



Supplementary Information

**Continuous Electrochemical Water Splitting from Natural Water
Sources via Forward Osmosis**

Samuel S. Veroneau and Daniel G. Nocera*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA
02138

* Corresponding author email: dnocera@fas.harvard.edu

Table of Contents

A. Literature Search.....	3
B. Analytical Methods.....	3
B.1 Phosphate concentration determination.....	3
Figure S1. Malachite absorption assay and concentration standard plot.....	3
B.2 Chloride concentration determination.....	3
Figure S2. Lucigenin fluorescence assay and concentration standard plot.....	4
B.1 HClO ⁻ /ClO ⁻ concentration determination.....	4
Figure S3. DPD absorption assay and concentration standard plot.....	4
C. Experimental Set-up of FOWS Cell.....	5
Figure S4. Image of FOWS cell.....	5
D. Faradaic Efficiency for Direct Saltwater Splitting.....	5
Figure S5. Faradaic efficiency over 24 h for H ₂ and O ₂ generation.....	5

A. Literature Review

An exhaustive literature review was performed using Google Scholar and Web of Science, among other databases. Keywords for searches included osmosis, forward osmosis, electrolysis, water-splitting, and seawater; queries were searched with permutations of these words and others. Additionally, a third-party performed a review of the patent literature at our request. To our knowledge based on these literature and patent searches, the approach described herein has not previously been reported.

B. Analytical Methods

B.1 Phosphate Concentration Determination

Absorption spectra of a Malachite green assay were measured and compared to a seven-point standard curve (Fig. S1) to furnish phosphate concentration in the outer electrolyte solution. An aliquot of samples taken from the outer electrolyte solution were diluted 200-fold for these measurements.

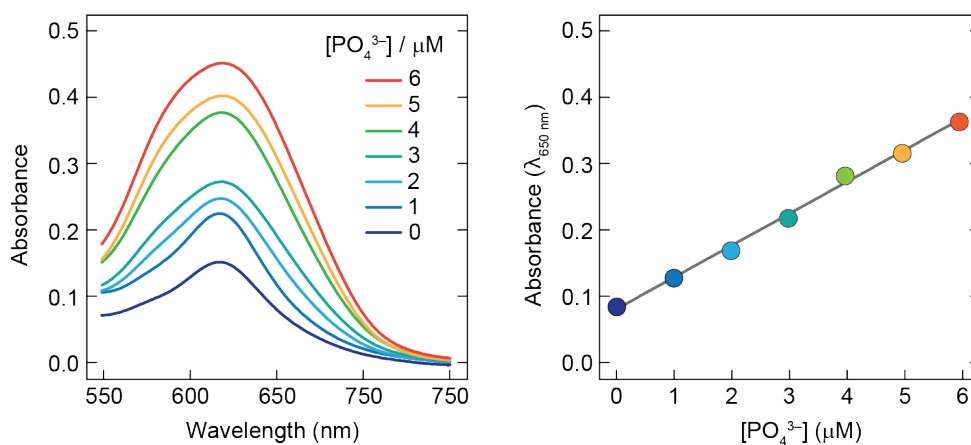


Figure S1. Absorption spectra (left) and standard curve fitting (right) for Malachite green phosphate assay (maximum absorption at $\lambda = 621$ nm) at the following $[\text{PO}_4^{3-}]$: 0 μM , 1 μM , 2 μM , 3 μM , 4 μM , 5 μM , and 6 μM . Additionally, these standard samples contained 3 mM NaCl to correspond with experimental samples and dilution.

B.2 Chloride Concentration Determination

Fluorescence emission spectra of a Lucigenin assay were measured and compared to a seven-point standard curve (Fig. S2) to furnish Cl^- concentrations. An aliquot of samples taken from the inner electrolyte solution were diluted 16-fold for these measurements.

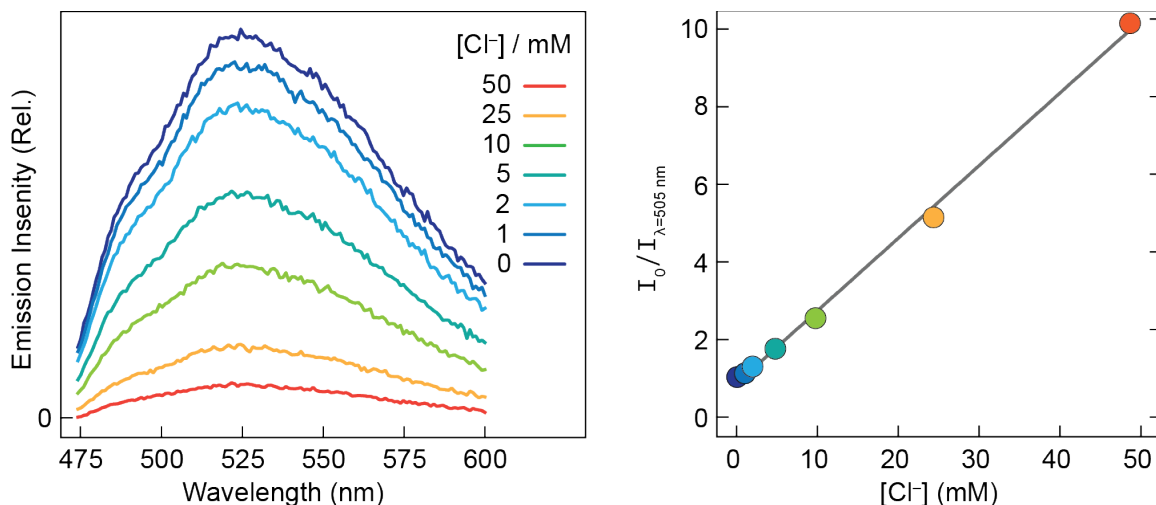


Figure S2. Emission spectra (left) and standard curve fitting (right) for Lucigenin assay ($\lambda_{\text{exc}} = 455 \text{ nm}$) at the following [Cl⁻]: 0 mM, 1 mM, 2 mM, 5 mM, 10 mM, 25 mM, and 50 mM. Additionally, these standard samples contained 50 mM NaP_i to correspond with experimental samples and dilution

B.3 HClO/ClO⁻ Concentration Determination

Absorption spectra of a DPD assay were measured and compared to a seven-point standard curve (Fig. S3) to furnish the total HClO/ClO⁻ concentration in the inner electrolyte solution. An aliquot of samples taken from the inner electrolyte solution were diluted 16-fold for these measurements.

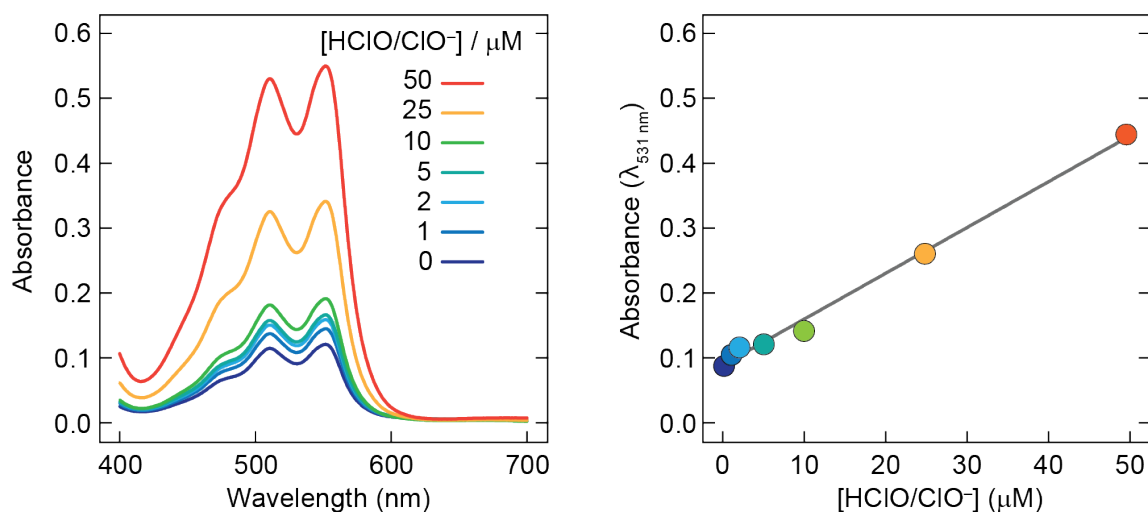


Figure S3. Absorption spectra (left) and standard curve fitting (right) for DPD assay (maximum absorption at $\lambda_{\text{max,abs}} = 531 \text{ nm}$) at the following [HClO/ClO⁻]: 0 μM, 1 μM, 2 mM, 5 μM, 10 μM, 25 μM, and 50 μM. Additionally, these standard samples contained 50 mM NaP_i to correspond with experimental samples and dilution.

C. Experimental Set-up

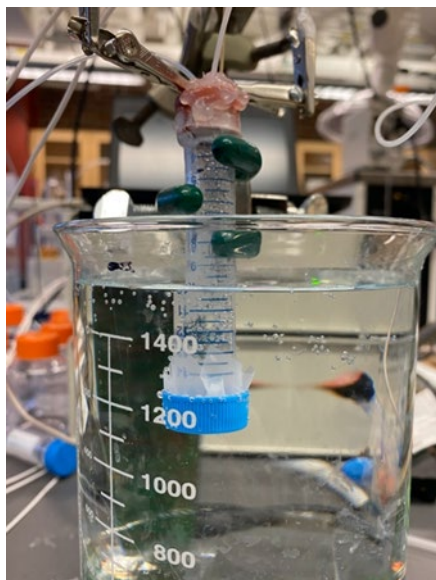


Figure S4. Image of FOWS cell in outer electrolyte of 0.6 M NaCl.

D. Faradaic Efficiency for Direct Saltwater Splitting

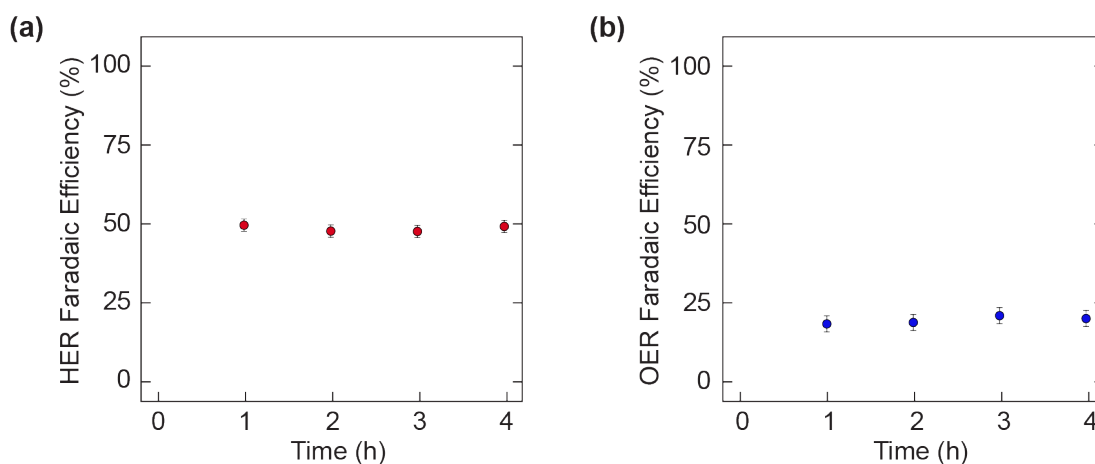


Figure S5. Faradaic efficiency plots for (a) O₂ and (b) H₂ generation from water-splitting directly from 0.6 M NaCl. Electrochemical experiments were conducted on a CH Instruments 760D bipotentiostat, using Pt flag electrodes for the anode and cathode in a single-compartment electrochemical cell operated at 250 mA.