Experimental Report

Operando PDF of novel electrode materials for rechargeable Li ion and Mg-ion batteries

Beamline P02.1 21st - 25th of September 2017, Dorthe B. Ravnbæk, Daniel R. Sørensen, Christian Henriksen, Jonas H. Kristensen, Christian L. Jakobsen, Jeanette Hvam

1) Short description of the actual experiment (including user provided setups) and typical example of the results obtained. Include DESY NanoLab experiments if applicable.

The goal of the proposed experiment was to investigate structural changes and phase transformations during battery charge and discharge in selected positive electrode materials for Li- and Mg-ion batteries by means of operando pair distribution function analysis and to some extant powder X-ray diffraction.

The cathode materials, present in the form of free-standing pellets, were mounted in the special designed operando battery test cells together with electrolyte and Mg- or Li-metal anodes. The cells were mounted at the diffractometer in a special cell-stage holding six cells (Figure 1), and connected to a battery cycler (galvanostat) from which charged/discharged current rates were controlled giving complete charge or discharge in between 2 and 20 hours. Simultaneously, operando diffraction data of all mounted cells were collected in parallel (stage moved circularly by macro for alternating data collection). The data was collected in transmission mode using the 2D Perkin Elmer detector and X-ray exposure times of 30 s. A CeO_2 standard was measured at all six positions for determination of sample to detector distance. Measurements of the empty cell as well as cell assemblies without cathode materials, i.e. cell, separator, and electrolyte, were collected for background subtraction. Idle time between operando measurements were used for ex-situ data collections and test measurements on different cell-stack composition such as cathode material coated on aluminium foil, or cell-stacks with Mg-metal in the X-ray beam to be used for optimization of future experiments.

During the experiment several cathode materials were investigated as described in the proposal: Several TiO_2 polymorphs of various particle size, a series of amorphous Mn-O compounds, V_2O_5 in both crystalline and amorphous state. Additionally, select novel battery systems of mixed metal phosphor-olivines were investigated for the first time.

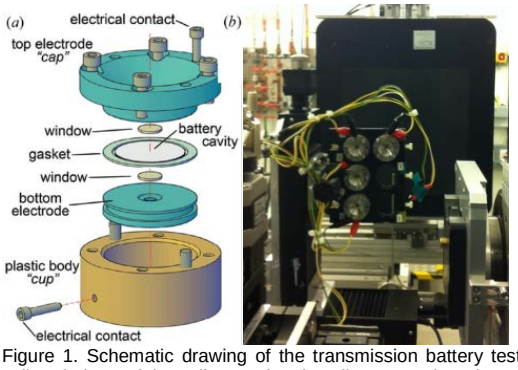

Figure 1. Schematic drawing of the transmission battery test cell and photo of the cell stage for six cells mounted on the Y-Z motors.

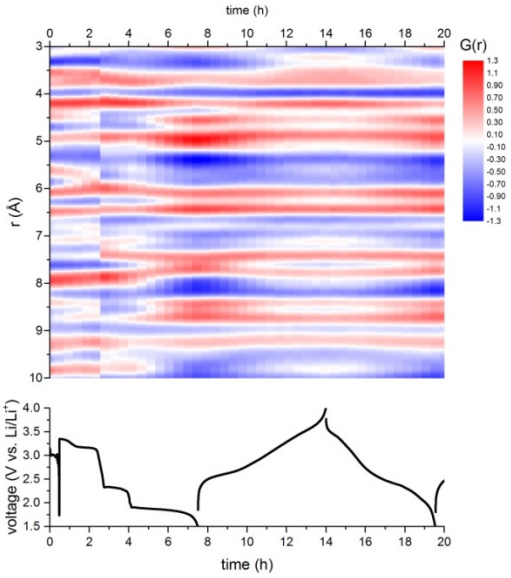

Figure 2 (top) Operando PDF data for the electrochemical insertion (discharge) and extraction (charge) of Li in V2O5 and (bottom) the corresponding galvanostatic voltage response.

2) If applicable: short description of any difficulties encountered during the experiment (beyond the information addressed in your beamtime feedback)

Some electrochemical problems were encountered but they were fixed by alterations in the cell assembly.

3) If applicable: Did you alter the originally proposed experiment or did you request a beamline setup different from the one requested in the proposal? If yes: explain details.

As usual, we tested the most interesting and best performing materials available prior to the beamtime. This means a few of the materials explained in the proposal were exchanged for newer ones. All materials were measured in the originally planned experimental setup.

4) Has the aim of the experiment been achieved? Are the data sufficient for publication? If not: which data/information would be needed in addition to the obtained results?

The aim of the experiment has been achieved and three manuscripts are in preparation for publication in peer reviewed journals. For the three materials in focus: TiO_2, Mn-O and V_2O_5 the obtained PDF data has been the key for understanding the structural changes these materials undergo during battery charge and discharge. In the case of Mn-O, we deal with a completely amorphous yet electrochemical active material. Very few details presently exist about ion storage in amorphous materials. For the other cases, it appears that we now can conclude that ion-intercalation induced formation of nano-crystals, likely as a strain relieving mechanism.

5) Do you expect DESY staff to be included as co-author?

No