PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Non-Traditional Methods for in situ Characterization of Interfaces

L. M. Peter

Phil. Trans. R. Soc. Lond. A 1996 **354**, 1613-1625
doi: 10.1098/rsta.1996.0068

Non-traditional methods for *in situ* characterization of interfaces

By L. M. Peter
School of Chemistry, University of Bath, Bath BA2 7AY, UK

Studies of electrochemical systems are traditionally based on electrical measurements, but in recent years there has been an upsurge of activity involving application of a wide range of *in situ* spectroscopic and structural techniques to characterize the interfacial region. This paper presents a brief overview of several of these techniques and provides experimental illustrations of their utility.

1. Introduction

The development of electrochemical power systems depends on selection and optimization of electrode and electrolyte components. Thermodynamic factors determine the cell voltage at open circuit, whereas interfacial kinetics, mass transport and conductivity influence the power output. Characterization of these processes at the electronic, molecular and structural level is a demanding task for which electrochemical measurements alone are inadequate. The need to obtain detailed information about systems under operating conditions stimulated the development of a formidable armoury of *in situ* techniques, ranging from infrared (IR) spectroscopy to X-ray scattering. Some of these methods require special facilities, for example, a synchrotron radiation source; others can be applied under normal laboratory conditions. When used in conjunction with electrochemical measurements, *in situ* techniques help to relate electrochemical processes to structure and reactivity at the atomic or molecular level. *In situ* methods will continue to make important contributions to the development of clean power sources for the next century.

One of the primary objectives of electrochemical measurements is to obtain information about the rates and mechanisms of interfacial reactions. The rate of electrochemical transformations is related directly to the measured current density by Faraday's laws, so that an electrode acts as a transducer. Similarly, the open-circuit voltage of an electrochemical cell provides a direct measure of the overall driving force or Gibbs energy change for a battery or fuel cell reaction. This convenient transformation of the rates and energetics of electrochemical reactions into current and voltage led to the evolution of techniques involving control and measurement of the electrical variables. Until recently, steady-state, transient, periodic and hydrodynamic measurements dominated studies of dynamic electrochemistry, and our understanding of the structure of the electrode solution interphase was largely based on experimental double-layer data for mercury. The link to surface science has now been firmly established by the development of reliable methods for the preparation of clean well defined monocrystalline metal electrodes and the introduction of acceptable vacuum transfer techniques that allow electrode specimens to be removed from

Phil. Trans. R. Soc. Lond. A (1996) **354**, 1613–1625
Printed in Great Britain

TEX Paper

an electrolyte while maintaining control of the potential. Subsequent structural and chemical characterization in UHV can be followed by reintroduction of the electrode into the electrochemical cell (Parsons 1989).

While electrical methods are powerful tools in experimental electrochemistry, there is a pressing need for supplementary methods, particularly in the case of complex reactions. For example, electrocatalysis in the direct methanol fuel cell involves complex adsorption–desorption reactions at specific sites on the surface of catalyst centres. Clearly, additional spectroscopic and structural information is essential for a fuller understanding of the mechanism of electrocatalysis and to assist the optimization of fuel cell electrodes. The last fifteen years have seen rapid expansion in the application of *in situ* spectroscopic and structural techniques to diverse electrochemical systems, with fuel cells, corrosion, battery systems, semiconductor processing and novel materials as major areas of impact. The recent rapid expansion of non-traditional methods has brought electrochemistry closer to surface science, and a new generation of textbooks is beginning to devote attention to *in situ* spectroscopic and structural techniques. Christensen & Hamnett's *Techniques and mechanisms in electrochemistry* (Christensen & Hamnett 1994) provides an excellent introduction to the field. Earlier reviews of *in situ* techniques are given elsewhere (Compton & Hamnett 1989; Abruña 1991).

2. *In situ* spectroscopic techniques in electrochemistry

(*a*) *Overview*

Table 1 lists some of the *in situ* optical and spectroscopic techniques that are used to characterize electrochemical systems.

Most of these methods rely on detection of a specularly reflected light beam, either in the UV/visible or in the IR. It follows that smooth electrodes are usually necessary in order to prevent losses by diffuse scattering. In the case of IR measurements, additional complications arise from the IR absorption of the solvent which limits the window–electrode gap to a few microns. Restrictions of this kind have important implications for the study of electrochemical systems for power generation, which can involve high surface area electrodes or dispersed catalyst centres on high surface area supporting materials. For this reason, many experiments have been carried out on model systems, and it is not always clear to what extent the interpretation of results obtained in this way may be extended to the description of real systems. Nevertheless, the insights gained from *in situ* techniques have made a substantial impact on the level of understanding in many technologically important areas; the discussion of methanol fuel cell electrocatalysis, for example, has been revolutionized by the application of *in situ* IR spectroscopy.

(*b*) *Ellipsometry*

Ellipsometry is a powerful method for the study of surface layers on smooth electrodes (Greef 1989). It involves measurement of the changes in polarization of a light beam that result from reflection at an interface. It has been used extensively to characterize oxide films on metals, and in its simplest form measurements are performed at a single wavelength, usually that of the helium–neon laser (633 nm). Ellipsometry can also be used to characterize absorbing films such as those of conducting polymers formed on metal substrates. The result are normally presented in terms of the ellipsometric parameters Δ and Ψ. tan Ψ is the ratio of the magnitudes of the p and

Table 1. *In situ optical and spectroscopic techniques used to characterize electrochemical systems*

technique	information provided	examples of systems studied
ellipsometry	optical constants, film thickness	oxide layers, polymer films
differential reflectance (UV–vis)	optical properties of films	corrosion layers
potential-modulated reflectance	optical properties, surface reactions	corrosion layers, conducting polymers
electroreflectance, electroabsorption	band gaps, composition, defects, strain	bulk semiconductors, thin films
electrochemically modulated IR spectroscopy (EMIRS)	identification of surface adsorbed species	CO on platinum
subtractively normalized interfacial Fourier transform IR (SNIFTIRS)	surface and bulk species, band shifts due to chemisorption	organic species on metal electrodes hydrogen on silicon
polarization-modulation IR reflection absorption spectroscopy (IRRAS)	surface adsorbed species	CO and CN
surface-enhanced Raman spectroscopy (SERS)	surface-bound molecular and ionic species	roughened surfaces with adsorbed organic molecules
surface second harmonic generation (SHG)	interfacial structure, electrode kinetics	overlayer deposition on metals
electron paramagnetic resonance (EPR)	identification of paramagnetic species	electrochemically generated radicals, conducting polymers
Mossbauer spectroscopy	electronic and magnetic properties	^{57}Fe in surface oxides, macrocylic catalysts
photocurrent spectroscopy	bandgap, film thickness, metal–oxide interface	semiconductors, oxide films on metals
modulated microwave reflectivity	changes in free-carrier density	silicon–electrolyte interface

s components and Δ is the difference between the phase changes experienced by the p and s components on reflection.

Figure 1 illustrates the changes in the ellipsometric parameters that accompany the electropolymerization of a polyaniline film on platinum by multiple cyclic potential scans. The insulating reduced form of polyaniline (leucoemeraldine) is transparent at 633 nm, whereas the oxidized conducting form (emeraldine) is coloured. The evolution of the $\Delta\Psi$ trace arises from growth of the film and switching between the oxidized and reduced forms; a full analysis of the ellipsometric data gives information about the thickness and optical properties of the films as it grows (Greef *et al.* 1989).

Single-wavelength measurements made with a laser source (usually He–Ne) are convenient experimentally, but the full power of the method is realized in spectroscopic ellipsometry, which provides information about the wavelength dependence

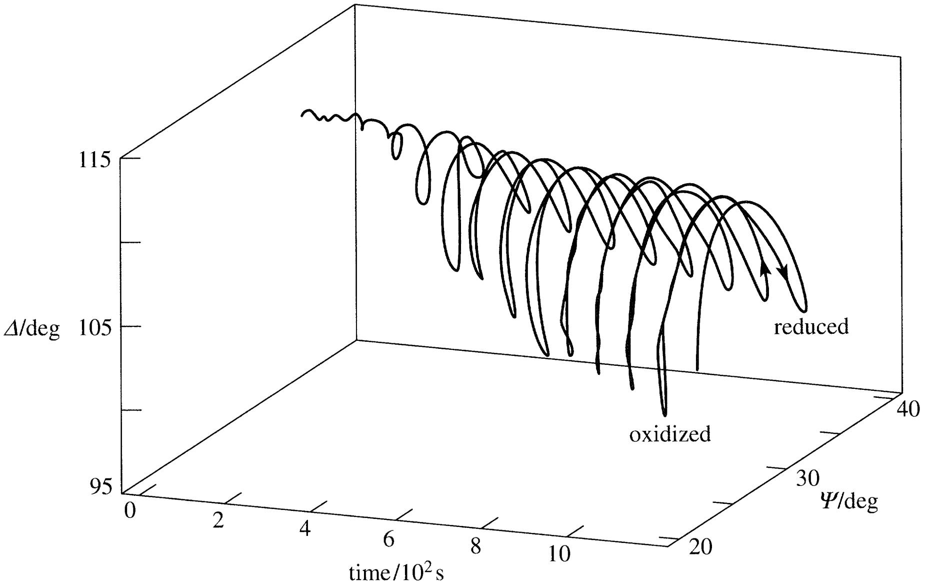

Figure 1. Three-dimensional plot illustrating the evolution of Δ and Ψ with time during electropolymerization of polyaniline by potential cycling between -0.2 V and $+0.7$ V versus SCE. The 'dinosaur's backbone' arises from film growth and switching between the transparent (reduced) and coloured (oxidized) states of the polymer. Adapted from Greef *et al.* (1989).

of the optical properties of the substrate and surface films. The main limitations of ellipsometry arise from the need to have smooth substrates and homogeneous films to allow straightforward interpretation.

(*c*) *UV–visible reflectance and transmittance*

Reflectance and transmittance measurements are commonly used to monitor electrode reactions. In many cases, however, the changes in the optical signal are small, and in the differential reflectance technique a reference beam is used to offset the reflectance signal so that changes can be measured. Sensitivity enhancement can also be achieved by modulating the potential of the electrode between two values. The perturbation ΔR of the reflectance is normalized to the unperturbed reflectance R to allow for changes in substrate reflectivity and incident light intensity. The spectra are related to the difference between the absorption spectra of the oxides present at two potentials chosen. Potential-modulated UV–visible reflectance (PMR) spectroscopy can be used to detect processes occurring in thin corrosion films on metals since a sensitivity of $\Delta R/R$ of 10^{-5} is readily achieved using a lock-in amplifier (Gutierrez & Martinez 1986). PMR can also be used under dynamic conditions where the electrode potential is scanned and the wavelength is held constant. Figure 2 illustrates the PMR responses obtained at two wavelengths for an iron electrode in alkaline solution. The large $\Delta R/R$ changes observed at 400 nm are clearly associated with the Fe(II)/Fe(III) region of the voltammogram, whereas the $\Delta R/R$ peak at 700 nm occurs in the oxygen evolution region. Analysis of the PMR spectrum in this region has shown that it is related to the Fe(III)/Fe(VI) couple (Peter, unpublished data).

Potential-modulated transmittance measurements have also been used to characterize the properties of conducting polymers such as polyaniline grown on optically transparent tin-oxide-coated glass electrodes In the case of polyaniline, the changes

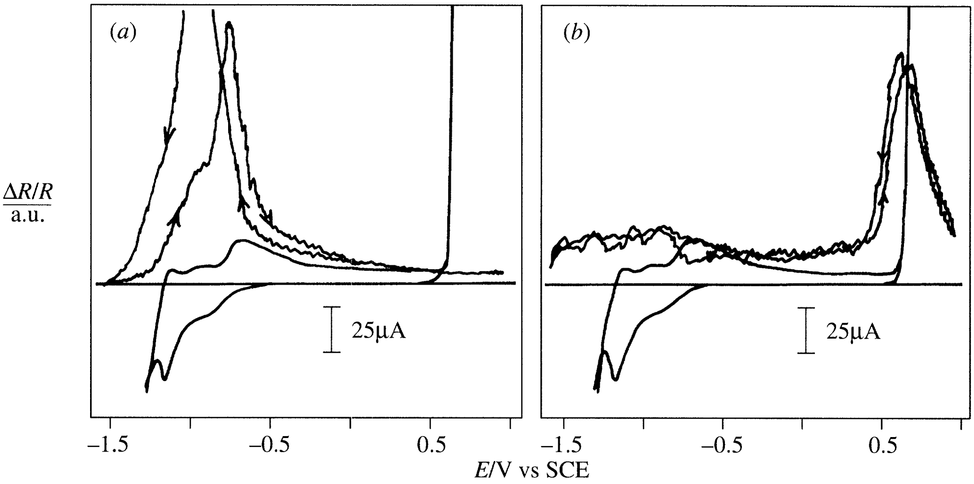

Figure 2. Potential-modulated reflectance signals $\Delta R/R$ measured at (*a*) 400 nm and (*b*) 700 nm during anodic oxidation of iron in 1 M KOH. The cyclic voltammograms recorded at the same time are also shown. 100 mV modulation, 27 Hz. Peter (unpublished data).

in optical absorption are associated with oxidation of the colourless insulating form to the green conducting polaron form. These measurements show that the 'supercapacitor' properties of conducting polymers are due to fast electron transfer reactions rather than to charging of the electrical double layer (Kalaji & Peter 1991).

Electroreflectance and electroabsorption are related techniques in which modulation of the electric field perturbs the optical constants of a solid. The best way to distinguish between true electroreflectance and changes in absorption arising from Faradaic processes is to measure the frequency dependence of the response; electroreflectance effects are generally frequency independent, whereas Faradaic processes are attenuated as the frequency increases because the change in absorbance depends on the Faradaic charge passed. Although electroreflectance is more commonly used to study semiconductor structures (Pollak & Shen 1993), it can also be used to characterize oxide films on metals such as titanium (Blackwood & Peter 1990).

(*d*) *Vibrational spectroscopy*

In situ IR spectroscopy of the electrode–solution interface was pioneered by Bewick and co-workers (Beden *et al.* 1981; Bewick & Pons 1985). A recent review of Fourier transform IR spectroscopy as a tool for the characterization of the metal–electrolyte interface gives an account of the explosion in activity that has occurred since then (Iwasita & Nart 1995).

The application of IR spectroscopy to study electrochemical interfaces *in situ* in the external reflection mode requires sensitivity enhancement and surface selectivity since the IR beam must traverse the solution. The difference in the properties of s- and p-polarized light at metal electrodes gives rise to the so-called 'surface selection rule' that predicts that IR absorption by surface species is limited to p-polarized light at non-normal incidence. For absorption to occur, the molecule must be oriented so that a component of its transition dipole moment is normal to the surface.

Sensitivity enhancement has been achieved in several ways. In the case of electrochemically modulated IR spectroscopy (EMIRS), the electrode potential is modulated between two values at a relatively low frequency (around 10 Hz), and the change in reflected IR signal is normalized by dividing by the DC reflectivity R. Since only the surface-adsorbed molecules are influenced by changes in electrode potential, the EMIRS difference spectrum is insensitive to species in the bulk. The spectra are related to changes in coverage or to shifts in IR absorption energy induced by changes in electrode potential (Stark effect). In the case of reflection absorption spectroscopy (IRRAS), the potential is held constant, but the polarization of the incident IR beam is switched repeatedly between the s- and p-states by a photoelastic modulator and the lock-in detector therefore records the difference between the reflectivity for the two polarizations. The surface selection rule limits absorption by surface-adsorbed species to p-polarized light, whereas absorption by species in the bulk phase is insensitive to polarization. Consequently, under ideal conditions the normalized difference signal can be attributed to surface-adsorbed species (Russell *et al.* 1982). The advantage of IRRAS is that it can supply absolute spectra rather than difference spectra. In fact, however, its sensitivity is limited by the fact that the electric field from the standing wave effectively samples the near-electrode region to a depth of 10^{-5} cm or more, so that contributions from bulk solvent absorption are still evident in IRRAS spectra.

The most widely used *in situ* IR technique is SNIFTIRS (subtractively normalized interfacial FTIR spectroscopy). It relies on averaging repeated scans in an FTIR spectrometer and subtracting them from an averaged baseline spectrum obtained at a suitable potential. The difference spectrum is then divided by the reference spectrum to give $\Delta R/R$. The main advantage of the method is that the speed performance and convenience of modern FTIR spectrometers is much better than that of the dispersive instruments used in EMIRS. Figure 3 shows an excellent example of how SNIFTIRS appears to have solved a long-standing controversy regarding the intermediate in the hydrogen evolution reaction (HER) on platinum (Nichols & Bewick 1988). It has been known for many years that platinum is covered by a monolayer of adsorbed hydrogen at potentials more positive than the reversible hydrogen potential (i.e. underpotential deposition). However, kinetic treatments of hydrogen evolution appear to indicate that the adsorbed intermediate in the HER is present at low coverage. This discrepancy was resolved by the IR study, which revealed that a new absorption peak appears at 2090 cm^{-1} at potentials close to the reversible hydrogen potential, whereas it is absent in the main underpotential region.

In situ FTIR has also been used to study the hydrogen termination of silicon under conditions of electrochemical dissolution (Blackwood *et al.* 1989).

Since their introduction a decade ago, *in situ* IR techniques have been applied to study systems relevant to fuel cell electrocatalysis. The main thrust of this effort is to establish a link between structure and reactivity at the atomic–molecular level, in order to design and optimize catalysts. The importance of surface structure and composition has been confirmed by studies of bulk single-crystal platinum and platinum alloys, but much remains to be done on real high surface area supported catalysts.

In situ Raman spectroscopy has also been used extensively to study the vibrational modes of species adsorbed at electrode surfaces (Hester 1989; Pemberton 1991). The Raman signal is greatly enhanced on silver, for example, when the surface is roughened by oxidation–reduction cycles in chloride solutions, and for this reason the method is known as surface-enhanced Raman spectroscopy (SERS). With improvements in instrumentation it has become possible to carry out measurements on a range of metals without the need to perform surface-roughening cycles, so that it is now possible to obtain results for better defined systems. Raman microprobe spec-

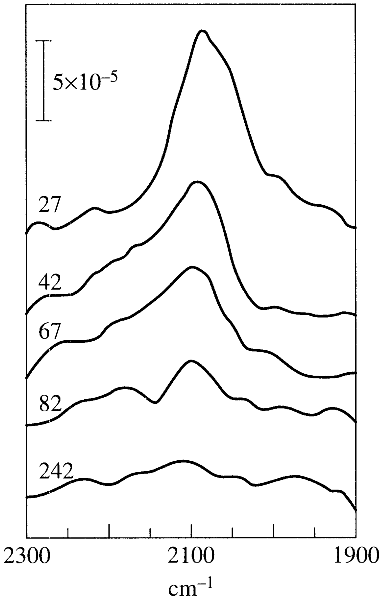

Figure 3. SNIFTIRS spectra for hydrogen adsorbed on polycrystalline platinum at different potentials (values shown in mV versus RHE). Adapted from Nichols & Bewick (1988).

troscopy has also been employed to characterize the local composition of corrosion layers on metals. The method has the advantage over IR spectroscopy that the solvent is transparent to the laser beam (usually an Ar or Kr laser line). The high intensities required can be a problem, however, since may materials are photoactive and change composition when illuminated. The advent of FT Raman may circumvent this problem by reducing exposure times substantially.

(*e*) *Nonlinear optical methods*

Nonlinear optical methods are now being applied with increasing success to characterize the solid–solution interface (Richmond 1991; Corn & Higgins 1994). Optical second harmonic generation (SHG), hyper-Raman scattering (HRS) and sum-frequency generation (SFG) are all nonlinear processes which arise from the symmetry-breaking properties of the interface. SHG has been used to examine ionic adsorption, the formation of overlayers on oriented monocrystalline metal substrates as well as to follow transient electrode processes.

(*f*) *Electron spin resonance spectroscopy*

Electron spin resonance (ESR) has been used for many years to study paramagnetic solution species formed electrochemically. Sophisticated flow cell systems have been developed for kinetic measurements, and the reader is referred to an authoritative review of progress (Waller & Compton 1989). More recently, the formation of radical ions or 'polarons' in conducting polymer films has been characterized by ESR measurements.

(*g*) *Mossbauer spectroscopy*

Mossbauer spectroscopy has also been developed as an *in situ* tool for studying electrochemical reactions involving iron species (Scherson 1991). The method requires high surface areas in order to achieve adequate sensitivity, but in spite of this limitation it has been used successfully to characterize iron corrosion chemistry and the reactivity of macrocyclic compounds containing iron.

(*h*) *Photocurrent spectroscopy*

Techniques based on the photoexcitation of charge carriers have made important contributions to our understanding of the electrochemistry of semiconductors and of semiconducting layers formed under electrochemical conditions. Photocurrent spectroscopy is a sensitive technique that can be used to identify surface phases and to measure film thickness (Peter 1989). UV–visible light incident on the electrode excites electrons across the forbidden gap, creating a hole in the valence band and an electron in the conduction band. The electric field in the solid separates the charge carrier pairs which are measured as a photocurrent in the external circuit. The sensitivity of the method is enhanced by interrupting the light with a mechanical chopper and using a lock-in amplifier to detect the current. Currents below 10^{-9} A can be measured routinely in this way, and the lock-in amplifier rejects unwanted currents due to processes occurring in the dark. An example of the application of photocurrent spectroscopy that is relevant to battery electrochemistry is the formation of a PbO layer on lead electrodes in sulphuric acid. Even in strongly acidic conditions, a layer of PbO forms under the lead sulphate passivating layer. This layer has been identified as tetragonal PbO by fitting the photocurrent excitation spectrum to the absorption spectrum of the solid, and the growth of the oxide layer at different temperatures has been monitored by observing the increase in photocurrent (Buchanan & Peter 1988). Figure 4 illustrates the photocurrent response for a lead electrode in sulphuric acid measured at the same time as the cyclic voltammogram. The figure shows that it is possible to measure a photocurrent in the presence of a dark current that is five orders of magnitude larger. Analysis of the photocurrent excitation spectrum has identified the photoactive material unambiguously as the tetragonal form of the oxide.

(*i*) *Modulated microwave reflectance spectroscopy*

A very recent development is the application of potential and light-modulated microwave reflection to semiconductor–electrolyte systems (Schlichthörl & Peter 1994). The microwave reflectivity of a sample is sensitive to changes in free-carrier density brought about by an external perturbation, and as with other techniques, the requisite sensitivity is achieved by using lock-in detection. It remains to be seen whether microwave measurements can be extended to the characterization of other classes of electrochemical systems such as conducting polymers.

3. *In situ* structural techniques in electrochemistry

(*a*) *Overview*

Table 2 lists some of the structural methods that have been used for *in situ* studies of electrochemical systems.

In the limited space of this review paper, only the main techniques are listed and references to some recent literature are provided.

(*b*) *Surface X-ray scattering*

In situ X-ray diffraction has received much less attention in electrochemistry than *in situ* spectroscopic techniques. However, it has the potential of providing essential

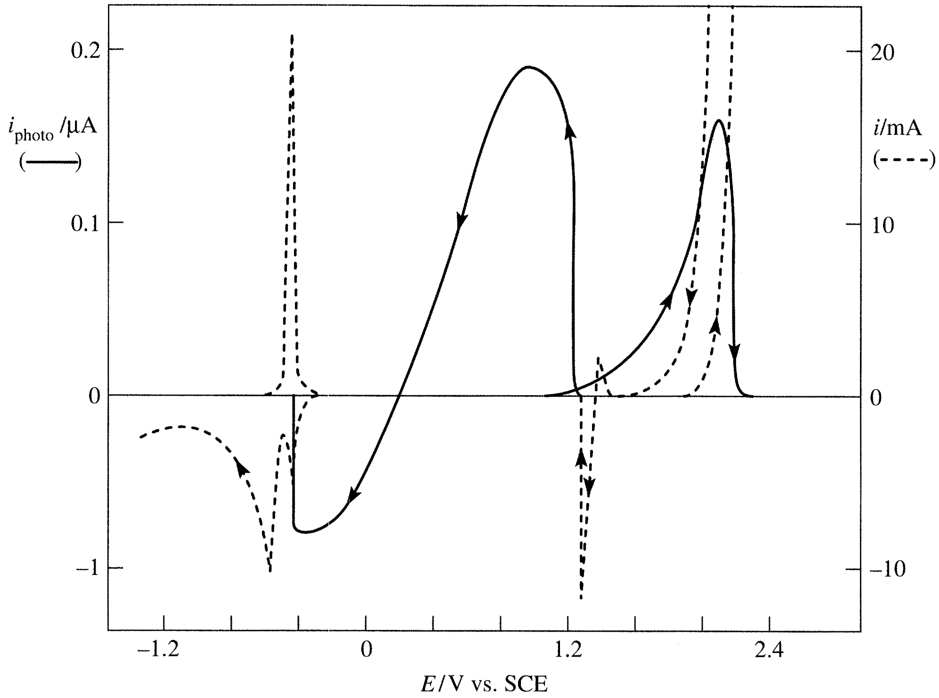

Figure 4. Simultaneous recording of cyclic voltammogram (broken line) and photocurrent response for a lead electrode in 0.5 M H_2SO_4. Sweep rate 20 mV s^{-1}. Wavelength 340 nm. Adapted from Buchanan & Peter (1988).

Table 2. *Structural methods used for* in situ *studies of electrochemical systems*

technique	information provided	examples of systems studied
(surface) X-ray scattering	surface and bulk structure	surface structure
EXAFS	local structure and composition	corrosion films batteries
X-ray standing waves	long-range surface order	underpotential deposited layers
scanning tunnelling microscopy (STM)	atomically resolved surface topology	metal and semiconductor electrodes
atomic force microscopy (AFM)	surface topology	insulators, semiconductors, surface films

structural information, and the availability of synchrotron sources has made its more widespread use possible (Toney & Melroy 1991). In addition, remarkable success has been achieved with conventional sources (Fleischmann *et al.* 1986).

(c) EXAFS

EXAFS (extended X-ray absorption fine structure) has been used to study a range of electrochemical systems, including oxide films, batteries and fuel cells and underpotential monolayers (Abruña 1991). Since EXAFS provides information about short-range order, it is particularly useful for the non-crystalline materials often encountered in electrochemical systems. For example, the nickel oxide electrode has been studied extensively using EXAFS in transmission mode and studies of carbon-supported platinum fuel cell catalysts have also been made by EXAFS.

(d) X-ray standing waves

The standing X-ray wave effect arises from coherent interference between two travelling waves at a strong reflection at a near perfect crystalline surface. The theory and application of the method are discussed by White (1991). The main application of the method has been to examine underpotential deposition on metals, for example, Tl on Cu. The experiments are difficult to perform, and it is not clear to what extent the method may find more general application to electrochemical systems of interest for power generation and energy storage.

(e) Scanning probe microscopy

The most exciting innovation in surface science in recent years has been the introduction of scanning tunnelling microscopy and later of atomic force microscopy (Behm *et al.* 1990). The realization that both these techniques could be applied to the electrode–solution interface has revolutionized the search for the links between structure and reactivity in electrochemical systems.

Scanning tunnelling microscopy (STM) is based on the phenomenon of quantum mechanical tunnelling of electrons between the tip of a metal probe and the substrate (Chen 1993). It has proved possible to achieve atomic resolution at the metal–electrolyte interface, and events such as surface reconstruction and electrodeposition can be followed in real time and related to the electrochemical behaviour (Batina *et al.* 1992; Siegenthaler & Gewirth 1996). The enormous impact of the method on electrochemistry arises from the fact that it is now possible to obtain structural information *in situ*, avoiding the need to transfer samples to UHV for LEED analysis, for example. The method can also be applied to semiconductor substrates, and reactions such as silicon etching have been imaged at high resolution (Allongue 1994). In addition to its imaging capabilities, STM offers a way to probe the local density of electron states by varying the tip–substrate potential difference.

Atomic force microscopy relies on measuring the attractive or repulsive forces between a tip and a substrate. It can be used on semiconducting or insulating substrates, and so has a potentially wider range of application than STM. However, in general its resolution is lower. Nevertheless, it is becoming clear that AFM is a versatile and useful tool for studying electrochemical transformations such as corrosion battery reactions and electrodeposition in electrochemical systems.

4. Other *in situ* techniques

(a) Overview

Several other experimental techniques that have been introduced into electrochemistry in recent years are listed in table 3.

Table 3. *Experimental techniques that have been introduced into electrochemistry in recent years*

technique	information provided	examples of systems studied
scanning electrochemical microscopy (SECM)	surface topology and reactivity	metal, semiconductors, modified electrodes
photoelectrochemical microscopy (PEM)	local electronic properties	semiconductors, oxide films on metals
quartz crystal microbalance (QCMB)	mass changes at surfaces	modified electrodes adsorption
differential electrochemical mass spectroscopy (DEMS)	product analysis	methanol oxidation

(*b*) *Scanning electrochemical microscopy (SECM) and related techniques*

This technique uses an ultramicroelectrode which is scanned across the substrate surface at which an electrochemical reaction is taking place (Bard *et al.* 1990). In its most sensitive mode, SECM involves regeneration of the electroactive species at the ultramicroelectrode, leading to a steep increase in current as the tip approaches the substrate. The technique can also be used to carry out localized electrochemical or chemical reactions, for example, tracks can be etched in a semiconductor substrate by generating bromine at the microelectrode tip.

(*c*) *Quartz crystal microbalance (QCMB)*

The quartz crystal microbalance is based on measurement of the small variations in frequency of an oscillating quartz crystal due to changes in the loading of its surface by a surface layer. The electrode material is usually a thin film of gold or platinum evaporated or sputtered on the quartz crystal. For rigid surface films, the change in frequency is linearly related to the mass change. The QCMB has been used extensively to characterize ion ingress and egress in electroactive polymers films as well as deposition and adsorption processes (Ward & Buttry 1990).

(*d*) *Differential electrochemical mass spectroscopy (DEMS)*

The DEMS technique (Wolter & Heitbaum 1984) involves coupling a high surface area electrocatalytic electrode to a mass spectrometer via a gas permeable porous PTFE membrane. The technique has been refined to reduce the response time sufficiently to allow simultaneous recording of cyclic voltammograms and product analysis at scan rates of 50 mV s^{-1}. One of the main applications of DEMS has been the study of methanol oxidation.

5. Conclusions

In situ techniques have made a substantial contribution to the evolution of modern electrochemistry. It seems likely that the already wide range of techniques will be added to as efforts are made to interface electrochemical cells to other measurement systems. This broadening of the experimental approaches used by electrochemists will further promote fruitful overlap with other areas of science and technology.

References

Abruña, H. D. 1991 *Electrochemical interfaces—modern techniques for in-situ characterization*, p. 580. New York: VCH.

Allongue, P. 1994 Scanning tunnelling microscopy of semiconductor electrodes. In *Advances in electrochemical science and engineering* (ed. H. Gerischer & C.W. Tobias), vol. 4, p. 66. Weinheim: VCH.

Bard, A. J., Denault, G., Lee, C., Mandler, D. & Wipf, D.O. 1990 Scanning electrochemical microscopy—a new technique for the characterization and modification of surfaces. *Acc. Chem. Res.* **23**, 357–363.

Batina N., Will, T. & Kolb, D. 1992 Study of the initial stages of copper deposition by *in-situ* scanning tunnelling microscopy. *Faraday Discuss. Chem. Soc.* **94**, 93–106.

Beden, B., Bewick, A., Kunimatsu, K. & Lamy, C. 1981 Infrared study of adsorbed species on electrodes—adsorption of carbon monoxide on platinum. *J. Electroanal. Interfac. Electrochem.* **121**, 343–347.

Behm, R. J., Garcia, R. & Rohrer, H. 1990 Scanning tunnelling microscopy and related methods. NATO ASI series E. vol. 184. Dordrecht: Kluwer Academic.

Bewick, A. & Pons, S. 1985 *In-situ* IR spectroscopy for the electrode/electrolyte solution interface. In *Advances in infrared and raman spectroscopy* (ed. R. J. H. Clark & R. E. Hester), vol. 12, p. 1. London: Wiley.

Blackwood, D. J, Peter, L. M. & Pons, S. 1989 *In-situ* characterization of the illuminated silicon-electrolyte interface by Fourier transform infrared spectroscopy. *Phys. Rev. Lett.* **62**, 308–311.

Blackwood D. J. & Peter, L. M. 1990 Potential modulated reflectance spectroscopy of anodic oxide films on titanium. *Electrochim. Acta* **35**, 1073–1080.

Buchanan, J. G & Peter, L. M. 1988 Photocurrent spectroscopy of the lead electrode in sulphuric acid. *Electrochim. Acta* **33**, 127–136.

Chen, C. J. 1993 *Introduction to scanning tunnelling microscopy*. Oxford University Press.

Christensen, P. & Hamnett, A. 1989 *In-situ* infrared studies of the electrode–electrolyte interface. In *Comprehensive chemical kinetics* (ed. R. G. Compton & A. Hamnett), vol. 29, pp. 1–78. Amsterdam: Elsevier.

Christensen, P. A. & Hamnett, A. 1994 *Techniques and mechanisms in electrochemistry*, p. 379. London: Blackie.

Corn, R. M. & Higgins, D. A. 1994 Optical second harmonic generation as a probe of surface chemistry. *Chem. Rev.* **94**, 107–125.

Fleischmann, M., Oliver, A. & Robinson, J. 1986 *In-situ* X-ray diffraction studies of the electrode solution interface. *Electrochim. Acta* **31**, 899–906.

Greef, R. 1989 *Ellipsometry. Comprehensive chemical kinetics* (ed. R. G. Compton & A. Hamnett), vol. 29, pp. 427–452. Amsterdam: Elsevier.

Greef, R., Kalaji, M. & Peter, L. M. 1989 Ellipsometric studies of polyaniline growth and redox cycling. *Faraday Disc. Chem. Soc.* **88**, 277–289.

Gutierrez, C. & Martinez, M. A. 1986 Potential modulated reflectance of the iron electrode in 0.1 M NaOH. *J. Electrochem. Soc.* **131**, 1874–1875.

Hester, R.E. 1989 Raman spectroscopic studies of species *in situ* at electrode surfaces. In *Comprehensive chemical kinetics* (ed. R. G. Compton & A. Hamnett), vol. 29, pp. 79–104. Amsterdam: Elsevier.

Iwasita, T. & Nart, F. C. 1995 *In-situ* Fourier transform infrared spectroscopy: a tool to characterise the metal–electrolyte interface at a molecular level. In *Advances in electrochemical science and engineering* (ed. H. Gerischer & C. Tobias), vol. 4, pp. 123–216. Weinheim: VCH.

Kalaji, M. & Peter, L. M. 1991 Optical and electrical a.c. response of polyaniline films. *J. Chem. Soc. Faraday Trans.* **87**, 853–860.

Nichols, R. J. & Bewick, A. 1988 Spectroscopic identification of the adsorbed intermediate in hydrogen evolution on platinum. *J. Electroanal. Interfac. Electrochem.* **243**, 445–453.

Parsons, R. 1989 The use of *ex-situ* uhv techniques to study electrode surfaces. In *Comprehensive chemical kinetics* (ed. R. G. Compton), vol. 29, pp. 105–128. Amsterdam: Elsevier.

Pemberton, J. E. 1991 Surface enhance Raman scattering. In *Electrochemical interfaces—modern techniques for* in-situ *surface characterization* (ed. H. D. Abruña), pp. 193–263. New York: VCH.

Peter, L. M. 1989 *Photocurrent spectroscopy. Comprehensive Chemical Kinetics* (ed. R.G. Compton & A. Hamnett), vol. 29, pp. 353–384. Amsterdam: Elsevier.

Pollak, F. H. & Shen, H. 1993 Modulation spectroscopy of semiconductors. *Mater. Sci. Eng.* **R10**, 275–374.

Pons, S., Davidson, T. & Bewick, A. 1984 Vibrational spectroscopy of the electrode–electrolyte interface 4. Fourier transform infrared spectroscopy—experimental conditions. *J. Electroanal. Interfac. Electrochem.* **160**, 63–71.

Richmond, G. L. 1991 Investigations of electrochemical interfaces by nonlinear optical methods. In *Electrochemical interfaces—modern techniques for* in-situ *surface characterization* (ed. H. D. Abruña), pp. 265–338. New York: VCH.

Russel, J. W., Overend, J., Scanlon, K, Severson, M. & Bewick, A. 1982 Infrared spectrum of CO on a platinum electrode in acidic solution. *J. Phys Chem.* **86**, 3066–3068.

Scherson, D. A.1991 Mossbauer spectroscopy. In *Electrochemical interfaces—modern techniques for* in-situ *surface characterization* (ed. H. D. Abruña), pp. 413–477. New York: VCH.

Schlichthörl, G. & Peter, L. M. 1994 Deconvolution of the impedance of the silicon/electrolyte interface by potential modulated microwave measurements. *J. Electrochem. Soc.* **141**, L171–L173.

Siegenthaler, H. & Gewirth, A. A. (eds) 1996 *Nanoscale probes of the solid/liquid interface.* NATO ASI series. Dordrecht: Kluwer Academic. (In the press.)

Toney, M. F. & Melroy, O. R. 1991 Surface X-ray scattering. In *Electrochemical interfaces—modern techniques for* in-situ *surface characterization* (ed. H. D. Abruña), pp. 55–129. New York: VCH.

Waller, A. M. & Compton, R. G. 1989 *In-situ* electrochemical ESR. In *Comprehensive chemical kinetics* (ed. R.G. Compton & A. Hamnett), vol. 29, pp. 297–352. Amsterdam: Elsevier.

Ward, M. D & Buttry, D. A. 1990 *In-situ* interfacial mass detection with piezoelectric transducers. *Science* **249**, 1000–1007.

White, J. H. 1991 Elucidation of structural aspects of electrode/electrolyte interfaces with X-ray standing waves. In *Electrochemical interfaces—modern techniques for* in-situ *surface characterization* (ed. H. D. Abruña), pp. 131–154. New York: VCH.

Wolter, O. & Heitbaum, J. 1984 Differential electrochemical mass spectrometry (DEMS). A new method for the study of electrode processes. *Ber. Bunsenges. Phys. Chem.* **88**, 2–6.