Chapter II.6
UV/Vis/NIR Spectroelectrochemistry

Andreas Neudeck, Frank Marken, and Richard G. Compton

## II.6.1 Introduction – Why Couple Techniques?

Voltammetric techniques used in electrochemistry monitor the flow of current as a function of potential, time, and mass transport. A huge variety of different experiments are possible, giving information about reaction energies, reaction intermediates, and the kinetics of a process [1–4]. However, additional data are often required and are accessible, in particular, via in situ spectroelectrochemical approaches. By coupling a spectroscopic technique such as UV/Vis/NIR spectroscopy [5, 6] to an electrochemical experiment, a wealth of complementary information as a function of the potential, time, and mass transport is available. In a recently published book dedicated to spectroelectrochemical techniques [7] the diversity of methods and new chemical information obtained is apparent. Both spectroscopic information about short-lived unstable intermediates and spectroscopic information disentangling the composition of complex mixtures of reactants can be obtained. Figure II.6.1 shows a schematic diagram for the case of a computer-controlled potentiostat system connected to a conventional electrochemical cell (working electrode WE, reference electrode RE, counter electrode CE) and simultaneously controlling the emitter and detector of a spectrometer. This kind of experimental arrangement allows the electrochemical and the spectroscopic data to be recorded simultaneously and, therefore, in contrast to the analysis of two independent data sets, direct correlation of data as a function of time and potential is possible.

Using electrochemical techniques it is possible to generate a well-defined amount of intermediates controlled by the charge forced through the working electrode. In this way, interesting intermediates (e.g. radicals or radical ions) can be generated electrochemically in a much more controlled and localised manner compared to, for example, what is possible with conventional photochemical methodology. In order to follow reactions of these intermediates, a wide range of spectroscopic methods are available, which have been successfully coupled to electrochemical systems. A

A. Neudeck (✉)

Textilforschungsinstitut Thüringen-Vogtland e.V., Stellv. Bereichsleiter Forschung und Entwicklung –Vorlaufforschung, Zeulenrodaer Str. 42, 07973 Greiz, Germany
e-mail: andreas.neudeck@t-online.de
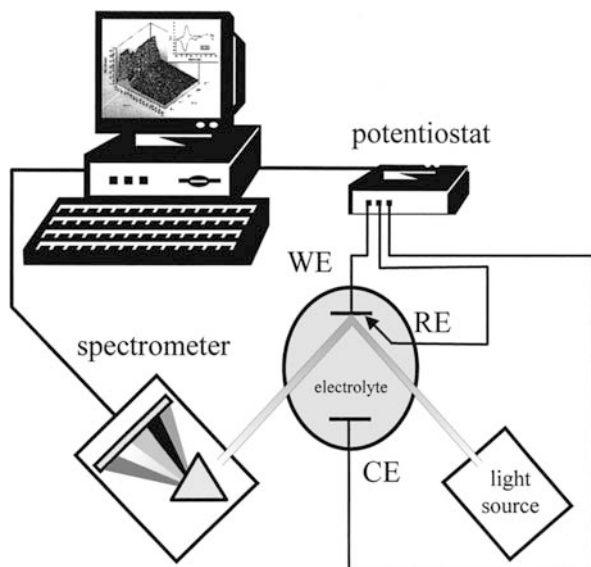
Fig. II.6.1 Schematic diagram of a spectroelectrochemical system with a conventional three-electrode electrochemical cell (*WE* working electrode, *RE* reference electrode, *CE* counter electrode) controlled by a computer-based potentiostat

list of some more commonly used coupled or 'hyphenated' spectroelectrochemical methodologies is given in Table II.6.1.

The techniques listed in Table II.6.1 have been chosen to demonstrate the capability of spectroelectrochemical methods to probe both processes in the solution adjacent to the electrode and heterogeneous processes occurring directly at the surface of the electrode. Given the wide range of existing in situ spectroelectrochemical techniques, Table II.6.1 can only highlight some of the more important methods.

Table II.6.1 Examples for spectroelectrochemical techniques probing both the solution phase in the vicinity of the working electrode (homogeneous) and the electrode surface (heterogeneous), which have been used in situ during the course of voltammetric experiments

Homogeneous Spectroelectrochemical Probes
In Situ Electron Spin Resonance (ESR) [8–11]
Molecules with unpaired electrons may be detected by microwave spectroscopy in the presence of a magnetic field. This technique is of considerable importance for the detection of radical reaction intermediates produced during electrolysis.
In Situ UV/Vis/NIR Optical Spectroelectrochemistry [12, 13]
The light absorption of reaction intermediates generated at the electrode surface can be monitored in transmission or in reflection mode, and this allows sensitive detection and/or quantitative kinetic studies. The sensitivity of this technique can be substantially improved by introducing cavity-ring-down cells [14] or multiple-reflection path cells.
In Situ Raman and Resonance Raman Spectroscopy or Microscopy [15, 16]
Raman allows the intensity and oscillator strength of vibrational bands to be measured with an optical laser system. The technique is particularly powerful in conjunction with confocal microscope.

Table II.6.1   (continued)

In Situ Luminescence Spectroscopy [17, 18]

Compared to the absorption of light in the visible wavelength range, luminescence is a much more sensitive technique due to the absence of background radiation. Even single photons may be counted and analysed in chemiluminescence processes [19].

In Situ Nuclear Magnetic Resonance Spectroscopy (NMR) [20]

NMR is very widely used and a powerful tool for structure determination. Although commonly used for diamagnetic compounds, it may also be applied to paramagnetic materials [21].

In Situ Differential Electrochemical Mass spectrometry (DEMS) [22]

Solution-phase reaction intermediates can be directly injected (within milliseconds) into appropriate mass spectrometers to provide localised solution composition information.

Heterogeneous Spectroelectrochemical Probes

In Situ UV/Vis/NIR Optical Spectroelectrochemistry [23–26]

UV/Vis/NIR spectroscopy may be employed directly for the characterisation of materials formed or deposited on electrode surfaces.

In Situ NMR Spectroscopy [27]

It has been demonstrated that NMR spectroscopy may be employed to study molecules adsorbed onto electrode surfaces during the course of electrochemical measurements. With higher magnetic field strengths and the availability of nano-particle samples this methodology becomes increasingly powerful.

In Situ Surface-Enhanced Raman Scattering (SERS) [28–31]

Raman scattering gives information about molecular or solid-state vibrations. In the presence of some electrode materials (e.g. silver or copper) a considerably enhanced sensitivity for molecules adsorbed at the electrode surface in the form of a monolayer can be achieved. This surface-enhanced Raman scattering effect can be transferred to other electrode materials coated in the form of a very thin layer onto a silver or copper substrate [32]. The recently developed TERS technique (Tip-Enhanced Raman Spectroscopy [33]) provides additional and highly resolved mapping information.

In Situ X-ray Diffraction (XRD) and Synchrotron Techniques [34–36]

XRD techniques are used mainly to study the crystal structure of crystalline solids at the electrode–solution interface. Structural changes, solid-state reactions, precipitation processes, dissolution processes, and intercalation processes can be followed as a function of applied potential and time. For non-crystalline samples, X-ray absorption and EXAFS allow the structure to be studied in more detail.

In Situ Mössbauer Spectroscopy [37]

Mössbauer transitions occur in atomic nuclei and involve absorption or emission of high-energy X-ray photons. Detailed information about the local chemical environment, oxidation state, and coordination symmetry of atoms can be obtained. However, the technique has been used for Fe and Sn only.

In Situ Spectroellipsometry [38] **and Optical Waveguide Techniques** [39]

Ellipsometry allows the optical properties of thin layers at electrode surfaces to be studied as a function of wavelength, time, and potential. Theoretical models allow conclusions about the film thickness and structure. Optical waveguide techniques improve the interaction of the electromagnetic wave with the sample for example in surface plamon resonance processes.

In Situ Non-linear Optical Methods and Second Harmonic Generation [40]

Steady-state electric field inhomogeneity at the electrode–solution interface causes submono-layer amounts of molecules to undergo 'unusual' but detectable two-photon transitions, which are 'forbidden' by selection rules in the bulk phase. Therefore, this technique allows molecules at a surface to be detected and studied independently and selectively.

In Situ Spectromicroscopy and Scanning Probe Methods [41]

A diverse range of scanning probe methods for use within electrochemical systems is now available.

Electrochemically generated intermediates are usually easier to detect spectroscopically than the substrate material itself. The electrochemical reduction or oxidation of many organic materials yields products, which are often coloured with high absorption coefficients (UV/Vis), or which give a characteristic radical 'signature' in electron spin resonance (ESR) spectroscopy [42]. Based on this highly sensitive detection, spectroelectrochemical detectors have been proposed and employed for analytical applications [43].

II.6.2 Flowing Versus Stagnant Systems – Achieving Spatial, Temporal, and Mechanistic Resolution

II.6.2.1 Steady-State or Transient Techniques

Voltammetric techniques may be broadly divided into *steady-state* techniques, such as channel flow cell [44–46], rotating disc [47, 48], or microelectrode [49] voltammetry at sufficiently low potential scan rate to give a current response *independent* of time, and *transient* techniques, such as cyclic voltammetry or chronoamperometry, giving a current response which is *dependent* on time.

The rotating-disc electrode voltammetry technique is a very commonly employed steady-state method. However, due to the moving parts in the experimental set-up, coupling to in situ spectroelectrochemical techniques has not been very widely used [50]. An elegant and extremely versatile approach to steady-state spectroelectrochemical measurements is based on the channel flow cell technique [51–53]. In this technique (see Fig. II.6.2), a continuous flow of electrolyte solution from a reservoir is allowed to pass through a rectangular duct with the working electrode embedded. The reference and counter electrodes are located outside of the flow cell in the upstream and downstream parts of the system. After setting the potential to a fixed value, downstream detection of the change in UV/Vis absorption, changes in ESR signal intensities, or changes in fluorescence signals may be monitored as a function of the flow rate. Data generated by this experimental technique have been analysed quantitatively with the help of computer models [54], which predict the spectroelectrochemical response based on a given reaction mechanism.

Transient spectroelectrochemical studies are possible with modern and fast spectroscopic probes, e.g. based on diode array spectrometers [55]. Compared to steady-state techniques, the design of transient spectroelectrochemical experiments is more challenging and the data analysis has to take into account the development of diffusion- and convection-driven concentration profiles [56]. However, these experiments open up the possibility to study time-dependent processes such as the development of a diffusion profile. For example, it is known, but usually ignored, that changing the redox state of a molecule changes its diffusivity. It has recently been shown [57] that, for the oxidation of N,N,N',N'-tetra-methylphenylenediamine (TMPD) in water, ethanol, and acetonitrile (Eq. II.6.1), the diffusion coefficients of the reduced form, TMPD, and the diffusion coefficient of the oxidised form,

Fig. II.6.2 Channel-flow system (**a**) with gravity-controlled solution flow from a reservoir, passing a reference electrode, flowing through a channel cell and a counter electrode, then passing through a capillary controlling the flow rate, and finally being collected. Rectangular channel cell corresponding to (**a**) with (**b**) transmission detection, (**c**) reflection detection, and (**d**) downstream transmission detection
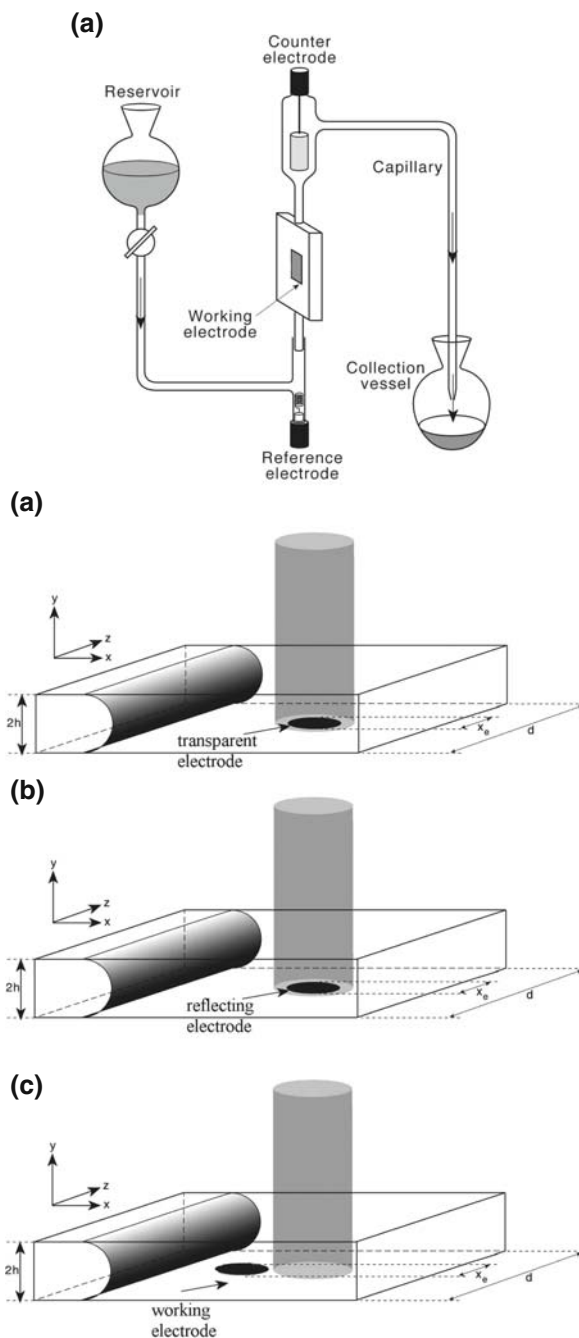
TMPD$^+$, can be determined separately and simultaneously in a single transient spectroelectrochemical experiment.

$$TMPD \rightleftarrows TMPD^+ + e^- \tag{II.6.1}$$

The experiment was based on a channel flow cell system (see Fig. II.6.2) with UV/Vis detection downstream of the working electrode (Fig. II.6.2d). Switching the electrode potential from the potential region with no faradaic current into a region with diffusion-limited faradaic current allowed the transient change in the UV/Vis absorption to be monitored. The data analysis for this transient UV/Vis response was based on a computer simulation model, which allowed D(TMPD) and D(TMPD$^+$) to be varied independently. Interestingly, the difference in D(TMPD) and D(TMPD$^+$) was relatively high in water and ethanol (15% slower diffusion of the radical cation) and considerably lower (5%) in the less polar solvent acetonitrile. This example demonstrates the ability of transient spectroelectrochemical experiments, in conjunction with computer simulation-based data analysis, to unravel even complex processes.

II.6.2.2 Cell Geometry and Experimental Design Considerations

The requirements for a successful spectroelectrochemical experiment may be summarised as (i) a cell with sufficiently good electrical properties (low iR$_U$ drop, homogeneous potential distribution over the entire working electrode surface area, sufficiently high counter electrode area), (ii) a potentiostat system with sufficient output current and output voltage to sustain potential steps and current transient without signal distortion, and (iii) a cell geometry which separates the working electrode from the counter electrode to avoid product generated at the counter electrode interfering with the electrochemical process at the working electrode and with the spectroscopic detection.
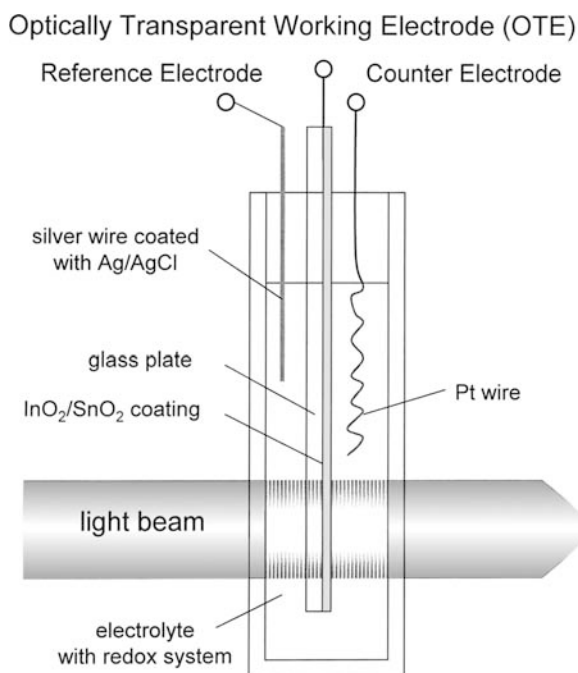
For a flow system such as that shown in Fig. II.6.2, the tubing connection between counter and reference electrode has to be kept reasonably short and with a not too narrow bore to avoid the uncompensated solution resistance R_U increasing. Further, even with a powerful potentiostat system, the lack of 'communication' between counter and reference electrode can cause the entire system to oscillate with high frequency (a check with a high-frequency oscilloscope is recommended) depending on the type of electrolyte solution used. These oscillations can be suppressed by improving the high-frequency 'communication' between counter and reference electrode, e.g. by introducing an additional counter electrode upstream of the reference or simply by connecting a small capacitor across reference and counter electrode. A good test for the quality of voltammetric data obtained with a channel-flow system can be based on cyclic voltammetry under stationary (no flow) conditions. Highly reversible electrochemical systems such as the oxidation of ferrocene in acetonitrile (1 mM ferrocene in 0.1 M NBu$_4$PF$_6$) can be employed and voltammograms are expected to give well-defined characteristics at sufficiently

high scan rate [58]. Any deviation from ideal behaviour is an indication of a cell design or potentiostat problem.

II.6.2.3 Time-Scale Considerations

Long-lived reactive intermediates are readily detected by voltammetric and spectro-electrochemical techniques after they have been generated electrochemically, e.g. by bulk electrolysis. In the simple UV/Vis/NIR spectroelectrochemical cell shown in Fig. II.6.3, the concentration of the electrolysis product will build up in the vicinity of the working electrode over several tens of minutes to give locally a relatively high and detectable concentration of the product. However, a short-lived reaction product or intermediate will be present in very low concentration and go undetected under these conditions.

Increasing the scan rate in cyclic voltammetry allows faster reactions to be studied. At a planar electrode, the diffusion layer grows into the solution phase during the progress of the potential cycle. The thickness of the diffusion layer at the time of the current peak, δ_{peak}, for the case of a reversible cyclic voltammetric response is given approximately by Eq. (II.6.2).

Optically Transparent Working Electrode (OTE)

Reference Electrode   Counter Electrode

silver wire coated with Ag/AgCl

glass plate

InO_2/SnO_2 coating

Pt wire

light beam

electrolyte with redox system

Fig. II.6.3 Simple in situ UV/Vis spectroelectrochemical cell based on a quartz cuvette with an optically transparent working electrode, counter electrode, and reference electrode immersed in solution

$$\delta_{\text{peak}} = \frac{1}{0.446}\sqrt{\frac{RTD}{nFv}} \tag{II.6.2}$$

In this equation 0.446^{-1} is a constant for the case of a reversible diffusion controlled process [59], R is the gas constant 8.31 J K^{-1} mol^{-1}, T is the temperature in Kelvin, D is the diffusion coefficient in m^2 s^{-1}, n denotes the number of electrons transferred per molecule diffusing to the electrode, F is the Faraday constant 96487 C mol^{-1}, and v is the scan rate in Vs^{-1}. The diffusion layer thickness may be compared to the reaction layer thickness, δ_{reaction}, which is given approximately by Eq. (II.6.3).

$$\delta_{\text{reaction}} = \sqrt{\frac{D}{k}} \tag{II.6.3}$$

In this expression D denotes the diffusion coefficient in m^2 s^{-1} and k is the first-order rate constant (s^{-1}) for a chemical reaction step. Similar expressions may be written for other types of chemical processes [60]. The scan rate required for the intermediate to be detected voltammetrically may be estimated based on matching the reaction layer and the diffusion layer (Eq. II.6.4).

$$v = \frac{1}{0.446^2}\frac{kRT}{nF} \tag{II.6.4}$$

For example, an intermediate generated at the electrode surface with $D = 1 \times 10^{-9}$ m^2 s^{-1}, which undergoes a first-order follow-up chemical reaction with $k = 100$ s^{-1}, requires a scan rate of ca. 13 V s^{-1} to be detectable in cyclic voltammetry. The reaction layer thickness in this case can be estimated as approximately 3 μm. During a fast-scan voltammogram, only a fraction of the charge is flowing compared to the experiment at slower scan rate. Therefore, the sensitivity of the spectroscopic detection is reduced considerably. An upper limit of the absorption of the intermediate generated at the electrode surface can be estimated based on the Beer–Lambert law [61] and by assuming $1/2\ \delta_{\text{reaction}}$ to be approximately the 'effective' optical path length. By repeating the experiment and by accumulation of the spectroscopic data, a considerable improvement in the signal-to-noise ratio is possible.

II.6.2.4 Spatial and Mechanistic Resolution

Apart from the detection and characterisation of reaction intermediates it is often desirable to gain quantitative mechanistic information in transient or steady-state electrochemical experiments. From voltammetric experiments, it is known that in some cases one type of voltammetric current response may be interpreted by more than one mechanism [62]. Depending on the type of experiment, coupling a spectroscopic method to a voltammetric experiment may provide complementary data, which then allows a definite decision on which reaction pathway is followed.

Therefore, spectroelectrochemical experiments may be used to obtain more than just data to identify the nature of the reaction intermediate. The spatial distribution and concentration gradients of reactants and products give direct insight into the reaction mechanism of a particular electrode process [63]. A spectroelectrochemical technique with high spatial resolution can yield very valuable data. However, the experimental approach shown, for example, in Fig. II.6.2 can be seen to give an absorbance measurement equivalent to the integral value of all the material produced in the diffusion layer without spatial resolution.

A very elegant approach overcoming this problem has been proposed based on a channel flow cell geometry with downstream detection (Fig. II.6.2d). The potential of the electrode is stepped during steady-state flow of the solution across the electrode. A downstream UV/Vis detector system is then employed to measure the time dependence of the concentration profile formation at the electrode surface. A computer program is employed to relate the time-dependent absorbance signal to the concentration profile of reactant and product at the electrode surface. Alternatively, direct measurement of the concentration profiles at the electrode surface has also been reported based on confocal Raman spectroelectrochemistry [16].

II.6.3 UV/Vis/NIR Spectroelectrochemical Techniques

II.6.3.1 Spectroelectrochemistry in Transmission Mode

A very powerful and convenient approach to couple a spectroscopic method with electrochemical experiments is based on the spectroscopy in the ultraviolet (UV), visible (Vis), and near infrared (NIR) range of the electromagnetic spectrum. This can be achieved with UV/Vis/NIR spectroscopy in transmission mode [64] with an optically transparent electrode employed as the working electrode. There are two distinct types of optically transparent electrodes useful in this approach, a partially transparent metal grid or mesh electrode or a glass plate coated with a conductive but optically transparent layer of indium tin oxide (ITO) as optically transparent electrode (OTE) in a glass or quartz cuvette (see Fig. II.6.4). Also, coatings of very thin metal layers (below 100 nm) on glass substrates can be employed as working OTE in spectroelectrochemical studies [65].

A very simple spectroelectrochemical experiment based on a conventional cuvette for UV/Vis spectroscopy with electrodes immersed in the solution phase is shown in Fig. II.6.4. The optically transparent working electrode is located directly in the beam path and additionally a large surface area counter electrode (Pt wire) and a reference electrode (e.g. a coated silver wire) are located in the solution phase above the beam path. After filling the cuvette with electrolyte solution, the reference spectrum can be recorded taking into account the transparency of the OTE and optical properties of the solution. This reference spectrum is later used to subtract the absorption of the cuvette, the electrolyte, and the OTE from experimental data obtained after applying a potential. Next, the redox reagent is added and the first spectrum of the starting material is recorded. The potential is applied

Fig. II.6.4 Simple in situ
UV/Vis/NIR
spectroelectrochemical cell
with an optically transparent
electrode prepared from a
partly transparent metal mesh,
grid, or gauze electrode
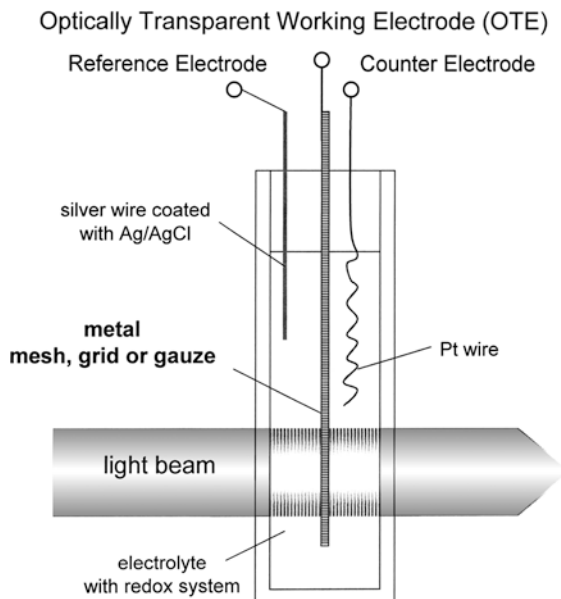
to the optically transparent working electrode using a potentiostat system. Initially, a potential in a zero current region is applied and then a step of the potential is applied (chronoamperometry) into a potential region in which the electrochemical conversion proceeds. By recording spectra at regular time intervals, the conversion of the starting material into products during the course of reduction or oxidation at the working electrode can be followed qualitatively (Fig. II.6.4). At the end-point of the electrolysis process in the limited volume of the cuvette, the product can be identified based on the change in absorption. In the case of an unstable intermediate being generated at the OTE, conclusions concerning the presence of intermediates or follow-up reactions may be possible. In the experimental set-up shown in Fig. II.6.4, reaction intermediates with a half-life in the order of minutes may be detected. In a cuvette with a shorter (1 mm) path length the conversion can be driven to completion.

In order to improve the detection of short-lived intermediates, the potential step or chronoamperometric experiment can be replaced by a cyclic voltammetric experiment, which involves applying a triangular potential ramp. With a fast UV/Vis spectrometer, e.g. a diode array system, additional UV/Vis/NIR spectroscopic information as a function of the potential can be recorded simultaneously to the voltammetric data. However, recording cyclic voltammograms with the simple cell shown in Fig. II.6.4 is complicated by the presence of ohmic drop in the solution phase, which is amplified by poor cell design. In this kind of cell, the peak-to-peak separation in cyclic voltammograms of a reversible redox couple may increase by several hundreds of millivolts. Voltammetric data (and simultaneously recorded spectroscopic data) are therefore very difficult to interpret quantitatively.

The size of the working electrode is large, and with the size the high current results in a high ohmic drop distortion. Additionally, resistance of the electrode itself in the case of a glass plate with a very thin conducting layer may further increase the ohmic iR_U drop problem. Considerable improvements can be achieved by minimising the active electrode area of the working electrode. This can be achieved by insulation of the OTE to leave only a small well-defined working electrode area exposed to the solution and by an optimal placement of reference close to the working electrode, as shown in Fig. II.6.5.

As a further requirement, many electrochemical investigations have to be carried out under an inert atmosphere of argon or nitrogen, and sometimes in pre-dried organic solvents. Therefore, a lid with gas inlet and gas outlet is used combined with a septum seal, which allows solvent to be introduced into the cell without it coming into contact with the ambient atmosphere. The insulation of the OTE requires a material resistant to commonly used organic solvents. Commercially available lamination foil, used for protecting documents, has been employed for this purpose and shown to be suitable even in organic solution [66, 67] (see Fig. II.6.5). The laminating foil is applied to the working electrode simply by thermal encapsulation leaving the active electrode area uncovered.

As a further practical tip, for an OTE based on a thin conductive optically transparent layer, the resistance of the working electrode can be reduced if an additional thicker metal layer is coated on the optically transparent film in the region not exposed to the light beam under the insulation layer. If the insulation is prepared through lamination, a thin metal foil can be simply inserted instead of the deposited metal layer. This new cell design (Fig. II.6.5) enables cyclic voltammograms as well as current time curves in the case of a potential step experiment (chronoamperograms) simultaneously with a series of time-resolved spectra to be recorded. This experimental approach allows absorbance–potential or absorbance–time curves to be recorded to analyse the reaction kinetics of the generation of intermediates and the final product up to a timescale of approximately 0.1 s lifetime.

Problems with cells with relatively long path length (1–10 mm) may arise when the starting material itself is strongly absorbing. As soon as a coloured starting material with broad absorption bands is investigated, the spectra of the intermediates and of the final product are superimposed onto the more intense spectrum of the starting material. This is caused by the fact that the overall absorbance is proportional to the thickness of the investigated layer – the optical path lengths through the material. For the intermediate or product the path length corresponds to the diffusion layer, which is in the range 0.01–1 mm. The size of the diffusion layer and reaction layer depends on the timescale of the experiment. For a cuvette with a size of 5 mm the layers of the products may be a factor 10–10000 times thinner than the layer for the starting material. By reducing the size of the cuvette from a thin layer cell down to a capillary slit cell this problem can be solved. Effectively, the optical path length of the cell and the diffusion layer for the electrochemical process can be matched.

Figure II.6.6 shows two possible designs of capillary slit cells. The second type of cell has the added advantage of being suitable also for in situ ESR spectroelectrochemical experiments. Capillary slit cells permit fast electrochemical conversion
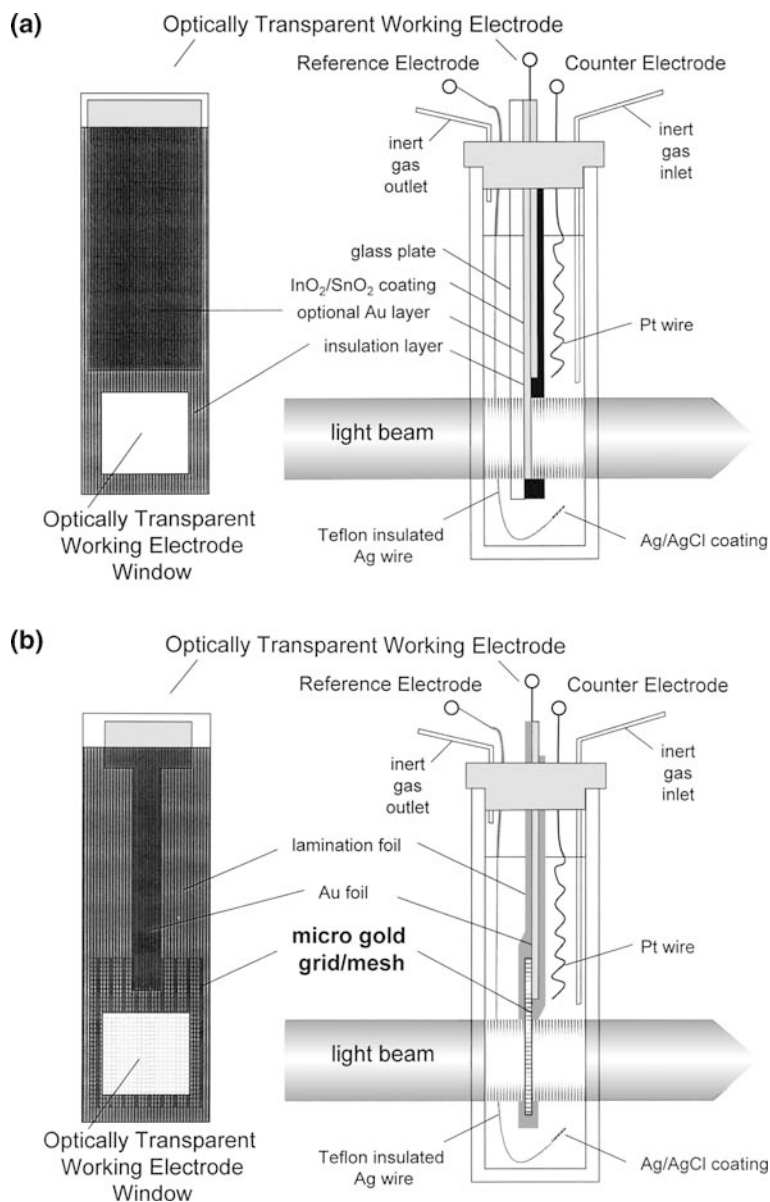
Fig. II.6.5 An improved in situ UV/Vis/NIR spectroelectrochemical cell design with an optically transparent electrode prepared from *top* a glass substrate coated by a thin conductive optically transparent ITO layer and *bottom* a metal mesh, grid, or gauze

of the starting material into unstable radical intermediates, which may be followed in time during follow-up chemical reaction steps. The thickness of the capillary slit, together with the diffusion coefficient D of the reactant, determine the approximate conversion time $\tau_{\text{diffusion}}$ (Eq. II.6.5).
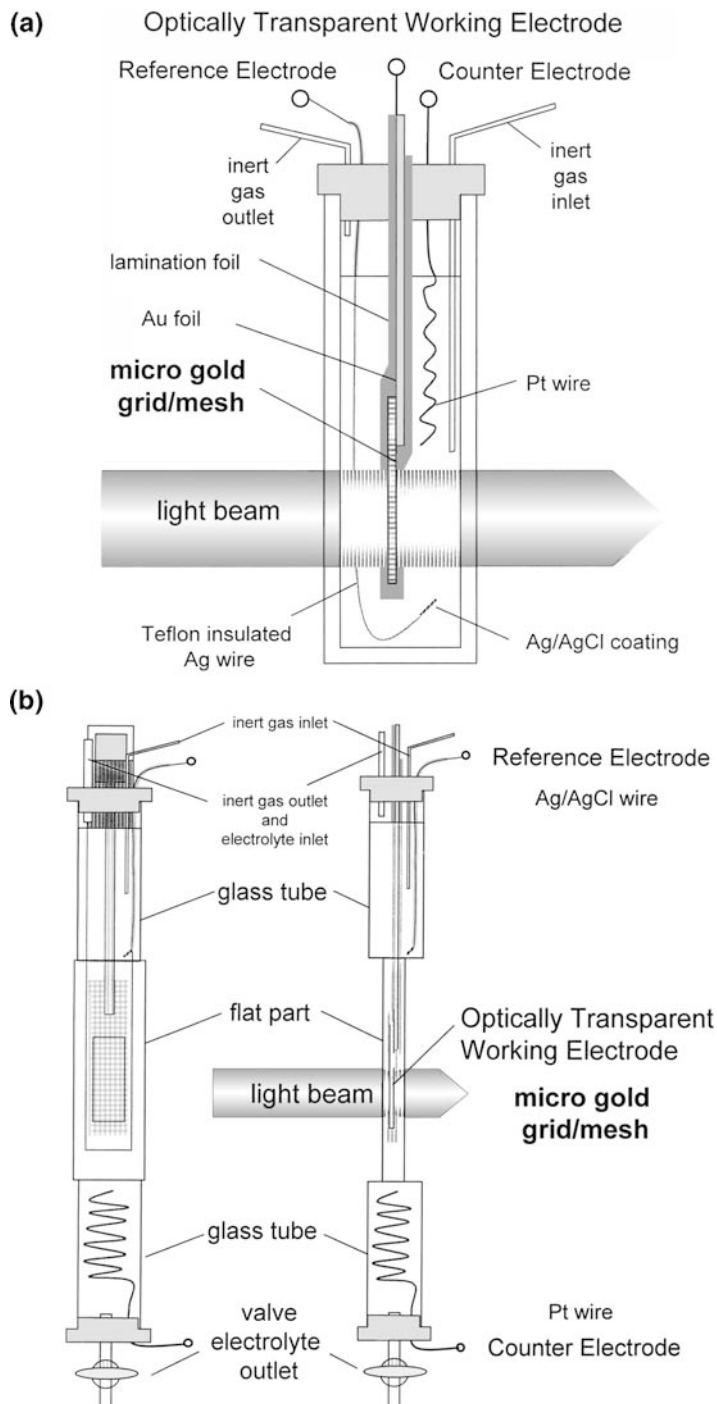
Fig. II.6.6 Capillary slit in situ UV/Vis/NIR spectroelectrochemical cells with an optically transparent electrode prepared from a metal mesh, grid, or gauze in a *top* cuvette cell and in a *bottom* flat cell with outlet allowing the solution to flow through the slit

$$\tau_{\text{diffusion}} = \frac{\delta^2}{D} \qquad\qquad (II.6.5)$$

Unfortunately, even when capillary slit cells are used in the experiment, the spectra of the different species are still superimposed. Therefore, it is necessary to separate or to 'deconvolute' the superimposed spectra in order to obtain information about the reaction kinetics of individual species. In the literature, techniques have been proposed for the deconvolution of the superimposed spectra [68, 69]. Data processing and deconvolution may be achieved with spreadsheet software on a suitable computer system. As soon as the time dependence of the concentration of each component is known, the absorbance–time curves and the charge–time curves calculated from the current passing the electrode can be used to determine rate or equilibrium constants for the chemical system under study.

Instead of a capillary slit, a thin partly transparent three-dimensional structure may also be employed in spectroelectrochemical studies. To achieve the same level of sensitivity compared to that in a capillary slit cell, grid-like optically transparent electrodes with micro-structured electrodes have been employed [70–72]. In the grid system the size of individual pores determines the size of the diffusion-layer thickness and therefore the timescale of the experiment. A more sophisticated approach has been introduced by replacing the simple grid electrode by a LIGA structure (prepared by the LIGA technique: lithographic galvanic up-forming based on a synchrotron radiation patterned template). A thick honeycombed structure (see Fig. II.6.7) has been used with hexagonal holes of micron dimension. The size of the holes restricts the diffusion-layer thickness into a fast timescale regime, although the optical-path length of the cell is kept relatively long to give strong absorption responses in the spectroscopic measurement.

Figure II.6.8 shows the data obtained from the UV/Vis spectroelectrochemical study of a oligo-thiophene (see structure in Fig. II.6.8) in a LIGA cell [73]. The oligo-thiophene was dissolved in a solution of 0.1 M NBu_4PF_6 in acetonitrile and voltammograms were recorded at two different temperatures, at (A) +20°C and (B) −40°C. What appears to be an electrochemically reversible oxidation process at +1.16 V can be seen to become much more complicated at lower temperature. The analysis of spectroelectrochemical data clearly indicates the presence of two distinct products of which one, the radical cation $A^{\bullet+}$, is detected at ambient temperature (Fig. II.6.8 A). A second product, the dimer A_2^{2+}, is present at 20°C in low concentration. However, upon reducing the temperature in the spectroelectrochemical cell to −40°C, the dimer becomes the dominant product (Fig. II.6.8B) causing a change in both the voltammetric and the UV/Vis spectroelectrochemical response.

The spectroelectrochemical cell based on the LIGA-OTE can be employed in a flow-through-type system. Then, this cell allows the rapid renewal of the solution inside the cell after a spectroelectrochemical experiment. Experiments can be repeated rapidly and with a small volume of sample. A series of experiments can be conducted by varying the conditions without the need to open the cell. The use of optical waveguides to connect the cell with a light source and the spectrometer offers further scope for improvements in the experimental methodology.
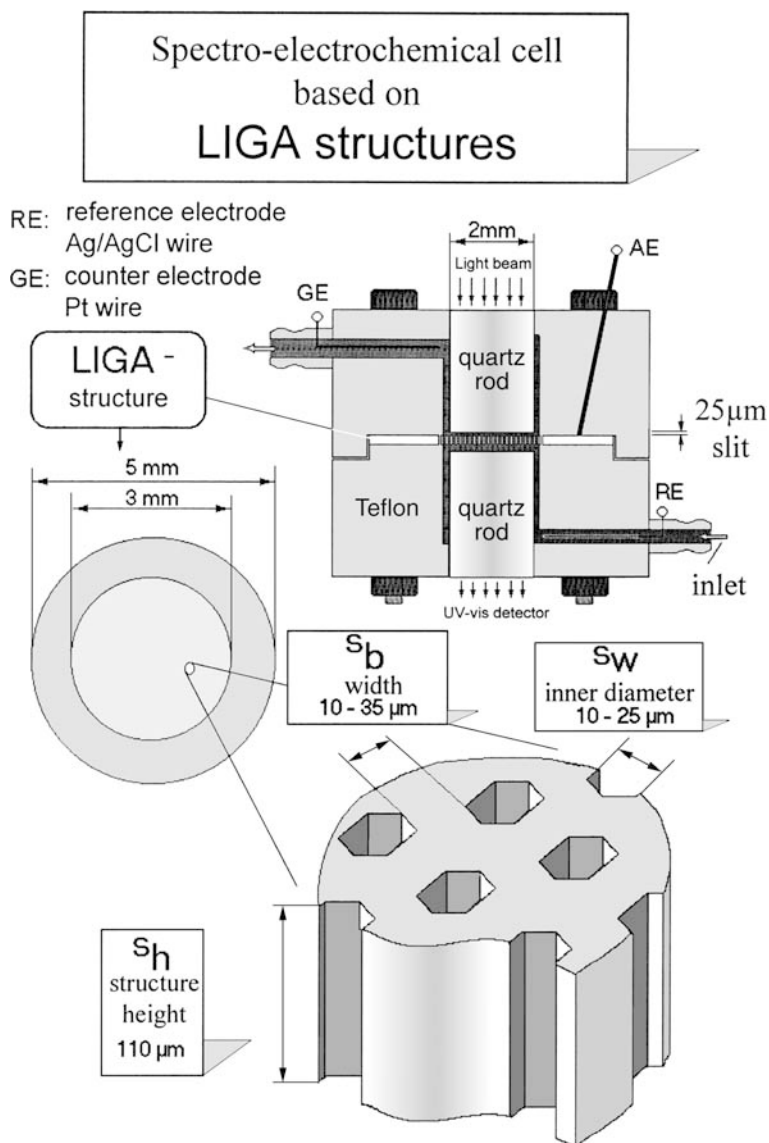
Fig. II.6.7 In situ UV/Vis/NIR spectroelectrochemical cell based on a microstructured optically partly transparent electrode with LIGA design

Conducting ITO-coated glass electrodes generate relatively simple 'planar' concentration profiles. The detected absorption of products generated at this type of electrode is easily related to the overall charge passed through the cell, because the absorption is directly proportional to the concentration integrated over the entire diffusion layer. Compared to optically transparent conductive glass electrodes, partly
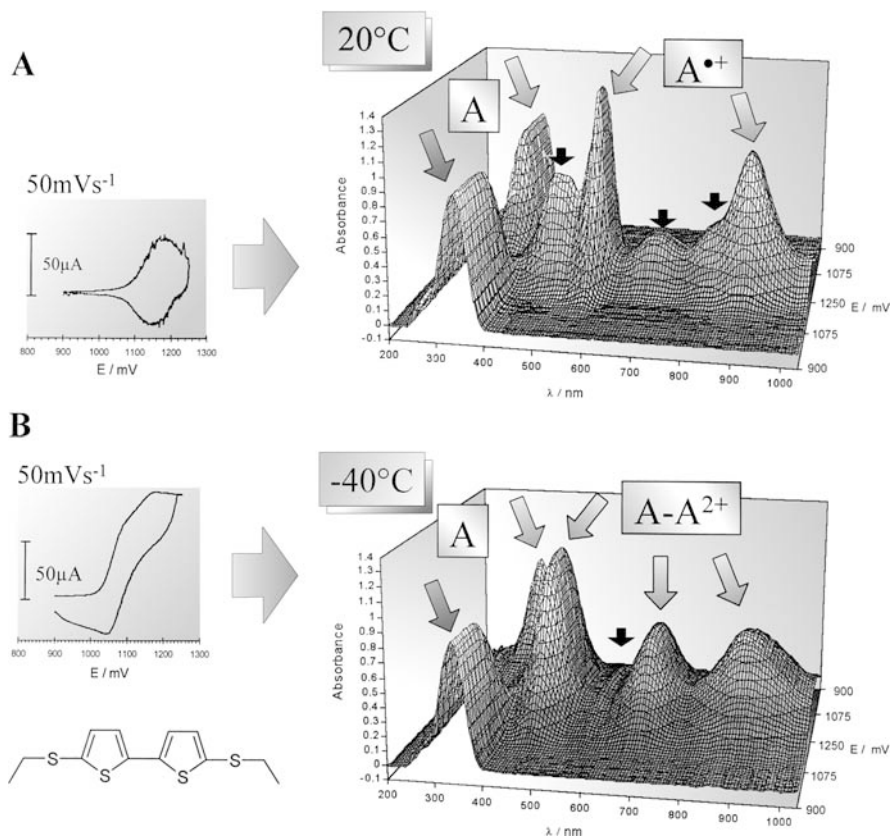
Fig. II.6.8 UV/Vis spectroelectrochemical detection of the oxidation products for the oxidation of an oligo-thiophene in acetonitrile (0.1 M NBu$_4$PF$_6$). The voltammetric and in situ spectroelectrochemical measurements were conducted at (**A**) 20°C and (**B**) −40°C in a LIGA cell system

transceptor electrodes, such as meshes, grids, gauzes, and micro-structures, give more complex concentration profiles, which change geometry as a function of time. For these latter types of electrodes, the absorption signal detected during electrolysis is *not* necessarily proportional to the amount of the product generated. For quantitative investigations, details of the geometry of the diffusion layer and the time dependence have to be taken into account. For example, locally, a concentration gradient is generated at each wire of a grid electrode orthogonal to the light beam.

The development of the concentration profile for a grid electrode may then be considered to occur in two steps. First, the concentration profile grows into the space between individual wire electrodes perpendicular or orthogonal to the incoming light beam. In this situation, the absorbance detected experimentally is not proportional to the concentration of product generated due to the complex shape of the concentration gradient. Next, the individual concentration gradients merge to a planar diffusion front, which then is proportional to the amount of electrogenerated

product similar to the case observed for ITO-coated electrodes. In cyclic voltam-
metric experiments with in situ spectroelectrochemical detection of the UV/Vis/NIR
absorbance one has to therefore carefully consider the grid size and the scan rate to
stay in the planar diffusion regime. This then allows the absorbance to be compared
to the charge passed determined by integrating the current response.

Based on the development of a diffusion front with dimension $d_{\mathrm{diffusion}}$ (Eq.
II.6.6), at very fine meshes, grids, or gauzes with a wire density of 1000 wires per
inch or more, the effect of the changing diffusion layer geometry becomes negligible
after a time t of ca. 50 ms.

$$\delta_{\mathrm{diffusion}} \approx \sqrt{Dt} \qquad\qquad\qquad \text{(II.6.6)}$$

However, diode array spectrometer systems permit spectra to be recorded in
about 0.5-ms steps. Therefore, it is necessary to analyse the data carefully with
respect to consistency by considering the type of diffusion profile at a given time in
the course of the experiment.

A very similar effect of a non-linear concentration to absorbance dependence
occurs in grazing angle or long path length cells. In this type of cell (see
Fig. II.6.9), the detector beam of the spectrometer passes parallel to the working
electrode through the electrochemical cell. The advantage of spectroelectrochemical
measurements in transmission through a long path length cell is the high sensitivity,
which can be achieved even with a small electrode.

The first long path length cell was described from Niu et al. [74] for ana-
lytical applications where high sensitivity is required. In order to overcome the
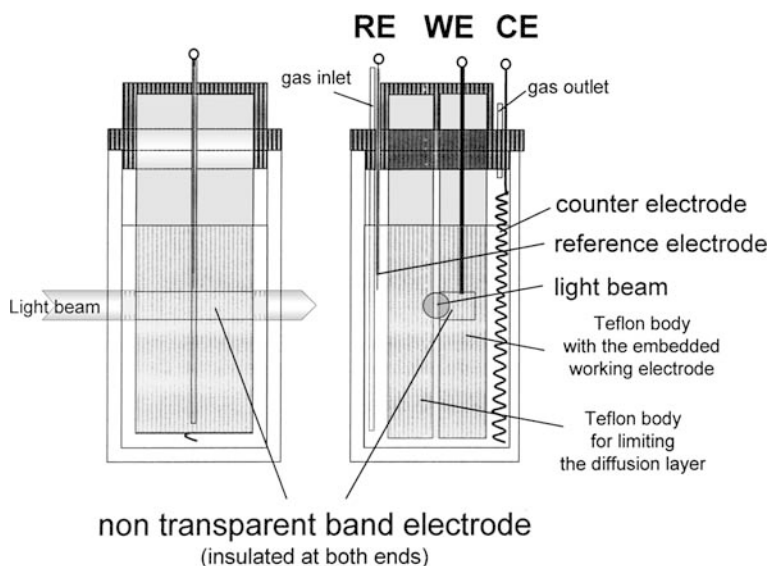
Fig. II.6.9 In situ UV/Vis/NIR spectroelectrochemical 'long path length cell' based on a non-
transparent band electrode in a capillary slit and a light beam focused through the diffusion layer
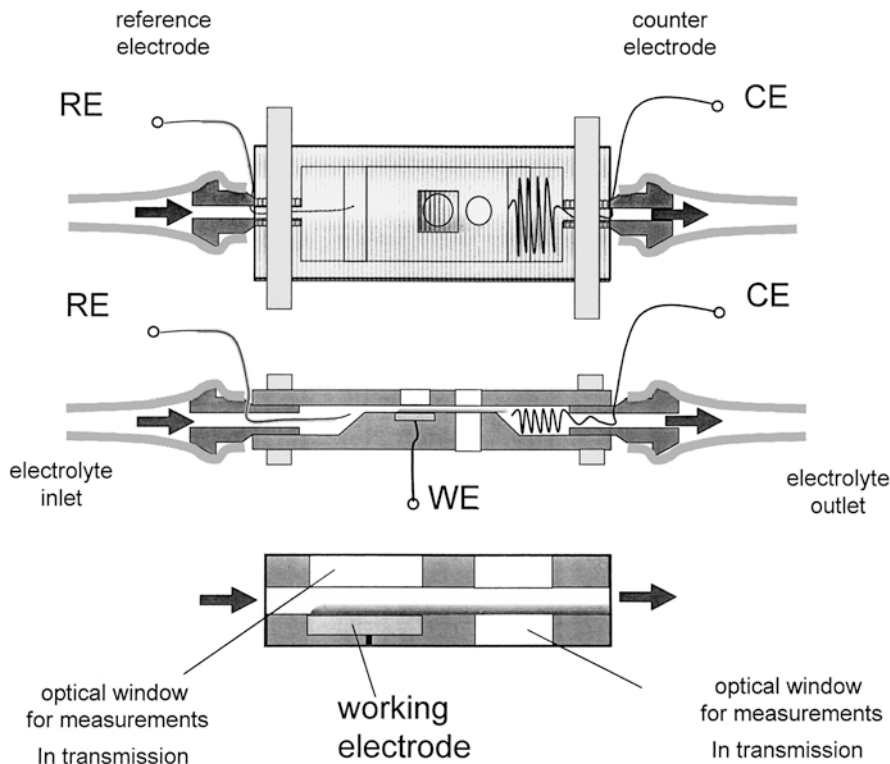
Fig. II.6.10 In situ UV/Vis/NIR spectroelectrochemical flow cell design, which allows spectra to be recorded in transmission and in reflection mode

non-linearity in the absorbance response, a capillary slit type cell is employed with a size similar to the diffusion layer. This allows the detection of all of the product generated electrochemically. For very thin slits, the total conversion of the starting material to the products occurs in only a few milliseconds. This short timescale permits the reaction kinetics of fast reactions to be followed. Instead of using a wall to limit the diffusion-layer thickness, it is also possible to focus the light beam into a very thin layer close to the electrode with a suitable lens system. In this configuration, only the concentration of reagent immediately at the electrode surface is measured in the spectroscopic detection. The current signal from a cyclic voltammogram can be processed by semi-integration [75] to give a signal directly proportional to the surface concentration and is, therefore, ideal for the analysis of the spectroelectrochemical data.

A laser beam focused into the diffusion layer in combination with a diode array detector may even be used to directly image the concentration profile inside the diffusion layer, as described by Posdorfer et al. [76, 77].

The in situ UV/Vis/NIR spectroelectrochemical cells shown in Figs. II.6.6 and II.6.7 permit solution to flow through the cell. However, the flow is only used to

renew the solution at the electrode and to allow repeat experiments under identical conditions or on different timescales. Experiments may also be conducted under flowing conditions at a fixed flow rate or as a function of flow rate. In the case of short-lived intermediates being formed a continuous electrolysis in a streaming electrolyte allows the steady-state concentration of intermediates to be measured independent of time. The concentration of the intermediate in the flowing solution might be low, but the concentration is constant over a long time and this permits spectra to be recorded over a long timescale and with high sensitivity. An in situ spectroelectrochemical cell system, which allows spectra to be recorded under flowing solution conditions, is shown in Fig. II.6.10. Both measurements in transmission and measurements in reflection mode are possible and software for modelling concentration profiles and reaction kinetics under flowing conditions has been described.

II.6.3.2 Spectroelectrochemistry in Reflection Mode

In the previous section, it was shown that detailed information about electrochemical processes and the kinetics of follow-up chemical reaction steps can be investigated by UV/Vis/NIR spectroelectrochemical experiments in transmission mode
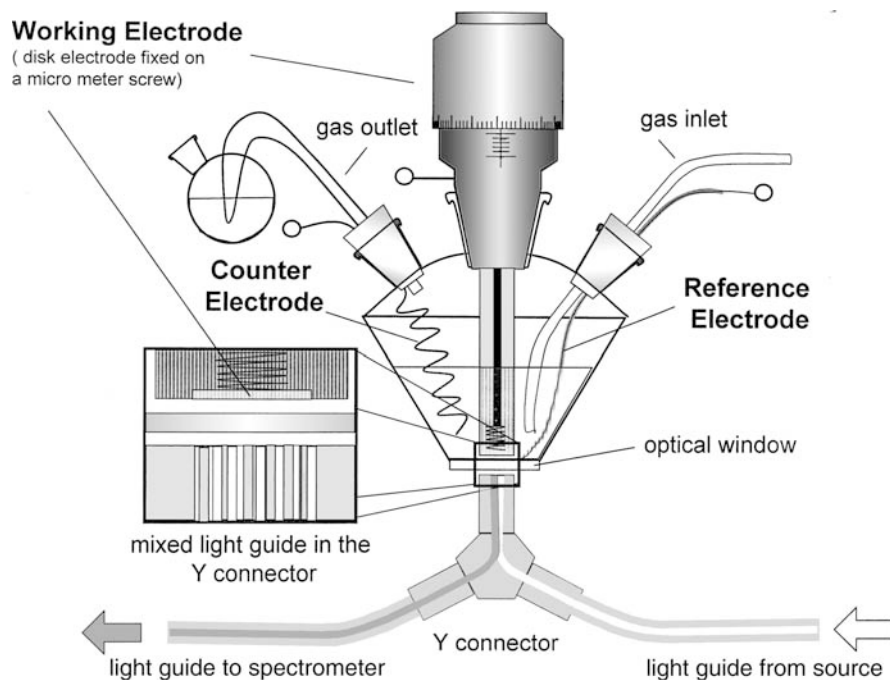
Fig. II.6.11 In situ UV/Vis/NIR spectroelectrochemical cell for measurements in reflection mode at conventional disc electrodes

in the diffusion layer at optically transparent or microstructured non-transparent electrodes. Many metal electrodes show a high reflectivity, and therefore optical spectra may also be recorded under in situ conditions in reflection mode [78, 79]. This approach is essential for the study of adsorbed species, the formation of solid layers at the electrode surface, reactions of solids [80–82], and the redox behaviour of conducting polymer layers [83–85]. Furthermore, in reflection mode, the angle of incidence may be modified and polarised light may be used in ellipsometry studies [86].

By using optical waveguides for illumination and detection, it is possible to record spectra at a disc electrode during the course of cyclic voltammetric measurements (see Fig. II.6.11). Fixing the disc electrode onto a micrometer screw allows the distance between the electrode and the optical window to be varied in a very much easier way compared with the procedure required in in situ spectroelectrochemical cells working in the transmission mode. In this experimental arrangement, the gap between the electrode surface and the wall with the optical waveguide defines the diffusion layer thickness and therefore the type of absorbance response or timescale.

In conclusion, UV/Vis/NIR spectroelectrochemistry in both transmission and reflection mode are extremely useful techniques that yield a wealth of complementary data additional to those obtained in pure electrochemical voltammetric experiments. Especially when based on computer simulation models, this data may be used to unravel the kinetics and thermodynamics of complex electrode processes.

References

1. Bard AJ, Faulkner LR (2001) Electrochemical methods – fundamentals and applications, 2nd edn. John Wiley, New York
2. Dong S, Niu J, Cotton TM (1994) Biochemical spectroscopy. In: Abelson JN, Simon MI (eds) Methods in enzymology. vol 246, Academic Press, Orlando, Florida
3. Broman RF, Heineman WR, Kuwana T (1973) Faraday Discuss Chem Soc 56: 816
4. Aylmer-Kelly AWB, Bewick A, Cantrill PR, Tuxford AM (1973) Faraday Discuss Chem Soc 56: 96
5. Heineman WR, Hawkridge FM, Blount HN (1984) Electroanal Chem 13: 55
6. Kuwana T, Winograd N (1974) Electroanal Chem 7: 74
7. Kaim W, Klein A (2008) Spectroelectrochemistry. RSC Publishing, Cambridge, UK
8. Goldberg IB, McKinney TM (1984) In: Kissinger PT, Heineman WR (eds) Laboratory techniques in electroanalytical chemistry. Marcel Dekker, New York, p 675
9. Compton RG, Waller AM (1988) ESR spectroscopy and electrode processes. In: Gale RJ (ed) Spectroelectrochemistry – theory and practice. Plenum Press, New York, p 349
10. McKinney TM (1977) Electroanal Chem 10: 77
11. Bagchi RN, Bond AM, Scholz F (1989) Electroanalysis 1: 1
12. Bard AJ, Faulkner LR (1980) Electrochemical methods – fundamentals and applications. John Wiley, New York, p 577
13. Hamann CH, Hamnett A, Vielstich W (1998) Electrochemistry. John Wiley, New York, p 247
14. Mazurenka M, Wilkins L, Macpherson JV, Unwin PR, Mackenzie SR (2006) Anal Chem 78: 6833
15. Browne WR, McGarvey JJ (2007) Coord Chem Rev 251: 454

16. Amatore C, Bonhomme F, Bruneel JL, Servant L, Thouin L (2000) J Electroanal Chem 484: 1
17. Compton RG, Fisher AC, Wellington RG (1991) Electroanalysis 3: 27
18. Kanoufi F, Bard AJ (1999) J Phys Chem B 103: 10469
19. Collinson MM, Wightman RM (1995) Science 268: 1883
20. Prenzler PD, Bramley R, Downing SR, Heath GA (2000) Electrochem Commun 2: 516
21. La Mar GN, Horrocks WDW, Holm RH (1973) NMR of paramagnetic molecules: principles and applications. Academic Press, New York
22. Silva-Chong JA, Guillen-Villafuerte O, Rodriguez JL, Pastor E (2008) J Solid State Electrochem 12: 517
23. Kolb DM (1988) UV-Visible reflectance spectroscopy. In: Gale RJ (ed) Spectroelectrochemistry – theory and practice. Plenum Press, New York, p 87
24. Beden B, Lamy C (1988) Infrared reflectance spectroscopy. In: Gale RJ (ed) Spectroelectrochemistry – theory and practice. Plenum Press, New York, p 189
25. Schröder U, Scholz F (2000) Inorg Chem 39: 1006
26. Kavan L, Dunsch L (2007) ChemPhysChem 8: 975
27. Tong YY, Rice C, Wieckowski A, Oldfield E (2000) J Am Chem Soc 122: 1123
28. Pemberton JE (1991) Surface enhanced Raman scattering. In: Abruna HD (ed) Electrochemical interfaces. VCH, Weinheim, p 195
29. Mrozek MF, Weaver MJ (2000) J Am Chem Soc 122: 150
30. Birke RL, Lu T, Lombardi JR (1991) Surface enhanced Raman spectroscopy. In: Varma R, Selman JR (eds) Characterization of electrodes and electrochemical processes. John Wiley, New York, p 211
31. Murgida DH, Hildebrandt P (2008) Chem Soc Rev 37: 937
32. Wasileski SA, Zou SZ, Weaver MJ (2000) Appl Spectrosc 54: 761
33. Bailo E, Deckert V (2008) Chem Soc Rev 37: 921
34. McBreen J (1995) In situ synchrotron techniques in electrochemistry. In: Rubinstein I (ed) Physical electrochemistry. Marcel Dekker, New York, p 339
35. Abruna HD (1991) Electrochemical interfaces. VCH, Weinheim
36. Robinson J (1988) X-ray techniques. In: Gale RJ (ed) Spectroelectrochemistry – theory and practice. Plenum Press, New York, p 9
37. Scherson DA (1991) Mössbauer spectroscopy. In: Abruna HD (ed) Electrochemical interfaces. VCH, Weinheim, p 413
38. Gottesfeld S, Kim YT, Redondo A (1995) Recent applications of ellipsometry and spectroellipsometry in electrochemical systems. In: Rubinstein I (ed) Physical electrochemistry. Marcel Dekker, New York, p 393
39. Grieshaber D, MacKenzie R, Voros J, Reimhult E (2008) Sensors 8: 1400
40. Richmond GL (1991) Investigations of Electrochemical interfaces by nonlinear optical methods. In: Abruna HD (ed) Electrochemical interfaces. VCH, Weinheim, p 267
41. Szunerits S, Pust SE, Wittstock G (2007) Anal Bioanal Chem 389: 1103
42. Drago RS (1977) Physical methods in chemistry. Saunders and Co., London
43. Xie QJ, Nie LH, Yao SZ (1997) Anal Sci 13: 453
44. Cooper JA, Compton RG (1998) Electroanal 10: 141
45. Brett CMA, Brett AMO (1993) Electrochemistry: principles, methods, and applications. Oxford University Press, Oxford
46. Wang ZH, Zhao M, Scherson DA (1994) Anal Chem 66: 4560
47. Rieger PH (1994) Electrochemistry. Chapman & Hall, London
48. Wang ZH, Zhao M, Scherson DA (1994) Anal Chem 66: 1993
49. Montenegro MI, Queiros MA, Daschbach JL (1991) Micro electrodes: theory and applications, Nato ASI Series, vol 197. Kluwer, London
50. Zhao M, Scherson DA (1992) Anal Chem 64: 3064
51. Compton RG, Dryfe RAW (1995) Prog Reaction Kinetics 20: 245
52. Albery WJ, Compton RG, Kerr IS (1980) J Chem Soc Perkin Trans 2: 825
53. Albery WJ, Chadwick AT, Coles BA, Hampson NA (1977) J Electroanal Chem 75: 229

54. Prieto F, Webster RD, Alden JA, Aixill WJ, Waller GA, Compton RG, Rueda M (1997) J
     Electroanal Chem 437: 183
55. Kress L, Neudeck A, Petr A, Dunsch L (1996) J Electroanal Chem 414: 31
56. Wang RL, Tam KY, Marken F, Compton RG (1997) Electroanalysis 9: 284
57. Wang RL, Tam KY, Compton RG (1997) J Electroanal Chem 434: 105
58. Marken F, Neudeck A, Bond AM, Cyclic Voltammetry this Volume
59. Marken F, Neudeck A, Bond AM, Cyclic Voltammetry this Volume
60. Marken F, Neudeck A, Bond AM,, Cyclic Voltammetry this Volume
61. Atkins PW (2000) Physical chemistry, 6th edn. Oxford Univ Press, Oxford
62. Marken F, Neudeck A, Bond AM, Cyclic Voltammetry this Volume
63. Amatore C, Szunerits S, Thouin L (2000) Electrochem Commun 2: 248
64. (a) Niu J, Dong S (1996) Rev Anal Chem 15: 1; (b) Salbeck J (1993) Anal Chem 65: 2169
65. Porter JD, Heller A, Aspnes DE (1985) Nature 313: 664
66. Neudeck A, Kress L (1997) J Electroanal Chem 437: 141
67. Rapta P, Neudeck A, Petr A, Dunsch L (1998) J Chem Soc Faraday Trans 94: 3625
68. Massart DL, Vandeginste BGM, Deming SN, Michotte Y, Kaufman L (1988) Chemometrics:
     a textbook. Elsevier, Oxford
69. Keesey RL, Ryan MD (1999) Anal Chem 71: 1744 and references cited therein
70. Neudeck A, Dunsch L (1995) Electrochim Acta 40: 1427
71. Neudeck A, Dunsch L (1995) J Electroanal Chem 386: 135
72. Neudeck A, Dunsch L (1993) Ber Bunsges Phys Chem 97: 407
73. Neudeck A, Audebert P, Guyard L, Dunsch L, Guiriec P, Hapiot P (1999) Acta Chem Scand
     53: 867
74. Niu J, Dong S (1995) Electrochim Acta 3: 1059
75. Oldham KB, Myland JC (1994) Fundamentals of electrochemical science. Academic Press,
     London
76. Posdorfer J, Olbrich-Stock M, Schindler RN (1994) Electrochim Acta 39: 2005
77. Posdorfer J, Olbrich-Stock M, Schindler RN (1994) J Electroanal Chem 368: 173
78. Hansen WN (1973) Internal reflection spectroscopy in electrochemistry. In: Muller RH (ed)
     Advances in electrochemistry and electrochemical engineering, vol 9. John Wiley, New York
79. McIntyre JDE (1973) Specular reflection spectroscopy of the electrode-solution interphase.
     In: Muller RH (ed) Advances in electrochemistry and electrochemical engineering, vol 9.
     John Wiley, New York
80. Ramaraj R, Kabbe C, Scholz F (2000) Electrochem Commun 2: 190
81. Bond AM, Marken F, Hill E, Compton RG, Hügel H (1997) J Chem Soc Perkin Trans 2: 1735
82. Schröder U, Scholz F (1997) J Solid State Electrochem 1: 62
83. Rapta P, Neudeck A, Petr A, Dunsch L (1998) J Chem Soc Faraday Trans 94: 3625
84. Neudeck A, Petr A, Dunsch L (1999) J Phys Chem B 103: 912
85. Aubert PH, Neudeck A, Dunsch L, Audebert P, Maumy M (1999) J Electroanal Chem 470: 77
86. Muller RH (1973) Principles of ellipsometry. In: Muller RH (ed) Advances in electrochem-
     istry and electrochemical engineering, vol 9. John Wiley, New York