The Effect of Electrode Active Material Particle Size on Li-Ion Battery Charging

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Introduction

With the demand for electric vehicles (EVs) rapidly increasing, the need for increasingly faster charging Lithium-ion (Li-ion) batteries has followed. The Vehicle Technologies Office (VTO), an office of the US Department of Energy, has stressed the importance of enhancing EV batteries in improving EVs economic, social, and environmental sustainability. The VTO has set ambitious goals to push EV technology forward, including a goal to decrease charge time to 15 minutes or less [1].

Previous research has focused on improvements to prevent Li plating on the electrodes or the benefits of low-viscosity solvents with highly concentrated electrolytes [2, 3]. This study focuses on the effects of the active material particle size in the anode and cathode on charging ability via the change in lithium mole fraction. The battery was modeled with a porous graphite (C_6) anode and a porous Lithium Carbonate Oxide (LCO) cathode. In addition, the electrolyte separator was $LiPF_6$ in a solvent of Ethylene Carbonate (EC):Dimethyl Carbonate (DMC). The components of the model battery are common materials for EV batteries [4].

Model Formulation

Assumptions

In order to isolate the effects of the graphite particle size, temperature was assumed to be constant at ambient temperature (298 K). It was assumed that all Li^+ that moved from the cathode to the anode reacted with the graphite surface and became lithiated. The symmetry factor, β, was assumed to be 0.5 for the forward and reverse reactions in the anode and cathode.

The charge fraction was set as 0.9, meaning the battery was charged to 90% of the total possible charge. This was done to prevent damage and extend the life of the battery [5]. The charge rate was set to 6C, meaning 6 charges per hour or one charge in ten minutes. This would put the battery well under the fast-charging goals listed above.

Model Derivation

A single particle model (SPM) was used to model all conservation equations. SPM assumes each electrode is composed of identical particles that all evolve uniformly within the electrode. Through this assumption, a single particle can be tracked and represents all particles in the electrode. Specific parameters were researched for each electrode as inputs to the model and the sources for those values can be found in the Jupyter notebook (*FCB_model FINAL*).

The overall conservation of charge equation for the anode is:

$$\frac{\partial Q_{an}}{\partial t} = 0 = -I_{ext} - i_{Far} A_{surf} - i_{dl} A_{surf} \tag{1}$$

Using the definition of current density gives:

$$I_{ext} = i_{ext} A_{geo} \quad (2)$$

Inserting eq (2) into eq (1) and rearranging to solve for i_{dl} results in:

$$i_{dl} = -i_{ext} \frac{A_{geo}}{A_{surf}} - i_{Far} \quad (3)$$

Using the equations for n_p, A_{surf}, and ε_s, an equation for i_{dl} was developed (for full derivation see Jupyter notebook *FCB_model FINAL*):

$$i_{dl} = -i_{ext} \frac{r_p}{3 H_{el} \varepsilon_s} - i_{Far} \quad (4)$$

Eq (4) is the double layer current equation that was used to solve for the electric potential in the anode. The external current, i_{ext}, is a function of the charge rate C, and the capacities of the electrodes. The Butler-Volmer equation was used to solve for i_{far}. A similar equation to eq (4) was developed for the cathode.

The bulk electrode species transport was modeled via surface reactions on the active material in each electrode. Lithium moving into the graphite was taken as a positive $\dot{s}_k$.

$$\frac{dN_k}{dt} = \dot{s}_k A_{surf} \quad (5)$$

Dividing (5) by the volume of the anode results in a change in concentration over time:

$$\frac{d(\varepsilon_s C_k)}{dt} = \frac{A_{surf}}{A} \frac{\dot{s}_k}{H_{an}} \quad (6)$$

Using the definition of X_k gives the change in the Li mole fraction over time:

$$\frac{dX_k}{dt} = \frac{1}{C^\circ} \frac{1}{\varepsilon_s} \frac{A_{surf}}{A} \frac{1}{H_{an}} \dot{s}_k \quad (7)$$

The molar production rate, $\dot{s}_k$, comes from Faraday's law:

$$\dot{s}_k = \frac{\nu_k}{nF} i_{Far} \quad (8).$$

Results

Figure 1 is a plot of the baseline data for X_{Li} in the anode using a graphite particle radius generally found in literature [6]. The curve increases to a steady state value for X_{Li} of as the
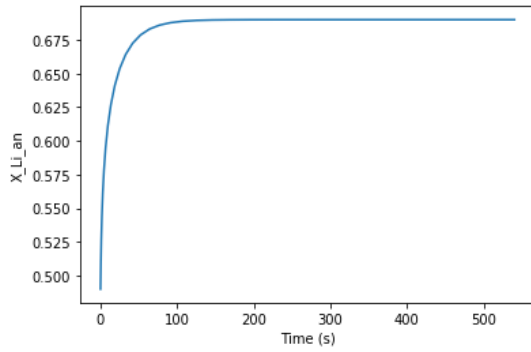
Figure 1: Baseline mole fraction of lithium in anode during charging

battery charges. Doubling the graphite particle size produced *Figure 2A*, while halving the particle size resulted in *Figure 2B*. While the Li$^+$ mole fraction reached the same steady state value for each scenario, the time at which the steady state was achieved differs. The steady state value was reached in half the time with repsect to the baseline when the particle size was halved, and the time doubled when the radius was doubled.

The plot of the Li$^+$ mole fraction in the cathode, *Figure 3*, exhibited a complementary decrease to the plot in *Figure 1*. The effect of the LCO particle size w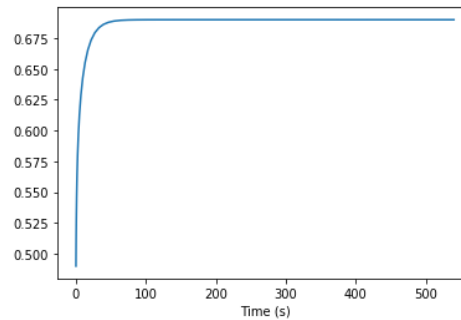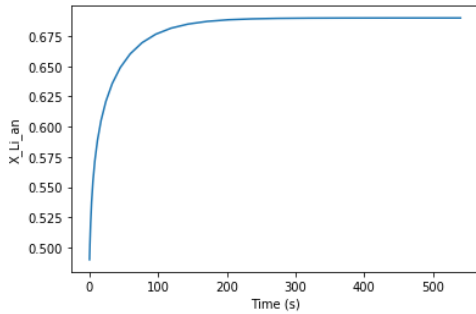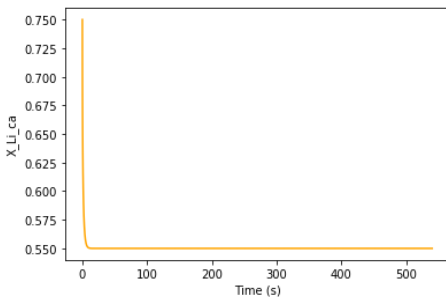as also observed. The radius was halved and doubled as with the graphite and similar changes were recorded. *Figure 4A & B* show how doubling the LCO radius resulted in the lithium mole fraction to decrease more slowly and halving the radius led to the mole fraction to decrease in a shorter time frame. The anode and cathode active particle size were observed separately, meaning the cathode particle size was not changed during the runs that the anode particle size was altered.
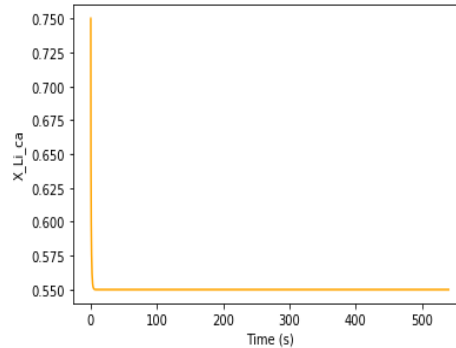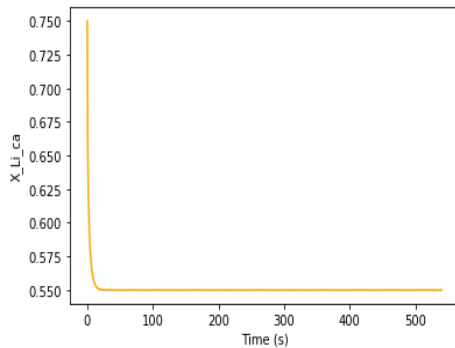

Figure 3: Mole fraction of lithium in anode with graphite particle A) doubled (left) and B) halved (right)

Figure 4: Mole fraction of lithium in cathode with LCO particle A) doubled (left) and B) halved (right)

Discussion

While an increase in the Li$^+$ mole fraction in the anode was expected during charging, the sharp increase close to time 0 was not expected. In the model, the mole fraction was only a function of the double layer potential; all other variables remained constant. The double layer potential was used to find i_{far} and the relationship between i_{far} and X_{Li} was linear, therefore the X_{Li} curve has the same shape as the i_{far} curve, as seen in *Figure 5A & B*.

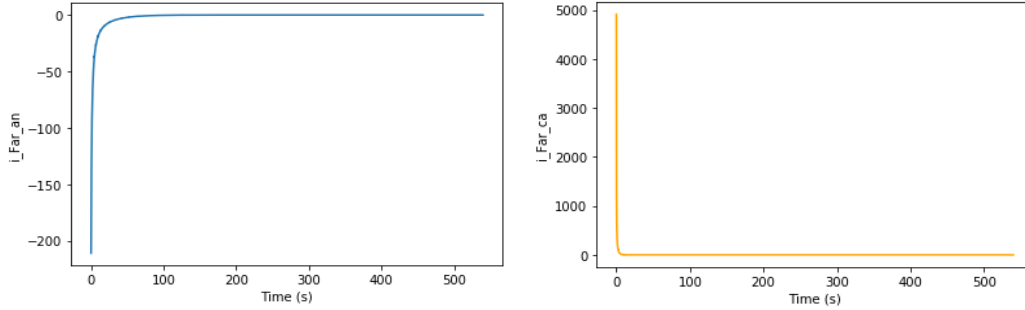*Figure 5: Faradaic current (A/m^2) over time in the A) anode (left) and B) cathode (right)*

The sharp increase of the lithium mole fraction in the anode closer to time 0 results from the higher number of open sites for the surface reactions on the graphite. The reverse was true for the cathode; there was a larger number of lithium ions moving out of the LCO particles at time 0 eventually tapering off at the steady state value.

The lithium was not expected to transport and react in such a short time frame, between 50 and 200 seconds for the anode depending on the graphite radius. By these times, the curves in the mole fraction graphs, *Figures 1* and *2*, first reached the steady state values. In the cathode, the lithium mole fraction decreased almost instantaneously. The reason for these sharp changes could be due to the lack of modeled forces that could slow down the transport of lithium, as well as the fact that the mole fraction was only a function of current.

The graphs all end at a time of 540 seconds due to the 10-minute charging rate and the 0.9 charge factor set in **Model Formulation**.

Conclusions

Fast charging batteries play a critical role in encouraging wide-scale adoption of EVs to help reduce the effects of climate change from conventional gasoline vehicle emissions. Battery technology is constantly improving, and in order to achieve charging in under 15 minutes this paper suggested an approach to study the effects of the active material size in each electrode.

A decrease in the active material radius was found to increase the rate at which the mole fraction reached a steady state level, meaning all of the lithium that could be reacted had been reacted after a shorter time interval. With smaller particles, the surface area increases, therefore there are more surface sites for the reaction to occur. While there is a limit to how small the active material particle size can be, literature suggests that 2 μm is the lower limit for graphite. This value was used as the lower limit in the model.

Future research should incorporate temperature effects during fast charging while also examining active material radius effects. Another suggestion for future research is to observe how the active material particle shape and surface defects play a role in the lithium surface reactions over time.

Acknowledgments

Bonus meme

References

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