Electronic Supplementary Information

Anodic Engineering towards High Performance Direct Methanol Fuel Cells with Non-precious Metal Cathode Catalyst

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Experimental Section

Synthesis of Fe-N-C catalyst: 1.63 g ZnO, 3.28 g and 69.6 mg ferric acetate were placed in an agate jar with 8 agate balls of Φ 6 mm and 2 agate balls of Φ 10 mm. The jar was sealed and placed in a planetary ball-miller to undergo ball-milling at 250 rpm for 1 h. The powder was subsequently transferred into a Teflon vial and suffered from microwave irradiation in a household microwave oven (2.45 GHz, 1000 W) for 15 min. The obtained light-yellow powder was the catalyst precursor. The electrocatalyst was prepared by placing the precursor in a quartz tube to pyrolyze at 1000 ºC for 3 h under N_2 atmosphere with a ramping rate of 5 ºC min-1 and a flow rate of 300 ml min^{-1}. The pyrolyzed sample was leached in 1 M HCl for 12 h at room temperature under continuous stirring. The sample was collected after washing with water and drying at 80 °C under vacuum overnight, and then pyrolyzed at 950 °C for 15 min under a NH_3 flow to obtain the catalyst.

Fabrication of GDLs: The anode GDL samples of Toray120, Toray060, and Toray030 were fabricated by spraying the mixture ink of carbon black powder (Vulcan XC72, Cabot Co., US) and polytetrafluoroethylene (PTFE, the weight ratio of carbon black to PTFE was 9:1) on the substrates of wet-proofed carbon paper (TGP-H-120, TGP-H-060, TGP-H-030, Toray Co., Japan). The carbon black loading was approximately 1.0±0.1 mg cm^{-2}. The home-made anode GDLs of CFCNT70 and CNT10 was fabricated by filtration procedures. Specifically, multiwall carbon nanotubes (MWCNTs, BTR Energy Materials Co., China) and PTFE (60 wt.% water dispersion, weight ratio of MWCNTs to PTFE was 9:1) were dispersed in N-methyl pyrrolidone (NMP, 20-time weight of MWCNTs) and ultrasonicated for 60 min, followed by high-speed stirring (20000 rpm) for 3 min. The as prepared ink was filtrated to form CNT membranes. The sample of CFCNT72 was fabricated by adding carbon fibres (CFs, average length is 5 mm, Nanjing Weida Composite Materials Co., China) to the as-prepared CNT ink (the weight ratio of carbon fibres to MWCNTs and PTFE was 6:3:1). Then the mixture ink was filtrated to form CF-CNT membranes. The as-prepared CNT and CF-CNT membrane was calcinated at 340 ^{o}C under air ambient for 30 min to form the anode GDL samples of CNT10 and CFCNT70, respectively. The cathode GDLs were purchased from commercial GDLs (29BC, SGL Co., Germany) for low temperature fuel cells.

Fabrication of MEAs: For Pt-C catalyst equipped MEAs, catalyst ink prepared from commercial Pt-C catalyst (60 wt.%, HiSPEC 9100, Johnson Matthey Co., UK), perfluorosulfonic acid (PFSA) ionomer (5 wt.% Nafion dispersion in alcohol, Sigmar Aldrich Co., weight ratio of Pt-C to Nafion was 4:1), and ethanol was sprayed on polymer electrolyte membranes (PEMs, Nafion 212, Dupont Co., or Gore Select, Gore Co.) with catalyst loading of 4 mg cm^{-2} to form catalyst coated membrane (CCM) cathodes. For Fe-N-C catalyst equipped MEAs,

the as-prepared Fe-N-C catalyst was dispersed in ethanol with the adding of Nafion dispersion (5 wt.% Nafion dispersion in alcohol, Sigmar Aldrich Co., weight ratio of Fe-N-C to Nafion was 2:1). The catalyst ink was then sprayed on PEMs (Nafion 212, Dupont Co., or Gore Select, Gore Co.) with catalyst loading of 4 mg cm^{-2} to form CCM cathodes. The anode gas diffusion electrodes (GDEs) were fabricated by spraying PtRu black (HiSPEC 6000, Johnson Matthey Co., UK), mixed with Nafion ionomer (5 wt.% Nafion dispersion in alcohol, Sigmar Aldrich Co., weight ratio of PtRu to Nafion was 17:3), on the above fabricated anode GDLs with catalyst loading of 4 mg cm^{-2}. MEAs were fabricated by sandwiching the cathode CCM between the anode GDE and the cathode GDL with a hot-press procedure (130 ^{o}C, 20 MPa, 2 min). The active area of each MEA was 2 cm^{-2}. The DMFC single cells were assembled by inserting the as-prepared MEAs into stainless steel polar-plates with serpentine flow channels.

Physical characterizations: Morphological details were obtained by scanning electronic microscopy (SEM, JSM-7800F, JEOL) and transmission electronic microscopy (TEM, JEM-2100F, JEOL). The pressure differences of gas pass through the samples were measured by a homemade instrument as shown in Fig. S6a.

Rotating ring disk electrode (RRDE) tests: The half-cell measurements were conducted in 0.1 M $HClO_4$ electrolyte on CHI760E electrochemical workstation with a RRDE work electrode (diameter of glass carbon = 5.61 mm), a graphitic counter electrode and a reference electrode of saturated calomel electrode (SCE). The potential was converted against reversible hydrogen electrode (RHE) by experimental calibration. The catalyst ink was prepared by ultrasonically dispersing 4 mg Fe-N-C catalyst and 30 μL Nafion isopropanol (5 wt %) in 2 mL ethanol. The ink was pipetted on the glass carbon and dried under ambient environment to give a loading of 0.8 mg cm^{-2}. The cyclic voltammetry (CV) curves were recorded in the N2-saturated 0.1 M $HClO_4$ electrolyte at a scan rate of 10 mV s^{-1}. The linear sweep voltammetry (LSV) curves were recorded in the O_2-saturated 0.1 M $HClO_4$ electrolyte at a scan rate of 10 mV s^{-1} and the potential on the Pt ring was held on 1.2 V constantly. The capacitive current had been deducted to obtain the LSV curves on ORR. The electron transfer number was calculated by the equation as follows:

$$n = \frac{4I_D}{I_D + {I_R}/{N}}$$

I_D-disk current; I_R-ring current; N-collection efficiency (0.37).

The methanol tolerance property was evaluated by recording the LSV curve and the i-t curve at 0.5 V with the addition of 1 M methanol (6 ml methanol in 150 ml electrolyte). The commercial Pt/C catalyst (20 wt%,

Johnson Matthey) with a loading of 0.1 mg cm^{-2} was introduced as the contrast sample.

DMFC single cell tests: The single cell tests on DMFCs were carried out by using a fuel cell test system (FCTS, Arbin Co.) and an electrochemical workstation (SI1287 and SI1260, Solartron Co.). The anode polarization curves were obtained by linear scanning applied to anodes with a scan rate of 5 mV s^{-1}. The methanol crossover polarization curves were obtained by linear scanning applied to cathodes with a scan rate of 5 mV s^{-1}. The single cell polarization curves were obtained without any back pressure and humidification. Other test conditions can be found in the specific figure descriptions.

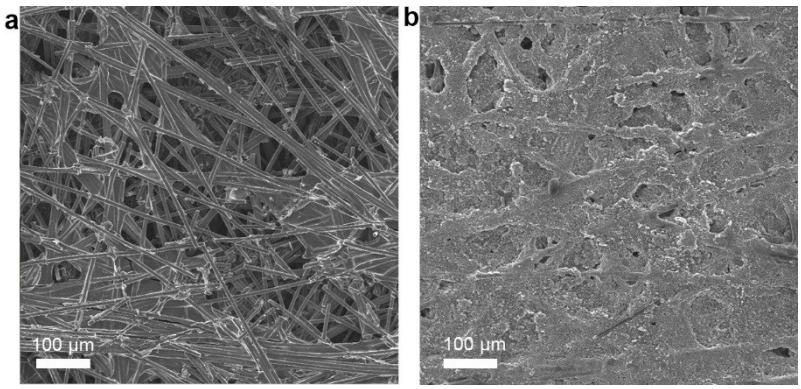

Fig. S1 Top views of the SEM images for the backing layer side (a) and microporous layer side (b) of the carbon paper (Toray060) based anode GDL.

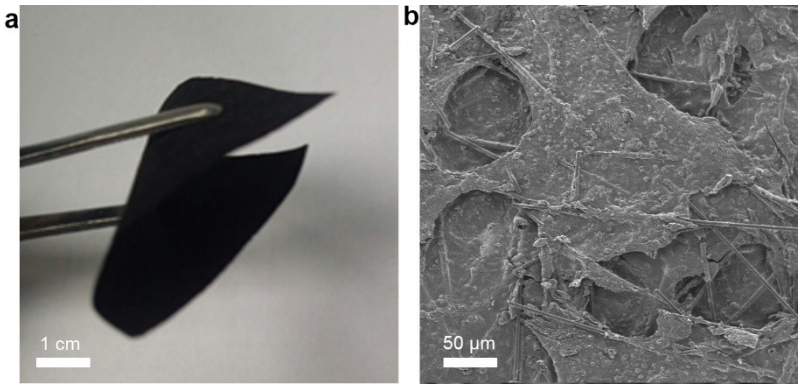

Fig. S2 Optical photograph (a) and top view of the SEM image (b) for the anode GDL of CFCNT70.

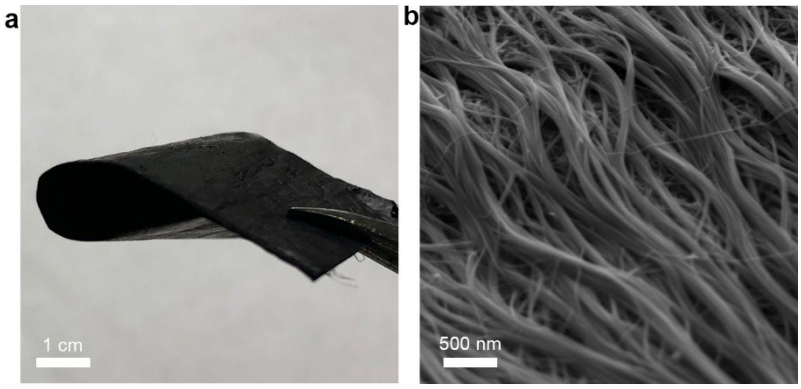

Fig. S3 Optical photograph (a) and top view of the SEM image (b) for the anode GDL of CNT10.

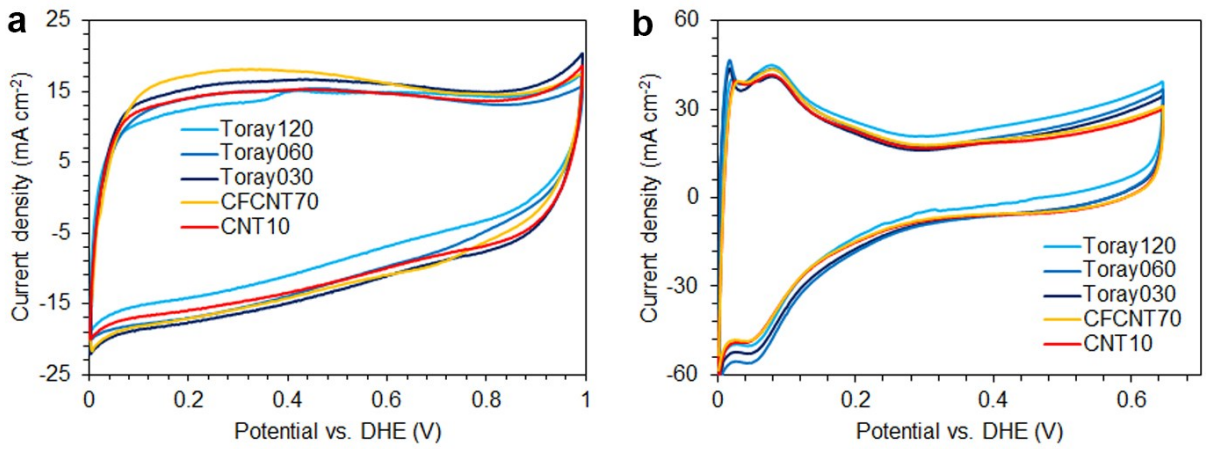

Fig. S4 Cathode (a) and anode (b) CV curves for MEA samples with different anode GDLs, scan rate is 20 mV s^{-1}, cell temperature is 80 ^{o}C.

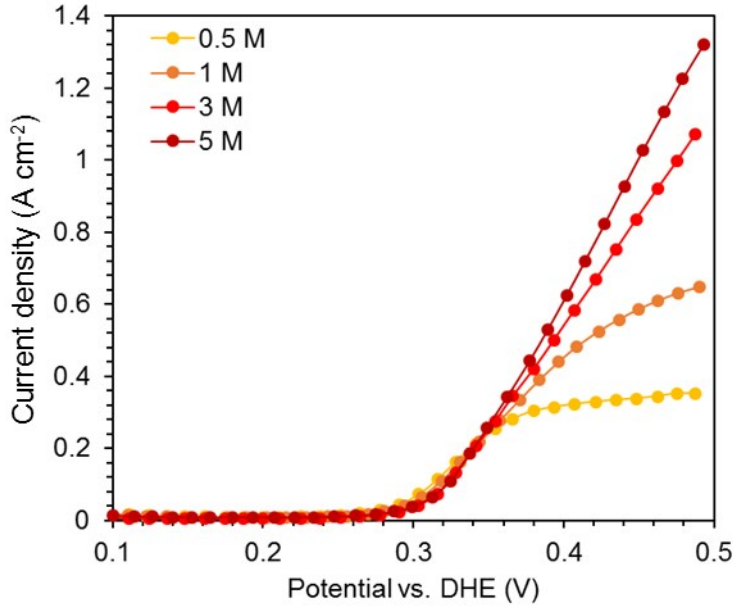

Fig. S5 Anode polarization curves for the sample with Toray060 GDL at different methanol concentration, anodes fed with methanol, cathodes fed with 40 mL min^{-1} H_2, scan rate is 5 mV s^{-1}, cell temperature is 80 ^{o}C.

Table S1 Properties of the different anode GDLs.

GDL sample	Thickness (μm)	Bulk density (g cm^{-3})	Porosity (%)	Gas permeability (mL cm^{-2} Pa^{-1} min^{-1})	Water contact angle (°)
Toray120	318	0.46	78	1.65	158
Toray060	169	0.44	80	2.14	157
Toray030	98	0.45	79	2.72	157
CFCNT70	72	0.37	85	3.15	152
CNT10	12	0.47	82	4.75	154

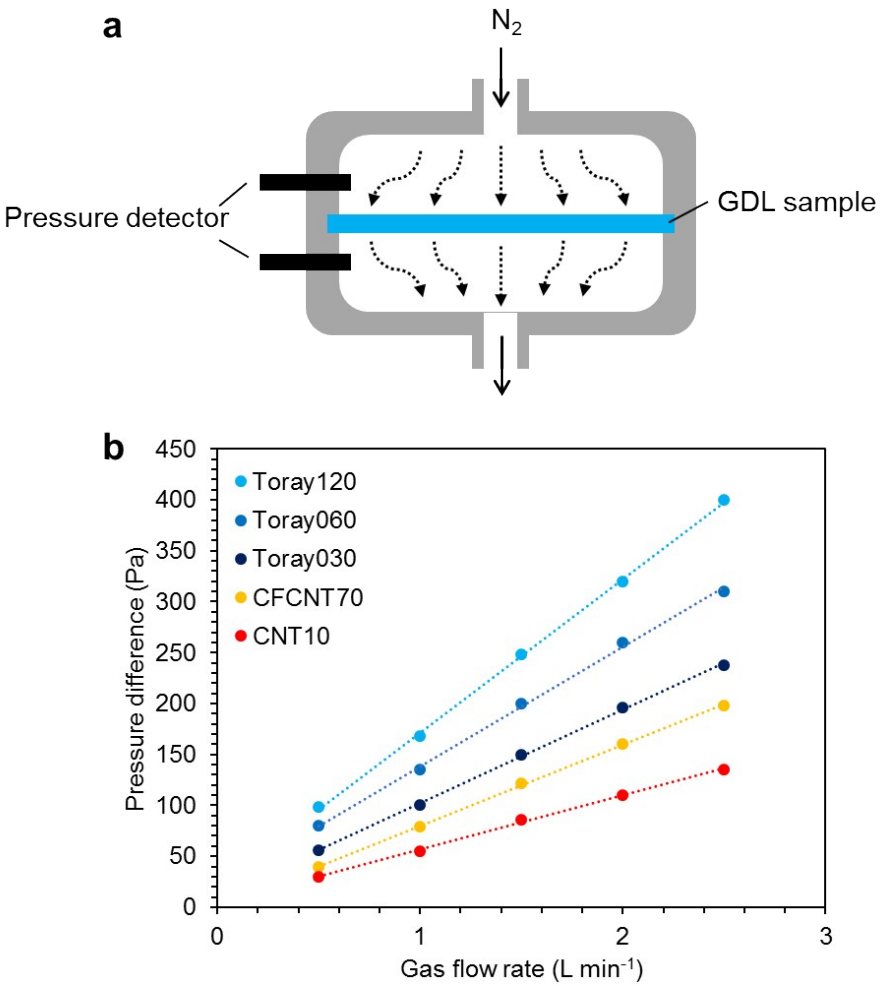

Fig. S6 Schematic (a) and results (b) of the gas permeability tests for different anode GDLs at room temperature (25 ^{o}C).

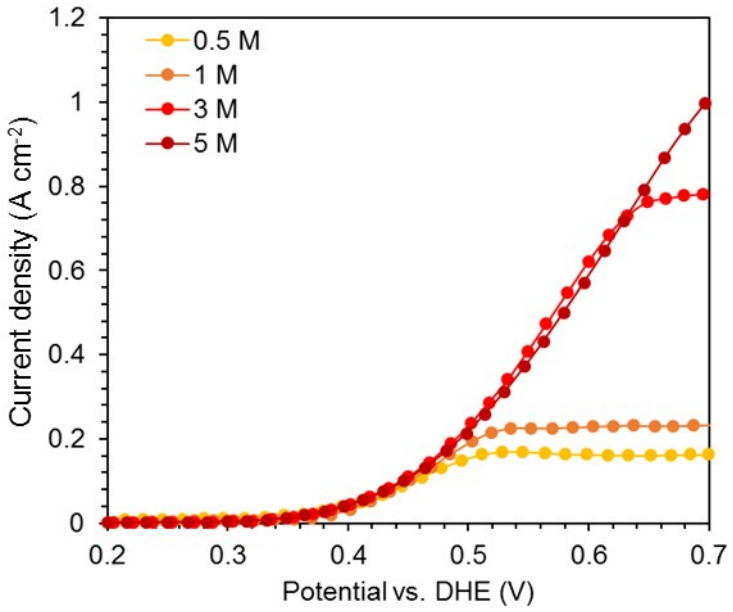

Fig. S7 Methanol crossover results for the sample with Toray060 GDL at different methanol concentration, anodes fed with methanol, cathodes fed with 40 mL min^{-1} N_2, scan rate is 5 mV s^{-1}, cell temperature is 80 ^{o}C.

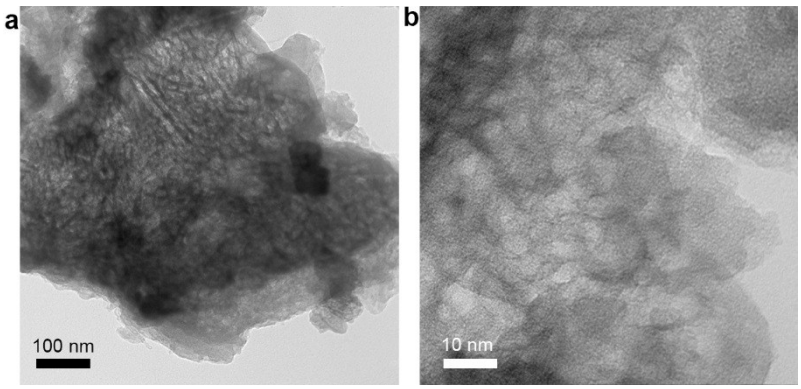

Fig. S8 TEM images for the as-prepared Fe-N-C catalyst.

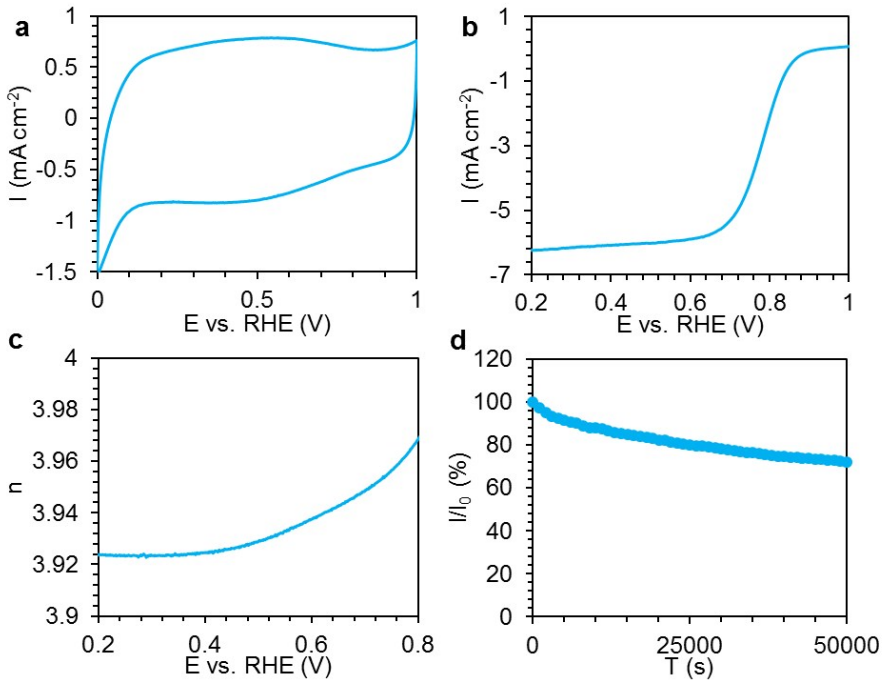

Fig. S9 Electrochemical test results for the as-prepared Fe-N-C catalyst at 0.1 M $HClO_4$. (a) CV curve, scan rate is 20 mV s^{-1}. (b) ORR polarization curve, rotation rate is 1600 rpm, scan rate is 10 mV s^{-1}. (c) Electron transfer numbers at different potential; (d) Chronopotentiometry test result at 0.5 V (vs. RHE).

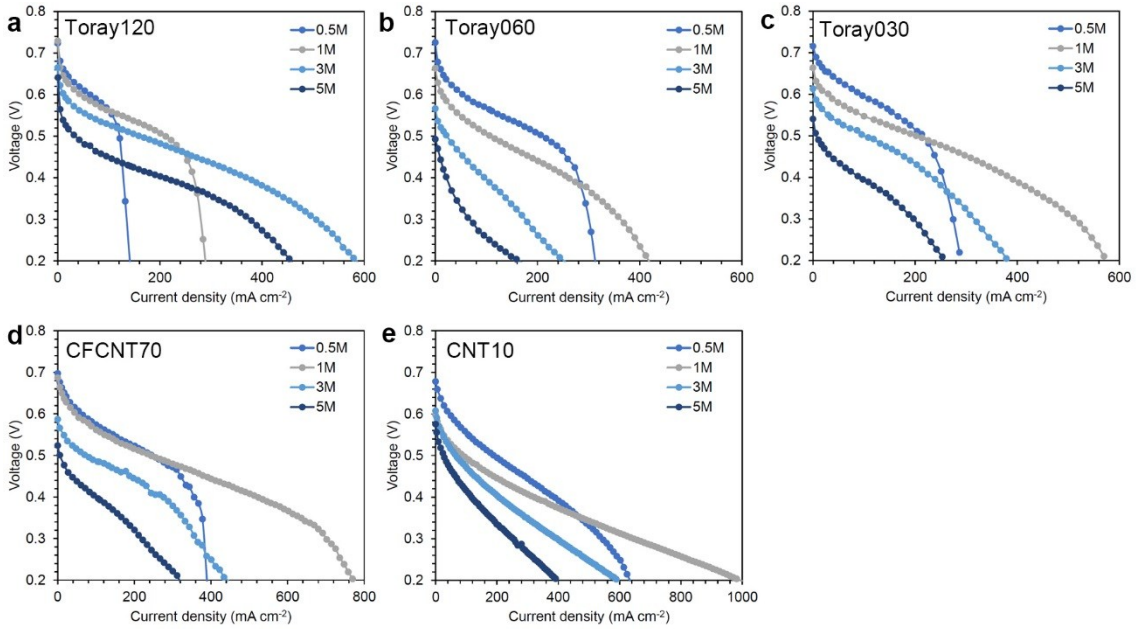

Fig. S10 DMFC polarization curves at different methanol concentration for Pt-C equipped cathodes with different anode GDLs, anodes fed with 1 mL min^{-1} methanol, cathodes fed with 80 mL min^{-1} O_2, cell temperature is 80 ^oC.

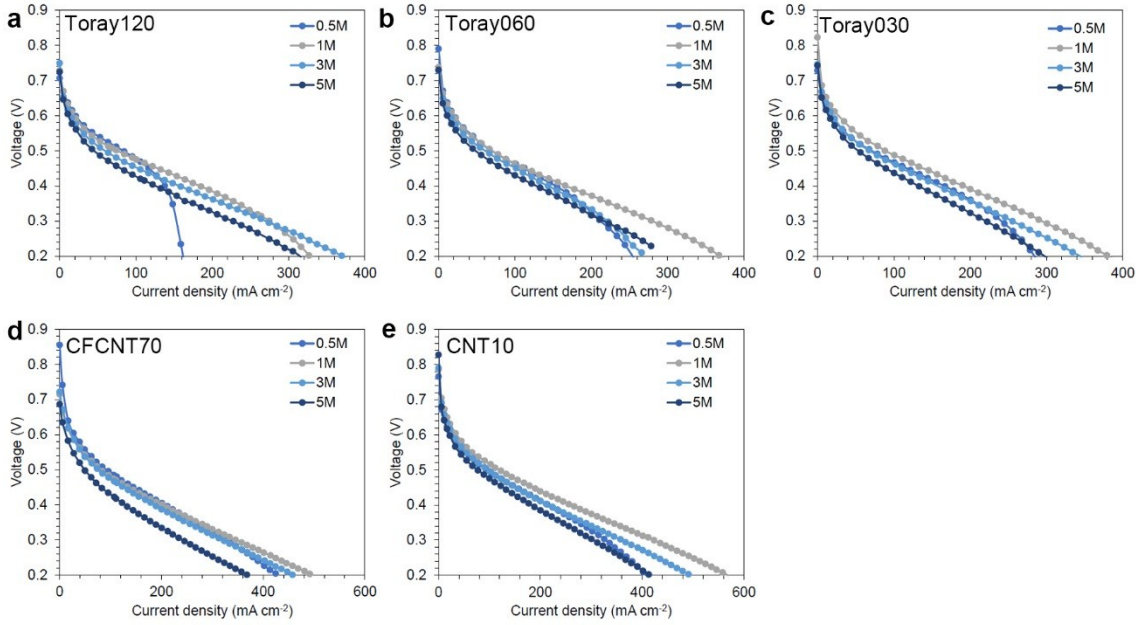

Fig. S11 DMFC polarization curves at different methanol concentration for Fe-N-C equipped cathodes with different anode GDLs, anodes fed with 1 mL min^{-1} methanol, cathodes fed with 80 mL min^{-1} O_2, cell temperature is 80 ^oC.

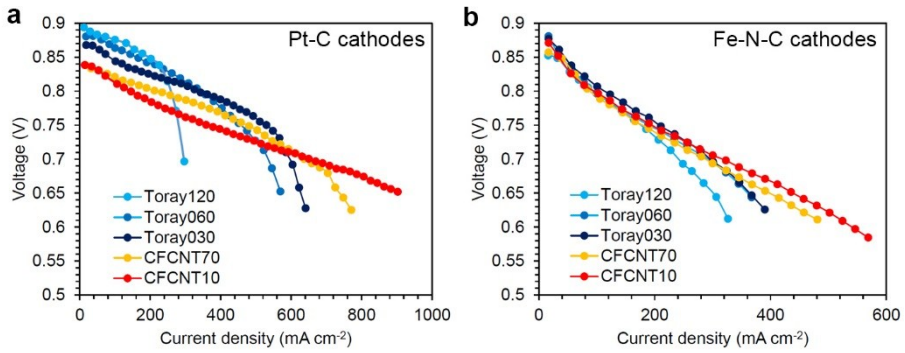

Fig. S12 Cathode polarization curves derived from single cell and anode polarization curves for Pt-C (a) and Fe-N-C (b) cathodes with different anode GDLs.

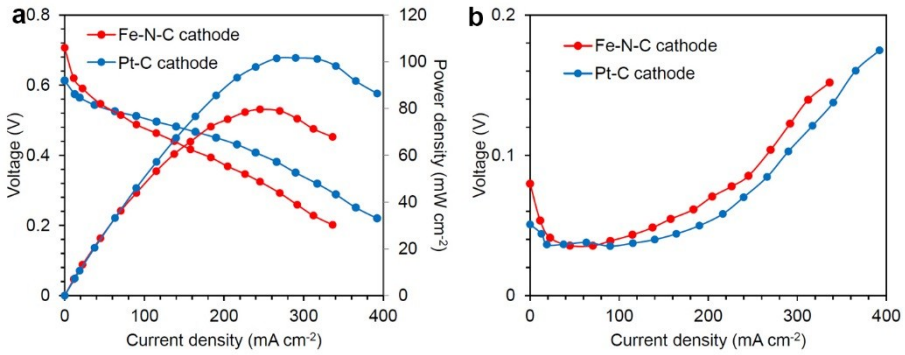

Fig. S13 DMFC performance tested with air (a) and oxygen gain (b) for MEAs with Fe-N-C and Pt-C cathodes, anodes fed with 1 mL min^{-1} 1 M methanol, cathodes fed with 80 mL min^{-1} air, cell temperature is 80 ^{o}C.

Table S2 Comparison of the DMFC performance published recently.

Cathode catalyst	Cathode loading (mg cm^{-2})	Anode loading (mg_{PtRu} cm^{-2})	$E_{1/2}$	Current density@0.5 V (mA cm^{-2})	P_{max} (mW cm^{-2})	Test conditions	Ref.
Fe-N-C	4	4	0.780	118	141	80 °C, 1 M methanol/O_2*	This work
	4	4		119	127		
	4	4		81	79	80 °C, 1 M methanol/air*	
Fe-N-C/DMS	5	4	0.800	85	130	80 °C, 3 M methanol/O_2*	[37]
ZIF/MIL-10-900	4	4	0.780	49	83	75 °C, 3 M methanol/O_2*	[29]
Fe-N-rGO	4	6	0.790	50	56	80 °C, 0.5 M methanol/air*	[30]
Co-Ppy/MWCNT	2.5	2.5	-	54	55	80 °C, 1 M methanol/O_2 (1 bar)	[43]
Fe-Nx-C-THT	4.5	1	0.730	25	50	90 °C, 5 M methanol/O_2*	[44]
GbC	2	5	0.740	20	32	80 °C, 1 M methanol/O_2*	[45]
Fe-N/MPC2	2.5	1.5	0.700	15	23	90 °C, 2 M methanol/O_2 (3 bar)	[46]
Fe-N-C	5	1.5	0.720	10	20	90 °C, 2 M methanol/O_2 (3 bar)	[47]
Fe-N/CNN	2.6	2.6	0.600	-	15	90 °C, 2 M methanol/O_2*	[48]

* Cathode flow with ambient pressure