

Supplementary material

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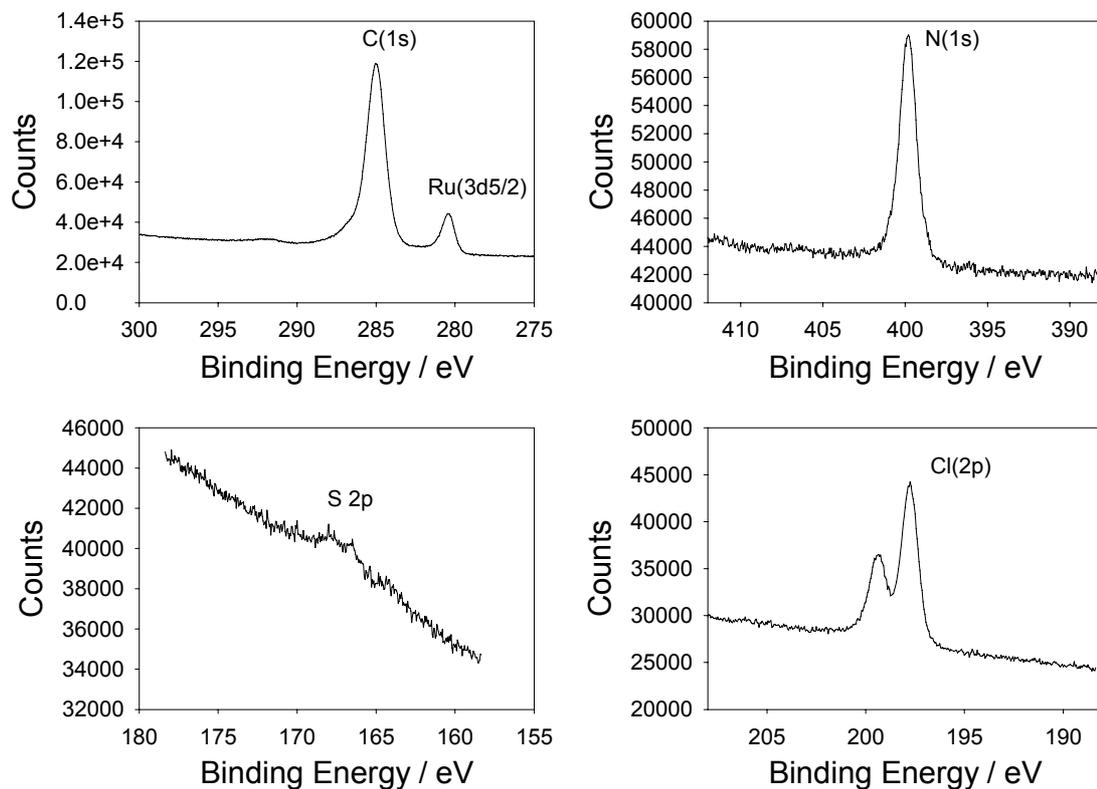


Fig. S1: XPS spectra for as deposited electropolymerised $\text{Ru}(\text{vpy})_4\text{Cl}_2$ film showing C(1s), Ru(3d), N(1s), S(2p) and Cl(2p) regions.

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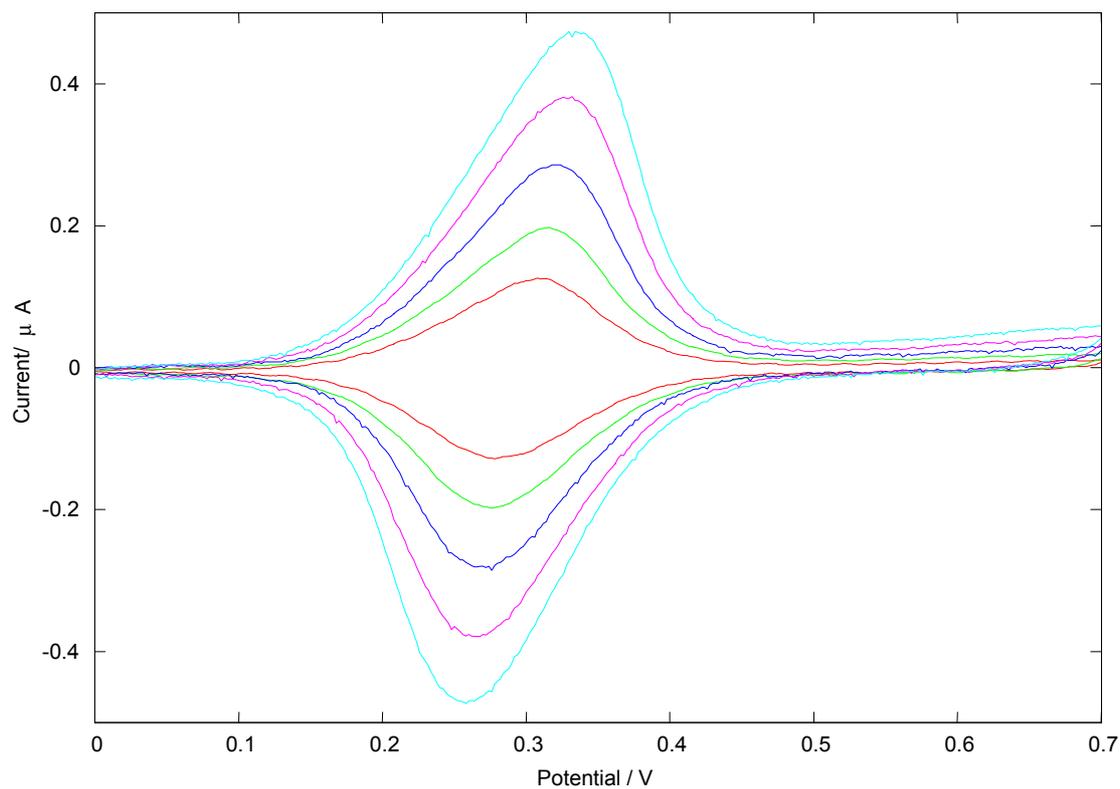


Fig S2: CVs for Ru polymer with a coverage of 28 nmol cm⁻² on a 25 μm diameter microelectrode with scan rates of 1,2,3,4,5 V s⁻¹.

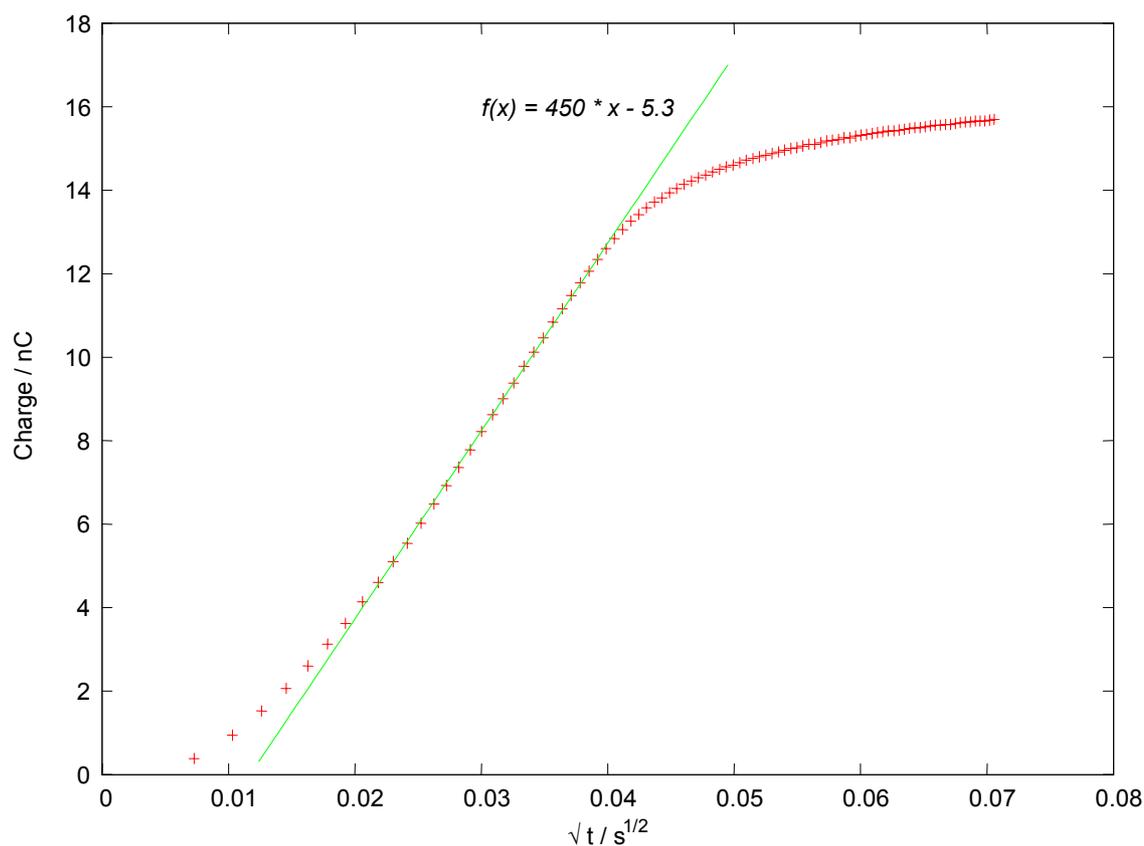
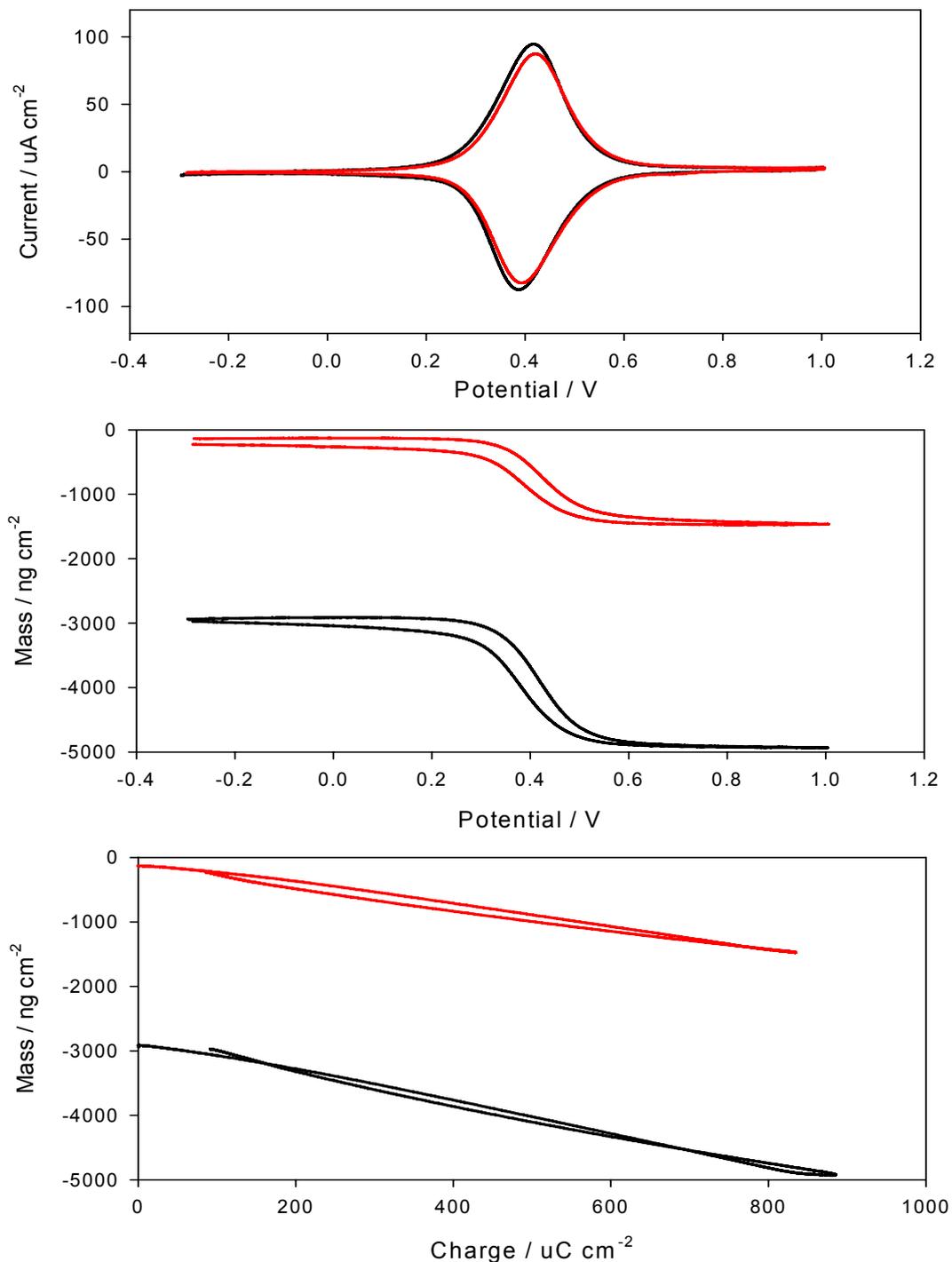
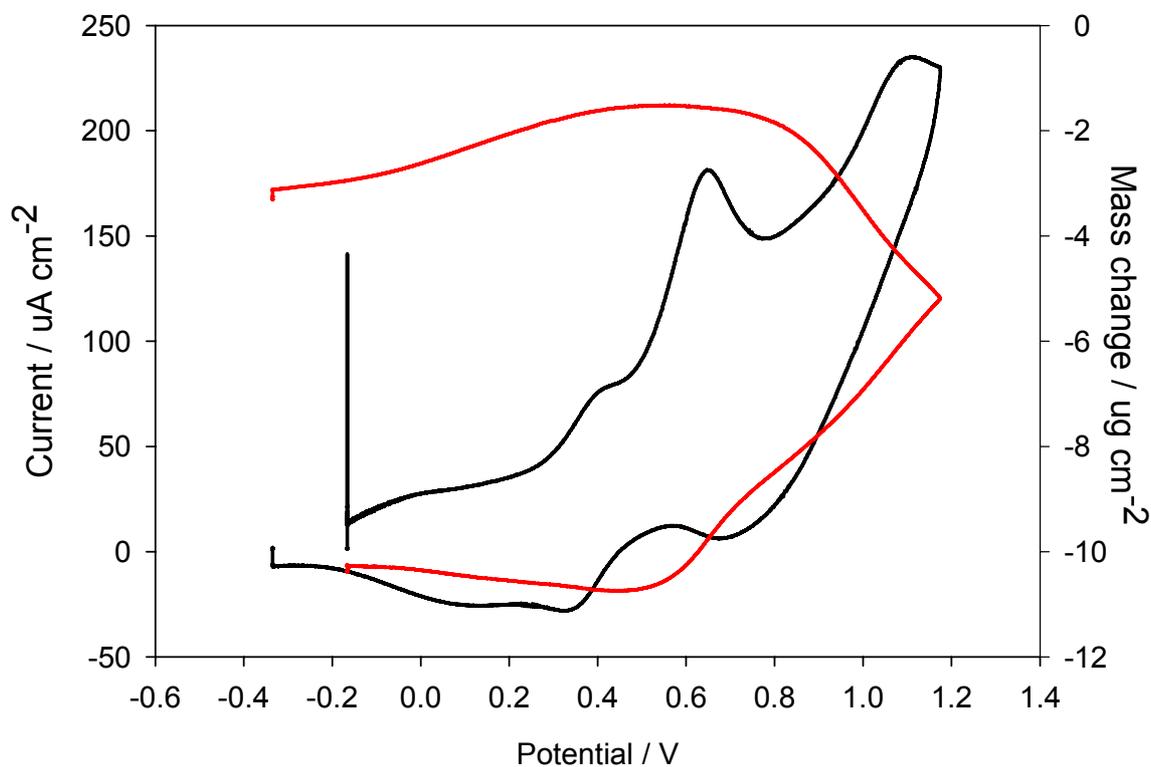


Fig S3: Chronocoulometry plot for Ru polymer with a coverage of 28 nmol cm^{-2} on a $25 \mu\text{m}$ diameter $15 \mu\text{m}$ microelectrode (as in Fig. S2) from 0.0 V to +0.6 V with step time of 5 ms. The slope was taken from the region of the plot between x values of 0.02 and 0.04. After this time the curve reaches the saturation charge associated with the full conversion of Ru(II) sites to Ru(III). The deviation at short times is associated with the resistance of the cell.



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Fig. S4: Black traces $\text{Ru}^{2+/3+}$ CVs vs. Ag/AgCl in background electrolyte I immediately after deposition (i.e. without drying the film); grey traces, CVs after rinsing and drying film followed by re-immersion background electrolyte. Mass zero offset to value of dried film immersed in solvent.



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Fig. S5: Mass changes (grey line) of a bare Au QCM electrode during redox sweep of bulk reduced Ru^{2+} solution after bulk reductive electrolysis. Black, current trace shows substantial loss of $\text{Ru}^{2+/3+}$ activity at 0.4 V (corresponding to Ru species with Cl^- ligands) and peak at +0.6 V is accompanied by mass loss indicating dissolution of the Au electrode. Ag/AgCl reference.

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