Supporting Information

Hexahydric component metal organic frameworks constructed by multiple ligands and mixed-valence ions

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Materials and methods

All of the materials for syntheses are obtained commercially and used without further purification. The powder X-ray diffraction (PXRD) data are characterized using a Rigaku D/Max-2500 diffractometer with a Cu-target tube and a graphite monochromator (40 kV, 100 mA). Simulated PXRD spectra are derived from modulating the single-crystal X-ray diffraction (SCXRD) data via the Mercury software. The electronic conductivity tests are carried out by PARSTAT MC (aka PMC) electrochemical workstation. Oxygen evolution reaction measurements are conducted on a CHI760E electrochemical workstation with a standard three-electrode system. ICP-OES data are tested by Aglient 5110. X-ray photoelectron spectroscopy (XPS) images were collected on a Thermo Scientific Escalab 250 Xi XPS spectrometer. The morphologies structures of the samples were measured by using the Scanning electron microscope (ZEISS MERLIN Compact).

Synthesis method

$[CH_3NH_2CH_3]_2[Fe^{III}_2Fe^{II}_{10}(tz)_{11}(HCO_2)_{12}(btc)_{5/3}]$ (**1**): A mixture of $FeCl_2{\cdot}4H_2O$ (0.5 mmol), $FeCl_3{\cdot}6H_2O$ (0.5 mmol), H_3btc (0.25 mmol), Htz (1 mmol), K_2CO_3 (0.25 mmol), N,N-Dimethylformamide (8 mL), and H_2O (4 mL) is sealed in a 25 mL Teflon-lined stainless steel autoclave. The autoclave is heated at 140 °C for 72 h under autogenous pressure and then cooled slowly to room temperature at a rate of 2 °C·h^{-1}. Yellow triangle block crystals are obtained.

$[CH_3NH_2CH_3]_2[Fe^{III}_2Fe^{II}_2Co^{II}_8(tz)_{11}(HCO_2)_{12}(btc)_{5/3}]$ (**2**): A mixture of $FeCl_2{\cdot}4H_2O$ (0.5 mmol), $CoCl_2{\cdot}6H_2O$ (0.5 mmol), H_3btc (0.25 mmol), Htz (1 mmol), K_2CO_3 (0.25 mmol), N,N-Dimethylformamide (8 mL), and H_2O (4 mL) is sealed in a 25 mL Teflon-lined stainless steel autoclave. The autoclave is heated and then cooled in the same way as **1**. Red triangle block crystals were obtained.

X-ray Crystallography

X-ray single-crystal diffraction data for these crystals were collected on a Rigaku Xtlab-Min diffractometer at 293(2) K with Mo Kα radiation (λ = 0.71073 Å) by ω scan mode. The program CrysAlisPro 1.171.39.7e[s1a] was used for the integration of the diffraction profiles. The structure was determined by intrinsic phasing method using ShelXT[s1b] and refined by full-matrix least-squares methods using ShelXL[s1c] with Olex2.[s1d] The crystal data of **1** and **2** are shown in **Table S1**. The selected bond lengths

and angles are given in **Table S2** and **Table S3**.

Electronic conductivity measurement

Electronic conductivity measurement is conducted by two-probe contact method. The compacted tablet used for conductivity measurements has a diameter of 0.5 cm with the thickness 0.12 cm for **1** and 0.14 cm for **2**, which are obtained by pressing crystal powders at 8 Mpa for 1 min. The tablet is sandwiched by two copper-plated electrodes. The electronic conductivity measurement is performed on the electrochemical workstation PMC under ambient condition. Linear *I-V* curve is obtained by sweeping the voltage from -1V to 1V.

The electronic conductor σ could be calculated by the express $\sigma = \frac{IL}{VS}$, where the *L* is the length of the crystal, *S* represents the cross-sectional area of the crystal, and the value of *I* and *V* could be obtained by the *I-V* curve.

Electrochemical impedance spectroscopy (EIS) of **1** and **2** are the fitting results under the Q(QR) and R(QR)(QR) circuit models, respectively, as shown in **Fig. S4**.

Oxygen evolution reaction (OER) measurement

A glassy carbon rotating disk electrode (RDE, diameter, 5 mm) or rotating ring-disk electrode (RRDE, disk diameter: 5.5 mm) is used as the working electrode, the carbon rod was used as counter electrode and an Ag/AgCl (3 M KCl) is used as reference electrode. To prepare the catalyst-coated working electrode, 6 mg of the as-synthesized catalyst (or 6mg catalyst and 6mg conductive carbon black) is dispersed in the mixing solution of 500 μL H_2O, 500 μL EtOH and 50 μL nafion (5%) under sonication for 1 h to form a homogeneous catalyst ink. A 12 μL amount of the mixture is dropped onto a polished glassy carbon electrode (5 mm in diameter) in sequence and dried in air. All the recorded potential has been converted to reversible hydrogen electrode (RHE) as follows:

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^{\theta} + 0.059\,pH$$

OER performances of as-prepared catalysts is measured in 1 M KOH aqueous solution at room temperature. The electrochemistry measurements are represented with 95% iR compensation rate. Linear sweep voltammetry (LSV) polarization curves is performed in O_2 saturated electrolyte. LSV polarization curves are measured with a sweep rate of 5 mV s^{-1}.

I-t stability measurement

The long-term stability test was carried on RRDE working electrode. The material configuration and test methods are shown in the OER measurement. The sample used for PXRD test before and after i-t test was obtained by coating the sample on 1.5*1cm^2 hydrophobic carbon paper. The PXRD pattern was collected before and after 2h i-t test.

TOF calculations

For OER, the TOF value is usually calculated by the equation:

$$TOF = (J\,A)/(4Fn)$$

where *J* is the current density after 95% iR corrected, *A* is the geometric area of the

electrode (0.196 cm^2), *F* is Faraday's constant and n is the molar number of active sites. In our study, we suppose Co and Fe as active sites for catalysts. For the structural transformation during electrocatalysis, there is no structural information for surface species. Therefore, we use all the metals in the catalyst as active species. And *n* is calculated by the following formula: $n= 12*m/M_W$.

References

S1. (a) CrysAlisPro 1.171.39.7e, Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Rigaku Oxford Diffraction, 2015. (b) G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv*., 2015, **71**, 3−8. (c) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem*., 2015, **71**, 3−8. (d) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339−341.

Table S1 Crystal data for **1** and **2**.

	1	**2**
Empirical formula	$C_{53}H_{55}Fe_{12}N_{35}O_{34}$	$C_{53}H_{55}Co_8Fe_4N_{35}O_{34}$
Formula weight	2396.52	2421.16
Temperature, K	293(2)	293(2)
Crystal system	hexagonal	hexagonal
Space group	*P-62m*	*P-62m*
A, b, Å	29.5235(14)	29.351(10)
c, Å	9.5830(5)	9.495(4)
$\alpha=\beta$, deg	90	90
γ, deg	120	120
Volume, $Å^3$	7233.8(7)	7084(5)
Z	3	3
ρ_{calc}, g/cm^3	1.65	1.703
μ, mm^{-1}	1.838	2.053
F (000)	3606	3630
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Reflections collected	30339	13642
Data/restraints/parameters	4610/18/375	4436/71/335
Goodness-of-fit on F^2	1.044	0.932
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0473, wR_2 =0.1151	R_1 = 0.0990, wR_2 = 0.2045
Final R indexes [all data]	R_1 = 0.0581, wR_2 = 0.1295	R_1 = 0.2504, wR_2 = 0.3048

$R_1=\sum||Fo|-|Fc||/\sum|Fo|$; $wR_2= [\sum w(Fo^2-Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

Table S2 The bonds lengths(Å) and angles(°) for **1**.

1			
Fe1-N1	2.139(8)	N2-Fe4	2.179(8)
Fe1-N1^{ii}	2.139(8)	Fe5-O8	2.143(8)
Fe1-O3	2.110(8)	Fe5-N8	2.156(7)
Fe1-O3^{ii}	2.110(8)	Fe5-N8^{viii}	2.156(7)
Fe1-O4	2.250(9)	Fe5-O11	2.201(6)
Fe1-O14^{iii}	2.211(8)	Fe5-O11^{viii}	2.201(6)
Fe2-O2	2.040(12)	O15-Fe5	2.092(9)
Fe2-O2^{v}	2.040(12)	Fe6-O9	2.045(8)
Fe2-N5^{iv}	2.056(11)	Fe6-O11^{viii}	2.235(6)
Fe2-N5	2.056(11)	Fe6-O11	2.235(6)
Fe3-N4	2.188(7)	Fe6-O12	2.067(9)
Fe3-N4^{ii}	2.188(7)	N3-Fe6^{iii}	2.173(8)
Fe3-O5	2.090(9)	Fe7-N7	2.05(2)
Fe3-N6	2.142(11)	Fe7-O10^{ii}	2.148(9)
Fe3-N9	2.174(7)	Fe7-O10^{vii}	2.148(9)
Fe3-N9^{ii}	2.174(7)	Fe7-O10^{xi}	2.148(9)
Fe4-O4	2.216(9)	Fe7-O10	2.148(9)
Fe4-O6	2.367(11)	Fe7-O13	2.06(2)
Fe4-N10	2.149(7)	Fe7-O13^{xi}	2.06(2)
Fe4-N10^{ii}	2.149(7)		
N1^{ii}-Fe1-N1	89.2(4)	O15-Fe5-O8	177.6(4)
N1^{ii}-Fe1-O4	83.4(3)	O15-Fe5-N8	86.9(3)
N1-Fe1-O4	83.4(3)	O15-Fe5-N8^{viii}	86.9(3)
N1^{ii}-Fe1-O14^{iii}	96.0(3)	O15-Fe5-O11	91.0(3)
N1-Fe1-O14^{iii}	96.0(3)	O15-Fe5-O11^{viii}	91.0(3)
O3-Fe1-N1^{ii}	89.8(3)	O8-Fe5-N8	91.5(2)
O3^{ii}-Fe1-N1^{ii}	172.8(3)	O8-Fe5-N8^{viii}	91.5(2)
O3-Fe1-N1	172.8(3)	O8-Fe5-O11	90.9(2)
O3^{ii}-Fe1-N1	89.8(3)	O8-Fe5-O11^{viii}	90.9(2)
O3-Fe1-O3^{ii}	90.4(5)	N8-Fe5-N8^{viii}	92.9(4)
O3^{ii}-Fe1-O4	89.4(3)	N8-Fe5-O11	95.2(2)
O3-Fe1-O4	89.4(3)	N8-Fe5-O11^{viii}	171.5(3)
O3^{ii}-Fe1-O14^{iii}	91.2(3)	N8^{viii}-Fe5-O11^{viii}	95.2(2)
O3-Fe1-O14^{iii}	91.2(3)	N8^{viii}-Fe5-O11	171.5(3)
O14^{iii}-Fe1-O4	179.2(4)	O11-Fe5-O11^{viii}	76.6(3)
O2-Fe2-O2^{v}	90.6(7)	N3^{ix}-Fe6-N3^{x}	99.2(4)
O2-Fe2-N5	115.3(3)	N3^{x}-Fe6-O11	92.8(3)

O2^{v}-Fe2-N5	115.3(3)	N3^{ix}-Fe6-O11^{viii}	92.8(3)
O2^{v}-Fe2-N5^{iv}	1153(3)	N3^{ix}-Fe6-O11	168.0(3)
O2-Fe2-N5^{iv}	115.3(3)	N3^{x}-Fe6-O11^{viii}	168.0(3)
N5^{iv}-Fe2-N5	105.3(6)	O9-Fe6-N3^{x}	90.3(3)
N4^{ii}-Fe3-N4	87.8 (4)	O9-Fe6-N3^{ix}	90.3(3)
N4^{ii}-Fe3-N9	90.8(3)	O9-Fe6-O11^{viii}	90.2(3)
N4-Fe3-N9	176.8(3)	O9-Fe6-O11	90.2(3)
N4-Fe3-N9^{ii}	90.8(3)	O9-Fe6-O12	174.5(4)
N4^{ii}-Fe3-N9^{ii}	176.8(3)	O11^{viii}-Fe6-O11	75.2(3)
O5-Fe3-N4^{ii}	88.8(3)	O12-Fe6-N3^{x}	86.2(3)
O5-Fe3-N4	88.9(3)	O12-Fe6-N3^{ix}	86.2(3)
O5-Fe3-N6	176.6(5)	O12-Fe6-O11^{viii}	94.1(3)
O5-Fe3-N9	94.0(3)	O12-Fe6-O11	94.1(3)
O5-Fe3-N9^{ii}	94.0(3)	N7-Fe7-O10	97.0(3)
N6-Fe3-N4^{ii}	88.7(4)	N7-Fe7-O10^{xi}	97.0(3)
N6-Fe3-N4	88.7(4)	N7-Fe7-O10^{vii}	97.0(3)
N6-Fe3-N9	88.3(4)	N7-Fe7-O10^{ii}	97.0(3)
N6-Fe3-N9^{ii}	88.3(4)	N7-Fe7-O13	163.8(6)
N9^{ii}-Fe3-N9	90.4(4)	N7-Fe7-O13^{xi}	163.8(6)
N2-Fe4-N2^{ii}	87.0(4)	O10-Fe7-O10^{vii}	83.7(6)
N2-Fe4-O4	85.3(3)	O10^{xi}-Fe7-O10^{ii}	83.7(6)
N2^{ii}-Fe4-O4	85.3(3)	O10-Fe7-O10^{xi}	165.9(6)
N2-Fe4-O6	89.3(3)	O10^{xi}-Fe7-O10^{vii}	94.6(5)
N2^{ii}-Fe4-O6	89.3(3)	O10^{ii}-Fe7-O10^{vii}	165.9(6)
O4-Fe4-O6	172.6(4)	O10-Fe7-O10^{ii}	94.6(5)
N10-Fe4-N2^{ii}	176.9(3)	O13-Fe7-O10^{xi}	94.0(5)
N10^{ii}-Fe4-N2	176.9(3)	O13-Fe7-O10^{vii}	94.0(5)
N10^{ii}-Fe4-N2^{ii}	91.9(3)	O13^{xi}-Fe7-O10^{vii}	72.3(5)
N10-Fe4-N2	91.9(3)	O13-Fe7-O10^{ii}	72.3(5)
N10^{ii}-Fe4-O4	97.5(3)	O13-Fe7-O10	72.3(5)
N10-Fe4-O4	97.5(3)	O13^{xi}-Fe7-O10^{xi}	72.3(5)
N10-Fe4-O6	87.7(3)	O13^{xi}-Fe7-O10^{ii}	94.0(5)
N10^{ii}-Fe4-O6	87.7(3)	O13^{xi}-Fe7-O10	94.0(5)
N10^{ii}-Fe4-N10	89.0(4)	O13-Fe7-O13^{xi}	32.5(12)

^{i} y, x, z	^{ii} x, y, 1-z	^{iii} y-x, 1-x, z	^{iv} x, y, 2-z
^{v} 1-y+x, 2-y, 2-z	^{vi} y, x, 2-z	^{vii} 1-y+x, 2-y, z	^{viii} x, y, -z
^{ix} 1-y, 1+x-y, -z	^{x} 1-y, 1+x-y, z	^{xi} 1-y+x, 2-y, 1-z	^{xii} 1-x, 1-x+y, 1-z
^{xiii} 1-y+x, 2-y, -z			

Table S3 The bonds lengths(Å) and angles(°) for **2**.

2			
Fe/Co1-O3^{i}	2.05(3)	Fe/Co4-N10^{i}	2.13(3)
Fe/Co1-O3	2.05(3)	Fe/Co5-O8	2.08(3)
Fe/Co1-O4	2.21(3)	Fe/Co5-O11^{v}	2.20(2)
Fe/Co1-O1^{ii}	2.18(3)	Fe/Co5-O11	2.20(2)
Fe/Co1-N1^{i}	2.15(2)	Fe/Co5-O15	2.09(4)
Fe/Co1-N1	2.15(2)	Fe/Co5-N8^{v}	2.17(2)
Fe/Co2-N5^{iii}	2.03(4)	Fe/Co5-N8	2.17(2)
Fe/Co2-N5	2.03(4)	Fe/Co6-O9	2.03(3)
Fe/Co2-O2^{iv}	1.93(4)	Fe/Co6-O11	2.22(2)
Fe/Co2-O2	1.93(4)	Fe/Co6-O11^{v}	2.22(2)
Fe/Co3-O5	2.06(3)	Fe/Co6-O12	2.07(3)
Fe/Co3-N4^{i}	2.16(2)	Fe/Co6-N3^{vi}	2.14(2)
Fe/Co3-N4	2.16(2)	Fe/Co6-N3^{vii}	2.14(2)
Fe/Co3-N6	2.02(3)	Fe/Co7-O10^{viii}	2.13(3)
Fe/Co3-N9	2.14(2)	Fe/Co7-O10^{i}	2.13(3)
Fe/Co3-N9^{i}	2.14(2)	Fe/Co7-O10^{ix}	2.13(3)
Fe/Co4-O4	2.16(4)	Fe/Co7-O10	2.13(3)
Fe/Co4-O6	2.34(4)	Fe/Co7-O13	1.84(9)
Fe/Co4-N2	2.16(2)	Fe/Co7-O13^{ix}	1.84(9)
Fe/Co4-N2^{i}	2.16(2)	Fe/Co7-N7	2.00(5)
Fe/Co4-N10	2.13(3)		
O3^{i}-Fe/Co1-O3	89.4(18)	O8-Fe/Co5-O11	89.6(8)
O3^{i}-Fe/Co1-O4	89.1(10)	O8-Fe/Co5-O11^{v}	89.6(8)
O3-Fe/Co1-O4	89.1(10)	O8-Fe/Co5-O15	176.9(12)
O3-Fe/Co1-O14^{ii}	91.7(11)	O8-Fe/Co5-N8^{v}	92.4(9)
O3^{i}-Fe/Co1-O14^{ii}	91.7(11)	O8-Fe/Co5-N8	92.4(9)
O3^{i}-Fe/Co1-N1	91.1(11)	O11-Fe/Co5-O11^{v}	77.2(10)
O3-Fe/Co1-N1	172.2(10)	O15-Fe/Co5-O11^{v}	92.8(9)
O3^{i}-Fe/Co1-N1^{i}	172.3(10)	O15-Fe/Co5-O11	92.8(9)
O3-Fe/Co1-N1^{i}	91.1(11)	O15-Fe/Co5-N8^{v}	85.4(9)
O14^{ii}-Fe/Co1-O4	178.8(15)	O15-Fe/Co5-N8	85.4(9)
N1-Fe/Co1-O4	83.2(10)	N8^{v}-Fe/Co5-O11^{v}	95.4(8)
N1^{i}-Fe/Co1-O4	83.2(10)	N8-Fe/Co5-O11^{v}	172.3(9)
N1^{i}-Fe/Co1-O14^{ii}	96.0(11)	N8^{v}-Fe/Co5-O11	172.3(9)
N1-Fe/Co1-O14^{ii}	96.0(11)	N8-Fe/Co5-O11	95.4(8)
N1-Fe/Co1-N1^{i}	87.4(13)	N8^{v}-Fe/Co5-N8	92.0(13)
N5-Fe/Co2-N5^{iii}	107(2)	O9-Fe/Co6-O11^{v}	90.0(8)

O2^{iv}-Fe/Co2-N5^{iii}	113.8(9)	O9-Fe/Co6-O11	90.0(8)
O2^{iv}-Fe/Co2-N5	113.8(9)	O9-Fe/Co6-O12	174.4(12)
O2-Fe/Co2-N5^{iii}	113.8(9)	O9-Fe/Co6-N3^{vi}	90.1(9)
O2-Fe/Co2-N5	113.8(9)	O9-Fe/Co6-N3^{vii}	90.1(9)
O2^{iv}-Fe/Co2-O2	94(2)	O11-Fe/Co6-O11^{v}	76.3(10)
O5-Fe/Co3-N4	87.4(9)	O12-Fe/Co6-O11	94.4(9)
O5-Fe/Co3-N4^{i}	87.4(9)	O12-Fe/Co6-O11^{v}	94.4(9)
O5-Fe/Co3-N9	94.3(8)	O12-Fe/Co6-N3^{vi}	86.3(9)
O5-Fe/Co3-N9^{i}	94.3(8)	O12-Fe/Co6-N3^{vii}	86.3(9)
N4^{i}-Fe/Co3-N4	87.7(12)	N3^{vi}-Fe/Co6-O11	92.8(8)
N6-Fe/Co3-O5	177.1(11)	N3^{vii}-Fe/Co6-O11	169.1(8)
N6-Fe/Co3-N4	90.5(8)	N3^{vi}-Fe/Co6-O11^{v}	169.1(8)
N6-Fe/Co3-N4^{i}	90.5(8)	N3^{vii}-Fe/Co6-O11^{v}	92.8(8)
N6-Fe/Co3-N9^{i}	87.7(8)	N3^{vii}-Fe/Co6-N3^{vi}	98.1(13)
N6-Fe/Co3-N9	87.7(8)	O10-Fe/Co7-O10^{viii}	84.8(16)
N9-Fe/Co3-N4^{i}	90.6(8)	O10^{i}-Fe/Co7-O10^{viii}	166(2)
N9^{i}-Fe/Co3-N4^{i}	177.5(9)	O10^{i}-Fe/Co7-O10^{ix}	84.8(16)
N9-Fe/Co3-N4	177.5(9)	O10-Fe/Co7-O10^{ix}	166(2)
N9^{i}-Fe/Co3-N4	90.6(8)	O10-Fe/Co7-O10^{i}	93.6(16)
N9-Fe/Co3-N9^{i}	91.1(12)	O10^{ix}-Fe/Co7-O10^{viii}	93.6(16)
O4-Fe/Co4-O6	173.4(13)	O13-Fe/Co7-O10^{i}	69.5(18)
N2^{i}-Fe/Co4-O4	85.2(9)	O13-Fe/Co7-O10^{ix}	97(2)
N2-Fe/Co4-O4	85.2(9)	O13-Fe/Co7-O10	69.5(18)
N2-Fe/Co4-O6	89.9(9)	O13-Fe/Co7-O10^{viii}	97(2)
N2^{i}-Fe/Co4-O6	89.9(9)	O13^{ix}-Fe/Co7-O10^{viii}	69.5(18)
N2-Fe/Co4-N2^{i}	85.4(13)	O13^{ix}-Fe/Co7-O10^{ix}	69.5(18)
N10^{i}-Fe/Co4-O4	97.2(10)	O13^{ix}-Fe/Co7-O10	97(2)
N10-Fe/Co4-O4	97.2(10)	O13^{ix}-Fe/Co7-O10^{i}	97(2)
N10-Fe/Co4-O6	87.4(10)	O13-Fe/Co7-O13^{ix}	42(5)
N10^{i}-Fe/Co4-O6	87.4(10)	O13-Fe/Co7-N7	159(2)
N10^{i}-Fe/Co4-N2	176.6(9)	O13^{ix}-Fe/Co7-N7	159(2)
N10-Fe/Co4-N2	92.6(9)	N7-Fe/Co7-O10^{viii}	96.8(11)
N10-Fe/Co4-N2^{i}	176.6(9)	N7-Fe/Co7-O10^{ix}	96.8(11)
N10^{i}-Fe/Co4-N2^{i}	92.6(9)	N7-Fe/Co7-O10^{i}	96.8(11)
N10-Fe/Co4-N10^{i}	89.4(13)	N7-Fe/Co7-O10	96.8(11)

^{i} x, y, 1-z	^{ii} y-x, 1-x, z	^{iii} x, y, 2-z	^{iv} 1-y+x, 2-y, 2-z
^{v} x, y, -z	^{vi} 1-y, 1+x-y, z	^{vii} 1-y, 1+x-y, -z	^{viii} 1-y+x, 2-y, z
^{ix} 1-y+x, 2-y, 1-z	^{x} 1-x, 1-x+y, 1-z	^{xi} 1-y+x, 2-y, -z	^{xii} y, x, z
^{xiii} y, x, 2-z			

Table S4 Valence bonds data of **1**.

Atom #1	Atom #2	Length	Fe2 r0	Fe3 r0	Fe2 s	Fe2 BVS	Fe3 s	Fe3 BVS
Fe1	N1	2.149	1.769	1.815	0.35807	1.910025	0.405472	2.234117
Fe1	N1	2.149	1.769	1.815	0.35807		0.405472	
Fe1	O14	2.193	1.7	1.765	0.263835		0.314505	
Fe1	O3	2.091	1.7	1.765	0.347581		0.414335	
Fe1	O3	2.091	1.7	1.765	0.347581		0.414335	
Fe1	O4	2.236	1.7	1.765	0.234887		0.279998	
Fe2	N5	2.058	1.769	1.815	0.457911	1.733368	0.51853	2.011618
Fe2	O2	2.031	1.7	1.765	0.408773		0.487279	
Fe2	N5	2.058	1.769	1.815	0.457911		0.51853	
Fe2	O2	2.031	1.7	1.765	0.408773		0.487279	
Fe3	N4	2.178	1.769	1.815	0.331077	2.026545	0.374906	2.315621
Fe3	N4	2.178	1.769	1.815	0.331077		0.374906	
Fe3	N6	2.139	1.769	1.815	0.367879		0.41658	
Fe3	N9	2.186	1.769	1.815	0.323995		0.366887	
Fe3	N9	2.186	1.769	1.815	0.323995		0.366887	
Fe3	O5	2.09	1.7	1.765	0.348522		0.415456	
Fe4	N10	2.151	1.769	1.815	0.35614	1.805958	0.403286	2.070247
Fe4	N10	2.151	1.769	1.815	0.35614		0.403286	
Fe4	O4	2.211	1.7	1.765	0.251307		0.299571	
Fe4	O6	2.353	1.7	1.765	0.17121		0.204091	
Fe4	N2	2.173	1.769	1.815	0.335581		0.380006	
Fe4	N2	2.173	1.769	1.815	0.335581		0.380006	
Fe5	N8	2.163	1.769	1.815	0.344774	1.836447	0.390417	2.147995
Fe5	O11	2.209	1.7	1.765	0.252669		0.301194	
Fe5	O8	2.146	1.7	1.765	0.299571		0.357103	
Fe5	O15	2.097	1.7	1.765	0.34199		0.40767	
Fe5	N8	2.163	1.769	1.815	0.344774		0.390417	
Fe5	O11	2.209	1.7	1.765	0.252669		0.301194	
Fe6	O11	2.23	1.7	1.765	0.238728	1.940011	0.284575	2.271114
Fe6	O12	2.062	1.7	1.765	0.37592		0.448116	
Fe6	O9	2.047	1.7	1.765	0.391473		0.466656	
Fe6	N3	2.16	1.769	1.815	0.347581		0.393595	
Fe6	O11	2.23	1.7	1.765	0.238728		0.284575	
Fe6	N3	2.16	1.769	1.815	0.347581		0.393595	
Fe7	N7	2.033	1.769	1.815	0.48992	2.035168	0.554777	2.396792
Fe7	O10	2.157	1.7	1.765	0.290795		0.346643	
Fe7	O10	2.157	1.7	1.765	0.290795		0.346643	
Fe7	O13	2.056	1.7	1.765	0.382066		0.455442	
Fe7	O10	2.157	1.7	1.765	0.290795		0.346643	
Fe7	O10	2.157	1.7	1.765	0.290795		0.346643	

Table S5 ICP-OES test data of **2**.

Sample	m_0/g	V_0/mL	element	C_o/mg/L	f	C_1/mg/L	C_x/mg/kg	W/%	W^c/%
1	0.0654	25	Fe	2.427	100	242.7	92775.2	9.28%	9.77%
1	0.0654	25	Fe	2.433	100	243.3	93004.6	9.30%	9.79
1	0.0654	25	Co	4.690	100	469	179281.3	17.93%	18.87
1	0.0654	25	Co	4.693	100	469.3	179396.0	17.94%	18.88

The thermogravimetric analysis of the prepared and activated **2** shows that **2** contains 5% by mass of low boiling point solvent (**Fig. S2**). These solvents are not localized in the crystal structure, thus, metal contents of the ICP test was converted according to the thermogravimetric result of the crystal molecular formula by $W^c/\%=W\%\div 0.95$. And the calculated molecular formula of **2** is $C_{53}H_{55}Co_{7.75}Fe_{4.25}N_{35}O_{34}$, which can be simplified to $C_{53}H_{55}Co_8Fe_4N_{35}O_{34}$ by accounting one significant digit of the metal ion.

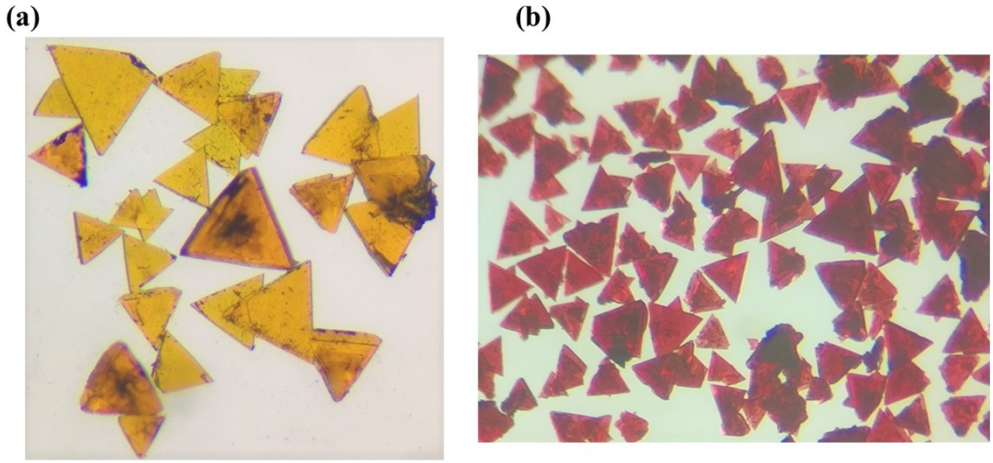

Fig. S1 Shape of single crystal **1** (a) and **2** (b).

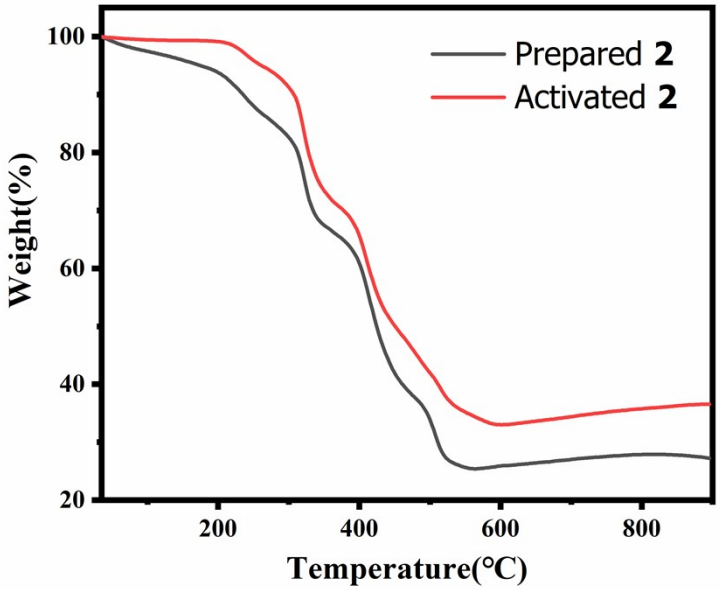

Fig. S2 TGA profiles recorded for **2** in N_2 atmosphere.

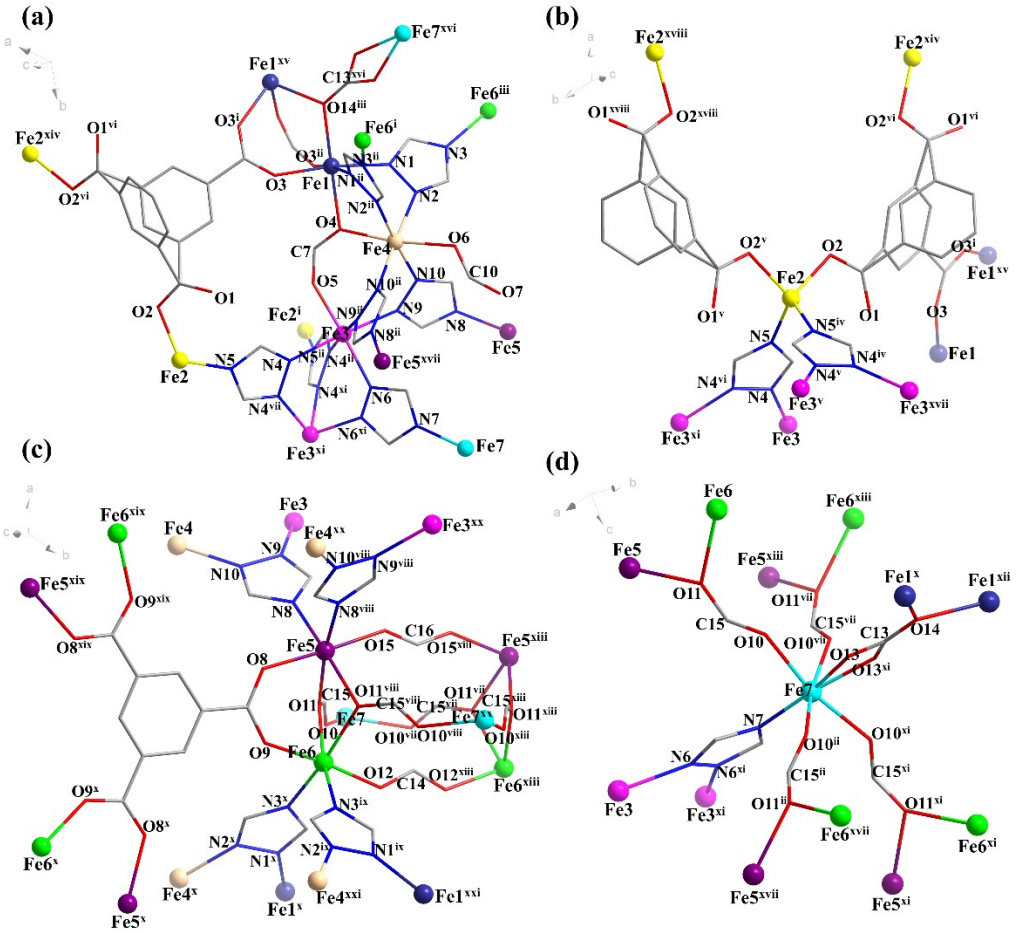

Fig. S3 Coordination modes and linkages of the metal ions and ligands in **1**. (a) for Fe1, Fe3 and Fe4; (b) for Fe2; (c) for Fe5 and Fe6; (d) for Fe7. Symmetric code: [i]y, x, z; [ii] x, y, 1-z; [iii]y-x, 1-x, z; [iv]x, y, 2-z; [v]1-y+x, 2-y, 2-z; [vi]y, x, 2-z; [vii]1-y+x, 2-y, z; [viii]x, y, -z; [ix]1-y, 1+x-y, -z; [x]1-y, 1+x-y, z; [xi]1-y+x, 2-y, 1-z; [xii]1-x, 1-x+y, 1-z; [xiii]1-y+x, 2-y, -z; [xiv]2-y, 1+x-y, z; [xv]y, x, 1-z; [xvi]y-x, 1-x, 1-z; [xvii] x, y, 1+z; [xviii]1-x+y, 2-x, 2-z; [xix]y-x, 1-x, -z; [xx]x, y, z-1; [xxi]1-y, 1+x-y, z-1.

As shown in **Fig. S3**, Fe1 is coordinated by two N atoms and four O atoms from two tz ligands, two formates and two carboxylate groups from btc or formate with disorder. The Fe1-N/O distances are in the normal range of 2.110-2.250 Å (**Table S2**). Fe3 is coordinated by one formate and five tz ligands, and Fe4 is coordinated by two formates and four tz ligands. The coordination environment of Fe5 and Fe6 are very similar which are both coordinated by three formates, one btc and two tz ligands. Fe7 ion locates in a slightly distorted octahedral geometry coordinated by five formate anions and one tz ligand, in which the formate containing O13 atom is disordered. Fe2 ion is four coordinated by two O atoms from two disorder btc or formate anions and two N atoms from two tz ligands.

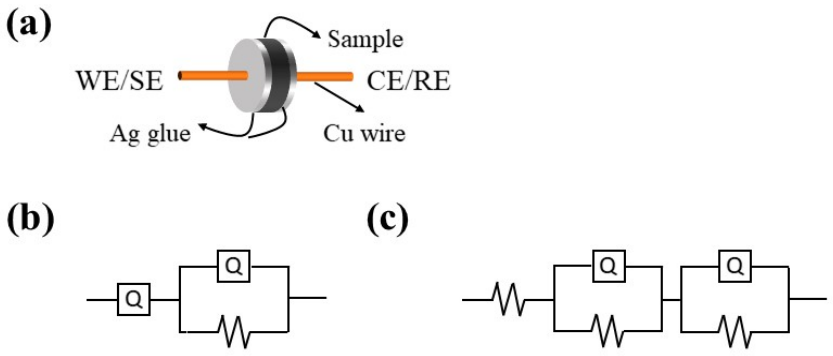

Fig. S4 The compacted tablet model (a) and circuit model of **1** (b), **2** (c)

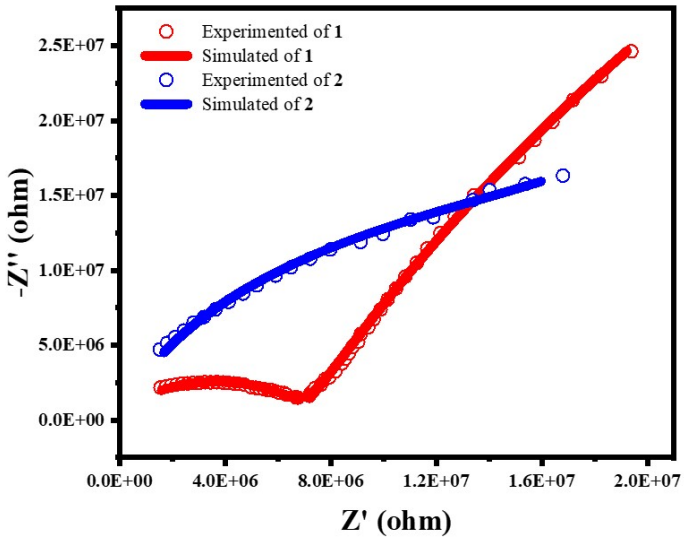

Fig. S5 Electrochemical impedance spectroscopy of **1**and **2**.

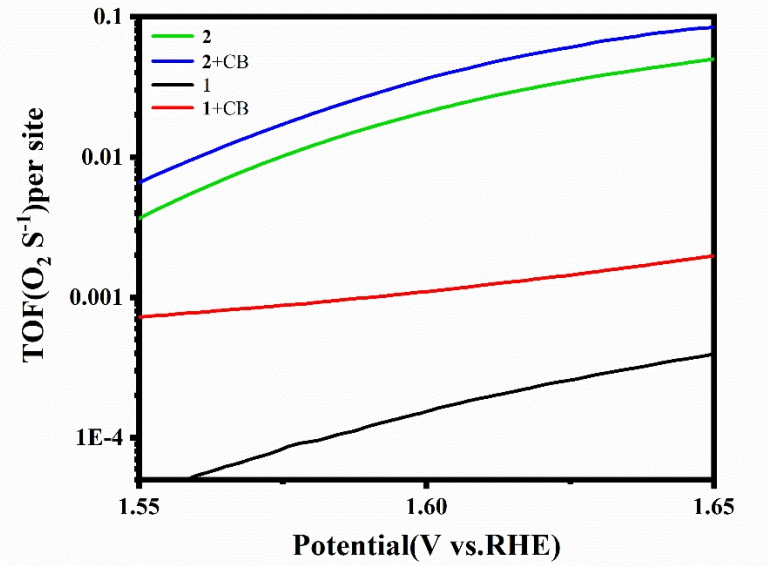

Fig. S6 TOF values collected at different potentials of **1**, **2**, **1** mixed CB and **2** mixed CB.

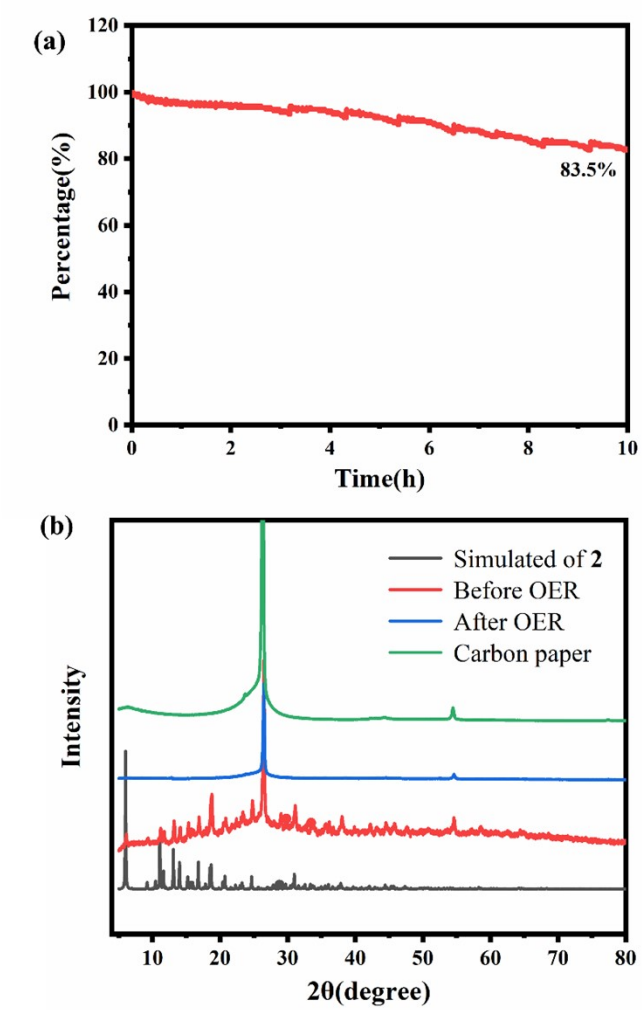

Fig. S7 a) Continuous OER i-t test for **2** at 1.62 V. b) the PXRD of carbon papers, **2** coated on carbon papers before OER i-t test and **2** coated on carbon papers after 2 h OER i-t test.

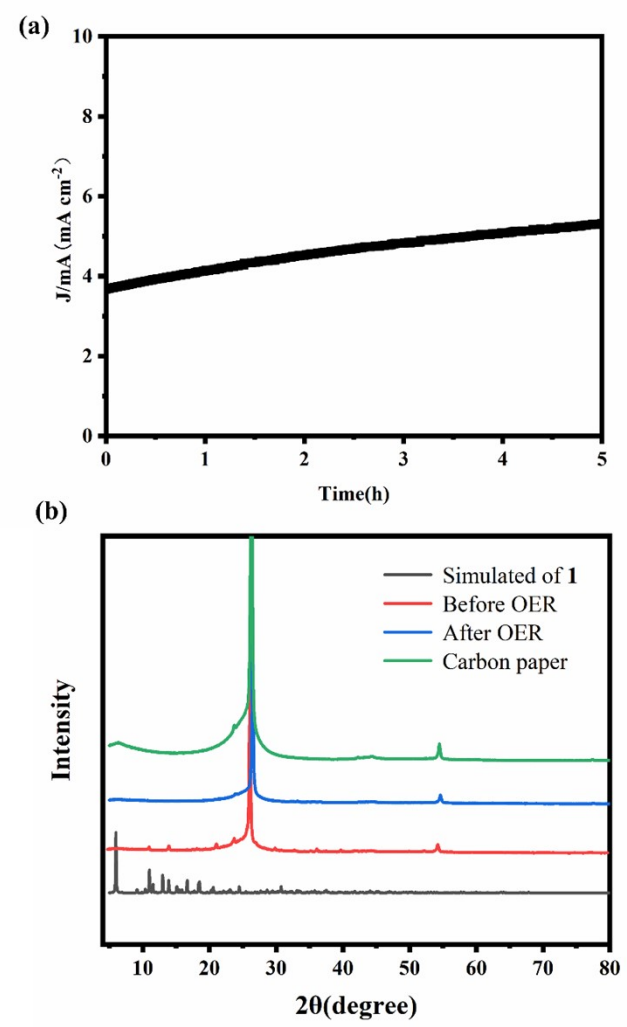

Fig. S8 a) Continuous OER i-t test for **1** at 1.62 V. b) the PXRD of carbon papers, **1** coated on carbon papers before OER i-t test and **1** coated on carbon papers after 2 h OER i-t test.

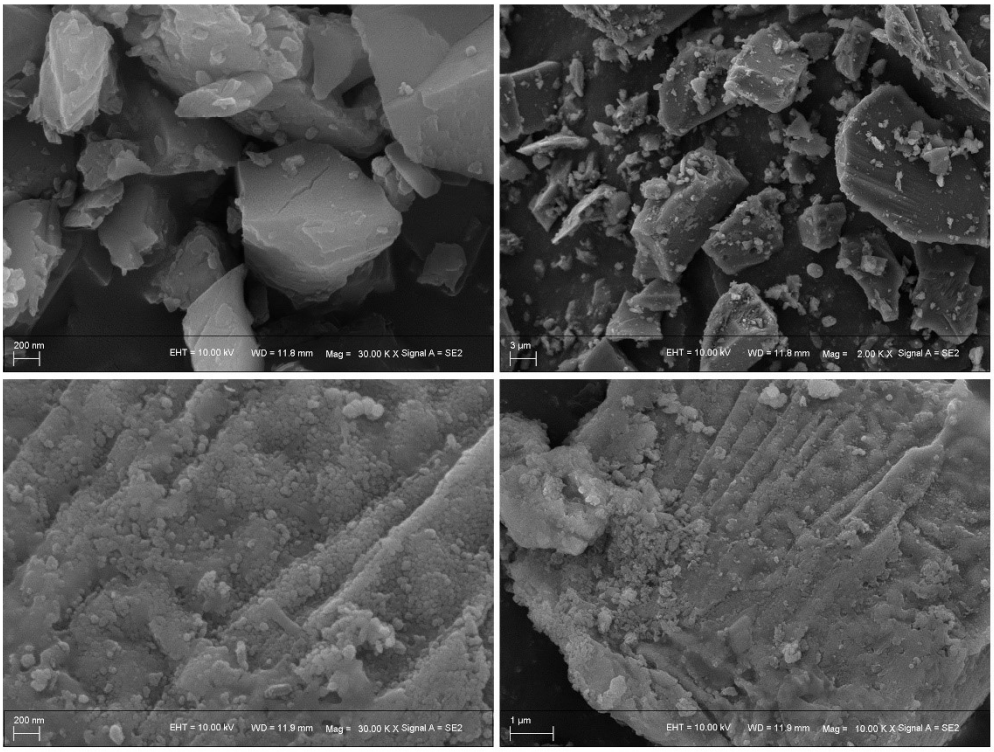

Fig. S9 SEM images of **1** before (top) and after (bottom) 2 h OER test.

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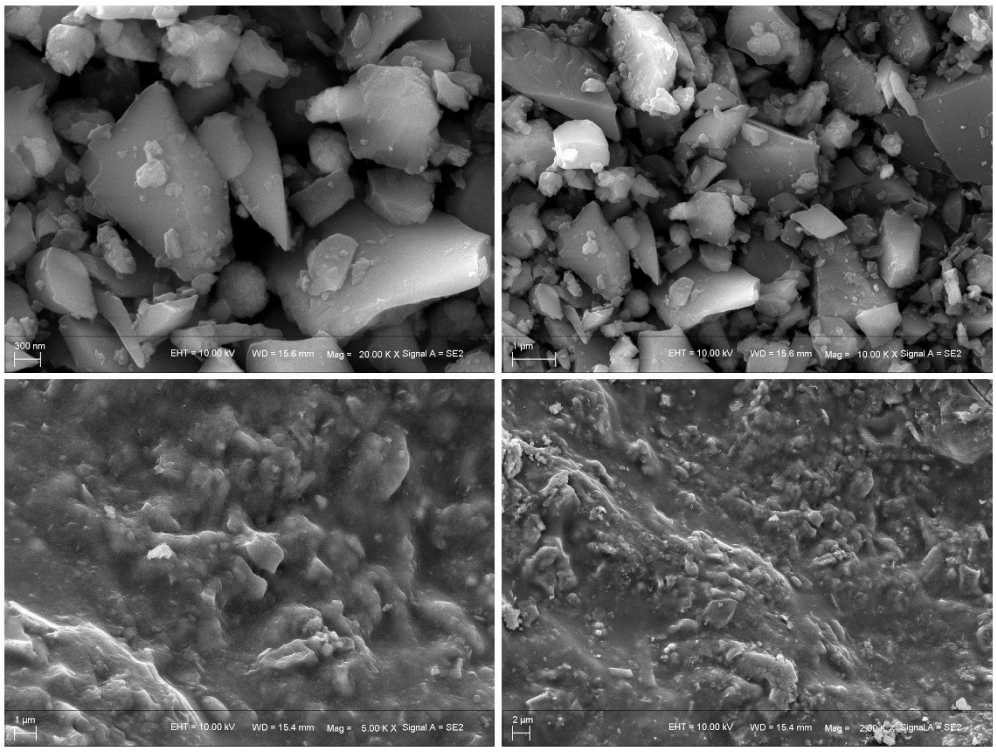

Fig. 10 SEM images of **2** before (top) and after (bottom) OER test.