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Supplementary information for:

Thin film fabrication and characterization of proton conducting lanthanum tungstate

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Representative Nyquist plots for LWO-1 in wet air are shown in Figure S1. The curves show essentially one large semicircle (R_1Q_1) at high frequencies, and a small semicircle (R_2Q_2) at lower frequencies. The first exhibits an uncorrected capacitance of ~$4 \cdot 10^{-12}$ F, which is associated to the stray capacitance of the ProboStat™ cell, wires, substrate and setup (C_{stray}, the reader is referred to the NorECs ProboStat manual [1]) and the resistance of the film. Given the geometry of our in-plane configuration (A/l ~10^{-3} cm), the capacitance expected for both grain interior (Cgi~10^{-15} F) and grain boundaries (Cgb~10^{-12} -10^{-13} F) are too low (or at best, overlapping with the stray capacitance of the setup) to be separated with this geometry, so both contributions are reflected in R_1 (=Rgi+Rgb). R_1Q_1 did not change as a function of oscillation voltage from 50 mV to 1 V, which supports that this semicircle corresponds to the film. The measurements shown in Figure S1 are the ones performed at 1 V, which reduces the overall noise of the sweep.

The second semicircle (not possible to deconvolute at 650 °C) exhibits an uncorrected capacitance of ~10^{-8} F, which represents an area specific capacitance in the order of 10^{-4} F/cm^2, clearly corresponding to the electrode contribution. Therefore, the conductivity of the film (including grain interior and grain boundary contributions) is calculated using R_1 and equation 1.

$$\sigma = \frac{L}{A} \cdot \frac{1}{R} \qquad (1)$$

	Area (cm^2)	A/l (cm)
LWO-1	10^{-4}	$2 \cdot 10^{-3}$

[1] http://www.norecs.com/index.php?page=Manuals, by 20th March 2014.

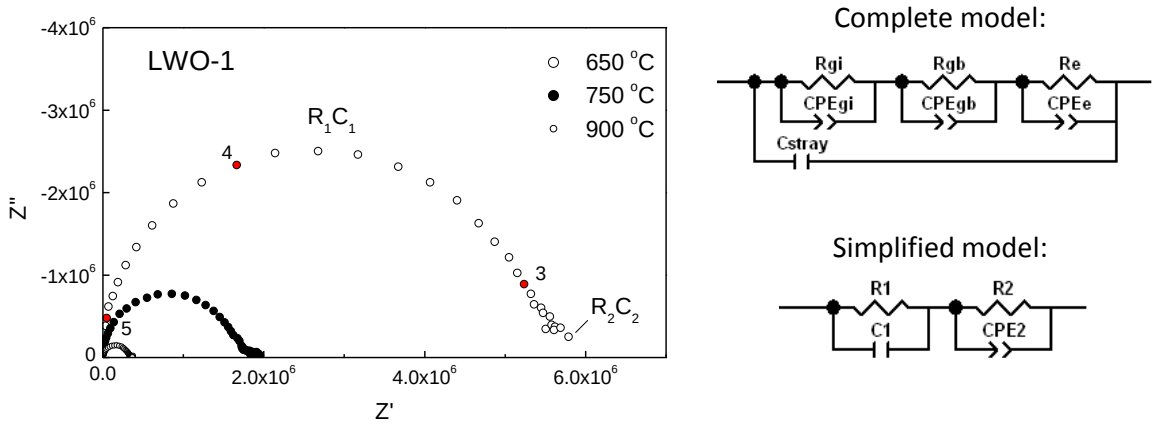

Figure S1: Representative Nyquist plots for LWO-1 in wet air (not corrected by geometrical factor) (left) and the equivalent circuit used to extract R1 (right). The numbers adjacent to points marked in red correspond to log frequency.

Figure S2 shows that the conductivity increases slightly with increasing water content in both inert and reducing conditions, showing that some protonic conductivity exists in the material. However, one can also conclude that protons are not the main charge carriers due to the relatively small slope.

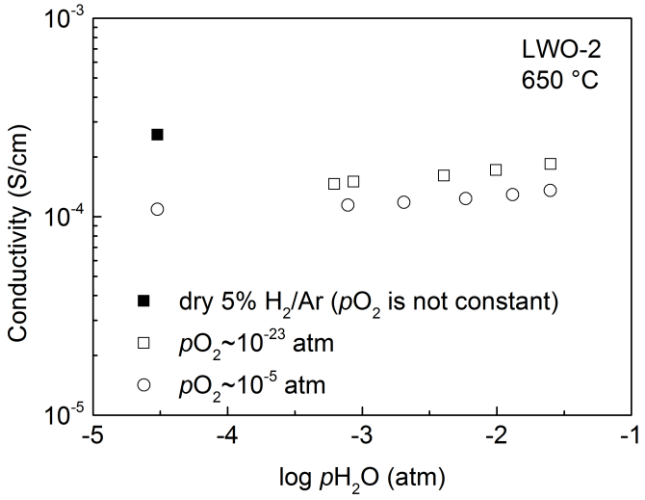

Figure S2: Variation of the film conductivity with water vapor partial pressure at 650 °C at constant pO_2.

Representative Nyquist plots for LWO-3 in wet air are shown in Figure S3. Due to the large geometrical factor inherent of this geometry, the grain interior and grain boundary contribution can be differentiated. The curves show essentially two contributions: one semicircle (R_1Q_1) at high frequencies, and a contribution involving one or more semicircles (R_2Q_2-R_3Q_3…) at lower frequencies. The first exhibits an area specific capacitance of ~$2 \cdot 10^{-12}$ F/cm, which is associated to the grain interior of the deposited LWO film, while the second semicircle presents an area specific capacitance ~10^{-5}-10^{-4} F/cm^2, clearly corresponding to the electrode contribution. No grain boundary contribution could be detected. Since we, in this work, are solely interested in the conductivity of the film and not the electrode polarization, the other semicircles overlapping with the electrode contribution were not deconvoluted (R_3Q_3…). Calculation of R_2Q_2 was performed to confirm the following contributions were only due to the electrode polarization. Therefore, the conductivity of the film (grain interior) is calculated using R_1 and equation 1.

	Area (cm^2)	A/l (cm)
LWO-3	$7 \cdot 10^{-2}$	$6 \cdot 10^{2}$

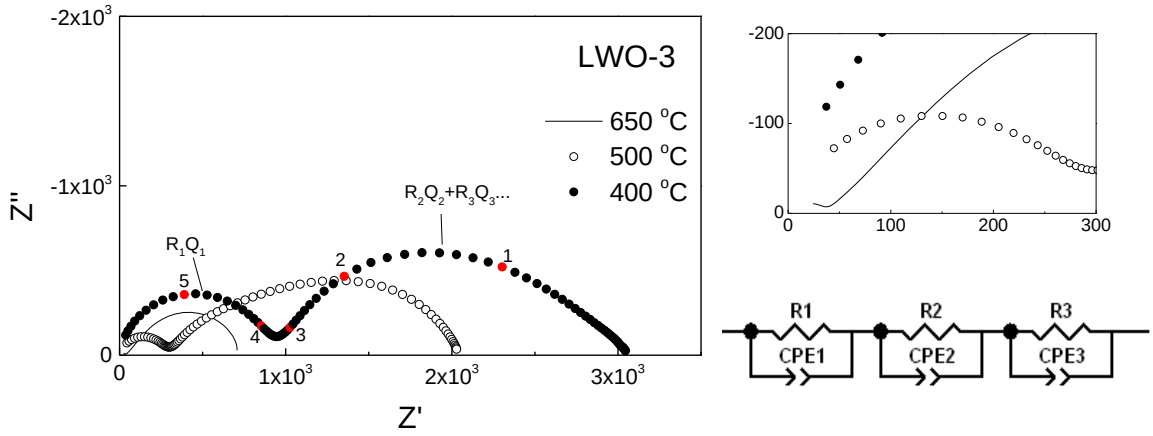

Figure S3: Representative Nyquist plots for LWO-3 in wet air (not corrected by geometrical factor) (left) and the equivalent circuit used to extract R1 (right). The numbers adjacent to points marked in red correspond to log frequency. The inset shows a magnified portion of the graph.