

Chemo-Mechanics of Energy Storage Materials (sponsors: DOE, NASA, NSF, Argonne National Laboratory, The State of Rhode Island)

Background and Scope: Here we examine a variety of questions in the context of the mechanics and electrochemistry of electrode materials in energy storage systems. The specific focus is on lithium ion battery materials, but the ideas and concepts are broadly applicable to other ion chemistries as well. Our approach is to study the underlying canonical phenomena by eliminating the geometric and material complexity as much as possible so that concrete and quantitative conclusions can be drawn, based on which predictive models can be developed. We employ carefully designed experiments, often involving design and construction of new instrumentation and infrastructure and new experimental techniques for quantitative characterization of the phenomena under consideration. Some examples of the projects include: characterization of the mechanical behavior of the solid electrolyte interphase (SEI) layers and their influence on surface roughening instabilities, real-time measurement of phase boundary kinetics in planar electrodes under one dimensional conditions, stress evolution and plasticity in electrode materials and chemo-mechanical coupling in electrode materials. Experimental measurements are used to develop analytical models of the materials or the phenomena in a suitable form for computational implementation. Representative examples of the projects pursued are summarized below.

Selected Significant Contributions

(i) Mechanical Behavior of Solid Electrolyte Interphase (SEI) and its Influence on Surface Roughening Instabilities: Mechanical integrity of the nanometer-scale solid electrolyte interphase (SEI) on anode surface plays an essential role in determining the life and performance of lithium-ion batteries. Fracture and continued formation of the SEI contribute to consumption of lithium, drying of electrolyte, increase in impedance, and growth of dendrites resulting in capacity fade and premature failure. Electrolyte additives such as fluoroethylene carbonate (FEC) have been known to improve performance, but the underlying reasons have been elusive. Despite its importance, reliable methods for mechanical characterization of SEI have been lacking. “Opinions” in the electrochemistry community regarding the elastic modulus of SEI have spanned from a few kPa to 100 GPa! Here, we developed an experimental technique that combines atomic force microscopy and a micro-membrane-bulge configuration, which for the first time, can accurately measure the stress-strain behavior of SEI, including the onset of inelastic response and fracture (Fig. 1). We demonstrated that the SEI elastic modulus can vary by an order of magnitude depending on the electrolyte composition. We also showed that the fracture strain of the SEI increases dramatically by the addition of fluoroethylene carbonate (FEC) electrolyte additive (Fig. 1d and 1e), which for the first time provides a mechanistic explanation for its beneficial role on the cell performance. The experimental technique and the results offer a platform for designing electrolyte compositions for optimizing the SEI mechanical behavior [1,2].

Formation of lithium dendrites is an important failure mechanism for realizing the promise of lithium metal anodes for the next generation of lithium ion batteries. Dendrites are often nucleated by surface roughening instabilities during electrodeposition of lithium during the charging cycle. There is some evidence that ionic liquid electrolytes retard dendrite growth, although the reasons behind have not been known. Our experiments (described above) revealed that the SEI formed with ionic liquid electrolytes have an order of magnitude higher modulus than that for organic solvent electrolytes. These observations motivated us to examine the role of the SEI stiffness on

surface roughening instabilities during lithium deposition. We carried out a stability analysis of surface being electrodeposited with respect to sinusoidal perturbations by accounting for the interfacial traction (between the SEI and the lithium metal surface), interface diffusion and inhomogeneous transport properties of the SEI [2]. The analysis provides design guidelines for the desired SEI mechanical properties in order to suppress roughening instabilities. To close the loop, we carried out an experimental investigation by measuring surface roughness evolution with different SEI stiffnesses, the results of which confirmed the theoretical predictions [2].

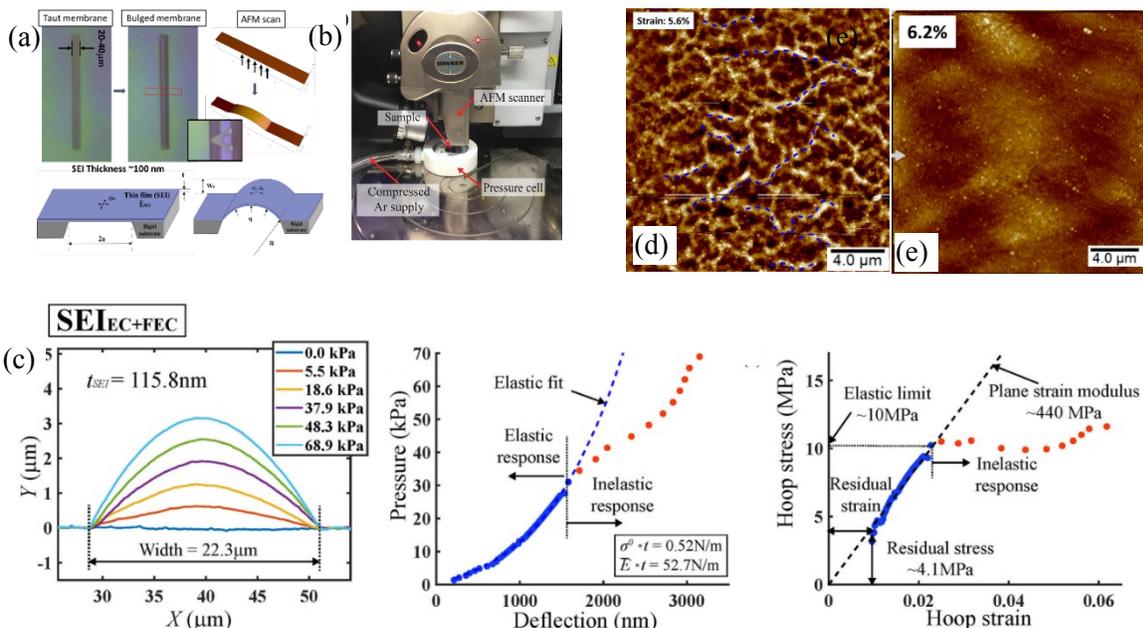


Figure 1. (a) A schematic illustration of the micro-membrane-bulge configuration to measure the mechanical properties. The PDMS membrane dimensions are $\sim 20\mu\text{m}$ width, $400\mu\text{m}$ length and $\sim 200\text{ nm}$ thickness. The SEI on top of the PDMS has a thickness of $\sim 100\text{ nm}$. (b) Experimental setup in which a specially designed electrochemical cell is integrated with an AFM. (c) Representative experimental results for membrane bulge profile, pressure vs. deflection relation and the stress-strain curve. Note that the SEI behaves like an elastic-plastic material. (d) Extensive cracking of SEI at a strain 5.6%. (e) However, when FEC additive is added, there is a dramatic increase in resistance to fracture. No cracking is seen at a strain of 6.2%.

(ii) Mechanics and Kinetics of Moving Phase Boundaries in Electrode Materials through Picosecond Ultrasonics: Phase transformations are ubiquitous in electrode materials during charging/discharging cycles. These are typically diffusive phase transformations with moving phase boundaries. Such boundaries are often associated with large discontinuities in stress, composition, crystal structure and compositional strain; and they play an important role in determining not only the electrochemical performance but also the mechanical degradation that can accrue during cycling. Predictive models of the mechanics, thermodynamics and kinetics of moving phase boundaries in electrode materials are essential in accurate computational modeling of the lithiation/delithiation cycles and the corresponding mechanical and electrochemical degradation that accrues. Such models must be based on definitive experimental measurements that are as direct as possible, requiring minimal assumptions in analyzing the data. Prior experimental investigations such as *in situ* TEM observations of nano-wires do not yield usable quantitative measurements; experiments involving planar single crystal specimens do not permit direct observation of the position of the phase boundary inside the specimen, hence require

assumptions in order to extract the relevant kinetic parameters. Ideally, what one needs is an experimental technique that combines the advantages of both approaches, i.e., the precise control of the electrochemical parameters and 1-D phase boundary propagation associated with planar single crystal specimens and the ability to physically visualize the progression of the phase boundary inside the specimen. Here, we developed an experimental technique that accomplishes these objectives by employing picosecond ultrasonics to accurately measure the velocity of 1-D moving phase boundaries in electrode materials under well controlled lithium flux and potential [3,4].

Picosecond ultrasonics is a pump-probe method in which a train of femtosecond laser pulses, i.e., the pump pulses, generates a periodic sequence of ultrasonic waves in the specimen at a high frequency (80MHz in our setup). Each wave travels through the thickness of the specimen and is partly reflected from the phase boundary and from the electrode/electrolyte interphase. The arrival of the reflected pulses is detected by an identical sequence of probe laser pulses which are progressively time delayed with respect to the pump pulses by gradually increasing their travel time in air through a set of moving retro-reflectors. When the reflected pulses arrive, since the dielectric constant of materials is a function of strain, the optical reflectivity of the surface changes, which modifies the intensity of the reflected probe pulse. By modulating the probe pulse sequence at a lower frequency of 1 MHz and by means of a lock-in amplifier that homes in on this frequency, the change in the reflected probe pulse intensity is detected accurately. The setup is shown in Fig.

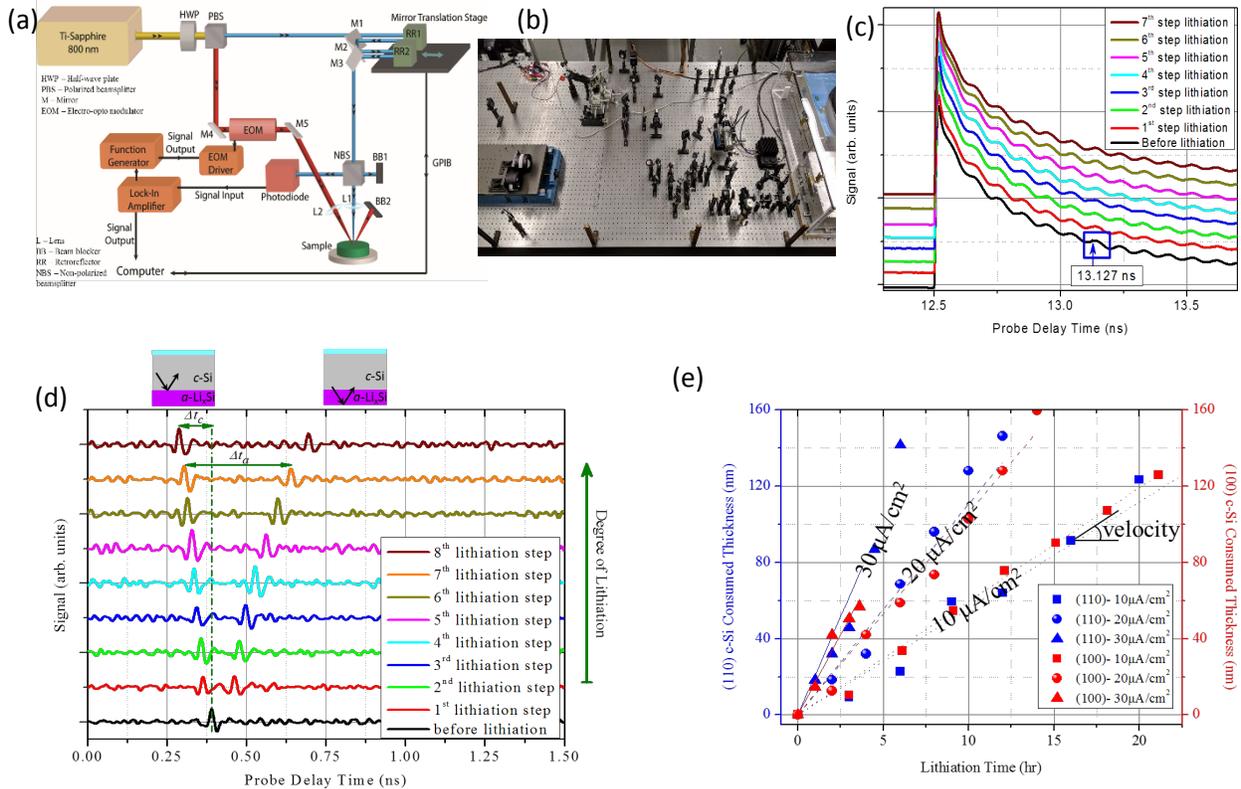


Figure 2. (a) The schematic experimental setup for the picosecond ultrasonics setup. (b) The experimental setup. (c) Typical measurements of the reflected probe beam intensity as a function of the probe delay time, showing Brillouin oscillations. (d) Reflected ultrasonic pulses as a function of the lithiation time. The two reflections correspond to those from the phase boundary and from the free surface. Note the increase in the time delay between the two reflected pulses as the thickness of the new phase grows. (e) Representative data of phase boundary displacement with lithiation time, from which phase boundary velocity is inferred.

2a and 2b. Fig. 2c shows the Brillouin oscillations in the reflected probe beam intensity due to the moving ultrasonic pulse in the adhesive layer that bonds the specimen to the glass substrate. Fig. 2d shows the reflected pump pulses as a function of the probe delay time for different lithiation times. By choosing phase transformation in silicon during initial lithiation as the model system, a systematic investigation is carried out to measure the phase boundary velocity for different crystallographic orientations (Fig. 2e). For the same driving force, it was found that the phase boundary propagates on the (110) planes at about 3 times the velocity on the (100) planes. These measurements provide direct measurements of the kinetic constants that determine the relative ease with which phase transformation occurs normal to the different crystallographic planes [4].

In order to extract the relevant kinetic parameters, a Cahn-Hilliard type phase field model is developed to solve the moving phase boundary problem. The model considers the diffusivity of lithium, stress, plastic deformation of lithiated silicon and an interface mobility that depends on the local lithium concentration [4]. Together, the experimental and modeling results provide a robust methodology for modeling phase transformations in electrode materials of interest in any ion electrochemistry.

(iii) Stress evolution and mechanical deformation in electrode materials during electrochemical cycling: Electrode materials undergo volumetric strain due to insertion or removal of lithium during electrochemical cycling. The resulting stresses lead to a variety of mechanical degradation mechanisms, which collectively contribute to loss of performance of lithium ion batteries (e.g. capacity fade with continued charge/discharge cycling). We have developed an experimental technique to measure stress evolution in electrode materials in real time during electrochemical cycling and applied it to a variety of electrode materials (amorphous silicon [5, 6, 8], crystalline silicon [8], tin [9], LiMn_2O_4 [10], composite electrodes [11, 12]), each of which has distinct canonical response features. Some of the useful insights that emerged from this work include: (a) electrode materials undergo significant plastic deformation, even in nominally brittle materials like silicon; (b) stress makes non-trivial contribution to the chemical potential and stress gradients provide significant driving force for diffusion of lithium in electrode materials, which must be taken into consideration; (c) the mechanical properties such as elastic modulus and the yield strength of the electrode materials is a strong function of lithium concentration [15]. Motivated by these experimental investigations, Bower and **Guduru** collaborated to develop an analytical framework to model the coupled mechanics-electrochemistry in these materials, which integrates stress, elastic and plastic deformations, diffusion and electrochemical reactions into a unified thermodynamic framework [13, 14]. The results and insights from this body of work have been widely used in the field for further experimental developments and modeling efforts (The first experimental paper [5] on silicon has been cited over 410 times and continues to be well-cited. The first modeling paper [13] has been cited nearly 270 times).

(iv) Stress-potential coupling in electrode materials:

A useful insight that emerges from the recognition of the non-trivial contribution of stress to the chemical potential in the electrode materials is that the electric potential of the electrochemical cell depends on the state of stress in the electrodes. In other words, mechanics and electrochemistry are inherently coupled through solution thermodynamics. Such a coupling becomes significant when the materials can sustain a large stress ($\sim 1\text{GPa}$) and when the compositional strain due to the solute (e.g. lithium) is large. Both of these conditions are met in anodes like silicon and cathodes like LiMn_2O_4 and LiCoO_2 . This coupling was first recognized

and expounded by **Guduru** and coworkers in a paper [16], which also presented an experimental technique to measure it. The experimental method relied on a simple recognition that when a thin film silicon electrode is in a state of plastic yield during lithiation, imposing an incremental reduction in its lithium concentration results in a corresponding change in the compositional strain, which is also an elastic unloading strain; hence it results in a large change in the state of stress. A reasonably good agreement was found between the theory and experiment. To address the stress-potential coupling more carefully, **Guduru** and his student **Chon** [7] developed an alternative experimental technique in which thin film specimens could be subjected to a controlled flexural strains that would result in elastic unloading of the lithiated silicon thin films while leaving the lithium concentration unchanged. These experimental results yielded more refined measurements. A revised theoretical effort is currently underway in which lithiation is treated as a sequence of phase transformations, which offers a pathway for good agreement between the experimental measurements and theory predictions (The initial paper on the stress-potential coupling in electrode materials [16] has been cited nearly 225 times). The main significance of this work is to highlight the necessity of considering the stress-electrochemistry coupling in designing battery electrodes and evaluating the stress effects in the electrochemical performance and its degradation in lithium ion batteries.

V. Relevant Publications:

1. Yoon, I., Jurng, S., Abraham, D.P., Lucht, B.L., Guduru, P.R. An Investigation of the Mechanical Properties and Fracture of the Solid Electrolyte Interphase in Lithium Ion Batteries. Under review at *Energy and Environmental Science*, 2019.
2. Yoon, I., Ph.D. Thesis, Brown University, June 2019.
3. Rezasadeh-Kalehbasti, S., Liu, L.W., Maris, H.J., Guduru, P.R., In *Situ* Measurement of Phase Boundary Kinetics during Initial Lithiation of Crystalline Silicon through Picosecond Ultrasonics. *Experimental Mechanics*. In press. <https://doi.org/10.1007/s11340-018-00460-5>. 2018.
4. Rezasadeh-Kalehbasti, S., An investigation of the phase transformation kinetics in silicon during initial lithiation: experiments and modeling. Ph.D. Thesis, June 2019.
5. V.A. Sethuraman, M.J. Chon, M. Shimshak, V. Srinivasan, P.R. Guduru, "In Situ Measurements of Stress Evolution in Silicon Thin Films during Electrochemical Lithiation and Delithiation", *J. Power Sources* 195, 5062-5066, 2010.
6. G.Bucci, S.P.V.Nadimpalli, V.A.Sethuraman, A.F.Bower, P.R.Guduru. "Measurement and modeling of the mechanical and electrochemical response of amorphous Si thin film electrodes during cyclic lithiation." *Journal of the Mechanics and Physics of Solids* 62: 276-294, 2014.
7. Chon, M.J., Ph.D. Thesis, Brown University, 2016.
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9. Chen, C-H., Chason, E., Guduru, P.R. Numerical solution of moving phase boundary and diffusion- induced stress of Sn anode in the Lithium ion battery. *Journal of the Electrochemical Society* 164: E3661-E3670. 2017.
10. Sheth, J., Karan, N.K. Abraham, D., Nguyen, C.C., Lucht, B.L. Sheldon, B.W., Guduru, P.R., In situ stress evolution in $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ thin films during electrochemical cycling in

- Li-ion cells. *Journal of the Electrochemical Society* 163: A2524-A2530, 2016.
11. Nadimpalli, S.P.V., Sethuraman, V.A., Abraham, D.P., Bower, A.F., Guduru, P.R. Stress Evolution in Lithium-Ion Composite Electrodes during Electrochemical Cycling and Resulting Internal Pressures on the Cell Casing. *Journal of the Electrochemical Society*. 162: A2656-A2663, 2015.
 12. V.Sethuraman, A. Nguyen, M.Chon, S. Nadimpalli, H.Wang, D.P.Abraham, A.F.Bower, V.Shenoy, P.R.Guduru. "Stress Evolution in Composite Silicon Electrodes during Lithiation/Delithiation." *Journal of the Electrochemical Society* 160: A739-A746 (2013).
 13. A.F. Bower, P.R. Guduru, V.A. Sethuraman, "A Finite Strain Model of Stress, Diffusion, Plastic Flow and Electrochemical Reactions in a Lithium-ion Half-cell", *Journal of the Mechanics and Physics of Solids* 59: 804-828 (2011).
 14. S.P.V.Nadimpalli, V.A.Sethuraman, G. Bucci, V. Srinivasan, A.F.Bower, P.R. Guduru. "On plastic deformation and fracture in Si films during electrochemical lithiation/delithiation cycling." *Journal of the Electrochemical Society*, DOI: 10.1149/2.098310jes, 2013.
 15. V.A. Sethuraman, M. Shimshak, M.J. Chon, N. Van Winkle, P.R. Guduru, "In Situ Measurement of Biaxial Modulus of Si Anode for Li-ion Batteries," *Electrochemistry Communications*, 12:1614- 1617(2010).
 16. V.A. Sethuraman, V. Srinivasan, A.F. Bower, P.R. Guduru, In situ Measurements of Stress-potential Coupling in Lithiated Silicon." *Journal of the Electrochemical Society* 157: A1253 (2010).