In understanding the performance of Li-battery materials, a holy grail is the ability to study the effect of particle size, particle boundaries, electrode-electrolyte interfaces, phase transitions, crystal defects, all independently during battery operation [1-2]. In practice however, scientists have to rely on macroscopic polycrystalline electrodes with several additives and binders, where the overall performance is determined by a combination of many parameters. Because thorough determination of the effects of all parameters requires very expensive many-parameters studies, in practice researchers restrict to a trial and error approach leaving too much room for interpretation.

In-situ TEM studies on the other hand allow the usage of submicron dimension single particles as electrodes without supplementary additives or binder; enabling easy interpretation of results during the battery operation, even on the atomic scale. These TEM studies can lead to valuable insights on understanding the (de)lithiation mechanism of different electrode materials. However most of the in-situ TEM battery setups are based on STM tip [3-4], where only one edge of the investigated electrode material (generally nanowires) is connected to the electrolyte (either ionic liquid or oxidised lithium). This design forces Li$^+$ ion exchange to take place from that edge alone and blocks the possibility of exchange from all directions. This restriction may lead to partial knowledge about the (de)lithiation mechanism of the electrode material.

We have designed an in-situ nano battery setup based on MEMS based chips, which ensures full coverage of the electrode with the electrolyte, allowing free exchange of Li$^+$ from every part of the electrode. Our in-situ nano battery setup to study the (de)lithiation mechanism of the much debated LiFePO$_4$ [5] is shown in Fig. 1. Here, during charging Li$^+$ ions de-intercalate from LiFePO$_4$ lamella and plate on the opposite gold line. While discharging, these Li$^+$ ions move through LiPON and intercalate back to the lamella.

EELS analysis was carried out during the (dis)charging of the battery. One of our important finding, shown in Fig. 2, is: (de)lithiation always starts from the interface of electrolyte, current collector and electrode irrespective of LiFePO$_4$ crystallite direction, signifying the importance of the interface for faster charging of the battery.

References:

Acknowledgement: This project is carried out in the framework of NWO-NANO project, No.-11498.
Fig. 1: Nano battery setup: (a) TEM chip (top view) prepared using electron beam lithography; (b) FIB-lamella is prepared from a LiFePO$_4$ crystal; (c) ion beam induced platinum deposition ensures good electrical contact between lamella and current collector (gold pad); (d) chip is placed into electrical TEM holder after sputtering thin LiPON layer.

Fig. 2: a) STEM image of LiFePO$_4$ lamella (highlighted with yellow line) on gold pad. EEL-scan was performed along the red line after charging of battery; b) presence of the edge around 4-7 eV for the position (i), due to presence of Fe$^{3+}$, indicates the formation of FePO$_4$, while the absence of this edge for position (ii) indicates absence of FePO$_4$. 