# Supporting Information: Towards Direct Electroanalysis in Seawater: Understanding the Role of the Buffer Capacity of Seawater in Proton-Coupled Electron Transfer Reactions

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## Section 1 Carbonate Equilibrium Constants in Seawater

In the oceanography stoichiometric constants are used to define the relevant chemical equilibria. For example the acid dissociation constant for the bicarbonate/carbonate system is:

#### $K2 = [H+][CO_3^{2-}]/[HCO^{3-}]$

where the concentrations are expressed in moles per kilogram of solution and not activities. Importantly using the above definition, since concentrations as opposed to activities are used, the stoichiometric acid dissociation constants vary as a function of ionic strength, temperature and pressure. Millero [1] provides an extensive overview of the marine inorganic carbon equilibria and their associated constants. In the literature the constants are reported to a high level of precision as a function of the salinity of the solution and the temperature. The practical salinity scale (S) is related to the conductivity of a standard solution of KCl solution, however, in this work we have simply taken a value of S=35 and T = 298 K to give us the stoichiometric acid dissociation constants as:

$H_2O(l)$ + $CO_2(aq)$ $\Rightarrow$ $HCO_3^-(aq)$ + $H^+(aq)$	$K_a^* = 1.4 \times 10^{-6} M$
$H_2CO_3(aq)$ $\rightleftharpoons$ $HCO_3^-(aq)$ + $H^+(aq)$	$K_{a1} = 1.2 \times 10^{-3} M$
$HCO_3^-(aq) \rightleftharpoons CO_3^2^-(aq) + H^+(aq)$	$K_{a2} = 1.1 \times 10^{-9} M$

Note the first  $pK_a^*$  as expressed above is the effective, 'apparent' or composite first acid dissociation constant where the \* is used to designate that this is the equilibria is comprised of two reactions, the protonation of bicarbonate to form carbonic acid and the dehydration of carbonic acid to yield dissolved carbon dioxide. From the above composite equilibrium and knowledge of the hydration constant [2] for carbon dioxide ( $K_{eq}$  = 848 in high ionic strength media) the 'true' first pK<sub>a</sub> for carbonic acid can be inferred to be 2.9 at ionic strengths comparable to seawater.

# Section 2 Formal potential of the hydrogen/proton redox couple

The Nernst equation for the hydrogen/proton redox couple is [3]:

$$\mathbf{E} = \mathbf{E}_{\mathrm{H}^{+}/\mathrm{H}_{2}}^{\Theta} + \frac{RT}{F} \ln \frac{a_{\mathrm{H}^{+}}/a^{\Theta}}{p_{\mathrm{H}_{2}}^{1/2}/p^{\Theta^{1/2}}}$$

where  $E_{H+/H2}^{\ominus}$  is the standard hydrogen electrode (SHE) potential and is by definition 0.00 V,  $a_{H+}$  is the proton activity (mol dm<sup>-3</sup>),  $a^{\ominus}$  is the standard activity (1 mol dm<sup>-3</sup>),  $p_{H2}$  is the hydrogen pressure (bar), and  $p^{\ominus}$  is the standard pressure (1.013 bar). In contrast to the above equation the formal potential is defined not at the standard state but at standard concentration (see equation 6 of the main text). Consequently, the difference between these two potentials can be analytically expressed as [4]:

$$E_{f}^{\ominus} = E_{H}^{\ominus}_{H_{2}} + \frac{RT}{F} \ln \frac{\gamma_{H} + p^{\ominus 1/2}}{K_{H_{2}}^{1/2} 10^{k_{s}[salt]/2} a^{\ominus 1/2}}$$

where  $\gamma_{H^+}$  is the proton activity coefficient,  $K_{H2}$  is the Henry constant for hydrogen (1292 dm<sup>3</sup> bar mol<sup>-1</sup>),  $k_s$  is the Sečenov parameter for the used electrolye and [salt] is the concentration of the used electrolyte. In the theory section we consider the situation in which the hydrogen oxidation reaction is occurring in a pure water solution, hence  $\gamma_{H^+}$ = 1 and [salt] = 0. In this case the formal potential for the hydrogen/proton redox couple can be calculated to be -0.0918 V vs SHE.

For the case in which the HOR is being studied in the presence of an electrolyte the situation is slightly more complicated. At a concentration of 0.7 M the proton activity coefficient will be approximately 0.772, as reported for HCl. Further the Sečenov parameter for NaCl is reported to be 0.114. Consequently, under these conditions the formal potential for the hydrogen/proton redox couple is - 0.1008 V vs SHE, this is a shift of 9 mV from the formal potential in the absence of electrolyte.

### Section 3 Simulation Details

The one-dimensional voltammetric response was simulated using a central fully implicit finite difference method, as covered in reference [5]. Although the results are presented herein in a dimensional form the simulation uses dimensionless variables as also introduced in the literature.[5] An exponential expanding grid was used with an expanding grid factor of 1.01 and an initial step size of 1x10<sup>-9</sup>. Notably due to the presence of non-linear terms an iterative Newton-Raphson method was employed to solve the system of equations. The convergence level for the Newton-Raphson iterations was set as being when the average concentration varied by no more than 1x10<sup>-8</sup>. The simulation was written in Python 3.6.8 and the resulting sparse matrix was solved using the spsolve function provided as part of the SciPy package. Using a potential step size of ~2mV the simulation time was less than a minute, for some of the simulations a smaller potential step size was used to increase the accuracy of the reported mid-point potential. Last the kinetics of the acid/base reaction are in all cases set to be fast enough as to ensure that the reaction is fully at equilibrium this can lead to the use of forward rate constants that are formally greater than the diffusion limited reaction rate for a bimolecular reaction.

In the simulation a Nernstian boundary condition is assumed to apply at the electrode surface, further as both the reactant and product are considered in the reaction scheme conservation of mass also needed to be accounted for where:

 $J_{H^+} = -2J_{H^2}$ 

where  $J_{H_{+}}$  and  $J_{H_{2}}$  are the flux at the interface of the protons and hydrogen respectively.

#### 3.1 Validation

DIGISIM (version 3.0, BASi Technicol, West Lafayette, IN) is a commercially available software package able to simulate 1D electrochemical problems. However, it is not able to be used for studying nonunity stoichiometric reactions such as the hydrogen/proton system without the introduction of fictitious chemical reactions. Consequently, to validate the results the simulation presented in this work the simulation needed to be modified so that the results could be directly compared to those obtained from DIGISIM. To this end an ECC reaction was simulated using DIGISIM where the simulation details were the same as presented in Figure 2 a) of the main text, the only change was that the interfacial reaction stoichiometry was altered to being a unity reaction (A - e = B). Figure S1 presents the comparison between the DIGISIM results (red dashed lines) and those produced by the lab-written simulation (solid black line) where the two sets of voltammograms superimpose. In comparison to the data presented for the non-unity stoichiometry reaction in Figure 2 of the main text there are a few notable differences between the two sets of voltammograms. First, the oxidative wave for the unity reaction occurs at a distinctly different potential despite having the same formal potential. Second, the voltammetric peak heights differ significantly due to both the change in the number of electrons transferred per reactant molecule and further due to the change in the voltammetric wave shape.



Figure S1: Comparison of an ECC reaction as simulated using the commercial software package DIGISIM (red dashed line) and the bespoke lab written simulation (black line). The two data sets are completely superimposed. The figure shows the simulated voltammetric response for the reversible oxidation of A to B (unity reaction one-electron) and the influence of the presence of species X in the solution phase which is able to undergo a bimolecular reaction with B to form species Y and where the formed species Y is able to undergo a further unimolecular reaction. A fixed concentration of species X is used  $C_x = 10 \text{ mM}$ and the forward rate constant of the unimolecular reaction  $k_f$  is varied from  $1x10^{-2} - 1x10^8 \text{ s}^- K_{eq1} = 1000 \text{ M}^{-1}$ ,  $K_{eq2} = 1000$ ,  $D_A$  $= 5.1x10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $D_B = 9.3x10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $D_X = D_Y = D_Z = 1x10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $[A]_{bulk} = 0.784 \text{ mM}$ ,  $E_f = -0.0918 \text{ V}$  (vs SHE), electrode radius = 1 mm and scan rate = 0.1 V s^{-1}.

Having validated the simulations voltammetric response for a unity reaction, the validity and accuracy of the implemented non-unity electrode boundary condition was considered. A simple reversible E reaction was simulated. Due to the change in the stoichiometry there is a corresponding change in the voltammetric peak shape leading to a change in the peak height. For a simple reversible process the simulated peak height is compared to known literature results.[6] In the case of the hydrogen oxidation reaction the reversible peak current is given by:

$$I_{p,H_2} = 0.7686FA[H_2] \sqrt{\frac{2vFD_{H_2}}{RT}}$$

Where the area A =  $3.14 \times 10^{-6} \text{ m}^2$ , [H<sub>2</sub>] = 0.784, D<sub>H2</sub> =  $5.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Consequently, at a scan rate of 0.1 V s<sup>-1</sup> the expected peak current is 36.403 uA. Figure S2 depicts the simulated voltammetric response for a reversible 1:2 stoichiometry electrochemical reaction, the simulated peak current is 36.400 uA. This discrepancy between the simulated and literature reported peak height is less than 0.01 %. This excellent agreement with the literature confirms that the non-unity stoichiometric Nernst boundary condition has been correctly implemented.



Figure S2: Simulated reversible voltammetric response for the reaction  $H_2 = 2H^+ + 2e^-$ , as measured at a macroelectrode with a radius of 1 mm and initially in a solution containing 0.784 mM hydrogen and no protons.  $D_{H2} = 5.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{H+} = 9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ 

## Section 4 Simulated HOR voltammetry in the presence of bicarbonate

In Figure 4 a of the main text the experimental voltammetric response of the hydrogen oxidation reaction is presented as a function of the concentration of bicarbonate (0-1.0 mM). For comparison here we provide in Figure S3 the simulated voltammetric response. All simulation details are the same as the main text apart from the use of a variable base concentration.



Figure S3 The simulated response for the hydrogen oxidation reaction in the presence of a variable concentration of bicarbonate (0-1.0 mM). Simulation details:  $[H_2] = 0.644 \text{ mM}$ ,  $pK_{a1} = 2.9$ ,  $K_{eq2} = 868$ ,  $D_{H2} = 4.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{H+} = 6.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{base} = D_{acid} = 10.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $E_f = -0.1008 \text{ V}$  (vs SHE), electrode radius = 0.83 mm and scan rate = 0.1 V s<sup>-1</sup>.

### Section 5 HOR in the presence of carbonate

Carbonate is a strong enough base ( $pK_{a2} = 8.95$ ) that the hydrogen oxidation reaction onsets outside of the voltammetric window. Figure S4 presents the hydrogen oxidation reaction in the presence of a finite concentration of carbonate. At low concentrations increasing carbonate leads to removal of the voltammetric back peak- similarly to the bicarbonate case the carbonate ion serves to titrate away the formed protons. However also notable is that the current at lower potentials (-0.7 – -0.6 V vs SCE) increases. Furthermore, at high carbonate concentrations (10 mM see inset) no clear voltammetric peak occurs, even at the start of the voltammogram ~10 uA of oxidative current are passed. Hypothetically if one could start the voltammogram at a lower potential one would expect to see a clear hydrogen oxidation wave; however solvent breakdown limits the potential range that can be studied, the onset of hydrogen evolution from the solvent obscures the process.



Figure S4 The oxidation of hydrogen on a platinum macroelectrode A) 0.7 M NaCl in the presence of increasing concentration of carbonate 0-0.5 mM (10 mM inset).

#### References

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