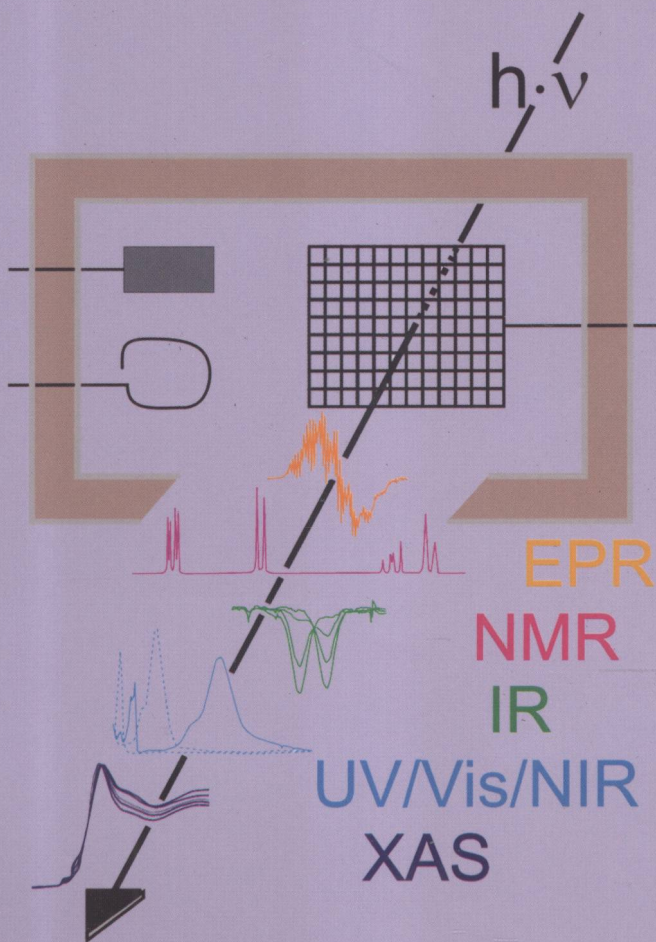


Edited by Wolfgang Kaim and Axel Klein

# Spectroelectrochemistry



RSC Publishing

# ***Spectroelectrochemistry***

Edited by

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## Spectroelectrochemistry

# Preface

As a truly interdisciplinary field of science, electrochemistry is involved in the transformation of materials, in the transfer of information (especially in living systems), and in the conversion and storage of energy. Furthermore, electrochemical processes constitute a major class of chemical reactions in the laboratory and on large industrial scales. Conventional analytical electrochemistry continues to be an excellent method to determine concentrations (sensor technology), to yield energy data in the form of redox potentials, and to elucidate formal reaction mechanisms *via* kinetic analysis. However, these techniques are not by themselves suitable to identify unknown species that are formed as intermediates or as products in a redox reaction. The combination of *reaction-oriented electrochemistry* with *species-focused spectroscopy*, in what is known as spectroelectrochemistry (SEC), can solve this problem and thus allow for a more complete analysis of electron-transfer processes and complex redox reactions. While the technique has been well developed during the last few decades, its application in various fields of chemistry has only recently become more widespread. Readily accessible, inexpensive equipment and lower barriers to application have contributed to this situation and, at the same time, it is becoming less and less acceptable in chemical research to assign redox transformations without spectral evidence. Yet, while the method has become more commonplace, there are still aspects to be considered that require sound knowledge and experience. This book is meant to serve as a guide and as an illustration of the kind of research where SEC can make a difference in the understanding of redox reactions through identification of their intermediates and products. The examples covered include organometallics, coordination compounds (mixed-valence complexes, metalloporphyrins), and compounds of biochemical interest such as iron-containing proteins. Solutions available from spectroelectrochemical investigation not only provide simultaneous reaction analysis and species identification but also an assessment of electronic situations, of intra- and intermolecular electron transfer. We hope that this presentation helps to familiarise the scientific

community with the method by describing the experimental approaches possible and by pointing out under what diverse circumstances this technique can be useful. We sincerely thank Mrs. Angela Winkelmann for her contribution in preparing this presentation.

Wolfgang Kaim  
Axel Klein

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## CHAPTER 1

# *Infrared Spectroelectrochemistry*

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## 1.1 Introduction

A set of electrochemical measurements may, with the aid of simulations, provide skeletal details of the redox-coupled reactions of a system, although the extent of the detail or uniqueness of the description depends on the complexity of the system and the relative rates of reaction. Since such an approach can, at best, yield only limited insight into the structure of intermediate species there is a clear need to supplement the electrochemical measurements by spectroscopic investigations. This need has spawned a number of approaches designed to provide the spectroscopic details of the electrogenerated intermediates/products. Spectro-electrochemical (SEC) techniques allow *in-situ* spectroscopic interrogation of electrogenerated complexes and this may permit the study of shorter-lived species and also establish the chemical reversibility of these reactions. This allows the building, testing and refinement of the mechanism and, crucially, provides insights into the structures of the intermediates.

The structure of the intermediate implicitly encompasses molecular, electronic, and vibrational components where the molecular structure is most commonly deduced by X-ray crystallography. More limited structural data may also be obtained from solute species through analysis of the X-ray absorption fine structure (XAFS) spectra and this will be discussed briefly in Section 1.6. Clearly the electronic and vibrational structure must be obtained from analysis of the spectra. The interconnection between these aspects of the structure is reinforced by *in-silico* techniques, where advances in DFT (density-functional theory) have greatly expanded the range of transition-metal compounds and

smaller clusters that are amenable to study. For systems of moderate complexity a combination of structural, spectroscopic and *in-silico* approaches is required in order to achieve a satisfactory understanding of the intermediates formed during reaction. This chapter focuses on the use of IR spectroscopy to delineate the chemistry following redox activation and the integration of these results with a range of electrochemical, spectroscopic and computational methods to characterise the charge state and structure of intermediate species. While the vibrational structure of a species would ideally be determined through the examination of both its IR and Raman spectra, in most cases the complementary nature of the physical constraints associated with the two techniques results in studies concentrating on one or the other approaches. In cases where the system under investigation incorporates strongly IR absorbing chromophores, such as CO or CN<sup>-</sup>, IR spectroscopy can be both effective and easily implemented.

Since the objective of the studies described herein is the characterisation of the solute species formed following redox reaction the very extensive research dealing with characterisation of the electrode/solute interface will not be discussed, excellent overviews of the experimental aspects of this subject are available.<sup>1</sup> While this contribution focuses on applications involving IR, Raman spectroscopy has proved to be invaluable to many SEC studies where surface-enhanced Raman spectroscopy (SERS) and resonance Raman spectroscopy dominate. Reviews and recent studies attest to the value of these approaches.<sup>2</sup>

In this contribution we aim to illustrate the impact of IR-SEC techniques on the elucidation of the chemistry following a redox reaction. The most effective experimental approach will depend on the stability of the redox products together with the rates or nature of the following reactions. In Section 1.5 we show the experimental results obtained from several systems chosen so as to highlight the different experimental approaches that can be applied to good effect. We have limited the discussion to studies of solute species and to concentrating on examples drawn from our own research, published and unpublished. This is driven, in large part, by the availability of the raw experimental data and the opportunity that this provides to recast the figures in a self-consistent form. As a result, there is an overrepresentation of studies conducted using external reflectance SEC cells.

## 1.2 Overview of IR-SEC Techniques for the Study of Solute Species

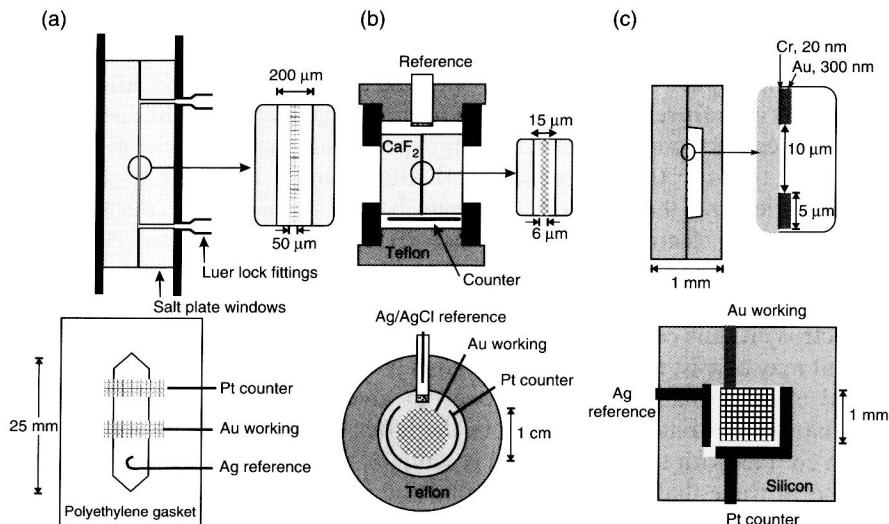
The marriage between the spectroscopic and electrochemical requirements of the SEC experiment necessarily involves compromise, the nature of which will be dictated by the objectives of the study. For thin-layer cells with large surface area electrodes uncompensated solution resistance will generally present problems and these will be accentuated for studies conducted in highly resistive solvents. In many cases it is not practicable to use a conventional reference

electrode and in these instances a pseudoreference consisting of a silver or platinum wire or foil is used. While such electrodes are susceptible to a drift in potential the impact of this deficiency may be minimised if the duration of the experiment is short relative to a change in the concentration of the species near the reference electrode. Several different experimental approaches have proved to be effective for the collection of IR-SEC results from electrogenerated solute species and these may be distinguished in terms of the characteristics of the working electrode. These include (i) optically transparent electrodes, (ii) perforated electrodes and (iii) reflective electrodes. To these may be added approaches in which a probe beam is brought close to the working electrode of an electrosynthesis cell by means of a waveguide or optical fibre. The sampling element may consist either of a pair of launch and collection fibres or include an optical element that is arranged so as to give near-total internal reflection (attenuated total reflection, ATR). In the latter case the spectrum of the solution in contact with the ATR crystal is sampled through its interaction with the evanescent wave that propagates beyond the reflecting surface. Depending on the cell geometry, and volume of solution, the time required for electrosynthesis can be substantial ( $>1$  h) in which case the distinction between *in-situ* and *ex-situ* spectroscopic interrogation is not clear cut. With careful attention to the design it is possible to reduce the volume of solution subject to electrosynthesis and thereby reduce the response time. An ATR IR-SEC cell featuring a sample chamber with a volume of  $20\ \mu\text{L}$  has recently been reported, although even in this case the cell requires *ca.* 6 min for redox equilibration following a potential step.<sup>3</sup>

### 1.3 Transmission Cells Using Optically Transparent or Perforated Electrodes

In optical terms the simplest SEC approach involves the use of transparent electrodes. For visible spectroscopy doped tin oxide affords a useful spectral window.<sup>4</sup> More recently boron-doped diamond has been shown to be suitable for UV-Vis and IR spectroscopy.<sup>5,6</sup> This material offers a wide potential range, inertness in chemically aggressive environments and biocompatibility.<sup>7</sup> The spectroscopic range and conductivity depends on the boron doping level. Diamond films with moderate levels of boron doping ( $0.5$  to  $0.05\ \Omega\text{cm}^{-1}$ ,  $1\text{--}10 \times 10^{19}\ \text{B cm}^{-3}$ ) retain a high transmittance in the region below  $1500\ \text{cm}^{-1}$ .<sup>6</sup>

An alternative strategy to the use of transparent electrodes is to use a conductor in the form of a grid or fine gauze. Cells constructed using this approach date back to the work of Murray *et al.*<sup>8</sup> and have been used for UV-Vis and IR spectroscopic studies. In the latter case the solution pathlength must be minimised in order to avoid problems associated with strong solvent absorption. The principle for construction of the cell is straightforward, generally involving modification of a solution IR cell by incorporation of a fine metal gauze working electrode located in the path of the IR beam. A good example of a compact, airtight cell based on this approach has been reported by Hartl and



**Figure 1.1** Schematic of transmission SEC cells (a) after Hartl,<sup>9</sup> (b) after Moss<sup>10</sup> and (c) after Yun.<sup>11</sup>

coworkers.<sup>9</sup> In this case the working, counter, and reference electrodes occupy the space between the salt plate windows as shown in Figure 1.1a. The working and counter gauze electrodes and silver pseudoreference electrode are melt-sealed into a single 200-μm thick polyethylene spacer. The working electrode has a dimension slightly larger than the IR beam (6 × 5 mm) and is formed from a highly transmitting (80%) Au minigrid (200 lines/mm). Platinum gauze of similar surface area serves as the counter electrode. The approach is well suited to the study of air-sensitive species since solutions may be transferred to the cell anaerobically using gas-tight syringes, however, the relatively long electro-synthesis time (up to 4 min for 5–10 mM solutions) limits the suitability of the approach for products that undergo following reaction.

A variation of this approach has been described by Moss *et al.*<sup>10</sup> who have reported a cell design that is optimised for IR-SEC studies of proteins. A schematic cross-sectional view of the Moss cell is shown in Figure 1.1.(b) The working electrode consists of a 6-μm thick, 70% transparent Au mini-grid and this, together with the Pt foil counter and Ag/AgCl reference electrodes, completes the three-electrode geometry. An important feature of the cell for applications using proteins is the low sample requirement, where a 3–5 μL drop of solution is sufficient to fill the 20 mm diameter × 15 μm thick space formed by the CaF<sub>2</sub> windows. The outer cavity of the cell is filled with buffer/salt solution. Despite the contact between the sample solution and the surrounding medium the rate of dilution was reported to be ~5% over 24 h. In order to improve the rate of heterogeneous electron transfer and reduce the effects of protein denaturation, electrode-surface modifiers or electron-transfer reagents may be added to the sample solution. Owing to the high electrode surface area to

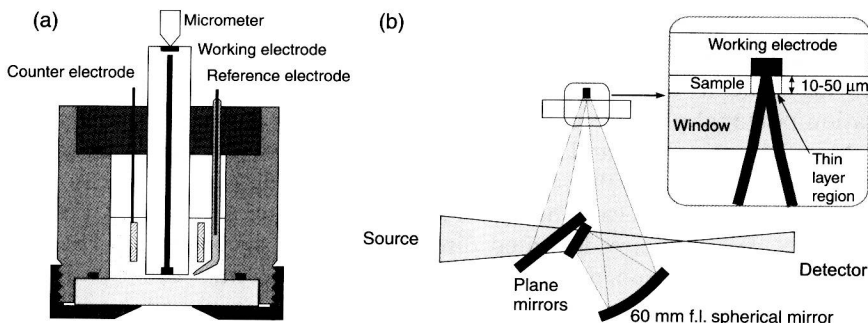
volume ratio the system rapidly equilibrates following a change in applied potential (1–2 min). Although factors such as the solution resistance within the cell may lead to an offset to the cell potential, excellent Nernstian concentration/potential plots were obtained for model studies of cytochrome *c*.<sup>10</sup>

More recently, Yun and coworkers<sup>11</sup> have reported the design of a transmission IR/UV-Vis cell that is micromachined from single-crystal silicon wafers (Figure 1.1(c)). In this case the Au minigrid, Au counter and Ag/AgCl pseudo-reference electrodes are deposited directly onto the silicon wafer. The cover plate is also etched from a single crystal, allowing fine control of the pathlength of the solution. The sample solution (*ca.* 0.1 mL) is placed between the two silicon wafers and these are clamped together in the cell mount. This arrangement was reported to work well for aqueous solutions but in the case of nonaqueous solvents it was necessary to enclose the edge of the thin-layer cell with Teflon tape so as to prevent solvent leakage. While transmission through silicon cells is lowered as a result of high reflectance losses at the interfaces this is offset by the control over the solution volume and electrode geometry provided by the microfabrication techniques.

## 1.4 External Reflection-Absorption SEC Cells

IR reflectance spectroscopy has proved to be highly effective for the examination of both the solute/electrode interface and the electrogenerated products. Two general approaches, designated internal and external reflection, may be employed in these studies.<sup>12</sup> For internal reflection the radiation passes through a transparent substrate and is reflected from a thin film of metal deposited thereon. The metal film also serves as the working electrode. The penetration of the electric vector of the radiation into the solution in contact with the reflecting surface provides a means of obtaining selective information related to the solute/electrode interface. For external reflectance the radiation passes through a suitable window and is specularly reflected from a solid electrode. The solution trapped between the electrode and window is interrogated by the IR beam. External reflectance approaches have been used to study both the electrode/electrolyte interface and the electrogenerated species. Since the study of monolayer or submonolayers of adsorbed species introduces significant challenges in terms of sensitivity, a number of different approaches have been developed that has spawned an extraordinarily diverse range of acronyms (EMIRS, IRRAS, SNIPTIRS, PM-FTIRS, LPSIRS). Briefly, discrimination between molecules bound to the electrode and those in the bulk solution may be achieved by examining the spectral changes that result from either potential or polarisation modulation. A good review of the techniques, and their physical basis has been outlined by Beden and Lamy.<sup>12</sup>

Examination of the solute species by external reflectance presents far fewer challenges and a variety of cell designs have been reported. These include strategies that permit the study of air-sensitive compounds<sup>13</sup> over a range of temperatures<sup>14,15</sup> and/or pressures.<sup>16</sup> A schematic diagram of a basic external reflection SEC cell is shown in Figure 1.2(a).<sup>14</sup> If the object of the investigation

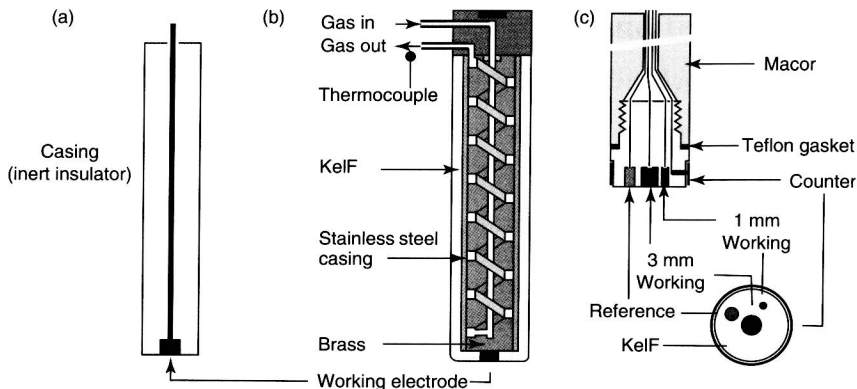


**Figure 1.2** (a) Cross section of an external reflectance SEC cell and (b) an example of an optical arrangement that permits its use in a conventional FTIR spectrometer.

is the study of solute species then the incident beam strikes the working electrode near to normal incidence, this minimises reflection losses from the air/IR-transmitting window interface and reduces the cross-sectional area of the focus of the IR beam when projected onto the electrode. Since the layer of solution under investigation is typically 10–20 μm the cells inevitably suffer from a substantial uncompensated solution resistance and this may best be controlled by minimising the surface area of the working electrode. Thus, the diameter of the working electrode should match the IR beam diameter. Depending on the instrument this typically translates into an electrode diameter of 3–5 mm. Naturally, the electrode must be fashioned from a material highly reflecting to radiation in the energy range of interest. While this is best achieved with metals such as Au and Pt, it is important to note that vitreous carbon has sufficient reflectivity in the IR to be suitable for such measurements. In its simplest form the working electrode is encased in an inert insulator, usually KelF or glass (Figure 1.3(a)). The thickness of the layer of solution under examination is determined by the position of the working electrode relative to the front window and this is adjusted under micrometer control. In most cases the counter and reference electrodes are located outside the thin-layer region where diffusion between the bulk solution and the solution in contact with the working electrode is negligibly small over the timescale of the SEC experiments.

In view of the need to restrict the size of the IR beam at the electrode plane the use of reflection absorption cells is generally limited to FTIR instrumentation where it is often necessary to use a high-sensitivity photovoltaic detector (*e.g.* liquid-nitrogen-cooled mercury cadmium telluride, MCT). Since in these cases the detector element is small, in addition to providing a flat, highly polished working electrode, it is necessary to provide an optical train that does not increase the size of the IR beam at the detector focus. The optical design used in our laboratory is shown in Figure 1.2(b). The IR beam is directed to the working electrode located at the beam focus using a plane mirror. The central ray of the IR beam makes an angle of  $14.3^\circ$  to the normal to the  $\text{CaF}_2$  window and  $10^\circ$  to that of the working electrode. The reflected beam is





**Figure 1.3** Working electrode designs for external reflectance SEC cells. (a) Single element, (b) temperature controlled,<sup>14</sup> and (c) multielectrode assembly.<sup>16</sup>

refocused using a spherical mirror to give a beam focus and path as close as possible to that of the undiverted beam. All three mirrors are built into a mount that allows rotation about axes coincident with their reflective surfaces and beam centre, in addition, the two plane mirrors have tilt axes normal to the rotation axis.

A schematic diagram of an electrode suitable for low-temperature use is shown in Figure 1.3(b).<sup>14</sup> The temperature of the brass pin attached to the working electrode is controlled by the flow rate and temperature of dinitrogen gas that passes through its structure. Using this approach it is difficult to monitor directly the temperature of the thin layer of solution, however, our experience (based on the freezing of solvent/supporting electrolyte) suggests only a small temperature difference ( $<ca. 10^{\circ}\text{C}$ ) between that of the outgoing gas. An approach that minimises the distance between the electrodes and also facilitates the construction of small solution volume cells involves incorporation of the working, counter and reference electrodes into a single KelF pin.<sup>16</sup> An additional small (1 mm diameter) working electrode is also incorporated into the assembly so as to provide a means of obtaining better electrochemical characterisation of the solution. In more recent designs (Figure 1.3(c)) the KelF pin is attached to a machineable ceramic cylinder (Macor). The greater dimensional stability provided by this material provides advantages in establishing an airtight seal between the electrode assembly and the cell body.

Relative to the transmission cells described in Section 1.3, external reflectance cells are less simple to construct and require additional optics for incorporation into the optical path of the spectrometer. The advantages associated with the approach relate to the well-defined nature of the working electrode, the wider range of materials suitable for this purpose, and the greater control over the thickness of the thin layer of solution. These factors contribute to a much faster ( $>10\times$ ) rate of electrosynthesis for external reflectance compared to transmission cells.