“Supporting Information”

Single-Atom Iron-Based Electrocatalysts for High-Temperature Polymer Electrolyte Membrane Fuel Cell: Organometallic Precursor and Pore Texture Tailoring

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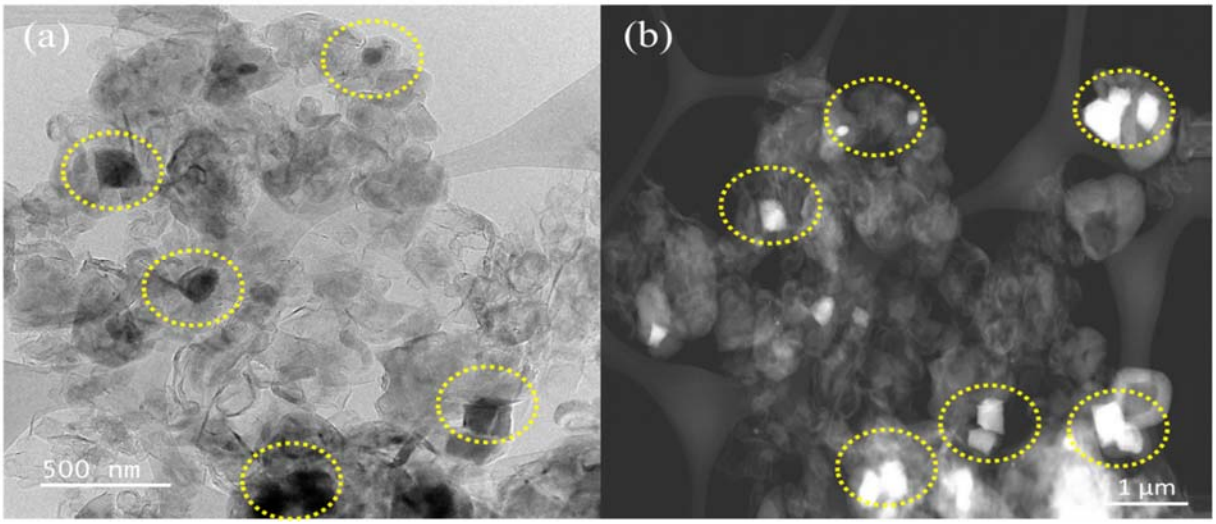

Figure S1. (a) HR-TEM and (b) STEM images of EDFe2-B.

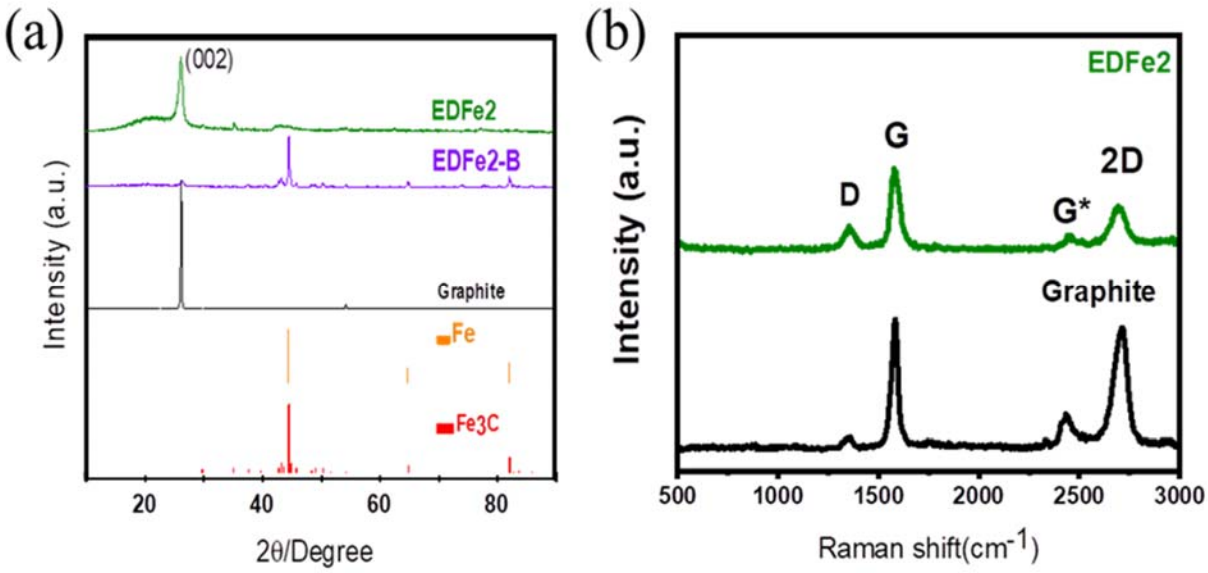

Figure S2. (a) XRD patterns of EDFe2-B and EDFe2 and (b) Raman spectra of EDFe2 and commercial graphite.

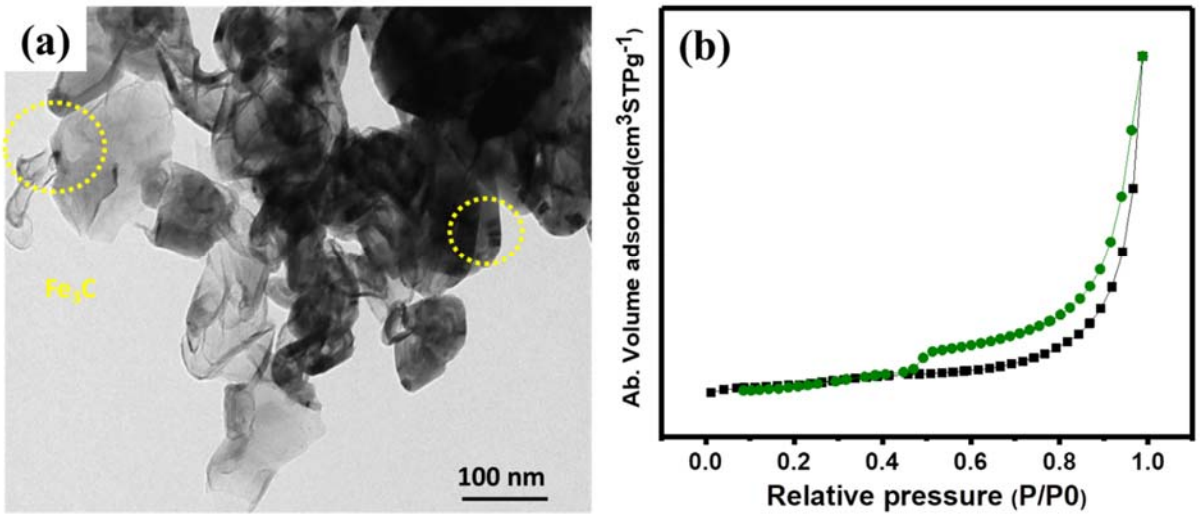

Figure S3. (a) HR-TEM image of carbon-encapsulated iron species in EDFe2 and (b) nitrogen adsorption-desorption isotherms of EDFe2.

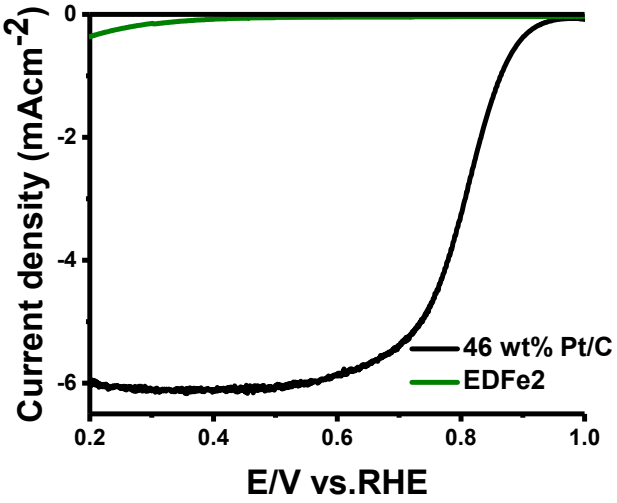

Figure S4. LSV profiles of EDFe2 and commercial Tanaka Pt/C in 0.1 M $HClO_4$ solution.

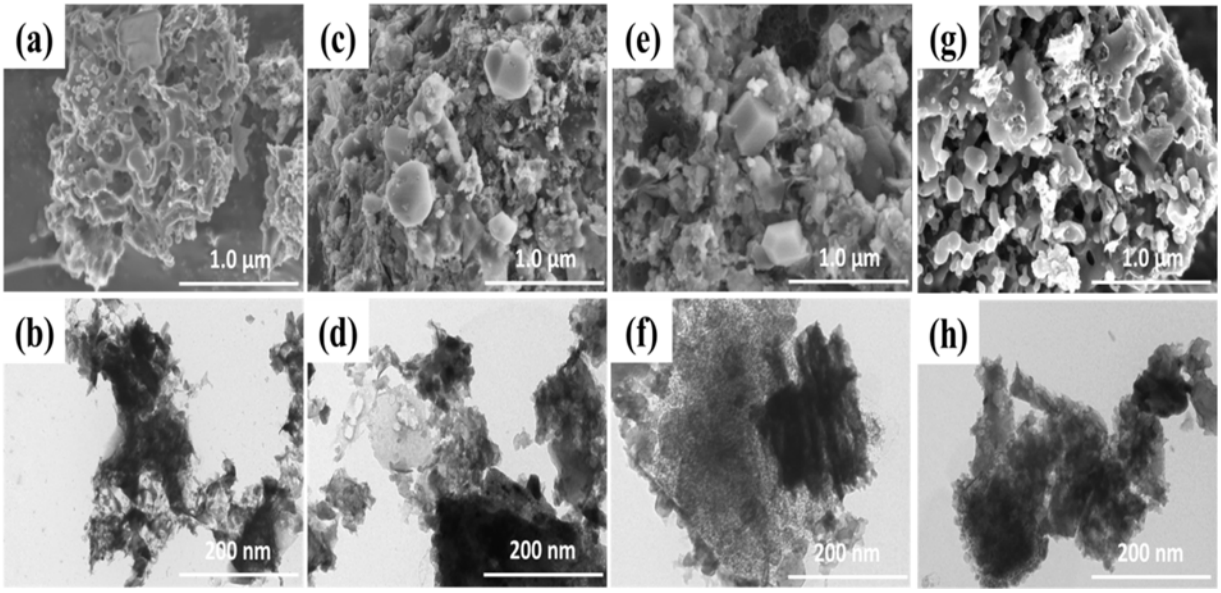

Figure S5. (a, c, e and g) SEM and (b, d, f and h) TEM images of EDFe3-B, EDFe4-B, EDFe5-B and EDFe6-B, respectively.

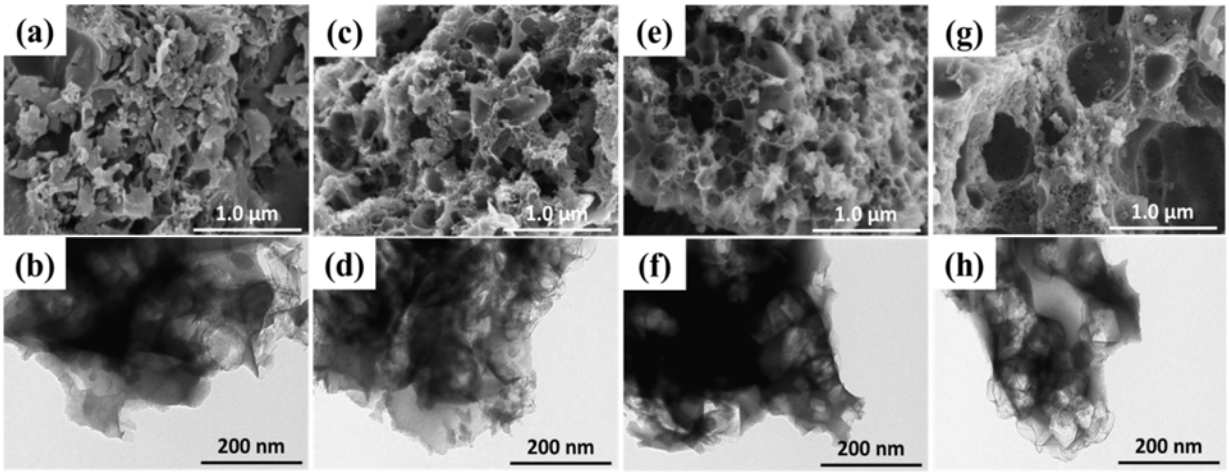

Figure S6. (a, c, e and g) SEM and (b, d, f and h) TEM images of EDFe3, EDFe4, EDFe5 and EDFe6, respectively.

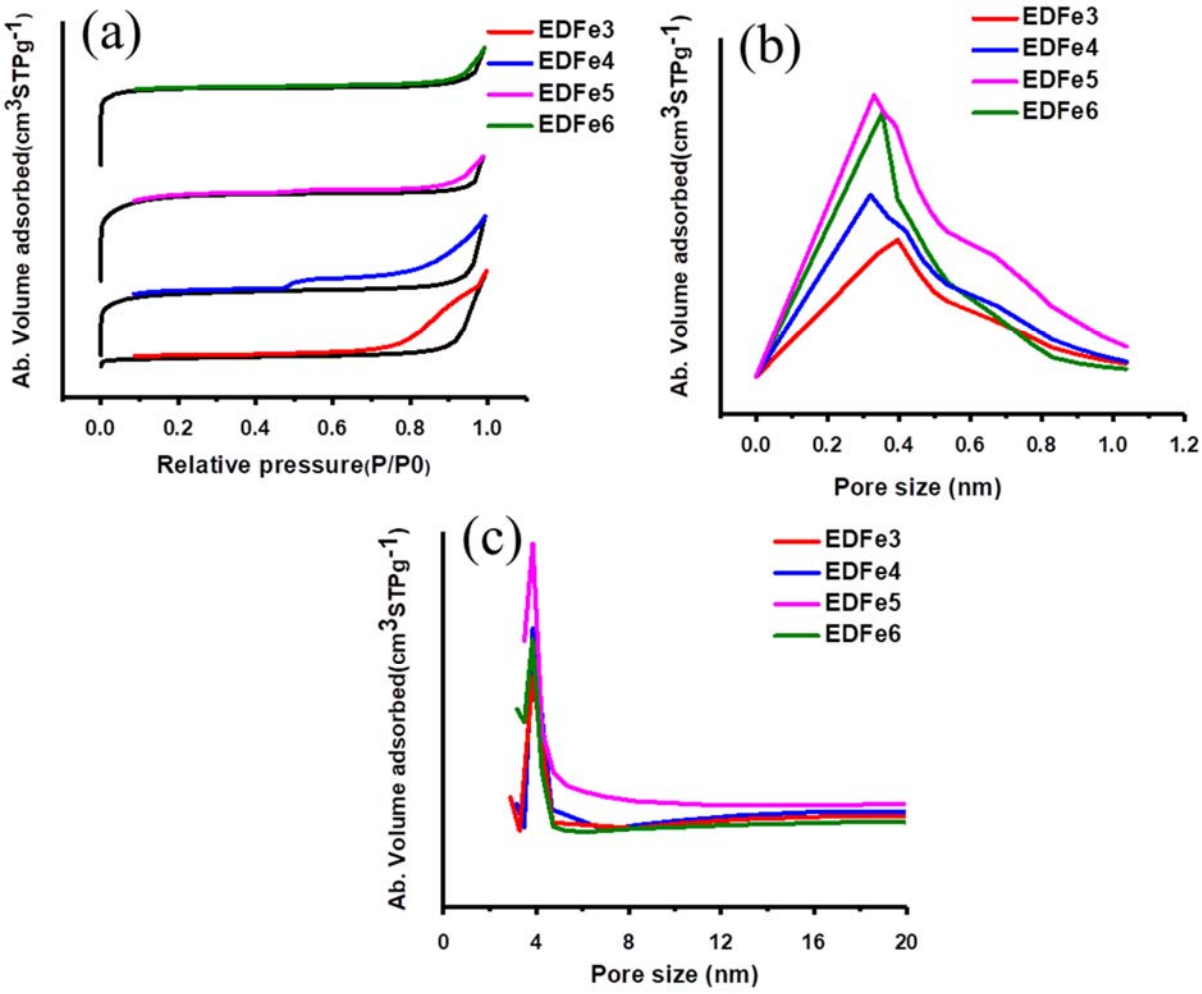

Figure S7. (a) Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of different EDFe catalysts determined from (b) H-K and (C) BJH methods.

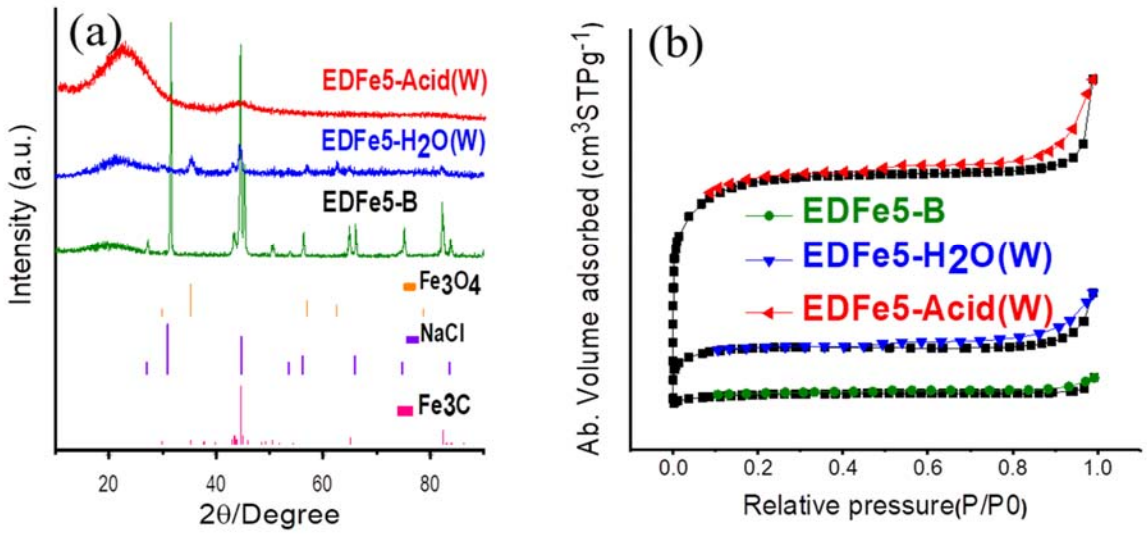

Figure S8. (a) XRD patterns and (b) nitrogen adsorption-desorption isotherms of EDFe5-B, EDFe5-H_2O (W) and EDFe5-Acid (W).

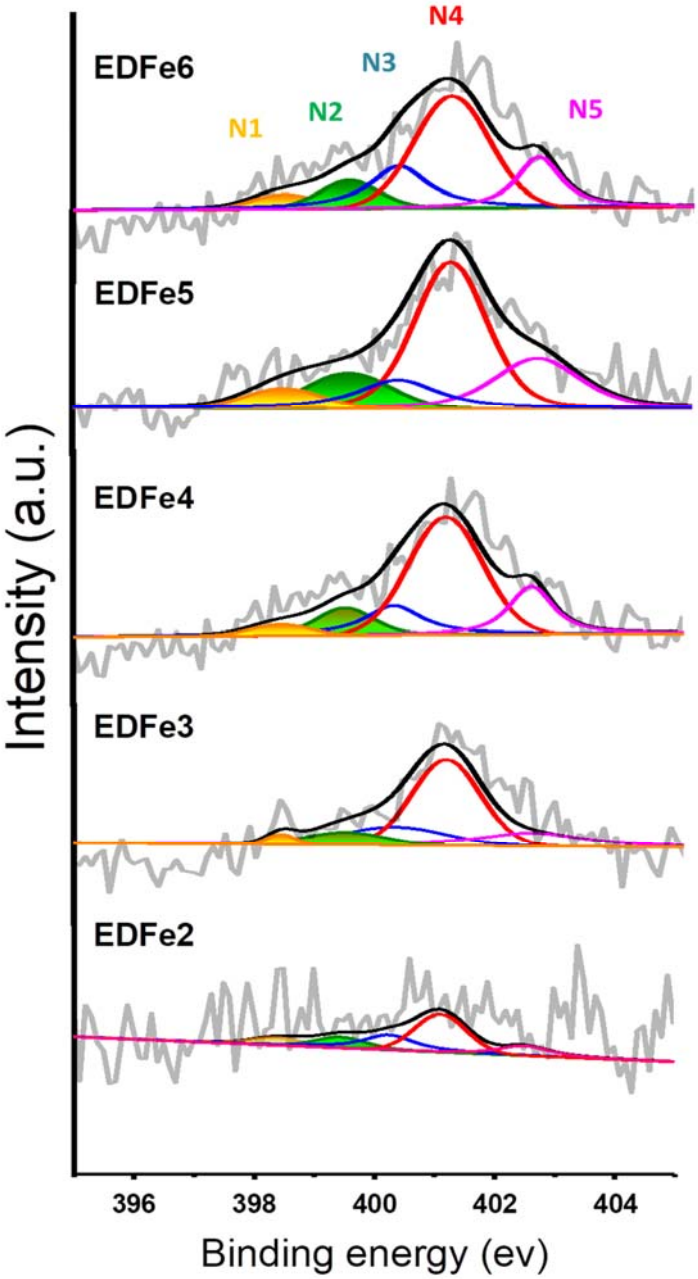

Figure S9. Deconvolution of N 1s XPS spectra of different samples. N1 corresponds to pyridinic-N, N2 to nitrogen coordinated with iron (Fe-N_x), N3 to pyrrolic-N, N4 to graphitic-N and N5 to oxidized forms of nitrogen (N-O).

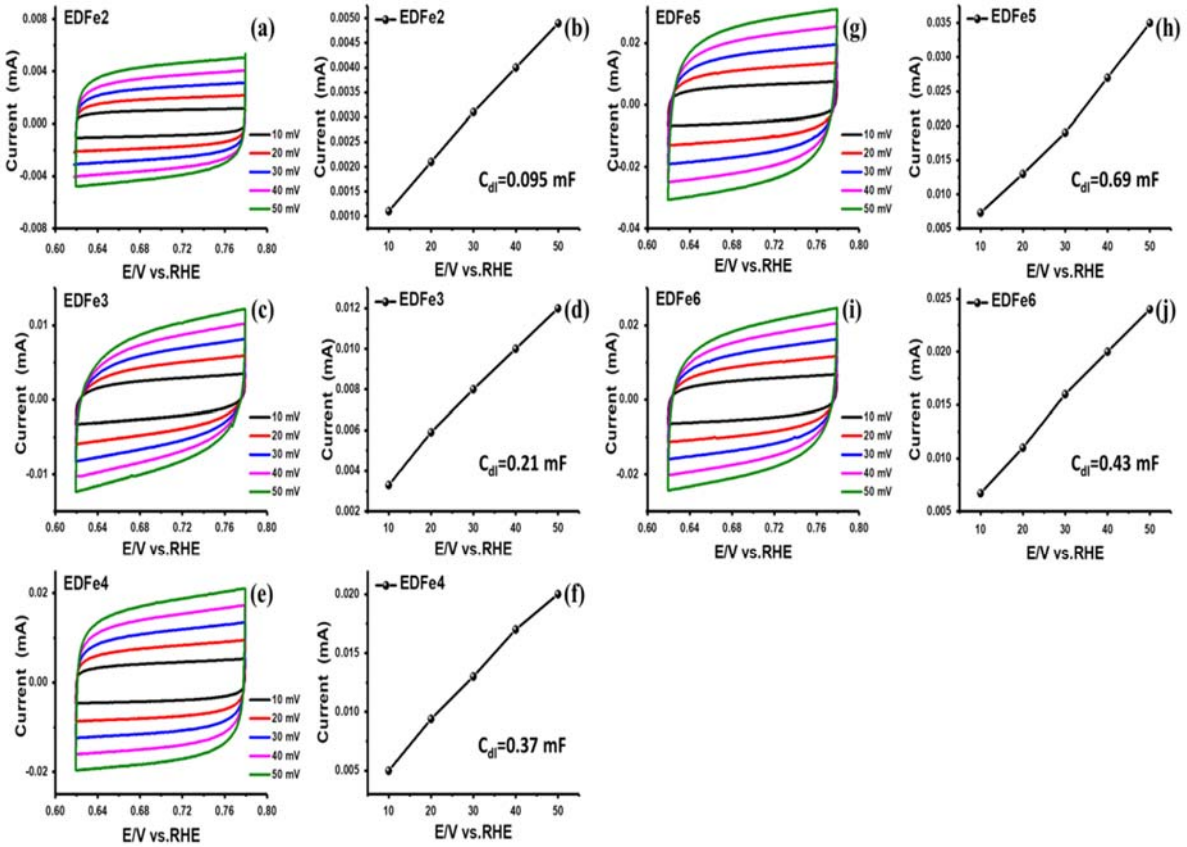

Figure S10. Cyclic voltammetry (CV) profiles of (a) EDFe2, (c) EDFe3, (e) EDFe4, (g) EDFe5 and (i) EDFe6, and electrochemical double layer capacitance (C_{dl}) estimations determined for (b) EDFe2, (d) EDFe3, (f) EDFe4, (h) EDFe5, and (j) EDFe6.

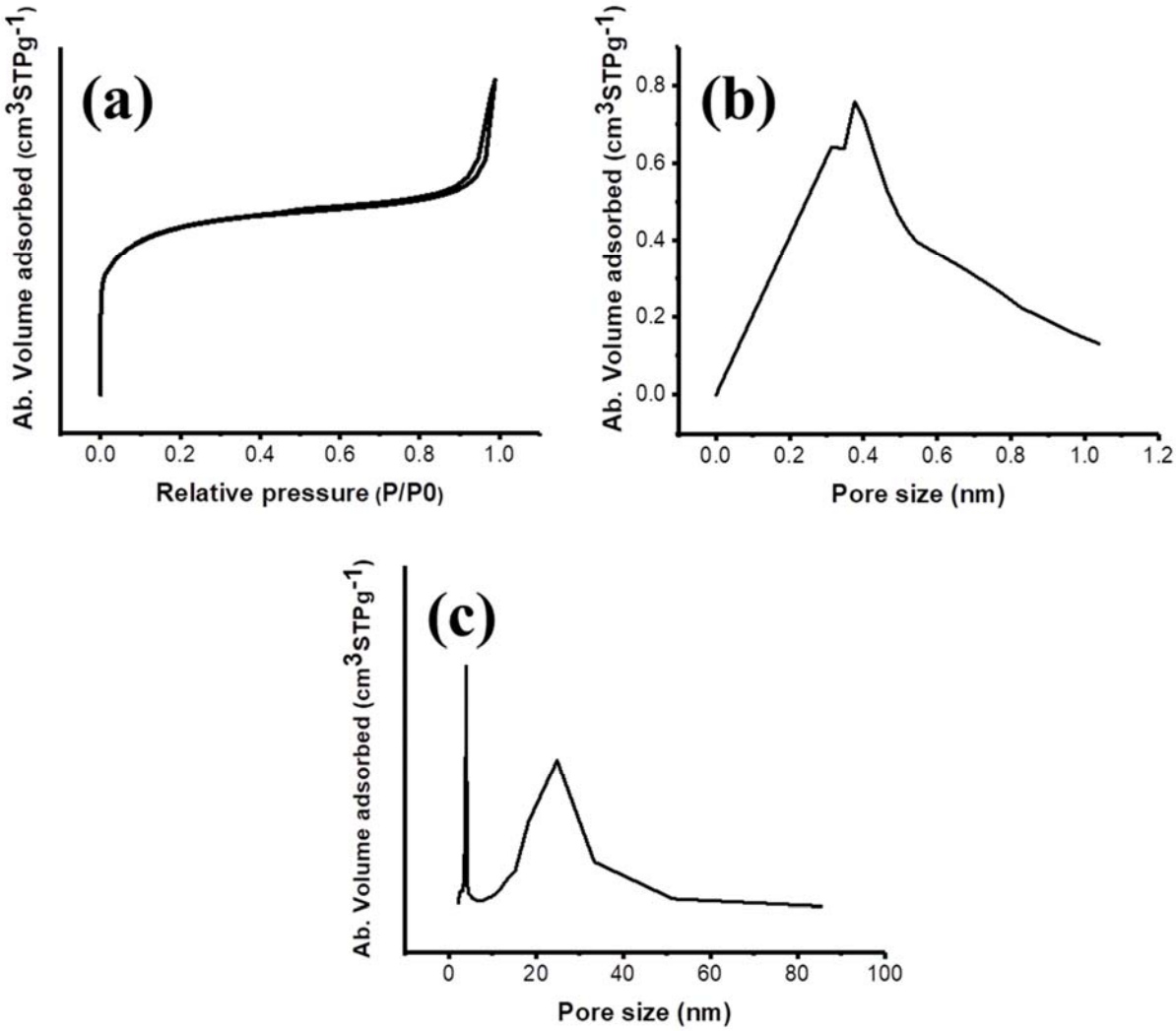

Figure S11. (a) Nitrogen adsorption-desorption isotherms, (b) the corresponding micropore size distribution curve obtained from the H–K method and (c) the corresponding pore size distribution curve obtained from the BJH method for LEDFe5.

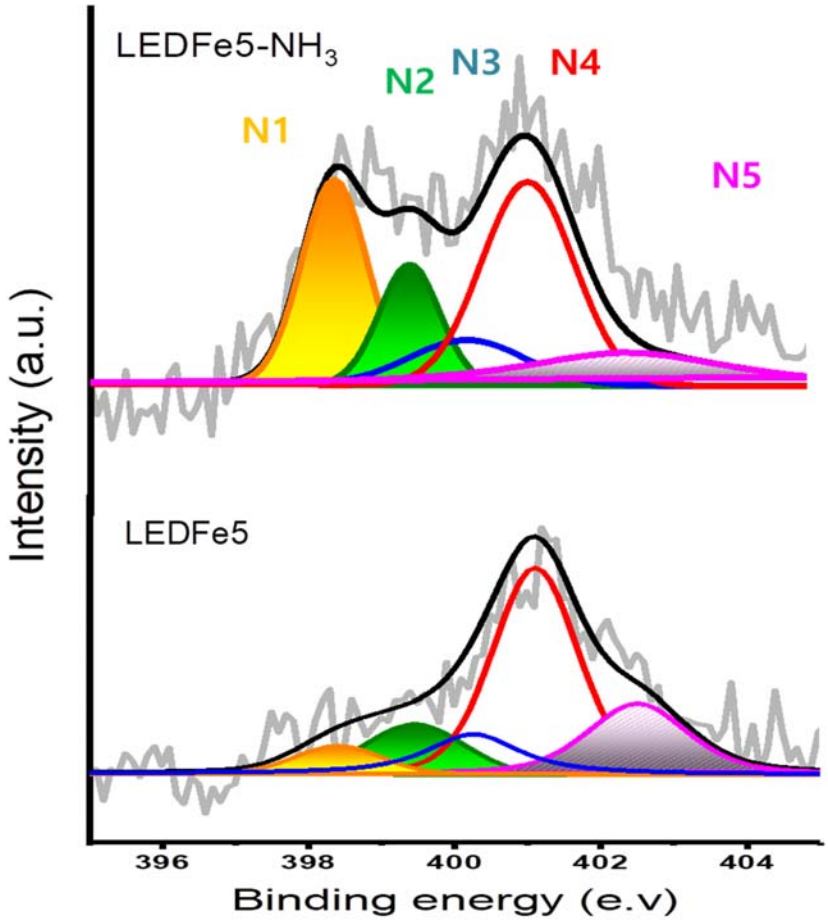

Figure S12. Deconvolution of N 1s XPS spectra of LEDFe5 and LEDFe5-NH_3 catalysts.

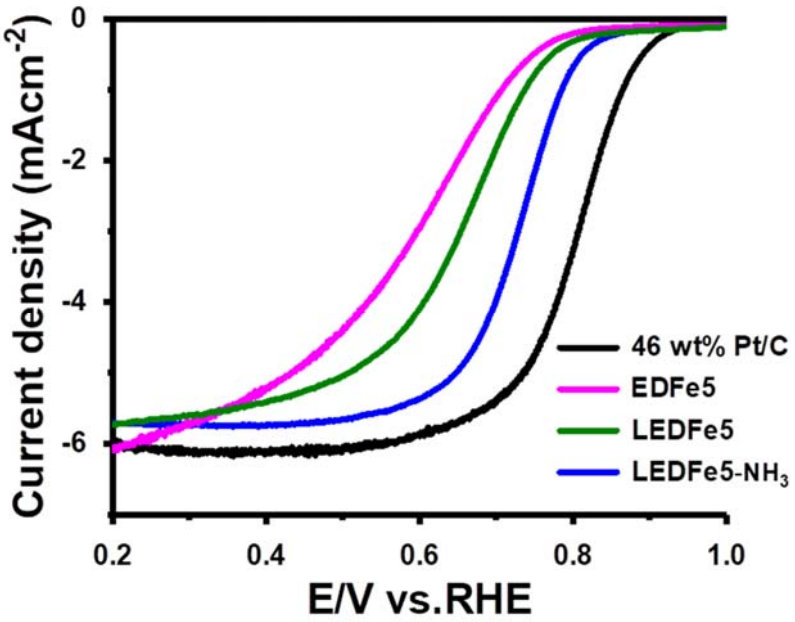

Figure S13. LSV curves of EDFe5, LEDFe5 and LEDFe5-NH_3 catalysts compared with commercial Pt/C.

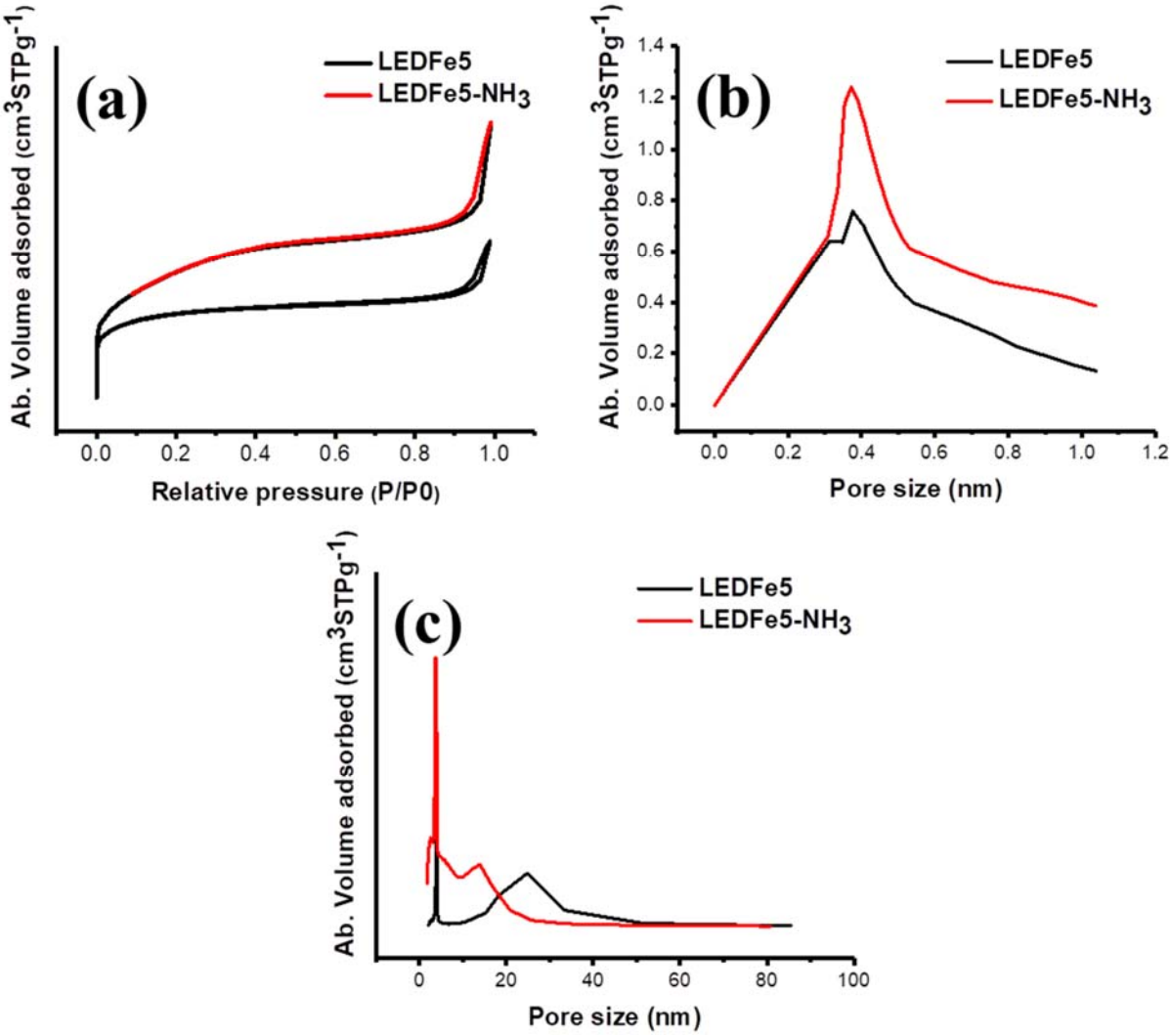

Figure S14. (a) Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves for LEDFe5 and LEDFe5-NH_3 catalysts obtained from (b) H-K and (c) BJH methods, respectively.

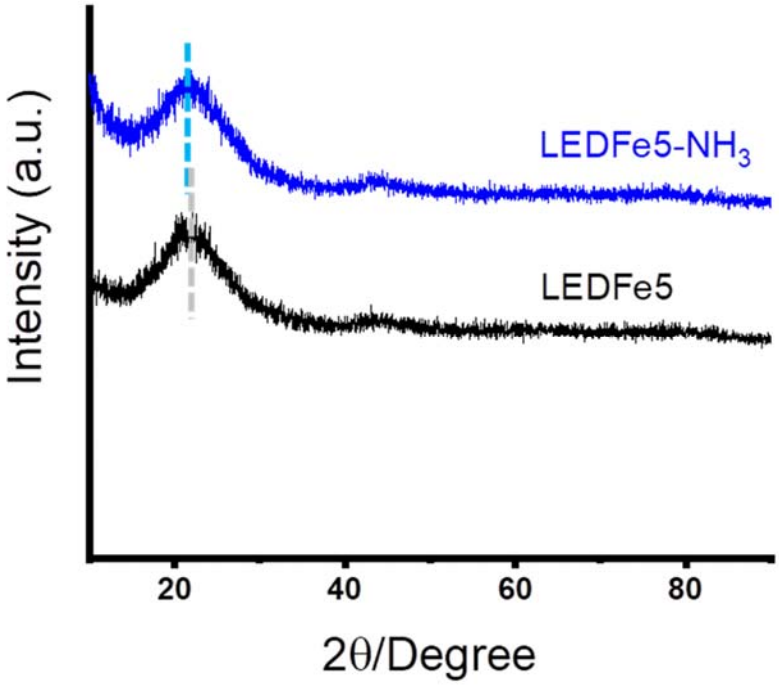

Figure S15. XRD patterns of LEDFe5 and LEDFe5-NH_3 catalysts.

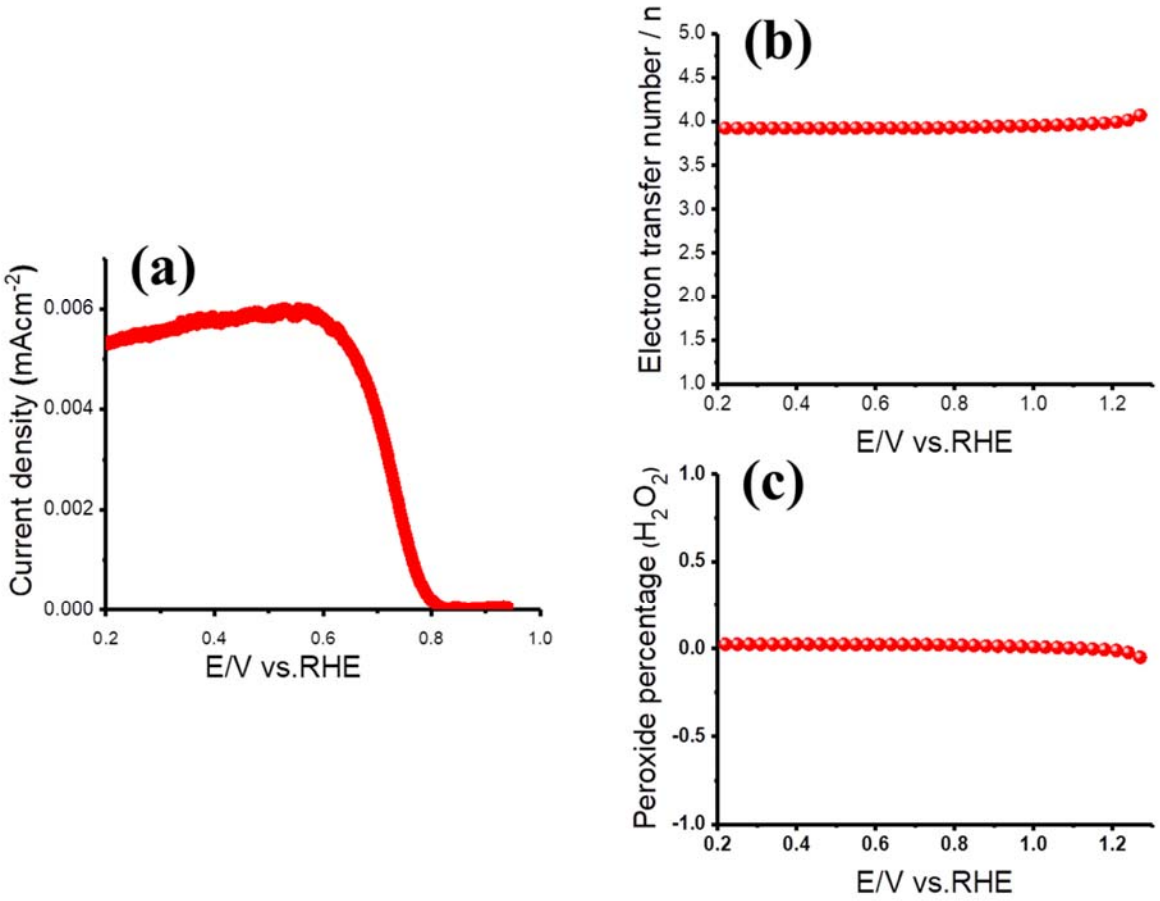

Figure S16. (a) Ring current and (b) electron transfer number (n) and (c) H_2O_2 production of LEDFe5-NH_3 catalyst.

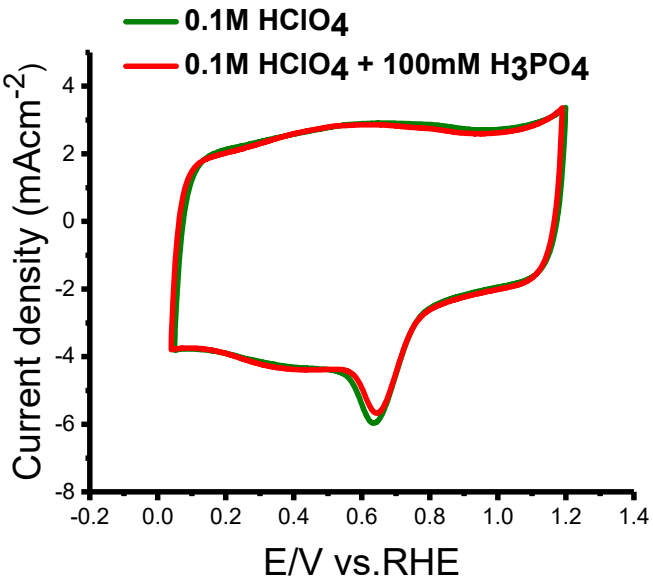

Figure S17. CV patterns of LEDFe5-NH_3 in O_2-saturated 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 100 mM H_3PO_4, respectively.

Table S1. Synthesis classification for all the prepared samples.

Sample	Na-EDTA (g)	$FeCl_3$ (g)	Ludox HS-40 (g)	N_2 (900 °C)	NH_3 (900 °C)
EDFe2	5	2	---	2h	---
EDFe3	5	3	---	2h	---
EDFe4	5	4	---	2h	---
EDFe5	5	5	---	2h	---
EDFe6	5	6	---	2h	---
LEDFe5	5	5	1	2h	---
LEDFe5-NH_3	5	5	1	2h	1h

Table S2. Physical characteristics by nitrogen sorption data for various EDTA-Fe based carbon catalysts.

Sample	BET total surface area (m^2g^{-1})	Micropore surface area (m^2g^{-1})	Mesoopore surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	micropore volume (cm^3g^{-1})	mesopore volume (cm^3g^{-1})
EDFe2	49	2.5	46.5	0.000135	------	------
EDFe3	106	68.6	37.4	0.31	0.28	0.03
EDFe4	524	435.7	88.3	0.49	0.31	0.18
EDFe5	684	592.6	91.4	0.61	0.39	0.22
EDFe6	658	583	75	0.57	0.35	0.22
LEDFe5	1094	896	198	0.84	0.47	0.37
LEDFe5-NH_3	1582	1211	371	1.46	0.87	0.59

Table S3. Surface element contents (at.%) obtained from XPS analyses for different catalysts.

Sample	C 1s	O 1s	N 1s	Fe 2p
EDFe2	93.83	5.43	0.70	0.04
EDFe3	86.56	10.97	2.37	0.1
EDFe4	84.87	12.28	2.69	0.16
EDFe5	83.92	13.1	2.76	0.22
EDFe6	86.91	10.88	2.09	0.12
LEDFe5	83.96	13.06	2.74	0.24
LEDFe5-NH_3	87.95	8.12	3.67	0.26

Table S4. Electrochemical single cell performance of Fe-N-C type catalysts in HT-PEMFC conditions.

Sample	Maximum power density (mW cm^{-2})	Current density @0.7V (mA cm^{-2})	Operating temperature (°C)	Catalyst loading (mg cm^{-2})	Absolute Pressure (bar)	Reference
LEDFe5-NH_3	**260**	**78**	**150**	**3.8**	**2.5**	**Present work**
Fe/N/C (5+12 nm)	17*	14*	150	21	1.0	(1)
BP-FeNC	185*	32*	160	7.8	1.0	(2)
FePhen@ MOF-ArNH_3	-§	129*	200	2	2.45	(3)
FeSA-G	276	62*	160	3.9	1.0	(4)
NCMI	-§	34*	160	2	2.5	(5)

* These values are not directly given in the papers and thus obtained by digging the I-V polarization curves or calculated by the data provided.

§ The I-power density curves are not given in corresponding reference.

References

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