

General Motivation

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 graphite-based lithium-ion cells

Open issues

- Mechanical degradation due to large volumetric expansion (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
- Capacity loss in solid-electrolyte interface formation

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 a Si anode during lithiation

Test and Calibration

- In situ measurements [Sethuraman et al., 2010] from ad hoc experiments are used to calibrate and verify the predictive capability of the model

Material parameters under investigation

- 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 electrochemical main and side reactions

Governing Equations

Finite element model in 1D spatial set

$$\rho_{Si} \frac{dc}{dt} = -\frac{\partial j_X}{\partial x} \quad j = -\frac{D}{RT} \rho_{Si} c \frac{\partial \mu}{\partial x} \quad \text{Diffusion equation}$$

$$\mu = \mu(c, \sigma) \quad \text{Chemical potential}$$

Boundary conditions in galvanostatic tests

$$j_X(H) = \frac{I_R + I_S}{F} \quad j_X(0) = 0 \quad \text{Cell voltage and stress computed}$$

Boundary conditions in potentiostatic tests

$$j_X(H) = \frac{I(V - U_0(c, \sigma))}{F} \quad j_X(0) = 0 \quad \text{Current density and stress computed}$$

Thermodynamics of a lithium-ion half cell

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

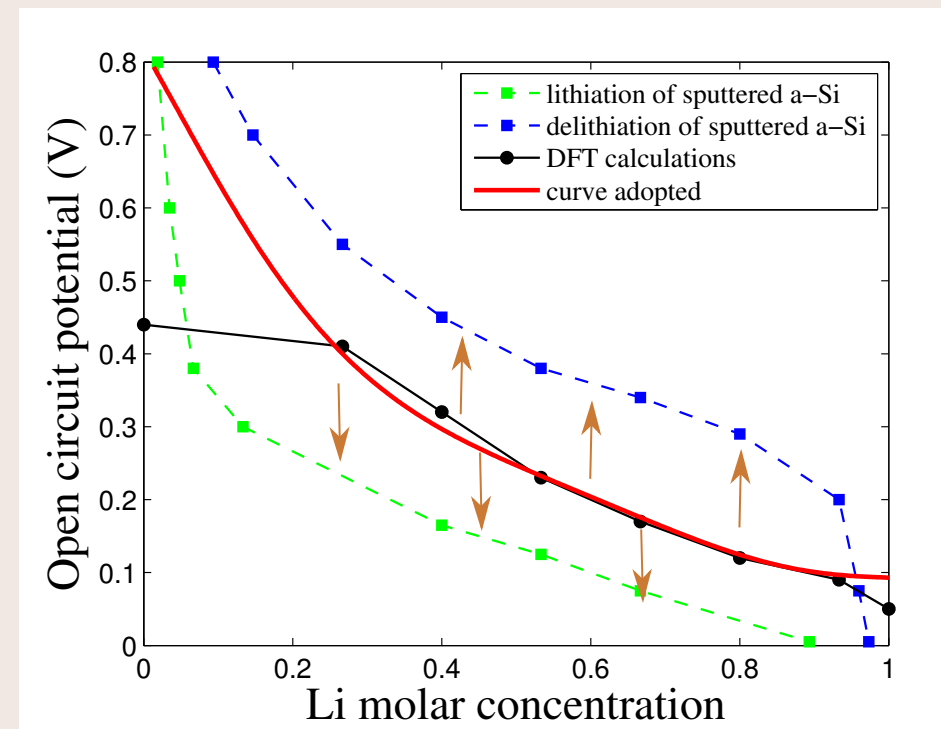
$$\mu = \mu^\theta + RT \ln \left(\frac{c\gamma}{c_{max} - c} \right) - \frac{\sigma^2}{\rho_{Si}} \frac{\partial}{\partial c} \left(\frac{1}{M} \right) - \frac{2\beta\sigma}{3(1+\beta)c\rho_{Si}}$$

It accounts for higher order interactions in non infinite dilute solutions (through the activity coefficient γ) and for the mechanical contribution.

As proposed in literature [Verbrugge et al. 1996], we assume the excess of free energy expressed as a series expansion in c/c_{max} . The open circuit potential can be written as

$$U_0 = U_0^\theta + \underbrace{\frac{RT}{F} \ln \left(\frac{c\gamma}{c_{max} - c} \right)}_{\text{ideal solution thermodynamics}} + \underbrace{\sum_{n=2}^N \Omega_n n \left(\frac{c}{c_{max}} \right)^{n-1}}_{\text{Li-Li interactions}} + \underbrace{\frac{\sigma^2}{F\rho_{Si}} \frac{\partial}{\partial c} \left(\frac{1}{M} \right) + \frac{2\beta\sigma}{3F(1+\beta)c\rho_{Si}}}_{\text{stress-potential coupling}}$$

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



The chemical effect on U_0 is represented by the red curve on the left. The hysteresis (orange arrows) is obtained through the stress-potential coupling.

The magnitude of the stress-potential coupling in lithiated silicon is estimated to be 62 mV/GPa in thin-film geometry [Sethuraman et al., 2010]

Electrochemical reactions

The total current density through the external circuit is divided into two contributions $I = I_R + I_S$

The current supplied to the desired Faradaic reaction is calculated as follows

$$I_R = i_0 \left[\exp \left(\frac{\alpha F \eta}{RT} \right) - \exp \left(-\frac{(1-\alpha) F \eta}{RT} \right) \right] \quad i_0 = F \left[k_c \rho_{Li+} \left(1 - \frac{c}{c_{max}} \right) \right]^\alpha \left(\frac{k_a c}{c_{max}} \right)^{1-\alpha}$$

For the electrolyte-reduction reaction a Tafel kinetics is assumed (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)

$$I_S = -i_{0,S} \left(1 - \frac{Q_t}{Q_S} \right) \exp \left[-\frac{\alpha_S F}{RT} (V - U_{0,S}) \right]; \quad Q_t = -\int_0^t I_S dt; \quad U_{0,S} = 0.8V$$

The total charge lost Q_S is assumed to be $0.05 C \cdot cm^{-2}$ [Nadimpalli et al. 2012].

Main Reference

G. Bucci, S.P.V. Nadimpalli, V.A. Sethuraman, A.F. Bower, and P.R. Guduru. Measurement and modeling of the mechanical and electrochemical response of amorphous Si thin film electrodes during cyclic lithiation, *J. Mech. and Phys. Solids* (accepted)

Mechanical deformation

The anode consists of amorphous Si-film bounded to a rigid substrate and it is modeled as an isotropic, elasto-viscoplastic solid.

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

$$\epsilon_{xx}^e = \epsilon_{yy}^e = \epsilon_{zz}^e = \log(1 + \beta c)/3.$$

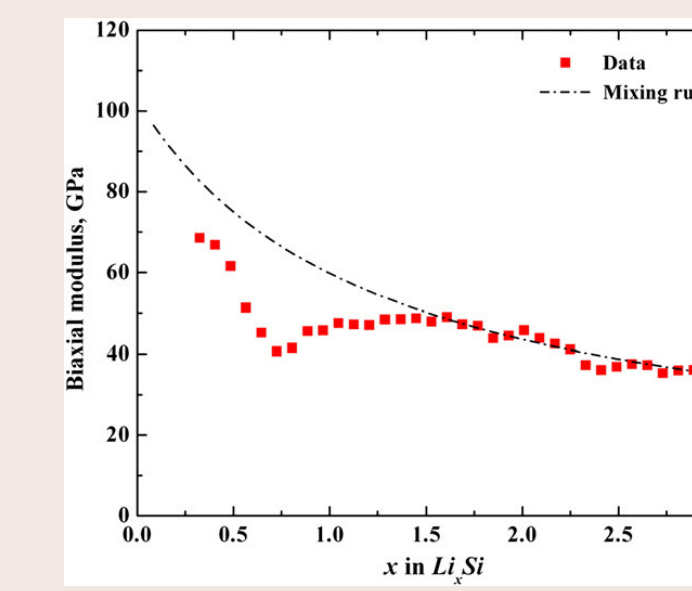
$$\frac{1}{3} \log(1 + \beta c) - 2 \log(\lambda^p) + \epsilon_{xx}^e = \log \left(1 + \frac{\partial u}{\partial X} \right)$$

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

1. 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 $M(c)$

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

$$M(c) = M_0 + M_1 \log(1 + c/c_0)$$



[Sethuraman et al., 2010]

2. The plastic deformation can be characterized by a viscoplastic constitutive equation relating the plastic stretch rate to stress

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

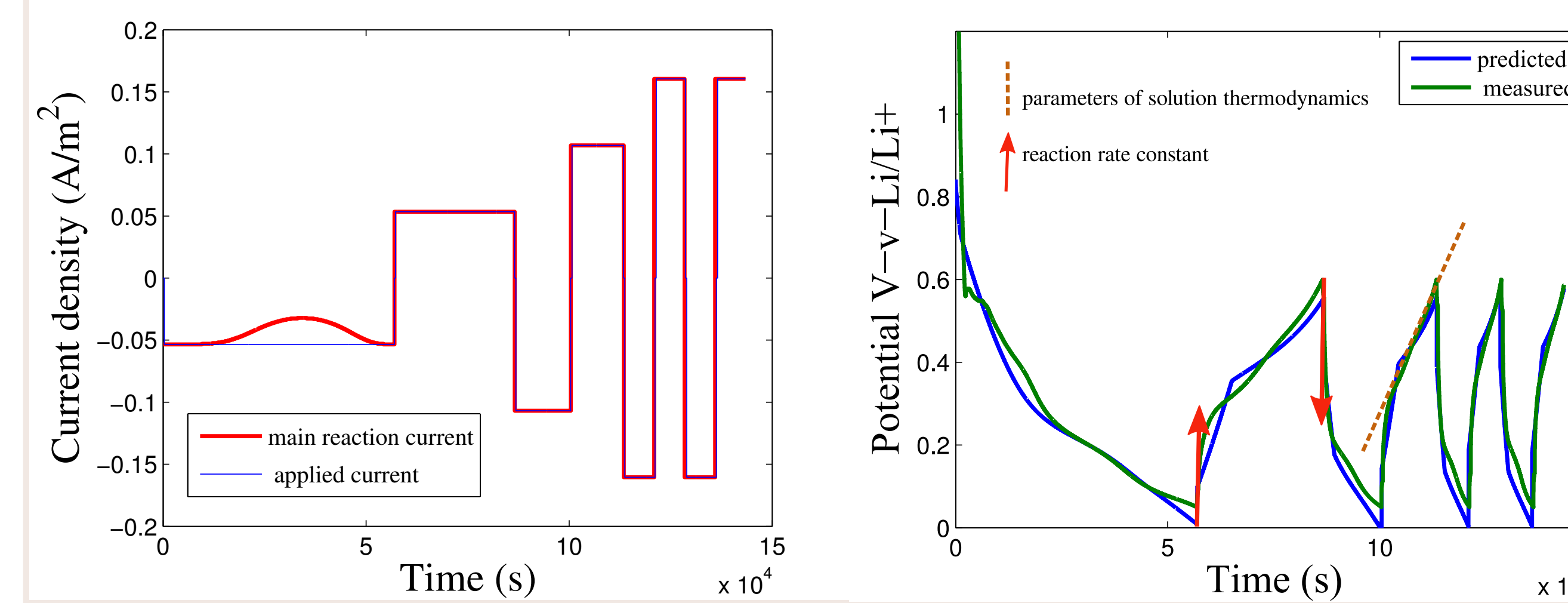
$$\dot{\epsilon}_{yy}^p = \dot{\epsilon}_{zz}^p = 0 \quad \text{if } |\sigma| < \sigma_0$$

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 σ_0 constitutive law is assumed to be a linear function of lithium concentration

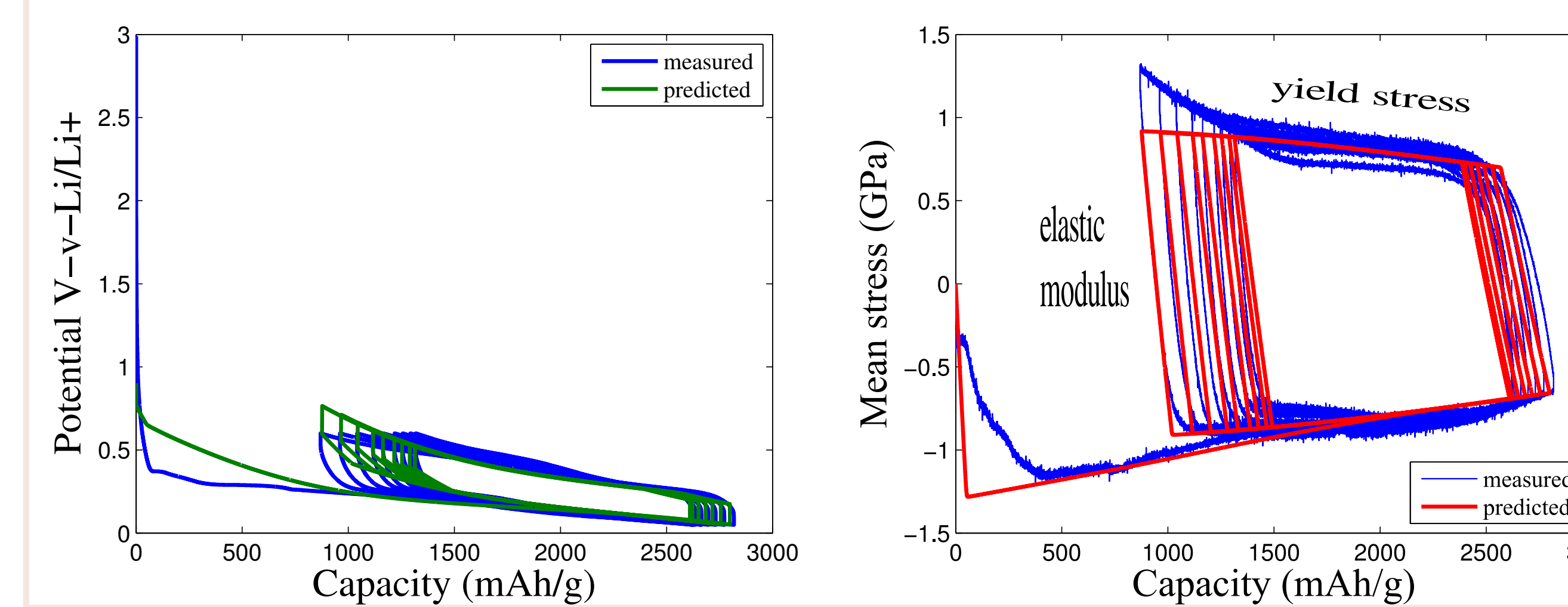
$$\sigma_0(c) = s_0 + s_1(c - c_0)$$

Experiment used for model calibration



a - Si film of 127nm thickness and $18.7 \cdot 10^{-4} m^2$ surface area. Initial residual stress of $-0.1 GPa$.

Validation of model prediction capability



a - Si film of 103nm thickness. Initial residual stress of $-0.36 GPa$. It undergoes cycles of alternate current of $175 \mu A$.

Conclusions

- The Young's modulus was found to vary from 80 GPa in the un-lithiated electrode to $50 \pm 15 GPa$ at full charge capacity. These values are in good agreement with previously reported data [Shenoy & Johari, 2010].
- The inelastic response is described by a rate-dependent elastic-viscoplastic constitutive model, with a linear concentration dependent flow stress varying from $0.49 \pm 0.08 GPa$ at zero concentration to $0.23 \pm 0.08 GPa$ at full capacity, and a stress exponent of 50.
- Secondary effects, such as capacity loss in SEI formation and Li - Li interactions, are taken into account.
- Reaction rate constants extracted from PITT experiment fit the cell voltage data

Li transport and reaction kinetics via PITT experiments

Motivation

- 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 and atomistic scale calculations) span several orders of magnitude.

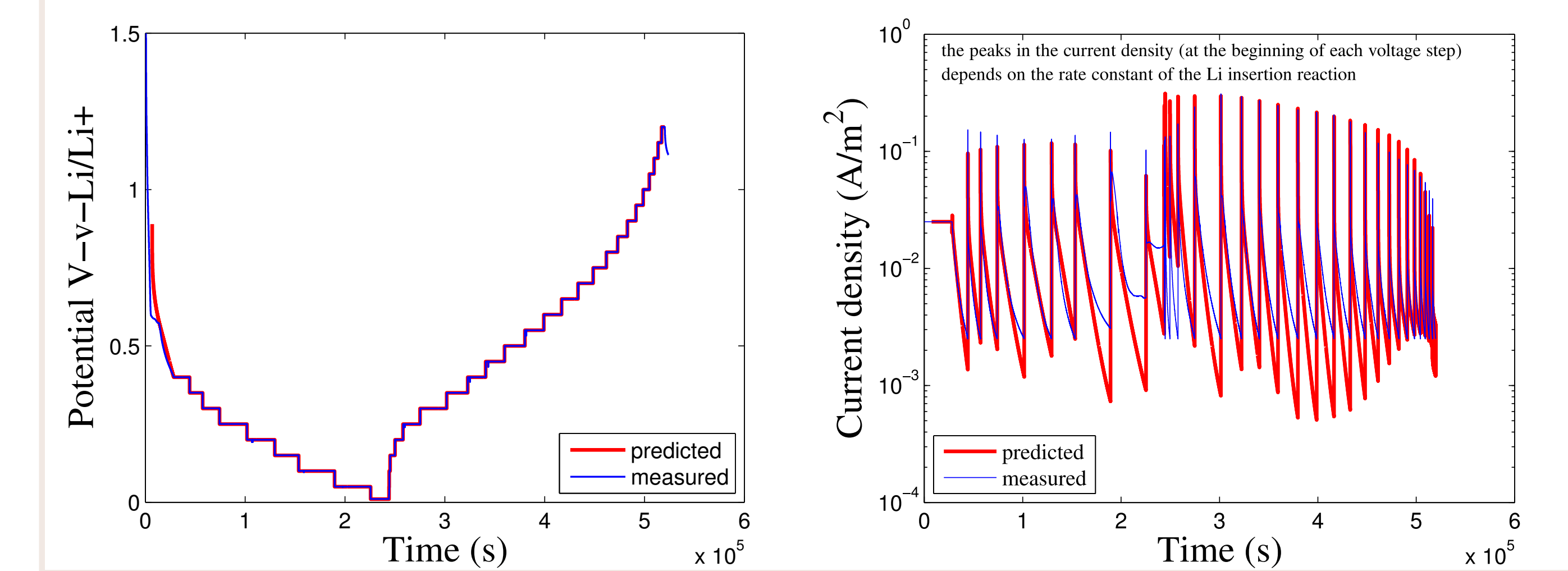
Experiment description

- In the potentiostatic intermittent titration technique experiment, the electrode was subjected to incremental step changes in potential, and the subsequent transient evolution of stress and electric current density in the anode were measured.

Our contribution

- Lithium diffusivity and reaction rate constants was determined by fitting full numerical simulations of the PITT experiment to the experimental data.
- Our approach respect to the classical model [Weppner et al, 1977] accounts rigorously for departures from the ideal diffusion model resulting from stress and free energy of mixing. It also accounts for nonlinearities arising from the Li insertion kinetics.

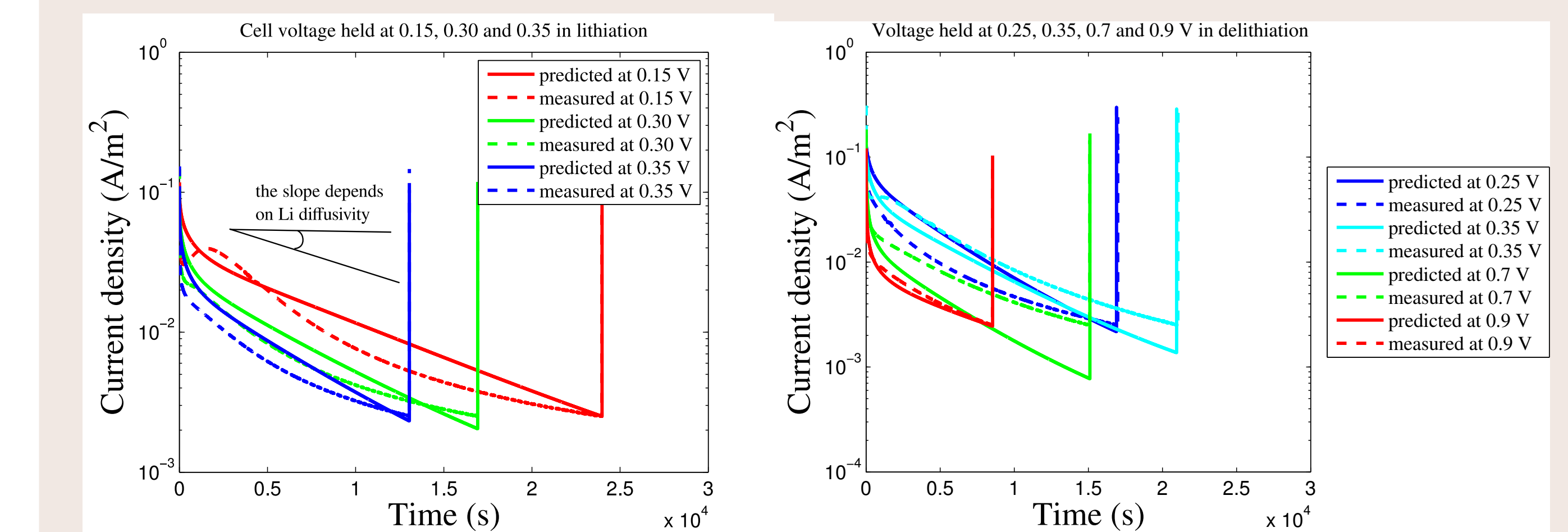
PITT experiment results



a - Si film of 104nm thickness. Each potentiostatic step was carried out until the current decayed to less than $0.25 \mu A/cm^2$

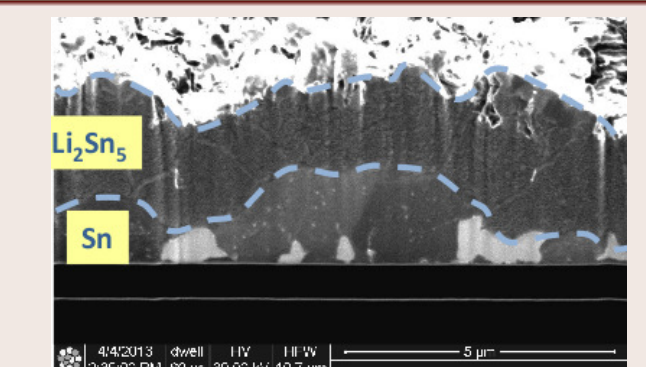
Conclusions

- Experimentally measured transients in the PITT test 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].
- 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 vary by several orders of magnitude.

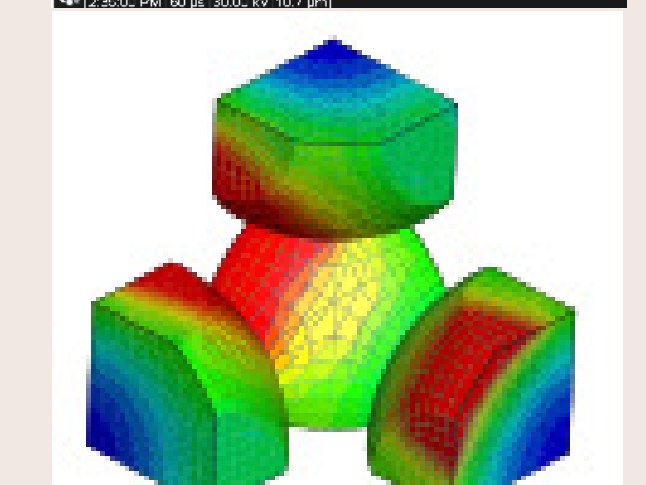


Future work

Model of phase boundary propagation in lithiated c-Si and Sn anodes in thin film and spherical particle configurations.



The 1D formulation, developed for the thin film anode case, is being extended to 3D composite configurations with the aim of simulating the interaction between active material, binder and electrolyte.



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