Chronoabsorptometric Imaging of Li^+ Insertion in Molybdenum Oxide Thin Films

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This presentation will focus on a newly developed spectroelectrochemical approach that integrates optical microscopy, atomic force microscopy, and electrochemical techniques to study heterogeneous ion/charge transfer reactivity at electrochromic metal oxide thin films. By collecting transmitted light images as a function of time following the application of a potential step to reducing (insertion) and subsequent oxidizing potentials (deinsertion) we are able to measure spatially-resolved insertion kinetics from heterogeneous regions in disordered thin films. Since the charge transfer reaction involves a simultaneous visible change in the optical density of the material, the electrocoloration response is used to study associated lithium insertion behavior and estimate apparent diffusion coefficients for mixed-phase materials. An example of this approach is shown in Figure 1 for lithium insertion in a disordered molybdenum oxide thin film. Clearly, anisotropic reactivity is observed, where energetically distinct phases and domain-specific reactivity exists. Three different regions of interest (ROI's) are indicated which highlight specific areas of unequal electrochemical activity representing reversible, irreversible, and quasi-reversible type insertion behavior. Structural changes are also seen during the insertion process where the semi-crystalline domains appear to undergo irreversible lattice expansions upon electrochemical reduction, which is consistent with AFM and voltammetric studies. In an effort to resolve associated electronic conductivity issues, we have also implemented a newly-developed variant of scanning probe microscopy, known as conductive probe atomic force microscopy (CP-AFM) to measure electronic transport properties. As shown in Figure 2, the (a) topography and (b) conductivity images show definitive evidence that the films are not only heterogeneous but that non-uniform conductive pathways exist which govern the observed anomalous electrochemical reactivity. Localized current-voltage curves acquired along these current carrying conduits and in electronically inactive regions will allow for the comparison of the nature of the electronic conductivity in these regions.

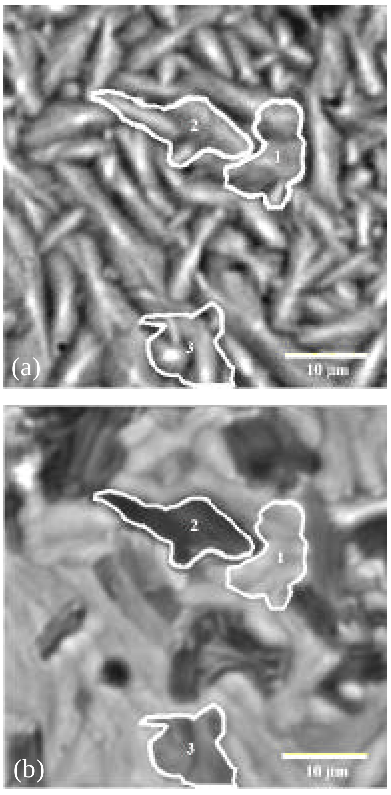

Figure 1. Chronoabsorptometric Imaging of Li^+ ion insertion into MoO_3. (a) film prior to ion insertion (b) film after 1 insertion/deinsertion cycle.

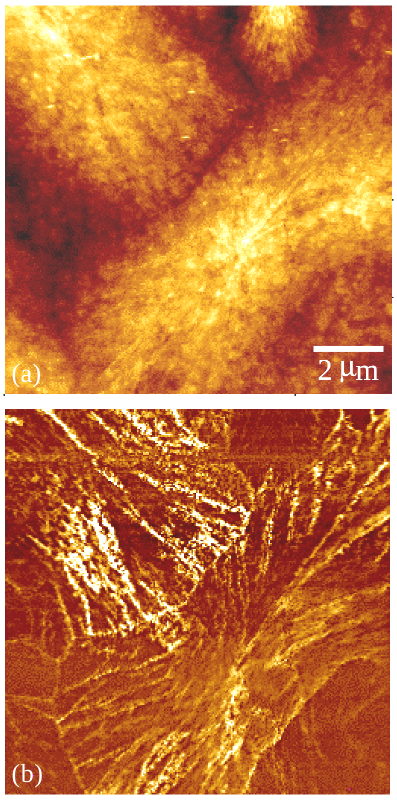

Figure 2. Simultaneously acquired (a) topography and (b) conductive AFM images of MoO_3 thin film prior to Li^+ insertion illustrating paths of current flow in the metal oxide.