# **Supporting information**

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Section 1 Microscope imaging of uncoated and coated iridium wire with cathodic electrophoretic paint



Fig. SI1 Microscope images of iridium wires before and after insulated with cathodic electrophoretic paint

# Section 2 Electrodeposition of iridium oxide onto iridium micro-disc electrode



**Fig. SI2** Cyclic voltammograms (15 cycles) at the iridium micro-disc electrode in a deposition solution containing 1.0 mM  $K_3IrCl_6$  (pH = 11.5); scan rate 50 mV s<sup>-1</sup>



Fig. SI3 Cyclic voltammograms of bare and iridium oxide modified the iridium micro-disc electrode in 0.01M  $HNO_3 + 0.1M$  KCl (pH 2); scan rate 100 mV s<sup>-1</sup>

# Section 3 Estimation of uncertainty of pH measurements using our electrode and a glass electrode as a reference pH values

3.1 Uncertainty of pH measurements of aqueous buffer solutions using cyclic voltammetry



**Fig. SI4** Plot of midpoint potentials from CV of iridium oxide on iridium micro-disc electrode in aqueous buffer solutions at variable pH against pH reading from pH meter.

pH from pH meter	Midpoint potential- measurement (E <sub>meas</sub> ) / V	Midpoint potential- calculation (E <sub>calc</sub> ) / V	$\Delta E = E_{meas} - E_{calc} / V$	Standard deviation of $\Delta E / V$
2.04	0.465	0.468	-0.004	0.006
2.99	0.406	0.409	-0.003	
4.22	0.333	0.332	0.001	
5.04	0.288	0.280	0.007	
6.05	0.225	0.217	0.008	
7.12	0.152	0.150	0.002	
7.41	0.127	0.132	-0.005	
6.67	0.181	0.178	0.003	
6.86	0.161	0.166	-0.005	
2.04	0.465	0.468	-0.004	
2.99	0.406	0.409	-0.003	
4.22	0.333	0.332	0.001	
5.04	0.293	0.280	0.013	

6.05	0.229	0.217	0.012	
7.12	0.148	0.150	-0.002	
7.41	0.122	0.132	-0.010	
6.67	0.175	0.178	-0.003	
6.86	0.160	0.166	-0.006	
2.04	0.465	0.468	-0.004	
2.99	0.406	0.409	-0.003	
4.22	0.333	0.332	0.001	
5.04	0.288	0.280	0.007	
6.05	0.225	0.217	0.008	
7.12	0.152	0.150	0.002	
7.41	0.127	0.132	-0.005	
6.67	0.181	0.178	0.003	
6.86	0.161	0.166	-0.005	

# Conversion of standard deviation (V) to pH units

Considering slope of the linear plot of midpoint potentials of iridium oxide on iridium microdisc electrode in aqueous buffer solutions using cyclic voltammetry at variable pH against pH reading from pH meter as shown in Fig.SI11,

Slope is 0.063 V per 1 pH units

Therefore, 0.006 V is  $\frac{1}{0.063} \times 0.006 = 0.095$  pH units

3.2 Uncertainty of pH measurements of sheep's blood using cyclic voltammetry



**Fig. SI5** Plot of midpoint potentials from CV of iridium oxide on iridium micro-disc electrode in sheep's blood sample at variable pH against pH reading from pH meter.

pH from pH meter	Midpoint potential- measurement (E <sub>meas</sub> ) / V	Midpoint potential- calculation (E <sub>calc</sub> ) / V	$\Delta E = E_{meas} - E_{calc} / V$	Standard deviation of ∆E / V
7.15	0.103	0.119	-0.017	0.006
6.79	0.142	0.152	-0.010	
6.64	0.161	0.165	-0.005	
6.58	0.166	0.171	-0.005	
7.43	0.089	0.094	-0.005	
7.01	0.132	0.132	0.000	
6.8	0.157	0.151	0.006	
6.68	0.166	0.162	0.004	
7.44	0.095	0.093	0.002	
7.28	0.113	0.108	0.005	
7.01	0.132	0.132	0.000	
6.8	0.161	0.151	0.010	
6.53	0.178	0.175	0.003	
7.45	0.098	0.092	0.006	

7.08	0.122	0.126	-0.004	
6.82	0.152	0.149	0.002	
6.68	0.166	0.162	0.004	
7.44	0.098	0.093	0.005	
7.18	0.117	0.117	0.000	
7.12	0.117	0.122	-0.005	
6.95	0.142	0.137	0.005	
6.95	0.137	0.137	0.000	

# Conversion of standard deviation (V) to pH unit

Considering slope of the linear plot of midpoint potentials of iridium oxide on iridium microdisc electrode in sheep's blood samples using cyclic voltammetry at variable pH against pH reading from pH meter as shown in Fig.SI12,

Slope is 0.090 V per 1 pH units

Therefore, 0.006 V is  $\frac{1}{0.090} \times 0.006 = 0.067$  pH units

3.3 Uncertainty of pH measurements of sheep's blood using square wave voltammetry



**Fig. SI6** Plot of midpoint potentials from SWV of iridium oxide on iridium micro-disc electrode in sheep's blood sample at variable pH against pH reading from pH meter.

		Midpoint		
	Midpoint potential-	potential-		Standard
pH from pH	measurement	calculation (E <sub>calc</sub> )	$\Delta E = E_{meas} - E_{calc}$ /	deviation
meter	(E <sub>meas</sub> ) / V	/ V	V	of ΔE / V
7.32	0.086	0.084	0.002	0.0035
7.14	0.102	0.103	-0.001	
6.96	0.123	0.121	0.002	
6.77	0.142	0.140	0.002	
6.64	0.158	0.153	0.005	
7.35	0.078	0.081	-0.004	
7.01	0.112	0.116	-0.004	
7.30	0.083	0.086	-0.004	
7.03	0.111	0.114	-0.003	
6.73	0.144	0.144	-0.001	
6.61	0.154	0.156	-0.003	
7.45	0.076	0.071	0.004	
7.01	0.113	0.116	-0.003	
6.64	0.148	0.153	-0.006	

6.70	0.151	0.147	0.003	
7.31	0.083	0.085	-0.003	
7.02	0.118	0.115	0.003	
7.25	0.097	0.091	0.006	
6.90	0.131	0.127	0.004	

Conversion of standard deviation (volts) to pH unit

Considering slope of the linear plot of midpoint potentials of iridium oxide on iridium microdisc electrode in sheep's blood samples using square wave voltammetry at variable pH against pH reading from pH meter as shown in Fig.SI13,

Slope is 0.101 V per 1 pH units

Therefore, 0.0035 V is  $\frac{1}{0.101} \times 0.0035 = 0.034$  pH units

No. of measurements	Buffer			Sheep's blood		
1	2.03	4.95	9.08	7.50	7.27	7.18
2	2.01	4.93	9.07	7.49	7.27	7.18
3	2.01	4.93	9.05	7.53	7.27	7.13
4	2.01	4.93	9.07	7.53	7.30	7.15
5	2.00	4.93	9.07	7.54	7.31	7.13
6	2.00	4.92	9.07	7.55	7.31	7.18
7	2.00	4.92	9.06	7.53	7.32	7.16
8	2.00	4.92	9.07	7.52	7.32	7.17
9	2.00	4.92	9.07	7.52	7.31	7.18
10	2.00	4.92	9.07	7.53	7.31	7.19
Mean	2.01	4.93	9.07	7.52	7.30	7.17
Standard deviation	0.01	0.01	0.01	0.02	0.02	0.02

Section 4 Estimation of uncertainties of using a conventional glass electrode for pH measurements in aqueous buffer solutions and in sheep's blood samples

# Section 5 Optimisation of iridium oxide thickness

The Ir/IrOx redox couple exhibits a well-defined peak with a small peak to peak separation in pH buffer system (*ca.* 50 mV at scan rate of 100 mV s<sup>-1</sup> for pH 2). However, in sheep's blood sample, the peaks were not as well defined as the CVs of buffer solutions as shown in Fig SI3 (15 scans). Moreover, the peaks were more distorted (peak to peak separation (*ca.* 280 mV).).

To improve the peak to peak separation the thickness of iridium oxide film was varied by changing the number of deposition cycles. As the thickness of the iridium oxide layer increased by increasing the number of deposition cycles, the obtained cyclic voltammograms tested in sheep's blood became less "reversible", as shown in Fig.SI4. The peak separation  $(\Delta E_p)$  values were 240mV, 200mV, 266mV, 284mV and 295 mV for 2, 5, 8, 15, and 30 deposition cycles respectively. Considering the peak to peak separation and the definition of the peak, 5 deposition cycles was chosen as an optimal condition to prepare iridium oxide film in this study.



**Fig. SI7** Comparision of cyclic voltametric responses of 0.1M phosphate buffer (pH7.4) and sheep's blood (pH 7.5) at iridium oxide on iridium micro-disc electrode; scan rate of  $100 \text{ mV s}^{-1}$ .



**Fig. SI8** Optimisation of iridium oxide thickness varying by differing number of scans (2, 5, 8, 15, and 30 scans). Normalised cyclic voltammetry response of electrodeposition of iridium oxide on iridium micro-disc electrode of *sheep's blood* samples; scan rate of 100 mV s<sup>-1</sup>. Inset: plot of peak to peak separation against number of electrodeposition cycles.

Section 6 Study of variability of apparent standard electrode potential of electrodes studied in buffer solutions and in sheep's blood



#### A) Aqueous buffer solutions

**Fig. SI9** Reproducibility of cyclic voltammetry measurements of our IrOx pH sensor in buffer solutions (A) plots of all values including oxidation, reduction, and midpoint potentials and (B) enlarged plots of midpoint potential.



#### **B)** Sheep's blood samples

**Fig. SI10** Reproducibility of cyclic voltammetry measurements of our IrOx pH sensor in sheep's blood samples (A) plots of all values including oxidation, reduction, and midpoint potentials and (B) enlarged plots of midpoint potential.

# Section 7 Optimisation of SWV parameters in sheep's blood sample



**Fig. SI11** Effect of the frequency parameter on the SWV signal tested in sheep's blood samples, performed with step potential and amplitude fixed at 1 mV and 20 mV respectively.



**Fig. SI12** Effect of the amplitude parameter on the SWV signal tested in sheep's blood samples, performed with step potential and frequency fixed at 1 mV and 10 Hz respectively.

Variable Step potential



**Fig. SI13** Effect of the step potential parameter on the SWV signal tested in sheep's blood samples, performed with frequency and amplitude fixed at 10 Hz and 20 mV respectively.



**Fig. SI14** Effect of the frequency parameter on the SWV signal tested in sheep's blood samples, performed with step potential and amplitude fixed at 1 mV and 10 mV respectively.

#### Section 8 Study of effect of albumin

Albumin is one of the important proteins in blood and has been reported as the potential matrix interference in some measurements. Therefore, the experiment to explore the effect of albumin on voltammetric responses of an iridium oxide electrode was conducted. The solution of 4% w/v albumin from bovine serum (Sigma-Aldrich) was prepared in phosphate buffer (pH = 7.2). Cyclic voltammetric responses of an iridium oxide electrode were recorded in blank solution (phosphate buffer without albumin) and in albumin solution. The results shown in Fig. SI15 suggest that albumin does not interfere voltammetric response of iridium oxide electrode in this case.



**Figure SI15** Comparison of cyclic voltammetry responses of iridium oxide on iridium micro-disc electrode in blank solution (phosphate buffer without albumin) and in 4% w/v albumin solution pH = 7.2; scan rate of 100 mV s<sup>-1</sup>.

# Section 9 Bland-Altman plot



**Fig. SI16** Bland-Altman plot for method comparison between measured pH values from pH meter and pH from our pH sensors for a) pH of buffer solutions, b) pH of sheep's blood via CV, and c) pH of sheep's blood via SWV.

# Section 10 Consecutive scans of CV of iridium oxide on iridium micro-disc electrode



**Figure SI17** Cyclic voltammetry responses of iridium oxide on iridium micro-disc electrode in aqueous solution pH = 2; scan rate of 100 mV s<sup>-1</sup>.

Figure SI17 shows three consecutive scans of CV of iridium oxide electrode in aqueous solution (pH=2) at potential window range from 0 V to +1.0 V. At potentials > +0.7 V, there is the changing of capacitance of the electrode and the increasing of anodic current which might be due to the electrolysis of water. However, considering the peak position, the responses from three consecutive scans do not change in peak positions suggesting that there is no significant pH change in the vicinity of the electrode caused by electrolysis of water.