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Fabrication of Hg/Pt Hemispherical Nanoelectrodes for Localized Quantitive Detection of Manganese $^{2+}$ Produced at Battery Material

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The spinel $LiMn_2O_4$ is one of the most promising cathode materials for lithium batteries. It exhibits very good electrochemical performance at room temperature. However, its capacity fades with charge-discharge cycling or storage. This capacity fading is due to numerous factors such the Jahn-Teller distortion and the dissolution of Mn^{2+} into the electrolyte. [1] Although the exact mechanism is still unclear, most research groups agree that dissolution of Mn^{2+} is the leading factor contributing decreased capacity. [2] Our ongoing research efforts focus on localized quantitative detection of Mn^{2+} produced at battery materials, collected using a platinum-mercury amalgam nanoelectrode under anaerobic conditions using shear-force constant-distance scanning electrochemical microscopy (SECM). This electrochemical method allows surface characterization by approaching an ultramicroelectrode (UME) in close proximity of it. In SECM, the characterization focuses on both topology and local reactivity of the surface. Our probe scanner also allows the local measurement of the topology and the reactivity the battery material as the reaction is ongoing with high resolution.

The work presented here directly relates to the development and characterization of shear force Hg/Pt hemispherical nanoelectrodes. The production of this type of electrochemical probe is performed by electrodeposition from a mercuric ion solution [3] on a Pt/quartz laser-pulled disk nanoelectrode [4]. The preliminary production of the laser-pulled nanoelectrodes has allowed the development of a reproducible procedure leading to perfectly concentric disk nanoelectrodes of well-controlled geometry. The diameters of the electroactive surfaces ranged from of a few nanometers to hundreds of nanometers. Previous work on laser-pulled nanoelectrode shows that their physical characteristics allow their implementation in our platform. These standard nanoelectrode tips exhibit very stable shear force behavior. This characteristic is essential to the SECM technique. Indeed, the signal obtained in conventional SECM combines the topological response and the electrochemical response. Shear force mode brings the opportunity to deconvolute the two signals by isolating a topological signal. The shear force allows constant distance scanning over the substrate. The whole Hg/Pt hemispherical nanoelectrodes fabrication procedure is based on the electrodeposition from a mercuric ion solution onto these Pt nanoelectrodes. Platinum has been shown be an ideal choice of substrate because formation of inter-metallic compounds at the base metal can occur. Additionally, it can be easily wetted and has a low solubility in mercury. [3] The electrochemical characterization of platinum-mercury amalgam tips is performed with methyl viologen, and hexamineruthenium (III) chloride in order to validate the geometry of the electrode. In addition to cyclic voltammetry, approach curves recorded during SECM experiments with both redox mediators over a conductive substrate were to fit theoretical plots for hemispherical electrodes.

It has been reported that amalgam electrodes can be used to perform the quantitative analysis of Mn^{2+} due to extension of the potential window to more negative potentials. [5] An enhanced sensitivity of the substrate generation-tip collection (SG-TC) results has also been reported. The enhancement in sensitivity of this SECM mode and positioning capability of our system will give us a competitive advantage in the mapping of Mn^{2+} hot spots at battery materials as the reaction is ongoing with high resolution.

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