

Electronic Supplementary Information

Electrochemical Neutralization Energy: From Concept to Devices

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(1) The second law in chemical thermodynamics

For a spontaneous chemical process in a closed system at constant temperature (T) and pressure (p) without non-PV work, the Clausius inequality $\Delta S > Q/T$ transforms into a condition for the change in Gibbs free energy: $\Delta G < 0$.

Thus, a negative value of the change in free energy (ΔG) is a necessary condition for a process to be spontaneous, where free-energy changes can be calculated from enthalpies of formation and standard molar entropies of reactants and products by the equation 1:

$$\Delta_r G^\theta = \Delta_r H^\theta - T\Delta S^\theta \quad (1)$$

where $\Delta_r G^\theta$ is standard Gibbs free energy change, $\Delta_r H^\theta$ is standard molar enthalpy change, ΔS^θ is standard molar entropy change, and T is the temperature the reaction taken place.

In addition, since G is a state function, $\Delta_r G^\theta$ can be calculated directly from the standard free energy of formation values (ΔG_f^θ) of products and reactants, by the equation 2:

$$\Delta_r G^\theta = \sum n\Delta G_f^\theta(\text{products}) - \sum m\Delta G_f^\theta(\text{reactants}) \quad (2)$$

Therefore, based on the data in **Table S1**, the standard Gibbs free energy change ($\Delta_r G^\theta$) of acid-base neutralization reaction ($H^+ + OH^- = H_2O$) can be calculated by:

$$\begin{aligned} \Delta_r G^\theta &= \Delta_r H^\theta - T\Delta S^\theta \\ &= \{\Delta_f H^\theta(H_2O) - \Delta_f H^\theta(H^+) - \Delta_f H^\theta(OH^-)\} - 298.15 \times \{S^\theta(H_2O) - S^\theta(H^+) - S^\theta(OH^-)\} \\ &= \{-285.83 - 0 - (-229.994)\} - 298.15 \times \{69.91 - 0 - (-10.75)\} \times 10^{-3} \\ &\approx -79.9 \text{ kJ/mol} \end{aligned}$$

Or it can be directly calculated by:

$$\begin{aligned} \Delta_r G^\theta &= \sum n\Delta G_f^\theta(\text{products}) - \sum m\Delta G_f^\theta(\text{reactants}) \\ &= \Delta G_f^\theta(H_2O) - \Delta G_f^\theta(H^+) - \Delta G_f^\theta(OH^-) = -237.129 - 0 - (-157.244) \\ &\approx -79.9 \text{ kJ/mol} \end{aligned}$$

Table S1 Thermochemical data (standard molar enthalpy of formation ($\Delta_f H^\theta$), standard molar entropy (S^θ), and standard Gibbs free energy of formation (ΔG_f^θ) of some substances at 298.15 K. (Data redirected from Ref¹)

Substance	Standard molar enthalpy of formation ($\Delta_f H^\theta$) (kJ mol ⁻¹)	Standard molar entropy (S^θ) (J K ⁻¹ mol ⁻¹)	Standard Gibbs free energy of formation (ΔG_f^θ) (kJ mol ⁻¹)
H ⁺	0	0	0
OH ⁻	-229.994	-10.75	-157.244
H ₂ O (l)	-285.83	69.91	-237.129
H ₂ (g)	0	130.684	0
O ₂ (g)	0	205.138	0
Na ⁺	-240.12	59.0	-261.905
K ⁺	-252.38	102.5	-283.27
SO ₄ ²⁻	-909.27	20.1	-744.53
Na ₂ SO ₄ (s)	-1387.08	149.58	-1270.16
NaOH (s)	-425.609	64.455	-379.494
Zn	0	41.6	0
Zn ²⁺	-153.89	-112.1	-147.06
ZnO (s)	-348.28	43.64	-318.30
Mn ²⁺	-220.75	-73.6	-228.1
MnO ₂ (s)	-520.0	53.1	-465.2

(2) Bipolar membrane electro dialysis (BMED)

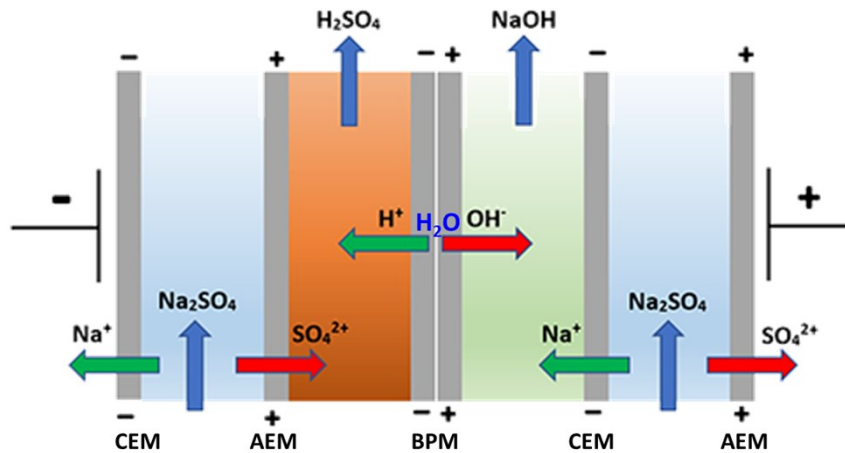


Fig. S1 Schematic diagram of bipolar membrane electro dialysis (BMED) process for production of acid and base.

Electrodialysis (ED) is a process that the salt ions transport from one solution through an ion-exchange membrane to another solution under the driven force from applied electric potential. **Bipolar membrane electro dialysis (BMED)** is a special form of ED that oppositely charged ions transport from the bipolar membrane to the opposite directions under applied potential. **Fig. S1** shows a representative device configuration of applying BMED for the production of acid and base. The electro dialytic cell consists of multiple compartments and separated by ion-exchange membranes (AEM and CEM) and bipolar membrane (BPM). As can be seen, when feeding salts solutions between the AEM and CEM, the cations (Na⁺) and anions (SO₄²⁻) move across the monopolar ion-exchange membranes under the applied potential, and combine with the OH⁻ and H⁺ ions generated from water dissociation at the BPM to form acid and base. The potential needed for the water dissociation in BPM is 0.828 V.²

(3) Reverse Electrodialysis (RED)

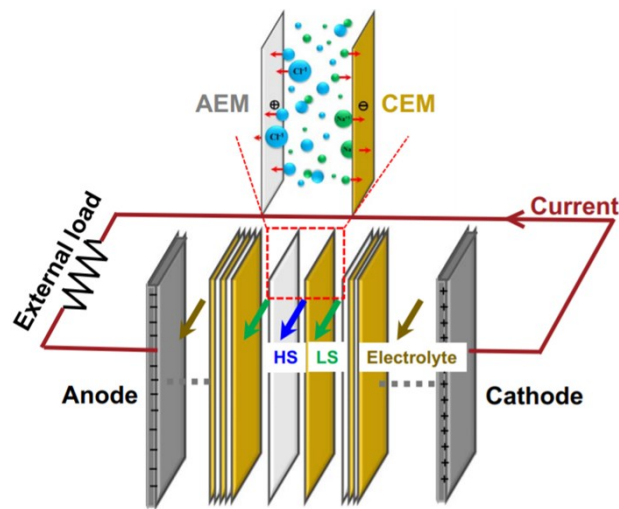


Fig. S2 Schematic diagram of a reverse electrodialysis (RED) stack connected to an external electric load. Reprinted with permission from ref.³. Copyright 2018 Elsevier Ltd.

Reverse electrodialysis (RED) is a technology for harvesting salinity gradient power (SGP).^{3, 4} A typical RED stack comprises of alternately stacked cation-exchange membranes (CEMs) and anion-exchange membrane (AEMs) to form flow compartments of high salinity streams (HSS) and low salinity streams (LSS), as shown in **Fig. S2**. Generally, seawater and fresh water are used as the HSS and LSS, respectively, to harvest the SGP. Cations and anions in the HSS transport to LSS through CEM and AEM in opposite directions under their respective concentration gradients, leading to convert the chemical potential difference between salt and fresh water to electricity by coupling redox reactions on the two electrodes.

(4) Device Configuration for Galvanic and Electrolytic Cells to Properly Harvest ENE

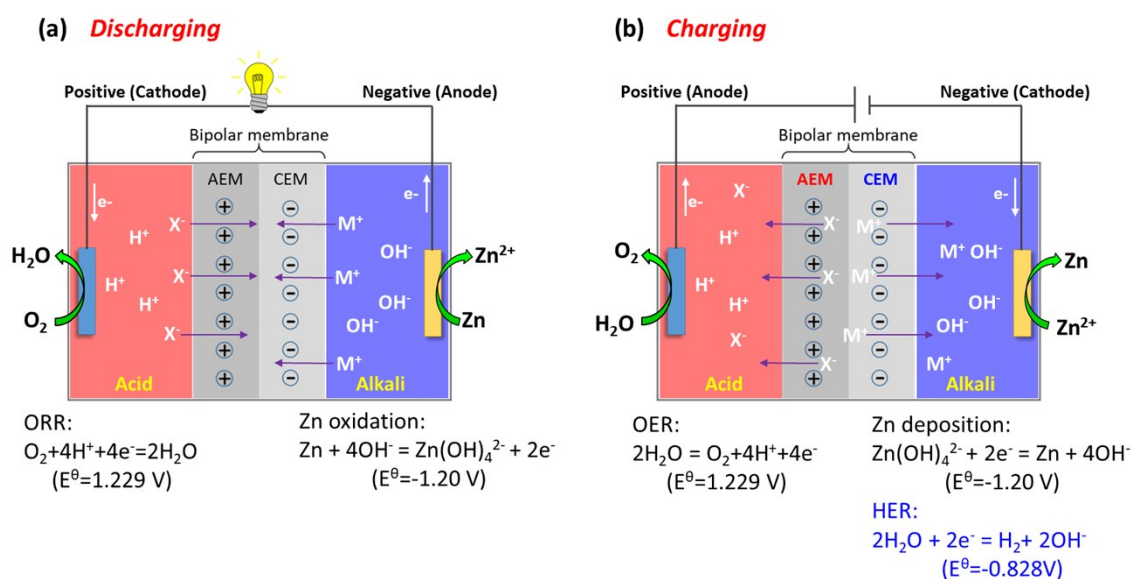


Fig. S3 Schematic illustration of the device configurations for an acid-base asymmetric galvanic cell (e.g., Zn-air battery) during discharging (a) and charging (b). During discharging, the H^+ and OH^- are consumed on positive (cathode) and negative (anode) electrodes, respectively; the ENE is contributing to enlarge the output voltage. During charging, the electrodes are reversed, the positive electrode (anode) is in the acidic electrolyte and the negative electrode (cathode). In this situation, the water decomposition potential is enlarged due to shift of HER and OER, thus widening the operating potential window. Noting that even though the potential for Zn reduction is more negative than HER in alkaline electrolyte, the overpotential for HER is high in practice, so the Zn reduction is still preferred to occur.

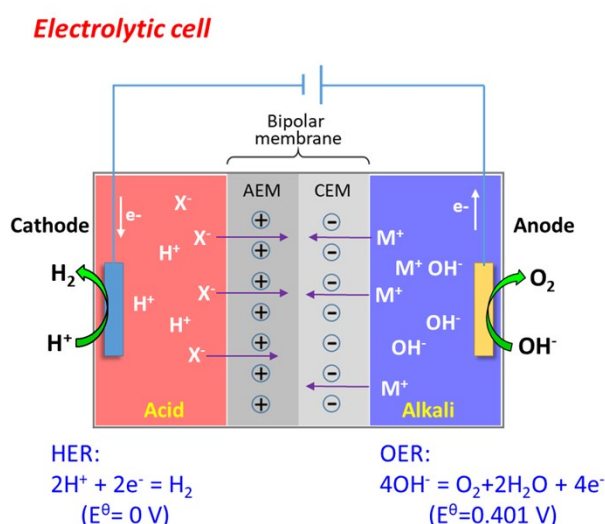
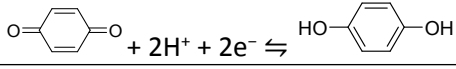


Fig. S4 Schematic illustration of the device configurations for an acid-base asymmetric electrolytic cell (e.g., water electrolysis).

(5) pH-sensitive Electrochemical Redox Reactions

Table S2. Half reactions and standard electrode potentials of some pH-sensitive redox reactions (Data redirected from Wikipedia⁵)

Electrode reaction Under acidic condition (pH=0)	Standard electrode potential (E^θ)
$\text{ZrO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Zr}(\text{s}) + 2\text{H}_2\text{O}$	-1.553 V
$\text{TiO}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ti}(\text{s}) + \text{H}_2\text{O}$	-1.31 V
$\text{SiO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Si}(\text{s}) + 2\text{H}_2\text{O}$	-0.91 V
$\text{B}(\text{OH})_3(\text{aq}) + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{B}(\text{s}) + 3\text{H}_2\text{O}$	-0.89 V
$\text{TiO}^{2+} + 2\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Ti}(\text{s}) + \text{H}_2\text{O}$	-0.86 V
$\text{Bi}(\text{s}) + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{BiH}_3$	-0.8 V
$2\text{TiO}_2(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ti}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}$	-0.56 V
$\text{MoO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Mo}(\text{s}) + 2\text{H}_2\text{O}$	-0.15 V
$\text{WO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{W}(\text{s}) + 2\text{H}_2\text{O}$	-0.12 V
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCOOH}(\text{aq})$	-0.11 V
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}$	-0.11 V
$\text{SnO}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s}) + \text{H}_2\text{O}$	-0.1 V
$\text{SnO}_2(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{SnO}(\text{s}) + \text{H}_2\text{O}$	-0.09 V
$\text{WO}_3(\text{aq}) + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{W}(\text{s}) + 3\text{H}_2\text{O}$	-0.09 V
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0 V
$\text{Fe}_3\text{O}_4(\text{s}) + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}$	0.085 V
$\text{H}_2\text{MoO}_4(\text{aq}) + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{Mo}(\text{s}) + 4\text{H}_2\text{O}$	0.11 V
$\text{HCHO}(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{OH}(\text{aq})$	0.13 V
$\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	0.19 V
$\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Sb}(\text{s}) + \text{H}_2\text{O}$	0.2 V
$\text{GeO}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ge}(\text{s}) + \text{H}_2\text{O}$	0.26V
$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O}$	0.34 V
$\text{H}_2\text{MoO}_4 + 6\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Mo}^{3+} + 2\text{H}_2\text{O}$	0.43 V
$\text{CH}_3\text{OH}(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}$	0.5 V
$\text{CO}(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{C}(\text{s}) + \text{H}_2\text{O}$	0.52 V
$\text{H}_2\text{MoO}_4(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MoO}_2(\text{s}) + 2\text{H}_2\text{O}$	0.65 V
	0.6992 V
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	0.7 V
$\text{NO}_3^-(\text{aq}) + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{NO}_2(\text{g}) + \text{H}_2\text{O}$	0.8 V
$\text{MnO}_4^- + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HMnO}_4^-$	0.9 V

$\text{MnO}_2(\text{s}) + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Mn}^{3+} + 2\text{H}_2\text{O}$	0.95 V
$\text{Ag}_2\text{O}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Ag}(\text{s}) + \text{H}_2\text{O}$	1.17 V
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.229 V
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23 V
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33 V
$\text{CoO}_2(\text{s}) + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Co}^{3+} + 2\text{H}_2\text{O}$	1.42 V
$\beta\text{-PbO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46 V
$\alpha\text{-PbO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.468 V
$2\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Br}_2(\text{l}) + 6\text{H}_2\text{O}$	1.48 V
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51 V
$\text{NiO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Ni}^{2+} + 2\text{H}_2\text{O}$	1.59 V
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$	1.7 V
$\text{AgO}(\text{s}) + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ag}^+ + \text{H}_2\text{O}$	1.77 V
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1.78 V
$\text{HMnO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$	2.09 V
$\text{F}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HF}(\text{aq})$	3.05 V
Electrode reaction	
Under alkaline condition (pH=14)	Standard electrode potential (E^0)
$\text{Al}(\text{OH})_4^- + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s}) + 4\text{OH}^-$	-2.33 V
$\text{Al}(\text{OH})_3(\text{s}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s}) + 3\text{OH}^-$	-2.31 V
$\text{BH}_4^- + 2\text{OH}^- \rightleftharpoons \text{BH}_3\text{OH}^- + \text{H}_2\text{O} + 2\text{e}^-$	-1.24 V
$\text{Zn}(\text{OH})_4^{2-} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s}) + 4\text{OH}^-$	-1.199 V
$\text{Fe}(\text{OH})_2(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s}) + 2\text{OH}^-$	-0.89 V
$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-$	-0.828 V
$\text{MH}_x + \text{OH}^- \rightleftharpoons \text{MH}_{x-1} + \text{H}_2\text{O} + \text{e}^-$	-0.8~-0.83 V
$\text{CH}_3\text{OH} + 6\text{OH}^- \rightleftharpoons \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$	-0.81 V
$\text{PbO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + 2\text{OH}^-$	-0.58 V
$\text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{Cu}(\text{s}) + 2\text{OH}^-$	-0.36 V
$\text{HgO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Hg}(\text{l}) + 2\text{OH}^-$	0.0977 V
$\text{N}_2\text{H}_4(\text{aq}) + 4\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{NH}_4^+ + 4\text{OH}^-$	0.11 V
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	0.401 V
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 4\text{OH}^-$	0.59 V
$2\text{FeO}_4^{2-} + 5\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + 10\text{OH}^-$	0.81 V

(6) Bipolar Membrane

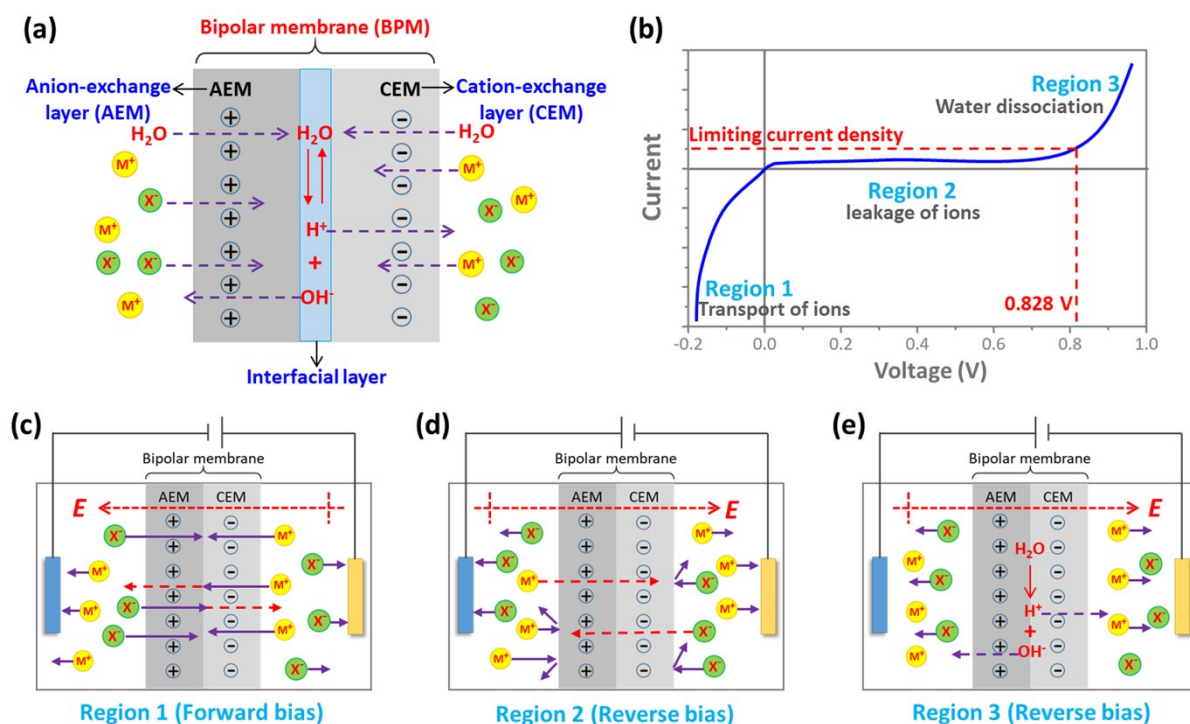
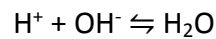


Fig. S5 Structure and electrochemical behavior of bipolar membrane: (a) Schematic illustration of the structure and function of bipolar membrane. (b) Typical I-V curve of bipolar membrane under forward and reverse bias (Reproduced based on Ref.⁶). (c-e) The membrane function and ions transport profiles under applied voltage bias corresponding to the three regions in the I-V curve.

Fig. S5a illustrates the representative structure and function of a BPM. As can be seen, only the oppositely charged ions can penetrate the membrane from each site (under open circuit or forward bias conditions); or H^+ and OH^- generated from water dissociation under a reverse bias can across the membrane to the two compartments. Due to the special architecture, BPM shows current rectification behavior under an electric field in aqueous solution, which is analogous to the p-n junction of inorganic semiconductors. **Fig. S5b** presents a typical I-V curve of a BPM at various applied voltage bias.⁶ The I-V curve can be divided into three regions. When applying a forward bias voltage (Region 1 in **Fig. S5b**), the BPM exhibits high conductivity due to the migration of ions into the membrane (**Fig. S5c**). However, in this case, the continuous accumulation of ions in the BPM will compensate the fixed charges in the membrane, resulting in the Donnan exclusion effect be less effective and then some ions may even cross the adjacent membrane and enter into the electrolyte on the other side (*i.e.*, ion crossover might happen). Under reverse bias, when a voltage is applied below the

thermodynamic potential of water dissociation (0.828 V) (Region 2 in **Fig. S5b**), the BPM shows a small current density less than a certain value, which called limiting current density.⁷ Below this limiting current density, the electric current is contributed by the leakage of counter-ions which migrate from one side to another (**Fig. S5d**), attributing to that the BPM is not strictly permselective. In other words, the limiting current density is indicative to the permselectivity of BPM. It has been reported that the water dissociation rate in the BPM is much higher than that in conventional bulk solution, due to the second Wien effect.⁸ In addition, the water dissociation might occur at a voltage lower than the theoretic potential of 0.828 V,⁹ and the water dissociation property in BPM could be further promoted by incorporation of water dissociation catalyst on the interfacial layer.^{8, 10} When applying a voltage exceeding the thermodynamic potential (0.828 V) of water dissociation (Region 3 in **Fig. S5b**), water will be split into H⁺ and OH⁻. Then, the transport of H⁺ and OH⁻ through AEM and CEM to the two compartments dominates the conduction in the membrane (**Fig. S5e**).

(7) Estimation of the wasted energy of acid-base neutralization



Assuming the global annual waste acids are equivalent to 100 million tons of concentrated H_2SO_4 , where the molar amount of protons (H^+) will be:

$$N = 2 \times \frac{100 \times 10^6 \times 10^3 \times 10^3 \times 98\% \text{ g}}{98.079 \text{ g mol}^{-1}} \approx 2.0 \times 10^{12} \text{ mol}$$

Then, if all of them are neutralized, the generated heat will be:

$$Q = 2.0 \times 10^{12} \times 55.84 \approx 1.11 \times 10^{14} \text{ kJ} \approx 30 \text{ TWh}$$

If they are harvested to convert to electricity, the generate power will be:

$$Q = 2.0 \times 10^{12} \times 79.9 \approx 1.6 \times 10^{14} \text{ kJ} \approx 44 \text{ TWh}$$

Noting the concentration of concentrated H_2SO_4 is 98%, the molar mass of H_2SO_4 is 98.079 g/mol, the standard molar enthalpy change ΔH^\ominus is -55.84 kJ/mol, and the standard molar Gibbs free energy change (ΔG^\ominus) is -79.9 kJ/mol⁻¹. 1 kJ=1/3.6 Wh.

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