

***In-situ* TEM Characterization of Electrochemical Processes in Energy Storage Systems**

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The accelerated development of materials for utilization in electrical energy storage systems will hinge critically upon our understanding of how interfaces (particularly electrode-electrolyte solid-liquid interfaces) control the physical and electrochemical energy conversion processes in energy storage systems. A prime example is found in Li⁺ ion-based battery systems, where a passive multiphase layer grows at the electrode/electrolyte interface due to the decomposition of the liquid electrolyte [1]. Once formed, this solid electrolyte interphase (SEI) protects the active electrode materials from degradation and also regulates the transport and intercalation of Li⁺ ions during battery charge/discharge cycling [2]. Due to the dynamically evolving nature of this *nm*-scaled interface, it has proven difficult to design experiments that will not only elucidate the fundamental mechanisms controlling SEI nucleation and growth, but will enable the SEI microstructural and chemical evolution as a function of charge/discharge cycling to be monitored in real time.

Recent advances in *in-situ* TEM characterization platforms have demonstrated the feasibility of conducting *in-situ* electrochemistry experiments on energy storage systems where lithium intercalation mechanisms [3] and the formation of surface compounds [4] on single SnO₂ nanowire anodes have been conducted. These microscopy experiments used an ionic liquid-based electrolyte, (LiTFSI) due to its relatively low vapor pressure and stability in the high vacuum environment of a TEM. Most commercially available electrolytes are, however, more volatile, and therefore cannot be utilized in the same manner. The use of closed environmental cells can overcome these issues by allowing imaging through a liquid that is wholly contained between thin electron-transparent silicon nitride (SiN) membranes that are supported on silicon microchips.

In this work, we have extended the versatility of a liquid cell [5] TEM holder and developed an *in-situ* electrochemical cell with flow-cell capabilities for use within a Hitachi HF3300 S/TEM operating at 300kV. The electrochemical cell *in-situ* TEM holder provides a liquid delivery system (microfluidic syringe pump and microfluidic tubing) for flow between the SiN windows comprising the cell. Biasing contacts are deposited onto the upper chip/window of the cell, which doubly serves as a platform for attaching battery electrodes and for interfacing with an external potentiostat for electrochemical testing. A 500nm spacer material patterned on the bottom chip controls the thickness of the liquid electrolyte layer in the cell. This device has been used to dynamically monitor the formation of the SEI on a graphite anode *in-situ* within an electrolyte consisting of 1M LiClO₄ in EC:DEC. Fig.1 shows the biasing chip platform (Fig. 1a) with a highly oriented pyrolytic graphite (HOPG) anode and LiCoO₂ cathode attached using a focus ion beam (FIB) instrument, experimental charging curve (Fig. 1b), and TEM micrographs of the HOPG anode through the silicon nitride viewing window before (Fig. 1c) and during an *in-situ* electrochemistry, which shows the formation of the SEI on the graphite anode (Fig. 1d). SEI phase identification is underway. Practical uses and limitations for performing this type of *in-situ* electrochemistry experiments will be addressed [6].

References

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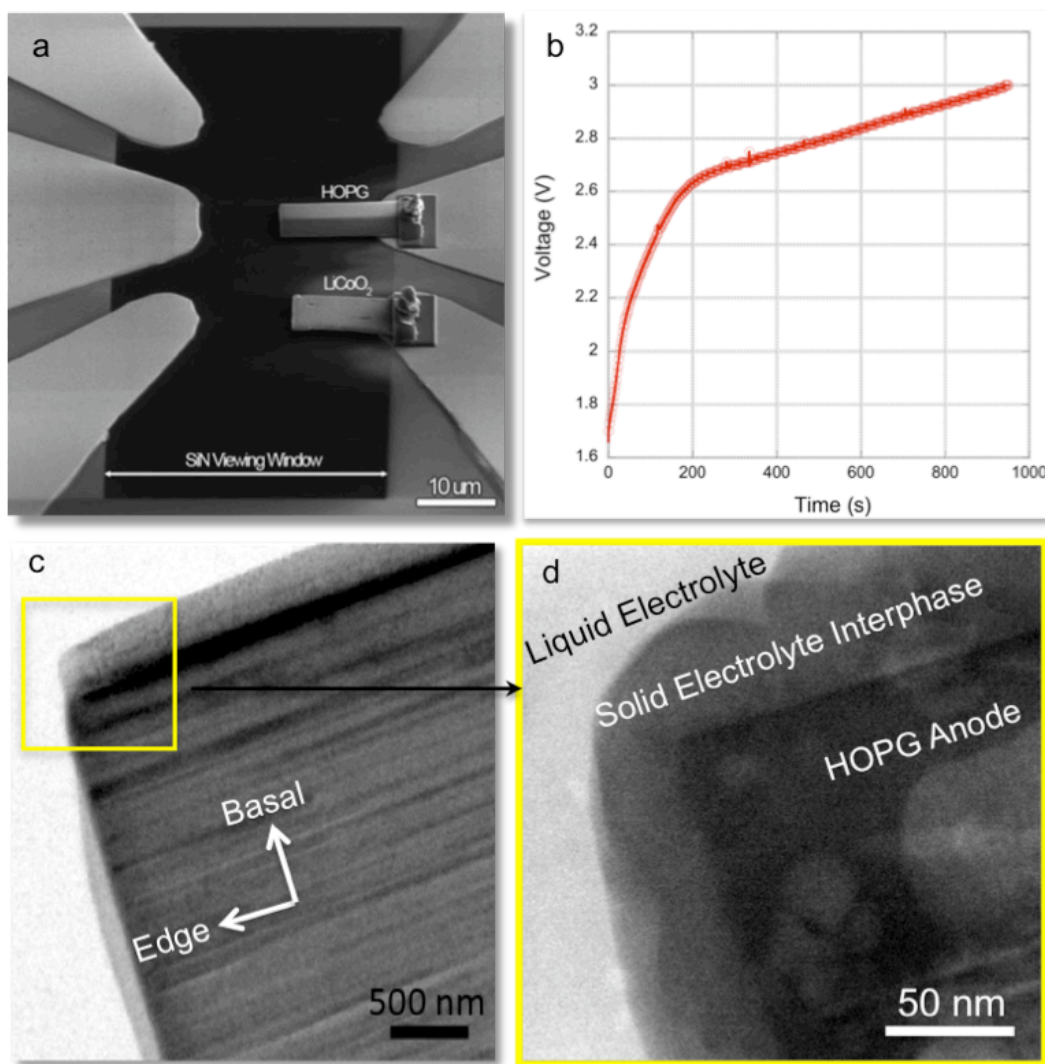


FIG 1. a) SEM micrograph of a FIB prepared "battery-on-chip" microbattery with HOPG anode and LiCoO₂ cathode before closing the *in-situ* TEM liquid flow cell. b) Charging curve of the microbattery in an organic liquid electrolyte consisting of 1M LiClO₄ in EC:DEC. c) BF-TEM micrograph of the HOPG anode within the *in-situ* electrochemical cell (sans liquid electrolyte). d) Individual frame-shot acquired during an *in-situ* electrochemistry experiment showing the formation of the SEI on the graphite anode.