Electronic Supplementary Information

Iron Phosphide Doped-porous Carbon as an Efficient Electrocatalyst for Oxygen Reduction Reaction

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Electrochemistry

Oxygen reduction reaction (ORR) in an alkaline electrolyte is expected to proceed via the combination of two reaction pathways, a two-step $2e^-$ and a single-step $4e^-$ reactions, as shown below:

A direct four-electron pathway: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (1)

A two-step two-electron pathway: $O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$ (2)

$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^-$ (3)

The first reaction pathway (eq.1) is kinetically fast and ensures higher efficiency as appose to the two-step two-electron reaction pathway (eq.2 and 3).

ORR in an acidic electrolyte proceeds via the combination of two reaction pathways, a two-step $2e^-$ and a single-step $4e^-$ reactions, as shown below:

A direct four-electron pathway: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (4)

A two-step two-electron pathway: $O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$ (5)

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ (6)

$2H_2O_2 \longrightarrow 2H_2O + O_2$ (7)

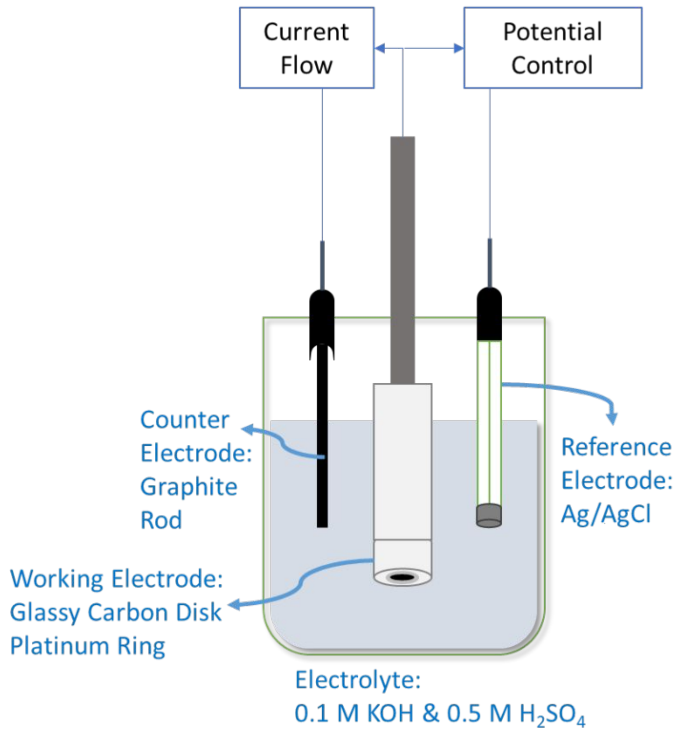
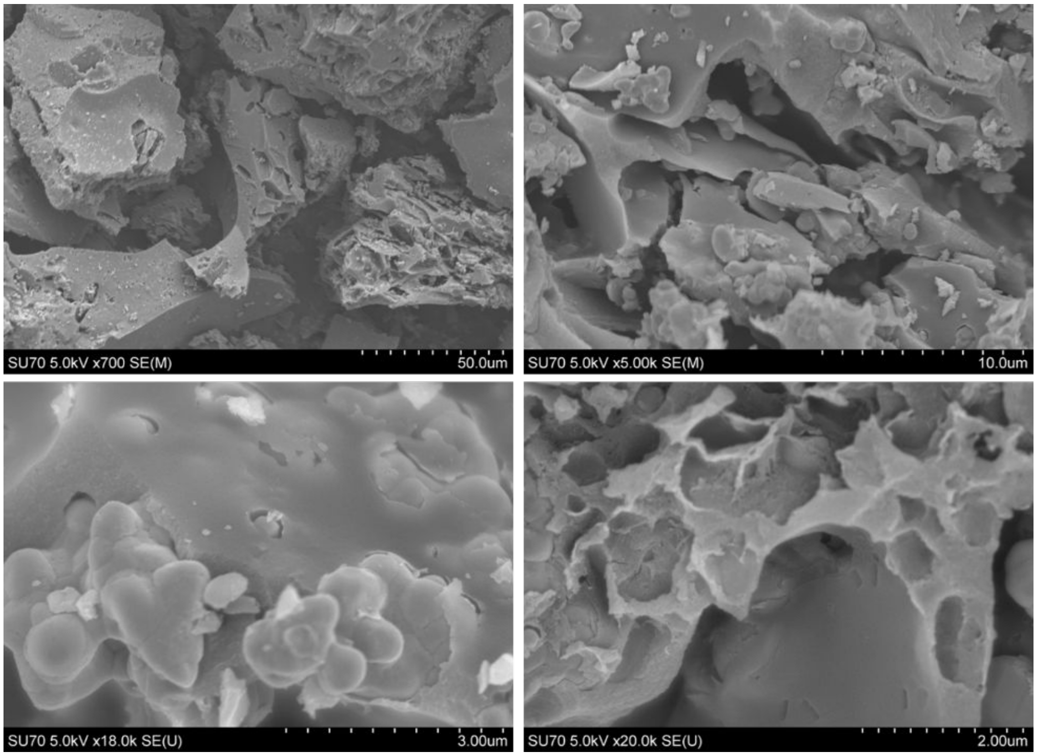


Figure S1. Schematic of an alkaline and acidic half-cell electrochemistry setup.

Surface Morphology

(a)



(b)

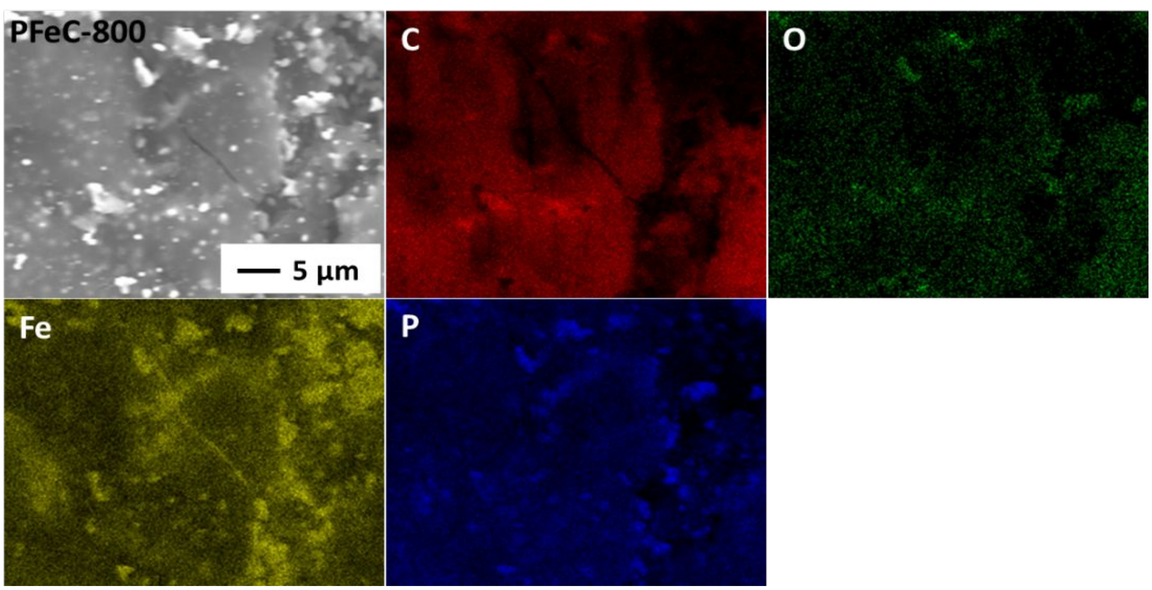
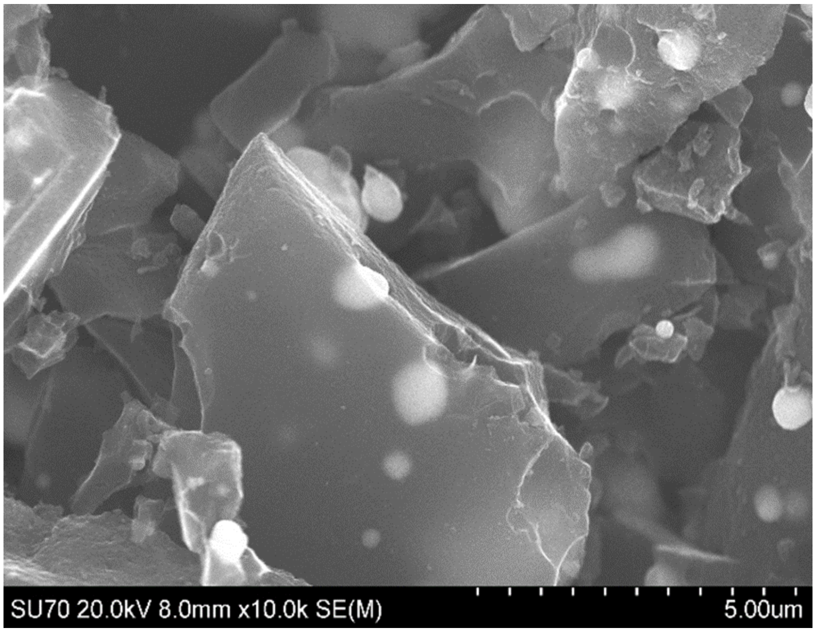


Figure S2. (a) SEM images (b) EDX elemental mapping of PFeC-800.

(a)



(b)

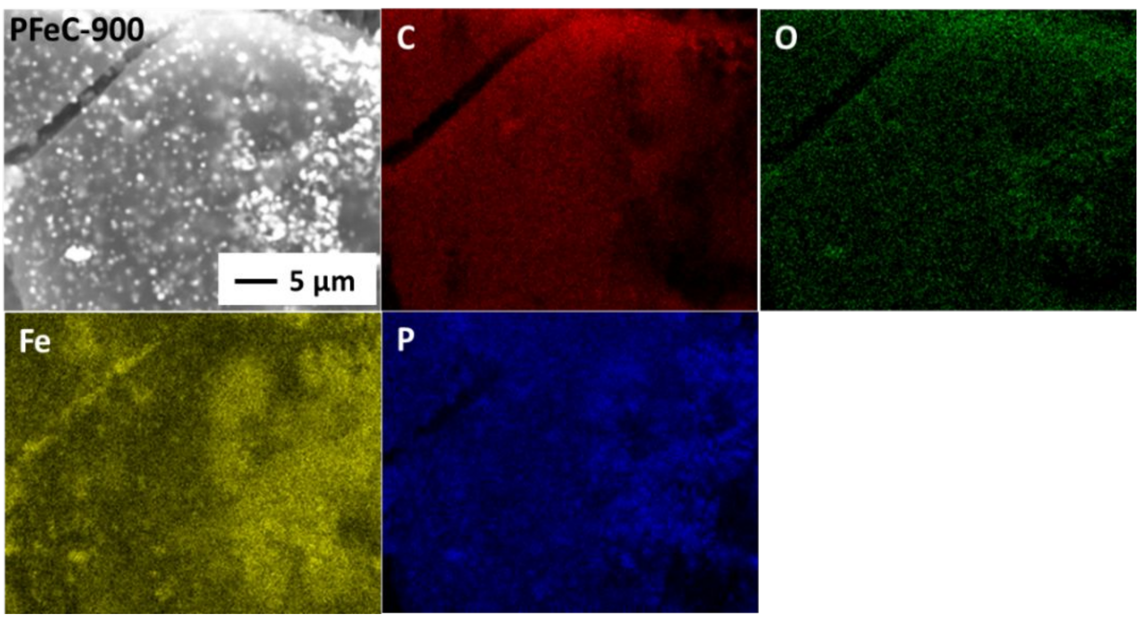


Figure S3. (a) SEM image of PFeC-900 without platinum sputter coating (b) EDX elemental mapping of PFeC-900.

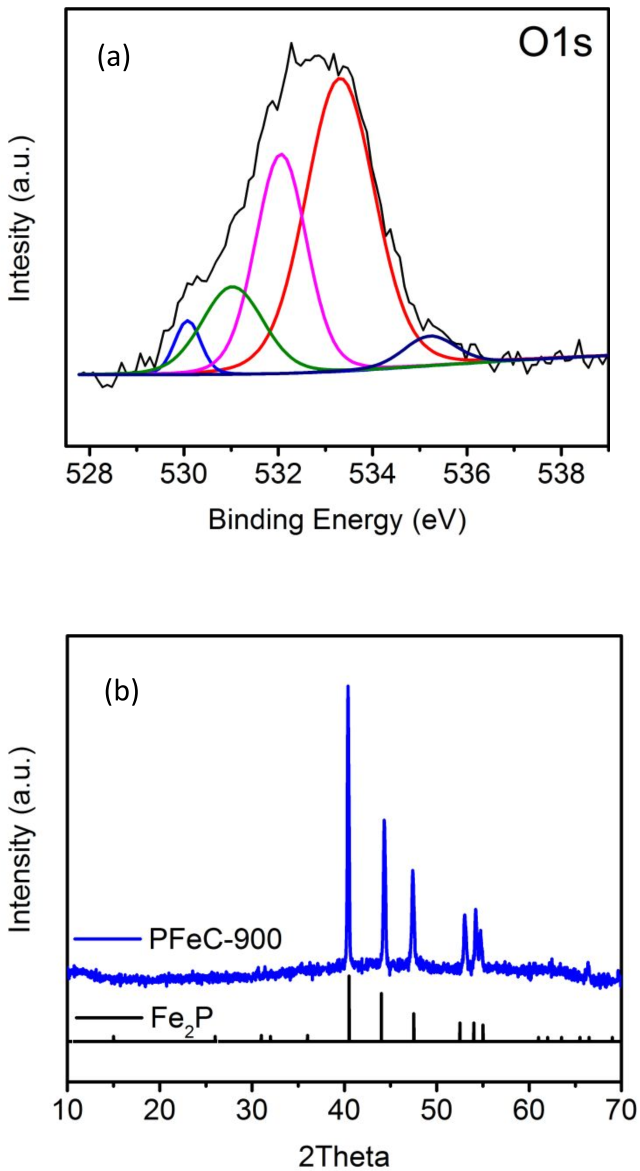


Figure S4. (a) Deconvolution O 1s spectra for PFeC-900, (b) XRD pattern of PFeC-900 and Fe_2P (JCPDS: 51-0942).

Scherrer equation: $B(2\theta) = \frac{k\lambda}{L\cos\theta}$ (8)

Where Scherrer constant k is 0.9, λ is 0.15418 nm.

(a)

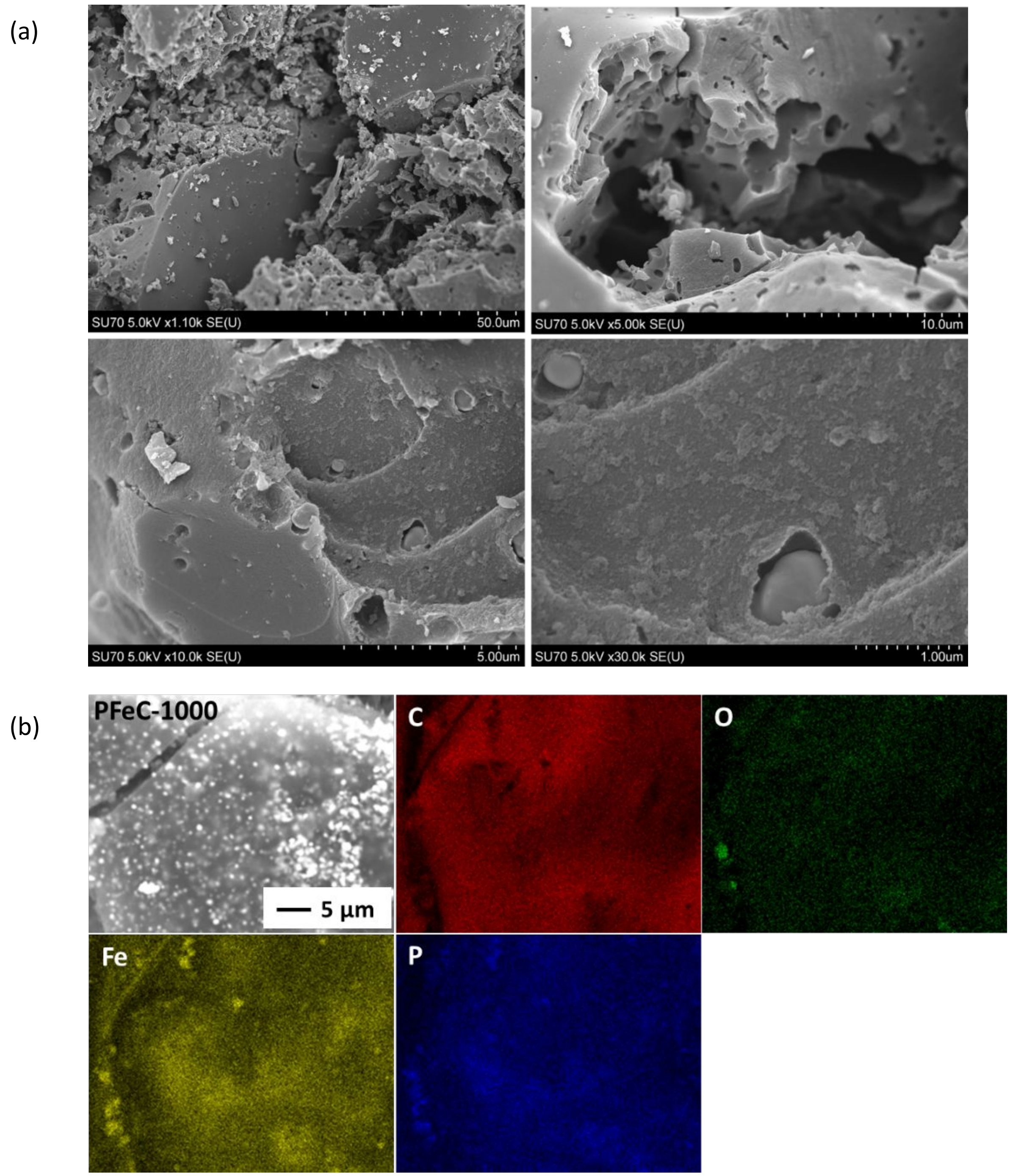
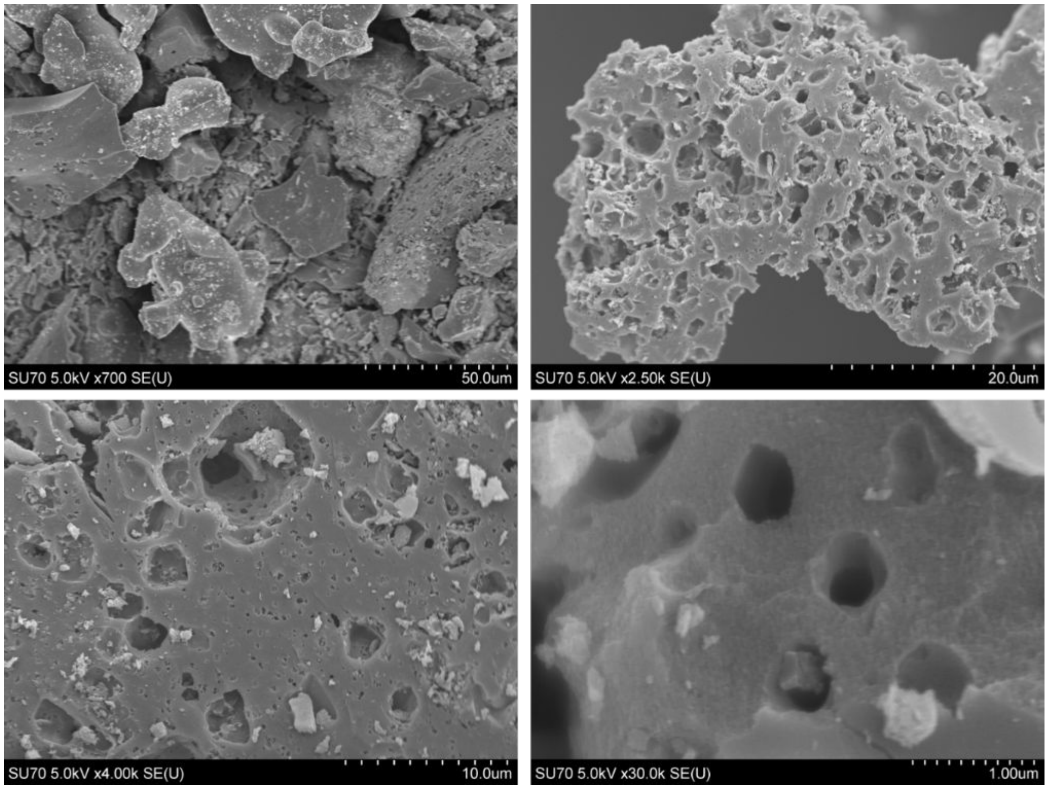


Figure S5. (a) SEM images (b) EDX elemental mapping for PFeC-1000.

(a)



(b)

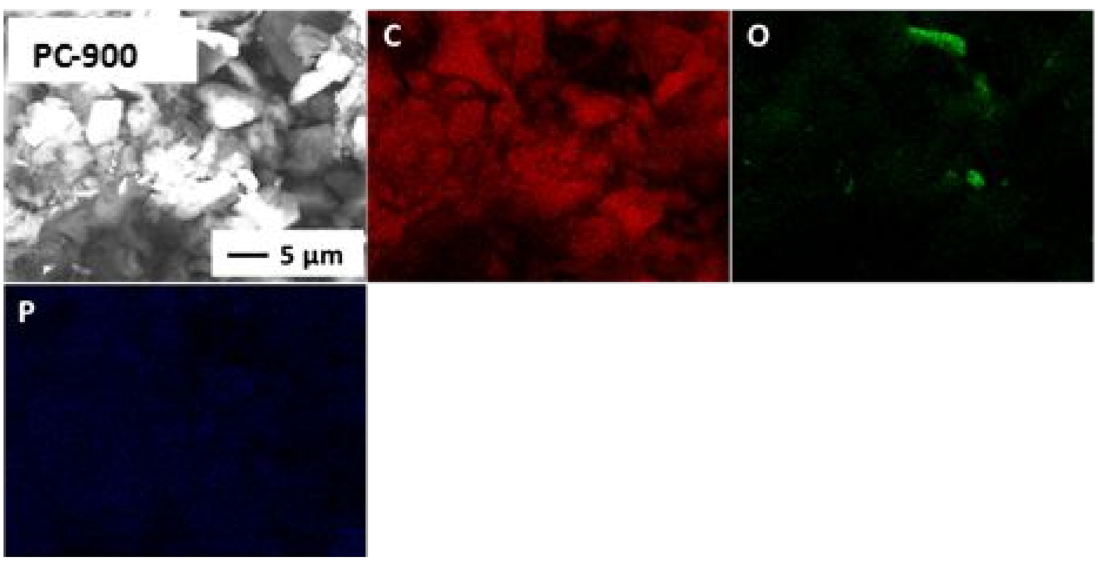


Figure S6. (a) SEM images (b) EDX elemental mapping for PC-900.

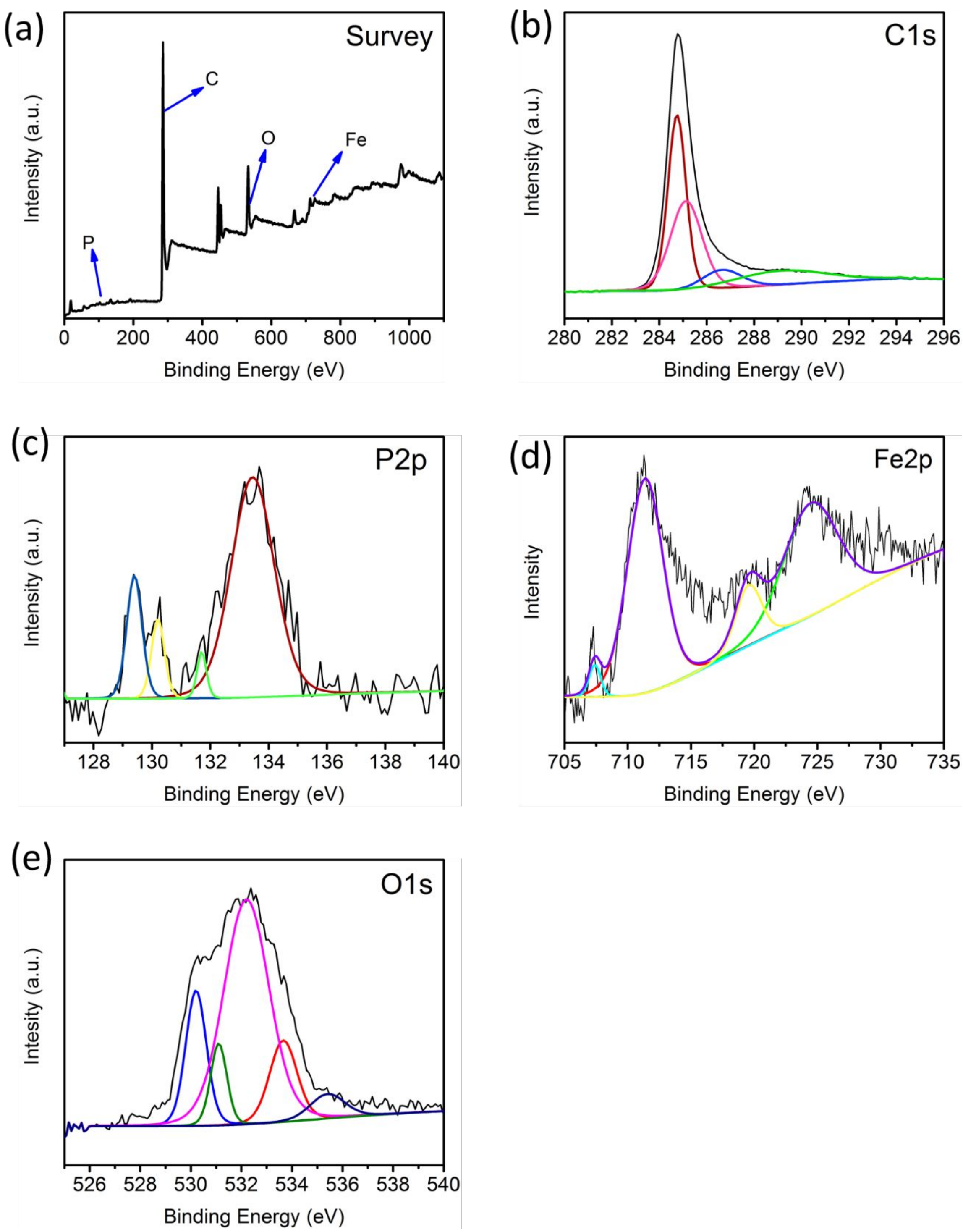


Figure S7. (a) Survey spectra of PFeC-800 (b) Deconvoluted C 1s spectra (c) Deconvoluted P 2p spectra (d) Deconvoluted Fe 2p spectra (e) Deconvoluted O 1s spectra.

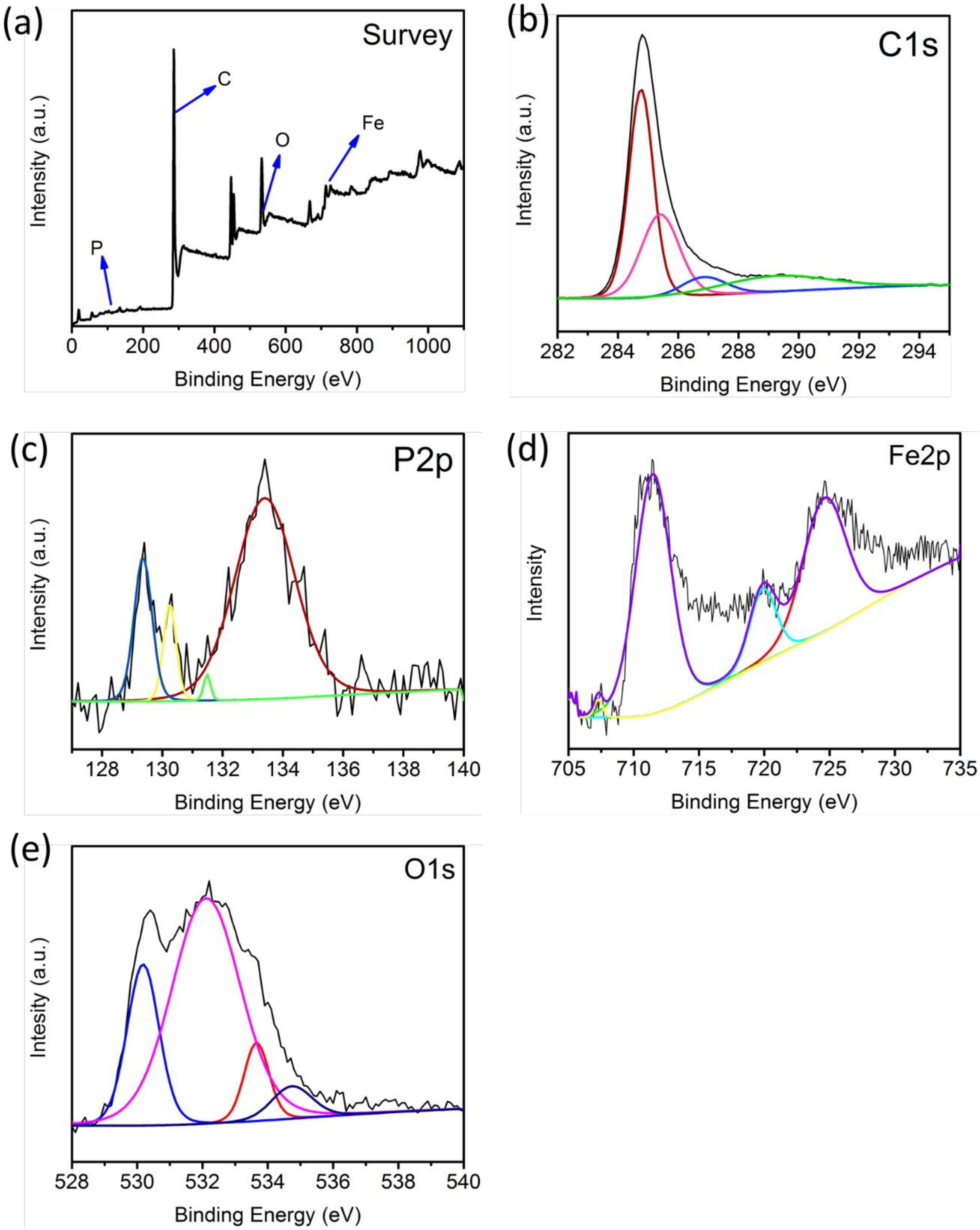


Figure S8. (a) Survey spectra of PFeC-1000 (b) Deconvoluted C 1s spectra (c) Deconvoluted P 2p spectra (d) Deconvoluted Fe 2p spectra (e) Deconvoluted O 1s spectra.

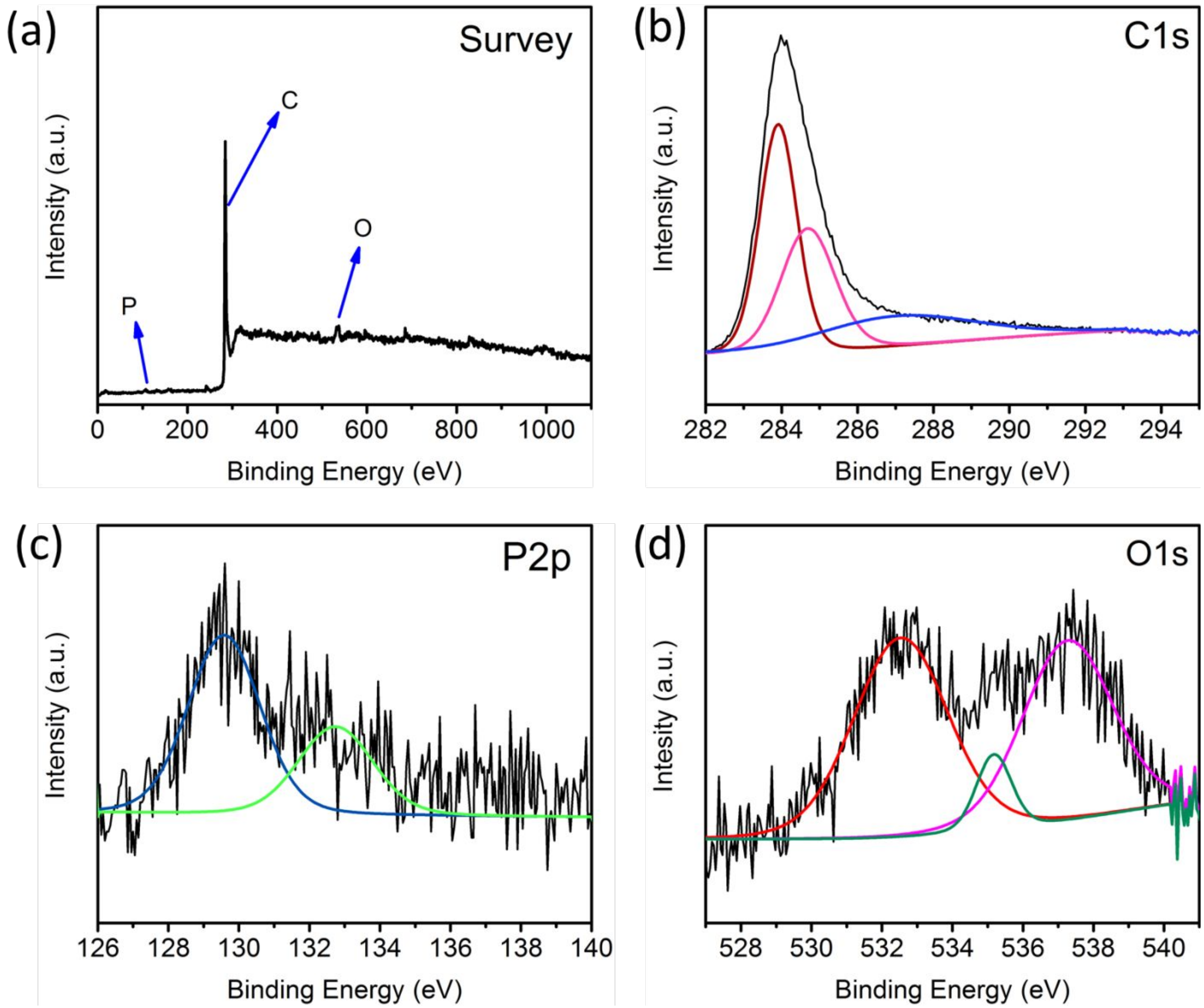


Figure S9. (a) Survey spectra of PC-900 (b) Deconvoluted C 1s spectra (c) Deconvoluted P 2p spectra (d) Deconvoluted O 1s spectra.

Table S1. Surface and bulk chemical composition of PFeC-800, 900, 1000 and PC-900 collected from XPS, EDX and the iron weight percent collected from ICP-OES.

Sample	C (At%) XPS/EDX	O (At%) XPS/EDX	P (At%) XPS/EDX	Fe (At%) XPS/EDX/ICP
PFeC-800	89.2/86.6	9.2/1	1.2/2.9	0.4/9.5/20(wt%)
PFeC-900	90.6/84	8/2.1	1.1/4.1	0.4/9.8/22(wt%)
PFeC-1000	88.9/88.4	9.5/1.9	1.1/3.1	0.5/6.6/30(wt%)
PC-900	95.4/92	3.6/7	1/1	0/0/0.5(wt%)

Electrochemistry

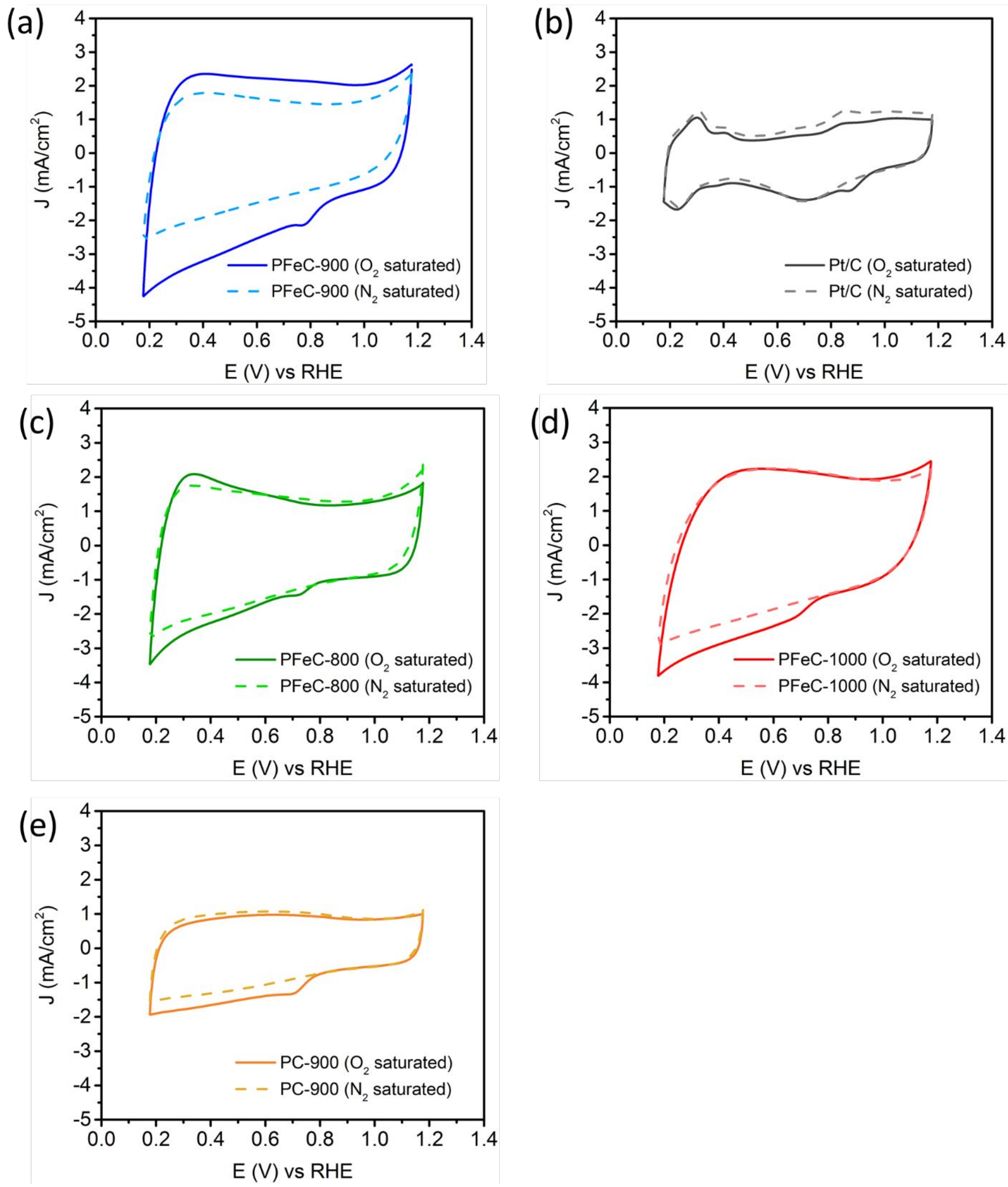


Figure S10. The CV of (a) PFeC-900 and (b) Pt/C (c) PFeC-800, (d) PFeC-1000 (e) PC-900 in N_2 and O_2 saturated 0.1 M KOH using RDE at scan rate of 50 mV s^{-1}

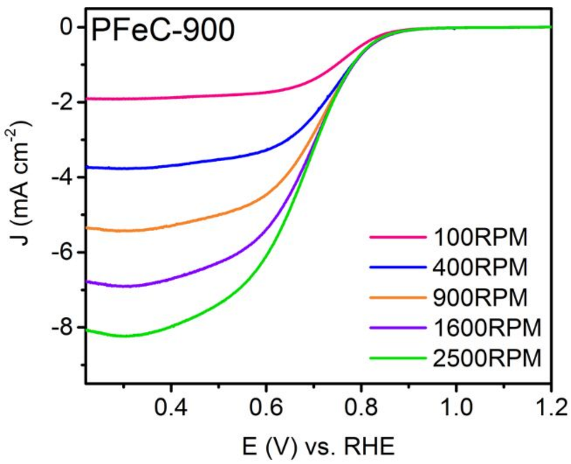


Figure S11. The polarization curves for PFeC-900 in O_2 saturated 0.5 M H_2SO_4 at rotation rates 100-2500 rpm

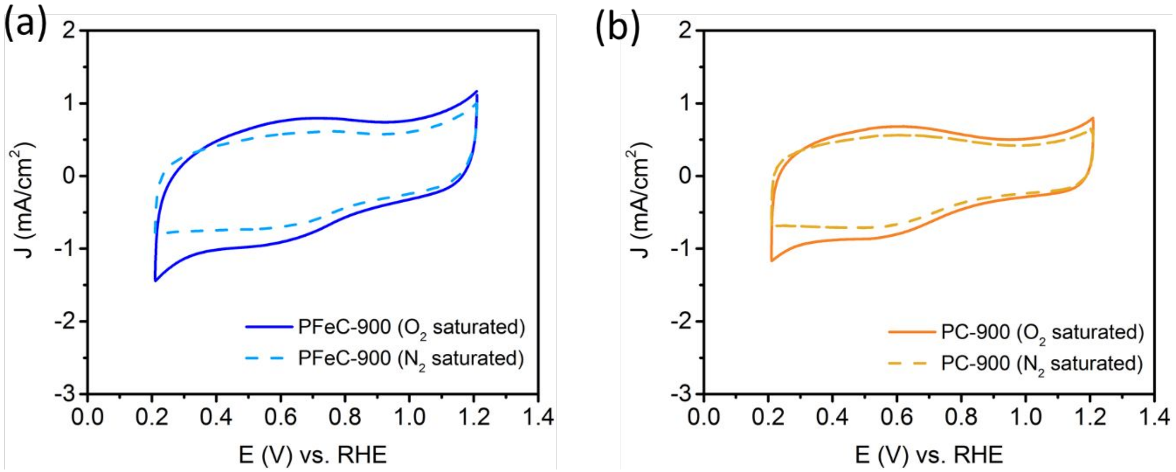


Figure S12. The CV of (a) PFeC-900 and (b) Pt/C in N_2 and O_2 saturated 0.5 M H_2SO_4 using RDE at scan rate of 50 mV s^{-1}

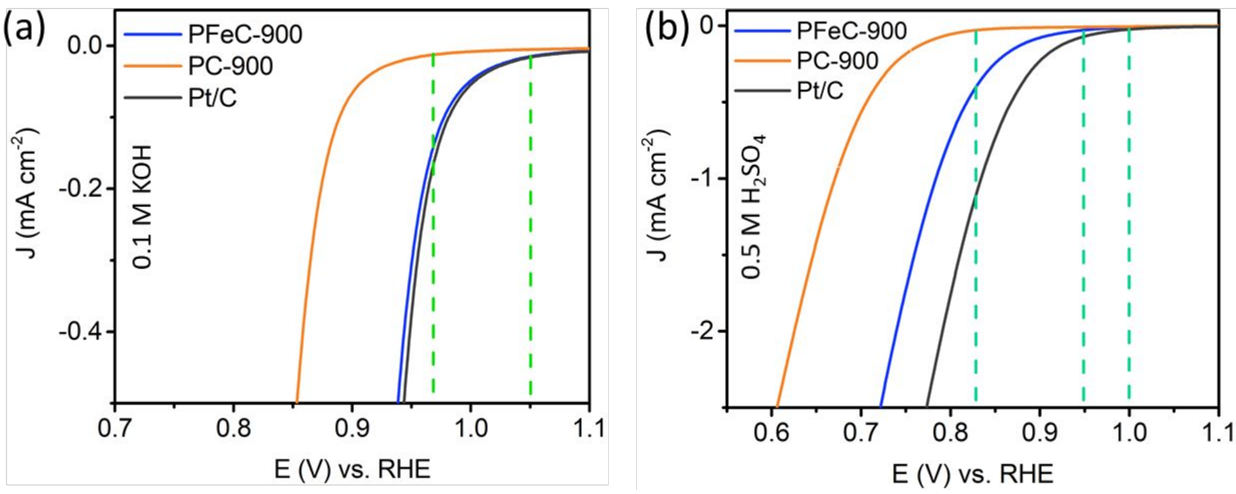


Figure S13. Comparision between onset potentials in O_2 saturated (a) 0.1 M KOH and (b) 0.5 M H_2SO_4 using RDDE at 1600 rpm and scan rate of 10 mV s^{-1}.

Table S2. Comparison of preparation methods and ORR activities of reported phosphorus-doped, Iron phosphorous-doped electrocatalysts with PFeC-900 and PC-900 in 0.1M KOH (Al.) medium or 0.1 M $HClO_4$ / 0.5 M H_2SO_4 (Ac.). (If the exact values are not mentioned in the paper, an estimated number from the corresponding graphs is used for this Table.)

Catalyst (given name)	Electrolyte	Onset Potential catalyst/Pt/C (V vs. RHE)	Half wave Potential catalyst/Pt/C (V vs. RHE)	Limiting Current Density (mA cm^{-2})	Electron Transfer Number, n	Surface Area (m^2g^{-1})	Reference
PFeC-900	Al.	1.01/1.04	0.88/0.90	-7.29 RRDE	3.97	967	This work
PFeC-900	Ac.	0.95/1.0	0.71/0.77	-6.61 RRDE	3.98	967	
PC-900	Al.	0.95/1.04	0.79/0.88	-8.51 RRDE	3.88	1137	
PC-900	Ac.	0.81/1.0	0.6/0.77	-6.22 RRDE	3.5	1137	
Fe-P-C	Al.	0.95/0.97	~ 0.78	-5.01 RRDE	3.61	1371	1
Fe-P-C	Ac.	0.84/~0.97	~ 0.6	-5.80 RRDE	3.8	1371	
GPFe	Al.	0.93/0.96	~ 0.82	-6.72 RRDE	3.6	612.15	2
GPFe	Ac.	0.62/0.84	~ 0.5/0.8	-4.11 RRDE	3.84	612.15	
Fe_2P(3nm) @BC	Al.	0.96/0.97	0.82/	-5.18 RDE	3.9	314.9	3
Fe_2P(3nm) @BC	Ac.	0.78/0.89	0.65/0.72	4.1 RDE	3.7	314.9	
FeP@PNC-900	Al.	0.92/0.92	0.84/0.82	-5.50 RDE	4.1	724	4
P(Co)-C	Al.	~ 0.85/0.97	~ 0.75/0.82	~ -6.1 RRDE	3.79	1349	5
POMC-3	Al.	~ 0.87/0.92	0.74/0.78	~ -5.50 RDE	3.91	1182	6
FeP@NPC	Al.	ΔV= 15 mV	ΔV= 15 mV	-5.85 RDE	4	381	7
P-doped graphite/GC	Al.	~0.87/0.98	~0.72/0.85	-5.50 RDE	3	3986	8

References

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