

Visualization of Electrochemical Reaction Dynamics in Liquids Using TEM

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The study of electrochemical processes using liquid environmental cell transmission electron microscopy (TEM) has attracted a lot of attention. Assisted by electrochemical liquid environmental cells, dynamic phenomena at electrode-electrolyte interfaces can be revealed in real time with high spatial resolution using TEM. So far, there have been many studies, for instance, electrochemical deposition of metal clusters, dendrite formation, using a custom-made or commercial liquid sample stage [1]. Here, using our own development of electrochemical cells and a sample stage, we have been able to observe a series of electrochemical phenomena at electrode-electrolyte interfaces. For example, the observation of growth and dissolution of Pb dendrites [2] and lithium dendrites [3], formation and characterization of composition and structure of solid electrolyte interphase (SEI) [3,4], lithiation/delithiation of MoS₂ nanosheets in a commercial electrolyte for lithium ion batteries [4], lithiation of Au electrode [5], in situ study of Mg deposition [6], Na deposition [7] and Li-S intermediate phases [8] in a nanobattery EM cell. These studies provide insights on battery operation and failure mechanisms.

As an example, Figure 1 shows the deposition and dissolution of Pb dendrites and a lithium dendrite in an electrochemical environmental cell [2,3]. Dendritic growth arises from the instabilities when the growth rate is limited by the diffusion rate of ions from the solution to the interface, which is ubiquitous in materials solidification and crystallization. Its complexity characterized as multilevel branching has attracted lots of attention. It may also introduce serious consequences, such as device failure due to dendrites connecting two electrodes. Real TEM time capturing of the dendrite formation and dissolution gives the opportunity to elucidate the mechanisms of growth. It may allow developing possible strategies to improve the device performance. Figure 2 shows the morphological evolution of MoS₂ nanosheets during initial charge cycles in a lithium- MoS₂ nanobattery cell, where LiPF₆/EC/DEC electrolyte was used. Upon discharge in a voltage range of 1.8-1.2 V, MoS₂ nanosheets on the Ti electrode underwent irreversible decomposition resulting in fast dissolution and vanish of the MoS₂ active nanoflakes (Figure 2a). Repeated experiments also indicate lithiation induced structural expansion and deformation of MoS₂ nanosheets. Energy dispersive x-ray spectroscopy (EDS) maps confirm Mo and S elements signals in the residual MoS₂ nanoflakes but not in the rest of areas (Figure 2b). 4D-STEM characterization of the decomposition products occurred near 1.1 V shows that some of MoS₂ nanosheets broke down into 5-10 nm MoS₂ nanoparticles instead of fully decomposed into Mo and Li₂S nanoparticles (Figure 2c). On the other side of the electrode, we observed SEI layer formation. Our detailed characterization including EDS mapping and 4D-STEM show the constitute elements and LiS nanocrystals (~5nm) uniformly distributed in SEI. At the end of this

paper, our newest study on Na deposition and formation of Li-S intermediate phases in a nanobattery EM cell will be discussed.

References:

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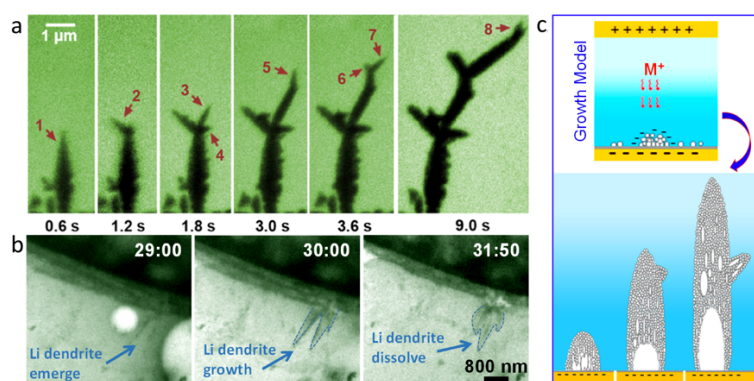


Figure 1. (a) Time series of TEM images show deposition and dissolution of Pb dendrites. (b) Time evolution of the growth and dissolution of a lithium dendrite. (c) A cartoon showing the electrochemical growth of lead dendrites based on both in situ and ex situ studies.

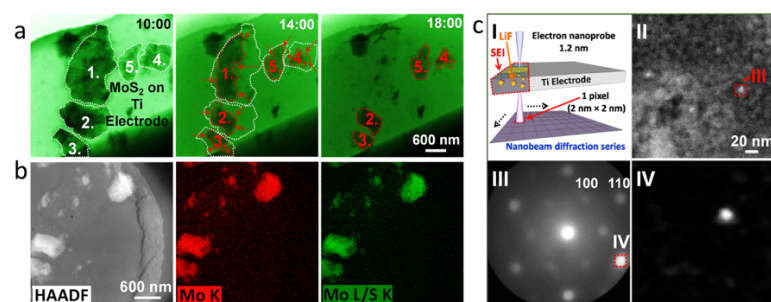


Figure 2. (a) Time series of TEM images show the morphological evolution of MoS₂ nanosheets upon the initial discharge. (b) HAADF image showing the reacted MoS₂ nanosheets and the corresponding Mo K-series, Mo L-series/S K-series elemental distribution from EDS mapping. (c) I. A schematic showing nano-beam diffraction characterization of SEI layer or residual MoS₂ products after the reaction. II. A STEM image with a marked red dash box area where nano-beam diffraction was acquired. III. Reconstructed virtual diffraction patterns from the marked region III with 16 pixels in Panel II. IV. Virtual dark-field image reconstructed by selecting single diffraction spot marked in panel III.