

Electronic Supplementary Information

Variation of nitrogen species in zeolite-templated carbon by low-temperature carbonization of pyrrole and the effect on oxygen reduction activity

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S1. Supporting experimental section

Determination of electron transfer number

The Koutecky–Levich (K–L) plots were derived at diverse potentials from the LSV curves obtained at various rotation speeds. The number of electrons transferred per oxygen molecule (n) was determined from the slope (B) of the K-L plot based on the K-L equation below:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.2nF(D_0)^{2/3}C_0\nu^{-1/6}$$

where j is the measured current density, j_K is the kinetic-limiting current density, ω is the electrode rotation rate, F is the Faraday constant (96 485 C mol⁻¹), D_0 is the diffusion coefficient of O₂ in 0.1 M KOH (1.9 × 10⁻⁵ cm² s⁻¹), C_0 is the bulk concentration of O₂ (1.2 × 10⁻⁶ mol cm⁻³), and ν is the kinetic viscosity (0.01 cm² s⁻¹).

RRDE measurements for determination of H₂O₂ selectivity

The rotating ring disk electrode (RRDE) measurements were performed using a similar electrochemical set up for the rotating disk electrode (RDE) measurements (described in the Experimental Section). Instead of an RDE, an RRDE consisted of a glassy carbon (GC) disk (0.126 cm²) and a Pt ring (0.188 cm²) was used to simultaneously monitor currents for ORR and H₂O₂ production. Prior to the measurement, both the GC disk and the Pt ring were electrochemically cleaned by cycling the potential between 1 and 0 V vs RHE 50 times at a scan rate of 500 mV s⁻¹ in N₂-saturated 0.1 M KOH. The H₂O₂ production activity was determined from the linear sweep voltammetry (LSV) curves obtained between 1 to 0 V vs RHE in O₂-saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm. The Pt ring potential was held constant at 1.45 V vs RHE. The H₂O₂ current was calculated considering the correction of the ring current with the collection efficiency of the Pt ring (35%). The H₂O₂ selectivity was determined based on the following equation:

$$H_2O_2 \text{ selectivity} = \frac{200i_r}{(Ni_d + i_r)}$$

Where i_r is the ring current, i_d is the disk current, and N is the collection efficiency of the ring.

S2. Supporting figures and table

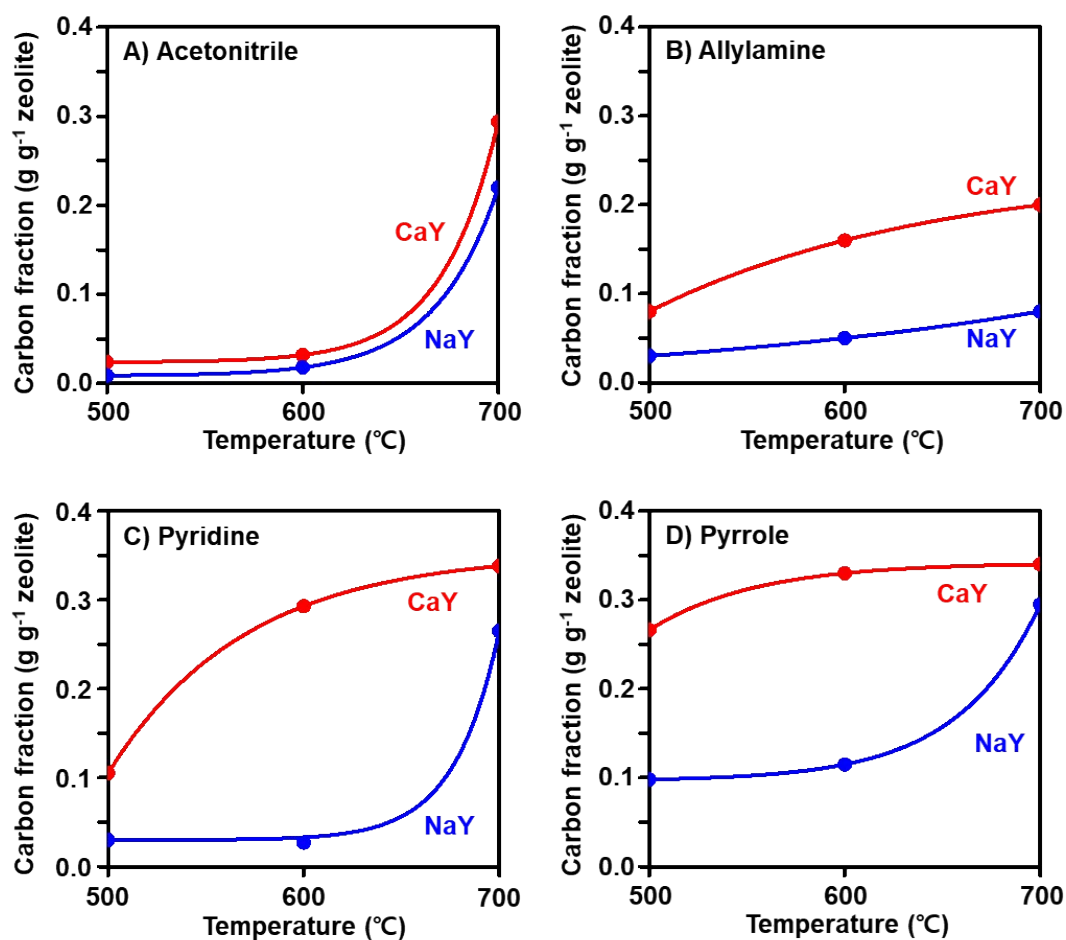


Figure S1. Amount of carbon deposited in Ca²⁺- and Na⁺-exchanged Y zeolite after 1 h of deposition plotted as a function of temperature. The precursors used for the carbonization were A) acetonitrile, B) allylamine, C) pyridine, and D) pyrrole.

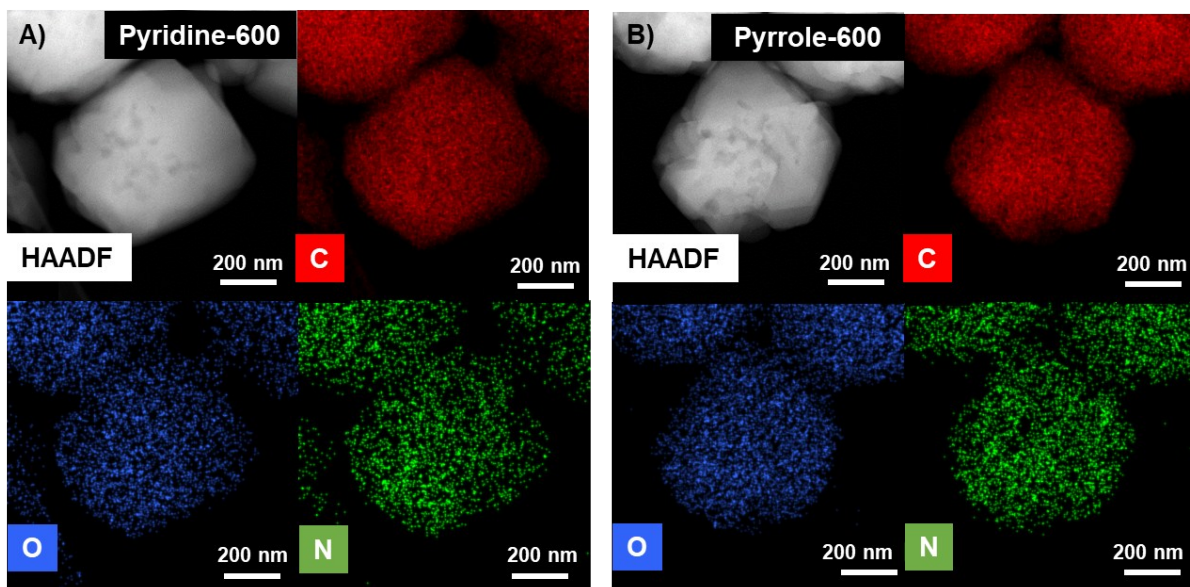


Figure S2. Energy dispersive X-ray spectroscopic mapping of N-ZTCs synthesized 600 °C using A) pyridine and B) pyrrole.

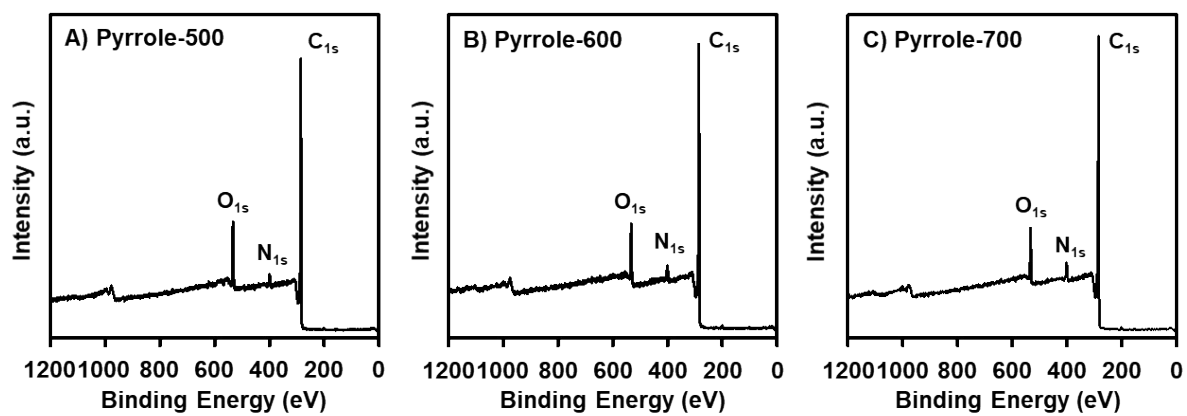


Figure S3. Survey XPS spectra of A) Pyrrole-500, B) Pyrrole-600, and C) Pyrrole-700.

Table S1. Nitrogen content and fraction of each N species of carbon deposits obtained before the framework-curing step

Sample*	N content (wt %)	Fraction (%)			
		Pyridinic N	Pyrrolic N	Graphitic N	N-oxides
Pyridine-600	7.8	56	21	12	11
Pyrrole-500	7.6	25	47	14	14
Pyrrole-600	6.3	33	31	21	15
Pyrrole-700	6.1	33	26	25	16

*Sample name = 'Precursor name-carbon deposition temperature in Celsius'.

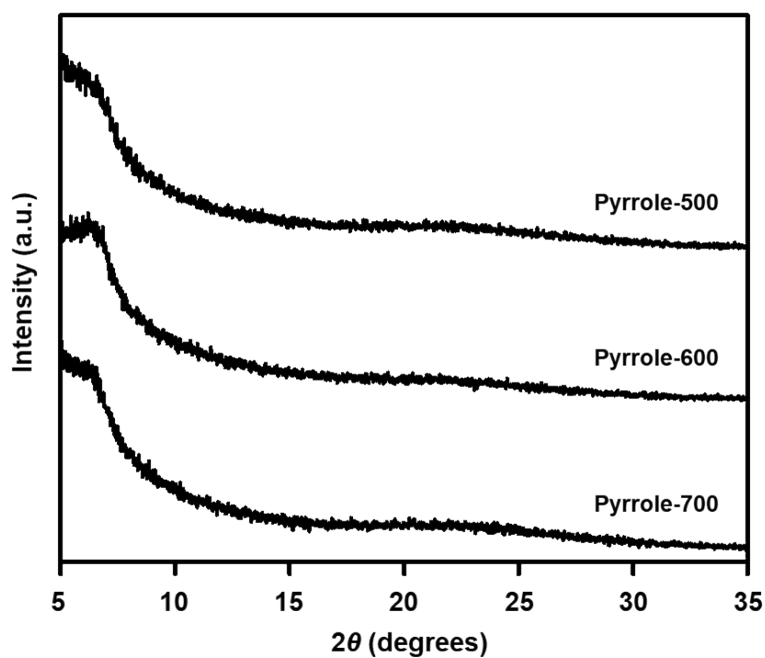


Figure S4. XRD patterns of Pyrrole-500, Pyrrole-600, and Pyrrole-700 samples.

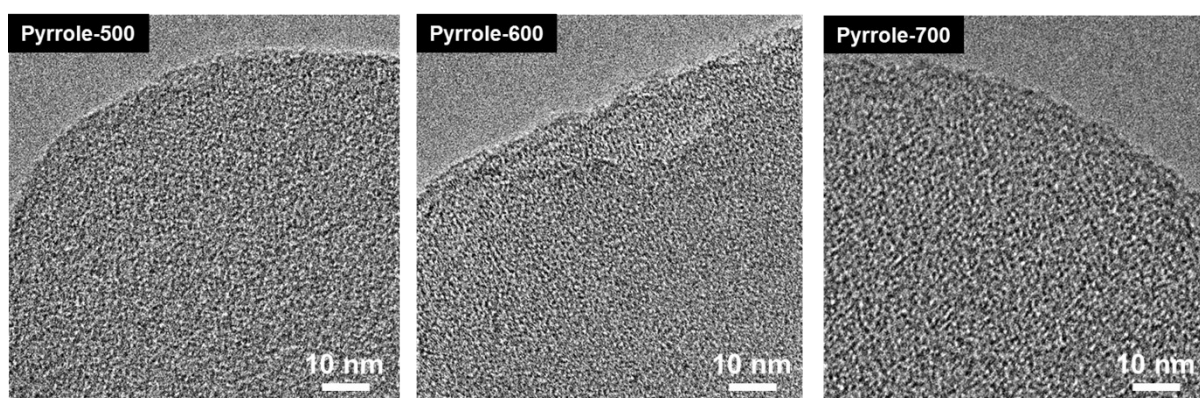


Figure S5. TEM images of Pyrrole-500, Pyrrole-600, and Pyrrole-700 samples.

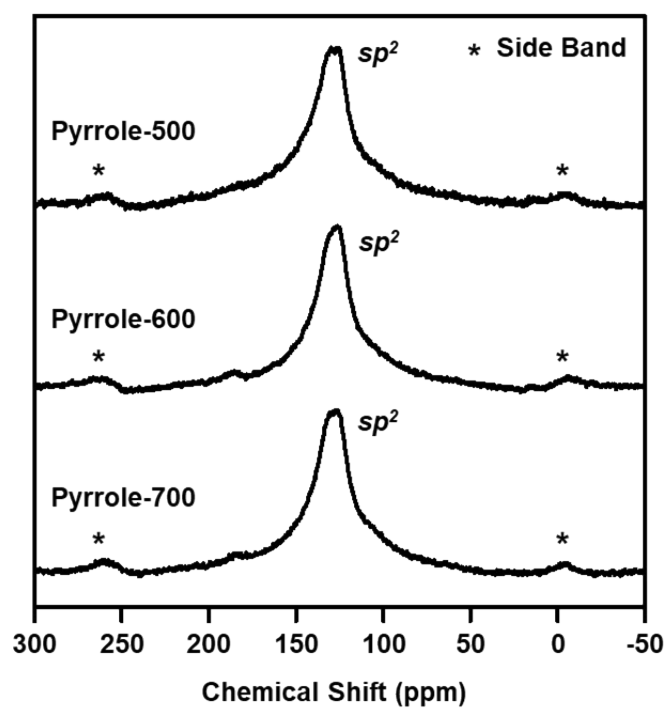


Figure S6. ¹³C solid-state NMR spectra of Pyrrole-500, Pyrrole-600, and Pyrrole-700 samples. The predominant peak over 120-160 ppm signifies the presence of sp²-hybridized carbons. The small peak at 180 ppm represents the presence of oxygen-containing surface functional groups.

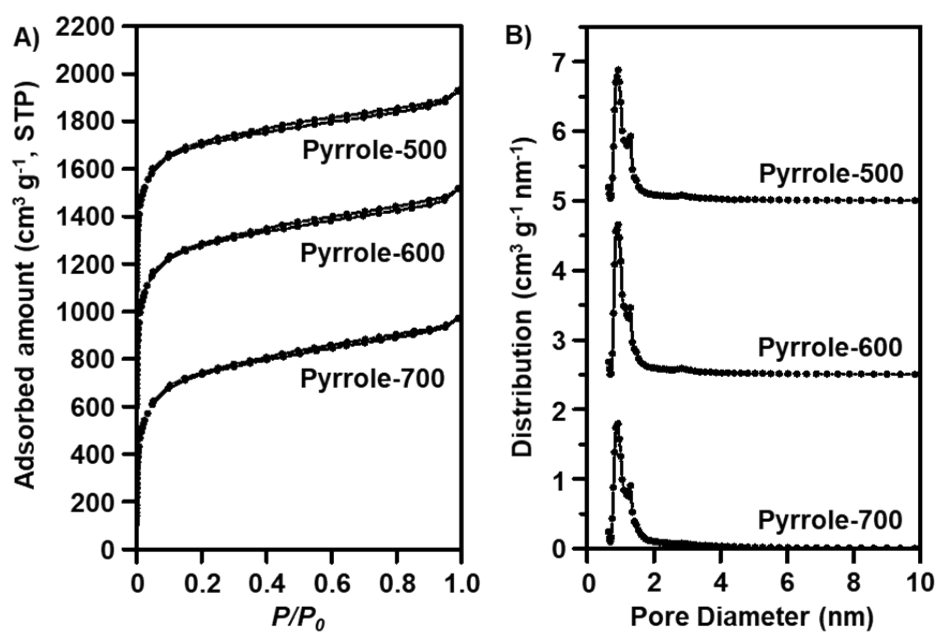


Figure S7. A) Argon adsorption-desorption isotherms and B) pore size distributions of Pyrrole-500, Pyrrole-600, and Pyrrole-700 (Offsets: A) $500 \text{ cm}^3 \text{g}^{-1}$, B) $2.5 \text{ cm}^3 \text{g}^{-1} \text{nm}^{-1}$).

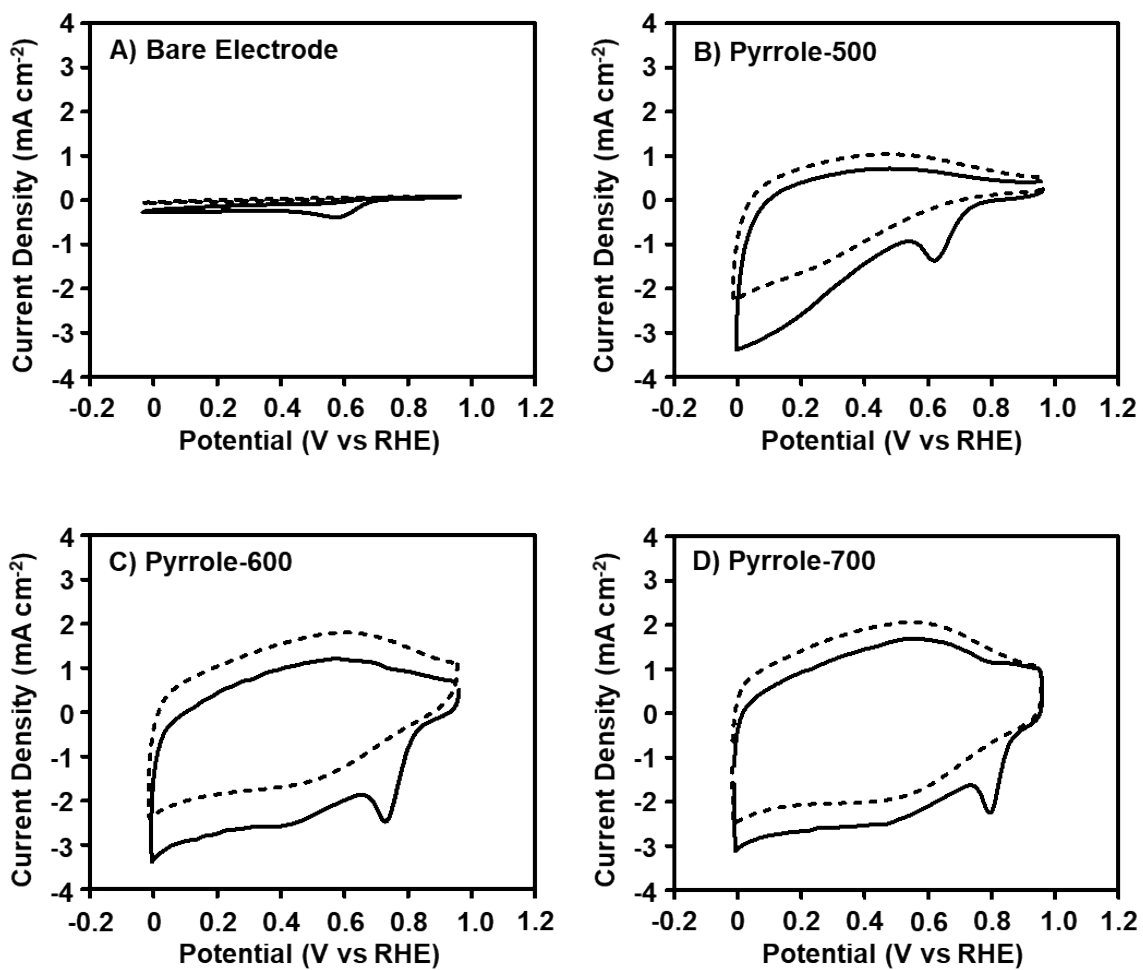


Figure S8. Cyclic voltammetry curves of A) bare electrode, B) Pyrrole-500, C) Pyrrole-600, and D) Pyrrole-700 obtained at a scan rate of 20 mV s^{-1} (dotted line: in N_2 -saturated 0.1 M KOH , solid line: in O_2 -saturated 0.1 M KOH).

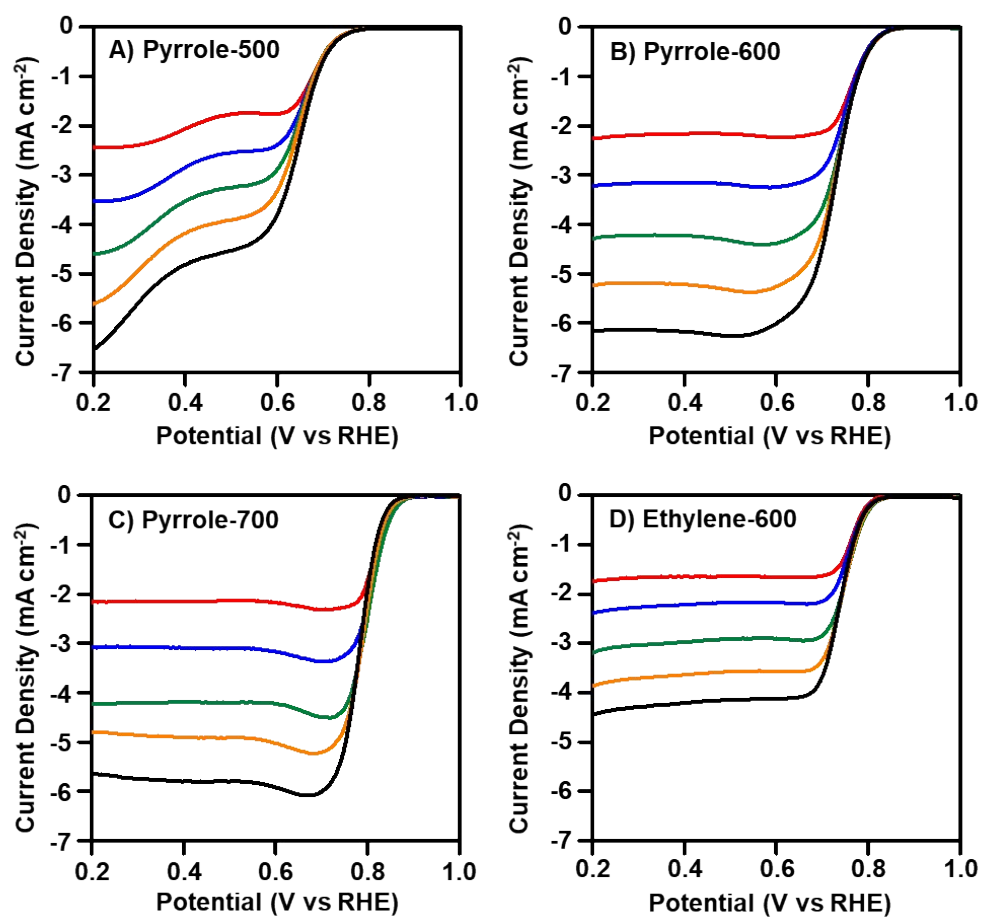


Figure S9. RDE curves of A) Pyrrole-500, B) Pyrrole-600, C) Pyrrole-700, and D) Ethylene-600 obtained at different rotating rates (from top to bottom: 400, 900, 1600, 2500, and 3600 rpm) and a scan rate of 5 mV s⁻¹ in an O₂-saturated 0.1 M KOH.

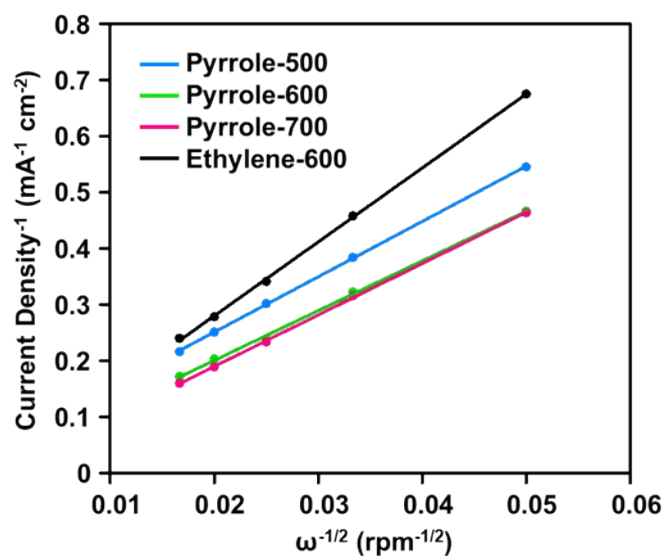


Figure S10. K-L plots determined from the RDE curves of Pyrrole-500, Pyrrole-600, Pyrrole-700 and Ethylene-600 at 0.5 V vs RHE.

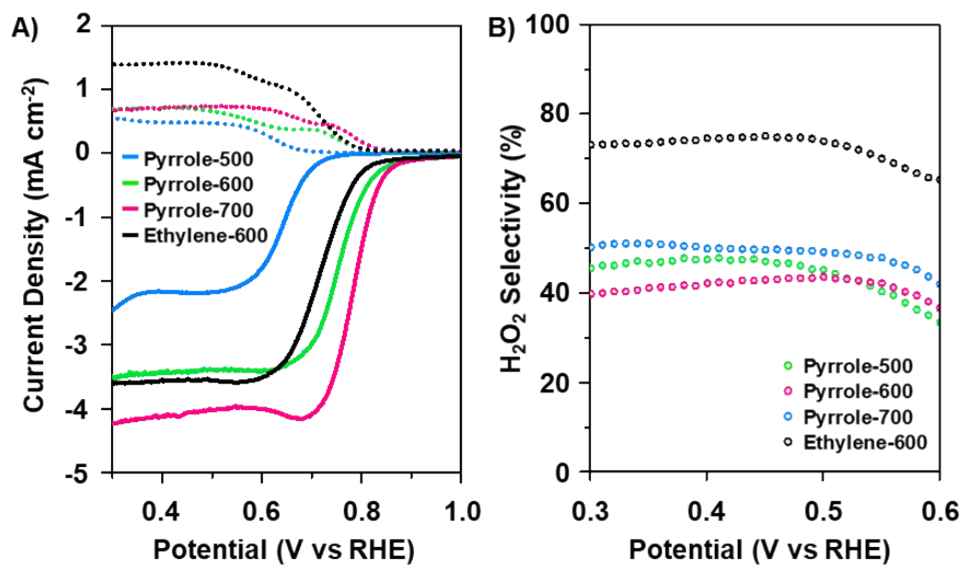


Figure S11. A) LSV curves of Pyrrole-500, Pyrrole-600, Pyrrole-700 and Ethylene-600 for ORR (solid lines) and H₂O₂ production (dotted lines) obtained at 1600 rpm and a scan rate of 5 mV s⁻¹ in an O₂-saturated 0.1 M KOH. The H₂O₂ current was calculated by the correction of the ring current with the collection efficiency of the Pt ring. B) H₂O₂ selectivity determined using the RRDE method.

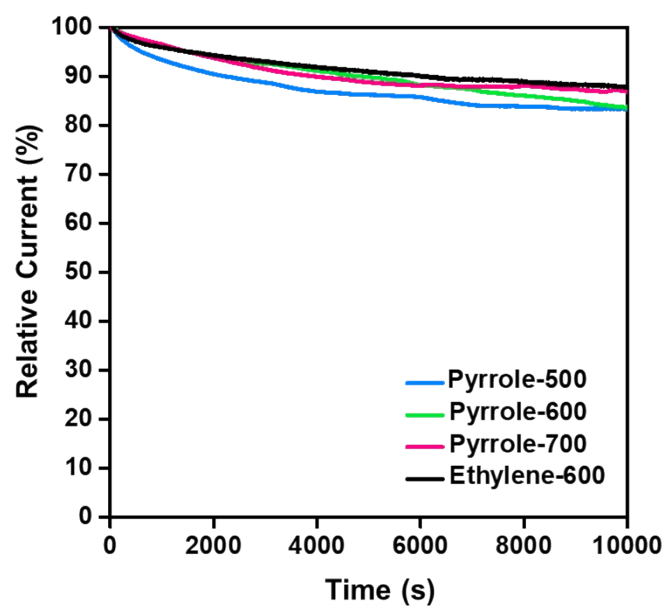


Figure S12. Chronoamperometric responses of Pyrrole-500, Pyrrole-600, Pyrrole-700 and Ethylene-600 measured at the half-wave potential in O_2 saturated 0.1 M KOH for 10000 s.

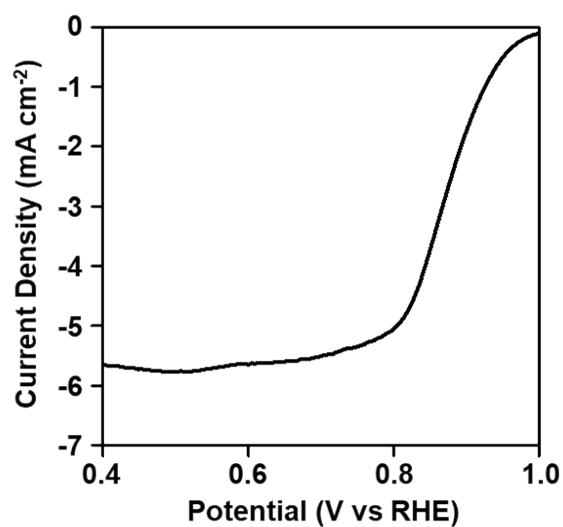


Figure S13. LSV curve of Pt/C benchmark catalyst (20 wt% Pt, purchased from Johnson Matthey) obtained at a scan rate of 5 mV/s.