Modeling Ion Transport and Dendrite Formation in All-Solid-State Lithium-Ion Batteries

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Introduction

All-solid-state lithium-ion batteries (ASSLIBs), which use Li metal as anode, are considered as more efficient and safer alternatives to traditional lithium-ion batteries due to their higher theoretical capacity and lower negative potential. [1]

Among the candidate solid electrolyte materials, Lithium Phosphorus Sulfide (LPS) with high Li ion conductivity is a promising candidate. However, there are major challenges such as the complicated porous geometries and multiple phases with different ion transport abilities. [2] Additionally, it is important to suppress dendrite growth at the anode/electrolyte interface during charging, which compromises battery performance. [3]

Many studies into dendrite suppression in ASSLIBs has focused on anode surface modifications. One study shows that simply creating a stamped micropattern at the anode surface is capable of suppressing lithium dendrite growth. [4]

In this study, we used the Lattice Boltzmann Method (LBM) to simulate charging processes in half-cells with a Li working electrode, virtual Li counter electrode, and LPS solid electrolyte. We identified the transport parameters of electrolyte that best promote ion transport and the anode morphologies that are best for forming smooth anode surface.

Lattice Boltzmann Method

Lattice Boltzmann Method (LBM) is a discrete method that traces the evolution of the "ensemble-averaged distribution function" $f_i(x,t)$ representing the probability of finding a particle at site x at time t with velocity c_i. The Lattice Boltzmann equation (LBE) can be written as

$$f_i\left(x + c_i \Delta t,\, t + \Delta t\right) - f_i(x,t) = -\frac{1}{\tau}\left(f_i - f_i^{eq}\right)$$

where the left side of the equation is referred to as the streaming step and the right side is called the collision step. f^{eq} is the equilibrium distribution function and τ is the relaxation time reflecting the timescale of the bringing the local distribution function to local equilibrium. We incorporated ion transport in the electrolyte into LBE which was described using the time-dependent Nernst-Planck equation, shown below:

$$J_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \varnothing$$

where J_j is the mass flux of species j; D_j is the diffusion coefficient; C_j is the local concentration; z_j is the charge on species j; F is the Faradic constant; R is the ideal gas constant; T is the system temperature; $\varnothing$ is the local electrical potential.

The electrochemical reactions on the anode/electrolyte interfaces are driven by the overpotential, and the current density can be computed by the modified Butler-Volmer (B-V) equation shown below:

$$j_c = j_0\, e^{\left((1-\alpha_1)\Delta \mu_e / RT\right)}\left(e^{\alpha_1 F\eta / RT} - e^{-\alpha_2 F\eta / RT}\right)$$

where j_0 is the exchange current density; α_1 and α_2 are symmetry factors (we set $\alpha_1 = \alpha_2 = 0.5$); R is gas constant; T is temperature; η is the local overpotential; $\Delta \mu_e$ is the electrochemical potential change in the electrons due to the change of local morphologies. [5]

Methodology

Dendrite Formation

In our simulations, we considered three interface morphologies – rough with no micropattern, smooth with micropattern, and rough with micropattern, as shown in Fig. 1 below:
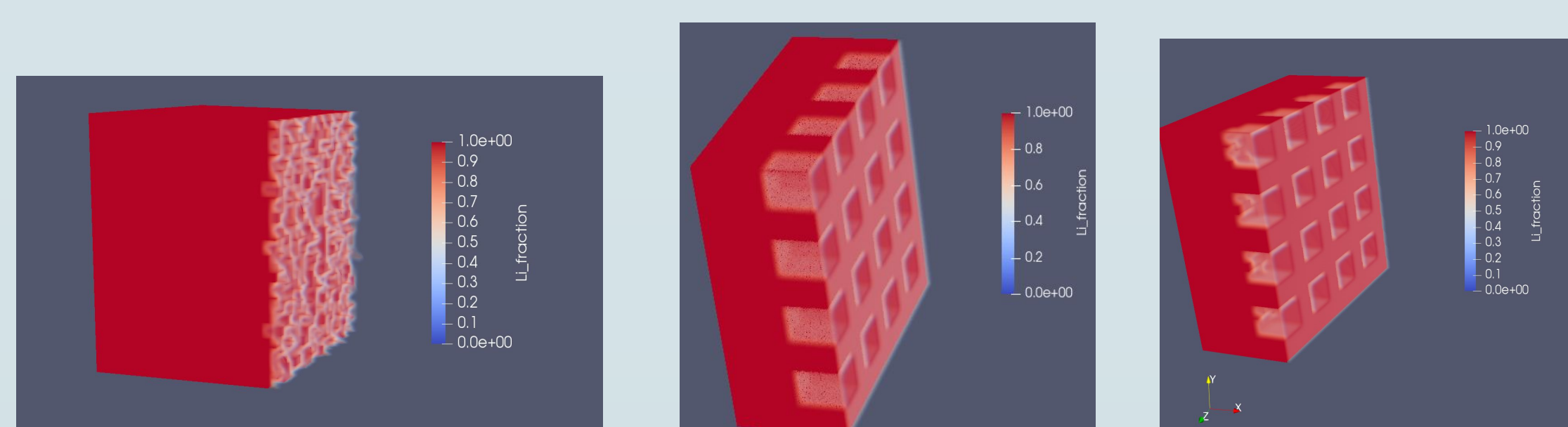

Fig. 1: (Left) Rough morphology with no micropattern; (Middle) Smooth morphology with micropattern; (Right) Rough morphology with micropattern

For the rough interface, we studied the effect of electrolyte porosity on dendrite growth. For the remaining interface morphologies, we measured dendrite formation at 0% porosity and varied charge current, surface roughness, and micropattern hole size.

We quantified dendrite growth between the working electrode and electrolyte by calculating the change in surface area for the working electrode, Li fraction at each node, and potential of the half-cell.
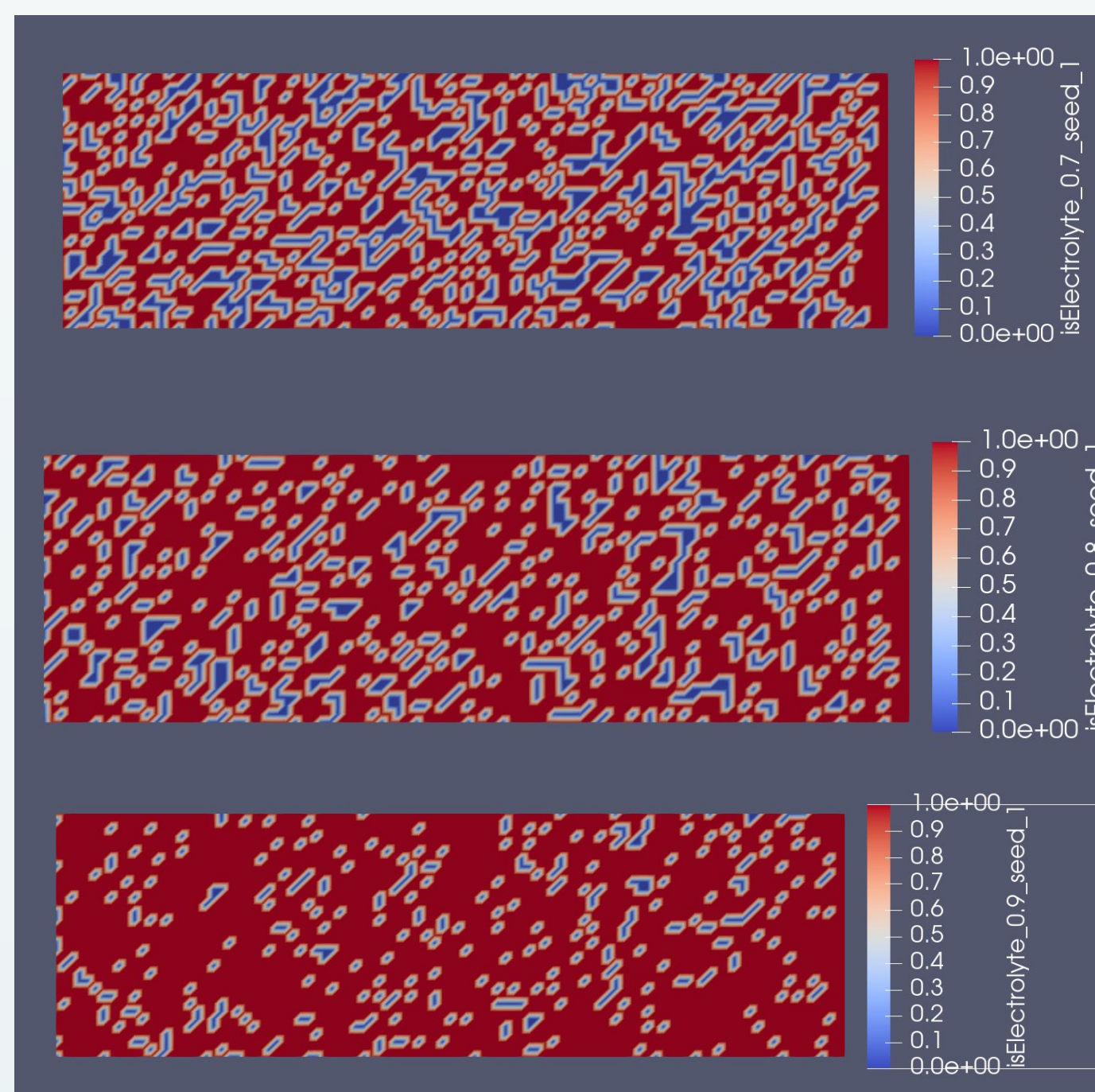
Ion Transport

Fig 2. The porous electrolytes with 10%, 20%, and 30% porosity(blue:pores, red: electrolyte).

To quantify ion transport through the electrolyte, diffusion limited current density values were taken from simulations with varying diffusivity (3.13×10^{-4}, 3.13×10^{-5}, 3.13×10^{-6} mm^2/s), porosity (0%, 10%, 20%, 30%), and mobility(1×10^{-4}, 1×10^{-5}, 1×10^{-6} mm^2/(sV)). Diffusivity and mobility were characterized at each node in the Lattice-Boltzmann Simulation, while porosity was modeled by removing nodes, preventing ion transport through those areas.

Results and Discussion

Dendrite Formation

We found that a higher porosity in the electrolyte increases dendrite formation, while in our trial with 0% porosity, the Li ions concentration at the anode was more uniform, creating a smoother surface with less dendrite growth.
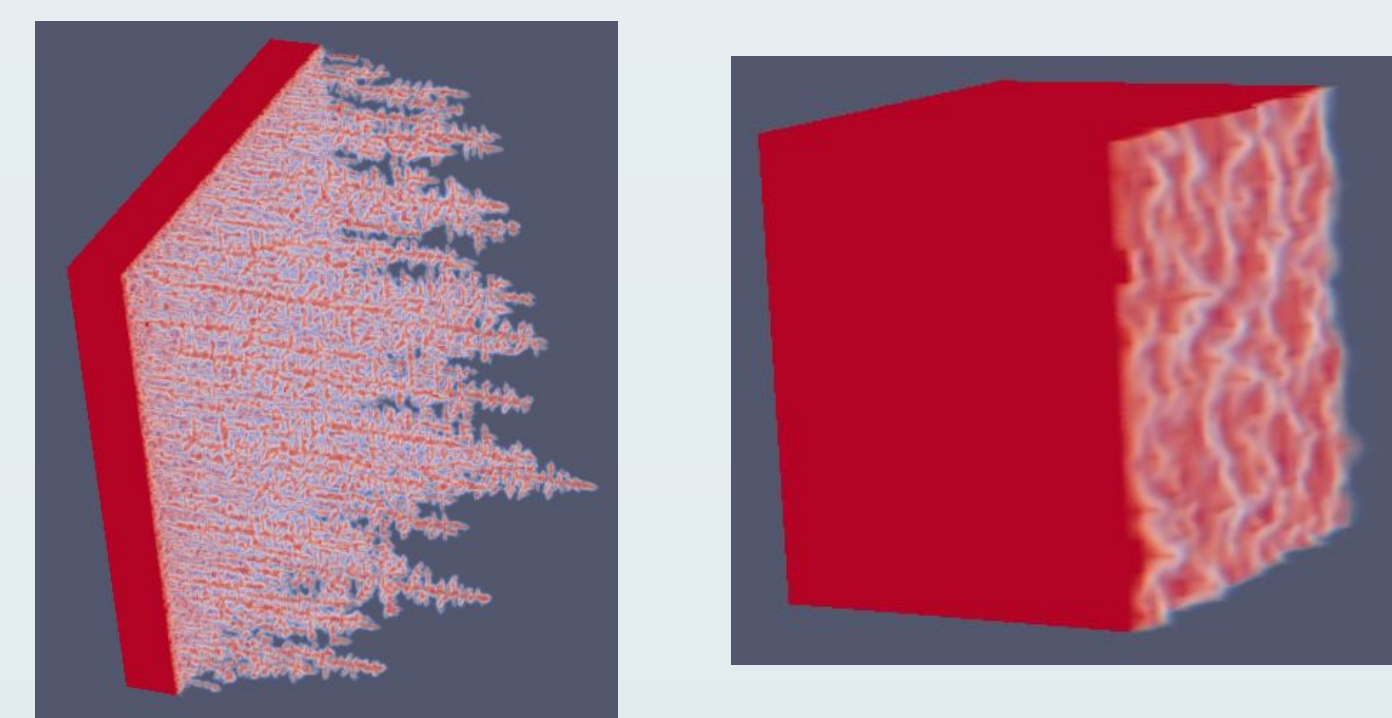

Fig. 3: (Left) 16.5% porosity; (RIght) 0% porosity

The results of our trials at 0% porosity are summarized in **Table 1** below. All trials shown were run with a surface standard deviation of 0.5 microns. We also ran trials with stdev at 0.1 and 1 microns but found similar trends. Current density was varied between low, medium, and high values (0.1, 0.5, and 1.0 mA/cm^2), and here, we expressed the current density in terms of the diffusion limited current density for our trials, which was 0.025 mA/cm^2.

Micropattern Hole Size (microns)	Current Density Over Diffusion Limited Current Density	Percent Change in RMS roughness
0	3.98016	-5.99%
0	19.9008	-12.84%
0	39.8016	-8.54%
2	3.98016	-77.88%
2	19.9008	-77.65%
2	39.8016	-77.86%
4	3.98016	-44.30%
4	19.9008	-44.30%
4	39.8016	-50.12%
6	3.98016	-35.01%
6	19.9008	-35.35%
6	39.8016	-42.65%

Table 1: Values for percent change in surface roughness for the flat rough morphology and the rough with micropattern morphology

Our data shows the greatest decrease in surface roughness at a hole size of 2, followed by a hole size of 4, then 6, and lastly the control flat surface. Therefore, we concluded that a micropattern with a hole size of 2 best suppresses dendrite growth. At larger hole sizes, we found that a higher current density to diffusion limited current density ratio increases the drop in surface roughness.
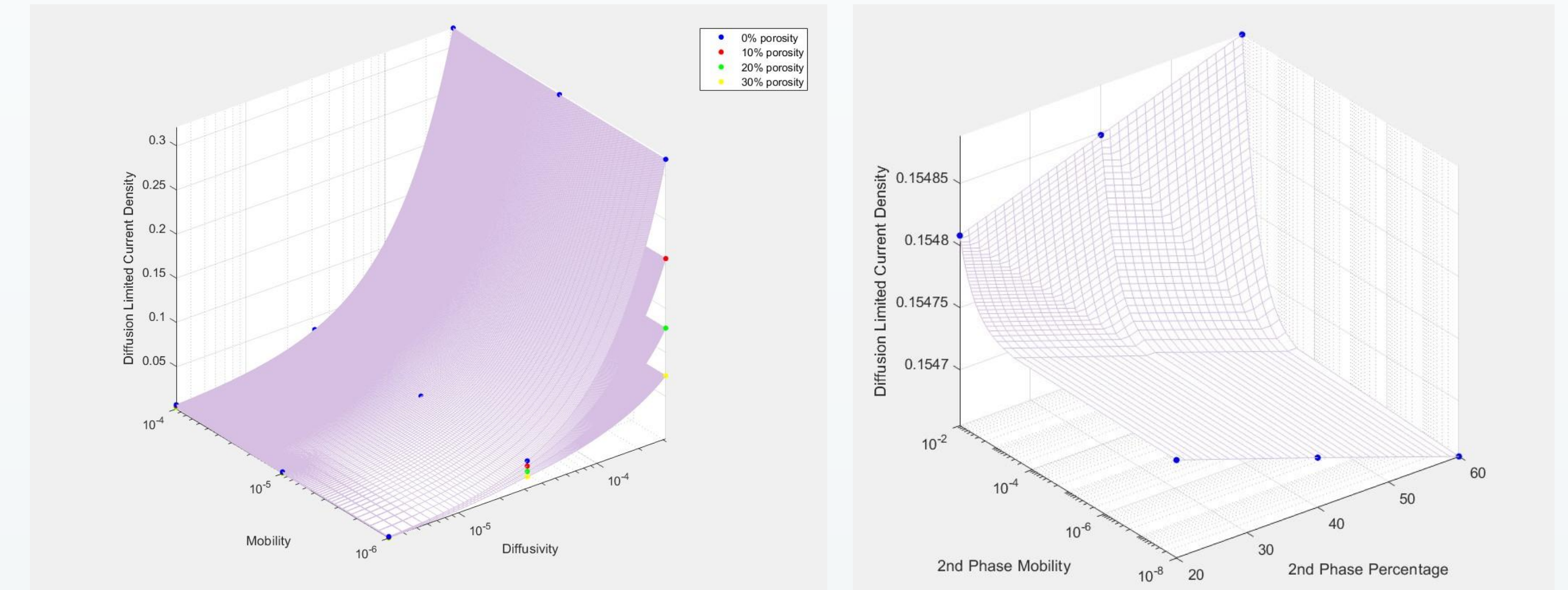
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Fig. 4 The Diffusion Limited Current Density showed limited changes when mobility was increased but increased drastically when diffusivity was increased.

Fig. 5 The Diffusion Limited Current Density was measured in a multiphase environment. A second phase was introduced to a 20% porous electrode with diffusivity = 3.13×10^{-5} mm^2/s, mobility = 10^{-5} mm^2/(sV).

We observed that mobility had a limited effect on current density while diffusivity had a pronounced effect on the current density. We also observed that raising the porosity decreased the measured diffusion limited current density with a peak forming at 0 porosity, diffusivity = 3.13×10^{-4} mm^2/s, and mobility = 1×10^{-4} mm^2/(sV).

For our multiphase simulations, we ran two different mobility values while the first phase was set at diffusivity = 3.13×10^{-5} mm^2/s, mobility = 1×10^{-5} mm^2/(sV), and an overall porosity of 20%. We tested second phase composition at 20%, 40%, and 60% with mobilities of 1×10^{-2} and 1×10^{-8}. We observed that increasing the second phase percentage when the second phase mobility was higher increased the diffusion limited current density while the opposite happened when the second phase mobility was lower than first phase mobility. However, we did not see a significant change, demonstrating that the second phase mobility had little impact on the overall diffusion limited current density.

Conclusion

Based on the dendrite formation trials, we concluded that adding a smaller micropattern to the Li-anode surface successfully mitigates dendrite growth. In the future, we plan to study different porosities and determine how adding micropatterns to the electrode-electrolyte interface can mitigate the larger dendrite growth associated with higher porosity. Additionally, in our trials, we added a simple stamping pattern, so in the future, we plan to investigate how other micropatterns can limit dendrite growth.

In the ion transport simulations, we concluded that diffusivity overall had a greater impact on the diffusion limited current density in the single phase simulations and that the second phase mobility could impact the observed current density if the mobility was different from the first phase in the multiphase simulations. Going forward, we would like to investigate how a greater data set of diffusivity/mobility combinations would impact the observed diffusion limited current density of single phase electrolytes while also investigating larger multiphase systems with a larger number of phases and various overall porosities.

References

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