

SUPPORTING INFORMATION

Mono-, bi- and tri-metallic Fe-based platinum group metal-free electrocatalysts derived from phthalocyanine for oxygen reduction reaction in alkaline media

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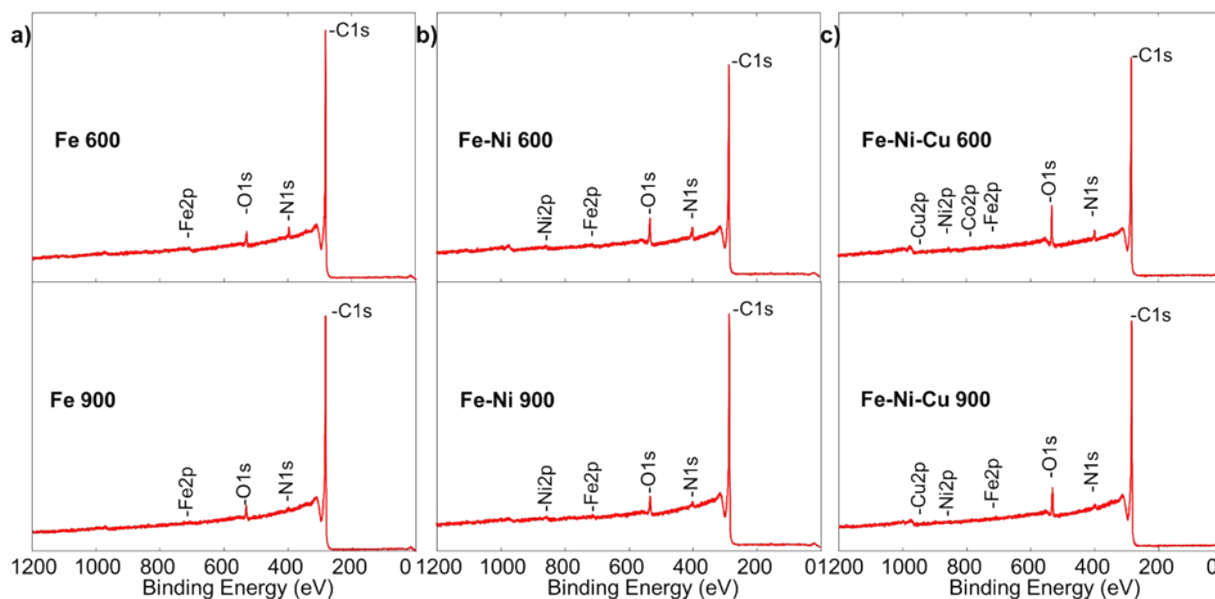


Figure S1: XPS survey spectra for a) Fe 600 and Fe 900, b) Fe-Ni 600 and Fe-Ni 900 and c) Fe-Ni-Cu 600 and Fe-Ni-Cu 900.

Table S1. Atomic percentage of C1s, N1s, Fe2p_{3/2}, Ni2p_{3/2}, Cu2p_{3/2} and O1s in the KB-supported catalysts derived from XPS analyses.

| Catalysts | C (1s) | N (1s) | Fe (2p _{3/2}) | Cu (2p _{3/2}) | Ni (2p _{3/2}) | O (1s) |
|---------------------|--------|--------|-------------------------|-------------------------|-------------------------|--------|
| Fe 600 | 93.4 | 3.2 | 0.3 | - | - | 3.1 |
| Fe 900 | 95.7 | 1.6 | 0.3 | - | - | 2.4 |
| Fe-Ni 600 | 89.4 | 4.4 | 0.2 | - | 0.3 | 5.7 |
| Fe-Ni 900 | 94 | 2.0 | 0.1 | - | 0.1 | 3.8 |
| Fe-Ni-Cu 600 | 89.4 | 3.0 | 0.2 | 0.3 | 0.1 | 7.0 |
| Fe-Ni-Cu 900 | 91.9 | 2.4 | ~0.1 | ~0.1 | <0.1 | 5.5 |

Table S2. Composition of nitrogen from N1s deconvolution spectra.

| KB-supported Catalysts | Composition of N (relative %) | | | | | | |
|------------------------|-------------------------------|------------------------------|----------------------|-----------------------------------|---------------------|----------------------|---------------|
| | N (at. %) | I _{mine} (397.7 eV) | Pyridinic (398.3 eV) | N-M (M=Fe, Cu, Ni) (399.1 eV±0.1) | Pyrrolic (400.9 eV) | Graphitic (402.1 eV) | N-O (>403 eV) |
| Fe 600 | 3.2 | - | 35.9 | 45.5 | 10.6 | 8.0 | - |
| Fe 900 | 1.6 | - | 29.3 | 32.5 | 38.2 | - | - |
| Fe-Ni 600 | 4.4 | - | 23.1 | 59.9 | 15.0 | 2.0 | - |
| Fe-Ni 900 | 2.0 | - | 29.3 | 31.8 | 35.6 | 3.3 | - |
| Fe-Ni-Cu 600 | 3.0 | - | 37.9 | 50.7 | 11.4 | - | - |
| Fe-Ni-Cu 900 | 2.4 | - | 35.2 | 1.8 | 63.0 | - | - |

Table S3. Composition of nitrogen from C1s deconvolution spectra.

| Catalysts | Composition of C (relative %) | | | | | | |
|---------------------|-------------------------------|----------------------|------------------------------|------------------------|--------------------------|----------------|-----------------|
| | C (at. %) | Graphitic (284.3 eV) | Secondary carbons (285.0 eV) | C-N defects (286.2 eV) | C-OH and C-OC (287.1 eV) | C=O (288.0 eV) | COOH (289.4 eV) |
| Fe 600 | 93.4 | 63.9 | 22.0 | 5.5 | 2.0 | 2.0 | 4.6 |
| Fe 900 | 95.7 | 55.3 | 29.0 | 4.5 | 3.6 | 1.1 | 6.5 |
| Fe-Ni 600 | 89.4 | 57.1 | 28.7 | 5.9 | 1.9 | 2.6 | 3.8 |
| Fe-Ni 900 | 94 | 54.9 | 30.5 | 3.8 | 3.9 | 1.4 | 5.5 |
| Fe-Ni-Cu 600 | 89.4 | 40.6 | 40.6 | 7.9 | 1.7 | 4.1 | 5.1 |
| Fe-Ni-Cu 900 | 91.9 | 44.8 | 40.7 | 4.3 | 2.9 | 3.1 | 4.2 |

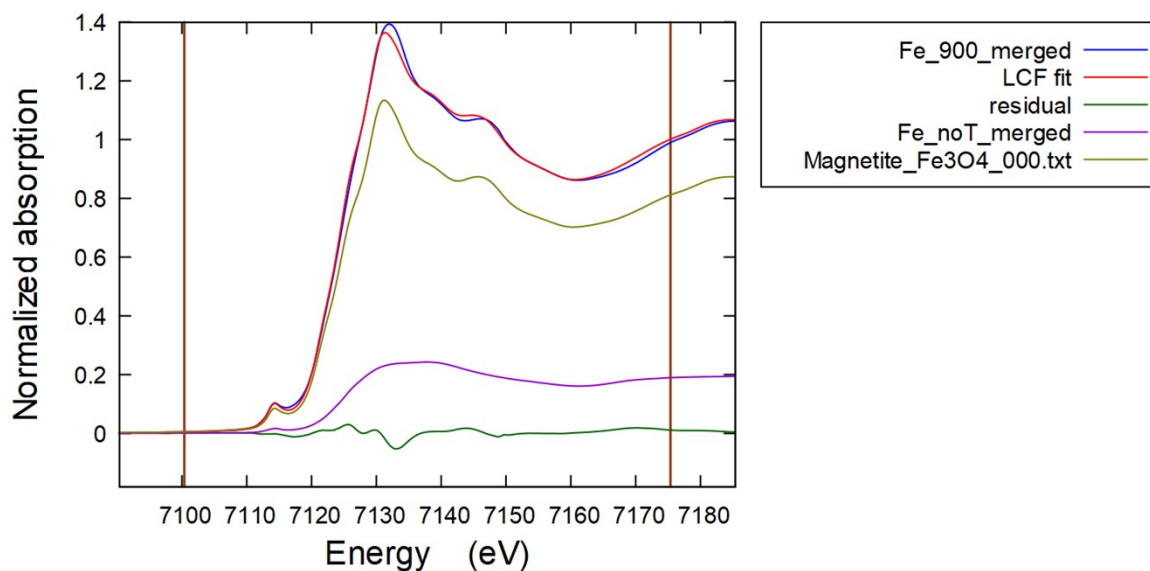


Figure S2: Spectrum of the sample treated at 900 °C (blue line) with the best LC fit (red line) obtained using 81% Fe_3O_4 (yellowish line) and 19% pristine Fe(Pc)/C (violet line).

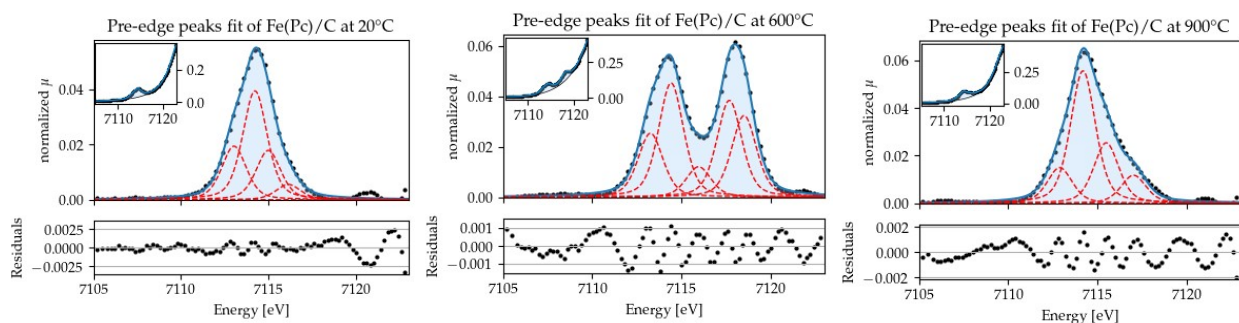


Figure S3: Pre-edge peaks fit: Black dots are the experimental data, blue lines the total fitted area, and in red the single components used. Upper-left small plate, the fit without the background subtraction.

Table S4. Onset-potential, half-potential, and limiting current density belong to the Fe-based electrocatalysts with the different (wt.%) of the FePc

| Sample | Onset-potential (V) | Half-potential (V) | Limiting current density (mA cm⁻²) |
|---------------------|--------------------------------|-------------------------------|--|
| Fe (30%) 600 | 0.96 | 0.90 | 6.2 |
| Fe (30%) 900 | 0.96 | 0.84 | 5.2 |
| Fe (20%) 600 | 0.95 | 0.88 | 5.8 |
| Fe (20%) 900 | 0.95 | 0.83 | 5.4 |
| Fe (10%) 600 | 0.94 | 0.86 | 5.2 |
| Fe (10%) 900 | 0.89 | 0.75 | 5.5 |
| Pt/C | 0.98 | 0.85 | 5 |

Table S5: Onset-potential, half-potential, and limiting current density belong to the Fe-based electrocatalysts with the different mono/bi/tri-metallic precursors.

| Sample | Onset-potential (V) | Half-potential (V) | Limiting current density (mA cm⁻²) |
|---------------------|--------------------------------|-------------------------------|--|
| Fe 600 | 0.96 | 0.90 | 5.3 |
| Fe 900 | 0.96 | 0.84 | 5.6 |
| Fe-Ni 600 | 0.89 | 0.78 | 4.5 |
| Fe-Ni 900 | 0.88 | 0.76 | 4.9 |
| Fe-Ni-Cu 600 | 0.96 | 0.90 | 5 |
| Fe-Ni-Cu 900 | 0.93 | 0.81 | 5 |
| Pt/C | 0.98 | 0.85 | 5 |

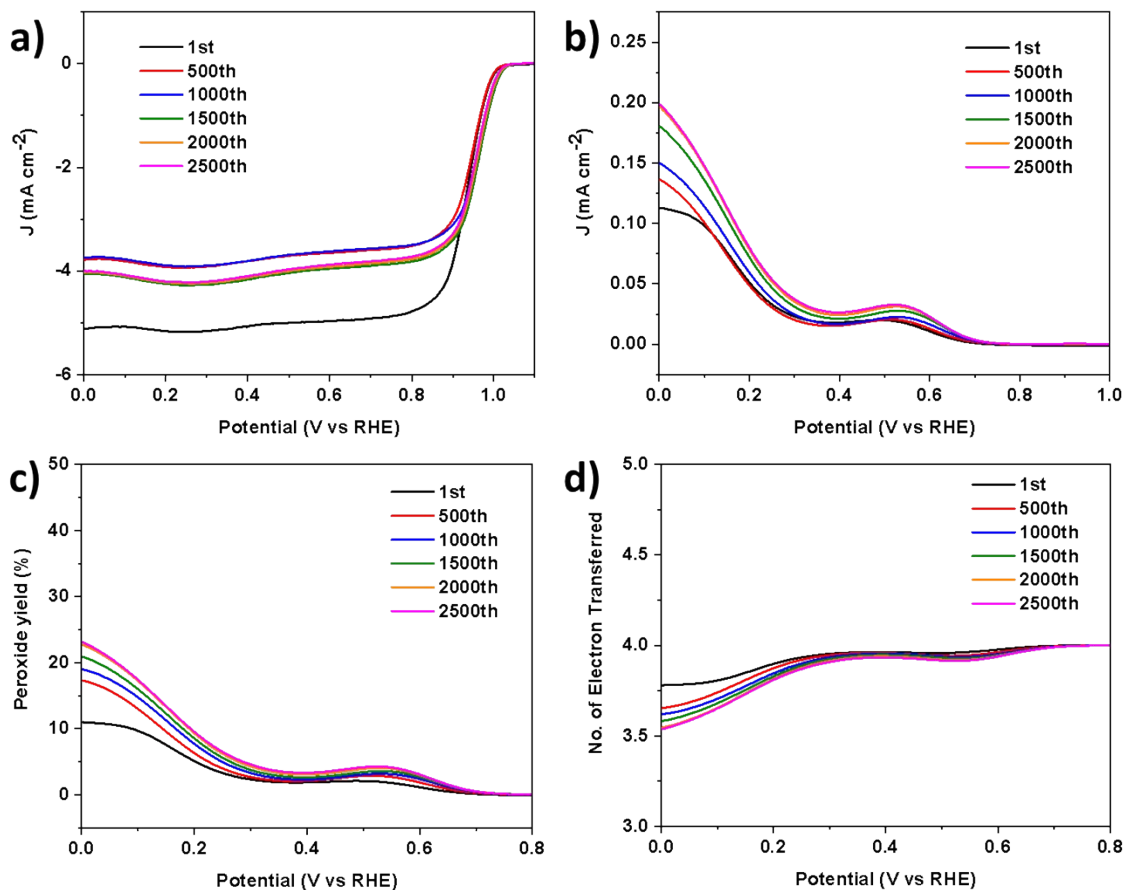


Figure S4. Accelerated ORR stability test performed over Fe 600 with the scan rate of 5 mVs⁻¹ in O₂ saturated 0.1 M KOH while operating RRDE at 1600 rpm; a) LSV for disk current, b) Ring current, c) Peroxide anion yield, and d) Number of electrons transferred. Pt/C in all plots is the benchmark.

| Sample | E _{on} (V) | E _{1/2} (V) | limited current density (J _d) (mA cm ⁻²) | Solution | cite |
|-----------------|------------------------|-------------------------|--|-------------------------|-----------|
| FeCoNi-CNF | - | 0.77 | - | 0.1 M KOH | [1] |
| Fe-BP(N) | 0.95 | 0.84 | -6.1 | 0.1 M KOH | [2] |
| Poly-FePc | 0.98 | 0.91 | -5.49 | 0.1 M KOH | [3] |
| PPcFeCo/3D-G | | 0.89 | -5.4 | 0.1 M KOH | [4] |
| CMP-CoFe/C | 0.95 | 0.83 | -6.5 | 0.1 M KOH | [5] |
| FePc-PcFe | 0.80 | 0.59 | - | 0.1 M HClO ₄ | [6] |
| CoFe-COP/OMC | 0.90 | - | -5.35 | 0.1 M KOH | [7] |
| Fe/12Zn/CoNCNTs | 1.02 | 0.88 | -5.59 | 0.1 M KOH | [8] |
| Fe 600 | 0.96 | 0.90 | -5.3 | 0.1 M KOH | This work |
| Fe-Ni-Cu 600 | 0.96 | 0.90 | -5 | 0.1 M KOH | This work |

Table S6: Comparison of ORR performance with similar electrocatalysts in other articles

Reference

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