Supporting information

In-situ Observation of pH Change during Water Splitting in Neutral pH Conditions: Impact of Natural Convection Driven by Buoyancy Effects

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Figure S1. Calibration curves of (a) pH fluorescence sensor foils in 0.1 M KP_i and 0.5 M KP_i and (b) O_2 fluorescence sensor foil in 0.1 M KP_i. The pH sensor foils incorporate green pH indicator dyes and red inert reference dyes. The O_2 sensor foil has red O_2 indicator dyes and green inert reference dyes. The ratio between the green and red signals (y-axis in a and b), which are obtained through the green and red channels in the RGB camera, is used for the calibration and the measurements. Digital photographs of the experimental setup for pH monitoring during water splitting from (c) top view and (d) front view.



Figure S2. Measured time-dependent ΔpH profile (a) in 0.5 M K₂SO₄ at 1 mA cm⁻² and in 0.1 M KP_i at (b) 1 and (c) 10 mA cm⁻².



Figure S3. pH distribution in 0.1 M KP_i during chronopotentiometry at (a) 5 and (b) 10 mA cm⁻².



Figure S4. Chronopotentiometry (voltage-time) curves at various current densities in (a) 0.5 M K₂SO₄, (b) 0.1 M KP_i and (c) 0.5 M KP_i.



Figure S5. pH distribution in 0.5 M K_2SO_4 during chronopotentiometry at 1 mA cm⁻². Note that in this measurement the anode and cathode are switched from the configuration used in other measurements in this study.



Figure S6. pH distribution after a period of 30, 60 and 90 seconds during chronopotentiometry at 5 mA cm^{-2} in 0.5 M K₂SO₄.



Figure S7. Reported electrolyte densities of (a) potassium phosphate, (b) sodium phosphate, (c) potassium carbonate buffer solutions and (d) potassium hydroxide solution as a function of concentrations.^{1,2} The electrolyte density of our bulk phosphate buffer electrolyte is also identified.



Figure S8. Schematics of our two-dimensional multiphysics model, showing the equations and boundary conditions for (a) mass-transport, (b) electrochemistry and (c) fluid dynamics. Further details are shown in Supplementary Note 1 below.

Supplementary Note 1

Mass-transport of dissolved species was simulated by solving Nernst-Planck equations with charge neutrality. A local equilibrium of buffer species was also assumed. At the electrode surface, mass fluxes were determined by the local current density (j_s) and the stoichiometry coefficients (v_i). The stoichiometry coefficients for H⁺, H₂ and O₂ are -4, 2 and -1, respectively, when the number of electrons involved (n) is 4.

$$v_{Ox}Ox + ne^{-} \rightleftharpoons v_{Red}Red \tag{S1}$$

The local electrode current density (j_s) was determined by Butler-Volmer equation.

$$j_{s} = j_{0} \left\{ exp\left(\frac{\alpha_{a}F\eta}{RT}\right) - exp\left(\frac{-\alpha_{c}F\eta}{RT}\right) \right\}$$
(S2)

 j_0 , α_a and α_c are exchange current density, anodic and cathodic transfer coefficient, respectively. The overpotential (η) was determined by the following equation, which contains concentration overpotential due to the pH gradient.

$$\eta_{Anode} = \phi_s - \phi_l - 1.23 + \frac{RT}{2F} \ln \frac{c_{H,bulk}}{c_H}$$
(S3)

$$\eta_{Cathode} = \phi_s - \phi_l - 0 + \frac{RT}{2F} \ln \frac{c_{H,bulk}}{c_H}$$
(S4)

The local electrolyte density was determined from the reported local ion concentrations, as shown in Fig. S7. Continuity equation and Navier-Stokes equation are solved with the consideration of the local electrolyte density.



Figure S9. (a) Relative error of ΔpH on anode and velocity (at 400 μ m from anode) for varying maximum mesh element sizes. The black arrow shows the chosen mesh element size for the simulation. **(b)** Optimized mesh used in our simulation.



Figure S10. (a) Simulated pH changes at the center of the electrodes as a function of time in 0.1 M KP_i at 1 mA cm⁻² with different electrode area. (b) Simulated velocity profile between the anode and the cathode after 200 s, as a result of buoyancy-driven convection. (c) Simulated pH shift along the anode surface after 200 s.



Figure S11. (a) Simulated local concentration profile of cation and sum of anions close to the anode. The vertical dashed line identifies the location 400 μ m away from the surface of the anode. (b) Simulated local change of electrolyte density with respect to local buffer anions concentrations at 400 μ m away from the surface of the anode. All the simulations are performed with the density function of KP_i after 300 s of electrolysis at 1 mA cm⁻². The values are compared to those obtained in a hypothetical case where either the diffusion coefficient of cation (D_{cation}) is decreased to that of sodium (magenta) or the diffusion coefficient of anions (D_{anion}) is increased to that of carbonates (green).



Figure S12. Simulated change of ΔpH as a function of time in KP_i (black) and KC_i (blue) at 1 mA cm⁻². In addition, additional curves (magenta) are shown in which KP_i is considered as the electrolyte, but with the diffusion coefficient and density function varied to those of KC_i. The difference between the black and magenta lines therefore represents the impact of higher D_{anion} and lower ρ in KC_i, while the difference between the magenta and blue lines highlights the influence of the higher bulk pH.



Figure S13. Simulated pH changes as a function of time in 0.1 M KOH (pH = 13) at 1 mA cm⁻² with and without buoyancy effect.

 Table S1. Parameters used for the multiphysics simulations.

Parameters for phosphate buffer solutions	Value	Ref.
Bulk H^+ concentration, $c_{H,bulk}$	$2.0 \times 10^{-7} \text{ mol/L}$	
Bulk H ₃ PO ₄ concentration, <i>CH3PO4,bulk</i>	$1.5 \times 10^{-6} \text{ mol/L}$	
Bulk H ₂ PO ₄ ⁻ concentration, <i>CH2PO4,bulk</i>	$5.7 \times 10^{-2} \text{ mol/L}$	
Bulk HPO ₄ ²⁻ concentration, <i>CHPO4,bulk</i>	$4.3 \times 10^{-2} \text{ mol/L}$	
Bulk PO ₄ ³⁻ concentration, <i>CPO4,bulk</i>	$4.6 \times 10^{-8} \text{ mol/L}$	
Bulk O ₂ concentration, <i>c</i> _{O2,bulk}	0 mol/L	
Bulk H ₂ concentration, <i>C</i> _{H2,bulk}	0 mol/L	
Diffusion coefficient of H^+ , D_H	$9.3 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of K^+ , D_K	$1.96 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of Na ⁺ , D _{Na}	$1.33 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of H ₃ PO ₄ , <i>D</i> _{H3PO4}	$0.76 \times 10^{-9} \text{ m}^2/\text{s}$	3
Diffusion coefficient of H ₂ PO ₄ ⁻ , D _{H2PO4}	$0.85 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of HPO4 ²⁻ , <i>D</i> _{HPO4}	$0.69 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of PO_4^{3-} , D_{PO4}	$0.72 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of H_2 , D_{H2}	$5.0 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of O_2 , D_{O2}	$2.4 \times 10^{-9} \text{ m}^{2/s}$	1
1st buffer equilibrium constant, K_{a1}	7.5×10^{-3}	1
2nd buffer equilibrium constant, K_{a2}	1.5×10^{-7}	4
3rd buffer equilibrium constant, K_{a3}	2.1×10^{-13}	1
Dynamic viscosity, μ	9.0×10^{-4} Pa s	1
Temperature, T	298 K	

Parameters for carbonate buffer solutions	Value	Ref.
Bulk OH ⁻ concentration, <i>c</i> _{OH,bulk}	$2.1 \times 10^{-4} \text{ mol/L}$	
Bulk HCO ₃ ⁻ concentration, <i>CHCO3,bulk</i>	$5.0 \times 10^{-2} \text{ mol/L}$	
Bulk CO_3^{2-} concentration, <i>c</i> _{CO3,bulk}	$5.0 \times 10^{-2} \text{ mol/L}$	
Diffusion coefficient of OH^- , D_{OH}	$5.3 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of K^+ , D_K	$1.96 \times 10^{-9} \text{ m}^2/\text{s}$	1

Diffusion coefficient of HCO_3^- , D_{HCO3}	$1.19 \times 10^{-9} \text{ m}^2/\text{s}$	1
Diffusion coefficient of CO_3^{2-} , D_{CO3}	$0.92 \times 10^{-9} \text{ m}^2/\text{s}$	1
2nd buffer equilibrium constant, K_{a2}	4.68×10^{-11}	1
Dynamic viscosity, μ	$9.0 \times 10^{-4} \text{Pa s}$	1
Temperature, T	298 K	

Parameter for electrochemistry	Value	Ref.
Exchange current density for OER, $j_{0,OER}$	$1 \times 10^{-5} \text{ mA/cm}^2$	5-8
Exchange current density for HER, <i>j</i> _{0,HER}	1 mA/cm^2	5,9
HER anodic transfer coefficient, $\alpha_{a,HER}$	0.5	
HER cathodic transfer coefficient, $\alpha_{c,HER}$	0.5	
OER anodic transfer coefficient, $\alpha_{a,OER}$	1.9	
OER cathodic transfer coefficient, $\alpha_{c,OER}$	0.1	

References

- 1 D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 84th ed., 2003.
- F. Chenlo, R. Moreira, G. Pereira and M. J. Vázquez, J. Chem. Eng. Data, 1996, 41, 906– 909.
- 3 O. W. Edwards and E. O. Huffman, J. Phys. Chem., 1959, 63, 1830–1833.
- 4 A. A. Green, J. Am. Chem. Soc., 1933, **55**, 2331–2336.
- 5 S. Haussener, C. Xiang, J. M. Spurgeon, S. Ardo, N. S. Lewis and A. Z. Weber, *Energy Environ. Sci.*, 2012, **5**, 9922–9935.
- 6 G. Lodi, E. Sivieri, A. De Battisti and S. Trasatti, J. Appl. Electrochem., 1978, 8, 135–143.
- 7 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446–6473.
- 8 K. Kinoshita, *Electrochemical oxygen technology*, John Wiley & Sons, Inc., 1992.
- 9 S. Trasatti, J. Electroanal. Chem. Interfacial Electrochem., 1972, **39**, 163–184.