Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic supplementary information

Fe-N-functionalized carbon electrocatalyst derived from zeolitic imidazolate framework for oxygen reduction: Fe and NH_3 treatment effects

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Reagent and chemicals

Zinc (II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, > 98.0%), 2-methylimidazole ($C_4H_6N_2$, 99%) and iron (III) acetylacetonate ($Fe(acac)_3$, 97%) were purchased from Sigma-aldrich (U.S.A.). Methanol (CH_3OH, 99.5%) and ethanol (CH_3CH_2OH, 99%)) were purchased from Samchun Pure Chemical Co., Ltd. (Korea). Ultrapure water (resistance > 18 $M\Omega cm^{-1}$) was used in all experiments.

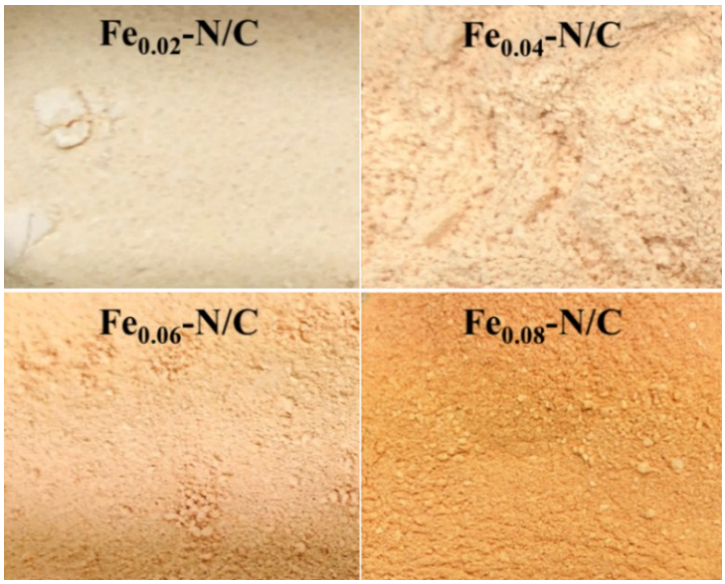

Fig. S1 Photographic images of Fe_x-N/C (x = 0.02, 0.04, 0.06, and 0.08) precursors, which correspond to the different mixtures of $Fe(acac)_3$ and ZIF-8.

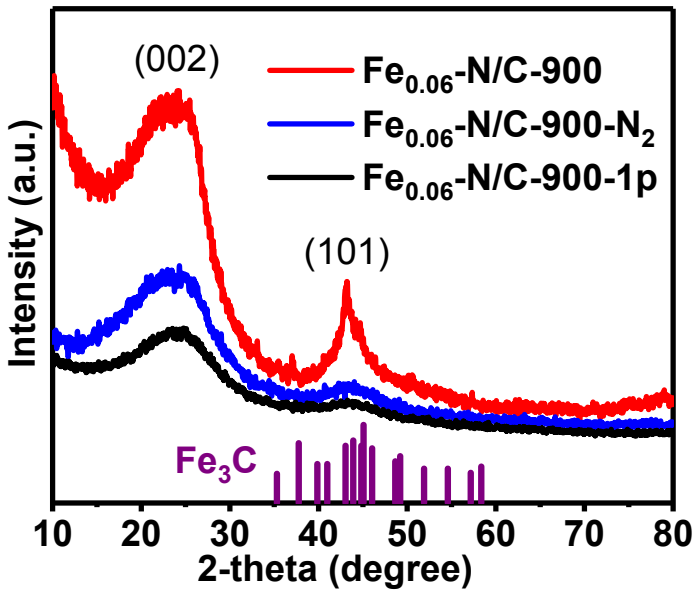

Fig. S2 XRD spectra of $Fe_{0.06}$-N/C-900-1p, $Fe_{0.06}$-N/C-900-N_2, and $Fe_{0.06}$-N/C-900.

Table S1 Physicochemical properties of all the as-prepared samples.

Samples	S_{BET}(m^2/g)	S_{micro} (m^2/g)	S_{micro}/S_{BET}	V (cm^3/g)	I_D/I_G	I_{AM}/I_G
$Fe_{0.06}$-N/C-900-N_2	1094.0	960.6	87.8%	0.57	0.97	0.71
$Fe_{0.02}$-N/C-900	2313.4	1426.2	61.6%	1.40	0.90	0.37
$Fe_{0.04}$-N/C-900	1498.5	831.6	55.5%	1.23	0.98	0.41
$Fe_{0.06}$-N/C-900	1288.7	826.2	64.1%	0.98	1.02	0.58
$Fe_{0.08}$-N/C-900	1186.4	891.1	75.1%	0.87	0.91	0.52

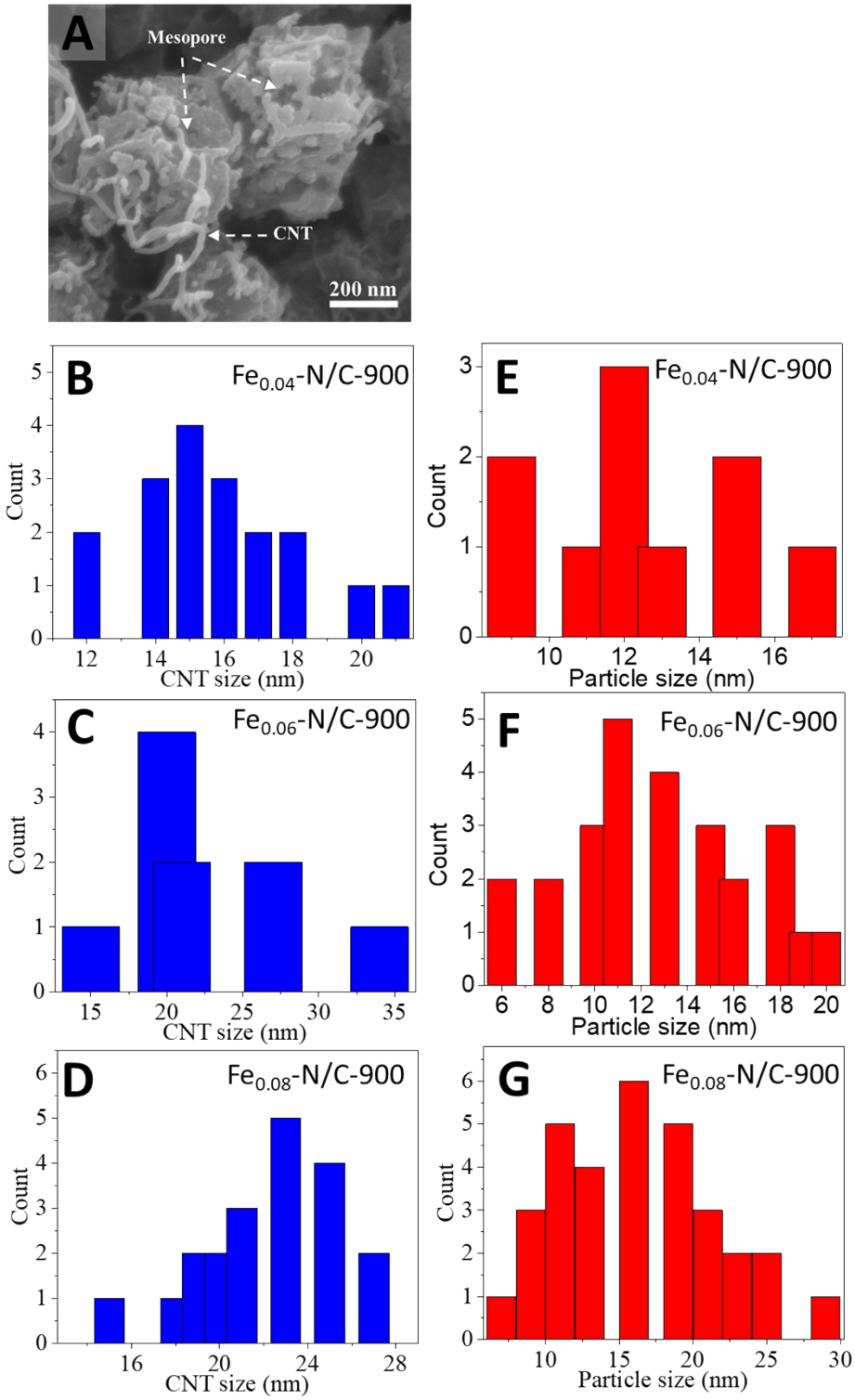

Fig. S3 A) SEM image of $Fe_{0.06}$-N/C-900 showing the development of pores and N-doped CNTs. B-D) size distribution histograms of CNTs from SEM images in Fig. 3B-D and E-G) particle size distribution from TEM images in Fig. 3F-H for $Fe_{0.04}$-N/C-900, $Fe_{0.06}$-N/C-900, and $Fe_{0.08}$-N/C-900, respectively.

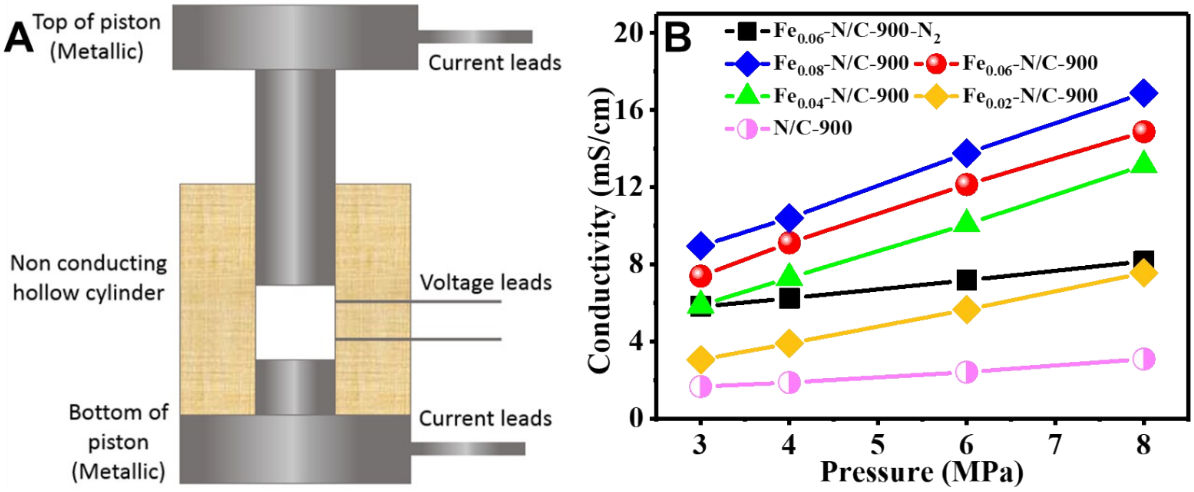

Fig. S4 A) Electrical conductivity cell with four-probe configuration, and B) electrical conductivity vs pressure profiles of Fe_x-N/C-900 and $Fe_{0.06}$-N/C-900-N_2.

Table S2 Atomic composition obtained from XPS spectra for the as-prepared samples.

Samples	C 1s (at. %)	Fe 2p (at. %)	N 1s (at. %)	O 1s (at. %)
$Fe_{0.06}$-N/C-900-N_2	84.13	0.18	3.93	11.76
N/C-900	88.89	N/A	3.62	7.49
$Fe_{0.02}$-N/C-900	88.68	0.23	4.36	6.73
$Fe_{0.04}$-N/C-900	88.06	0.27	5.10	6.57
$Fe_{0.06}$-N/C-900	87.27	0.37	7.12	5.24
$Fe_{0.08}$-N/C-900	87.87	0.30	5.94	5.89

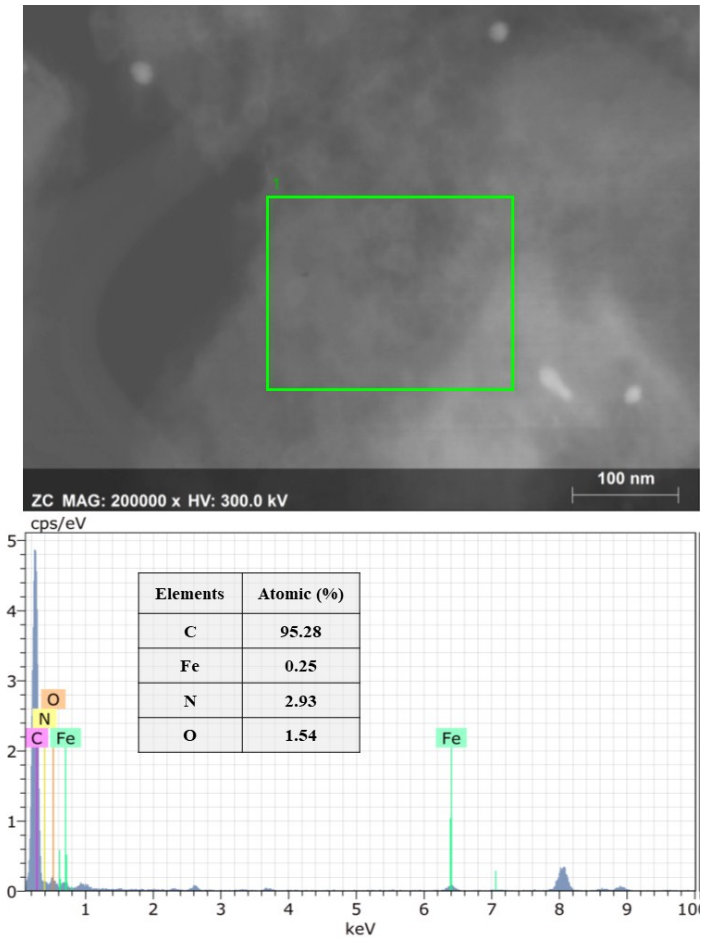

Fig. S5 STEM image and EDS spectrum of a selected area along with a table of elemental atomic percentage (inset) of $Fe_{0.06}$-N/C-900 catalyst.

Table S3 Summary of ORR activities of $Fe_{0.06}$-N/C-900 and recently reported non-precious Fe-N-C catalysts in acidic medium (electrode rotating speed 1600 rpm).

Materials	**Electrolyte**	**E_{onset} relative to Pt/C**	**$E_{1/2}$ relative to Pt/C**	**Current density at 0.15 V (vs. RHE) (mA/cm^2)**	**Ref.**
FeNC-20-1000	0.1 M $HClO_4$	Negative shift ~ 70 mV	Negative shift ~ 57 mV	6.20	[1]
C-Fe-Z8-Ar	0.1 M $HClO_4$	Negative shift ~ 70 mV	Negative shift ~ 40 mV	7.40	[2]
C-2PANI/PBA	0.5 M H_2SO_4	Negative shift ~ 150 mV	Negative shift ~ 100 mV	6.00	[3]
C-Z8Nc/FePc-900	0.1 M $HClO_4$	Negative shift ~ 50 mV	Negative shift ~ 50 mV	5.60	[4]
C-FeZIF-900-0.84	0.1 M $HClO_4$	Negative shift ~ 100 mV	Negative shift ~ 80 mV	5.70	[5]
5% Fe-N/C	0.5 M H_2SO_4	Negative shift ~ 157 mV	Negative shift ~ 39 mV	5.12	[6]
NH_3-$Fe_{0.25}$-N-C-900	0.1 M $HClO_4$	Negative shift ~ 110 mV	Negative shift ~ 100 mV	5.98	[7]
C-AFC© ZIF-8	0.1 M $HClO_4$	Negative shift ~ 80 mV	Negative shift ~ 36 mV	5.95	[8]
$Fe_{0.06}$-N/C-900	**0.1 M $HClO_4$**	**Negative shift ~ 39 mV**	**Negative shift ~ 33 mV**	**6.66**	**This Work**

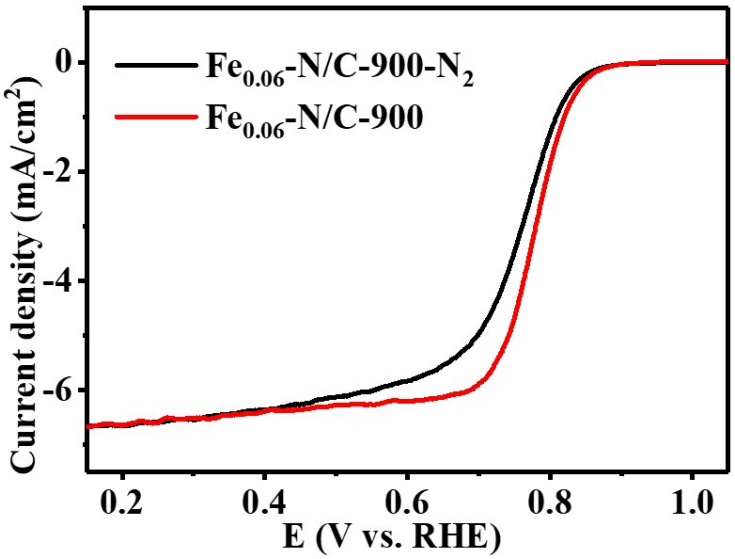

Fig. S6 LSV curves of $Fe_{0.06}$-N/C-900 and $Fe_{0.06}$-N/C-900-N_2 with rotation speed 1600 rpm at scan rate of 10 mV/s in O_2-saturated 0.1 M $HClO_4$.

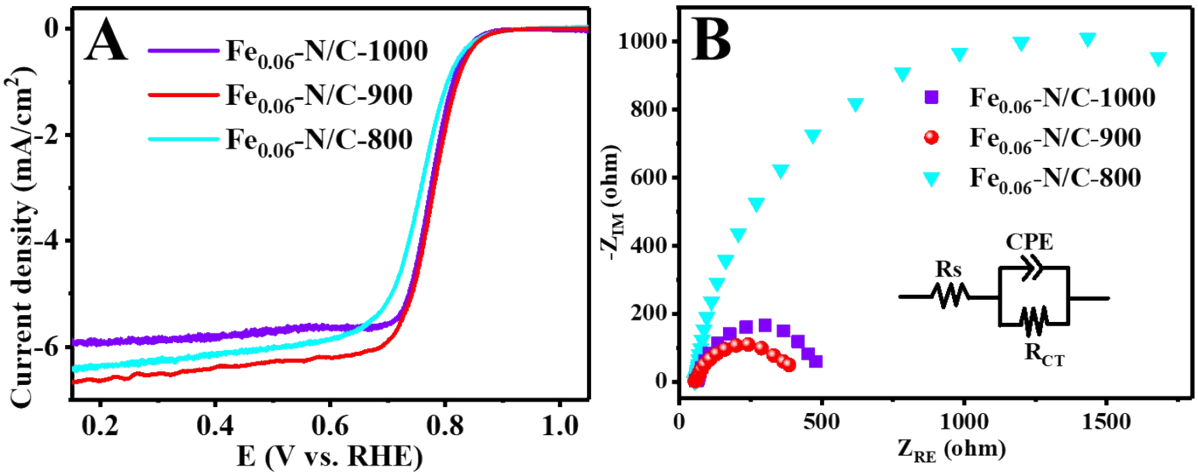

Fig. S7 A) LSV curves, and B) Nyquist plots (inset: equivalent circuits) of the $Fe_{0.06}$-N/C-800, $Fe_{0.06}$-N/C-900, and $Fe_{0.06}$-N/C-1000 prepared at different pyrolysis temperatures in O_2-saturated 0.1 M $HClO_4$.

Table S4 EIS parameters of $Fe_{0.06}$-N/C-T obtained from analysis of Nyquist plot.

Samples	R_S (Ω)	R_{CT} (Ω)	CPE ($mFs^{1/\alpha}$)
$Fe_{0.06}$-N/C-1000	55.6	445.8	3.53
$Fe_{0.06}$-N/C-900	57.4	345.3	4.31
$Fe_{0.06}$-N/C-800	56.5	2238.0	1.62

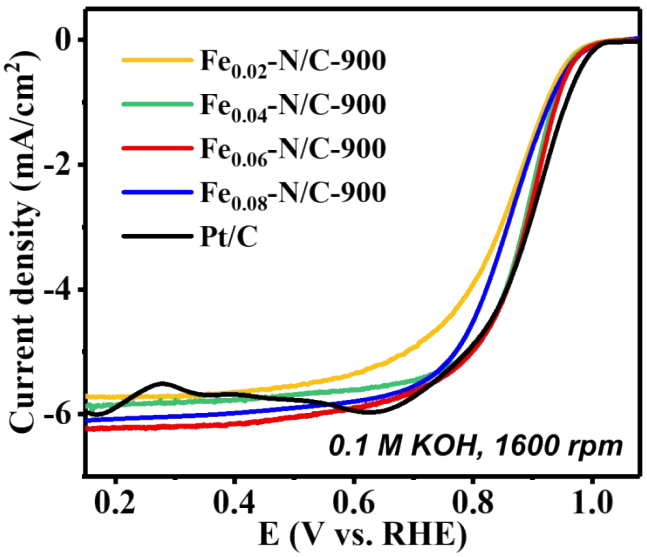

Fig. S8 LSV curves of as-prepared catalysts Fe_x-N/C-900 and Pt/C-TKK in O_2-saturated 0.1 M KOH.

Table S5 Single cell performances in H_2/O_2 PEMFC of $Fe_{0.06}$-N/C-900 and recently reported non-precious Fe-N-C catalysts.

Materials	**Precursors**	**Operation conditions: temperature, backpressure, cathode catalyst loading.**	**P_{max} (mW/cm^2)**	**I at 0.6 V (mA/cm^2)**	**Ref.**
py-Fe-FA/C	$FeCl_3$, vitamin B19, carbon Vulcan.	80 °C, 1 bar, 6 mg/cm^2	330	140	[9]
Fe-N-C	Iron (II) phthalocyanine with silica template.	60 °C, 3 bar , 2.5 mg/cm^2	105	70	[10]
Fe–N/CNN3	$Fe(ac)_2$, 2,4,6-Tris(2-pyridyl)-s-triazine.	60 °C, 2 bar, 2.6 mg/cm^2	121	40	[11]
Fe-NCB	$Fe(NO_3)_3$, nicarbazin, silica template.	80 °C, 1.5 bar, 4 mg/cm^2	500	520	[12]
FeCoTETA/C	$CoCl_2$, $FeCl_2$ triethylenetetramine, carbon black.	50 °C, 2 bar, 2 mg/cm^2	256	200	[13]
(CM+PANI)-Fe-C	$FeCl_3$, Cyanamide, Aniline	80 °C, 2 bar, 4 mg/cm^2	940	1100	[14]
$Fe_{0.06}$-N/C-900	**ZIF-8, $Fe(acac)_3$**	**80 °C, 2 bar, 3.5 mg/cm^2**	**503**	**564**	**This work**

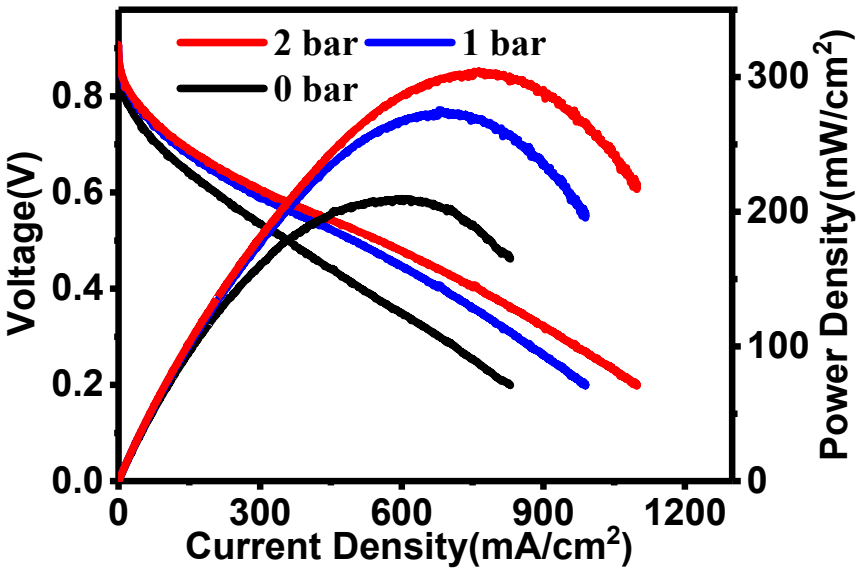

Fig. S9 H_2/air fuel cell polarization curves and corresponding power density at 80 °C with various backpressure from 0 to 2 bar (the cathode catalyst loading is 3.5 mg/cm^2, and membrane of MEA is nafion 212) of $Fe_{0.06}$-N/C-900.

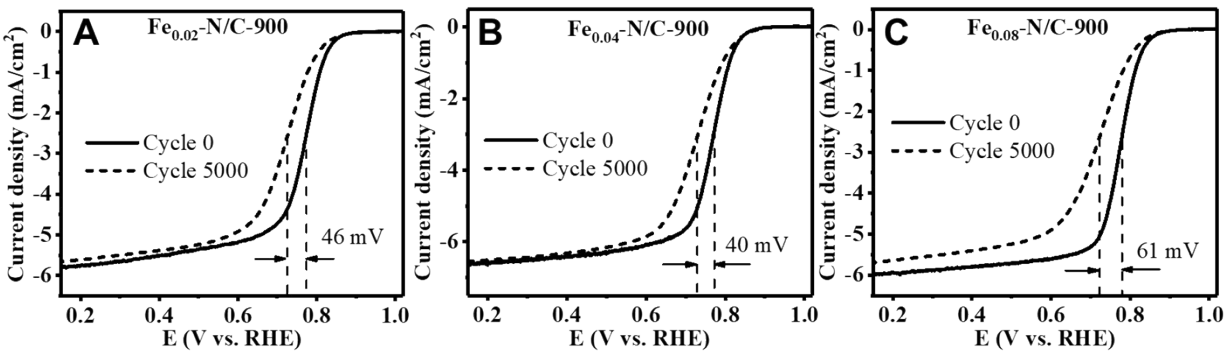

Fig. S10 LSV curves at before (cycles 0) and after 5000 potential cycles (Cycle 5000) in O_2-saturated $HClO_4$ of $Fe_{0.02}$-N/C-900, $Fe_{0.04}$-N/C-900 and $Fe_{0.08}$-N/C-900.

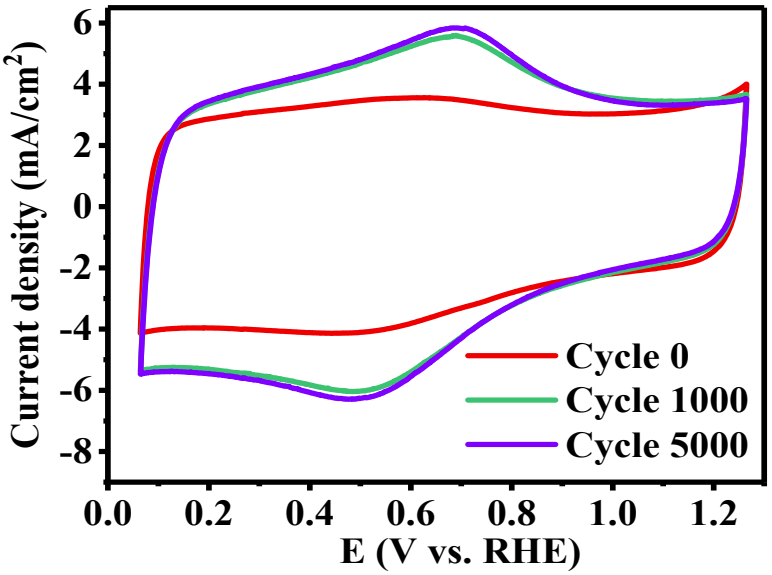

Fig. S11 Cyclic voltammograms of $Fe_{0.06}$-N/C-900 electrode in N_2-saturated 0.1 M $HClO_4$ solution at different potential cycles of N = 0, 1000, 5000.

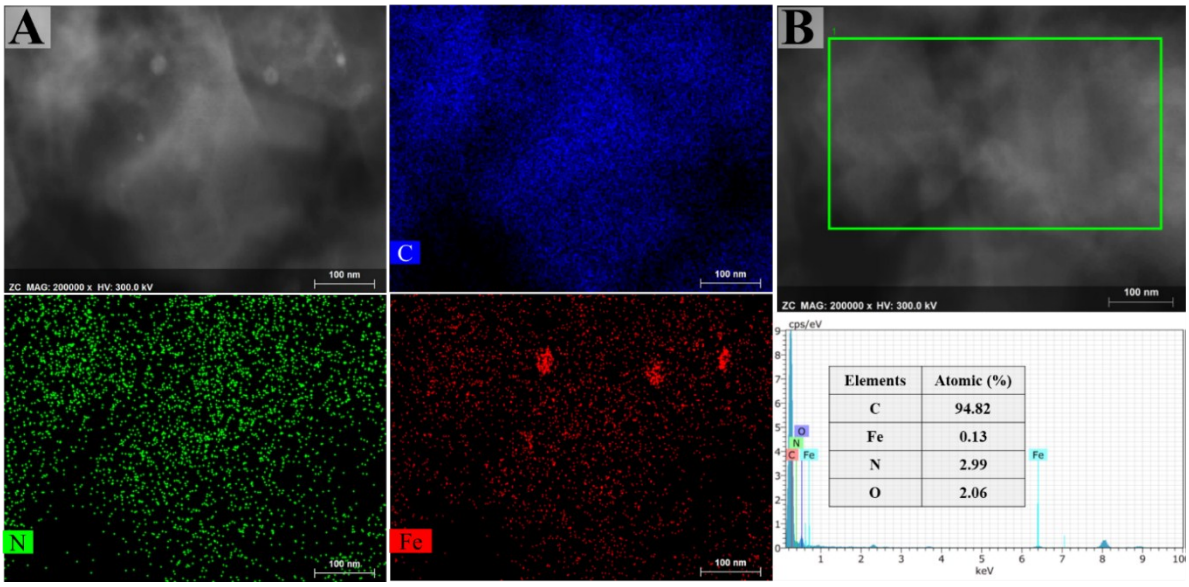

Fig. S12 A) STEM images with elemental mapping for C, N, and Fe, and B) a selected area EDS spectrum with a table of elemental atomic percentages (inset) of $Fe_{0.06}$-N/C-900 sample after 5000 potential cycles.

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