A bilayer electrolyte design to enable high areal-capacity composite cathodes in polymer electrolytes based solid-state lithium metal batteries

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Abstract

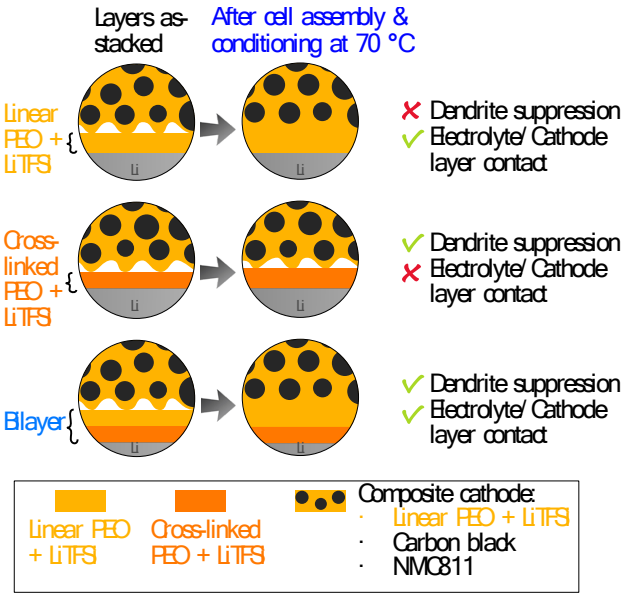
High-areal-capacity cathodes are needed for energy-dense solid-state batteries. Here, we demonstrate a bilayer polymer electrolyte design for cycling 3-6 mAh/cm^2 NMC811 composite cathodes. The bilayer electrolyte comprises a cross-linked PEO-based electrolyte layer and a linear PEO-based electrolyte layer. The former provides dendritic resistance, and the latter provides a seamless interface with the cathode during cycling. Using a single layer of either membrane led to severe shorting or extremely low Coulombic efficiency (C.E.) in the first cycle. The general concept of a rigid dendrites-inhibiting electrolyte facing Li anode, and a softer, cathode-integrated electrolyte that ensures contact with the cathodes during cycling may present a pattern for enabling high-energy-density cathodes.

Research on solid-state batteries (SSBs) has been invigorated in the past few years owing to the push to enable lithium metal anodes for achieving >400 Wh/kg cell-level energy densities, the timely discovery of several room temperature inorganic solid electrolytes, as well as to address the safety concerns of conventional lithium-ion batteries. Solid polymer electrolytes, one of the solid-electrolyte classes, will play an important role in the development of scalable solid-state batteries due to their higher processibility, flexibility, and soft nature, which can lead to intimate interfaces with the electrode materials resulting in lower contact resistances and compensate for volume changes of active materials during cycling. The past decade has also seen rapid development of novel polymeric electrolytes with improved room temperature ionic conductivities, transference

numbers, high voltage stability, and lithium dendrite resistance, all of which were lacking in poly-ethylene oxide (PEO), the oldest and most studied polymer electrolyte.[1-3]

Achieving >400 Wh/kg cell-level energy density in SSBs requires high areal capacity cathodes of at least 4 mAh/cm^2, which corresponds to a mass loading of ~21-25 mg/cm^2 of the nickel-rich $LiNi_xMn_yCo_zO_2$ or NMC cathode active material (assuming a capacity of 160-190 mAh/g depending upon the NMC-type).[4] Even higher loadings will be needed for LFP-based cathodes due to their lower nominal cell voltage (3.3 vs. 3.7 V). Increasing the cathode capacity or thickness in SSBs can introduce several new challenges apart from the more obvious rate capability limitations, such as higher volume changes during cycling which can put dynamic stresses at the various interfaces.[5, 6] For example, a larger amount of lithium would get plated and stripped during cycling of thicker cathodes. However, reports on the fabrication and testing of solid-state cells with high loading cathodes, especially with polymer electrolytes, remain scarce.[7] Relatively more reports with high loading cathodes can be found for all inorganic solid electrolyte-based cells, but their cell assembly typically involves several pressing and sintering steps for integrating the various layers, and testing is done under a continuous application of megapascals of pressure, which is not commercially viable.[8-10]

In this work, we report a cell design with a bilayer electrolyte/separator that allows cycling of 3-6 mAh/cm^2 composite cathodes made with NMC811, linear PEO + LiTFSi (3:1 by weight), and carbon black, in coin cell format SSBs. The cathodes were fabricated via the standard slurry-processing approach, followed by cold calendering to reduce the electrode porosity. The two electrolytes in the bilayer were 1) linear PEO with LiTFSi salt (same composition as the catholyte), and 2) cross-linked PEO-based polymer (made via thermally cross-linking PEO-based precursors poly(ethylene glycol) diglycidyl ether (PEGDGE) and Jeffamine 2000) mixed with LiTFSi salt. Both electrolytes contained no plasticizer (see supporting information for details). We found that the bilayer electrolyte mitigates the issues observed during cycling with either one of these membranes at a time, as shown schematically in Scheme 1. The detailed results are discussed next.



Scheme 1. Schematic representation of the three different cell designs and the associated benefits and issues during cycling. The left column shows the cell stacks as made, whereas the right column highlights the cathode/electrolyte layer interface changes after the cells were conditioned at 70 °C for two days.

Coin cells were fabricated via stacking the various layers, including the composite cathode (described above), either the linear PEO or cross-linked PEO based membrane, or both stacked on top of each other (linear PEO on the cathode side), and the commercial Li metal (600 µm thick) anode. After assembly, all cells underwent conditioning or rest step at 70 °C for two days to allow the various interfaces at the anode and cathode to become as conformal as possible, followed by charge/discharge cycling at a constant current of 0.05 mA/cm^2 at 70 °C. Cathode loadings were either ~3, ~4, or ~6 mAh/cm^2, calculated based on the theoretical capacity of 200 mAh/g for NMC811 charged till 4.3 V vs. Li/Li$^+$.

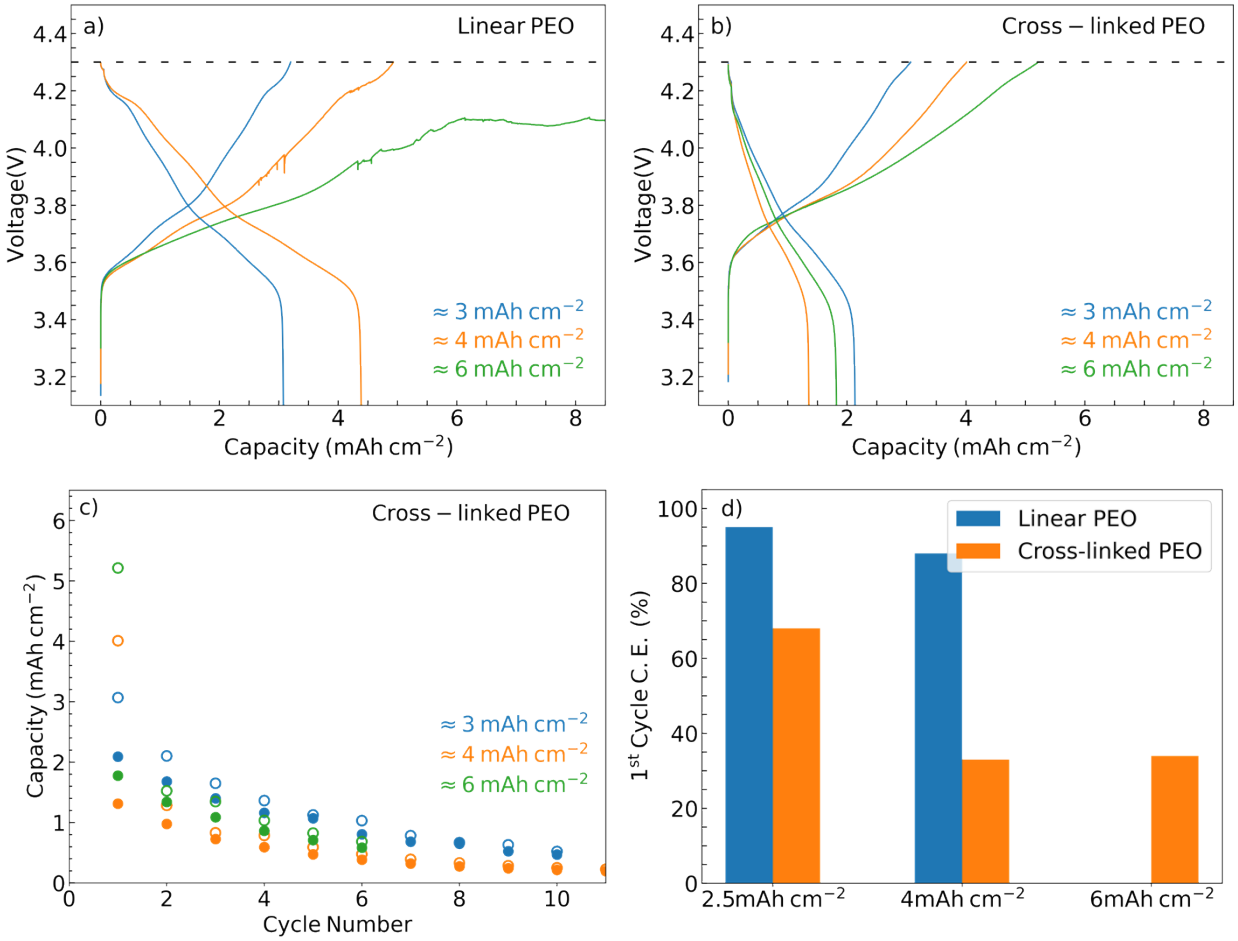


Figure 1. (a, b) Voltage profiles of the Li//NMC811 half cells containing cathodes of three different areal capacities and containing either linear PEO or cross-linked PEO as the separator layer, galvanostatically cycled with 0.05 mA/cm^2 current between 2.9-4.3 V and at 70 ºC. c) Charge (hollow circles) and discharge (filled circles) capacity of the Li//NMC811 half cells with different cathode loadings and cross-linked PEO as the separator layer. d) First cycle coulombic efficiency of Li//NMC811 half cells as a function of cathode areal capacity and polymer electrolyte separator type.

Cells containing only the linear PEO membrane showed well-defined plateaus for all cathode loadings suggesting low cell resistances (Figure 1a). However, cells with cathode loading of 4 and 6 mAh/cm^2 exhibited "voltage noise" during the first charge, which is known to be due to the formation of soft shorts,[11, 12] and which gets exacerbated as more lithium is cycled per half cycle.[13] It is worth mentioning that the soft short formation is quite unpredictable for this cell configuration. Statistically, higher loading (≥4 mAh/cm^2) cathodes always led to soft shorts with varying severity, but some soft short occurrences with loadings as low as 2 mAh/cm^2 were also observed. For the cells made with cross-linked electrolyte only, "voltage noise" during charging was not observed even for the thickest composite cathode (Figure 1b). This is consistent with several reports in the literature that have shown improved dendrite suppression ability of cross-linked PEO-based polymer electrolytes compared to their linear counterpart, primarily due to poorer mechanical properties of linear PEO-based electrolytes at elevated temperatures.[14, 15] The voltage plateaus, in this case, were lesser defined compared to the previous case, and overall cell polarization during charging was also higher, reflecting higher cell resistances (Figure S1). However, the bigger issue with this configuration was that a very small fraction of charge capacity (which matched well with the nominal cathode capacity based on the areal mass loading of NMC811) could be retrieved during discharge. The Coulombic efficiency (C.E.) seemed to improve in the following cycles when much less capacity was available to be cycled (Figure 1c). Nonetheless, the cells retained less than 20% of their nominal capacities after 10 cycles. In contrast, the linear PEO based cells did not show this severe capacity loss during the initial discharge, as can be seen from the first cycle C.E. comparison in Figure 1d (95% vs. 68% for 3 mAh/cm^2 loading, 88% vs. 33% for 4 mAh/cm^2 loading). Data for the cell containing 6 mAh/cm^2 loading cathode and linear PEO is not presented because of the severe soft-shorting during charge, which manifests as artificially high charge capacity. Some amount of soft-shorting observed for the cell containing 4 mAh/cm^2 cathodes and linear PEO caused its C.E. to be calculated lower than the 3 mAh/cm^2 cell. Interestingly, the C.E. for the cells with cross-linked PEO decreased dramatically with cathode loading.

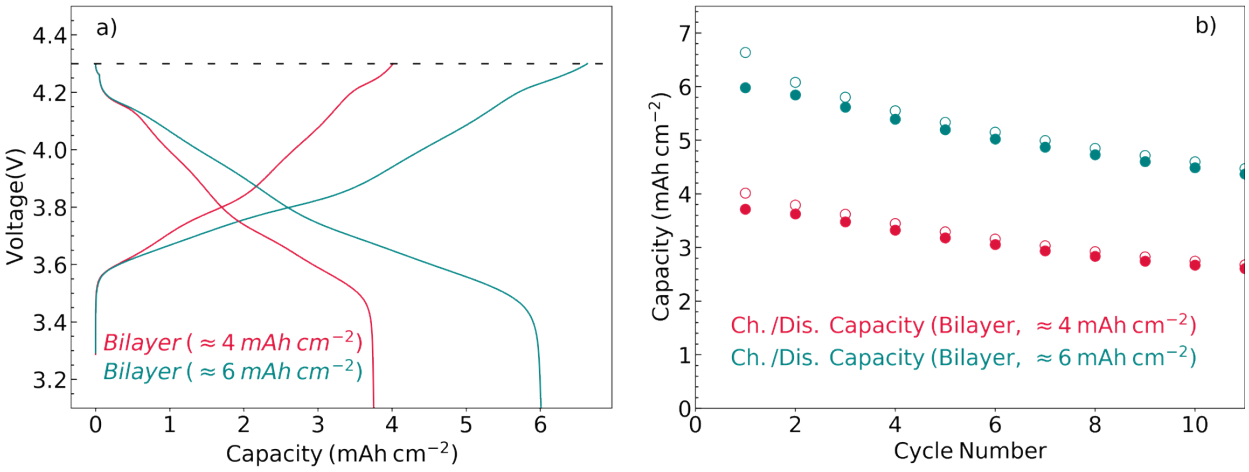


Figure 2. a) Voltage profile of the first charge/discharge cycle of Li//NMC811 half-cells containing bi-layer polymer electrolyte separator (cross-linked PEO on Li metal side, and linear-PEO on the cathode side) and cathodes of two different areal capacities, galvanostatically cycled with 0.05 mA/cm^2 current between 2.9-4.3 V and at 70 ºC. b) Long-term cycling of the two bilayer cells, with charge capacities shown as hollow circles and discharge capacities as filled circles.

Initial interpretation of the differences in cell performance between the two polymer electrolytes leads one to suggest electrochemical instability of the cross-linked PEO electrolyte at the lithium metal anode to be the contributing factor. However, that does not explain the decreasing trend of C.E. observed as a function of cathode loading. Instead, we found that inserting a linear PEO layer between the composite cathode and cross-linked PEO layer (a configuration called 'bilayer' here) completely mitigated the first cycle capacity loss observed with single-layer cross-linked PEO based cells. Figure 2a shows the first cycle charge/discharge profile of bilayer cells containing 4 or 6 mAh/cm^2 NMC811 composite cathodes. The C.E. observed was 92.5 % and 90.1 %, respectively. Voltage plateaus are well defined, and despite the presence of an extra layer, cell overpotentials are lower than cross-linked PEO-only cells (Figure S1). This is likely due to the chemical compatibility between the two polymer electrolytes used here, as polymer/polymer interface between two dissimilar polymer electrolytes can potentially add significant impedance to the cell.[16] In addition, because of the presence of cross-linked PEO, no soft-shorts were observed even for the highest loading cathode either in the first cycle or any time later during cycling. Longer-term cycling performance is shown in Figure 2b. The two cells retained 72% and 75% of their initial discharge capacities after 10 cycles, respectively. Most of the capacity loss occurring in these cells is likely due to the poor oxidative stability of linear PEO-based catholyte in the cathode with the high-voltage NMC811.[17, 18] The rapid capacity fade observed is similar to other reports of dry PEO-containing SSBs with high-voltage cathodes of lower loadings.[18-20]

The improvement in C.E. due to insertion of the linear PEO between cross-linked PEO and cathode layer rules out the Li metal interface to be the issue. Another possibility is the presence of a mechanically poor interface between the composite cathode and cross-linked PEO layer, which could not buffer greater volume changes in the cells containing thicker cathodes and resulted in capacity loss during discharge. Unlike linear PEO, which is soft and can easily undergo plastic deformation at 70 ºC, cross-linked PEO is not plastically deformable at this temperature and coin-cell pressure,[14] which may prevent the formation of a conformal contact with the microscopically rough surface of the composite cathode, and may make it prone to delamination/contact loss during cycling. Cell pressure increases during charging as a new layer of Li gets plated,[21] which might have improved the contacts during charging to allow almost complete delithiation even for the highest loading cathode (Figure 1b). To investigate this hypothesis, we prepared a cross-section of the whole-cell stack using a microtome and imaged it via SEM. Figure 3 shows the cross-section SEM images of the bilayer cell. Two main observations should be noted. One, the thickness of the linear PEO was significantly reduced from an initial 140 μm to ~30 μm, which is expected because of its undesired plastic deformation. As expected, cross-linked PEO maintained its initial thickness of ~80 μm. Second, the cathode/linear PEO layer interface appears seamless, with linear PEO completely conformed to the cathode's surface roughness, eliminating any gaps. Linear PEO is also self-healing at 70 °C, which means the linear PEO separator can irreversibly fuse with the linear PEO catholyte within the cathode, which can prevent interfacial delamination during cycling stresses. The cathode layer could also not be peeled off by hand. On the other hand, the cathode could be very easily separated from the cell stack, for the cell containing only a cross-linked PEO electrolyte layer. Therefore, corresponding cross-section images of that cell could not be obtained as the electrolyte delaminated from the cathode during microtome sectioning.

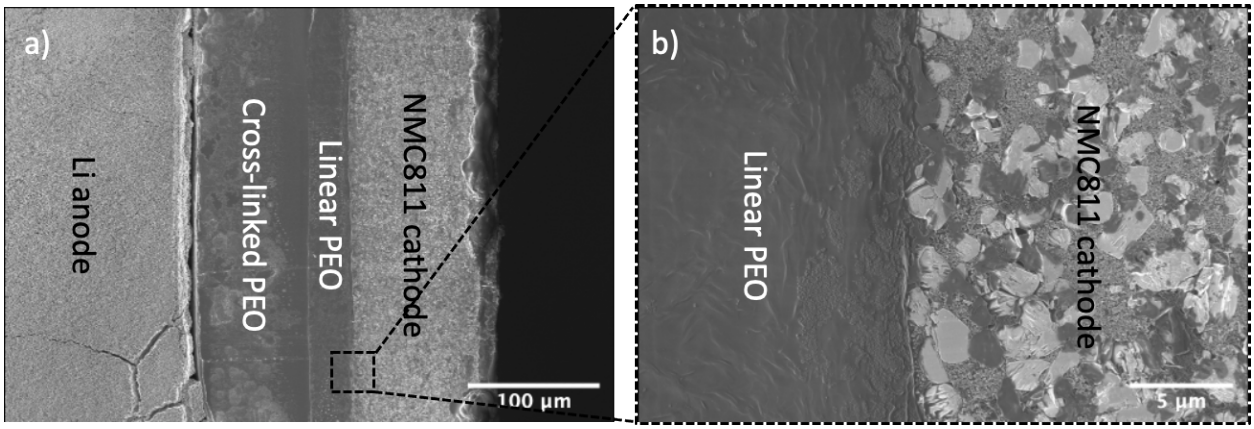


Figure 3. a) SEM image of the cross-section of complete cell stack of the Li/bilayer electrolyte/NMC811 (6 mAh/cm^2) cell, disassembled after one charge/discharge cycle. b) Magnified SEM micrograph of the linear PEO/cathode layer interface.

The energy density for the cell containing 6 mAh/cm^2 cathode, based on the weight of the whole-cell stack, including the two electrodes and electrolytes and a nominal cell voltage of 3.8 V, is 236 Wh/kg (Table S1). This is further increased to 307 Wh/kg when a 10 µm thick lithium on Cu foil substrate was used as the anode (Figure S2, Table S1). Reducing the electrolyte thickness to 50 µm can further bring this energy density to 428 Wh/kg (Table S1). Future works will focus on improving the cell-level energy density by reducing the thickness of electrolyte layers and reducing the capacity fade during cycling by employing high-voltage stable polymer electrolytes as catholyte. Reducing the electrolyte thickness to practical range will require adoption of alternative cell assembly routes because of difficulty in handling self-standing membranes of such low thicknesses.

In conclusion, we have demonstrated the cycling of lithium metal SSBs containing thick composite cathodes (3-6 mAh/cm^2) in coin cell format, using a bilayer electrolyte design that utilized the benefits of individual electrolyte layers while mitigating their corresponding shortcomings. Cross-linked PEO provided higher mechanical stability and suppression of dendrites, whereas the linear PEO likely helped provide a mechanically more robust interface with composite cathode layer. The results presented indicate the importance of an integrated electrolyte/catholyte cell design,[7, 22-24] especially for high loading cathodes, which can prevent the delamination or contact loss issue at the separator/cathode interface during cycling-induced volumetric changes and associated stresses generated within cell stack. While this strategy is presented here for a specific set of materials, and the current densities/high temperatures used are still less than ideal, the general concept of a more rigid electrolyte that inhibits dendrites and a softer, cathode-integrated electrolyte that ensures contact with the cathodes during cycling, may be a pathway for enabling high-energy-density cathodes with room-temperature solid-electrolytes.

Supporting Information

Experimental method details including fabrication of electrolyte membranes and composite cathodes, electrochemical testing, and SEM characterization; Figures S1-2 including first charge profile comparisons, cycle life performance of the bilayer configuration cell with a thin Li anode; Table S1 showing stack-level energy density calculations.

Acknowledgments

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