

Interphases of Magnesium Metal Anodes Enabled by Cryogenic Electron Microscopy

Daniel Long, Scott McClary, Nathan Hahn, Kevin Zavadil and Katherine Jungjohann

Sandia National Laboratories, Albuquerque, New Mexico, United States

Since its inception in the 1970s[1] cryogenic electron microscopy(cryo-EM) has allowed researchers to image and characterize aqueous, soft, and beam sensitive materials at length scales that were previously inaccessible via electron microscopy. Historically cryo-EM has been most prominent in the biological and soft matter sciences; however, recent advances in cryo-EM preparation have allowed for scanning transmission electron microscopy (STEM) investigation of energy materials with preserved solid-liquid interfaces that are both beam sensitive and chemically reactive.[2] With new Thermo Fisher Scientific and Leica transfer tools available at the Center for Integrated Nanotechnologies, we have implemented cryogenic focused ion beam (cryo-FIB) and cryo-STEM for the characterization of next-generation energy storage anodes.

Multivalent-ion batteries (MIBs), including Mg^{2+} , are promising high-energy density technologies that contain more abundant materials which are cheaper than lithium, making them ideal for use in all-electric vehicles or localized grid residential/commercial energy storage.[3] Realizing the high theoretical energy density of MIBs requires the native multivalent-ion metal to be used as the anodic electrode, where densely controlled metal plating and stripping has yet to be achieved. The mechanisms governing plating/stripping of MIBs and the resulting impact of microstructure and interphases on the battery performance must be understood before MIBs can be employed commercially. Solving the structure and chemistry of the solid-electrolyte interface (SEI) in multivalent-ion metal plating/stripping may lead to strategies for controlling reversible anodic cycling. Here we present results of our chemical and microstructural investigation of plated and stripped Mg^{2+} anodes, collected with cryo-FIB preparation, cryo-transfer, and cryo-STEM.

Mg was deposited onto Pt working electrodes in a two-electrode flat electrochemical cell with a Mg rod functioning as the counter and reference electrode. Mg was galvanostatically deposited to a thickness of 1-2 microns onto a Pt surface, after the electrolyte was introduced into the cell and subjected to several cyclic voltammetry (CV) cycles to activate the Pt surface and condition the electrolyte. Electroplated Mg deposits on the Pt substrate were immediately transferred into a 20 mL vial containing fresh electrolyte solution. The Mg deposit, interphases, and native electrolyte were preserved intact, frozen, and transferred inertly from glovebox to a Leica cryogenic SEM suite. This was accomplished by transfer into a 20 mL vial in the glovebox followed by freezing the sample in the vial in an insulated container and then submerging the vial into a nitrogen gas curtain and dropping the sample into liquid nitrogen in the Leica VCT. It must be noted that freezing behavior of these electrolytes and solvents is similar to that of ceramic glass, i.e. cooling too quickly results in excess mechanical stress that leads to fracture and cooling too slowly leads to crystallization or devitrification.

Cryo-transfer and cryo-FIB were performed with the Leica cryogenic preparation suite and a Thermo Fisher Scientific Scios 2 outfitted with the Lecia cryogenic suite, respectively. The Lecia cryogenic suite includes 1) a VCM cryogenic loading station for sample transfer between Vitrobot, VCT, the SEM/FIB, and cryo-STEM holder, 2) a VCT transfer module for movement between the VCM, ACE, and SEM/FIB, 3) an ACE600 system for cryogenic sputtering and freeze fracture, and 4) components attached-to and within the SEM/FIB including a VCT transfer feedthrough and an LN2 cold finger to the stage and liftout

needle. The sample was maintained at or below $-150\text{ }^{\circ}\text{C}$ during all transfers and characterization steps. A 10 nm Pt coating was sputtered onto the frozen electrolyte surface to mitigate charging in the ACE600 tool prior to deposition of the protective cap of GIS Pt that was condensed and cured onto the region of interest. EDXS was used in the SEM/FIB to map the chemistry of large portions of the sample surface in order to locate a region of interest and both EDXS and EBSD were used to characterize the lifted-out lamella. The region of interest identification, protective cap deposition and liftout and thinning are shown in figure 1. Cryo-STEM, -EDXS, and -EELS were performed in a FEI Titan operated at 300kV with a Gatan double-tilt cryo holder. Further details will be presented on the anode porosity, grain orientation maps, chemical maps from the electrode/electrolyte interfaces, and high-resolution structural imaging of the electrode interfaces. Correlating the Mg^{2+} and interphase structures and chemistries to energy density, coulombic efficiency and cyclability will enable more-informed battery design which will expedite commercialization of Mg secondary batteries [4].

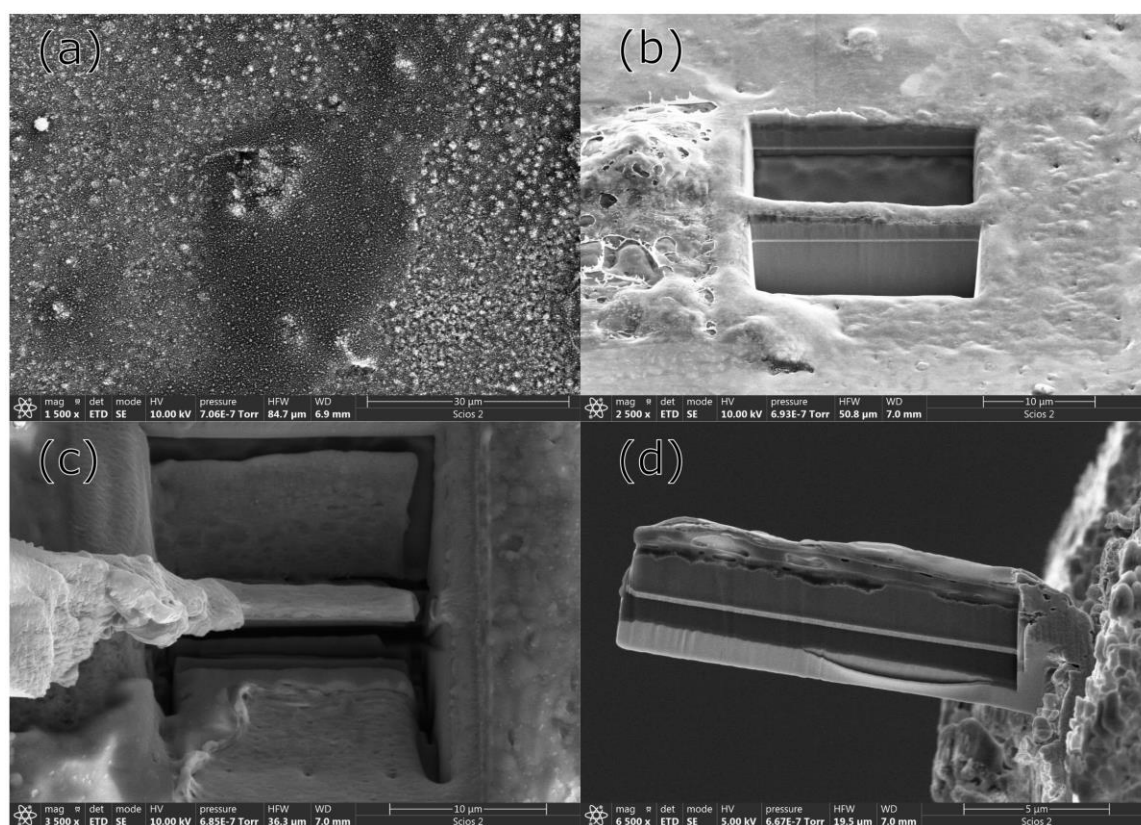


Figure 1. Cryogenic-FIB preparation of a cross section of an electrochemically deposited Magnesium anode. (a) Imaging the surface texture and identifying the region of interest, (b) bulk milling the region of interest, (c) needle attachment and lift-out of the cross-section, and (d) final thinning to electron transparency.

References

1. Henderson, R. and P.N.T. Unwin, *Three-dimensional model of purple membrane obtained by electron microscopy*. Nature, 1975. **257**(5521): p. 28-32.
2. Zachman, M.J., et al., *Cryo-STEM mapping of solid-liquid interfaces and dendrites in lithium-metal batteries*. Nature, 2018. **560**(7718): p. 345-349.

3. Ponrouch, A., et al., *Multivalent rechargeable batteries*. *Energy Storage Materials*, 2019. **20**: p. 253-262.

4. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.