

Supporting Information

A Rational Synthesis of Hierarchically Hierarchically Porous, N-Doped Carbon from Mg-Based MOFs: Understanding the Link between Nitrogen Content and Oxygen Reduction Electrocatalysis

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Experimental details

Synthesis of HMgNTA and KMgNTA

This synthesis is a modified version of a previously reported one.^[1] All chemicals were purchased from commercial sources and used as received. Nitrilotriacetic acid ($\text{N}(\text{CH}_2\text{COOH})_3$, 22.937 g, 0.120 mol, 99%, Alfa Aesar A11936) was added to 300 mL of de-ionized (DI) water at 85 °C in a 2000 mL beaker, followed by addition of basic magnesium carbonate ($(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2$, 11.657 g, 0.120 mol Mg; 99%, <0.02% Fe, Strem 93-1220), to give a 1:1 molar ratio of nitrilotriacetate (NTA^{3-}) to Mg^{2+} . The solution became clear yellow within 1 minute. Different amounts of potassium carbonate (K_2CO_3 , Alfa Aesar) were added (0 to 6 g) and the pH was measured after cooling to RT. To precipitate the solid reproducibly, 1500 mL ethanol were flowed continuously over 5-6 minutes from a burette, with stirring and without heating. This produced off-white goo, with different degrees of graininess (more with higher pH values). After addition of ethanol, the solution was chilled in an ice bath for 1-2 hours, and the precipitate was collected and vacuum dried at 40 °C for 48 hours. The precipitate was ground by mortar and pestle to a fine white powder. The end cases (as defined by TGA) were recrystallized, and their structure and composition was determined by single crystal X-ray diffraction (see below) to have the formulas of $[\text{MgNH}(\text{CH}_2\text{COO})_3(\text{H}_2\text{O})_3] \cdot \text{CH}_3\text{CH}_2\text{OH}$ (previously identified by elemental analysis)^[1] and $[\text{KMgN}(\text{CH}_2\text{COO})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$.

Carbon synthesis

The precursor salts used were either HMgNTA, a ready-made mixture of HMgNTA with KMgNTA, or commercial magnesium citrate ($\text{Mg}_3(\text{C}_6\text{O}_7\text{H}_5)_2 \cdot 9\text{H}_2\text{O}$, sc-215279A, Santa Cruz Biotechnology, USA). 20-25 g of the salt were transferred into a quartz boat, and loaded into a quartz tube. The tube was loaded into a tube furnace inside a fume hood, and heated to 900 °C at 10 °C/min, held at 900 °C for 1 hr, and let cool naturally. **CAUTION: pyrolysis wastes pose an environmental hazard, and must be collected by scrubber water.** Argon gas (99.999%) was flowed through the tube at a flow rate of 100 sccm for 90 mins before heating started, and continuously during pyrolysis. Note that turning off argon flow prematurely (when the temperature is still high) may suck up water from the scrubber into the carbon, and convert the MgO into $\text{Mg}(\text{OH})_2$. The carbons were removed from the tube and added directly into 500 mL of 0.5 citric acid. **CAUTION: the K-containing carbons produce a KC_8 bronze that coats the quartz walls and tube; upon contact with air, this bronze heats rapidly and may ignite and consume the carbon powder. Therefore, the powders are transferred into the acid immediately upon opening the tube, directly with the boats, to neutralize the bronze in solution.** The quartz boats and tubes are therefore not reusable.

Each carbon was stirred in the acid for over 10 hours, and then vacuum filtered, washed by 5 L of DI water, and dried for several hours at 120 °C. Then each carbon was loaded again into a tube furnace and heated to 1000 °C at 5 °C/min, held for 1 hr, and let cool naturally. The total yield of each process is 5-15% (lower with higher KMgNTA fraction). All carbons were black and fine.

Characterization procedures

Gas adsorption isotherms were measured on a Thermo Scientific Surfer instrument using N_2 at 77 K. The samples were dried in a vacuum ($1 \cdot 10^{-3}$ mbar) for 3 h at 200 °C prior to the measurement. Helium density was measured on a Micromeritics multi volume pycnometer 1305. Data were analyzed by the ThermoFischer Advanced Data Processing 6.0 software. Specific surface areas and micropore volumes were calculated using the BET2 and the Dubinin-Radushkevitch methods, respectively.

The microstructure of the powders was examined by TEM on a Tecnai Osiris Microscope at an accelerating voltage of 200 kV. Raman spectroscopy was performed on a Thermo Nicolet Almega XR confocal Raman microscope, at a 532 nm laser wavelength (University of Alberta).

X-Ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany). Analysis was performed using a monochromatic Al K α X-ray source of 24.8 W power with a beam size of 100 μm . The spherical capacitor analyser was set at 45° take-off angle with respect to the sample surface. The pass energy was 46.95 eV yielding a full width at half maximum of 0.91 eV for the Ag 3d 5/2 peak. Peaks were calibrated using the C1s position. Integration was performed and adjusted to remove the occasionally occurring Si 2p peaks (< 3%), arising from visible quartz pieces that broke off the tube. Curve fitting was performed using the XPSPeak 4.1 freeware. In the assignment of nitrogen functionalities, we avoided using pyrrolic functionalities, because they are known to decompose at temperatures above 800 °C to either pyridinic or graphitic nitrogens.^[2]

The KMgNTA single crystal structure was determined on a Rigaku R-Axis RAPID II diffractometer using graphite monochromated Mo-K α radiation. A colorless plate crystal having approximate dimensions of 0.400 x 0.150 x 0.100 mm was mounted on a glass fiber. The crystal-to-detector distance was 127.40 mm. The HMgNTA single crystal structure was based on crystallographic data collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab. Samples were mounted on MiTeGen kapton loops and placed on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON100 CMOS detector operating in shutterless mode. The samples were in a 100 K nitrogen cold stream provided by an Oxford Cryostream 800 Plus low temperature apparatus. Diffraction data were collected using synchrotron radiation monochromated by using silicon(111) to a wavelength of 0.7749 (1) Å. The structure was solved by intrinsic phasing (SHELXT) and refined by full-matrix least-squares on F2 (SHELXL-2014). Crystallographic data are registered at the Cambridge Structural Data Base as CCDC-1470252 (HMgNTA) and CCDC-1470491 (KMgNTA).

Electrochemical procedures

Catalytic powders used included home-made N-doped carbons C0, C22, C42, C68, C91 and C_{MgCit} (derived from Mg citrate pyrolysis), as well as commercial Pt/C (20% wt Pt on Vulcan XC 72, fuel cell grade, Premetek, USA). Inks of the catalytic powders were prepared according to the following proportions: 0.80 mL DI water, 0.20 mL ethanol, 10 μL Nafion® (D-521 dispersion 5%wt in water/isopropanol, Alfa Aesar 42117), and 1.0 mg powder. The inks were sonicated and stirred overnight. The working electrode substrate was a $\phi = 5$ mm ($A = 0.196$ cm²) glassy carbon electrode (Gamry, USA), which was polished by diamond polishing films with 1 and 0.1 μm particles (Allied High Tech Products, USA), and rinsed well. Inks were deposited by dropcasting 10 μL portions x 3, with air drying at 50°C between the drops. The total catalyst loading was 30 μg , or 153 $\mu\text{g}/\text{cm}^2$.

Electrochemical experiments were performed in a 3-electrode home-made glass cell, filled with KOH (0.1 M, 150 mL), stabilized at 25.0 ± 0.1 °C in a water bath. A Gamry Reference 600 potentiostat was employed, together with a Gamry RDE710 Rotating Electrode setup. Saturated calomel electrode (SCE, Gamry, USA) separated from the solution by a 10 cm bridge was used as a reference electrode, and a graphite rod (Gamry, USA) as a counter electrode. Potentials were reported vs. reversible hydrogen electrode (RHE) by adding 1.011 for pH 13. Nitrogen (99.999%) or oxygen (99.999%) were bubbled for 30 minutes to saturate the solution, and were flowed above the solution ('gas blanket') during the experiments. Linear scan voltammograms were measured from 1.01 to 0.31 V vs. RHE with a scan rate of 10 mV/s at rotating speeds of

2400, 2000, 1600, 1200, 900, 600 and 400 rpm. Reported current densities represent Faradaic currents, after subtraction of capacitive charging background current. Cyclic voltammetry was measured with the same parameters but without rotation. At the beginning of each measurement set, the solution resistance was measured (typically 44–48 Ohm in base, 4-6 Ohm in acid). A positive feedback automatic iR correction of 95% was used in the alkaline solutions only in voltammetric and chronoamperometric measurements. Before measurements, surface adsorbed oxygen was reduced and the wetting was improved by cycling the electrode between +0.2 and –0.2 V vs. SCE for 50 cycles (200 mV/s) and 5 cycles (20 mV/s). Electrochemical impedance spectroscopy was measured potentiostatically at ± 5 mV around the half-wave potential of each carbon, while bubbling oxygen and rotating at 1600 rpm. The EIS frequency range was 0.2 Hz to 10^6 Hz.

Koutecký-Levich analysis

Number of electrons transferred per mol O₂ was estimated by the Koutecký-Levich equation:

$$\frac{1}{J} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

Where J is the measured current density (mA/cm²), J_K the kinetic (exchange) current density (mA/cm²), ω is the RDE rotation rate (rpm), and B is given by:

$$B = 0.2nFC_O D_O^{2/3} \nu^{-1/6}$$

Where 0.2 is the arithmetic correction factor for ω in rpm, n is the number of electrons transferred per mol, F is Faraday's constant (96,485 C/mol), C_O is the concentration of dissolved O₂ (1.2 mM at 25 °C in 0.1 M KOH), D_O is the diffusion coefficient of O₂ ($1.9 \cdot 10^{-5}$ cm²/s at 25 °C in 0.1 M KOH), and ν is the kinematic viscosity of the 0.1 M KOH electrolyte at 25 °C (0.01 m²/s). By plotting $1/J$ versus $1/\omega^{1/2}$ at different potentials and fitting linear equations to the data, the number of electrons could be calculated from the slope ($1/B$).

Additional Tables and Figures

Table S1. Compositional and structural data for the carbon series.

	HMgNTA: KMgNTA fractions	XPS (total at%)						N ₂ adsorption at 77K		Raman I _D /I _G ratio
		C1s	N1s	O1s	N-pyr	N-graph	N-oxy	BET2 SSA (m ² /g)	Micropore volume (cm ³ /gr)	
C0	100:0	91.58	5.70	2.70	1.90	2.93	0.87	1831	0.601	0.94
C22	78:22	94.09	3.75	2.16	1.16	2.09	0.49	1809	0.664	1.00
C42	58:42	92.58	3.42	3.95	1.20	1.88	0.33	1101	0.444	0.93
C68	32:68	93.57	1.34	5.09	0.28	0.96	0.10	1508	0.597	0.98
C91	9:91	90.28	1.29	8.44	0.21	0.90	0.18	1250	0.420	0.93
C _{undoped}	-	-	-	-	-	-	-	1845	0.648	-

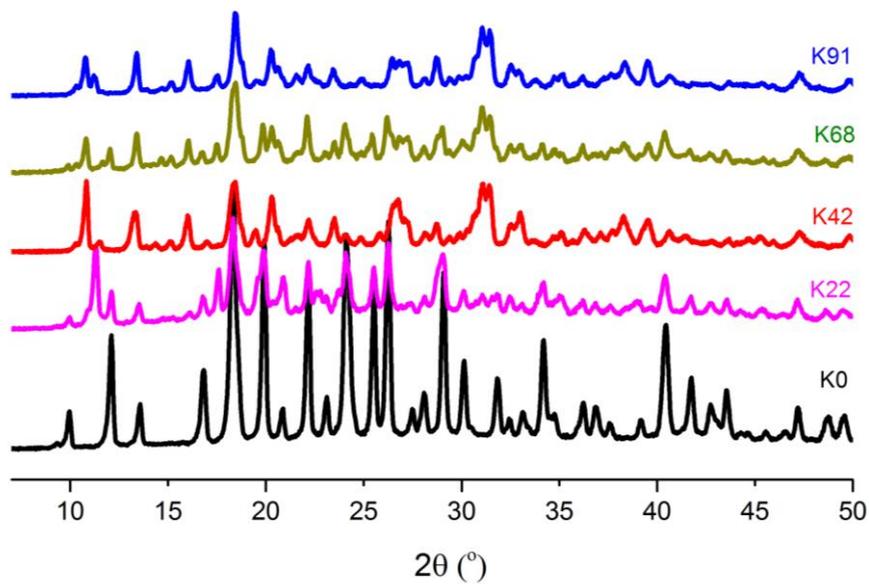


Figure S1. X-ray diffraction patterns of the precursor series.

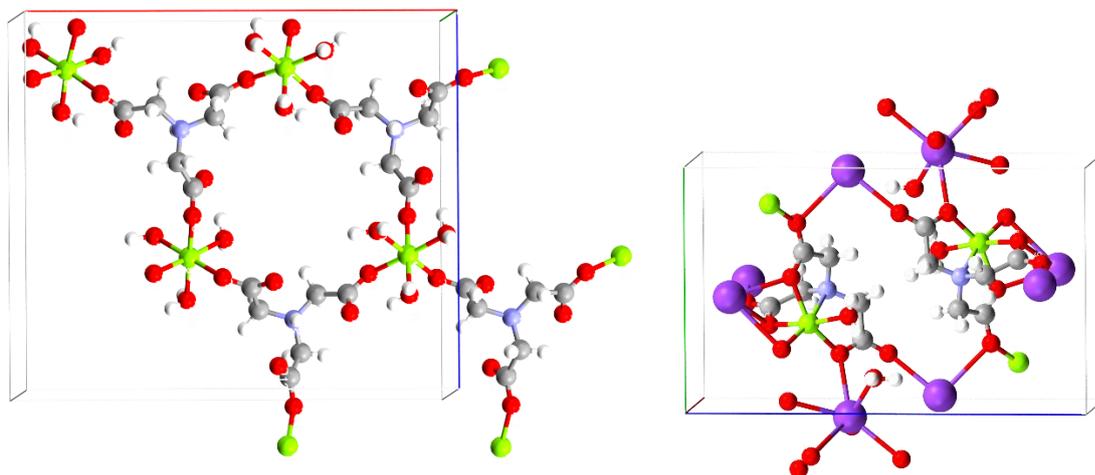


Figure S2. Unit cells of HMgNTA (left) and KMgNTA (right). Lattice solvent molecules were removed for clarity.

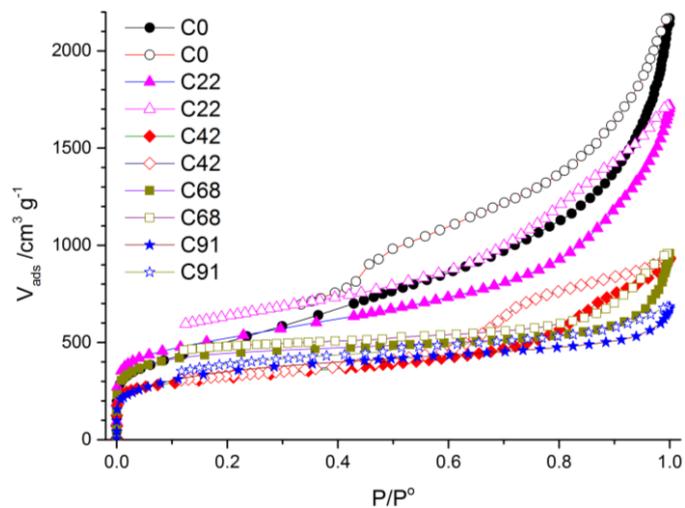


Figure S3. N_2 adsorption isotherms at 77K along the carbon series. All the samples show a sharp initial rise corresponding to micropore sorption, and a final rise corresponding to mesopore condensation.

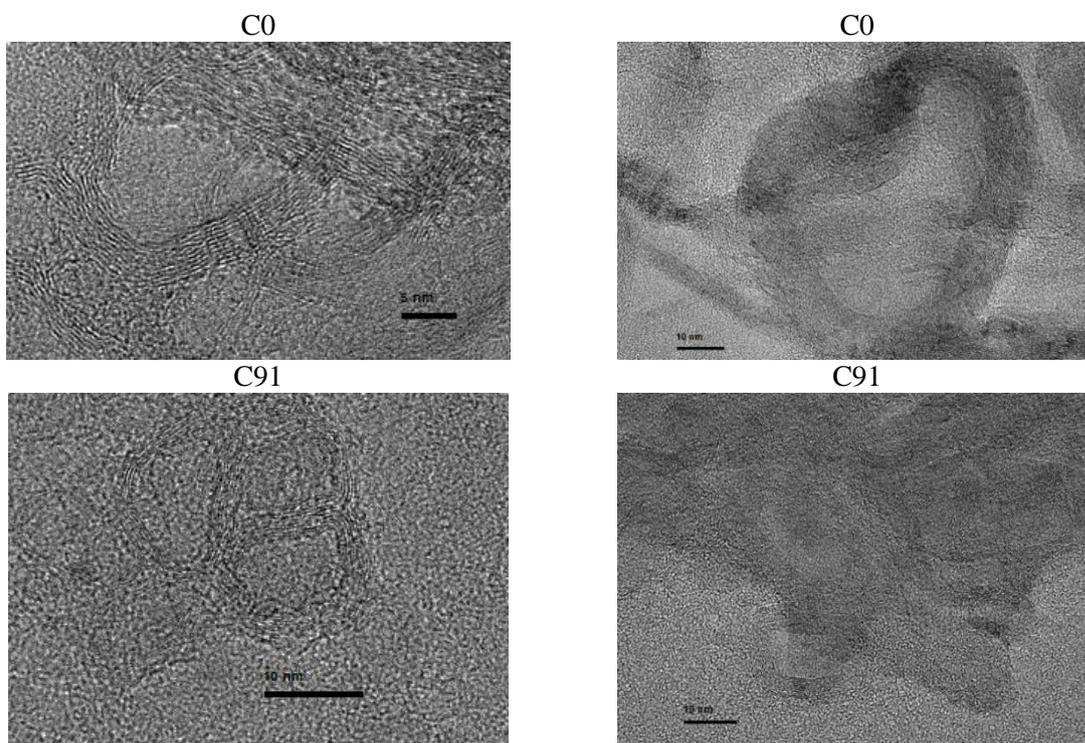


Figure S4. Transmission electron micrographs of the end-case carbons.

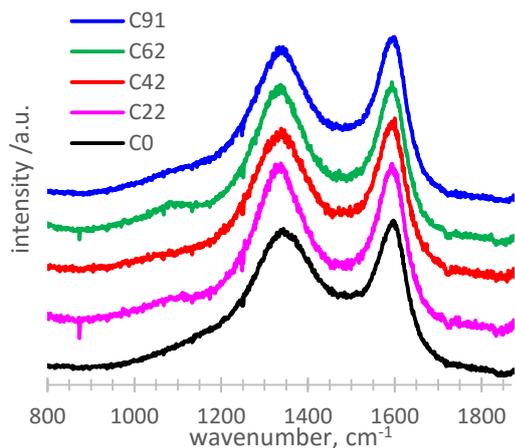


Figure S5. Raman spectra along the carbon series.

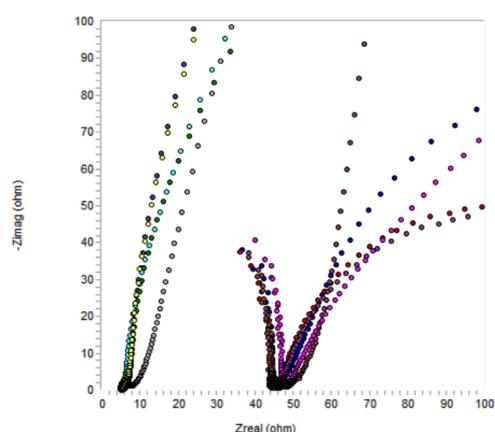


Figure S6. Electrochemical impedance spectroscopy in H_2SO_4 0.5 M (left group) and in KOH 0.1 M (right group) measured around the half-wave potential in O_2 -saturated solutions. The semicircles' intersection with the x axis correlates with the equivalent serial resistance of the system, including the resistance of the electrocatalyst layer. In both cases, the values span about 4 Ohms, suggesting that the catalyst layers have similar conductivities.

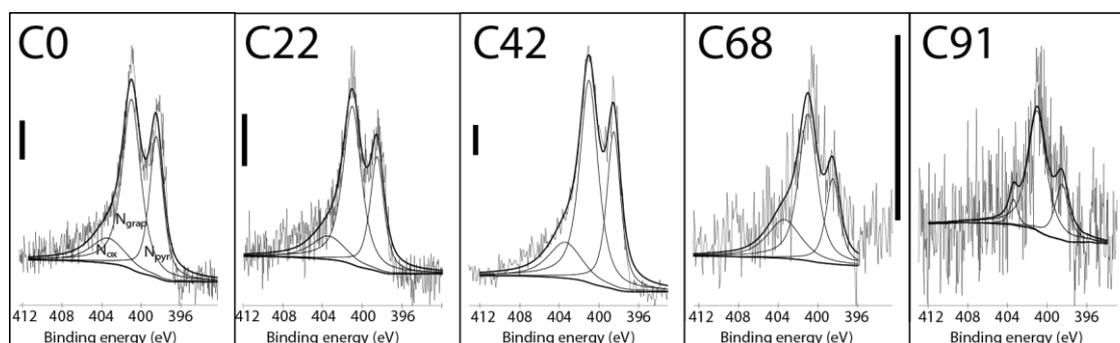


Figure S7. X-ray photoelectron spectra in the N-1s region, along the carbon series, fitted with pyridinic (398.5 ± 0.84 eV), graphitic (401.0 ± 1.1 eV) and oxidized (403.4 ± 2.0 eV) nitrogen peaks. The vertical scalebars corresponds to 50 counts per second.

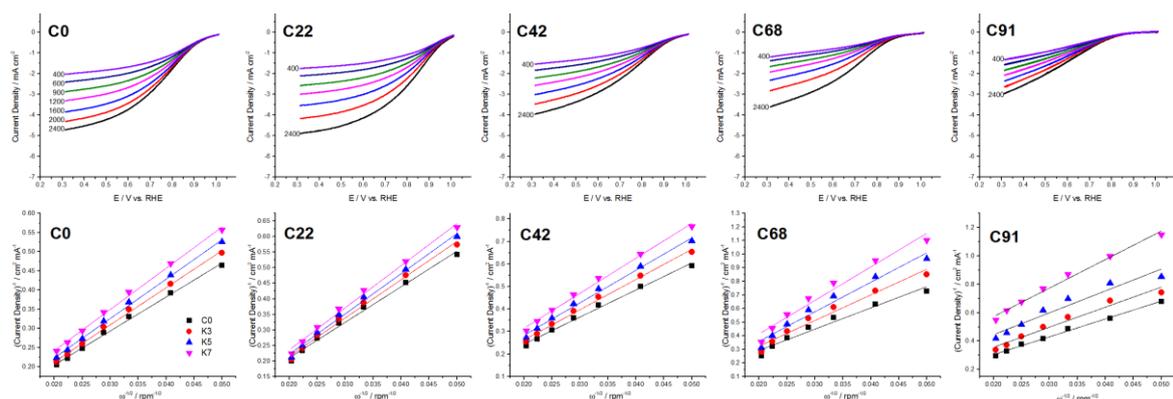


Figure S8. Rotating disk electrode (RDE) studies of ORR electrocatalysis in 0.5 M H₂SO₄ along the carbon series. *Top row:* LSVs at different rotation speeds, in rpm. *Bottom row:* Koutecký-Levich plots

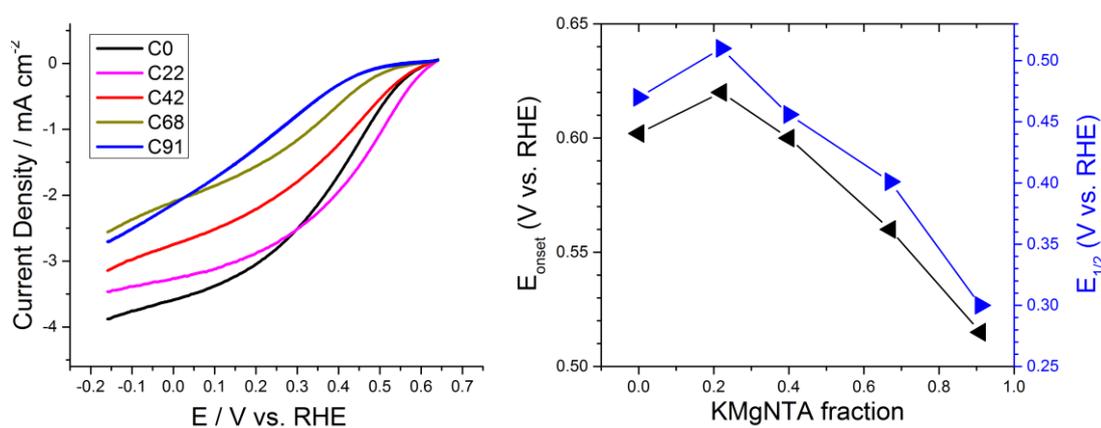


Figure S9. Oxygen reduction activity in acid (0.5 M H₂SO₄, pH 0). (a) Linear scan voltammetry, 10 mV/s, 1600 rpm, O₂-saturated solution. (b) Onset and half-wave potentials for ORR along the carbon series.

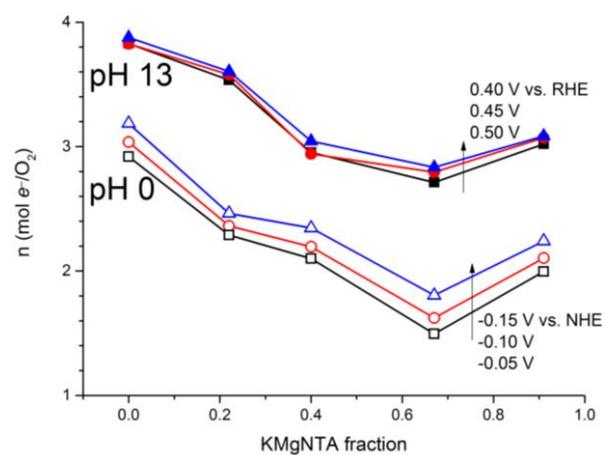


Figure S10. Number of electrons transferred per mol O₂ along the carbon series. Calculated from the Koutecký-Levich plots, in 0.1 M KOH (pH 13), and 0.5 M H₂SO₄ (pH 0).

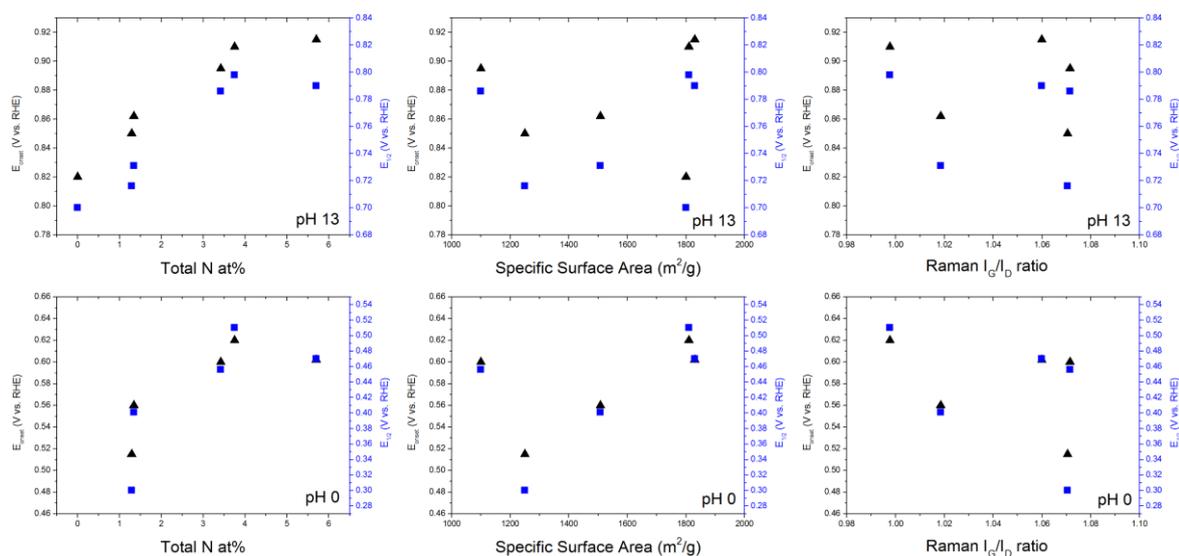


Figure S11. Possible structure-activity correlations for ORR along the carbon series. ORR activity measures include onset potential (black triangles, left axis) and halfwave potential (blue squares, right axis); structural and compositional parameters include total N at% (from XPS), specific surface area (from N₂ adsorption at 77K) and the Raman I_G/I_D peak ratio. *Top row:* in 0.1 M KOH. *Bottom row:* in 0.5 M H₂SO₄.

References

- [1] D. Eisenberg, W. Stroek, N. J. Geels, C. S. Sandu, A. Heller, N. Yan, G. Rothenberg, *Chem. - Eur. J.* **2016**, 22, 501–505.
- [2] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* **1995**, 33, 1641–1653.