

Lithium Metal Batteries: The Future?

An Electrochemical Impedance Spectroscopy study of Lithium metal anode performance



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Abstract

Lithium metal batteries (LMB's) could be the answer to the 30-year quest for a high energy storage device. These lithium anode batteries are a promising alternative to conventional lithium-ion batteries. Low electrode potential and a high theoretical specific capacity nearly 10 times greater than traditional graphite anode/lithium cobalt oxide cathode technology gives LMB's the edge in the evolving energy sector^[1].

In this project, the effect of electrolyte concentrations and ambient temperatures on formation of the solid electrolyte interface (SEI) on the lithium anode in separator-free lithium symmetric cells was investigated with a liquid electrolyte lithium bis(fluorosulfonyl) imide in tetraglyme (LIFS/G4).

Motivation

- LMB's face several obstacles in their mass development, such as dendrite growth of high surface area lithium material deposited during charging (due to an inhomogeneous Solid Electrolyte Interface) that can short circuit the cell, leading to overheating and thermal runaway^[2].
- Investigating the effect of concentration and temperature on SEI formation can help inform future cell designs to mitigate LMB short circuiting.

Cell assembly Methodology

- Lithium metal electrode symmetric cells (n=100) were prepared in a glove box environment at 0.25, 1 and 2 molal concentrations over a range of temperatures (20,30,40,50 °C) followed by Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) experiments in an environment chamber. Electrode design was optimised to 300µm followed by hexane assisted brushing and pressing. The cells were encased in parafilm with 300 microlitres of LFS/G4.
- The finished cells were assessed by Electrochemistry Impedance spectroscopy over 12 hours and results were fitted to an equivalent circuit model^[4]. Thirty-six cells were selected for their R0 reproducibility values within +/- 10 ohms of the average R0 value at each concentration and the optimal 3 cells in each of the 12 conditions tested were averaged for analysis.

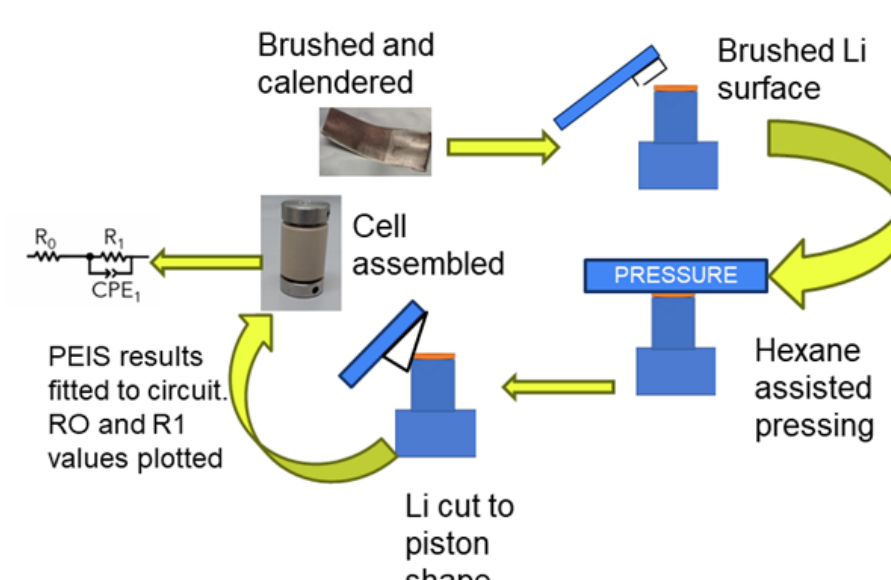


Figure 1: Project design.

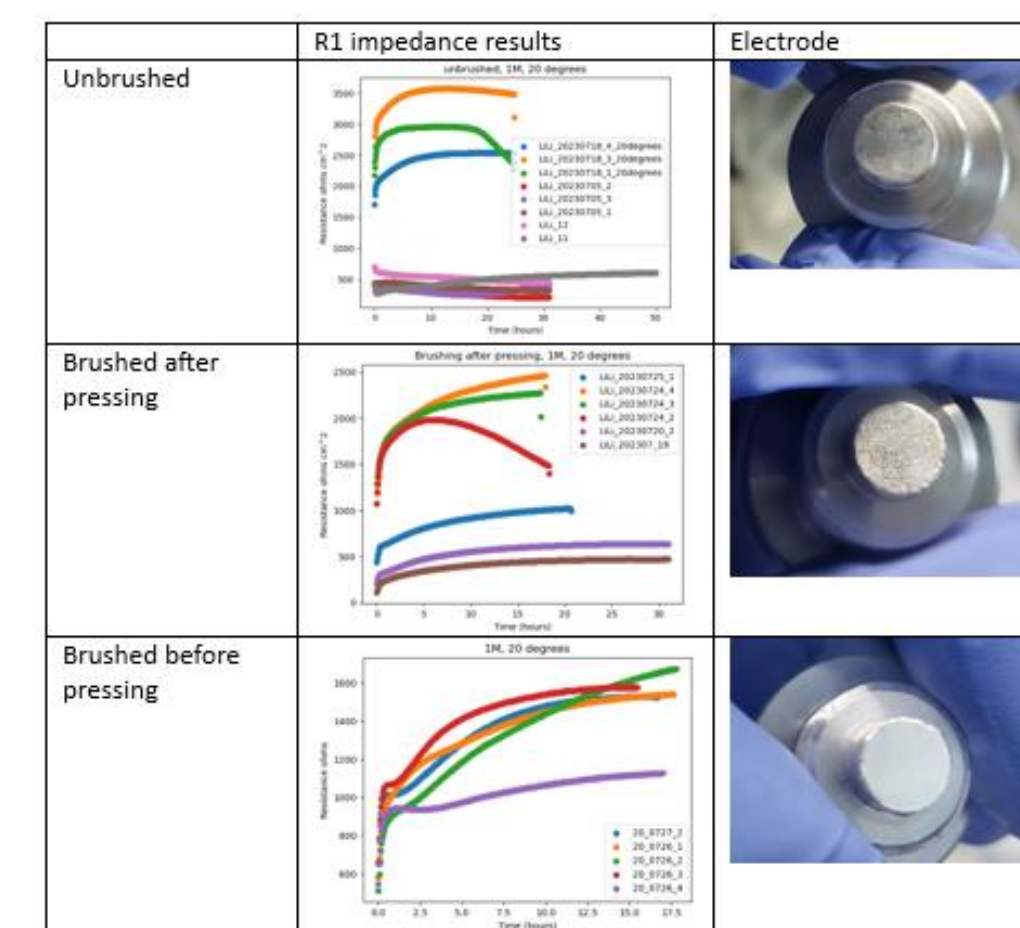


Table 1: Comparison of three assembly techniques. Post assembly, an impedance reproducibility check was performed at 20 °C by Potentiostatic electrochemical impedance spectroscopy (PEIS) in a 200kHz to 100mhz frequency range. This was conducted across the initial cell designs before finalization of the hexane assisted pressing method and was used to identify unsuitable cells to cycle.

Results: Equivalent Circuit Model Fitting

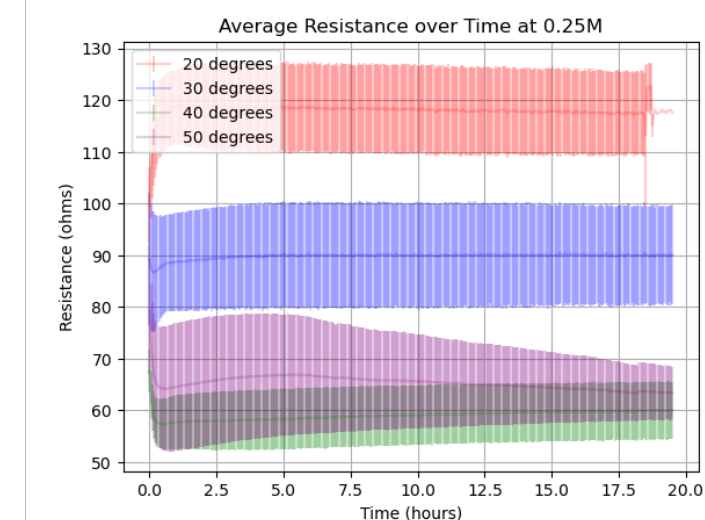


Figure 2: Average electrolyte resistance (R0) at 0.25M against time. R0 resistance error bars overlap at 40/50 °C with no noticeable variation.

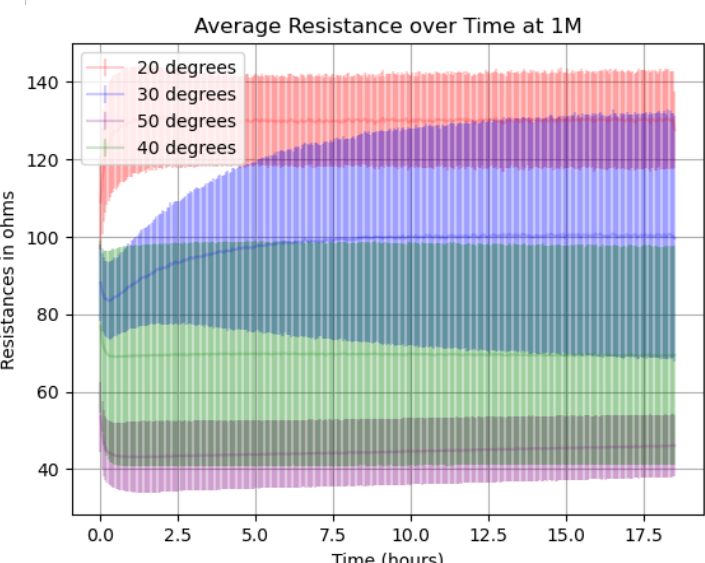


Figure 3: Average electrolyte resistance (R0) at 1M against time. Resistance error bars overlap at all temperatures suggesting limited result variation.

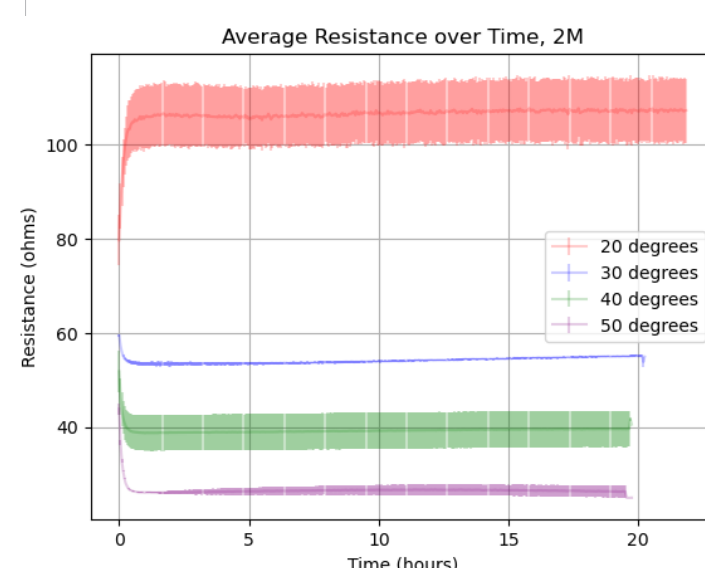


Figure 4: Average electrolyte resistance (R0) at 2M against time. R0 is highest at 20 °C.

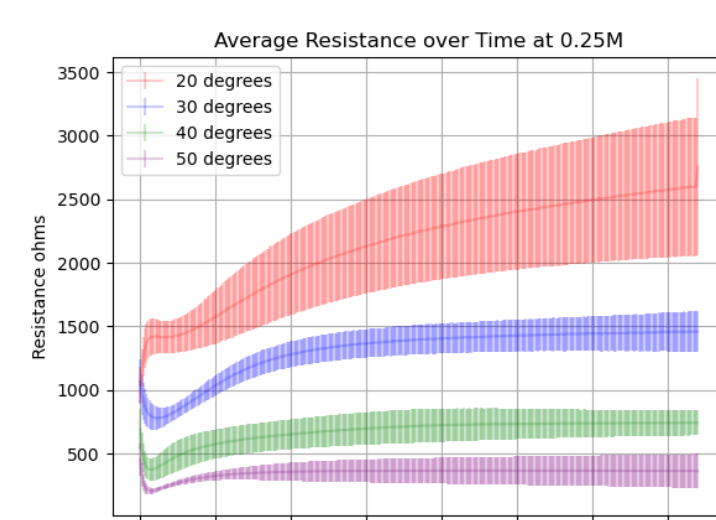


Figure 5: Average SEI resistance (R1) at 0.25M against time. R1 is highest at 20 °C.

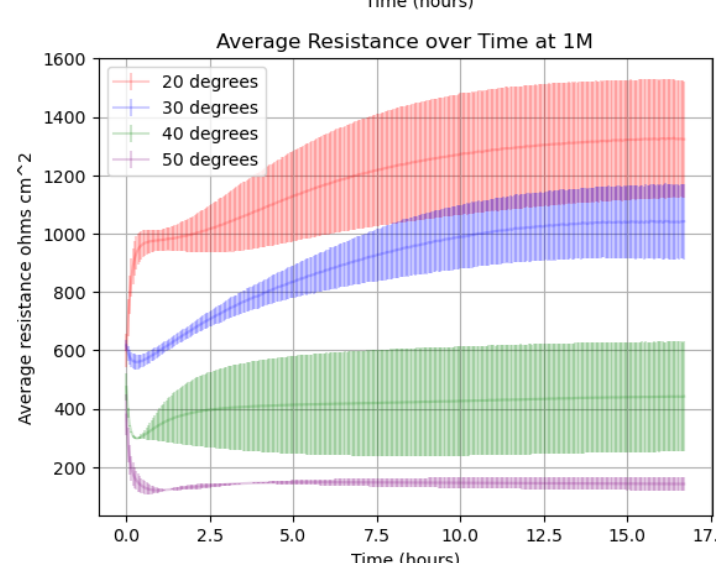


Figure 6: Average SEI resistance (R1) at 1M against time. R1 is lowest at 50 °C.

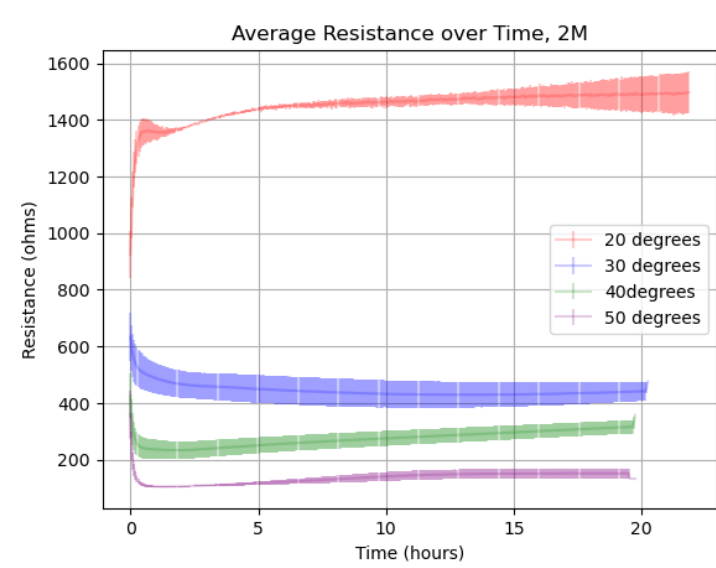


Figure 7: Average SEI resistance (R1) at 2M against time. R1 overlaps at 20/30 °C.

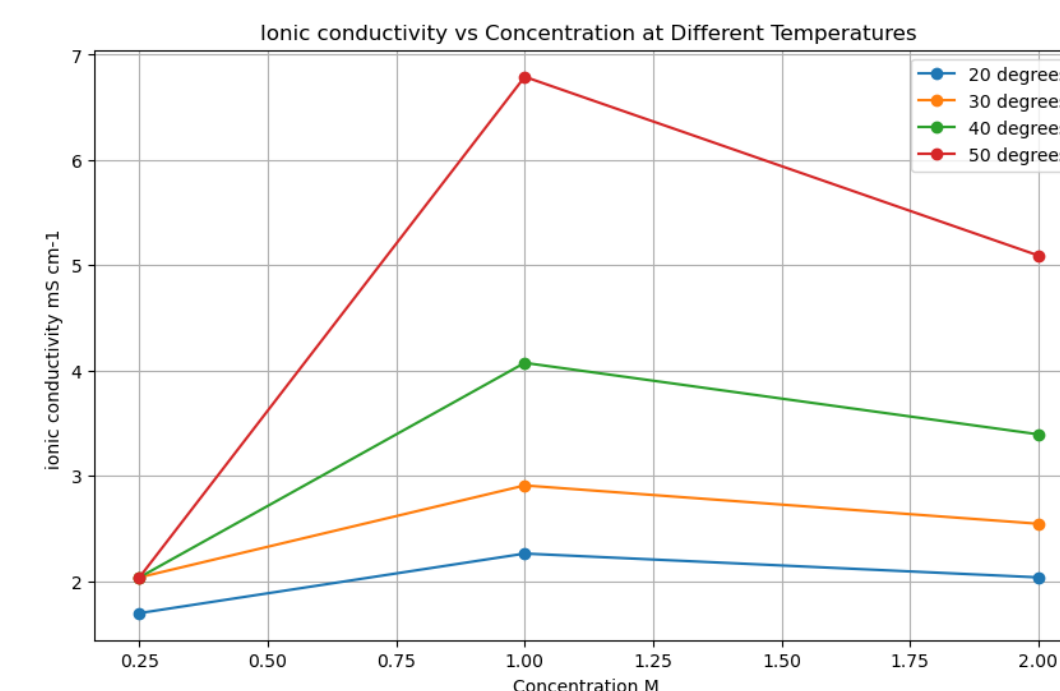


Figure 8: The ionic conductivity increases with concentration at all temperatures, with a steep downward gradient after 1M. A proportional relationship is observed between ionic conductivities to temperatures up to 1M, a trend that is expected for the LIFS/G4 electrolyte. The results indicate a small rise in temperature can increase the ionic conductivity at each concentration, with a notably high ionic conductivity at 1M, 50 °C, perhaps because the ions have higher kinetic energy at this temperature.^[3,5]

Conclusions

- An EIS reproducibility protocol was successfully optimized by modifications to the lithium electrode preparation. Circuit fitting provided insights into SEI formation.
- SEI resistance (R1) was maximal at 20°C across all the tested electrolyte concentrations. There appears to be an inverse correlation with temperature. This could be because lower temperatures inhibit SEI formation at the electrolyte-electrode interface.
- The proportional increase in LIFS/G4 ionic conductivity to concentration can explain the initial rise in the R0 (electrolyte resistance). Beyond this concentration, the electrolyte viscosity potentially emerges as a dominant factor, reducing the R0 resistance.

Impact / Next steps

- The influence of solvation on the SEI formation can be investigated further to identify solvation structure changes at different concentrations.
- The data will be fitted to an advanced equivalent circuit model followed by collaboration with international research group on Pade approximants.
- The influence of higher temperatures on faster SEI formation can be explored further with AFM microscopy to determine SEI thickness and applied to different cell setups, including ones with a magnesium cathode.

References

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Manav is an M.Eng student interested in the rapidly developing renewable technology field especially in energy storage and alternative fuel innovations. He believes that developments in battery technology underpinned by novel materials and nanotechnology can offer cutting-edge solutions for global energy challenges.

