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Comparison of Nanoscale Focused Ion Beam and Electrochemical Lithiation in β -Sn Microspheres

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Abstract

The development of Li focused ion beams (Li-FIB) enables controlled Li ion insertion into materials with nanoscale resolution. We take the first step toward establishing the relevance of the Li-FIB for studies of ion dynamics in electrochemically active materials by comparing FIB lithiation with conventional electrochemical lithiation of isolated β -Sn microspheres. Samples are characterized by cross-sectioning with Ga FIB and imaging via electron microscopy. The Li-FIB and electrochemical lithiated Sn exhibit similarities that suggest that the Li-FIB can be a powerful tool for exploring dynamical Li ion-material interactions at the nanoscale in a range of battery materials.

Introduction

There is increasing interest in leveraging host materials such as Si, Sn, Al or Ge as high capacity negative electrodes in Li-ion batteries. For example, $\text{Li}_{4.4}\text{Sn}$, with a theoretical capacity of 993 mAh g^{-1} , could achieve an energy density more than twice that of the conventional graphite electrodes used today.¹ Recently, it has been found to be advantageous to disperse these materials at the nanoscale into composite electrodes. This reduces failure due to volume expansion and cracking; however, it significantly complicates our understanding of the lithiation process within the individual particles. The inhomogeneous nature of these composite electrodes leads to spatial variations in state-of-charge throughout the electrode during cycling. This has led to several attempts to characterize these high capacity composite electrodes with *in-situ* transmission electron microscopy (TEM),² *in-situ*

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synchrotron transmission X-ray microscopy (TXM),³ and electrochemical strain microscopy (ESM).⁴

Tools that can probe lithiation mechanisms at the nanoscale are critically needed to optimize and improve these composite electrodes. Here we introduce the use of a nanoscale focused Li ion beam (Li-FIB) as a new approach to this problem. In the Li-FIB lithiation process, a focused ion beam with spot size of a few tens of nanometers and kinetic energy of a few kiloelectronvolts is directed at a sample in vacuum and scanned across the area of interest. Unlike electrochemical lithiation, the precise dosage and spatial distribution of the lithiation can be controlled through the spot size, beam positioning, beam current, and time of exposure. Furthermore, because lithiation occurs under vacuum, in the absence of electrolytes and counter ions, no solid-electrolyte interface (SEI) is formed. Without an SEI, it becomes possible to study lithiation effects solely in the electrode material, without the confounding influences that the interfacial material can have.

While Li-FIB lithiation appears to be attractive for nanoscale ion transport studies, it is important to examine whether there are any fundamental differences in the lithiation process that result from the fact that the ions enter the material at high energy under vacuum, rather than through diffusion at a potential of a few volts from a liquid or solid electrolyte. To begin to address this question, the present study was conducted to qualitatively compare the morphology of β -Sn microspheres lithiated by Li-FIB and by conventional electrochemical means. The work presented here is a first step towards the realization of Li-FIB lithiation as a battery research and development tool.

Experimental

Li-FIB

Focused Li ions were produced in a Li-FIB system consisting of a magneto-optical trap ion source, in which laser-cooled atoms at $\approx 600 \mu\text{K}$ are photoionized, extracted, and coupled into a conventional FIB focusing column.^{5–7} The ion beam is accelerated to an energy of 3.9 keV and electrostatically focused to a $\approx 50 \text{ nm}$ spot. The Sn spheres (Ted Pella, Inc. 600-A⁸, monocrystalline tetragonal polymorphs of β -tin) were lithiated under a vacuum of approximately $2 \times 10^{-4} \text{ Pa}$ by rastering a $(1.0 \pm 0.2) \text{ pA}$ beam over a $1 \mu\text{m} \times 1 \mu\text{m}$ square area for 6 hours to deposit $(9.6 \pm 1.9) \times 10^{10}$ ions (Fig. 1a).⁹ Sn spheres with diameter $\approx 3 \mu\text{m}$ were chosen for lithiation to ensure significant volumetric filling. Target spheres were chosen adjacent to similarly-sized unlithiated spheres, so that direct comparison could be made. Numerical simulation of ion beam dynamics using SRIM calculations¹⁰ indicates that 99 % of the ions stop within 60 nm of the surface, and that 29 % of the ions backscatter from the sample. Fig. 1(b) illustrates how a point source of Li ions is calculated to stop in bulk Sn—here the local Li number density is plotted relative to tin as $\tilde{n} = \frac{n_{\text{Li}}}{n_{\text{Sn}}}$ for 1 pC of injected charge. Importantly, the Li interacts with the first 60 nm of the Sn bulk, not just the surface.

Electrochemistry

Using a sample identical to the Li-FIB lithiation sample, Sn spheres on a carbon substrate were electrochemically lithiated in a three-electrode cell assembled in an Ar atmosphere. A

schematic of the reaction is shown in Fig. 2(a), and a typical cyclic voltammogram is shown in Fig. 2(b). The sample was lithiated by holding the working electrode at 0.35 V relative to Li/Li⁺ for 1 hour. This voltage was chosen to drive Sn lithiation to at least Li₅Sn₂, based on the coulometric titration (see Supplemental for additional details).¹¹

Analysis

All samples were transported to the focused ion beam/field emission scanning electron microscope (FIB/FESEM) chamber in an air-tight jar to minimize air exposure. Images were obtained with a beam current of 0.2 nA at an energy of 10 keV. Cross-sectioning was performed with 30 keV Ga⁺ ions, revealing interior changes resulting from the lithiation.

Results and Discussion

Directly after lithiation, ion-induced secondary electron imaging in the Li-FIB showed surface contrast of the lithiated area (Fig 1a, inset). In subsequent FESEM imaging, increased surface roughness was seen in comparison with the nearby unlithiated control sphere of similar size (Fig 1c). This roughness, which extends across a large portion of the surface of the sphere, indicates surface expansion and diffusion from the implantation area. Cross sectional FESEM images of the lithiated sphere after milling with a Ga⁺ FIB (Fig. 1d) show a band of contrast starting in the implantation volume and expanding into the sphere. No contrast changes were observed in the nearby unlithiated sphere of similar dimensions. We associate this band of contrast with the lithiated volume. As the spheres are physically isolated, the average Li/Sn ratio can be calculated from the ion dose and the estimated volume of the modified-contrast region. This ratio is found to be of order unity and supports the hypothesis that the contrast change is associated with local Li concentration.

The traditional electrochemical lithiation of the Sn spheres is illustrated in Fig. 2. In this case the lithiation mechanism is complicated by interfacial layers on the Sn sphere, which impede ion transport, and reduction of solvents at the electrode surface during formation of the SEI. Reduction of the solvent is unavoidable as lithiation of Sn occurs at potentials below the anodic electrochemical stability potential of most organic solvents.¹² Intercalation of Li⁺ into the carbon substrate and formation of the carbon SEI further complicate this reaction. The electrochemical cyclic voltammogram (CV) representing the sum of all four reactions is shown in Fig. 2b. Also shown is a CV of the back side of the sample, which consisted of just the carbon substrate, with no Sn spheres. A small difference is observed in the CV current between the Sn-on-carbon and carbon sides of the sample, indicating the presence of Sn lithiation (see Supplemental). However, quantification of the Sn lithiation rate from the current alone is complicated by the mixed contribution of the four possible reactions. Dramatic surface undulations on the Sn spheres are observed in the FESEM imaging, most likely due to volume expansion, and also side reactions, including the SEI formation. The expected volume change from Sn to Li₅Sn₂ is a factor of ≈ 2.3 , consistent with the appearance of the spheres in the FESEM image of Figs 2c and 2d. Cross sections of the electrochemically lithiated spheres (Fig. 2d) show bands of contrast near the surface indicating spatially varying Li concentration. The appearance of these bands is remarkably

similar to those observed in the Li-FIB lithiated sample, suggesting that the behavior of the Li within the Sn sphere is comparable for both lithiation methods.

Summary

Direct Li-FIB lithiation of individual β -Sn micron-sized spheres was compared with electrochemical lithiation. We observed similar SEM contrast changes in the interior of the spheres, suggesting the lithiation method did not have an impact on Li diffusion. Both methods resulted in morphological changes to the surface of the sphere, with the electrochemical spheres experiencing more pronounced changes, most likely due in part to SEI formation and uncontrolled lithiation dose.

This study suggests that Li-FIB lithiation may have significant advantages for exploring ion transport in heterogeneous samples. Complications due to interfacial chemistry are absent, and the focused nature of the Li-FIB allows for precise Li^+ “titration” into specific nanoscale regions of a sample. Detailed knowledge of the local Li concentration will allow for studies of Sn changes without electrolyte-specific effects. Future work will couple local scale injection with accurate electronic measurements to quantify and analyze local electrochemical regions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Bruce PG, Scrosati B, Tarascon JM. *Angew Chem Int Ed*. 2008; 47:2930–2946.
2. Liu XH, Huang JY. *Energy Environ Sci*. 2011; 4:3844–3860.
3. Chao SC, Yen YC, Song YF, Chen YM, Wu HC, Wu NL. *Electrochem Commun*. 2010; 12:234–237.
4. Kalinin SV, Balke N. *Adv Mater*. 2010; 22:E193–E209. [PubMed: 20730814]
5. Knuffman B, Steele AV, Orloff J, McClelland JJ. *New J Phys*. 2011; 13:103035.
6. Knuffman B, Steele AV, McClelland JJ. *J Appl Phys*. 2013; 114:044303.
7. Twedt KA, Chen L, McClelland JJ. *Ultramicroscopy*. 2014; 142:24–31. [PubMed: 24751577]
8. Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.,.
9. All uncertainties in this paper are intended to be interpreted as one-standard-deviation, combined standard uncertainty.,.
10. Ziegler, J., Biersack, J., Ziegler, M. www.srim.org<http://www.SRIM.org>
11. Wen C, Huggins R. *J Electrochem Soc*. 1981; 128:1181–1187.

12. Fok, ECW., Madden, JDW. Energy Technology/Battery (general) - 223rd Ecs Meeting. Manthiram, A.Manivannan, A., Narayan, SR., editors. Vol. 53. Electrochemical Soc Inc; Pennington: 2013. p. 131-142.

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Figure 1.

Li-FIB Lithiation: (a) schematic of Li-FIB lithiation of Sn sphere; inset shows ion-beam-induced-secondary-electron image of lithiated sphere; (b) numerical simulation of the distribution of Li to Sn densities for every picocoulomb of deposited charge; (c) FESEM image of Li-FIB lithiated Sn sphere (left) and pristine Sn sphere (right); (d) FESEM image of Ga^+ FIB-cross-sectioned spheres shown in (c).

Figure 2. Electrochemical Lithiation: (a) schematic of electrochemical lithiation of Sn sphere; (b) cyclic voltammograms of Sn sphere on carbon sample and plain carbon; dashed line at 0.35 V indicates chosen lithiation voltage; (c) FESEM image of an electrochemically lithiated Sn sphere; (d) FESEM image of Ga⁺ FIB-cross-sectioned, electrochemically lithiated Sn sphere.