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Transient study of the oxygen reduction reaction on reduced Pt and Pt alloys: evidence for the reduction of pre-adsorbed oxygen species linked to dissolved oxygen

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Supporting Information

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Voltammograms in absence and presence of oxygen

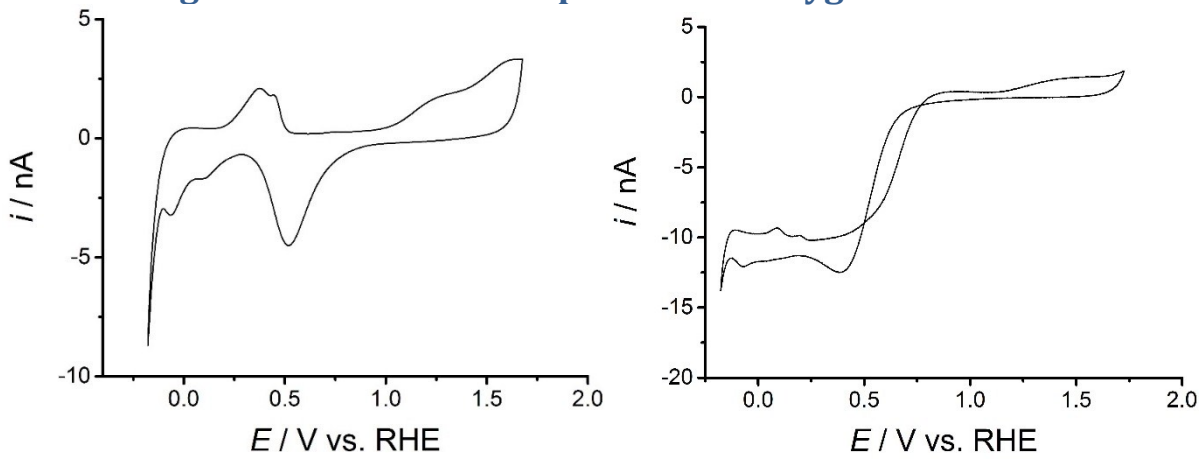

Figure SI-1: Cyclic voltammogram for a 25 µm Ø Pt microdisc recorded in Ar purged (left) and aerated (right) 0.1 M $KClO_4$ at 200 mV s^{-1}.

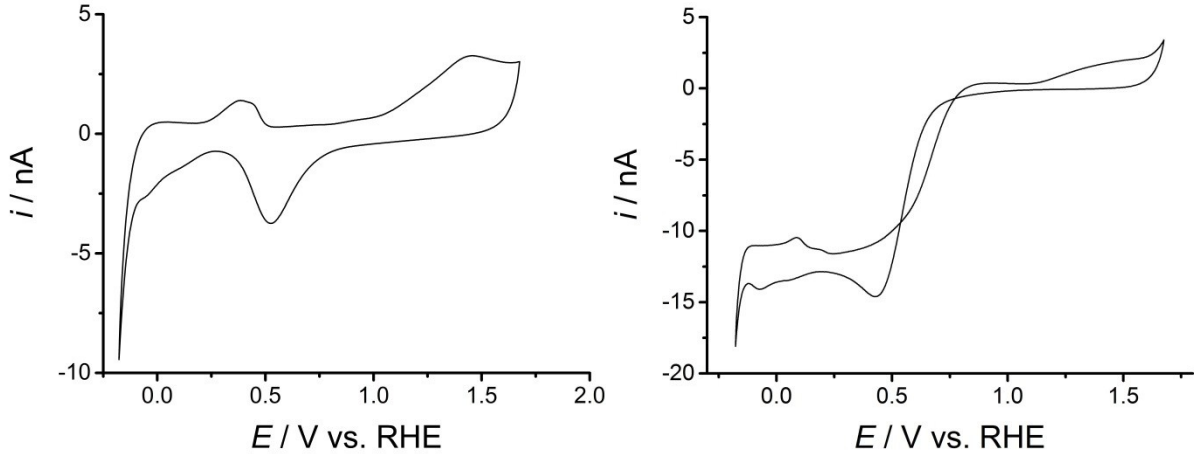

Figure SI-2: Cyclic voltammogram for a 25 µm Ø $Pt_{0.9}Rh_{0.1}$ microdisc recorded in Ar purged (left) and aerated (right) 0.1 M $KClO_4$ at 200 mV s^{-1}.

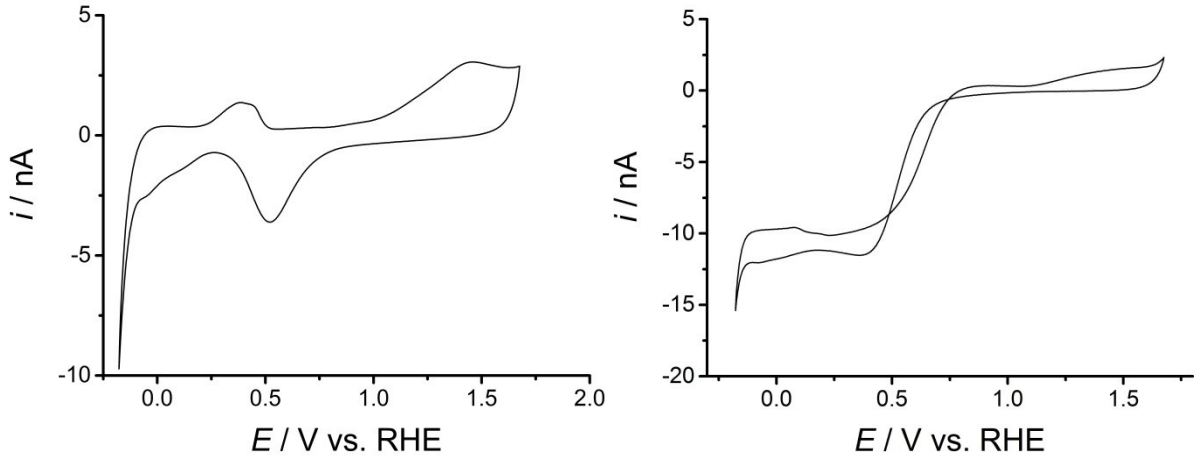

Figure SI-3: Cyclic voltammogram for a 25 µm Ø $Pt_{0.9}Ir_{0.1}$ microdisc recorded in Ar purged (left) and aerated (right) 0.1 M $KClO_4$ at 200 mV s^{-1}.

Chronoamperograms for the Pt alloys

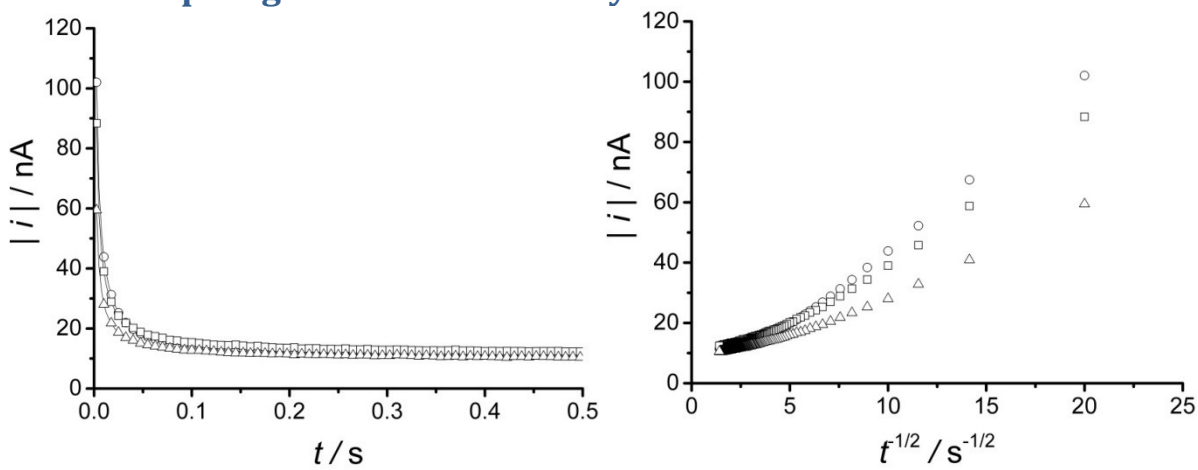

Figure SI-4: (Left) Chronoamperograms for the reduction of oxygen in aerated 0.1 M $KClO_4$ with a 25 µm Ø Pt (○), $Pt_{0.9}Ir_{0.1}$ (Δ) and $Pt_{0.9}Rh_{0.1}$ (□) electrode. Each electrode was conditioned as shown in figure 1 of the article. (Right) same data but plotted versus $t^{-1/2}$.

Correction for atmospheric pressure on the oxygen solubility

Deviations in atmospheric pressure were taken into account using equation 1:[1]

$$c_{aq} = \frac{c_{aq,760\ mm\ Hg}\,(P_t - p)}{760\ mm\ Hg - p} \tag{1}$$

where c_{aq} is the concentration of dissolved oxygen, $c_{aq,760\ mm\ Hg}$ is the saturation concentration of dissolved oxygen at 760 mm Hg pressure, P_t is the barometric pressure and p is the vapour pressure of water at 298 K. Barometric pressure was measured and updated hourly by a barometer from the University of Southampton weather station.

Estimation of the double layer charging duration

The time taken to charge or discharge 95% of the double layer is estimated[2] as

$$\tau = 3R_u C_{dl} \tag{2}$$

where R_u is the uncompensated solution resistance and C_{dl} the double layer capacitance. For a microdisc of radius a and roughness factor R_f, C_{dl} is given by

$$C_{dl} = \pi a^2 R_f C \tag{3}$$

where C is the capacitance per unit area. The microdisc uncompensated solution resistance is given by[3]

$$R_u = \frac{1}{4\kappa a} \tag{4}$$

where κ is the conductivity of the solution. Combining equations 2-4 the time needed to charge / discharge 95% of the double layer is given by

$$\tau \cong \frac{3\pi a R_f C}{4\kappa} \tag{5}$$

Assuming a roughness factor of 3, a capacitance of 20 μF cm^{-2} (typical for Pt in water) and a conductivity of 0.0115 Ω^{-1} cm^{-1} (typical for 100 mM $KClO_4$), it takes less than 20 μs to charge or discharge the double layer at a 25 μm diameter Pt microdisc.

Estimation of the electrode electroactive area

For Pt the electroactive area, A, was found from the charge under the hydride adsorption region of a 20 mV s^{-1} CV in 1 M H_2SO_4,

$$A = \frac{0.77}{210\ \mu C\ cm^{-2}} \int_{0.02\ V\ vs.\ RHE}^{0.35\ V\ vs.\ RHE} i\ dt \tag{6}$$

where integrating the current between the double layer region and the trough in the hydride adsorption region prior to hydrogen evolution for the acid CV gives 0.77 monolayers of hydride and a single monolayer of hydride corresponds to 210 μC cm^{-2} of charge[4].

This method was only possible for the platinum electrode thanks to its well defined and well-studied hydrogen adsorption region. For the Pt alloys, the electroactive area was calculated by multiplying their geometric area by the roughness factor of the platinum electrode (R_f), which is taken as the ratio between the electrode electroactive surface area and its geometric area. After undergoing a standard polishing regime, the R_f was found to be 2.6. As all electrodes underwent the same polishing regime, it is a reasonable assumption that they will exhibit the same roughness factor.

Estimation of oxygen coverage

This was done by first calculating the number of moles of oxygen that would make up a complete monolayer (N_{O_2}) from

$$N_{O_2} = \frac{A\ N_{Pt,\ cm^{-2}}}{2N_A} \tag{7}$$

where $N_{Pt,\ cm^{-2}}$ is the average number of Pt surface atoms found in polycrystalline platinum (1.5×10^{15} atom cm^{-2}), N_A is Avogadro's number and A is the electroactive surface area of the electrode. The factor of two is needed as oxygen is assumed to bind side on, such that one Pt atom is bonded to one oxygen atom within the diatomic molecule. For a 25 μm Pt microdisc electrode, the number of adsorption sites for O_2 was found to be 3.68×10^{9}, which equates to 6.11×10^{-15} mol in a complete monolayer. The number of moles of oxygen that was actually present on the electrode surface was found from the extra charge passed using Faraday's law of electrolysis. The charge for the direct reduction of the adsorbed oxygen corresponds to 1.5×10^{-15} mol adsorbed oxygen. The extra charge seen in fully aerated solution corresponds to 1.9×10^{-15} mol. These values respectively correspond to 0.08 and 0.10 monolayers of adsorbed oxygen.

References

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