Supporting information for

The oxygen reduction reaction at silver electrodes in high chloride media and the implications for silver nanoparticle toxicity

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Section 1: Calibration of electrode

Electrode radii were confirmed using cyclic voltammetry at variable scan rates from 20 mV s^{-1} to 400 mV s^{-1} at 25 ^{o}C in nitrogen degassed solutions of 0.1 M potassium chloride and 1 mM hexaammineruthenium(III) chloride using the fully electrochemically reversible version Randles–Ševčík equation, where the variation of the peak current (I_p) with the square root of the scan rate (v):

$$I_p = 2.69 \times 10^5 n\, A {D_{O_2}}^{0.5} C_{O_2} v^{0.5}$$

Where n = 1, $C_{O_2} = 1.0\, mol\, m^{-3}$, $D_{O_2} = 8.4 \times 10^{-10}\, m^2 s^{-1}$. [1]

The term $2.69 \times 10^5 n\, A {D_{O_2}}^{0.5} C_{O_2}$ was calculated from the slope of the inlay in **Fig. S1a** and **b**, giving radii of the silver electrode (1.36 mm) and the glassy carbon electrode (1.49 mm)

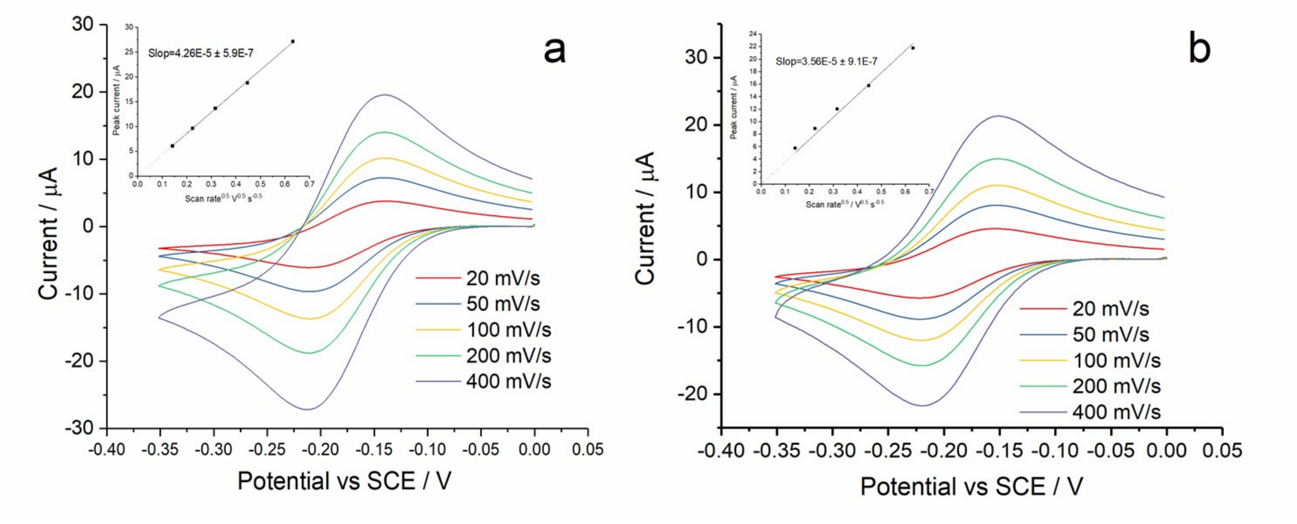

Fig S1. Calibration of electrode a) GC, r=1.49 mm, Technical, UK) and b) Ag, homemade, r=1.36 mm.

The measured diameter of GC electrode is 2.97±0.05 mm which is in agreement with electrochemical results, however the measured diameter of Ag electrode (1.98±0.01 mm) is much smaller than that obtained from **Fig. 1b**, possibly due to surface roughness which increased the effective surface area.

Section 2: ORR on glassy carbon electrodes

2.1 Seawater composition

Table S1. Chemical compositions of synthetic seawater[2, 3] and authentic seawater[4]

Composition	Simple synthetic seawater / mol L[-1]	Standard synthetic seawater / mol L[-1]	Authentic seawater / mol L[-1]
Na^+	4.20E-01	4.80E-01	4.69E-01
K^+	9.39E-03	1.02E-02	1.02E-02
Mg^{2+}	5.46E-02	5.46E-02	5.28E-02
Ca^{2+}	□	1.05E-02	1.03E-02
Sr^{2+}	□	6.40E-05	9.10E-05
Cl^-	5.39E-01	5.60E-01	5.46E-01
SO_4^{2-}	□	2.88E-02	2.82E-02
HCO_3^-	□	2.38E-03	1.72E-03
CO_3^{2-}	□	□	2.39E-04
Br^-	□	8.40E-04	8.42E-04
F^-	□	7.20E-05	6.80E-05
H_3BO_3	□	4.90E-05	□
$B(OH)_4^-$	□	□	1.01E-04
$B(OH)_3$	□	□	3.14E-04
OH^-	□	□	8.00E-06
CO_2	□	□	1.00E-05

2.2 Oxygen diffusion coefficient in aqueous solutions

Table S2. Reported diffusion coefficients of oxygen in various solutions.
*Data obtained for solution at a) 20 ℃, b) 25 ℃ and c) 24 ℃.

D_{O_2} (× 10^{-9}) / m^2 s^{-1}	Solution
2.42 [5-7]	H_2O [b]
1.98 [8]	H_2O [a]
3.40 [9]	H_2O [b]
2.26 [10]	H_2O [b]
1.96 [11]	H_2O [b]
1.7 [12]	Britton-Robinson buffer solution containing 0.1 M NaCl [b]
1.9 [63]	0.01M Na_2SO_4 aq [a]
1.46 [8]	0.552M NaCl aq. [a]
2.08 [9]	0.5M NaCl aq. [b]
2.17 [10]	0.5642M NaCl aq. [b]
1.4 [13]	Seawater [b]
2.3 [14, 15]	Seawater [c]
1.26 [16]	0.5M H_2SO_4 aq. [b]
1.93 [17, 18]	0.1M NaOH aq. [b]

Table S3. Reported diffusion coefficients of oxygen in different NaCl concentration aq. solutions
*Data obtained at a) 25 °C b) Data at 22 °C c) Data at 20 °C.

Literature value reported by	NaCl concentration in M	D_{O_2} (× 10^{-9}) / m^2 s^{-1}
Stroe et. al [10 a]	0	2.26

	0.0846	2.2
	0.154	2.22
	0.282	2.21
	0.4231	2.12
	0.5642	2.17
Ju et. al [19 b]	0	2.08
	0.2	1.80
	0.5	1.60
Jamnongwong et. al [8 c]	0	1.98
	0.103	1.44
	0.552	1.46

2.3 Oxygen solubility in aqueous solutions

Table S4. Literature solubility of O_2 in various solutions.
*Data obtained for solution at a) 25 °*C*, b) 30 °*C.*

Solubility in mM	Solution
1.15 [20]	H_2O [b]
1.01[20]	H_2O [b]
1.26 [21]	H_2O [a]
1.25 [12]	Britton-Robinson buffer solution containing 0.1 M NaCl [a]
0.23 [20]	5M NaCl aq. [a]
1.28 [22]	1mM H_2SO_4 aq. [a]
1.25 [23]	0.5M H_2SO_4 aq.[a]
1.43 [16]	0.5M H_2SO_4 aq.[a]

Table S5. Literature solubility of O_2 in solution with varied salinity at 25°C.
*Data obtained a) with air saturated solution b) with oxygen saturated solution c) from Figure 8 in reference cited

Solubility in mM	Solution
0.2591[20 a]	H_2O

0.2791 [20 a]	H_2O
0.2598 [20 a]	H_2O
0.2631 [20 a]	H_2O
1.26 [21 b]	20mM KCl aq.
1.25 [12 b]	Britton-Robinson buffer solution containing 0.1 M NaCl
1.24 [24 c]	0.1 M NaCl aq.
1.07 [24 c]	0.42 M NaCl aq.
1.01 [24 c]	0.54 M NaCl aq.
0.2508 [20 a]	Seawater Salinity = 7.816 g Kg^{-1}
0.2350 [20 a]	Seawater Salinity = 18.985 g Kg^{-1}
0.2226 [20 a]	Seawater Salinity = 28.986 g Kg^{-1}
0.2054 [20 a]	Seawater Salinity = 35.77 g Kg^{-1}
0.2096 [20 a]	Seawater Salinity = 38.792 g Kg^{-1}

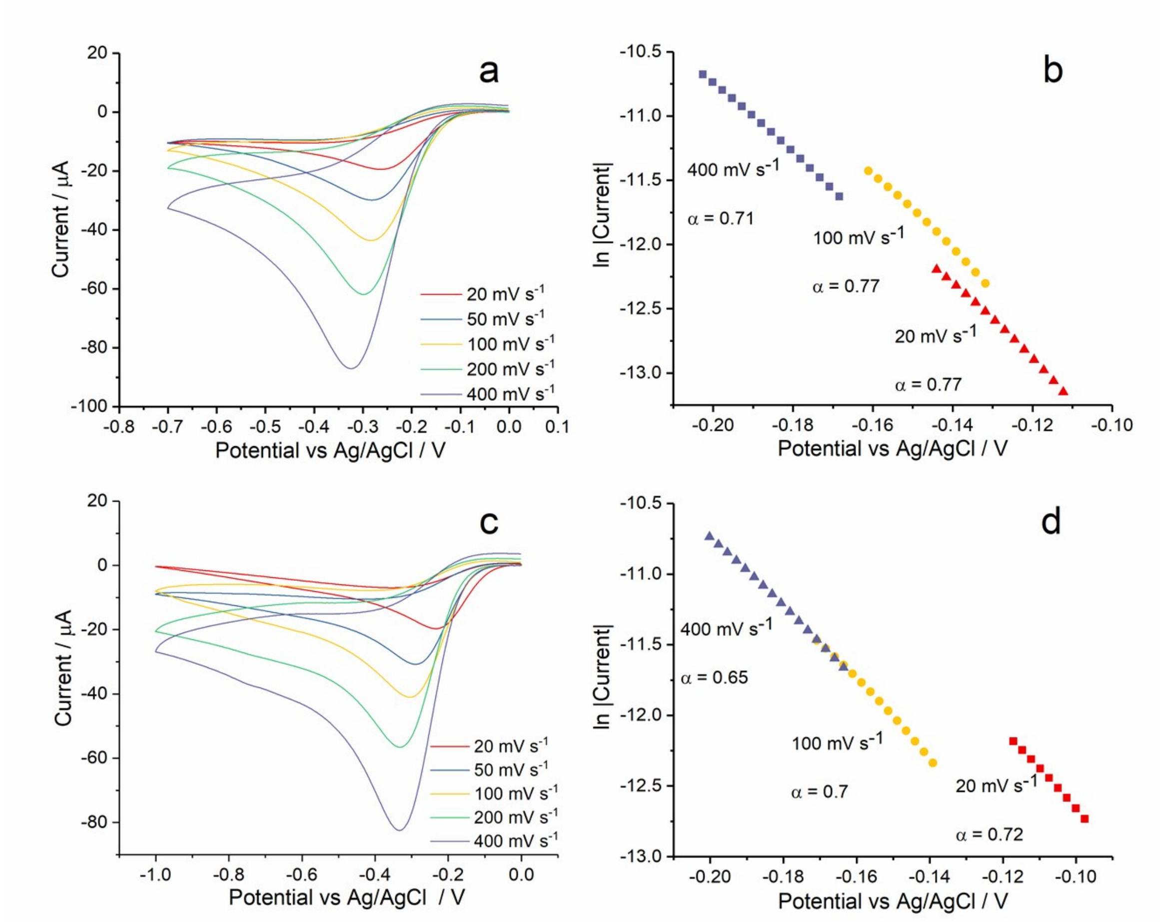

Fig S2. Reductive voltammetry studies on a silver macroelectrode. a) Voltammagrams in oxygen saturated 0.1 M KNO_3 with varying scan rates from 20 mV s^{-1} to 400 mV s^{-1} and Tafel analysis in b); c)Voltammagrams in oxygen saturated 0.1 M $NaClO_4$ with varying scan rates from 20 mV s^{-1} to 400 mV s^{-1} and Tafel analysis in d)

Section 3: ORR on silver electrode in KNO_3 and $NaClO_4$

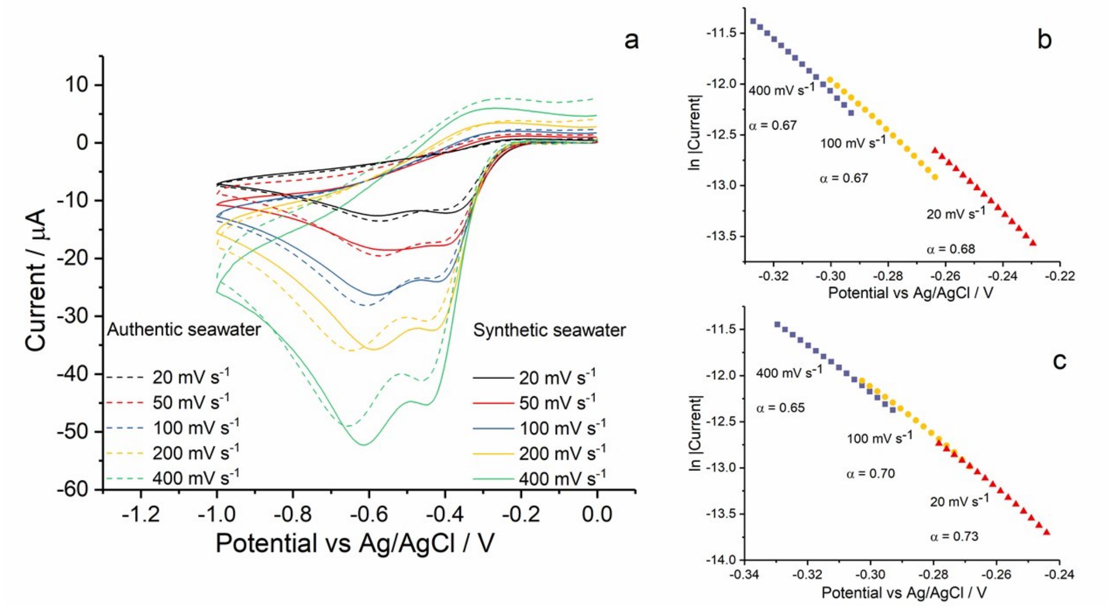

Fig S3. O_2 reduction in seawater on silver electrode a) Voltammagrams in synthetic seawater (solid line) and authentic seawater (dash line) with varying scan rates from 20 mV s^{-1} to 400 mV s^{-1} b) Tafel analysis in authentic seawater and c) Tafel analysis in synthetic seawater

Section 4: ORR on silver electrode in seawater

Section 5: Digisim fitting of ORR on silver in synthetic seawater

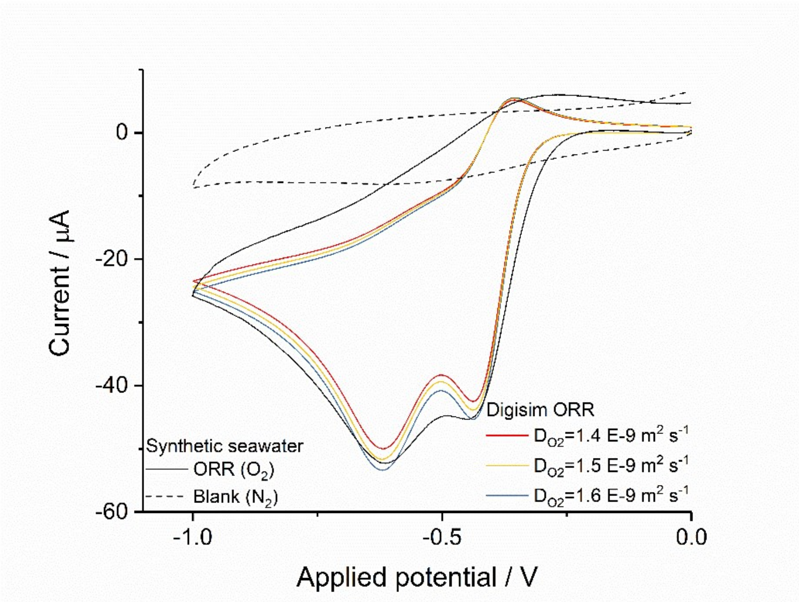

Fig. S4 Digisim analysis of ORR in seawater. The effect of diffusion coefficient and background (experiment in nitrogen saturated seawater) at 400 mV s^{-1}.

Table S6. Electron transfer kinetics of the oxygen reduction at bulk silver at 298 K in synthetic seawater.

* k_0 and E^0 refer to the kinetic constant and the formal potential of each step,

** The values of k_0 and α for the first step are arbitrary to model a quasi-reversible behaviour.

Step 1		Step 2	
$A + e^- \rightarrow B$ (quasi-reversible)		$B + e^- \rightarrow P$ (irreversible)	
C_{O_2}=1.1 mM			
D_{O_2}=1.6 × 10^{-9} $m^2 s^{-1}$			
α	0.5	$k = k_0 \exp\left(\frac{\alpha E^0 F}{RT}\right)$ cm s^{-1}	$4.9 \pm 1.8 \times 10^{-11}$
k_0 / cm s^{-1}	1.0		
E^0 / V	-0.4		

Section 6: ORR on silver in 0.1 M KCl and 0.42 M KCl

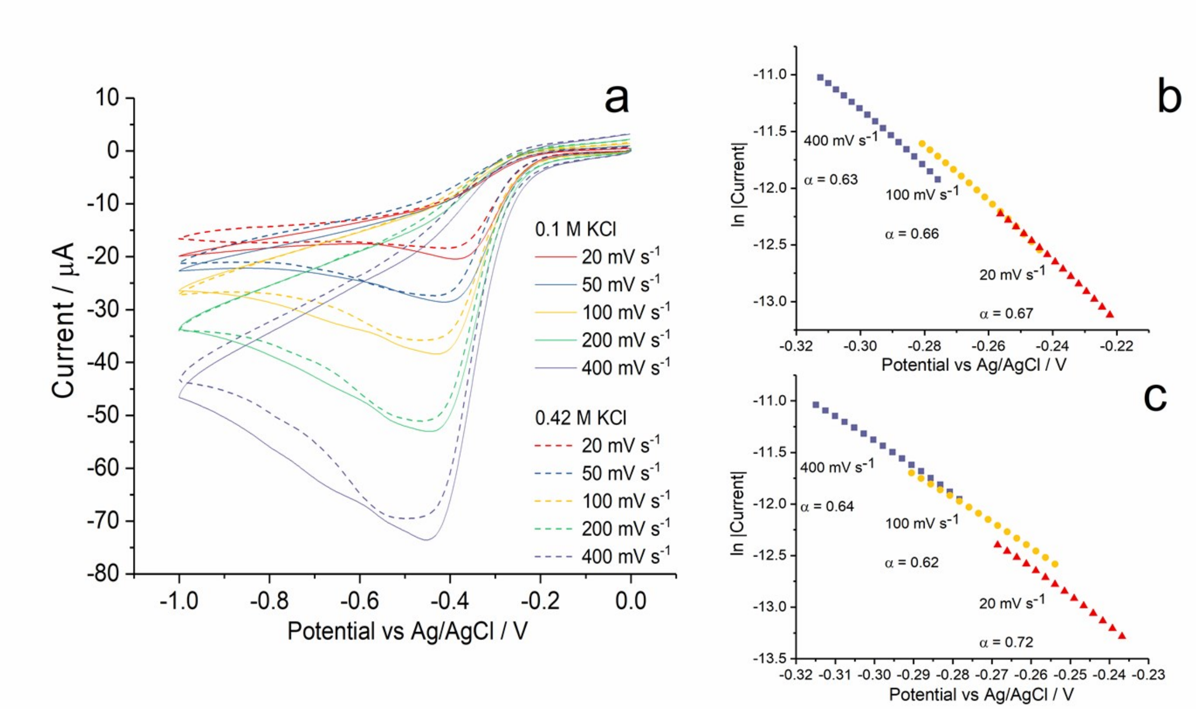

Fig. S5 ORR on silver in potassium chloride solutions a) Voltammagrams in oxygen saturated 0.1 M KCl and 0.42 M KCl with varying scan rates from 20 mV s^{-1} to 400 mV s^{-1} b) Tafel analysis for 0.1 M KCl c) Tafel analysis for 0.42 M KCl

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