Electronic Supplementary Information

Synthesis of an ε-MnO₂/metal-organic-framework composite and its electrocatalysis towards oxygen reduction reaction in an alkaline electrolyte

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Fig. S1 Horvath-Kawazoe pore size distributions for the (a) MOF(Fe) and (b) ϵ -

MnO₂/MOF(Fe) samples.



Fig. S2 TEM images of samples and EDX spectroscopic profiles from the selected TEM images. The element contents of the samples are listed in Table S1.

Table S1

Element	Area 1 ^a		Area 2 ^b			Area 3 ^c	
	Weight%	Atomic%	Weight%	Atomic%		Weight%	Atomic%
C (K)	80.51	89.87	64.99	80.59		45.87	69.83
O (K)	9.11	7.63	15.11	14.05		15.04	17.19
Fe (<i>K</i>)	10.38	2.50	11.49	3.07		6.51	2.13
Mn (<i>K</i>)			8.41	2.29		32.58	10.85

The weight and atomic percentage of the elements from selected area of TEM images

^a the blue area shown in Fig. S2

^{*b*} the orange area shown in Fig. S2

^c the red area shown in Fig. S2



Fig. S3 (a) TEM, (b) STEM image of MOF(Fe). (c-h) Element mapping of

corresponding C-, O-, Fe-, Fe+C- and Fe+O- performed at the region of the STEM

image, respectively.



Fig. S4 (A) Deconvoluted C 1s and (B) deconvoluted O 1s XPS spectra for the (a) MOF(Fe) and (b) ϵ -MnO₂/MOF(Fe) samples.

<u>Reference electrode calibration</u>

A KCl-saturated Ag/AgCl reference electrode was used for all electrochemical tests. The KCl-saturated Ag/AgCl was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was conducted in a H₂-saturated 0.1 M KOH by using a Pt wire as a working electrode. The CV was run at a sweep rate of 1 mV·s⁻¹ and the average of two potentials at which current crossed zero was regarded as the thermodynamic potential of hydrogen electrode reaction. In this work, $E_{(RHE)}=E_{(Ag/AgCl)}+0.953$ V.



Fig. S5 CV curves of hydrogen oxidation/evolution reactions run at a sweep rate of 1 $mV \cdot s^{-1}$ by using Pt wire as a working electrode in H₂-saturated 0.1 M KOH.

Electrochemical impedance spectra (EIS) for iR-compensation

EIS were recorded at a constant potential with amplitude of 5mV, and the frequency scan range was from 1M Hz to 1 Hz. The value at second intersection of the semicircle and the real axis was regarded as the solution resistance (~20 Ω) in this work. Therefore, all the catalytic activity data shown in this work were *iR*-corrected with *R* value of ~20 Ω .



Fig. S6 Electrochemical impedance spectra of electrolyte resistance under different

conditions in 0.1 M KOH.



Fig. S7 ORR activities at 1600 rpm in $\mathrm{O}_2\text{-saturated}$ 0.1 M KOH for the $\epsilon\text{-}$

 $MnO_2/MOF(Fe)$ composites with different $\epsilon\text{-}MnO_2$ loadings.



Fig. S8 (A-C) RDE voltammograms for the ORR in 0.1 M KOH under different rotational speeds with a sweep rate of 5 mV·s⁻¹ and (a-c) corresponding K-L curves at various potentials for ε-MnO₂/MOF(Fe)-*l*, ε-MnO₂/MOF(Fe) and ε-MnO₂/MOF(Fe)-*h*, respectively.



Fig. S9 CV curves of the MOF(Fe) sample in N_2 - or O_2 -saturated 0.1 KOH solution at

a sweep rate of 50 mV \cdot s⁻¹, respectively.



Fig. S10 (A-D) RDE voltammograms for the ORR in 0.1 M KOH under different rotational speeds with a sweep rate of 5 mV·s⁻¹ and (a-d) corresponding K-L curves at various potentials for MOF(Fe), ε-MnO₂, ε-MnO₂+MOF(Fe) and 20% Pt/C, respectively.

Table S2

ORR catalytic activities obtained by RDE with a rotational speed of 1600 rpm for several developed MnO_2 catalysts

Catalyst	MnO ₂ loading on GC electrode	i _{measured} @ 0.75 V vs. RHE (mA∙cm ⁻²)	<i>i_{measured} @ -</i> 0.20 V vs. Ag/AgCl (mA∙cm ⁻²)	Electrolyt e	Ref. #
ε-MnO ₂ /MOF(Fe)	36 μg·cm ⁻²	-0.47	-0.47	0.1 M KOH	This work
α -MnO ₂ nanoflakes	30.6 µg·cm ⁻² a	\sim -0.65 b		0.1 M KOH	S 1
α -MnO ₂ rods	318 μg·cm ⁻² a	~ -1.10 <i>b</i>		0.1 M KOH	S2
β-MnO ₂	101 μg·cm ⁻² <i>a</i>	\sim -0.20 ^{b, c}		0.1 M KOH	S3
α -MnO ₂ nanowires	50 μg <i>«</i>		~ -1.25 ^b	0.1 M KOH	S4
β -MnO ₂ nanowires	50 μg <i>a</i>		\sim -0.87 b	0.1 M KOH	S4
γ -MnO ₂ nanowires	50 μg <i>a</i>		\sim -0.80 b	0.1 M KOH	S4
α-MnO ₂ /C	56 μg·cm ⁻²		\sim -1.01 b, d	1.0 M KOH	S5
ε-MnO ₂ /C	31 μg·cm ⁻²		\sim -1.74 b, d	1.0 M KOH	S5

a the values are calculated from available experimental details in the corresponding papers *b* "~" indicates that the values are read directly from figures in the corresponding papers *c* the values are obtained by RDE under 2500 rpm

^d the values are obtained by RDE under 900 rpm at -0.20 V vs. saturated calomel electrode



Fig. S11 (a) ORR LSV curve performed at 1600 rpm in O₂-saturated 0.1 KOH solution at a sweep rate of 5 mV·s⁻¹ and (b) HORR LSV curve performed at 1600 rpm in N₂-saturated 0.1 KOH solution with a H₂O₂ concentration of 1.3 mM at a sweep rate of 5 mV·s⁻¹ for the ϵ -MnO₂/MOF(Fe) composite.



Fig. S12 Chronoamperometric curves performed in O₂-saturated 0.1 M KOH at 0.55 V at a rotational speed of 1600 rpm for the (a) ε-MnO₂/MOF(Fe) and (b) 20% Pt/C samples. (Methanol crossover tests were conducted by injecting 3 mL methanol within chronoamperometry tests).

References

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