Supporting Information:
Electrode kinetics at carbon electrodes and the density of electronic states

Rita Nissim, Christopher Batchelor-McAuley, Martin C. Henstridge and Richard G. Compton*

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford OX1 3QZ, United Kingdom

*Corresponding author

Fax: +44 (0) 1865 275410; Tel: +44 (0) 1865 275413. Email: richard.compton@chem.ox.ac.uk

1 Marcus-Hush theory

This section presents the most commonly used forms of Marcus-Hush theory, for further details beyond that outlined below the reader is referred to the recent review by Henstridge *et al.*.[1] One of the main features in the Marcus-Hush expressions for the rate of heterogeneous electron transfer is the reorganisation energy λ. The reorganisation energy does not have a classical equivalent and as such it does not appear within the Butler-Volmer equation. The value of λ represents the energy required to distort the electronic configuration of the reactants such that they are equal to the equilibrium position of the products but in the absence of electron transfer. The reorganisation energy is regularly expressed in terms of inner (intramolecular vibrations) and outer (solvation) sphere contributions.

Consideration of the electrode as being a continuum of energy levels gives - and through the use of Fermi's golden rule - the following Marcus-Hush expressions for describing the reductive (k_{red}) and oxidative (k_{ox}) rate constants are obtained;

$$k_{red} = k^o e^{-(1/2)\theta} \frac{I(\theta,\Lambda)}{I(0,\Lambda)} \quad (1)$$

$$k_{ox} = k^o e^{+(1/2)\theta} \frac{I(\theta,\Lambda)}{I(0,\Lambda)} \quad (2)$$

where k^o is the standard electrochemical rate constant, $\theta = F/RT(E - E_f^0)$ and $\Lambda = (F/RT)\lambda$. Within these equation E_f^0 is the formal potential, λ is the reorganisation energy, F the Faraday constant (96,485 C mol^{-1}), R the gas constant 8.314 J K^{-1} mol^{-1}, T the absolute temperature K. $I(\theta, \Lambda)$ is an integral;

$$I(\theta,\Lambda) = \int_{-\infty}^{\infty} \frac{\exp[-(\varepsilon-\theta)^2/4\Lambda]}{2\cosh[\varepsilon/2]} \mathrm{d}\varepsilon \quad (3)$$

As stated in the main text the standard electrochemical rate constant (k^o) is defined as

$$k^o = \frac{(2\pi)^2 \rho \mathrm{H}_{DA}^{o2}}{\beta h \sqrt{4\pi\Lambda}} exp\left[-\frac{\Lambda}{4}\right] I(0,\Lambda) \tag{4}$$

where ρ is the density of electronic states in the electrode material H_{DA}^{o} is the electronic coupling matrix at the closest distance of approach and β is its associated electronic coupling attenuation coefficient.

2 Simulation and fitting

For a known concentration of an electroactive species the diffusion coefficient may be readily determined through measurement of the steady state limiting current, via the following equation;

$$i_{ss} = 4nFCDr \tag{5}$$

i_{ss} is the steady state limiting current (A), n is the total number of electrons transferred, F is the Faraday constant (96,485 C mol^{-1}), C is the concentration of the electroactive species (mol cm^{-3}) D is the diffusion coefficient (cm^2 s^{-1}) and r is the radius of the microdisc (cm).

In order to find the value of k^o for each of the five quinone species, the steady-state voltammetric response was recorded at the microdisc electrodes at 25°C in 0.1M TBAP at 25 mVs^{-1}. The voltammetric responses were fitted to a simulated response from an in house program based upon modeling the electron transfer as following Butler-Volmer kinetics. It should be noted that both the Butler-Volmer and Marcus-Hush models are equivalent as the system tends towards the reversible limit.[1] The fitting of the simulated results to the expreimental system was under taken with the aim of extracting physically significant data from the experimental voltammetry.

The quantification of the accuracy of the fitting and hence the accuracy of the obtained values, was achieved through measurement of the difference in current between the experimental and simulated responses. This difference in current was expressed as a *mean scaled absolute deviation* (MSAD). The MSAD is defined as,

$$\%\ \mathrm{MSAD} = \frac{1}{n}\sum_{n}\left|\frac{i_{\mathrm{exp}} - i_{\mathrm{sim}}}{i_{\mathrm{exp}}}\right| \times 100 \tag{6}$$

where i_{exp} and i_{sim} are experimental and simulated current respectively and n is the number

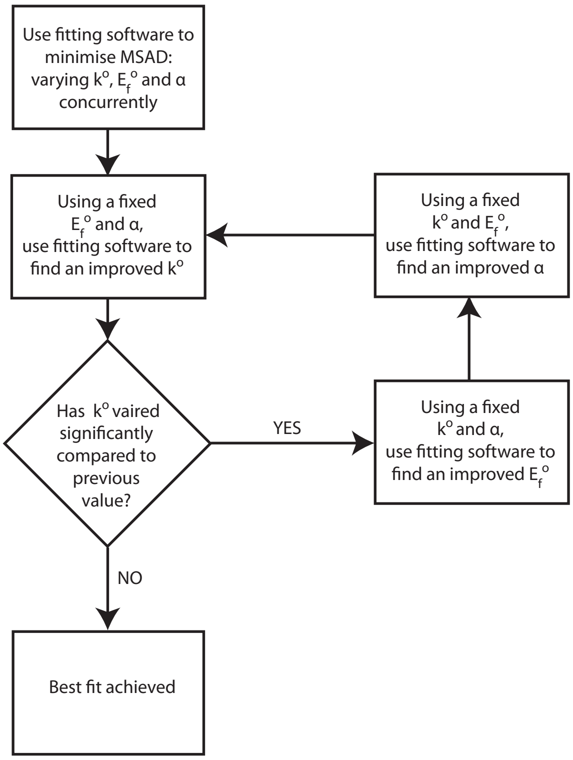

Figure 1: Flow chart depicting the procedure utilised in order to find the best fit for the experimental results.

of data points. Since the points of the simulated voltammetry are not necessarily aligned at the same potential values as those of the experimental voltammetry, spline interpolation was used to calculate i_{sim} at the potentials of the experimental points. Additionally a narrow strip of the experimental voltammetry near $i = 0$ was omitted from the MSAD calculations because dividing by a very small value of i_{exp} yields a very large value of MSAD even if $i_{\mathrm{exp}} - i_{\mathrm{sim}}$ is small. The MSAD values at each point considered are then averaged to yield a final value of average MSAD per point. In order to obtain the best fit for each of the voltammetric responses the procedure as outlined in figure 1 was followed. The plots shown in figures 2, 3, 4 and 5 depict the voltammetric response for AQ, BQ, CBQ and DDQ, respectively, on both a gold and carbon microdisc, the experimental results for DCQ can be found in the main body of the text. Also depicted in figures 2, 3, 4 and 5 is the variation in the MSAD for the fitting of the simulation to the experimental results as a function of the simulated k^o. The minimum in the MSAD versus k^o plots represents the best fit. Further from these plots the *relative* errors in the k^o may be assessed, where the values quoted in the main text represent the k^o value where the MSAD is +10% greater than the minimum. In all experimental cases the fit of plot of MSAD versus k^o is asymmetric about the minimum, this is most apparent in the case of the reduction of DDQ on a gold electrode. This asymmetry arises due to the fact that at the high rates of electron transfer the influence of the electron transfer rate decreases, as the system tends towards the fully reversible (Nernstian) limit. Consequently the errors for the simulated best fit k^o's within the text are given different upper and lower bounds. Table 1 gives all of the experimental data obtained from the fitting, where the formal potentials have been stated against the Ag pseudo reference electrode. It should also be highlighted that although the values of alpha have been stated, due to the system being close to the revesible limit, alpha does not have a significant influence upon the simulated voltammetry. If error bars are applied to the simualted alpha values in an analogous manner to that done for the standard rates of electron transfer the variation will on average be $\alpha \pm 0.05$ units.

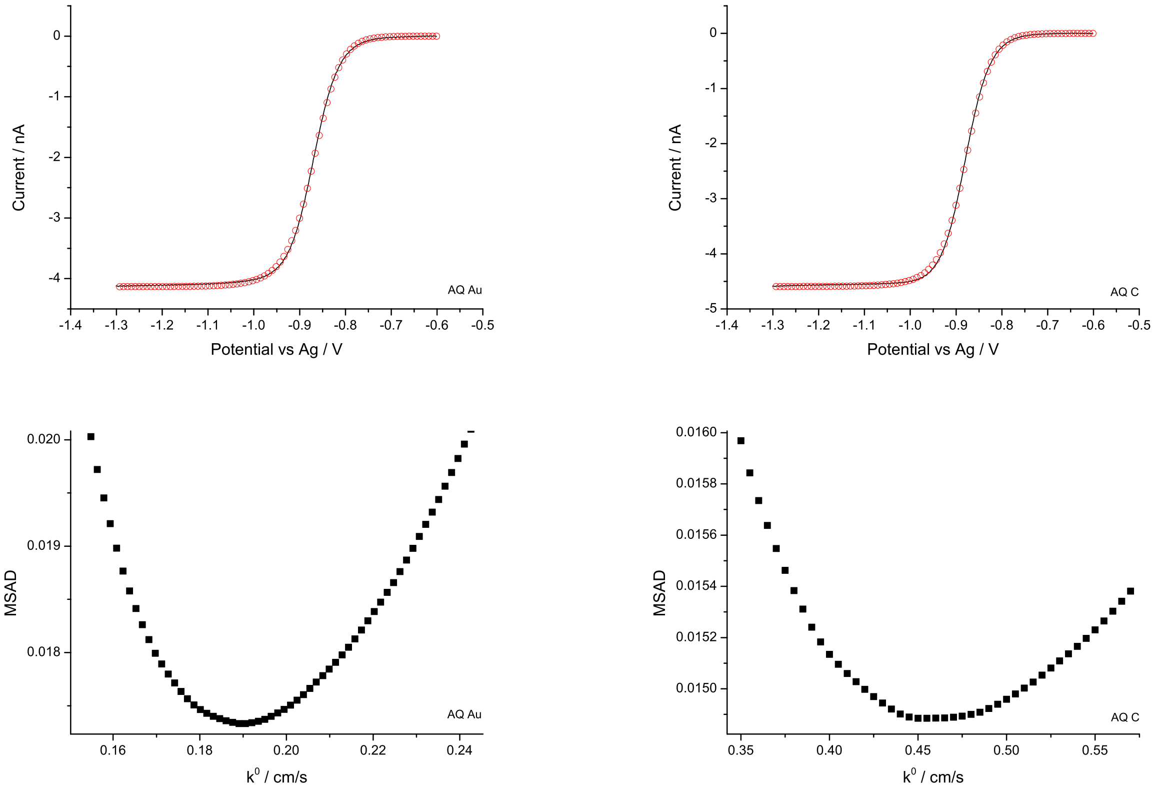

Figure 2: Experimental and simulated best fits for the reduction of AQ (1mM) on both a gold and carbon microdisc at a scan rate of 25 mVs^{-1}. Also depicted in the plot of MSAD versus the value of k^o used within the simulation.

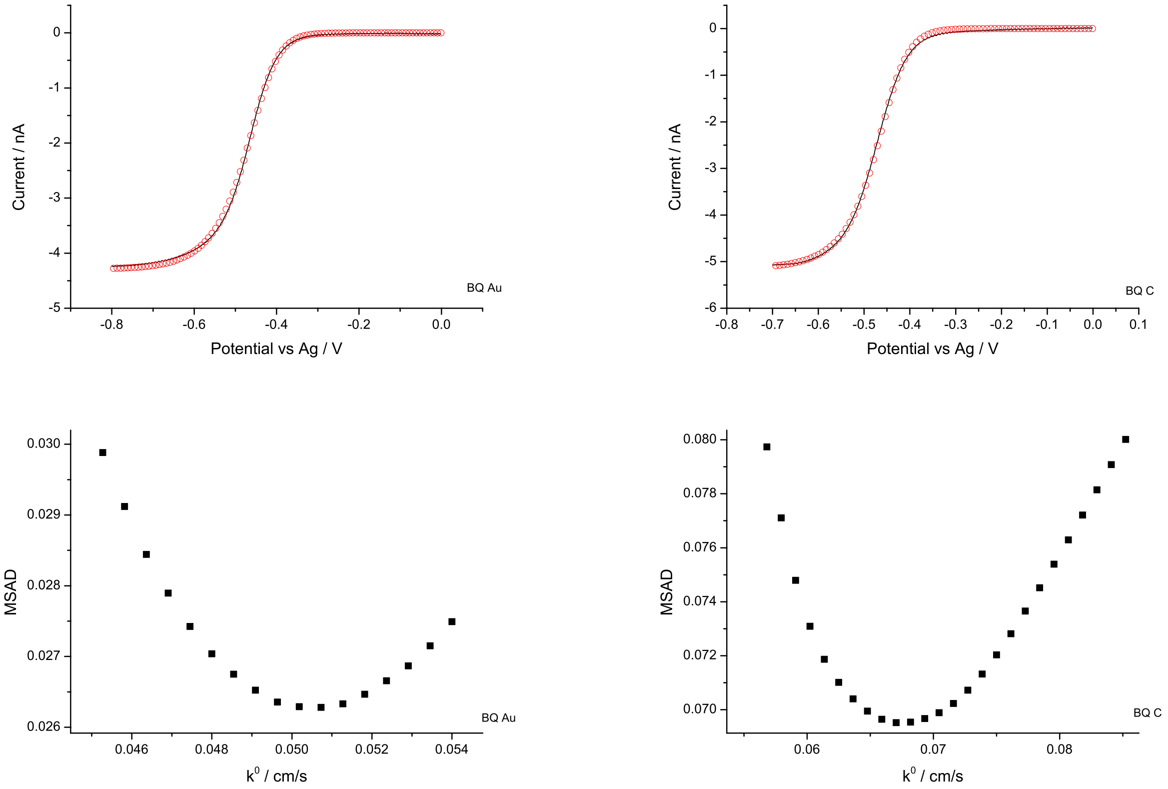

Figure 3: Experimental and simulated best fits for the reduction of BQ (1mM) on both a gold and carbon microdisc at a scan rate of 25 mVs^{-1}. Also depicted in the plot of MSAD versus the value of k^o used within the simulation.

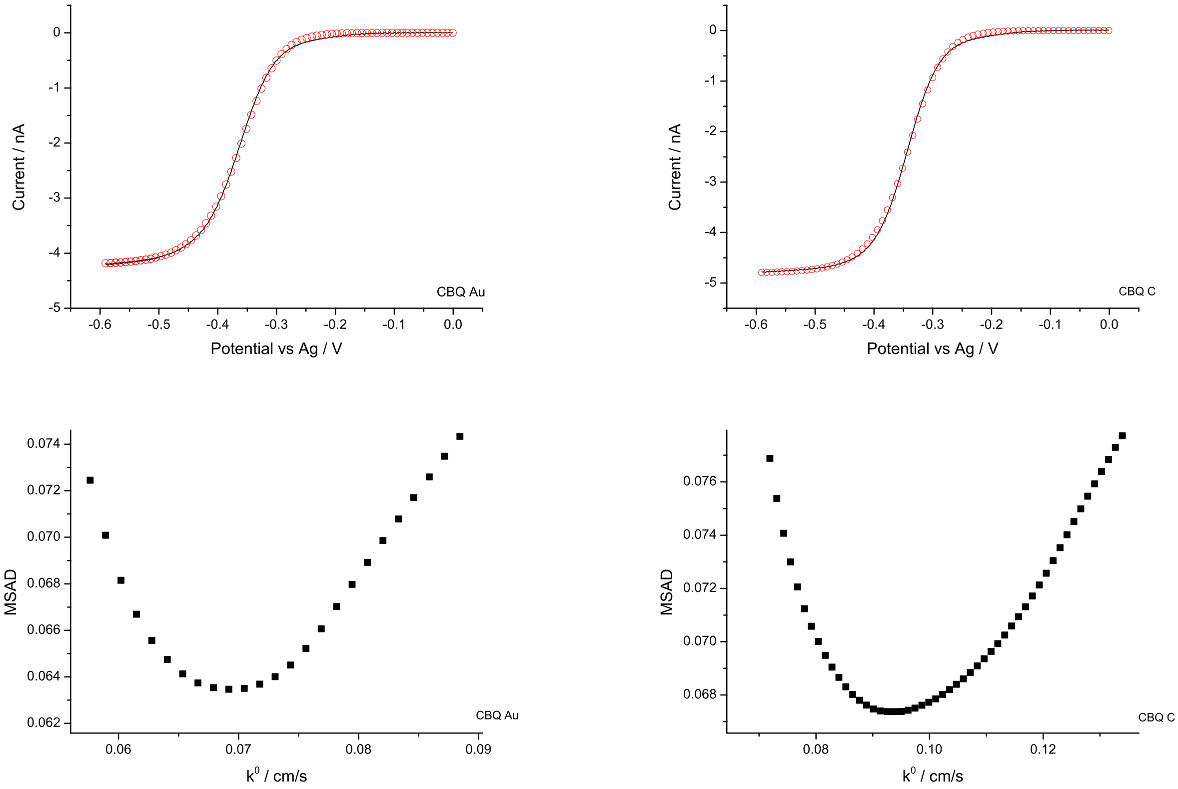

Figure 4: Experimental and simulated best fits for the reduction of CBQ (1mM) on both a gold and carbon microdisc at a scan rate of 25 mVs^{-1}. Also depicted in the plot of MSAD versus the value of k^o used within the simulation.

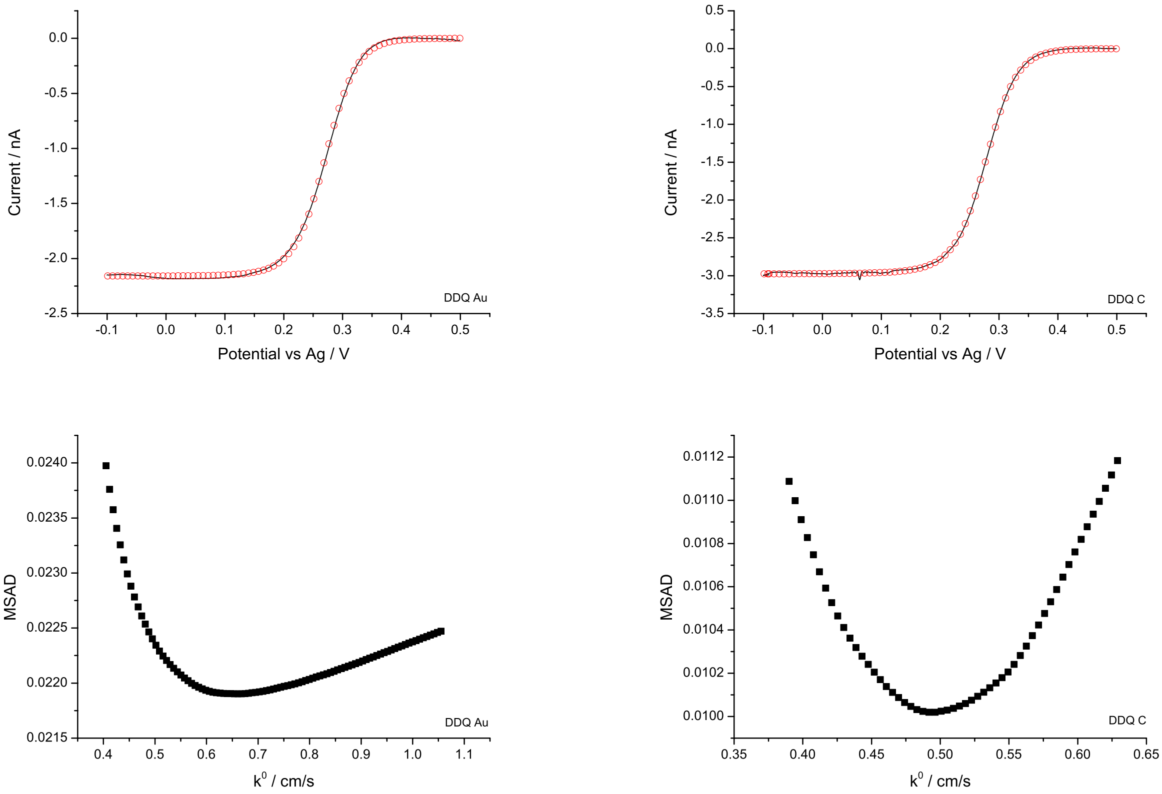

Figure 5: Experimental and simulated best fits for the reduction of DDQ (1mM) on both a gold and carbon microdisc at a scan rate of 25 mVs^{-1}. Also depicted in the plot of MSAD versus the value of k^o used within the simulation.

Species		Au micro	C micro
AQ	k^o (cm s^{-1}) =	0.19054	0.45
	alpha =	0.584	0.489
D = 2.43 x 10^{-5} cm^2 s^{-1}	E_f^0 vs. Ag (V) =	-0.86	-0.8746
	MSAD =	0.01733	0.01488
BQ	k^o (cm s^{-1}) =	0.05072	0.06704
	alpha =	0.468	0.477
D = 2.18 x 10^{-5} cm^2 s^{-1}	E_f^0 vs. Ag (V) =	-0.4436	-0.4541
	MSAD =	0.02627	0.06952
CBQ	k^o (cm s^{-1}) =	0.06941	0.093
	alpha =	0.575	0.6
D = 2.16 x 10^{-5} cm^2 s^{-1}	E_f^0 vs. Ag (V) =	-0.3426	-0.32857
	MSAD =	0.06346	0.06737
DCQ	k^o (cm s^{-1}) =	0.5007	0.4951
	alpha =	0.385	0.515
D = 1.97 x 10^{-5} cm^2 s^{-1}	E_f^0 vs. Ag (V) =	-0.22357	-0.2175
	MSAD =	0.01772	0.009997
DDQ	k^o (cm s^{-1}) =	0.6677	0.496
	alpha =	0.498	0.453
D = 1.47 x 10^{-5} cm^2 s^{-1}	E_f^0 vs. Ag (V) =	0.2725	0.27925
	MSAD =	0.0219	0.01001

Table 1: Experimental values obtained from fitting of the simulated data. Where, D is the diffusion coefficient k^o is the rate of electron transfer and E_f^o is the measured formal potential.

3 Measurement of the 'potential of zero charge'

As stated in the main body of the text, the *potential of zero charge* (PZC) correlates in the absence of adsorption effects to the position Fermi level of the material.[2] Measurement of the PZC can only be achieved under experimental conditions containing limited levels of supporting electrolyte.[3] Consequently, the capacitance of the system was measured as a function of potential using cyclic voltammetry in the presence of 0.1 mM tetrabutyl ammonium perchlorate. Each cyclic voltammogram was recorded of a potential range of 50 mV and at a scan rate of 2 Vs^{-1}, the results of this can bee seen in figure 6.

The difference in current between the forward and backward scan (i_{cap}) is readily correlated to the specific capacitance of the of the electrode,[3]

$$i_{cap} = 2\nu C_{DL} \tag{7}$$

where ν is the scan rate (Vs^{-1}) and C_{DL} is the double layer capacitance. C_{DL} is equal to the area of the electrode times the specific capacitance. Hence, given the area of the electrode is known the specific capacitance, as depicted in figure 2 in the main body of the text, can be readily determined.

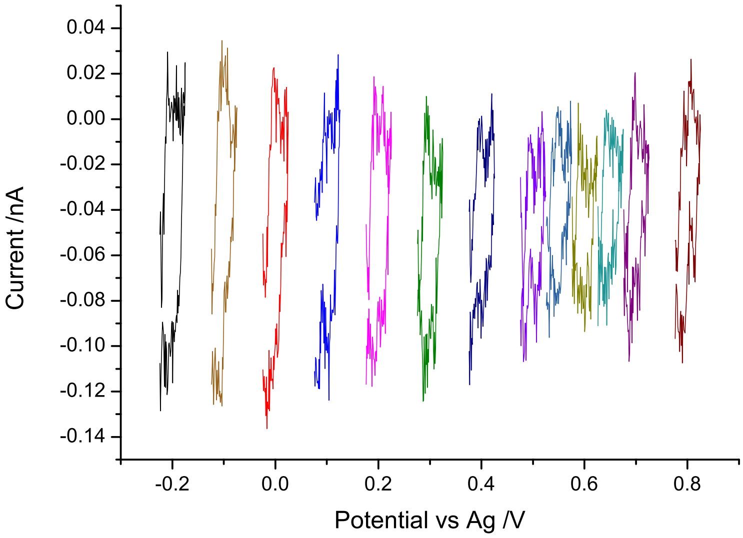

Figure 6: The voltammetric response of a carbon microelectrode in the presence of 0.1mM TBAP, at a scan rate of 2 Vs^{-1}.

4 Experimental

All reagents were purchased from Aldrich (Gillingham, U.K.) and were used as recieved without further purification. All solutions were prepared using deionised water of resistivity not less 18.2 MΩcm at 298 K (Viviendi water systems, U.K.). electrochemical measurements were recorded using a computer controlled μAutolab potentiostat (EcoChemie) with a standard three-electrode configuration in an acetonitrile solution containing unless stated otherwise 0.1M tetrabutyl ammonium perchlorate. A polycrystalline gold (BASi Technicol, West Lafayette, IN) or carbon fibre microelectrode (BASi Technicol, West Lafayette, IN) was used as the working electrode, a platinum wire (99.99% GoodFellow, Cambridge, U.K.) counter electrode and a silver wire (GoodFellow, Cambridge, U.K.) reference electrode completed the assembly. Both the Au and C electrodes were polished using alumina slurries of decreasing size from 3.0 to 0.1μm (Buehler Micropolishing II, Lake Bluff, IL) with the electrode briefy sonicated between each polishing step to remove any adhered alumina particles. All experiments were carried out in a thermostated water bath at a temperature of $25 \pm 0.1°$C.

References

[1] Henstridge, M. C.; Laborda, E.; Rees, N. V.; Compton, R. G. *Electrochim. Acta* **2011**, in press.

[2] Hahn, M.; Baertschi, M.; Barbieri, O.; Sauter, J.-C.; Ktz, R.; Gallay, R. *Electrochem. Sol.-State Lett.* **2004**, *7*, A33–A36.

[3] Bard, A. J.; Faulkner, L. R. *Electrochemical methods: fundamentals and applications*; Wiley,

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