

Supplementary Information for

**Operando Elucidation of Hydrogen Production Mechanisms on Sub-Nanometric
High-Entropy Metallenes**

Li et al.

Supplementary Note 1

Electrochemical Measurements

The reference electrode was calibrated by a three-electrode electrochemical cell with working electrode (Pt foil), counter electrode (Pt foil), reference electrode (Ag/AgCl or Hg/HgO), and gas (H₂) inlet. In this work, the calibration of reference electrode against reversible hydrogen electrode (RHE) was conducted in H₂-saturated electrolytes (0.5 M H₂SO₄, 1.0 M PBS or 1.0 M KOH). The cyclic voltammetry (CV) in the voltage range of hydrogen electrocatalysis with the scan rate of 2 mV s⁻¹. The HER CV has two voltage intercepts at zero current. The calibrated E is the average value of two voltages, which was estimated to be -0.228 V for Ag/AgCl electrode in 0.5 M H₂SO₄, -0.604 V for Ag/AgCl electrode in 1.0 M PBS and -0.917 for Hg/HgO electrode in 1.0 M KOH (Supplementary Fig. 17). The RHE was thus determined by using the following equation:

$$0.5 \text{ M H}_2\text{SO}_4: E (\text{vs. RHE}) = E \left(\text{vs. } \frac{\text{Ag}}{\text{AgCl}} \right) + 0.228 \text{ V} \quad (1)$$

$$1.0 \text{ M PBS: } E (\text{vs. RHE}) = E \left(\text{vs. } \frac{\text{Ag}}{\text{AgCl}} \right) + 0.604 \text{ V} \quad (2)$$

$$1.0 \text{ M KOH: } E (\text{vs. RHE}) = E \left(\text{vs. } \frac{\text{Hg}}{\text{HgO}} \right) + 0.917 \text{ V} \quad (3)$$

Supplementary Note 2

Computational details

The first principle calculations were performed by the Vienna *ab initio* simulation package (VASP) using the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) method based on density functional theory (DFT). The projector augmented wave (PAW) was used to describe ions and electron interaction. The kinetic energy cutoff was set at 450 eV.

PdRh, PdMoFeMn, RhMoFeMn, and PdRhMoFeMn were employed as models to further determine the intrinsic mechanism for excellent catalytic activity according to the ICP results. All the cell parameters of PdRh, PdMoFeMn, RhMoFeMn, and PdRhMoFeMn are $a=b=10.58010 \text{ \AA}$, $c=21.84430 \text{ \AA}$. In the vertical direction, a vacuum layer of about 15 $\text{\AA}$ in thickness was introduced to avoid the interaction between neighboring image structures.

In all the calculations, we use $3 \times 2 \times 1$ for the Monkhorst-Pack k-point for periodic crystal structure and surface model. The convergence threshold for energy was set at 10^{-5} eV . The equilibrium lattice constants were optimized with maximum stress on each atom within $0.05 \text{ eV/\AA}$. To precisely reflect the calculations, the DFT+U corrections for transition metal (Rh: 2.0 eV, Pd: 2.0 eV, Fe: 2.5 eV, Mo: 3.5 eV, and Mn: 4.0 eV) were employed.

The adsorption energy (ΔE_{ads}) was defined as follows:

$$E_{\text{ads}} = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}}$$

where $E_{\text{ad/sub}}$, E_{ad} , and E_{sub} are the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate respectively. Usually, a more negative E_{ads} value reflects stronger adsorption.

The free energy was calculated using the equation:

$$\Delta G = \Delta E + \Delta \text{ZPE} - \Delta TS$$

Where ΔG , ΔE , ΔZPE , and TS represented the free energy, total energy from DFT calculations, zero-

point energy, and entropic contributions (T was set to be 300 K), respectively.

Our modeling process begins by creating a 5x5x5 supercell of FCC-Pd. Then, we proportionally replace Pd atoms and obtain a high-entropy alloy PdRhMoFeMn. Since the lattice atomic configurations of high-entropy alloys are disordered, we need to generate many models and select the one with the lowest energy. When generating a new model, we use a different set of random numbers to replace the Pd atoms, ensuring that each configuration is unique.

To handle the generation of many models, we utilize shell scripting in the LAMMPS program and incorporate LAMMPS' looping commands. The following is the LAMMPS script for PdRhMoFeMn.

```
# LAMMPS script for high-entropy alloy modeling
```

```
# Set up the initial FCC-Pd supercell
```

```
lattice fcc 2.28
```

```
region box block 0 5 0 5 0 5
```

```
create_box 1 box
```

```
create_atoms 1 box
```

```
label loop
```

```
variable a loop 1000
```

```
log log.$a
```

```
# Proportional replacement of Fe atoms
```

```
variable rand1 equal random (0, 1)
```

```
variable rand2 equal random (0, 1)
```

```
variable rand3 equal random (0, 1)
```

```
variable rand4 equal random (0, 1)
```

```
mass 1 106.42 #Pd
```

```
mass 2 55.84 #Fe
```

```
mass 3 54.94 #Mn
```

```
mass 4 95.95 #Mo
```



```
mass 5 102.91 #Rh
group Pd type 1
group Fe type 2
group Mn type 3
group Mo type 4
group Rh type 5
group all type 1 2 3 4 5
group PdRhMoFeMn region box
delete_atoms group Pd
delete_atoms group Mn
delete_atoms group Fe
delete_atoms group Mo
delete_atoms group Rh
create_atoms 1 random 0 4 PdRhMoFeMn
create_atoms 2 random 0 4 PdRhMoFeMn
create_atoms 3 random 0 4 PdRhMoFeMn
create_atoms 4 random 0 4 PdRhMoFeMn
create_atoms 5 random 0 4 PdRhMoFeMn
#To call a shell script and change random numbers for creating new models.
shell ./mseed.sh
next
A jump PdRhMoFeMn.in loop
# Perform structure optimization and energy calculations
```

By running the script, we obtained 1000 models. Additionally, we performed optimization on each model using conjugate gradient and fast descent methods to obtain the energy of their optimized structures.

After submitting the computational tasks using PBS, we can see that the computation folder now contains 1000 structure data files for PdRhMoFeMn high-entropy alloys, along with corresponding log files for each optimization process. Since we ensured that each model is unique during the modeling process, after static structural optimization, the system's free energy can be arranged from lowest to highest. The target structure we are looking for will have the lowest energy. Upon opening any log file, you will see the output of the free energy after each optimization completion.

Minimization stats:

Stopping criterion = energy tolerance

Energy initial, next-to-last, final=

-15233.1467809 -15233.1478714 -15233.1453834

```
#!/bin/bash
```

```
echo `echo -e "Number""\t""Energy_(eV)"` >>result.txt
```

```
for i in {1..1000}^1
```

```
do
```

```
energy=$(echo ``grep -A 1 'Energy initial' log.$i | tail -1|awk '{printf "%12f\n", $3}'`)
```

```
echo `echo -e $i"\t"$energy` >> result.txt
```

```
done
```

```
echo "print(''.join(sorted(open('result.txt'), key=lambda s: s.split()[1],reverse=1)))" > sort.py
```

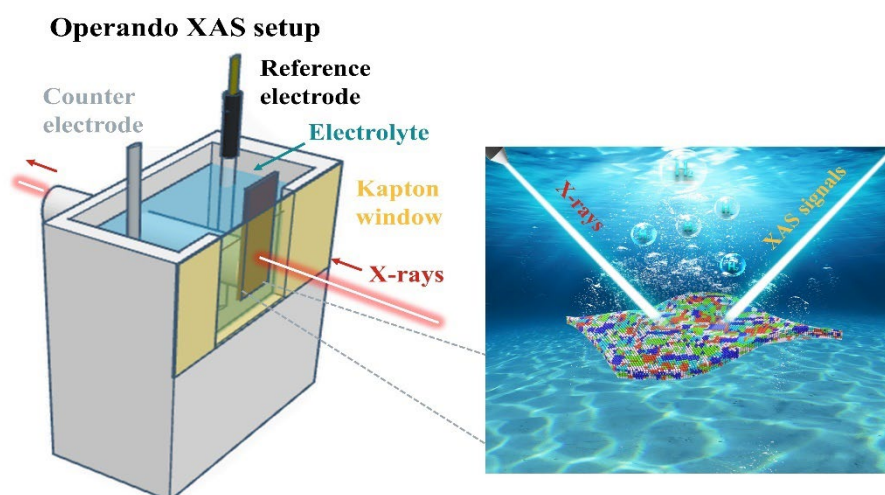
```
python sort.py > sorted.txt
```

```
rm sort.py
```

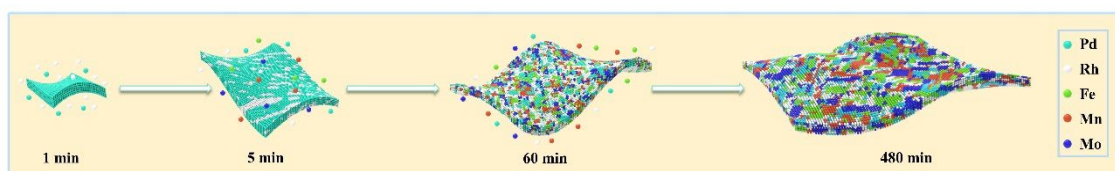
The program is named ad.sh. By running "./ad.sh" in the computational task folder, we can obtain the sorted file named sorted.txt. Opening sorted.txt, we find that the first line corresponds to the minimum energy, which represents the optimal structure we are looking for.

As shown in Supplementary Fig. 38a, we determined that the energy of the 359th model is the lowest according to the sorting. Therefore, we selected model number 359 as the model for our subsequent

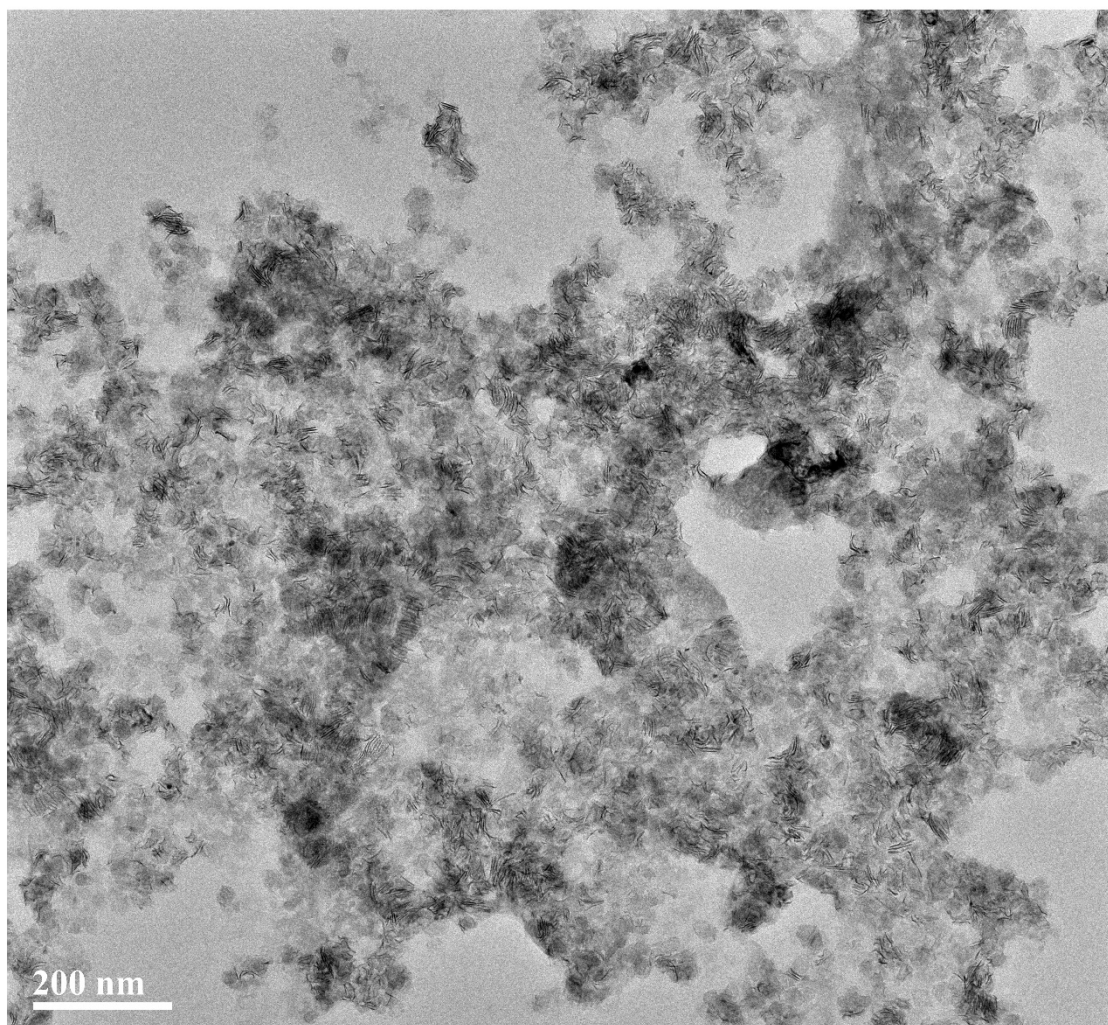
simulation. Supplementary Fig. 38b shows the selected model, which is a PdRhMoFeMn high-entropy alloy.



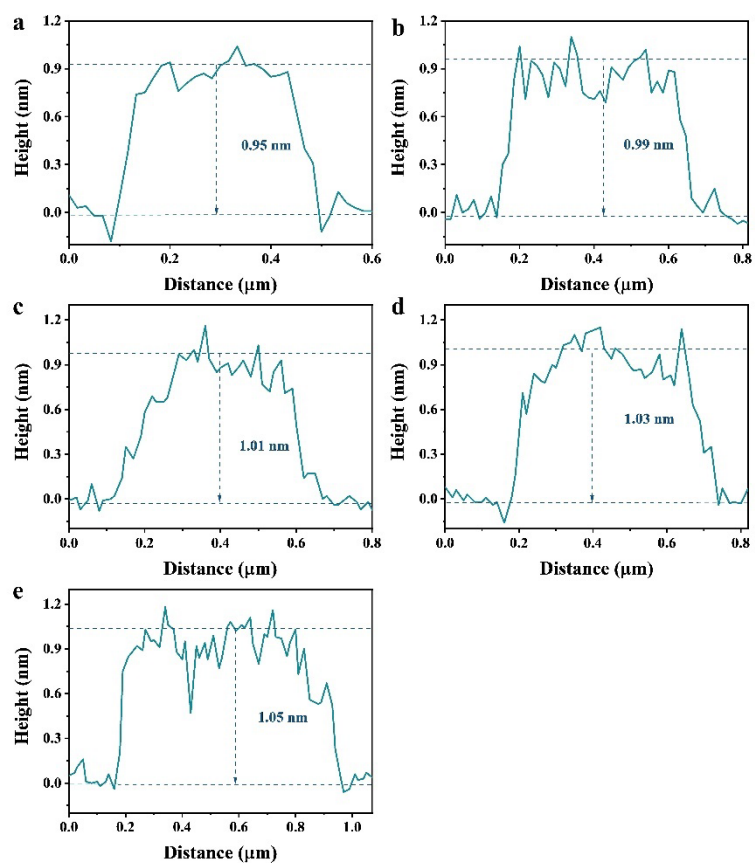
Supplementary Fig. 1 Identifying active sites and reaction mechanisms of HEMs by operando X-ray absorption spectroscopy spectra.



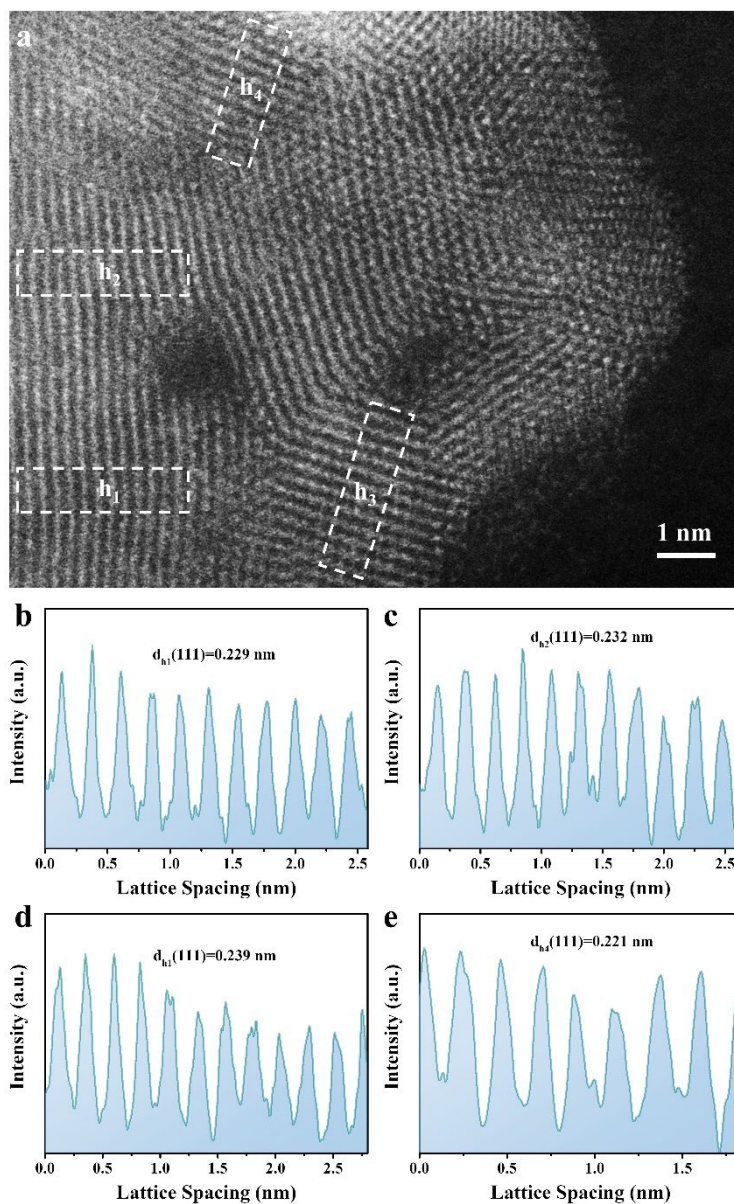
Supplementary Fig. 2 Schematic illustration of the growth process of PdRhMoFeMn HEMs.



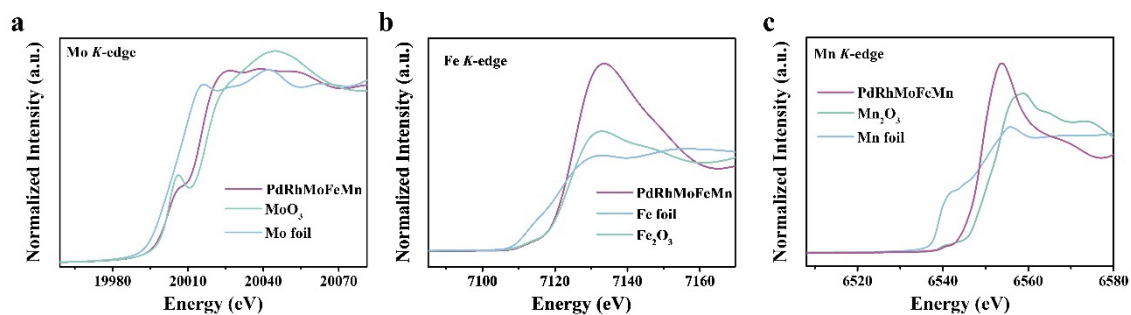
Supplementary Fig. 3 Low-magnification TEM image of monolayer PdRhMoFeMn HEMs.



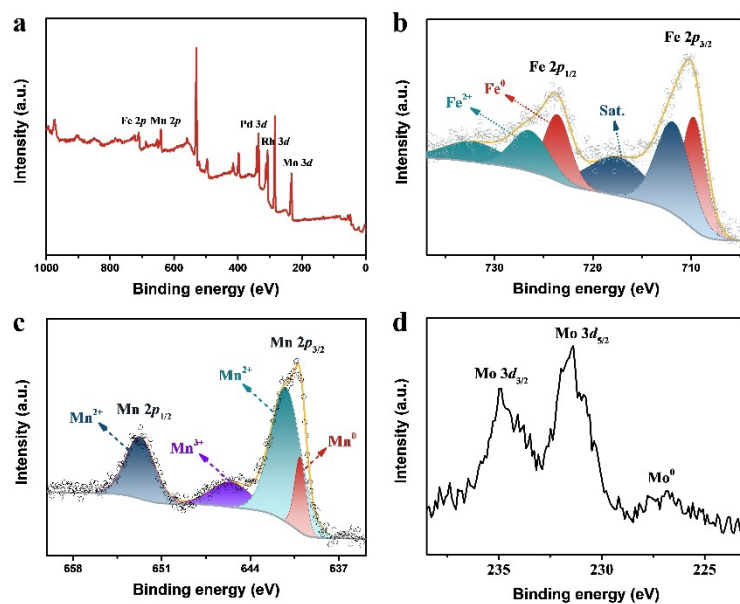
Supplementary Fig. 4 AFM characterization of PdRhMoFeMn HEMs. (a-e) The corresponding height profiles of monolayer PdRhMoFeMn HEMs in Fig. 2e.



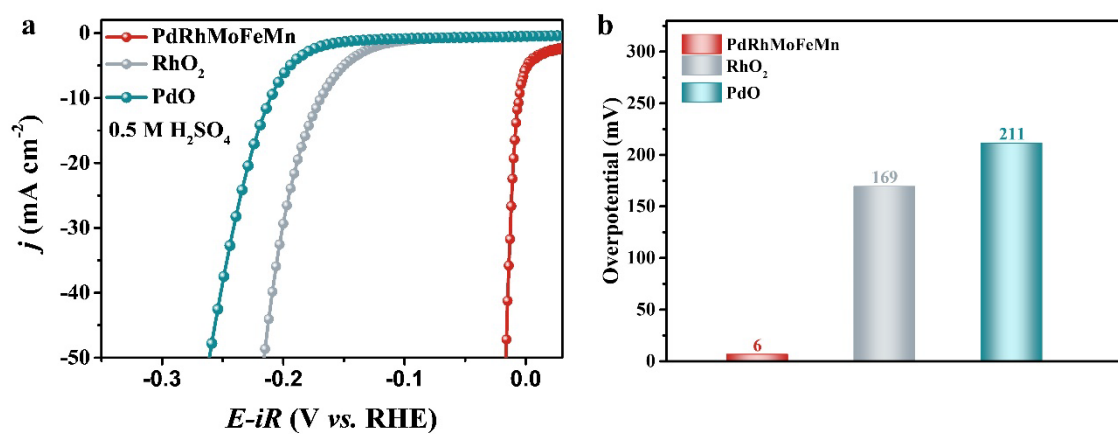
Supplementary Fig. 5 Aberration-corrected HRSTEM characterization of PdRhMoFeMn HEMs. (a) Aberration-corrected HRSTEM image of the surface atomic arrangement on PdRhMoFeMn HEMs and (b-e) the corresponding integrated pixel intensities of the HEA phase taken from the white dashed rectangles in (a).



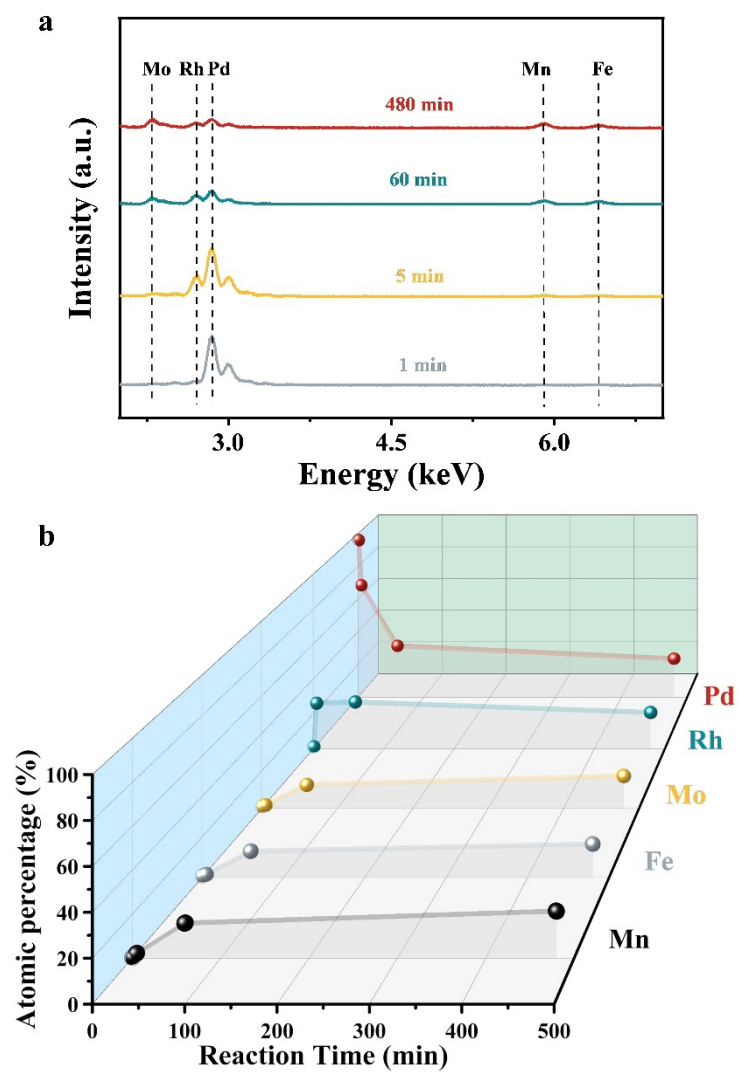
Supplementary Fig. 6 XANES analysis of HEMs. (a) The Mo *K*-edge XANES spectra of PdRhMoFeMn HEMs, MoO₃, and Mo foil. (b) The Fe *K*-edge XANES spectra of PdRhMoFeMn HEMs, Fe₂O₃, and Fe foil. (c) The Mn *K*-edge XANES spectra of PdRhMoFeMn HEMs, Mn₂O₃, and Mn foil.



Supplementary Fig. 7 XPS compositional analysis of PdRhMoFeMn HEMs. (a) XPS survey spectrum, (b) Fe 2p XPS spectrum, (c) Mn 2p XPS spectrum, and (d) Mo 3d XPS spectrum of PdRhMoFeMn HEMs.

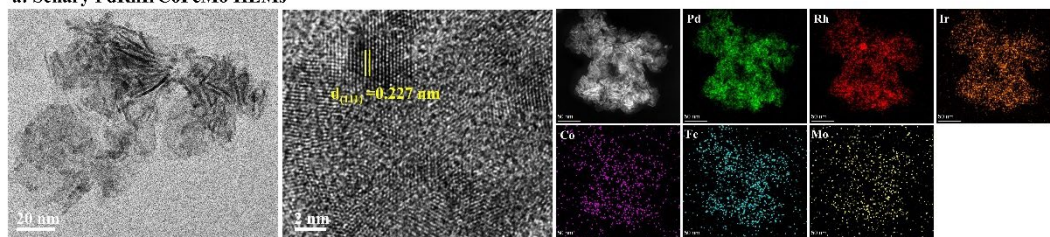


Supplementary Fig. 8 Electrocatalytic HER performance evaluation of PdRhMoFeMn HEMs, RhO₂, and PdO. (a) Polarization curves and (b) the histogram for overpotentials at 10 mA cm⁻² of PdRhMoFeMn HEMs, RhO₂, and PdO in 0.5 M H₂SO₄ electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05, electrolyte resistance: 6.4 ± 0.3 Ω.

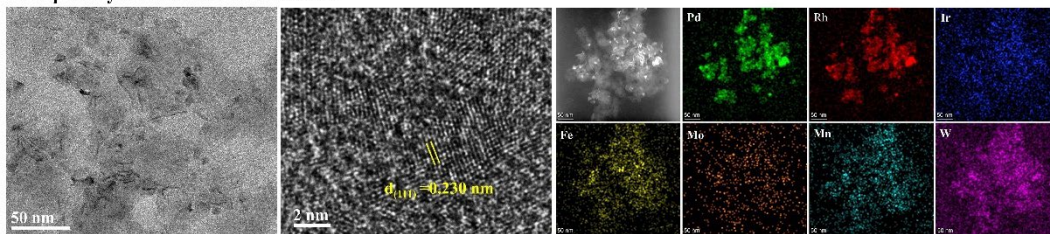


Supplementary Fig. 9 Growth mechanism of PdRhMoFeMn HEMs. (a) EDS spectrums and **(b)** the atomic ratio of Pd, Rh, Mo, Fe, and Mn of the products at different reaction time.

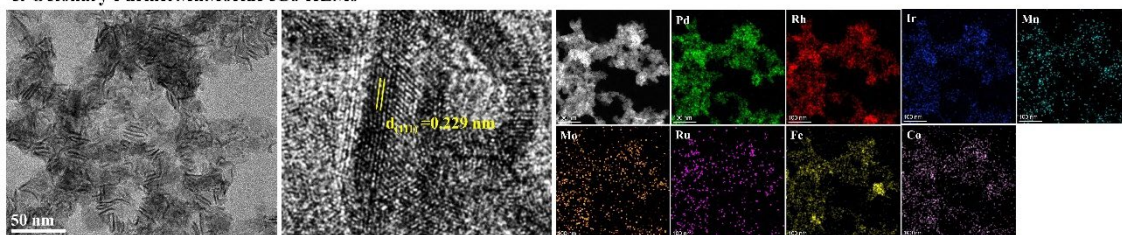
a: Senary PdRhIrCoFeMo HEMs



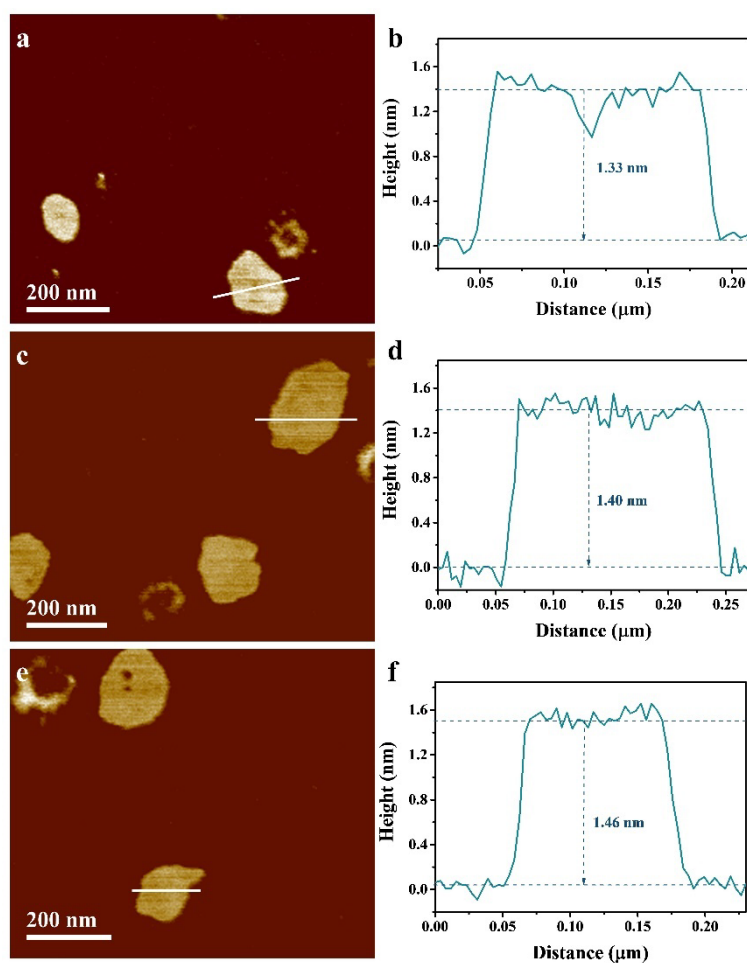
b: Septenary PdRhIrFeMoMnW HEMs



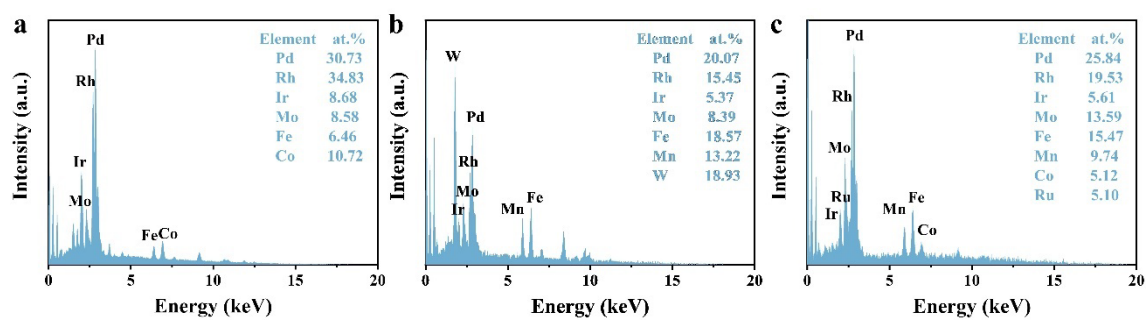
c: Octonary PdRhIrMnMoRuFeCo HEMs



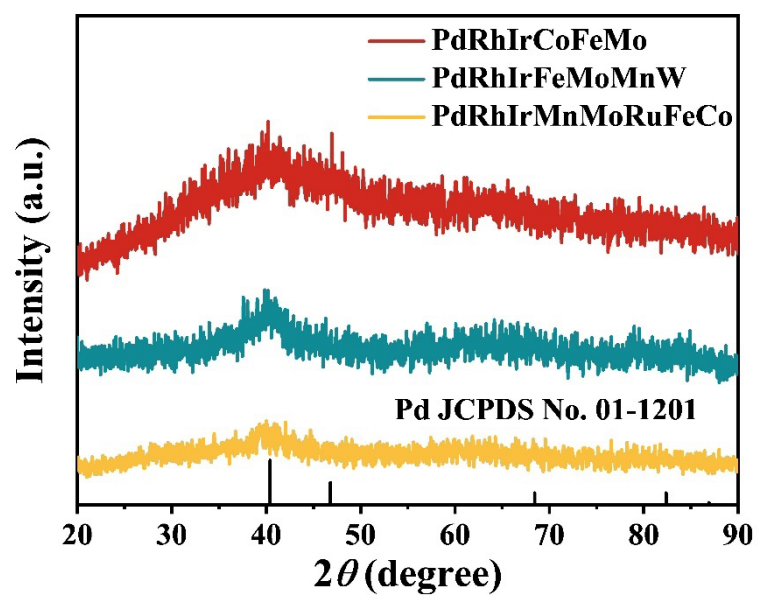
Supplementary Fig. 10 TEM, HRTEM, and EDS elemental mapping images of HEMs with different compositions. TEM, HRTEM, and EDS elemental mapping images of (a) senary PdRhIrCoFeMo HEMs, (b) septenary PdRhIrFeMoMnW HEMs, and (c) octonary PdRhIrMnMoRuFeCo HEMs.



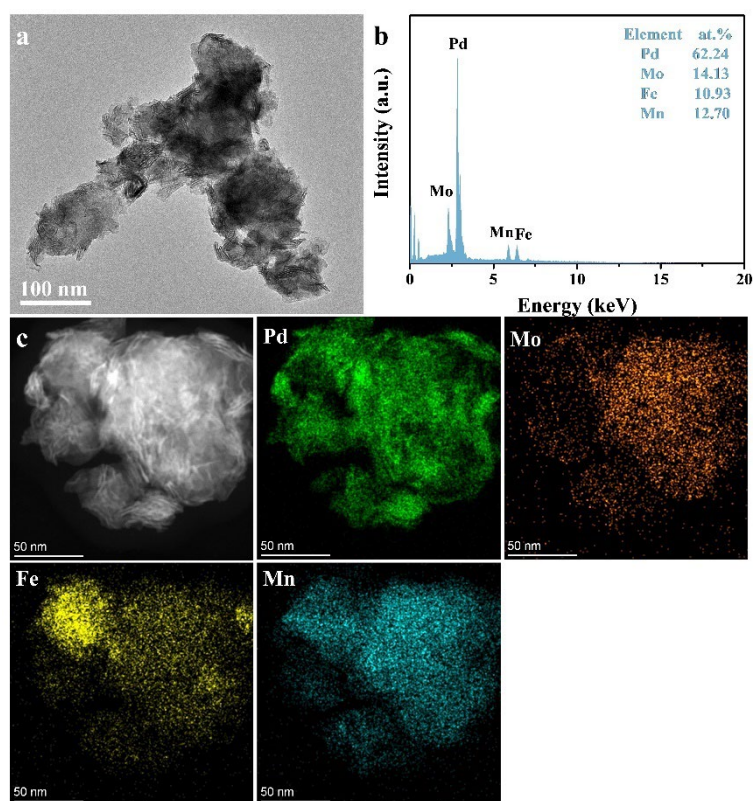
Supplementary Fig. 11 AFM analysis of HEMs with different compositions. AFM image (a) and corresponding height profiles (b) of senary PdRhIrCoFeMo HEMs. AFM image (c) and corresponding height profiles (d) of septenary PdRhIrFeMoMnW HEMs. AFM image (e) and corresponding height profiles (f) of octonary PdRhIrMnMoRuFeCo HEMs.



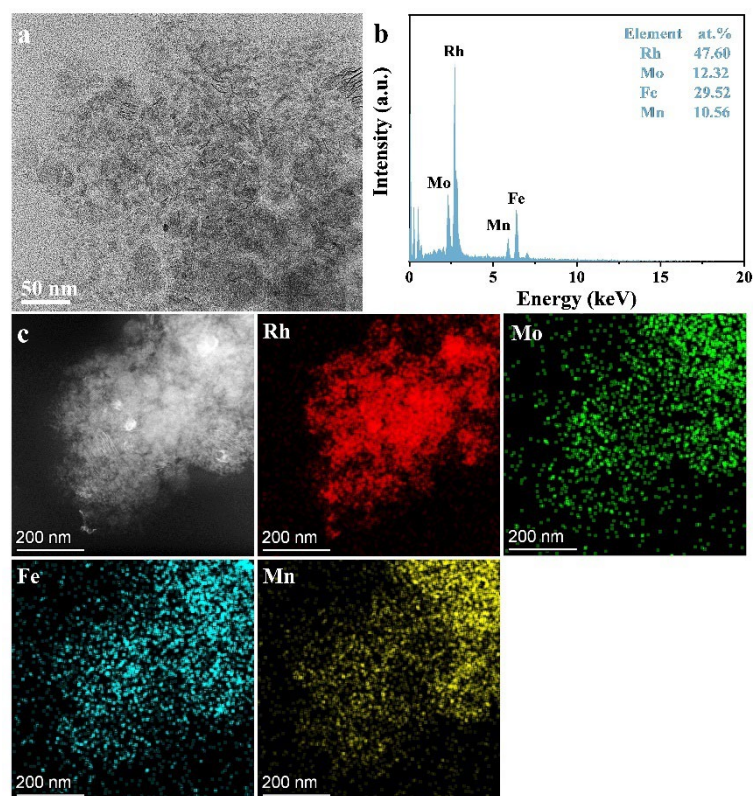
Supplementary Fig. 12 SEM-EDS analysis of HEMs with different compositions. SEM-EDS analysis of **(a)** senary PdRhIrCoFeMo HEMs, **(b)** septenary PdRhIrFeMoMnW HEMs, and **(c)** octonary PdRhIrMnMoRuFeCo HEMs.



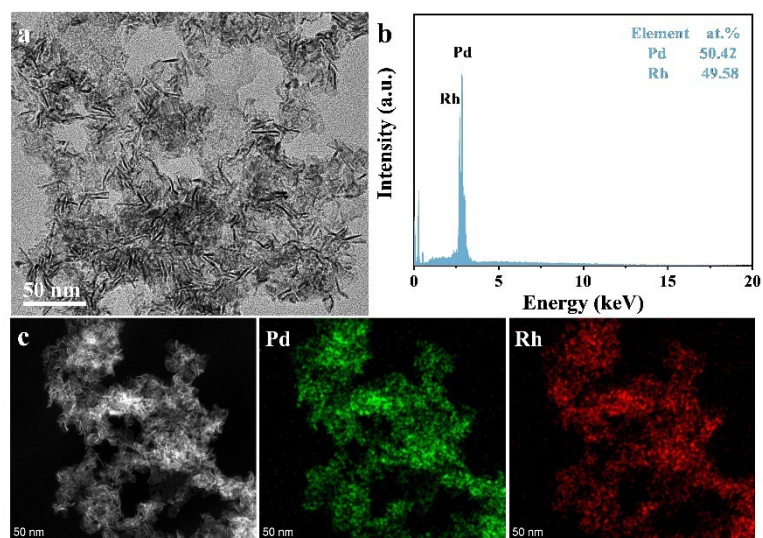
Supplementary Fig. 13 XRD patterns of senary PdRhIrCoFeMo HEMs, septenary PdRhIrFeMoMnW HEMs, and octonary PdRhIrMnMoRuFeCo HEMs.



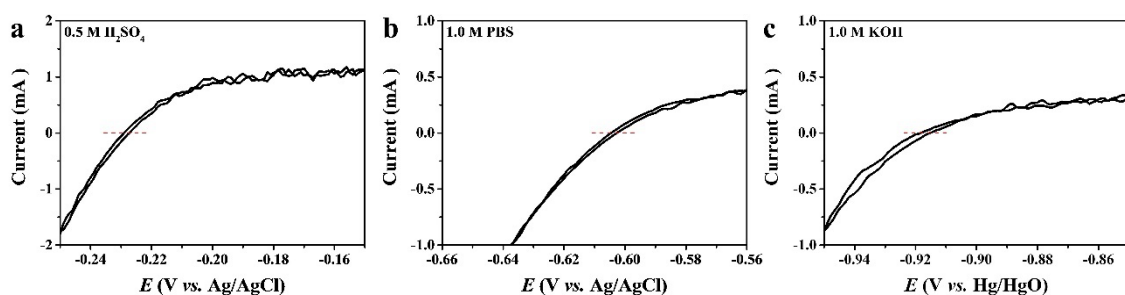
Supplementary Fig. 14 Characterizations of PdMoFeMn metallenes. (a) TEM image, **(b)** SEM-EDS, and **(c)** EDS elemental mapping images of PdMoFeMn metallenes.



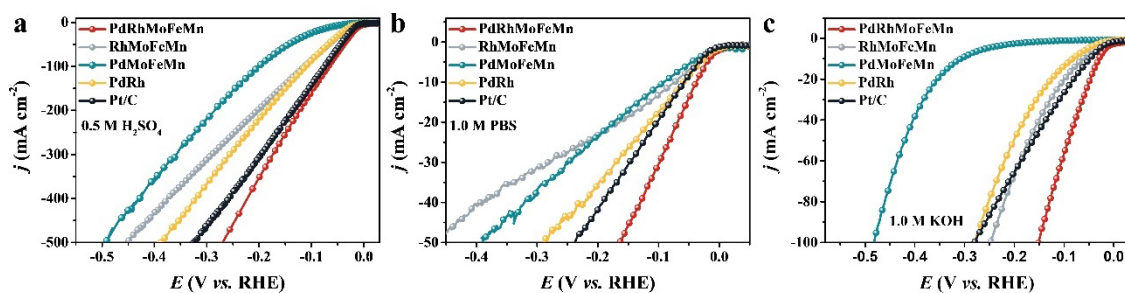
Supplementary Fig. 15 Characterizations of RhMoFeMn metallenes. (a) TEM image, **(b)** SEM-EDS, and **(c)** EDS elemental mapping images of RhMoFeMn metallenes.



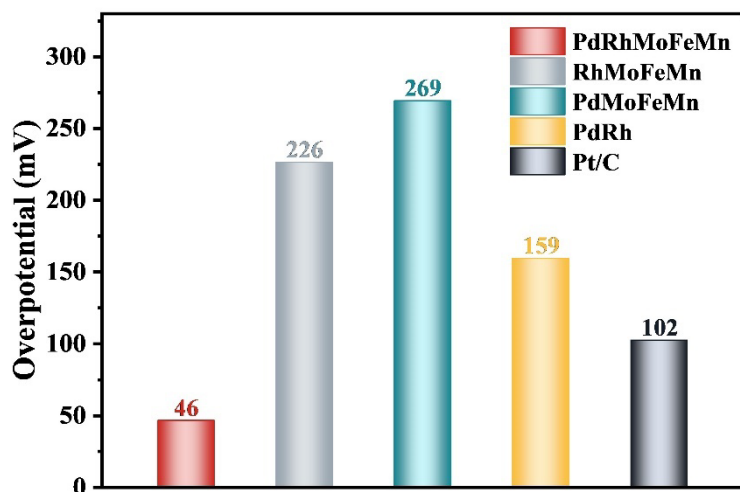
Supplementary Fig. 16 Characterizations of PdRh metallenes. (a) TEM image, **(b)** SEM-EDS, and **(c)** EDS elemental mapping images of PdRh metallenes.



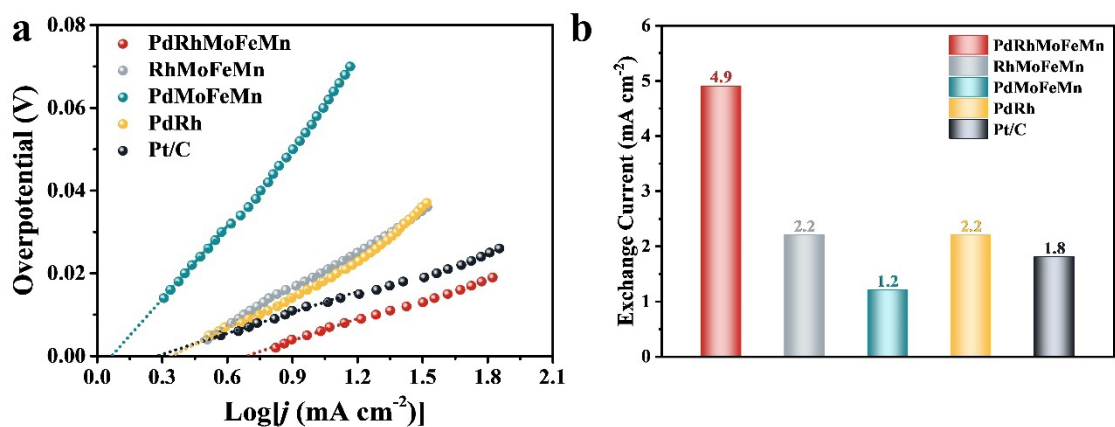
Supplementary Fig. 17 Calibration of reference electrodes. Calibration of **(a)** Ag/AgCl electrode in H_2 -saturated 0.5 M H_2SO_4 , **(b)** Ag/AgCl electrode in H_2 -saturated 1.0 M PBS and **(c)** Hg/HgO electrode in H_2 -saturated 1.0 M KOH. The testing conditions include electrolyte pH: 0.37 ± 0.05 (0.5 M H_2SO_4), 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $6.4 \pm 0.3 \Omega$ (0.5 M H_2SO_4), $21.6 \pm 0.6 \Omega$ (1 M PBS), and $5.5 \pm 0.4 \Omega$ (1 M KOH).



Supplementary Fig. 18 Non-iR-compensated polarization curves of the samples in various electrolytes. Polarization curves with iR-compensation of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C in **(a)** 0.5 M H₂SO₄, **(b)** 1.0 M PBS, and **(c)** 1.0 M KOH electrolytes. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05 (0.5 M H₂SO₄), 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $6.4 \pm 0.3 \Omega$ (0.5 M H₂SO₄), $21.6 \pm 0.6 \Omega$ (1 M PBS), and $5.5 \pm 0.4 \Omega$ (1 M KOH).

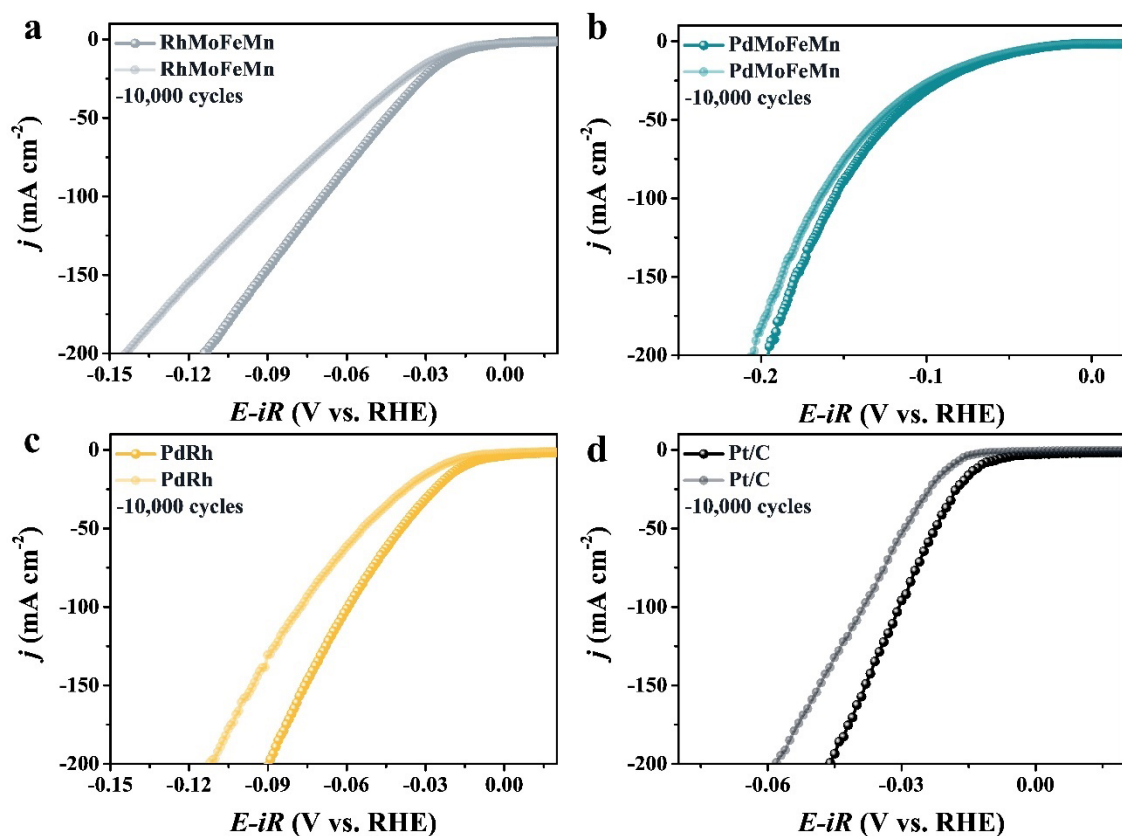


Supplementary Fig. 19 The histogram for overpotentials of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C at 500 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 0.37 ± 0.05 , electrolyte resistance: $6.4 \pm 0.3 \Omega$.



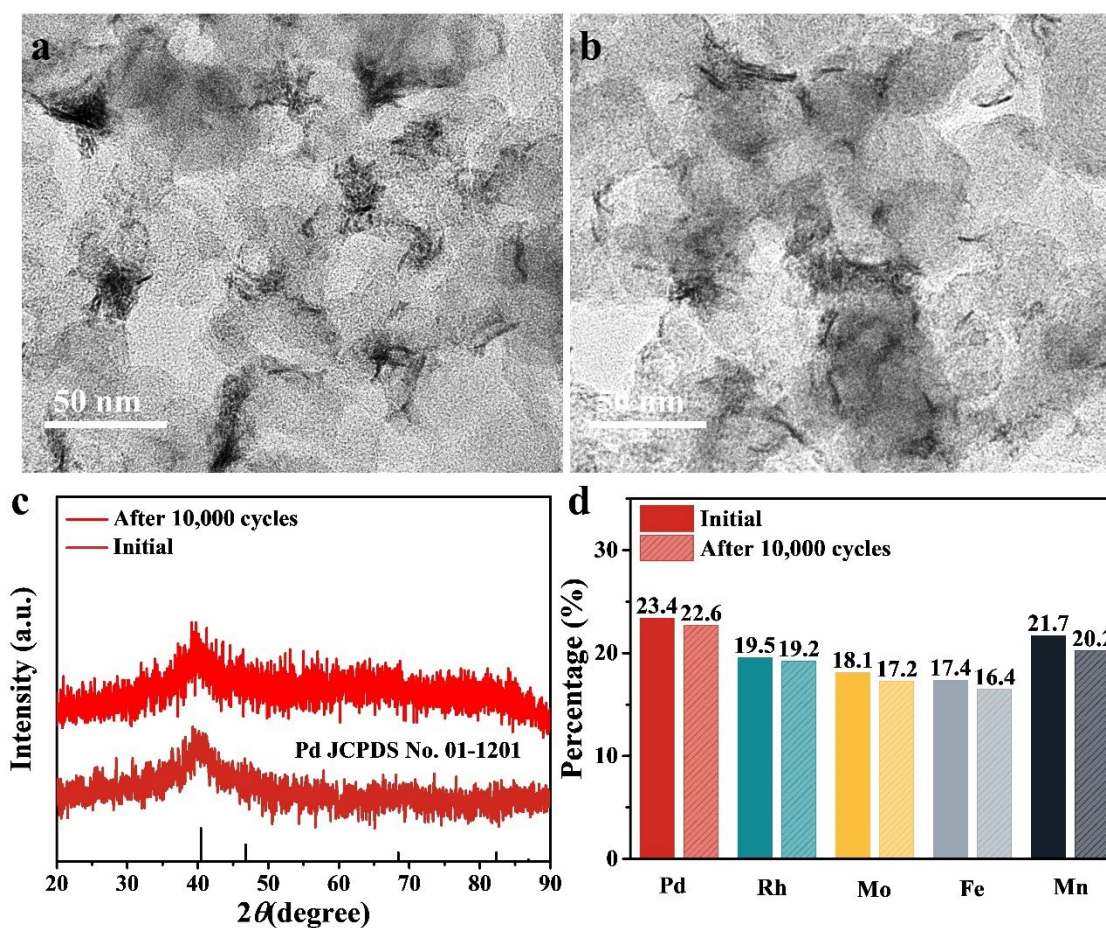
Supplementary Fig. 20 Exchange current density analysis in 0.5 M H₂SO₄ electrolyte.

Exchange current densities **(a)** and the corresponding histogram **(b)** of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C calculated from Tafel plots by extrapolation method in 0.5 M H₂SO₄ electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05, electrolyte resistance: 6.4 ± 0.3 Ω.

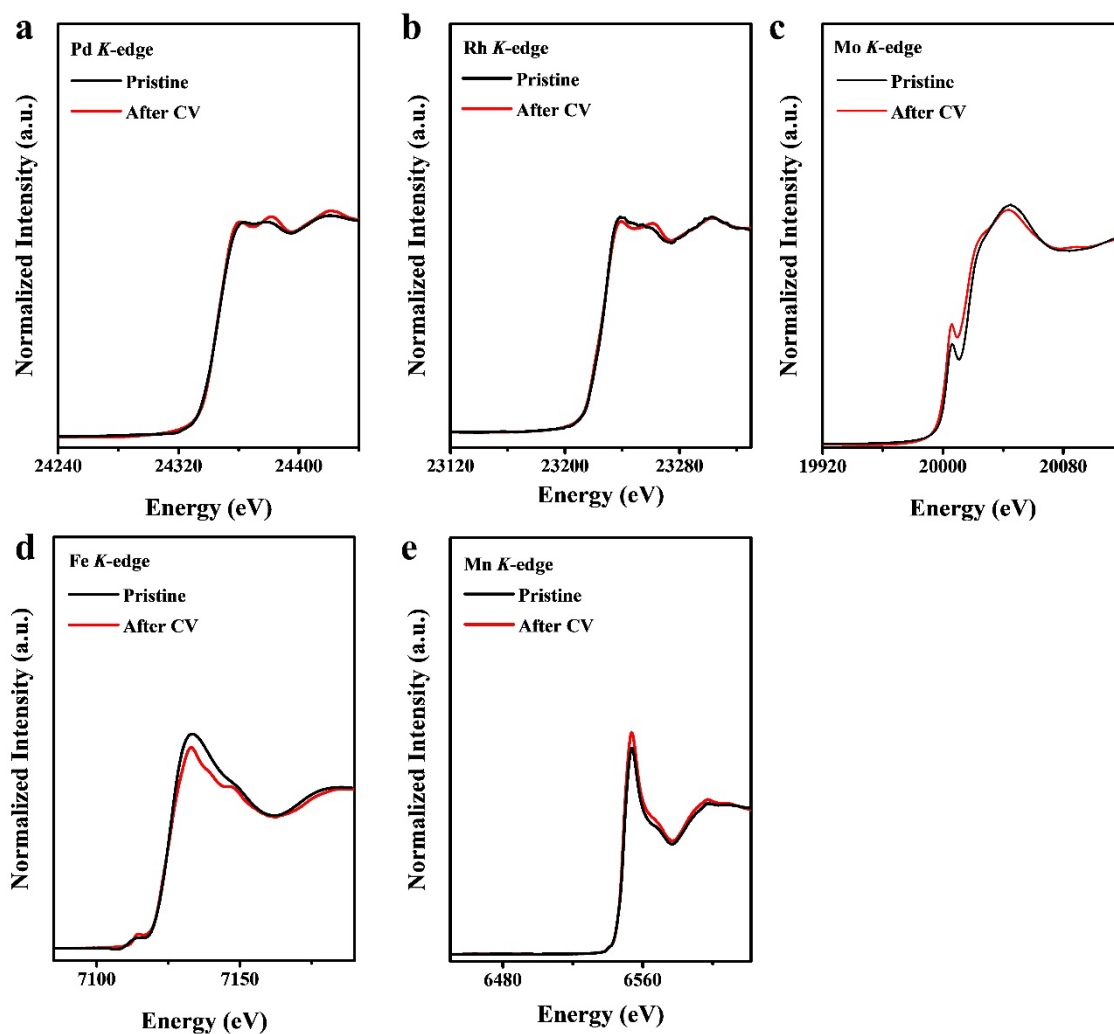


Supplementary Fig. 21 The stability tests of different catalysts in 0.5 M H_2SO_4 electrolyte.

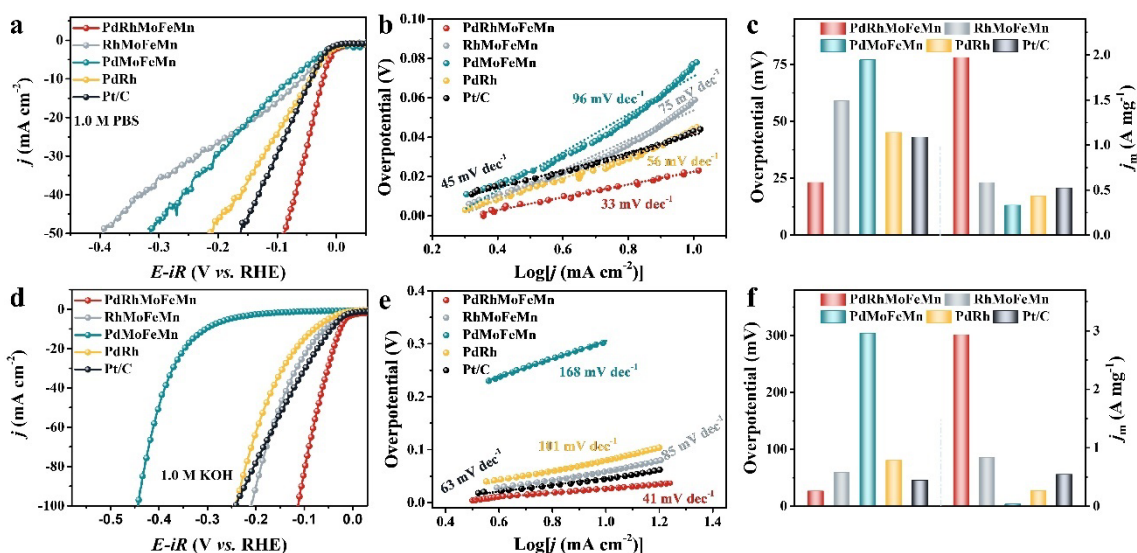
Polarization curves of **(a)** RhMoFeMn metallenes, **(b)** PdMoFeMn metallenes, **(c)** PdRh metallenes, and **(d)** Pt/C before and after 10000 CV cycles with iR-compensation in 0.5 M H_2SO_4 electrolyte. The testing conditions include GCE surface area: $0.07\ cm^2$, catalyst loading: $0.286\ mg\ cm^{-2}$, electrolyte pH: 0.37 ± 0.05 , electrolyte resistance: $6.4 \pm 0.3\ \Omega$.



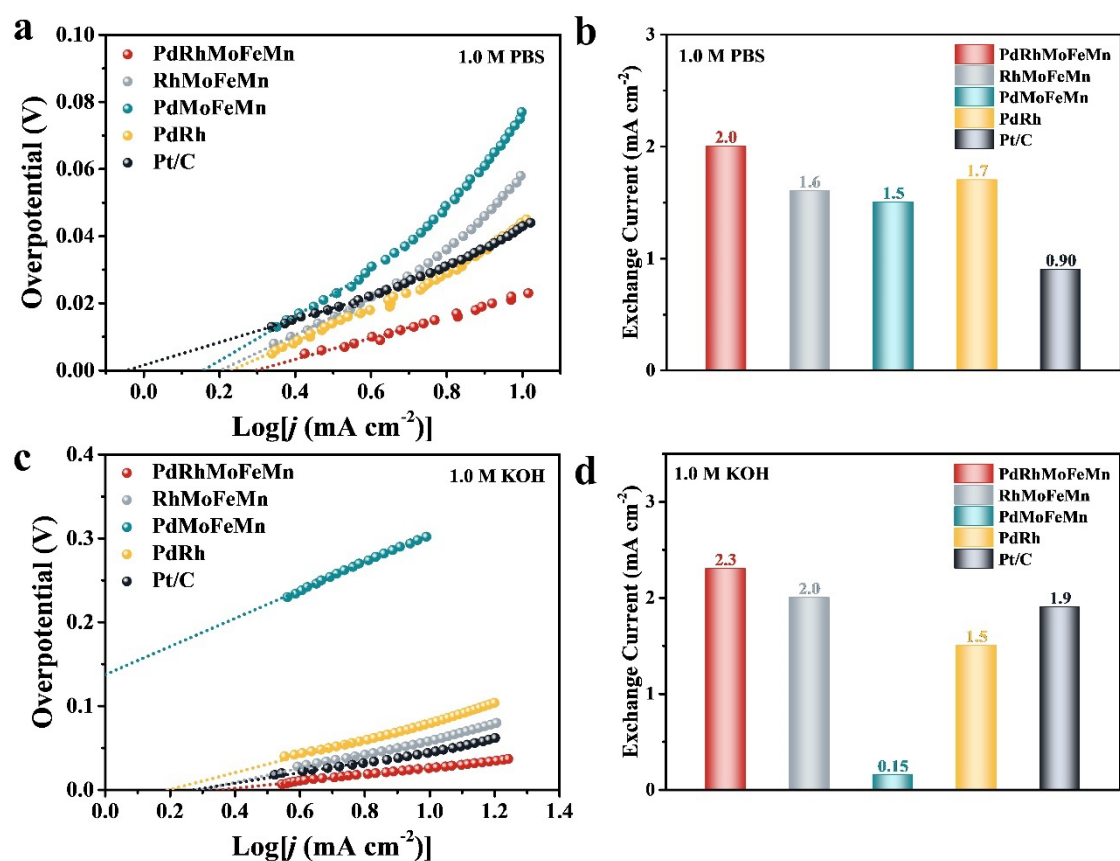
Supplementary Fig. 22 Characterizations of PdRhMoFeMn HEMs before and after 10,000 CV cycles. TEM images **(a)** before and **(b)** after 10,000 CV cycles. **(c)** XRD pattern before and after 10,000 CV cycles. **(d)** ICP-OES results before and after 10,000 CV cycles.



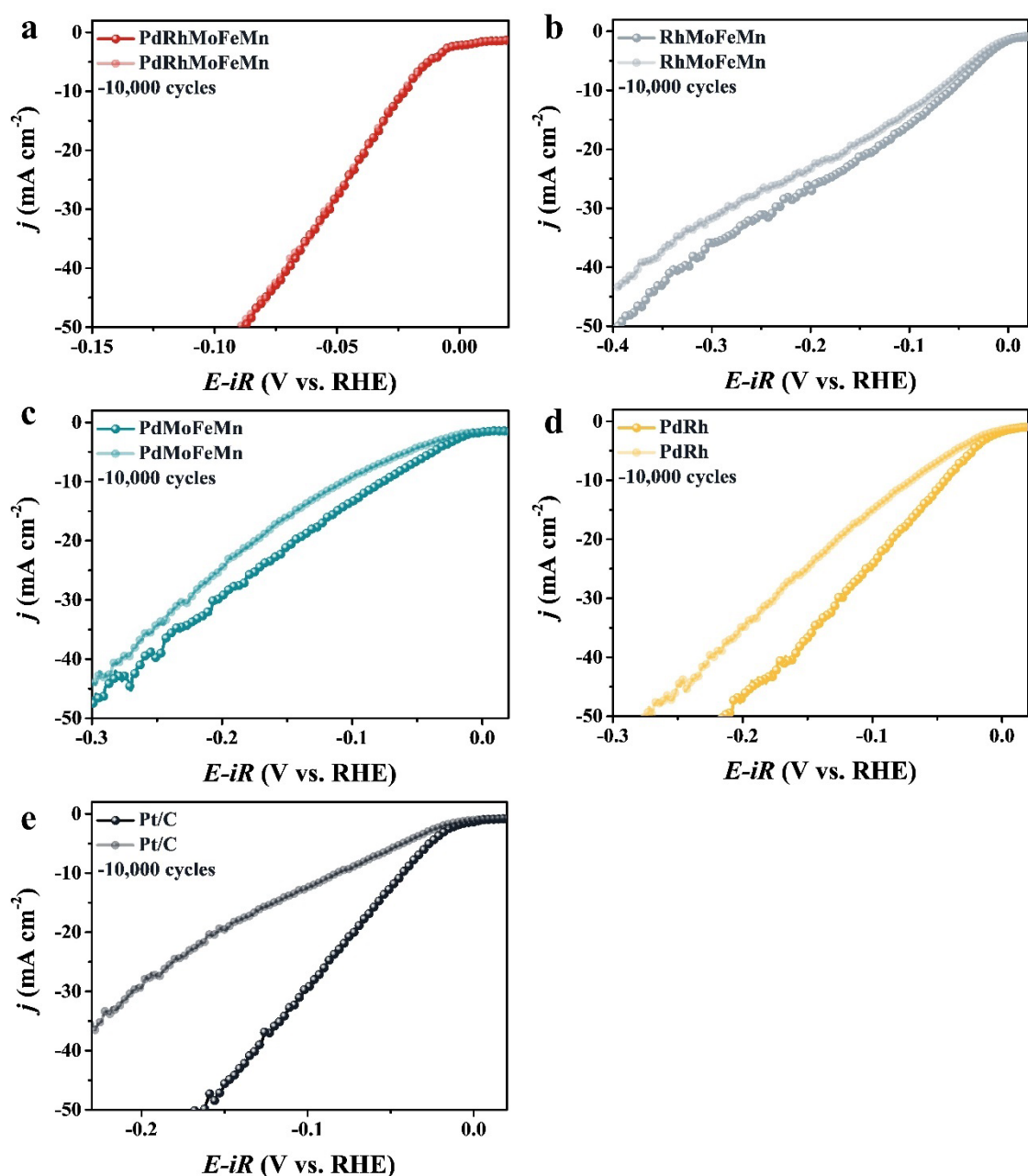
Supplementary Fig. 23 The XAS Characterization of PdRhMoFeMn HEMs before and after 10,000 CV cycles. The XANES spectra of (a) Pd, (b) Rh, (c) Mo, (d) Fe, and (e) Mn before and after 10,000 CV cycles.



Supplementary Fig. 24 Electrocatalytic HER performance evaluation of different catalysts in 1.0 M PBS and 1.0 M KOH electrolytes. (a) Polarization curves with iR-compensation and (b) corresponding Tafel plots of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C in 1.0 M PBS electrolyte. (c) Overpotentials at 10 mA cm^{-2} (left) and mass activities (right) at an overpotential of 100 mV of these nanocatalysts in 1.0 M PBS electrolyte. (d) Polarization curves with iR-compensation and (e) corresponding Tafel plots of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallene,s, and Pt/C in 1.0 M KOH electrolyte. (f) Overpotentials at 10 mA cm^{-2} (left) and mass activities (right) at an overpotential of 100 mV of these nanocatalysts in 1.0 M KOH electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , nobel metal loading: 0.028 mg cm^{-2} (PdRhMoFeMn HEMs), 0.027 mg cm^{-2} (RhMoFeMn metallenes), 0.039 mg cm^{-2} (RhMoFeMn metallenes), and 0.057 mg cm^{-2} (PdRh metallenes and Pt/C), electrolyte pH: 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $21.6 \pm 0.6 \Omega$ (1 M PBS), and $5.5 \pm 0.4 \Omega$ (1 M KOH).

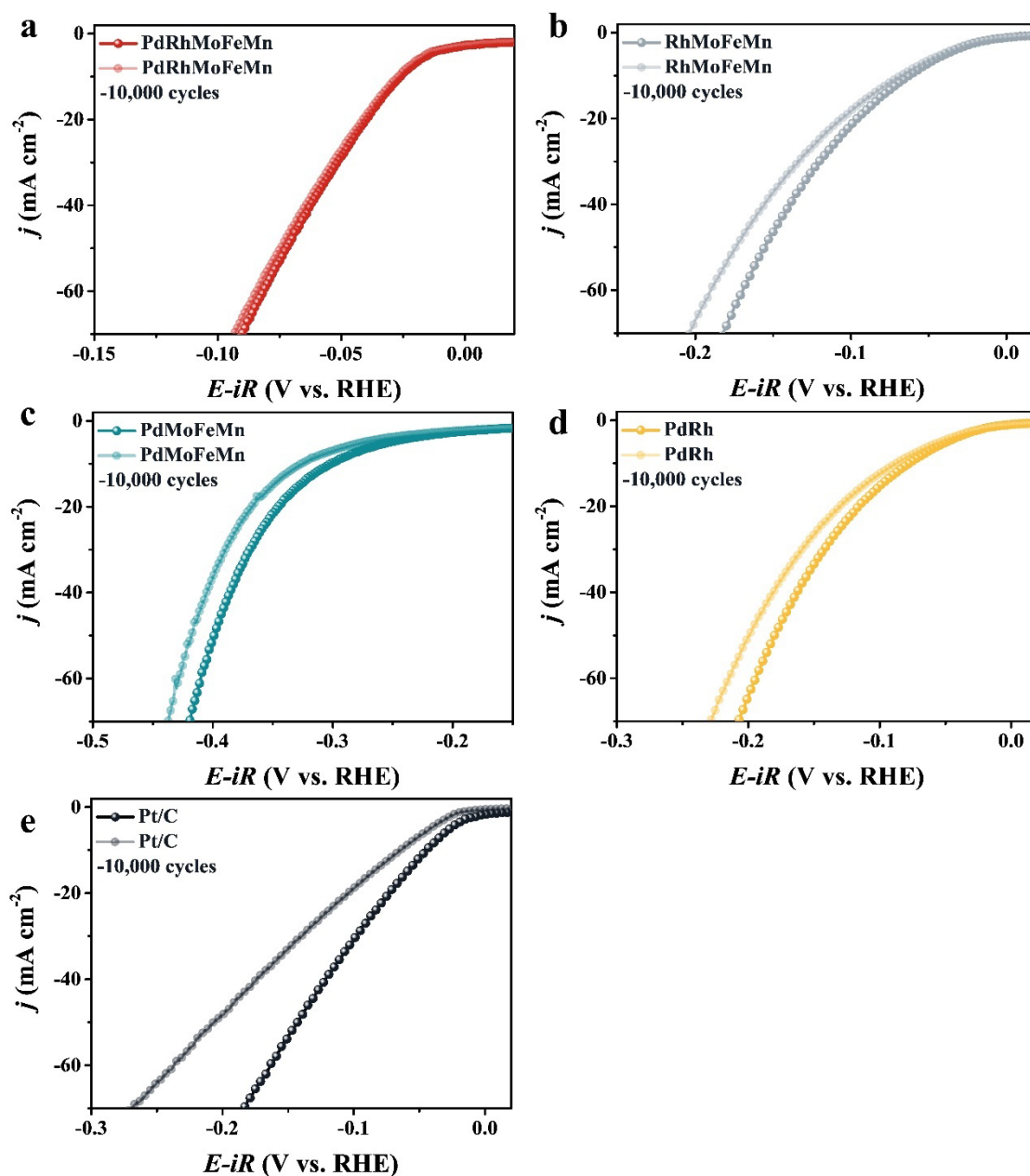


Supplementary Fig. 25 Exchange current density analysis in 1.0 M PBS and 1.0 M KOH electrolytes. Exchange current densities (a) and the corresponding histogram (b) of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C calculated from Tafel plots by extrapolation method in 1.0 M PBS electrolyte. Exchange current densities (c) and the corresponding histogram (d) of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallene,s and Pt/C calculated from Tafel plots by extrapolation method in 1.0 M KOH electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $21.6 \pm 0.6 \Omega$ (1 M PBS), and $5.5 \pm 0.4 \Omega$ (1 M KOH).



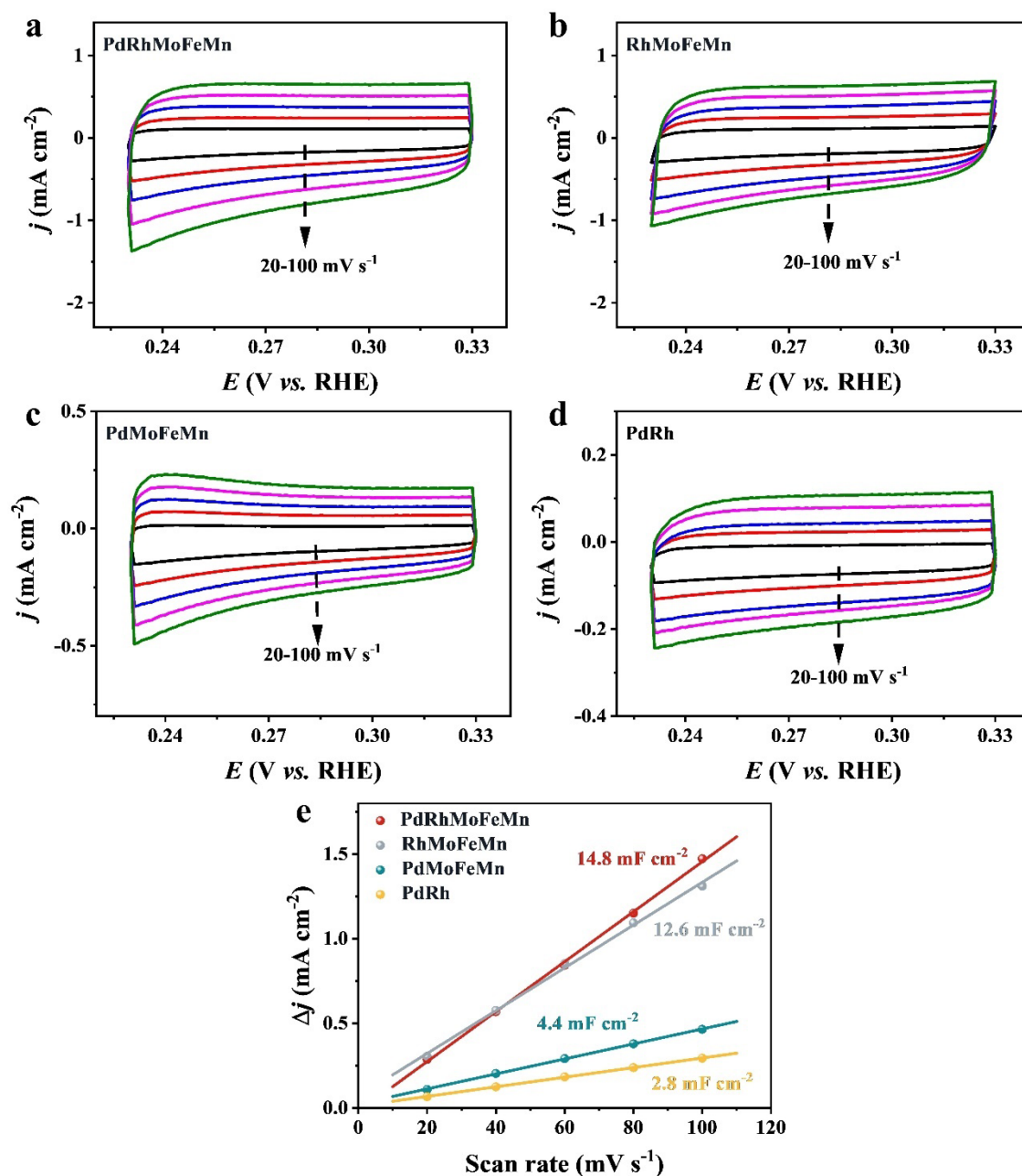
Supplementary Fig. 26 The stability tests of different catalysts in 1.0 M PBS electrolyte.

Polarization curves of (a) RhMoFeMn HEMs, (b) RhMoFeMn metallenes, (c) PdMoFeMn metallenes, (d) PdRh metallenes and (e) Pt/C with iR-compensation before and after 10000 CV cycles in 1.0 M PBS electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 6.96 ± 0.03 (1 M PBS), electrolyte resistance: $21.6 \pm 0.6 \Omega$ (1 M PBS).

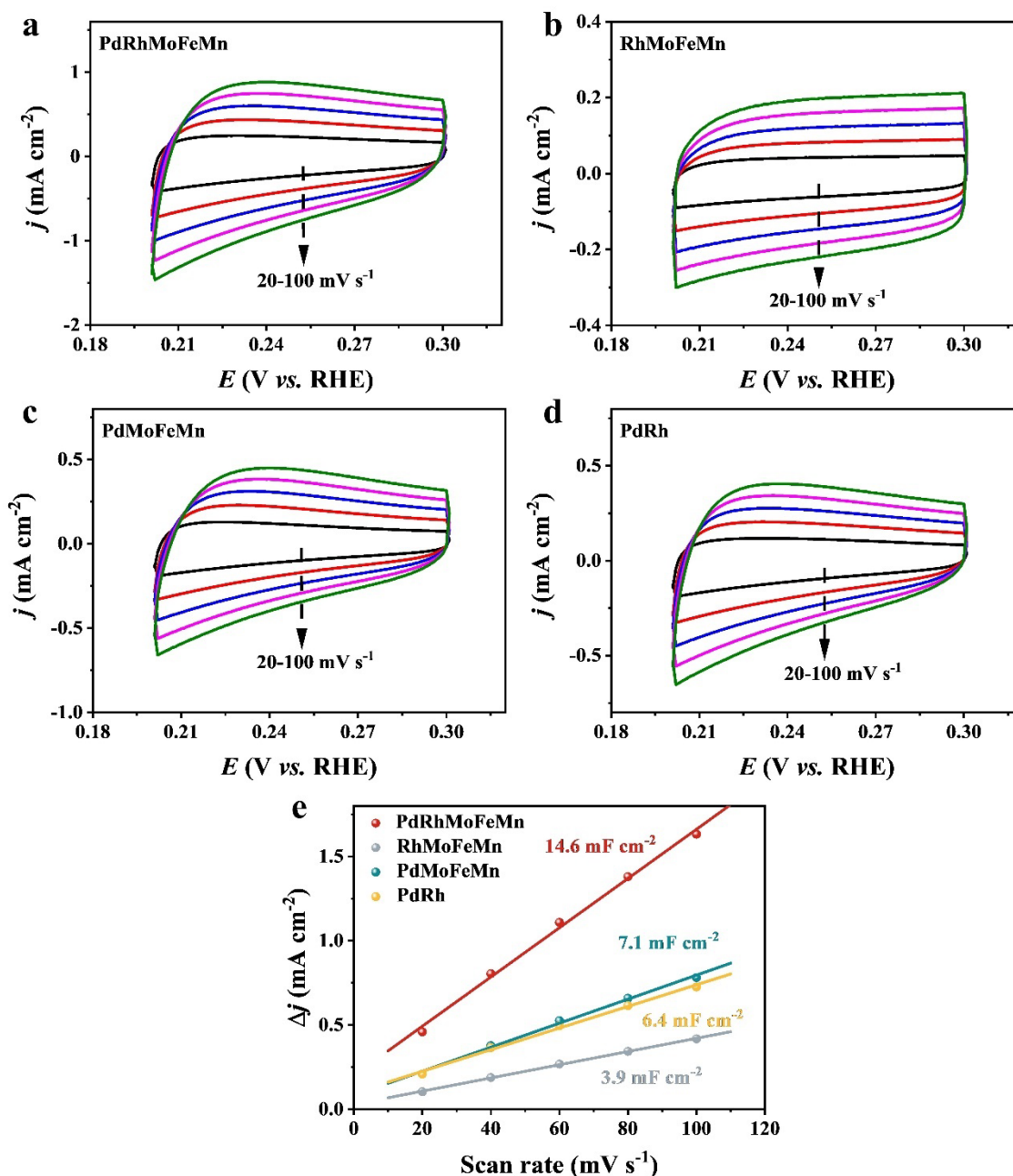


Supplementary Fig. 27 The stability tests of different catalysts in 1.0 M KOH electrolyte.

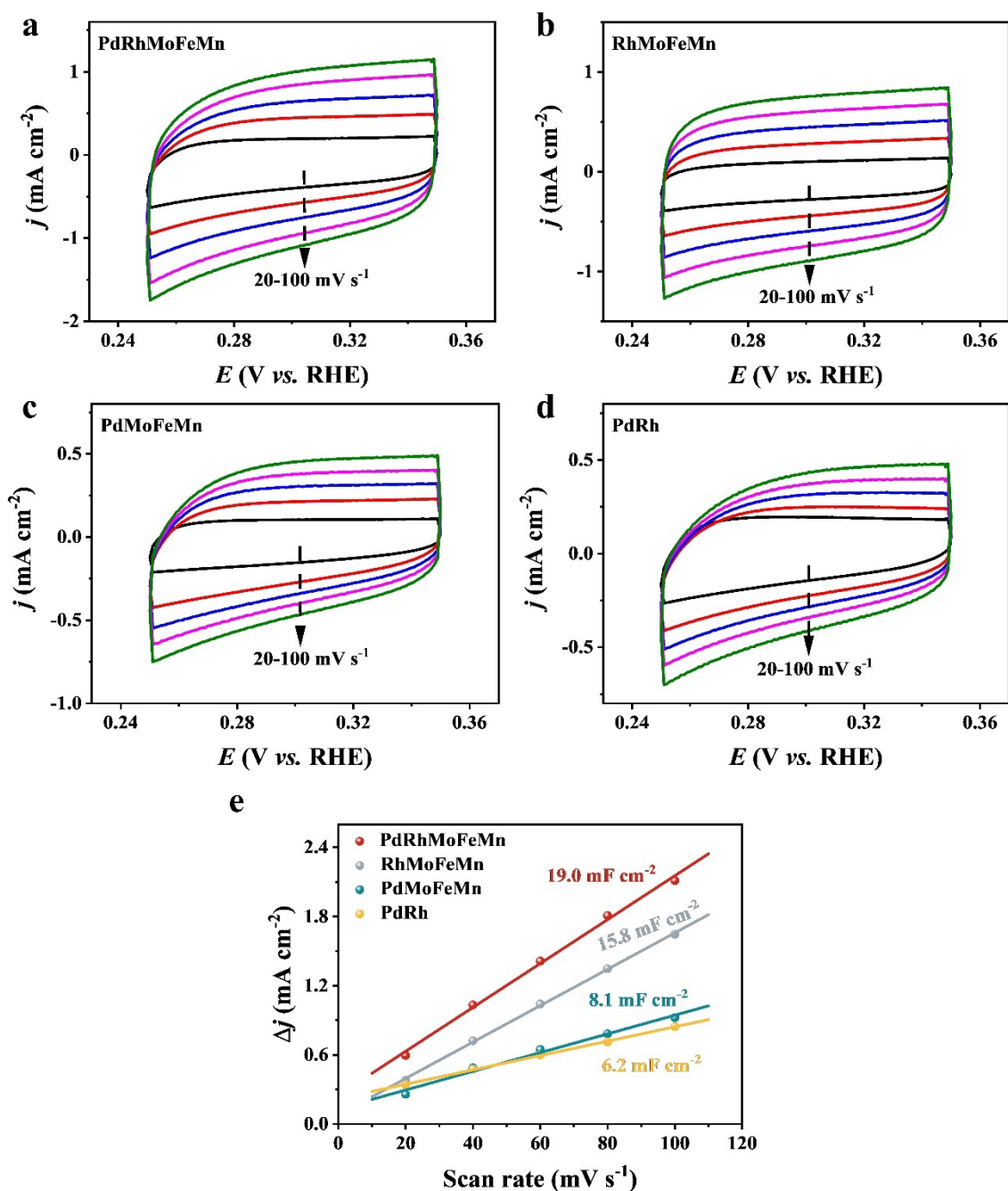
The polarization curves of (a) PdRhMoFeMn HEMs, (b) RhMoFeMn metallenes, (c) PdMoFeMn metallenes, (d) PdRh metallenes and (e) Pt/C with iR-compensation before and after 10000 CV cycles in 1.0 M KOH electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $5.5 \pm 0.4 \Omega$ (1 M KOH).



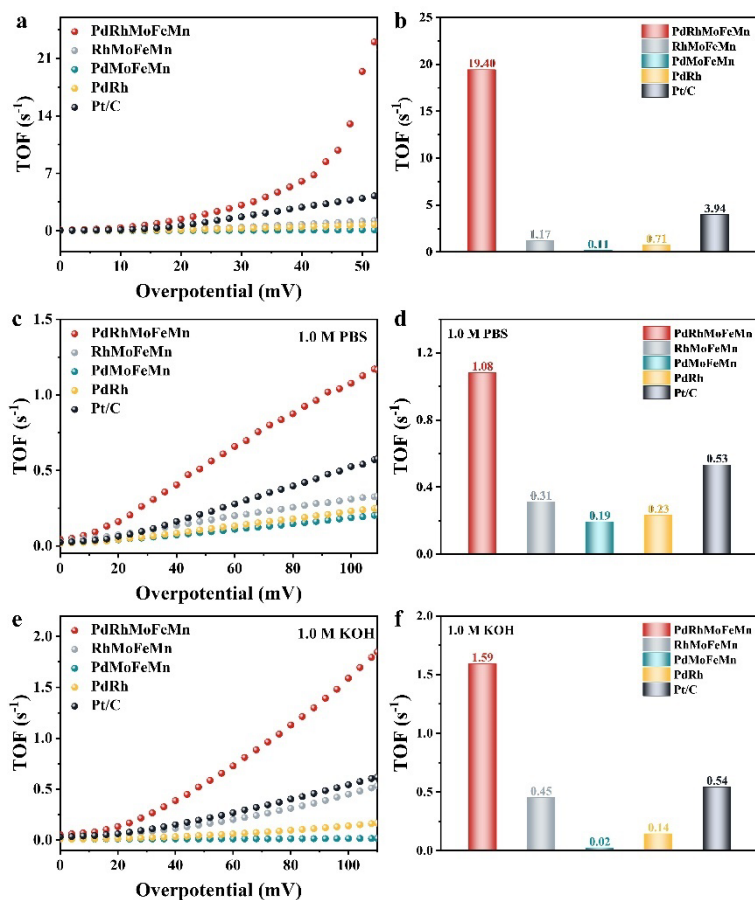
Supplementary Fig. 28 CV plots and C_{dl} in 0.5 M H_2SO_4 electrolyte. CV plots of (a) PdRhMoFeMn HEMs, (b) RhMoFeMn metallenes, (c) PdMoFeMn metallenes, and (d) PdRh metallenes at varying scan rates from 20 to 100 mV s⁻¹ in 0.5 M H_2SO_4 electrolyte. (e) C_{dl} of these nanocatalysts in 0.5 M H_2SO_4 electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05 , electrolyte resistance: $6.4 \pm 0.3 \Omega$.



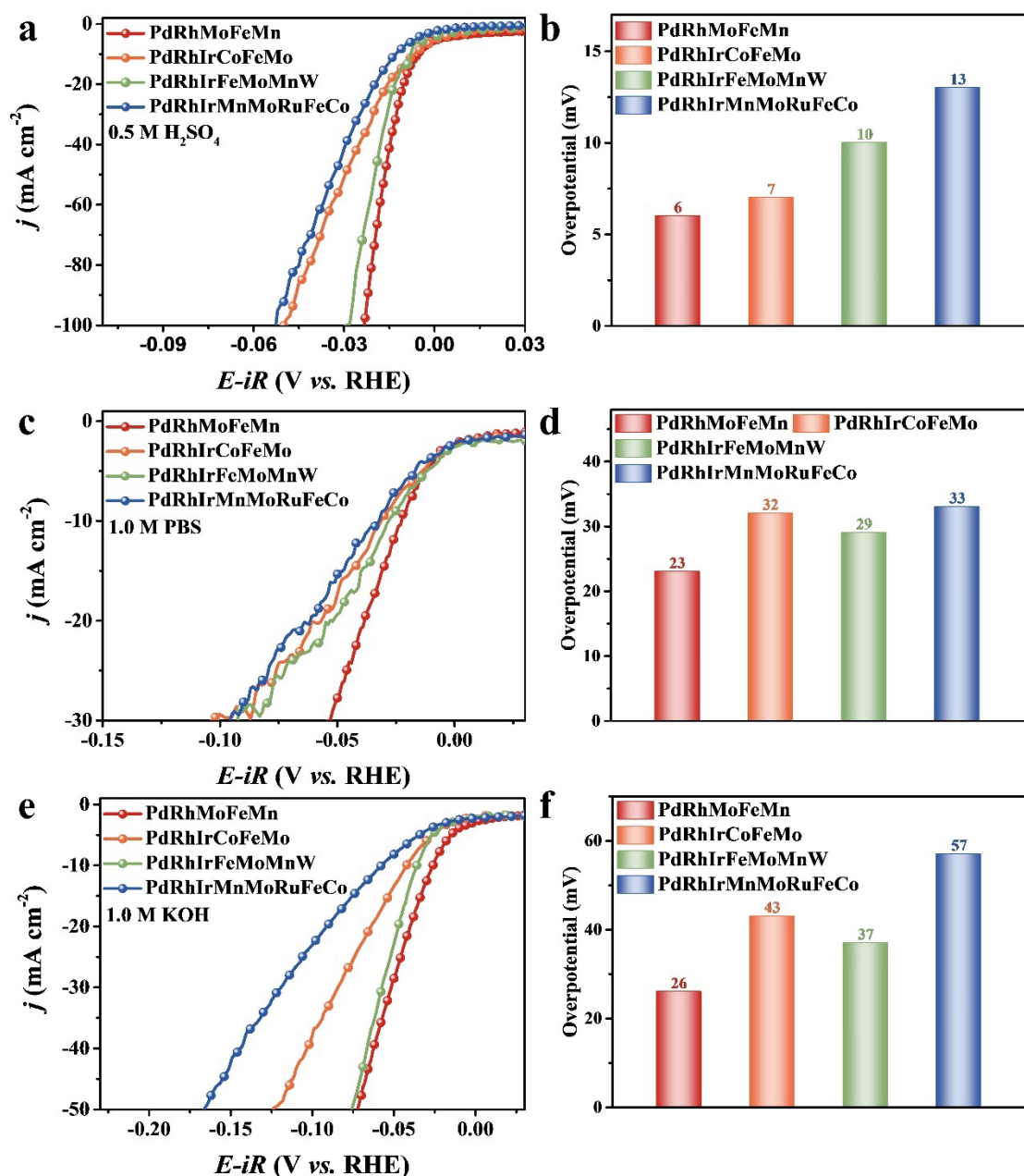
Supplementary Fig. 29 CV plots and C_{dl} in 1.0 M PBS electrolyte. CV plots of (a) PdRhMoFeMn HEMs, (b) RhMoFeMn metallenes, (c) PdMoFeMn metallenes, and (d) PdRh metallenes at varying scan rates from 20 to 100 mV s⁻¹ in 1.0 M PBS electrolyte. (e) C_{dl} of these nanocatalysts in 1.0 M PBS electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 6.96 ± 0.03 (1 M PBS), electrolyte resistance: 21.6 ± 0.6 Ω (1 M PBS).



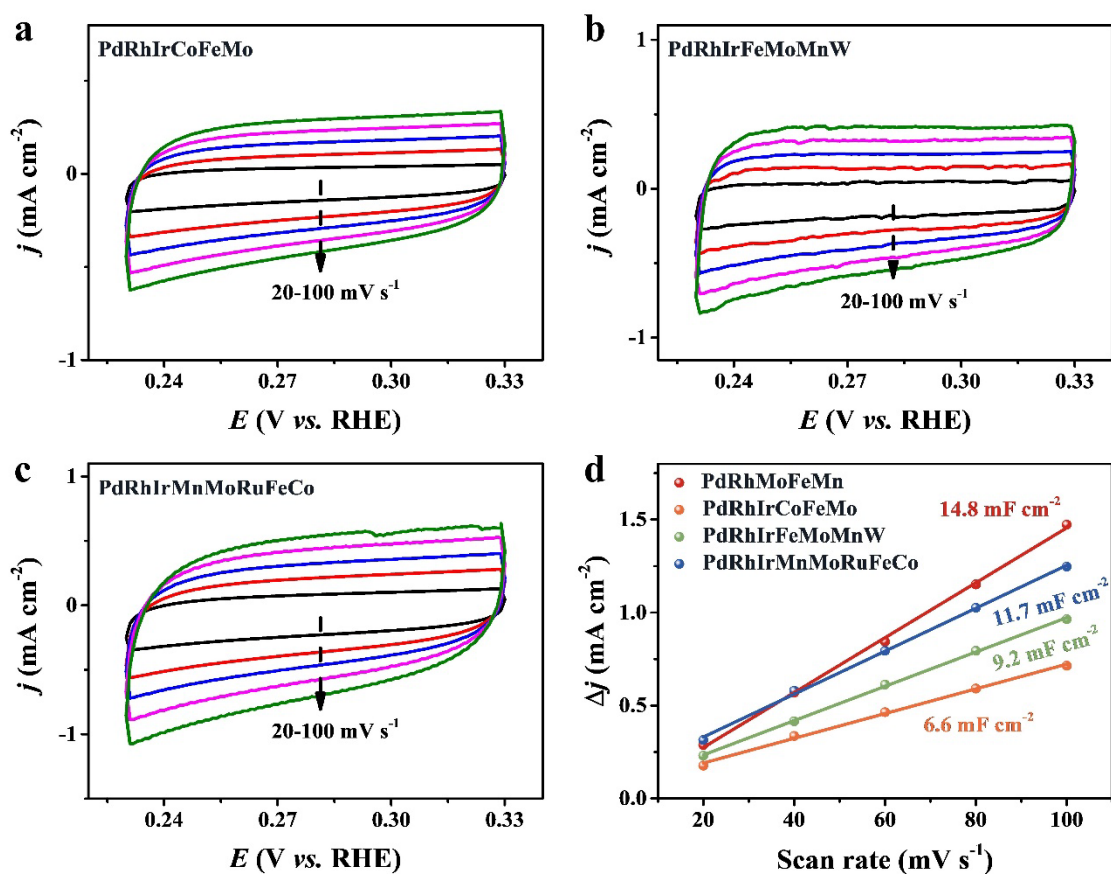
Supplementary Fig. 30 CV plots and C_{dl} in 1.0 M KOH electrolyte. CV plots of (a) PdRhMoFeMn HEMs, (b) RhMoFeMn metallenes, (c) PdMoFeMn metallenes, and (d) PdRh metallenes at varying scan rates from 20 to 100 mV s^{-1} in 1.0 M KOH electrolyte. (e) C_{dl} of these nanocatalysts in 1.0 M KOH electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 13.81 ± 0.14 (1 M KOH), electrolyte resistance: $5.5 \pm 0.4 \Omega$ (1 M KOH).



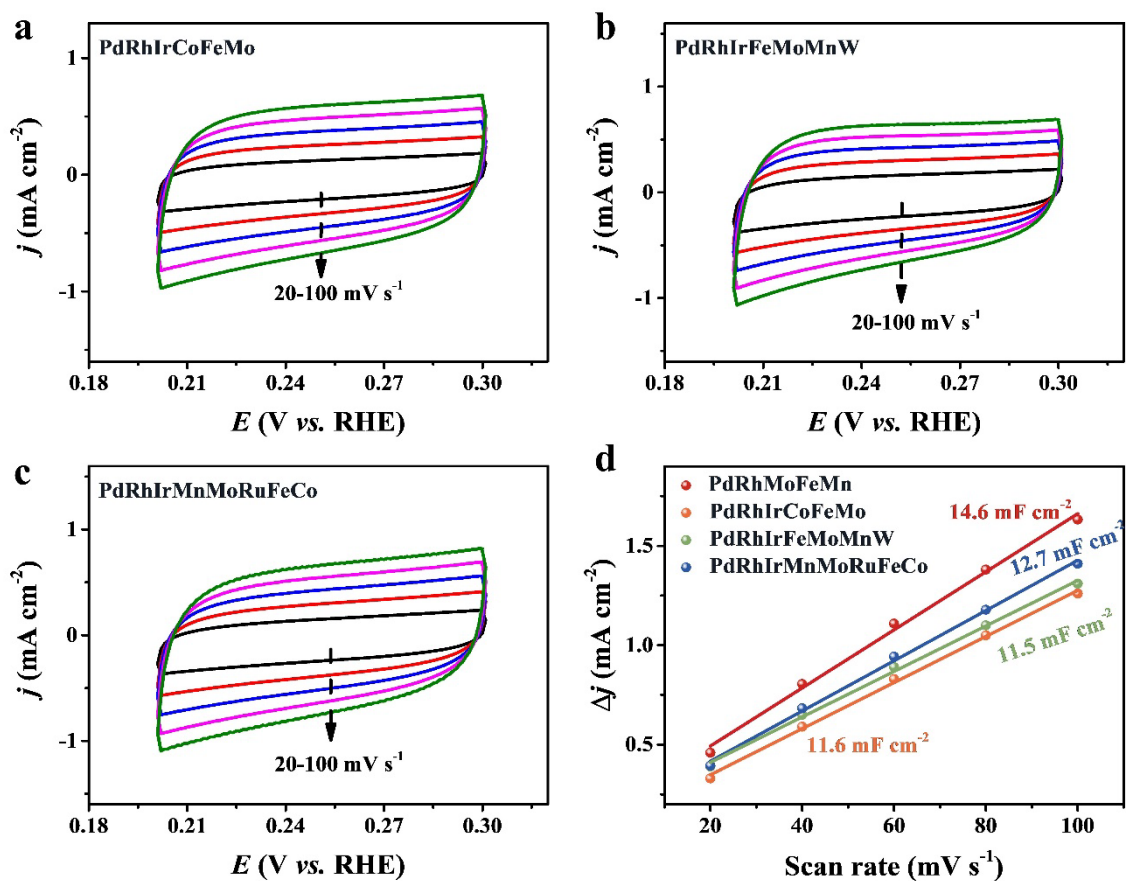
Supplementary Fig. 31 The calculations of TOFs for different catalysts in different electrolytes. The comparison of TOFs at different overpotentials (a) and the corresponding histogram (b) for the TOFs at the overpotential of 50 mV of PdRhMoFeMn HEMs, RhMoFeMn metallenes, PdMoFeMn metallenes, PdRh metallenes, and Pt/C in a 0.5 M H₂SO₄ electrolytes. The comparison of TOFs at different overpotentials (c) and the corresponding histogram (d) for the TOFs at the overpotential of 100 mV of different catalysts in 1.0 M PBS electrolytes. The comparison of TOFs at different overpotentials (e) and the corresponding histogram (f) for the TOFs at the overpotential of 100 mV of different catalysts in 1.0 M KOH electrolytes. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², noble metal loading: 0.028 mg cm⁻² (PdRhMoFeMn HEMs), 0.027 mg cm⁻² (RhMoFeMn metallenes), 0.039 mg cm⁻² (RhMoFeMn metallenes), and 0.057 mg cm⁻² (PdRh metallenes and Pt/C), electrolyte pH: 0.37 ± 0.05 (0.5 M H₂SO₄), 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: 6.4 ± 0.3 Ω (0.5 M H₂SO₄), 21.6 ± 0.6 Ω (1 M PBS), and 5.5 ± 0.4 Ω (1 M KOH).



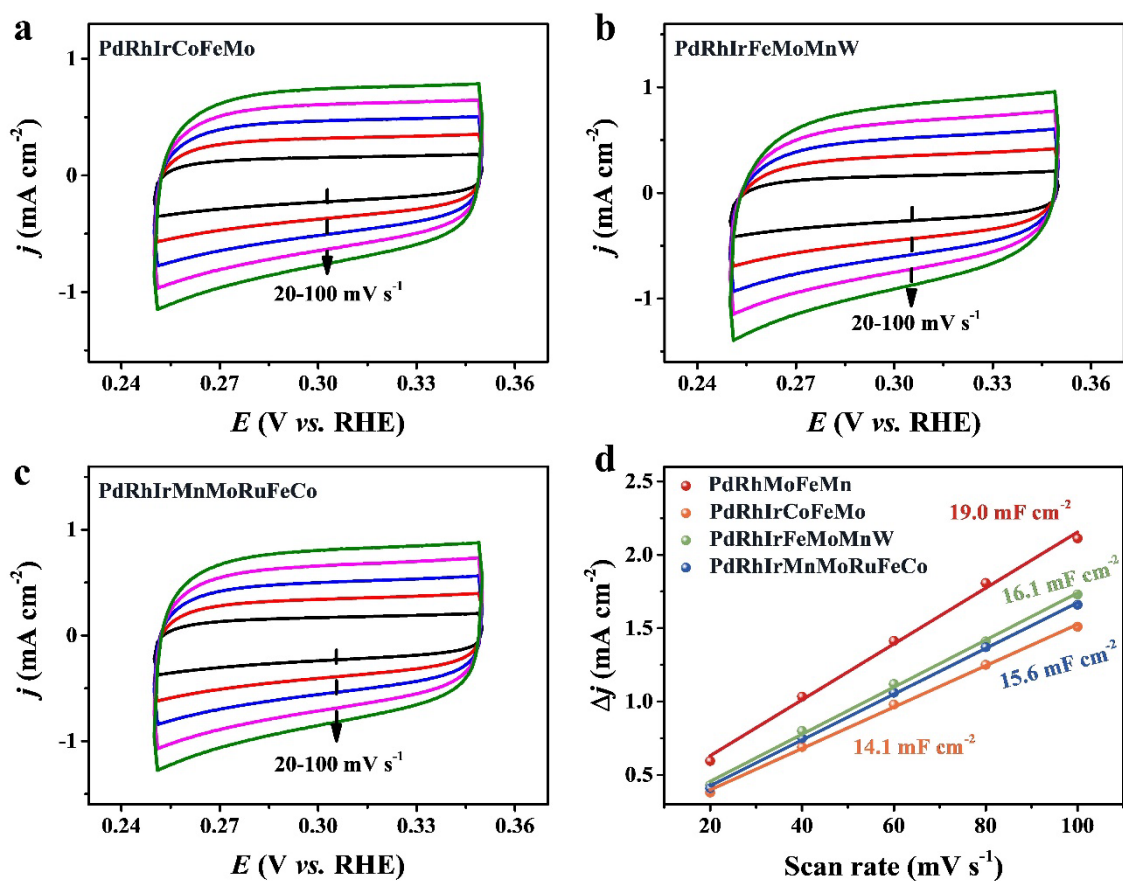
Supplementary Fig. 32 Electrocatalytic HER performance evaluation of quinary PdRhMoFeMn, senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. (a) Polarization curves with iR-compensation and (b) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 0.5 M H₂SO₄. (c) Polarization curves and (d) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M PBS. (e) Polarization curves and (f) corresponding overpotentials at 10 mA cm⁻² of HEMs with different composition in 1.0 M KOH. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05 (0.5 M H₂SO₄), 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: 6.4 ± 0.3 Ω (0.5 M H₂SO₄), 21.6 ± 0.6 Ω (1 M PBS), and 5.5 ± 0.4 Ω (1 M KOH).



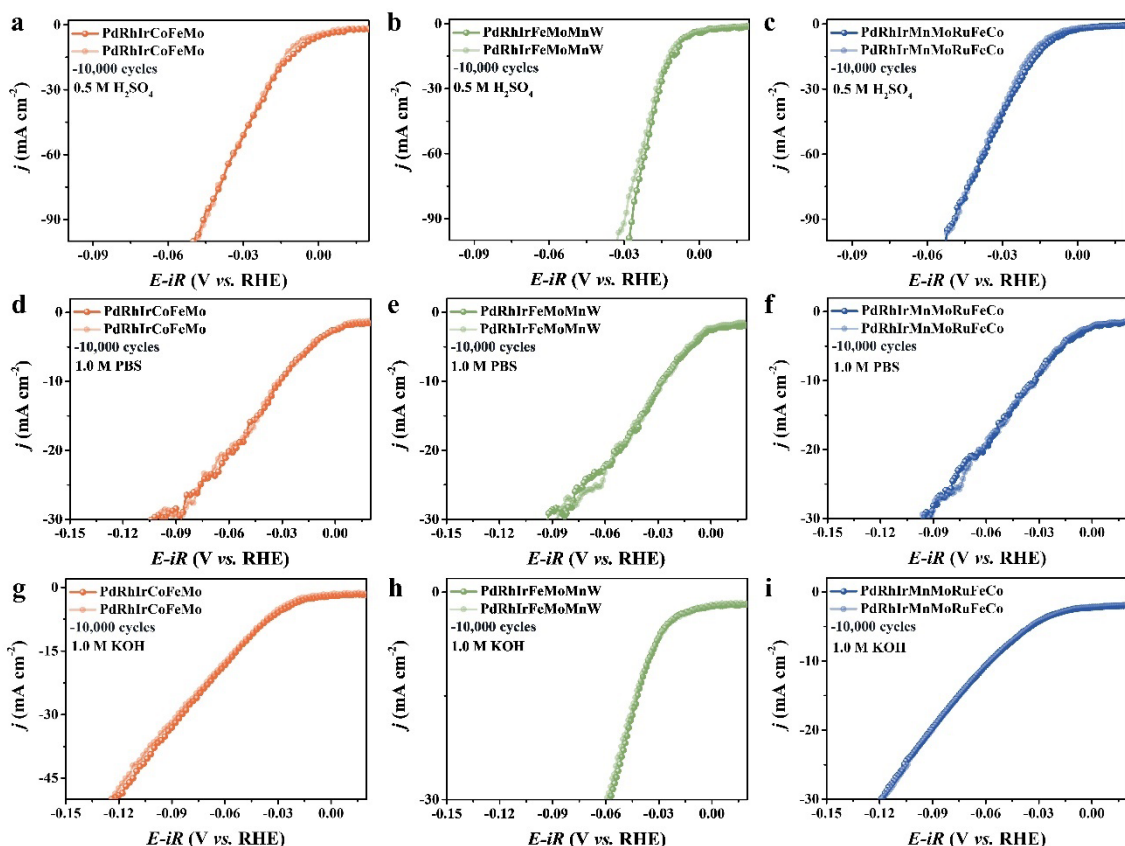
Supplementary Fig. 33 CV plots and C_{dl} in 0.5 M H_2SO_4 electrolyte. CV plots of (a) senary PdRhIrCoFeMo, (b) septenary PdRhIrFeMoMnW, and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s⁻¹ in 0.5 M H_2SO_4 electrolyte. (d) C_{dl} of these nanocatalysts in 0.5 M H_2SO_4 electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05 , electrolyte resistance: $6.4 \pm 0.3 \Omega$.



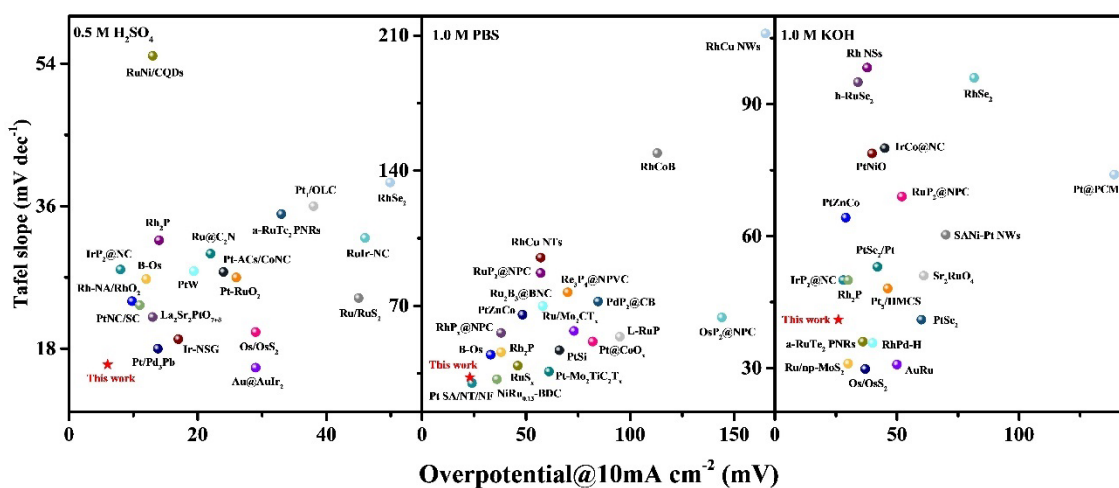
Supplementary Fig. 34 CV plots and C_{dl} in 1.0 M PBS electrolyte. CV plots of (a) senary PdRhIrCoFeMo , (b) septenary PdRhIrFeMoMnW , and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s^{-1} in 1.0 M PBS electrolyte. (d) C_{dl} of these nanocatalysts in 1.0 M PBS electrolyte. The testing conditions include GCE surface area: 0.07 cm^2 , catalyst loading: 0.286 mg cm^{-2} , electrolyte pH: 6.96 ± 0.03 (1 M PBS), electrolyte resistance: $21.6 \pm 0.6 \Omega$ (1 M PBS).



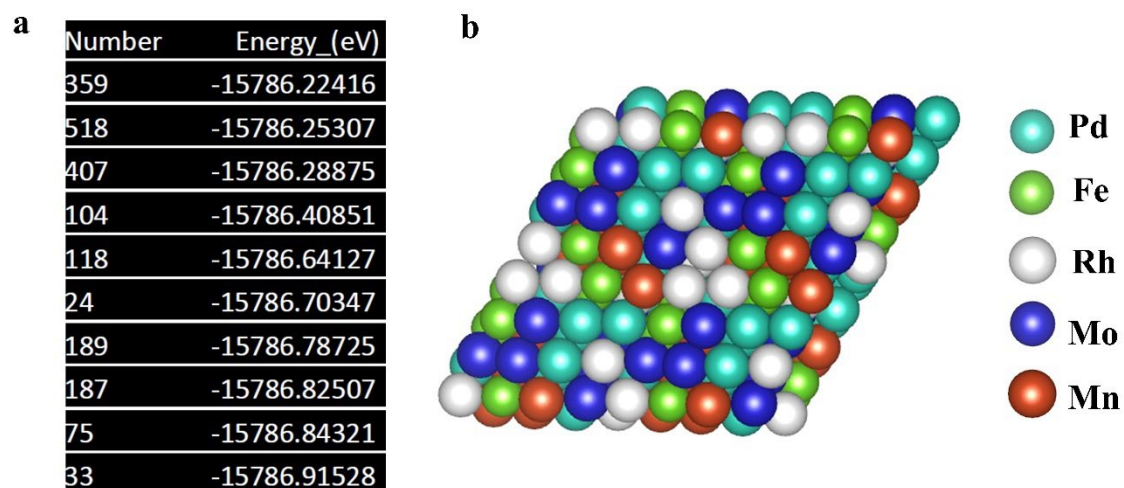
Supplementary Fig. 35 CV plots and C_{dl} in 1.0 M KOH electrolyte. CV plots of (a) senary PdRhIrCoFeMo, (b) septenary PdRhIrFeMoMnW, and (c) octonary PdRhIrMnMoRuFeCo HEMs at varying scan rates from 20 to 100 mV s⁻¹ in 1.0 M KOH electrolyte. (d) C_{dl} of these nanocatalysts in 1.0 M KOH electrolyte. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 13.81 $\pm$ 0.14 (1 M KOH), electrolyte resistance: 5.5 $\pm$ 0.4 Ω (1 M KOH).



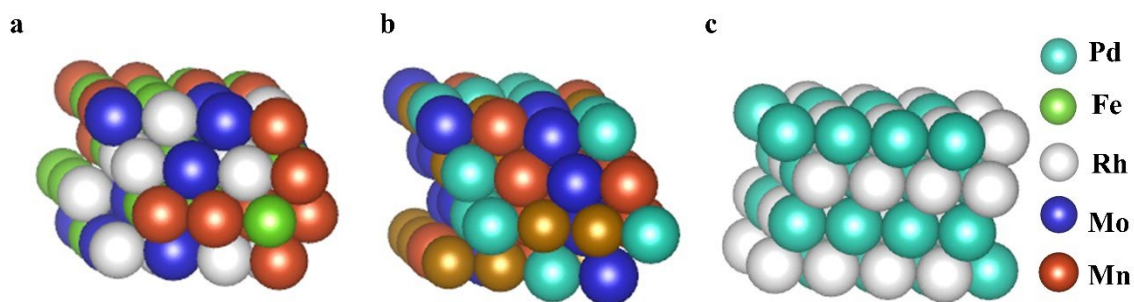
Supplementary Fig. 36 Electrocatalytic HER stability tests of senary PdRhIrCoFeMo, septenary PdRhIrFeMoMnW, and octonary PdRhIrMnMoRuFeCo HEMs. Polarization curves of (a) senary HEMs, (b) septenary HEMs, and (c) octonary HEMs with iR-compensation before and after 10,000 CV cycles in 0.5 M H₂SO₄. Polarization curves of (d) senary HEMs, (e) septenary HEMs, and (f) octonary HEMs with iR-compensation before and after 10,000 CV cycles in 1.0 M PBS. Polarization curves of (g) senary HEMs, (h) septenary HEMs, and (i) octonary HEMs with iR-compensation before and after 10,000 CV cycles in 1.0 M KOH. The testing conditions include GCE surface area: 0.07 cm², catalyst loading: 0.286 mg cm⁻², electrolyte pH: 0.37 ± 0.05 (0.5 M H₂SO₄), 6.96 ± 0.03 (1 M PBS), and 13.81 ± 0.14 (1 M KOH), electrolyte resistance: 6.4 ± 0.3 Ω (0.5 M H₂SO₄), 21.6 ± 0.6 Ω (1 M PBS), and 5.5 ± 0.4 Ω (1 M KOH).



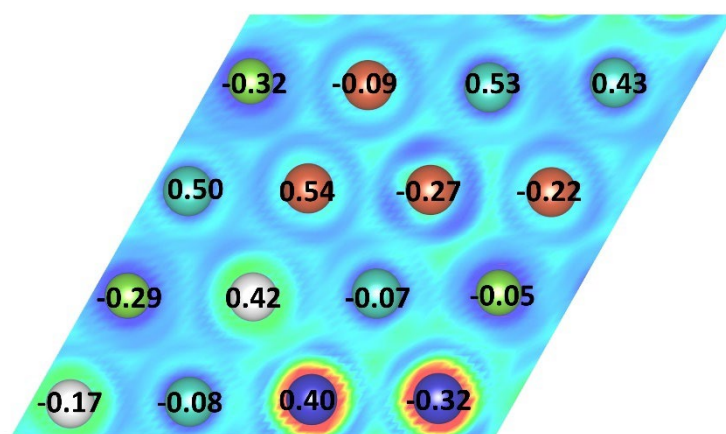
Supplementary Fig. 37 Performance comparison of PdRhMoFeMn HEMs with other reported noble metal based HER catalysts with high activity in 0.5 M H_2SO_4 , 1.0 M PBS, and 1.0 M KOH electrolytes, respectively.



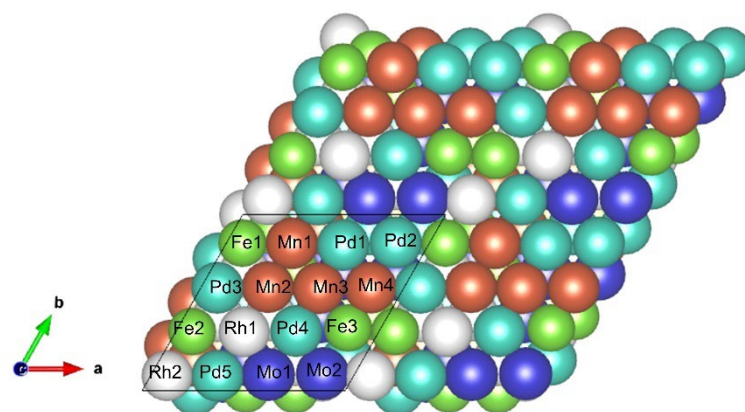
Supplementary Fig. 38 Computational modeling of PdRhMoFeMn HEMs. (a) Top 10 energy rankings of PdRhMoFeMn HEMs. **(b)** The top view of the lowest energy of PdRhMoFeMn HEMs.



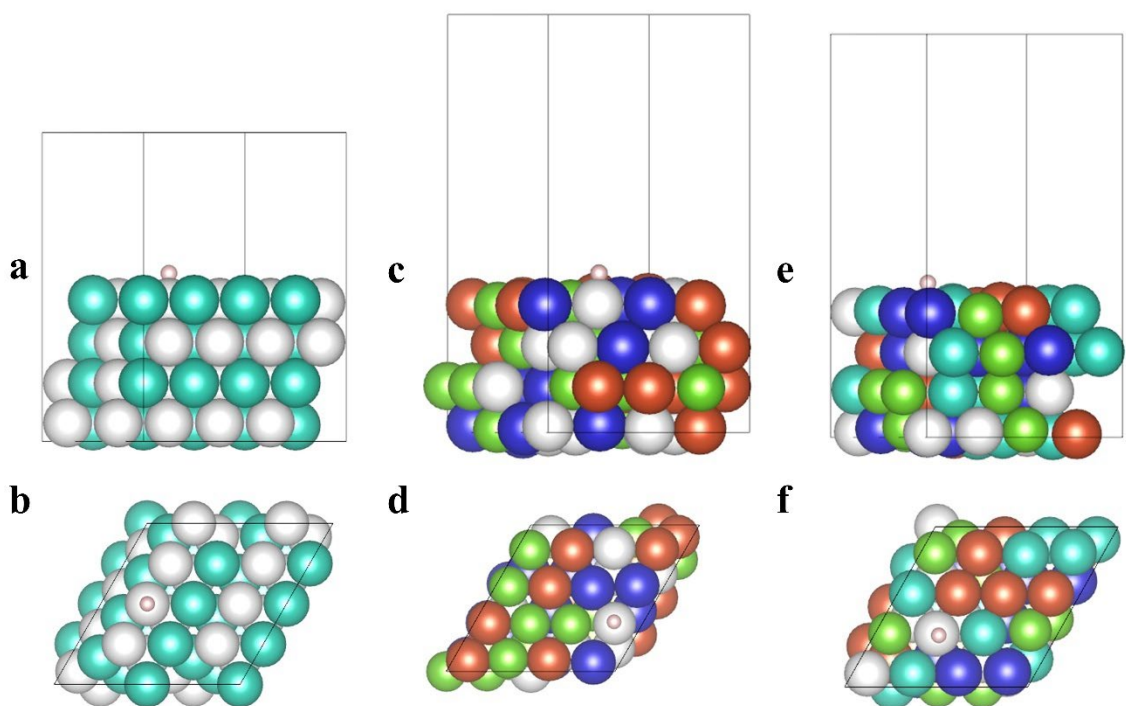
Supplementary Fig. 39 The DFT calculated structural models of reference samples. Computational modeling of **(a)** RhMoFeMn metallenes, **(b)** PdMoFeMn metallenes, **(c)** PdRh metallenes.



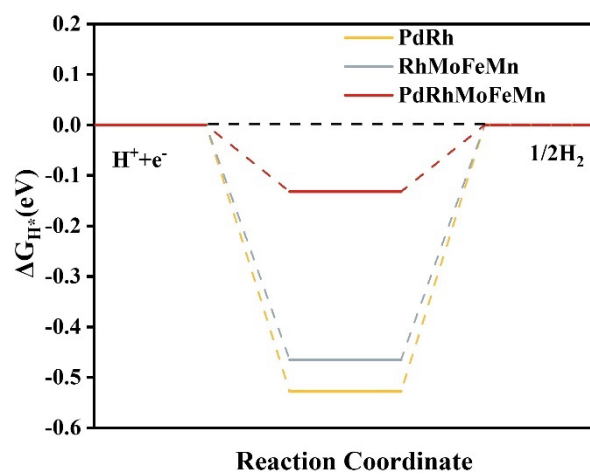
Supplementary Fig. 40 The Bader charge analysis of PdRhMoFeMn HEMs.



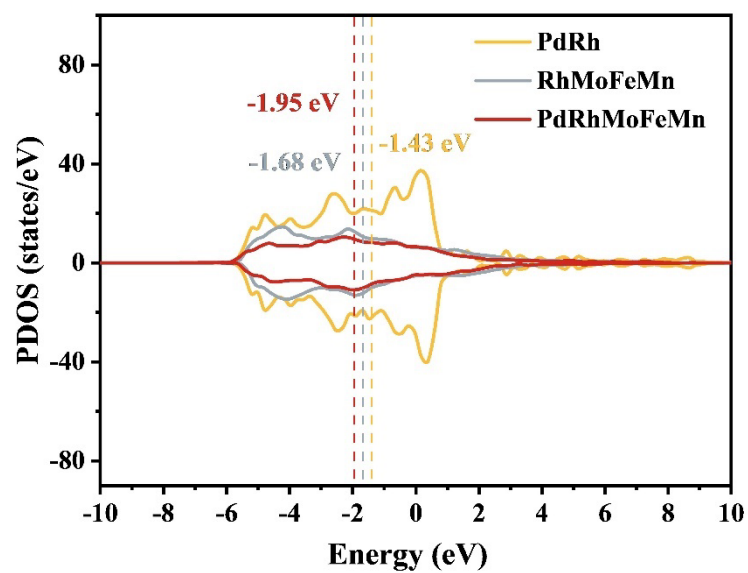
Supplementary Fig. 41 The atomic configurations of various H* adsorption sites in PdRhMoFeMn HEMs.



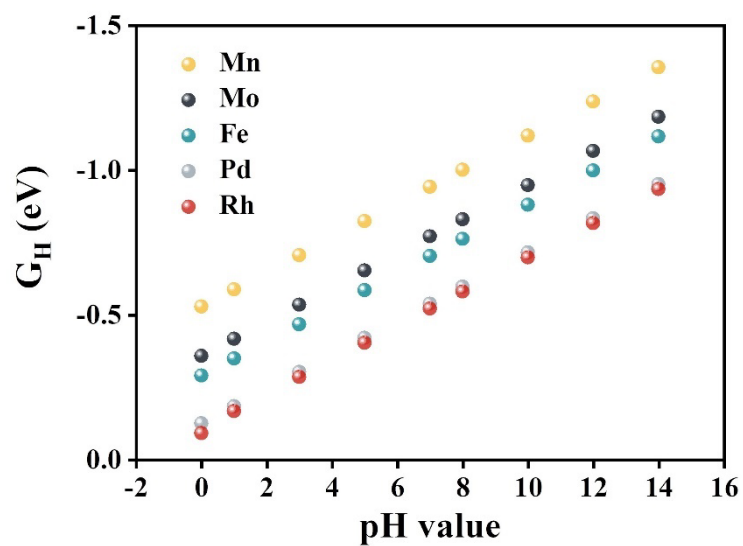
Supplementary Fig. 42 The DFT calculated structural models of H* adsorption on different catalysts. The optimized structure models of (a,b) PdRh, (c,d) RhMoFeMn, and (e,f) PdRhMoFeMn, showing both the side view and top view of each structure.



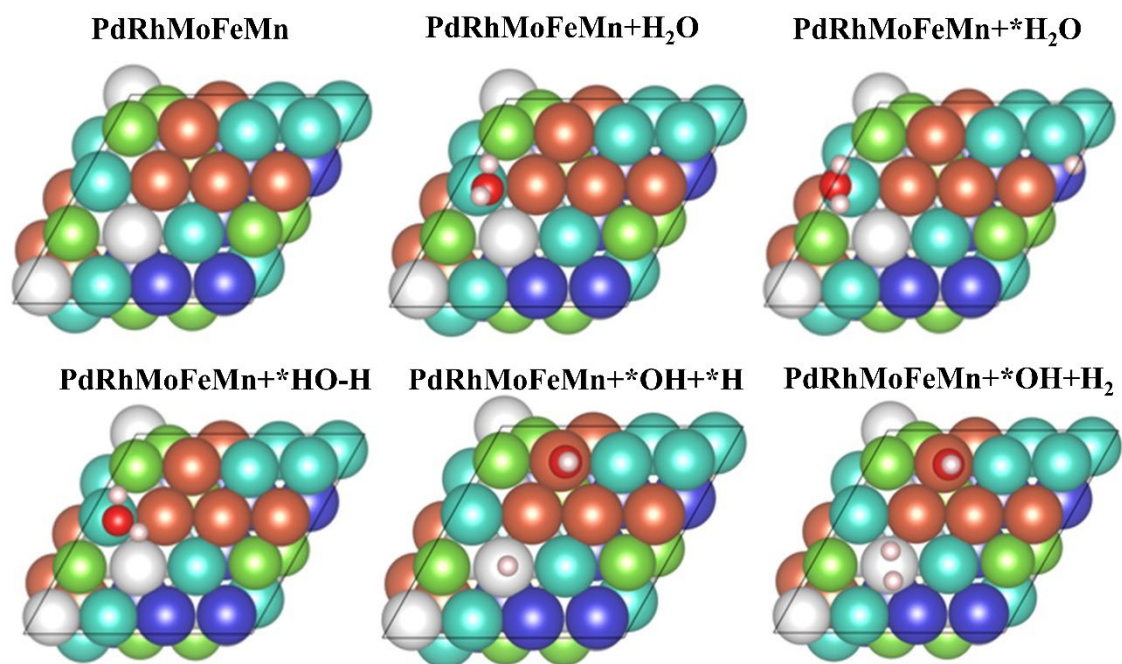
Supplementary Fig. 43 The adsorption energies of H_{ads} on PdRh, PdMoFeMn, RhMoFeMn, and PdRhMoFeMn.



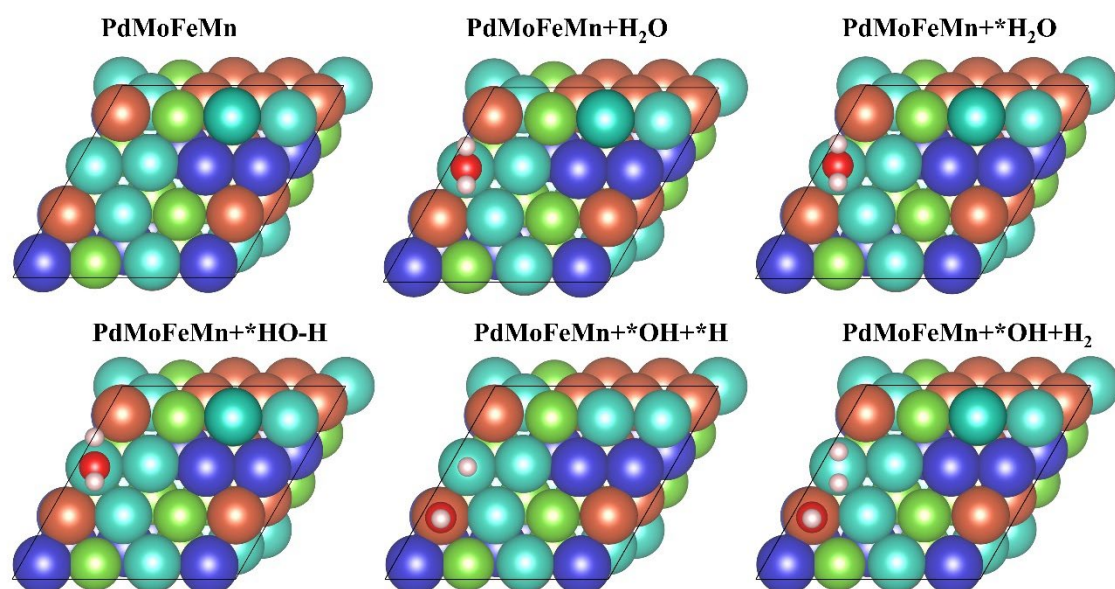
Supplementary Fig. 44 PDOS calculations for PdRh, RhMoFeMn, and PdRhMoFeMn.



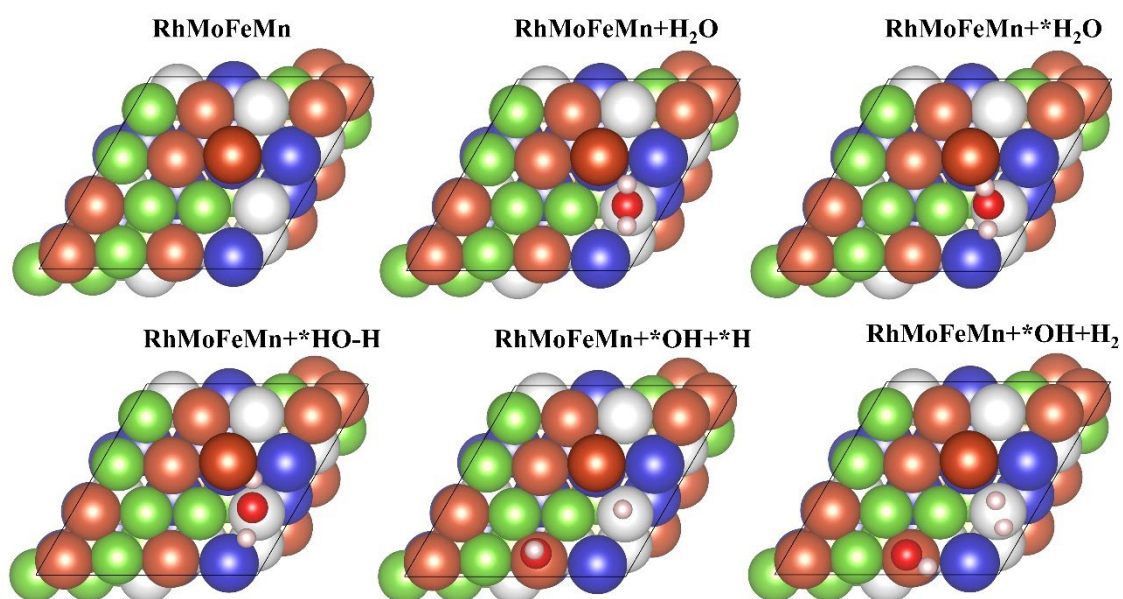
Supplementary Fig. 45 The ΔG_{H^*} diagrams on various catalytic sites of PdRhMoFeMn HEMs at different pH values.



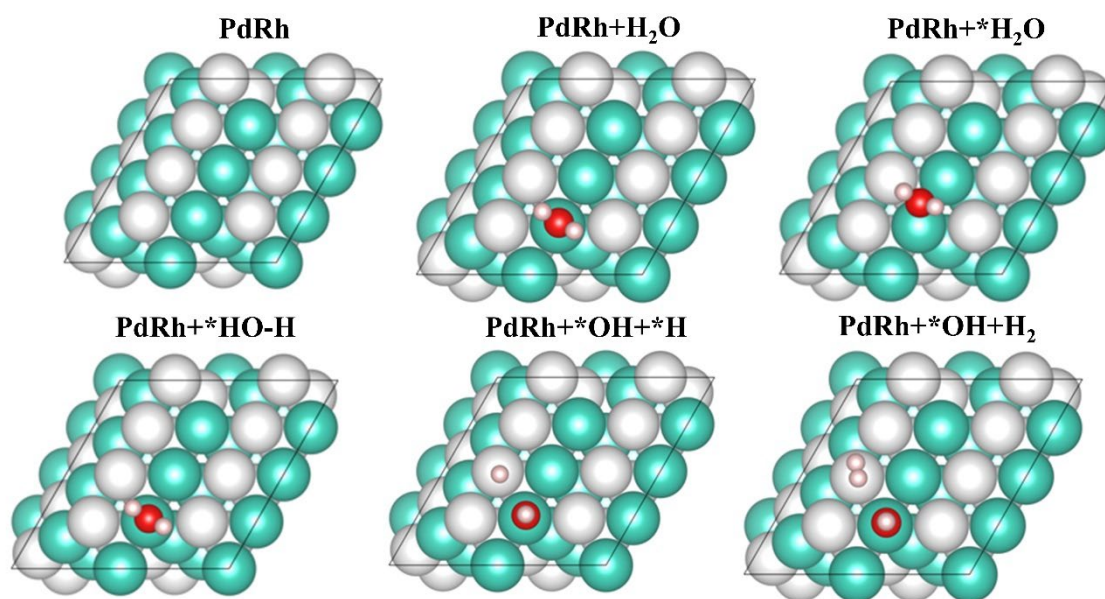
Supplementary Fig. 46 The DFT calculated structural models of water dissociation on PdRhMoFeMn HEMs.



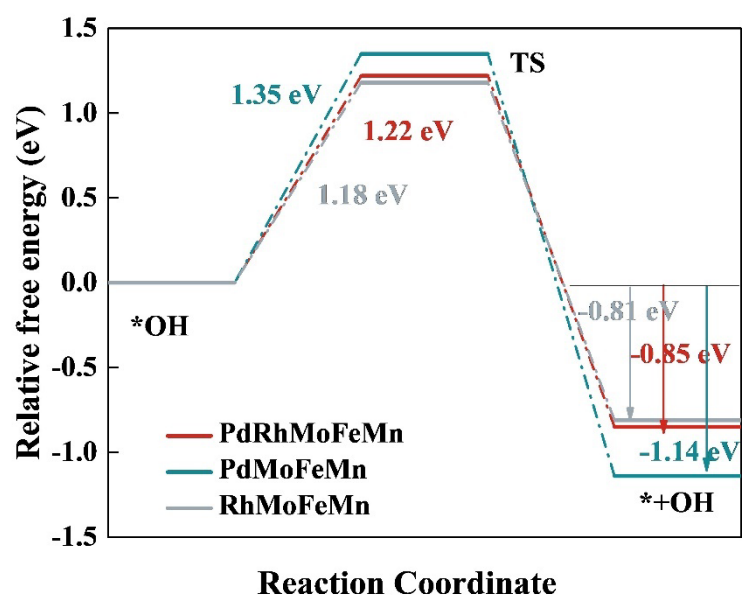
Supplementary Fig. 47 The DFT calculated structural models of water dissociation on PdMoFeMn metallenes.



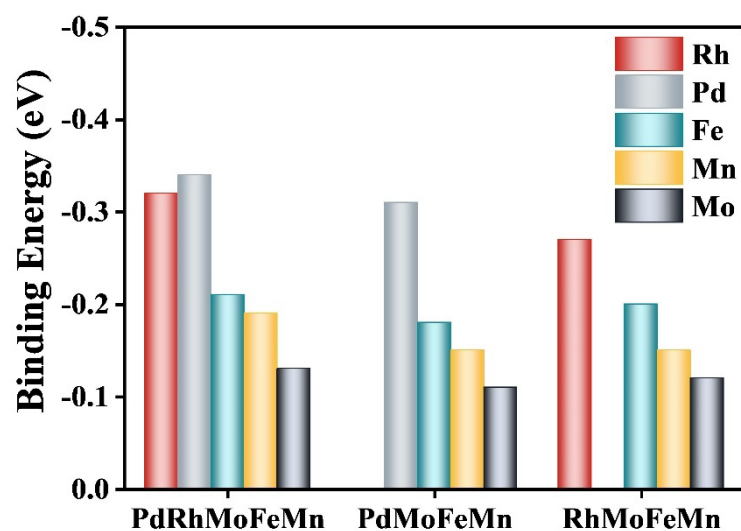
Supplementary Fig. 48 The DFT calculated structural models of water dissociation on RhMoFeMn metallenes.



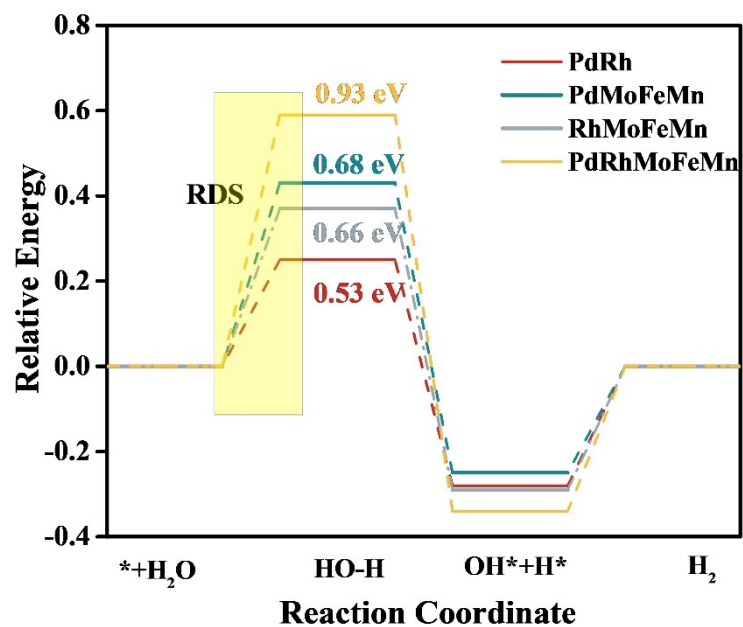
Supplementary Fig. 49 The DFT calculated structural models of water dissociation on PdRh metallenes.



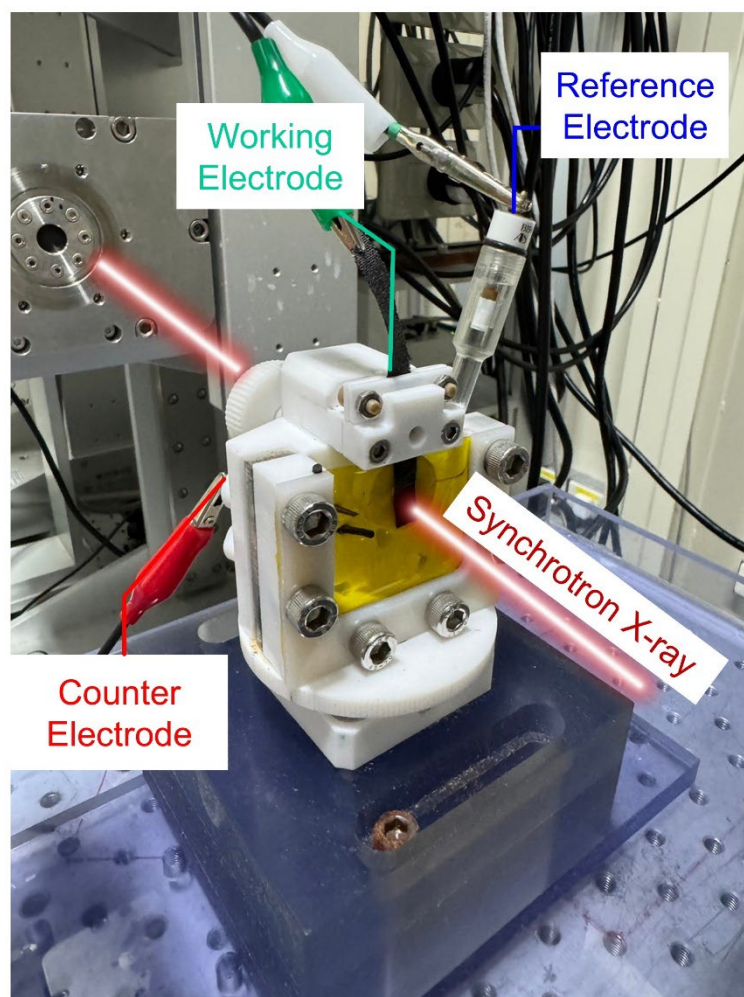
Supplementary Fig. 50 The calculated transition state of OH desorption kinetics at the Mn sites of PdRhMoFeMn, PdMoFeMn and RhMoFeMn.



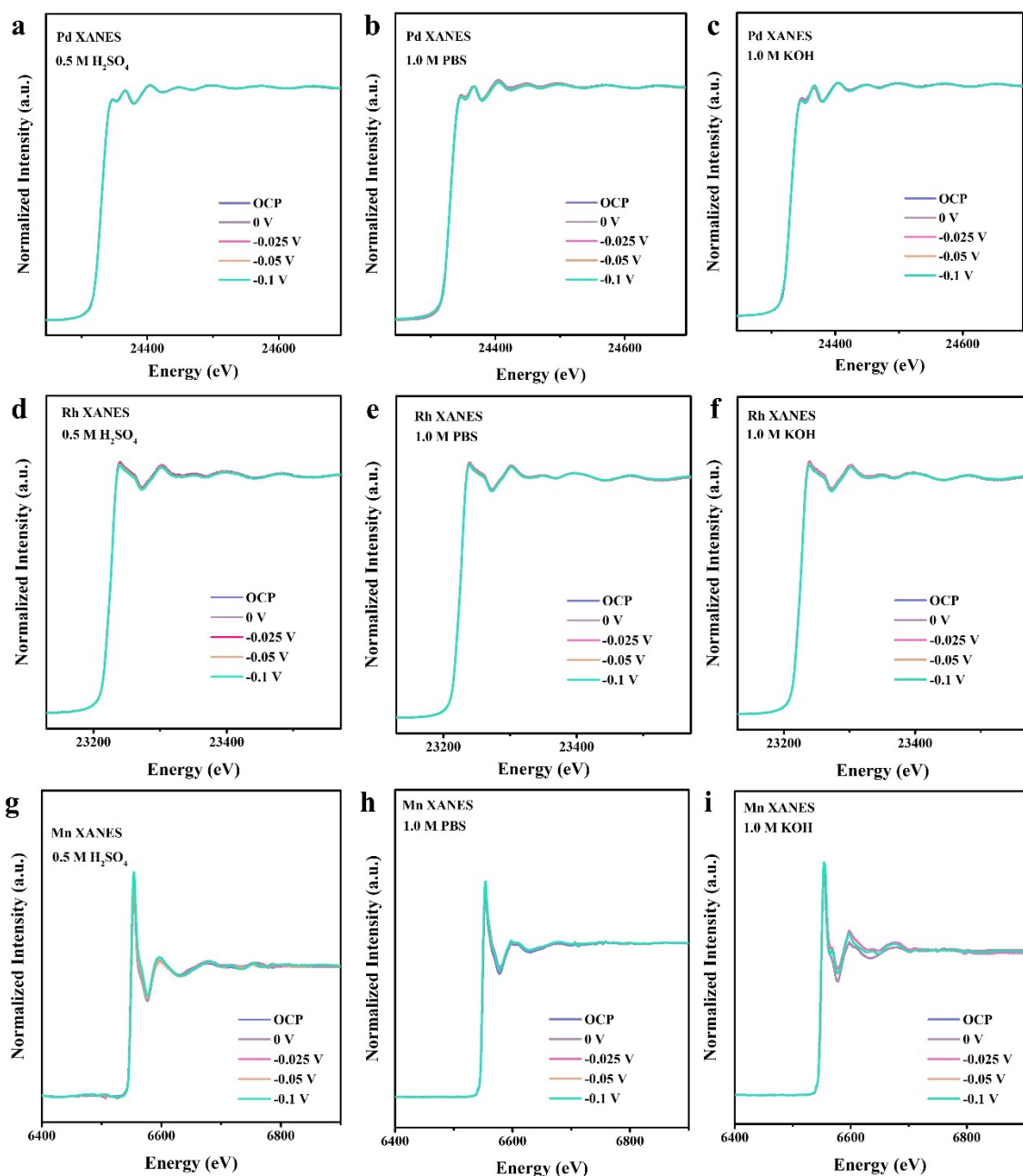
Supplementary Fig. 51 The binding energy profile for water adsorption on PdMoFeMn, RhMoFeMn, and PdRhMoFeMn.



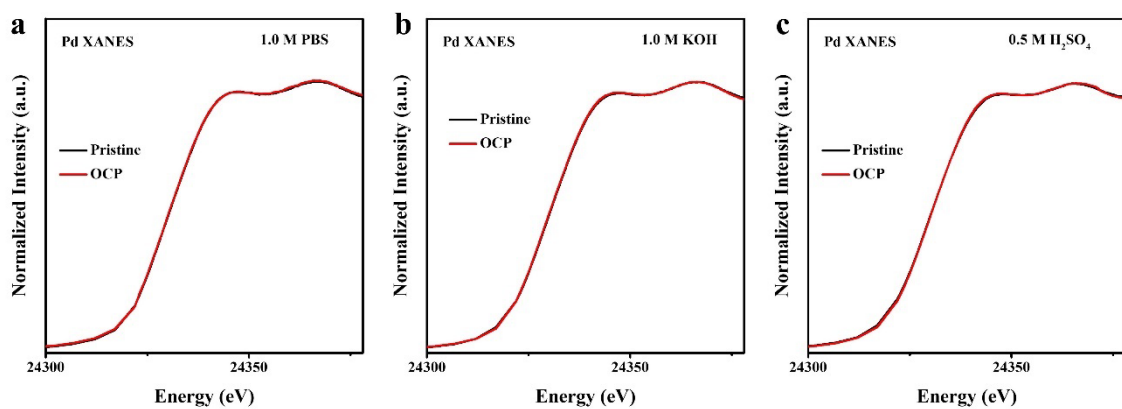
Supplementary Fig. 52 The NEB calculated the energy profile for water dissociation on PdRh, PdMoFeMn, RhMoFeMn, and PdRhMoFeMn.



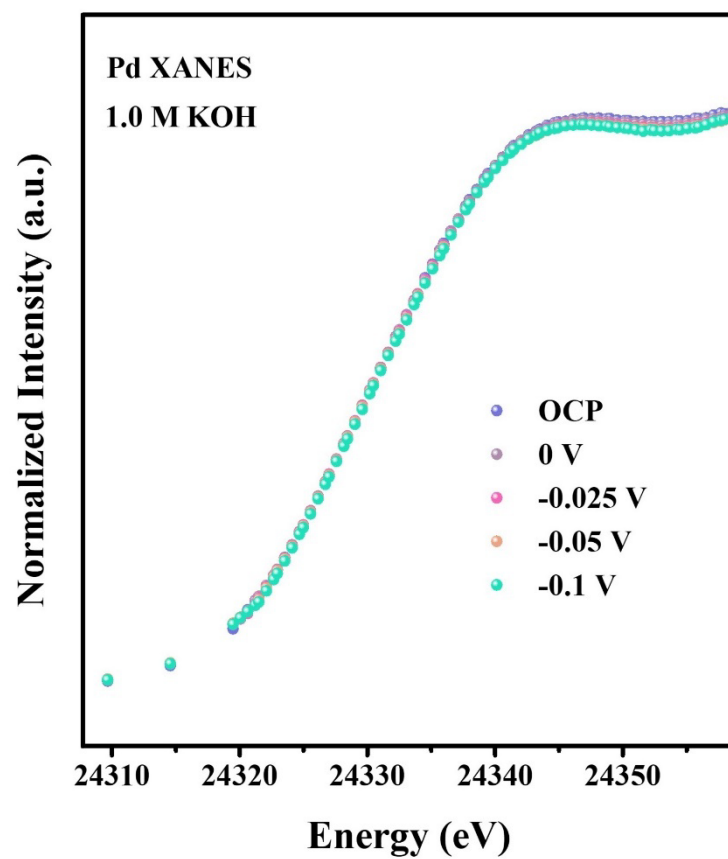
Supplementary Fig. 53 Photograph of operando quick-XAS. The counter electrode is platinum, reference electrode is an Ag/AgCl electrode, and a work electrode is carbon cloth with loaded catalysts.



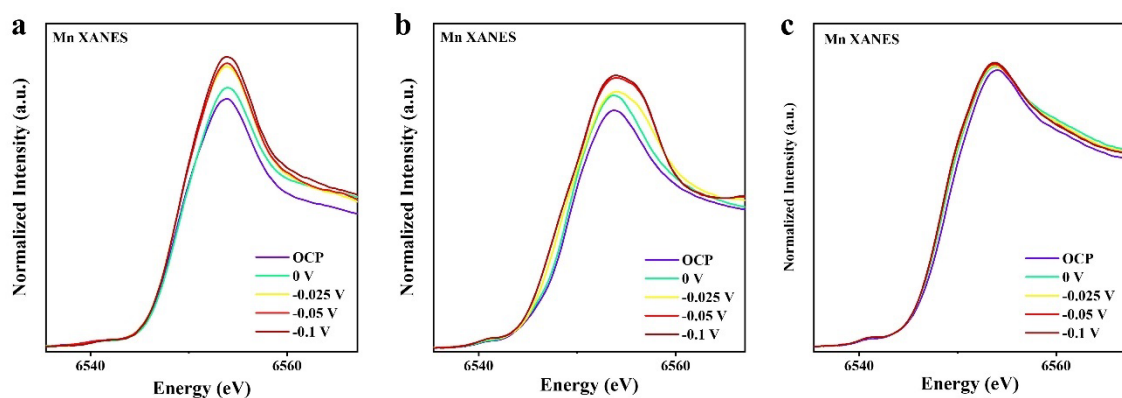
Supplementary Fig. 54 The broad range XANES spectra in different electrolytes. The broad range XANES spectra of (a-c) Pd, (d-f) Rh, and (g-i) Mn in 0.5 M H₂SO₄, 1.0 M PBS, and 1.0 M KOH electrolyte, respectively.



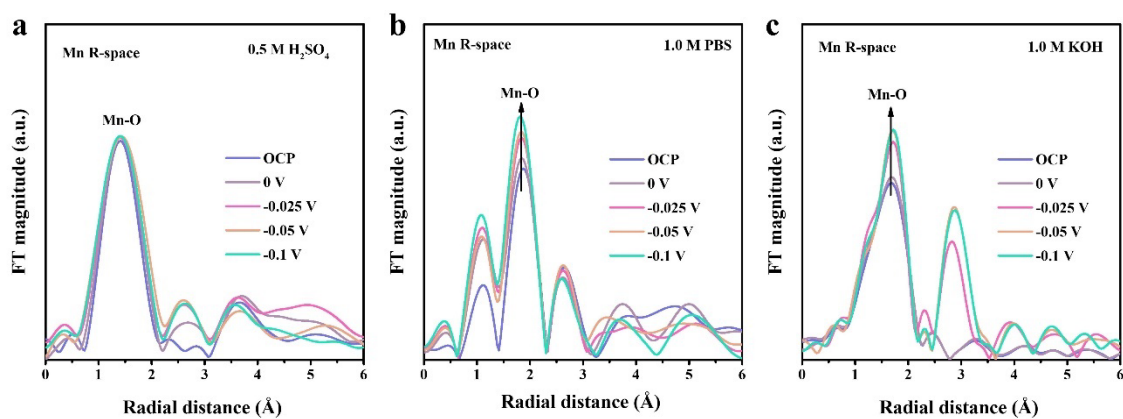
Supplementary Fig. 55 The Pd XANES spectra of pristine sample compared to OCP state in different electrolytes. The Pd XANES spectra of pristine sample compared to OCP state in (a) 1.0 M PBS, (b) 1.0 M KOH, and (c) 0.5 M H₂SO₄ electrolyte, respectively.



Supplementary Fig. 56 Pd scattered XANES spectra under 1.0 M KOH.



Supplementary Fig. 57 Operando XANES spectra of Mn at various potentials in different electrolytes. Operando XANES spectra of Mn at various potentials in **(a)** 0.5 M H₂SO₄, **(b)** 1.0 M KOH, and **(c)** 1.0 M PBS solution, respectively.

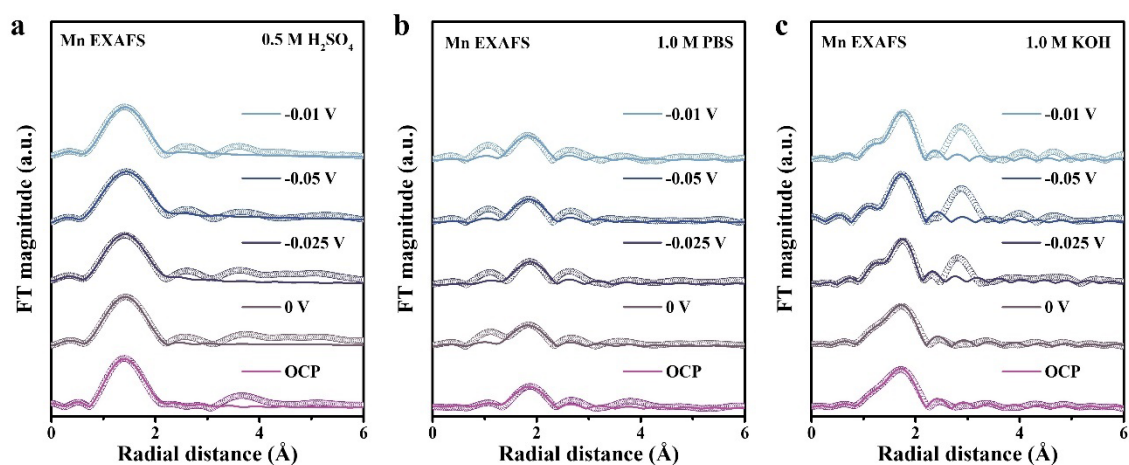


Supplementary Fig. 58 Operando XANES spectra of Mn at various potentials in different electrolytes. Operando XANES spectra of Mn at various potentials in (a) 0.5 M H₂SO₄, (b) 1.0 M PBS, and (c) 1.0 M KOH solution without phase correction, respectively.

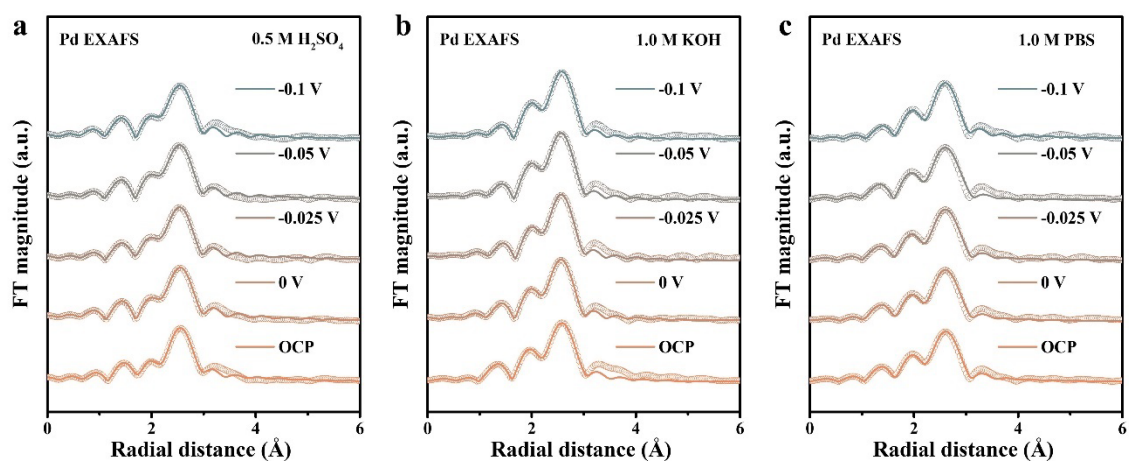
EXAFS measurements and analysis

EXAFS data were collected at the TPS BL44A beamline in NSRRC. The acquired data were processed using the ATHENA module implemented in the Demeter software packages [Ravel B., Newville M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 2005, 12 (4), 537-541]. Initially, the post-edge background was subtracted from the overall absorption, and then normalization was performed with respect to the edge jump step to obtain the k^3 -weighted EXAFS spectrum. Subsequently, the k^3 -weighted $\chi(k)$ data in the k-space (within the range of 3-11 Å⁻¹) were Fourier-transformed into R-space using a Hanning window ($dk=1$ Å⁻¹) to separate the contributions from different coordination shells.

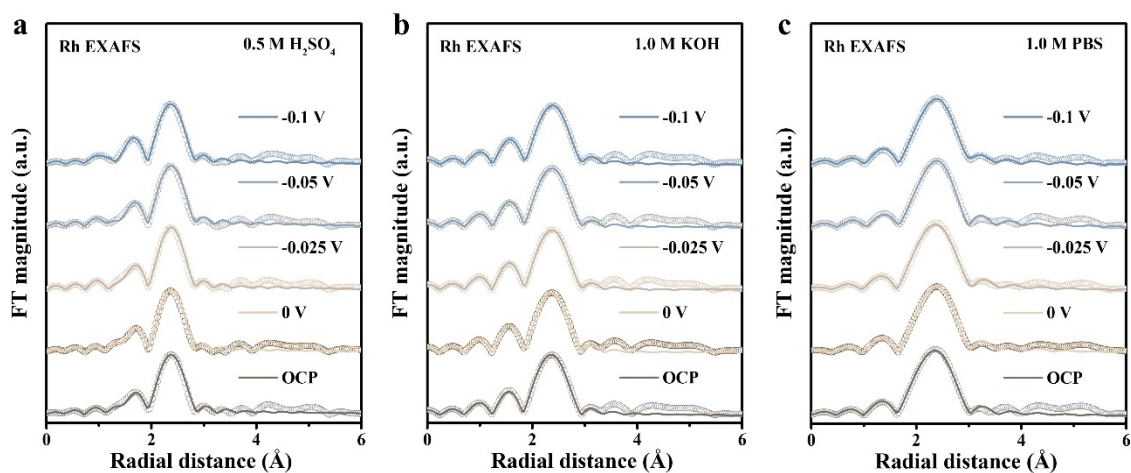
To obtain quantitative structural parameters for the high-entropy atoms, a least-squares curve fitting was performed using the ARTEMIS module of the Demeter software packages [Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12, 537-541 (2005)]. The fitting of the multi-path EXAFS data was conducted on the k^3 -weighted EXAFS function $\chi(k)$ data within the R-range of 1-3 Å. The amplitude reduction factor (S_0^2) was fixed at 1 for each group. Coordination numbers (CN), atomic distances (R), Debye-Waller factors (σ^2), and edge-energy shift (ΔE_0) were allowed to vary freely. In the first step, coordination numbers were added with absolute values to avoid intensity cancellation. In the second step, atoms with similar atomic numbers, such as Mo (42), Pd (44), and Rh (45), as well as Fe (26) and Mn (25), were considered as two groups for fitting the EXAFS data of Pd and Rh. Following this fitting strategy, satisfactory curve-fitting results were obtained, as shown in Supplementary Figs. 55-57, and the obtained parameters are listed in Supplementary Tables 7-15.



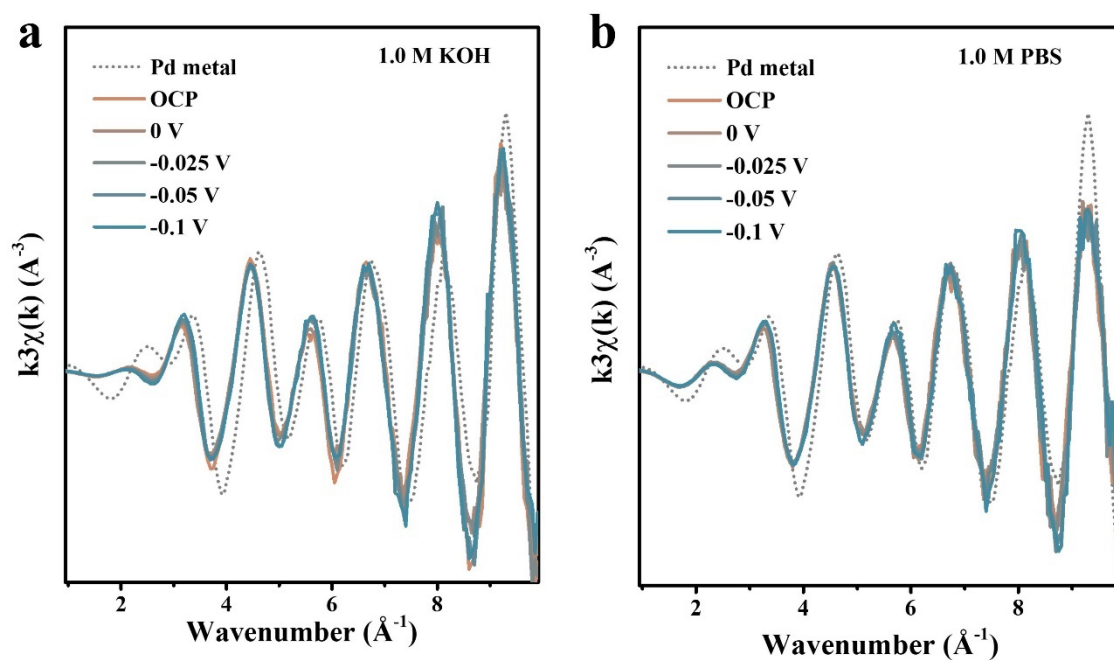
Supplementary Fig. 59 Operando Mn EXAFS spectra at various potentials in different electrolytes. Operando Mn EXAFS spectra at various potentials in (a) 0.5 M H₂SO₄, (b) 1.0 M PBS and (c) 1.0 M KOH solution without phase correction, respectively. The detailed fitting results are listed in Supplementary Tables 7-9.



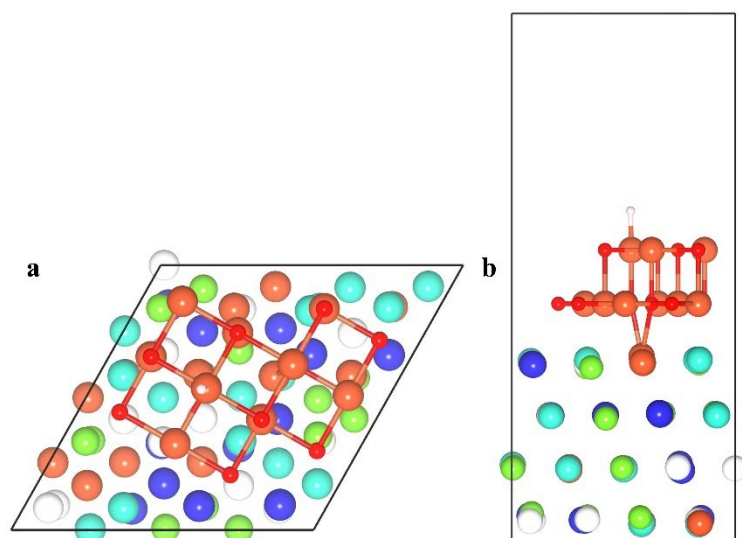
Supplementary Fig. 60 Operando Pd EXAFS spectra at various potentials in different electrolytes. Operando Pd EXAFS spectra at various potentials in (a) 0.5 M H_2SO_4 , (b) 1.0 M KOH and (c) 1.0 M PBS solution without phase correction, respectively. The detailed fitting results are listed in Supplementary Tables 10, 12, and 14.



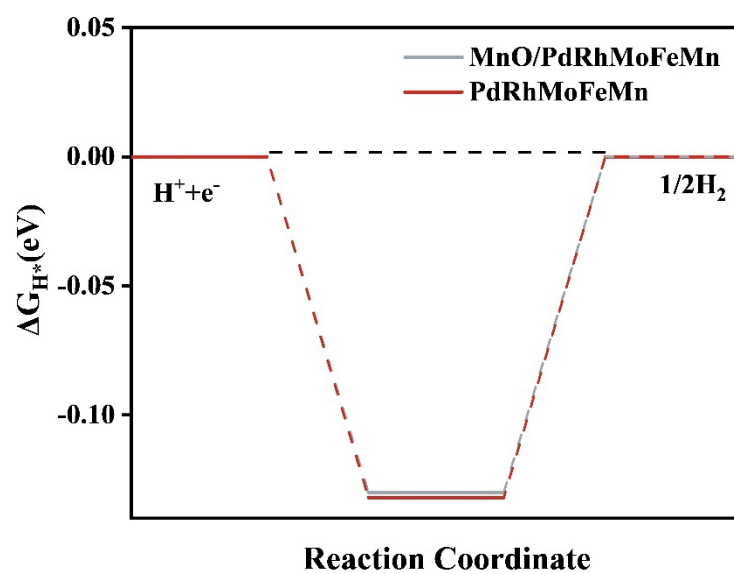
Supplementary Fig. 61 Operando Rh EXAFS spectra at various potentials in different electrolytes. Operando Rh EXAFS spectra at various potentials in (a) 0.5 M H₂SO₄, (b) 1.0 M KOH, and (c) 1.0 M PBS solution without phase correction, respectively. The detailed fitting results are listed in Supplementary Tables 11, 13, and 15.



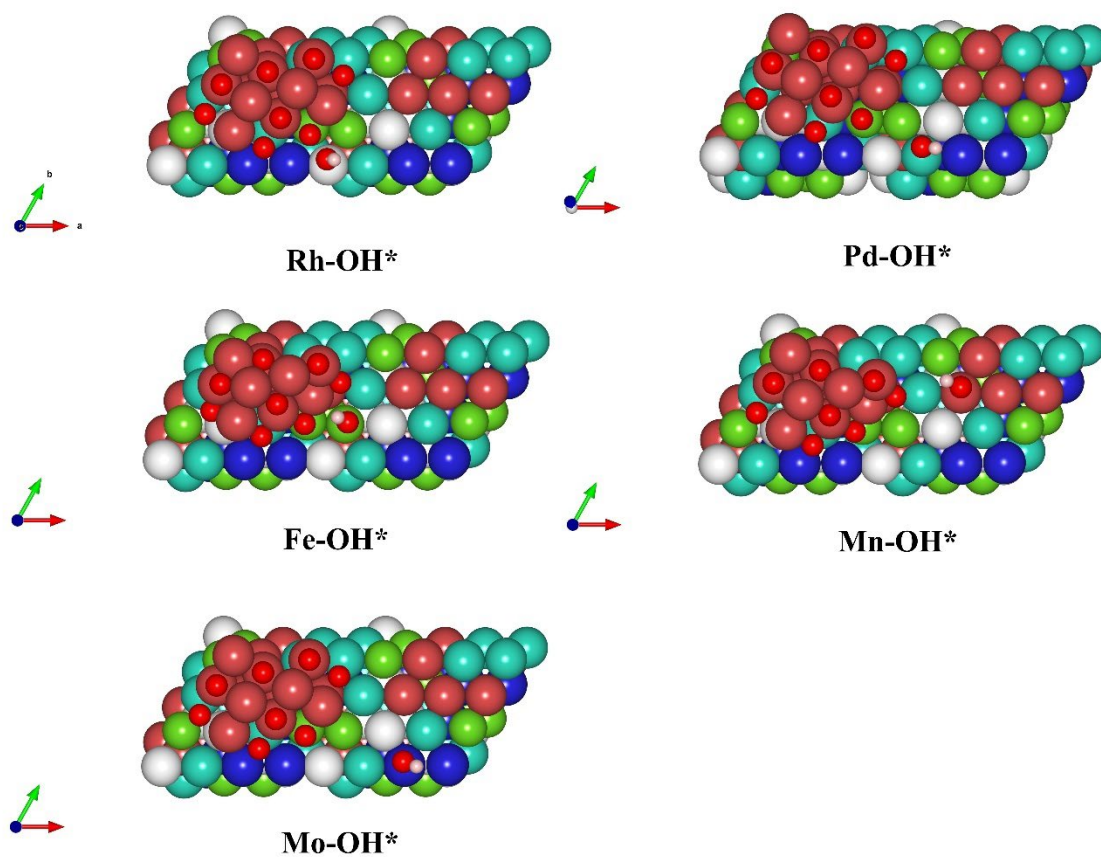
Supplementary Fig. 62 The corresponding $k^3\chi(k)$ oscillation functions for Pd in different electrolytes. The corresponding $k^3\chi(k)$ oscillation functions for Pd in **(a)** 1.0 M KOH and **(b)** 1.0 M PBS electrolyte, respectively.



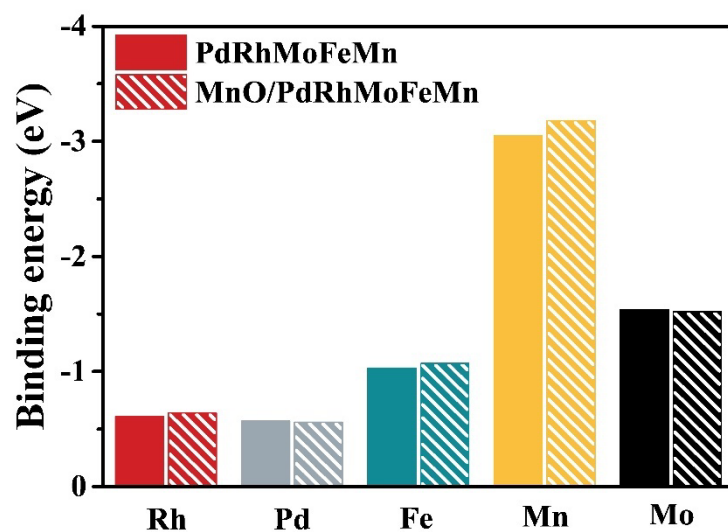
Supplementary Fig. 63 The DFT calculated structural models of MnO/ PdRhMoFeMn HEMs. (a) Top and (b) side view computational modeling of MnO/ PdRhMoFeMn HEMs.



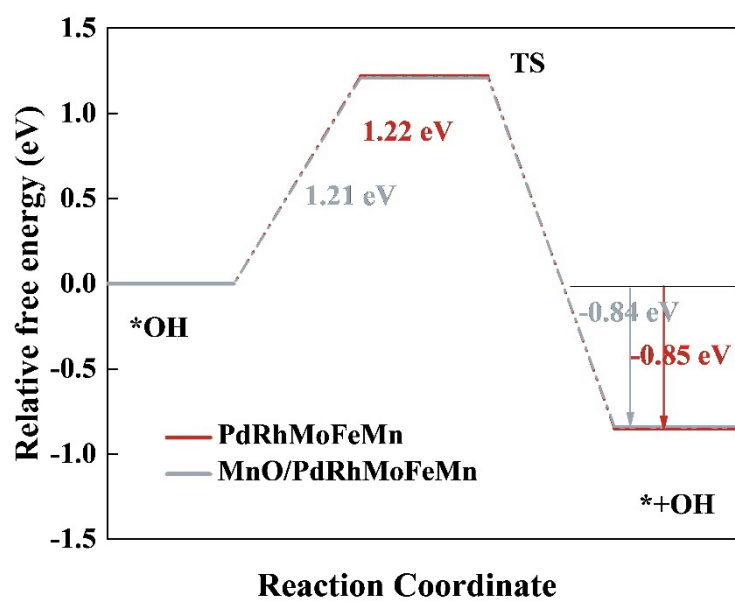
Supplementary Fig. 64 The ΔG_{H^*} profiles of PdRhMoFeMn and MnO/ PdRhMoFeMn HEMs.



Supplementary Fig. 65 The atomic configurations of different sites in MnO/PdRhMoFeMn HEMs during the OH* adsorption process.



Supplementary Fig. 66 The adsorption energy of hydroxide at different sites for PdRhMoFeMn and MnO/PdRhMoFeMn HEMs.



Supplementary Fig. 67 The desorption energy of hydroxide at different sites for PdRhMoFeMn and MnO/PdRhMoFeMn HEMs.

Supplementary Table 1. ICP-OES results of different catalysts.

Element content (At%) Samples	Pd	Rh	Mo	Fe	Mn	Ir	Co	W	Ru
Quinary PdRhMoFe Mn HEMs	23.37	19.53	18.07	17.35	21.68				
Senary PdRhIrCoFe Mo HEMs	29.55	27.44	11.35	7.63		9.45	14.58		
Septenary PdRhIrFeMo MnW HEMs	21.15	13.24	10.76	17.22	14.37	5.83		17.43	
Octonary PdRhIrMnM oRuFeCo HEMs	25.23	17.15	14.76	14.31	10.08	6.58	6.17		5.72
RhMoFeMn Metallenes		47.95	18.71	23.26	10.08				
PdMoFeMn Metallenes	68.93		15.89	7.66	7.52				
PdRh Metallenes	56.24	43.76							

Supplementary Table 2. Summary of recently reported catalysts for HER in acidic electrolyte.

Catalyst	Electrolyte	Overpotential @10 mA cm ⁻²	Tafel slope / mV.dec ⁻¹	References
PdRhMoFeMn HEMs	0.5 M H ₂ SO ₄	6	16	This work
Pt/C	0.5 M H ₂ SO ₄	13	17	This work
IrP ₂ @NC	0.5 M H ₂ SO ₄	8	28	1
Rh-NA/RhO ₂	0.5 M H ₂ SO ₄	9.8	24	2
PtNC/SC	0.5 M H ₂ SO ₄	11	23.5	3
B-Os	0.5 M H ₂ SO ₄	12	26.8	4
La ₂ Sr ₂ PtO _{7+δ}	0.5 M H ₂ SO ₄	13	22	5
RuNi/CQDs	0.5 M H ₂ SO ₄	13	55	6
Pt/Pd ₃ Pb	0.5 M H ₂ SO ₄	13.8	18	7
Rh ₂ P	0.5 M H ₂ SO ₄	14	31.7	8
Ir-NSG	0.5 M H ₂ SO ₄	17	19.2	9
PtW	0.5 M H ₂ SO ₄	19.4	27.8	10
Ru@C ₂ N	0.5 M H ₂ SO ₄	22	30	11
Pt-ACs/CoNC	0.5 M H ₂ SO ₄	24	27.7	12
Pt-RuO ₂	0.5 M H ₂ SO ₄	26	27	13
Au@AuIr ₂	0.5 M H ₂ SO ₄	29	15.6	14
Os/OsS ₂	0.5 M H ₂ SO ₄	29	20.1	15
a-RuTe ₂ PNRs	0.5 M H ₂ SO ₄	33	35	16
Pt ₁ /OLC	0.5 M H ₂ SO ₄	38	36	17
Ru/RuS ₂	0.5 M H ₂ SO ₄	45	24.4	18
RuIr-NC	0.5 M H ₂ SO ₄	46	32	19
RhSe ₂	0.5 M H ₂ SO ₄	49.9	39	20

Supplementary Table 3. Summary of recently reported catalysts for HER in neutral electrolyte.

Catalyst	Electrolyte	Overpotential @10 mA cm ⁻²	Tafel slope / mV.dec ⁻¹	References
PdRhMoFeMn HEMs	1.0 M PBS	23	33	This work
Pt/C	1.0 M PBS	43	45	This work
Pt SA-NT-NF	1.0 M PBS	24	30	21
B-Os	1.0 M PBS	33	44.7	4
NiRu _{0.13} -BDC	1.0 M PBS	36	32	22
Rh ₂ P	1.0 M PBS	38	46	8
RhP _x @NPC	1.0 M PBS	38	56	23
RuS _x	1.0 M PBS	46	39	24
PtZnCo	1.0 M PBS	48.3	65.4	25
RuP ₂ @NPC	1.0 M PBS	57	87	26
RhCu NTs	1.0 M PBS	57	95	27
Ru ₂ B ₃ @BNC	1.0 M PBS	58	69.9	28
Pt-Mo ₂ TiC ₂ T _x	0.5 M PBS	61	36	29
PtSi	1.0 M PBS	66	47	30
Re ₃ P ₄ @NPVC	1.0 M PBS	70	77	31
Ru/Mo ₂ CT _x	1.0 M PBS	73	57	32
Pt@CoO _x	1.0 M PBS	82	51.5	33
PdP ₂ @CB	1.0 M PBS	84.6	72.3	34
L-RuP	1.0 M PBS	95	54	35
RhCoB	1.0 M PBS	113	149.1	36
OsP ₂ @NPC	1.0 M PBS	144	64	37
RhCu NWs	1.0 M PBS	165	211	27

Supplementary Table 4. Summary of recently reported catalysts for HER in alkaline electrolytes.

Catalyst	Electrolyte	Overpotential @10 mA cm ⁻²	Tafel slope / mV.dec ⁻¹	References
PdRhMoFeMn HEMs	1.0 M KOH	26	41	This work
Pt/C	1.0 M KOH	45	63	This work
IrP ₂ @NC	1.0 M KOH	28	50	1
PtZnCo	1.0 M KOH	29	64.2	25
Rh ₂ P	1.0 M KOH	30	50	8
Ru/np-MoS ₂	1.0 M KOH	30	31	38
h-RuSe ₂	1.0 M KOH	34	95	39
a-RuTe ₂ PNRs	1.0 M KOH	36	36	16
Os/OsS ₂	1.0 M KOH	37	29.8	15
Rh NSs	1.0 M KOH	37.8	98.3	40
PtNiO	1.0 M KOH	39.8	78.8	41
RhPd-H	1.0 M KOH	40	35.7	42
PtSe ₂ /Pt	1.0 M KOH	42	53	43
IrCo@NC	1.0 M KOH	45	80	44
Pt ₅ /HMCS	1.0 M KOH	46.2	48.1	45
AuRu	1.0 M KOH	50	30.8	46
RuP ₂ @NPC	1.0 M KOH	52	69	26
PtSe ₂	1.0 M KOH	60	41	47
Sr ₂ RuO ₄	1.0 M KOH	61	51	48
SANi-Pt NWs	1.0 M KOH	70	60.3	49
RhSe ₂	1 M KOH	81.6	96	20
Pt@PCM	1.0 M KOH	139	74	50

Supplementary Table 5. Adsorption energy of H species (ΔE_{H^*}), the relevant contributions to the free energy (ΔZPE and $T\Delta S$), and the free energy of adsorbed H^* (ΔG_{H^*}) on different sites on the surfaces of HEMs.

ΔG_{H^*} (eV)	ΔE_{H^*} (eV)	ΔZPE (eV)	$T\Delta S$ (eV)	Site
-0.615	-0.760178	0.157852	0.012674	Fe1 top
-0.642	-0.783684	0.157655	0.015971	Mn1 top
-0.242	-0.373501	0.145014	0.013513	Pd1 top
-0.238	-0.36369	0.142526	0.016836	Pd2 top
-0.272	-0.406013	0.149499	0.015486	Pd3 top
-0.682	-0.815997	0.151355	0.017357	Mn2 top
-0.682	-0.809863	0.143828	0.015965	Mn3 top
-0.687	-0.825537	0.153059	0.014522	Mn4 top
-0.436	-0.574556	0.153052	0.014496	Fe2 top
-0.132	-0.256948	0.140729	0.015781	Rh1 top
-0.242	-0.376385	0.148027	0.013642	Pd4 top
-0.425	-0.570145	0.157793	0.012648	Fe3 top
-0.145	-0.285793	0.156215	0.015422	Rh2 top
-0.23	-0.360034	0.143693	0.013659	Pd5 top
-0.524	-0.667479	0.157513	0.014034	Mo1 top
-0.557	-0.700467	0.157501	0.014034	Mo2 top
-0.782	-0.891416	0.123952	0.014536	Mn1Mn2 bridge1
-0.782	-0.914873	0.148336	0.015463	Mn1Mn3 bridge2
-0.782	-0.92433	0.157793	0.015463	Mn2Mn3 bridge3
-0.782	-0.925568	0.157793	0.014224	Mn3Mn4 bridge4
-0.29	-0.421217	0.145145	0.013928	Pd1Pd2 bridge1
-0.546	-0.679138	0.146852	0.013714	Mo1Mo2 bridge1
-0.674	-0.816518	0.156215	0.013697	Mn1-Mn2-Mn3 Hollow

Supplementary Table 6. Adsorption energy of H species (ΔE_{H^*}), the relevant contributions to the free energy (ΔZPE and $T\Delta S$), and the free energy of adsorbed H^* (ΔG_{H^*}) on Rh or Pd sites over PdRh, PdMoFeMn, RhMoFeMn, and HEMs.

Species	ΔE_{H^*} (eV)	ΔZPE (eV)	$-T\Delta S$ (eV)	ΔG_{H^*} (eV)
H ₂		0.287212	0.410024	
H* on Rh site of HEMs	-0.256948	0.140729	0.015781	-0.132
H* on Rh site of RhMoFeMn	-0.596889	0.147255	0.015366	-0.465
H* on Rh site of PdRh	-0.537682	0.154264	0.144582	-0.528

Supplementary Table 7. Model-fitted operando Mn EXAFS spectra in 0.5 M H₂SO₄.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Mn-O	6.0±0.3	2.09±0.08	5.8±0.1	-8.1±6.8	0.001
0 V	Mn-O	5.9±0.4	2.07±0.08	4.8±0.1	-9.0±8.2	0.001
-0.025 V	Mn-O	5.8±0.9	2.10±0.07	4.5±0.1	-6.2±-2.5	0.001
-0.05 V	Mn-O	6.0±0.9	2.17±0.06	5.6±0.1	-5.1±1.8	0.001
-0.1 V	Mn-O	6.0±0.9	2.14±0.06	6.8±0.1	-5.3±1.4	0.001

Supplementary Table 8. Model-fitted operando Mn EXAFS spectra in 1.0 M KOH.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Mn-O	4.9±0.4	2.14±0.02	7.7±0.1	-0.9±3.7	0.001
0 V	Mn-O	5.1±0.6	2.15±0.03	7.8±0.1	-0.1±5.5	0.002
-0.025 V	Mn-O	5.2±0.6	2.15±0.03	7.7±0.1	3.2±0.6	0.003
-0.05 V	Mn-O	5.9±1.0	2.15±0.06	7.6±0.1	-4.1±10.0	0.003
-0.1 V	Mn-O	5.9±0.9	2.16±0.04	7.6±0.1	6.0±5.7	0.001

Supplementary Table 9. Model-fitted operando Mn EXAFS spectra in 1.0 M PBS.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Mn-O	2.4±0.2	2.22±0.02	3.0±0.1	7.6±5.7	0.002
0 V	Mn-O	2.4±0.2	2.20±0.03	3.3±0.1	9.1±9.8	0.002
-0.025 V	Mn-O	2.5±0.5	2.18±0.02	3.0±0.1	15.2±2.2	0.002
-0.05 V	Mn-O	2.5±0.5	2.19±0.03	3.0±0.1	13.5±2.8	0.002
-0.1 V	Mn-O	2.7±0.5	2.18±0.03	3.0±0.1	13.4±2.9	0.002

Supplementary Table 10. Model-fitted operando EXAFS spectra results for Pd in 0.5 M H₂SO₄.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.03	4.0±0.1	1.3±5.4	0.013
	Pd-Pd/Rh/Mo	5.1±0.7	2.73±0.01	8.6±0.1		
	Pd-Fe/Mn	1.2±0.2	2.73±0.04	7.2±0.1		
0 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	1.3±2.4	0.007
	Pd-Pd/Rh/Mo	5.0±0.6	2.69±0.03	8.1±0.1		
	Pd-Fe/Mn	1.0±0.1	2.71±0.05	7.4±0.1		
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	1.3±0.4	0.008
	Pd-Pd/Rh/Mo	4.9±0.8	2.69±0.05	8.9±0.1		
	Pd-Fe/Mn	1.1±0.1	2.72±0.03	7.1±0.1		
-0.05 V	Pd-O	0.2±0.1	2.12±0.01	3.9±0.1	1.3±5.4	0.006
	Pd-Pd/Rh/Mo	5.0±1.0	2.68±0.03	8.2±0.1		
	Pd-Fe/Mn	1.1±0.1	2.71±0.03	7.9±0.1		
-0.1 V	Pd-O	0.2±0.1	2.12±0.01	4.2±0.1	1.3±3.6	0.009
	Pd-Pd/Rh/Mo	5.1±0.9	2.69±0.03	8.1±0.1		
	Pd-Fe/Mn	1.1±0.1	2.71±0.02	7.2±0.1		

Supplementary Table 11. Model-fitted operando EXAFS spectra results for Rh in 0.5 M H₂SO₄.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	4.4±0.3	0.005
	Rh-Rh/Pd/Mo	6.8±1.1	2.69±0.02	8.8±0.1		
	Rh-Fe/Mn	2.2±0.3	2.71±0.04	7.7±0.1		
0 V	Rh-O	0.3±0.2	1.88±0.01	5.7±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	6.9±0.7	2.69±0.01	8.2±0.1		
	Rh-Fe/Mn	2.0±0.4	2.68±0.03	7.4±0.1		
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.1±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	7.0±1.0	2.70±0.02	8.4±0.1		
	Rh-Fe/Mn	2.1±0.2	2.69±0.03	7.6±0.1		
-0.05 V	Rh-O	0.3±0.2	1.88±0.01	6.2±0.1	4.4±1.1	0.007
	Rh-Rh/Pd/Mo	6.8±1.0	2.70±0.02	8.3±0.1		
	Rh-Fe/Mn	2.2±0.3	2.69±0.03	7.5±0.1		
-0.1 V	Rh-O	0.3±0.1	1.88±0.01	6.3±0.1	4.4±1.3	0.008
	Rh-Rh/Pd/Mo	7.1±0.7	2.69±0.02	8.1±0.1		
	Rh-Fe/Mn	2.3±0.2	2.72±0.03	7.3±0.1		

Supplementary Table 12. Model-fitted operando EXAFS spectra results for Pd in 1.0 M KOH.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.01	4.0±0.1	-0.1±2.0	0.009
	Pd-Pd/Rh/Mo	5.1±0.4	2.72±0.03	8.0±0.1		
	Pd-Fe/Mn	1.0±0.1	2.67±0.01	7.1±0.1		
0 V	Pd-O	0.4±0.1	2.12±0.02	3.6±0.1	-0.1±0.2	0.012
	Pd-Pd/Rh/Mo	5.0±0.8	2.66±0.02	7.6±0.1		
	Pd-Fe/Mn	1.1±0.1	2.64±0.04	7.0±0.1		
-0.025 V	Pd-O	0.5±0.1	2.12±0.03	4.2±0.1	-0.1±2.6	0.011
	Pd-Pd/Rh/Mo	5.1±0.9	2.70±0.02	7.9±0.1		
	Pd-Fe/Mn	1.2±0.1	2.72±0.04	7.1±0.1		
-0.05 V	Pd-O	0.6±0.1	2.12±0.02	5.1±0.1	-0.1±0.4	0.010
	Pd-Pd/Rh/Mo	5.1±0.7	2.71±0.03	8.3±0.1		
	Pd-Fe/Mn	1.4±0.1	2.73±0.04	7.1±0.1		
-0.1 V	Pd-O	0.7±0.1	2.12±0.01	6.1±0.1	-0.2±2.0	0.008
	Pd-Pd/Rh/Mo	5.0±0.5	2.69±0.05	8.6±0.1		
	Pd-Fe/Mn	1.5±0.1	2.70±0.04	7.5±0.1		

Supplementary Table 13. Model-fitted operando EXAFS spectra results for Rh in 1.0 M KOH.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.8±0.8	0.008
	Rh-Rh/Pd/Mo	6.8±0.9	2.70±0.04	8.4±0.1		
	Rh-Fe/Mn	2.3±0.1	2.73±0.02	7.6±0.1		
0 V	Rh-O	0.2±0.1	1.88±0.01	6.2±0.1	0.9±2.7	0.007
	Rh-Rh/Pd/Mo	6.9±0.9	2.69±0.03	8.1±0.1		
	Rh-Fe/Mn	2.4±0.3	2.74±0.05	7.3±0.1		
-0.025 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	0.8±3.1	0.011
	Rh-Rh/Pd/Mo	6.9±0.7	2.71±0.02	8.3±0.1		
	Rh-Fe/Mn	2.2±0.1	2.70±0.06	7.3±0.1		
-0.05 V	Rh-O	0.3±0.1	1.88±0.01	6.2±0.1	0.8±2.2	0.008
	Rh-Rh/Pd/Mo	7.1±1.1	2.69±0.03	8.1±0.1		
	Rh-Fe/Mn	2.1±0.1	2.71±0.03	7.1±0.1		
-0.1 V	Rh-O	0.3±0.2	1.88±0.02	6.2±0.1	0.8±1.9	0.008
	Rh-Rh/Pd/Mo	6.9±0.3	2.72±0.03	8.4±0.1		
	Rh-Fe/Mn	2.4±0.1	2.70±0.05	7.3±0.1		

Supplementary Table 14. Model-fitted operando EXAFS spectra results for Pd in 1.0 M PBS.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{Å}^2)$	ΔE_0 (eV)	R-factor
OCP	Pd-O	0.2±0.1	2.12±0.02	4.0±0.1	-2.0±1.1	0.012
	Pd-Pd/Rh/Mo	5.2±0.9	2.73±0.03	8.5±0.1		
	Pd-Fe/Mn	0.9±0.1	2.67±0.03	7.6±0.1		
0 V	Pd-O	0.2±0.1	2.12±0.08	4.1±0.1	-2.2±1.0	0.009
	Pd-Pd/Rh/Mo	5.3±0.7	2.69±0.02	8.6±0.1		
	Pd-Fe/Mn	1.1±0.2	2.71±0.06	7.5±0.1		
-0.025 V	Pd-O	0.2±0.1	2.12±0.01	4.1±0.1	-2.2±1.0	0.011
	Pd-Pd/Rh/Mo	5.2±1.0	2.71±0.03	8.3±0.1		
	Pd-Fe/Mn	1.2±0.1	2.72±0.05	7.8±0.1		
-0.05 V	Pd-O	0.2±0.1	2.12±0.02	4.1±0.1	-2.0±3.7	0.009
	Pd-Pd/Rh/Mo	5.2±0.9	2.70±0.03	8.5±0.1		
	Pd-Fe/Mn	1.4±0.2	2.71±0.05	7.2±0.1		
-0.1 V	Pd-O	0.3±0.1	2.12±0.02	4.1±0.1	-2.0±1.0	0.007
	Pd-Pd/Rh/Mo	5.3±0.7	2.71±0.02	8.3±0.1		
	Pd-Fe/Mn	1.4±0.2	2.69±0.05	7.7±0.1		

Supplementary Table 15. Model-fitted operando EXAFS spectra results for Rh in 1.0 M PBS.

Potential	Path	CN	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$	ΔE_0 (eV)	R-factor
OCP	Rh-O	0.2±0.1	1.88±0.05	5.3±0.1	1.1±0.2	0.013
	Rh-Rh/Pd/Mo	7.1±1.2	2.66±0.02	7.6±0.1		
	Rh-Fe/Mn	1.8±0.5	2.64±0.08	8.1±0.1		
0 V	Rh-O	0.1±0.1	1.88±0.05	5.2±0.1	1.1±0.1	0.010
	Rh-Rh/Pd/Mo	6.9±1.1	2.65±0.01	7.4±0.1		
	Rh-Fe/Mn	1.8±0.4	2.62±0.04	8.1±0.1		
-0.025 V	Rh-O	0.1±0.1	1.88±0.03	5.2±0.1	1.0±0.4	0.009
	Rh-Rh/Pd/Mo	7.1±0.8	2.66±0.02	7.2±0.1		
	Rh-Fe/Mn	2.0±0.2	2.63±0.06	8.3±0.1		
-0.05 V	Rh-O	0.1±0.1	1.88±0.01	5.2±0.1	1.0±0.1	0.007
	Rh-Rh/Pd/Mo	7.2±1.0	2.64±0.03	7.8±0.1		
	Rh-Fe/Mn	1.9±0.2	2.61±0.07	8.4±0.1		
-0.1 V	Rh-O	0.1±0.1	1.88±0.04	5.1±0.1	1.1±0.2	0.008
	Rh-Rh/Pd/Mo	7.0±1.3	2.65±0.01	7.0±0.1		
	Rh-Fe/Mn	1.8±0.5	2.60±0.03	7.9±0.1		

Supplementary Table 16. Content of each metal salt in the precursor solutions.

Metal Salts (mg) Products	Pd(acac) ₂	Rh ₆ (C ₂ O ₄) ₁₆	Fe ₃ (CO) ₁₂	Mn ₂ (C ₂ O ₄) ₁₀	Mo(CO) ₆	Ir ₄ (C ₂ O ₄) ₁₂	Co ₂ (C ₂ O ₄) ₈	W(CO) ₆	Ru ₃ (C ₂ O ₄) ₁₂
Quinary PdRhMo FeMn HEMs	9.5	5.5	5.5	5.0	35.0				
Senary PdRhIrCo FeMo HEMs	9.5	2.0	3.0		35.0	3.0	3.0		
Septenary PdRhIrFe MoMnW HEMs	9.5	5.0	6.0	4.0	15.0	7.0		20.0	
Octonary PdRhIrMnMoRuFe Co HEMs	9.5	5.0	6.0	4.0	25.0	7.0	6.0		8.0

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