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Supplementary Information

Oxygen Reduction Reaction of $PrBaCo_{2-x}Fe_xO_{5+\delta}$ compounds as H^+-SOFC cathode: correlation with physical properties

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Oxygen Reduction Reaction, H^+-SOFC cathode, Rate Determining steps, Double Perovskites, Oxygen diffusion, Water formation mechanism

Electrical Conductivity Relaxation data fitting

The analytical solution to the ECR profile was solved by Crank[1]; considering a pellet with 2x, 2y and 2z dimensions, the ratio between the oxide ions diffusing between *t* to infinite time can be written:[2-4]

$$\frac{M_t}{M_\infty} = 1 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\sum_{p=1}^{\infty} \frac{2L_x^2 \exp\left(\frac{-\beta_m^2 D_{Chem} t}{x^2}\right)}{\beta_m^2(\beta_m^2 + L_x^2 + L_x)} \times \frac{2L_y^2 \exp\left(\frac{-\gamma_n^2 D_{Chem} t}{y^2}\right)}{\gamma_n^2(\gamma_n^2 + L_y^2 + L_y)} \times \frac{2L_z^2 \exp\left(\frac{-\delta_p^2 D_{Chem} t}{z^2}\right)}{\delta_p^2(\delta_p^2 + L_z^2 + L_z)} \quad (1)$$

$$L_x = x\frac{k_{Chem}}{D_{Chem}} \; ; \; L_y = y\frac{k_{Chem}}{D_{Chem}} \; ; \; L_z = z\frac{k_{Chem}}{D_{Chem}} \quad (2)$$

with k_{Chem} and D_{Chem} being the chemical surface exchange and diffusion coefficients, respectively, β_m, γ_n and δ_p the non-null solutions of the following equation:

$$\beta_m \tan\beta_m = L_x \; ; \; \gamma_n \tan\gamma_n = L_y \; ; \; \delta_p \tan\delta_p = L_z \quad (3)$$

Using a sufficiently small pO_2 step, the charge carrier mobility is considered as constant and the relation between this mobility and the conductivity can be considered as linear and the ratio $\frac{M_t}{M_\infty}$ can be written:

$$\frac{M_t}{M_\infty} = \frac{\sigma_t - \sigma_0}{\sigma_\infty - \sigma_0} \quad (4)$$

σ_t, σ_0 and σ_∞ are the conductivity values at t, t = 0 and t = ∞, respectively.

These equations were fitted using a homemade program.

Table S1 Chemical diffusion and surface exchange coefficients obtained for $PrBaCo_2O_{5+\delta}$ by the electrical conductivity relaxation (ECR) method and γ thermodynamic factor measured by thermal gravimetric analysis under 0.21 and 10^{-2} bar O_2.

Temperature (˚C)	D_{Chem} (cm^2/s)	**k_{Chem} (cm/s)**	γ
800	$1.8\ 10^{-5}$	$3.4\ 10^{-4}$	90.8
700	$6\ 10^{-6}$	$3.2\ 10^{-4}$	106.9
650	$4.5\ 10^{-7}$	$1.8\ 10^{-4}$	116.0
600	$3.7\ 10^{-6}$	$1\ 10^{-4}$	125.0

Mobile oxygen – Ionic conductivity calculation

For the ionic conductivity calculation, the mobile oxygen concentration $[O^{2-}] = N / V_M$, with N the amount of mobile oxygen in the structure and $V_M = V/Z$ the volume of a unit cell divided by the number of formula unit, is required.

Several N can be chosen for the double perovskite structure:

- $N = \delta$ if only the oxide ions located in the oxygen vacancy planes are mobile.
- $N = 4 + \delta$ if the oxide ions from the CoO_2 planes are also mobile
- $N = 5 + \delta$ if all oxide ions are mobile (*i.e*. those from the BaO planes can also be mobile).

Calculations by molecular dynamics from Parfitt *et al.* and Hermet *et al.* describe a similar oxygen diffusion mechanism for which the oxygen diffuses mainly in the rare earth and cobalt planes, with oxygen from the barium planes not being involved in the diffusion process.[5, 6] This can be explained by a larger distance in between the cobalt and barium planes than between the cobalt and rare earth planes. Despite these studies, we have considered that all oxide ions are mobile in the double perovskite structure and $N = 5 + \delta$.

The unit cell volume is estimated at each temperature using thermal expansion coefficient reported in the literature and equal to $20\text{x}10^{-6}\ K^{-1}$ for both x = 0 and x = 0.5.[7, 8]

Elementary steps of the oxygen reduction reaction at the H^+-SOFC cathode

Starting from kinetics equations,[3, 4] for a given elementary step of a reaction, a general expression of the corresponding polarization resistance Rp can be written as follows:

$$R_p \,\alpha\, pO_2^{-n} \,.\, pH_2O^{-m}$$

n and m being the reaction orders with respect to pO_2 and pH_2O, respectively.

Regarding the complexity of the oxygen reduction and water formation at the H^+-SOFC cathode and that both reactions can be coupled through the presence and concentration of defects, we kept these reactions as simple as possible. For instance, the step 5 being:

$$2OH_{O(cath)}^{\bullet} = H_2O_{(ads)} + V_O^{\bullet\bullet} + O_{O(cath)}^{x}$$

$$K = \frac{[OH_O^{\bullet}]^2}{pH_2O.[V_O^{\bullet\bullet}]}$$

and

$$[V_O^{\bullet\bullet}] \propto pO_2 \qquad \text{but also} \quad \propto pH_2O$$

As $[V_O^{\bullet\bullet}]$ is dependent on pO_2 but also on pH_2O when the electrode is hydrated under wet atmosphere, it gives $j \propto pH_2O^{-(1-x)}$. However, the determination of the x value is very difficult to obtain via normal TGA analysis (*cf.* ref 9).

Table S2 Elementary steps of the oxygen reduction reaction at a H^+-SOFC cathode and their reaction orders with respect to pO_2 (n) and pH_2O (m).

			$Rp \propto pO_2^{-n}.pH_2O^{-m}$	
	Elementary steps		**n**	**m**
1	$O_{2(g)} \rightarrow O_{2(ads)}$	Oxygen adsorption	1	0
2	$O_{2(ads)} \rightarrow 2O_{(ads)}$	Oxygen dissociation	½	0
3	$O_{(ads)} + 2e^- + V_{\ddot{O}} \rightarrow O_{O(cath)}^x$	Charge transfer	¼	0
4	$OH_{O(electrolyte)}^{\bullet} + O_{O(cath)}^x \rightarrow O_{O(electrolyte)}^x + OH_{O(cath)}^{\bullet}$	Proton transfer	0	½
5	$2OH_{O(cath)}^{\bullet} \rightarrow H_2O_{(ads)} + V_{\ddot{O}} + O_{o(cath)}^x$	Water formation	0	1
6	$H_2O_{(ads)} \rightarrow H_2O_{(g)}$	Water exhaust	0	1

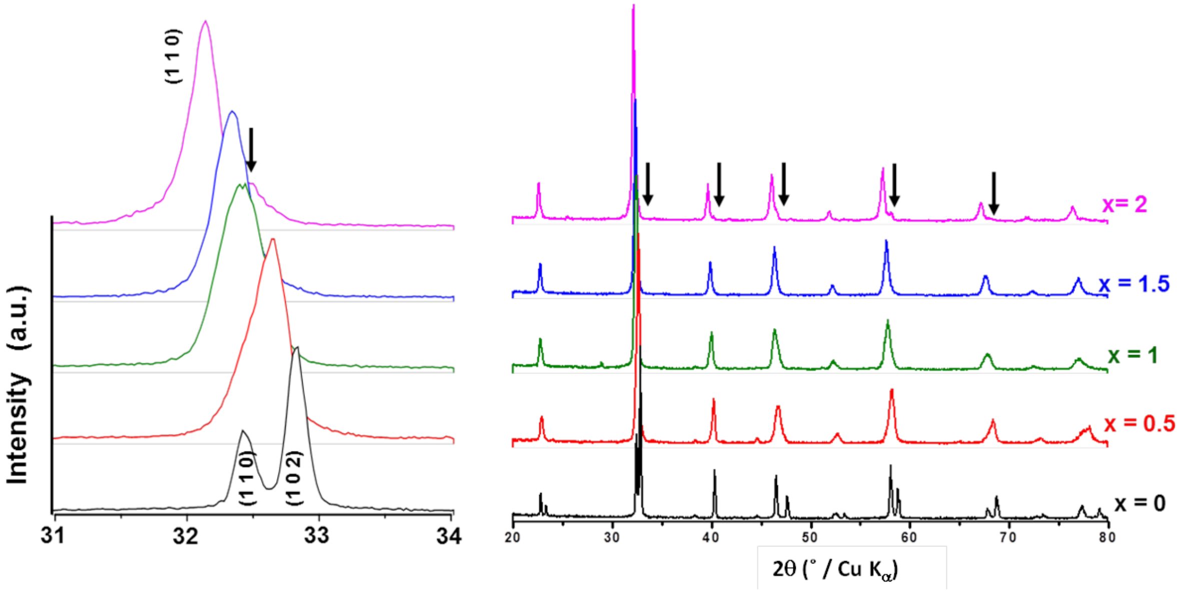

Figure S1. XRD data obtained for $PrBaCo_{2-x}Fe_xO_{5+\delta}$ oxides sintered at 1100˚C under air.

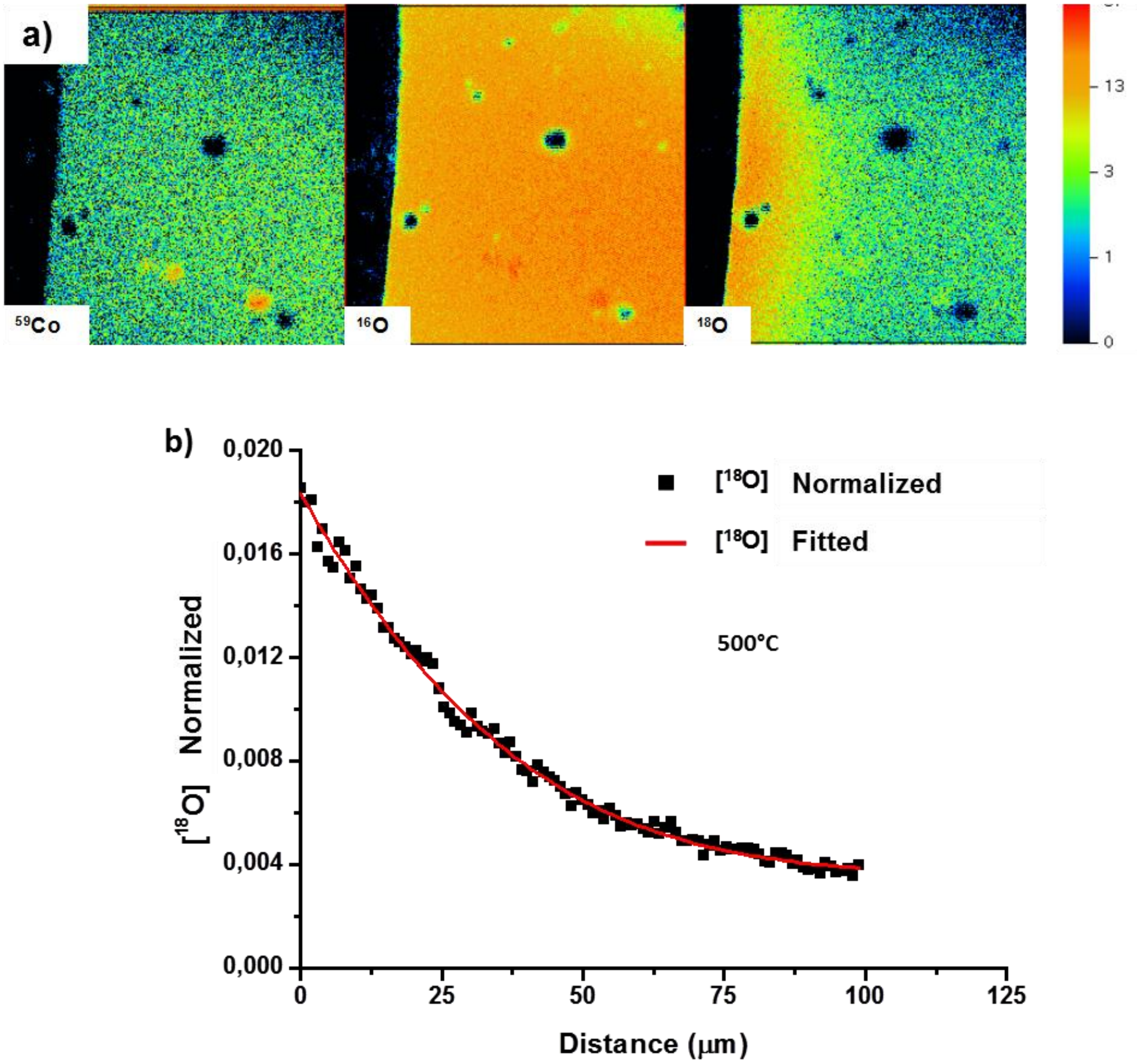

Figure S2. a) Secondary Ion Mass Spectroscopy (SIMS) maps of ^{59}Co, ^{16}O and ^{18}O obtained for $PrBaCo_2O_{5+\delta}$ exchanged at 500°C and b) [^{18}O] normalized profile obtained from SIMS maps and fitted profile.

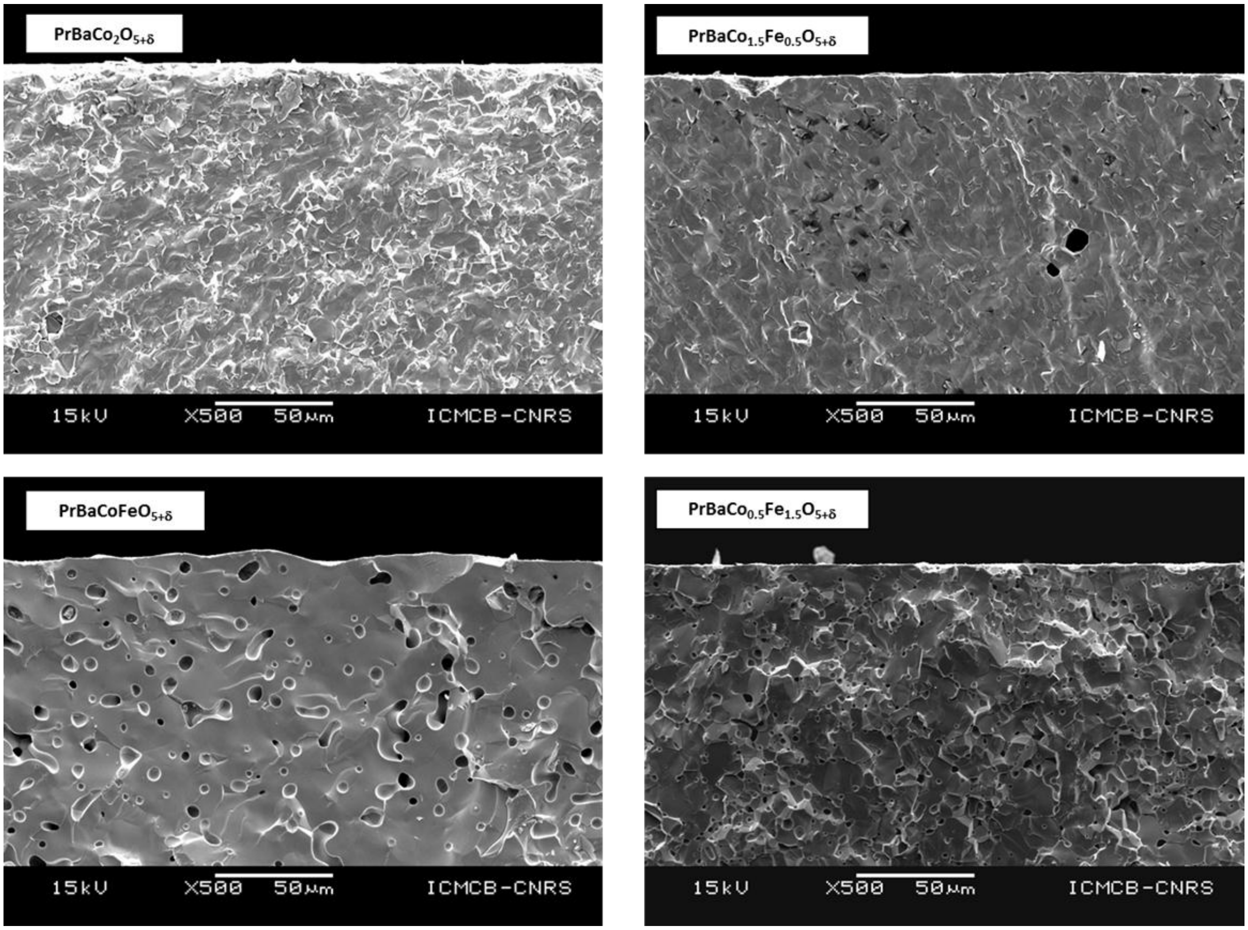

Figure S3. SEM micrographs of dense $PrBaCo_{2-x}Fe_xO_{5+\delta}$ pellets used for ECR and IEDP-SIMS measurements. They were obtained by isostatic pressure at 3000 bar for 10 min followed by a sintering process at 1300°C for 12 hours.

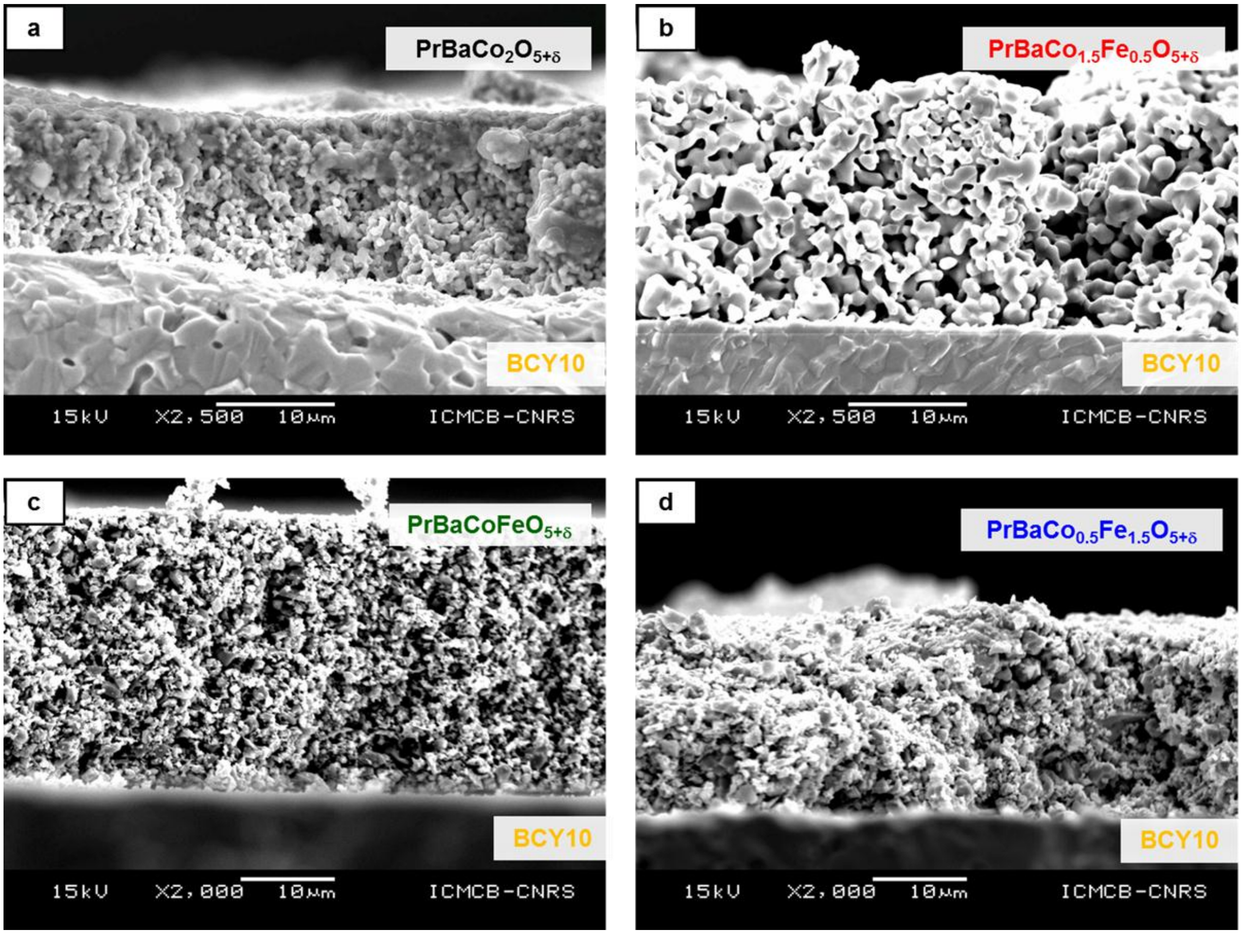

Figure S4. SEM micrographs of PrBaCo$_{2-x}$Fe$_x$O$_{5+\delta}$ electrodes after electrochemical experiments.

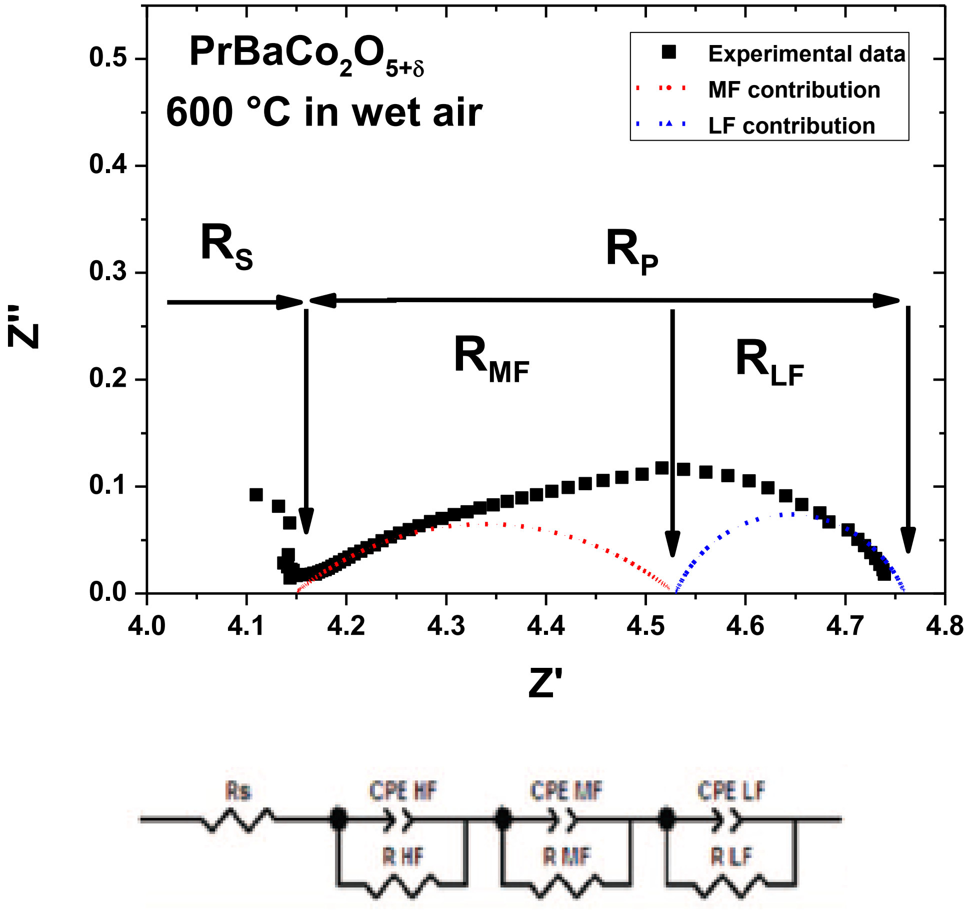

Figure S5. Typical fit of an impedance spectroscopy diagram obtained for $PrBaCo_2O_{5+\square}$ in wet air at 6000 °C. The inset shows the equivalent circuit used for fitting the data.

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