Surface Modified Electrodes

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1 Introduction

In 1975 Murray and co-workers[1] introduced the term 'chemically modified electrodes' to describe electrodes that had foreign molecules deliberately immobilized on their surfaces. Research on such modified electrodes has been expanding rapidly in the past few years and these modifications are now being performed by adsorption as well as by chemical or covalent bonding. It therefore seems that a more generally appropriate term for such electrodes is 'surface modified electrodes'. This will be used in the present review.

Research on surface modified electrodes has involved studies of the electrochemistry of the attached molecules, the catalysis and inhibition of various electrochemical processes, and specific applications to such widely varying areas as photoelectrodes and analytical determinations.

A brief review of this field has appeared recently.[2] The present review covers the early work, the types of modification methods that have been used, and the results obtained in their applications. It also discusses possibilities for future study and applications.

2 Early Work

Lane and Hubbard[3,4] were among the first to study in detail electrode reactions at a metallic surface which had been deliberately coated with an organic substance. Taking advantage of the strong absorption of olefinic compounds on platinum,[5] they formed such coated electrodes by simply soaking the platinum in a dilute solution of the organic compound. By using olefinic molecules with different terminal groups, a variety of surface functional groups was obtained. They concluded from measurements of surface coverage that loss of π-bonds and formation of Pt—C σ-bonds had occurred.

The adsorbed molecules were found to have pronounced effects on electrochemical reactions at the metal surface. By varying the electrode potential, the tendency of an ionic substituent to chelate with metal ions in solution could be changed.[3] The rate of electron transfer reactions between the metal surface and ionic complexes in solution was found to be increased by an ionic olefin of the opposite charge on the surface, and decreased by an ionic olefin of the same

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[1] P. R. Moses, L. Wier, and R. W. Murray, *Anal. Chem.*, 1975, **47**, 1882.
[2] W. R. Heinemann and P. T. Kissinger, *Anal. Chem.*, 1978, **50**, 166R.
[3] R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, 1973, **77**, 1401 and references therein.
[4] R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, 1973, **77**, 1411.
[5] 'Electrosorption', ed. E. Gileadi, Plenum Press, New York, 1967.

charge on the surface.[4] This presumably occurred due to the effect of the ionic olefin charge on the ion distribution in the double layer. Variations in the orientation of adsorbed molecules perpendicular to the surface was found in some cases to inhibit normal reversible redox behaviour.[3] Equations to describe these kinetic and electrochemical results were also derived.

In other early work on surface modified electrodes, Miller and co-workers[6] were able to attach optically active amino-acids to a graphite surface. A standard procedure used in organic chemistry to derivatize carboxylic acids was employed. Surface acid-groups were formed on a graphite electrode by air oxidation and these were treated with $SOCl_2$. The resulting acid chlorides were then allowed to react with (*S*)-(−)-phenylalanine methyl ester.

The modified electrode was called a 'chiral' electrode and was visually and electrochemically indistinguishable from an untreated electrode. However, this 'chiral' electrode could be used to produce optically active alcohols by the electrochemical reduction of ketones. Racemic mixtures resulted when an unmodified electrode was used.

Other early work on surface modified electrodes performed by Murray and co-workers[1] consisted of attaching a hydrolysis-sensitive trialkoxy or trichloro silane to a SnO_2 electrode by reaction with surface hydroxy-groups. Such a procedure had previously been used to modify chromatographic supports[7] and glass slides[8] for use in trace metal analysis. Murray's group was also the first to use *X*-ray photoelectron spectroscopy (XPS or ESCA) to study the modified surface. ESCA was able to provide evidence for the formation of a Si—O—Sn bond and to confirm the presence of the surface immobilized compound. The electrically insulating silane layer was extremely stable and able to influence the double layer charging currents for the electrode. This was discovered by observing the effects of changing the pH of the electrolytic solution. The silanized SnO_2 electrode underwent the same electrochemical reactions with solution species as did clean SnO_2. However, some loss of reversibility was observed with some species due, apparently, to a decrease in effective electrode area by the presence of the surface silane layer. A pyridino silane on the surface was able to complex Cr^{2+} from solution, suggesting that the chemistry of the bound compound was not significantly altered, and that further reactions with this surface species might be possible.

The interest in surface modified electrodes has increased rapidly in the past few years. Surface immobilized molecules have been found to influence chemical and electrochemical reactions and also to retain their chemical behaviour. It will be seen that these properties of surface modified electrodes have been exploited in many different ways to yield surprising and exciting results. The three early modification methods (adsorption, silanization, and graphite surface group reactions) have been extensively used since. In addition, many different techni-

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[6] B. F. Watkins, J. R. Behling, E. Kariv, and L. L. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 3549.

[7] K. F. Sugawara, H. H. Weetall, and G. D. Schucker, *Anal. Chem.*, 1974, **46**, 489.

[8] D. M. Hercules, L. E. Cox, S. Osinick, G. D. Nichols, and J. C. Carver, *Anal. Chem.*, 1973, **45**, 1973.

ques have been developed or adapted from other fields to allow the making of useful modified electrodes. These are discussed in the following sections.

3 General Methods of Preparation

A. Silanization.—The modification of surfaces with different types of silane compounds is possible due to the sensitivity of these reagents to water. The application of this procedure to electrodes was first demonstrated by Murray and co-workers.[1] Surface hydroxy-groups, formed by the action of atmospheric moisture or concentrated NaOH on surface oxides, react with trialkoxy or trichloro silanes to form one to three bonds with the electrode material. Studies have indicated an average of two surface bonds are formed.[9–11] Silane monolayers are usually formed under anhydrous conditions. However, if small amounts of water are present in the reaction, multilayers can form, presumably due to polymerization of the surface silanes. In a recent report,[12] Lenhard and Murray observed that these multilayers, although difficult to form consistently, gave rise to more nearly ideal cyclic voltammetric behaviour than monolayers. This may be due to a more flexible two-dimensional structure for the silane layer.

Successful silanizations have been carried out on SnO_2,[1,9,10,13–26] TiO_2,[10,15,18,21,27] Pt/PtO,[10,12,25,26,28–30] carbon,[19,31] RuO_2,[10,25,26,32] Al_2O_3,[11] 'DSA' (a mixture of Ta and Ir oxides),[33] In_2O_3,[22] Au,[30] and Si[34,35] and Ge[36]

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[9] V. S. Srinivasan and W. J. Lamb, *Anal. Chem.*, 1977, **49**, 1639.

[10] P. R. Moses, L. M. Wier, J. C. Lennox, H. O. Finklea, J. R. Lenhard, and R. W. Murray, *Anal. Chem.*, 1978, **50**, 576.

[11] A. F. Diaz, U. Uetzler, and E. Kay, *J. Amer. Chem. Soc.*, 1977, **99**, 6780.

[12] J. R. Lenhard and R. W. Murray, *J. Amer. Chem. Soc.*, 1978, **100**, 7870.

[13] M. Fujihira, T. Matsue, and T. Osa, *Chem. Letters*, 1976, 875.

[14] M. Fujihira, T. Matsue, and T. Osa, *Sov. Electrochem.* (*Engl. Transl.*), 1977, **13**, 1449.

[15] P. R. Moses and R. W. Murray, *J. Amer. Chem. Soc.*, 1976, **98**, 7435.

[16] A. Diaz, *J. Amer. Chem. Soc.*, 1977, **99**, 5838.

[17] R. J. Burt, G. J. Leigh, and C. J. Pickett, *J.C.S., Chem. Comm.*, 1976, 940.

[18] G. J. Leigh and C. J. Pickett, *J.C.S., Dalton Trans.*, 1977, **18**, 1797.

[19] D. F. Untereker, J. C. Lennox, L. M. Wier, P. R. Moses, and R. W. Murray, *J. Electroanal. Chem.*, 1977, **81**, 309.

[20] A. Diaz and K. K. Kanazawa, *J. Electroanal, Chem.*, 1978, **86**, 441.

[21] T. Osa and M. Fujihira, *Nature*, 1976, **264**, 349.

[22] N. R. Armstrong, A. W. C. Lin, M. Fujihira, and T. Kuwana, *Anal. Chem.*, 1976, **48**, 741.

[23] D. D. Hawn and N. R. Armstrong, *J. Phys. Chem.*, 1978, **82**, 1288.

[24] K. Itaya and A. J. Bard, *Anal. Chem.*, 1978, **50**, 1487.

[25] H. S. White and R. W. Murray, *Anal. Chem.*, 1979, **51**, 236.

[26] D. F. Smith, K. Willman, K. Kuo, and R. W. Murray, *J. Electroanal. Chem.*, 1979, **95**, 217.

[27] H. O. Finklea and R. W. Murray, *J. Phys. Chem.*, 1979, **83**, 353.

[28] J. R. Lenhard and R. W. Murray, *J. Electroanal. Chem.*, 1977, **78**, 195.

[29] M. S. Wrighton, R. G. Austin, A. B. Bocarsly, J. M. Bolts, D. Haas, K. D. Legg, L. Nadjo, and M. C. Palazzatto, *J. Electroanal. Chem.*, 1978, **87**, 429.

[30] M. S. Wrighton, M. C. Palazzatto, A. B. Bocarsly, J. M. Bolts, A B. Fischer, and L. Nadjo, *J. Amer. Chem. Soc.*, 1978, **100**, 7264.

[31] C. M. Elliott and R. W. Murray, *Anal. Chem.*, 1976, **48**, 1247.

[32] P. R. Moses and R. W. Murray, *J. Electroanal. Chem.*, 1977, **77**, 393.

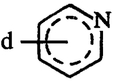
[33] B. E. Firth and L. L. Miller, *J. Amer. Chem. Soc.*, 1976, **98**, 8272.

[34] M. S. Wrighton. R. G. Austin, A. B. Bocarsly, J. M. Bolts, D. Haas, K. D. Legg, L. Nadjo, and M. C. Palazzatto, *J. Amer. Chem. Soc.*, 1978, **100**, 1602.

[35] I. Haller, *J. Amer. Chem. Soc.*, 1978, **100**, 8050.

[36] J. M. Bolts and M. S. Wrighton, *J. Amer. Chem. Soc.*, 1978, **100**, 5257.

semiconductor surfaces. Pretreatment of metal oxide surfaces with concentrated NaOH has sometimes been used to maximize surface hydroxy-groups. However, pretreatment procedures are not usually found to be necessary for coupling to occur.

By attaching silanes containing terminal functional groups (such as -NH_2, -CN, -SH, and ), reactions to further modify the surface with specific electroactive groups, using the electrically insulating silane as a linking chain, have been performed. The bound electroactive group is thought to be able to approach the electrode surface for electron transfer since the length of the silane compound could allow for 'floppiness' in the structure and therefore bending of the chain. As will be seen, this method of using the silane chain to bind species to electrode surfaces has been the major preparation route.

B. Adsorption.—Irreversible adsorption of compounds on electrode surfaces can be induced by an electrodic potential (electrosorption) or by the soaking of an electrode in a solution containing the species of interest. It is possible that some type of bonding is a factor in the adsorption process. Olefins on platinum are thought to form Pt—C bonds[3] and enzyme disulphide bonds may interact with a Hg electrode.[37] However, this technique is not considered to produce covalently modified surfaces.

The strength of adsorption is usually a function of the type of compound being adsorbed. Many organic compounds adsorb on graphite as a function of the number of aromatic rings they contain, with an increasingly stronger adsorption for an increasing number of aromatic rings.[38] Other reagents are absorbed only after they have been electrochemically reduced or oxidized or if a potential exists on the electrode, a process known as electrosorption. Regardless of how the adsorption occurs, the adsorbed layer usually exhibits characteristics similar to those observed if it had been attached through some type of covalent bonding. However, slow desorption has usually caused a loss of the modified surface.

Although it is not as widely utilized as silanization, adsorption is still an important preparation method. It is one that has been studied, not only in electrochemistry, but also in other areas prior to the interest in surface modified electrodes.

C. Polymer Coatings.—The methods used for modifying electrodes with polymers, such as substituted styrenes and polyvinyl ferrocenes, are primarily adsorption techniques. However, since several reports of polymer modified electrodes have appeared in the literature, the use of polymers is worthy of a

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[37] K. S. V. Santhanam, N. Jespersen, and A. J. Bard, *J. Amer. Chem. Soc.*, 1977, **99**, 274.
[38] A. P. Brown, C. Koval, and F. C. Anson, *J. Electroanal. Chem.*, 1976, **72**, 379.

separate treatment. Platinum has been the usual electrode material so far.[39-43] The use of SnO_2,[24] which was silanized prior to the attachment of the polymer, and of carbon,[39,44] has recently been reported.

The majority of electrodes were prepared by simple adsorption from a dilute solution of the polymer.[40,42-44] Electrochemical anodic deposition,[41] where the oxidized form of the polymer electrosorbs on the electrode, and glow-discharge polymerization[39] methods have also been utilized. All of these methods yield quite stable surfaces which have produced some interesting electrochemical results. These results are reviewed in a later section.

D. Carbon Surface Reactions.—The discussion of the preparation of covalently modified carbon surfaces has been divided into three separate schemes. One involves the use of surface oxide functional groups, the second involves oxide-free surfaces, and the third is the silanization method, which has been discussed previously. The first successful modification by Miller and co-workers[6] involved treating surface carboxylic acid groups (generated by air oxidation at 160 °C) with $SOCl_2$ to form easily derivatized acid chlorides. This is the most common route now used for modified carbon electrodes,[45-51] although direct derivatization of the acids[46,52,53] using dicyclohexylcarbodi-imide (DCC) as a dehydrating agent[54] has also been successful. The acid groups have generally been treated with amine-containing compounds, forming amide bonds which show good stability on the surface. Coupling with surface quinone structures[31] and surface hydroxyls[55,56] has also resulted in stable surface modified electrodes.

The concentration of surface oxide functional groups has been increased by several techniques, including air or chemical oxidation, anodization and radio-frequency oxygen-plasma treatment. Varying amounts of different functional groups can be selectively produced in this manner. Treatment of oxidized surfaces with $LiAlH_4$ reduces a large percentage of the functional groups to hydroxyls.

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[39] K. Doblhofer, D. Nölte, and J. Ulstrup, *Ber. Bunsengesellschaft Phys. Chem.*, 1978, **82**, 403.

[40] L. L. Miller and M. R. Van De Mark, *J. Amer. Chem. Soc.*, 1978, **100**, 639.

[41] A. Merz and A. J. Bard, *J. Amer. Chem. Soc.*, 1978, **100**, 3222.

[42] M. R. Van De Mark and L. L. Miller, *J. Amer. Chem. Soc.*, 1978, **100**, 3223.

[43] L. L. Miller and M. R. Van De Mark, *J. Electroanal. Chem.*, 1978, **88**, 437.

[44] N. Oyama and F. C. Anson, *J. Amer. Chem. Soc.*, 1979, **101**, 739.

[45] C. A. Koval and F. C. Anson, *Anal. Chem.*, 1978, **50**, 223.

[46] M. Fujihira, A. Tamura, and T. Osa, *Chem. Letters*, 1977, 361.

[47] M. Sharp, *Electrochim. Acta*, 1978, **23**, 287.

[48] B. E. Firth, L. L. Miller, M. Mitani, T. Rogers, J. Lennox, and R. W. Murray, *J. Amer. Chem. Soc.*, 1976, **98**, 8271.

[49] J. C. Lennox and R. W. Murray, *J. Amer. Chem. Soc.*, 1978, **100**, 3710.

[50] J. C. Lennox and R. W. Murray, *J. Electroanal. Chem.*, 1977, **78**, 395.

[51] L. Horner and W. Brich, *Justus Liebigs Ann. Chem.*, 1978, 1354.

[52] J. F. Evans and T. Kuwana, *Anal. Chem.*, 1977, **49**, 1632.

[53] J. F. Evans, T. Kuwana, M. T. Henne, and G. P. Royer, *J. Electroanal. Chem.*, 1977, **80**, 409.

[54] N. F. Albertson, *Organic Reactions*, 1962, **12**, 205.

[55] A. M. Yacynych and T. Kuwana, *Anal. Chem.*, 1978, **50**, 640.

[56] M. F. Dautartas, J. F. Evans, and T. Kuwana, *Anal. Chem.*, 1979, **51**, 104.

Oxide-free surface modifications involve reactions with surface carbon atoms. Vacuum pyrolysis of graphite has produced oxide-free surfaces which have then undergone reaction with the π-bond of acrylyl chloride,[57] forming an immobilized acid chloride group. Mechanical abrasion of glassy carbon under a nitrogen atmosphere apparently generates an oxide-free surface which was capable of undergoing further reactions.[58] Radio-frequency argon-plasma treatments have reduced the oxide concentration, allowing the bonding of ammonia or diethylenetriamine to the surface to serve as new functional groups capable of further derivatization.[59,60] Both of these results indicate that desired functional groups can be introduced on the electrode surface which otherwise might not be present, thereby making more modification routes available.

The same reactions that are used in normal organic syntheses appear to be useful for carbon surface modifications. Thus, the attachment of many different types of compounds has been accomplished. Although silanization is the most commonly used technique, the derivatization of the surface functional groups on carbon electrodes is a frequently utilized route for obtaining surface modified electrodes.

4 Specific Surface Modifications

A. **Covalently Bonded Surfaces.**—As was previously mentioned, the use of a silane chain to modify a surface and to attach specific electroactive centres is by far the most common route for preparing surface modified electrodes. Since the introduction of this method by Murray and co-workers[1], who modified SnO_2 surfaces, it has been found to work equally well for many other electrode surfaces.

There are probably three reasons for this wide usage. One is that, since the chain is electrically insulating, no electrochemical interference from the silane layer is observed. Second, the layer appears to be 'porous' enough to allow the diffusion of species to the electrode surface so that electron transfers may occur. The third reason is that silanes of sufficient molecular chain length can be selected that could allow for good chain flexibility and presumably permit attached electroactive centres to approach the surface within distances short enough for electrochemical processes to occur. (Silane monolayers have chain lengths[10] of $\sim$0.9—1.2 nm) This flexing of the chain has been suggested as a factor in the efficiency of electron transport at the surface.[10,23] However, the length of the chain may not rule out the possible occurrence of long-range electron transfers similar to those observed for molecular rectifiers.[61]

Since their first report on silanized SnO_2 electrodes,[1] Murray and co-workers have further demonstrated that the immobilized molecules appear to retain their

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[57] S. Mazur, T. Matusinovic, and K. Cammann, *J. Amer. Chem. Soc.*, 1977, **99**, 3888.

[58] R. Nowak, F. A. Schulto, M. Umaña, H. Abruña, and R. W. Murray, *J. Electroanal. Chem.*, 1978, **94**, 219.

[59] N. Oyama and F. C. Anson, *J. Electroanal. Chem.*, 1978, **88**, 289.

[60] N. Oyama, A. P. Brown, and F. C. Anson, *J. Electroanal. Chem.*, 1978, **87**, 435.

[61] D. G. Davis and M. A. Ratner, *Chem. Phys. Letters*, 1974, **29**, 277.

chemical behaviour. ESCA was able to detect that amino and pyridino silanes on SnO_2[1] and carbon[31] were capable of undergoing protonation in acidic media. Pyridino silanes on SnO_2 and TiO_2 have also been successfully methylated with methyl iodide.[15] This surface complex was verified by ESCA and by its electroreducibility in cyclic voltammetric scans. Chelation of Cu^{2+} by a covalently bound 3-(2-aminoethylamino)propylsilane (ethylenediaminosilane) has also been observed.[31]

The attachment of reversible electroactive centres has been another area of success. 3,5-Dinitrobenzamide structures have been bound to RuO_2[32] and PtO[28] surfaces by an amino silane, which readily undergoes amidization reactions. Both modified surfaces exhibited extremely good reversibility for the nitro groups in non-aqueous solvents, with the surface redox potentials very similar to those observed in solution. For the RuO_2 electrode, the modification was able to extend the anodic limit of the electrode, permitting electrochemical scans that were not possible with unmodified RuO_2 surfaces. Evidence that the Ru—O—Si and Pt—O—Si bonds remained intact after exhaustive cycling had resulted in the loss of the nitro groups was obtained from ESCA spectra. Wrighton and co-workers,[29] attached a ferroceno silane to platinum and observed similar results for stability of the surface bonding and reversibility of the bound electroactive centre. Haller[35] has bonded an amino silane to the oxide layer on silicon wafers. The terminal amine group remained reactive as it was able to undergo many different types of derivatizations.

By immobilizing redox centres on electrode surfaces, the study of these species can be greatly enhanced, since diffusion will not occur and no other interfering species need be present at the surface. Leigh and Pickett[18] were able to bond dinitrogen complexes of molybdenum and tungsten to SnO_2 by co-ordination with a cyano silane. They have also been succesful with the attachment of iron–sulphur clusters *via* a thiol silane.[17] These clusters exhibited good Fe^{2+}/Fe^{3+} reversibility. Due to this, their use as 'mediators' in electron transfer processes between the electrode and solution species appears quite possible.

Dansyl chloride was immobilized on metal oxide electrodes by reaction with a surface bound ethylenediamino silane.[25] The resulting sulphonamide was cleared from the surface by a KOH–ethanol solution, and fluorescent studies performed on the resultant solution allowed the calculation of the surface concentration of the sulphonamide. ESCA was also used to help determine the efficiency of coupling between the silane and dansyl chloride and the silane coverage.

Not all modification attempts have met with success. An interesting result was reported by Davis and Murray[62] when they attempted to bond iron porphyrins to silanized SnO_2, using an amidization procedure. Instead of forming amide linkages, the porphyrins were strongly adsorbed on the surface, and apparently catalysed the electrochemical reduction of the SnO_2 electrode.

Silane compounds have not been the only reagents used that are capable of being derivatized after bonding to the electrode surfaces. Although other im-

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[62] D. G. Davis and R. W. Murray, *Anal. Chem.*, 1977, **49**, 194.

mobilized chains have not been applied to widely different electrode materials, they too, have been found to provide good, stable attachments. Graphite has been the major, although not exclusive, electrode modified by these types of compounds.

Kuwana and co-workers[55,56,63] have prepared high concentrations of surface hydroxyls on graphite by radio-frequency oxygen-plasma treatments followed by $LiAlH_4$ reduction. These hydroxy-groups reacted readily with cyanuric chloride,[55,56,63] a linking species previously used to bind covalently enzymes to chromatographic supports. Cyanuric chloride was also found to react with surface hydroxyls of SnO_2 and In_2O_3 electrodes[63] where pretreatment with NaOH maximized the hydroxyl concentration.

Since cyanuric chloride also reacts easily with amines, hydrazines, and alkyl and aryl Grignard reagents, the unreacted chlorines on the surface bound molecule were capable of undergoing further modification. A hydroxymethylferrocene compound was attached to the electrode *via* the electroinactive cyanuric chloride.[56,63] The ferrocene group remained electroactive while thus immobilized. Similar results were obtained by using *o*-tolidine.[56] Its surface electrochemistry was found to be close to that observed in solution.

The use of surface bound 4-aminomethylpyridine to co-ordinate a pentammine ruthenium(II) complex has been reported by Koval and Anson.[45] The pyridine compound was attached *via* amidization of a $SOCl_2$-treated graphite electrode. This immobilization of the ruthenium(II) complex by the pyridino ligand was found to produce a more stable, or long-lived, electroactive surface, than that formed by adsorption of the complex.

The use of oxide-free graphite surfaces has attracted attention for immobilizing linking agents. After elimination of the oxygen groups, direct bonding with the surface carbon atoms is possible. Mazur and co-workers[57] discovered that acrylyl chloride apparently reacts with a graphite surface that has undergone high temperature vacuum pyrolysis by substitution across the double bond. The acid chloride functional group is then able to react with β-aminoanthraquinone, thus binding the quinone to the electrode. Studies of this modified electrode by first harmonic a.c. voltammetry, a more discriminating technique than cyclic voltammetry, showed that the surface quinones exhibited persistent redox voltammetric waves closely corresponding to those observed for the quinones in solution.

Oyama and Anson[59,60] have used radio-frequency argon-plasma treatments to reduce the oxide concentration on graphite, thereby allowing amines to anchor themselves to the surface. These amine groups are then able to be used as linking agents. A quinquedentate EDTA[59] or a pentammine[60] complex of ruthenium(II) was then immobilized on the graphite electrode by either an amidization reaction between the surface amine and the ligands of the complex ion or with nicotinic acid,[60] which then co-ordinated the complex. In the case of the EDTA complex, the bonding was *via* the free carboxylic acid group, and a

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[63] A. W. C. Lin, P. Yeh, A. M. Yacynych, and T. Kuwana, *J. Electroanal. Chem.*, 1978, **84**, 411.

solvent molecule occupied the sixth co-ordinate site. Ligand substitution in this sixth site was easily achieved after surface immobilization. The reversibility of the Ru^{2+}/Ru^{3+} couple was seen for both types of complexes.

The possibility of these surface species serving as useful catalysts has been suggested[59] because of the ease of electron transport between the electrode and the metal ion, because the anchoring covalent bond is isolated from the metal ion, and because ligand substitution in the complex, which can have an effect on the electrochemistry of the metal ion couple, is easily accomplished. Covalently attached catalysts on electrode surfaces would be quite useful, since they would allow a specific catalyst easily to be added to and removed from a reaction mixture.

Another technique that was used to obtain oxide-free glassy carbon surfaces and to carry out reactions with them has been reported.[58] Mechanical abrasion of the electrode in a puddle of vinyl pyridine under a nitrogen atmosphere produced a surface that was modified by the olefinic compound. This surface group was able to co-ordinate bis(2,2′-bipyridine)Ru^{II}, as evidenced from the succeeding electrochemical studies. Argon plasma treatments, followed by exposure to diethylenetriamine and co-ordination of the ruthenium(II) compound, produced similar electrochemical results but with more pronounced background currents.

Carbon electrodes have been the primary electrodes modified by methods that do not involve derivatizations of surface-bound molecules. Due to its many surface groups, the carbon electrode has lent itself quite well to direct attachments of the molecules of interest. Normal organic synthesis procedures can be used for these reactions. Direct modification of SnO_2 electrodes without the use of an immobilized chain has recently been reported[64,65] and is discussed in a later section of this review. All of the results below were obtained with carbon electrodes.

The earliest report of direct modification was the work of Elliot and Murray,[31] who formed an azo linkage to the electrode through the reaction of 2,4-dinitrophenylhydrazine with a surface quinone group. Although the irreversible cyclic voltammetric waves for the surface bound nitro groups were poorly resolved from the charging current, ESCA was able to detect their presence on the electrode.

The majority of these carbon surface modifications have involved the carboxylic functions, either in the acid or acid chloride form. These groups have then been treated with amine compounds, forming stable amide bonds. The attachment of benzidine[52] and alkyl amines[46] to graphite by the reaction with the acid groups has been reported. Evans and Kuwana[52] oxidized the carbon by radiofrequency oxygen-plasma treatment, while Fujihira and co-workers[46] used air oxidation techniques. ESCA provided evidence for the bonding in both cases, and voltammetric studies revealed the electroactivity of the molecules. Fujihira and co-workers were also able to achieve the same result using surface acid chloride groups.

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[64] T. Osa, N. Ohishi, and M. Fujihira, *Nature*, 1977, **268**, 226.

[65] M. Fujihira, T. Osa, D. Hursh, and T. Kuwana, *J. Electroanal. Chem.*, 1978, **88**, 285.

Lennox and Murray[49,50] have reported success in the attachment of amino porphyrins to carbon electrodes by the acid chlorides formed in the treatment of carbon electrodes with $SOCl_2$. Once again ESCA was used for evidence of the modification. The bound porphyrin exhibited poorly resolved reduction waves using cyclic voltammetry. Better results were obtained by differential pulse and a.c. voltammetry. Changes in the voltammetric waves upon metallation of the porphyrin with Co^{2+} were observed.

The use of linking agents is much more common than the use of this direct route, since the linking compounds allow the use of a greater variety of terminal functional groups than are possible to create on an electrode surface. However, this direct method can be used to eliminate an insulating chain (such as a silane chain) or to permit the electroactive centre to be bonded closer to the surface. This does not always produce better results, but studies of the stereochemical requirements of redox species and their electron transfer properties could conceivably be performed with more control this way than with a long, floppy chain. Uses of this method to prepare modified electrodes for specific applications are discussed later in this paper.

B. Adsorbed Coatings.—Since the early work of Lane and Hubbard,[3,4] who found that absorbed olefins on Pt were capable of undergoing chemical processes, studies of absorbed species on electrodes have produced results indicating that the molecules remain chemically and electrochemically active. Even though surfaces modified by absorption do not usually last as long as covalently modified ones, many interesting results have been obtained from these types of modifications.

Platinum and carbon have been the major electrode materials used for adsorption study. Recently a new type of electrode, polymeric sulphur nitride, $(SN)_x$, has also found use in these adsorption studies.

After their success with olefins, Lane and Hubbard[66] continued their work in adsorption by investigating how halides are adsorbed on platinum electrodes. Their results indicated that all halides adsorb in the anionic form, with the exception of I^-, which adsorbs as I. Its adsorption involves H_2O in order to produce the transformation. I^- adsorption on platinum is extremely strong, and this has allowed the use of I^- adsorption on a previously modified platinum electrode to determine the surface coverage of the modifying species.[43] The redox behaviour of platinum(II) and platinum(IV) complexes was not altered by the halide adsorption in Lane's and Hubbard's study.

As was stated earlier, aromatic compounds adsorb strongly on graphite electrodes. Anson *et al.* have adsorbed 9,10-phenanthrenequinone[38,67] and Fe^{II}-tetraphenyl porphyrins[38] on carbon electrodes. The strong, irreversible adsorption facilitated the use of slow cyclic and differential pulse voltammetry to study the stability of the adsorbed layer. They found that the electrochemical behaviour was influenced by changes in the pH of the solution, ligand concentrations, and other solution parameters, indicating that the adsorbed com-

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[66] R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, 1975, **79**, 808.
[67] A. P. Brown and F. C. Anson, *Anal. Chem.*, 1977, **49**, 1589.

pounds remained responsive to chemical changes. By adsorbing compounds containing varying numbers of aromatic rings, they determined that the strength of the adsorption increased with an increase in the number of aromatic rings. Compounds with only one ring showed very little irreversible adsorption.

The anchoring of the $Ru(NH_3)_5$[1-(9-phenanthrene)-2-(4-pyridine)-ethene]$^{2+}$ ion to graphite has been reported by Anson and co-workers.[45,68] This presumably occurs through the large aromatic structure in the ligand. The adsorption of this ion was found to be irreversible, but the layer was not as stable as that obtained by the co-ordination of a Ru^{2+} complex by a pyridino ligand covalently attached to a graphite surface.[45]

A modification of an adsorption method introduced by Davis[69] was used by Pool and Buck[70] to absorb a dinuclear ruthenium complex on glassy carbon. They allowed one to two microlitres of an acetonitrile solution containing the complex to evaporate on the electrode. This resulted in a surface film whose concentration was about ten times larger than a film obtained by dipping techniques. Measurements of the amount of charge transferred during the electrochemical studies indicated that all the ruthenium centres participated in electron transfer, and that the surface multilayer of ruthenium complex apparently offered little impediment to the transfer of electrons from the electrode.

The use of polymeric sulphur nitride, $(SN)_x$, as an electrode material has been demonstrated by Mark and co-workers.[61-63] This electrode, which is composed of fibre bundles, contains two types of crystal surfaces, and in this respect is similar to pyrolytic graphite (which contains basal plane and edge surfaces). $(SN)_x$ has one type of surface, designated as a 'parallel' surface, which seems to consist mostly of conjugated π-bonds, and a second surface perpendicular to the first, referred to as a 'perpendicular' surface.

Metal cations have been observed to adsorb strongly on and interact with the parallel surface,[71] Strong adsorption on perpendicular surfaces has also been detected.[71-73] Catalytic and inhibitory effects with this type of surface modified electrodes are presented in a later section of this review.

C. Polymer Coated Electrodes.—The modification of electrodes with polymeric films has recently been reported by many workers. The polymer layers have been formed by adsorption, electrosorption, glow-discharge polymerization, and covalently bound linkages. All of these methods have produced very electrochemically stable electrode surfaces. The electroactivity of the electrode material is usually not destroyed by these films, although some small hindrances of electron transfer have been noted. These polymer films have also been observed

[68] A. P. Brown and F. C. Anson, *J. Electroanal. Chem.*, 1977, **83**, 203.

[69] D. G. Davis, *J. Electroanal. Chem.*, 1977, **78**, 383.

[70] K. Pool and R. P. Buck, *J. Electroanal. Chem.*, 1979, **95**, 241.

[71] H. B. Mark, Jr., R. J. Novak, W. Kutner, J. F. Johnson, and A. G. MacDiarmid, *Bioelectrochem. Bioenerg.*, 1978, **5**, 215.

[72] A. N. Voulgaropoulos, R. J. Nowak, W. Kutner, and H. B. Mark, Jr., *J.C.S., Chem. Comm.*, 1978, 244.

[73] R. J. Nowak, W. Kutner, H. B. Mark, Jr. and A. G. MacDiarmid, *J. Electrochem. Soc.*, 1978, **125**, 232.

to retain their own chemical behaviour, such as catalytic properties, when immobilized on the surface.

Miller and Van De Mark[40,42,43] have reported the successful adsorption of polymers on platinum. This was accomplished by dipping the electrode into a dilute solution of the polymer. Poly-*p*-nitrostyrene, when adsorbed on platinum, exhibited reversible nitro voltammetric waves and was capable of reducing solution species when it was negatively charged.[42] The attachement of the 3,5-dinitrobenzoyl moiety to a polypeptide layer (60% lysine, 40% alanine) adsorbed on platinum was verified by ESCA.[40]

The platinum surface structure appeared to be unchanged by the polymer modification when analysed with a scanning electron microscope (SEM) of 5 nm resolution.[40,43] The polymer films were found to be about 2.5—3.0 nm thick. Analysis of the modified surfaces by ESCA and Auger electron spectroscopy yielded C, N, and O peak-intensity ratios corresponding to those predicted for the bulk polymer.[40,43] The films were stable even under oxidizing conditions.

Similar results were reported by Bard and co-workers, who electrosorbed polyvinyl ferrocene (PVF) on platinum[41] and poly(methacryl chloride) on platinum and SnO_2[24] electrodes by anodic deposition of the oxidized polymer. The latter polymer was also successfully linked to SnO_2 *via* a covalently bound amino silane, and was further modified by the attachment of hydroxymethylferrocene.[24] Good reversibility was observed for this ferrocene group during the electrochemical scans.

PVF exhibited easily reversible cyclic voltammetric waves after immobilization on platinum. It was also capable of electron transfer with a solution of 9,10-diphenylanthracene (DPA), although an instability in the film was noted when a large potential range was used for this reaction.

Experimental results indicated that the polymeric film may not have been uniform.[41] This was partially due to the presence of attenuated ESCA spectrum peaks from the underlying platinum. It is unlikely that platinum photoelectrons would be able to penetrate the film if its thickness, which was found to be approximately 21 nm, was uniform. A second observation was that DPA could be reduced by the modified electrode at a potential where the surface PVF itself was not reduced. Since it seems unlikely that electron transfer through the the film would occur under that condition, non-uniformity was again suggested.

Pyrolytic graphite basal planes were coated with polyvinylpyridine (PVP) and polyacrylonitrile (PAN) by Oyama and Anson.[44] Strong, rapid binding of $Ru^{III}EDTA$ and $Ru(NH_3)_5OH_2^{2+}$ by these surface polymers was observed. Surface concentrations of $Ru^{III}EDTA$ were about fifty times higher than that expected for a monolayer. A slight anodic shift in the surface redox potential from the solution potential was observed after immobilization of the complex, presumably due to symmetry and potential differences. A second, more anodic wave, appeared with time for the PVP/$Ru^{III}EDTA$ electrode when ruthenium(II) was maintained on the surface by the electrode potential. This second peak was believed to arise from electroactivity of Ru^{2+} while co-ordinated by two pyridine groups. This assignment was made because the potential compared closely to the observed redox potential for $Ru^{III}EDTA$ in solution in the presence of excess pyridine.

Glow-polymerization produces films containing a large number of electronic states. Doblhofer and co-workers[39] formed layers of polyacrylonitrile on platinum, carbon, and stainless steel electrodes using this method, and found that the ease of electron transfer through the film was directly dependent on the concentration of electronic states. These states are capable of being oxidized and reduced, thereby allowing an electron to hop through the film. Direct tunnelling is improbable due to the 10—100 nm thick polymer films. SEM observations showed the electrode surface structure to be essentially unchanged by the polymer modification at a resolution of 1.5 nm. The stable polymer layer was removed only by very strong oxidation on the electrode.

Extremely stable and concentrated polymeric films of vinyl ferrocene have been produced on glassy carbon and platinum electrodes by the introduction of the olefin vapour during argon-plasma etching of the electrode surfaces.[58] This method may present a new approach to preparing modified surfaces.

These results show that insulating polymer films can chemically modify electrodes and are able to effect electron transfer when charged. Polymers could be used to modify almost any electrode material, since their adsorption is rather non-specific. This suggests that the properties of polymers could be extended to an electrode for use in many types of applications.

5 Structure of Surface Layers

The study of the surface layers on modified electrodes has focused on three areas—the bonding, the orientation and structure, and the thickness of the layer. This has included the effect of the modified surface on the Helmholtz double layer of the electrode, as measured by capacitance and resistivity changes on the electrode surface.

The usefulness of ESCA, Auger, Inelastic Electron Tunnelling Spectroscopy (IETS), and Raman spectroscopy to probe the types and number of bonds present in the modified layer has been demonstrated. Also, for pyrolytic graphite, the specific regions of modification on the surface have been investigated.

The use of trichloro and trialkoxy silanes has introduced the problem of how many Si—O—M (M = metal electrode) bonds are formed in the modification process. There is a possible maximum of three. Recent spectroscopic studies of silanized surfaces by ESCA,[10] IETS,[11] and Raman[9] have indicated that an average of two bonds are present. This was because the spectra contained peaks corresponding to unreacted alkoxy or chloro groups. These dangling groups were apparently able to react with 3,5-dinitrobenzoyl chloride in a reaction intended to derivatize the surface silane,[28] producing voltammetric waves that were not as 'cleanly' resolved as those produced by a silanized electrode derivatized with 3,5-dinitrobenzoic acid by the DCC procedure.[54] This latter procedure eliminates the possibility of a dangling-group reaction.

The formation of four surface bonds is possible when tetra(aminophenyl) porphyrins are attached to graphite electrodes. Quantitative ESCA measurements, made after 3,5-dinitrobenzoyl chloride was added to react with the non-bonded amine groups, indicated an average of two surface amide bonds.[49]

Measurements of the extent of reaction of the amine groups on the surface silane chains with derivatizing compounds have been made with quantitative ESCA spectra. Monoamino silanes have been seen to be fairly unreactive toward derivatization, as coverages ranging from 6 to 27% have been obtained.[10,13] Surface coverages for derivatization reactions with diamino silanes have been from 50 to 90%.[32,45]

Murray and co-workers[10] have suggested that this inertness of the monoamino silanes is due to a cyclic structure that could form by hydrogen bonding between a γ-position amine and a SiOH function on the chain. The SiOH could result from the hydrolysis of the dangling, unreacted alkoxy function. Support for this structure was obtained when the surface coverage for the derivatization of a monoamino silane was dramatically increased to 74% when the electrode was continuously maintained in an anhydrous atmosphere.[10] These conditions would inhibit the hydrolysis of the dangling group and not allow the postulated hydrogen-bonded cyclic structure to form.

Information on the thickness and surface coverage of the modifying layer has been reported. Kuwana and co-workers[22] estimated the silane layer thickness on SnO_2 to be 2.4 nm. This was done by using argon sputtering with Auger spectroscopy to determine the depth at which the spectrum of the surface showed a 'clean' Sn:O peak ratio. White and Murray[25] used fluorescent measurements of cleaved surface species and ESCA spectra to calculate the ethylenediamino silane surface coverage on different electrodes. The coverages were in the range of 2—8×10^{-10} mol cm^{-2}, which compared closely with values obtained from ESCA and electrochemical determinations[1,19,32] and from molecular models.[10]

Resistivity and capacitance measurements have indicated that a modified layer is present on the surfaces of these electrodes. Lower surface capacitances have been measured for silanized SnO_2[13,22,46] and In_2O_3[22] electrodes, and a higher surface resistivity (by the four-point probe method) was determined for silanized SnO_2.[9] These results are in agreement with an increase in the thickness of the Helmholtz double layer of the electrode, which would be expected for a surface modified electrode.

Pyrolytic graphite electrodes consist of basal plane and plane edge surfaces. Distinct differences in the behaviour of these two surfaces towards modification have been observed. Selective modification reactions with predominantly one type of surface at a time showed that covalent bonding occurs primarily at the plane edge.[45,48] Presumably the plane edges contain most of the oxygen functional groups which react with the modifying species. Adsorption occurred on either type of surface,[45] although smaller and cleaner background currents have resulted with the basal planes.[44]

The investigation and study of species immobilized on the electrode surface is of importance in order to gain information on the surface structures and orientations involved in electrochemical reactions at an electrode. This information is important in order to understand and investigate how electron transfer occurs at an electrode–solution interface. Modified electrodes seem to present a viable approach to studying this process. More research aimed at investigating the structure of the surface layer is needed to pursue this area of interest, as it is almost certain that the electrode surface structure has a bearing on the mechanism of transfer.

Some investigations of adsorbed species on electrodes have begun through the use of Raman spectroscopy. The use of this method for adsorbed amines and pyridines on silver[74, 75] and platinum[75] has indicated that the orientation of surface-adsorbed species depends on the potential of the electrode. Pyridine normally adsorbed in a 'head-on' position on silver, but, as the potential increased more positively, the molecule apparently was attracted towards the surface and assumed an orientation more parallel to the electrode.[74] The use of Raman spectroscopy may be one technique for use in future surface studies of modified electrodes.

6 Non-ideal Redox Behaviour

The major thrust of the research on surface modified electrodes has been qualitative studies of the attached molecules. These studies have included observing the redox behaviour, possible catalytic effects, use in analytical determinations, and the stability of electrochemically generated products of the modifying compound.

However, recently more attention has begun to be devoted to fundamental studies of molecular interactions that occur on the surface of the modified electrode between the immobilized molecules. These interactions could be comparable, in some respects, to those occurring in solution, except that diffusion does not occur. Thus, a static system of interacting species is present on the surface, and quantitative studies of this could lead to information on electrode/solute interactions at unmodified electrode surfaces as well.

Murray and co-workers[76] have compiled tables comparing the redox potentials observed for many species in solution and immobilized on electrode surfaces. The surface potentials have corresponded quite closely to the solution potentials, and this indicates that the formal redox potential of a molecule is relatively insensitive to irreversible attachment on electrodes. This has allowed the use of voltammetric waves of surface species to suggest the success of a modification procedure. Murray and co-workers also discussed factors that could have an effect on the redox potential. These included stereochemical limitations of the surface molecules during charge transfers, interactions between the molecules and the electrode, or interactions between the molecules themselves in their reduced and oxidized forms.

This latter interaction has been incorporated into equations derived by Brown and Anson[67] for the study of reactants irreversibly attached to electrodes by

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[74] D. L. Jeanmarie and R. P. Van Duyne, *J. Electroanal. Chem.*, 1977, **84**, 1.

[75] G. Hagen, B. S. Glavaski, and E. Yeager, *J. Electroanal. Chem.*, 1978, **88**, 269.

[76] J. R. Lenhard, R. Rocklin, H. Abruña, K. Willman, K. Kuo, R. Nowak, and R. W. Murray, *J. Amer. Chem. Soc.*, 1978, **100**, 5213.

cyclic voltammetry. This was accomplished by defining surface activity coefficients as being exponentially dependent on the surface concentration and molecular interaction parameters. The following equations for the potential and current were then derived from the Nernst equation, using the total concentration of surface species:

$$E = E^{0'} - \frac{RT\Gamma}{nF}\left\{\mathrm{f}(\mathrm{r_O} + \mathrm{r_R}) - \mathrm{r_R}\right\} + \frac{RT}{nF}\ln\left[\frac{\mathrm{f}}{1 - \mathrm{f}}\right] \tag{1}$$

$$i = \frac{-n^2F^2\Gamma\nu\,\mathrm{f}(1 - \mathrm{f})}{RT\,[1 - \mathrm{f}\Gamma(\mathrm{r_O} + \mathrm{r_R})(1 - \mathrm{f})]} \tag{2}$$

$E^{0'}$ is the formal potential for the surface redox couple, Γ is the total surface concentration, ν is the scan rate of the potential, f is the fraction of surface molecules in the oxidized form, and the other symbols have their usual significance. The non-ideality parameters $\mathrm{r_O}$ and $\mathrm{r_R}$ represent the molecular interactions for the oxidized and reduced forms of the surface species respectively.

The peak potential and peak current are obtained by setting $\mathrm{f} = 0.5$ in equations 1 and 2. This results in equations 3 and 4:

$$E_\mathrm{a} = E_\mathrm{c} = E^{0'} - \frac{RT\Gamma(\mathrm{r_O} - \mathrm{r_R})}{2n\,F} \tag{3}$$

$$i_\mathrm{P} = \frac{n^2\,F^2\Gamma\nu}{RT\,[4 - \Gamma(\mathrm{r_O} + \mathrm{r_R})]} \tag{4}$$

where E_a and E_c are the anodic and cathodic peak potentials and i_p is the peak current. Murray and co-workers[26] have utilized a computer program to give the best fit with their data for the case of *p*-aminophenylferrocene covalently bound on metal oxide electrodes.

The non-ideality parameters are believed to be related to stabilizing and destabilizing processes on the surfaces. These parameters so far have been found to be very large negative numbers, typical values calculated by Brown and Anson,[67] and Lenhard and Murray[12] being around -1×10^9 cm^2 mol^{-1}. Equations 1 and 2 produced very good fits to the experimental curves. These negative values suggest that a destabilizing process of some kind is responsible for the non-ideality observed so far in the redox behaviour of the attached reagents.

Equation 3 predicts that no shift in the observed peak potentials will occur with a change in concentration or temperature as long as $\mathrm{r_O} = \mathrm{r_R}$. This condition was observed by Brown and Anson for the irreversible adsorption of aromatic quinones and iron porphyrins on graphite electrodes. However, they did not speculate as to the possible origins of the non-ideal behaviour.

Similar equations were derived by Brown and Anson[67] for differential pulse voltammetric studies, but the fit between the calculated and experimental curves was not as close as that seen for the cyclic voltammetric case. However, after incorporating extra uncompensated resistance in series with the working electrode, the use of an appropriately modified equation showed improved agreement between the two curves.

Insufficient experimental work has been performed at this time to discuss confidently the implications of these non-ideality parameters. Brown and Anson's theory is a preliminary step in trying to understand the current potential behaviour observed with modified electrodes. Lenhard and Murry[12] have reported that r (the non-ideality parameter when $r_O = r_R$) decreased with increasing Γ but found a constant $r.\Gamma$ product for ferrocene carboxylic acids attached to silane monolayers on platinum. This is not allowed for in the theory, and it is likely that modifications to the theory will be needed as more results are obtained from specific studies. As an example, Lenhard and Murray[12] stated that, by inclusion of a third interaction parameter, a shift of $E^{0'}$ with time, which they observed, is predicted.

This area of research with surface modified electrodes holds forth the possibility of gaining useful information on the mechanisms of electrode processes. Data obtained with tailormade modified electrodes should also help in the investigation of the processes that give rise to the non-ideality parameters. Hopefully, these results will allow extension to unmodified surfaces as well.

7 Applications

A. Catalysis and Inhibition.—Some of the compounds that have been used to modify electrode surfaces are able to catalyse different types of electrochemical reactions when in solution. This catalytic property apparently can be retained when the compounds are attached to an electrode surface. Other instances of electrochemical catalytic and inhibitory effects have been observed with electrodes modified by normally inactive compounds. This catalysis or inhibition is exhibited in the rate of electron transfer between the electrode and molecules in solution.

The catalytic electrode surfaces have been applied to the study of various electrochemical reactions. Although some of the catalytic effects that have been observed were unexpected and appeared during the course of studying the modified electrodes, there has been some success with the preparation of modified electrode surfaces that are specific for the catalysis of particular reactions.

The first report of the use of a covalently bonded electrode in a catalytic reaction was by Kuwana and co-workers,[53] who demonstrated that the electrochemical oxidation of ascorbic acid was catalysed by a graphite electrode modified by the attachment of benzidine. It is possible that benzidine acted as a 'mediator' in the electron transfer process between the electrode and the ascorbic acid. Tse and Kuwana[77] were also successful in catalysing the electrochemical oxidation of dihydronicotinamide adenosine diphosphate (NADH) by the use of a quinone modified graphite electrode. Either 3-hydroxytyramine or a 3,4-dihydroxybenzylamine was attached to the electrode using the DCC amidization method[54] and was then oxidized electrochemically to the quinone form. NADH normally reacts with quinones in solution to give NAD^+. Since the

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[77] D. C. Tse and T. Kuwana, *Anal. Chem.*, 1978, **50**, 1315.

modified surface was able to achieve the same result, it seems clear that this property was extended to the graphite electrode.

The capability of electrodes to reduce O_2 would be useful for applications in such practical areas as fuel cells. A platinum electrode, coated with polyacrylonitrile,[39] reduced O_2 to OH^-. Formation of the intermediate HO_2^- species was not observed with this electrode as it was with a graphite electrode. Polyacrylonitrile normally catalyses the decomposition of HO_2^- in alkaline solutions and apparently this capability is retained while it is on the platinum electrode. A layer of poly-*p*-nitrostyrene on platinum[42] decreased the reduction overpotential for O_2 by about 200 mV and increased the current over that observed for clean platinum electrodes.

Another example of electrocatalytic reduction of O_2 by a modified surface was demonstrated by Zagal and co-workers.[78] This was achieved by adsorbing cobalt (II) tetrasulphonatephthalocyanine complexes, which reduce O_2 when in solution, on the basal planes of pyrolytic graphite. A kinetic study of this reduction indicated a first order reaction.

Many reports of electrocatalysis by halides adsorbed on platinum electrodes have appeared in the literature.[79] A recent example was the catalytic reduction of ferric ion in perchloric acid solutions.[79] This reduction was studied by cyclic voltammetry and by the changes in half-wave potential *vs.* time.

The inhibition of ferrous ion oxidation was observed at a polyester-coated platinum electrode by Miller and Van De Mark.[43] Normal reduction of Fe^{3+} to Fe^{2+} occurred at the electrode but the oxidation did not take place. They also found[40] that surface-bound nitro groups, obtained on a polypeptide-covered platinum electrode by reaction of the adsorbed polymer with 3,5-dinitrobenzoyl chloride, were able to be reduced but their oxidation was inhibited when studied with cyclic voltammetry.

The ability of a viologen compound that was electrosorbed on a gold electrode to increase the rate of electron transfer between the electrode and a solution species has been observed by Hawkridge and co-workers.[80,81] Surface immobilized methyl and benzyl viologen both catalysed the oxidation and reduction of whale myoglobin,[80] and methyl viologen sped up the rate of reduction of spinach ferrodoxin.[81] This catalytic behaviour is apparently due to the viologens acting as electron 'mediators'. In the myoglobin reaction, the interaction occurred at a potential that was quite different from the redox potentials of the viologen compounds. These results were significant because unmodified gold electrodes oxidized or reduced the ferrodoxin or myoglobin only at a very slow rate.

Andrieux and Saveant[82] have presented a theoretical treatment comparing catalytic effects from modified electrodes (primarily polymer electrodes) and homogeneous solutions. They assumed that the catalytic reaction was the rate-determining step and that the substrate concentration at the surface polymer

[78] J. Zagal, R. K. Sen, and E. Yeager, *J. Electroanal. Chem.*, 1978, **83**, 207.

[79] D. C. Johnson and E. W. Resnick, *Anal. Chem.*, 1977, **49**, 1918 and references therein.

[80] J. F. Stargardt, F. M. Hawkridge, and H. L. Landrum, *Anal. Chem.*, 1978, **50**, 930.

[81] H. L. Landrum, R. T. Salmon, and F. M. Hawkridge, *J. Amer. Chem. Soc.*, 1977, **99**, 3154.

[82] C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.*, 1978, **93**, 163.

film remains constant. The derived equations predict an increasing catalytic efficiency with an increasing polymer-layer thickness up to the point where the substrate concentration assumption is no longer valid. Little, if any, catalytic behaviour would be expected with monolayer-polymer electrodes, since the surface is essentially unchanged from the bare metal, at least as far as outer sphere electron transfers would be concerned. Polymer electrodes would be expected to produce slightly less reversible behaviour when compared to homogeneous solutions, contributing to slightly lower efficiencies. However, the use of polymer electrodes does appear to be a useful and promising route for catalytic studies.

An interesting electrolyte effect on current-potential curves was observed by Wrighton and co-workers[30] in the study of ferroceno silanes attached to anodized gold electrodes. By using electrolytes of varying cation and anion sizes, they noticed that only changes in anion sizes produced differences in the measured currents. The presence of BPh_4^-, a large anion, produced a smaller current than ClO_4^-, a smaller anion. The authors postulated that this effect could be related to how well the anion penetrates into the surface film, presumably a function of the anion size. Another possibility could be solubility differences of the anions in the film.

This electrolyte effect is evident since the oxidation of one ferrocene centre requires the close presence of a counteranion. If this close contact is hindered, the magnitude of the current will decrease. No cation effect was observed in this study. Further investigations will be necessary for a better understanding of the effect.

Catalytic results have also been measured after adsorbing transition metal ions and complexes on the perpendicular surfaces of $(SN)_x$ polymer electrodes.[72,73] The magitude of the current observed for the oxidation of I^- to I_2 at an electrode that had been modified by the adsorption of $Ru(NH_3)_5Cl^{2+}$ was 100—200% larger than that measured at an unmodified electrode.[43] No such catalysis was seen when $Ru(NH_3)_6{}^{3+}$ was the adsorbed species nor when pyrolytic graphite was used as the electrode. Similarly, the rate of reduction for IO_3^- in solution was increased after the adsorption of Cr^{3+} onto a $(SN)_x$ electrode.[73]

These results have shown that surface modified electrodes can function as electrochemical catalysts. Thus, it is easy to imagine further tailoring of surfaces for application to specific reaction systems. Of equal interest is the observation of catalytic and inhibitory behaviour where none was expected. Further studies of these occurrences should help increase the understanding of how the electron transfer processes occur at electrode surfaces.

B. Photoelectrodes.—The use of sunlight to generate electrical current is a fast-growing area of research interest due to the world energy problems. Most photoelectrodes that do not become passivated during irradiation in aqueous media cannot respond to the visible region of sunlight. Electrodes such as TiO_2 and SnO_2 are more sensitive to the ultraviolet wavelengths. These wavelengths, of course, are not easily passed through the earth's atmosphere and therefor only very small photocurrents can be obtained with these electrodes.

However, many highly-coloured dyes, when in the solution with the immersed electrodes, are able to sensitize the electrode to the visible wavelength that the dye absorbs. An obvious extension of this would be physically to attach the dye to the electrode surface. Then, the electrode could be placed into a solution free of the dye and it would still be responsive to the specific visible wavelength.

The application of surface modified electrodes in this area has been studied by Fujihira and co-workers[21,64,65] by immobilizing the dye rhodamine B on the surface of SnO_2 electrodes. This was accomplished in two ways. The first was to silanize the electrode with an amino silane and then attach the dye by an amidization reaction.[21] The second method was direct coupling between the dye and the surface hydroxy-groups[64] using the DCC procedure.[54] The observed photocurrent at the electrode with the silyl attachment was less than that from the direct covalent attachment. This apparently arose because the distance between the dye and the electrode for the directly coupled surface is less than for the dye linked to the electrode by the insulating silane chain, where the shorter distance would allow for a greater amount of electron injection by the excited dye molecule into the conduction band of the electrode. Another reason could be due to the amide form of rhodamine B being less sensitive to visible light than the ester form. In further work[65] with the ester-linked rhodamine B photoelectrode, a quantum efficiency of 0.09 ± 0.03 was measured.

Another type of dye-sensitized electrode surface was studied by Hawn and Armstrong.[23] They attached erythrosin to SnO_2 electrodes by electrosorption of the oxidized dye, silane linkages using amino and thiol terminal functional groups, and direct coupling with surface hydroxyls. Photocurrents were observed for all types of surface modification, although the covalently modified electrodes gave higher currents than electrodes modified by adsorption. The photocurrent was sustained when a reducing agent was put into the solution, as it reduced the photo-oxidized dye and permitted a cycling process for the dye molecules.

In a different approach to obtaining a bound dye on an electrode surface, Fujihira and co-workers[14] attempted to synthesize a dye after attaching a starting material to a silanized SnO_2 electrode. However, under the derivatizing conditions used, the silane surface bonds were broken and the experiment was unsuccessful.

Rapid passivation of n-type silicon and germanium semiconductor electrodes occurs when they are photoanodized in aqueous solutions. This passivation is caused by a buildup of surface oxide. However, by attaching a ferroceno silane to these electrodes, Wrighton and co-workers.[34,36] prepared photoelectrodes with longer lives. The silane layer apparently inhibits the further formation of surface oxide, thereby increasing the usefulness and efficiency of the photoelectrodes. These electrodes could be cycled more than 50 times with very little change in response or change in their cyclic voltammetric scans, thereby allowing their use as stable photoelectrodes.

Similar results were hoped for by Finklea and Murray[27] when they bonded silanes to TiO_2 electrodes. They found that the silanes did not appear to affect the semiconductor properties and that the Ti—O—Si bond was stable to irradiation by band-gap light. Unfortunately, if their assumption that electron transfer occurs only at TiOH sites is correct, the silane coverage did not appear to be complete, since 'normal' ferricyanide reduction and weak phosphate buffer adsorption still occurred after the silanization treatment. Trapping of photogenerated hole oxidations by the surface silane layer, which inhibited the SiO_2 buildup on silicon,[34] was not observed with the modified TiO_2 electrodes, thereby not increasing the photoefficiency.

Photoactive porphyrins were adsorbed on platinum[83] by a method similar to that of Davis.[69] Stable photocurrents that decayed with time were observed, with a maximum photocurrent measured when the surface coverage was about 30 monolayers. No photocurrent was detected until multilayers of the porphyrins were present on the electrode, which differs from dye monolayers on semiconductor electrodes giving rise to appreciable photosensitization.

These initial beginnings suggest a promising application of surface modified electrodes. It seems likely that this area of research is one that will command a great degree of interest.

C. Analytical.—Surface modified electrodes have been applied to the area of analytical chemistry. Lane and Hubbard[84] have taken advantage of the strong adsorption of I^- on platinum electrodes to study the concentration of catecholamines in solution. Under normal conditions, the detection of these compounds by electrochemical means was hampered by the solid reaction products adsorbing onto the electrode and quickly passivating it. Adsorbed I^- inhibits this process, thereby allowing for more accurate determinations of the catecholamines in a live rat's brain.[85] Double differential pulse voltammetry was used to aid in measuring the small concentrations.

Lane and Hubbard also used the Pt/I^- system to observe the conversions of Pt^{II} complexes to Pt^{IV} complexes in non-aqueous solvents.[86] Common solvents such as dimethylsulphoxide, acetonitrile, and pyridine were found to adsorb strongly on plain platinum, thereby blocking the adsorption of the platinum complexes on the surface and inhibiting the conversion. Adsorbed I^- was again seen to inhibit this solvent adsorption, allowing the conversions to be studied.

Surfaces can be modified with biological molecules, such as proteins, by a method developed by Weetall and Detar,[87] which utilizes cyanogen bromide. Yamamoto and co-workers[88] used this method to modify titanium wire electrodes with either antigens or antibodies. When an antigen was present on the electrode and the electrode was placed into a solution that contained the antibody for which it was specific, a positive potential shift occurred. A negative shift was observed when the antibody was on the electrode and the antigen was in the

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[83] Y. Umezawa and T. Yamamura, *J. Electroanal. Chem.*, 1979, **95**, 113.

[84] R. F. Lane and A. T. Hubbard, *Anal. Chem.*, 1976, **48**, 1287.

[85] R. F. Lane, A. T. Hubbard, K. Fukunaga, and R. J. Blanchard, *Brain Res.*, 1976, **114**, 346.

[86] R. F. Lane and A T. Hubbard, *J. Phys. Chem.*, 1977, **81**, 7341.

[87] H. H. Weetall and C. C. Detar, *Biotechnol. Bioeng.*, 1975, **17**, 295.

[88] N. Yamamoto, Y. Nagasawa, S. Shuto, M. Sawai, T. Sudo, and H. Tsubomura, *Chem. Letters*, 1978, 245.

solution. No potential shift was seen if the antibody and antigen were not specific for each other. The potential shift was found to be proportional to the concentration of the species in the solution and it followed first order kinetics. This technique would allow the sensitive detection of biologically active substances.

Cheek and Nelson[89] measured Ag^+ concentrations by the use of a modified carbon-paste electrode. The electrode was silanized with an ethylenediamino silane or amidized with diethylenetriamine. The latter method produced the better results. The Ag^+ ion was complexed by the surface ligands in both cases. Measurements of 10^{-6} M concentrations were possible by this method, and it appears to be promising for applicability in the measurement of the picomolar concentrations. This result and those preceding indicate that there are many possible analytical applications and that the recognition and investigation of these possibilities have just begun.

D. Electrochemical Synthesis.—The use of a graphite electrode, whose surface had been modified by the attachment of an optically active amino-acid, in the preparation of optically active alcohols was one of the first reports on surface modified electrodes.[6] A similar 'chiral' surface was also prepared on silanized SnO_2 and DSA electrodes[33] by the attachment of (−)-camphoric anhydride. These latter electrodes were used to prepare optically active sulphoxides from sulphide compounds.

Horner and Brich[51] bonded chiral and achiral amines to graphite electrodes and then electrochemically reduced acetophenone with the modified electrodes. However, unlike Miller and co-workers,[6] no chiral products were isolated. Rather, the carbinol and pinacol forms of the reduction product were formed by this reaction. The ratio of carbinol to pinacol was dependent on the acidic or basic nature of the modified surface. The pinacol product predominated with basic and neutral surfaces, while acidic surfaces favoured the carbinol form.

Although there has been only a small handful of synthetic applications, the potential has been demonstrated. It does appear that the surface layer has an effect on the reactions occurring at the electrodes. However, more studies must be carried out to gain more detailed information on the surface layer structure, so that specifically designed electrodes may be used to achieve desired results in this area.

E. Study of Immobilized Molecules.—Sharp[47] bonded 1-amino and 2-amino-9,10-anthraquinone to graphite electrodes by the standard acid chloride procedure, and then studied these two isomers by cyclic voltammetry. Both of these isomers of the anthraquinone exhibit redox behaviour in solution, yet electrical activity was observed only for the 1-amino isomer after the surface modification. This difference apparently arose due to an orientation effect. Maximum electron transfer would occur with a parallel orientation of the aromatic group to the

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[89] G. T. Cheek and R. F. Nelson, *Anal. Letters*, 1978, **A11**, 393.

electrode surface, as this would afford the largest electronic interaction. Only the 1-amino-9,10-anthraquinone is able seemingly to achieve this configuration while bonded to the surface, and therefore electron transfer to the 2-amino isomer is hindered. An interesting observation from these results is that apparently no electron transfer occurs through the surface amide linkage since the 2-amino isomer was unresponsive.

The formation and stability of electrochemically generated pyrazoline radicals was studied by Diaz and Kanazawa.[16,20] The pyrazolines were bonded to SnO_2 electrodes by an amino silane chain. By the use of cyclic voltammetry, Diaz found[16] that some amount of reversibility in the radical formation was lost for the surface bound pyrazolines, reflecting a lower stability when on the surface than in solution. The amount of reversibility lost was dependent on the structure of the particular pyrazoline being studied. The instability was apparently due to the radical not being able to diffuse into the electrolytic solution and thus stabilize itself.

The ability of electrode surfaces to immobilize molecules from solution can be used to study intermediates in solution reactions. For example, a trimethylsilane radical, formed by the electrochemical reduction of chlorotrimethylsilane, was observed to bond to a platinum electrode,[90] but only when a potential existed on the electrode. Evidence for this modification was obtained from ESCA measurements.

Kinetic studies of surface immobilized molecules have also been made. Lenhard and Murray[12] found the decay of the ferricinium state of ferrocenylphenylacetic acid appears to follow second order kinetics when attached to platinum electrodes and immersed in acetonitrile solutions, while it follows first order kinetics when dissolved in aqueous solutions. No difference in order between mono- and multi-layer silane coverages was observed. The decay on the surface apparently occurs through the loss of iron. The rate of decay was found to be dependent on the electron-withdrawing abilities of substituents present in the molecule. The decay rate constant measured on monolayer electrodes was ~10 times larger than that on multilayer electrodes.

Electron transfer rate constants of immobilized species are important in determining their possible use as catalysts. Brown and Anson[91] measured the rate constant for 9,10-phenanthrenequinone, adsorbed on pyrolytic graphite, by an open circuit charge injection technique. They assumed first order kinetics for the electron transfer process and found it to follow typical Arrhenius behaviour for temperature variations. Sharp and co-workers[92] adsorbed allylamine on platinum and used it to bind ferrocene carbaldehyde. They then measured k^0, the standard electron transfer rate constant, and α and β, the cathodic and anodic transfer coefficients respectively, for this quasi-reversible system.

The ability to use modified surfaces in the study of electrochemical properties

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[90] A. L. Allred, C. Bradley, and T. H. Newman, *J. Amer. Chem. Soc.*, 1978, **100**, 5081.

[91] A. P. Brown and F. C. Anson, *J. Electroanal. Chem.*, 1978, **92**, 133.

[92] M. Sharp, M. Petersson, and K. Edstrom, *J. Electroanal. Chem.*, 1979, **95**, 123.

of molecules has been demonstrated. By making comparisons between solution and surface studies, it seems likely that valuable information can be gained on electron transfer processes and the parameters involved.

8 Summary

This review has presented the many different results obtained with surface modified electrodes. Their usage in such widespread areas as photoelectrodes, synthesis, catalysis, and basic research on the properties of immobilized molecules has demonstrated many possible applications. There are still many uncertainties in this field that need to be investigated more fully, including surface orientation, bonding and structure, mechanisms and orientations involved in electron transfer processes, origins of non-ideal redox behaviour and equations to describe them, and how to increase the efficiency of catalytic behaviour, just to list a few. This is a field that is growing quickly and appears to offer applications to a wide variety of interests, including areas not yet explored. It seems safe to predict that interest in this field will continue to increase as more of the capabilities of surface modified electrodes become evident and are refined for specific purposes.