Electrochemically-Driven Solid-State Amorphization in Lithium-Metal Anodes

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Metal-based anodes have received much interest as alternatives to carbon for lithium-ion negative electrodes due to their intrinsically high gravimetric and volumetric capacity [1-5]. Although the basic thermodynamics and electrochemistry of most of the simple alloys are known, [6-7] the fundamental materials response at the micro- and nanostructural scale upon electrochemical cycling remains poorly understood, for both anodes and cathodes. This behavior is especially important to long-term cycling.

Fracture, dislocation damage, and phase transformations are commonly observed in both cathodes and anodes subjected to electrochemical cycling. Fracture can nominally be attributed to electrochemically-induced strain, and occurs in both intercalation oxides[8] and metal anodes.[9] However, metal anodes have been observed to undergo increased disorder at the atomic level upon electrochemical cycling, the cause of which has not been understood. In this paper, we propose a new mechanism - *electrochemically driven solid –state amorphization* to explain this transformation from crystalline to disordered phases.

Solid-state amorphization through diffusive reactions have been observed in multilayer thin film systems, in which the film thickness is comparable to an interface thickness.[10] Amorphization occurs when a thermodynamically preferred crystallline intermediate compound is unable to nucleate, and a glassy phase that is metastable yet lower in free energy than the pure reactants forms instead. We propose that a similar phenomenon can occur when alloying is electrochemically-driven. The basic criteria necessary for transformation from a crystalline to amorphous state, bypassing the equilibrium intermediate compound, is a negative heat of mixing, large size differences between atoms, high alloying concentration, and large differences in diffusivities of atoms.[11-14] These criteria are easily met in various Li-Me systems.

We have obtained direct evidence that the proposed phenomenon occurs. Several metal systems including Al, Ag and Sn, were lithiated and then characterized using X-ray diffraction calibrated with internal standards, high-resolution transmission electron microscopy (HREM) and scanning transmission electronmicroscopy (STEM). Figure 1 shows an HREM image of Sn metal after 5 cycles against a Li electrode. The observed nanostructure consists of nanocrystallites of $d < 5$ nm coexisting with an amorphous metallic phase. Details of the electrochemically-driven solid state amorphization mechanism, supporting experimental results and comparision with solid-state thin film experiments will be presented at the meeting.

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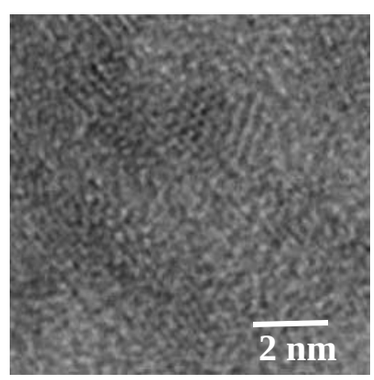

Figure 1. High-resolution transmission electron image of a Sn particle after 5 cycles between 0.005-2 V against Li at 10 mA/g, showing coexistence of nanocrystalline and amorphous phase.