

Tunable Electrolytes for Studies on Dendrite Growth in Lithium Metal Batteries

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It has long been recognized that many of the battery chemistries that provide high theoretical energy densities employ lithium metal anodes. Unfortunately, batteries with lithium metal anodes may fail catastrophically upon repeated cycling, due to uneven, dendritic metallic lithium deposition during recharge. Lithium dendrites that cross the cell create a short-circuit that ends limits lifetime and may result in fire or explosion. Though lithium dendrite formation and propagation has been observed experimentally by several groups by optical imaging, electron microscopy, and monitoring cell potential during polarization or cycling, the relationship of the parameters governing dendrite formation and growth is still unclear. It is known that the common organic liquid electrolytes for Li-ion batteries (ex. EC/DMC + LiPF₆) significantly react with lithium, creating an inhomogeneous SEI that leads to uneven deposition. This is not the case for cells employing non-reactive polymer electrolytes, yet other than the recognition that delamination of the electrolyte initiates dendrite growth, these systems are not well characterized. Understanding what results in varying dendrite onsite times among cells employing varying polymer electrolyte compositions could enable the development of safe, rechargeable lithium metal batteries. In this talk, we will report on the quantitative effects of varying electrolyte modulus, interfacial impedance, ionic conductivity, mobile ion concentration, and lithium transference number on dendritic lithium growth, studies enabled by the development of tunable electrolyte platforms.

Systematic testing of the parameters that effect dendrite onset time and propagation has been limited due to the intrinsic coupled nature of these parameters. For example, it is difficult to increase the ionic conductivity of the electrolyte without significantly decreasing the interfacial impedance and mechanical modulus. In our studies, we have employed two different platforms – a nanoscale hybrid organic-inorganic electrolyte and a crosslinked co-polymer electrolyte – to differentiate the effects of these parameters. Each of the platforms may be systematically tuned.

In our previous work,¹⁻⁴ we have demonstrated the tunability of a nanoscale hybrid organic-inorganic electrolyte platform, where inorganic nanoparticles are functionalized with polymeric or ionic ligands and doped with lithium salt. Both dry and plasticized versions of the platform have been investigated. Use of appropriate organic ligands allows for the electrolyte modulus to be tuned over several orders of magnitude while the ionic conductivity changes relatively little by varying the inorganic content. Materials of this type display nearly athermal mechanical modulus, thus variations in temperature effect ion transport, but not the modulus. Use of ionic ligands (ionic-liquids or lithiated tethered anions) affords additional tailorability in supporting electrolyte content and/or ion transference. Similar tailorability, but higher modulus, can also be achieved using a crosslinked co-polymer platform.⁵ Figure 1 displays schematics of several different electrolytes employed.

Using these tunable platforms, we quantitatively measure the effects of change in electrolyte parameters on dendritic lithium growth as determined via the galvanostatic polarization and cycling methods. Results from galvanostatic polarization testing are compared with the predicted short-circuit time by Chazalviel,⁶⁻⁷ a summation of dendrite onset time τ_s (Sand's time) and the dendrite growth time t_g :

$t_{sc\ predicted} \sim \tau_s + t_g = \pi D \left(\frac{eC_0}{2Jt_a} \right)^2 + \frac{\sigma L}{\mu_a J}$, a function of the ambipolar diffusion coefficient D , ion concentration C_0 , current density J , anion transference number t_a , ionic conductivity σ , interelectrode distance L , and anion mobility μ_a . We find significant deviations between the experimentally determined and predicted short-circuit times, particularly for electrolytes with a shear storage modulus approaching 1 MPa or greater. We will compare our results from galvanostatic cycling tests to recent literature⁸ that suggests a linear correlation between electrolyte modulus and total charge passed until short-circuit, and demonstrate that longer cell lifetimes may be achieved at lower moduli by several mechanisms, including reducing interfacial resistance, addition of a supporting electrolyte, and anion immobilization.

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FIGURES

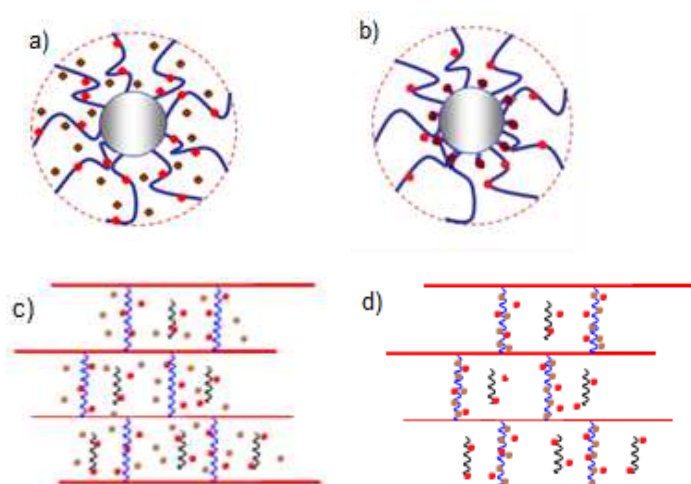


Figure 1. Schematics of tunable organic-inorganic hybrid (a, b) and crosslinked polymer (c, d) electrolyte platforms with free dopant lithium salt (a, c) and lithium exchanged, immobilized anions (b, d).