Supplementary Information

A Non-isothermal Water Formation Cell for Electrochemical Heat Recovery

Ritwik Mondal‡, Shyaam Srirangadhamu Yuvaraj‡, Bhojkumar Nayak, Hemanga Pradhan, Musthafa Ottakam Thotiyl*

Department of Chemistry, Indian Institute of Science Education and Research, Pune, Dr. Homi Bhabha Road, Pune, 411008, India.

*Correspondence: musthafa@iiserpune.ac.in

‡These authors contributed equally

Experimental Section

Materials

Chemicals such as H_2SO_4 (98%), NaOH (97%), oxalic acid (98%), AgCl (98%), KCl (99%), H_2O_2, agar-agar, $K_4[Fe(CN)_6]$ (99.9%), $K_3[Fe(CN)_6]$ (99.9%), and phenolphthalein were bought from Sigma Aldrich. The platinum-carbon catalyst (0.5 mg/cm² Pt/C) and Nafion-117 membrane were purchased from Fuel Cell Store, USA.

Electrochemical Study (Three electrode configuration)

Electrochemical measurements were carried out using a Biologic VMP-300 electrochemical workstation. A platinum electrode with a surface area of 0.031 cm² was employed as the working electrode, while a larger platinum mesh served as the counter electrode. An Ag/AgCl electrode (3.5 M KCl) was used as the reference electrode in a three-electrode setup for cyclic voltammetry experiments. Each measurement utilized 15 mL of electrolyte.

In-situ Electrochemical Mass Spectrometry

In-situ electrochemical mass spectrometry was performed using an HPR-40 quadrupole mass analyzer (Hiden Analytical) equipped with a standard QIC inlet. The setup included a T-shaped connector with three ports: one connected to the mass spectrometer inlet, one to the cell outlet, and the third serving as an exhaust to the surroundings. For the cathodic half-cell experiments, argon (Ar) was used as the carrier gas, while for the anodic half-cell experiments, hydrogen gas was supplied directly to the mass spectrometer. The gas flow generated from the electrochemical cell was directed to the mass spectrometer inlet via the T-shaped connector.

Electrochemical Study (Device configuration)

Polyacrylic sheets were used to construct a two-compartment laboratory prototype of the water formation cell. Electrolytes were pumped into the half-cells at a constant flow rate of 10 mL/min using peristaltic pumps. The two half-cells were separated by a Nafion-117 membrane, which was pretreated in an acidic H_2O_2 solution at 80°C before use. To prevent intercompartment leakage, the membrane was secured between two silicone washer gaskets. The cathodic electrocatalyst for the water formation cell consisted of platinum electrodeposited on titanium mesh (prepared by applying a continuous current of 5 mA/cm² for 10 minutes in a chloroplatinic acid solution), while the anodic electrocatalyst was Pt/C supported on Toray carbon paper. For the ferrocyanide-ferricyanide redox-based thermogalvanic system, carbon sheets were employed as both the cathode and anode. Hydrogen generation was quantified using the water displacement method. The concentrations of the anolyte and catholyte were determined through acid-base titration with phenolphthalein as an indicator. Oxalic acid served as the primary standard for these experiments. First, NaOH was standardized using oxalic acid. The catholyte from the cell was then titrated with the standardized NaOH to estimate its concentration, while the anolyte concentration was determined by titration with oxalic acid.

Temperature Dependent Study

Temperature-dependent studies were conducted in the device mode as well as three-electrode mode. In the case of the three-electrode assembly mode, the working and counter electrodes were connected to the reference electrode via a salt bridge (Fig. S11), and the potential values were measured non isothermally (by keeping the temperature of the reference electrode constant while that of the working electrode is scanned). The salt bridge was prepared by mixing agar-agar and KCl in an aqueous solution at 75^{o}C. The chamber with working and counter electrodes was heated to different temperatures, and the reference electrode was kept at room temperature to avoid fluctuations in the reference electrode's potential. The heating mantle was used to heat the working electrode compartment. The potential of the working electrode was measured at a temperature of 298 K to 358 K. In the device mode, a temperature gradient of 55 K was maintained between the half-cells.

Calculation S1

Net cell reaction for hydrogen system

$H^+ + OH^- \leftrightarrow H_2O$

Enthalpy change for the reaction

$\Delta H^0 = H^0\,(H_2O) - H^0\,(H^+) - H^0\,(OH^-)$

$= -285.8 - 0 - (-230)$

$= \mathbf{-55.8\ kJ/mol}$

Entropy change for the reaction

$\Delta S^0 = S^0\,(H_2O) - S^0\,(H^+) - S^0\,(OH^-)$

$= 69.91 - 0 - (-10.75)$

$= \mathbf{0.08066\ kJ/K\ mol}$

Gibbs free energy of the reaction

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$= -55.8 - (298 * 0.08066)$

$= \mathbf{-79.875\ kJ/mol}$

Amount of extracted heat from surrounding

$T\Delta S^0 = 298 * 0.08066$

$= \mathbf{24.075\ kJ/mol}$

Percentage of extracted heat from surrounding $= {}^{T\Delta S^0}/_{\Delta G^0}$

$= {}^{24.075}/_{79.875}$

$= \mathbf{30.14\ \%}$

30 % of overall energy output is extracted from the surroundings at room temperature and pressure.

$\Delta G^0 = -\,nFE^0$

$E^0 = -\,\Delta G^0 / nF$

$E^0 = -\,(-\,79875)/1*96500$

$E^0 = \mathbf{0.82\ V}$

0.82 V of electromotive force can be harvested from the hydrogen system.

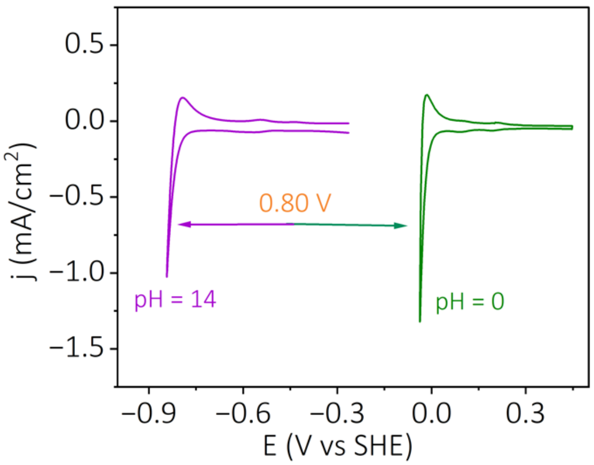

Fig. S1: Cyclic voltammograms of hydrogen redox reactions in acidic (pH 0) and alkaline (pH 14) electrolytes on a polycrystalline platinum electrode at a scan rate of 10 mV/s.

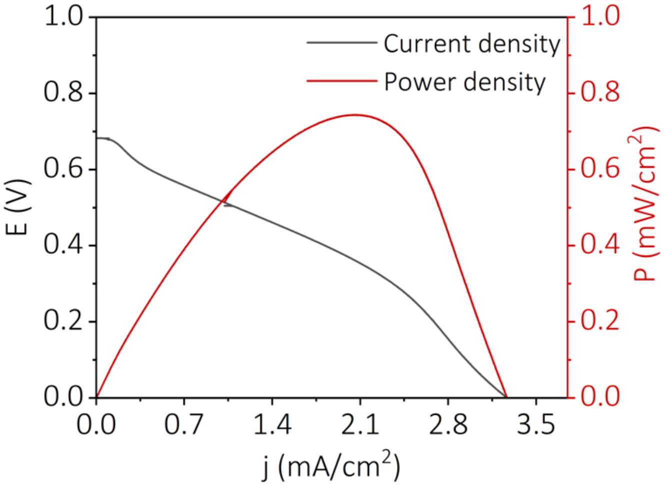

Fig. S2: Polarisation curve for electrochemical water formation energy harvesting device without a H_2 redox. The anolyte is 2 M NaOH and the catholyte is 1 M H_2SO_4.

Calculation S2

The total cell reaction for the water formation cell:

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$

The free energy change for that reaction can be written as follows:

$\Delta G = \Delta G^o + RT \ln ({[H_2O]}/{[H^+][OH^-]})$

$\Delta G = \Delta G^o - RT \ln [H^+] - RT \ln [OH^-]$

$\Delta G = \Delta G^o - RT\ 2.303 (\log[H^+] + \log [OH^-])$

$\Delta G = \Delta G^o + RT\ 2.303 (pH + pOH)$

$\Delta G = \Delta G^o + RT\ 2.303 (pH_A + 14 - pH_B)$,

where pH_A = pH of acidic electrolyte and pH_B = pH of alkaline electrolyte

$\Delta G = \Delta G^o + RT\ 2.303 (pH_A - pH_B) + RT\ 2.303*14$

$\Delta G = \Delta G^o - RT\ 2.303\ \Delta pH + RT\ 2.303*14 \qquad (pH_B > pH_A)$

$\Delta G = -79.8 - 5.7\Delta pH + 79.8$

$\Delta G = -5.7\ \Delta pH$

$E = {-\Delta G}/{nF} = 0.059\ \Delta pH$.

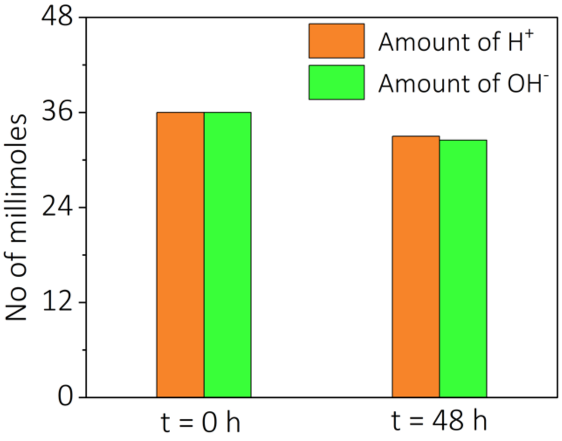

Fig. S3: Amount of H^+ in the catholyte and OH^- in the anolyte before and after keeping the system under open circuit condition for nearly 48 hours.

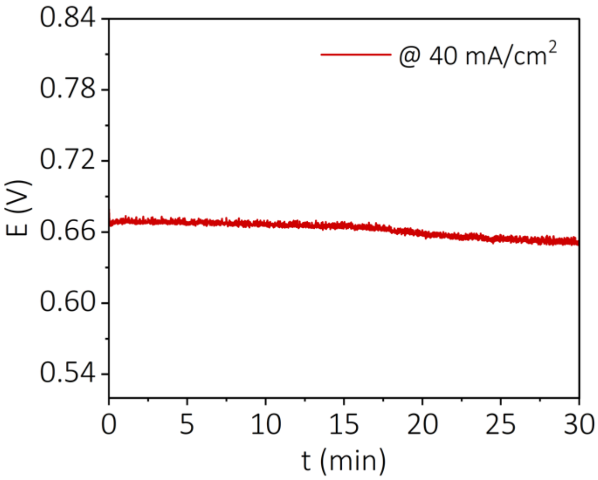

Fig. S4: Galvanostatic discharge of the isothermal water formation cell at a constant current density of 40 mA/cm^2.

Calculation S3

Quantification of hydrogen

From Fig. 1b

The overall charge passed = 2717.99 C.

Moles corresponding to the charge passed = (2717.99/96500) = 0.02817 mol = 28.17 mmol.

To evolve one H_2 molecule there is a requirement of 2 electrons.

So, theoretically the amount of evolved H_2 = (28.17/2) = 14.085 mmol

At room temperature (298 K), 1 mol of gas equals 24.45 L.

So, the theoretical amount of evolved H_2 gas = $(24.45 * 14.085 * 10^{-3})$ = 344.37 mL.

From the experiment, the amount of evolved H_2 gas = 331.25 mL.

Faradaic efficiency = (331.25 / 344.37) * 100 = **96.2%**

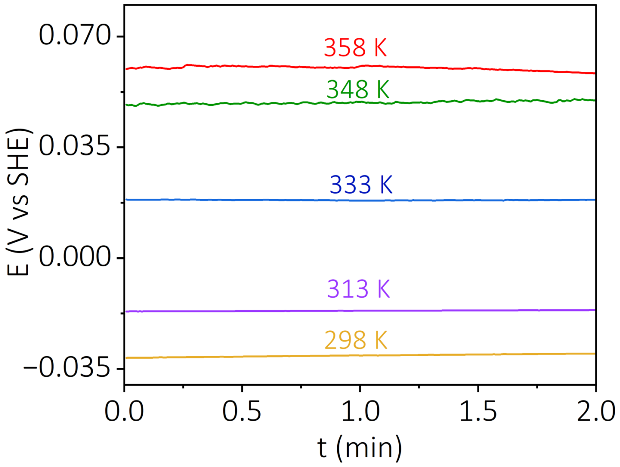

Fig. S5: The temperature dependence of the potential for the hydrogen redox in the acidic electrolyte of pH = 0.

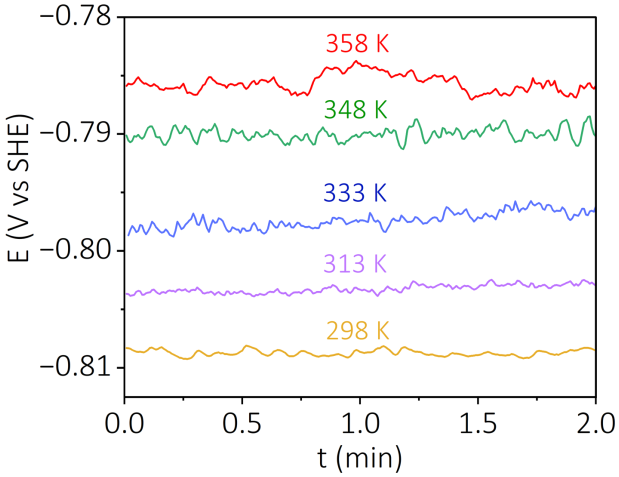

Fig. S6: The temperature dependence of potential for the hydrogen redox in the alkaline medium of pH= 14.

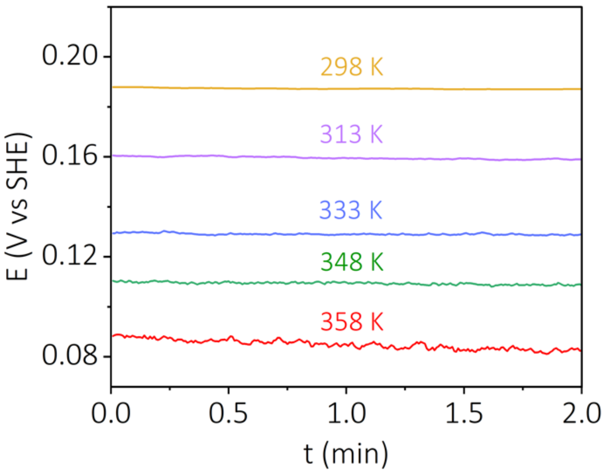

Fig. S7: The temperature dependence of potential for the oxygen redox in the alkaline medium of pH= 14.

Calculation S4

For water formation cell,

The Seebeck coefficient (α) for the water formation cell = 1.30 ± 0.12 mV/K

No. of electrons = 2

Faradaic constant = 96484 C. mol^{-1}

Partial molar entropy change (ΔS) = n. F. α

= 2 * 96484 * (1.30 ± 0.12)

= **251± 23.55 J mol^{-1} K^{-1}**

For the H_2 - O_2 fuel cell,

The Seebeck coefficient (α) for the fuel cell = − 1.96 ± 0.06 mV/K

No. of electrons = 4

Partial molar entropy change (ΔS) = n. F. α

= 4 * 96484 * (− 1.96 ± 0.06)

= **− 756.43 ± 23.1 J mol^{-1} K^{-1}**

Calculation S5

From Fig. 3b

Power density output at $\Delta T = 55$ (area under the orange potential trace) = 106.76 mW/cm^2

Power density output at $\Delta T = 0$ (area under the blue potential trace) = 86.19 mW/cm^2

Thermal contribution = Shaded area between orange and blue trace

= {(106.76 − 86.19)/106.76} * 100

= (20.57/106.76) * 100

= **19.26 %**

Galvanic contribution = (100 −19.26) %

= **80.74 %**

Increment in performance under non-isothermal condition = (20.57/86.19)*100 = **23.86 %**

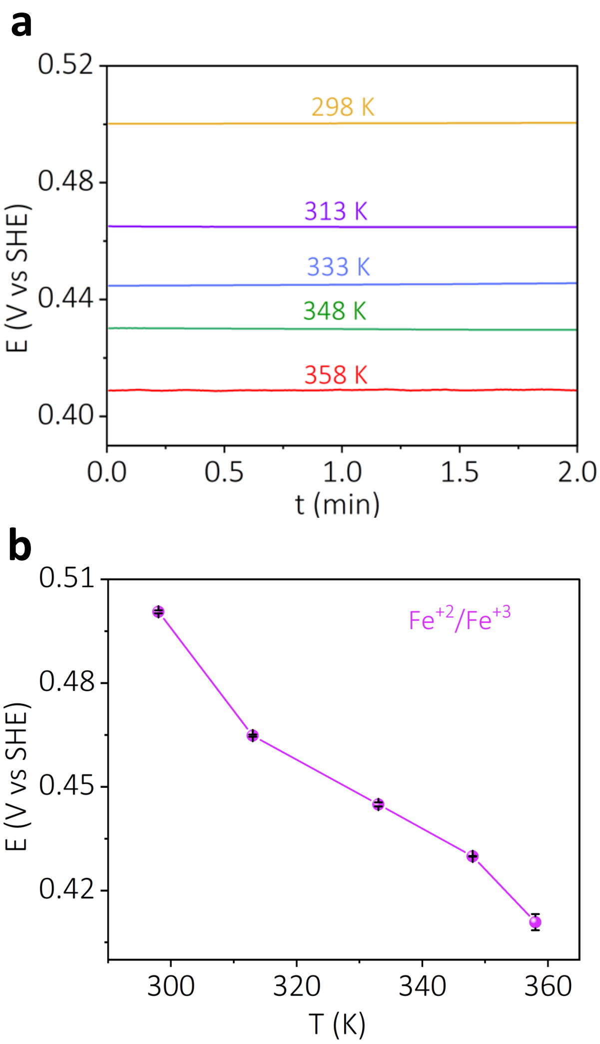

Fig. S8: (a) and **(b)** The temperature dependence of the potential for ferrocyanide-ferricyanide redox. The electrolyte is an equimolar ferrocyanide-ferricyanide (0.4 M Fe^{2+} + 0.4 M Fe^{3+}) in the 1 M KCl solution.

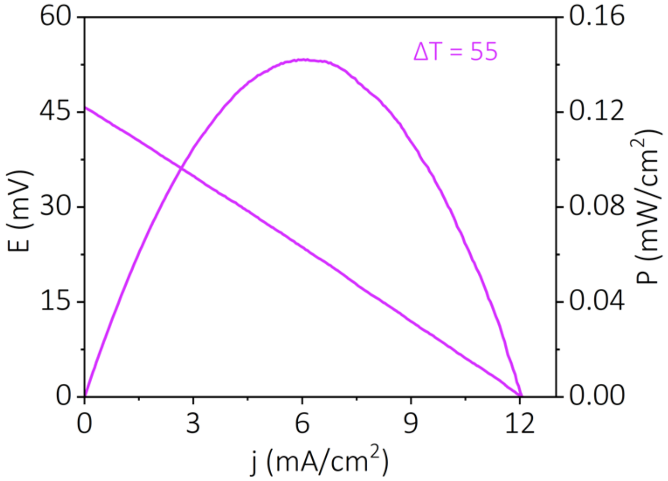

Fig. S9: Polarization curve for the ferrocyanide/ferricyanide (Fe^{2+}/Fe^{3+}) redox-based thermogalvanic device when a temperature gradient of ΔT = 55 K is applied.

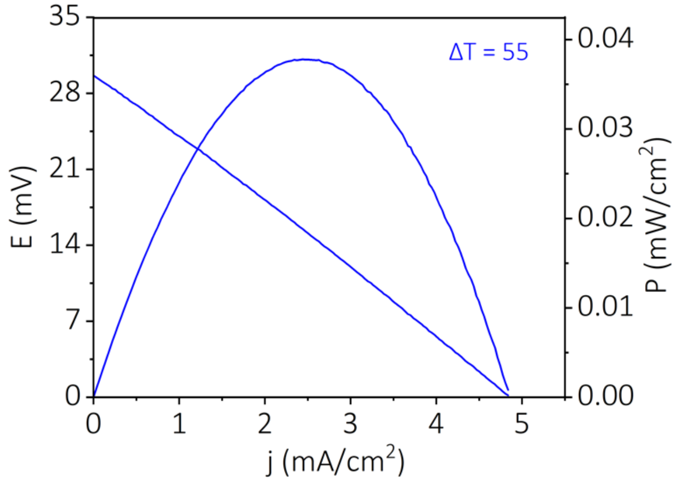

Fig. S10: Polarization curve for the Iodide/triiodide (I^-/I_3^-) redox-based thermogalvanic device when a temperature gradient of ΔT = 55 K is applied.

Calculation S6

For water formation reaction-based thermogalvanic system,

From Fig. 3b,

Peak power density (P_{max}) at ΔT = 55 K = 53.23 mW/cm^2

Peak power density (P_{max}) at ΔT = 0 K = 43.08 mW/cm^2

ΔP_{max} = 10.15 mW/cm^2

ΔT = 55K

Temperature-insensitive maximum power density ($^{\Delta P_{max}}/_{\Delta T^2}$) $= {}^{10.15}/_{55^2}$

$= 0.003355$ mWcm^{-2}K^{-2}

= **33.55 mWm^{-2}K^{-2}**

For ferrocyanide/ferricyanide redox-based thermogalvanic system,

From Fig. S9,

Peak power density (P_{max}) at ΔT = 55 K = 0.143 mW/cm^2

ΔT = 55 K

Temperature-insensitive maximum power density ($^{\Delta P_{max}}/_{\Delta T^2}$) $= {}^{0.143}/_{55^2}$

$= 0.000047$ mWcm^{-2}K^{-2}

= **0.47 mWm^{-2}K^{-2}**

For iodide/triiodide redox-based thermogalvanic system,

From Fig. S10,

Peak power density (P_{max}) at $\Delta T = 55$ K = 0.0378 mW/cm^2

$\Delta T = 55$ K

Temperature-insensitive maximum power density ($\Delta P_{max}/\Delta T^2$) $= 0.0378/55^2$

$= 0.00001249$ mWcm^{-2}K^{-2}

= **0.125 mWm^{-2}K^{-2}**

Table S1: Thermogalvanic device performance comparison of water formation cell with state-of-the-art systems reported in the literature (ref-22,28,30,42-44).

S.No	**Electrochemical system**	**$\lvert\alpha\rvert$ (mV/K)**	**ΔT (K)**	**P_{max} (mW/cm^2)**	**$P_{max}/\Delta T^2$ ($mW\ m^{-2}K^{-2}$)**	**Ref**
1	**$H^+ – OH^-$ (2 M each) (Pt‖Pt)**	**1.38**	**55 (298 K – 353 K)**	**10.15**	**33.55**	**This work**
2	$[Fe(CN)_6]^{-4}$ / $[Fe(CN)_6]^{-3}$ (0.4 M each) (C‖C)	1.4	10 (293 K – 303 K)	0.0041	0.41	22
3	I^-/I_3^- (0.8 M I^- + 0.4 M I_2) (Pt‖Pt)	0.86	34 (276 K – 310 K)	1.8 μW	0.00155 μWK^{-2}	42
4	$[Fe(CN)_6]^{-4}$ / $[Fe(CN)_6]^{-3}$ [0.4 M each + 2.6 M guanidine chloride] (C‖C)	2.7	10 (293 K – 303 K)	0.0095	0.95	22
5	$[Fe(CN)_6]^{-4}$ / $[Fe(CN)_6]^{-3}$ [0.4 M each + 2.6 M guanidine chloride + 24 M Urea] (C‖C)	4.2	10 (293 K – 303 K)	0.011	1.10	22
6	$[Fe(CN)_6]^{-4}$ / $[Fe(CN)_6]^{-3}$ [0.4 M each + 20 wt% Methanol] (C‖C)	2.9	4.1	0.001	0.64	30
7	Quinone/Hydroquinone (80 mM) + 1 M HCl (Cu‖Cu)	1.23	30	0.009783	0.11	28
8	I^-/I_3^- (12.5 mM I^- + 2.5 mM I_2 + 60 mM Starch + 2 M KCl) (Pt‖Pt)	1.5	34 (276 K – 310 K)	3.6 μW	0.00311	42
9	I^-/I_3^- (0.08 M I^- + 0.04 M I_2 + 2.4 M Cs^+ ion) (C‖C)	1.2	50	0.074	0.3	43
10	$[Fe(CN)_6]^{-4}$ / $[Fe(CN)_6]^{-3}$ (0.4 M) +1 M $(Gdm)_2SO_4$	5.58	30	1.07	11.9	44

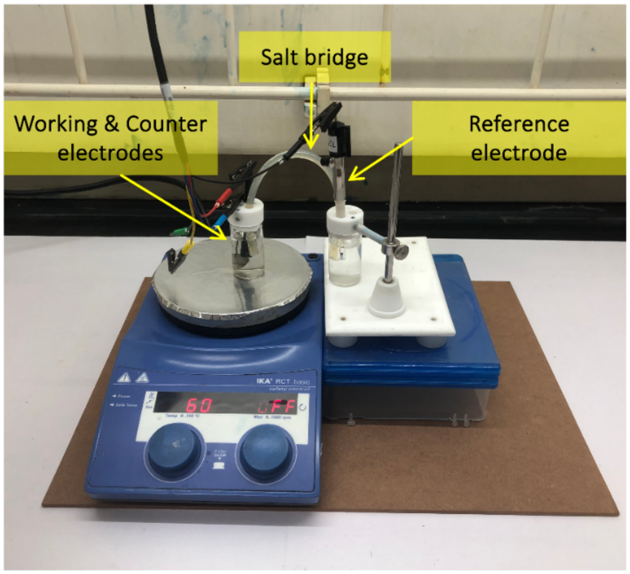

Fig. S11: Photograph of the three-electrode setup employed to measure the temperature-dependent electrochemical half-cell reaction voltages.