Comment [NC]: Reviewer 3.1

Supplementary Information

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Heat-treatment temperature effect

This material was pyrolyzed at a wide range of temperatures (600°C-1000°C). The activity, in terms of the ORR onset and half-wave potentials in the RDE plots, undergoes a significant increase after the sample was heat-activated under nitrogen atmosphere at temperatures up to 700°C and then drops for the material pyrolyzed at higher temperatures(800-1000°C), as shown in Fig. S1. An optimal performance was achieved for the sample pyrolyzed at a temperature of 700°C with an onset potential of 0.87 V.

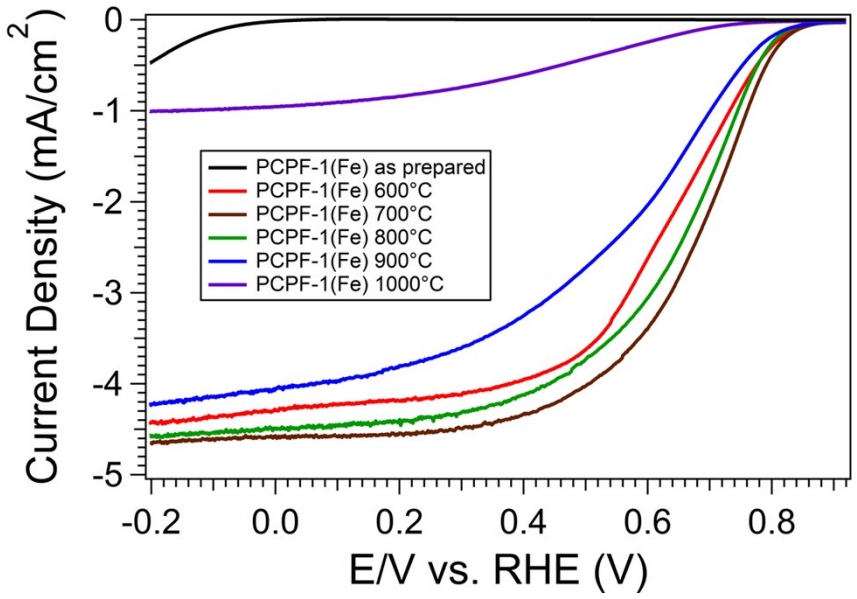

Fig. S1 RDE curves for the untreated and pre-treated iron porphyrin framework at different heat-treatment temperatures (600-1000°C). 1600 rpm, 10 mV/s scan rate, room temperature, 0.1 M H_2SO_4 electrolyte, Hg/Hg_2SO_4 reference electrode and Au wire counter electrode.

The best-performing PCPF-1(Fe) sample, heat treated at 700°C, exhibits the lowest hydrogen peroxide yield over the potential range from -0.2 to 0.9 V (Fig. S2). This suggests that the oxygen reduction reaction is mainly proceeding through an overall four-electron transfer path: either by the direct four-electron oxygen reduction or by the two-electron reduction to produce hydrogen peroxide and its subsequent oxidation. Further experimentation would be necessary to determine this, which is beyond the scope of this paper. Hydrogen peroxide yields for the heat treated material are comparable to that of Pt-based catalysts (5% H_2O_2 yield at 0.4 V for PCPF-1(Fe) heat-treated at 700°C *vs* 3-4% H_2O_2 yield at 0.4 V on 14 $\mu g_{Pt} cm^{-2}$ Pt/C).

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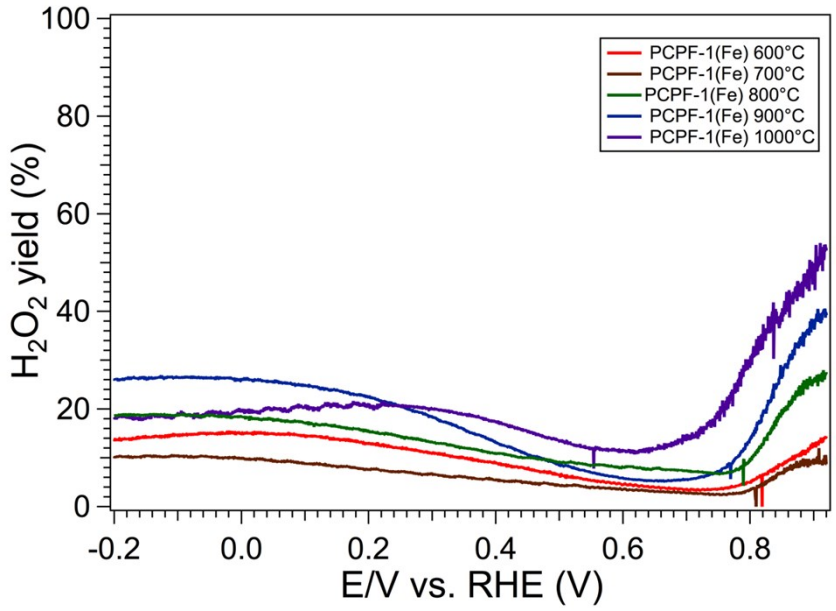

Fig. S2 H_2O_2 yield plots measured for the pre-treated iron porphyrin framework at different heat-treatment temperatures (600-1000°C). 1600 rpm, 10 mV/s scan rate, room temperature, 0.1 M H_2SO_4 electrolyte, Hg/Hg_2SO_4 reference electrode and Au wire counter electrode. Ring electrode is kept at 1.2 V.

Catalyst Layer Nafion Content

A study was carried out to determine the best ionomer (Nafion®) ratio in terms of fuel cell performance. Three different catalyst inks were prepared with a fixed catalyst powder amount (15 mg), 1 ml of deionized water, 2 ml of isopropanol and a variable weight of Nafion® solution. The Nafion®:catalyst ratios were set to 30:70, 50:50 and 70:30, and the catalyst loading on the cathode electrode was $2mg_{cat}/cm^2$ in all cases. The highest Nafion®:catalyst ratio (70:30) ink presented agglomeration issues, which prevented a suitable electrode preparation and subsequent fuel cell testing . The results obtained with the 30:70 and 50:50 Nafion®:catalyst

ratios are shown in Fig. S3. Although both ratios exhibit a similar behavior at high voltages, the 50:50 Nafion®:PCPF-1 electrode undergoes a more significant drop at lower voltages. The current density for the 30:70 PCPF-1:Nafion electrode, at 0.4 V, is 40% higher than for he 50:50 PCPF-1:Nafion electrode. This could be related to a higher extent of ionomer agglomeration, which affects the global structure of the electrode.

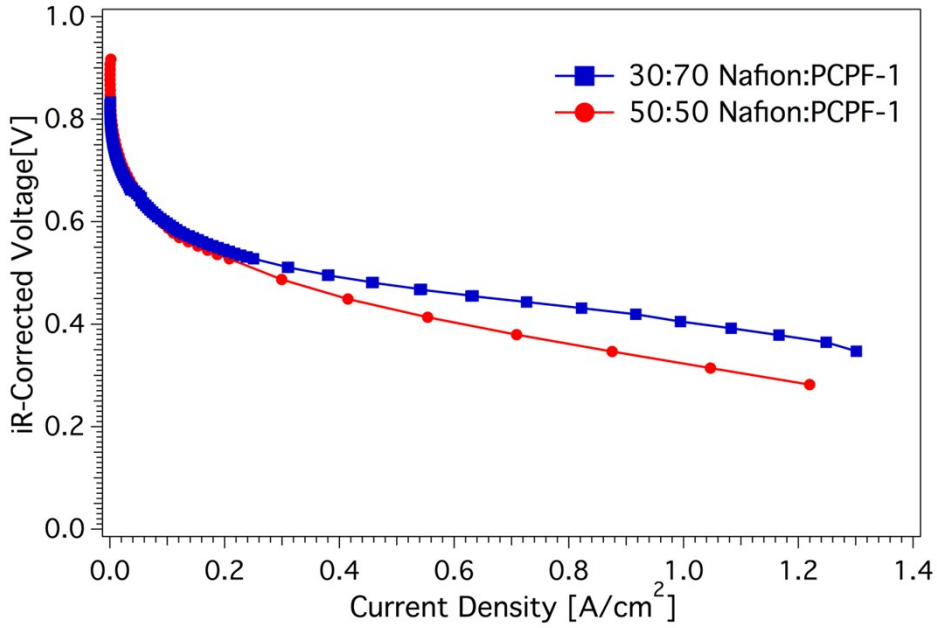

Fig. S3 *P*olarization and resistance curves for H_2-O_2 PEM fuel cells with a 2 mg_{cat}/cm^2 cathode catalyst loading and different catalyst:Nafion ratios (30:70 and 50:50). The curves were obtained with inlet gases heated and humidified to 83 °C, 2 atm backpressure and the cell

Material Stability

The polarization curves, showing the stability of the material through cycling according to the testing protocol described, are shown in Fig. S3. A significant performance loss is observed over the entire voltage range, approximately 0.37 $A \cdot cm^{-2}$ was observed at 0.4 V after 49 cycles (~49 hours).

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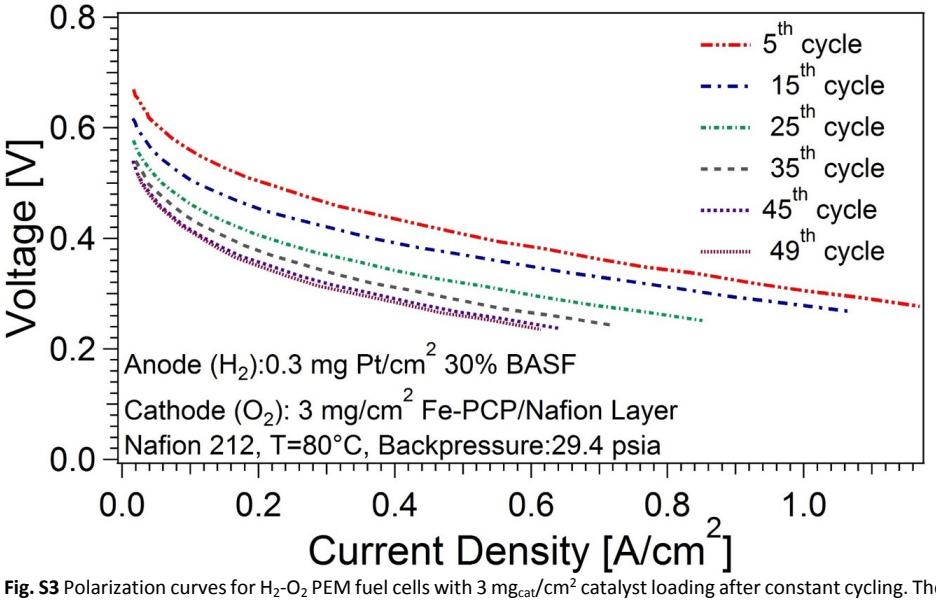

Fig. S3 Polarization curves for H_2-O_2 PEM fuel cells with 3 mg_{cat}/cm^2 catalyst loading after constant cycling. The curves were obtained with inlet gases heated and humidified to 83 °C, 2 atm backpressure and the cell temperature was held at 80°C.

Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out through a BioLogic VSP3 potentiostat with a 10 A booster on the Fuel Cell setup described. All AC impedance spectra reported here were measured between the fuel cell cathode and the fuel cell anode. The EIS measurements were carried out at each point of the polarization curve. The frequency scan was performed from 10 kHz down to 1 Hz. The measured impedance responses for each oxygen pressure are shown in Fig. S4 for a set of voltages throughout the Tafel region. At higher oxygen pressures (20% and up), the typical high voltage pattern of the EI spectra is observed:[1,2] a single depressed semicircle with diameter R_p, which decreases with voltage). As seen from the Bode plots presented in Fig. S5, the characteristic frequencies of this loop increase with decreasing potential and increasing oxygen concentration.

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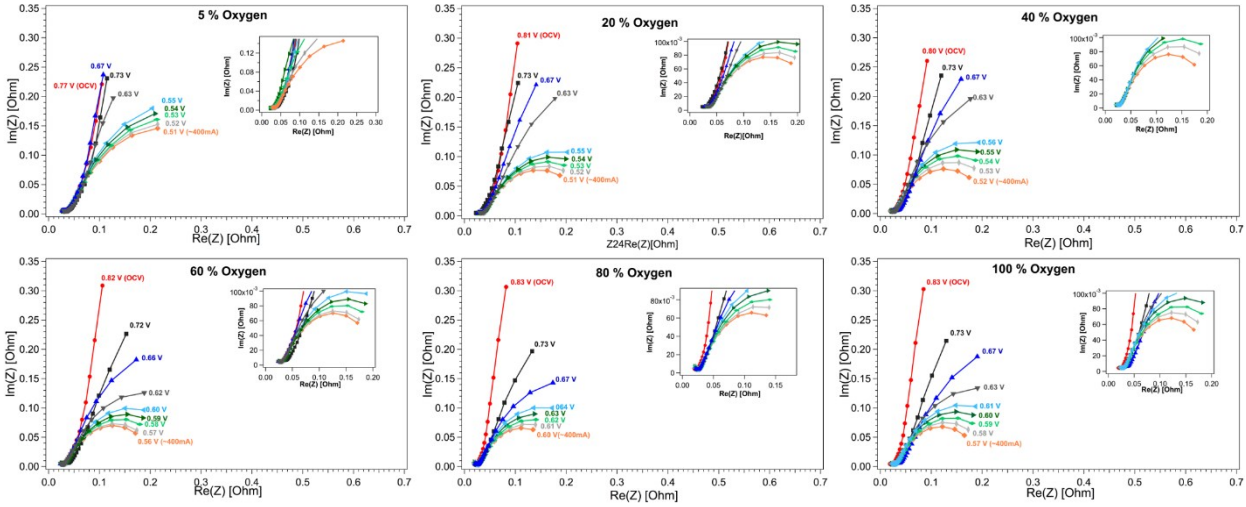

Fig. S4 Measured impedance response for PEM fuel cell with 2 mg_{cat}/cm^2 cathode catalyst loading and oxygen partial pressure variation. Plots at different voltage values are shown for each oxygen pressure.

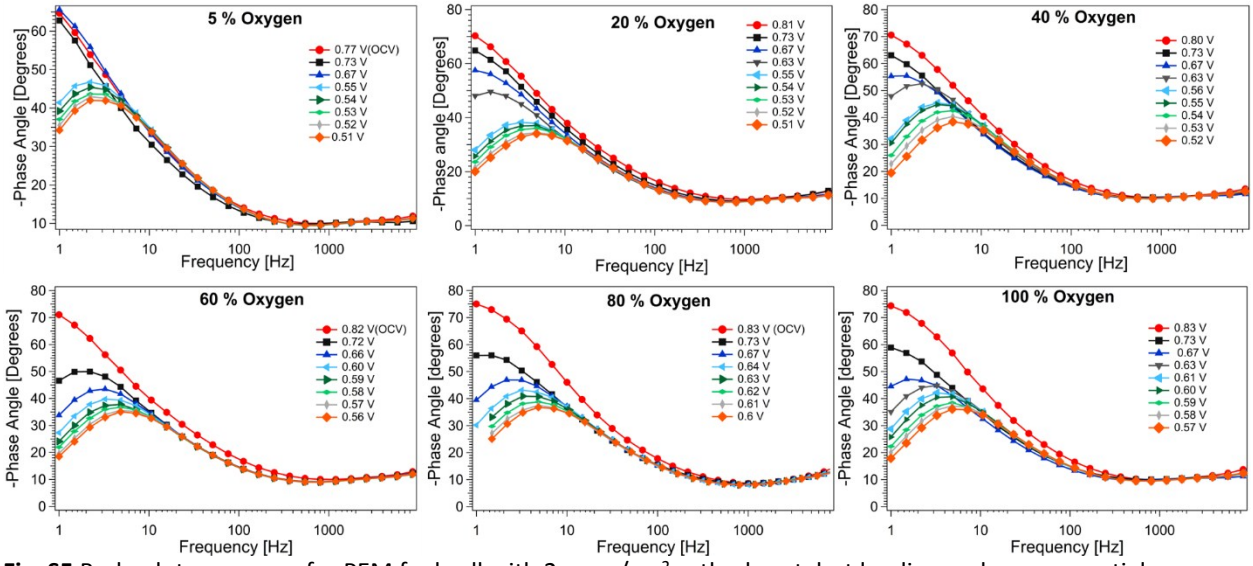

Fig. S5 Bode plots response for PEM fuel cell with 2 mg_{cat}/cm^2 cathode catalyst loading and oxygen partial pressure variation. Plots at different voltage values are shown for each oxygen pressure.

Given the absence of a second (low-frequency) semicircle or any sign of concavity change of the first loop, R_p could be associated with the charge transfer across the catalyst-electrolyte interface.[3] An equivalent circuit (Fig. S6)) taking into account the ohmic and contact resistance (R_Ω) of the electrochemical cell, a constant phase element T_1, which accounts for the effect of the porous electrode on the double-layer capacitance and the charge transfer resistance R_1. Fitting of the impedance plots was carried out to calculate the parameter values (T_1, R_1 and R_Ω) as shown in Fig. S6 for the 2 mg_{cat}/cm^2 cathode catalyst loading at 100% oxygen partial pressure and 0.6 V. The calculated values are shown in Table S1 for each oxygen pressure.

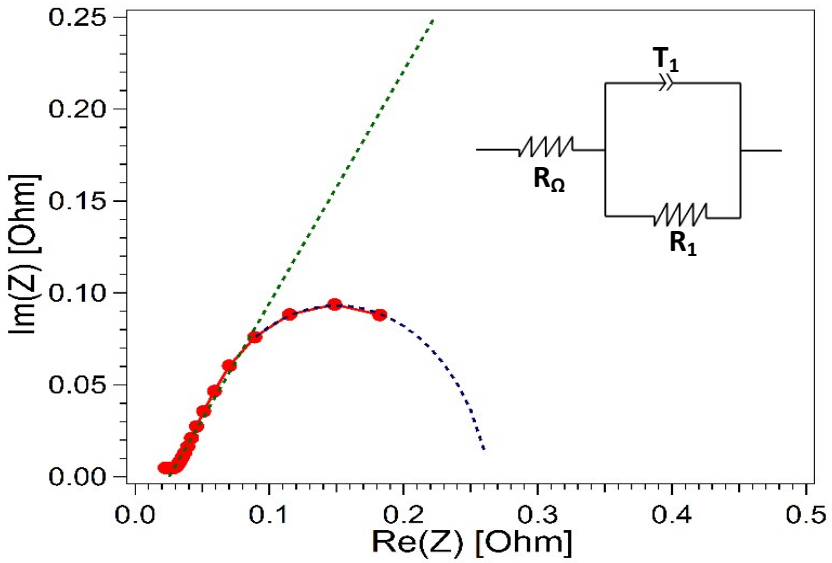

Fig. S6 Measured Impedance response for PEM fuel cell with 2 mg_{cat}/cm^2 cathode catalyst loading at 100% oxygen partial pressure and 0.6 V, semicircle and CPE fitting included.

Table S1. Charge transfer resistance and CPE calculations

O_2 Partial Pressure							
100%	**Voltage [V]**	**0.57**	**0.58**	**0.59**	**0.6**	**0.61**
	$R_\Omega[\Omega]$	0.2009	0.2196	0.2416	0.2639	0.2918
	$R_1[\Omega]$	0.1641	0.1822	0.2033	0.2270	0.2534
	T_1	0.0207	0.0291	0.0272	0.0207	0.0368
80%	**Voltage [V]**	**0.60**	**0.61**	**0.62**	**0.63**	**0.64**
	$R_\Omega[\Omega]$	0.1837	0.2006	0.2225	0.2440	0.2630
	$R_1[\Omega]$	0.1508	0.1649	0.1857	0.2110	0.2279
	T_1	0.0360	0.0354	0.0363	0.0348	0.0309
60%	**Voltage [V]**	**0.56**	**0.57**	**0.58**	**0.59**	**0.60**
	$R_\Omega[\Omega]$	0.2126	0.2289	0.2501	0.2683	0.3075
	$R_1[\Omega]$	0.1725	0.1876	0.2073	0.2250	0.2683
	T_1	0.0283	0.0347	0.0385	0.0472	0.0178
40%	**Voltage [V]**	**0.52**	**0.53**	**0.54**	**0.55**	**0.56**
	$R_\Omega[\Omega]$	0.2134	0.2317	0.2509	0.2710	0.2977
	$R_1[\Omega]$	0.1743	0.1923	0.2114	0.2319	0.2575
	T_1	0.0342	0.0362	0.0313	0.0479	0.0430
20%	**Voltage [V]**	**0.60**	**0.61**	**0.62**	**0.63**	**0.64**
	$R_\Omega[\Omega]$	0.4817	0.5494	0.6507	0.7843	1.0060
	$R_1[\Omega]$	0.4224	0.4912	0.5959	0.7318	0.9560
	T_1	0.0238	0.0923	0.0873	0.0476	0.0443
5%	**Voltage [V]**	**0.51**	**0.52**	**0.53**	**0.54**	**0.55**
	$R_\Omega[\Omega]$	0.6810	0.6954	0.8884	0.9846	1.0660
	$R_1[\Omega]$	0.6341	0.6442	0.8443	0.9390	1.0192
	T_1	0.0467	0.0454	0.0268	0.0224	0.0395

In order to be able to determine if there are other contributions, the cathode potential (iR-corrected cell voltage) was represented as a function of log R_p^{-1} (Fig. S7). The linear relationship between the cathode potential (E_{cath}) and log R_p^{-1} can be associated to a Tafel plot,[1] where charge transfer represents the main contribution to R_p:

$E_{cath} = E_o - b log R_p^{-1}$

where $b = 2.3b'$ ($b' = RT/\propto nF$). In Fig. S7 the values of b calculated from the different plots have been included. In general terms, the plots corresponding to higher oxygen pressures present a good fitting to a linear behavior. Lower oxygen concentrations (5-20%) show a larger deviation from the linear behavior, which could suggest a larger mass transport contribution.

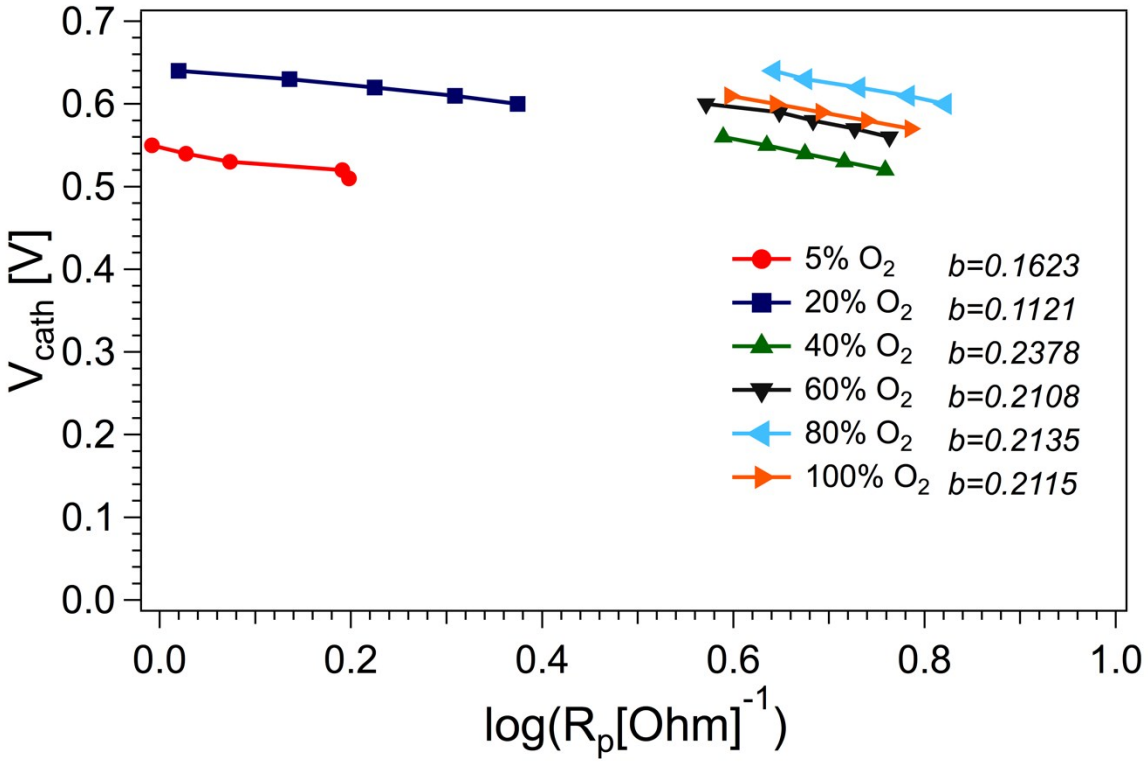

Fig. S7 Cathode potential as a function of log(R_p^{-1}) at different oxygen pressures

References

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3 C. Boyer, S. Gamburzev, O. Velev, S. Srinivasan and A. J. Appleby, *Electrochim. Acta*, 1998, **43**, 3703–3709.