BIO Web of Conferences **129**, 25013 (2024) https://doi.org/10.1051/bioconf/202412925013
EMC 2024

PFIB-preparation and STEM-characterization of electrochemically plated lithium at the interface to the solid electrolyte Li6PS5Cl

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Solid-state batteries are of particular interest when it comes to safe high-energy storage as they potentially enable the usage of lithium anodes. Theoretically, a lithium metal anode has a more than 10 times higher specific charge capacity than graphite [1], which is typically used as anode material in commercially available lithium-ion batteries. But, industrial production of highly reactive lithium metal anodes is challenging. One approach is to electrochemically deposit lithium in a so-called anode-free cell. The lithium is plated between a current collector and the solid electrolyte during charging. In the half-cell assembly investigated throughout this study, the current collector consists of stainless steel and the solid electrolyte of argyrodite-type Li6PS5Cl. The latter is a promising solid electrolyte candidate due to its high ionic conductivity, but comes along with a solid electrolyte interphase (SEI) formation when in contact with lithium metal [2]. Therefore, the characterization of interfacial side reactions at the micro- and nanoscale is crucial.

Scanning transmission electron microscopy (STEM) offers structural insights at atomic resolution. Still, it comes with a challenging sample preparation that is further complicated by moisture and ion beam sensitivity of the battery materials. Furthermore, lithium metal and sulfide electrolytes like Li6PS5Cl require cryogenic conditions during ion- and electron-beam exposure to withstand the beam doses. The plasma focused ion beam (PFIB) system Helios 5 Hydra CX is capable of an inert-gas transfer from and to the glove box as well as sample preparation at temperatures around -190 °C. In the PFIB, the sample is thinned to electron-transparency (< 100 nm), from where it is transferred to the glove box and mounted in a sealed transfer holder (Mel-Build) for further investigation in a STEM (JEOL JEM-2200FS). Low-dose electron imaging and STEM-EDX (energy dispersive X-ray spectroscopy) at cryogenic temperatures are performed.

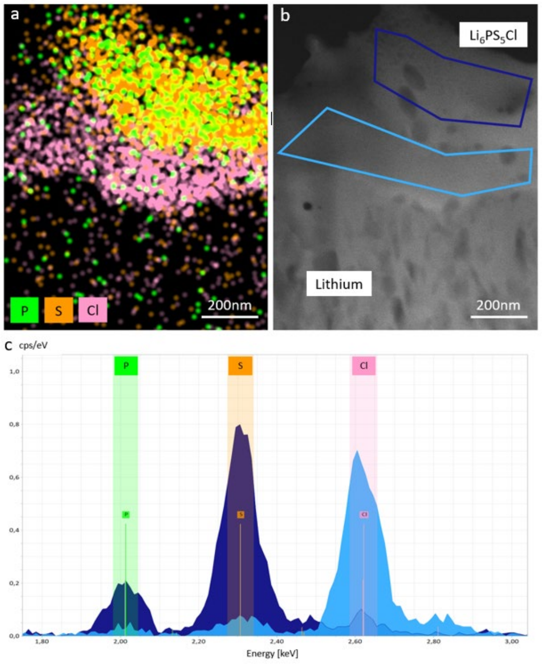
The lamella preparation of the highly sensitive lithium metal and Li6PS5Cl requires adapted preparation steps: low ion currents to preserve the Li | Li6PS5Cl interface as well as eliminating tungsten deposition. Usually, tungsten deposition is used to protect the sample during thinning and to attach the sample to the manipulator needle for lift-out and attachment of the lamella to the copper TEM grid. The high mobility of ions in Li6PS5Cl makes it impossible to distribute the tungsten atoms of the precursor gas locally. Hence, a complete gas-free workflow is needed. The manipulator needle is attached to the lamella gas-free using redeposition of the needle material. Also, the lamella is attached to the copper grid using redeposition of the grid. The steel current collector serves as a protection layer during thinning.

The thinned lamella is investigated in the STEM. A cryo-STEM EDX map and spectrum are depicted in Figure 1. The dark blue area (Figure 1b) encircles Li6PS5Cl with its characteristic peak relation of phosphorus, sulfur, and chlorine, as seen in the corresponding EDX spectrum (dark blue graph Figure 1c). Between lithium and Li6PS5Cl is a roughly 200 nm thick SEI, colored in light blue in Figure 1b, showing chlorine enrichment in the EDX map (Figure 1a) as well as in the corresponding EDX spectrum (light blue graph Figure 1c). Lithium is not detectable using EDX, as it's characteristic X-rays have too low energy and are absorbed by the detector's window.

The preparation of electrochemically plated lithium and Li6PS5Cl using the PFIB is highly complex and requires the absence of air as well as cryogenic conditions. Nonetheless, the effort is necessary to gain structural and chemical information on the SEI. An approximately 200 nm thick chlorine-rich layer between plated lithium and argyrodite-type Li6PS5Cl is already observed. Further measurements like STEM-EELS (electron energy loss spectroscopy) to detect lithium and TEM-PED (precession electron diffraction) for structural information need to be carried out.

Graphic:

Figure 1



Keywords:

Plasma-FIB, Battery, Inert-gas-transfer, Anode-free-cell

Reference:

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