

Bulk Properties of Amorphous Lithium Dendrites

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ABSTRACT

The formation of dendrites is a critical drawback for the utilization of lithium in secondary batteries. These amorphous crystals can pierce into the polymer electrolyte and short the cell. Therefore the design/selection criterion requires the mechanical compatibility of the grown dendrites from electrode and the solid polymer electrolyte. Hereby we grow the morphology of lithium. We compute the porosity and consequently, we perform force field calculations to extract its effective bulk modulus. We show that despite extremely high porosity, the dendrite bulk modulus yet remains significant.

INTRODUCTION

Lithium metal is arguably one of the most promising anode candidate materials for use in high-energy and high-power density rechargeable batteries.[1] Possessing the lowest density and smallest ionic radius, lithium has a very high gravimetric energy density ($\rho = 0.53 \text{ g.cm}^{-3}$). Furthermore lithium is the most electropositive metal ($E^0 = -3.04 \text{ V vs HSE}$), therefore coupling with any other cathode compound, it will likely provide the highest possible voltage, making it suitable for high-power applications such as electric vehicles.[2] The prominent issue with the lithium comes from its very low surface energy, leading to the formation of thermodynamically favorable branched dendrites during electrodeposition during each charge period.[3]

Earlier model of dendrites evolution had focused on the electric field and space charge as a responsible mechanism [4] while the later models focused on how ionic

concentrations affect diffusion limited aggregation (DLA). [5] These mechanisms all relate to the electrochemical potential [6], indicating that each could be dominant, depending on the localizations of the electric potential or ionic concentration in the cell domain. However in various instances, each mechanism appear dominant, depending on the magnitude of electric field and the electrolyte concentration.

Therefore their interplay would be the final determining factor, especially in continuum scale and large time periods. Therefore, we developed coarse grained computationally affordable algorithm that allowed us to reach to the experimental time scale (ms), which provided insights for current study. [7]

Previously we have approached the dendrites mechanics by constructing the pillars of lithium in oxygen-free glovebox, and subjecting them under compression load, until failure. We realized the importance of size effect on the elastic, bulk and shear modulus. [8] In this paper, we grow such dendrites for the lithium in a free solution. We quantify the porosity and bulk modulus of the microstructure. The results would be useful for designing mechanically compliant solid polymer electrolytes for prevention of short circuit.

METHODOLOGY

We have utilized the monte carlo coarse grained method (CG) for the creating the evolving dendrites is based on coarse-grained method, which has been part of our previous study. In the coarse grained method, the movement of individual ions is described by simultaneous cooperation of displacements from diffusion and migration. Therefore the electrochemical flux is generated from the gradients of concentration (∇C) and electric potential ($\nabla \phi$). At the atomic scale, the ions of higher concentration regions tend to collide and repel more and, given enough time, they diffuse to lower concentration regions following Brownian dynamics. In the continuum scale and time intervals larger than in inter-collision scales (fs), these random movements lead to the *diffusive* displacement $\delta \vec{r}_D$ that can be described by the diffusion length as: [9]

$$\delta \vec{r}_D = \sqrt{2D^+ \delta t} \hat{g} \quad (1)$$

where D^+ is the cationic diffusion coefficient in the electrolyte, δt is the large time interval and is a random normal vector in space, representing Brownian dynamics. Given

enough time, the multidirectional random vector \hat{g} will abolish any existing concentration gradient. The diffusion length represents the average progress of a diffusive wave in time, which is obtained from diffusion equation. [10]. On the other hand, within a small period of time, the ions tend to acquire drift velocity in the electrolyte medium, and their electromigrative displacement $\delta\vec{r}_M$ is given as:

$$\delta\vec{r}_M = \mu^+ \vec{E} \delta t \quad (2)$$

where μ^+ is the mobility of cations in electrolyte and \vec{E} is the local electric field.

The vector sum indicates the importance of directionality in equation 1. The diffusion either can help the migration or can hurt it based on local gradients of concentration and electric potential. While *electromigrative* displacement is toward electric field, the diffusive displacement is in random direction (due to vector \hat{g}) and tends to even out the existing concentration gradients.

Following CG simulations, we perform reactive force field (reaxFF) simulation on created morphologies to get the relative volume change, when subjected to a certain pressure. In reaxFF method the energy of the system is defined as function of bond order as below:

$$E_{sys} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdw} + E_{Coulomb} \quad (3)$$

Detailed explanation of Equation 3 can be found in the literature. [11]

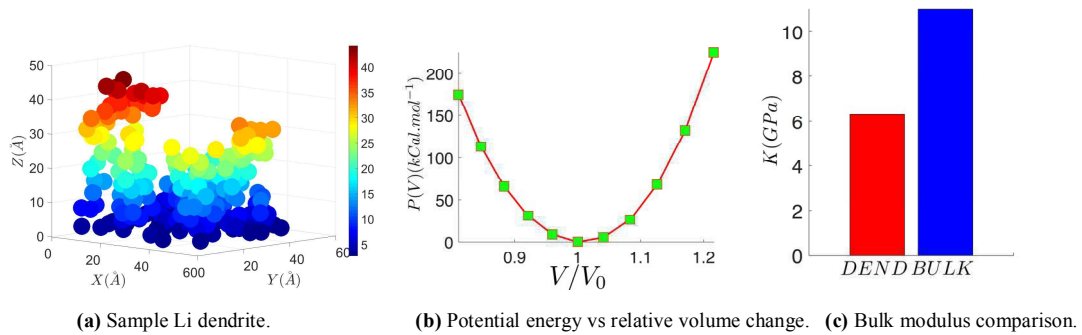


Figure 1: Simulation results.

RESULTS AND DISCUSSIONS

The CG method has been run for the lithium for deposition of 250 atoms and a sample result is shown in Figure 1a, with respective porosity of $\sim 80\%$.

The bulk moduli of these amorphous phases can be derived by fitting into the EOS to Birch-Murnaghan equation as follows: [12]

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 - \frac{3}{4} (B_0' - 4) \right\} \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \quad (4)$$

where $P(V)$ is the potential energy of the system, V_0 and V is the reference and deformed volumes. B_0 is the bulk modulus defined as:

$$B_0 = -V \left(\frac{\partial P}{\partial V} \right)_{p=0} \quad (5)$$

and B_0' is the derivative of bulk modulus B_0 with respect to pressure:

$$B_0' = \left(\frac{\partial B}{\partial P} \right)_{p=0} \quad (6)$$

The reaxFF framework has been trained for lithium and the amorphous phases is subjected to isotropic volume change. The respective trend is shown in Figure **1b**. The concave curves is fitted into the 4 which is the so-called equation of state (EOS).

Although the porosity of dendrite is very high with a significant amount of voids, the resulting bulk modulus is still a considerable amount. (Figure **1c**) This either can be attributed to the size effect that we have shown in our previous work. [8] or the geometrical effect of the existing pores inside the microstructure, which have convex geometry and act as a resistance for collapsing. Therefore assisting the strength of the structure, albeit very high fraction of voids.

CONCLUSIONS

In this paper, we have studied the electrochemical growth of lithium dendrites in a free solution. Performing reactive force field training for lithium we have obtained respective potential energy of the microstructure, when subjected to isotropic expansion/compression. We prove that the bulk modulus of the amorphous dendritic crystals remains significant despite the extremely low porosity relative to bulk phase. This study implies the importance of mechanics dendrites for application of metal electrodes in rechargeable batteries.

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