Supporting information for

A bespoke chloride sensor for seawater: Simple and fast with a silver electrode

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Content

Section 1: The calibration of the silver electrode

The silver electrode radius was evaluated using cyclic voltammetry of the two electron reduction of oxygen. Experiments were conducted using variable scan rates from 20mV s^{-1} to 400mV s^{-1} at 25°C in oxygen saturated solution of pure 0.1M KNO_3 and analysed using the irreversible version of Randles–Ševčík equation (Eqn 1) and Tafel analysis. The variation of the peak current (I_p) with the square root of the scan rate (v):

$$I_p = 2.99 \times 10^5 n \sqrt{\alpha} {D_{O_2}}^{0.5} C_{O_2} A v^{0.5} \quad \text{Eqn 1[1]}$$

where the number of electrons transferred is n = 2, the concentration of saturated dissolved oxygen[2] is $C_{O_2} = 1.26$ mol m^{-3}, the diffusion coefficient of oxygen in solution[3] is $D_{O_2} = 1.96 \times 10^{-9}$ $m^2 s^{-1}$, the area of electrode is A (m^2). The transfer coefficient obtained at 20mVs^{-1} was α=0.78 from the Tafel plot in Fig. S1 b, in agreement with data in previous paper[4]. The Tafel analysis was performed on the voltammetry section starting from 10% to 30% of the peak height. The term $2.99 \times 10^5 n \sqrt{\alpha} {D_{O_2}}^{0.5} C_{O_2} A$ was calculated from the slope of Fig. S1 inset, giving the silver electrode radius of 1.13mm, very close to the nominal radius of 1.0mm.

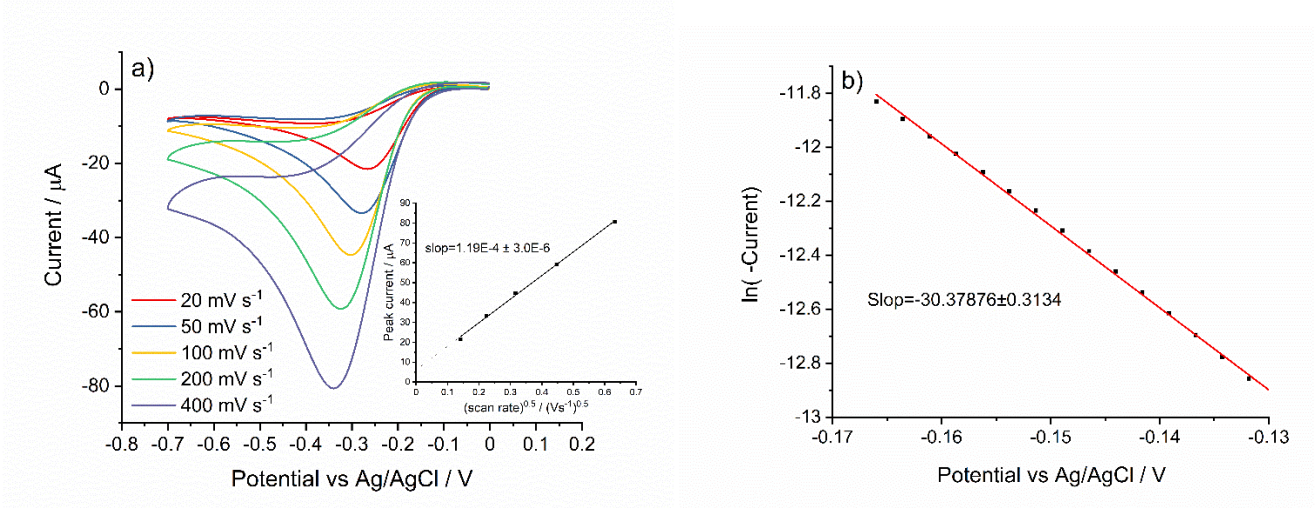

Fig S1. Calibration of silver electrode in oxygen saturated 0.1M KNO_3 solution at 25°C. a) Voltammetry conducted at 20mVs^{-1} to 400mVs^{-1}, inset: scan rate dependancy of the peak current. b) Tafel plot for data at 20mVs^{-1}.

Section 2: The synthetic seawater recipe

Table S1. Chemical compositions of synthetic seawater[5, 6]

Composition	**Concentration mol L^{-1}**
Na^+	4.80E-01
K^+	1.02E-02
Mg^{2+}	5.46E-02
Ca^{2+}	1.05E-02
Sr^{2+}	6.40E-05
Cl^-	5.60E-01
SO_4^{2-}	2.88E-02
HCO_3^-	2.38E-03
Br^-	8.40E-04
F^-	7.20E-05
H_3BO_3	4.90E-05

Section 3: Monolayer peaks of silver chloride

Silver chloride monolayer was studied voltammetrically in a nitrogen degassed 0.564M NaCl solution using a silver electrode. The electrode was first held at -1.0V for 1min followed by scans from -0.15V to +0.060V with reversal at +0.060V. The scan was conducted at a scanrate ranges from 20mVs^{-1} to 400mV s^{-1}.Two peaks were observed, regarding the silver chloride monolayer formation at -0.025V and stripping at -0.10V. The peak current of silver chloride monolayer formation signal is proportional to scanrates (Fig S2 a, inset). The total formation charge of the monolayer was calculated via polynomial baseline

subtractions (Fig. 2 b). For instance using the data in Fig 2a, 400mVs^{-1}, the peak between point a and b was first removed from the full voltamogram. Next, a polynomial fitting was conducted on the remaining data (-0.15V to point a, and point b to -0.050V).Then, the fitted polynomial data was subtracted from raw data at 400mVs^{-1} (Fig. S2, b). The actual charge of oxidation peaks were calculated as 1.2±0.1μC cm^{-2} via integration of current from -0.10V to +0.060V, consistent with the literature reported by Jaya et al. (4.62μC cm^{-2})[7].

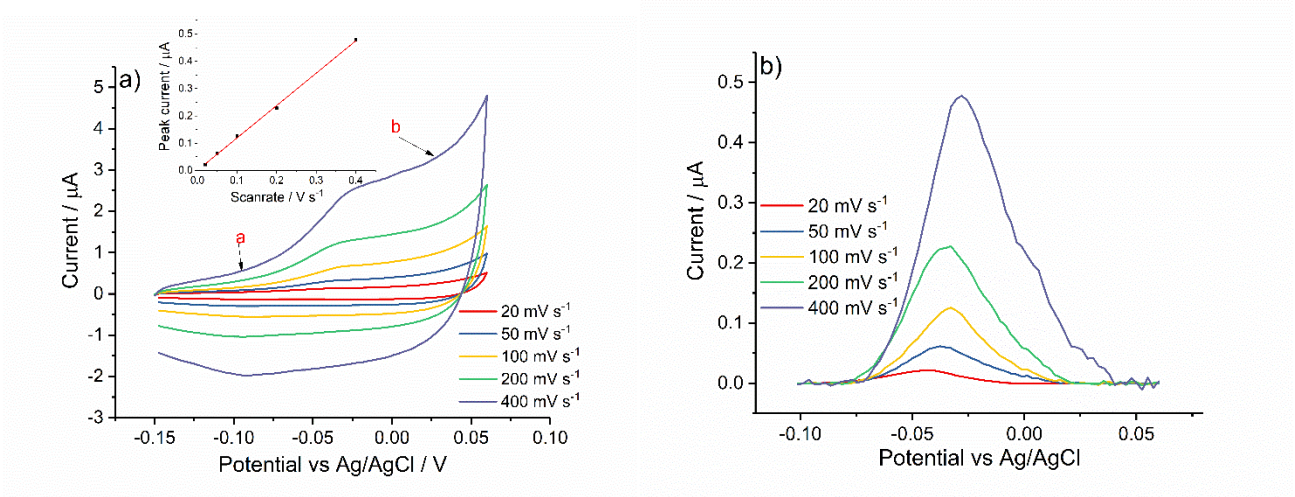

Fig S2. Scan rate dependency of silver chloride monolayer peaks. a) Raw data with peak current to scanrate dependency in the inset. b) Baseline subtratcted data.

Section 4: The superoxide peak studied in synthetic seawater

The stability of the superoxide peak in synthetic seawater with chloride concentrations in the range from 0.484M to 0.593M was analysed (Fig. 6 in the main text). The voltammetry was conducted at 20mVs^{-1} scanning from -0.20V to -1.0V, then scanned positively to +0.1V before returning to -0.2V. Each experiment was repeated four times for every concentration. The superoxide peak was observed at -0.39±0.01V with a peak height of 2.51±0.08μA. Within the range of 0.484M to 0.624M both peak potential and peak current of the superoxide feature are almost unchanged, thus the superoxide peak can be used as a stable internal reference potential

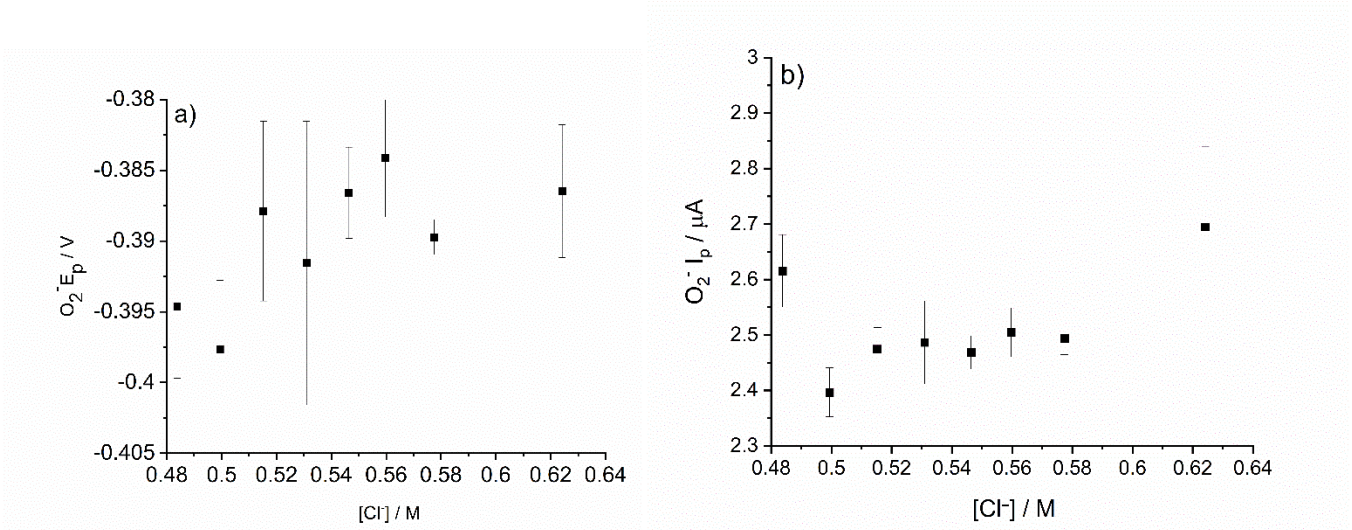

Fig S3. The superoxide peak in synthetic seawater with the chloride concentration ranges from 0.484M to 0.624M a) Peak potentials. b) Peak currents.

References

[1] R.G. Compton, C.E. A Banks, Understanding Voltammetry, 2nd ed.2010.

[2] K. Shimizu, L. Sepunaru, R.G. Compton, Innovative catalyst design for the oxygen reduction reaction for fuel cells, Chem Sci 7(5) (2016) 3364-3369.

[3] C.C.M. Neumann, E. Laborda, K. Tschulik, K.R. Ward, R.G. Compton, Performance of silver nanoparticles in the catalysis of the oxygen reduction reaction in neutral media: Efficiency limitation due to hydrogen peroxide escape, Nano Research 6(7) (2013) 511-524.

[4] Y.J. Guo, M.J. Yang, R.C. Xie, R.G. Compton, The oxygen reduction reaction at silver electrodes in high chloride media and the implications for silver nanoparticle toxicity, Chem. Sci. 12(1) (2021) 397-406.

[5] F.M.M. Morel, J.G. Rueter, D.M. Anderson, R.R.L. Guillard, AQUIL: A CHEMICALLY DEFINED PHYTOPLANKTON CULTURE MEDIUM FOR TRACE METAL STUDIES12, J. Phycol. 15(2) (1979) 135-141.

[6] N.M. Price, G.I. Harrison, J.G. Hering, R.J. Hudson, P.M.V. Nirel, B. Palenik, F.M.M. Morel, Preparation and Chemistry of the Artificial Algal Culture Medium Aquil, Biological Oceanography 6(5-6) (1989) 443-461.

[7] S. Jaya, T.P. Rao, G.P. Rao, Mono-and multilayer formation studies of silver chloride on silver electrodes from chloride-containing solutions, J. Appl. Electrochem. 17(3) (1987) 635-640.