

INVESTIGATING DEGRADATION OF THE CURRENT COLLECTORS IN LIB

Exploring the effects of C-rate and UCV on the degradation of the current collectors in lithium-ion batteries



Poppy Mullins supervised by Aigerim Omir Khan and Ramin Jannat, Mary Ryan Research Group

ABSTRACT

The ongoing climate crisis has driven research in 'greener' energy options, such as lithium-ion batteries (LIBs). However, degradation of LIBs provide major limitations in their lifetime and performance. Thus, imploring a more comprehensive understanding of the mechanisms of degradation in LIBs is key to improving the lifetime, performance and safety of these energy sources in the future.

- Current collectors are metal foils, usually metallic copper at the anode and aluminum at the cathode, which bridge the electrical current produced at electrodes and the external circuits. Both current collectors show signs of degradation, particularly under over-discharge conditions [1]. The key forms of corrosion for both Cu and Al are pitting and crevice corrosion.

MOTIVATION AND AIMS

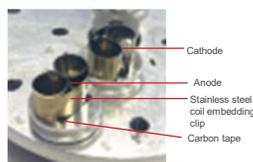
- Produce reliable coin cells using Faraday suggested protocol and cycle with experimental matrix (2 Upper cutoff voltage (UCV) and 2 C-rates) using BioLogic battery tester
- Use SEM to compare the degradation of current collectors vs pristine samples

RESULTS

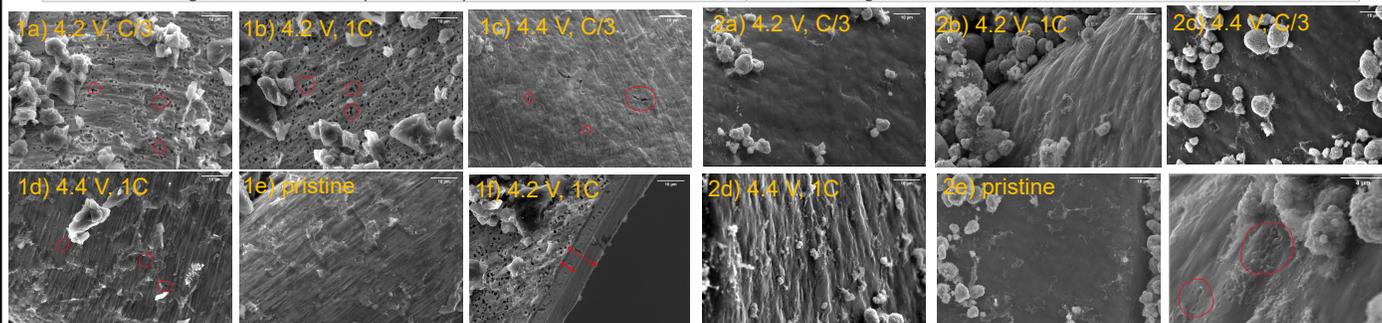
- Pits of approximately $< 1.0 - 5.0 \mu\text{m}$ were seen on the copper current collector charged to 4.2 V, with more dense pits seen at a C-rate of 1C. Interestingly much fewer pits were seen in the UCV of 4.4 LIBs regardless of the C-rate. Figure 1f illustrates the depth of the pits of the Cu in figure 1b, reaching up to $4.47 \mu\text{m}$ of a total thickness of the copper of $11.43 \mu\text{m}$.
- The aluminium current collector is generally more resistant to corrosion, with far less pitting seen. However, in all cycled cells, more roughness is seen on the surface and larger and more shallow pits and scrapes were seen in the 1C to 4.4 V cell, as shown in Figure 2f.

METHOD

- Following protocol recommended by the Faraday institute, NMC811 cathode (1.73 cm^2) and graphite anode (1.77 cm^2) were used.
- A spring and two spacers (1 mm) were utilized at the negative case before the anode was added. The cathode was placed in the positive cap followed by a glass fibre separator. 70 μL of 1M LiPF_6 in EC:EMC electrolyte was added, and the coin cell crimped.
- Using constant current, constant voltage protocol to 2 UCVs (4.2 and 4.4 V) and 2 C-rates (C/3 and 1C)
- Cycled cells were disassembled. Both anode and cathode were washed using 1 ml of DMC at least three times before further characterisation

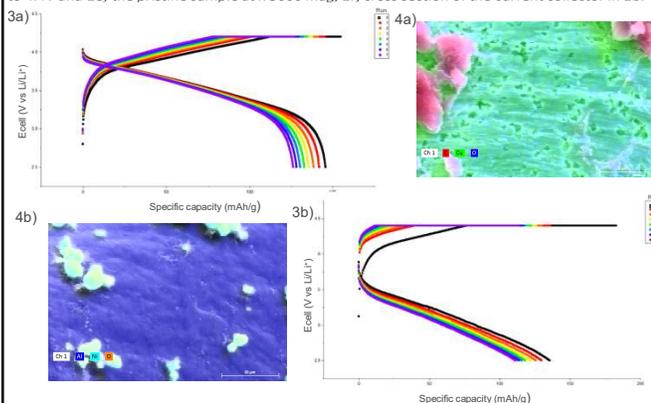


- The current collectors were imaged using an Auriga FIB-SEM; the samples were held in place using embedding clips to image the cross-section of the current collectors, as well as to provide the conductivity for electron imaging



Copper current collector cycled at; 1a) C/3 to a UCV of 4.2 V, 1b) 1C to 4.2 V, 1c) C/3 to 4.4 V, 1d) at 1C to 4.4 V and 1e) the pristine sample at x 5000 mag, 1f) cross section of the current collector in 1b.

Aluminium current collector cycled at; 2a) C/3 to a UCV of 4.2 V, 2b) 1C to 4.2 V, 2c) C/3 to 4.4 V, 2d) 1C to 4.4 V and 2e) the pristine sample at x 5000 mag, 2f) x20000 magnification of the corrosion seen in 2b



Specific capacity (mAh/g) vs Ecell (V vs Li/Li+) plots for 8 cycles of charging/discharging for 3a) C/3 to 4.2 V and 3b) 1C to 4.4 V (formation cycles not included). 4a) Energy Dispersive X-Ray Analysis (EDX) of Cu illustrating the presence of Cu with a protective oxide and graphite particles 4b) EDX of Al illustrating presence of Al surface and Ni and O in NMC particles

CONCLUSIONS

- SEM results suggest the density and size of pits in the Cu current collectors increase with increasing C-rate [2]; these pits can have significant effects on the electrode coating adhesion and hence the electrical contact in the cell.
- Reduced electrical contact may result in reduced cell capacity and poor current distribution.
- Interestingly, copper dissolution is also affected by the state of the electrolyte. The electrolyte used, LiPF_6 , was opened in April 2022 (5 months aged), which can increase copper dissolution by up to several hundred ppm due to higher concentrations of HF. Potential effect of copper corrosion is Cu deposits occurring on the cathode surface, which was seen using EDX. Copper deposits are said to increase as the C rate is decreased as the copper experiences the potential at which corrosion occurs for much longer.
- Aluminium forms passive fluoride layer preventing corrosion; the AlF_3 component of this film in LiPF_6 is seen to increase in thickness with applied potential (3.8 - 4.2 V) protecting the current collectors from degradation [1]
- The surface roughness makes Al more susceptible to crevice corrosion, suggesting Al degradation may be more significant after more cycles
- Larger cracks are formed at higher potentials of 5.3 V for aluminium hence why corrosion appeared to a lesser extent for Al than Cu [3]
- The reduced appearance of pits and surface roughness between UCV of 4.2 and 4.4 V for Cu is unexpected and needs further investigation

IMPACT / NEXT STEPS

- Having only had 6 weeks of my internship so far further research into the effects of aged/fresh electrolyte and different varieties of electrolyte would be an interesting next step
- Baseline experiments with LIB soaking in electrolytes
- Characterization of disassembled cells at 2C
- Using other methods, such as Linear Scanning Voltammetry or Cyclic Voltammetry, to determine the extent of Cu deposits on cathode, and how this varies with C-rate

REFERENCES

- [1] Degradation in lithium ion battery current collectors. Guo, L. et al. *Journal of Physics: Energy*, 3(3), p.032015 (2021)
- [2] Effects of cycle times and C-rates on mechanical properties of copper foil and adhesive strength of electrodes in commercial LiCoO_2 LIBs. Dai, C. et al., *Engineering Failure Analysis*, 101, pp.193-205 (2019)
- [3] Corrosion of aluminium current collector in lithium-ion batteries: A review. Gabryelczyk, A. et al., *Journal of Energy Storage*, 43, p.103226 (2021)

INTERN BIO

I am going into my final year studying Chemistry at the University of Durham. Interested predominantly in inorganic chemistry, I am completing my integrated masters in a supramolecular inorganic chemistry research group. However, the electrochemistry and materials aspects that I have gained insight into throughout this project has urged me to explore these areas further in the future.

