

Understanding Lithium Alloy Induced Volumetric Expansion in Silicon Electrodes via *in situ* High Resolution Spectroelectrochemical Diffraction Microscopy

Sankaran Murugesan, Kjell W. Schroder, Lauren J. Webb, and Keith J. Stevenson*

Department of Chemistry and Biochemistry,
The University of Texas at Austin,
Austin, Texas 78712, USA

To replace the existing limited capacity graphitic carbon electrodes (372 mAh/g) in lithium ion batteries, considerable attention has been paid towards lithium alloying type electrodes such as Si and Sn due to its higher storage capacity (4200 mAh/g). Though Sn and Si based compounds have higher capacity, they suffer the drawback of volume expansion leading to strain in the electrodes which causes pulverization. *In situ* experiments were performed to measure the volume change in these electrodes by transmission X-ray microscopy and AFM measurements. However, the results could not conclude the real picture of volume expansion due to electrochemical amorphization of the electrodes in few cycles of lithiation/delithiation and these experimental methods are very expensive and requires special experimental setups. Here, we present volume expansion/contraction behavior of amorphous Sn and Si electrodes by *in situ* high resolution spectroelectrochemical diffraction based microscopy.

Diffraction-based imaging is an emerging optical based sensing technique that employs diffraction of visible light as signal for detection of receptor/analyte interactions. Earlier our group has shown diffraction based imaging of electrochemically induced Li-insertion/deinsertion in metal oxides and mixed metal oxides.¹ Here we have used this technique to understand volume expansion/contraction in electrochemical Li-alloying reaction by monitoring the diffraction intensities and profile movements. Any spatially periodic material patterned on an appropriate length scale can act as a diffraction grating, when it is differentiated from its surroundings by a component of its complex refractive index ($n' = n + ik$) by modulation of n or k . For instance, monochromatic light propagating through a 1-D patterned array (e.g. periodically spaced set of parallel features) will be diffracted forming a row of bright spots. The intensity of these diffracted spots depends on both the thickness of the pattern and the degree of contrast between the complex refractive index of the pattern and the surroundings. As a consequence, any electrochemical or volumetric change occurring at the grating material or its surroundings will result in detectable modulation of the position and intensity of diffracted light due to changes in the volume (spacing between diffracting elements) and complex refractive index of the system. The figure of merit used to describe the degree of diffraction is called diffraction efficiency (DE) and is related to n and k using an easily derived expression.

First we have developed theoretical models to understand modulation in the diffraction due to volume change. Mathematical formulas are derived from Fraunhofer diffraction equation for predicting diffraction efficiency of gratings made on a transparent substrate. This formula is used in two situations: 1) when the gratings are active and undergo lithiation which leads to

change in thickness of the grating (Fig. 1A); 2) when the gratings are inert and the underlying substrate undergoes lithium alloying causing movement of gratings. The change in center to center distance of grating by lithiation is monitored as shown in Fig. 1C. From the theoretical analysis it is clear that the diffraction intensity profile of lithiated gratings are decreased compared to original gratings (Fig. 1B). In case of inert gratings with active underlying layer during lithiation shows diffraction intensity profile movement (Fig. 1D) due to volume change. The effect of expansion causes increase in spacing between centers of each slit, leading to a change in the peak position of the diffraction maxima. Additionally, the opening of the slits results in decreased intensity.

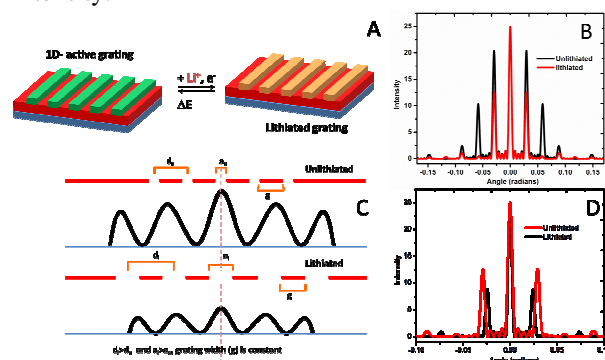


Figure 1. A. Schematic representation electrochemical alloying of active 1-D gratings. B. The diffraction intensity patterns generated by simulation with active 1-D gratings. C. Schematic representation electrochemical alloying of active underlying layer causing inert 1-D gratings movements. D. Shows the intensity patterns generated by simulation with active underlying layer and inert 1-D gratings.

The theoretical predictions are validated experimentally by preparing 1-D gratings over optically transparent carbon (OTC) electrodes. For lithium alloying active grating we developed amorphous Sn gratings over OTC. In case of active underlying layer with inert gratings, amorphous Si active layer and Pt inert gratings were used. The *in situ* high resolution diffraction imaging experiments were performed with a home built electrochemical cell using Li as the reference and Pt counter electrodes in 1 M LiPF₆ DEC/EC electrolyte. Lithiation-delithiation experiments were performed by cycling between 2 V to 10 mV vs Li. The Sn grating electrodes completely lithiate at 0.12V vs Li during lithiation causing decrease in intensity of diffraction as predicted from theoretical model (situation1). From the DE analysis Sn gratings show about 10% of thickness raise during lithiation. In the case of amorphous Si with inert Pt gratings lithiation takes place at 0.2V vs Li. During lithiation the diffraction intensity changes due to increase in thickness and also diffracted spot movement takes place due to change in slit distance as predicted in the theoretical model (situation 2). We will also demonstrate real time volume change during lithiation-delithiation of amorphous Si.

References:

1. Kondrachova, L.V.; May, R.A.; Cone, C.; Vanden Bout, D. A.; Stevenson, K.J. "Evaluation of Lithium Ion Insertion Reactivity Via Electrochromic Diffraction-Based Imaging," *Langmuir* **2009**, 25(4), 2508-2518.

*Corresponding author e-mail: stevenson@cm.utexas.edu
Ph (512) 232-9160, Fax (512) 471-8696