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Detailed "mapping" of internal resistance in Li-S batteries

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1. Introduction and principle

Frequent and continuous determination of battery internal resistance by a simple current-interrupt method through the creation of resistance "maps", showing changes in resistance as a function of both capacity and cycle number. This new approach is demonstrated here with an investigation of cell failure in the lithium-sulfur system with Li electrode excesses optimised towards practically relevant specifications.

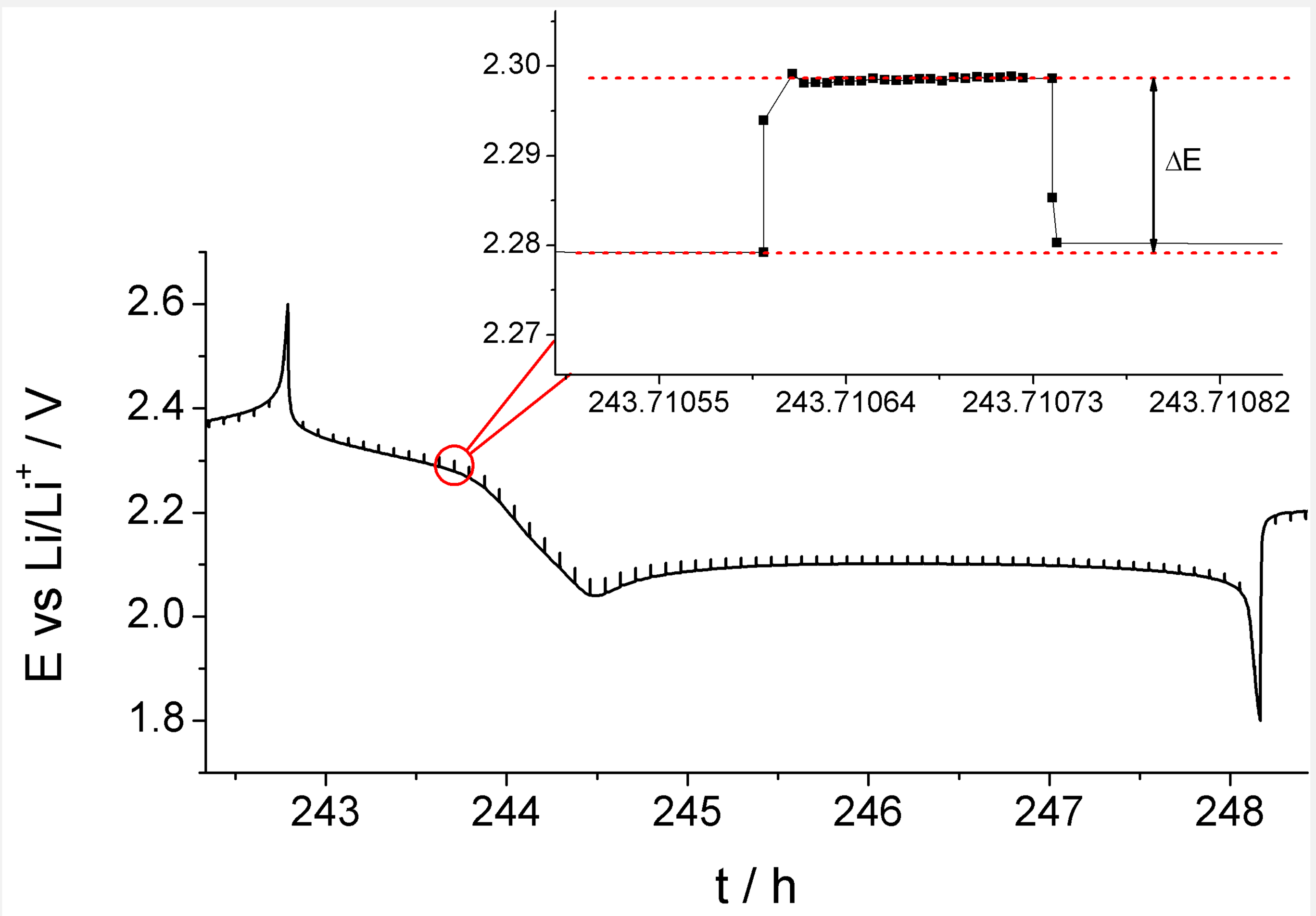

Figure 1: Typical discharge voltage profile showing repeated current interruptions. Inset is a zoomed view of a single current interruption, indicating the voltage difference over which the resistance is determined.

In this work, internal resistance was followed by by modifying a standard C/10 constant current cycling program to include regular current interruptions (0.5 seconds interruption every 5 minutes). Internal resistance was estimated from each current interruption assuming Ohmic behaviour. Analysis and plotting of the datasets is easily automated with a simple program written in the freely available programming language R.

In this case, measurements with this frequency gives approx. 100-150 individual measurements of resistance per cycle but only increases the duration of the experiment relative to the standard cycling program by less than 0.2%.

Compared with common techniques, particularly impedance spectroscopy as widely used in academic research, the technique benefits from ease of implementation, lack of requirement for sophisticated instrumentation and simplicity of analysis.

2. Validation

The current-interrupt approach was validated by comparison with other conventional measurements, specifically impedance spectroscopy and current pulse approaches. The comparison was made by measuring the resistance at approximately the same point every cycle (1 hour after the start of the charge cycle).

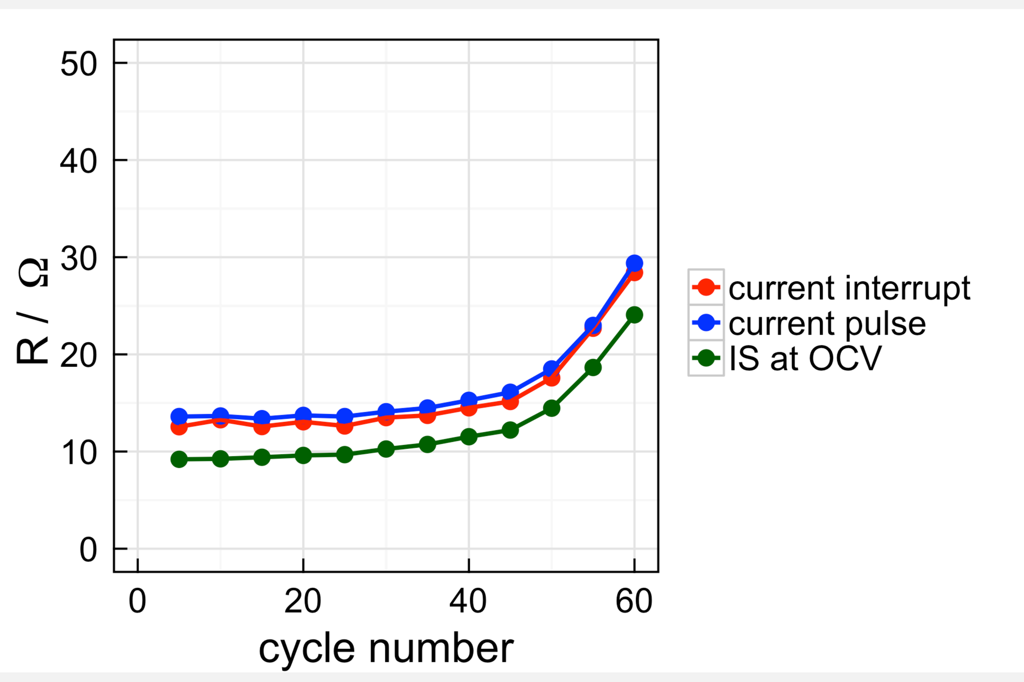

Figure 2: internal resistance for a Li-S cell measured at approximately the same state of charge over 60 cycles by three different techniques.

The resistance as determined by the current-interrupt method is approximately the sum of electronic and ionic resistances in the electrodes and electrolyte, plus charge transfer (kinetic) resistances, as determined by comparison with impedance spectroscopy.

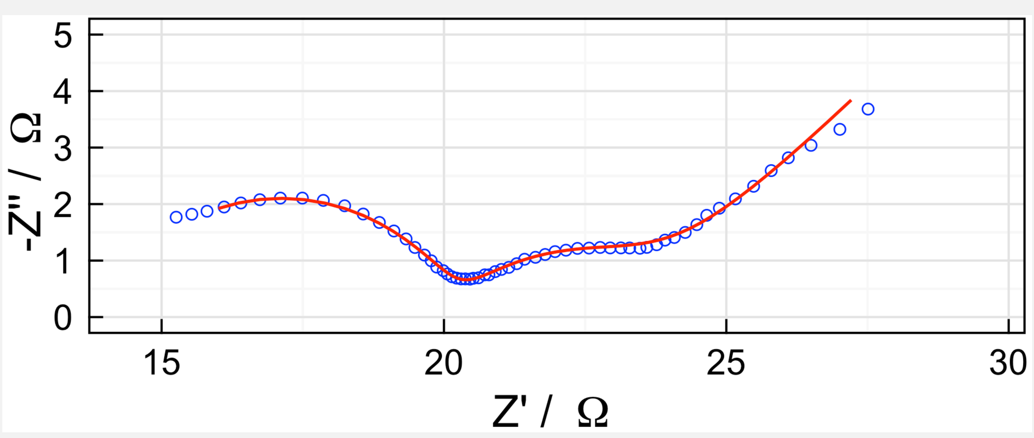

Figure 3: typical impedance spectrum for a Li-S cell.

References and acknowledgements

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3. Results and discussion

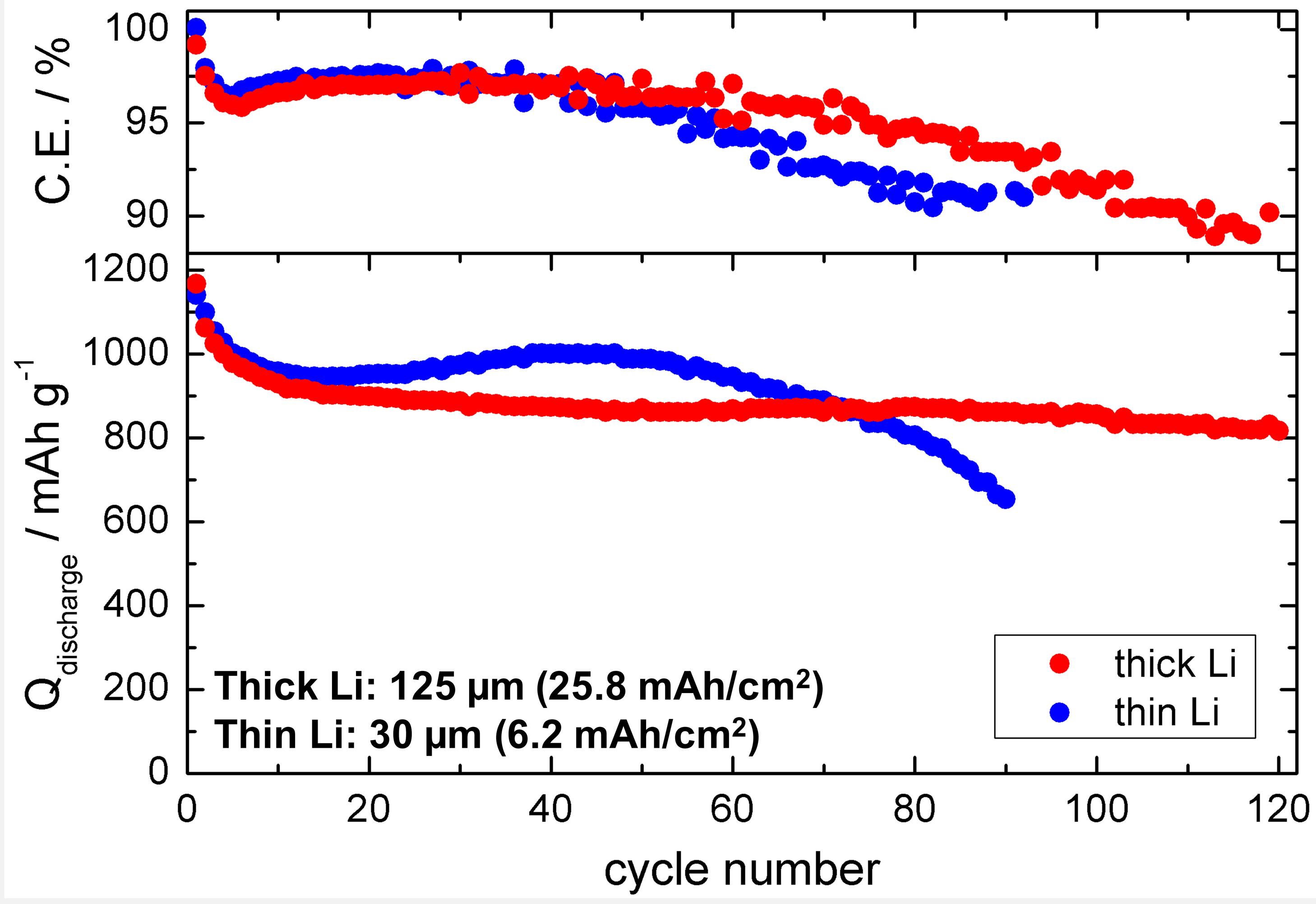

Figure 4: Specific discharge capacity and coulombic efficiency vs cycle number for lithium-sulfur cells containing thick (125 mm) or thin (30 mm) Li foil negative electrodes cycled until failure.

Fig. 4 shows the cycling behaviour of two lithium-cells using negative electrodes of different thicknesses. The positive electrodes are optimised towards realistic specifications (65% S in electrode, ~2 mAh/cm², water-based functional binder), and the electrolyte/sulfur ratio is reduced to 6 µL/mg$_S$$^{-1}$.

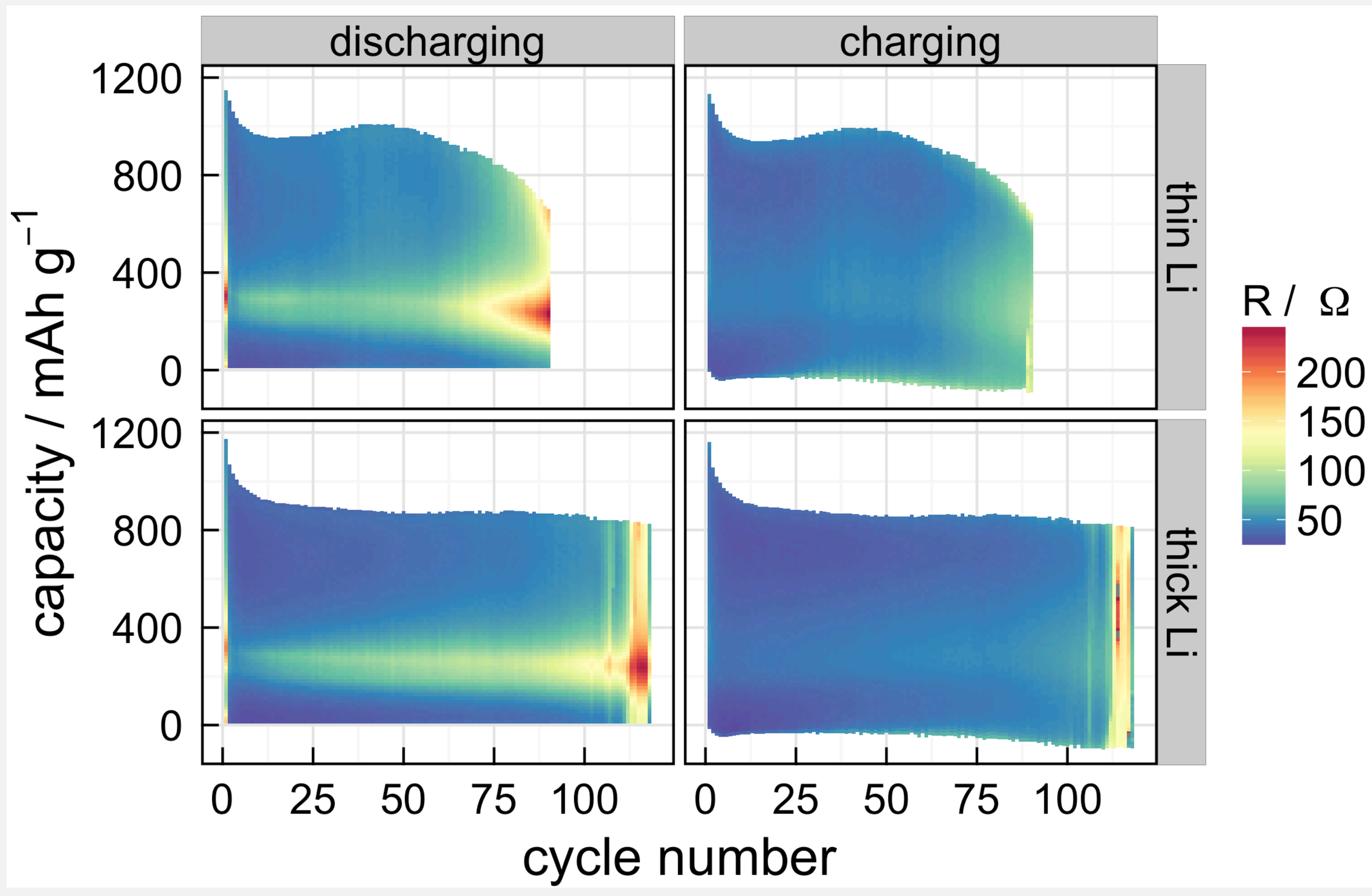

Figure 5: Specific capacity vs cycle number plots for lithium-sulfur cells with different negative electrode thicknesses, coloured according to the calculated internal resistance at each given point.

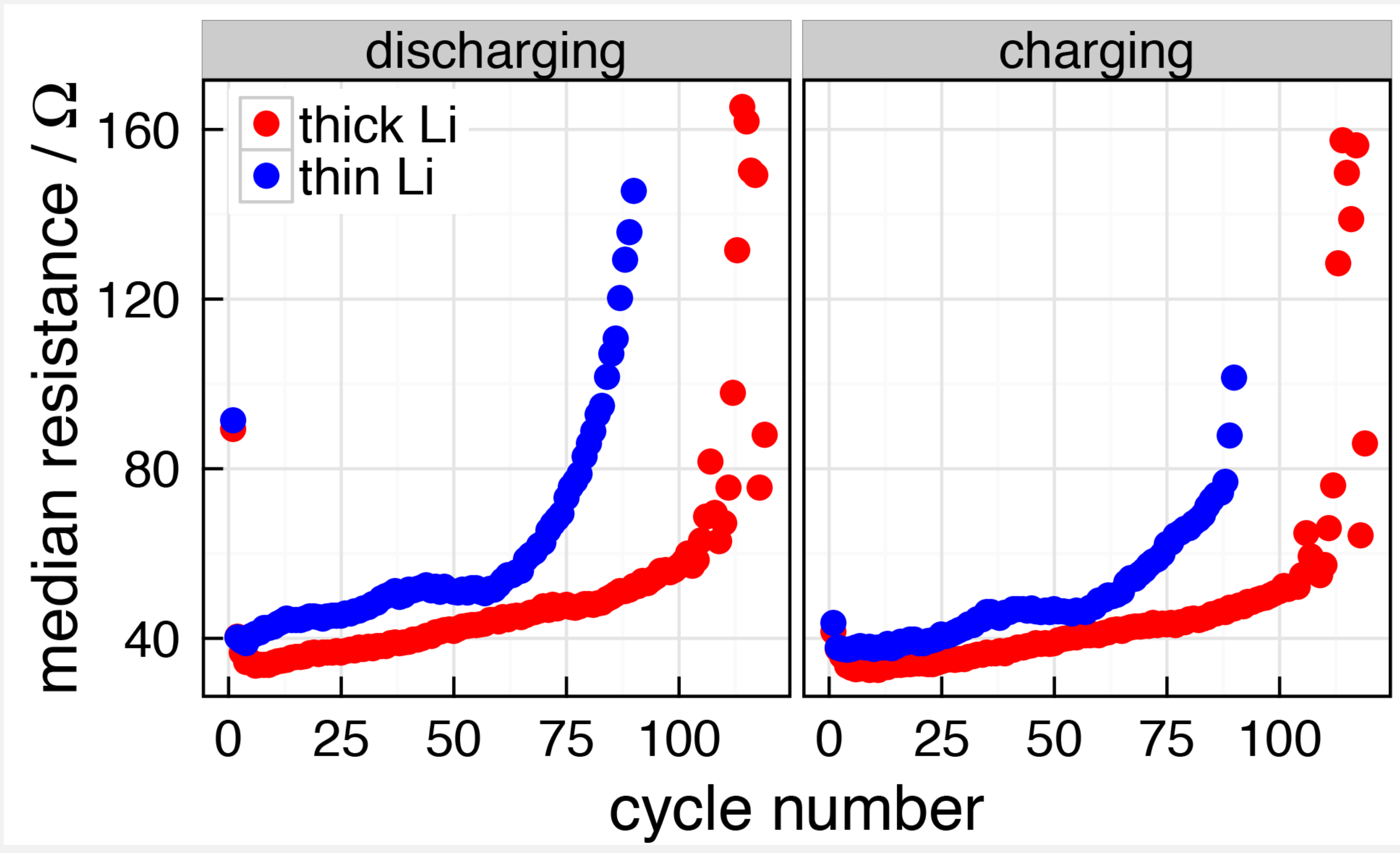

Figure 6: Median internal resistance for each (dis)charge step vs cycle number, as calculated from the data given in Fig. 2.

Figs. 5 and 6 show the "raw" results of a typical experiment and a simple statistical analysis of the results respectively. In this case the effect of reducing the negative electrode excess on the cycle life and the changes in cell resistance is clear. Supplementary experiments/analysis can reveal further information on the processes governing cell failure, including:

- SoC-dependent variation in resistance, and changing distribution with increasing cycles
- Asymmetry in charge and discharge
- Evidence of electrolyte decomposition leading to cell failure

4. Summary

The behaviour of Li-S cells optimised towards realistic specifications deserves greater attention. Reduction of Li excess results in earlier onset of capacity fade and/or cell failure. The resistance "mapping" approach is a simple method for extracting detailed information on changes in cell resistance. Such information is highly valuable in evaluating stability of batteries, especially those where resistance varies with SoC.