

# In situ neutron radiography of lithium-ion batteries during charge/discharge cycling

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## Abstract

Commercial, prismatic lithium-ion cells, type ICP-340848 (Renata AG, Switzerland), were investigated using neutron radiography. The measurements revealed that an excess of electrolyte initially present in the cell was consumed after first cell charging and solid electrolyte interphase formation. In situ neutron radiography of the lithium-ion cells during the first charge/discharge cycles showed a displacement of such excess electrolyte owing to volume changes of the electrode assembly as well as to an evolution of gases in the first charging cycle.

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## 1. Introduction

In situ techniques are useful tools for investigating the processes occurring in lithium-ion cells during electrochemical cycling [1–3]. Frequently, specially designed laboratory test cells are used for electrochemical in situ measurements, and the properties of commercial lithium-ion batteries are inferred from such measurements. Applying in situ measurements directly to commercial lithium-ion cells would be advantageous for a correct identification of certain processes taking place therein. Neutron radiography (NR) is a non-destructive inspection method that has been applied to the investigation of various technical devices [4,5]. This imaging method should be a useful tool for the investigation of lithium-ion cells, since the neutrons have favorable properties with respect to mass attenuation in the various materials used in lithium-ion cells. Specifically, neutrons are strongly attenuated<sup>1</sup> both by Li and by the H atoms of the organic electrolyte used in lithium-ion cells, whereas the metallic parts of the lithium-ion cell, i.e. the aluminum cell casing and the electrode current collectors made of Al and Cu, are rather transparent to neutrons [4,6].

The electrode active components, which are fabricated of a carbonaceous material and a transition metal oxide, respectively, also give rise to a comparatively low neutron beam attenuation in their de-lithiated state. Fig. 1 shows the mass attenuation coefficients of the various elements. Thus, NR can be used to visualize electrochemical processes involving macroscopic changes in the organic electrolyte and in the lithium-ion distribution of lithium-ion cells. In contrast, X-ray radiography as another conceivable imaging method for in situ electrochemical investigations, would not be suited for the study of such lithium-ion batteries, because the X-ray mass attenuation coefficients for the various elements contained in the lithium-ion battery are in the same range, see Fig. 1 [4]. Therefore, a large part of the X-rays would be attenuated by the cell casing and the electrode current collectors.

The application of NR for a qualitative investigation of several commercial lithium batteries with metallic lithium or a lithium alloy as the anode material has been reported [6]. In that NR study, changes of the lithium distribution occurring within the battery at different charge and discharge stages were observed. To our knowledge, no in situ NR study on the behavior of lithium-ion batteries during electrochemical cycling has been published up to now. We therefore applied NR to the in situ study of a commercial, rechargeable lithium-ion cell, type ICP-340848 (Renata AG, Switzerland), and we observed macroscopic changes that occurred inside the cell during cycling.

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<sup>1</sup>Attenuation of a neutron beam is caused by scattering and/or absorption of neutrons.

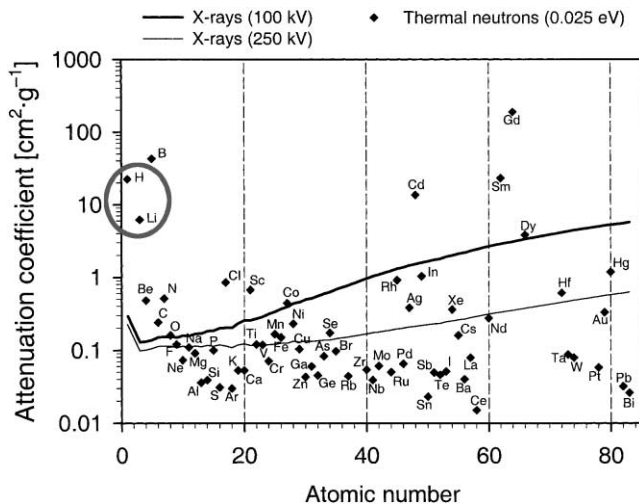


Fig. 1. Neutron and X-ray mass attenuation coefficients for the elements. Data were taken from [4].

## 2. Experimental

### 2.1. Lithium-ion cells and electrochemical cycling

Prismatic lithium-ion cells, type ICP-340848 from Renata AG, Switzerland, having a nominal capacity of 950 mAh and an aluminum casing, were investigated. The external dimensions of the casing are 48 mm × 34 mm × 8.8 mm. Two types of cells were investigated in the in situ experiments: fresh, sealed cells with no prior electrochemical charging, and cells that had been charged to 380 mAh at a  $C/3$  charging rate (320 mA) in an argon-filled dry-box before sealing of the cell. For the second type of cell, the gases that evolved during this initial charging step (cell formation) were allowed to escape through a small hole at the top of the cell for several hours, and then the cell was sealed with aluminum epoxy glue. Note that the cells investigated in the in situ experiments, unlike the commercially available lithium-ion cells, did not undergo a factory-manufactured cell formation step before the experiments described.

In the electrochemical cycling experiments, the cells were charged up to a cell voltage of 4.1 V at a current rate of 1C (950 mA), then the voltage was maintained at 4.1 V for 2.4 h (CCCV mode = constant current constant voltage). Discharge was performed galvanostatically, at a current rate of 1C, down to a cell voltage of 3.0 V (CC mode = constant current).

### 2.2. Neutron radiography

NR images were taken at the NEUTRA facility [7] of the spallation neutron source SINQ at the Paul Scherrer Institute [8]. For in situ measurements, the prismatic lithium-ion cells were fixed between two aluminum plates (thickness 3 mm) setup in the neutron beamline and preventing mechanical

dislocation during the measurement. Aluminum is highly transparent to neutrons due to its low neutron mass attenuation coefficient (see Fig. 1). NR images were taken for every 10–20 min during electrochemical cycling; two successive NR images were taken each time. The exposure time per image was about 30 s. The neutrons passing through the samples were absorbed on a neutron-sensitive scintillation screen (zinc sulfide doped with  $^6\text{Li}$ ), and the scintillation light was reflected to a nitrogen-cooled CCD camera by a mirror. Alternatively, a Gd-doped imaging plate (resolution 50  $\mu\text{m}$ ) was used for high-resolution NR images.

## 3. Results and discussion

### 3.1. Measurements before/after electrochemical cycling

Fig. 2 shows an NR image of a fresh lithium-ion cell. The electrode assembly comprising the anode, the cathode and the separator sheets, occupies almost all of the space available in the aluminum casing. The electrode assembly is soaked with an organic electrolyte containing a lithium salt, and appears dark in the NR image due to the strong neutron beam attenuation of the H and the Li atoms. The aluminum casing is hardly visible because of its weak neutron beam attenuation. At the lower left and right edges of the casing, a small excess of liquid electrolyte is seen which was not taken

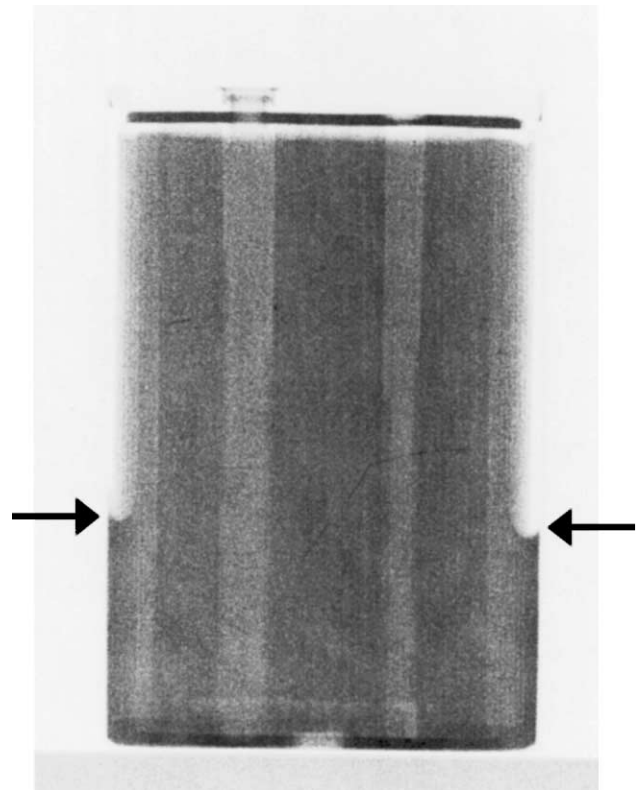


Fig. 2. NR image of a fresh lithium-ion cell (ICP-340848 from Renata AG). The arrows point to the electrolyte level.

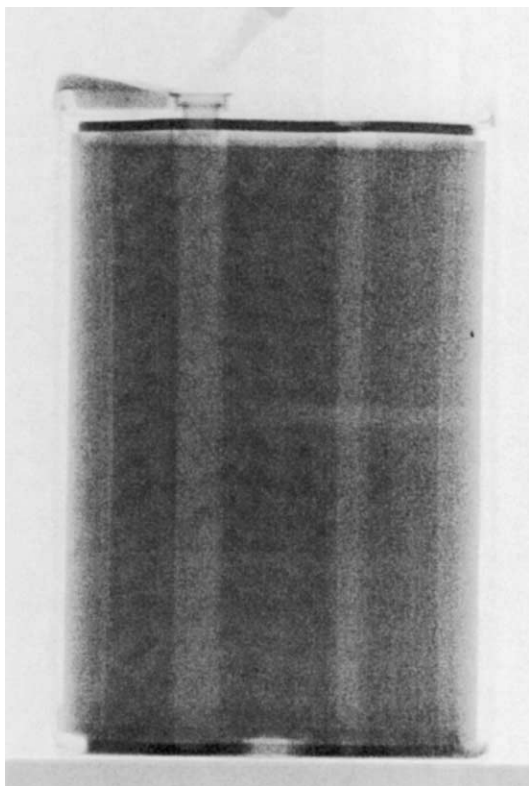


Fig. 3. NR image of a lithium-ion cell after 70 full charge/discharge cycles.

up by the electrode assembly. Fig. 3 shows an NR image of a lithium-ion cell taken after 70 electrochemical charge/discharge cycles. No excess electrolyte is left in this cell, showing that it was irreversibly consumed during cycling.

We further recorded a series of NR images on lithium-ion cells that had undergone a factory-manufactured cell formation step and, subsequently, either an electrochemical charge/discharge cycling (6 or 200 cycles, respectively) or a 1 month storage. We found that the excess electrolyte had almost vanished in most cells, showing that irreversible consumption of the excess electrolyte had taken place. This observation can be accounted for by the formation of a protecting solid electrolyte interphase (SEI) on the electrode surfaces, which may be attended by gas evolution [9,10]. The SEI layer is built up mainly in the first charging cycle (formation cycle), but part of this process can extend beyond the first charging and may even continue at open circuit, which we have recently observed with in situ electrochemical mass spectrometry on thick graphite electrodes [11]. We conclude that NR is a fast, useful and non-destructive tool to optimize the electrolyte soaking and the formation process in the industrial development of lithium-ion cells in aluminum casings.

### 3.2. In situ measurements

When the lithium-ion cells were electrochemically charged and discharged, macroscopic changes occurred

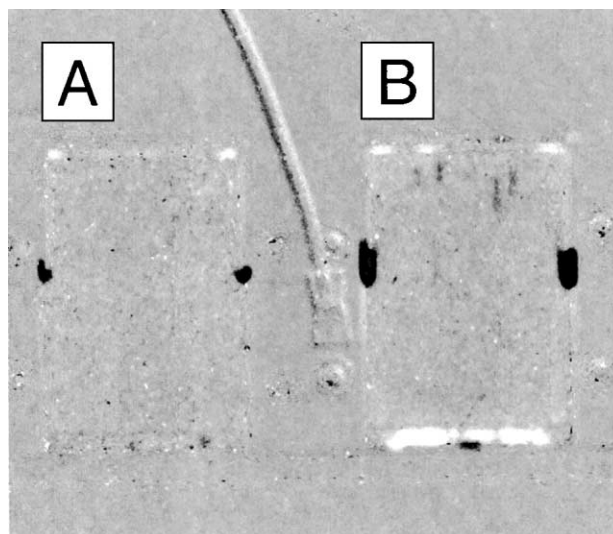


Fig. 4. Referenced image (see text) of two lithium-ion cells placed side by side in the neutron beamline. The referenced image was constructed from NR images taken after a 1.8 h charging time of the cells and at  $t = 0$ . The cell A had been charged to 380 mAh, 1 day before the experiment, whereas the cell B was fresh (uncharged) at the beginning of the experiment.

inside the cells. These changes can best be visualized by creating a “referenced image”, i.e. by constructing an intensity ratio image from two NR images taken at different charging stages, and subsequently normalizing the resulting image. An image analysis software (Image-Pro, Media Cybernetics) was used for processing the data. Fig. 4 shows an example of such a referenced image. To construct Fig. 4, an NR image of two charged cells (A and B), taken during the first charging cycle after a 1.8 h charging time, was graphically divided by an NR image of the same cells taken before charging, at  $t = 0$ , and the resulting image was then normalized to obtain an appropriate grey-scale image. Note that the two cells, A and B shown in Fig. 4, were placed side by side in the neutron beamline, and both cells were electrochemically cycled simultaneously. The cell A on the left-hand side of Fig. 4 had been charged to 380 mAh (about one-third of a full charge) 1 day before the NR experiment, whereas the cell B on the right was fresh (uncharged) at the beginning of the experiment. Dark areas in the referenced image indicate a stronger neutron beam attenuation of the NR image taken at  $t = 1.8$  h, while bright areas indicate a weaker attenuation. The referenced image in Fig. 4 shows that the excess electrolyte filling level had increased in both cells. This is due to the following reasons: (i) during the charging of the lithium-ion cells, the thickness of the electrodes increased to some extent because of an expansion of the lattice constants of the electrode materials during lithium insertion or extraction, respectively [12].<sup>2</sup>

<sup>2</sup>The graphite (negative electrode) interlayer distance increases from 3.35 to 3.70 Å when  $\text{LiC}_6$  is formed, and the  $\text{LiCoO}_2$  (positive electrode) intersheet distance increases from  $\sim 4.7$  to  $\sim 4.8$  Å at the first phase transition occurring in the course of lithium extraction.

Therefore, part of the electrolyte was displaced and increased the filling level of the cells; (ii) in the cell B on the right of Fig. 4, the bright area indicates that a displacement of electrolyte had taken place at the bottom of the cell, which was presumably due to gas evolution under initial charging of the cell. The gas produced at the bottom of the cell was held back by the electrode assembly, and therefore it could not immediately rise to the top of the battery casing. This effect further increased the electrolyte filling level, and therefore, the filling level change was more pronounced in the cell B of Fig. 4. The cell A did not show this displacement related to gas formation, because it had already been charged to 380 mAh before the beginning of the experiment (see experimental section). Therefore, all or most of the gas evolution had already occurred before the in situ experiment. An inspection of the complete series of referenced images taken at various stages of the charging cycle showed that the bright area in the cell B of Fig. 4, most probably indicating gas evolution, had developed during the first 10 min of electrochemical charging. For a more detailed description of gas evolution on electrodes for lithium-ion batteries, we refer to [9] dealing with ethylene and hydrogen gas evolution during the decomposition of a carbonate electrolyte and the formation of a SEI layer on graphite electrodes, and to [10] investigating gas evolution (mainly  $\text{CO}_2$ ) on lithiated transition metal oxide electrodes.

Figs. 5 and 6 display how the electrolyte filling level of the cells shown in Fig. 4 varied during the first three electrochemical half-cycles. The level increased at the beginning of a charging cycle, and it decreased during discharge. This observation correlates well with the corresponding expansion/contraction processes of the electrodes and is also reflected by a change in thickness of the lithium-ion cells

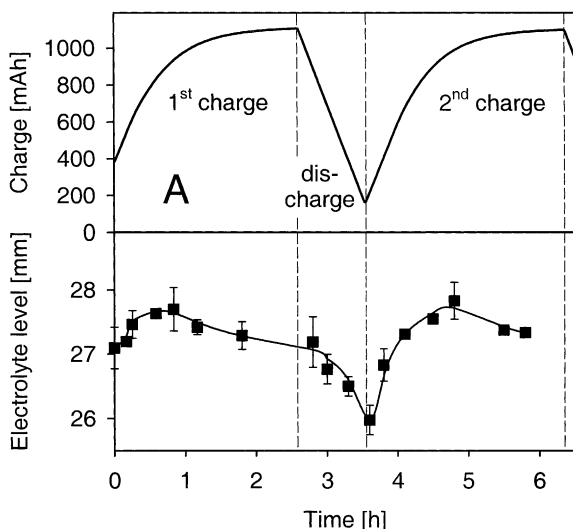


Fig. 5. Charge and electrolyte filling level of a lithium-ion cell as functions of time during initial cycling. The cell had been charged to 380 mAh, 1 day before the experiment (cell A of Fig. 4). Square symbols with error bars indicate average values of two successive NR images in each case.

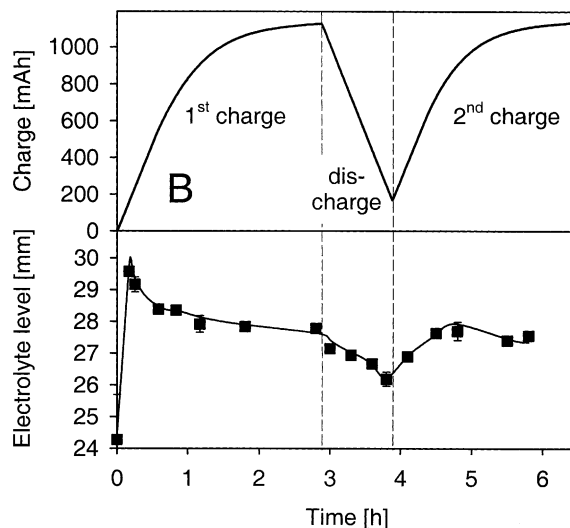


Fig. 6. Same as Fig. 5, with a lithium-ion cell that was fresh (uncharged) at the beginning of the experiment (cell B of Fig. 4).

amounting to several hundred micrometers. The initial increase occurring at the beginning of the first charging cycle (during the first 10 min) was more pronounced for the uncharged cell (cell B of Fig. 4) than for the pre-charged cell (cell A of Fig. 4), the reason being gas evolution as described above. However, in both cells one sees a slow decrease in the electrolyte filling level during further charging that probably indicates a consumption of electrolyte due to SEI formation.

#### 4. Conclusion

Neutron radiography is a useful tool for the non-destructive investigation of macroscopic changes that occur during cycling in lithium-ion cells. NR measurements carried out before/after electrochemical cycling revealed a consumption of excess electrolyte, most probably as a consequence of initial cell charging and SEI formation, and can be used to optimize the electrolyte soaking and the formation process in the industrial development of lithium-ion batteries. In situ NR measurements of the lithium-ion cells revealed displacements of excess electrolyte during initial cycling, occurring due to an expansion/contraction of the electrodes as well as an evolution of gases during SEI formation.

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