Supplementary Material

Highly-active ZIF-8@CNT composite catalysts as cathode materials for anion exchange membrane fuel cells

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Tables

Table S1 Amounts of ZIF-8, MWCNT and Fe/Co salts used to prepare ZIF-8 based catalyst materials.

Catalyst	MWCNTs (mg)	Fe(OAc)$_2$ (mg)	Co(OAc)$_2$ (mg)	ZIF-8 (mg)
ZNT-900	100	-	-	104.9
Fe-ZNT-900	100	8.2 (2.5 wt%)	-	104.9
Co-ZNT-900	100	-	15.37 (5 wt%)	104.9
Fe$_1$Co$_2$-ZNT-900	100	5.4 (1.65 wt%)	10.3 (3.35 wt%)	104.9
Fe$_1$Co$_1$-ZNT-900	100	16.36 (5 wt%)	15.37 (5 wt%)	104.9

Table S2 The value of R2, I_{D1}/I_G, W_{D1}, and W_G calculated from the deconvolution of Raman bands for all the catalyst materials.

Catalyst	R2	I_{D1}/I_G	W_{D1}, cm^{-1}	W_G, cm^{-1}
ZNT-900	0.53	1.52	78	59
Fe-ZNT-900	0.53	1.58	79	58
Co-ZNT-900	0.55	1.60	86	61
Fe$_1$Co$_2$-ZNT-900	0.57	1.78	104	65
Fe$_1$Co$_1$-ZNT-900	0.56	1.73	90	63

Table S3. Surface elemental composition and functional forms of the catalysts obtained from XPS analysis.

| Catalyst		ZNT-900		Fe-ZNT-900		Co-ZNT-900		Fe$_1$Co$_2$-ZNT-900		Fe$_1$Co$_1$-ZNT-900	
Elements	Functional form	BE (eV)	at. %	BE (eV)	at. %	BE (eV)	at. %	BE (eV)	at. %	BE (eV)	at. %
C	sp^2	284.3	47.19	284.3	41.93	284.3	41.93	284.3	40.27	284.3	40.69
	sp^3	284.8	12.46	284.8	21.24	284.8	21.24	284.8	19.57	284.8	21.10
	C-O	285.8	16.73	286.0	12.32	286.0	12.32	285.9	14.39	286.0	12.98
	C=O	289.5	3.55	289.5	3.25	289.5	3.25	289.5	3.39	289.5	3.63
	C=O	287.7	5.43	287.7	5.76	287.7	5.76	287.7	5.5	287.7	5.47
	pi-pi*	291.4	6.94	291.3	7.41	291.3	7.41	291.3	7.05	291.4	6.71
	Carbide	283.0	3.95	283.0	3.89	283.0	3.89	283.0	3.8	283.0	3.84
N	Imine	397.5	0.17	397.7	0.16	397.7	0.16	397.3	0.07	397.5	0.14
	Pyridinic	398.4	0.64	398.4	0.55	398.4	0.55	398.4	0.91	398.4	0.90
	Amines/Metal-N$_x$	399.4	0.31	399.2	0.56	399.2	0.56	399.4	0.62	399.2	0.58
	Pyrrolic	400.5	0.34	400.5	0.41	400.5	0.41	400.5	0.46	400.5	0.59
	Graphitic	401.8	0.18	401.6	0.21	401.6	0.21	401.5	0.35	401.7	0.25
	Bulk N-H	402.9	0.04	402.9	0.08	402.9	0.08	402.9	0.12	403.0	0.05
	NO	404.0	0.06	404.9	0.01	404.8	0.01	404.4	0.05	404.0	0.02
Metal oxide		530.0	0.18	530.2	0.32	530.3	0.25	530.1	0.03	530.1	0.39
O=C-OH carboxyl		531.2	0.49	531.2	0.36	531.2	0.46	531.2	0	531.2	0.77
C=O carbonyl		532.0	0.56	532.1	0.41	532.1	0.51	532.1	0.11	532.1	0.51
C-O		532.9	0.51	532.9	0.37	532.9	0.27	532.9	0.07	532.9	0.38
C-OH		533.9	0.21	533.8	0.22	533.8	0.21	533.9	0.05	533.9	0.21
Water, chemisorbed O		535.2	0.08	535.3	0.07	535.5	0	535.0	0.03	535.0	0.01
Total Fe (at.%)		-		0.1				0.34		0.2	
Total Co (at.%)		-		0		0.5		0.41		0.6	
Total N (at.%)		1.74		1.1		2.0		2.58		2.5	

Figures
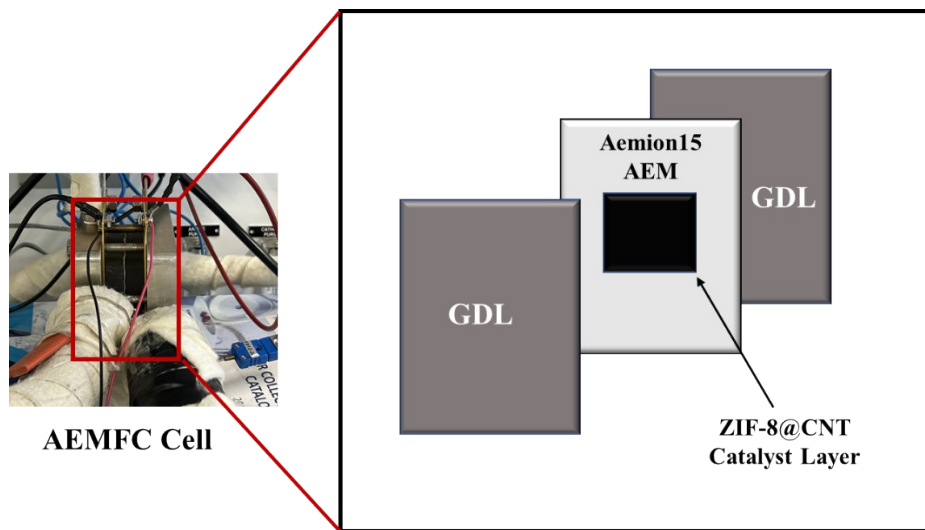
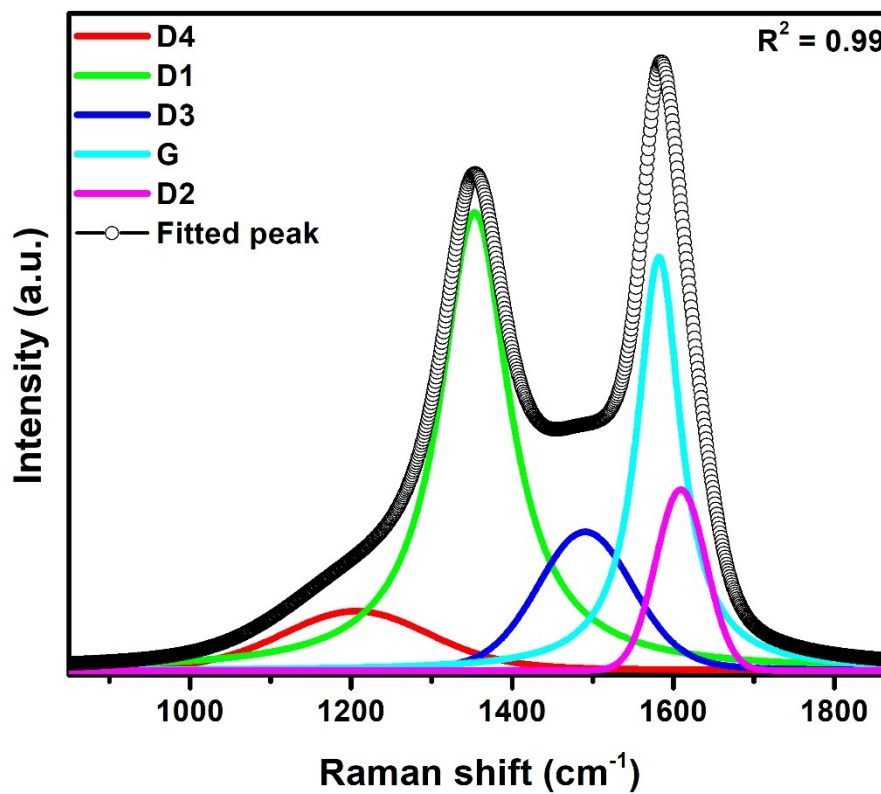**Fig. S1** Pictorial representation of the membrane-electrode assembly used for AEMFC tests.

Fig. S2 Deconvoluted Raman spectra recorded for Fe_1Co_2-ZNT-900 catalyst [R-Square fitting parameter (R^2) is 0.998].
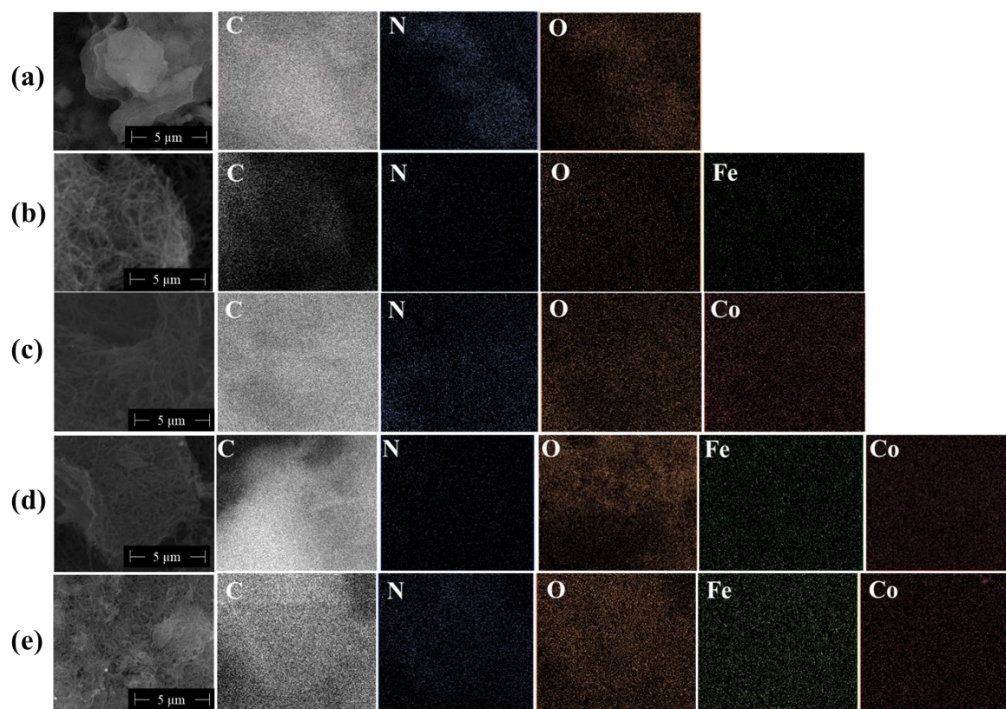
Fig. S3 SEM-EDX analysis with elemental mapping of (a) ZNT-900, (b) Fe-ZNT-900 and (c) Co-ZNT-900, (d) Fe_1Co_1-ZNT-900 and (e) Fe_1Co_2-ZNT-900 catalysts.
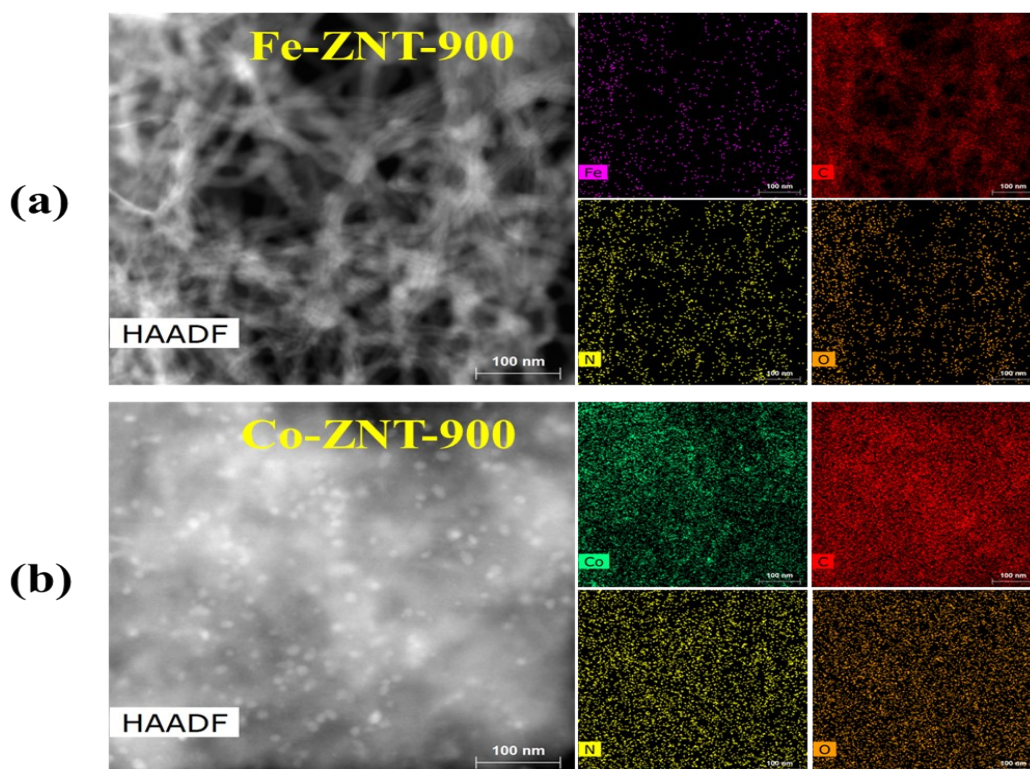

Fig. S4. HAADF-STEM images for (a) Fe-ZNT-900 and (b) Co-ZNT-900 catalysts captured at 100 nm with their corresponding EDX mapping for C, N and O elements.
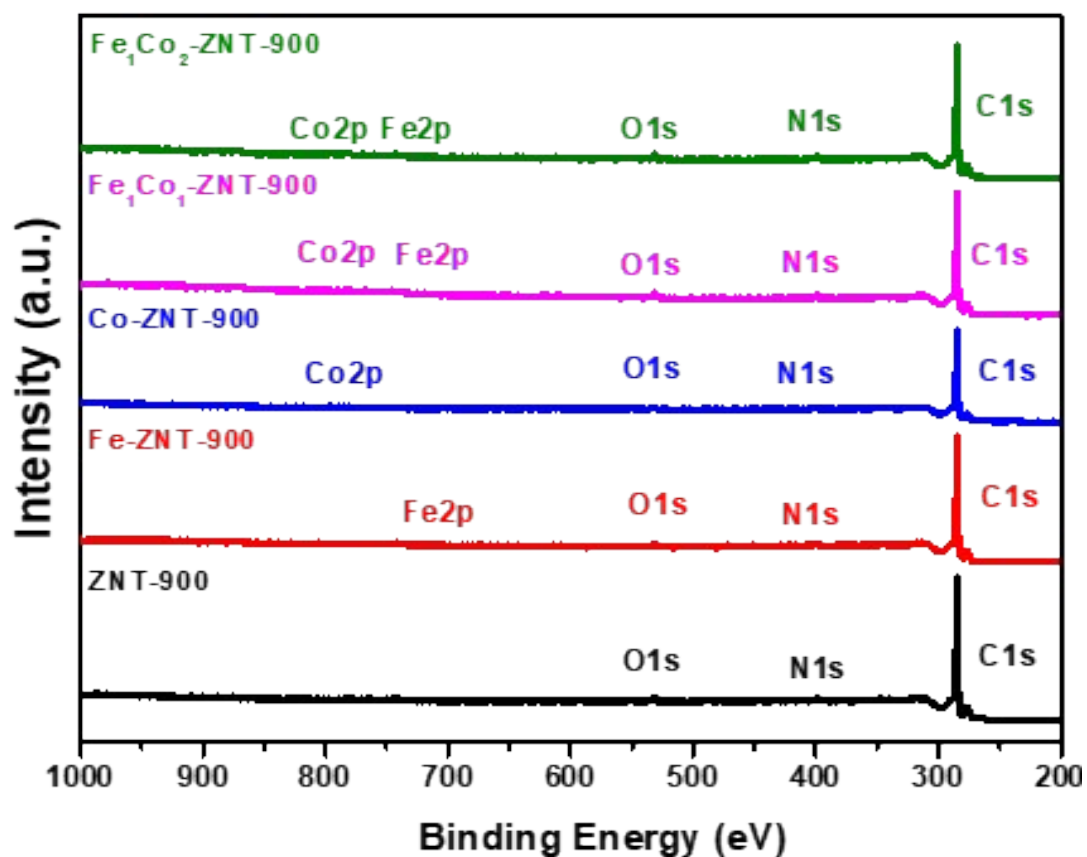
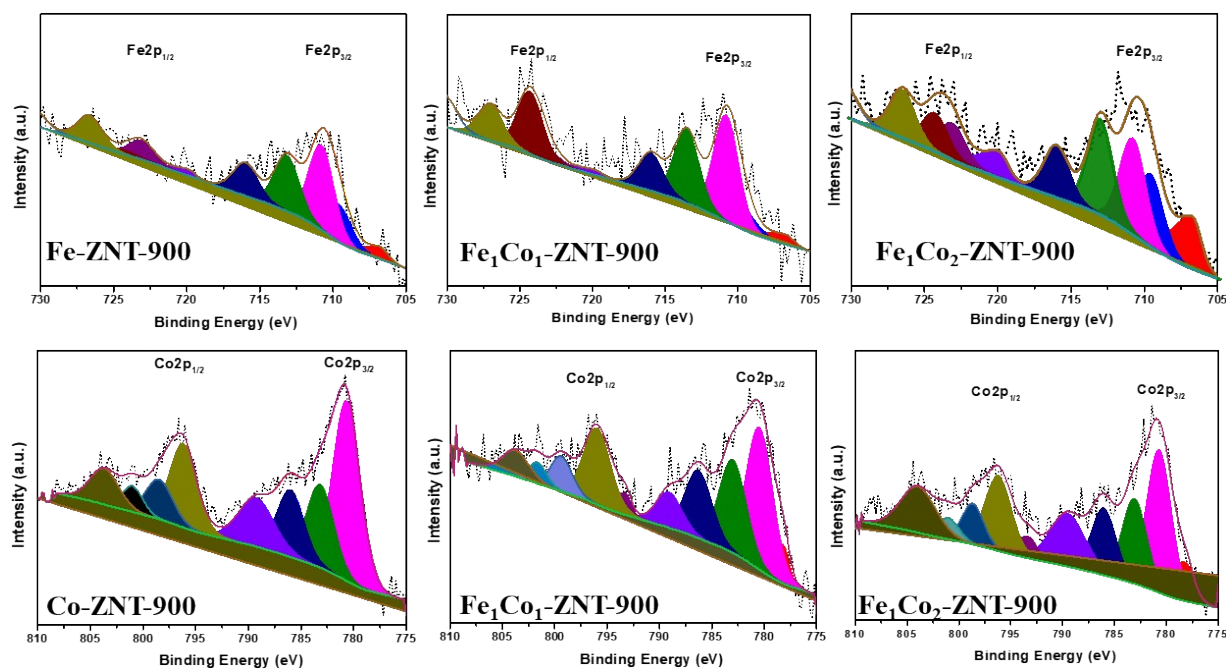**Fig. S5.** XPS survey spectra of ZIF-8@CNT catalysts representing the presence of C, N, O, Fe and Co elements.

Fig. S6. High-resolution XPS spectra recorded in the Fe2p and Co2p regions for transition metal doped ZIF-8@CNT catalysts.
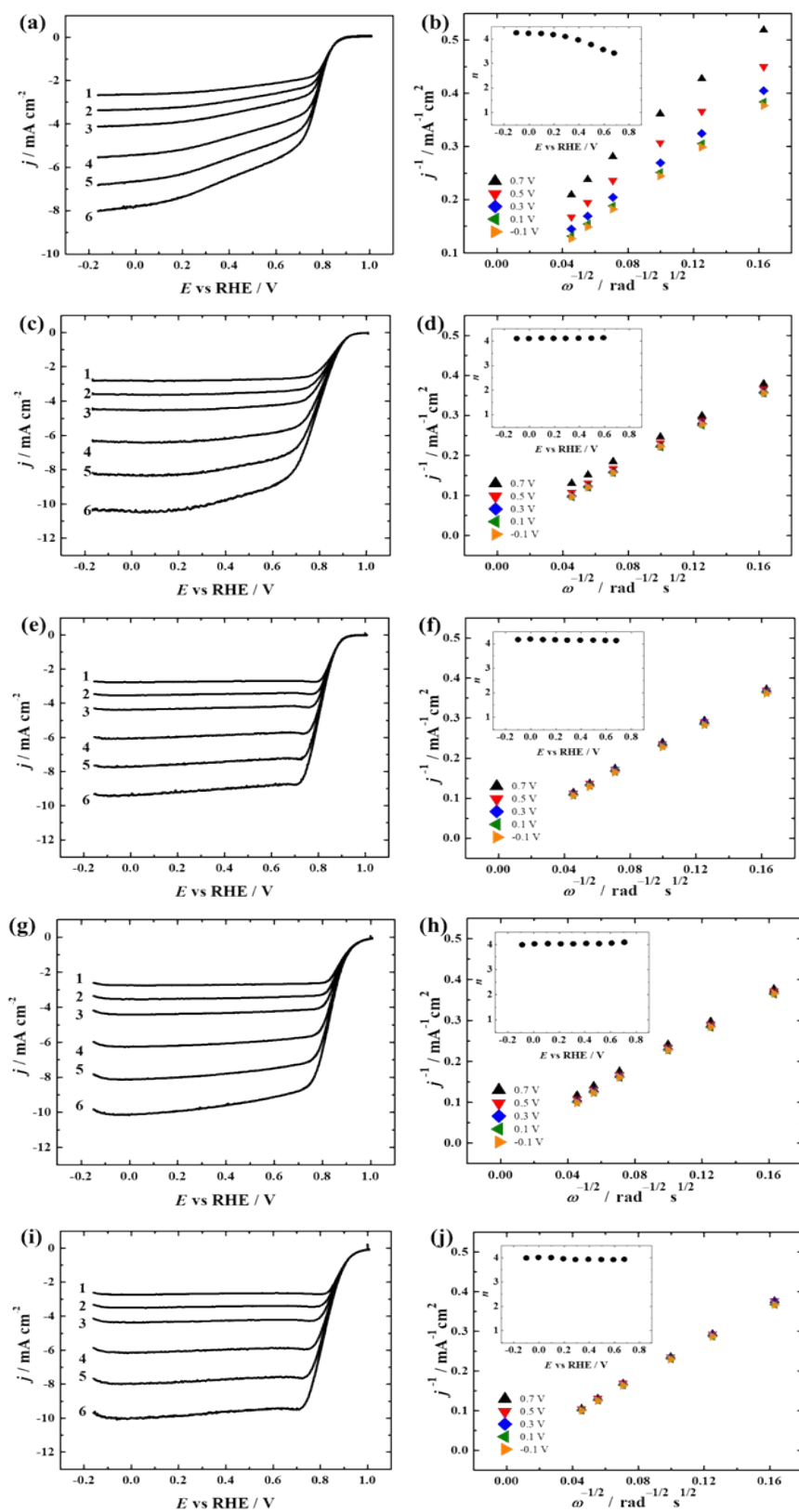
Fig. S7. The RDE voltammetry curves and K-L plots for oxygen reduction on (a, b) ZNT-900, (c, d) Fe-ZNT-900, (e, f) Co-ZNT-900, (g, h) Fe_1Co_1-ZNT-900 and (i, j) Fe_1Co_2-ZNT-900. Scan rate: 10 mV s^{-1}. Rotation rate (ω): (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm. Insets to the K-L plots show the number of electrons transferred per O_2 molecule as a function of potential.