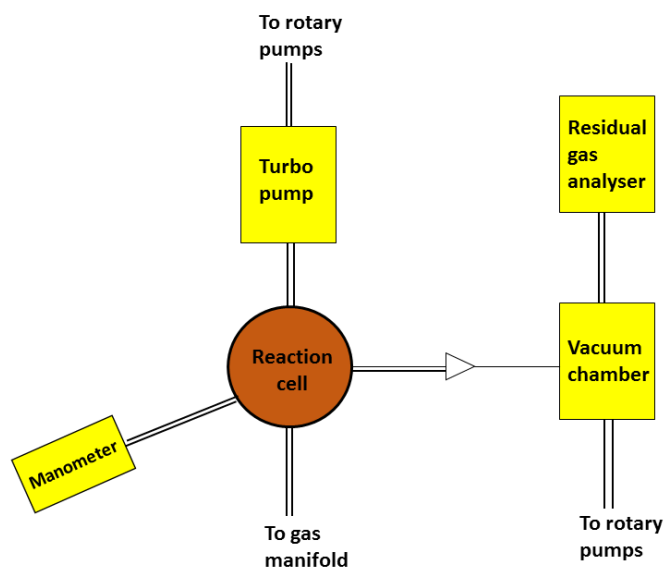


Supporting information

S1: Thermometric -Mass spectrometer analysis

The thermometric-MS experiment was carried out using a custom-built high temperature pulsed-gas sampling equipment which was coupled with a mass spectrometer for real-time analysis of the gaseous mixture (Scheme S1) [1]. The reaction cell is in contact with a copper block containing a 100 W heater cartridge controlled by a proportional-integral-derivative (PID) temperature controller (CAL Controls, Cal 3300) and K-type thermocouple mounted to the cell. A piezo-resistive manometer (Keller, Leo Record series, 30 bar range) measures the pressure. Pulsed nozzle (Parker, Series 9 Pulse Valve) connected to the cell, which is used to pulse controlled amounts of gas from the reaction cell via a 1/16" stainless steel tube into the vacuum system, comprised of a residual gas analyser (RGA, RGA 200, Stanford Research Systems, USA) for sampling of the gas mixture (*vide infra*). For our analysis, we loaded 10 mg of samples into the reaction cell and ramped for different temperatures including 30 °C to 200 °C and 200 °C–250 °C and 250 °C–275 °C and paused the temperatures at 200 °C, 250 °C and 275 °C to determine any evolved gases.



Scheme S1. Schematic representation of custom-build high temperature pulsed-gas sampling equipment.

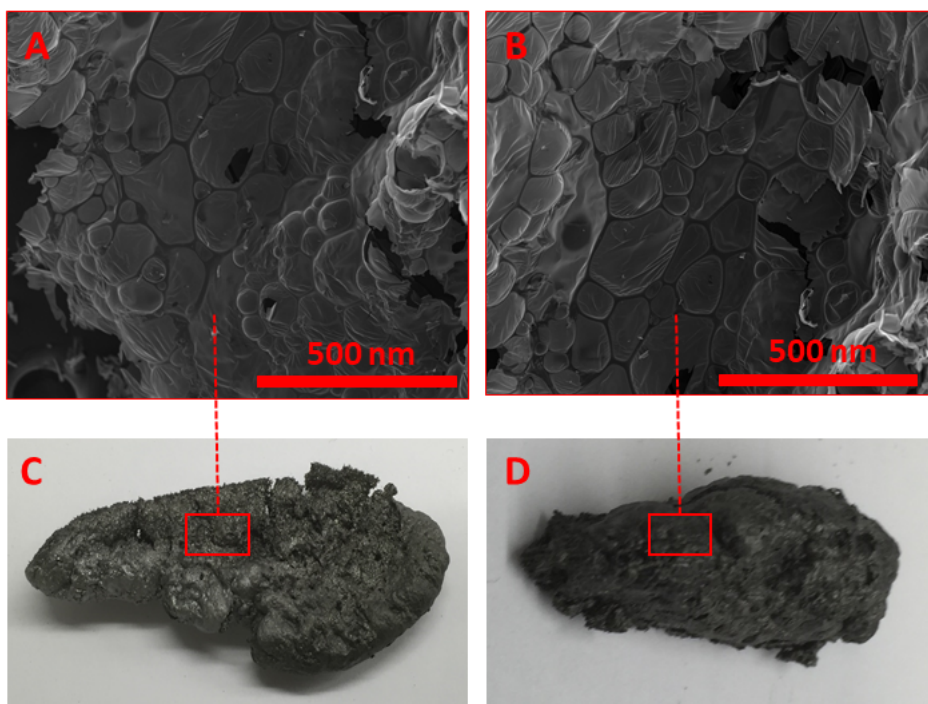


Figure S1: SEM images of (A) P-SAOPF and (B) P-SAOrgO. Synthesised macroporous (C) P-SAOPF and (D) P-SAOrgO.

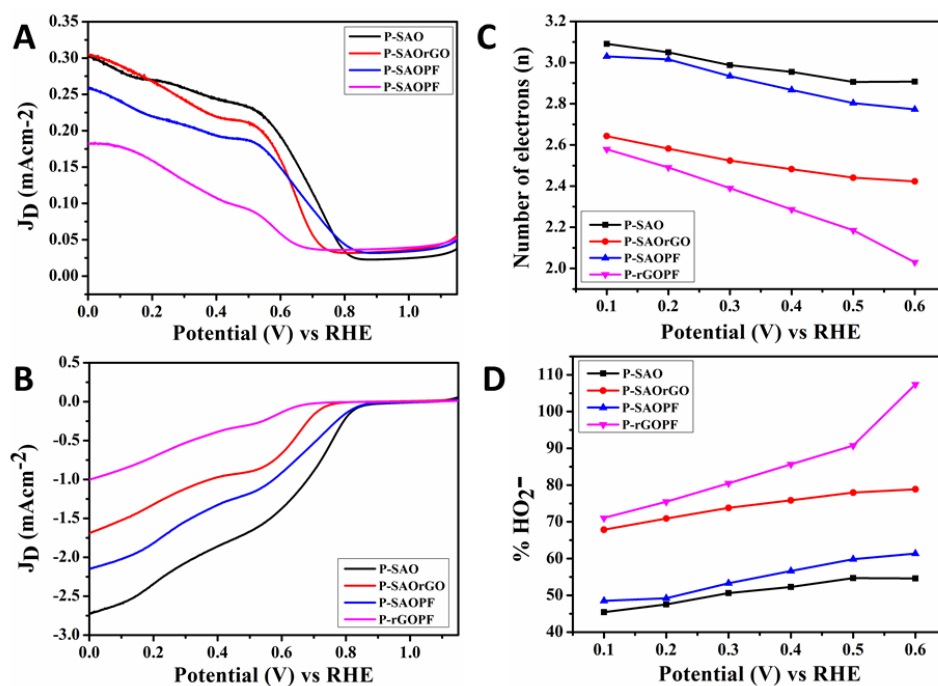


Figure S2. Rotating ring disc voltammograms of (A) ring current, (B) disc current of P-SAO, P-SAOrgO, P-SAOPF and Pt/C electrodes in oxygen saturated 0.1M KOH at 2000 rpm at a scan rate of 10 mV/s. (C) number of electrons and (D) percentage peroxide of P-SAO, P-SAOrgO, P-SAOPF and Pt/C electrodes at various potential calculated according to RRDE data.

Table S1. Electrochemical properties of the pyrolysed aniline oligomers and composite of aniline oligomers catalysts.

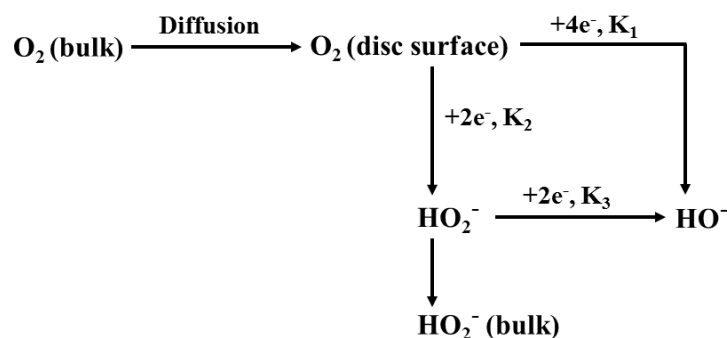
Catalysts	Current density (mA/cm ²) at 0.00 V (RHE)	Onset potential (RHE) (V)	Number of electrons (n) (0.10–0.80 V) (RHE)	% HO ₂ ⁻ (0.10–0.80V) (RHE)
P-SAO	2.73	0.81	3.09–2.90	45.45–54.60
P-SAO _r GO	1.69	0.74	2.64–2.42	67.84–78.68
P-SAOPF	2.16	0.84	3.03–2.77	48.50–61.35
P-rGOPF	1.01	0.64	2.57–2.03	71.06–107.40

Table S2: Mean onset set potential, current density, number of electrons and % HO₂⁻ of pyrolysed and N-doped carbon materials synthesised.

Onset potential RHE (V)						
	Mean Pyrolysed	SD	Mean Doped	SD	-	SD
SAO	0.81	0.02	0.87	0.01	-	-
SAO _r GO	0.789	0.01	0.93	0.01	-	-
SAOPF	0.84	0.03	0.98	0.01	-	-
rGOPF	0.84	0.01	0.78	0.02	-	-
Pt/C	-	-	-	-	0.98	0.005
Current density (mVcm ⁻²)						
	Mean Pyrolysed	SD	Mean Doped	SD	-	SD
SAO	2.73	0.06	6.29	0.14	-	-
SAO _r GO	1.59	0.10	7.89	0.20	-	-
SAOPF	2.16	0.08	5.18	0.10	-	-
rGOPF	1.01	0.13	3.99	0.11	-	-
Pt/C	-	-	-	-	5.85	0.12
Number of electrons (n)						
	Mean Pyrolysed	SD	Mean Doped	SD	-	SD
SAO	2.91	0.01	3.22	0.04	-	-
SAO _r GO	2.69	0.13	3.38	0.04	-	-
SAOPF	2.81	0.04	3.62	0.04	-	-
rGOPF	2.19	0.09	3.21	0.05	-	-
Pt/C	-	-	-	-	3.88	0.01
% HO ₂ ⁻						
	Mean Pyrolysed	SD	Mean Doped	SD	-	SD
SAO	54.69	4.24	39.05	2.98	-	-
SAO _r GO	65.37	4.07	30.84	3.05	-	-
SAOPF	59.84	4.10	19.02	2.50	-	-
rGOPF	90.74	4.80	40.19	3.60	-	-
Pt/C	-	-	-	-	10.21	1.30

S2: Electron transfer kinetics

The electron transfer kinetic of the ORR was identified using RRDE voltametry (Scheme S2) [2, 3]. According to Damjanovic [2] *et al.* [2] the electron transfer mechanism follows a direct four-electron pathway via K_1 kinetics (Scheme S1), in which oxygen is directly reduced to hydroxide anion (OH^-) or could be driven through a two-electron pathway via K_2 kinetics producing peroxide intermediates (HO_2^-), followed by reduction to hydroxide anion (OH^-) through another two electron pathway through K_3 kinetics.



Scheme S2: Proposed model for electrochemical reduction of oxygen proposed by Damjanovic et al. and Hsueh et al.

Hsueh *et al.*[3] suggested a series of equations (3, 4 and 5) to calculate the rate constants K_1 , K_2 and K_3 , where I_d , I_r , I_{dL} and ω are the disc current, ring current, limiting disc current and the rotation speed, respectively.

$$k_1 = S_1 Z_1 \frac{I_1^{N-1}}{I_1^{N+1}} \quad (3)$$

$$k_2 = \frac{2 S_2 Z_1}{I_1^{N+1}} \quad (4)$$

$$k_3 = \frac{N S_1 Z_2}{I_1^{N+1}} \quad (5)$$

Where S_1 and I_1 are the slope and intercept correspond to the I_d / I_r vs $\omega^{-1/2}$ plots and S_2 and is the slope of $I_{dL} / I_{dL} - I_d$ vs $\omega^{-1/2}$ plot. $Z_1 = 0.62 D_{\text{O}_2}^{2/3} V^{-1/6}$, $Z_2 = 0.62 D_{\text{H}_2\text{O}_2}^{2/3} V^{-1/6}$, $D_{\text{H}_2\text{O}_2}$ is $6.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and N is the collection efficiency [4].

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