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In situ neutron diffraction study of Li insertion in $Li_4Ti_5O_{12}$

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ABSTRACT

Developing an efficient *in situ* electrochemical cell for neutron diffraction of electrode materials for Li-ion batteries remains a major technical challenge. We recently published the results of the first experiment carried out with such a cell developed by our group. In order to improve the quality of data we optimized the preparation of the electrode, introduced a gradient in the carbon content, and controlled the porosity. $Li_4Ti_5O_{12}$ was used as a model material to demonstrate the advantages of the new approach. 10 diffractograms were recorded *in situ* during the first electrochemical cycle and then refined to obtain the evolution of unit cell parameters, oxygen position, and of the quantitative ratio between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$.

1. Introduction

The comprehension of lithium insertion mechanism is a crucial step in the improvement of electroactive materials for lithium-ion batteries. Potential electrode materials have been extensively studied through *ex situ* X-ray and neutron diffraction. However to obtain more dynamical information on the insertion of lithium during cycling, different groups developed *in situ* X-ray diffraction tools [1–3]. Unfortunately, although X-ray diffraction gives important information about the global structure changes, it doesn't allow a simple localization of lithium. To this point, neutron diffraction is the method of choice. Despite some past attempts [4], and some *in situ* experiments carried out on commercial cells [5], a reliable *in situ* electrochemical cell for neutron diffraction has not been described yet.

The difficulty in designing such a cell is due to the contradictory needs of both electrochemical cycling and neutron diffraction. As the interaction of neutrons with matter is weak, high amount of electroactive powder should be used to acquire a good diffractogram in a given time. But this big quantity of material is detrimental to the electrochemical cycling as a thick electrode increases the overpotentials in the cell. Furthermore, the presence of a H-containing electrolyte in the cell also lowers the quality of neutron diffraction patterns. These difficulties often lead the groups to study lithium localization by *ex situ* neutron diffraction on chemically inserted materials rather than on their electrochemically inserted relatives.

We recently developed such an *in situ* electrochemical cell, whose preliminary test was very promising [6]. But to retrieve good structural data, the quality of the patterns had to be improved. We identified the electrode engineering as the bottleneck to achieve this goal. Thus we investigated two major issues related to the electrode architecture, namely the porosity and the volumetric current distribution. In order to demonstrate the advantages of this new electrode architecture, *in situ* neutron diffraction had to be carried out on a model material. Such a model material had to be a well described material so that the results obtained with our cell could be easily compared to the expected results. The model material should also enlighten the specificity of neutron diffraction. For these reasons $Li_4Ti_5O_{12}$ was selected as a good model material. The Li insertion–deinsertion mechanism is indeed well documented for this compound [7,8]. The starting material crystallizes in a spinel type structure and can be formulated as $Li[Li_{1/3}Ti_{5/3}]O_4$ where the tetrahedral sites are occupied by lithium and the octahedral sites by both titanium and lithium. The insertion of lithium occurs through a biphasic process whose second end member is $Li_7Ti_5O_{12}$ and can be formulated as $Li_2[Li_{1/3}Ti_{5/3}]O_4$. In this material the $[Li_{1/3}Ti_{5/3}]O_4$ skeleton remains intact but the tetrahedral sites are now empty due to the migration of lithium ions in the vacant octahedral sites resulting in a rock-salt type structure. Interestingly, only the position of lithium differs significantly in the two end members, so it will be a good test for the data quality of our *in situ* diffractograms as the intensity changes would be directly related to the lithium migration.

2. Experimental

Neutron powder diffraction studies were performed in an in-house built electrochemical cell that is capable of cycling large quantities of material and permits diffraction characterization of the required active material without interference from other components of the cell. The design of the assembled *in situ* neutron cell was published elsewhere [6].

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Commercial $Li_4Ti_5O_{12}$ powder obtained from Süd-Chemie AG (Moosburg, Germany) is mixed with appropriate amount of graphite KS6 and Super P carbon both from TIMCAL SA (Bodio, Switzerland). Celgard 2400 (Celgard, LLC, Charlotte, North Carolina, USA) was used as a separator and lithium metal (Aldrich, 99.9%) was used as counter electrode. The electrolyte used was 1 M $LiPF_6$ in EC/DMC (Ferro, Ohio, USA, EC = ethylene carbonate, DMC = dimethyl carbonate). Note that the use of deuterated electrolyte was planned but due to the very high water content in the delivered solution the electrochemistry failed. Thus a standard (protonated) electrolyte was used.

Our preliminary experiments with the *in situ* cell [6] showed the importance of the active material to carbon ratio. Only few intense peaks of the studied $Li_{1.1}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1.9}O_2$ were indeed detectable. This led us to put stress on the improvement of the electrode preparation procedure. Two issues have been identified as critical. Firstly, as the current path to the current collector, and consequently the ohmic resistance, increases with the increasing distance, the content of conductive additives should be optimized along the current paths to ensure homogeneous bulk current density distribution. Thus, the electrode was divided into three layers, called bottom, middle and top layer going from the current collector to the separator. The content of graphite was set to be maximum in the top layer, which is far from the current collector, and then decreased through the middle and bottom layer. Secondly, to get a better diffraction signal we also had to minimize the content of Super P carbon. The primary role of Super P in our electrode mass is to bring porosity of the electrode to get a good wetting of all particles independent of their location. To reduce the amount of Super P, the porosity was controlled by the following method. First NH_4HCO_3 was mixed with the other components of the electrode mass, and the mass was pressed into the current collector. Then the electrode was heated at 150 °C under vacuum, which provoked the complete decomposition of NH_4HCO_3, resulting in a release of gases that left behind a well-defined porous network running through the electrode [9]. Using this technique the average active material to carbon ratio was increased to 6:1, compared to the 1:1 used in Ref. [6], without compromising the electrochemical properties of the cell.

The electrochemical cycling used during the *in situ* neutron diffraction experiment was similar to a GITT protocol; a step consisting of an 80 min galvanostatic charging (or discharging) at C/25 rate followed by a 100 min at OCV was repeated 3 times, and then followed by a 9 h OCV step during which the neutron diffraction pattern was acquired (Fig. 1). This protocol was chosen to ensure equilibrium during the pattern acquisition and to reduce the polarization effects in the extremely thick electrode. During the three steps of active cycling, a second, identical cell running simultaneously allowed the recording of additional patterns, thus using the beam time more effectively. One cell was devoted to the pattern collection during the first charge, while the other one was charged before the neutron experiment and was devoted to the acquisition of patterns during the first discharge.

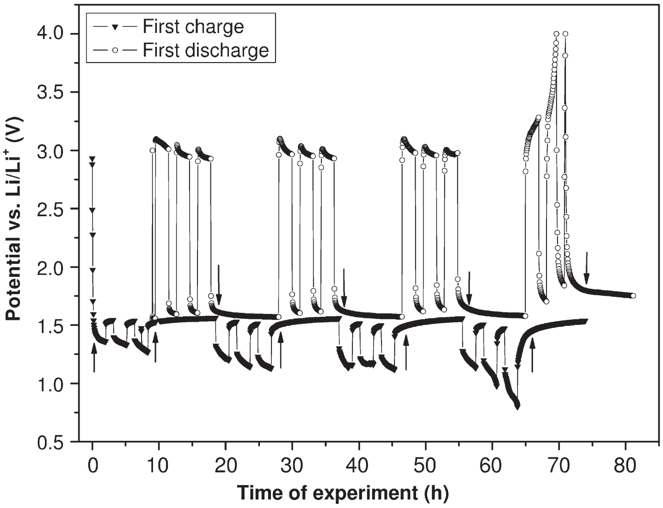

Fig. 1. Electrochemical data obtained with two *in situ* cells. The arrows show the time when the acquisition of a new diffraction pattern starts.

The patterns were acquired at the High Resolution Powder Diffractometer for Thermal Neutrons (HRPT) beamline at the Swiss Spallation Neutron Source (SINQ, Paul Scherrer Institut) using a 1.494 Å wavelength. The Rietveld refinements were carried out using Fullprof software [10].

3. Results

The precise structure of the pristine $Li_4Ti_5O_{12}$ material was first determined *ex situ* by neutron diffraction using a vanadium tube as a sample container. As expected, the compound crystallized in the $Fd\bar{3}m$ space group with a cell parameter $a = 8.3636$ Å, which is in accordance with the literature [7,11]. Refinement of occupancies did not bring any improvement in the fitting of data so they were fixed to their theoretical value. The results of the refinement are given in Table 1.

The electrochemical data are shown in Fig. 1. Along this article we will use the nomenclature used for full cells, thus the insertion of lithium in $Li_4Ti_5O_{12}$, which is an anode material will be called charge. We can observe that, during the galvanostatic part of the cycling, the polarization reaches high values which were expected due to the extreme thickness of the working electrode (around 4 mm) and the high current used (15 mA for 2.2 g of electroactive material). But when the current flow was stopped, the system relaxation was sufficiently fast and a potential close to the expected equilibrium (1.57 V vs. Li^+/Li) was reached at the end of the OCV step. This is obviously due to the good repartition of the electrolyte through the electrode. The acquisition of diffraction pattern then took place when the system was in a quasi-equilibrium state. A specific charge of 163 mAh/g was achieved at the end of the first charge which means that 93% of the material reacted. During the successive discharge a small irreversible charge loss of 5% was noticed. These results prove that using a proper design of the electrode allows overcoming challenges raised by the high amount of material required for neutron diffraction.

The diffraction patterns obtained during the cycling are shown in Fig. 2. The background shows a characteristic bend shape due to the protonated electrolyte, but still peaks due to the active material are clearly visible. The structural model obtained during the *ex situ*

Table 1
Crystallographic data for $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$.

		$Li_4Ti_5O_{12}$			
Space group: $Fd\bar{3}m$		Cell parameter a (Å) = 8.36363(5)		$\chi^2 = 2.6$	
Atom	Wyckoff site	x	y	z	Occupancy
Li1	8a	0.125	0.125	0.125	1.0
Li2	16d	0.5	0.5	0.5	0.1667
Ti	16d	0.5	0.5	0.5	0.8333
O	32e	0.2625(1)	0.2625(1)	0.2625(1)	1.0
		$Li_7Ti_5O_{12}$			
Space group: $Fd\bar{3}m$		Cell parameter a (Å) = 8.35805(2)		$\chi^2 = 1.7$	
Atom	Wyckoff site	x	y	z	Occupancy
Li1	16c	0	0	0	1.0
Li2	16d	0.5	0.5	0.5	0.1667
Ti	16d	0.5	0.5	0.5	0.8333
O	32e	0.2576(3)	0.2576(3)	0.2576(3)	1.0