Electronic Supplementary Information: Experimental and numerical analysis to identify the performance limiting mechanisms in solid-state lithium cells under pulse operating conditions†

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A new cell was overcharged with a small current (C/10) beyond 4.2 V to estimate the upper voltage limit. The initial characterisation result shows that the cell reaches a maximum cell voltage at 5.0 V before a sharp drop. Also, the gradient of the voltage profile begins to increase sharply after 4.6 V, which indicates possible irreversible reactions at high voltage.[1] Hence, the upper voltage limit was estimated to be 4.5 V before this sharp gradient change (Figure S1(a)). Likewise, the cell was overdischarged with a small current (C/10) beyond 3.0 V to estimate the lower voltage limit. A voltage plateau can be observed around 1.25 V. In another experiment following the procedures described in Section 3.2, the impedance of the cell was monitored during overdischarge. A significant change in the cell impedance can be observed when the cell voltage drops below 3.0 V (Figure S1(c)), indicating an unstable positive electrode. Based on this initial characterisation results, the voltage window was set to [3.0, 4.5 V]. Another new cell was cycled first between the voltage windows defined by the manufacturer 3.0 − 4.2 V and then the initial voltage limits in Figure S1.

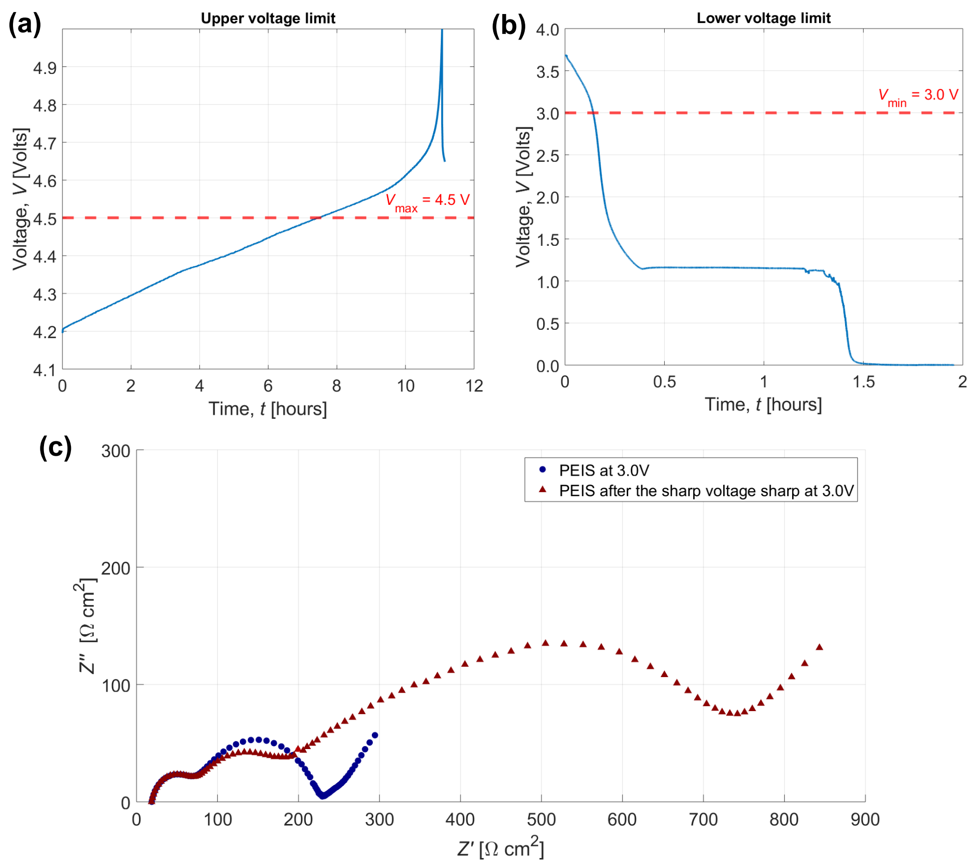

Fig. S1 Initial overcharge (a) and overdischarge characterisation experiment (b) to estimate the upper and lower voltage limits of the cell, which are used as a basis to estimate the maximum and minimum lithium content in the cell. (c) PEIS impedance measurement at the OCV of 3.0 V and 1.5 V.

Figure S2 shows the experimental results of cycling between these voltage limits. Because a hysteresis effect is observed between the discharge and charge curves of the fresh cell at [3.0, 4.5 V] for a C-rate at C/40, [3.0, 4.2 V] was chosen to be the subsequent voltage limit in this work. For a cell configuration that uses metallic lithium as the negative electrode, the maximum and minimum lithium content in the cell can be estimated from the voltage-capacity curves by aligning and normalising the voltage-capacity curves of these voltage windows.

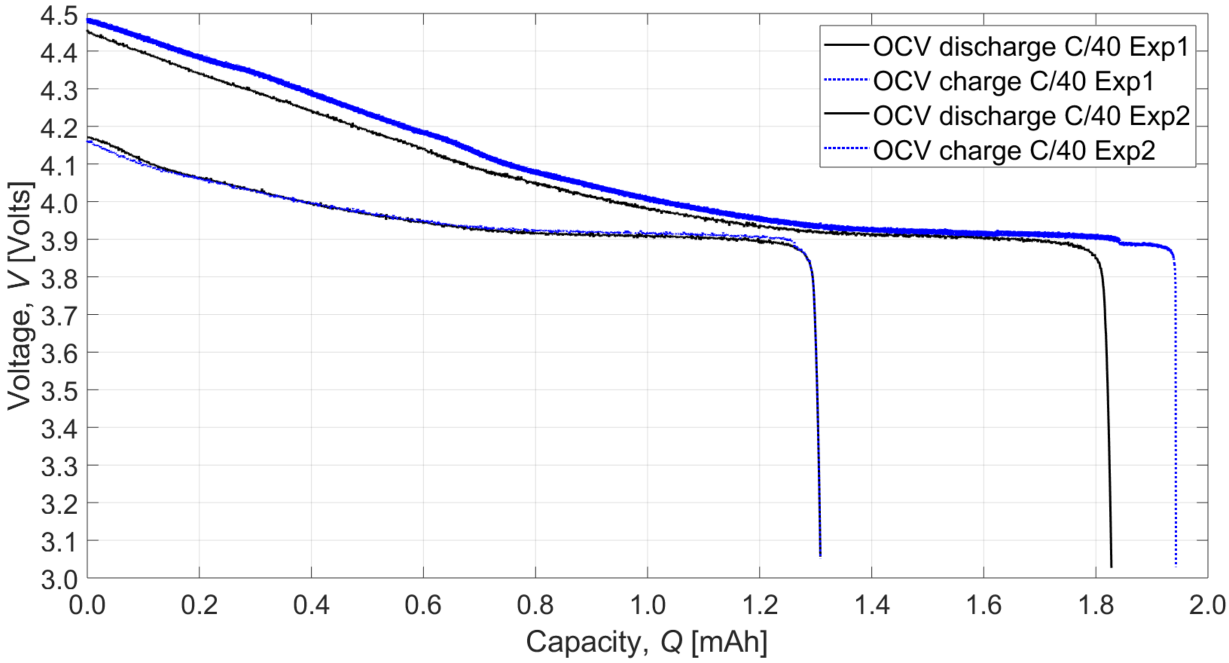

Fig. S2 Cycling between the voltage limits of 4.2 V - 3.0 V (blue curve: discharge at C/40; red curve: charge at C/40) and 4.5 V - 3.0 V (black curve: discharge at C/40; blue curve: charge at C/40). The offset between the discharge and charge curves is the rest period between the discharge and charge sequence.

Figure S3 shows the percentage of deviation between experimentally measured and simulated pulse discharge and charge curves, whereas Figure S4 shows the voltage deviation in percentage for the dynamic pulses. Both experimental and simulation model have the same timestep. The sharp peak in the voltage deviation is due to the immediate voltage jump at a short timescale of 1s.

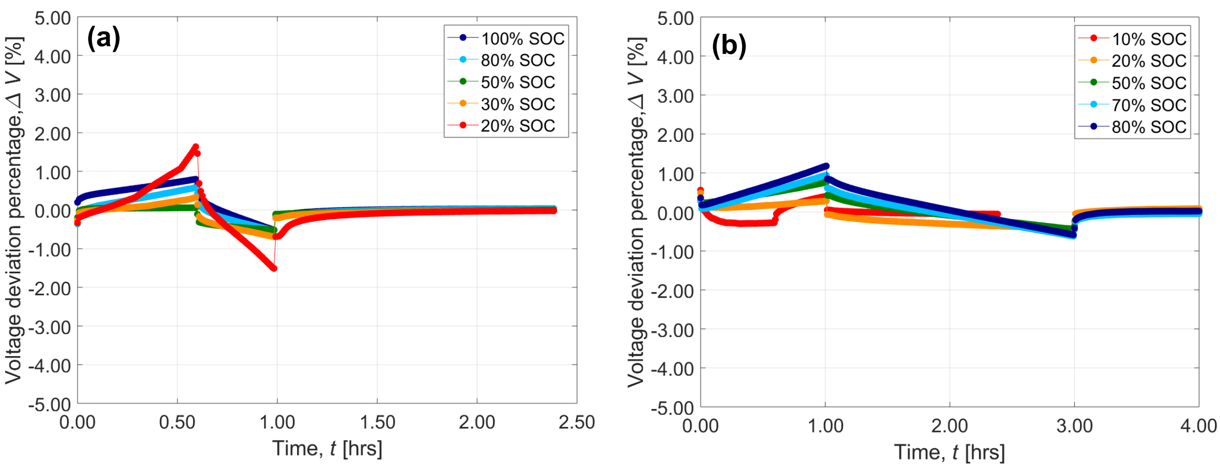

Fig. S3 The voltage deviations in percentage for the pulse discharge and charge profiles. Both experimental and simulated profiles have a maximum deviation percentage of $\approx 2\%$.

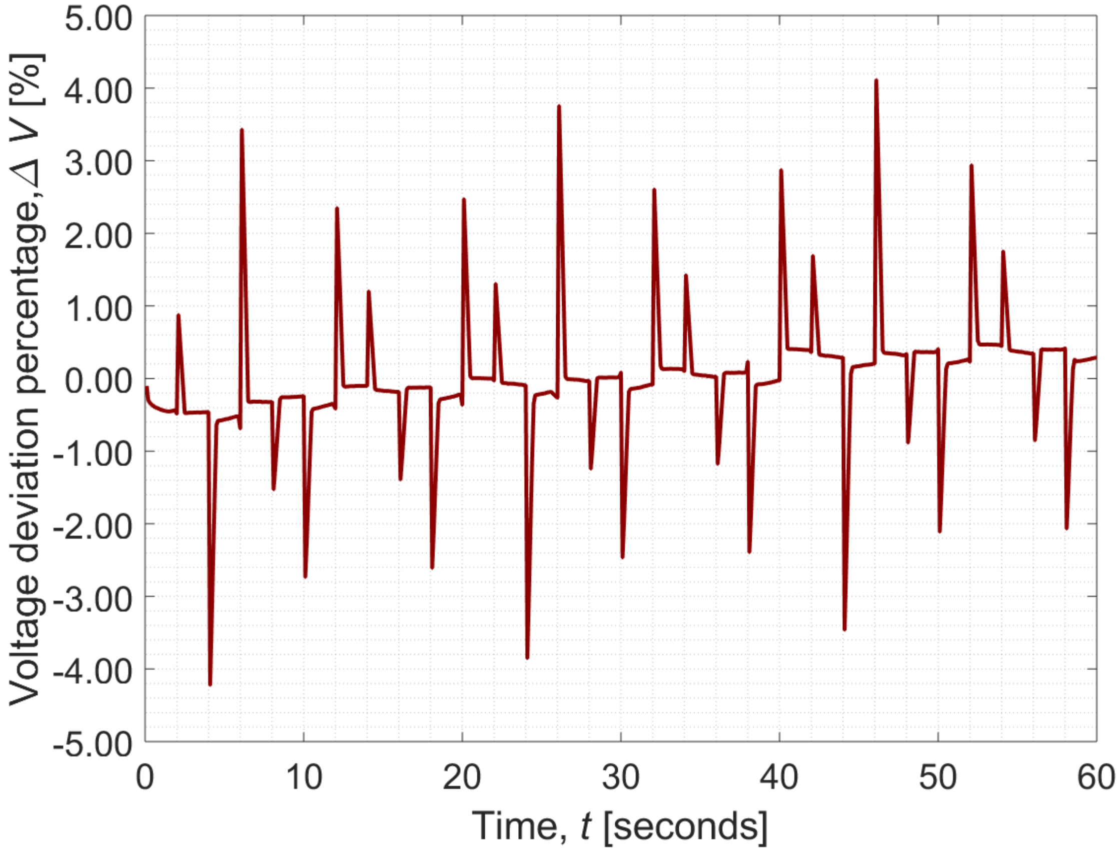

Fig. S4 The voltage deviations in percentage for the dynamic pulse profiles, which has a maximum deviation in percentage of approximately 4%. The sharp peak in the deviations is caused by the immediate voltage jump when the current profile changes.

References

1 Z. Yang, R. Li and Z. Deng, *Scientific reports*, 2018, **8**, 863.