

SUPPORTING INFORMATION

Dual Function of Phosphate Buffer in Untreated Seawater Electrolysis: Boosting Oxygen Evolution Reaction Efficiency and Inhibiting Cathode Scaling

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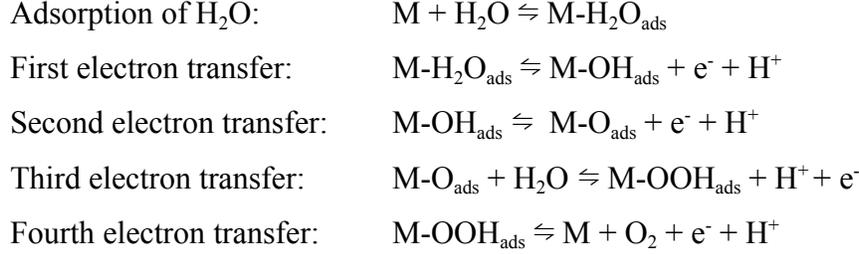
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S1. Microkinetic Tafel Model for OER

The proposed elementary steps for the oxygen evolution reaction for single site (M) mechanism are the following,



The rate expressions for each elementary steps can be written as,

$$r_1 = r_{-1} \Rightarrow k_1(1 - \theta) [\text{H}_2\text{O}] = k_{-1}\theta_1 \quad (\text{S1})$$

$$r_2 = r_{-2} \Rightarrow k_2\theta_1 = k_{-2}\theta_2[\text{H}^+] \quad (\text{S2})$$

$$r_3 = r_{-3} \Rightarrow k_3\theta_2 = k_{-3}\theta_3[\text{H}^+] \quad (\text{S3})$$

$$r_5 = r_{-5} \Rightarrow k_5\theta_4 = k_{-5}(1 - \theta)[\text{O}_2][\text{H}^+] \quad (\text{S4})$$

Considering the third electron transfer as rate determining step (RDS) for OER,

$$r_4 = k_4\theta_3[\text{H}_2\text{O}]$$

From (S1)

$$(1 - \theta) = \left(\frac{k_{-1}}{k_1[\text{H}_2\text{O}]} \right) \theta_1 \quad (\text{S5})$$

Substitute (S5) in (S4)

$$k_5\theta_4 = \left[k_{-5} \left(\frac{k_{-1}}{k_1[\text{H}_2\text{O}]} \right) [\text{O}_2][\text{H}^+] \right] \theta_1$$

$$\theta_4 = \left(\frac{k_{-1}k_{-5}[\text{O}_2][\text{H}^+]}{k_5k_1[\text{H}_2\text{O}]} \right) \theta_1 \quad (\text{S6})$$

From (S2)

$$k_2\theta_1 = k_{-2}\theta_2[\text{H}^+]$$

$$\theta_2 = \left(\frac{k_2}{k_{-2}[H^+]} \right) \theta_1 \quad (S7)$$

Substitute (S7) in (S3)

$$k_{-3}\theta_3[H^+] = k_3 \left[\left(\frac{k_2}{k_{-2}[H^+]} \right) \theta_1 \right]$$

$$\theta_3 = \left(\frac{k_3 k_2}{k_{-3} k_{-2} [H^+]^2} \right) \theta_1 \quad (S8)$$

Substitute (S6), (S7) & (S8) in (S1)

$$k_1[H_2O](1 - (\theta_1 + \theta_2 + \theta_3 + \theta_4)) = k_{-1}\theta_1$$

$$1 - (\theta_1 + \theta_2 + \theta_3 + \theta_4) = \left(\frac{k_{-1}}{k_1[H_2O]} \right) \theta_1 \quad (S9)$$

Substitute (S6), (S7) & (S8) in (S7)

$$\theta_1 = \frac{1}{1 + \left(\frac{k_{-5} k_{-1} [O_2] [H^+]}{k_5 k_1 [H_2O]} \right) + \left(\frac{k_2 k_3}{k_{-2} k_{-3} [H^+]^2} \right) + \left(\frac{k_2}{k_{-2} [H^+]} \right) + \left(\frac{k_{-1}}{k_1 [H_2O]} \right)}$$

$$\theta_1 = \frac{1}{1 + \left(\frac{\exp(-f\eta) [O_2] [H^+]}{K_5^0 K_1 [H_2O]} \right) + \left(\frac{K_2^0 K_3^0 \exp(-2f\eta)}{[H^+]^2} \right) + \left(\frac{K_2^0 \exp(f\eta)}{[H^+]} \right) + \left(\frac{1}{K_1 [H_2O]} \right)} \quad (S10)$$

Substitute (S10) in (S8)

$$\theta_3 = \frac{K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta)}{\left(1 + \left(\frac{\exp(-f\eta) [O_2] [H^+]}{K_5^0 K_1 [H_2O]} \right) + \left(\frac{K_2^0 K_3^0 \exp(-2f\eta)}{[H^+]^2} \right) + \left(\frac{K_2^0 \exp(f\eta)}{[H^+]} \right) + \left(\frac{1}{K_1 [H_2O]} \right) \right) [H^+]^2}$$

$$\theta_3 = \frac{K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta)}{[H^+]^2 + \left(\frac{\exp(-f\eta) [O_2] [H^+]^3}{K_5^0 K_1 [H_2O]} \right) + \left(K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta) \right) + \left(\left(K_2^0 \exp(f\eta) \right) [H^+] \right) + \left(\frac{[H^+]^2}{K_1 [H_2O]} \right)} \quad (S11)$$

By assuming step 1 is fast and at anodic potential 2nd term can be neglected

$$\theta_3 = \frac{K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta)}{[H^+]^2 + K_2^0 \exp(f\eta) (K_3^0 \exp(f\eta) + [H^+])} \quad (S12)$$

Substitute (S12) in RDS

$$r_4 = k_4 \left(\frac{K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta)}{[H^+]^2 + K_2^0 \exp(f\eta) (K_3^0 \exp(f\eta) + [H^+])} \right) [H_2O]$$

$$r_4 = \frac{k_4^0 \exp[(1-\alpha)f\eta] \cdot K_2^0 \exp(f\eta) \cdot K_3^0 \exp(f\eta) \cdot [H_2O]}{[H^+]^2 + K_2^0 \exp(f\eta) (K_3^0 \exp(f\eta) + [H^+])}$$

At high over potential,

$$r_4 = k_4^0 \exp[(1 - \alpha)f\eta][H_2O] \quad (S13)$$

Assuming first electron transfer step as rds, the rate of OER can be described as,

$$r_2 = \frac{k_2^0 k_1 [H_2O] \exp((1-\alpha)f\eta)}{k_1 [H_2O] + k_{-1}} \quad (S14)$$

The derivation of Equation (S14) is provided in our previous work [1].

Since $k_1 \ll k_{-1}$, the Equation (S14) gets reduced to,

$$r_2 = \frac{k_2^0 k_1}{k_{-1}} \exp[0.5f(E - E_{eq})][H_2O]$$

S2. Linear sweep voltammograms (LSV) in natural seawater electrolyte

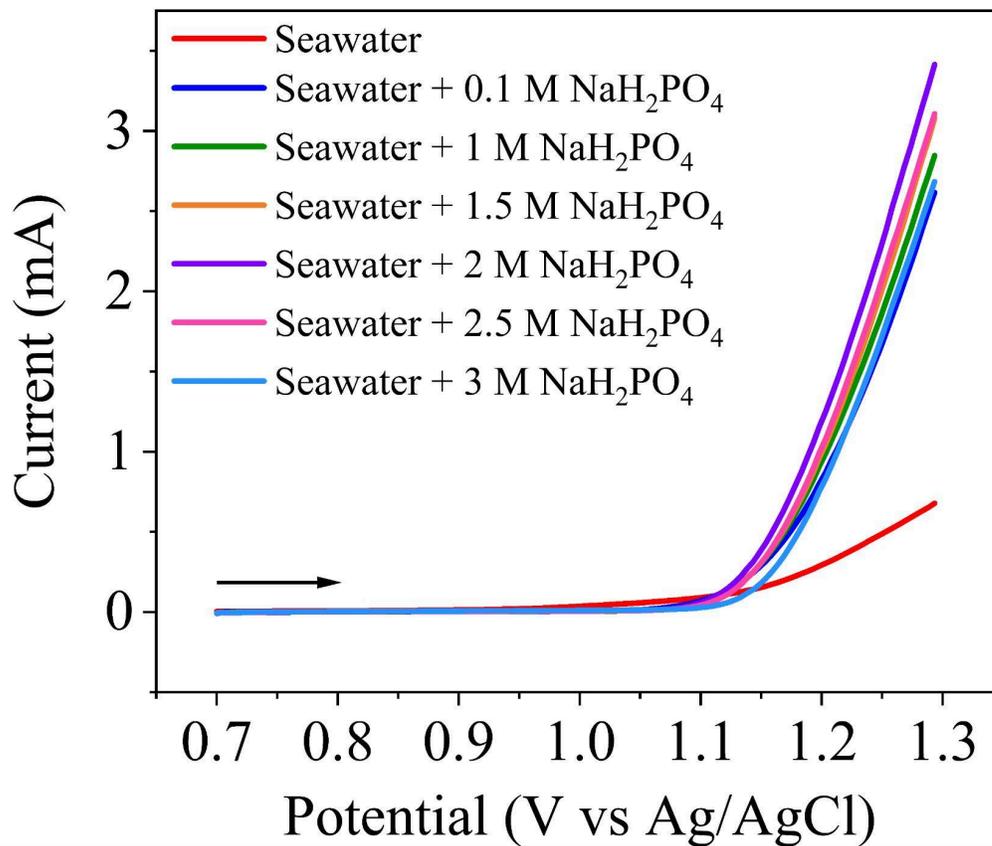


Figure S1: Linear sweep voltammograms in Ar-saturated natural seawater electrolyte for varying concentrations of NaH_2PO_4 in Ir/C catalyst at 10 mV/s scan rate and 1000 rpm electrode rotation rate

S3. Tafel plots of segregated currents from LSVs in natural seawater electrolyte

S3.1. For Chlorine Evolution Reaction (CER)

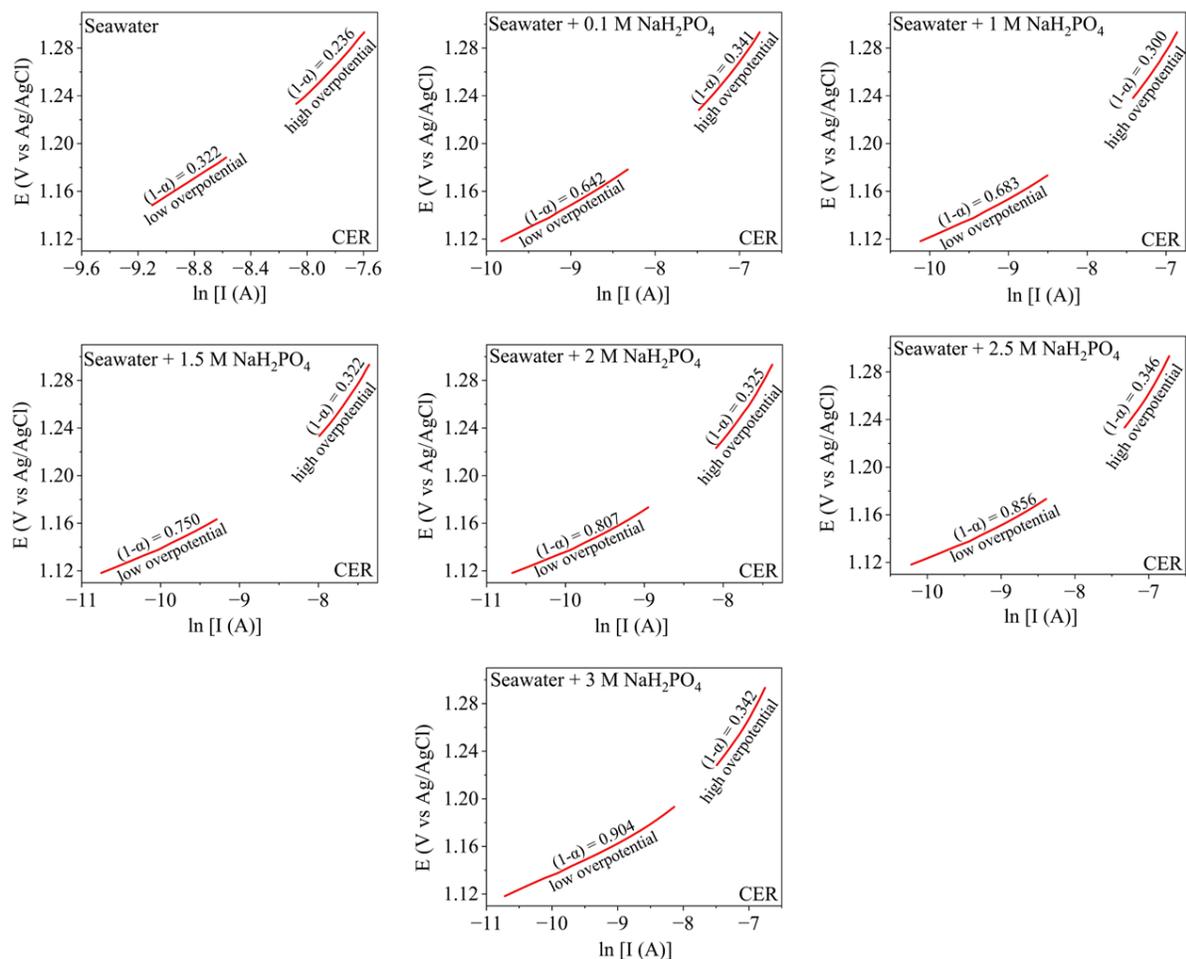


Figure S2: Tafel plots of segregated CER currents, for varying concentrations of NaH_2PO_4 in Ir/C catalyst for Ar-saturated natural seawater electrolyte, at 10 mV/s scan rate and 1000 rpm electrode rotation rate

S3.2. For Oxygen Evolution Reaction (OER)

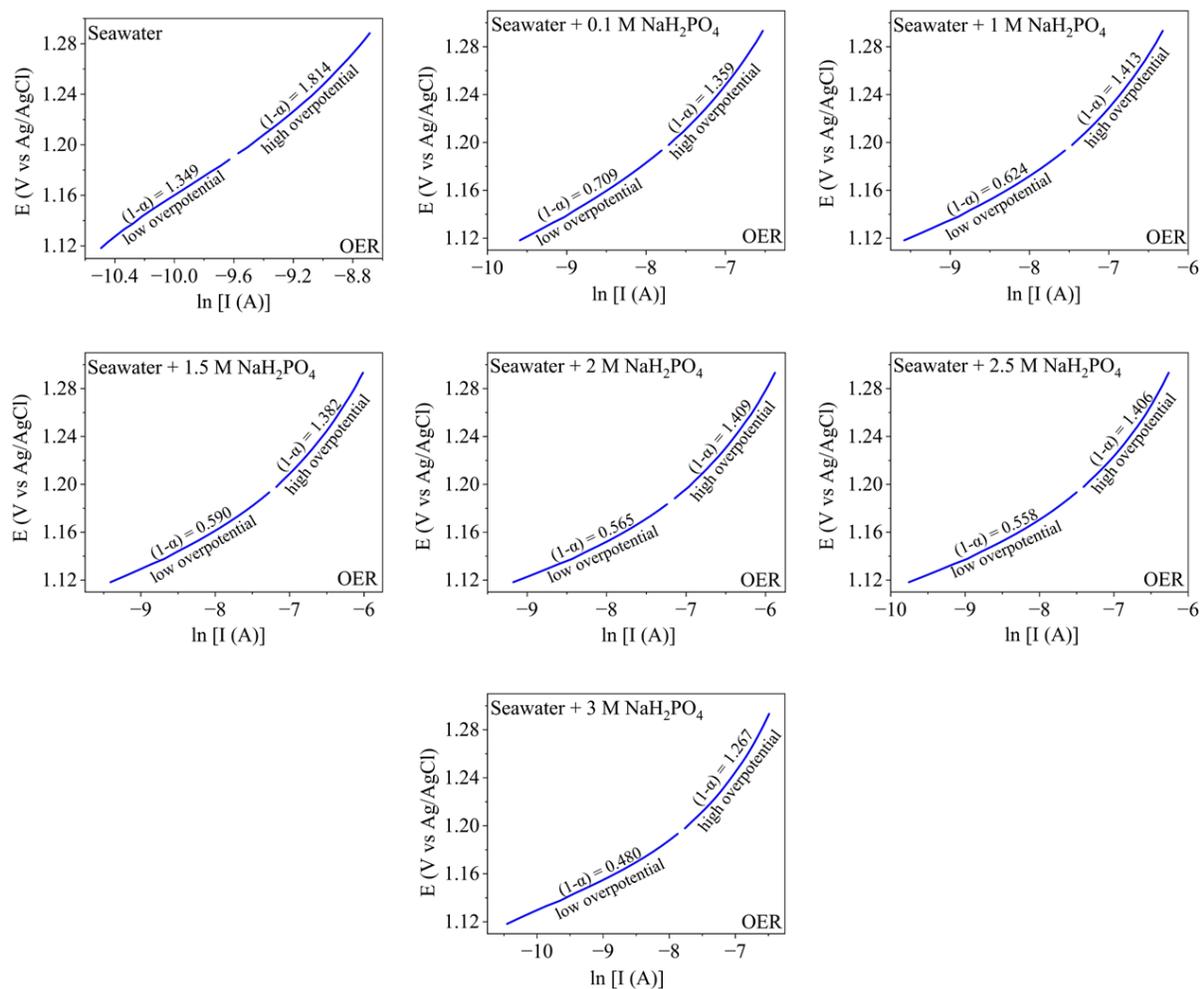


Figure S3: Tafel plots of segregated OER currents, for varying concentrations of NaH_2PO_4 in Ir/C catalyst for Ar-saturated natural seawater electrolyte, at 10 mV/s scan rate and 1000 rpm electrode rotation rate

S4. Inductively Coupled Plasma - Optical Emission Spectroscopy Characterization

Table S1: Metal ion concentration in the natural seawater obtained from Bay of Bengal in winter season (Chennai Area)

Metal ion	Concentration (mM)
Na	428
Mg	62.94
Ca	14.7
K	8.39
Zn	1.423
Sr	0.1255
Li	0.144

S5. Bulk pH measurements

Table S2: Bulk pH of 20 mL Ar-saturated electrolytes with and without chloride ions, measured using a Hanna Instruments pH meter before and after electrolysis at 200 mA/cm² with Ir/C as electrocatalyst for 20 minutes

Electrolyte	pH before electrolysis	pH after electrolysis
0.8 M NaClO ₄	6.071	6.069
0.8 M NaCl	6.104	8.529

S6. Ionic conductivity values

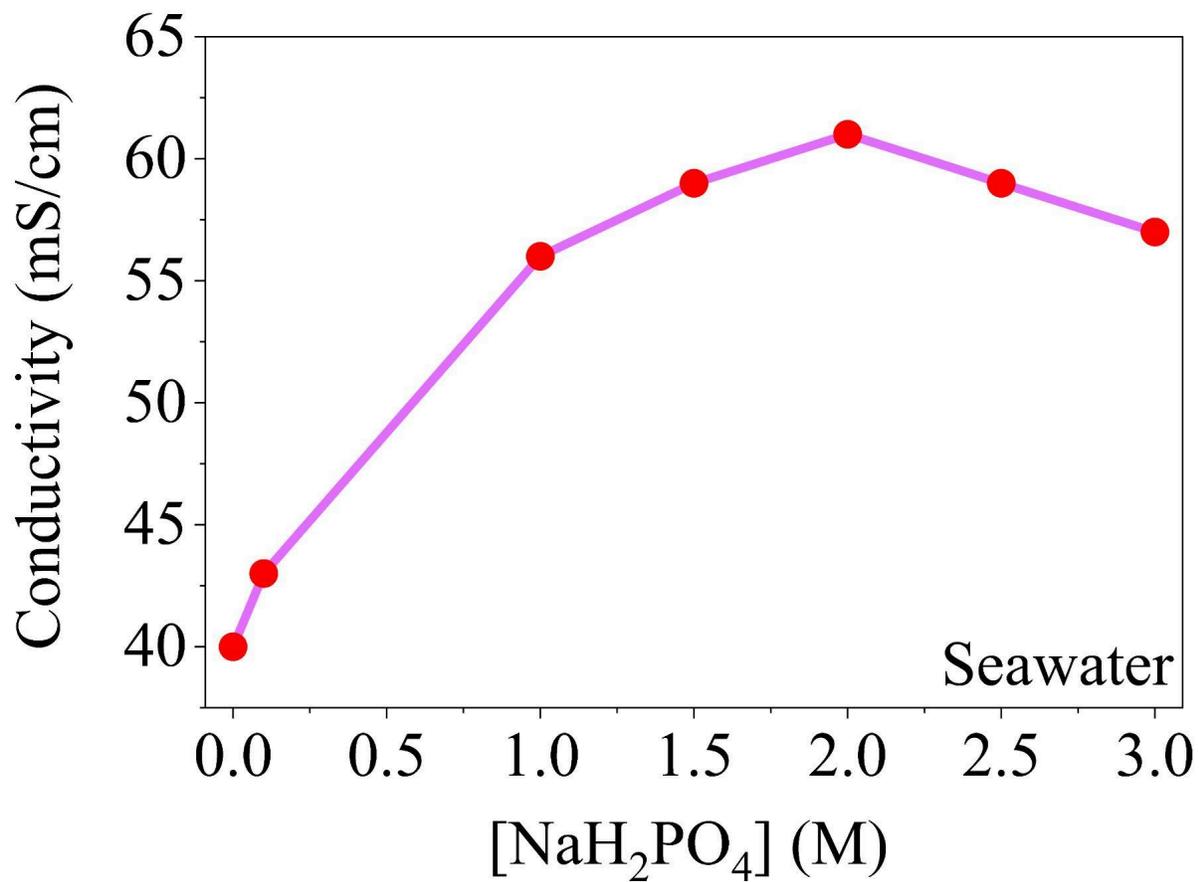


Figure S4: Ionic conductivity values of the natural seawater electrolytes supplemented with different concentrations of NaH_2PO_4 (0-3 M), measured at 298 K

S7. UV-Vis Analysis

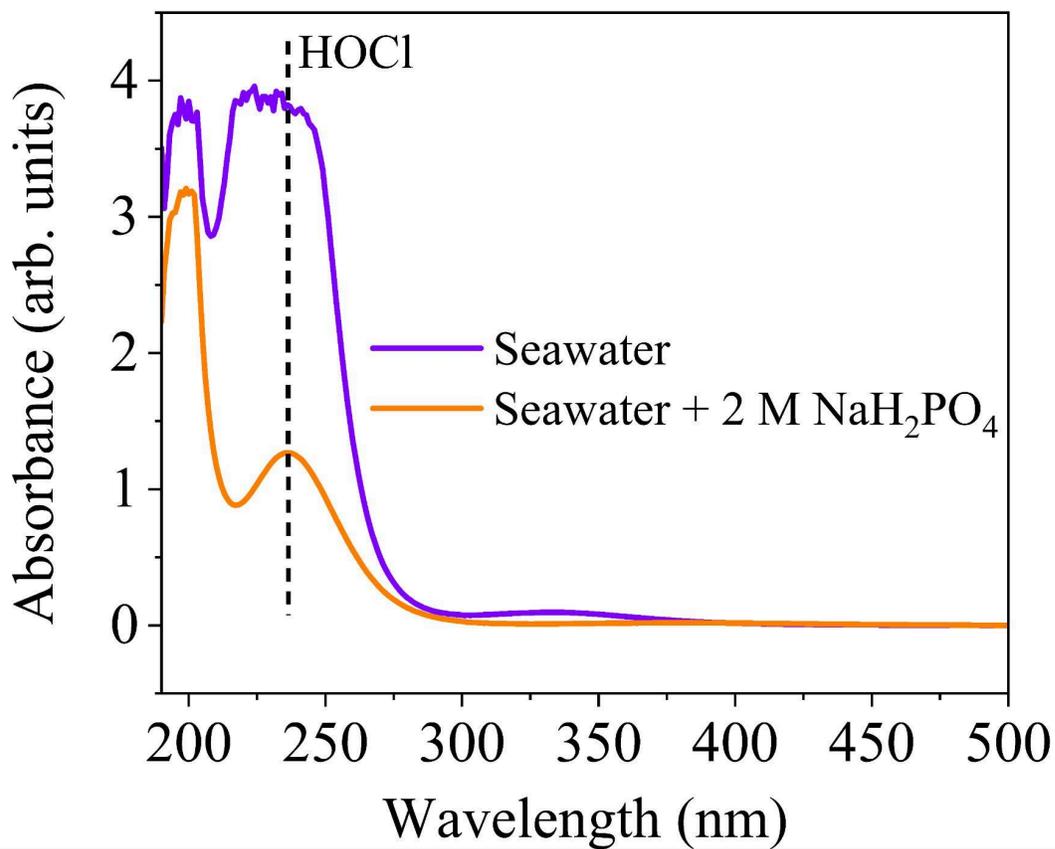


Figure S5: UV-vis spectra of untreated natural seawater electrolytes with and without 2 M NaH₂PO₄, post-electrolysis at 200 mA/cm² for 20 minutes.

S8. OER Faradaic efficiency values in seawater with different concentrations of NaH₂PO₄

Table S3: OER Faradaic efficiency values in seawater with varied concentrations of NaH₂PO₄ (0-3 M), obtained by iodometric titration

Electrolyte	Experiment-1	Experiment-2	Experiment-3	Average FE _{OER} %
Seawater	25.70	26.26	24.09	25.35 ± 1.13
Seawater + 0.1 M NaH ₂ PO ₄	57.27	55.80	55.18	56.08 ± 1.07
Seawater + 1 M NaH ₂ PO ₄	63.15	64.92	63.03	63.70 ± 1.14
Seawater + 1.5 M NaH ₂ PO ₄	80.53	78.17	78.64	79.11 ± 1.25
Seawater + 2 M NaH ₂ PO ₄	82.47	82.1	80.53	81.7 ± 1.03
Seawater + 2.5 M NaH ₂ PO ₄	62.92	61.27	60.37	61.52 ± 1.29
Seawater + 3 M NaH ₂ PO ₄	55.03	57.73	55.6	56.13 ± 1.42

S9. H-type electrochemical cell



Figure S6: H-type electrochemical cell separated by a glass frit

Reference

1. P. V. Raja , P. Vishnu , T. K. Panigrahi , R. Sankannavar , S. P. Vangala and I. Mahesh , Hydrated Electrocatalysis: To Boost the Selectivity for the Oxygen Evolution Reaction in Seawater Electrolysis, *J. Phys. Chem. C*, 2025, **129**, 262–270.