

Supporting Information

Broad Applicability of Electrochemical Impedance Spectroscopy to the Measurement of Oxygen Non-stoichiometry in Mixed Ion and Electron Conductors

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Further information regarding impedance data reported in Figure 3 of the main text is provided here. Figure S1 is a zoomed in representation of Figure 3a, showing the ohmic offset due primarily to the YSZ substrate. Table S1 provides the complete set of parameters used for describing the spectra, and in Figure S2 are plotted the electrochemical surface reaction resistance values derived from the fits. Additionally, van't Hoff analysis of undoped ceria is documented in Figure S3.

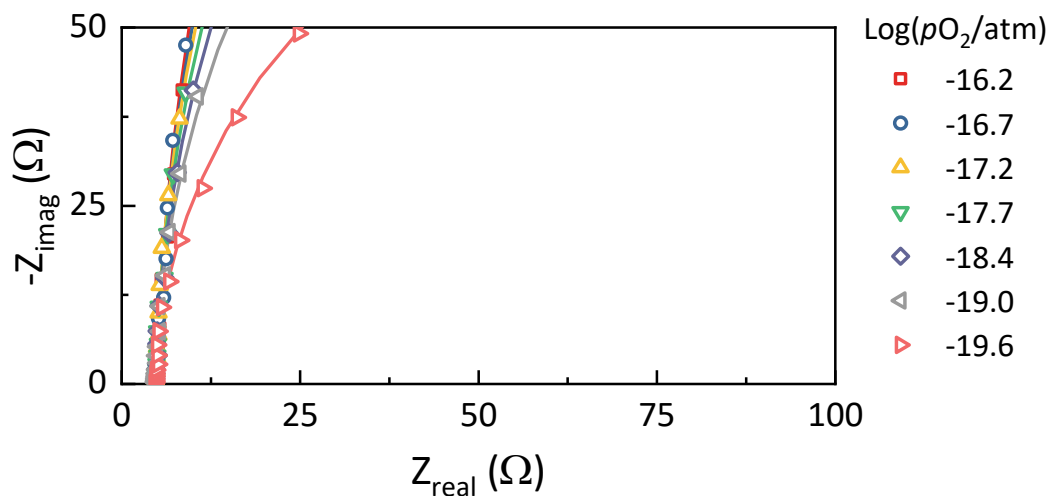


Figure S1. Zoomed in view of high frequency region of the impedance spectra collected from the 1050 nm thick film at 750 °C and the oxygen partial pressures indicated (corresponds to Figure 3a of the main text). Ohmic offset is visible at this scale.

Table S1. Fit parameters obtained by equivalent circuit fitting to the spectra shown in Figure 3 of the main text. The films are deposited on both sides of 8YSZ substrates, $1 \times 1 \times 0.05 \text{ cm}^3$ in size, with an active film area of 0.75 cm^2 . [Continued on next page.]

A. Ceria, $R_0(\text{RQ})$; values obtained by fitting using ZView® software¹

$\log(p\text{O}_2)$ atm	χ^2 10^{-4}	R_0^a Ω	Error %	R_{ion}^{surf} Ω	Error %	Q 10^{-3} *	Err %	n_q unitless	Err %	C mF	Err %
-19.6	5.75	4.688	0.40	155.0	0.67	12.64	0.46	0.979	0.23	0.053	0.85
-19.0	5.14	4.731	0.40	286.3	0.60	8.78	0.40	0.989	0.18	0.033	0.75
-18.4	3.67	4.752	0.36	380.5	0.51	6.26	0.35	0.988	0.15	0.021	0.63
-17.7	2.94	4.778	0.35	477.5	0.50	4.54	0.33	0.986	0.13	0.014	0.61
-17.2	1.78	4.800	0.29	570.7	0.38	3.53	0.26	0.987	0.10	0.009	0.47
-16.7	3.22	4.841	0.41	708.7	0.51	2.82	0.35	0.982	0.13	0.009	0.64
-16.2	2.56	4.871	0.39	825.0	0.45	2.34	0.32	0.981	0.11	0.007	0.56

^aimplies an ionic conductivity of the substrate of $1.39 \times 10^{-2} \text{ S/cm}$ at $750 \text{ }^\circ\text{C}$.

B. CZO20, Eq. A1 or modification thereof with C_{chem} replaced with a constant phase element, analyzed using in-house code written in Python²

$\log(p\text{O}_2)$ atm	$R_0^{a,b}$ Ω	Err %	$R_{ion}^{surf\ b}$ Ω	Err %	$C_{ion}^{surf\ b}$ mF	Err %	R_{ion}^c Ω	Err %	C_{chem}^b mF	Err %	$C_{eon}^{int\ b,d}$ μF	Err %
-0.68	2.67	0.25	30.4	1.5	0.12	27	10.7	4.2	1.06	5.3	0.78	42
-1.30	2.65	0.22	37.7	1.1	0.19	22	9.03	4.4	1.25	5.8	1.10	26
-1.93	2.64	0.24	43.6	0.93	0.22	25	7.77	4.9	1.48	6.0	1.58	18
-2.77	2.61	0.28	49.3	0.70	0.33	21	5.92	5.0	1.84	6.1	2.18	16
-2.94	2.61	0.25	52.4	0.69	0.34	24	5.66	5.5	1.93	6.2	2.47	20
-3.35	2.61	0.23	66.0	0.57	0.35	28	5.11	5.9	2.15	5.4	2.79	15
-3.77	2.60	0.23	98.3	0.47	0.37	37	4.56	7.1	2.41	3.4	3.14	18
-0.68 ^e	2.68	0.26	32.7	1.5	0.12	30	10.8	4.4	1.07	5.1	0.82	41

^aImplies an ionic conductivity of the substrate of $2.50 \times 10^{-2} \text{ S/cm}$ at $800 \text{ }^\circ\text{C}$. ^bValue obtained from fitting to a modification of Eq. A1 in which C_{chem} was replaced with a constant phase element ^cValue obtained from fitting to Eq. A1 as written. ^dThis capacitance term is effectively zero and can be ignored; fits in which C_{int} was fixed at the very small value of 1 pF produced values of the other parameters that were unchanged within the errors reported here. For convenience, C_{int} was retained as a varied parameter across all analyses. ^eAt the completion of the $p\text{O}_2$ cycle of measurements, the material was returned to the most oxidizing condition and remeasured, yielding values that are unchanged within the error of the measurement.

Table S1. Continued.

C. CZO20, $R_0(RQ)$; values obtained by fitting using ZView® software¹

$\log(pO_2)$ atm	χ^2 10^{-4}	R_0^a Ω	Error %	R_{ion}^{surf} Ω	Err %	Q 10^{-3*}	Err %	n_q unitless	Err %	C mF	Err %
-19.5	12.74	4.82	0.24	41.7	0.68	35.6	0.50	0.955	0.30	36.2	0.89
-18.3	15.10	4.86	0.27	73.1	0.72	28.8	0.47	0.967	0.28	29.6	0.90
-17.1	11.39	4.88	0.25	121	0.61	24.9	0.37	0.974	0.21	25.7	0.75
-16.2	15.77	4.91	0.30	182	0.71	21.7	0.42	0.975	0.23	22.5	0.85
-15.2	11.99	4.94	0.28	199	0.61	18.2	0.38	0.978	0.20	18.7	0.75
-14.4	15.20	4.98	0.32	190	0.74	16.1	0.45	0.980	0.23	16.5	0.90

^aimplies an ionic conductivity of the substrate of 1.36×10^{-2} S/cm at 746 °C.

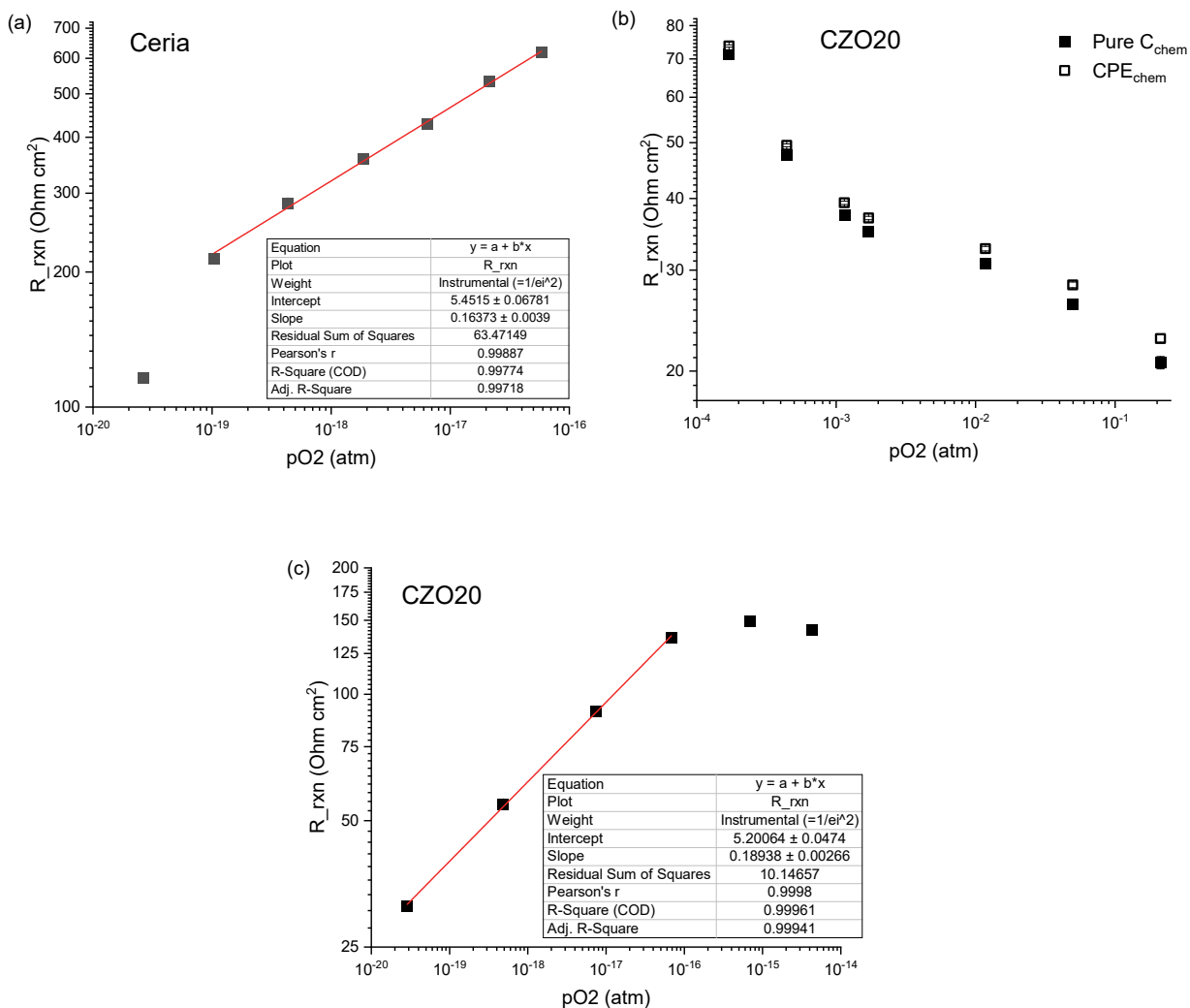


Figure S2. Electrochemical reaction resistance, R_{ion}^{surf} , of (a) ceria under reducing conditions ($T = 750 \text{ }^\circ\text{C}$), (b) CZO20 under oxidizing conditions ($T = 800 \text{ }^\circ\text{C}$), and (c) CZO20 under reducing conditions ($T = 746 \text{ }^\circ\text{C}$). Results in (a) and (c) are derived from $R_0(RQ)$ fitting and uncertainties are smaller than the symbol sizes. In (b) slight differences result from choice of capacitor used to represent C_{chem} in Eq. A1. An electrochemical reaction resistance which decreases with decreasing pO_2 under highly reducing conditions as evident in (a) and (c) has been reported previously for doped ceria.³ That previous study furthermore showed a transition in behavior under oxidizing conditions, resulting in trends similar to that evident in (b). Because of the role of the Pt paste current collector and the influence of unknown impurities, detailed interpretation of these results is premature.

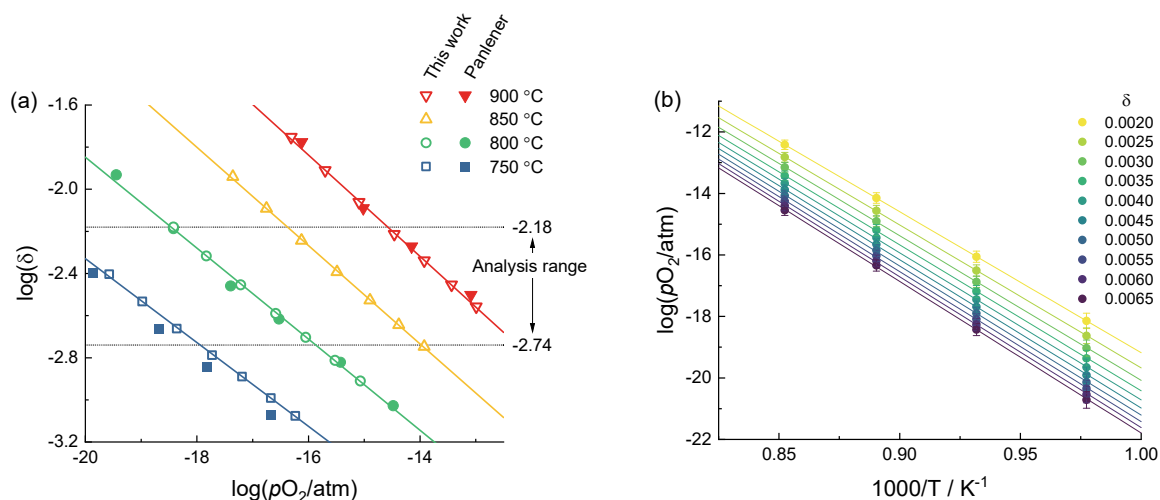


Figure S3. van't Hoff analysis of ceria nonstoichiometry: (a) double-logarithmic plot of nonstoichiometry as a function of oxygen partial pressure used to facilitate interpolation between measured data points, shown in comparison to Panlener data⁴; and (b) Arrhenius plot of isostoichiometric temperature and oxygen partial pressure conditions. Slope and intercept values in (b) yield, respectively, the standard partial molar enthalpy and the standard partial molar entropy of oxygen in the solid. Takacs et al.⁵ have suggested that the thermodynamic properties of ceria may be temperature dependent, and at first glance, the discrepancies noted here agree with those authors' observation that the magnitude of the enthalpy increases with temperature (the TGA results are obtained at substantially higher temperature than the electrochemical results). However, the thermodynamic parameters obtained from analysis of only the data collected between 800-900 °C from the work of Panlener et al. are essentially identical to the values obtained from analysis of the data collected at all temperatures (up to 1500 °C). Thus, an inherent temperature dependence of the thermodynamic properties cannot explain the discrepancies between the enthalpy and entropy values obtained here and those of Panlener. Instead, a slight difference in the measured nonstoichiometries at 750 °C, panel (a), appears to be the source of the discrepancies.

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² <https://github.com/hailegroup/ECIF>; https://github.com/hailegroup/LSM-type_fitting

³ W. Lai and S. M. Haile, "Impedance Spectroscopy as a Tool for Chemical and Electrochemical Analysis of Mixed Conductors: A Case Study of Ceria," *J. Amer. Cer. Soc.* **88**, 2979–2997 (2005).

⁴ Panlener, R. J.; Blumenthal, R. N.; Garnier, J. E., Thermodynamic Study of Nonstoichiometric Cerium Dioxide. *J. Phys Chem Solids* **1975**, *36* (11), 1213-1222.

⁵ Takacs, M.; Scheffe, J. R.; Steinfeld, A., Oxygen nonstoichiometry and thermodynamic characterization of Zr doped ceria in the 1573-1773 K temperature range. *Physical Chemistry Chemical Physics* **2015**, *17* (12), 7813-7822.