Electronic Supplementary Material (ESI) for Energy & Environmental Science

Electronic Supplementary Information

Resistance and polarization losses in aqueous buffer-membrane electrolytes for water-splitting photoelectrochemical cells

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Tafel Plots

Current-voltage data were obtained using a BAS 100B electrochemical workstation in a three-electrode cell. A glassy carbon rotating disc electrode modified with $IrO_x \bullet nH_2O$ served as the working electrode, while a Pt coil and Ag/AgCl electrode, served as counter and reference electrodes, respectively.[1, 2] The solution resistance was measured with a clean glassy carbon RDE using the iR test function of the BAS 100B. All Tafel plots are shown with potentials corrected for series resistance. The overpontential for the oxygen evolution reaction at -25 mA/cm^2 was determined by extrapolation from the equation of the trend lines. The Ir surface coverage, Γ_{Ir}=1.2 x 10^{-7} mol/cm^2, was determined by integration of the Ir V/IV wave in the cyclic voltammogram (Fig. S-1D).

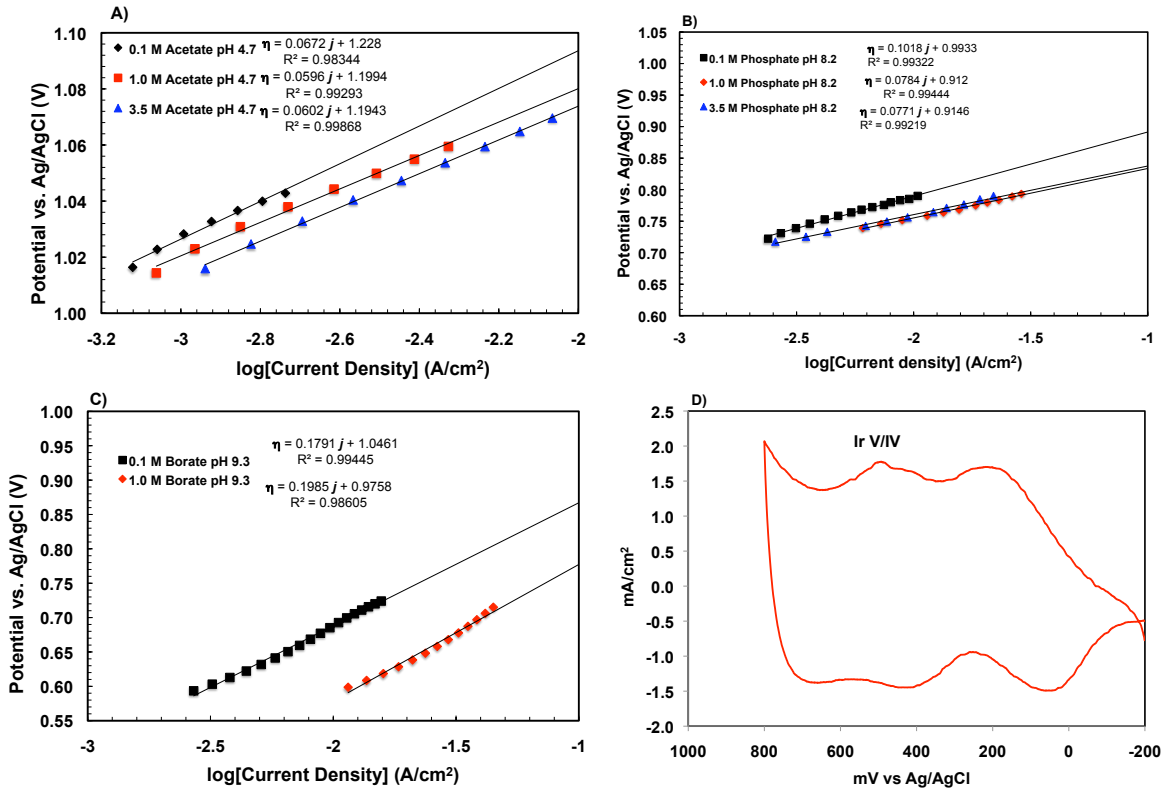

Figure S-1. Tafel plots for oxygen evolution reaction on IrO_x film in A) acetate, B) phosphate, and C) borate buffers. D) Cyclic Voltammogram for a $IrO_x \bullet nH_2O$ modified GC-RDE in 0.1 M Phosphate buffer at a scan rate of 10 mV/s.

Solution resistance and conductivity

This resistance was converted to conductivity (σ, mS/cm) using equation S-1:

$$\sigma = \frac{K}{R_{sol}} \quad \text{(S-1)}$$

Here, K is the cell constant (cm^{-1}) and R_{sol} is the resistance of the solution. K gives the parameter $\frac{l}{A}$ for the cell, which was obtained by using a 10,000 μS/cm NIST conductivity standard.

$$K = \sigma_{std} R_{std} \quad \text{(S-2)}$$
$$K = (0.09990\ \Omega^{-1} cm^{-1})(127\ \Omega) = 12.6\ cm^{-1}$$

The conductivity σ can be converted to equivalent conductivity by dividing by the buffer concentration C (S-3). The square root dependence of equivalent conductivity on ionic strength follows Kohlrausch's law (S-4).[3]

$$\Lambda = \frac{\sigma}{C} \quad \text{(S-3)}$$
$$\Lambda = \Lambda^0 - AI^{1/2} \quad \text{(S-4)}$$

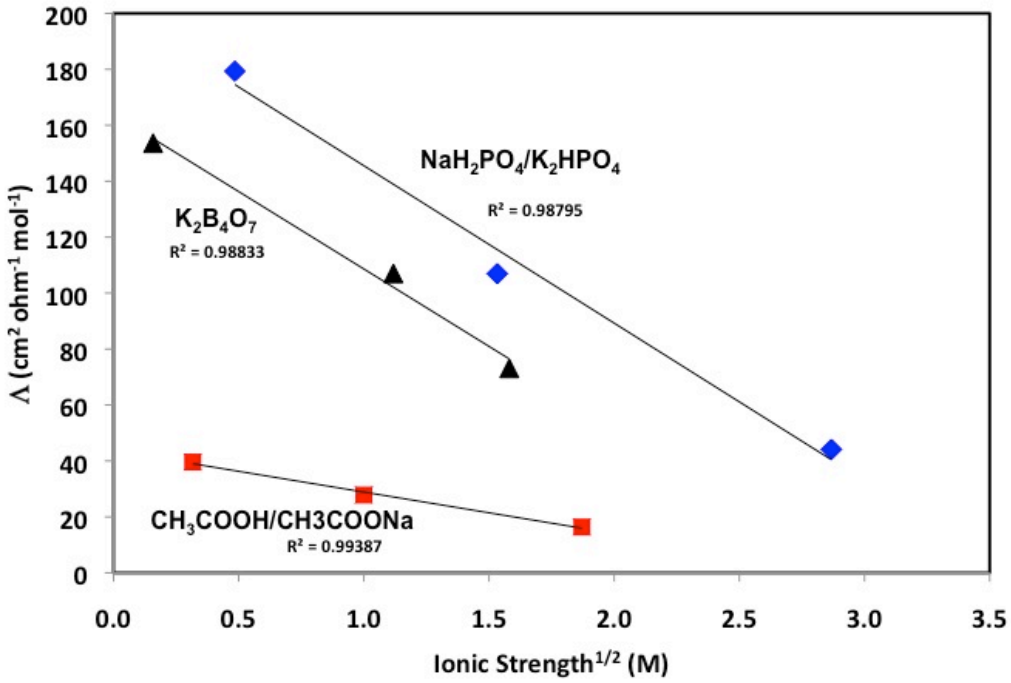

Figure S-2. Equivalent conductance as a function of the square root of the ionic strength.

Solution resistance

The potential drop associated with the solution resistance was calculated using equation (S-5). Here j, A_{ele}, S, A_{cell}, and σ_{sol}, are the current density, the area of the electrodes, the solution path length, the area of the cell, and the solution conductivity, respectively.

$$E = jA_{ele}\frac{S}{A_{cell}\sigma_{sol}} \qquad \text{(S-5)}$$

For the 3.5 M phosphate buffer example described in Section 3.2 the potential drop was calculated as:

$$E = \left(25\ \frac{mA}{cm^2}\right)\left(\frac{0.1\ cm}{154\ x\ 10^{-3}\ \Omega^{-1}cm^{-1}}\right) = 16\ mV$$

The values used are for a PEC cell operating at a current density of 25 mA/cm^2, where the area of the cell, the photoelectrodes, and the membrane are equal to 1 cm^2 (A_{cell} = $A_{electrode}$ = $A_{membrane}$ = 1 cm^2) and the solution path length is 0.1 cm.

Membrane resistance

The resistance of the membrane, R_M, was determined as follows:

$R_M = \left(R_{M+sol} - R_{sol}\right)A$, where R_{M+sol} is the resistance of the buffer solution measured with the membrane, R_{sol} is the resitance measured for the buffer solution without a membrane, and A, the area in contact with the solution was 0.38 cm^2. In both cases, the resistance was determined from the slope of i-V curves.

Balance sheet analysis

For the balance sheet analysis, which is intended to be illustrative rather than quantitative, a number of approximations were made. The diffusion coefficient of the ions in the membrane was assumed to be similar to that in water, and it was also asssumed that all anions have the same partition coefficient for exchanging into the membrane. It was assumed that the ionic conductivity, λ, of each ion is close to its value at infinite dilution, λ_0. The transport numbers were then calculated using equation (S-8), where z_j, C_j, and λ_φ are the charge, concentation, and ionic conductivity of the *j*th ion, respectively. The values for λ_0 were obtained from Lange's Handbook of Chemistry.[4] The concentration of the buffer solutions used for electrolysis was 3.5 M, and because the pH of the solution was equal to the pK_a, the concentration of both species is taken as 1.75 M.

$$t_j = \frac{|z_j| C_j \lambda_j}{\sum_k |z_k| C_k \lambda_k} \qquad \text{(S-8)}$$

The contribution of the ions to migration and diffusion currents are given by:

$$i_m = \pm \frac{n}{z} t_j i \qquad \text{(S-9)}$$

$$i_d = i - i_m \qquad \text{(S-10)}$$

A more detailed explanation can be found in reference (5).

Migration of phosphate anions through AMX membranes

Titrations were performed to determine the total number of moles of both $H_2PO_4^-$ and HPO_4^{2-} in the phosphate buffer stock solution. Prior to the titrations, the NaOH and HCl solutions were standardized to 1.002 ± 0.008 and 1.001 ± 0.002 M, respectively. Also, the pipet used to extract the samples was calibrated to 518 ± 2 µL. For the determination of the number of moles of both $H_2PO_4^-$ and HPO_4^{2-}, forward and back-titrations were employed. A 2.00 mL aliquot of standardized HCl was added to a 518 µL aliquot of the as-prepared buffer and a basic titration was performed (Fig. S-3A). From this titration, a second derivative plot (Fig. S-3B) was used to determine the endpoints to calculate (eqn. S-11) the total moles of phosphate in the sample.

$$mmoles\ phosphate = [NaOH](V_2 - V_1) = (1.002\ M)(2760 - 966) \times 10^{-3}\ L$$

$$= 1.798\ mmoles \left(\frac{4 \times 10^{-3}\ L}{518 \times 10^{-6}\ L} \right) = 13.88\ mmoles\ phosphate \approx 13.9\ mmoles \qquad \text{(S-11)}$$

An acidic titration of a second 518 µL aliquot from the as-prepared buffer was done and its second derivative plot was used to calculate (S-12) the number of moles of HPO_4^{2-} in 4.00 mL.

$$mmoles\ HPO_4^- = [HCl](V) = (1.001\ M)(893 \times 10^{-3}\ L)$$

$$= 0.894\ mmoles \left(\frac{4 \times 10^{-3}\ L}{518 \times 10^{-6}\ L} \right) = 6.903\ mmoles\ HPO_4^- \approx 6.9\ mmoles\ HPO_4^- \qquad \text{(S-12)}$$

Therefore, the amounts of $H_2PO_4^-$ and HPO_4^{2-} in each 4 mL compartment of the cell prior to electrolysis were 7.0 and 6.9 mmoles, respectively.

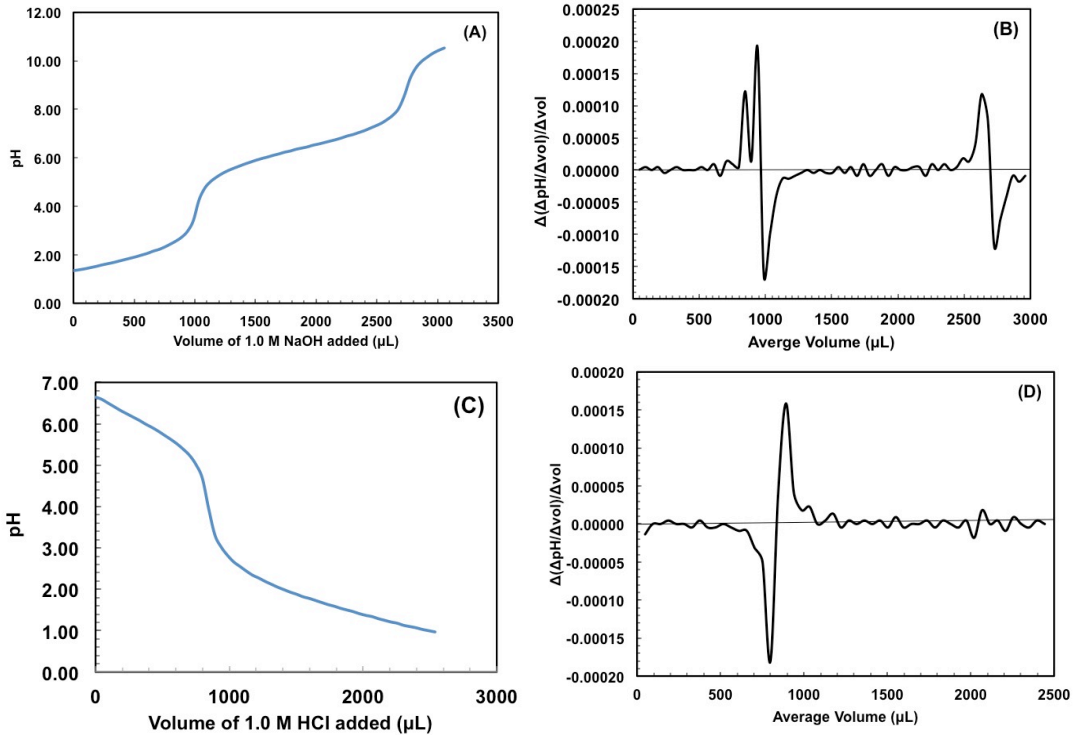

Figure S-3. A) Back-titration curve and B) second derivative plot of as-prepared 3.5 M phosphate buffer stock solution. C) Acid titration and D) second derivative plot of the buffer stock solution.

After a 24 hr continuous electrolysis (25 mA/cm^2) of the phosphate buffer solution, the solution in the cathode compartment was analyzed by titration. The initial pH of the solution was close to 11.3, and acidic titrations were performed in triplicate to calculate the total amount of phosphate ions in solution. Aliquots of 518 μL were analyzed with standardized HCl. Figure S-4 shows a sample titration and its second derivative plot. A sample calculation for the phosphate content of the cathode compartment is given in (S-13):

$$mmoles\ phosphate = [HCl](V_2 - V_1) = (1.001\ M)(1574 - 772) \times 10^{-3}\ L$$
$$= 0.8028\ mmoles\left(\frac{4 \times 10^{-3}\ L}{518 \times 10^{-6}\ L}\right) = 6.20\ mmoles\ phosphate \qquad \text{(S-13)}$$

The average number of mmoles of phosphate remaining in the 4.0 mL cathode compartment was **6.3 ± 0.1** Therefore the number of mmoles of phosphate that migrated from the cathode to the anode compartment during the experiment was given by (S-14):

$$mmoles_{initial} - mmoles_{final} = 13.9 - 6.3 = 7.6\ mmoles \qquad \text{(S-14)}$$

The number of equivalents that migrate through the membrane can be calculated from the current and time using Coulomb's law (S-15):

$$mequiv_{theoretical} = \frac{it}{F} = \frac{9.5\times10^{-3} A \times 8.64\times10^{4} s}{96.484\ C/mequiv} = 8.5\ mequiv \qquad \text{(S-15)}$$

If the current was carried entirely by $H_2PO_4^-$ anions, we would expect 8.5 mmol to migrate from the cathode to the anode compartment. In the case of the doubly charged HPO_4^{2-} anion, we would expect 4.25 mmol. The observed 7.6 mmol indicates that about 75% of the migration current is carried by $H_2PO_4^-$ and about 25% by HPO_4^{2-}.

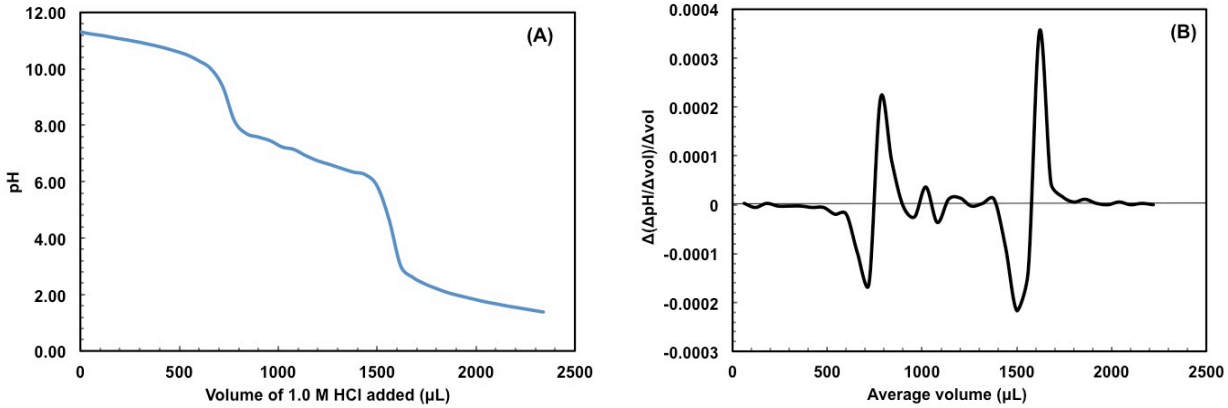

Figure S-4. A) Acid titration and B) second derivative plot of 518 μL of post-electrolysis phosphate buffer solution from the cathode compartment.

Diffusion experiments

For the simple case of monoprotic buffers (acetate and imidazole), one can calculate the diffusion flux, J_D, of each species from equation (S-16). Here ΔC, V, A, t, are the concentration difference after 24 hr in mol/L, the total volume of solution in L, the area in cm^2, and the time in seconds, respectively. The value of ΔC was determined from the change in pH using the Henderson-Hasselbach equation.

$$J_i = \frac{\Delta CV}{tA} \qquad \text{(S-16)}$$

$$J_{HOAc} = \frac{(0.13M)(0.01L)}{(8.64x10^4 s)(0.38cm^2)} = 4.0x10^{-8}\frac{mol}{cm^2 s}$$

For the more complicated case of the phosphate buffer system, the distribution coefficient of each form of the buffer was calculated from the following set of equations:

$$\alpha_0 = \frac{[H_3PO_4]}{C_T} = \frac{[H^+]^3}{D} \qquad \text{(S-17)}$$

$$\alpha_1 = \frac{[H_2PO_4^-]}{C_T} = \frac{[H^+]^2 K_{a1}}{D} \qquad \text{(S-18)}$$

$$\alpha_2 = \frac{[HPO_4^{2-}]}{C_T} = \frac{[H^+]K_{a1}K_{a2}}{D} \qquad \text{(S-19)}$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{C_T} = \frac{K_{a1}K_{a2}K_{a3}}{D} \qquad \text{(S-20)}$$

where C_T is the total phosphate concentration, the K_a's are the successive acid dissociation constants, and D is given by:

$$D = [H^+]^3 + [H^+]^2 K_{a1} + [H^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3} \qquad \text{(S-21)}$$

At each initial and final pH, the α values were calculated from the experimental pH values and C_T on the acid and base sides of the membrane was obtained algebraically using $C_{T,anode} + C_{T,cathode}$ = constant. Phosphoric acid pK_a values at 3.5 M concentration were determined experimentally from titration curves (1.8, 6.2, and 11.3).

The flux due to migration, J_m, was calculated from equation (S-22). Here j, is the current density in A/cm^2, and F, is Faraday's constant.

$$J_m = \frac{j}{F} \qquad \text{(S-22)}$$

$$J_m = \frac{2.5\ x\ 10^{-2}}{9.648\ x\ 10^4\ A \cdot s} = 2.6\ x\ 10^{-7}\ \frac{mol}{cm^2\ s}$$

Titration analysis of solutions: Acetate buffer

Under the conditions of electrolysis it is possible that acetate could be decomposed anodically. For this reason a titration analysis was performed before and after electrolysis. First, 500 μL of an acetate buffer stock solution (~3.5 M, pH 4.7) was placed in a vial and 1.6 mL of 1.00 M HCl was added to convert all the OAc^- to HOAc + excess HCl. This solution was titrated with 1.00 M NaOH. The total moles of OAc^- + HOAc were obtained by subtracting the moles calculated from the first inflection point (Fig. S-5), which corresponds to OH^- reacting with the excess acid, from the moles of base need to reach the second inflection point (S-23). Based on these results the concentration of the stock solution is 3.5 M.

$$moles\ of\ OAc^- + HOAc = [total\ moles\ of\ OH^-] - [moles\ of\ excess\ acid] \qquad (S-23)$$

$$moles\ of\ OAc^- + HOAc = [(1.0\ M)(2.35\ x\ 10^{-3}\ L)] - [(1.0\ M)(6.0\ x\ 10^{-4}\ L)] = 1.75\ mmol$$

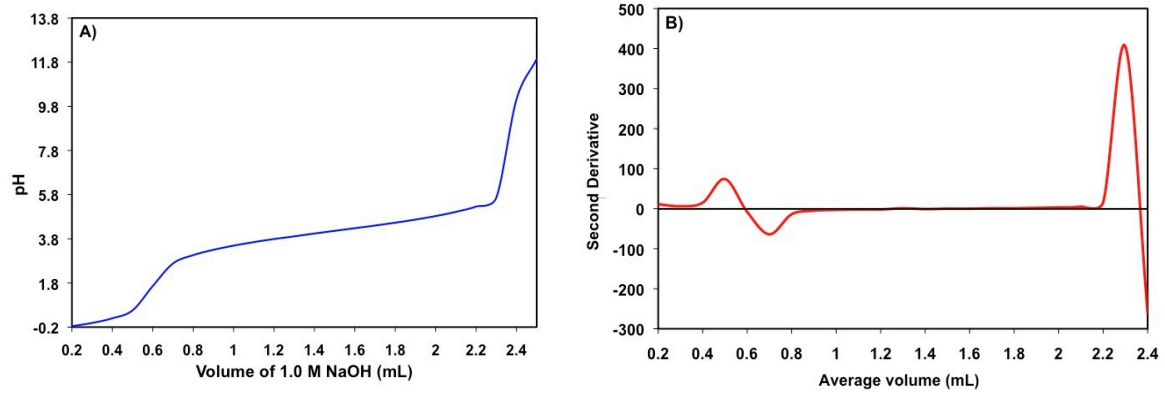

Figure. S-5. A) Titration curve and B) second derivative curve for a 3.5 M acetate buffer stock solution.

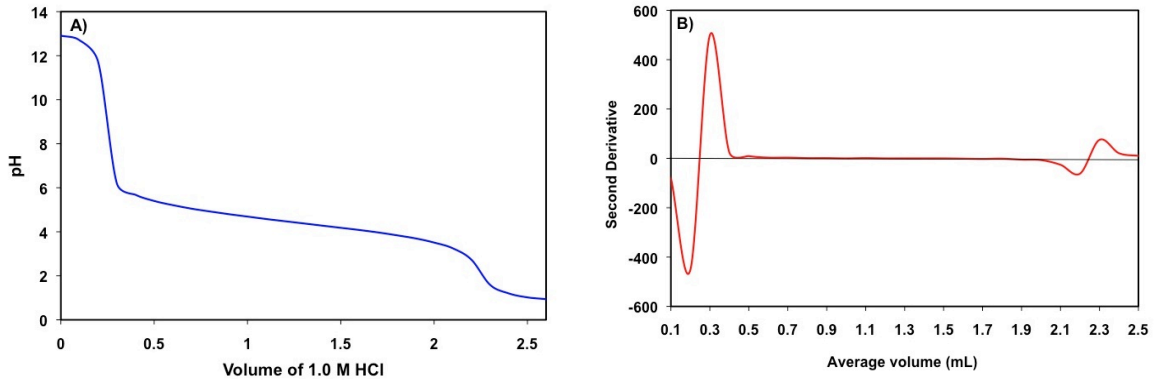

Figure S-6. A) Titration curve and B) second derivative curve for a combined anolyte/ catholyte aliquot after electrolysis of 8 mL 3.5 M acetate buffer, initially at pH 4.7, at 25 mA/cm^2 for 48 hr.

A cell containing a total volume of 8 mL of acetate buffer (i.e. 28 mmoles) was electrolyzed at 25 mA/cm^2 for 48 hr. After electrolysis, 500 μL of catholyte and anolyte were combined and titrated with 1.0 M HCl, as the intial pH of the solution was ~12. The total moles of OAc^- + HOAc were also obtained by subtracting the moles calculated from the first inflection point (Fig. S-6), which corresponds to H^+ reacting with the excess base, from the moles of base needed to reach the second inflection point (S-24).

$$moles\ of\ OAc^- + HOAc = [total\ moles\ of\ H^+] - [moles\ of\ excess\ base] \quad (S-24)$$

$$moles\ of\ OAc^- + HOAc = [(1.0\ M)(2.45x\ 10^{-3}\ L)] - [(1.0\ M)(2.5\ x\ 10^{-4}\ L)] = 2.2\ mmol$$

From the titration of the stock solution, the aliquot taken from the post-electrolysis solution should contain close to 3.5 mmoles of the acetate species. Titration analysis of the electrolyzed solution yielded 2.2 mmoles, corresponding to a 37% difference. A total charge of 1.642 x 10^3 C, equivalent to 17 mmoles of electrons, was passed during the electrolysis experiment. This charge would be enough to decompose 63 % of the acetate in solution, assuming a 1-electron Kolbe mechanism for acetate oxidation. The estimated error in the titration analysis is ±10%, suggesting that approximately 20% of the acetate does decompose after an exhaustive electrolysis. A similar analysis was carried with the acetate buffer solution used for the "on-off" electrolysis experiments. After electrolysis, 500 μL of catholyte and anolyte were combined and and 2.8 mL of 1.0 M HCl was added to convert all the OAc^- to HOAc + excess HCl. This solution was titrated with 1.0 M NaOH (Fig. S-7) and the moles of acetate species was determined as described for the stock solution (S-13). This aliquot, taken from the post-electrolysis solution, should contain close to 3.5 mmoles of the acetate species. The titration analysis yielded a value of 3.1 mmoles, corresponding to an 11% difference. This suggests that if the buffer is decomposing in the experiment, the amount is with in the error of the titration analysis.

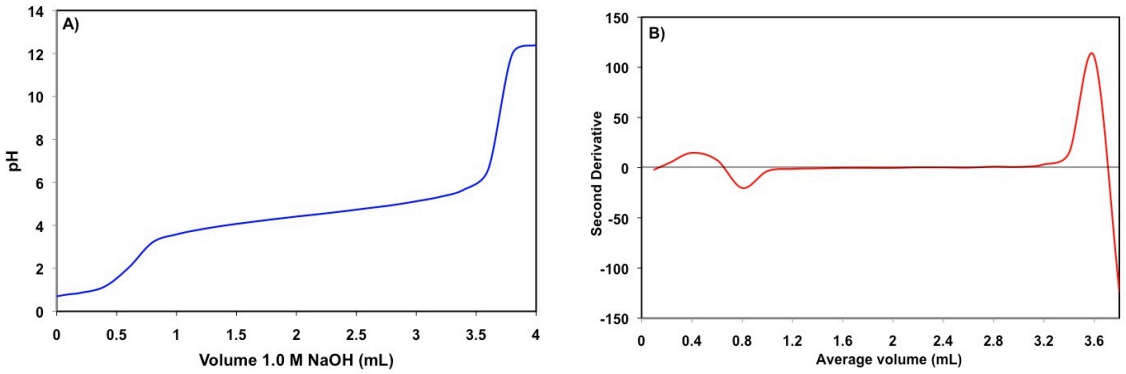

Figure S-7. A) Titration curve and B) second derivative curve for aliquot after on-off electrolysis of 8 mL of 3.5 M acetate buffer at an initial pH of 4.7. The on-off experiments consisted on performing electrolysis for 8 hr at 25 mA/cm^2, followed by 16 hrs off. This cycle was repeated three times prior to the titration.

On-off electrolysis of Imidazole buffer

During the on-off electrolysis experiment with the imidazole/CMX system a slow recovery is seen in the pH gradient (Table S-1). However the recovery is limited as the buffer capacity is rapidly decreased by electropolymerization of imidazole at the anode.[6]

After electrolysis the platinum electrode is covered by a black film, consistent with oxidative polymerizatio of imidazole, and the anolyte turns dark with a precipitate. The catholyte and anolyte were analyzed by proton NMR and evidence of decomposition was found (Figure S-8 & S-9).

Table S-1. On-off electrolysis with 3.5 M Imidazole/CMX

Time	pH anode	pH cathode
0	6.97	6.97
On (8 hrs)	5.95	7.29
Off (16 hrs)	6.12	7.19
On	4.35	7.43
Off	4.86	7.27
On	1.8	7.52
Off	2.29	7.26

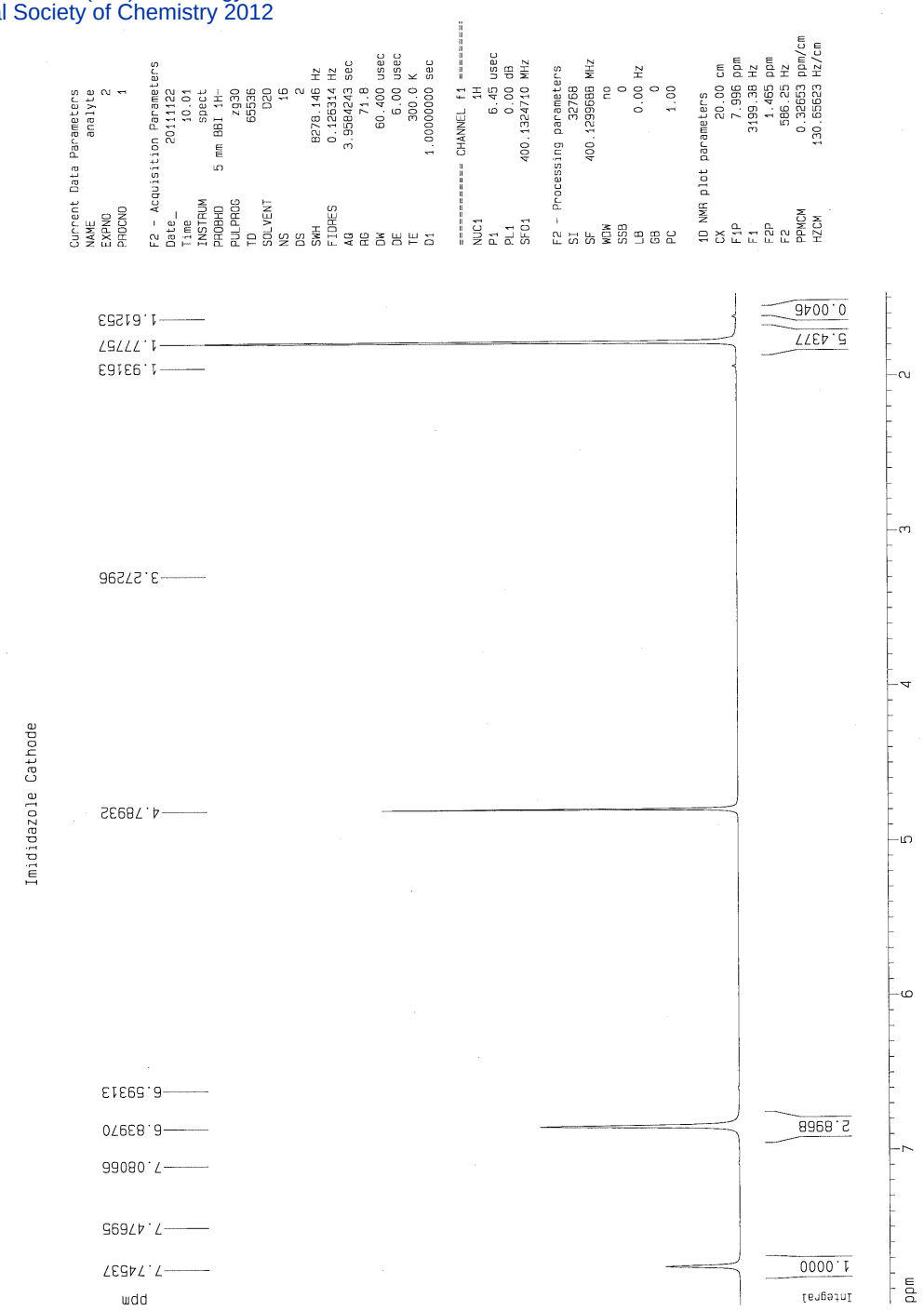

Figure S-8. Proton NMR spectrum of imidazole buffer after 16 hrs (anolyte) of electrolysis in D_2O with acetone added as a standard.

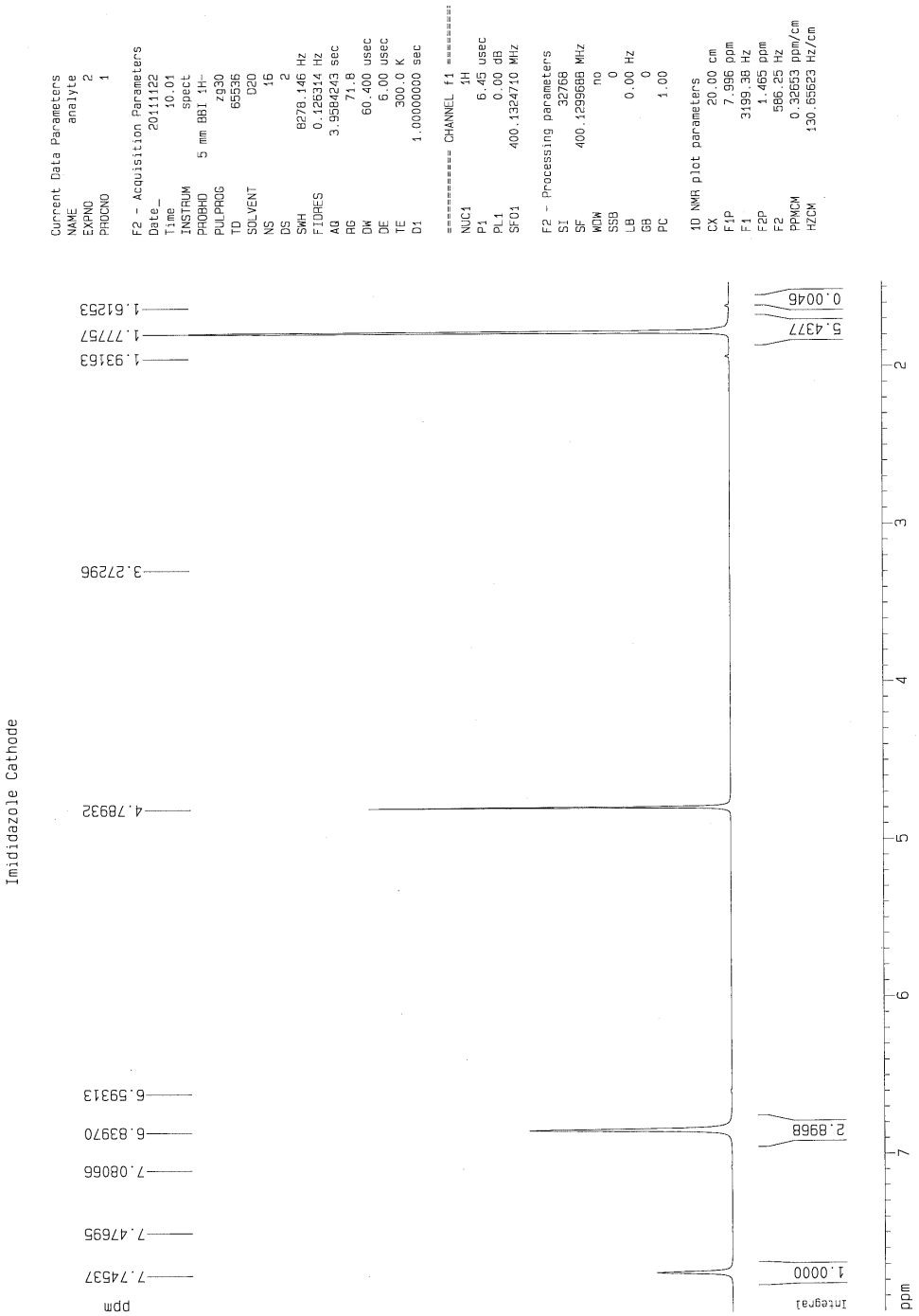

Figure S-9. Proton NMR spectrum of Imidazole buffer after 16 hrs (catholyte) of electrolysis in D_2O with acetone added as "standard".

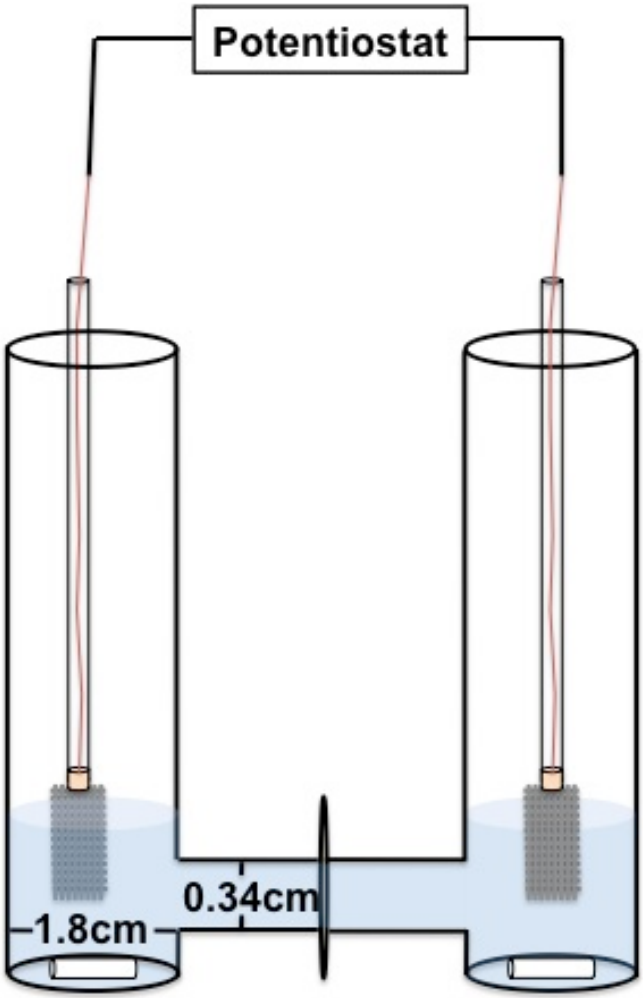

Figure S-10. Schematic of cells used for the pH gradient measurements and on-off electrolysis.

Borate buffer

We calculated the species distribution of electrolytes in the buffer solutions as a function of pH using the MINEQL+ code.[7] Developed at MIT in the mid 1970's, MINEQL+ is a chemical equilibrium code capable of calculating aqueous speciation, solid phase saturation states, precipitation-dissolution, and adsorption. MINEQL+ uses a thermodynamic database that contains the entire USEPA MINTEQA2 and USGS WATEQ database and allows the user to input data for chemical components that the database does not include. However ion pairing equilibria, which are likely to be significant at high concentration, are not included in the model. To simulate the species distribution, the equilibria shown below were considered. The model shows that in addition to boric acid, several borate species including $H_2BO_3^-$, $H_8(BO_3)_3^-$, and $H_5(BO_3)_2^-$ are present in appreciable concentration at pH 9.3 and 0.5 M total boron concentration. Notably, all the basic borate species have a -1 charge, and the acid form, H_3BO_3, is uncharged.

$$H_2O \leftrightarrow H^+ + OH^- \qquad K = \left[H^+\right]\left[OH^-\right] = 10^{-13.997}$$

$$B(OH)_3 + 2H_2O \leftrightarrow B(OH)_4^- + H_3O^+ \qquad K = \frac{\left[B(OH)_4^-\right]\left[H_3O^+\right]}{\left[B(OH)_3\right]} = 10^{-9.236}$$

$$3B(OH)_3 + H_2O \leftrightarrow H_8(BO_3)_3^- + H_3O^+ \qquad K = \frac{\left[H_8(BO_3)_3^-\right]\left[H_3O^+\right]}{\left[B(OH)_3\right]^3} = 10^{-7.306}$$

$$2B(OH)_3 + H_2O \leftrightarrow H_5(BO_3)_2^- + H_3O^+ \qquad K = \frac{\left[H_5(BO_3)_2^-\right]\left[H_3O^+\right]}{\left[B(OH)_3\right]^3} = 10^{-9.306}$$

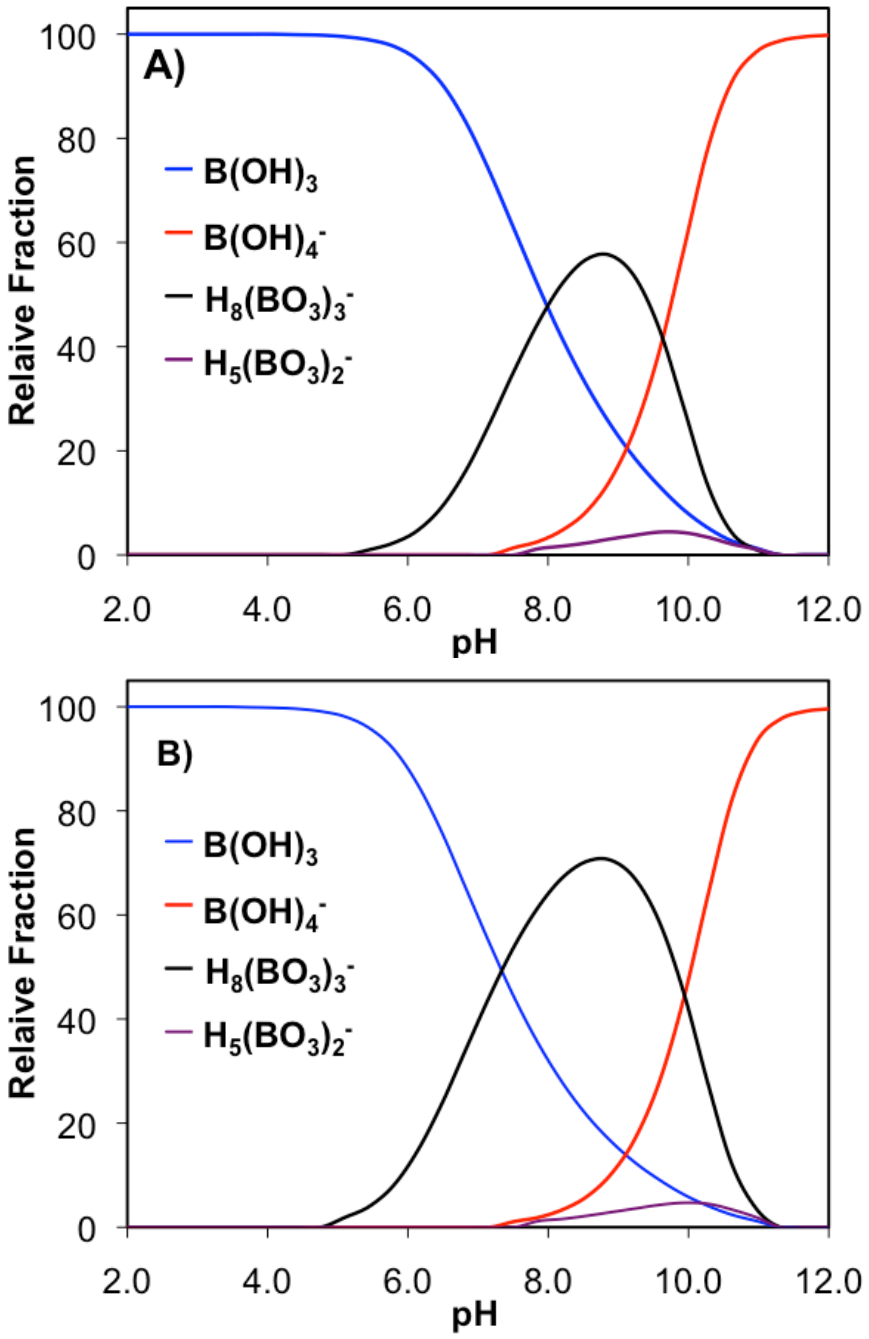

Figure S-11. Species distribution as function of pH for A) 0.5 M borate and B) 1.0 M borate buffers obtained from MINEQL+.

References

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