# In-situ Electrochemical Scanning Probe Microscopy for Observing Electrode Surfaces under Operating Conditions

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The ongoing study of electrochemical energy storage and conversion devices is of great importance owing to higher possible efficiencies over current combustion technologies for automotive applications. Key to the development of improved electrochemical energy devices is the understanding of electrode behavior under operating conditions. Although traditional electrochemical techniques may be utilized to analyze electrode reactions and post-mortem analysis can provide information on electrode structural changes, these do not provide the ability to directly observe as a function of potential and time the evolution of the electrode surface. To bridge this gap, in-situ electrochemical scanning probe microscopy (EC-SPM) has been implemented to aid our research in a variety of electrochemical systems

To demonstrate the capability of EC-SPM, we investigated the formation and decomposition of Li-oxygen products on gold electrodes in 0.1 M $LiClO_4$ DMSO electrolyte as recently reported by Peng et al. [1]. EC-SPM and cyclic voltammetry (CV) were performed on various Au substrates in an oxygenated 0.1 M $LiClO_4$ DMSO electrolyte. A typical 3-compartment electrochemical cell comprised of a Li counter electrode and a $Ag/Ag^+$ reference electrode was utilized for the CV experiments. For EC-SPM experiments, a two electrode configuration was utilized where Li metal served as both the counter and reference electrodes. SPM images were acquired as a function of potential

Figure 1 displays EC-AFM discharge/charge images as a function of applied potential on a Au(111) film. Each potentiostating step was approximately 2 to 3 minutes as dictated by the time required to achieve an image (taken every 0.05 V). As the potential is reduced from open circuit (~3 V vs. $Li^+/Li$), the onset of discharge product formation was observed to occur at ~2.85 V. As potential was further decreased to 2.7 V, product formation was observed to occur layer by layer as indicated by the loss of terrace details on individual particles as well as filling of gaps between individual particles. From 2.7 to 2.3 V, nanoparticle formation was observed with average diameters and heights of 20 nm and 7 nm, respectively. At 2.3 V, the measured current rapidly declined corresponding to a total product thickness of ~10 nm indicating the electrode surface was passivated. Upon charging, no change in product morphology was observed until the potential was increased to above 3 V. Decomposition onset was primarily observed at 3.1 to 3.2 V and complete decomposition was not observed until 4 volts after which Au particle terraces were again observed. These results are in good agreement with the results of Peng et al.; however, comparison with the CV curves displayed in Figure 2 clearly indicates that reversibility is strongly influenced by the scan rate. Whereas the EC-AFM measurements were conducted at essentially very slow scan rates, the CVs were acquired at 100 mV/sec and show rapid passivation of the electrode surface (within 20 cycles). These findings qualitatively agree with recent studies that battery operating conditions (rate and depth of discharge) can significantly influence the reversibility of Li-O batteries [2,3].

It will be shown that in-situ observations of these types of processes provide direct insight into understanding the influence of the formation parameters (potential, current, time) on the morphology and stability of the solid product.

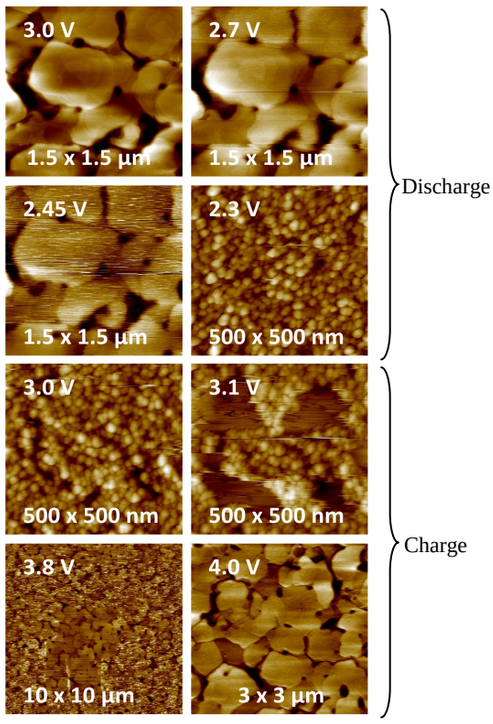


Figure 1. Representative EC-AFM images taken during discharge and charge. See text for details.

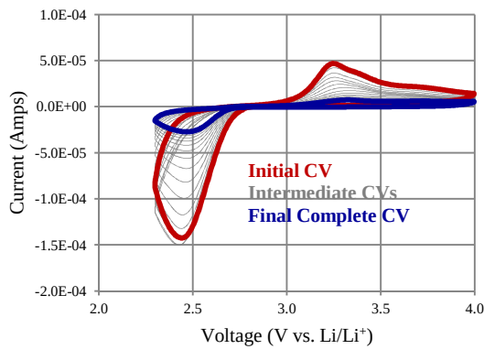


Figure 2. Cyclic voltammograms of polycrystalline Au disk from 2.3 to 4 V vs. Li. Scan rate is 100 mV/sec.

References

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[3] R. Mitchell, B. Gallant, Y. Shao-Horn, and C. Thompson, *J. Phys. Chem. Lett.* 2013, 4, 1060-1064