

Near-Field IR Investigations of the Solid Electrolyte Interphase Layer on Sn

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A strong understanding of the solid electrolyte interphase (SEI) (1,2) layer in lithium-ion batteries is necessary for further development of the technology, leading the path to application of high energy density intermetallic anodes. However, the identification of chemical compounds in this surface layer, as well as their spatial distribution, has been limited by diffraction to the 5-10 μm wavelength scale available to traditional Fourier Transform Infrared spectroscopy (FTIR). Here we demonstrate, for the first time, deeply subwavelength imaging of the SEI using infrared (IR) near-field scanning optical microscopy (NSOM).

NSOM (3) is a technique based on light confinement at the apex of an atomic force microscope (AFM) probe. The tight optical focusing combined with the placement of the probe within small fractions of a wavelength allow resolution well below the classical diffraction limit, while simultaneously obtaining topographic information about the sample surface and the present SEI. Additionally, this microscope is highly surface-sensitive, allowing selective optical imaging of the interfacial layers. The NSOM used here is configured as part of a pseudo-heterodyne interferometer, which allows high signal-to-noise ratio as well as collection of the optical phase.

A mechanically flattened polycrystalline tin anode was cycled five times between 2.5 and 0.8 V vs Li/Li⁺, then removed from the cell, rinsed three times with DMC and imaged with the IR NSOM at a range of wavelengths in the mid-infrared region (9.2 μm -10.4 μm). The potential range of the scans limits the tin-lithium alloying and therefore the SEI layer on top is not broken and reformed in each subsequent cycle.

The signal was demodulated at the sum of the pseudo-heterodyne modulation frequency and the second harmonic of the probe oscillation frequency. Sample results of the topography and optical images at three different wavelengths are shown in Figure 1. The optical images display some correlation to the topography but also indicate the presence of clear differences, demonstrating that major parts of the optical contrast is due to materials' chemical composition and/or structure variations rather than topographically-induced artifacts. There is a visible spectral variation in the images, further demonstrating this point and making possible the identification of the materials.

By correlating spectral data to already known reference spectra, these results allow the identification of the chemical structure of the SEI layer at high resolution. With further investigation, it will be possible fully to characterize the inhomogeneous surface layer at its natural length scale and to find solutions to overcome this hindrance.

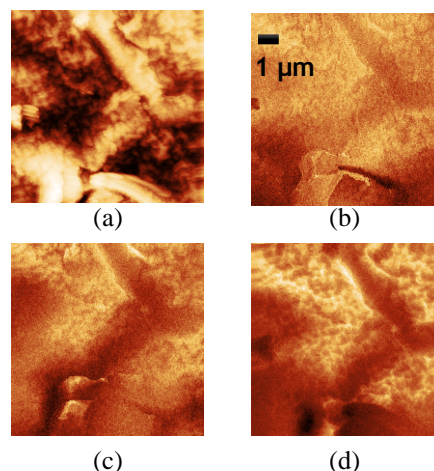


Figure 1: IR NSOM images of the SEI. (a) Topography (b-d) Second-harmonic optical images. (b) 9.2 μm (c) 9.6 μm (d) 10.0 μm

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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