Journal of Electroanalytical Chemistry, Volume 549, 5 June 2003, Pages 119-127

The Electrochemistry of the Ferri/Ferrocyanide couple at a Calix[4]resorcinarenetetrathiol modified Gold Electrode as a study of novel electrode modifying coatings for use within Electro-analytical Sensors.

Stuart D. Collyer[a], Frank Davis[a], Andrew Lucke[b], Charles J. M. Stirling[c] and Séamus P. J.Higson[a*].

[a]Institute of Bioscience and Technology, Cranfield University at Silsoe, Silsoe, MK45 4DT.

[b]Institute for Molecular Bioscience, University of Queensland, Brisbane, Queensland, Australia.

[c]Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK.

[*] To whom correspondence should be addressed. Fax (+44) 01525 863433,

email s.p.j.higson@cranfield.ac.uk

Abstract:

The electrochemistry of the ferri/ferrocyanide redox couple has been studied at Au electrodes modified with calix[4]resorcinarenetetrathiol. Cyclic voltammetry in $Fe(CN)_6^{3-}$ solutions yields three separate pairs of faradaic peaks. Evidence is given for these redox couples corresponding to the reduction of $Fe(CN)_6^{3-}$ and the subsequent re-oxidation of $Fe(CN)_6^{4-}$ in three differing steric arrangements. One pair of peaks suggest that when the $Fe(CN)_6^{3-}$ ion resides within the calix[4]resorcinarene bowl, electron transport is facilitated by the calix[4]resorcinarene acting as a charge transfer mediator; in this arrangement the activation energy is found to be lowered by ~24kJmol^{-1}. Another pair of peaks is thought to correspond to the reduction of $Fe(CN)_6^{3-}$ as it approaches the Au electrode by packing itself in-between adjacent calix[4]resorcinarene molecules. The third pair of redox peaks is attributed to the reduction and subsequent re-oxidation of $Fe(CN)_6^{3-}$ /$Fe(CN)_6^{4-}$ when the ion resides above a saturated calix[4]resorcinarene coating; in this case the activation energy was raised by ~45kJmol^{-1}. FTIR spectroscopy of calix[4]resorcinarene-coated Au electrodes and calix[4]resorcinarene-coated Au electrodes exposed to $Fe(CN)_6^{3-}$ lends further support to this argument, by demonstrating that the $Fe(CN)_6^{3-}$ ion resides within at least two and possibly three differing environments.

Calix[4]resorcinarene modified electrodes previously exposed to ferricyanide lose the calix[4]resorcinarene coating together with a surface layer of gold when subsequently scanned in a phosphate buffer. It therefore appears that the calix[4]resorcinarene/$Fe(CN)_6^{3-}$ association is stronger than the Au binding to the underlying glass material.

Keywords: Calixarene, ferri/ferrocyanide, electrode coatings, sensors.

1. Introduction

Electrode modification has been widely employed to optimise the performance of many electrochemical analyses[1-3], with potential benefits including enhanced selectivity[4], stability[5] and sensitivity[6]. *Chemically* Modified Electrodes (CMEs) in particular have been used to facilitate electron transfer reactions[7] and the preferential accumulation of analytes at electrode surfaces[8]. A variety of coatings have been used in this context with common examples including conducting polymers[9], ion-exchange polymers (*viz. Nafion®*)[10] and metallic complex films such as the bipyridine complexes[11]. CMEs have already been previously reviewed elsewhere[12-13].

Calix[4]resorcinarenes form a family of resorcinol/aldehyde oligomers linked in macrocyclic arrays by alkylene bridges[14-15], and may be synthesised by acid-promoted condensation of resorcinols with aldehydes[16]. The term calixarene first appeared in print in 1978[17], and is derived from the Greek *calix* meaning ‘vase’ or ‘chalice’ with the *arene* adjunct indicating the presence of aryl residues in the macrocyclic array[14]. Among their properties, calixarenes allow for the preferential uptake of ions from solution and may be used to coat, and thereby modify electrode surfaces[18]. Structural and functional group modification of a calixarene, offers the prospect of tailor designing molecules suitable for use as selective electrode coatings for molecular or ionic analytes of differing radii, charge and even chirality[14]. A variety of regimes might be possible here; for example a polymeric calixarene ester has been used as an electrode modifier for the voltammetric analysis of lead (II), copper (II) and mercury (II) ions[18], while a commercially available calix[4]resorcinarene, C-undecylcalix[4]resorcinarene, (Fluka Chemicals, Gillingham, England, UK.) has also been shown to be capable of imparting high selectivity for the amperometric detection of

neurotransmitters such as dopamine and epinephrine[19]. Further examples include calixarene derivatives that have been used within potentiometric ion-selective electrodes[20], chemically sensing field effect transistors (CHEMFET's)[21] and gaseous sensors[22].

Calix[4]resorcinarenetetrathiols linked to gold, reside with the bowl pointing away from the metal surface, and have been found to show varying selectivities towards the adsorption of specific solutes, such as Vitamin C and glutaric acid[23]. Coatings of this type have also been shown[24] to spontaneously self-assemble to form multilayers via a previously unreported van der Waals inter-digitation - hydrogen-bonding alternation process, as opposed to the better documented covalent, covalent - co-ordinate, covalent - ionic and hydrogen-bonding mechanisms[25]. SPR measurements have been made by other authors[26] on an identical compound and have shown that the calix[4]resorcinarenetetrathiol forms good quality monolayers with a thickness of about 21 Å, consistent with an array of well packed vertically orientated molecules. Alkyl-substituted calix[4]resorcinarenes have been shown to give thinner, less well-ordered layers[26]. The electrochemistry for ferricyanide at these substituted calix[4]resorcinarene coated electrodes has been previously reported[27].

This paper reports on the electrochemical behaviour of the ferri/ferrocyanide couple at a calix[4]resorcinarenetetrathiol coated gold electrode; the electrochemistry of the calix[4]resorcinarene modified electrode is discussed with respect to the approach trajectory of the $Fe(CN)_6^{3-}$ ion and the possible charge transfer mechanisms by which it is (a) first reduced to $Fe(CN)_6^{4-}$, and then (b) re-oxidised back to the ferricyanide ion. This work is focussed towards characterising the electrochemical properties of such coatings for their possible exploitation within electrochemical sensors.

2. Experimental

2.1 Electrochemical Apparatus

All experiments were conducted with a purpose designed cell, **Fig. 1**. The Ag/AgCl reference, Au counter and working electrodes were all mounted within 'Suba-Seal' rubber septa and placed so that they were suspended within the cell. A side-arm water-filled air lock prevented the ingress of air, whilst a gas bubbler permitted de-oxygenation of the cell's contents.

Measurements were performed using an '*Eco Chemie* PGSTAT20 Autolab' potentiostat, linked via an IEEE interface to a Dell PC.

2.2 Reagents and Solutions

A 1 x 10^{-3} M solution of $K_3Fe(CN)_6$ (A.C.S. grade, Aldrich Chemical Co., Gillingham, England, UK.) was prepared in a *p*H 7.4 phosphate buffer supporting electrolyte, consisting of 5.28 x 10^{-2} M Na_2HPO_4 and 1.30 x 10^{-2} M NaH_2PO_4 (both of 'AnalaR' grade, B.D.H. Ltd., Poole, England, UK.) in doubly distilled de-ionised water together with 0.1 M KCl as a supporting electrolyte. Calix[4]resorcinarenetetrathiol (structure in **Fig. 2**), was prepared as previously reported[23]. Solutions (0.25 mmol dm^{-3}) of the calix[4]resorcinarene were prepared in a 9:1 v:v EtOH-DMSO mixture for the coating of the gold electrodes.

2.3 Electrode Preparation

A custom made Ag/AgCl reference electrode of 1.5mm diameter was fabricated by sealing a length of silver wire within a hollow soda glass tube, to leave approximately 15 mm exposed metal. The electrode was pre-anodised for 10 mins in a saturated KCl solution at +1.0 V (vs. Standard Calomel Electrode) to form an Ag/AgCl interface. The counter electrode was constructed using a similar technique, but with gold wire of 0.5mm diameter consisting of a coiled length of metal to provide a large surface area.

The calix[4]resorcinarene-coated gold electrodes were prepared by first evaporating a 50 Å layer of Cr, followed by 500 Å of Au onto a clean glass slide. Wires were attached using '*Electrolube*' silver paint which was subsequently coated with epoxy resin to both insulate the electrical junction and provide additional mechanical strength to the junction. The final geometric area of the electrode was ~4cm^2. In this study, slides were placed in the calix[4]resorcinarene solution overnight and then washed thoroughly with clean ethanol. The formation and reproducibility of gold-thiol linked calix[4]resorcinarene monolayers was verified by grazing angle reflection FTIR spectroscopy, as a quality control procedure[25].

2.4 Cell Preparation

Prior to each measurement, all glassware was cleaned in chromic acid (25g $K_2Cr_2O_7$ / 500ml H_2SO_4 - Fisons, Loughborough, England, UK.) for 1 hour and then rinsed thoroughly with doubly distilled de-ionised water. After being allowed to dry in air, the cell was assembled and 100ml of the prepared $K_3Fe(CN)_6$ solution was placed in the cell. The reference, counter and working electrodes were then all fixed in 'Suba-Seal' rubber septa and mounted into the

cell. The cell was purged with argon for 20mins to remove any dissolved oxygen whilst agitating the cell contents.

2.5 FTIR Analysis

FTIR spectra were recorded using a Perkin-Elmer 1725 X spectrometer fitted with a Harrick FT80 reflection accessory and a MCT detector. The samples used for grazing incidence were calix[4]resorcinarene-thiol monolayers adsorbed on a 500 Å Au film which had been sputter coated on top of a 50 Å Cr-coated glass slide. Spectra were recorded for the samples before and after 1 hr exposure to a 1 mM aqueous K_3FeCN_6 solution. The IR spectrum of K_3FeCN_6 was measured within a disc of ground KBr.

3 Results and Discussion

3.1 Voltammetry of $Fe^{(III)}(CN)_6^{3-/4-}$ couple at Au-calix[4]resorcinarene modified electrodes.

Cyclic voltammograms were recorded at a calix[4]resorcinarene modified electrode in a *p*H 7.4 phosphate buffer (0.1M KCl) and at a potential scan rate of $20mVs^{-1}$, **Fig. 3**. The voltammograms are clearly devoid of any faradaic peaks; it may therefore be assumed that at least within the +0.8V to -0.8V (vs. Ag/AgCl) potential window, the calix[4]resorcinarene displays no electrochemical redox activity of its own.

The ferri/ferrocyanide couple provides an ideal electrochemical probe for the study of chemically modified surfaces, since its reduction and oxidation both proceed via simple one electron transfer redox processes, **Eqn. 1**:

Eqn 1: $Fe^{(III)}(CN)_6^{3-} \rightleftharpoons Fe^{(II)}(CN)_6^{4-}$

Cyclic voltammograms were therefore recorded for the ferri/ferrocyanide couple at (a) a calix[4]resorcinarene coated electrode, and (b) at a plain gold electrode for comparison, **Fig. 4**. For a diffusion controlled reversible reaction at a planar electrode surface, reversible redox peaks would be expected to show a 59/n mV separation (where in this case n=1 corresponds to a one electron transfer)[28]. However as we have shown previously gold-sputtered electrodes of the type we are using offer faster electrode kinetics than polished planar gold electrodes due to their crystalline, granular structure and so induce some irreversibility to the behaviour observed with some redox reactions[29]. Electrodes of this type were used in this study since they provide an ideal surface for the thiol-linked anchorage of calix[4]resorcinarenes[24].

3.2 Identification of Redox Peaks

From **Fig. 4**, it is immediately obvious that the single pair of ferri/ferrocyanide redox peaks for the bare gold electrode transmute into three *separate* and discernible pairs of peaks at a calix[4]resorcinarene modified gold electrode surface. It is clear here that a one electron reduction/oxidation couple may not be further differentiated into simpler component steps, and that the presence of three redox peak pairs must therefore correspond to three *separate* reduction/oxidation processes for each of the redox couples. The redox peaks were matched by running voltammograms over smaller potential windows. Voltammograms between +800mV through to +250mV vs Ag/AgCl exhibited only one redox pair of peaks, **Fig 5**, which allowed the identification of the β redox couple. Voltammograms between +800mV through to -200mV vs Ag/AgCl, **Fig 6**, allowed the identification of the α redox couple. The γ redox peaks were then assigned by deduction as denoted within Fig 4. It should also be noted that each of the three pairs of peaks obtained for the calix[4]resorcinarene coated electrode are smaller than the original peaks seen for the plain gold electrode. For clarity the ferri/ferrocyanide redox potentials at the bare gold electrode are compared with those for the calix[4]resorcinarene coated electrodes; (**table 1**).

These results differ from those reported previously for alkyl-substituted calix[4]resorcinarene which gave much simpler single peaks[27]. However it should be noted that the voltammograms shown in this paper were for calix[4]resorcinarenes which had been substituted at the hydroxy group. This would greatly alter the binding of these materials as it would be impossible for them to act as hydrogen bond donors and may also alter their conformation as substituted calix[4]resorcinarenes often display mobile structures in solution rather than a fixed cone conformation[27]. Calix[4]resorcinarenes in that work with compact headgroups tended to block the electron transfer reaction. Several materials with bulkier

headgroups showed presence of pinhole defects, shown by oxidation/reduction cycles close to that of a bare gold electrode. The authors also report that the alkyl-substituted calix[4]resorcinarene with unreacted hydroxy groups forms monolayers with surface defects (voltammogram not shown), confirming SPR studies[26].

3.3. Steric Effects in the $Fe^{(III)}(CN)_6^{3-/4-}$/ Au-calix[4]resorcinarene electrode system.

If three separate redox processes are occurring, then it is probable that these each correspond to location of the $Fe(CN)_6^{3-}$ ion in three different environments.

Several interesting points should be noted: The first and most interesting observation relates to the ($\beta_{(RED)}$) and ($\beta_{(OX)}$) redox couple. These peaks are nearly coincident in potential, pointing first towards their match (which may be further verified by comparing their integrated charge values), and second towards a *surface* bound redox process. Variation of the potential sweep rate from 5 through to 50 mV s-1 also yielded peaks coincident in potential providing further confirmation that this redox couple corresponds to a surface-based process. ($\beta_{(OX)}$) is at a *lower* overpotential relative to the single ferricyanide reduction potentials observed at the bare Au electrode. Two scenarios could possibly explain this behaviour; the first explanation could involve the $Fe(CN)_6^{3-}$ approaching the gold surface in a more favourable position for the electrochemical charge transfer to occur relative to the bare gold electrode surface; the second could possibly indicate a *facilitated* electron transport, with the calix[4]resorcinarene within this context performing the role of a charge transfer mediator between the ferricyanide ion and the gold surface. The most obvious charge transfer mechanism here could involve the approach and possible retention of the $Fe(CN)_6^{3-}$ ion directly into the bowl of the calix[4]resorcinarene. An ion residing within the calix[4]resorcinarene bowl could clearly explain the observation of a surface bound

electrochemical reaction. Estimates within the literature for the ionic diameter for $Fe(CN)_6^{3-}$ range from 6.2Å[30] through to 7.2Å[31], while the calix[4]resorcinarene has a bowl diameter which may be calculated to be of approximately 13.2Å, which should therefore should permit easy access. Even if we take the shortest Oxygen-Oxygen distance around the perimeter of the bowl (~10Å) - the ferricyanide should be able to enter and reside within the calix[4]resorcinarene structure.

It should be remembered in this context that the ion/calix[4]resorcinarene interactions will occur via hydrogen bonding between the oxygen atoms around the perimeter of the calix[4]resorcinarene bowl and the ion, and that the bowl itself will, by its structure, possess some flexibility. It therefore follows that it should be possible for ions to reside in the perimeter of the calix[4]resorcinarene bowl without having to enter the cavity of the calix[4]resorcinarene itself.

If a $Fe(CN)_6^{3-}$ ion does reside within the calix[4]resorcinarene bowl, it might be expected to be held at a distance of between 18 and 21Å from the Au surface, as calculated by geometrical modelling and comparison with SPR results[26]. One possibility here could be that the $Fe(CN)_6^{3-}$ might pass through the calix[4]resorcinarene molecule and directly access the Au surface; steric hindrance would however make such an approach highly unlikely since the diameter at the base of the calix[4]resorcinarene bowl is calculated to be approximately 5.2Å, whilst the diameter of the ferricyanide ion (7.2Å) is at least 1-2Å than the passage through which it would have to pass. It appears clear therefore, that the ferricyanide ion must here be held at some distance *in excess* of 14Å from the Au surface as its plane of closest approach.

A simple consideration of the Marcus[28] or Intersecting State theories[32] for charge transfer mechanisms shows that molecular or ionic coupling - and therefore electron transfer rates decrease exponentially with distance, **Eqn. 2**:-

Eqn 2: $$V_R^2 = V_O^2 \exp^{(-\beta R)}$$

where V_o^2 represents the maximum electric coupling, R is the distance and β is the exponential electron tunnelling coefficient.

Indeed, variations of 20Å have been shown to change electron transfer rates by as much as 10^{12} fold[33].

It should be remembered that the empirical results of **Fig. 4**, show a ***facilitation*** in the electron transfer process and so suggest that the ferricyanide is being held in a favourable steric environment and that charge transfer species (*eg* H^+ or even OH^- ions) permit transfer between the environment of the calix[4]resorcinarene bowl and the gold surface. It should not be forgotten that the calix[4]resorcinarene molecule is immobilised on the gold surface via thiol linkages. While insulating proteins typically show an electron tunnelling coefficient of $1.4Å^{-1}$ [33], β values for Au-thiol linked saturated hydrocarbons have been reported as low as $0.98Å^{-1}$ [34], showing that charge transfer of this nature may occur far more easily than was previously thought possible.

If a $Fe(CN)_6^{3-}$ ion resides within the calix[4]resorcinarene bowl, the components of the complex must undergo electronic orbital coupling with each other; although data for the calix[4]resorcinarene/$Fe(CN)_6^{3-}$ interaction is not available, it would appear that the

entrapment of ferricyanide ion enhances electronic coupling which facilitates electron transport to the electrode via the thiol-linked/calix[4]resorcinarene structure. The overall lowering of the activation barrier, may however be calculated from the change in reduction potential, calculated from **Eqn. 3**:-

Eqn 3: $\Delta E = nF\ (\alpha_{RED} - \beta_{RED})$

where F = Faraday Constant and n = no. of electrons involved in reaction.

In this instance, the activation energy for the reduction of $Fe(CN)_6^{3-}$ has been found to be lowered by approximately 24kJ mol^{-1}. Possible interactions include hydrogen bonding of the phenolic groups to the negatively charged ferricyanide ions and interactions of the ion with the electron rich aromatic groups. Should the more electron rich $Fe^{II}(CN)_6^{4-}$ interact more strongly than $Fe^{III}(CN)_6^{3-}$, this would cause a net stabilisation of the ferrocyanide and make the reduction of ferricaynide more energetically favourable.

The next pair of peaks to be considered are those denoted as $\alpha_{(RED)}$ and $\alpha_{(OX)}$ respectively. The $\alpha_{(RED)}$ now occurs at a more negative overpotential (approximately -25mV vs Ag/AgCl) indicating a slightly less favourable environment with respect to the bare gold surface. In this instance the activation energy is calculated to have increased by approximately 10kJ mol^{-1}. The corresponding re-oxidation peak $\alpha_{(OX)}$, moreover exhibits some loss in reversibility again indicating a less favourable environment for the re-oxidation of the $Fe(CN)_6^{4-}$ ion with respect to the bare gold electrode surface.

It is possible in this situation that the $Fe(CN)_6^{3-}$ ion approaches the gold electrode by migration under the influence of electric field, but encounters considerable steric hindrance from adsorbed $Fe(CN)_6^{3-}$ as it is pulled against the calix[4]resorcinarene layer. It is known that direct contact may not be necessary to permit efficient electron transport[33]. The ferricyanide ions are held against the layer but not immobilised inside the bowls. The absence of any smaller shoulder peaks on the ($\alpha_{(RED)}$) peak suggests that the ferricyanide ion is being prevented from directly accessing the gold electrode surface which in turn would point towards a complete and homogeneous calix[4]resorcinarene coating at the Au electrode surface which is consistent with SPR results[26].

In this model one pair of redox peaks ($\gamma_{(RED)}$ and $\gamma_{(OX)}$) has still to be accounted for. A third environment for the approach of the Fe $(CN)_6^{3-}$ ion could involve a stacking of Fe $(CN)_6^{3-}$ ions above a layer of Fe $(CN)_6^{3-}$ filled calix[4]resorcinarene cavities; this is indeed probable as the ferricyanide will be drawn to the surface of the gold electrode during the cathodic sweep. Once the calix[4]resorcinarene cavities are filled, the closest possible approach of the $Fe(CN)_6^{3-}$ ion to the electrode will be in excess of 21Å.

It is therefore proposed that ($\gamma_{(RED)}$ and $\gamma_{(OX)}$) may correspond to the reduction of $Fe(CN)_6^{3-}$ and the subsequent oxidation of $Fe(CN)_6^{4-}$ respectively when the ion is held above the calix[4]resorcinarene coating. An increased reduction overpotential of approximately 320mV (**table 1**), shows that the activation energy for this process has been increased by ~45kJ mol^{-1}. If the process has become *less* favourable energetically, then electronic coupling of the $Fe(CN)_6^{3-}$ ion with either the calix[4]resorcinarene or gold surface must also have been impaired and this may indeed be probable if the ions are situated some distance from either the calix[4]resorcinarene structure - or indeed the Au surface.

This model for the reduction of $Fe(CN)_6^{3-}$ ions of three environments could account for all of the considerations thus far. It has been established for some time that ions do indeed reside within that calix[4]resorcinarene bowl[24], and it is probable that the electrical migration of ions towards the Au surface will cause further ions to be firstly pulled in between and then stacked above the individual calix[4]resorcinarene molecules; an electrical double layer type arrangement of ion association around the electrode might be envisaged here.

To summarise it is therefore that the three observed pairs of redox peaks observed respectively correspond to the electron transfer processes of ferricyanide ions residing:

(i) directly within the calix[4]resorcinarene bowl ($\alpha_{(RED)}$ & $\alpha_{(OX)}$); and

(ii) against the calix[4]resorcinarene layer, ($\beta_{(OX)}$ & $\beta_{(RED)}$),

(iii) stacked above the calix[4]resorcinarene layer ($\gamma_{(RED)}$ & $\gamma_{(OX)}$).

3.4 IR Spectroscopy of the $Fe^{(III)}(CN)_6^{3-/4-}$ couple on the Au-calix[4]resorcinarene surface.

Further supporting evidence for this model was found by infra-red spectroscopy of a calix[4]resorcinarene coated Au surface, a calix[4]resorcinarene coated Au surface which has been exposed to $Fe(CN)_6^{3-}$ and the $Fe(CN)_6^{3-}$ complex. The spectra of the Au/calix[4]resorcinarene and Au/calix[4]resorcinarene/$Fe(CN)_6^{3-}$ surfaces were obtained using FTIR spectroscopy; the infra-red spectrum of the $Fe(CN)_6^{3-}$ was measured within a ground and compressed KBr disc, **Fig 7**. The $Fe(CN)_6^{3-}$ spectrum displays a pronounced peak at ~2135 cm^{-1}, **Fig 7a** (not to scale with a and b). Two discernible peaks are seen for the calix[4]resorcinarene/ferricyanide coating at ~2115 and 2086 cm^{-1}, **Fig 7b**, which might

correspond to the $Fe(CN)_6^{3-}$ residing between adjacent calix[4]resorcinarene molecules and within the calix[4]resorcinarene bowl respectively. Alternatively they could arise because of the difference between axial and equatorial cyano groups in an immobilised ion. The peaks are noticeably broader and of lower wavenumber than in the solid, indicating the presence of a pronounced interaction with the calix[4]resorcinarene, however due to the almost spherical symmetry of the ferricyanide ion, no orientation data can be found. As a control the FTIR spectrum of the calix[4]resorcinarene layer on its own was measured and shows no distinguishable peaks within the range studied, **Fig 7c**.

3.5 Stability of the $Fe^{(III)}(CN)_6^{3-/4-}$ calix[4]resorcinarene-Au association.

It is known that ion-calix[4]resorcinarene associations may remain stable for some time[24], the stability of the association between the ferricyanide and the calix[4]resorcinarene coatings was therefore evaluated electrochemically. Electrodes which had already been voltammetrically scanned in a $Fe(CN)_6^{3-}$/ phosphate buffer solution were immersed and then repeatedly voltammetrically scanned within a plain phosphate buffer, **Fig. 8**. The magnitudes of the ferri/ferrocyanide faradaic peaks clearly diminish with each sweep. This may be explained in terms of loss of ferricyanide with time and successive potential sweeping. Only one discernible oxidation peak on the anodic sweep (which itself diminishes with each successive cycle) is observed. The position for this peak is also curious (~ -0.05 to -0.15 V vs Ag/AgCl), since this is considerably less anodic than each of the $\alpha_{(OX)}$, $\beta_{(OX)}$ or $\gamma_{(OX)}$ peaks. It is believed that when the electrode is placed in fresh buffer, loosely associated ferricyanide ions, in positions other than the calix[4]resorcinarene bowl, are lost under the action of a diffusion gradient. The packing arrangement once disrupted may also possibly perturb the $Fe(CN)_6^{3-}$/calix[4]resorcinarene bowl association, which in turn may give rise to an altered oxidation potential, **Fig 8**.

Even more interestingly however, it became apparent that the *Au* surface is progressively lost from the glass backing support of the electrode with each successive potential sweep, **Fig. 9**. By contrast, a calix[4]resorcinarene coated gold electrode that has never been exposed to ferricyanide, remains stable indefinitely, when voltammetrically scanned in the same phosphate buffer. A plain gold electrode also remains indefinitely stable when voltammetrically scanned in buffer. In a similar manner a plain gold electrode voltammetrically scanned in a buffered solution of ferricyanide again remains stable. The stripping of the gold therefore *only* occurs at electrodes that have been calix[4]resorcinarene coated and exposed to ferricyanide. It is not surprising that during the anodic sweep - and following the oxidation of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ ions will tend to be repelled from the working electrode. If gold is lost during these potential cycles it would therefore appear that $Fe(CN)_6^{4-}$ - calix[4]resorcinarene interaction is greater than the adhesive bonding of the Au/Cr film to the underlying glass substrate. In this case the gold/calix[4]resorcinarene/$Fe(CN)_6^{4-}$ is stripped as one entity from the glass backing.

Unfortunately, it is difficult to calculate the work expended in removing the gold-thiol linkage as the observed faradaic peak corresponds not solely to the removal of the calix[4]resorcinarene coating, but principally to the oxidation of $Fe(CN)_6^{4-}$.

4 Conclusions

Three different redox peaks are observed for the reduction of $Fe(CN)_6^{3-}$ and the subsequent re-oxidation of $Fe(CN)_6^{4-}$ at calix[4]resorcinarene - modified Au electrodes. Each pair of peaks is thought to correspond to the inorganic ion residing in three different environments. It is thought that one redox pair corresponds to the ion residing in the calix[4]resorcinarene bowl, another to the ion between the bowls and the third to ions stacked above a $Fe(CN)_6^{3-}$ saturated calix[4]resorcinarene layer. It is also postulated that the calix[4]resorcinarene coating acts as a charge transfer mediator towards $Fe(CN)_6^{3-}$ ions residing within the bowl structure. FTIR spectroscopy lends further support to this argument.

It appears that the $Fe(CN)_6^{3-}$/calix[4]resorcinarene association may be stronger than bonding of the Au/Cr film to the glass backing of the electrode, since electrodes exposed to ferricyanide lose their gold and calix[4]resorcinarene coating when voltametrically scanned in a fresh phosphate buffer.

References:

1. J. Wang, Electroanalysis. 3 (1991) 255.
2. R.P. Baldwin, K.N. Thomsen, Talanta. 38 (1991) 1.
3. J. Wang, Anal. Chem. 65 (1993) 450R.
4. Q.T Cai, S.B. Khoo, Anal. Chem. 24 (1994) 4543.
5. J.M. Zen, S.Y. Huang,. Anal. Chim. Acta. 256 (1994) 77.
6. J.M. Zen, J.S. Tang, Anal. Chem. 67 (1995) 208.
7. M. Watanabe, H. Nagasak, N. Ogata, J. Phys. Chem. 32 (1995) 12294.
8. S.B. Khoo, Q.T. Cai, Electroanalysis. 6 (1996) 549.
9. M. Josowicz, M. Analyst. 120 (1995) 1019.
10. C.M.A Brett, A.M.O. Brett, F.M. Matysik, S. Matysik, S. Kumbhat, Talanta. 43 (1996) 2015.
11. C. Lopez, J.C. Moutet, E. Saintaman, J.Chem. Soc. Faraday Trans. 92 (1996) 1527.
12. K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, Electroanalysis. 7 (1995) 5.
13. P. Ugo, L.M. Moretto, Electroanalysis. 7 (1995) 1105.
14. C.D. Gutsche, Calixarenes; Royal Society of Chemistry: Cambridge, 1989; p 20-47.
15. J. Vicens, V. Bohmer, Calixarenes. A Versatile Class of Macrocyclic Compounds; Kluwer: Dordrecht, 1990.
16. D. Diamond, M.A. McKervey, Chem. Soc. Rev. 25 (1996) 15.
17. C.D. Gutsche, R. Muthukrishnan,. J. Org. Chem. 43 (1978) 4905.
18. D.W.M. Arrigan, G. Sevhla, S.J. Harris, M.A. McKervey, Electroanalysis. 6 (1994) 97.
19. J. Wang, J. Liu, Anal. Chim. Acta. 294 (1994) 201.
20. K. O'Connor, G. Svehla, S.J. Harris, M.A. McKervey, Talanta. 39 (1992) 1549.

21. P. Cobben, R. Egberink, J. Bomer, P. Berveld, W. Verboom, D. Reinhoudt, J. Am. Chem. Soc. 114 (1992) 10573.

22. M. McMarrick, S.J. Harris, D. Diamond, J. Mater. Chem. 4 (1994) 217.

23. H. Adams, F. Davis, C.J.M. Stirling, J. Chem. Soc. Chem. Comm. 21 (1994) 2527.

24. F. Davis, C.J.M. Stirling, J. Am. Chem. Soc. 117 (1995) 10385.

25. S.W. Keller, H. –N. Kim, T.E. Mallouk, J. Am. Chem. Soc. 116 (1994) 8817.

26. J. D. Faull, V. K. Gupta, Langmuir. 18 (2002) 6584.

27. E. U. Thoden van Velzen, J. F. J. Engbersen, P. J. de Lange, J. W. G. Mahy, D. N. Reinhoudt, J. Am. Chem. Soc. 117 (1995) 6853.

28. R. Greef, R.L. Peat, L.M. Peter, D. Pletcher, J. Robinson. Instrumental Methods in Electrochemistry; Ellis Horwood Ltd.: Chichester, 1985; p 185.

29. S. D. Collyer, S. Bradbury, J. V. Hadfield, S. P. J. Higson, Electroanlysis 15 (2001) 332.

30. H.B. Weiser, W.O. Milligan and J.B. Bates, J. Phys. Chem., 42 (1942) 99.

31. A.G. Sharpe, Inorganic Chemistry – 3rd Edition, Longman, Harlow, UK, 1992; p.540.

32. J.M. Hale, in Reactions of Molecules at Electrodes; N. S. Hush Editor, Wiley Interscience: London, 1971; p 247.

33. L.G. Arnault, S.J. Formosinho, J. Photochem & Photobiol A: Chemistry. 100 (1996) 15.

34. C.C. Moser, J.M. Keske, K. Warncke, R.S. Farid, P.L. Dutton, P.L. Nature. 355 (1992) 796.

Legends to Figures

Fig 1: Schematic of electrochemical cell

Fig 2: Calix[4]resorcinarenetetrathiol structure

Fig 3: Cyclic voltammogram recorded at a calix[4]resorcinarene-coated gold electrode in *p*H 7.4 phosphate buffer: (scan rate: $20mVs^{-1}$ between +0.8V and -0.8V vs. Ag/AgCl).

Fig 4: Cyclic voltammograms recorded at bare gold and calix[4]resorcinarene-coated gold electrodes in 1mM $K_3Fe(CN)_6$ solution: (scan rate: $20mVs^{-1}$ between +0.8V and -0.8V vs. Ag/AgCl).

(—— : calix[4]resorcinarene coated electrode; ----- : bare gold electrode).

Fig5: Cyclic voltammogram recorded at a calix[4]resorcinarene-coated gold electrode in *p*H 7.4 phosphate buffer containing 1mM $K_3Fe(CN)_6$ solution: (scan rate: 20 mVs^{-1} between +0.8V and +0.25V vs. Ag/AgCl).

Fig 6: Cyclic voltammogram recorded at a calix[4]resorcinarene-coated gold electrode in *p*H 7.4 phosphate buffer containing 1mM $K_3Fe(CN)_6$ solution: (scan rate: 20 mVs^{-1} between +0.8V and –0.2V vs. Ag/AgCl).

Fig 7: FTIR spectra of (a) $K_3Fe(CN)_6$ as a KBr disk

(b) Calix[4]resorcinarene following 1 hr exposure to 1 mM $K_3Fe(CN)_6$

(c) Calix[4]resorcinarene modified Au surface

Fig 8: Cyclic Voltammogram recorded at a calix[4]resorcinarene-coated gold electrode in *p*H 7.4 phosphate buffer, after original scan in 1mM $K_3Fe(CN)_6$ solution (scan rate: $20mVs^{-1}$ for 10 sweeps between +0.8V and -0.8V vs. Ag/AgCl).

Fig 9: Figure showing removal of the calix[4]resorcinarene and gold electrode surface from a glass backing support, after; a) 1 scan; b) 10 scans and c) 15 cyclic potential scans.

Table 1.

Comparison of redox peak potentials for a bare gold electrode and a calix[4]resorcinarene coated electrode in a 1mM $K_3Fe(CN)_6$ solution. (All potentials expressed vs. Ag/AgCl).

Redox Peaks	Bare Gold Electrode Peak Potentials (mV)		Calix[4]resorcinarene Coated Electrode Peak Potentials (mV)	
	REDUCTION	OXIDATION	REDUCTION	OXIDATION
α	125	195	-25 ($\alpha_{(RED)}$)	185 ($\alpha_{(OX)}$)
β	-	-	370 ($\beta_{(RED)}$)	395 ($\beta_{(OX)}$)
γ	-	-	-340 ($\gamma_{(RED)}$)	490 ($\gamma_{(OX)}$)



https://dspace.org/

The electrochemistry of the ferri/ferrocyanide couple at a calix [4]resorcinarenetetrathiol-modified gold electrode as a study of novel electrode modifying coatings for use within electro-analytical sensors

Collyer, Stuart D.; Davis, Frank; Lucke, Andrew; Stirling, Charles J. M.; Higson, Seamus P. J.

2003-06-05T00:00:00Z
Elsevier Science B.V., Amsterdam.
http://dx.doi.org/10.1016/S0022-0728(03)00270-5
Stuart D. Collyer, Frank Davis, Andrew Lucke, Charles J. M. Stirling and Séamus P. J. Higson, The electrochemistry of the ferri/ferrocyanide couple at a calix[4] resorcinarenetetrathiol-modified gold electrode as a study of novel electrode modifying coatings for use within electro-analytical sensors, Journal of Electroanalytical Chemistry, Volume 549, 5 June 2003, Pages 119-127

Downloaded from a DSpace repository. https://dspace.org/