Supporting Information

A Bespoke Reagent-free Amperometric Bromide Sensor for Seawater

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Section 1 Calculation of Transfer coefficients from Tafel Analysis

This section reports the use of Tafel analysis for obtaining the transfer coefficient β for the bromide oxidation reaction (BOR) at a Pt macro-disc electrode. As shown in SI.1a, cyclic voltammograms in degassed 0.84 mM Br^- with 0.1 M KNO_3 at variable scan rates of 20, 50, 100, 200 and 400 mV s^{-1} were recorded. The potential started at 0 V vs. SCE, swept towards 1.7 V before returning to 0 V. an oxidation peak is seen at 0.98 V *vs.* SCE and one reduction peak at 0.85 V *vs.* SCE were observed at different scan rates, consisted with the observation of Chen and Kumar *et al.* [1]. We infer that $peak_1$ (oxidation) and $peak_{1'}$ (reduction) correspond to the following redox reaction:

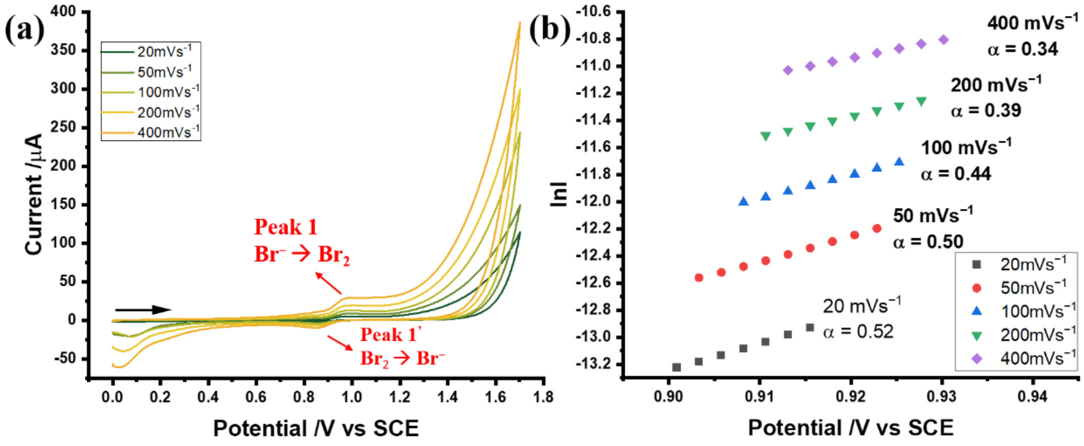
$$Br^- \rightleftharpoons \frac{1}{2}Br_2 + e^- \qquad (8)$$

Note that at the concentrations of bromide used, the formation of the tribromide anion is negligible. Chen *et al.* reported simulations showing that a concentration of ca 0.1 M of bromide would be needed for sufficient tribromide ion to be generated[1] The transfer coefficient β can be calculated from the following expression 1. [2]

$$\beta = \frac{RT}{F}\frac{\partial ln|I_{ox}|}{\partial E} \qquad (1)$$

where I_{ox} is the oxidative current.

For the BOR at Pt macro-disc electrode in of 0.84 mM Br^- ions supported by 0.1 M KNO_3 recorded with different scan rates (20, 50, 100, 200 and 400 mVs^{-1}), Tafel plots of $ln|I_{ox}|$ vs potential (V vs SCE) are shown as SI.1b. An average β value was calculated to be 0.44 ± 0.07 for BOR indicating that in the media studied the reaction is electrochemically irreversible.



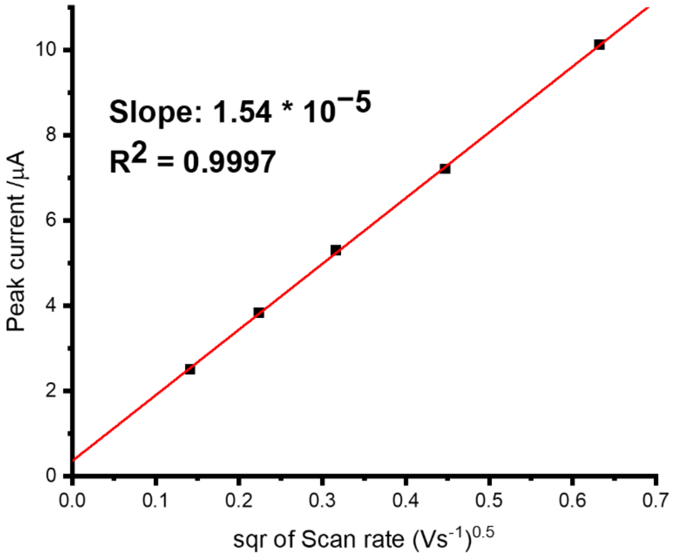
SI.1 *(a) Cyclic voltammograms in degassed 0.84 mM* Br^- *with 0.1 M* KNO_3 *at variable scan rates of 20, 50, 100, 200 and 400 mV* s^{-1}*. The potential started at 0 V vs. SCE, swept towards 1.7 V before returning to 0 V. (b) The Tafel plots for the BOR at Pt macro-disc electrode in of 0.84 mM* Br^- *ions supported by 0.1 M* KNO_3 *recorded with different scan rates (20, 50, 100, 200 and 400* mVs^{-1}*). 10% - 30% of the current range of the forward wave was used.*

Section 2 Calculation of the Bromide Diffusion Coefficient

This section explains the calculation of the diffusion coefficients, D, for Br^- and Br_2 from the voltammograms obtained as a function of scan rate for BOR. The Randles–Ševčík equation for an irreversible one-electron transfer reaction, $A - e^- \rightleftharpoons B$, was used to estimate the D for Br^- [2]:

$$I_p = 2.99 \times 10^5 \sqrt{\beta} [A]_{bulk} D^{0.5} A \upsilon^{0.5} \tag{1}$$

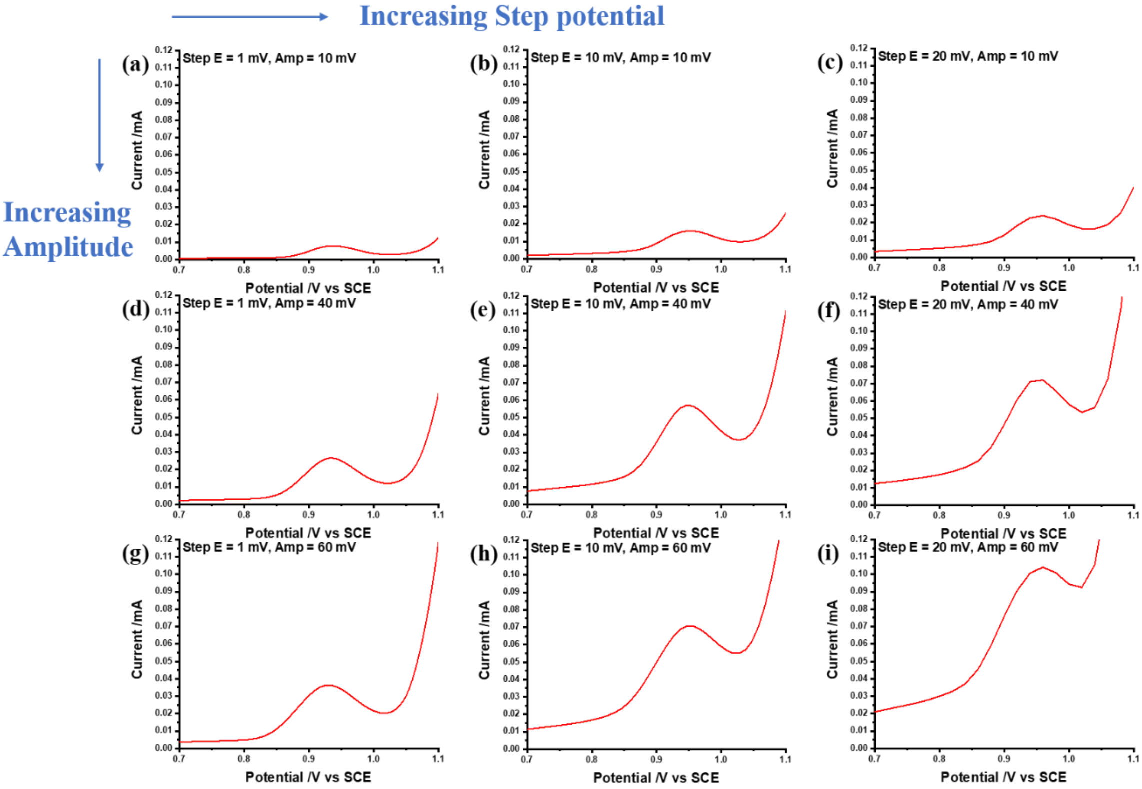
where I_p is the oxidative peak current, β is the transfer coefficient calculated from the Tafel analyses discussed in previous section, A is the area of the Pt macro-disc electrode (0.02 cm^2). $[A]_{bulk}$ is the bulk concentration of the bromide ions (0.84 mM). SI.2 shows that the peak current scales with the square root of the voltage scan rate as predicted. The linearity confirms a diffusion-controlled electrode process. The diffusion coefficient of the bromide ion in 0.1 M KNO_3 was measured with a value of 2.1×10^{-5} cm^2/s which compares well with the literature value of 2.08×10^{-5} cm^2/s [3] and 2.1×10^{-5} cm^2/s [1].



***SI.2** The calibration plot of the peak current of I_p against the concentration of bromide ions measured with a scan rate of 20 mVs^{-1}.*

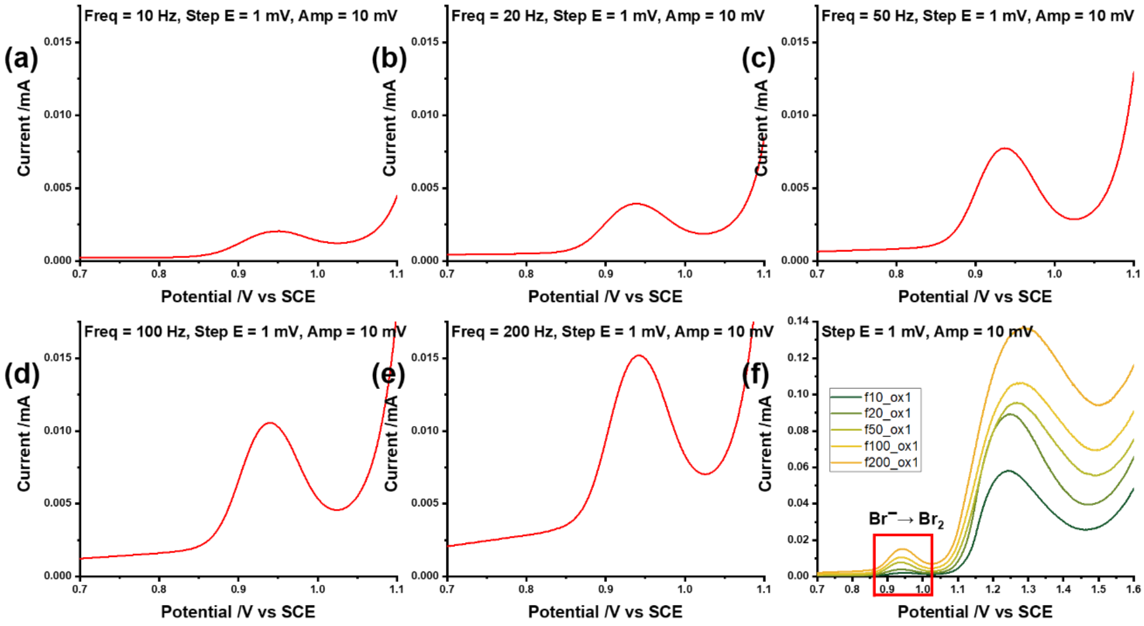
Section 3 The Optimisation of SWV parameters

This section reports the effect of three parameters (frequency, step potential and amplitude) on the SWV signal as tested for the oxidation of bromide ions. Voltammograms were conducted in a degassed ASW from a potential of 0 V *vs.* SCE, and stop at 1.7 V *vs.* SCE for an oxidative scan. The optimisation of step potential and amplitude was first performed with a fixed frequency of 50 Hz whilst varying the step potential and amplitude. SI 3 shows recorded SWVs with a potential window from 0.7 to 1.1 V focusing on the bromide peak (0.94 V *vs.* SCE). Comparison of all the SWVs showed that an amplitude of 10 mV, and a step potential of 1 mV gave a well-defined peak with the best resolution (SI. 3a).



SI. 3 *Effect of increasing step potential (from left to right) and increasing amplitude (downward) on the SWV (focusing on bromide oxidation peak) with a fixed frequency of 50 Hz in a degassed ASW. (a) Step E = 1 mV, Amp = 10 mV, (b) Step E = 10 mV, Amp = 10 mV, (c) Step E =20 mV, Amp = 10 mV, (d) Step E = 1 mV, Amp = 40 mV, (e) Step E = 10 mV, Amp = 40 mV, (f) Step E = 20 mV, Amp = 40 mV, (g) Step E = 1 mV, Amp = 60 mV, (h) Step E = 10 mV, Amp = 60 mV, (i) Step E = 20 mV, Amp = 60 mV.*

Then, adopting an amplitude of 10 mV and the step potential of 1 mV, the optimisation of the frequency was conducted (SI. 4). SI. 4f indicates overlaid SWVs to demonstrate the effect of varying frequency on the peaks. There are again two oxidation peaks observed, namely of bromide (ca. 0.94 V *vs.* SCE) and of chloride (ca. 1.26 V *vs.* SCE), the peak currents of which increase with the frequency. An acceptable peak shape of bromide oxidation relative to the background at a frequency of 50 Hz was obtained as shown by SI. 4c. Thus, the optimised SWV with a frequency of 50 Hz, amplitude of 10 mV and step potential of 1 mV was applied to record the electroanalytical responses of bromide ions in the presence of high levels of chloride.



SI. 4 *Effect of frequency on the SWV (focusing on bromide oxidation peak) with fixed step potential (1 mV) and amplitude (10 mV) in a degassed ASW. (a) Freq = 10 Hz, (b) Freq = 20 Hz, (c) Freq = 50 Hz, (d) Freq = 100 Hz, (e) Freq = 200 Hz, (f) Overlaid SWV with various frequencies, Step E = 1 mV and Amp = 10 mV.*

Section 4 The composition of natural seawater obtained by Ion chromatography measurements

Ion chromatography measurements were made using a Dionex (Thermo Scientific, Sunnyvale, CA, USA) ICS-5000+ SP instrument. Separations were carried out using a Dionex IonPac AS23-4um analytical column. The three samples of seawater were each diluted 200-fold with deionized water prior to the analysis. The composition of three samples was summarised in Table S1.

Table S1. Composition of natural seawater

	Fluoride/ ppm	Chloride/ ppm	Nitrite/ ppm	Bromide/ ppm	Nitrate/ ppm	Phosphate/ ppm	Sulfate/ ppm
Sample 1-Rep 1	0.0076	126.63	n.a.	0.41	n.a.	n.a.	12.08
Sample 1-Rep 2	0.0077	123.90	n.a.	0.41	n.a.	n.a.	11.75
Sample 2-Rep 1	0.0070	102.62	n.a.	0.33	n.a.	n.a.	9.44
Sample 2-Rep 2	0.0063	102.96	n.a.	0.37	n.a.	n.a.	8.89
Sample 3-Rep 1	0.0066	102.17	n.a.	0.33	n.a.	n.a.	14.31
Sample 3-Rep 2	0.0067	103.19	n.a.	0.34	n.a.	n.a.	14.49

References:

[1] H. Chen, A. Kaliyaraj Selva Kumar, H. Le, R.G. Compton, Non-unity stoichiometric reversible electrode reactions. The effect of coupled kinetics and the oxidation of bromide, J. Electroanal. Chem. 876 (2020) 114730.

[2] R.G. Compton, C.E. Banks, Understanding Voltammetry, World Scientific, 3rd edition, 2018.

[3] R.E. White, S.E. Lorimer, A model of the bromine/bromide electrode reaction at a rotating disk electrode, J. Electrochem. Soc. 130(5) (1983) 1096-1103.