Modeling Voltage of a Lithium Ion Battery with a Silicon-Graphite Composite Anode

Zoey Huey

MEGN 570: Electrochemical Systems Engineering

December 16, 2020

1 Introduction

The goal of this project was to create a model of a composite silicon-graphite electrode to determine the impact of particle sizes on voltage. Particle size, particularly regarding the Si particles, is a point of discussion because it is believed that Si nanoparticles produce the best performance because of reduced deformation and mechanical damage during lithiation and delithiation.[1] However, in terms of scalability, larger Si particles (micron regime) will likely be more feasible and economical from a mass production standpoint.[2] Graphite sizes may also impact performance, as particle size affects available surface area for reactions. By creating a model to understand the exact impact of particle sizes on performance, informed decisions can then be made by researchers on whether the cost impacts of Si nanoparticles are worth the performance increase.

2 Model Formulation

2.1 Battery specifications

The initial data for the material properties, including particle sizes and compositions, and electrode compositions comes from standard CAMP electrodes and the listed manufacturers (silicon from Paraclete Energy, graphite from Hitatchi, and NMC 811 from Targray).[3,4]

The two anode particle types (Si and Gr) will have radii r_{Si} and r_{Gr}. The total number of particles, N_p is equal to

$$N_p = N_{Si} + N_{Gr} \tag{1}$$

The volume fraction of active material is similarly defined:

$$\epsilon_s = \epsilon_{Gr} + \epsilon_{Si} \tag{2}$$

The electrode dimensions are Δx_{an}, Δy_{an}, $\Delta z_{an} = H_{an}$ and $\Delta x_{ca}\Delta y_{ca}$, $\Delta z_{ca} = H_{ca}$.

Since it is common for the graphite and silicon amounts to be described in weight percentages rather then volume fractions, as is done for the CAMP reference electrodes, the volume fraction for component x is calculated as follows

$$\epsilon_x = \frac{\frac{M_x}{\rho_x}}{V_{an}} = \frac{\frac{M_x}{\rho_k}}{H_{an}\Delta x \Delta y} \tag{3}$$

To determine the solid phase volume,

$$\epsilon_{Gr} + \epsilon_{Si} = \epsilon_s = \frac{N_{Gr}\pi\frac{4}{3}r_{Gr}^3}{\Delta x_{an}\Delta y_{an}\Delta z_{an}} + \frac{N_{Si}\pi\frac{4}{3}r_{Si}^3}{\Delta x_{an}\Delta y_{an}\Delta z_{an}} = \frac{4(N_{Gr} + N_{Si})\pi(r_{Gr}^3 + r_{Si}^3)}{3AH_{an}} \tag{4}$$

If $n_p = n_{Gr} + n_{Si} = \frac{N_p}{A}$, then

$$n_p = \frac{3H_{an}(\epsilon_{Gr} + \epsilon_{Si})}{4\pi(r_{Gr}^3 + r_{Si}^3)} \tag{5}$$

2.2 Conservation of charge in anode

Conservation of charge and charge neutrality dictate that

$$\frac{dQ_{an}}{dt} = 0 = \dot{Q}_{in} - \dot{Q}_{out} = I_{ext} - i_{Far}A_{surf} - i_{dl}A_{surf} \tag{6}$$

This can be rewritten as

$$i_{dl} = i_{Far} - i_{ext}\frac{A}{A_{surf}} \tag{7}$$

There will be an A_{surf} term for each component, since they will have individual double layer currents.

$$A_{surf,x} = 4\pi r_x^2 A N_p \tag{8}$$

$$\frac{A}{A_{surf,x}} = \frac{1}{4\pi r_x^2 n_{p,x}} \tag{9}$$

$$n_{p,x} = \frac{r_{p,x}}{3H_{an}\epsilon_x} \tag{10}$$

In the anode, it is assumed that the surface fraction of each component is the same as the volume fraction. Therefore,

$$i_{dl,x} = i_{Far,x} - i_{ext}\epsilon_x\frac{A}{A_{surf,x}} \tag{11}$$

If we assume that the two double layer currents, which are local to the domains of each component, contribute to the total anode double layer current proportional to their surface fractions, then

$$i_{dl,an} = i_{dl,gr}\epsilon_{gr} + i_{dl,si}\epsilon_{si} \tag{12}$$

The i_{Far} is calculated using the Butler-Volmer equation:

$$i_{Far,x} = i_{o,x}(exp(\frac{-n_x F\beta_x\eta_x}{RT}) - exp(\frac{n_x F(1-\beta_x)\eta_x}{RT})) \tag{13}$$

The overpotential η is defined as

$$\eta_x = V - U_x \tag{14}$$

where V is the cell voltage and U is the equilibrium potential. The equilibrium for the graphite was assumed to be -0.125 V, the equilibrium potential for silicon was calculated to be -1.05 V, and the equilibrium potential for NMC was calculated to be 4.07 V assuming an intercalation fraction of 0.5 for all components.[5,6]

2.3 Capacity

The anode capacity also needs to account for the Si and Gr components

$$Cap = \rho_{AM}\epsilon_{AM}H_{el} = (\rho_{Gr}\epsilon_{Gr} + \rho_{Si}\epsilon_{Si})H_{el} \tag{15}$$

The equation for the cathode is similarly derived.

$$Cap = \rho_{NMC}\epsilon_{NMC}H_{el} \tag{16}$$

The actual capacity is the minimum of these two values. Additionally, the current applied is determined by

$$i_{ext} = C * Cap \tag{17}$$

where C is the C rate of the battery.

3 Results

Initially the model was formulated to test the impact of changing the radius of each particle type in the anode across a range of 100 μm to 100 nm. However, it was determined that with the current model functionality, changing the radius does not appreciably alter the voltage of the battery, as shown in Figure 1.
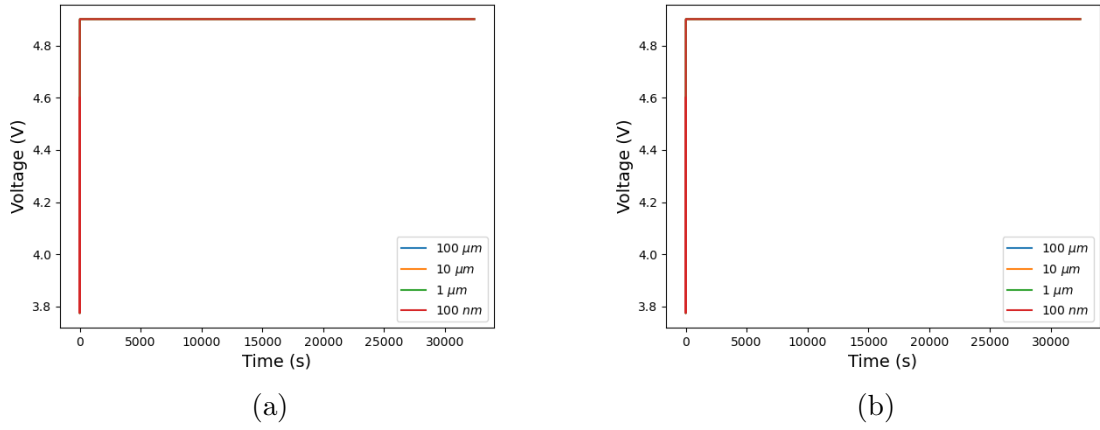
Figure 1: (a) Voltage vs. time plot at a range of Si radii. (b) Voltage vs time at a range of Gr radii.

For this reason, the model was modified to cycle over a range of compositions (in weight fraction) of Si and Gr to observe the impact on voltage, which is shown in Figure 2.
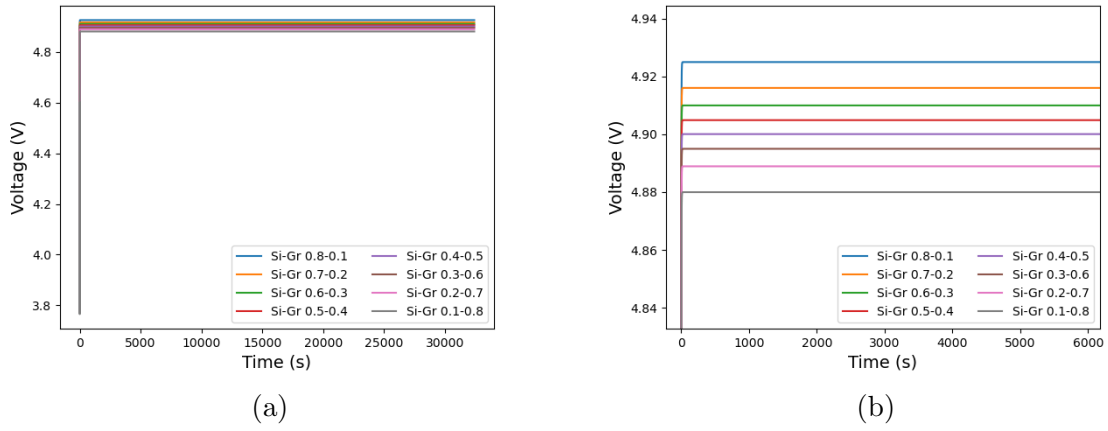

Figure 2: (a) Voltage vs. time plot at a range of Si-Gr compositions. (b) Voltage vs time at a range of Si-Gr compositions, smaller scale.

The capacity as a function of weight percent Si was also modeled, as shown in Figure 3.
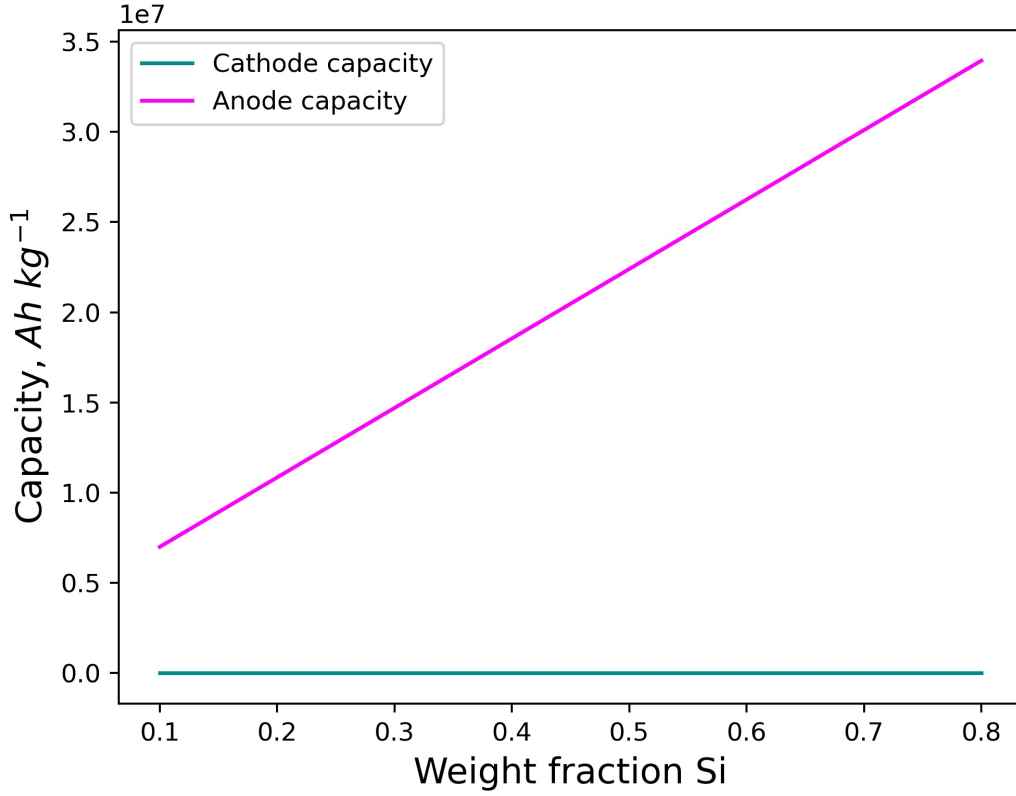
Figure 3: Anode and cathode capacity as a function of weight percent Si.

4   Discussion

With the model as is, changing the Si and Gr particle radii from micron to nanometer size has virtually no impact on the voltage results of the model. This lack of change is likely due to simplifications or assumptions made during model formulation, rather than a lack of physical relationship between particle size and voltage. Some changes that may impact these results are more fully accounting for the surface area of the particles and for the degree of porosity that may be present.

The model also showed that the voltage increased from 4.88 V to 4.925 V when the Si content was increased from 0.1 to 0.8 weight fraction. This increase is because a lower equilibrium potential of Si relative to Gr causes the overall anode equilibrium potential to decrease as fraction of Si increases. The implications of this voltage increase are that under equivalent conditions, a cell with more Si will run at a higher

6

current than one with less Si.

Although the anode capacity was shown to increase as Si content increases, in this particular cell, the capacity, which is the minimum of the two electrodes, is limited by the cathode, which has a much lower capacity that the Si anode. Thus, to fully exploit the high theoretical capacity of Si, a higher capacity cathode material must be used as well.

5 Conclusion

The model found no relationship between Si and Gr particle sizes and cell voltage. However, a more sophisticated model may prove otherwise. It was also determined that increasing the weight fraction of Si and decreasing that of Gr increased the cell voltage, and that the cell capacity was limited by the cathode.

References

(1) Gan, C.; Zhang, C.; Wen, W.; Liu, Y.; Chen, J.; Xie, Q.; Luo, X. *ACS Applied Materials & Interfaces* **2019**, *11*, 35809–35819.

(2) Mu, T.; Zhang, Z.; Li, Q.; Lou, S.; Zuo, P.; Du, C.; Yin, G. *Journal of Colloid and Interface Science* **2019**, *555*, 783–790.

(3) Stetson, C.; Huey, Z.; Downard, A.; Li, Z.; To, B.; Zakutayev, A.; Jiang, C.-S.; Al-Jassim, M. M.; Finegan, D. P.; Han, S.-D.; DeCaluwe, S. C. *Nano Letters* **2020**, *20*, 8081–8088.

(4) NMC Battery Material for Li-ion Cells (LiNiMnCoO2), https://www.targray.com/li-ion-battery/cathode-materials/nmc, 2020.

(5) Mai, W.; Colclasure, A.; Smith, K. *Journal of The Electrochemical Society* **2019**, *166*, A1330–A1339.

(6)   Allart, D.; Montaru, M.; Gualous, H. *Journal of The Electrochemical Society*
       2018, *165*, A380–A387.

A   Memes