



**Amplified Electron Transfer at Poly-Ethylene-Glycol (PEG)
Grafted Electrodes**

Journal:	<i>Physical Chemistry Chemical Physics</i>
Manuscript ID:	CP-ART-03-2015-001244.R1
Article Type:	Paper
Date Submitted by the Author:	25-Mar-2015
Complete List of Authors:	Hotchen, Christopher; University of Bath, Chemistry Maybury, Ian; University of Bath, Chemistry Nelson, Geoffrey; Oxford University, Chemistry Foord, J; University of Oxford, Physical Chemistry Laboratory Holdway, Philip; Oxford University, Department of Materials Marken, Frank; Bath University, Department of Chemistry

ARTICLE

Amplified Electron Transfer at Poly-Ethylene-Glycol (PEG) Grafted Electrodes

Cite this: DOI: 10.1039/x0xx00000x

Christopher E. Hotchen ^a, Ian J. Maybury ^a, Geoffrey W. Nelson ^b, John S. Foord ^c, Philip Holdway ^d, and Frank Marken ^{a*}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

“Amplified” electron transfer is observed purely based on electron transfer kinetic effects at modified carbon surfaces. An anodic attachment methodology is employed to modify the surface of glassy carbon or boron doped diamond electrodes with poly-ethylene glycols (PEGs) for polymerisation degrees of $n = 4.5$ to 9.1 (PEG200 to PEG400). Voltammetry and impedance data for aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ suggest systematic PEG structure-dependent effects on the standard rate constant for heterogeneous electron transfer as a function of PEG deposition conditions and average polymer chain length. Tunnel distance coefficients are polymerisation degree dependent and estimated for shorter PEG chains, $\beta = 0.17 \text{ \AA}^{-1}$ for aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$, consistent with a diffuse water – PEG interface. In contrast, electron transfer to 1,1'-ferrocene-dimethanol (at 1 mM concentration) appears un-impeded by PEG grafts. Mediated or “amplified” electron transfer to $\text{Fe}(\text{CN})_6^{3-/4-}$ based on the 1,1'-ferrocene-dimethanol redox shuttle is observed for both oxidation and reduction with estimated bimolecular rate constants for homogeneous electron transfer of $k_{\text{forward}} = 4 \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$ and $k_{\text{backward}} = 1 \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$. Digital simulation analysis suggests an additional resistive component within the PEG graft double layer.

Introduction

Poly-ethylene-glycol (PEG) derivatives play a central role as low-volatility additives and solvents,¹ in carbon dioxide capture,² in consumer products and green engineering,³ for electroless metal deposition,⁴ and in functional surfaces.⁵ Important surface applications of PEGs are in anti-fouling treatments to prevent non-specific protein adsorption⁶ or cell-adhesion,⁷ and as barrier layers.⁸ PEG grafting can be beneficial in membrane⁹ or sensor technologies employed for example in blood separation and analysis.

In electrochemistry PEG solvents and PEG surface modification have received only relatively little attention. The electron transfer to ferrocenes in viscous and highly viscous PEG solvents has been reported.^{10,11} Zhou et al. investigated dimethyl-ferrocene reactivity in poly-ethylene-glycols.¹² Viscous PEG environments are of interest in battery applications^{13,14} and in solar cells.¹⁵ Williams and Murray studied charge transport in redox active PEG-melts.¹⁶

PEG-grafted carbon surfaces have been employed to immobilise redox active proteins.¹⁷ In this case a chemical PEG attachment method based on reaction with acid chloride functional groups on the carbon surface has been utilised. Also the use of PEG-silanes for patterning of ITO electrode surfaces has been reported.¹⁸ Electrochemical grafting onto glassy carbon at anodic potentials was pioneered by Maeda initially in octanol.¹⁹ The same group then systematically studied several alkyl-alcohols, glycols, and poly-ethylene-glycols and reported slower electron transfer for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system at modified glassy carbon surfaces.²⁰

Reviews for a wider range of electrochemical attachment²¹ and electro-grafting protocols have appeared.²²

In this report an anodic attachment protocol (following the methodology of Maeda²⁰) is employed to modify both glassy carbon and boron-doped diamond electrode surface with poly-ethylene-glycols of polymerisation degree n (see Figure 1). A permanent modification is observed (and optimised as a function of grafting potential for both glassy carbon and boron-doped diamond) with interesting (and possibly very useful) effects on the rate of heterogeneous electron transfer for hydrophilic ($\text{Fe}(\text{CN})_6^{3-/4-}$) versus more hydrophobic (1,1'-ferrocene-dimethanol) redox systems. The results imply (i) a highly diffuse PEG-water boundary and (ii) a high degree of selectivity in the electron transfer process leading to signal “amplification” effects for combined redox systems: a trace amount of redox mediator shows a high current response due to bimolecular reaction with the second redox system in solution.

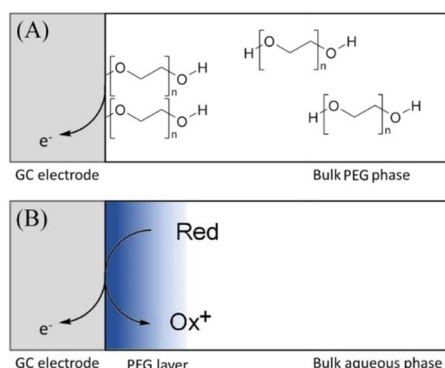


Figure 1. Schematic drawing of (A) the PEG attachment process and (B) electron transfer at a PEG-modified glassy carbon electrode.

Experimental

Reagents. Poly-ethylene-glycols with average molecular weight 200 g mol^{-1} (PEG200), 300 g mol^{-1} (PEG300) and 400 g mol^{-1} (PEG400) were obtained from Aldrich and used as the solvent for grafting solutions with lithium perchlorate (LiClO_4 , Sigma-Aldrich, $\geq 95.0\%$) as electrolyte. Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, Sigma-Aldrich, 99%), potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$, Fisons Scientific, $\geq 95.0\%$), and 1,1'-ferrocenedimethanol ($\text{Fc}(\text{CH}_2\text{OH})_2$, Aldrich, 98%) were used as redox probes for voltammetry with potassium nitrate (KNO_3 , Sigma-Aldrich, $\geq 99.0\%$) as electrolyte.

Instrumentation. Electrochemical measurements were performed using an Autolab PGSTAT12 potentiostat (Autolab, Utrecht, NL) and in a three-electrode glass cell with platinum wire counter electrode and KCl-saturated calomel electrode (SCE) at room temperature ($20 \pm 2^\circ \text{C}$). Working electrodes were either a 3 mm diameter glassy carbon (BAS Analytical, UK) or a 3 mm diameter bulk-boron-doped diamond (polished to mirror finish, DiafilmTM, Windsor Scientific, UK). The GPES software package (version 4.9005, Autolab, Utrecht, NL) was employed for data acquisition with a potential step parameter not higher than 1 mV. Electrochemical impedance measurements were performed using a Solartron 1286 potentiostat and 1250 frequency response analyser over a frequency range of 10 kHz to 0.1 Hz and with an amplitude of 10 mV. Field emission scanning electron microscopy (FESEM) images were taken using a JEOL FESEM6301F microscope. Digital simulation of voltammetry data was performed with commercial DigiElch (version 4.F) PC software package.

XPS experiments were conducted using a Thermo K Alpha (Thermo Scientific) spectrometer (operating at $\approx 10^{-8} - 10^{-9}$ Torr), a 180° double focusing hemispherical analyzer running in constant analyzer energy (CAE) mode with a 128-channel detector. A monochromated Al K α radiation source (1486.7 eV) was used. Peak fitting was conducted using XPS Peak Fit (v. 4.1) software using Shirley background subtraction. Peaks were referenced to the adventitious carbon C1s peak (284.6 eV) and peak areas were normalized to the photoelectron cross-section of the F1s photoelectron signal using atomic sensitivity factors.²³

Procedure: Attachment of Poly-ethylene-glycol Films. The working electrode – either a 3 mm diameter glassy carbon (GC) disc or 3 mm diameter boron doped diamond (BDD) disc – was polished with wet alumina paste with particle diameter $0.3 \mu\text{m}$ followed by rinsing

with de-ionised water ($18.2 \text{ M}\Omega \text{ cm}^2$). Cyclic voltammetry of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KNO_3 was performed prior to deposition of PEG films to confirm that any previous PEG deposits had been successfully removed. Deposition of PEG films was achieved by applying a fixed anodic potential for a fixed time to the working electrode immersed in a neat PEG solution with 20 mM LiClO_4 electrolyte. After deposition, the working electrode was rinsed with de-ionised water (in order to remove residual PEG from the electrode surface) and dried in a nitrogen flow prior to further experimentation. The PEG film can be removed from the electrode surface by either mechanical polishing of the electrode or by scanning the potential to +1.5 V vs. SCE in aqueous 0.1 M KNO_3 solution.

Results and discussion

PEG Attachment to Glassy Carbon or Boron-Doped Diamond: XPS Analysis

Survey spectra show photoelectron signals from nearly contaminant free surfaces containing primarily C and O. This is evident from the representative set of survey spectra pertaining to BDD and modified-BDD substrates shown in Figure 2. Al2s and Al2p signal can be seen and this likely arises from the alumina powders used in the electrode cleaning process. As BDD (or GC) is modified with PEG layers, the Al signal is attenuated, which is consistent with the addition of over-layers to the initial substrate.

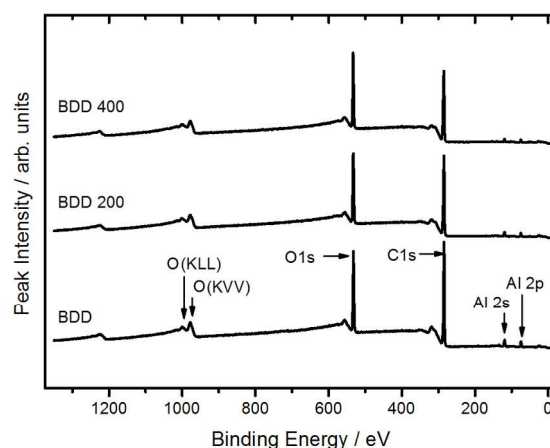


Figure 2. Representative XPS survey scan of PEG-modified samples, with spectra shown originating from bare BDD, PEG200 on BDD, and PEG400 on BDD.

The C1s photoelectron signal shows evidence for systematic changes in surface chemistry due to PEG grafting. An overlay of all C1s spectra is shown in Figure 3A. The spectra were fitted into five chemical environments, as has been done for carbon-based electrodes such as BDD and GC: adventitious carbon (284.6 eV), hydrocarbon (C-H, $\approx 285.1 \text{ eV}$), ether (C-O, $\approx 286.1 \text{ eV}$), carbonyl (C=O, $\approx 287.1 \text{ eV}$) and carboxyl (C=O(OH), $\approx 288.1 \text{ eV}$).²⁴ Notably, as either BDD or GC is modified by PEG, the intensity of the ether component increases in proportion to chain length (cf. Fig. 3 and Table 1). This result is consistent with the sequential addition of poly-(ethylene)glycol moieties to the surface.

The O1s photoelectron signal in Figure 3B was curve fitted using the model established by Schlapak *et al.*²⁵ as follows: hydroxyl (-OH, ≈ 531 eV), ether (C-O, ≈ 532.2 eV), water (H₂O, ≈ 533.3 eV). As the carbon-based electrodes are modified with PEG layers, the intensity of the ether component increases - in proportion to chain length - relative to the two minor components (-OH and H₂O). The increase in the ether component is entirely consistent with PEG chemistry. The attenuation of the hydroxyl and water signal suggests that the underlying carbon electrode has a higher concentration of these two species, than the PEG films, despite the fact that water is known to bind strongly to PEG.

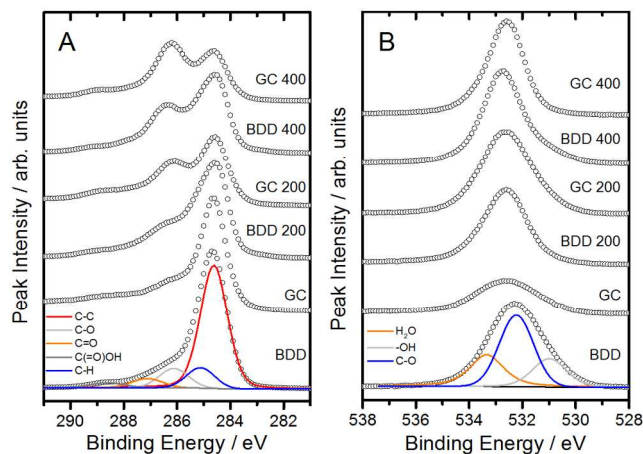


Figure 3. XPS data: C1s (left) and O1s (right) XPS core level spectra of BDD, GC, and PEG-modified BDD and GC, with representative curve fits associated with unmodified BDD shown in the figure.

Table 1. Summary of XPS data for bare and modified samples in terms of ratios and composition.

Sample	O1s/C1s	% O1s signal			% C1s signal				
		OH	C-O	H ₂ O	C-C	C-H	C-O	C=O	C=O(OH)
BDD	2.58	50	21	29	70	11	11	5	3
GC	1.29	12	55	33	66	4	11	11	8
BDD200	2.72	18	63	19	51	14	18	13	4
GC200	2.61	9	70	21	46	6	26	10	12
BDD400	2.75	22	66	12	43	16	33	5	3
GC400	2.99	2	81	17	28	14	37	14	7

XPS data clearly confirm the covalent surface modification. Importantly, it can be inferred from data in Table 1 that the C-O ether bond is dominating at modified electrode surfaces consistent with the attachment of alkoxy radicals. The decrease in O-H could be linked to the attachment of PEGs at both ends, although this appears less probable when grafting in neat PEG. More quantitative coverage information is difficult to extract from these XPS data, but can be obtained in electrochemical experiments.

PEG Attachment to Glassy Carbon or Boron-Doped Diamond: Effect on Fe(CN)₆^{3-/4-} Electron Transfer

The one-electron Fe(CN)₆^{3-/4-} redox system (equation 1) is commonly employed to detect surface modification and changes on

carbon electrodes²⁶ in particular when the surface is modified via covalent attachment.²⁷

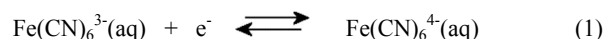


Figure 4A shows a typical cyclic voltammogram for the Fe(CN)₆^{3-/4-} redox system in aqueous 0.1 M KNO₃ and at a glassy carbon disc electrode. With a scan rate of 50 mV s⁻¹ the voltammetric response appears quasi-reversible with a peak-to-peak separation of ca. 0.14 V and a midpoint potential of E_{mid} = 0.19 V vs. SCE. The peak current of ca. 55 μA when analysed with the one-electron Randles-Sevcik equation²⁸ (see equation 2) is consistent with a diffusion coefficient of D_{ferrocyanide} = 0.6 $\times 10^{-9}$ m² s⁻¹, which is consistent with literature values.²⁹

$$D = \frac{I_{\text{peak}}^2 RT}{(0.466 \times AFc)^2 \nu F} \quad (2)$$

In this expression the diffusion coefficient D is given by I_{peak} , the peak current, R , the universal gas constant, T , the absolute temperature, A , the electrode area, F , the Faraday constant, c , the bulk concentration, and ν , the scan rate.

After anodic treatment of the electrode in PEG400/20 mM LiClO₄ (see Experimental), a clear shift of both anodic peak and cathodic current peak suggests slowing down of interfacial electron transfer (Figure 4A). Both the duration of the anodic treatment (Figure 4A) and the applied potential during treatment (Figure 4B) systematically affect the magnitude of the observed effect. Data in Figure 4B clearly show that for PEG400 a treatment of 20 minutes at +1.6 V vs. SCE can be used to completely suppress the electron transfer process in the 1 V potential window. In order to better quantify this effect impedance methods were employed.

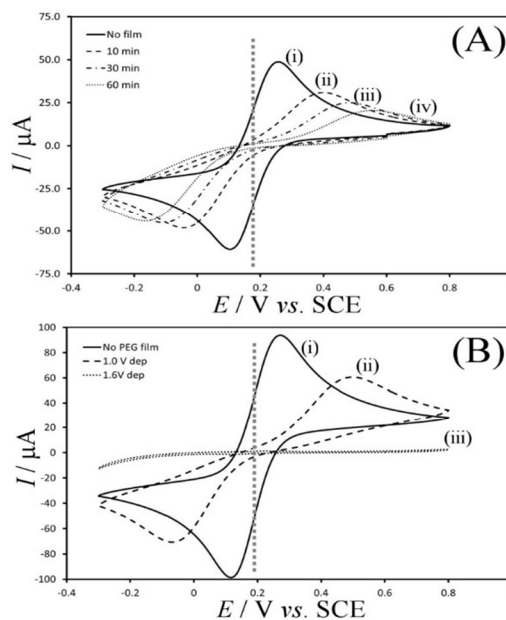


Figure 4 (A) Cyclic voltammograms (scan rate 50 mV s⁻¹, second cycle shown) for a solution containing 5 mM K₃Fe(CN)₆, 5 mM K₄Fe(CN)₆ and 0.1 M KNO₃ at a 3 mm diameter glassy carbon working electrode before PEG400 attachment (i), after 10 min (ii), after 30 min (iii), and after 60 min (iv) at +1.2 V vs. SCE. (B) As

above, but with no PEG film (i) and a PEG400 film attached by anodic treatment for 20 min at (ii) 1.0 V and (iii) +1.6 V vs. SCE.

A change in heterogeneous standard rate constant for electron transfer k_o can be observed either by cyclic voltammetry or determined more quantitatively using electrochemical impedance spectroscopy. The effect of PEG attachment was investigated using PEG400 for both glassy carbon (GC) and for boron doped diamond (BDD) electrodes. Impedance measurements were performed in aqueous solution containing 5 mM $K_3Fe(CN)_6$, 5 mM $K_4Fe(CN)_6$ and 0.1 M KNO_3 at open circuit potential (OCP). Figure 5A and 5B show Bode plots for data obtained as a function of attachment potential. Equivalent circuit data fitting based on a simple Randles circuit³⁰ (see inset Figure 3A) was used to determine the charge transfer resistance, R_{ct} , which enabled the standard rate constant for heterogeneous electron transfer, k_o , for the $Fe(CN)_6^{3-/4-}$ redox couple to be calculated based on equation 3.

$$k_o = \frac{RT}{F^2 c A R_{ct}} \quad (3)$$

In this expression, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, F is Faraday's constant, A is the geometric surface area, and c is the bulk concentration for the case that $c = c(Fe(CN)_6^{3-}) = c(Fe(CN)_6^{4-})$.

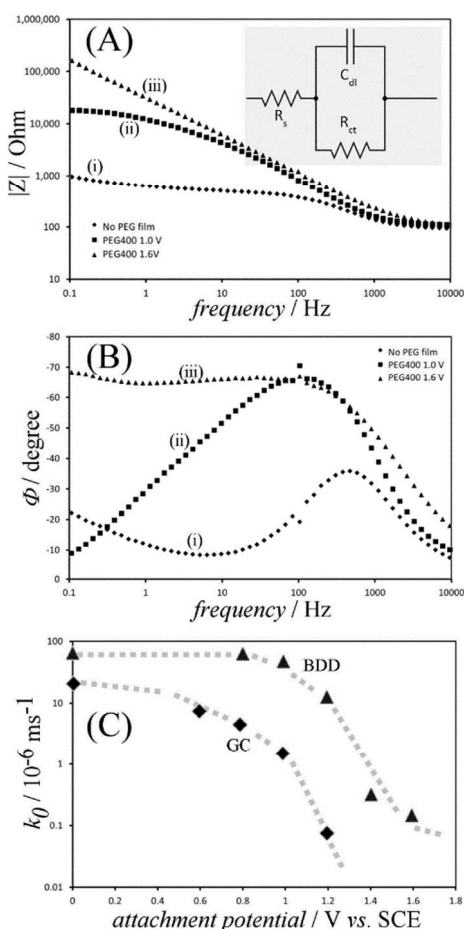


Figure 5. (A,B) Bode impedance plots for a solution containing 5 mM $K_3Fe(CN)_6$, 5 mM $K_4Fe(CN)_6$ and 0.1 M KNO_3 at a 3 mm diameter glassy carbon working electrode recorded at OCP (i) with

no PEG film, and with a PEG400 film attached at (ii) 1.0 V, and at 1.6 V vs. SCE for 20 min deposition. (C) Plot of the standard heterogeneous rate for electron transfer versus attachment potential for glassy carbon ($\blacklozenge$) and for boron-doped diamond ($\blacktriangle$). Line provided to aid the eye.

As the PEG attachment potential was increased, R_{ct} for the $Fe(CN)_6^{3/4-}$ redox system increased, which indicates the rate of electron transfer for the process is decreasing (see Figure 5C). The solution resistance, R_s , was typically 114Ω in all experiments and the double layer capacitance, C_{dl} , was typically $1.7 \mu F$ and $2.4 \mu F$ on glassy carbon and on boron-doped diamond, respectively. These values were independent of PEG deposition potential and therefore insensitive to the coverage with PEG. It is proposed that the anodic treatment of the electrodes in a PEG solution causes oxidative coupling between the polymer and the carbon substrate consistent with reports by Maeda,²⁰ and that due to high miscibility of PEGs and water there is no significant change in the double layer capacitance. Higher deposition potentials lead to faster rates of oxidative coupling, which appears to result in a more dense PEG film attachment with improved surface coverage. For glassy carbon, attachment potential of 1.4 V and 1.6 V vs. SCE gave highly effective films with R_{ct} values too low to be quantified under these conditions (therefore omitted in Figure 5C).

Field emission scanning electron microscopy (FESEM) was used to observe the passivating PEG film on a BDD electrode. The PEG film is very thin and cannot be seen directly by FESEM. Figure 6A and 6B show typical poly-crystalline domain structures with or without PEG coating. There are no significant morphology changes, however, due to the insulating nature of the PEG film, modified regions of the electrode appear darker (see Figure 6C).

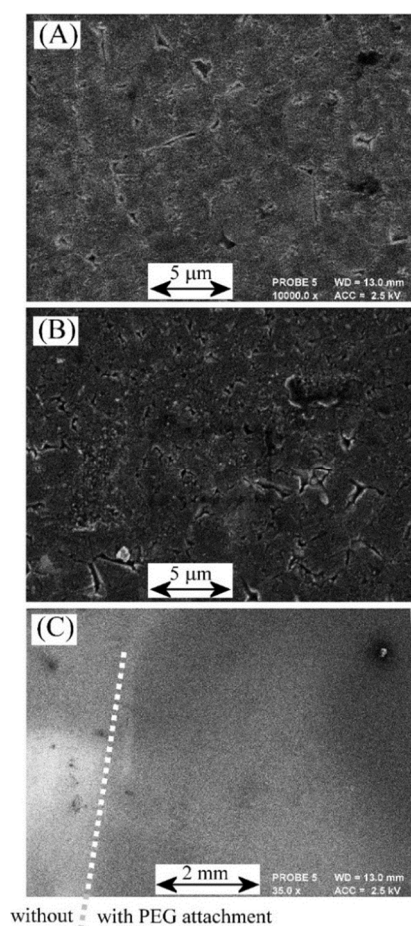


Figure 6. Scanning electron micrographs for (A) a bare boron-doped diamond, (B) a PEG400 attached boron-doped diamond (20 min at 1.6 V vs. SCE), and (C) a partially PEG400 attached boron-doped diamond electrode surface.

The minimum potential at which electrodes can be modified with a PEG layer is dependent upon the nature of the surface. A threshold potential of +1.0 V vs. SCE had to be overcome for PEG400 to attach to the boron-doped diamond surface. In contrast, the glassy carbon surface was modified with PEG400 at about 0.4 V lower potentials (Figure 5C) but with a second threshold at +1.0 V vs. SCE for higher coverages. These two thresholds for glassy carbon are likely to reflect surface reactivity, for example for binding to sp^2 and sp^3 type carbons and/or edge and plane reactivity on graphite. The doping-level dependent³¹ rate of electron transfer at boron-doped diamond may also contribute to the difference in reactivity. At attachment potentials above +1.2 V vs. SCE for glassy carbon and +1.6 V vs. SCE for boron-doped diamond, both PEG400-GC and PEG400-BDD electrodes had similarly low k_o values (between 10^{-7} and 10^{-8} m s⁻¹) for the $Fe(CN)_6^{3/4-}$ redox couple (Figure 5C). PEG films attached to glassy carbon or boron-doped diamond electrode surfaces are somewhat sensitive to potential cycling over a wider potential window in aqueous media. Beyond a potential of +1.2 V vs. SCE in aqueous 0.1 M KNO_3 a clear loss of the PEG film is observed (see Experimental).

PEG Attachment to Glassy Carbon: Effect of Chain Length on Electron Transfer

With attachment parameters optimised, the properties of the PEG film can be tuned systematically by altering the chain length of the

polymer. PEGs with an average molecular weight up to 400 are liquid at room temperature and can therefore be used directly to attach to electrode surfaces from neat solutions containing 20 mM $LiClO_4$ (see Experimental). In order to investigate the effect of PEG chain length, PEG films with average molecular weights 200, 300 and 400 g mol⁻¹ were deposited onto a glassy carbon electrode. The standard heterogeneous rate constant for electron transfer for the $Fe(CN)_6^{3/4-}$ redox system was then determined from data recorded in impedance measurements (see Figure 7). Values for R_s and C_{dl} were not significantly affected.

The rate of electron transfer sequentially decreased as the average molecular weight of the polymer increased. The longer PEG chains are likely to form a thicker layer on the electrode surface and thereby cause an increase in the tunnelling distance for electron transfer. The increased tunnelling distance decreases the rate of electron transfer exponentially (with a Gamov-type exponential decay law for tunnelling through a monolayer³²) as predicted by quantum mechanics (equation 4).

$$k_o(\text{monolayer}) = k_o(\text{substrate}) \times \exp(-\beta d) \quad (4)$$

In this expression the standard heterogeneous rate constant for electron transfer through a monolayer, $k_o(\text{monolayer})$, is given by the limiting value $k_o(\text{substrate})$, the tunnel distance coefficient, which is approximately $\beta = 1 \text{ \AA}^{-1}$ for alkyl chains,^{33,34} and the tunnel distance $d \text{ (\AA)} = 5.6 + 1.3xCH_2$ (where x is the number of CH_2 units) estimated for alkyl chains. When PEG is attached to the glassy carbon surface, it can be considered to act as a similar insulating layer, however, with the important difference of being water miscible and therefore not creating a separate phase. As the chain length of the polymer increases, the thickness of the insulating layer does so accordingly, and the rate of electron transfer is reduced. However the rate of decrease exhibits more complexity. A non-linear plot (Figure 7C) suggests that the effect of PEG films of higher molecular weight is higher compared to that of lower molecular weight (the β -value seems to increase). For the initial part of the plot, the β -value (ca. $0.17 \text{ \AA}^{-1}$) for all PEG attachments is estimated to be much lower compared to that for alkyl chains (β -value $1.0 \text{ \AA}^{-1}$). Both, the fact that water penetrates into the film (through the diffuse phase boundary) and the unknown (less than perfect) coverage may contribute to this effect.

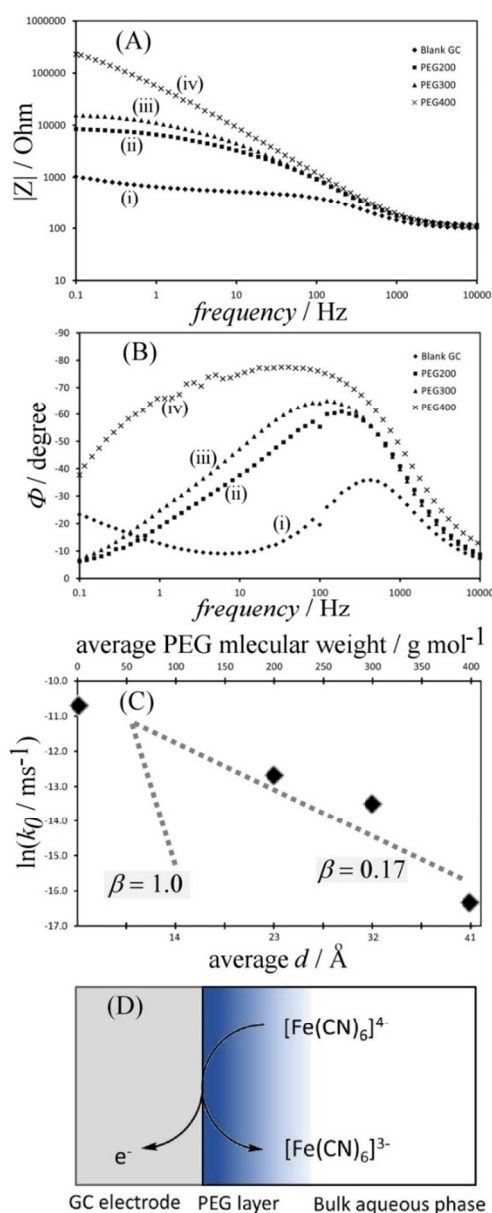
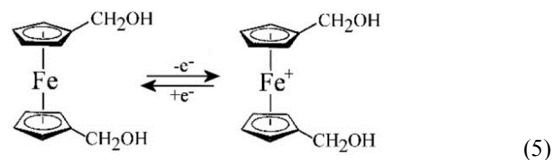


Figure 7. (A,B) Bode impedance plots for a solution containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M KNO_3 at a 3 mm diameter glassy carbon working electrode recorded at OCP (i) with no PEG film, (ii) PEG200-GC, (iii) PEG300-GC, and (iv) PEG400-GC after a 20 min attachment at +1.2 V vs. SCE. (C) Plot of $\ln(k_0)$ as a function of PEG average molecular weight. Also shown is the “average d ” scale based on tunnel distance $d (\text{\AA}) = 5.6 + 3.9n(\text{O}-\text{CH}_2-\text{CH}_2)$. (D) Schematic drawing of the interfacial electron transfer.

PEG Attachment to Glassy Carbon: Effect on 1,1'-Ferrocene-dimethanol Electron Transfer and Mediation

Although PEG is completely miscible with water, a thin and dense film of PEG attached to an electrode surface can be considered as a separate surface phase with diffuse phase boundary to the bulk solution. Species which are insoluble in PEG will not be able to penetrate into the film, whereas compounds that solubilise in PEG should pass through unhindered. This can be demonstrated with the

more hydrophobic one-electron redox system 1,1'-ferrocene-dimethanol (equation 5).



The voltammetry of 1,1'-ferrocene-dimethanol ($\text{Fc}(\text{CH}_2\text{OH})_2$) without and with the PEG attachment at the electrode surface was examined. The cyclic voltammetry data for $\text{Fc}(\text{CH}_2\text{OH})_2$ (see Figure 8A) shows highly reversible characteristics with $E_{\text{mid}} = 0.22$ V vs. SCE consistent with literature³⁵ with no change in peak-to-peak separation between an unmodified electrode and an electrode with different types of PEG grafted onto the surface. When analysed based on equation 2, the peak current of ca. 7 μA is consistent with the previously reported³⁶ diffusion coefficient of $D_{\text{ferrocenedimethanol}} = 0.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

This voltammetric behaviour was observed on both GC and BDD electrodes. For $\text{Fc}(\text{CH}_2\text{OH})_2$ the rate of electron transfer appears to remain fast (reversible) and is therefore likely to be independent upon attachment time, attachment potential, and length of the surface-attached PEG chain. It is proposed that the rate of electron transfer does not significantly decrease at a PEG-modified electrode (for both glassy carbon and boron-doped diamond) for $\text{Fc}(\text{CH}_2\text{OH})_2$ because the more hydrophobic redox species can diffuse more deeply into the PEG layer (Figure 8E) with less effect on the electron tunnelling distance compared to that for $\text{Fe}(\text{CN})_6^{3-/4-}$. The apparent selectivity of the PEG-modified electrode between the two one-electron redox systems could have implications and applications in electrochemical sensing, for example when exploited for suppressing unwanted background current responses or when “amplifying” the signal for low concentration mediators (*vide infra*).

Both redox systems, $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{Fc}(\text{CH}_2\text{OH})_2$, exhibit similar electron transfer kinetics at an unmodified electrode and similar E_{mid} values, 0.19 V and 0.22 V vs. SCE, respectively. With $\text{Fc}(\text{CH}_2\text{OH})_2$ having a marginally higher reversible potential, a redox mediation process should be possible. $\text{Fc}(\text{CH}_2\text{OH})_2$ has been employed as redox mediator previously, for example for redox proteins.³⁷ $\text{Fc}(\text{CH}_2\text{OH})_2$ is employed here to mediate the oxidation of $\text{K}_4\text{Fe}(\text{CN})_6$ at a PEG400 modified glassy carbon electrode.

An optimised PEG400 modified glassy carbon electrode was prepared using a fixed deposition potential of +1.6 V (vs. SCE) for 20 minutes. Cyclic voltammetry was then performed using a mixture of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{Fc}(\text{CH}_2\text{OH})_2$. Figure 8B shows voltammetric responses for 0 to 50 μM $\text{Fc}(\text{CH}_2\text{OH})_2$ and 10 mM $\text{Fe}(\text{CN})_6^{4-}$. The mediated electron transfer is clearly observed even for 5 μM $\text{Fc}(\text{CH}_2\text{OH})_2$ with a gradually increasing limiting current (kinetically limited, see Figure 8Bii and 8Biii). For concentrations of 50 μM or 100 μM $\text{Fc}(\text{CH}_2\text{OH})_2$ peak-shaped current response features are observed due to the onset of mass transport effects. The gradually increasing nature of the kinetically limited current with applied potential suggests either (i) the rate is in part limited by slow (non-Butler-Volmer) $\text{Fc}(\text{CH}_2\text{OH})_2$ oxidation at the electrode surface or (ii), may be less likely, the positive applied potential can affect the bimolecular electron transfer, for example by allowing $\text{Fe}(\text{CN})_6^{4-}$ to penetrate deeper into the PEG layer.

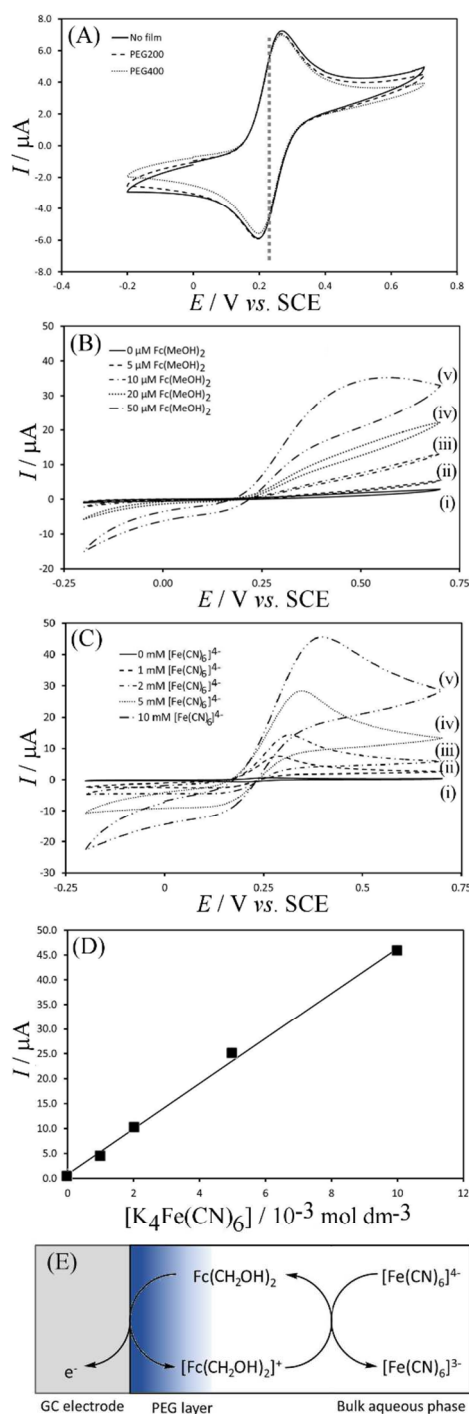


Figure 8. (A) Cyclic voltammogram (scan rate 50 mVs⁻¹, second cycle) for the oxidation of ca. 0.5 mM Fc(CH₂OH)₂ in 0.1 M KNO₃ with different PEG length surface modifications on glassy carbon. (B) Cyclic voltammograms (scan rate 50 mVs⁻¹, second cycle) for fixed 10 mM Fe(CN)₆⁴⁻ in 0.1 M KNO₃ with increasing concentration ((i) 0 μM, (ii) 5 μM, (iii) 10 μM, (iv) 20 μM, (v) 50 μM) of Fc(CH₂OH)₂ at a PEG400-GC electrode (attachment 20 min +1.6 V vs. SCE). (C) As above, but with fixed 100 μM Fc(CH₂OH)₂ and with increasing concentrations ((i) 0, (ii) 1, (iii) 2, (iv) 5, and (v) 10 mM) of K₄Fe(CN)₆. (D) Plot of peak current versus K₄Fe(CN)₆ concentration. (E) Schematic drawing of the mediated electron transfer.

For a concentration of 10 μM Fc(CH₂OH)₂ and 10 mM Fe(CN)₆⁴⁻, the kinetically limited current is approximately 10 μA (see Figure 8B). This case can be considered a transition case between slow electron transfer to the Fc(CH₂OH)₂ (for lower Fc(CH₂OH)₂ concentrations) and onset of Fe(CN)₆⁴⁻ depletion (for higher Fc(CH₂OH)₂ concentrations). This limiting current, 10 μA, corresponds to a diffusion layer thickness of $\delta_{diffusion} = \frac{FDAC}{I_{lim}} =$

380 nm (with $D = 0.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). This diffusion layer thickness can then be equated with a reaction layer thickness of approximately $\delta_{reaction} = \sqrt{\frac{D}{k_{forward} \times [Fe(CN)_6^{4-}]}}$ for the homogeneous bimolecular

electron transfer, which is rate limiting here. The bimolecular rate constant for forward electron transfer is estimated as $k_{forward} = 4 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Forward and backward rate constants are linked via equation 6 and therefore $k_{backward} = 1 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

$$-F\Delta E_{mid} = RT \ln \frac{k_{forward}}{k_{backward}} \quad (6)$$

For a fixed concentration of 100 μM Fc(CH₂OH)₂ present in the solution (Figure 8C), the voltammetric current response increases with Fe(CN)₆⁴⁻. The peak current shows approximately linear increase with K₄Fe(CN)₆ consistent with the bimolecular mediation mechanism (Figure 8D and 8E). It is interesting to note that the redox mediation mechanism operates for both oxidation and reduction due to the small difference in E_{mid} for the two redox systems. Data in Figure 8B and 8C show significant reduction responses indicative for the conversion of Fe(CN)₆³⁻ back to Fe(CN)₆⁴⁻. The mediator effect of Fc(CH₂OH)₂ is versatile and potentially useful for future sensor applications with PEG-modified electrode surfaces.

A confirmation for the validity of the complete set of kinetic and thermodynamic parameters (E_{mid} , D , $k_{forward}$, $k_{backward}$) can be obtained from digital simulation (employing the commercial DigiElch 4.F package). Figure 9B and 9C show simulated data contrasting with Figure 8B and 8C experimental data. The relatively good match of experiment and theory confirms the parameters derived above, but also reveals a further effect. In order to obtain these simulation data sets, uncompensated resistance has to be introduced. The value of $R = 2 \text{ k}\Omega$ for 100 μM, 4 kΩ for 50 μM, 10 kΩ for 20 μM, 20 kΩ for 10 μM, 40 kΩ for 5 μM Fc(CH₂OH)₂ appear to scale inversely with the mediator concentration suggesting that a higher concentration of mediator can reduce the effect (e.g. via Fc(CH₂OH)₂⁺NO₃⁻ in the PEG layer). This resistance also appears to be potential dependent as can be seen from gradually increasing currents in Figure 8B. The schematic drawing in Figure 9A suggests a role of the nitrate anion, but further experimental work will be required to confirm this hypothesis.

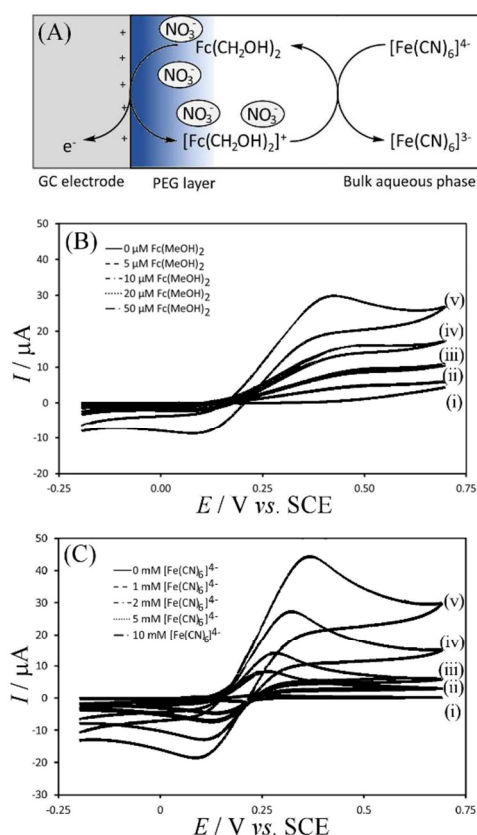


Figure 9. (A) Schematic drawing indicating the role of nitrate anions in the PEG film. (B) Digital simulation of cyclic voltammograms (scan rate 50 mVs^{-1} , second cycle) for fixed $10 \text{ mM Fe}(\text{CN})_6^{4-}$ in 0.1 M KNO_3 with increasing concentration ((i) $0 \mu\text{M}$, (ii) $5 \mu\text{M}$, (iii) $10 \mu\text{M}$, (iv) $20 \mu\text{M}$, (v) $50 \mu\text{M}$) of $\text{Fc}(\text{CH}_2\text{OH})_2$. (C) As above, but with fixed $100 \mu\text{M Fc}(\text{CH}_2\text{OH})_2$ and with increasing concentrations ((i) 0 , (ii) 1 , (iii) 2 , (iv) 5 , and (v) 10 mM) of $\text{K}_4\text{Fe}(\text{CN})_6$. Parameters for the digital simulation were as given in the text except an additional uncompensated resistance of $R = 2 \text{ k}\Omega$ for $100 \mu\text{M}$, $4 \text{ k}\Omega$ for $50 \mu\text{M}$, $10 \text{ k}\Omega$ for $20 \mu\text{M}$, $20 \text{ k}\Omega$ for $10 \mu\text{M}$, $40 \text{ k}\Omega$ for $5 \mu\text{M Fc}(\text{CH}_2\text{OH})_2$.

Conclusions

Systematic mono-layer attachment of PEGs of various chain lengths has been investigated at carbon and boron-doped diamond electrodes at appropriate anodic potentials. The thickness and coverage of the deposited PEG layer depend upon the attachment potential, attachment time, and the average molecular weight of the PEG. For more hydrophilic redox systems, such as $\text{Fe}(\text{CN})_6^{3-/4-}$, the PEG film effectively passivates the surface of the electrode and reduces the heterogeneous rate of electron transfer. In contrast, electron transfer for more hydrophobic species, such as ferrocene-dimethanol, appears not significantly impeded by a PEG attachment. Combining these two redox systems leads to a mediated or “amplified” electrochemical response whereby the hydrophobic ferrocene derivative mediates the oxidation of ferrocyanide. Some aspects of the mechanism for the amplification process (e.g. novel double phenomena) require further investigation.

The selectivity of the modified electrode for both glassy carbon and boron-doped diamond for hydrophobic redox systems could be beneficial in electroanalytical sensing, for example for detection of hydrophobic drug molecules. Selective

amplification based on (i) electrode surface design and (ii) a suitable redox reservoir system could significantly increase sensitivity and reveal the presence of traces of materials. The limit in this type of amplification is given by the bimolecular electron transfer process, which in turn is dependent on the difference in midpoint potentials for analyte mediator and amplifier redox systems.

Acknowledgements

C.E.H. thanks the University of Bath for a Ph.D. scholarship.

Notes and references

- ^a Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK
- ^b Imperial College London, Department of Materials, Royal School of Mines, Exhibition Road, London, SW7 2AZ, UK
- ^c Chemistry Research Laboratories, Oxford University, South Parks Road, Oxford OX1 3TA, UK
- ^d Department of Materials, Oxford University Begbroke Science Park, Begbroke Hill, Oxford OX5 1PF, UK

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- ¹ (a) H.F. Zhou, Q.H. Fan, Y.M. He, L.Q. Gu and A.S.C. Chan, *Progress Chem.*, 2007, **19**, 1517-1528. (b) Z.Z. Yang, Q.W. Song, Capture and utilization of carbon dioxide with polyethylene glycol. Springer, Berlin, 2012.
- ² P. Styring and O. Aschenbrenner, *Energy Environ. Sci.*, 2010, **3**, 1106-1113.
- ³ J. Chen, S.K. Spear, J.G. Huddleston and R.D. Rogers, *Green Chem.*, 2005, **7**, 64-82.
- ⁴ C.E. Hotchen, G.A. Attard, S.D. Bull and F. Marken, *Electrochim. Acta*, 2014, **137**, 484-488.
- ⁵ M.D. Howard, M. Jay, T.D. Dziubal and X.L. Lu, *J. Biomed. Nanotechnol.* 2008, **4**, 133-148.
- ⁶ R.K. Bose, S. Nejati, D.R. Stuffle and K.K.S. Lau, *Macromolecules*, 2012, **45**, 6915-6922.
- ⁷ S. Kaneko, H. Nakayama, Y. Yoshino, D. Fushimi, K. Yamaguchi, Y. Horiike and J. Nakanishi, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4051-4059.
- ⁸ Z. Wang, H.Y. Ma, B.S. Hsiao and B.M. Chu, *Polymer*, 2014, **55**, 366-372.
- ⁹ P. Wang, K.L. Tan, E.T. Kang and K.G. Neoh, *J. Membrane Sci.*, 2002, **195**, 103-114.
- ¹⁰ K. Aoki, Y. Guo and J.Y. Chen, *J. Electroanal. Chem.*, 2009, **629**, 73-77.
- ¹¹ Y. Guo, K. Aoki, J.Y. Chen and T. Nishiumi, *Electrochim. Acta*, 2011, **56**, 3727-3730.
- ¹² H.F. Zhou, N.Y. Gu and S.J. Dong, *J. Solid State Electrochem.*, 1999, **3**, 82-86.
- ¹³ Y.K. Kang, H.J. Kim, E. Kim, B. Oh and J.H. Cho, *J. Power Sources*, 2001, **92**, 255-259.

- ¹⁴ Y. Kato, S. Yokoyama, H. Ikuta, Y. Uchimoto and M. Wakihara, *Electrochem. Commun.*, 2001, **3**, 128-130.
- ¹⁵ A.F. Nogueira, C. Longo and M.A. De Paoli, *Coord. Chem. Rev.*, 2004, **248**, 1455-1468.
- ¹⁶ M.E. Williams and R.W. Murray, *J. Phys. Chem. B*, 1999, **103**, 10221-10227.
- ¹⁷ Y.L. Wen, H.X. Wu, S.H. Chen, Y.H. Lu, H.B. Shen and N.Q. Jia, *Electrochim. Acta*, 2009, **54**, 7078-7084.
- ¹⁸ S.S. Shah, M.C. Howland, L.J. Chen, J. Silangcruz, S.V. Verkhoturov, E.A. Schweikert, A.N. Parikh and A. Revzin, *ACS Appl. Mater. Interfaces*, 2009, **1**, 2592-2601.
- ¹⁹ H. Maeda, T.X. Li, M. Hosoe, M. Itami, Y. Yamauchi and H. Ohmori, *Anal. Sci.*, 1994, **10**, 963-965.
- ²⁰ H. Maeda, M. Itami, Y. Yamauchi and H. Ohmori, *Chem. Pharm. Bull.*, 1996, **44**, 2294-2299.
- ²¹ A.J. Downard, *Electroanalysis*, 2000, **12**, 1085-1096.
- ²² D. Belanger and J. Pinson, *Chem. Soc. Rev.*, 2011, **40**, 3995-4048.
- ²³ C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. M. Raymond and L. H. Gale, *Surf. Interface Anal.*, 1981, **3**, 211 and are reproduced here from Appendix 6 of "Practical Surface Analysis", Vol. 1., 2nd Edition, by C. D. Wagner, eds. D. Briggs and M.P. Seah, Published by J. Wiley and Sons in 1990, ISBN 0-471-92081-9 by kind permission of the Authors and publishers.
- ²⁴ S. Ferro, M. Dal Colle and A. De Battisti, *Carbon*, 2005, **43**, 1191-1203.
- ²⁵ R. Schlaak, D. Caruana, D. Armitage and S. Howorka, *Soft Matter*, 2009, **5**, 4104-4112.
- ²⁶ L.H.J. Xiong, C. Batchelor-McAuley, K.R. Ward, C. Downing, R.S. Hartshorne, N.S. Lawrence and R.G. Compton, *J. Electroanal. Chem.*, 2011, **661**, 144-149.
- ²⁷ K.K. Cline, L. Baxter, D. Lockwood, R. Saylor and A. Stalzer, *J. Electroanal. Chem.*, 2009, **633**, 283-290.
- ²⁸ F. Scholz, *Electrochemical methods*. Springer, Berlin, 2005, p. 64.
- ²⁹ R.N. Adams, *Electrochemistry at solid electrodes*, Marcel Dekker, New York, 1969, p. 220.
- ³⁰ D. Pletcher, R. Greef, R. Peat, L.M. Peter and J. Robinson, *Instrumental methods in electrochemistry*, Horwood Publishing, Chichester, 2001, p. 266.
- ³¹ R.G. Compton, J.S. Foord and F. Marken, *Electroanalysis*, 2003, **15**, 1349-1363.
- ³² A. Kiani, M.A. Alpuche-Aviles, P.K. Eggers, M. Jones, J.J. Gooding, M.N. Paddon-Row and A.J. Bard, *Langmuir*, 2008, **24**, 2841-2849.
- ³³ H.Z. Yu, H.B. Shao, Y. Luo, H.L. Zhang and Z.F. Liu, *Langmuir*, 1997, **13**, 5774-5778.
- ³⁴ J.R. Winkler and H.B. Gray, *J. Amer. Chem. Soc.*, 2014, **136**, 2930-2939.
- ³⁵ S.J. Stott, R.J. Mortimer, K.J. McKenzie and F. Marken, *Analyst*, 2005, **130**, 358-363.
- ³⁶ R.W. French, A.M. Collins and F. Marken, *Electroanalysis*, 2008, **20**, 2403-2409.
- ³⁷ A. Konash and E. Magner, *Anal. Chem.*, 2005, **77**, 1647-1654.