Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supplemental Information**

Lithium Vanadium Oxide ($Li_{1.1}V_3O_8$) Thick Porous Electrodes with High Rate Capacity: Utilization and Evolution upon Extended Cycling Elucidated via *Operando* Energy Dispersive X-ray Diffraction and Continuum Simulation

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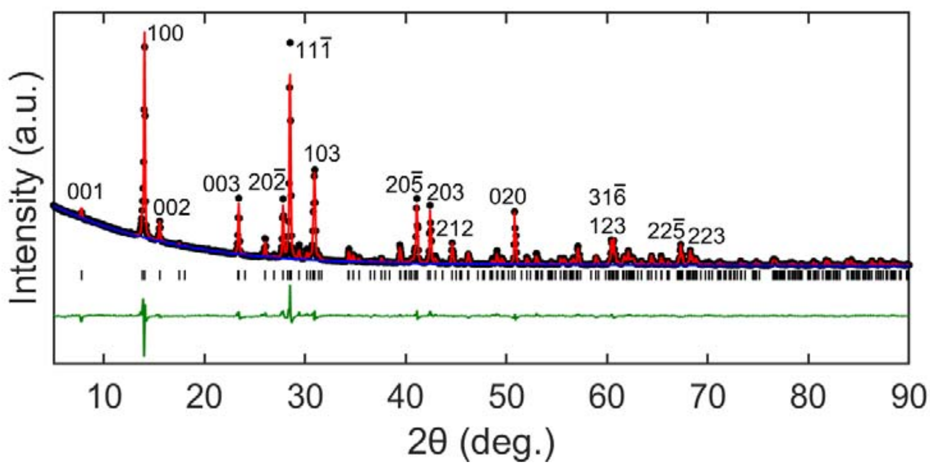


**Figure S1.** Rietveld refinement of the XRD pattern collected on pristine LVO. The black is the experimental data, the red is the calculated fit, the blue is the background, and the green is the difference between the experimental data and the calculated fit. The black lines and indices are the expected α-LVO reflections from PDF #01-073-8145.

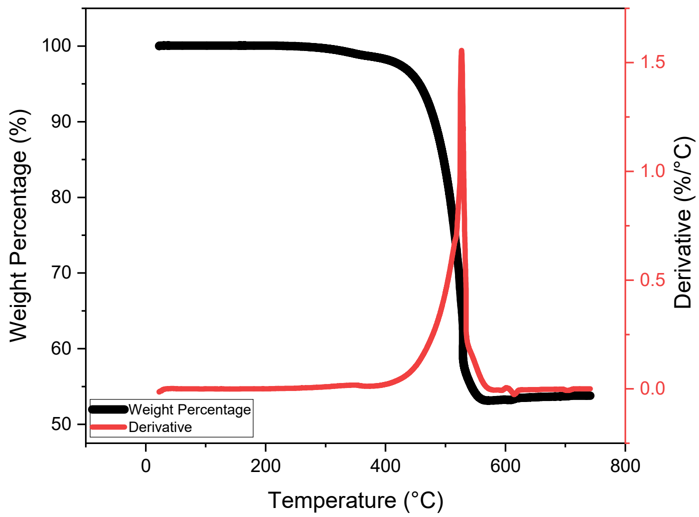


**Figure S2**.TGA results of the composite thick porous electrode (TPE) from 25°C to 750°C (black) with the derivative of the weight percentage (red).

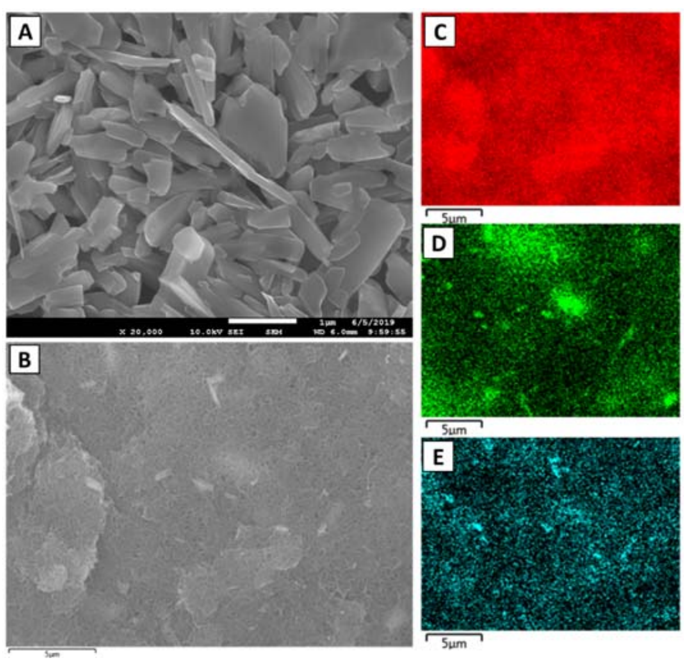


**Figure S3**. SEM of pristine LVO500 material (A) and EDS Maps of composite TPE(B-E). The (B) original image was scanned for different elemental mapping with (C) carbon in red, (D) vanadium in green, and (E) oxygen in blue.

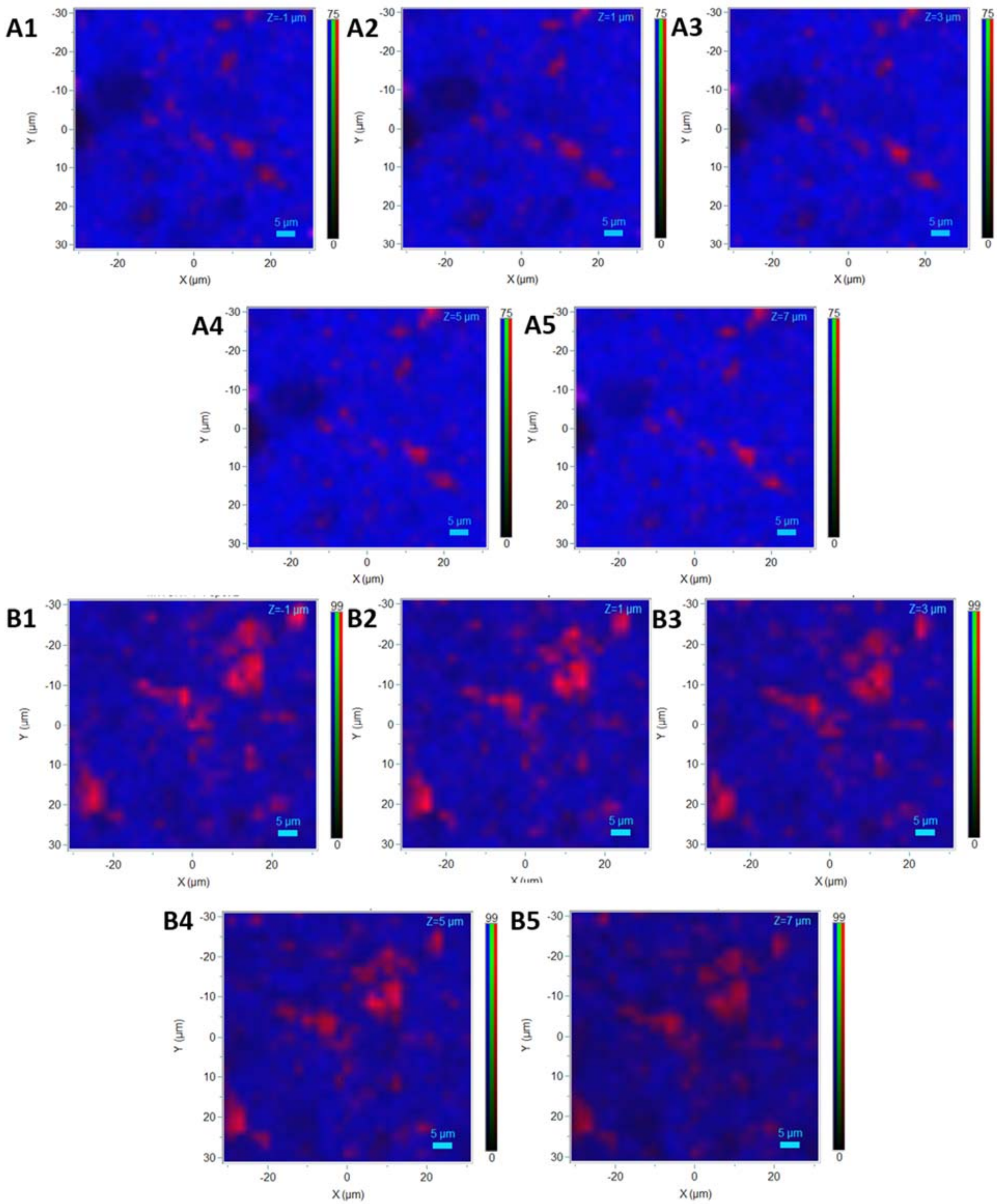


**Figure S4.** 2D CLS Raman figures of TPE (A1-5) and dense electrode (B1-5) from electrode surface to 8 µm below the surface.

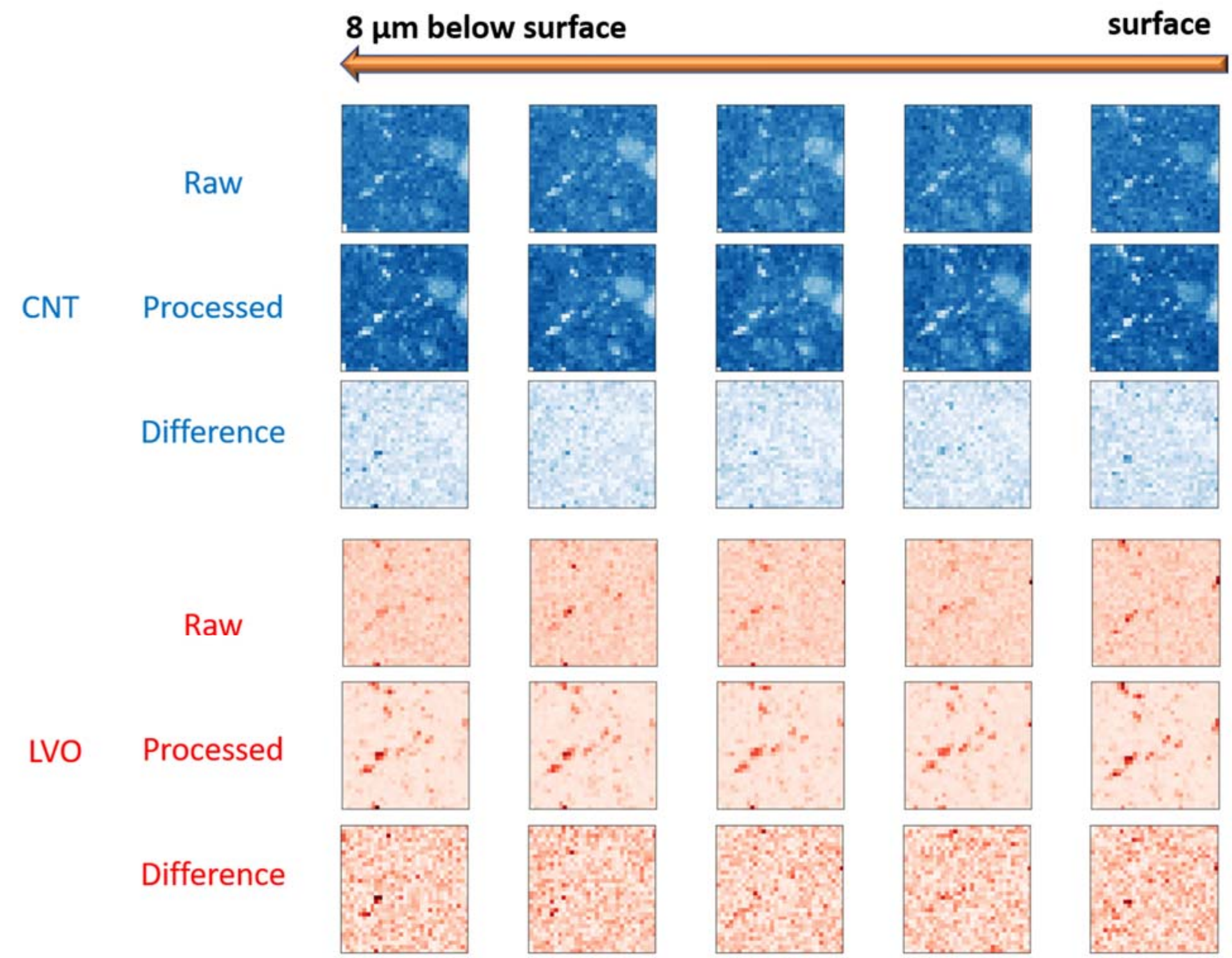


**Figure S5.** 2D NMF Raman slices along vertical z axis arranged in ascending order from left to right.

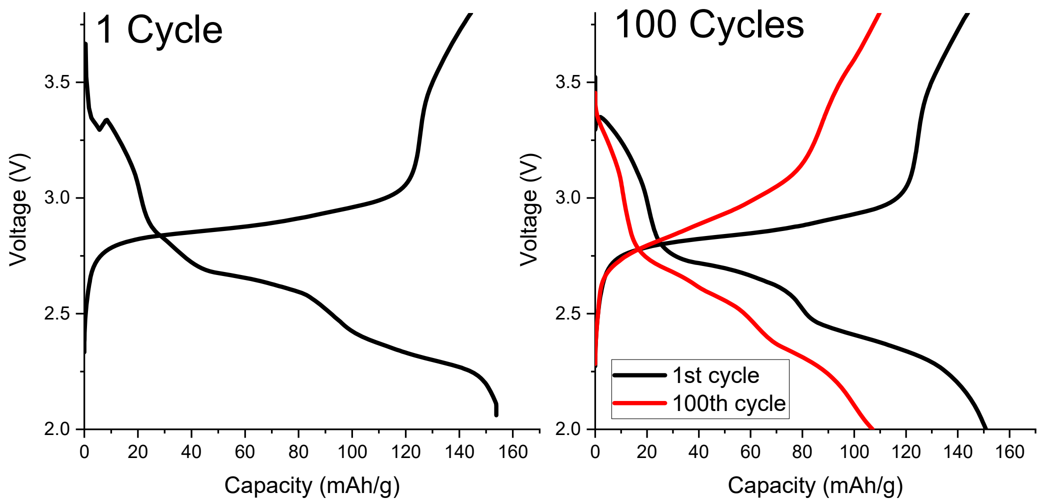


**Figure S6.** Electrochemistry from *ex situ* XRD and SEM cells. Left side is the voltage profile of the one cycle cell while the right side is the voltage profile from the first and last cycle for the cell cycled 100 times.

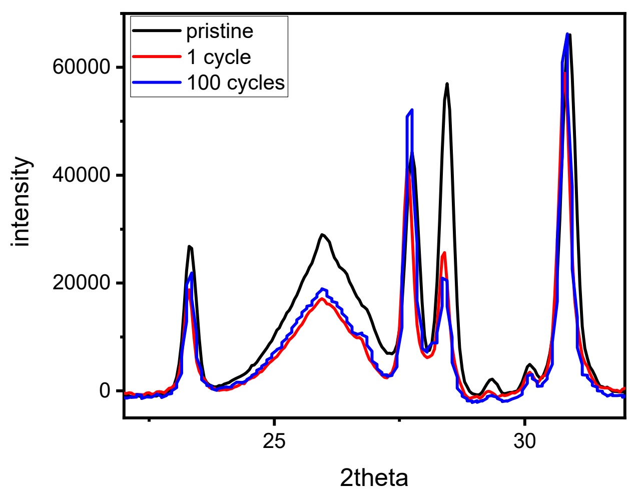


**Figure S7.** *Ex situ* XRD scans of the TPEs prior to cycling and after both 1 and 100 cycles between 22° and 32°. The broad peak around 26° can be assigned to CNTs while the rest of the peaks can be assigned to α-LVO.

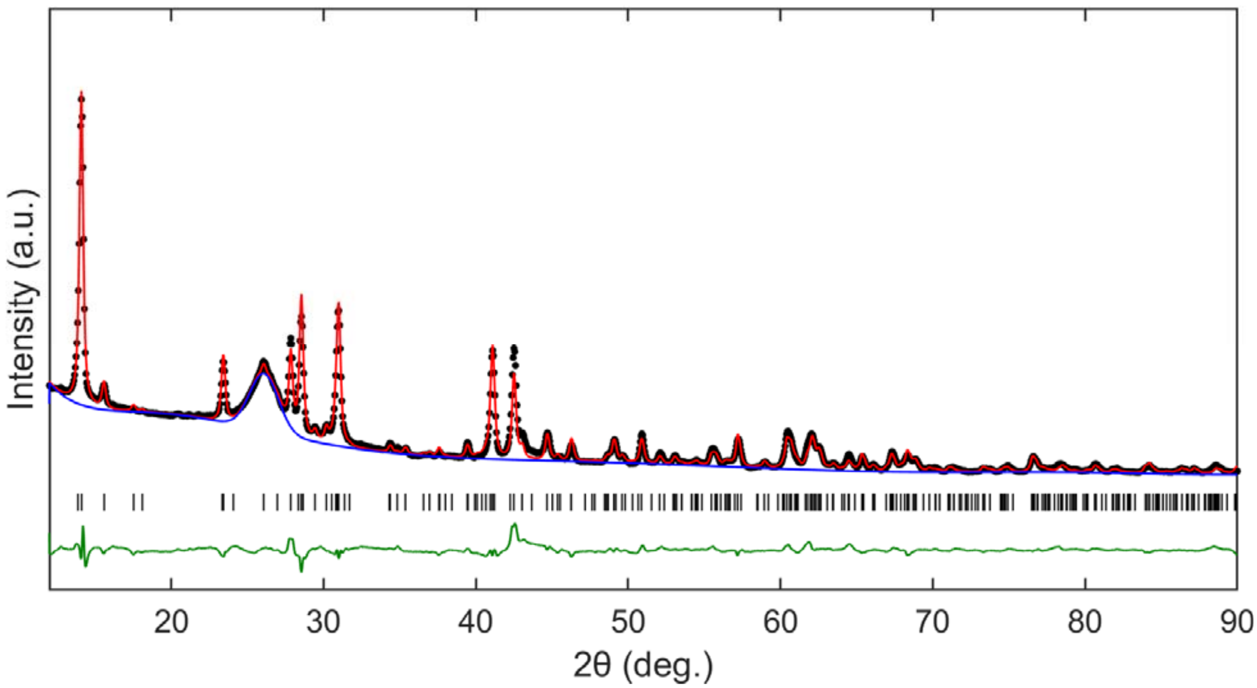


**Figure S8.** Rietveld refinement of the XRD pattern collected on a pristine TPE. The black is the experimental data, the red is the calculated fit, the blue is the background where the peak at ~26° is from the CNT's, and the green is the difference between the experimental data and the calculated fit. The black lines are the expected α-LVO reflections from PDF #01-073-8145.

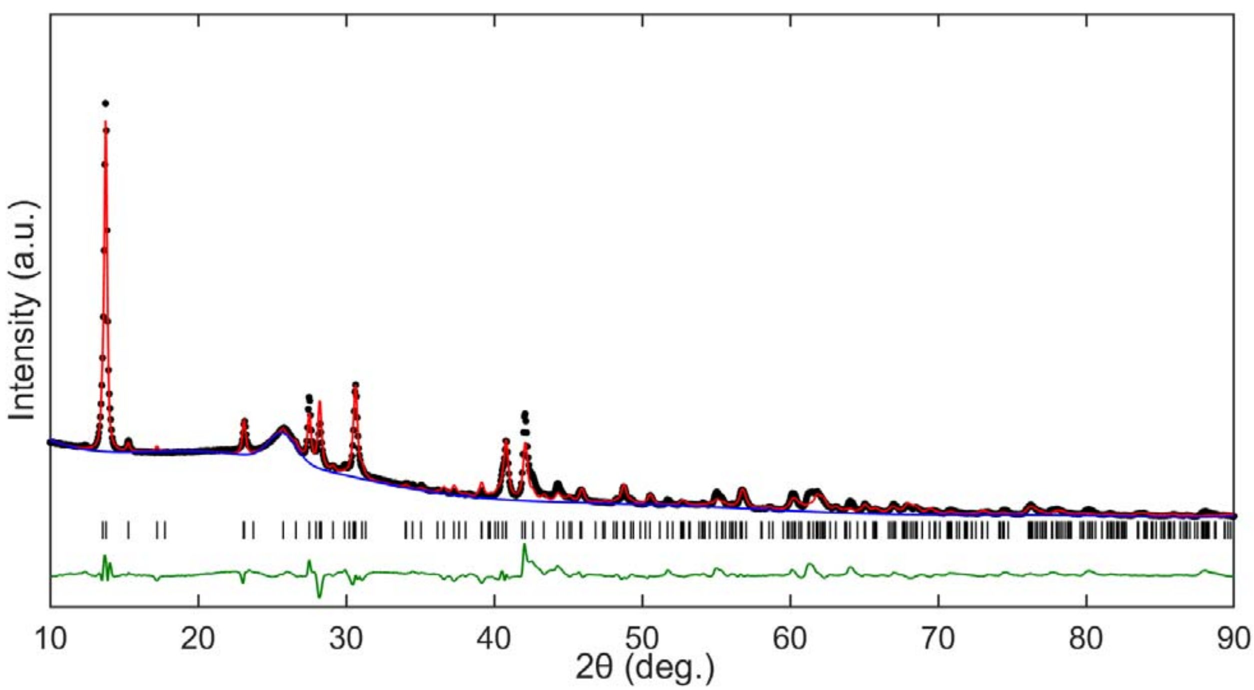


**Figure S9.** Rietveld refinement of the XRD pattern collected on a once cycled TPE. The black is the experimental data, the red is the calculated fit, the blue is the background where the peak at ~26° is from the CNT's, and the green is the difference between the experimental data and the calculated fit. The black lines are the expected α-LVO reflections from PDF #01-073-8145.

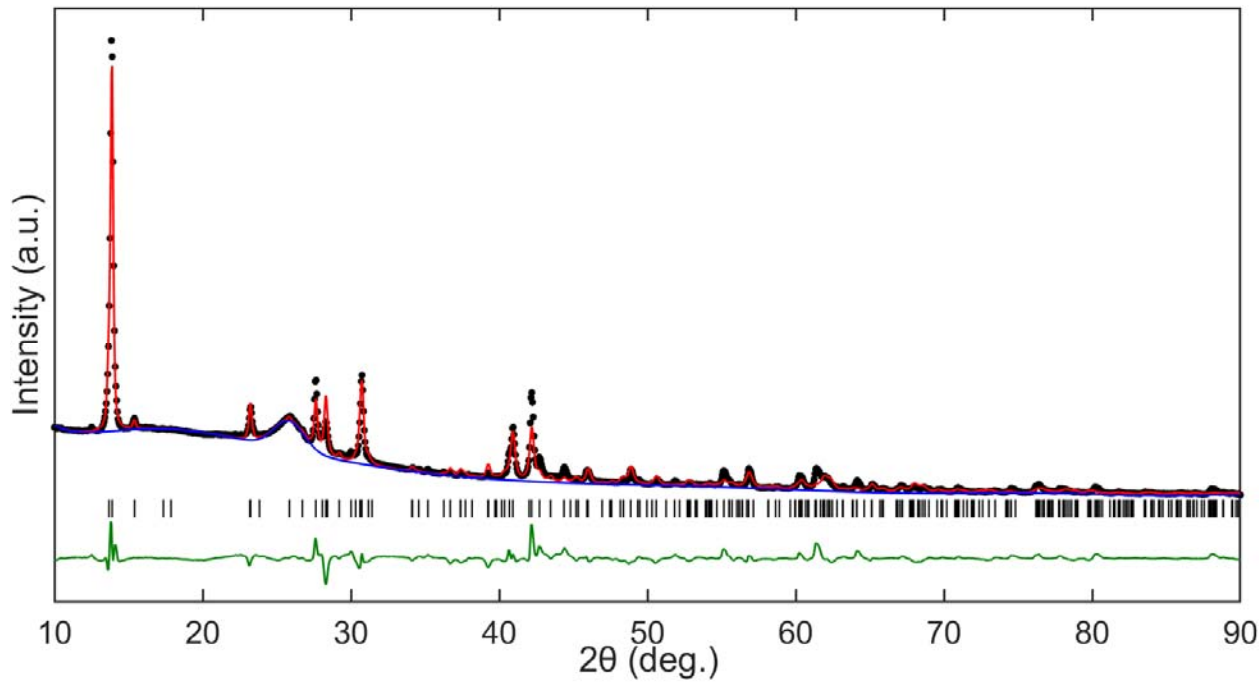


**Figure S10.** Rietveld refinement of the XRD pattern collected on a 100X cycled TPE. The black is the experimental data, the red is the calculated fit, the blue is the background where the peak at ~26° is from the CNT's, and the green is the difference between the experimental data and the calculated fit. The black lines are the expected α-LVO reflections from PDF #01-073-8145.

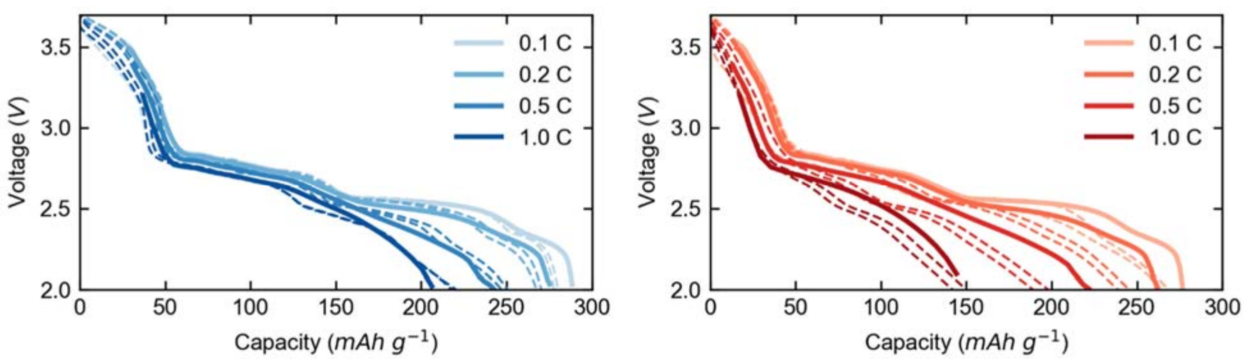


**Figure S11**. Experimental (dotted lines) and simulated (solid lines) potential during discharge over four discharge rates from C/10 to 1C for the TPE (left) and dense electrode (right).

**Table S1.** Refinement parameters of LVO as obtained by Rietveld refinement of the XRD patterns.

| | |
|---|---|
| **Space Group** | P21/m |
| **a (Å)** | 6.6403(4) |
| **b (Å)** | 3.59439(6) |
| **c (Å)** | 11.997(1) |
| **β (deg.)** | 107.818(2) |
| **C.S. (nm)** | 169(6) |
| **Microstrain (%)** | 0.016(9) |
| **%$R_{wp}$** | 5.88 |

**Table S2.** Refinement parameters of TPE as obtained by Rietveld refinement of the XRD patterns.

| **Parameter** | **Pristine** | **1XCycled** | **100XCycled** |
|---|---|---|---|
| **Phase** | **α-LVO** | **α-LVO** | **α-LVO** |
| ***a*** **(Å)** | 6.636(2) | 6.650(3) | 6.650(3) |
| ***b*** **(Å)** | 3.5941(4) | 3.5969(8) | 3.6003(8) |
| ***c*** **(Å)** | 12.012(4) | 12.009(8) | 12.011(8) |
| **β (deg.)** | 107.886(7) | 107.79(1) | 107.75(1) |
| **C.S. (nm)** | 49(2) | >180 | >180 |
| **Microstrain (%)** | 0.06(4) | 1.03(7) | 1.08(3) |
| **M-D (110)** | 1.47(1) | 1.67(3) | 1.67(3) |
| **%$R_{wp}$** | 5.44 | 6.35 | 7.26 |