

# IN-SITU SEM CHARACTERIZATION OF LITHIUM-ION BATTERY CREATED ON MEMS CHIP

**Ondřej Klvač**

Doctoral Degree Programme (1), FEEC BUT

E-mail: xklvac02@vutbr.cz

Supervised by: Tomáš Kazda

E-mail: kazda@feec.vutbr.cz

**Abstract:** The aim of the work is to develop an in-situ method for electrode nanostructure investigation by scanning electron microscopy. In the first part, the preparation of a model battery using FIB-SEM system is described, which consists of lithium titanate oxide (LTO) and metallic lithium material cutting by the focused ion beam, transport to the MEMS chip, and contacting by carbon deposition. After that the electrodes were soaked by the electrolyte, the voltage changes were measured on two created battery systems. Finally, a current was applied to the cell. However, cycling failed due to technological problems. Challenges connected with battery preparation are described and possible solutions for future testing are proposed. The work is evolved in cooperation with Thermo Fisher Scientific Brno.

**Keywords:** SEM, FIB, MEMS, in-situ, Li-ion, LTO, battery characterization

## 1 INTRODUCTION

Lithium-ion batteries (LIBs) are currently the most commonly used cells for high-performance applications. There are several reasons, they have a high energy density, low self-discharge, high number of charge/discharge cycles, low maintenance, no “memory effect”, and high nominal voltage. This makes them a suitable candidate for future applications such as energy storage for renewable electricity sources or electric vehicle propulsion [1,2,3].

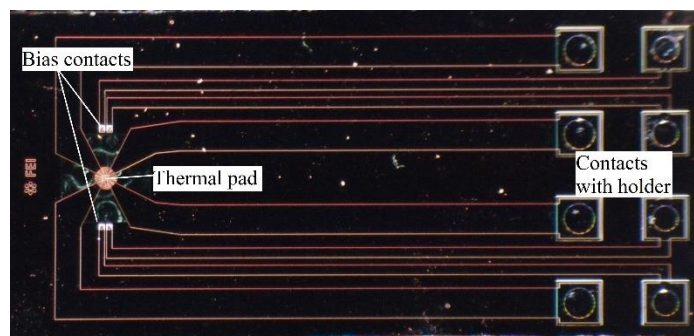
However, there are still some issues that need to be solved before they can be spread on a massive scale.  $\text{LiCoO}_2$ , a widely used cathode material in the past, was gradually replaced, due to its high cost and poor stability, by  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC) [4,5]. Achieving higher capacity while maintaining stability has been the subject of research in recent years [6,7]. Today, this material reaches its limits and although there are other promising and cheaper materials (sulfur, silicon), they are not very widespread due to technological problems (solubility, poor conductivity, cracking, and delamination induced by high expansion) [8,9].

During the investigation by electrochemical methods, only spatial averages can be derived. Scanning electron microscopy (SEM) allows seeing mentioned phenomena in detail directly which is essential for modern nanostructures [10]. In most cases, the battery is discharged after a defined number of cycles, disassembled, and the electrode surface or cross-section is scanned [11,12]. However, for safety reasons (manipulation with charged cell), charging phenomena such as lithium plating cannot be observed [13]. In-situ SEM characterization can be helpful, but it needs to prevent electrolyte evaporation and material degradation caused by air exposure. The ionic liquid is often used in combination with special cells for transfer and cycling [14].

This work follows the diploma thesis of Ing. Hujňák [15], where the whole battery is created inside the SEM chamber from active electrode materials only. The materials are observed from the first soaking with the electrolyte and the presented method is universally applicable for various materials. Because this procedure is new a stable LTO and lithium were used for the first steps.

## 2 EXPERIMENTAL

The battery was connected to biasing contacts of a MEMS chip [16] designed for in-situ heating and biasing experiments in Thermo Fisher Scientific tools [17] (**Figure 1**).



**Figure 1:** Used MEMS chip

In standard conditions, the chip is contacted in a holder on the SEM stage and connected to the controller at the air side of the vacuum feedthrough via a 25 pin CANON connector. For this experiment, the controller was used for connectivity test only, then it was dismantled and pins connected directly with bias contacts were used for measurements.

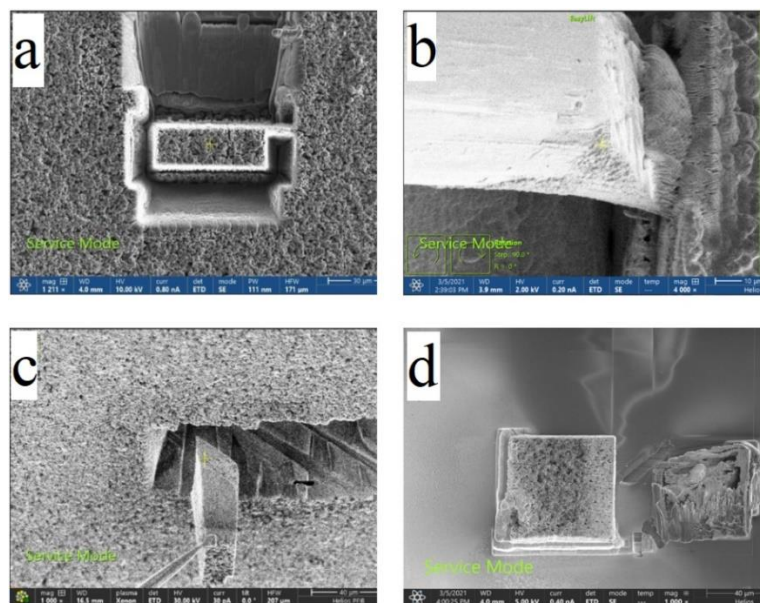
Firstly, a chunk of approx.  $50 \times 50 \times 20 \mu\text{m}$  was cut from an electrode with LTO active material coated on aluminum foil produced by CUSTOMCELLS<sup>®</sup> using xenon plasma focused ion beam (PFIB) system Helios Hydra 5 UX DualBeam (Thermo Fisher Scientific).

The sample was not cut completely, a small „bridge“ for fixation was left (**Figure 2a**). Then, the EasyLift micromanipulation needle was attached on the top-left chunk corner, glued by carbon deposition using MultiChem Gas Delivery System and the „bridge“ was removed (**Figure 2b**). Afterward, the chunk was lifted-up (**Figure 2c**), aligned with bias pad on MEMS, fixed by carbon deposition and the needle was cut-off finally (**Figure 2d**).

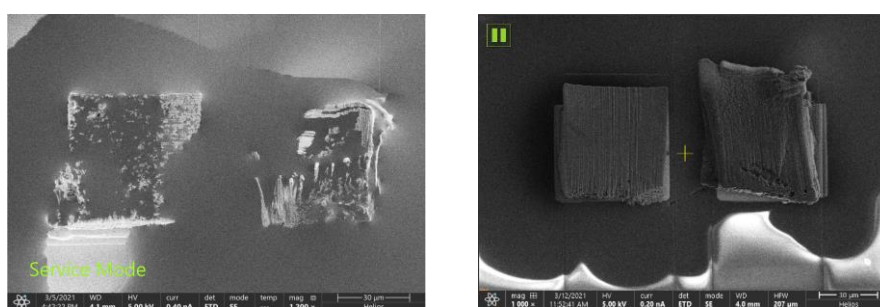
In the case of air-sensitive lithium, a small piece from 99.9% pure ribbon (SigmaAldrich) was cut with a knife in Ar-filled glovebox, enclosed to a glass vial, and the cap was tightened with PARAFILM<sup>®</sup>. To minimize the air exposure time, the vial was opened once everything inside the Dual-Beam chamber was ready. After opening, the lithium was placed on a sample stub, the chamber was closed and pumped immediately. The chamber was then kept closed through the rest of the experiment.

For lithium chunk preparation, Helios 5 UC DualBeam (Thermo Fisher Scientific) with gallium FIB was used similarly. However, lithium has a lower melting point than LTO, it is very soft, and strong redeposition occurs during ion milling. Moreover, carbon is deposited slowly and has poor adhesion. Tungsten deposition was tested too, it is faster, but the deposited layer was nested into lithium after a short time and a chemical reaction probably occurred. Therefore, it was problematic to prepare the chunk with the same dimensions precisely. After tuning appropriate conditions of the FIB sample preparation, a  $30 \times 50 \times 20 \text{ Li}$  sample was placed on the second biasing contact of the MEMS chip.

As an ionic liquid, 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF  $\geq 98\%$ , SigmaAldrich) in a mixture with  $\text{LiBF}_6$  salt in 0.5M concentration was used. The liquid was applied to the MEMS chip near the LTO in an amount of 0.5 microliters with a pipette. Once both active materials were connected to the biasing contacts, the electrolyte was moved between them using stage tilt (**Figure 3**).



**Figure 2:** Cut chunk from electrode (a); contacting with EasyLift needle (b); chunk lift out (c); connection with MEMS chip by carbon deposition, both electrodes (d)



**Figure 3:** Soaking of electrodes by electrolyte, first (left) and second (right) battery system

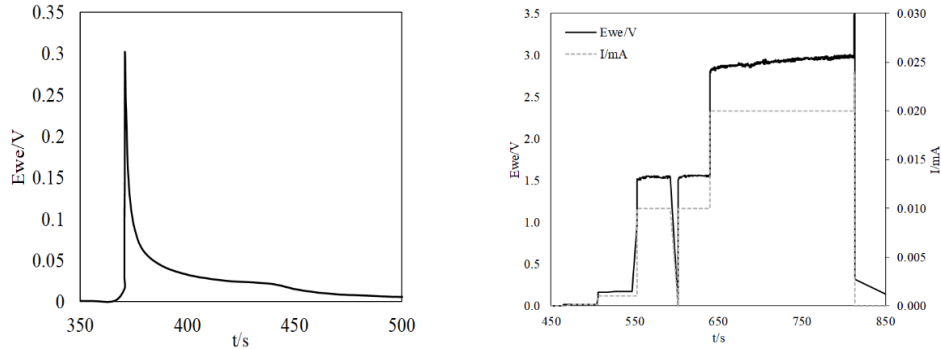
For electrochemical characterization, BioLogic SP-150 potentiostat which allows setting currents below nano amperes was used. For instance, the capacity of used LTO given by datasheet is  $1\text{mAh}/\text{cm}^2$ , and measured active material thickness is around  $30\text{ }\mu\text{m}$ . Then, the calculated capacity of the created battery is approximately  $16\text{ nAh}$ . The device was connected with a shared reference electrode (RE) and the counter electrode (CE) to the lithium, LTO was on the working electrode. The ground electrode was on the microscope frame.

### 3 RESULTS AND DISCUSSION

Before the IL was moved between electrodes, an open-circuit voltage was measured with a  $0.5\text{ s}$  period. Since the electrodes were not connected, the voltage was zero (only noise in microvolts was present). Once the electrolyte soaked both electrodes, the voltage increased to  $302.3\text{ mV}$  within  $4.5\text{ s}$ . However, it immediately began to decline, after  $2.5\text{ s}$  it was  $150\text{ mV}$ ,  $23\text{ mV}$  after  $1\text{ min}$ , and  $5.7\text{ mV}$  after  $2\text{ min}$  (Figure 4 – right).

Many battery recovery attempts have been performed with different currents in galvanostatic mode. At  $2.5\text{ nA}$ , the voltage fluctuated around  $5\text{ mV}$ , but charging was not visible. At  $100\text{ nA}$ , the voltage was increased to stable  $16\text{ mV}$ , at  $1\text{ mA}$  it was stable  $167\text{ mV}$ , and  $1.5\text{ V}$  at  $10\text{ mA}$ . As soon as the current source was disconnected the voltage dropped to units of millivolts immediately. At  $20\text{ mA}$  there was a visible increasing voltage trend, however, these currents are in the order of millions of C-rate and it is probably polarization only (Figure 4 – left).

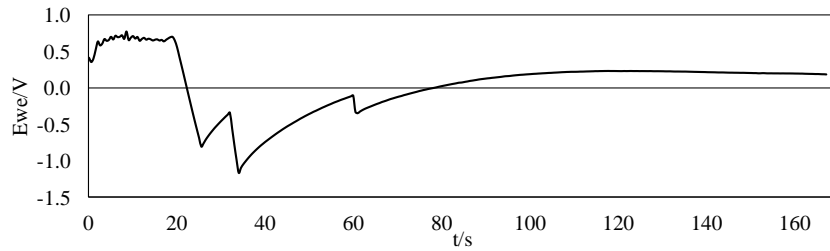
It is clear that the current flows here, but the battery is not charged. The IL was on the surface of the chip for 8 days and solid particles were floating on its surface. MEMS surface could be dissolved and might become conductive for electrons. It is also possible that during cutting of the needle, re-deposition of tungsten occurred and paths were partially connected. During the experiment, the LTO chunk extended by 13%.



**Figure 4:** Open circuit voltage measurement (left); applied current and voltage response (right)

In the next experiment, it was tried to pass a current of 100 nA through the circuit before the electrolyte soaked the electrodes. The current flowed here and a voltage drop of 1.5 V was measured. It turned out that a very thin layer of material is redeposited between the contacts, which forms a parallel resistance of about 15 M $\Omega$ . The layer was not visible, but during the milling of the area between the contacts, the voltage drop gradually increased to 10 V, and then it was not possible to maintain the current. After wetting the electrodes with the electrolyte, the voltage rose to about 0.65 V, which was stable for the 20 s (**Figure 5**). Then, the electrodes were irradiated with an electron beam and the polarity was reversed.

Charging and local lithium deposition induced by electron beam was described for a system where the lithium was connected with the sample stage (ground) [13], however in this case, although the voltage began to return to normal, the battery was destroyed completely and the cycling failed. Only strong noise was present even after turning off the beams and low voltages could not be measured. Obviously, it is necessary to modify the connection.



**Figure 5:** Open circuit voltage measurement affected by ion and electron beam

#### 4 CONCLUSION

An experimental setup for in-situ research of electrode materials by scanning electron microscopy has been described and will be used for the characterization of nanostructures during doctoral study.

Two batteries from commercially available LTO electrode material, metallic lithium, and ionic liquid were created on a MEMS chip inside the SEM chamber. In the first case, the battery had a voltage of 0.3 V when both electrodes were soaked by the electrolyte. However, it was found, that conductive materials can be redeposited between electrodes during preparation and a parallel load is created. Therefore, the battery was discharged very fast. In the case of the second battery, the load was removed by ion cleaning. There was a stable voltage of 0.65 V for 20 sec, then the battery was damaged

by an electron beam and cycling was not possible. It has been shown that the electron and probably also the ion beam can strongly influence the result and damage the battery.

During the work, it is planned to create a best practice document describing individual steps of the battery preparation, which consists of FIB cut-out of electroactive samples, transfer of these samples on micromanipulation needle, and connection of the samples with the MEMS pads by carbon deposition. The experiment is still in progress, the usage of platinum deposition for better contacting, another ionic liquid, and modification of measurement connection is planned. The described procedure can be used for the characterization of sulfur electrodes in the future.

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