Side Reaction Correction and Non-linear Exchange Current Density for Mathematical Modeling of Silicon Anode Based Lithium Ion Batteries

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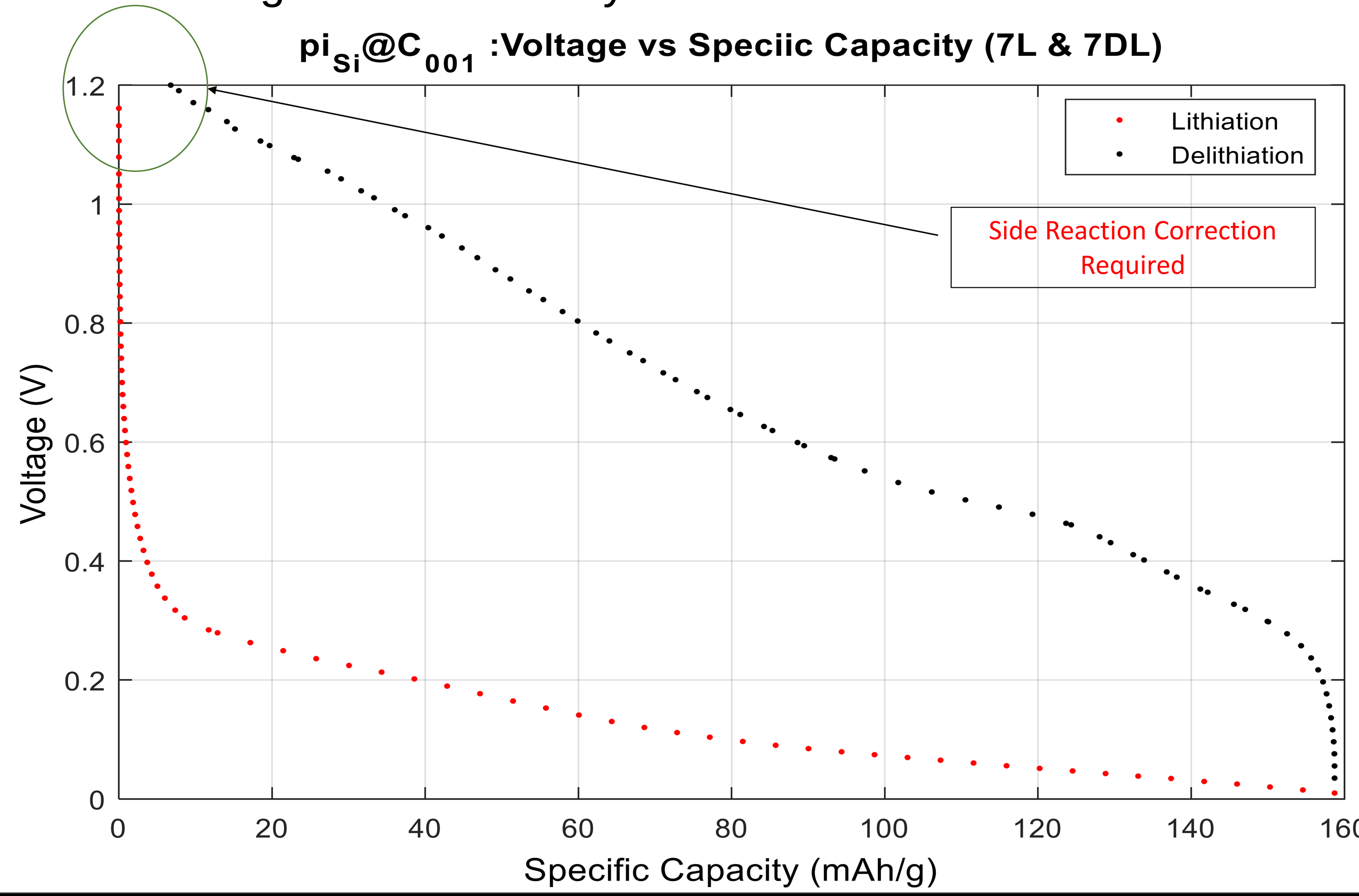
Abstract

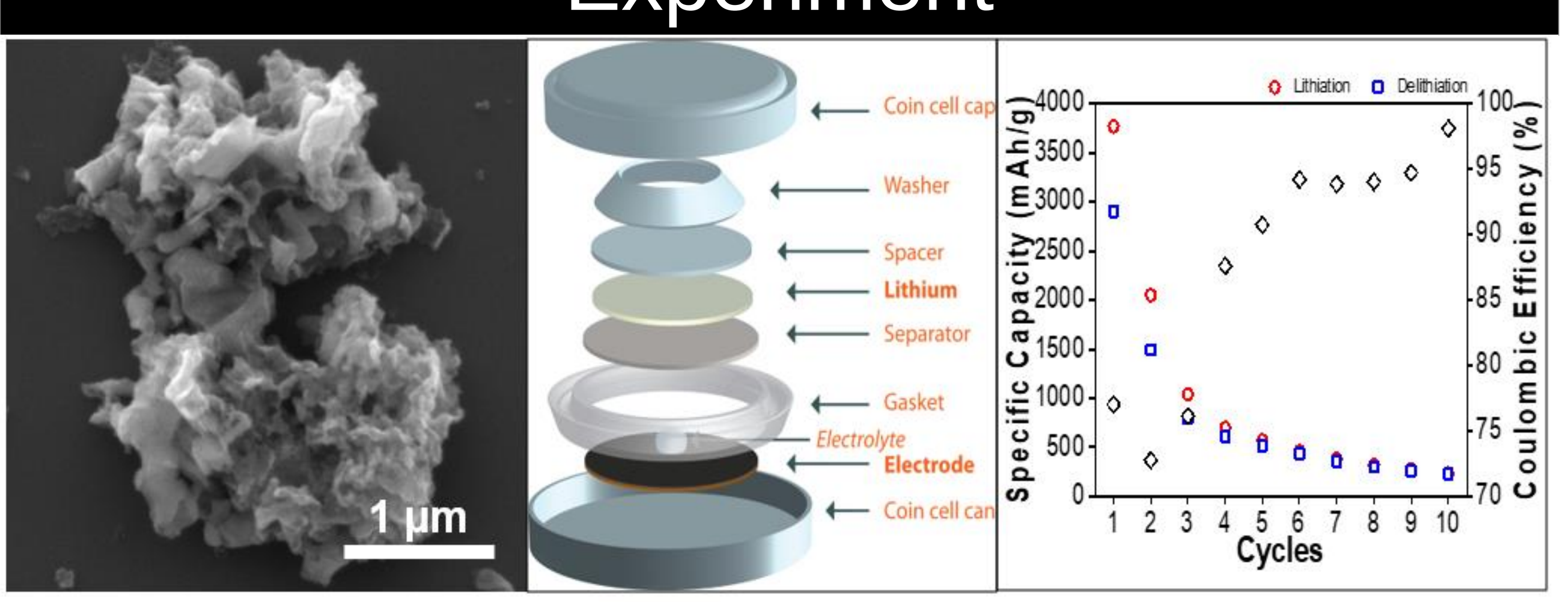
A physics-based electrochemical model has been developed to investigate overall performance and sensitivity analysis of Silicon anode based Lithium-ion batteries. Lithiation-Delithiation cycling has been done on the porous Si anode coin cell. Then side reaction has been corrected on the exchange current density, i_0_SR of the cell. i_0_SR as a function of cycle numbers have been plotted in the graph. It has been noticed, side reaction exchange current density in the initial cycles just because of SEI layer formation at the interphase of anode and separator of the battery. In the later cycles, it reduces to small values. Then, a single particle half-cell model has been developed and simulated to validate the experimental result. In the model, different equations (logarithmic, linear, average) to evaluate side-reaction exchange current density. It has been observed logarithmic i0_SR as a function of the state of charge(SOC) has been fitted the best with the experimental results.

Introduction/Motivation

- It has been suggested that the performance of the Lithium-ion Batteries can be improved if the graphite in anode could be replaced with silicon because of its high capacity.
- Silicon experiences a large volume change during battery cycling, which can cause cracks at the surface of the electrodes, failure at the separator-electrodes interface and large volumetric changes to the cell.
- To optimize the Si-anode-battery design, side reaction must be corrected on the exchange current density of the cell.

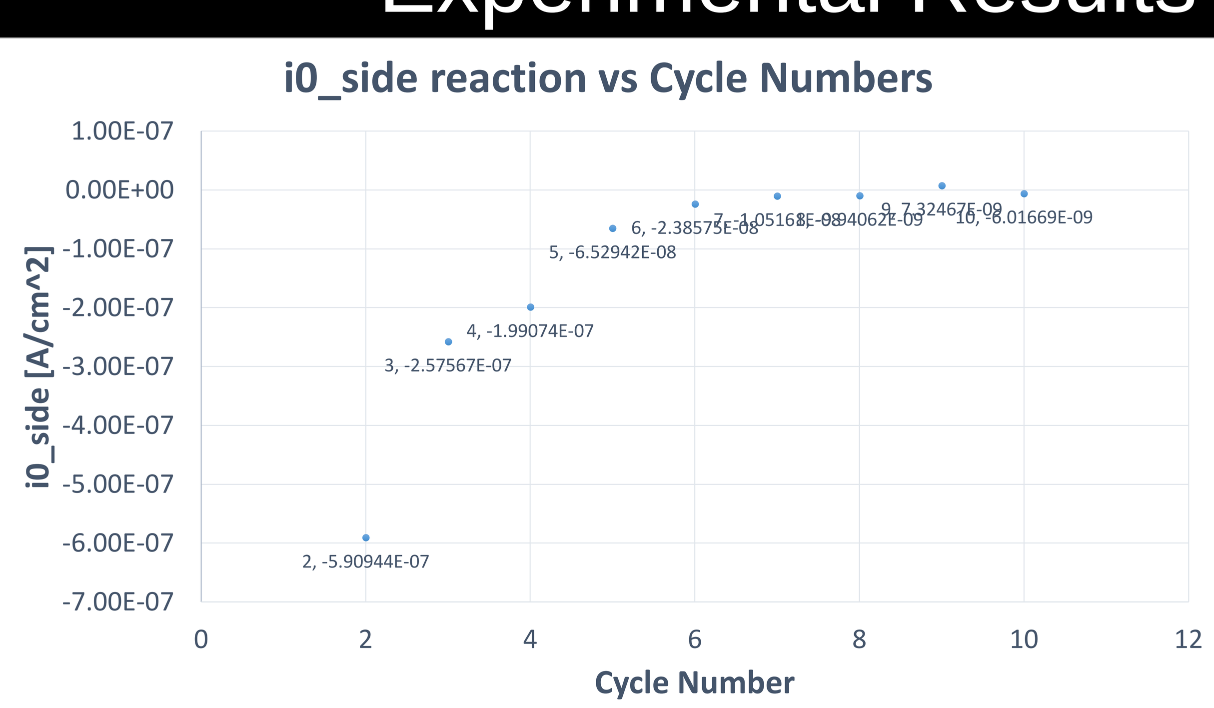


Experiment



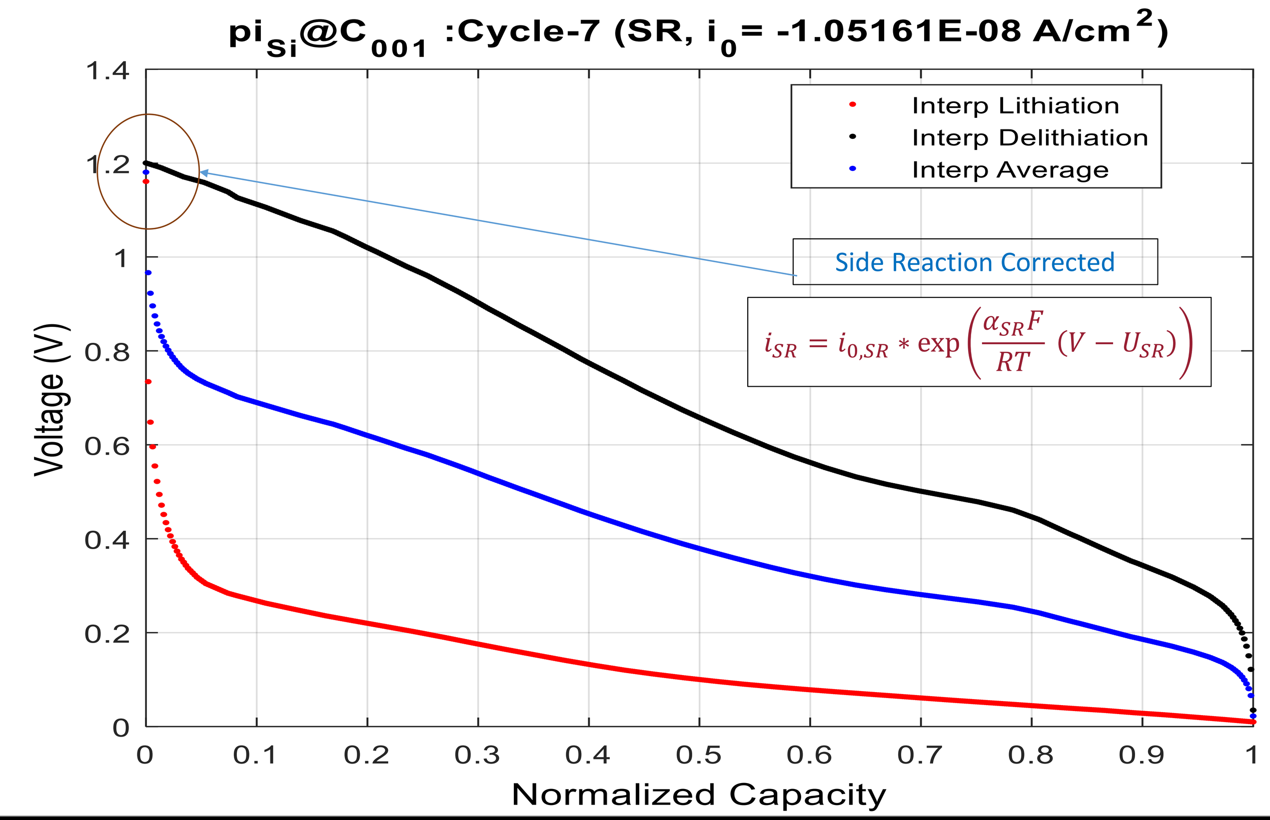
Carbon coated Macroporous Si (pSi@C)

Experimental Results



Cycle No.	i0_side [A/cm^2]
1	N/A
2	-5.90944E-07
3	-2.57567E-07
4	-1.99074E-07
5	-6.52942E-08
6	-2.38575E-08
7	-1.05161E-08
8	-9.94062E-09
9	7.32467E-09
10	-6.01669E-09

Side Reaction Correction



Modeling Parameters

Name	Value	Units	Description
r_0	500	[nm]	Particle Radius
D_s	2E-15	[m²/S]	Diffusivity
$i0_1$	1.46E-3	[A/m²]	Exchange Current Density-1
$i0_2$	8.46E-6	[A/m²]	Exchange Current Density-2

Mathematical Model

Mass diffusion equations can be written as,

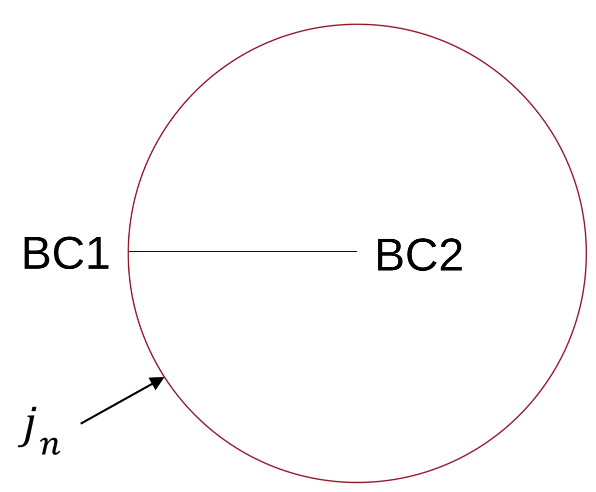
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial r^2} + 2\frac{D}{r}\frac{\partial c}{\partial r}$$

Boundary Condition-1:

$$D\frac{\partial c}{\partial r} = -j_n \quad \text{for} \quad r = R$$

Boundary Condtion-2:

$$D\frac{\partial c}{\partial r} = 0 \quad \text{for} \quad r = 0$$



j_n is net flux, mol/m²/s

σ_h is hydrostatic stress at the surface layer of electrode, N/m²

Use $\alpha = 0.5$ Then, Butler Volmer (BV) equation becomes[3],

$$j_n = \frac{i_0}{F}\left\{\exp\left[\frac{F(V-U)-\sigma_h\Omega}{2RT}\right] - \exp\left[-\frac{F(V-U)-\sigma_h\Omega}{2RT}\right]\right\}$$

i_0 for Side Reaction (logarithmic), linear and average express

$$i_0 = 10\text{^}(\log_{10} i0_2 - \log_{10} i0_1 * SOC) \qquad [1]$$

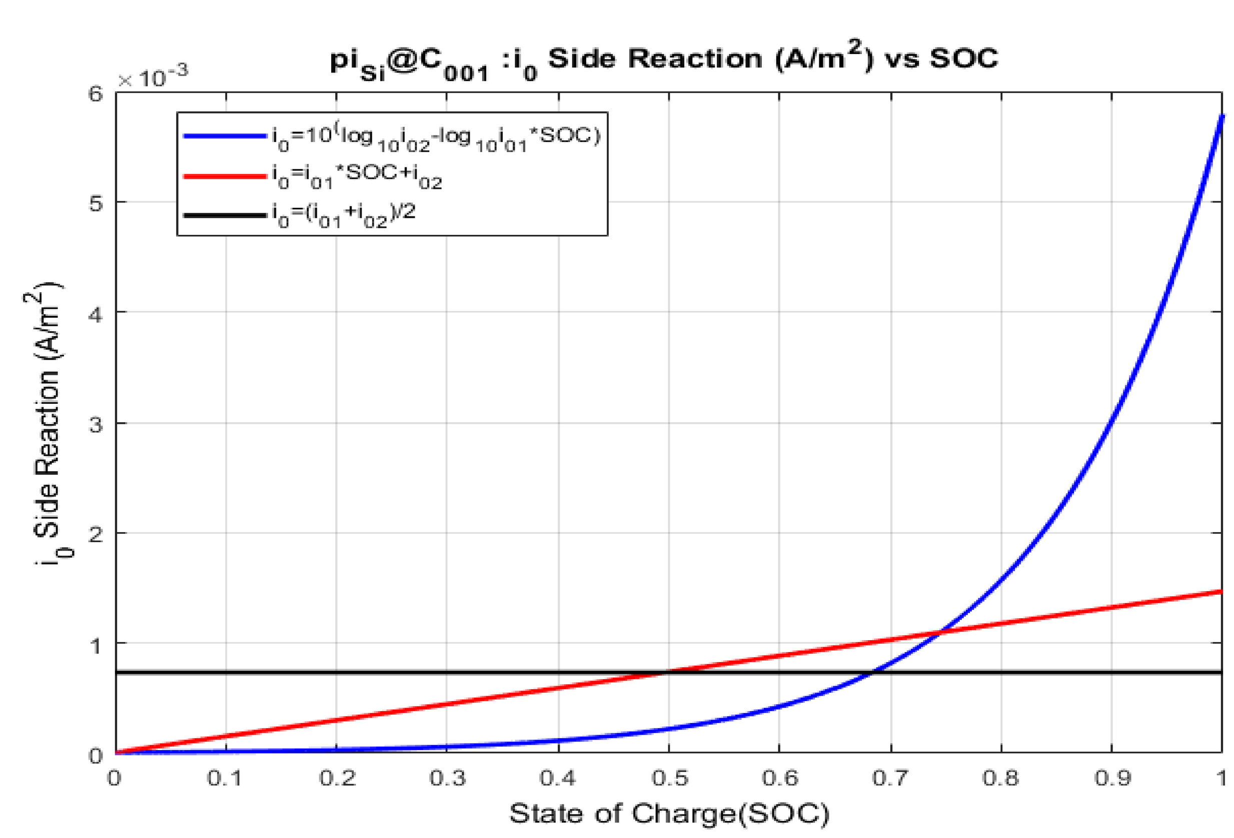
$$i_0 = i0_1 * SOC + i0_2 \qquad [2]$$

$$i_0 = (i0_1 + i0_2)/2 \qquad [3]$$

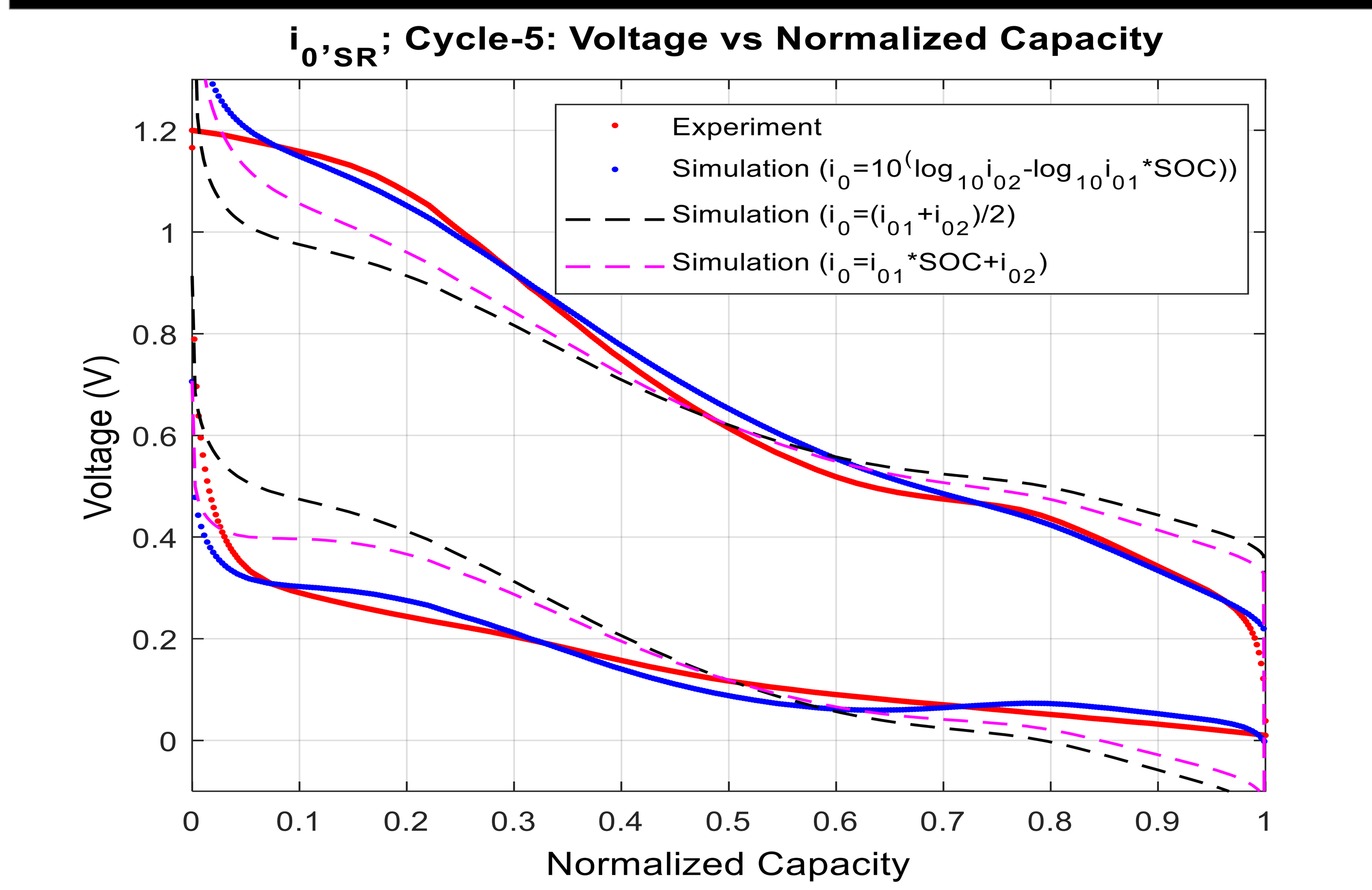
Here, $SOC = State\ of\ charge = c/c\_\max$

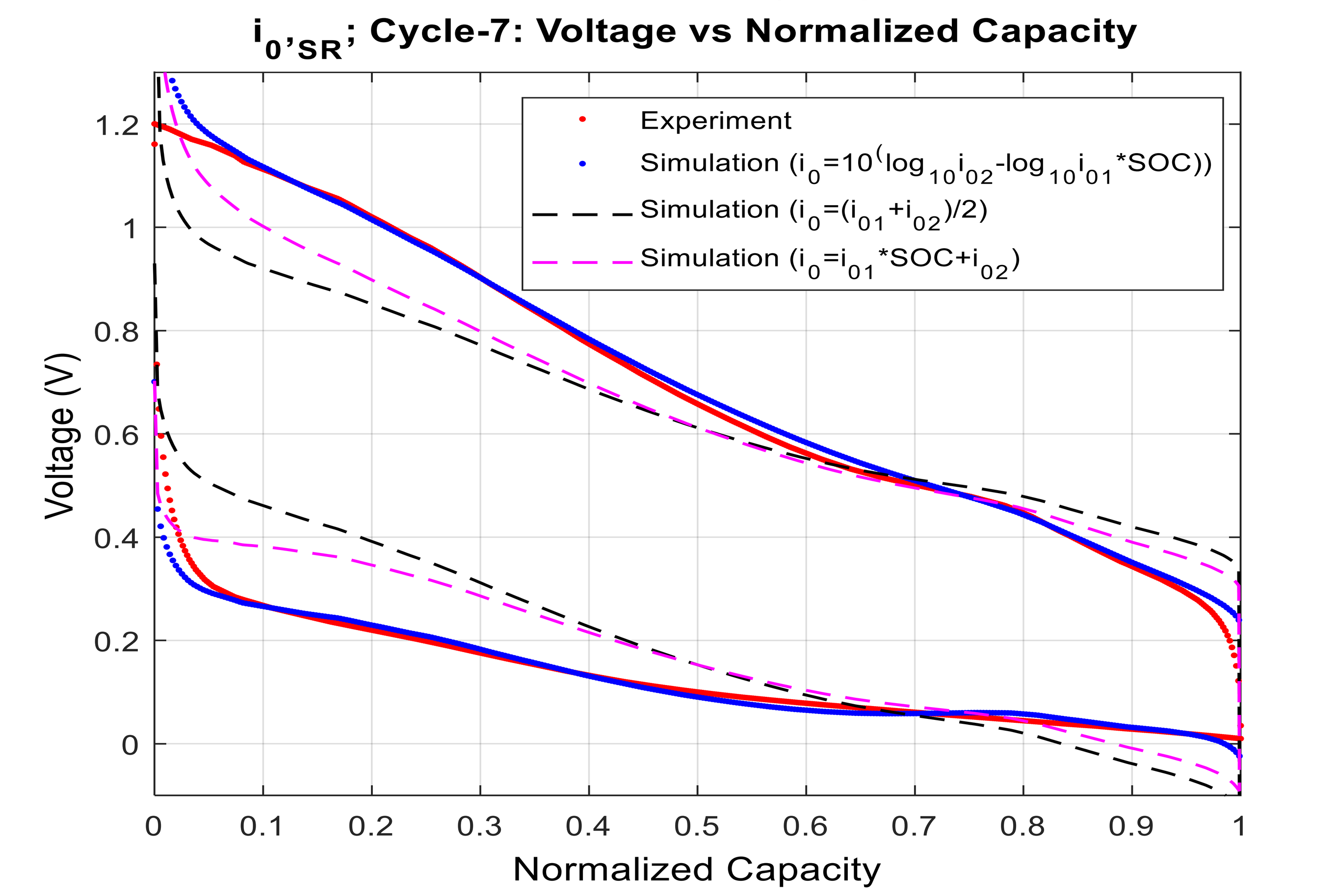
Hydrostatic Equation was generated for Cheng and Verbrugge's solution[1]. At the surface, the stress becomes then,

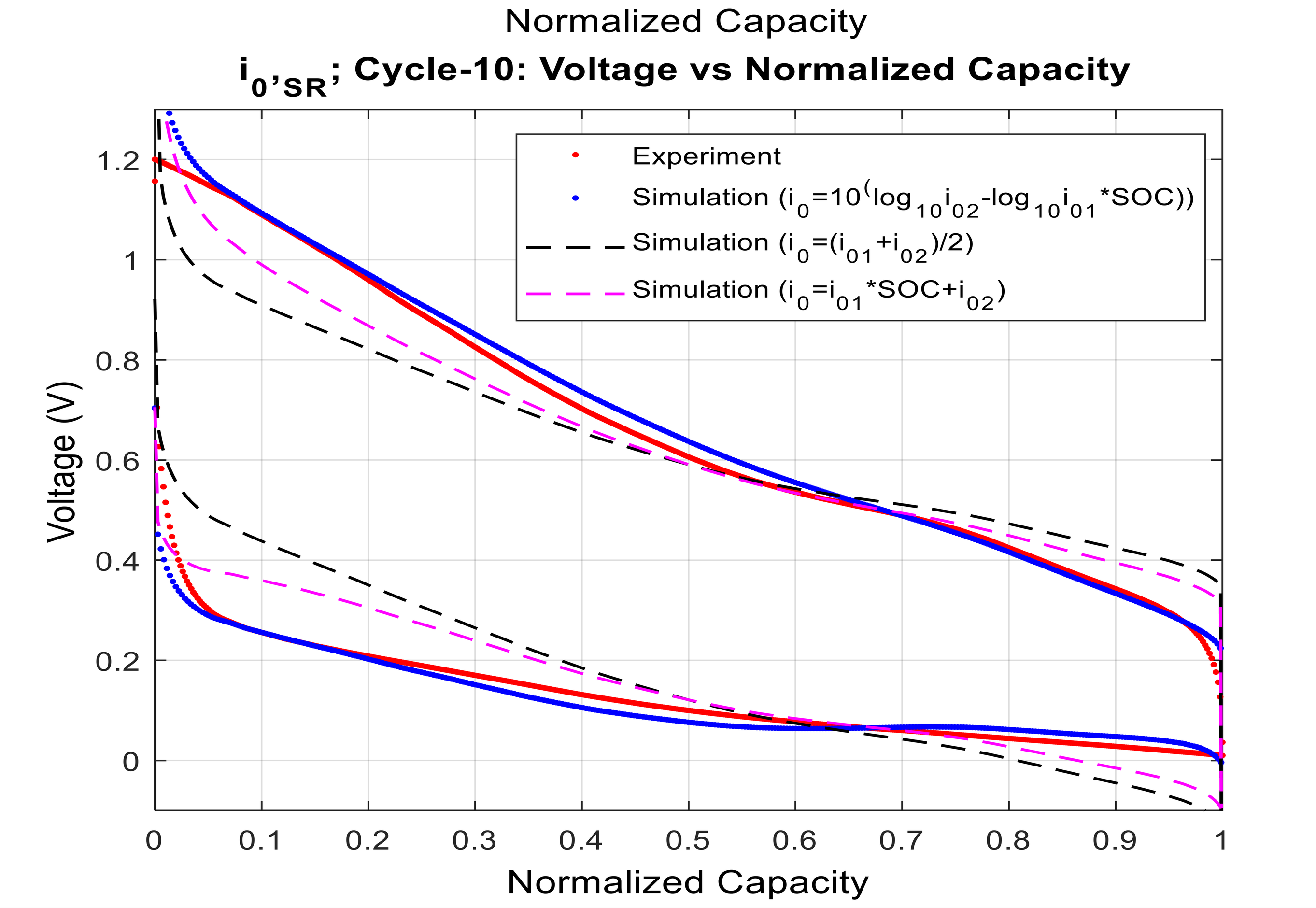
$$\sigma_h(R) = \frac{2E\Omega}{9(1-\nu)}[S_1 c_{av}(R) - c(R)] + S_2$$



Simulated Validation







Conclusions

- Battery cycling was done in the silicon anode coin cell.
- Side-reaction in the exchange current density was corrected.
- A physics-based model has been developed and simulated in COMSOL Multiphysics 5.5.
- It was observed the exchange current as a function of SOC fitted best with the experimental result as showed in the graph.
- Experiment and simulation were conducted for ten different cycles and best of the three cycles' results have been exhibited here.

References

[1] Cheng, Y. and Verbrugge, M., 2008. The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles. *Journal of Applied Physics*, 104(8), p.083521.

[2] Sethuraman, V., Srinivasan, V. and Newman, J., 2012. Analysis of Electrochemical Lithiation and Delithiation Kinetics in Silicon. *Journal of The Electrochemical Society*, 160(2), pp.A394-A403.

[3] Jin, C., Li, H., Song, Y., Lu, B., Soh, A. and Zhang, J., 2019. On stress-induced voltage hysteresis in lithium ion batteries: Impacts of surface effects and interparticle compression. *Science China Technological Sciences*, 62(8), pp.1357-1364

2207