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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In-situ electronic structure study of novel Li-ion batteries	**Experiment number**: HE 1265
Beamline: ID 16	**Date of experiment**: from: 8 May 2002 to: 12 May 2002	**Date of report**: 22 August 2002
Shifts: 12	**Local contact(s)**: Gyorgy Vanko	*Received at ESRF:*

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Report:

Li-ion batteries have been in the focus of substantial interest as power sources for portable telecommunication, IT and hybrid electric vehicles. In order to improve Li-ion battery technology further, understanding the electronic structure of novel battery materials, such as $LiNiO_2$, is of fundamental importance. There are conflicting reports regarding the redox chemistry of Ni and the role of oxygen during battery cycling in $LiNiO_2$ based cathode materials. In some experiments the hole doping following lithium removal from the cathode during battery operation is observed to happen mostly on oxygen sites while in other experiments the charge compensation is observed to happen trough further oxidation of the transition metal ions.

This experiment aimed to answer these discrepancies by measuring the evolution of Non-Resonant Inelastic X-ray Scattering (NRIXS) spectra of O in a series of $Li_xNi_{0.85}Co_{0.15}O_5$ samples with a varying degree of Lithium content *x*. In NRIXS, by tuning the energy transfer over the core electron binding energies, an equivalent of conventional inner shell absorption spectrum can be measured. In this experiment we tuned the energy transfer over oxygen 1*s* binding energy and thus we were able to measure the O K-edge absorption spectra using hard x-rays, making this a bulk sensitive experiment.

Two incidents, however, prevented us from reaching the full objectives of the experiment. After getting the samples aligned on Friday, 10th of May, we were able to measure NRIXS spectrum from one $LiNi_{0.85}Co_{0.15}O_5$ sample before the malfunction of the storage ring control computers on the night of Friday, due to the sabotage in the control room and followed by a 2-day shutdown, prevented the further use of the beamline. Secondly, we experienced severe difficulties with getting the samples delivered to ESRF on time. The French shipping company Ziegler was unable to deliver the samples by the start of the experiment due to delays caused by the US shipping company used by the Brookhaven National Laboratory, from where the samples originated, and due to problems with the French customs. The bank holiday on Thursday, 9th of May, caused

further delays in the delivery. The total delivery time turned out to be 10 days instead of three days promised by the shipping company, causing altogether a delay of several shifts in starting the experiment. However, if we had been able to proceed normally with the experiment till the end of the allocated beam time, we would have been able to achieve the objectives of the experiment despite the sample delivery problems.

The obtained NRIXS data from $LiNi_{0.85}Co_{0.15}O$ sample, with energy transfer corresponding to O 1*s* binding energies, is shown in figure 1. together with O K-edge absorption spectra of some Li oxycompounds recorded using soft x-rays. The data clearly shows that meaningful results are obtainable with the used experimental technique at ID 16. Further analysis of the data is currently under work.

We would also like to emphasize, that during the experiment we have gained expertise on several complicated technical issues. The samples require inert gas atmosphere and during the conducted experiment we have been able test and improve the procedures needed for sample preparation, transportation to the beamline and manipulations at the experimental station under the required special conditions. Further, we have gained information on the expected count rates and on the radiation damage to the samples. We expect this information to very valuable in continuing this experiment in the future.

Notwithstanding the sample delivery problems we were able to use the first half of the allocated beam time efficiently for scientific work after being granted by the beamline staff a permission to work on a MgB_2 sample using NRIXS. The Helsinki group had previously done experiments on this sample on ESRF beamline ID15 and the unexpected opportunity to further study the sample has supported the efforts to understand the properties of this compound.

We conducted investigations i) on the collective charge excitations of the MgB_2 system as evidenced by momentum transfer dependant dispersion of plasmon like excitations at few eV energy transfer range, and ii) on the free electronic states of Boron by recording NRIXS spectra at energy transfers corresponding to boron K-shell energy at varying momentum transfers to the electronic system.

Although the MgB_2 investigation was planned to be only a preliminary one, the obtained data seems to be of high enough quality to merit publication. Currently, a paper on the results of experiment ii) is under preparation and the results of experiment i) are being analyzed.

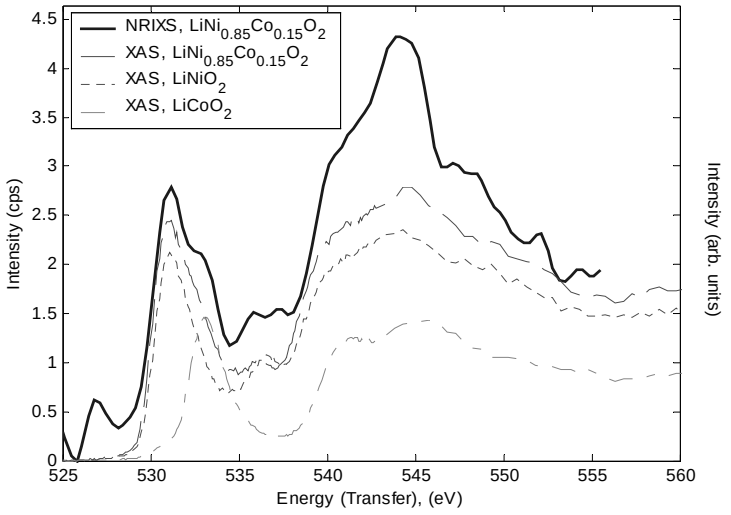

Figure 1. The NRIXS spectrum from $LiNi_{0.85}Co_{0.15}O$ (blue line, in units of cps) at energy transfers corresponding to O K-edge energies. The obtained data is compared with soft x-ray O K-edge absorption measurements of $LiNi_{0.85}Co_{0.15}O$, $LiNiO_2$ and $LiCoO_2$ (in arb. units).