

Matthew Charlton Proposal Abstract

Atomic Layer Deposition of Model Metal Oxide Electrode Architectures

A thorough knowledge of chemical and electrochemical processes that occur at the electrode interface is paramount to the development of improved materials for electrochemical energy storage. One approach is to study model systems with well-defined structures and geometries (architectures) more amenable to systematic and careful study of such materials. The goal of this work is to develop new approaches for creation of well-defined metal oxide electrode architectures from titanium and vanadium precursors utilizing atomic layer deposition (ALD). ALD is an emerging synthetic method that enables atomic-level control over the physical and chemical structure of deposited materials. These model systems are designed specifically to facilitate high-resolution, spatially resolved surface analytical measurements to elucidate complex lithium ion coupled electron transfer processes in heterogeneous material interfaces. Additionally, by promoting such charge transfer processes through the addition and integration of redox-active thin films supported on carbon electrodes (current collectors), the performance of the composites should be superior to that of single component electrodes.

Carbon films derived from pyrolyzed photoresist films (PPFs) will be used as the deposition substrate and current collecting layer. The quality and thickness of the PPF can be tuned to some extent to yield both optically opaque and transparent varieties, which will enable characterization using state-of-the-art surface analytical methods. A standard ALD technique is being used to conformally deposit anatase titanium dioxide (TiO₂) onto the carbon surfaces. However, a specific method is being developed for deposition of vanadium pentoxide (V₂O₅) onto carbon substrates. The physical and electrochemical characteristics of TiO₂ and V₂O₅ thin films of a series thicknesses will be investigated. The structure and other material properties will be studied via Raman spectroscopy, grazing incidence X-ray diffraction (GI-XRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The primary mechanisms of Li insertion will be determined using cyclic voltammetry, galvanostatic cycling, and in situ UV-Vis absorption spectroscopy. Chemical changes in the electrode as well as the formation of surface deposits during cycling will be investigated by time-of-flight secondary ion mass spectroscopy (TOF SIMS) and XPS. TOF SIMS will be a particularly valuable technique to investigate the effectiveness of fluorinated versus non-fluorinated salt electrolytes to promote lithiation by conversion in the electrodes.

All together, these experiments will provide information that can be used correlate the differences in Li⁺ insertion characteristics with variations in electrode or electrolyte chemistry as well as geometric changes such as the electrode surface area to volume ratio. They will allow a more detailed analysis of the specific mechanisms that are governing charge transfer in these materials systems. Through these studies, it will be shown that the high quality thin film composite electrodes achievable through ALD are ideal candidates to be used to investigate the fundamental chemical and electrochemical processes that occur during charge transfer and storage.