A Cross-linked Polymer Artificial Solid Electrolyte Interphase for Stable Li Metal Anodes

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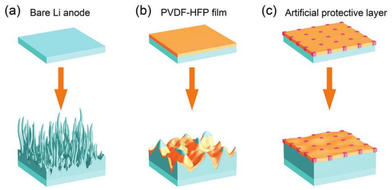
Research Background

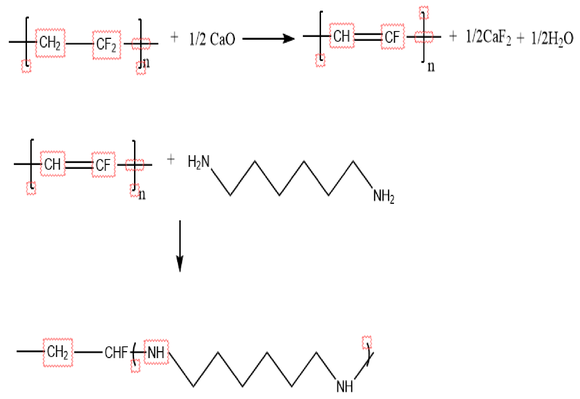
Graphite is currently used as the anode in commercially sold lithium-ion batteries. However, this restricts the energy density of the batteries. The energy storage capacity could potentially be doubled by using lithium metal batteries (LMBs) instead, which have an anode made of lithium metal instead of the conventionally used graphite. A higher energy density would make it possible to use LMBs in electric automobiles and energy storage grids for renewable sources of energy.



Schematic illustrations of Li deposition a.) without protection b.) with a pure PVDF-HFP layer c.) with a layer composed of organic PVDF-HFP and inorganic LiF [1]

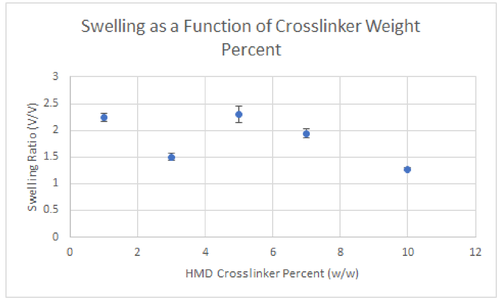
However, there are three major problems with LMBs: dendrite growth, ion isolation, and cell death. A possible solution to these problems is to use a flexible and mechanically stable crosslinked artificial solid electrolyte interphase (SEI) passivation layer as seen in the above figure. The purpose of this layer would be to suppress dendrite growth, increase ion selectivity as well as increase the life of the battery, and to overall improve the efficiency of the battery.

Crosslinking



Reaction Scheme of the crosslinking of the PVDF copolymer

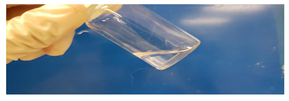
The SEI layer is a passivation layer formed on an electrode surface and acts as a barrier between the anode and the electrolyte reducing unfavorable side reactions by chemical selectivity. Polymer materials such as Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), is used as an artificial SEI layer thanks to its flexibility as well as its ability prevent direct interactions between the anode and electrolyte.[2] Crosslinking the polymer helps to increase the mechanical stability of the polymer as well as the flexibility of the material. This makes it a good candidate for an artificial SEI, as it would act as a protective layer with sufficient mechanical strength for the electrode to suppress dendrites growth.



The swelling of the crosslinking polymer was analyzed as a function of crosslinker Hexamethylenediamine (HMD). As the percent weight of HMD was increased in the polymer, so did the percentage of crosslinking and therefore the swelling of the polymer decreased as %HMD increased due to crosslinking limiting the amount of swelling the polymer could do.

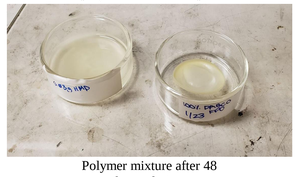
Methodology

- We used 1%, 3%, 5%, 7% and 10% of our crosslinking agent to create the polymer film and determine its relationship with polymer swelling. As the weight percent of our crosslinker increases the crosslinking in the polymer should increase as well.

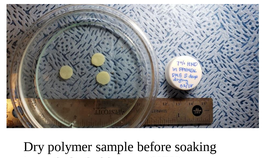


Polymer Mixture

the polymer mixture in a petri dish



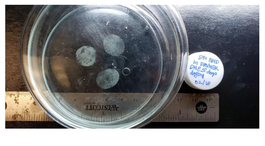
Polymer mixture after 48 hours drying



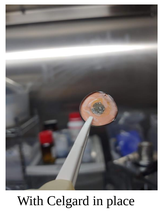
Dry polymer sample before soaking in methyl ethyl ketone (HEK)

48 Hours

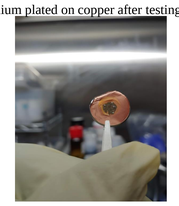
Wet polymer sample after soaking in HEK



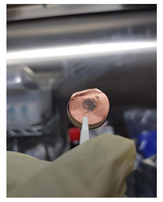
Lithium plated on copper after testing in cells



With Celgard in place

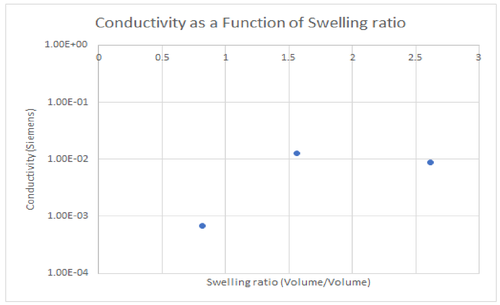


With Celgard removed (Lithium plated on top)

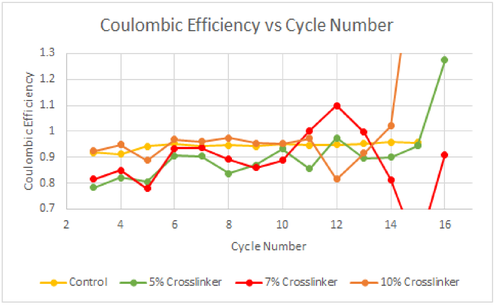


With PVDF layer removed (lithium plated on bottom)

Results

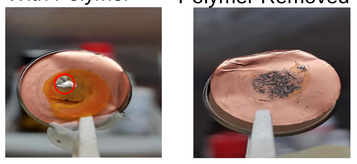


The relationship of ionic conductivity and swelling were analyzed. As the swelling increased the conductivity increased as well due to the availability of ions in the swollen polymer. Which agrees with previous studies.[3]

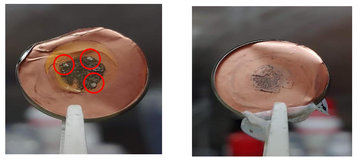


The coulombic efficiency (cycling efficiency) of the various crosslinked polymers were plotted as a function of cycle number. 10% has the possibility of performing better than the control given more testing.

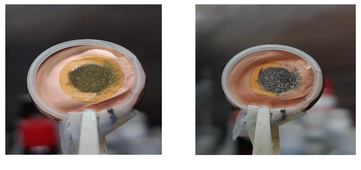
With Polymer | Polymer Removed



10% Crosslinker



7% Crosslinker



5% Crosslinker

At very high crosslinking the polymer film tends to break and in other cases lithium plates on top. At lower concentrations of crosslinker, the lithium plates underneath the film. As it can be seen in this image, there is no lithium that plates on top. This may be the case because of the films relatively higher ionic conductivity.

Summary

- Swelling decreases with increased crosslinking
- Ionic conductivity increases with increased swelling
- Crosslinked polymer samples show potential for being an Artificial SEI
- At very high crosslinking the film breaks and lithium plates on top and at lower crosslinking the film holds and lithium plates below.

Future work

- Given more time, the artificial SEI has the potential to maintain a coulombic efficiency higher than that of the control cell.
- The absorptivity of various crosslinked polymers could be further studied to determine the optimum level of cross-linking.
- Look at CaO as it is a possible cause of an uneven film and may need to be purified from the polymer.
- Regulate film thickness and uniformity more closely to create a film has less impurities and pores.

References

1. Xu, R., Zhang, X. Q., Cheng, X. B., Peng, H. J., Zhao, C. Z., Yan, C., & Huang, J. Q. (2018). Artificial soft–rigid protective layer for dendrite-free lithium metal anode. *Advanced Functional Materials*, *28*(8), 1705838..
2. Luo, J., Fang, C. C., & Wu, N. L. (2018). High Polarity Poly (vinylidene difluoride) Thin Coating for Dendrite-Free and High-Performance Lithium Metal Anodes. *Advanced Energy Materials*, *8*(2), 1701482
3. Chung, N. K., Kwon, Y. D., & Kim, D. (2003). Thermal, mechanical, swelling, and electrochemical properties of poly (vinylidene fluoride)-co-hexafluoropropylene/poly (ethylene glycol) hybrid-type polymer electrolytes. *Journal of power sources*, *124*(1), 148-154.