

Introduction

A key challenge in the development of lithium-ion battery materials is combating the formation of lithium dendrites on the electrode surface after repeated charge/discharge cycles. Fundamental to this process is the formation of the solid electrolyte interphase (SEI) layer. The SEI layer is an intermediate solid-liquid layer formed at the surface of the electrode by the interaction of lithium with the electrolyte. If the SEI layer is unstable it can lead to crack formation, thus increasing the surface roughness of the electrodes, and the formation of lithium dendrites. As dendrites form over repeated cycles, so-called “dead” lithium no longer participates in ion transport, and causes reduction in battery capacity while increasing the potential for the formation of a short circuit between the anode and the cathode. The Poseidon system enables the simultaneous acquisition of correlative electrochemical results, such as cyclic voltammogram (CV) curves, which enables quantification of process reversibility and electrochemical cell capacity, key parameters affecting the battery performance of many consumer devices.

The Poseidon electrochemistry liquid cell system

facilitates the study of dynamic nanoscale processes in the transmission electron microscope (TEM) while simultaneously collecting correlative electrochemical data. Researchers can probe complex processes, such as lithium-ion batteries, fuel cells, and corrosion at the nanoscale in order to better understand the fundamental mechanisms and develop new materials. The Poseidon system includes a dedicated *in situ* microfluidic TEM holder, potentiostat and syringe pump. Samples are contained in a liquid environment between a large and a small microchip (called E-chips), both of which have an electron beam transparent, amorphous 50 nm membrane of silicon nitride (SiN). In order to simultaneously acquire electrochemical data and images in the TEM, a three electrode circuit, which includes a working, reference and counter electrode, is integrated into an E-chip device loaded in the tip of the TEM holder, as shown in Figure 1. When the large Poseidon E-chip is inverted, it rests against the small E-chip (shown positioned in the tip of the Poseidon TEM holder) and the integrated electrodes of the large E-chip make contact with the electrode pad in the holder to form a closed circuit. A 500 nm insulating layer on the surface of the E-chip prevents

electrolyte from interacting with the electrodes outside the viewing region, which improves electrical signal and provides a flow channel for the electrolyte.

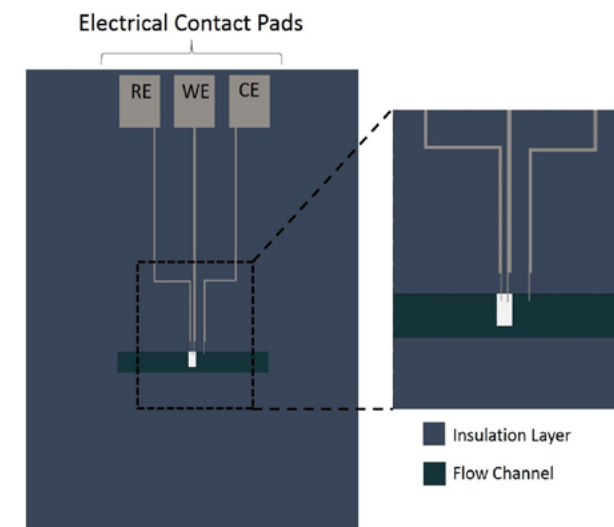
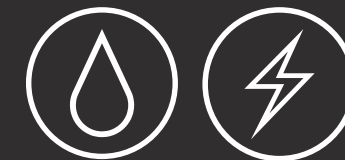


Figure 1: Posiedon E-chips

Experiment

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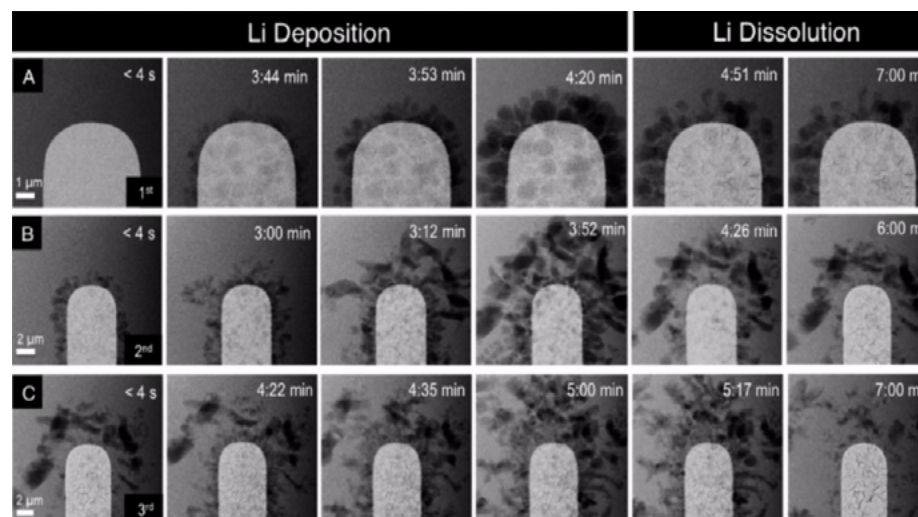


system to observe the charge/discharge process of lithium-ion batteries in solution using scanning TEM (STEM). The Poseidon system enables TEM imaging of hydrated samples, enabling the researchers to image and quantify the growth and evolution of the SEI layer as well as the resulting formation of lithium dendrites on the surface of the anode during successive charge/discharge cycles.

The configuration of the battery cell used in the study was as follows: The reference, working and counter electrodes were platinum, patterned linearly on the surface of the large Poseidon E-chip, with the working electrode (anode) patterned onto the 50 nm SiN. An insulating layer on the surface of the E-chip confined the electrolyte to localized regions of the electrodes and provided a 500 nm spacer for electrolyte to be flowed through the cell. An additional 150 nm spacer was used on the corresponding E-chip (Part # EPB-55BF) for a chamber liquid thickness of 650 nm at the edge of the liquid cell. Lithium was introduced into the system via the electrolyte, 1.0 M lithium hexafluorophosphate in propylene carbonate (LiPF₆/PC), at a flow rate of 3 μ L/minute using a syringe pump. the

entire the system was assembled under argon using a glove box because the electrolyte is air and water sensitive. Current was supplied to the system using a Gamry Reference 600 potentiostat.

Images were recorded using an FEI Cs corrected Titan operated in scanning TEM (STEM) mode at 300 kV. The electron dose was maintained below ≤ 0.3 electrons/ $\text{\AA}^2/\text{s}$ to prevent breakdown of the electrolyte, beam induced precipitation and bubble formation.



Results and Discussion

A series of real-time STEM images of the working electrode (WE) was acquired as the electrochemical potential of the cell was simultaneously cycled from 0 to -4 volts. Figure 2 shows high angle dark field (HAADF)-STEM images of the formation of lithium dendrites on the surface of the platinum WE over the course of three charge/discharge cycles. For each cycle (Figure 2 A-C) lithium deposition (charging) is shown in the first four frames and lithium dissolution (discharging) is shown in the final two frames. At the start of the first cycle the surface of the platinum working electrode

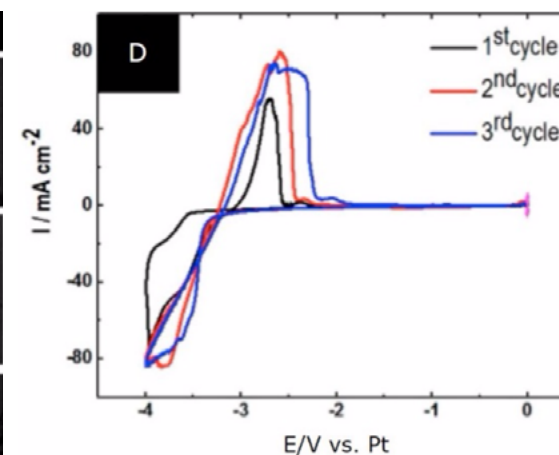
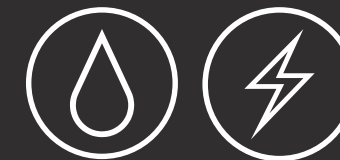


Figure 2A-D: Lithium dendrite growth and dissolution over repeated battery cycling



is pristine and all the lithium is dissolved in the electrolyte solution. As the battery is charged, lithium is deposited on the surface of the working electrode and surface roughening is observed as the lithium is not deposited in an even layer. Discharging of the battery during the first cycle leads to a reduction in lithium on the electrode surface, however lithium dendrites remain on the surface of the electrode and do not re-dissolve in the electrolyte. This process is continued in cycles two and three, and each subsequent cycle leads to an increase in the number and size of the lithium dendrites on the electrode surface.

Also present after the second and third cycle are regions of “dead” lithium, which are deposits of lithium metal no longer in contact with the electrode surface, and consequently does not participate in charge transport. The formation of these regions of dead lithium in an electrochemical cell causes capacity fading, resulting in shorter battery lifetimes between charging cycles. Real-time movies of the charge/discharge cycle are available online at: <http://pubs.acs.org/doi/suppl/10.1021/acs.nanolett.5b00175>. The corresponding electrochemical data (CV curves) are shown

in Figure 2D. As the number of charge cycles increases, an increase in irreversibility of the electrochemical cell is observed, which corresponds to the formation of lithium dendrites and “dead” lithium regions visible in the STEM images. Also visible in the CV curves are characteristic peaks at -2 and -2.5 volts, which indicate alloying between the platinum electrode and the lithium in the electrolyte.

To accurately interpret the electrochemical results, it was necessary to understand the distribution of the electric field within the liquid chamber of Poseidon. Using the dimensions of the liquid chamber and electrodes the researchers simulated the electrical field that results from a constant galvanostatic discharge 0.1 mA/cm² in a LiPF₆/PC electrolyte by performing an Ansoft Maxwell static 3D simulation.

The Maxwell simulation of the reference and working electrode configuration of the E-chip used in this study is shown in Figure 3A. A region of high electric field gradient, or hotspot, is predicted to occur at the right hand tip of the working electrode (anode) between the anode and cathode in the original work. This region

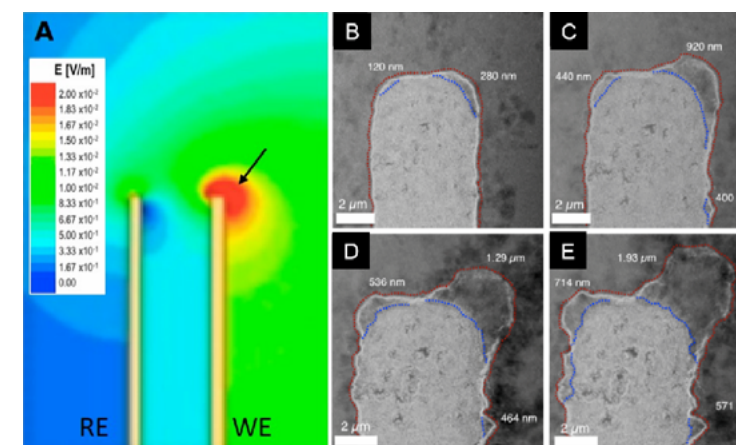


Figure 3: Modelled Electrode Hotspot and Corresponding Experimental Data. A: Maxwell simulation reference and working electrode of the E-chip used in this study. Dark field STEM image of the working electrode after the fifth (B), sixth (C), seventh (D) and the eighth cycle (E).

of increased electric field density is confirmed in the experimental data. HAADF-STEM images shown in Figure 3 B-E of the working electrode (area indicated by the blue line) after the fifth cycle (B), sixth (C), seventh (D) and the eighth cycle (E) show the localized formation of a lithium dendrite at the same location as the predicted hotspot position, which increases in size with each subsequent charge/discharge cycle.



Also visible in the images is a region of bright contrast at the edge of the electrode (indicated by the red line). This region is the SEI layer, which becomes increasingly irregular with each subsequent cycle, corresponding to the increase in the growth of the lithium dendrites on the electrode surface.

Conclusions:

Using the Poseidon system researchers successfully imaged the formation of lithium dendrites during battery charge/discharge cycles while simultaneously collecting electrochemical data using STEM. The experimental results were further confirmed through computer simulations, which identified regions on the working electrode in which dendrites were likely to form. *In situ* S/TEM analysis of fundamental battery mechanisms combined with quantitative electrochemical results, such as the study presented here, represents a fundamental advancement in the development of the next generation of high performance battery materials. Contact us to discuss the full range of capabilities of the Poseidon. We can be reached at (919) 377-0800 or contact@protochips.com.