

Supplementary Information

Engineering all-organic electrocatalysts with asymmetric dual-active sites for uncommon oxygen-evolving pathway

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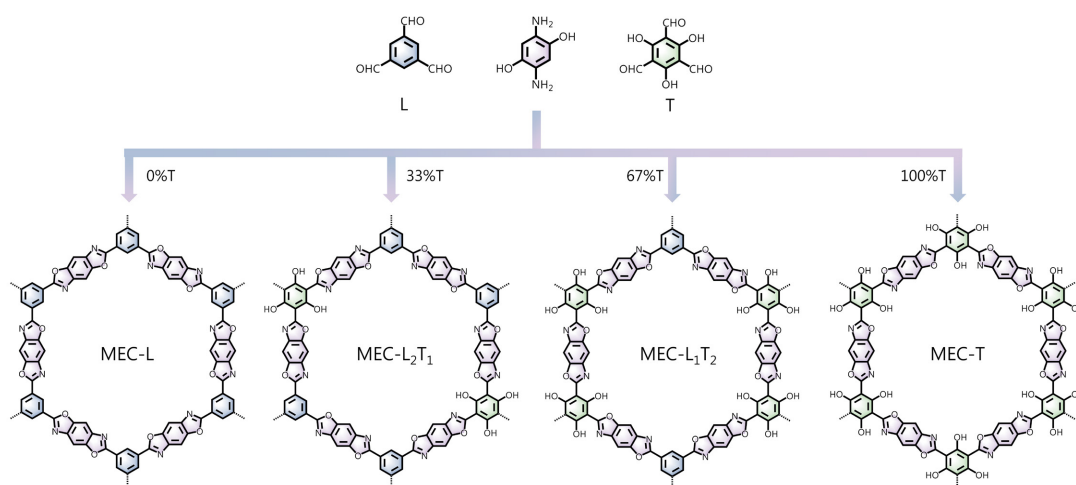
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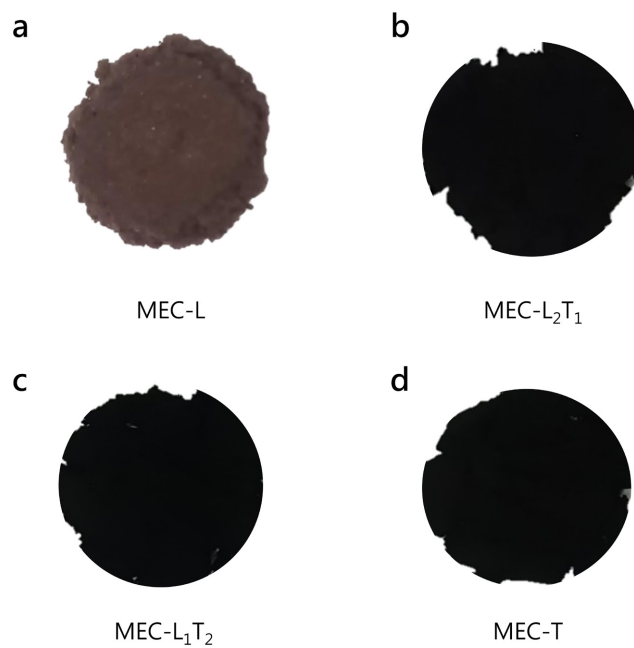
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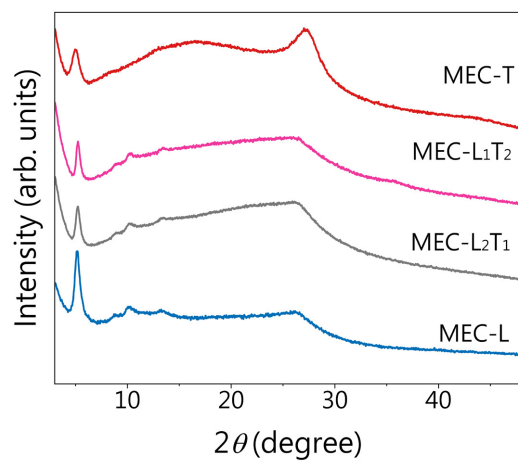
Catalyst characterization



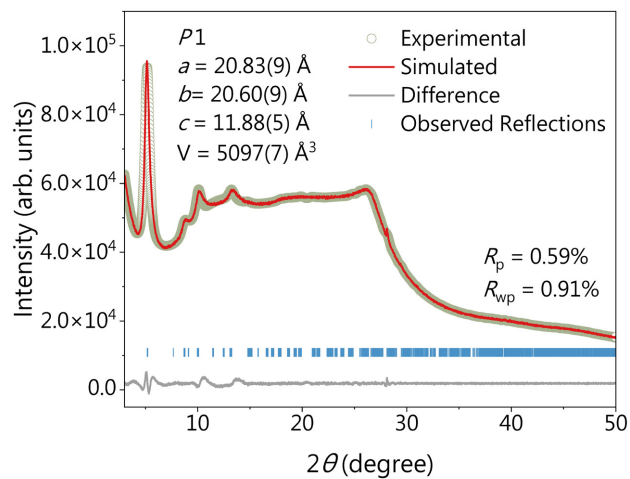
Supplementary Fig. 1. Schematic diagram of the synthesis of catalysts. Controlled synthesis of COFs with tunable oxygen content via gradient variation of trial-aldehyde phloroglucinol (TP) feeding ratio.



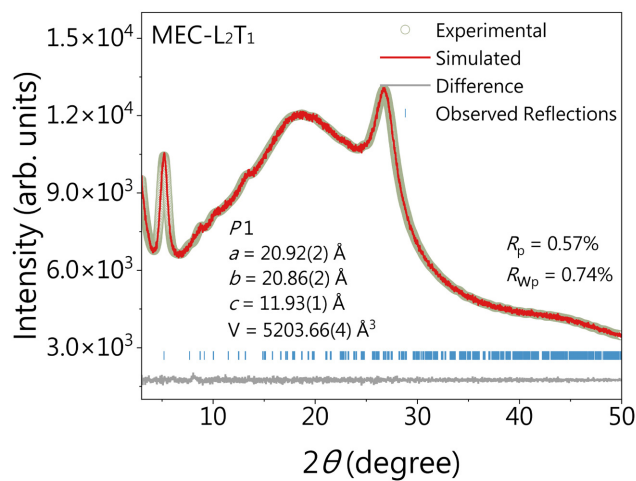
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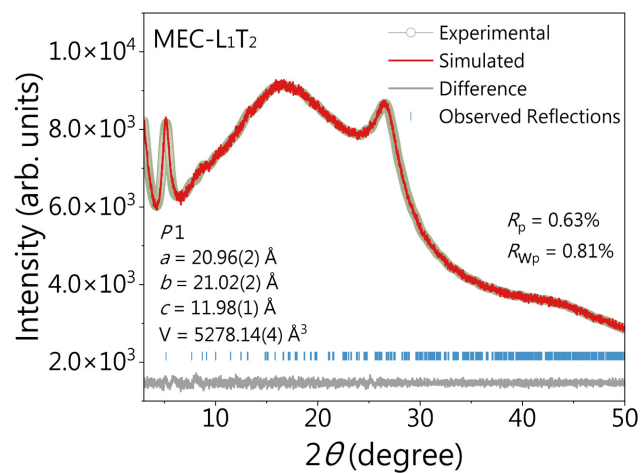
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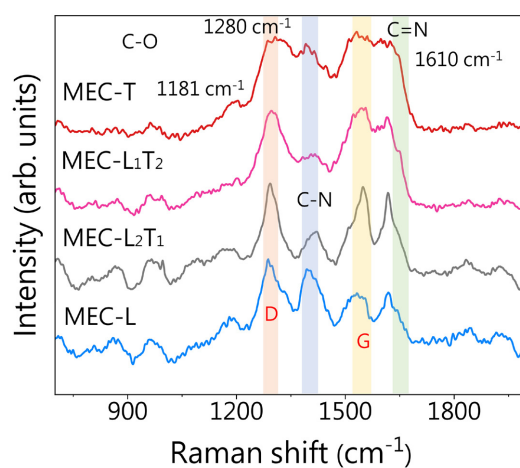
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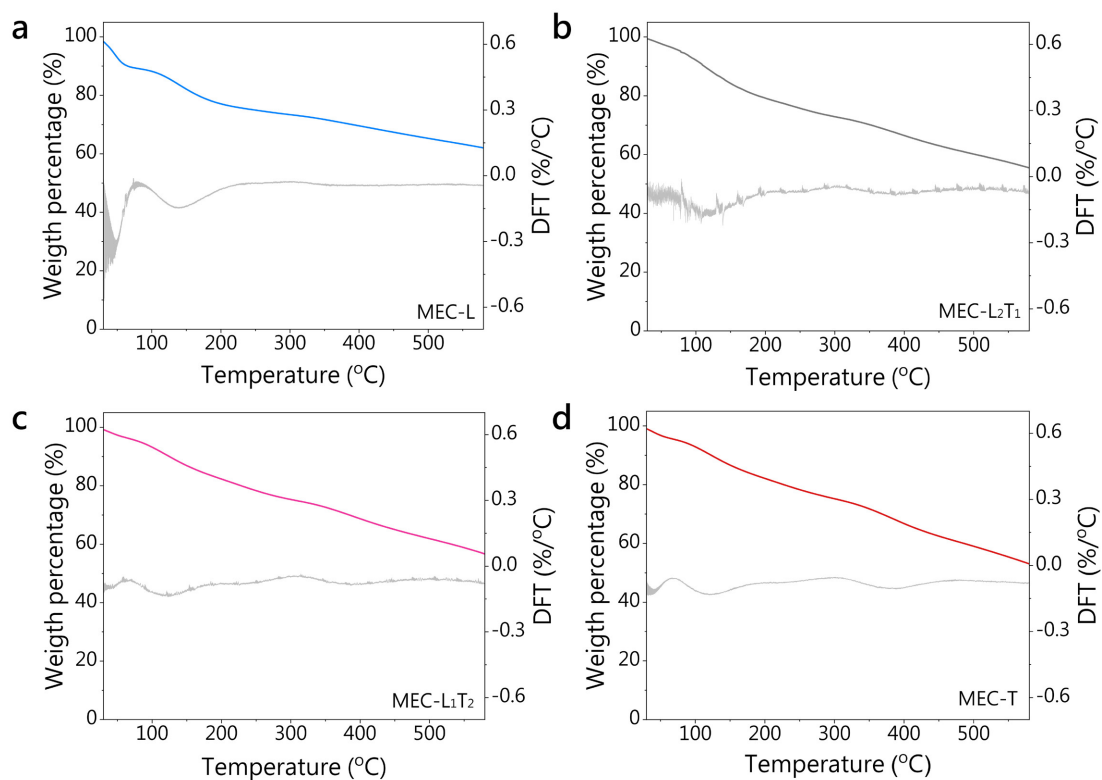
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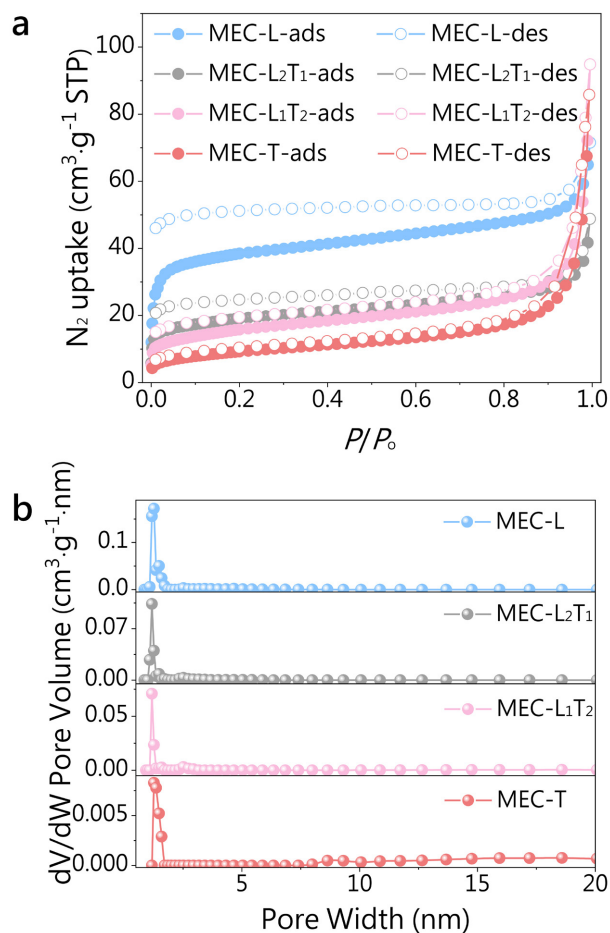
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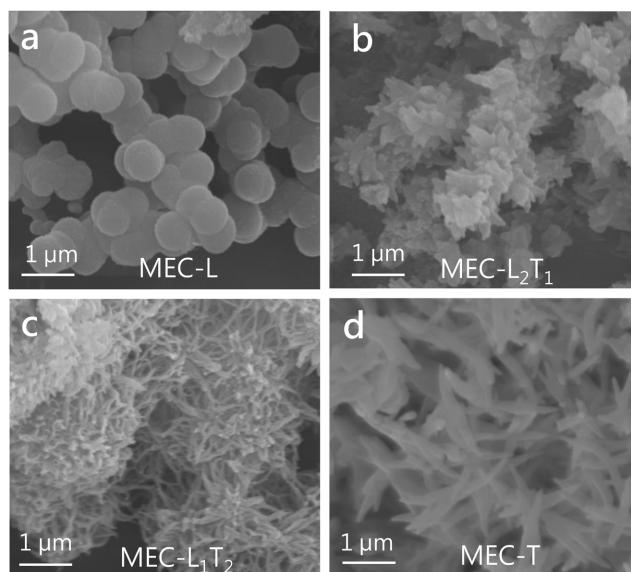
Supplementary Fig. 7. Raman spectra of catalysts. The presence of the G-band at 1580 cm^{-1} confirms that the structure is a two-dimensional porous honeycomb framework constructed from benzene and oxazole rings. Meanwhile, the characteristic peaks of C–O (1181 and 1280 cm^{-1}), C–N (1386 cm^{-1}), and C=N (1610 cm^{-1}) observed in the Raman spectra of all samples demonstrate the successful synthesis of COFs. Source data are provided as a Source Data file.



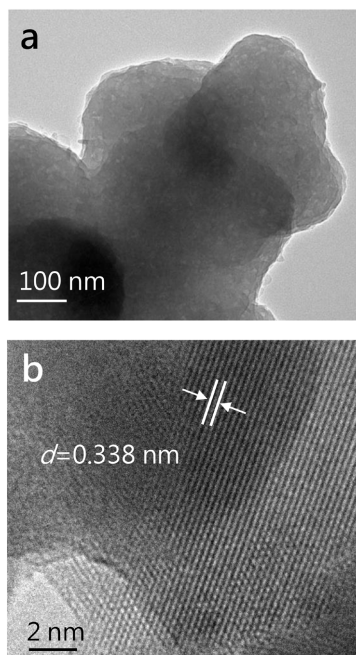
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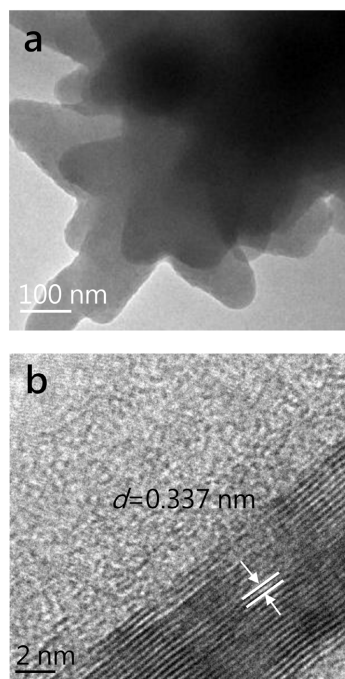
Supplementary Fig. 9. N₂ sorption curves and pore size distributions of catalysts. **a** 77 K nitrogen adsorption isotherms of COFs, **b** Pore size distributions of COFs. The specific surface areas of MEC-L, MEC-L₂T₁, MEC-L₁T₂ and MEC-T are 146.7 m²·g⁻¹, 68.8 m²·g⁻¹, 56.3 m²·g⁻¹ and 33.0 m²·g⁻¹, respectively. The pore size distribution of the catalysts was calculated by NLDFT method, which showed that the pore size was about 1.4 nm. Source data are provided as a Source Data file.



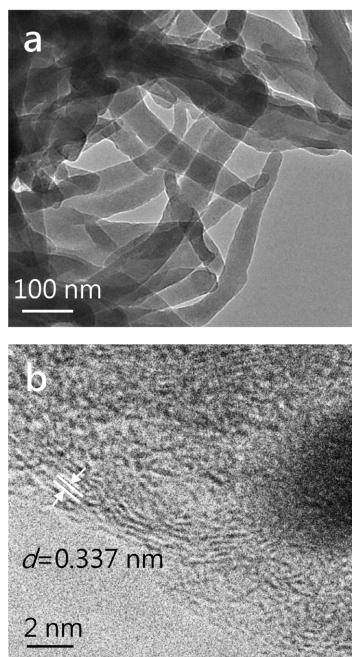
Supplementary Fig. 10. SEM images of catalysts. SEM images of **a** MEC-L, **b** MEC-L₂T₁, **c** MEC-L₁T₂ and **d** MEC-T.



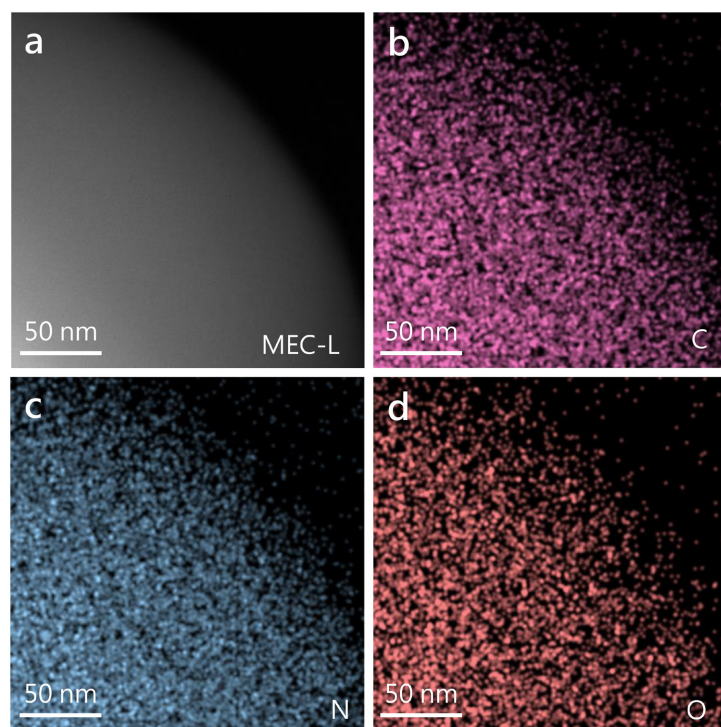
Supplementary Fig. 11. TEM image and HRTEM image of MEC-L. **a** TEM image of MEC-L, **b** HRTEM image of MEC-L. The lattice fringe spacing in the image of MEC-L was measured as $d = 0.338$ nm, corresponding to the diffraction peak of 26.3° in the PXRD pattern.



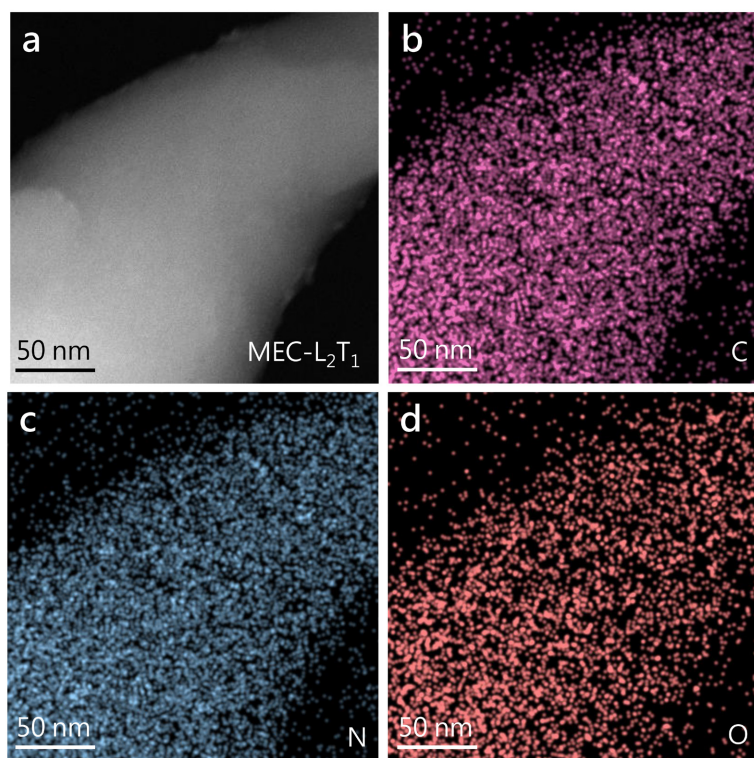
Supplementary Fig. 12. TEM image and HRTEM image of MEC-L₂T₁. **a** TEM image of MEC-L₂T₁, **b** HRTEM image of MEC-L₂T₁. The lattice fringe spacing in the image of MEC-L₂T₁ was measured as $d = 0.337$ nm, corresponding to the diffraction peak of 26.3° in the PXRD pattern.



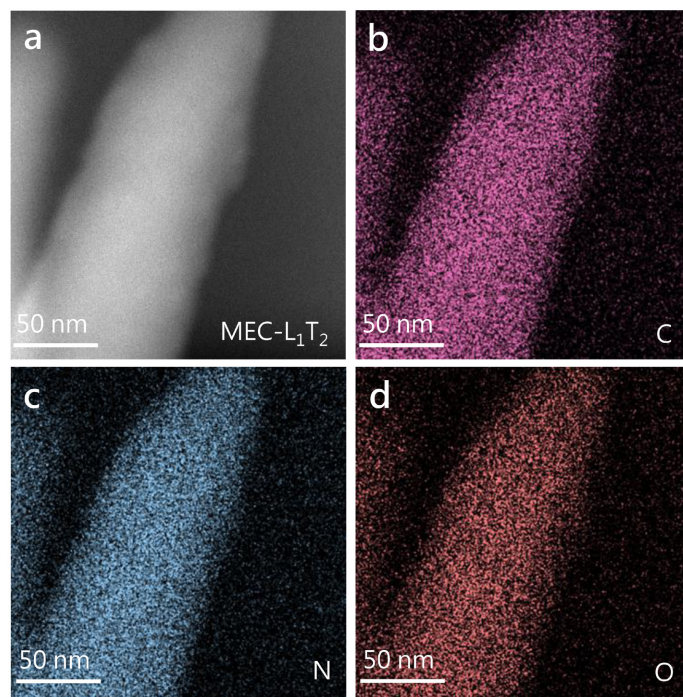
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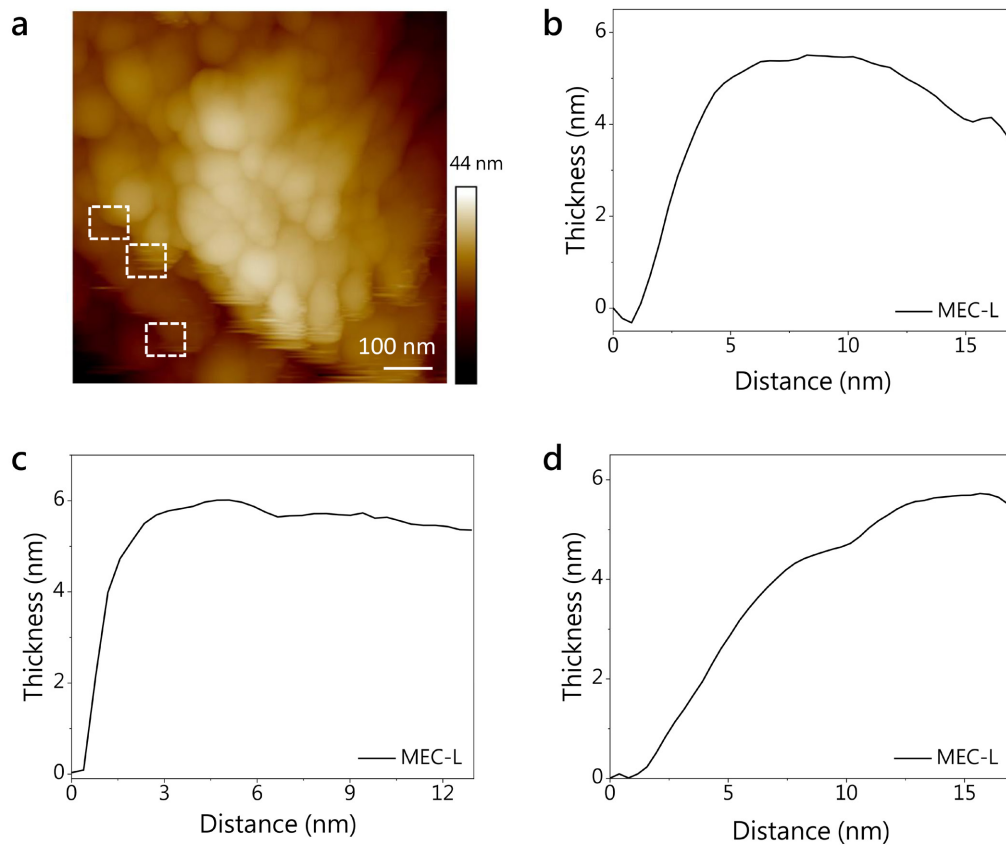
Supplementary Fig. 14. TEM-Mapping of MEC-L. The C, N, and O elements are uniformly distributed in MEC-L.



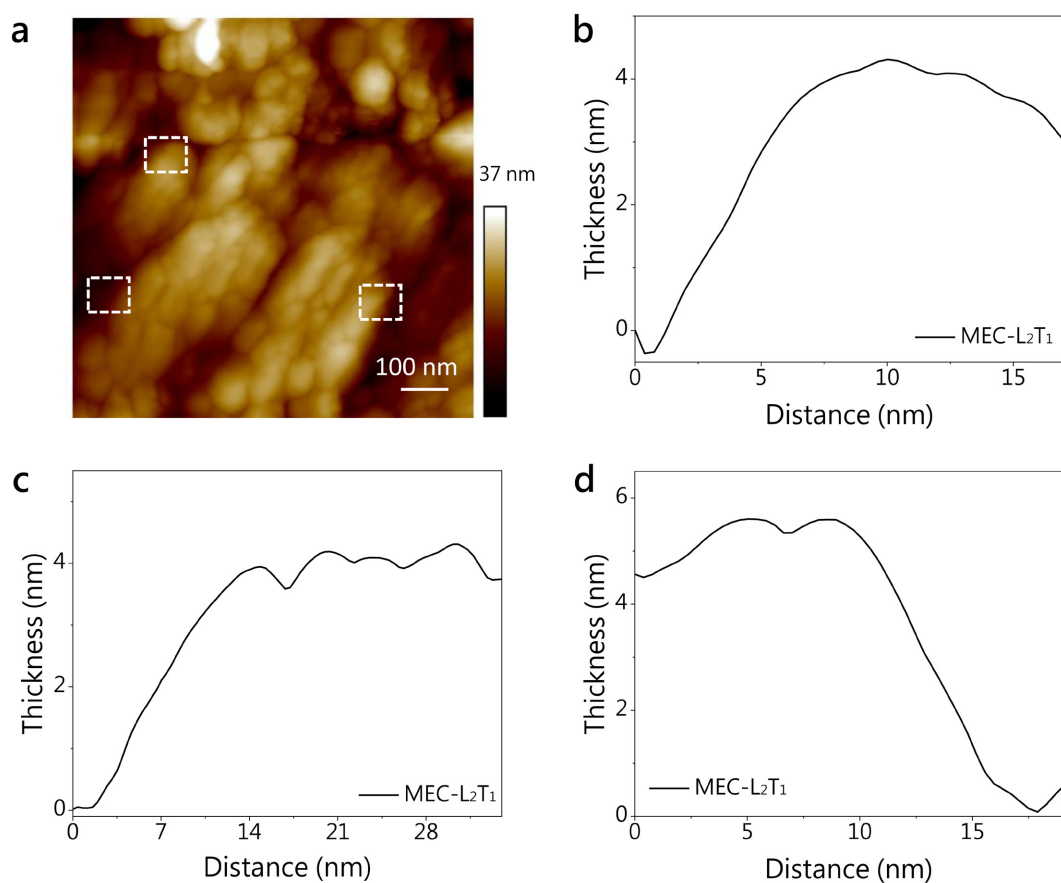
Supplementary Fig. 15. TEM-Mapping of MEC-L₂T₁. The C, N, and O elements are uniformly distributed in MEC-L₂T₁.



Supplementary Fig. 16. TEM-Mapping of MEC-Li₁T₂. The C, N, and O elements are uniformly distributed in MEC-Li₁T₂.

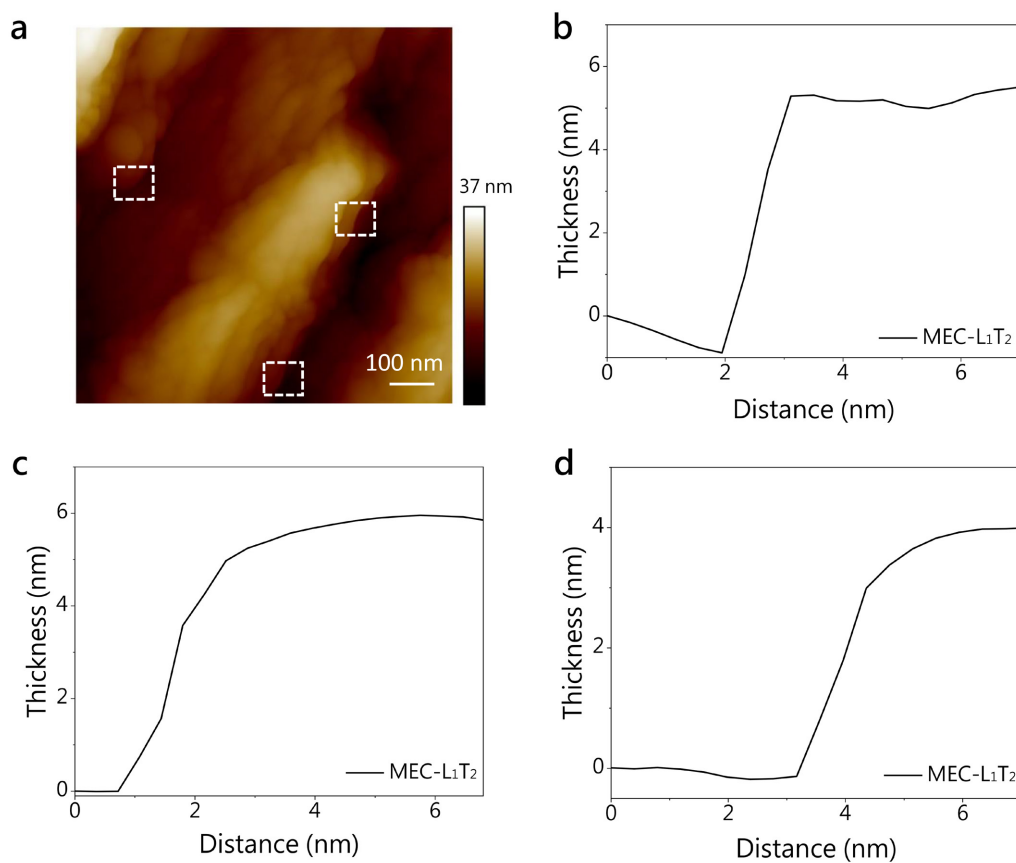


Supplementary Fig. 17. AFM image of MEC-L. **a** AFM image of MEC-L. **b, c, d** The thickness of MEC-L at different selected areas. The AFM image size is $1 \times 1 \mu\text{m}$. The thickness of MEC-L is $5.7 \pm 0.1 \text{ nm}$. Source data are provided as a Source Data file.



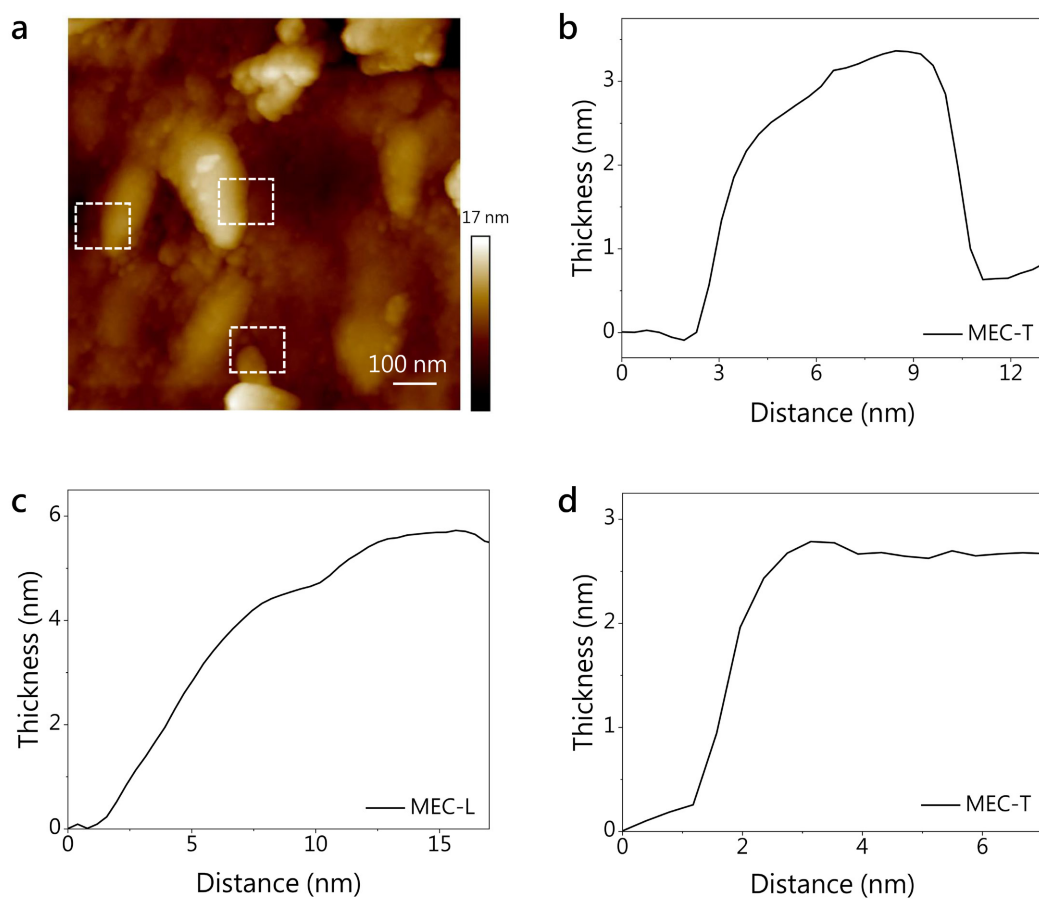
Supplementary Fig. 18. AFM image of MEC-L₂T₁. **a** AFM image of MEC-L₂T₁. **b, c, d** The thickness of MEC-L₂T₁ at different selected areas. The AFM image size is $1 \times 1 \mu\text{m}$. The thickness of MEC-L₂T₁ is $4.8 \pm 0.6 \text{ nm}$.

Source data are provided as a Source Data file.

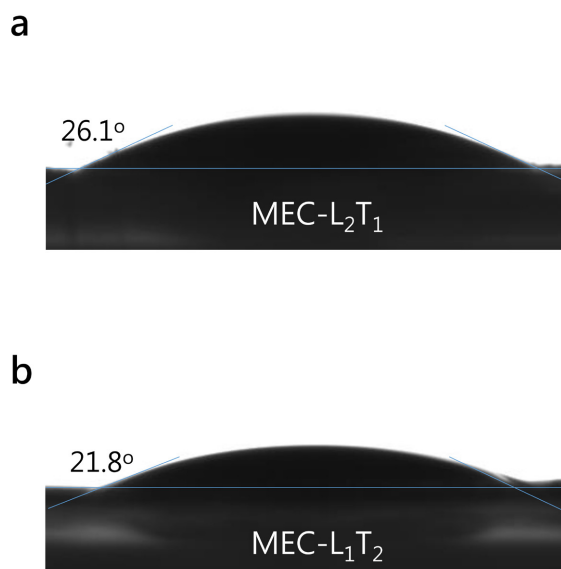


Supplementary Fig. 19. AFM image of MEC-LiT₂. **a** AFM image of MEC-LiT₂. **b, c, d** The thickness of MEC-LiT₂ at different selected areas. The AFM image size is $1 \times 1 \mu\text{m}$. The thickness of MEC-LiT₂ is $5.2 \pm 1.0 \text{ nm}$.

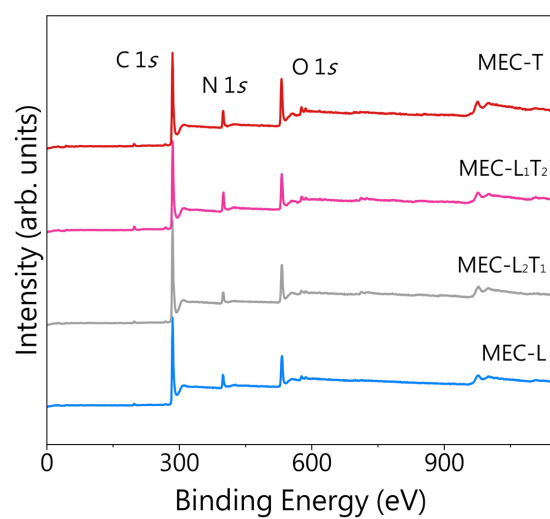
Source data are provided as a Source Data file.



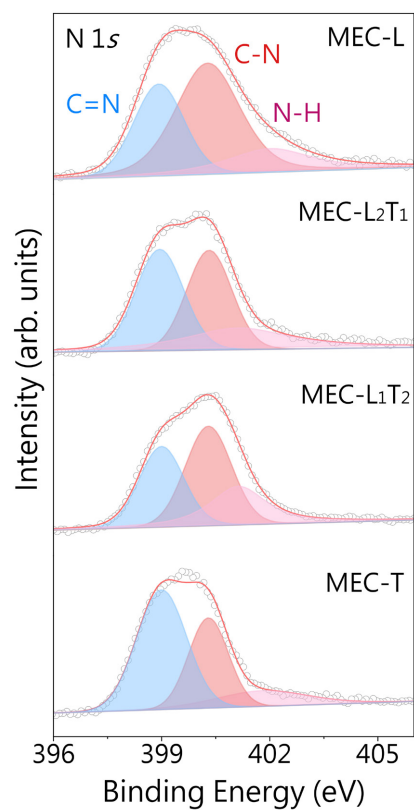
Supplementary Fig. 20. AFM image of MEC-T. **a** AFM image of MEC-T. **b, c, d** The thickness of MEC-T at different selected areas. The AFM image size is $1 \times 1 \mu\text{m}$. The thickness of MEC-T is $3.2 \pm 0.2 \text{ nm}$. Source data are provided as a Source Data file.



Supplementary Fig. 21. Images of static water-droplet contact for catalysts. Static Contact Angle of **a** MEC-L₂T₁ and **b** MEC-L₁T₂. The enhanced incorporation of the third monomer TP elevates the hydroxyl density within the COF framework, consequently decreasing the water contact angle.

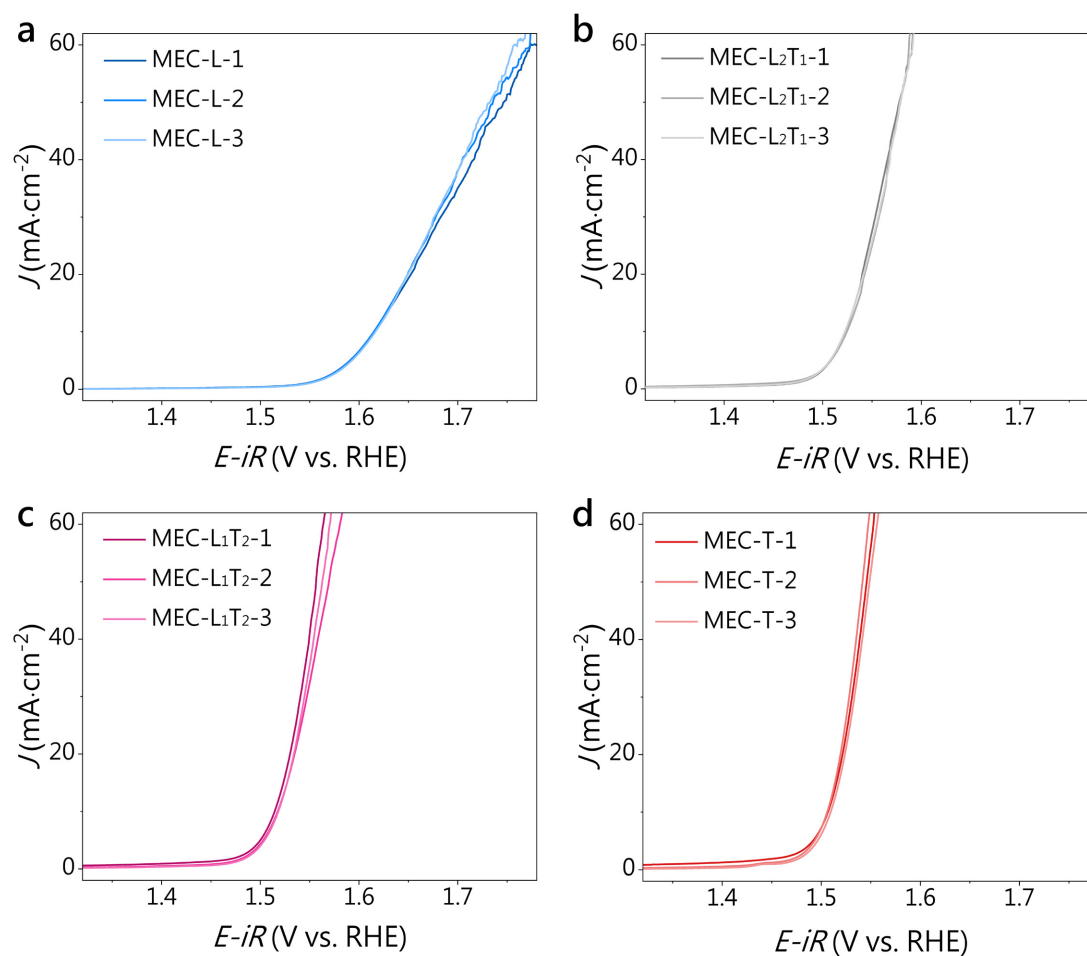


Supplementary Fig. 22. XPS survey scans of catalysts. According to the intensity of the oxygen peaks, it can be inferred that the oxygen content in the structure increases with the increase of TP proportion in the reaction. Source data are provided as a Source Data file.

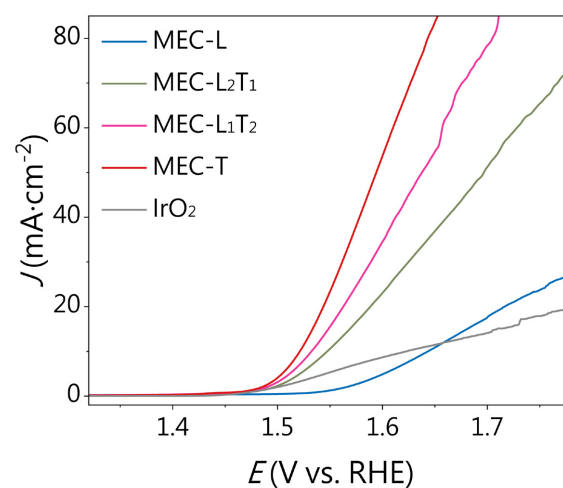


Supplementary Fig. 23. High-resolution N 1s XPS spectra of catalysts. N 1s XPS spectra of MEC-L, MEC-L₂T₁, MEC-L₁T₂ and MEC-T. Source data are provided as a Source Data file.

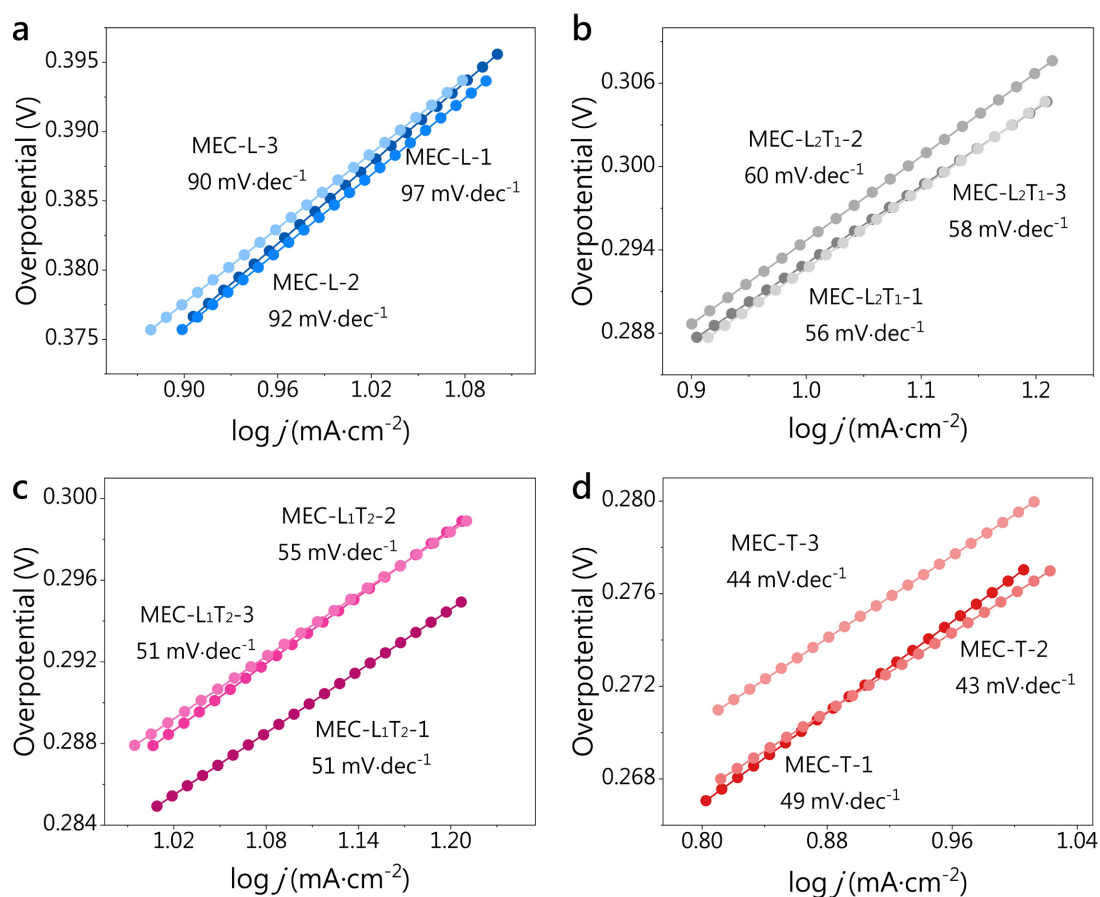
Electrocatalytic activity evaluation



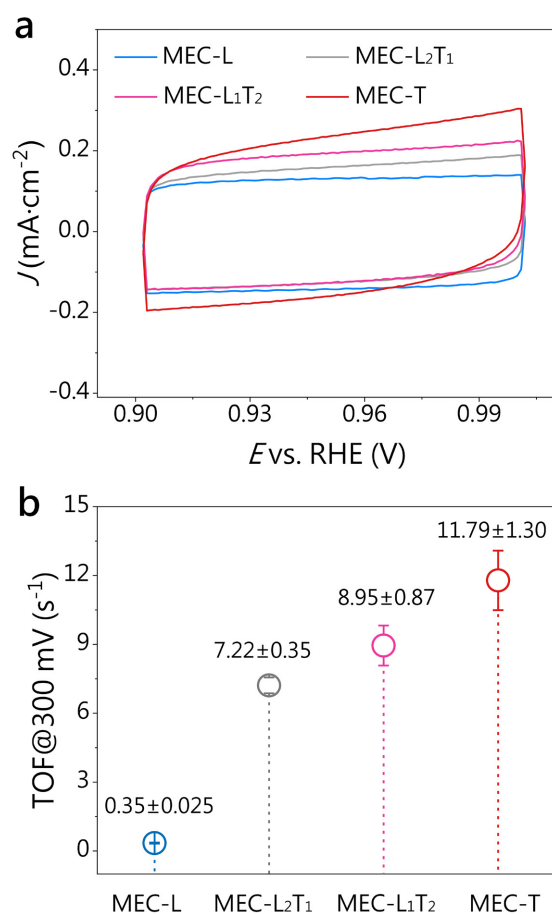
Supplementary Fig. 24. OER LSV curves of catalysts. LSV curves of **a** MEC-L, **b** MEC-L₂T₁, **c** MEC-L₁T₂, and **d** MEC-T. LSV curves were obtained with 95% iR compensation on GCE with a sweep rate of 5 mV·s⁻¹ in O₂-saturated 1.0 M KOH (pH = 13.6 ± 0.2) at 25°C. Each sample tested 3 times on different GCE. At the current density of 10 mA·cm⁻², the overpotential of MEC-L, MEC-L₂T₁, MEC-L₁T₂, and MEC-T were 386.0 ± 1.0 mV、293.7 ± 1.2 mV、287.3 ± 2.1 mV and 277.7 ± 2.1 mV, respectively. J : current density. E : potential. RHE: reversible hydrogen electrode. Source data are provided as a Source Data file.



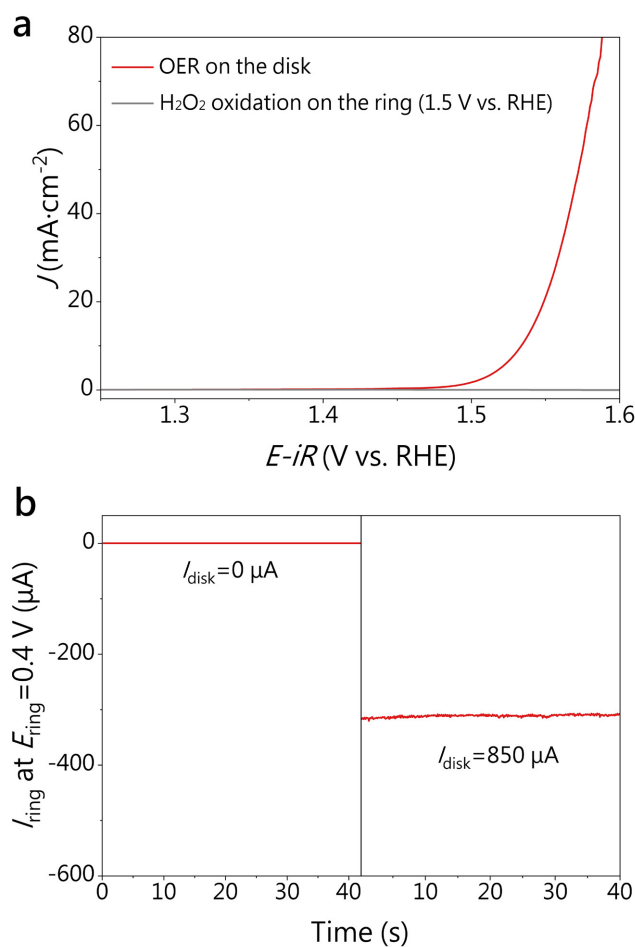
Supplementary Fig. 25. OER LSV curves of catalysts without iR compensation. The LSV curves for COF electrocatalysts and IrO₂ on GCE with a sweep rate of 5 mV·s⁻¹ in 1.0 M KOH at 25°C. Source data are provided as a Source Data file.



Supplementary Fig. 26. Corresponding Tafel slopes of LSV curves in Supplementary Fig 24. Tafel slopes of **a** MEC-L, **b** MEC-L₂T₁, **c** MEC-L₁T₂, and **d** MEC-T. The Tafel slopes of MEC-L, MEC-L₂T₁, MEC-L₁T₂, and MEC-T were 93.0 ± 3.6 mV·dec⁻¹, 58.0 ± 2.0 mV·dec⁻¹, 52.3 ± 2.3 mV·dec⁻¹ and 45.3 ± 3.2 mV·dec⁻¹, respectively. Source data are provided as a Source Data file.

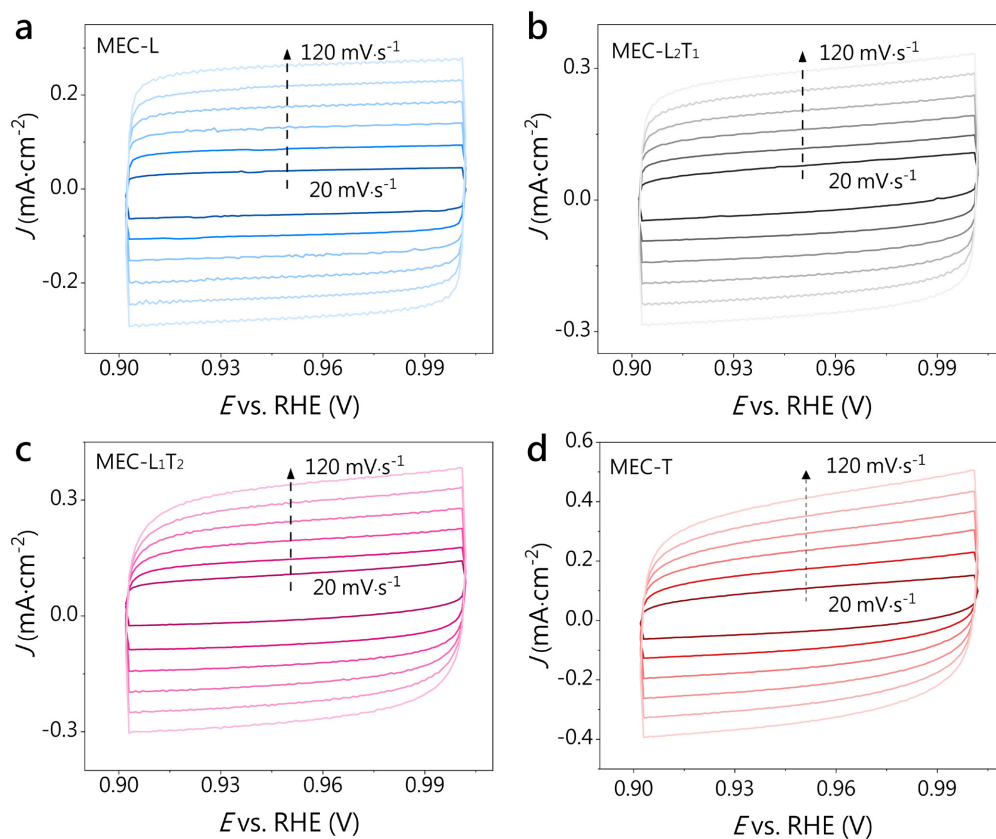


Supplementary Fig. 27. Redox area curves and TOF values of catalysts. **a** Redox area curves (in both cases the employed scan rate was 60 mV·s⁻¹) and **b** TOF values for MEC-L, MEC-L₂T₁, MEC-L₁T₂, and MEC-T. Error bars represent standard deviation, derived from three replicate experiments. Source data are provided as a Source Data file.

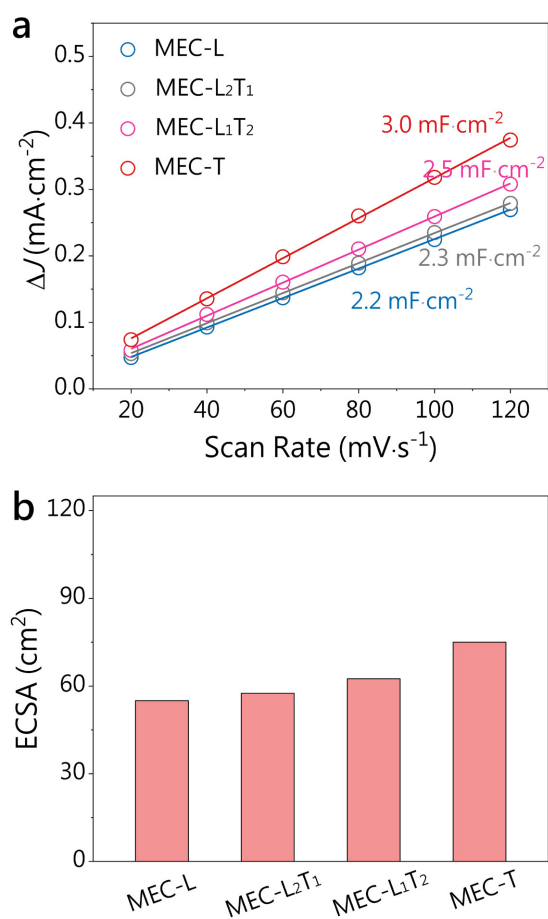


Supplementary Fig. 28. Faradaic efficiency testing of MEC-T using the rotating-ring disk electrode technique.

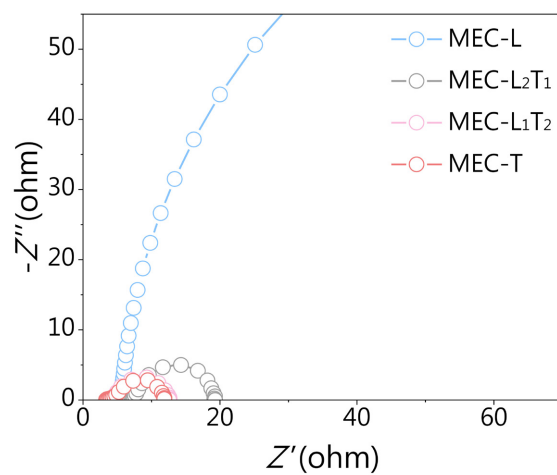
a Detection of H_2O_2 generation via RRDE measurements. Ring current responses of MEC-T recorded on a RRDE at a rotation speed of 1500 rpm in O_2 -saturated 1.0 M KOH aqueous solution (ring electrode potential: 1.50 V). **b** Ring current responses of MEC-T recorded on a RRDE at 1500 rpm in O_2 -saturated 1.0 M KOH aqueous solution (ring electrode potential: 0.40 V). We employed the RRDE in N_2 saturated 1.0 M KOH with the Pt ring electrode at a constant potential of 0.40 V versus RHE to reduce O_2 . In addition, the oxygen collection coefficient of electrode configuration is about 0.37. At a disk current of 850 μA , a ring current of ca. 314 μA was detected, suggesting that MEC-T operates with 99.68% Faradaic efficiency. Source data are provided as a Source Data file.



Supplementary Fig. 29. CV curves of catalysts on GCE. CV curves of **a** MEC-L, **b** MEC-L₂T₁, **c** MEC-L₁T₂, and **d** MEC-T. CV curves were investigated in non-faraday efficient regions (0.901-1.01 V vs. RHE) at different sweep rates (20, 40, 60, 80, 100, 120 mV·s⁻¹) on GCE in 1.0 M KOH at 25°C. All of the CV curves were obtained without *iR* compensation. Source data are provided as a Source Data file.

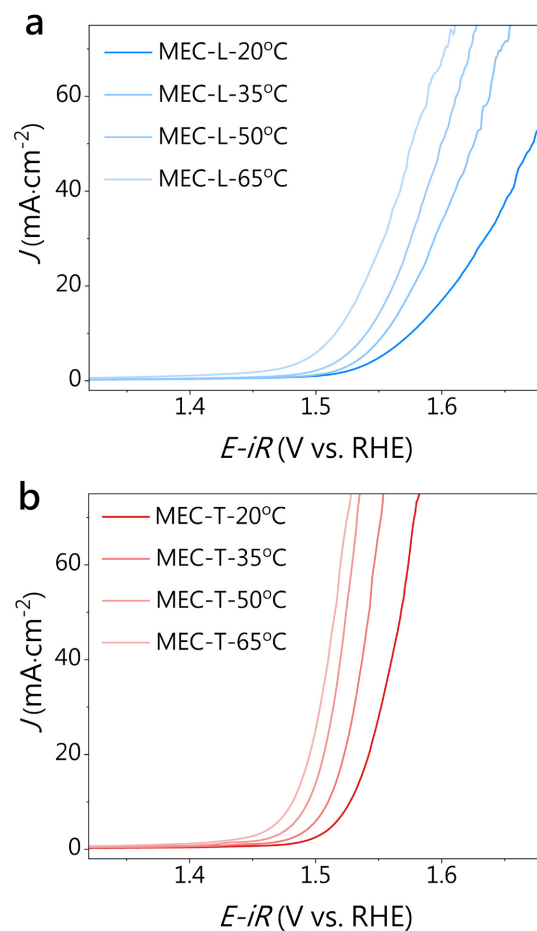


Supplementary Fig. 30. C_{dl} plots and ECSA values of catalysts. **a** C_{dl} plots and **b** ECSA values of MEC-L, MEC-L₂T₁, MEC-L₁T₂, and MEC-T. When the C_s value is 0.04 mF·cm⁻², the electrochemical specific surface area of the electrocatalysts increases with the rise of hydroxyl group content in the structure. Source data are provided as a Source Data file.

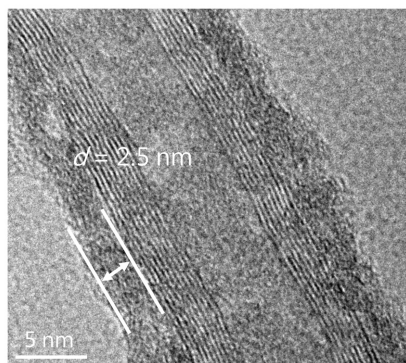


Supplementary Fig. 31. Nyquist plots of catalysts. Nyquist plots of MEC-L, MEC-L₂T₁, MEC-L₁T₂, and MEC-T.

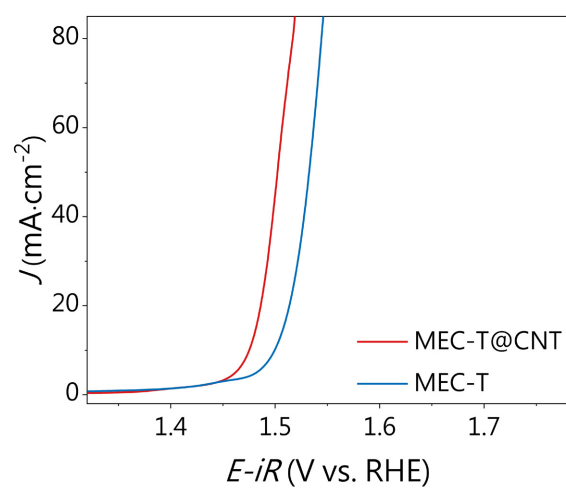
From the Nyquist plots of various catalysts, it can be observed that MEC-L₁T₂ and MEC-T exhibit similar interfacial charge transfer impedances, which are significantly smaller than those of MEC-L and MEC-L₂T₁ catalysts. The R_{ct} values for these catalysts are 148.5, 12.0, 8.5, and 7.4 Ω , respectively. Source data are provided as a Source Data file.



Supplementary Fig. 32. Apparent activation energies of MEC-L and MEC-T. a LSV curves of MEC-L at different temperatures. **b** LSV curves of MEC-T at different temperatures. LSV curves were obtained with 95% iR compensation on GCE with a sweep rate of 5 mV·s⁻¹ in O₂-saturated 1.0 M KOH solution at 20, 35, 50, 65°C, respectively. Source data are provided as a Source Data file.

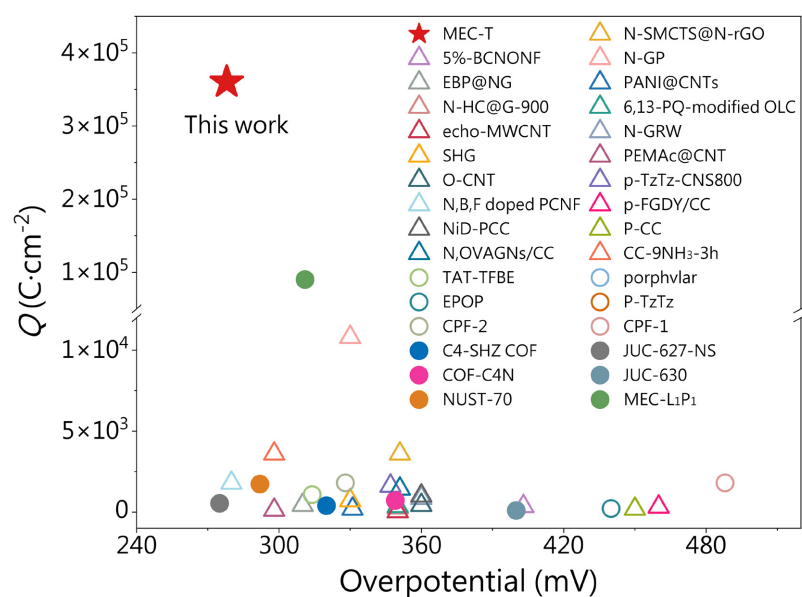


Supplementary Fig. 33. TEM image of MEC-T@CNT. MEC-T grows uniformly on the outer layer of CNT, with a thickness of approximately 2.5 nm.



Supplementary Fig. 34. LSV curves of catalysts of MEC-T@CNT. LSV curves of MEC-T@CNT and MEC-T.

The LSV curves for electrocatalysts and on GCE with a sweep rate of $5 \text{ mV} \cdot \text{s}^{-1}$ in 1.0 M KOH at 25°C. Source data are provided as a Source Data file.



Supplementary Fig. 35. Electrocatalytic stability and activity metrics for MEC-T against state-of-the-art metal-free electrocatalysts. Electrocatalytic stability (total charge transfer) and activity (overpotential at 10 mA·cm⁻²) metrics for MEC-T against state-of-the-art metal-free electrocatalysts. Symbols represent metal-free COFs (solid circles), carbon-based catalysts (hollow triangles), and porous organic polymers (hollow circles). Source data are provided as a Source Data file.

Table S1. OER performance evaluation. Comparison of OER performance of metal-free electrocatalysts in 1.0 M KOH electrolyte.

Catalysts	Q(C·cm ⁻²)	T (°C)	Carrier	Loading	η_{10} (mV)	Tafel (mV·dec ⁻¹)	Reference
COF							
MEC-T	360000	25	GCE	0.23 mg·cm ⁻²	278	45	This work
COF-C ₄ N	720	25	GCE	/	349	64	ACS Energy Lett. 2019 ¹
C4-SHz COF	396	/	GCE	0.07 mg·cm ⁻²	320	39	ACS Catal. 2020 ²
JUC-627-NS@G-2	540	/	GCE	0.20 mg·cm ⁻² (CC)	275	137	Chem. Eng. J. 2023 ³
JUC-630	97.2	/	GCE	0.86 mg·cm ⁻²	400	104	Acta Phys. Chim. Sin. 2023 ⁴
NUST-38	/	/	NiF	2.0 mg·cm ⁻²	303	73.2	ACS Appl. Eng. Mater. 2025 ⁵
NUST-70	1728	/	GCE	/	292	65.49	J. Mater. Chem. A, 2025 ⁶
MEC-2	900000	25	GCE	0.18 mg·cm ⁻²	257	26	Nat Commun. 2025 ⁷
MEC-L ₁ P ₁	90000	25	GCE	0.23 mg·cm ⁻²	311	53	Adv. Sci. 2025 ⁸
I-TTA COF	/	23	CC	0.982 mg·cm ⁻²	283	202	Angew. Chem. Int. Ed. 2025 ⁹
iCOP-CB[7]-2	/	/	CC	0.10 mg·cm ⁻²	296	55	Small 2024 ¹⁰
PT-30	/	25	CC	/	390	69	Langmuir 2024 ¹¹
POP							
P-TzTz	216	/	GCE	0.43 mg·cm ⁻²	583	110	Mater. Today Chem. 2023 ¹²
TAT-TFBE	1080	/	CC	0.69 mg	314	42	Adv. Mater. 2023 ¹³
porphvlar	2160	/	CC	0.05 mg·cm ⁻²	700	131	Chem. Sci. 2022 ¹⁴
EPOP	216	25	CC	2.0 mg·cm ⁻²	440	169	ACS. Omega. 2018 ¹⁵
CPF-2	1800	25	GCE	0.03 mg	328	89	ACS Appl. Mater. Inter. 2023 ¹⁶
CPF-1	1800	25	GCE	0.03 mg	488	56	ACS Appl. Mater. Inter. 2023 ¹⁶
THT-PyDAN	/	/	CC	0.83 mg	283	81	Adv. Mater. 2024 ¹⁷
TpCalix	/	/	CC	0.93 mg	290	120	Angew. Chem. Int. Ed. 2025 ¹⁸
Other metal-free electrocatalysts							
N-SMCTs@N-rGO	3600	25	RDE	0.20 mg·cm ⁻²	351	/	Chem. Eng. J. 2022 ¹⁹
5%-BCNONF	360	/	RDE	0.30 mg·cm ⁻²	403	73	Nano Energy 2021 ²⁰
EBP@NG(1:8)	432	25	GCE	0.30 mg·cm ⁻²	310	89	J. Am. Chem. Soc. 2019 ²¹
PANI@CNTs75	198	/	GCE	0.38 mg·cm ⁻²	331	85	Chem Asian J. 2020 ²²
N-HC@G-900	270	25	GCE	0.25 mg·cm ⁻²	350	88	Angew. Chem. Int. Ed. 2018 ²³
6,13-PQ-modified OLC	360	25	GCE	0.051 mg·cm ⁻²	350	62	J. Am. Chem. Soc. 2018 ²⁴
N-GP	10800	/	GCE	/	330	55	J. Am. Chem. Soc. 2022 ²⁵
echo-MWCNTs	48.6	/	GCE	0.025 mg	350	41	J. Am. Chem. Soc. 2015 ²⁶
SHG	720	/	GCE	0.65 mg·cm ⁻²	330	71	Adv. Mater. 2017 ²⁷

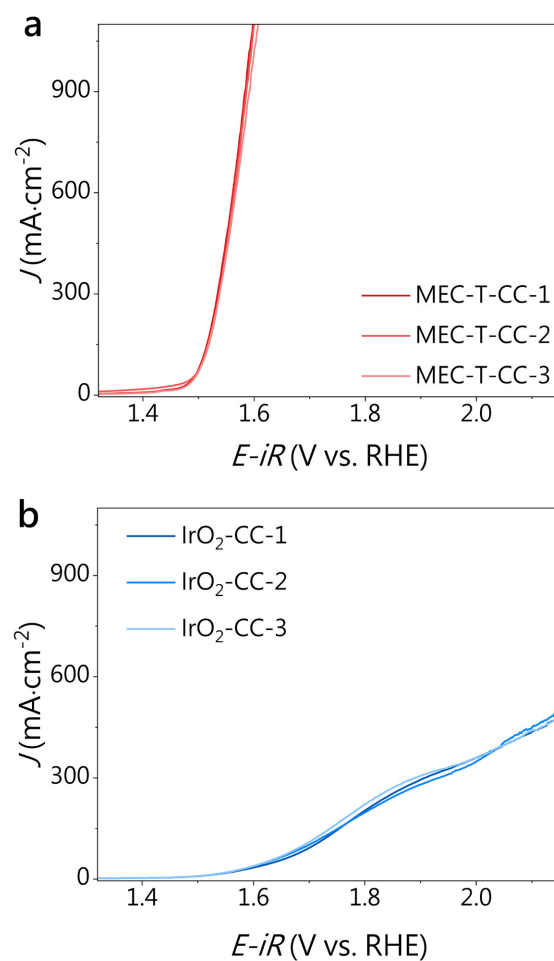
PEMAc@CNTs 90	135	25	GCE	0.30 mg·cm ⁻²	298	52	Energy Environ Sci. 2017 ²⁸
N-GRW	864	25	GCE	0.30 mg·cm ⁻²	360	47	Sci. Adv.2016 ²⁹
O-CNT	432	25	GCE	0.125 mg·cm ⁻²	360	48	ACS Energy Lett. 2017 ³⁰
P-TzTz-CNS800	1620	/	GCE	0.43 mg·cm ⁻²	347	129	Mater. Today Chem. 2023 ¹²
N, B, F doped PCNFs	1800	25	GCE	0.50 mg·cm ⁻²	280	83	J. Mater. Chem. A. 2024 ³¹
g-C ₃ N ₄ NS-CNT	/	/	GCE	0.20 mg·cm ⁻²	370	83	Angew. Chem. Int. Ed. 2014 ³²
g-CN	/	25	GCE	1.05 mg	316	125	ChemCatChem 2019 ³³
G-P	/	/	GCE	0.20 mg·cm ⁻²	330	62	Chem. Commun. 2016 ³⁴
G-NC(1.5)	/	/	GCE	0.30 mg·cm ⁻²	330	52.6	ChemSusChem 2019 ³⁵
G-EX-ST	/	25	GCE	0.35 mg·cm ⁻²	349	44	Chem. Commun. 2019 ³⁶
LIG-O	/	25	GCE	0.15 mg·cm ⁻²	360	49	Adv. Mater. 2018 ³⁷
S-doped BP	/	/	GCE	/	410	75	Nanotechnology 2019 ³⁸
B, N-Carbon	/	/	GCE	0.29 mg·cm ⁻²	380	84	Adv. Sci. 2018 ³⁹
NDGs-800	/	/	GCE	0.20 mg·cm ⁻²	450	132	ACS Energy Lett. 2018 ⁴⁰
S, S'-CNT1000°C	/	/	GCE	0.28 mg·cm ⁻²	350	95	Adv. Energy Mater. 2016 ⁴¹
NPCNF-O	/	/	GCE	0.90 mg·cm ⁻²	326	178	ACS Catal. 2022 ⁴²
g-CN _x	/	/	GCE	/	480	146	Small 2017 ⁴³
p-FGDY/CC	324	/	CC	/	460	128	Angew. Chem. Int. Ed. 2019 ⁴⁴
NiD-PCC	1008	/	CC	/	360	98	Energy Environ. Sci. 2016 ⁴⁵
P-CC	198	/	CC	/	450	/	Adv. Mater. 2017 ⁴⁶
N, OVAGNs/CC	1440	/	CC		351	38	J. Mater. Chem. A 2018 ⁴⁷
CC-9NH ₃ -3h	3600	25	CC	/	298	62	Appl. Catal. B: Environ. 2021 ⁴⁸
PANa	/	25	CC	0.8 ± 0.2 mg·cm ⁻²	316	42	Nat commun. 2023 ⁴⁹
NSGF(GFLs)	/	25	/	/	346	78	Adv. Energy Mater. 2016 ⁵⁰
PA-PPy/CC	/	/	CC	0.40 mg·cm ⁻²	340	55	Angew. Chem. Int.Ed. 2019 ⁵¹
CC-AC	/	25	CC	/	360	52	Adv. Energy Mater. 2019 ⁵²
PCN-CFP	/	/	CC	/	400 (η ₁₀₀)	62	Angew. Chem. Int.Ed.
G-C ₃ N ₄ film	/	/	CC	0.10 mg·cm ⁻²	414 (η ₁₀₀)	128	Adv. Sci. 2015 ⁵⁴
ONPPGC/OCC	/	/	CC	0.10 mg·cm ⁻²	410	83	Energy Environ. Sci.

GCE = glassy carbon electrode; NiF = nickel foam; POP = porous organic polymer; RDE = rotating disk electrode; CC = carbon cloth.

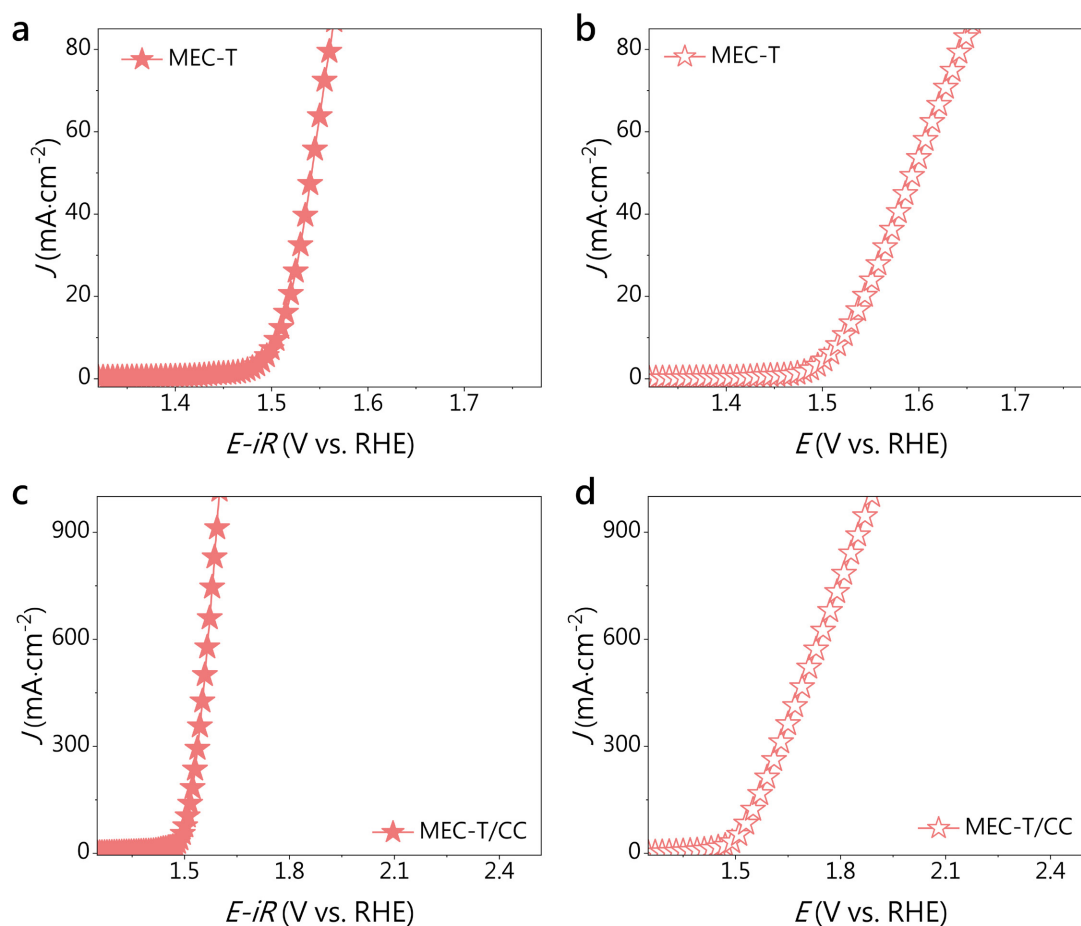
Table S2. OER performance evaluation. Comparison of OER performance of metal electrocatalysts in 1.0 M KOH electrolyte.

Catalysts	Q(C·cm ⁻²)	T (°C)	Carrier	Loading	η_{10} (mV)	Tafel (mV·dec ⁻¹)	Reference
MEC-T	360000	25	GCE	0.23 mg·cm ⁻²	278	45	This work
Mn-NG	4320	/	GCE	-	337	55	Nat. Catal. 2018 ⁵⁶
NiSA-O/Mo ₂ C	576	25	GCE	0.7 mg·cm ⁻²	299	89.36	Nat Commun. 2024 ⁵⁷
PSCFM	720	25	GCE	0.51 mg·cm ⁻²	315	54.5	Nat Commun. 2024 ⁵⁸
Ir ₁ /Ni LDH-V	3600	25	GCE	0.55 mg·cm ⁻²	301	62	Nat Commun. 2024 ⁵⁹
Ni(Fe)OOH	-	/	GCE	-	293	30	Nat Commun. 2023 ⁶⁰
FeO _x H _y -Co	-	/	GCE	-	319	35	Nat Commun. 2023 ⁶¹
Co-N ₃ P-HCS	-	25	GCE	0.43 mg·cm ⁻²	320	121.5	Adv. Mater. 2022 ⁶²
FeCo-DACs/NC	-	/	GCE	-	370	82.7	Adv. Mater. 2022 ⁶³
Ni SAs@S/N-CMF	2160	/	CP	1.0 mg·cm ⁻²	285	50.8	Adv. Mater. 2022 ⁶⁴
γ -FeOOH/NF-6M	5184	/	NF	0.50 mg·cm ⁻²	286	51	Adv. Mater. 2021 ⁶⁵
Co ₃ O ₄ -Vco	432	/	GCE	-	268	38.2	J. Am. Chem. Soc. 2023 ⁶⁶
ZnCo ₂ O _{4-x} F _x /CNTs	468	/	GCE	-	350	59.2	Angew. Chem. Int. Ed. 2023 ⁶⁷
Ce-NiCo ₂ O ₄	900	/	GCE	-	270	-	Angew. Chem. Int. Ed. 2024 ⁶⁸
Fe-NiO/NiS ₂	360	25	GCE	-	270	40	Angew. Chem. Int. Ed. 2022 ⁶⁹
NiCoFe-HO@NiCo-LDH YSMR	396	/	GCE	0.33 mg·cm ⁻²	278	49.7	Angew. Chem. Int. Ed. 2022 ⁷⁰
HEOs	-	/	GCE	-	320	45	Adv. Funct. Mater. 2022 ⁷¹
Co-CoN ₄ @NCNs	-	25	GCE	0.26 mg·cm ⁻²	310	78.1	Adv. Funct. Mater. 2022 ⁷²
VO _x -CoMoVO _x	21600	/	GCE	-	248	74.2	Adv. Funct. Mater. 2025 ⁷³
2D/2D BNHNSs	~ 720	/	GCE	-	297	-	Adv. Energy. Mater. 2022 ⁷⁴

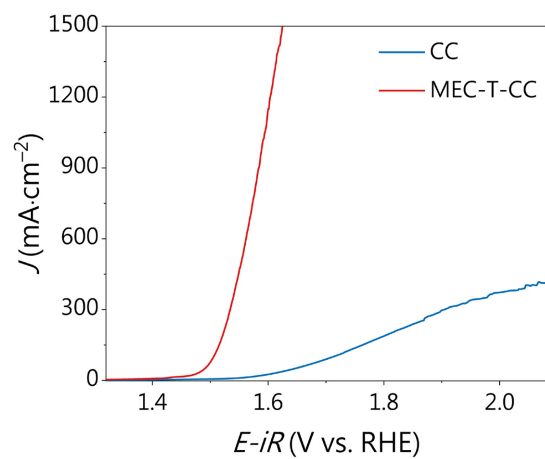
CP = carbon paper; NF = nickel foam.



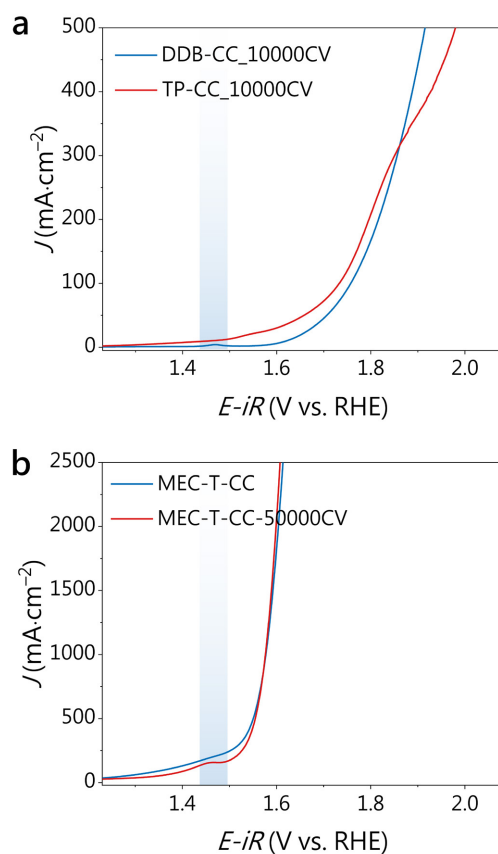
Supplementary Fig. 36. LSV curves of catalysts supported on carbon cloth. **a** LSV curves of MEC-T supported on carbon cloth. **b** LSV curves of IrO₂ supported on carbon cloth. Each sample tested 3 times on different carbon cloth. The LSV curves for COF electrocatalysts and IrO₂ on CC with a sweep rate of 5 mV·s⁻¹ in 1.0 M KOH at 25°C. Source data are provided as a Source Data file.



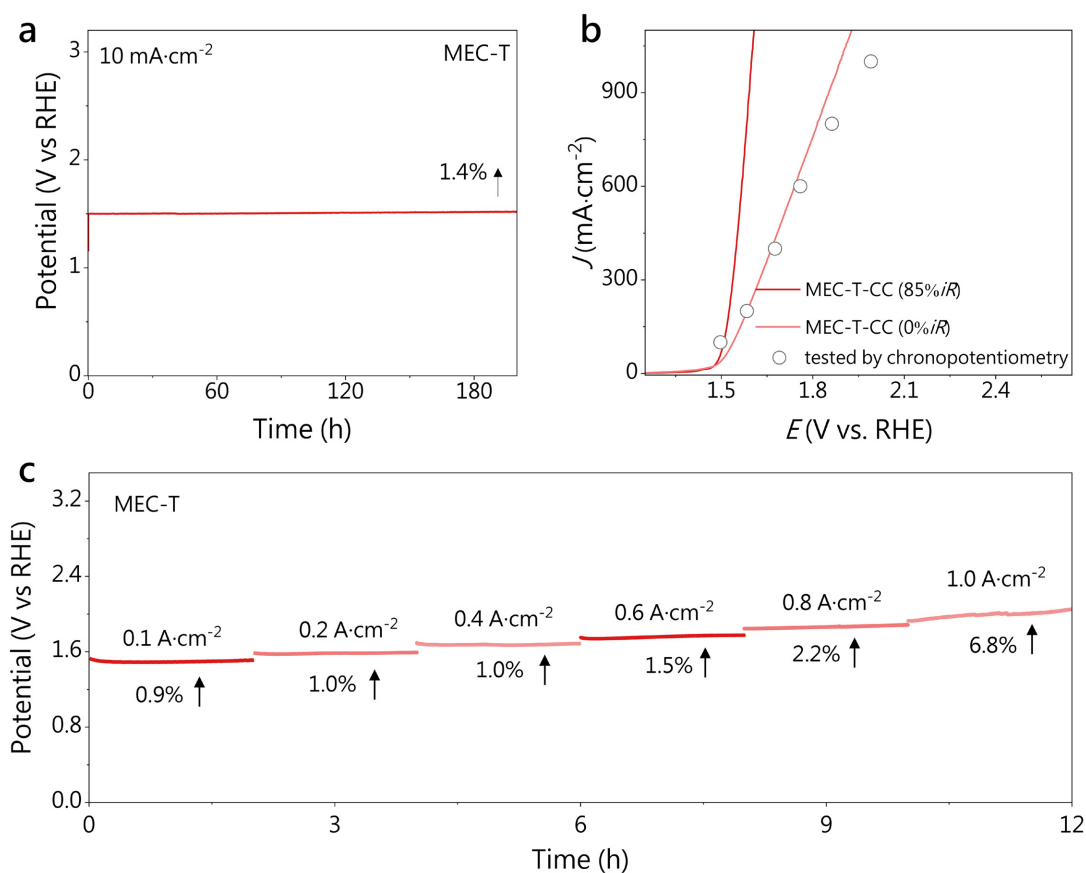
Supplementary Fig. 37. LSV curves of catalysts with and without iR compensation. **a** LSV curves of MEC-T supported on GCE with 95% iR compensation. **b** LSV curves of MEC-T supported on GCE without iR compensation. **c** LSV curves of MEC-T supported on carbon cloth with 85% iR compensation. **d** LSV curves of MEC-T supported on carbon cloth without iR compensation. The LSV curves for COF electrocatalysts on GCE or CC with a sweep rate of $5 \text{ mV} \cdot \text{s}^{-1}$ in 1.0 M KOH at 25°C . Source data are provided as a Source Data file.



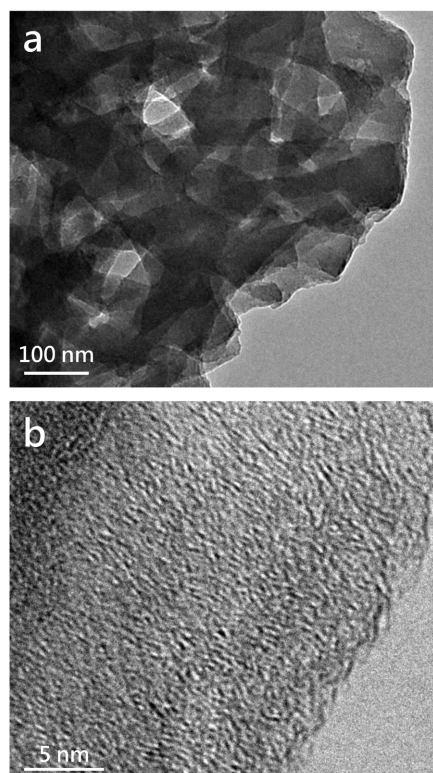
Supplementary Fig. 38. LSV curves of catalysts supported on carbon cloth and the catalyst-free carbon cloth substrate. The LSV curves for electrocatalysts on CC with a sweep rate of $5 \text{ mV}\cdot\text{s}^{-1}$ in 1.0 M KOH at 25°C. Source data are provided as a Source Data file.



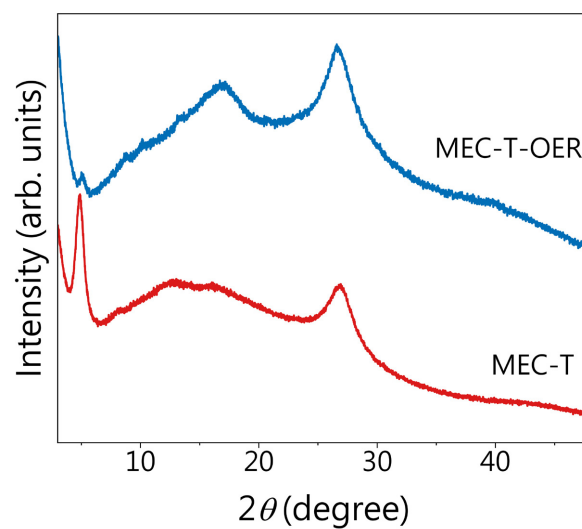
Supplementary Fig. 39. OER polarization curves of MEC-T supported on CC before and after CV scans. LSV curves of **a** 2,5-diamino-1,4-benzenediol dihydrochloride (DDB) and 2,4,6-triformylphloroglucinol (TP), **b** MEC-T. After 50000 CV cycles, the oxidation peak in the LSV curve of MEC-T should originate from residual DDB monomers in the COF. The LSV curves for electrocatalysts on CC with a sweep rate of 5 mV·s⁻¹ in 1.0 M KOH at 25°C. Source data are provided as a Source Data file.



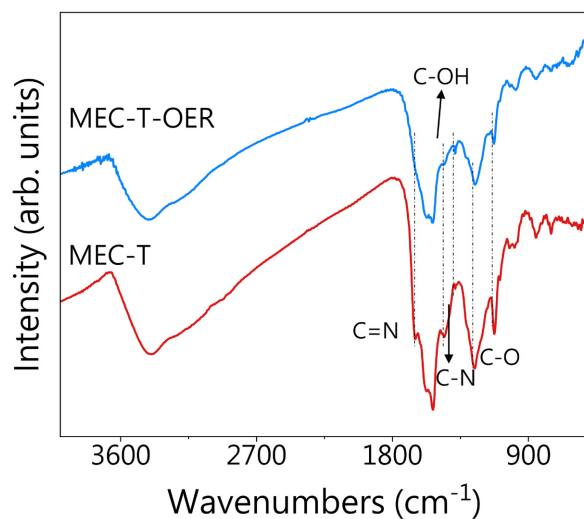
Supplementary Fig. 40. Electrochemical durability of electrocatalysts. **a** The electrochemical stability of MEC-T was evaluated by chronopotentiometry at a current density of 10 mA cm^{-2} . The catalyst exhibited excellent durability, with only a 1.4% potential decay after continuous operation for approximately 200 hours. **b** LSV curves of catalysts with and without iR compensation. **c** The electrochemical stability of MEC-T was evaluated by chronopotentiometry at different current densities. Decay rate = $\Delta E/E_0$, where E_0 is the initial potential at the start of the constant-current stability test, and ΔE is the increase in potential relative to the initial potential after a certain period of time. Source data are provided as a Source Data file.



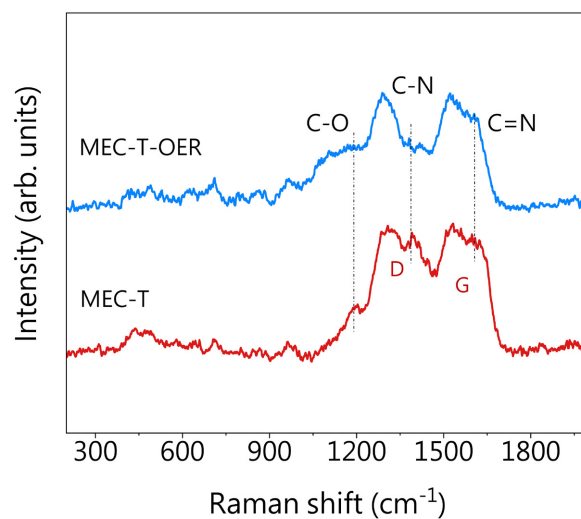
Supplementary Fig. 41. TEM image and HRTEM image of MEC-T after OER. a TEM image of MEC-T-OER, **b** HRTEM image of MEC-T-OER.



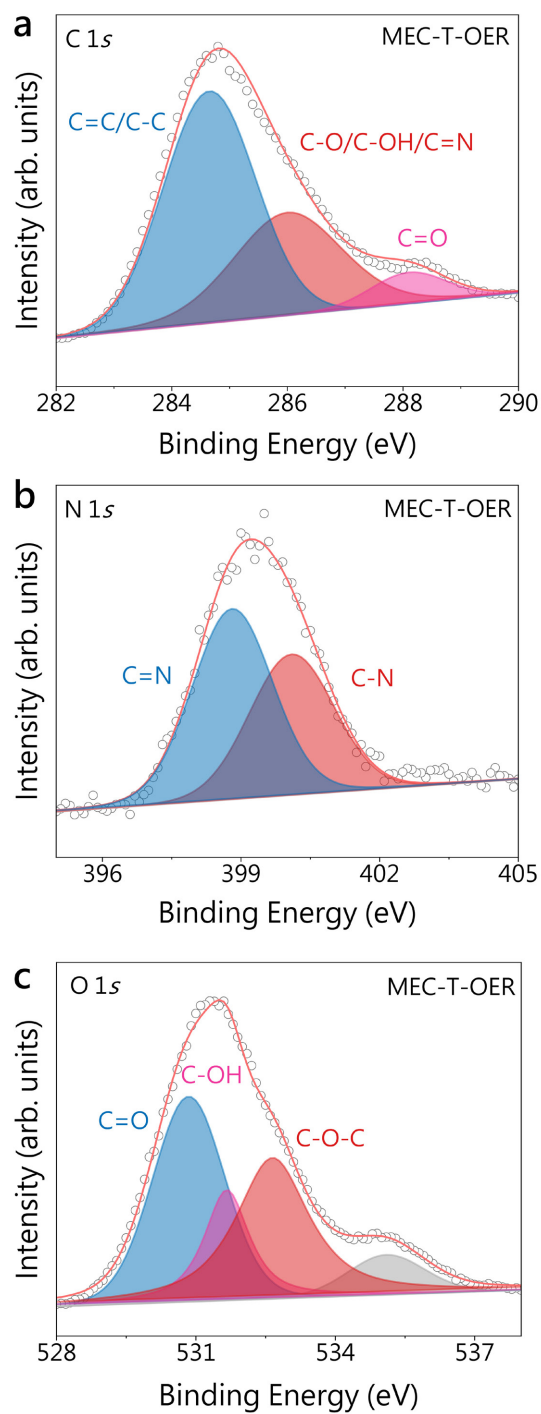
Supplementary Fig. 42. PXRD pattern of MEC-T and MEC-T-OER. The post-OER sample MEC-T-OER exhibited attenuated powder diffraction peak intensities compared to MEC-T, particularly for the characteristic peak at $2\theta = 5.06^\circ$. Source data are provided as a Source Data file.



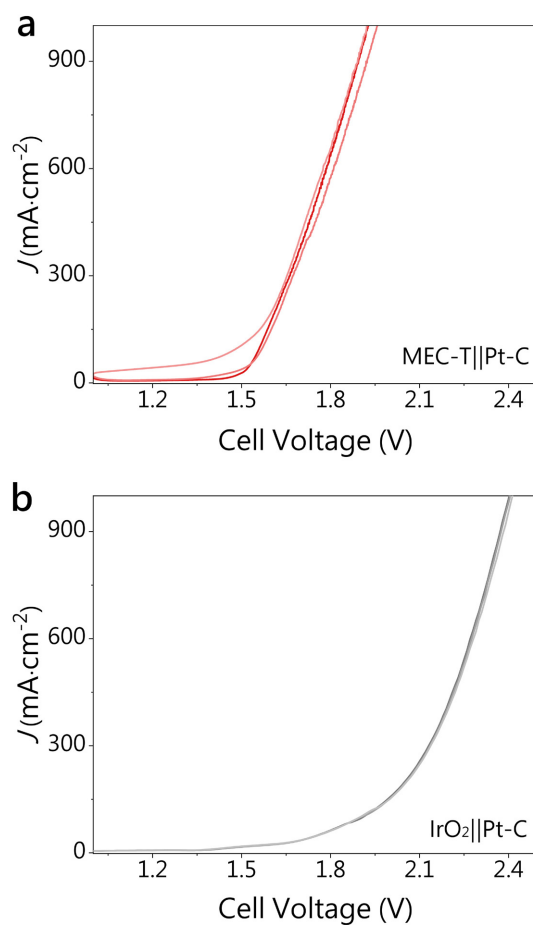
Supplementary Fig. 43. FT-IR spectra of MEC-T and MEC-T-OER. In the FTIR spectrum, the high consistency of the characteristic peaks of MEC-T before and after the reaction indicates that the structure of the sample can be maintained after the electrochemical reaction. Source data are provided as a Source Data file.



Supplementary Fig. 44. Raman spectra of MEC-T and MEC-T-OER. The persistence of characteristic Raman bands at 1202 cm^{-1} (C–O stretching), 1393 cm^{-1} (C–N vibration), and 1619 cm^{-1} (C=N stretching) demonstrates the structural retention of the material following the oxygen evolution reaction. Source data are provided as a Source Data file.

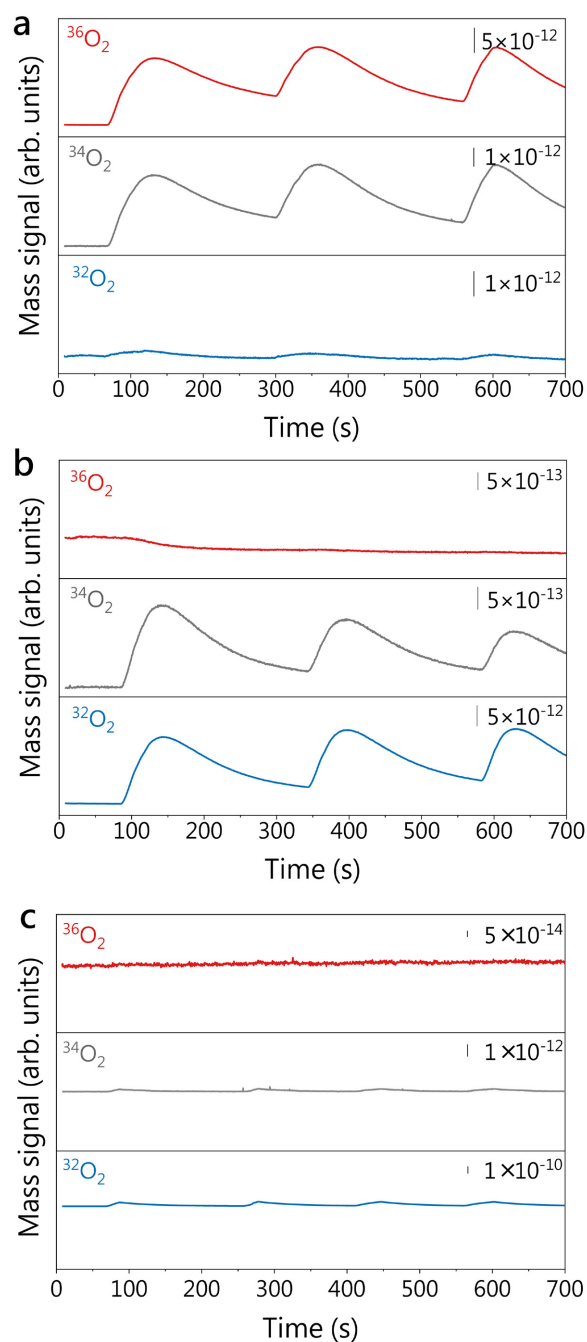


Supplementary Fig. 45. Structural characterization of MEC-T after OER. **a** High-resolution C 1s XPS spectra of MEC-T-OER, **b** High-resolution N 1s XPS spectra of MEC-T-OER, **c** High-resolution O 1s XPS spectra of MEC-T-OER. Source data are provided as a Source Data file.

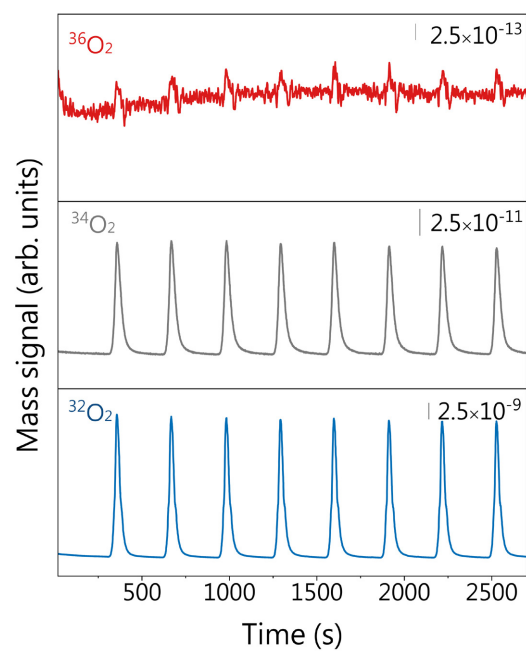


Supplementary Fig. 46. Polarization curves of MEC-T||Pt/C and IrO₂||Pt/C toward overall water splitting.

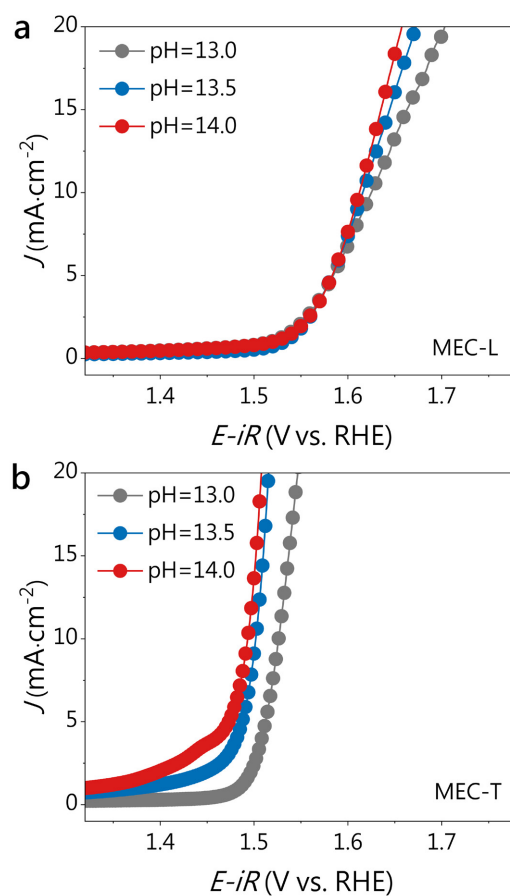
LSV curves of **a** MEC-T||Pt/C and **b** IrO₂||Pt/C in 1.0 M KOH at 25°C without iR -compensation. Each sample tested 3 times on different carbon cloths. Source data are provided as a Source Data file.



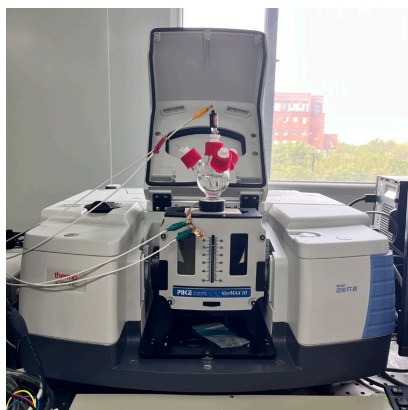
Supplementary Fig. 47. DEMS signals of O₂ products for MEC-L. **a** DEMS signals of O₂ products for MEC-L using H₂¹⁸O as the electrolyte during CV scans. **b** DEMS signals of O₂ products for MEC-L using H₂¹⁶O as the electrolyte during CV scans. **c** Baseline background of the DEMS signal of O₂ products in H₂¹⁶O aqueous KOH electrolyte. Source data are provided as a Source Data file.



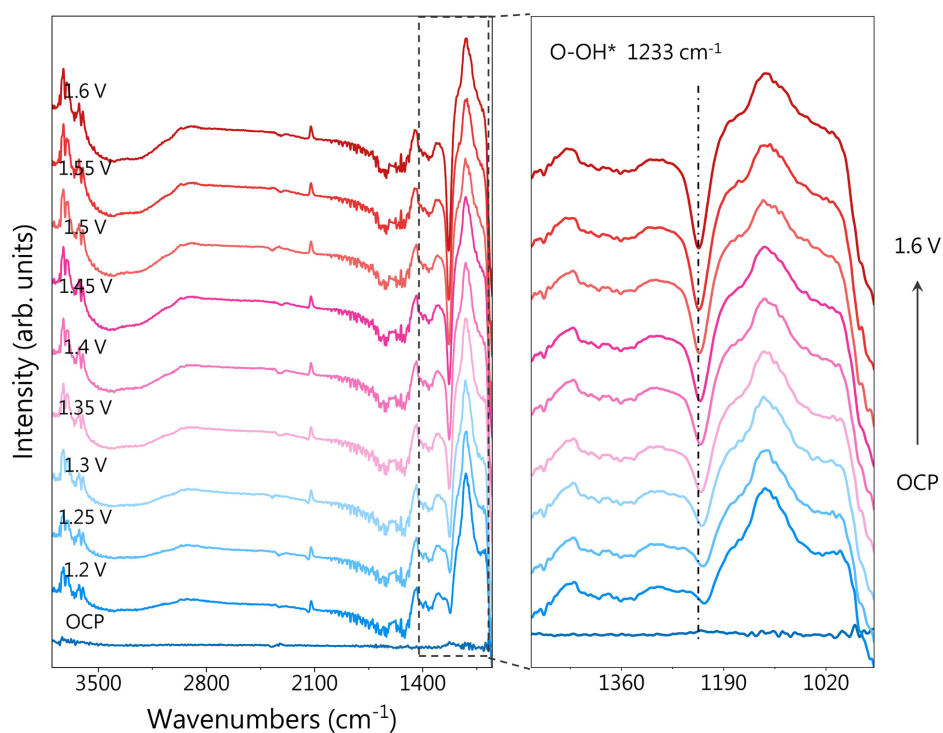
Supplementary Fig. 48. DEMS signals of O_2 products for MEC-T using H_2^{16}O as the electrolyte solvent. Source data are provided as a Source Data file.



Supplementary Fig. 49. pH dependence. The LSV curves with 95% iR correction on GCE with a sweep rate of 5 $\text{mV}\cdot\text{s}^{-1}$ in 1.0 M KOH solution with pH=13-14 of **a** MEC-L, **b** MEC-T. Source data are provided as a Source Data file.

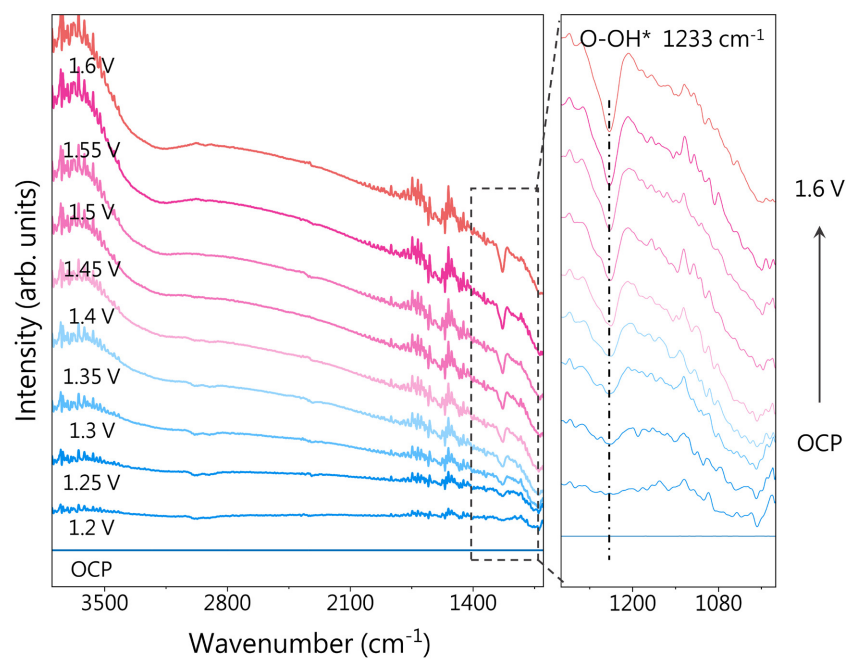


Supplementary Fig. 50. A photograph of the operando ATR-SEIRAS system configuration.



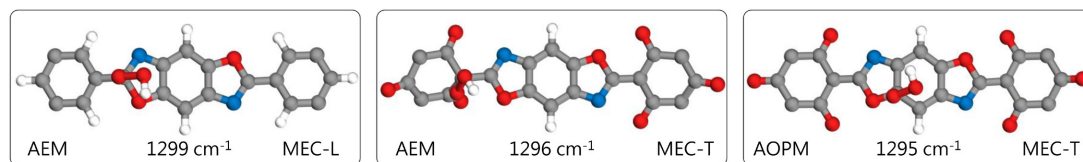
Supplementary Fig. 51. Potential-dependent *operando* ATR-SEIRAS of MEC-T in 1.0 M KOH solution.

Potential-dependent *operando* ATR-SEIRAS was measured in the potential range of 1.2-1.6 V vs. RHE. The appearance of an infrared signal peak attributed to *O-OH at 1233 cm^{-1} . Source data are provided as a Source Data file.

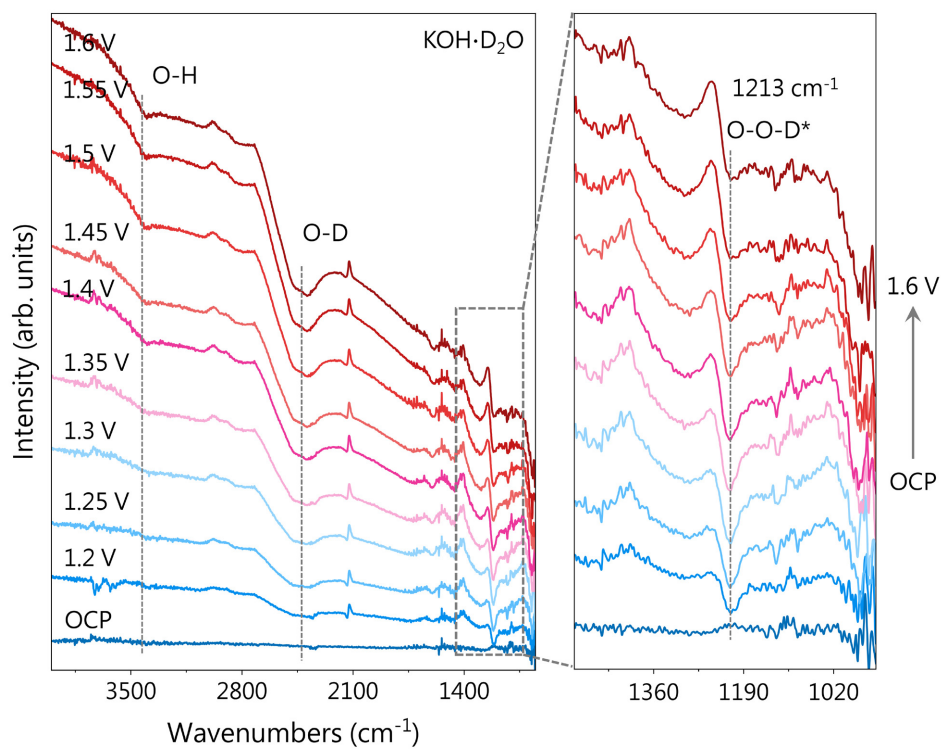


Supplementary Fig. 52. Potential-dependent *operando* ATR-SEIRAS of MEC-L in 1.0 M KOH solution.

Potential-dependent *operando* ATR-SEIRAS was measured in the potential range of 1.2-1.6 V vs. RHE. The appearance of an infrared signal peak attributed to *O–OH at 1233 cm⁻¹. Source data are provided as a Source Data file.



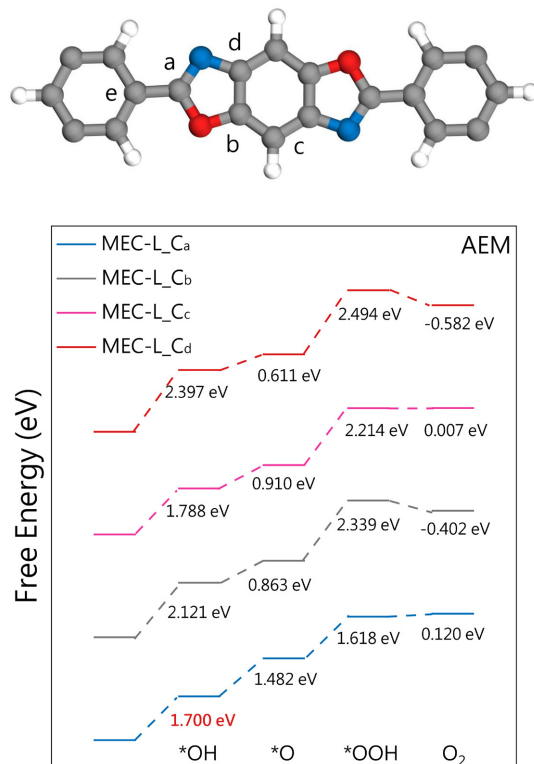
Supplementary Fig. 53. The theoretical *OOH infrared spectral peak positions for MEC-L and MEC-T. The theoretical *OOH spectral peak positions for MEC-L (AEM pathway) and MEC-T (AOPM pathway) are 1299 cm^{-1} and 1295 cm^{-1} , respectively. For reference, we also calculated the theoretical *OOH peak position for MEC-T under the AEM pathway, which is 1296 cm^{-1} . Source data are provided as a Source Data file.



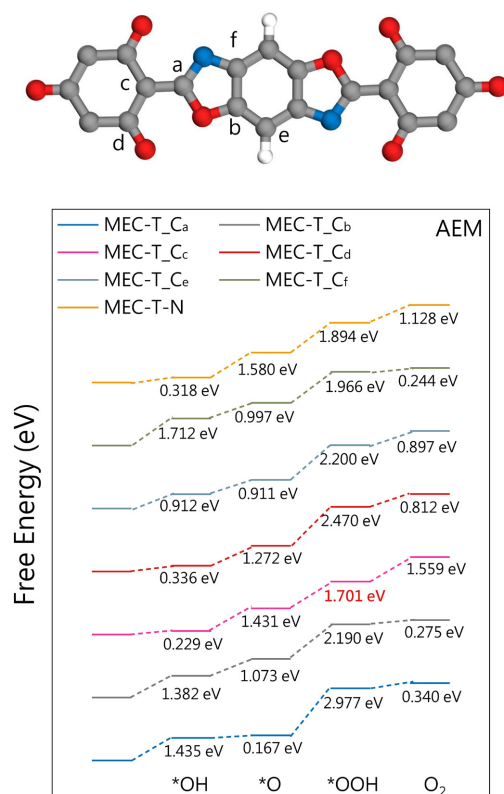
Supplementary Fig. 54. Potential-dependent *operando* ATR-SEIRAS of MEC-T in 1.0 M KOH-D₂O solution.

Potential-dependent *operando* ATR-SEIRAS was measured in the potential range of 1.2-1.6 V vs. RHE. The appearance of an infrared signal peak attributed to *O-OH at 1213 cm⁻¹. Source data are provided as a Source Data file.

Mechanistic analysis of OER activity



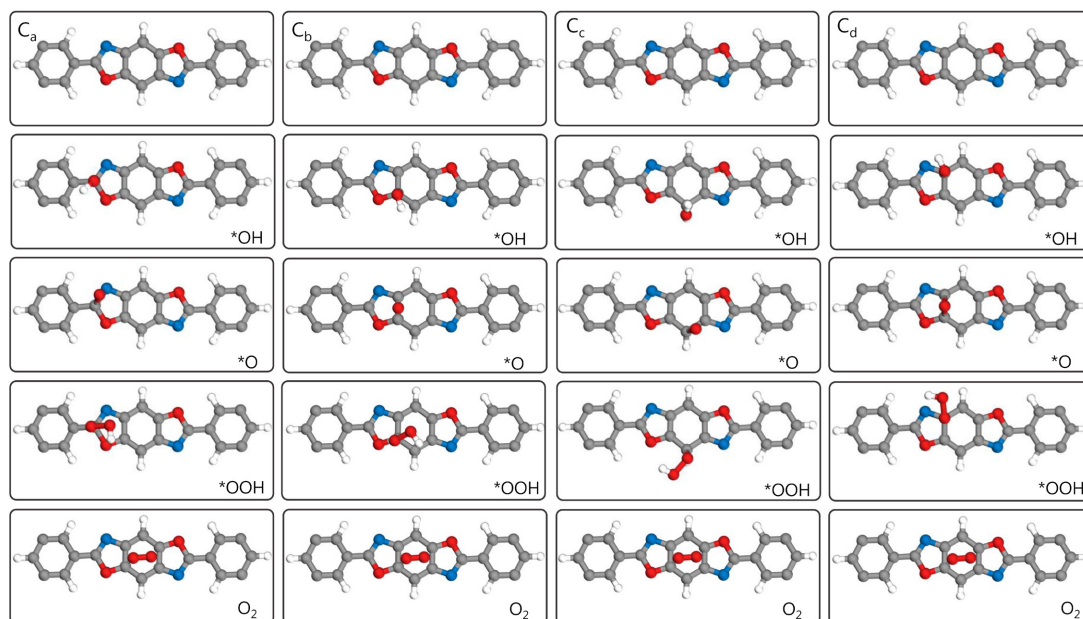
Supplementary Fig. 55. DFT calculations of the AEM mechanism on different C sites in MEC-L. Structural model of MEC-L with 6 kinds of C atoms labeled. Color codes: grey, C; blue, N; red, O; white, H, and Gibbs free energy profiles of different C sites on MEC-L. Source data are provided as a Source Data file.



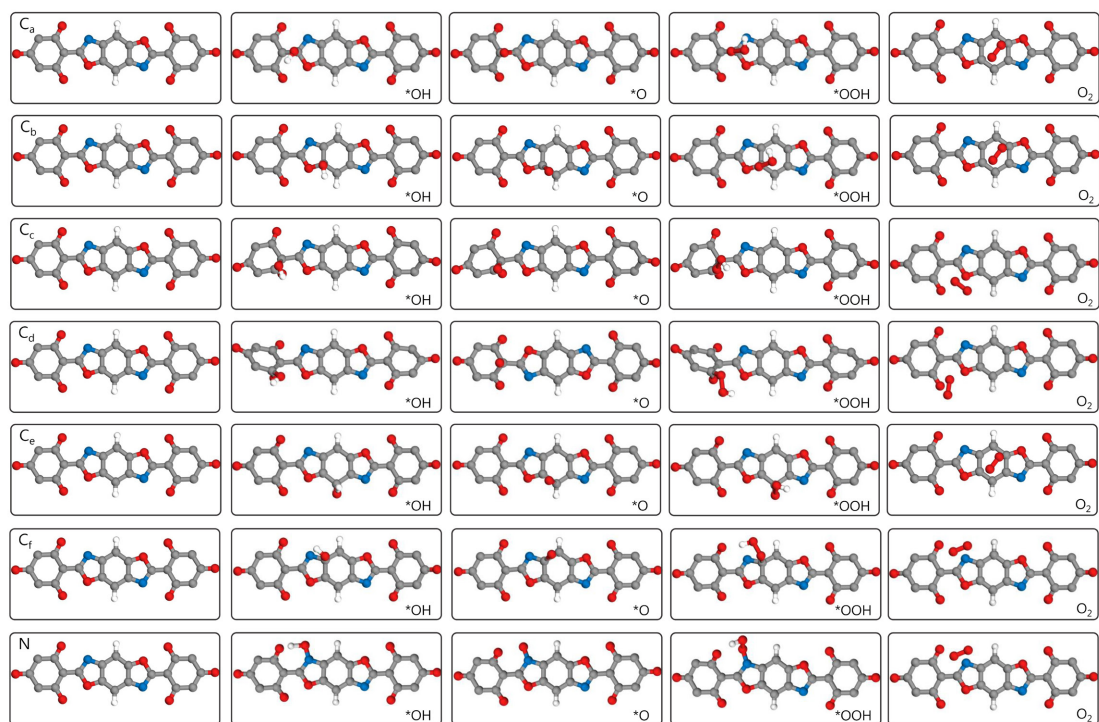
Supplementary Fig. 56. DFT calculations of the AEM mechanism on different C sites and N site in MEC-T.

Structural model of MEC-T with 6 kinds of C atoms labeled. Color codes: grey, C; blue, N; red, O; white, H, and

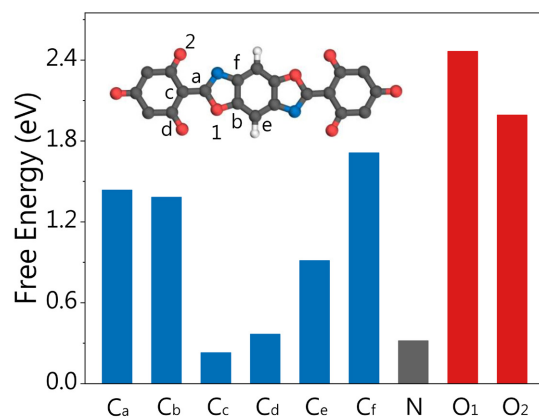
Gibbs free energy profiles of different C sites on MEC-T. Source data are provided as a Source Data file.



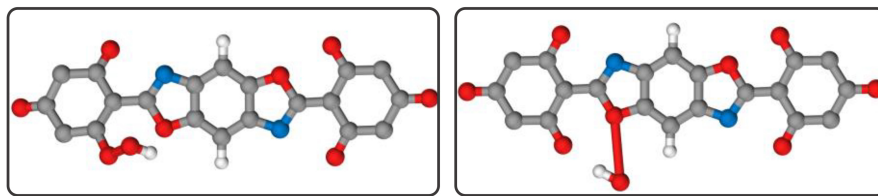
Supplementary Fig. 57. Structure models of MEC-L for key intermediates of AEM reaction pathway. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



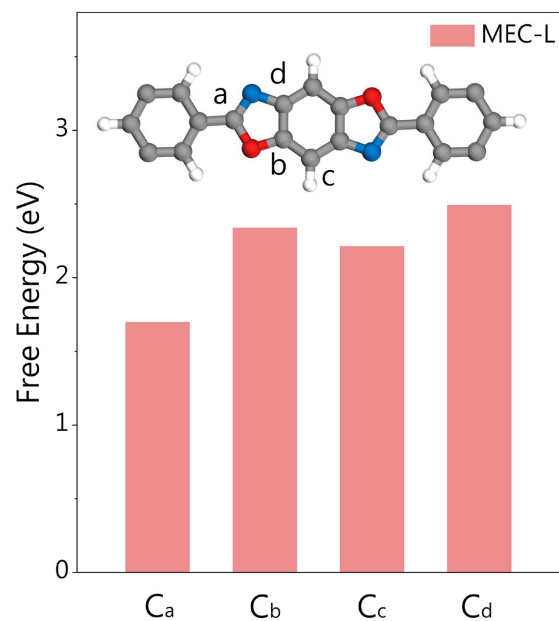
Supplementary Fig. 58. Structure models of MEC-T for key intermediates of AEM reaction pathway. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



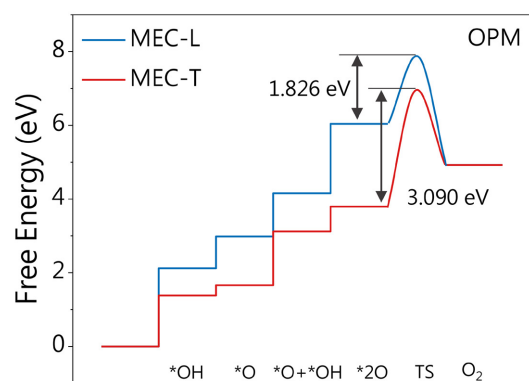
Supplementary Fig. 59. The OH adsorption free energy of each atom in the MEC-T. Color codes: grey, C; blue, N; red, O; white, H. Source data are provided as a Source Data file.



Supplementary Fig. 60. Structure models of MEC-T for OH adsorption onto O atoms. Color codes: grey, C; blue, N; red, O; white, H.

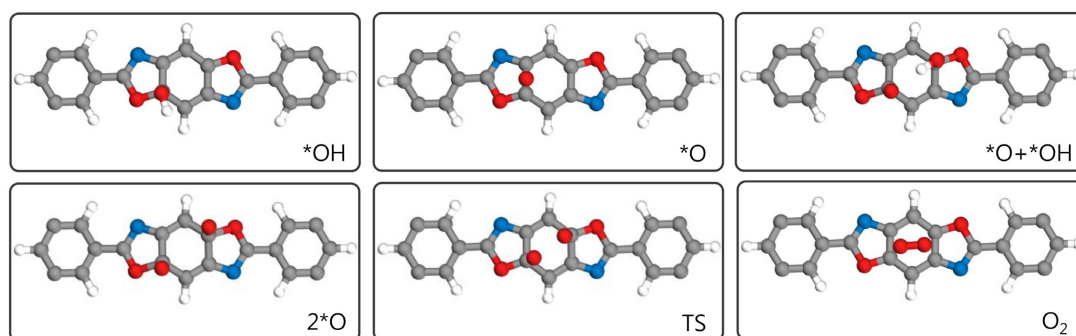


Supplementary Fig. 61. Free energy changes of the rate-determining step (RDS) of MEC-L. Free energy changes (ΔG) of the rate-determining step (RDS) at distinct carbon sites on MEC-L following the AEM pathway (inset: spatial distribution of four potential active sites on MEC-L). Color codes: grey, C; blue, N; red, O; white, H. Source data are provided as a Source Data file.

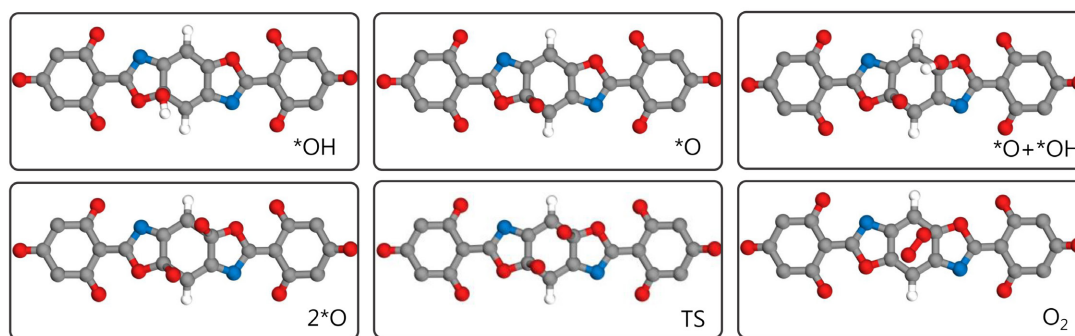


Supplementary Fig. 62. Gibbs free energy diagrams of MEC-L and MEC-T for the OPM pathway. The overall

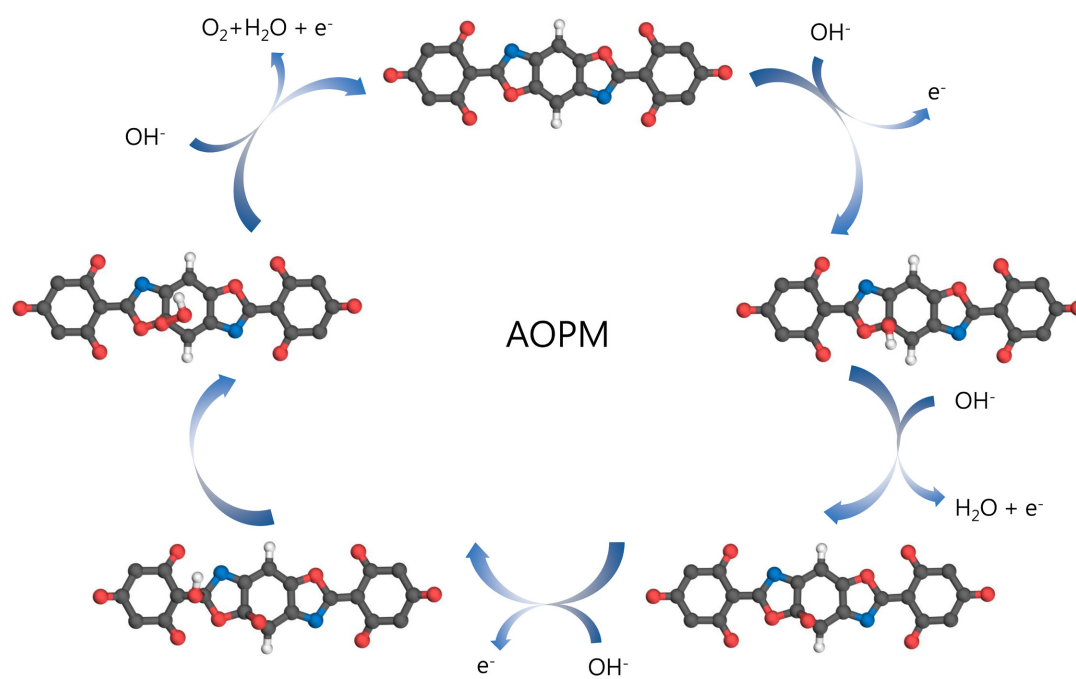
Gibbs free energy profiles of MEC-L and MEC-T. Source data are provided as a Source Data file.



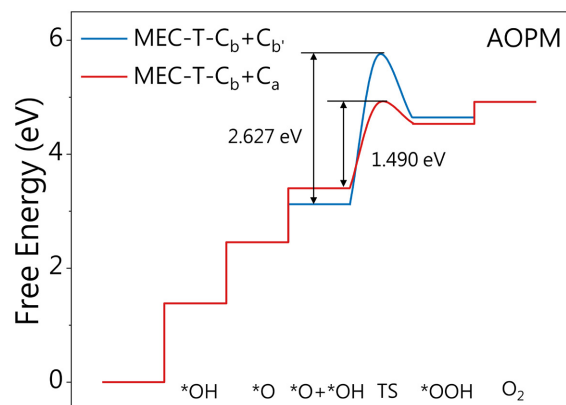
Supplementary Fig. 63. Structure models of MEC-L for key intermediates of OPM reaction pathway. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



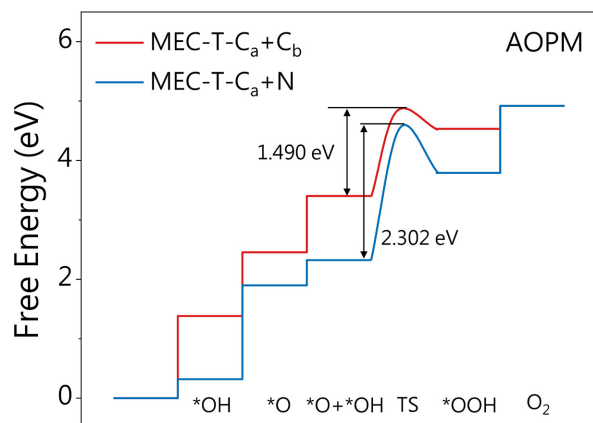
Supplementary Fig. 64. Structure models of MEC-T for key intermediates of OPM reaction pathway. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



Supplementary Fig. 65. The schematic diagram of the AOPM pathway of MEC-T.

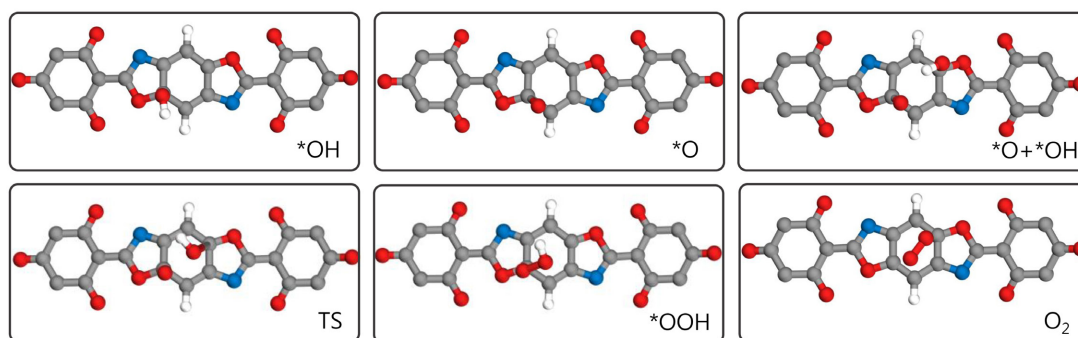


Supplementary Fig. 66. Gibbs free energy diagrams of MEC-T for the AOPM pathway on C_b+ $\text{C}_{b'}$ and C_b+ C_a . The overall Gibbs free energy profiles of MEC-T on different active sites. Source data are provided as a Source Data file.

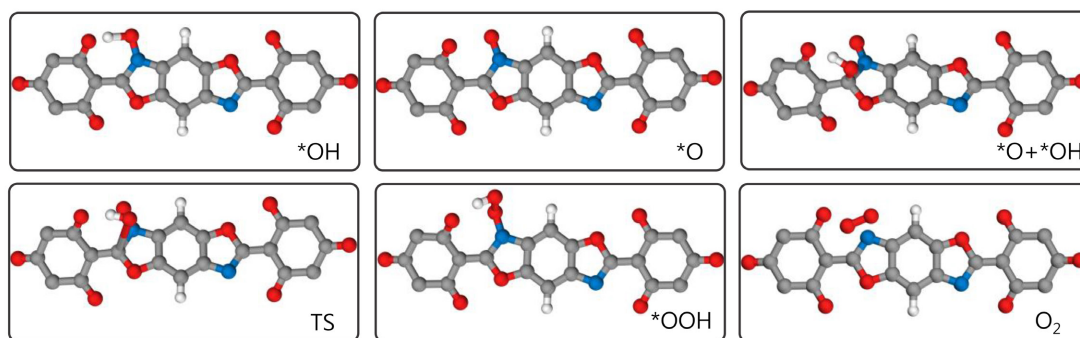


Supplementary Fig. 67. Gibbs free energy diagrams of MEC-T for the AOPM pathway on C_a+C_b and C_a+N .

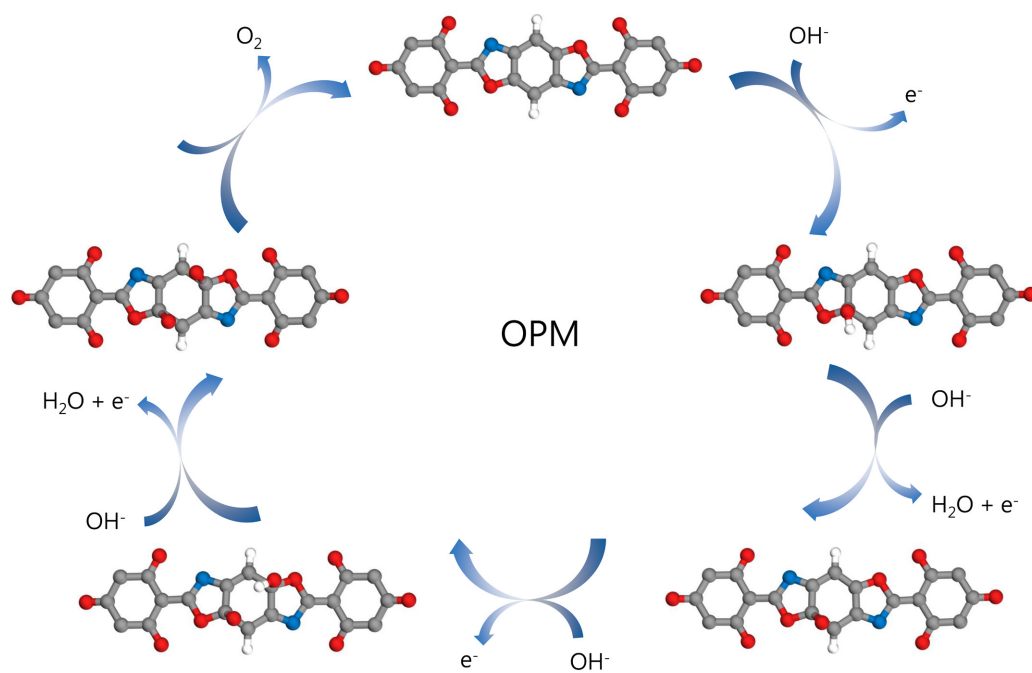
The overall Gibbs free energy profiles of MEC-T on different active sites. Source data are provided as a Source Data file.



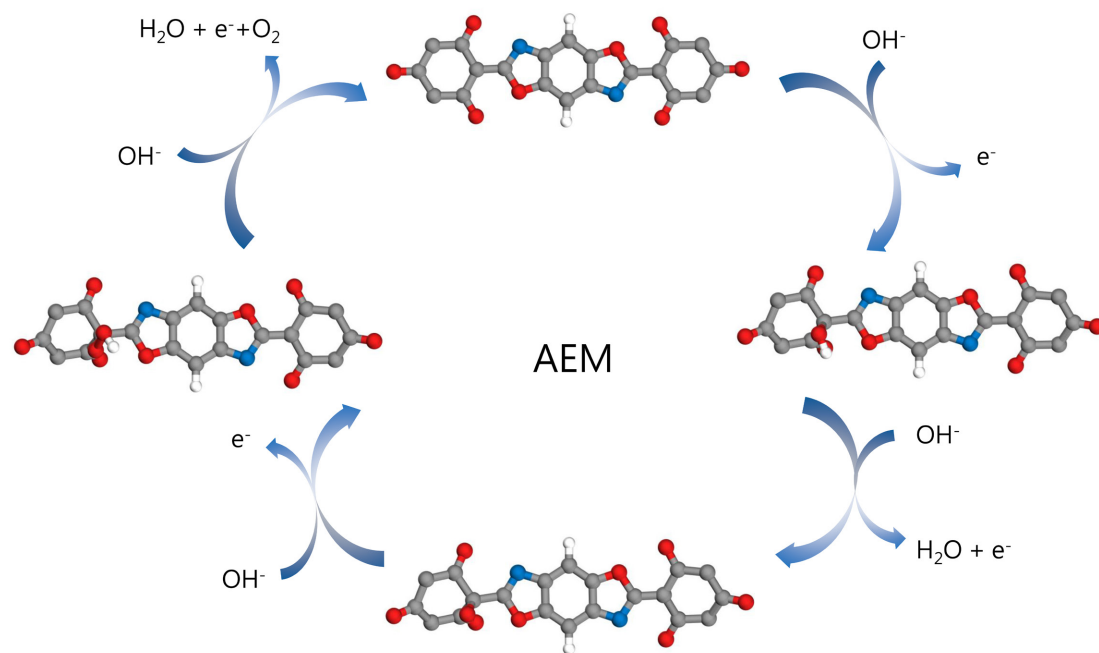
Supplementary Fig. 68. Structure models of MEC-T for key intermediates of AOPM reaction pathway at active site $C_b + C_b$. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



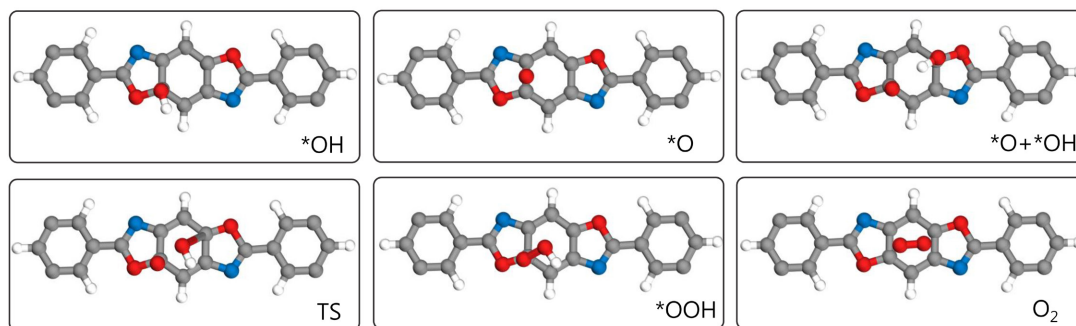
Supplementary Fig. 69. Structure models of MEC-T for key intermediates of AOPM reaction pathway at active site $C_a + N$. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



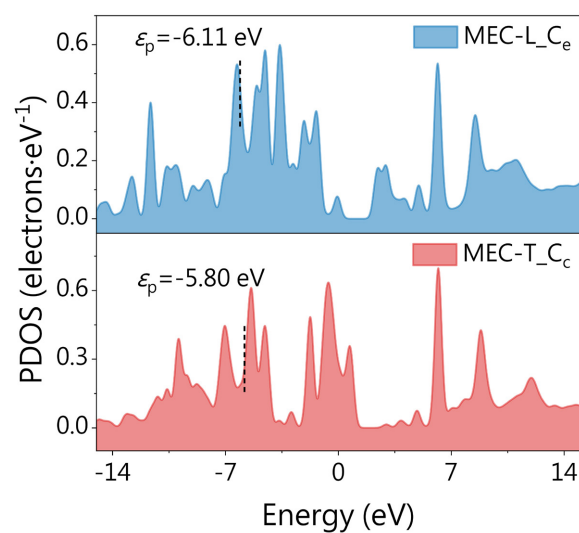
Supplementary Fig. 70. Schematic diagram of the OPM pathway for MEC-T.



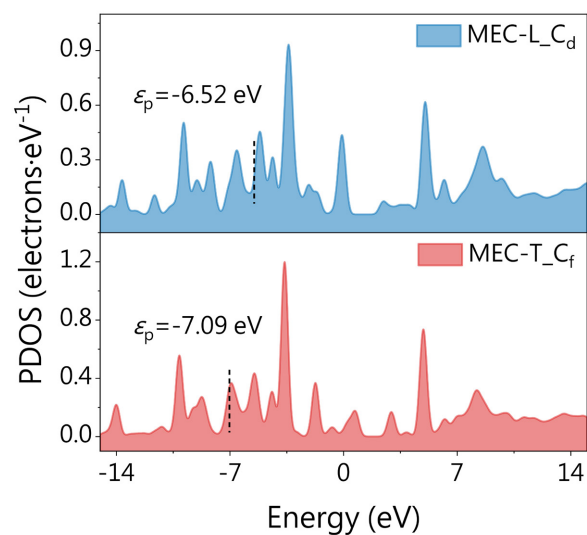
Supplementary Fig. 71. Schematic diagram of the AEM pathway for MEC-T.



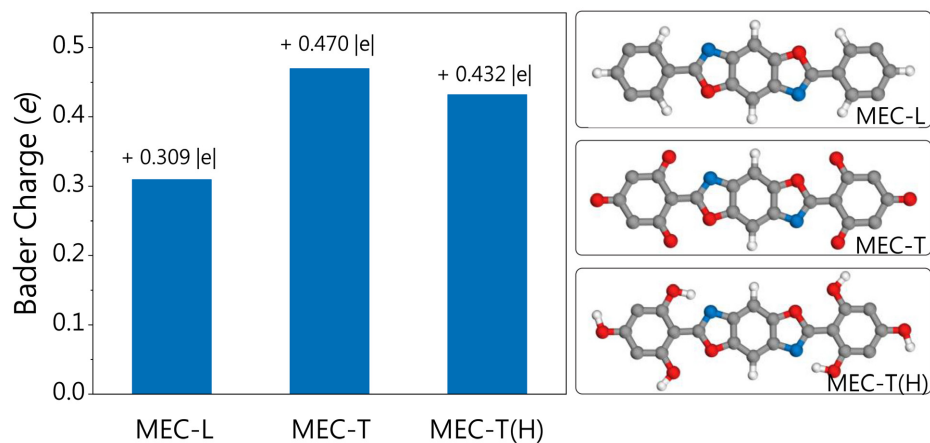
Supplementary Fig. 72. Structure models of MEC-L for key intermediates of AOPM reaction pathway. The colors in the structure are represented: the gray ball represents carbon, the blue ball represents nitrogen, the red ball represents oxygen, and the white ball represents hydrogen.



Supplementary Fig. 73. PDOS of *p* orbital for the same C atoms on catalysts. PDOS of *p* orbital for C_e and C_c atoms on MEC-L and MEC-T, respectively. Their corresponding *p*-band centers were labeled, ϵ_p : *p*-band center. Source data are provided as a Source Data file.

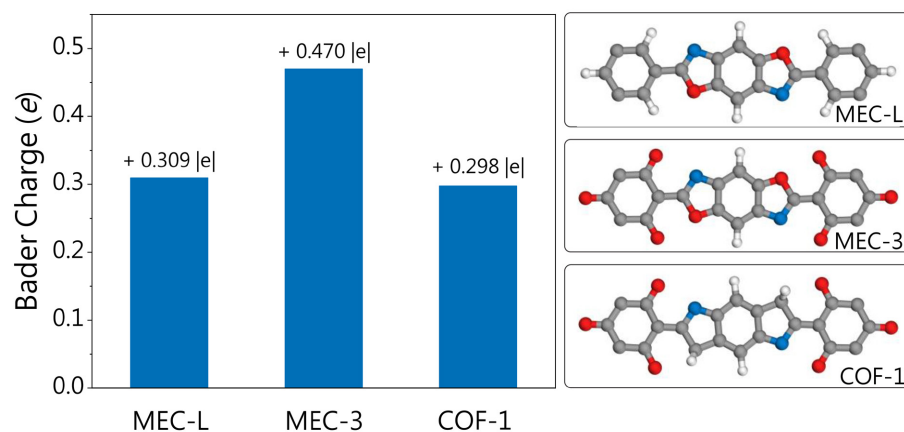


Supplementary Fig. 74. PDOS of p orbital for the same C atoms on catalysts. PDOS of p orbital for C_d and C_f atoms on MEC-L and MEC-T, respectively. Their corresponding p -band centers were labeled, ϵ_p : p -band center. Source data are provided as a Source Data file.

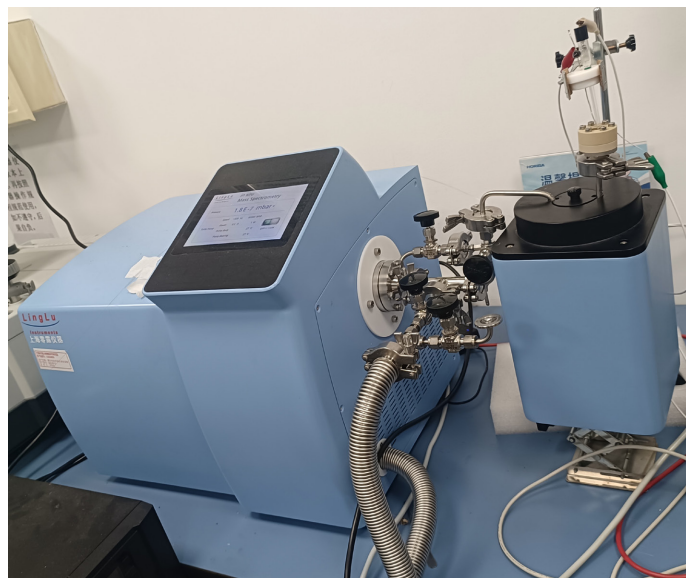


Supplementary Fig. 75. Comparison of Bader charge analysis results for MEC-L, MEC-T and MEC-T(H).

MEC-T(H) represents the case where the hydroxyl group forms a hydrogen bond with the N atom. The Bader charges of the carbon atoms in MEC-T(H) and MEC-T are +0.432 $|e|$ and +0.470 $|e|$, respectively, indicating that the hydrogen bond only slightly reduces the positive charge at the carbon atom. In contrast, the Bader charge of the carbon atom in MEC-L is +0.309 $|e|$, which is significantly lower than that of the hydroxyl-containing system, confirming that the introduction of the hydroxyl group enhances the positive charge on the carbon atom. Color codes: grey, C; blue, N; red, O; white, H. Source data are provided as a Source Data file.



Supplementary Fig. 76. Comparison of Bader charge analysis results for MEC-L, MEC-T and COF-1. The control model COF-1 are constructed by replacing the oxygen atom in the benzoxazole unit with a carbon atom. The Bader charges of the carbon atoms in MEC-T and COF-1 are +0.470 $|e|$ and +0.298 $|e|$, respectively, confirming that the oxygen atom in the benzoxazole can significantly enhance the positive charge on the carbon atoms. Color codes: grey, C; blue, N; red, O; white, H. Source data are provided as a Source Data file.



Supplementary Fig. 77. A photograph of the operando DEMS experiments.

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