Exploring the stability and protonic conductivity in W- and Mo-substituted $LaNbO_4$ under reducing atmospheres

Kehan Huang[a§], Yidong Han[a§], Mark A. Isaacs[b, c] and Stephen J. Skinner[a, d*]

[a] Department of Materials, Imperial College London, Exhibition Road, London, SW7 2AZ, United Kingdom

[b] Department of Chemistry, University College London, London, WC1H 0AJ, United Kingdom

[c] HarwellXPS, Research Complex at Harwell, Rutherford Appleton Labs, Harwell Campus, Didcot, OX11 0FA, United Kingdom

[d] International Institute for Carbon Neutral Energy Research, Kyushu University, Fukuoka, Japan

§ Kehan Huang and Yidong Han both contributed equally to this work

* s.skinner@imperial.ac.uk

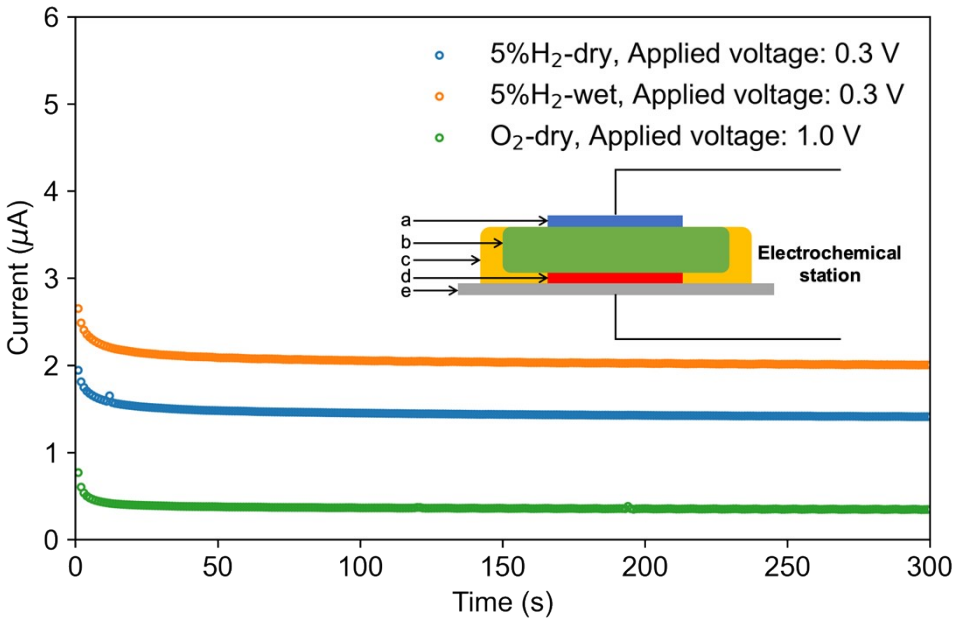

Figure S1. Exemplified current relaxation curves of the ion-blocking cell measured at 578°C under different conditions. Inset shows a schematic diagram of the ion-blocking cell configuration for the DC polarization measurements: (a) porous Pt current collector; (b) pellet sample; (c) high temperature ceramic adhesive; (d) Pt paste (current collector); and (e) dense Pt disk.

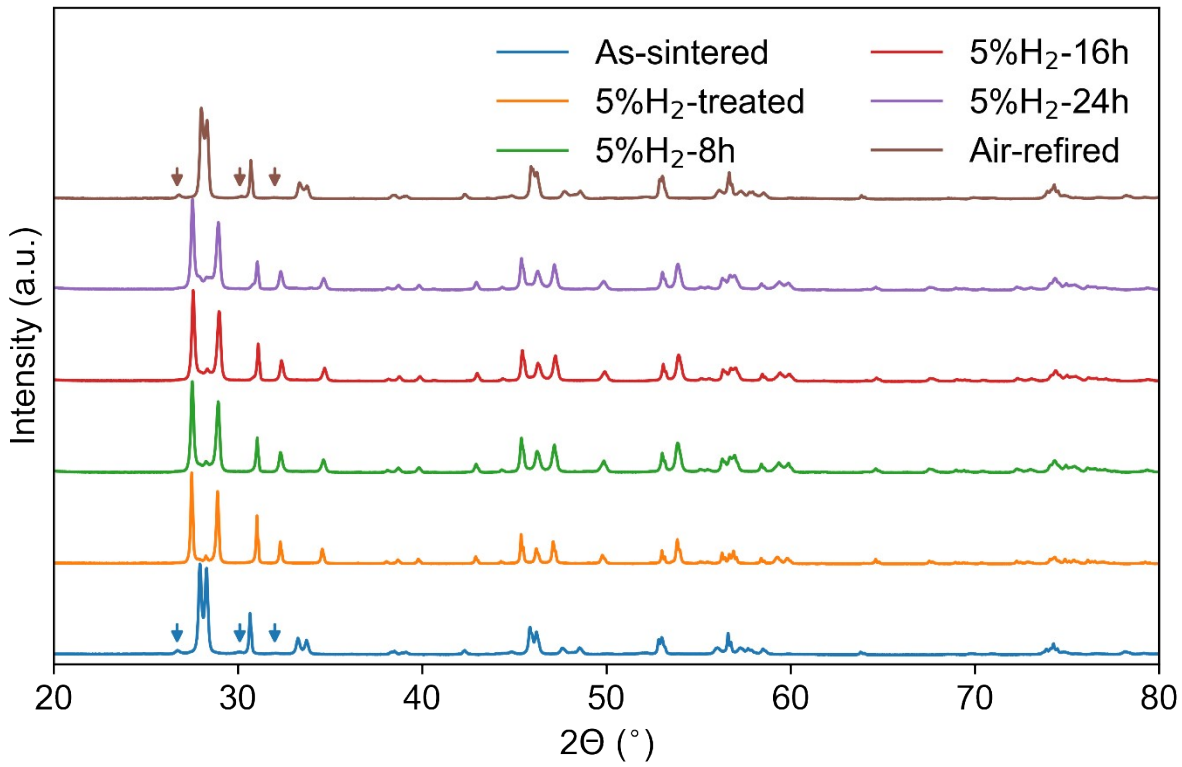

Figure S2. XRD patterns of as-sintered, 5%H_2-treated LNM16 and after the 5%H_2-annealing for 8, 16 and 24 hours, respectively. The 24h 5%H_2-treated sample was then air-annealed at 800°C for 4 hours, and is labelled as "Air-refired". The satellite peaks are marked by the arrows. All patterns show the monoclinic phase (*I2/a*). However, the as-sintered sample (β=90.9685°) has a smaller monoclinic distortion and is close to tetragonal symmetry with the presence of the modulated structure, while 5%H_2-treated sample (β=94.0040°) is an analogue of pristine $LaNbO_4$ without the modulated structure. The modulated structure reappears after the air annealing.

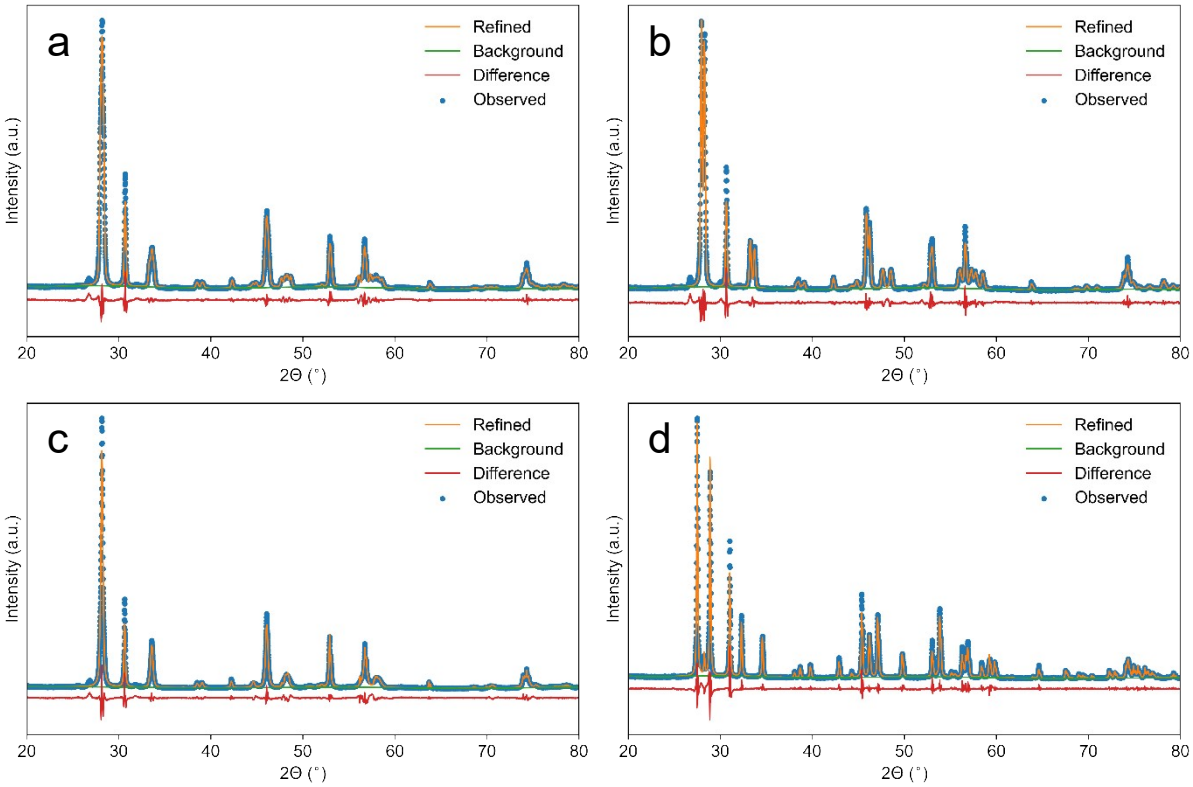

Figure S3. Rietveld refinement results of LNW16 (a) before and (c) after 5%-H_2 treatments and LNM16 (b) before and (d) after 5%-H_2 treatments. Note the modulation reflections previously identified are not included in the refinement as only the simple parent cell is included in the refinement and not the supercell.

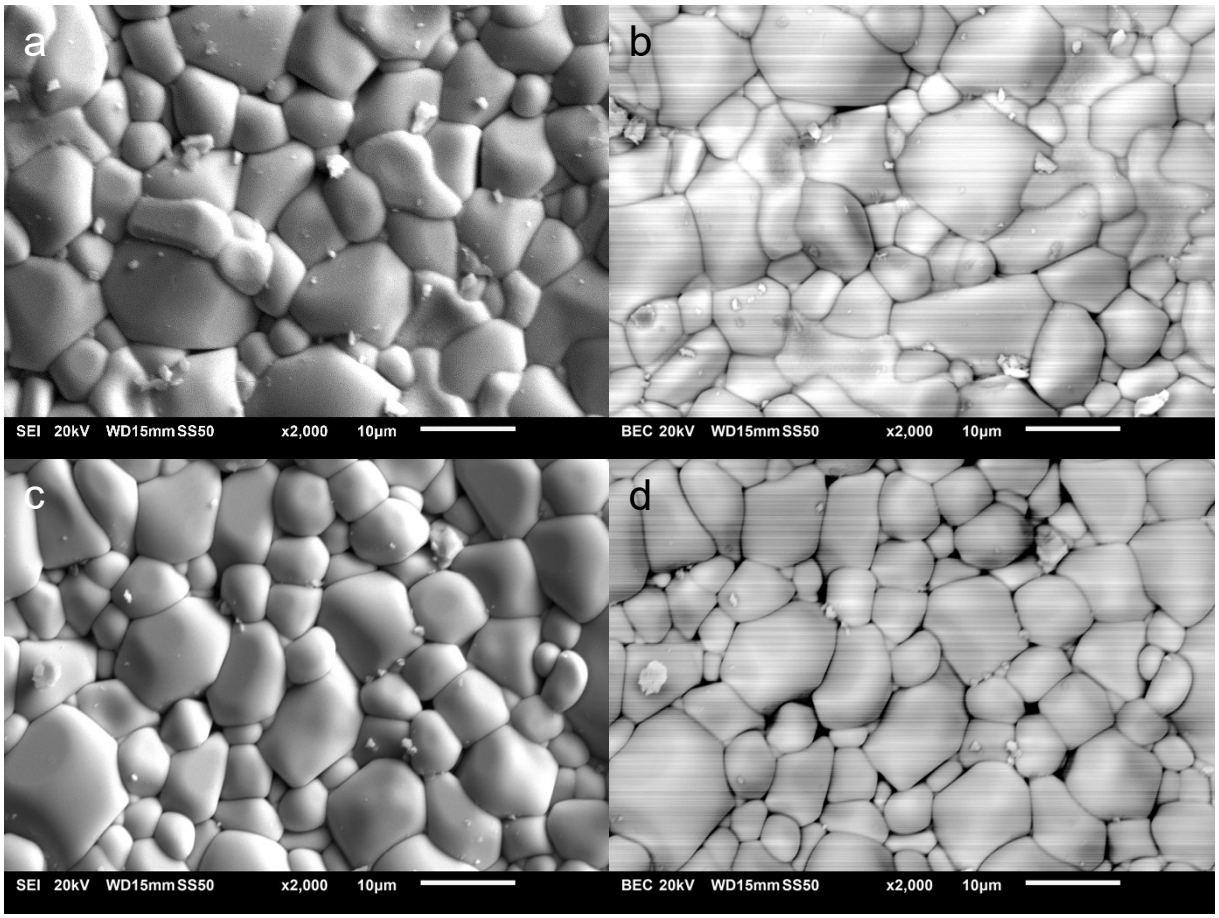

Figure S4. (a) and (b) SEI and BSE images of as-sintered LNW16; (c) and (d) SEI and BSE images of hydrogen-treated LNM16.

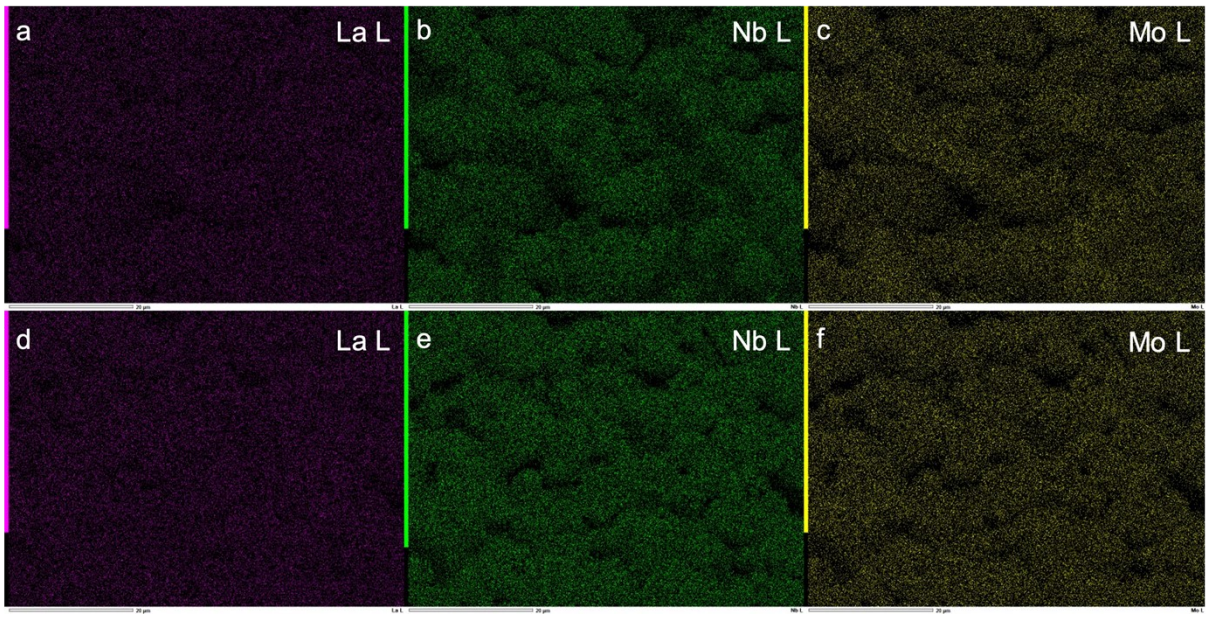

Figure S5. (a), (b) and (c) corresponding EDS maps of SEM images in Figure S4(a); (d), (e) and (f) corresponding EDS maps of SEM images in Figure S4(c).

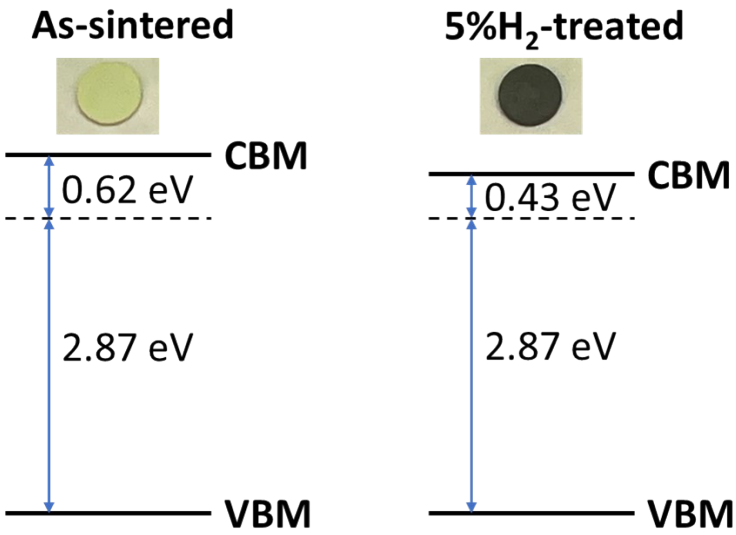

Figure S6. Schematic diagrams of band structure, and the visual appearance of as-sintered and 5%H_2-treated LNW16.

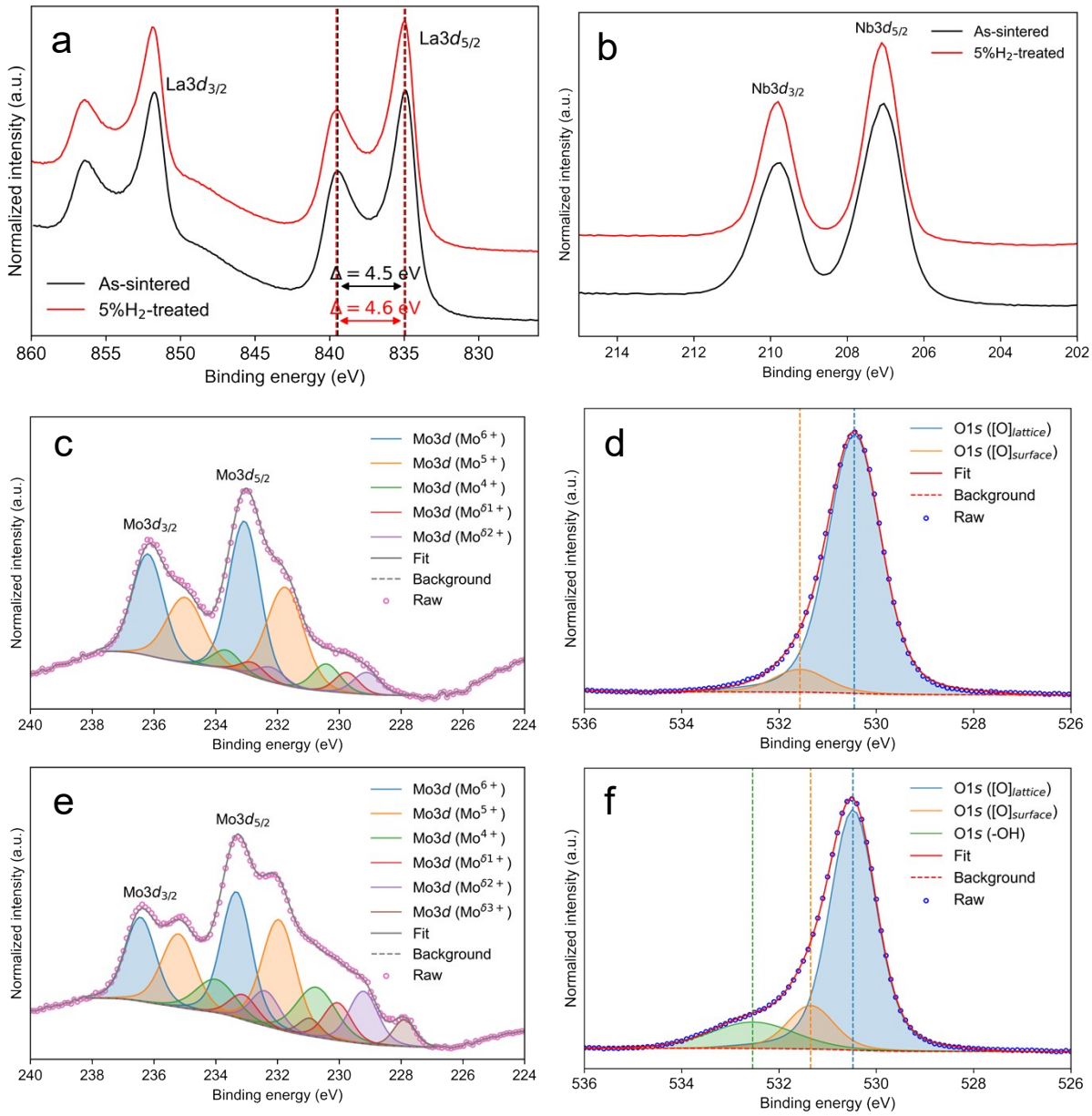

Figure S7. Normalized XPS spectra of (a) La3*d*, (b) Nb3*d*; Fitted XPS spectra of Mo3*d* in (c) as-sintered and (e) 5%H_2-treated LNW16; Fitted XPS spectra of O1*s* in (d) as-sintered and (f) 5%H_2-treated LNW16. (δ+ and ε+: the oxidation state of Mo cations in between 0 and 4+.)

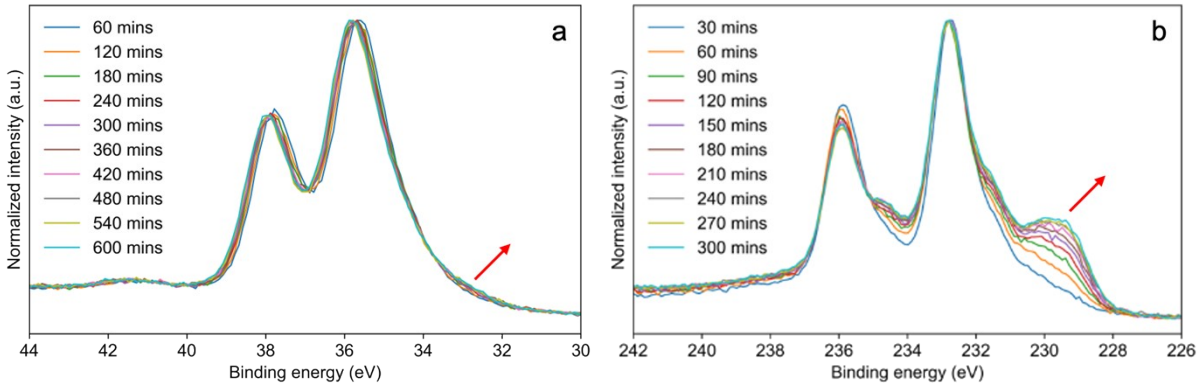

Figure S8. Normalized XPS iteration spectra of (a) W4*f* and (b) Mo3*d*. The red arrow clearly shows the emergence of the feature corresponding to lower oxidation states of W and Mo species. Significant reduction is observed in the case of the Mo3d.

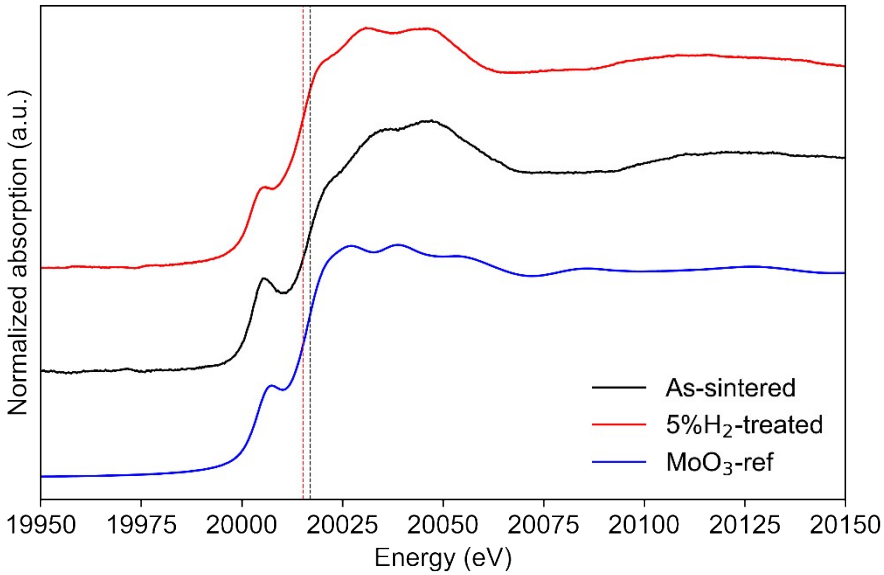

Figure S9. Normalized synchrotron XANES spectra of the Mo K-edge measured under ambient atmosphere and temperature. The edge position (E_0) of as-sintered LNM16 is the same as MoO_3 reference at 20017 eV (black dash line), while the E_0 position of 5%H_2-treated LNM16 is at 20015.2 eV (red dash line) indicating the reduction of Mo^{6+}.

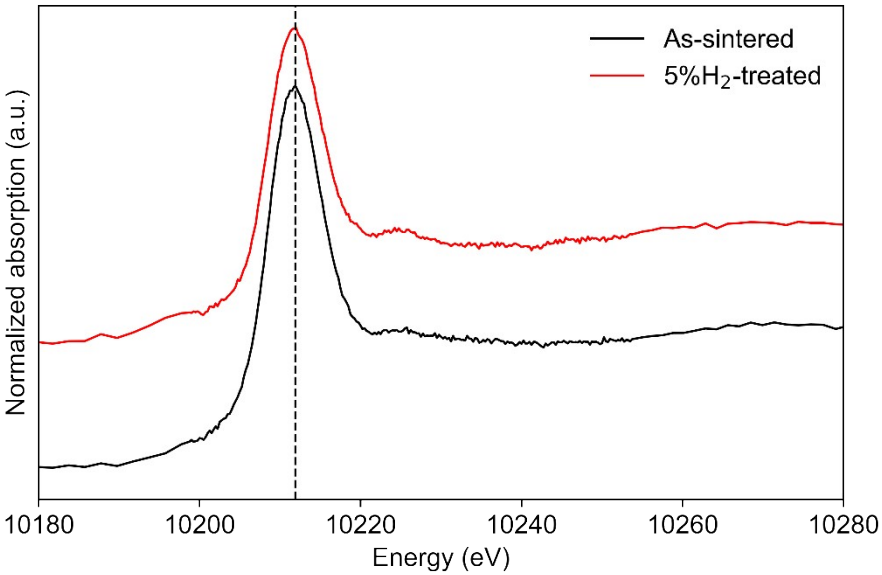

Figure S10. Normalized benchtop XANES spectra of W L_3-edge measured under ambient conditions. The white line of both samples is identical at 10212 eV indicating W^{6+} oxidation state.

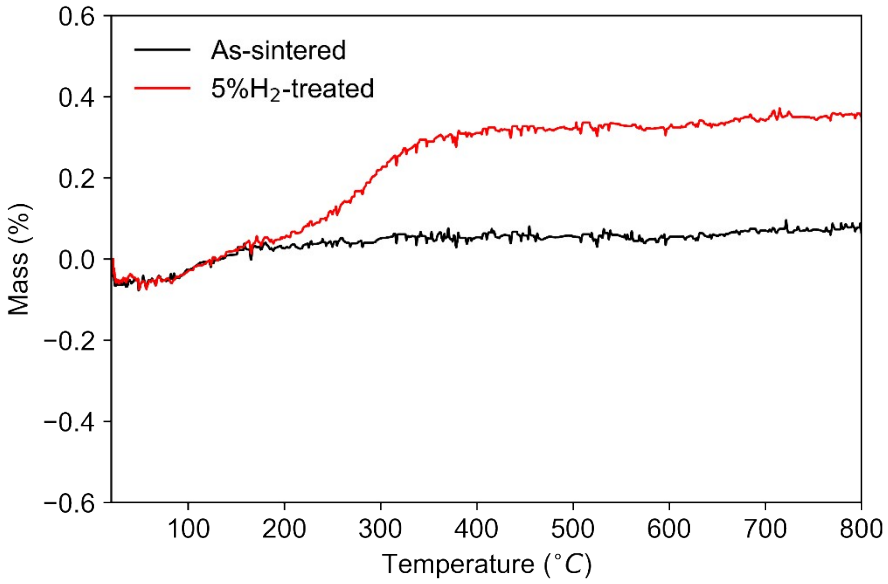

Figure S11. TGA data of as-sintered and 5%H_2-treated LNM16 measured from room temperature to 800°C under flowing air atmosphere.

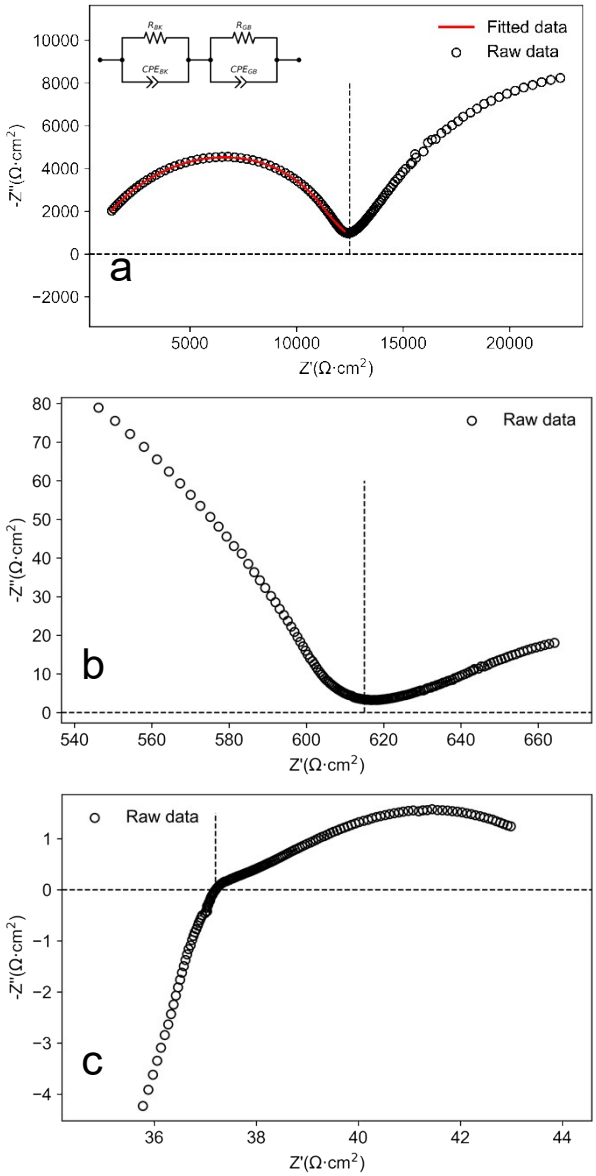

Figure S12. Impedance spectra of LNW16 measured under dry air at (a) 570°C, (b) 765°C and (c) measured under dry 5%H_2 conditions at 765°C. The fitting result is obtained using the equivalent circuit model in the inset. The subscripts of "BK" and "GB" are short for bulk and grain boundary, respectively. The fitting parameters in (a) are R_{BK} = 3.02 x 10^3 Ω·cm², CPE-T_{BK} = 1.21 x10^{-10} F, CPE-P_{BK} = 0.99; R_{GB} = 9.67 x 10^3 Ω·cm², CPE-T_{GB} = 1.76 x 10^{-9} F, CPE-P_{GB} = 0.71 and the Chi-squared of the fitting is 1.31 x 10^{-5}. For higher temperature points no clear BK and GB components are observed and the high frequency intercept is selected as the total conductivity.

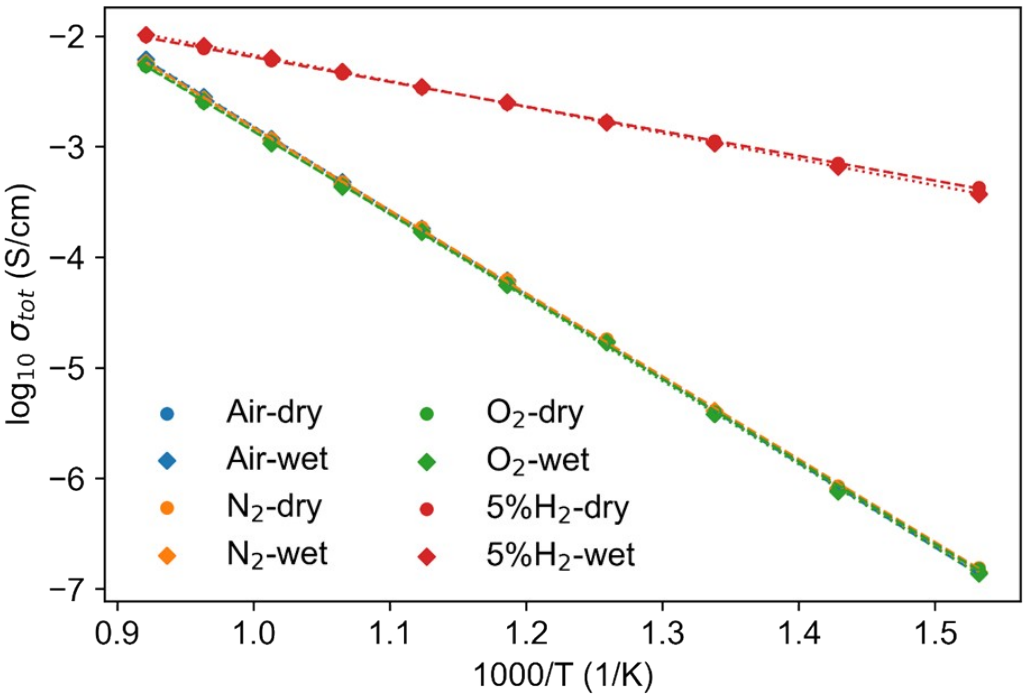

Figure S13. Total conductivity of LNM16 measured under different atmospheres. The fitting results of the activation energies are presented in Table S4.

Table S1. Refined lattice parameters of all samples from Rietveld refinements.

	As-sintered LNW16	5%H_2-treated LNW16	Air-refired LNW16	As-sintered LNM16	5%H_2-treated LNM16
a (Å)	5.3694(2)	5.3474(3)	5.3480(2)	5.3834(2)	5.5583(1)
b (Å)	11.6707(4)	11.6848(4)	11.6793(4)	11.6555(7)	11.5332(1)
c (Å)	5.3238(2)	5.3463(3)	5.3517(3)	5.3140(2)	5.2023(1)
β (°)	90.663(3)	90.390(4)	90.432(4)	90.968(3)	94.004(1)
V ($Å^3$)	333.58(1)	334.31(2)	334.26(2)	333.38(2)	332.68(1)
R_{wp} (%)	8.28	9.81	9.25	8.35	9.51
χ^2	3.45	3.93	3.37	3.46	3.90

Table S2. Normalized EDS atomic ratios of B- site cations in LNM16.

Cation	As-sintered (at%)	5%H_2-treated (at%)	Theoretic (at%)
Nb	84.6 ± 0.5	84.0 ± 0.5	84.0
Mo	15.4 ± 0.6	16.0 ± 0.6	16.0

Table S3. Normalized atomic ratios of Mo cations with different oxidation states and different oxygen species in LNM16 obtained from XPS fittings. δ1+, δ2+ and δ3+ represent the oxidation state of Mo cations in between 0 and 4+. The binding energy of each fitted Mo3$d_{5/2}$ and O1*s* peak after C1*s* calibration is listed in the brackets.

Oxidation state	As-sintered (at%)	5%H_2-treated (at%)
Mo^{6+}	46.4 (233.1 eV)	30.0 (233.3 eV)
Mo^{5+}	35.6 (231.8 eV)	34.0 (231.9 eV)
Mo^{4+}	7.4 (230.4 eV)	11.9 (230.6 eV)
$Mo^{\delta 1+}$	4.8 (229.8 eV)	9.5 (229.9 eV)
$Mo^{\delta 2+}$	5.8 (229.1 eV)	10.0 (229.5 eV)
$Mo^{\delta 3+}$	-	4.6 (227.9 eV)
Oxygen species	**As-sintered (at%)**	**5%H_2-treated (at%)**
$[O]_{lattice}$	91.3 (530.4 eV)	74.8 (530.5 eV)
$[O]_{surface}$	8.7 (531.6 eV)	12.7 (531.3 eV)
-OH	-	12.5 (532.4 eV)

Table S4. Calculated activation energy of LNM16 measured at different atmospheres.

Atmosphere	Humidity	E_a (eV)	R^2
Air	Dry	1.51	0.99
	Wet	1.51	0.99
N_2	Dry	1.49	0.99
	Wet	1.50	0.99
O_2	Dry	1.48	0.99
	Wet	1.50	0.99
5%H_2	Dry	0.44	0.99
	Wet	0.47	0.99