Electrochemistry of carbon nanofibre composite films

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Electrochemistry of Carbon Nanofibre Composite Films

by

Maria A. Murphy

Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy
of
Loughborough University

June 2006
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Acknowledgments

I would like to thank my supervisors, Drs. Frank Marken and Geoff Wilcox, for their guidance throughout my PhD studies and my Director of Research, Prof. Steve Fletcher. I would also like to acknowledge John S. Bates for his invaluable help with obtaining and discussing electron microscopy data and Gary Critchlow for Auger spectra and analysis. Financial support from the Faculty of Science, and from Dana Glacier Vandervell Bearings (Rugby) is gratefully acknowledged.
Abstract

The work carried out for this thesis focussed on four main areas: (i) the examination and optimisation of the conditions for carbon nanofibre (CNF) growth, both unsupported and as films on substrates, (ii) the electrochemical characterisation of the CNF material before (as-grown) and after solubilisation (oxidation), (iii) the formation and investigation of CNF thin film electrodes, and (iv) the (co-) deposition of the CNFs with metals from aqueous plating solutions.

CNFs are grown at an iron nanoparticle catalyst produced from an iron oxide precursor. After exploratory work with different types of iron oxide precursors, a suitable and universally applicable catalyst is identified. CNFs are characterised by electron microscopy, spectroscopy, and electrochemistry. When grown onto a ceramic substrate, the ‘as-grown’ CNF material is shown to act as a porous, high surface area electrode with the ability to strongly adsorb aromatic molecules, such as hydroquinone, benzoquinone, and phenol.

Following the oxidation of the bulk CNFs in concentrated nitric acid the resulting oxidised fragments are soluble in alkaline aqueous solution. Deposition onto inert carrier electrodes and immersion into acidic aqueous electrolyte allows a new electrochemical signal to be detected, consistent with a surface bound quinone. The layer-by-layer and sol-gel deposition of the solubilised CNF material with chitosan (a natural poly-cationic ionomer) and silicates, respectively, allows novel carbon structures to be grown and used as electrodes.

CNF/metal (zinc and copper) composites were electrodeposited. Conventional and pulse plating methods were investigated under various conditions of agitation, current density, and time. The electrochemistry of the Cu and Zn plating solutions was explored. The metal/CNF composite films grown were characterised using the quartz crystal microbalance (QCM), field emission gun scanning electron microscopy (FEGSEM), energy dispersive X-ray analysis (EDX), and Auger electron spectroscopy (AES) techniques.
Keywords
Carbon nanofibre growth, electrochemistry, hydrophobic carbon nanofibres, supported carbon nanofibres, hydrophilic carbon nanofibres, composite electrodes, thin film electrodes, metal/carbon nanofibre electrodeposition, QCM
Chapter 1
Introduction
1.1. Aims

The work described in this thesis was a collaboration between the Department of Chemistry and the Institute of Polymer Technology and Materials Engineering. The main aims were to explore and exploit the properties of Carbon Nanofibre (CNF) materials in novel electrochemical and electrodeposition processes, more specifically:

(1) to develop a reliable synthesis for carbon nanofibres
(2) to characterise the properties of carbon nanofibre materials
(3) to form and investigate thin film electrodes containing carbon nanofibres
(4) to develop metal/carbon nanofibre codeposition techniques based on electrodeposition

1.2. Carbon Materials

CNFs have been known for many years as an unwanted product from the catalytic conversion of carbon containing gases. However, the discovery of the structure of carbon nanotubes (CNT) by Iijima in 1991 [1] has given CNF technology a recent boost. CNFs exhibit some similarities to fullerenes and nanotubes. They combine the attributes of active carbon, possessing high surface area, e.g., the activated carbons used in supercapacitors, whose energy density is proportional to the surface area per unit volume of the carbon, and the electrical conducting properties of graphite. Carbon fibres, which have previously been referred to as carbon filaments, have been known since the 19th century. In 1889 a process describing the growth of carbon filaments from carbon containing gases was patented [2]. The growth took place in a metallic container, which, it was later realised, acted as a catalyst for the reaction. Robertson was one of the first to appreciate that graphitic carbon could be produced at relatively low temperatures by the interaction of methane and metal surfaces [3].

The arc-discharge and laser ablation methods, used for the growth of fullerenes and nanotubes, lead to mixtures of carbon products, which results in awkward purification to yield the desired material. From a practical point of view the catalytic vapour growth of nanofibres seems a reasonable alternative with a number of advantages over these methods [4, 5]. The arc technique is a batch process, so the amount of material which can be generated is limited and the deposits produced contain significant
amounts of nanoparticles. Using the catalytic vapour deposition technique, very pure CNFs with good size uniformity can be achieved, controlled by the size of the catalyst particles, and the process can be scaled up to produce large amounts of fibres.

A number of metal/metal alloy catalysts are used to produce graphitic CNFs. These include iron, copper, and nickel [6], chromium, vanadium, and molybdenum. The metals can be used as either bulk particles, typically 100 nm in diameter, or as supported particles, 10 - 50 nm in diameter. Various sources of carbon are possible, e.g., methane, carbon monoxide, synthesis gas (H₂/CO), ethyne, or ethene. The usual temperature for CNF growth is between 700 and 1200 K.

The steady state growth of CNFs from a catalyst particle is represented schematically in Fig. 1.1.

![Figure 1.1. Schematic representation of the catalytic growth of a CNF using a carbon containing gas.](image)

The schematic is taken from the review of de Jong and Geus [5]. The first step, (1), is the decomposition of a carbon containing gas on the metal surface. Carbon atoms are deposited on the surface with an associated release of gaseous products, such as molecular hydrogen, carbon dioxide, and water, depending on the carbon gas used. Then, (2), carbon atoms dissolve in and diffuse through the bulk of the metal, with surface diffusion possibly playing a part in this. Finally, (3), precipitation of carbon in the form of a CNF consisting of graphene occurs.

It turns out that the structure of the CNF growth at the catalyst surface can be
modified and controlled. The schematic in Fig. 1.2 (a) illustrates the tubular type of fibres that can be obtained from iron particles [7] and from nickel particles at elevated temperatures [8].

![Schematic representation of (a) the parallel or tubular fibre structure and (b) the fishbone/herringbone structure [5].](image)

Figure 1.2. Schematic representation of (a) the parallel or tubular fibre structure and (b) the fishbone/herringbone structure [5].

In the tubular type of fibre only the basal plane of graphite is exposed at the surface. The herringbone type of CNF has only graphite edge sites exposed and should therefore exhibit a very different reactivity during adsorption processes. This is as a consequence of the number of graphite edge atoms exposed in (a) being relatively small compared to (b), and therefore, the surface area of the parallel fibre expected to be significantly lower than that of the herringbone fibre. The latter form is mainly observed with nickel or nickel/iron alloys and methane as the carbon source.

Snoeck et al. used a theoretical model to explain the growth of both full and hollow fibres from supported metal particles [8]. The nucleation of filamentous carbon requires the supersaturation of carbon in nickel, followed by reconstruction and faceting of the particle and precipitation of graphitic layers. Deformation of the nickel particle takes place upon carbon filament formation. It was proposed that the deformation of the nickel particle and the appearance of the carbon filaments are related to their relative rates of nucleation and of the diffusion of carbon through the nickel and to differences in the diffusional path length on the metal/carbon interface causing differences in the rate of carbon supply leading to the formation of either hollow or full carbon filaments.

The addition of excess hydrogen is required, when either C₂H₄ or CO are used as the
carbon source, to balance the amount of carbon atoms in the nanofibre growth process. Hydrogen reduces the amount of carbon atoms formed and can therefore prevent encapsulation, and thus, deactivation of the catalyst [9].

1.3. Soluble Carbon Nanosols
Since this work includes the solubilisation of CNFs soluble carbon nanosols are now briefly discussed. Colloidal carbon refers to carbon sols in which both the amorphous and crystalline forms are dispersed in water or organic media. Colloidal carbon has many applications including use in inks and paints, as a lubricant, fuel and as an adsorbent.

Soluble or colloidal forms of carbon have been known for over 100 years [10], when Bartoli and Papasgoli obtained stable suspensions of elemental carbon during a study of the products obtained by the electrolysis of acids and alkalis with a carbon anode. In each case the anode disintegrated to yield soluble black products.

Carbon sols can be produced by a number of methods [11]. Anodic disintegration involves the electrolysis of ammonia or alkali; the carbon anode is consumed resulting in the sol. In electric arc disintegration stable organosols can be derived from an organic liquid, e.g., carbon tetrachloride, chloroform, rather than from the disintegration of the electrodes [12]. Decomposition of organic compounds yields a sol mixture, e.g., the action of sulphuric acid on sucrose [13]. The sols can also be prepared by peptisation, e.g., aquadag and oildag, which are colloidal dispersions of graphite in water and oil, respectively.

1.4. Applications of Carbon Nanofibres/tubes
Nano carbons, in the form of single walled nanotubes (SWNT), multi walled nanotubes (MWNT), nanofibres or nanostructured carbon, have varied applications. These include being utilised in the areas of electrochemistry, composites, field emission, and electronics. The largest current commercial use of CNTs is within thermoplastic matrices for the purpose of anti-static dissipation, particularly in the automotive and electronics industries. Such applications exploit the bulk properties of relatively defective catalytically grown materials, while other applications exploit the
properties of individual perfect CNTs. The thermal conductivity, thermal stability, wear resistance and other properties are also of interest.

The areas of application mentioned above are now discussed in more detail:

(A) Electrochemistry
Carbon in the form of graphite is a common and well established stable electrode material, which does not undergo oxidation or reduction over a wide potential range. Consequently, CNTs with their large surface area and low resistivity have become an interesting material with potential novel uses in electrochemistry.

Porous carbons are used as capacitors because of their high surface area, \( A \), and low double layer thickness, \( d \), since \( C = \varepsilon A/d \), where \( \varepsilon \) is the dielectric constant and \( C \) is the capacitance, as discussed in [14]. Although SWNTs have the highest surface area to volume ratio of any carbon material and so should make the ultimate capacitor, the surface area and energy density of activated carbon is already near the theoretical maximum. The advantage to using CNTs is their lower resistance compared to activated carbon, which could greatly increase their power density. The problem is contacting the CNTs to a polymer backing at low temperature and low cost.

CNFs are also being used to increase the conductivity of porous carbon electrodes in Li batteries to improve their power density [15]. CNTs exhibit numerous advantageous characteristics when used as a filler in lithium ion battery electrodes, including [16]:

a) the small CNT diameter allowing homogeneous distribution in the thin electrode material, introducing a larger surface area to react with the electrolyte
b) improved electrical conductivity due to the high electrical conductivity of the CNTs, acting as an electrical bridge between graphite particles
c) highly flexible electrode due to the CNT mat structure
d) improved electrolyte penetration due to the homogeneous distribution of the CNTs surrounding the anode material
e) the presence of CNTs absorbs stress caused by the intercalation of lithium
Points (a) to (d) above are relevant advantages to many potential applications of CNT, whereas points (e) and (f) are more specific to applications in Li ion batteries.

CNTs decorated with metal nanoparticles, acting as fuel cell electrodes, have doubled the performance of certain fuel cells, due to the increased catalytic activity of CNT based electrodes [17, 18]. Matsumoto et al. have demonstrated that CNTs can significantly reduce the Pt catalyst loading in polymer electrolyte fuel cells in comparison with commercial carbon black materials [19].

It has been shown that CNFs are capable of providing the required porosity and pore structure, as well as excellent electrical conductivity, in order to be used as a material for gas diffusion electrode production for use in fuel cell cathodes [20].

Ryu et al. studied the effect of the mechanical grinding of the catalyst on the resulting CNFs. They established that the size and uniformity of the as-grown CNFs could easily be tailored by tuning the mechanical grinding time. It was found that no Pt agglomeration occurred on the homogeneous bundles and twisted CNFs produced with mechanically ground catalyst, which have surface pits that may help to disperse the loaded Pt. These CNFs exhibited superior fuel cell performance, compared to those produced with unground catalyst [21].

CNTs and CNFs can be grown on a variety of substrates, which can be used directly as electrodes. This includes the growth of CNTs on fuel cell support materials, which subsequently have Pt particles deposited on them. Consequently, a composite electrode with an electrical path between the Pt catalyst and the carbon backing was obtained [22].

A MWNT/chitosan modified glassy carbon electrode has been used for the electrochemical determination of bromide. The CNTs were in the form of a porous meshy structure and the chitosan can effectively absorb halogen ions due to its amino
and hydroxyl groups. It is this combination of properties that led to the remarkable enhancement in the peak current observed compared to the use of chitosan or MWNTs alone [23].

MWNTs grown onto a platinum substrate have been used for the development of an amperometric biosensor. The opening and functionalisation by oxidation of the CNT array allows for the efficient immobilisation of the glucose oxidase enzyme, while the platinum substrate provides the direct transduction platform for signal monitoring [24]. The structure dependent metallic character of CNT should facilitate the promotion of electron transfer reactions at low overpotentials. This, along with their high surface area, provides the basis for unique biochemical sensing systems.

A hemin-modified MWNT electrode (hemin immobilised through π-π porphyrin-CNT interaction) was successfully constructed by Sheu et al. [25]. Cyclic voltammetry showed that the magnitude of the current for oxygen reduction was four times greater than that observed on the same MWNT electrode without immobilised hemin. The increase in the peak current and the positive shift in potential indicate that the hemin adsorbed at the surface of the CNTs electrocatalyses the reduction of \( \text{O}_2 \). The modified electrode retained the electrical and structural properties of the CNTs, while adopting the electrocatalytic properties of hemin.

It was found that the electro-oxidation of hydrazine was greatly improved at a CNT powder microelectrode; the CNTs could catalyse the anodic process. It was also shown that this type of electrode had a high sensitivity for hydrazine and could thus be used as a sensor for its detection [26].

A recent review by Banks et al. questions the use of multi walled CNT [27]. They highlight the advantages of edge plane pyrolytic graphite electrodes as electrode substrates in electroanalysis, due to the highly reactive edge plane sites, which allow low detection limits, high sensitivities, improved signal to noise characteristics and low overpotentials to be achieved. It was shown that, in a number of cases, edge plane electrodes can replace CNT modified electrodes due to their ease of preparation, cost, and relative advantages of reactivity.
(B) Composite Materials

The strong mechanical properties of CNTs, due to the carbon/carbon covalent bond, are highly dependent on the atomic structure of the CNTs and on the number of shells present; they also exhibit useful electrical and thermal conductivity properties. Therefore, CNTs have been extensively studied as fillers in various matrices, especially polymers [28, 29].

Conducting carbon/epoxy composites generally consist of carbon black in a polymer as discussed by Robertson in [14], where it is illustrated that less than 0.01 % MWNTs is required compared to about 1 % carbon black to reach the percolation threshold, which gives a continuous path across the sample. This type of composite was first exploited by Hyperion to electrostatically apply paint to car components [30].

CNTs have been used as fibres or whiskers to toughen nanocomposites. For instance, they have been used to enhance the hardness and toughness of alumina films and are a good candidate for wear-resistant coatings [31]. Toughness enhancement was obtained through crack deflection, crack bridging, and fibre pullout.

Indium tin oxide (ITO) is used as a transparent conducting material in displays. Flexible displays are of current interest but ITO is brittle and suffers from poor adhesion to plastics. CNTs are flexible and compatible with polymer substrates and are transparent if thin enough [32], giving them huge potential for application in this area.

The mechanical properties achieved have not reached expectation. Much lower than anticipated Young’s moduli have been achieved since the SWNTs are generally distributed as bundles and also only small amounts of the CNTs are dispersed in the host, with insufficient bonding across the nanotube/host interface. These composites tend to fail either by fracture at the CNT/host interface, or in the case of MWNTs, by pull out of the different shells of the MWNTs. This is discussed further in [14].

Tu et al. produced Ni-P-CNT composite coatings and CNT/copper matrix composites by electroless plating and powder metallurgy techniques, respectively [33]. Their
results demonstrated that the Ni-P-CNT electroless composite coating exhibited higher wear resistance and a lower friction coefficient than Ni-P-SiC and Ni-P-graphite composite coatings. After annealing, the wear resistance of the CNT composite improved. CNT/copper matrix composites showed a lower wear rate and friction coefficient compared with pure copper.

Chen et al. also prepared cobalt nanoparticle coated CNT by electroless plating. The CNTs underwent an oxidative treatment and surface modification (Sn$^{2+}$ and Pd$^{2+}$ activation) prior to plating, which resulted in the formation of Pd/Sn particles as active sites that initiate the deposition of cobalt [34]. They demonstrated the feasibility of electroless plating for the preparation of a one-dimensional nanoscale composite, suggesting that this might be useful in the generation of high strength adhesion between nanotubes and a metal matrix, using the CNT as a template.

CNTs have also been investigated for the formation of electrodeposited metal/CNT composites, which is discussed in Sec. 1.5.2.

(C) Field Emission Devices

Field emission, FE, is the emission of electrons from a solid under an intense electric field. The advantages of CNTs over other field emitting materials have been outlined by de Jonge [35]. An application of CNTs in FE is as an electron gun for scanning electron microscopes and transmission electron microscopes [36], further details are available in [14].

FE displays are another potential application. CNTs have advantages in that the technology is relatively simple compared to previously used materials and the CNT display is robust [35].

(D) Electronic Devices

Room temperature field effect transistors (a three terminal switching device, here consisting of a SWNT and two metal electrodes) have been fabricated. The fabrication of this three terminal switching device at the level of a single molecule represents an important step towards molecular electronics [37]. Furthermore, Avouris et al. have reported the selective tailoring of the properties of bundles of SWNTs allowing the
generation of arrays of nanoscale field effect transistors [38].

1.5. Composite Electrodeposition

In this section, composites will be discussed in terms of the manner in how composite electrodeposition occurs and with specific literature examples of metal/CNF electrodeposits.

A composite material is a three-dimensional combination of at least two chemically distinct materials, with a distinct interface separating the components, created to obtain properties that cannot be achieved by any of the components acting alone [39]. Composite electrodeposition (also known as electrolytic co-deposition), or the ability to co-deposit inert particles within a metal matrix, can be traced back to the early days of electrodeposition. Though inert, the combination of the metal with this second phase results in a new functionality in the composite material. The formation of rough deposits was attributed to the presence of impurities in the electrolyte, which co-deposited during electrolysis.

The particles that may be entrapped include ceramic, polymer, and metal powders suspended in the electroplating bath. The amount of particles co-deposited with the metal depends on a number of factors including current density, potential, temperature, bath agitation, and particle concentration.

In this work the formation of novel Zn/CNF and Cu/CNF composite electrodeposits is investigated. A number of the factors listed above are considered and are discussed in more detail in subsequent chapters.

1.5.1. Metal/Non-metal Composite Electrodeposition Processes

The simultaneous deposition of particles and metal can cause interesting changes in the physical and mechanical properties of the coatings. For example, it has been shown by Fransaer et al. that the co-deposition of liquid-containing microcapsules enables the production of self-lubricating coatings through the inclusion of oil [40].

Guglielmi was the first to attempt to describe the mechanism of electrolytic co-
deposition [41]. The mechanism proposed is based on two consecutive adsorption steps. The first step is postulated to be mainly physical in character and to produce a layer of loosely adsorbed particles at high coverage. The second step is thought to be field assisted, therefore substantially electrochemical in character, and produces a strong adsorption of the particles onto the electrode. The strongly adsorbed particles are then progressively submerged by the growing metal. In the first step the particles are still coated by a thin layer of adsorbed ions and solvent molecules, which screens the interaction between the electrode and the particles. In the second step, the electrical field existing at the interface helps to uncover the particles, producing a stronger field assisted adsorption. An analogy exists between the two stages of particle adsorption and the adsorption of ions in the inner and outer Helmholtz planes of the electrode. Guglielmi verified his model for the co-deposition of titania and silicon carbide with nickel from a nickel sulfamate bath. Also, Celis and Roos validated the above mechanism for the co-deposition of alumina and copper from an acidified copper plating bath [42].

More recently, Celis et al. proposed a new model, based on a statistical approach. Two systems were considered; Cu/Al₂O₃ from an acidic sulphate bath and Au/Al₂O₃ from an additive free potassium cyanide bath [43]. The general applicability of Guglielmi’s model, which does not predict the effect of parameters such as the hydrodynamics, the effect of particle size, type, and pre-treatment, the effect of the bath constituents, pH, and temperature, is considered. Foster and Kariapper proposed a mathematical expression that could describe the effect of hydrodynamics [44]. A number of the parameters incorporated in the formulas of Guglielmi and Foster et al. cannot be evaluated but the model from Celis et al. contains measurable parameters so that the prediction of the amount of co-deposited particles becomes more feasible. The basis of this more recent model is: (1) the adsorption of a layer of ionic species around the inert particles at the time the particles are added to the plating solution or during the pre-treatment of these particles in ionic solution; (2) the replacement of some of these adsorbed ionic species, which is required for the incorporation of particles into the metal matrix. In effect, a particle must proceed through 5 stages to get from bulk solution to the site of incorporation, Fig. 1.3 [43].
Figure 1.3. Five stages in the co-deposition of a particle [43].

These stages are:

1) adsorption of ionic species onto the particle surface
2) movement of the particle, by forced convection, towards the hydrodynamic boundary layer, $\delta_0$, at the cathode
3) diffusion of the particle through the diffuse double layer, $\delta$
4) adsorption of the particle at the cathode surface
5) replacement of some of the adsorbed ionic cloud, the particle becomes irreversibly incorporated into the metal matrix

Overall, the model can be summarised as follows: a particle is only incorporated when a certain amount of the adsorbed ions are reduced.

1.5.2. Metal/Carbon Nanofibre Composite Electrodeposition Processes

It has been found that the co-deposition of conducting particles can prove problematic. Bazzard and Boden studied nickel/chromium composite electrodeposition and discovered that the deposits suffered from severe dendritic growths, chromium particles were used as the second phase [45]. Stankovic and Gojo observed that since graphite is conductive, these particles in contact with the current feeder (cathode) are polarised and deposition occurs onto the particles as well as onto the cathode [46]. The incorporating particle provides a raised spot on the coating but since the particle is conducting it provides an area of localised high current density, Fig. 1.4.
Fransaer et al. highlighted two significant problems that hamper the development of composite plating with nano-sized particles [48]. In aqueous plating electrolytes, particles easily agglomerate due to the compression of the diffuse double layer surrounding the particles by high ionic strength. This effect is more pronounced for particles of submicron size as the shearing forces on the agglomerates, created by the agitation of the plating bath decreases with particle size. The result is the co-deposition of agglomerates and the anticipated mechanical, chemical and/or physical properties are not reached. Secondly, the co-deposition of particles decreases with particle size. The volume percent of co-deposited particles in aqueous electrolytes drops from 5 - 15 vol. % for micron sized particles to 0.1 vol. % or less for submicron sized particles.

Composite electrodeposition techniques were used by Arai and Endo to produce CNF/copper composites [49]. Motivation for their work included the fact that high temperature processes are required when melting metals to produce carbon filler/metal composites. These melting points are usually higher that the oxidation point of the carbon material. Also, suppressing the formation of metal carbide at the interface is important, since it could degrade the performance of the resultant composite. Therefore, attempts were made to develop a low temperature composite formation method. The images in Fig. 1.5 show SEMs of the surface of a Cu/CNF film electrodeposited from a Cu/sulphuric acid bath (containing the dispersant, polyacrylic acid and CNF) at 25 °C.
CNF/Cu powder composites were prepared by electrodeposition from the same bath as detailed in Fig. 1.5. The CNFs were tightly incorporated into the deposited Cu as spiky structures surrounding individual Cu grains. The resulting composite could easily be separated from the electrode by ultrasonication to give a powdered CNF/Cu composite, Fig. 1.6 [50].
In addition, Arai et al. electrodeposited Ni-deposited MWNT. Once again poly acrylic acid was used to disperse the MWNT in the plating bath, a "dull Watt's" type bath [51].

Chen et al. produced CNT/Ni composite coatings from a conventional nickel plating bath [52]. Acid treated CNTs were utilised. The CNTs were ball milled, which shortened them, and ultrasonic agitation was used for their dispersion in the nickel bath. Sediment electrodeposition was used to form the composite coating. The co-deposit was found to depend on the CNT length, cathodic current density, and agitation rate. CNTs are a low density material, which agglomerate easily in solution. At low CNT concentration in the plating bath, the CNT content in the deposit is low. However, for high CNT concentrations the content of CNTs in the deposit decreases gradually. This is caused by the agglomeration of CNTs in the plating bath at higher concentrations.

Another study considered the tribological behaviour of CNT reinforced nickel matrix composite coatings. In this study ultrasound agitation and sedimentation electrodeposition were employed [53]. In a further investigation Chen et al. investigated the corrosion behaviour of CNT/Ni composite coatings produced by sediment electrodeposition [54]. A cationic surfactant was used to improve the hydrophilic nature of the CNTs. Ultrasonic agitation was used to disperse the CNTs in the nickel sulphate bath. The incorporation of the CNTs significantly increased the corrosion resistance. This was due to the CNTs acting as a physical barrier to the corrosion process by filling in crevices, gaps, and micro holes on the surface of the nickel coating. The CNTs also make the corrosion potential of the composite coating more positive, restricting localised corrosion, resulting in mainly homogenous corrosion.

Shi et al. produced Ni-P binary alloy deposits with both 5 wt. % ultrafine diamond (5 - 10 nm) and 0.5 wt. % CNT, these were ultrasonically dispersed with the help of surfactants [55]. The Ni-P-CNT resulted in a clearly rougher surface. The objective of the study was to investigate the properties of these composites for electrolytic hydrogen evolution in alkaline and acidic environments. The Ni-P-CNT composite performed with the highest catalytic activity.
1.6. Electrochemical Techniques

1.6.1. Equilibrium Techniques

The investigation of equilibrium electrode processes is performed using a two-electrode set-up, i.e., a working electrode, where the reaction of interest occurs, and a reference electrode, which provides a stable and fixed potential so that the potential at the working electrode is precisely defined. If no current is drawn through the cell then the potential, $E$, rapidly reaches a steady state value corresponding to equilibrium. For the general charge transfer reaction

$$O_{(aq)} + ne^{-}_{(m)} \leftrightarrow R_{(aq)}$$ \hspace{1cm} (1.1)

$n$ electrons are transferred. Nernst showed that the potential established at the electrode under equilibrium conditions is given by

$$E_e = E^o + \frac{RT}{nF} \ln \frac{[O]}{[R]}$$ \hspace{1cm} (1.2)

where the equilibrium potential, $E_e$ (V), of the electrode results from the standard electrode potential, $E^o$ (V), of the reaction and the activities of $O$ and $R$ at the electrode surface, which are the same as their bulk solution activities under equilibrium conditions. $R$ is the gas constant, J K$^{-1}$ mol$^{-1}$; $T$ is the temperature, K; and $F$ is the Faraday constant, F mol$^{-1}$.

1.6.2. Steady State Techniques

Electrochemical measurements, which give data independent of time, are ‘steady state’ techniques. The basic dynamic electrochemical experiment approaching steady state is to use a three-electrode cell and to step to a fixed voltage between the working and reference electrodes. When a steady state has been reached the current is measured. Alternatively a constant current is sent through the cell and the voltage between the WE and RE is measured. The results are usually plotted as current versus voltage plots or as Tafel plots. For an electrochemical system to reach a steady state, microdisc electrodes or an agitated solution (rotating disc voltammetry, sonovoltammetry), are required.
1.6.3. Transient Techniques

1.6.3.1. Linear Sweep Voltammetry

With transient methods a third variable, time, is introduced. In voltammetric methods the voltage is changed and the current is measured with time. In chronopotentiometry the current is changed and the voltage measured with time.

Linear sweep voltammetry (LSV), which is closely related to cyclic voltammetry, is relatively easy to perform, and rapidly provides both complex and useful information about the system under investigation. The experiment is conducted in stationary solution and relies only on diffusion to transport material to the electrode surface. The mass transport of species A to the electrode can be predicted using Fick's laws

\[ J_d = -D_A \frac{\partial [A]}{\partial x} \quad (1.3 \text{ (a)}) \]

\[ \frac{\partial [A]}{\partial t} = D_A \frac{\partial^2 [A]}{\partial x^2} \quad (1.3 \text{ (b)}) \]

\( J_d \) is the diffusional flux, the number of moles of material diffusing through a unit of area in one second, mol m\(^{-2}\) s\(^{-1}\); \( D_A \) is the diffusion coefficient of species A, m\(^2\) s\(^{-1}\); \([A]\) is the concentration of A, and \( x \) is the distance from the electrode surface. The potential of the working electrode is swept from a value \( E_h \), where A cannot undergo reduction, to a potential \( E_2 \), where electron transfer is driven rapidly. The applied potential, \( E \), is a function of the speed at which the potential is swept, \( \nu_s \) (V s\(^{-1}\)), and the time of the sweep, \( t \) (s)

\[ E(t) = E_1 - \nu_s t \quad (1.4) \]

Fig. 1.7 shows the potential sweep and the corresponding current response for a reduction process \( A + e^- \rightarrow B \).
Figure 1.7. The potential sweep, (a), and the corresponding current response, (b), for an irreversible electron transfer reaction [56].

The A/B couple has irreversible electrode kinetics, i.e., the standard rate constant, $k^*$, is relatively slow compared to diffusion, $k^* < \frac{FvD}{RT}$. Initially, at positive potentials no current, $i$ (A), passes, since the applied potential is insufficient to induce significant electron transfer. As the potential is swept to more reducing values, it reaches a point where it is capable of inducing the reduction of A to B at the electrode, and current is passed. As E is made more negative, the electrochemical rate constant, $k_{\text{red}} = k^* \exp\left(-\frac{\alpha nF(E-E_f)}{RT}\right)$, for the reduction of A increases, and initially the current rises exponentially with potential, or time; $\alpha$ (dimensionless) is the transfer coefficient. As more negative potentials are applied the increase becomes less than exponential and eventually a maximum is reached, after which the current falls off. The maximum in the current/voltage curve reflects a balance between an increasing heterogeneous rate constant and a decrease in surface concentration. The maximum current is known as the peak current, $i_p$. The peak currents in amperes for reversible and irreversible electron transfer are given by the Randles Sevcik equation, Eqs. (1.5 (a)) and (1.5 (b)), respectively.

\begin{align}
    i_p &= -2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} [A]_0 \\
    (1.5 \text{ (a)}) \\

    i_p &= -2.12 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} [A]_0 \\
    (1.5 \text{ (b)})
\end{align}
In these expressions, \( n \) is the number of electrons appearing in the half reaction for the redox couple; \( A \) is the electrode area, \( \text{m}^2 \); \( D_A \) is the diffusion coefficient, \( \text{m}^2 \text{s}^{-1} \); \( v \) is the rate at which the potential is scanned, \( \text{V s}^{-1} \); \([A]_0\) is the concentration of \( A \) in the bulk solution, \( \text{mol m}^{-3} \); and the numerical constant (assuming \( \alpha = 0.5 \)) has the units \( \text{C mol}^{-1} \text{V}^{-1/2} \). It can be seen that \( i_p \) varies with the square root of the sweep rate. Once the peak current is attained, the magnitude of the current flowing is simply controlled by the rate at which fresh \( A \) can diffuse to the electrode surface. The fall in current can be accounted for in terms of Eq. (1.3 (b)) and a steadily increasing diffusion layer thickness resulting from progressive electrolysis of the solution.

Reversible redox systems can only be observed if both oxidant and reductant are stable and the kinetics of the electron transport are fast, so that at all potentials and potential scan rates, the electron transfer process at the surface is in equilibrium (this is dependent on a comparison of the rates of the forward and back electron transfer reactions with the rate of diffusion of material to and from the surface) so that surface concentrations follow and may be calculated from the Nernst equation. For the reversible case, \( E_p \) is independent of sweep rate.

The value of the half wave potential can be obtained from data under reversible conditions where the chemical reaction does not interfere (i.e., at high sweep rates) when \( E_p \) and \( E_{1/2} \) are related by

\[
E_p = E_{1/2} - 0.028/n \quad (1.6)
\]

at 25 °C [57]. The half peak potential \( E_{p/2} \), the potential at 1/2 \( i_p \), is also related to \( E_p \)

\[
|E_p - E_{p/2}| = 2.2RT/nF = 0.0565/n \quad (1.7)
\]

If the difference between the peak potential and half peak potential is a multiple of 56.5 mV then the number of electrons can be determined, Eq. (1.7).

Fig. 1.8 (a) shows a voltammogram for the case where the A/B couple now has reversible kinetics, compared in the diagram to (b), the irreversible case.
In the reversible case, appreciable current flows when the electrode reaches a potential more negative than $E_e$, which is consistent with the half wave potential, $E_{1/2}$. As soon as the reduction becomes thermodynamically viable it takes place as a result of the rapid electrode kinetics implicit for a reversible couple. No current flows in the irreversible case until the potential is considerably more negative than $E_e$.

Two other points to note when comparing the reversible and irreversible cases are:

1) In the reversible case, the peak potential, $E_p$, is constant and independent of sweep rate, whereas for the irreversible case $E_p$ shifts to more negative potentials at faster sweep rates.

2) The peak current is larger for a reversible couple than for an irreversible couple for the same voltage sweep rate.

These differences reflect the contrasting electrode kinetics of the two systems. For both reversible and irreversible systems, $i_p$ is directly proportional to the concentration of A and increases with voltage sweep rate.

1.6.3.2. Cyclic Voltammetry (CV)

Cyclic linear sweep voltammetry, CV, consists of LSV in two directions. Once the potential has been swept to the highest value the potential is reduced, at the same sweep rate, to the original value. It is conventional to show current as a function of voltage, Fig. 1.9.
Figure 1.9. Cyclic voltammogram for a reversible electron transfer reaction.

The voltage and current are shown with respect to time in Fig. 1.10.

Figure 1.10. Voltage and current changes during cyclic voltammetry.

The forward sweep of the cyclic voltammogram is identical to the LSV, but, on reaching \( E_2 \) the potential is swept back, oxidising species B, formed on the electrode during the forward scan, to species A. When all of B present in the diffusion layer is converted back to A, the current drops to zero. The peak potential and the peak size seen on the reverse scan again reflect the reversibility of the A/B couple. In the case of Fig. 1.9, the heights of the forward and reverse peaks are of the same magnitude and are separated by a potential of 56 mV approx. (at 298 K), which is independent of scan rate. If \( n \) electrons are transferred in a reversible electrode process the separation is
1.6.4. Sonoelectrochemistry

Sonoelectrochemistry is concerned with the coupling of power ultrasound to electrochemical systems [58]. Sonoelectrochemistry can be compared to other synergistic approaches in which two independent energy or activation sources are coupled. It has emerged over recent years as a powerful tool for both electroanalytical [59] and electrosynthetic [60] processes. Ultrasound emitted from a horn transducer and directly applied to the working electrode in an electrochemical cell has a major effect on the redox process, predominantly due to (i) very fast mass transport conditions induced by macro- and micro-streaming events [61], (ii) in situ cleaning of interfaces (removal of gas bubbles and weakly adsorbed materials) [62], (iii) in situ emulsification of two phase systems [63], and (iv) chemical effects due to cavitation [64]. A schematic representation of the ultrasonically induced cavitation process at interfaces is shown in Fig. 1.11.

![Figure 1.11. Schematic of the collapse of a cavitation bubble [65].](image)

Microjets, resulting from cavitation bubble collapse, propel fresh analyte to the electrode surface, dramatically increasing the current. Bombardment of the electrode surface by these jets can aid retention of electrode activity in highly fouling media.

It is well known that ultrasound causes considerable mass transport enhancement, not only at flat interfaces, but also at porous interfaces, e.g., during leather dyeing processes [66]. The quantitative comparison between ultrasound induced mass
transport effects at flat and at porous interfaces is a complex task. However, some mechanistic insights are possible, when the mass transport is detected electrochemically, in the form of a current at flat and porous electrodes. This will be demonstrated in the current study for electrochemical processes at CNF electrodes.

1.7. Metal Electrodeposition Processes
Firstly, the general principles of metal electrodeposition processes are described. Conventional metal electrodeposition processes are contrasted with pulse plating methods. Subsequently, the benefits of pulse plating and its physical principles are discussed.

1.7.1. Conventional Metal Electrodeposition Processes
The electrodeposition of metals involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. The reaction, in aqueous media, occurring at the cathode is as follows, Fig. 1.12,

\[ \text{M}^{n+} + \text{n}e^- \rightarrow \text{M} \quad (1.9) \]

with a corresponding anodic reaction.

Figure 1.12. Schematic of an electrolytic cell, where metal M from a metal salt solution plates onto the cathode.

The anode material is either the metal being deposited, in which case the electrode reaction is anodic dissolution, or it can be an inert material, usually producing oxygen by the electrolytic decomposition of water. The anode reaction can involve oxygen or
carbon dioxide evolution. In electrodeposition, electrons are supplied by an external power source. The following equation gives the charge required to reduce \( m \) moles of metal

\[
Q = mnN_aQ_e
\]

(1.10)

\( Q \) is the total cathodic charge used in the deposition, \( n \) is the charge on the metal ion, \( N_a \) is Avogadro's number, and \( Q_e \) is the charge per electron. \( N_aQ_e \) is the Faraday constant, \( F \), so substitution and rearrangement gives the number of moles reduced by a charge, \( Q \),

\[
m = \frac{Q}{nF}
\]

(1.11)

If the deposition current is held constant then the total charge used in the deposition, \( Q \), is the product of the current and the time of deposition. If the current varies during the deposition then

\[
Q = \int Idt
\]

(1.12)

and the number of moles deposited is

\[
m = \frac{1}{nF} \int Idt
\]

(1.13)

The weight of the deposit, \( w \), can be obtained by multiplying Eq. (1.13) by the atomic weight of the metal, \( M_w \). The thickness can be calculated using the density of the metal, \( D \),

\[
D = \frac{w}{V} = \frac{w}{AT}
\]

(1.14)

with \( D \) in g/cm\(^3\); volume of deposited metal, \( V \), cm\(^3\); the area of the deposit, \( A \), cm\(^2\);
and thickness, \( T \), cm. Using Eqs. (1.13) and (1.14) and solving for \( T \) gives

\[
T = \frac{w}{AD} = \frac{M_w}{nFAD} \int I dt
\]  

(1.15)

As mentioned above, at constant current the integral becomes \( It \).

1.7.2. Pulse Plating

Pulse plating is a method of depositing metal on a substrate using interrupted direct current, DC. This method favours the initiation of grain nuclei and increases the number of grains per unit area. The result is a finer grained deposit with improved properties, compared to conventionally plated coatings [67].

In electrolysis, the rate of reaction can be controlled easily by using a particular current density or potential. Pulse plating takes full advantage of the fact that current or potential can be applied as virtually any function of time. A number of variations are used, some of which are shown schematically in Fig. 1.13.

![Figure 1.13. Examples of square wave modulated current systems, with subscripts (a) and (b) denoting anodic and cathodic current, respectively [67].](image)

Typical waveforms include a cathodic pulse followed by off-time and/or an anodic...
pulse, galvanostatic or potentiostatic pulses, etc. The technique has two main limiting factors: electrical double layer charging at the metal/electrolyte interface and mass transport considerations:

(1) Capacitance Effects
The electrical double layer at the electrode/solution interface can be approximated to a plate capacitor with an interplate distance of a few ångstroms and therefore with a high capacitance. Charge is supplied to the double layer, which raises its potential to the value required for metal deposition at a rate corresponding to the applied pulse current, supplied by the generator. The electrode behaves as a capacitor with a parallel resistance, Fig 1.14, the resistance being a function of current density.

![Equivalent circuit of the electrode/electrolyte interface.](image)

Double layer charging (through a further external resistor) requires a certain time, which is dependent on, amongst other parameters, current density. The charging time needs to be much shorter than the pulse duration to avoid distortion of the current pulse. Also, the time required for the discharge of the double layer should be much shorter than the off-time between pulses. The current required, at the beginning of the pulse, for double layer charging is not lost for metal deposition: the charge is recovered at the end of the pulse while the capacitor is discharging. If the pulses are at a frequency where capacitive effects are relevant, current efficiency is not affected significantly, but the amplitude of the pulse is affected, and therefore the energy of the deposition reaction.

(2) Mass Transport
Mass transport effects arise with the depletion of cations from the diffusion layer.
Two cathodic diffusion layers occur in pulse plating with short pulse durations. A pulsating diffusion layer exists close to the cathode, Fig. 1.15.

![Figure 1.15](image_url)

Figure 1.15. Concentration profiles of the two diffusion layers existing at the end of a pulse. c is concentration, x is distance from the electrode, $\delta_p$ is the pulsating diffusion layer thickness, $\delta_s$ is the stationary diffusion layer thickness [67].

In the immediate vicinity of the cathode, the concentration pulsates with the frequency of the pulsating current, decreasing during the pulses and relaxing in the interval between pulses. A short pulse duration means that the diffusion layer does not extend into the region where convection controls mass transport. Therefore, the metal deposited during the pulse is transported by diffusion, so a concentration gradient also builds up into the bulk of the electrolyte. The thickness of this diffusion layer essentially corresponds to that which would be established under the same hydrodynamic conditions (diffusion and convection) in DC electrolysis. During the off-time, cations are also supplied in the direction of the cathode through this outer diffusion layer, this supply allows the pulsating diffusion layer to relax during the off-time. The outer diffusion layer is essentially stationary. The depletion of the cationic concentration in the pulsating diffusion layer limits the pulse current density, and the depletion of the stationary diffusion layer limits the average current density.

Pulse reverse is a common mode of current modulation. When the technique was first used, relatively long periods of forward and reverse cycles, longer than the on-time used in pulse plating, were used. This is also called periodic reverse. Pulse reverse is not restricted to shorter cycles and applies to periodic reverse also. The main purpose of inverting the current from cathodic to anodic during a short fraction of the total period is to remove metal preferentially from areas that tend to overplate during the
cathodic part of the cycle. It is possible to considerably retard dendrite formation or improve the electrodeposits thickness distribution over complicated shapes. Changes in the deposit structure can also be achieved due to the forced nucleation with each new cathodic pulse.

Pulse reverse is usually carried out when the deposit is easily soluble in the electrolyte, otherwise passivation may occur. Pulse reverse can be very useful in equalising the electrodeposit thickness distribution. Areas exposed to concentrations of current density are preferentially plated in the cathodic cycle, and metal is preferentially removed in the anodic cycle. To maximise the benefits of pulse reverse, the cathodic and anodic current densities should be independently adjustable. This allows an increase in the dissolution rate of raised regions by applying very high anodic current densities for short durations. Obviously, the net charge must be cathodic.

Kollia et al. investigated the influence of pulse reversed current on the crystal orientation and surface morphology of nickel electrodeposits [68]. They found that the reversed current technique exerts an effect analogous to that of organic additives, without the associated fouling problems. At low frequencies, < 1 Hz, colloidal nickel hydroxide is precipitated during the dissolution time, which is adsorbed on the metal surface and inhibits the growth of crystallites. The result of this inhibition is the development of randomly oriented, microcrystalline, bright and smooth deposits.

Electroplated zinc is widely used for corrosion protection, especially for iron base metals, but relatively little work has been done in the field of pulsed electrodeposition. The main reason for this is that the most important advantage of pulse plating, the reduced amount of metal required due to a reduction in the layer thickness, is not particularly important for relatively cheap non noble metals. Pulsed current zinc electrodeposition has the advantage of producing a finer grain sized layer, resulting in a more homogeneous surface appearance.

Zinc electrodes in storage batteries have the problem of the formation of dendritic deposits during the discharge and charging processes. For cycle life and efficiency,
good adherent deposits of high porosity are needed. Pulsed current electrodeposition has been used to produce porous zinc layers for battery operation using concentrated alkaline zincate solutions [69]. Also, Despic and Popov have shown that compact deposits can be achieved by pulse plating using the same average current density at which dendrites are formed under direct current electrodeposition conditions from an alkaline zincate bath [70]. Work was carried out using a three-component impulse current consisting of high cathode and low anode current pulses, followed by a break time [71]. An adherent deposit of about 50 % porosity was formed. It was proposed that the anodic current pulses result in the dissolution of raised regions in the deposited zinc, increasing the zincate concentration at the electrode surface.

1.8. The Electrochemical Quartz Crystal Microbalance

1.8.1. Introduction

The electrochemical quartz crystal microbalance (EQCM) is comprised of a thin quartz crystal sandwiched between two metal electrodes; it resonates in a mechanical shear mode by applying an alternating high frequency electric field across the crystal, causing the vibrational motion of the crystal. It is a piezoelectric device capable of extremely sensitive mass measurements. Sauerbrey was the first to recognise that these devices could be used to measure mass changes at the crystal surface [72]. The mass sensitivity arises from a dependence of the oscillation frequency on the total mass of the crystal, its electrodes, and any material present at the electrode surface. It was thought that these crystals would not oscillate in liquids due to excessive energy loss to the solution as a result of viscous effects. In the early 1980s it was shown that the QCM could be used in a liquid environment for the determination of mass changes at the crystal surface [73, 74]. The QCM was first used in an electrochemical context by Jones and Meure to monitor trace metal mass changes by electrodepositing the metal onto the QCM electrode and measuring the change in resonance frequency of the crystal in air following its removal from the cell [75, 76]. Nomura et al. developed the first in-situ application of the QCM to an electrochemical problem (EQCM). It was used to determine Cu(II) and Ag(I) by electrodeposition. In the EQCM one of the electrodes is used to provide the alternating electric field, which drives the oscillation of the crystal and as the working electrode in the electrochemical cell. The EQCM experiment involves the measurement of the potential, current, and charge at one of
the EQCM electrodes and the simultaneous measurement of the oscillation frequency of the piezoelectric crystal, which can indicate minute mass changes at the electrode. EQCM has been used to study monolayer and multilayer deposition and dissolution [77], mass transport in polymer films, corrosion processes, electroless deposition, and mass changes caused by protein adsorption at electrodes.

1.8.2. The Piezoelectric Effect

In 1880 Jacques and Pierre Curie discovered that a mechanical stress applied to the surface of various crystals, including quartz, gave a corresponding electrical potential across the crystal whose magnitude was proportional to the applied stress. This is referred to as the piezoelectric effect. The Curies also experimentally verified the converse piezoelectric effect in which a voltage applied across the crystal gives a corresponding mechanical strain, Fig. 1.16, this effect is the basis of the QCM.

![Figure 1.16. Schematic of the converse piezoelectric effect for shear motion [78].](image)

Fig. 1.16 illustrates the shear motion of an AT-cut quartz resonator, which consists of a thin quartz wafer prepared by slicing through a quartz rod at an angle of approximately 35° with respect to the x-axis. The electric field induces a reorientation of the dipoles of the material, resulting in lattice strain and shear deformation. The direction of the shear is dependent on the applied potential. The extent of the shear strain depends on the magnitude of the applied potential. In quartz the deformation is elastic. The opposite polarity produces an identical strain, but in the opposite direction. Fig. 1.17 shows a schematic representation of the transverse shear wave in a quartz crystal and a composite resonator comprised of a quartz crystal and a layer of foreign material.
1.8.3. Piezoelectric Crystals

Most reported applications of the QCM use AT-cut alpha quartz crystals because of the superior mechanical and piezoelectric properties of the alpha quartz and because of the nearly zero temperature coefficients of the AT-cut crystals at one or two temperatures [79]. However, temperature effects for crystals immersed in liquids far outweigh the intrinsic temperature dependence of the crystals themselves and must be taken into account in most electrochemical applications.

The thin, disk shaped transducers, typically used as QCM crystals oscillate in a pure shear mode when an alternating electric field of the appropriate frequency is applied across the disk, i.e., the electric field lines are normal to the disk surface. A pure shear mode indicates that the motion of the disk surface is precisely parallel to the disk face. Typical EQCM frequencies are between 1 and 10 MHz.

In addition to the thickness shear mode described above, other modes of vibration can also arise due to the applied electric field. While most other modes are only weakly coupled to the shear mode, the flexural modes are sometimes strongly coupled [80].
When the frequencies of the flexural modes are near that of the shear mode, deviations in the resonant frequency can occur such that the response of the QCM to mass changes is no longer linear. This problem can be eliminated by the appropriate design of the crystal and electrodes. The unwanted modes can be suppressed by a number of methods, e.g., bevelling and contouring [81]. Bevelling is part of the contouring of crystals but is important in its own right in the design of resonators for mode suppression. Typically, the edge of a circular crystal is bevelled. Initially, crystals were mounted at the bevelled edge to avoid disturbing the thickness-shear vibration but it was also shown that with circular disks spurious modes could be avoided, especially when bevelled. Bevelling spatially separates the flexural and thickness shear modes, consequently, reducing or eliminating any coupling between the two. Contoured crystals have been studied both theoretically and experimentally. The mode suppression arises because the thickness shear mode is confined to the central region and the flexural waves are concentrated at the edges.

1.8.4. Sauerbrey Equation

For shear mode oscillation, there are several frequencies that correspond to resonant conditions including the frequency of maximum displacement of the crystal surface (at a constant driving voltage). This condition corresponds to the establishment of a standing acoustic wave within the bulk of the crystal with a node existing in the centre of the disk and the antinodes at the two surfaces, Fig. 1.18, the acoustic wavelength is equal to $2t_\phi$ [82].

\[ \text{Node} \] \hspace{1cm} \text{Shear Distortion}

**Figure 1.18.** Edge view of a QCM disk under shear deformation [82].

When a uniform layer of a foreign material is added to the surface of the quartz crystal the acoustic wave will travel across the interface between the quartz and the layer, and will propagate through the foreign layer, Fig. 1.17. This assumes that particle displacement and shear stress are continuous across the interface. Assuming that the acoustic properties of the foreign layer and the quartz are identical then the system can be treated as a composite resonator. A fractional change in thickness, $\Delta t$, ...
results in a fractional change in frequency. The resonant frequency can be related to the thickness of the crystal by the following equation

\[ f_0 = \frac{v_q}{2t_q} = \frac{\mu_q}{2 \rho_q} \]  

(1.16)

where \( v_q \) is the velocity of the acoustic wave in quartz, \( f_0 \) is the resonant frequency of the quartz prior to mass change, and \( t_q \) is the thickness. Using Eqs. (1.16) and (1.17), the Sauerbrey equation is obtained, Eq. (1.18).

\[ \frac{\Delta f}{f_0} = -\frac{\Delta t}{t_q} = -2f_0 \frac{\Delta m}{\rho_q} \]  

(1.17)

\[ \Delta f = -2f_0^2 \frac{\Delta m}{A\sqrt{\mu_q \rho_q}} \]  

(1.18)

\( \Delta f \) is the frequency shift, \( \Delta m \) is the mass change, \( A \) is the piezoelectrically active area, \( \rho_q \) is the density of the quartz, and \( \mu_q \) is the shear modulus of quartz.

The dimensions of the electrodes and the crystal disk have a strong influence on the coupling of other modes to the thickness shear mode. This coupling represents a source of spurious frequency changes, which must be addressed. Many of the design criteria, which suppress these unwanted modes, are described by the frequency, amplitude, and the shape of the vibrations in the quartz crystal [81]. The critical dimensions are the thickness of the quartz disk, \( t_q \), the diameter of the crystal, \( d_c \), and the diameter of the concentric electrode pad, \( d_e \). With \( \frac{d_c}{t_q} > 50 \) and \( \frac{d_e}{t_q} > 18 \) unwanted modes can be suppressed by 40 dB [81]. The values for the quartz crystals used are 76 and 30, respectively, satisfying the above conditions to allow the excitation of the thickness shear mode without significant coupling to other modes.

Most QCM investigations assume ideal rigid behaviour, using the Sauerbrey equation
when interpreting frequency changes. The QCM measures frequency changes and not mass changes so there is the potential for interferences, which can result in non-ideal behaviour, defined as a lack of conformance with the Sauerbrey equation.

A number of factors can lead to non-ideal behaviour. The investigation of redox polymer films is used to evaluate the equivalent mass changes in films during redox cycling, establishing the number of counterions and solvent molecules involved in the transport process. In the absence of impedance analysis, it is recommended that QCM measurements of polymer films be performed over a range of thicknesses. A linearity of response can generally be taken as evidence of rigid film behaviour and/or the absence of changes in the viscoelasticity of the film. High mass loadings reduce the sensitivity of the QCM; this effect can be understood readily by inspection of the Sauerbrey equation.

The microscopic roughness of the QCM electrode can play an important role in the behaviour of the QCM in liquid media. Trapped liquid in surface cavities results in an additional mass component, the magnitude of which depends on the amount of trapped liquid and the size of the cavities. The effect has been seen for Au oxidation in neutral and basic media, the observed frequency change during oxidation was significantly larger than expected from oxide formation [83]. This was attributed to water trapped in surface cavities formed during oxidation. 80% of the observed frequency shifts could be attributed to roughness effects.

QCM experiments are usually performed with one side of the AT-cut quartz crystal immersed under a column of liquid with the opposite side facing air. This results in a stress on the quartz crystal due to the hydrostatic pressure exerted by the column of liquid. The effect of this pressure has not been established, but it seems likely that it is not important since the pressure is generally constant throughout a typical experiment.

The radial sensitivity of the QCM requires a uniform mass distribution if accurate measurements are to be made using the Sauerbrey equation. The film uniformity required is macroscopic. Actual electrode surfaces, including those with redox active films, are unlikely to possess truly uniform films. As long as the roughness is not longer than the acoustic wavelength or the non-uniformities are randomly distributed,
conformance to the Sauerbrey equation can be expected and the average thickness will be measured. The electrochemical parameters and the frequency changes are related by

$$\Delta f = 10^6 MW \frac{C_f Q}{n F}$$  \hspace{1cm} (1.19)$$

where MW is the apparent molar mass, g mol$^{-1}$, $C_f$ is the sensitivity factor for the crystal used. The charge is a measure of the total number of electrons involved in the redox process and so should be directly proportional to the frequency change, which is a measure of the total mass change. $\Delta f$ is directly proportional to $Q$, plotting $\Delta f$ vs. $Q$ reveals the extent to which the above statement holds and should give the apparent molar mass of the depositing species. Deviations are caused by various effects, including deposit surface roughness, along with solvent, and/or supporting electrolyte incorporation. The current involved is the instantaneous rate of electron transfer at the interface. Therefore, it is related to the derivative of the frequency with respect to time (or potential in the case of a constant sweep rate cyclic voltammetry experiment)

$$i = \frac{(d(\Delta f)/dE)(10^{-6} n F)}{(MW C_f)}$$ \hspace{1cm} (1.20)$$

$\nu$ is the sweep rate, V/s; $10^{-6}$ is a unit conversion factor.

1.9. Surface and Compositional Analysis Techniques

1.9.1. Scanning Electron Microscopy

In a scanning electron microscope (SEM), a minute electron beam is scanned across the sample. Simultaneously, the generated signals are being recorded, and an image is formed pixel by pixel. In SEM, the signals are observed on the same specimen site as the incoming electron beam. In contrast to TEM methods needing very thin samples, compact samples can thus be investigated by SEM. Valuable information about morphology, surface topology, and composition can be obtained. SEM microscopes achieving resolutions below 1 nm are now commonly available.
The SEM consists of an electron optical column, a vacuum system and control electronics [84]. The electron gun at the top of the column produces an electron beam, which is focused into a fine spot on the sample, Fig. 1.19 [85].

![Diagram of a SEM](image)

Figure 1.19. Schematic representation of a SEM [85].

The electron gun consists of a filament and Wehnelt cylinder (also known as a cathode-ray tube grid or shield; a cylindrically shaped electrode containing the cathode of a cathode-ray tube with opposite potential, which is designed to focus and control the electron beam). The illumination system consists of an electron gun, an anode, and condenser lenses. The final lens focuses the beam onto the surface of the sample being studied.

The electrons produced when the primary beam strikes the sample are detected and turned into an electrical signal. During electron bombardment a number of phenomena occur:

1. emission of secondary electrons from the sample
2. some primary electrons are reflected (backscattered electrons)
3. electron adsorption by the sample
4. X-ray emission from the sample
5. occasional emission of photons from the sample
The above effects are interrelated and are dependent, to an extent, on topography, atomic number, and the chemical state of the sample. The number of backscattered, secondary, and absorbed electrons is mainly dependent on the topography of the sample. This is why these effects are used for surface imaging.

When an electron beam hits matter, it begins to broaden because of strong elastic scattering effects. Simultaneously, inelastic interactions cause an energy loss of the electrons. If the sample is very thick, the energy will be completely transferred to the sample. The overall result is a pear-shaped interaction volume, Fig. 1.20 [85].

![Interaction between incident electrons and specimen](image)

**Figure 1.20.** Interaction between incident electrons and specimen [85].

The penetration depth depends on the electron energy ($t \sim V$) and on the material ($t \sim 1/\text{atomic mass}$).

The three main signals measured by SEM, which provide different information about the sample, are secondary electrons, back-scattered electrons and X-ray emissions:

**Secondary Electrons:** Since electrons in the conduction or valence band only need a small amount of energy (work function) to be transferred into vacuum, the energy of the secondary electrons (SE) is low ($> 50$ eV). Because of their low energy, SEs can only escape from the sample if they are generated close to the surface. Therefore, SE images are a means to obtaining topographic images.

**Back-scattered Electrons:** The collision of an electron from the beam with a nucleus leads to the deflection of its path as a result of Coulombic forces (Rutherford elastic
scattering). Sometimes, the electrons are completely back-scattered and leave the surface of the sample, Fig. 1.21.

![Diagram of electron scattering](image)

Figure 1.21. Possible path of an incident electron through an atom [85].

Since heavy atoms with a high atomic number are stronger scatterers than light ones, they cause a larger signal. Therefore, images with back-scattered electrons contain compositional information.

**FEGSEM:** In the case of the Field Emission Gun SEM, electrons are pulled out of a very fine pointed tungsten tip by a very high electric field. Electron densities up to 1000 times those from conventional tungsten emitters can be obtained with the FEG. The increased electron density permits a reduction in beam diameter, which results in better resolution.

The instrument used to record the images obtained for this report was a Leo 1530VP field emission SEM (FEGSEM) capable of nanometre-scale resolution and equipped with a variable pressure facility and EDAX/TSL Pegasus system, allowing simultaneous electron backscattering diffraction and energy-dispersive X-ray analysis.

### 1.9.2. Energy Dispersive X-ray Spectrometry

Energy dispersive X-ray (EDX) spectrometers can be installed within an SEM, providing laterally resolved information about sample composition. The electrons bombarding the sample cause it to emit X-rays (outer to inner orbital transitions)
whose energy is determined by the elemental composition. It is possible to detect minute quantities of an element, down to the picogram level. Spectra are acquired, showing distinctive peaks for the elements present and the peak height indicates the concentration of the element.

1.9.3. Auger Electron Spectroscopy

Auger electron spectroscopy (AES) uses an electron beam, the energy and wavelength of which can be adjusted by changing the potential within the electron gun, to probe the surface of a sample. The electron beam brings about a change in the electronic levels within the atoms of the sample. Core level electrons are ejected, leaving the atom in an excited state. To fill the vacancy, an electron from an outer shell moves in, releasing a photon of energy. In Auger processes, this energy is in turn transferred to an electron in the outer shell, which is ejected with a characteristic energy. The kinetic energy of the ejected Auger electron is related to the binding energy of the electrons in the three shells involved in the transition.

Each element has a characteristic Auger electron spectrum corresponding to various preferred combinations of the contributing levels, and the compositional analysis is made by identifying peaks in the Auger electron spectrum. The Auger electron peaks are superimposed on a large background due to the different types of electrons involved. The Auger peaks are fairly sharp, and the background can be eliminated by plotting $dN/dE$ ($N$ is the number of Auger electrons) as a function of the electron energy, $E$. Correcting for the sensitivity of the detector and the probability of a particular transition, the area of the $dN/dE$ peak can be related to the number of atoms in the sample.

If the electron is scattered inelastically, during its passage through the sample, its kinetic energy, in vacuo, will differ from the characteristic Auger energy and will only contribute to a broad continuum on which the Auger electrons are superimposed. Therefore, AES is strictly a surface technique; atoms more than 20 Å from the surface can contribute unscattered electrons.

AES has a depth-profiling feature. The sample is etched with a beam of high-energy ions, e.g., $\text{Ar}^+$. The spectrum is recorded after the period of etching. Potential
problems are the homogenisation of the sample by the high-energy ion beam and differential sputtering, which involves the removal of one component at a faster rate than another. The instrument used was a JEOL 7100 Auger electron spectrometer. The instrument allows elemental analyses to be made on most surfaces with a spatial resolution of 50 nm. By removing surface material using ion beam sputtering, bulk analyses can also be made.

1.9.4. Fourier Transform Infrared Spectroscopy

Infrared spectroscopy concerns the interaction of molecules with infrared energy. The infrared region of the electromagnetic spectrum ranges from $10^{-4}$ to $10^2$ cm. Fourier transform infrared spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation. There are several methods for measuring the temporal coherence of the light, including the Fourier transform spectrometer.

The absorption spectra achieved result from irradiating the sample with energy of many different wavelengths and seeing which wavelengths are absorbed and which pass through. Molecules are in constant motion with the bonds vibrating, rotating, and bending. When a molecule absorbs infrared radiation these molecular motions increase in intensity. Since each radiation frequency corresponds to a specific motion, therefore, the infrared spectrum shows the kinds of molecular motions the sample has [86].

1.9.5. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic technique that measures the empirical formula, chemical state, and electronic state of the elements that exist within a material [87]. XPS spectra are obtained by irradiating a material with a beam of X-rays, while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.

A typical XPS spectrum is a plot of the number of electrons detected versus the binding energy of those electrons. Each element produces a characteristic set of XPS
peaks at specific binding energy values that directly identify each element that exists in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of electrons detected in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" and normalized over all of the elements detected.

1.9.6. Raman Spectroscopy

When light is scattered from a molecule most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in $10^7$ photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons leading to Stokes radiation [88]. Other photons collect energy from excited molecules emerging with higher energy; termed anti-Stokes radiation. The process leading to this inelastic scattering is termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. The vibrational Raman effect is of most significance. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a Raman spectrum.
References

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Chapter 2
Carbon Nanofibre Synthesis and Electrochemistry
2.1. Introduction
Carbon nanofibres and nanotubes have a considerable impact on science and technology and offer a new type of conducting carbon for electrochemical technologies. The combination of high surface area and good electrical conductivity is crucial in many areas of electrode performance and energy storage systems. The mesoporous character of the carbon nanomaterials plays a dominant role in their electrochemical properties [1]. Compared to conventional carbon materials, carbon nanotubes have a higher rate of electron transfer. Their tangled network and central canal are at the origin of pseudo capacitive effects, allowing easy access of the ions to the electrode/electrolyte interface.

Porous carbons, e.g., activated carbon, are used as electrodes in supercapacitors, whose performance is judged in terms of their energy density, which is proportional to the surface area per unit volume of carbon [2]. CNTs are a possible replacement due to their large and controllable surface area and their unique network of pores, as mentioned above [1].

Porous carbon electrodes are used in Li batteries. CNF are now being used to increase the conductivity and thus improve the power density of the battery. Endo et al. described the basic properties and applications of vapour grown carbon fibres to batteries [3]. Their use as a filler in the electrode of a lead-acid battery and a Li-ion battery system exploits properties, such as their relatively high mechanical strength and electrical conductivity, including their network-like morphology, improving the performance of the electrodes in these battery systems, especially their cycle characteristics. In addition, the small diameter of the fibres makes it possible to homogeneously distribute them in the electrode material introducing a larger surface area for reaction. The electrode exhibits high endurance due to the presence of the carbon nanofibres, which absorb stresses caused by the intercalation of Li$^+$ ions.

A multiwalled carbon nanotube chitosan-modified glassy carbon electrode has been shown to be capable of highly sensitive cathodic stripping voltammetric measurements for bromide [4]. It was found that, at low pH, the amino groups on chitosan and the hydroxyl groups on the MWNT were protonated thus promoting an
interaction between these protonated groups and the Br⁻ ions in solution, aided by the porous meshy structure of the MWNT, leading to the enhanced voltammetric response observed.

Aligned MWNT grown on a platinum substrate have been used for the development of an amperometric biosensor [5]. The opening and functionalisation of the nanotube array allowed for the efficient immobilisation of the enzyme. The carboxylated open ends of the nanotubes immobilised the enzyme, while the platinum substrate provided the direct transduction platform for signal monitoring, as mentioned in Chap. 1.

Hofmann et al. have reported low temperature growth of CNT and CNF on plastic, using plasma enhanced CVD [6]. It has also been shown that the catalyst can be delivered to the surface as an organo-metallic precursor liquid [7], allowing for the opportunity to grow CNT onto complex shapes, polymers, and in printable patterns. It could be possible to grow CNTs as an electrode material on polymer membranes for fuel cells [8].

MWNT are also of interest in terms of their use as an electrocatalyst support in direct methanol fuel cells. The use of composite electrodes, made by the direct growth of MWNT on carbon backing paper and the subsequent deposition of platinum particles, suitable for electrocatalysis has been investigated [9]. It was found that highly dispersed and very small Pt particles were successfully deposited on the MWNTs grown on carbon paper, and cyclic voltammetry confirmed the electrical contact.

The similarities to, and advantages, of edge plane pyrolytic graphite electrodes over MWNT modified electrodes in the areas of gas sensing, stripping voltammetry, and biosensing have been illustrated by Compton et al. [10].

In this thesis carbon nanofibre materials are employed as a relatively low cost/high efficiency alternative to more structurally well-defined materials.

In this chapter, the formation of carbon nanofibre materials in an ambient pressure chemical vapour phase deposition process is described. For many applications it is beneficial to employ solution deposition processes and therefore the solubilisation via
oxidation of carbon nanofibre materials is investigated. Aqueous solutions are obtained for later use in metal codeposition processes. Next, the characterisation of both the as grown and oxidised nanofibre materials is described.

Electrochemical processes at carbon nanofibre materials, produced by the direct growth of carbon nanofibres onto a suitable ceramic, are discussed. Redox systems are studied diffusing into and through the porous carbon nanofibre material and adsorbing onto the carbon nanofibre surface.

2.2. Experimental

2.2.1. Chemicals

FeCl₃, Ru(NH₃)₆Cl₃, hydroquinone, H₃PO₄ (85 wt.-%), NaOH, KCl, KOH, and HClO₄ (Aldrich); phenol (BDH); ethanol (Fisons); and HNO₃ (70 %) (Fisher) were obtained commercially and used without further purification. For the chemical vapour deposition (CVD) synthesis of carbon nanofibres ethylene, hydrogen, and argon (all BOC) were used. Demineralised and filtered water was taken from an ELGA (ELGA, Bucks, UK) water purification system with a resistivity of not less than 18 MΩ cm.

2.2.2. Instrumentation

The carbon nanofibres were grown in an Elite tube furnace, model TSH 12/65/550. Voltammetry experiments were performed with an Autolab PGSTAT20 system, Eco Chemie, Netherlands. Field emission gun scanning electron microscopy (FEGSEM) images were obtained on a Leo 1530VP Field Emission Gun SEM system. Samples were gold coated (ca. 3 nm) in a sputter coating unit prior to imaging, as necessary. Transmission Electron Microscopy images were obtained on a Jeol 100CX TEM system operating at 100 kV, or a Jeol 2000FX operating at 200 kV. XPS data were obtained with an 8.5 kV X-ray source. Diffuse Reflectance Infrared Fourier Transform Spectroscopy, DRIFTS, experiments were carried out using a Nicolet 20 DXC FTIR spectrometer with a DRIFTS attachment. RAMAN spectra were run on a standard LabRAM 300 system, configured with a 532 nm excitation laser.

Power ultrasound was introduced into the electrochemical cell using an ultrasound processor (Hielscher UP 200G, 24 kHz, maximum output power approximately 8 W
cm$^2$ based on a calorimetric calibration [11]) fitted with a 13 mm diameter glass horn.

The cell used for standard electrochemical experiments is shown in Fig. 2.1, with a saturated calomel reference electrode (SCE, Radiometer) and a platinum gauze counter electrode (2 cm x 2 cm). Prior to voltammetric experiments the solutions were de-aerated with argon (BOC). Experiments were generally conducted at a temperature of 22 +/- 2 °C. Variations are noted in the appropriate sections.

![Figure 2.1. Standard electrochemical cell, where R is a saturated calomel reference electrode (SCE), W is the working electrode, C is the counter electrode (Pt mesh).](image)

The working electrode was usually a 3 mm diameter glassy carbon disc electrode (BAS, polished on a polishing cloth with an aqueous slurry of 1 μm Al$_2$O$_3$, Kemet). For measurements with carbon nanofibre electrodes, a 4 or 7 mm diameter disc of the carbon nanofibre/ceramic composite material was attached to the glassy carbon electrode with a Lycra™ membrane [12]. Sonoelectrochemical experiments were carried out in a special sonoelectrochemical cell, Fig. 2.2, where the glass horn, delivering the power ultrasound, was placed opposite the working electrode.
2.3. Synthesis of Carbon Nanofibres (CNF)

2.3.1. Catalyst Preparation

A number of variations were considered in order to find a suitable, reproducible, method for carbon fibre growth. In general, an oxidised form of iron in nanoparticulate form is required as the precursor for the catalyst, which is formed during reduction with hydrogen. As a convenient starting point, the direct use of commercially available Fe(II) oxalate was investigated. It is thermally unstable and gives an oxide at elevated temperatures. The intermediate oxide is then reduced and the resulting iron particles act as the catalyst for carbon nanofibre growth. Fig. 2.3 shows FEGSEM images of the carbon nanofibres grown via this approach.

![FEGSEM images of carbon nanofibres grown using Fe(II) oxalate as the catalyst precursor](image)

Figure 2.3. FEGSEM image of carbon nanofibres grown using Fe(II) oxalate as the catalyst precursor, (a) low magnification, (b) high magnification.

Unfortunately, this rather simple process turned out to be of low efficiency, typically
growing 2 g carbon nanofibre for 1 g catalyst precursor, with large fluctuations in yield and quality.

A better approach proved to be the preparation of Fe$_2$O$_3$ nanoparticles following Sorum’s procedure [13, 14]. The basic method was as follows: 50 mL of 0.2 M FeCl$_3$ was added dropwise to 450 mL of boiling H$_2$O. The resulting solution was boiled for a further 5 min. The red solution was cooled and then dialyzed by pouring it into a dialysis membrane and immersing the tubing in a beaker of dilute HClO$_4$, pH 3.5, which was replaced with fresh solution after 24 h. This process removed Cl$^-$ impurities from the colloidal iron oxide solution. The resulting dark orange sol of Fe$_2$O$_3$ (0.02 M in Fe) was stable and consisted of nanoparticles of approximately 6-12 nm in diameter [15]. Fig. 2.4 shows a typical TEM image of the colloidal catalyst precursor solution prepared in this way.

![Figure 2.4. TEM of Fe$_2$O$_3$ catalyst nanoparticles, the particles are 6-12 nm in diameter.](image)

The composition of the nanoparticles is best described as hydrous iron oxide [16] and is known to change slowly with time [17].

### 2.3.2. Bulk Synthesis of Carbon Nanofibres

The carbon nanofibres were grown in a tube furnace, Fig. 2.5, following a literature procedure [18, 19, 20].
The furnace consists of a quartz tube surrounded by heating elements, which are controlled by a programmable panel on the front of the instrument. The required gases, Ar, H₂, and C₂H₄, are supplied from cylinders connected via a gas flow system. The flow rates and pressures can be adjusted, as appropriate. The atmosphere is maintained by the insertion of glass stoppers into the reaction tube and by connecting a bubbler to the gas outlet.

A catalyst particle bed was prepared by the evaporation of an appropriate amount of the Fe sol pre-catalyst solution (prepared as described in Section 2.3.1) into a combustion boat. Carbon nanofibres were grown from ethylene at 600 °C in contact with the iron catalyst formed by the reduction of the Fe₂O₃ precursor, following a known procedure [18, 19].

The nanofibre growth consists of the following steps:

1) in air, ramp to 450 °C at a rate of 600 °C/h and hold for 90 min.,
2) insert stoppers, flow Ar at 1 bar at a rate of 200 ccm for 5 min. to remove air,
3) turn on H₂, also to 1 bar, flow at 50 ccm for 120 min. at 450 °C,
4) the system then ramps to 600 °C,
5) open ethylene cylinder to 1 bar, C₂H₄ and H₂ both flowing at a rate of 250 ccm for 150 min.,
6) turn off gases, flush system with Ar while cooling.

The yield of carbon nanofibres obtained with this approach was typically 7 g CNF per
0.1 g catalyst precursor. A typical FEGSEM image of the resulting carbon nanofibres is shown in Fig. 2.6.

![FEGSEM Image](image)

Figure 2.6. FEGSEM of as grown carbon nanofibres.

### 2.3.3. Surface Synthesis of Carbon Nanofibres on Ceramic Substrates

It is also possible to grow carbon nanofibres directly onto a solid support, e.g., ceramic paper. In this case, the catalyst for the carbon nanofibre growth was deposited onto a ceramic paper (Fisher, HCR-350-W) by adsorption and carbon nanofibres were grown directly into the three dimensional structure. The resulting carbon nanofibre electrode material is both electrically conducting and mechanically robust. Fig. 2.7 shows SEM images of the ceramic substrate and the resulting carbon nanofibre growth.
The heat resistant, highly porous ceramic paper was cut into 20 × 120 mm rectangular pieces. It was approximately 1 mm thick and had an overall weight of 18 mg cm⁻². The ceramic paper was thoroughly impregnated with the catalyst precursor, nanoparticulate Fe₂O₃, by dipping into the sol. The catalyst precursor impregnated ceramic paper was then dried and transferred into the tube furnace. The procedure for carbon nanofibre growth was as described in the previous section.

In the absence of catalyst no carbon growth was detected. The FEGSEM images in Fig. 2.7 (b) and (c) show the carbon nanofibre growth. The fibres are long and intertwined with a typical diameter of 100 nm. The weight of the deposit was typically 21 mg cm⁻² (this value was obtained by getting the difference in weight between a ceramic paper sample with and without CNF growth), which (assuming a density of 2.2 g cm⁻³) amounts to 1,200 m carbon nanofibre length, or 0.38 m² area per cm² geometric area (this corresponds to approximately 20 m² g⁻¹ carbon surface

Figure 2.7. FEGSEM images of (a) the ceramic paper substrate, (b) and (c) carbon nanofibres of typically 100 nm diameter, grown from ethylene gas directly onto the catalyst impregnated ceramic paper. The thickness of the carbon nanofibre coating on individual fibres is estimated as typically 10 - 20 μm.
per gram of carbon fibre material, in good agreement with earlier reports [21]). FEGSEM images were used to estimate the CNF diameter and length as 100 nm and 20 µm, respectively.

The value of the surface area estimated above, 20 m² g⁻¹, is the area that contributes to the faradaic current and is the area of significance in the context of electrochemistry. It is the voltammetric area, which is a function of the diffusional path length and the time scale of the experiment. This is the area that is readily penetrated by electrolyte solution under the conditions of an electrochemical experiment. BET surface area measurements were also conducted, by N₂ adsorption. A value of 114 m² g⁻¹ was obtained, which is the surface area that contributes to the non-faradaic current, e.g., this is the area of significance in supercapacitor measurements.

In addition to their growth onto ceramic paper, carbon nanofibres could also be grown onto individual ceramic fibres in a similar fashion. Bundles of fibres 11 µm in diameter and made from alumina/silica/boria (Al₂O₃:SiO₂:B₂O₃/70:28:2) were employed. Fig. 2.8 shows that the diameter of the fibres increased to about 30 µm after carbon nanofibre growth, i.e., the fibres were coated in a carbon film of approximately 10 µm.

![Figure 2.8. FEGSEM images of a carbon nanofibre deposit grown onto individual ceramic fibres, (a) & (b) showing different magnifications.](image)

2.3.4. Surface Synthesis of Carbon Nanofibres on Metal Substrates

The synthesis of supported carbon nanofibres is useful for their direct application as electrode materials. It has recently been demonstrated that stainless steel mesh can act
as a combined catalyst precursor and supporting material for CVD carbon nanofibre growth [22]. Emmenegger et al. also synthesised carbon nanotubes from an iron nitrate precursor solution spin coated onto an aluminium substrate [23]. Highly oriented carbon nanotubes have been produced on polycrystalline and single crystal nickel substrates by plasma enhanced hot filament CVD [24]. Carbon nanotubes have been synthesised directly onto stainless steel plates by the sequential combination of PECVD and thermal CVD [25]. A titanium substrate with a Ni layer as catalyst, deposited by magnetron sputtering, has been shown to give well-aligned carbon nanotubes by PECVD [26].

In this work, the direct growth of carbon nanofibres onto metallic substrates was feasible by depositing the iron oxide catalyst precursor onto a suitable metal substrate. The iron oxide catalyst was deposited onto a copper surface with the subsequent growth of carbon nanofibres by CVD. The images in Fig. 2.9 show the carbon nanofibre growth on copper produced using the standard procedure.

Figure 2.9. SEM of fibres grown using Fe$_2$O$_3$ nanoparticle solution coated onto a Cu sheet, 3 different magnifications shown. Cu particles are seen along the CNF.
The underlying copper surface was roughened during the carbon growth process. The carbon nanofibres are seen to adhere well. Fig. 2.9 (c) shows the presence of catalyst particles along the length of the nanofibres, as a result of the nucleation and growth mechanism occurring, and axial fibre growth can be observed.

2.4. Solubilisation of Carbon Nanofibres

2.4.1. Introduction

The chemical vapour deposition grown carbon nanofibre material was obtained under a strictly reducing atmosphere. The ‘as grown’ carbon nanofibres are highly hydrophobic and entirely insoluble in aqueous solution. However, for many applications it is crucial for the carbon nanofibre material to be soluble in aqueous environments. The soluble form of the carbon nanofibres can be used for the deposition of well-defined carbon electrodes (Chap. 3) or employed for co-deposition with metals (Chaps. 5 & 6).

In order to achieve solubilisation in water either (i) additives have to be employed (e.g., surfactants [27] or adsorbing polymers [28]) or (ii) the surface of the carbon has to be made hydrophilic. Hu et al. successfully obtained carboxyl modified carbon nanotubes by treating their raw carbon nanotubes with concentrated nitric acid [29]. Using a mixture of concentrated nitric and sulphuric acids Windle et al. introduced acidic groups onto nanotubes. This was verified with X-ray micro-analysis, which confirmed that they contained significant concentrations of carbon and oxygen [30].

Work on single walled carbon nanotubes has shown that they are soluble in an aqueous starch-iodine complex, where the amylose in starch is pre-organised into a helical formation by the iodine. The carbon nanotubes displace iodine molecules from the amylose helix [31]. Jia et al. reported the breaking of carbon nanotubes by boiling in nitric acid [32]. They found that the average length of the nanotubes was reduced and that the shorter tubes were relatively straight. The mechanism responsible is believed to be the oxidation of the nanotube wall at defect sites.

Here, the solubilisation of carbon nanofibres in water without additives is undertaken. Hence, an oxidative treatment under reflux in strongly oxidizing, concentrated nitric acid was applied to introduce polarity and hydrophilicity to the carbon surface.
2.4.2. Oxidative Breakdown and Solubilisation of Carbon Nanofibres

The furnace grown carbon nanofibres were oxidised in HNO₃ as follows. The fibres were placed in a 100 ml round bottomed flask and 60 ml of HNO₃ was added. A condenser was fitted to the flask, which was then heated to a gentle reflux, 135 °C approx., in a thermostatically controlled oil bath. The solution was heated at this temperature for 4 h during which time it turned from yellow to brown. The solution was allowed to cool and the fibres were washed several times with distilled water followed by sedimentation, until the fibres began to form a more stable suspension. The remaining solution was evaporated in an oven (100 °C).

The oxidised carbon nanofibres are hydrophilic and therefore more water-soluble. They are easily suspended in distilled water and form stable suspensions in alkaline aqueous media. They form less stable suspensions in acidic solution with the fibres settling out after 1 - 2 h.

Comparison of the As Grown and Oxidised Nanofibres by Microscopy and Spectroscopy

The as-grown carbon nanofibres are long and intertwined, as shown in (Sec. 2.3), and as illustrated in Fig. 2.10 (a). The acid treatment introduced carboxyl groups at the ends, and at weak points, of the fibres. From the FEGSEM image of the oxidised carbon nanofibres shown in Fig. 2.10 (b), it can be seen that the long fibres were broken into much shorter fragments. At higher magnification, Fig. 2.10 (c), the individual inter-grown components can be observed.
Figure 2.10. FEGSEM images of carbon nanofibres: (a) as grown, (b) after nitric acid digestion, and (c) after nitric acid digestion at high magnification.

The image in Fig. 2.10 (c) suggests a hierarchical structure with smaller individual fibres combining to make the larger diameter fibres. This image gives an important insight into the growth process. Individual fibres appear to form bundles, likely to be dependent on the density of the catalyst particles.

Next, the carbon nanofibre materials were compared via spectroscopy. Fig. 2.11 shows diffuse reflectance FTIR (DRIFTS, requires an instrument attachment - used for solid samples) spectra for (a) the as grown and (b) the oxidised carbon nanofibres, described in Chap. 1.9.4.
Figure 2.11. DRIFTS of carbon nanofibres (a) as grown and (b) after oxidation in HNO₃.

The peaks common to both spectra are located at 2856.6 and 2926 cm⁻¹, both -CH stretching absorptions. The carbonyl absorption peak is present at 1743.4 cm⁻¹ in the oxidised spectrum. It also exhibits a C-O stretching frequency at 1239 cm⁻¹. The as grown spectrum has a peak at 882 cm⁻¹ attributable to olefin C-H adsorption.

XPS can be used for elemental composition (qualitative and quantitative) analysis, described in Chap. 1.9.5. It can also provide chemical state information, with appropriate deconvolution of the spectrum. The technique has a detection limit of about 1 at.% and it requires a high vacuum, 10⁻⁶ mbar for the instrument used in this work. Fig. 2.12 shows the XPS spectrum of the as grown (unoxidised) carbon nanofibres.
Figure 2.12. XPS spectra of as grown carbon nanofibres (a) 1 - 1100 eV (85 eV, 20 mS, 5 scans) and (b) 268 - 298 eV (25 eV, 40 mS, 25 scans).

The only peak present is that of carbon at 285 eV. The Fe catalyst is not apparent; if present it would appear at 55 eV. XPS is surface sensitive, to a depth of 30 Å, so the Fe may still be present inside the carbon nanofibres.

The spectrum for the oxidised carbon nanofibres shows peaks for carbon and oxygen at 285 and 532 eV, respectively, Fig. 2.13 (a). Nitrogen as well as other elements are absent.
Figure 2.13. XPS spectra of oxidised carbon nanofibres (a) 1 - 1100 eV (85 eV, 20 mS, 5 scans) and (b) 268 - 298 eV (25 eV, 40 mS, 25 scans).

Fig. 2.13 (b) shows an expanded spectrum around the carbon peak showing a shoulder at higher energy than the main peak. The shoulder was not present in the unoxidised sample and is attributed to the hydroxyl, carbonyl, and carboxyl groups [33, 34, 35].

Raman spectra were recorded for the as grown and oxidised forms of the carbon nanofibres, more detail on Raman spectroscopy in Chap. 1.9.6. The signals observed at ~1350 cm\(^{-1}\) and ~1600 cm\(^{-1}\), Fig. 2.14, are indicative of the signals seen for a carbon spectrum. They are the first order graphite bands known as the D (disorder) and G (graphite) bands.
The first peak is the D band and can be assigned to sp$^3$ defects on the carbon nanofibres. The second peak, the G band, is caused by the Raman active $E_{2g}$ mode analogous to that of graphite [36]. It is due to the presence of sp$^2$ C [37]. The expanded region from 2250 - 3300 cm$^{-1}$ shows a distinct difference between the two spectra. The peaks observed are due to the symmetrical/asymmetrical C-H stretching modes of -CH$_2$ and -CH$_3$ and may overlap with the second order combination modes of the D and G bands. The decrease in the peak at $\sim$ 2700 cm$^{-1}$ is to be expected with a decrease in the number of CH$_x$ groups on oxidation of the carbon nanofibres. It is also expected that the ratio of the first order graphite peaks would change [38]. As the fibres are oxidised, sp$^2$ hybridised C changes into sp$^3$ C. A small increase in the ratio of the D:G intensity can be seen after oxidation.

McCreary attempted to describe a relationship between electrode structure and electroanalytical performance, showing the potential significance of the functional groups identified above [39]. The presence of chemisorbed oxygen, oxygen containing functional groups, and surface oxides was discussed. Possible surface oxide groups include quinone, phenol, carbonyl, etc. Variations in the surface oxides (type and quantity) was seen to be a major source of variability in the electrochemical performance. Several electrochemical observations, which are affected by surface structure, were discussed, including the voltammetric background, electron transfer kinetics, and adsorption.
Clear examples were discussed, where surface oxides accelerate electron transfer, such as cytochrome c, NADH oxidation, and O₂ reduction. In some cases a H/D isotope effect was observed, which was attributed to proton transfer to or from surface phenols. For these cases a clean surface is not sufficient for fast electron transfer. Redox mediation, proton assisted electron transfer and interaction with the oxide binding sites are three examples where surface oxides are directly involved with electron transfer.

A number of factors were seen to affect electron transfer at carbon, including the physicochemical properties of basal plane carbon which retarded electron transfer (e.g., low density of electronic states) [40]. Also, it was observed that the kinetics of aquated ions were very sensitive to the density of surface oxides on modified carbon electrodes, while those of various other redox systems were not [41]. The long term aim of this work was to provide a structural basis for electron transfer reactivity [40].

2.5. Electrochemical Processes at Immobilised Carbon Nanofibre Materials

2.5.1. Introduction

Carbon nanofibre materials are superb electrode materials due to their relatively high electrical conductivity and surface area [42]. The high electrical conductivity allows three dimensional carbon frameworks to be built and electrically connected. The high surface area is important for (i) conducting kinetically slow processes, (ii) accumulation of molecules from the solution phase by adsorption onto the surface at the solid/solution interface, and (iii) achieving high current densities.

The voltammetry of ‘as grown’ carbon nanofibres has been reported based on a simple ‘teabag’ technique [21]. The carbon nanofibre material was placed on a glassy carbon electrode and immobilised with a polymer membrane. The alternative immobilisation of carbon nanofibres in an inert dielectric such as paraffin has also been reported [43]. This resulted in the formation of a random array of carbon fibre electrodes exposed to the solution. This type of electrode was proposed for the analytical detection of zinc.
Carbon nanotubes, nanofibres, and other types of carbon nano-structures [44] have found wide-spread applications in electrochemistry, electroanalysis [45], and in bioelectrochemistry [46]. Novel electrodes have been prepared in the form of pastes [47], by mechanical abrasion onto suitable electrode surfaces [48], or as composite films with polymeric binders [49, 50]. The attraction of carbon as a relatively cheap and versatile material for electrode processes is associated with its abundance, high charge storage ability, and good conductivity, as well as the ease of chemical surface modification [51, 52, 53].

The rest of this chapter explores the characteristics of the novel carbon nanofibre/ceramic substrate as an electrode material. The material is shown to have interesting electrochemical properties.

2.5.2. Voltammetry of Carbon Nanofibres Grown onto Ceramic Supports I: Stagnant Solution

Carbon nanofibres were grown directly onto a ceramic substrate after impregnation of the surface with iron oxide catalyst precursor and transfer of the sample into the furnace, as described earlier in Sec. 2.3, and as illustrated by the SEM image of the resulting material, shown in Fig. 2.7.

This type of novel electrode combines mechanical stability, introduced by the ceramic backbone, and electrical conductivity/high surface area, introduced by the carbon growth. In order to use this type of material as an electrode, a disc was attached to a glassy carbon electrode and held in place with a Lycra membrane. The electrochemical properties of this electrode material will be described in stagnant solution, in this subsection, and in agitated solution, in the subsequent subsection.

Electrodes composed of carbon nanofibres grown onto ceramic paper substrates show well-defined electrochemical characteristics. When immersed in aqueous electrolyte solution (at pH 7) an essentially featureless potential window from $-0.6$ to $+0.8$ V vs. SCE becomes accessible and voltammetric signals due to the catalyst employed in the carbon nanofibre growth process are not observed. This behaviour is in contrast to that of the oxidised carbon nanofibres, which show peak-shaped signals due to
quinoid surface functionalities. Noticeable oxidation of the carbon surface occurs at potentials positive of 0.8 V vs. SCE.

Next, aqueous redox couples were investigated. In Fig. 2.15 voltammograms for the one electron reduction of 5 mM $\text{Ru(NH}_3\text{)}_6^{3+}$ in aqueous 1.0 M KCl are shown (Eq. 2.1).

![Cyclic voltammograms for the reduction of 5 mM $\text{Ru(NH}_3\text{)}_6^{3+}$ in 1.0 M KCl obtained (i) at a 3 mm diameter glassy carbon electrode (current scaled to be comparable with the voltammograms obtained at a 7 mm diameter carbon nanofibre electrode (ii-iv)).](image)

The $\text{Ru(NH}_3\text{)}_6^{3+/2+}$ redox couple is a well known reversible outer sphere electron transfer system.

$$\text{Ru(NH}_3\text{)}_6^{3+} + e^- \rightarrow \text{Ru(NH}_3\text{)}_6^{2+}$$  \hspace{1cm} (2.1)

The voltammogram shown in Fig. 2.15 (i) was recorded at a 3 mm diameter glassy carbon electrode and the current was scaled to be comparable with the voltammograms obtained at a 7 mm diameter carbon nanofibre electrode (ii-iv). The reversible reduction of $\text{Ru(NH}_3\text{)}_6^{3+}$ occurs with a half wave potential of $E_{1/2} = \frac{1}{2} (E_{p,\text{ox}} + E_{p,\text{red}}) = -0.21 \text{ V vs. SCE}$. At glassy carbon electrodes, a well-defined diffusion controlled voltammetric signal with an approx. 60 mV peak-to-peak separation is detected. The symmetric shape and position of the voltammetric signal detected at the carbon nanofibre electrode indicates a considerably different kind of process. The charge under the voltammetric signal, ca. 5 mC, is much higher than that expected for
diffusion to a disc electrode (compare to Fig. 2.15 (i)) and is in agreement with Ru(NH$_3$)$_6$$_{3+}$ trapped in the solution phase within the carbon nanofibre electrode. For experiments in a 5 mM Ru(NH$_3$)$_6$$_{3+}$ solution, a charge of 5 mC corresponds to a solution volume of ca. 0.01 cm$^3$, which is in good agreement with the approximate free volume in the carbon nanofibre/ceramic composite disc. The approximately symmetric shape of the voltammogram is indicative of thin film behaviour. However, the peak width at half height only approaches the theoretical limit of 91 mV [54] at very slow scan rates, Fig. 2.15 (ii). The increased capacitive background current in the cyclic voltammograms observed for the carbon nanofibre electrodes relative to the glassy carbon electrode is not surprising and is in agreement with the increased total electrode area, as approximated in Sec. 2.3.3. The peak-to-peak separation of 160 mV at a scan rate of 5 mV s$^{-1}$, Fig. 2.15 (iv), is consistent with an overall resistance effect equivalent to a resistor of approximately 100 $\Omega$.

Following this, the oxidation of an aromatic molecule, hydroquinone, was studied. Hydroquinone is oxidised in a 2 electron - 2 proton process, Eq. 2.2 [55].

\[
\begin{align*}
\text{Cyclic voltammograms for the oxidation of 5 mM hydroquinone in aqueous 1.0 M phosphate buffer (pH 7) at glassy carbon and at carbon nanofibre electrodes are shown in Fig. 2.16. The reversible potential for hydroquinone/benzoquinone, } & E_{1/2} = \frac{1}{2} (E_{p^{\text{ox}}} + E_{p^{\text{red}}}) = 0.04 \text{ V vs. SCE, is observed at both glassy carbon, Fig. 2.16 (i), and carbon nanofibre electrodes, Fig. 2.16 (ii-vi). However, the shape of the voltammetric peaks at these two types of electrode at identical scan rate, Fig. 2.16 (i) and (iv), are very different. The charge under the voltammetric peak observed for the carbon nanofibre electrodes, ca. 80 mC, is an order of magnitude higher than that expected for solution trapped in the electrode.}
\end{align*}
\]
Figure 2.16. Cyclic voltammograms for the oxidation of 5 mM hydroquinone in 1.0 M phosphate buffer (pH 7) obtained at (i) a 3 mm diameter glassy carbon electrode (current scaled to an electrode area of 0.38 cm²) and (ii-iv) a 7 mm diameter carbon nanofibre electrode (electrode area approx. 0.38 cm², scan rate (i) 10 mV s⁻¹, (ii) 2 mV s⁻¹, (iii) 5 mV s⁻¹, (iv) 10 mV s⁻¹). Cyclic voltammograms (scan rate 10 mV s⁻¹) for (v) the background current obtained with a fresh 7 mm diameter carbon nanofibre electrode in 1.0 M phosphate buffer (pH 7) and for (vi) the background current detected with a thoroughly rinsed 7 mm carbon nanofibre electrode after use in a solution containing 5 mM hydroquinone and 1.0 M phosphate buffer (pH 7) are also shown.

It is more interesting that the voltammetric signal for the hydroquinone/benzoquinone redox system remains, Fig. 2.16 (vi), when the electrode is thoroughly rinsed with water and re-immersed into an aqueous 1.0 M phosphate buffer solution (pH 7), which does not contain hydroquinone. Strong adsorption of the hydroquinone/benzoquinone system onto carbon nanofibre materials can explain this observation. The concentration dependence of this adsorption process was investigated over a wide range of hydroquinone concentrations, 1 mM to 0.5 M. Comparing with a Langmuir adsorption model, an approximate limit for monolayer adsorption at ca. 600 μC cm⁻² (based on the estimated total surface area) and an approximate equilibrium constant of ca. 2 mol¹ dm⁻³ were estimated. Monolayer coverage with benzoquinone is consistent with the surface area.

The hydroquinone adsorbate is removed from the surface of the carbon nanofibre electrode by immersion in ethanol for 30 min. Therefore, physisorption of both
hydroquinone and benzoquinone appears to occur. These compounds have a high affinity for the carbon nanofibre material. The voltammetric responses are dominated by the presence of adsorbed material. The asymmetric shape of the voltammetric responses is, at least in part, due to resistance effects.

Another system studied was the electrochemical oxidation of phenol and phenol derivatives, which is an important process for the analytical detection of phenols [56] and for the oxidative destruction of phenol impurities in aqueous systems [57]. The electrochemical oxidation of phenol is known to proceed predominantly via a one-electron transfer and the formation of insoluble and non-conducting polymeric products (e.g., poly-oxyphenylenes [58]), which lead to electrode ‘fouling’. This process is demonstrated at a glassy carbon electrode in Fig. 2.17 (i).

Figure 2.17. Multi-cycle cyclic voltammograms (scan rate 10 mV s⁻¹) for the oxidation of 50 mM phenol in 1.0 M phosphate buffer (pH 7) obtained at (i) a 3 mm diameter glassy carbon electrode and (ii) a 7 mm diameter carbon nanofibre electrode (geometric electrode area approx. 0.38 cm²). (iii) shows multi-cycle voltammograms obtained in 1.0 M phosphate buffer (pH 7) after 30 min. immersion of a fresh carbon nanofibre electrode in a 1.0 M phosphate buffer solution containing 50 mM phenol and thorough rinsing in water. Ar sparged solution.
At a glassy carbon electrode, immersed in 50 mM phenol in aqueous 1.0 M phosphate buffer (pH 7), a significant oxidation response is only detected during the first potential cycle of a multi-cycle cyclic voltammogram. The charge under the oxidation peak amounts to a deposition of \( \text{ca. } 120 \times 10^{-9} \text{ mol cm}^{-2} \) (assuming one electron is transferred per phenol molecule).

A carbon nanofibre disc electrode immersed in 50 mM phenol in aqueous 1.0 M phosphate buffer (pH 7) solution also shows the characteristic phenol oxidation response at a potential of approximately 0.74 V vs. SCE, Fig. 2.17 (ii). However, in this case the electrode continues to function for several potential cycles. Integration of the charge under the oxidation peak at 0.74 V vs. SCE, observed during the first potential cycle, (\( \text{ca. } 0.3 \text{ C} \)) suggests that phenol accumulates by adsorption onto the carbon nanofibres (and/or transfer of several electrons per phenol molecule). Immersion of a fresh carbon nanofibre electrode into a solution of 50 mM phenol in 1.0 M phosphate buffer (pH 7) followed by thorough rinsing with water and re-immersion of the electrode into pure phosphate buffer also allows the characteristic oxidation response for adsorbed phenol to be detected, Fig. 2.17 (iii). From the estimated electrode area for the carbon nanofibre electrode (\( \text{ca. } 0.15 \text{ m}^2 \)), Sec. 2.3.3, it can be deduced that the average current density at the carbon nanofibre electrode immersed in 50 mM phenol solution, compared with that observed at the glassy carbon electrode, is substantially smaller (by a factor of 60, approximately).

There may also be a resistance effect due to the nature of the ceramic supported CNFs. An uncompensated resistance has the effect of drawing out the peaks along the potential axis, shifting peaks, and decreasing peak heights [59]. Under steady state conditions the effect of an IR drop is greatly diminished.

A new voltammetric signal, with \( E_{1/2} = 0.04 \) V vs. SCE, is detected. This reversible oxidation/reduction response is observed at the same potential and with similar characteristics compared to those observed for the hydroquinone/benzoquinone redox system. Therefore, multi-electron oxidation of phenol adsorbed onto the carbon nanofibres seems to occur. However, a second weaker signal at \( E_{1/2} = 0.29 \) V vs. SCE is also observed and after rinsing with ethanol the new voltammetric signals remain.
This suggests that under the high concentration conditions employed here, the phenol oxidation process follows a multi-electron pathway with a complex mixture of products remaining adsorbed at the carbon surface.

Both strong adsorption and the relatively high electrode area of the carbon nanofibre electrodes (lower average current density) seem to change the reaction pathway for phenol oxidation. A plausible (and oversimplified) mechanism for the detection of the hydroquinone/benzoquinone signal after phenol oxidation is proposed in Fig. 2.18.

![Figure 2.18. Reaction scheme for the proposed mechanism for multi-electron phenol oxidation.](image)

Oxidation of the adsorbed phenol may occur in two steps and without polymerization. Nucleophilic attack at the phenoxonium intermediate [60] and a further two electron – two proton oxidation finally yield benzoquinone.

In conclusion, carbon nanofibre electrodes have been grown onto a porous ceramic substrate. The resulting electrode material, although to some extent electrically resistive, shows promising properties for applications in electrochemistry. In particular, the observation of strong adsorption of some aromatic compounds onto the surface of the carbon nanofibre composite electrode could be of potential importance for future applications in electroanalysis.

2.5.3. Voltammetry of Carbon Nanofibres Grown onto Ceramic Supports II: Agitated Solution

Introducing fast mass transport into electrochemical reactions is often required to improve the efficiency of processes and the flux of materials to the electrode surface in general. An unusual, but very versatile, way of improving mass transport is to apply ultrasound to electrode surfaces. In the literature, there are numerous examples of ultrasound applied to flat electrode surfaces, but no account of the effects of
ultrasound at highly porous electrodes. Here, ultrasound from a glass horn emitter is applied to carbon nanofibre composite electrodes.

Hydroquinone is oxidised in aqueous solution in a reversible 2-electron - 2-proton process leading to quinone as the main product (see Eq. 2.2). The process has already been studied and compared at glassy carbon and carbon nanofibre electrodes, see previous section. The process is diffusion controlled and therefore predicted to be strongly affected by the mass transport increase in the presence of ultrasound.

Fig. 2.19 (A) shows typical sonovoltammograms in 1.0 M phosphate buffer solution, pH 7 obtained at a 3 mm diameter glassy carbon electrode. As expected, a linear increase in the mass transport controlled limiting current with concentration is observed.

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Figure 2.19. Sonovoltammograms for the oxidation of hydroquinone in aqueous 1.0 M phosphate buffer solution at pH 7 (5 mm horn to electrode distance, 24 kHz, 8 W cm\(^{-2}\)) at a scan rate of 0.02 V s\(^{-1}\) obtained at (A) a 3 mm diameter glassy carbon electrode and (B) a carbon nanofibre electrode (geometric electrode area 0.38 cm\(^2\)). In (C) a plot of the diffusion layer thickness, \(\delta_{\text{sono}}\), determined from the steady state limiting currents versus the horn to electrode distance is shown (errors estimated).
Sonovoltammograms obtained at a carbon nanofibre ceramic composite electrode are shown for comparison, Fig. 2.19 (B). The carbon nanofibre/ceramic composite structure remains essentially undamaged in the presence of 8 W cm$^{-2}$ ultrasound, evidenced by the fact that voltammograms can be obtained over prolonged periods of time without loss of signal. In part, this is because the ultrasound intensity applied in these experiments is lower and less violent compared to that applied in work reported with titanium horn transducers [61]. It can be observed that the sonovoltammetric response at carbon nanofibres is very different compared to that shown in Fig. 2.19 (A) for the oxidation of hydroquinone at glassy carbon. There are three distinct current components associated with (i) hydroquinone adsorbed onto the carbon nanofibre surface, resulting in a peak response, (ii) hydroquinone from the solution phase being transported to the electrode and oxidised to quinone in a sigmoidal steady state response, and (iii) a considerable capacitive charging or background current. The peak current, due to the electrochemically reversible oxidation of adsorbed hydroquinone, is concentration dependent and has been shown to follow Langmuir adsorption characteristics, see Sec. 2.5.2. The capacitive background current (obtained from cyclic voltammograms shown in Fig. 2.19 (B)) observed for the carbon nanofibre/ceramic composite electrode is a factor of 2000 higher, compared to that for the glassy carbon electrode, consistent with the increased surface area. Here, the main point of interest is the sigmoidal steady state response observed at potentials positive of the peak response, because it can be used to calculate the average rate of mass transport from the limiting current.

The mass transport to a solid surface in sonoelectrochemical processes can generally be understood in terms of two factors: (i) macroscopic streaming (a turbulent flow of liquid from the horn probe towards the electrode surface [62]) and (ii) microstreaming processes (due to oscillating and collapsing bubbles at the solid/solution interface [63, 64, 65]). The latter type of process dominates at short time scales and at small electrodes. Both processes contribute to the average limiting current, $I_{\text{sono}}$, detected at a macroscopic electrode. In order to describe the average mass transport to a first approximation, fluctuations in the current can be ignored and the average mass transport coefficient, $m_{\text{sono}}$, can be determined from the average limiting current, $I_{\text{sono}}$, (see Eq. 2.3) assuming a planar diffusion mode [66]. In some cases it is advantageous
to express $m_{\text{sono}}$ in terms of the diffusion coefficient, $D$, and the average diffusion layer thickness, $\delta_{\text{sono}}$. The implicit assumption, $I_{\text{sono}} \propto D$, made in this step does not necessarily hold [67] and may introduce the need for correction [68]. However, in general, Eq. 2.3 is relatively robust [69] and can be applied to voltammetric data to give the average diffusion layer thickness, $\delta_{\text{sono}}$.

$$\frac{I_{\text{sono}}}{A} = n F c m_{\text{sono}} = n F c \frac{D}{\delta_{\text{sono}}}$$

(2.3)

In this equation, the current density, $\frac{I_{\text{sono}}}{A}$, is related to $n$, the number of electrons transferred per molecule of reactant diffusing to the electrode, $F$ is Faraday’s constant, $D$ is the diffusion coefficient, $c$ is the concentration in bulk solution, and $\delta_{\text{sono}}$ is the average diffusion layer thickness. The diffusion coefficient for hydroquinone in aqueous solution has been reported to be $D_{\text{hydroquinone}} = 0.85 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [70]. An analysis of the diffusion layer thickness as a function of the electrode/horn distance is shown in Fig. 2.19 (C). At glassy carbon, the diffusion layer thickness is typically 4 - 10 $\mu$m (depending on distance and power), whereas at the porous carbon nanofibre composite electrode the diffusion layer thickness is approximately an order of magnitude smaller, under otherwise identical conditions. So, for the same geometric area, a much higher current and, therefore, a faster conversion are possible.

In order to explain the observation, two arguments are plausible: (i) the interfacial cavitation process and therefore the mass transport inducing step may depend on the type and extent of the electrode surface, or (ii), and probably more important, the turbulent mass transport conditions allow a higher surface area to be accessed locally.
In Fig. 2.20, the idea of a higher surface area becoming accessible in the presence of ultrasound is shown schematically. The turbulent flow pattern allows 'pockets' in the electrode material to be accessed efficiently. Therefore, an increased surface area, rather than the apparently thinner diffusion layer thickness, is responsible for the higher average limiting currents. The value of the surface area estimated earlier was 20 m$^2$ g$^{-1}$, which is the voltammetrically active area contributing to the faradaic current and is a function of the diffusional path length and the time scale of the experiment. This area becomes increasingly penetrable under the mass transport conditions attained with ultrasound. More of the porous structure becomes accessible. The BET surface area of 114 m$^2$ g$^{-1}$ is the surface area that contributes to the non-faradaic current, and remains inaccessible under the timescale involved.

In order to gain further insight into the sonovoltammetric process in the presence of the carbon nanofibre ceramic composite electrode, the reversible one electron reduction of Ru(NH$_3$)$_6^{3+}$, Eq. 2.1, was also investigated.
Figure 2.21. Sonovoltammograms obtained at a 3 mm diameter glassy carbon electrode for the reduction of 5 mM \( \text{Ru(NH}_3\text{)}_6^{3+} \) in aqueous 1.0 M KCl (5 mm horn to electrode distance, 24 kHz, 8 W cm\(^{-2}\)) at a scan rate of (A) 0.02 V s\(^{-1}\), (B) 1 V s\(^{-1}\), and (C) 4 V s\(^{-1}\).

The voltammograms shown in Fig. 2.21 were recorded at a 3 mm diameter glassy carbon disk electrode immersed in 5 mM \( \text{Ru(NH}_3\text{)}_6^{3+} \) in 1.0 M KCl in the presence of ultrasound. At slow scan rates a typical quasi steady state current response with a limiting current density of approximately 5 mA cm\(^{-2}\) is detected. Based on Eq. 2.3 and assuming a diffusion coefficient of \( D_{\text{Ru}} = 0.91 \times 10^{-9} \text{ m}^2\text{s}^{-1} \) [71], this limiting current is consistent with an average diffusion layer thickness of 9 ± 2 \( \mu \text{m} \) and is in agreement with the results observed for hydroquinone. Next, Fig. 2.21 (B) and (C) show the voltammetric responses for the case of faster scan rates. Clearly, the peak response characteristics for a cyclic voltammogram are emerging at fast scan rates. The observation of forward and back current peaks in the cyclic voltammogram can be understood as a sign that the time between reduction and oxidation (the voltammetric time scale) becomes too fast for molecules to escape from the diffusion layer.
Figure 2.22. Plot of the limiting and peak current densities for sonovoltammograms obtained at a flat glassy carbon (squares) and at a porous carbon nanofibre/ceramic composite electrode (x's) (see Figs. 2.21 & 2.23) versus 'voltammetric time scale', $\tau = \frac{RT}{vF}$ (errors estimated). The shaded regions correspond to the transition zones between the steady state and transient behaviour and are associated with $\tau_{\text{flat}}$ and $\tau_{\text{porous}}$ (see text).

Fig. 2.22 shows a plot of the peak current density (black squares) versus the voltammetric time, $\tau = \frac{RT}{vF}$, which corresponds to the inverse of the scan rate, $v$, multiplied by $\frac{RT}{F}$. At slow scan rates (short time scales) a steady state limiting current is observed and at very fast scan rates (long/fast time scales) a strong peak current is detected. The expected increase in the peak current with the square root of scan rate is observed at fast scan rates (see dotted line), in agreement with the appropriate Randles-Sevčík expression for the peak current [72]. The intersection between the two linear regions in the plot (see Fig. 2.22) allows the average time $\tau_{\text{NH}_3}_{6}^{3+}$ molecules spent within the diffusion layer to be estimated as $\tau_{\text{flat}} \approx 50$ ms. A very similar estimate can be derived directly from the known diffusion layer thickness and $\tau = \frac{D^{2}}{D}$. 

79
Figure 2.23. Sonovoltammograms obtained at a carbon nanofibre composite electrode (geometric electrode area 0.38 cm²) for the reduction of 5 mM Ru(NH₃)₆³⁺ in aqueous 1.0 M KCl (5 mm horn to electrode distance, 24 kHz, 8 W cm⁻²) at a scan rate of (A) 0.15 V s⁻¹, (B) 0.05 V s⁻¹, and (C) 0.02 V s⁻¹. For these measurements 8 Ω compensation was applied to minimise distortions due to the IR drop.

Voltammograms for the reduction of Ru(NH₃)₆³⁺ at a 4 mm diameter carbon nanofibre/ceramic disk electrode are shown in Fig. 2.23. As expected, a considerable capacitive background current is observed. However, in addition, a steady state current component and a peak current component (at sufficiently high scan rates) can be identified. The steady state limiting current, approximately 25 ± 3 mA cm⁻², is consistent with an average diffusion layer thickness of approximately 1.6 ± 0.2 μm, which again suggests that the current expressed per geometric electrode area is increased at carbon nanofibre/ceramic composite electrodes when compared to flat glassy carbon. However, the plot of the peak current versus voltammetric time (see Fig. 2.22) suggests that the average time spent by the Ru(NH₃)₆³⁺ molecules in the diffusion layer of the porous electrode, τporous ≈ 600 ms, is substantially increased compared to that observed at flat glassy carbon. Therefore, the porous carbon nanofibre/ceramic composite electrode, in the presence of power ultrasound, leads to (i) an overall faster mass transport effect, and (ii) an increased contact time between reactant and electrode.

As a possible application of carbon nanofibre/ceramic composite electrodes, one can envisage electrode reactions, which proceed at a slow rate or which require several collisions between reactant and electrode surface. One extreme case of this type of redox reaction is the electron transfer between an electrode and a colloidal particle [73]. It has recently been shown [15] that Fe₂O₃ nanoparticles in aqueous solution give voltammetric responses in the presence of power ultrasound. However, electron
transfer appeared to be slow and sensitive to the composition of the aqueous electrolyte. The overall redox process can be expressed as a multi-electron transfer associated with dissolution (see Eq. 2.4). The number of iron cations per particle, \( n \), is approximately 2500 in this experiment (particle size ca. 4 - 5 nm [15]).

\[
[Fe_2O_3]_{n+2}(\text{solid}) + ne^- + 3nH^+(aq) \rightarrow Fe^{2+}(aq) + 1.5nH_2O \quad (2.4)
\]

Experiments employing a glassy carbon electrode immersed in aqueous 0.1 M KCl, containing different concentrations of hydrous iron oxide with and without ultrasound, failed to give any voltammetric signature for the reduction of Fe(III) to Fe(II).

![Figure 2.24. Sonovoltammograms obtained at a carbon nanofibre electrode (geometric electrode area 0.13 cm\(^2\)) for the reduction of colloidal hydrous iron oxide (particle size approximately 4 - 5 nm) with (A) 0 mM, (B) 1.8 mM, (C) 3.3 mM, and (D) 4.0 mM Fe content in aqueous 0.1 M KCl (5 mm horn to electrode distance, 24 kHz, 8 W cm\(^{-2}\)) at a scan rate of 0.02 V s\(^{-1}\).](image)

Figure 2.24. Sonovoltammograms obtained at a carbon nanofibre electrode (geometric electrode area 0.13 cm\(^2\)) for the reduction of colloidal hydrous iron oxide (particle size approximately 4 - 5 nm) with (A) 0 mM, (B) 1.8 mM, (C) 3.3 mM, and (D) 4.0 mM Fe content in aqueous 0.1 M KCl (5 mm horn to electrode distance, 24 kHz, 8 W cm\(^{-2}\)) at a scan rate of 0.02 V s\(^{-1}\).

A considerable change is observed when the carbon nanofibre/ceramic composite electrode is employed. The voltammograms in Fig. 2.24 show that with an increasing concentration of hydrous iron oxide a new voltammetric reduction response is detected. It is composed of (i) a steady state reduction response commencing at approximately \(-0.2 \text{ V vs. SCE} \) and (ii) anodic peak responses at \(-0.5 \text{ and } -0.2 \text{ V vs. SCE} \). The peak responses have to be attributed to forms of Fe\(^{2+}\) trapped in the structure of the carbon nanofibre/ceramic composite electrode. However, the steady state response is consistent with Fe\(_2\)O\(_3\) particles being reduced in the porous electrode environment (Eq. 2.4). An analysis of the increase in the limiting current as a function of concentration (Fig. 2.24) allows an estimate for the diffusion layer thickness to be
obtained (Eq. 2.3). From the number of electrons transferred per nanoparticle, \( n = 2500 \), the estimated diffusion coefficient \( D_{HFO} = 8.5 \times 10^{-11} \text{ m}^2\text{s}^{-1} \) [15], and the voltammetric data shown in Fig. 2.24, an approximate value of \( \delta_{\text{sono}} = 0.7 \pm 0.2 \mu \text{m} \) is obtained. This value is reasonable and suggests that \( \text{Fe}_2\text{O}_3 \) nanoparticles are fully reduced during their interaction with the porous electrode.

In conclusion, it has been shown that porous electrodes, such as carbon nanofibre/ceramic composite electrodes, can be employed beneficially in the presence of power ultrasound. Mass transport to and into the porous electrode is enhanced and extremely fast even at a modest ultrasound intensity. The effect of ultrasound on mass transport in the porous electrode has been determined quantitatively. In spite of the increase in mass transport, even slow electrode reactions may proceed due to a longer contact time between the reagent and the electrode. However, details about the distribution of the contact times are currently not known, and the impact of the porous electrode topography on sonoelectrochemical reaction mechanisms may be more complex, as suggested by a longer contact time.
References

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Chapter 3
Electrochemical Characterisation of Ultra-thin Carbon Nanofibre/Chitosan Films
3.1. Introduction

Very thin films of carbon can be prepared, e.g., by evaporation coating or by various chemical vapour deposition techniques [1]. Carbon electrodeposition from organic solvent systems has been reported [2]. New wet chemical methods for the assembly and deposition of charged nano-particulate materials from solution have been developed [3, 4]. In particular, layer-by-layer deposits formed using ionomeric binder molecules have attracted attention [5]. Also, the layer-by-layer deposition of carbon nanotube materials has been reported recently [6]. It is shown here, that this versatile strategy is also successful for the formation of ultrathin carbon nanofibre films. For the deposition process to work, the negatively charged carbon nanofibre material, oxidised carbon nanofibres (Chap. 2.4), has to be suspended in a suitable solution (here aqueous 0.1 M acetate buffer at pH 5), and a cationic binder (here chitosan) has to be employed to promote layer-by-layer binding to a substrate surface.

Chitosan (or poly(D-glucosamine)) is a modified carbohydrate polymer derived from chitin (see structure in Fig. 3.1).

Figure 3.1. Molecular structural unit of the chitosan polymer.

Chitosan is chemically stable and has been used in electrochemical applications such as chitosan-modified glassy carbon electrodes for total iron determination [7], as a glucose sensor [8], as a biosensor matrix [9], and for the determination of EDTA species in water [10].

In this chapter, well-defined amounts of oxidised carbon nanofibre material were deposited onto tin-doped indium oxide (ITO) electrodes by solvent evaporation, which could then be characterised electrochemically. Also, a novel methodology for the layer-by-layer deposition of very thin layers of carbon nanofibres with a chitosan...
binder was developed. Electrically conducting and electrochemically active films were formed; their thickness was controlled by the number of deposition cycles.

The films were characterised by electron microscopy, conductivity measurements, and quartz crystal microbalance gravimetry.

This new type of electrode has the properties of a transparent carbon electrode due to the extremely thin carbon coating. The capacitive background current and the Faradaic current for the aqueous hydroquinone/benzoquinone redox system were investigated and compared for carbon nanofibre deposits formed with and without chitosan. In the presence of chitosan and for relatively high hydroquinone concentrations, the electron transfer between the ITO substrate and the carbon nanofibre deposit becomes rate limiting.

3.2. Experimental

3.2.1. Chemicals
Chitosan (poly(D-glucosamine, low molecular weight, Aldrich), and HCl (32 %, Fisher) were obtained commercially and were used without further purification. For further details see Chap. 2.2.1.

3.2.2. Instrumentation
The working electrodes were made from tin-doped indium oxide (ITO) coated glass (1 cm x 6 cm, 30 Ω per square, Image Optics, Basildon, UK). ITO is a commonly used substrate due to its conductivity and the fact that it can act as a support for various species. The ITO electrode was rinsed with ethanol, heat treated in a furnace for 1 h at 500 °C, and re-equilibrated to ambient conditions prior to use. Quartz crystal microbalance experiments were conducted with a lab-made oscillator and a Fluke PM6680B counter at 9.1 MHz ITO coated quartz crystals (QA-A9M-ITOM, Advanced Measurement Technology, Wokingham, UK). Layer by layer deposits were prepared using a dip coating robot (DSG Dip Carousel, Nima Technology, Coventry, UK). For further details see Chap. 2.2.2.
3.2.3. Formation of Water Soluble Carbon Nanofibre Fragments

The carbon nanofibres were grown from ethylene at 600 °C in contact with the iron catalyst formed by the reduction of the Fe₂O₃ precursor, as described earlier (Chap. 2.3) and following a literature procedure [11, 12]. The oxidation of the CNFs with HNO₃ was also carried out as outlined earlier in Chap. 2.4.

The fibres were broken down into shorter fragments, which under high magnification allowed the components of the individual bundles to be observed. The carbon nanofibre fragments are easily suspended in distilled water and form stable suspensions in alkaline aqueous media.

3.2.4. Layer-by-Layer Formation of Carbon Nanofibre/Chitosan Composite Films

Solutions of chitosan (ca. 0.25 mg in 1 cm³) and carbon nanofibres (ca. 1 mg in 1 cm³) were prepared in 0.1 M acetate buffer at pH 5. The deposition process relies on the interaction of the positively charged chitosan ionomer with the negatively charged carbon fragments. A robotic dip coating method was developed to perform the layer-by-layer deposition, which is shown schematically in Fig. 3.2.

![Figure 3.2. Schematic drawing of the layer-by-layer deposition process, employing the chitosan binder and carbon nanofibre fragments, alternately.](image)

A single deposition cycle consisted of the following steps:

1) dipping a clean ITO electrode into stirred chitosan solution, holding for 30 s,
raising the electrode and holding for 5 s,

2) dipping into stirred water, holding for 30 s, raising the electrode and holding for 5 s (twice),

3) dipping into stirred carbon nanofibre solution, holding for 30 s, raising the electrode and holding for 5 s,

4) dipping into stirred water, holding for 30 s, raising the electrode and holding for 5 s (twice).

These steps were repeated for the required number of layers. The colour of the ITO electrode was observed to darken with an increasing number of deposition cycles. Typical FEGSEM images of a 10 layer chitosan/carbon nanofibre deposit are shown in Fig. 3.3. The film thickness is similar to the nanofibre diameter (50 - 200 nm).

![FEGSEM image of a 10 layer carbon nanofibre/chitosan layer-by-layer deposit on ITO at (a) lower and at (b) higher magnification.](image)

**Figure 3.3.** FEGSEM image of a 10 layer carbon nanofibre/chitosan layer-by-layer deposit on ITO at (a) lower and at (b) higher magnification.

### 3.2.5. ITO Conductivity Probes and Conductivity Measurements

In order to determine the conductivity (lateral) of ultrathin carbon nanofibre/chitosan films, ITO electrodes (1 cm × 6 cm) were patterned by etching. Two electrodes, with a 1 mm gap, were made by masking the two electrode areas with tape (Scotch tape, 3M), etching the exposed ITO layer with HCl vapour, and rinsing with distilled water. After removing the tape, two electrodes separated by an insulating glass surface were formed. These electrodes were then used for the layer-by-layer film growth (over a length of 1 cm) and the resistances of the resulting films were measured across the non-conducting area using a potentiostat in two electrode mode. Very low currents were measured and from the current/voltage plot true ohmic behaviour was inferred.
Typical conductivities measured for the films (after drying and equilibrating in air) were $2 \pm 1 \times 10^9$ Ohm, independent of the number of layers deposited (independent of the thickness of the carbon deposit). From this behaviour it was concluded that the resistance measured is not a bulk resistance, but the contact resistance between the carbon nanofibre fragments and the ITO surface and due to the chitosan binder film, see below.

3.3. Results and Discussion

3.3.1. Deposition and Characterisation of Hydrophilised Carbon Nanofibre Fragments at ITO Electrodes

Carbon nanofibres are of considerable interest as electrode materials and methods of depositing carbon nanofibres have been developed based on direct growth onto an electrode [13] or onto a ceramic substrate, as described earlier in Chap. 2, membrane immobilisation [14], composite formation [15], and abrasion techniques [16]. Uniform films with good stability and controlled thickness are difficult to achieve using these techniques. In this section an alternative layer-by-layer deposition approach for the formation of well-defined and electrochemically active films containing carbon nanofibre fragments is described.

Carbon nanofibres in the hydrophobic ‘as grown’ state have been studied electrochemically, [14] and Chap. 2.5, but due to their complex structure (Fig. 2.10 (a)) are difficult to deposit in the form of a film. However, after oxidation, causing fragmentation (Fig. 2.10 (b) and (c)), the carbon nanofibres are hydrophilic due to extensive surface functionalisation with carboxylate, quinone, and other oxygen containing groups. The presence of the oxygen containing groups was confirmed using spectroscopic techniques, as described earlier, Chap. 2.4. After oxidation in nitric acid the carbon nanofibres become soluble in alkaline aqueous media and temporarily soluble in neutral aqueous buffer media.

3.3.2. Electrochemical Characterisation of Carbon Nanofibre Deposits I: The Capacitive Background Current

A solution of hydrophilised carbon nanofibres in water (2 µg per 1 µL) was prepared and deposited by solvent evaporation onto tin-doped indium oxide electrodes. Fig. 3.4
shows typical cyclic voltammetric current responses obtained as a function of the amount of deposit.

![Cyclic voltammograms](image)

**Figure 3.4.** (A) Cyclic voltammograms (scan rate 50 mV s⁻¹) obtained in aqueous 1.0 M phosphate buffer solution, pH 2, for varying amounts of oxidised carbon nanofibres deposited onto an ITO electrode: (a) no carbon nanofibres deposited, (b) 2 µg, (c) 4 µg, (d) 11 µg, and (e) 22 µg. (B) Graph of peak current vs. the amount of carbon nanofibre deposited onto the ITO electrode surface (conditions as in (A)).

It can be seen clearly that the peak signal is (pseudo-)capacitive in nature and directly proportional to the weight of carbon nanofibres deposited (Fig. 3.4 (B)). The capacitance is typically 150 F g⁻¹ over a 1 V potential window, with a reduced capacitive response outside this potential region. The reasons for the high capacitive current response (in comparison to the as grown material, 20 F g⁻¹ [14]) are fragmentation and the presence of quinone/quinol surface functional groups.

The effect of scan rate on the voltammetric current signal is shown in Fig. 3.5.
Figure 3.5. (A) Cyclic voltammograms (scan rates (a) 5 mV s\(^{-1}\), (b) 20 mV s\(^{-1}\), (c) 50 mV s\(^{-1}\), and (d) 100 mV s\(^{-1}\)) obtained in aqueous 1.0 M phosphate buffer, pH 2, for 11 \(\mu\)g of carbon nanofibres deposited onto an ITO electrode. (B) Variation of peak current with scan rate, obtained at an ITO electrode modified with 11 \(\mu\)g carbon nanofibres (conditions as in (A)).

As expected for a surface immobilised redox system, a linear increase in current with increasing scan rate is observed, up to a certain scan rate, 50 mV s\(^{-1}\). The widening peak-to-peak separation, observed at higher scan rates, is indicative of the onset of slow electron transport across the ITO|carbon contact or through the carbon nanofibre film deposit. The deposit formed by solvent evaporation is uneven in nature but suitable for the study of the redox behaviour of the hydrophilised carbon in acidic aqueous buffer media.

3.3.3. Electrochemical Characterisation of Carbon Nanofibre Deposits II: The Aqueous Hydroquinone/Benzoquinone System

Next, the electron transfer reactivity of the carbon nanofibre deposit was investigated. The hydroquinone/benzoquinone redox system is kinetically very slow on ceramic electrode surfaces such as tin-doped indium oxide (ITO). In Fig. 3.6 (a) typical voltammetric current responses are shown for the oxidation of 5 mM hydroquinone in 1.0 M phosphate buffer, pH 2, at a clean ITO electrode.
Oxidation is observed at a potential of ca. +1 V vs. SCE and after reversal of the scan direction, the reduction of benzoquinone to hydroquinone is observed at -0.3 V vs. SCE. The substantial (and symmetrical) gap between the oxidation and reduction process is a sign of slow electron transfer at the ITO surface. The presence of carbon nanofibres on the ITO electrode, deposited by solvent evaporation, allows for much faster redox processes. In the presence of 11 µg of hydrophilised carbon nanofibres an almost reversible voltammetric response is observed at 0.33 V vs. SCE, Fig. 3.6 (b) – (e). Electron transfer occurs indirectly via the carbon nanofibres, which act as a dense array of carbon nano-electrodes.

3.3.4. Layer-by-Layer Deposition and Characterisation of Hydrophilised Carbon Nanofibre/Chitosan Films at ITO Electrodes

Next, in order to form electrode surfaces with an even and homogeneous film of hydrophilised carbon nanofibres, a layer-by-layer deposition process was developed. Many examples of layered films formed due to the electrostatic interaction of two components are known [17] but this is the first instance of a carbon nanofibre film being formed by employing this process. Hydrophilised carbon nanofibre fragments
are negatively charged and require a positively charged binder. Here chitosan (Fig. 3.1) is employed as a well-known positively charged ionomer, which has been used, e.g., for the deposition of layered silica films [18].

The films were grown as described in the experimental section, Sec. 3.2.4. Direct evidence for the deposition process comes from quartz crystal microbalance measurements. Fig. 3.7 shows mass data for a dry 9.1 MHz ITO coated quartz crystal resonator after each chitosan and hydrophilised carbon nanofibre deposition step.

![Graph showing weight of chitosan and CNF](image)

Figure 3.7. Graph, from QCM data, of the weight of chitosan (●) and CNF (■) added with each layer deposited onto an ITO coated quartz crystal resonator.

From the data it can be seen that typically 50 ng chitosan and 80 ng hydrophilised carbon nanofibres were deposited onto the $20 \times 10^{-6}$ m$^2$ resonator surface per deposition step. This amount of deposit is not inconsistent with the electron micrographs shown in Fig. 3.3. With this deposition technique, it is now possible to immobilise very small amounts of hydrophilised carbon nanofibres evenly (from FEGSEM images) at the ITO electrode surface.

3.3.5. Electrochemical Characterisation of Ultra-thin Carbon Nanofibre/Chitosan Composite Films I: The Capacitive Background Current

Hydrophilised carbon nanofibres, when co-deposited in layers with chitosan onto ITO electrodes and immersed in aqueous phosphate buffer at pH 7, typically result in peak-shaped current responses similar to those observed for deposits formed via solvent evaporation (compare Fig. 3.8 and Fig. 3.4).
Figure 3.8. Cyclic voltammograms (scan rate 50 mV s\(^{-1}\)) at ITO electrodes (1 cm\(^2\) exposed area) with different numbers, as marked, of carbon nanofibre/chitosan layers, 0.1 M PBS, pH 7.

For the initial 5 layers, the (pseudo-)capacitive current response increases with the number of layers deposited (Fig. 3.8), but for higher numbers of layers more complex and less reproducible behaviour was observed. The approximate charge stored per gram of hydrophilised carbon nanofibre material, ca. 180 F g\(^{-1}\), was estimated from knowing the amount of deposit (Fig. 3.7) and the current response (Fig. 3.8). This result is consistent with the value observed for hydrophilised carbon deposited by solvent evaporation, discussed above. It is likely that smaller fragments deposit more readily/preferentially causing the slightly higher value.

3.3.6. Electrochemical Characterisation of Ultra-thin Carbon Nanofibre/Chitosan Composite Films II: The Hydroquinone/Benzoquinone System

Subsequently, the ability of the carbon nanofibre/chitosan composite film to enhance electron transfer from the ITO electrode to aqueous redox systems was investigated. A one layer film deposited on ITO was immersed in a solution of 5 mM hydroquinone in 0.1 M phosphate buffer. As expected, the oxidation of hydroquinone was highly irreversible (a wide potential gap between the oxidation and reduction responses, Fig. 3.9 (a)) in the absence, and highly reversible in the presence, of the carbon nanofibre film deposit.
Figure 3.9. Cyclic voltammograms for the oxidation of 5 mM hydroquinone in 0.1 M phosphate buffer at pH 7 at (a) a bare ITO electrode (scan rate 50 mVs⁻¹), (b) a 1 layer electrode (scan rate 10 mVs⁻¹), (c) a 1 layer electrode (scan rate 20 mVs⁻¹), and (d) a 1 layer electrode (scan rate 50 mVs⁻¹), all with 1 cm² exposed area.

The reversible hydroquinone/benzoquinone redox process was detected at a potential of 0.03 V vs. SCE (at pH 7) consistent with the measurement obtained with carbon nanofibre deposits at pH 2 (Fig. 3.6). The 300 mV shift in equilibrium potential for a proton activity change of 5 pH units is expected and consistent with the behaviour of a 2 electron – 2 proton redox system. However, the voltammetric responses at the carbon nanofibre/chitosan composite film are strongly distorted and both the oxidation as well as reduction responses show almost ohmic characteristics with a 2500 Ω resistance, Fig. 3.9 (b) - (d). The peculiar shape of the voltammetric responses is essentially independent of the number of layers deposited (for the first 5 layers).

An analysis of the results indicates an ohmic contact, i.e., highly resistive but still conducting, between the carbon nanofibre deposit and the ITO electrode surface. It is very likely that the presence of the chitosan ionomer between the carbon nanofibres and the ITO substrate causes a barrier for electron tunnelling, sufficient to act as the rate-determining step for the hydroquinone oxidation process.

3.3.7. Electrochemical Characterisation of Ultra-thin Carbon Nanofibre/Chitosan Composite Films III: Conductivity Measurements

Further evidence for the presence of a barrier to electron movement between the hydrophilised carbon nanofibre/chitosan deposit and the ITO electrode comes from the measurement of the conductivity of the ultra-thin carbon film deposits. A
conductivity probe was made by removing a 1 mm wide section of ITO from the centre of the electrode surface leaving two separate 0.45 cm x 6 cm electrodes on a 1 cm x 6 cm glass slide. A hydrophilised carbon nanofibre/chitosan film was deposited and used to bridge the two electrodes. The conductivity of the film was measured with a two probe technique at low current (and over a range of potentials to ensure ohmic characteristics). The ultra-thin carbon film deposits clearly conduct electricity and a typical resistance of $2 \pm 1 \times 10^9$ Ohm is measured. This value is recorded independent of the number of layers deposited onto the probe. Again a contact resistance rather than the true bulk resistance of the film is measured. The contact resistance of the dry film appears to be substantially higher compared to the contact resistance of the film immersed in aqueous buffer solution.

Both the dry resistivity measurement and the voltammetric measurement of the contact resistance in solution, probe the gap between the carbon nanofibres and the ITO substrate and it is interesting to ask how this resistivity, due to the tunnelling gap, can be affected. It has been reported that, under relatively mild conditions, chitosan can be converted to carbon [19] and this would allow a better coupling between carbon nanofibre electrodes and substrate. Alternatively, a different type of cationic binder layer could be employed, initially between the first carbon layer and the ITO substrate.

3.4. Conclusions

It has been shown that small fragments of hydrophilised carbon nanofibres deposited in the form of an ultra-thin film on ITO electrodes can be formed and have a considerable effect on the voltammetric characteristics of the electrode. Important electrochemical processes such as the oxidation of hydroquinone, which occurs with a substantial overpotential at a bare ITO electrode, proceeds with a high rate of electron transfer and essentially reversibly. However, the chitosan binder employed to bind a thin layer of carbon nanofibres to the electrode surface also acts as a barrier for electron transfer. Current flow under both dry and wet conditions is limited by the ohmic carbon/substrate contact.
The presence of an ultra-thin carbon film at the ITO electrode surface imposes the electrochemical properties of carbon without significant changes in transparency. Potential future applications of this type of electrode could be in spectroelectrochemical studies or as sensors with covalently modified carbon nanofibres.
References

Chapter 4
Electrochemical Characterisation of Carbon Nanofibre/Sol-gel Silicate Films
4.1. Introduction

Sol-gel materials have been used in many coating and thin film studies [1]. This wet coating method is based on silane precursors, such as tetramethoxysilane or methyltrimethoxysilane, which are soluble in methanol and sensitive to hydrolysis in the presence of acids [2]. Typically, dilute precursor solutions are mixed with HCl and applied to a suitable substrate surface. Over a period of hours the solvent evaporates and a uniform microporous silicate film is formed [3]. Sol-gel methods are very attractive for the incorporation of sensitive chemicals (e.g., proteins [4]) or for the preparation of very thin functional films [5]. In this study, the sol-gel approach is employed to embed carbon nanofibres in a thin film at an electrode surface.

Prior to the development of the carbon nanofibre/sol-gel silicate films, carbon nanofibre containing composite electrodes in the form of carbon ceramic electrodes (CCE) and carbon paste electrodes (CPE) were investigated [6]. A hydrophobic sol-gel matrix based on a methyl-trimethoxysilane precursor was employed in combination with carbon nanofibres or a carbon nanofibre/carbon particle mixture to form the CCEs, while the CPEs were made by simply pasting carbon nanofibres with the redox probe solution under investigation. Carbon nanofibre CCEs, in comparison with conventional graphite particle based CCEs, exhibited higher capacitive currents. Both the CCE and CPE systems demonstrated good efficiencies and consistent voltammetric characteristics. The addition of graphite particles into the carbon nanofibre CCE was seen to improve electrode stability.

In this study, the development of thin film electrodes involved embedding carbon nanofibres into thin films of a hydrophobic sol-gel material and casting onto tin-doped indium oxide (ITO) electrodes. The carbon nanofibres consisted predominantly of ca. 100 - 200 nm diameter fibres, which promote electrical transport and allow the study of electrochemical reactions at liquid | liquid interfaces. In order to prevent carbon nanofibre aggregation, 7 nm diameter silica nanoparticles were added to the sol-gel mixture and homogeneous high surface area films were obtained.

This novel electrode material was employed for the oxidation of ferrocenedimethanol in aqueous solution and for the oxidation of tert-butylferrocene as either the pure
liquid or immobilised in hydrophobic 2-nitrophenyloctylether (NPOE) and immersed in aqueous solution. In the absence of an organic phase, partial blocking of the electrode was observed, but well defined voltammetric responses were obtained with an organic liquid immobilised in the hydrophobic mesoporous film. Due to the formation of an extended liquid | liquid | electrode triple phase junction, cyclic voltammograms were recorded, which allow the transfer potential for a range of anions to be determined directly from the peak potentials. Measurements in the presence of tetrabutylammonium perchlorate (TBAP) and tetraoctylammonium perchlorate (TOAP) reveal that a gradual transition from anion transfer dominated to cation transfer dominated processes occurs as the hydrophilicity of the anion increases.

The recent development of “ion transfer” electrodes based on small amounts of immobilised organic liquids composed of a pure redox liquid [7] or of a redox probe solution in an organic hydrophobic solvent [8] or in a room temperature ionic liquid [9], which is immersed in an aqueous electrolyte solution, has attracted much interest. This is connected with potential applications in, e.g., ion partitioning analysis [10], photoelectrochemistry at liquid | liquid interfaces [11], and in liquid | liquid electro-organic synthesis [12]. The mechanism of the electrode process involves electron transfer at the electrode | organic liquid interface and ion transfer across the liquid | liquid interface [13, 14], to maintain charge neutrality. The close proximity of the electrode surface and the two liquid phases (at the triple phase junction) has been shown to be a condition for efficient electrode processes for unsupported organic liquids, where no electrolyte salt has intentionally been added into the organic phase. Currently, new and better electrode materials are being developed for this kind of redox process.

Heterogeneously structured electrodes, with electronically conductive particles or fibres as one of the components, are potentially interesting in terms of their ability to provide favourable conditions for extended triple phase junction formation. An electrode composed of graphite particles suspended in a hydrophobic silicate matrix (Carbon Ceramic Electrode, CCE) has already proved to be an appropriate support for ion transfer measurements in unsupported [15, 16] or supported [17] systems. Thin porous films, based on hydrophobic silicate films [5, 18] and layer-by-layer deposited
nanoparticle films [19, 20] provide appropriate supports for diluted or undiluted redox liquids. The use of a porous layer covered by a thin metallic (gold) film to support the liquid | liquid electrode has been reported [3]. The efficiency of the electrode processes for such electrodes is affected by the size of the conducting particles [21].

In the search for novel electrode supports for efficient “ion transfer” electrodes attention turned to carbon nanofibres (CNFs), formed as described earlier in Chap. 2.3. The electrochemistry of these CNFs has been explored in composites [22], in thin films (discussed in Chap. 3), and for materials grown directly onto ceramic substrates (discussed in Chap. 2). As mentioned above, CNFs were used as a component in CCEs in order to improve the characteristics of these liquid | liquid “ion transfer” electrodes [6]. Here, the immobilisation of CNFs into thin and hydrophobic silicate films is investigated. The hydrophobic silicate matrix is known to support redox liquid deposits on electrode surfaces [5, 18]. In addition, novel 7 nm diameter hydrophobic SiO₂ nanoparticles are employed to prevent the aggregation of CNFs during the sol-gel curing process. This methodology helps to overcome CNF aggregation and improves the homogeneity and quality of the films deposited, which is a considerable improvement over a recently published sol-gel procedure [23]. Voltammetric measurements in aqueous and in two phase organic | aqueous media are reported. Firstly, the hydrophobic CNF/silica composite film modified electrodes are examined for the oxidation of ferrocenedimethanol in aqueous solution. Then, their electrochemical characterisation was performed after the modification of the hydrophobic mesoporous film with unsupported and supported redox liquid systems. Tert-butylferrocene (tBuFc) and solutions of tBuFc in 2-nitrophenyloctylether (NPOE) were employed. The CNF composite film is shown to have a significant effect on the efficiency of electrochemically driven ion transfer processes at liquid | liquid interfaces.

4.2. Experimental

4.2.1. Chemicals

Methyltrimethoxysilane (MTMOS) (99 %) and t-butylferrocene (tBuFc) (98 %) (ABCR); ferrocenedimethanol (FcDM) (Aldrich); 2-nitrophenyloctylether (NPOE) (99+ %) and tetraoctylammonium perchlorate (TOAP) and (C₄H₉)₄NBr (Fluka); NaF,
NaSCN, KBr, KCl, KSCN, KClO₄, and KNO₃ (analytical grade) (POCh); and KPF₆ (98+ %) (Merck) were obtained commercially and used without further purification. Tetrabutylammonium perchlorate (TBAP) was prepared by the metathesis of (C₄H₉)₄NBr with HClO₄ in water. The product was recrystallised twice from water and dried under reduced pressure at 100 °C for 24 h. Hydrophobic SiO₂ nanoparticles, Aerosil R812 (d = 7 nm), were obtained from the ETC Group. Water was filtered and demineralised with an ELIX system (Millipore). For further details see Chap. 2.2.1.

4.2.2. Instrumentation

Differential pulse voltammetry, as well as cyclic voltammetry were performed with an Autolab (Eco Chemie) electrochemical system. For further details see Chap. 2.2.2.

4.2.3. Electrodes and Electrode Preparation

The working electrode was an ITO or modified ITO electrode. A platinum wire (0.5 mm diameter) counter electrode and a Ag|AgCl|KCl(saturated) reference electrode were used. The "ion transfer" electrodes were immersed into the aqueous salt solutions.

Thin films were obtained on tin-doped indium oxide (ITO) surfaces by a sol-gel process involving sol drop deposition and solvent evaporation. The sol was prepared by mixing 0.5 mL of methyltrimethoxysilane (MTMOS) with 0.75 mL of methanol. After the addition of 50 μL of 11 M HCl the mixture was sonicated for 2 min. Following this, the stock sol solution was diluted 1:10 with methanol and sonicated for a further 2 min. Then 10 mg of the hydrophobic SiO₂ nanoparticles and 40 mg of CNFs were added and the mixture was further sonicated for 2 min. The resulting 4 μL of mixture was immediately placed onto the ITO support. The electrode area was defined by masking off a 0.2 cm² area with Scotch tape. The electrode was dried overnight at room temperature. Further electrode modification was carried out by placing 4 μL of redox liquid (tBuFc diluted with hexane) onto the electrode surface. Other experiments utilised 0.5 μL of tBuFc solution in NPOE, which was deposited directly. These electrodes, with redox liquid deposits, can be re-used after an experiment by carrying out a simple rinsing step.
4.3. Results and Discussion

4.3.1. Electrochemical Processes at Hydrophobic Carbon Nanofibre/Silica Film Electrodes in Aqueous Solution

The CNFs have to be broken up, or dispersed effectively, in order to form a homogeneous suspension for film deposition. It was observed that the addition of silica particles of 7 nm diameter improved the CNF solubilisation and prevented the aggregation of CNFs during the sol-gel curing process. By casting a suspension of MTMOS, in acidified methanol containing SiO$_2$ nanoparticles and CNFs (1:4 weight ratio), stable high-quality films suitable for electrochemical measurements were obtained. Typical FEGSEM images of these hydrophobic CNF/silica films, prepared on ITO substrates, are shown in Fig. 4.1.

![FEGSEM images of hydrophobic CNF/silica films](image)

Figure 4.1. Typical FEGSEM images of the surface of hydrophobic CNF/silica films on ITO substrates at (A) low, (B) intermediate, and (C) high magnification.

At low magnification globular deposits of up to 100 µm diameter can be seen. Closer inspection (see Fig. 4.1 (B) and (C)) reveals the presence of densely packed carbon nanofibres and silica nanoparticles. Both particles and fibres are clearly visible in Fig. 4.1 (C) and the structure can be seen to be essentially mesoporous. The addition of
hydrophobic SiO$_2$ nanoparticles is crucial to reduce the size and increase the homogeneity of the aggregates.

In order to study the electrical and electrochemical properties of the CNF/silica composite films, voltammetric experiments with a solution of 0.001 M ferrocenedimethanol in aqueous 0.1 M KNO$_3$ were undertaken. Ferrocenedimethanol is water soluble and undergoes a reversible one electron oxidation at a midpoint potential of $E_{\text{mid}} = 0.25$ V vs. Ag/AgCl (sat. KCl) (see Eq. 4.1).

$$\begin{align*}
\text{Fe} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \text{Fe}^+ \\
\text{OH} & \text{OH} \\
\text{OH} & \text{OH}
\end{align*}$$

(4.1)

The shape of the cyclic voltammograms obtained during continuous scanning of the potential (0.01 V s$^{-1}$) applied to the CNF/silica modified ITO electrode in the presence of ferrocenedimethanol in aqueous solution indicates the characteristics of a partially blocked electrode (Fig. 4.2, solid line). The characteristic capacitive current generally seen for a carbon nanofibre electrode is not observed.

Figure 4.2. Cyclic voltammograms for the oxidation of 0.001 M ferrocenedimethanol in 0.1 M aqueous KNO$_3$ at (i) a bare ITO electrode (surface area 0.02 cm$^2$) at a scan rate 0.01 V s$^{-1}$ (dashed line) and (ii, iii) hydrophobic CNF/silica film modified ITO electrodes (surface area 0.02 cm$^2$) at scan rates of (ii) 0.01 and (iii) 0.001 V s$^{-1}$ (solid lines).

The typical sigmoidal cyclic voltammogram shape is clearly seen at slower scan rates
(0.001 V s⁻¹) (Fig. 4.2 (iii)), where ultramicroelectrode-like behaviour is observed. This perhaps surprising observation can be rationalised by assuming that the globular structures visible in Fig. 4.1 (A) are effectively partially insulating the electrode surface. They are highly hydrophobic and it is likely that they are not wetted by the aqueous solution. The remaining electrode area acts as an assembly of ultramicroelectrodes with mixed diffusion (planar and spherical). The smaller current in comparison to an unmodified ITO electrode (Fig. 4.2 (i)) also indicates substantial blocking of the active ITO surface by the hydrophobic CNF/silica matrix. It will be shown that after wetting with organic solvents, the porous CNF structure is electrochemically active; significant effects are observed in the cyclic voltammograms due to the presence of the high surface area CNFs.

4.3.2. Electrochemical Processes at Hydrophobic Carbon Nanofibre/Silica Film Electrodes with a Liquid Tert-butylferrocene Deposit and Immersed in Aqueous Solution

Next, the hydrophobic electrodes were modified with organic liquids prior to measurement in aqueous solution. The CNF/silica film modified ITO electrodes were modified with well-defined amounts of the redox liquid tert-butylferrocene (tBuFc) by solvent evaporation of a solution in n-hexane. The resulting electrodes, when immersed in aqueous 0.1 M NaClO₄ solution, allow the oxidation of tert-butylferrocene, accompanied by the transfer of the perchlorate anion from the aqueous into the organic phase, to be observed (Eq. 4.2).

\[
\text{Fe} + \text{ClO}_4^-(aq) \rightleftharpoons \text{Fe}^+ + \text{ClO}_4^-(org)
\]

(4.2)

The cyclic voltammograms obtained with this tBuFc liquid modified electrode (modified with 1960, 196, 19.6, and 7.2 nmol) are presented in Fig. 4.3.
Substantial voltammetric signals are observed. The CNF/silica film strongly enhances the signal when compared to films without CNFs or at a bare ITO electrode, see below. Two important effects can be seen from these data. Firstly, the hydrophobic CNF/silica film is electrochemically active and electrically connected to the ITO substrate. Secondly, for a larger amount of redox liquid deposit a larger electrical charge passes during a single scan. However, this dependence is not linear and higher conversion efficiency is observed at lower coverage. This behaviour is probably connected with the development of triple phase junctions at the carbon nanofibre | tert-butylferrocene | aqueous electrolyte interface, which is expected to be more extended for a smaller amount of deposit. The efficiency of the electrode process (calculated for the 3rd scan with a scan rate of 10 mV s⁻¹), determined as the ratio of the anodic charge (Qₐ) to the electrical charge corresponding to the complete electrooxidation of the deposit (Qₑₜₓ), increases going from the largest to the smallest amount of deposit with \( \frac{Qₐ}{Qₑₜₓ} = 2, 5, 12, \text{ and } 32 \% \) for 1960, 196, 19.6, and 7.2 nmol tBuFc, respectively.

The ratio of the anodic charge, Qₐ, to the cathodic charge, Qₑ, corresponding to the reversibility of the electrode process (Eq. 4.2), also decreases going from larger to
smaller amounts of deposit with $\frac{Q_e}{Q}$ = 2.4, 1.4, 1.3, and 1.5 for 1960, 196, 19.6, and 7.2 nmol tBuFc, respectively. This suggests that perchlorate anion transfer is more efficient and side reactions such as the expulsion of tert-butylferricinium into the aqueous phase can be avoided. As a result, the voltammograms are unstable during subsequent potential cycles for the two largest amounts of deposit and a decrease in the peak current is observed.

Fig. 4.4 shows stable cyclic voltammograms for the oxidation of 19.6 nmol tBuFc immobilised in the hydrophobic CNF/silica film at various scan rates.

![Figure 4.4](image)

Figure 4.4. Cyclic voltammograms (scan rate (i) 0.16, (ii) 0.08, (iii) 0.04, (iv) 0.02, (v) 0.01, and (vi) 0.005 V s\(^{-1}\)) obtained for the oxidation of 19.6 nmol tBuFc immobilised in a hydrophobic CNF/silica film modified ITO electrode (surface area 0.02 cm\(^2\)) immersed in aqueous 0.1 M NaClO\(_4\).

It can be seen that although at slower scan rates a well-defined response, with only slightly increased peak-to-peak separation, is observed, at faster scan rates the voltammetric response becomes very broad. It can be seen that the time constant for the electrode is slow, from the shape of the curves at the reversal potential. Both the substantial surface area of the carbon nanofibres and resistance in the electrical contact between CNFs and ITO substrate may contribute to this effect.

In these experiments, no electrolyte was initially added to the redox liquid deposit.
Therefore, the electron transfer processes occur at the triple phase junction and the extent of this triple phase junction is the major factor affecting the efficiency of redox liquid based electrode processes. Fig. 4.5 shows a comparison of the voltammograms obtained for the oxidation of 19.6 nmol tBuFc immobilised in (i) a hydrophobic CNF/silica film and (ii) a similar film without CNFs.

![Voltammograms](image)

**Figure 4.5.** Cyclic voltammograms (scan rate 0.01 V s⁻¹) obtained for the oxidation of 19.6 nmol tBuFc immobilised in (i) a hydrophobic CNF/silica film and (ii) a similar film without CNFs, deposited onto ITO substrates (surface area 0.02 cm²) and immersed in aqueous 0.1 M NaClO₄.

Scan (i) is stable for several potential cycles in contrast to scan (ii). The presence of CNFs contributes to the high efficiency of the electrode process. Therefore, the presence of a high surface area due to CNF immobilisation seems to create a much more extended electrode | tBuFc | aqueous electrolyte triple phase junction. Moreover, the presence of CNFs contributes to the stability of the voltammetric response over several potential cycles (Fig. 4.6).

![Voltammograms](image)

**Figure 4.6.** Cyclic voltammograms (1ˢᵗ, 2ⁿᵈ, 3ʳᵈ, 4ᵗʰ, and 20ᵗʰ scan, scan rate 0.01 V s⁻¹) obtained for the oxidation of 19.6 nmol tBuFc immobilised in a hydrophobic silica film without CNFs deposited onto ITO substrates (surface area 0.02 cm²) and immersed in aqueous 0.1 M NaClO₄.
The rapid decrease in the peak current for tBuFc oxidation in the absence of CNFs indicates that the expulsion of tBuFc\(^+\) into the aqueous solution and the loss of active material from the electrode play a significant role. It is possible that the presence of CNFs creates a more extended hydrophobic interface with sufficient electrical conductivity to give stable voltammetric responses. The stabilising role of the CNF film deposits can also be discussed based on the experimental results, which showed that large amounts of deposit result in unstable voltammetric behaviour (Fig. 4.3). In that case the mesoporous structure was "flooded" with redox liquid, re-deposition of tBuFc\(^+\)(aq) after reduction is less likely, and its loss during oxidation is predominant.

4.3.3. Electrochemical Processes at Hydrophobic Carbon Nanofibre/Silica Film Electrodes with a Tert-butylferrocene in 2-Nitrophenyloctylether Deposit, with and without Supporting Electrolyte

Subsequently, solutions of tBuFc in 2-nitrophenyloctylether (NPOE, a highly water-insoluble solvent) are studied rather than the pure tBuFc liquid. In this way currents can be kept low and anion transfer processes are easier to measure. An attempt to immobilise 5 μL of a 0.01 M tBuFc solution in NPOE onto hydrophobic CNF/silica modified ITO electrodes resulted in irreversible and unstable voltammetric responses (Fig. 4.7).

![Cyclic voltammograms](image)

_Figure 4.7. Cyclic voltammograms (1\(^{\text{st}}\), 2\(^{\text{nd}}\), 5\(^{\text{th}}\), and 10\(^{\text{th}}\) scan, scan rate 0.01 V s\(^{-1}\)) obtained for the oxidation of 0.5 μL of 0.01 M tBuFc solution in NPOE immobilised in a hydrophobic CNF/silica film deposited onto ITO substrates (surface area 0.02 cm\(^2\)) and immersed in aqueous 0.1 M NaClO\(_4\)._
The efficiency of the electrode process is much lower than that for the pure redox liquid. It decreased from 4 % to less than 0.4 % (after correction for background current) during the first 10 potential cycles. Furthermore, with this amount of deposit, the CNFs in the composite film did not contribute to the background current, and therefore, seemed to be inactive. This can be explained by the “flooding” of the mesoporous structure with effectively insulating NPOE liquid with electrochemical reactivity in only small regions within the triple phase junction. Therefore, the use of a supporting electrolyte within the organic NPOE phase was considered.

Two types of supporting electrolyte, tetrabutylammonium perchlorate (TBAP) and tetraoctylammonium perchlorate (TOAP), were added into NPOE at a 0.1 M concentration and compared. In the presence of supporting electrolyte in the organic phase, both the Faradaic and capacitive currents observed for the hydrophobic CNF/silica film electrodes increase by approximately one order of magnitude (in comparison to the unsupported system). The voltammograms shown in Fig. 4.8 demonstrate the effect of the high CNF surface area on the capacitive current and the enhancing effect of the CNF film on the Faradaic current for tBuFc oxidation. Both TOAP and TBAP gave similar effects.

![Figure 4.8. Cyclic voltammograms (5th scan, scan rate 0.01 V s⁻¹) obtained for the oxidation of (i) 0.5 µL of 0.01 M tBuFc and 0.1 M TOAP solution in NPOE (dotted) and (ii) the same solution in the absence of tBuFc (dashed) immobilised in a hydrophobic CNF/silica film film deposited onto ITO substrates (surface area 0.02 cm²) and immersed in aqueous 0.1 M NaClO₄. (iii) The solid line corresponds to the same experiment performed with a bare ITO electrode.](image-url)
For supported ioniically conductive systems the existence of a triple phase junction is not a prerequisite and the locations for electron transfer (electrode | NPOE junction) and for ion transfer (NPOE | aqueous electrolyte junction) become separated. The observed voltammograms are much more stable and the electrode process efficiency decreased from 27 % to only 14 % during 10 potential cycles at a scan rate of 10 mV s⁻¹. Most of the electrogenerated tBuFc⁺ cations are not in direct contact with the aqueous solution phase and therefore they remain in the organic phase. The role of the extended surface of the CNFs in the electrode process is important as can be seen from the comparison of the peak currents for voltammograms obtained in the presence, and in the absence, of the hydrophobic CNF/silica film (Fig. 4.8 (i) and (iii)). The capacitive currents for CNF modified electrodes are significant due to good wetting of the CNFs by the NPOE solvent and the presence of supporting electrolyte in the organic phase.

Subsequently, the hydrophobic CNF/silica electrode was used to study a wider range of anion transfer reactions across the NPOE | water interface, generated by the immobilisation of a solution of tBuFc in NPOE with supporting electrolyte. The contribution of the capacitive currents, due to the high surface area of the CNF material, was suppressed by employing differential pulse voltammetry. In Fig. 4.9, typical differential pulse voltammograms for the oxidation of 10 mM tBuFc in 0.1 M TOAP NPOE solution, obtained at an ITO electrode modified with a hydrophobic CNF/silica film and immersed in various aqueous electrolytes, are shown.

![Figure 4.9. Differential pulse voltammograms (step potential 0.01 V, modulation amplitude 0.01 V, modulation time 0.05 s, interval time 1 s) for the oxidation of 0.5 μL of 0.01 M tBuFc solution in NPOE immobilised in a hydrophobic CNF/silica film deposited onto ITO (0.02 cm²) and immersed in aqueous 0.1 M KPF₆, KClO₄, KBF₄, and KBr.](image-url)
Well-defined peaks are observed for the transfer of the more hydrophobic anions with broadened peaks for the hydrophilic anions. The characteristic shift in peak potential, $E_{\text{peak}}$, clearly indicates that anion transfer dominates the overall process. For a coupled electron/ion transfer reaction (Eq. 4.3) the peak potential of the differential pulse voltammogram, $E_{\text{peak}}$, is expected to show a Nernstian dependence on the aqueous electrolyte concentration, $c_{X^-}$, since to a first approximation the activities in the Nernst equation can be replaced by concentrations [8, 13],

$$E_{\text{peak}} = E_{E_{\text{org}+/ \text{org}^-}} + \Delta_{\text{eq}}^{\text{NPOE}} \phi_{X^-}^0 + \frac{RT}{F} \ln c_{X^-} + \frac{RT}{F} \ln \frac{c_{\text{org}^{+}}}{2}$$  (4.3)

In this equation $E_{E_{\text{org}+/ \text{org}^-}}^0$ is the standard redox potential for the tBuFc$^+/t$BuFc couple in organic solution, $\Delta_{\text{eq}}^{\text{NPOE}} \phi_{X^-}^0$ - is the standard transfer potential of anion $X^-$ from water into the NPOE phase, and $c_{X^-}$ and $c_{\text{org}^{+}}$ denote the initial concentrations of $X^-$ and DMFc in the organic phase. If the reaction mechanism is formally given by Eqs. 4.1 and 4.2, one would expect a linear plot of $E_{E_{\text{org}+/ \text{org}^-}}^0$ vs. $\Delta_{\text{eq}}^{\text{NPOE}} \phi_{X^-}^0$ with unit slope for measurements of a range of different anions.

The decrease of the slope from a value close to the theoretical value, to much lower values, can be seen for the more hydrophilic anions, from the voltammetric data obtained in four different electrolytes (Fig. 4.10 (A)).

This effect is much more striking for TBAP solutions than for TOAP solutions in NPOE. Therefore, it is likely that cation transfer, with tetrabutylammonium or tetraoctylammonium being transferred, from the organic to the aqueous phase is important. Since the transfer potentials for nitrobenzene (NB) are known for a wider range of anions, these were employed for further data analysis. The tabulated values of the standard transfer potentials of $X^-$ from water to nitrobenzene ($\Delta_{\text{eq}}^{\text{NB}} \phi_{X^-}^0$) were used [24]. This procedure is justified because of the dominant effect of anion solvation in water compared to solvation effects in the organic phase.
Figure 4.10. Plot of the peak potential from differential pulse voltammograms, $E_{\text{peak}}$, versus the standard transfer potential for anion transfer (A) from aqueous media to nitrophenyloctylether (NPOE) $\Delta_{Ag}^{NPOE} \phi_X^0$ and (B) to nitrobenzene (NB) $\Delta_{Ag}^{NB} \phi_X^0$. $E_{\text{peak}}$ values were determined from differential pulse voltammograms for the oxidation of 5 µL of 0.01 M tBuFc and 0.1 M TOAP/TBAP solution in NPOE immobilised in a hydrophobic CNF/silica film deposited onto ITO substrates and immersed in aqueous 0.1 M electrolyte solutions. The sequence of anions is indicated and the dotted line corresponds to the ideal Nernstian behaviour for a simple anion transfer process.

Fig. 4.10 (B) shows a plot with data from a wider range of anions. An almost linear dependence of $E_{\text{peak}}$ vs. $\Delta_{Ag}^{NB} \phi_X^0$, with a slope close to unity, can be seen from the hydrophobic PF$_6^-$ to the relatively hydrophilic Cl$^-$. A deviation from this dependence is only seen for the most hydrophilic anion, F$^-$, and in the presence of tetrabutylammonium cations, indicating the important contribution of cation ejection. The broad shape of the differential voltammograms for the more hydrophilic anions may be interpreted as the effect of competing reaction mechanisms involving two
different pathways: (i) transfer of the anion from the aqueous to the organic phase or (ii) transfer of the electrolyte cation from the organic to the aqueous phase. Komorsky-Lovric et al. reported similar effects for electrolytes dissolved in an electrochemically active organic phase [25]. They deposited small droplets of nitrobenzene solutions onto paraffin impregnated graphite electrodes. The effect was also observed recently for droplet deposits of redox probe solution in room temperature ionic liquids [9].

4.4. Conclusions
Films of a hydrophobic carbon nanofibre/silica composite were prepared using a sol-gel methodology. The benefit of adding silica nanoparticles to the films was noted and the resulting thin film electrodes on ITO were characterised with voltammetric techniques. The electrodes, when immersed in purely aqueous solution, seem to have gas trapped in the hydrophobic mesoporous structure and partial blocking of the electrode was observed. In contrast, when the electrodes were wetted with organic redox liquids, such as tBuFc or solutions of tBuFc in NPOE, well-defined voltammetric responses were observed and the effect of the CNFs on the voltammetric signal was clearly seen. The efficiency of the electrode process on such hydrophobic film electrodes was considerable, if the volume of organic phase was adjusted, appropriately. The presence of the CNFs stabilised the voltammetric response for the oxidation of tBuFc during continuous potential cycling. The effect of adding electrolyte into the organic phase was dramatic and good quality ion transfer data for a wide range of anions was recorded in the presence of tetraoctylammonium perchlorate as the added as electrolyte.

The above carbon nanofibre/silica thin film composite electrodes were also used in the study of ion transfer processes at the room temperature ionic liquid (RTIL) | aqueous solution interface [26]. It was shown that heterogeneously structured bulk modified electrodes based on a carbon particle/hydrophobic silica composite can be used as a support for electroactive RTILs [17]. However, these composites are not suitable for the formation of thin films. It has been demonstrated that hydrophobic CNF/hydrophobic silica composite thin films can be used successfully as a support for hydrophobic redox liquids in order to monitor ion transfer processes in contact with
aqueous solutions. These thin film composite electrodes provide an ideal porous support for measurements employing electroactive RTIL phases.

Hydrophobic CNF/silica film modified ITO electrodes were shown to give well-defined voltammetric signals and to support solutions of a redox probe in a hydrophobic ionic liquid. The presence of the hydrophobic CNF/silica film enhances both the capacitive background and the magnitude of the Faradaic current response.
References


Chapter 5

Copper/Carbon Nanofibre Co-deposition
5.1. Introduction
The first recorded discovery of copper electrodeposition was the work of Bessemer. In 1831, he plated castings by immersion in a copper sulphate solution contained in a zinc tray. Electroplating from an external current source quickly followed the development of the Daniell cell in 1836 and from 1840 the electrodeposition of copper from sulphate and cyanide baths became widespread. Further information regarding the development of copper plating can be found in Greenwood’s publication [1].

Lowenheim covered the fundamental principles of electroplating extensively as well as dealing with the specific details relating to various electrodeposited metals including copper, where the particulars of various electrolytes are considered [2]. Similarly, Pinner described various copper electrolytes, coating applications, methods of surface preparation, and also gave details for deposit testing and electroplating bath control [3].

Copper is a relatively soft and ductile metal and combines readily with other metals to produce alloys, e.g., brasses and bronzes [4]. It has good electrical and thermal conductivities. It is widely used for both decorative and industrial purposes.

Copper had long been recognised as superior to aluminium for the wiring of microelectronic chips, but chips with copper interconnect were not successfully developed until IBM’s 1997 announcement and their subsequent production of the industry’s first copper interconnect chips in 1998 using the dual-damascene manufacturing process, setting in motion the copper generation [5]. The damascene process, an electroplating technique, leads to void free deposition in trenches [6]. The advantage of using copper, as an alternative metallisation material to aluminium and aluminium alloys, is due to its low resistivity and ability to reliably carry high current densities [7]. Copper also exhibits an order of magnitude improvement in electromigration characteristics relative to aluminium alloys, due to its higher melting point and atomic weight [8].

Copper has many recent technological applications. Current research includes the
formation of a diamond/copper composite, which could prove useful in electronic packaging. As the level of integration of ICs (integrated circuits) continues to increase, thermal considerations have become more important due to the effect of heat on the reliability of electronic parts. Materials are required that exhibit the appropriate thermal conductivity to allow for the efficient cooling of the ICs. Yoshida et al. prepared a diamond/copper composite using high pressure sintering technology [9]. The composite has a high thermal conductivity and the coefficient of thermal expansion could be tailored according to the semiconductor material in the electronic device.

There have been various attempts at utilising carbon nanofibres in IC applications with the aim of improving the thermal and electronic properties. Vertically aligned, free standing CNF arrays were fabricated on silicon wafers [10]. Copper electrodeposition was used to create a CNF/Cu composite array. The mechanical strength and efficient interfacial heat conduction of the CNF/Cu composite array makes it suitable for next-generation heat-sink devices, with potential for use in IC packaging. Lin et al. studied the high temperature degradation of a carbon fibre reinforced copper composite formed by hot pressing a stack of monolayers of Cu coated carbon fibres, which were aligned and woven with Cu wire [11]. This type of composite is of interest due to its promising high thermal conductivity relevant in hypersonic and power systems for space exploration.

A series of copper/graphite materials produced by powder metallurgy, which exhibited a self-lubricating function were developed by He et al. [12]. This effect was achieved by the formation of a carbonaceous layer on the counterparts surface. One of the aims of the development of this type of material is for application in pantograph strips for railway power connection systems, with the possibility of reduced wear and therefore maintenance costs, and an improvement in the power transmission efficiency. Electrodeposition was used in conjunction with hot pressing to fabricate a PAN (polyacrylonitrile) carbon fibre reinforced copper composite [13]. The effects of the hot-pressing temperature, pressure and duration, and the reinforcement content, on the properties of the composite were investigated.

Carbon nanotube/copper composite electrodes based on the co-mixing of CNT and Cu
powders within mineral oil were prepared by Wang et al. [14]. The electrode was used for improved amperometric detection of carbohydrates following their capillary electrophoresis microchip separations. The composite electrode displayed enhanced sensitivity compared to detectors based on copper or CNTs alone.

There is great interest in metal matrix composites reinforced with carbon nanofibres due to their superior mechanical, thermal and electrical properties. Carbon nanofibre reinforced copper composites were fabricated using the liquid infiltration process [15]. The tensile strength increased twofold with 13 % added carbon nanofibres, despite the weak chemical bonding between the carbon and copper.

A useful route to metal/carbon nanofibre composite deposits is via electro-co-deposition. In the current work, an acidic copper electrodeposition bath was investigated by cyclic voltammetry, FEGSEM, and quartz crystal microbalance (QCM) studies. It was hoped that FEGSEM imaging would provide evidence for the incorporation of carbon nanofibres as well as information on the structure and surface morphology of the deposit.

The study of metal/carbon nanofibre co-deposition by QCM has not been previously reported. Copper metal was chosen due to its high current efficiency and lack of side reactions, e.g., hydrogen evolution. As a result, all current passed is associated with metal deposition. The aim of the QCM studies was to monitor any mass changes associated with the deposition process and any differences between the process in the absence and presence of carbon nanofibres, i.e., mass changes associated with the co-deposition of the carbon nanofibres. The co-deposition experiments are reported here with evidence for the co-deposition of copper metal with carbon nanofibres. The determination of the mass of deposit per mole of electrons passed is used as a novel probe for indication of CNF incorporation in the co-deposit.

5.2. Experimental
5.2.1. Chemicals
Poly acrylic acid (partial sodium salt, Mw 5000) and CuSO4.5H2O (Aldrich); HNO3 (70 %), and H2SO4 (98 %) (Fisher) were obtained commercially and used without
further purification.

5.2.2. Instrumentation
The carbon nanofibre growth, voltammetry experiments, ultrasound agitation, and electrode analysis were performed as described earlier. For further details see Chap. 2.

Quartz crystal microbalance experiments were conducted with a home-made oscillator based on an Oxford Electrodes oscillator circuit and a Fluke PM6680B counter at a 10 MHz AT-cut gold-coated oscillator quartz crystal, Fig. 5.1.

![Figure 5.1](image)

**Figure 5.1.** Schematic drawing of a quartz crystal resonator with a gold electrode evaporated onto the surface.

The quartz crystal was mounted in a Faraday cage to minimise electrical noise interference. The analogue output of the counter was fed into the ADC input of an Autolab potentiostat system (Eco Chemie, Netherlands) with data processing made possible with GPES software (Eco Chemie, Netherlands).

Solution phase experiments were carried out with the crystal mounted in the wall of a specially made glass cell (volume 20 mL). Using this setup, only one face of the crystal was immersed in solution and frequency changes as a function of concentration could be recorded as a function of time and potential. Magnetic stirrer agitation was used to control and stabilise mass transport to the crystal sensor.

5.2.3. Electrode Preparation
For the electrodeposition experiments, the working electrode was a mild steel cathode with an exposed area of 5 cm². Electrode preparation consisted of washing with detergent and then rinsing with distilled water and ethanol. The electrode was then
degreased electrochemically using the following solution: NaOH/Na₂CO₃/Na₃PO₄, which leads to the evolution of H₂. The final step involved immersing in HCl and rinsing with distilled water. The cathode was dried in hot air between each step and after final rinsing.

For the voltammetric investigations, mild steel electrodes with a well-defined electrode area (ca. 5 mm diameter disc, defined with insulating tape, cleaned as above) or glassy carbon disc (BAS, 3 mm diameter), contacted with a crocodile clip, were employed as working electrodes. A saturated calomel electrode (SCE) served as the reference and platinum gauze as a high surface area counter electrode; variations are noted in the text, as appropriate.

5.2.4. Plating Bath Composition
A conventional plating bath formulation was employed in order to study the co-deposition process with carbon nanofibre materials. The following bath composition and conditions were investigated.

**Copper Bath**
An acid copper bath with the following constituents was used:

- 212 g/L (0.85 M) CuSO₄·5H₂O
- 54 g/L (0.55 M) H₂SO₄
- 2 g/L as-grown CNF
- pH 1
- (+ 2 x 10⁻⁵ M poly acrylic acid, where stated)

Two forms of CNF, either as-grown or oxidised, were used for the experiments described in this chapter. The as-grown fibres are hydrophobic and were used either mechanically ground or sonicated with poly acrylic acid, PAA. The PAA was used as an additive to aid the formation of a suspension of as-grown CNFs by the interaction of the hydrophobic polymer backbone with the CNFs, Fig. 5.2. When sonicated the CNFs disperse well in the electrodeposition solutions.
The oxidised fibres, produced as described in Chap. 2.4, are hydrophilic, i.e., more water-soluble. They formed very stable suspensions in alkaline plating baths and less stable ones in acidic baths, the fibres settling out after 1-2 h.

5.2.5. Plating Bath Agitation
Two methods of agitation were investigated: 1) a conventional magnetic stirring instrument and 2) ultrasound agitation. The ultrasound method provided very fast interfacial mass transport conditions induced by macro- and micro-streaming, and lead to the removal of gas bubbles, discussed in more detail in Chap. 1.

PAA containing solutions were agitated ultrasonically for 30 min. prior to electrodeposition. A conventional magnetic stirring instrument was used for solution agitation during electrodeposition.

5.3. Electrodeposition of Copper and Copper/Carbon Nanofibre Composites
5.3.1. Voltammetry of Copper Electrodeposition from Acidic Solution
Firstly, the electrodeposition of copper on mild steel and glassy carbon electrodes was studied using cyclic voltammetry, Fig. 5.3, in acidic solution, 0.85 M CuSO₄·5H₂O, 0.55 M H₂SO₄, pH 1. The $E^\circ$ value for the reduction of copper is

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad \quad E^\circ = 0.3419 \text{ V (SHE)} \quad (5.1)$$

At a mild steel electrode, Fig. 5.3 (A), immediate electrodeposition was observed due to the dissolution of iron. The voltammetric responses shown in Fig. 5.3 (A) are therefore consistent with electrodeposition of copper onto copper. The potential of zero current is observed at 0.05 V vs. SCE.
Figure 5.3. Cyclic voltammograms recorded at (A) mild steel (0.28 cm$^2$) and (B) at a 3 mm diameter (0.07 cm$^2$) glassy carbon electrode (successive scans), 100 mV s$^{-1}$, 0.85 M CuSO$_4$-5H$_2$O, 0.55 M H$_2$SO$_4$, pH 1.

At glassy carbon electrodes, Fig. 5.3 (B), the deposition process commences at a potential of 0.05 V vs. SCE and leads to the formation of copper metal. In Fig. 5.3 (B) the potential scan is successively reversed at three different values (~ -0.3, -0.2, -0.1 V vs. SCE) and the amount of copper metal deposited varies accordingly; the amount of charge observed is dependent on the lower potential limit with the most charge seen for a limit of -0.3 V vs. SCE. A well-defined stripping response is detected after reversing the scan direction and scanning the potential positive of 0.05 V vs. SCE. The deposition process is not affected by the scan rate or agitation due to the high concentration of Cu$^{2+}$ available at the electrode surface, i.e., it is not mass transport limited. The deposition process is entirely dominated by the deposition kinetics, following ion diffusion to the electrode. An important detail in these voltammetric responses is the current loop observed during deposition of copper onto carbon, Fig. 5.3 (B). The current loop observed is caused by the relatively slow nucleation of copper on carbon, compared to copper on copper, due to the poor contact between the carbon and metal. The deposition current is initially low and increases after reversal of the scan direction. This is an indication of a nucleation and growth type process, where copper is preferentially plated onto copper. A nucleation overpotential is
5.3.2. Electrodeposition of Copper/Carbon Nanofibre Composites
Electrodeposition experiments were then conducted on mild steel electrodes, utilising both a conventional stirrer and ultrasound agitation. On visual inspection the Cu\(^{2+}\) ions in solution appeared to facilitate the dispersion of as-grown CNFs in the aqueous electrolyte and therefore as-grown CNF material was used directly rather than oxidised CNFs. The images in Fig. 5.4 show typical copper growths for a stirred copper plating solution in the presence of carbon nanofibres.

![Figure 5.4: FEGSEM images of the copper/CNF composite formed with conventional stirring at a mild steel electrode, 0.85 M CuSO\(_4\)·5H\(_2\)O, 0.55 M H\(_2\)SO\(_4\), 2 g L\(^{-1}\) CNF, -0.1 A, 1800 s.](image)

The lowest magnification image, Fig. 5.4 (a), on the top left shows the bulk deposit with characteristic surface nodules. The FEGSEM images in (b) and (c) show higher magnification images of the bulk of the deposit and of the nodules on the surface, respectively. The bulk image, (b), shows the growth of relatively small copper crystals in the background. More interesting is the FEGSEM image in (c), which shows the nodular growths, clearly illustrating the growth of larger copper crystals.
with the incorporation of the CNF. The final image, (d), is a higher magnification image of the nodules showing CNF incorporation more clearly. From these images it can be concluded that carbon nanofibres are inter-grown into the copper deposit. The fact that copper growth is unfavourable on the carbon surface causes well-defined inclusion and easy detection of the carbon nanofibre fragments. The nodular characteristics of the composite growth are believed to be due to carbon nanofibre aggregation, which allow nodules to form. This effect will also be demonstrated and discussed in detail for zinc deposition processes in Chap. 6.

Agitation is believed to strongly affect the deposition process and an attempt was undertaken to explore the effect of high rates of mass transport introduced by ultrasound. An ultrasonic horn system (1.3 cm diameter, 20 kHz, ca. 20 W cm\(^{-2}\), Chap. 2) was directed towards the electrode during growth of a copper carbon composite film.

Figure 5.5. FEGSEM images of the copper/CNF composite formed on mild steel using ultrasound agitation, 0.85 M CuSO\(_4\)•5H\(_2\)O, 0.55 M H\(_2\)SO\(_4\), 2 g L\(^{-1}\) CNF, -0.1 A, 1800 s.

Fig. 5.5 shows typical images obtained for deposits grown under ultrasound
conditions. Generally, the coatings were less well facetted and more irregular, compared to those formed using stirrer agitation. Carbon nanofibres appear to be better integrated into the copper metal deposit. It would be expected that ultrasonic agitation would destroy agglomerates of carbon nanofibres and therefore could effectively prevent nodule formation.

However, while the presence of incorporated CNFs can be observed in the SEM images, the amount of carbon nanofibre material in the co-deposit cannot be determined from the electron micrographs. An improved alternative method is required in an attempt to quantify the amount of carbon nanofibres in the co-deposits.

In Sec. 5.4 a novel application of the quartz crystal microbalance (QCM) will be introduced and demonstrated. In situ QCM monitoring of the co-deposition process allows the weight of carbon nanofibres co-deposited with the metal to be determined. The initial application of this method as a probe for the copper CNF system is described in detail and further experiments for its application in quantitative analysis are suggested.

5.3.3. Voltammetry of Copper Electrodeposition from Acidic Solution containing Poly Acrylic Acid

In addition to the deposition of copper/CNF composites from the conventional acidic copper electrodeposition bath, a bath containing poly acrylic acid was also investigated. There have been a number of reports of copper/carbon nanofibre composites in the literature, including those of Arai and Endo whose electrolyte contained poly acrylic acid, which proved useful for the homogeneous dispersion of the carbon nanofibres in solution, e.g., [16, 17]. More details of their work and of other systems used to produce copper/carbon nanofibre composites are discussed in Chap. 1.

Voltammetric responses, at 100 mV s⁻¹, in both the absence and presence of poly acrylic acid and at two types of electrode, namely mild steel and glassy carbon, were recorded. The responses at the mild steel electrode are shown in Fig. 5.6.
Figure 5.6. Cyclic voltammograms recorded at a mild steel electrode, 0.2 cm\(^2\), (A) reduction potential limit varied: -1.2, -1.25, -1.3 V, (B) as (A) but with the addition of 2 \(\times\) \(10^{-5}\) M PAA. 0.85 M CuSO\(_4\)·5H\(_2\)O, 0.55 M H\(_2\)SO\(_4\), scan rate: 100 mV s\(^{-1}\).

In the absence of poly acrylic acid, as already shown in Fig. 5.3 (A), immediate electrodeposition was observed at a mild steel electrode due to the dissolution of iron. Here, the voltammetric responses are again consistent with the electrodeposition of copper onto copper, Fig. 5.6 (A). The potential of zero current is again observed at 0.05 V vs. SCE. The response on the addition of poly acrylic acid is shown in Fig. 5.6 (B). The current observed is of the same magnitude as observed in the absence of the poly acrylic acid, suggesting that its presence does not have a significant affect on the electrochemistry of the system.

The responses at a 0.07 cm\(^2\) glassy carbon electrode are shown in Fig. 5.7. Again, cyclic voltammograms were recorded in the absence, Fig. 5.7 (A), and presence, Fig. 5.7 (B), of 2 \(\times\) \(10^{-5}\) M poly acrylic acid.
In Fig. 5.7 (A) the response is as observed in Fig. 5.3 (B). The potential scan is reversed at three different values (−1.2, −1.25, −1.3 V vs. SCE) and the amount of copper metal deposited varies accordingly. A well-defined stripping response is detected after reversing the scan direction and scanning the potential positive of 0.05 V vs. SCE. The deposition process is not mass transport limited but is entirely dominated by the deposition kinetics. Again a current loop is observed during the deposition of copper onto carbon. The deposition current is initially low and increases after reversal of the scan direction, indicating a nucleation and growth type process, where as seen earlier, Fig. 5.3, copper is once more preferentially plated onto copper. A nucleation overpotential is responsible for slow electrodeposition onto carbon. The reaction is slower kinetically in the presence of PAA, i.e., a slightly higher resistance is observed, Fig. 5.7 (B), suggesting that there is poorer electrical contact between the copper nuclei and the carbon surface with the PAA present. This may be due to metal/PAA complexation in solution or PAA adsorption onto copper nucleation sites on the carbon surface. While the kinetics of the process seems slower from the electrochemical study, the structure of the deposit may in fact be superior with the PAA present, since the additive could lead to an enhancement of the desired deposit properties, e.g., uniformity, smoothness, etc. The potentially complicated deposition
process for the metal/PAA system is discussed further in Chap. 6.

5.3.4. Electrodeposition of Copper/Carbon Nanofibre Composites from Poly Acrylic Acid containing Electrolytes

The deposit shown in the surface FEGSEM images in Fig. 5.8 was produced from the poly acrylic acid containing acidic copper electrolyte with a current of -0.5 A applied for 60 min.

![Figure 5.8. Cu/CNF composite formed from an acidic copper electrolyte containing PAA, 0.85 M CuSO₄·5H₂O, 0.55 M H₂SO₄, 2 x 10⁻⁵ M PAA, -0.5 A, 3600 s.](image)

Large nodules of about 20 μm in diameter are observed, which can be seen distributed over the deposit surface, Fig. 5.8 (a). A higher magnification image is shown in Fig. 5.8 (b) showing the nodular growths more clearly. On closer inspection, Fig. 5.9, the composite can be observed with the regular appearance of CNF dispersed in the crystalline copper structure.

![Figure 5.9. FEGSEM image of Cu/CNF composite formed from an acid copper solution containing PAA, 0.85 M CuSO₄·5H₂O, 0.55 M H₂SO₄, 2 x 10⁻⁵ M PAA, -0.5 A, 3600 s.](image)
Similar images were recorded for both the nodular protrusions and the background layer. This is in contrast to the observations in the absence of PAA when CNF were only present in the nodular growths, Fig. 5.4. This is supported by the appearance of the electrolyte after the addition of PAA, when the CNF were much more well-dispersed in the solution. The following high magnification image shows the presence of CNF incorporated in a copper crystal, Fig. 5.10.

Figure 5.10. High magnification image of Cu/CNF composite formed from an acid copper solution containing PAA: 0.85 M CuSO₄·5H₂O, 0.55 M H₂SO₄ 2 x 10⁻⁴ M PAA; -0.5 A, 3600 s.

Hence, the presence of the PAA in the electrodeposition solution appears to promote the inclusion of CNFs in the co-deposit, to some extent.

The aim of the remainder of this chapter is to demonstrate the application of the QCM as a probe for the detection of CNF inclusion in the co-deposits. Once the proof of principle for its use as a detection probe is established, possible directions for optimisation of the technique in quantifying the amount of CNFs in a co-deposit will be outlined.

5.4. Quartz Crystal Microbalance Studies

The quartz crystal microbalance system responds to adsorption or deposition processes at the gold surface with a shift in resonance frequency. The theoretical frequency response for the resonator can be calculated from the Sauerbrey equation, Eq. 5.2 [18], as discussed in Chap. 1. Note that the decrease in resonance frequency reflects an increase in the mass of material on the crystal surface:
\[ \Delta f = -2 \frac{f_0^2 \Delta m}{A \sqrt{\mu_q \rho_q}} \] (5.2)

In this equation \( \Delta f \) is the change in resonance frequency, \( f_0 = 10 \times 10^6 \) Hz is the resonance frequency of the crystal, \( \Delta m \) is the deposited mass, \( A = 0.196 \text{ cm}^2 \) is the area of the electrode, \( \mu_q = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2} \) is the shear modulus of quartz, and \( \rho_q = 2.648 \text{ g cm}^{-3} \) is the density of quartz. Based on this equation, the sensitivity of the quartz crystals employed is \( \Delta m/\Delta f = 0.87 \text{ ng Hz}^{-1} \). This equation was originally derived for processes in the gas phase, but, as mentioned earlier, can be employed for solution phase studies, Chap. 1.8. Here, the deposition of copper is studied and is generally employed as a calibration check for the system [19].

5.4.1. QCM Study of Deposition from an Acidic Copper Bath

The ability of the QCM to be employed in electrochemical studies (EQCM) allows for the recording of CVs and simultaneous mass changes at the electrode surface due to processes such as adsorption, electrodeposition, and dissolution. This setup has been used, e.g., to discuss the concept of massograms and to describe their application to electrode processes [20]. Fig. 5.11 shows a cyclic voltammogram for the reduction and oxidation of Cu from an acidic copper electrolyte and the corresponding mass data from the QCM.

![Cyclic voltammogram and mass data](image)

**Figure 5.11.** Cyclic voltammogram and mass data for the oxidation and reduction of 0.8 M Cu\(^{2+}\) at a gold-coated quartz crystal.
The negative part of the cyclic voltammogram shows the deposition of Cu at potentials below about 0.05 V vs. SCE and on the positive scan dissolution occurs and continues up to about 0.14 V. The corresponding mass data illustrates that as Cu begins to plate, the mass on the crystal surface increases and reaches a maximum at the potential of the onset of oxidation and continues to decrease until all the Cu has dissolved back into the solution. The mass change recorded simultaneously, is consistent with the deposition and stripping process.

5.4.2. Deposition from an Acidic Copper Bath Containing Oxidised Carbon Nanofibres

Both as-grown and oxidised CNF were used for the experimental QCM study. Firstly, oxidised CNF were added to the Cu plating bath and a deposit was grown on a Au coated quartz crystal resonator. Theoretically, for the deposition of Cu alone, a value of 31.8 g mol\(^{-1}\) of electrons is expected, since Cu reduction is a 2 e\(^-\) process. The following plots, Fig. 5.12, consider the total mass deposited just before dissolution starts, as described in Fig. 5.11.

\[ \text{Figure 5.12. Plot of the integrated charge under the reduction signal and the maximum weight change as a function of the addition of between 0 and 8 g L}^{-1} \text{ of oxidised CNFs to the Cu plating bath.} \]

It can be seen that the presence of the carbon nanofibres affects the deposition process. Both the charge and the mass increase for solutions with increasing concentrations of oxidised CNF, at least initially. The increasing electrode surface area effect of the carbon nanofibre deposit is believed to be responsible. Charge and mass values increase but then level off, and dividing mass by charge and multiplying by the Faraday constant gives a molar mass of the deposit (in g mol\(^{-1}\) of electrons). These values are presented in Tab. 5.1.
<table>
<thead>
<tr>
<th>ox. CNF g/L</th>
<th>g mol$^{-1}$ of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.8</td>
</tr>
<tr>
<td>1</td>
<td>32.8</td>
</tr>
<tr>
<td>2</td>
<td>32.2</td>
</tr>
<tr>
<td>4</td>
<td>32.2</td>
</tr>
<tr>
<td>8</td>
<td>31.5</td>
</tr>
</tbody>
</table>

Table 5.1. Mass of deposit per mole of electrons at various concentrations of oxidised CNF.

These values are almost constant suggesting little or no carbon incorporation in the case of oxidised carbon nanofibres. This may be caused by a number of factors. The lack of apparent incorporation of nanofibres is possibly due to preferential copper deposition. However, due to the difference in molar mass between copper and carbon, it is also a possibility that there could be some carbon incorporation that goes undetected by the quartz crystal microbalance technique.

Since these experiments are intended to act as a demonstration of the application of the QCM as a probe for the detection of CNFs in co-deposits and the results from the above table are inconclusive (although the SEM images show CNF inclusion), a further investigation was undertaken using as-grown CNFs.

5.4.3. QCM Study of Deposition from an Acidic Copper bath with as-grown Carbon Nanofibres

Following on from the previous section, the experiments were repeated with as-grown carbon nanofibres. These were surprisingly dispersable in the presence of Cu$^{2+}$ cations and could be used without the addition of surfactants. For the case of the as-grown CNF, both the mass and charge appear to increase with increasing additions of CNF to the solution, Fig. 5.13.
Unlike the case of the oxidised CNFs, a clear increase in both charge and weight of deposit are observed with higher carbon concentrations causing greater effects. It is likely that the increase in charge is associated with charging occurring at the incorporated CNFs. Again, the molar weight of deposit per electron is determined.

<table>
<thead>
<tr>
<th>As-grown CNF g/L</th>
<th>g mol⁻¹ of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.8</td>
</tr>
<tr>
<td>1</td>
<td>28.8</td>
</tr>
<tr>
<td>2</td>
<td>31.6</td>
</tr>
<tr>
<td>4</td>
<td>35.1</td>
</tr>
<tr>
<td>8</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Table 5.2. Mass of deposit per mole of electrons at various concentrations of as-grown CNF.

Nevertheless, taking the molar weight per electron value with 0 g/L as-grown CNF in solution as the baseline, it appears that a clear increase in the molar weight per electron was detected. This suggests that more and more carbon was incorporated as the carbon nanofibre concentration was increased. The experiments with the as-grown CNFs demonstrate that the QCM may be applied as a probe for the detection of CNFs in co-deposits. The quantitative results obtained with the QCM system are in agreement with qualitative results obtained by SEM.
Figure 5.14. With the addition of 8 g/L of unoxidised CNF to the Cu bath the following data was recorded. (a): cyclic voltammogram, I vs. E; (b): massogram, dm/dt vs. E; (c) = (b)/(a), (dm/dt)/(dQ/dt) vs. E.

From Fig. 5.13, the addition of 8 g/L of unoxidised CNF gave a value of 34 g mol\(^{-1}\) of electrons for the deposit. This value was calculated from the peak maximum as shown earlier, Fig. 5.11. The cyclic voltammogram in Fig. 5.14 (a) shows the current response to an applied potential. Part (b) is the derivative of the mass vs. potential data ("massogram"), which can be compared to the cyclic voltammogram to verify the mass mol\(^{-1}\) value over the full deposition/dissolution potential range. As in the previous case, mass is divided by charge, but in this case dm/dQ is obtained, i.e., taking into account the full potential range, this gives about 37 g mol\(^{-1}\) of electrons during the deposition part of the cycle and 30 - 37 g mol\(^{-1}\) of electrons for the dissolution part of the scan. The lower initial value, for the dissolution, may be more representative of just Cu oxidation; it then increases to incorporate the slower CNF removal from the quartz crystal, in the sense of a physical detachment of the carbon.
rather than electro-dissolution.

Nevertheless, the results act as a quantitative indicator for the inclusion of CNFs into copper co-deposits and serve as a proof of principle for the use of the QCM as a probe in quantifying the co-deposition process.

5.5. Conclusions

The results in this chapter detail the work undertaken to study copper/CNF co-deposition processes from acidic solution. The electrochemistry of copper and copper/CNF composite electrodeposition was presented. FEGSEM images provided evidence for the inclusion of as-grown CNF into copper electrodeposits and allowed a comparison of the effect of different agitation methods. Although ultrasound would be expected to aid the dispersion of the CNFs, no distinct differences were observed between the FEGSEM images obtained for it and conventional stirrer agitation. Future work could include attempts to eliminate nodular growths, e.g., by pulse plating.

A brief study of the effect of adding PAA to the electrodeposition solution on the deposition process was undertaken. An increase in resistance was observed in the electrochemical results, which may be due to metal/PAA complexation or PAA adsorption. From the FEGSEM images the presence of the PAA in the plating solution appears to promote the incorporation of CNFs in the co-deposit.

It would also be interesting to consider species that would potentially promote the incorporation of CNF with the Cu electrodeposit. This could be achieved through the functionalisation of the Cu with activating groups, e.g., containing N (amines) or S (thiols) functionalities to interact with the oxidised form of the CNFs.

The application of the QCM as a probe for the detection of the inclusion of the CNFs in copper co-deposits was demonstrated by experiments involving oxidised and as-grown CNF materials. Unlike the oxidised fibres, where it is uncertain from the results whether CNF co-deposition occurred or not, in the case of the as-grown fibres, the quantity incorporated appears to increase with higher concentrations of CNF in the plating solution. Hence, the proof of principle for the application of the QCM as a
probe for the determination of the level of CNF co-deposition has been established. Further experiments to optimise the approach for the quantification of the amount of CNFs in the deposits would need to be undertaken. These include a possible study of the affect of adding PAA to the electrodeposition solution.
References


Chapter 6
Zinc/Carbon Nanofibre Co-deposition
6.1. Introduction

Due to its high specific energy, low cost, low toxicity and reversibility, zinc has been extensively studied by electrochemists with a view to battery production and development [1, 2, 3, 4]. Zinc's well-established electrochemistry includes its electrodeposition from acidic or alkaline solution, as required, which is of particular relevance in the current study [5, 6, 7]. This, in combination with the experience and knowledge of zinc electrodeposition available in the laboratory made it an obvious choice for the further study of metal/carbon nanofibre electrodeposition systems, e.g., [7, 8, 9], and including the investigation of other Zn composite systems, e.g., Zn-SiO$_2$ [10].

The role of zinc in electrochemistry originates with Volta, who in 1800 developed the silver-zinc pile [11]. Zinc has been a favoured material for many battery systems due to its favourable technological and economic properties. Its low equivalent weight and relatively high voltage place it high on the list of energy densities for aqueous systems and it has always been readily available.

A number of reviews have appeared in the literature, which discuss developments in zinc-air, Rechargeable Alkaline Manganese dioxide (RAM)/zinc, and nickel/zinc batteries [2, 3, 4]. Recent advances in the field of batteries and energy storage devices include the work of Deiss et al. who studied a rechargeable battery that utilised a porous Zn/ZnO anode, their model is expected to be useful in the optimisation of zinc cell design [12]. Research has also been undertaken to explore the effect of electrocatalysts on oxygen reduction in a zinc-air battery [13]. Freitas investigated the recycling of zinc from Zn-MnO$_2$ batteries, electrochemical recycling being favourable from an environmental point of view [14].

In addition to the important area of batteries, zinc and zinc materials have found uses in a wide variety of applications. These include zinc-nickel alloy electrodeposits formed for use as cathodes for alkaline water electrolysis. High surface area Ni and Ni-Co coatings were obtained by an electrodeposition methodology that allows the complete removal of Zn, generating a highly porous surface suitable for alkaline water hydrolysis [15].
In an effort to make the production of dye sensitised solar cells more economical, Karuppuchamy et al. studied the electrodeposition of ZnO thin films [16]. This method avoids the commonly used heat treatment step, which requires the use of a relatively expensive heat resistant material, the conductive nature of their film is guaranteed without applying heat. Another area of semiconductor research looked at the electrodeposition of cadmium and zinc sulphides and selenides [17]. The ternary compounds deposited are of interest due to the possibility of varying the band gap with composition.

Electrodeposited zinc and zinc-based coatings find extensive use in applications such as the corrosion protection of steel in the automotive industry, and it is often assumed that the service life of the part is directly proportional to the thickness of the zinc layer. However, the corrosion characteristics were shown by Bouroushian et al., in the case of an acid sulphate bath, to strongly depend on the texture and microstructure, which, in turn, depend on the specific deposition procedure employed [18]. They showed that the variation of the deposition current density from very low (0.5 A dm\(^{-2}\)) to moderately high values (40 A dm\(^{-2}\)), under DC electrodeposition conditions, was related to changes in the texture, grain structure, and surface morphology of the zinc coating, depending on bath pH.

Raeissi explained changes in the morphology and texture of zinc deposits on steel in terms of the nucleation and growth mechanism [19]. At pH 2 instantaneous nucleation is predominant. Increasing the pH of the electrodeposition bath reduces the number of active sites for nucleation on the steel substrate due to zinc hydroxide adsorption, which may cause their observed shift towards progressive nucleation. At pH 2, increasing the current density reduced the zinc crystal size. At pH 4, increasing the current density increased the zinc crystal size.

Since the 1960's, increasing pressure to reduce, and to eventually eliminate, the use of cyanide solutions, due to the serious safety issues associated with exposure to, and containment of, large quantities of solution in industry, has led to the development of zincate solutions. The zincate process proves to be quite efficient but not as reliable as cyanide solutions, mainly related to the quality of the deposits. Mirkova et al. found that in the presence of additives the zinc deposition process from a zincate electrolyte
is kinetically limited but in the absence of additives the deposition is mass transport limited [20]. The attempts to find cyanide free electrodeposition solutions also extend to copper/zinc alloy deposition, which is widely used in industry due to the corrosion protection it provides. One such bath was developed by Carlos et al., who investigated the effect of various concentrations of copper and zinc ions in a sorbitol (sorbitol complexes the Cu, which then reduces at a potential near that of the zincate ion, so that codeposition is achieved) containing alkaline solution [21]. They illustrated how these ratios and the deposition conditions influenced the alloy composition, surface morphology, current efficiency, and brightness of the Cu-Zn electrodeposits.

New zincate electrolytes have proved interesting in terms of improving the brightness of Zn coatings and also in working towards reducing the hydrogen embrittlement of zinc deposits, as a result of the simultaneous discharge of hydrogen ions or water molecules during Zn deposition. Mirkova et al. found that the evolution of hydrogen decreased with increasing ZnO and decreasing NaOH concentrations in the electrolyte [22]. The hydrogen permeation through the steel membrane is suppressed by the deposition of the Zn coating.

In this chapter, zinc is codeposited with carbon nanofibres. A potential application for carbon nanofibres is as a coating on crankshaft bearings, e.g., as a lubricating and wear-resistant film, in the form of a metal/carbon nanofibre composite. In the absence of a bearing material and when the pressure generated in the lubricating oil film is insufficient to keep the two moving surfaces apart, then there is the possibility of the two surfaces seizing or welding together. Conventionally, the coating materials generally consist of lead, tin, and copper, providing the desirable properties of both hardness and lubricity. Lead acts as a solid lubricant, particularly during engine start-up, but it is one of the heavy metals whose use is being phased out under the EU's end of life vehicles directive [23], so an alternative is required. The material must also have a soft surface so that small foreign objects can be included in it. Carbon, in the form of carbon nanofibres, has the potential to act as a lubricating and wear-resistant material. The seizing/welding effect is potentially avoidable by the inclusion of carbon nanofibres in a Pb free coating.

One route to metal/carbon nanofibre composite deposits is via electro-codeposition, as
discussed in Chap. 5 for copper. In the current work, although not directly applicable as a bearing material, two well-established Zn electrodeposition baths were chosen for preliminary investigations, due to their familiarity and ease of deposition, as discussed at the beginning of this chapter. It is hoped that, in the future, these model systems would have the potential to be adapted for more wear resistant/lubricious Sn, and/or Cu/carbon nanofibre composite coatings. The second phase, the carbon nanofibres, were suspended in the electrolyte to allow the formation of a composite coating during electrodeposition.

The co-deposition experiments are reported here with evidence for the co-deposition of zinc metal with carbon nanofibres.

6.2. Experimental
6.2.1. Chemicals
NaOH, poly acrylic acid (partial sodium salt, Mw 5000) (Aldrich); HCl (32 %), HNO₃ (70 %), ZnO, ZnSO₄.7H₂O, and H₂SO₄ (98 %) (Fisher); Na₂SO₄ (99 %) (Acros Organics); were obtained commercially and used without further purification.

6.2.2. Instrumentation
A computer aided pulse plating unit (CAPP, Axel Akermenn A/S) was used for the pulse plating experiments.

The electrochemical cell employed for the preliminary investigations, Fig. 6.1, was designed to minimise the solution volume while still allowing controlled mass transport conditions to be applied.
Figure 6.1. Electrochemical cell used for the initial Zn electrodeposition experiments. \( W = \) stainless steel working electrode, \( R = \) SCE reference electrode, and \( C = \) Pt mesh counter electrode. Cell is placed on a magnetic stirrer, there is also a cover for the cell, not shown for clarity.

The solution was stirred using a magnetic stirrer. A flow of argon was maintained to remove traces of oxygen. The current was supplied by a potentiostat in galvanostatic mode. This cell was used for initial experiments up to and including Sec. 6.3.2.

The carbon nanofibre growth, subsequent voltammetry experiments, and electrode analysis were performed as described earlier. For further details see Chap. 2.2.

6.2.3. Electrode Preparation

For the electrodeposition experiments, the working electrode was a 10 cm\(^2\) mild steel cathode (a low carbon steel, 0.02 wt.-% C). Electrode preparation was undertaken as in Chap. 5.2.3, to include; washing, rinsing with distilled water and ethanol. Then there was an electrochemical degreasing step followed by immersion in HCl and final rinsing with distilled water. The cathode was dried in hot air between each step and after final rinsing. A sacrificial, zinc, metal anode was used in the bulk electrodeposition trials.

In the case of the voltammetric investigations, stainless (AISI 316) and mild steel electrodes with a well-defined electrode area (ca. 1 cm\(^2\) and 0.28 cm\(^2\), respectively) or a glassy carbon disc (BAS, 3 mm diameter) were employed as the working electrodes. A saturated calomel electrode (SCE) served as the reference and platinum gauze as a high surface area counter electrode; variations are noted in the text, as appropriate.
6.2.4. Plating Bath Composition

a) The initially investigated electrolyte solution was prepared by dissolving 1 g of ZnO in 100 mL of a 2 M solution of NaOH. Stainless steel electrodes were obtained commercially (AISI 316 - foil, Goodfellow, UK) and cut into 1 x 5 cm specimens. The surface of stainless steel is typically coated with Cr2O3. The electrode area was masked off using an insulating tape and contact was made through a crocodile clip. Prior to zinc electrodeposition, the surface was cleaned by rinsing with ethanol and water to remove impurities. All experiments were conducted at a temperature of 22 ± 2 °C.

This initial electrolyte was used in conjunction with the cell described in Sec. 6.2.2 for the work described up until Sec. 6.3.3, from which point the electrolytes used were as described below. Any variations are noted as appropriate.

b) Subsequently, as was the case for the copper investigations, conventional plating bath formulations were employed in the study of the co-deposition process with carbon nanofibre materials. The bath compositions and conditions investigated were as follows.

Alkaline Zincate:
The alkaline zincate bath consisted of:

- 10 g/L (0.12 M) ZnO
- 105 g/L (2.6 M) NaOH
- 1 g/L of oxidised CNF
- pH 14

Zinc Sulphate:
The constituents of the acidic zinc sulphate bath were:

- 250 g/L (0.87 M) ZnSO₄·7H₂O
- 80 g/L (0.56 M) Na₂SO₄
- 1 g/L of as-grown CNF
- pH 2 (adjusted with H₂SO₄)
- (+ 2 x 10⁻⁵ M poly acrylic acid or tetraphenylphosphonium bromide (PPh₄⁺), where stated)
Both the as-grown and oxidised form of CNFs were used in the experiments undertaken in this chapter. Details about their growth and oxidation are given in Chap. 2. The as-grown fibres are hydrophobic and were used either mechanically ground, wet milled with the surfactant, PPh$_4$Br, or sonicated with poly acrylic acid in order to improve their dispersibility.

Tetraphenylphosphonium bromide was used as a cationic surfactant to aid the formation of a suspension of as-grown CNFs by the adsorption of the aromatic cation onto the hydrophobic carbon nanofibres, Fig. 6.2.

![Tetraphenylphosphonium ion](image)

**Figure 6.2.** Tetraphenylophosphonium ion.

The other additive used was poly acrylic acid, PAA, which was described earlier in Chap. 5.2.4; the hydrophobic polymer backbone interacts with the CNFs and when sonicated the CNFs disperse well in the electrodeposition solutions.

As stated earlier, the oxidised fibres are hydrophilic and form a very stable suspension in the alkaline plating bath and a less stable one in the acidic bath, with the fibres settling out after an hour or two.

**6.2.5. Plating Bath Agitation**

The first method of agitation investigated was the vibromix, Fig. 6.3, which provided vibratory agitation, inducing good particulate mixing and buoyancy with low interfacial convection.
It consisted of a rod, which was attached to a vibrating plate with a number of truncated holes, through which flow occurred; the transformer controlled the rate of displacement of the plate. This method demonstrated the Venturi effect: the flow of fluid through short, tapered holes, which causes an increase in the velocity of the fluid and a corresponding decrease in pressure.

A conventional magnetic stirring instrument was also considered.

PAA containing solutions were agitated ultrasonically for 30 min. prior to electrodeposition, typically in a 1 L beaker. A conventional magnetic stirring instrument was used for solution agitation during electrodeposition.

6.2.6. Electrode Surface and Compositional Analysis
After electrodeposition, sample preparation was not required for surface analysis. Cross sections of the samples were prepared using a Struers Labotom cut-off saw, the sample was then smoothed with a belt surfacer. Subsequently, the samples were mounted in a conducting resin in a hot mounting press. The next step was the manual grinding of the samples with progressively finer, silicon carbide, abrasive papers. Then, the samples were polished with 6 and 1 μm diamond polish on a polishing wheel. Finally, the samples were etched with ferric chloride etchant, if required.
6.3. Electrodeposition of Zinc and Zinc/Carbon Nanofibre Composites from Alkaline Solution

Zinc electrodeposition is an important industrial process, in particular for the corrosion protection of steel. Here it is investigated for the incorporation of carbon nanofibres during electrodeposition. Traditionally, two types of zinc electrodeposition baths have been employed using either alkaline or acidic conditions, the case of acidic solution will be dealt with later in Sec. 6.4. The alkaline bath takes advantage of the amphoteric nature of ZnO. ZnO can be dissolved in the presence of high concentrations of hydroxide and can be employed for the electrodeposition of zinc on steel [24]. Under these conditions hydrogen evolution can be suppressed. ZnO dissolves in strongly basic solution forming a zinc-hydroxide ion complex. The predominant species present is the Zn(OH)\(^{2-}\) ion. Zinc electrodeposition from zincate solutions has been reviewed [7]. As mentioned earlier, interest in this process developed from the fact that the well established cyanide based electrolytes had safety concerns due to the inherent toxicity and difficulty in the removal of complexed zinc. The search was prompted by the increasingly stringent anti-pollution laws introduced in a number of countries in the 1960's. Alkaline zincate formulations were one of the non-cyanide alternatives developed.

As pointed out earlier, it has been found that oxidised carbon nanofibres are soluble in alkaline aqueous environments (Chap. 2.4) and therefore co-deposition of zinc and carbon nanofibres from an alkaline zincate solution becomes feasible. However, it will be shown that, depending on the conditions employed, both alkaline zincate and acidic baths (Sec. 6.3 and 6.4) are suitable for carbon nanofibre co-deposition.

Electrochemical investigations were conducted in terms of the influence of scan rate and the mass transport properties of the system. Initially, cyclic voltammograms were recorded to characterise the behaviour of the stainless steel electrodes immersed in electrolyte solution; 0.12 M ZnO, 2.0 M NaOH. Fig. 6.4 shows typical cyclic voltammograms obtained for the reduction of Zn(OH)\(^{2-}\) to zinc metal at a stainless steel (AISI 316 foil) electrode, recorded at various scan rates; 10, 50, and 200 mV s\(^{-1}\).
Two reactions are possible when a steel electrode is cathodically polarised in an alkaline zinc solution [25]. The first is the electrolytic deposition of zinc, Eq. 6.1. The second is the hydrogen evolution reaction, Eq. 6.2. The standard electrode potentials indicate that, thermodynamically speaking, hydrogen discharge should appear in preference to zinc. However, due to the much higher hydrogen overpotential on zinc compared to steel, the cathode efficiency for zinc deposition varies from 60 - 90% [25].

\[
\text{Zn(OH)}_4^{2-} + 2 e^- \rightarrow \text{Zn} + 4 \text{OH}^- \quad E^0 = -1.199 \text{ V (SHE)} \quad (6.1)
\]

\[
2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad E^0 = -0.828 \text{ V (SHE)} \quad (6.2)
\]

In this work, a characteristic deposition signal is detected commencing at approximately - 1.45 V vs. SCE followed by a ‘stripping’ response after reversal of the scan direction (Eq. 6.1). From the unequal charge under the reduction and stripping signals it can be concluded that a side reaction, in this instance hydrogen evolution, occurs, Eq. 6.2. During the deposition process the evolution of gas bubbles can also be observed. From the magnitude of the currents and the known concentration of \text{Zn(OH)}_4^{2-} it can be calculated that the electrochemical cell (conditions as shown in Fig. 6.4) is operating far from mass transport control; a decreasing current is observed with increasing scan rate.
Since all the scan rates investigated in Fig. 6.4, 10 - 200 mV s\(^{-1}\), gave well defined responses a scan rate of 100 mV s\(^{-1}\) was chosen for subsequent experiments. Further cyclic voltammograms were obtained to characterise the electrodeposition processes for both carbon and stainless steel electrodes again in alkaline zincate solution; 0.12 M ZnO, 2.6 M NaOH, pH 14, scan rate: 100 mV s\(^{-1}\), Fig. 6.5. Zn deposition and stripping occur at a negative potential of \(-1.55\) V vs. SCE on stainless steel. It can be seen in Fig. 6.5 (A), that the deposition commences and, depending on the potential at which the scan is reversed, a mass transport controlled peak appears. Upon reversal of the direction of the scan a stripping peak is detected. On glassy carbon electrodes, Fig. 6.5 (B), the deposition of zinc commences at a slightly lower potential and a loop consistent with nucleation and growth is observed. The drawn out (almost ohmic) oxidation peak, which occurs at the glassy carbon electrode, shows that Zn is reduced at a considerably slower rate than at the steel electrode.

![Cyclic voltammogram](image)

**Figure 6.5.** Cyclic voltammograms recorded at (A) stainless steel (0.28 cm\(^2\)) and (B) glassy carbon (0.07 cm\(^2\)) electrodes, 0.1 V s\(^{-1}\). 0.12 M ZnO, 2.6 M NaOH, pH 14.

The metal to carbon contact for nuclei could be poor and may be responsible for this effect. Sonneveld et al. studied the nucleation and growth of zinc on glassy carbon from a zincate solution [26]. They concluded, using cyclic voltammetry, that a crystallisation overpotential was observed during zinc deposition on glassy carbon in
alkaline zincate solution. Therefore, no interaction between the electrode surface and the deposit occurs and a poor deposit adherence can be expected. Hence, and from the voltammetric responses shown in Fig. 6.5, it can be predicted that zinc in alkaline baths will electrodeposit preferentially onto steel and zinc, but not onto the carbon inclusions.

6.3.1. Morphology of Zinc Electrodeposits from Alkaline Solution

Based on these preliminary voltammetric studies, the bulk deposition of zinc on stainless steel was then attempted by applying a constant current density to the electrode.

At a relatively high current density, 10 A dm\(^{-2}\), zinc nucleation on the steel surface and growth of well-defined crystals can be observed, Fig. 6.6. The lower magnification FEGSEM micrograph shows the partial coating of the steel substrate, Fig. 6.6 (a). The steel appears dark in the FEGSEM image and the zinc is the lighter coloured material. Faceted zinc crystals are observed at higher magnification, Fig. 6.6 (b).

![Figure 6.6. FEGSEM images of Zn deposited on stainless steel from an alkaline zincate bath (Sec. 6.2.4. (a)), obtained at high current density, 10 A dm\(^{-2}\), 2 min; (a) low magnification, (b) high magnification.](image)

However, at lower current densities, 1 A dm\(^{-2}\), 'mossy' zinc deposits are observed. The zinc nuclei observed in Fig. 6.7 (a), on closer inspection, Fig. 6.7 (b), reveal the mossy zinc type deposit. This effect, leading to nanostructured zinc, is well known and part of the complex deposition process at lower current density or in the presence
of additives [27, 28].

Figure 6.7. FEGSEM images of “mossy” Zn deposited on stainless steel from an alkaline zincate bath (Sec. 6.2.4. (a)), obtained at low current density, 1 A dm^-2, 18 min; (a) low magnification, (b) high magnification.

It has been mentioned in the literature that the deposit morphologies produced during the deposition of zinc from an aqueous solution of potassium hydroxide saturated with zinc oxide vary with current density. At high current densities of 10 A dm^-2 the deposits were dendritic, at 2 A dm^-2 they consisted of layer and some granular growths, and at 0.4 A dm^-2 mossy growths formed [29].

6.3.2. The Electrodeposition of Zinc/Carbon Nanofibre Composites

The next part of the investigation involved the repetition of the zinc electrodeposition experiment but with oxidised carbon nanofibres (7 mg mL^-1) added to the solution, with the aim of incorporating them into the coating. The low current density experiment in the presence of carbon nanofibres were difficult to interpret due to the similar topography of mossy zinc and carbon nanofibres. Chemical identification of the exact regions of Zn and C may be possible with, e.g., localised EDX analysis. However, the high current density experiments, 10 A dm^-2 for 2 min, in the presence of carbon nanofibres gave the first clear evidence for co-deposition, as demonstrated by the high magnification FEGSEM image shown in Fig. 6.8.
Both zinc nuclei and carbon nanofibre fragments are visible (compare to Fig. 2.10 (b), a FEGSEM image of oxidised carbon nanofibres). At this stage the extent of incorporation of the carbon nanofibres is not known. Both individual carbon nanofibres and carbon nanofibre aggregates are clearly observable in the image, Fig. 6.8, possibly suggesting their non-ideal dispersion in the electrodeposition solution.

Subsequent work involved the formation of coatings of considerably increased thickness, of between 10 and 50 μm approx., (enabling cross section analysis) as well as the investigation of an acidic Zn bath and bath additives (to aid CNF dispersion), Sec. 6.4 - 6.6.

6.3.3. Variation of Electrochemical Conditions and Agitation

As mentioned earlier in Sec. 6.2.4, the baths and electrodes used subsequently are as described in Chap. 6.2.3 and 6.2.4. (b).

Coatings from the alkaline zincate bath discussed above were deposited under various electrodeposition conditions and agitation methods. Only relatively high current densities were used due to the mossy deposits encountered at low current densities, as described in the previous section. The preparation of the cross section samples is also detailed in Chap. 6.2.6. Both cross section and surface images of the deposit formed using vibratory agitation at 2 A dm$^{-2}$ for 30 min are shown in Fig. 6.9. The cross sectional image shows the electrodeposited zinc sandwiched between the mild steel substrate (top layer) and the conducting polymeric mounting material (bottom layer), Fig. 6.9 (a), with (b) showing the layered zinc surface. Vibratory agitation appears to
result in a reasonably dense deposit (compared to magnetic stirrer agitation, see subsequent data).

Figure 6.9. FEGSEM image of Zn deposit formed on mild steel from alkaline zincate solution (0.12 M ZnO, 2.6 M NaOH, pH 14) with vibratory agitation, 2 A dm\(^{-2}\), 30 min; (a) cross section (the layers from top to bottom are the mild steel substrate, electrodeposited zinc, polymeric mounting material), (b) surface.

Increasing the current density, to 4 A dm\(^{-2}\), leads to a finer grain structure caused by the formation of more nuclei, Fig. 6.10, again both cross section (a) and surface images (b) are presented.

Figure 6.10. As Fig. 6.9 but with applied current of 4 A dm\(^{-2}\) for 15 min; (a) cross section, (b) surface.

The different thicknesses observed with the same amount of charge passed are probably due to the effect of hydrogen evolution. Hydrogen ions can adsorb at active sites, related to zinc nucleation, and be released as hydrogen gas [30]. Nucleation sites are more abundant on fine and randomly orientated zinc surfaces than on unidirectionally grown large crystalline surfaces. Hydrogen is preferentially adsorbed
onto the nucleation sites rather than onto uniformly stacked crystalline surfaces. The high current efficiency is the result of the preferred texture of the deposit that has less defects and grain boundaries providing nucleation sites for H₂ gas evolution. In this case, the lower current density, Fig. 6.9, produced a layered type deposit supplying fewer sites for hydrogen adsorption, compared to the case illustrated in Fig. 6.10, and, therefore, has a higher current efficiency. Also, it is likely that the layered type deposit will adhere better to the substrate, while the granular type deposit is more likely to detach prior to/during mounting.

Figure 6.11. FEGSEM of the deposit formed on mild steel from alkaline zincate solution (0.12 M ZnO, 2.6 M NaOH, pH 14) under vibratory agitation in the presence of 1 g L⁻¹ of oxidised CNFs, 2 A dm⁻², 60 min. [7.1, Tab. 6.1]⁺

Fig. 6.11 shows the deposit formed in the presence of 1 g L⁻¹ of oxidised CNFs at a current density of 2 A dm⁻² for 60 min using vibratory agitation. It is a surface SEM of the zinc/CNF electrodeposited formed; the oxidised CNFs are evident on the surface of the Zn deposit, though incorporation is not yet observable. Carbon nanofibre inclusion could be shown by an investigation of the structure of the bulk of the deposit.

At higher current density, 4 A dm⁻² for 30 min, Zn crystals seem to be better intermingled with the oxidised CNFs as shown below in Fig. 6.12.

⁺ Numbers in brackets, after the figure captions, refer to the samples detailed in Tab. 6.1.
Figure 6.12. FEGSEM of Zn/CNF deposit formed on mild steel under the conditions in Fig. 6.5 except at a current density of 4 A dm$^{-2}$ for 30 min. [7.2, Tab. 6.1]

The overall deposit formed is less compact than that formed at 2 A dm$^{-2}$, compare to Fig. 6.11.

Figure 6.13. Zn electrodeposited on mild steel from the alkaline zincate magnetically stirred bath (0.12 M ZnO, 2.6 M NaOH, pH 14) at 2 A dm$^{-2}$ for 30 min; (a) cross section, (b) surface.

A relatively low-density deposit was formed from magnetically stirred solution, at 2 A dm$^{-2}$ for 30 min, Fig. 6.13. The surface image shows platelets growing perpendicular to the substrate surface.

At the higher electrodeposition current density of 3 A dm$^{-2}$, the deposit has a similar morphology but the process is much less efficient, Fig. 6.14. This effect, of reduced efficiency at higher current densities, was seen earlier comparing Figs. 6.9 and 6.10, and again may be related to hydrogen evolution effects [30], but differences in the grain structure are much less apparent in this case. Looking at the cross sectional images it can be seen that at 2 A dm$^{-2}$ about 9 \(\mu\)m thickness was obtained, Fig. 6.13,
but at 3 A dm\(^{-2}\), the deposit was only about 5 µm thick, Fig. 6.14.

**Figure 6.14.** As above but at 3 A dm\(^{-2}\) for 20 min; (a) cross section, (b) surface.

On addition of 1 g L\(^{-1}\) of oxidised CNF to the electrodeposition bath the following images were obtained, Fig. 6.15. A layer type growth was obtained, typical for the current density used [29]. There is some evidence of incorporation of the oxidised CNF between the growing zinc crystals in the deposit. The differences in the size and compactness of the Zn grain structure show that the oxidised CNFs alter the growth process. Nucleation in the presence of the CNFs is slower leading to the larger grains evident in the SEM, Fig. 6.15. The CNF fragments appear to modify the substrate surface causing the reduced rate of nucleation.

**Figure 6.15.** Zinc electrodeposited on mild steel from the alkaline zincate magnetically stirred bath (0.12 M ZnO, 2.6 M NaOH, pH 14) but with the addition of 1 g/L of oxidised CNF, 2 A dm\(^{-2}\) for 30 min; (a) high magnification, (b) lower magnification.

A comparison between Figs. 6.9 and 6.13, which illustrate deposition from the alkaline zincate bath in the absence of CNF with vibratory and magnetic stirrer
agitation, respectively, under otherwise identical conditions, can be made. In the case of vibratory agitation a relatively compact, dense deposit was obtained compared to the low density, platelet growth observed for the magnetically stirred bath. In both cases, increasing the current density led to less efficient deposition, which is illustrated by reduced deposit thickness.

On the addition of CNFs to either vibratory agitated or magnetically stirred solution, the CNFs are evident agglomerated on the surface of quite similar zinc deposits, with the possibility that the CNFs are incorporated at the grain boundaries with continued deposit growth, Figs. 6.11 and 6.15.

6.4. Electrodeposition of Zinc and Zinc/Carbon Nanofibre Composites from Acidic Solution

The behaviour of the acid Zn electrodeposition bath at mild steel and glassy carbon electrodes was also studied, Fig. 6.16. Initially, cyclic voltammograms were recorded to characterise the behaviour of the mild steel and glassy carbon electrodes immersed in acidic solution, 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, pH 2.

![Cyclic voltammograms](image)

Figure 6.16. Cyclic voltammograms recorded at (A) mild steel (0.28 cm²) and (B) glassy carbon (0.07 cm²) electrodes. 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, pH 2.
In the current work, for the acidic zinc electrodeposition bath, Zn oxidation and reduction occur at a much more positive potential (-1.05 V vs. SCE) than in the alkaline bath, Sec. 6.3. Mass transport control is absent for both electrodes (glassy carbon and mild steel) under the high concentration conditions used for Fig. 6.16. Fig. 6.16 (B) shows an overpotential for the nucleation of zinc onto glassy carbon, similar to that shown in Fig. 6.5. The overpotential exists since metal deposition is occurring at an inert glassy carbon cathode. This involves the formation of initial stable nuclei, with subsequent nucleation and growth, leading to the overlapping of the nuclei, eventually resulting in the growth of a complete layer. Thus, zinc deposition from acidic baths will also occur preferentially onto metal (non-carbon) surfaces. From the slope of the deposition and stripping responses in Fig. 6.16, it can also be seen that a characteristic resistance exists, associated with zinc electrodeposition onto carbon. It is believed that the poor electrical contact between zinc nuclei and the carbon surface is responsible. McBreen studied zinc deposition on glassy carbon from acid electrolyte and observed a similar effect to that already mentioned for zinc deposition from alkaline electrolyte, in terms of a crystallisation overpotential and the lack of interaction between the electrodeposited zinc and the glassy carbon [31].

Raeissi et al. have shown that, from an acidic zinc sulphate bath, in the potential range from -0.65 to -1.0 V the current density does not increase rapidly [19]. This potential range is predominantly associated with hydrogen evolution [32]. Zinc hydroxide is formed by hydrolysis due to the predominant hydrogen evolution and consequent local pH increase near the cathode surface [32, 33]. The zinc hydroxide acts as an inhibitor, limiting the number of deposition sites for hydrogen, giving an additional overvoltage for hydrogen evolution [32]. Eventually, hydrogen evolution is suppressed and zinc starts to deposit, Fig. 6.17.
Zinc deposition started at about -1.0 V after complete passivation of the cathode surface by zinc hydroxide. So, during zinc electrodeposition on a steel substrate the rate of hydrogen evolution is initially high leading to the rapid formation of a zinc hydroxide layer in the solution near the cathode. Subsequent zinc nucleation occurs with a high current efficiency and the resulting contribution of hydrogen evolution is minor.

Zinc electrodeposition is accompanied by a simultaneous hydrogen reduction reaction. The hydrogen evolution reaction and entry of hydrogen into iron and steels during zinc electrodeposition have been studied extensively because it may induce hydrogen embrittlement of the substrate, modify the mechanical properties of the material, and sometimes cause stress-corrosion cracking [30, 34, 35, 36]. In this work, at high current density, 5 A dm\(^{-2}\), gas evolution (hydrogen) was evident at the cathode during the electrodeposition process, causing the undesirable voids and bubble inclusion patterns, which can be seen in the FEGSEM image below, Fig. 6.18.
Figure 6.18. Surface FEGSEM of a Zn deposit formed on a mild steel substrate at 5 A dm$^{-2}$ for 12 min. 0.9 M ZnSO$_4$.7H$_2$O, 0.6 M Na$_2$SO$_4$, pH 2.

A higher magnification image is illustrated in Fig. 6.19 showing the grain structure of the deposit.

Figure 6.19. Higher magnification surface FEGSEM image of the sample in Fig. 6.18, 5 A dm$^{-2}$ for 12 min. 0.9 M ZnSO$_4$.7H$_2$O, 0.6 M Na$_2$SO$_4$, pH 2.

Similarly, Wiart et al. observed numerous holes of different sizes, corresponding to the formation of hydrogen bubbles in electrodeposits formed from an acidic zinc sulphate electrolyte at a current density of 5 A dm$^{-2}$ [37].

6.4.1. Electrodeposition of Zn/Carbon Nanofibre Composite from a PPh$_4^{+}$ Containing Solution

As mentioned earlier, Sec. 6.2.4, tetraphenylphosphonium bromide (PPh$_4$Br) was used as a cationic surfactant to aid the formation of a suspension of as-grown CNFs by the presumed adsorption of the aromatic cation onto the carbon nanofibre walls. Infrared
and mass spectroscopies could be applied to assess the adsorption process. The hydrophobic phenyl rings associate with the hydrophobic CNF structure and the cationic nature of the PPh₄⁺ promotes deposition at the steel electrode (cathode). In this way the laborious CNF oxidation procedure can be avoided with the direct use of the as-grown uncharged CNFs.

The following images were obtained on samples following the addition of the CNFs and PPh₄⁺ to the acidic solution, at 2 and 4 A dm⁻², Figs. 6.20 and 6.21, respectively, both utilising vibratory agitation.

![Figure 6.20. Surface FEGSEMs of the electrodeposited Zn deposit formed on mild steel from ZnSO₄·7H₂O/CNF/PPh₄⁺ solution, 2 A dm⁻², 60 min, vibratory agitation. [8.1, Tab. 6.1]](image)

These surface images show the incorporation of CNF in the growing Zn deposit, Fig. 6.20, 2 A dm⁻², 60 min. In Fig. 6.20 (a) a raised “nodular” area can be identified where CNF incorporation is evident; no CNF are evident in the background area “base layer”. Part (b) of Fig. 6.20 shows another area of nodular growth with further CNF incorporation. The following images, which demonstrate a deposit similar to that shown above, were obtained at a higher current density, 4 A dm⁻², 30 min, Fig. 6.21. Figs. 6.20 (a) and (b) and 6.21 (b) and (c) show comparable FEGSEM images in terms of zinc crystal size and CNF inclusion.
Figure 6.21. FEGSEM images of the electrodeposit formed on mild steel from ZnSO$_4$.7H$_2$O/CNF/PPh$_4^+$ solution, 4 A dm$^2$, 30 min, vibratory agitation, (a) cross section, (b) surface, (c) surface - higher magnification. [8.2, Tab. 6.1]

Fig. 6.21 (a) clearly illustrates one of the major problems encountered during this work (though also evident in Fig. 6.20), the presence of a base layer plus a surface, nodular type, growth. While CNFs are obviously incorporated, the inclusions exist as large aggregates; the nodular areas shown in cross section in (a) correspond to the areas in the foreground of (b) showing CNF intertwined with the zinc crystals. Fig. 6.21 (a) shows a cross section of the coating deposited from the acid electrolyte, with a surface layer of Zn (apparent when compared to the surface image in (b)) with aggregates (of CNF) forming nodular growths with the metal. The higher magnification image shown in Fig. 6.21 (c) shows more clearly the lack of CNF in the base, metal, layer. This problem was also encountered earlier with copper, Chap. 5.

The next three images show micrographs obtained for electrodeposits from the acid bath with magnetic stirrer agitation, Figs. 6.22 – 6.24.
Again, there is evidence for the incorporation of CNFs with the growing Zn crystals, 2 A dm\(^{-2}\), Fig. 6.22. Under similar conditions, but at higher current density, 4 A dm\(^{-2}\), a comparable deposit is formed and again the image on the right hand side shows a base layer with nodular growth, Fig. 6.23.

The behaviour for both vibratory and magnetic stirrer agitation appears to be similar. The incorporation observed by FEGSEM imaging would seem to be independent of the method of solution agitation, though an elemental analysis of the constituents was not achieved.

In order to determine if the presence of the CNFs affected the deposit morphology, the above experiment was also conducted in the absence of CNFs, 4 A dm\(^{-2}\) and 30 min, Fig. 6.24.
When compared to Fig. 6.23, it clearly illustrates the effect of the CNFs or the PPh₄⁺ on deposit morphology. The nodular deposit shown in Fig. 6.23 is in stark contrast to the Zn deposit formed on steel in the absence of CNFs showing a nodule free compact deposit with hexagonal stacking platelets.

In addition to the FEGSEM analysis used to investigate the composite coatings other techniques were also investigated. These were energy dispersive X-ray analysis (EDX) and Auger electron spectroscopy (AES). Both EDX and AES can provide chemical compositional analysis of the deposits. The techniques were introduced earlier, in Chap. 1, and the data obtained will be discussed as it arises in subsequent sections.

6.4.2. Energy Dispersive X-Ray (EDX) Analysis
EDX (discussed in Chap. 1) was used to give elemental analysis of the Zn/CNF composite coatings produced. It was used to compare the alkaline zincate, Sec. 6.3, and acid sulphate baths, and also for the comparison of the two agitation methods, vibratory and magnetic stirrer agitation. Details of the baths and electrodeposition conditions used to prepare the samples for EDX analysis are given in Table 6.1. The first two samples are from the alkaline bath and the remainder are from the acidic zinc bath.
Table 6.1. Baths and electrodeposition conditions used, and results obtained for the samples analysed by EDX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bath</th>
<th>Conditions</th>
<th>Agitation</th>
<th>wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Fig.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>6.11</td>
<td>ZnO/ox. CNF</td>
<td>2 A/dm$^2$</td>
<td>Vib 180</td>
</tr>
<tr>
<td>7.2</td>
<td>6.12</td>
<td>ZnO/ox. CNF</td>
<td>4 A/dm$^2$</td>
<td>Vib. 180</td>
</tr>
<tr>
<td>8.1</td>
<td>6.20</td>
<td>ZnSO$_4$/CNF/PPh$_4^+$</td>
<td>2 A/dm$^2$</td>
<td>Vib 180</td>
</tr>
<tr>
<td>8.2</td>
<td>6.21</td>
<td>ZnSO$_4$/CNF/PPh$_4^+$</td>
<td>4 A/dm$^2$</td>
<td>Vib. 180</td>
</tr>
<tr>
<td>10.1</td>
<td>6.22</td>
<td>ZnSO$_4$/CNF/PPh$_4^+$</td>
<td>2 A/dm$^2$</td>
<td>stir</td>
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<tr>
<td>10.2</td>
<td>6.23</td>
<td>ZnSO$_4$/CNF/PPh$_4^+$</td>
<td>4 A/dm$^2$</td>
<td>stir</td>
</tr>
</tbody>
</table>

ZnO is the alkaline zincate electrolyte, ZnSO$_4$ is the acidic zinc sulphate electrolyte, ox. CNF are oxidised CNF, PPH$_4^+$ is the tetraphenyl phosphonium cation, vib. is vibratory agitation, and stir is magnetic stirrer agitation.

EDX can analyse to a depth of 1 - 2 µm so surface/adsorbed C may distort the values obtained. From the wt.-% of the C and Zn present, the acid bath appears to promote higher inclusion rates for the CNF compared to the alkaline bath. The elemental qualitative analysis was performed by the use of standardless analysis. Vibratory agitation seems to be a more effective agitation method than the magnetic stirrer; this may be due to the improved buoyancy of the particles in the solution with vibratory agitation [38]. Lower current and longer electrodeposition times seem preferable. The values obtained were localised rather than averaged. Therefore, they were treated with caution and were only taken as a roughly quantitative indication, in addition to the ease with which surface contamination can occur, the surface nature of the technique (1 - 2 µm), and the lack of uniformity between different areas within the samples, as has been illustrated readily by the FEGSEM images, appropriate references to the images given in Table 6.1.

6.5. Pulsed Electrodeposition of Zinc/Carbon Nanofibre Codeposits

As discussed in Chap. 1, pulse electrodeposition is a method of depositing metal on a substrate using interrupted direct current, DC. This method favours the initiation of grain nuclei and increases the number of grains per unit area, since each new cathodic pulse forces nucleation to occur. The result is a finer grained deposit with improved
properties, compared to conventionally electrodeposited coatings [39]. Periodic pulse reverse, i.e., having an anodic component to the cycle, removes metal preferentially from areas that tend to over-electrodeposit during the cathodic part of the cycle. Therefore, it is possible to considerably retard dendrite formation or to improve the electrodeposit thickness distribution over complicated shapes. Preliminary experiments have been conducted in both alkaline and acidic electrolytes. The waveform used for these initial experiments is shown in Fig. 6.25.

![Figure 6.25. Waveform consists of a cathodic current of 0.4 A for a duration $T_c = 2$ s; an off time with zero current for a duration $T_{off} = 1$ s; and an anodic current of -0.4 A for a duration $T_A = 0.5$ s.](image)

The net current density and electrodeposition times used were similar to those used to produce the direct current (DC) deposits.

The variations in the texture and morphology of DC and pulse current (PC) deposits were studied by Vasilakopoulos et al. [18]. They found that PC effectively modified the properties obtained over a limited range of conditions, though at high current densities PC resembled DC electrodeposition.

One of the methods adopted in an attempt to reduce shape change and dendritic growth in zinc-based secondary cells was pulse charging, including periodically reversing the current and multi-component pulse charging. This and other methods were reviewed by Bass et al. [9]. It was found that the application of a high current peak created a high surface overvoltage, thus activating a large number of nucleation sites. The subsequent rest period allows local zinc concentration gradients to relax by diffusion into the depleted diffusion layer. Thus, a more uniform deposit is obtained by electrodeposition from this replenished diffusion layer.
6.5.1. Pulsed Electrodeposition of Zinc in Alkaline Conditions

This sample was prepared from an alkaline zincate/CNF bath with vibratory agitation, Fig. 6.26. The pulse reverse waveform, detailed in Fig. 6.25, was applied. The net current applied was 4 A dm$^{-2}$ for 60 min. The FEGSEM shows the deposit formed, consisting of 20 μm crystals, Fig. 6.26.

![Figure 6.26](image)

Figure 6.26. FEGSEM images of a pulse electrodeposited sample on mild steel from alkaline zincate solution with vibratory agitation, 4 A dm$^{-2}$, 60 min.

At higher magnification, it can be seen that the CNFs are trapped at grain boundaries, Fig. 6.26. During the reverse part of the pulse the least coordinated zinc i.e., at kink and step locations in the growth, is removed but the carbon is likely to remain, and since the CNFs are negatively charged in this environment further CNFs may be attracted to the cathode, so that the forward pulse will aid CNF incorporation by entrapment. This deposit consists of larger crystals and is much denser than that obtained in the absence of the reverse pulse as can be seen by comparison with the next image, Fig. 6.27.
Looking at mounted and polished cross sectioned samples gave no further information, regarding the presence/absence of CNFs in the bulk of the deposit. In an attempt to obtain such information a sample was treated as above but, in addition, was etched. The aim of etching was to reveal the CNFs. A standard etching solution, 2 vol.-% nital, was used. It consists of 2 % HNO$_3$ in ethanol. The solution is non-aqueous to avoid sample corrosion. This should etch the metal content but leave the carbon intact. These cross sectional FEGSEM images demonstrate the effect of etching, Fig. 6.28.

It is obvious that a layer of Zn has been removed and it reveals the grain structure of the Zn but it did not expose the CNF. Once again, it provides further evidence for the problem of large nodular growths.
6.5.2. Pulsed Electrodeposition of Zinc in Acidic Conditions

Initial studies of the pulse electrodeposition of zinc from the acidic zinc bath were also carried out. The same pulsed waveform as previously detailed was used. The type of deposit formed can be seen in the FEGSEM images Fig. 6.29.

The CNFs are apparent in the surface image of the deposit (a) but in (b), the cross section, there are no CNFs evident after etching. Fig. 6.29 (c) illustrates that nodular type growths also occurred under these pulse plating conditions.

6.5.3. Auger Electron Spectroscopy (AES)

The principles of Auger Electron Spectroscopy (AES) were discussed previously, Chap. 1. Auger spectra were obtained for the sample in Fig. 6.29 (zinc/CNF electrodeposited onto mild steel from ZnSO$_4$.7H$_2$O/CNF/PPh$_4^+$ solution, 4 A dm$^{-2}$, 30 min, vibratory agitation); these are illustrated in Fig. 6.30.
An Auger spectrum plots a function of electron signal intensity vs. electron energy. A table of the electron energies of the relevant elements is given, Table 6.2. The peak areas are used to quantify the amount of a particular element present.

<table>
<thead>
<tr>
<th>Element</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>272</td>
</tr>
<tr>
<td>Zn</td>
<td>996, 1017</td>
</tr>
<tr>
<td>O</td>
<td>510</td>
</tr>
</tbody>
</table>

Table 6.2. Auger energies associated with the elements studied.

Depth profiling can only be carried out destructively and up to 1 nm depth of the surface can be analysed. Ion bombardment will not give a uniform erosion of the sample. As a consequence a light Ar$^+$ etch was performed on the sample with the aim of revealing whether the carbon present in the initial spectrum was due to contaminants or due to carbon in the composite. The values obtained are quantified using AES standards. The peak-to-peak height, $H_{pp}$, relates to the concentration and sensitivity as follows:
\[
\frac{H_{pp,Zn}}{H_{pp,C}} = \frac{c_{Zn} - s_{Zn}}{c_c - s_c}
\]  

(6.3)

where \(c_{Zn}\) and \(c_c\) are the concentration terms and \(s_{Zn}\) and \(s_c\) are the sensitivity factors for zinc (Zn) and carbon (C).

The following data were obtained after Ar\(^+\) etching, Table 6.3.

<table>
<thead>
<tr>
<th>Etch time (s)</th>
<th>C</th>
<th>O</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.8</td>
<td>42.7</td>
<td>47.4</td>
</tr>
<tr>
<td>10</td>
<td>3.5</td>
<td>14.3</td>
<td>82.3</td>
</tr>
<tr>
<td>30</td>
<td>3.6</td>
<td>7.1</td>
<td>89.3</td>
</tr>
</tbody>
</table>

Table 6.3. AES data: composition in atom %.

About 10 at.-% C was present at the 0 s measurement, with 43 % O and 47 % Zn. The 10 and 30 s etchings both gave a value for C of about 3.5 at.-%, the value seems to have become steady, suggesting that the 0 s reading did contain C from contaminants and also that a realistic value for C is 3.5 at.-% (the steel itself contains 0.02 wt.-% C). The value for Zn also remains reasonably steady for the 10 and 30 s readings though the value for O continues to drop, the oxygen may have been associated with both the carbon contaminants and the zinc in the form of zinc oxide.

6.6. Electrodeposition of Zn/Carbon Nanofibre Composites from Poly Acrylic Acid containing Electrolytes

As discussed in more detail in Chap. 1, Arai and Endo used composite electrodeposition techniques to produce carbon nanofibre/copper composites [40] in an attempt to develop a low temperature composite formation method. Films were electrodeposited from a Cu/sulphuric acid bath (containing the dispersant, PA (polyacrylic acid), and 2 g/L CNF). CNF/Cu powder composites were prepared by electrodeposition from the same bath as detailed above. The resulting composite could easily be separated from the electrode by ultrasonication to give a powdered CNF/Cu composite [41]. The same workers also electrodeposited Ni-deposited MWNT. Once again poly acrylic acid was used to disperse the MWNT in the plating bath [42].
In the context of this work, PAA ($\text{pK}_a 4.25$) was chosen as a dispersant for CNF in the acidic zinc electrodeposition solution. It has a hydrophobic backbone, which interacts with the hydrophobic as grown CNF structure and hydrophilic carboxylic acid groups, which allow for its suspension in aqueous electrolyte. It proved to be very successful for the suspension of the CNF in the electrolyte resulting in the uniform dispersion of the CNF.

In addition to the effect of dispersing the CNFs other interactions are likely to occur. Poly acrylic acid, present in weak polyelectrolyte multilayers, has been used to produce metal nanoparticles [43]. Carboxylic acid groups in the multilayers bind metal cations by exchange with the acid protons. Subsequent reduction forms metallic nanoparticles. Poly acrylic acid has a pH-dependent degree of ionisation, the lower the pH the more non-ionised carboxylic acid groups are present, whose protons can exchange with metal cations. The interactions observed in Rubner's work [43, 44] may also have occurred in the present study, the low pH would have made numerous sites available for zinc cation exchange. Therefore, as well as aiding CNF dispersion, the poly acrylic acid may have had a more direct influence over the electrodeposition process through cation exchange with zinc. The rate of deposition could be reduced, since a zinc/PAA complex may be present and when the metal is reduced the associated PAA could block the electrode surface and slow further deposition, a complicated mechanism for deposition may exist in the presence of PAA. The cyclic voltammograms shown below verify that PAA does affect the deposition process, Figs. 6.31 and 6.32.

Cyclic voltammograms were recorded for the acidic zinc sulphate bath in the absence and presence of poly acrylic acid. In the case of zinc electrodeposition on mild steel in the absence of poly acrylic acid, Fig. 6.31 (A), a similar cyclic voltammogram was recorded to that observed in Fig. 6.16, and subsequently explained.

$$\text{ZnSO}_4\cdot7\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Zn} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \quad -0.799 \text{ V (SHE)}$$ (6.4)

A resistance effect is clearly seen during the deposition and stripping of the zinc metal and almost no overpotential for metal deposition is detected (deposition and stripping
start from the same potential value) Fig. 6.31 (A).

![Cyclic voltammograms](image)

**Figure 6.31.** Cyclic voltammograms recorded at a mild steel electrode, 0.2 cm$^2$, (A) reduction potential limit varied: - 1.2, - 1.25, - 1.3 V, (B) as (A) but with the addition of 2 x $10^{-5}$ M PAA, 0.9 M ZnSO$_4$·7H$_2$O, 0.6 M Na$_2$SO$_4$, pH 2, scan rate: 100 mV s$^{-1}$.

Slower kinetics were observed with the addition of poly acrylic acid, zinc electrodeposition did not begin until a potential of about -1.15 V vs. SCE was reached and a "potential gap" is observed between the deposition and stripping processes. The potential for deposition is shifted to a lower value. However, the magnitude of the current remained and therefore the rate of zinc deposition was not affected. The overpotential for zinc deposition and for zinc stripping can be understood as a kinetic effect possibly due to a film of poly acrylic acid and the zinc | aqueous solution interface and the cation exchange effect mentioned earlier [44].

Additional information about the effect of poly acrylic acid on the zinc deposition process was obtained for experiments at glassy carbon electrodes, Fig. 6.32. The CVs shows data recorded in the absence and in the presence of poly acrylic acid. The overpotential, relative to $E^0$, for deposition and stripping that exists in the absence of PAA (due to nucleation and deposition on the inert glassy carbon electrode) is not
very high and was discussed earlier, Fig. 6.16 (B). However, the “resistance effect” is substantial.

![Cyclic voltammograms recorded at a glassy carbon electrode, 0.07 cm², (A) reduction potential limit varied: - 1.2, - 1.25, - 1.3 V, (B) 2 x 10⁻⁵ M PAA added, scans 1 - 3 (initial 3 scans) shown. 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, pH 2, scan rate: 100 mV s⁻¹.](image)

Figure 6.32. Cyclic voltammograms recorded at a glassy carbon electrode, 0.07 cm², (A) reduction potential limit varied: - 1.2, - 1.25, - 1.3 V, (B) 2 x 10⁻⁵ M PAA added, scans 1 - 3 (initial 3 scans) shown. 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, pH 2, scan rate: 100 mV s⁻¹.

A dramatic change is observed in the presence of poly acrylic acid, Fig. 6.32 (B). The separation between the deposition and stripping processes is much wider and currents are an order of magnitude smaller. At carbon electrodes, poly acrylic acid almost completely suppresses the formation of zinc deposits. The current increase with each scan shows that although Zn deposition is inhibited in the presence of PAA, zinc nuclei remain on the surface of the electrode and more deposition occurs with each cycle. The implications from these experiments are (i) PAA slows down the deposition of zinc onto steel and (ii) PAA strongly inhibits the deposition of zinc onto carbon.

The reason for this dramatic difference can be seen in the way the zinc metal interacts with the substrate. For metal on steel deposition, good contact between the nuclei and the substrate is achieved and growth continues. For the deposition of zinc onto carbon nuclei show poor electrical contact to the substrate due to the presence of PAA and electrical resistance suppresses further growth. This also explains the peak shape of voltammograms in Figure 6.32 (B). A very similar effect was described for the electrical contact between carbon nanofibres and an ITO substrate in the presence of
chitosan polyelectrolyte (Chap. 3). Overall, the growth of zinc onto steel is not strongly inhibited in the presence of poly acrylic acid but its growth directly onto carbon nanofibres seems unlikely under these conditions.

The cross sectional FEGSEM image below, Fig. 6.33, shows the Zn/CNF composite formed on the addition of PAA to the acidic ZnSO₄ electrodeposition bath. A nodule free deposit was formed.

![Figure 6.33](image)

**Figure 6.33.** Cross sectional FEGSEM image of the Zn/CNF composite formed on mild steel from 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, 2 x 10⁻⁵ M PAA, 2 A dm⁻², 180 min, magnetically stirred solution, (a) low magnification, (b) high magnification.

Fig. 6.33 (a) clearly shows the nodule free Zn/CNF composite electrodeposit formed with the higher magnification image, Fig. 6.33 (b), illustrating its relatively uniform and compact nature.

![Figure 6.34](image)

**Figure 6.34.** Cross sectional FEGSEM image of the Zn/CNF composite formed on mild steel from 0.9 M ZnSO₄·7H₂O, 0.6 M Na₂SO₄, 2 x 10⁻⁵ M PAA, 2 A dm⁻², 180 min, magnetically stirred solution, (A) highlighting a Zn platelet area and (B) a “carbon rich” area.
Distinct areas were identified in the deposits formed from the acidic zinc sulphate solution containing poly acrylic acid. The above high magnification image demonstrates the individual areas seen, Fig. 6.34 (A) and (B). These two areas, (A) highlighting a Zn platelet area and (B) a “carbon rich” area, were again analysed using EDX spectroscopy. The spectra recorded are shown in the next two images, Figs. 6.35 and 6.36.

![Figure 6.35. EDX spectrum of (A) a Zn platelet area, as highlighted in Fig. 6.34.](image)

The spectrum for the Zn platelet area, Fig. 6.35, shows the presence of zinc with nothing identifiable in the carbon region except normal background noise.

In the case of the “carbon rich” area, identified in Fig. 6.34, the EDX spectrum shows a distinct carbon peak as well as the zinc peak, Fig. 6.36. The oxygen peak, which is also apparent, may be due to the presence of ZnO.

![Figure 6.36. EDX spectrum of (B) a “carbon rich” area, as highlighted in Fig 6.34.](image)

Individual carbon nanofibres were also identified, as shown in the high magnification FEGSEM images in Figs. 6.37 and 6.38. The Zn/CNF association is very apparent,
especially when compared to earlier images of previous composites formed, e.g., Fig. 6.20.

![Figure 6.37. High magnification FEGSEM image showing incorporated CNFs.](image)

In order to confirm the presence of carbon, an EDX spectrum of the individual fibre highlighted in Fig. 6.38 was recorded and is shown on the right hand side of the figure.

![Figure 6.38. FEGSEM highlighting an individual CNF and an EDX spectrum of the CNF.](image)

Once again, from the EDX spectrum, the presence of carbon is apparent, together with zinc from adjacent areas.

Overall, on addition of poly acrylic acid to the electrodeposition solution, a much improved composite deposit is achieved when compared to the composites described earlier. This is supported by the FEGSEM and EDX data provided.
6.7. Conclusions

A number of Zn/CNF composite coatings were produced from both alkaline and acidic baths and in the case of the acidic bath two different additives (PPh₄⁺ and PAA) were also investigated. The presence of CNF was confirmed with EDX, AES, and FEGSEM analysis.

On the addition of CNFs to either vibratory agitated or magnetically stirred alkaline solution, the CNFs are evident agglomerated on the surface of morphologically quite similar zinc deposits, as shown by FEGSEM analysis. The behaviour for both vibratory and magnetic stirrer agitation is also similar for the acidic zinc sulphate/CNF/PPh₄⁺ bath. The fibre incorporation observed by FEGSEM imaging, showed nodular growth on a smoother base layer of zinc. This morphology seemed to be independent of the method of solution agitation. Pulse electrodeposition also led to nodular type deposits. In the case of the acidic zinc sulphate solution, with the addition of PAA as a CNF dispersant, clear evidence was provided by FEGSEM analysis for the incorporation of CNFs into a uniform compact deposit.

AES analysis, conducted in the case of the acidic zinc sulphate/CNF/PPh₄⁺ bath, confirmed, by depth profiling, the presence of carbon in the deposit.

A comparison was made between the alkaline zincate bath and the acidic zinc sulphate baths by EDX in terms of solution agitation and current density. The acidic bath appeared to promote a higher inclusion rate of CNF compared to the alkaline zincate bath. In addition, the vibratory agitation seemed to be a more effective agitation method than magnetic stirring, due to the increased buoyancy of the CNF and therefore increased opportunity for incorporation. Although in each experimental run the charge passed is constant, the conditions of electrodeposition with lower current density consistently gave a higher percentage of carbon inclusion. EDX was also used to confirm the composition of the zinc/CNF composites electrodeposited from the acidic zinc sulphate, PAA-containing, bath.

Improvements in the processes were observed, which meant the properties of the composites formed varied from agglomerated CNF present at the electrodeposited
zinc surface to nodular growths, where CNF were thought to have incorporated but not uniformly, to the highest quality deposits produced, which were nodule free and compact and where the CNFs were well incorporated and distributed. These observations are backed up by the physical appearance of the electrolytes with the CNF added, the best deposits were obtained with the most disperse solution.

Further investigations are necessary to discover the properties of the zinc/CNF deposits formed, wear and hardness testing, corrosion resistance, and where improvements could be made in the process. Pulse electrodeposition investigations of the PAA containing bath could be prepared for comparison. The principles developed here could also be adapted to establish the viability of a Sn and/or Cu CNF electrodeposition system, the resulting composites potential could then be investigated with a view to future use in bearing overlay materials.
References


7. Conclusions/Summary

The primary aims of the work undertaken for this thesis were to explore and exploit the unique properties of carbon nanofibre materials in novel electrochemical and electrodeposition processes.

The focus of the research concerned four key areas: (i) the examination and optimisation of the conditions for carbon nanofibre (CNF) growth, both unsupported and as films on substrates, (ii) the electrochemical characterisation of the CNF material before (as-grown) and after solubilisation (oxidation), (iii) the electrochemical characterisation and chemical analysis of (co-) deposited CNFs and (iv) the formation of novel CNF/metal composite coating materials by electrodeposition.

CNFs were grown at an iron nanoparticle catalyst produced from an iron oxide precursor, following process optimisation. The CNFs were characterised by surface and bulk analysis techniques including electron microscopy, spectroscopy, and electrochemistry. When grown onto a ceramic substrate, the 'as-grown' CNFs were shown to act as a porous, high surface area electrode with the ability to strongly adsorb aromatic molecules, such as hydroquinone, benzoquinone, and phenol. The strong adsorption of aromatic compounds onto the surface of the CNF composite electrode could be of potential importance for future applications in electroanalysis. In the presence of ultrasonic agitation, this type of electrode allowed unusually high current densities to be achieved. Interestingly, it was also shown that a colloidal redox system (colloidal iron oxide) was trapped within the CNF structure, and underwent highly efficient redox processes. This was the first reported observation of the reduction of a large colloidal species.

After the oxidation of the CNFs in concentrated nitric acid, there was clear evidence from XPS and electron microscopy that a high surface coverage of oxygen functionalities (carboxylic acid and quinone) was achieved, and that the fibres were broken into smaller fragments. These oxidised fragments were soluble in alkaline aqueous solution. Deposition onto inert carrier electrodes and immersion into acidic aqueous electrolyte allowed a new electrochemical signal to be detected, consistent
with a surface bound quinone. Layer-by-layer deposition of the solubilised CNF material with chitosan (a natural poly-cationic ionomer) allowed novel carbon structures to be grown and used as electrodes. Electrochemical processes such as the oxidation of hydroquinone, which occurs with a substantial overpotential at a bare ITO electrode, proceeded with a very high rate of electron transfer and essentially reversibly. However, current flow was limited by the ohmic carbon/substrate contact.

Novel Composite CNF sol-gel film modified ITO electrodes were also formed and were shown to give well defined highly efficient voltammetric signals. The high surface area of the CNFs led to the formation of an extended electrode | tBuFc | electrolyte triple phase junction. The CNFs created an extended hydrophobic interface; without CNF the tBuFc⁺ was expelled. The presence of the CNF stabilised the voltammetric response for the oxidation of tBuFc during continuous potential cycling. The hydrophobic CNF/silica film enhanced both the capacitive background and the magnitude of the Faradaic current response. It was also shown that heterogeneously structured bulk modified electrodes, based on a carbon particle/hydrophobic silica composite, can be used as a support for electroactive ionic liquids.

Electrodeposition was used to form unusual CNF/metal composites, in this particular case with the industrially important metals, zinc and copper. The electrochemistry of the plating baths was explored in detail. Conventional and pulse plating methods were investigated under various conditions of agitation, current density, and time with the aim of determining the optimum conditions for CNF inclusion.

Both the as-grown and oxidised forms of the CNFs were used in the plating baths. The as-grown fibres were hydrophobic and were used with additives, e.g., PAA and PPh₄Br, to improve their dispersibility in aqueous solution. The oxidised fibres were hydrophilic and formed a very stable suspension in alkaline electrolyte and a less stable one in acidic electrolyte. Various plating baths were investigated; acid copper, alkaline zinicate, and acidic zinc sulphate.

The composite deposits formed from the various baths were analysed using the quartz crystal microbalance (QCM), field emission gun scanning electron microscopy
(FEGSEM), energy dispersive analysis of X-rays (EDX), and Auger electron spectroscopy (AES) techniques. The QCM was applied in a novel manner as a probe for the detection of the inclusion of CNFs in the copper co-deposits in experiments involving both oxidised and as-grown CNF materials. This resulted in the proof of principle for the application of the QCM in the determination of the CNF inclusion level. However, further experiments are required to optimise the QCM approach for quantification of the total amount of CNFs in the deposit.
8. Publications


