## Supporting Information

# High-Entropy Alloy Catalysts for Advanced Hydrogen-Production Zinc-Based Batteries

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#### **Experimental Section**

#### Materials

All chemicals are of analytical grade and used without further purification. FeCl<sub>3</sub>, ethanol, zinc acetate, triethylamine and N,N-dimethylformamide(DMF) were purchased from Sinopharm. NiCl<sub>2</sub>·6H<sub>2</sub>O, WCl<sub>6</sub>, commercial RuO<sub>2</sub>, Glycerinum and DL-Glyceric acid were purchased from Aladdin. CuCl<sub>2</sub>·2H<sub>2</sub>O was purchased from General-Reagent. RuCl<sub>3</sub> was purchased from Bidepharm. Trimesic acid was bought from Macklin. HCl, DL-Glyceraldehyde, Glycolic acid and Dihydroxyacetone were purchased from Adamas. Nickel foam and titanium foam were purchased from Kunshan Guangjiayuan New Material Co., Ltd. The proton membrane was purchased from Dupont. Commercial Pt/C (20 wt%) was purchased from Shanghai Hesen Electric Co., Ltd. Potassium formate was purchased from Sigma-Aldrich.

#### **Materials Synthesis**

The nickel foam and titanium foam were ultrasonically pretreated in 1 M HCl for 15 minutes, then washed with deionized water and ethanol, respectively, and then dried.

In a typical process for the synthesis of high-entropy alloy nanoparticles on nickel or titanium foam, 0.5 mmol FeCl<sub>3</sub>, 0.5 mmol NiCl<sub>2</sub>· $6H_2O$ , 0.25 mmol CuCl<sub>2</sub>· $2H_2O$ , 0.75 mmol WCl<sub>6</sub>, 0.5 mmol RuCl<sub>3</sub> metal salts and 2.5 mmol trimesic acid were added sequentially to a 32 ml DMF solution containing 4 ml anhydrous ethanol. Then, the mixed solution was stirred continuously for 12 hours and 3 ml triethylamine was added to the above mixed solvent. Next, the solution was transferred to the 50 ml reactor liner and the nickel foam or titanium foam substrate (2 cm×2 cm) was sunk to the bottom of the solution. Finally, the reactor was held at 130 °C for 40 hours. The resulting substrates loaded with high-entropy alloy nanoparticles were washed with ethanol, dried and prepared for use. The catalyst loading was about 1.1 mg cm<sup>-2</sup>. The high-entropy alloy nanoparticle powder samples used for XRD and ICP were synthesized by a similar method, without the addition of a metal foam substrate.

For comparison, ternary and quaternary alloys were synthesized by a similar method, but without the addition of one or two metal salts.

#### **Materials Characterization**

X-ray powder diffraction (XRD) was performed on a (Miniflex 600, Rigaku) powder x-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å, 40 kV, 15 mA) at a scan rate of 10 °/min. The microscopic morphology and structure of the samples were investigated by scanning electron microscopy (SEM, JSM6700-F) and transmission electron microscopy (TEM, TECNAI G2 F20). *In-situ* Raman spectra were acquired with a 532 nm laser on a LabRAM HR. The x-ray photoelectron spectra (XPS) were obtained on an XPS spectrometer Thermo Scientific K-Alpha using Al K $\alpha$  rays (hv=1486.66 eV) as the excitation source. The mass ratios of the elements were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110). NMR spectra were gathered on a 600 MHz Bruker spectrometer.

#### **Electrochemical Characterization**

The electrochemical performance of catalysts HER and OER was tested using a standard three-electrode system in the CHI 660E electrochemical workstation. For HER and OER measurements, the electrolyte was pre-saturated with Ar and O<sub>2</sub>, respectively. In the HER measurements,  $0.5 \text{ M H}_2\text{SO}_4$  was used as the electrolyte, an electrode (1 cm×1 cm) as the working electrode, a graphite rod as the counter electrode, and an Ag/AgCl electrode as the reference electrode. As for the OER performance test, 1 M KOH was used as the electrolyte, and the Hg/HgO electrode was used as the reference electrode. As for the oER performance test, 1 m KOH was used as the electrolyte, and the Hg/HgO electrode was used as the reference electrode. As for the oER performance test, 10 mg of Pt/C or RuO<sub>2</sub> was dissolved in a mixture of 500 µL of deionized water, 400 µL of ethanol and 100 µL of Nafion and sonicated well. Then 100 µL of the ink was applied uniformly dropwise to a 1 cm<sup>2</sup> area of metal foam substrate.

Cyclic voltammetry (CV) was performed at a scan rate of 100 mV s<sup>-1</sup> and a series of linear scanning voltammetry (LSV) was conducted with a scan rate of 5 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was recorded in the range of 100 kHz ~ 0.1 Hz. The electrochemical surface area (ECSA) value was obtained by the doublelayer capacitances (C<sub>dl</sub>), which was estimated by the CV curves at various scan rates. Specifically, ECSA was estimated by the equation: ECSA = C<sub>dl</sub>/C<sub>s</sub>, where the specific capacitance value (C<sub>s</sub>) was taken 0.04 mF cm<sup>-2</sup>. The long-term stability tests of HER and OER were performed by chronopotentiometry. All the potentials reported herein are without iR correction, which is given versus reversible hydrogen electrode (RHE) according to  $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$  and  $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059 \times pH$ .

#### In-situ Raman experiments

The *in-situ* Raman spectroscopy electrochemical experiments were carried out in a homemade electrochemical cell with Pt sheet as the counter electrode, Hg/HgO as the reference electrode and the prepared catalyst as the working electrode, respectively. A 532 nm light source was used as the excitation source for the Raman test, and each spectrum was scanned three times, with each scan exposed for 60 seconds. Raman signals were recorded in situ at open circuit voltage (OCP) and different applied potentials, from 1.07 to 1.47 V *vs.* RHE.

#### The assembly of rechargeable H<sub>2</sub>-generation zinc batteries

To assemble the rechargeable H<sub>2</sub>-generation Zn-based battery, nickel foam modified by FeNiCuWRu high-entropy alloy nanoparticles (1 cm×1 cm) and commercially available zinc plates (99.99 % purity) were immersed in an alkaline solution (4 M NaOH + 0.1 M zinc acetate) and titanium foam modified by FeNiCuWRu high-entropy alloy nanoparticles (1 cm×1 cm) was immersed in an acidic solution (2 M H<sub>2</sub>SO<sub>4</sub>). In particular, when the zinc plate was charged with glycerol, the anode and anolyte were changed to commercial Pt/C and 4 M NaOH + 0.1 M zinc acetate + 0.5 M glycerol, respectively. In addition to the selection of high ion-conducting N117, it is crucial to minimize the distance between the anode and cathode (currently around 2 mm) to accelerate ion migration and reduce the overall resistance of the battery circuit, ultimately enhancing the reaction kinetics of the battery. Moreover, the acidic electrolyte and alkaline electrolyte were separated by a proton membrane, and the electrolyte was circulated through the liquid flow pump, delivery tube and electrolyte tank in order to speed up mass transfer and maintain a stable electrolyte pH gradient for a long time. For the symmetrical electrolyte H<sub>2</sub>-generation Zn-based battery control group, the electrolyte was replaced by 4 M NaOH (anolyte) and 4 M NaOH (catholyte). Performance study of rechargeable H<sub>2</sub>-generation zinc batteries

The entire battery system was pre-filled with Ar gas before performing

electrochemical tests on all H<sub>2</sub>-generation Zn-based batteries to avoid the influence of oxygen from the air and electrolyte. Power density curves for fuel battery discharging were obtained by performing LSV tests at a scan rate of 5 mV s<sup>-1</sup> on a CHI 660E workstation and CHI 680C current amplifier. Discharge rate performance and long-term stability were evaluated on the Land CT3002K multi-channel battery test system. The corresponding specific capacity and energy density were obtained by testing the mass lost from the zinc anode at different current densities during the 5 hours of fuel battery discharge. When conducting galvanostatic charge/discharge cycle testing, manually switch the Land battery test system (CT3001A) to connect the charge/discharge circuit.

#### Theoretical electrochemical properties of H<sub>2</sub>-generation zinc batteries

Cathodic hydrogen evolution reaction(2 M  $H_2SO_4$ ):  $2H^+ + 2e^- \rightarrow H_2$ 

$$E_{c} = E_{H^{+}}^{\theta} - 2.303 \frac{RT}{2F} \log \left[ \frac{\alpha_{H_{2}}}{(\alpha_{H^{+}})^{2}} \right] = 0 V + 0.059 * \log (\alpha_{H^{+}}) = 0.035 V$$

$$E_{H^{+}}^{\theta} = 0 V vs. SHE$$

$$(H^{+})^{2} = 0 V vs. SHE$$

$$(Eq. 1)$$
Anodic zinc oxidation reaction(4 M NaOH): Zn - 2e^{-} + 2 OH^{-} \rightarrow H\_{2}O + ZnO
$$E_{a} = E_{a} \frac{\theta}{2^{+}} - 2.303 \frac{RT}{2F} \log \left[ (\alpha_{OH^{-}})^{2} \right] = -1.249 V - 0.059 * \log (\alpha_{OH^{-}}) = -1.285 V$$

$$E_{\frac{Zn^{2}+}{Zn}}^{\theta} = -1.249 \text{ V vs. SHE}$$
(Eq. 2)

Zn ) The entire reaction:  $Zn + 2H^+ + 2 OH^- \rightarrow ZnO + H_2 + H_2O$ 

$$V_{cell} = E_{c} - E_{a} = E_{d}^{\theta} - E_{d}^{\theta} - E_{d}^{\theta} - E_{d}^{\theta} + 0.059 * \left[ \log \left( \alpha_{H}^{\theta} + \right) + \log \left( \alpha_{OH}^{\theta} - \right) \right] = 1.32 V$$
(Eq. 3)

Notes: R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $\alpha$  is the corresponding activity, F is the faraday constant, 96485 C mol<sup>-1</sup>, T is 298.15 K.

The theoretical energy density of the H<sub>2</sub>-generation Zn-based battery should be:

$$E_{\text{theo}} = C_{\text{theo}} V_{\text{cell}} = 0.82 \text{ Ah g}^{-1} \times 1.32 \text{ V} = 1082.4 \text{ Wh kg}^{-1}$$
 (Eq. 4)

#### **Faraday efficiency calculations**

In order to monitor the H<sub>2</sub> production, we recorded the volume (V) of hydrogen produced every 10 min at a current density of 500 mA cm<sup>-2</sup> using the drainage method. The molarity of H<sub>2</sub> (n) can be expressed by the following equation:

$$n = \frac{V}{V_m}$$

where  $V_m$  is the molar volume of the gas (24.5 L/mol)

The theoretical H<sub>2</sub> volume can be calculated by the following equation:

$$n_{\text{theo}} = \frac{Q}{N * F} = \frac{I * t}{N * F}$$

where Q is the charge transfer, N is the number of electrons transferred to produce each  $H_2$  molecule (N = 2), F is the Faraday constant (96,500 C mol<sup>-1</sup>), I is the discharge current (mA), and t is the operating time (s).

Therefore, the Faraday efficiency (FE) of H<sub>2</sub> can be calculated as follows:

$$FE(\%) = \frac{n}{n_{theo}} \times 100\%$$

#### Design of H<sub>2</sub>-generation zinc batteries stacks

In order to ensure the simplicity of the battery structure, the cathodes and anodes of several fuel battery monomers were stacked together in a sandwich-like structure. Among them, the electrolytes of many cathode and anode chambers were connected separately in parallel through the liquid flow pipeline, and formed a circulation through the liquid flow pump and electrolyte tank. The electrons generated by the external circuit of several battery units were exported in series through wires, while the prepared high-purity hydrogen was collected at the cathode electrolyte tank.

#### **Theoretical Calculations Section**

#### S1. High-throughput screening based on pre-trained machine learning potential

The advancement of theoretical calculation methodologies, exemplified by first principles, alongside the progress in data science, notably through machine learning techniques, has established preliminary material screening from databases as a critical research paradigm before proceeding to experimental stages. Despite this progress, the high-throughput screening of high-entropy materials remains an elusive goal. This challenge primarily arises from the combinatorial explosion associated with the extensive variety of elemental combinations and configurations in high-entropy materials, which substantially hinders the efficacy of first-principle methods and other data-driven strategies.

To overcome the limitations in high-throughput screening of high-entropy materials, the adoption of machine learning potentials (MLPs)<sup>1</sup> has emerged as a vital solution. MLPs notably diminish the reliance on extensive density functional theory (DFT) data volumes by extrapolating force fields across the complete range of conformational space, derived from DFT data. Nonetheless, prevailing MLP frameworks typically treat each element independently, resulting in a parameter count proportional to the number of elements involved, which subsequently slows down the operation when the element count exceeds seven, thereby compromising the efficiency of MLPs. In response to this issue, recent developments by DeepMD-Kit<sup>2</sup> have introduced pre-trained potentials that leverage type-embedding to recognize elemental similarities and utilize self-attention mechanisms to enhance the learning of coordination environments vital for energy calculation. This innovative approach, termed the Large Atom Model (LAM),<sup>3,4</sup> facilitates the creation of an MLP capable of incorporating up to 56 elements by learning from material databases, thus proving exceptionally advantageous for the high-throughput screening of high-entropy materials in this research.

### S2. An overview of elemental distributions and calculations of activities at all sites The simulations contain three key issues:

(i) Monte Carlo simulations are imported to achieve the elemental distribution of these nanoparticles, which are detailed in sec. S2.1.

(ii) The computational hydrogen electrode (CHE) method proposed by Norskov's method<sup>5</sup> is introduced to predict the activities of a certain site via the binding energies (sec. S2.2).

(iii) The above two steps are executed via a force field (FF) instead of DFT to ensure the calculation efficiency in such a large NP. However, we introduce a firstprincipal-based high-dimensional neutral work potential (HDNNPs)<sup>6</sup> to ensure our FF has the DFT accuracy. Additionally, an active learning skill is attached to ensure the FF well represent the DFT result. The details for this process are shown in sec. S2.3.

#### S2.1 MC process for elemental distribution

The elements in HEA will not distributed randomly. Instead, like the people in the society, each element will have a different "personality". Some elements have higher affinities to each other, and some elements tend to be located at the surface instead of staying in bulk. The distribution preference closely connects with the apparent activity. So achieving the appropriate distribution via simulation is an important method. In this paper, as the crystal structure is known to be fcc, it is facile for us to implement a Metropolis Monte Carlo (MC) to identify the most probable distribution of every element atom in the model of HEA-Alloys. We use a truncated octahedron of 405 atoms as a reaction model with lattice constants taken from a weighted average of the lattice constants of all atoms. This structure is named NP<sub>405</sub> in the following. For each new step, we will randomly switch one element's atom with another element of other types,

then using the Metropolis algorithm (acceptance probability  $P = min[(1,exp[m](-\frac{\Delta E}{RT}))]$ ,  $\Delta E$  is the energy cost for the switch, T=300 K) to check whether to accept such a switch. For each structure, a total of 1E6 MC step was performed. The cross-section drawn of the MC processes for FeCuNiWRu, FeNiRuW, and FeNiRu is shown in Fig. 5a and Fig. S14. From it we can see the elemental distribution nearly stays unchanged after 1E5 MC steps, which indicates the final structure after the MC steps are thermodynamically appropriate.

#### S2.2 The implementation of a force field-based CHE method on HEA-NP.

CHE method is popular in theory study in electrocatalysis. Instead of directly calculating the exact PES of an electrocatalytic reaction, the CHE method uses the adsorption energy to represent it. Unlike the PES which has a tremendous degree of freedom (because of the involvement of electrolytes)<sup>5</sup>, adsorption energy is only a point in PES. That is, it only contains one degree of freedom. Though inevitably lacks precision, it still well captures most of the trends in electrocatalysis. Therefore, the CHE

method can somehow be regarded as the "first-order approximation" of the exact reaction potential energy surface (PES).

For HEA-NP, we can still apply these CHE methods to discuss the associated activities. Similar to the previous works, we use adsorption energies of H\* and O\* respectively as the descriptor for HER and OER. The former is denoted as  $\Delta G_{H*}$ , which is defined as:

$$\Delta G_{H*} = G(MH) - G(M) - \frac{1}{2}u_{H2(g)}$$

The latter is denoted as  $\Delta G_{O^*}$ , which is defined as:

$$\Delta G_{0*} = G(M0) - G(M) - u_{H20(g)} + u_{H2(g)}$$

The volcano relation from Koper's work is introduced, where the volcano apex for HER and OER is located at 0 and 2.85  $eV^6$ . Therefore, the TOF for a certain site I is expressed as:

$$TOF_{HER}(i) = k_{0}^{HER} \exp\left(-\frac{\left|\Delta G_{H*}(i)\right|}{RT}\right)$$
(Eq.5)  
$$TOF_{OER}(i) = k_{0}^{OER} \exp\left(-\frac{\left|\Delta G_{O*}(i) - 2.85\right|}{RT}\right)$$
(Eq.6)

The results of  $|\Delta G_{H*}(i)|$ ,  $\Delta G_{H*}(i)$ ,  $|\Delta G_{0*}(i) - 2.85|$  and  $\Delta G_{0*}(i) - 2.85$  in each site is plotted in Fig. 5f in the main text. Based on the expressions of TOF, we can write the potential dependent expression of current density via Bulter-Volmer equations:

$$j_{HER} = 2Fk_0^{HER} \exp\left(-\frac{\left|\Delta G_{H*}(i)\right|}{RT}\right) exp^{[m]} \left[-\frac{\alpha\left(U - U_0^{HER}\right)}{RT}\right]$$
(Eq.7)

$$j_{OER} = 2Fk_{0}^{OER} \exp\left(-\frac{|\Delta G_{0*}(i) - 2.85|}{RT}\right) exp^{[m]} \left[-\frac{\alpha\left(U - U_{0}^{OER}\right)}{RT}\right]$$
(Eq.8)

Where  $k_{0}^{HER}$  and  $k_{0}^{0}$  are the standard reaction kinetic constant for HER and OER. These two expressions generate the calculated LSV in Fig. S17.

#### S2.3 ML scheme to the force field of MC process and adsorption energy.

#### (1) Basic simulation strategy

The two issues we discuss in this paper, namely, the elemental distribution in  $NP_{405}$ , and the adsorption energy of H\* on O\* on the surface site, are both too expensive

to calculate directly. Therefore, we use the ML scheme to train the neural network with a sufficient amount of DFT results, and then let the trained neural network act as a force field for MC, as well as to calculate the H\* and O\* adsorption energies for all sites. The high-dimensional neutral network potentials (HDNNPs)<sup>7-9</sup> are used as the ML scheme to generate a force field. The HDNNPs is a neural network paradigm that is initialized by Behler and Parrinello. It decouples the total energy of the system to a sum of atomic energies, and uses the concept of "nearsightedness" to regard the atomic potential as the functionals of the local chemical environment up to a cutoff radius and are computed by individual atomic neural networks (NN). After fine training, NN can represent functions of many variables in a continuous way and interpolate within the training set. Thus, it will allow obtaining a faithful representation of the ab initio potential energies and forces, at a much-reduced cost<sup>8</sup>.

In addition, we also want to improve the sampling efficiency during the construction of HDNNPs. For this purpose, we will use DP-GEN (DP-Generator)<sup>10</sup>, an active learning scheme for DP. The core of the DP-GEN scheme lies in the "model deviation" strategy: a DP force field set is trained with different random seeds from the same training set, and the error size of the upper atomic forces on a given configuration is viewed by this force field set (expression given in Fig. S15 for the DPGEN original indicator), and thus determine whether the DP is already "familiar" with this configuration. The larger the error, the less familiar it is. If it is not "familiar", then continue to mark it; if it is "familiar", then skip it. In this way, the structures that are worth marking can be continuously filtered. Eventually, the force field can be improved. We give the default mode of DP-GEN to the DPGEN original slab in Fig. S15. More details for DP-GEN can be found in the original paper<sup>10</sup>.

# (2) The corresponding DPGEN workflows for the elemental distribution and adsorption energies.

When using DP-GEN for structural acquisition of this project's system, it is important to note that the default mode of the DP-GEN workflow set is built with MD as a sampler, which places more emphasis on force information. As in this paper, the MC is used as the sampler, force information is not useful. Similar to the adsorption energy, where we will discuss the adsorption on all the sites, indicating the force information is also not useful. Therefore, some adjustments need to be made to the DPGEN scheme.

#### a. Elemental distribution

The first is the elemental distribution. As we will discuss this through MC, for the labelling process, the sampler will be switched to MC. Compared with MD, MC simulation contains two characters, one is the forces are less important as we do not use force to run MC. This makes it unnecessary to get the force information when labeling; the second is atomic energy is especially important, because MC uses atomic energy to determine whether to accept the trial move.

Driven by this, the main attention should be paid to the handling of atomic energy. Firstly, it is important to note that in DP, although the construction of the force field is based on atomic energy, it only imposes a limit on the sum of the atomic energy of all the atoms. Therefore, if we only remove the force term in the loss function (see the indicator in DPGEN\_A panel in Fig. S15), but do not directly feed the atomic energy information into DP, the atomic energy predicted by DP will be very inaccurate. So the first thing to do is to add the atomic energy to the loss function (see loss function term in DPGEN\_A panel in Fig. S15), which can be done from the DeepMD-kit code. Secondly, this also means that we need to specify the atomic energy directly in the labelling process. However, unlike atomic forces, atomic energy cannot be generated during the running of the DFT code. So we choose to label the atomic energy information through a post-processing process, via the DFT energy difference between the presence/absence of each atom in the structure.

Gidden by this strategy, we will then propose our workflow for elemental distribution. Similar to DPGEN\_A, it also contains exploring, labelling and training processes.

For the labelling process, for a given MC structure Si, we use the following expression to calculate the atomic energy:

$$ae_{ij} = E_{S_i}^{DFT} - E_{S_i - j}^{DFT}$$
(Eq.9)

with  $E_{S_i}^{DFT}$  and  $E_{S_i-j}^{DFT}$  the DFT-based total energy of  $S_i$  and that of  $S_i$  without the *j*th atom. Both of them are single-point energy (*i.e.*, without structure optimization). Correspondingly, in the training process, the loss function will be switched into pure atomic energy term as well:

$$L(p_{ae}) = \frac{p_{ae}}{N} \Sigma_j |\Delta ae_j|^2$$
(Eq.10)

with  $\Delta ae_j$  root mean square (RMS) error in atomic energy. In addition, in the exploration process, the indicator for model deviation will be on the basis of the atomic energy:

$$\varepsilon = \max_{j} \sqrt{(\|ae_j - ae_j\|^2)}$$
(Eq.11)

Besides, for a miniature system of NP<sub>405</sub>, we will use a small slab model (with pbc and a total atomic number of 35) that contains 111, 100 surfaces along with the edges. The atomic ratio is the same as in the large NP<sub>405</sub>. The view of the structures is shown in Fig. S16.

The associated workflow, named DPGEN\_B, is put in the B panel in Fig. S15. One can compare the difference between it and DPGEN\_A, and the three subprocesses are marked as '1b. Exploration', '2b. Labeling' and '3b. Training', respectively.

#### **b.** Adsorption energies

Close to elemental distribution, we also used atomic energy to label the adsorption energy. We used the Alloy Catalysis Automated Toolkit (ACAT) to generate adsorption sites (1053 sites were generated, see Fig. S16). Afterwards, an initial force field was trained by calculating the adsorption energy of a certain number of sites. Then, the adsorption energies of all sites are obtained by model deviation, and the deviation converges after several iterations. The workflow we give in Fig. 1b.

It is worth noting that the following situation may occur during the structure optimization: for example, the original is in the bridge site, and during the optimization process, it runs to the fcc site. This situation should be avoided. Therefore, we invented a limited structure optimization method (denoted as lim\_str\_opt) to perform structure optimization. The abstracted algorithm of lim\_str\_opt is that once the program finds that the adsorbate has run into other sites during the structure optimization, it stops,

resets the adsorbate, fixes it, and re-optimizes it. In this way, it is ensured that the unstable sites are still labeled with an unstable energy. It does not matter if this unstable energy is in error or not, because the contribution of the unstable energy to the final result is small. The associated DPGEN workflow is given in Fig. S15.

#### S2.4 Machine learning and DFT parameters.

The training process was executed by DeePMD-kit package<sup>11</sup>. The codes achieve a high-dimensional neural network that preserves all the natural symmetries during structure analysis. Meanwhile, efficiently repeating indistinguishable with the DFTbased data will generate a small volume of the force field. During the learning process, the cut-off radius is set to be 5 Å. The maximum number of neighbor atoms that are treated by full relative coordinates is set as 50 for all atoms. The smoothing is set to begin from 1/5 to 2. The number of neurons in each hidden layer numbers of the embedding nets are 10, 20 and 40. The hidden layer numbers of the fitting net are 240, 240 and 240. The prefactors of energy and force loss at the start of the training are set to be 0.02 and 1000, while those at the limit of the training are set to be 2 and 1. The starting learning rate, the decay step and the decay rate are set as 0.001, 1000 and 0.95.

The structures selected by the exploration process will be calculated by DFT and then added to the DFT data set. It is carried on by Quantum Espresso. Perdew-Burke-Ernzerhof (PBE) functional for exchange-correlation and the ultrasoft pseudopotentials for nuclei and core electrons. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry.

#### S3 The definition of Af

Af is defined as the number of elements that meet a constraint divided by the total number of elements. The constraint can be a certain location, for instance, the surface, or a certain bond, for instance, the CuRu bond. The former is written as, *e.g.*, Af(Cu,Sur), which means the total surface Cu number divided by the total Cu number. The latter can be written as, for example, Af(Cu,Ru), which is defined as the total Cu number. Af for these two cases can be written generally as Af(M,sur) and  $Af(M_1,M_2)$ .



Fig. S1 Schematic of the synthesis procedures for HEA-NPs/TF, HEA-NPs/NF electrodes.



**Fig. S2** SEM images of a) FeNiCuWRu-NPs, b) FeNiCuWRu/TF, c) FeNiWRu/TF, c) FeNiRu/TF.



Fig. S3 SEM images of a) FeNiCuWRu/NF, b) FeNiWRu/NF, c) FeNiRu/NF.



**Fig. S4** a-b) Atomically resolved HAADF-STEM image of FeNiCuWRu (inset: corresponding FFT pattern), c) The elemental distribution obtained by line scan along the direction of the yellow arrows in Fig. 2g.



**Fig. S5** Strain curves obtained along the direction of the yellow arrow in Fig. 2f. Note: The closer to the stacking layer faults, the greater the strain.



Fig. S6 Cyclic voltammograms (CVs) of the prepared samples stripping between 0.5 V and 0.6 V vs. Ag/AgCl in 0.5 M  $H_2SO_4$ , respectively.



**Fig. S7** EDS elemental maps of Fe, Ni, Cu, W, Ru and O for FeNiCuWRu before (a) and after (b) HER testing.



**Fig. S8** The concentration of each metal ion in the electrolyte after 100 hours of HER and OER stability tests at a current density of 100 mA cm<sup>-2</sup>.



**Fig. S9** Using FeNiCuWRu as the working electrode: a) An H-type electrolytic cell was used, and the volume of hydrogen generated was measured every ten minutes using the water displacement method, with three parallel experiments conducted; b) The Faradaic efficiency of hydrogen evolution was obtained in the current density range of 10 mA cm<sup>-2</sup> to 250 mA cm<sup>-2</sup>.



**Fig. S10** a) Polarization curves of the electrocatalyst and its individual components in 1 M KOH for HER, b) Tafel plots for the HER derived from the LSV curves in Fig. S13a, c) EIS Nyquist plots of the set of samples, d) Chronopotentiometric curve of FeNiCuWRu at different current densities.



**Fig. S11** Cyclic voltammograms (CVs) of the prepared samples stripping between 0 V and 0.1 V *vs.* Hg/HgO in 1 M KOH, respectively.



Fig. S12 a-c) SEM images of FeNiCuWRu after 60 hours of long-term stability testing.



**Fig. S13** a) CV curves of FeNiCuWRu measured at 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution saturated with Ar and O<sub>2</sub>, respectively, b) LSV curves of FeNiCuWRu and Pt/C for ORR at 1600 rpm.

**Note:** The FeNiCuWRu-based high-entropy alloy exhibits almost no four-electron redox activity.



Fig. S14 Sections views of the MC process for FeNiWRu and FeNiRu.

ult MD	
<ul> <li>2a.Labeling</li> <li>Input: {S<sub>i</sub>}</li> <li>Labeler: DFT based forces and energy</li> <li>Output: {F<sub>ij</sub>}, {E<sub>i</sub>}</li> </ul>	<b>Ja. Training</b> <b>Input:</b> $\{F_{ij}\}, \{E_i\}$ <b>Trainer:</b> Deepnd-kit <b>Loss function:</b> $L(p_c, p_f) = \frac{P_c}{N} \Delta E^2 + \frac{P_f}{3N} \sum_i  \Delta F_i ^2$ Output: EE
nental Distribution	Output.11,
2b.Labeling ·	→ 3b.Training
<b>Input:</b> $\{S_i\}$ <b>Labeler:</b> DFT based atomic energy: $ae_{ij} \equiv E_{S_l}^{PFT} - E_{S_l-j}^{PFT}$	Input: $\{ae_{ij}\}$ Trainer: Deepmd-kit Loss function:
Output: {ae <sub>ij</sub> }	$L(p_{ae}) = \frac{rae}{N} \sum_{i}  \Delta ae_{i} ^{2}$ Output: FF <sub>b</sub>
<b>&gt;</b> 2c.Labeling	3c.Training
Input: $\{S_i^H\}$ Labeler: $\Delta G_{Hi}$ calculated by DFT based lim_str_opt. $ae_i^H \equiv \Delta G_{Hi}$ Output: $\{ae_i^H\}$	Input: $\langle ae_{ij} \rangle$ Trainer: modified Deepmd-kit Loss function: $L(p_{ae^H}) = \frac{p_{ae^H}}{N} \sum_i  \Delta ae_i^H ^2$
	ult MD - 2a.Labeling Input: $\{S_i\}$ Labeler: DFT based forces and energy Output: $\{F_{ij}\}, \{E_i\}$ nental Distribution - 2b.Labeling Input: $\{S_i\}$ Labeler: DFT based atomic energy: $ae_{ij} \equiv E_{S_i}^{PFT} - E_{S_i-j}^{PFT}$ Output: $\{ae_{ij}\}$ orption energy - 2c.Labeling Input: $\{S_i^H\}$ Labeler: $\Delta G_{Hi}$ calculated by DFT based Im_str_opt. $ae_i^H \equiv \Delta G_{Hi}$ Output: $\{ae_{ij}^H\}$

s<sub>i</sub>: *i*th structure  $S_i^H$ : local structure of *i*th H adsorption site cut model with the radius of 5A to H) ij: *j*th atomic forces for S<sub>i</sub> **ae<sub>ij</sub>:** *j***th atomic energy for S<sub>i</sub>**  $ue_{i}^{H}$  atomic energy of *i*th H  $p_arepsilon, p_f, p_{ae}$  : prefactors of total energy, orces, and atomic energy that are free to change during the optimization process **LE,**  $\Delta f_{i_i} \Delta a e_i$ ,  $\Delta a e_i^H$  :root mean square RMS) error in energy, force, atomic energy, and atomic energy of H on site i. **N**: total number of the atoms.  $S_{S_i}^{DFT}$ : DFT based total energy of  $S_i$  $S_{S_i-j}^{DFT}$ : DFT based total energy of  $S_i$  without he *j*th atom Fa, FFb, FFc: The trained force field for DEPGEN panel A, B and C.

**Fig. S15** The DPGEN workflow scheme was employed for calculating elemental distribution and adsorption energy, with reference to the default version of DPGEN.



**Fig. S16** The structures of NP405 for FeNiRu, FeNiRuW and CuFeNiRuW. The grid is assigned by ACAT.



Fig. S17 Computed activity for HER and OER.



Fig. S18 a) The histograms of  $\Delta G_0$  for FeNi-LDH. b) The spatial-specific values are plotted alongside, with the boxes representing the positions and the colors indicating the  $\Delta G_0$ .



**Fig. S19** a) The chemical potentials of Fe and Ni in FeNiCuWRu, FeNiWRu and FeNiRu. b) Computational modeling. The value of the chemical potential is calculated based on the energy difference between the cases with and without the studied atoms (labeled in red).



Fig. S20 The bonding modes for the active sites of HER and OER.



Fig. S21 The physical picture of rechargeable zinc-based hydrogen battery.



**Fig. S22** Polarization curves (left-hand y-axis) and power densities (right-hand y-axis) of proton exchange membrane and bipolar membrane.



Fig. S23 a) OCV for FeNiCuWRu-equiped  $H_2$ -generation zinc battery (inset shows the digital photograph of OCV), b) Polarization curves (left-hand y-axis) and power densities (right-hand y-axis) for the  $H_2$ -generation zinc battery, c) Plot of voltage versus specific capacity.



**Fig. S24** Polarization curves (left-hand y-axis) and power densities (right-hand y-axis) for the H<sub>2</sub>-generation zinc battery using FeNiCuWRu, FeNiWRu, FeNiRu, TF in symmetric electrolyte 1 M H<sub>2</sub>SO<sub>4</sub> (cathode) + 1 M Na<sub>2</sub>SO<sub>4</sub> (anode).



Fig. S25 a) OCV of  $H_2$ -generation zinc battery based on FeNiCuWRu, b) Polarization curves (left-hand y-axis) and power densities (right-hand y-axis) for the  $H_2$ -generation zinc battery using FeNiCuWRu, FeNiWRu, FeNiRu, TF in symmetric electrolyte 4 M NaOH (cathode) + 4 M NaOH (anode).



Fig. S26 a) The charging and discharging voltage platforms correspond to different current densities during OER charging, b) Galvanostatic discharge and charge profiles of  $H_2$ -generation zinc battery at a current density of 200 mA cm<sup>-2</sup>.



Fig. S27 a) Physical photo of the zinc anode after charging, b) XRD image of the powder scraped from the deposited surface.



**Fig. S28** a) CV curve of Pt/C in 1 M KOH + 0.1 M glycerol solution saturated with Argas. Scan rate: 50 mV s<sup>-1</sup>, b) Charge/Discharge polarization curves for FeNiCuWRuequiped H<sub>2</sub>-generation zinc battery (Black: FeNiCuWRu as anode, Purple: Commercial Pt/C as anode).



Fig. S29 <sup>1</sup>H NMR standard spectra of the organic products that could be formed by oxidizing glycerol. For each NMR measurement, the sample is made by mixing 100  $\mu$ L of D<sub>2</sub>O (containing the dimethyl sulfoxide (DMSO) internal standard) with 500  $\mu$ L of 4 M NaOH + 0.1 M zinc acetate solution.



**Fig. S30** Digital photograph of a fuel battery stack consisting of six H<sub>2</sub>-generation zinc batteries stacked in series with electrolyte. a) Open circuit voltage for six single HEA-equiped batteries connected in series, b) a fan and a set of LEDs can be powered up simultaneously, c) The open circuit voltage of the battery stack can reach 3.91 V when the external circuit is connected with three batteries in series and two groups in parallel, d) Digital photograph of a one-button start prototype that charges a cell phone while generating hydrogen.



Fig. S31 Assembly diagram of the  $H_2$ -generation zinc fuel battery stack.

Note: The cathode lattice-type flow field structure facilitates the rapid removal of hydrogen gas.



Fig. S32 a) Polarization curves (left-hand y-axis) and power (right-hand y-axis) for the single stack structure using Pt/C ( $6 \text{ cm} \times 6 \text{ cm}$ ), b) long-term durability tests for the single stack structure at a current of 1 A.

**Video S1.** Video of the actual operation of a prototype with one-touch start-stop functionality, which is based on six high-power zinc-based hydrogen production batteries (cathode area:  $3 \text{ cm} \times 3 \text{ cm}$ ).

**Video S2.** Video of the actual operation of a single stack component designed based on Fig. 7e and Fig. S31 (Pt/C: cathode area  $6 \text{ cm} \times 6 \text{ cm}$ ).

Table S1. Summarized overpotentials at 10 mA cm<sup>-2</sup> ( $\eta_{10}$ ) and Tafel slopes of electrocatalysts for HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Catalysts	η 10 (mV)	Tafel slope (mV dec <sup>-1</sup> )	References
FeNiCuWRu	49	32.4	This work
$Al_{80}Ni_6Co_3Mn_3Y_5Au_3\\$	70	39	12
CoPS nanoplates	48	56	13
PdCu@Pd NCs	68	35	14
MoNiCoFeCr-1150	107	41	15
IrNiTa/Si	99	35	16
Pt ML/Au NF	100	53	17
Pt <sub>1</sub> /OLC	38	36	18
Pt-MoS <sub>2</sub>	80	40	19
Pt@PCM	105	63.7	20
Li-PPS NDs	91	29	21
MoS <sub>x</sub> /NCNT	110	40	22
FeP NPs	50	37	23
MoP S	64	50	24
Ni <sub>2</sub> P pellet	42	38	25
Ru/MeOH/THF	83	46	26
Ni@Ni <sub>2</sub> P-Ru	51	35	27

Catalysts	Substrates	η <sub>10</sub> (mV)	Tafel slope (mV dec <sup>-1</sup> )	References
FeNiCuWRu	Nickel foam	267	43	This work
Fe-Mn-ONSs /CC	Carbon cloth	273	63.9	28
Mo-NiP <sub>x</sub> /NiS <sub>y</sub>	Nickel foam	137	49	29
P-Ni <sub>0.5</sub> Fe@C	GCE	256	65	30
NiFe LDH	GCE	300	40	31
$Co_3Fe_{1.5}$ -O	GCE	284	60	32
Fe <sub>3</sub> N/Fe <sub>4</sub> N	Nickel foam	238	44.5	33
HEAN@NPC/CC- 450	Carbon Cloth	263	43	34
$CoS_{4.6}O_{0.6}$	GCE	290	67	35
NiCoP/C	GCE	330	96	36
Co <sub>3</sub> O <sub>4</sub> /N-G	Nickel foam	310	67	37

Table S2. Summarized overpotentials at 10 mA cm<sup>-2</sup> ( $\eta_{10}$ ) and Tafel slopes of electrocatalysts for OER in 1 M KOH.

GCE stands for Glassy Carbon Electrode.

Table S3. Comparison of the assembled  $H_2$ -generation zinc battery with other

Catalysts	Electrolyte (catholyte//anolyte)	Open circuit voltage(V)	Actual operating current density (mA cm <sup>-2</sup> )	Power density <sub>max</sub> (mW cm <sup>-2</sup> )	Energy density /Wh Kg <sub>Zn</sub> <sup>-1</sup> (@mA cm <sup>-2</sup> )	Ref.
FeNiCuWRu @TF	2 M H <sub>2</sub> SO <sub>4</sub> // 4 M NaOH	1.31	500	537	934.51@100	This work
Mo-WC@NCS	0.5 M H <sub>2</sub> SO <sub>4</sub> // 1 M KOH	1.08	10	41.4	-	38
Mo <sub>2</sub> C-Ru/C	2 M H <sub>2</sub> SO <sub>4</sub> // 4 M NaOH	1.23	10	54	-	39
Pt/CNTs	2 M H <sub>2</sub> SO <sub>4</sub> // 4 M NaOH	1.249	10	80	934@10	40
Cu <sub>6</sub> S <sub>6</sub> / CP	0.05 M H <sub>2</sub> SO <sub>4</sub> // 4 M NaOH	1.18	10	65.6	875@10	41
Ru/3DNCN	2 M H <sub>2</sub> SO <sub>4</sub> // 4 M NaOH	1.26	20	126.5	966@10	42
Siloxene-p-Pt-2h	2 M H <sub>2</sub> SO <sub>4</sub> // 6 M KOH	1.27	15	157	-	43
MoP@NMC	2 M H <sub>2</sub> SO <sub>4</sub> // 4 M KOH	1.19	10	89.7	809@10	44
Co <sub>2</sub> P-CuP <sub>2</sub> /NF	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub>	0.93	10	19.8	-	45
$Co_2N_{0.67}/CoMoO_4$	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub>	-	10	20	-	46
CrP-Re <sub>2</sub> P/NF	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub>	1.04	10	8.8	-	47
Ni-MOF/Ni <sub>2</sub> P @EG	1 M KOH	-	5	4.1	-	48
Mo-Co <sub>0.85</sub> Se <sub>VSe</sub>	1 M KOH	-	10	3.9	-	49

recently reported  $H_2$ -generation Zn-based batteries.

Catalysts	Electrolyte	Power density <sub>max</sub> /mW cm <sup>-2</sup>	Specific Capacity /mAh g <sub>Zn</sub> <sup>-1</sup> (@mA cm <sup>-2</sup> )	Energy density /Wh Kg <sub>Zn</sub> <sup>-1</sup> (@mA cm <sup>-2</sup> )	Ref.
FeNiCuWRu@ TF	(catholyte) 2 M H <sub>2</sub> SO <sub>4</sub> // (anolyte) 4 M NaOH	537	819@300	934.51@100	This work
Fe-N-C	6 M KOH <sup>a</sup>	175	775.7@10	1040@10	50
Co <sub>2</sub> Fe <sub>1</sub> @NC	6 M KOH <sup>b</sup>	423.7	812.5@20	1011.5@20	51
Co–N <sub>x</sub> /C NRA	6 M KOH <sup>a</sup>	193.2	-	853.12@5	52
PtIr	6 M KOH	166.5	-	-	53
np-AlFeCoNiCr	6 M KOHª	125	800@20	943.7@20	54
Ni-MnO/rGO	6 M KOH <sup>b</sup>	123	758@5	930@5	55
Co/Co <sub>3</sub> O <sub>4</sub> @PGS	6 M KOHª	118.27	-	-	56
Meso- CoNC@GF	6 M KOH	154.4	-	-	57
Co <sub>4</sub> N/CNW/CC	6 M KOH <sup>a</sup>	174	701@50	-	58
Mn <sub>3</sub> O <sub>4/</sub> C	4 M KOH	317	-	-	59
Pt <sub>1.1%</sub> Fe <sub>8.8%</sub> Ni PF	6 M KOH <sup>a</sup>	175	816@20	856.4@50	60
Co <sub>3</sub> O <sub>4</sub> @carbon cloth	CCNF-PDIL SSEs	135	700@5	847@5	61
NiO/ CoN PINWs	6 M KOH <sup>a</sup>	79.6	690@5	945@5	62
C-MOF-C2	6 M KOH	105	768@5	-	63
Mn-RuO <sub>2</sub>	6 M KOH <sup>a</sup>	119	812@10	-	64
NiFe@NC <sub>X</sub>	6 M KOH	88	583.7@10	732.3@10	65
Porous carbon nanosphere	6 M KOH	224	786@20	874@20	66
Mn-SAS/CN	6 M KOH	220	780@10	-	67
FeCo/Co <sub>2</sub> P@NP CF	6 M KOH <sup>a</sup>	154	-	-	68
Bambooshaped fibrous	30wt% KOH solution-filled A-PAA hydrogel	160	745@5	915@5	69
(Co,Fe) <sub>3</sub> N_2D	6 M KOH <sup>a</sup>	234	-	-	70

**Table S4.** Comparison of  $H_2$ -generation Zn-based battery with the best recentlyreported conventional alkaline Zn-air batteries.

<sup>a</sup> Because the application is focused on rechargeable Zn-air batteries, the electrolyte is combined with a zinc salt such as  $0.2 \text{ M Zn}(\text{CH}_3\text{COO})_2$ .

 $^{\text{b}}$  the electrolyte is combined with 0.2 M ZnCl\_2.

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