Photoelectron Spectroscopic Studies of Electrode and Related Surfaces

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1 Introduction

X-Ray photoelectron spectroscopy (XPS or ESCA) is now a very well established technique for the examination of surfaces. There is a rapidly growing interest in the application of this spectroscopy, and other surface sensitive spectroscopies, to the solid–liquid interface. This has taken the form of an examination of films or adsorbed layers formed on the surfaces of electrode materials. Such studies have often been combined with the electrochemical experiments and increasingly have been concerned with corrosion problems.

In a review such as this there is not enough space to give a comprehensive coverage of the area, for there are now more than five hundred papers in the field. The author has reviewed the area in some depth.[1] A number of other reviews relevant to the area have been published in English,[2] French,[3] and Japanese.[4] Review articles on corrosion which include electrochemical studies have been written by Joshi,[5] Larson,[6] Castle,[7] Baer and Thomas,[8] McIntyre,[9,10] Hashimoto and Asami[11] (written in Japanese), and Oudar[12] (written in French). In addition there have been a number of reviews on aspects of the area such as films on stainless steel and metal alloys,[13–16] ion selective electrodes,[17] and chemically modified

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[1] P. M. A. Sherwood, in 'Contemporary Topics in Analytical and Clinical Chemistry', Vol. 4, ed. D. M. Hercules, G. M. Hieftje, L. R. Snyder, and M. A. Evenson, Plenum, 1982, pp. 205–293.

[2] J. Augustynski and L. Balsenc, in 'Modern Aspects of Electrochemistry', Vol. 13, ed. B. E. Conway and J. O'M. Bockris, Plenum Press, New York, 1979, pp. 251—360.

[3] D. Landolt and H. J. Mathieu, *Oberfläche-Surf.*, 1980, **21**, 8.

[4] T. Nakajima and N. Watanabe, *Yoyuen*, 1976, **19**, 239.

[5] A. Joshi, *Rev. Coat. Corros.*, 1979, **3**, 51.

[6] D. T. Larson, *Corros. Sci.*, 1979, **19**, 657.

[7] J. E. Castle, *Surf. Sci.*, 1977, **68**, 583.

[8] D. R. Baer and M. T. Thomas, ACS Symp. Ser., No. 199, 'Industrial Applications of Surface Analysis', 1982, p. 251.

[9] N. S. McIntyre, *Chem. Anal. (N.Y.)*, 1982, **62** (Appl. Electron Spectros. Chem. Anal.), 89.

[10] N. S. McIntyre, in 'Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy', ed. D. Briggs and M. P. Seah, John Wiley and Sons, Chichester, New York, Brisbane, Toronto, and Singapore. 1983, Chapter 10.

[11] K. Hashimoto and K. Asami, *Boshoku Gijutsu*, 1977, **26**, 375.

[12] J. Oudar, *J. Microsc. Spectrosc. Electron.*, 1979, **4**, 439.

[13] M. Hirochi and C. Yoshimura, *Hyomen Gijutsu*, 1980, **31**, 596.

[14] H. Fischmeister and I. Olefjord, *Relat. Etats Surf. Corros., Colloq. A.I.A.C.-CEFRACOR*, 1980, 17.

[15] M. Janik-Czachor, *Pr. Nauk. Inst. Technol. Nieorg. Nawozow Miner. Politech. Wroclaw.*, 1979, **16**, 9.

[16] H. Fischmeister and I. Olefjord, *Mater. Tech. (Paris)*, 1982, **70**, 306.

[17] M. F. Ebel, *Anal. Chem. Symp. Ser., No. 8*, (Ion-Sel. Electrodes, 3), 1981, p. 89.

electrodes.[18] This review will attempt to illustrate the main features of the field with a range of appropriate examples.

The interface between the solid and the liquid electrolyte plays a very important role in any electrochemical process. This process may be one corresponding to a system of known composition under careful electrochemical control, or it might be a general corrosion system (many corrosion processes are electrochemical in nature). It is only in the past twenty years that really effective methods have become available for the study of the detailed chemistry at the surface, especially where the surface has a different nature from that of the bulk. The occurrence of a different surface nature is common in electrochemical situations. Thus metals frequently oxidize to form an insulating oxide film that prevents further current flow. Films often form on the surface due to adsorbed materials. In any corrosion situation the ability of the surface film to allow the transfer of electrolyte and/or gaseous materials to the bulk determines the progress of the corrosion.

Yeager[19] has provided an excellent overview of the non-traditional approaches that can be taken to the study of the solid–electrolyte interface. The non-traditional methods have the advantage of greater molecular specificity over the traditional methods, and the combination of both approaches is now more common in the investigation of electrochemical behaviour. Any method for examination of the solid–liquid interface is best carried out *in situ* since the interface may change when it is removed from the liquid. A number of methods can be applied in this way including ellipsometry, Mössbauer spectroscopy, i.r. and Raman spectroscopy, and visible and u.v. spectroscopy. The use of synchrotron radiation opens up new possibilities,[20] and, in particular, extended *X*-ray absorption fine structure (EXAFS) can produce valuable structural information. As with all physical methods for analysis these methods are often complementary, and it is best to apply as many as possible in order to get a full understanding of the surface. The problem with the *in situ* methods is that they sometimes lack sensitivity and may be limited to particular surfaces. Most modern surface science techniques are of necessity *ex situ* methods and often require the surface to be studied in a high vacuum. They present the problem that the electrode must be removed from the liquid in such a way as to minimize any changes to the surface. In these studies this is usually achieved by removing the electrodes from the cell without disconnecting the potentiostat, and by trying to eliminate any reactions of the surface during transfer from the cell to the spectrometer. In many cases electrolyte is often left attached to the electrode and may be slow to be removed even in a vacuum system. The most widely applied *ex situ* techniques have been XPS, ultraviolet photoelectron spectroscopy (UPS), Auger spectroscopy, electron energy loss spectroscopy (EELS), secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), and low energy electron diffraction (LEED). The important area of *in situ* photoemission (the photoelectron emission from an electrode

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[18] M. Umana, D. R. Rolison, R. Nowak, P. Daum, and R. W. Murray, *Surf. Sci.*, 1980, **101**, 295.

[19] E. Yeager, *Surf. Sci.*, 1980, **101**, 1.

[20] D. W. Lynch, *J. Electroanal. Chem.*, 1983, **150**, 229.

into an electrolytic solution leading to a current resulting from the conversion of the photons in the electrode, see for example *ref.* 21) will not be discussed here.

A number of surface science methods may be destructive of the surface as a result of electron beam damage (Auger, *X*-ray emission, electron diffraction) or ion beam damage (SIMS and ISS). This is especially true when small intense beams are used in order to maximize spatial information. This is not to say that these methods are not of great value in studies of electrode and related surfaces, and it is the spatial information that they can provide that is often of greatest importance. Some mention will be made of these methods, but most space will be given to XPS since it gives useful chemical information and is generally less destructive than the other methods. It does not, however, provide much information about small variations on different parts of the surface but rather gives an average view of the surface.

XPS studies involve the subjection of the sample in an ultra-high vacuum environment to a beam of almost monochromatic *X*-radiation. Photoelectrons are ejected from the sample surface and their kinetic energy is measured, allowing their binding energy to be calculated. Normally only those electrons that suffer no collision give rise to a distinct peak in the spectrum, the other electrons contributing to the spectral background. This means that the effective sampling depth is less than 10 nm, allowing films of submonolayer thickness to be studied. The valence band and core region of the spectrum provide important and often complementary information. Thick films can be examined by etching the surface away by methods such as argon-ion etching leading to a composition and concentration profile with depth (*e.g. ref.* 22). This method may lead to significant alteration in surface chemistry as a result of the etching process,[23] and for thinner films angle resolved studies in the core region are more appropriate (*e.g. ref.* 24).

The core region gives rise to chemical shifts in the essentially core atomic energy levels as a result of the small energy changes resulting from the interaction of the core electrons with the outer-lying electrons from the same atom and the surrounding atoms. This means that the difference in chemical shift between the atom in some standard environment (*e.g.* the metal) and compound of interest mainly depends upon the charge on the atom in question, the charges on the surrounding atoms, and extra-atomic relaxation energy differences. These chemical shifts can be compared with known values for bulk compounds, though such an approach may present problems due to differences in the surface and bulk compositions for the standards, and calibration and charging problems. Identification may be assisted by using simple calculations to predict the core chemical

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[21] J. K. Sass, *Surf. Sci.*, 1980, **101**, 507.

[22] P. A. Breeze, H. L. Hartnagel, and P. M. A. Sherwood, *J. Electrochem. Soc.*, 1980, **127**, 454.

[23] K. S. Robinson and P. M. A. Sherwood, *Surface and Interface Analysis*, 1984, **6**, 261.

[24] R. O. Ansell, T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Electron Spectros. Relat. Phenom.*, 1977, **11**, 301.

shifts.[25] The spectrum represents the number of electrons arriving at the detector for a particular electron kinetic energy (determined by the pass energy of the electron energy analyser). The peak intensities in the core region, measured as the areas under the peaks, can be related to the amount of material with a particular chemical shift present. In suitable, mainly simple, cases (such as a uniform oxide layer lying on a metal surface) it is possible to obtain information about the thickness of the surface films from the intensities. This is particularly true of thin films where the underlying material may be present, such as in the case of a metal covered by a metal oxide where the metal and metal oxide core peaks have a different chemical shift.

Significant differences may be seen in the valence region for two different compounds whose core chemical shifts are accidentally the same, but the analysis of the valence band region is more difficult than the core region, and generally requires band structure or molecular orbital cluster calculations. Valence band spectra are complicated by the need to unravel the spectrum of interest from overlapping valence band spectra from the various components, including contamination, which will probably all give features in this region. Single crystal studies of high purity systems under carefully controlled conditions can reveal important information, especially when combined with angle resolved photoemission[26,27] and X-ray photoelectron diffraction.[28,29] Much more work using single crystal electrodes has been carried out recently.

2 The Importance of Obtaining Data of High Quality and Careful Data Analysis

While there are cases when the X-ray beam may cause some decomposition, this is rare and it is generally possible to collect spectral data for considerable periods of time without compound decomposition. Indeed this is a particularly valuable feature of the soft radiation used in XPS, in contrast to the problems that are often found with small area electron beams. In fact most decomposition is caused by sample heating from the X-ray gun. Of course spectra collected at high resolution will have poorer statistics, but normally the best resolution is selected in order to detect closely overlapped spectral features more easily. This means that spectra may have to be collected for a longer time in order to obtain the appropriate statistics to allow these overlapped spectral features to be analysed by curve fitting methods with appropriate confidence. The availability of cheap microcomputer systems makes the collection and analysis of such data much easier. The aim of data analysis techniques is to resolve spectra which arise from overlapping chemically shifted signals into their component peaks. Many methods are now available for the analysis of this situation.[30]

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[25] P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1791.

[26] F. J. Himpsel, *Adv. Phys.*, 1983, **32**, 1.

[27] E. W. Plummer and W. Eberhardt, *Adv. Chem. Phys.*, 1982, **49**, 533.

[28] E. S. Crawford, S. Evans, and E. Raftery, *Surface and Interface Analysis*, 1983, **5**, 28.

[29] C. S. Fadley, *Inn.-Shell X-Ray Phys. At. Solids. (Proc. Int. Conf. X-Ray Processes Inn-Shell Ioniz.)*. ed. D. J. Fabian, H. Kleinpopper, and L. M. Watson, Plenum, New York, N.Y., 1980 (Pub. 1981), p. 467.

[30] P. M. A. Sherwood. in 'Practical Surface Analysis by Auger and Photo-Electron Spectroscopy', ed. D. Briggs and M. P. Seah. Appendix 3, J. Wiley and Sons, Chichester, New York. Brisbane, Toronto. Singapore, 1983.

3 Overview of the Information Available by Combining XPS and Electrochemical Studies

The combination of XPS with electrochemical studies gives complementary information from the two techniques. The main information provided by XPS has been discussed above. The two techniques relate to one another as shown below. Thus electrochemical studies provide:

(*a*) a highly controlled environment for the formation of films or adsorbed layers,
(*b*) measurements that give information on film thickness and changes in film type.

The XPS studies of the electrode surface gives the following main information:

(*a*) information about the chemical nature of the film,
(*b*) information about the thickness of the film which can be shown to agree with electrochemical measurements of the film thickness.

Further, the use of surface spectroscopies involve experimental conditions (*e.g.* a clean high vacuum system) which may allow the generation of a well-defined surface which can be monitored by the spectroscopy before any electrochemistry is carried out. The initial state of the electrode surface generally has a profound effect upon any subsequent electrochemistry.

4 A Simple System

Cyclic voltammetry is a useful electrochemical method for investigating the electrochemical behaviour of a system. In this process the current passing between the electrode of interest (whose potential is monitored by a reference electrode) and a counter electrode (generally made of platinum) is measured under the control of a potentiostat. The potential of the electrode of interest is subjected to a triangular sweep (where the potential rises from the start value to a final value then back to the start at a sweep rate that varies linearly with time) controlled by a signal generator. The current measured during this process (often shown as the current density where the current is divided by the electrode area) is then plotted as a cyclic voltammogram.

The first application of XPS to the study of electrode surface was made on platinum electrodes by Kim, Winograd, and Davis in 1971.[31] Noble metal systems sometimes show simple behaviour and present less problems over sample transfer than non-noble metal systems where oxidation may occur during transfer. In a non-noble metal system, such as aluminium, the metal is readily oxidized and is normally found with a thin oxide layer on the surface. Unoxidized aluminium will oxidize in the transfer process as a result of the high activity of aluminium metal to water and oxygen. The ways to reduce or eliminate chemical changes occurring during the transfer process will be discussed below. If an aluminium metal sample is taken which has its normal air-formed oxide film, then a cyclic voltammogram for this sample in dilute sodium hydroxide solution [32] can be obtained, and appears as in Figure 1. As the potential is increased the current increases until a peak is given at −0.25 V (*vs.* an Hg/HgO electrode) corresponding to oxide thickening and then oxygen evolution gives the cusp on the extreme right-hand side. When the

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[31] K. S. Kim, N. Winograd, and R. E. Davis, *J. Am. Chem. Soc.*, 1971, **93**, 6296.
[32] H. Al-Bayati and P. M. A. Sherwood, to be published.

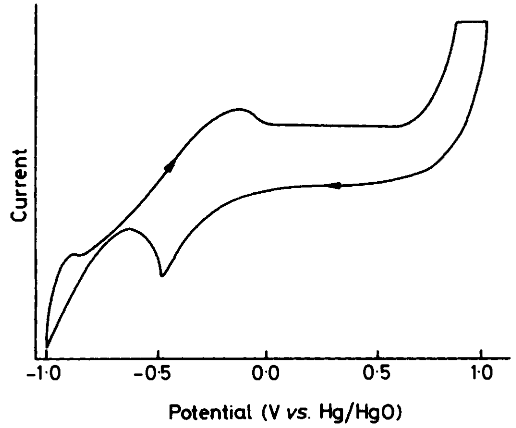

Figure 1 *Cyclic voltammogram of aluminium metal in* 0.5M NaOH *solution for a sweep rate of* 0.03125 V s^{-1} *and a sweep limit of* -1.0 *to* $+1.0$ V (vs. Hg/HgO *reference electrode*) (H. Al-Bayati and P. M. A. Sherwood, to be published)

potential is decreased the current rises sharply due to oxide thinning and then falls before hydrogen evolution, indicated by the cusp on the extreme left-hand side of Figure 1. Figure 2 shows the spectra seen from aluminium electrodes polarized in 1M sodium hydroxide solution to various potentials for five minutes. The spectra clearly show the presence of both aluminium metal (the narrow peak on the right-hand side) and aluminium oxide (the broader peak on the left-hand side) in all cases except for the -0.25 V case. At -0.75 V aluminium metal has a thin oxide layer on the surface, thinner than the air-formed oxide film. The amount of oxide rises at -0.5 V and finally at -0.25 V the oxide film is so thick that the underlying metal is obscured. The spectra show the aluminium 2*p* region, which is in fact two overlapping spin orbit doublets (area ratio 1:2). In many cases the spin orbit doublets are sufficiently widely separated that each component in the spectrum gives two clear peaks. This example illustrates a simple system, which nevertheless is an important system in chemistry and materials science. The corrosion resistance of aluminium is highly relevant in many applications and we are currently investigating aluminium and its alloys in a number of electrolytes.

The initial state of the electrode is of great importance in its subsequent electrochemical behaviour. Many electrochemists clean their electrodes by chemical methods. When such cleaned electrodes are investigated by XPS, however, one sometimes finds that the electrode surface is oxidized. Thus a rhodium metal electrode that has been cleaned by argon-ion etching[33] shows only a spin orbit doublet peak (now separated by some 5 eV with intensity ratio of 1 : 1.5) for the metal. If this electrode is now immersed in concentrated sulphuric acid, oxide is formed (Figure 3). When this electrode is polarized to 0.3 V (which might

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[33] H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc.*, *Faraday Trans. 1*, 1984, **80**, 2867.

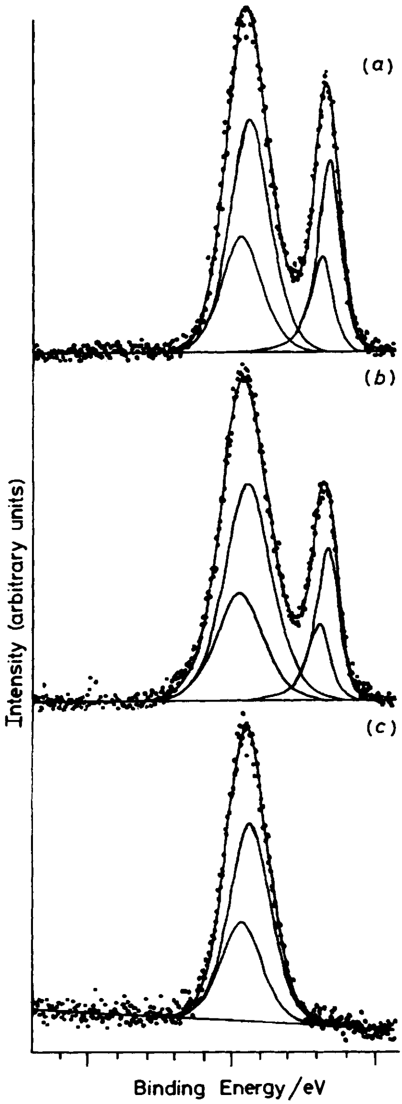

Figure 2 *Aluminium 2p region after steady-state polarization for five minutes in* 1M NaOH *solution* (a) *after polarization to* −0.75 V (vs. Hg/HgO *reference electrode*), (b) *after polarization to* −0.5 V, (c) *after polarization to* −0.25 V
(H. Al-Bayati and P. M. A. Sherwood, to be published)

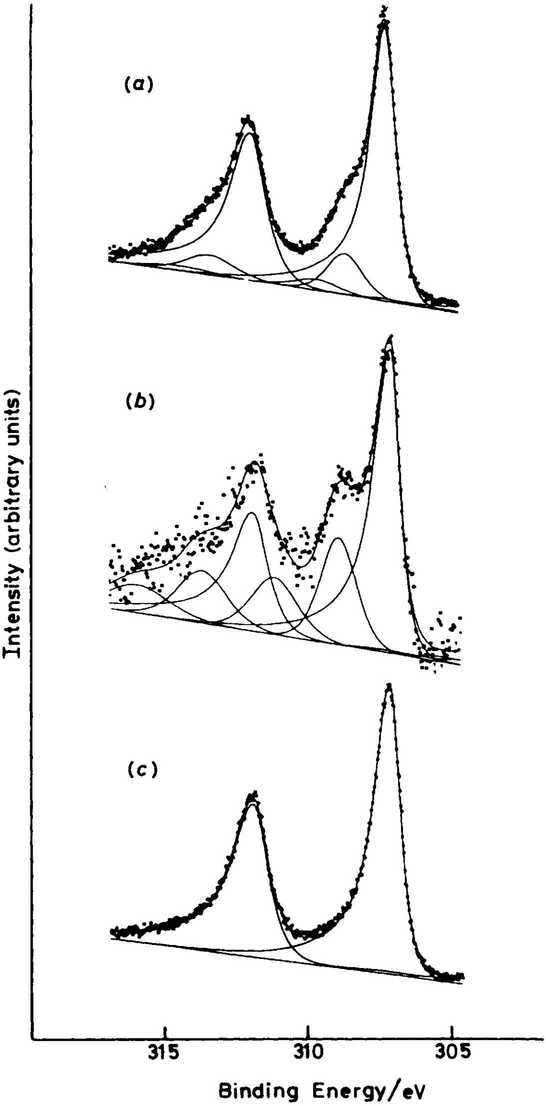

Figure 3 *Rhodium* 3*d region showing the effect of pre-treatment of a rhodium metal electrode* (a) *etched and then immersed in concentrated sulphuric acid.* (b) *after polarization at* 0.3 V *for* 15 min (c) *etched and polarized at* 0.3 V *for* 15 min
(Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2867)

be expected to reduce any oxide) there is actually an increase in the amount of oxide formed. XPS can be used to monitor electrodes cleaned by methods such as argon-ion etching *in vacuo* before any electrochemistry is carried out as an important check on surface purity. The importance of a really clean electrode surface will now be discussed in more detail

5 Some Fundamental Points

A. The Electrode Surface.—Very careful electrode surface preparation and cleaning are thus seen to be valuable features of surface science techniques. Hubbard[34] has given a very complete discussion of the electrochemistry of well-defined surfaces. The ultimate well-defined surface consists of a single crystal electrode prepared under ultra-high vacuum conditions with a surface crystallography that has been analysed by LEED, and a surface chemistry that has been monitored by XPS and other surface sensitive techniques. This requires that the crystal first be oriented, using *X*-ray diffraction methods to check the orientation,[35]then that the crystal be suitably cleaned. The argon-ion etching method discussed above is suitable for polycrystalline materials and many single crystal metal surfaces, but may render some single-crystal compound surfaces amorphous.[36]

Single crystal studies of this type[37] are very important in trying to obtain a complete understanding of the solid–electrolyte interface. Most of the experiments have been carried out with single crystal metals, mainly Pt(100), Pt(111), Au(100), Au(111), and Rh(111) surfaces (*e.g.* 38–56).

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[34] A. T. Hubbard, *Acc. Chem. Res.*, 1980, **13**, 177.

[35] E. A. Wood, 'Crystal Orientation Manual', Columbia University Press, New York, 1963.

[36] P. M. A. Sherwood, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 201.

[37] A. T. Hubbard, *J. Vac. Sci. Technol.*, 1980, **17**, 49.

[38] R. M. Ishikawa and A. T. Hubbard, *J. Electroanal. Chem.*, 1976, **69**, 317.

[39] J. A. Schoeffel and A. T. Hubbard, *Anal. Chem.*, 1977, **49**, 2330.

[40] T. E. Felter and A. T. Hubbard, *J. Electroanal. Chem.*, 1979, **100**, 473.

[41] A. T. Hubbard, J. L. Stickney, S. D. Rosasco, M. P. Soriaga, and D. Song, *J. Electroanal. Chem.*, 1983, **150**, 165.

[42] J. L. Stickney, S. D. Rosasco, D. Song, M. P. Soriaga, and A. T. Hubbard, *Surf. Sci.*, 1983, **130**, 326.

[43] G. A. Garwood, jun. and A. T. Hubbard, *Mater. Sci. Res.*, 1983, **15**, 91.

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[45] A. Wieckowski, S. D. Rosasco, B. C. Schardt, J. L. Stickney, and A. T. Hubbard, *Inorg. Chem.*, 1984, **23**, 565.

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[49] W. E. O'Grady, M. Y. C. Woo, P. L. Hagans, and E. Yeager, *J. Vac. Sci. Technol.*, 1977, **14**, 365.

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[51] W. E. O'Grady, M. Y. C. Woo, P. L. Hagans, and E. Yeager, in 'Electrode Materials and Processes for Energy Conversion and Storage', ed. J. D. E. McIntyre, S. Srinivasan, and F. G. Will, The Electrochemical Society, Princeton, N.J., 1977, p. 172.

[52] P. L. Hagans, A. Homa, W. E. O'Grady, and E. Yeager, *Report*, 1979, TR-51, Order No. AD-AD-A082822.

[53] P. N. Ross, jun., *J. Electroanal. Chem.*, 1977, **76**, 139.

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[55] M. Peuckert, F. P. Coenen, and H. P. Bonzel, *Surf. Sci.*, 1984, **141**, 515.

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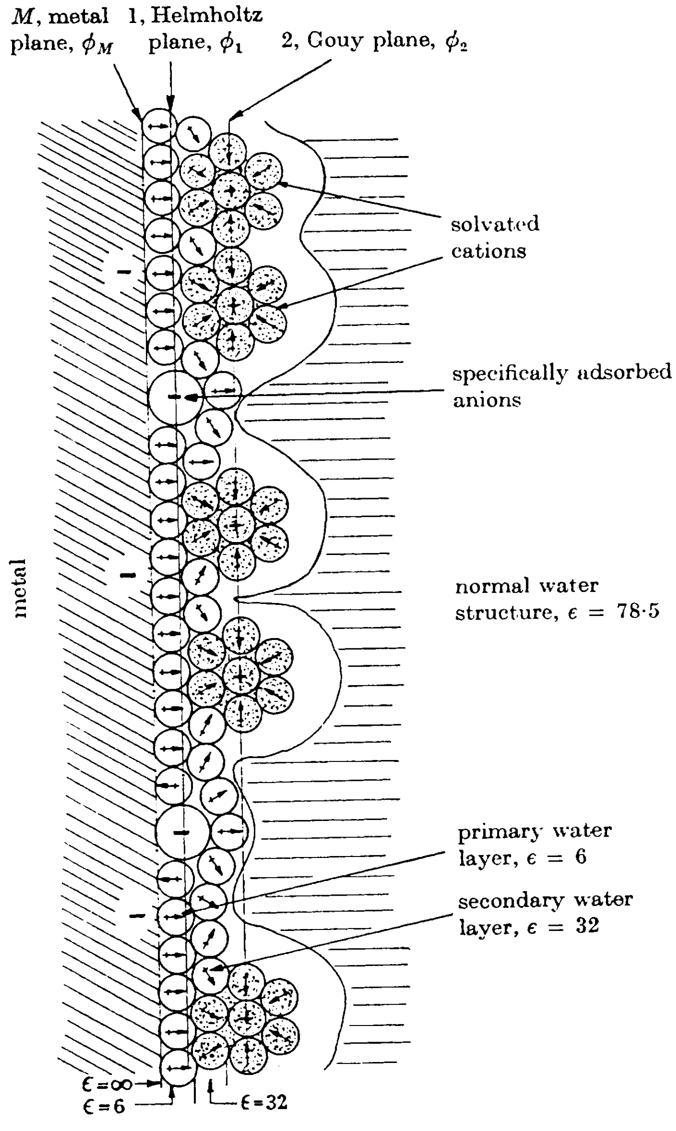

Figure 4 *Model for the electrochemical double layer*
(Reproduced by permission from J. O'M. Bockris, M. A. Devanathan, and K. Muller, *Proc. R. Soc. London, Ser. A*, 1963, **274**, 55)

B. The Electrochemical Double Layer.—The central problem of all *ex situ* methods is that the electrode must be removed from the electrolyte and placed in the high vacuum conditions of the spectrometer. When an electrode is in solution the solid–electrolyte surface interface can be considered to consist of the electrochemical double layer, often called the interphase. This double layer, which is only around a nanometre in thickness, is considered as an inner layer of water molecules with an orientation and structure dependent upon the interaction with the electrode surface and the electric field, and an outer layer of solvated cations. In addition, specifically adsorbed anions may be found in direct contact with the electrode surface. The line of centres of the specifically adsorbed anions is known as the inner Helmholtz plane, and the line of centres of the solvated cations is known as the outer Helmholtz plane. The situation is illustrated in Figure 4. There is a potential difference across the double layer of around a volt, but owing to the small width of the interphase there is a large potential gradient (of the order of 10^7 V cm^{-1}) across the layer. The potential distribution becomes increasingly more complex as the electrolyte concentration increases.

Any attempt to study the surface of an electrode after an electrochemical process has taken place would ideally be carried out if the double layer could be carried intact into the surface spectrometer. As a starting point for a study of the surface and interphase, the interaction of the surface with electrolyte vapour should be investigated. Such a study has been carried out by Ishikawa and Hubbard[38] for water, Garwood and Hubbard[43] for polar solvents and other electrolytic materials such as I_2 and hydrogen halides, and by Schoeffel and Hubbard[57] for a range of organic and other solvents on single-crystal platinum surfaces under ultra-high vacuum (UHV) conditions. The latter study was used to calibrate Auger spectroscopy for adsorbed layers. Ordered solvent layer structures are commonly found for certain solvent coverages. Experiments such as this have to be carried out with care to prevent accumulation of solvents on the surfaces of the vacuum system. One very valuable feature of such an approach is that an adsorbed electrolyte layer formed on the surface tends to inhibit or eliminate the adsorption of other species onto the electrode surface, hence allowing transfer of an uncontaminated electrode from the vacuum system into the electrolyte of an electrochemical cell. There have been a number of experimental and theoretical studies of the adsorption of water onto metal surfaces. The O1*s* core region binding energy of water adsorbed on metals[58–70] is in the region of 529—536 eV depending upon the temperature

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[69] P. N. Norton, *J. Catal.*, 1975, **36**, 211.

[70] R. Kotz, H. Neff, and S. Stucki, *J. Electrochem. Soc.*, 1984, **131**, 72.

and nature of the surface. At room temperatures and above, water normally dissociatively absorbs. This leads to a peak in the range 529 to 531 eV resulting from oxide formation or the formation of chemisorbed oxygen, though some intensity in the hydroxide region may also be seen (around 531—533 eV). Oxygen may chemisorb molecularly or atomically, depending upon the conditions and the nature of the metal surface. The former situation gives rise to a peak in the range 532—533 eV, but this is usually lost by desorption and dissociation at temperatures below room temperature. In fact Benndorf, Nobl, and Thieme[66] have shown that water will adsorb to an oxygen precovered Ni(110) surface to give two O1*s* peaks at 530.8 and 532.8 eV at 300 K which may be due to hydrogen bonded $O_{ads} \cdots HOH$ species on the surface. This situation might be a general feature on 'messy' surfaces where a peak around 532—533 eV may be seen in the O1*s* region, together with a peak around 531—532 eV. At lower temperatures (below 175 K) peaks due to oxide, hydroxide (around 531—533 eV), and ice (around 533—536 eV) can be seen, the ice peaks tending to predominate at high coverage and low temperatures. At low temperature, in the presence of oxygen, the water may form the $O_{ads} \cdots HOH$ species as discussed above[66] or may dissociate to form two adsorbed –OH species.[67] The binding energy ranges for the O1*s* peaks given above take into account real variations, and variations due to different methods of calibration. Further information is provided about this complex situation by EELS studies. Thus Ibach and Lehwald,[71] using EELS, have found that the structure depends upon coverage for water adsorbed on Pt(100) at 150 K. For adsorbed multilayers the situation represents that of the highly hydrogen-bonded ice, but for submonolayer quantities below one half of a monolayer water forms clusters containing three different forms of hydrogen. There are –OH vibrations due to free –OH groups in addition to vibrations due to hydrogen bonding between water molecule clusters and vibrations due to hydrogen bonding to the metal. There is also oxygen lone-pair bonding to the surface. Such a situation could be explained by a cyclic hexamer cluster which can tilt with respect to the surface to accommodate both hydrogen bonding and oxygen lone-pair bonding. Similar results were found by Sexton[72] for water adsorbed on Pt(111) at 100 K. A detailed UPS study[73] of the adsorption of water on various metal surfaces at 160 K and below gives some similar results, suggesting single-adsorbed water molecules at temperatures close to the desorption point (160 K), partially hydrogen-bonded water for coverages of a monolayer or less, and fully hydrogen-bonded water with an ice-like structure at low temperatures and several monolayers coverage. These results support the double-layer situation in Figure 4 where the water molecules may be oriented differently to the surface (corresponding to oxygen and hydrogen bonded forms). Model calculations[74] suggest that the equilibrium H–O–H bond angle does not change on water adsorption, in contrast to experimental measurements.[75]

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[71] H. Ibach and S. Lehwald, *Surf. Sci.*, 1980, **91**, 187.

[72] B. A. Sexton, *Surf. Sci.*, 1980, **94**, 435.

[73] D. Schmeisser, F. J. Himpsel, G. Hollinger, B. Reihl, and K. Jacobi, *Phys. Rev. B*, 1983, **27**, 3279.

[74] S. Holloway and K. H. Bennemann, *Surf. Sci.*, 1980, **101**, 327.

[75] T. E. Madey and J. T. Yates, *Surf. Sci.*, 1977, **51**, 77.

Once the electrode has been transferred from the vacuum system of the surface spectrometer into the electrolyte of the electrochemical cell, by a suitable transfer method (*in situ* cells will be discussed below) that attempts to minimize electrode surface contamination, the major problem of the *ex situ* methods must be considered. This problem is the transfer of the electrode after electrochemical treatment from the electrolyte into the surface spectrometer. It has already been pointed out that ideally one would like the double layer to remain intact in the vacuum system so that the electrode surface remains the same in the vacuum system as its state in solution. There has been considerable debate as to just how much if any of the double layer is retained in the spectrometer. Clearly one would be surprised if the double layer, which consist largely of water, were to be retained in a full UHV system. Of course water is difficult to remove from a vacuum system, and, to achieve UHV conditions, contaminants (including water) are 'baked off' the walls of the vacuum system. Although ideally surface spectroscopies are carried out under UHV conditions, the achievement of those conditions might well destroy the double layer. Thus Neff and Kotz[76] have shown that the double layer can be removed from electrochemically treated gold electrodes by examining the UPS spectrum (using HeII radiation under UHV conditions) of the electrode. No trace of the characteristic adsorbed water peaks were found in the spectrum. Other workers[77–79] have suggested that the double layer can be routinely removed from its electrolyte essentially unchanged, and then be subjected to detailed *ex situ* analysis. Neff and Kotz[76] have criticized the validity of some of the measurements upon which this conclusion is based. However, while the water in the double layer may or may not be present, it appears that the ions of the double layer are retained on the electrode surface. Ishikawa and Hubbard[38] find that LEED studies of a Pt(100) surface after exposure to liquid water shows a layer of chemisorbed water on the surface as well as oxygen intensity in the Auger spectrum. Certainly if the electrode surface is studied at low pressures outside the UHV range the author finds that water vapour can be seen to be strongly held as recorded by a mass spectroscopic investigation of the vacuum system over a considerable time period (several hours), loss of water being noted when the sample is heated. Also one needs to consider that water may be more strongly retained by some surfaces (*e.g.* those that are appreciably oxidized to give a porous oxide) than others. In the author's view this area must be treated with considerable care, with a careful note of the vacuum and temperature conditions, and the careful attempt to monitor other experimental evidence before coming to firm conclusions. Thus one might assume that all the O1*s* XPS signal was due to surface species on the electrode, though if any water from the double layer were present the results would be invalidated. A good example of bringing other evidence to bear is found in a study of the oxide film on Pt(111) oxidized by polarizing to 3 V [*vs.* standard hydrogen reference

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[76] H. Neff and R. Kotz, *J. Electroanal. Chem.*, 183, **151**, 305.

[77] W. N. Hansen, D. M. Kolb, D. L. Rath, and R. Wille, *J. Electroanal. Chem.*, 1980, **110**, 369.

[78] W. N. Hansen, *J. Electroanal. Chem.*, 1983, **150**, 133.

[79] D. M. Kolb, D. L. Rath, R. Wille, and W. N. Hansen, *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 1108.

electrode (SHE)] for 16 hours. An EELS study combined with XPS[80] shows that the oxide film is $Pt(OH)_4$ under UHV conditions. The O1*s* spectrum shows the presence of OH^- at 531 eV and the EELS study shows Pt–OH vibrations. Further evidence may be obtained by monitoring thermal decomposition (or the lack of it) of the film (*e.g. refs.* 80 and 70).

6 Anaerobic Transfer Electrochemical Cells

Various methods have been used to attempt to reduce or eliminate atmospheric oxidation or contamination in the transfer of the electrode from the electrochemical cell to the spectrometer. In addition, as discussed above, consideration must be given to operating under conditions where the electrode has an uncontaminated surface before any electrochemistry is carried out.

The simplest approach is to transfer the electrode in the air in the hope the surface is sufficiently inert to be unaffected by the atmosphere. Even in the case of inert surfaces, such an approach may lead to the collection of contaminants on the surface. Such a contamination layer may be unimportant, but could seriously inhibit the performance of the surface analytical technique by causing a severe loss of intensity of signals arising from the sample surface species of interest. Highly surface sensitive techniques such as SIMS are especially prone to such problems. The transfer method may be refined by attempting to protect the sample's surface after removal from the cell by means such as, rapid transfer to keep the surface covered with electrolyte (*vide supra*) (*e.g. ref.* 80), or rapid transfer after immersing the surface in an appropriate oxygen scavenger. This latter approach has been used by Sukhotin *et al.*[81] who first replaced the electrolyte after electrochemistry by deoxygenated water and then liquid hydrazine. The sample was then brought into the air and the excess liquid removed by filter paper. The electrode surface now wetted with a thin film of hydrazine was then inserted into the high vacuum of the spectrometer when the hydrazine evaporated off the electrode surface. The idea is that the hydrazine removes oxygen:

$$N_2H_4 + O_2 \longrightarrow 2H_2O + N_2$$

This method allowed a chromium metal sample to be abraded under hydrazine and be studied by XPS to reveal no signal due to surface Cr_2O_3 seen on the untreated metal sample. Further electrochemical experiments using the hydrazine transfer method indicated that Cr_2O_3 peaks were due to electrochemical rather than atmospheric oxidation.

The simplest method for transfer using environmental control is to place the electrochemical cell in a glove bag or glove box and carry out the electrochemistry under an atmosphere of deoxygenated nitrogen gas. Transfer to the spectrometer can be carried out using appropriate containers and glove bags and boxes attached

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[80] M. Peuckert and H. Ibach, *Surf. Sci.*, 1984, **136**, 319.

[81] A. M. Sukhotin, M. N. Shlepakov, Yu. P. Kostikov, and V. S. Strykanov, *Elektrokhimiya*, 1982, **18**, 285 (*Soviet Electrochemistry*, 1982, **18**, 255).

to the spectrometer (*e,g. refs.* 82 and 83).

The best approach is to design a system where the electrochemical cell is physically attached to the vacuum system allowing passage of an electrode with a clean surface from the spectrometer after cleaning (*e.g.* argon-ion etching) and passage of the electrode back into the spectrometer after electrochemical treatment. Various groups have designed such cells for use with XPS and other surface spectrometers. The cells have sometimes been of conventional size and in other cases have been of very small size with the electrolyte solution occupying a very small volume. This approach minimizes the amount of trace impurities in the solution that might contaminate the electrode. Miniature cells are not, however, appropriate to studies where high current densities are needed such as in gas evolution or corrosion reactions.

Complex glove-box systems have been constructed by a number of workers. Thus Hammond and Winograd[84] have built miniature cells into a glove box attached to the spectrometer. McIntyre and co-workers[85] have used a similar arrangement with a standard three-compartment, three-electrode cell. Oxygen contamination in such a system was kept to less than 50 $\mu l\ l^{-1}$. Neff, Foditsch, and

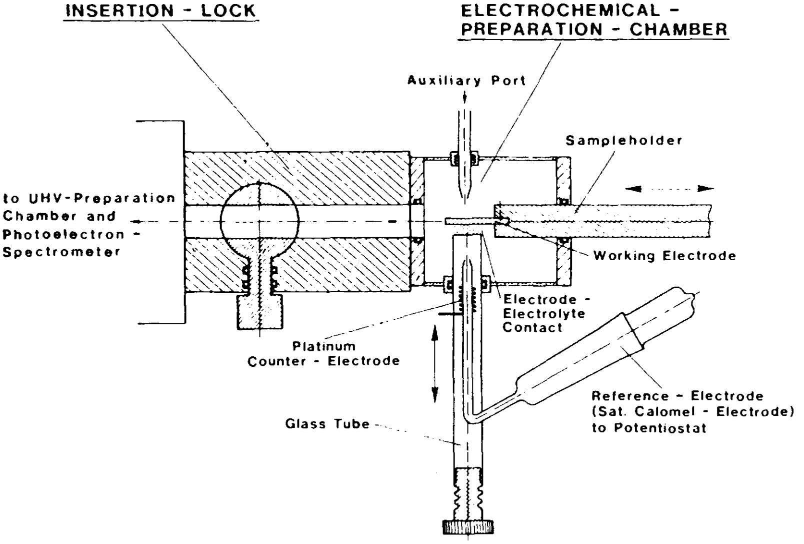

Figure 5 *Schematic diagram of electrochemical preparation chamber in combination with a fast insertion lock*
(Reproduced by permission from N. Neff, W. Foditsch, and R. Kotz, *J. Electron Spectros. Relat. Phenom.*, 1984, **33**, 171)

[82] T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 327.

[83] T. E. Pou, O. J. Murphy, V. Young, J. O'M. Bockris, and L. L. Tongson, *J. Electrochem. Soc.*, 1984, **131**, 1243.

[84] J. S. Hammond and N. Winograd, *J. Electroanal. Chem. Interfacial. Electrochem.*, 1977, **78**, 55.

[85] N. S. NcIntyre, S. Sunder, D. W. Shoesmith, and F. W. Stanchell, *J. Vac. Sci. Technol.*, 1981, **18**, 714.

Kotz[86] have constructed an electrochemical cell in the insertion lock of the spectrometer (Figure 5). The arrangement consists of a three-electrode design where the working electrode is attached to the insertion shaft, and the counter-electrode and the reference electrode are attached *via* a glass tube at the bottom of the lock. The lock is overpressured with high purity argon to keep out the atmosphere. The electrolyte can be added *via* an auxiliary port at the top of the lock to give a meniscus between the solution in the glass tube and the working electrode. Lowering the glass tube breaks contact of the electrolyte with the electrode, which may then be studied in the spectrometer.

A number of workers have constructed electrochemical cells that are directly associated with the vacuum system of the surface-sensitive technique. One of the earliest designs was reported by Revie, Bockris, and Baker[87] for a study of the passive film on iron by Auger spectroscopy. This particular design has the electrochemical cell in a chamber (which can be evacuated) connected to the vacuum system of the spectrometer by a UHV valve, the electrode being mechanically transferred from the cell to the spectrometer. Hubbard and co-workers[38,41,88] have developed a system for use with a combined LEED and Auger system. Their design[38,41] used a miniature cell (a thin layer cell) shown in Figure 6. The single crystal sample, held at the end of a sample manipulator, was arranged so that it was in contact with the ends of a pair of Pyrex glass capillaries. The thin layer cell was constructed by sealing the tips of the capillaries together and forming a circular recess 0.02 mm deep and 5 mm wide in the tip so that the sample and the cavity formed a thin layer cavity. The outside of the capillary (except the tip) were coated with platinum and earthed to prevent charging during LEED–Auger experiments. Electrolyte was introduced from microburets using miniature valves and fittings made of inert materials such as Teflon, Kel-F, platinum, and glass. The reference electrode and counter electrodes were located outside the vacuum system (see the diagram in *ref.* 38). During electrochemical experiments the chamber was brought to atmospheric pressure with pure argon. The sample chamber was separated from the LEED optics by an isolation valve and both chambers were separately pumped. Pressures of 2×10^{-9} Torr could be achieved after evacuation for about five minutes. Of course such miniature cells present much less of a problem for evacuation after electrochemistry since the volume of electrolyte that must be removed is much less than in a conventional cell. Figure 7 shows a recent schematic diagram of the LEED–electrochemistry instrument[41] where the electrochemical cell is separated from the sample chamber *via* gate valves. Yeager and his co-workers[19,49,89] have constructed a LEED–Auger system incorporating a thin-layer electrochemical cell. The system consists of two UHV chambers, one housing the LEED–Auger spectrometer and the other the thin-layer electrochemical cell, the two chambers being separated by an

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[86] H. Neff, W. Foditsch, and R. Kotz, *J. Electron Spectros. Relat. Phenom.*, 1984, **33**, 171.

[87] R. W. Revie, J. O'M. Bockris, and B. G. Baker, *Surf. Sci.*, 1975, **52**, 664.

[88] A. T. Hubbard, R. M. Ishikawa, and J. Katekaru, *J. Electroanal. Chem.*, 1978, **86**, 271.

[89] E. Yeager. W. E. O'Grady, M. Y. C. Woo, and P. Hagans, *J. Electrochem. Soc.*, 1978, **125**, 348.

isolation valve. Samples can be moved between the two chambers by a manipulator which can be cooled by liquid nitrogen. Samples can be taken from this manipulator into the electrochemical cell by another manipulator operating at right angles to the first. The design is shown in Figure 8. An important feature of the design is the combination of the counter and reference electrode as a single palladium–hydrogen alloy electrode with a carefully cleaned (by argon-ion etching) surface kept under a hydrogen atmosphere before use. Electrochemical experiments are carried out with the cell under an atmosphere of pure argon. Electrolyte is placed on the combined counter-reference electrode and the electrode being studied is then brought into contact with the electrolyte to form the thin-layer cell. Wagner and Ross[54,90] report a LEED apparatus connected to a miniature electrochemical cell in two separate vacuum chambers. Olefjord and Vannerberg[91] and Elfstrom and Olefjord[92] have attached an electrochemical cell *via* an isolation valve to a reaction chamber and have fitted this to the spectrometer with a transfer system which allows the sample to be moved from the cell to the UHV chamber under an inert gas. A similar approach has been taken by Miller and co-workers[93]

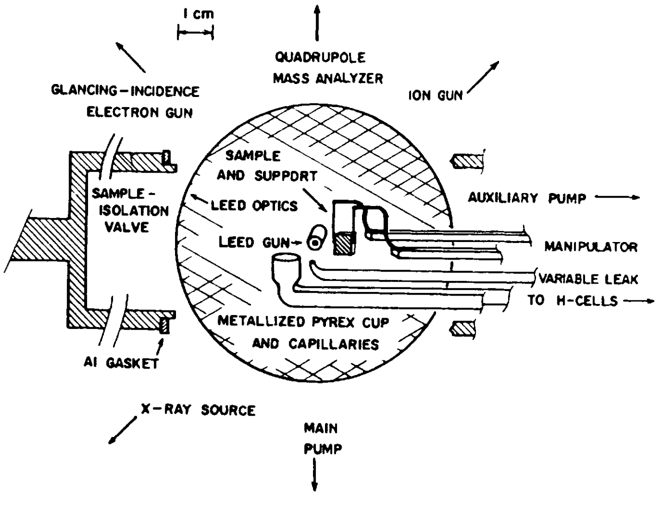

Figure 6 *Single-crystal electrode and electrolysis compartment of a LEED–electrochemistry system, as seen through the viewport of the vacuum system*
(Reproduced by permission from A. T. Hubbard, R. M. Ishikawa, and J. Katekaru, *J. Electroanal. Chem.*, 1978, **86**, 271)

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[90] F. T. Wagner and P. N. Ross, jun., *J. Electrochem. Soc.*, 1983, **130**, 1789.

[91] I. Olefjord and N. G. Vannerberg, *Scand. Corros. Congr. (Proc.), 7th*, 1975, 434.

[92] B. O. Elfstrom and I. Olefjord, *Phys. Scr.*, 1977, **16**, 436.

[93] C. W. Miller, J. R. Fagan, D. H. Karweik, and T. Kuwana, *Appl. Surf. Sci.*, 1981, **9**, 214.

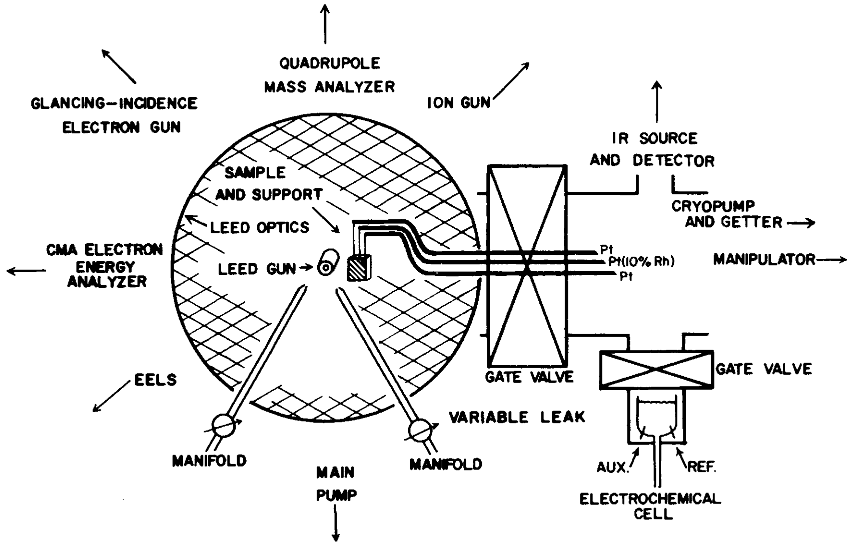

Figure 7 *Schematic diagram of LEED–electrochemistry instrument*
(Reproduced by permission from A. Wieckowski, S. D. Rosasco, B. C. Schardt, J. L. Stickney, and A. T. Hubbard, *Inorg. Chem.*, 1984, **23**, 565)

who have produced a system which allows both electrochemical and other sample treatment in various ways. Thus radio-frequency plasma surface modification can be carried out in one chamber, and chemical and electrochemical treatment in another chamber, with transfer in a UHV system. Similar systems have been used for transfer between different types of spectrometer and an electrochemical cell.[94]

The author and his co-workers[95,96] have constructed an apparatus consisting of a high-vacuum chamber attached to the spectrometer and containing a glass electrochemical cell of conventional size. Such a full sized cell can be used for the full range of electrochemical reactions, though, of course, much more electrolyte must be handled and removed from the vacuum system before evacuation. In common with the cells described above the design allows the surface of the electrode to be analysed and prepared before any electrochemistry is carried out. The electrochemical cell is kept under vacuum except when liquid is about to be added, when it is filled with deoxygenated nitrogen gas.

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[94] T. Fleisch, A. T. Shepard, T. Y. Ridley, W. E. Vaughn, N. Winograd, W. E. Baittinger, G. L. Ott, and W. N. Delgass, *J. Vacuum Sci. Technol.*, 1978, **15**, 1756.

[95] R. O. Ansell, T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **98**, 69.

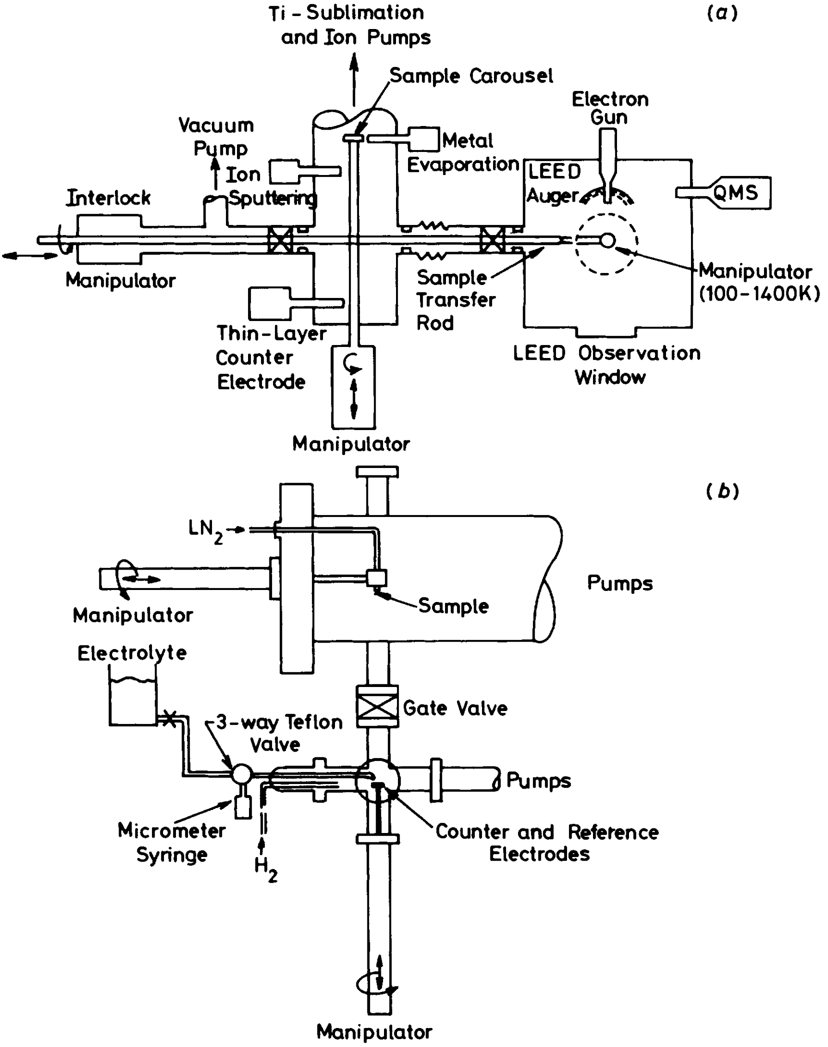

Figure 8 *Schematic diagram of LEED–Auger–electrochemistry system is shown in* (a), *with the details of the solution injection and thin-layer cell system shown in* (b)
(Reproduced by permission from W. E. O'Grady, M. Y. C. Woo, P. L. Hagans, and E. Yeager, *J. Vac. Sci. Technol.*, 1977, **14**, 365)

This cell has been used to examine molybdenum electrochemistry and the oxidation of molybdenum.[96] It is found that molybdenum metal (etched to remove

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[96] R. O. Ansell, T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **98**, 79.

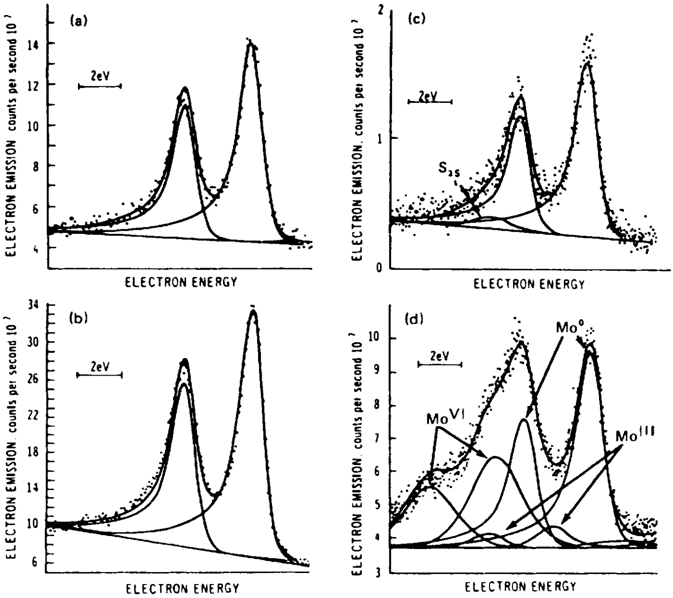

Figure 9 *Molybdenum 3d region for molybdenum metal subjected to various surface treatments.* (a) *Argon-ion etched metal,* (b) *etched metal exposed to oxygen* (1 atm *for* 10 min). (c) *etched metal exposed to deoxygenated dilute sulphuric acid in an anaerobic cell, and* (d) *etched metal exposed to oxygenated water*
(Reproduced by permission from P. M. A. Sherwood in 'Contemporary Topics in Analytical and Clinical Chemistry', Vol. 4, ed. D. M. Hercules, G. M. Hieftje, L. R. Snyder, and M. A. Evenson, Plenum, Chapter 7, 1982, pp. 205—293)

any oxide) shows no surface oxidation when exposed to dry oxygen at room temperature, even when the spectra are run at low take-off angles to improve surface sensitivity. When the etched metal is exposed to deoxygenated sulphuric acid solution or water in the cell very little oxidation occurs, but when oxygenated water is used considerable oxidation results. The spectra (Figure 9*a*—*c*) are fitted to molybdenum metal, together in one case with a single sulphur 2*s* peak due to adsorbed sulphate ions. In the oxidized case (Figure 9*d*), there are two peaks for each different molybdenum species (spin-orbit splitting with an intensity ratio of 1:1.5 and a fixed separation), the six peaks correspond to molybdenum metal, Mo^{III} oxide, and Mo^{VI} oxide. It is possible to attempt to fit Figure 9*d* to four peaks rather than six peaks. Statistical analysis of these two fits to the same data indicate that the χ^2 value falls by 20% when Mo^{III} is included in the fit, though as expected the errors (95% confidence limits) in position and width for the Mo^{III} peaks are much greater than those of the other molybdenum peaks.

The cell has been completely redesigned to allow easier use and incorporates additional features. For example, electrodes of any geometry within about

5 mm × 15 mm cross section can be studied, including fibre and single-crystal electrodes. The cell, constructed of glass, can be easily removed from the apparatus to enable cleaning (essential for accurate electrochemistry), and the admission and expulsion of electrolyte is easier to carry out. The apparatus can be used to transfer samples between different surface analytical methods. Thus when used in conjunction with SIMS complementary information can be obtained.[97,98] The *in situ* arrangement substantially reduces the amount of hydrocarbon found on electrodes transferred in air and results in less complex and more easily interpreted SIMS spectra. SIMS also gives valuable information about hydrogen-containing species (*vide infra*).

7 Non-aqueous Electrolyte Studies

A. Molten Salt Systems.—There have been a number of studies of electrode surfaces in molten salt electrolytes at high temperature. Such studies provide valuable information about the electrochemistry of the systems. The corrosion of the electrode by the melt must be examined, and the problem of the dissolution of some species in the melt must be considered. In noble metal systems such as platinum[99,100] oxidation of the metal occurs. In systems such as tungsten oxidation occurs, but there are substantial differences between the aqueous and molten salt electrolyte cases. Thus in aqueous nitrate electrolytes W^{VI} oxide is formed,[101] with a thickness that increases with anodization voltage. In molten equimolar sodium and potassium nitrate at 230 °C, lower oxidation-state tungsten oxides are found in addition to W^{VI} oxide, W^{IV} and W^{V} being formed under suitable conditions.[102] The electrode examined in molten salts is tungsten(VI) oxide rather than the metal.

B. Solid Electrolyte Systems.—Electrochemical cells using solid electrolytes have the advantage that they can be examined completely under UHV conditions without any of the transfer and associated problems discussed above. Therefore, in this special case, XPS and other surface-science techniques are genuinely *in situ* methods for examining the electrode surface.

A number of studies have been carried out that have used the high control of the electrochemical experiment to form oxide films. Chemical oxidation experiments (of which a very large number have been studied by surface analytical techniques), which involve the exposure of a pure metal surface at a known temperature to oxygen gas of known dosage, suffer from difficulties in controlling the reaction, making the initial stages difficult to observe. Another advantage of the electro-

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[97] D. M. Hercules, P. M. A. Sherwood, and I Welsh, to be published.

[98] J. G. Helliwell and P. M. A. Sherwood, *J. Microscopie Spectros. Electron.*, 1983, **8**, 321.

[99] L. Sabbatini, P. G. Zambonin, E. Desimoni, and B. De Angelis, *Chim. Ind. (Milan)*, 1977, **59**, 493.

[100] L. Sabbatini, F. Palmisano, P. G. Zambonin, and B. De Angelis, *Ann. Chim. (Rome)*, 1978, **67**, 525.

[101] T. A. Carlson and G. E. McGuire, *J. Electron Spectros. Relat. Phenom.*, 1972/1973, **1**, 161.

[102] L. Sabbatini, P. M. A. Sherwood, and P. G. Zambonin, *J. Electrochem. Soc.*, 1983, **130**, 2199.

chemical approach is that one can perform repeated oxidation–reductions of the metal–metal-oxide films reversibly in the vacuum system, without the need to expose the sample to oxygen gas or a reducing agent. Appropriate systems for electrochemical oxidation need the equilibrium pressure of oxygen for metal-oxide formation at high temperature to be in the range of pressure in the vacuum system, and the oxides should be formed at a reasonable rate. Further the vapour pressures of the metal and oxide should be very low at the temperature studied, so that the vacuum system can be operated under UHV conditions. The electrochemical experiments generally involve an electrochemical cell of the type:

$$\begin{array}{ccc} \text{Oxygen}(p_1),\text{Metal} & | \text{ Solid Electrolyte } | & \text{Metal}',\text{Oxygen}(p_2) \\ \text{Metal Oxide} & & \text{Metal}' \text{ Oxide} \end{array}$$

where one of the metal/metal oxides is the system of interest, and the other is a metal/metal oxide reference electrode and where p_1 and p_2 represent the oxygen partial pressures at the two different electrodes.

The solid electrolyte used has often been an oxygen-ion conducting electrolyte based on zirconia (ZrO_2). Such electrolytes are used for oxygen sensors, high-temperature fuel cells, and oxygen pumps. Stout and co-workers[103,104] have used Auger[103] and Auger–XPS[104] to study iron oxides formed electrochemically at 850 °C. Their cell (Figure 10) consisted of a cylindrical cap of zirconia stabilized with calcium oxide, with an iron electrode vapour-deposited to a thickness of about one micron on the flat end of the cap. The reference electrode was made up of copper and cuprous oxide (Cu_2O) powder pressed into the cap and held by a copper cylinder. The whole cell was heated by a concentric cylinder heater. Three different types of iron oxide were identified, namely wustite (Fe_xO), magnetite (Fe_3O_4), and haematite (α-Fe_2O_3) which had Fe $^2P_{3/2}$ binding energies of 709.5, 710.4, and 710.6 eV respectively. The oxygen–iron intensity ratios could also be used to identify the oxides. The counter electrode consisted of a platinum foil spot-welded to a platinum–platinum–rhodium thermocouple. Yang and O'Grady[105] have studied the electrochemical oxidation of iron and nickel using a yttria-stabilized (8 wt.%) zirconia electrolyte in an *in situ* cell (Figure 11) with a metal–metal oxide reference electrode. They measured the rate of oxidation of nickel at 500 °C and they also obtained cyclic voltammograms for the nickel film in the UHV cell (Figure 12). The cyclic voltammogram shows separations between the peaks consistent with oxide formation which is also seen in the XPS spectrum. More than one peak is seen on both the anodic and cathodic sides of the voltammogram due to the temperature discontinuities caused by non-uniform heating. Watanabe and Kuwana[106] examined the oxidation of copper using a similar cell to that in Figure 10. The experiment allowed them to prepare known non-stoicheiometric compositions of cuprous oxide by partial oxidation. XPS studies showed that the Cu2*p* and O1*s* binding energies were independent of the

[103] D. A. Stout, G. Gavelli, J. B. Lumsden, and R. W. Staehle, *Surf. Sci.*, 1977, **69**, 741.

[104] D. A. Stout, G. Gavelli, J. B. Lumsden, and R. W. Staehle, *Appl. Surf. Anal.*, ASTM STP 699, 1980, 42.

[105] C. Y. Yang and W. E. O'Grady, *J. Vac. Sci. Technol.*, 1982, **20**, 925.

[106] N. Watanabe and T. Kuwana, *Anal. Chem.*, 1980, **52**, 1657.

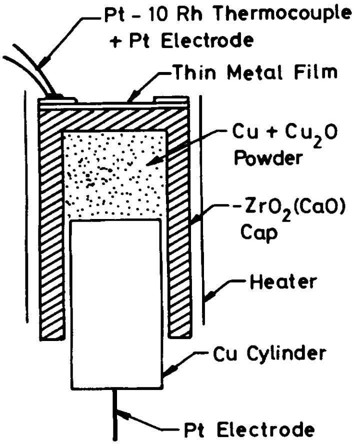

Figure 10 *Solid state electrochemistry* in situ *cell*
(Reproduced by permission from D. A. Stout, G. Gavelli, J. B. Lumsden, and R. W. Staehle, *Appl. Surf. Anal.*, ASTM STP 699, 1980, 42)

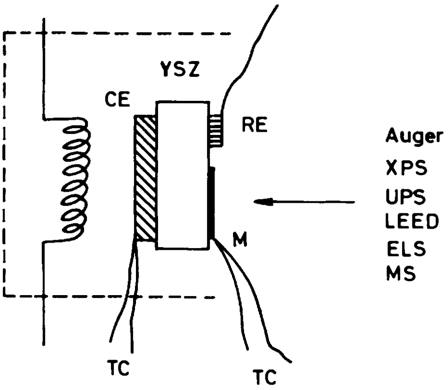

Figure 11 *Solid state electrochemistry* in situ *cell*
(Reproduced by permission from C. Y. Yang and W. E. O'Grady, *J. Vac. Sci. Technol.*, 1982, **20**, 925)

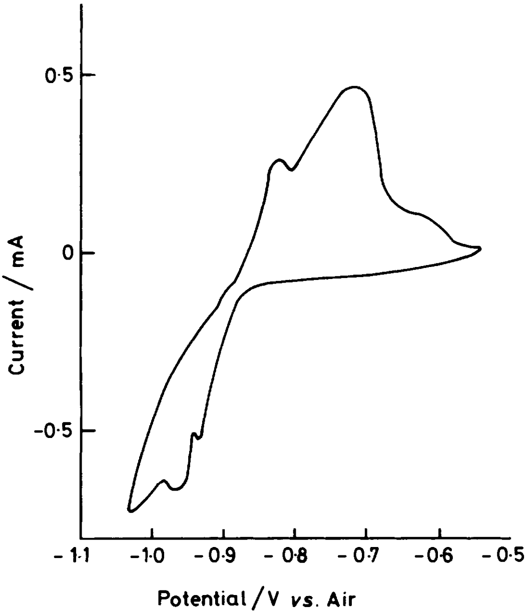

Figure 12 *Cyclic voltammogram of a nickel film in a UHV system (pressure* 2×10^{-8} Torr) *at* 500 °C *with a sweep rate of* 50 mV s^{-1}
(Reproduced by permission from C. Y. Yang and W. E. O'Grady, *J. Vac. Sci. Technol.*, 1982, **20**, 925)

extent of oxidation, but the copper L_3M_{45} M_{45} Auger peak in the XPS spectrum varied substantially with oxidation (Figure 13). Arakawa, Saito, and Shiokawa[107] have monitored the O1*s* and Ag3*d* binding energies in a cell with a silver electrode in zirconia stabilized with calcium oxide (11 mol%) at 325 and 400 °C. Oxidation of the silver occurs at 400 °C.

Solid electrolytes have been used in a number of electrochemical systems. The high ionic conductivity of these electrolytes often arises because of the possibility of the mobile cation being able to occupy different sites in the crystal lattice. Dickinson, Povey, and Sherwood[108] have investigated a range of such electrolytes. Different sites could not be distinguished in solid electrolytes involving Ag^1 and Cu^1 compounds. However different sites could be distinguished in β-alumina solid electrolytes, silver β-alumina gave rise to a Ag3*d* electron peak that could be fitted to two peaks with an intensity ratio of 2:1 corresponding to the ratio of different sites expected from *X*-ray crystallography.

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[107] T. Arakawa, A. Saito, and J. Shiokawa, *Chem. Phys. Lett.*, 1983, **94**, 250.
[108] T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Solid State Chem.*, 1975, **13**, 237.

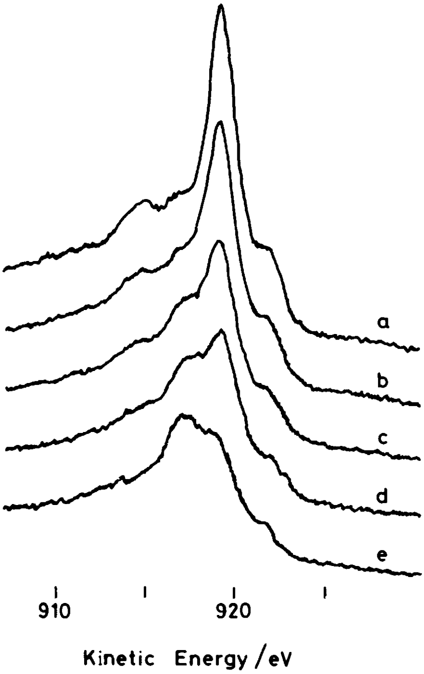

Figure 13 *Copper* $L_3M_{4,5}M_{4,5}$ *Auger spectra of copper oxidized in an* in situ *electrochemical cell at high temperature.* (a) *The reduced film,* (b) *the one quarter oxidized film,* (c) *the half oxidized film.* (d) *the three quarter oxidized film. and* (e) *the fully oxidized film*
(Reproduced by permission from N. Watanabe and T. Kuwana, *Anal. Chem.*, 1980, **52**, 1657)

8 Complex Systems with Mixed Oxidation State Oxides and Variations with Electrolyte Concentration

One of the great strengths of XPS is its ability to distinguish between different chemical environments on a surface. In electrochemical situations this feature can be of great value in trying to understand more complex chemical situations on an electrode surface. This behaviour is well illustrated by the electrochemistry of the noble metals iridium and rhodium in acid and base at different concentrations. Rhodium behaves in a much more simple manner in acid than it does in base. Iridium on the other hand behaves in a more simple manner in base than it does in acid. In both cases the more complex behaviour is associated with the formation of much larger amounts of oxidized product.

Noble metals are important in many electrochemical applications, such as their ability to act as good electrocatalysts for the oxygen evolution reaction and their use in fuel cells. In any of these applications the presence of an oxide layer on the surface can have a marked effect on the kinetics and mechanism of the reactions. Further, the oxide films formed may passivate the metal, thus a knowledge of the nature of this layer is of considerable relevance. In applications such as the production of hydrogen from the electrolysis of water, there is a real need for a greater understanding of all the processes which can occur at electrodes in aqueous solutions. Further discussion of gas evolution electrodes is given later in Section 10.

Most of the work carried out on noble-metal electrochemistry has been devoted to platinum, and many of the single-crystal studies mentioned above have used platinum. Thus subtle features such as the fact that electrolytic reduction of aqueous H^+ to form adsorbed hydrogen

$$H^+ + e \rightleftharpoons H_{ads}$$

is energetically more favourable at a Pt(100) surface than at a Pt(111) surface, and that the maximum amount of chemisorbed hydrogen corresponds to one hydrogen atom per surface platinum atom in the former case can be revealed by LEED.[49,54,88,89,109] Other electrochemical processes that show a marked dependence upon the particular single-crystal surface include underpotential deposition of metals,[110] the reduction of oxygen and the oxidation of organic molecules on the surface. Thus Adzic and co-workers[47,48] find that the kinetics of oxygen reduction on Au(100) and Au(111) surfaces differ, the half-wave potential for the former surface being the most positive. Underpotential deposition is a phenomenon that arises when monolayer quantities of metal cations on a foreign metal substrate electrode are deposited at applied potentials that are more anodic than the thermodynamic Nernstian potential. Hammond and Winograd[111,112] have studied the underpotential deposition of silver and copper at platinum electrodes and find that the XPS spectra show a shift of about 1 eV to lower binding energy for the underpotential deposited copper. It is clear that the binding energy corresponds to copper atoms and a similar shift could be obtained by vacuum evaporation of copper atoms under appropriate circumstances. Paul and Sherwood[113] find a similar negative shift for trace elements that have diffused to the surface of platinum and other metals after heating.

The ability of XPS to distinguish oxide films has been exploited for a number of electrode surfaces. These oxide films are of importance in their own right, thus iridium oxide films are known to act as a better catalyst than the metal itself in the oxygen-evolution reaction. Some of these oxide films (*e.g.* IrO_2) also show electrochromic properties (the ability to change colour on the application of a voltage or current).

Complex behaviour for iridium and rhodium is revealed when the cyclic voltammograms are examined. Thus Figure 14*a* shows a typical cyclic voltammogram for polycrystalline noble metals such as platinum, palladium, rhodium, and gold in 0.5 M sulphuric acid. These voltammograms are essentially superimposable when the cycle is repeated. Figure 14*b* shows the same cyclic voltammogram for iridium in 0.5 M sulphuric acid where it can be seen that there is a steady increase in current as the number of cycles increases, leading to an

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[109] A. S. Homa, E. Yeager, and B. D. Cahan, *J. Electroanal. Chem.*, 1983, **150**, 181.

[110] K. Juttner and J. W. Lorenz, *Z. Phys. Chem. N.F.*, 1980, **122**, 163.

[111] N. Winograd, *Gov. Rep. Announce Index* (*U.S.*), 1976, **76**, 102.

[112] J. S. Hammond and N. Winograd, *J. Electroanal. Chem.*, 1977, **124**, 826.

[113] A. Paul and P. M. A. Sherwood, to be published.

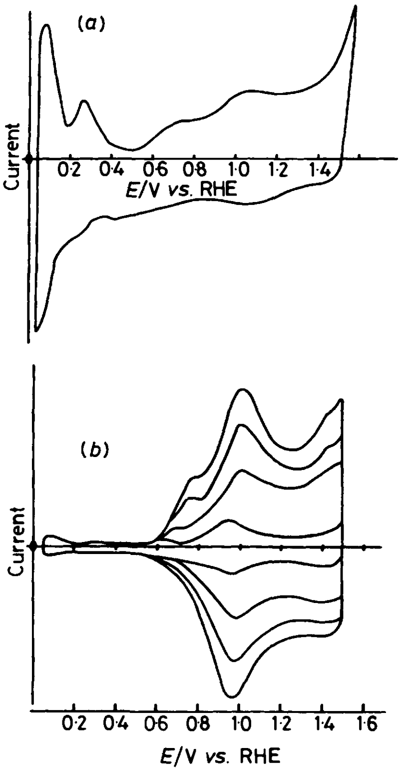

Figure 14 *Cyclic voltammograms for etched iridium in* (a) 5M *and* (b) 0.5M *sulphuric acid. The current increases with the number of cycles for* (b). *Voltammograms are shown for* 150, 350. 1 500, *and* 2 500 *cycles for* (b)
(Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc.. Faraday Trans. 1*, 1984, **80**, 135)

almost symmetric voltammogram about the potential axis. When the iridium electrode system is studied in base (1M sodium hydroxide) the cyclic voltammogram has an appearance similar to that of Figure 14*a* which is superimposable when the cycle is repeated. The rhodium electrode in base (1M sodium hydroxide) has a more complex behaviour than that in acid electrolyte. Thus while the behaviour of Figure 14*b* is not seen, the voltammogram does show more extensive hydrogen and oxygen regions on the anodic sweep and incomplete removal of oxygen on the cathodic sweep. This complex behaviour can be much more fully understood with the aid of XPS studies of the electrodes. In the work of the author and his co-workers, discussed below, the electrode surfaces were cleaned and characterized by XPS, before electrochemistry was carried out, in order to eliminate the problems associated with some electrochemical cleaning methods discussed in Section 4.

Iridium metal in 0.5M sulphuric acid shows only a very small amount of oxide formation under steady-state polarization conditions,[114,115] there appearing to be a competition between oxide formation and dissolution. Thick oxide films can be formed by cycling from 0.05 V to 1.5 V (RHE)[115,116] and the steady growth of iridium oxides can be seen from the Ir4*f* spectrum shown in Figure 15. The spectra can be fitted to two 'oxide' peaks, one with a constant binding energy of 61.8 eV (Ir$4f_{7/2}$) and a width that varies with the number of cycles as shown in Figure 16 and the other peak with a binding energy that varies over the range 61.8 to 63.9 eV with a variable width. The separation of the first oxide peak of 1.5 eV[115] from that of the metal is similar to that found in a number of studies of the anodic oxide film.[116,117] The first oxide peak may be due to IrO_2, though its initially greater width may be due to an overlap between a peak due to IrO_2 and Ir_2O_3. The second peak of variable width and position is consistent with a mixture of oxy/hydroxide. Some of the IrO_2 may be in the form of $Ir(OH)_4$.[116] Significant intensity is seen in the hydroxide region of the O1*s* spectrum supporting this suggestion. It is impossible conclusively to identify these species by XPS alone because any model compounds studied may provide misleading results caused by differences between the surface and bulk composition (*e.g. ref.* 118). Further the lack of detailed crystallographic data makes calculations difficult. However, in order to get some idea of the range of binding energies molecular orbital cluster calculations[115] for octahedral iridium oxide ions corresponding to iridium in formal oxidation states Ir^{VI}, Ir^{V}, Ir^{IV}, and Ir^{III} suggest that the oxides should lie in a binding energy range of about 3 eV, with binding energies increasing with formal oxidation state in the order $V < VI < III < IV$. The mechanism for the electrochemical process may thus be due to the formation of reversibly and irreversibly formed oxide. Irreversible oxide, associated with the first 'oxide' peak, may be formed by the process:

$$Ir + 2H_2O \longrightarrow 4H^+ + IrO_2 + 4e$$

with some Ir_2O_3 formed as discussed above:

$$2Ir + 3H_2O \longrightarrow 6H^+ + Ir_2O_3 + 6e$$

and the reversible oxide, associated with the second 'oxide' peak may be associated with a range of complex oxy/hydroxide reactions such as:

$$IrO_a(OH)_b \rightleftharpoons IrO_{a+c}(OH)_{b-c} + cH^+ + ce$$

The reversibility in the cyclic voltammogram may be associated with reversible stoicheiometric changes within the irreversibly formed oxide. Angle-resolved XPS studies[115] clearly show that the oxides lie on the surface, the second oxide

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[114] R. Kotz, H. J. Lewerenz, P. Bruesch, and S. Stucki, *J. Electroanal. Chem.*, 1983, **150**, 209.

[115] H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 135.

[116] J. Augustynski, M. Koudelka, J. Sanchez, and B. E. Conway, *J. Electroanal. Chem.*, 1984, **160**, 233.

[117] R. Kotz, H. Neff, and S. Stucki, *J. Electrochem. Soc.*, 1984, **131**, 72.

[118] A. F. Povey and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1240.

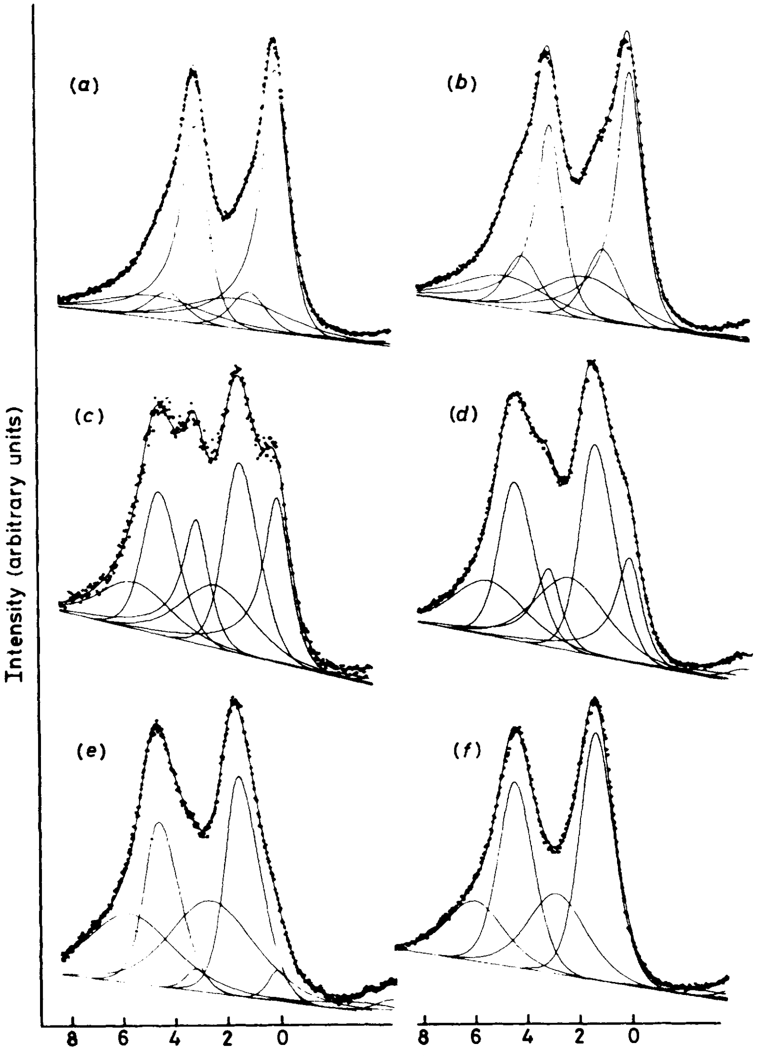

Figure 15 *Iridium 4f region of electrodes cycled to* 1.5 V *at* 31.25 mV s^{-1} *in* 0.5M *sulphuric acid. The fixed width at half maximum of the first oxide peak is at* 1.54 eV. *Electrodes cycled* (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, *and* (f) 200 *times*
(Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 135)

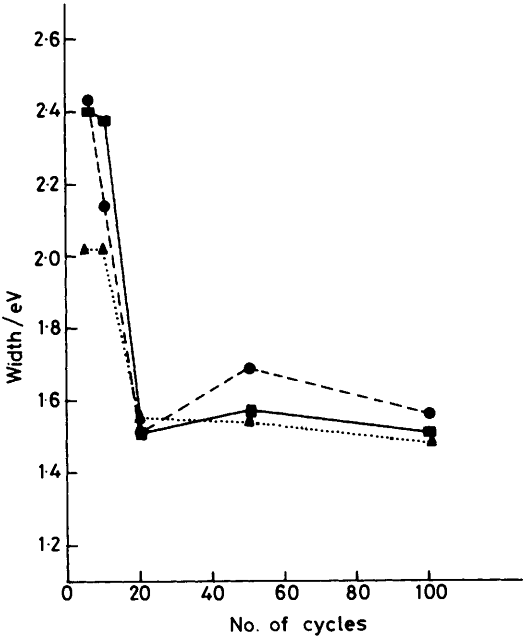

Figure 16 *Graph showing the effect of change in width of the first oxide peak in the iridium* 4*f* *region on cycling an iridium electrode to* 1.5 V *in* 0.5M *sulphuric acid.* ■. 10; ●, 31.25, *and* ▲, 100 mV s^{-1}
(Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1,* 1984, **80**, 135)

peak appearing to lie closer to the surface than the first oxide peak (Figure 17).

Iridium metal in 5M sulphuric acid displays a different behaviour, giving the cyclic voltammogram shown in Figure 14*a*. The XPS spectra[115] show (Figure 18) that much less oxide is formed, and the second oxide peak is not seen. There appears to be competion between formation and dissolution of the oxide as in the steady-state studies in 0.5M sulphuric acid.

Electrochemical and XPS studies of thick anodic oxide films on iridium[117] show no change in the position of the Ir4*f* peaks with electrode potential for polarization in 0.5 M sulphuric acid, though there appears to be a change in the width of the peaks. The O1*s* region, however, shows a significant dependence upon electrode potential, moving to lower binding energy as the steady-state polarization potential is increased. These results may be explained by iridium hydroxide species at low potentials becoming deprotonated at higher potentials to form oxide species. Above 1.5 V (SCE) the anodic oxide starts to corrode (in agreement with the results discussed above), and the O1*s* binding energy shifts back to the hydroxide region. Heating these thick anodic oxide films causes a shift in O1*s* and

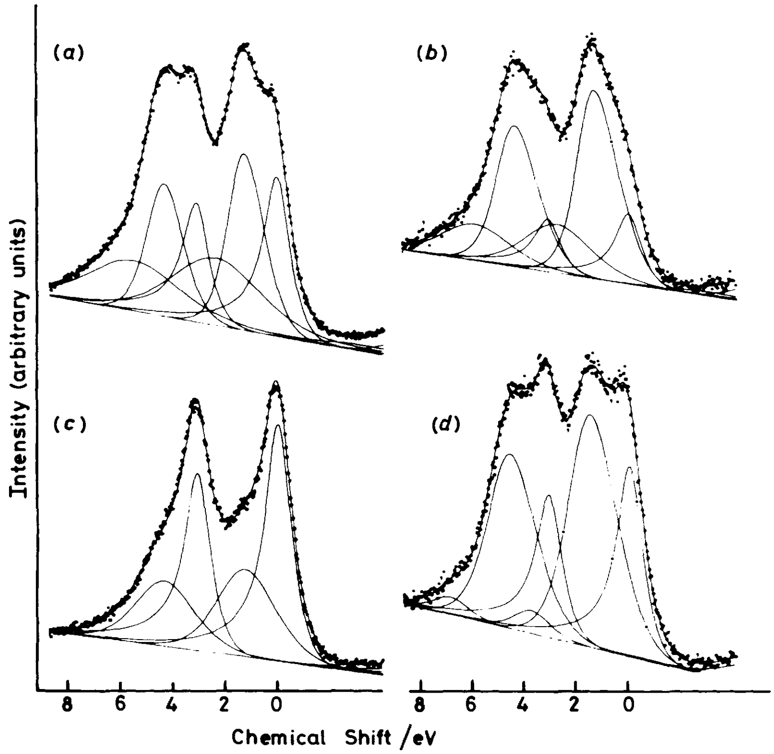

Figure 17 *Angle-resolved studies on an iridium electrode with oxide coverage:* (a) *and* (c) *correspond to the optimum angle;* (b) *and* (d) *correspond to spectra run at a surface-sensitive angle* (Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 135)

Ir4*f* binding energies, corresponding probably to dehydration or decomposition.

When iridium is cycled and polarized in base (1M sodium hydroxide) it behaves in a much simpler way to the behaviour in acid.[119] Steady-state polarization in base does produce an oxide film which never accounts for more than 27% of the total Ir4*f* intensity. There is hardly any increase in the amount of oxide on repeated cycling, which in any case never accounts for more than 19% of the total Ir4*f* intensity. As in the acid case, two different types of iridium oxide can be identified, though at slightly different binding energies. Surface-sensitive experiments clearly show the presence of the oxides on the surface of the electrode since the amount of oxide can be increased to represent around 60% of the total Ir4*f* intensity in such experiments.

Rhodium metal polarized (for between 15 minutes and one hour) in 0.5 M

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[119] J. G. Helliwell and P. M. A. Sherwood, to be published.

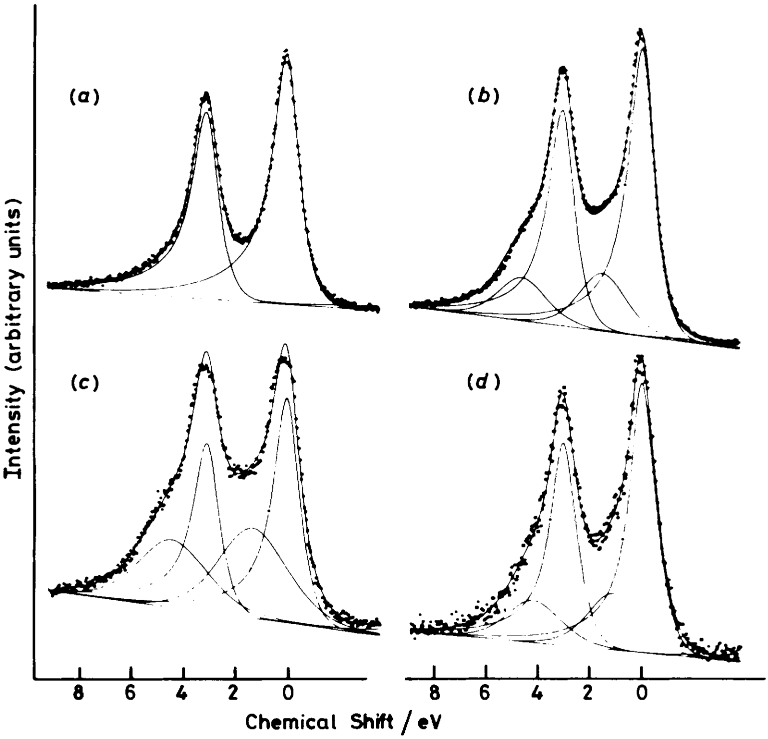

Figure 18 *Iridium 4f region of an argon-ion etched iridium electrode cycled in* 5M *sulphuric acid at* 31.25 mV s^{-1}. (a) *Upper limit* 1.2 V, *cycled twenty times.* (b) *Upper limit* 1.5 V, *cycled twenty times.* (c) *Upper limit* 1.5 V, *cycled fifty times.* (d) *Upper limit* 1.8 V, *cycled twenty times* (Reproduced by permission from H. Y. Hall and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 135)

sulphuric acid results in the formation of Rh_2O_3 (at a chemical shift of 1.23 eV from the metal peak) at low potentials, and RhO_2 (at a chemical shift of 2.72 eV from the metal peak) in addition to Rh_2O_3 at higher potentials.[33] The maximum amount of oxide never rises above 46% of the total Rh3*d* area. The highest potential of this study was 2.4 V (SCE). Peuckert[120] suggests that the oxide formed by polarization to 3 V (SCE) for 16 hours is RhOOH on the basis of a slightly lower (0.4 eV) chemical shift and greater linewidth (suggested as being due to an overlap with the metal peak) as compared to a sample of Rh_2O_3 prepared by thermal oxidation. In the work of Hall and Sherwood[33] the metal peak could be clearly resolved from the oxide peaks (Rh_2O_3 and RhO_2) in the Rh3*d* spectrum, and the RhO_2 peak was suggested by careful curve fitting of the same spectrum. RhO_2 was detected as the predominant species when rhodium was studied after cycling in base.[121]

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[120] M. Peuckert, *Surf. Sci.*, 1984, **141**, 500.

[121] J. G. Helliwell and P. M. A. Sherwood, to be published.

Rhodium metal polarized and cycled in 1M sodium hydroxide shows complexities similar to those found for iridium in acid.[121] Thus steady-state polarization studies (for 15 minutes) show a level of oxidation similar to that of rhodium metal in acid and the main oxide is Rh_2O_3 (the maximum amount of oxide never rises above 27% of the total Rh3*d* area). When the electrode is cycled repeatedly the type and amount of oxide is different from that obtained by steady-state polarization. Thus the amount of oxide rises steadily with the number of cycles until it becomes the predominant feature of the spectrum, almost completely obscuring the metal peak. The binding energy of this oxide is clearly measured as being separated by 1.9 to 2.3 eV from the metal, since during this process the metal and oxide peaks are clearly resolved. For the reasons that follow, this oxide is attributed to RhO_2. The peak shows the oxide to suffer from thermal decomposition to give the metal and a lower oxide. The oxide imparts a distinctive green colour to the electrode surface, the green colour becoming more marked as the amount of RhO_2 increases. The green colour is consistent with hydrated RhO_2. The samples appear yellow/brown after removal from the spectrometer, consistent with anhydrous RhO_2.

9 Electrochemically Prepared Surfaces

There have been many studies of surfaces that have been prepared using electrochemistry, and many of these surfaces have been studied by surface-science techniques. This approach has the advantage that the highly controlled conditions possible using electrochemistry allow reproducible surfaces to be prepared.

A. Anodic Oxide Films.—An enormous number of anodic oxide films have been prepared and studied using surface spectroscopies. A useful collection of XPS binding energies for oxide films can be found in the work of Barr[122,123] and Holm and Storp.[124]

Tantalum pentoxide films grown on tantalum foil provide an example of a film that is of such good quality when prepared electrochemically that it is used as a calibrant for depth profiling experiments using Auger and XPS (*e.g. refs.* 125 and 126). Thus films of 28.4 ± 1.7 nm and 96.3 ± 2.8 nm show resolutions at the Ta_2O_5/Ta interface of 1.41 ± 0.07 and 1.74 ± 0.10 nm respectively for oxygen Auger electrons. High reproducibility is found for different batches of anodic oxide film and different instruments.

A good example of an important anodic oxide film is that formed on the mixed II–VI semiconductor system cadmium mercury telluride ($Hg_{1-x}Cd_xTe$). This material is a useful i.r. detector, often being used in the n-type form where $x = 0.2$ for the 8—14 μm i.r. region. These materials are stabilized by the formation of an

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[122] T. L. Barr, *J. Phys. Chem.*, 1978, **82**, 1801.
[123] T. L. Barr, *J. Vac. Sci. Technol.*, 1977, **14**, 660.
[124] R. Holm and S. Storp, *Appl. Phys.*, 1976, **9**, 217.
[125] M. P. Seah, *Commun. Eur. Communities*, (*Rep.*) *EUR*, 1984, EUR 8839.
[126] M. P. Seah, H. J. Mathieu, and C. P. Hunt, *Surf. Sci.*, 1984, **139**, 549.

anodic oxide film which acts as a passivating and insulating layer. The film also appropriately terminates the lattice, creating the minimum perturbation to the crystal lattice at the surface. The nature of the anodic oxide film has been studied by XPS and other techniques.[127-135] The film is complex and may consist of mixed oxides such as $CdTe_2O_5$ and TeO_2, though a range of other oxides have been suggested. Argon-ion depth-profile experiments have been carried out, but decomposition probably occurs (such as ion-induced reduction of Te^{4+}) and preferential sputtering effects occur (the relative sputter yields of Cd, Te, and Hg are 0.14, 0.27, and 0.59.[136] It is interesting to find that although XPS and Auger experiments suggest that the layer is homogeneous, SIMS indicates appreciable inhomogeneity in the layer.[134] A combined electrochemical and XPS study of the formation and reduction of the anodic oxide layer has been carried out[133] which suggests a CdO-rich oxide film in alkaline solutions. The insulator properties of the oxide film and its continuous nature are indicated by the fact that no oxygen evolution occurs on the oxidized electrode up to potentials greater than five volts (RHE). Anodic sulphide films have been used to passivate and insulate cadmium mercury telluride.[137] The anodic sulphide films formed have advantages over the oxide films for p-type cadmium mercury telluride.

Anodic oxide films on aluminium are of considerable interest and have been the subject of many XPS studies (*e.g. refs.* 138—154). These films are important because of the role they play in the corrosion (and prevention of corrosion) of aluminium and in applications such as solar energy absorption. Batra and Kleinman[155] have written a comprehensive review of the chemisorption of oxygen on aluminium surfaces that covers the range of chemisorption to oxide formation.

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[127] T. S. Sun, S. P. Buchner, and N. E. Byer, *J. Vac. Sci. Technol.*, 1980, **17**, 1067.

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[129] A. Benninghoven, O. Ganschow, U. Kaiser, J. Neelsen, L. Wiedmann, H. Brendecke, H. Maier, and U. Ziegler, *Springer Ser. Electrophys.*, 1981, **7**, 303.

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[131] R. F. C. Farrow, P. N. J. Dennis, H. E. Bishop, N. R. Smart, and J. T. M. Wotherspoon, *Thin Solid Films*, 1982, **88**, 87.

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[135] A. B. Christie, I. Sutherland, and J. M. Walls, *Surf. Sci.*, 1983, **135**, 225.

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[137] Y. Nemirovsky and L. Burstein, *Appl. Phys. Lett.*, 1984, **44**, 443.

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[141] J. Augustynski, H. Berthou, and J. Painot, *Chem. Phys. Lett.*, 1976, **44**, 221.

[142] M. Koudelkova, J. Augustynski, and H. Berthou, *J. Electrochem. Soc.*, 1977, **124**, 1165.

[143] J. Augustynski, in 'Passivity in Metals', ed. R. P. Frankenthal and J. Kruger, The Electrochemical Soc. Inc., Princeton, 1978, pp. 989—1020.

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[145] H. Kaneno, S. Kobayashi, H. Takahashi, and M. Magayama, *Aruminyumu Kenkyu Kaishi*, 1979, **137**, 40.

[146] H. Yamada, T. Nakajima, and N. Watanabe, *Aruminyumu Kenkyu Kaishi*, 1977, **118**, 19.

[147] M. Hirochi and C. Yoshimura, *Kinzoku Hyomen Gijutsu*, 1980, **31**, 596.

The formation of anodic oxide films on gallium arsenide is a simple technique for producing barrier-type insulating films on this semiconductor. Such films are used for the construction of MOS (metal-oxide-semiconductor) devices. Many XPS studies (*e.g. refs.* 156—164) have been carried out in order to try to understand the nature of the films. Since the films are generally much thicker than the sampling depth of XPS, many of the studies have employed argon-ion depth profile methods for the investigation, and problems of ion damage and preferential sputtering have been encountered. It is found (*e.g. ref.* 22) that there is an excess of metallic arsenic at the interface between the anodic oxide and the gallium arsenide, and this may have interesting effects on the MOS characteristics.

Nickel is a very important element used on its own, or as a basic component of many alloy systems. Anodic oxide films on nickel have been extensively studied by surface science techniques (*e.g. refs.* 82, 97, and 165—177). The nature of the oxide film depends upon the anodization conditions and is composed of NiO, as well as $Ni(OH)_2$ and NiOOH, under appropriate conditions. Thus in neutral and acid solutions a porous precursor film of $Ni(OH)_2$ is formed and a passive film of NiO and some $Ni(OH)_2$ (the latter on top of the former) of 1—2 nm thickness is formed, while in a neutral borate buffer solution films several hundred nanometres thick can be formed. Such a thick film is thought[171] to consist of a porous film of β-NiOOH [which may be cathodically reduced to $Ni(OH)_2$] and a compact NiO film of around 1 nm thickness.

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[163] K. M. Geib and C. W. Wilmsen, *J. Vac. Sci. Technol.*, 1980, **17**, 952.

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B. Carbon Fibre Surfaces.—Carbon fibres are treated before incorporation into a matrix material (resin) in a composite structure as a means of increasing the strength of the fibre/matrix bond. The methods used have included chemical 'wet' methods (such as nitric acid, potassium permanganate, chromic acid, or sodium hypochlorite), electrochemical methods, 'dry' methods (such as catalytic oxidation, oxidation by air, oxygen, or ozone) and 'coatings' (such as pyrolytic graphite or silicon carbide). Electrochemical oxidation offers a method with a large degree of control over the oxidation process.

There have been a number of XPS studies of carbon fibre surfaces (*e.g. ref.* 178 and the references therein, and *refs.* 179—190). Lowde and co-workers[191] have used electrochemistry and XPS to study carbon-fibre paper. The paper consisted of an interwoven network of carbon fibres with a smooth, uniform coverage of pyrographite. It was treated either by chemical or electrochemical oxidation. The latter method used galvanstatic treatment in dilute nitric acid. The effect of electrochemical treatment was investigated by cyclic voltammetry on the untreated carbon-fibre paper. The C1*s* XPS spectra showed surface oxidation after electrochemical treatment. Similarities were found between some of the spectral features and those found for graphitic oxide. Proctor and Sherwood[192] and Kozlowski and Sherwood[193–195] have examined the electrochemical treatment of carbon fibres using sulphuric acid, ammonium bicarbonate, nitric acid, phosphoric acid, and electrolytes with a range of pH, both under laboratory and sometimes commercial conditions. The extent of oxidation and the type of surface functionality is shown to depend upon a number of factors such as the nature of the electrolyte, the anodic potential, the reaction time, the structure of the fibre surface, the pH of the electrolyte solution, and the electrolyte concentration. In acidic solutions the fibres are extensively oxidized. While the functionality of the oxide layer produced is very similar, the amount and type of surface oxide varies considerably depending upon the pH of the electrolyte. Much more surface oxide

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[195] C. Kozlowski, J. Harvey, and P. M. A. Sherwood, to be published.

is produced in acidic environments where extensive oxidation can occur. Carbon dioxide is evolved during treatment in acidic environments, and oxygen, together with clouding of the solution, in basic environments. In basic environments the carbon-fibre surface breaks up giving rise to small carbon-fibre fragments in the electrolyte. Different oxidation mechanisms probably occur at different pH values. Figure 19 illustrates the changes observed in the C1*s* region for fibres polarized to 2.0 V (SCE) for 20 minutes in solutions of different pH. Figure 20 shows the corresponding change in the O1*s* region which reflect the changes in the C1*s* region (*vide infra*). The two major peaks in the spectrum correspond to $>$C=O (531.5 eV) and $>$C–OH (533.5 eV). At low pH only one peak is seen, with a binding energy intermediate between $>$C=O and $>$C–OH due to the presence of both groups in proximity to one another, and as the pH is increased more individual $>$C–OH and $>$C=O character is present giving two clearly separable peaks. Carboxylic acid/ester groups increase with pH and these groups also add intensity to the main two peaks in the O1*s* region. When the C1*s* spectra are fitted, the various groups present on the carbon-fibre surface can be identified. Shifts from the 'graphitic' C1*s* peak (the peak at lowest binding energy) of 1.6 eV can be ascribed to the presence of $>$C–OH groups, of around 2.1 eV to the presence of $>$C=O and/or quinone-type groups, of around 4.0 eV to the presence of ester-type groups and above 6.0 eV to the presence of possible $-CO_3$-type groups. There may be some plasmon intensity associated with the latter group. These assignments were confirmed by Fourier transform i.r. (FTIR) spectroscopy.[193] Figure 21 illustrates how the C1*s* region of the spectrum changes with potential (SCE) for fibres polarized in 10% NH_4NO_3. The surface geometry of the fibres was investigated[193–195] by SEM. Surface treatment in acid generally causes splitting and pitting on the carbon-fibre surface together with the formation of an oxide 'skin', whereas in base, circular holes are formed in the fibre surface and no oxide 'skin' is seen. The electrochemical control of surface treatment allows for the preparation of fibre-resin composites of varying interlaminar shear strengths (ILSS). When the fibres are formed into composites with low ILSS the composites consist of areas of high fibre concentration and others of only resin. When the ILSS is high the composites shows a more even distribution of fibre in the resin and the fibres are well coated with resin.

10 Gas Evolution Electrodes

A number of electrode systems which can be used for gas evolution have been studied by XPS. The gas evolution process is markedly dependent upon the electrode surface and XPS studies can help in the understanding and optimization of the process. The use of noble metals and their oxides (*e.g.* IrO_2[117]) for this purpose has already been mentioned.

A. Ruthenium and Related Electrodes.—These electrodes have been used for oxygen and chlorine production. Ruthenium and ruthenium dioxide based anodes have amongst the lowest oxygen evolution overpotentials known, and thus find a

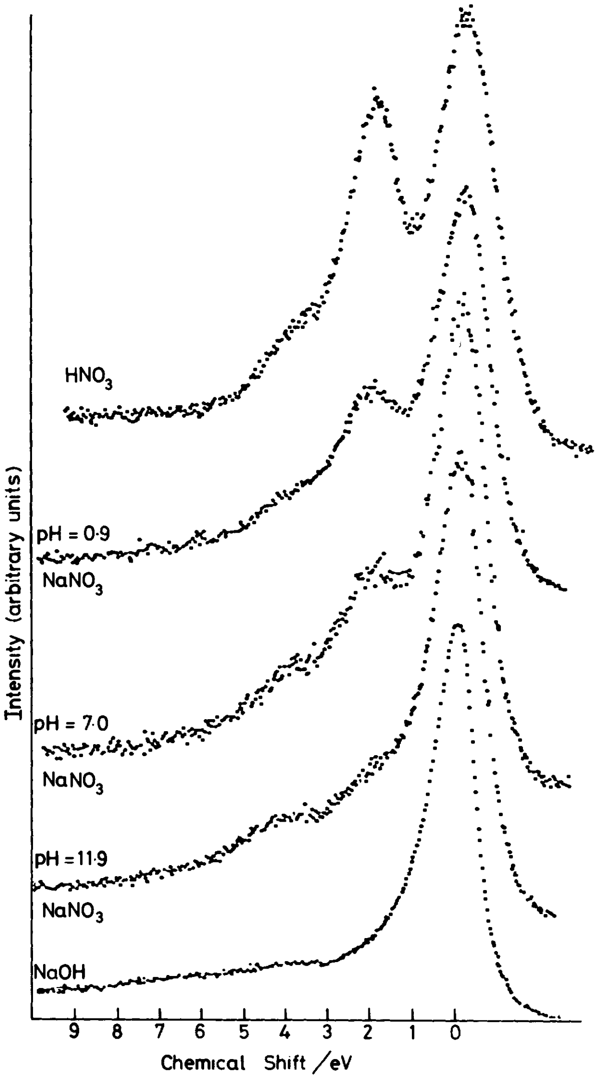

Figure 19 *Carbon 1s region of carbon fibres polarized in solutions of different pH* (C. Kozlowski and P. M. A. Sherwood, to be published)

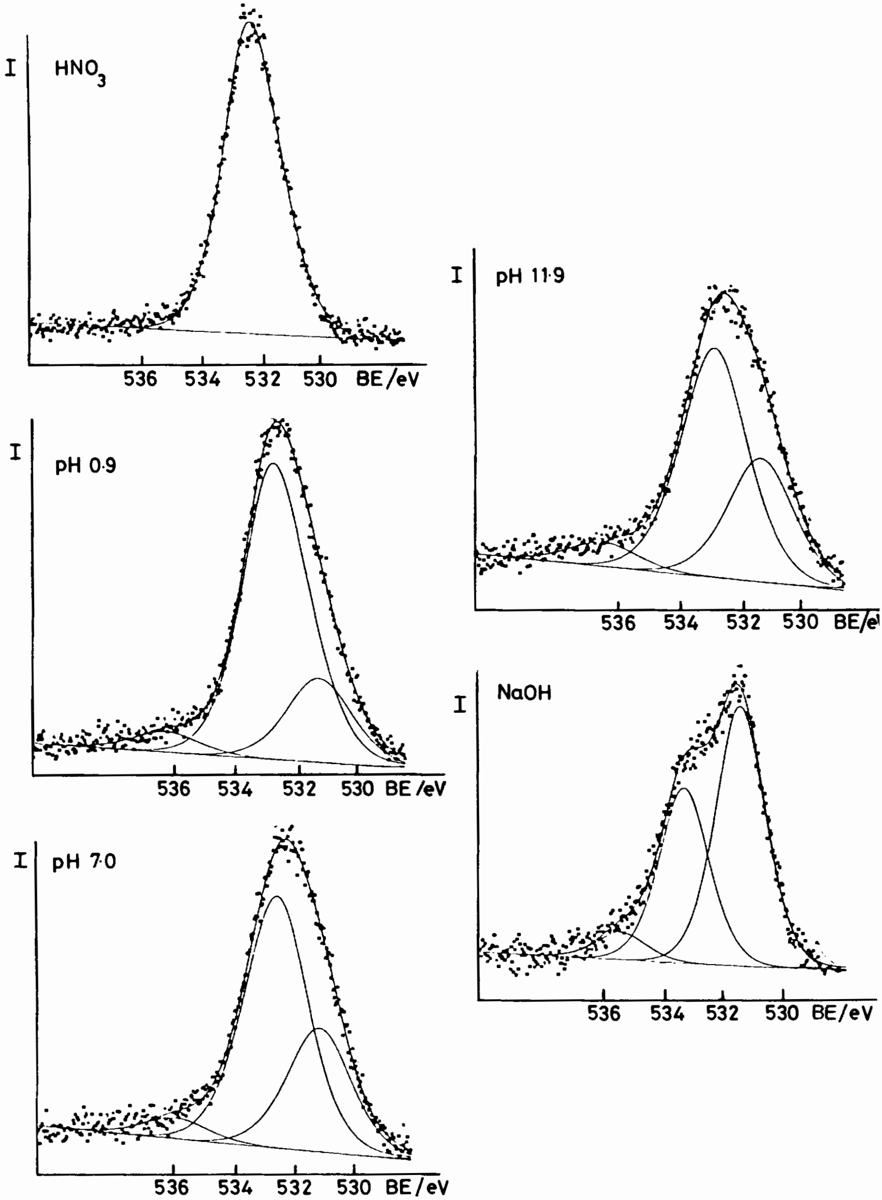

Figure 20 *Oxygen 1s region of carbon fibres polarized in solutions of different pH*
(C. Kozlowski and P. M. A. Sherwood, to be published)

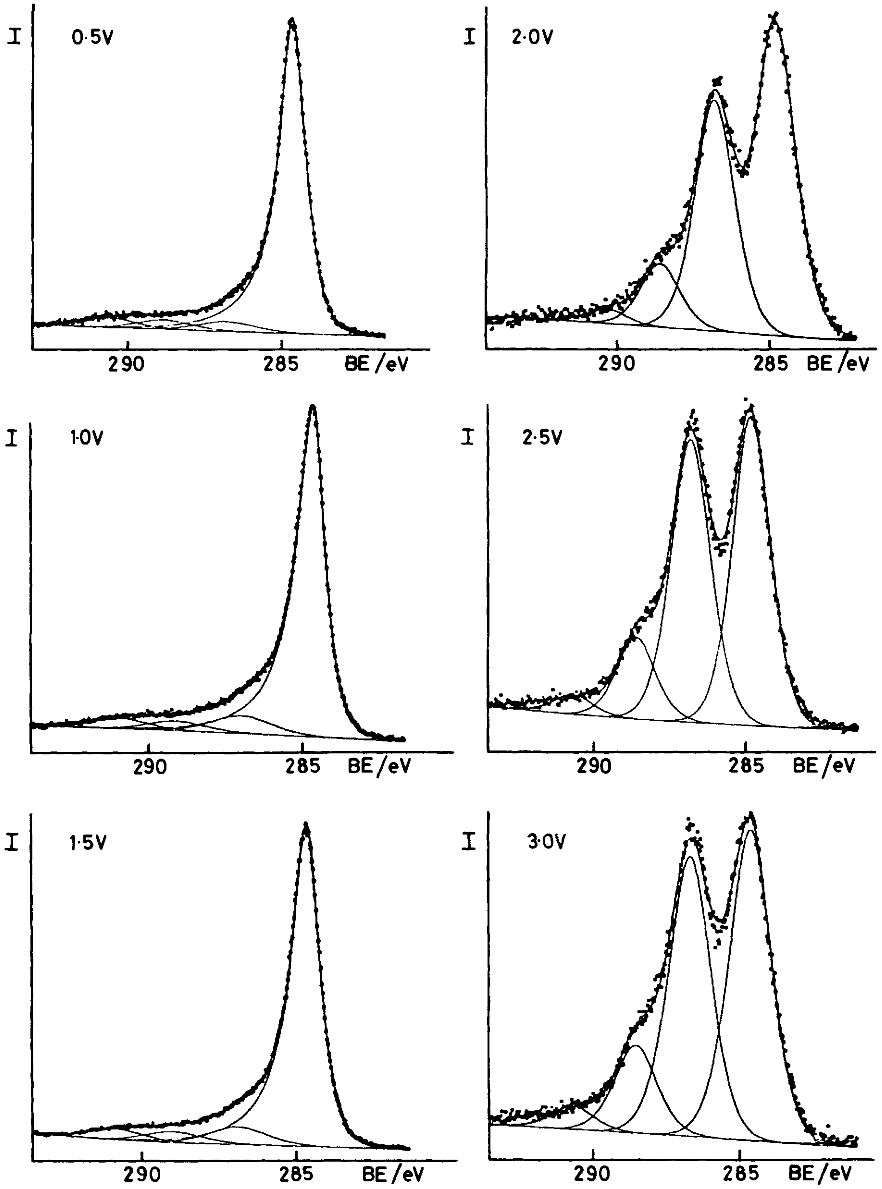

Figure 21 *Carbon* 1*s region of carbon fibres polarized in* 10% *ammonium nitrate solutions to different potentials (SCE) for one minute*
(C. Kozlowski and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2099)

role as O_2-evolving electrodes in hydrogen production by water electrolysis, and in fuel cells. Ruthenium dioxide is preferable to the metal since the latter corrodes during oxygen evolution to form a non-protecting oxide layer with a lower catalytic activity than that of the pure metal. Mixed ruthenium and titanium oxide electrodes have also been used. The catalytic performance of such electrodes depends upon the conditions of preparation. The surface chemistry of these electrode used for both oxygen and chlorine production have been investigated during operation by XPS. Thus Augustynski *et al.*[196] have investigated RuO_2 and RuO_2 deposited on TiO_2 film electrodes after electrolysis in 4M sodium chloride solution to form chlorine. The electrode surfaces showed surface enrichment of TiO_2, and the presence on the electrode surface of Ru^{VI} and two different chlorine species, one due to chloride ions and the other due to adsorbed atomic chlorine or ClO . Similar results were obtained from an Auger study by Gorodetskii and co workers.[197] Kotz and co-workers[198,199] have studied oxygen evolution on ruthenium and RuO_2 anodes. They have shown that a thick hydrous oxide film of RuO_2 is formed during oxygen evolution on the metal. In the case of the RuO_2 electrode, a higher oxide (Ru^{VI}) is formed on the electrode surface. It is thought that RuO_4 is formed in the case of the metal and the oxide electrode, but the relative stability of the Ru^{VI} intermediate determines whether the electrode corrodes (as in the case of the metal) or dissociates into oxygen and Ru^{VI} (as in the case of the oxide). Rolinson and co-workers[200] have examined the RuO_2 electrode in various non-aqueous electrolytes where it acts as a well-behaved electrode. As in the aqueous electrolyte case, Ru^{VI} is found on the electrode surface after electrochemistry in the non-aqueous electrolytes.

Ruthenates have been studied as electrodes for the efficient reduction of O_2 for use in fuel cells. Egdell and co-workers[201] have used electrochemistry and core-level and valence-level XPS to investigate the use of pyrochlore ruthenates with the general form $Bi_{2-2x}Pb_{2x}Ru_2O_{7-y}$ for this purpose. They discuss the behaviour of these oxides with respect to the electrochemical double-layer during oxygen reduction, and consider the factors that determine the catalytic activity of the metal oxides with respect to the noble metals.

B. Noble Metal and Alloy Electrodes.—Chlorine evolution has been studied on noble metal electrodes, and indeed such electrodes are used for chlorine evolution in the chlor-alkali industry. Hara and co-workers[202] have monitored the catalytic activity of palladium, rhodium, iridium, and platinum in such an application by

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examining the surface film formed on the electrode after action by XPS. In the case of platinum the film changes from Pt^{II} to Pt^{IV} oxychlorides with decreasing chloride presence, with increasing potential leading to an increase in chlorine overpotential. Only one oxidation-state compound was seen on the other metal surfaces. The chlorine evolution activity decreases in the order platinum, palladium, iridium, and rhodium which also corresponds to a decreasing chloride and increasing hydroxyl content in the film. A palladium–titanium–phosphorus alloy was found to give more chlorine gas evolution in a sodium chloride electrolyte when the amount of palladium on the surface of the film was greatest,[203] metallic and oxidized palladium being seen on the surface.

11 Anodic Oxidation of UO_2

UO_2 is an oxide of particular interest. It is the only product of uranium oxidation at higher temperatures (around 800 °C), and it is used in the form of sintered UO_2 pellets as a reactor fuel in the nuclear industry. It is important to understand how the oxide reacts in the appropriate environmental conditions when the material is disposed of (*e.g.* in stable geological formations such as salt and hard rock), or in the case of reactor failure. Shoesmith and co-workers[85,204,205] have examined the anodic oxidation of the oxide (which is an electrical conductor) by combining electrochemistry with XPS measurements. These studies show that the oxidation yields a range of other oxides such as non-stoicheiometric oxides UO_{2+x} (where x can have values between 0 and 1), and U_3O_8, U_2O_5, and UO_3.

12 Studies of Corrosion

There has been a very large number of studies where electrochemistry and XPS (and other surface-sensitive techniques) have been applied to problems of corrosion. Some of the work already mentioned has relevance to this area. The subject is too large to cover in any detail in this review, so a particular corrosion system (iron) has been chosen to illustrate the features of such studies.

Iron was one of the first materials whose corrosion behaviour was studied. Since iron, its alloys, and stainless steels are essential materials it is important to understand the mechanisms of their possible passivation in the environment of their application. Passivation means that the surface has a much lower activity or complete inertness towards its environment. Faraday first discovered that iron could be passivated by placing it into concentrated nitric acid. It was found that this passivation depended upon the formation of a protective passive film on the surface of the metal. The nature of the surface passive film formed either in air or by electrochemical treatment has been the subject of many studies. Thus Hoar *et al.*[206] found that the film that formed on pure iron exposed to air was Fe_2O_3, and that anodic polarization into the passive region produced a surface film that

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contained Fe_3O_4 underneath an oxide film of Fe_2O_3. This suggestion agreed with earlier work where electron diffraction and coulometry[207] and Mossbauer spectroscopy[208] were used to study the film. Experiments using *ex situ* methods may of course cause structural changes to the film after its removal from the passivating medium. Revie *et al.*[87,209] suggested that the film was polymeric, consisting of hydrated iron oxide having di-hydroxy bridging bonds that could be dehydrated by heating to 150 °C to give a film containing Fe_3O_4 and some γ-Fe_2O_3. O'Grady[210] has examined the film by *in situ* Mössbauer spectroscopy and has found that the film was not in the form of any of the known stoicheiometric oxides or hydroxides of iron. He proposed a chain-like structure of FeO_6 octahedra bonded together by di-oxy and di-hydroxy bridging bonds, the chains being linked by water molecules. There is a continuing debate as to the extent of water and hydroxyl content[211–213] in these films that revolves around the problems of *ex situ* measurements such as XPS and SIMS. This debate has led to the consideration of two models, sometimes called the 'crystalline oxide model' and the 'hydrated polymeric oxide model'. In the latter model it is water that transforms the properties of 'iron oxide' to those of a protective passive film, the water pulling together' the iron oxide in such a way that it is difficult for Fe^{2+} ions from the metal surface underneath the film to diffuse to the hydration sites at the oxide–solution interface. Of course the exact nature of the film depends upon the electrochemical and other conditions used in its formation (*e.g. refs.* 91 and 214 218). Further, when chloride ions are present the passive film is broken down and corrosion occurs. The nature of the passive film after polarization in chloride-containing solutions has been the subject of a number of studies. Thus Szklarska-Smialowska *et al.*[219] find no chloride ions in the film at negative potentials (−0.2 and −0.4 V NHE). Bockris and co-workers,[83,220] working at positive potentials (+0.3 V NHE) find that the nature of the film is strongly time dependent. Thus they find that increasing amounts of chloride ions penetrate the films with time (reaching right up to the metal–passive-film interface) until the passive film breaks down, after which there is a decrease in the chloride content in the passive film. They suggest that chloride ions may remove water from the film, leading to depassivation. The result supports, but does not prove, the 'hydrated polymeric oxide model'.

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[211] S. C. Tjong and E. Yeager, *J. Electrochem. Soc.*, 1981, **128**, 2251.
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[213] S. C. Tjong and E. Yeager, *J. Electrochem. Soc.*, 1982, **129**, 1276.
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The corrosion system of iron alloys and steels is much more complex. Many XPS studies have been carried out in this area and the surface films are found to contain not only iron oxides, but also oxides of the alloying elements. It is, of course, the passivation properties of these surface films that is so important in the choice of a particular alloy system. Space does not allow any detailed discussion of this important area (see, for example, *ref.* 1).

13 Chemically Modified Electrodes

A considerable amount of important work has been devoted to the study of chemically modified electrodes. There are many materials that have potentially useful properties as electrodes, but which do not behave well as electrode materials. Such materials can be used as electrodes by modification of the surface of well-behaved electrodes by the deposition of the desired material onto the electrode surface. This treatment causes the electrode to display the chemical and electrochemical properties of the deposited substance as if this substance were itself a well-behaved electrode material. The author has given a short review of this area,[1] and *refs.* 18 and 221—228 contain a selection of papers in the field.

14 Concluding Comments

Surface science has now come of age as a method for investigating electrochemical problems. XPS has played an important role in this area, and more and more studies have used a range of complementary surface-sensitive techniques that have included XPS. Much more attention has been given in recent years to the problems associated with *ex situ* methods and careful experimental approaches have been developed. Investigations have covered well-defined electrode surfaces of simple systems to the complex electrode surfaces found in corrosion and 'messy' systems. This comprehensive approach has greatly assisted our understanding of the electrode surface, and will continue to make an important contribution for many years to come.

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