In Situ Analytical Electron Microscopy for Probing Nanoscale Electrochemistry

by Ying Shirley Meng, Thomas McGilvray, Ming-Che Yang, Danijel Gostovic, Feng Wang, Dongli Zeng, Yimei Zhu, and Jason Graetz

Oxides and their tailored structures are at the heart of electrochemical energy storage technologies and advances in understanding and controlling the dynamic behaviors in the complex oxides, particularly at the interfaces, during electrochemical processes will catalyze creative design concepts for new materials with enhanced and better-understood properties. Such knowledge is not accessible without new analytical tools. New innovative experimental techniques are needed for understanding the chemistry and structure of the bulk and interfaces, more importantly how they change with electrochemical processes *in situ*.

Analytical Transmission Electron Microscopy (TEM) is used extensively to study electrode materials *ex situ*[1-8] and is one of the most powerful tools to obtain structural, morphological, and compositional information at nanometer scale by combining imaging, diffraction and spectroscopy, e.g., EDS (energy dispersive X-ray spectrometry) and Electron Energy Loss Spectrometry (EELS). Determining the composition/structure evolution upon electrochemical cycling at the bulk and interfaces can be addressed by new electron microscopy technique with which one can observe, at the nanometer scale and *in situ*, the dynamic phenomena in the electrode materials. In electrochemical systems, for instance in a lithium ion battery (LIB), materials operate under conditions that are far from equilibrium, so that the materials studied *ex situ* may not capture the processes that occur *in situ* in a working battery. *In situ* electrochemical operation in the ultra-high vacuum column of a TEM has been pursued by two major strategies. In one strategy, a "nano-battery" can be fabricated from an all-solid-state thin film battery using a focused ion beam (FIB). The electrolyte is either polymer based or ceramic based without any liquid component. As shown in Fig. 1a, the interfaces between the active electrode material/electrolyte can be clearly observed with TEM imaging, in contrast to the composite electrodes/electrolyte interfaces in conventional lithium ion batteries, depicted in Fig.1b, where quantitative interface characterization is extremely difficult if not impossible. A second strategy involves organic electrolyte, though this approach more closely resembles the actual operation conditions of a LIB, the extreme volatility of the organic electrolytes present significant challenges for designing an *in situ* cell that is suitable for the vacuum environment of the TEM.

Significant progress has been made in the past few years on the development of *in situ* electron microscopy for probing nanoscale electrochemistry. In 2008, Brazier et al.[9] reported the first cross-section observation of an all solid-state lithium ion nano-battery by TEM. In this study the FIB was used to make a "nano-battery," from an all solid-state battery prepared by pulsed laser deposition (PLD). *In situ* TEM observations were not possible at that time due to several key challenges such as the lack of a suitable biasing sample holder and vacuum transfer of sample. In 2010, Yamamoto et al.[10] successfully observed changes of electric potential in an all-solid-state lithium ion battery *in situ* with electron holography (EH). The 2D potential distribution resulting from movement of lithium ions near the positive-electrode/electrolyte interface was quantified. More recently Huang et al. [11] and Wang et al.[12,13] reported the *in situ* observations of the electrochemical lithiation of a single SnO_2 nanowire electrode in two different *in situ* setups. In their approach, a vacuum compatible ionic liquid is used as the electrolyte, eliminating the need for complicated membrane sealing to prevent the evaporation of carbonate based organic electrolyte into the TEM column. One main limitation of this approach is that EELS spectral imaging is not possible due to the high plasmon signal of the ionic liquid.

To this end, we have developed a novel *in situ* instrumental system combining analytical electron microscopy with advanced spectroscopy to probe the dynamic phenomena in an all solid-state nano-battery. *In situ* electron microscopy is a versatile technique that yields insights into challenging questions that could not be obtained using other techniques. However, in order to fully exploit the capabilities, a very carefully thought-out plan of action is essential. It is important to recognize that this is not just a simple characterization tool, but a collection of tools that make up a complete experimental set-up: the choice of FIB operation conditions, specimen holder for biasing, grid materials and design as well as microscope environment must be thoroughly considered before performing an experiment. To ensure electron beam transparency and minimize artifacts, the nano-battery must be thinned down to a thickness below 100 nm for quantitative analysis. In performing EELS, artifacts due to plural scattering have been an issue, particularly when the shallow Li K-edge is of interest. Radiation damage, through radiolysis or sputtering, has been a big concern in studying Li-containing materials. Some strategies on reducing undesirable plural scattering and radiation damage have been developed for this project; generally operating TEM at a higher voltage (i.e., 300 kV) can be beneficial.[14] One of the key issues for observing and studying electrochemical reactions *in situ* under TEM is to assure that the very thin cross section samples (nano-batteries) are still electrochemically functional after the FIB fabrication. Other important barriers that we have overcome include (i) solid-state nano-battery fabrication and *in situ* monitoring of electrochemistry functionality; (ii) custom designed TEM sample grids that enable robust electric contacts and electrochemical testing; and (iii) coupled imaging, diffraction, and spectroscopy for comprehensive structural and chemical analysis of nano-batteries under biasing; particularly tracking the Li may be possible by developed Li K-edge spectroscopy and mapping.

All Solid State Nano FIB Fabrication

Pulsed laser deposition (PLD) is capable of producing thin-films of lithium transition metal oxides with dense and smooth morphology. Various PLD films can be arranged in a multi-layer structure to form a complete all-solid-state battery. Fig. 1a shows an example with the following configuration: Au (current collector) / SnO_2 (anode) / $Li_{3.4}V_{0.6}Si_{0.4}O_4$ (electrolyte) / $LiCoO_2$ (cathode) / Pt (current collector). PLD has been widely recognized as a very promising, versatile and efficient technique for the growth of high quality films from a variety of materials even containing volatile components with complex stoichiometries. By carefully controlling the laser energy, target-substrate distance and angle, substrate temperature and the atmosphere in the PLD chamber, one can not only deposit films with accurate stoichiometry,

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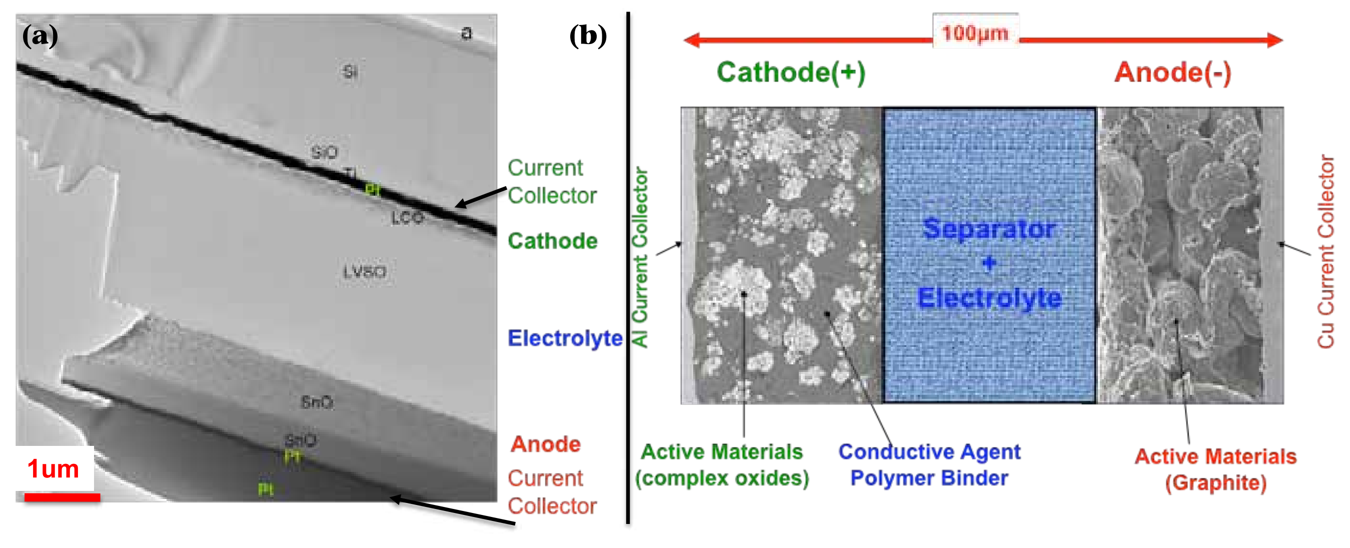

Fig. 1. *TEM micrograph of a FIB prepared nanoscale all-solid-state lithium ion cell and SEM micrograph of a conventional lithium ion cell.*

but also control the crystallographic orientation of the films, if they are crystalline. In our nano-battery, the electrodes are crystalline materials while the lithium vanadium silicon oxide (LVSO) is amorphous with a reported ionic conductivity 10^{-3}-10^{-4}S/cm^2.[15] More importantly, the PLD grown films are much denser than films prepared by other deposition techniques such as sputtering, and are therefore well suited for FIB processing (porous films are difficult to handle with the focused ion beam).

The nano-battery was fabricated by first preparing a cross section sample (from a solid-state battery) and cutting it down to a micron-sized battery (about a few micrometers thick) using a focused ion beam in a dual beam SEM equipped with a micromanipulator. As shown in Fig. 2, the electrochemical measurements were conducted throughout the FIB preparation process to monitor the status of the battery. In Fig. 2b, we applied constant current charging mode on an isolated cross section trench with 1nA (current density about 0.5mA/cm^2). The voltage rises and shows a plateau at 3.4 V, indicating the de-intercalation of Li from $LiCoO_2$. The reversible capacity is observed upon discharging with 1nA though it is clear that polarization in this particular nano-battery is high. The *in situ* monitoring of the status of the nano-battery is critical to ensure the electrochemical functionality of the nano-battery remains intact throughout FIB processing. Ion beam damage of the active components and possible shorting of the battery can be prevented by optimizing the FIB operating conditions.

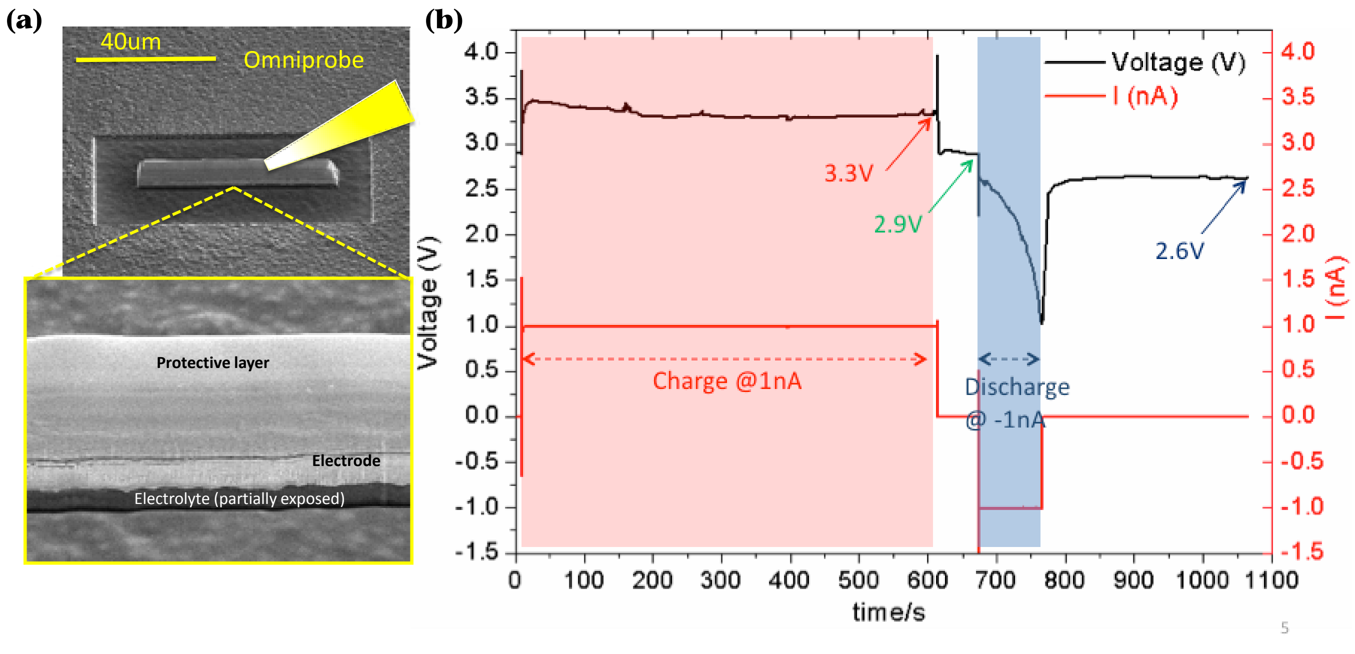

Fig. 2. *Electrochemical activity of the all-solid-state battery can be preserved during FIB process. The electrochemical response is from the isolated trench shown in the SEM micrograph.*

Biasing Setup for NanoElectrochemisty

To ensure good electric contacts between the TEM holder and sample grid, extra care has to be taken to make sure the sample biasing setup is repeatable and robust. As shown in Fig. 3, our custom designed TEM grids (by TEMwindows) have an insulating TEMwindow (made of SiN), which holds an electron transparent cross-section of an electrochemical device (i.e., solid state battery). Two gold pads deposited on a Si frame with a 40 µm opening gap provide electronic contacts for both electrodes. It should be noted that in order to prevent shorting between the electrodes, additional milling steps need to be taken to isolate the cathode and anode when establishing the contacts on Au pads, as depicted in Fig. 3.

This setup ensures the solid-state battery cross section area can be accessed by the electron beam while the mechanical stability of the sample on the grid is well maintained. Fig. 3a shows a graphic representation of the entire sample on the grid, which has been transported from one microscope to another. The mechanical stability of the sample on the grid is essential since the cross section has to be further thinned down (from 2000 nm to <100 nm) to enable quantitative EELS characterization. It should also be pointed out that solid electrolytes such as LVSO or polymer electrolytes such as LiPON are sensitive to moisture (though to a lesser extent compared with a carbonate based organic electrolyte), air exposure of the nano-battery must be minimized or eliminated.

In Situ TEM Observations

A nano-battery cross section of lithium nickel manganese oxides with a LVSO electrolyte was analyzed in a JEOL 3000F TEM equipped with a Gatan image filter (GIF). One of the typical cross-section TEM images of the nano-batteries is given in Fig. 4a, showing all of the components. The LVSO electrolyte layer is amorphous as confirmed by electron diffraction from the area, giving diffuse rings typical of amorphous phase structure. Below the LVSO electrolyte is the crystalline lithium nickel manganese oxide cathode, where crystallites in random orientations may be distinctly seen. Under the cathode there is an interfacial phase that appears to have epitaxially grown into the SiO_2 film below it. At the bottom of the image we see the silicon bulk substrate. Lithium and transitional metal elements were mapped using EELS, for direct visualization of their distribution in the electrolyte and electrode. Fig. 4b shows the nickel, vanadium, and lithium distributions, indicating that nickel is not evenly distributed but highly concentrated in some particles, and vanadium is evenly distributed throughout the electrolyte phase. One can clearly see that transition metal oxide electrode is indeed the lithium source. Fig. 4c displays the lithium intensity, which was highest in the center of the electrode region. The interface between the electrode and the current collector is atomically flat while the interface between the electrode and electrolyte is relatively rough (tens of nm). A more thorough examination by SEM/EDX of the entire nano-battery shows little or no Ga signal, indicating that unwanted ion implantation can be minimized during the FIB preparation.

The completed nano-battery has extremely small dimensions (about 10 µm × 30 µm × 100 nm), which present another set of challenges for *in situ* TEM. The suitable current range for such a functional nano-battery should be in the range of a few pA (10^{-12} A). If a 100 nA current is applied to such a nano battery, the actual current density is equivalent of 2 to 3A/cm^2 (a typical LIB operates at a few or tens of mA/cm^2), the battery will fail catastrophically. Figure 5, shows the results from one of the first trials of biasing a nano-battery with 100 nA current *in situ*. The battery "exploded" inside the TEM column—the current collector (Pt), electrode, and electrolyte were completely smeared and platinum (the current collector) was deposited throughout the cross sectional area. With the recent advancement in nano metrology, it is now possible to probe nano devices with fA accuracy.

Concluding Remarks

Understanding and controlling the interfaces in energy systems is identified as one of the Grand Challenges of Science by the Basic Energy Sciences Advisory Committee (BESAC).[16] The development of our new *in situ* analytical electron microscopy is in response to this dedicated and coordinated effort to invent, design, and employ novel and sophisticated analytical systems underpinning of the challenge. We believe that the *in situ* analytical electron microscopy for probing nanoscale electrochemistry will enable us to understand dynamic changes—particularly those that happen

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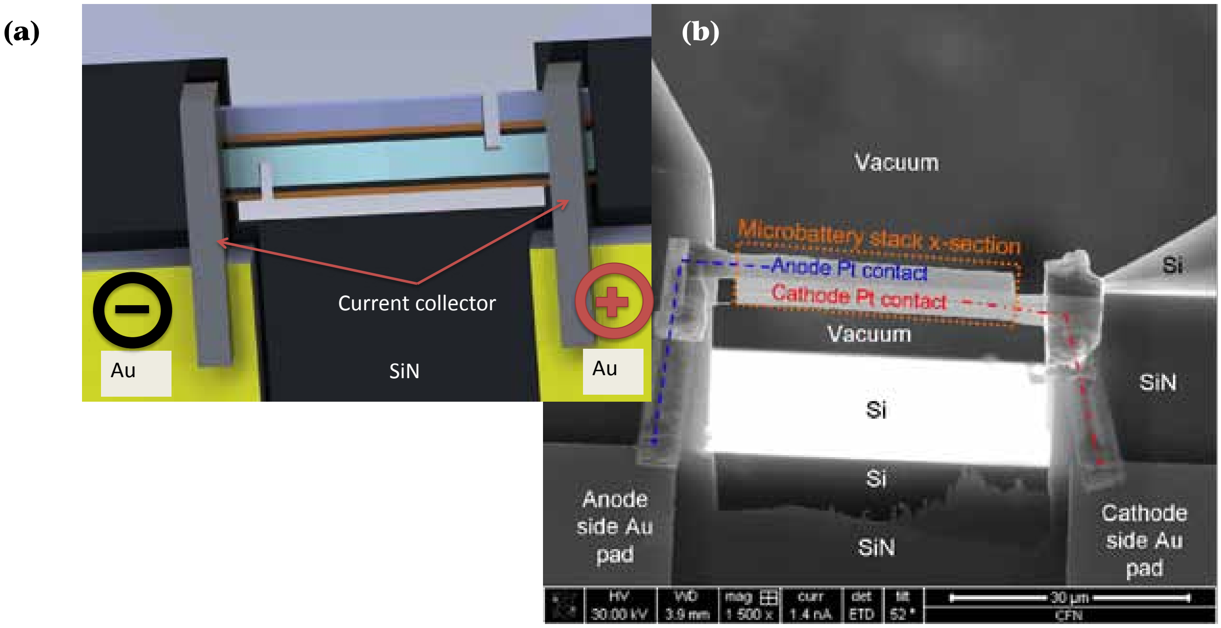

Fig. 3. In situ *biasing setup of a lithium ion cell on a custom-designed TEM grid. The thickness of the battery is in the order of 100 nm.*

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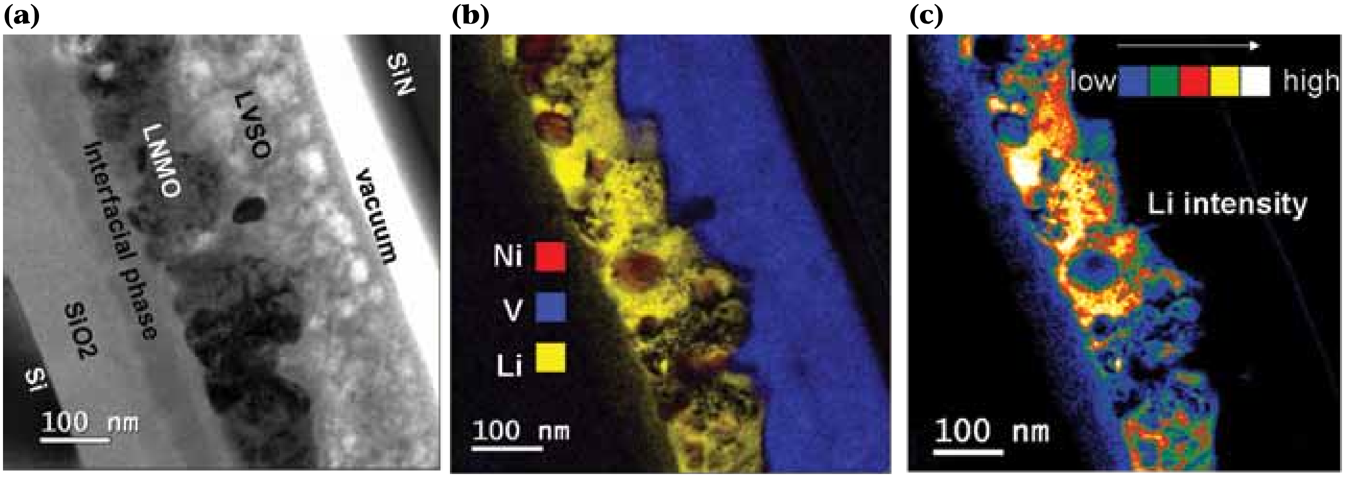

TEM micrograph

Ni, V, Li EELS map

Li intensity EELS map

Fig. 4. *The unique capability of analytical transmission electron microscopy, combining imaging and chemical analysis with high spatial resolution.*

at the interfaces during the active operation of electrochemical cells—and ultimately learn to control the dynamic phenomena for design and develop the next generation of materials for energy storage.

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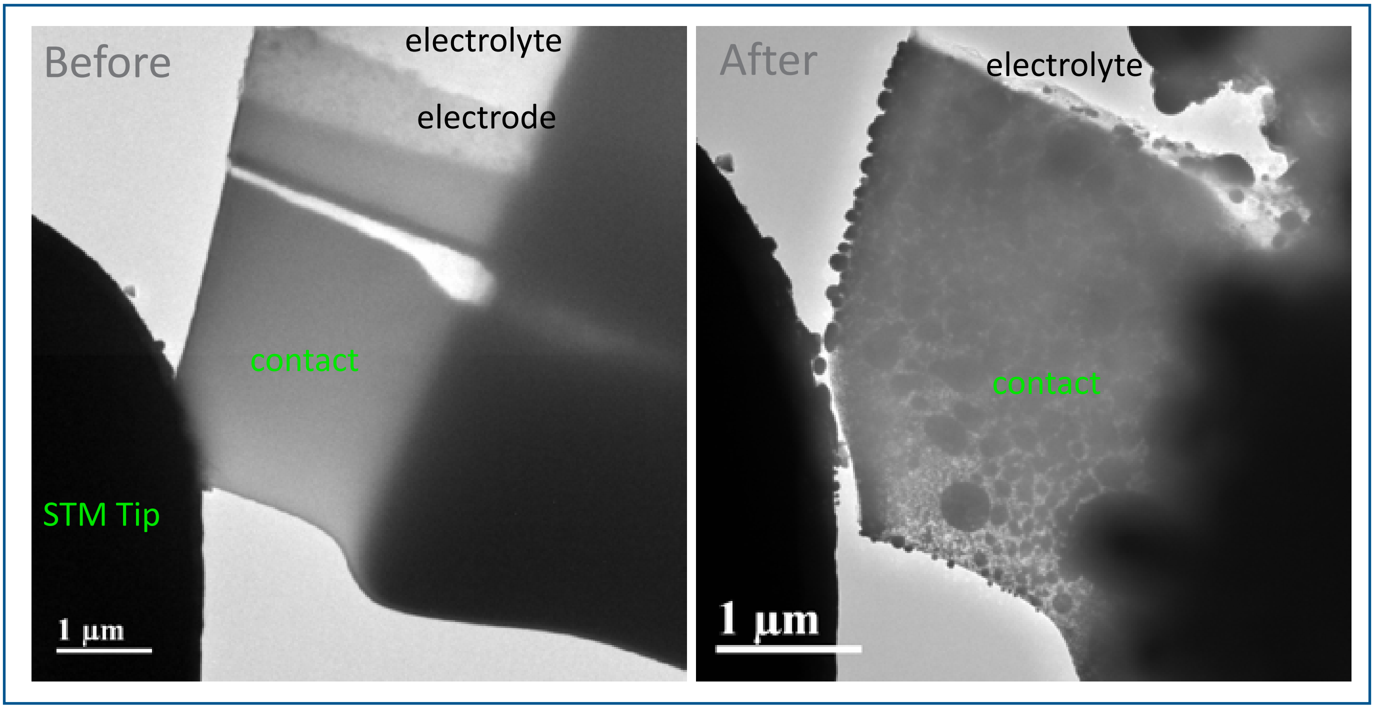

Fig. 5. *Effect of high current density (in the order of 2500 mA/cm²) on the all solid state lithium ion cell.*

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