



***Electrochemical properties of redox
mediators at carbon electrodes***

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Thesis submitted for the degree of DPhil
in Physical and Theoretical Chemistry

September 2011

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Abstract

Chapter 1 gives an overview of the basic principles of electrochemistry.

A rigorous electrochemical study on the solution phase and solid phase cobalt phthalocyanine (CoPC) is presented in chapter 2. The form of CoPC on carbon electrodes was characterized by scanning electron microscope (SEM). The use of CoPC modified edge plane pyrolytic graphite (CoPC-EPPG) for sensing nitrite (NO_2^-) was also investigated. It was found that the claimed mediator CoPC has no influence on the process. A bare glassy carbon (GC) electrode was successfully applied for the quantitative determination of nitrite as a simple alternative to the modified electrodes reported in the literature (chapter 3).

Chapter 4 compares the voltammetric responses of an edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) and solution phase anthraquinone monosulphonate (AQMS) in the presence of a limited concentration of protons. The solution phase and surface bound species show analogous responses resulting in split waves. DigisimTM simulation of the AQMS voltammetry have shown that the pH adjacent to the electrode may be altered by up to 5–6 pH units in low buffered solutions; this is caused by the consumption of protons during the electrochemical reaction.

Chapters 5 and 6 compare the electrochemical properties of 2-anthraquinonyl groups covalently attached to an edge plane pyrolytic graphite (EPPG) and to a gold electrode. In both cases simulations using newly developed Marcus-Hush-Chidsey theory for a $2e^-$ process assuming a uniform surface did not achieve a good agreement between theory and experiment. Subsequently two models of surface inhomogeneity were investigated: a distribution of formal potentials, $E^{\ominus'}$, and a distribution of electron tunneling distances, r_0 . For both EPPG-AQ2 and Au-AQ2 modified electrodes the simulation involving $E^{\ominus'}$ distribution turned out to be the most adequate. This is the first time that Marcus-Hush-Chidsey theory has been applied to a $2e^-$ system.

Chapter 7 briefly summarizes the obtained results.

Publications

The results presented in this thesis have been published by the following journals:

1. **B. R. Kozub**, N. V. Rees, and R. G. Compton,
Sensors and Actuators B: Chemical, 2010, 143, 539–546
2. **B. R. Kozub** and R. G. Compton,
Sensors and Actuators B: Chemical, 2010, 147, 350–358
3. C. Batchelor-McAuley, **B. R. Kozub**, D. Menshykau, and R. G. Compton,
Journal of Physical Chemistry C, 2011, 115, 714–718
4. **B. R. Kozub**, M. C. Henstridge, C. Batchelor-McAuley, and R. G. Compton,
ChemPhysChem, 2011, 12, 2806–2815
5. **B. R. Kozub**, M. C. Henstridge, C. Batchelor-McAuley, and R. G. Compton,
International Journal of Electrochemical Science, 2011, 6, 6047–6062

Acknowledgements

I would like to thank **Professor Richard Compton** for his help, encouragement, guidance, support and enthusiasm over the past three years.

This thesis would not have been possible without other members of the group who have contributed to my research. I am very grateful especially to: Dr Neil Rees for the DigisimTM analysis of nitrite oxidation mechanism in section 3.3.1, Dr Lei Xiao for SEM images and EDS spectra in section 2.3.3, Chris Batchelor-McAuley for many conversations about anthraquinone, for the solution phase voltammetry of AQMS in chapter 4, and Martin Henstridge for Marcus-Hush-Chidsey theory section 5.2 and also for providing the simulation programs which were used in chapters 5 and 6.

I am also very grateful to many of my colleagues for their insightful, intelligent and funny comments on research, food, driving, traveling, jobs and life in general. They are (in no particular order): Emma Rogers, Laura Barrosse-Antle, Kathryn Toghill, Jane Panchompoo, Yige Zhou, Qian Li, Min Lu, Rahmat Wibowo, Neil Rees, Ian Cutress, Danu Suwatchara, Konstantin Zhurov, Thomas Doneux and Leon Freitag.

I would like to thank **St John's College, University of Oxford**, for a Sir John Kendrew Scholarship which provided me with full funding towards my DPhil studies.



Dziękuję wszystkim, którzy zawsze, a zwłaszcza przez te ostatnie trzy lata trzymali za mnie kciuki. Dziękuję w szczególności mojej rodzinie – mamie Stanisławie i bratu Dawidowi – oraz moim znajomym za życzliwość, wsparcie, poświęcony mi czas, a przede wszystkim za długie, ciekawe i pomocne rozmowy (telefoniczne i w cztery oczy).



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Fundamentals of electrochemistry

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This chapter gives a short overview of the basic principles of electrochemistry and describes experimental methods relevant to the research presented in this thesis. More detailed information can be found in many electrochemistry textbooks [1–9].

The chapter also briefly outlines modified electrodes and explains the aims of this thesis.

1.1. Introduction

Electrochemistry is a branch of chemistry which studies the kinetics and thermodynamics of processes involving a charge transfer which occurs heterogeneously at the electrode/solution interface. The processes studied in this thesis are all heterogeneous, i.e. between solid (bare or modified) electrodes in an electrolyte solution (with or without electroactive species).

1.1.1. Electrochemical cells

The magnitude of the potential difference at an electrode/solution interface controls the direction and the rate of charge transfer. In reality the potential of a single interface cannot be measured. The potential *difference* between two electrodes in an electrochemical cell can however be determined. In electrochemical experiments usually only one of the electrodes is the subject of study. It is called a working (indicator) electrode (WE). The second one is a reference electrode (RE) (see Appendix A.1) which has a fixed composition so its potential is constant [1–7].

1.1.2. Galvanic and electrolytic cells

Electrochemical cells in which electrode reactions take place spontaneously are called galvanic cells (Fig. 1.1a). They convert chemical energy into electrical energy. Electrochemical cells in which electrode reactions are caused by an external voltage are electrolytic cells (Fig. 1.1b).

A galvanic cell important commercially is e.g. primary (nonrechargeable) Leclanché Zn-MnO₂ cell. An example of an electrolytic cell used industrially is e.g. for electrorefining of copper.

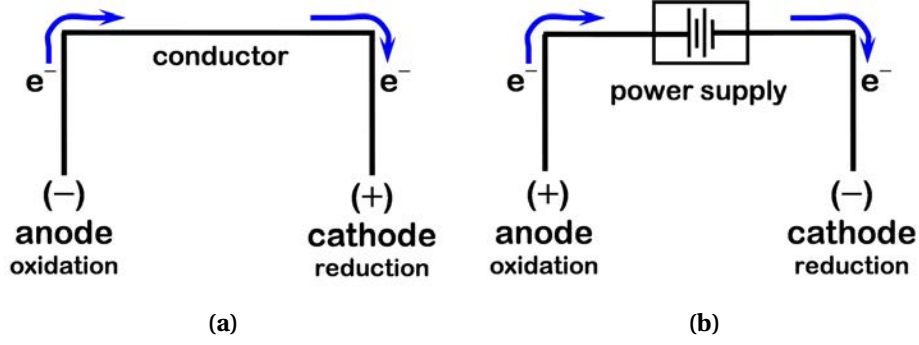
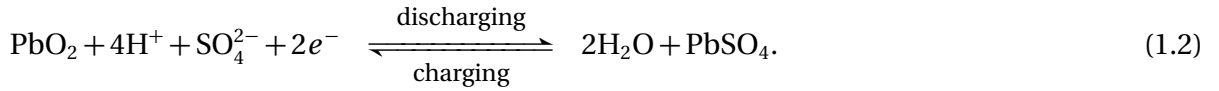
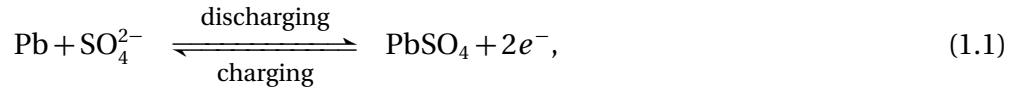


Fig. 1.1: Types of electrochemical cells: (a) galvanic and (b) electrolytic.

Some cells can behave as galvanic and electrolytic cells. A well-known example is the lead-acid car battery:



Under discharge it is a galvanic cell and on recharging it is an electrolytic cell [1, 3].

1.1.3. Electron transfer

Metals are conductors due to a large number of electrons which are free to move in the metal lattice. Atomic orbitals on the very strongly interacting neighbouring atoms in the lattice form a continuum of energy levels, termed a band. The highest occupied energy level at 0 K is the Fermi level, E_F [8].

The occupation of the electronic levels in a metallic electrode close to the E_F level is:

$$f = \frac{1}{1 + \exp \frac{(E - E_F)}{k_B T}}, \quad (1.3)$$

where f is the probability of occupation of a level of energy E and k_B is

the Boltzmann constant ($1.38065 \cdot 10^{-23}$ J/K). When $E = E_F$, $f = 0.50$ and when $E = E_F - k_B T$, $f = 0.73$. For a solid metallic electrode only electrons with energies within $k_B T$ of E_F can be transferred [3].

Electron transfer occurs between the highest available occupied energy level in the electrode (the Fermi level, E_F) and the lowest energy orbital on a solution species ($O_{(aq)}$ or $R_{(aq)}$), which can undergo a reaction:



at the electrode/solution interface. When the Fermi level of a metallic electrode immersed in a solution of $O_{(aq)}$ has a higher energy than the lowest vacant orbital on $O_{(aq)}$, then the electrons leave the electrode and reduce $O_{(aq)}$ to $R_{(aq)}$. The transfer of electrons from the electrode makes it positively charged (i.e. the potential of the electrode, ϕ_M , becomes more positive), the Fermi level lowers, whereas the solution becomes negatively charged (i.e. the potential of the solution, ϕ_S , becomes more negative). Electron transfer continues until the energies of the Fermi level and the orbital on $O_{(aq)}$ are equal and the dynamic equilibrium is reached [2].

The Fermi level of an electrode can be easily affected by external voltage since energies of electrons in an electrode correspond to the electrode potentials. When an applied potential is more negative than E_F , the energy of electrons is raised and they flow from the electrode to solution species $O_{(aq)}$ and a reduction occurs (Fig. 1.2a). When an applied potential is more positive than E_F then the electrons flow in the opposite direction and an oxidation takes place (Fig. 1.2b). The magnitude of the potential difference at the electrode/solution interface affects

the relative energies of electrons in the electrode and ions in the solution. Control of this potential difference governs the direction and the rate of electron transfer [1, 5, 6].

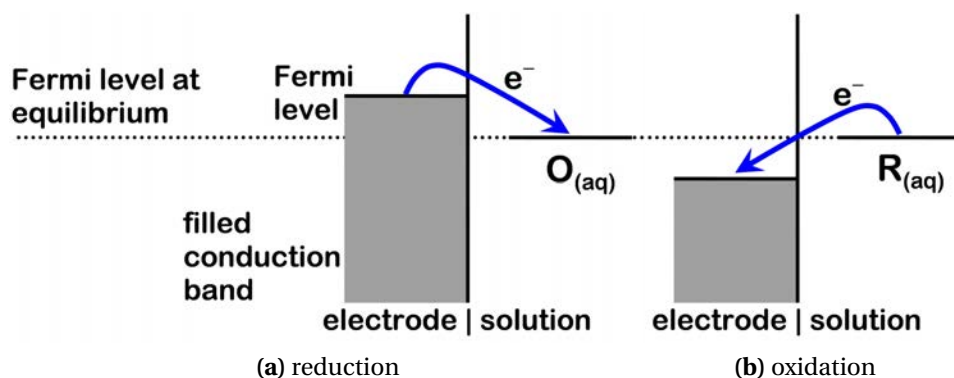


Fig. 1.2: Electron transfer at the electrode/solution interface. Fermi level is varied by application of potential: (a) by driving the electrode to more negative potentials the energy of electrons is raised; (b) by driving the electrode to more positive potentials the energy of electrons is lowered.

1.1.4. Faradaic and nonfaradaic processes

There are two types of processes which take place at electrodes and contribute to the resulting current. Reactions in which charge is transferred between the electrode and electroactive solution species (oxidation or reduction) are called faradaic processes, because they are governed by Faraday's first law (see Appendix A.2), i.e. the amount of reduced or oxidized species is proportional to the amount of charge passed. The current flows also when nonfaradaic processes occur. These can be caused by changes of the electrode/solution interface, e.g. adsorption/desorption. The current resulting from nonfaradaic processes is called a charging (capacitive) current, I_c :

$$I_c = C_{dl} \frac{dE}{dt} = C_{dl} v, \quad (1.5)$$

where C_{dl} is double layer capacitance and $\frac{dE}{dt} = \nu$ is the scan rate. Nonfaradaic processes happen in a range of potentials where oxidation or reduction are thermodynamically or kinetically impossible. When an electrode exhibits lower capacitative currents, the faradaic process of interest may be more easily resolved from the background. The double layer capacitance, C_{dl} , (usually $10 - 40 \mu\text{F}/\text{cm}^2$ in aqueous solutions) is often a function of potential [1].

1.1.5. Electrical double layer

When an electrode is immersed in a solution, a potential difference develops across the electrode/solution interface. As a result ions of opposite charge are attracted to the electrode surface and ions of the same charge are repelled. The region of charge separation at the electrode/solution interface is called the electrical double layer. It resembles a parallel plate capacitor.

When a potential is applied across a capacitor, charge will accumulate on its plates. During charging the charging current will flow. In the case of the electrode/solution interface there is a charge on the electrode Q^E and a charge in the solution Q^S , and always $Q^E = -Q^S$ (Fig. 1.3) to assure electroneutrality.

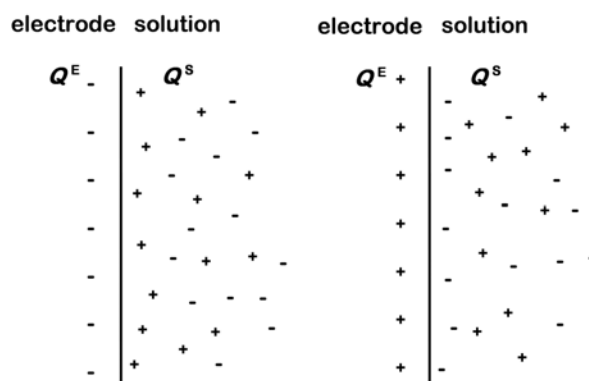


Fig. 1.3: The metal/solution interface as a capacitor.

The charge on the electrode exists in a very thin layer ($<0.1\text{ \AA}$) and comes from an excess or deficiency of electrons. The charge in the solution is located near the electrode surface and represents an excess of either cations or anions.

An electrode in an electrolytic cell at which no charge transfer (oxidation or reduction) can occur over a specified potential range is called the ideal polarizable electrode. The behaviour of an electrode/solution interface of the ideal polarizable electrode, when the potential across it is changed, is analogous to that of a parallel plate capacitor:

$$Q = CE, \tag{1.6}$$

where Q is the charge stored on the plates, E is the potential difference between the plates and C is a proportionality constant – the capacitance (in farads). In the case of the double layer, Q corresponds to the charge on the electrode or on the solution side of the interface and E to the potential difference between metal and solution interiors. However, even when $Q=0$ there still is a potential difference between metal and solution due to the solvent dipole layer at the electrode surface. If the dipole layer does not change greatly with potential, the Eq. (1.6) can be written as:

$$Q = C(E - E_{\text{pzc}}), \tag{1.7}$$

where E_{pzc} is the potential of zero charge which is the potential of an electrode on which surface there are no specifically adsorbed ions [1, 8].

There are various models proposed to describe the structure of the double layer at an electrode/solution interface:

- **Helmholtz-layer model:** It is the simplest model which describes the electrical double layer as a capacitor comprised of two parallel rigid layers of equal and opposite charge: one on the metal surface and one with solvated ions which approach the surface of the electrode as closely as possible. The plane passing through the centre of charge of the ions is called the Helmholtz plane. The potential between the electrode and the Helmholtz plane drops (or rises) linearly with distance.

- **Gouy and Chapman (diffuse layer) model:** This model takes into account the effect of thermal motion on the ions near an electrode surface. The double layer is not as compact as in Helmholtz's model. It has a variable thickness depending on the applied potential and electrolyte concentration and it consists of solvated ions in a quite extended region near the electrode surface which is called the diffuse layer. The potential drops (or rises) exponentially over the diffuse layer and tends to the bulk solution value, ϕ_S .

- **Stern model:** Stern combined the Helmholtz-layer and the diffuse layer models. Stern also pointed out that the Helmholtz plane should be divided into two planes. The inner Helmholtz plane (IHP) contains ions able to lose their solvation sheaths and approach the surface very closely, e.g. specifically adsorbed ions, and the outer Helmholtz plane (OHP) includes ions which may only approach the electrode to a distance determined by their solvation sheaths. The potential will fall (or rise) linearly from the surface of the electrode, ϕ_M , to the outer Helmholtz plane, ϕ_{OHP} , and then exponentially from OHP to the bulk of the solution, ϕ_S , across the diffuse double layer (Fig.1.4).

Some anions can undergo specific adsorption through van der Waals interactions

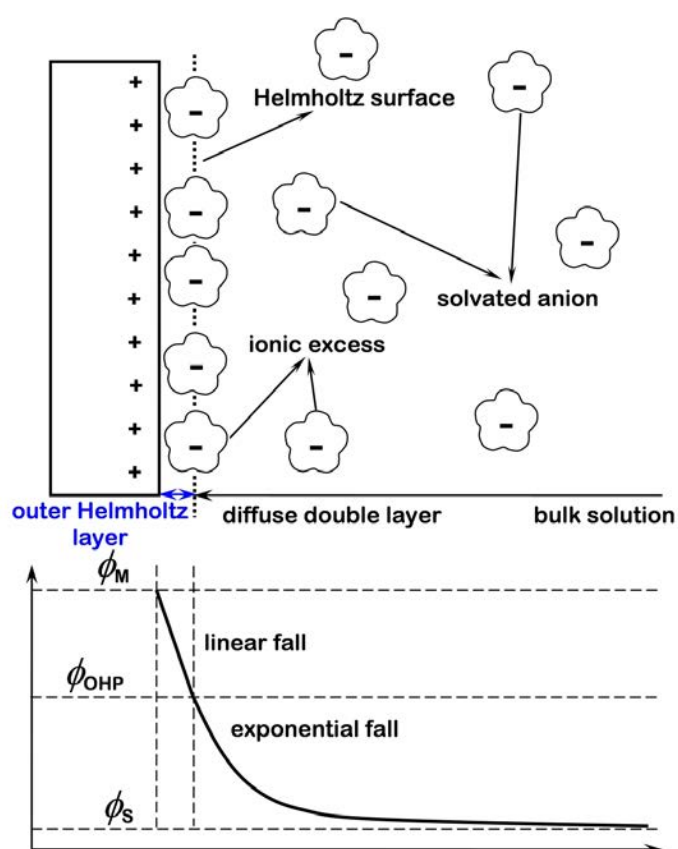


Fig. 1.4: Potential distribution at double layer: ϕ_M – potential of the metal electrode, ϕ_{OHP} – potential of the outer Helmholtz layer and ϕ_S – potential of the solution.

and therefore they can be adsorbed on an electrode surface even if it is negatively charged.

The structure of the interfacial region between electrode and solution affects the electrode processes. The thinner the interfacial region the better. The thickness of the double layer depends on the ionic strength of the solution. To minimize its size a large concentration of inert supporting electrolyte is added. For a 0.1 M concentration the thickness of the double layer can be of the Helmholtz layer itself; the thickness of the diffuse layer will be negligible [1, 3, 8].

1.1.6. Modes of mass transfer

Mass transfer is the movement of neutral molecules and ions from one location in solution to another. It affects the rates of reactions taking place at the electrode/solution interface and therefore the magnitude of current observed. Mass transfer occurs by diffusion, migration and convection:

- **Diffusion:** Diffusion is a movement of charged or neutral species under the influence of a concentration gradient from an area of high concentration to an area of low concentration. It is described by Fick's first law:

$$J_i = -D_i \frac{\partial c_i}{\partial x}, \quad (1.8)$$

where J_i (mol/cm²·s) is the flux of species i of concentration c_i in direction x and $\frac{\partial c_i}{\partial x}$ is the local concentration gradient at point x . D_i (cm²/s) is the proportionality factor between flux and concentration gradient known as the diffusion coefficient. Typically D_i is $10^{-6} - 10^{-5}$ cm²/s at room temperature in all of the solvents, except for room temperature ionic liquids (RTILs). It depends on the size of the diffusing species, solvent viscosity and temperature. The negative sign in Eq.(1.8) implies that the flux of species tends to annul the concentration gradient.

The rate of concentration change with time due to diffusion is described by Fick's second law:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}. \quad (1.9)$$

- **Migration:** Migration is a movement of a charged species under the influence of a gradient of electrical potential. In the presence of an applied

external electric field of strength $\frac{\partial \phi}{\partial x}$, the flux of ion i due to migration is:

$$J_i = -u_i c_i \frac{\partial \phi}{\partial x} = -c_i D_i \frac{z_i F}{RT} \cdot \frac{\partial \phi}{\partial x}, \quad (1.10)$$

where u_i is the mobility of ion i .

In the bulk solution concentration gradients are generally negligible and the mass transfer occurs mainly due to migration. The force affecting the ion due to the electric field is:

$$F = z_i e_0 \cdot \frac{\partial \phi}{\partial x}, \quad (1.11)$$

where e_0 is the elementary charge ($1.602 \cdot 10^{-19}$ C), and it is counterbalanced by a viscous force given approximately by Stoke's equation:

$$F = 6\pi\eta r v_i, \quad (1.12)$$

where η is the solution viscosity, r is the radius of solvated ion i and v_i is the velocity of the ion. The maximum velocity is:

$$v_i = \frac{z_i e_0 \cdot \frac{\partial \phi}{\partial x}}{6\pi\eta r} = u_i \cdot \frac{\partial \phi}{\partial x}, \quad (1.13)$$

where u_i is the ion mobility. There is a direct proportionality between diffusion coefficient, D_i , and mobility, u_i , given by the Einstein relation:

$$D_i = \frac{u_i RT}{z_i F}. \quad (1.14)$$

D_i depends on temperature, the size of the ion and solution viscosity:

$$D_i = \frac{k_B T}{6\pi\eta r}, \quad (1.15)$$

where k_B is the Boltzmann constant ($1.38065 \cdot 10^{-23}$ J/K).

• **Convection:** There are two types of convection: natural and forced. Natural convection is the motion of solution due to density gradients, which can be caused by e.g. exothermic reactions or by imperfect thermostating of electrochemical cell. Natural convection is generally unreproducible and therefore undesirable. Forced convection is usually achieved by either stirring the solution or rotating the electrode or by using channel flow electrodes. Controlled forced convection dominates the mass transport and gives well defined and easily interpreted results therefore it is widely employed in hydrodynamic electrochemical experiments. The convective mass transport can be described by:

$$J_i = c_i v, \quad (1.16)$$

where v is the velocity of solution relative to the electrode.

Overall mass transfer to an electrode is governed by the Nernst-Planck equation (written for one-dimensional mass transfer along the x -axis):

$$J_i = -D_i \frac{\partial c_i}{\partial x} - c_i D_i \frac{z_i F}{RT} \cdot \frac{\partial \phi}{\partial x} + c_i v, \quad (1.17)$$

which includes diffusion, migration and convection. Solving this equation is not easy when all three forms of mass transfer are present, therefore usually one or more of the contributions are prevented. Migration is avoided by adding an inert (supporting) electrolyte at a concentration much larger than that of the electroactive species (usually 0.1 M). Natural convection can usually be eliminated by limiting the duration of experiments to ca 10–20 s [1–3].

1.1.7. General aspects of electrochemical experiments

There are many important parameters in electrochemical experiments including electrode material, its surface area and geometry, concentration of electroactive species, concentration of supporting electrolyte, pH, solvent, potential, current, temperature, pressure, time etc. To investigate the electrochemical behaviour of a redox system some variables are kept constant while other are varied.

The rate of a homogeneous reaction, ν (mol/s), is:

$$\nu = \frac{dN}{dt} = \frac{I}{nF}, \quad (1.18)$$

whereas the rate of a heterogeneous reaction (mol/s·cm²) is expressed as:

$$\nu = \frac{I}{nFA}, \quad (1.19)$$

where A is the electrode area (cm²). The magnitude of current, I , which flows when a potential different from the equilibrium potential is applied to the cell, is:

$$I = nFAJ, \quad (1.20)$$

where J (mol/cm²s) is the flux of molecules reacting at the electrode area. It can be considered the rate of the electrochemical reaction:

$$J = k_c[O]_0, \quad (1.21)$$

e.g. a reduction reaction of solution phase electroactive species:



where k_c is the heterogeneous rate constant for a cathodic process (reduction) and

$[O]_0$ is the concentration of the reactant, $O_{(aq)}$, at the electrode surface (which is not the same as in bulk solution). Often (but not always) heterogeneous electron transfer reactions are first order. The units of the first order heterogeneous rate constants are cm/s in contrast to the units of the first order homogeneous rate constants, which are 1/s.

For any multistep process, the overall rate is determined by the slowest step. For heterogeneous reaction occurring at a working electrode, it may be any one of the following, depending on the system:

- rate of mass transport of the electroactive species to or from the electrode surface,
- rate of adsorption or desorption at the electrode surface,
- rate of the electron transfer between the electroactive species and the electrode, or
- rates of the individual chemical reactions which are part of the overall reaction scheme [1–3].

1.1.8. Electrochemical equilibrium

Thermodynamics predicts the direction (not the rate) of chemical reactions. It can be applied only to systems at equilibrium. For an electrochemical reaction:



equilibrium means that the rates of forward (reduction) and backward (oxidation) reactions are exactly the same, i.e. the rate at which electrons flow from the electrode to $O_{(aq)}$ is precisely balanced by the rate at which electrons flow

from $R_{(aq)}$ to the electrode. If electrochemical equilibrium is rapidly achieved and maintained as the electrode potential is varied, i.e. the electron transfer is fast, the reaction is called electrochemically reversible. A redox system with relatively slow electrode kinetics is called electrochemically irreversible. In this case equilibrium is not achieved on the timescale of the experiment. Reactions which demonstrate intermediate behaviour are called quasireversible. Electrochemical reversibility therefore gives an indication of the rate of the electron transfer kinetics [1, 2].

1.1.9. Electrode potential under equilibrium conditions: Nernst equation

Thermodynamic equilibrium for chemical reactions is defined by a balance between chemical potentials, μ , of the reactants and those of the products. Electrochemical equilibrium at constant temperature and pressure is controlled by electrochemical potentials, $\bar{\mu}$. The definition of $\bar{\mu}$ for component i in phase α is:

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi_\alpha = \left(\mu_i^{\ominus \alpha} + RT \ln a_i \right) + z_i F \phi_\alpha, \quad (1.24)$$

where z_i is the charge of i , F is the Faraday constant (96485 C/mol) and ϕ_α is the potential of phase α . $\bar{\mu}_i^\alpha$ is the sum of a term due to the chemical potential in a non-ideal solution ($\mu_i^\alpha = \mu_i^{\ominus \alpha} + RT \ln a_i$) and the contribution from the charge of the component i , ($z_i F \phi_\alpha$). The electrical energy of species i is analogous to the chemical Gibbs energy per mole: $\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i} \right)_{p, T, n_j \neq i}$, but it contains the electrical effects of the environment: $\bar{\mu}_i^\alpha = \left(\frac{\partial \bar{G}^\alpha}{\partial n_i} \right)_{p, T, n_j \neq i}$. In case of a species without charge: $\bar{\mu}_i^\alpha = \mu_i^\alpha$. For a pure phase that has unit activity (e.g. solid metals): $\bar{\mu}_i^\alpha = \mu_i^{\ominus \alpha}$.

For electrons in a metal ($z_{e^-} = -1$) activity effects can be neglected, therefore:

$$\bar{\mu}_{e^-}^\alpha = \mu_{e^-}^{\ominus\alpha} - F\phi_\alpha. \quad \text{For species } i \text{ in equilibrium between two phases } \alpha \text{ and } \beta:$$

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta.$$

For an electrode reaction of soluble species O^z and $R^{(z-n)}$:



a balance between electrochemical potentials of the reactants (O^z and ne^-) and those of the products ($R^{(z-n)}$) at equilibrium is:

$$\bar{\mu}_{O^z}^S + n\bar{\mu}_{e^-}^M = \bar{\mu}_{R^{(z-n)}}^S; \quad (1.26)$$

$$(\mu_{O^z}^S + zF\phi_S) + n(\mu_{e^-}^M - F\phi_M) = \mu_{R^{(z-n)}}^S + (z-n)F\phi_S, \quad (1.27)$$

$$\mu_{O^z}^S + n\mu_{e^-}^M + (z-n)F\phi_S - nF(\phi_M - \phi_S) = \mu_{R^{(z-n)}}^S + (z-n)F\phi_S, \quad (1.28)$$

$$\phi_M - \phi_S = \frac{\mu_{O^z}^S + n\mu_{e^-}^M - \mu_{R^{(z-n)}}^S}{nF}. \quad (1.29)$$

Since:

$$\mu_{O^z}^S = \mu_{O^z}^{\ominus S} + RT \ln a_{O^z}, \quad (1.30)$$

$$\mu_{R^{(z-n)}}^S = \mu_{R^{(z-n)}}^{\ominus S} + RT \ln a_{R^{(z-n)}}, \quad (1.31)$$

then:

$$\phi_M - \phi_S = \frac{\Delta\mu^{\ominus}}{nF} + \frac{RT}{nF} \ln \frac{a_{O^z}}{a_{R^{(z-n)}}}, \quad (1.32)$$

where

$$\Delta\mu^{\ominus} = \mu_{O^z}^{\ominus S} + n\mu_{e^-}^{\ominus M} - \mu_{R^{(z-n)}}^{\ominus S}, \quad (1.33)$$

which is a constant at a given temperature and pressure. Eq.(1.32) is the Nernst equation in a form appropriate to a single electrode/solution interface.

If a system follows the Nernst equation or an equation derived from it, the electrode reaction is often said to be electrochemically reversible (or nernstian). A given system may behave reversibly in one experiment and irreversibly in another, depending on experimental conditions.

In practice it is impossible to measure the absolute value of $\phi_M - \phi_S$ at a single electrode/solution interface. The measurement of potential has to be carried out relative to another electrode, usually one of the reference electrodes (see Appendix A.1), therefore:

$$\Delta\phi = (\phi_M - \phi_S)_{\text{working}} - (\phi_M - \phi_S)_{\text{reference}}. \quad (1.34)$$

If a chosen reference electrode is the calomel electrode then:

$$\Delta\phi = \frac{\Delta\mu_{\text{working}}^{\ominus}}{nF} - \frac{\Delta\mu_{\text{calomel}}^{\ominus}}{F} + \frac{RT}{nF} \ln \frac{a_{\text{O}^z}}{a_{\text{R}}^{(z-n)}} - \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (1.35)$$

The Eq.(1.35) is an example of Nernst equation in a form appropriate to a two electrode system. The activities of reactants and products in reference electrodes are kept constant, i.e. $\ln a_{\text{Cl}^-}$ does not influence the measured potential, therefore the Eq.(1.35) is usually presented as:

$$E = E^{\ominus} + \frac{RT}{nF} \ln \frac{a_{\text{O}^z}}{a_{\text{R}}^{(z-n)}}, \quad (1.36)$$

where E is the potential applied to working electrode and $E^{\ominus}$ is the standard potential.

The number of electrons transferred, i.e. the current, is directly proportional to the concentration, not to activity. Therefore a form of the Nernst equation in

which concentrations appear is more often used:

$$E = E^{\ominus'} + \frac{RT}{nF} \ln \frac{[O^z]}{[R^{(z-n)}]}, \quad (1.37)$$

where $E^{\ominus'}$ is the formal potential:

$$E^{\ominus'} = E^{\ominus} + \frac{RT}{nF} \ln \frac{\gamma_{O^z}}{\gamma_{R^{(z-n)}}}. \quad (1.38)$$

$\gamma_{R^{(z-n)}}$ and γ_{O^z} are the activity coefficients [1, 2, 5]:

$$a_{R^{(z-n)}} = \gamma_{R^{(z-n)}} \cdot [R^{(z-n)}], \quad (1.39)$$

$$a_{O^z} = \gamma_{O^z} \cdot [O^z]. \quad (1.40)$$

1.1.10. Three electrode cell

In voltammetric experiments a three-electrode cell (Fig. 1.5) is usually used in order to fully control the potential, E , of the working electrode (WE). In two-electrode cells E measured between the electrodes would gain the additional term:

$$E = (\phi_M - \phi_S)_{\text{working}} - (\phi_M - \phi_S)_{\text{reference}} + IR, \quad (1.41)$$

where IR is the electrical resistance of the bulk solution. Changes in E would result in unknown changes in IR . The $(\phi_M - \phi_S)_{\text{reference}}$ might also be affected by the flowing current and therefore the $(\phi_M - \phi_S)_{\text{working}}$ would no longer be controlled.

The three-electrode cell offers important advantages compared to a two-electrode cell in experiments, when relatively large currents may flow. When a setup is comprised of only a working (WE) and a reference (RE) electrode, the resulting current, which is induced by potential E , flows through both electrodes: WE and

RE. The current can cause chemical changes in RE and alter its potential if it is high enough. When the RE potential changes by an unknown value during the experiment, the potential of the WE changes as well by the same unknown value, therefore it is no longer fully controlled. When a third electrode, a counter (CE), is present in the system, the potential of the working electrode (WE) is still monitored relative to the reference electrode (RE), but the resulting current flows through the WE and CE, instead of RE. Consequently the RE potential remains constant and equal to its open circuit value.

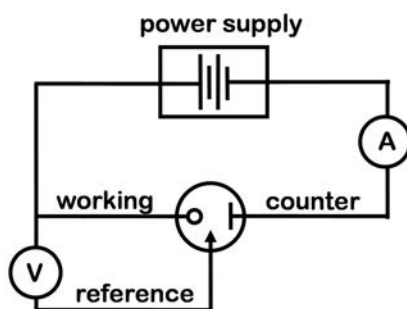


Fig. 1.5: Three electrode cell. A – amperometer, V – voltmeter; the potential is measured between the working electrode (WE) and a reference electrode (RE), the current flows between the working electrode (WE) and a counter (auxiliary) electrode (CE).

The three-electrode cell is also advantageous in experiments involving solutions of low conductivities, i.e. where the electrical resistance of the bulk solution between the working (WE) and a reference (RE) electrode (IR , ohmic drop potential) is high. Changes in E would cause unknown changes in IR . Introduction of the counter electrode (CE) helps to minimise IR and avoid serious complications from the ohmic drop in solution. In order to further reduce the resistance of the solution, a large excess concentration of inert supporting electrolyte is added (usually 0.1 M).

In experiments involving a microelectrode as WE, a two electrode set up (WE+RE) may be sufficient, because the resulting current is of the order of

ca 10^{-9} A and therefore the changes in RE are negligible. Also the IR term for microelectrodes is small enough to neglect.

1.1.11. Rate of electron transfer: Butler-Volmer equation

Transition state theory predicts that for an electrode reaction of soluble species O^z and $R^{(z-1)}$:



the cathodic (for reduction) and anodic (for oxidation) rate constants are:

$$k_c = A_c \exp \frac{-\Delta G_c}{RT}, \quad (1.43)$$

$$k_a = A_a \exp \frac{-\Delta G_a}{RT}, \quad (1.44)$$

where ΔG_c and ΔG_a are the energies of activation and A_c and A_a are pre-exponential frequency factors.

For interfacial electron transfer the activation energy of the process and therefore its rate can be varied by the applied potential ($\Delta G = -F(E - E^{\ominus'})$). For a fixed temperature and pressure the energies of activation for forward and backward reactions are:

$$\Delta G_c = G^\ddagger - (G_{O^z} + G_{e^-}), \quad (1.45)$$

$$\Delta G_a = G^\ddagger - G_{R^{(z-1)}}, \quad (1.46)$$

where $G^\ddagger$ is the Gibbs energy of the transition state. Since the electrochemical potential of a species i in phase α is:

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi_\alpha = \left(\mu_i^{\ominus\alpha} + RT \ln a_i \right) + z_i F \phi_\alpha, \quad (1.47)$$

and $\bar{\mu}_i^\alpha = \left(\frac{\partial \bar{G}^\alpha}{\partial n_i} \right)_{p,T,n_j \neq i}$, then:

$$G_i^\alpha = z_i F \phi_\alpha + \text{constant}. \quad (1.48)$$

The Eqs. (1.45) and (1.46) can be rewritten as:

$$\Delta G_c = G^\ddagger - (zF\phi_S - F\phi_M + \text{constant}_2), \quad (1.49)$$

$$\Delta G_c = G^\ddagger - ((z-1)F\phi_S - F(\phi_M - \phi_S) + \text{constant}_2), \quad (1.50)$$

$$\Delta G_a = G^\ddagger - ((z-1)F\phi_S + \text{constant}_3). \quad (1.51)$$

Comparison of both equations for ΔG_c and ΔG_a shows that in respect of potential difference they differ by $F(\phi_M - \phi_S)$. The Butler-Volmer model assumes that the transition state has a Gibbs energy in between the energy of the reactants and that of the products. This is described by the transfer coefficient, β , where $0 < \beta < 1$:

$$G^\ddagger = (z-1)F\phi_S - \beta F(\phi_M - \phi_S) + \text{constant}_4, \quad (1.52)$$

If β is close to zero, the transition state is product like, whereas if β is near unity, the transition state is reactant like in terms of the potential dependence of its Gibbs energy. A value of 0.5 means that the activated complex is exactly halfway between reagents and products on the reaction coordinate; its structure reflects reagent and product equally. Substituting Eq. (1.52) to (1.50) and (1.51) gives:

$$\Delta G_c = (1 - \beta)F(\phi_M - \phi_S) + \text{constant}_5, \quad (1.53)$$

$$\Delta G_a = -\beta F(\phi_M - \phi_S) + \text{constant}_6. \quad (1.54)$$

Substituting these equations into the Arrhenius equations (Eqs. (1.43) and (1.44)) gives the electrochemical rate constants:

$$k_c = A_c \exp \frac{-\text{constant}_5}{RT} \exp \frac{-(1-\beta)F(\phi_M - \phi_s)}{RT}, \quad (1.55)$$

$$k_a = A_a \exp \frac{-\text{constant}_6}{RT} \exp \frac{+\beta F(\phi_M - \phi_s)}{RT}. \quad (1.56)$$

The exponential terms containing the constants are independent of potential and may therefore be moved in the pre-exponential term, therefore for a two electrode system:

$$k_c = k_{c,0} \exp \frac{-(1-\beta)F(E - E^{\ominus'})}{RT}, \quad (1.57)$$

$$k_a = k_{a,0} \exp \frac{+\beta F(E - E^{\ominus'})}{RT}. \quad (1.58)$$

When the reaction:



is at equilibrium, the fluxes of O^z and $\text{R}^{(z-1)}$ are equal:

$$k_c[\text{O}]_0 = k_a[\text{R}]_0, \quad (1.60)$$

where $[\text{O}]_0$ and $[\text{R}]_0$ are the concentrations of O^z and $\text{R}^{(z-1)}$ at the electrode.

When the electrode potential E equals $E^{\ominus'}$, then $k_{c,0} = k_{a,0} = k_0$, where k_0 is the standard electrochemical rate constant. $k_{c,0}$ and $k_{a,0}$ do not depend on potential therefore they are equal even when $E \neq E^{\ominus'}$. Also assuming $\alpha + \beta = 1$, the equations for cathodic and anodic electrochemical rate constants can be written as:

$$k_c = k_0 \exp \frac{-\alpha F(E - E^{\ominus'})}{RT}, \quad (1.61)$$

$$k_a = k_0 \exp \frac{(1-\alpha)F(E - E^{\ominus'})}{RT}. \quad (1.62)$$

The net flux is the difference between the rate of oxidation and reduction reactions at the electrode surface:

$$J_{\text{net}} = k_c[\text{O}]_0 - k_a[\text{R}]_0, \quad (1.63)$$

therefore the net current is:

$$I_{\text{net}} = I_a + I_c = FA(k_c[\text{O}]_0 - k_a[\text{R}]_0), \quad (1.64)$$

where A is the electrode area, which is fully described as:

$$I_{\text{net}} = FAk_0 \left[\exp \frac{-\alpha F(E - E^{\ominus'})}{RT} [\text{O}]_0 - \exp \frac{(1 - \alpha)F(E - E^{\ominus'})}{RT} [\text{R}]_0 \right]. \quad (1.65)$$

The Eq. (1.65) is the final form of Butler-Volmer macroscopic model, which provides a satisfactory description of many electrochemical systems under usual experimental conditions [1–3].

1.1.12. Irreversible reactions: Tafel law

For a simple electrode process:



the net current is:

$$I_{\text{net}} = FAk_0 \left[\exp \frac{-\alpha F(E - E^{\ominus'})}{RT} [\text{O}]_0 - \exp \frac{(1 - \alpha)F(E - E^{\ominus'})}{RT} [\text{R}]_0 \right], \quad (1.67)$$

where $[\text{O}]_0$ and $[\text{R}]_0$ are the concentrations of O^z and $\text{R}^{(z-n)}$ at the electrode.

When $E \gg E^{\ominus'}$ or $E \ll E^{\ominus'}$ it is possible to neglect one term or another, therefore

the current is either:

$$I_c = k_0 n F A \left[\exp \frac{-\alpha F(E - E^{\ominus'})}{RT} \right] [O]_0 \quad (1.68)$$

or:

$$I_a = k_0 n F A \left[\exp \frac{(1 - \alpha) F(E - E^{\ominus'})}{RT} \right] [R]_0. \quad (1.69)$$

If $[O]_0$ and $[R]_0$ are not substantially changed from their constant bulk values, then:

$$\ln |I_c| = \frac{-\alpha F E}{RT} + \text{constant}_7, \quad (1.70)$$

$$\ln |I_a| = \frac{(1 - \alpha) F E}{RT} + \text{constant}_8, \quad (1.71)$$

where I_c and I_a are the reduction and oxidation currents respectively. Plots of $\ln |I_c|$ vs. E or $\ln |I_a|$ vs. E are called Tafel plots and provide the magnitude of the transfer coefficient α [1–3].

1.1.13. Marcus-Hush-Chidsey theory

For a heterogeneous electron transfer reaction between an electrode and an electroactive species O in solution:



Marcus theory assumes that the Gibbs energy profiles of the reactant, O, and the product, R, are parabolas in accordance to Hooke's law, which says that the potential energy of a spring is $\frac{1}{2} k x^2$, where k is the force constant and x is the distance of the spring's end from its equilibrium position. If a mass is attached to the end of such a spring, the system becomes a harmonic oscillator.

In Marcus theory the nuclei of the reactant and the product behave like a harmonic oscillator therefore the Gibbs energies depend on the square root of the distance. Changes in nuclear coordinates (the relative positions of the atoms) occur from vibrational and rotational motion of O and R and from fluctuations in the position and orientation of the solvent molecules.

Fig. 1.6 shows a plot of the Gibbs energy of species O and R as a function of reaction coordinate. The point $\ddagger$ is the transition state where O and R have the same configuration. It corresponds to the intersection of the parabolas, where the Franck-Condon and energy conservation principles are fulfilled. Electron transfer occurs only at $\ddagger$. ΔG is the Gibbs energy change between the reactants and products, $\Delta G^\ddagger$ is the activation energy, λ is the reorganization energy. Assuming that the bottom of the O parabola is at (x_O, G_O) and its equation is $G(x) = G_O + \frac{1}{2}k(x - x_O)^2$ and the bottom of the R parabola is at (x_R, G_R) and its equation is $G(x) = G_R + \frac{1}{2}k(x - x_R)^2$, the equations for the Gibbs energy of the transition state, $G^\ddagger$, are:

$$G^\ddagger = G_O + \frac{1}{2}k(x^\ddagger - x_O)^2, \quad (1.73)$$

$$G^\ddagger = G_R + \frac{1}{2}k(x^\ddagger - x_R)^2. \quad (1.74)$$

Solving these equations for $x^\ddagger$ gives:

$$x^\ddagger = \frac{1}{2}(x_O + x_R) - \frac{G_R - G_O}{k(x_O - x_R)}. \quad (1.75)$$

Gibbs energy of activation, $\Delta G^\ddagger$, is:

$$\Delta G^\ddagger = G^\ddagger - G_O, \quad (1.76)$$

therefore substituting Eq. (1.75) gives:

$$\Delta G^\ddagger = \frac{\frac{1}{4}k^2(x_O - x_R)^4 + (G_R - G_O)^2 + k(G_R - G_O)(x_O - x_R)^2}{2k(x_O - x_R)^2}. \quad (1.77)$$

Assuming $\lambda = \frac{1}{2}k(x_O - x_R)^2$ and $\Delta G = G_R - G_O$ the Gibbs energy of activation is:

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G)^2}{4\lambda} = \frac{\lambda}{4} \left(1 + \frac{\Delta G}{\lambda} \right)^2. \quad (1.78)$$

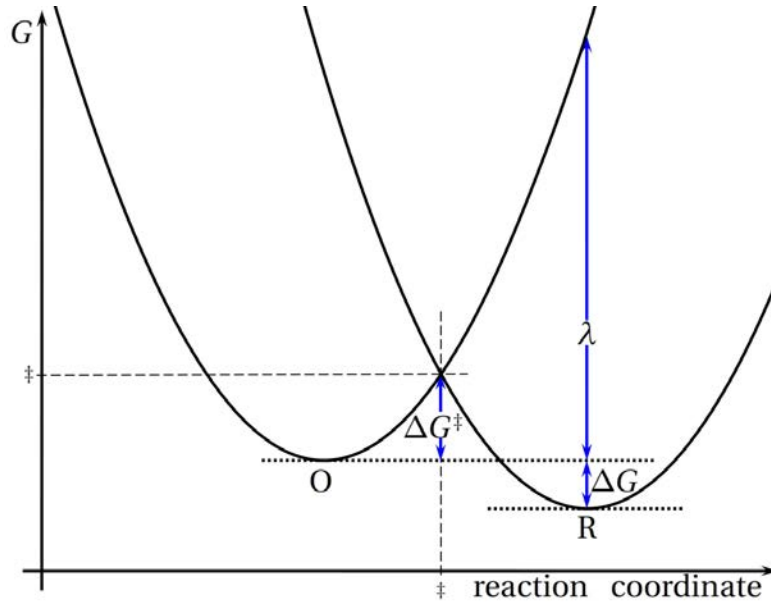


Fig. 1.6: Representation of a reaction coordinate.

In Marcus theory the reorganization energy, λ , represents the energy necessary to transform the nuclear configurations in the reactant and its solvation shell to the product state in the absence of electron transfer. It is related to the curvature of the Gibbs energy curves. Reorganization energy can be separated into inner λ_i and outer λ_o parts. λ_i represents changes in bond lengths and bond angles (intramolecular vibrations) and λ_o represents changes in solvation (fluctuation of the solvent dipoles around the species of interest):

$$\lambda = \lambda_i + \lambda_o. \quad (1.79)$$

The inner component can be calculated by summing over the normal vibrational modes of the reactant:

$$\lambda_i = \sum_j \frac{1}{2} k_j (x_{O,j} - x_{R,j})^2 \quad (1.80)$$

where k_j are the force constants and x are the displacements in the normal mode coordinates. The solvent reorganization energy is calculated by assuming that the solvent is a dielectric continuum, and the reactant is a sphere of radius a_O . For an interface electron transfer:

$$\lambda_o = \frac{e_0^2}{8\pi\epsilon_0} \left(\frac{1}{a_O} - \frac{1}{2d} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right), \quad (1.81)$$

where e_0 is the elementary charge, ϵ_0 is the permittivity of free space, a_O is the radius of the reactant, ϵ_{op} is the optical permittivity, ϵ_s is the static permittivity and d is the distance from the reactant to the metal surface. Typical values of λ are in the range of 0.5 eV to 1 eV. When both forms of the adsorbed electroactive molecule have similar structures the main contribution to the activation barrier is reorganization of the solvent.

The calculation of α from the rate constant, k :

$$k = A \exp \frac{-\Delta G^\ddagger}{RT} = A \exp \frac{-(\Delta G + \lambda)^2}{4\lambda RT} = A \exp \frac{-(-F(E - E^{\ominus'}) + \lambda)^2}{4\lambda RT}, \quad (1.82)$$

$$\alpha = \frac{RT}{F} \frac{\partial \ln k}{\partial E} = \frac{1}{2} \left(1 + \frac{-F(E - E^{\ominus'})}{\lambda} \right) = \frac{1}{2} \left(1 + \frac{\Delta G}{\lambda} \right), \quad (1.83)$$

links Marcus theory and Butler-Volmer kinetics. The transfer coefficient, α , is a function of the applied potential, not a constant, but at small overpotentials it is predicted to be ca 0.5. When:

- $\lambda \gg \Delta G$ – the kinetics is slow, $\alpha \approx 0.5$ (this is the case for many reactions),
- λ is small (fast reactions):

- $\Delta G \approx 0$ ($E \sim E^{\ominus'}$), $\alpha \approx 0.5$,
- $\lambda \approx \Delta G$, (the reaction is thermodynamically uphill) $\alpha \rightarrow 1$,
- $\lambda \approx -\Delta G$, (the reaction is driven hard by the electrode potential) $\alpha \rightarrow 0$.

It shows that Tafel plots can be curved as a consequence of the parabolic shape of the Gibbs energy curves.

The Marcus model [10, 11] was developed for homogeneous outer-sphere electron transfers processes (i.e. the reactant and product do not interact strongly with electrode surface; electron transfer takes place at a distance of at least a solvent layer) and later extended by Hush to inner-sphere reactions. Chidsey applied Marcus-Hush theory to interfacial electron transfers by assuming a metal electrode as an electron donor/acceptor with a continuum of energy levels. According to Marcus-Hush-Chidsey theory k_0 for a redox species confined at the electrode surface is:

$$k_0 = \frac{4\pi^2}{h} \rho H_{\text{DA}}^2 S(\Lambda, 0) \exp(-\beta r_0) \quad (1.84)$$

where h is Planck's constant, ρ (eV^{-1}) is the density of states in the electrode, r_0 ($\text{\AA}$) is the distance separating the redox centre from the electrode surface, H_{DA} (eV) is the electronic coupling between donor and acceptor at this distance and β ($\text{\AA}^{-1}$) is the electronic coupling attenuation coefficient. The facility of the electron transfer is related to the electrode material (density of electronic states, ρ) and the structural changes in the solution (reorganization energy, λ) [1–3, 12–16]. More information on Marcus-Hush-Chidsey model can be found in the theory section 5.2.

1.1.14. Types of reaction mechanisms

There are reactions where a charge transfer at the electrode is preceded or followed by homogeneous reactions in solution. The letter E is used to denote a heterogeneous electron transfer step and the letter C to indicate a homogeneous step.

- **EC reaction:** When an electron transfer yields a product that is unstable (like a radical) a homogeneous chemical reaction will follow producing an electrochemically inactive product. If the chemical step is irreversible the label is EC_{irr}. When the chemical step is second order (e.g. dimerisation) the mechanism is denoted as EC₂. The EC scheme is:



where k_f and k_b are forward and backward homogeneous reactions rate constants.

- **ECE reaction:** The chemical step following an electrode reaction yields a product which is itself electrochemically active in the experimental potential range:



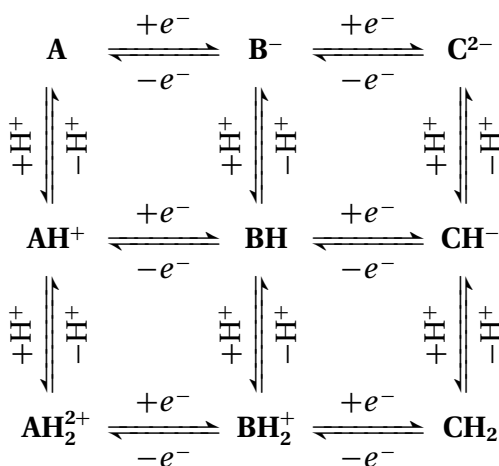
• **CE reaction:** In a CE process the reagent undergoes a homogeneous chemical step prior to electron transfer (e.g. the reduction of a weak acid).



• **EC' reaction:** This is a catalytic process. The homogeneous reaction regenerates $\text{O}_{(\text{aq})}$ from $\text{R}_{(\text{aq})}$.



• **Two electron transfers and two protonation steps reaction:** Reduction or oxidation of many organic compounds involves the addition or removal of hydrogen which proceeds via electron plus proton transfer. Such mechanisms are commonly summarized in the scheme of squares (Tab. 1.1). A typical example is the quinone/hydroquinone system [1–3].



Tab. 1.1: Scheme of squares for the 2H^{+} , $2e^{-}$ redox behavior.

1.2. Experimental methods

1.2.1. Cyclic voltammetry

Cyclic voltammetry (CV) is a relatively simple, inexpensive and versatile electrochemical technique; it is therefore widely used. It is very useful especially for initial studies of new systems. Usually the potential of the working electrode is scanned back and forth linearly with time between two extreme values using a triangular potential waveform (Fig. 1.7a). The rate at which the potential varies with time is scan rate, $\nu = \frac{dE}{dt}$. The plot of resulting current vs. potential is called a voltammogram (Fig. 1.7b).

When the potential of the working electrode is more positive than that of a redox couple, the corresponding species may be oxidized and produce an anodic current. When the working electrode potential becomes more negative than the potential of a redox couple, reduction may occur and produce a cathodic current. By IUPAC convention, anodic currents are positive and cathodic currents negative.

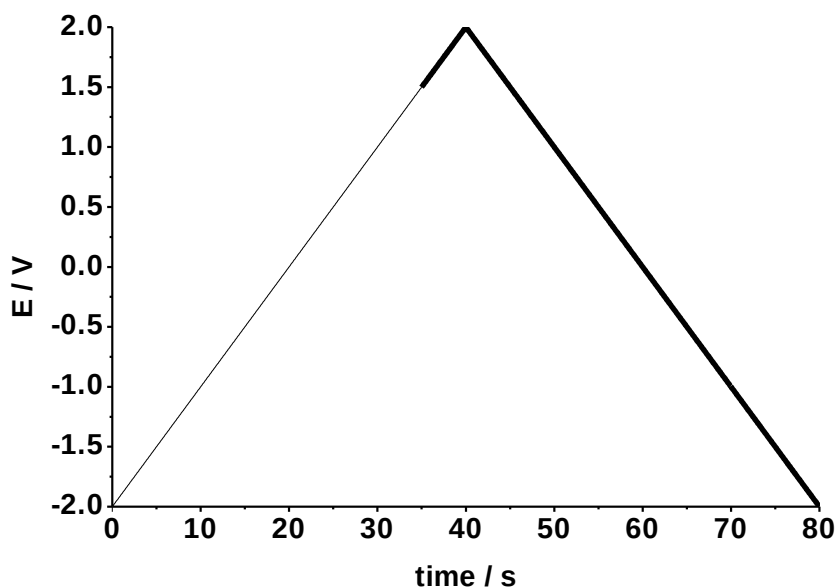
If the reaction involving n electrons:



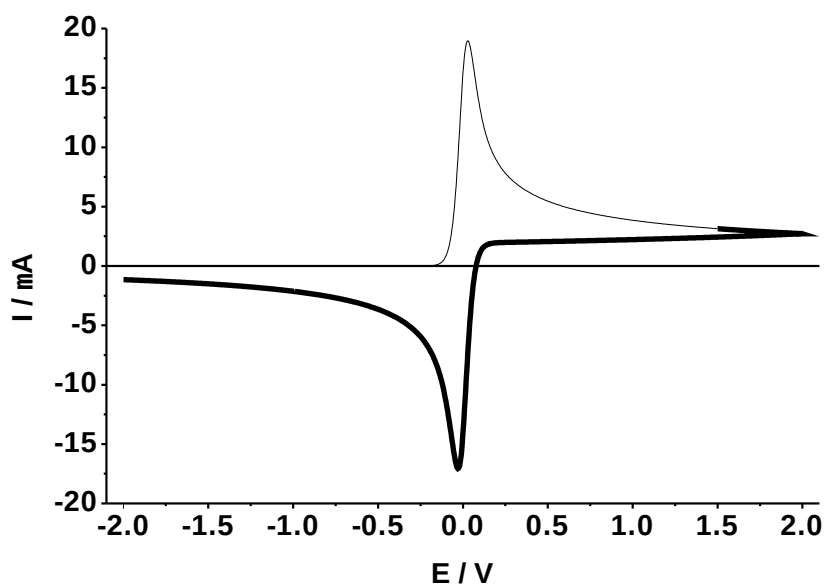
is fast (reversible), i.e. the rate of electron transfer is large compared to the rate of mass transport, the reaction is at equilibrium during the potential sweep, therefore surface concentrations of O and R obey the Nernst equation:

$$E = E^{\ominus'} - \frac{RT}{nF} \ln \frac{[R]_0}{[O]_0}, \quad (1.95)$$

where E is the applied potential and $E^{\ominus'}$ is the formal potential of the couple; $[O]_0$ and $[R]_0$ represent surface concentrations at the electrode/solution interface,



(a) time vs. potential



(b) current vs. potential

Fig. 1.7: (a) Start potential: -2.0 V, switch/vertex potential: 2.0 V, scan rate $\nu = 0.1$ V/s. (b) Simulation of a one electron oxidation process for a homogeneous reaction according to Butler-Volmer theory.

$\alpha = 0.5$, $D_O = D_R = 1 \cdot 10^{-5}$ cm²/s, $E^{\ominus'} = 0$ V, $\nu = 0.1$ V/s, $A = 0.0707$ cm², $[O]_{\text{bulk}} = 0.001$ M, $k_0 = 1$ cm²/s.

not bulk solution concentrations. The Nernst equation applies to reversible electron transfer reactions therefore it may or may not be obeyed depending on the system or on the experimental conditions (scan rate, ν).

An example of a simulated ideal voltammogram is shown in Fig.1.7b. The scan starts at a more negative potential than $E^{\ominus'}$ up to a positive switching

value at which the scan is reversed back to the starting potential. The peak is first observed at E_{pa} (with value I_{pa}) indicating that oxidation is taking place and then it drops due to depletion of the reacting species from the diffusion layer. The current becomes diffusion controlled and the diffusion layer extends. During the return scan the processes are reversed (reduction occurs) and a peak current is observed at E_{pc} (corresponding value I_{pc}). Providing that the charge transfer reaction is reversible, that there is no surface interaction between the electrode and the reagents, and that the redox products are stable (at least in the time frame of the experiment):

- the ratio of the oxidation and the reduction current is $\frac{I_{pa}}{I_{pc}} = 1$,
- the corresponding peak potentials E_{pa} and E_{pc} are independent of scan rate and concentration,
- the formal potential for a reversible couple, $E^{\ominus'}$, is centered between E_{pa} and E_{pc} (when $D_O = D_R$):

$$E^{\ominus'} = \frac{E_{pa} + E_{pc}}{2}, \quad (1.96)$$

- the separation between peaks is:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{59}{n} \text{mV} \quad (\text{at } 25^\circ\text{C}) \quad (1.97)$$

(for n electron transfer reaction) at all scan rates. Larger values of ΔE_p , which increase with increasing scan rate, are characteristic of slow electron transfer kinetics.

When the electron transfer reaction is slow compared to mass transport, the Butler-Volmer equation applies. Irreversible kinetics results in a large peak-to-peak

separation in cyclic voltammograms (Fig. 1.8) [1–3].

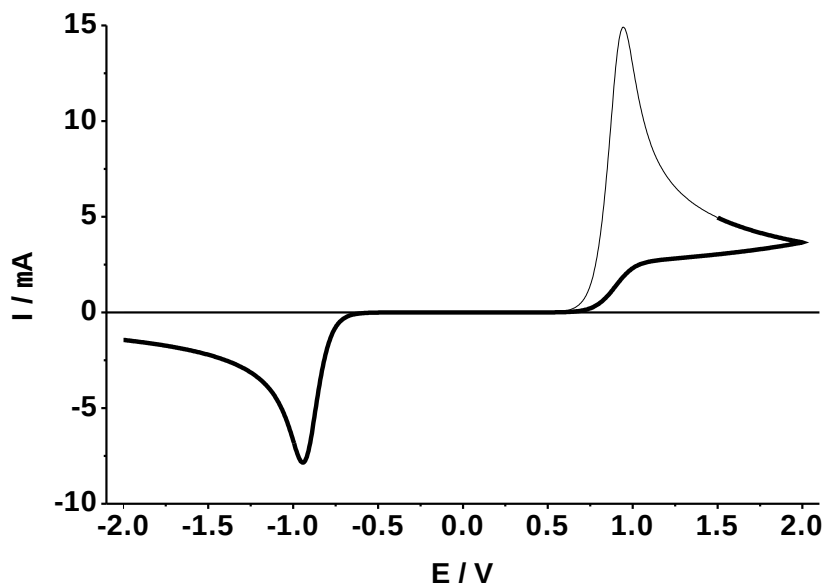


Fig. 1.8: Simulation of a one electron oxidation process for a homogeneous reaction according to Butler-Volmer theory. $\alpha = \beta = 0.5$, $D_O = D_R = 1 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $E^{\ominus'} = 0 \text{ V}$, $\nu = 0.1 \text{ V/s}$, $A = 0.0707 \text{ cm}^2$, $[O]_{\text{bulk}} = 0.001 \text{ M}$, $k_0 = 1 \cdot 10^{-10} \text{ cm}^2/\text{s}$.

- **Randles-Ševčík equation:** Potential scan rate can be used to distinguish between a reversible (diffusion-controlled) and irreversible (charge-transfer controlled) kinetics of an electrode process. For the electron transfer to occur, the molecules in solution have to approach the electrode. In a cyclic voltammetry experiment mass transport occurs only by diffusion due to concentration gradients created around the electrode surface. The magnitude of the observed peak current for the forward sweep in a reversible system is given by the Randles-Ševčík equation:

$$I_p = 0.446 n F A [O_{(\text{aq})}]_{\text{bulk}} \left(\frac{n F D_{O(\text{aq})} \nu}{R T} \right)^{1/2}, \quad (1.98)$$

$$I_p = 2.69 \cdot 10^5 n^{3/2} A D_{O(\text{aq})}^{1/2} \nu^{1/2} [O_{(\text{aq})}]_{\text{bulk}}, \quad (1.99)$$

where n is the number of electrons exchanged during the redox process, A (cm^2) the active area of the working electrode, $D_{O(\text{aq})}$ (cm^2/s) the diffusion coefficient, $[O_{(\text{aq})}]_{\text{bulk}}$ (mol/cm^3) the bulk concentration of the electroactive species and ν is

the scan rate (V/s). For irreversible processes the individual peaks are reduced in size and widely separated (Fig. 1.8). Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E^{\ominus'} - \frac{RT}{\alpha n_a F} \left[0.780 + \ln \frac{D_{O(aq)}^{1/2}}{k_0} + \ln \left(\frac{\alpha n_a F \nu}{RT} \right)^{1/2} \right] \quad (1.100)$$

where α is the transfer coefficient and n_a is the number of electrons involved in the charge-transfer step. Assuming $n_a = 1$:

$$E_p = E^{\ominus'} - \frac{RT}{\alpha F} \left[0.780 + \ln \frac{D_{O(aq)}^{1/2}}{k_0} \right] - \frac{RT}{\alpha F} \ln \left(\frac{\alpha F \nu}{RT} \right)^{1/2} = K - \frac{RT}{2\alpha F} \ln \nu, \quad (1.101)$$

where K is a constant. The peak potential, E_p , and the half-peak potential, $E_{1/2}$, (at 25°C) will differ by $\frac{47.7}{\alpha n_a}$ mV. The voltammogram becomes more drawn-out as α decreases. The peak current:

$$I_p = 0.496 n F A [O_{(aq)}]_{\text{bulk}} \left(\frac{\alpha n_a F D_{O(aq)} \nu}{RT} \right)^{1/2}, \quad (1.102)$$

$$I_p = 2.99 \cdot 10^5 n (n_a \alpha)^{1/2} A [O_{(aq)}]_{\text{bulk}} D_{O(aq)}^{1/2} \nu^{1/2} \quad (1.103)$$

is still proportional to the bulk concentration, but will be lower (depending on the value of α). Assuming $\alpha = 0.5$, the ratio of the reversible-to-irreversible current peaks for a one electron process is 1.27 (i.e. the peak current for the irreversible process is about 80% of the peak for a reversible one). For quasi-reversible systems the current is controlled by both the charge transfer and mass transport. The shape of the cyclic voltammogram is a function of the ratio:

$$\Lambda = \frac{k_0}{\left(\frac{n F D_{O(aq)} \nu}{RT} \right)^{1/2}}. \quad (1.104)$$

As the ratio increases, the process approaches the reversible case. For small values of it, the system exhibits an irreversible behavior. For reversible systems: $\Lambda \geq 15$

($k_0 \geq 0.3\nu^{1/2}$ cm/s), for quasireversible reactions: $15 > \Lambda > 10^{-2(1+\alpha)}$ ($0.3\nu^{1/2} > k_0 > 2 \cdot 10^{-5}\nu^{1/2}$ cm/s) and for irreversible processes: $\Lambda \leq 10^{-2(1+\alpha)}$ ($k_0 \leq 2 \cdot 10^{-5}\nu^{1/2}$ cm/s).

• **Adsorbed species:** The peak current, I_p , and the current at each point of a cyclic voltammogram of adsorbed species $O_{(ads)}$ undergoing a reaction:



is proportional to scan rate, ν :

$$I_p = \frac{n^2 F^2}{4RT} \nu A \Gamma, \quad (1.106)$$

where Γ is the surface coverage (mol/cm²), in contrast to the solution phase voltammetry (diffusing species) where I_p is proportional to square root of scan rate, $\nu^{1/2}$. The area under oxidation or reduction peak minus residual (background) current corresponds to the charge, Q , necessary to fully oxidize or reduce the layer:

$$Q = nFA\Gamma. \quad (1.107)$$

If both species do not desorb during the experiment the surface coverage, Γ , is constant and equal to:

$$\Gamma = \Gamma_O + \Gamma_R, \quad (1.108)$$

where $\Gamma_O = b_O[O]$ and $\Gamma_R = b_R[R]$. b_O and b_R are the adsorption coefficients. The peak potential is given by:

$$E_{p,ads} = E_{ads}^{\ominus'} - \frac{RT}{nF} \ln \frac{b_O}{b_R}, \quad (1.109)$$

where $E_{ads}^{\ominus'}$ is the formal potential of the adsorbed couple which is typically

different from the formal potential of solution species. The pair of peaks for adsorbed species can appear at potentials either higher ($b_O > b_R$) or lower ($b_O < b_R$) than $E^{\ominus'}$ which corresponds to solution phase species. When the O is more strongly adsorbed than R, the peak related to adsorbed species is situated after the solution phase peak. When R is adsorbed more strongly than O, the adsorbed peak appears before solution phase peak.

For an ideal reversible reaction: $E_{pa,ads} = E_{pc,ads}$ and the total width at half-height of either the cathodic or anodic wave is:

$$3.53 \frac{RT}{nF} = \frac{90.6}{n} \text{mV} \quad (\text{at } 25^\circ\text{C}). \quad (1.110)$$

A common method for differentiating between surface bound and diffusional systems is the analysis of the logarithm of peak current, $\log|I_p|$ vs. logarithm of scan rate, $\log \nu$. When the plot is linear and its gradient is 0.5 then the system is purely diffusional. When the gradient is 1 there are only adsorbed species. Gradients between 0.5 and 1 represent mixed systems, where the value indicates the level of contribution from the two environments [1, 2, 17].

• **The influence of pH on cyclic voltammetry:** The position of peaks: E_{pa} , E_{pc} and $E_{1/2} = \frac{E_{pa} + E_{pc}}{2}$ for some redox processes in aqueous solutions can shift with pH. For a fully electrochemically reversible process:



involving the transfer of n electrons and m protons, the Nernst equation is:

$$E = E^{\ominus'} - \frac{RT}{nF} \ln \frac{[R]_0}{[O]_0 [H^+]_0^m} = E^{\ominus'} - \frac{RT}{nF} \ln \frac{[R]_0}{[O]_0} - 2.303 \frac{mRT}{nF} \text{pH}. \quad (1.112)$$

It shows that the peak potentials (E_{pa} , E_{pc} , $E_{1/2}$) vary by $-2.303 \frac{mRT}{nF}$ per pH unit [2].

For quinones which undergo a $2e^-$, $2H^+$ reduction (full reaction scheme: Tab. 4.1, page 110):



a plot of $E_{1/2}$ vs. pH should give a slope of -59 mV/pH up to $\text{pH} = pK_{a1}$ for AQH_2 (at 25°C). At pHs higher than pK_{a1} up to pK_{a2} AQH^- form exists so the process becomes $2e^-$, $1H^+$. It gives the slope of -30 mV/pH . At pHs higher than pK_{a2} quinone is fully deprotonated, AQ^{2-} , therefore the reaction is $2e^-$, $0H^+$ what means that peak potentials do not change with pH [18].

For HNO_2 the measurement of the peak potential, E_p , vs. pH shows that oxidation of nitrite is essentially independent of pH for solutions of pHs higher than 3.3 (the pK_a for nitrous acid, HNO_2 , is between 3.2 and 3.4 [19–21]).

1.2.2. Potential step chronoamperometry

In potential step chronoamperometry the potential of the working electrode is stepped from the value E_1 , where no electrolysis takes place to E_2 , where partial or complete conversion of substrates into products occurs:



The magnitude of the current is controlled by the rate of diffusion of $O_{(aq)}$ to the electrode surface. The concentration gradient shortly after the step is very

large and consequently so is the current. Gradually, the diffusion layer thickness increases and the current decreases ultimately to zero. The current response for processes where planar diffusion dominates (macroelectrodes) as a function of time is described by the Cottrell equation:

$$|I| = \frac{nFAD_{\text{O(aq)}}^{1/2}[\text{O(aq)}]_{\text{bulk}}}{\pi^{1/2}t^{1/2}}, \quad (1.116)$$

where $D_{\text{O(aq)}}$ is the diffusion coefficient of O(aq) and $[\text{O(aq)}]_{\text{bulk}}$ is the bulk concentration of O(aq) . When $|I|$ is proportional to $t^{-1/2}$ the process is diffusion controlled over the rate of electrolysis and the diffusion coefficient can be calculated. The Cottrell equation is valid when only the substrate is present in solution, its concentration far from the electrode approaches the bulk value and the concentration of substrate is reduced to zero immediately after the potential step. In potential step chronoamperometry E_2 is usually chosen to be more negative (for a reduction) than the cyclic voltammetry peak and therefore the chronoamperometric experiment does not provide any information about the electrode kinetics, because the mass transport is rate limiting [1, 6].

1.2.3. Scanning electron microscope

Resolution of optical microscopes is limited by the wavelength of visible light. A scanning electron microscope (SEM) uses electrons instead of light therefore it exceeds the 1000-fold magnification achieved by optical microscopes. SEM can also provide information about the topography, composition and electrical conductivity of the sample.

• **Limitations of light optical microscopes:** The amount of information a microscope can provide depends on its resolution. The maximum resolution depends on the wavelength of the radiation, λ , the index of refraction of the surrounding medium, μ , and the aperture semi angle, α , formed by the optical axis and the edge beam. The resolution limit, r , is determined by:

$$r = \frac{0.61 \lambda}{\mu \sin \alpha}, \quad (1.117)$$

where r is the distance between two diffraction maxima. When normal light-optical microscopes are used, the maximum resolution using wavelengths of visible light (400 – 700 nm) is limited to about 200 nm, which determines magnification to 1000x.

• **Employing electron beams:** Electron microscopes use a beam of high-energy electrons. The wavelength of an electron beam is considerably smaller than the wavelength of visible light. It can be varied depending on the voltage set to accelerate the electrons towards the sample. The velocity of a single electron can almost reach the velocity of light, c . An accelerating voltage of 20 kV results in wavelength of $\lambda = 8.6 \cdot 10^{-3}$ nm. Electrons in scanning electron microscopes are accelerated at voltages in the range of 2–40 kV. The use of electrons therefore allows for much greater magnification in comparison to an optical microscope.

• **Design and function:** The SEM microscope consists of an electron gun (cathode), Wehnelt cylinder (anode used for focusing and control of the electron beam), lens system and the specimen chamber.

A beam of electrons is generated by the electron gun, located at the top of the column. This beam is attracted through the anode, condensed by a condenser

lens, and focused on the sample by the objective lens. The beam hits the sample and generates various signals which are collected by relevant detectors, converted to a voltage, and amplified. The image consists of thousands of spots of varying intensity that correspond to the topography of the sample.

- **Interactions between electrons and specimen:** The primary electrons from the beam interact in various ways with the surface layers of the sample producing secondary electrons (SE), back scattered electrons (BSE), X-rays, Auger electrons and cathodoluminescence. While all these signals are always present, not all of them are detected and used for information. The signals most commonly exploited are secondary electrons, backscattered electrons and X-rays.

- **Detectors:** Detectors transform the signals produced into electrical signals. Each signal (secondary electrons, back scattered electrons, X-rays) requires a special detector.

Secondary electron (SE) imaging is the standard detection mode of most SEMs. Secondary electrons are generated by inelastic collisions between the electrons from the beam and electrons from the sample, which in effect are emitted. Their energy is ≤ 50 eV. Back scattered electrons (BSE) are the electrons from the electron beam that are elastically scattered back off the sample surface. The electrons are more energetic than the SE, ranging from 50 eV to the energy of the primary electron. BSE also provide information regarding the distribution of different elements in a sample due to a direct relation between the backscattering coefficient and the mean atomic number of the area of interaction. The third possible detector is energy dispersive X-ray spectroscopy (EDS) which may be used to detect characteristic X-rays from the sample. The X-rays are emitted when

the electron beam removes an inner shell electron from the sample, causing a higher electron to migrate to the position of the lost electron. The migration emits excess energy in the form of X-ray.

- **The vacuum:** The electron beam in an air filled environment would interact with any ions in its path and therefore lose its energy. This would lead to a high instability of the beam and therefore lower the contrast and obscure detail in the image. In order to avoid complications from ionization of the beam a high vacuum is required in an electron microscope.

- **The limitations of SEM:** A major limitation of SEM is that there must be a vacuum in the chamber. It has no impact on dry samples but e.g. modified electrodes must be removed from the solution and dried first, therefore SEM is an ex situ technique. The images in this thesis (Fig.2.10a and Fig.2.10b) of modified electrodes which are dried in air are still highly informative.

Another limitation of SEM is that non-conductive or partially conductive samples must be coated with a fine layer of conductive material, usually gold or platinum. When non-conductive materials are imaged the electrostatic charging occurs due to an accumulation of electrons from the beam [1, 22, 23].

1.3. Modified electrodes

Modified electrodes (ME) are of great interest due to their possible practical applications. If a given process exhibits slow kinetics, a modification can significantly change the electron transfer rates, and therefore increase observed currents. The modified electroactive layer can act as a mediator (or sometimes as an inhibitor) in electron transfer between the solution species and the conductive substrate

electrode. A substrate is typically a material that is also used in an unmodified form as an electrode. It can be a metal, carbon or semiconductor. MEs are frequently used to decrease oxidation potentials, to improve rate of electron transfer, to inhibit a reaction or to obtain selectivity toward a particular process (e.g. glucose detection in blood). For all mediated electron transfer reactions, the driving force is dependent on the formal potential, $E^{\oplus'}$, values of the substrate and the electrocatalyst.

Some of the most common ways to modify electrodes are: irreversible physical or chemical (covalent bonding of specific species) adsorption, coating the electrode with films of polymers or other materials (such as carbon nanotubes CNTs) or in the form of self assembled monolayers. Other possible modifications include inorganic materials such as metal oxides, clays and zeolites.

Carbon is one of the typical electrode materials along with metals and semiconductors. It is a conductor, i.e. it provides a relatively large density of charge carriers at the electrode/solution interface, therefore it shows metal-like behaviour. Carbon is an ideal electrode substrate. The main advantages of carbon materials are low cost, relatively wide potential window and inert electrochemistry. Various types of carbon have been used as electrodes in analytical and industrial electrochemistry. These include glassy carbon (GC), edge plane pyrolytic graphite (EPPG), basal plane pyrolytic graphite (BPPG), carbon powders and pastes (graphite particles incorporated in an inert matrix).

Glassy carbon (GC) (Fig. 1.9) is a material composed of thin convoluted microfibrils of the graphite structure. This structure makes GC much harder than graphite and impermeable to gases and liquids.

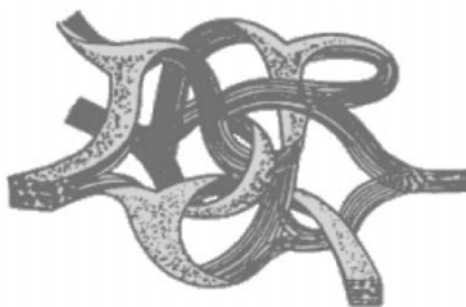


Fig. 1.9: Structure of glassy carbon [2, 3, 24].

Edge plane pyrolytic graphite (EPPG) electrodes are fabricated by cutting highly ordered pyrolytic graphite (HOPG) (Fig. 1.10) perpendicularly to graphite layers. Basal plane pyrolytic graphite (BPPG) electrodes are produced by cutting HOPG the way that graphite layers are parallel to the electrode surface. Kinetics at edge plane sites are at least three times faster than at basal plane sites.

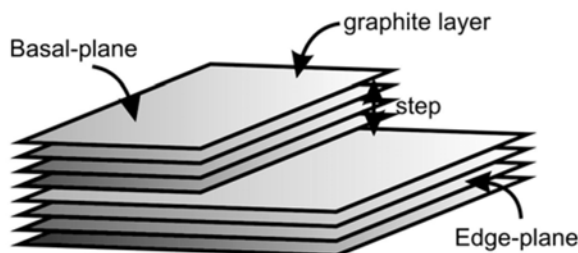


Fig. 1.10: Schematic structure of highly ordered pyrolytic graphite (HOPG) [24].

Carbon materials used in electrochemistry share some electronic properties of metals, but their surface chemistry is completely different due to the presence of oxygen-containing functional groups (Fig. 1.11), which occur especially on edge plane sites. These groups can be used to modify the surface of carbon in order to change its properties.

Many organic compounds (especially those containing aromatic rings, double bonds and long hydrocarbon chains), e.g. CoPC (Fig. 1.12) adsorb strongly on carbon from solution allowing a simple and quick modification by e.g. casting (Fig. 1.13) or dipping procedures.

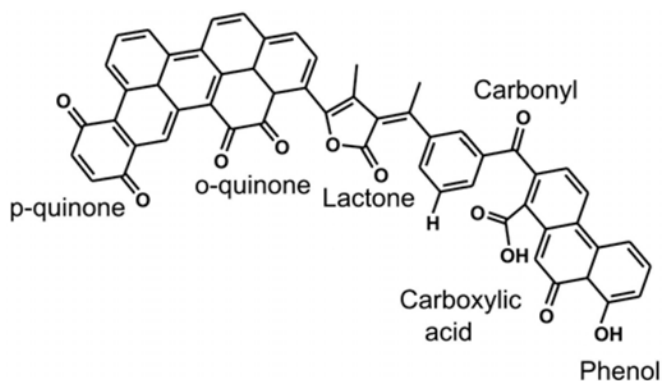


Fig. 1.11: Oxygen containing functional groups at a carbon surface [24].

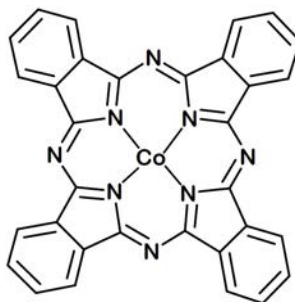


Fig. 1.12: Structure of cobalt (II) phthalocyanine ($\text{Co}^{2+}\text{PC}^{2-}$) [25].

The defect free basal plane is nonpolar and hydrophobic whereas the edge plane carbon atoms terminated by oxygen groups make the surface polar and hydrophilic. It has a higher affinity for water soluble ionic compounds such as AQDS and AQMS (Fig. 1.14). Adsorption at EPPG can occur due to the dipole-dipole and ion-dipole interactions between the polar surface and the polar and charged adsorbate [26].

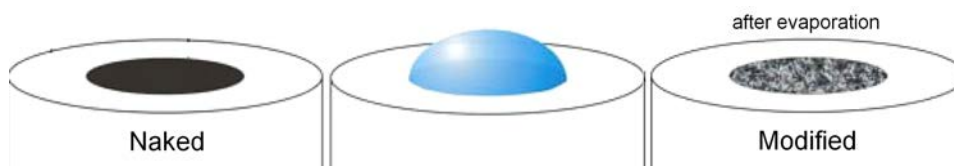


Fig. 1.13: Casting procedure for modifying a carbon electrode with a solution/suspension containing CoPC [2, 27].

Anthraquinone can also be covalently attached to surface groups present on carbon by reduction of diazonium salts (Fig. 1.15). The electrochemical modification of e.g. a gold or carbon electrode with 2-anthraquinonyl groups can be performed

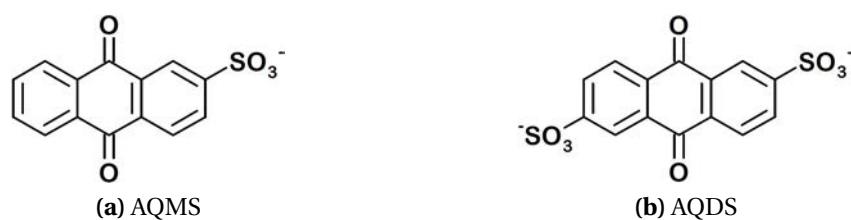


Fig. 1.14: Structures of: (a) anthraquinone-2-sulfonate (anthraquinone monosulfonate) and (b) anthraquinone-2,6-disulfonate.

by using a μM solution of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) dissolved in acetonitrile with 0.1 M TBAP as supporting electrolyte. The diazonium salt is then reduced using the electrode surface as a cathode. It is also possible to derivatize an electrode by simple immersion of the surface in a diazonium salt solution. The spontaneous modification is simpler and quicker but not very reproducible and controllable.

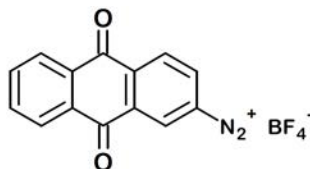


Fig. 1.15: Structure of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$).

Electrodes, such as carbon, can also be modified with biologically active molecules (e.g. enzymes), which interact with a target analyte and produce an electrochemically detectable signal (electrochemical sensors).

Other possible modifications include e.g. polymers or materials such as carbon nanotubes, CNTs, which usually form thicker films than monolayers. Analysis of results for such MEs is usually more complex, because mass transfer and reaction kinetics within the film (Fig.1.16) must also be considered.

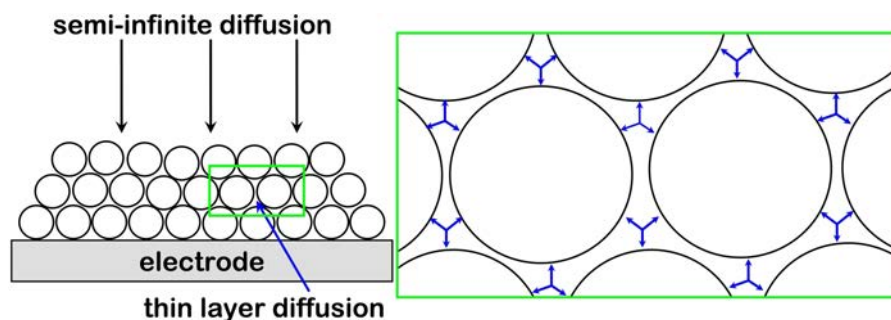


Fig. 1.16: Schematic illustration of possible diffusion regimes to an electrode modified with relatively thick layers.

Electrons tunnel through the film and cause faradaic current to flow. The electron transfer rate constant, k_0 , for a redox species confined at the surface is:

$$k_0(r_0) = k_0(r_0 = 0) \exp(-\beta r_0), \quad (1.118)$$

where r_0 is the distance between the redox centre and the electrode surface and β ($\text{\AA}^{-1}$) is the electronic coupling attenuation coefficient. The equation assumes that β is essentially independent of potential. The exponential decrease in the rate of tunneling with distance and the magnitude of β , usually ca $1 \text{\AA}^{-1}$, implies that electron tunneling will only be important with films thinner than about 1.5 nm. For electron tunneling studies the films should have a well defined and known structure, so that the distance between substrate and electroactive group is constant and known.

Rate constants can be determined by potential step chronoamperometry, in which case the faradaic current, I_F , follows a simple exponential decay:

$$I_F = k_{\text{app}} Q \exp(-k_{\text{app}} t), \quad (1.119)$$

where k_{app} is the sum of the forward and backward electron transfer rate constants for the process investigated, $Q = nFA\Gamma$, and Γ is the surface coverage of electroactive centers [1, 3, 24, 26, 28, 29].

• **Calculation of detection limits:** Quantitative analysis of experimental results is extremely important because it can lead to commercial applications of the investigated modified electrode (ME) provided that the limit of detection (LOD) is low enough. Direct comparison of various MEs is sometimes difficult because in the literature, the limit of detection is sometimes ambiguously defined. In general LOD is the minimum value of the signal that is significantly different from the signal of the blank solution. It is common to see in the literature: "LOD is based on $S/N=3$ (signal to noise ratio equals 3)" without any equations or justifications and sometimes even with: "Figure not shown". This approach makes comparisons of MEs very difficult because usually the noise in question is not defined at all, not even at least depicted in a plot with experimental results.

The unambiguous way of presenting a LOD is based on the calculation from the calibration plot which is constructed from points of response, e.g. I_p , vs. concentrations. The relationship between concentrations and responses must be linear. The intercept of the linear plot, $y = a + bx$, is the value of blank solution response ($y_{\text{blank}} = a$), and the limit of detection (LOD) is $3\frac{s_B}{b}$, where s_B is the standard deviation. In this case $S/N=3$ means that the response, e.g. I_p , is $y = y_{\text{blank}} + 3s_B$.

If the calibration plot gives very small s_B (R^2 very close to 1), then the calculated LOD may be so low that it cannot be resolved from the blank solution response. It is therefore important to remember that $\text{LOD} = 3\frac{s_B}{b}$ is not always a detection limit possible to reach in practice [5].

1.4. Aims of this thesis

It is widely reported in the literature that the ‘mediator’ cobalt phthalocyanine (CoPC) facilitates a variety of redox processes. The possible target molecules include nitrite, glutathione and hydrogen peroxide. Often CoPC modified electrodes are claimed to be superior to unmodified ones without any comparison of analytical parameters (such as sensitivity and detection limit) for the reaction at both CoPC modified and a bare unmodified electrode. There is also a lack of full and proper study of the electrochemical properties of dissolved and adsorbed CoPC in the literature. It is also reported that the nature of active form of CoPC at the surface of carbon electrodes is always a monolayer. In this thesis all these issues will be addressed: a thorough electrochemical study of the solution phase and solid phase CoPC will be presented, the surface of carbon electrodes modified with CoPC will be investigated with scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) and also the use of CoPC modified and a bare carbon electrode for sensing one of the possible target molecules, nitrite (NO_2^-), will be studied.

The voltammetric responses of 2H^+ , $2e^-$ systems in fully buffered aqueous solutions, i.e. the DNA intercalators: anthraquinone disulfonate (AQDS) and anthraquinone monosulfonate (AQMS), has been thoroughly investigated across the full pH range by Batchelor-McAuley et al. (C. Batchelor-McAuley, Q. Li, S. Dapin, and R. G. Compton, *Journal of Physical Chemistry B*, 2010, 114, 4094–4100). The voltammetry of processes involving a proton transfer is known to be altered in the presence of a limited concentration of protons and this will be investigated for solution phase and surface confined anthraquinone species, i.e. an edge

plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) and solution phase anthraquinone monosulphonate (AQMS).

Marcus-Hush-Chidsey theory, which can provide more insight into electron transfer reactions than Butler-Volmer analysis, has been previously successfully applied to various one electron processes involving species adsorbed on electrode surfaces, usually as self-assembled monolayers (SAMs). In this thesis the theory will be applied for the first time to a two-electron redox system, namely to an edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) and the obtained results will be compared to an AQ2 modified gold electrode (Au-AQ2). In both cases cyclic voltammograms simulated using Marcus-Hush-Chidsey theory for $2e^-$ process assuming a uniform surface will be investigated along with two models of possible surface inhomogeneity: a distribution of formal potentials, $E^{\ominus'}$, and a distribution of electron tunneling distances, r_0 .

1.5. References

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Voltammetric studies of the redox mediator, cobalt phthalocyanine, with regard to its claimed electrocatalytic properties

The work presented in this chapter has been published in
Sensors and Actuators B: Chemical, 2010, 147, 350–358.

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It is widely reported in the literature that cobalt phthalocyanine (CoPC) facilitates a wide variety of redox processes. This conclusion is often made without any comparison of analytical parameters (such as sensitivity and detection limit) for the reaction at both CoPC modified and a bare unmodified electrodes. Another important issue is a lack of full and proper study of the electrochemical properties of dissolved and adsorbed CoPC before adding an analyte to the solution. It is

also generally reported, without presenting convincing argument, that the nature of the active form of CoPC at the surface of carbon electrodes is always a monolayer. In this chapter a thorough electrochemical study on the solution phase and solid phase cobalt phthalocyanine with regard to its claimed electrocatalytic properties towards oxidation of nitrite is presented. The cyclic voltammetry of cobalt phthalocyanine has been examined in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) at a glassy carbon (GC) electrode. In both solvents three redox couples are present: one ring based and two cobalt based processes. The aqueous voltammetry of CoPC adsorbed on basal plane pyrolytic graphite (BPPG) and edge plane pyrolytic graphite (EPPG) was also studied in phosphate buffer solution. Two couples are present: Co(II/I) and Co(III/II). Cyclic voltammetry experiments suggest that the number of electroactive adsorbed CoPC molecules on EPPG is approximately 3.5 times higher than on BPPG. The surface properties of both electrodes modified by immersing in 0.1 mM CoPC in dimethylformamide (DMF) solution were characterized by SEM and energy dispersive X-ray spectroscopy (EDS). It was observed that CoPC adsorbed on EPPG and BPPG electrodes exists as microcrystals, not a monolayer as reported in the literature for other carbon electrodes. The use of an EPPG-CoPC modified electrode for sensing nitrite (NO_2^-) was also investigated. It was found that CoPC on EPPG has no influence on the oxidation of nitrite.

2.1. Introduction

Cobalt (II) phthalocyanine (CoPC) and structurally similar molecules have been utilised extensively as mediators for electrochemical processes. In particular the

ability to use CoPC and analogs in conjunction with carbon electrodes of diverse forms has seen significant advances in the fabrication of screen printed and carbon paste electrodes [1–16] for the study of processes such as:



This allows the mediated detection of a wide variety of target species in an electrocatalytic fashion with the potential required for the mediated oxidation being lower than for the direct process:



Significant targets claimed for analysis included nitrite [17–19], glutathione [20–22] and hydrogen peroxide [7, 23, 24]. Tab.2.1, page 55, gives a full range of analytes for which CoPC based sensors have been realized. The mediation implied by Eqs. (2.1) and (2.2) requires, for a complete mechanistic investigation, that the phase of CoPC when undergoing the electron transfer shown in Eq. (2.1) is defined and it is evident that this minimum insight is needed for anything other than entirely empirical sensor optimization. That said, given that CoPC is generally added to a solid to form screen printed electrodes and carbon paste electrodes, it is possible that the active form of CoPC might be that of a solid probably in microcrystalline form, or as a small amount of dissolved CoPC in equilibrium with the solid present in the electrode, or, as a third possibility, as adsorbed molecular CoPC on the electrode surface present after dissolution of the solid CoPC followed by reprecipitation.

Tab. 2.1: Analytes and CoPC based electrodes used for their determination from the literature; MWCNTs – multiwalled carbon nanotubes, SWCNTs – singlewalled carbon nanotubes, GC – glassy carbon, OPG – ordinary pyrolytic graphite.

analyte	electrode
2-aminoethanethiol	CoPC adsorbed on OPG [25]
amitrole	CoPC modified carbon paste [26]
ascorbic acid	drop-coated with nano-CoPC colloid GC [27] CoPC modified screen printed carbon [9] nano-CoPC modified carbon paste [28] CoPC modified carbon-epoxy composite [10]
aziprotrotryne	CoPC modified carbon paste [29]
carbaryl	CoPC and acetylcholinesterase modified carbon paste [30]
coenzyme A	CoPC modified screen printed carbon [9]
cysteine	CoPC modified sol-gel carbon composite [24]
dichlorvos	CoPC and acetylcholinesterase modified screen printed graphite [31]
2',3'-dideoxyinosine	CoPC modified carbon paste [32]
dimethyldisulfide	CoPC modified screen printed carbon [33]
dopamine	nano-CoPC modified carbon paste [28] CoPC modified MWCNTs on GC [34]
ethanethiol	CoPC modified screen printed carbon [33]
ethanol	alcohol oxidase and CoPC modified screen printed carbon [4]
methanol-ethanol mixtures	alcohol oxidase and CoPC modified screen printed carbon [35]
ephedrine	CoPC modified carbon paste [36]
fructose	CoPC modified carbon paste [37]
galactose	CoPC modified carbon paste [37]
glutathione	CoPC adsorbed on OPG [20, 21] CoPC modified surfactant-induced sol-gel carbon [22] CoPC modified screen printed carbon [9] CoPC modified screen printed graphite [38]
glucose	CoPC modified carbon paste [37] cellulose acetate and glucose oxidase coated CoPC modified screen printed carbon [11] CoPC and glucose oxidase screen printed carbon [5, 12] CoPC adsorbed on OPG [39]

continued on next page

Tab. 2.1 – continued

analyte	electrode
hydrazine	CoPC modified carbon paste [40–42] CoPC adsorbed on GC [43] polymeric CoPC modified GC [44] CoPC modified SWCNTs on GC [45] CoPC modified sol-gel carbon composite [24]
hydrogen peroxide	immobilised CoPC-cobalt porphyrin pentamer at GC [23] CoPC modified screen printed carbon [7, 14, 15] CoPC modified sol-gel carbon composite [24]
hydrogen sulfide	CoPC modified screen printed carbon [33]
hydroxylamine	polymeric CoPC GC [46]
lactose	CoPC modified carbon paste [37]
maltose	CoPC modified carbon paste [37]
2-mercaptoacetate	CoPC adsorbed on OPG [47]
2-mercaptoethanesulfonic acid	CoPC adsorbed on OPG and vitreous carbon [48]
2-mercaptoethanol	CoPC modified screen printed graphite [38]
methanethiol	CoPC modified screen printed carbon [33]
nitric oxide	CoPC adsorbed and electrodeposited on GC [49] solution phase voltammetry [50] CoPC modified carbon fiber [51]
nitrite	CoPC adsorbed on vitreous carbon [18] heat-treated CoPC supported on high area carbon [19] CoPC synthesized on a sol-gel derived $\text{SiO}_2/\text{SnO}_2$ and mixed with graphite powder [17]
oxygen	CoPC vacuum-deposited on OPG [52, 53] CoPC adsorbed on OPG [54] CoPC adsorbed on GC [43]
oxalic acid	CoPC synthesized on a sol-gel derived $\text{SiO}_2/\text{SnO}_2$ and mixed with graphite powder [55] CoPC modified sol-gel carbon composite [24]
paraquat pesticide	CoPC adsorbed on OPG [56]
propanethiol	CoPC modified screen printed carbon [3]
ribose	CoPC modified carbon paste [37]
sucrose	CoPC modified carbon paste [37]

continued on next page

Tab. 2.1 – continued

analyte	electrode
thiocholine	CoPC modified screen printed carbon [16]
thioglycolic acid	CoPC modified carbon paste [57]
2-thiobarbituric acid	CoPC modified carbon paste [58]
2-thiouracil	CoPC modified carbon paste [58]
thiourea	CoPC modified sol-gel carbon composite [24]
uric acid	uricase-cellulose acetate CoPC modified screen printed carbon [13, 59]
	uricase-cellulose acetate CoPC modified graphite-epoxy resin [59]

In beginning to study the mode of operation of CoPC as a mediator, and guided particularly by the works of Bedioui [18, 60], Hart [8] and others we were first surprised to find that the claimed electrocatalytic oxidation of nitrite by CoPC [17, 19] could be reproduced on bare carbon electrodes in the absence of CoPC! [61]. Accordingly and prior to full mechanistic reexamination of various sensing systems we have undertaken a re-evaluation of the voltammetry of CoPC in various forms – solid and dissolved – using both aqueous and non-aqueous solvents in order to better define the nature of its electrochemistry in various phases, in the context of its possible mode of action as a mediator of electron transfer.

2.2. Experimental

All reagents were used as received without further purification. Cobalt phthalocyanine (CoPC) was obtained from Fluka. Electrochemical measurements were carried out using an Autolab PGSTAT20 computer-controlled potentiostat

(EcoChemie, Utrecht, the Netherlands) with a standard three-electrode configuration. Deionised water used for rinsing electrodes and preparing solutions was of resistivity not less than $18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C (Millipore Water Systems, UK).

2.2.1. Voltammetry of cobalt phthalocyanine in organic solvents

Tetrabutylammonium perchlorate (TBAP) was obtained from Fluka, dimethyl sulfoxide (DMSO) was obtained from Aldrich and tetrahydrofuran (THF) was supplied by Rathburn Chemicals Ltd. (UK). Glassy carbon (GC, 3 mm diameter, BAS, Technicol, UK) was the working electrode, a platinum wire was the counter electrode and a silver wire was the reference electrode. The glassy carbon electrode was polished with diamond lapping compounds (Kemet, Kent, UK) of decreasing size ($3 \mu\text{m}$, $1 \mu\text{m}$, $0.1 \mu\text{m}$), sonicated in deionised water in an ultrasound bath and dried in air prior to use. The electrochemical cell for DMSO solutions had a volume of 50 mL and was covered with parafilm. The electrochemical cell for THF solutions was a 50 mL three-neck round-bottom glass flask covered with rubber bungs. DMSO and THF solutions contained 0.1 M TBAP as a supporting electrolyte. DMSO solutions were thoroughly deoxygenated with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solutions during experiments. THF solutions were also deoxygenated with nitrogen and a nitrogen atmosphere was maintained throughout measurements using inflatable plastic balloons filled with nitrogen. Due to the relatively high volatility of THF (boiling point: 65°C) the round-bottom flask was immersed in a water-ice bath, so the temperature of THF solutions during experiments was approximately 2°C . Solutions of CoPC in DMSO and THF were saturated and of only approximately known concentration

because in practice CoPC dissolves with difficulty in DMSO and THF.

2.2.2. Voltammetry of adsorbed cobalt phthalocyanine

Potassium dihydrogen phosphate (KH_2PO_4) was obtained from Sigma, potassium hydrogen phosphate (K_2HPO_4) was obtained from May & Barker and dimethylformamide (DMF) was purchased from Aldrich. Edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG, 4.9 mm diameter, Le Carbone, Ltd. Sussex, UK) were the working electrodes, a platinum wire was the counter electrode and a saturated calomel (SCE, Radiometer, Copenhagen, Denmark) was the reference electrode. Discs of pyrolytic graphite were machined to a 4.9 mm diameter and oriented with the disc face parallel with the edge plane or basal plane as required. The edge plane pyrolytic graphite electrode was polished on alumina lapping compounds (Buehler) of decreasing sizes ($1.0\ \mu\text{m}$, $0.3\ \mu\text{m}$) on soft lapping pads, sonicated in deionised water in an ultrasound bath and dried in air prior to use. The basal plane pyrolytic graphite electrode was prepared by renewing the electrode surface with cello tape. Both edge plane and basal plane electrodes were modified by immersing in 0.1 mM CoPC in dimethylformamide (DMF) solution, rinsed with pure DMF, then with deionised water and placed into the electrochemical cell. Modified electrodes are referred to as BPPG-CoPC and EPPG-CoPC. The 50 mL electrochemical cell was covered with parafilm to reduce ingress of oxygen. Phosphate buffer solution (pH 7.2) contained 0.05 M KH_2PO_4 and 0.14 M K_2HPO_4 : it was thoroughly deoxygenated with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solution during experiments.

2.2.3. Electrocatalytic properties of adsorbed cobalt phthalocyanine

Potassium nitrite (KNO_2) was obtained from Sigma-Aldrich. Bare EPPG and EPPG-CoPC modified electrodes were the working electrodes (described in section 2.2.2), platinum wire was the counter electrode and a saturated calomel (the same as in section 2.2.2) was the reference electrode. The 50 mL electrochemical cell was covered with parafilm to retain nitrogen above the solution. All experiments were performed in phosphate buffer solution (pH 7.2) (the same as in section 2.2.2). Phosphate buffer solution was thoroughly deoxygenated with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solution during experiments. Nitrite stock solutions in water were prepared daily prior to experiments and kept in the fridge when not in use.

2.3. Results and discussion

2.3.1. Voltammetry of cobalt phthalocyanine in organic solvents

The solution redox properties of cobalt phthalocyanine (CoPC) were studied using cyclic voltammetry (CV) in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) on a glassy carbon (GC) electrode.

Figures 2.1, 2.2a, 2.2c and 2.2e show the cyclic voltammograms of CoPC in DMSO solution. Figures 2.3, 2.4a, 2.4c and 2.4e show the cyclic voltammograms of CoPC in THF solution; three redox couples are present. Peak potentials for CoPC in DMSO at 0.5 V/s from Fig. 2.1 and peak potentials for CoPC in THF at 0.5 V/s from Fig. 2.3 are reported in Tab. 2.2.

CoPC in DMSO				CoPC in THF			
	E_{pa}	E_{pc}	$E_{1/2}$		E_{pa}	E_{pc}	$E_{1/2}$
process 1	-1.28	-1.35	-1.32	process I	-0.65	-0.90	-0.78
process 2	-0.39	-0.44	-0.42	process II	0.15	0.06	0.10
process 3	0.99	0.96	0.98	process III	0.71	0.50	0.60

Tab. 2.2: Peak potentials for CoPC in DMSO and THF solutions on GC electrode at 0.5 V/s (units: V vs. Ag); E_{pa} – anodic peak potential, E_{pc} – cathodic peak potential, $E_{1/2} = \frac{E_{pa} + E_{pc}}{2}$.

2.3.1.1. Dimethyl sulfoxide

Bedioui et al. [62] investigated the electrochemical behaviour of CoPC in DMSO containing 0.1 M tetrabutylammonium tetrafluoroborate (TBAF₄) on a vitreous carbon disk electrode and reported only two well-defined pairs of peaks. One at -1.43 V vs. SCE for a phthalocyanine ring reduction process $[\text{Co(I)PC}(-2)]^- / [\text{Co(I)PC}(-3)]^{2-}$ and a second one at -0.50 V vs. SCE for a metal-based electron transfer $[\text{Co(II)PC}(-2)] / [\text{Co(I)PC}(-2)]^-$. They described obtained voltammograms as "not very well-defined at potentials > 0.4 V, where the Co(III)/Co(II) redox process is supposed to take place". By comparison with those results it is possible to assign the most negatively situated pair in DMSO, labeled as 1 in Fig. 2.1 and in Fig. 2.2a to ring-based process: $\text{PC}(2- / 3-)$ and the middle pair, labeled as 2 in Fig. 2.1 and in Fig. 2.2c to metal-based process Co(II/I).

CoTSPC in DMSO	E
ring process	-1.35
Co(II)/Co(I)	-0.42
Co(III)/Co(II)	0.38

Tab. 2.3: Peak potentials for tetrasulphonated cobalt phthalocyanine (CoTSPC, TSCoPC) in DMSO with 0.05 M TBAP on a Pt electrode [63] (units: V vs. SCE).

CoPC in pyridine	E
$[\text{Co(I)PC}(2- / 3-)]^{-/2-}$	-1.42
$[\text{Co(II/I)PC}(2-)]^{0/-}$	-0.60
$[\text{Co(III/II)PC}(2-)]^{+/0}$	0.19

Tab. 2.4: Peak potentials for CoPC in pyridine containing 0.2 M TBAP on Pt wire electrode [64] (units: V vs. SCE).

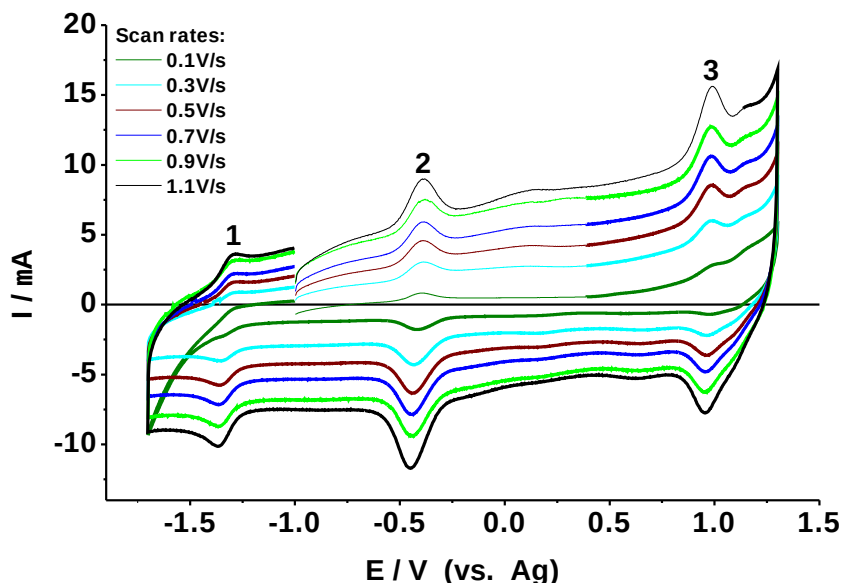


Fig. 2.1: Cyclic voltammograms of CoPC in DMSO solution.

A widely reported example of a substituted CoPC is tetrasulfonated cobalt phthalocyanine (CoTSPC, TSCoPC). It is studied because CoPC itself is poorly soluble in water and most of organic solvents [64] whereas the sulphonated metal phthalocyanines are water soluble [63]. Tab.2.3 shows peak potentials for CoTSPC in DMSO on a platinum electrode [63]. Again, two potentials correspond well to the results obtained for unsubstituted cobalt phthalocyanine in DMSO (Tab.2.2). The process at -1.35 V vs. SCE is described as a ligand based and not involving a $\text{Co}(0)$ species, the process at -0.42 V vs. SCE as involving Co(II)/Co(I) and the last one at 0.38 V vs. SCE as involving Co(III)/Co(II) species [63].

Substituted CoPCs in DMSO sometimes show more than three pairs of peaks – Tab.2.5. It is clear that potentials for **B**, **C** and **D** are very similar and also confirm the origin of two first pairs of peaks for the unsubstituted CoPC in DMSO. Although the potential for the third pair is more similar to the $\text{PC}(-/2-)$ process for **A**, it is very unlikely that this process corresponds to another ring-based process. Unsubstituted CoPC in DMSO in the positive potential range most likely

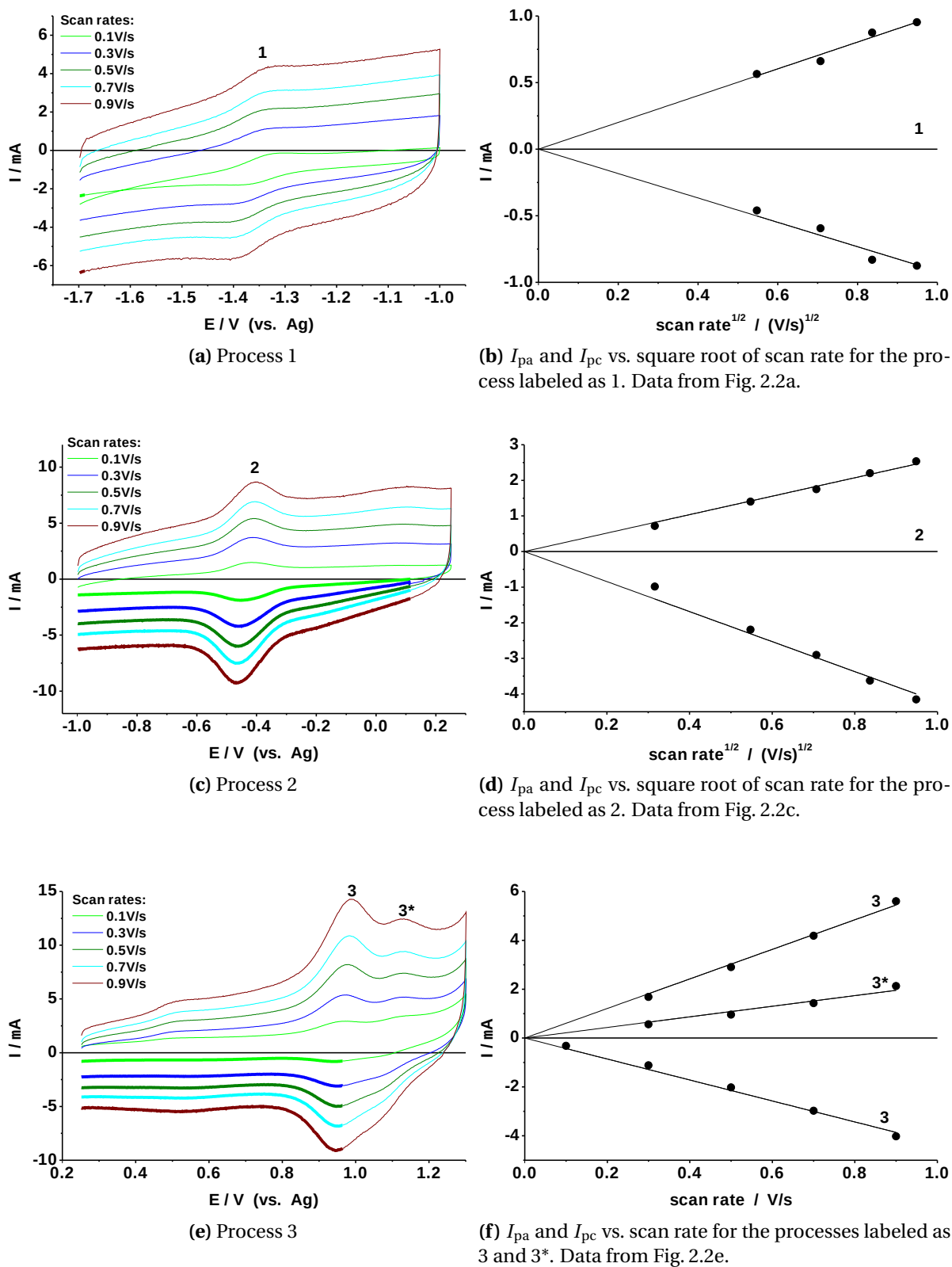


Fig. 2.2: Cyclic voltammograms of CoPC in DMSO solution.

exhibits oxidation of Co(II) to Co(III) [65] and we suggest this is the origin of the peaks labeled as 3 and III reported in Tab.2.2.

	A [64]	B [66]	C [67]	D [68]
Co(I)sub.PC(2 – /3 –)	–1.58	–1.34	–1.27	–1.30
Co(II/I)sub.PC(2 –)	–0.51	–0.41	–0.36	–0.42
Co(II/III)sub.PC(–)	0.28	0.43	0.47	0.45
Co(III)sub.PC(–/2 –)	0.80	—	—	—

Tab. 2.5: Peak potentials for substituted CoPC in DMSO on Pt electrode (units: V vs. SCE); sub.PC: substituted phthalocyanine ring; **A:** CoTNPC – cobalt tetraneopentoxypthalocyanine; **B:** 2,9,16,23-tetrakis-6-(-thiophene-2-carboxylate)-hexylthiocobalt phthalocyanine; **C:** 2,9,16,23-tetrakis-(6-hydroxyhexylsulfanyl) cobalt phthalocyanine; **D:** cobalt phthalocyanine with tetra-tricarbethoxyethyl substituents at the peripheral position.

The literature data for unsubstituted cobalt phthalocyanine [64] in pyridine on Pt wire (Tab.2.4) also confirm that the first two pairs of peaks correspond to PC(2 – /3 –) and Co(II/I) respectively.

Fig. 2.2a illustrates the PC(–2/–3) in DMSO process, which is labeled as 1, and Fig. 2.2b shows the corresponding dependence of peak currents (I_{pa} and I_{pc}) on the square root of scan rate. The linearity of I_p vs. square root of scan rate suggests a diffusional process and solution species are responsible for voltammetric signals. Fig. 2.2c depicts the Co(II/I) in DMSO process labeled as 2. The dependence of I_{pa} and I_{pc} on the square root of scan rate for the Co(II/I) process (Fig. 2.2d) is characteristic of a diffusion controlled process. Fig. 2.2e illustrates reversible Co(III/II) in DMSO reaction, which is labeled as 3. The additional peak (labeled as 3*) is probably due to reorganisation of adsorbed CoPC at the surface of GC electrode [43]. It is more apparent after recording several cyclic voltammograms than after just few (compare to Fig. 2.1). Fig. 2.2f shows that peak currents for processes labeled as 3 and 3* are proportional to scan rate indicating surface

electron transfer processes.

2.3.1.2. Tetrahydrofuran

There are no voltammetric data available in the literature for unsubstituted CoPC in THF. The main difference between electrochemical results for CoPC in THF and CoPC in DMSO may be due to the fact that THF is a nondonor solvent whereas DMSO is a donor solvent. Donor solvents (DMSO) favor Co(III) species and the oxidation to Co(III) in donor solvents takes place before the ring oxidation process. In nondonor solvents (THF) the ring oxidation occurs first before oxidation of Co(II) to Co(III) [69]. That said the data shown in Tab.2.2 reports potentials against the Ag wire quasi-reference electrode, so absolute comparison is difficult.

Substituted CoPC (namely cobalt phthalocyanine carrying tetrakisdiethoxymalonyl substituents) in THF exhibits four reduction processes and two oxidation processes [69] (Tab.2.6). By comparison of the data obtained for CoPC in THF (Tab.2.2) with those results it is possible to assign the most negatively situated pair of peaks labeled as I in Fig.2.3 and in Fig.2.4a to diffusional (Fig.2.4b) Co(II/I) process; the middle pair labeled as II in Fig.2.3 and in Fig.2.4c to a ring-based redox PC(2−/1−) and the pair labeled as III in Fig.2.3 and in Fig.2.4e to a Co(III/II) process.

The linear dependence of peak currents (I_{pa} and I_{pc}) on the square root of scan rate for Co(II/I) (Fig.2.4b) is associated with a diffusional process for solution species over the investigated range of scan rates. Fig.2.4d shows the dependence of I_{pa} and I_{pc} on the square root of scan rate for the PC(2−/1−)

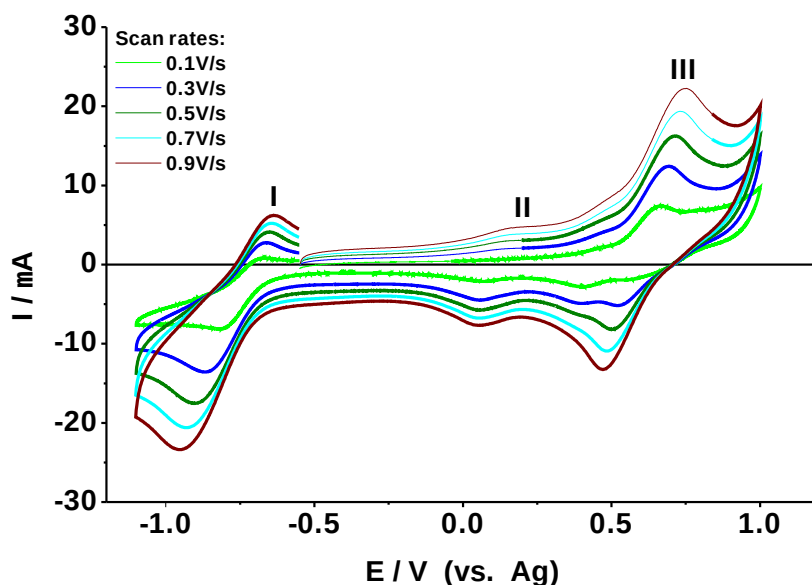


Fig. 2.3: Cyclic voltammograms of CoPC in THF solution.

sub.CoPC in THF	$E_{1/2}$
	-1.436
	-1.247
	-1.031
Co(II)sub.PC(-2)/Co(I)sub.PC(-2)	-0.216
Co(II)sub.PC(-2)/Co(II)sub.PC(-1)	0.321
Co(II)sub.PC(-1)/Co(III)sub.PC(-1)	0.762

Tab. 2.6: Peak potentials for cobalt phthalocyanine carrying tetrakisdiethoxymalonyl substituents in THF containing 0.1M TBAP on Pt plate electrode [69] (units: V vs. SCE); sub.CoPC: substituted cobalt phthalocyanine, sub.PC: substituted phthalocyanine ring

process. It is characteristic of a diffusion controlled process. Fig.2.4f depicts only I_{pa} vs. square root of scan rate. It is because the reduction process at lower scan rates exhibits two peaks and at higher scan rates it shows only one peak.

2.3.2. Voltammetry of adsorbed cobalt phthalocyanine

The redox properties of cobalt phthalocyanine (CoPC) adsorbed by immersion into a DMF solution of 0.1 mM CoPC on edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG) electrodes were studied in phosphate

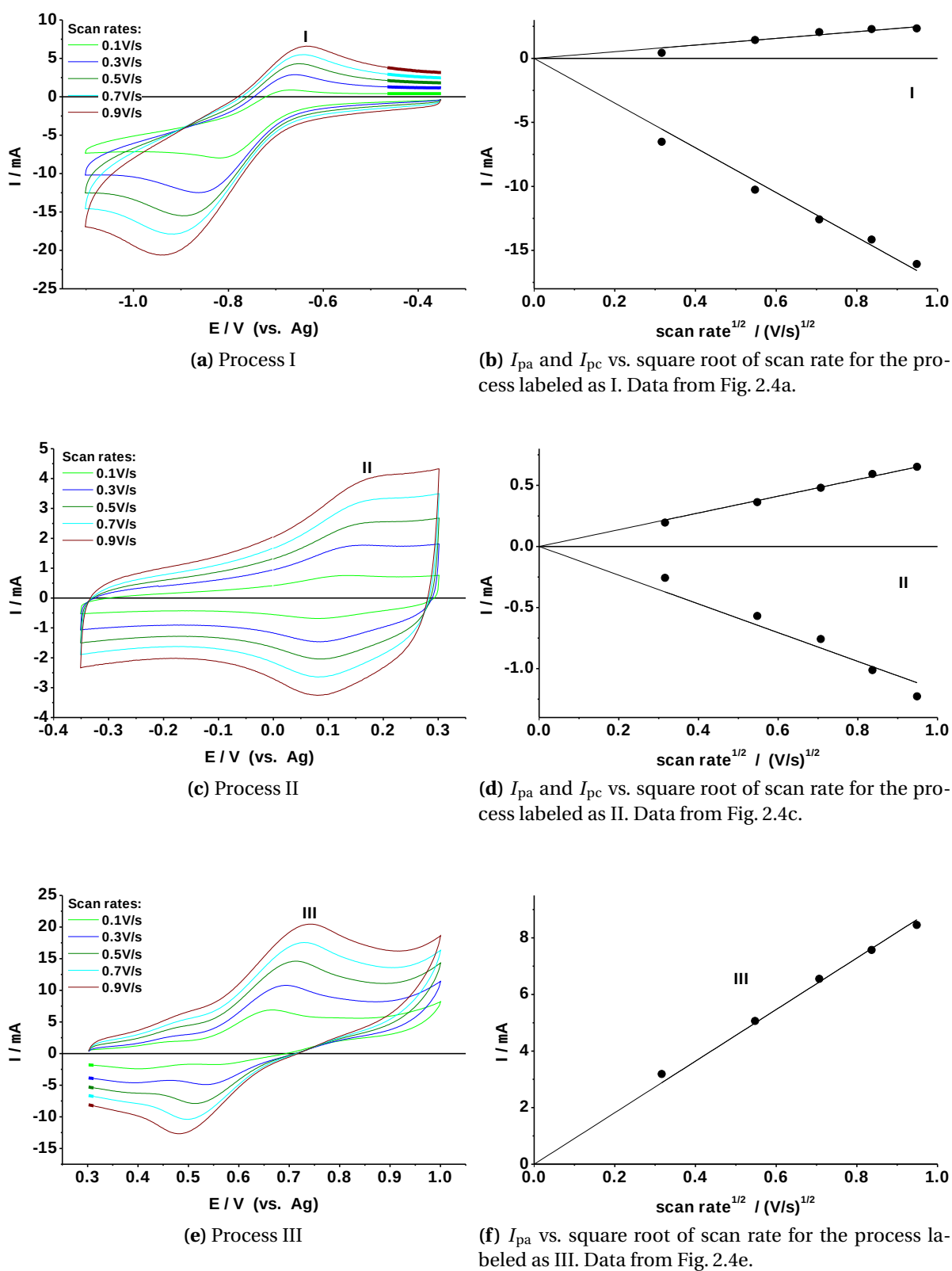


Fig. 2.4: Cyclic voltammograms of CoPC in THF solution.

buffer solution (pH 7.2) using cyclic voltammetry (CV).

Fig. 2.5 shows the cyclic voltammograms of bare EPPG electrode and EPPG-CoPC modified electrode. Peak potentials for CoPC adsorbed on EPPG electrode at 0.1 V/s from Fig. 2.5 are: $E_{pa} = -0.59$ V; $E_{pc} = -0.60$ V and $E_{pa} = 0.78$ V; $E_{pc} = 0.49$ V vs. SCE. The reversible pair of peaks can be assigned to the redox Co(II/I) process of the adsorbed CoPC [21, 25, 39, 43, 60]. The other pair corresponds to the Co(III/II) couple [43].

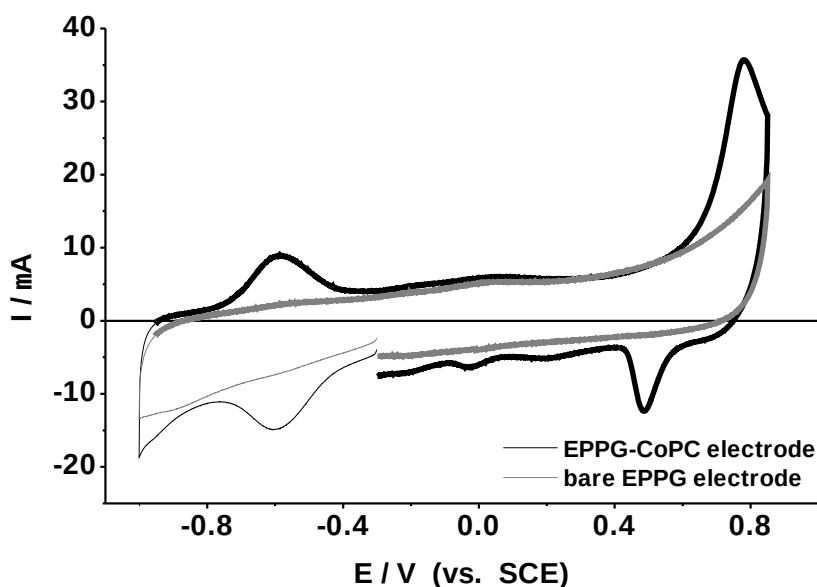


Fig. 2.5: Cyclic voltammograms of bare EPPG electrode and EPPG-CoPC modified electrode; modification time: 2:00 hours, scan rate: 0.1 V/s.

Fig. 2.6a and Fig. 2.6b show the cyclic voltammograms of EPPG-CoPC and BPPG-CoPC modified electrodes. It is clear that CoPC molecules adsorb on edge plane pyrolytic graphite electrode more than on basal plane pyrolytic graphite. The charge under the forward peak (reductive) (Fig. 2.6a), corrected for a residual current, is $4.5 \cdot 10^{-5}$ C/cm² for EPPG-CoPC modified electrode and $1.3 \cdot 10^{-5}$ C/cm² for BPPG-CoPC. It is due to the difference in surface properties between these two types of carbon electrodes. It has been well known that the electrode kinetics at EPPG are at least three times faster than on BPPG electrodes [70, 71]. It is

very likely that edge plane sites are the reason for approximately 3.5 times higher number of adsorbed CoPC molecules on EPPG than on BPPG.

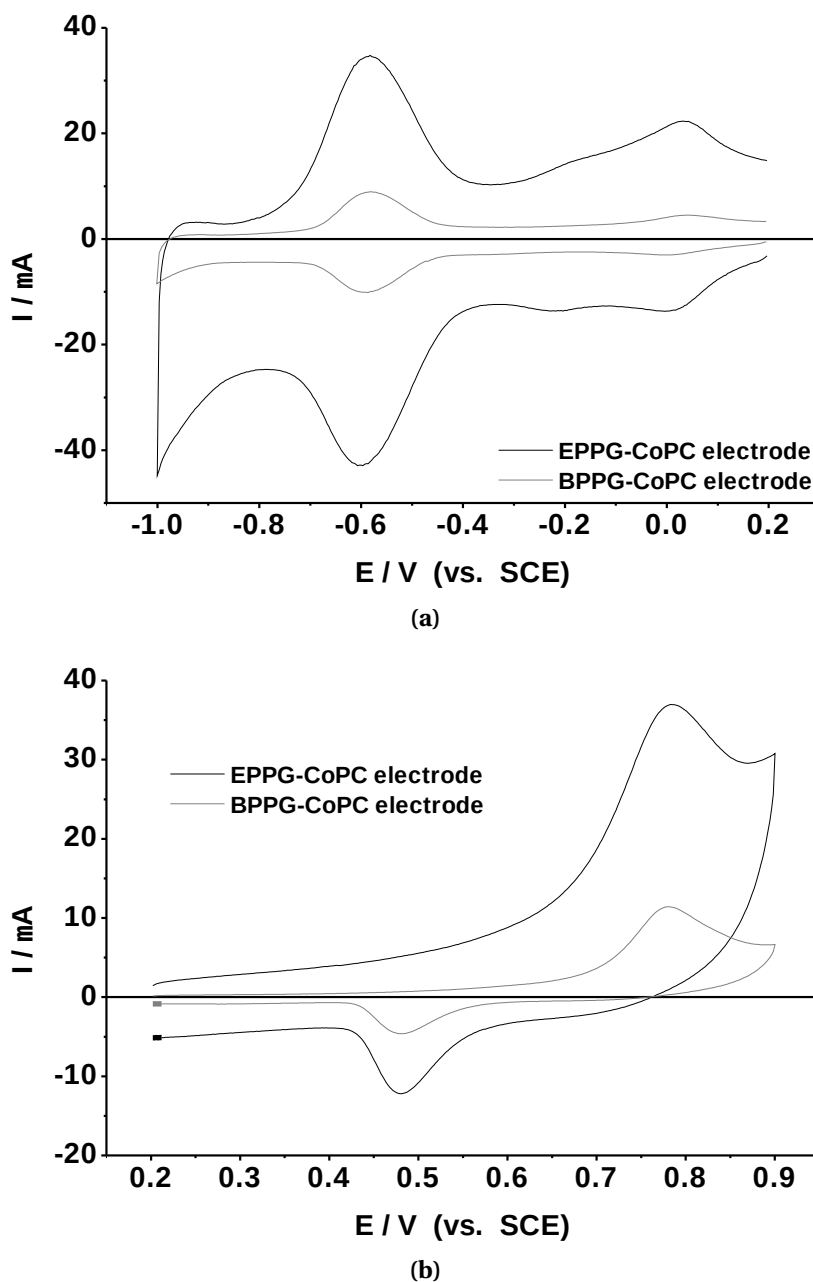


Fig. 2.6: Cyclic voltammograms of EPPG-CoPC and BPPG-CoPC modified electrodes: (a) modification time: 1:00 hour, scan rate: 0.5 V/s, (b) modification time: 2:00 hours, scan rate: 0.1 V/s.

The heights of the oxidation and reduction peaks related to Co(II/I) redox process vary linearly with the scan rate (Fig.2.8) according to equation:

$$I_p = \frac{n^2 F^2}{4RT} \nu A \Gamma \quad (2.4)$$

where n is the number of electrons, F is Faraday constant, R is the gas constant, T is the temperature, ν is the potential scan rate, A is the electrode surface area, Γ is the surface concentration, as expected for surface confined species [72]. I_{pa} (back scan) to I_{pc} (forward scan) ratio is 1.17. The area under the peak is the charge, Q , required for the full reduction of the layer [72]:

$$Q = nFA\Gamma. \quad (2.5)$$

Assuming $n = 1$, $F = 96485 \text{ C/mol}$ and A – geometrical electrode area (without any surface roughness correction), Γ for EPPG-CoPC is $4.6 \cdot 10^{-10} \text{ mol/cm}^2$. Cobalt phthalocyanine is a square, planar molecule of size $\text{ca } 1.2 \text{ nm} \cdot 1.2 \text{ nm}$ [21] so it is possible to estimate that 1 cm^2 of monolayer of CoPC (on an ideally flat surface) should consist of $1.2 \cdot 10^{-10} \text{ mol}$ of CoPC molecules (ca 4 times less). It is therefore likely that microcrystallites are present rather than monolayer of adsorbed species: we address this in the next section 2.3.3 below.

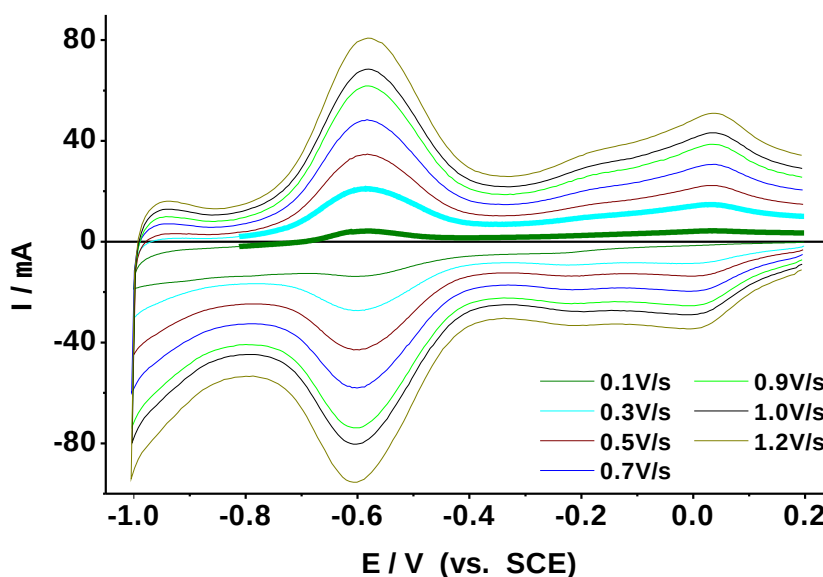


Fig. 2.7: Cyclic voltammograms of EPPG-CoPC modified electrode; modification time: 1:00 hour.

Fig. 2.9 shows ten subsequent cyclic voltammograms of the Co(III/II) couple. Due to the irreversible nature of the redox process the peak currents decrease

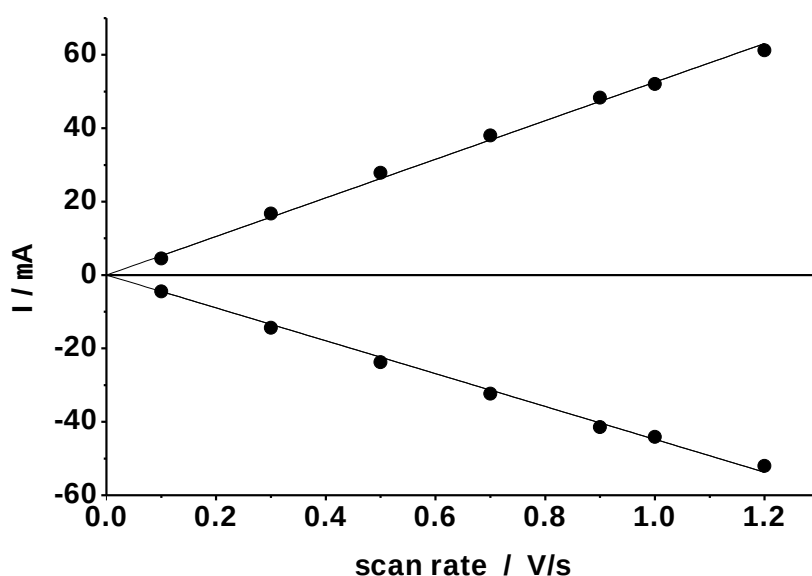


Fig. 2.8: I_{pa} and I_{pc} vs. scan rate for EPPG-CoPC modified electrode. Data from Fig. 2.7.

rapidly and by the tenth scan there is no oxidation peak visible and I_{pc} is only 8% of the current in the first scan. This is also likely due to desorption of Co(III)PC (oxidized CoPC). This behaviour is in contrast to the Co(II/I) couple (Fig. 2.7) which is much more stable. This difference between Co(III/II) and Co(II/I) has implications in the sensing properties of CoPC modified electrodes because one of the most important features of a good sensor is its stability.

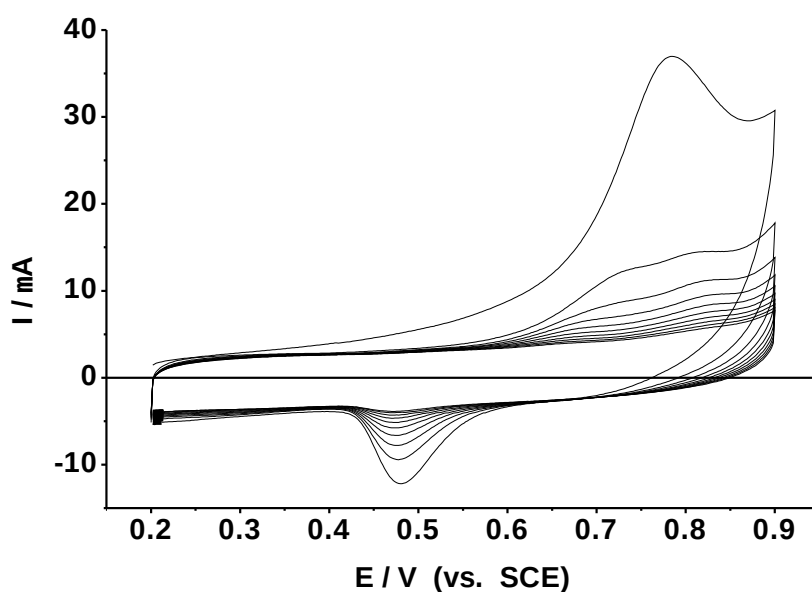


Fig. 2.9: Cyclic voltammograms of EPPG-CoPC modified electrode; modification time: 2:00 hours, scan rate: 0.1 V/s.

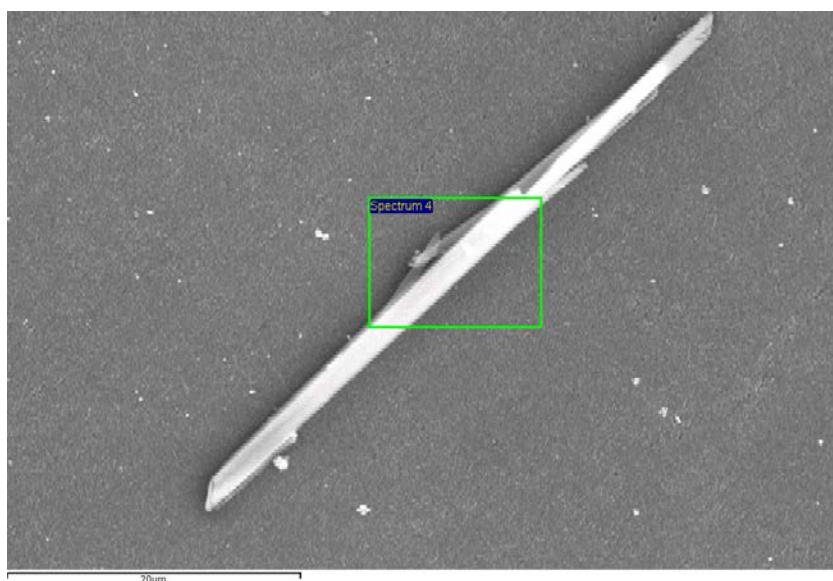
2.3.3. Characterization of the BPPG-CoPC and EPPG-CoPC modified electrodes surface

The surface properties of EPPG-CoPC and BPPG-CoPC modified electrodes were investigated by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

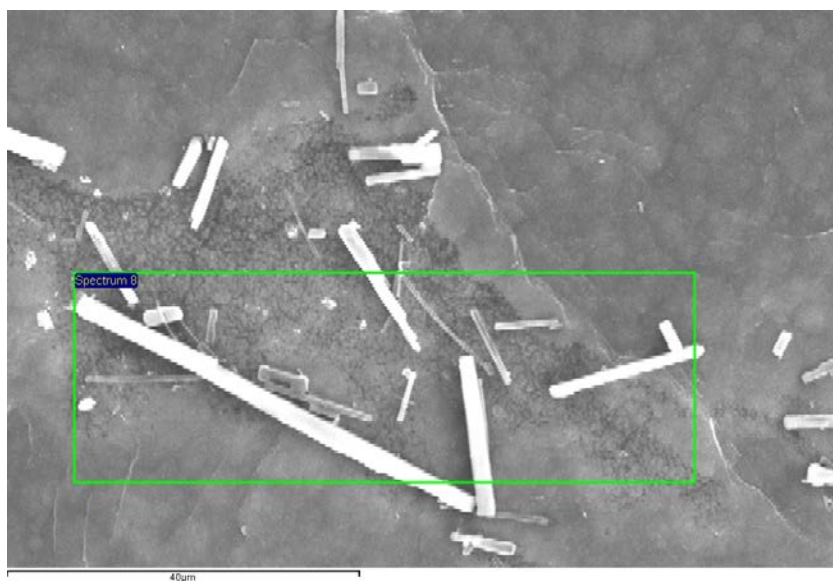
The SEM images (Fig. 2.10a and Fig. 2.10b) show that cobalt phthalocyanine forms thin microcrystals up to ca 70 μm long distributed irregularly on the surface of both electrodes. The cyclic voltammetry results for EPPG-CoPC and BPPG-CoPC modified electrodes (Fig. 2.6a and Fig. 2.6b) suggest that there should be ca 3.5 times more molecules adsorbed on EPPG than on BPPG (section 2.3.2) whereas SEM pictures show that there are ca 6 times more crystals on BPPG than on EPPG. The reason for much lower peak current for BPPG-CoPC modified electrode than for EPPG-CoPC in cyclic voltammetry experiments is probably due to the differences in conductivity between edge plane and basal plane sites. Edge plane defects act as electrochemically active microbands and the basal plane defects as electrochemically inert material [71, 73, 74]. For this reason only crystals located on top of edge plane defects contribute to the current observed.

Energy dispersive X-ray spectroscopy (EDS) measurements of the modified surfaces showed peaks corresponding to the C and O atoms (at ca 0.28 keV and ca 0.53 keV respectively) and also three peaks characteristic of Co (at ca 0.70 keV, 6.89 keV and 7.68 keV).

SEM and EDS indicate that CoPC adsorbed on EPPG and BPPG electrodes exists as microcrystals, not as, or as well as, a monolayer as reported in the literature for ordinary pyrolytic graphite [20, 21, 39, 54]. The crystalline form of



(a) scale bar: 20 μm



(b) scale bar: 40 μm

Fig. 2.10: SEM images of (a) EPPG-CoPC modified electrode and (b) BPPG-CoPC modified electrode. Modification time: 2:00 hours.

adsorbed CoPC may influence its stability in the cyclic voltammetry experiments and may be the reason for fast desorption observed for the Co(III/II) couple (Fig. 2.9).

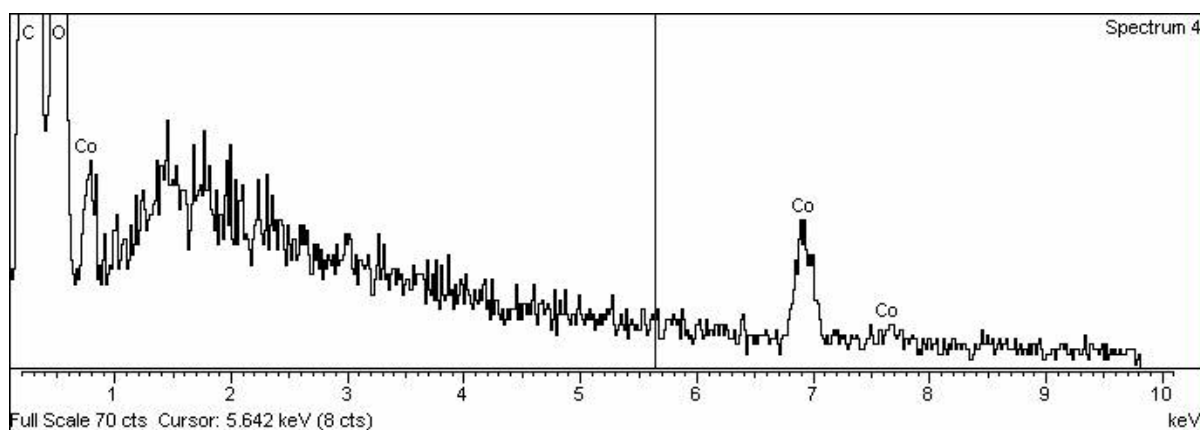


Fig. 2.11: EDS spectrum of EPPG-CoPC modified electrode (Fig. 2.10a).

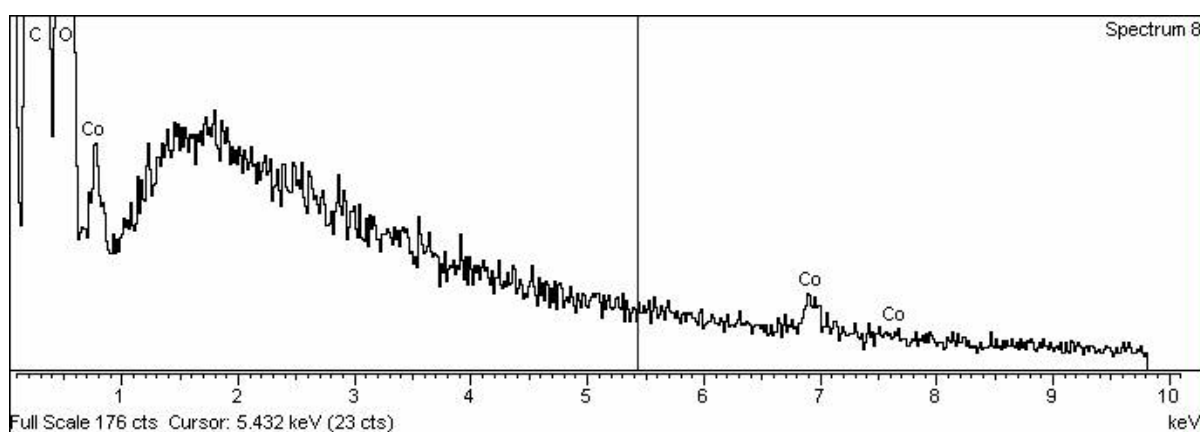


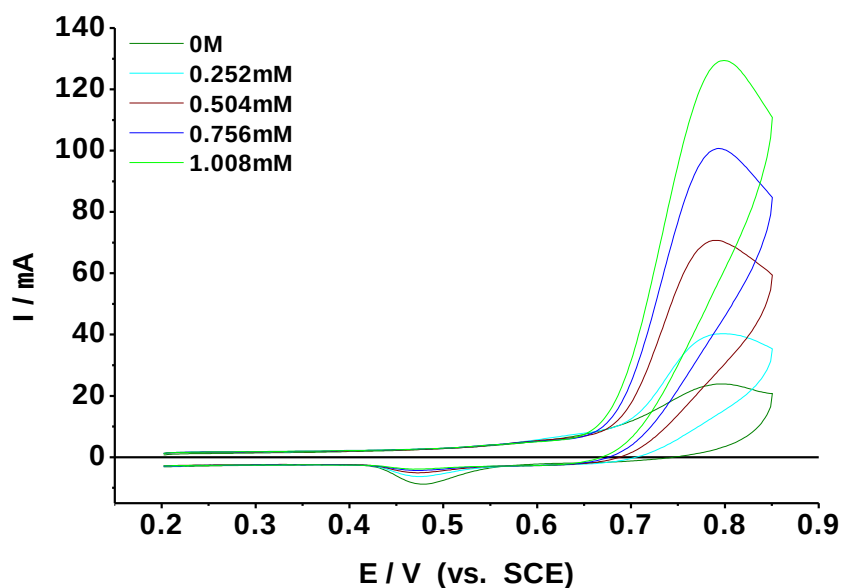
Fig. 2.12: EDS spectrum of BPPG-CoPC modified electrode (Fig. 2.10b).

2.3.4. Electrocatalytic properties of adsorbed cobalt phthalocyanine

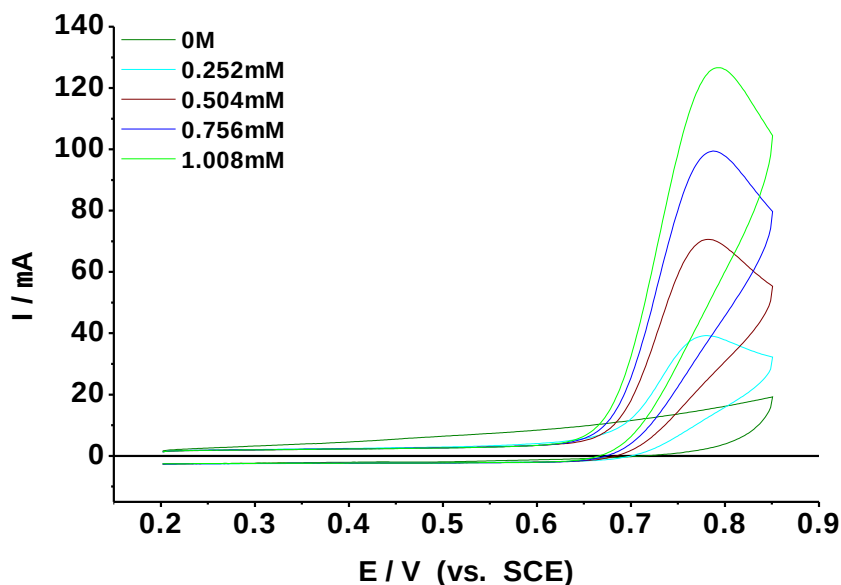
The claimed electrocatalytic properties of EPPG-CoPC modified electrode towards nitrite were studied in phosphate buffer solution (pH 7.2) using cyclic voltammetry (CV).

Fig. 2.13a illustrates cyclic voltammograms of CoPC adsorbed on EPPG electrode in NO_2^- solution for concentrations ranging from 0.25 mM to 1 mM. The same dependence but recorded using bare EPPG electrode is depicted in Fig. 2.13b. It is clear that the main difference between those two figures is the first unlabeled cyclic voltammogram obtained in the absence of NO_2^- . The CoPC-EPPG modified electrode in the investigated potential range exhibits a peak which is growing

upon addition of NO_2^- . It turns out that the next labeled scans look almost the same. The difference between the slopes of standard addition plots for CoPC-EPPG modified electrode and bare EPPG electrode is smaller than 2% (both R^2 0.998). It is clear that CoPC present on the EPPG surface has no influence on the oxidation of nitrite.



(a) EPPG-CoPC



(b) EPPG

Fig. 2.13: Cyclic voltammograms of NO_2^- at (a) EPPG-CoPC modified electrode and at (b) unmodified EPPG electrode (modification time: 2:00 hours) at increasing NO_2^- concentrations. Scan rate: 0.1 V/s.

2.4. Conclusions

The results in this chapter show that CoPC undergoes three distinct types of redox processes in non-aqueous solution and that the thermodynamics of these couples are solvent sensitive. When CoPC is immobilized on graphite (as BPPG or EPPG) it is found to take the form of water insoluble microcrystallites of CoPC which when oxidized from Co(II)PC to Co(III)PC likely undergoes solubilization with loss of surface modification. The role of microcrystallites, as opposed to molecularly adsorbed CoPC, has been neglected in the study of CoPC mediated oxidations, as has the scope for loss of modification from the surface. Moreover careful examination has shown that the reported mediated oxidation of nitrite anions occurs readily on unmodified electrodes! This will be closely addressed in chapter 3.

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Electrochemical determination of nitrite at a bare glassy carbon electrode; why chemically modify electrodes?

The work presented in this chapter has been published in
Sensors and Actuators B: Chemical, 2010, 143, 539–546.

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This chapter describes the oxidation of nitrite which was studied at a bare glassy carbon (GC) electrode in aqueous solution using cyclic voltammetry, square wave voltammetry and chronoamperometry. A mechanism for the electrode reaction is proposed. A limit of detection (LOD) of $4 \cdot 10^{-7}$ M was obtained for amperometry

and this is evaluated with reference to literature reports for NO_2^- detection; in particular the possible merits of using chemically modified electrodes as compared to 'bare' unmodified electrodes are critically assessed.

3.1. Introduction

The need for accurate, rapid and simple methods of nitrite determination comes from its potential toxicity to human health. It may form carcinogenic N-nitrosoamines with secondary amines in the stomach [1–7]. NO_2^- is present in food as a preservative (in different kinds of meat and cheese) or as a natural component (in vegetables). It is also found in water due to chloramination which may give rise to the formation of nitrite within the water distribution system. The concentration of nitrite may increase as the water moves towards the extremities of the network [8]. da Silva and Mazo suggest that the allowable residue of nitrite in potable water is $2.17 \mu\text{M}$ [9] although a value of $4 \mu\text{M}$ is also reported by Gao et al. [10].

The analytical techniques used for detection and determination of nitrate and nitrite have been described in the review by Moorcroft et al. [11]. These include spectroscopic, chromatographic, electrochemical and capillary electrophoresis. Electrochemical methods are often favoured over others because they are faster, cheaper and simpler [3, 12]. Generally, electrochemical methods involve either oxidation or reduction of nitrite at different solid electrodes either bare or modified. Oxidation is usually preferred since the major limitations in cathodic determination of nitrite, namely interferences from reduction of nitrate and molecular oxygen, are avoided [5, 7, 13]. Nitrite is electroactive at glassy carbon, platinum, diamond,

gold, copper and transition metal oxide electrodes [7, 9, 12, 14–17]. However, the application of bare electrodes is said to be limited because several species can poison the electrode surface and decrease the sensitivity and accuracy [7, 15, 18].

Our interest in employing bare GC electrodes for the determination of nitrite comes from a large number of papers on modified GC electrode available and little quantitative data on NO_2^- at a bare one. To our knowledge there is no analytical information available for oxidation/reduction of nitrite at GC such as limit of detection, sensitivity and the range of linear response. It is widely reported that oxidation products and intermediates of nitrite adsorb irreversibly at the surface of the glassy carbon electrode causing its passivation [5, 13, 19, 20] and thus the common approach for determination of nitrite is to use modified GC often without any comparison to bare GC voltammetry. After presenting data for the bare electrode we assess the merits of modified GC electrodes in comparison to the unmodified cases and critically assess the mechanisms, notably ultrasonic cleaning of the electrode, by which surface modification may improve the electrode response.

3.2. Experimental

3.2.1. Reagents

All reagents were used as received without further purification. Hydrochloric acid, acetic acid, sodium acetate, sodium hydroxide and dibasic sodium phosphate were obtained from Aldrich, sodium phosphate monobasic dihydrate from Sigma-Aldrich, disodium tetraborate and sodium nitrite from BDH, potassium chloride from

Riedel-de Haën and sodium nitrate from Fisons. Sodium nitrite solutions were prepared daily prior to experiments. All solutions were prepared using deionised water of resistivity not less than $18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C (Millipore Water Systems, UK).

Solutions in the range pH 1 to pH 12 were prepared as follows: pH 1–pH 3: 0.1 M – 10^{-3} M hydrochloric acid, pH 4.6: 0.1 M acetic acid and 0.1 M sodium acetate, pH 6.8: 0.025 M dibasic sodium phosphate and 0.025 M sodium phosphate monobasic dihydrate, pH 9.2: 0.05 M disodium tetraborate, pH 10–pH 12: 10^{-4} M – 0.01 M sodium hydroxide. All solutions contained 0.1 M potassium chloride as supporting electrolyte. pH measurements were performed using a pH 213 Microprocessor pH Meter (Hanna Instruments).

3.2.2. Instrumental

Electrochemical measurements were conducted using an Autolab PGStat 20 computer-controlled potentiostat (Eco-Chemie, Utrecht, the Netherlands) with a standard three-electrode configuration.

Glassy carbon (3 mm diameter, BAS, Technical, UK) was the working electrode, platinum wire was the counter electrode and a saturated calomel (Radiometer, Copenhagen, Denmark) the reference electrode. For sonoelectrochemical experiments the reference electrode was $\text{Ag}|\text{AgCl}|0.1 \text{ M KCl}$. The glassy carbon electrode was polished with diamond lapping compounds (Kemet, Kent, UK) of decreasing size ($3 \mu\text{m}$, $1 \mu\text{m}$, $0.1 \mu\text{m}$) and sonicated in an ultrasound bath prior to use.

For sonoelectrochemical experiments a 20 kHz ultrasound horn transducer system (Sonics & Materials, VCX400) with a stepped 3 mm microtip (titanium alloy, Jencons,

Leyton Buzzard, U.K.) was used.

3.2.3. Electrochemical experiments

For deaerated experiments the electrochemical cell was a 50 mL beaker covered with parafilm. All solutions were thoroughly deoxygenated with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solutions during experiments (unless stated otherwise).

For sonoelectrochemical experiments the cell was a tube with open top and counter and reference electrodes placed horizontally opposite to each other. The working electrode was placed vertically opposite the ultrasonic horn from the bottom of the tube (in 'face-on' orientation) similar to the setup depicted in ref. [21]. The working volume for all silent experiments was 20 cm³ and 12 cm³ for sonoelectrochemical experiments.

Square wave voltammetry was performed as follows: the electrode was held at the conditioning potential -0.5 V for 5 s, then equilibrated for 2 s; the analytical experiment was carried out at 25 Hz frequency from the initial potential -0.5 V to the end potential 1.2 V , where the step potential was 0.00195 V and amplitude 0.01245 V .

Chronoamperometry was conducted by holding the electrode at a conditioning potential of 0.35 V before stepping to 1.0 V for the rest of experiment (1000 s).

3.3. Results

3.3.1. Voltammetric dependence on the solution pH and the mechanism of nitrite oxidation

In order to find the pH dependence of the nitrite oxidation on a glassy carbon electrode (GC), cyclic voltammograms (CVs) were recorded at a scan rate of 0.1 V/s in 2 mM nitrite solutions of various pHs from 1 to 12. The obtained CVs show an oxidation peak appearing at ca +0.8 V (vs. SCE) (Fig.3.1). These were analyzed to extract the peak current, I_p , and peak potential, E_p , at each pH. The peak current increases significantly for solutions of pH up to ca 4 after which the value is approximately constant (Fig.3.2a). Measurement of the peak potential vs. pH (Fig.3.2b) shows that oxidation of nitrite is essentially independent of pH for solutions of pHs rather higher than 3.3 (the pK_a for nitrous acid, HNO_2 , is between 3.2 and 3.4 [22–24]). These observations are in agreement with previous literature reports [20, 25, 26].

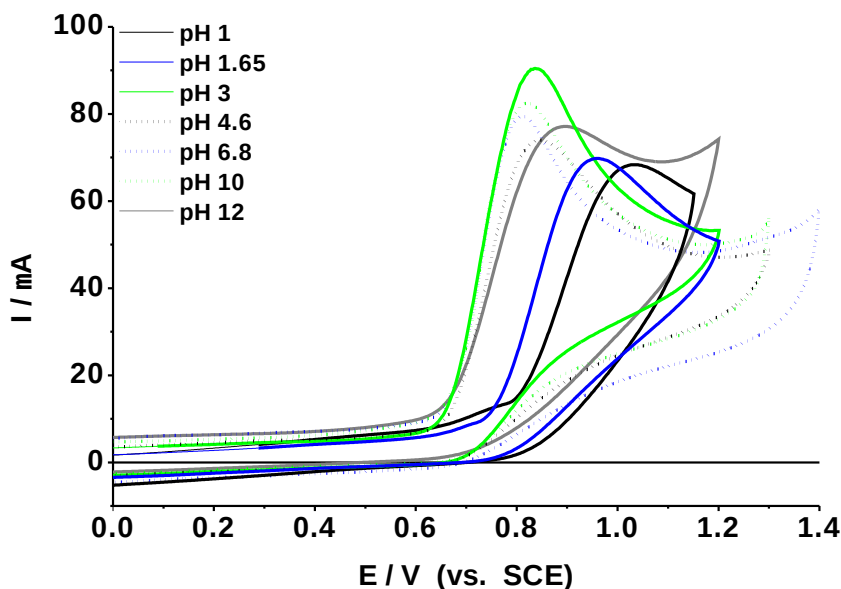


Fig. 3.1: Cyclic voltammograms of a bare GC electrode in 2 mM nitrite solutions of various pHs. Scan rate: 0.1 V/s.

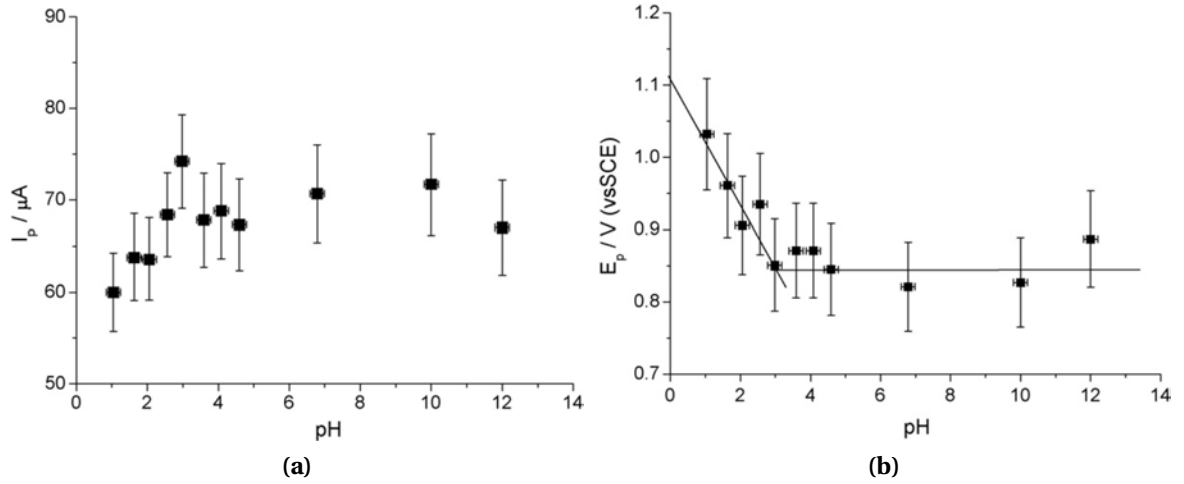


Fig. 3.2: (a) Peak current and (b) peak potential dependence on solution pH for oxidation of nitrite on GC electrode (data from experiments in Fig. 3.1).

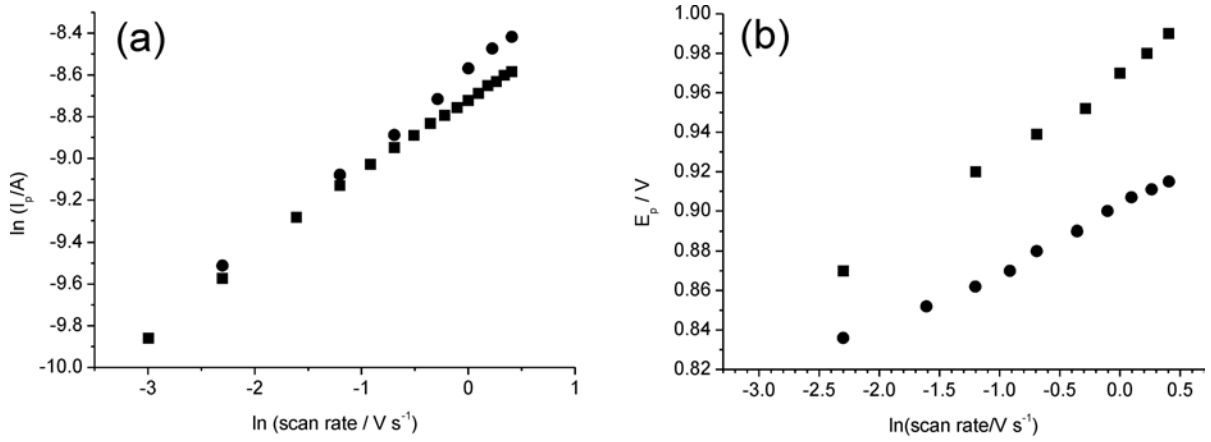


Fig. 3.3: Variations of (a) peak current, and (b) peak potential with scan rate for experiments conducted at pH 3 (●) and pH 7.3 (■).

The mechanism for nitrite oxidation at solid electrodes has been thoroughly investigated [26–28], and the following proposed:



where k_0 is the standard electrochemical rate constant, k_a is the association rate constant for nitrous acid (HNO_2) and k_d is the rate constant for the final disproportionation step. The chemical step (3.1) accounts for the reduction in

current at pH values below the pK_a of HNO_2 .

Piela and Wrona [26] conducted rotating disk studies on solid gold and glassy carbon (GC) electrode surfaces. From an analysis of their steady-state voltammetry obtained on GC, following a method due to Ulstrup [29], they were able to derive values for the following. The rate constant for the final disproportionation step, k_d , was $(1.1 \pm 0.1) \cdot 10^6 \text{ dm}^3/\text{mol} \cdot \text{s}$, and the diffusion coefficient for NO_2^- (which was assumed to be equal with that of NO_2) was $1.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$.

Cyclic voltammetric experiments were conducted in solutions of pH 3 and pH 7.3, to measure the oxidation of nitrite at a range of scan rates from 0.1 V/s to 5 V/s. Fig. 3.3 shows the variations in oxidative peak current and potential with scan rate.

A value of $(1 - \alpha)$ can be extracted from Fig. 3.3b using the expression:

$$E_p = \frac{RT}{2(1 - \alpha)F} \ln \nu + K \quad (3.4)$$

for the variation of peak potential with voltage scan rate, ν , R , T , and F have their usual meaning, and K is a constant [30], with the result of $(1 - \alpha) = 0.65 \pm 0.07$.

The experimental waveshapes were then fitted using Digisim™, according to the CE mechanism described in steps (3.1) and (3.2) above. Using the above literature values combined with the pK_a for nitrous acid of 3.3 [26], very good fits were obtained between simulation and experiment for a range of scan rates from 0.1 V/s to 5 V/s at solution pH 3 and 7.3 (Fig. 3.4). For these simulations the acid association rate constant, k_a , in step (3.1) was found to be $50 \pm 5 \text{ dm}^3/\text{mol} \cdot \text{s}$. Since the voltammetry is electrochemically irreversible, the formal potential, $E^{\ominus'}$, and heterogeneous electron transfer rate, k_0 , are not separately measurable in the

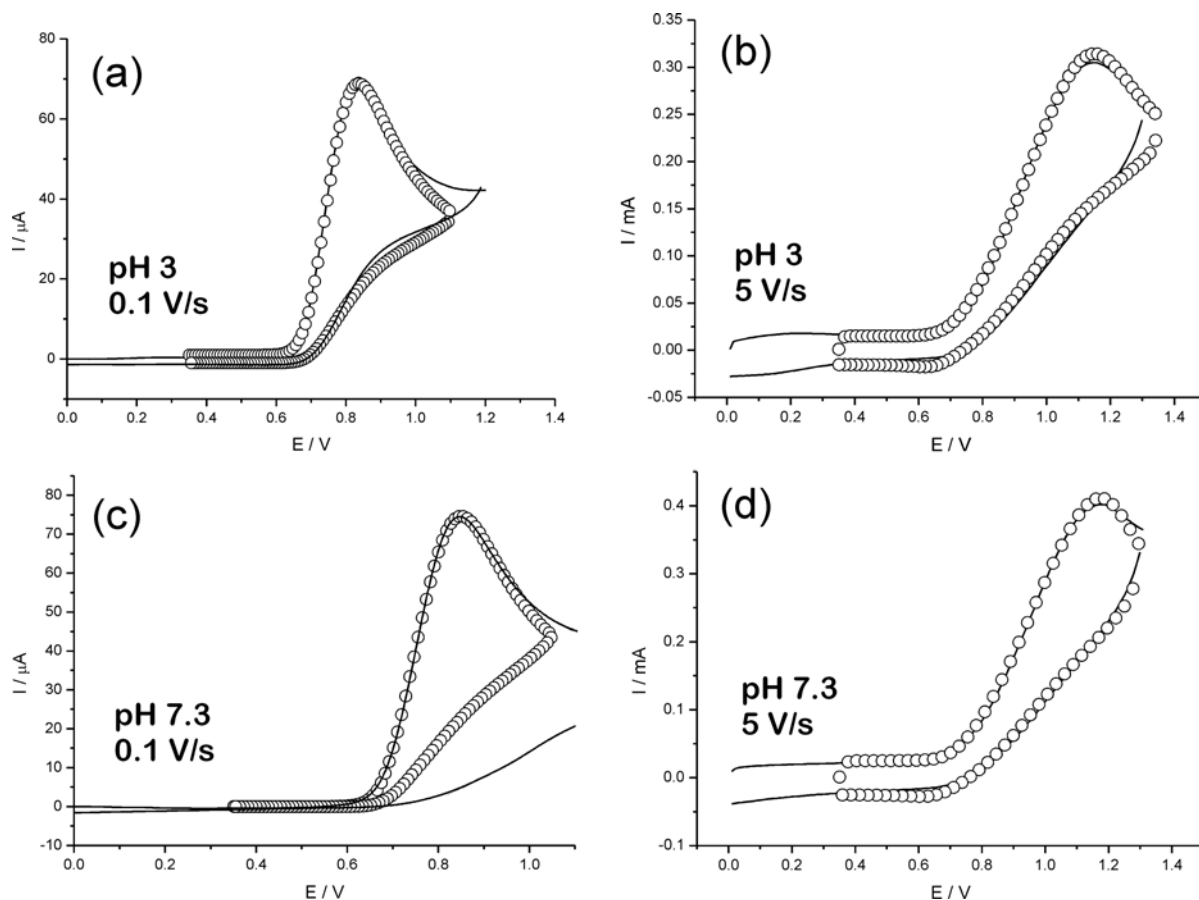


Fig. 3.4: Representative fits of simulation (○) and experiment (—) for different pH and scan rates (ν).

experiment reported. The value $k_0 \exp \frac{-(1-\alpha)FE^{\ominus'}}{RT}$ was found from Digisim™ to be $3.8 \cdot 10^{-11}$ cm/s for pH 7.3 and $8.9 \cdot 10^{-11}$ cm/s for pH 3.

3.3.2. Analytical applicability

The possible analytical application of the bare, unmodified GC electrode for electrochemical detection of nitrite was tested using the standard addition method for cyclic voltammetry, square wave voltammetry and amperometry, all being methods widely used in the relevant literature [5–7, 10, 13, 15, 22, 23, 31–42]. All analytical experiments were conducted at pH 3, unless stated otherwise.

3.3.2.1. Cyclic voltammetry

First, a 'blank' voltammogram was recorded for the GC electrode response in 20 mL of pH 3 solution (containing 10^{-3} M HCl and 0.1 M KCl) at a scan rate of 0.1 V/s. Then, a $10\ \mu\text{L}$ aliquot of 0.02 M NaNO_2 stock solution was added to the beaker, stirred vigorously to ensure thorough mixing, and another CV was recorded. This procedure was repeated for the 0.02 M, 0.2 M and 0.4 M stock solutions of nitrite (so that the volume of additions did not exceed 10% of the total volume) until the level of nitrite was $5.5 \cdot 10^{-3}$ M as shown in Fig. 3.5a.

A plot of peak current vs. concentration (Fig. 3.5b) was found to be linear in the range $5 \cdot 10^{-5}$ M to $4.7 \cdot 10^{-3}$ M with correlation coefficient 0.999. The calculated limit of detection (LOD) (based on 3σ) was $2 \cdot 10^{-4}$ M and the sensitivity was $3.3 \cdot 10^{-2}$ A/M.

3.3.2.2. Square wave voltammetry

Initially, a 'blank' square wave voltammogram (all parameters in section 3.2) was recorded in 20 mL of pH 3 solution, then a $10\ \mu\text{L}$ aliquot of 0.02 M NaNO_2 stock solution was added to the beaker, stirred vigorously to ensure thorough mixing, and another square wave voltammogram was recorded. This procedure was repeated for the 0.02 M, 0.2 M and 0.8 M stock solutions until the level of nitrite was $1 \cdot 10^{-2}$ M as shown in Fig. 3.5c. A plot of peak current vs. concentration was found not to be linear in any range (figure not shown), whereas the plot of peak area vs. concentration (Fig. 3.5d) is linear in the range $2 \cdot 10^{-5}$ M to $6.4 \cdot 10^{-3}$ M with correlation coefficient 0.998. The calculated limit of detection (LOD) (based on 3σ) was $3 \cdot 10^{-4}$ M and the sensitivity was $1.6 \cdot 10^{-3}$ A·V/M.

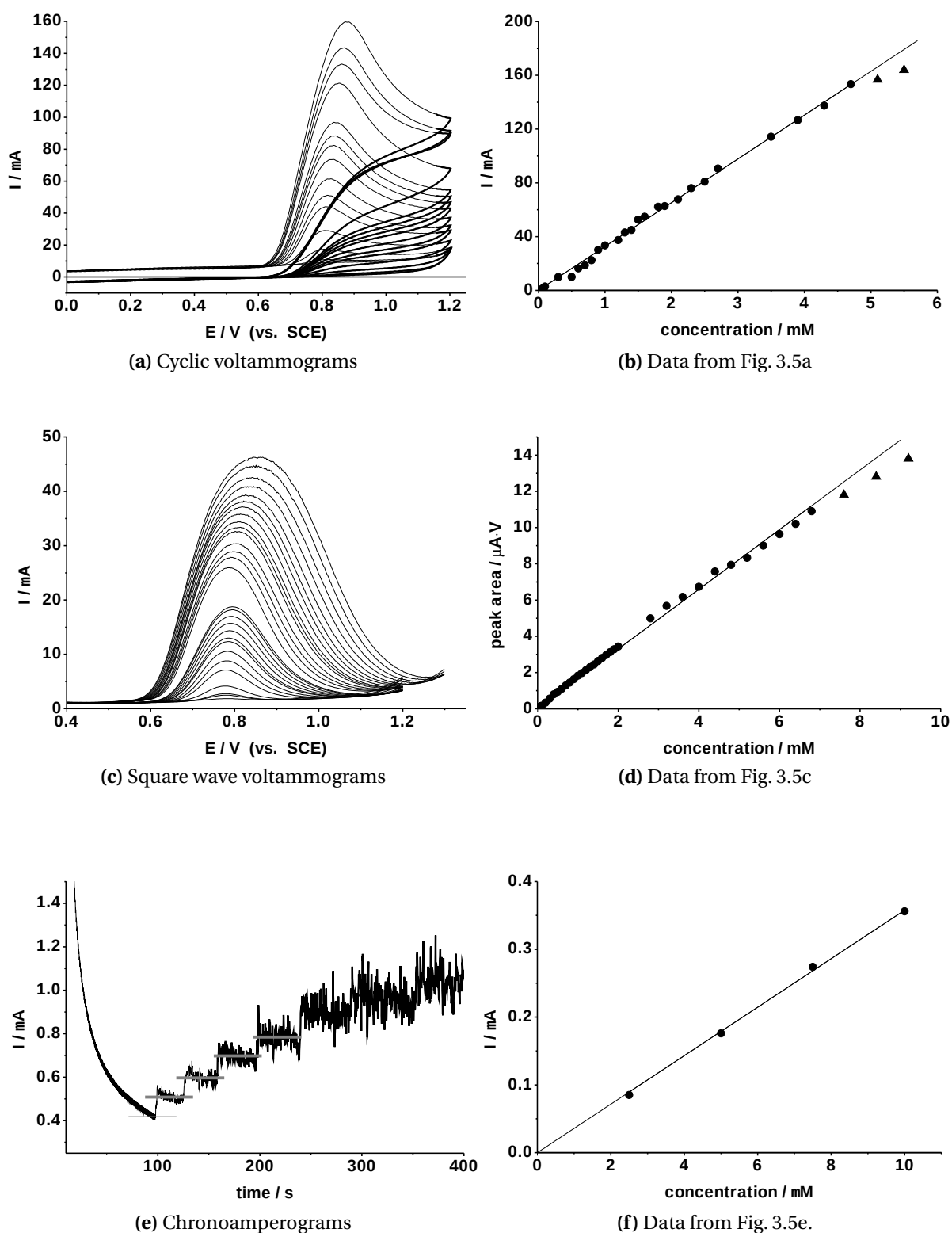


Fig. 3.5: (a) Cyclic voltammograms, (c) square wave voltammograms and (e) chronoamperograms for the oxidation of nitrite at GC electrode in pH 3 solution increasing the NO_2^- concentration at scan rate of 0.1 V/s. (b), (d), (f): Standard addition plots ($\blacktriangle$ – points which deviate from linearity).

3.3.2.3. Chronoamperometry

At the beginning of the experiment (all parameters in section 3.2) the beaker contained only 20 mL of pH 3 solution which was stirred during the experiment at a constant speed with a magnetic bar. After ca 100 s the first 10 μ L aliquot of 0.02 M NaNO₂ stock solution was added to the beaker. After just four additions ($2.5 \cdot 10^{-6}$ M each) the electrode response became less well-defined as the signal to noise ratio decreased significantly, such that the determination of current was ambiguous. A plot of the current vs. concentration (Fig. 3.5f) was found to be linear in the range $2.5 \cdot 10^{-6}$ M to $1.0 \cdot 10^{-5}$ M with correlation coefficient 0.9996. Calculated limit of detection (LOD) (based on 3σ) was $4 \cdot 10^{-7}$ M and the sensitivity was $3.6 \cdot 10^{-2}$ A/M. The same experiment was carried out in the presence of ultrasound but no improvement was found. A sonoelectrochemical experiment was carried out with a low intensity of ultrasound (12 W/cm²), below the cavitation threshold. This intensity was chosen because at higher levels the nitrite oxidation wave was shifted to such positive potentials, that it merged with the onset of solvent breakdown. Another reason for using low intensity was minimizing the noise detected in the chronoamperogram which was already significant for the silent chronoamperometric experiment (Fig. 3.5e).

3.3.2.4. Sonoelectrochemical GC electrode cleaning

It has been reported that NO₂⁻ oxidation products and intermediates adsorb at the surface of the glassy carbon electrode [5, 13, 19, 20]. One possible way to maintain the sensitivity of glassy carbon electrode is to ensure its surface is kept free from adsorbates during the standard addition experiment. Fig. 3.6 illustrates

how the electrode response changes in the second cycle in NO_2^- solution. The peak current in the second scan is smaller by ca 35%. In order to minimize the current decrease, the electrode was then sonicated at 34.5 W/cm^2 (above cavitation threshold) in between the first and the second scan. Using this procedure the second scan now did not differ from the first one. This clearly indicates that sonication provides better stability of the GC electrode response.

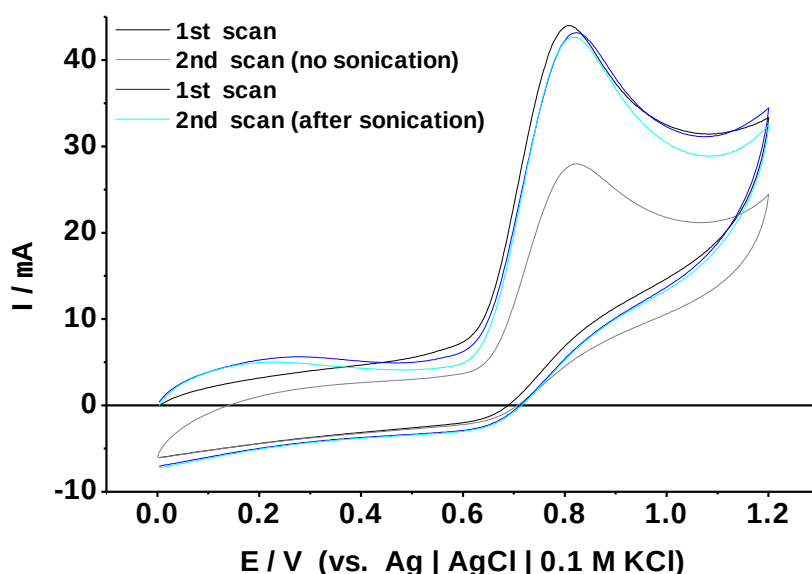


Fig. 3.6: Cyclic voltammograms for the oxidation of nitrite at bare GC electrode in pH 3 solution without sonication and after 30 s of sonication at amplitude 5% (scan rate: 0.1 V/s, no deoxygenating, nitrite concentration: 2 mM).

3.3.2.5. Comparison of results

The experimental results obtained for oxidation of nitrite at glassy carbon electrode show that it is possible to use bare GC for the determination of NO_2^- . Sonication in between scans ensures clean electrode surface and stability of GC response. The most sensitive technique for the determination of nitrite (without sonication) was found to be chronoamperometry. The lowest limit of detection (based on 3σ) was calculated also from chronoamperometry. It is important to note that in terms of analytical applicability voltammetry may offer the advantage

of having a wider range of linear response than chronoamperometry (Fig. 3.7) with slightly lower sensitivity.

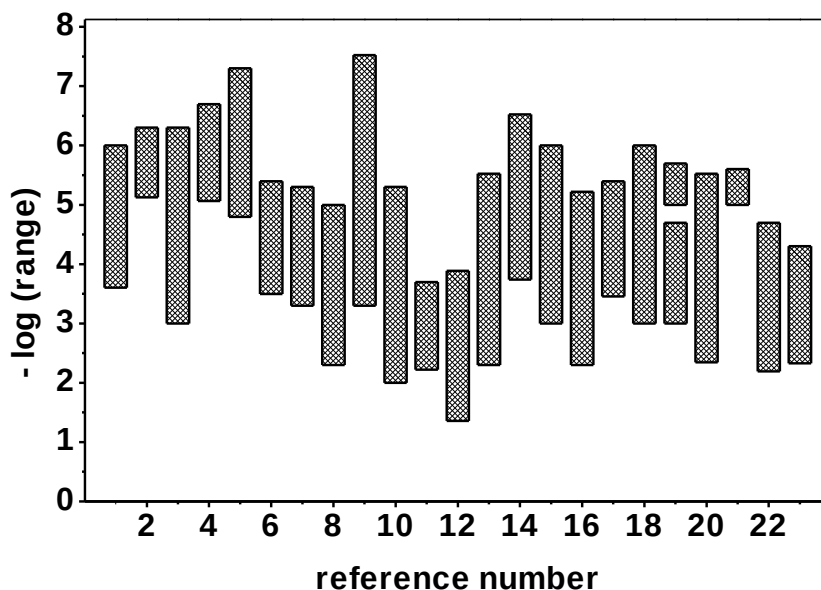


Fig. 3.7: Ranges of linear response for the electrochemical detection of nitrite. The list of references: 1. [23], 2. [34], 3. [43], 4. [33], 5. [13], 6. [36], 7. [7], 8. [40], 9. [32], 10. [39], 11. [41], 12. [42], 13. [31], 14. [6], 15. [22], 16. [38], 17. [15], 18. [10], 19. [35], 20. [37], 21. this chapter — chronoamperometry, 22. this chapter — SWV, 23. this chapter — CV.

3.3.2.6. Edge plane pyrolytic graphite (EPPG) vs. glassy carbon (GC)

Fig. 3.8 presents the cyclic voltammograms for NO_2^- oxidation at a bare GC and bare EPPG electrode, with current normalized by area to account for different electrode sizes. The voltammetry appears more electrochemically reversible on EPPG than on GC as reflected by the lower overpotential required for the oxidation. The peak current for EPPG is 1.32 ± 0.05 times higher than for GC electrode. This difference is discussed below in section 3.4.

3.3.2.7. Nonelectroactivity of nitrate

Fig. 3.9 illustrates cyclic voltammograms of bare glassy carbon electrode in solutions containing either NO_2^- or NO_3^- . Clearly, there is an oxidation peak only

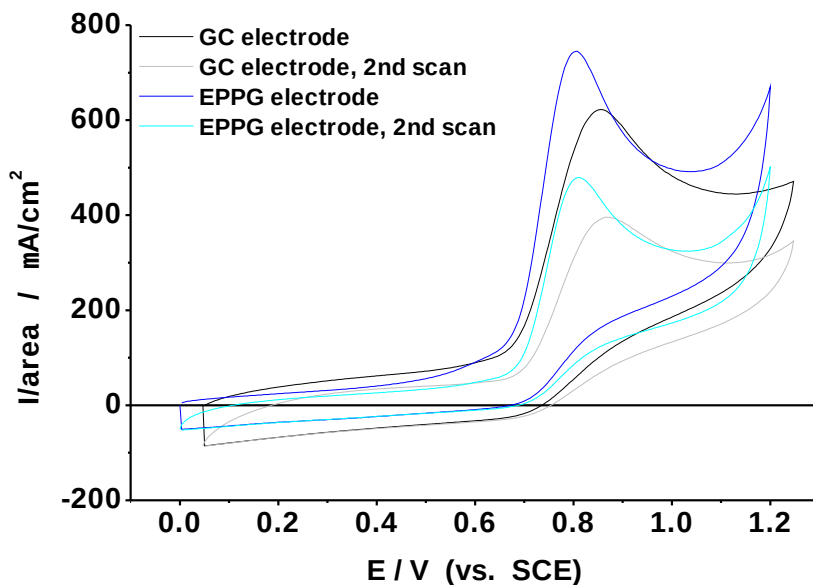


Fig. 3.8: Comparison of GC and EPPG electrode response in pH 3 solution containing 1 mM NO_2^- (scan rate: 0.1 V/s, no deoxygenating).

for nitrite, thus we conclude that the determination of NO_2^- using bare GC is also possible in solutions containing both nitrite and nitrate. This is analytically very important as both species are usually found together, because their chemistries are linked [11].

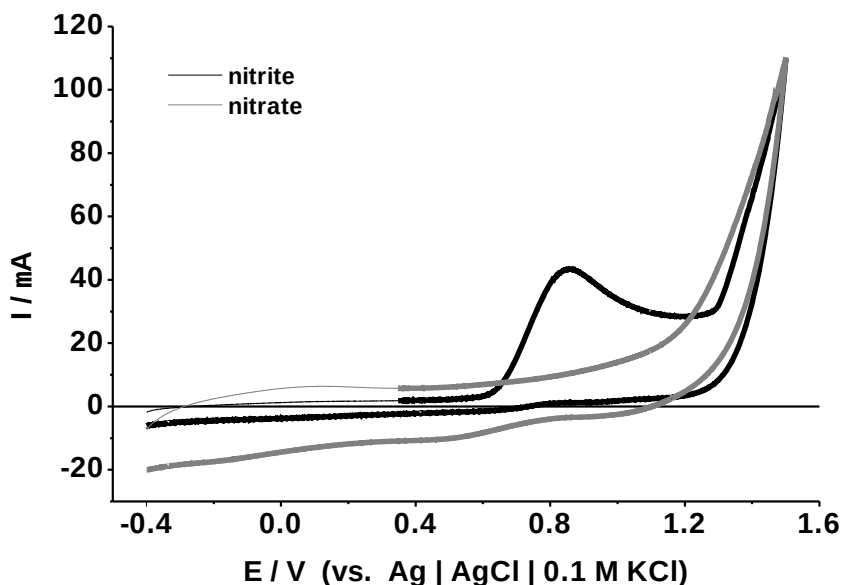


Fig. 3.9: Cyclic voltammograms for GC electrode in pH 3 solution of 2 mM with nitrite or with nitrate (scan rate: 0.1 V/s, no deoxygenating).

3.4. Discussion

Much work has been undertaken modifying GC for the electroanalytical detection of NO_2^- . The variety of reported modifications of glassy carbon electrode is vast (Tab. 3.1, page 103). The list includes and is not limited to metal and metal oxide nanoparticles and nanoclusters, carbon nanotubes, electrocatalytically active molecules (hemoglobin (Hb), metal phthalocyanines (MPCs)), organic and inorganic electropolymerized films, sol-gel and modifications and combinations of these.

The variety of detection limits (Tab. 3.1, page 103) and ranges of linear response (Fig. 3.7) are also great. In the following we focus on a comparative account of the different electrodes and their responses to nitrite.

In discussing the rationale for the modification of GC with gold nanoparticles Huang et al. [22] say "Generally, compared with bulk gold electrode, the nano-Au layer on the surface would enable fast electron transfer kinetics and make a decrease in the overpotential needed, which made [sic] the voltammetry appear reversible, and the redox reaction become kinetically viable." Similar arguments are often presented for modifying electrode surfaces with many of the wide range of materials mentioned above. It is interesting therefore to consider, in general, the effects of varying the electrode kinetics, keeping all other parameters constant. In particular assuming planar Fickian diffusion to a flat surface, conventional theory recognizes two limiting cases. For an oxidation as with NO_2^- detection above:



In the fully reversible limit where the electrode kinetics are fast compared to the prevailing mass transport a voltammogram such that in Fig. 3.10 ($k = 1 \text{ cm/s}$) is

seen where the average of the forward (oxidative) and back (reductive) potentials correspond to the formal potential. Adopting a Butler-Volmer parameterization, so that the net rate of electrochemical reaction is given by:

$$J_{\text{net}} = k_a[\text{R}]_0 - k_c[\text{O}]_0, \quad (3.6)$$

where

$$k_a = k_0 \exp \frac{(1 - \alpha)F(E - E_{\text{O/R}}^{\ominus'})}{RT}, \quad (3.7)$$

$$k_c = k_0 \exp \frac{-\alpha F(E - E_{\text{O/R}}^{\ominus'})}{RT} \quad (3.8)$$

and $[\text{R}]_0$ denotes the surface concentration of R and $[\text{O}]_0$ the surface concentration of O, then as the electrochemical rate constant is decreased an ‘overpotential’ develops for the electrode process and the peak potential for the R to O oxidation shifts to more positive potentials. Fig. 3.10 shows for a range of k_0 values, for the case of $\alpha = 0.5$, $D_{\text{R}} = D_{\text{O}} = 1 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $E^{\ominus'} = 0 \text{ V}$, $\nu = 0.1 \text{ V/s}$, electrode area: 0.0707 cm^2 and $[\text{R}]_{\text{bulk}} = 0.001 \text{ M}$ ($[\text{R}]_{\text{bulk}}$ is the bulk concentration of R) how the current, I , varies with the applied potential E . As k_0 decreases the peak current, I_p , tends to a constant value characteristic of the fully irreversible limit according to Randles and Ševčík:

$$I_p = 2.99 \cdot 10^5 (1 - \alpha)^{1/2} A [\text{R}]_{\text{bulk}} D_{\text{R}}^{1/2} \nu^{1/2} \quad (3.9)$$

for a one electron process, ν is scan rate (V/s), A is an electrode area (cm^2), $[\text{R}]_{\text{bulk}}$ is a bulk concentration of R (mol/cm^3) and D_{R} is the diffusion coefficient of R (cm^2/s). The fully reversible limit for a one-electron process according to

the Randles-Ševčík equation is:

$$I_p = 2.69 \cdot 10^5 A [R]_{\text{bulk}} D_R^{1/2} \nu^{1/2}. \quad (3.10)$$

The peak currents for the fully reversible and fully irreversible limits differ only by a factor of 1.27 (assuming $(1 - \alpha) = 0.5$):

$$\frac{I_{p, \text{rev.}}}{I_{p, \text{irrev.}}} = \frac{2.69 \cdot 10^5 A [R]_{\text{bulk}} D_R^{1/2} \nu^{1/2}}{2.99 \cdot 10^5 (1 - \alpha)^{1/2} A [R]_{\text{bulk}} D_R^{1/2} \nu^{1/2}} = \frac{2.690}{2.99 \cdot (0.5)^{1/2}} = \frac{2.690}{2.114} = 1.27. \quad (3.11)$$

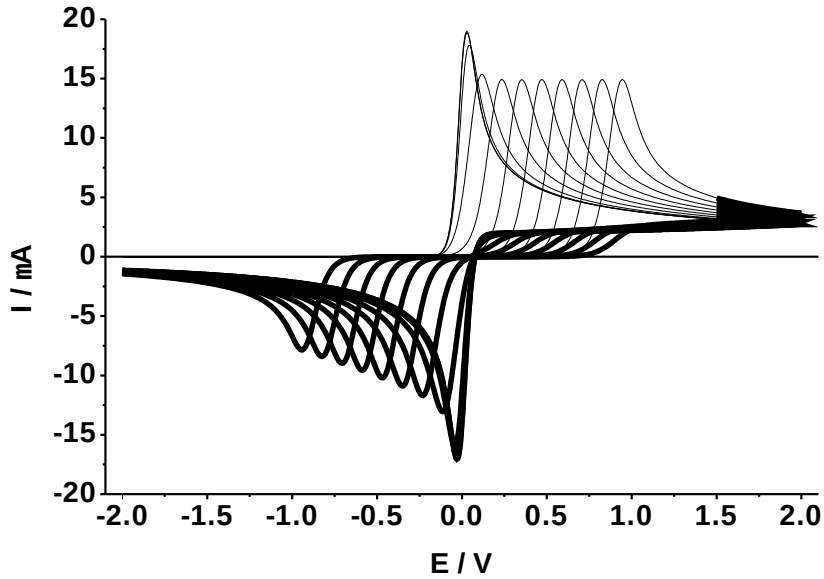


Fig. 3.10: Simulation of one-electron oxidation process. $\alpha = 0.5$, $D_R = D_O = 1 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $E^{\ominus'} = 0 \text{ V}$, $\nu = 0.1 \text{ V/s}$, $A = 0.0707 \text{ cm}^2$, $[R]_{\text{bulk}} = 0.001 \text{ M}$, k_0 ranges from 1 to $1 \cdot 10^{-10} \text{ cm/s}$.

It is clear from the above that the effect of much altered electrode kinetics is a significant change in a peak potential but only a tiny change in the peak current. It follows that the former are best suited to identify electrocatalysis rather than the latter. Moreover if as a result of surface modification the currents change by a more than a factor of 1.27 then it is clear that physical reasons other than a change in electrode kinetics must be found to explain the change. The difference in peak currents between GC and EPPG electrodes noted above (section 3.3.2.6, page 93) is close to the factor of 1.3 suggesting that diffusion

controlled irreversible and reversible peaks are being observed.

From an analytical perspective it is the peak current that is of analytical use. It follows from the above argument that unless the surface modification makes voltammetrically visible a response which is otherwise outside of the solvent window, then simply altering the electrode kinetics per se will be unlikely to have a major benefit in terms of analytical sensitivity.

There are many examples in the literature in which surface modification leads to a significant enhancement of peak currents in excess of those predicted for semi-infinite diffusion to a planar electrode. Such increases are often accompanied by a decrease or an apparent decrease in overpotential. Such behaviour is reported by Huang et al. [22] in the context of nitrite oxidation by making a (porous) film of gold nanoparticles in the form of a composite with the polymer poly(3-methylthiophene). Electrodes covered with films of carbon nanotubes show analogous responses in respect of the oxidation of ferrocyanide [44], dopamine and epinephrine [45]. In these cases the nanoparticles or the nanotubes provide an electrode of high effective area and so the target molecules within the film are electrolysed as if in a thin layer cell, since the distance of diffusion to the conducting material, nanotubes or nanoparticles dispersed in the film is short. Such behaviour not only can lead to a significant current enhancement but also, because of the change of diffusion regime, to a peak potential closer to the formal potential, than seen for planar, semi-infinite diffusion. Note it has been shown [44] that there must not be enhanced electron kinetics for electrolysis on the nanoparticles or nanotubes for this to occur. Such thin layer effects may also explain supposed 'electrocatalysis' seen at C₆₀ film-modified electrodes [46, 47].

A very sensitive LOD of $1.5 \cdot 10^{-8}$ M for NO_2^- oxidation has been reported by Casella and Salvi [32], who formed a Pt-CME of polydispersed platinum on a glassy carbon electrode. The responses of the Pt-CME to nitrite were in excess of the maximum factor of 1.27 for the irreversible and reversible transfer discussed above. It follows that the thin film model may account, at least in part, for the success of the approach. It also prompts the question as to what are the mechanisms by which nanoparticles can influence voltammetric response.

By virtue of mass transport via convergent rather than planar diffusion the current density at an isolated nanoparticle for mass transport controlled conditions is greater than at a planar electrode. For the case of an isolated spherical nanoparticle sitting upon a planar electrode, assuming electrolysis occurs only at the nanoparticle surface, the mass transport controlled limiting current is:

$$I_{\text{lim}} = -8.71 F D r [\text{O}]_{\text{bulk}}, \quad (3.12)$$

for a one electron process, r is the radius of the sphere and $[\text{O}]_{\text{bulk}}$ is the bulk concentration of the electroactive species, O, which has a diffusion coefficient D [48]. If the surface coverage of nanoparticles is increased then, as the diffusion fields of the individual nanoparticles began to overlap, the average current per particle begins to decrease although the overall current increases; the voltammetric response becomes peak shaped. Assuming at most only monolayer coverage of spheres, the average current drops until there is full overlap of the diffusion layers in which limit the current to the substrate electrode as a whole reflects that predicted by the Randles-Ševčík equation [30] for geometric area of the substrate. That is to say the current to the substrate electrode can never be larger than

that predicted by the Randles-Ševčík equation for the geometric substrate area in operation provided the coverage of spherical nanoparticles is monolayer. The only exception to this is at such extremely high scan rates that the diffusion layer thickness corresponding to the peak current is constrained to a very thin 'skin' that reflects the surface area of the spheres rather than that of the substrate [49].

It follows from the above arguments that if surface modification with a large number of nanoparticles results in a significant increase in peak current then this must in part reflect the film formation and the change from planar thin layer mass transport. Of course nanoparticles may be electrocatalytic compared to bulk electrodes of the same material but it is clear from the above discussion of reversible vs. irreversible processes that a monolayer of nanoparticles can at most produce the reversible current for planar diffusion to an area corresponding to that of the underlying electrode. It follows that substantial increases in peak currents likely reflect mass transport rather than electrode kinetic effects providing a diffusion controlled current is observed.

The above discussion has indicated that LODs are related to the mass transport regime operating at the electrodes of interest. It is important therefore when comparing reported LODs to compare the transport regimes under which measurements are made. It is clear from Tab.3.1, page 103, that the most sensitive LODs are those recorded under 'hydrodynamic' or stirred conditions. The role of convection in increasing transport is significant and thus is the basis of sonovoltammetry [50–53]. Similarly LODs measured using pulse voltammetry of some sort (SWV, DPV, etc.) will be more sensitive than those measured from dc voltammetry since the potential steps which are intrinsic to the voltammetry will

lead to steeper concentration gradients than found near the peak currents in dc voltammetry [54].

In order to discriminate the faradaic signals from background currents (which are increased by capacitative charging), the use of potentiostatic conditions (or as a close equivalent, a pulse voltammetry with time steps sufficiently long that any charging has effectively decayed to zero when the current is sampled), will produce more reliable measurements of low LODs. It follows that the so-called ‘amperometry’ method of measuring limits of detection is superficially attractive for obtaining low LODs. In this method an electrode is potentiostatted at an optimal potential for the detection of the target and standard additions made. Plots of current vs. time are then used to find the LOD value. Whilst low LODs result from this method the approach is rather different from what would be used in usual analytical procedures so it should be viewed with caution. In the case of nitrite oxidation this approach leads to the lowest LOD values reported using this electrolytic reaction [13, 32].

Analysis of amperometry and other data should proceed via an approach close to the excellent summary given by Brett and Oliveira Brett [54] in which a linear calibration plot $y = a + bx$ is analyzed to give values of standard deviation, s_B , and slope b ; the value $3\frac{s_B}{b}$ is the resulting LOD. As Brett and Brett point out this method may, for reasons of experimental procedure or instrumental limitations such as noise and drift at low signal levels, give values of signal which cannot in practice be resolved from the background. In many of the cases reported in Tab.3.1, page 103, it is not clear how the LOD has been evaluated (e.g. [7, 22]); in the case of reference [13] the plot of peak current vs. $[\text{NO}_2^-]$ shows a positive

intercept and the reader is told that the LOD of $3.4 \cdot 10^{-10}$ M is based on "S/N=3 (Figure not shown)".

A final issue for comparison is that of reproducibility and electrode fouling. It is clear from the discussion above that prolonged oxidation of nitrite at GC leads to a slight signal decrease probably due to adsorption on the electrode surface either slowing down the electrode kinetics of the oxidation, or partially blocking the reaction completely. One value of surface modification [13] is that prior adsorption of suitable material can prevent this occurring. Alternatively, as seen above, sonication can preserve electrode activity. The latter provides a general method for surface activation whilst the former may explain the success of some of the surface modifications in Tab.3.1, page 103.

3.5. Conclusions

In this chapter it has been demonstrated that a bare glassy carbon (GC) electrode can be used for the quantitative determination of nitrite in aqueous solutions, and a limit of detection $4 \cdot 10^{-7}$ M was obtained using chronoamperometry. Sonoelectrochemical cleaning of GC electrode was shown to maintain the electrode surface activity. Moreover, some possible misinterpretations of analytical results obtained with chemically modified electrodes widely reported in the literature were critically reviewed.

In the next chapter the influence of unbuffered media on voltammetric responses of surface bound and solution phase anthraquinone moieties will be described.

Tab. 3.1: GC electrode modifications from the literature. Abbreviations: **PdSiW₁₁** – potassium salt of palladium(II)-substituted Keggin type heteropolytungstate, **K₆[(H₂O)PdSiW₁₁O₃₉]**, **CME** – chemically modified electrode, **p-ATT** – electropolymerized film of 5-amino-1,3,4-thiadiazole-2-thiol, **GCE** – glassy carbon electrode, **FeT4MPyP/CoTSPc** – alternated layers of iron(III) tetra-(N-methyl-4-pyridyl)-porphyrin (FeT4MPyP) and cobalt(II) tetrasulfonated phthalocyanine (CoTSPc), **Hb** – hemoglobin, **HS-CdS** – CdS hollownanospheres, **FeT4MPyP/CuTSPc** – alternated layers of iron(III) tetra-(N-methyl-4-pyridyl)-porphyrin (FeT4MPyP) and copper tetra-sulfonated phthalocyanine (CuTSPc), **PPy-Pt** – Pt nanoclusters deposited in polypyrrole (PPy) nanowires nanocomposite, **CuHNF** – copper-heptacyanonitrosylferrate, **GC** – glassy carbon, **poly-LS** – polymerized sodium lignosulfonate (LS), **CNT** – carbon nanotube, **NG** – nano-gold, **RTIL** – a room temperature ionic liquid, 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIT), **MWCNTs** – multi-walled carbon nanotubes, **poly-TiTAPc** – polimerized titanium tetraamino phthalocyanine, **PAA** – poly(azure A), **CNTs** – carbon nanotubes, **Pd-Fe** – film of Pd-Fe oxide layers, **TiO₂ Sol-Gel** – titania sol-gel matrix/film, **nano-Au** – gold nanoparticles, **P3MT** – poly(3-methylthiophene), **CSNs** – colloidal silver nanoparticles, **PGCE** – pretreated glassy carbon electrode.

modification	LOD [M]	ox/red of NO ₂ ⁻	technique	sensitivity
PdSiW ₁₁ CME [31]	$2.4 \cdot 10^{-11}$	red	hydrodynamic voltammetry (flow injection analysis)	$y[\text{nA}] = 1.1 + 363.8x[\text{mM}]$
p-ATT-GCE [13]	$3.4 \cdot 10^{-10}$	ox	amperometry (stirred sol.)	320nA/ μM
Pt-CME [32]	$1.5 \cdot 10^{-8}$	ox	amperometric detector in flowing streams ion chromatography	21 μA /mM
FeT4MPyP/CoTSPc [33]	$4.0 \cdot 10^{-8}$	ox	amperometry	0.37 μA ·l/ μmol
Hb/HS-CdS [6]	$8.0 \cdot 10^{-8}$	NO red	amperometry (stirred sol.)	not given
FeT4MPyP/CuTSPc [34]	$1.0 \cdot 10^{-7}$	ox	differential pulse voltammetry	$I(\mu\text{A}) = 0.4(\pm 0.2) + 20(\pm 3.0)c(\mu\text{mol/l})$
PPy-Pt [43]	$1.5 \cdot 10^{-7}$	red	cyclic voltammetry	0.566 μA / μM
CuHNF CME [10]	$3.0 \cdot 10^{-7}$	red	amperometry in a flowing system	not given
GC poly-LS [23]	$3.0 \cdot 10^{-7}$	red	amperometry	128nA/ μM ·cm ²
CNT-modified GC [35]	$5.0 \cdot 10^{-7}$	red	differential pulse voltammetry	not given
NG/GC [7]	$5.0 \cdot 10^{-7}$	ox	cyclic voltammetry	$ip(\mu\text{A}) = 0.2195 + 0.2636c(10\mu\text{M})$
Hb/RTIL/MWCNTs [36]	$8.1 \cdot 10^{-7}$	red	amperometry (stirred sol.)	$I(\mu\text{A}) = 1.00154 + 0.04592C(\mu\text{M})$
poly-TiTAPc [5]	$1.0 \cdot 10^{-6}$	ox	cyclic voltammetry	not given
PAA/CNTs/GC [37]	$1.0 \cdot 10^{-6}$	red	amperometry (stirred sol.)	not given
Pd-Fe/GCE [38]	$1.0 \cdot 10^{-6}$	red	differential pulse amperometry (stirred sol.)	not given
Hb/colloidal gold nanoparticles sol-gel TiO ₂ film-modified GCE [15]	$1.2 \cdot 10^{-6}$	red	amperometry	not given

continued on next page

Tab. 3.1 – continued

modification	LOD [M]	ox/red of NO ₂ ⁻	technique	sensitivity
catalase-MWCNTs-modified-GC [39]	1.35 · 10 ⁻⁶	red	amperometry (stirred sol.)	I _p (μA)=0.007c(μM)+0.006μA
nano-Au/P3MT/GCE [22]	2.3 · 10 ⁻⁶	ox	amperometry	not given
nano-Au/GCE [40]	2.4 · 10 ⁻⁶	ox	cyclic voltammetry	I _p (μA)=0.098+22.2C[mM]
GCE/Hb-CSNs/TiO ₂ Sol-Gel [41]	3.4 · 10 ⁻⁵	red	amperometry (stirred sol.)	-5.84μA/mM·cm ²
nanometer-sized gold colloid ethylenediamine/PGCE [42]	4.5 · 10 ⁻⁵	red	amperometry (stirred sol.)	i(μA)=0.1568+3.1516c[mM]

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Voltammetric responses of surface-bound and solution-phase anthraquinone moieties in the presence of unbuffered aqueous media

The work presented in this chapter has been published in
Journal of Physical Chemistry C, 2011, 115, 714–718.

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The voltammetry of solution-phase redox species involving proton transfer are known to be qualitatively altered under conditions of nonbuffered media [1]. This chapter reports first the voltammetric response of solution-phase anthraquinone monosulphonate on a gold macroelectrode in the presence of a limited concentration of protons; further it provides quantitative analysis of the voltammetry under unbuffered conditions whereby it is possible to demonstrate through simulation that in some conditions the pH at the electrode may alter by up to 5–6 pH

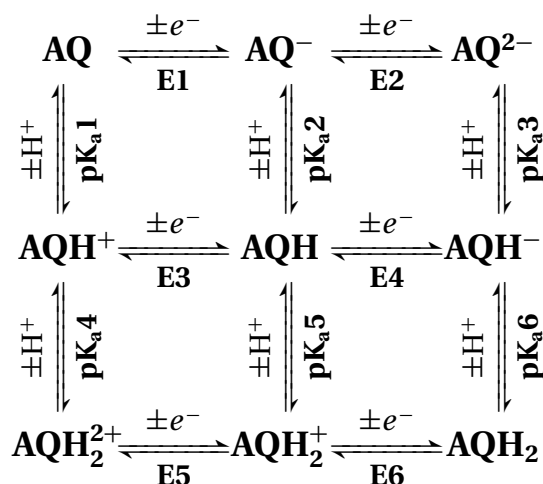
units as compared to that of the bulk solution. This change in local environment adjacent to the electrode is caused by the consumption of protons during the electrochemical process. As a result, in conditions of low buffering the electrochemical reduction is limited by the availability of protons, leading to a measured voltammetric signal with two voltammetric waves. Second, the work in this chapter is developed through the study of an anthraquinone modified pyrolytic graphite electrode under conditions of finite proton concentration. It is demonstrated experimentally how analogous split wave results occur for surface confined species. These results provide physical insight into the consumption of protons during the electrochemical process and highlight how methods of pH measurement based upon the use of redox modified electrode surfaces are nonpassive.

4.1. Introduction

Acid-base reactions are ubiquitous throughout chemistry and biology, and the understanding of their fundamental role has been the focus of huge amounts of research. Within biology pH gradients are utilized within a cell for energy conversion and storage [2]. Attempts to chemically mimic biological functions have also focused on the use of protonation as a source of energy [3, 4]. Apart from these more complex examples, changes in pH have also recently been used within the literature for both the exploration of electrochemical mechanisms [5] and as a method of controlling the rate of chemical reactions [6].

Numerous redox processes involve the coupled transfer of both protons and electrons [7]. The study of the influence on the local pH of these reactions at an

electrode interface has been investigated using methods such as interferometry [8], Raman spectroscopy [9], and the fluorescence of pH sensitive probes [10, 11]. Of the species able to undergo multiple electron and proton transfers anthraquinone and its derivatives have been well studied as model systems. A theoretical description of the 2H^+ , $2e^-$ system was first proposed by Jacq [12] whereby a scheme of squares mechanism was proposed in which the protonations are at equilibrium and the electron transfers are the rate determining steps. A generalized scheme for the redox behavior of anthraquinone (AQ) is presented in Tab.4.1.



Tab. 4.1: A generalized scheme of squares for the 2H^+ , $2e^-$ redox behavior of anthraquinone.

The mechanistic pathway taken is highly dependent upon the pK_{a} s associated with the intermediate species, where under differing conditions (nonaqueous media and pHs) it is possible for the process to stop at either lower protonated or reduced states. Recent work by Quan et al. demonstrated how the somewhat incongruously large difference in redox behavior for quinones in protic and nonprotic media may be explained in terms of hydrogen bonding of the reduced dianion species [1]. This was achieved through the investigation of the influence of the concentration of buffer present in the electrolyte solution upon the observed voltammetry.

Voltammetric simulations based upon the ‘scheme of squares’ for two-proton two-electron systems are surprisingly limited within the literature. Work by Barber et al. provided the first attempt at the simulation of such a system, where the redox chemistry of flavin adenine dinucleotide was modeled over a limited pH range [13, 14]. Recent work by Batchelor-McAuley et al. provides the first complete model of a 2H^+ , $2e^-$ system across the full pH range, in which the solution-phase voltammetric response of the DNA intercalators anthraquinone disulfonate (AQDS) and anthraquinone monosulfonate (AQMS) were studied [15]. Both of these previous examples are of the modeling of systems in which the redox species is fully buffered. Guo et al. have undertaken a quantitative analysis of the voltammetric response of $[\alpha_2 - \text{Fe}^{\text{III}}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-} \text{1H}^+$, $1e^-$ in conditions of limited concentrations of buffer [16]; the influence of proton consumption during the redox process was clearly demonstrated to cause a second voltammetric feature.

Carbon surfaces are of particular interest to electrochemists due to the relative ease by which they may be modified as compared to metal-based materials [17]. Chemical modification of the surfaces may be achieved through a variety of methods, but the use of diazonium salt chemistry is widely employed [18]. As a result of their highly reactive nature diazonium salts allow the production of surfaces with high surface coverages. The use of anthraquinone modified carbon electrodes has previously been utilized for the production of reagentless electrochemical pH probes, able to accurately measure the pH of buffered media across a large range of pHs [19, 20]. A recent review of the use of carbon derivatized carbon materials for pH measurement has been undertaken by Kahlert [21]. The effect of low buffered media upon these pH probes has not been investigated and as

will be shown, the voltammetric response in low buffered media is significantly altered.

The work in this chapter investigates the influence of low buffered media upon the voltammetric response of 2H^+ , $2e^-$ systems for both solution-phase and surface-bound species. The cyclic voltammetry of anthraquinone monosulfonate is shown to exhibit two waves under conditions of low buffer concentrations. This system is demonstrated to be readily simulated providing quantitative information about the variation in the local pH adjacent to the electrode. Furthermore the modification of a graphitic electrode with anthraquinone moieties is achieved through the use of diazonium salt chemistry. This modified electrode is voltammetrically characterized and shown to be highly reversible with the peak potentials for the redox feature varying in a Nernstian manner. The response of this electrode in conditions of limited buffer also exhibits significant proton consumption, as a result of the high surface loading. As such, this work provides physical insight into how surface-bound anthraquinone under conditions of limited buffering exhibits a distorted voltammetric response involving split waves; this result is analogous to that found for solution-phase anthraquinone. Hence, this demonstrates that a significant change in the pH of the solution adjacent to the electrode is occurring as a result of consumption of protons during the electrochemical experiment.

4.2. Experimental methods

4.2.1. Chemicals and reagents

All reagents were used as received without further purification. The anthraquinone monosulfonate has the sulfonate group situated in the 2-position. Hydrochloric acid, acetic acid, sodium acetate, sodium hydroxide, dibasic sodium phosphate and monobasic sodium phosphate dihydrate were obtained from Sigma–Aldrich (Gillingham, U.K.), disodium tetraborate (borax) from BDH Limited (Poole, U.K.) and potassium chloride from Riedel-de Haën (Seelze, Germany). All solutions were prepared using deionised water of resistivity not less than 18.2 M Ω ·cm at 23°C (Millipore Water Systems, UK). Solutions of various pH were prepared as follows: pH 1.10: 1 M hydrochloric acid, pH 4.55: 0.1 M acetic acid and 0.1 M sodium acetate, pH 6.71: 0.025 M sodium phosphate dibasic and 0.025 M sodium phosphate monobasic dihydrate, pH 9.15: 0.05 M disodium tetraborate, pH 12.06: 0.01 M sodium hydroxide, pH 3.35 and 3.91: diluted hydrochloric acid. All solutions contained 0.1 M potassium chloride as supporting electrolyte. pH measurements were performed using a pH 213 Microprocessor pH Meter (Hanna Instruments, Leighton Buzzard, U.K.). Electrochemical measurements were conducted using an Autolab PGStat20 computer-controlled potentiostat (Eco–Chemie, Utrecht, Netherlands) with a standard three-electrode configuration. Either an edge plane pyrolytic graphite (EPPG) electrode (4.9 mm diameter, Le Carbone, Ltd. Sussex, UK) or a polycrystalline gold macro electrode (1.6 mm diameter, BASi Technicol, West Lafayette, IN) was the working electrode, platinum wire the counter electrode and a saturated calomel (Radiometer, Copenhagen, Denmark) the reference electrode.

The working electrodes were polished prior to use on alumina lapping compounds (Buehler, Coventry, U.K.) of decreasing sizes ($1.0\ \mu\text{m}$, $0.3\ \mu\text{m}$) on soft lapping pads and sonicated in deionised water in an ultrasound bath for 3 min. All solutions of various pH were thoroughly deoxygenated for at least 15 minutes with nitrogen prior to measurements and a nitrogen atmosphere was kept over the solutions during experiments.

4.2.2. Electrode preparation

4.2.2.1. Synthesis of anthraquinone-2-diazonium tetrafluoroborate

Anthraquinone-2-diazonium tetrafluoroborate was synthesized according to the method developed by Milner [22]. 0.5 g of 2-aminoanthraquinone (Sigma-Aldrich, Gillingham, U.K.) was added to 0.4 g of nitrosonium tetrafluoroborate (ca 50% molar excess) (Sigma-Aldrich, Gillingham, U.K.) in 50 ml of dichloromethane (DCM) (Fisher Scientific, Loughborough, U.K.). The slurry was kept in an ice-water bath. It was stirred for 1 h and after that DCM was removed under vacuum. The resulting anthraquinone-2-diazonium tetrafluoroborate product was stored at -5°C .

4.2.2.2. Modification of EPPG electrode with 2-anthraquinonyl groups

The polished EPPG electrode was immersed in a stirred solution of ca 0.04 g of synthesized anthraquinone-2-diazonium tetrafluoroborate product in 25 ml of water for about 30 minutes. The solution of diazonium salt was prepared using deionized water cooled to a temperature below 5°C . After that the EPPG electrode modified with 2-anthraquinonyl groups (EPPG-AQ2) was rinsed with acetonitrile, DMF and deionised water to remove any unreacted salt.

4.2.3. Modeling

The simulation of the voltammetric response for the solution-phase anthraquinone-2-monosulfonate was achieved through the use of the commercially available software package DigisimTM (version 3.0, BASi Technicol, USA). DigisimTM is based on a fully implicit finite difference (IFD) method as proposed by Rudolph [23, 24]. Protonation steps were modeled as:



to enable the system to be fully equilibrated at all points the rate of the protonation was set as being larger than $1 \cdot 10^{10} \text{ dm}^3/\text{mol} \cdot \text{s}$. This simplification ensures that it is unnecessary to include all of the possible mechanistic pathways leading to a change in the level of protonation of the intermediate species. Included within the simulation was the self-ionization of water, where the concentration of water was set as 55.56 M and the value of K_w taken as $1.0 \cdot 10^{-14} \text{ mol}^2/\text{dm}^6$ [25]. Control of the pH of the system was modeled through the inclusion of 0.1 M buffer (as per the experimental section).

The values used for the standard potentials, electron transfer rates, and pK_a s associated with the solution-phase AQMS system were taken from work by Batchelor-McAuley et al. [15]. Further the diffusion coefficient was set as being $4.7 \cdot 10^{-6} \text{ cm}^2/\text{s}$, as measured from the reductive steady state current at a Pt microdisc electrode in aqueous media [15]. The diffusion coefficient of the proton varies between $5.0 \cdot 10^{-5}$ and $9.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$ depending on the ionic strength of the solution [26], but in accordance with the theoretical value as given by the Grothus

mechanism [27] and from experimental work by Unwin [28] a value of $7 \cdot 10^{-5} \text{ cm}^2/\text{s}$ was used within the simulations. In reference to the nomenclature used within this chapter the double reduced and unprotonated form of anthraquinone is referred to as the dianion species (AQ^{2-}). As such in the case of AQMS this ignores the charge associated with the sulfonate group: this is done to simplify the discussion and ease direct comparison between the solution-phase and surface-bound species.

4.3. Results and discussion

4.3.1. Solution-phase voltammetry of AQMS

The cyclic voltammetric response of 1 mM AQMS at a gold macroelectrode was measured in aqueous media containing varying concentrations of HCl as depicted in Fig. 4.1a.

The voltammetric response of AQMS has previously been shown to be a reversible 2H^+ , $2e^-$ system and to exhibit near Nernstian behavior across the full aqueous pH range. From the literature the pK_a values associated with the reduced form are found to be 7.6 and 11 [29], consequently below ca pH 7 the peak potentials for the voltammetry vary with 59 mV/pH and above pH 11 the system is found to be insensitive to the proton concentration [15]. In the presence of 4 mM HCl the reduction of 1 mM AQMS is found to exhibit one voltammetric feature (at -0.21 V vs. SCE), corresponding to the transfer of 2H^+ and $2e^-$. As the concentration of protons is decreased to 0.25 mM a second voltammetric feature is apparent at a higher potential. In the case where no HCl has been added to the electrolyte, a single voltammetric feature is observed at -0.59 V (vs. SCE).

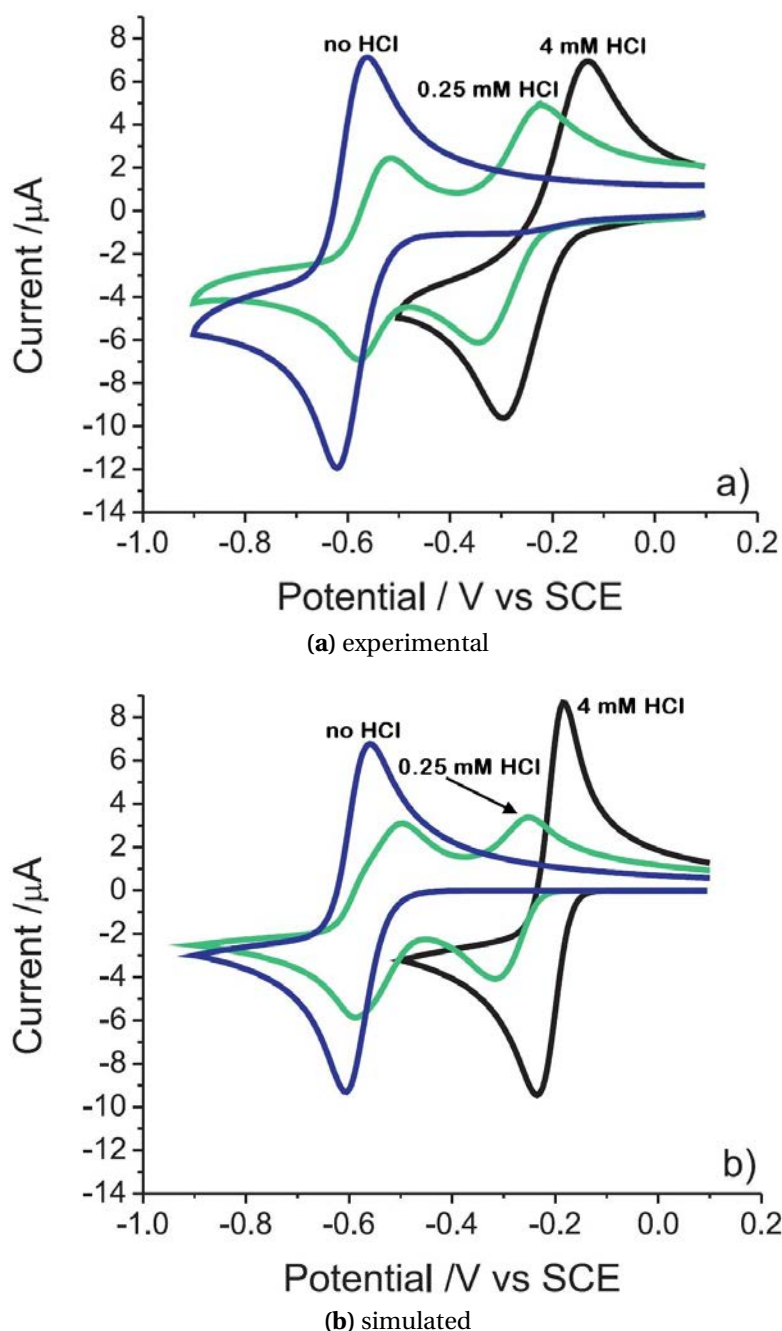


Fig. 4.1: The cyclic voltammetric response of 1 mM AQMS in the presence of a finite solution-phase proton concentration as controlled through decreasing concentrations of HCl (black: 4 mM, green: 0.25 mM, blue: no HCl) for both (a) experimental and (b) simulated results at a scan rate of 0.1 V/s.

This observed behavior may be explained as being a result of the consumption of protons upon reduction of the anthraquinone species. When under conditions of limited buffering, the reduction process may alter the pH adjacent to the electrode. As such in the case of 0.25 mM HCl the reduction of AQMS is effectively limited by the availability of the protons, in the absence of protons the reduction

proceeds via the formation of the dianion species (AQ^{2-} in Tab.4.1), this reduction occurs at -0.59 V (vs. SCE) as evidenced by the voltammetric response of AQMS in the absence of HCl. Note that the second voltammetric wave observed for the 0.25 mM HCl does not occur at exactly -0.59 V (vs. SCE) and this is likely as a result of the formation of equilibrium concentrations of dianion, monoprotonated and diprotonated species [1].

4.3.2. Modeling of the solution-phase voltammetry

Modeling of the voltammetric response of 1 mM AQMS at a gold macroelectrode was under taken so as to allow quantitative information to be obtained about the extent of change in pH at and adjacent to the electrode in aqueous solutions containing low buffer concentrations. The simulation used was based upon that given by Batchelor-McAuley et al. [15] where pK_a3 and pK_a6 are set as being 7.6 and 11, respectively, and the standard potentials used for electron transfers are given in Tab.4.2. Further details of this model are given within the experimental section. As can be seen the voltammetric simulation results closely follow that found experimentally (Fig.4.1). As a result of assuming that the protonations are fully equilibrated the simulated voltammetry has a smaller peak-to-peak separation than is experimentally found. A least-squares methodology was not used to improve the simulated voltammetric response, this is as a result of the inherent number of variables present in the system and as such use of this methodology may lead to obtaining nonphysically correct values. It is of significance that this simulation is able to accurately predict (as a function of pH) the shift in voltammetric response from that of a one voltammetric feature to that of two

waves. Hence this leads to the confirmation that the model is accurately able to describe the proton concentrations at and adjacent to the electrode surface. It should be noted that the second peak observed in 0.25 mM HCl shows a shoulder on the voltammetric wave, which is not observed experimentally. It is surmised that this is due to a further possible mechanistic pathway by which the reduced product may equilibrate, which is not present within the simulation. For the three proton concentrations outlined above (4, 0.25, and 0 mM) the simulation was used to describe the variation in the pH adjacent to the electrode surface. Fig.4.2 depicts the results obtained at the switching potentials.

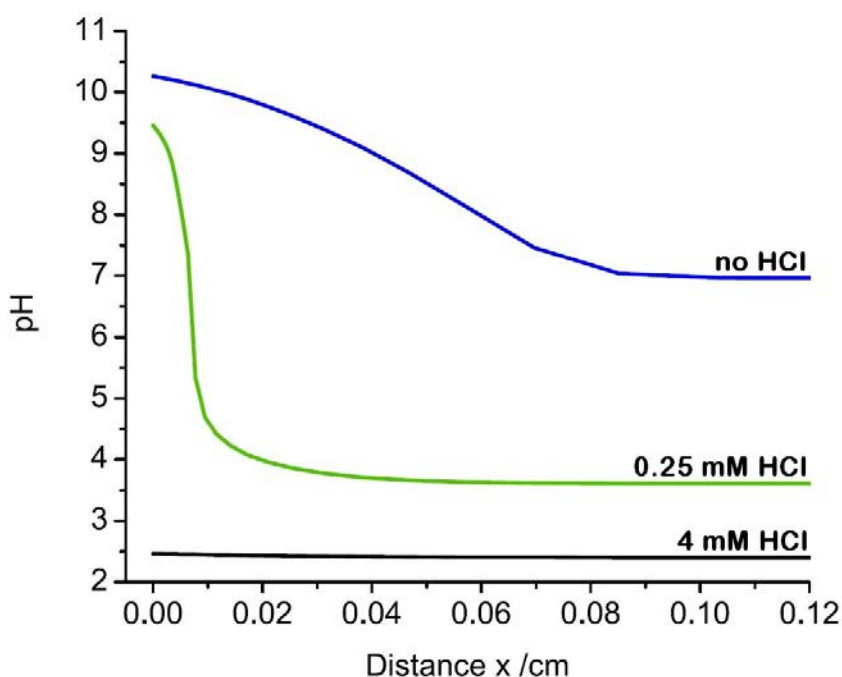


Fig. 4.2: The theoretical variation of the pH with distance from the electrode at the switching potentials for the cyclic voltammetry depicted in Fig. 4.1b.

As can be seen in relatively high proton concentrations the reduction of the anthraquinone species has little influence upon the levels of acidity adjacent to the electrode. As the initial proton concentration is decreased to 0.25 mM a significant change in the pH of the solution occurs at distances close to the electrode surface, where the pH at the electrode interface is roughly 5–6 pH units greater

than that of the bulk solution. This region of high pH is confined to a layer close to the electrode interface (<0.01 cm). In the case where no HCl is present in the solution, a significant alteration in the solution pH occurs at distances further from the electrode (<0.08 cm). This simulation clearly demonstrates how due to the transfer of protons to the electrochemically reduced species the pH adjacent to the electrode is significantly altered. Hence systems based on such chemistry for the measurement of pH are going to be significantly influenced by the buffer concentrations and will not give readily analyzable results.

redox couple:	standard potential: V vs. SCE	electron transfer rate: cm/s
E_1	-0.6061	10
E_2	-0.62101	0.38067
E_3	-0.3995	10
E_4	-0.22681	10
E_5	0.03813	10

Tab. 4.2: Values for the standard potentials and electron-transfer rates used used for the simulation for AQMS.

4.3.3. Surface-bound AQMS

The cyclic voltammetry of an AQ2 modified EPPG electrode was run from 0.0 V to -1.0 V (vs. SCE) in buffers of various pH from 1 to 14 (Fig.4.3). The cyclic voltammetry exhibits a large surface-bound wave, which is ascribed as being a 2H^+ , $2e^-$ process. From the geometric area of the EPPG electrode it is possible to calculate that a full monolayer of vertically aligned 2-anthraquinonyl groups leads to a surface coverage of $2.5 \cdot 10^{-9}$ mol/cm²; this value is an underestimation due to the actual surface area of the electrode being greater than its geometric

area as a result of the surface not being atomically flat. Hence from analysis of the voltammetry it is concluded that the anthraquinone modified EPPG electrode has a high surface coverage of 2-anthraquinonyl groups $((2.1 \pm 0.2) \cdot 10^{-9} \text{ mol/cm}^{-2})$. Because of this high surface coverage there is a distinct possibility that the modification of the surface with anthraquinone may have led to the formation of partial multilayers. At all pHs the voltammetric peak-to-peak separation is nonzero ($\sim 70 \text{ mV}$), whereas for an ideal fully reversible surface-bound species the peak-to-peak separation is predicted as being zero. Fig. 4.4 depicts the variation of the peak potentials for the AQ2 modified EPPG with pH; below pH 9 the reductive and oxidative peaks are found to vary with -59 and -58 mV/pH , respectively. These values are very close to those expected for a fully reversible two electron two proton system as given by the Nernst equation (59 mV/pH ; 25°C), thus suggesting that although the peak-to-peak separation is larger than expected for an ideal surface-bound species the system is reversible in nature and the nonzero peak-to-peak separation is likely a result of the surface-bound species being nonideal [30, 31]. Above pH 9 the gradient for the plot of peak potential vs. pH deviates away from being that of a two proton two electron system. This is a result of the pH being greater than the pK_a s associated with the doubly reduced anthraquinone species $\text{pK}_a 3$ and $\text{pK}_a 6$ as shown in Tab. 4.1. It is of interest that it is also possible to modify the EPPG surface with AQ1, the midpoint potentials for the voltammetric response of both AQ2- and AQ1-modified EPPG electrodes occur at the same potential below pH 12 (within experimental error). Although the reduction of these species is thermodynamically similar, the AQ1 exhibits a less reproducible wave which also shows a greater peak-to-peak

separation. Consequently for this present study AQ2 modified EPPG electrodes were used for the experimental investigation of the influence of low buffered media. The influence of low proton concentrations upon the voltammetry of the AQ2-modified EPPG electrode was investigated. Fig. 4.5 depicts the recorded voltammetric response of the AQ2-modified electrode in 0.3, 0.1, and 0 mM HCl at a scan rate of 0.1 V/s. As for the fully buffered species the voltammetric response of the modified electrode in 0.3 mM HCl exhibited a single two-electron two-proton feature at -0.34 V vs. SCE.

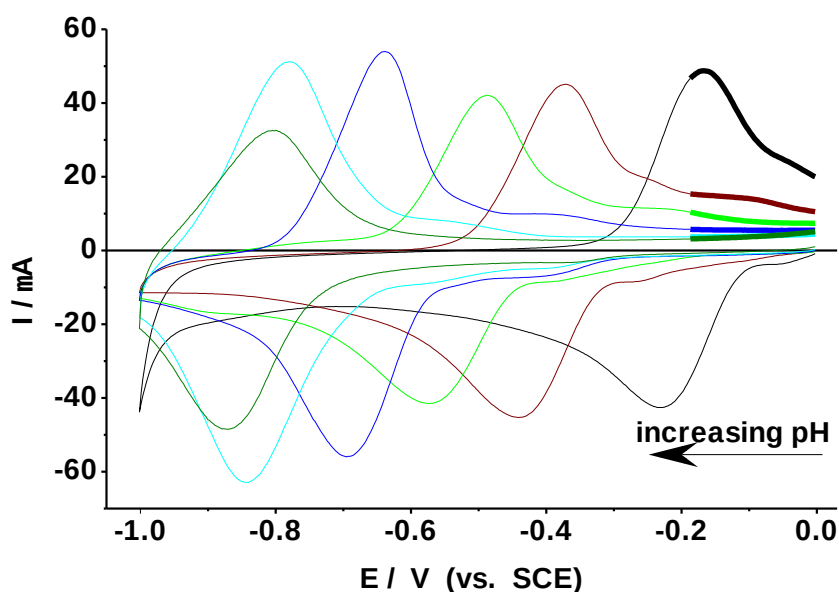


Fig. 4.3: The cyclic voltammetry of an AQ2 modified EPPG electrode in fully buffered media (0.1 M) with varying pH (1–14), scan rate 0.1 V/s.

As the proton concentration is further reduced (0.1 mM HCl) a second voltammetric feature becomes apparent. This second voltammetric feature occurs at the same potential (-0.73 V vs. SCE) as that found for the reduction of the surface-bound AQ in the absence of HCl. It should be noted that for the response at 0.3 mM HCl although only one voltammetric wave is observed the peak is significantly distorted from that expected for a fully buffered system where the peak-to-peak separation is measured as 59 mV as opposed to 67 mV for the

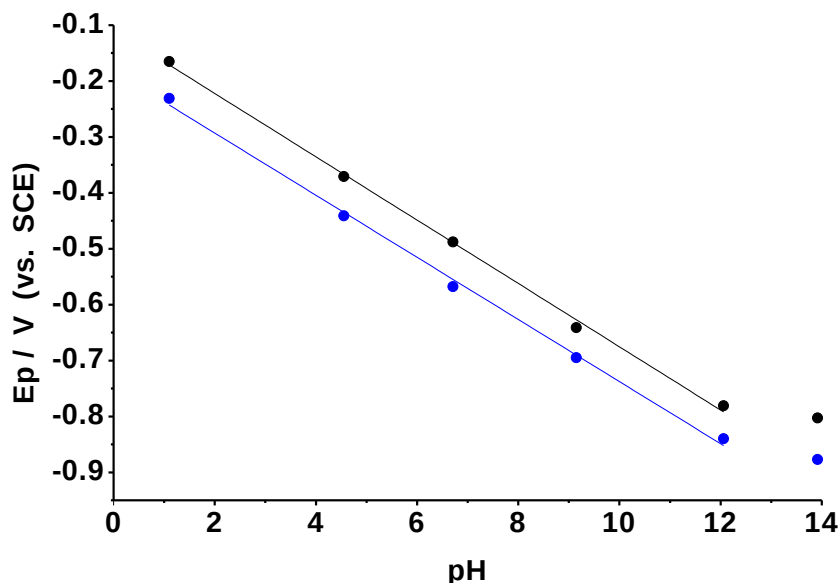


Fig. 4.4: A plot of peak potentials (E_{pc} blue, E_{pa} black) for an AQ2 modified EPPG electrode in fully buffered media (0.1 M) of varying pH (data from Fig. 4.3). The lines are the best fits for both the E_{pc} and E_{pa} as a function of pH.

fully buffered system and the midpoint potential has been shifted negatively by ~ 12 mV. This result is analogous to that found for the solution-phase species and demonstrates how in the case of high surface coverages of redox active species involving the transfer of protons the measured voltammetry is significantly altered in low buffering conditions. From the simulation it can be seen that for the solution-phase species when the concentration of the buffer is less than twice that of the AQMS, significant deviations are observed in the voltammetry. As such, for the present experimental case with 1 mM AQMS, concentrations of less than 2 mM HCl exhibit voltammetry which is distorted from that of a fully buffered system. In comparison it is observed experimentally that for the surface-bound species concentrations of ≤ 5 mM HCl lead to distorted peaks, where the voltammetric peak-to-peak separation is increased, and there is a shift in the apparent midpoint potential. This occurs as a result of the relatively high levels of proton consumption adjacent to the electrode and hence alteration of the local environment. This result is significant as it highlights how pH measurements

based on such a methodology are restricted to the use of media in which there are high concentrations of buffer. Furthermore, as a proof of concept it highlights how such a modified electrode may be used to effectively control the pH adjacent to an electrode surface.

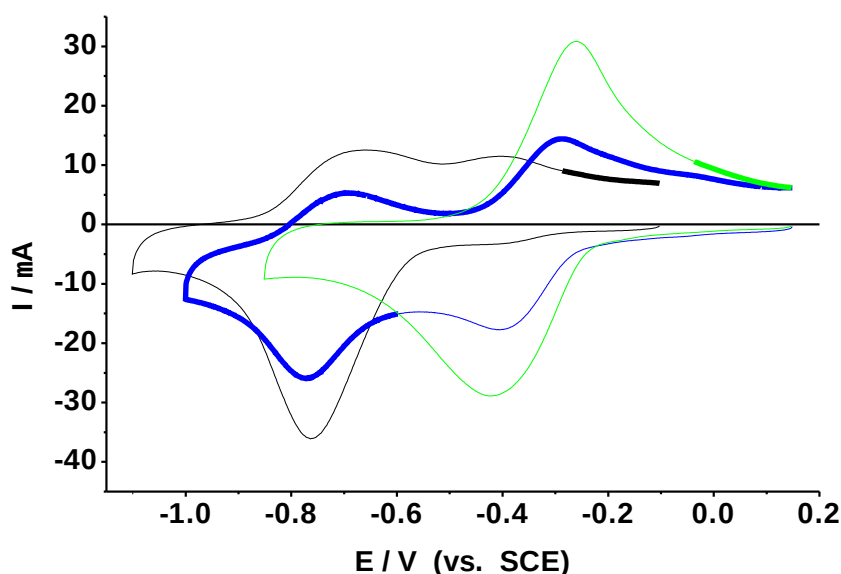


Fig. 4.5: The cyclic voltammetry an AQ2-modified electrode in the presence of a finite solution-phase proton concentration as controlled through the concentration of HCl (green: 0.3 mM; blue: 0.1 mM; black: no HCl).

4.4. Conclusions

This chapter has demonstrated through the use of a solution phase species which may undergo a 2H^+ , $2e^-$ process how the measured voltammetry is significantly altered when under conditions of low buffering, as exemplified through the use of anthraquinone monosulfonate. As a result of proton consumption upon reduction of the electro-active species the pH adjacent to the electrode is altered, leading to, in some situations the observation of two voltammetric features. The response for the AQMS system in low buffered aqueous media has been modeled through the use of the commercially available software package DigisimTM. Through the use of these simulations it was possible to ascertain

that the pH adjacent to the electrode may be altered by up to 5–6 pH units as compared to that of the bulk solution. Further, the modification of an EPPG electrode with 2-anthraquinonyl groups was achieved through the use of diazonium salt chemistry. This EPPG-AQ2 modified electrode was shown to exhibit near reversible behavior in fully buffered aqueous media. In the case of the use of low buffered media the voltammetry of the surface-bound species altered significantly, leading to the observation of split voltammetric waves, in a manner analogous to that found for the solution-phase species. This distortion is a result of the significant consumption of protons during the electrochemical experiment. As such it is concluded that this EPPG-AQ2 modified electrode may cause a significant shift in pH adjacent to the electrode interface. This is of importance due to the use of similar methodologies for the voltammetric measurement of pH. Further it is demonstrated as a proof of concept that such modified electrodes may be used for the effective control of the pH adjacent to an electrode. In the next chapter the EPPG-AQ2 modified electrode will be used as the first $2e^-$ system to be analyzed according to Marcus-Hush theory.

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Edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups: theory and experiment. Application of Marcus-Hush theory to two electron systems.

The work presented in this chapter has been accepted for publication in
ChemPhysChem, 2011, 12, 2806–2815.

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In this chapter an edge plane pyrolytic graphite (EPPG) electrode was modified by electrochemical reduction of anthraquinone-2-diazonium tetrafluoroborate (AQ2-N₂⁺BF₄⁻) giving an EPPG-AQ2 modified electrode of a surface coverage below a monolayer. Cyclic voltammograms simulated using Marcus-Hush theory for a 2e⁻ process assuming a uniform surface gave unrealistically low values of reorganisation

energies, λ , for both electron transfer steps. Subsequently two models of surface inhomogeneity based on Marcus-Hush theory were investigated: a distribution of formal potentials, $E^{\ominus'}$, and a distribution of electron tunneling distances, r_0 . The simulation of cyclic voltammograms involving the distribution of formal potentials showed better fit than the simulation with the distribution of tunneling distances. Importantly the reorganization energies used for the simulation of $E^{\ominus'}$ distribution were similar to the literature values for adsorbed species.

5.1. Introduction

Carbon is one of the most widely used electrode materials along with metals and semiconductors mainly because it is very versatile and inexpensive. It also has a wide potential window and a reproducible surface and exists in a variety of forms suitable for electrochemical applications, e.g. glassy carbon (GC), edge plane pyrolytic graphite (EPPG), basal plane pyrolytic graphite (BPPG), highly oriented pyrolytic graphite (HOPG), carbon powders and pastes etc. Although carbon materials used in electrochemistry have similar electronic features to metals, their surface chemistry is different and plays an important role in the observed electrochemical and chemical reactivity of carbon and modified carbon electrodes. It is well known that a wide variety of oxygen-containing functional groups are present on carbon surfaces, especially on edge plane sites and that enables a quick and easy chemical derivatization of carbon based materials. These are hydroxyl, carbonyl, ether, carboxylic acid, cyclic esters and also quinone- and lactone-like groups. The ratio of edge plane to basal plane sites also determines electrode properties like kinetics, adsorption and electrocatalysis due to the fact

that electron transfer is at least three times faster at edge plane sites than at basal plane sites [1, 2]. The complexity of carbon surfaces often results in more complex cyclic voltammetry and chronoamperometry than for metallic electrodes. It is caused by the nature of carbon surfaces which usually can not be considered as homogeneous [1–6].

Quinones are one of the most popular and well-studied examples of organic compounds. The majority of them take part in biological electron and proton transfer processes in living creatures. The practical applications of quinones and quinone modified electrodes include: dyes [7, 8], oxygen reducing agents [9], pH probes [10] and capacitors [11, 12]. More importantly quinones are model organic redox molecules for electrochemical studies playing very important roles in developing understanding of organic redox chemistry [11, 13, 14]. Redox reactions of various aromatic compounds, often biologically active, very often involve transfer of two (or more) electrons and therefore it is important to study these processes.

The covalent attachment of molecular species to surfaces by electrochemical and spontaneous reduction of diazonium cations has been widely investigated [15–32]. The reduction of diazonium salts can be used to modify carbon, metal and semiconductor electrodes. It is very simple: 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. 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. Diazonium salts are easily and rapidly synthesized in one step from a wide range of aromatic amines. Tetrafluoroborates (BF_4^-) are especially recommended since they

are stable and there is no risk of explosion. It is also possible to derivatize an electrode by simple immersion of the surface in a diazonium salt solution. The spontaneous modification is simpler and quicker but not very reproducible and controllable [5, 33–36].

Chronoamperometry (CA) is considered to be a more direct technique to measure the reaction kinetics than cyclic voltammetry (CV) although the current transients have to be slow enough to be accurately recorded. In potential step experiments the kinetics at different potentials (different reaction energies) are not convoluted by a potential scan, the kinetic homogeneity of the sites can be easily judged from the plot of the logarithm of the electron transfer current ($\ln|I|$) vs. time (t) which is linear for uniform layers and the electron transfer rates can be measured at large overpotentials [37]. The first order reaction of an adsorbed species displays an exponentially decaying current:

$$I(t) = k_{\text{app}} Q \exp(-k_{\text{app}} t), \quad (5.1)$$

where k_{app} is the sum of the forward and backward electron transfer rate constants for the redox process investigated and Q is the charge passed in the electron transfer reaction [38].

In cyclic voltammetry the peak current, I_p , is proportional to the scan rate, v :

$$I_p = \frac{n^2 F^2}{4RT} v A \Gamma. \quad (5.2)$$

The surface coverage, Γ , can be calculated from the slope of the I_p vs. ν plot or from the charge, Q , of the background-subtracted peaks for each scan rate:

$$\Gamma = \frac{Q}{nFA}. \quad (5.3)$$

The full width at half of the peak maximum height (FWHM) is:

$$\text{FWHM} = 3.53 \frac{RT}{nF} = \frac{90.6}{n}. \quad (5.4)$$

For a completely reversible system at slow scan rates the peak separation should be zero. Ideal reversible electrochemical behaviour results when both the reduced and oxidized form of the redox species are strongly adsorbed to the electrode [39].

Voltammetric results are usually interpreted according to Laviron analysis [40] for irreversibly adsorbed redox active groups which uses the classical Butler-Volmer model of electrochemical kinetics to calculate how electron transfer rate constants vary with applied potential. This method relies on α , the transfer coefficient, which is a measure of the symmetry of the energy barrier of the redox reaction. Ideally, $\alpha = 0.5$ for all overpotentials, however in many cases α deviates from 0.5, therefore it is very important to determine α in order to find k . Plots of peak potentials vs. $\log \nu$ at higher scan rates where $\Delta E_p > \frac{200}{n}$ mV should be straight lines. The slope of the line for the cathodic peak is $-\frac{2.3RT}{\alpha nF}$ and $\frac{2.3RT}{(1-\alpha)nF}$ for the anodic peak:

$$E_{pc} = E_c - \frac{RT}{\alpha nF} \ln \frac{RTk_c}{\alpha nF\nu_c}, \quad (5.5)$$

$$E_{pa} = E_a - \frac{RT}{(1-\alpha)nF} \ln \frac{RTk_a}{(1-\alpha)nF\nu_a}, \quad (5.6)$$

where E_c and E_a are peak potentials at low scan rates. The intercepts of the lines for the anodic and the cathodic branches give ν_a and ν_c – critical scan

rate values that are used to calculate k [39, 41]:

$$k_c = \frac{\alpha n F v_c}{RT}, \quad (5.7)$$

$$k_a = \frac{(1 - \alpha) n F v_a}{RT}. \quad (5.8)$$

The Laviron method is widely used for determining the electron transfer rate constants, however experimental kinetics can very often deviate from the Butler-Volmer behaviour so that the transfer coefficient, α , depends on electrode potential. The molecular theory of electrode kinetics developed by Marcus [42, 43] predicts that the rate of electron transfer for a simple, reversible reaction:



between an electron donor and an electron acceptor depends on the reaction's Gibbs energy, ΔG , reorganization energy, λ , temperature, T , and the electronic coupling between donor and acceptor, H_{DA} :

$$k = \frac{4\pi^2 H_{DA}^2}{h \sqrt{4\pi\lambda k_B T}} \exp \frac{-(\Delta G + \lambda)^2}{4\lambda k_B T}, \quad (5.10)$$

where h is the Planck's constant and k_B is the Boltzmann's constant. Reorganization energy, λ , is the energy required to reorient all atoms (from equilibrium state to the product state) without allowing the electron to transfer and consists of two parts: $\lambda = \lambda_i + \lambda_o$. The inner contribution, λ_i , is the energy required to change bonds. The outer contribution, λ_o , is the energy needed to reorient the solvent. When both forms of the adsorbed electroactive molecule have similar structures the main contribution to the activation barrier is reorganization of the solvent [37, 39].

Marcus theory predicts that when λ is similar to the applied potential, the rate

constants do not increase exponentially with η as as predicted by Butler-Volmer theory, but they reach a maximum at $\eta = \lambda$ and decrease at larger overpotentials (classical Marcus inverted region). The heterogeneous electron transfer rates however do not decrease at $\eta \gg \lambda$ as predicted for homogeneous reactions because of the continuum of electronic states in the metal electrode. When $\eta \gg \lambda$, the entire distribution of redox active sites overlaps with states in the electrode that are available for electron transfer. Increasing the driving force, η , does not make new states available for electron transfer and does not increase the probability of electron transfer. When $\eta \ll \lambda$ Marcus equations reduce to Butler-Volmer equations [37, 39, 44].

The original Marcus theory [42, 43], later extended by Hush [45], was formulated for electron transfer reactions occurring in solutions. When electron transfers happens heterogeneously between a redox molecule and a metal electrode it is necessary to take the energy distribution of electrons near the Fermi level in the metal into account. It was mainly Chidsey [37] who developed Marcus-Hush theory for heterogeneous reactions at metallic electrodes. For redox reactions between a metal electrode with a continuum of electronic states, cathodic and anodic rate constants are sums of the individual rates for each electronic state of the metal weighted by the Fermi-Dirac probability of occupancy or vacancy of that state and they can be calculated by numerical integration of donor and acceptor levels over a range of energies [37, 39, 44, 46].

When adsorbates behave ideally interpretation of cyclic voltammograms and chronoamperograms is relatively simple. In reality electroactive films are rarely ideal. The adsorbed molecules can react with the electrode at different rates from

large to small. This phenomenon is called the dispersion or distribution of the rate constant and it is clearly evident from curved rather than linear plots of $\ln|I(t)|$ vs. time from potential step experiments (chronoamperometry). In potential sweep experiments (cyclic voltammetry) kinetic dispersion causes broadening and tailing of the voltammetric peaks and makes them generally assymmetric. Kinetic dispersion can arise from a spread in the formal potentials of the electroactive sites or from a distribution of tunneling distances [44]. It was previously reported that the distribution of formal potentials of 60 mV explains the broadening of the experimental voltammograms of an edge plane pyrolytic graphite electrode covalently modified with ferrocene (EPPG-Fc) [47].

Marcus-Hush theory has been previously successfully applied to various one electron processes involving species adsorbed on electrode surfaces, usually as self-assembled monolayers (SAMs) [37–39, 44]. In this chapter Marcus theory is applied to a two-electron redox system, namely to edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2).

5.2. Theory

We consider the reaction scheme:



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:

$$\frac{d\Gamma_A}{dt} = -k_1\Gamma_A + k_2\Gamma_B, \quad (5.12)$$

$$\frac{d\Gamma_B}{dt} = -(k_2 + k_3)\Gamma_B + k_1\Gamma_A + k_4\Gamma_C, \quad (5.13)$$

$$\frac{d\Gamma_C}{dt} = -k_4\Gamma_C + k_3\Gamma_B, \quad (5.14)$$

where Γ_A , Γ_B and Γ_C (mol/cm²) 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:

$$I = FA \left[\frac{d\Gamma_A}{dt} - \frac{d\Gamma_C}{dt} \right], \quad (5.15)$$

where F is the Faraday constant (C/mol) and A (cm²) is the electrode area.

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

$$E(t) = |E_1 - \nu t - E_2| + E_2, \quad (5.16)$$

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

Simultaneous solution of Eqs. (5.12) – (5.14) yields the following analytical expressions for the coverage of each species as a function of time:

$$\begin{bmatrix} \Gamma_A \\ \Gamma_B \\ \Gamma_C \end{bmatrix} = \alpha \begin{bmatrix} \frac{k_2}{k_1 - a} \\ 1 \\ \frac{k_3}{k_4 - a} \end{bmatrix} e^{-at} + \beta \begin{bmatrix} \frac{k_2}{k_1 - b} \\ 1 \\ \frac{k_3}{k_4 - b} \end{bmatrix} e^{-bt} + \gamma \begin{bmatrix} \frac{k_2}{k_1} \\ 1 \\ \frac{k_3}{k_4} \end{bmatrix}, \quad (5.17)$$

where

$$a = \frac{1}{2}(k_1 + k_2 + k_3 + k_4) + \frac{1}{2}\sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_1 k_3 + k_1 k_4 + k_2 k_4)}, \quad (5.18)$$

$$b = \frac{1}{2}(k_1 + k_2 + k_3 + k_4) - \frac{1}{2}\sqrt{(k_1 + k_2 + k_3 + k_4)^2 - 4(k_1 k_3 + k_1 k_4 + k_2 k_4)}, \quad (5.19)$$

and

$$\alpha = \left[\frac{k_1(k_4 - a)}{a(a - b)} \right] \Gamma_A^* + \left[\frac{(k_1 - a)(k_4 - a)}{a(a - b)} \right] \Gamma_B^* + \left[\frac{k_4(k_1 - a)}{a(a - b)} \right] \Gamma_C^*, \quad (5.20)$$

$$\beta = \left[\frac{k_1(k_4 - b)}{b(b - a)} \right] \Gamma_A^* + \left[\frac{(k_1 - b)(k_4 - b)}{b(b - a)} \right] \Gamma_B^* + \left[\frac{k_4(k_1 - b)}{b(b - a)} \right] \Gamma_C^*, \quad (5.21)$$

$$\gamma = \left[\frac{k_1 k_4}{ab} \right] \Gamma_A^* + \left[\frac{k_1 k_4}{ab} \right] \Gamma_B^* + \left[\frac{k_1 k_4}{ab} \right] \Gamma_C^*, \quad (5.22)$$

where Γ_A^* , Γ_B^* and Γ_C^* are the coverages of A, B and C at the beginning of the pulse.

As can be seen from Eqs. (5.17) – (5.22), a knowledge of the coverage of each species at the beginning of a pulse is sufficient to evaluate the current at any arbitrary time during that pulse. Due to the pulses being consecutive, the coverage at the beginning of one pulse is equal to the coverage at the end of the preceding pulse. By induction it is therefore sufficient to know the coverage of each species at the beginning of the first pulse to evaluate the current at any time during the entire cyclic voltammogram, assuming the values of the four

rate constants are also known.

For each timestep during the cyclic voltammogram the rate constants are calculated in accordance with the Marcus-Hush kinetic formalism [37, 46, 48]. The rate constants are given by:

$$k_1 = k_0^{\text{AB}} \exp \left[-\frac{\theta^{\text{AB}}}{2} \right] \frac{S(\Lambda^{\text{AB}}, \theta^{\text{AB}})}{S(\Lambda^{\text{AB}}, 0)}, \quad (5.23)$$

$$k_2 = k_0^{\text{AB}} \exp \left[+\frac{\theta^{\text{AB}}}{2} \right] \frac{S(\Lambda^{\text{AB}}, \theta^{\text{AB}})}{S(\Lambda^{\text{AB}}, 0)}, \quad (5.24)$$

$$k_3 = k_0^{\text{BC}} \exp \left[-\frac{\theta^{\text{BC}}}{2} \right] \frac{S(\Lambda^{\text{BC}}, \theta^{\text{BC}})}{S(\Lambda^{\text{BC}}, 0)}, \quad (5.25)$$

$$k_4 = k_0^{\text{BC}} \exp \left[+\frac{\theta^{\text{BC}}}{2} \right] \frac{S(\Lambda^{\text{BC}}, \theta^{\text{BC}})}{S(\Lambda^{\text{BC}}, 0)}, \quad (5.26)$$

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:

$$\theta^{\text{XY}} = \frac{F}{RT} (E - E_{\text{XY}}^{\ominus}), \quad (5.27)$$

$$\Lambda^{\text{XY}} = \frac{F}{RT} \lambda^{\text{XY}}, \quad (5.28)$$

where E (V) is potential, $E_{\text{XY}}^{\ominus}$ (V) is the formal potential of the XY couple, λ^{XY} (eV) is the reorganization energy, R is the gas constant and T (K) is the temperature.

The integral:

$$S(\Lambda, \theta) = \int_{-\infty}^{\infty} \frac{\exp \left[\frac{-(\epsilon - \theta)^2}{4\Lambda} \right]}{2 \cosh \left[\frac{\epsilon}{2} \right]} d\epsilon \quad (5.29)$$

where ϵ is an integration variable, is evaluated numerically using the trapezium rule. It should be noted that in the limit $\lambda \rightarrow \infty$ the rate constants given by the Marcus-Hush model become identical to those given by Butler-Volmer model for $\alpha = 0.5$.

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:

$$I_{\text{total}} = \frac{\sum_j Q_j I_j}{\sum_j Q_j} \quad (5.30)$$

with Q_j , the weighting of the j th simulation, given by the Gaussian function:

$$Q_j = \exp \left[-\frac{(\chi_j - \mu)^2}{2\sigma^2} \right] \quad (5.31)$$

and I_j is the current of the j th simulation, given by Eq.(5.15).

For a redox species confined at the electrode surface, k_0 is related to tunneling distance by [49, 50]:

$$k_0 \propto \exp(-\beta r_0), \quad (5.32)$$

where r_0 (Å) is the distance separating the redox centre from the electrode surface and β (Å⁻¹) is the electronic coupling attenuation coefficient which takes a value of 1.59 Å⁻¹ in water [51]. Thus, in contrast to the distribution of formal potentials, a Gaussian distribution of electron tunneling distances is not manifested as a Gaussian distribution of k_0 values.

k_0 is more precisely given by [49, 50]:

$$k_0 = \frac{4\pi^2}{h} \rho H^2 S(\Lambda, 0) \exp(-\beta r_0), \quad (5.33)$$

where h is Planck's constant, ρ (eV⁻¹) is the density of states in the electrode and H (eV) is the electronic coupling matrix at the distance r_0 (Å).

It should be noted that values of k_0 quoted in this and in the next chapter are defined at the electrode surface and are subject to Eq.(5.32), thus a value of 10^6 s^{-1} at the electrode surface is equal to 0.113 s^{-1} at a distance of $10 \text{ \AA}$ from the electrode, assuming β takes the value $1.6 \text{ \AA}^{-1}$ [51].

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.

5.3. Experimental

5.3.1. 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 Haën (Seelze, Germany), tetrabutylammonium 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 $18.2 \text{ M}\Omega\cdot\text{cm}$ at 25°C (Millipore Water Systems, UK).

Electrochemical measurements were conducted using a μ Autolab 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/s . The response of a redox modified electrode to staircase cyclic voltammetry is not, under all conditions, equivalent to that of an analogous 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 $\nu > 10k_0E_{\text{step}}$ [52], i.e. for the current system, when the scan rate, ν , is greater than ~ 12.8 V/s. These differences between the two methods are further minimised through the use of a low α 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.

Edge plane pyrolytic graphite (EPPG) electrode (4.9 mm diameter, Le Carbone, Ltd. Sussex, UK) 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.

5.3.2. Synthesis of anthraquinone-2-diazonium tetrafluoroborate

See section 4.2.2.1, page 114.

5.3.3. Electrochemical modification of EPPG electrode with 2-anthraquinonyl groups

The edge plane pyrolytic graphite (EPPG) electrode was polished on alumina lapping compounds (Buehler, Coventry, U.K.) of decreasing sizes ($1.0\ \mu\text{m}$, $0.3\ \mu\text{m}$) on soft lapping pads and sonicated in deionised water in an ultrasound bath for 3 minutes and dried in air.

Surface modification of the EPPG electrode was carried out by electrochemical reduction of a ca $5\text{ }\mu\text{M}$ solution of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) in a 0.1 M TBAP solution in acetonitrile. The modification solution was kept in an ice-water bath in order to minimize spontaneous reaction between diazonium salt and carbon surface as it is much less controllable and generally it can lead to a relatively high surface coverage. Reduction was carried out by scanning the potential between 0.8 and -1.3 V vs. Ag wire at 0.1 V/s starting at 0.8 V for 13 times.

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

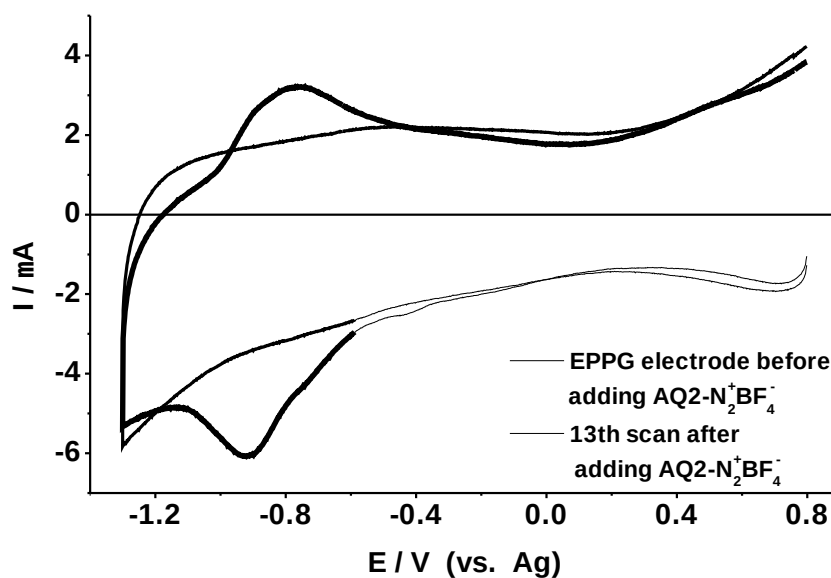
5.3.4. Voltammetric and chronoamperometric characterization of EPPG-AQ2 modified electrode

The EPPG-AQ2 modified electrode was characterized in aqueous solution of 0.1 M NaOH with 0.1 M KCl as supporting electrolyte between -0.3 and -1.3 V vs. SCE over a wide range of scan rates ($1\text{--}50\text{ V/s}$). The step potential for all scan rates was 0.01281 V , because the ratio $\frac{\text{scan rate}}{\text{step potential}}$ must be $\leq 4000/\text{s}$, therefore it is not possible to keep the step potential very low for all scan rates. To avoid the influence of various step potentials 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 theory for a uniform surface and with distribution of either formal potentials or tunneling distances, were also performed using a potential staircase (0.01281 V). Chronoamperograms of EPPG-AQ2 and EPPG electrodes were recorded from -0.3 V vs. SCE (for 5 s) to a range of more negative potentials, up to -1.3 V , for 0.1 s (sample time:

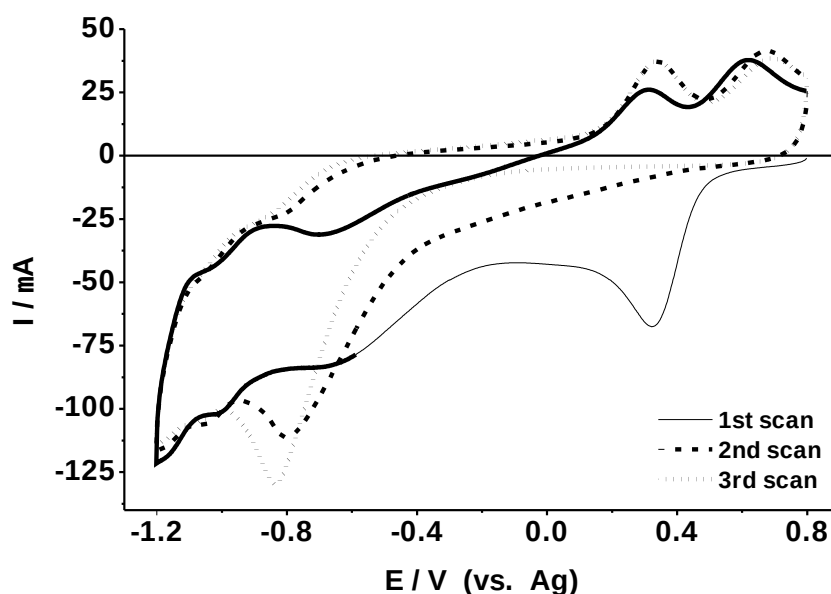
0.0001 s), also in a deoxygenated aqueous solution of 0.1 M NaOH with 0.1 M KCl.

5.4. Experimental results

5.4.1. Electrochemical modification of EPPG electrode with 2-anthraquinonyl groups



(a) $\text{AQ2-N}_2^+\text{BF}_4^-$ concentration: $5 \mu\text{M}$



(b) $\text{AQ2-N}_2^+\text{BF}_4^-$ concentration: 3.18 mM

Fig. 5.1: Electrochemical modification of an EPPG electrode with 2-anthraquinonyl groups in a deoxygenated with nitrogen acetonitrile solution containing (a) ca $5 \mu\text{M}$ or (b) 3.18 mM solution of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) and 0.1 M TBAP. Scan rate: 0.1 V/s.

Fig. 5.1a shows the electrochemical modification of edge plane pyrolytic graphite (EPPG) electrode with 2-anthraquinonyl groups. Anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) dissolved in acetonitrile with 0.1 M TBAP as supporting electrolyte, was reduced using the EPPG surface as a cathode. Reduction was carried out by scanning the potential between 0.8 and -1.3 V vs. Ag wire at 0.1 V/s, starting at 0.8 V for 13 times. The voltammogram of the EPPG-AQ2 modified electrode (thick line in Fig. 5.1a) reveals only oxidation and reduction peaks for surface bound 2-anthraquinonyl groups (at ca -0.8 V vs. Ag). It is possible to observe the diazonium cation (AQ2-N_2^+) reduction peak in solutions of higher concentrations. Fig. 5.1b shows the modification using 3.18 mM solution of $\text{AQ2-N}_2^+\text{BF}_4^-$. In the first scan (solid line) the reduction peak of diazonium cation appears at ca $+0.3$ V vs. Ag. It can only be observed in the first scan, in subsequent ones (second – dashed line, third – dotted line) it disappears because of blocking by thick polymeric layers. Electrochemical modifications using high concentration solutions of diazonium salts lead to maximum surface coverage but this can give a complex electrochemical response due to the intrinsic heterogeneity of polymeric layers, as also seen in Fig. 5.1b. However this method, unlike spontaneous modification, is reproducible and controllable and more importantly, it can give very low surface coverage, even lower than a monolayer, simply by reducing the concentration of diazonium salt solution and/or the number of scans.

5.4.2. Voltammetric and chronoamperometric characterization of EPPG-AQ2 modified electrode

The EPPG-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. 5.2. The voltammetric response of AQ at edge plane pyrolytic graphite electrode corresponds to the following redox reaction:



however at pH higher than 12.05 the reduction product is present in anionic form (AQ^{2-}) [27, 53].

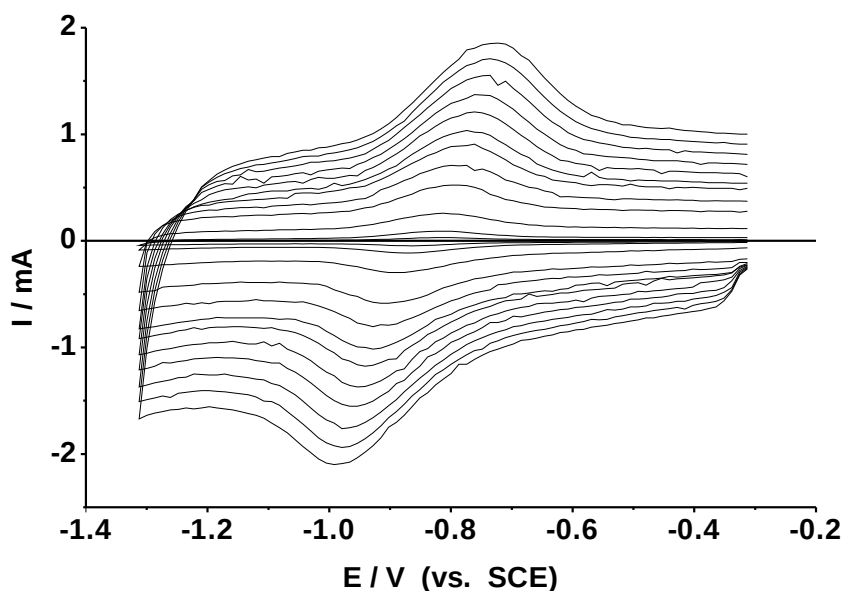


Fig. 5.2: Cyclic voltammograms of the EPPG-AQ2 modified electrode in a N_2 -deoxygenated aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Scan rate range: 1–50 V/s.

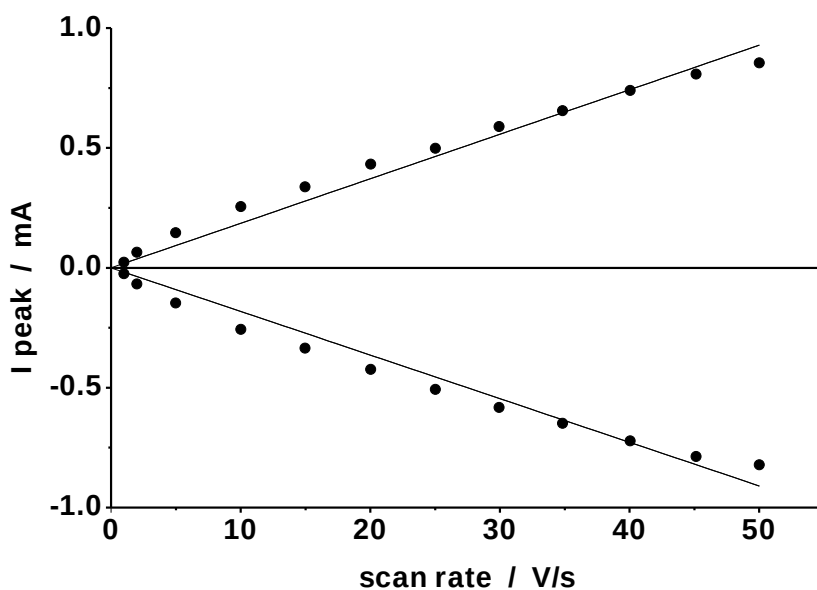


Fig. 5.3: Plot of oxidation and reduction peak current against scan rate (data from Fig. 5.2, R^2 : 0.992 – anodic branch and 0.990 – cathodic branch).

The relationship between peak current and scan rate (Fig. 5.3) was found to be linear, demonstrating that anthraquinone was indeed surface bound. The average surface coverage calculated from Eq. (5.2), page 131, for the whole scan rate range was $\text{ca } 2.62 \cdot 10^{-11} \text{ mol/cm}^2$. The literature value of a monolayer coverage of anthraquinone-2-monosulfonate, which is a bigger molecule than anthraquinone, is $\text{ca } 1.4 \cdot 10^{-10} \text{ mol/cm}^2$ assuming a flat orientation of the molecules on the surface [53, 54]. For 2,6-AQDS (anthraquinone-2,6-disulfonate) the value is $1.32 \cdot 10^{-10} \text{ mol/cm}^2$, also assuming a flat orientation [55]. It is possible to roughly estimate Γ_{AQ} for a monolayer coverage from the surface area of the molecule. Assuming all C–C bonds 140 pm (as in benzene) and C=O 123 pm (as in carbonyl compounds) for a flat orientation of the adsorbate Γ_{AQ} would be around $4.4 \cdot 10^{-10} \text{ mol/cm}^2$. Anthraquinone-2 groups are also likely to be 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 $2.4 \cdot 10^{-9} \text{ mol/cm}^2$. These values are only estimates which do not take spaces between molecules and any imperfections into account but they illustrate the order of magnitude expected for a monolayer coverage of either vertically or horizontally aligned anthraquinone. Due to the intrinsic roughness of the EPPG surface, the actual surface area is larger than the geometric one which was used to calculate Γ_{AQ} from Eq. (5.2), page 131, therefore the real surface coverage of anthraquinone for the EPPG-AQ2 electrode used in all of our experiments was certainly much lower than a monolayer. Such low surface concentration helps to avoid interactions between the adsorbed anthraquinone molecules.

Chronoamperograms of both the bare EPPG and the EPPG-AQ2 modified

electrodes were recorded from -0.3 V vs. SCE (where a negligible reduction of anthraquinone occurs) to a range of potentials where partial or full conversion from AQ to AQ^{2-} takes place, up to -1.3 V vs. SCE. Fig. 5.4 shows the $\ln|I(t)|$ against time plots for step -1.3 V/s (full conversion) for bare EPPG and EPPG-AQ2 electrodes and also for the difference between them ($\ln|I_{\text{EPPG-AQ2}} - I_{\text{EPPG}}|$). The subtraction was an attempt to remove the electrode charging current as it probably occurs over a very similar timescale as the reduction of anthraquinone (there are no two distinct regions of significantly different slopes at very short times). Moreover, the $\ln|I_{\text{EPPG-AQ2}}|$ vs. time plot is not linear but curved and therefore it is not possible to extract an apparent rate constant by measuring the slope of the linear region of the plot as various parts of the plot have significantly different slopes. The subtraction clearly does not deconvolute faradaic and capacitance signals completely as the shape of $\ln$ of subtracted current vs. time is not typical for a simple reduction process and therefore it leads to uncertainty of apparent rate constants obtained this way. In order to get kinetic and thermodynamic parameters, in the present case at least, cyclic voltammograms have to be used, because it is possible to subtract capacitance current more accurately.

5.4.3. Simulations of cyclic voltammograms according to Marcus-Hush theory

Cyclic voltammetry is advantageous to chronoamperometry, especially for relatively fast reactions as it makes the background current subtraction possible (Fig. 5.5). This allows us to simulate the exact faradaic process and avoid errors originating from the overlap of charging and faradaic currents. However both peaks for EPPG-AQ2 modified electrode are very broad, even at low scan rates. At 1 V/s

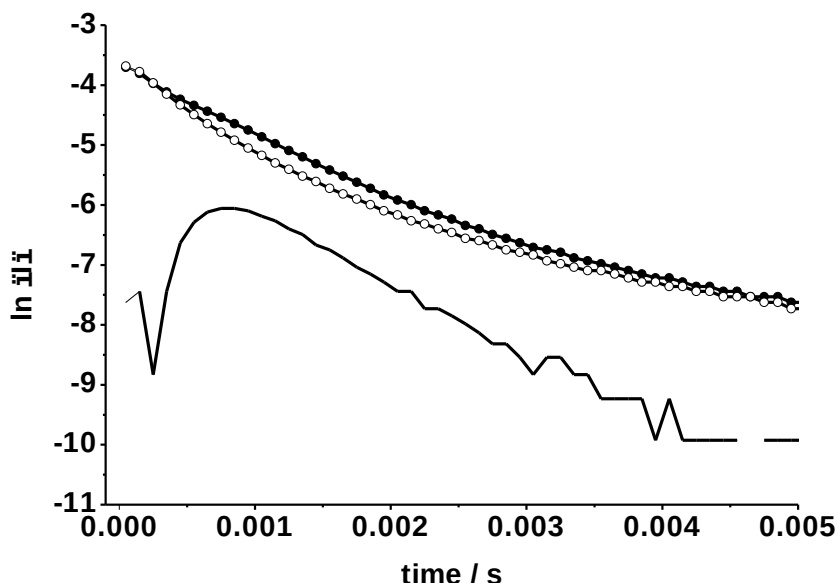


Fig. 5.4: The $\ln|i(t)|$ against time plots for the current-time transients for bare EPPG (open circles), EPPG-AQ2 modified electrode (solid circles) and for $|I_{\text{EPPG-AQ2}} - I_{\text{EPPG}}|$ (solid line). Step: -1.3 V/s; aqueous solution containing 0.1 M NaOH and 0.1 M KCl.

the full width at half of the peak maximum height (FWHM), which is diagnostic of the homogeneity of the monolayer, was 148 mV for the oxidation peak and 135 mV for the reduction peak. These values are only approximate because of tailing of the both peaks making baseline subtraction and therefore the values of peak heights somewhat uncertain. Values of FWHM that are larger or smaller than $\frac{90.6}{n}$ mV at 25°C , which is expected for identical and independent sites, suggesting that the adsorbates do not react with the electrode at the same rate [39].

The baseline-subtracted experimental voltammetry shows very good agreement when compared to simulation of Marcus-Hush theory for a uniform surface (Fig. 5.6a). However, to achieve so close a fit it is necessary to use probably unrealistically small reorganisation energies of 0.12 eV for the first and 0.1 eV for the second electron transfer step (Tab. 5.1a). λ values of 0.1 eV are probably realistic for reactions of organic molecules only in hydrocarbon-like solvents where the dipolar reorientation energies are small [44]. Ferrocene containing self assembled

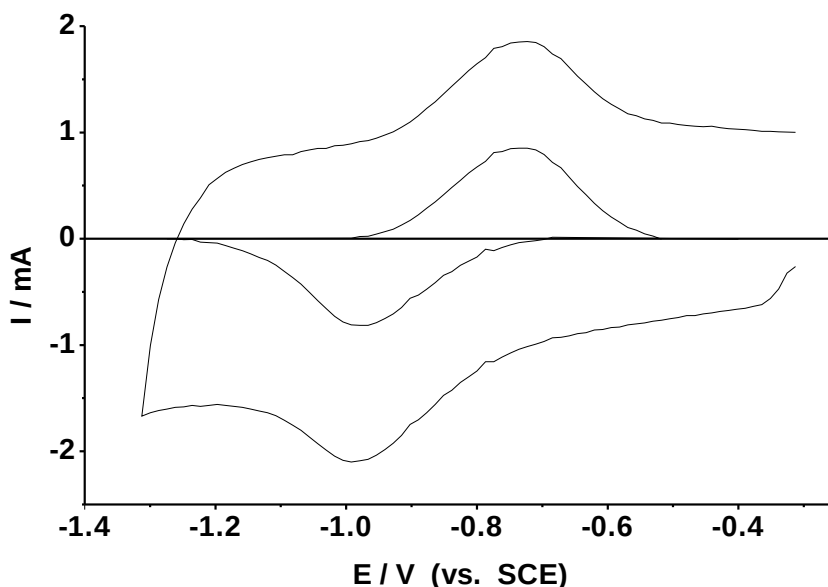
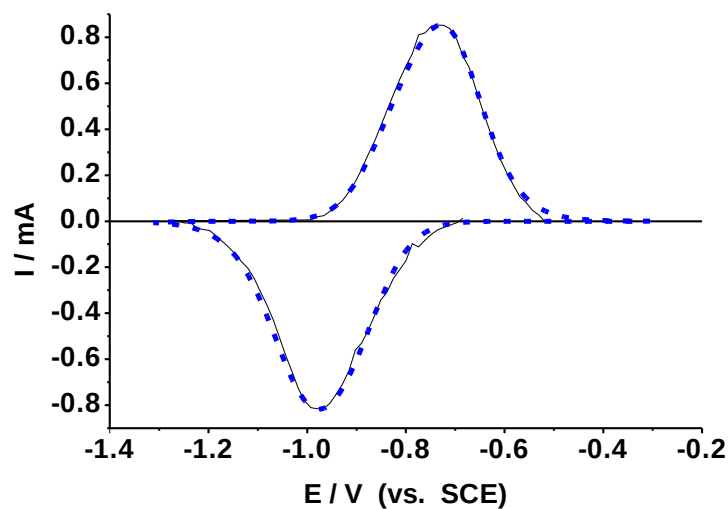


Fig. 5.5: Comparison of an experimental cyclic voltammogram (thin line) with the baseline-subtracted voltammogram (thick line). Scan rate: 50 V/s.

monolayers at gold electrodes in 0.1 M aqueous HClO_4 have $\lambda = 0.85$ eV [37, 44] or $\lambda = 0.87$ eV [56].

The comparison of the baseline-subtracted experimental voltammetry with the simulation which includes distribution of r_0 shows a worse fit (Fig. 5.6b) as far as the shape of the peaks is concerned while the peak potentials are in good agreement. This simulation permits us to use only slightly higher reorganisation energies when compared with Marcus-Hush theory for a uniform surface (Tab. 5.1b) and it also requires very high values of k_0 .

The simulation which includes a distribution of $E^{\ominus'}$ is depicted in Fig. 5.6c. The values of reorganisation energies (Tab. 5.1c) are much higher than for Marcus-Hush theory for a uniform surface (Tab. 5.1a) and for simulated distribution of tunneling distances (Tab. 5.1b). Reorganisation energies of 0.7 eV and 1.0 eV correspond to 67.5 and 96.5 kJ/mol respectively, whereas in potential step experiments the largest overpotential ($\eta = E - E^{\ominus'}$) was ca 0.5 V which is equivalent to 48.2 kJ/mol – slightly too low for the inverted region to become apparent. According to Marcus theory



(a) uniform surface

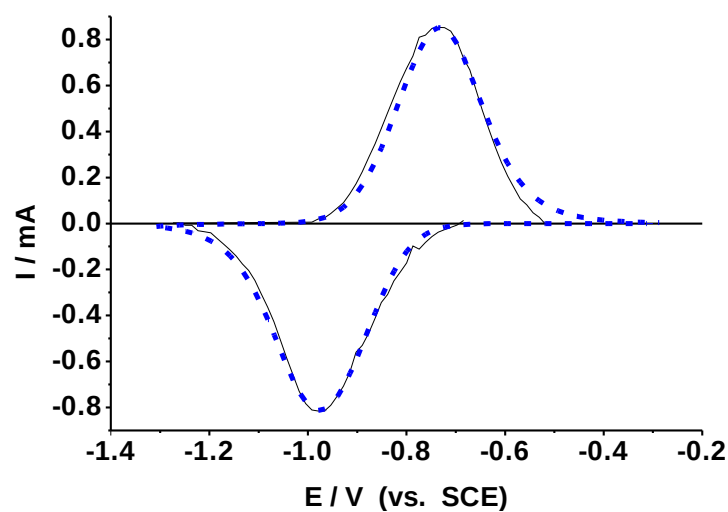
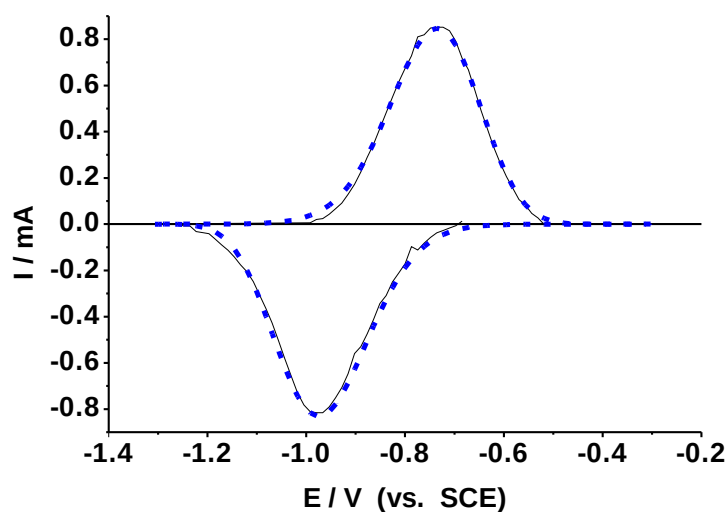

(b) distribution of r_0

(c) distribution of $E^{\ominus'}$

Fig. 5.6: Comparison of baseline-subtracted experimental voltammetry (solid line) with simulated cyclic voltammetry for Marcus-Hush theory for: (a) uniform surface, (b) simulated distribution of tunneling distances and (c) simulated distribution of formal potentials. Scan rate: 50 V/s.

	first step: EPPG-AQ/EPPG-AQ ⁻	second step: EPPG-AQ ⁻ /EPPG-AQ ²⁻
$E^{\ominus'}$	-0.825 V	-0.895 V
k_0	140 s ⁻¹	120 s ⁻¹
λ	0.12 eV	0.1 eV

(a) uniform surface (Fig. 5.6a)

	first step: EPPG-AQ/EPPG-AQ ⁻	second step: EPPG-AQ ⁻ /EPPG-AQ ²⁻		
$E^{\ominus'}$	-0.825 V	-0.885 V	r_0	1.8 Å
k_0	700 s ⁻¹	600 s ⁻¹	β	1 Å ⁻¹
λ	0.15 eV	0.18 eV	$\sigma(r_0)$	0.6 Å

 (b) distribution of r_0 (Fig. 5.6b)

	first step: EPPG-AQ/EPPG-AQ ⁻	second step: EPPG-AQ ⁻ /EPPG-AQ ²⁻
$E^{\ominus'}$	-0.82 V	-0.89 V
k_0	110 s ⁻¹	100 s ⁻¹
λ	0.7 eV	1.0 eV
$\sigma(E^{\ominus'})$	0.06 V	

 (c) distribution of $E^{\ominus'}$ (Fig. 5.6c)

Tab. 5.1: Parameters used in the simulated cyclic voltammetry for Marcus-Hush theory for (a) uniform surface, (b) distribution of tunneling distances and (c) distribution of formal potentials for 50 V/s.

the rate constants reach a maximum at $\eta = \lambda$ and for homogeneous solution reactions start to decrease, for heterogeneous reactions at metal electrodes, rates reach a plateau. To observe this kind of behaviour the reorganization energy, λ , would have to be much lower or the overpotential higher. As figures of the variation of λ for the first (EPPG-AQ/EPPG-AQ⁻) and the second (EPPG-AQ⁻/EPPG-AQ²⁻) electron transfer steps (Fig. 5.7a and 5.7b) suggest, significant deviations from the experimental voltammograms are evident for λ_{first} and $\lambda_{\text{second}} = 0.001$ up to ca 0.2 and for values ca 0.5 – 0.7 simulated voltammograms start to be very similar to

experimental ones. For both λ there is no upper limit, as even simulations with λ_{first} and $\lambda_{\text{second}} = 1000$ do not significantly deviate from the shape and the size of the experimental voltammograms and actually they are the same as simulated voltammograms for Butler-Volmer theory assuming $\alpha = 0.5$ (Fig. 5.8). In order to make inverted region to appear the overpotential would have to be at least 0.7 V, what would make solvent breakdown effects more likely to start to interfere with the measurement and also it would make charging current more difficult to resolve from the faradaic transient.

The values of formal potentials, $E^{\ominus'}$, for the first (EPPG-AQ/EPPG-AQ⁻) and the second (EPPG-AQ⁻/EPPG-AQ²⁻) electron transfer steps are rather fixed. A ± 10 mV alteration of either $E_{\text{first}}^{\ominus'}$ or $E_{\text{second}}^{\ominus'}$ shifts both peaks slightly and changes their heights. Similarly, a ± 10 s⁻¹ modification of either $k_{0,\text{first}}$ or $k_{0,\text{second}}$ starts to influence peak heights and peak potentials. For the standard deviation, $\sigma(E^{\ominus'})$, even a ± 5 mV change affects the sizes of both peaks significantly.

All three simulations of cyclic voltammograms according to Marcus-Hush theory (a uniform surface, $E^{\ominus'}$ distribution and r_0 distribution) show very good agreement with experimental voltammograms as far as peak potentials are concerned (Fig. 5.9). In order to be able to interpret the results of simulations for the EPPG-AQ2 modified electrode correctly it is crucial to analyze closely all the parameters used for simulations, not only the shapes and the sizes of peaks.

5.5. Conclusions

To the best of our knowledge, this is the first time that Marcus-Hush theory has been applied to two electron redox system, namely to edge plane pyrolytic

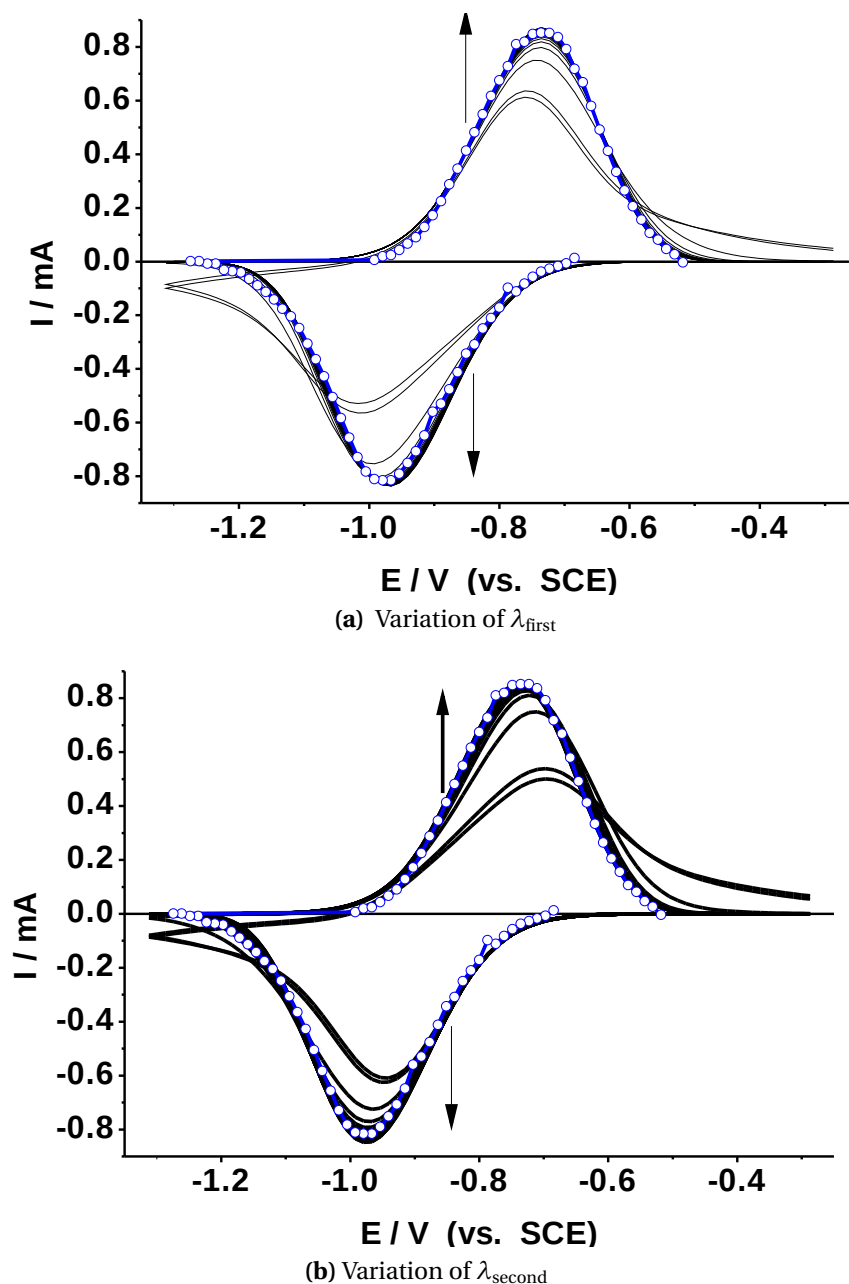


Fig. 5.7: Variation of (a) λ_{first} and (b) λ_{second} . λ values = 0.001, 0.01, 0.1 – 1.5 (every 0.1), 2, 3, 5, 10, 100 and 1000. Baseline-subtracted experimental voltammetry (open circles) at 50 V/s. Arrows show the direction of λ increase.

graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2). Cyclic voltammograms were fitted with simulations of Marcus-Hush theory for a uniform surface and also with a distribution of either standard potential, $E^{\ominus'}$, or tunneling distance, r_0 . The values of reorganisation energies, λ , used for the simulation of $E^{\ominus'}$ distribution of 60 mV gave the best fits to the experimentally observed broad cyclic voltammograms and also were consistent with the literature

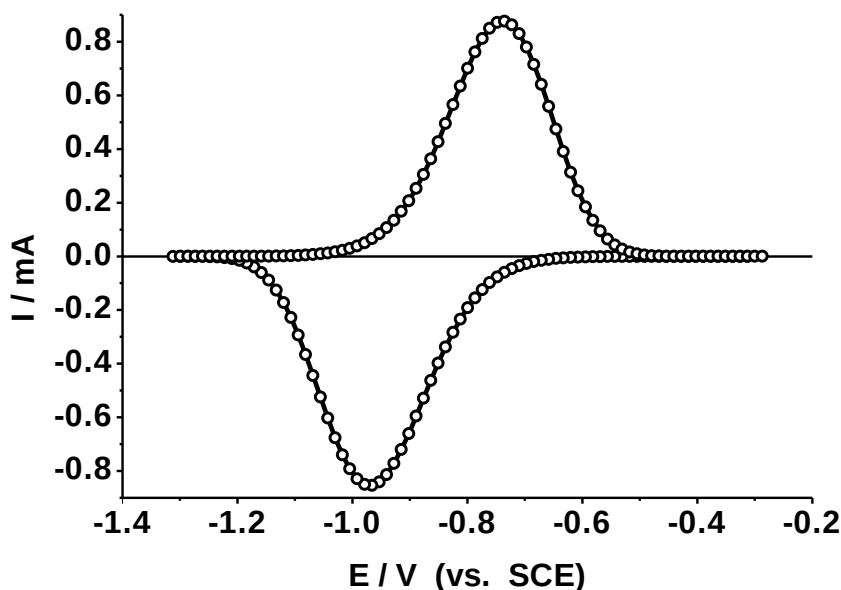


Fig. 5.8: Comparison between cyclic voltammograms obtained from simulations of Butler-Volmer theory (black line) and Marcus-Hush theory (open circles). For both simulations: $E_{\text{first}}^{\ominus'} = -0.82$ V, $E_{\text{second}}^{\ominus'} = -0.89$ V, $k_{0,\text{first}} = 110$ s $^{-1}$, $k_{0,\text{second}} = 100$ s $^{-1}$, scan rate = 50 V/s, $\sigma(E^{\ominus'}) = 60$ mV. For Butler-Volmer simulation: $\alpha_{\text{first}} = 0.5$ and $\alpha_{\text{second}} = 0.5$. For Marcus-Hush simulation: $\lambda_{\text{first}} = 1000$ eV and $\lambda_{\text{second}} = 1000$ eV.

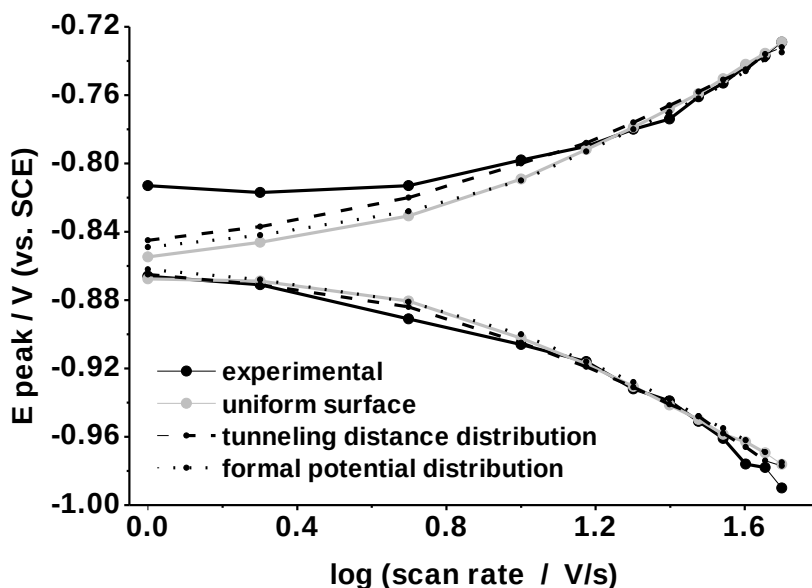


Fig. 5.9: Experimental peak potentials for EPPG-AQ2 modified electrode compared with peak potentials obtained from simulations of cyclic voltammograms according to Marcus-Hush theory.

values for adsorbed redox systems. The standard deviation $\sigma(E^{\ominus'}) = 60$ mV was previously reported for the edge plane pyrolytic graphite electrode covalently modified with ferrocene (EPPG-Fc) [47]. Moreover EPPG-AQ2 modified electrode at overpotentials lower than ca 0.7 V can be analyzed according to Butler-Volmer model. The influence of the electrode material on the electro-reduction kinetics

of covalently attached 2-anthraquinonyl groups will be presented in chapter 6.

5.6. References

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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.

The work presented in this chapter has been published in
International Journal of Electrochemical Science, 2011, 6, 6047–6062.

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A gold electrode was derivatized by electrochemical reduction of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) 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, $E^{\ominus'}$, 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-AQ2²⁻ process compared to the parameters of the EPPG-AQ2/EPPG-AQ2²⁻ process described in chapter 5 show much faster kinetics, attributed to the higher density of electronic states for a gold electrode.

6.1. 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 $E^{\ominus'}$ 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, $\nu_e(E)$, is:

$$\nu_e(E) = k_e(E)[O_{(s)}], \quad (6.1)$$

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 states/eV [4]. 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 than 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 chapter the two electron redox system attached to a gold electrode is explored 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.

6.2. Theory

See section 5.2, page 135.

6.3. Experimental

6.3.1. 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 Haën (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 M Ω ·cm at 25°C (Millipore Water Systems, UK).

Electrochemical measurements were conducted using a μ Autolab 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 $\nu > 10k_0E_{\text{step}}$ [34], i.e. for the current system, when the scan rate, ν , 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.

6.3.2. Synthesis of anthraquinone-2-diazonium tetrafluoroborate

See section 4.2.2.1, page 114.

6.3.3. 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 ($1.0\ \mu\text{m}$, $0.3\ \mu\text{m}$) 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 $2\ \mu\text{M}$ solution of anthraquinone-2-diazonium tetrafluoroborate (AQ2- $\text{N}_2^+\text{BF}_4^-$) in a 0.1 M TBAP solution in acetonitrile, because the ca $5\ \mu\text{M}$ 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 and $-1.3\ \text{V}$ vs. Ag wire at $0.1\ \text{V/s}$ starting at $0.8\ \text{V}$ 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.

6.3.4. 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 and $-1.2\ \text{V}$ vs. SCE in

a wide range of scan rates (1–50 V/s) (Fig. 6.3). The step potential for all scan rates was 0.01281 V, because the ratio $\frac{\text{scan rate}}{\text{step potential}}$ must be $\leq 4000/\text{s}$, 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).

6.4. Results

6.4.1. Electrochemical modification of a gold electrode with 2-anthraquinonyl groups

At first the gold electrode was modified using the same concentration of the anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) 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. 6.1), 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 .

Fig. 6.2 shows the electrochemical modification of the gold electrode with 2-anthraquinonyl groups using a 2 μM solution of anthraquinone-2-diazonium

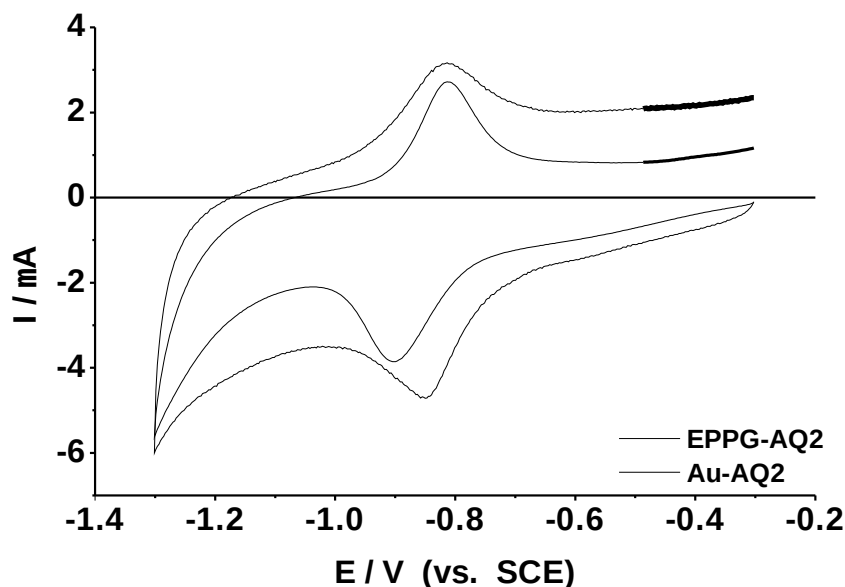


Fig. 6.1: Cyclic voltammograms of EPPG-AQ2 (thick line) and Au-AQ2 (thin line) modified electrodes in a deoxygenated with nitrogen aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Scan rate: 0.1 V/s. Both EPPG and Au electrodes modified electrochemically in an acetonitrile solution containing ca 5 μ M of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) and 0.1 M TBAP. The ratio between geometric surface area of the EPPG to the gold electrode was 7.41.

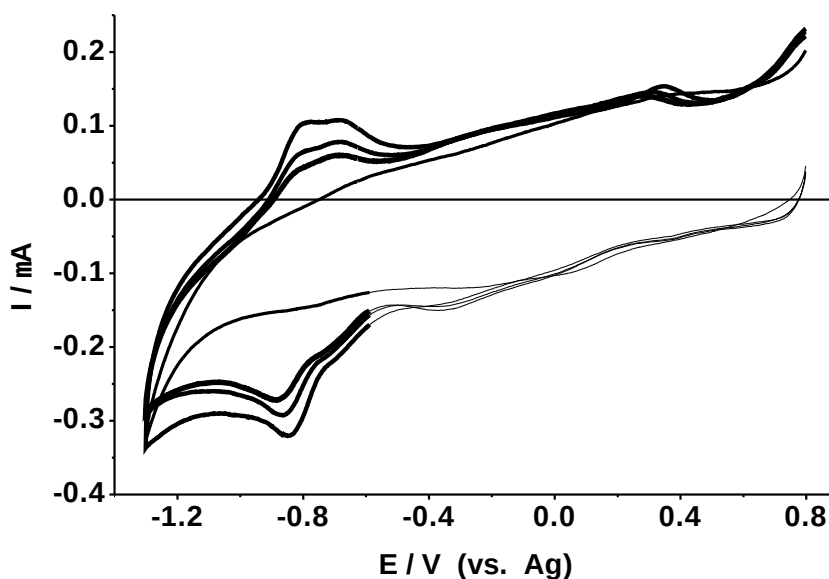


Fig. 6.2: Electrochemical modification of the gold electrode with 2-anthraquinonyl groups in a deoxygenated with nitrogen acetonitrile solution containing ca 2 μ M of anthraquinone-2-diazonium tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) and 0.1 M TBAP. Scan rate: 0.1 V/s; thin line: Au electrode before adding $\text{AQ2-N}_2^+\text{BF}_4^-$; thick lines: 7th, 14th and 23rd scan after adding $\text{AQ2-N}_2^+\text{BF}_4^-$.

tetrafluoroborate ($\text{AQ2-N}_2^+\text{BF}_4^-$) 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 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. 6.2) 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].

6.4.2. 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. 6.3. The voltammetric response of Au-AQ2 at pH higher than 12.05 corresponds to the following redox reaction [17, 35]:

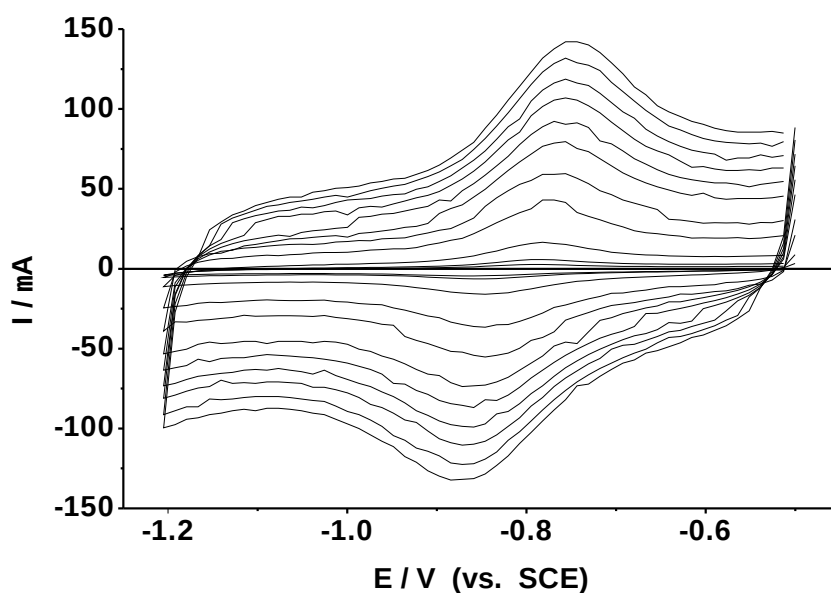


Fig. 6.3: Cyclic voltammograms of the Au-AQ2 modified electrode in a deoxygenated with nitrogen aqueous solution containing 0.1 M NaOH and 0.1 M KCl. Scan rate range: 1–50 V/s.

The 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 $2 \mu\text{M}$ $\text{AQ2-N}_2^+\text{BF}_4^-$ 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. 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. ν plot:

$$I_p = \frac{n^2 F^2}{4RT} \nu A \Gamma. \quad (6.3)$$

Γ of 2-anthraquinonyl groups at the gold electrode for the whole scan rate range was ca $1.51 \cdot 10^{-11}$ mol/cm². 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/cm². 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/cm². 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/cm² [36]. The surface concentration of 2-anthraquinonyl groups equal to ca $1.5 \cdot 10^{-11}$ mol/cm² is lower than the literature value and estimations mentioned above, therefore it can be

confidently assumed that the $\Gamma_{\text{Au-AQ2}}$ in the experiments described in this chapter 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.

6.4.3. Simulations of cyclic voltammograms according to Marcus-Hush-Chidsey theory

Baseline subtraction of experimental cyclic voltammetry (Fig. 6.4) allows us to simulate the exact faradaic process and avoid errors originating from the overlap of charging and faradaic currents.

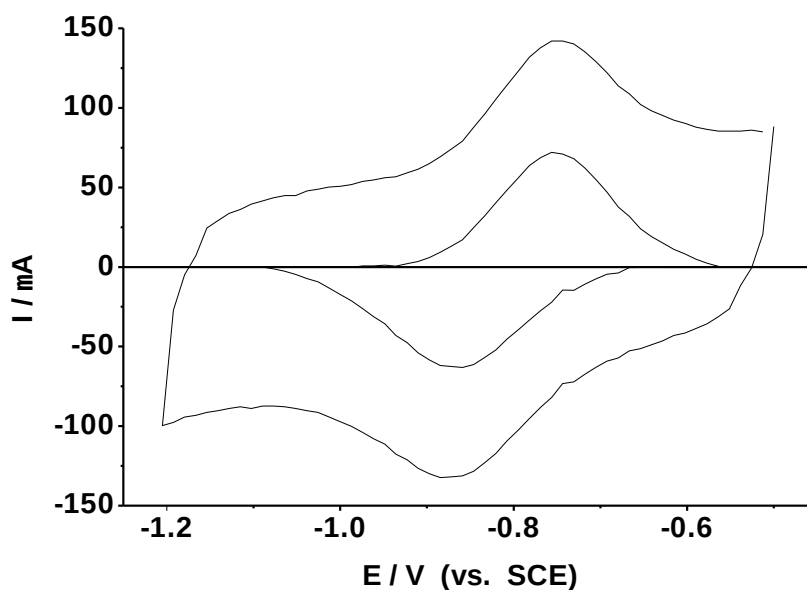


Fig. 6.4: Comparison of an experimental cyclic voltammogram (thin line) with the baseline-subtracted voltammogram (thick line). Scan rate: 50 V/s.

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 are 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 $\frac{90.6}{n}$ 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-AQ2²⁻ two electron redox process cannot be fitted with Marcus-Hush-Chidsey theory assuming a uniform surface (Fig. 6.5a and Tab. 6.1a). 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.

The comparison of the baseline subtracted experimental voltammetry with the simulation which includes distribution of tunneling distances, r_0 , shows a closer fit (Fig. 6.5b) 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. 6.1b). As mentioned in chapter 5, 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].

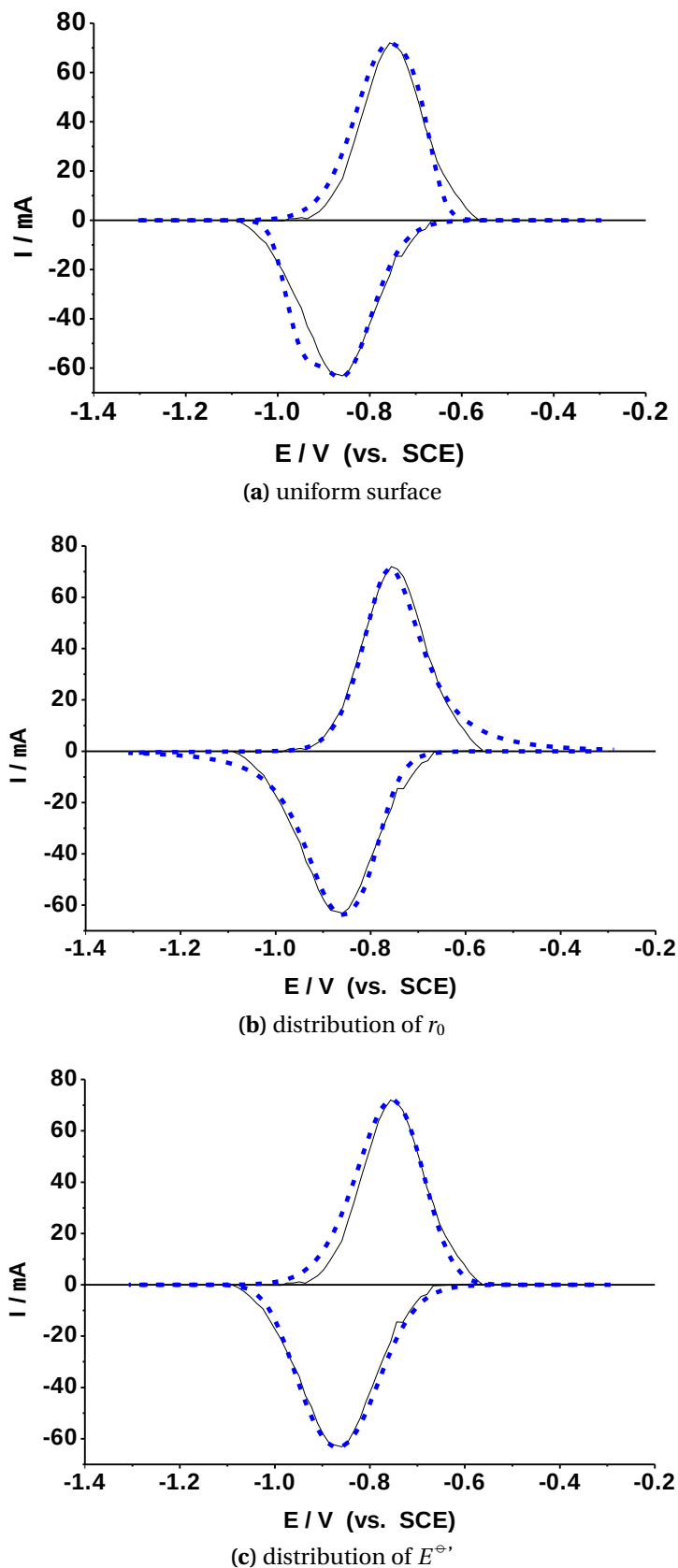


Fig. 6.5: Comparison of baseline-subtracted experimental voltammetry (solid line) with simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for: (a) uniform surface, (b) simulated distribution of tunneling distances and (c) simulated distribution of formal potentials. Scan rate: 50 V/s.

	first step: Au-AQ2/Au-AQ2⁻	second step: Au-AQ2⁻/Au-AQ2²⁻
$E^{\ominus'}$	-0.778 V	-0.865 V
k_0	360 s ⁻¹	290 s ⁻¹
λ	0.7 eV	1 eV

(a) uniform surface (Fig. 6.5a)

	first step: Au-AQ2/Au-AQ2⁻	second step: Au-AQ2⁻/Au-AQ2²⁻		
$E^{\ominus'}$	-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

 (b) distribution of r_0 (Fig. 6.5b)

	first step: Au-AQ2/Au-AQ2⁻	second step: Au-AQ2⁻/Au-AQ2²⁻
$E^{\ominus'}$	-0.78 ± 0.005 V	-0.85 ± 0.005 V
k_0	500 ± 50 s ⁻¹	330 ± 40 s ⁻¹
λ	0.7 eV*	1.0 eV*
$\sigma(E^{\ominus'})$	0.04 ± 0.003 V	

 (c) distribution of $E^{\ominus'}$ (Fig. 6.5c)

Tab. 6.1: Best fit parameters used in the simulated cyclic voltammetry for Marcus-Hush-Chidsey theory for (a) uniform surface, (b) distribution of tunneling distances and (c) distribution of formal potentials for 50 V/s. * – For $\pm$ analysis of both λ see text.

The simulation which includes a distribution of formal potentials, $E^{\ominus'}$, is depicted in Fig. 6.5c. 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⁻ process are 0.04 V less negative than for EPPG-AQ2/EPPG-AQ2⁻ [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-AQ2²⁻ ($k_{0,\text{first}} = 500 \text{ s}^{-1}$ and $k_{0,\text{second}} = 330 \text{ s}^{-1}$) are higher than for EPPG-AQ2/EPPG-AQ2²⁻ ($k_{0,\text{first}} = 110 \text{ s}^{-1}$ and $k_{0,\text{second}} = 100 \text{ s}^{-1}$) [33], while the reorganizational energies remain the same within experimental error (Tab.6.1c). 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-AQ2²⁻ and EPPG-AQ2/EPPG-AQ2²⁻ illustrates the dependence of the heterogeneous electron transfer rate on the DOS of the electrode material [1].

The $\sigma(E^{\ominus'}) = 40 \text{ mV}$ is lower for the Au-AQ2⁻/Au-AQ2²⁻ 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, $E^{\ominus'}$, for the first (Au-AQ2/Au-AQ2⁻) and the second (Au-AQ2⁻/Au-AQ2²⁻) electron transfer steps are fixed. A $\pm 5 \text{ mV}$ alteration of either $E_{\text{first}}^{\ominus'}$ or $E_{\text{second}}^{\ominus'}$ shifts both peaks slightly and changes their heights. A $\pm 50 \text{ s}^{-1}$ modification of $k_{0,\text{first}}$ or a $\pm 40 \text{ s}^{-1}$ modification of $k_{0,\text{second}}$ starts to influence peak heights and peak potentials. For the standard deviation, $\sigma(E^{\ominus'})$, even a $\pm 3 \text{ mV}$ 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 $\lambda_{\text{second}} = 0.001$ 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 $\lambda_{\text{second}} = 1000$ 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.

6.5. 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] (chapter 5), this chapter 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 voltammetrically 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, $E^{\ominus'}$, 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-AQ2²⁻ process demonstrate much faster kinetics than for EPPG-AQ2/EPPG-AQ2²⁻ [33], which can be expected on the basis of higher electronic density of states (DOS) for gold.

6.6. References

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Conclusions

In recent years a great attention has been focused on the preparation and optimization of modified carbon electrodes in order to improve electron transfer rates of reactions of many target analytes. Carbon electrodes are an attractive alternative to more expensive metal electrodes, moreover their surface properties, for example the presence of oxygen containing functional groups, allow a simple and quick modification.

The claimed effectiveness of cobalt phthalocyanine (CoPC) as a redox mediator for many compounds has led to creation of a variety of CoPC based modified carbon electrodes used as electrochemical sensors, but the electrochemical properties of the CoPC mediator itself have not been properly examined. In this thesis a thorough study on the solution phase and solid phase cobalt phthalocyanine is provided. One ring based and two cobalt based redox couples were found in dimethyl sulfoxide (DMSO) and in tetrahydrofuran (THF) at a glassy carbon electrode. Two processes: Co(II/I) and Co(III/II) were observed for CoPC adsorbed on basal plane pyrolytic graphite (BPPG) and edge plane pyrolytic graphite (EPPG) electrodes in phosphate buffer solution. The surface properties of both EPPG-CoPC and BPPG-CoPC modified electrodes were characterized by SEM and energy dispersive X-ray spectroscopy (EDS). It was observed that CoPC forms microcrystals, not a

monolayer as reported in the literature. The use of EPPG-CoPC modified electrode for sensing nitrite (NO_2^-) was also investigated and it was found that CoPC has no influence on the process. A bare glassy carbon electrode was proposed for the quantitative determination of nitrite as a simple alternative to some of the complexly modified electrodes reported in the literature.

The voltammetry of processes involving a proton transfer is known to be altered in the presence of unbuffered aqueous media. In this thesis the voltammetric responses of an edge plane pyrolytic graphite electrode covalently modified with 2-anthraquinonyl groups (EPPG-AQ2) and solution phase anthraquinone monosulphonate (AQMS) in the presence of a limited concentration of protons is presented. The solution phase and surface bound species show analogous response resulting in split waves. DigisimTM simulation of the AQMS voltammetry have shown that the pH adjacent to the electrode may be altered by up to 5–6 pH units in low buffered solutions which is caused by the consumption of protons during the electrochemical reaction.

Marcus-Hush-Chidsey theory has been previously successfully applied to various one electron processes involving species adsorbed on electrode surfaces, usually as self-assembled monolayers (SAMs). In this thesis the theory was applied to a $2e^-$, namely the 2-anthraquinonyl groups covalently attached to an edge plane pyrolytic graphite electrode (EPPG-AQ2) and the obtained results were compared to an AQ2 modified gold electrode (Au-AQ2). In both cases cyclic voltammograms simulated using Marcus-Hush-Chidsey theory for $2e^-$ process assuming a uniform surface were not able to achieve a good agreement between theory and experiment. Subsequently two models of surface inhomogeneity based on Marcus-Hush-Chidsey

theory were investigated: a distribution of formal potentials, $E^{\oplus'}$, and a distribution of electron tunneling distances, r_0 . For both EPPG-AQ2 and Au-AQ2 modified electrodes the simulation involving $E^{\oplus'}$ distribution turned out to be the most adequate. The parameters of the Au-AQ2/Au-AQ2²⁻ process compared to the parameters of the EPPG-AQ2/EPPG-AQ2²⁻ process showed much faster kinetics, attributed to the higher density of electronic states for a gold electrode. This is the first time that Marcus-Hush-Chidsey theory has been applied to a $2e^-$ system.



Additional information

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A.1. Reference electrodes

Potential can only be registered as a difference with respect to a chosen reference value (reference electrode). A good reference electrode needs to have a potential that is stable with time and with temperature and which is not altered by the passage of a small current.

A.1.1. The standard (or normal) hydrogen electrode (SHE or NHE)

In cell notation the standard (or normal) hydrogen electrode is written as: Pt/H₂/H⁺. All components are at unit activity.

It is used to define the standard electrode potential scale. It is very reproducible, showing differences of only 10 μ V between different hydrogen electrodes. A typical design (construction) consists of a platinum foil that is platinized in order to

catalyse easily the reaction:



The Nernst equation for the electrode is:

$$E = -\frac{RT}{F} \ln \frac{\left(\frac{p_{\text{H}_2}}{p^0}\right)^{1/2}}{a_{\text{H}^+}}, \quad (\text{A.2})$$

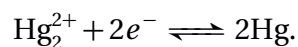
where p^0 is standard pressure (10^5 Pa).

Various procedures for platinizaion exist but normally involve the deposition of platinum black from a solution of 3 % chloroplatinic acid (H_2PtCl_6) containing a small quantity of lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$, 0.005 %) to prolong electrode life [1–3].

A.1.2. Saturated calomel electrode (SCE)

In cell notation the saturated calomel electrode is written as: $\text{Pt}/\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$, where KCl is saturated in water.

The electrode reactions are:



Overall reaction is:



The Nernst equation for the electrode is:

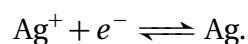
$$E = E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^\ominus - \frac{RT}{2F} \ln(a_{\text{Cl}^-})^2 = E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^\ominus - \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (\text{A.5})$$

Its potential is 0.242 V vs. NHE.

A.1.3. Silver-silver chloride electrode (Ag/AgCl)

In cell notation the silver-silver chloride electrode is written as: Ag/AgCl/KCl, where KCl saturated in water.

The electrode reactions are:



Overall reaction is:



The Nernst equation for the electrode is:

$$E = E_{\text{AgCl/Ag}}^\ominus - \frac{RT}{F} \ln a_{\text{Cl}^-}. \quad (\text{A.8})$$

Its potential is 0.197 V vs. NHE.

A.1.4. Quasi-reference electrodes

Quasi-reference electrodes such as a platinum wire, silver wire or mercury pool are sometimes used in voltammetric experiments. The advantage is low electrical resistance, but their potential may vary up to 20 mV.

A.2. Faraday's laws

The first Faraday's law states that mass changes during electrolysis are proportional to the transferred electric charge, Q : $m = kQ$, where k is a constant.

The charge depends on the time of electrolysis, t , and the current, I : $Q = It$, therefore $m = kIt$. The proportionality constant k is comprised of molar mass M , ionic charge z of the discharged ions and the Faraday constant F which is the electric charge of one mole of electrons and equals 96485 C/mol: $k = \frac{M}{zF}$, thus the first Faraday's law is:

$$m = \frac{M}{zF} It. \quad (\text{A.9})$$

The second Faraday's law says that during electrolysis the same amount of charge passes through both electrode/solution interfaces in a cell, therefore mass changes on both electrodes are proportional [4]:

$$\frac{m_1}{m_2} = \frac{\frac{M_1}{z_1}}{\frac{M_2}{z_2}}. \quad (\text{A.10})$$

A.3. References

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