

Supporting Information

Strategic Usage of Redox Active Materials and Sacrificial Zinc Electrode for Spontaneous Hydrogen Evolution Reaction

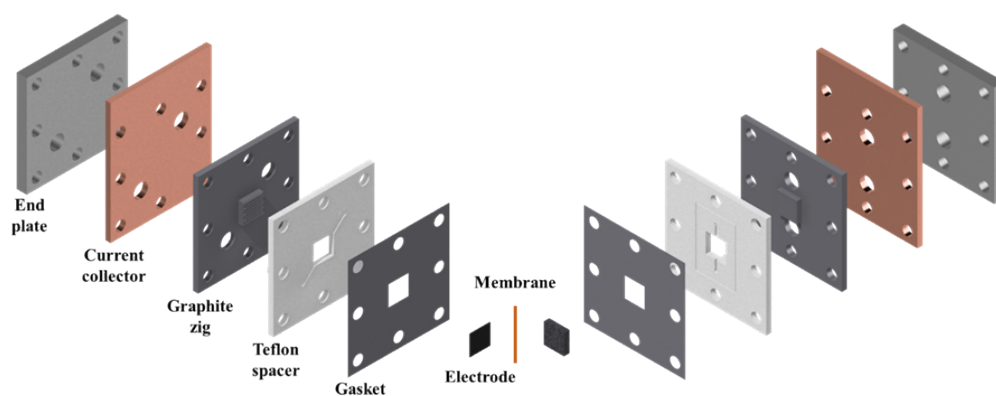
Tae Yup Jeong,^{a,‡} Chandan Chandru Gudal,^{a,‡} Byeongkyu Kim,^a Yong Seok Kim,^a Tae Yeon
Ha,¹ Anki Reddy Mule,^a Pil J. Yoo,^a Chan-Hwa Chung^{*a}

School of Chemical Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

*E-mail: chchung@skku.edu

‡ These two authors contributed equally to this work

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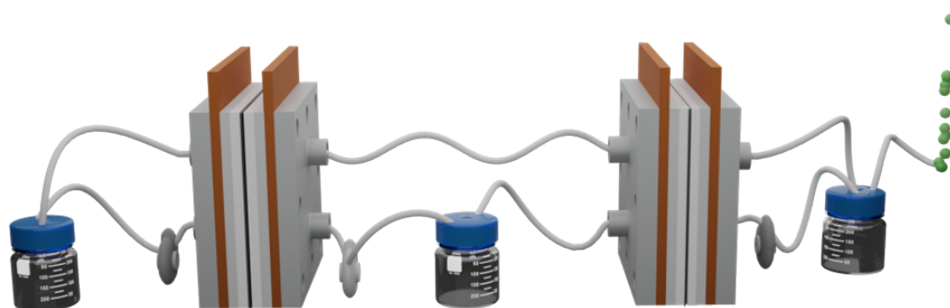


Fig. S1 (a) Open arrangement of individual parts in a typical module and (b) 3D perspective view of the assembled modules.

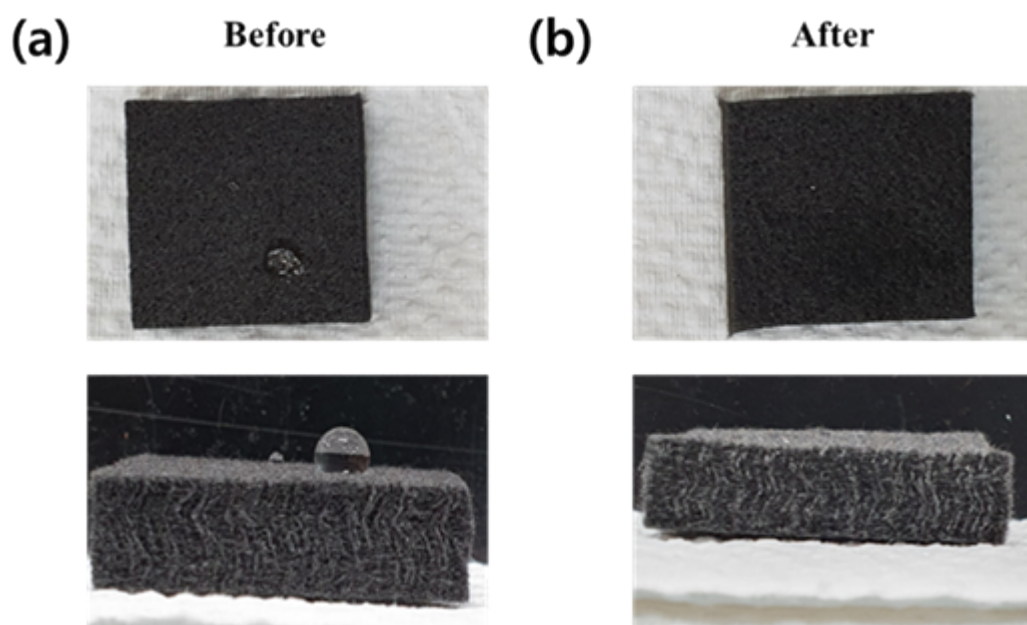


Fig. S2 Digital images of carbon felt (a) before and (b) after pretreatment process.

S1. Half-cell Electrochemical measurements

Prior to the implementation of the electrodes and electrolytes including the RAM in the designed system. These are analyzed electrochemically for a better understanding of their behavior under conditions similar to full-cell tests. The half-cell tests were carried out in ZENNIUM, ZAHNER (Germany) system. Cyclic voltammetry (CV) of DHBQ is done where the electrolyte concentration is 0.01 M DHBQ with 1 M KOH solution. Here, the size of $1 \times 1 \text{ cm}^2$ bare CF, $1 \times 3 \text{ cm}^2$ Pt plate, and silver chloride (Ag/AgCl, 3 M NaCl) are used as working (WE), counter (CE), and reference electrodes (RE), respectively. The linear sweep voltammetry (LSV) of Zn foil as WE, Pt plate as CE, and Ag/AgCl, 3 M NaCl as RE in 5 M KOH solution, and Pt/C on carbon paper as WE, Pt plate as CE, and mercury sulfate ($\text{Hg}/\text{Hg}_2\text{SO}_4$, 1 M K_2SO_4) in 1 M HCl solution are analyzed. The reversibility of the reduction/oxidation reactions of DHBQ (5, 10, 20, and 50 mV/s) is confirmed in Fig. S1(a). At the current density of $10 \text{ mA}/\text{cm}^2$, Zn foil in 5 M KOH and CF in 0.01 N DHBQ with 1.02 M KOH performed -1.37 and -0.74 V (vs. SHE) (Fig. S2(b)). At the current density of $10 \text{ mA}/\text{cm}^2$, Pt/C in 1 M KOH and CF in 0.01 M DHBQ with 1.02 M KOH performed -0.67 and -0.10 V (vs. SHE) (Fig. S2(b)).

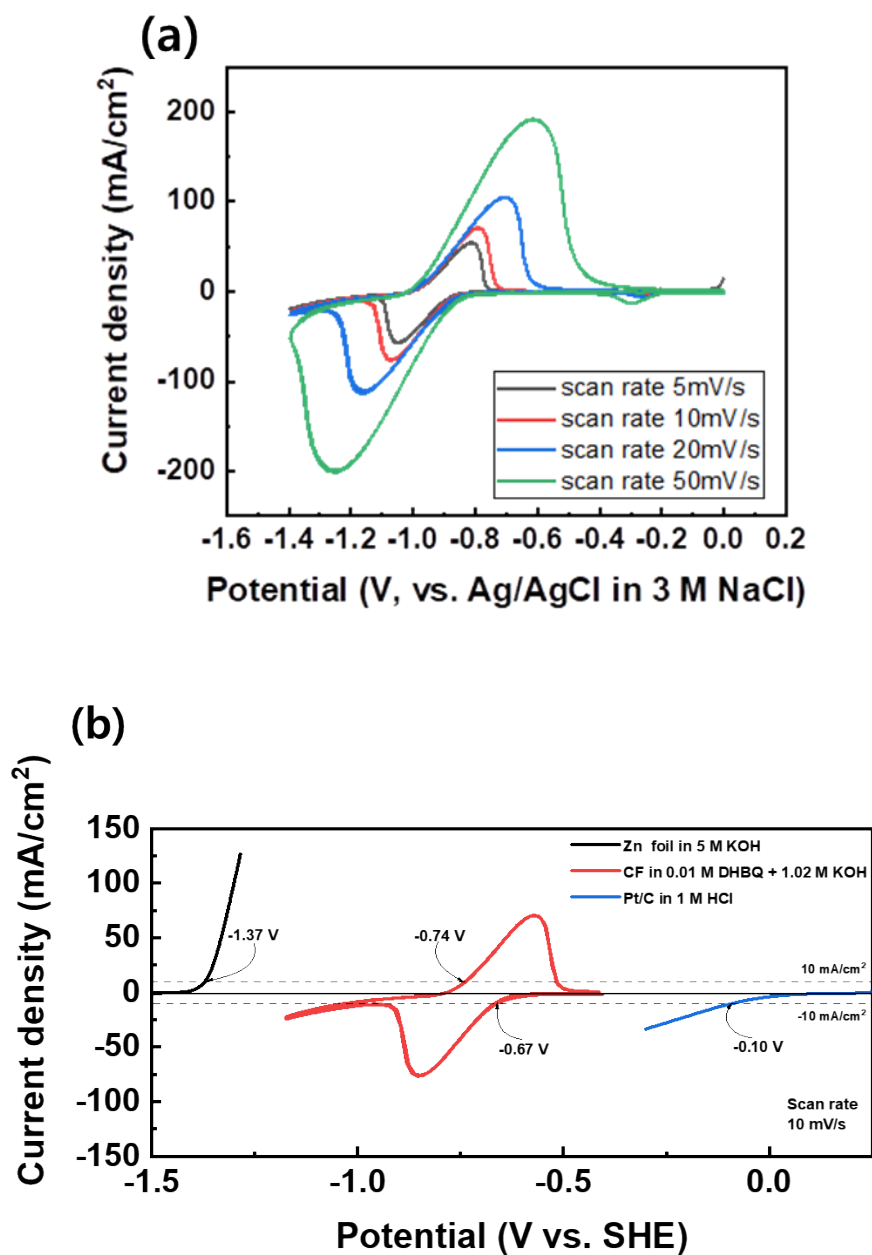


Fig. S3. (a) CV analysis of DHBQ of 0.01 M with 1 M KOH solution and (b) the CV (red color) with DHBQ as an RAM in alkaline electrolyte, and the LSV (black and blue color) of sacrificial Zn and Pt/C electrodes, respectively.

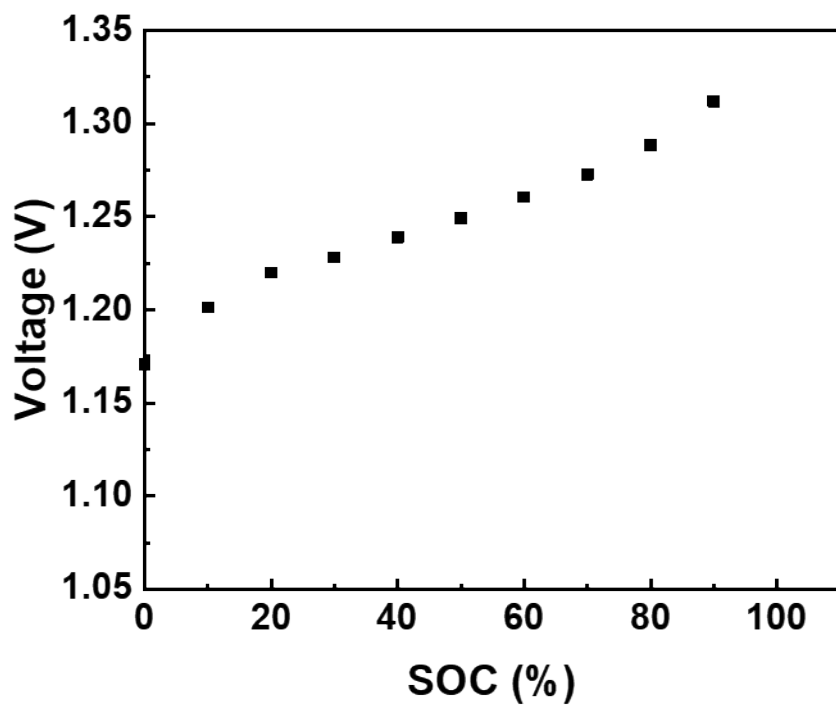


Fig. S4. SOC-voltage profile of RFB cell

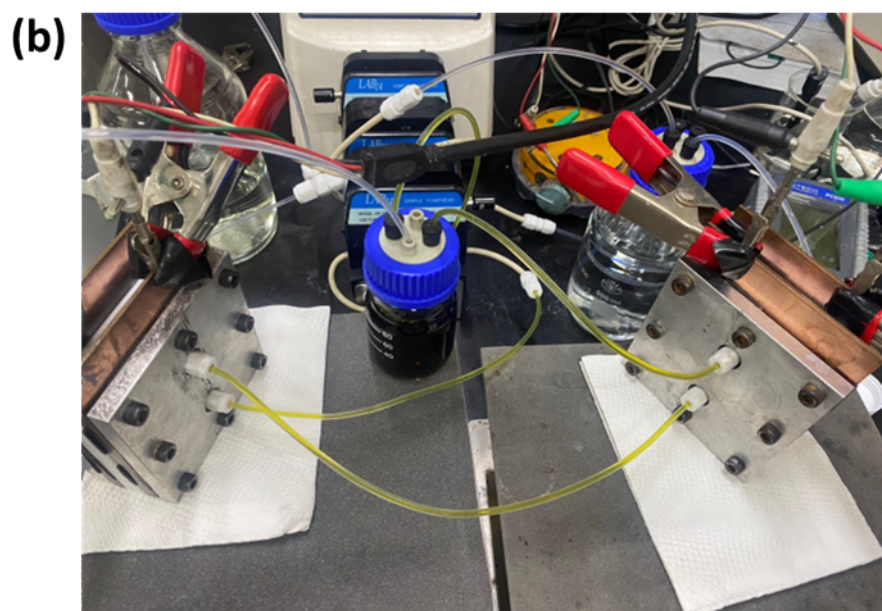
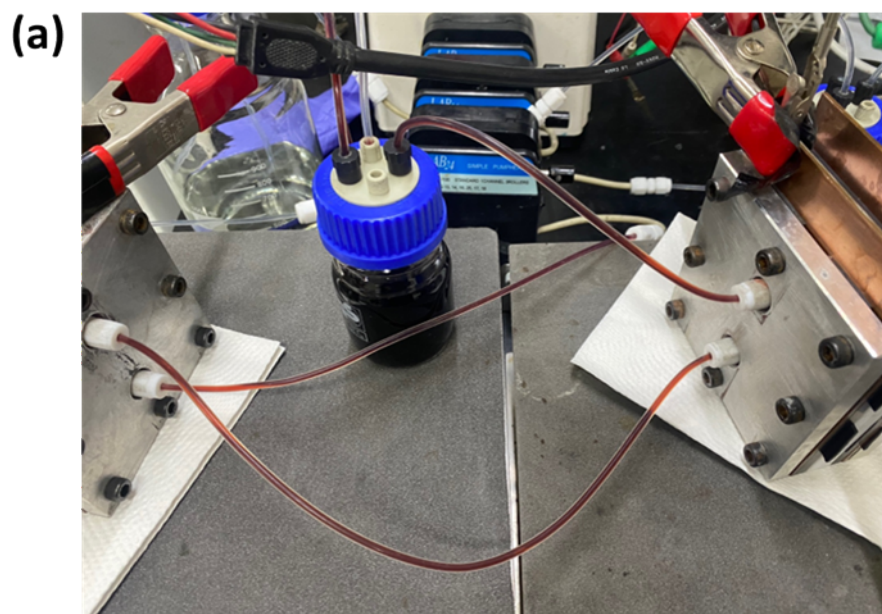


Fig. S5. Digital images of the DHBQ RAM changing color (a) before and (b) after charging

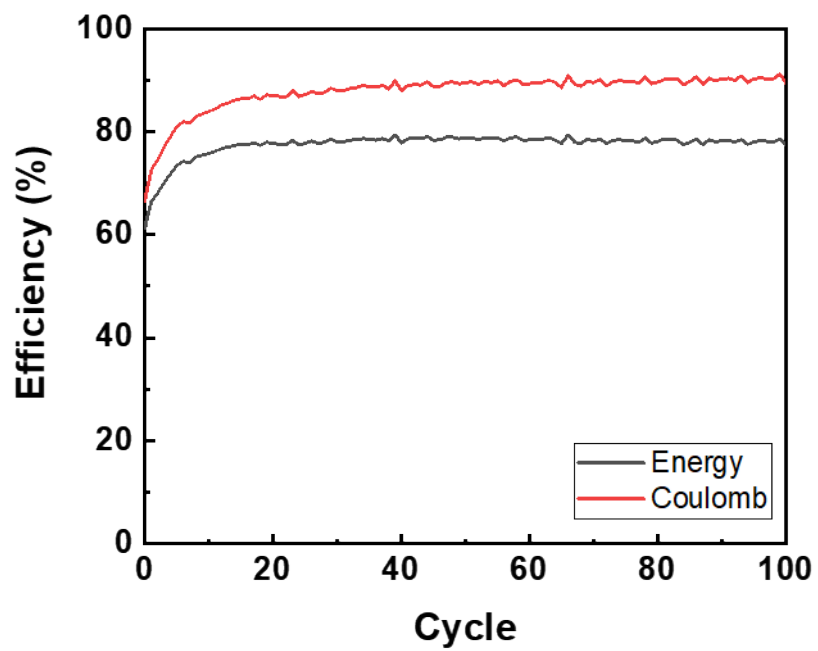


Fig. S6. Cycle number-efficiency (EE & CE) profile of RFB cell.

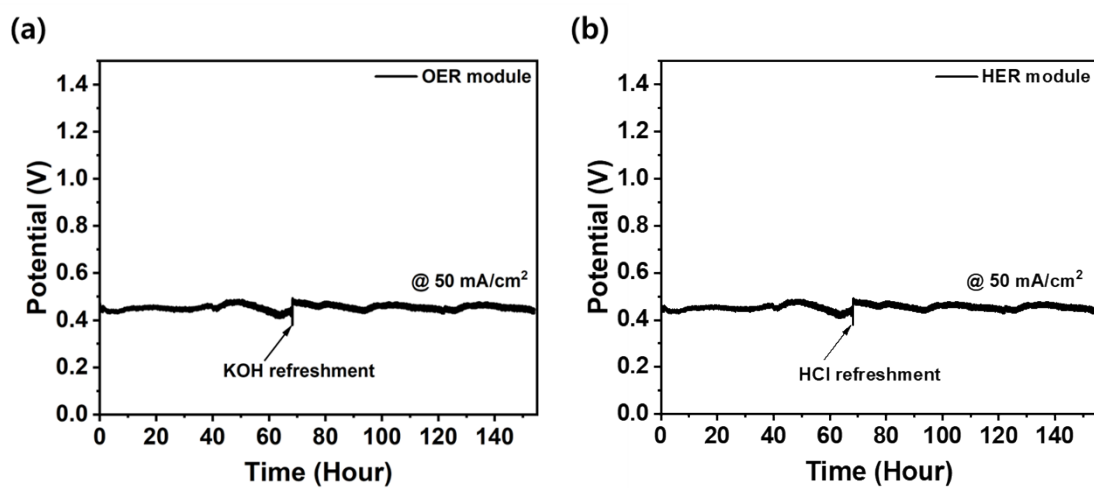


Fig. S7. Chronopotentiometry curves of the (a) OER and (b) HER modules at a current density of 50 mA/cm².

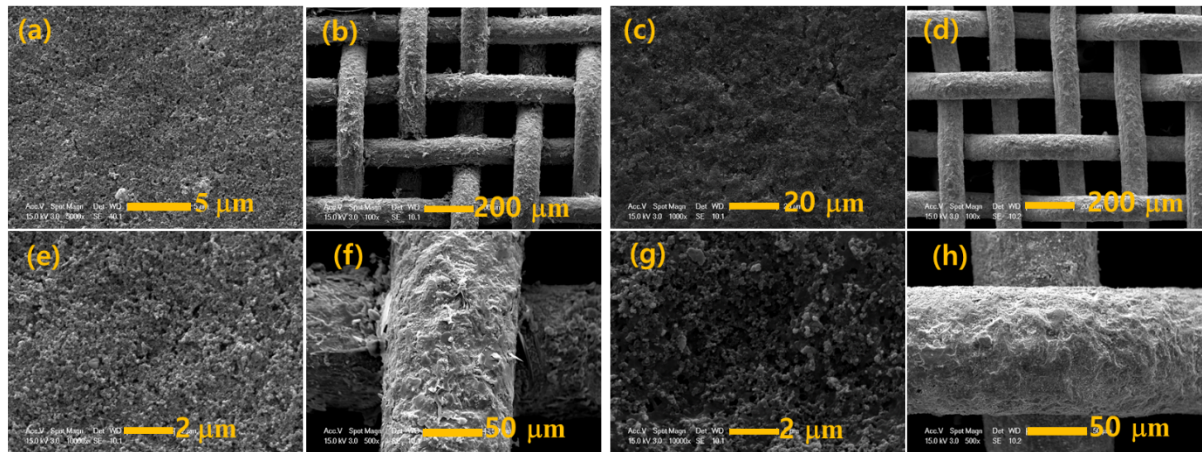


Fig. S8. : ESEM images of (a, e) Pt/C on CP and (b, f) IrO₂ mesh before chronopotentiometry. ESEM images of (c, g) Pt/C on CP and (d, h) IrO₂ mesh after chronopotentiometry.

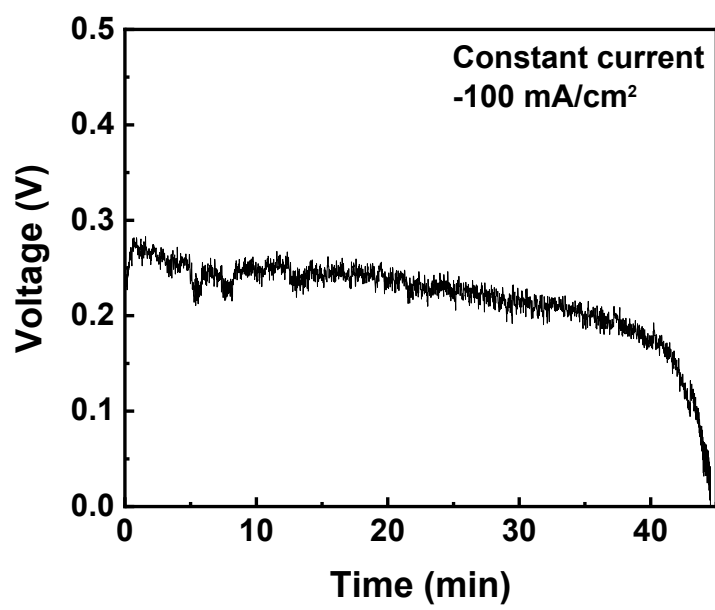


Fig. S9. Time-voltage profiles of HER module under a constant current with the DHBQ as an RAM in the alkaline condition.

S2. Price comparison calculations to produce H₂ (per kg)

In the OER-HER module, our system consumes electricity (0.75 Wh) for the OER module and generates electricity (0.175 Wh) and green hydrogen from the HER module (spontaneous reaction). In terms of the energy consumed for 1 kg of H₂ generation will be 39.26 kWh. In addition, the average price of electricity in the US is \$0.2246/kWh. Taking all these factors into consideration, the total cost of producing 1 kg of H₂ in this system was \$8.819.

In the Zn-HER module, we used the same electrolyte. However, both the Zn and HER modules generated electricity via spontaneous reactions (0.189 and 0.175 Wh, respectively) with a combined output of 24.674 kWh/kg_{H₂}. The zinc consumed to produce 1 kg of H₂ was 37.792 kg, and the cost was \$2.374/kg. The total cost to produce 1 kg of H₂ in this system amounts to \$84.199 [= \$-5.541 (for energy output) + \$89.74 (for consumed zinc metal)]. For the ideal case, to utilize Zn slurry, the cost of Zn metal can be nullified, amounting to \$ -5.541.

Table S1: Different H₂ production methods and their costs

Method	Source	Cost (\$/kg of H ₂)
Photoelectrolysis	Solar	10.36 ^{S1}
Proton-exchange membrane fuel cells	Solar PV	12.6 ^{S2}
Water electrolysis	Wind Solar thermal	5.10-23.37 ^{S3} 7.00 ^{S3}
Thermochemical water electrolysis	Solar	7.98-8.40 ^{S3}
Our system OER-HER module Zn-HER module	Electricity Spontaneous (Zn foil) Spontaneous (Zn slurry)	8.819 84.199 -5.541

\$: United States Dollar

Note: The above calculations were performed assuming the utilization of waste acidic and alkaline electrolytes.

- S1. M. Kayfeci, A. Keçebaş and M. Bayat, in *Solar Hydrogen Production*, eds. F. Calise, M. D. D'Accadia, M. Santarelli, A. Lanzini and D. Ferrero, Academic Press, 2019, pp. 45-83.
- S2. M. R. Shaner, H. A. Atwater, N. S. Lewis and E. W. McFarland, *Energy & Environmental Science*, 2016, **9**, 2354-2371.
- S3. M. H. Hasan, T. M. Mahlia, M. Mofijur, I. M. Rizwanul Fattah, F. Handayani, H. C. Ong and A. S. Silitonga, *Journal*, 2021, **14**.