

Electrochemical Impedance Spectroscopy of Lithium-Ion Cells at Progressive States of Charge



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Abstract and Motivations

- Development of **efficient batteries** is key to enabling a global transition away from **fossil fuels**; lithium-ion batteries serve as a model chemical system for liquid electrolyte cells.
- As Lithium-ion cells **charge**, the graphite anode is progressively reduced, and lithium ions migrate to it from the cathode. Ion transport speeds vary across different cell components, depending on local reactions occurring. As Li^+ is loaded into and unloaded from electrodes, **cell impedance characteristics change**; migration processes in cells of different sizes and structures vary due to factors such as diffusion distances, contact surface area and electrode materials.
- Electrochemical Impedance Spectroscopy (EIS)** can measure cell impedance (complex resistance) at **different timescales** and track the change in resistive/charge transfer processes.
- Understanding changes in impedance with **state of charge (SOC)**, cell structure and charging **current rate** give insight into what chemical processes may be occurring on different **timescales** and how phenomena such as double layer capacitance and component resistance change with Li^+ concentration. This can inform development of improved **models** for cell cycling, enabling **optimisation** of cell structure for **fast charging** and other **diverse uses**.

Results and Discussion

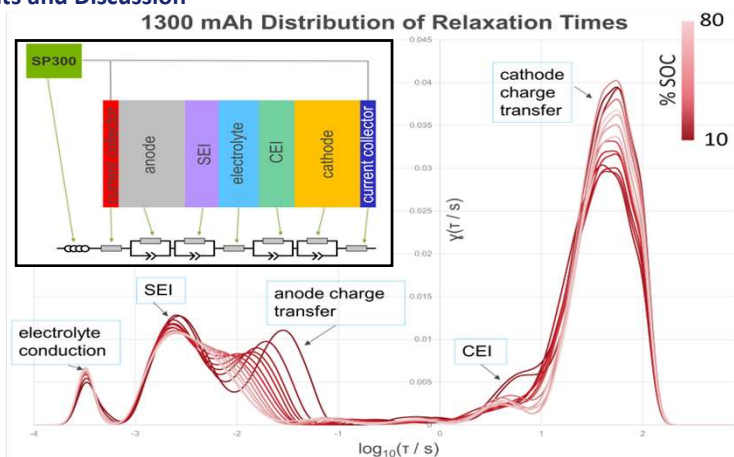


Figure 3 – each DRT peak is modeled by an ECM element, $\lambda=0.0001$

- Result:** Electrolyte resistance was much greater in the 1300 than 750 mAh cell (see Figure 2). **Hypothesis** \rightarrow Electrolyte composition of the cells differ.
- Result:** Electrolyte conduction is the fastest Li^+ transport mechanism, followed by SEI, anode charge transfer and cathode charge transfer^[1, 2] (see Figure 3). **Hypothesis** \rightarrow This leads to the accumulation of Li^+ at the electrolyte/SEI interface as the cell is charged.
- Result:** SEI resistance decreases with SOC for the larger pouch cell; no significant difference for the smaller cell. **Hypothesis** \rightarrow SEI thickens in 1300 mAh cell as accumulated Li^+ reacts with the electrolyte: lithium is incorporated into the SEI as lithium alkoxides ($\text{ROLi}^{[3]}$). Thicker SEI means more space for lithium, so lower resistance. \rightarrow Difference in anode structure / electrolyte composition in the 750 mAh cell means SEI thickness does not change significantly.
- Result:** Anode charge transfer resistance and time constant decrease with SOC. This is more significant in the 1300 mAh cell. **Hypothesis** \rightarrow Li^+ build-up increases its concentration gradient, so diffusion into the anode happens more quickly. ROLi catalyse movement of Li^+ across the SEI, so SEI resistance decreases. This is most significant in the 1300 mAh cell. In addition, graphite stage change from $n=2$ to $n=1$ with progressive SOC^[4] increases surface site availability for intercalation.
- Result:** CEI resistance is very small and decreased linearly with SOC ($R^2=0.94$; $p=E-16$) and Li^+ movement got faster with SOC; 750 mAh double layer capacitance increases with charge. **Hypothesis** \rightarrow Resistance and τ decrease due to increased diffusion gradients; \rightarrow double layer capacitance increases with cell potential increase due to cathode oxidation.
- Result:** Cathode resistance is highest at top and bottom of charge; a clear hysteresis is seen in the double layer capacitance (paired t-test $p<<E-5$). **Hypothesis** \rightarrow Li^+ high Li^+ concentration at 0% SOC slows further lithiation; crystal structure changes with increasing oxidation decrease Li^+ intercalation sites.

Further work

- Repeat all measurements taken; compare results to *operando* EIS measurements.
- Determine electrode and electrolyte materials; investigate chemical reactions behind impedance and time constant changes observed using small angle neutron scattering.
- The Warburg diffusive tail was not observed in the frequency range measured: recording EIS data at lower frequencies could provide a fuller picture of cell processes.

Researcher Bio

Heledd Jones is entering her third year as an undergraduate Natural Sciences student at the University of Cambridge. Hoping to play a role in enabling a green energy transition, she is interested in the use of diverse electrode materials in different battery cell systems.

connect here!



Summary of Work

- Optimised GEIS perturbation amplitude**
- 5% SOC GEIS measurements of 750 mAh cell at 1 C and 4.2 C**
- 5% SOC GEIS measurements of 1300 mAh cell at 1C**

Galvanostatic Electrochemical Impedance Spectroscopy GEIS Perturbation

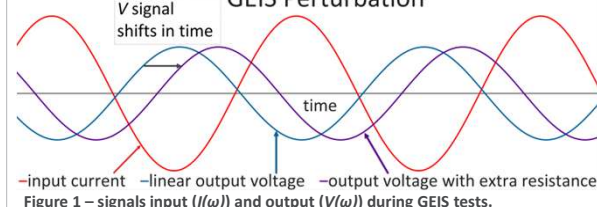


Figure 1 – signals input ($I(\omega)$) and output ($V(\omega)$) during GEIS tests.

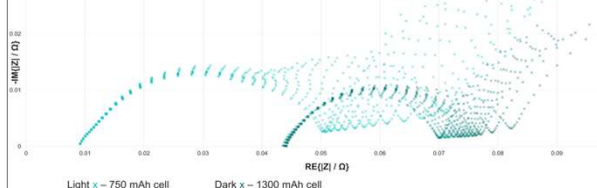
- A **sinusoidal current** is supplied to a cell at fixed amplitude and varying frequency; **output potential difference** is measured.
- Cells are rested between charging and GEIS, so the system is assumed to be **linear** (no ions moving).
- If the perturbation frequency is similar to or slower than the frequency of a certain reaction process in the cell, the **resistance of that process** will increase the **phase angle of output voltage**, shifting the signal detected in time (see **FIGURE 1**).
- The impedance, Z , of the system is measured using

$$Z(\omega) = \frac{\tilde{V}(\omega)}{\tilde{I}(\omega)} = \left| \frac{\tilde{V}(\omega)}{\tilde{I}(\omega)} \right| (\cos(\phi\omega) + i \sin(\phi\omega)) = \text{Re}\{|Z|\} + i\text{Im}\{|Z|\}$$

Experimental

- GEIS measurements were taken on 1300 mAh and 750 mAh pouch cells (C/5 perturbation: 130 mA and 260 mA respectively) at 5% SOC increments between 10% and 80% SOC – during charging and discharging cycles – at 1C and 4.2C.
- Cells were rested for an hour before each measurement to ensure system linearity.
- Equivalent circuit models (ECMs)** motivated by **distribution of relaxation times (DRT)** and fit residual error analysis were fitted to the impedance data using relaxIS software (see **FIGURE 2**).

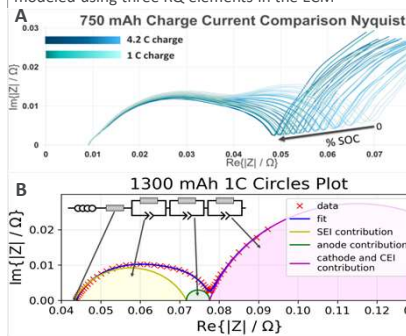
FIGURE 2 – NYQUIST PLOT FOR 1C CHARGE DATA



Conclusions

- Cell size and composition significantly affect the resistances and time constants of charge transfer processes.
- Overall impedance decreases with increasing SOC.
- Charge and discharge cycles did not differ significantly for most processes; charge rate did not affect impedance (**FIGURE 4A**).

Figure 4 – A: see text; B: some 1300 mAh SOCs were modeled using three RQ elements in the ECM



References

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