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# Single step synthesis of W-modified $LiNiO_2$ using an ammonium tungstate flux

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## Supporting Information

***Table S1.*** *Elemental composition determined using TEM-EDX, measured from grains at the interior of secondary particles.*

| Annealing Temp. / °C | W / mol % | at. % | | |
|---|---|---|---|---|
| | | O | Ni | W |
| 700 | 0 | 56.10 | 43.90 | 0.00 |
| 700 | 1 | 53.64 | 46.32 | 0.04 |
| 800 | 1 | 50.12 | 49.59 | 0.29 |
| 900 | 1 | 61.22 | 38.66 | 0.12 |
| 700 | 5 | 61.76 | 36.89 | 1.35 |

***Table S2.*** *Elemental composition of W-doped LNO materials as determined by ICP-OES and CGHE (for O).*

| Annealing Temp. / °C | W / mol % | Molar equivalents (mol) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Li | ± | O | ± | Ni | ± | W | ± |
| 700 | 0 | 1.03 | 0.04 | 2.05 | 0.19 | 1.00 | 0.01 | | |
| 700 | 1 | 1.03 | 0.04 | 2.03 | 0.18 | 0.98 | 0.01 | 0.0095 | 0.0003 |
| 750 | 1 | 1.03 | 0.04 | 2.04 | 0.19 | 0.97 | 0.01 | 0.0106 | 0.0004 |
| 800 | 1 | 1.00 | 0.04 | 2.03 | 0.18 | 0.99 | 0.01 | 0.0103 | 0.0004 |
| 850 | 1 | 0.99 | 0.04 | 2.03 | 0.18 | 0.99 | 0.01 | 0.0100 | 0.0004 |
| 900 | 1 | 0.99 | 0.04 | 2.03 | 0.18 | 0.99 | 0.01 | 0.0101 | 0.0004 |
| 700 | 0.5 | 1.04 | 0.04 | 2.08 | 0.19 | 0.99 | 0.01 | 0.0050 | 0.0002 |
| 700 | 1.5 | 1.04 | 0.04 | 2.06 | 0.19 | 0.95 | 0.01 | 0.0146 | 0.0005 |
| 700 | 5 | 0.98 | 0.04 | 1.90 | 0.17 | 0.88 | 0.01 | 0.0475 | 0.0017 |

***Table S3.*** *Models tested for placement of cations on 3a and 3b sites of the LNO structure and their resulting refined atomic parameters. The sample is 1 mol % W $LiNiO_2$ synthesised at 700 °C. In model III, the total amount of W is fixed to the amount found by ICP.*

| | Cations in Li (3b) site | Cations in Ni (3a) site | $R_w$ / % | W on Li site | Ni on Li site | W on Ni site | $U_{iso}$ (3b) / Å² | $U_{iso}$ (3a) / Å² |
|---|---|---|---|---|---|---|---|---|
| I | Li, Ni | Ni, W | 6.772 | 0 (fixed) | 0.045(1) | 0.022(12) | 0.00937(69) | 0.00309(28) |
| II | Li, W | Ni | 6.825 | 0.0156(3) | 0 (fixed) | 0 (fixed) | 0.01383(72) | 0.00252(6) |
| III | Li, W, Ni | Ni, W | 6.774 | -0.0035(11) | 0.055(4) | 0.0135(11) | 0.0084(8) | 0.00291(7) |

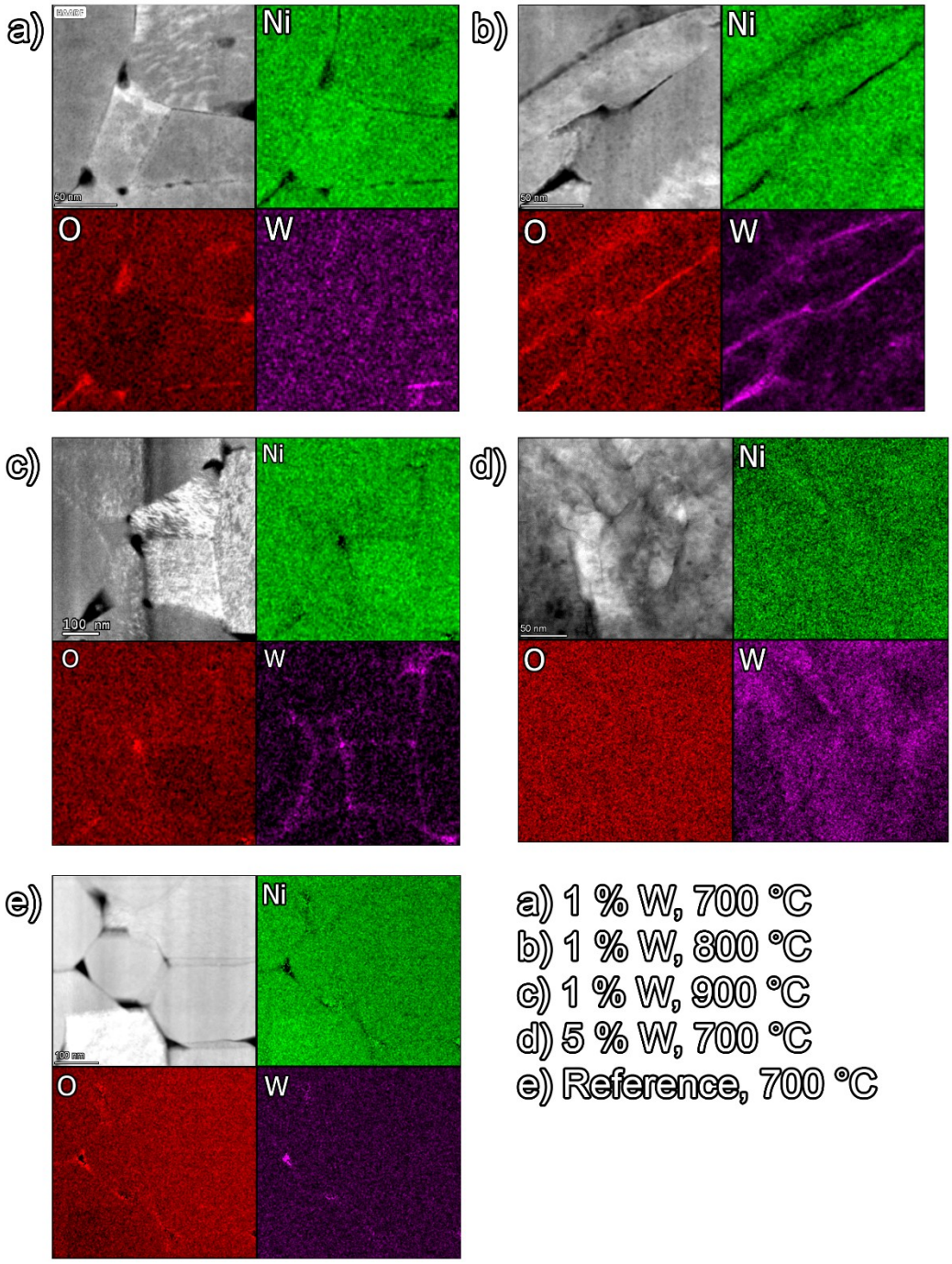


**Figure S1.** TEM-EDS maps and corresponding HAADF-TEM images collected from the reference and W-doped LNO samples.

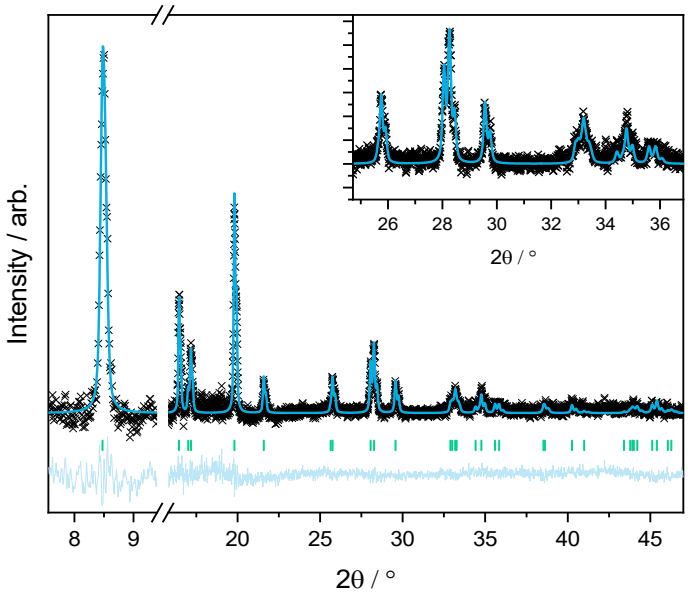


**Figure S2.** Rietveld refinement profile showing quality of fit achieved during the variable temperature XRD experiment. Pattern collected from the reference LNO material at 700 °C (*t* ≈ 190 min).

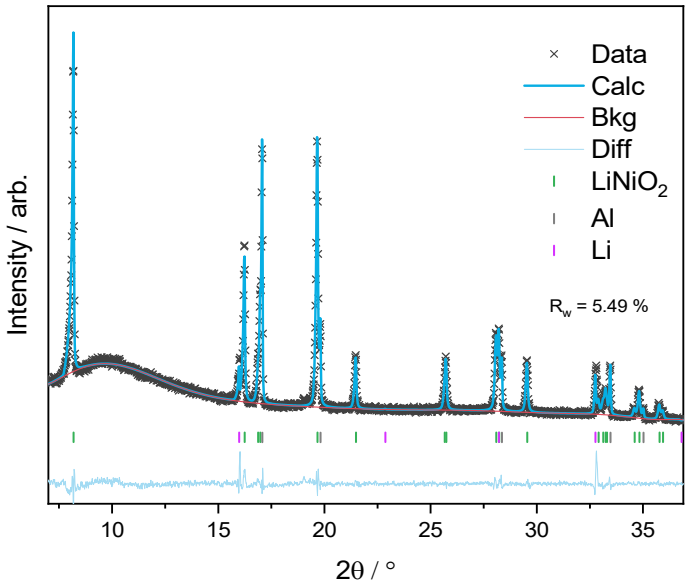


**Figure S3.** Rietveld refinement profile showing quality of fit achieved during the *operando* electrochemical-XRD experiment. First pattern collected from the LNO reference material.

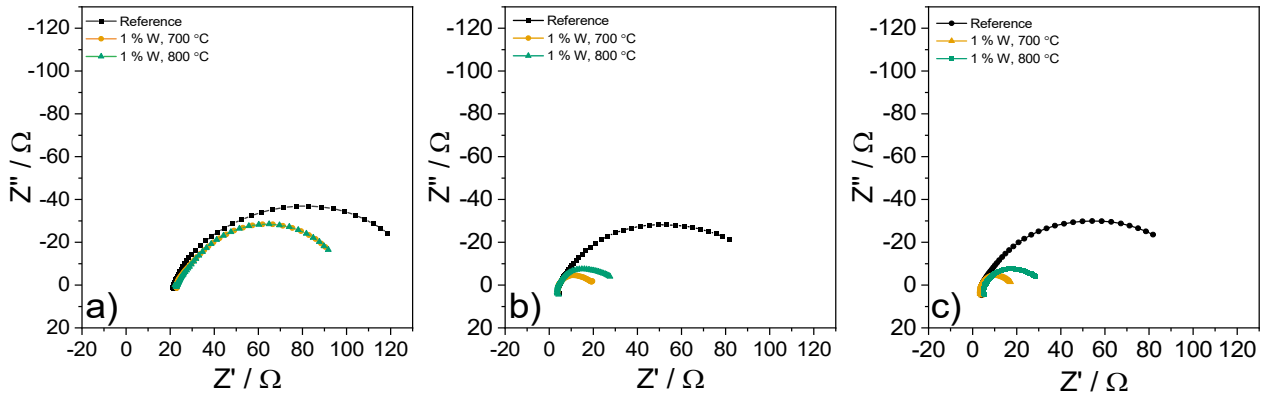


**Figure S4.** Electrochemical impedance spectroscopy recorded from coin cells before and after cycling. a) 1st cycle b) 55th cycle c) 106th cycle

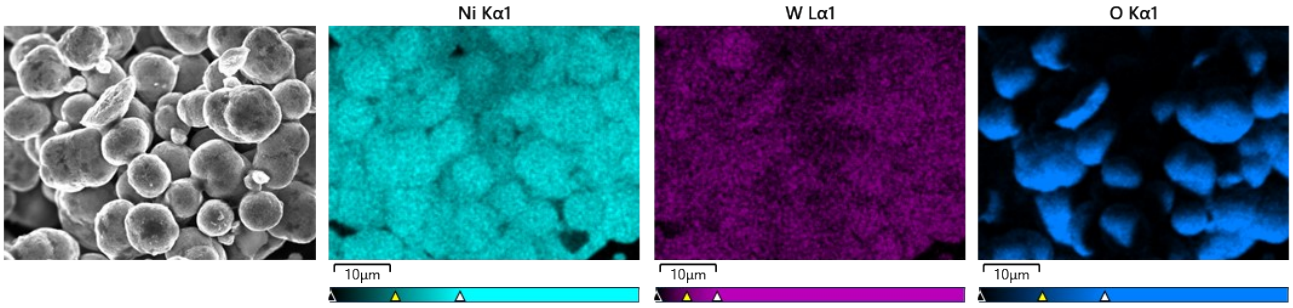


**Figure S5.** Electron microscopy data collected from the 1 mol % W sample prepared at 700 C, and corresponding EDX spectra.