Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Heat-treated carbon supported Fe(II) phthalocyanine ORR catalysts: elucidation of structure activity relationship using XAS

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Supporting Information:

A. Cyclic voltammetry figures (CV)

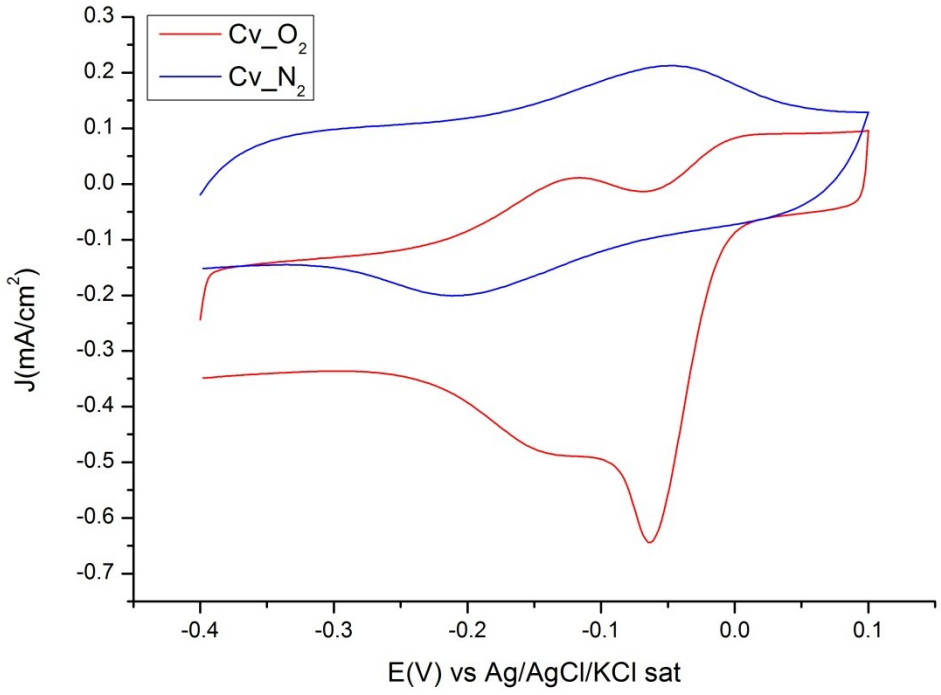


Fig. S1 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C(400). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

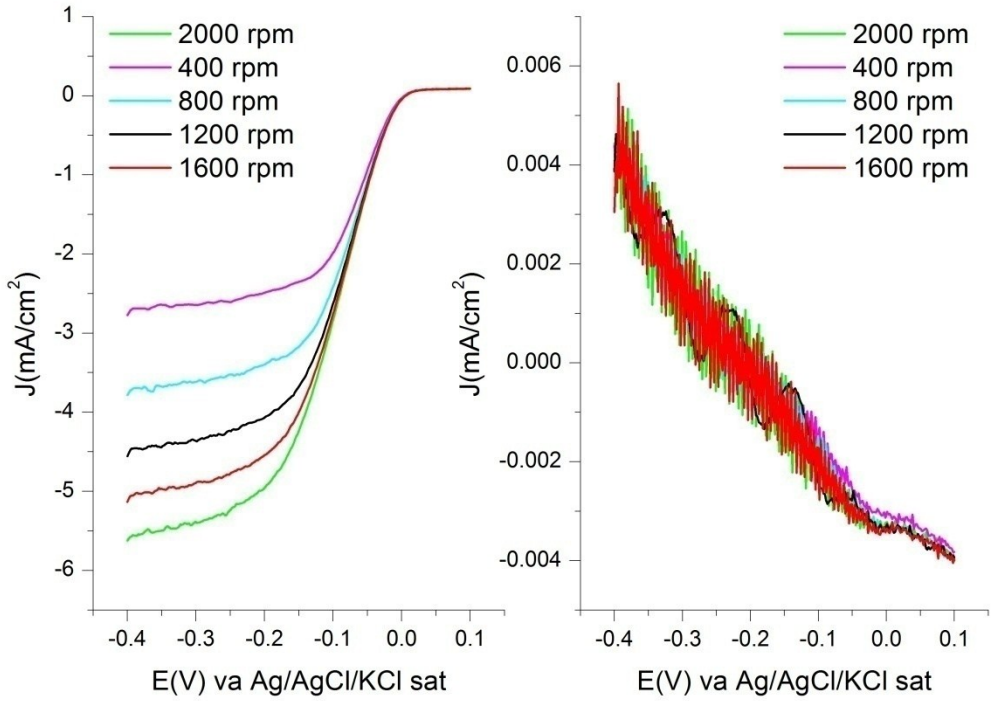


Fig. S2 CVs of FePc/C(400) using RRDE at different rotation speeds left (disk) and right (ring).

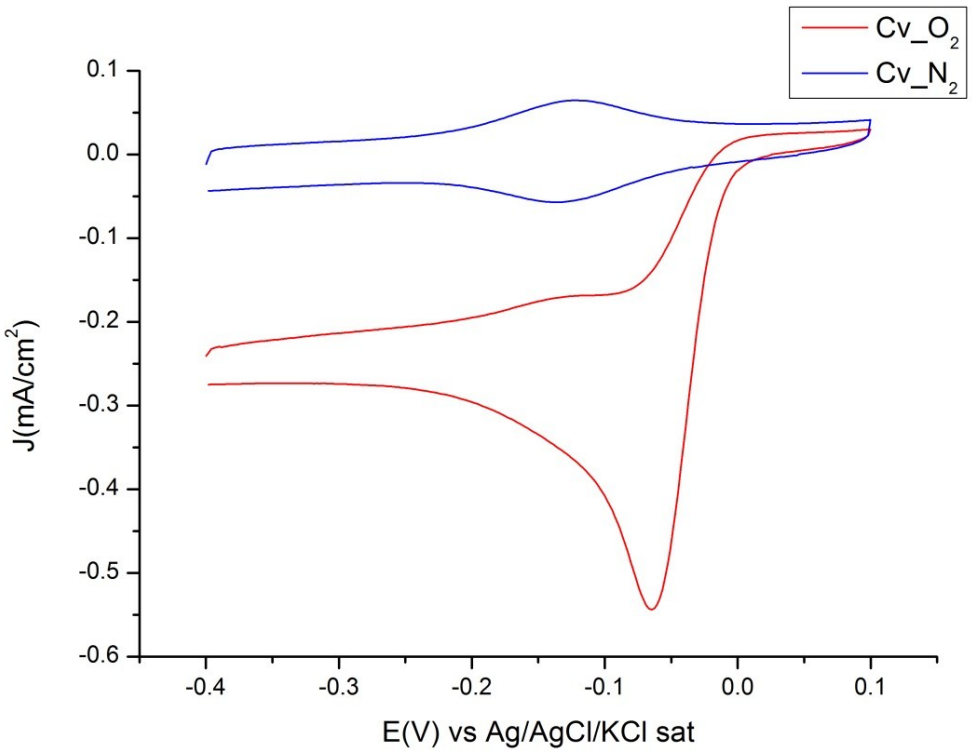


Fig. S3 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C(500). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

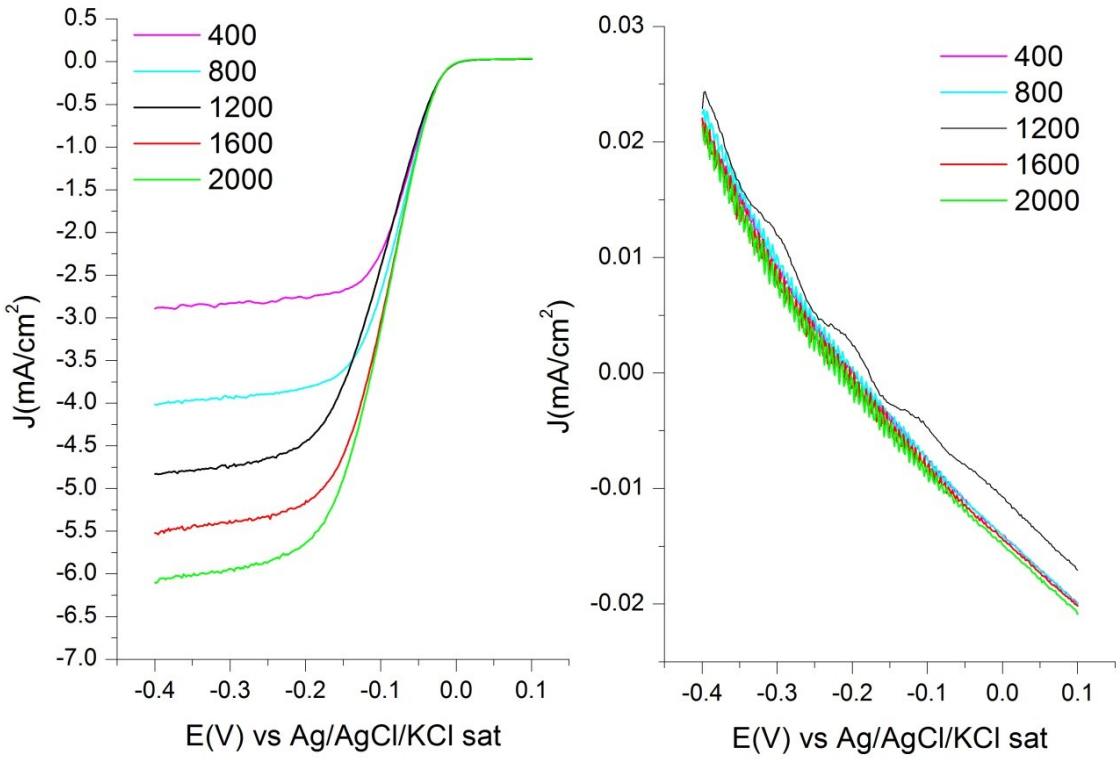


Fig. S4 CVs of FePc/C(500) using RRDE at different rotation speeds left (disk) and right (ring).

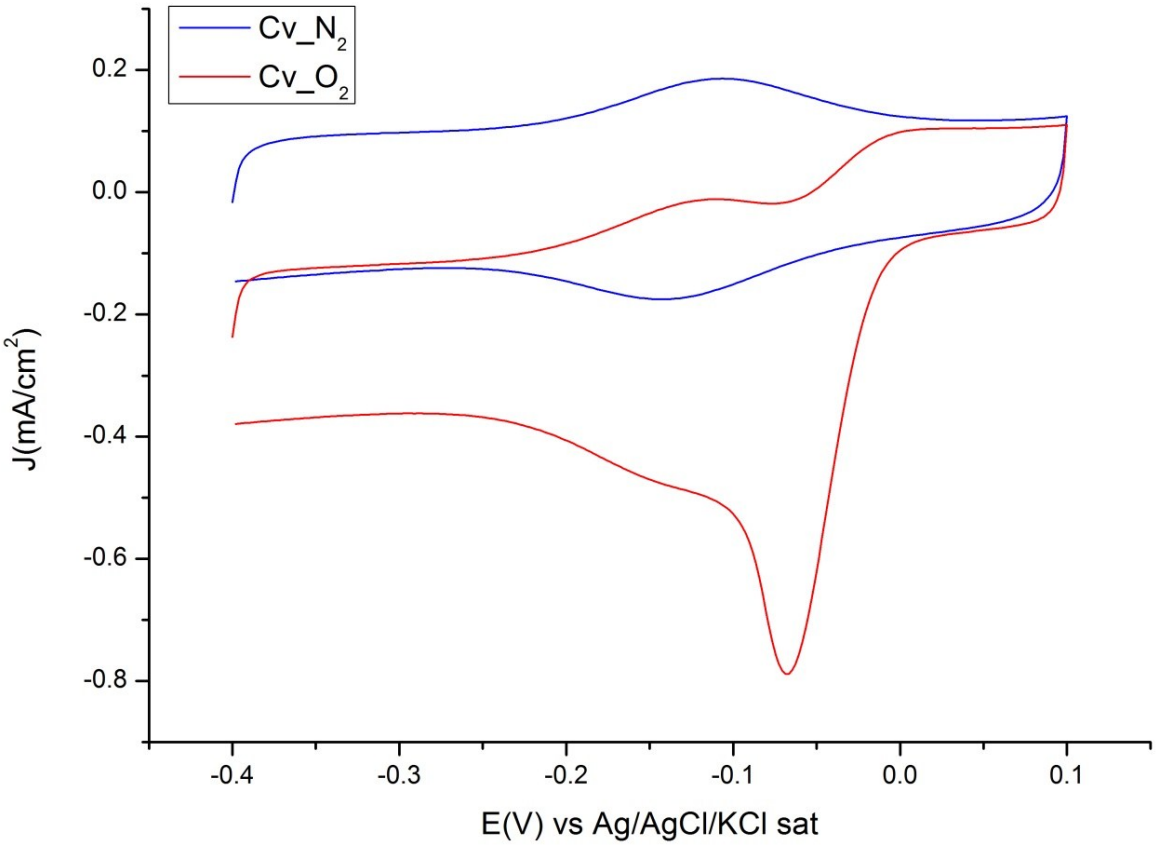


Fig. S5 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C(600). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

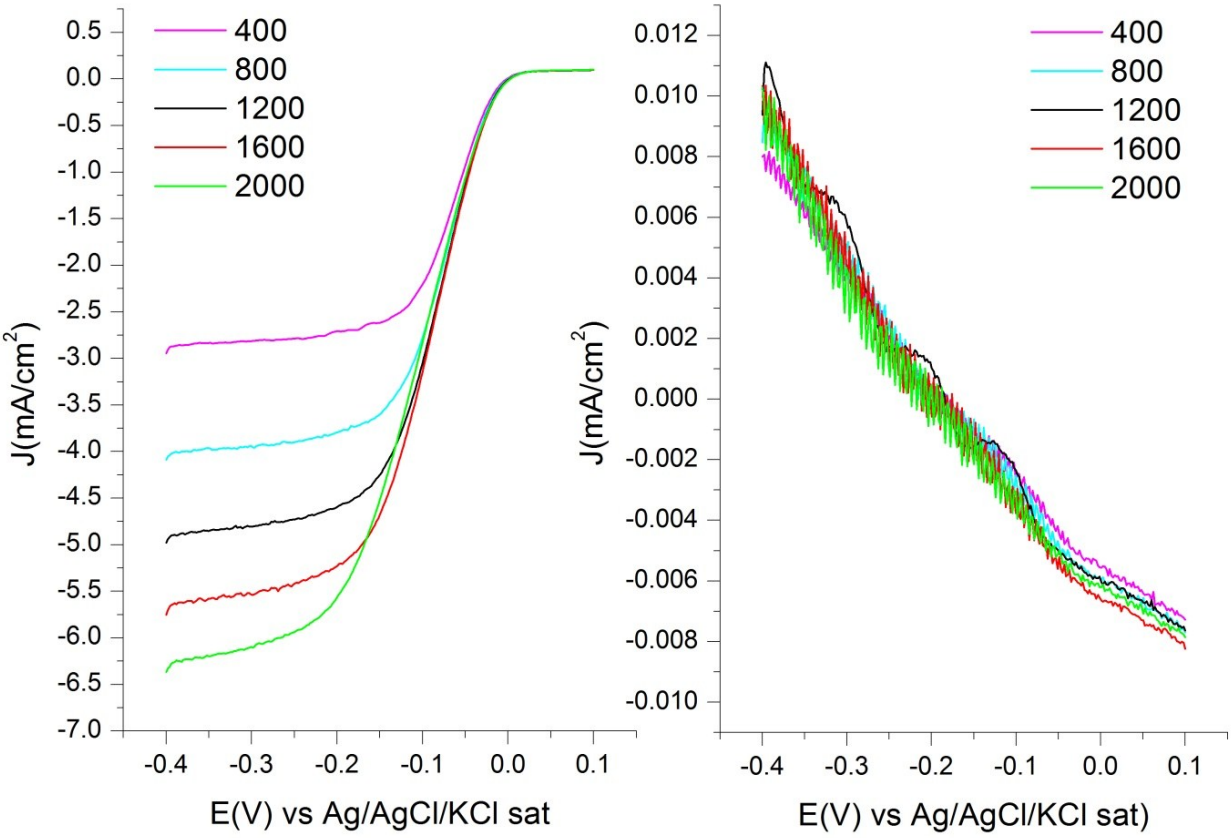


Fig. S6 CVs of FePc/C(600) using RRDE at different rotation speeds left (disk) and right (ring).

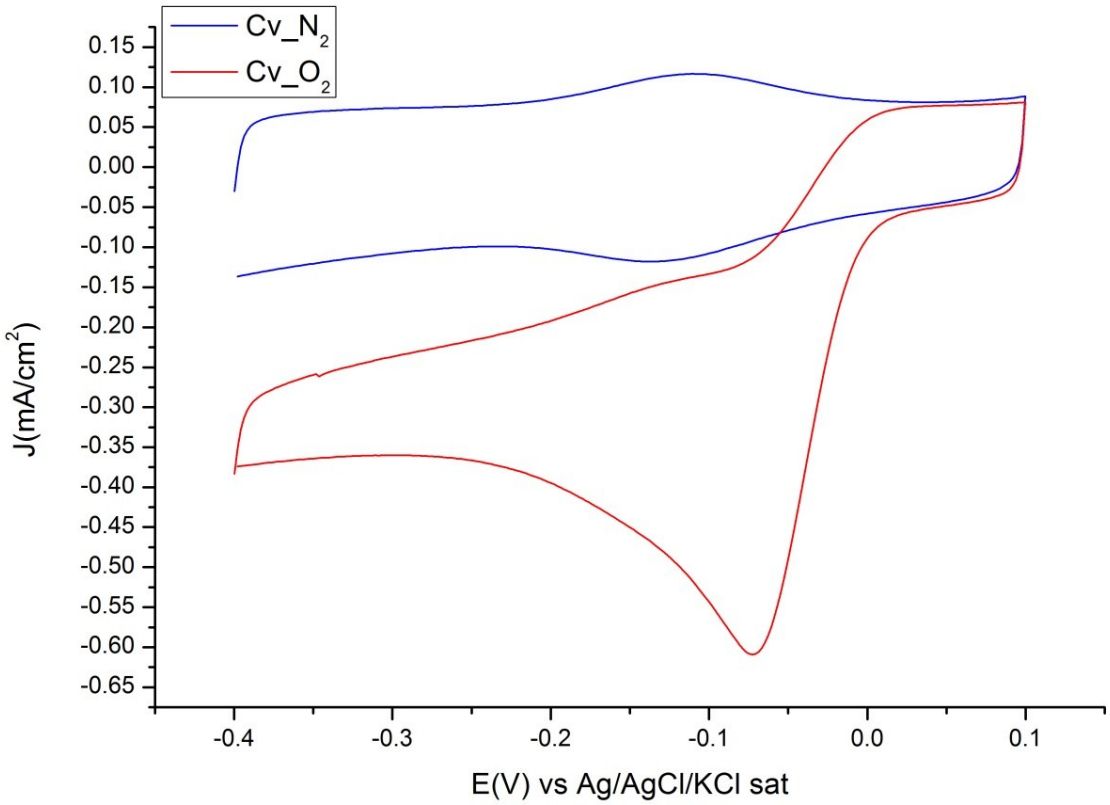


Fig. S7 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C (700). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

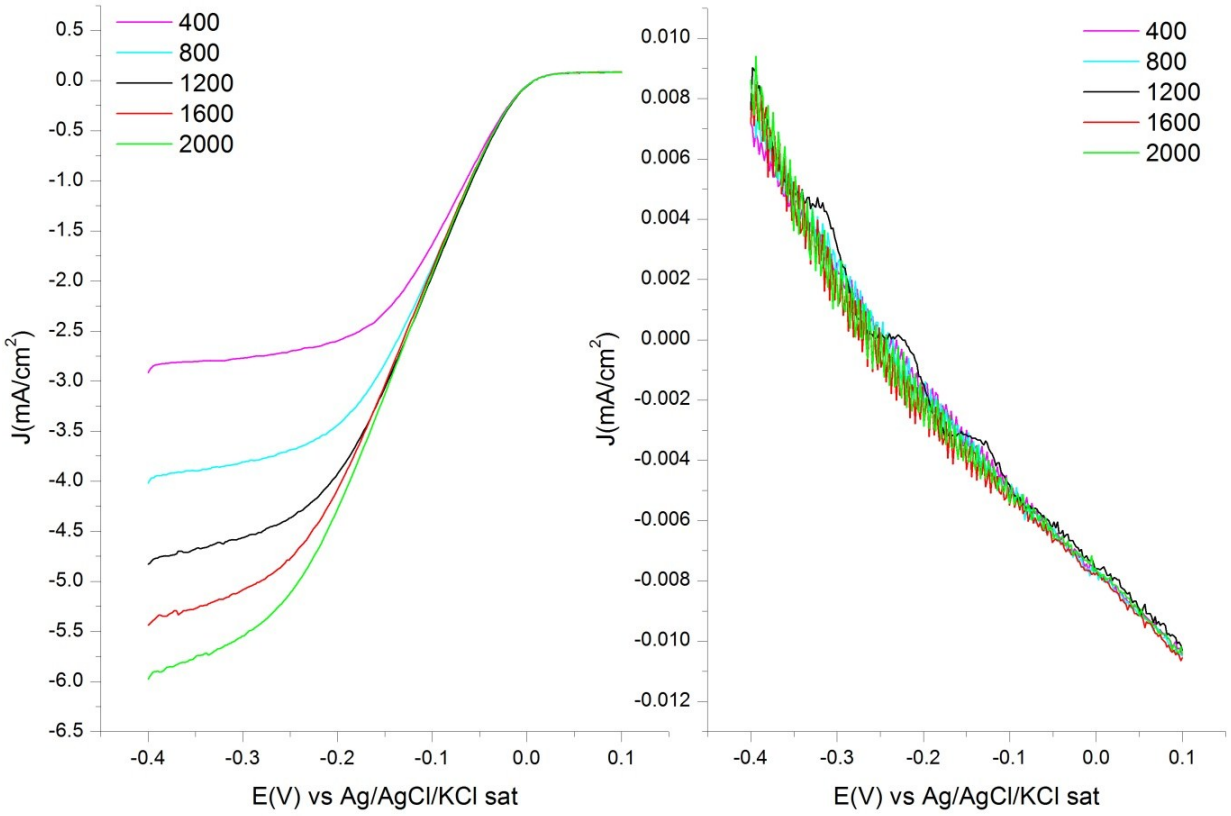


Fig. S8 CVs of FePc/C (700) using RRDE at different rotation speeds left (disk) and right (ring).

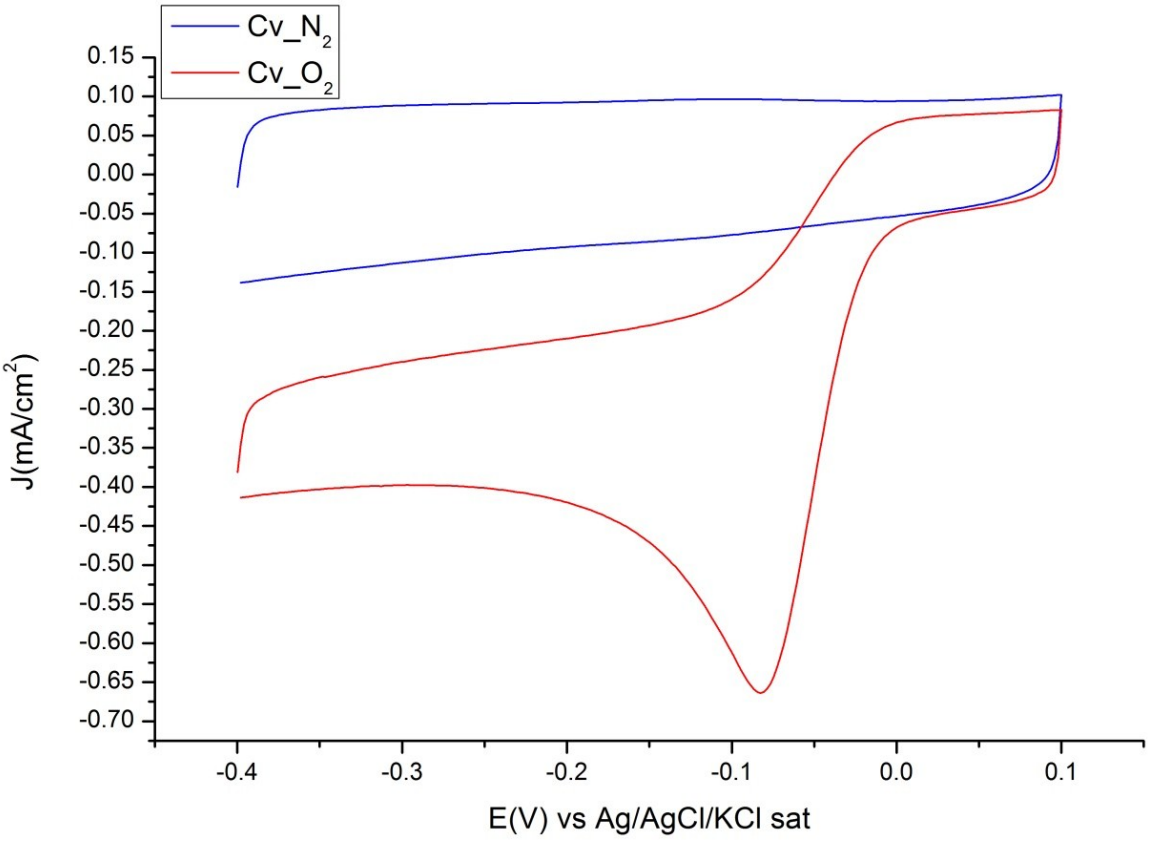


Fig. S9 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C (800). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

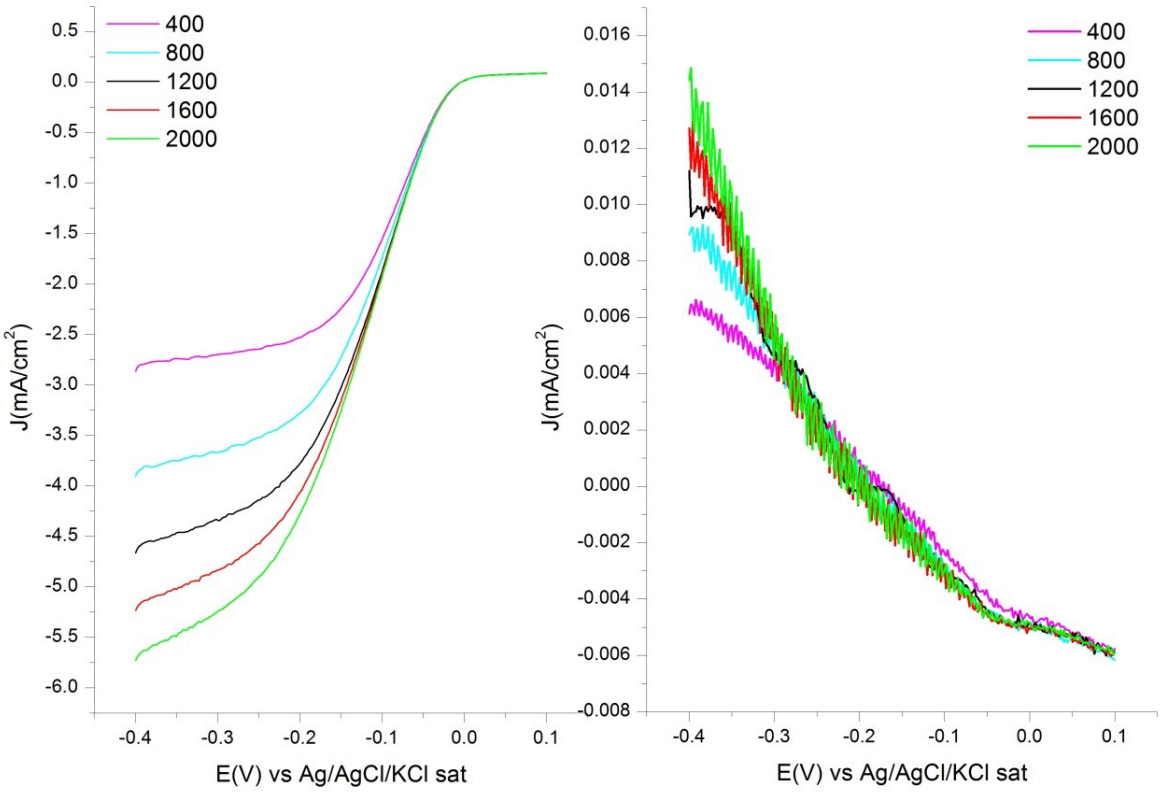


Fig. S10 CVs of FePc/C(800) using RRDE at different rotation speeds left (disk) and right (ring).

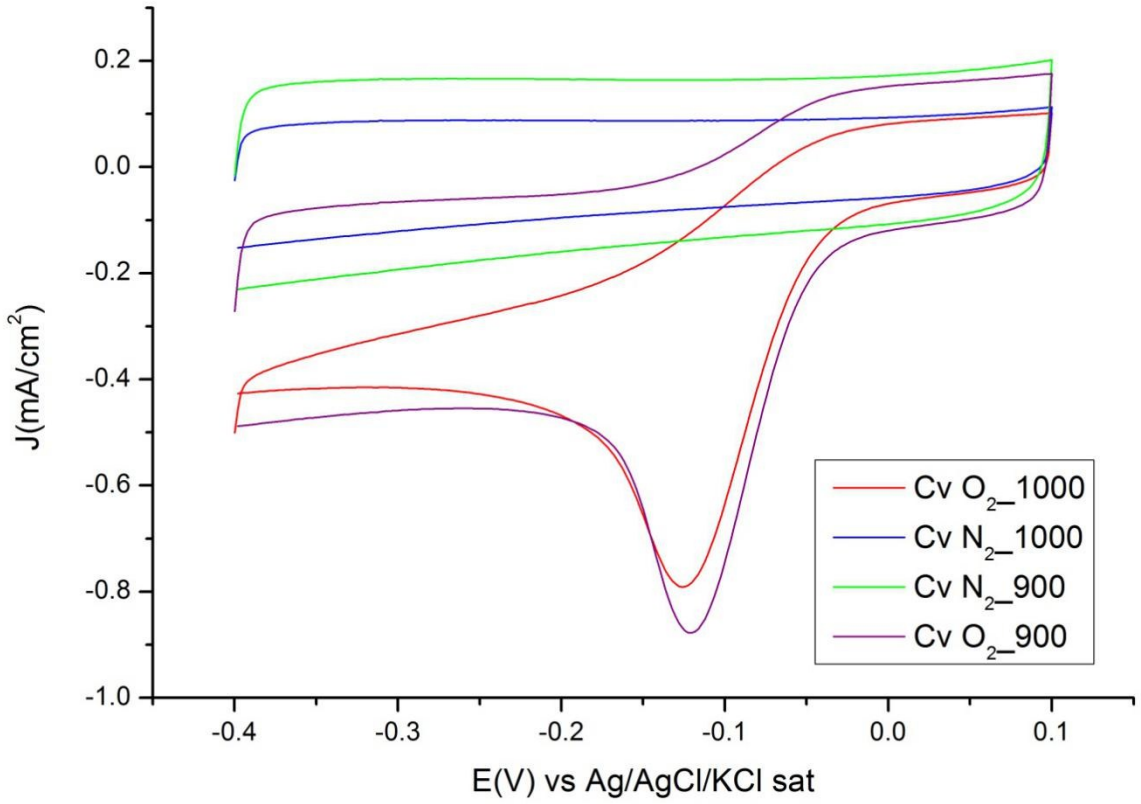


Fig. S11 CVs in 0.1 M KOH N_2-saturated (blue-line) and O_2-saturated solutions (red-line) of FePc/C(900) and FePc/C(1000). Sweeping potentials linearly from −0.4 V to 0.1 V with a scan rate of 20 mV s^{-1}.

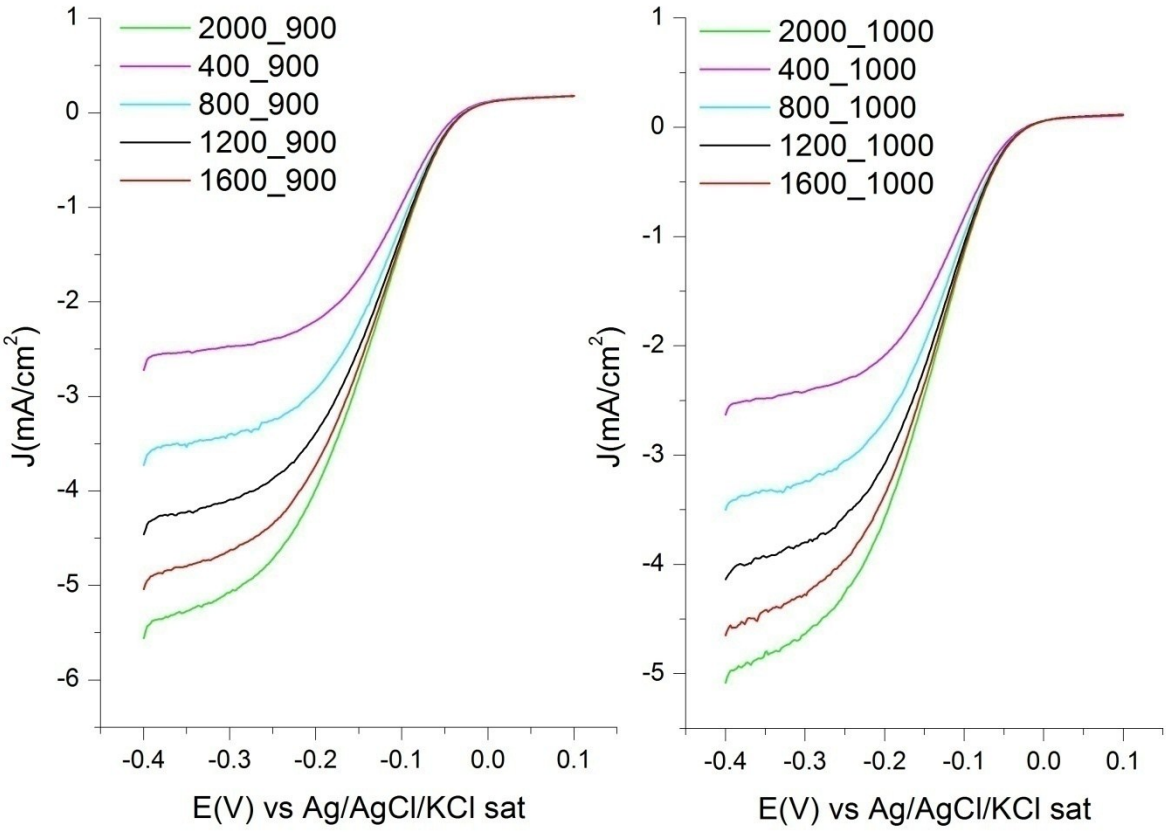


Fig. S12 CVs of FePc/C(900) and FePc/C(1000) using RRDE at different rotation speeds left (disk)

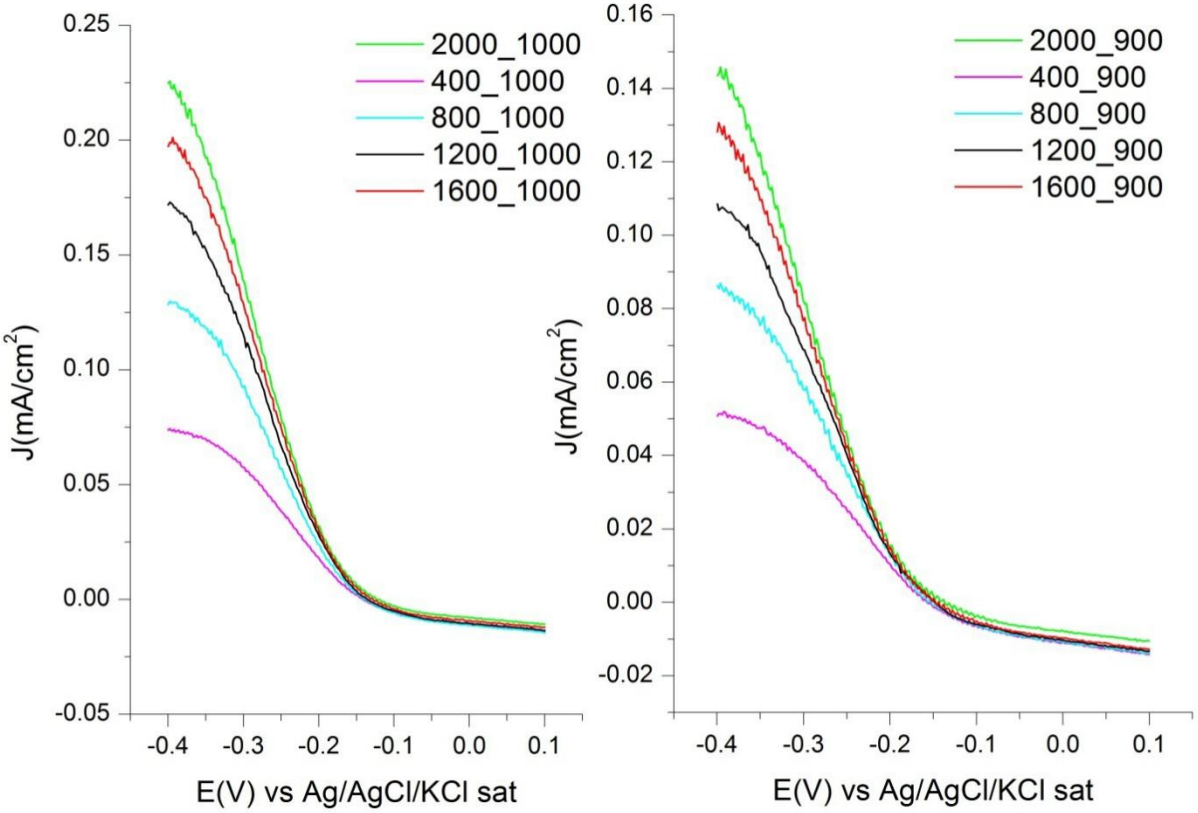


Fig. S13 CVs of FePc/C(900) and FePc/C(1000) using RRDE at different rotation speeds left (ring)

B. Koutecky–Levich Plots:

Koutecky–Levich plots were obtained based upon the following equations:[1]

$$\frac{1}{i} = \frac{1}{i_{cc}} + \frac{1}{k_d \sqrt{\omega}} \qquad (1)$$

and $$k_d = 0.620nFACD^{\frac{2}{5}}v^{-\frac{1}{6}} \qquad (2)$$

A plot of i vs $\sqrt{\omega}$ is non linear with $i = i_{cc}$ for $\omega^{1/2} \rightarrow 0$.

Equation (1) can be changed substituting the current (i) with the current density (j) and using f instead of ω to describe the rotation speed to give:

$$\frac{1}{J} = \frac{1}{J_{cc}} + \frac{1}{nK_f \sqrt{f}}$$

A plot of $\frac{1}{J} VS \frac{1}{\sqrt{f}}$, should be a linear plot with the slope of;

$m_{KL} = \frac{1}{nfK}$ combined with $q = \frac{1}{J_{cc}}$ we can obtain the number of electrons exchanged during the process using:

$$n_{KL} = \frac{1}{K_f m_{KL}}$$

With the following values; *C, D, v* for a solution of KOH 0.1M saturated with O_2 to obtain the value of K_f:

- $C_{o2} = 1.15*10^{-5}$
- $D_{o2} = 1.95*10^{-5} cm^2/s$ $\Rightarrow K_f = 0.03538$
- $v = 8.98*10^{-3} cm^2/s$

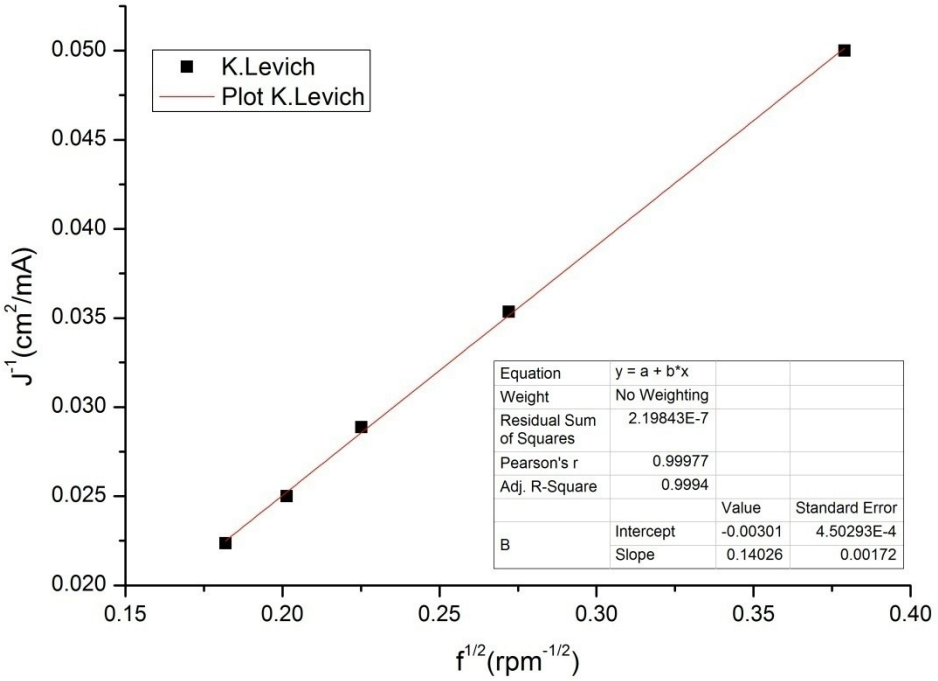


Fig. S14 Koutecky–Levich plot for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(400 ^oC)

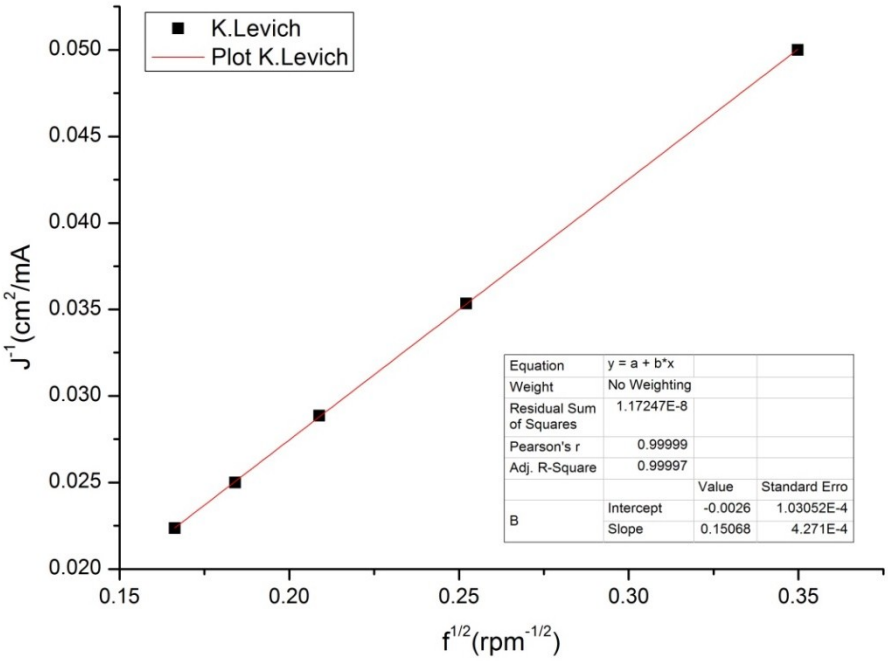


Fig. S15 Koutecky–Levich plot for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(500 °C).

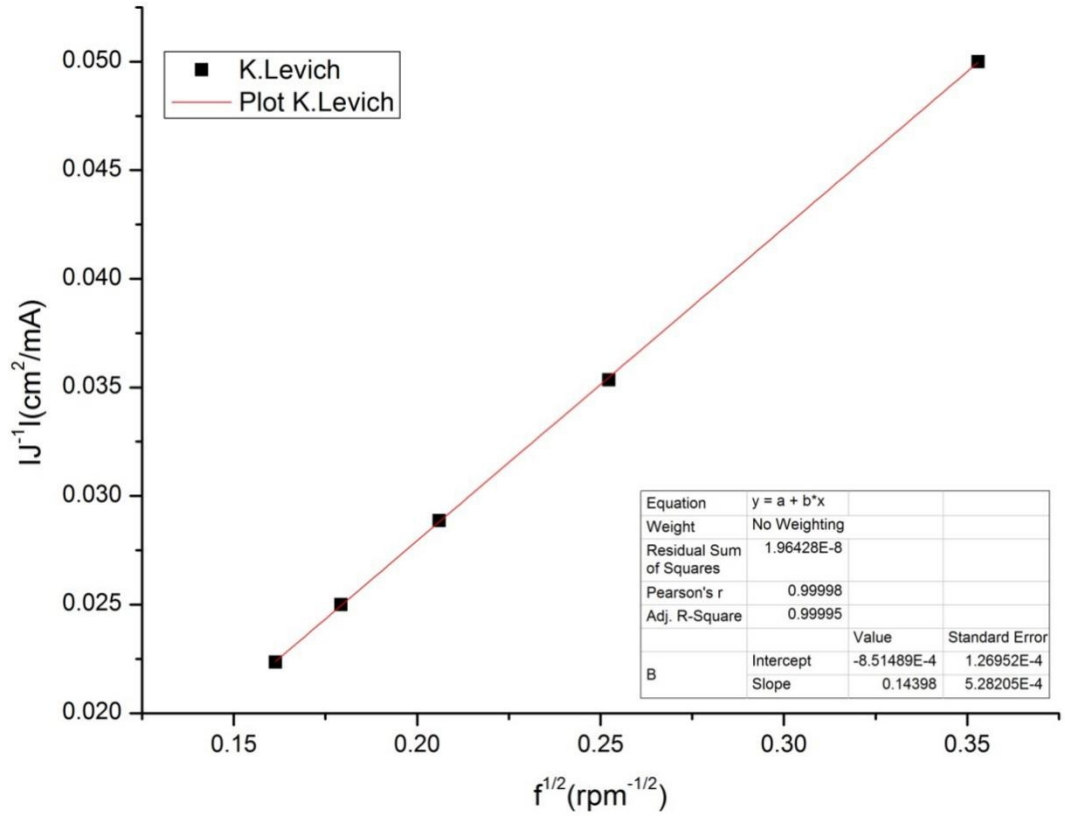


Fig. S16 Koutecky–Levich plot for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(600 °C).

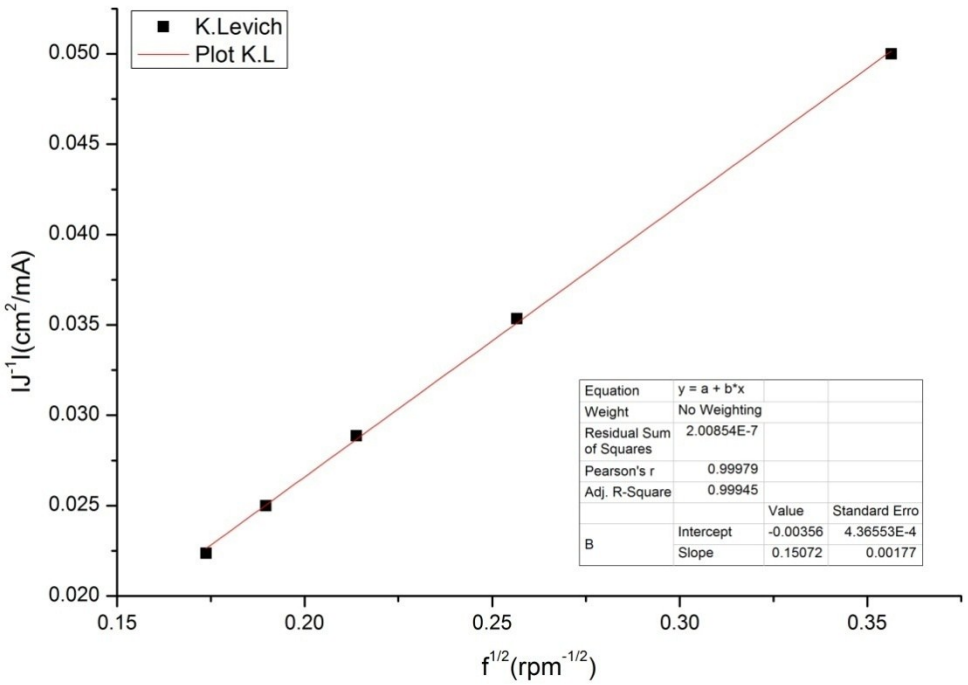


Fig. S17 Koutecky–Levich plot for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(700 ^oC).

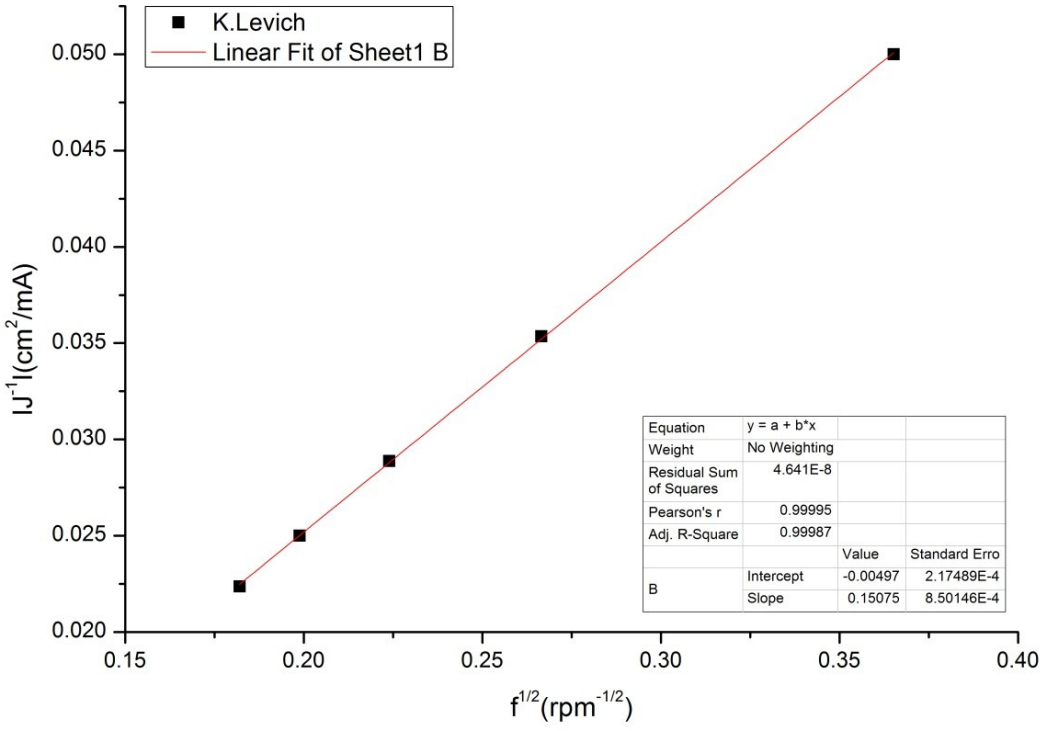


Fig. S18 Koutecky–Levich plot for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(800 ^oC).

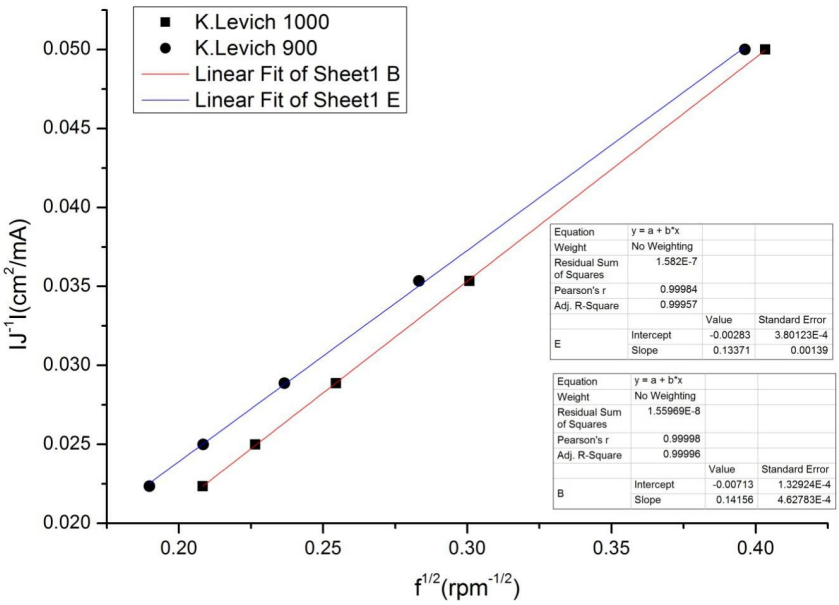


Fig. S19 Koutecky–Levich plots for ORR in O_2-saturated 0.1 M KOH solution of FePc/C(900 ^oC) and FePc/C(1000 ^oC).

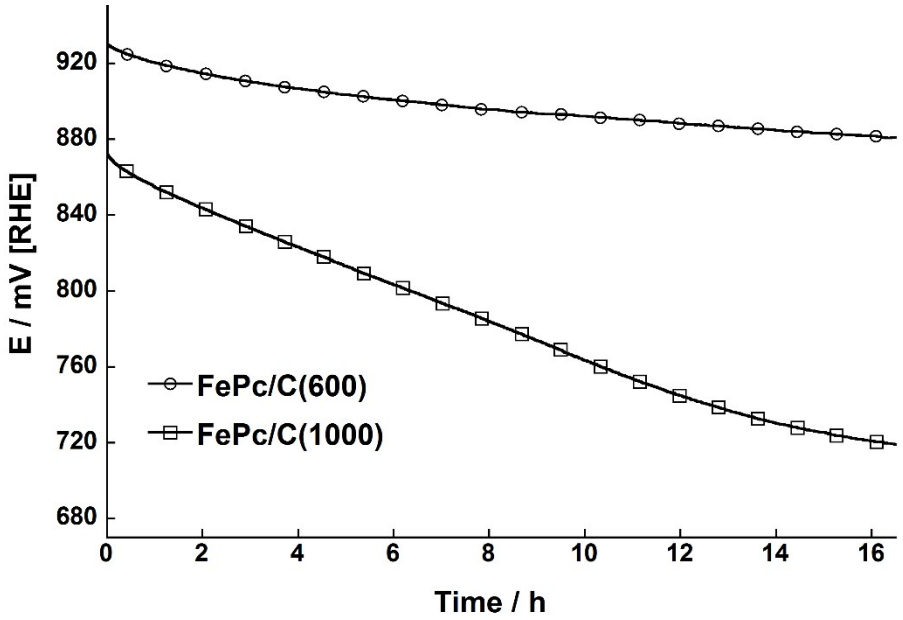


Fig. S20 Chronopotentiometric curves for the ORR. Experimental conditions: KOH 0.1 M, O_2 saturated, RDE Ω = 1600 rpm, constant current chronopotentiometry at 2.5mA cm^{-2}, ref. electrode $Ag|AgCl|KCl_{sat}$ (all potentials are also referred to RHE).

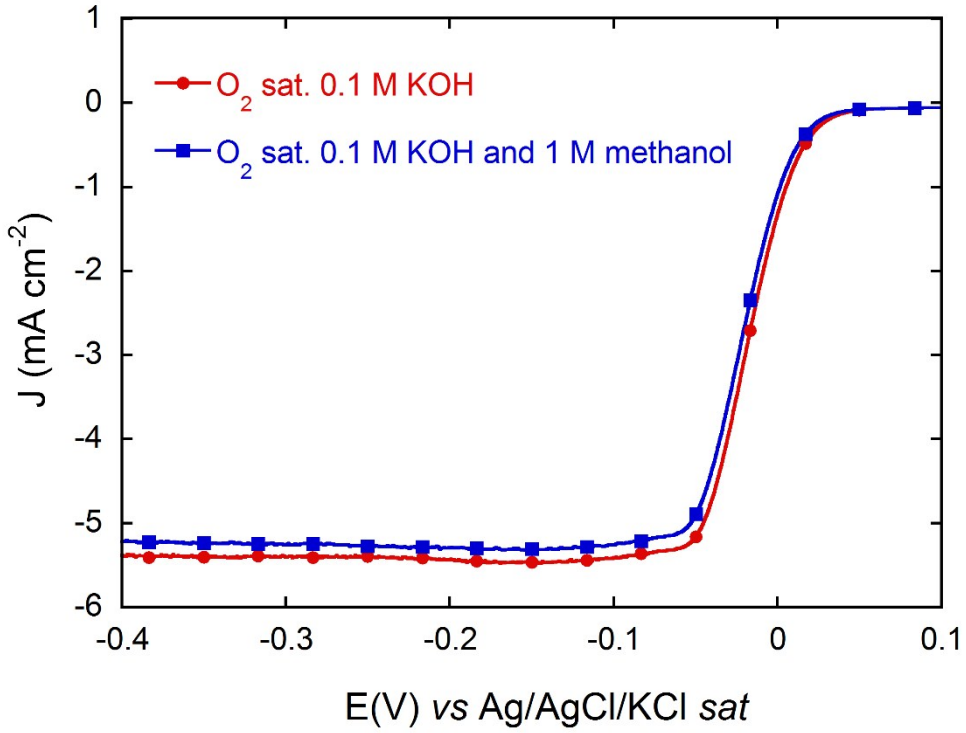


Fig. S21 Linear polarization experiments in O_2 sat. 0.1M KOH and in O_2 sat. 0.1M KOH with 1M methanol.

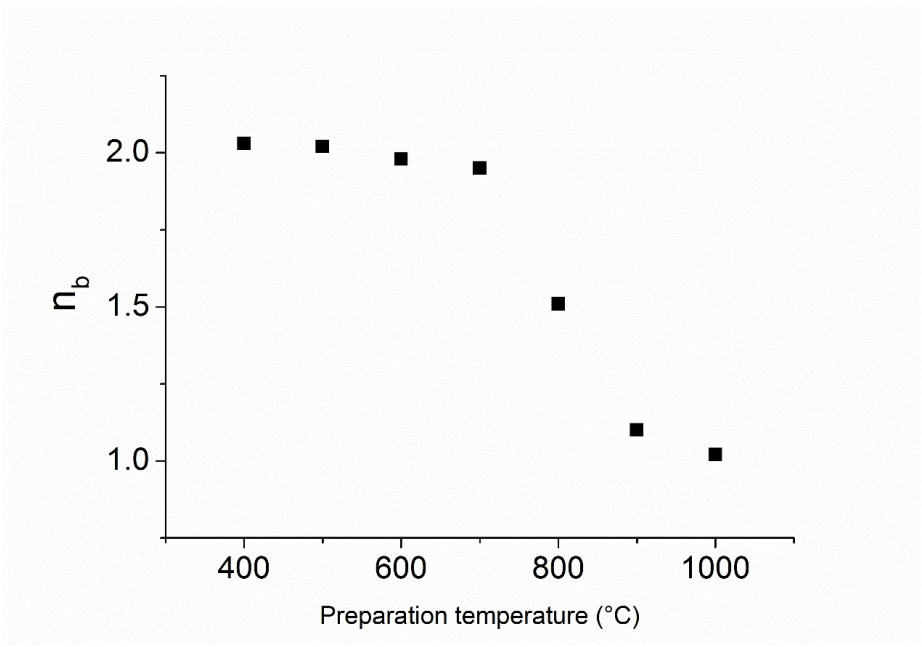


Fig. S22**.** Number of exchanged electrons (n_b) before the rds plotted against the heat treatment temperature.

C. XAS fittings

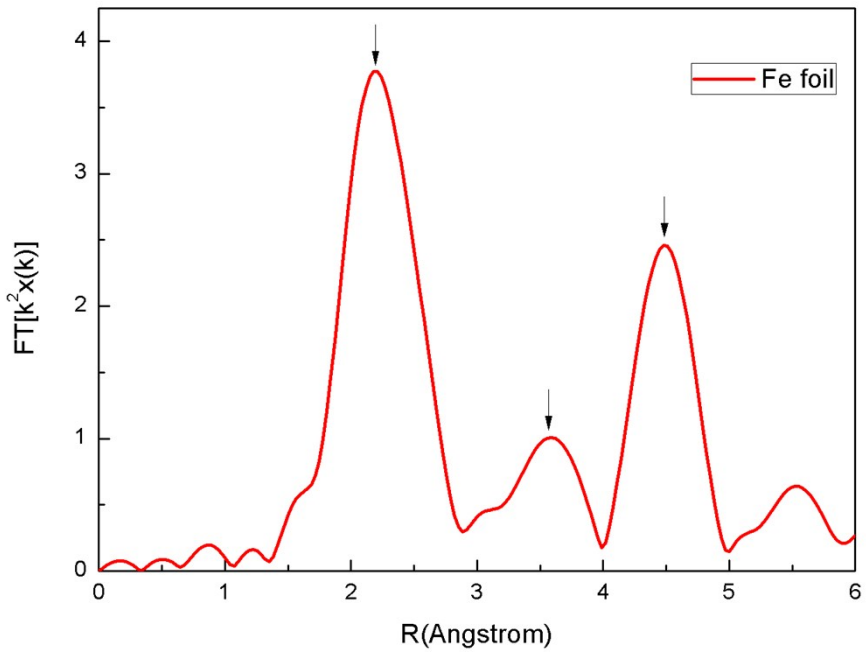
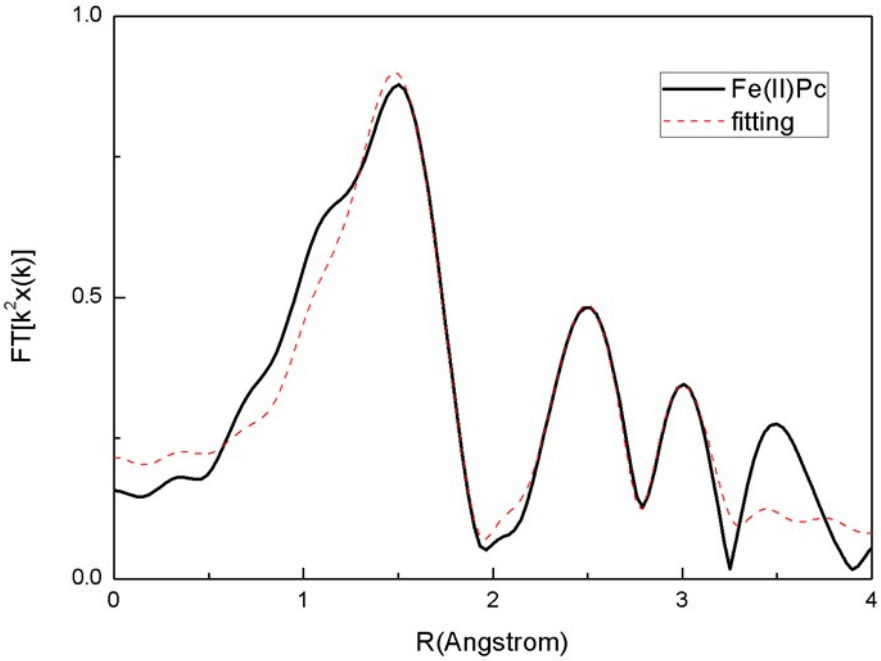
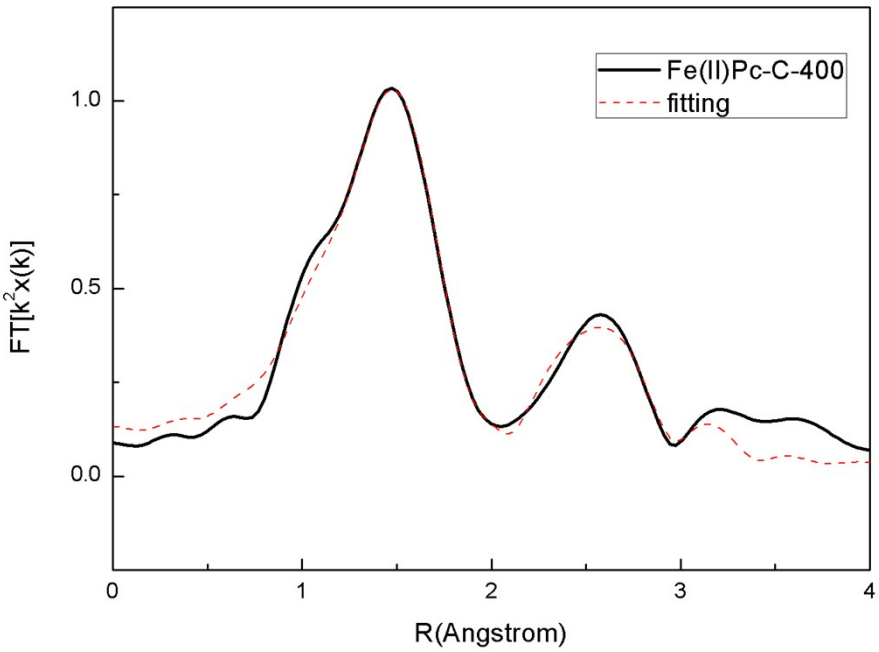
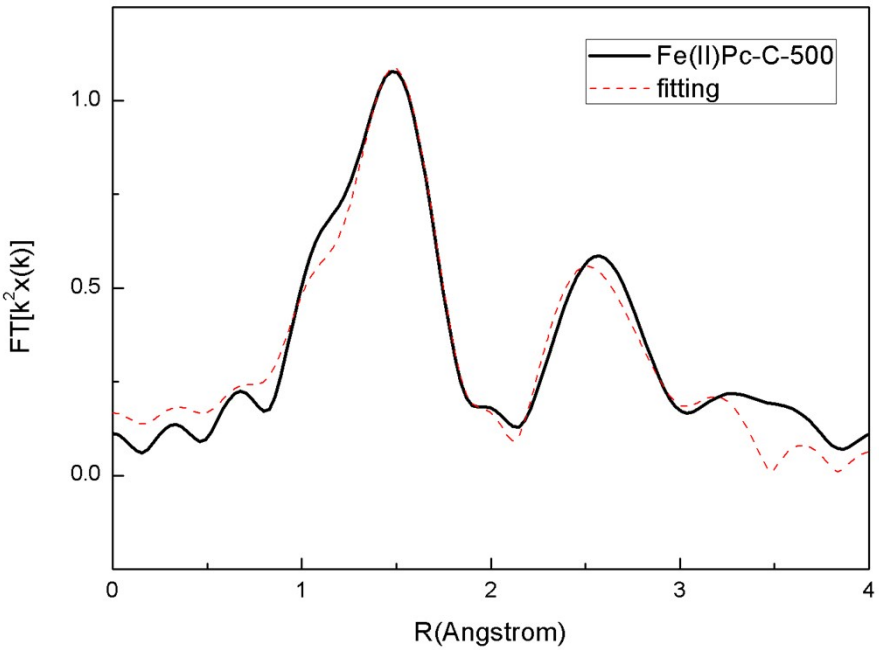
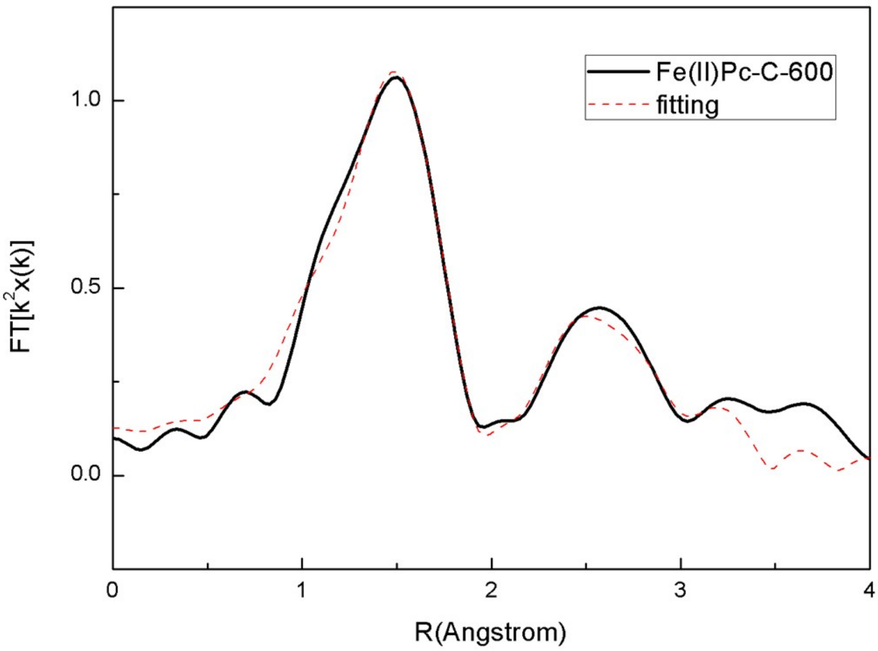


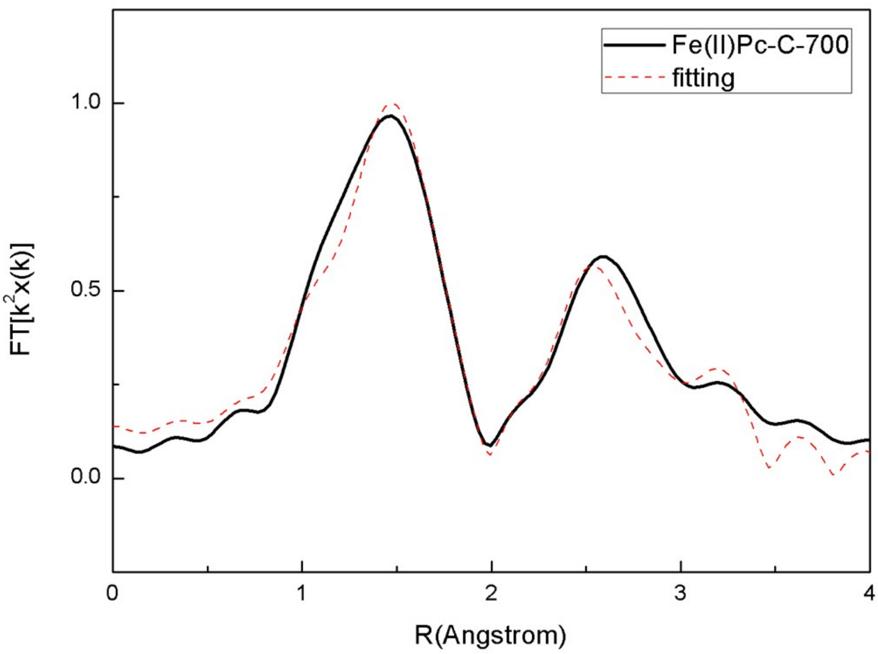
Fig. S23 Fourier transform of the Fe K edge EXAFS spectrum of metallic Fe foil. The Fe-Fe peaks are marked by arrows.


1.0
0.5
0.0
0
1
2
3
4
FT[k²x(k)]
R(Angstrom)
Fe(II)Pc
fitting


Fe(II)Pc-C-400
fitting
FT[k²x(k)]
R(Angstrom)
0.0
0.5
1.0
0
1
2
3
4


Fe(II)Pc-C-500
fitting
FT[k²x(k)]
R(Angstrom)
0.0
0.5
1.0
0
1
2
3
4


Fe(II)Pc-C-600
fitting
FT[k^{2}x(k)]
1.0
0.5
0.0
0
1
2
3
4
R(Angstrom)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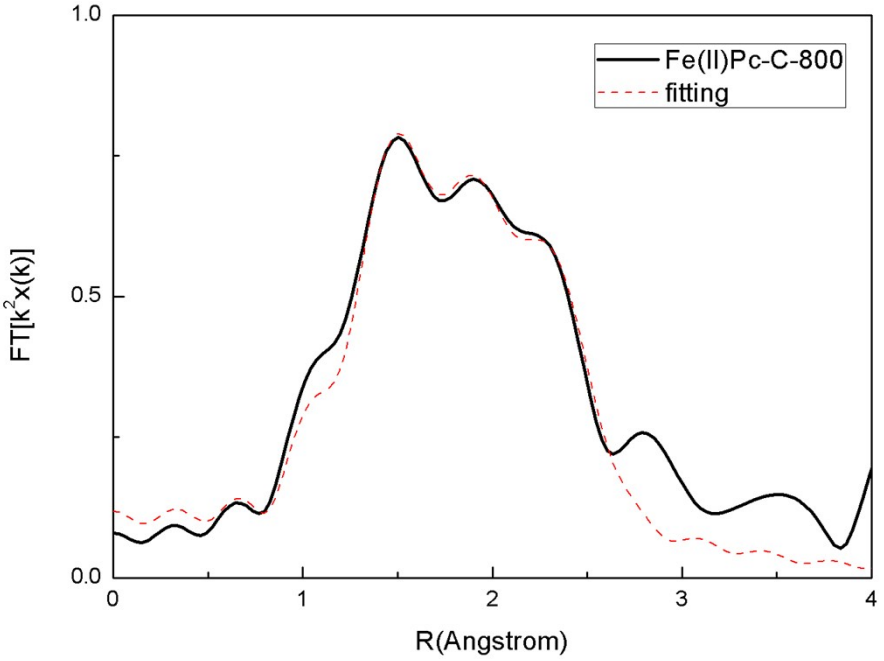
1
2
3
4
R(Angstrom)


Fe(II)Pc-C-800
fitting
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R(Angstrom)
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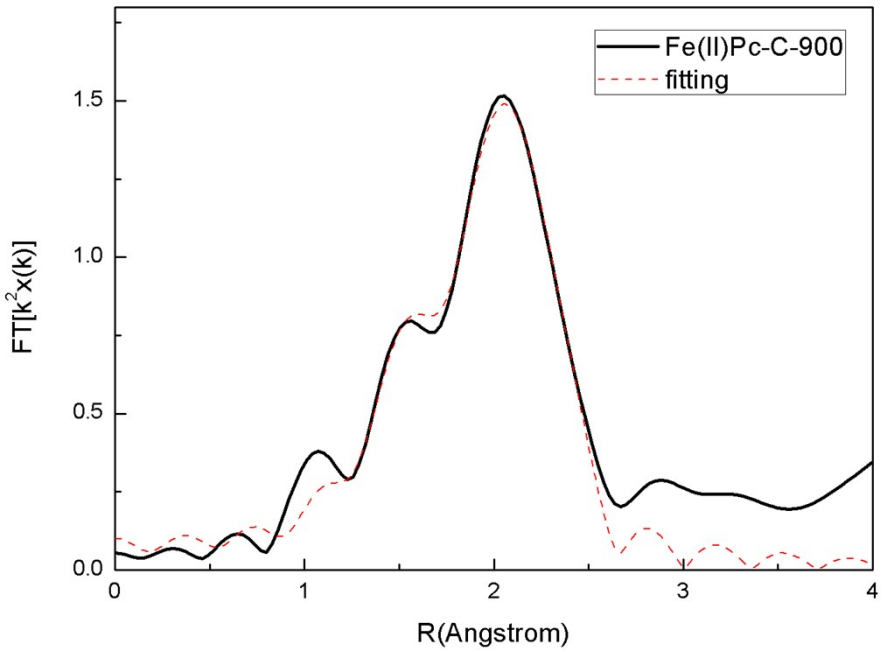
1
2
3
4


Fe(II)Pc-C-900
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0
1
2
3
4

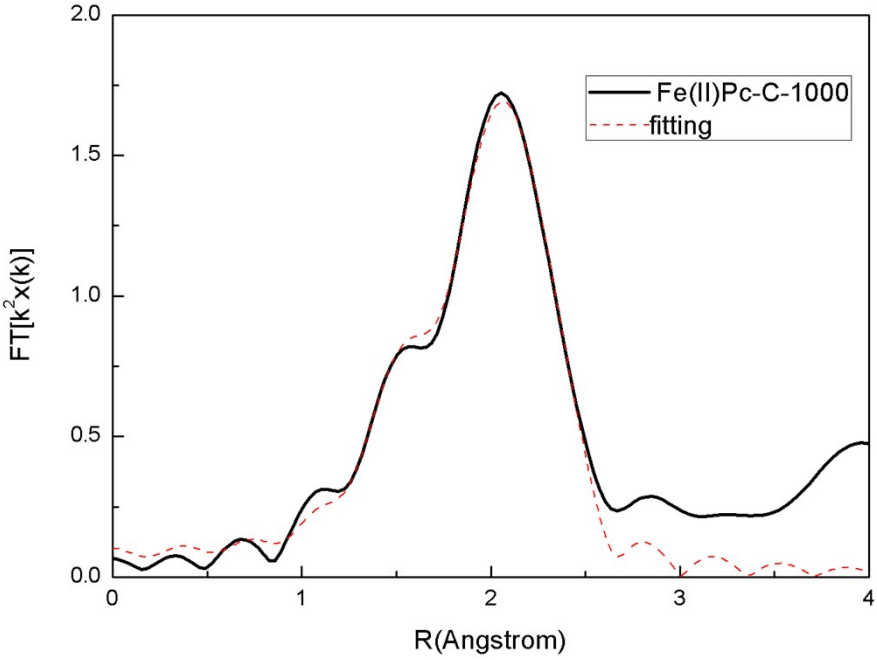

Fig. S24 Fourier transform EXAFS spectra of FePc reference and samples treated from 400 – 1000℃. k^2: Δk = 2.8 – 11.8Å^{-1},Δr=1.1 – 3.2Å

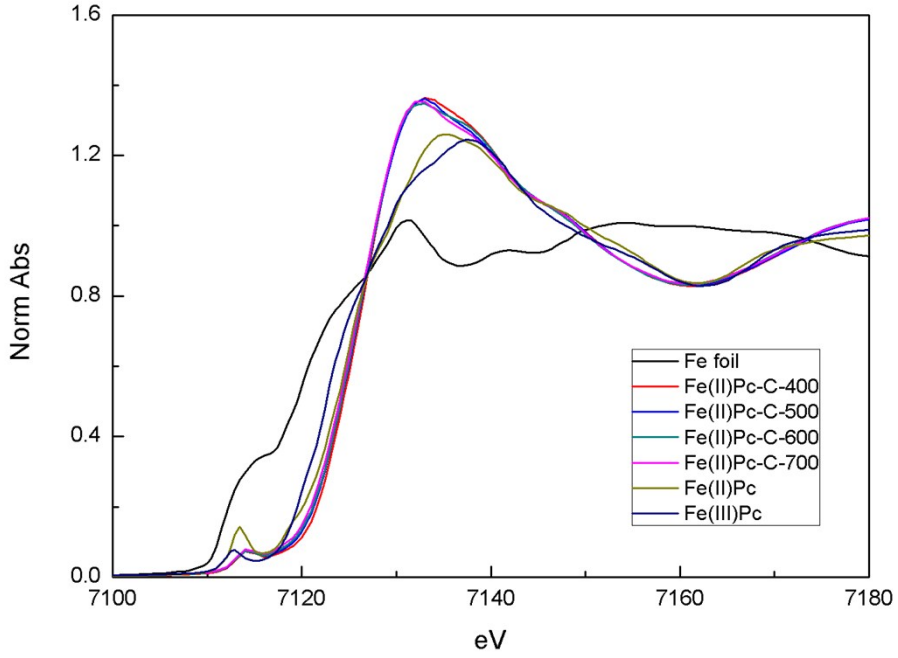

Fig. S25 Fe Kedge XANES spectra of Fe(II)Pc-C treated between 400 – 700 °C with respect to references.

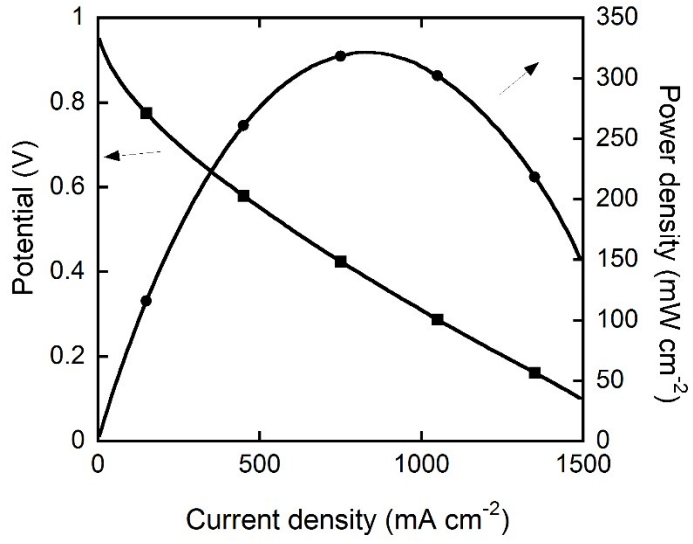

Fig. S26. Typical power density and IV curves (scan rate: 50 mA s^{-1}) for H_2/O_2 monoplanar AEM-FCs with Pt/C as both anode and cathode catalysts (0.4 mg_{Pt} cm^{-2}). T_{cell} = 55 °C. H_2/O_2 (100% relative humidity, RH) with the flow rate of 100 and 200 mL min^{-1} respectively.

References:

1. E. Higuchi, H. Uchida and M. Watanabe, *J Electroanal Chem*, 2005, 583, 69-76.