

Electronic Supporting Information

Aqueous Surface Chemistry of Gold Mesh Electrode in a Closed Bipolar Electrochemical Cell

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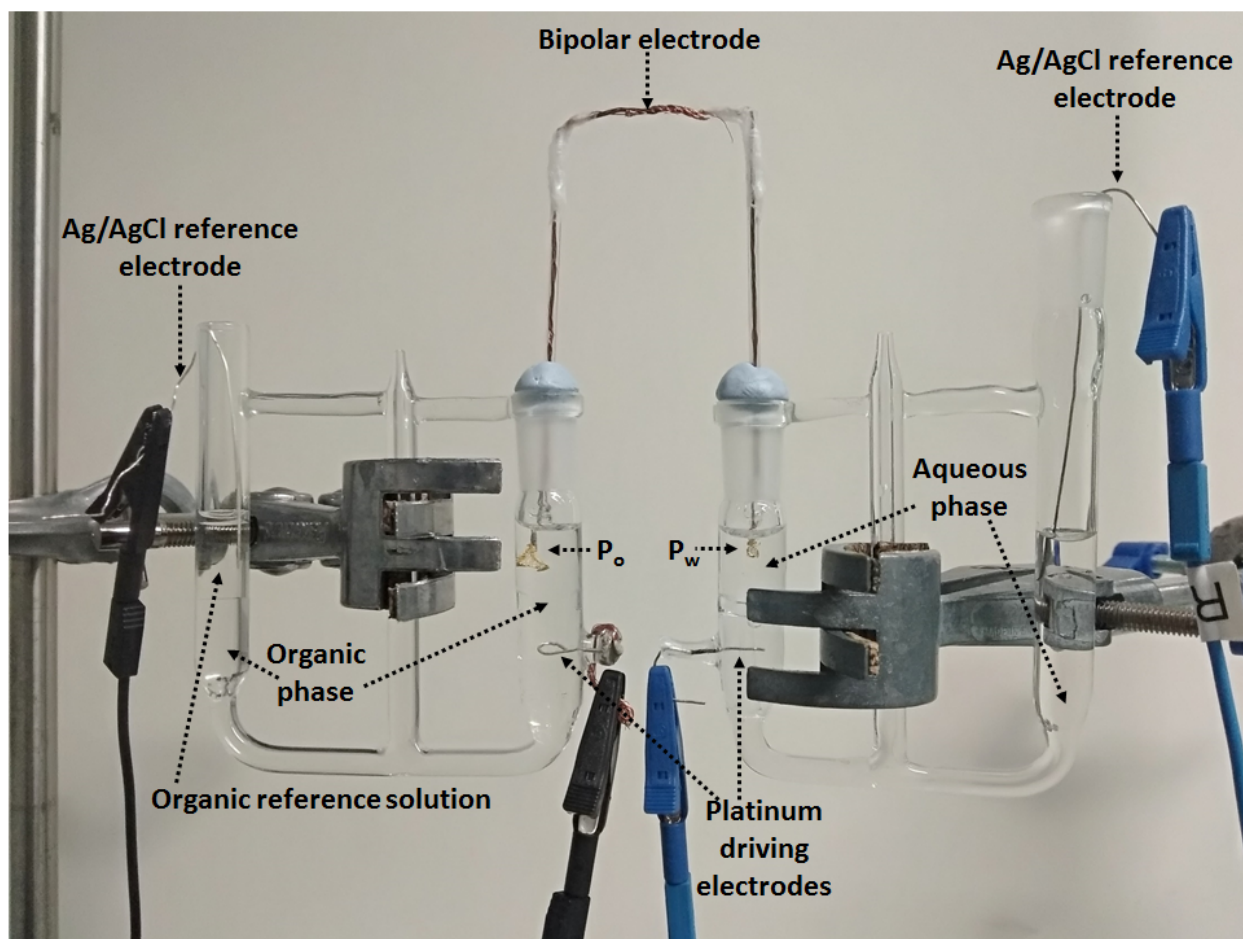


Fig. S1. Image of the 4-electrode closed bipolar electrochemical cell (CBPEC) used in this study. Each pole of the bipolar electrode consisted of gold mesh wires, with one immersed in each compartment, denoted P_w in the aqueous phase and P_o in the organic phase, and connected with an electric wire.

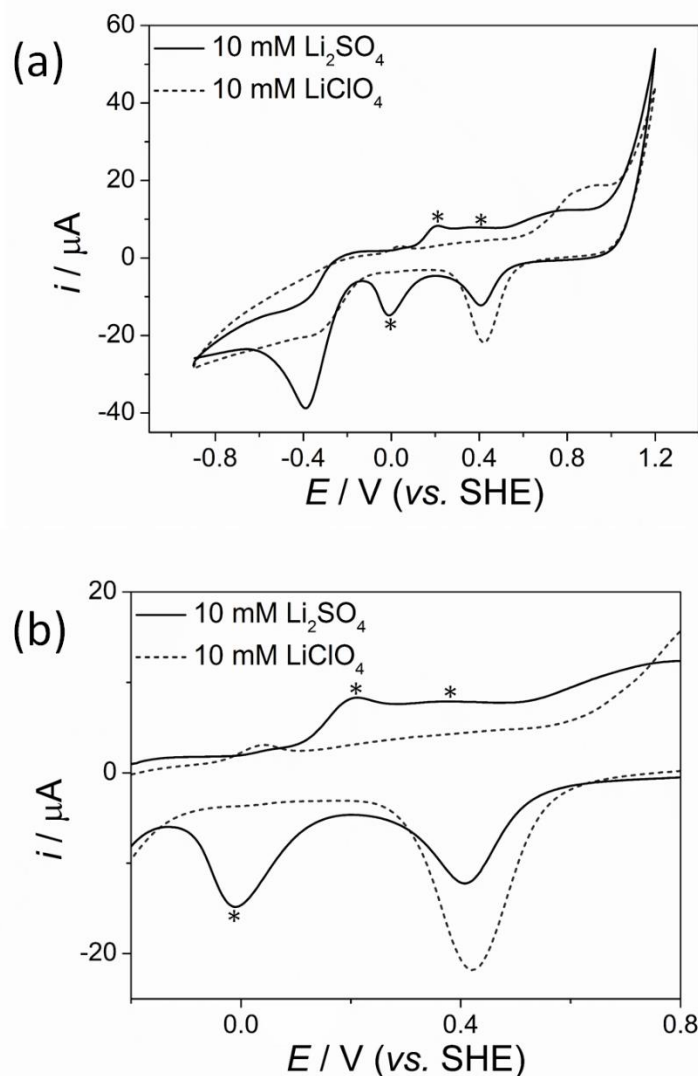


Fig. S2. Varying the aqueous electrolyte anion. **(a)** CVs obtained using a 3-electrode cell with 10 mM Li_2SO_4 and 10 mM LiClO_4 aqueous electrolytes and a gold mesh working electrode. Sulphate anions (SO_4^{2-}) adsorb strongly at the gold surface giving rise to characteristic electrochemical features, as indicated by the asterisks. Perchlorate anions (ClO_4^-) adsorb more weakly to the gold surface, with the CV containing noticeably less features by comparison. The scan rate used was $20 \text{ mV}\cdot\text{s}^{-1}$. **(b)** Enhanced view of the region of the CV in part (a) involving significant SO_4^{2-} adsorption. Notably the additional voltammetric peak on the forward sweep at more positive potentials with Li_2SO_4 as the aqueous electrolyte appeared within the key potential range of +0.410 to +0.630 V vs. SHE (the potential window experienced by P_w during the 4-electrode CPBEC experiments).

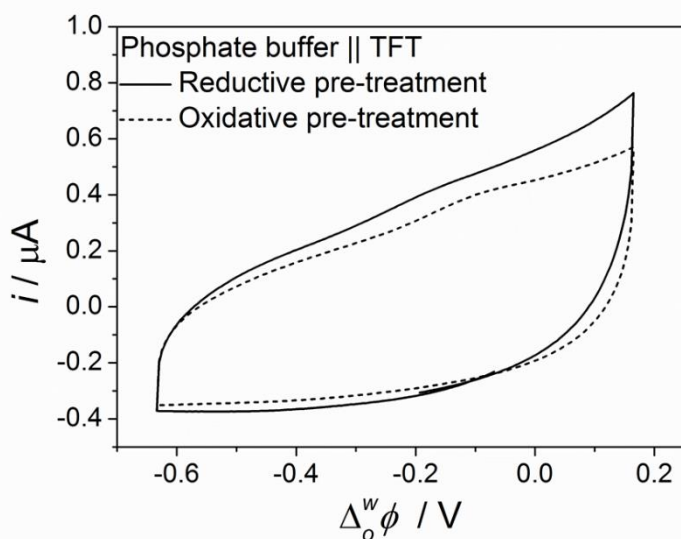


Fig. S3. Reductive and oxidative pre-treatment of the aqueous pole of the bipolar electrode (P_w). CVs were obtained with a 2 mM phosphate buffer solution and no electron donor species present in the TFT organic phase. Just prior to the 4-electrode CBPEC experiment, the gold mesh electrode acting as P_w underwent either electrochemical oxidative (+1.2 vs. SHE) or reductive (−0.9 V vs. SHE) pre-treatment for 100 seconds. The scan rate used was $20 \text{ mV}\cdot\text{s}^{-1}$. The full configuration for the 4-electrode CBPEC experiments is shown in Scheme 1.

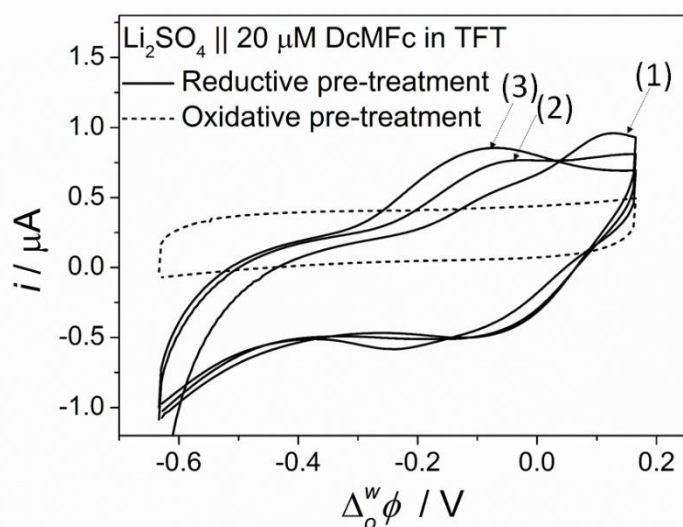


Fig. S4. Reductive and oxidative pre-treatment of the aqueous pole of the bipolar electrode (P_w). CVs were obtained with a 10 mM Li_2SO_4 aqueous electrolyte and $20 \mu\text{M}$ DcMFC present in the TFT organic phase after electrochemical oxidative (+1.2 V vs. SHE) or reductive (−0.9 V vs. SHE) pre-treatment of the gold mesh electrode acting as P_w . For the latter, the first 3 CV scans are shown. The scan rate used was $20 \text{ mV}\cdot\text{s}^{-1}$ in all experiments, see the full configuration for 4-electrode CBPEC experiments in Scheme 1.

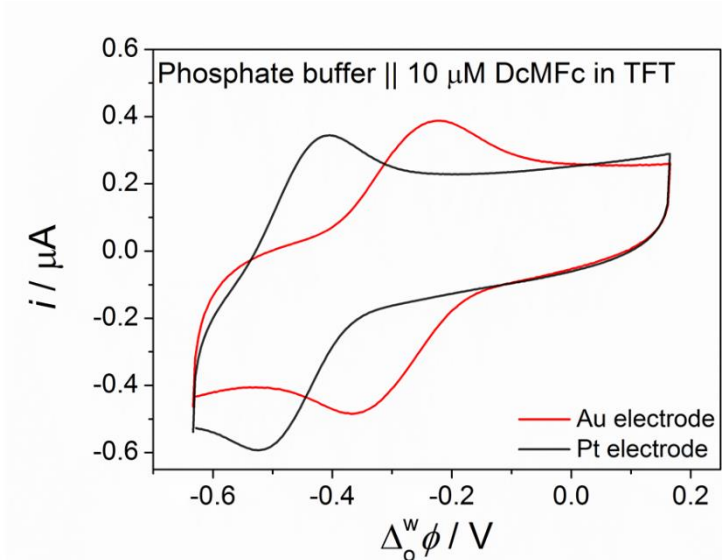


Fig. S5. *Nature of the aqueous pole of the bipolar electrode.* Platinum mesh electrodes and gold mesh electrodes were used as both P_w and P_o . CVs were obtained with a 2 mM phosphate buffer solution and 10 μM DcMFC present in the TFT organic phase. P_w was investigated without pre-treatment. Scan rate used was 20 $\text{mV}\cdot\text{s}^{-1}$. The full configuration for the 4-electrode CBPEC experiments is shown in Scheme 1.

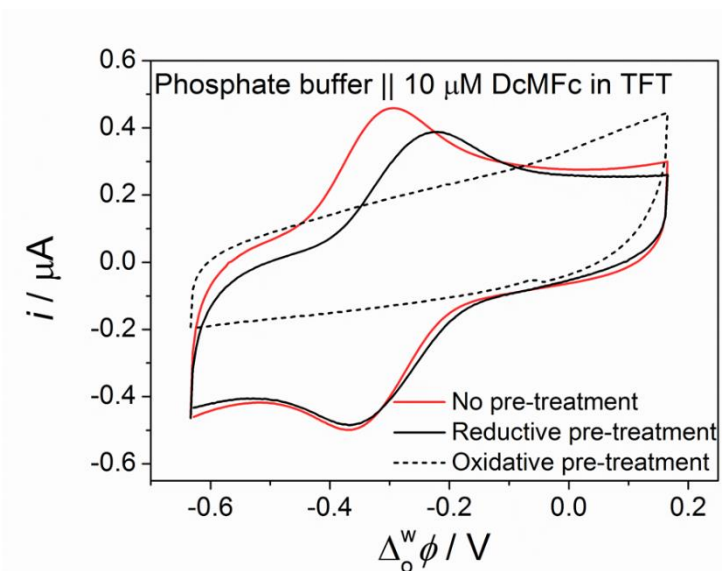


Fig. S6. *Anaerobic conditions.* CVs were obtained with a 2 mM phosphate buffer solution (degassed with N_2 for 30 minutes prior to the experiment beginning and then maintained under a flow of N_2 that was saturated with organic solvent), and 10 μM DcMFC present in the TFT organic phase. The scan rate used was 20 $\text{mV}\cdot\text{s}^{-1}$. The full configuration for the 4-electrode CBPEC experiments is shown in Scheme 1. P_w was investigated without pre-treatment, and after reductive and oxidative electrochemical pre-treatment.

Table S1. Monitoring the potential window of the oxidatively or reductively pre-treated gold mesh electrode acting as P_w using a multimeter and an auxiliary Ag/AgCl *pseudo*-reference as an electric contact while the Galvani potential difference in the 4-electrode CBPEC was scanned from -1.200 to $+0.200$ V. Li_2SO_4 was the aqueous electrolyte and $50 \mu M$ DcMFC was present in the TFT organic phase. The scan rate used was $20 \text{ mV}\cdot\text{s}^{-1}$. The full configuration for the 4-electrode CBPEC experiments is shown in Scheme 1.

Oxidative pre-treatment of P_w (+1.2 V vs. SHE) for 100 seconds	
CV cycle number	Potential window measured on P_w
1	+1.159 to +0.787 V
2	+1.059 to +0.555 V
3	+0.997 to +0.296 V
5	+0.834 to +0.191 V
6	+0.898 to +0.148 V
Reductive pre-treatment of P_w (-0.9 vs. SHE) for 100 seconds	
CV cycle number	Potential window measured on P_w
1 to 6	+0.725 to -0.062 V