

# Understanding the limits of Li-NMC811 half-cells

Rory C. McNulty,<sup>1,2</sup> Elizabeth Hampson,<sup>1</sup> Lewis N. Cutler,<sup>1</sup> Clare P. Grey,<sup>2,3</sup> Wesley M. Dose<sup>†,2,3</sup> and Lee Johnson<sup>\*1,2</sup>

<sup>1</sup>Nottingham Applied Materials and Interfaces Group, School of Chemistry, University of Nottingham, NG7 2TU, UK

<sup>2</sup>The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot, OX11 0RA, UK

<sup>3</sup>Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

<sup>†</sup>Current address: School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

\*lee.johnson@nottingham.ac.uk

## Supporting Information

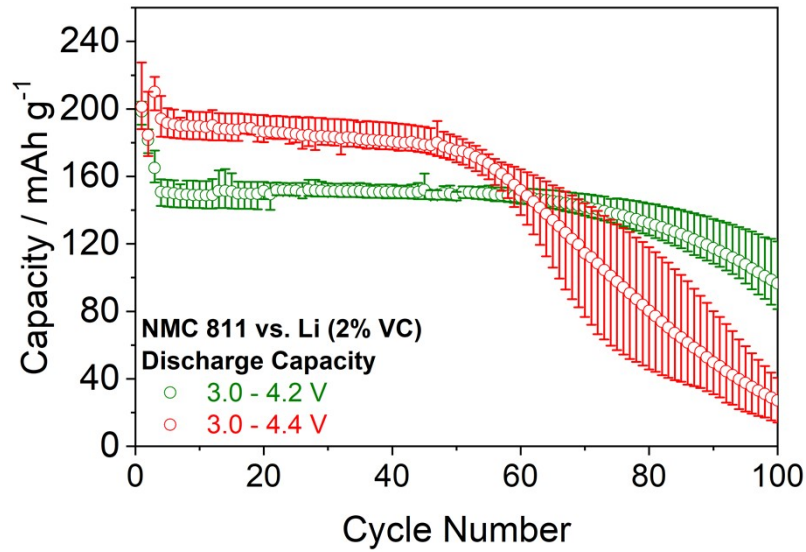
**Materials.** LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> (NMC811, 16.9 mg cm<sup>-2</sup>, ca. 3.19 mAh cm<sup>-2</sup>) and graphite (Gr, 11.3 mg cm<sup>-2</sup>, 3.8 mAh cm<sup>-2</sup>) electrodes were manufactured by LiFun. NMC811 electrodes were comprised of 95.5% active material, 2.5% conductive carbon support, and 2% binder coated on aluminium foil. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO, 25 mg cm<sup>-2</sup>, 3.7 mAh cm<sup>-2</sup>) electrodes were manufactured at the Argonne National Laboratory. Lithium metal was purchased from Sigma Aldrich (99.9% purity). The base electrolyte (LP57) and the formulated electrolyte with 2 wt. % vinylene carbonate (VC) additive were purchased from Solvionic (99.9 % purity, H<sub>2</sub>O <20 ppm). NMC811, LTO, and Gr electrodes were dried under vacuum at 120 °C for 24 hours before being transferred into an Ar-filled glovebox without exposure to air.

**Electrochemical testing.** Battery cells were assembled inside an Ar-filled glovebox (MBraun, O<sub>2</sub> and H<sub>2</sub>O ≤ 0.1 ppm). All measurements were carried out at 40 °C with an initial equilibration time of 1 hr allowed for electrode wetting and temperature uniformity. Whatman glass microfiber filter paper functioned as the separator, soaked in 120 μL of LP57 (1 M LiPF<sub>6</sub> in EC:EMC = 30:70 v/v) either with or without the presence of 2 wt. % VC additive. Li-, Gr-, and LTO-NMC811 cells were cycled using a two-electrode Swagelok format cell, pairing 12 mm disc electrodes. C-rates were calculated assuming a practical NMC811 capacity of 190 mAh g<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was carried out in a 3-electrode Swagelok format cell consisting of a 12 mm NMC811 electrode, a 12 mm lithium metal counter electrode, and a 6mm lithium metal reference electrode. EIS measurements were taken at 3.6 V vs. Li<sup>+</sup>/Li after a 1-hour voltage hold step when the discharge voltage reached 3.6 V vs. Li<sup>+</sup>/Li on the subsequent discharge step. Battery cycling and electrochemical impedance spectroscopy were carried out on IviCycle200 and Ivium Octostat30, respectively. Cycling data were analysed using the GalvAnalyze executable.<sup>1</sup>

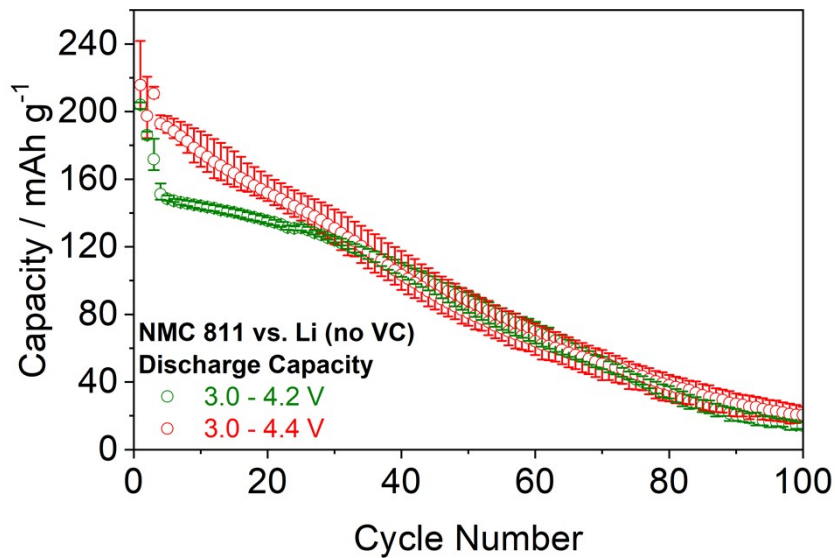
**Post-cycling electrolyte analysis.** After cycling, the cells were disassembled in an Ar-filled glovebox and the glass microfiber filter paper was soaked in 1.5 mL CDCl<sub>3</sub> (Sigma Aldrich, 99.0% purity, H<sub>2</sub>O <100 ppm) for >30 minutes, taking inspiration from procedures by Dahn *et al.*<sup>2</sup> The solution was split between an airtight NMR tube fitted with a Young's tap (1 mL) and sealed GC-MS vials (250 μL). One-dimensional <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>31</sup>P NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer with data analysed using the TopSpin software. GC-MS samples were analysed using a Thermo Fisher TRACE1300/1310 gas chromatograph coupled to an ISQ single quadrupole mass

spectrometer. A 30 m Rtx-1701 column with an inner diameter of 0.25 mm and a coating thickness of 0.25  $\mu\text{m}$  was equipped to the inlet. The carrier gas was helium (99.999%) at a constant flow of 1.5 mL/min. Samples were injected into the inlet with a splitless flow at 200  $^{\circ}\text{C}$  and carried onto the column preheated to 40  $^{\circ}\text{C}$  and held for 3 minutes. The oven temperature was ramped at 2  $^{\circ}\text{C}/\text{min}$  for 10 mins, followed by 10  $^{\circ}\text{C}/\text{min}$  for 3 minutes, 2  $^{\circ}\text{C}/\text{min}$  for 10 minutes, and finally 10  $^{\circ}\text{C}/\text{min}$  for 13 minutes to a temperature of 240  $^{\circ}\text{C}$ , where all compounds were evolved from the column. The mass spectrometer transfer line and ion source were held at 250  $^{\circ}\text{C}$ . A blank injection (HPLC grade methanol) was run between each injection to prevent contamination between sample injections. Data was analysed using the Chromeleon software to identify the composition of chromatogram peaks through cross referencing mass spectra with the NIST database.

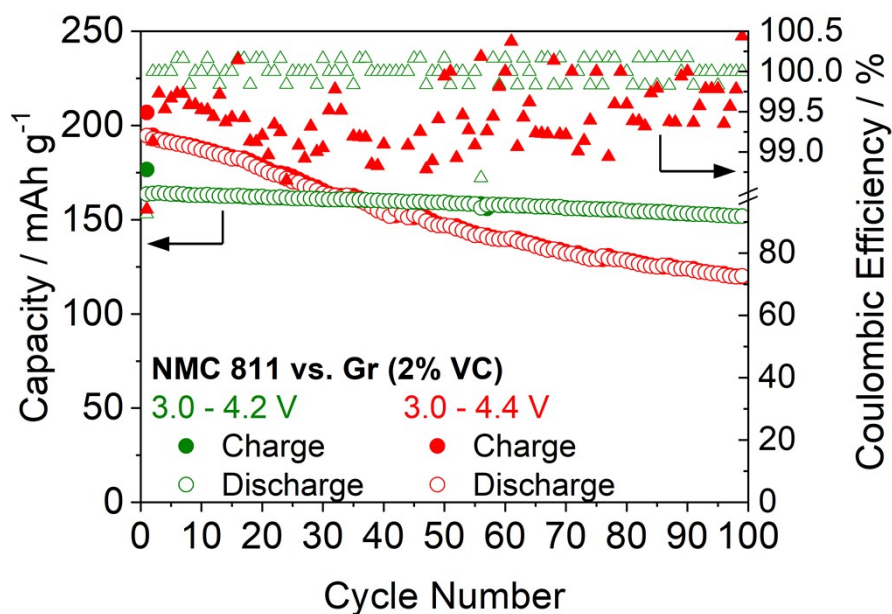
**Cell reconstitution procedure.** Two electrode NMC811-Li cells were assembled as described above and cycled for 2 C/20 formation cycles between 3.0 – 4.2 V vs  $\text{Li}^+/\text{Li}$ . For the data shown in Figure 4, the cells were cycled for a further 100 cycles at C/2 under either standard (3.0 – 4.2 V vs  $\text{Li}^+/\text{Li}$ ) or stressed (3.0 – 4.4 V vs  $\text{Li}^+/\text{Li}$ ) conditions before being reconstituted. The cells were disassembled, taking care to separate the components by exposing the separator-separator interface between the two soaked Whatman glass microfiber filter paper discs. Each of the cycled electrode-separator pairs was then reassembled in a fresh cell with the addition of an additional pristine separator, fresh electrolyte and a pristine partner electrode. The result was two cells, one with the cycled NMC811 paired with a pristine lithium metal electrode, and the other the cycled lithium paired with a pristine NMC811 electrode. By separating the components at the separator-separator interface, the mechanical disturbance of the SEI and CEI was kept to a minimum. The cells were allowed to rest at 40  $^{\circ}\text{C}$  for 1 hour before the cycling procedure was initiated. To validate the cell reconstitution procedure, 10 C/2 cycles were carried out after formation cycling under standard conditions (3.0 – 4.2 V vs  $\text{Li}^+/\text{Li}$ ) before the same reconstitution procedures described above were carried out.



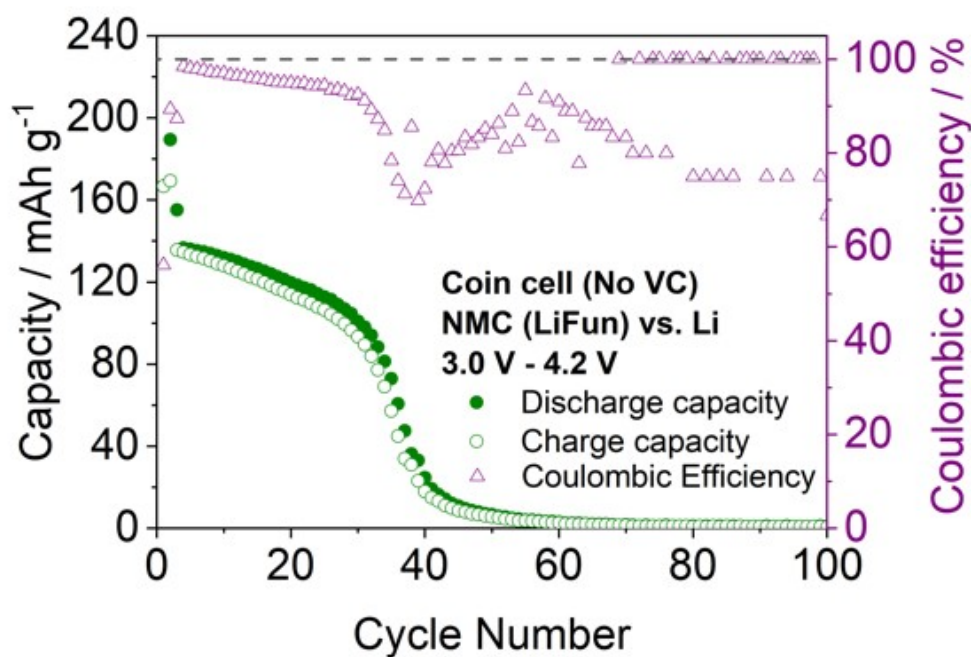
**Fig S1.** Comparison of the error in the first 100 cycle discharge capacity (circles) of multiple Li-NMC 811 half-cells with an LP57 electrolyte (1M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), with 2 wt. % VC additive, under standard (3.0 – 4.2 V vs. Li<sup>+</sup>/Li, green) and stressed (3.0 – 4.4 V vs. Li<sup>+</sup>/Li, red) conditions. A total of 10 cells for each set of conditions are compared, with 4 being cycled to 100 cycles. Error bars represent the spread of data.



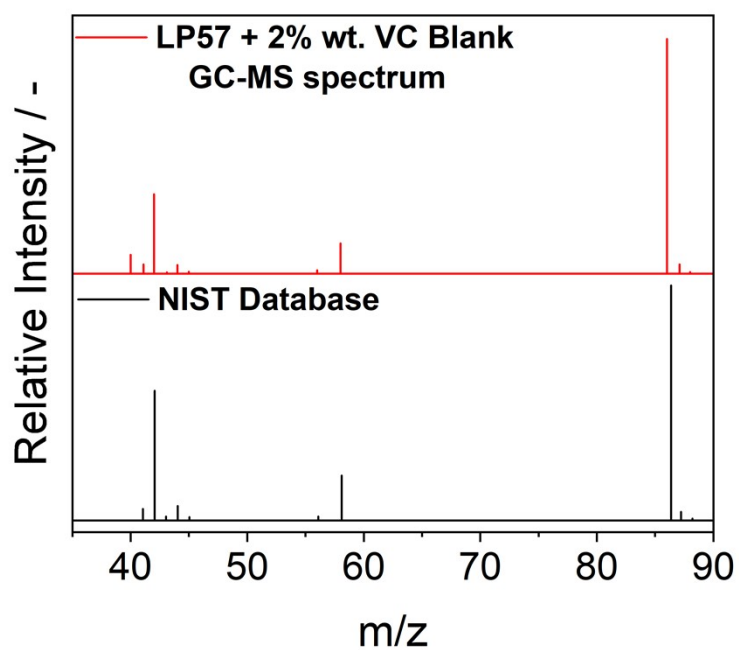
**Fig S2.** Comparison of the error in the first 100 cycle discharge capacity (circles) of multiple Li-NMC 811 half-cells with an LP57 electrolyte (1M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), with no VC additive, under standard (3.0 – 4.2 V vs. Li<sup>+</sup>/Li, green) and stressed (3.0 – 4.4 V vs. Li<sup>+</sup>/Li, red) conditions. A total of 9 cells for each set of conditions are compared, with 3 being cycled to 100 cycles. Error bars represent the spread of data.



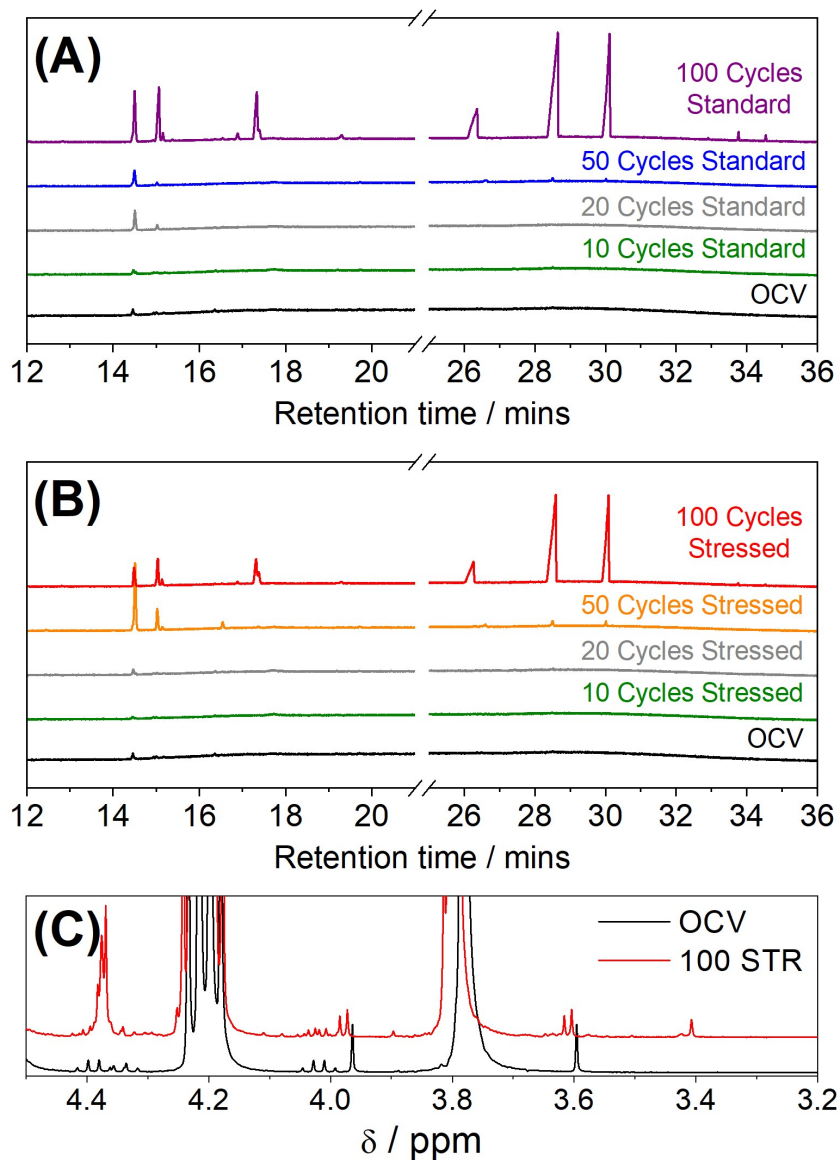
**Figure S3.** Comparison of the first 100 cycle capacities (circles) of Gr-NMC 811 full-cells with an LP57 electrolyte (1M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), with 2 wt. % VC additive, under standard (3.0 – 4.2 V vs. Li<sup>+</sup>/Li, green) and stressed (3.0 – 4.4 V vs. Li<sup>+</sup>/Li, red) conditions. The capacity performance of the Gr-NMC811 cell cycled under standard conditions with 2 wt. % VC additive has a comparative performance to Li-NMC811 cells up to 50 cycles.



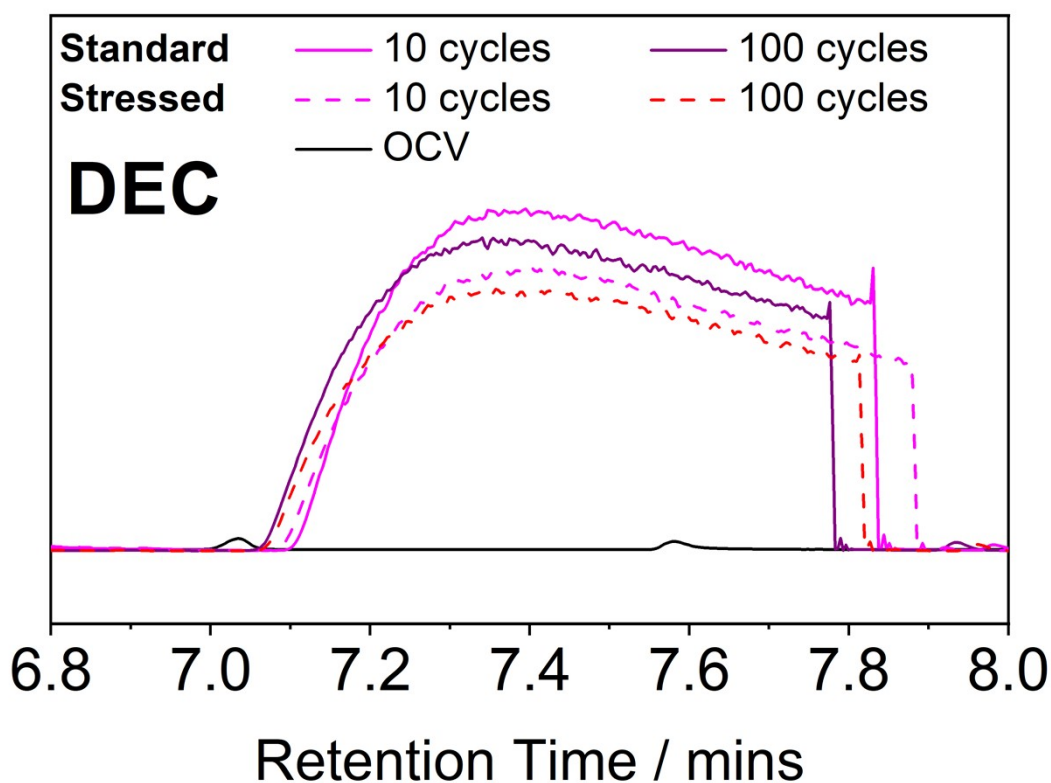
**Fig S4.** Charge and discharge capacities (circles) and cycle coulombic efficiency (triangles) of the first 100 cycles of a NMC811-Li half-cell containing a LP57 electrolyte with no VC additive cycled using a coin cell format.



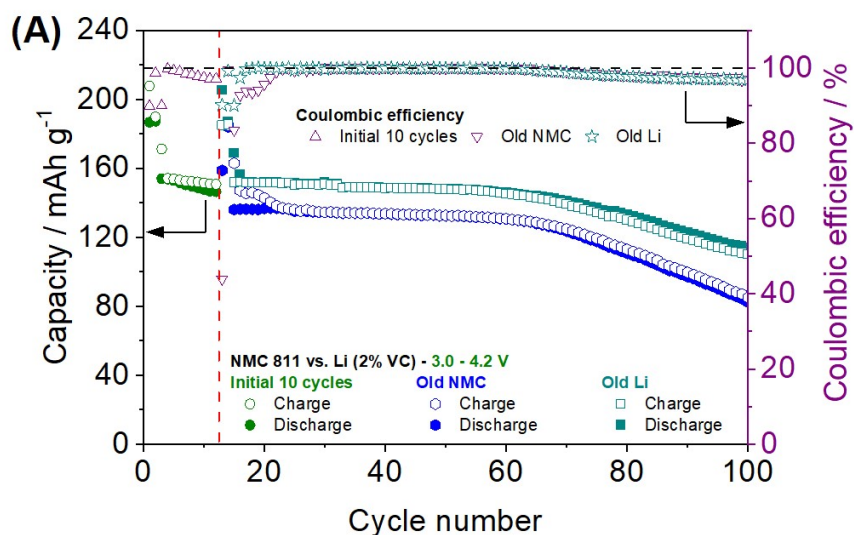
**Fig S5.** Comparison of the mass spectrum of VC produced during GC-MS analysis to the NIST database spectrum highlighting the three key identification fragments above 40 Da as 86 Da (molecular ion), 58 Da and 42 Da.



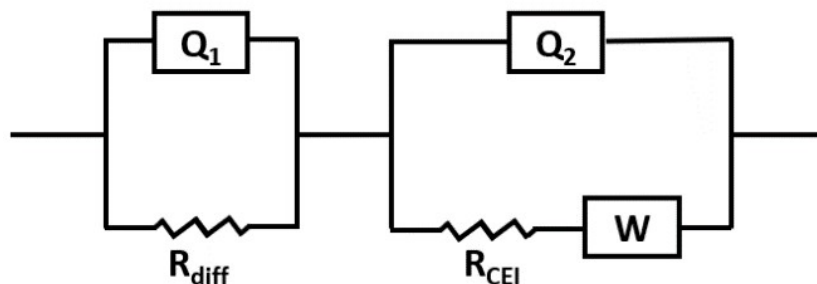
**Fig S6.** (A, B) GC-MS chromatograms of cells cycled under (A) standard (3.0 – 4.2 V vs Li<sup>+</sup>/Li) and (B) stressed (3.0 – 4.4 V vs Li<sup>+</sup>/Li) conditions, showing retention times between 12 – 36 mins, with 21 – 25 minutes removed to remove the intense EC peak. (C) NMR spectra showing the difference in the electrolyte composition between an 80 hr OCV period (black) and 100 cycles (red) under stressed conditions. Cell conditions were the same as those used in Figure 2 and 3.



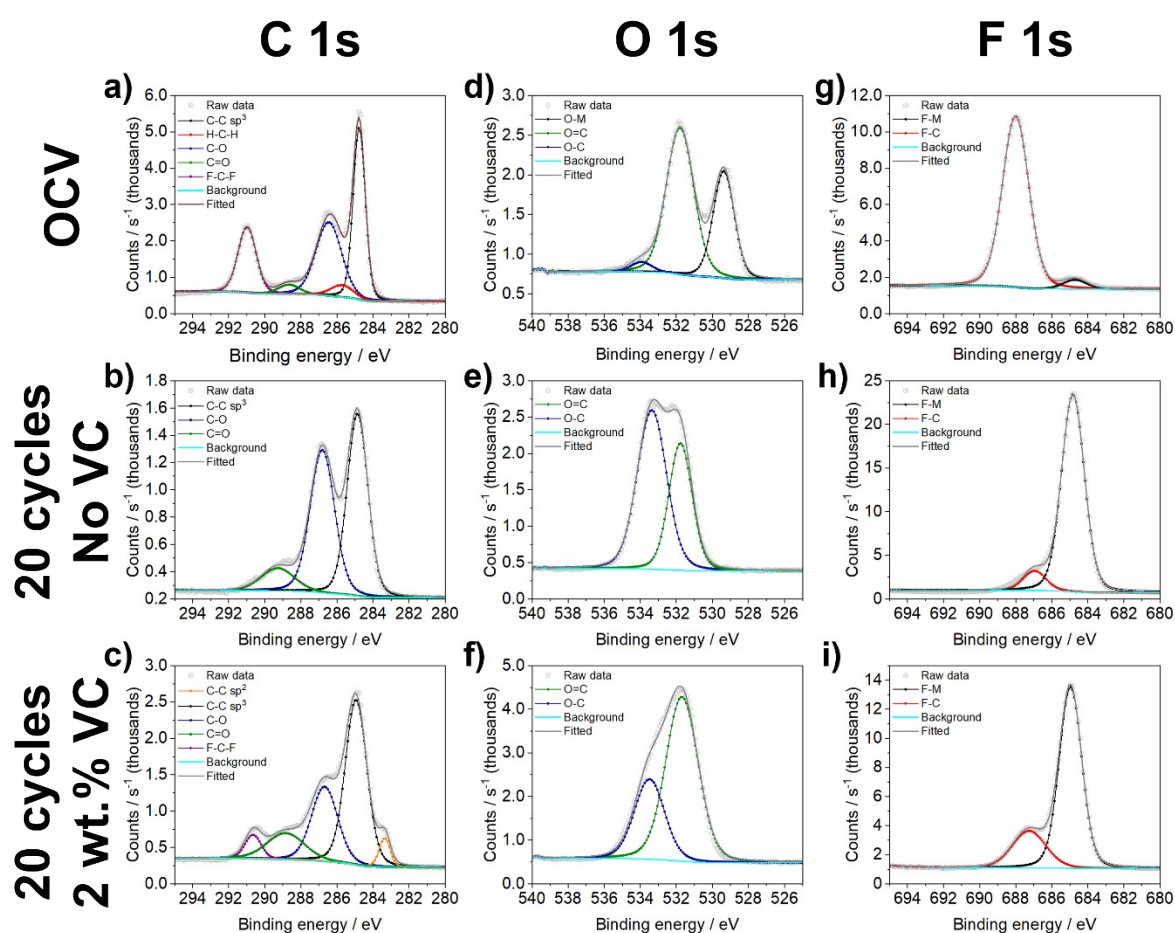
**Fig S7.** GC-MS chromatogram showing the formation of DEC in early stage cycling of Li-NMC 811 cells with an LP57 electrolyte (1M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), with no VC additive. Cells were cycled under standard (3.0 – 4.2 V vs Li<sup>+</sup>/Li) and stressed (3.0 – 4.4 V vs Li<sup>+</sup>/Li) conditions.



**Fig S8.** Comparison of the charge and discharge capacities (circles, hexagons, squares) and cycle coulombic efficiency (triangles, stars) of a Li-NMC811 half-cell containing an LP57 electrolyte (EC:EMC 3:7 v/v) and 2% VC additive cycled under standard conditions (3.0 – 4.2 V vs. Li<sup>+</sup>/Li). C/20 SEI formation cycling and 10 cycles at C/2 are shown for the pristine cell (green circles, purple triangles) before reconstitution is performed (dashed line). The performance of the cycled NMC (hexagons, triangles) and cycled Li (squares, stars) reconstituted with a pristine partner electrode are shown for comparison to the pristine cell.

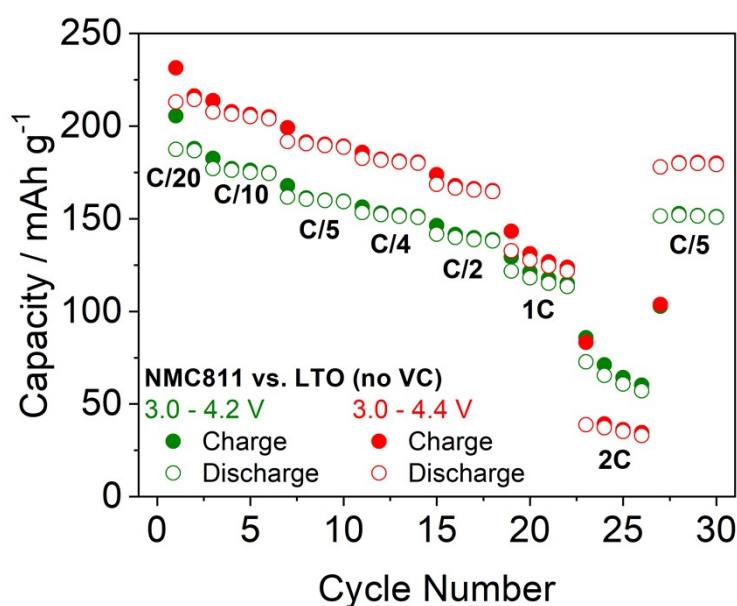


**Figure S9.** Schematic representation of the equivalent circuit diagram used to fit the isolated impedance response of an NMC811 electrode in a Li-NMC811 half-cell under a 3-electrode configuration with a lithium metal reference electrode.



**Figure S10.** XPS spectra of NMC811 electrodes after cycling in NMC811-Li half-cells containing an LP57 base electrolyte (c, f, i) with and (b, e, h) without 2 wt.% VC. (a – c) C 1s, (d – f) O 1s, and (g – i) F 1s spectra. Cells were cycled at C/2 for two formation cycles and subsequent cycles were at C/2. (a, d, g) Spectra of the NMC811 electrode after 80 hours at OCV within a NMC811-Li half-cell containing an LP57 base electrolyte with 2%wt. VC.





**Fig S11.** Comparison of the capacity performance of LTO-NMC811 cells with an LP57 electrolyte (1 M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), and with no VC additive, as a function of charge-discharge rate between C/20 (20 hour charge) to 2C (30 minute charge). Cell performance is examined under standard (3.0 – 4.2 V vs. Li<sup>+</sup>/Li, green) and stressed (3.0 – 4.4 V vs. Li<sup>+</sup>/Li, red) conditions and compared to the initial discharge capacities of Li-NMC811 cells cycled at C/2 under the same conditions.

**Fig S12.** Comparison of the capacity performance of LTO- (red), Gr- (blue) and Li-NMC811 (purple) cells with an LP57 electrolyte (1 M LiPF<sub>6</sub> in EC:EMC 3:7 v/v), and with no VC additive, under stressed conditions (UCV = 4.4 V vs. Li<sup>+</sup>/Li)

## References

1. McNulty, R.C., and Rier, L. (2023) GalvAnalyze: Streamlining Data Analysis of Galvanostatic Battery Cycling. Batter. Supercaps, e202300038. 10.1002/batt.202300038.
2. Thompson, L.M., Stone, W., Eldesoky, A., Smith, N.K., McFarlane, C.R.M., Kim, J.S., Johnson, M.B., Petibon, R., and Dahn, J.R. (2018). Quantifying Changes to the Electrolyte and Negative Electrode in Aged NMC532/Graphite Lithium-Ion Cells. J. Electrochem. Soc. 165, A2732. 10.1149/2.0721811jes.

