimental data for any of the tested Li insertion materials. The initial open circuit potential of cells containing intended cathode materials such as Li_3FeF_6, $Na_2Ti_6O_{13}$ or $Li_2Ti_6O_{13}$, was always found to be significantly lower (more than 1 Volt) than the expected one (Fig. 2). Furthermore cells showed clear signs of self-discharge with a continuous decrease of potential with time, which was probably due to some internal short-cut of the experimental cell. Taking then in mind the difficulties to prepare this type of electrochemical cells (non accurate operativity of the cell; prohibition of handling solvents, including liquid electrolytes for lithium batteries, in the glove-box located at the on-site Chemistry Lab), we run electrochemical tests with CR2032 coin cells.

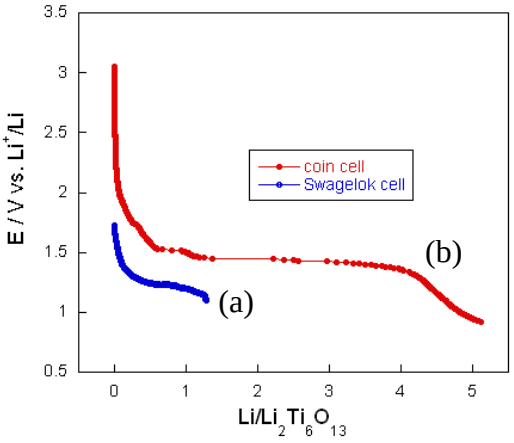

Figure 2: First discharge curves of Li cells bearing $Li_2Ti_6O_{13}$ as the cathode using (a) an electrochemical Swagelok cell and (b) a coin cell.

These had been assembled well in advance to the experiment at the home institution CEU, with the intended insertion materials as the cathode and Li as the anode. Coin cell technology is succesfully being applied in our research group to investigate Li insertion materials, giving very reliable and reproducible results. A typical discharge-charge curve of coin cells bearing $Li_2Ti_6O_{13}$ as the cathode is given in Fig. 2. Although the coin cells presented a good Li insertion electrochemical behaviour, the absorption was now to severe to obtain accurate diffraction data in transmission geometry (components of the coin cell such as (–) and (+) cases, each 0,25 mm thick, and a spacer disk 0, 5mm thick, all of them made were of stainless steel).

In order to overcome the absorption problem it is planned to develop an operating electrochemical cell based on coin cell technology, components of which will be provided with appropriate 5mm diameter concentric holes on both (–) and (+) cases and the spacer disk. A first design of such a cell can be depicted in Fig. 3.

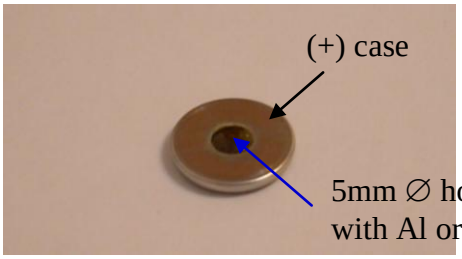

Figure 3: Modified CR2032 coin cell suitable for investigations with transmission high energy synchrotron X-ray diffraction (planned).

[1] E. Gonzalo, A. Kuhn, F. García-Alvarado, *Journal of the Electrochemical Society* (2010).
[2] J.C. Pérez Flores, A. Kuhn, F. García-Alvarado, *Journal of Power Sources* (2010).
[3] A. Kuhn, E. Gonzalo, J.C. Pérez Flores, F. García-Alvarado, C. Baehtz, to be published.