Experimental report

05/02/2016

Proposal:	**7-03-146**	**Council:**	4/2015
Title:	Quasi Elastic Neutron Scattering on Li2VO2F, a high performance electrode material for lithium ion battery		
Research area:	Other...		

This proposal is a new proposal

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Samples: Li2VO2F

Instrument	Requested days	Allocated days	From	To
IN16B	5	5	12/11/2015	17/11/2015

Abstract:

The proposed experiments aim to obtain detailed atomic scale information about mechanisms governing the lithiation/delithiation of the new promising Li2VO2F cathode material for lithium batteries. This is a novel cathode material with unprecedented high capacity and energy density (462 mAh/g, 1000 Wh/ kg respectively). In comparison to previously reported vanadium-based compounds, the lithium insertion reaction is reversible. We want to gain an understanding of lattice reordering and stabilisation resulting from ion migration during charge/discharge reactions. We anticipate that the mobility of vanadium is a key parameter, assuring the stability of the crystal structure during the delithiation and therefore its reversibility. Vanadium atoms could move to the free lithium lattice sites, jumping to the defect sites to accommodate its oxidation state. To confirm this hypothesis we would like to study the vanadium dynamics in Li2-xVO2F with different stoichiometry, fully lithiated (x=0), half lithiated(x=1) and nearly fully delithiated (x~1.7). We will combine (QENS) with DFT calculation to investigate the vanadium jump diffusion and the lattice site migration.

Experimental Report – 7-03-146 IN16b

Quasi Elastic Neutron Scattering on Li2VO2F, a high performance electrode material for lithium ion battery

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The proposed experiment aimed to obtain detailed atomic scale information about mechanisms governing the lithiation/delithiation of the new promising Li_2VO_2F cathode material recently developed at KIT [1]. This is a novel cathode material with unprecedented high capacity and energy density (462 mAh/g, 1000 Wh/ kg respectively). In comparison to previously reported vanadium-based compounds, the lithium insertion reaction is reversible, thus it is important to understand the mechanisms governing the lithiation/delithiation reaction. We anticipate that in such compound, the mobility of vanadium is a key parameter, assuring the stability of the crystal structure during the delithiation and therefore its reversibility. Vanadium atoms could move to the free lithium lattice sites, jumping to the defect sites to accommodate its oxidation state. To confirm this hypothesis we planned to study the vanadium dynamics in $Li_{2-x}VO_2F$ with different stoichiometry, fully lithiated (x=0), half lithiated(x=1) and nearly fully delithiated (x~1.7). However, due to the unexpected leave of the person in charge of the synthesis, another colleague had to learn from scratch the synthesis of the cathode material and we did not get in time the three different samples but only the fully lithiated (x=0).

The *Figure 1* presents the results obtained from different elastic/inelastic temperature scans performed on Li_2VO_2F. A first scan (0 μeV, 2 μeV at 1^{o}K/min form 2 to 550K, red and green plots in *Figure 1*) was performed. The elastic intensities decreased mainly above 250 K with two peculiar features observed at ~250K and ~450K. A second scan (0 μeV at 0.5^{o}K/min from 240 to 540 K, blue plots in *Figure 1*) was performed with longer acquisition time at each temperature. This second scan shows the same monotonic decrease with temperature but with the better statistic, the two peculiar events of the first scan are not any more visible and thus might have resulted from the poor statistic of the first temperature scan. During the first scan, the inelastic intensities (2 μeV at 1^{o}K/min form 2 to 550K, green plots in *Figure 1*) didn't seem to change much but because of the limited statistic, we performed inelastic measurements at three different temperatures and three different energies (2, 5 and 10 μeV, at 240, 350 and 500 K, pink plots in *Figure 1*) with much longer acquisition time (20 min. vs 2 min.). These measurements show that no clear changes in the inelastic signals could be recorded. It was therefore concluded that the observed decrease in the elastic intensity during the first and second scans might originate only form thermal vibrations (Debye Waller) and we decided to stop any further investigation on this compound. For that fully lithiated Li_2VO_2F it is thus concluded that if any vanadium dynamics, such as jump diffusion, exist it is not possible to probe them. Most probably, because of the stoichiometry, only small fractions of the vanadium are mobiles, if any, and thus this is not detectable. More favourable samples i.e. $Li_{2-x}VO_2F$ with x from 1 to 1.7 should be investigated in the future.

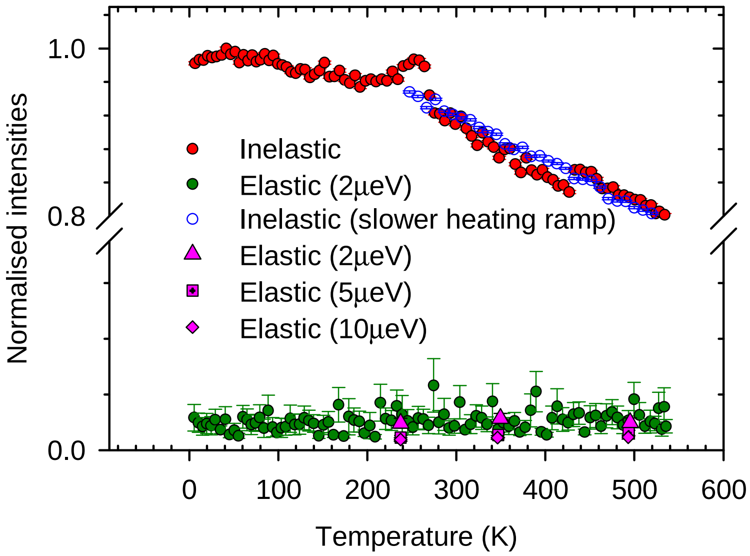

Figure 1: *Elastic/Inelastic temperature scans performed on fully lithiated* Li_2VO_2F

The last days of this beam time were successfully used to investigate the BH_4^- mobility in a composite made of $LiBH_4$ ball-milled with SiO_2 aerogel. Such composites exhibit high Li^+ conductivity and can be used as solid-electrolyte in all-solid-state lithium –ion batteries. Indeed, we propose to develop all-solid-state lithium-sulfur batteries, of higher robustness, prolonged lifetime and higher energy and power densities than current state-of-the art Li-ion batteries. The development of better batteries for cost effective electricity storage is paramount for large market penetration of electrical vehicle and integration of renewable, but intermittent, energy sources into the grid system. For today's best technology, *i.e.* state-of- the-art lithium-ion battery, limited improvement in capacity and cost are expected because of the use of liquid or gel electrolytes which limits the choice of electrode materials and exposes to safety concerns. Finding a solid-state electrolyte, to replace the liquid ones, with adequate properties is a challenging task but we found that if a lithium-ion containing light metal hydride (LiBH4) is confined in a nano-porous SiO_2 scaffold, the lithium conductivity is multiplied by 1000! [2]. We also found that the high Li^+ conductivity is most probably due to the interface existing between SiO_2 and $LiBH_4$ and not an intrinsic property of the nanoconfinement. Ball milled samples are ideal to investigate this latter finding. A clear correlation exists between the BH_4^- rotational diffusion and Li^+ mobility as proved by NMR measurements and explained by the "paddle to wheel" mechanism. Therefore Quasi-Elastic Neutron Scattering characterization on $LiBH_4$ ball-milled with SiO_2 aerogel should bring valuable information on this solid-electrolyte mainly to probe the fraction of highly mobile BH_4^- located at the interface between $LiBH_4$ and SiO_2.

Figure 2 displays the change in the inelastic counts at 2μeV during a temperature scan from 2 to 280 K at 1 K/min. Clearly there is a large increase on the counts until above 210 K and then a decrease when the lorentzians become too broad. For pure $LiBH_4$, only the two last peaks (~ 210 k and 240K) are expected and correspond to rotational diffusion along the C3 and C4 axis of the BH_4- anions. This is well documented. More interestingly and as expected form the conductivity measurements, the inelastic intensity began to increase at rather low temperature, ~60K and it is possible to distinguish two components as illustrated by the quick fitting displayed in Figure 2.

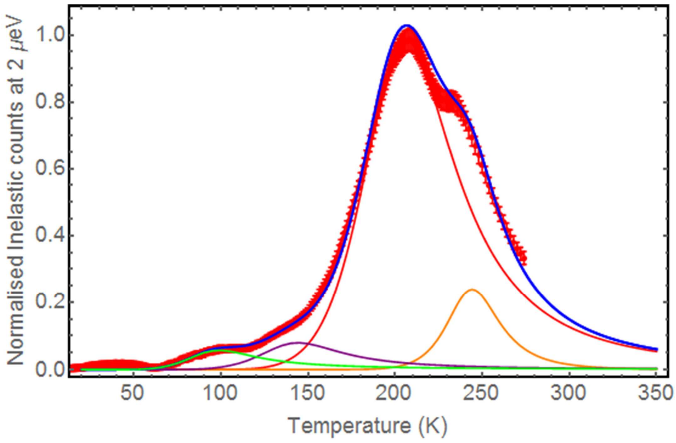

Figure 2: Inelastic temperature scan performed on LiBH4/SiO2 composite.

From that measurement, it was decided to record QENS spectra at the following temperatures: 50, 80, 110, 120, 130, 140, 150, 160, 180, 200, 225, 250 and 290 k with energy windows of 5 and 30 μeV.

Figure **3** displays some of the QENS spectra recorded with the energy windows of 5μeV. The quasi-elastic broadenings are unambiguous. The full analysis of the different spectra is currently undergoing and hopefully it will be possible to extract the exact fraction of the BH_4^- being highly mobiles at low temperatures, i.e the ones at the interface with SiO_2.

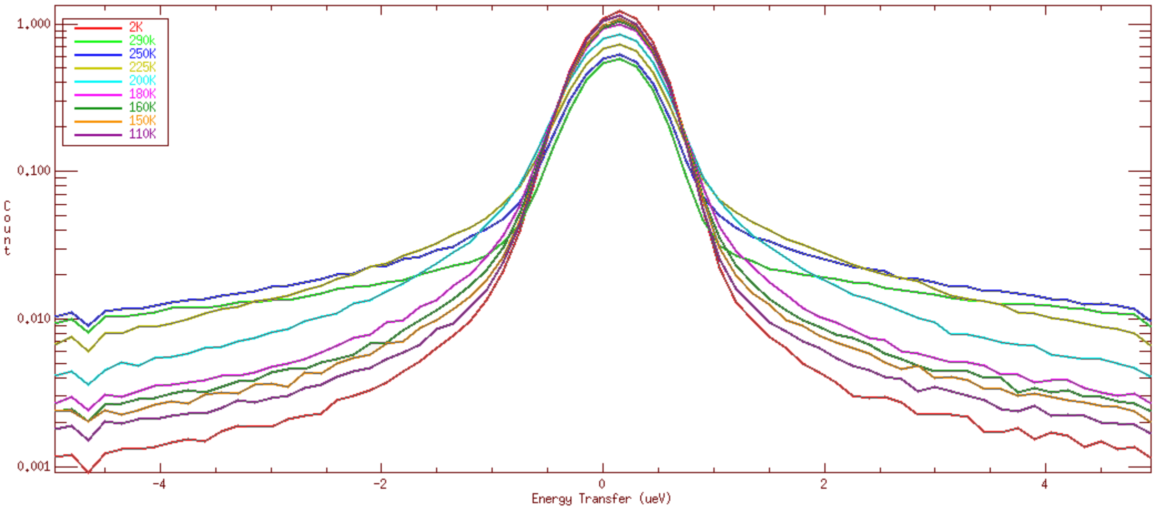

Figure 3: QENS spectra for $LiBH_4/SiO_2$ composites recorded at different temperatures. Summation over all detectors. Energy window 5μeV

[1] R. Chen, S. Ren, S. Indris, M. Fichtner, H. Hahn, Patent application, EP 14160894.3, 2014.

[2] Blanchard, Didier, Angeloclaudio Nale, Dadi Sveinbjörnsson, Tamara M Eggenhuisen, Margriet H W Verkuijlen, Suwarno, Tejs Vegge, Arno P M Kentgens, and Petra E de Jongh. 2015. “Nanoconfined LiBH4 as a Fast Lithium Ion Conductor.” *Advanced Functional Materials* 25(2): 184–92.