

## ***Project – Lithium Electrolyte Characterization***

DATE: February 20, 2026

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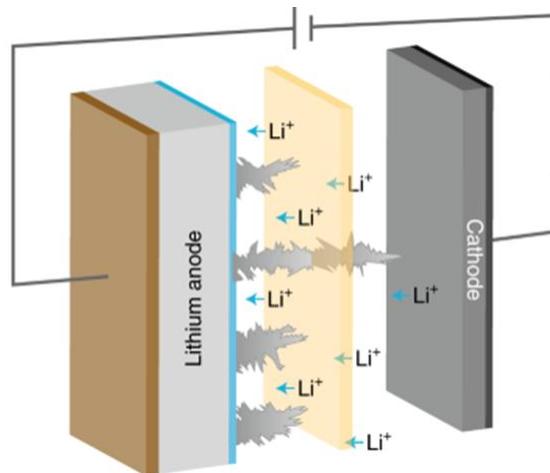
### **Guidelines:**

1. You have **3 days (72 hours) to complete the project.** You may select the optimal 3-day window for your schedule between Friday, February 20 at noon to Monday, March 2 at 9:00 pm to start and complete your project.
  2. **This project should be completed independently.** You are not permitted to discuss the project with other students in the class or anyone else. The course instructor and TAs are the only people with whom you may discuss the project and seek assistance. Questions should initially be directed to Prof. Stoykovich via email at [stoykovich@uchicago.edu](mailto:stoykovich@uchicago.edu). Inquiries will be addressed as quickly as possible during standard working hours (9 am ~ 5 pm) but response times will not be immediate particularly during off hours (*i.e.*, weekends, late at night, etc.), so plan accordingly.
  3. For this project, you are allowed to use the Chapra and Canale textbook, your notes from lecture, or your problem sets. In addition, you are allowed to use any code that you have written thus far for the purposes of the course.
  4. You are allowed to use the materials posted on the course Canvas page.
  5. You are allowed use the official Python resource pages:  
<https://www.python.org/>  
<https://matplotlib.org/>  
<https://www.scipy.org/>  
<http://www.numpy.org/>  
<https://pandas.pydata.org/docs/>
  6. **No other online resources are allowed.**
  7. **Submit your solution to the project to Canvas, both** in the format of a single Jupyter notebook and PDF of that notebook.
  8. The project will be graded with respect to (i) the accuracy of your solution, (ii) the methodology applied, (iii) your presentation of the results with a focus on clarity and professionalism, (iv) your creativity in developing your solution, and (v) your engineering interpretation of the results.
  9. The project should be viewed as an open-ended engineering project, so you are encouraged to analyze the system more than is specifically prompted and to take the analysis and presentation of results in directions of interest to you.
  10. **Any violation of these rules will be viewed as a breach of academic ethics** and subject to severe repercussions.
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## Background

Lithium (Li) ion batteries have revolutionized portable technologies and enabled near ubiquitous devices such as mobile phones, tablets, and laptops. However, they still fall short for certain demanding applications such as in electric transportation and storage of renewably generated energy. One exciting frontier in battery research is the Li-metal battery which, instead of intercalating  $\text{Li}^+$  ions in a graphene electrode (intercalation here means “insertion between layers in a crystal lattice”), plates Li metal onto the surface of the electrode. Due to the higher density of Li metal as compared to intercalated Li ions, these Li-metal batteries could offer much higher energy densities than state-of-the-art Li-ion batteries.

Despite these potential benefits, Li-metal batteries must address several technical challenges that have thus far limited their applicability. One of the most significant issues is that, rather than plating uniformly, Li metal often plates as spiky dendrites that pierce the separator that keeps the electrodes from contacting and causing an electrical short in the device (see Fig. 1). An approach that many researchers have explored to address this issue is the development of specialized electrolytes that inhibit this dendritic growth. In this project, we will process electrochemical data to extract the  $\text{Li}^+$  ion diffusivity of several potential electrolytes and then use a simplified diffusion model, along with other provided transport properties, to predict how resistant the electrolytes are to the growth of dendrites.



**Figure 1.** Illustration of Li metal dendrites growing from electrode surface. Adapted from Babu and Ajayan, “Good riddance, dendrites”, *Nature Energy*, 4, 631-632 (2019).

### 1. Characterizing diffusivity in Li electrolytes

One method electrochemists have for characterizing the  $\text{Li}^+$  ion diffusivity in an electrolyte is rotating disk electrode (RDE) experiments. Typically, RDE measurements are performed by collecting voltammograms (*i.e.*, plots of current or current density versus applied potential) at different rotation speeds of the electrode, extracting the limiting current density at each rotation speed, and then fitting the resulting data to the Levich equation to determine the  $\text{Li}^+$  ion diffusivity ( $D$ ). The Levich equation is

$$i_L = (0.620)nFD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C$$

where

$D$  =  $\text{Li}^+$  ion diffusivity in the electrolyte

$i_L$  = mass transfer limited current density

$\omega$  = angular velocity

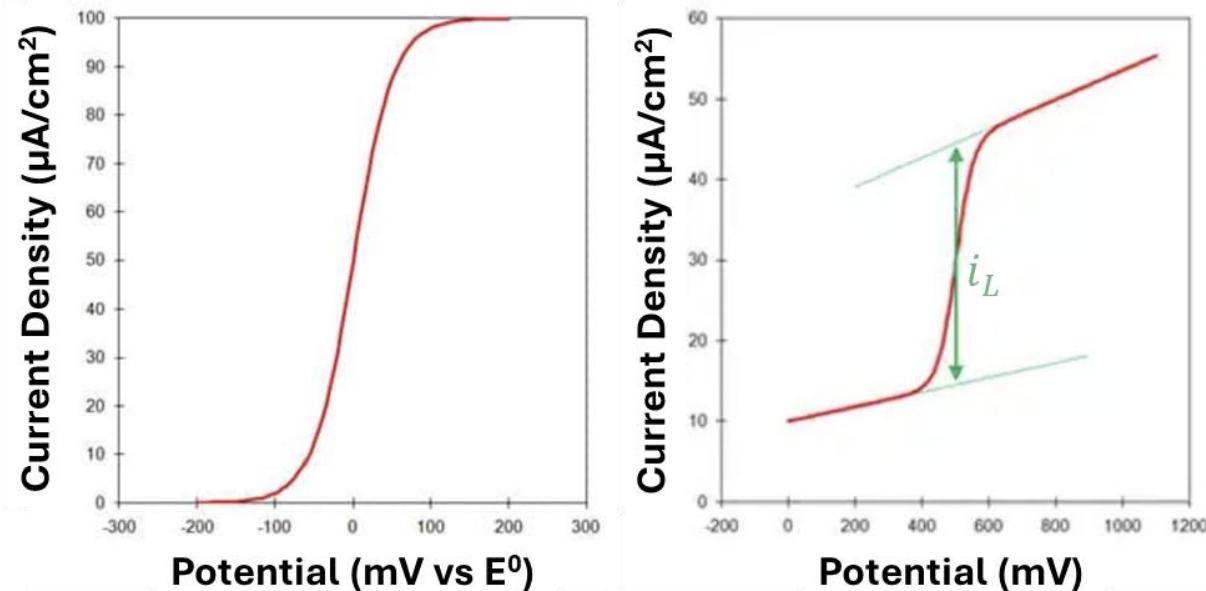
$\nu$  = kinematic viscosity

$C$  = electrolyte concentration

$F$  = Faraday constant,  $9.64853321 \times 10^4$  C/mol

$n$  = number of electrons involved in the electrochemical reaction of interest; in this case for Li,  $n = 1$  ( $\text{Li}^+ \leftrightarrow \text{Li}^0$ )

The voltammograms are generated by gradually increasing (also known as “sweeping”) the potential at the electrode and measuring the current response. In ideal conditions, this data will form a perfect sigmoidal curve, the height of which is  $i_L$  (see left panel of Fig. 2, with  $i_L = 100 \mu\text{A}/\text{cm}^2$ ). In practice, however, there is often a background current caused by reactions with the solvent or impurities and for which corrections must be made in the data analysis process. This background current can be different on the low- and high-voltage sides of the curve, and thus to estimate the limiting current density  $i_L$  one must take the height of the upper plateau compared to the lower plateau at the midpoint of the curve (as illustrated in the right panel of Fig. 2). The midpoint of the curve can be approximated by finding the point of inflection of a background corrected current or current density versus potential signal.



**Figure 2.** Left, an idealized voltammogram. Right, common shape of empirically measured voltammograms and illustration in green of how the mass transport limited current density ( $i_L$ ) is estimated.

- (a) Three electrolytes are being studied here, with Table 1 detailing some information already known about them.

**Table 1.** Physical parameters of electrolytes under investigation.

Concentration (M)	Kinematic Viscosity (cm <sup>2</sup> /s)	$t_p$
Electrolyte 1	1	0.025
Electrolyte 2	4	0.1
Electrolyte 3	1	0.2

In addition, RDE experiments have been performed at 4 different electrode rotation speeds for each electrolyte. The raw voltammogram data are provided as Excel files (.xlsx) for each electrolyte, with individual worksheets in each file reserved for a specific rotation speed (noted in rotations per minute or rpm). Using pandas, read the data from each of the RDE\_data Excel files for Electrolytes 1, 2, and 3 (*Note: Artificial data sets generated with the assistance of AI for illustrative purposes*). On a separate figure for each electrolyte, plot the 4 potential sweep curves. Please be sure to provide clear labels for the plots and make them presentation-quality.

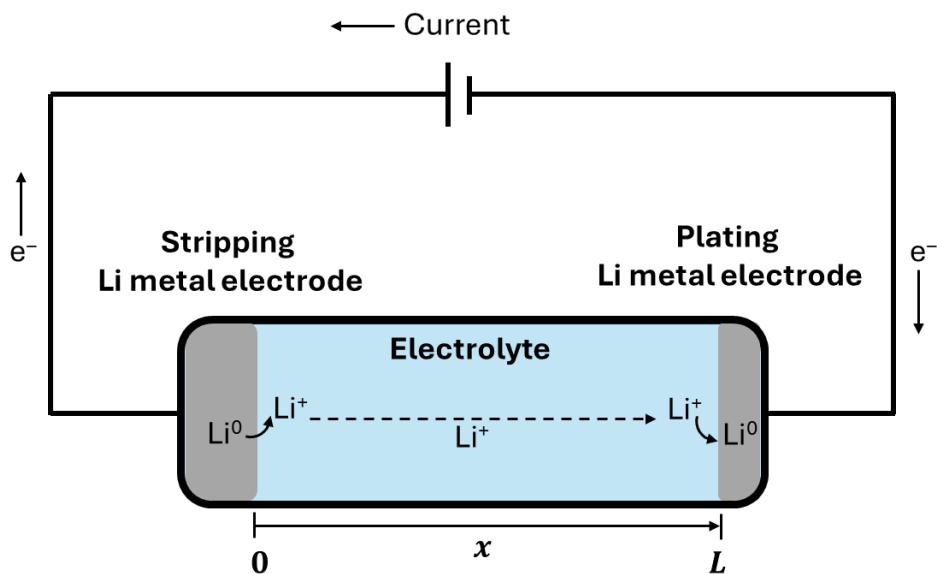
- (b) Create a function that accepts as arguments the data for one potential sweep curve along with a user-defined potential range (*i.e.*, a lower potential and a higher potential). The function should then perform a linear regression on the voltammogram data between the two potential bounds and return the fitting data.
- (c) Create a function that accepts as arguments the data and two bounds over which you want to find the baseline plateau (*i.e.*, the plateau in current or current density on the sigmoidal curve at the smaller potentials and with lower currents) and perform a background subtraction. This function should apply the function from part (b) to determine the background signal for the baseline plateau and then subtract that signal from the whole data set.  
Have the function also generate a figure with subplots. In the first subplot, provide the original data, two vertical lines representing the bounds, and the fitted background signal. In the second subplot, provide the dataset after the background subtraction has been performed.
- (d) Identify the upper plateaus in the baseline corrected datasets. Use your function from part (b) and plot the fitted upper plateaus alongside the data.
- (e) Next, define a function that accepts as arguments the baseline corrected data and finds the point of inflection. Here is a recommendation for how to go about it:
  - (i) Downsample the data by choosing every N data points.
  - (ii) Calculate the second derivative and plot. Manually adjust to find an appropriate value of N that is small enough to give sufficient resolution around the point of inflection, but is also large enough that the calculated derivative is not dominated by the noise in the data.
  - (iii) Interpolate to generate a smooth function for the second derivative and then apply a root finding method to identify where the second derivative is equal to zero.
- (f) Evaluate the height of the upper plateau at the point of inflection and record this as  $i_L$ . Report the results for all available data as a plot of  $i_L$  versus angular velocity  $\omega$ .
- (g) Fit this data to the Levich equation to determine the  $\text{Li}^+$  ion diffusivity in each electrolyte. Demonstrate and discuss the quality of the fit of the theory to the empirically measured data. For a sanity check, the diffusivities of  $\text{Li}^+$  ions in liquid electrolytes should generally be in the range of  $10^{-8}$  to  $10^{-6} \text{ cm}^2/\text{s}$ .
- (h) What are the units of the 0.620 constant in the Levich equation?

## 2. Modeling time-dependent concentration profiles and dendrite formation

It is beneficial to be able to predict how well an electrolyte will resist dendrite formation. One metric researchers have used for this purpose is “Sand’s time” which specifies how long it takes

for dendrites to start forming, and thus the transition from stable to dendritic growth, when running a symmetric Li cell at an elevated current. Molecular-level research has shown that dendrites begin to form at elevated currents when the concentration of  $\text{Li}^+$  ions approaches 0 at the electrode where the Li metal is being plated. In a  $\text{Li}^+$  ion starved environment, Li metal will favor dendritic deposition as opposed to uniform plating.

Figure 3 illustrates the system to be modeled. Here the model will only be used to analyze half of the cell, from the electrode where Li is being stripped to the center of the cell. The concentration gradient should be symmetric given the symmetric nature of the cell being modeled, and this approach will simplify the boundary conditions.



**Figure 3.** Diagram of a symmetric Li metal cell.

The governing equation that describes the concentration of  $\text{Li}^+$  ions as a function of the position in the cell and operation time ( $c(x, t)$ ) is a simple model given by Fick's second law of diffusion.

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

Although there are electrostatic, convective, and intermolecular forces at play in real Li cells, such complicating factors are not captured by this model. Therefore, this simple model is only valid for very dilute electrolytes. Real electrolytes are typically used at higher concentrations than what would be considered sufficiently dilute for this model to hold, however, the simplicity of the model is such that it is still frequently used to provide estimates of the  $\text{Li}^+$  ion concentration profiles in Li cells.

The boundary conditions for the model in Li cells are given as follows:

$$-D \frac{\partial c}{\partial x} \Big|_{x=0} = (1 - t_p) \frac{i}{F}$$

$$c(x = L/2, t) = c_0$$

The first boundary condition can be interpreted as the flux of  $\text{Li}^+$  at  $x = 0$  due to generation from the stripping electrode. The second condition is based on the observation that if  $\text{Li}^+$  is being consumed and produced at the same rate at each electrode, then the concentration profile will always be symmetric and the concentration at the center of the cell (*i.e.*,  $x = L/2$ ) is constant throughout. There is also an initial condition at  $t = 0$  that  $c(x, 0) = c_0$  because the concentration of the  $\text{Li}^+$  ions are uniform throughout the cell.

In these equations, the variables are defined as:

$c$  = concentration of  $\text{Li}^+$  ions

$c_0$  = initial concentration of  $\text{Li}^+$  ions in the electrolyte, as provided in Table 1

$D$  =  $\text{Li}^+$  ion diffusivity in electrolyte

$i$  = current density

$t_p$  = transference number, as provided in Table 1. The transference number is a transport property of the electrolyte that can be understood as the fraction of the current that is carried by  $\text{Li}^+$  ions versus the anion. A  $t_p = 1$  means the current is carried only through  $\text{Li}^+$  ions, *i.e.*, the anion is completely immobile which theoretically can occur for certain solid-state electrolytes. A lower  $t_p$  means the anion is moving along with the  $\text{Li}^+$  ions which leads to greater concentration polarization.

$L$  = distance between the surfaces of the stripping and plating electrodes

$F$  = Faraday constant,  $9.64853321 \times 10^4 \text{ C/mol}$

- (a) Convert this differential equation into a form that allows it to be solved using finite difference methods. Provide your work in a markdown cell of your jupyter notebook.

*Hints:*

- Use the notation  $c_i^l$  to represent the concentration at position  $i$  and at time  $l$ .
- Develop an implicit method that relates  $c_i^{l+1}$  to  $c_i^l$  and other information at time  $l + 1$ . No concentrations at neighboring nodes at time  $l$  should be used (*e.g.*, do not use  $c_{i-1}^l$  or  $c_{i+1}^l$ ).
- Use first-order and second-order finite difference approximations for the  $\partial c / \partial t$  and  $\partial^2 c / \partial x^2$  terms, respectively. In other words, the errors of the approximations should scale as  $O(\Delta t)$  and  $O(\Delta x^2)$ .
- Clearly identify the defining equations at internal nodes, as well as for the boundary nodes at  $x = 0$  and  $x = L/2$ .

- See Ch. 27.1.2 in the Chapra and Canale textbook for general guidance on the finite difference method and implementation of Dirichlet and Neumann boundary conditions. Chapter 30 may also be beneficial.
  - Be careful with units when implementing, as some provided data may need to be converted prior to running the calculations.
- (b) Create a function that accepts as arguments the necessary model parameters and returns the coefficient matrix for the equations that define the system at each time step. Create a second similar function that returns the constant vector for the equations that define the system at each time step.
- (c) Define a function that accepts as arguments the  $\text{Li}^+$  ion concentration profile at the time  $l$  and any other necessary model parameters, and then solves for and returns the  $\text{Li}^+$  ion concentration profile at the time  $l + 1$ . In other words, this function should perform an integration over one  $\Delta t$  time step only and should not iterate further with respect to time.
- (d) Next, define a function that accepts as arguments the initial  $\text{Li}^+$  ion concentration profile, the time step for integration ( $\Delta t$ ), the time duration over which to integrate the model, and any other necessary model parameters. This wrapper function should then call the subroutines written in parts (b) and (c) to calculate and store the  $\text{Li}^+$  ion concentration profile over time.
- (e) Now apply the model to calculate the concentration profile for a cell of length  $L = 50 \mu\text{m}$  and a current density of  $i = 1 \text{ A/cm}^2$ . Use 100 nodes in position to approximate the  $\text{Li}^+$  ion concentration profile. (*Note: This is a much higher current density than that at which ordinary Li cells operate, but it is used here to better illustrate the differences between the electrolytes.*)
- (f) Prove that your model results satisfy the boundary conditions for this system for all times.
- (g) Create a function that accepts the array containing your  $\text{Li}^+$  ion concentration profile over time (*i.e.*,  $c(x, t)$ ) and plots  $\text{Li}^+$  ion concentration versus position. Colorize each curve using a color map to visualize how the  $\text{Li}^+$  ion concentration profile evolves with time. Make sure to include a color bar and labels as appropriate. For ease of comparison between electrolytes, report the concentration divided by the initial concentration.
- (h) Estimate the Sand's time ( $\tau_{sand}$ ) for each electrolyte (*i.e.*, Electrolytes 1-3) at the given conditions. The Sand's time is reached when the  $\text{Li}^+$  ion concentration at the surface of the plating electrode is 0, or alternatively by symmetry arguments, when the  $\text{Li}^+$  ion concentration at the surface of the stripping electrode is twice its initial concentration.
- (i) Given the simplicity of this model, there exists an analytical solution that specifies the Sand's time for known system parameters:

$$\tau_{sand} = \frac{\pi}{4} D \left( \frac{Fc_0}{(1 - t_p)i} \right)^2$$

Check to see if the Sand's time approximated numerically matches the analytical expectations and discuss.

- (j) Based on the predictions of the model and your analysis, which electrolyte is likely to be the most resistant to dendrite formation? Provide a reason why you may not expect this

electrolyte to perform well in a Li cell and explain how other factors influence the decision on which electrolyte to choose when designing a Li-metal battery.

(k) Explore the behavior of this system more deeply, if you wish. Some potential ideas for further exploration:

- Implement the integration across the full cell (*i.e.*, from  $x = 0$  to  $L$ ) using appropriate boundary conditions. Demonstrate the system is symmetric around the midpoint of the cell.
- Perform a sensitivity analysis by exploring the parameter space to determine which electrolyte properties (*e.g.*,  $D$  and  $t_p$ ) and cell design features (*e.g.*,  $L$  and  $i$ ) impact the Sand's time most significantly.
- Consider the behavior of the  $\text{Li}^+$  ion concentration profile if the polarization of the cell is reversed at the Sand's time. Does the concentration profile revert to the initial uniform concentration ( $c_0$  at all  $x$ ) by reversibly following the time evolution computed in part (g)? Or does the system exhibit hysteresis? Demonstrate and explain.
- What happens to the  $\text{Li}^+$  ion concentration profile if the current is turned off at the Sand's time? How long does it take for the  $\text{Li}^+$  ion concentration to achieve a steady-state profile through the system?
- Any other ideas that you find interesting and that can be addressed via analysis of the model...