Application of Marcus-Hush-Chidsey Theory to Two Electron Systems. The Influence of Electrode Material on the Electro-Reduction Kinetics of Covalently Attached 2-Anthraquinonyl Groups: Gold Vs. Carbon.

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A gold electrode was derivatized by electrochemical reduction of anthraquinone-2-diazonium tetrafluoroborate (AQ2-$N_2^+BF_4^-$) giving an Au-AQ2 modified electrode of a surface coverage below a monolayer. Simulations of cyclic voltammograms using Marcus-Hush-Chidsey theory for 2e^- process and assuming a uniform surface were *not* able to achieve a good fit for the overall shape of the baseline subtracted experimental voltammograms. Subsequently two models of surface inhomogeneity based on Marcus-Hush-Chidsey theory were investigated: a distribution of formal potentials, $E°'$, and a distribution of electron tunneling distances, r_0. The simulation of cyclic voltammograms involving the distribution of formal potentials allowed a good agreement between theory and experiment. The parameters of the Au-AQ2/Au-AQ2^{2-} process compared to the parameters of the EPPG-AQ2/EPPG-AQ2^{2-} process reported previously by Kozub et al. (*ChemPhysChem*, 12 (2011) 2806) show much faster kinetics, attributed to the higher density of electronic states for a gold electrode.

Keywords: Marcus-Hush-Chidsey theory, two electron process, cyclic voltammetry, modified gold electrode, distribution of formal potentials, density of electronic states

1. INTRODUCTION

Generally, the electronic density of states (DOS) of carbon materials is very different from that of metals and these differences can affect electrode kinetics. Metals have a large number of atomic orbitals to form bands and a high density of electronic states.

A higher DOS means a higher probability of electrons of correct energy available for an electron transfer to a redox system. Accordingly heterogeneous electron transfer rates are dependent on

the DOS of the electrode material. Electron transfer is faster when there is a high density of electronic states in the electrode at the $E^{\circ\prime}$ of the redox system involved. Disordered carbon materials such as glassy carbon conduct electrons similarly to metals because they have a relatively even DOS distribution, but the density of DOS at the Fermi level is generally lower than for metal materials [1].

For redox acceptors attached to a metallic or a semimetallic electrode, $O_{(s)}$, the potential dependent charge transfer flux, $v_e(E)$, is:

$$v_e(E) = k_e(E) \cdot [O_{(s)}], \tag{1}$$

where $k_e(E)$ is the potential dependent rate constant and $[O_{(s)}]$ is the surface concentration of redox acceptors. $k_e(E)$ for a metallic or a semimetallic electrode is proportional to ρ which is the energy dependent effective density of states/eV of the electrode that takes part in the electron transfer process [2].

Gold has a DOS of 0.28 states/eV and this value is relatively constant with energy [1]. The density of states in carbon is energy dependent. At a potential of -1.0 V vs. SCE the total DOS of graphite is ca 0.08 [3] - 0.083 [4] states/eV. Therefore it can be expected that the rate constants of reactions taking place on gold electrodes at -1.0 V vs. SCE will be ca 3.5 times faster that on carbon electrodes, other factors remaining constant.

The covalent attachment of anthraquinonyl groups by both electrochemical and spontaneous reduction of diazonium cations has been widely investigated [5-23]. A large variety of materials have been modified this way: GC, HOPG, carbon fibers, carbon nanotubes, silicon, aluminum alloys and metals such as gold, platinum, copper and iron. A diazonium salt dissolved in aprotic solvent or in acidic aqueous solution with a supporting electrolyte is reduced using the surface to be modified as a cathode. It is also possible to derivatize electrodes by simple immersion of the surface in a diazonium salt solution.

The spontaneous modification is simpler and quicker but generally not very reproducible and controllable [1, 24-27].

Marcus-Hush-Chidsey theory has been previously successfully applied to one electron processes involving species adsorbed on electrode surfaces, usually as self-assembled monolayers (SAMs) [28-31] but also to ferrocene attached to an edge plane pyrolytic graphite electrode (EPPG-Fc) [32].

More recently Marcus-Hush-Chidsey theory has also been employed to a two electron redox system, namely to edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) [33].

In this work we explore the two electron redox system attached to a gold electrode in order to compare the electrochemical behaviour and the kinetic parameters of 2-anthraquinonyl groups covalently attached to two types of surfaces: an EPPG and a gold electrode.

2. THEORY

We consider the reaction scheme:

$$A + e^- \overset{k_1}{\underset{k_2}{\Leftrightarrow}} B, \quad B + e^- \overset{k_3}{\underset{k_4}{\Leftrightarrow}} C \tag{2}$$

for which species *A*, *B* and *C* are all confined on the surface of an electrode. This system is described by the following rate equations:

$$\frac{d\Gamma_A}{dt} = -k_1\Gamma_A + k_2\Gamma_B, \tag{3}$$

$$\frac{d\Gamma_B}{dt} = -(k_2 + k_3)\Gamma_B + k_1\Gamma_A + k_4\Gamma_C, \tag{4}$$

$$\frac{d\Gamma_C}{dt} = -k_4\Gamma_C + k_3\Gamma_B, \tag{5}$$

where Γ_A, Γ_B and Γ_C (mol/cm^2) are the coverages of species *A*, *B* and *C* respectively, *t* (s) is time and k_1, k_2, k_3 and k_4 (s^{-1}) are the rate constants for their interconversion. The current, *I* (A), passed to the electrode is given by:

$$I = FA\left[\frac{d\Gamma_A}{dt} - \frac{d\Gamma_C}{dt}\right] \tag{6}$$

where *F* is the Faraday constant (C/mol) and *A* (cm^2) is the electrode area.

In this paper we consider cyclic voltammetry as a series of consecutive pulses, thus the potential applied at the electrode varies as a discrete function of time according to:

$$E = |E_1 - vt - E_2| + E_2 \tag{7}$$

where E_1 and E_2 (V) are the starting and vertex potentials respectively, *v* (V/s) is the scan rate and *t* takes discrete values at which the current is measured.

Simultaneous solution of Eqs.(3)-(5) yields the analytical expressions for the coverage of each species as a function of time [33].

For each timestep during the cyclic voltammogram the rate constants are calculated in accordance with the Marcus-Hush kinetic formalism [28, 34, 35]. The rate constants are given by:

$$k_1 = k_0^{AB} \exp\left[-\frac{\theta^{AB}}{2}\right] \frac{S(\Lambda^{AB}, \theta^{AB})}{S(\Lambda^{AB}, 0)} \tag{8}$$

$$k_2 = k_0^{AB} \exp\left[+\frac{\theta^{AB}}{2}\right] \frac{S(\Lambda^{AB}, \theta^{AB})}{S(\Lambda^{AB}, 0)} \qquad (9)$$

$$k_3 = k_0^{BC} \exp\left[-\frac{\theta^{BC}}{2}\right] \frac{S(\Lambda^{BC}, \theta^{BC})}{S(\Lambda^{BC}, 0)} \qquad (10)$$

$$k_4 = k_0^{BC} \exp\left[+\frac{\theta^{BC}}{2}\right] \frac{S(\Lambda^{BC}, \theta^{BC})}{S(\Lambda^{BC}, 0)} \qquad (11)$$

where k_0^{XY} is the standard electrochemical rate constant (defined at the electrode surface) for the *XY* couple, Λ^{XY} and θ^{XY} are dimensionless reorganization energy and dimensionless overpotential for the *XY* couple. These are defined thus:

$$\theta^{XY} = \frac{F}{RT}\left(E - E_{XY}^{\circ'}\right), \qquad (12)$$

$$\Lambda^{XY} = \frac{F}{RT} \lambda^{XY}, \qquad (13)$$

where E (V) is potential, $E_{XY}^{\circ'}$ (V) is the formal potential of the *XY* couple, Λ^{XY} (eV) is reorganization energy, R is the gas constant and T (K) is the temperature. The integral:

$$S(\Lambda, \theta) = \int_{-\infty}^{\infty} \frac{\exp\left[\dfrac{-(\varepsilon - \theta)^2}{4\Lambda}\right]}{2\cosh\left[\dfrac{\varepsilon}{2}\right]} d\varepsilon, \qquad (14)$$

where ε is an integration variable, is evaluated numerically using the trapezium rule.

For a redox species confined at the electrode surface, k_0 is given by [2, 36]:

$$k_0 = \frac{4\pi^2}{h} \rho \cdot H^2 \cdot S(\Lambda, 0) \cdot \exp(-\beta \cdot r_0) \qquad (15)$$

where h is Planck's constant, ρ (eV^{-1}) is the density of states in the electrode, r_0 (Å) is the distance separating the redox centre from the electrode surface, H (eV) is the electronic coupling matrix at this distance and β (Å^{-1}) is the electronic coupling attenuation coefficient which takes a value of 1.59 Å^{-1} in water [37].

The inhomogeneity of the electrode surface was modeled as a Gaussian distribution of parameter χ (either formal potential or tunneling distance) with mean μ and standard deviation σ. A

total of 300 cyclic voltammograms were simulated, spread evenly across the range $\chi = \mu \pm 3\,\sigma$. A weighted sum was then calculated to give the total current:

$$I_{total} = \frac{\sum_{j} Q_j I_j}{\sum_{j} Q_j} \tag{16}$$

with Q_j, the weighting of the jth simulation, being given by the Gaussian function:

$$Q_j = \exp\left[\frac{(\chi_j - \mu)^2}{2\sigma^2}\right] \tag{17}$$

and I_j is the current of the jth simulation, given by Eqn. (6).

It should be noted that values of k_0 quoted in this work are defined at the electrode surface and are subject to Eqn. (15), thus a value of 10^6 s^{-1} at the electrode surface is equal to 0.113 s^{-1} at a distance of 10 Å from the electrode, assuming β takes the value 1.6 Å^{-1} [37].

The program was written in C++ and run on a desktop PC. Typical simulation times were ca 40 s for tunneling distance distribution and ca 60 s for formal potential distribution.

3. EXPERIMENTAL

3.1 Reagents and equipment

All reagents were used as received without further purification. Sodium hydroxide was obtained from Sigma-Aldrich (Gillingham, U.K.), potassium chloride from Riedel-de Haen (Seelze, Germany), tetra-n-butylammonium perchlorate (TBAP) from Fluka (Buchs, Switzerland) and acetonitrile from Fisher Chemical (Loughborough, U.K.). All aqueous solutions were prepared using deionised water of resistivity not less than 18.2 MΩ cm at 25˚C (Millipore water systems, UK).

Electrochemical measurements were conducted using a μAutolab computer-controlled potentiostat (Eco-Chemie, Utrecht, Netherlands) with a standard three-electrode configuration. Cyclic voltammetry was performed using a staircase step potential (E_{step}) of 0.01281 V. The response of a redox modified electrode to staircase cyclic voltammetry, is not, under all conditions equivalent to that of an analogy cyclic voltammogram. In situations where k_0 is large relative to the scan rate, significant deviations between the two procedures can occur. These deviations are minimal when $v > 10 k_0 E_{step}$ [38], i.e. for the current system, when the scan rate, v, is greater than ca 42.3 V/s. These differences between the two methods are further minimised through the use of a low alpha value (experimentally set at 0.3). Simulations of the voltammetric system were achieved through the use of a model in which the applied potential had a staircase waveform, so that any variations in the voltammetry at lower scan rates arising from the use of this procedure could be accounted for.

A polycrystalline gold electrode (1.8 mm diameter, BASi Technicol, West Lafayette, IN) was the working electrode, platinum wire the counter electrode and either a saturated calomel (SCE) (Radiometer, Copenhagen, Denmark) or a silver wire the reference electrode.

All solutions were thoroughly deoxygenated for at least 15 minutes with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solutions during experiments.

3.2 Synthesis of anthraquinone-2-diazonium tetrafluoroborate

The anthraquinone-2-diazonium tetrafluoroborate salt, used in the surface modification of a gold electrode, was synthesized according to the method developed by Milner [39]. 1.00 g of 2-aminoanthraquinone (Sigma-Aldrich, Gillingham, U.K.) was added to a slurry of ca 50 % molar excess of nitrosonium tetrafluoroborate (Sigma-Aldrich, Gillingham, U.K.) in 100 ml of dichloromethane (DCM) (Fisher Scientific, Loughborough, U.K.). The reaction mixture was placed in an ice-water bath and stirred for 1 h and after that DCM was removed under vacuum in an ice-water bath. The resulting anthraquinone-2-diazonium tetrafluoroborate product was stored at -5˚C.

3.3 Electrochemical modification of a gold electrode with 2-anthraquinonyl groups

The gold electrode was polished on alumina lapping compounds (Buehler, Coventry, U.K.) of decreasing sizes (1.0 μm, 0.3 μm) on soft lapping pads and sonicated in deionised water in an ultrasound bath for 3 minutes and dried in air.

Surface modification of the gold electrode was carried out by electrochemical reduction of ca 2 μM solution of anthraquinone-2-diazonium tetrafluoroborate (AQ2-$N_2^+BF_4^-$) in a 0.1 M TBAP solution in acetonitrile, because the ca 5 μM concentration of the diazonium salt used previously for electrochemical modification of an edge plane pyrolytic graphite (EPPG) electrode [33] turned out to give too high surface coverage on gold. The modification solution was kept in an ice-water bath in order to minimize spontaneous reaction between diazonium salt and gold surface as it was much less controllable and generally it could lead to a relatively high surface coverage in case of an EPPG electrode [33]. Reduction was carried out by scanning the potential between 0.8 V and -1.3 V vs. Ag wire at 0.1 V/s starting at 0.8 V for 23 times. Diazonium stock solution was prepared on a daily basis and kept in an ice-water bath to prevent decomposition.

The gold electrode modified with 2-anthraquinonyl groups (Au-AQ2) was then thoroughly rinsed with acetonitrile and dried in air.

3.4 Voltammetric characterization of Au-AQ2 modified electrode

The Au-AQ2 modified electrode was characterized in aqueous solution of 0.1 M NaOH with 0.1 M KCl as supporting electrolyte between -0.5 V and -1.2 V vs. SCE in a wide range of scan rates (1-50 V/s) (Fig. 3). The step potential for all scan rates was 0.01281 V, because the ratio scan rate : step potential must be ≤ 4000/s, therefore it is not possible to keep step potential very low for all

scan rates. To avoid the influence of various step potential on cyclic voltammograms it was kept constant for the whole range of scan rates and it was high enough for 50 V/s. All simulations of cyclic voltammograms for Marcus-Hush-Chidsey theory: for a uniform surface and with distribution of either formal potentials or tunneling distances, were also performed using a potential staircase (step height was 0.01281 V).

4. RESULTS

4.1 Electrochemical modification of a gold electrode with 2-anthraquinonyl groups
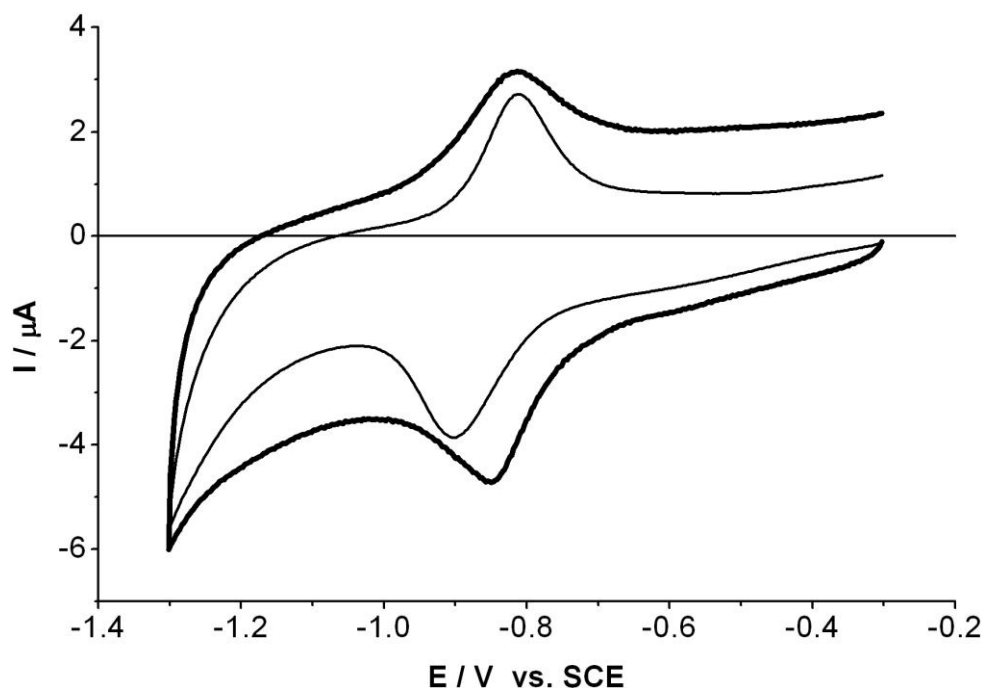
Figure 1. Cyclic voltammograms of EPPG-AQ2 (thick line) and Au-AQ2 (thin line) modified electrodes in a deoxygenated with nitrogen aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Scan rate: 0.1 V/s. Both EPPG and Au electrodes modified electrochemically in an acetonitrile solution containing ca 5 µM of anthraquinone-2-diazonium tetrafluoroborate (AQ2-$N_2^+BF_4^-$) and 0.1 M TBAP. The ratio between geometric surface area of the EPPG to the gold electrode was 7.4.

At first the gold electrode was modified using the same concentration of the anthraquinone-2-diazonium tetrafluoroborate (AQ2-$N_2^+BF_4^-$) solution as for the derivatization of an edge plane pyrolytic graphite (EPPG) electrode [33] (ca 5 µM) via electroreduction using potential cycling. However, after just seven scans the reduction peak of the surface bound 2-anthraquinonyl groups at the gold electrode was bigger than at EPPG (Fig. 1), even though the geometric area of the EPPG electrode was 7.4 times higher than that of the gold electrode pointing to multilayer and/or polymer formation. In order to decrease the surface coverage of 2-anthraquinonyl groups at the gold electrode, the concentration of diazonium salt in following experiments was reduced to ca 2 µM.
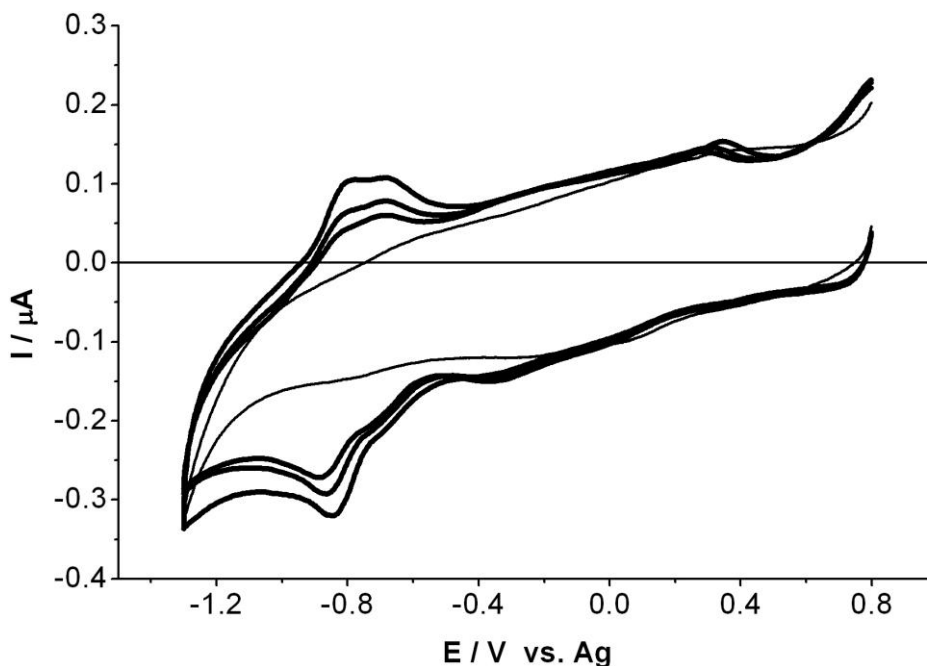
Figure 2. Electrochemical modification of the gold electrode with 2-anthraquinonyl groups in a deoxygenated with nitrogen acetonitrile solution containing ca 2 μM of anthraquinone-2-diazonium tetrafluoroborate (AQ2-N$_2^+$BF$_4^-$) and 0.1 M TBAP. Scan rate: 0.1 V/s; thin line: Au electrode before adding AQ2-N$_2^+$BF$_4^-$; thick lines: 7th, 14th and 23rd scan after adding AQ2-N$_2^+$BF$_4^-$.

Fig. 2 shows the electrochemical modification of the gold electrode with 2-anthraquinonyl groups using a 2 μM solution of anthraquinone-2-diazonium tetrafluoroborate (AQ2-N$_2^+$BF$_4^-$) dissolved in acetonitrile with 0.1 M TBAP as supporting electrolyte. The diazonium salt was reduced using the gold surface as a cathode. Reduction was carried out by scanning the potential between 0.8 V and -1.3 V vs. Ag wire at 0.1 V/s, starting at 0.8 V for 23 times. The voltammograms of the Au-AQ2 modified electrode (thick lines in Fig. 2) reveal oxidation and reduction peaks for the surface bound 2-anthraquinonyl groups at the same potentials as at EPPG electrode (ca -0.8 V vs. Ag) [33].

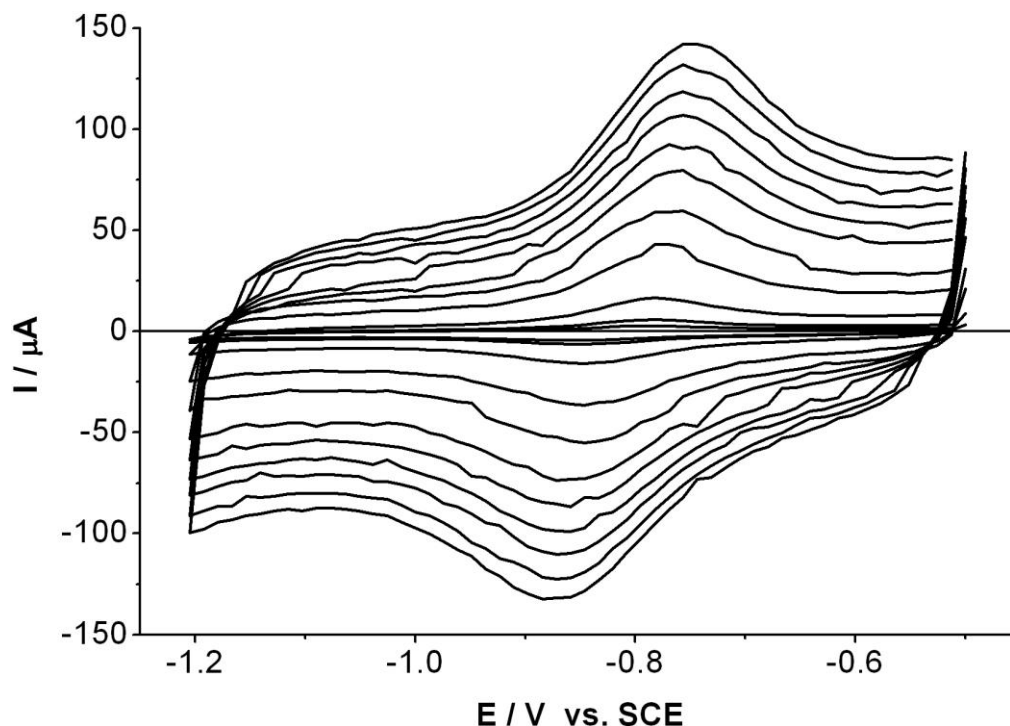*4.2 Voltammetric characterization of the Au-AQ2 modified electrode*

The Au-AQ2 modified electrode was characterized by cyclic voltammetry in aqueous solution containing 0.1 M NaOH and 0.1 M KCl over a wide range of scan rates (1-50 V/s), as shown in Fig. 3. The voltammetric response of Au-AQ2 at pH higher than 12.05 corresponds to the following redox reaction [17, 40]:

$$\text{Au-AQ2} + 2e^- \leftrightarrow \text{Au-AQ2}^{2-}. \tag{18}$$

The relationship between the baseline subtracted peak current and scan rate was found to be approximately linear. The electrode was modified in acetonitrile solution containing ca 2 μM

AQ2-N$_2^+$BF$_4^-$ and 0.1 M TBAP, then rinsed thoroughly with acetonitrile, dried in air and transferred to aqueous solution containing only 0.1 M NaOH and 0.1 M KCl, therefore no molecules other than attached 2-anthraquinonyl groups could contribute to the observed voltammetric signals.

Figure 3. Cyclic voltammograms of the Au-AQ2 modified electrode in a deoxygenated with nitrogen aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Scan rate range: 1-50 V/s.

The slight observed deviation from linearity was probably due to the difficulty of accurate background correction as the electrode capacitance appears markedly different at potentials either side of the peak. The average surface coverage, Γ, can be calculated from the slope of the I_p vs. v plot:

$$I_p = \frac{n^2 F^2}{4RT} v A \Gamma .$$ (19)

Γ of 2-anthraquinonyl groups at the gold electrode for the whole scan rate range was ca $1.51 \cdot 10^{-11}$ mol/cm^2. As pointed out in ref. [33], it is possible to roughly estimate Γ_{AQ} for a monolayer coverage from the surface area of the molecule. Assuming a C-C bond length of 140 pm (as in benzene) and a C=O bond length of 123 pm (as in carbonyl compounds) for a flat orientation of the adsorbate Γ_{AQ} would be around $4.4 \cdot 10^{-10}$ mol/cm^2. Anthraquinone-2 groups are however likely to be more vertically aligned with the surface of the electrode. Assuming that the thickness of the molecule is a covalent diameter of carbon (0.77 Å) Γ_{AQ} would be around $2.4 \cdot 10^{-9}$ mol/cm^2. These values are only estimates which do not take spaces between molecules and any imperfections into account but they illustrate the row of magnitude expected for a monolayer coverage of either vertically or horizontally

aligned anthraquinone. Ernst et al. report that the theoretical coverage of a densely-packed monolayer assuming a planar orientation of the 2-anthraquinonyl groups calculated from X-ray bond lengths and non-bonded van der Waals radii yields a surface coverage of $3.45 \cdot 10^{-10}$ mol/cm^2 [41]. The surface concentration of 2-anthraquinonyl groups equal to ca $1.5 \cdot 10^{-11}$ mol/cm^2 is lower than the literature value and estimations mentioned above, therefore it can be confidently assumed that the Γ_{Au-AQ2} in the experiments described in this paper was below a monolayer. When more 2-anthraquinonyl groups are present on the surface, the average distances decrease and as a consequence, lateral interactions are likely to become greater making the voltammetric response more complex. The surface concentration below a monolayer prevents significant interactions between the attached anthraquinone molecules.

4.3 Simulations of cyclic voltammograms according to Marcus-Hush-Chidsey theory

Baseline subtraction of experimental cyclic voltammetry (Fig. 4) allows us to simulate the exact faradaic process and avoid errors originating from the overlap of charging and faradaic currents.
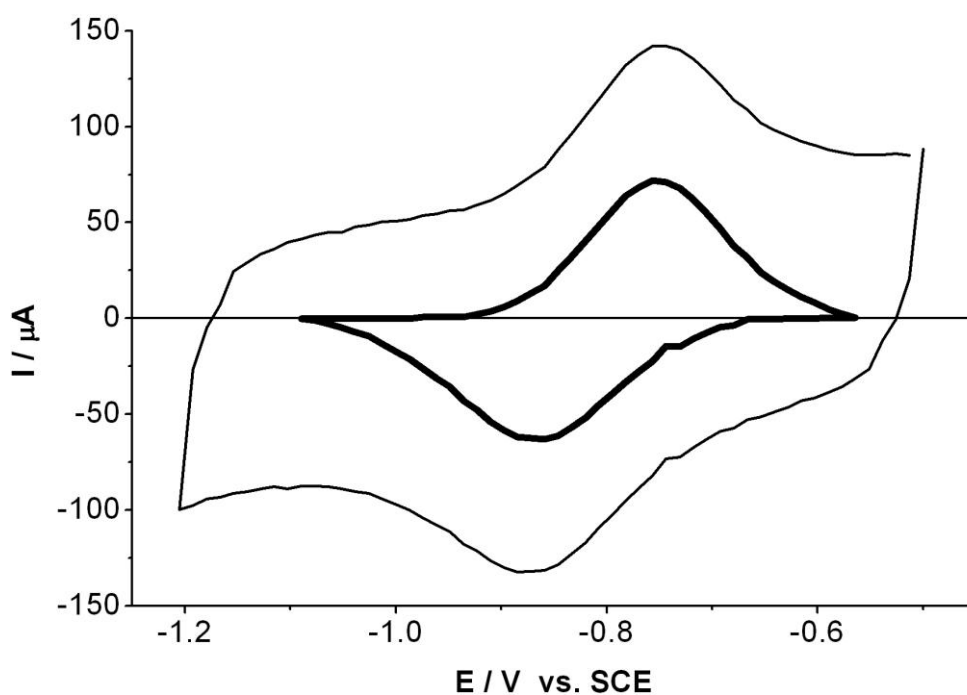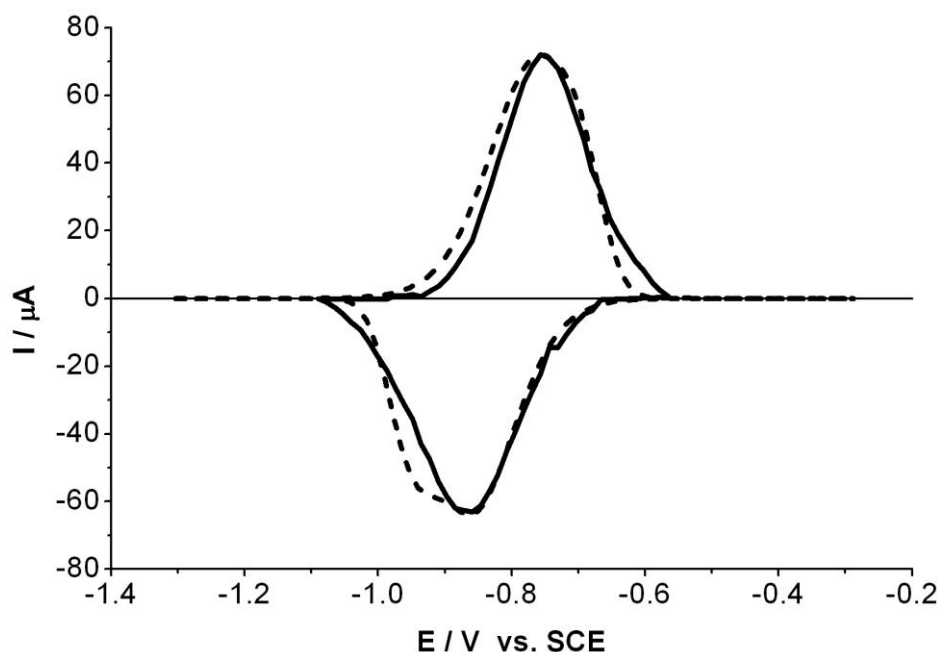

Figure 4. Comparison of an experimental cyclic voltammogram (thin line) with the baseline-subtracted voltammogram (thick line). Scan rate: 50 V/s.

Both peaks for Au modified electrode are very broad, even at relatively low scan rates. At 1 V/s the full width at half of the peak maximum height (FWHM), which is diagnostic of the homogeneity of the monolayer, was 115 ± 2 mV for the oxidation peak and 135 ± 8 mV for the reduction peak. These values are approximate because of the limitation of baseline subtraction (see above) and therefore the values of peak heights and widths somewhat uncertain. Broadening and tailing of the voltammetric peaks can arise from a spread in the formal potentials of the electroactive sites or from a distribution of

tunneling distances [30]; that is the values of FWHM that are larger or smaller than 90.6/n mV at 25°C, which is expected for identical and independent sites, suggest that the adsorbates do not react with the electrode all at the same rate for a given potential [31].

Despite the low surface coverage and a lack of lateral interactions the Au-AQ2/Au-AQ2^{2-} two electron redox process cannot be fitted with Marcus-Hush-Chidsey theory assuming a uniform surface (Fig. 5 and Tab. 1). The contrast between experimental subtracted voltammogram and the simulation is particularly apparent for the reduction peak. It indicates that the model is probably incomplete and the surface bound 2-anthraquinonyl groups are likely to react with the gold electrode in a non-uniform way.
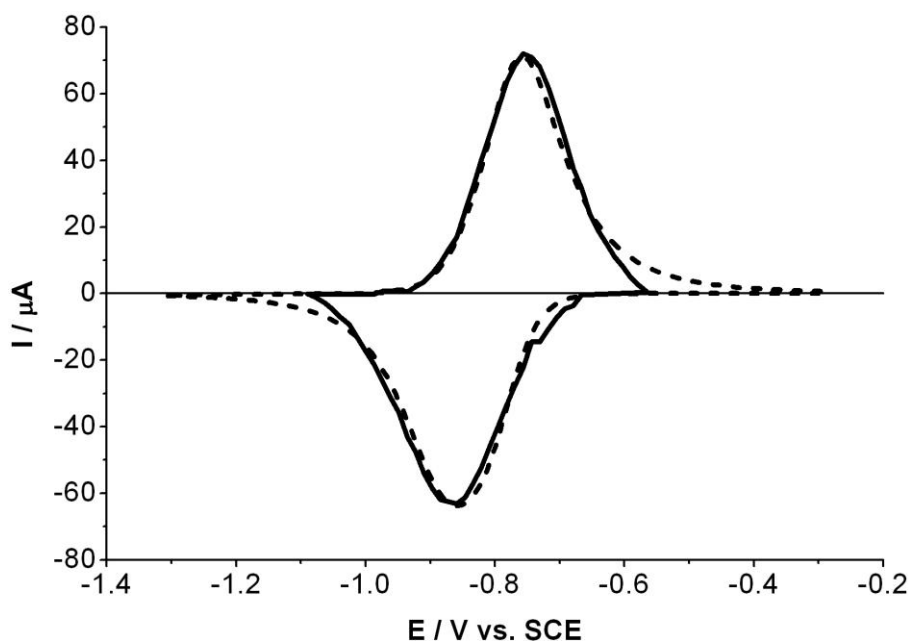

Figure 5. Comparison of baseline-subtracted experimental voltammetry (solid line) with simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for a uniform surface. Scan rate: 50 V/s.

Table 1. Best fit parameters used in the simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for a uniform surface (Fig. 5). Scan rate: 50 V/s.

	first step: Au-AQ2/Au-AQ2^{-}	second step: Au-AQ2^{-}/Au-AQ2^{2-}
$E^{\circ'}$	-0.778 V	-0.865 V
k_0	360 s^{-1}	290 s^{-1}
λ	0.7 eV	1 eV

The comparison of the baseline subtracted experimental voltammetry with the simulation which includes distribution of tunneling distances, r_0, shows a closer fit (Fig. 6) as far as the overall shape of the peaks is concerned; also the peak potentials are in good agreement. However, to achieve

so close a fit it is necessary to use unrealistically small reorganisation energies of 0.001 eV for the first and 0.04 eV for the second electron transfer step (Tab. 2). For reactions of organic molecules in hydrocarbon-like solvents, where the dipolar reorientation energies are small, λ can reach values not lower than 0.1 eV [30].
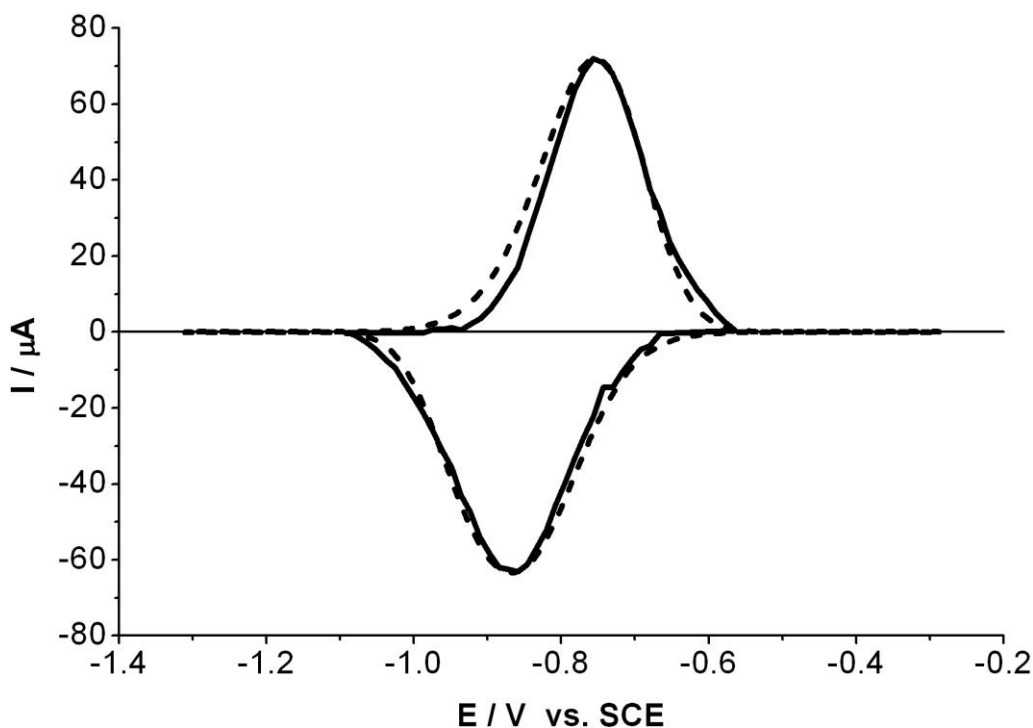

Figure 6. Comparison of baseline-subtracted experimental voltammetry (solid line) with simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for simulated distribution of tunneling distances. Scan rate: 50 V/s.

Table 2. Best fit parameters used in the simulated distribution of tunneling distances for 50 V/s (Fig. 6).

	first step: Au-AQ2/Au-AQ2$^-$	second step: Au-AQ2$^-$/Au-AQ2^{2-}		
$E^{\circ\prime}$	-0.79 V	-0.83 V	r_0	1.8 Å
k_0	3000 s^{-1}	2000 s^{-1}	β	1 Å^{-1}
λ	0.001 eV	0.04 eV	$\sigma(r_0)$	0.6 Å

The simulation which includes a distribution of formal potentials, $E^{\circ\prime}$, is depicted in Fig. 7. This model enables a good agreement between theory and experiment, matching peak currents, peak potentials and achieving a close fit for the overall shape of the subtracted experimental voltammogram. The values of both formal potentials for Au-AQ2/Au-AQ2^{2-} process are 0.04 V less negative that for EPPG-AQ2/EPPG-AQ2^{2-} [33] indicating that the reduction of surface confined 2-anthraquinonyl groups at gold electrode is more highly driven than at EPPG. Moreover, the values of the standard rate constants for Au-AQ2/Au-AQ2^{2-} ($k_{0,\text{first}} = 500$ s^{-1} and $k_{0,\text{second}} = 330$ s^{-1}) are higher than for EPPG-AQ2/EPPG-AQ2^{2-} ($k_{0,\text{first}} = 110$ s^{-1} and $k_{0,\text{second}} = 100$ s^{-1}) [33], while the reorganizational

energies remain the same within experimental error (Tab. 3). The differences in k_0 values between gold and EPPG electrodes reflect, as discussed in the introduction, the higher electronic density of states (DOS) for gold, which increases the probability that an electron of the correct energy will be available for electron transfer to a redox system [1]. The comparison of parameters between Au-AQ2/Au-AQ2^{2-} and EPPG-AQ2/EPPG-AQ2^{2-} illustrates the dependence of the heterogeneous electron transfer rate on the DOS of the electrode material [1].

Figure 7. Comparison of baseline-subtracted experimental voltammetry (solid line) with simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for simulated distribution of formal potentials. Scan rate: 50 V/s.

Table 3. Best fit parameters parameters used in the simulated distribution of formal potentials for 50 V/s (Fig. 7). For ± analysis of both λ see text.

	first step:	**second step:**
	Au-AQ2/Au-AQ2^{-}	Au-AQ2^{-}/Au-AQ2^{2-}
$E^{\circ\prime}$	-0.78 ± 0.005 V	-0.85 ± 0.005 V
k_0	500 ± 50 s^{-1}	330 ± 40 s^{-1}
λ	0.7 eV	1 eV
σ ($E^{\circ\prime}$)	0.04 ± 0.003 V	

The $\sigma\,(E^{\circ\prime}) = 40$ mV is lower for the Au-AQ2$^-$/Au-AQ2^{2-} process than 60 mV reported previously for an edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) and for the edge plane pyrolytic graphite electrode covalently modified with ferrocene (EPPG-Fc) [32, 33]. The fact that the distribution of formal potentials is smaller on gold than on an EPPG electrode reflects a more uniform surface of polycrystalline gold.

The values of formal potentials, $E^{\circ\prime}$, for the first (Au-AQ2/Au-AQ2$^-$) and the second (Au-AQ2$^-$/Au-AQ2^{2-}) electron transfer steps are fixed. A ± 5 mV alteration of either $E^{\circ\prime}_{first}$ or $E^{\circ\prime}_{second}$ shifts both peaks slightly and changes their heights. A ± 50 s^{-1} modification of $k_{0,\,first}$ or a ± 40 s^{-1} modification of $k_{0,\,second}$ starts to influence peak heights and peak potentials. For the standard deviation, $\sigma\,(E^{\circ\prime})$, even a ± 3 mV change affects the sizes of both peaks significantly. The analysis of both λ shows that deviations from the experimental voltammograms are evident only for λ_{first} and $\lambda_{second} = 0.001$ and 0.01. Values from 0.1 produce voltammograms which start to be very similar to experimental ones. For both λ there is no upper limit, as even simulations with λ_{first} and $\lambda_{second} = 1000$ do not noticeably deviate from the shape and the size of the experimental curves and therefore Au-AQ2 modified electrode can be analyzed according to Butler-Volmer kinetics.

5. CONCLUSIONS

Following the study of Marcus-Hush-Chidsey theory applied to two electron redox system, namely to an edge plane pyrolytic graphite electrode modified with 2-anthraquinonyl groups (EPPG-AQ2) [33], this work explores the influence of the electrode material on the extracted kinetic parameters. The AQ2 groups were covalently attached to a gold electrode by electrochemical reduction of diazonium salt in acetonitrile solution and characterized voltammetricaly in aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Experimental subtracted cyclic voltammograms were fitted with simulations of Marcus-Hush-Chidsey theory for a uniform surface and also with a distribution of either formal potential, $E^{\circ\prime}$, or tunneling distance, r_0. The values of the formal potentials, the standard rate constants and reorganisation energies used for the simulation of a formal potential distribution of 40 mV gave the best fits to the experimentally observed cyclic voltammograms. The parameters from the distributed formal potentials simulation for Au-AQ2/Au-AQ2^{2-} process demonstrate much faster kinetics than for EPPG-AQ2/EPPG-AQ2^{2-} [33], which can be expected on the basis of higher electronic density of states (DOS) for gold.

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