Measurement and modeling of the mechanical and electrochemical response of amorphous *Si* thin film electrodes during cyclic lithiation

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Mechanical-Electrochemical response of *Si* thin film anodes

Potential impact

> **Silicon high capacity** $(3579 Ah/kg)$ can increase the theoretical energy density and specific energy of the cell of 25-30% respect to existing graphite-based lithium-ion cells

Open issues

> **Large deformations** (a volumetric strain of about 270%) generate plastic flow and substantial stresses in the material, leading to mechanical failure after a few charge-discharge cycles
>
> First-lithiation **capacity loss** due to solid-electrolyte interface formation and **side reactions**, continuously occurring during cycling, have been detrimental to the commercialization of the system

Our contribution

> **To aid the development of failure tolerant architectures**, we develop a continuum model that predicts stress, plastic flow, diffusion and the electrochemical response of *Si* during lithiation

Test and Calibration

> **In situ measurements** from **ad hoc experiments** are used to calibrate and verify the predictive capability of the model

State of art

An extensive literature exists on the electrochemical and mechanical response of *Si* anodes and variety of designs have been explored, including

- thin films
- single particles
- nanowires
- patterned electrodes
- composites

Panasonic Corporation announced commercialization of high-capacity lithium-ion batteries with silicon-alloy anode

Accurate predictions require reliable values for *material parameters*, in particular:

- **mechanical properties** of *Si* as functions of *Li* concentration
- **transport properties** of *Li* through *Si*
- parameters related to the **solution chemistry** of *Li* in *Si* (i.e. the concentration dependent activity coefficient)
- parameters characterizing the **electrochemical** main and side **reactions**

Mechanical parameters in constitutive laws of lithiated *Si*

Literature data

Continuum models, following results form experimental measurements [Sethuraman et al., 2010] and first principle calculations [Shenoy & Johary, 2010], typically assume that Young's modulus decrease linearly with *Li* concentration [Deshpande et al., 2010] [Bower et al., 2010]

In [Shenoy & Johary, 2010], the authors attribute the elastic softening to the reduced stiffness of *Li-Si* bonds in comparison to *Si-Si* bonds.

Plastic flow has been observed [Sethuraman & Guduru, 2010] when the stress reaches approximately $1GPa$

Our contribution

Through a systematic combination of numerical simulations and experimental measurements of the resulting cycle of stress in *a-Si* film electrodes, we determined the parameters characterizing the variation of elastic modulus with concentration, together with the parameters that govern the rate dependent plastic flow in the film.

Lithium transport and kinetics, modeling and measurements of PITT experiments

Literature data

Power density of *Li*-ion cells is strictly related to the **diffusion coefficient** for *Li* transport through electrode materials. The range of values available in literature, from experiments [Xiao et al., 2012] and atomistic scale calculations [Tritsaris et al., 2012], span over several orders of magnitude.

Parameters characterizing solution thermodynamics and *Li* insertion reactions can be extracted from the potential vs. composition curve available in literature from experimental measurements [Hatchard et al., 2004] and ab-initio DFT calculations [Chevrier & Dahn, 2009].

Our contribution

Lithium diffusivity and reaction rate constant were determined by fitting full numerical simulation of PITT tests to the experimental data.
Our approach respect to the classical model [Weppner & Huggins, 1977] accounts rigorously for **departures from the ideal diffusion model**

Governing Equations

Finite element model in 1D spatial set

$$\rho_{Si}\frac{dc}{dt} = -\frac{\partial j_X}{\partial X} \qquad j = -\frac{D}{RT}\rho_{Si}\,c\frac{\partial \mu}{\partial x}$$

$$\mu = \mu(c,\sigma)$$

Diffusion equation

Chemical potential eq.

Boundary conditions in galvanostatic tests

$$j_X(H) = \frac{I_R + I_S}{F} \qquad j_X(0) = 0$$

Cell voltage computed through Newton's procedure applied to the Butler-Volmer eq

Boundary conditions in potentiastatic tests

$$j_X(H) = \frac{I\left(V - U_0(c,\sigma)\right)}{F} \qquad j_X(0) = 0$$

Cell voltage V assigned

Mechanical Model of a half-cell with a thin-film *Si* anode

Li insertion causes the stress-free Si network to increase its volume by a fraction $dV/dV_0 = 1 + \beta c$ proportional to *Li* molar concentration c, with a corresponding true strain $\epsilon_{xx}^c = \epsilon_{yy}^c = \epsilon_{zz}^c = \log(1 + \beta c)/3$.

Since the substrate prevents the film from expanding in its own plane, the strains are related by the compatibility conditions

$$\frac{1}{3} \log(1 + \beta c) - 2 \log(\lambda^p) + \epsilon_{xx}^e = \log \left(1 + \frac{\partial u}{\partial X} \right)$$

$$\frac{1}{3} \log(1 + \beta c) + \log(\lambda^p) + \epsilon_{yy}^e = 0$$

$$\frac{1}{3} \log(1 + \beta c) + \log(\lambda^p) + \epsilon_{zz}^e = 0$$
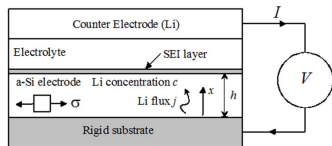
Assuming a plane stress condition, the Cauchy stress $\sigma(x) = \sigma_{yy} = \sigma_{zz}$ is related to (small) elastic strains by a concentration dependent biaxial modulus

$$\sigma = M(c)\epsilon_{yy}^e$$

Experimental measurements [Sethuraman et al. 2010] suggest that

1. A suitable constitutive law for the biaxial modulus can be a logarithmic function of the kind

$$M(c) = M_0 + M_1 \log\left(1 + \frac{c}{c_0}\right)$$
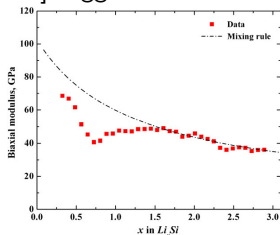
2. The plastic deformation can be characterized by a viscoplastic constitutive equation relating the plastic stretch rate to stress

$$\dot{\epsilon}^p_{yy} = \dot{\epsilon}^p_{zz} = \frac{\dot{\lambda}^p}{\lambda^p} = \frac{\dot{\epsilon}_0}{2}\left(\frac{|\sigma|}{\sigma_0} - 1\right)^m \frac{\sigma}{|\sigma|} \qquad \text{if} \quad |\sigma| \geq \sigma_0$$

$$\dot{\epsilon}^p_{yy} = \dot{\epsilon}^p_{zz} = 0 \qquad\qquad\qquad\qquad \text{if} \quad |\sigma| < \sigma_0$$

where σ_0 is a concentration dependent yield stress; $\dot{\epsilon}_0$ is a characteristic strain rate, and m a stress exponent

3. The yield stress constitutive law is assumed to be a linear function of lithium concentration

$$\sigma_0(c) = s_0 + s_1(c - c_0)$$

Solution thermodynamics and *Li* transport

Diffusion of *Li* through the *Si* electrode is driven by a chemical potential

$$\mu = \mu^\theta + RT \ln \left(\frac{c\gamma}{c_{max} - c} \right) - \frac{\sigma^2}{\rho_{Si}} \frac{\partial}{\partial c} \left(\frac{1}{M} \right) - \frac{2\beta\sigma}{3(1 + \beta c)\rho_{Si}}$$

It accounts for higher order interactions in non infinite dilute solutions (through the activity coefficient γ) and for the mechanical contribution, whose derivation is described by several authors [Larché & Cahn, 1973] [Li, 1978] [Bower et al. 2011].

As proposed in literature [Verbrugge et al. 1996], we assume the excess of free energy expressed as a series expansion in $c/cmax$ and we adopt the following form for the activity coefficient

$$RT \ln \gamma = \sum_{n=2}^{N} \Omega_n n \left(\frac{c}{c_{max}} \right)^{n-1}$$

where Ω_n are self-interaction coefficient, c_{max} the maximum number of hosting sites available.

The open circuit potential is expressed by $U_0(c, \sigma) = -\mu(c, \sigma)/F$

Solution thermodynamics and *Li* transport

Series expansion coefficients Ω_n are calibrated respect the to potential-v-capacity curves available in literature [Baggetto et al., 2008], [Chevrier & Dahn, 2009].

$$U_0 = U_0^\theta - \frac{RT}{F} \ln \left(\frac{c\gamma}{c_{max} - c} \right) - \sum_{n=2}^{N} \Omega_n n \left(\frac{c}{c_{max}} \right)^{n-1} +$$

$$\frac{\sigma^2}{F\rho_{Si}} \frac{\partial}{\partial c} \left(\frac{1}{M} \right) + \frac{2\beta\sigma}{3F(1 + \beta c)\rho_{Si}}$$
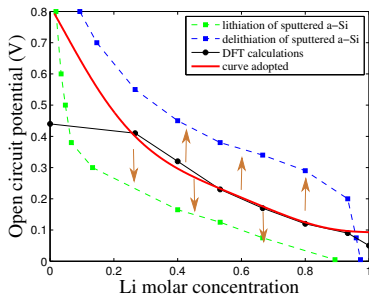
In [Sethruramna et al., 2010] the magnitude of the **stress-potential coupling** in lithiated silicon is estimated to be $62mV/GPa$ in thin-film geometry

- $\sigma = -1GPa \rightarrow -62mV$
- $\sigma = 1GPa \rightarrow 62mV$

Electrochemical reactions

At discharging, an electrochemical reaction takes place at the Si/electrolyte interface, where Li ions in the electrolyte combine with electrons and are inserted into host sites S in the Si network

$$Li^+ + e^- + S \rightleftarrows \left[Li^\delta - S^{-\delta} \right] \tag{1}$$
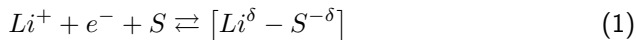
The Butler-Volmer equation relates the current density I_R of the Faradaic reaction to the over-potential η at the solid/electrolyte interface as follows

$$I_R = i_0 \left[\exp\left(\frac{\alpha F \eta}{RT} \right) - \exp\left(\frac{(1-\alpha)F\eta}{RT} \right) \right] \tag{2}$$

where the exchange current density may be expressed

$$i_0 = F \left[k_c \rho^+ \left(1 - \frac{c}{c_{max}} \right) \right]^\alpha \left(k_a \frac{c}{c_{max}} \right)^{(1-\alpha)}$$

k_c and k_a are the concentration dependent cathodic and anodic rate constants; ρ^+ is the molar density of Li^+ per unit of reference volume in electrolyte.

$$(\rho_{Li+} k_c)^\alpha \, k_a^{1-\alpha} = k_0 + k_1 \sin\left(\frac{\pi}{2} \frac{c}{c_{max}} \right)$$

Modeling of the capacity loss due to SEI layer formation

Side reactions occur at the negative electrode/electrolyte interface whenever the electrode potential falls below the value $U_{0,SEI}$ necessary to reduce the electrolyte.

Standard SEI models predict that the SEI thickness and total capacity loss vary with time as $t^{1/2}$ and give a good fit to measurements over a long time period [Pinson & Bazant, 2013] but do not fit our experimental data for a small number of cycles.
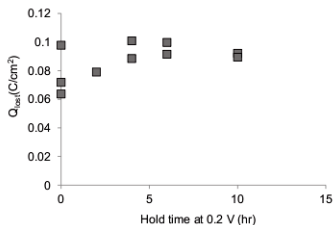

Figure: [Nadimpalli et al., 2012]

We have therefore used a simple phenomenological relation to fit our data

$$I_S = -i_{0,SEI} \left(1 - \frac{Q_{loss}}{Q_{SEI}} \right) \exp \left(-\frac{2\alpha_{SEI}F}{RT} \left(V - U_{0,SEI} \right) \right); \quad Q_{loss} = -\int I_S dt$$

Discussion of the results

Experiment description Half cell made with sputtered amorphous *Si* thin film electrodes and *Li* metal counter-electrode have been subjected to cyclic galvanostatic tests

> lower cut-off voltage of $0.05V$ vs. $Li/Li+$ to prevent crystallization
>
> upper cut-off voltage of $0.6V$ vs. $Li/Li+$ to prevent film cracking

Output of interest

- Cell Voltage
- Mean stress over the film thickness

Procedure

- **Cell 151** experimental results adopted for calibrating the model
- **Cell 200** used for verifying the predictive capability of the model

Numerical results Cell 151

Amorphous Si film of $100nm$ thickness and $18.7 \cdot 10^{-4} m^2$ surface area. Initial residual stress of $-0.1\ GPa$.
It undergoes cycles of alternate current of $100, 200, 300, \mu A$.
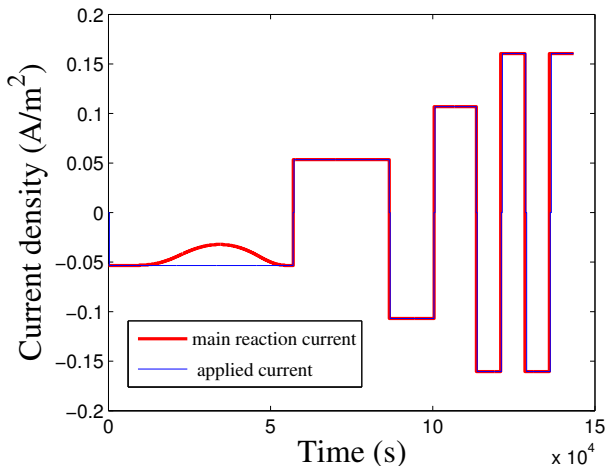
Numerical results Cell 151
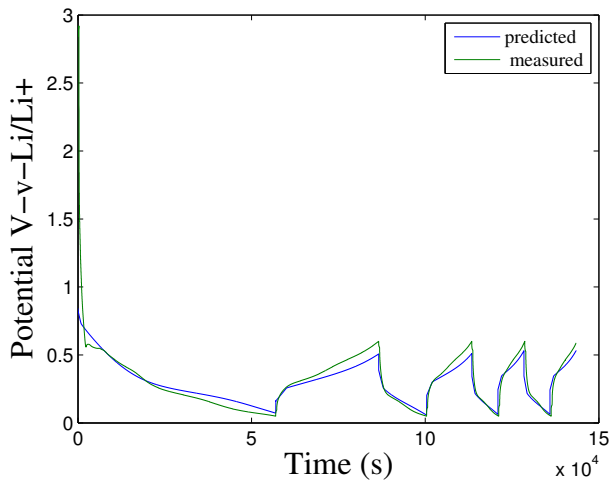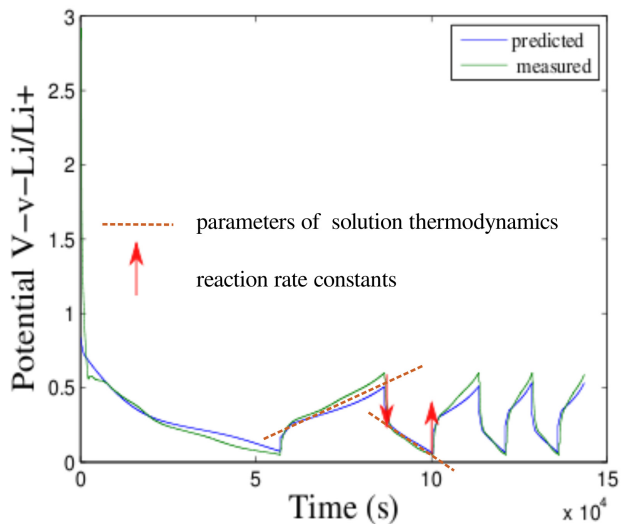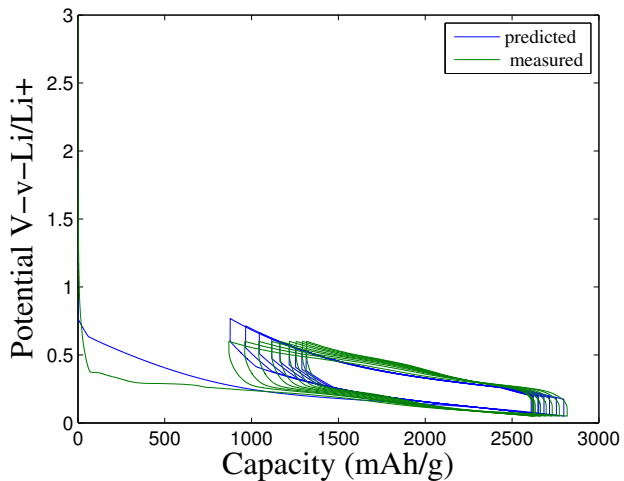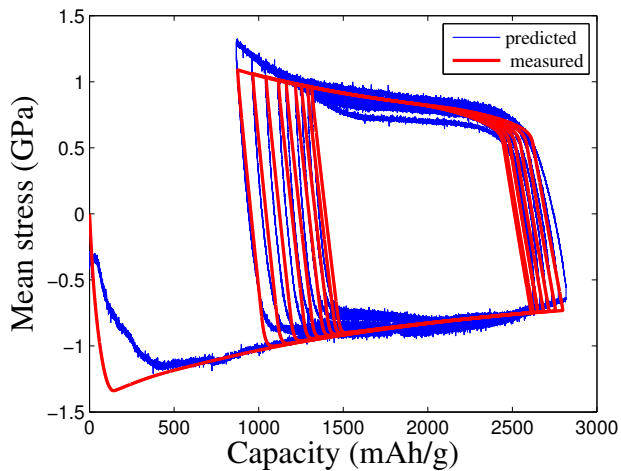
Numerical results Cell 151
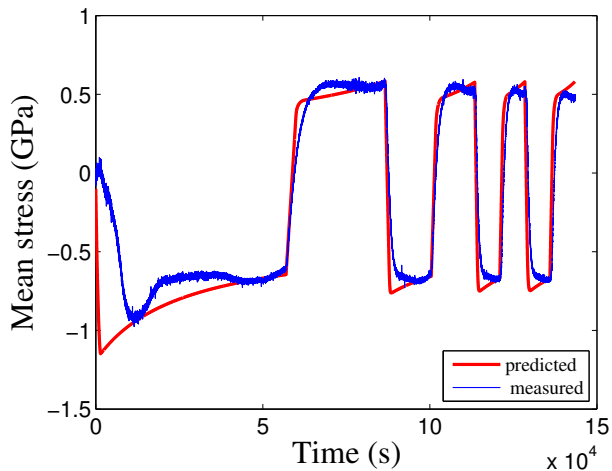
Numerical results Cell 200

Amorphous Si film of $123nm$ thickness and $18.7 \cdot 10^{-4}m^2$ surface area.
Initial residual stress of $-0.36\,GPa$.
It undergoes cycles of alternate current of $175\,\mu A$.
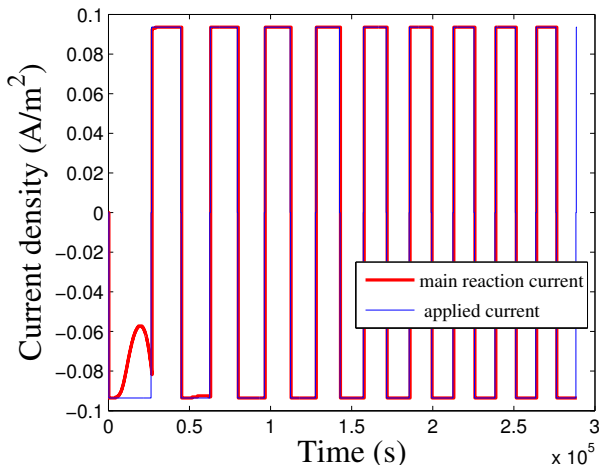
Numerical results Cell 200
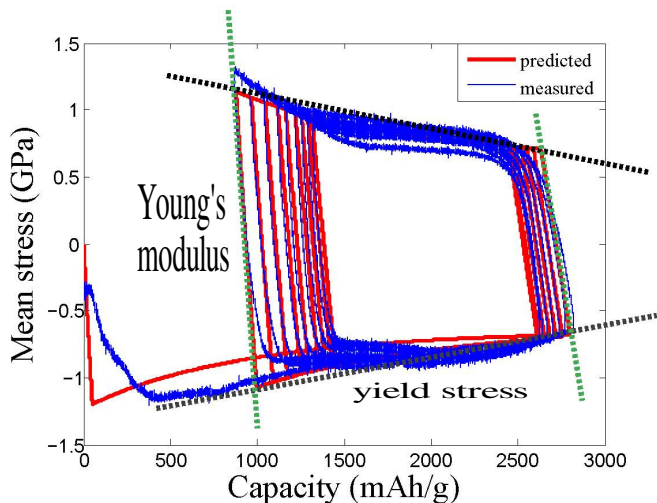
PITT experiment

Experiment description

- Half cell made of $104nm$ *a-Si* thin film electrode against a lithium metal reference and counter electrode
- Lithium insertion was carried out galvanostatically at $2.5\mu A/cm^2$ until the electrode potential reached $0.4V$ vs. *Li/Li+*
- Incremental step changes in potential of $50mV$ are applied until $0.05V$ vs. *Li/Li+*. Each potentiostatic step was carried out until the current decayed to less than $0.25\mu A/cm^2$
- Identical potentiostatic steps in the delithiation direction followed till $1.2V$ vs. *Li/Li+*
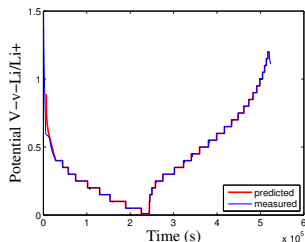
Output of interest Transient evolution of stress and electric current density

PITT experiment

Standard PITT measurements rely on the following hypotheses:

- transport in the electrode obeys Fick's law
- *Li* insertion reaction occurs sufficiently rapidly to ensure that transport in the electrode is the rate limiting process

which are not satisfied by our system.

For small perturbations in concentration δc relative to an initial concentration, the governing equations of diffusion (combined and linearized) yield

$$\frac{\partial \delta c}{\partial t} = \tilde{D} \frac{\partial^2 \delta c}{\partial x^2} \qquad \tilde{D} = D \frac{c}{RT} \left[\frac{\partial \mu}{\partial c} \bigg|_{\sigma} + \frac{\partial \mu}{\partial \sigma} \bigg|_{c} \frac{\partial \sigma}{\partial c} \right]$$

where the apparent diffusion coefficient $\tilde{D}$, extracted for PITT measurements, is history dependent.

The effects of stress can be minimized by ensuring that the voltage step δV tends to deform the electrode plastically.

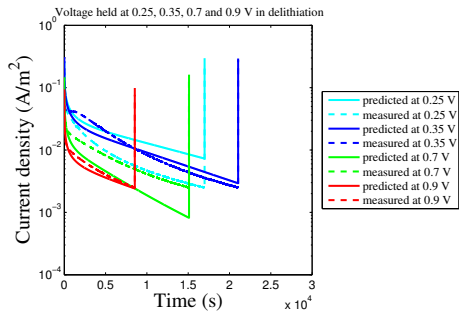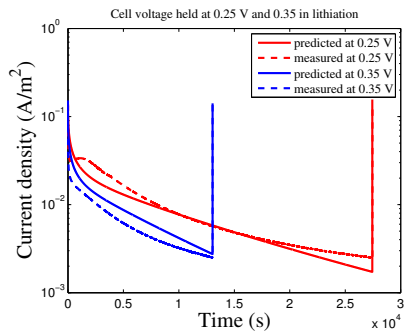This is the reason to prefer PITT to GITT experiments.

PITT experiment

Comparison of transient electric current density measured and predicted by assuming in the model $D = 10^{-19} m^2 s^{-1}$
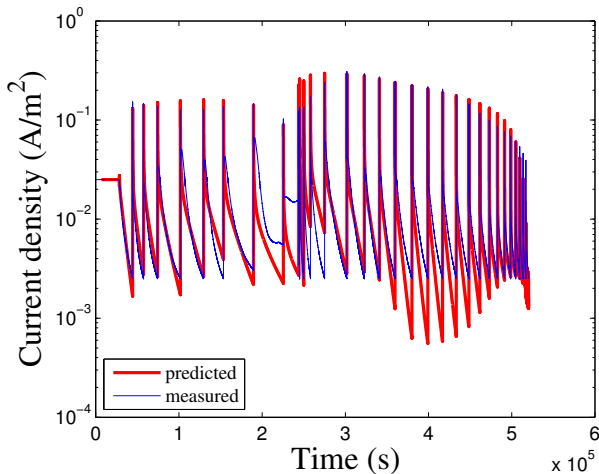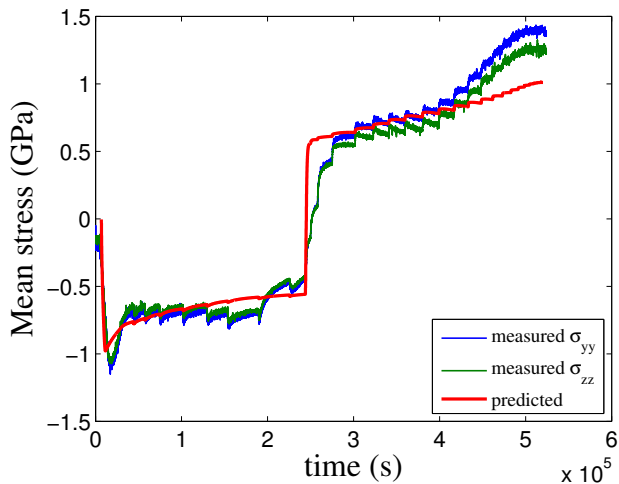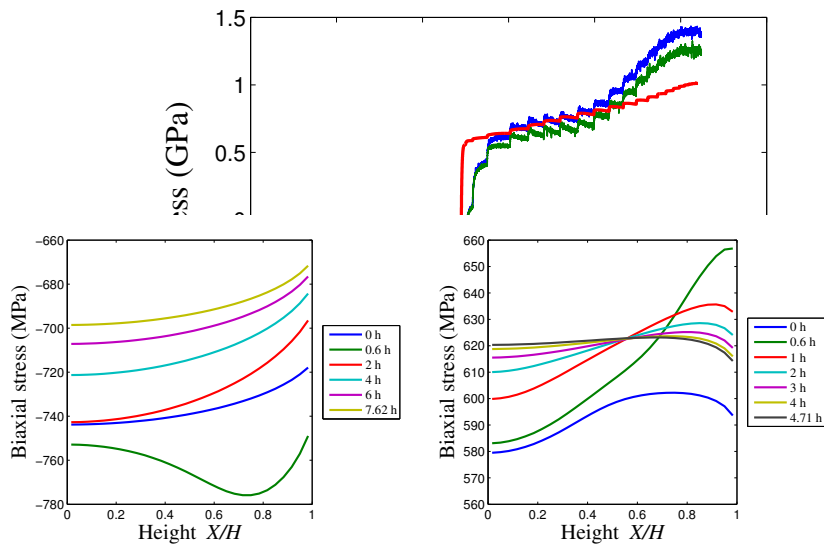
PITT experiment

PITT experiment

video

PITT experiment

PITT experiment

Conclusions and Future work

1. Combination of **experiments and modeling** to determine mechanical and electrochemical response of amorphous Si films under cyclic Li insertion.

2. The variation of **elastic biaxial modulus** was fit using a logarithmic variation with *Li* concentration. The Young's modulus was found to vary from $80\,GPa$ in the un-lithiated electrode to $36.8\,GPa$ at full charge capacity. These values are in good agreement with previously reported data [Shenoy & Johari, 2010].

3. The inelastic response is described by a rate-dependent **elastic-viscoplastic** constitutive model, with a linear concentration dependent **flow stress** varying from $0.60 \pm 0.04\,GPa$ at zero concentration to $1.05 \pm 0.04\,GPa$ at full capacity, and a stress exponent of 50.

4. Secondary effects, such as capacity loss in SEI formation and $Li - Li$ interactions, are taken into account. The activity coefficient of the *Li-Si* solid solution was characterized by a series expansion in c/c_{max} and it was calibrated to match the potential vs. capacity curves available in literature.

Conclusions and Future work

1. PITT measurements, in combination with numerical simulations, were used to determine the **diffusion coefficient** for *Li in a-Si*. Experiments were best fit with a diffusion coefficient $10^{-15} cm^2 s^{-1}$, which is comparable to, but on the low end of the range $10^{-16} - 10^{-10} cm^2 s^{-1}$ measured in previous experiments [Ding et al., 2009] [Ruffo et al., 2009] [Xiao et al., 2012] [Hüger et al., 2013].

2. The experiments were also used to estimate the variation of **exchange-current density** in the *Li* insertion reaction with concentration. It was found to be $i_0 \sim O(10\,A\,cm^{-2})$, comparable to the one obtained in [Chandrasekaran et al., 2010], while the values reported in literature for *Li-Si* battery systems [Bernardi & Newman, 1987] [Baggetto et al., 2009] vary by several orders of magnitude.

3. The 1D formulation, developed for the thin film anode case, is being extended to 3D composite configurations, where the active material is in the form of particles connected by a binder.