**General Motivation**

Potential impact

- Si: High capacity (1675 mAh/g) 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 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 dependence activity coefficient).
- Parameters characterizing electrochemical main and side reactions.

**Equations Governing**

- Finite element model in 3D spatial set
- Boundary conditions in galvanostatic tests
- Boundary conditions in potentiostatic tests

**Thermodynamics of a lithium-ion half-cell**

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

\[
\frac{\mu}{\rho_0} = \frac{1}{2} \frac{\partial F}{\partial c} \quad \text{Diffusion equation}
\]

\[
\mu = \mu(\sigma, \theta)
\]

Chemical potential

Boundary conditions in galvanostatic tests:

\[j(x, t) = j_0 \quad j(x, t) = 0\]

Cell voltage and stress computed

Boundary conditions in potentiostatic tests:

\[j(x, t) = j_0 \quad j(x, t) = 0\]

Current density and stress computed

**Electrochemical reactions**

The total current density through the external circuit is divided into two contributions \(j_0 = j_E + j_L\).

The current supplied to the desired Faradic reaction is calculated as follows:

\[
j_0 = j_{E,0} \quad j_{L,0} = j_{E,0} \quad j_{L,0} = j_{E,0} \quad j_{L,0} = j_{E,0}
\]

The electrode reaction reaction a Table kinetic is assumed [Sethuraman et al., 2010] predict that the SEI thickness and total capacity vary very little with time as \(1/t^2\) and give a good fit to measurements over a long time period [Piersini & Bassani, 2015] but do not fit our experimental data for a small number of cycles.

\[
j_E = \frac{Q_{\text{in}}}{t} \quad j_L = \frac{Q_{\text{out}}}{t}
\]

The total charge balance \(Q_{\text{in}}\) is assumed to be \(1/t^2\). [Piersini & Bassani, 2015].

**Mechanical deformation**

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

**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.

**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 were recorded.

**Our approach respect to the classical model** [Weppner et al., 1977] accounts rigorously for departures from the ideal diaphragm model resulting from stress and free energy of mixing. It also accounts for nonlinearities arising from the Li insertion kinetics.

**Future work**

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