Electrochemistry of Ferrocene Derivatives
Relevant to their use In Measuring State of
Charge of Lead Acid Batteries

By

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I declare that this thesis is my own account of my research and contains as its main content work, which has not previously been submitted for a degree at any tertiary education institute.

Touma B. Issa

2001
ABSTRACT

The electrochemistry of some ferrocene compounds coated on gold electrodes in concentrated sulphuric acid solutions in the concentration range 1–5 M has been investigated. The objective of this work was to investigate whether such compounds could be used to determine, potentiometrically, the state of charge of lead-acid batteries. The investigated ferrocenes included, simple ferrocene, poly(vinylferrocene), bridged ferrocenes in which the two cyclopentadienyl groups are linked by –CH₂– chains of vary lengths and alkanethiol substituted ferrocenes.

Each of the investigated ferrocenes were found to undergo one electron reversible oxidation/reduction at the surface of the electrode. Their anodic and cathodic peak potentials were independent of pH in the range 2–10 in aqueous solutions of K₂SO₄, KCl and NaClO₄. However, in concentrated acid solutions (H₂SO₄, HCl and HClO₄) the anodic and cathodic peak potentials shifted, almost linearly, to less positive potentials with increasing acid concentration. The attachment of alkanethiol group to the ferrocene molecules improved the retainability at the gold electrode surface which is possibly linked to strong chemisorption of the thiol group on the gold surface. The retainability and chemical stability of the ferrocene compounds at the gold electrode surface were found to be higher in ClO₄⁻ than in Cl⁻ and SO₄²⁻ media which is postulated to be related to the salt formation between the anion and the ferricenium ion generated on oxidation. The bridged ferrocenes were found to be chemically more stable than simple ferrocene. The presence of a carbonyl group in the alkanethiol chain
generally decreased the chemical stability of the ferrocene compounds in aqueous acidic media but more so in SO$_4^{2-}$ than in ClO$_4^-$ media. Of all the investigated ferrocenes, the potentiometric response of the 1,1`-Bis(11-mercaptoundecyl)ferrocene redox couple was found to be the most stable and reproducible in concentrated sulphuric acid. Hence this couple has the potential of measuring the change in the acid concentration corresponding to the state of charge of lead-acid battery. Long term stability of the material in concentrated sulphuric acid, however, is not good. The material survived for only 15 days. Further work on identifying more stable ferrocene couples is needed.
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To my family, without your constant love, support, and encouragement none of this would be possible.

“Let every man be swift to hear and slow to speak and slow to anger. James 1:19”
PUBLISHED WORK

The following papers and conference presentations have been published from the work described in this thesis.

Papers


Conference Presentations

1. Touma B. Issa; Pritam Singh; Murray Baker, “Cyclic Voltammetry at electrodes modified by ferrocene derivatives in sulphuric acid media.” EDRACI Winter School in Electrochemistry, Wollongong, Australia, 1999.


ABBREVIATIONS

\[\lambda\] reorganisation barrier energy
\[\mu\] electronic coupling
\[\rho\] density of metallic states
\[\Gamma\] or \[\Gamma_{\text{max}}\] surface coverage (mol cm\(^{-2}\))
(a) strongly bonding
(bipy) 2,2'-bipyridine
\[\Delta E_p\] or \[\Delta E\] peak potential separation
\[A\] area of the electrode (cm\(^2\))
AC atomic concentration
Au gold electrode
BE binding energy
Bu\(_4\) tetrabutyl
cp cyclopentadienyl ligand
CV cyclic voltammetry
DME dropping mercury electrode
DMF N,N- dimethylformamide
DMSO dimethylsulphoxide
\[E_{02}\] value for reduction of ferricenium ion
\(e_1\) weakly bonding degenerate
\(e_2\) degenerate antibonding
\(E_{pa}\) anodic peak potential
\(E_{pc}\) cathodic peak potential
EQCM  electrochemical quartz crystal microbalance
EQCN  electrochemical quartz crystal nanobalance
Et₄  tetraethyl
F  faraday’s constant = 9.648×10⁴ C mol⁻¹
Fc⁺  ferricenium ion
Fcs  any ferrocene

Ferrocenes

Fc: Ferrocene
PVFc: Poly(vinylferrocene)

Fc1: 11-Mercaptoundecylferrocene or 11-ferrocenylundecanethiol
Fc2: (1,1’)-Bis(11-mercaptopoundecyl)ferrocene
Fc3: 11-mercaptopoundecanoylferrocene
Fc4: 1,1'-Bis(11-mercaptopoundecanoyl)ferrocene
Fc5: [3](1,1')ferrocenophane
Fc6: [32](1,1')(3,3')ferrocenophane
Fc7: [33](1,1')(2,2')(4,4')ferrocenophane
Fc8: [5](1,1')ferrocenophane
Fc9: 2-(11-Mercaptoundecyl)[3](1,1')ferrocenophane
Fc10: 4-(11-Mercaptoundecyl)[32](1,1')(3,3')ferrocenophane
Fc11: 3-(11-Mercaptoundecyl)[33](1,1')(2,2')(4,4')ferrocenophane
Fc12: 3-(11-Mercaptoundecyl)[5](1,1')ferrocenophane

FTIR  fourier transform infrared spectroscopy
FTMS  fourier transform mass spectroscopy
GC  glassy carbon electrode
HMPTA  hexamethylphosphorotriamide

ᵢₚ  peak current
Ipₐ  anodic peak current.
Ipₑ  cathodic peak current.
K₁  equilibrium constant
LCAO-MO’s  linear combination of atomic orbitals-molecular orbitals
LPJ  liquid junction potential
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Me</td>
<td>Methyl group</td>
</tr>
<tr>
<td>n</td>
<td>number of equivalents per mole</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl group</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum electrode</td>
</tr>
<tr>
<td>Q</td>
<td>charge ($\mu$C/cm$^2$)</td>
</tr>
<tr>
<td>R</td>
<td>gas constant</td>
</tr>
<tr>
<td>$R^2$</td>
<td>the coefficient of determination</td>
</tr>
<tr>
<td>RE, Pt</td>
<td>rotating platinum electrode</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>sat. KCl</td>
<td>saturated potassium chloride</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SME</td>
<td>surface modified electrode</td>
</tr>
<tr>
<td>T</td>
<td>temperature in kelvin</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet visible spectroscopy</td>
</tr>
<tr>
<td>$v$</td>
<td>scan rate</td>
</tr>
<tr>
<td>XPS</td>
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The use of lead-acid batteries is considered to be the fundamental component of any power supply system utilising renewable as well as conventional energy sources. For a long battery life and efficient energy management it is necessary that the state of charge of the battery be monitored during operation (Kordesch, 1977). The concentration of the battery electrolyte, sulphuric acid, decreases on charge and increases on discharge, which provides means of indicating the state of charge of the lead acid battery. Generally the state of charge estimation is achieved by examining any property of the electrolyte, which changes as a function of sulphuric acid concentration during the charge/discharge cycle. For example variation of properties of the electrolyte such as conductivity, refractivity, heat capacity, impedance of the quartz crystal oscillatory, optical absorption, magnetic permeability, equilibrium vapour pressure, and ionic activities have been considered (Bode, 1977, Kordesch, 1977, Weininger and Briant, 1982, McNicol and Rand, 1984, Makino et al., 1994, Charlesworth, 1996, Weiss, 1999). However, specific gravity measurement by hydrometer is the most frequently used method at the present (Kordesch, 1977). This is a good reliable method, however it is messy, time wasting and labour intensive. It is especially unsuitable when banks of batteries are considered and when they are located in isolated areas. In such conditions remote monitoring is extremely practical. Determination of the state of
charge of lead acid batteries by using potentiometric methods becomes very attractive in these cases.

The potentiometric measurement of the change in hydrogen ion concentration \( [H^+] \) in the lead-acid battery electrolyte by a pH-measuring device would provide a simple route to the state-of-charge determination. Unfortunately the pH sensors such as the glass electrode and the antimony oxide electrode cannot be used because the concentrated battery electrolyte contains a high concentration (1–5 M) of sulphuric acid. There is therefore an urgent need to develop alternative devices.

One of the major aims of this thesis is to explore the possibility of exploiting surface modified electrode (SME) chemistry in developing an inexpensive, rugged, miniaturised probe for measuring \( [H^+] \) in the battery electrolyte as a means of monitoring the battery state of charge. The use of SMEs in measuring hydrogen ion concentration is not new. For example, a Nernstian response to \( [H^+] \) has been reported for poly(1,2-diaminobenzene) films on platinum and glassy carbon (Heineman et al., 1980, Cheek et al., 1983). Similarly, Rubinstein (Rubinstein, 1984) could measure the pH of solutions by measuring the reduction peak potential values of surface-bound poly(1,2-diaminobenzene) with respect to surface-bound \( \text{Ru(bipy)}_3^{3+/2+} \) (in nafion) reference SME. However, study of SMEs directed towards measuring \( [H^+] \) in concentrated sulphuric acid solutions similar to that in the lead-acid battery electrolyte has not been hitherto reported.
This thesis examines the use of SMEs made from various ferrocene compounds for monitoring change in H⁺ ion concentration in lead-acid batteries as a function of the state of charge of the battery.

Ferrocene is one of the most stable organometallic compounds. The one-electron oxidation of ferrocene to ferricenium ion proceeds in a straightforward manner. Consequently, the ferrocene/ferricenium ion system is routinely used by electrochemists as a model redox system (Gritzner and Kuta, 1984). Ferrocene and its derivatives have found numerous applications in electrochemistry. These include use as electroactive material of batteries (Tsutsumi and Matsuda, 1993), electron transfer agents for enzyme-based glucose sensors (Carlson et al., 1984, Dicks et al., 1993), and as reference materials for electrochemical pH sensors (Hickman et al., 1991). Electrochemical reference electrodes based on the ferrocene/ferricenium redox couple in non-aqueous media have been investigated extensively (Gritzner and Kuta, 1984). In aqueous media, this couple tends to undergo hydrolysis and hence its chemical stability limits its use in electrochemical devices for aqueous systems. Thus, this thesis examines the use of various ferrocene derivatives, which are expected to be more stable in aqueous acid media (Hisatome and Yamakawa, 1971, Ortaggi et al., 1979, Clara et al., 2000). These include poly(vinylferrocene) and ferrocenes whose cyclopentadienyl groups are linked by varying number of (CH₂–CH₂)n groups.

The attachment of thiol groups to ferrocene provides a mechanism through which ferrocene/ferricenium couples can be attached to a gold surface (Finklea, 1996). Thus,
SMEs consisting of thiol substituted ferrocenes chemisorbed on gold have been included in this study.

The investigations focus on the electrochemistry and chemical stability of the various ferrocenes in 1–5 M H₂SO₄ solutions. The potentiometric behaviour of these ferrocene/ferricenium couples, which were found to be reasonably stable in the acid media, was also investigated.

A literature review of the properties of ferrocenes and bridged ferrocenes is presented in Chapter 2. Chapter 3 includes a general review of surface modification and surface modified electrodes. The experimental details of the work described in the thesis are given in Chapter 4. The Chapter 5 describes and discusses the electrochemistry of a simple ferrocene molecule, $\text{Fc}$, coated on a gold substrate, while the electrochemistry of poly(vinylferrocene), $\text{PVFc}$, in concentrated sulphuric acid media is included in Chapter 6. Chapter 7 examines the characteristics of SME electrodes consisting of gold surfaces with immobilised thin layers of alkanethiol ferrocenes. A systematic study of the electrochemistry of surface modified electrodes made of bridged ferrocenes is described in Chapter 8. The electrochemistry of the thiol derivatives which additionally contain a $(\text{CH}_2)_{11}\text{SH}$ group attached to the cyclopentadienyl group of the ferrocene molecules discussed in Chapter 8 is given in Chapter 9. Based on the results described in Chapters 5–9, $(1,1')$-bis(11-mercaptopoundecyl)ferrocene, $\text{Fc}_2$, has been identified to be the most appropriate material for using as an SME type potentiometric sensor in concentrated sulphuric acid in the
range 1–5 M. The properties of this compound in relation to its use in a potentiometric device for measuring state of charge of lead-acid batteries are discussed in Chapter 10.

References


2.1 Introduction

Following the synthesis of ferrocene, Fe(C₅H₅)₂, in 1951–1952 (Kealy and Paulson, 1951, Miller et al., 1952) many researchers have studied the properties of this compound. Ferrocene, (dicyclopentadienyliiron(II)), is the first known metallocene in which the pi-electron system of the cyclopentadienyl (C₅H₅⁻) ion is bound to an iron ion. It has the structure known commonly as that of a “sandwich”. A large number of experimental observations have accumulated to suggest that in solution or in the vapour phase, the energy barrier to rotation of the rings is small. The cyclopentadienyl rings are able to rotate more or less freely with an estimated barrier of 4 kJ mol⁻¹. (Haaland and Nilsson, 1968) This results in two possible conformations of ferrocene, eclipsed (D₅h) and staggered (D₅d).

Ferrocene has 18 valence electrons. Six are considered to be from the iron(II), and six from each C₅H₅⁻ ring. The bonding in ferrocene is commonly treated by the linear combination of atomic orbitals (LCAO-MO’s) approximation, as shown in Figure 2.1. (Cotton and Wilkinson, 1988) Each C₅H₅⁻ ion has five $\pi$ molecular orbitals, one
strongly bonding (a), a weakly bonding degenerate pair \((e_1)\), and a degenerate antibonding pair \((e_2)\). The staggered \((D_{5d})\) symmetry is assumed for ferrocene since it lacks steric hindrance and is therefore assumed more stable. The valence shell orbitals of the iron atom \((3d^64s^2)\) interact with the \(\pi\) orbitals of the \(C_5H_5^-\) ring to form nine bonding and/or nonbonding molecular orbitals in ferrocene.

Figure 2.1 Linear combination of atomic orbitals (LCAO-MO’s) approximation for ferrocene. (Cotton and Wilkinson, 1988)
Several investigators have examined reactions of ferrocene to determine whether the cyclopentadienyl rings are similar to benzene in their chemical reactivity. It is now well known that substitution reactions on the cyclopentadienyl rings do occur, and ferrocene undergoes these reactions more readily than benzene. These reactions lead to the formation of derivatives of ferrocene. (Laskoski et al., 2001)

A vast wealth of information on ferrocene and its derivatives has become available since the preparation of ferrocene. Several reviews on this subject can be found in the literature, especially Marr and Rockett in their annual survey of ferrocene covering the years 1971 – 1989 in The Journal of Organometallic Chemistry. Since the work described in this thesis relates particularly to simple ferrocene and bridged ferrocenes derivatives, the following review focuses on the electrochemical behaviour of these compounds.

2.2 Electrochemistry of Ferrocene

Ferrocene is only sparingly soluble in water, with a reported solubility of the order $10^{-5}$ M in the presence of electrolyte. (Kolthoff and Thomas, 1965) It is an interesting electrochemical compound, since it contains iron(II) which is an electroactive centre.

Most of the modern electrochemical methods such as polaraography voltammetry, potentiometry, chronopotentiometry, etc., have been used to study the oxidation-reduction reactions of ferrocene and its derivatives. These methods are useful
in investigating the distribution of electron density in the molecule and the relative positions of the highest occupied and lowest vacant orbitals, not only in ferrocene but also for a number of other compounds with similar structure. (Denisovich and Gubin, 1977) A short review of the electrochemistry of ferrocene and its derivatives follows.

2.2.1 Oxidation of Ferrocene

Shortly after the preparation of ferrocene, Page and Wilkinson were the first to study the electrochemical behaviour of ferrocene at a dropping mercury electrode in 90% ethanol, 0.1 M NaClO₄. (Page and Wilkinson, 1952) They found that ferrocene undergoes reversible oxidation at 0.310V vs SCE forming dicyclopentadienyliron(III) which is also known by the name ferricenium ion, $\text{Fc}^+$. Several researchers have measured the potential of ferrocene in different solvents, supporting electrolytes and solute concentrations. Table 2.1 shows some of these data.
Table 2.1 Oxidation potential values for ferrocene in different media and working electrodes.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supporting Electrolyte</th>
<th>Fe Concentration (mM)</th>
<th>Working Electrode</th>
<th>Potential $E_{1/2}$ (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.280</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.385</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.460</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.2M LiClO$_4$</td>
<td>0.82 to 3.25</td>
<td>Pt-foil</td>
<td>0.307</td>
<td>(Kuwana et al., 1960)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M Et$_4$NClO$_4$</td>
<td>0.20 to 10</td>
<td>DME</td>
<td>0.379</td>
<td>(Kolthoff and Thomas, 1965)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M Bu$_4$NBF$_4$</td>
<td>1.00</td>
<td>DME</td>
<td>0.420</td>
<td>(Gubin et al., 1971)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M Bu$_4$NBF$_4$</td>
<td>1.00</td>
<td>Pt</td>
<td>0.480</td>
<td>(Gubin et al., 1971)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.350</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Acetylacetone</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.355</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Allyl Alcohol</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.365</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.1M LiClO$_4$</td>
<td>0.50</td>
<td>RE (Pt)</td>
<td>0.445</td>
<td>(Nelson and Iwamoto, 1963)</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Concentration</td>
<td>RE Potential</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>---------------</td>
<td>--------------</td>
<td>------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.410</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.370</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>0.1M Et₄NCIO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.335</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.420</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.445</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.505</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M LiClO₄</td>
<td>0.50</td>
<td>RE (Pt) 0.160 b</td>
<td>(Nelson and Iwamoto, 1963)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M Et₄NCIO₄</td>
<td>0.20</td>
<td>DME 0.147 b</td>
<td>(Kolthoff and Thomas, 1965)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M Li₂SO₄</td>
<td>0.33</td>
<td>GC 0.164 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M NaF</td>
<td>0.30</td>
<td>GC 0.161 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M Li₂SO₄</td>
<td>0.33</td>
<td>Au 0.156 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M NaF</td>
<td>0.30</td>
<td>Au 0.158 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M Li₂SO₄</td>
<td>0.33</td>
<td>Pt 0.160 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>0.1M NaF</td>
<td>0.30</td>
<td>Pt 0.159 c</td>
<td>(Bond et al., 1987)</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2.1: Potential Values for Reduction of Ferricenium Ion

<table>
<thead>
<tr>
<th>Medium</th>
<th>Concentration</th>
<th>Potential</th>
<th>Electrode</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.1M Li$_2$SO$_4$</td>
<td>0.35</td>
<td>Pt</td>
<td>0.165$^c$</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>-</td>
<td>Pt</td>
<td>0.400$^b$</td>
</tr>
</tbody>
</table>

(a) Saturated Calomel electrode (SCE), DME Dropping mercury electrode, RE (Pt) Rotating platinum electrode, Au Gold electrode, GC Glassy carbon electrode, Pt Platinum electrode, Bu$_4$= tetrabutyl, Et$_4$=tetraethyl

(b) $E_{1/2}$ value for reduction of ferricenium ion

(c) $E_{1/2} = (E_p^{ox} + E_p^{red})/2$

*More potential values could be found in Mann et al. and Janz et al.* (Mann and Barnes, 1970, Janz and Tomkins, 1973)
The Fe$^+$ solution colour is a blue or green in dilute form, but blood red in concentrated solution (Rosenblum, 1965). Fe$^+$ in solution, however, is unstable. It decomposes, to several products, through exchange of a cyclopentadienyl ligand (cp) with another nucleophile like hydroxide ion, (Prins et al., 1972, Holecek et al., 1979, McDowell et al., 1984) according to equation (2.1).

$$3[\text{Fe cp}_2]^+ + 3\text{OH}^- \rightarrow 2[\text{Fe cp}_2] + \text{Fe(OH)}_3 + 2\text{cp}^0 \quad (2.1)$$

$\text{cp}^0$ is a one electron oxidation product of cp$^-$. (Holecek et al., 1979)

Prins et al. studied the decomposition of the ferricenium Fe$^+$ cation by nucleophilic reagents. (Prins et al., 1972) Using electron spin resonance, electronic absorption spectroscopy, and magnetic susceptibility measurements they demonstrated that whereas the Fe$^+$ was stable in acetonitrile, acetone and nitromethane, it was decomposed by Cl$^-$ and Br$^-$ to Fc and FeX$_4^-$ (X = Cl, Br) and by N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), hexamethylphosphorotriamide (HMPTA), o-phenanthroline, and 2,2'-bipyridine to Fc and an Fe(II) complex, octahedrally coordinated by the added donor molecules. These results were explained by a reaction mechanism in which the primary step consisted of ligand exchange around the Fe(II) ion. The cp$^-$ ions which separated had a high reducing power, and so reduction of Fe$^+$ and the formation of the Fe(II) complex took place in secondary reactions. They also found that, because of the coupling of the ligand exchange reaction to the reduction reactions and the irreversible transformation of cp
radicals, even donors that were much weaker than cp\(^-\) could decompose Fe\(^+\). Similarly they found that iodide ions reduced Fe\(^+\) to Fe.

Holecek et al. studied the kinetics of decomposition of Fe\(^+\) in aqueous alkaline medium (Holecek et al., 1979). They found that the reaction stoichiometry was dependent on the type of ferricenium salt used (e.g., perchlorate or tetrafluoroborate). The decomposition rate of Fe\(^+\) ion was affected significantly by the presence of anions of inorganic salts with which Fe\(^+\) ion forms relatively stable complexes like \([\text{Fe(cp)}_2\text{X}]^{(n-1)}^{-}\), where X\(^{n-}\) = Cl\(^-\), Br\(^-\), NO\(_3^-\), ClO\(_4^-\), SO\(_4^{2-}\), cp = C\(_5\)H\(_5^-\). The authors suggested a complex mechanism for the decomposition reaction.

Matveev and Poroshenko studied the reaction of Fe\(^+\) with iodide ion in aqueous sodium chloride and sodium iodide salt solutions (Matveev and Poroshenko, 1989b). They found that Fe\(^+\) decomposed by a ligand-exchange mechanism, involving an outer-sphere complex with I\(^-\) ion. They noted that the stability of the Fe\(^+\) in these solutions was governed largely by the salt concentration. They also investigated the effect of pH in the range 5.41-6.71 on the stability of Fe\(^+\) in aqueous media (Matveev and Poroshenko, 1989a) and found that the decomposition reaction of Fe\(^+\) was irreversible and depended on the pH of the solution. In acetate-, propionate-, or formate-buffered solutions, Fe\(^+\) is unstable and the rates of decomposition of Fe\(^+\) ion decrease in the stated order of anion buffer. In weakly acidic solutions (pH 4.0-7.0), Fe\(^+\) is hydrolysed, with formation of associated complexes of the cation with the carboxylate anions. They found that these complexes increase in stability in the order formate < acetate < propionate.
Following Page and Wilkinson, who studied the oxidation of ferrocene (Page and Wilkinson, 1952), other researchers studied the oxidation of ferrocene derivatives.

Ferrocene and its derivatives could be oxidised both by chemical and by electrochemical methods. Inorganic oxidising agents such as HNO\textsubscript{3}, FeCl\textsubscript{3}, I\textsubscript{2}, Ag\textsuperscript{+}, etc. and organic oxidising agents like quinone, N-bromosuccinimide, etc. have been used for chemical oxidation of ferrocene (Mann and Barnes, 1970, Deeming, 1982). A typical oxidation reaction involving FeCl\textsubscript{3} as oxidising agent is shown in the equation (2.2).

\[
[\text{Fe(cp)}\textsubscript{2}] + 2\text{FeCl}_3 \rightarrow [\text{Fe(cp)}\textsubscript{2}][\text{FeCl}_4]^- + \text{FeCl}_2 \quad (2.2)
\]

The effect of substituents on the ease of oxidation of various substituted metalloccenes was investigated by Kuwana et al. (Kuwana et al., 1960). They showed that electron withdrawing substituents decreased the ease of oxidation, while electron donating substituents increased the ease of oxidation with respect to the parent metalloccene. The effect of substituents on the oxidation potential of ferrocenes has also been studied by many researchers (Mason and Rosenblum, 1960, Hoh et al., 1961, Sabbatini and Cesarotti, 1977, Grimes and Logan, 1980, Gallucci et al., 1993, Zanello et al., 1993b, Zanello et al., 1993a, Cinquantini et al., 1993, Zanello et al., 1994, Jiang et al., 1995). It has been reported that the progressive introduction of alkyl groups decreased the oxidation polarographic E\textsubscript{1/2} by 0.047 V irrespective of the position of the groups on the cyclopentadienyl rings. Some data are given in Table 2.2. While alkyl
groups favour oxidation, phenyl and CO$_2$H groups stabilise ferrocene with respect to oxidation to ferricenium ions, with polarographic $E_{1/2}$ increased by 0.023 and 0.280 V for the introduction of each of these groups respectively. However, 2-methoxycarbonyl-1-carboxyferrocene is more easily oxidised than it should be on this basis. This result has been explained in terms of intramolecular H-bonding between the two substituents (Sabbatini and Cesarotti, 1977).

Table 2.2 Half-wave potentials for different ferrocene derivatives measured in 90% ethanol at 25°C versus saturated calomel electrode (Sabbatini and Cesarotti, 1977, Grimes and Logan, 1980).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$</th>
<th>Compound</th>
<th>$E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.34</td>
<td>1-CO$_2$H-1'-CO$_2$Me-Fc</td>
<td>0.85</td>
</tr>
<tr>
<td>Me-Fc</td>
<td>0.28</td>
<td>1-CO$_2$H-2-CO$_2$Me-Fc</td>
<td>0.79</td>
</tr>
<tr>
<td>1,1,2-Et$_3$-Fc</td>
<td>0.19</td>
<td>Ph-Fc</td>
<td>0.37</td>
</tr>
<tr>
<td>1,1',3-Et$_3$-Fc</td>
<td>0.20</td>
<td>1,1-Ph$_2$-Fc</td>
<td>0.39</td>
</tr>
<tr>
<td>1,1'-Me$_2$-2,2'-Et$_2$-Fc</td>
<td>0.16</td>
<td>1,2,4-Ph$_3$-Fc</td>
<td>0.42</td>
</tr>
<tr>
<td>1,1',2,2',3,3',4,4'-Et$_8$-Fc</td>
<td>-0.05</td>
<td>1,1',3,3'-Ph$_4$-Fc</td>
<td>0.45</td>
</tr>
<tr>
<td>CO$_2$H-Fc</td>
<td>0.62</td>
<td>1,2,3,4-Ph$_4$-Fc</td>
<td>0.43</td>
</tr>
<tr>
<td>1-CO$_2$H-1',3'-Me$_2$-Fc</td>
<td>0.52</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bashkin et al. found the Fe was unstable to oxygen in aqueous and nonaqueous solvents. However, the stability is improved with sufficient methyl substitution of the
cyclopentadienyl rings. For example they have reported that bis(pentamethyl
cyclopentadienyl)iron is very stable in aqueous solutions in air (Bashkin and Kinlen,
1990).

Sato et al. examined the effect of the presence of trace amounts of dissolved
oxygen on the electrolytic oxidation of ferrocene (Sato et al., 1980) and found that a
portion of the ferricenium formed rapidly decomposed according to some unidentified
chemical processes. This effect was also studied by Fehlhammer et al. and Bashkin et

Grimes et al. investigated the effect of various substituents on the
cyclopentadienyl group on the ease of oxidation of ferrocene by measuring the
equilibrium constant of the reaction,

\[
Fcs + \frac{3}{2} I_2 \xleftarrow{K_1} \xrightarrow{} Fcs^+I_3^- \quad (2.3)
\]

(where \(Fcs\) is any ferrocene)

and polarographic \(E_{1/2}\) of the compounds in various media. They found that electron
withdrawing substituents made the ferrocene difficult to oxidise and electron donating
substituents made oxidation occur more readily. Some of Grimes data are in Table 2.3.
Table 2.3 Equilibrium constants and $E_{1/2}$ values for ferrocene derivatives oxidised by iodine (Grimes and Logan, 1980).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_1$</th>
<th>$E_{1/2}/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocene</td>
<td>175±3</td>
<td>0.34</td>
</tr>
<tr>
<td>Methylferrocene</td>
<td>635±35</td>
<td>0.28</td>
</tr>
<tr>
<td>Ethylferrocene</td>
<td>595±30</td>
<td>-</td>
</tr>
<tr>
<td>1,1´-dimethylferrocene</td>
<td>3314±150</td>
<td>0.24</td>
</tr>
<tr>
<td>1,1´-diisopropylferrocene</td>
<td>1482±60</td>
<td>-</td>
</tr>
<tr>
<td>Phenylferrocene</td>
<td>35±2</td>
<td>0.37</td>
</tr>
<tr>
<td>1,1´-diphenylferrocene</td>
<td>145±10</td>
<td>0.37</td>
</tr>
<tr>
<td>[3]ferrocenophane</td>
<td>1675±60</td>
<td>0.27</td>
</tr>
</tbody>
</table>

2.2.2 Reduction of Ferrocene

Although the oxidation of Fe has been studied very extensively, the reduction of Fe has also been investigated by few authors (Mugnier et al., 1980, Ito et al., 1983, Saji and Ito, 1985). The reduction is generally more difficult and unless reaction proceeds to metallic iron and cyclopentadiene the products are very unstable.

Trifan et al. studied the reduction of Fe with lithium metal in ethylamine at room temperature and reported that the reaction resulted in cleavage of the Fe molecule into metallic iron and cyclopentadiene molecules (Trifan and Nicholas, 1957). Mugnier et al. suggested the formation of Fe$^-$ by the reversible one electron reduction step in a cyclic
voltammogram of Fe in N,N-dimethylformamide (DMF) at −30°C corresponding to (Equation 2.4). (Mugnier et al., 1980)

\[ \text{Fc} + e^- \rightleftharpoons \text{Fc}^- \]  \hspace{1cm} (2.4)

However, at higher temperatures, a two electron reductive cleavage of the molecule occurred. They proposed the following ECE mechanism (Equations 2.5 - 2.7)

\[ \text{Fc} + e^- \rightleftharpoons \text{Fc}^- \]  \hspace{1cm} (2.5)

\[ \text{Fc}^- \rightarrow \text{Product} \]  \hspace{1cm} (2.6)

\[ \text{Product} + e^- \rightarrow 2\text{cp}^- + \text{Fe} \]  \hspace{1cm} (2.7)

Ikuta et al. reported the formation of \( \text{Fe}^- \) by the \( \gamma \)-ray irradiation of Fe in frozen matrices (Ikuta et al., 1981). Ito et al. also studied the electrochemical formation of stable ferrocene anion in 1,2-dimethoxyethane (Ito et al., 1983) using cyclic voltammetry. They showed that the formal rate constant, or charge transfer rate, of the \( \text{Fc}/\text{Fc}^- \) couple at −45°C, is \( ca. 10^{-3}\text{cm s}^{-1} \). This value is much lower than that of the analogous constant for the \( \text{Fc}^+//\text{Fc} \) couple which is \( >10^{-1}\text{cm s}^{-1} \).

Saji et al. studied the reduction of haloferrocenes (FcX; X = Cl, Br and I) at −45°C in 1,2-dimethoxyethane using cyclic voltammetry and the absorption spectrum of the solution after the exhaustive controlled-potential reduction. They found that the
reduction caused a cleavage of the carbon-halogen bond of FeX with quantitative formation of Fe (Saji and Ito, 1985).

2.3 Protonation of Ferrocene

The acid-base behaviour of ferrocene and several of its derivatives has been studied extensively (Curphey et al., 1960, Kotz and Pedrotty, 1969, Floris et al., 1972, Cerichelli et al., 1977, Bitterwolf and Ling, 1977, Bitterwolf, 1981, Bitterwolf and Ling, 1981). It is well established that ferrocene can be classified as a weak base. In strong acid, or high proton-donor medium, ferrocene is known to accept a proton, forming [FeH(C₅H₅)₂]⁺ (Curphey et al., 1960) as follows:

\[
\begin{align*}
\text{Fe} & \xrightarrow{\text{Acidic Media}} \left[ \text{Fe-H} \right]^{+} \\
\end{align*}
\]

The hydride ligand of [FeH(C₅H₅)₂]⁺ might be transferred to give [Fe(η⁵-C₅H₅)(η⁴-C₅H₆)]⁺, so the structure of ferrocene in acid solution exists as the following rapid equilibrium:

\[
\begin{align*}
\left[ \text{Fe-H} \right]^{+} & \rightleftharpoons \left[ \text{Fe-H} \right]^{+} \\
\end{align*}
\]
In the above equilibrium, the endocyclic proton is rapidly exchanged with all ten ring protons.

### 2.4 Bridged Ferrocenes

Bridged ferrocenes are ferrocene derivatives in which the two cyclopentadienyl group are linked by alkyl bridges.

The preparation of a bridged ferrocene was first reported by Rinehart et al. who synthesised 1,1′-(-ketotrimethylene)ferrocene. (Rinehart and Curby, 1957) In 1962 they studied the cyclisation of ferrocenylaliphatic acids. (Rinehart et al., 1962) Rosenblum et al. (Rosenblum et al., 1963) prepared the trimethylene bridged ferrocene and in the same year Rinehart et al. (Rinehart et al., 1963) synthesed the isomeric bis- and tris-(trimethylene)-ferrocenes. Barr et al. (Barr and Watts, 1968) studied the conformational properties of [m]ferrocenophanes (m=2,3,4,5) where the relative importance of cyclopentadienyl ring tilting, ring-ring torsion, and bridge mobility was estimated for systems of differing bridge length. Structure, reactivity and electronic properties of [4]ferrocenophanes were examined by Pudelski et al. (Pudelski and Callstrom, 1994)

These studies indicated that in a ferrocenophane having a three carbon bridge the cyclopentadienyl rings are tilted by approximately 9°. (Jones et al., 1965) The introduction of a second three-carbon bridge gives a conformation with approximately the same angle of tilt. The angle observed in a derivative which contains three adjacent bridges was 12.5°. (Spaulding et al., 1978)
The redox behaviour of bridged ferrocenes has been investigated by several authors (Gorton et al., 1971, Hillman et al., 1978, Ogata et al., 1981, Fujita et al., 1981, Chao et al., 1983, Toma et al., 1985, Hillman and Austin, 1987, Ushijima et al., 1987, Scholl and Sochaj, 1990, Scholl and Sochaj, 1991, Zanello et al., 1993a). For example, the polarographic half-wave potentials of some bridged ferrocenes was studied by Gorton et al. The results showed that the oxidation potentials of ferrocene derivatives were sensitive to structural, conformational, electronic, and possibly field effects (Gorton et al., 1971).

Hillman et al. (Hillman et al., 1978) studied the correlations between electrode potentials and the number of bridges in trimethylene bridged ferrocene derivatives. All the bridged ferrocene have lower redox potential than ferrocene. The positioning of the bridges with respect of each other had a strong influence on the redox potential of the ferrocenophane.

Similar to Hillman et al., (Hillman et al., 1978) Ogata et al. (Ogata et al., 1981) also observed a linear relation between the half-wave potential and the number of methylene groups for ferrocene and ferrocenophanes other than [3]$_2$ferrocenophane and [3]$_3$ferrocenophane.

The correlation of redox potentials with structure of bridged ferrocenes was also studied by Fujita et al. (Fujita et al., 1981). They measured the redox potentials for oxidation of ferrocenes with hydrocarbon bridges and of corresponding ketoferrocenes. For the compounds with hydrocarbon bridges only, correlations were observed between the potentials and the iron-to-ring distances. For the ketoferrocenes, the importance of alignment of the carbonyl with respect to the cyclopentadienyl rings was noted.

Scholl et al. compared the electrode potential of substituted ether– and thioether–bridged ferrocenes using cyclic voltammetry in acetonitrile solvent and Et$_4$NCIO$_4$ as a supporting electrolyte. (Scholl and Sochaj, 1991) The studied derivatives were as follows:

\[
\begin{align*}
\text{Fe} & \quad \text{R}_1 \quad \text{C} \\
& \quad \text{H} \quad \text{X} \\
& \quad \text{H} \quad \text{C} \\
& \quad \text{R}_2
\end{align*}
\]

where $R_1 = R_2 = \text{H}$

$R_1 = \text{H}, R_2 = \text{CH}_3$
R₁=R₂=CH₃
R₁=R₂=phenyl
X=O or S

It was concluded that the ether bridged ferrocene have a higher electrode potential than the thioether analogue (0.083V and 0.039V respectively), but methylene groups substituted in place of hydrogen atoms decrease this potential. On the other hand, phenyl groups increased the potential with diminishing electron density around the iron atom.

Ushijima et al. studied the electrode potential of 1,2,3-trithia[3]ferrocenophane and 1,2,3-triselena[3]ferrocenophanes. Their structures were as follows.

They found that the inhibition of the free rotation of the two cyclopentadienyl rings by bridging caused the interaction between sulphur atoms in the bridge and the iron atom through the d-electrons of the iron atom. This affected the Eₚ/₂ values, which were found to be in the order CH₂ < Se < S. (Ushijima et al., 1987)
2.5 Ferrocene Systems for pH-Insensitive Electrodes

The majority of ferrocene/ferricenium systems that have been used for modification of the surfaces of electrodes have been poly(vinylferrocene) (PVFc) systems. Most of these have been investigated in non-aqueous solutions and their use suffered from a range of problems. Generally the behaviour of such surface modified electrodes varied with the experimental details of the procedure through which the polymer is attached to the electrode surface, and the amount of material which is attached to the surface (Singh et al., 1990). The nature of the voltammetric response of electrodes coated with PVFc has been reported to vary with time, due to interactions between the polymer and the medium in which the electrode is immersed (Inzelt, 1989, Singh et al., 1990). The interpretation of the voltametric response of the PVFc is further complicated by such factors such as non-equivalent redox sites (present due to the heterogeneous nature of the polymer) and diffusion within the polymer film (Peerce and Bard, 1980). As well, although PVFc electrodes can be stored for long periods without apparent degradation, the poly(vinylferrocene) films lose their electrochemical response on prolonged use (Singh et al., 1990). The reason for this loss of activity is not well understood, but presumably, involves reactivity of ferricenium cations in the oxidised form of the polymer.

Many of the complications associated with the use of polymeric ferrocene derivatives could be avoided by use of monomeric ferrocene derivatives and a few studies have been made of electrodes modified with these. Wrighton and his co-workers
(Hickman et al., 1991) prepared a voltammetric pH sensor that involved electrodes derivatised with a quinone and a ferrocene. They found that the electrodes could be used intermittently over a period of several weeks, but did not investigate the long-term durability of the ferrocene- or quinone-based coatings on the electrodes. Earlier studies by Lenhard et al. (Lenhard and Murray, 1978) however, showed that for ferrocene/ferricenium groups immobilised on a platinum electrode, a slow decay in the voltammetric response of the electrode occurred when the electrode was cycled between ferrocene and ferricenium states or statically potentiostated at +0.70 V. Kinetic studies indicated that the half-life of electroactive groups on the surface was about 9 hours, with the ferricenium form being the less stable form of the electroactive groups. Presumably, surface-bound ferricenium groups undergo the same sorts of decomposition reactions as ferricenium ions in solution, (Matveev and Poroshenko, 1989a, Matveev and Poroshenko, 1989b, Prins et al., 1972) and one would expect that the ferricenium groups involved in Wrighton's pH-sensing electrode would exhibit similar instability.

2.6 References


3.1 Introduction

A Surface Modified Electrode (SME) consists of an inert substrate (metal or carbon), which has been chemically or physically coated with some material or functional groups, generally called modifiers, that alter the physicochemical properties of the substrate. For the SME to work, the bond between the substrate and the materials must be strong enough to resist any chemical, mechanical, and electrochemical interactions with the surroundings. Traditionally most electrode coatings were designed to contain electro active groups, which can be monitored and characterised by electrochemical methods, i.e. the coating can exchange electrons with the underlying inert substrate and this may be oxidised or reduced. The surface modified electrodes have been studied extensively during the last 20 years. This is because SMEs have found applications in a variety of fields including electrosynthesis of inorganic, organic and biological materials (Chao et al., 1983), biosensors (Janata et al., 1994, Buerk, 1993), (especially as a glucose detectors (Dicks et al., 1993)), analytical chemistry (Peerce and Bard, 1980a), corrosion protection of metals (Buttry and Ward, 1992, Finklea, 1996), semiconductor electrochemistry (Ulman, 1996), electronic and
Several reviews on SMEs are already accessible in the literature (Murray, 1980, Bard, 1983, Murray, 1984, Faulkner, 1984, Durst and Blubaugh, 1986, Murray et al., 1987, Wallace, 1988, Merz, 1990, Murray, 1992, Kutner et al., 1998, Leddy, 2000, Anderson et al., 2000). This chapter is primarily concerned with the preparation of SMEs, with some examples, and it will focus on the chemisorption of alkanethiols on gold surfaces.

3.2 Preparation of surface modified electrodes (SMEs)

The preparation of SMEs has been investigated by several authors (Murray, 1980, Murray, 1984, Durst and Blubaugh, 1986, Murray et al., 1987, Merz, 1990). Generally speaking, all electrodes could be identified as SMEs because they are chemically modified to some extent by the presence of various functional groups on their surface and by substances adsorbed from solutions.

The nature of the surface to be modified is known and the surface is pretreated in order to obtain a homogenous and reproducible modifying layer and attain the highest possible modifying effect.

The main drawback of present SMEs is their poor stability with time, especially on loading with electric current or in an unstable system (unstable with respect to the
modifier). For example, some SMEs last no longer than a few voltage cycles in cyclic voltammetry, and their stability depends on the media. Therefore the practical use of SMEs is less extensive than would be wanted, and new methods of modification are needed primarily to improve SME stability.

The preparation of SMEs is usually based on simple organic chemistry. There are three major methods for preparing the SME, namely physisorption, chemisorption and polymer coating. In physisorption the modifier is dispersed through the electrode by dip coating or drop evaporation techniques. It is the simplest and the oldest way of preparation of SMEs (Miller and Van de Mark, 1978, Daum and Murray, 1981, Murray, 1984). These SMEs are easy to prepare in a very short time and are cheap, but their lifetime is not long and their application is limited to systems that do not dissolve the modifier. Controlling the amount of the modifier is very difficult and in most cases not reproducible. For the chemisorption technique, the modifier is chemically bonded directly to the electrode. For example Figure 3.1 shows the schematic of surface modification of carbon electrodes which are prepared by attaching unsaturated compounds such as alkenes, vinylferrocene, or vinylpyridine to thermally deoxygenated carbon fibre. (Nowak et al., 1978)

![Figure 3.1 Schematic of attaching unsubstituted compounds to carbon substrate.](image)

Figure 3.1 Schematic of attaching unsubstituted compounds to carbon substrate.
Likewise, Oyama et al. bound amines to oxide free pyrolytic graphite using argon radio frequency (RF) plasma etching. (Oyama et al., 1978)

Various modifiers have also been attached to oxygenated carbon surfaces by using techniques described in the literature (Watkins et al., 1975, Firth et al., 1976, Elliott and Murray, 1976, Lennox and Murray, 1977, Lennox and Murray, 1978, Yacynych and Kuwana, 1978). As shown in the schematic diagram (Figure 3.2), such techniques involve creation of hydroxyl groups on the surface, usually by treatment of the carbon with radiofrequency oxygen plasma and subsequent lithium aluminium hydride reduction. The modifier molecules (eg. silanes) are then chemically attached to the carbon surface via the bonded O-atoms on the carbon surface (Yacynych and Kuwana, 1978).

![Figure 3.2 Schematic of the steps involved in surface modification of carbon electrode with substituted silanes group.](image-url)

If the R group of the modifier is a reactive group then it can be used to covalently bind other groups to the surface. (Fischer et al., 1979b, Fischer et al., 1979a, Fischer et al., 1982, Diaz et al., 1990, Elliker et al., 1994, Wrighton et al., 1978, Moses and Murray, 1976)
Surfaces containing carbonyl groups have been used for introducing modifiers such as carbonyl chloride or amides (Figure 3.3) (Rocklin and Murray, 1979, Firth et al., 1976).

\[
\begin{align*}
\text{C} & \text{O} \\
\text{OH} \\
\text{SOCl}_2 \quad \rightarrow \quad & \text{C} \quad \text{O} \\
\text{Cl} \\
\text{R-NH}_2 \quad \rightarrow \quad & \text{C} \quad \text{O} \\
\text{NHR}
\end{align*}
\]

Figure 3.3 Schematic of attaching carbonyl chloride or amides group on carbon electrode.

Polymer coating, a simple and robust method of SME preparation, can be done by several ways. Polymer coated SMEs have been prepared by immersing the electrode into a mediator solution and evaporating the solvent. Another method involving electrodeposition of the polymeric material has also been used (Peerce and Bard, 1980a). Electrochemically-initiated polymerisation of monomers on the electrode surfaces has also been suggested (Wallace, 1988, Elliott and Martin, 1982). Some of the most commonly investigated polymers include poly(p-nitrostyrene), poly(vinylferrocene) (Merz and Bard, 1978, Daum and Murray, 1979), viologen (De Long and Buttry, 1990), poly(vinylpyridine) and poly(acrylonitrile) (Oyama and Anson, 1979).

The methods of producing surface modified electrodes described above usually lead to films of irreproducible size and electrochemical characteristics. The technique
of producing self-assembled monolayers (SAMs) has lately attracted much more attention for surface modified electrode fabrication. SAMs can be highly ordered and oriented and can incorporate a wide range of groups both in the alkyl chain and at the chain termini as shown in Figure 3.4. Therefore, a variety of surfaces with specific interactions can be produced with fine chemical control.

Figure 3.4 A self-assembled monolayer of alkanethiols on a gold surface (Finklea, 1996).

While the majority of papers in recent years deal with thiols on gold, this system is by no means the only system which has been considered. For example, spontaneous adsorption of long chain \( n \)-alkanoic acids (\( C_nH_{2n+1}COOH \)) has been achieved on metal oxide surfaces. (Tao, 1993) The mechanism for this adsorption is considered to be acid-base type reaction with the formation of a surface salt between the carboxylate
anion and a surface metal cation. A schematic description of fatty acid monolayers on AgO and on Al₂O₃ is shown in Figure 3.5.

Figure 3.5: A schematic description of fatty acid monolayers on AgO and on Al₂O₃. (Ulman, 1991)

Monolayers of organosilicon derivatives have also been investigated. These require hydroxylated surfaces as substrates for their formation. The driving force for this self-assembly is the in situ formation of polysiloxane, which is connected to surface silanol groups (–SiOH) via Si–O–Si bonds. Substrates on which these monolayers have been successfully prepared include oxidised silicon wafers, aluminium oxide, quartz, glass, mica, zinc selenide, germanium oxide and gold (Ulman, 1991). A schematic description of this kind of SAM is shown in Figure 3.6.
SAMs have been formed from alkyltrichlorosilanes bearing various terminal functional groups, including halogen, cyanide, thiocyanide, methyl ether, acetate, thioacetate, α-haloacetate, vinyl, (trimethylsilyl)ethynyl, methyl ester, and p-chloromethylphenyl. (Ulman, 1991)

Surface modification by chemical reaction of a SAM provides a route for engineering of surface energy and interfacial properties such as wetting, adhesion and friction, and providing active surfaces for the attachment of molecules with different properties.

SAMs involving surface-active organosulphur compounds that form monolayers on gold have attracted particularly strong interest in recent years. Sulphur compounds have a strong affinity to transition metal surfaces. This is because they can form
multiple bonds with surface metal clusters. The SAMs of sulphur containing compounds on gold which have been reported include, among others, di-n-alkyl sulphides, di-n-alkyl disulphides, thiophenols, mercaptopyridines, mercaptoanilines, thiophenes, cysteines, xanthates, thiocarbaminates, thiocarbamates, thioureas, and mercaptoimidazoles. However the most studied, and probably most understood SAM is that of alkanethiolates on Au(III) surfaces. A schematic diagram of surface-active organosulphur compounds that form monolayers on gold is shown in Figure 3.7.

Several functionalised alkanethiolate SAMs have been investigated with a view to engineering surface properties and for further chemical reactions. The reported functionalities include CH₃, CF₃, CH=CH₂, C≡CH, Cl, Br, CN, OH, OCH₃, NH₂, N(CH₃)₂, SO₃H and Si(OCH₃)₃, COOH, COOCH₃, CONH₂, as well as more complex functionalities e.g., ferrocenyl, biotinyl 2,2' -bipyridyl, tetrahiafulvalenecarboxylate, tetraphenylporphyrin, and ferrocenylazobenzene. These monolayers are thus becoming the system of choice for studies of surface phenomena, electron transfer, molecular recognition, etc.
Figure 3.7 A schematic diagram of surface-active organosulphur compounds that form monolayers on gold.

Electroactive SAMs with attached ferrocenes have been investigated extensively (Finklea, 1996). The four most common linkages which have been studied, include (i) simple alkylferrocenes (Fc–R, R = mercapto-alkyl, etc.), (ii) ferrocene carboxylic ester (FcCOOR), (iii) amides (FcCONHR), and (iv) ketones (FcCOR). The adsorbing moiety is most commonly a thiol, but examples of SAMs based on disulphides, thiocarbamates, and isonitriles are known. Preparation of the SAM is usually accomplished by soaking the electrode for hours to days in a dilute solution of the ferrocene thiol; deposition
solvents range from ethanol to hexane. Besides gold and platinum, indium-tin oxide is a suitable substrate.

3.3 Chemisorption of alkanethiols onto gold surface

In 1983, Nuzzo and Allara reported that stable, oriented, polyfunctional organised monolayers on gold surfaces can be formed by solution adsorption of organic disulphides. They demonstrated that both polar and nonpolar organic functional groups can be placed at an ambient interface with known packing densities and selected orientations (Nuzzo and Allara, 1983). Since then it was found that sulphur (disulphide, alkanethiols…etc) compounds coordinate very strongly to gold, silver, copper and platinum surfaces, but most of the work has been done on gold because gold does not have a stable oxide, so its easier to handle in air (Ulman, 1991).

Many studies have characterised the properties of these monolayers like Nuzzo et al. (Nuzzo et al., 1987) and Sabatani et al. (Sabatani et al., 1987), demonstrated the use of self-assembled monolayers as electrochemical barriers (Li and Weaver, 1984) and using them as thin insulating films sandwiched between conducting films (Baker and Landau, 1995).

When an alkanethiol compound (R–S–H) or disulphide (R–S–S–R) is adsorbed on a gold surface it gives a Au(I) thiolate (R–S–) species as in equation (3.1) (Finklea, 1996).

\[
RSH + Au_n \rightarrow RS^-Au^+.Au_{n-1} + \frac{1}{2} H_2 \leftarrow Au_n + \frac{1}{2} RSSR
\]  

(3.1)

The mechanism involved in this reaction is not completely understood, but there is evidence by several methods, (XPS, FTIR, FTMS, electrochemistry and Raman spectroscopy) (Sellers et al., 1993), that the species chemisorbed on the gold surface is indeed a thiolate. Widrig et al. proved that the H of the thiol group is lost and the S atom is oxidised by 1 electron (Widrig et al., 1991).

Chidsey et al. described a structural model for the arrangement of alkanethiol chains on the surfaces, in which the chains exist in a crystalline - like environment with hexagonally packing in an \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice with a lateral spacing of 5Å, and tilted 20° to 30° from the normal to the gold surfaces (Chidsey et al., 1989, Chidsey et al., 1990, Chidsey and Loiacono, 1990), as shown earlier in Figure 3.3.

While the bonding of the thiolate group to the gold surface is very strong (homolytic bond strength is \(\sim 184 \text{ kJ mol}^{-1}\) (Dubois and Nuzzo, 1992), the rate of formation of monolayers is affected by several factors, including temperature, solvent, concentration of adsorbate, chain length of the alkyl group, and cleanliness of the substrate.
Bain et al. suggested that the properties of the interfaces between the SAMs and their environment are largely independent of chain length when \( n > 10 \); in particular, wetting is not directly influenced by the proximity of the underlying gold substrate. The adsorption of simple \( n \)-alkanethiols generates hydrophobic surfaces whose free energy (19 mJ m\(^{-2}\)) is the lowest of any hydrocarbon surface studied to date. In contrast, alcohol and carboxylic acid terminated thiols generate hydrophilic surfaces that are wet by water (Bain et al., 1989b).

Zhang et al. and Norrod et al. studied independently the mechanism of oxidation of self-assembled monolayers of alkanethiols on metal surfaces when irradiated with UV light in air. They concluded that chemical oxidation by ozone and not direct UV irradiation is responsible for the oxidation. (Zhang et al., 1998, Norrod and Rowlen, 1998)

Monolayers of thiols on Au appear to be stable indefinitely at room temperature, but their constituents desorb when heated to 80°C in hexadecane. Long-chain thiols form films that are thermally more stable than films formed from short-chain thiols. (Bain et al., 1989b)

Porter et al. studied the effect of the alkanethiol chain length on the properties of the monolayers in a series of \( n \)-alkanethiols \( \text{CH}_3(\text{CH}_2)_n\text{SH} \) where \( n = 1, 3, 5, 7, 9, 11, 15, 17, \) and 21) (Porter et al., 1987). The measured thickness of the monolayer shows two different regions of dependence on \( n \); the first between \( n = 1 \) and \( n = 9 \), and the second
between $n = 9$ and $n = 21$. They showed that there are clear differences in structure between long and short chain thiol monolayers. The value of $n$ for the sharpest change varies between 5 and 11 depending upon the specific measurement. The long-chain thiols form a densely packed, crystal-like assembly with full extended alkyl chains tilted from normal to the surface 20-30º. As the chain length decreases, the structure becomes increasingly disordered with lower packing density and coverage. The long-chain monolayers are free of measurable pinholes, provide substantial barriers to electron transfer, and are strongly resistant to ion penetration. With decreasing chain length the barrier properties become weaker (Porter et al., 1987). Also Bain et al. preferred long chain adsorbates to short chain ones, but until now it is not clear whether these monolayers are formed under kinetic or thermodynamic control. (Bain et al., 1989a)

### 3.4 Ferrocene Alkanethiol Derivatives Coated SME’s

It is understood now from the above discussion that ferrocenes derivatized with alkanethiol groups, can be used to modify a clean gold surface.

Numerous papers and several reviews (Finklea, 1996) report studies of the electrochemical characteristics of gold electrodes modified with self-assembly monolayer of ferrocene derivatives contain alkanethiols. Figure 3.8 illustrates the concept of a perfect electroactive monolayer. Close packing prevents motion of the redox centre (ferrocene) toward the electrode and motion of the ferrocene toward a pinhole or defect (Porter et al., 1987, Finklea, 1996).
Bain et al. studied the controlling of the chemical functionality at a gold substrate surface by varying the tail group attached to the alkanethiol chain. They concluded that any functional group that is comparable with the thiol can be introduced to the surface, but sterically bulky tail groups may interfere with the packing of the hydrocarbon chains. (Bain et al., 1989b, Bain et al., 1989a)

Several researchers measured the potential of ferrocene alkanethiol derivatives with different pendant groups in different supporting electrolyte and electrode material. Table 3.1 shows some of these potential values. (Finklea, 1996)
Table 3.1 Potential values for ferrocene alkanethiol derivatives in different supporting electrolyte and working electrodes

<table>
<thead>
<tr>
<th>Redox centre</th>
<th>Tether/diluent</th>
<th>Electrolyte</th>
<th>Electrode</th>
<th>$\Gamma_{\text{max}}$ (mol/cm$^2$)</th>
<th>$E^0$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$\Delta E_{\text{fwhm}}$ (mV)</th>
<th>Reference</th>
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<td>Fe</td>
<td>C$_4$SH</td>
<td>0.1M HClO$_4$</td>
<td>Au</td>
<td>$6 \times 10^{-10}$</td>
<td>0.21$^b$</td>
<td>30</td>
<td>Large</td>
<td>(Kondo et al., 1995)</td>
</tr>
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<td>1M HClO$_4$</td>
<td>Au</td>
<td>$4.6 \times 10^{-10}$</td>
<td>0.30$^c$</td>
<td>-</td>
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<td>(Rowe and Creager, 1991)</td>
</tr>
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<td>Bu$_4$NPF$_6$.CP</td>
<td>Au</td>
<td>-</td>
<td>-</td>
<td>$&gt;0$</td>
<td>-</td>
<td>(Richardson et al., 1995)</td>
</tr>
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<td>C$_n$SH, $n=6,11$</td>
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<td>Au</td>
<td>-</td>
<td>0.30$^c$</td>
<td>-</td>
<td>-</td>
<td>(Collard and Fox, 1991)</td>
</tr>
<tr>
<td>Fe</td>
<td>C$_{11}$SH</td>
<td>1M HClO$_4$</td>
<td>Au</td>
<td>$4 \times 10^{-10}$</td>
<td>0.30$^b$</td>
<td>20</td>
<td>110</td>
<td>(Shimazu et al., 1992)</td>
</tr>
<tr>
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<td>1M HClO$_4$</td>
<td>Au</td>
<td>-</td>
<td>0.25–</td>
<td>-</td>
<td>Spike</td>
<td>(Sato et al., 1993, Uosaki et al., 1991b, Sato et al., 1994)</td>
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<td>0.33$^c$</td>
<td>-</td>
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<td>-</td>
<td>Spike</td>
<td>(Shimazu et al., 1994a)</td>
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<tr>
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<td>Au</td>
<td>$5.5 \times 10^{-10}$</td>
<td>0.27$^b$</td>
<td>-</td>
<td>50</td>
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<td>Au</td>
<td>5.8 x 10⁻¹⁰</td>
<td>0.2²b</td>
<td>30</td>
<td>-</td>
<td>(Kondo et al., 1995)</td>
</tr>
<tr>
<td>-----</td>
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<td>1M HClO₄</td>
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<td>-</td>
<td>0.3⁵c</td>
<td>-</td>
<td>-</td>
<td>(Rowe and Creager, 1991)</td>
</tr>
<tr>
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<td>1M HClO₄</td>
<td>Au</td>
<td>4 x 10⁻¹⁰</td>
<td>0.2⁰-</td>
<td>-</td>
<td>-</td>
<td>(Creager and Rowe, 1991, Rowe and Creager, 1994)</td>
</tr>
<tr>
<td>Fe</td>
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<td>0.1M MeSO₃H</td>
<td>Au</td>
<td>-</td>
<td>0.3³c</td>
<td>-</td>
<td>-</td>
<td>(Creager and Rowe, 1993)</td>
</tr>
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<td>0.4¹c</td>
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<td>-</td>
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<td>1M HClO₄</td>
<td>Au</td>
<td>-</td>
<td>0.2⁰c</td>
<td>-</td>
<td>Large</td>
<td>(Chidsey et al., 1990)</td>
</tr>
<tr>
<td>Fe</td>
<td>C₁₂NC</td>
<td>Bu₄NPF₆, AN</td>
<td>Pt</td>
<td>4 x 10⁻¹⁰</td>
<td>0.3⁸c</td>
<td>-</td>
<td>-</td>
<td>(Hickman et al., 1992)</td>
</tr>
<tr>
<td>Fe</td>
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<td>Bu₄NPF₆, AN</td>
<td>Pt</td>
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<td>0.6⁸e</td>
<td>50</td>
<td>-</td>
<td>(Hickman et al., 1989)</td>
</tr>
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<td>FeCO</td>
<td>C₃SH</td>
<td>0.1M HClO₄</td>
<td>Au</td>
<td>5.2 x 10⁻¹⁰</td>
<td>0.5²b</td>
<td>10</td>
<td>-</td>
<td>(Kondo et al., 1995)</td>
</tr>
<tr>
<td>FeCO</td>
<td>C₁₀SH</td>
<td>1M NaClO₄</td>
<td>Au</td>
<td>4 x 10⁻¹⁰</td>
<td>0.5²a</td>
<td>-</td>
<td>-</td>
<td>(Hickman et al., 1991a)</td>
</tr>
<tr>
<td>FeCO</td>
<td>C₁₅SH</td>
<td>0.1M NaClO₄</td>
<td>Au</td>
<td>-</td>
<td>0.3-0.4⁶e</td>
<td>-</td>
<td>Large</td>
<td>(Abbott and Whitesides, 1994)</td>
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<td>(C₁₀S)₂</td>
<td>1M HClO₄</td>
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<td>0.5²a</td>
<td>23</td>
<td>90</td>
<td>(Clark et al., 1992)</td>
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<tr>
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<td>(C₁₀S)₂</td>
<td>Bu₄NPF₆, AN</td>
<td>Au</td>
<td>5 x 10⁻¹⁰</td>
<td>0.5²d</td>
<td>43</td>
<td>120</td>
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<td>FcCO</td>
<td>(C\textsubscript{10}S)\textsubscript{2}</td>
<td>Molten Salt</td>
<td>Au</td>
<td>5 x10\textsuperscript{-10}</td>
<td>0.52\textsuperscript{f}</td>
<td>35</td>
<td>110</td>
<td>(Clark et al., 1992)</td>
</tr>
<tr>
<td>-------</td>
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<tr>
<td>FcCO</td>
<td>(C\textsubscript{10}S)\textsubscript{2}</td>
<td>Bu\textsubscript{4}NPF\textsubscript{6}, AN</td>
<td>Au</td>
<td>4 x10\textsuperscript{-10}</td>
<td>0.6\textsuperscript{e}</td>
<td>-</td>
<td>-</td>
<td>(Hickman et al., 1992)</td>
</tr>
<tr>
<td>FcCOO</td>
<td>C\textsubscript{11}SH</td>
<td>1M HClO\textsubscript{4}</td>
<td>Au</td>
<td>5 x10\textsuperscript{-10}</td>
<td>0.58\textsuperscript{c}</td>
<td>20</td>
<td>100</td>
<td>(Popenoe et al., 1992)</td>
</tr>
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<td>C\textsubscript{n}SH n=4,8,12</td>
<td>Bu\textsubscript{4}NPF\textsubscript{6}, CP</td>
<td>Au</td>
<td>-</td>
<td>-</td>
<td>&gt;0</td>
<td>-</td>
<td>(Curtin et al., 1993)</td>
</tr>
<tr>
<td>FcCOO</td>
<td>C\textsubscript{n}SH n=8,11</td>
<td>1M HClO\textsubscript{4}</td>
<td>Au</td>
<td>4-5 x10\textsuperscript{-10}</td>
<td>0.52\textsuperscript{c}</td>
<td>&lt;10</td>
<td>150</td>
<td>(Walczak et al., 1991)</td>
</tr>
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<td>FcCOO</td>
<td>C\textsubscript{n}SH n=11,15</td>
<td>1M HClO\textsubscript{4}</td>
<td>Au</td>
<td>6 x10\textsuperscript{-10}</td>
<td>0.6\textsuperscript{c}</td>
<td>-</td>
<td>&gt;250</td>
<td>(Chidsey et al., 1990)</td>
</tr>
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<td>FcCOO</td>
<td>C\textsubscript{n}SH n=11,16</td>
<td>1M HClO\textsubscript{4}</td>
<td>Au</td>
<td>5 x10\textsuperscript{-10}</td>
<td>0.53\textsuperscript{c}</td>
<td>-</td>
<td>100</td>
<td>(Collard and Fox, 1991)</td>
</tr>
<tr>
<td>FcCOO</td>
<td>C\textsubscript{11}SH/HSC\textsubscript{6}CH\textsubscript{3}</td>
<td>1M HClO\textsubscript{4}</td>
<td>Au</td>
<td>-</td>
<td>0.51\textsuperscript{c}</td>
<td>0</td>
<td>90</td>
<td>(Chidsey et al., 1990)</td>
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<td>0.08\textsuperscript{d}</td>
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<td>(Chidsey, 1991)</td>
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<td>Au</td>
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<td>0.82\textsuperscript{b}</td>
<td>30</td>
<td>-</td>
<td>(Kondo et al., 1995)</td>
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</table>

\(a = \text{value vs SCE}; \ b = \text{value vs NaCl saturated SCE}; \ c = \text{value vs Ag/AgCl saturated KCl}; \ d = \text{value vs Ag/Ag}^+; \ e = \text{value vs Ag quasi reference electrode}; \ f = \text{value vs Al/Al(III)}.\)

\(Bu_4 = \text{tetrabutyl}; \ AN = \text{acetonitrile}; \ CP = 2:1 \text{chloroethane:propanenitrile}\)
3.4.1 Electron Transfer Kinetics

Long distance electron transfer plays a crucial role in numerous technological processes. Changing the number of carbon atoms in the polymethylene tether can be used to change the electron transfer distance in a controlled manner. The long distance electron transfer rate decays exponentially with the number of methylene groups between 10 and 18 (Dubois and Nuzzo, 1992).

Stable, electroactive self-assembled monolayers were prepared by Chidsey et al. (Chidsey et al., 1990) through the coadsorption of ferrocene-terminated alkanethiols and unsubstituted n-alkanethiols on evaporated gold films. They proposed a model (Figure 3.9) explaining the arrangement of this mixed monolayer in which the electroactive ferrocene groups, modelled as spheres with a diameter of 6.6Å (Seiler and Dunitz, 1979) are connected to the electrode through alkanethiol chains, modelled as cylinders with a distance of 4.6Å (Chidsey and Loiacono, 1990). These monolayers had low concentrations of alkanethiols linked to ferrocene by a polar ester group [FcCO2(CH2)nSH]. Electrochemical methods in 1.0 M HClO4 show that the ferrocene groups are homogeneous and noninteracting, ie, a thermodynamically ideal surface.

Higher surface concentrations or use of alkanethiols linked directly to the nonpolar ferrocene group (Fc(CH2)nSH) lead to broadening of the cyclic voltammetry peak, indicating interactions among ferrocene groups or inhomogeneous sites. Longer chain lengths and lower ferrocene surface concentration result in slower electron-transfer kinetics with the ferrocene group (Chidsey et al., 1990).
Figure 3.9 Model of a mixed monolayer containing ferrocene-terminated (Fc) and unsubstituted alkanethiols coadsorbed on the Au(III) surface (Chidsey et al., 1990).

The rate constant of the electron-transfer reaction between a gold electrode and an electroactive ferrocene group has been measured by Chidsey et al. (Chidsey, 1991) at a structurally well-defined metal-electrolyte interface at temperatures from 1 to 47°C and reaction free energies from −1.0 to +0.8 eV. The ferrocene group was positioned at a fixed distance from the gold surface by the self-assembly of a mixed thiol monolayer of FcCO₂(CH₂)₁₆SH and CH₃(CH₂)₁₅SH. Rate constants from 1 s⁻¹ to 2 x 10⁴ s⁻¹ in 1.0 M HClO₄ give a reasonable fit with a reorganisation energy of 0.85 eV and a prefactor
for electron tunnelling of $7 \times 10^4 \text{ s}^{-1} \text{ eV}^{-1}$. Such self-assembled monolayers can be used to systematically probe the dependence of electron-transfer rates on distance, medium, and spacer structure, and to provide an empirical basis for the construction of interfacial devices such as sensors and transducers that utilise macroscopically directional electron-transfer reactions.

Guo et al. studied the distance dependence of electron transfer rates in bilayers consisting of ferrocene (16-ferrocenyhexadecanoic acid) Langmuir-Blodgett monolayer and a self-assembled alkanethiol monolayer of variable chain length on gold, where the ferrocene groups resided at the monolayer. Interfacial electron transfer rates ($k^\circ$) for ferrocene electron transfer across the alkanethiol spacer monolayer were measured by cyclic voltammetry. The rates fell off exponentially with increasing alkanethiol chain length, giving a decay constant, $\beta$, of $\sim -1.0$ per methylene. The electron transfer rate with a dodecanethiol spacer layer ($k^\circ = 12 \text{ s}^{-1}$) was almost 2 orders of magnitude lower than those for the analogous ferrocenes chemically bound on Au through alkanethiols of similar length (Guo et al., 1995).

The electron-transfer rate of ferrocene alkanethiolate monolayers in ether and polyether solvents was measured by Ingram et al. The rate measurements of the ferrocene-ferricenium electron transfer, which presumably occurs by electron tunnelling through the alkane chain linker, were made using cyclic voltammetry at Au electrodes, as a function of potential sweep rate and temperature (Ingram and Murray, 1996).
The measurements were accomplished by analysing the cyclic voltammogram peak potential separation $\Delta E_p$, as a function of the potential scan rate. The analysis followed a Marcus-DOS model (Chidsey, 1991, Ingram and Murray, 1996) that takes into account the continuum of electronic states in the metal electrode by integration of the Marcus equation over those states as follows: (Ingram and Murray, 1996)

$$\int_{-\infty}^{\infty} \exp \left[ - \left( x - \frac{(\lambda \pm \eta)}{k_B T} \right)^2 \left( \frac{k_B T}{4\lambda} \right) \right] \frac{1}{1 - \exp(x)} \, dx$$

where $k_\eta$ is the rate constant at electrode overpotential $\eta$

$\lambda$ = reorganisation barrier energy

$\mu$ = electronic coupling

$\rho$ = density of metallic states

According to the authors Ingram et al. (Ingram and Murray, 1996) the electron-transfer rate constant is larger in dimethoxyethane (DME) than in polyethers, and slowest in the longer chain polyether, whereas the activation barriers for electron transfer are approximately the same. The behaviour of voltammetric peak broadening and apparent rate constant variation with potential sweep rate is indicative of a kinetic dispersion in the ferrocene electron-transfer kinetics; this dispersity increases in the polymeric solvents and at lower temperature. The ferrocene kinetics are faster in DME solvent than in aqueous $\text{HClO}_4$, which is rationalised on the basis of differences in
dielectric properties and a consequent lower outer sphere reorganisational barrier in DME.

Acevedo et al. suggested that in a redox-active self-assembling monolayer the standard rate constant for the electron transfer in an aqueous solution shows a very fast electron transfer with a lower limit of the order of 10^5 s\(^{-1}\). (Acevedo and Abruna, 1991)

### 3.4.2 Ion Pairing and redox potential

A coulombic interaction force between the two oppositely charged ions, ferricenium ion (positive ion) and the electrolyte anion (negative ion) leads to formation of an ion pair which is in equilibrium with the dissociated ions as in equation 3.3.

\[
\text{Fe}^{+} + \text{X}^{-} \rightleftharpoons \text{Fe}^{+} \text{X}^{-} \tag{3.3}
\]

*where X\(^{-}\) is the anion present in the solution*

The redox potential of hydroxymethylferrocene in water is 0.21V vs Ag/AgCl. This value is independent of both the nature and the concentration of electrolyte. This led to the "Ferrocene Assumption" which states that the potential of the ferricenium/ferrocene couple is unvarying with solvent and electrolyte. This is useful in
circumstances where the redox potentials of new compounds in unusual solvents can be preferably referenced against ferricenium/ferrocene rather than against an external electrode (Rowe and Creager, 1991).

On the other hand, the redox potential of an alkanethiol ferrocene immobilised on a gold surface shows an unexpected dependency on the nature of the electrolyte (Rowe and Creager, 1991, Creager and Rowe, 1991). Rivera et al. and Rowe et al. studied the thermodynamics of the redox and the ion-pairing in self-assembled monolayers, Self-assembled mixed monolayers composed of ferrocenylhexanethiol (\(\text{Fc(CH}_2\text{)}_6\text{SH, and n-alkanethiols} were prepared on polycrystalline bulk gold electrodes. They explained the unexpected dependence of the redox potentials on concentration of \(\text{ClO}_4^-\) and \(\text{PF}_6^-\) by the formation of ion pairs between \(\text{Fe}^+\) and these ions (Rivera and Cabrera, 1993, Rowe and Creager, 1991). Acevedo et al. also indicated that ion-pair formation between perchlorate anions (from supporting electrolyte) and the cationic head groups strongly influences the energetics of the system (Acevedo and Abruna, 1991).

Figure 3.10 shows the effect of increasing the concentration of \(\text{ClO}_4^-\) ion in \(\text{H}_2\text{SO}_4\) media, on the half-wave potential of a ferrocene alkanthiol electrode. The redox potential shows a dependency on the \(\text{ClO}_4^-\) ion concentration; which shifts negatively with log [\(\text{HClO}_4\)]. This behaviour is consistent with the consumption of a single \(\text{ClO}_4^-\) ion on ferrocene oxidation. Ion pairing of ferricenium could occur either from a free ferricenium ion or from a ferricenium that is already ion paired with bisulphate, which is
the predominant anion in 0.1 – 1.0 M H₂SO₄ media. In the presence of ClO₄⁻ ion, the predominant ion pairing is the ferricenium perchlorate.

Three more anions, hexafluorophosphate (PF₆⁻), trifluoroacetate (CF₃CO₂⁻) and methanesulphonate (CH₃SO₃⁻), were tested in the presence of sulphuric acid. Only PF₆⁻ ion underwent ion pairing. Rowe et al. attribute this result to the similarities of the ionic size and solvation free energy of PF₆⁻ with those of perchlorate ion.

Figure 3.10 Effect of perchlorate ion on the half-wave potential of ferrocene adsorbed from 0.1 mM FcC₆SH and 0.9 mM n-hexanethiol solution in ethanol (Creager and Rowe, 1991).
Effective formation constants for forming ion pairs between ferricenium and several anions were calculated and compared; the values scale roughly with the energies of solvation of the anions. Rowe and Creager suggested a model for ion pairing between ferricenium and perchlorate Figure 3.11 shows this model.

![Figure 3.11 Model for ion pairing of surface-bound ferricenium with perchlorate (Rowe and Creager, 1991).](image)

On the other hand, the relation between anion concentration and the peak potential was also studied by Shimazu et al. in a pure HClO$_4$ solution (Shimazu et al., 1994b). They showed that the peak potential shifts in a positive direction, as the concentration of HClO$_4$ becomes lower. They used an electrochemical quartz crystal microbalance (EQCM) to examine the mass transport accompanying the redox process of ferrocenylundecanethiol monolayers for both compact and loosely packed layers with different surface coverages prepared by self-assembly methods. The ferricenium cations (formed on the oxidation of the ferrocene groups) form ion pairs with the anions in the solution. The anion association was not accompanied by water incorporation into the
layers independent of the surface coverage, unless the layers were pretreated with water before the measurements were made. Immersion of the thiol-modified electrode in water caused a drastic increase in interfacial mass transport upon oxidation, particularly at a loosely packed layer. This increase is the result of the incorporation of water molecules into the space between the alkyl chains of the oriented ferrocenylundecanethiol. Uosaki et al. also showed that the position of the redox potential is varied with anion nature (Uosaki et al., 1991a). The peak potential for Fe in the presence of different anions follows the order \( \text{ClO}_4^- < \text{NO}_3^- < \text{SO}_4^{2-} \). Uosaki et al. also explained these results by the formation of ion pairs.

Shimazu et al. also confirmed the ion-pairing by using the electrochemical quartz crystal microbalance (EQCM). The EQCM was used to follow the mass change during the oxidation/reduction of ferrocenylundecanethiol monolayers. It was concluded that anions are incorporated into the self-assembled layer upon oxidation of the ferrocene group (Shimazu et al., 1992).

The redox process of ferrocene can be expressed by

\[
(Fc)_M + X^- \rightarrow (Fc^+X^-)_M + e^- \tag{3.4}
\]

where \((Fc)_M\) and \((Fc^+X^-)_M\) are Fe and Fe\(^+\)X\(^-\) respectively immobilised on the surface.

The redox potential can be written (Inzelt and Szabo, 1986),
\[ E = E^\circ - \frac{RT}{F} \ln K + \frac{RT}{F} \ln \left( \frac{[Fc^+ X^-]}{[Fc]^M} \right) - \frac{RT}{F} \ln [X^-] \quad (3.5) \]

where \( K \) is the formation constant of the ion pairs \((Fc^+X^-)_M\).

Since \([X^-]\) and \(Fc\) are constant, equation 3.5 can be written as

\[ E = E^\circ - \frac{RT}{F} \ln K + \frac{RT}{F} \ln \left( [Fc^+ X^-] \right)_M + C \quad (3.6) \]

where \( C \) is a constant.

If \([Fc^+X^-]_M\) is constant then equation 3.6 can be written as

\[ E = E^\circ - \frac{RT}{F} \ln K + C' \quad (3.7) \]

where \( C' \) is a constant.

The effect of the anion is governed by \( K \) only. The larger the value of \( K \) is, the more negative the redox potential becomes. The tendency of the peak shift suggests that \( K \) decreases in the order of \( \text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} \).

The detection of the mass transport accompanying the redox reaction of a ferrocenylundecanethiol monolayer was examined by Shimazu et al. and Ye et al. using
a novel combined FTIRRAS/EQCM system constructed to observe structural change and a quantitative measurement of mass transport simultaneously. FTIR spectra of ferrocenylundecanethiol SAMs suggest strongly that the alkyl chain of the monolayer becomes more perpendicular upon oxidation, when it was oriented initially more parallel to the surface Figure 3.12.

![Figure 3.12 SNIFTIRS spectra of FcC\textsubscript{11}S-monolayer (Shimazu et al., 1994c).](image)

The magnitude of the orientation change depends linearly on the degree of oxidation and following anion association. Such a structural change can explain the excess mass change indicated from the frequency response (Shimazu et al., 1994c) and (Ye et al., 1997). Popenoe et al. did not observe any changes in orientation of the polymethylene chains as a function of applied voltage (Popenoe et al., 1992).

### 3.4.3 Stability of the monolayer in different electrolytes

As stated in Chapter 2, ferricenium cation decomposes through exchange of a cyclopentadienyl ligand with another nucleophile like hydroxide (Prins et al., 1972,
Holecek et al., 1979, McDowell et al., 1984), so it should not be surprising that ferrocenes immobilised at surfaces follow similar modes of decomposition.

The stability of the ferricenium ion depends on the nature of the ferrocene derivative, the nature of the electrolyte and the way of attachment of ferrocene to the electrode. Popenoe et al. (Popenoe et al., 1992) studied the characterisation of ferrocene-terminated alkanethiolate monolayers on gold by cyclic voltammetry and in situ IR reflection-absorption spectroscopy. The results of these studies indicated that the ferrocenyl monolayers are relatively unstable at pH > 2, except when perchlorate is the dominant anion present. In 1.0 M HClO₄, loss of ferrocene coverage in an immobilised FcCOOC₁₁SH is minimal if the redox centre is kept predominantly in the reduced state. Significant loss >50% occurs over several hours if the redox centre is held in the oxidised state. Walczak et al. reported a cleavage at the ester bond. (Walczak et al., 1991) Rapid loss of coverage, >90% in a few scans, is observed if the monolayer film is cycled in alkaline or neutral electrolyte containing chloride, bromide, nitrate or sulphate anions. (Walczak et al., 1991, Popenoe et al., 1992) Popenoe et al. also show that (FcCOO(CH₂)₁₀SH) was unstable in sulphate media, even though it was attached to the gold surface by the thiol group, but it was more stable in perchlorate media. (Popenoe et al., 1992)

3.4.4 Properties of cyclic voltammograms immobilised monolayer

Cyclic voltammetry (Nicholson, 1965, Nicholson, 1966, Mabbott, 1983, Gossler, 1993) has been used very widely to determine the behaviour and characteristics of

The total quantity of attached electroactive sites or the surface coverages $\Gamma_a$ (anodic) and $\Gamma_c$ cathodic can be determined by integrating the area under the faradaic anodic current or the faradaic cathodic current peaks of the cyclovoltammogram (CV) after subtracting an extrapolated baseline of charging current to get the charge as shown in Figure 3.13.

Figure 3.13: Cyclic voltammogram for a monolayer of an immobilised redox system (Finklea, 1996).
\[ \Gamma = \frac{Q}{nFA} \]  

where \( Q = \text{charge (µC/cm}^2) \)

\( n = \text{number of equivalents per mole, the number of equivalents for our purposes} \)

will be equal to the number of electrons transferred in the reaction.

\( F = \text{Faraday’s constant}= 9.648 \times 10^4 \text{ C mol}^{-1} = 9.648 \times 10^4 \text{ J mol}^{-1} \text{ V}^{-1} \)

\( A = \text{Area of the electrode (cm}^2) \)

Chidsey et al. calculated the theoretical surface coverage of a ferrocene monolayer, as \( 2.7 \times 10^{14} \text{ molecule cm}^{-2} \) (Chidsey et al., 1990). This maximum coverage was obtained by assuming hexagonal close packing and by treating ferrocene as a sphere of diameter \( 6.6 \text{ Å} \) (Figures 3.14 and 3.15). (Seiler and Dunitz, 1979)
The faradic current $i$ for an immobilised redox species can be described as follows (Finklea, 1996)

$$i = \frac{4i_p e^\theta}{(1 + e^\theta)^2} \quad (3.9)$$

where

$$i_p = \frac{n^2 F^2 \nu \Gamma}{4RT} \quad (3.10)$$

$$\theta = \frac{nF}{RT} \left( E - E^{o'} \right) \quad (3.11)$$

where

- $i_p =$ peak current.
- $\nu =$ scan rate.
- $R =$ gas constant.
T = temperature in kelvin.

Γ = surface coverage (mol cm\(^{-2}\))

\(E''\) = formal potential of a redox couple = \(\frac{E_{pa} - E_{pc}}{2}\)

\(E_{pa}\) and \(E_{pc}\) = anodic and cathodic peak potentials respectively

**An ideal immobilised redox system has the following properties:** (Finklea, 1996)

1- \(\Gamma_a = \Gamma_c\)

2- Equal peak potentials \(\Delta E = (E_{pa} - E_{pc}) = 0\)

3- The peak is symmetrical with a peak-half width \(\Delta E_{fwhm} = 90.6/n\) mV at 25°C.

4- \(i_p\) is linearly proportional to scan rate \(v\) or the slope of \(\log i_p\) versus \(\log v\) = 1.

5- \(\Gamma_T\) is independent of scan rate \(v\).

6- Identical waveshapes for anodic and cathodic current-potential curves.

The current potential curve observed for a monolayer often differs from the ideal behaviour and indeed ideal behaviour is rarely obtained. (Rusling and Suib, 1994)

Typically, \(\Delta E > 0\), with curve shapes broader or more narrow than the ideal value can be observed, with \(\Delta E_{fwhm}\) often larger than 100mV (100–250mV) or smaller than 90mV.

According to Murray (Murray, 1984) this broadening behaviour in the cyclic voltammogram can be explained as (1) in an ensemble of attached species, slight variation in the surface structure, solvation which can lead to the existence of multiple formal potentials. (2) variation of surface activity coefficients with \(\Gamma_a, \Gamma_c\).
3.4.5 Monolayer order and shape of cyclic voltammograms.

The peak shape of the cyclic voltammogram of an electroactive alkanethiolate self-assembled monolayer depends on the immersion time of the electrode in the thiol solution. Also the peak shape and potentials of anodic and cathodic peaks are influenced by interactions between electroactive species in the layer. (Finklea, 1996)

Uosaki et al. examined electrochemical characteristics of a gold electrode modified with self-assembled monolayers of ferrocenylalkanethiols. The studied symmetrical reversible redox CV’s in HClO$_4$ solution, and effects of modification conditions on CV’s of the modified electrodes are summarised in Figure 3.16. It was shown that although the adsorption of the thiols was complete within 1 hour, the ordering of the adsorbed monolayer required a much longer time (Uosaki et al., 1991a) approximately 24 hours (Hickman et al., 1991b).
Figure 3.16 Cyclic voltammograms of gold electrodes modified by immersion in 50 μM FcC\textsubscript{11}SH hexane solution at 0°C for various time durations (a) 10s, (b) 30s, (c) 2min, (d) 5min, (e) 10min, (f) 45min, (g) 2h, (h) 4h, and (i) 17h. Electrolyte was 1.0 M HClO\textsubscript{4}. Sweep rate was 100 mVs\textsuperscript{−1} (Uosaki et al., 1991a).

CV’s for electroactive SAMs can contain spike peaks. For example, when a self-assembled monolayer formed from concentrated thiol solutions at temperatures higher than 25°C and immersion time higher than two hours, a very sharp current spike seems to reflect a different structure of the self-assembled monolayer (Figure 3.17). The shape of these spike peaks also depends on the cleanliness of the substrate. (Uosaki et al., 1991a, Willman et al., 1980)
Mixed monolayer films were studied by Creager and Row. (Creager and Rowe, 1991, Rowe and Creager, 1991) They examined the redox properties of ferrocenylalkanethiols coadsorbed with linear C₄–C₁₀ n-alkanethiols on polycrystalline bulk gold electrodes. Figure 3.18 shows the cyclic voltammograms of these electrodes in 1.0 M HClO₄. It was shown that as the alkanethiol chain length increases the amount of immobilised ferrocene decreases and the redox potential for ferrocene oxidation becomes more positive. The redox potential ranges from +0.20 V vs. Ag/AgCl for the shorter homologues to +0.39 V for coadsorption with n-decanethiol.
Figure 3.18 Cyclic voltammograms in 1.0 M HClO$_4$ of electrodes coated FeC$_6$SH and different $n$-alkanethiols. (Rowe and Creager, 1991)

The positive shift in potential was explained by the progressively more alkane-like environment created by the coadsorbed alkanethiols, which destabilises ferricenium relative to ferrocene. (Rowe and Creager, 1991)
3.4.6 Effect of functional groups

The electrostatic effects of functional groups are critically important during self-assembly. The affinity of ferrocenyl-alkanethiols with different functional groups for the surface of the electrode, relative to that of the corresponding alkanethiols, is a function of the polarity of the functional group linking ferrocene to the alkanethiol chain. In general, nonpolar linking groups like methylene show a stronger affinity for the surface than do polar groups like carboxamides and charged groups, for example quaternary ammonium salts. Also the redox potentials of these derivatives scale approximately with the electron donating/withdrawing effects of the functional groups on the cyclopentadiene rings. However, redox potentials for the surface-confined molecules are consistently more positive than for the identical molecules in bulk solutions (Creager and Rowe, 1994).

The effects of acyl and alkyl groups attached to the ferrocene ring on the adsorption behaviour of functionalised ferrocenylalkanethiols and disulphide onto electrodes was discussed by Kondo et al. When acyl groups were introduced into the ferrocene ring, the redox potentials of the modified electrodes in 0.1 M HClO₄ shifted in the positive direction by approximately 300 mV per acyl group. This shift is due to the electron-withdrawing effect of the carbonyl group. Introduction of a butyl group into the ring shifted the redox potential about 15 mV in the positive direction, possibly because of steric hindrance of counterion movement (Kondo et al., 1995).


3.4.7 Bifunctional monolayer

A mixed monolayer consisting of thiolated quinone and a thiolated ferrocene was used as functionalised surface for probing the pH in the absence of a reference electrode. (Hickman et al., 1991a, Lahav et al., 1998)

Hickman et al. examined the molecular self-assembly of a ferrocenyl thiol and a quinone thiol onto gold microelectrodes, to form a voltammetric microsensor with reference and sensor functions on the same electrode. The detection was based on measurement of the difference of current peaks for oxidation and reduction of the reference (ferrocene) and indicator (quinone) in aqueous electrolyte in a two-terminal system. The quinone has a half-wave potential, $E_{1/2}$, is pH-sensitive and can be used as a pH indicator; the ferrocene centre has an $E_{1/2}$ that is a pH-insensitive reference. The key advantages are that such sensors require no separate reference electrode and function as long as current peaks can be located for reference and indicator molecules. The range of the pH covered by this microsensor was between pH 2–10. (Hickman et al., 1991a)

Lahav et al. (Lahav et al., 1998) improved the idea by using single bifunctional redox active monolayer consisting of a covalently linked quinone and ferrocene assembly associated with a gold electrode. The bifunctional quinone-ferrocene monolayer was prepared by incubating a cleaned gold electrode an aqueous solution of disulphide functionalised quinone (0.02 M of 2-chloro-3-(DL-cystine)-1,4-naphthoquinone) for 2h, followed by coupling with an amine functionalised ferrocene
(10 mM of 2-aminoethyl ferrocenylmethyl ether) in 0.05 M 4-(2-hydroxymethyl)-1-piperazineethane sulphonic acid (HEPES) buffer, pH 7.2 in the presence of 10 mM of 1-(3-dimethyl- aminopropyl)-3-ethylcarbodiimide (EDC) for 3h as shown in Figure 3.19.

Figure 3.19 Assembly of the bifunctional quinone-ferrocene monolayer Au-electrode (Lahav et al., 1998).

3.5 References


Chapter 4 Experimental - 81 -

Experimental

4.1 Introduction

This chapter describes the experimental techniques for preparation and chemical characterisation of the various ferrocenes, together with investigation of their electrochemistry in the form of surface modified electrode on gold substrate.

4.2 Synthesis and chemical characterisation of ferrocenes

The ferrocenes investigated are summarised in Table 4.1.
Table 4.1 The structure of ferrocene and its derivatives used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocene</td>
<td>Fc</td>
<td><img src="image" alt="Fc" /></td>
</tr>
<tr>
<td>Poly(vinylferrocene)</td>
<td>PVFc</td>
<td><img src="image" alt="PVFc" /></td>
</tr>
<tr>
<td>11-Mercaptoundecylferrocene or 11-ferrocenylundecanethiol</td>
<td>Fc1</td>
<td><img src="image" alt="Fc1" /></td>
</tr>
<tr>
<td>(1,1')-Bis(11-mercaptoundecyl)ferrocene</td>
<td>Fc2</td>
<td><img src="image" alt="Fc2" /></td>
</tr>
<tr>
<td>11-mercaptoundecanoylferrocene</td>
<td>Fc3</td>
<td><img src="image" alt="Fc3" /></td>
</tr>
<tr>
<td>Name</td>
<td>Code</td>
<td>Structure</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>------</td>
<td>--------------------</td>
</tr>
<tr>
<td>1,1'-Bis(11-mercaptoundecanoyl)ferrocene</td>
<td>Fc4</td>
<td><img src="image" alt="Fc4 Structure" /></td>
</tr>
<tr>
<td><a href="1,1'">3</a>ferrocenophane</td>
<td>Fc5</td>
<td><img src="image" alt="Fc5 Structure" /></td>
</tr>
<tr>
<td><a href="1,1'">3,2</a>(3,3')ferrocenophane</td>
<td>Fc6</td>
<td><img src="image" alt="Fc6 Structure" /></td>
</tr>
<tr>
<td><a href="1,1'">3,3</a>(2,2')(4,4')ferrocenophane</td>
<td>Fc7</td>
<td><img src="image" alt="Fc7 Structure" /></td>
</tr>
<tr>
<td><a href="1,1'">5</a>ferrocenophane</td>
<td>Fc8</td>
<td><img src="image" alt="Fc8 Structure" /></td>
</tr>
<tr>
<td>Name</td>
<td>Code</td>
<td>Structure</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
<td>------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>2-(11-Mercaptoundecyl)<a href="1,1'">3</a>ferrocenophane</td>
<td>Fc9</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>4-(11-Mercaptoundecyl)<a href="1,1'">32</a>(3,3')ferrocenophane</td>
<td>Fc10</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>3-(11-Mercaptoundecyl)<a href="1,1'">33</a>(2,2')(4,4')ferrocenophane</td>
<td>Fc11</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>3-(11-Mercaptoundecyl)<a href="1,1'">5</a>ferrocenophane</td>
<td>Fc12</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
The ferrocene derivatives were synthesised from ferrocene as the starting material using procedures described in Appendix (I). All the reactions were carried out under a nitrogen atmosphere. All products were purified by chromatography on silica gel and characterised by NMR spectroscopy (300 MHz $^1$H; 75 MHz $^{13}$C).

Chemicals and solvents were of commercial origin and were used as received. All solutions used were prepared from analytical reagent grade chemicals and high purity water obtained from a Millipore Milli-Q system. The poly(vinylferrocene) was obtained from Polyscience. Ferrocene and ceric sulphate, Ce(SO$_4$)$_2$ were obtained from Aldrich. Potassium sulphate, K$_2$SO$_4$, sodium perchlorate, NaClO$_4$, potassium chloride, KCl, n-hexane, tetrahydrofurane and acetonitrile were supplied by BDH Chemicals. Sulphuric acid, H$_2$SO$_4$, perchloric acid, HClO$_4$, and sodium hydroxide, NaOH, were supplied by Ajax Chemicals. Hydrochloric acid, HCl, and potassium dihydrogen phosphate, KH$_2$PO$_4$ were supplied by Sigma Chemicals.

### 4.3 Ferrocene surface modified gold electrode preparation

#### 4.3.1 Pre-cleaning

A schematic diagram of the gold electrode used in this work is given in Figure 4.1. It consists of a gold rod connected to a copper wire, which was encased in epoxy resin. The exposed area of the electrode was 17mm$^2$. The gold rod was polycrystalline gold (99.99% fine gold; Australian Gold Refineries, Perth.).
Prior to the surface modification with the ferrocenes, the electrode was polished with silicon carbide waterproof papers starting with 800 grade and finishing with 1200 grade. The cleaned electrode was then dipped in dilute aqua regia (1 HCl: 3 HNO₃: 4 H₂O) for 1 minute. The cleaned electrode was then potentiostated for 5 minutes at –0.9 V vs SCE in 1.0 M H₂SO₄ where hydrogen gas was vigorously evolved at the electrode surface. During these experiments the electrode was rotated at 1000 rpm to let the bubbles of the gas escape from the surface of the electrode. Such treatment has the effect of removing any chemisorbed impurities on the surface. Then the electrode was rinsed with high purity water obtained from Millipore Milli-Q system and dried with nitrogen.
4.3.2 Preparation of surface modified electrodes

The cleaned electrode was coated with the required ferrocene material either by drop evaporation (Miller and Van de Mark, 1978, Daum and Murray, 1981, Murray, 1984) or by dip coating method (Hickman et al., 1991, Uosaki et al., 1991, Shimazu et al., 1994a, Shimazu et al., 1994b) as described earlier in Chapter 3. For the drop evaporation method, one drop (ca. 0.05 mL) of 1.0 mM solution of the derivative in hexane was placed on the gold surface and allowed to dry for ten minutes in air leaving a film on the electrode surface. In the case of PVFc, the solvent used was tetrahydrofuran (THF) with solution concentration of 0.5 mg mL\(^{-1}\) PVFc.

In the dip coating method the gold electrode was dipped in a 1.0 mM deoxygenated solution of the alkanethiol ferrocene derivative of interest in hexane for 12 hours. It was then rinsed with n-hexane, followed by distilled water, and finally with n-hexane.

4.4 Electrochemical characterisation of the modified electrode

Electrochemical measurements were carried out with E G & G Potentiostat/Galvanostat Model 173 with Model 276 interface, Universal Programmer Model 175. A platinum wire (0.5mm diameter) was used as an auxiliary or counter electrode. The reference electrode to which all potentials are referred throughout this study was Hg/HgCl (sat. KCl) SCE. The reference electrode was connected to the
Potentiostat / Galvanostat 173 by EG&G Model 178 Electrometer Probe. Voltammograms were recorded using a Rikadenki X-Y recorder, or an analogue to digital converter connected to an IBM compatible computer recording the current and voltage, or through the IEEE connector in the 276 interface and M270/250 EG&G software. The solution pH was measured with a Präzisions pH meter E510 Metrohm Herisau and a Model GK 2401C combined glass electrode.

The electrochemistry of the material was studied by using cyclic voltammetry (CV). The CV experiments were carried out by scanning the potential of the working electrode, measured against saturated calomel electrode as reference electrode, while measuring the resulting current as a function of the applied potential. A schematic diagram of the electrochemical cell used for this study is shown in Figure 4.2. For each experiment, the electrolyte solution was deoxygenated by bubbling high purity nitrogen gas, supplied by BOC Gases Australia Limited, through the system for 10 minutes, and the nitrogen atmosphere over the electrolyte was maintained by flowing the nitrogen gas over the surface of the solution. All experiments were done at room temperature. The pH of the electrolyte solution used for the electrochemical studies was adjusted by the addition of their acids or sodium hydroxide.
Figure 4.2 Schematic diagram of the electrochemical cell used in this study

4.5 Fourier Transform Infrared Spectroscopy (FTIR) Studies

FTIR spectra were acquired with a Nicolet Magna – IR 850 spectrometer series II equipped with a Deuteride Triglyceride Sulfide (DTGS) detector. A diffuse reflection cell (Spectra-Tech) was used to collect the spectra of the films (Figure 4.3).
4.6 X-ray Photoelectron Spectroscopy (XPS) Studies

Two rotating disk electrodes designed specifically for the XPS experiment were manufactured. The electrodes were 3mm in thickness including the base to fit inside the XPS instrument. A schematic diagram of the electrode used in the XPS studies is shown in Figure 4.4.
The XPS measurements were made with Kratos Ultra Axis X-ray photoelectron spectrophotometer at Murdoch University using monochromatised Al K\(\alpha\) radiation (1486.6eV) (150 watts). This instrument has an energy resolution of 350 meV and a spatial resolution of 2 \(\mu\)m in the imaging mode. The samples were under Ultra High Vacuum (UHV) conditions below \(10^{-9}\) millibar.

The XPS spectra were analysed with Kratos software that uses a simplex algorithm supplied by the instrument manufacturers for non-linear least squares fitting of the data. The binding energy of the peaks are characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface.

4.7 Electrochemical quartz crystal nanobalance (EQCN)

An electrochemical cell was manufactured specially for the EQCN system, Figure 4.5. The EQCN working electrode is an AT-cut polished quartz crystal with fundamental frequency of 10MHz. The quartz had a diameter of 15mm (0.538") and a thickness of 160 \(\mu\)m (0.0065"), and was coated with a 100 Å of titanium underlayer followed by 1000Å of gold overlayer forming a keyhole pattern with an active area 0.1963cm\(^2\) (gold disk diameter = 5mm (0.201"), flag width: 2.78mm). The crystals were supplied by ELCHEMA and/or International Crystal Manufacturers, ICM, USA. The quartz crystal was mounted between O-rings to the bottom of the cell so that one side of it faced the solution, which is at hard ground, while the opposite side faced air.
The experimental setup is shown in Figure 4.5. This consists of the EQCN cell, ELCHEMA nanobalance model 700, a 173/175 potentiostat, and an IBM PC with analogue/digital – digital/analogue converter. Because the potentiostat used in this study is a conventional and not a Wenking potentiostat, the working electrode is at virtual and not hard ground. The current was usually measured at the working electrode side, which requires that the current be measured by the voltage drop across a resistor in series with the counter electrode. A 1.0 k\(\Omega\) resistor was used for this purpose.

Figure 4.5 The EQCN electrochemical cell with the AT-cut quartz crystal used in this study
Figure 4.6 Schematic representation for the EQCN system used in this study.

4.8 References


Electrochemistry of Ferrocene in Aqueous Acidic Media

5.1 Introduction

Even though the electrochemistry of the ferrocene/ferricenium couple is well known in the literature (Page and Wilkinson, 1952, Rosenblum, 1965) particularly in relation to its use as a potentiometric reference couple (Gritzner and Kuta, 1984), its behaviour in concentrated sulphuric acid is not well understood. Since an important objective of this work is to establish whether ferrocene materials could be used for measuring change in $\text{H}^+$ activity in lead-acid battery electrolytes, the knowledge of how a simple ferrocene molecule behaves in this electrolyte is essential. This chapter is, therefore, aimed at investigating the electrochemistry of simple ferrocene (Fe), coated on a gold substrate by the drop evaporation method. The specific objective is to determine how the oxidation/reduction behaviour of the Fe responds to the change in the concentrations of $\text{H}_2\text{SO}_4$ in aqueous media. The effect of the different aqueous media on the electrode potential, and the stability of the ferrocene in $\text{H}_2\text{SO}_4$, is also included.
5.2 Results and Discussion

5.2.1 Cyclic voltammetry of Ferrocene

Typical cyclic voltammetry (CV) behaviour of Fe on a gold electrode in aqueous H₂SO₄ electrolyte can be seen from the results in Figure 5.1. For this, a gold electrode coated with Fe by the drop evaporation method (Chapter 4) was scanned between the potential limits –0.1 to 0.4 V in 1.0 M H₂SO₄ electrolyte. As can be seen the Fe shows well-defined anodic and cathodic peaks with the potential difference between these peaks (ΔEp) being 140 mV.

Figure 5.1  Cyclic voltammogram of ferrocene in 1.0 M H₂SO₄ at a gold electrode (sweep rate 100 mVs⁻¹).
The slope of the plot of log anodic peak current $I_{pa}$ versus log scan rate ($\nu$) for Fe is found to be 0.53 (Figure 5.2). It is known that the slope of the log–log plot of peak current versus scan rate should be 1.0 for electron transfer to a surface immobilised species, and 0.5 for a truly diffusion controlled system (Gomez and Kaifer, 1992, Gosser, 1993, Sa and Rangel, 1997). Thus, the observed result for the ferrocene (0.53 slope) suggests that the electron transfer corresponds to a diffusion mechanism rather than electron transfer to a surface adsorbed species. This is not unexpected because $\text{Fe}^+$ is soluble in the medium.

![Figure 5.2](image-url)  

Figure 5.2 Log (anodic peak current ($I_{pa}$)) against Log (scan rate ($\nu$)) for the cyclic voltammogram for ferrocene (Fe) in 1.0 M $\text{H}_2\text{SO}_4$ at a gold.
Effect of pH on anodic peak potential

The effect of pH on the anodic peak potential (Ep\textsubscript{a}) of Fe in SO\textsubscript{4}\textsuperscript{2−} media was investigated. As can be seen from Figure 5.3 the Ep\textsubscript{a} is found to be independent of pH in the range 2–10. This is consistent with what would normally be expected for a redox system which does not involve proton transfer during the electron transfer reaction. In fact, this is the basis of ferrocene/ferricenium being used as a reference electrode whose potential is independent of [H\textsuperscript{+}].

![Graph showing the relationship between pH and Ep\textsubscript{a}](image)

Figure 5.3 Anodic peak potential (Ep\textsubscript{a}) against pH for ferrocene in 0.1 M K\textsubscript{2}SO\textsubscript{4} solution.
Effect of acid concentration on anodic peak potential

As noted in the introduction (section 5.1) one of the objectives of this work is to determine whether materials like \( \text{Fc} \) could be used as potentiometric reference electrodes in concentrated \( \text{H}_2\text{SO}_4 \) media. Thus, the electrochemical behaviour of \( \text{Fc} \) in sulphuric acid solutions in the concentration range 1 – 5 M has been investigated. It is found that as the acid concentration is increased, the anodic (\( \text{E}_{\text{pa}} \)) and cathodic (\( \text{E}_{\text{pc}} \)) peak potentials both shift to less positive values. This is in contrast to what has been noted earlier *i.e.* that the peak potentials are independent of \( \text{H}_2\text{SO}_4 \) concentration in dilute solutions in the pH range 2–10. High concentration of the acid affect the \( \text{E}_{\text{pa}} \) and \( \text{E}_{\text{pc}} \) quite strongly, causing them to shift linearly to less positive values by *ca.* –53 mV per unit molar concentration of the acid. Typical data for the variation of \( \text{E}_{\text{pa}} \) with the acid concentration are shown in Figure 5.4. The linear regression equation for the curve in Figure 5.4 is,

\[
\text{E}_{\text{pa}} \, (\text{V}) = -0.053 \, [\text{H}_2\text{SO}_4] + 0.167, \quad R^2 = 0.9933.
\]
Figure 5.4  The anodic peak potential against concentration of sulphuric acid for ferrocene.

The Figure 5.5 shows the effect of repeated voltammetric cycling in the potential range of −0.1 to 0.4 V on the anodic peak current of the ferrocene. The $I_{pa}$ for each cycle was measured and the data used to calculate $(I_{pa})_n/(I_{pa})_1 \times 100$ where $n$ is the cycle number. The function $(I_{pa})_n/(I_{pa})_1 \times 100$ on the y-axis defines the percentage of the electroactive material left at the electrode surface at each cycle. The results plotted in Figure 5.5 show the residual ferrocene material on the electrode surface after each voltammetric cycle decreases rapidly. Only 2% of the material is left at the electrode surface at the end of 100$^{th}$ cycle.
5.3 Conclusion

The cyclic voltammetric behaviour of \textbf{Fc} on a gold electrode in concentrated \textbf{H}_2\textbf{SO}_4 solutions suggests that the \textbf{Fc} undergoes a fast reversible redox reaction. The electron transfer corresponds to a diffusion controlled mechanism. The anodic and cathodic peak potentials are independent of pH over the range 2–10 in \textbf{K}_2\textbf{SO}_4 solutions. However, in concentrated sulphuric acid solutions they shift to less positive potentials. They vary linearly (slope 0.53) with the concentration of sulphuric acid in the range 1–5 M. It is also found that on a repeated voltammetric cycling the \textbf{Fc} material is lost from the electrode surface. For example only 2\% of the ferrocene material remains at the electrode.

Figure 5.5 Percentage of the material remaining on the electrode surface for \textbf{Fc} against number of cycles in 1.0 M \textbf{H}_2\textbf{SO}_4.
surface at the end of the 100th cycle. This may be related to decomposition of the ferricenium ion or dissolution of the ferricenium ($\text{Fe}^+$) ionic species from the surface of the electrode (as explained in Chapter 2). Thus, simple Fe itself cannot be considered as a candidate for monitoring change in sulphuric acid concentrations in aqueous electrolytes. This is because its stability and or retainability is very poor in acidic media.

### 5.4 References


Electrochemistry of Poly(vinylferrocene) in Aqueous Acidic Media

6.1 Introduction

In Chapter 5 the point was made that the simple ferrocene molecule is either unstable in sulphuric acid media or is shed from the surface of the electrode because of the solubility of the ferricenium ion. Thus, a surface modified electrode capable of sensing H⁺ activity in concentrated sulphuric acid cannot be made using a simple ferrocene/ferricenium couple. With this in view poly(vinylferrocene) (PVFc) has been selected for further study. The PVFc/PVFc⁺ material is expected to be insoluble in the electrolyte. This chapter is, therefore, aimed at investigating the electrochemistry of PVFc in concentrated sulphuric acid media. The specific objective is to determine how the oxidation/reduction behaviour of the PVFc responds to change in the acid concentration solutions in aqueous media.
6.2 Results and Discussion

6.2.1 Cyclic voltammetry of poly(vinylferrocene)

Figure 6.1 shows typical cyclic voltammetric (CV) behaviour of PVFc attached to a gold electrode in 1.0 M H$_2$SO$_4$. The electrode was prepared by coating a thin film of PVFc, which was prepared by the drop evaporation method as explained in Chapter 4. A 0.5 mg mL$^{-1}$ solution of PVFc in THF was used for this purpose. Well-defined oxidation and reduction peaks of PVFc/PVFc$^+$ couple are seen. The $\Delta E$ value for the scan is 45 mV.

![Cyclic voltammogram of poly(vinylferrocene) in 1.0 M H$_2$SO$_4$ at a gold electrode (sweep rate 100 mVs$^{-1}$).]
Figure 6.2 shows the plot of log anodic peak current ($I_{pa}$) against log scan rate ($\nu$). The plot is linear with a slope of 0.77. This value of the slope indicates that the electron transfer to $\text{PVFc}$ occurs through a mechanism which is intermediate between diffusion in solution and electron transfer to a surface adsorbed species.

$$y = 0.7678x - 3.0251$$

$R^2 = 0.9991$

As discussed in Chapter 5, the log–log plot of peak current versus scan rate should have a slope of 1.0 for electron transfer to a surface immobilised species. Its value should be 0.5 for a truly diffusion controlled system. (Gomez and Kaifer, 1992; Gosser, 1993) The plots for redox reactions which involve...
species immobilised at the electrode surface with slow diffusion of a counter ions through the immobilised film can have slopes in between 0.5 – 1.0. Since the observed value of the slope for $\text{PVFc}$ lies in between 0.5 – 1.0, it is reasonable to conclude that the electron transfer mechanism in this case lies in between the two mechanisms.

**Effect of pH on anodic peak potential**

(a) Effect of $H^+$ at low concentration ($pH$)

In order to establish how different concentrations of sulphuric acid effect, the electrochemical behaviour of $\text{PVFc}$, firstly the effect of low concentration of $H^+$ on the anodic peak potential $E_{pa}$ was investigated. The results are shown in Figure 6.2. The results show that the $E_{pa}$ is independent of pH in the range 2 –10. This is consistent with what would normally be expected from a ferrocene (Chapter 5) because the electrode reaction should not involve protons (Equation 6.1).

$$\text{PVFc} \rightleftharpoons \text{PVFc}^+ + e^- \quad (6.1)$$
Figure 6.3  Anodic peak potential ($E_{pa}$) vs pH for PVFc in 0.1 M K$_2$SO$_4$ solution.

(b) Effect of $H_2SO_4$ in the concentration range (1–5 M)

The results in Figure 6.4 show that as the acid concentration is increased, the anodic and cathodic peak potentials shift to less positive values. This shift is linear with a slope of $ca. -33$ mV per unit molar concentration of the acid. The linear regression equation for the curve is

$$E_{pa} (V) = -0.0325 \ [H_2SO_4] + 0.4135, \ R^2 = 0.9899.$$
Figure 6.4 The anodic peak potential against concentration of sulphuric acid for PVFc.

This unexpected result is similar to that discussed earlier for Fc in Chapter 5 and deserves closer examination. One explanation could well be the contribution of the liquid junction potential (LJP) to the reference electrode (SCE) used in this work. Since the SCE is in contact with a fairly concentrated H₂SO₄ medium, the liquid junction potentials could make a significant contribution to the measured Eₚₐ values. To test this possibility the liquid junction potential was calculated using the method described by Senanayake and Muir. (Senanayake and Muir, 1988) These authors have shown that these values could be calculated in concentrated acid media (0.1 – 6 M) by using the Henderson equation (Equation 6.2), (Ives et al., 1961) provided the ionic mobilities are known.
\[ E_j = \frac{RT}{F} \left( \frac{U_1 - V_1}{U_1} \right) - \left( \frac{U_2 - V_2}{U_2 + V_2} \right) \ln \left( \frac{U_1 + V_1}{U_2 + V_2} \right) \]  

(6.2)*

* \[ U = \Sigma C_i u_i \text{ for cations and } V = \Sigma C_i u_i \text{ for anions} \]

where \( C \) is the concentration, \( u \) is ionic mobility of individual ions.

The \( E_h \text{–pH} \) diagram of aqueous/sulphur species media (Figure 6.5) shows that at the acid concentration of interest to this work, the predominant anion is \( \text{HSO}_4^- \). Thus to calculate the LPJ for our system the ionic mobility of \( \text{HSO}_4^- \) ion is needed. This is calculated from the ionic conductance data of Lange. (Lange, 1985) The data for other ions needed for the calculation \( i.e. \text{H}^+, \text{K}^+, \text{and } \text{Cl}^- \) were taken from Bard and Faulkner. (Bard and Faulkner, 1980) The calculated LJP values are shown in Table 6.1. This table also includes the data for HCl taken from Senanayake and Muir. (Senanayake and Muir, 1988)
Figure 6.5 Pourbaix diagram for aqueous/sulphur species media. (Pourbaix et al., 1963)
Table 6.1 Liquid junction potentials of Saturated Calomel Electrode in various media.

<table>
<thead>
<tr>
<th>Concentration of the acid</th>
<th>Experimental</th>
<th>Calculated †</th>
<th>Calculated ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl / sat. KCl</td>
<td>HCl / sat. KCl</td>
<td>H₂SO₄ / sat. KCl</td>
</tr>
<tr>
<td>1</td>
<td>16</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>19</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
<td>23</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>32</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>42</td>
<td>29</td>
<td>33</td>
</tr>
</tbody>
</table>

† (Senanayake and Muir, 1988) ‡ This study

The LJP values for the H₂SO₄ media are only slightly different from the Cl⁻ media, indicating that the ion type is not a dominant factor. The important point to note here is that the LJP values are quite small compared to the actual shift in the Epₐ values observed in this work. Thus, the LJP model cannot explain the observed dependence of the Epₐ values of PVFc on H₂SO₄ concentration.

Figure 6.6 shows the Epₐ values corrected for the LJP as a function of H₂SO₄ concentration. The slope of the graph suggests that either the oxidation of PVFc does include H⁺ ions in the electron transfer mechanism or some other factors are included. This needs further investigation. The following section addresses this issue.
Figure 6.6 The anodic peak potential against concentration of sulphuric acid for PVFc with LJP correction.

**Effect of anions (Cl\(^-\), SO\(_4^{2-}\), and ClO\(_4^-\)) on anodic peak potential**

In order to establish the mechanism by which a high concentration of H\(_2\)SO\(_4\) affects the Ep\(_a\) of PVFc, as discussed in section 6.4, the effect on Ep\(_a\) of other acids with anions other than SO\(_4^{2-}\) was investigated. The CV of PVFc was recorded in 1 – 5 M solutions of HCl, and HClO\(_4\).

The experimental Ep\(_a\) values were corrected for the LPJ as before by using Equation 6.2. The ionic mobility data for H\(^+\), K\(^+\), Cl\(^-\), and ClO\(_4^-\) required for the calculation were taken from Bard and Faulkner. (Bard and Faulkner, 1980)
calculated LJP values for the Cl\(^-\), SO\(_4\)^{2-}\), and ClO\(_4\)^{−}\) systems are compared in Table 6.2.

Table 6.2 Calculated liquid junction potentials for SCE in concentrated HCl, HClO\(_4\) and H\(_2\)SO\(_4\) media.

<table>
<thead>
<tr>
<th>Concentration of the acid M</th>
<th>H(_2)SO(_4) / sat. KCl, mV</th>
<th>HClO(_4) / sat. KCl mV</th>
<th>HCl / sat. KCl mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>27</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>33</td>
<td>30</td>
<td>29</td>
</tr>
</tbody>
</table>

As can be seen from Table 6.2 the LJP values are quite small and hence do not change the Ep\(_a\) values significantly. The corrected Ep\(_a\) values are plotted against acid concentration in Figure 6.7. The results clearly show that there is a linear relationship between the acid concentration and Ep\(_a\) for both of HCl and HClO\(_4\). Thus, all the investigated acids show the same effect. However, the slopes of the plot for the three acids are different (H\(_2\)SO\(_4\) = −33 mV, HClO\(_4\) = −44 mV, and HCl = −34 mV), suggesting that the anion types do play some role.
The Table 6.3 lists the Ep_a and Ep_c values for PVFe oxidation / reduction in 1.0 M concentration solution of each of HCl, HClO_4 and H_2SO_4 at of each of the acids. The results indicate that the anion type of the acids does have a significant influence on the Ep_a and Ep_c values of PVFe which occur at quite different positions on the scan. The oxidation of PVFe in ClO_4^- media occurs at the least positive potential as compared to the other two anions media. Furthermore the ΔEp for the ClO_4^- media is the highest. The results suggest that ClO_4^- stabilises the PVFe^+ more strongly than do either Cl^- or SO_4^{2-}. This is probably related to the salt formation between the anion and the ferricenium ion generated on oxidation. Such salt formation would change the activity of Fe^+ at the surface of the electrode. Similar observations were also made by Inzelt et al. and Uosaki et al. (Inzelt and Szabo, 1986, Inzelt and Horanyi, 1989, Inzelt, 1989,
Thus the observed dependence of $E_{p_a}$ on acid concentration ($> 1$ M) is probably related to $\text{Fe}^+$ – anion salt or ion pair formation.

Table 6.3 The peak potentials of poly(vinylferrocene) in different 1.0 M acid electrolyte (All values ±10 mV).

<table>
<thead>
<tr>
<th>Anion</th>
<th>$E_{p_a}$ / V</th>
<th>$E_{p_c}$ / V</th>
<th>$\Delta E_p$ / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>0.385</td>
<td>0.335</td>
<td>50</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>0.320</td>
<td>0.210</td>
<td>110</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.435</td>
<td>0.375</td>
<td>60</td>
</tr>
</tbody>
</table>

6.2.2 Stability of PVFc on Repeated Voltammetric Cycling

The electrochemical stability of PVFc physically adsorbed on gold electrodes was tested by subjecting a freshly prepared SME to repeated voltammetric cycling in the potential range -0.1 to 0.6V. The $I_{p_a}$ for each cycle was measured and the data used to calculate $(I_{p_a})_n/(I_{p_a})_1 \times 100$ where $n$ is the cycle number. The function $(I_{p_a})_n/(I_{p_a})_1 \times 100$ defines the percentage of the electroactive material left at the electrode surface at each cycle. These data are plotted in a Figure 6.8, which also includes similar data for simple ferrocene Fe.
The results show that the residual material left at the electrode surface during cycling decreases much more rapidly for Fe than for PVFc. For example at the 100th cycle mark 98% of Fe was lost from the electrode surface as compared to 69% PVFc.

A variation in the method of preparing SME was also investigated. This involved deposition of PVFc at the electrode surface by electrodeposition procedure described by Peerce and Bard. (Peerce and Bard, 1980) The SME electrodes prepared by this method were also subjected to repeated cycling as described earlier, and change in Ip_a noted. The results show that the residual material left at the electrode surface during cycling also decreases in a similar
manner to that observed for the SME electrodes prepared by the drop evaporation method.

Information on the stability of the PVFc SME’s as function of repeated voltammetric cycling on the SME’s was further obtained by using Fourier Transform Infrared Spectroscopy (FTIR) studies. A reflective gold electrode was designed specifically to fit a diffuse reflectance FTIR cell (Spectra-Tech). The infrared spectra of fresh films before cycling and after the 100th repeated voltammetric cycle were recorded for the wavelength region 4000 – 400 cm$^{-1}$. The relevant data are shown in Figures 6.9 and 6.10.

In general, the signal was rather weak as may be expected for a relatively thin film. The infrared spectra (Figures 6.9 and 6.10) showed bands consistent with the presence of PVFc. A sharp band occurred near 1100 cm$^{-1}$, characteristic of monosubstituted ferrocene groups (Pittman et al., 1970). The CH out-of-plane deformation of cyclopentadienyl rings was present at 810 cm$^{-1}$ and medium intensity bands near 3090 and 2920 cm$^{-1}$ were assigned to aromatic and aliphatic CH stretching (Pittman et al., 1970). It can be seen from these results that the intensity of these peaks after 100 repeated voltammetric cycling decreased and in some cases became too weak to detect, but no new peaks were observed. This suggests that the PVFc material is lost from the electrode surface during repeated cycling. The absence of new peaks would suggest that the loss of the material involves either only physical desorption or loss by chemical reactions which give rise to products soluble in the electrolyte. Unfortunately, the available data do not
give a clear cut answer to this.

Figure 6.9 FTIR spectrum (1400 – 700 cm\(^{-1}\) region) of PVFc on a gold electrode surface before and after 100 cycles in 1.0 M H\(_2\)SO\(_4\).

Figure 6.10 FTIR spectrum (3200 – 2700 cm\(^{-1}\) region) of PVFc on a gold electrode surface before and after 100 cycles in 1.0 M H\(_2\)SO\(_4\).
6.3 Conclusion

PVFc on gold electrodes in H₂SO₄ solutions gives well-defined oxidation and reduction peaks corresponding to the PVFc/PVFc⁺ couple. The electron transfer corresponds to a mechanism which is intermediate between diffusion in solution and electron transfer to a surface adsorbed species. The anodic and cathodic peak potentials are independent of solution pH in the range 2–10, while in concentrated acids solutions (1–5 M) they shift to progressively less positive potentials. It has been shown that the observed dependence of Epₐ and Epₖ values cannot be explained in terms of liquid junction potential (LJP) of the reference electrode in the concentrated acid solutions. The retainability of PVFc on the gold surface in concentrated sulphuric acid media is moderate. Approximately 69% of the material is lost from the electrode surface during the 100th repeated cycling of the material.

6.4 References


7.1 Introduction

In chapter 5, the electrochemistry of simple ferrocene was studied in acidic aqueous media. It was noted in that chapter that such a ferrocene molecule could not be retained at the electrode surface, hence a surface modified type potentiometric sensor cannot be fabricated from this material. To produce a surface modified electrode, it is essential that the electroactive material is immobilised effectively on the surface of the electrode. This could be achieved through thiol groups, which bind strongly on to gold electrodes (Chapter 3), and accordingly ferrocene compounds with attached thiol groups are now considered. For such compounds, the immobilisation of the electroactive material could be achieved through the thiol groups, which bind strongly on to gold electrodes (Chapter 3). The specific aim of this study is to establish whether an electrode consisting of a gold surface coated with an immobilised thin layer of alkanethiol ferrocene (SME) would have characteristics beneficial to its application in measuring state of charge of lead-acid batteries. The compounds used in this chapter are the alkyl and keto thiol derivatives of ferrocene with an 11-carbon
chain. The reason for the choice of the 11-carbon chain was its availability in our laboratory. The names of the investigated compounds and their codes for referring to them in this thesis are given in Chapter 4 and repeated below for convenience.

<table>
<thead>
<tr>
<th>Ferrocene Derivative</th>
<th>Type</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-mercaptoundecylferrocene</td>
<td>Alkanethiol</td>
<td>Fc1</td>
</tr>
<tr>
<td>(1,1’)-Bis(11-mercaptoundecyl)ferrocene</td>
<td>Alkanethiol</td>
<td>Fc2</td>
</tr>
<tr>
<td>11-mercaptoundecanoylferrocene</td>
<td>Ketothiol</td>
<td>Fc3</td>
</tr>
<tr>
<td>1,1’-Bis(11-mercaptoundecanoyl)ferrocene</td>
<td>Ketothiol</td>
<td>Fc4</td>
</tr>
</tbody>
</table>

The electrochemistry of the above thiol ferrocenes, attached to a gold substrate by drop evaporation method and dip coating (self-assembly) in concentrated acid media is described in this chapter.

7.2 Results and Discussion

7.2.1 Cyclic Voltammetry of alkanethiol ferrocenes

Figures 7.1 and 7.2 show the cyclic voltammogramic behaviour of the SMEs with Fc1 and Fc2 respectively on gold electrodes in 1.0 M H$_2$SO$_4$. Each of the compounds gives a well defined anodic peak and a corresponding cathodic peak consistent with a one electron reversible process.
Figure 7.1  Cyclic voltammogram of Fc1 in 1.0 M H₂SO₄ on a gold electrode
(sweep rate 100 mVs⁻¹).
Figure 7.2  Cyclic voltammogram of \textbf{Fc2} in 1.0 M H$_2$SO$_4$ on a gold electrode (sweep rate 100 mVs$^{-1}$).
The relevant anodic and cathodic peak potentials and surface coverage \((\Gamma_{\text{max}} \text{ in mol cm}^{-2})\) for the two compounds \textbf{Fc1} and \textbf{Fc2} are noted in Table 7.1.

Table 7.1: The peak potentials and the surface coverage of \textbf{Fc1} and \textbf{Fc2} in 1.0 M H\textsubscript{2}SO\textsubscript{4} electrolyte

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Gamma_{\text{max}} \text{ mol cm}^{-2})</th>
<th>(E_{\text{pa}} / \text{V})</th>
<th>(E_{\text{pc}} / \text{V})</th>
<th>(\Delta E_{\text{p}} / \text{mV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{Fc1}</td>
<td>5.35 \times 10^{-10} \ (4.5 \times 10^{-10}) \†</td>
<td>0.455</td>
<td>0.455</td>
<td>0</td>
</tr>
<tr>
<td>\textbf{Fc2}</td>
<td>5.58 \times 10^{-10}</td>
<td>0.520</td>
<td>0.510</td>
<td>10</td>
</tr>
<tr>
<td>\textbf{Fc}</td>
<td>-</td>
<td>0.110</td>
<td>-0.030</td>
<td>140</td>
</tr>
</tbody>
</table>

† Calculated value (Chidsey et al., 1990)

The surface coverage was calculated by integrating the current under the oxidation portion of the CV as discussed in Chapter 3. The table also includes calculated surface coverage value for \textbf{Fc1} taken from (Chidsey et al., 1990). For this calculation, Chidsey assumed the diameter of the ferrocene molecule to be 6.6Å forming a monolayer at the electrode surface. The experimentally found value for the surface coverage is higher than that of the calculated value. This could be related to the possibility of some ferrocene molecules folded between the poorly packed polymethylene chains (Chidsey et al., 1990), or uncertainty in the true surface area (Finklea, 1996) due to roughness. The surface coverage of related self-assembled monolayers (SAMs) prepared by other workers has been reported to be in the range 3 to 7 \times 10^{-10} \text{ mol cm}^{-2} (Shimazu et al., 1994, Creager and Rowe, 1991, Rowe and Creager, 1994, Rowe and Creager, 1991, Uosaki et al., 1991, Shimazu et al.,
Thus the surface coverage of Fc1 and Fc2 obtained experimentally in this work is consistent with the literature.

The plots of Log (anodic peak current (Ipa)) against Log (scan rate (ν)) are linear for both the compounds (Figures 7.4 and 7.5) with slopes of 0.96 and 0.97.
respectively for \textbf{Fc1} and \textbf{Fc2}. These values confirm that the redox process is for surface adsorbed material (Gomez and Kaifer, 1992, Gosser, 1993). Thus, the attachment of thiol groups does provide enhanced surface adsorption of ferrocene on gold substrate.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.4.png}
\caption{Log (anodic peak current ($I_{pa}$)) against Log (scan rate ($\nu$)) for the cyclic voltammogram for \textbf{Fc1} in 1.0 M H$_2$SO$_4$ at a gold electrode.}
\end{figure}
Effect of $H_2SO_4$ concentration on anodic peak potential

The dependence of $E_{pa}$ on [$H^+$] for $Fe1$ and $Fe2$ can be seen from Figures 7.6 and 7.7. The $E_{pa}$ values for both $Fe1$ and $Fe2$ are independent of [$H^+$] at low concentrations ($pH$ 2–10).
Figure 7.6 Anodic peak potential ($E_{pa}$) against pH for Fc1 and Fc2 in 0.1 M $\text{K}_2\text{SO}_4$ solution.

Figure 7.7 The anodic peak potential against concentration of sulphuric acid for Fc1 and Fc2.
However, as can be seen from Figure 7.7, the anodic peak potentials shift linearly to less positive values as the acid concentration is increased in the range 1–5 M. These observations are very similar to those seen for Fe and PVFe under similar conditions as discussed in Chapters 5 and 6. Presumably, the mechanism of this behaviour is similar to that discussed in Chapter 6. To confirm this, the behaviour of these compounds has been studied in HCl, H2SO4, and HClO4 in a manner similar to that for PVFe as noted in Chapter 6. The results are discussed below.

The Figures 7.8, 7.9, 7.10, and 7.11 show cyclic voltammograms of the two compounds in 1.0 M HCl and 1.0 M HClO4 solutions. The relevant $E_{pa}$, $E_{pc}$ and $\Delta E_p$ data are recorded in Table 7.2.

Table 7.2 The peak potentials of Fe1 and Fe2 in 1.0 M HCl, HClO4, and H2SO4 electrolyte (All values are ±10 mV).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Media</th>
<th>H2SO4</th>
<th>HClO4</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa}$/V</td>
<td>$E_{pc}$/V</td>
<td>$\Delta E_p$/mV</td>
<td>$E_{pa}$/V</td>
</tr>
<tr>
<td>Fe1</td>
<td>0.455</td>
<td>0.455</td>
<td>0</td>
<td>0.305</td>
</tr>
<tr>
<td>Fe2</td>
<td>0.520</td>
<td>0.510</td>
<td>10</td>
<td>0.205</td>
</tr>
</tbody>
</table>
Figure 7.8  Cyclic voltammogram of Fc1 in 1.0 M HCl on a gold electrode (sweep rate 100 mV s\(^{-1}\)).
Figure 7.9  Cyclic voltammogram of Fe2 in 1.0 M HCl on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 7.10  Cyclic voltammogram of Fc1 in 1.0 M HClO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 7.11 Cyclic voltammogram of Fe₂ in 1.0 M HClO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
The electrochemical behaviour is strongly dependent on the nature of the anion of the acid. The $E_{pa}$ and $E_{pc}$ values in $\text{HClO}_4$ are the least positive and in $\text{HCl}$ most positive. The $\Delta E_{p}$ value for all the acids lies between 0 and 10 mV which is very close to the theoretical value of zero millivolts for an electroactive species involving electron transfer whose oxidised and reduced forms are ideally adsorbed at the surface of an electrode. Since this behaviour is very similar to that observed for $\text{PVFc}$ (Chapter 6), the mechanism for the dependence of $E_{pa}$ values on acid concentration should be the same as that discussed in Chapter 6.

The effect of higher concentrations (1–5 M) of perchloric and hydrochloric acid on the anodic peak potentials of $\text{Fc}_1$ and $\text{Fc}_2$ was also investigated. As can be seen from the data in Figures 7.12 and 7.13, the anodic peak potentials shift linearly to less positive values as the acid concentration is increased. The linear regression equation and the slopes of the plots of $E_{pa}$ against acid concentration are listed in Table 7.3. The slopes are found to be of the same order of magnitude as those for $\text{PVFc}$ (Chapter 6).
Figure 7.12 The anodic peak potential against concentration of sulphuric, perchloric and hydrochloric acid for $\text{Fc1}$.

Figure 7.13 The anodic peak potential against concentration of sulphuric, perchloric and hydrochloric acid for $\text{Fc2}$.
Table 7.3 Linear regression equations of the anodic peak shifts in sulphuric, perchoric and hydrochloric acids.

<table>
<thead>
<tr>
<th>Media</th>
<th>Fc1</th>
<th>Fc2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>( E_{pa} (V) = -0.029 \ [H₂SO₄] + 0.477 )</td>
<td>( E_{pa} (V) = -0.031 \ [H₂SO₄] + 0.517 )</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.9953 )</td>
<td>( R^2 = 0.9887 )</td>
</tr>
<tr>
<td>HClO₄</td>
<td>( E_{pa} (V) = -0.034 \ [HClO₄] + 0.356 )</td>
<td>( E_{pa} (V) = -0.032 \ [HClO₄] + 0.341 )</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.9977 )</td>
<td>( R^2 = 0.9757 )</td>
</tr>
<tr>
<td>HCl</td>
<td>( E_{pa} (V) = -0.028 \ [HCl] + 0.498 )</td>
<td>( E_{pa} (V) = -0.026 \ [HCl] + 0.525 )</td>
</tr>
<tr>
<td></td>
<td>( R^2 = 0.9899 )</td>
<td>( R^2 = 0.9971 )</td>
</tr>
</tbody>
</table>

7.2.2 Stability/Retainability of thiol ferrocenes on repeated voltammetric cycling

The retainability of Fc1 and Fc2 chemisorbed on gold electrodes was tested by subjecting a freshly prepared SME to repeated voltammetric cycling in the potential range 0 to 0.7 V. The percentage of the material remaining on the electrode surface after each voltammetric cycle was measured in the form of \( (I_{pa})_n/(I_{pa})_1 \times 100 \), where \( n \) is the cycle number, as discussed in Chapter 6. The data is plotted in Figure 7.14. For comparison, the data for PVFc and Fc are also included in Figure 7.14. The alkanethiol compounds are retained at the electrode surface more strongly than PVFc or Fc. At the 100th cycle only 13% of the Fc2 which contains two thiol groups and 23% of Fc1 with only one thiol group is lost from the electrode surface. Under identical conditions, 69% of PVFc and 98% of Fc is lost. Thus, it can be concluded that the attachment of thiol groups to ferrocene allows the material to effectively stay on the gold electrode surface.
The larger the number of the thiol groups in the Fe structure, the better the retainability. Slow degradation of the electrode response in concentrated acid media, however, still occurs. For example, even for the best of the investigated ferrocenes Fe2 13% of the material was lost at the 100th cycle.

![Figure 7.14 Percentage of the remaining Fe, PVFc, Fe1, and Fe2 on the electrode surface against number of cycles in 1.0 M H₂SO₄.](image)

**7.2.3 Cyclic Voltammetry of keto alkyl thiol**

The retainability of alkane thiols on gold surface in concentrated sulphuric acid solutions has been found to be good (Section 7.2.3). However, as discussed in Section 7.2.3, some degradation of these compounds still occurs. The keto thiols were synthesised previous of the alkyl thiols and were thus available. Their electrochemical behaviour was studied.
The electrochemical behaviour of \( \text{Fc3} \) is found to be similar to that of the ferrocenes discussed earlier. \( \text{Fc3} \) also shows well-defined anodic and cathodic peaks (Figure 7.15) but these peaks occur at potentials more positive, \( ca. 550 \text{ mV} \), than those for the simple ferrocene.

![Cyclic voltammogram of Fc3](image)

**Figure 7.15** Cyclic voltammogram of \( \text{Fc3} \) in 1.0 M \( \text{H}_2\text{SO}_4 \) at a gold electrode (sweep rate 100 mVs\(^{-1}\)).

Unfortunately, the peak heights rapidly drop on repeated cycling. Almost all the \( \text{Fc3} \) material was lost from the electrode surface in eight cycles. \( \text{Fc4} \) was worst in this regard \( i.e. \) no oxidation reduction peaks were seen even in its first
cycle. This suggests that the carbonyl group adjacent to the ferrocene nucleus results in the instability of both \( \text{Fc3} \) and \( \text{Fc4} \) in sulphuric acid media.

To get further information on this, the CV behaviour of \( \text{Fc3} \) was investigated in 0.1 M \( \text{K}_2\text{SO}_4 \). In this medium, the number of cycles which could be obtained was higher (34 cycles) than in \( \text{H}_2\text{SO}_4 \) media, suggesting that \( \text{H}^+ \) ions contribute to the instability of the keto ferrocenes. Interestingly it is found that both the ferrocenes are relatively more stable in perchloric acid than in sulphuric acid media.

The repeated cycling behaviour of the ferrocenes in 1.0 M \( \text{HClO}_4 \) is shown in Figures 7.16 and 7.17 respectively. In 1.0 M \( \text{HClO}_4 \), \( \text{Fc3} \) could be cycled for 1200 cycles before losing all the material for the surface of the electrode. \( \text{Fc4} \) lasted for 20 cycles under the same conditions. Thus \( \text{ClO}_4^- \) ion provides some mechanism through which higher stability is possible. The mechanism may be similar to that proposed by Popenoe et al. who investigated 11-mercaptoundecylferrocenecarboxylate (\( \text{FcCOO(CH}_2\text{)}_{11}\text{SH} \)) which contained the carboxyl group (Popenoe et al., 1992) and found an identical dependence of stability of the ferrocene on the presence of \( \text{ClO}_4^- \) ion.
Figure 7.16  Cyclic voltammogram of $\text{Fc}3$ in 1.0 M $\text{HClO}_4$ at a gold electrode (sweep rate 100 mVs$^{-1}$).
7.3 Conclusion

The cyclic voltammetric behaviour of alkanethiol ferrocenes [Fc1 and Fc2] on gold electrodes in concentrated H$_2$SO$_4$ solutions suggests that alkanethiol ferrocenes undergo a one electron reversible redox reaction. The electron transfer mechanism involves surface adsorbed species. The anodic and cathodic peak potentials of the investigated ferrocene depend on the nature of the anion of the acid. The anodic peak potentials of the ferrocenes are independent of H$^+$.
concentration in the pH range 2–10. However, they shift to less positive values as a function of acid concentration in the range 1–5 molar. The attachment of thiol groups provides enhanced surface adsorption of ferrocene on gold substrate. The retainability of Fc1 and Fc2 at the gold electrode surface is higher than that for PVFc or Fc. The extent of retention at the electrode surface is higher for Fc2, which contains two thiol groups, than for Fc1, which has only one thiol group. The presence of a carbonyl group in the alkanethiol chain results in instability of both Fc3 and Fc4 in sulphuric acid media. The ketothiol ferrocenes are somewhat more stable in ClO4− media.

7.4 References


8.1 Introduction

As discussed in earlier chapters, the major limitation to the use of ferrocenes as a component of sensors and/or other electrochemical devices is that the ferricenium salts tend to be soluble and or have limited stability in the electrolyte. It is thought that both of these limitations could be overcome by using ferrocene derivatives in which the two cyclopentadienyl rings are bridged by one or more hydrocarbon chains consisting of methylene groups \( (\text{CH}_2)_n \) where \( n=3 \) or 5. As noted in chapter 2, most of the studies of bridged ferrocenes in the past have mainly been devoted to structural aspects rather than their electroreactivity and chemical stability (Rosenblum et al., 1963, Jones et al., 1965, Spaulding et al., 1978, Hillman and Nagy, 1980). In early 1970, Gorton et al. reported some polarographic half-wave potentials of bridged ferrocenes (Gorton et al., 1971). Other early reports on the study of the electrochemical properties of bridged ferrocenes come from Hillman et al. (Hillman et al., 1978) and Ogata et al. (Ogata et al., 1981); these authors found the oxidation of bridged ferrocenes a
straightforward one electron reversible process. However, no studies of the stability of bridged ferrocenes or bridged ferricenium ions under conditions likely to be encountered in electrochemical devices have been reported. This chapter deals with the results of a systematic study of the electrochemistry and electro and chemical stability of some relevant bridged ferrocenes. The investigated ferrocenes and their codes are listed in Table 8.1. These ferrocene molecules differ in their number of bridges (1 – 3) with each bridge containing methylene groups \((\text{CH}_2)_n\) where \(n=3\) or \(5\).

Table 8.1 The investigated bridged ferrocenes.

<table>
<thead>
<tr>
<th>Ferrocene Derivative</th>
<th>Code</th>
<th>((\text{CH}_2)_n)</th>
<th>No. of bridges</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="1,1'">3</a>ferrocenophane</td>
<td>Fc5</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td><a href="1,1'">32</a>(3,3')ferrocenophane</td>
<td>Fc6</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td><a href="1,1'">33</a>(2,2')(4,4')ferrocenophane</td>
<td>Fc7</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><a href="1,1'">5</a>ferrocenophane</td>
<td>Fc8</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

8.2 Results and Discussion

8.2.1 Cyclic Voltammetry of Bridged Ferrocenes

The bridged ferrocene molecule in each case was coated on a gold electrode in the form of a SME (Chapter 4), and its CV investigated in 1.0 molar aqueous solutions of \(\text{H}_2\text{SO}_4\), \(\text{HClO}_4\), and \(\text{HCl}\). Each of these compounds gave a
well defined anodic peak and a corresponding cathodic peak consistent with a one
electron reversible process. However it was found that the anodic peak potential,
$E_{pa}$, varied with cycle number. The oxidation peak during the first scan of a freshly
formed SME always occurred at a potential more positive than the subsequent
cycles. A typical CV is shown in Figure 8.1. This is probably related to the
conditioning of the film during the first cycle. This kind of behaviour is generally
observed if the electroactive material film at the surface of the electrode is not
readily wetted by the electrolyte (Murray, 1984). The anodic ($E_{pa}$) and cathodic
($E_{pc}$) peak potentials taken from the second cycle for each of the bridged ferrocenes
investigated in this work are summarised in Table 8.2.

Table 8.2 The peak potentials of $\text{Fc}_5$, $\text{Fc}_6$, $\text{Fc}_7$, and $\text{Fc}_8$ (second cycle) in 1.0 M
$\text{H}_2\text{SO}_4$, $\text{HClO}_4$, and $\text{HCl}$ electrolyte (All values are ±10 mV).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Media</th>
<th>$E_{pa}$/V</th>
<th>$E_{pc}$/V</th>
<th>$\Delta E$/mV</th>
<th>$E_{pa}$/V</th>
<th>$E_{pc}$/V</th>
<th>$\Delta E$/mV</th>
<th>$E_{pa}$/V</th>
<th>$E_{pc}$/V</th>
<th>$\Delta E$/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{HClO}_4$</td>
<td>$\text{HCl}$</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{HClO}_4$</td>
<td>$\text{HCl}$</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{HClO}_4$</td>
<td>$\text{HCl}$</td>
<td>$\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{Fc}_5$</td>
<td></td>
<td>0.090</td>
<td>0.040</td>
<td>50</td>
<td>0.040</td>
<td>-0.010</td>
<td>50</td>
<td>0.115</td>
<td>0.075</td>
<td>40</td>
</tr>
<tr>
<td>$\text{Fc}_6$</td>
<td></td>
<td>0.160</td>
<td>0.110</td>
<td>50</td>
<td>0.108</td>
<td>0.025</td>
<td>83</td>
<td>0.200</td>
<td>0.140</td>
<td>60</td>
</tr>
<tr>
<td>$\text{Fc}_7$</td>
<td></td>
<td>0.200</td>
<td>0.150</td>
<td>50</td>
<td>0.160</td>
<td>0.140</td>
<td>20</td>
<td>0.280</td>
<td>0.190</td>
<td>90</td>
</tr>
<tr>
<td>$\text{Fc}_8$</td>
<td></td>
<td>0.120</td>
<td>0.055</td>
<td>65</td>
<td>0.085</td>
<td>-0.005</td>
<td>90</td>
<td>0.140</td>
<td>0.090</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 8.1 Cyclic voltammogram of Fc6 in 1.0 M H₂SO₄ at a gold electrode (sweep rate 100 mVs⁻¹).
The results in the Table 8.2 show that the $E_{pa}$ value depends strongly on the nature of the bridging chain joining the two cyclopentadienyl groups. As the number of the bridging chains is increased there is a linear increase in the oxidation potential (Figure 8.2).

![Graph showing the effect of the number of bridges on $E_{pa}$ in various acids.](image)

**Figure 8.2** Effect of the number of bridges joining the two cyclopentadienyl rings of ferrocene on the anodic peak potential ($E_{pa}$) in 1.0 M $\text{H}_2\text{SO}_4$, $\text{HClO}_4$, and $\text{HCl}$.

It must however be mentioned that the dependence of $E_{pa}$ on the number of bridges observed in this work is opposite to that reported in the literature by others for the same compounds in acetonitrile solution (Hillman et al., 1978) (Chapter 2). In aqueous media these compounds are, however, insoluble. Thus, their behaviour in aqueous acid media may be the consequence of increased resistance imposed by the bridges to the anions diffusion into the solid film during
oxidation. The effect of the identity of the anion can be seen from the results in Figure 8.2. The plot of $E_{p\alpha}$ vs number of the bridges in each case is linear but their slopes are different. The number of $\langle \text{CH}_2 \rangle$ groups in the bridged chain also has influence on the $E_{p\alpha}$ values. The results in Table 8.2 show that higher the number of methylene groups the higher the $E_{p\alpha}$ value.

**Effect of acid concentration on anodic peak potential**

The effect of $H^+$ at low concentration in the pH range 2 – 10 on the $E_{p\alpha}$ values of the investigated bridged ferrocenes in sulphate, perchlorate and chloride media can be seen from the results plotted in Figures 8.3 to 8.5. Clearly for all the ferrocenes the $E_{p\alpha}$ values are independent of the solution pH in the range 2 – 10. This behaviour is similar to that noted earlier for PVFc (Chapter 6).
Figure 8.3  Anodic peak potential ($E_{pa}$) against pH in 0.1 M $K_2SO_4$ solution.

Figure 8.4  Anodic peak potential ($E_{pa}$) against pH in 0.1 M $NaClO_4$ solution.
The effect of H⁺ at high concentrations *i.e.* in 1 – 5 molar H₂SO₄, HClO₄, and HCl on the anodic peak potential of the various bridged ferrocenes can be seen from Figures 8.6 to 8.9. The Epₐ values are linearly related to acid concentration. The slopes of the plots of Epₐ vs concentration lie in the range 28 – 44 mV. The regression analysis of the variation of the peak potential as a function of concentration for each of the acids is given in Table 8.3. This observation is similar to that noted earlier for Fc and PVFc (Chapter 5 and Chapter 6). Thus, it appears that the dependence of the peak potential on acid concentration (1 – 5) is a general phenomenon for all the ferrocenes.

Figure 8.5   Anodic peak potential (Epₐ) against pH in 0.1 M KCl solution.
Figure 8.6 The anodic peak potential against $\text{H}_2\text{SO}_4$ concentration.

Figure 8.7 The anodic peak potential against $\text{HClO}_4$ concentration.
Figure 8.8  The anodic peak potential against HCl concentration.
Table 8.3 Linear regression equations of the anodic peak variation of various ferrocenes in sulphuric, perchloric and hydrochloric acid.

<table>
<thead>
<tr>
<th>Ferrocene</th>
<th>Sulphuric Acid</th>
<th>Perchloric Acid</th>
<th>Hydrochloric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc5</td>
<td>$E_{pa} \ (V) = -0.042 \ [H_2SO_4] + 0.130$  \  \  \ $R^2 = 0.9955$</td>
<td>$E_{pa} \ (V) = -0.032 \ [HClO_4] + 0.074$  \  \  \ $R^2 = 0.9983$</td>
<td>$E_{pa} \ (V) = -0.029 \ [HCl] + 0.142$  \  \  \ $R^2 = 0.9953$</td>
</tr>
<tr>
<td>Fc6</td>
<td>$E_{pa} \ (V) = -0.033 \ [H_2SO_4] + 0.193$  \  \  \ $R^2 = 0.9973$</td>
<td>$E_{pa} \ (V) = -0.041 \ [HClO_4] + 0.132$  \  \  \ $R^2 = 0.9899$</td>
<td>$E_{pa} \ (V) = -0.029 \ [HCl] + 0.228$  \  \  \ $R^2 = 0.9991$</td>
</tr>
<tr>
<td>Fc7</td>
<td>$E_{pa} \ (V) = -0.044 \ [H_2SO_4] + 0.255$  \  \  \ $R^2 = 0.9835$</td>
<td>$E_{pa} \ (V) = -0.039 \ [HClO_4] + 0.200$  \  \  \ $R^2 = 0.9860$</td>
<td>$E_{pa} \ (V) = -0.044 \ [HCl] + 0.312$  \  \  \ $R^2 = 0.9739$</td>
</tr>
<tr>
<td>Fc8</td>
<td>$E_{pa} \ (V) = -0.027 \ [H_2SO_4] + 0.145$  \  \  \ $R^2 = 0.9959$</td>
<td>$E_{pa} \ (V) = -0.033 \ [HClO_4] + 0.138$  \  \  \ $R^2 = 0.9937$</td>
<td>$E_{pa} \ (V) = -0.029 \ [HCl] + 0.168$  \  \  \ $R^2 = 0.9983$</td>
</tr>
</tbody>
</table>
8.2.2 Retainability/Stability of bridged ferrocenes on gold electrode on repeated voltammetric cycling

The retainability of each of the bridged ferrocenes coated on a gold electrode was tested by subjecting freshly prepared SME’s to repeated voltammetric cycling in the potential range –0.1 to 0.5V and analysing the data as explained in chapter 5. The percentage of the ferrocene left on the electrode as a function of cycle number for the investigated ferrocenes is plotted in Figure 8.9. For direct comparison the data for the 100\textsuperscript{th} cycle are noted in Table 8.4, which also includes data for PVFc taken from Chapter 6.

![Figure 8.9](image)

**Figure 8.9** Percentage of the bridged ferrocene material remaining on the electrode surface against number of cycles in 1.0 M H\textsubscript{2}SO\textsubscript{4}. 
Table 8.4 The percentage loss of the various ferrocenes from the electrode surface at the 100\textsuperscript{th} cycle (All values are ±5% loss).

<table>
<thead>
<tr>
<th>Ferrocene</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe5</td>
<td>98</td>
</tr>
<tr>
<td>Fe6</td>
<td>97</td>
</tr>
<tr>
<td>Fe7</td>
<td>92</td>
</tr>
<tr>
<td>Fe8</td>
<td>98</td>
</tr>
<tr>
<td>PVFc</td>
<td>69</td>
</tr>
</tbody>
</table>

It is clear from Figure 8.9 and Table 8.4 that for all the bridged ferrocenes the active material is either physically shed or dissolved away from the electrode surface, or is chemically decomposed, on repeated cycling between the potential limits of the experiment. At the 100\textsuperscript{th} cycle, almost all of the bridged ferrocene material is lost as against 69\% for PVFc. Clearly, PVFc is retained at the electrode surface more than the bridged ferrocenes. The mechanism for the loss of these ferrocenes from the electrode surface is not known. However it is most probably related to the greater the solubility of the oxidised form of these ferrocenes and / or their relative chemical instability in the aqueous acidic media. In order to get some insight into this, the following experiments were carried out on Fe7 which was chosen as a model of the other bridged ferrocenes.

The Fe7 was oxidised by reacting with Ce(IV) using a technique similar to that reported by Holecek et al. (Holecek et al., 1979a) and extracted into a 0.2 M aqueous H\textsubscript{2}SO\textsubscript{4} solution. The UV–Vis spectrum of a portion of this solution was
recorded immediately and then after 20 minutes. The results are shown in Figure 8.10. The presence of an absorption peak ($\lambda_{\text{max}}$) at 617 nm indicates that the solution does contain dissolved ferricenium salt (Huang and Jwo, 1991), confirming that the oxidised form of the investigated ferrocene is soluble in aqueous media. The spectra recorded after 20 minutes was virtually the same as at the beginning. This indicates that the dissolved material was chemically stable.

In another experiment, 0.1 M KH$_2$PO$_4$ was added to a portion of the solution of Fe$_7^+$ to increase the pH. After leaving the solution under these conditions for about 20 minutes, H$_2$SO$_4$ was added again to adjust the final pH of the solution 1.5 and its UV–Vis spectrum recorded. The spectrum was found to be identical to that obtained in the first experiment (Figure 8.10). This indicates that even exposure of the ferricenium ion to a higher pH, which is conducive to hydrolysis (Prins et al., 1972, Holecek et al., 1979b, McDowell et al., 1984), did not cause any chemical change in the ferricenium ion. Thus, the ferricenium ion of the bridged ferrocene is very stable chemically. In contrast, when the above experiments were reported with simple ferricenium the spectra changed rapidly (Figure 8.11). It could thus be concluded that while the oxidised form of the simple ferrocene is unstable in aqueous media, that of the bridged ferrocene [Fe$_7$] is stable. This means that bridging of the two cyclopentadienyl groups of the ferrocene molecules does provide chemical stability to the oxidised form of the ferrocene.
Figure 8.10 UV/Vis spectra for ferricenium ion of the triply bridged ferrocene (Fc7) (First: extracted into a 0.2 M aqueous H2SO4. Second: addition of 0.1 M KH2PO4 for 20 min. then H2SO4).
8.2.3 Potentiometric behaviour of Fe/Fc⁺ couple

As discussed in Chapter 5 the relationship of the electrode potential of Fe/Fc⁺ couple with acid concentration is more useful for its application in analytical chemistry such as potentiometric measurement of acid concentration. This property of the bridged ferrocene was investigated as follows.

For each of the ferrocenes, a gold electrode was coated with the ferrocene of interest by drop evaporation method. The coating on the electrode was then partially anodically oxidised in a 1.0 M H₂SO₄ solution. The polarisation was
then switched off and the equilibrium potential of the electrode was monitored against a saturated calomel electrode as a function of time in the same solution. The results are shown in Figure 8.12.

![Figure 8.12 Equilibrium potential against time for bridged ferrocenes.](image)

As can be seen from Figure 8.12 the equilibrium potential for all the investigated bridged ferrocenes changed rapidly to less positive potential, levelling out to some irreproducible value close to that before the partial oxidation step. Such a behaviour would be expected if the oxidised form of the active material is either poorly retained at the electrode surface or is chemically decomposed or is soluble in the electrolyte and hence is removed from the electrode surface.
8.3 Conclusion

The cyclic voltammetric behaviour of the bridged ferrocenes [Fc5, Fc6, Fc7, and Fc8] coated on a gold electrode in aqueous acid solutions suggests that these ferrocenes undergo a one electron reversible redox reaction. The oxidation peak during the first scan of freshly coated films (SME) always occurred at a potential more positive than in the subsequent cycles. This is related to the conditioning of the film during the first cycle. The Epa and Epc of the investigated bridged ferrocenes depend on the nature of the anion of the acid. They are independent of H⁺ concentration in the pH range 2–10, but they shift to less positive values as the acid concentration is increased in the range 1–5 molar. The retainability of the bridged ferrocenes on the surface of the electrode is very poor. The active material is either physically shed or dissolved away from the electrode surface on repeated voltammetric cycling between the potential limits where the ferrocene undergoes oxidation/reduction reaction.

8.4 References


9.1 Introduction

In Chapter 8, the electrochemical behaviour of the bridged ferrocenes [Fc5, Fc6, Fc7, and Fc8] was discussed. It was found that these ferrocenes, though chemically stable were not retained at the electrode surface. With a view to improving the retainability of these materials at the electrode surface, attachment of the (CH$_2$)$_{11}$SH group to the bridged ferrocene molecules has been considered. The sulphur atom in the –SH group is known to have a strong interaction with gold surface (Chapter 3 and Chapter 7) and hence should bind strongly to the gold substrate. This chapter describes the electrochemistry of the above bridged ferrocenes which additionally contain a (CH$_2$)$_{11}$SH group attached one cyclopentadienyl group. The work described in this Chapter is aimed at determining whether the attached thiol group provides effective adherence of the ferrocenes to an inert gold substrate and how it affects the electrochemistry of the parent ferrocene. For quick reference the investigated ferrocenes and their codes are listed Table 9.1.
Table 9.1 The investigated bridged ferrocene thiol derivatives.

<table>
<thead>
<tr>
<th>Ferrocene Derivative</th>
<th>Code</th>
<th>(\text{CH}_2)(_n)</th>
<th>No. of bridges</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(11-Mercaptoundecyl)<a href="1,1'">3</a>ferrocenophane</td>
<td>Fc9</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4-(11-Mercaptoundecyl)<a href="1,1'">3(_2)</a>(3,3')ferrocenophane</td>
<td>Fc10</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>3-(11-Mercaptoundecyl)<a href="1,1'">33</a>(2,2')(4,4')ferrocenophane</td>
<td>Fc11</td>
<td>3</td>
<td>3</td>
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<tr>
<td>3-(11-mercaptoundecyl)<a href="1,1'">5</a>ferrocenophane</td>
<td>Fc12</td>
<td>5</td>
<td>1</td>
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</tbody>
</table>

9.2 Results and Discussion

9.2.1 Cyclic voltammetry of alkylthiol bridged ferrocene

The cyclic voltammetric (CV) behaviour of the alkanethiol bridged ferrocenes [Fc9 – Fc12] was investigated in various aqueous acid electrolytes (H\(_2\)SO\(_4\), HClO\(_4\), HCl). The results are shown in Figures 9.1 to 9.10. The relevant data is noted in Table 9.2, which also includes data for the corresponding ferrocenes without the \(\text{CH}_2\)\(_{11}\)SH group for comparison.

The anodic and corresponding cathodic peaks for (Fc9, Fc10 and Fc12) occur at potentials significantly more positive than those for the corresponding ferrocenes without the attached \(\text{CH}_2\)\(_{11}\)SH group. Thus the presence of the \(\text{CH}_2\)\(_{11}\)SH group has a significant influence on the electron transfer process.
The cyclic voltammograms of all the ferrocenes [Fe9, Fe10 and Fe12] in SO4²⁻ and ClO4⁻ media consisted of perfectly symmetrical anodic and cathodic peaks. However in Cl⁻ media Fe10 behaved differently from Fe9 and Fe12. Only for Fe10 in Cl⁻ media the Ipₐ and Ipₐ heights decreased rapidly on repeated cycling (Figure 9.4). Similar observations were also made when the CV behaviour of Fe10 was compared with those of Fe9 and Fe12 in 1–5 M HCl and 0.1 M KCl. This is surprising, given the fact that the corresponding bridged ferrocenes without the attached (CH₂)₁₁SH groups (Fe5, Fe6, Fe7 and Fe8) behaved similarly in all the investigated media. It appears that the presence of Cl⁻ in the media has some unique effect on the properties of Fe10. At this stage no explanation can be put forward for this observation. However, this should be investigated in more detail in the future.
Table 9.2 The peak potentials of Fc9, Fc10, Fc11, and Fc12 in 1.0 M H₂SO₄, HClO₄, and HCl electrolyte

<table>
<thead>
<tr>
<th>Compound</th>
<th>Media</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>H₂SO₄</td>
<td>HClO₄</td>
<td>HCl</td>
<td>H₂SO₄</td>
<td>HClO₄</td>
<td>HCl</td>
<td>H₂SO₄</td>
<td>HClO₄</td>
<td>HCl</td>
<td>H₂SO₄</td>
<td>HClO₄</td>
</tr>
<tr>
<td></td>
<td>Epₐ/V</td>
<td>Epₐ/V</td>
<td>ΔEp/mV</td>
<td>Epₐ/V</td>
<td>Epₐ/V</td>
<td>ΔEp/mV</td>
<td>Epₐ/V</td>
<td>Epₐ/V</td>
<td>ΔEp/mV</td>
<td>Epₐ/V</td>
<td>Epₐ/V</td>
</tr>
<tr>
<td>Fc9</td>
<td>0.415 (0.090)</td>
<td>0.400 (0.040)</td>
<td>15 (50)</td>
<td>0.285 (0.040)</td>
<td>0.265 (-0.010)</td>
<td>20 (50)</td>
<td>0.445 (0.115)</td>
<td>0.430 (0.075)</td>
<td>15 (40)</td>
<td></td>
<td></td>
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<tr>
<td>Fc10</td>
<td>0.410 (0.160)</td>
<td>0.390 (0.110)</td>
<td>20 (50)</td>
<td>0.270 (0.108)</td>
<td>0.255 (0.025)</td>
<td>15 (83)</td>
<td>0.550† (0.200)</td>
<td>0.450† (0.140)</td>
<td>10 (60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc11</td>
<td>0.525 (0.200)</td>
<td>0.430 (0.150)</td>
<td>95 (50)</td>
<td>- (0.160)</td>
<td>- (0.140)</td>
<td>- (20)</td>
<td>- (0.280)</td>
<td>- (0.190)</td>
<td>- (90)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fc12</td>
<td>0.380 (0.120)</td>
<td>0.365 (0.055)</td>
<td>15 (65)</td>
<td>0.245 (0.085)</td>
<td>0.235 (-0.005)</td>
<td>10 (90)</td>
<td>0.430 (0.140)</td>
<td>0.420 (0.090)</td>
<td>10 (50)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Peak position of the anodic peak observed in the second scan.
All values are ±10 mV
The data in parenthesis are for the corresponding ferrocene without the attached (CH₂)₁₁SH group.
Figure 9.1  Cyclic voltammogram of Fe9 in 1.0 M HCl on a gold electrode (sweep rate 100 mV/s⁻¹).
Figure 9.2  Cyclic voltammogram of Fe9 in 1.0 M HClO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 9.3  Cyclic voltammogram of **Fe9** in 1.0 M H₂SO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 9.4  Cyclic voltammogram of Fc10 in 1.0 M HCl on a gold electrode (sweep rate 100 mV s$^{-1}$).
Figure 9.5  Cyclic voltammogram of Fe10 in 1.0 M HClO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 9.6  Cyclic voltammogram of Fc10 in 1.0 M H₂SO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
Figure 9.7  Cyclic voltammogram of Fc11 in 1.0 M H$_2$SO$_4$ on a gold electrode (sweep rate 100 mVs$^{-1}$).
Figure 9.8  Cyclic voltammogram of Fe12 in 1.0 M HCl on a gold electrode (sweep rate 100 mVs$^{-1}$).
Figure 9.9  Cyclic voltammogram of Fc12 in 1.0 M HClO₄ on a gold electrode (sweep rate 100 mV s⁻¹).
Figure 9.10  Cyclic voltammogram of Fc12 in 1.0 M H₂SO₄ on a gold electrode (sweep rate 100 mVs⁻¹).
The log ($I_p_a$) against log ($v$) plots for the ferrocenes are shown in Figures 9.11 – 9.14. All these plots are linear. Their slopes are listed in Table 9.3. The slopes are very close to the theoretical value of 1.0, indicative of the redox process involving species immobilised at the surface of the electrode (Gomez and Kaifer, 1992, Gosser, 1993). The data have also been analysed by plotting $I_p_a$ vs $v$. All the plots are also found to be linear confirming that the electron transfer involves confined electroactive species. (Bard and Faulkner, 1980) It may be noted however that the $\Delta E_p$ values are greater than zero as predicted by theory of such electron transfer reactions. (Bard and Faulkner, 1980) This is certainly due to resistance of the electrode coating. (Gomez and Kaifer, 1992)

Table 9.3 The slope values of the plots of log anodic peak current against log scan rate for alkane thiol bridged ferrocenes in 1.0 M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Ferrocene</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe9</td>
<td>0.86</td>
</tr>
<tr>
<td>Fe10</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe11</td>
<td>0.81</td>
</tr>
<tr>
<td>Fe12</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Figure 9.11 Log (anodic peak current \( I_{pa} \)) against Log (scan rate \( \nu \)) for the cyclic voltammogram for \textbf{Fc9} in 1.0 M H\(_2\)SO\(_4\) at a gold electrode.

\[
y = 0.8591x - 3.188 \\
R^2 = 0.9994
\]

Figure 9.12 Log (anodic peak current \( I_{pa} \)) against Log (scan rate \( \nu \)) for the cyclic voltammogram for \textbf{Fc10} in 1.0 M H\(_2\)SO\(_4\) at a gold electrode.

\[
y = 0.8008x - 3.3636 \\
R^2 = 0.9974
\]
Figure 9.13  Log (anodic peak current ($I_{pa}$)) against Log (scan rate ($ν$)) for the cyclic voltammogram for Fe11 in 1.0 M H$_2$SO$_4$ at a gold electrode.

Figure 9.14  Log (anodic peak current ($I_{pa}$)) against Log (scan rate ($ν$)) for the cyclic voltammogram for Fe12 in 1.0 M H$_2$SO$_4$ at a gold electrode.
**Effect of $H^+$ concentration on anodic peak potential**

The dependence of $E_{pa}$ of $\text{Fc9}$, $\text{Fc10}$ and $\text{Fc12}$ on $H^+$ at low concentration (pH 2 – 10) can be seen from the results in Figures 9.15 – 9.17. The $E_{pa}$ values for all these ferrocenes are independent of pH in the range 2 – 10, as has been found for all the other ferrocenes noted in this thesis.

![Diagram showing the relationship between $E_{pa}$ and pH for different anions in 0.1 M K$_2$SO$_4$, NaClO$_4$ and KCl solutions.](image)

**Figure 9.15**  Anodic peak potential ($E_{pa}$) against pH for $\text{Fc9}$ in 0.1 M K$_2$SO$_4$, NaClO$_4$ and KCl solutions.
Figure 9.16  Anodic peak potential ($E_{pa}$) against pH for $\text{Fc10}$ in 0.1 M $\text{K}_2\text{SO}_4$, $\text{NaClO}_4$ and $\text{KCl}$ solutions.

Figure 9.17  Anodic peak potential ($E_{pa}$) against pH for $\text{Fc12}$ in 0.1 M $\text{K}_2\text{SO}_4$, $\text{NaClO}_4$ and $\text{KCl}$ solutions.
The $E_{pa}$ values, however, shift linearly to less positive potentials as the acid concentration is increased from 1 to 5 M (Figures 9.18 – 9.20). The slopes of these graphs are different for the different acids (HCl, HClO$_4$, and H$_2$SO$_4$) but were in the approximate range 24–35 mV per unit molar concentration of the acid (Table 9.4). These slopes were almost of the same order as those for the corresponding ferrocenes without the attached (CH$_2$)$_{11}$SH group. The results confirm that the introduction of the thiol groups into the structure of the bridged ferrocenes does not significantly alter their electrochemical response to the change in H$^+$ concentration.

Figure 9.18 The anodic peak potential against concentration of H$_2$SO$_4$, HClO$_4$, and HCl for Fe9.
Figure 9.19  The anodic peak potential against concentration of H$_2$SO$_4$, HClO$_4$, and HCl for Fe10.

Figure 9.20  The anodic peak potential against concentration of H$_2$SO$_4$, HClO$_4$, and HCl for Fe12.
Table 9.4 Linear regression equations of the anodic peak shifts for bridged ferrocene thiols in sulphuric, perchloric and hydrochloric acids.

<table>
<thead>
<tr>
<th>Ferrocene</th>
<th>Sulphuric Acid</th>
<th>Perchloric Acid</th>
<th>Hydrochloric Acid</th>
</tr>
</thead>
</table>
| **Fc9**   | \( E_{pa} (V) = -0.0235 \ [H_2SO_4] + 0.4355 \)  
\( R^2 = 0.9950 \) | \( E_{pa} (V) = -0.034 \ [HClO_4] + 0.309 \)  
\( R^2 = 0.9940 \) | \( E_{pa} (V) = -0.0285 \ [HCl] + 0.4695 \)  
\( R^2 = 0.9942 \) |
| **Fc10**  | \( E_{pa} (V) = -0.0235 \ [H_2SO_4] + 0.4325 \)  
\( R^2 = 0.9986 \) | \( E_{pa} (V) = -0.035 \ [HClO_4] + 0.308 \)  
\( R^2 = 0.9976 \) | \( E_{pa} (V) = -0.0285 \ [HCl] + 0.4825 \)  
\( R^2 = 0.9810 \) |
| **Fc12**  | \( E_{pa} (V) = -0.0245 \ [H_2SO_4] + 0.4065 \)  
\( R^2 = 0.9954 \) | \( E_{pa} (V) = -0.0325 \ [HClO_4] + 0.2785 \)  
\( R^2 = 0.9993 \) | \( E_{pa} (V) = -0.03 \ [HCl] + 0.463 \)  
\( R^2 = 0.9967 \) |
9.2.2 Retainability of alkane bridged ferrocenes at the electrode surface

A major objective of investigating the thiol derivatives of bridged ferrocenes is to confirm whether the presence of a $(\text{CH}_2)_{11}\text{SH}$ group in their structure improves the retainability of bridged ferrocenes at the gold substrate. This property was, therefore, investigated by subjecting the thiol derivatives, chemisorbed on gold electrodes, to repeated voltammetric cycling in 1.0 M H$_2$SO$_4$ in the potential range 0.0 – 0.7 V. The data were analysed the same way as for the corresponding bridged ferrocenes without $(\text{CH}_2)_{11}\text{SH}$ groups (Chapter 8). The % of the material left on the electrode surface as a function of the cycle number is shown in Figure 9.21. The introduction of $(\text{CH}_2)_{11}\text{SH}$ groups improves the retainability of the electroactive material at the electrode surface markedly. As can be seen from the results in Figure 9.21, the loss of the material is much less than that for the corresponding ferrocene without the thiol groups. The data in Table 9.5, which compares % loss of the electroactive material of the two classes of the bridged ferrocenes at the 100th voltammetric cycle, give more quantitative information on their retainability of the gold electrode surface. The difference of retainability of these classes of compounds is very large.
Figure 9.21  Percentage of the bridged ferrocene material remaining on the electrode surface against number of cycles in 1.0 M H$_2$SO$_4$.

Table 9.5 Comparison of the % loss of thiol and non-thiol derivatives of bridged ferrocene at 100$^{th}$ repeated voltammetric cycle in 1.0 M H$_2$SO$_4$ (All values are ± 5% loss).

<table>
<thead>
<tr>
<th>Non thiol derivative</th>
<th>% loss</th>
<th>Thiol derivative</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc5</td>
<td>98%</td>
<td>Fc9</td>
<td>32%</td>
</tr>
<tr>
<td>Fc6</td>
<td>97%</td>
<td>Fc10</td>
<td>27%</td>
</tr>
<tr>
<td>Fc7</td>
<td>92%</td>
<td>Fc11</td>
<td>25%</td>
</tr>
<tr>
<td>Fc8</td>
<td>98%</td>
<td>Fc12</td>
<td>28%</td>
</tr>
</tbody>
</table>

Thus, the presence of a (CH$_2$)$_n$SH group enhances the retention of the thiol derivatives on the electrode surface significantly. Hence, construction of
stable surface modified electrodes of these ferrocenes should be possible.

9.3 Conclusion

Cyclic voltammetric behaviour of alkanethiol bridged ferrocenes [Fc9, Fc10, Fc11, and Fc12] shows that their oxidation/reduction occurs at potentials more positive than the corresponding molecules without the an attached \((\text{CH}_2)_{11}\text{SH}\) group. The response of Fc10 in Cl\(^-\) media is different from that of Fc9 and Fc12 in that its \(I_{p_a}\) and \(I_{p_c}\) values decrease rapidly on repeated cycling. Generally, the \(E_{p_a}\) and \(E_{p_c}\) of the investigated bridged ferrocenes depended on the nature of the anion of the acid. The \(E_{p_a}\) and \(E_{p_c}\) values were found to be independent of H\(^+\) concentration in the pH range 2–10. However, they shift to less positive values as the acid concentration is increased in the range 1–5 molar.

The retainability of the alkanethiol bridged ferrocenes on the surface of a gold electrode is superior to that of the corresponding bridged ferrocenes without the \((\text{CH}_2)_{11}\text{SH}\) group.

9.4 References


Potentiometric Behaviour and Chemical Stability of (1,1')-Bis(11-mercaptoundecyl)ferrocene in Concentrated Sulphuric Acid

10.1 Introduction

As stated in chapter 1, a major objective of the work has been to study whether an electrode consisting of an immobilised ferrocene/ferricenium couple on a conducting substrate could be used as a potentiometric sensor for the monitoring change in H$_2$SO$_4$ concentration (1 – 5M) simulating state of charge of lead acid batteries. Most of the ferrocenes investigated in this work were found to have oxidation/reduction characteristics, which could allow them to be used for such an application. However, their chemical instability in the H$_2$SO$_4$ media and or physical shedding of the electroactive material from the conducting substrate made them unsuitable. (1,1')-Bis(11-mercaptoundecyl)ferrocene, Fc2, was identified to be most suitable for this application as discussed in Chapter 7. The properties of this material relevant to this application are investigated in more detail and its potential for measuring state of charge of lead acid batteries is discussed in this Chapter.
10.2 Results and Discussion

10.2.1 Potentiometric behaviour of the ferrocene redox couple

A surface modified electrode (SME) consisting of a thin layer of $\text{Fc}_2$ chemisorbed on a gold substrate was prepared as described in Chapter 4. The $\text{Fc}_2$ layer of the SME was partially oxidised (Peerce and Bard, 1980) by way of anodic polarisation in a 1.0 M $\text{H}_2\text{SO}_4$ solution. The SME was then washed with deionised water, and wiped dry before transferring to a series of sulphuric acid solutions of concentrations varying from 1 to 5M. In each solution, the potential of the SME versus a saturated calomel electrode was monitored for up to 5–10 minutes before transferring to the next solution. The experiments were conducted starting with the solution of the lowest sulphuric acid concentration 1.0 M and then transferring to solutions of higher concentrations up to 5.0 M in steps of 1.0 M unit. The experiment was then repeated in the reverse direction i.e. decreasing the acid concentration in steps of 1.0 M unit back to 1.0 M. The experiments were repeated three times. Consistently reproducible potentials corresponding to each of the concentrations of the acid investigated were recorded. Typical experimental data are shown in Figure 10.1. The results indicate that the SME can be used to potentiometrically determine the concentration of sulphuric acid in the range 1–5 M, which simulates the change in the acid concentration during charge/discharge cycles of lead-acid battery.
10.2.2 Stability of the ferrocene in H₂SO₄ Media

If the SME consisting of Fc₂ is to find application in measuring the state of charge of lead-acid batteries, both its oxidised and reduced forms must be chemically stable and should maintain electrical contact with the substrate over long periods. This property of Fc₂ was tested as follows:

After completing the series of experiments described in section 10.2.1, the SME was placed in 1.0 M H₂SO₄ solution and periodically subjected to cyclic voltammetric scans in the potential range where reversible oxidation/reduction of Fc₂ occurs. The peak current, Iₚa, of the anodic peak for each cycle was noted. It was found that the peak current fell to half of its value in seven days and to zero in fifteen days. This suggests that the active material at the electrode surface was
either slowly decomposed or desorbed from the electrode surface during its contact with 1.0 M \( \text{H}_2\text{SO}_4 \) and subsequent cyclic voltammetric scans.

The chemical stability of \textbf{Fc2} was studied by Fourier Transform Infrared Spectroscopy (FTIR) studies. The procedure for this study was the same as described in Chapter 6. Thus, the FTIR spectrum of the \textbf{Fc2} film on the SME was recorded before the oxidation / reduction cycling in 1.0 M \( \text{H}_2\text{SO}_4 \) and compared with that obtained at the end of the 100\(^{th}\) cycle. The spectra in the high frequency region 3200 – 2700 cm\(^{-1}\) are shown in Figure10.2. This region corresponds to the C–H stretching of the \textbf{Fc2} molecule. The main two vibrational bands for both spectra are observed at 2923, and 2851 cm\(^{-1}\) and are assigned as the asymmetric methylene stretching mode \( (\nu_{\text{as}}(\text{CH}_2)_{\text{Fc}}) \), and the symmetric methylene stretching mode \( (\nu_{\text{s}}(\text{CH}_2)_{\text{Fc}}) \) respectively. The 3100 cm\(^{-1}\) peak which corresponds to CH stretching mode of the ferrocene ring \( (\nu(\text{CH})_{\text{Fc}}) \) was very weak. The positions of these bands are essentially the same as those reported in literature (Popenoe et al., 1992, Sato et al., 1994). The comparison of absorption peaks indicates that there is no change in the spectra before and after the voltammetric cycling suggesting that no chemical change occurred. Quantitative analysis of the spectra is not possible but it could be estimated by peak area that approximately 15±5\(\%\) of the material was lost from the surface. Thus, some material has been lost which may well be due to physical desorption of the material from the electrode surface.
Figure 10.2 FTIR spectrum (3200 – 2700 cm\(^{-1}\) region) of Fc2 on a gold electrode surface before and after 100 cycles in 1.0 M H\(_2\)SO\(_4\).

The chemical stability of Fc2 was further investigated by X-ray Photoelectron Spectroscopy (XPS) studies. For this purpose a gold electrode was specially fabricated of dimensions such that it could be held and manipulated in the XPS instrument (AXIS ULTRA X-ray Photon Spectroscopy Instrument). The details of this electrode are given in Chapter 4.

The electrode was cleaned as described in Chapter 4, and its XPS recorded as follows:

Experiment 1: Spectra of the freshly cleaned gold electrode.

Experiment 2: Spectra of the freshly formed thin film of Fc2 on the gold surface from experiment 1.
Experiment 3: Spectra of the Fe₂ on gold from Experiment 2 after it undergone 100 cyclic voltammetric cycles in the range 0 – 0.7 V in 1.0 M H₂SO₄. The resultant scans are shown in Figures 10.3, 10.4, and 10.5 respectively.

The spectrum in Figure 10.3 is similar to that reported by Li et al. (Li and Lieberman, 1999). Only gold, carbon and oxygen peaks are observed.

![XPS spectrum of polished and cleaned gold electrode.](image)

The carbon and oxygen peaks which appear in the bare gold electrode (at 285 eV and 533 eV respectively) were explained by Li et al as a surface contamination ("adventitious carbon") which is present to some extent on all the samples. No peaks for sulphur and iron were observed in this scan.
The XPS spectra of Figures 10.3 to 10.6 were quantified by evaluating the area under each peak with the curve fitting algorithm described in Chapter 4. The results of this analysis are summarised in Table 10.1. The binding energy (BE) and the calculated percent atomic concentration for each of the elements are listed in this table. The Au/C ratio and O/C ratio for each of the experiments was calculated and are noted in Table 10.2.

Table 10.1 Corrected Binding Energies (BE / eV) and Intensities (% AC) of XPS Peaks for Experiments 1, 2, and 3.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>O (1s)</th>
<th>C (1s)</th>
<th>Au (4f)</th>
<th>Fe (2p)</th>
<th>S (2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE</td>
<td>%AC</td>
<td>BE</td>
<td>%AC</td>
<td>BE</td>
</tr>
<tr>
<td>1</td>
<td>533.0</td>
<td>14.18</td>
<td>285.5</td>
<td>68.04</td>
<td>84.5</td>
</tr>
<tr>
<td>2</td>
<td>532.5</td>
<td>6.67</td>
<td>285.5</td>
<td>90.28</td>
<td>84.5</td>
</tr>
<tr>
<td>3</td>
<td>533.0</td>
<td>7.52</td>
<td>285.5</td>
<td>85.58</td>
<td>85.0</td>
</tr>
</tbody>
</table>

Table 10.2 Gold/Carbon and Oxygen/Carbon ratios

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Au/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>0.015</td>
<td>0.074</td>
</tr>
<tr>
<td>3</td>
<td>0.080</td>
<td>0.088</td>
</tr>
</tbody>
</table>
Figure 10.4 Low resolution, wide scan XPS spectrum of polished and cleaned gold electrode modified with Fe2.

Figure 10.5 Low resolution, wide scan XPS spectrum of polished and cleaned gold electrode modified with Fe2 after 100 cycles.
The spectrum in Figure 10.4 shows additional iron and sulphur peaks corresponding to the \textbf{Fc2} film compared to the gold, carbon, and oxygen peaks which were seen for the bare gold (Figure 10.3). The results can be interpreted in terms of the binding energies reported in the literature. (Briggs and Seah, 1990, Li and Lieberman, 1999, Ulman, 1991) Sulphur groups at 163 BE can be assigned to thiol group attached to gold (Li and Lieberman, 1999), and the 708 binding energy can be related to the presence of Fe of the ferrocene molecule on the surface of gold. (Briggs and Seah, 1990) As expected the intensity of the gold peak is lower and that of carbon is higher in Figure 10.4 than in Figure 10.3. This is also reflected in the relative Au/C and O/C ratios (Table 10.2). The Au/C and O/C ratios for the spectra of the \textbf{Fc2} film after 100 voltammetric cycles lies in between that of the bare gold (Experiment 1) and that of gold freshly coated with \textbf{Fc2} (Experiment 2). This indicates that some of the \textbf{Fc2} material has been lost during the voltammetric cycling process. This loss is estimated to be approximately 5\% based upon the change in the percentage of carbon for experiments 2 and 3.

The stability of the \textbf{Fc2} film was also studied by using the electrochemical quartz crystal nanobalance (EQCN) technique (Bruckenstein and Shay, 1985, Varineau and Buttry, 1987, Ward, 1988). This technique enables one to monitor, simultaneously, the mass changes which occur during an electrochemical experiment, and has been used extensively by several workers and found to be valuable in measuring the mass changes at electrode surfaces after electrodeposition of metals (Buttry and Ward, 1992, Ward, 1995) also in studies on using the EQCN as a modified electrode to study surface processes in a

The crystal were coated with the ferrocene derivative as described in Chapter 4. After modification the crystals were rinsed with hexane followed by Millipore water, and fitted to the EQCN cell (Chapter 4) containing 1.0 M H₂SO₄.

Figure 10.6 shows the cyclic voltammogram of the Fe₂ coated on the quartz crystal.

Figure 10.6 (A) cyclic voltammetry of Fe₂ film on a gold EQCN in 1.0 M H₂SO₄, scan rate was 100 mVs⁻¹. (B) mass response obtained simultaneously with the cyclic voltammogram.
The mass increase and decrease is in line with the oxidation followed by reduction during cyclic voltammetric cycle. This indicates that as $\text{Fc}_2^+$ is formed by oxidation of $\text{Fc}_2$, the mass increases as a result of incorporation of counter anions into the immobilised film of $\text{Fc}_2$. This process is reversed when the $\text{Fc}_2^+$ is reduced back to $\text{Fc}_2$ during the reverse cycle. However, as can be seen from Figure 10.7, the base line mass of the ferrocene film increases as repeated cycling. The change in mass ($\Delta \text{mass}$) as a function of the cycle number is plotted in Figure 10.8. The increase in mass is at a maximum during the first cycle but levels out after about four cycles. This can be explained by assuming that the sharp increase in mass during the first few cycles results from the retention of the solvent molecules associated with the counter anion in the film. Conditioning or opening of the otherwise insoluble ferrocene film by oxidation/reduction and consequent quenching of the material with the solvent is well known (Murray, 1984).

The fact that $\Delta \text{mass}$ becomes constant suggests that the material undergoes reversible oxidation without being lost from the surface. However, this conclusion is valid only up to the number of the repeated voltammetric cycles carried out in this study i.e. 7 cycles. To be more meaningful, the results for at least 100 cycles should be collected. Unfortunately, this was not possible because of the difficulties associated with maintaining the quartz crystal in working order over extensive periods necessary for 100 CV cycles.
Figure 10.7 Mass response obtained during continuous voltammetric cycles of Fc2 film on a gold EQCN in 1.0 M H2SO4.

Figure 10.8 Difference in mass between the voltammetric cycles.
10.3 Conclusion

The potentiometric behaviour of the redox couple of $\text{Fc}_2$ immobilised on a gold substrate in concentrated $\text{H}_2\text{SO}_4$ has been investigated. The results show that the couple responds to acid concentration reversibly in the range 1–5 M and hence could be used to measure the change in acid concentration in a lead-acid battery. However, the reproducibility of the results tends to degrade over approximately 15 days. The chemical stability of the material has been investigated by fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and electrochemical quartz crystal nanobalance (EQCN) technique. It is found that some of the material is lost from the surface of the electrode during repeated oxidation/reduction cycling. The estimates for the loss of the material by various methods used in the study vary but are of the order 10±5% over 100 cycles.

10.4 References


The electrochemistry of some ferrocene derivatives coated on gold substrate in the form of surface modified electrodes (SME) in concentrated sulphuric acid solutions simulating state of charge of lead-acid batteries has been investigated. The objective was to determine whether such SME’s could be used to determine state of charge of lead-acid batteries potentiometrically. The investigated ferrocenes included, simple ferrocene, poly(vinylferrocene), bridged ferrocenes in which the two cyclopentadienyl groups are linked by –CH₂– chains of varying lengths and alkanethiol substituted ferrocenes. The study involved examination of cyclic voltammetry of the ferrocene derivatives in various acids particularly sulphuric acid in the concentration range 1–5 M, which simulates the state of charge of lead acid battery.

The important conclusions of the work are

- all of the investigated ferrocenes undergo one electron reversible oxidation/reduction at the surface of gold electrode in aqueous media.

- the anodic and cathodic peak potentials of all the investigated ferrocenes are independent of pH in the range 2–10 in aqueous solutions of K₂SO₄, KCl and NaClO₄.
• in concentrated acid solutions (H$_2$SO$_4$, HCl and HClO$_4$) the anodic and cathodic peak potentials shift, almost linearly, to less positive potentials with increasing acid concentration in the range 1–5 M.

• the attachment of alkanethiol group to the ferrocene molecules improves the retainability of the ferrocene molecules at the surface of gold electrode. This is possibly linked to strong chemisorption of the thiol group on the gold surface.

• the retainability of the ferrocene compounds at the gold electrode surface is higher of ClO$_4^-$ than in Cl$^-$ and SO$_4^{2-}$ media. This may be related to salt formation between the anion and the ferricenium ion generated on oxidation. Such salt formation changes the activity of ferricenium ion at the surface of the electrode.

• bridged ferrocenes are chemically more stable than simple ferrocenes in concentrated H$_2$SO$_4$ media.

• in ketothiol ferrocenes the presence of a carbonyl group in the alkanethiol chain decreases stability of the ferrocene compounds in aqueous SO$_4^{2-}$ and ClO$_4^-$ media. The relative stability of ketothiol the ferrocenes is somewhat higher in ClO$_4^-$ than in SO$_4^{2-}$ media.
the redox potential of 1,1'-Bis(11-mercaptoundecyl)ferrocene couple varies linearly with sulphuric acid concentrations in the range 1–5 M. Of all the investigated ferrocenes, the potentiometric response of this couple is the most stable and reproducible in concentrated sulphuric acid. Hence this couple has the potential of measuring state of charge of lead-acid batteries. However, its chemical stability (about 15 days) limits its application. Thus, Further work on identification more stable ferrocene couples is needed.
Synthesis of 11-Mercaptoundecylferrocene (V) (Scheme 1)

Ferrocene I was acylated with 11-bromoundecanoylchloride in the presence of aluminium chloride (Okahata et al., 1989) to produce 11-bromoundecanoylferrocene II in 45% yield. Reaction of II with thiolacetic acid and sodium methoxide (Bain et al., 1989) afforded 11-mercaptoundecanoylferrocene III in 42% yield.

11-Bromoundecylferrocene IV was prepared in good yield by reduction of the acylferrocene II with zinc amalgam and hydrochloric acid. (Okahata et al., 1989) Treatment of IV with thiolacetic acid and sodium methoxide (Bain et al., 1989) afforded 11-mercaptopoundecylferrocene V in 40% yield.
1,1'-Bis-(11-mercaptopoundecyl)ferrocene (IX) (Scheme 2)

1,1'-Bis-(11-bromoundecanoyl)ferrocene VI was prepared in 50% yield by acylation of ferrocene I with 11-bromoundecanoyl chloride in the presence of aluminium chloride. (Okahata et al., 1989) On treatment with thiolacetic acid in the presence of sodium methoxide (Okahata et al., 1989), VI was converted into 1,1'-Bis-(11-mercaptopoundecanoyl)ferrocene VII in 74% yield.

1,1'-Bis-(11-bromoundecyl)ferrocene VIII was prepared by reduction of the diacyl ferrocene VI with zinc amalgam and hydrochloric acid. (Bain et al., 1989) Treatment of
with thiolacetic acid and sodium methoxide afforded 1,1'-Bis-(11-mercaptoundecyl)ferrocene IX in 43% yield.

Scheme 2

Synthesis of 2-(11-Mercaptoundecyl)[3](1,1')ferrocenophane (XVII) (Scheme 3)

Ferrocene I was formylated with N-methylformanilide in presence of phosphorus oxychloride (Rosenblum et al., 1963) to produce formylferrocene X in 73% yield. Compound X on treatment with malonic acid in presence of piperidine and pyridine (Osgerby and Pauson, 1958) afforded β-ferrocenylacrylic acid XI in 73% yield, which on hydrogenation over Pd-C (Rosenblum et al., 1963) gave β-ferrocenylpropionic acid
XII in 80% yield. β-Ferrocenylpropionic acid XII was cyclised by treatment with trifluoroacetic anhydride (Rosenblum et al., 1963) to give α-keto-1,1'-trimethyleneferrocene XIII in 80% yield. Reduction of XIII with lithium aluminium hydride and aluminium chloride (Rinehart et al., 1962) gave [3](1,1')ferrocenophane XIV in 45% yield.

[3](1,1')ferrocenophane XIV was acylated with 11-bromoundecanoyl chloride in the presence of aluminium chloride (Okahata et al., 1989) to produce 1,1'-trimethylene-3-(11-bromoundecanoyl)ferrocene XV in 55% yield. Reduction of XV with zinc amalgam in hydrochloric acid (Okahata et al., 1989) afforded 1,1'-trimethylene-3-(11-bromoundecyl)ferrocene XVI in 62% yield. Treatment of XVI with thiolacetic acid and sodium methoxide (Bain et al., 1989) produced 2-(11-Mercaptoundecyl)[3](1,1')ferrocenophane XVII in 55% yield.
Scheme 3
Synthesis of 4-(11-Mercaptoundecyl)[32](1,1')(3,3')ferrocenophane (XXV) (Scheme 4)

[3](1,1')ferrocenophane XIV on formylation with N-methylformanilide (Rosenblum et al., 1963) gave 1,1'-trimethylene-3-formylferrocene XVIII in 66% yield. Condensation of XVIII with malonic acid in presence of piperidine and pyridine (Osgerby and Pauson, 1958) afforded 1,1'-trimethylene-3(β-acrylic acid) ferrocene XIX in good yield. Compound XIX was hydrogenated in absolute ethanol over Pd-C (Rosenblum et al., 1963) to give 1,1'-trimethylene-3-(β-propionic acid)ferrocene XX in 90% yield, and cyclisation of this compound using trifluoroacetic anhydride (Rosenblum et al., 1963) produced 3,3'-(α-ketotrimethylene)-1,1'-trimethyleneferrocene XXI in 80% yield. Compound XXI was reduced with lithium aluminium hydride and aluminium chloride (Rinehart et al., 1962) to give [32](1,1')(3,3')ferrocenophane XXII in 80% yield.

The doubly-bridged ferrocene XXII was acylated with 11-bromoundecanoyl chloride in the presence of aluminium chloride (Okahata et al., 1989) to produce 1,1'-3,3'-bis(trimethylene)-2-(11-bromoundecanoyl)ferrocene XXIII in 40% yield. Reduction of the carbonyl group of XXII with zinc amalgam and hydrochloric acid (Okahata et al., 1989) afforded 1,1'-3,3'-bis(trimethylene)-2-(11-bromoundecyl)ferrocene XXIV in 56% yield. Compound XXIV was treated with thiolacetic acid and sodium methoxide (Bain et al., 1989) to give 4-(11-Mercaptoundecyl)[32](1,1')(3,3')ferrocenophane XXV in 60% yield.
APPENDIX I

Scheme 4
Synthesis of 3-(11-Mercaptoundecyl)[33](1,1')(2,2')(4,4')ferrocenophane XXXIII (Scheme 5)

Formylation of [32](1,1')(3,3')ferrocenophane XXII with N-methylformanilide (Rosenblum et al., 1963) gave 1,1'-3,3'-bis(trimethylene)-4-formyl ferrocene XXVI in 63% yield. Reaction of XXVI with malonic acid (Osgerby and Pauson, 1958) produced 1,1'-3,3'-bis(trimethylene)-4-(β-acrylic acid)ferrocene XXVII in 54% yield, and hydrogenation of this compound over Pd-C (Rosenblum et al., 1963) afforded 1,1'-3,3'-bis(trimethylene)-4-(β-propionic acid)ferrocene XXVIII in 74% yield. Compound XXVIII, on cyclization in presence of trifluoroacetic anhydride (Rosenblum et al., 1963) gave 4,4'-(α-ketotrimethylene)-1,1'-3,3'-(trimethylene)ferrocene XXIX in 80% yield. Reduction of keto group with lithium aluminium hydride and aluminium chloride (Rinehart et al., 1962) produced [33](1,1')(2,2')(4,4')ferrocenophane XXX in 86% yield. Acylation of this compound with 11-bromoundecanoyl chloride in presence of aluminium chloride (Okahata et al., 1989) gave 3-(11-Bromoundecanoyl)[33](1,1')(2,2')(4,4')ferrocenophane XXXI in 51% yield. Reduction of the keto group in the acyl chain (Okahata et al., 1989) produced 3-(11-Bromoundecyl)[33](1,1')(2,2')(4,4')ferrocenophane XXXII in 95% yield. Compound XXXII, on reaction with thiolacetic acid in presence of sodium methoxide (Bain et al., 1989), gave 3-(11-Mercaptoundecyl)[33](1,1')(2,2')(4,4')ferrocenophane XXXIII in 38% yield.
Synthesis of 3-(11-Mercaptoundecyl)[5](1,1')ferrocenophane XXXX (Scheme 6):

Acetylferrocene XXXIV was prepared by the reaction of ferrocene with acetyl chloride and aluminium chloride. (Barr and Watts, 1968) Reaction of XXXIV with β-chloropropionyl chloride in presence of aluminium chloride (Barr and Watts, 1968) gave 1-acetyl-1'-(β-chloropropionyl)ferrocene XXXV in 73% yield. Compound XXXV on cyclised in presence of sodium hydroxide in ethanol (Barr and Watts, 1968) produced
1,1’-(1,5-diketopentamethylene)ferrocene **XXXVI** in 93% yield. Reduction of keto groups of **XXXVI** with lithium aluminium hydride and aluminium chloride (Barr and Watts, 1968) gave [5](1,1’)ferrocenophane **XXXVII** in 86% yield. Acylation of this compound with 11-bromoundecanoyl chloride in presence of aluminium chloride (Okahata et al., 1989) gave 1,1’-(pentamethylene)-3-(11-bromoundecanoyl) ferrocene **XXXVIII** in 17% yield. Reduction of the keto group in the acyl chain (Okahata et al., 1989) produced 1,1’-(pentamethylene)-3-(11-bromoundecyl)ferrocene **XXXIX** in 67% yield. Compound **XXXIX**, on reaction with thiolacetic acid in presence of sodium methoxide, (Bain et al., 1989) gave 3-(11-Mercaptoundecyl)[5](1,1’)ferrocenophane **XXXX** in 81% yield.

![Scheme 6](image-url)
References


