Determining the Mechanism of Cell Degradation

Using cyclic voltammetry and direct current internal resistance techniques

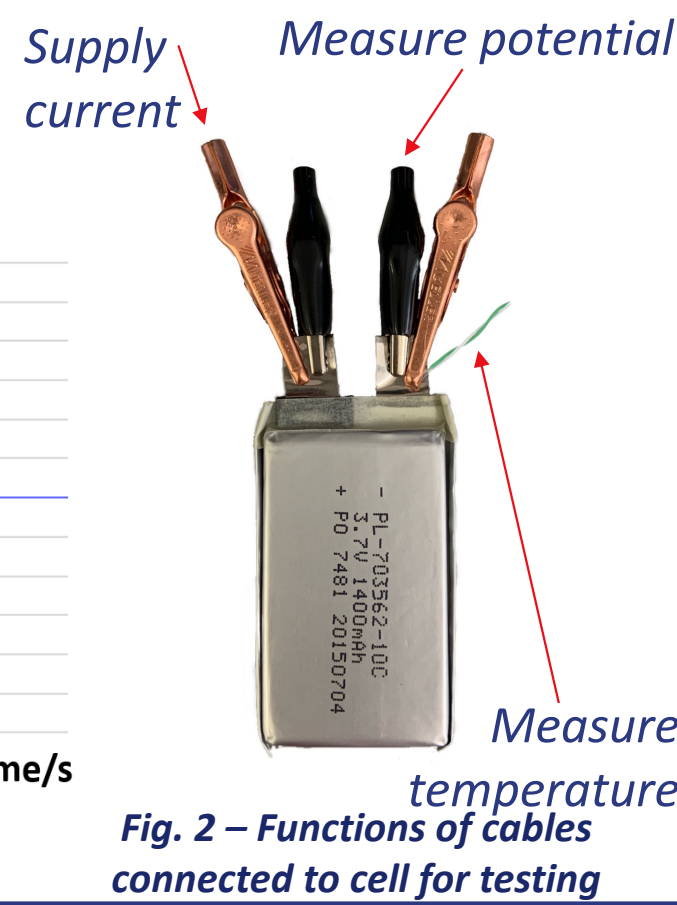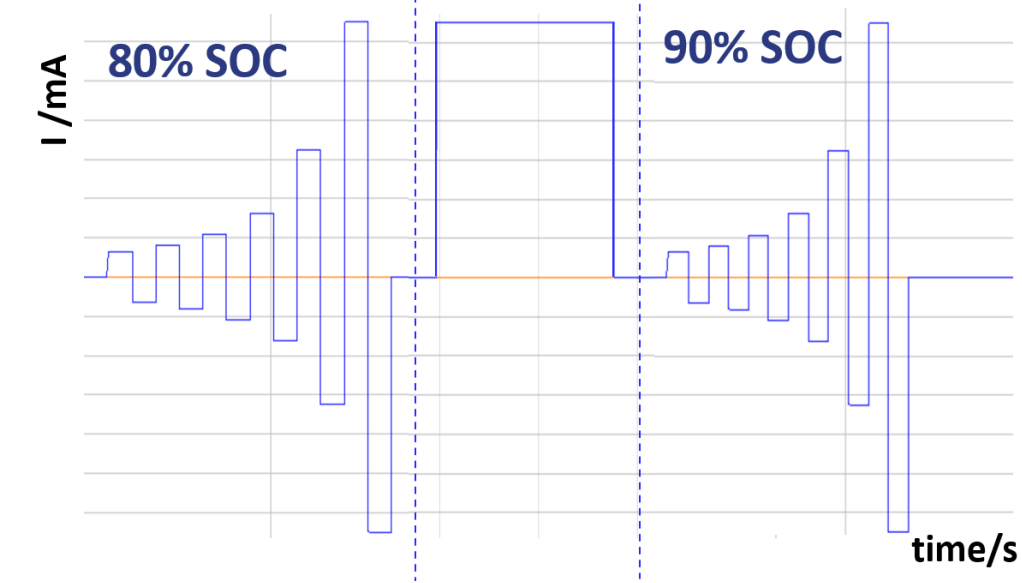**Eugenie Lumsdon,** Michael Johnson, Chun Tan, Thomas Heenan

Introduction

- Cyclic voltammetry (CV) is a technique in which the potential is varied linearly to a maximum and then back down to a minimum
- The rate at which the voltage is changed is the scan rate
- A cyclic voltammogram is a plot of the current as a function of the applied potential

- Direct current internal resistance (DCIR) is the the total electronic resistance of the materials of the battery as well as the resistance involved in the electrochemical processes

Motivation

Due to the climate crisis, many companies are striving towards net zero carbon emissions. A main goal is the transition away from petrol vehicles, an alternative being electric. These use chemical energy stored in battery packs to run, however there are many issues associated with them, including short ranges and long charging times. While it may seem intuitive to decrease charging times by simply charging at a higher current, this causes the battery to degrade faster. I used cyclic voltammetry and DCIR techniques to probe the degradation mechanism, as knowing how the battery degrades is vital for development of prevention methods.

Methods

- Cyclic voltammograms were obtained at scan rates from 0.05-0.10mVs^{-1} for a pristine polymer lithium pouch cell (PL-703562-10C)
- They were also taken after every 25 charge/discharge cycles, up to 125 cycles
- To find the DCIR, pulse currents are applied in the charge and discharge regions, and the potential measured
- A graph of V/I was drawn for each state of charge (SOC), and DCIR calculated from the gradient
- This is repeated after charging the cell in 10% increments
- A constant current-constant voltage (CCCV) process was used while charging to minimise overpotentials
- Safety limits were in place to stop the test if the temperature exceeded 60°C or the voltage 4.25V – as stated by the cell manufacturer

Fig. 1 – Current/time test profile for DCIR

Fig. 2 – Functions of cables connected to cell for testing

Cyclic Voltammetry results

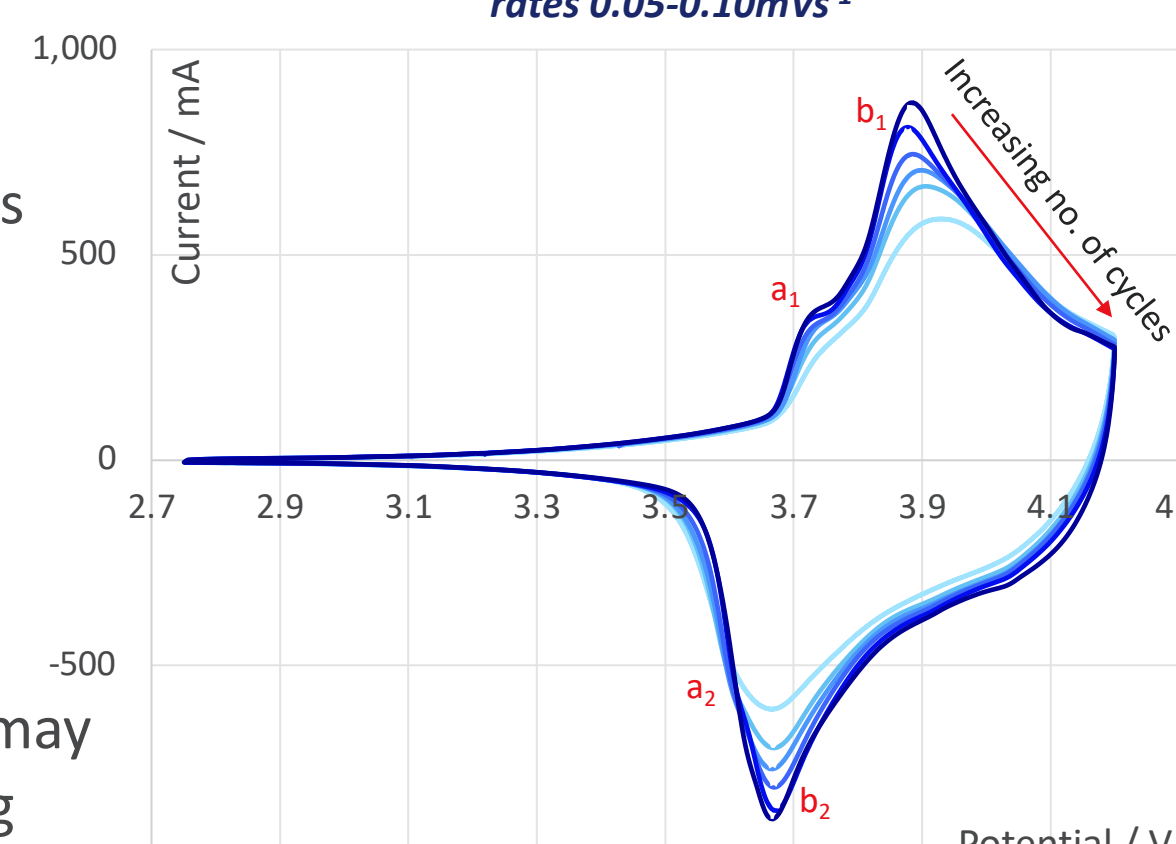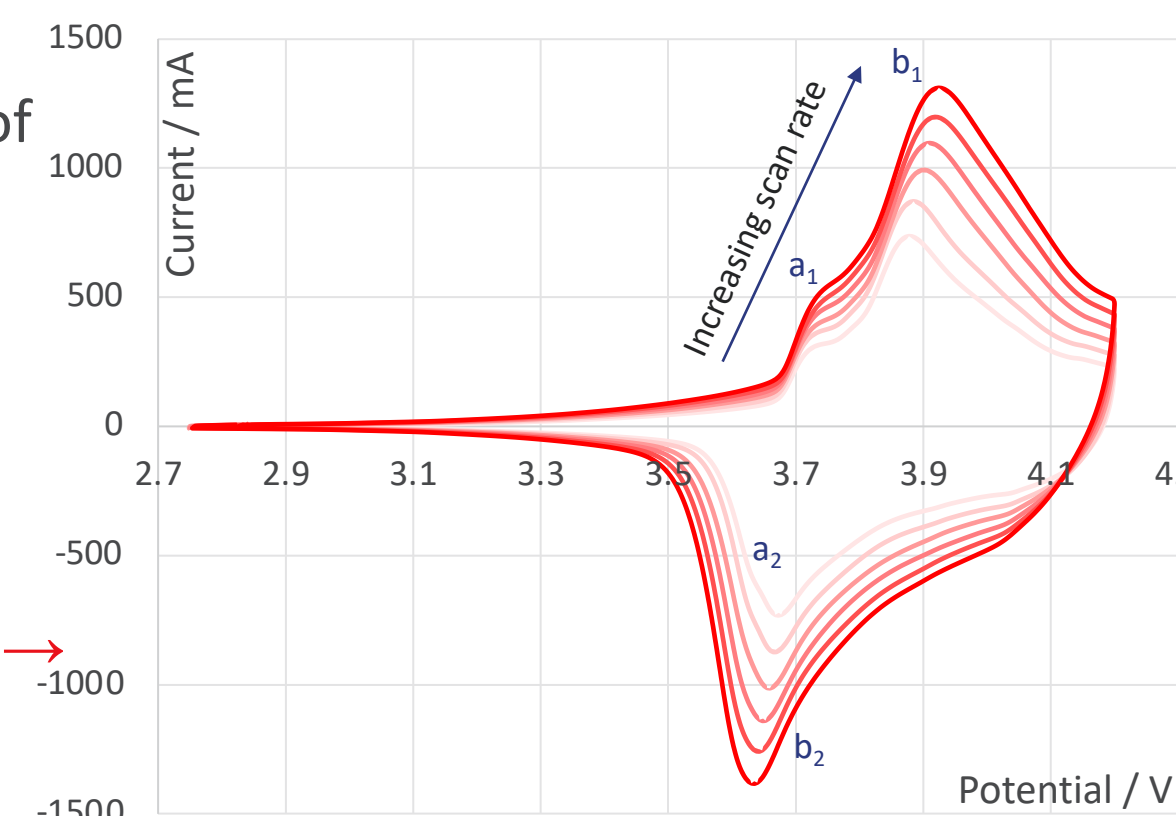The forward scan peaks correspond to delithiation of cathode, and reverse peaks to lithiation of cathode

Observation → Hypothesis

Pristine CVs

- Dual peaks a_1 and b_1 → two step de/lithiation process[1]
- Peak-to-peak separation increases with scan rate → quasi reversible process[2]
- Graph of current/(scan rate)$^{1/2}$ is linear → diffusion is rate limiting step[3]

Aged CVs

- All peaks show decreasing current → capacity loss
- Ratio of I_{anodic}/$I_{cathodic}$ decreases with ageing → degradation at anode
- Graph of current/scan rate is linear → reaction is surface controlled[4]

- Change from diffusion control to surface control may suggest active surface area of anode is decreasing

Fig. 3 – Cyclic voltammograms of pristine cell at scan rates 0.05-0.10mVs^{-1}

Fig. 4 – Cyclic voltammograms of cell after 0-125 cycles

DCIR results

- Resistance at 0% SOC is high but drops quickly with charging
- Stays low up to 100%

Fig. 5 – DCIR of pristine cell at various states of charge

Possible explanation

- Near 0% SOC, most Li$^+$ should be in cathode, but Li$^+$ ions can build up around cathode as intercalation is not instant. Diffusion gradient becomes unfavourable, increasing resistance[5]
- There are also few spaces for incoming Li$^+$ to occupy, so resistance is high
- Capacity of anode is typically higher than cathode, which could explain lack of resistance increase at 100% SOC[6]

Fig. 6 – DCIR at 20, 50 and 80% SOC after ageing

Fig. 7 – Capacity retention of cell after cycling

- As battery aged, resistance at high SOCs increased more significantly than other SOCs
- High SOCs correspond to intercalation of Li$^+$ into anode, so this may suggest loss of capacity at anode
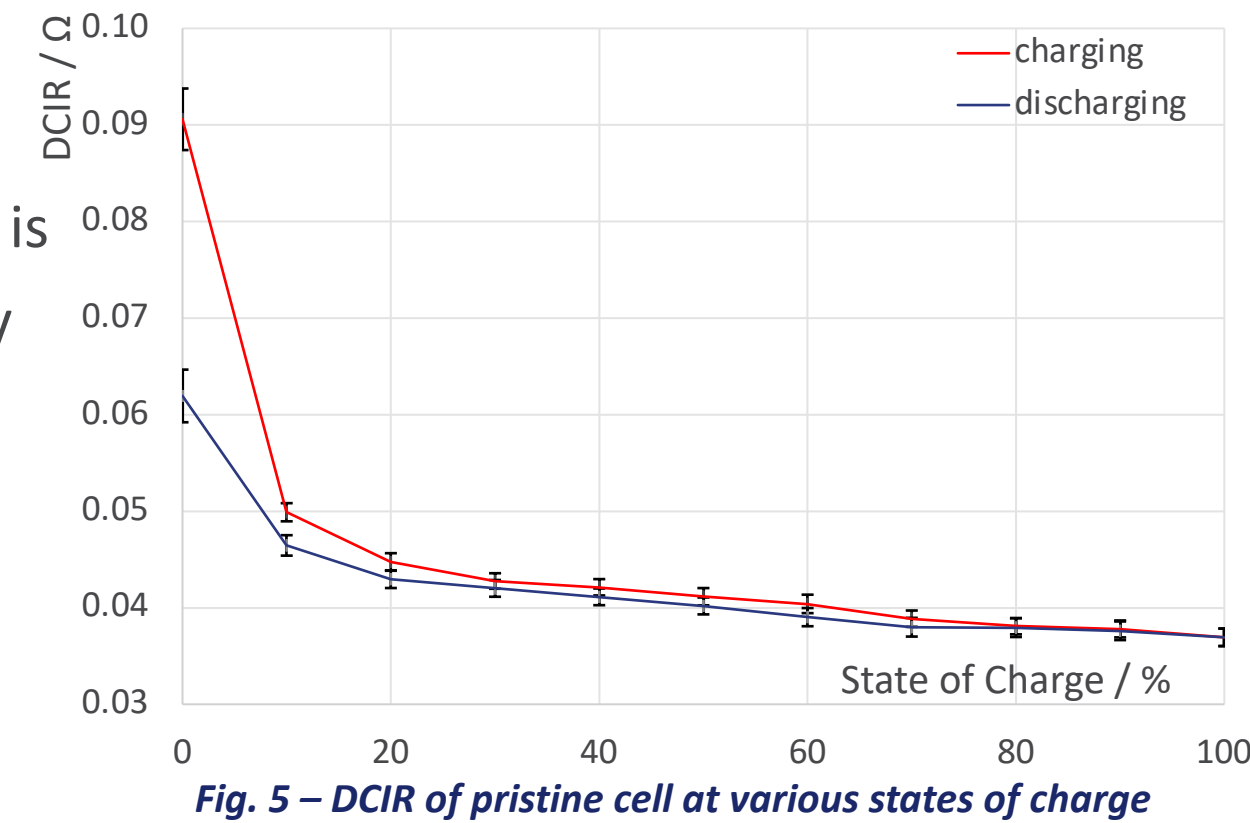
Conclusions

- Both techniques indicate the main cause of capacity loss is degradation at the anode
- Cyclic voltammograms also suggest a reduction in the active surface area of the anode
- A possible cause of both is **lithium plating** at the anode
- Instead of intercalating into the graphite electrode, lithium ions are reduced and metal gets deposited on the surface
- This reduces the active surface area for lithium deposition and the capacity of the battery
- Can also develop into dendrite formation, which introduces safety concerns due to short circuiting
- Especially significant for fast charging, where more Li$^+$ ions are moved to the anode in a short time, and plating is more likely[7]
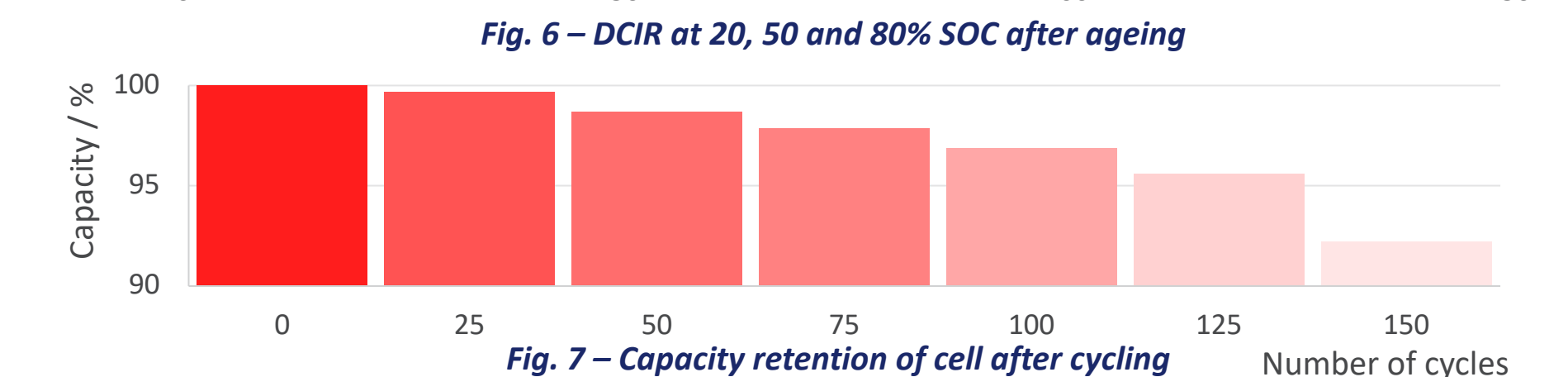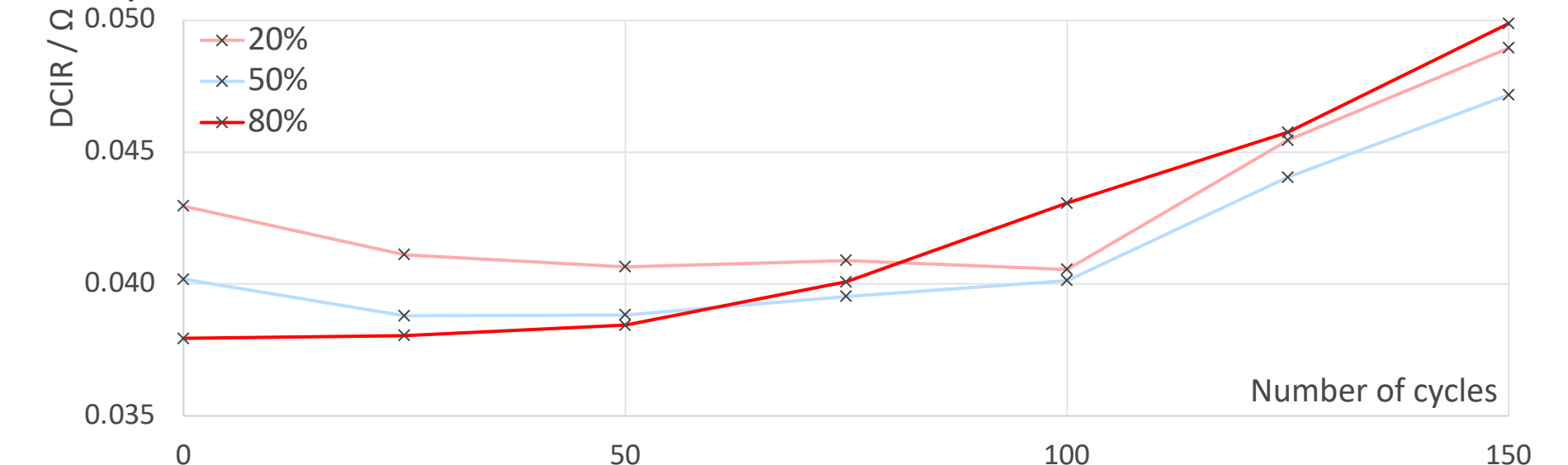
Impact / Next Steps

- Post-mortem analysis and cell disassembly could help confirm if lithium plating is occurring and offer a qualitative assessment of the extent
- Having an idea of the degradation mechanism allows for more relevant testing and development of mitigation techniques

- Repeat the experiments with faster charge/discharge cycles to identify the effects of fast charging
- Alter the charge/discharge protocols (i.e., cycle with fast charge and slow discharge) to mimic real life applications

References

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Intern Bio

Eugenie has completed her second year studying Chemistry at the University of Oxford. She is interested in developments in renewable energy and green technology, with a focus on the physical and mathematical side.

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