

## Introduction/Motivation

This paper looks at the molar fractions of Lithium in the anode and cathode of a Lithium-ion battery through simulations using Jupyter notebook. The model battery is composed of a graphite ( $C_6$ ) anode and a cobalt oxide ( $CoO_2$ ) cathode with an electrolyte separator composed of hexafluorophosphate ( $PF_6$ ) as well as ethylene carbonate ( $(CH_2O)_2CO$ ) and dimethyl carbonate ( $(OC(OCH_3)_2)$ ).

Lithium-ion batteries are used for batteries in electric vehicles, making them a good candidate for research. Fast charging these batteries is essential as the convenience and practicality of electric vehicles are linked to the time it takes to charge. Research is now going into achieving the stated goals of the United States Department of Energy which looks to attain Extreme Fast Charging, defined as 80% capacity charged in 15 minutes or less. [1] One such example of this research is “Electrolyte Design for Fast-Charging Li-Ion Batteries” where different low-viscosity species are used to improve battery design. In order to reflect this push toward Extreme Fast Charging, a charge time of fifteen minutes was used, with a charge fraction of 80%.

Using this battery, the molar fractions of Lithium in the anode and cathode were calculated. The size of graphite and cobalt oxide particles were then altered to show the effect this has on the molar fractions.

## Model Formulation

The first step in creating a model was establishing the conservation of charge and the effect it would have on a battery. This gives Equation 1:

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

Given the following:

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

$$A_{surf} = 4\pi r_p^2 N_p \quad (3)$$

$$n_p = \frac{N_p}{A_{geo}} \quad (4)$$

$$A_{fac} = \frac{A_{geo}}{A_{surf}} \quad (5)$$

Eventually the equation becomes:

$$i_{dl} = -i_{ext} \frac{r_p}{3H_{el}\epsilon_s} - i_{Far} \quad (6)$$

The Faradaic current was calculated using the Butler Volmer equation:

$$i_{Far} = i_o \left( e^{\frac{-nF\beta\eta}{RT}} - e^{\frac{nF(1-\beta)\eta}{RT}} \right) \quad (7)$$

while the external current was found using the charge rate and capacity of the cell. Using these values and given properties of the cell, the double layer current was established. This was then used to calculate the change in double layer potential over time applying the equations below.

Using the following balance equation:

$$\frac{dQ_{dl}}{dt} = i_{dl} A_{surf} \quad (8)$$

And given:

$$Q_{dl} = A_{surf} C_{dl} \Delta\phi_{dl} \quad (9)$$

$$\Delta\phi_{dl} = \phi_{elyte} - \phi_{an} \quad (10)$$

The equation becomes:

$$\frac{d\Delta\phi_{dl}}{dt} = \frac{d(\phi_{elyte} - \phi_{an})}{dt} = \frac{i_{dl}}{C_{dl}} \quad (11)$$

This change in double layer potential was used to calculate the changing Faradaic current over time.

The final piece to calculating the mole fractions over time used the following equation:

$$\frac{dX_k}{dt} = \frac{1}{C^o} \frac{1}{\varepsilon_s} \frac{A_{surf}}{A} \frac{1}{H_{an}} \dot{S}_k \quad (12)$$

$$\text{Where: } \dot{S}_k = \frac{-i_{Far} * v_{Li}}{n_{an} * F} \quad (13)$$

By integrating this change in mole fraction over the amount of time it takes to charge the battery, a plot can be created for the total mole fraction versus time. The total time modeled is 720 seconds, based on the 15-minute (900-second) charge time and a charge fraction of 0.8, as defined for extremely fast charging. Using this approach, the mol fractions of Lithium in both the anode and cathode were simulated.

## Results

Using the above methods, Figure 1 was created for a particle radius of  $4 \times 10^{-6}$  meters [2] for graphite, and  $8.5 \times 10^{-6}$  meters [3] for cobalt oxide.

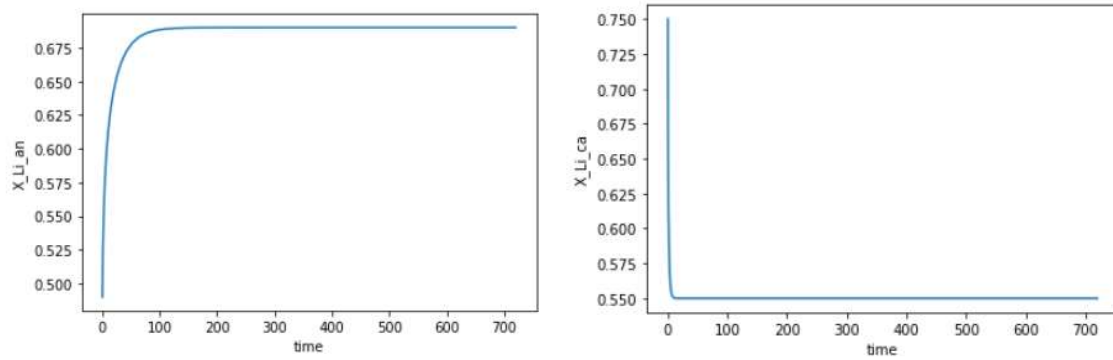


Figure 1: Lithium mole fractions with  $r_{p\_an}=4 \times 10^{-6}$  m (left) and  $r_{p\_ca}=8.5 \times 10^{-6}$  m (right)

Then, to capture the effect of a reduction in particle radius, the radius was reduced by a factor of 10. These results are shown in Figure 2.

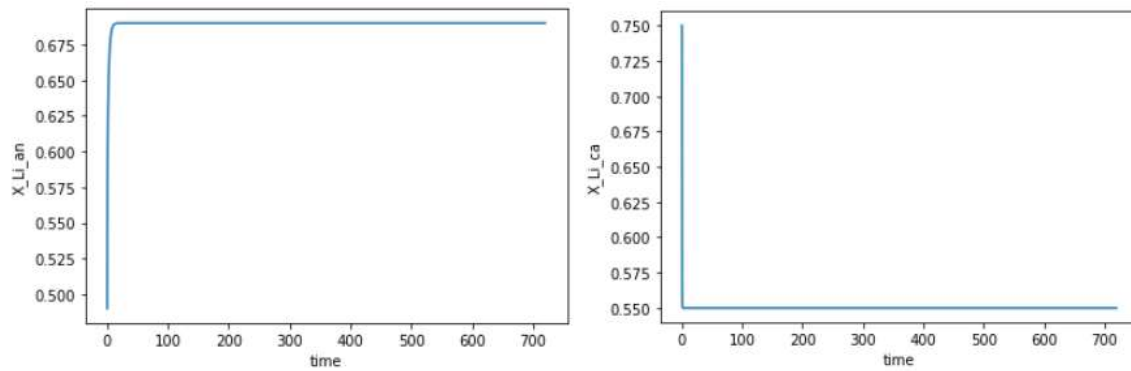


Figure 2: Lithium mole fractions with  $r_{p\_an}=4 \times 10^{-7}$  m (left) and  $r_{p\_ca}=8.5 \times 10^{-7}$  m (right)

Finally, in order to see the effect of an increase in particle radius and to help establish a pattern, the radius was increased from the original model by a factor of 10. The results are shown in Figure 3.

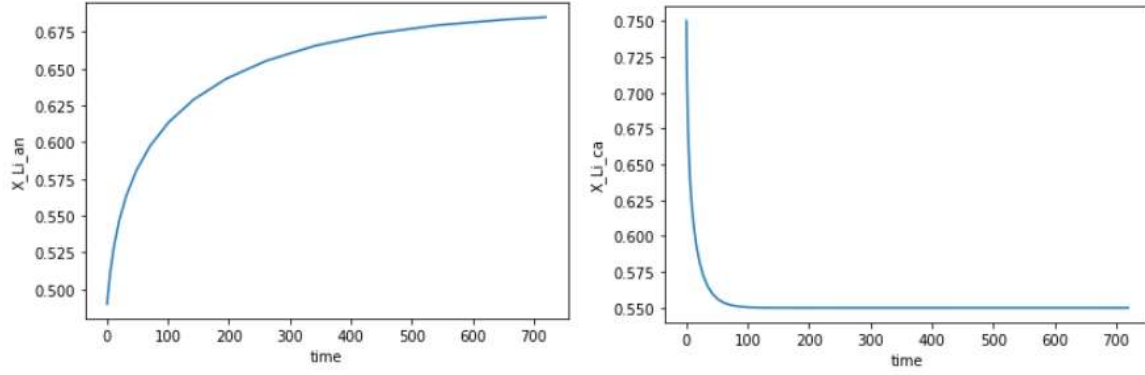


Figure 3: Lithium mole fractions with  $r_{p\_an}=4 \times 10^{-5}$  m (left) and  $r_{p\_ca}=8.5 \times 10^{-5}$  m (right)

### Discussion

As expected, the amount of Lithium grows in the anode as the battery charges and decreases in the cathode. Charging the battery essentially moves Lithium from the cathode back to the anode in order to build the battery's chemical potential for when it needs to discharge again.

However, given the beginning and ending mole fractions, it was expected the Lithium would transfer at a more stable rate, instead of mostly within the first 100 seconds and then leveling out as seen in Figure 1. This phenomenon can be explained by looking at the Faradaic current. As seen in Equation 13, the species production rate ( $\dot{s}_k$ ) is dependent on the Faradaic current. Figure 4 shows the Faradaic current compared with the mole fraction of Lithium for the anode while still at the original radius.

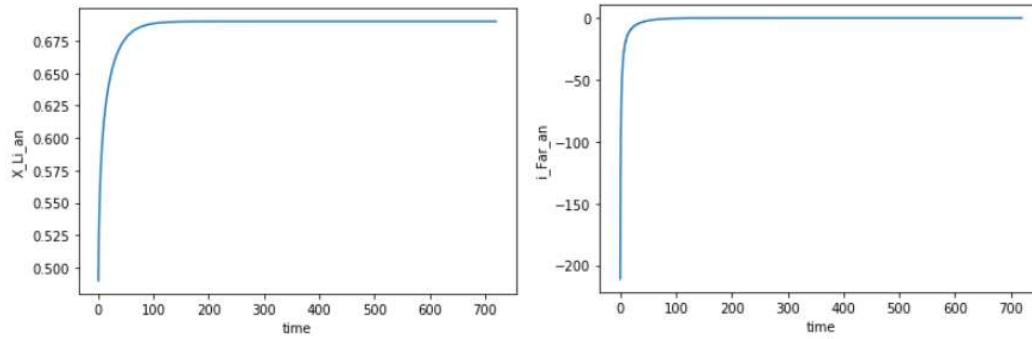


Figure 4: The mole fraction of Lithium in the anode (left) and the corresponding Faradaic current (right)

Figure 4 shows that the mole fraction does indeed reflect the Faradaic current, although the change in Faradaic current leads the change in the molar fractions slightly. This explains the rate of change in the molar fractions. Next the effects of changes in radius size are observed.

Comparing Figure 2 to Figure 1 shows the reduced radius sizes result in Lithium mole fractions changing more quickly. This is expected, as the reduced radius size leads to more surface area. While Equation 3 would seem to imply the opposite due to the  $r_p^2$  term, this is actually overpowered by the increase in the total number of particles. This total number of particles is calculated using the following equation:

$$N_p = \frac{3H\epsilon_k A_{geo}}{4\pi r_p^3} \quad (14)$$

Because this equation has the  $r_p^3$  term, the decrease in radius increases  $N_p$  more than it decreases the surface area from the  $r_p^2$  term. In other words, the smaller the particles, the more that fit, and therefore the higher the surface area.

Figure 4 confirms the pattern. As expected, the rate of mole fraction change is much slower than the previous trials. This again can be explained by the relationship of surface area and particle radius.

## Conclusions

Using this model and the results discussed, it is shown that the finer the particles of active material in the anode and cathode, the quicker the Lithium mole fractions will change. Because speed is the goal for batteries going forward, it makes sense to use the smallest particles of graphite and cobalt oxide possible.

## Sources

[1] Logan, E.R. and J.R. Dahn. "Electrolyte Design for Fast-Charging Li-Ion Batteries." Trends in Chemistry. April 2020, Vol. 2, No. 4

[2] "Particle size and particle shape of graphite powder." Application Graphite.

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[3] Cheng, Eric Jianfeng, Nathan John Taylor, Jeff Wolfenstine, Jeff Sakamoto. *Elastic properties of lithium cobalt oxide (LiCoO<sub>2</sub>)*. Journal of Asian Ceramic Societies. June 2017. Volume 5, Issue 2. P. 113-117.

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