Display and Imaging, Vol. 2, pp. 229–248
Reprints available directly from the publisher
Photocopying permitted by license only

In Situ Spectroelectrochemical Techniques as Tools for Investigating the Properties of Electroactive Systems[†]

TOMASZ JAROSZ[*], PRZEMYSLAW DATA AND MIECZYSLAW LAPKOWSKI[*]

*Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology,
9 Marcina Strzody street, 44-100 Gliwice, Poland*

Received: November 1, 2016. Accepted: December 12, 2016.

Spectroelectrochemical analysis techniques allow both charge transfer processes and the species that take part in these processes to be followed. The spectroelectrochemical methodology has found extensive application since its conception in the mid-twentieth century and the array of different experimental procedures and their applications reported in literature continues growing on a yearly basis. Although the current work discusses the most significant and most recent developments in the field of spectroelectrochemical methods, attention is given to the variety of systems and processes that can be investigated, as well as providing a brief overview of the practical aspects of conducting such measurements.

Keywords: Spectroelectrochemistry, instrumental analysis, UV-Vis spectroscopy, EPR spectroscopy, IR spectroscopy, conjugated polymers, organic semiconductors

1. INTRODUCTION

Electrochemical analysis techniques are one of the primary methods of evaluating the electronic properties of inorganic, organic and polymeric conductors and semiconductors. The use of these techniques allows the nature and kinetics of charge transfer and capacitive processes taking place in conduct-

---

*Corresponding author e-mail: Tomasz.Jarosz@polsl.pl and mieczyslaw.lapkowski@polsl.pl

†The research leading to these results received funding from the H2020-MSCA-ITN-2015/674990 project “EXCILIGHT”.

ing systems to be examined. A wealth of information can be acquired by using voltammetric, chronoamperometric and impedance measurements: concentrations of species taking part in redox reactions (sensor technology), energetics of the species (through redox potentials) and the mechanisms and rates of the reactions (through kinetic analysis) can all be determined based on the acquired electrochemical data. Even so, electrochemical analysis is by definition limited to electronic phenomena and cannot provide structural information about the investigated systems. When well-known species, whose reactivity is predictable, are investigated, such a limitation bears no impact; when new systems are tested, however, being limited to electronic phenomena and properties can prove to be crippling for any attempts to understand the transformations occurring in the electro-active species.

The most straightforward approach to the issue is to subject the products of the electrochemical process to an array of spectroscopic methods, aimed at identifying the obtained species. Such ex situ procedures are known and can be used to thoroughly identify any precipitated products of an electrochemical experiment. One issue, limiting the usefulness of such techniques is that not all products can be precipitated from a post-reaction solution in quantities sufficient for identification and some products may have lifetimes short enough that they are rapidly consumed in consecutive reactions when the electrochemical stimuli is removed. Consequently, over time, more and more spectroscopic techniques have been integrated with electrochemical analysis to give rise to the modern in situ spectroelectrochemical methods.

This state of the art has long been recognised by IUPAC [1], which endorses the use of the term "*spectroelectrochemistry*" to refer to in situ techniques, in which an electrochemical process is monitored using spectroscopy. Interestingly, the source work also makes a note of ex situ methods being the subject of another IUPAC report; no literature reference is, however, given.

2. OVERVIEW OF SPECTROELECTROCHEMICAL TECHNIQUES

Electrochemical and spectroscopic methods were used alongside each other in a number of early works [2]; the first such experimental procedures to become truly established, however, were electron paramagnetic resonance (EPR) spectroelectrochemistry [3] and UV-Vis spectroelectrochemistry [4]. In the case of UV-Vis spectroelectrochemistry, intense development has been brought on by the, recent at the time, advent of optically transmissive electrodes (OTEs). The abovementioned work by Kuwama et al. utilised the new methodology to follow the redox behaviour of o-toluidine. Although the evolution of optical absorption was monitored only at a single wavelength, due to technical limitations, this work sparked great interest in spectroelectrochemical techniques [5,6,7,8]. Interestingly, the procedure presented in the original work still remains in use, as a tool for measuring the performance of electrochromic materials [9,10], even though the development of instruments allowing multi-channel time-resolved spectroelectrochemical techniques [11,12], has long since been incorporated into its scope.

Even though UV-Vis and EPR spectroscopy were the first spectroscopic methods to be employed alongside electrochemical analysis, other types of spectroelectrochemical measurements were developed, with Raman [13], infrared (IR) [14] and even nuclear magnetic resonance (NMR) [15,16] spectroscopy being soon used for numerous investigations, becoming a widespread and integral part of electrochemical methodology [17].

Since the inception of the first spectroelectrochemical methods, many novel procedures were developed, tailored to the individual requirements of different fields and taking advantage of the improving performance and availability of analytical instruments. The late professor Dunsch, who himself is known for the development of a triply-coupled technique, linking electrochemical analysis with UV-Vis-NIR sand EPR spectroscopy [18], published a summary of progress in the field several years ago [19]. More recently, Jarosz et al. [20] compiled a general, basic review of the subject, illustrating the use of both standard spectroelectrochemical methods and the coupled EPR/UV-Vis-NIR technique. The developments in fluorescence spectroelectrochemical methodologies, in turn, were recently reviewed by Audebert and Miomandre [21], who illustrated a number of experimental approaches to the subject. The most recent reports, as well as some of the more significant works mentioned in the two reviews are briefly discussed herein, focusing primarily on the different combinations of spectroscopic and electrochemical techniques, the architecture of the experimental systems and the advantages and limitations of each technique.

2.1. "Standard" spectroelectrochemical methodology

Even though numerous spectroelectrochemical techniques and, correspondingly more numerous, applications of these techniques are known and continuously reported, some procedures, i.e. UV-Vis-NIR and EPR spectroelectrochemistry, appear to be more widespread than others. This is both due to the more universal nature of the two spectroscopic methods (although IR and Raman spectroscopy would be expected to have primacy over EPR spectroscopy), as well as due to the relatively simple architectures of the experimental cells and not very strict technical requirements to be fulfilled, in order to successfully carry out such measurements.

The UV-Vis-NIR spectroelectrochemical setup is a standard three electrode configuration, which can be condensed into the confines of a standard spectroscopic cuvette. Depending on whether the light beam is passed through this system parallel or perpendicular to the plane of the working electrode, either the electrolysed solution or species adsorbed at the surface of the electrode can be investigated.

In experiments, in which the light beam is passed in parallel (i.e. through the experimental solution between the electrodes) to the working and auxiliary electrodes, the opacity of the electrodes has no impact on the experiment. Consequently, no limitations are imposed on the choice of electrode materials. Conversely, when the optical path is perpendicular to the working and auxiliary electrodes, the use of at least one optically transparent electrode (OTE) is required (by choosing a mirror surface as the second electrode, experiments with a doubled optical path length can be performed).

The general scheme of the most common architecture of the UV-Vis-NIR spectroelectrochemical cell is shown in Figure 1. The cell consists of an optically transparent working electrode (often consisting of a conductive indium-tin oxide (ITO) layer deposited on a glass or quartz slide), a PTFE spacer, into which a window is cut to accommodate the light beam and an auxiliary electrode. A second ITO/glass slide can obviously be used as the counter electrode, but such a choice limits the operating potential window, as ITO is prone to irreversible reduction, when sufficiently negative potentials are

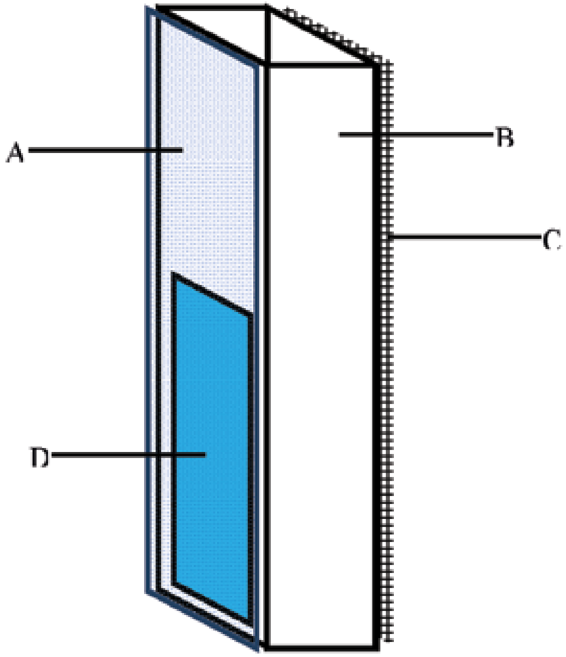

FIGURE 1
General scheme of the experimental cell (drawn not to scale for clarity) used for UV-Vis-NIR spectroelectrochemical measurements. A – ITO/quartz optically transparent electrode, B – PTFE spacer, C – platinum mesh auxiliary electrode, D – window for light beam passing through the spectroelectrochemical cell cut into the PTFE spacer. The silver wire pseudo-reference electrode (not shown) was inserted into a niche in the window cut into the spacer.

applied. Another option is to use a conducting mesh (typically platinum) auxiliary electrode, which is impervious to reductive degradation. This choice allows performing measurements in a wider potential window, but can lead to issues with light scattering on the electrode, resulting in distorted UV-Vis-NIR spectra being recorded.

Light scattering issues can be entirely avoided by cutting a window, matching that in the PTFE spacer, in the auxiliary electrode; this choice, however, disturbs the distribution of potentials in the spectroelectrochemical cell. Such a disturbance is relatively benign in the case of well-equilibrated experiments, in which each change of the applied potential is followed by an equilibration period. In the case of dynamic experiments, involving rapid changes in the applied potential, a distorted electrochemical response is expected, particularly in the case of low-conductance systems, in which the ohmic potential drop across the length of the cell will be most significant.

Alternatively, light scattering effects can be minimised by developing a scheme for repeatable and stable placement of the mesh electrode in the spectroelectrochemical cell and eliminating them at the stage of recording the reference spectrum for a blank sample placed in the experimental cell.

The architecture of the experimental cell for EPR spectroelectrochemical cell can vary significantly, depending on the mode of the resonating cavity of the EPR spectrometer. Regardless of resonating cavity mode, however, the experimental cell should have the least possible effect on the loading of the resonating cavity, i.e. should introduce the least possible disturbance of the magnetic field within the cavity.

Consequently, capillary cells are often used (Figure 2), in which the working and reference electrodes are inserted into a capillary, filled with a supporting electrolyte and attached to a wider section of the cell, housing the auxiliary electrode and serving as a reservoir of the supporting electrolyte. In the case of such cells, only the capillary section is inserted into the resonating cavity of the spectrometer, with the “bulk” section of the cell being attached outside the cavity. The material of the cell itself can vary, with glass being the standard choice and thin-walled quartz used as a solution when improved sensitivity is required.

The EPR spectroelectrochemical cell operates, as in the case of the UV-Vis-NIR cell, in a standard, three electrode configuration. The use of a coil as the auxiliary electrode (as pictured in Figure 2) is an interesting concept, as the working and reference electrodes can be run through it, stabilising their placement and improving the axial symmetry of the experimental setup.

Although the capillary cell is well-suited for detecting low spin concentrations, the electrochemical conditions in such a system are sub-optimal. Consequently, while performing well in potential step-equilibration time experiments, the capillary architecture can lead to issues in experiments involving rapid scanning of the applied potential.

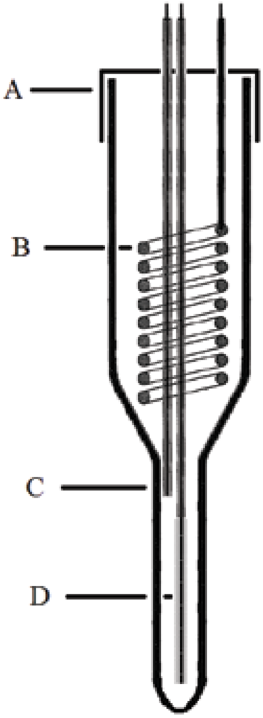

FIGURE 2
General scheme of the cell used for EPR spectroelectrochemical measurements (drawn not to scale for clarity). A – Cell cap holding the electrodes in position, B – long platinum coil auxiliary electrode, C – silver wire pseudo-reference electrode in a PTFE sheath, D – platinum wire working electrode in a PTFE sheath, with a deposited polymer layer indicated by the light grey section.

2.2. Review of recent progress in the development of spectroelectrochemical methods

Rather than developing a different experimental setup, Bancroft et al. [22], report an alternative data treatment scheme for the relatively standard coupling of either cyclic voltammetry or linear sweep voltammetry with time-resolved UV-Vis spectroscopy. In the authors' methodology, the first derivative of the absorption spectrum over applied potential is used instead of the absorption spectrum itself. A model system (tri-p-anisylamine), which undergoes reversible oxidation via one electron transfer, was investigated using this procedure, revealing that the derivative absorbance signal of the radical cation electrolysis product closely mirrors the shape of the current versus potential curve. The homomorphism of the derivative absorbance and current signals, plotted versus the potential applied to the working electrode was further analysed and a detailed theoretical explanation was provided in the work. The authors report a detection threshold of $1.5 \cdot 10^{-6}$mole·dm^{-3}; modification of the experimental procedure, however, may allow lowering this threshold. An important limitation of this methodology is that it relies on the occurrence of a single electrochemical process, yielding a distinct and isolated (non-overlapping other signals) absorption signal. Consequently, the occurrence of potential-dependent absorption signals, which partially overlap the absorption of the investigated species, can result in discrepancies in the shape of the two curves, which may prove to be an issue when attempting the use of this approach for analysis of more complex systems, exhibiting multiple absorption signals in the UV-Vis-NIR range or undergoing a sequence of charge transfer processes at similar values of the applied potential.

Although solid state electrochemical cells are primarily investigated and applied in terms of battery and fuel cell technology, the possibility of utilising to produce high-purity vapours was also explored. Interestingly, even when using a relatively straightforward experimental system, vapours of highly reactive species, such as potassium [23,24] can be produced. The technical requirements for generating reactive species vapours are easily adapted to match the conditions required for performing mass spectroscopy measurements, as exemplified by the report by Roy and Bruce [25], who developed a mass spectroelectrochemical setup in order to investigate the contents of vapours emitted from a solid state electrochemical cell (Figure 3) at different applied potentials. The only significant limitations of the described method stem from the use of ultra-high vacuum, required for mass spectroscopic measurements, making it impossible to investigate non-solid state electrochemical systems or solid state systems that contain volatile components.

An interesting concept for the investigation of species present and generated in solutions is reported by Shaw et al. [26]. The authors utilise a polished platinum working electrode to act as a mirror, reflecting the incident light beam, coming from a dip probe, back through the solution and onto the dip probe, effectively doubling the optical path length in the system (Figure 4). The procedure was employed by the authors in a time-resolved regime, in order to allow monitoring the evolution and decay of the intermediates and products of the electrolysis of a manganese complex, with the spectra of even highly unstable intermediates being easily recorded. The most obvious drawback of this technique, however, is that any loss of reflectance of the working electrode surface will rapidly lower the sensitivity of the spectroscopic component of the technique. The procedure can also be used to monitor the evolution of species on the working electrode, via reflectance measurements. In such a case, any significant light absorption on the part of the solution would prove detrimental to the quality of the measurement.

Rather than only allowing the investigation of setups, in which the investigated solution is static, spectroelectrochemical analyses can also be conducted for flow systems, as shown by Daniel and Gutz [27,28]. The authors report the development of one of the relatively rare spectroelectrochemical flow techniques, in which an experimental setup used for flow injection anal-

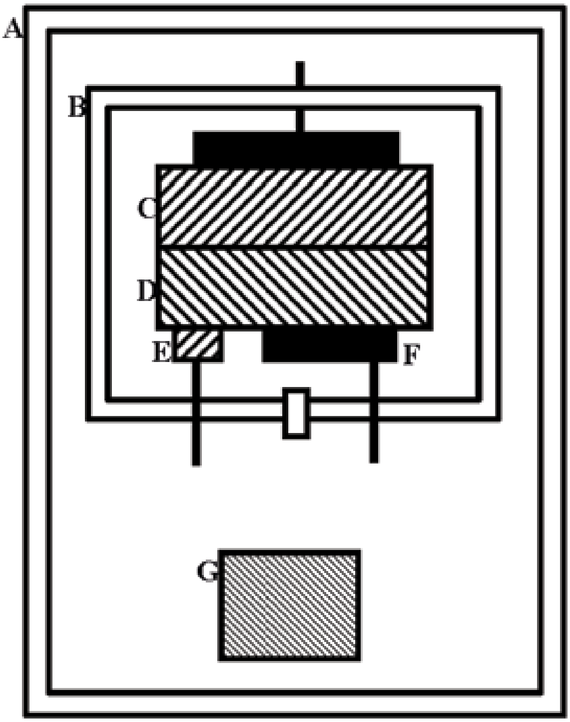

FIGURE 3
General scheme of the experimental setup for mass spectroelectrochemical measurements. A – high vacuum chamber, B – heated cell holder (non-hermetic, allowing the evolving gasses to penetrate into the vacuum chamber), C – sodium cobalt oxide counter electrode, D – sodium βalumina solid electrolyte, E – sodium cobalt oxide reference electrode, F – stainless steel working electrode, G – quadrupole mass spectroscopic detector. Based on the more detailed experimental setup scheme found in [24].

ysis continuously supplies the spectroelectrochemical cell (Figure 5) with the investigated solution. The abovementioned report details the investigation of a relatively straightforward system, in which the sample, containing promethazine hydrochlorate, is oxidised electrochemically to produce a red-coloured species. Although the concentrations of the two species can be independently monitored by either electrochemical or spectroscopic methods, the coupling of the two types of measurements allows the potential impact of contaminants, which may interfere with either measurement, to be minimised, as emphasised by the authors. The detection thresholds for the spectroscopic and electrochemical methods are reported respectively as $1.3 \cdot 10^{-6}$ mole·dm^{-3} and $3.0 \cdot 10^{-5}$ mole·dm^{-3}.

Ikeda et al. [29] report a different flow UV-Vis spectroelectrochemical technique, in which a flow column is utilised to directly monitor the progress of an electrochemical reaction for a number of proteins, with a detection threshold of $1 \cdot 10^{-7}$ mole·dm^{-3} being reported.

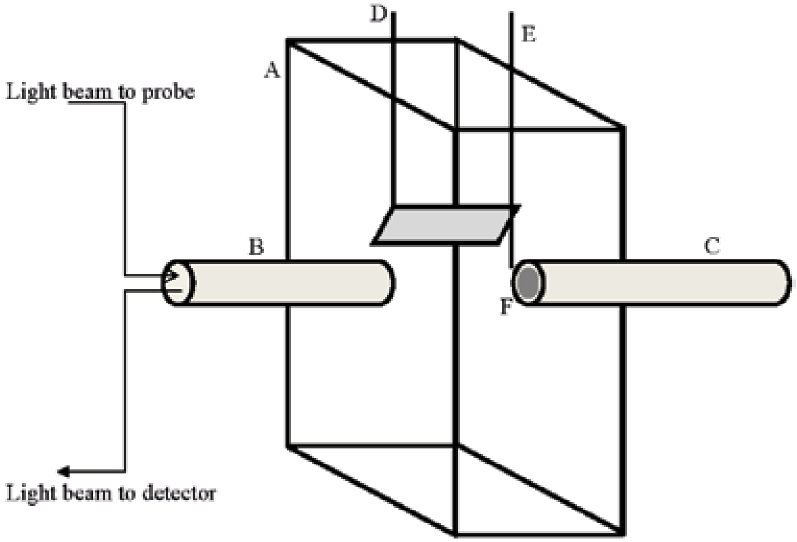

FIGURE 4
General scheme of the experimental setup for reflected light spectroelectrochemical measurements. A – experimental cell, B – Fibre optic probe, C – mount and electrical connector for F, D – auxiliary electrode, E –reference electrode, F –polished (mirror-like, to facilitate reflection) disk working electrode. Based on the more detailed experimental setup scheme found in [25].

An interesting novel coupling between UV-Vis spectroelectrochemistry and microscopy is reported by Gyurcsanyi and Lindner [30], who employed a prism attachment for a microscope to allow simultaneous recording of a microscopic image and the acquisition of UV-Vis spectra for a slice of this image. By recording the spectra (240 individual spectra) of pixels constituting a slice of the microscopic image, the authors are able to follow the concentration of light absorbing species at different locations of the observed cell area. The novel procedure was used to investigate the behaviour of a system consisting of an ion-selective membrane, which was loaded with an absorbing ionophore. Whereas an even distribution of the ionophore was observed across the membrane in open circuit conditions, upon the application of a potential difference to the solutions on both sides of the membrane, a concentration gradient soon developed reflecting the changes induced in the electrochemical cell. Although no detection threshold was reported, the architecture of the setup suggests that it should not deviate strongly from the parameters of the utilised detector, with only the prism attachment acting as a possible source of interference. The nature of the procedure allows it to be tailored to individual requirements, even though it is geared particularly towards studying heterogeneous phenomena. Provided that adequate magnification is feasible, this technique could also be

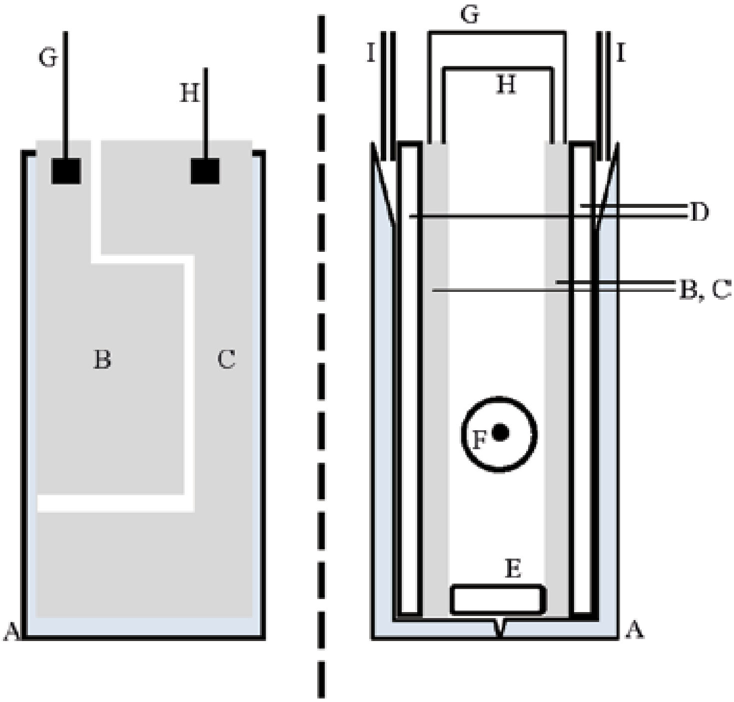

FIGURE 5
General scheme of the flow spectroelectrochemical cell used by Daniel and Gutz, based on the more detailed scheme found in [26,27]. A – body of the standard cuvette for spectroscopy, B – working electrode area, C – auxiliary electrode area, D – acrylic back plate, E – PTFE spacer, F – indication of the direction of the light beam passing through the cell, G – electrical connection between the two working electrodes, H – electrical connection between the two auxiliary electrodes, I – solution inlet / outlet

used to study such heterogenic processes as the precipitation and swelling/ contraction of conjugated polymer systems during respectively electrochemical polymerisation and doping / dedoping.

Ruiz et al. [31] employed a different approach to acquiring more versatile spectral data and developed an experimental setup, in which absorbance both normal and parallel to the working electrode plane was continuously recorded during a potential sweep. This experimental procedure was used to monitor the electrochemical polymerisation of a bithiophene derivative allowing the development of the absorption of the incipient polymer film on the working electrode and of the intermediate oligomeric species present in the solution neighbouring the working electrode to be simultaneously followed.

Rather than focus on the optical absorption of the experimental system, Feng et al. [32] explored the concept of reflectance-mode UV-Vis spectroelectrochemistry. Electrochemical impedance spectroscopy was employed to apply a sinusoidal potential signal to the working electrode and to vary its frequency. Simultaneously UV-Vis spectroscopy was used to record the reflectance spectra of a dye adsorbed on the working electrode. This experimental approach allowed the authors to determine the electrode reaction rate constants for two model dyes – hemin and Nile Blue A. In a later work, the authors departed from model systems and successfully demonstrated the application of this technique [33] to study the electron transfer rates to cytochrome c across organic monolayers.

A reflected beam approach, similar to the one discussed above was conceived and reported by Rosa-Montanez et al. [6]. Rather than utilising UV-Vis spectroscopic measurements, the authors employed IR spectroscopy as the method of identifying the species taking part in the reaction. Similar to the case of Shaw et al. [25], the authors also used a polished platinum disk as the "mirror" element. A triruthenium dodecacarbonyl, $Ru_3(CO)_{16}$ solution was used as the model system; potential-induced changes to the recorded IR spectra were observed at milimole $Ru_3(CO)_{16}$ concentrations, with the detection limit being reported in the range of $0.5\div1.0$mmole·dm^{-3}. Similarly to the previously discussed technique, loss of working electrode reflectance is a potentially significant drawback.

Jeanmaire et al. [35] report a Resonance Raman spectroelectrochemical procedure, which utilises a "sandwich-type" spectroelectrochemical cell to achieve semi-infinite diffusion conditions. Simultaneously, the construction of the cell allows high-resolution spectra of the electrolysed solution of tetracyanoethylene to be harvested. The authors, having observed the spectrum of the electrogenerated tetracyanoethylene radical anion, report being able to differentiate between the C≡N signals of the radical anion, at a concentration of 3mmole·dm^{-3}, and the signals of the solvent (acetonitrile), at a concentration of 19mole·dm^{-3}. The authors observe that the primary potential limitation of this procedure is the issue of sample fluorescence, which in some conditions may render spectral acquisition impossible; this issue can, however, be mitigated to some extent.

Surface-enhanced Raman spectroscopy (SERS) is often coupled with electrochemical methods, initially being even referred to as "Electrode SERS" [36], with a number of cell designs being in widespread use as early as 1986. Prior to that, SERS spectroelectrochemistry was reported in a number of works, one of which being by Ervin et al. [37], who investigated nucleic acid components adsorbed at a silver electrode. The authors later explored the subject in more detail [38], utilising the applied potential to promote adsorption at the electrode and elucidating the effects of adsorption on the spectra of purine and pyrimidine bases.

Further evolution of SERS spectroelectrochemical techniques brought about biological applications, with El-Said et al. [39] utilising Au nano-dots to investigate the species produced during electrolysis of dopamine in immobilised bulk cell and single cell systems.

Ogle et al. [40] reported another flow technique, coupling electrochemical methods with atomic emission spectroscopy and later used the technique to investigate dealloying phenomena in stainless steel samples [41]. The experimental system was set up so that up to thirty one atomic emission wavelengths can be monitored, allowing for comprehensive qualitative and quantitative analysis of the electrolysed solution to be carried out, with detection limits for the investigates elements (Fe, Cr, Ni, Mn, Mo, Cu) reported in the range of $0.37 \div 9.7 \mathrm{mg} \cdot \mathrm{dm}^{-3}$.

An interesting experimental setup for investigating the kinetics of protein adsorption was developed by Asanov and Larina [42], who coupled polarography with total internal reflectance fluorescence spectroscopy. Time-resolved studies have also been carried out, with the authors able to follow the impact of altering the applied potential on the concentration of protein adsorbed on the working electrode, determined by in situ fluorescence measurement. Although no detection limit is given, the technique is sufficiently sensitive to discern between desorption and reorientation of the protein molecules, caused by respectively rapid or slow changes in the potential applied to the working electrode.

Fluorescence spectroelectrochemical methodology was also implemented by Doneux et al. [43], who utilised fluorescence confocal microscopy to investigate the reduction of resazurin taking place at the surface of the working electrode. Although the authors did not investigate the systems quantitatively and, as such, no detection threshold is given, it can be seen that the methodology also allows performing time-resolved experiments, affording relatively good chronological resolution. A similar approach was earlier taken by Miomandre et al. [44], as indicated in the review work dedicated to fluorescence spectroelectrochemical methods [21], who, in turn, coupled fluorescence microscopy with electrochemical methods.

Rather than using microscopy, as in the works mentioned above, Moretto et al. [45] utilised a CCD camera as their detector, enabling real time imaging of the fluorescent species taking part in an on-going electrochemical process. The authors utilised a model system, consisting of a Nafion film deposited using a Langmuir-Blodgett procedure and loaded with tris(2,2'-bipirydyl)ruthenium (II) chloride, which can be reversibly oxidised to a ruthenium (III) complex.

An altogether different spectroelectrochemical methodology was proposed by Matencio and Vieil [46], who monitored an electrochemical process by passing a laser beam parallel to the surface of the working electrode and investigated its angular deviation, caused by changes in the refractive index of a polyaniline film upon doping / dedoping. Later work by the authors saw the application of this technique to the study of ion exchange in poly(paraphenylene) [47] and later, in conjunction with electrochemical quartz crystal microbalance measurements, for studying poly(o-toluidine) films [48].

2.3. Time-resolved spectroelectrochemical techniques

Standard spectroelectrochemical methodology often focuses on taking spectral "snapshots" at different points of the electrochemical experiment, to monitor the changes brought by the electrode process. These snapshots are often recorded when the investigated system is at a steady state, as is in the case of potential staircasing spectroelectrochemical techniques, where the spectra are recorded at a set applied potential, following a short "equilibration" time period.

Conversely, in the case of time-resolved experiments, the roles of the two types of measurements are typically reversed. That is to say that many time-resolved works continuously monitor the spectral characteristics of the investigated system, utilising electrochemical stimuli to either induce the monitored process or to act as a driving force for spectral changes. This approach is well exemplified by the current methodology of investigating colour switching times of electrochromic devices, which is aimed at determining the "spectral inertia" of a system, i.e. the time that is required for the system to change its spectral properties upon application of a potential stimulus.

The two approaches are complementary to each other, with one focusing on the steady state spectral characteristics and the other focusing on the dynamic changes of these characteristics. Consequently, both approaches are often used alongside each other, as has been noted in several instances of techniques reviewed in the earlier sub-section. The below works were instead chosen for review due to their use of time-resolved spectroelectrochemical measurements as the primary methodology, making it possible to focus on the developments in this area as well.

An interesting application of time-resolved UV-Vis spectroelectrochemical measurements is reported by Renault et al. [49], who investigated the reduction dynamics of microperoxidase-11 adsorbed on a porous indium-tin oxide (ITO) optically transparent electrode (OTE). The reduction/oxidation sequence was cycled multiple times, with a progressively decreasing reduction potential and the experiment appears to have been carried out numerous times, based on the presented dataset. Correlation between the reduction potential and magnitude of observed absorbance changes in a reduction/oxidation sequence was shown and utilised by the authors to determine the electron transfer rate constant. No detection limit is given; the authors, however, claim to be able to achieve a 50ms spectral resolution, allowing many reactions to be investigated by this methodology. An example of such a reaction was later reported by the authors themselves, who harnessed the capabilities of their experimental setup to investigate the catalytic reduction of O_2 on a microperoxidase-11-modified electrode [50].

Time-resolved UV-Vis spectroelectrochemical experiments were also carried out by Kadish et al. [51] and Yilmaz et al. [52], however, only the trends of changes were presented rather than the time-scale on which they were taking place. The former work deals with the mechanisms of redox processes of porphyrins containing iron (III), whereas the latter deals with the redox properties of tetrathia-bridged phthalocyanines. An earlier work by Mu and Kadish [53] utilises the same methodology for the investigation of iron nitrosyl porphyrins, however, it is worth mentioning that, in that instance, the authors also investigate the system by IR spectroelectrochemistry. Due to the fact that the three works are all qualitative in nature, no detection limits or spectral resolutions are unfortunately given.

An important early work dedicated to time-resolved UV-Vis spectroelectrochemistry was published by Gaillard and Levillain [54], dealing with the investigation of the electrochemical reduction of sulphur in dimethylformamide. The process was monitored with a 10ms (100Hz) resolution, allowing the species taking part in the electrode reaction and following chemical reaction to be identified and their concentrations to be closely monitored.

Wu et al. [55], report a time-resolved investigation of electron transfer in cytochrome c, utilising UV-Vis reflectance spectroelectrochemical measurements. The dynamics of the formation of new bands are carefully followed, with a resolution of 20ms, revealing that the electrochemical reaction is accompanied by a conformation change of the cytochrome c moleucle.

Although time-resolved UV-Vis spectroelectrochemical experiments are most commonly reported, other types of time-resolved spectral measurements may be used in place of UV-Vis spectroscopy. This is exemplified by Yan and Jin [56], who report the use of time-resolved IR spectroscopy to follow the electrochemical oxidation of formaldehyde. The authors, knowing that oxidation of formaldehyde to formic acid takes place through a gem-diol intermediate, were able to follow the process, by monitoring the IR bands of the intermediate gem-diol, the formate anion and water produced in the reaction; the latter was observed due to the process being carried out in D_2O. A resolution of about 14ms was achieved (70 spectra being acquired per second) and no detection limit of the utilised experimental setup was reported.

3. APPLICATIONS OF SPECTROELECTROCHEMICAL TECHNIQUES

Quantitatively, the use of spectroelectrochemical techniques is becoming increasingly widespread, as shown by the increasing number of published reports (Figure 6). The compilation focuses on the IUPAC-endorsed terms only, due to the fact that the commonly used non-IUPAC terms often coincide with other research fields. Consequently, their inclusion would obscure the observed trend more significantly than their omission. The differences between the three bibliographic databases are relatively minor up until the turn of the century, at which point Google Scholar begins to register significantly larger amounts of published articles. This is thought to be an issue arising due to multiple sources being available for a given report; the exact reason for this discrepancy is, however, unclear.

Qualitatively, the array of different systems and processes that can be investigated by spectroelectrochemical techniques is extremely wide, encompassing both organic and inorganic systems and their numerous applications.

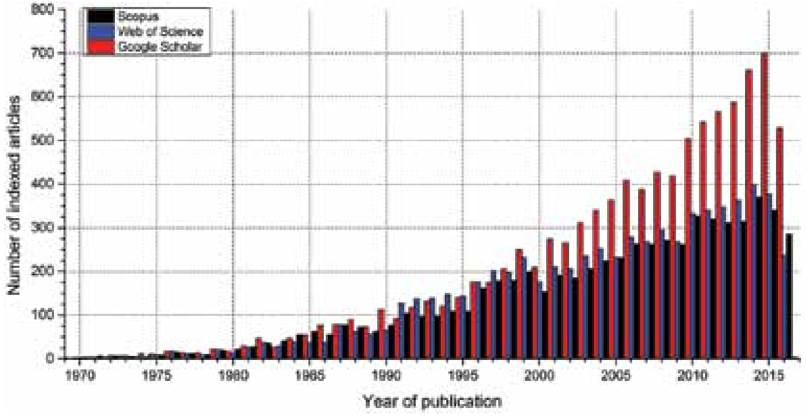

FIGURE 6
Year-by-year analysis of the number of research articles dedicated to spectroelectrochemical methods, found in the main bibliographic databases (Scopus, Web of Science, Google Scholar). Articles containing the terms "spectroelectrochemistry" and "spectroelectrochemistry" and "spectroelectrochemical" in their title or abstract were queried for, to provide a rough estimate of the current trend. Data for 2016 and 2017 is presented only as a supplement, due to the fact that final publishing data is unavailable for either year.

Examples of the areas of study, explored by selected recent works, are summarised briefly in Table 1.

4. SUMMARY

The increasing interest in spectroelectrochemical methods is well evidenced by the increasing numbers of reports pertaining to the development and applications of such methods. Similarly, the array of the different types of systems, whose properties are uncovered through spectroelectrochemical investigations and reported, keeps expanding on a yearly basis, with both materials and devices being subjected to, often ingenious, instrumental analyses.

Spectroelectrochemical analysis is quickly becoming one of the most important groups of techniques, whose development benefits from the fact that it bridges the gap between structural identification of chemical species and the evaluation of the properties of materials for highly specific applications, particularly in the rapidly expanding field of organic optoelectronics.

Despite many reports on the subject of spectroelectrochemical techniques, much room for further advances remains, with the concept of integrating numerous instrumental methods having barely been proven, with the development and popularisation of methods, in which two types of spectroscopic measurements are being performed during the application of electrochemical stimuli. Better investigation and understanding of the interplay of the techni-

TABLE 1
Compilation of applications of spectroelectrochemical techniques in recently published reports

Investigated systems, processes and properties	Spectroscopic methods used in conjunction with electrochemical stimuli	Reference
• Electrochemical polymerisation of a pyrrole derivative; • Investigation of electrochromic properties	• Time-resolved UV-Vis spectroscopy; • EPR-UV-Vis-NIR spectroscopy	[57]
• Electrochemical copolymerisation of an array of co-monomers; • Electrochromic properties of obtained copolymers	• Time-resolved UV-Vis-NIR spectroscopy; • UV-Vis-NIR spectroscopy	[58]
• Electrochromism and electrofluorochromism of a dithienopyrrole derivative	• UV-Vis-NIR spectroscopy; • Fluorescence spectroscopy	[59]
• Electrochromism of an EDOT-carbazole copolymer	• UV-Vis-NIR spectroscopy	[60]
• Redox and electronic properties of linked organic-inorganic systems	• UV-Vis-NIR spectroscopy	[61]
• Process of electrochemical oxidation of salicylic acid	• Time-resolved UV-Vis spectroscopy	[62]
• Process of electrochemical reduction of dinitrobenzene	• IR spectroscopy	[63]
• Performance of a vanadium-based redox electrolyte for battery applications	• UV-Vis-NIR spectroscopy	[64]
• Performance of an boron-doped diamond OTE; • Electrochemical dissolution of Au nanoparticles from the electrode surface	• Surface enhanced IR spectroscopy	[65]
• Corrosion of Cu-Au alloy electrodes	• X-ray diffraction spectroscopy	[66]
• Redox switching of a tetrazine fluorescent dye	• Fluorescence spectroscopy • Time-resolved fluorescence spectroscopy	[67]
• Redox and acid-base switching of a triphenylamine-based fluorescent dye	• UV-Vis-NIR spectroscopy • Fluorescence spectroscopy • Time-resolved fluorescence spectroscopy	[68]

cal requirements of different spectroscopic and electrochemical analysis techniques, as well as their benefits and drawbacks are fundamental for achieving further developments in this field, ideally leading to producing a fully integrated analytical workshop for simultaneously investigating and evaluating a large variety of conducting systems, providing a complete picture of their properties and responses.

REFERENCES

[1] Plieth W., Wilson G.S., Gutierrez De La Fe C. (1998). Spectroelectrochemistry: A survey of in situ spectroscopic techniques (Technical Report). Pure and Applied Chemistry, 70, 1395-1414.

[2] Winterbottom A.B. (1946). Optical methods of studying films on reflecting bases depending on polarisation and interference phenomena. Transactions of the Faraday Society, 42, 487–495.

[3] Maki A.H., Geske D.H. (1959). Detection of Electrolytically Generated Transient Free Radicals by Electron Spin Resonance, Journal of Chemical Physics, 30, 1356–1357.

[4] Kuwama T., Darlington R.K., Leedy D.W. (1964). Electrochemical Studies Using Conducting Glass IndicatorElectrodes. Analytical Chemistry, 36, 2023-2025.

[5] Krawczyk J., Łapkowski M., Strojek J.W. (1983). Minicomputer control of measurements of spectroelectrochemical processes : Part 1. Instrumentation and computer programs. Analytica Chimica Acta, 152, 45-52.

[6] Łapkowski M., Strojek J.W., Nemeth M., Mocak J. (1985). Minicomputer control of measurements of spectroelectrochemical processes: Part 2. A New Measurement System for Simultaneous Coulometric and Spectrophotometric Investigations. Analytica Chimica Acta, 171, 77–87.

[7] Gale R.J. (1988). Spectroelectrochemistry Theory and Practice. Springer (ISBN-13: 978-1461282785).

[8] Kaim W., Klein A. (2008). Spectroelectrochemistry. RSC Publishing (ISBN-13: 978-0854045501).

[9] Cho S.I., Kwon W.J., Choi S.J., Kim P., Park S.A., Kim J., Son S.J., Xiao R., Kim S.H., Lee S.B. (2005). Nanotube-Based Ultrafast Electrochromic Display. Advanced Materials, 17, 171-175.

[10] Argun A.A., Cirpan A., Reynolds J.R. (2003). The First Truly All-Polymer Electrochromic Devices. Advanced Materials, 15, 1338-1341.

[11] Kadish K.M., Cornillon J.L., Cocolios P., Tabard A., Guilard R. (1985). Electrochemistry and spectroelectrochemistry in indium(III) porphyrins. Reactions of five-coordinate ionic complexes. Inorganic Chemistry, 24, 3645–3649.

[12] Kadish K.M., Boisselier-Cocolios B., Simonet B., Chang D., Ledon H., Cocolios P. (1985). Electrochemistry and spectroelectrochemistry of easily reducible and easily oxidizable iron porphyrins. Reactions of monomeric and dimeric pyrrole-substituted tetracyano and phenyl-substituted diethylamino complexes of iron tetraphenylporphyrins. Inorganic Chemistry, 24, 2148–2156.

[13] Jeanmaire D.L., Van Duyne R.P. (1977). Surface Raman spectroelectrochemistry Part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. Journal of Electroanalytical Chemistry, 84, 1-20.

[14] Yaniger S.I., Vidrine W. (1985). Dynamic approach to FT-IR spectroelectrochemistry. SPIE Proceedings 0553, Fourier and Computerized Infrared Spectroscopy, 199, doi:10.1117/12.970770.

[15] Mincey D.W., Popovich M.J., Faustino P.J., Hurst M.M., Caruso J.A. (1990). Monitoring of electrochemical reactions by nuclear magnetic resonance spectrometry. Analytical Chemistry, 62, 1197–1200.

[16] Bussy U., Boujtita M. (2015). Review of advances in coupling electrochemistry and liquid state NMR. Talanta, 136, 155–160.

[17] Widrig C.A., Porter M.D., Ryan M.D., Strein T.G., Ewing A.G. (1990). Dynamic Electrochemistry: Methodology and Application. Analytical Chemistry, 62, 1R-20R.

[18] Petr A., Dunsch L., Neudeck A. (1996). In situ uv-vis esr spectroelectrochemistry. Journal of Electroanalytical Chemistry, 412, 153-158.

[19] Dunsch L. (2011). Recent Advances in in situ multi-spectroelectrochemistry. Journal of Solid State Electrochemistry, 15, 1631–1646.

[20] Jarosz T., Krukiewicz K., Lapkowski M., Domagala W. (2015). Spectroelectrochemical techniques as modern tools for investigating charge transfer processes in conjugated polymers. CHEMIK, 69, 485-490.

[21] Audebert P., Miomandre F. (2013). Electrofluorochromism : from molecular systems to set-up and display. Chemical Science, 4, 575.

[22] Bancroft E.E., Sidwell J.S., Blount H.N. (1981). Derivative Linear Sweep and Derivative Cyclic Voltabsorptometry. Analytical Chemistry, 53, 1390-1394.

[23] Bruce P.G., Abrahams I., Prior K.A., Stewart H. (1992). Spectroelectrochemical studies of alkali metal generation from solid state cells. Solid State Ionics, 53, 1371-1378.

[24] Bruce P.G., Roy S., Stewart H., Prior K.A. (1993). Potassium Beams from Solid State Electrochemical Cells. MRS Proceedings, 293, 93.

[25] Roy S.C., Bruce P.G. (1996). Spectroelectrochemical studies of alkali metal generation from solid state cells. Solid State Ionics, 86-88, 1371-1378.

[26] Shaw M.J., Cranford D.L., Rodgers K.W., Eilers J.E., Noble B., Warhausen A.J., Richter-Addo G.B. (2010). acile Determination of the Spectra of Unstable Electrode Products Using Simultaneous Fiber-Optic Chronoabsorptometry and Chronoamperometry. Inorganic Chemistry, 49, 9590–9598.

[27] Daniel D., Gutz I.G.R. (2001). Long-Optical-Path Thin-Layer Spectroelectrochemical Flow Cell with Inexpensive Gold Electrodes. Electroanalysis, 13, 681-685.

[28] Daniel D., Gutz I.G.R. (2003). Flow injection spectroelectroanalytical method for the determination of promethazine hydrochloride in pharmaceutical preparations. Analytica Chimica Acta, 494, 215–224.

[29] Ikeda T., Sato A., Takagi K., Torimura M., Kano K. (2000). Continuous-Flow Column Electrolytic Spectroelectrochemical Method for Determination of Protein Redox Potentials - Application to Quinoproteins, Biochemistry and Molecular Biology of Vitamin Ba and PQQ-dependent Proteins. Springer. ISBN 978-3-0348-9549-1.

[30] Gyurcsanyi R.E., Lindner E. (2005). Spectroelectrochemical Microscopy: Spatially Resolved Spectroelectrochemistry of Carrier-Based Ion-Selective Membranes. Analytical Chemistry, 77, 2132-2139.

[31] Ruiz V., Colina A., Heras A., Lopez-Palacios J., Seeber R. (2002). Bidimensional chronoabsorptometric study of electropolymerisation of 4,4'-bis(2-methylbutylthio)-2,2'-bithiophene. Electrochemistry Communications, 4, 451–456.

[32] Feng Z.Q., Sagara T., Niki K. (1995). Application of Potential-Modulated UV-Visible Reflectance Spectroscopy to Electron Transfer Rate Measurements for Adsorbed Species on Electrode Surfaces. Analytical Chemistry, 67, 3564-3570.

[33] Feng Z.Q., Imabayashi S., Kakiuchi T., Niki K. (1997). Long-range electron-transfer reaction rates to cytochrome c across long- and short-chain alkanethiol self-assembled monolayers: Electroreflectance studies. Journal of the Chemical Society, Faraday Transactions, 93, 1367-1370.

[34] Rosa-Montanez M.E., De Jesus-Cardona H., Cabrera-Martinez C.R. (1998). Airtight in Situ Thin-Layer Reflection-Absorption FT-IR Microspectroelectrochemical Cell for the Study of Nonaqueous Systems. Analytical Chemistry, 70, 1007-1011.

[35] Jeanmaire D.L., Suchanski M.R., Van Duyne R.P. (1975). Resonance Raman Spectroelectrochemistry. I. The Tetracyanoethylene Anion Radical. Journal of the American Chemical Society, 97, 1699-1707.

[36] Koglin E., Sequaris J.M. (1986). Surface enhanced raman scattering of biomolecules, Topics in Current Chemistry 134. Springer. ISBN: 978-3-540-16403-6.

[37] Ervin K.M., Koglin E., Sequaris J.M., Valenta P., Nürnberg H.W. (1980). Surface enhanced Raman spectra of nucleic acid components adsorbed at a silver electrode. Journal of Electroanalytical Chemistry, 114, 179-194.

[38] Koglin E., Sequaris J.M., Valenta P. (1982). Surface enhanced Raman spectroscopy of nucleic acid bases on Ag Electrodes. Journal of Molecular Structure, 79, 185-189.

[39] El-Said W.A., Kim T.H., Chung Y.H., Choi J.W. (2015). Fabrication of new single cell chip to monitor intracellular and extracellular redox state based on spectroelectrochemical method. Biomaterials, 40, 80-87.

[40] Ogle K., Weber S. (2000). Anodic Dissolution of 304 Stainless Steel Using Atomic Emission Spectroelectrochemistry. Journal of Electrochemical Society, 147, 1770.

[41] Ogle K., Baeyens J., Swiatowska J., Volovitch P. (2009). Atomic emission spectroelectrochemistry applied to dealloying phenomena: I. The formation and dissolution of residual copper films on stainless steel. Electrochimica Acta, 54, 5163–5170.

[42] Asanov A.N., Larina L.L. (1992). Electrochemical Control Of Protein Interactions With Solid Surfaces, Charge and Field Effects in Biosystems—3. Springer. ISBN: 978-1-4615-9839-8.

[43] Doneux T., Bouffier L., Goudeau B., Arbault S. (2016). Coupling Electrochemistry with Fluorescence Confocal Microscopy To Investigate Electrochemical Reactivity: A Case Study with the Resazurin-Resorufin Fluorogenic Couple. Analytical Chemistry 88, 6292–6300.

[44] Miomandre F., Meallet-Renault R., Vachon J., Pansu R.B., Audebert P. (2008). Fluorescence microscopy coupled to electrochemistry: a powerful tool for the controlled electrochemical switch of fluorescent molecules. Chemical Communications, 16, 1913–1915.

[45] Moretto L.M., Kohls T., Chovin A., Sojic N., Ugo P. (2008). Epifluorescence Imaging of Electrochemically Switchable Langmuir-Blodgett Films of Nafion. Langmuir 24, 6367-6374.

[46] Matencio T., Vieil E. (1991). Optical beam deflection study of ionic movements during the charge transfer of polyaniline and poly(alkylanilines) in NH4F;2.3HF medium. Synthetic Metals, 44, 349-356.

[47] Vieil E., Meerholz K., Matencio T., Heinze J. (1994). Mass transfer and convolution: Part II. In situ optical beam deflection study of ionic exchanges between polyphenylene films and a 1:1 electrolyte. Journal of Electroanalytical Chemistry, 368 183-191.

[48] Henderson M.J., Hillman A.R.a, Vieil E. (1998). A combined electrochemical quartz crystal microbalance (EQCM) and probe beam deflection (PBD) study of a poly(o-toluidine) modified electrode in perchloric acid solution. Journal of Electroanalytical Chemistry 454, 1–8.

[49] Renault C., Harris K.D., Brett M.J., Balland V., Limoges B. (2011). Time-resolved UV-visible spectroelectrochemistry using transparent 3D-mesoporous nanocrystalline ITO electrodes. Chemical Communications, 47, 1863–1865.

[50] Renault C., Andrieux C.P., Tucker R.T., Brett M.J., Balland V., Limoges B. (2012). Unraveling the Mechanism of Catalytic Reduction of O 2 by Microperoxidase-11 Adsorbed within a Transparent 3D-Nanoporous ITO Film. Journal of the American Chemical Society, 134, 6834–6845.

[51] Kadish K.M., Van Caemelbecke E., D'Souza F., Medforth C.J., Smith K.M., Tabard A., Guilard R. (1995). Electrochemistry and Spectroelectrochemistry of a-Bonded Iron(II1) Porphyrins with Nonplanar Porphyrin Rings. Reactions of (OETPP)Fe(R) and (OETPP) FeCl, Where R=C6H5, C6F4H, or C6F5 and OETPP Is the Dianion of 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraphenylporphyrin. Inorganic Chemistry, 34, 2984-2989.

[52] Yilmaz I., Kocak M.B. (2004). Electrochemical, spectroelectrochemical, and pyridine binding properties of tetrathia macrocycle-bridged dimeric cobalt phthalocyanine. Polyhedron, 23, 1279–1285.

[53] Mu X.H., Kadish K.M. (1988). In Situ FTIR and UV-Visible Spectroelectrochemical Studies of Iron Nitrosyl Porphyrins in Nonaqueous Media. Inorganic Chemistry, 27, 4120-4125.

[54] Gaillard F., Levillain E. (1995). Visible time-resolved spectroelectrochemistry: application to study of the reduction of sulfur (S8) in dimethylformamide. Journal of Electroanalytical Chemistry, 398, 77-87.

[55] Wu L.L., Huang H.G., Li J.X., Luo J., Lin Z.H. (2000). Time-resolved UV-vis spectroelectrochemical studies of the electron transfer process of cytochrome c. Electrochimica Acta, 45, 2877 – 2881.

[56] Yan R.W., Jin B.K. (2013). Study of the electrochemical oxidation mechanism of formaldehyde on gold electrode in alkaline solution. Chinese Chemical Letters, 24, 159–162.

[57] Jarosz T., Brzeczek A., Walczak K., Lapkowski M., Domagala W. (2014). Multielectrochromism of redox states of thin electropolymerised films of poly(3-dodecylpyrrole) involving a black coloured state. Electrochimica Acta, 137, 595–601.

[58] Tao Y., Zhang K., Zhang C., Cheng H., Jiao C., Zhao Y. (2016). Electrochemical synthesis of copolymers based on 2-(anthracen-9-yl)thiophene: A facile and efficient route to a series of multicolor electrochromic polymers. Materials Science in Semiconductor Processing, 56, 66–75.

[59] Zhang J., Chen Z., Yang L., Hu F., Yu G.A., Yin J., Liu S.H. (2017). Dithienopyrrole compound with twisted triphenylamine termini: Reversible near-infrared electrochromic and mechanochromic dual-responsive characteristics. Dyes and Pigments, 136, 168-174.

[60] Akbayrak M., Cansu-Ergun E.G., Önal A.M. (2016). Synthesis and electro-optical properties of a new copolymer based on EDOT and carbazole. Designed Monomers and Polymers, 19, 679-687.

[61] Chanawanno K., Rhoda H.M., Hasheminasab A., Crandall L.A., King A.J., Herrick R.S., Nemykin V.N., Ziegler C.J. (2016). Using hydrazine to link ferrocene with Re(CO)3: A modular approach. Journal of Organometallic Chemistry, 818, 145-153.

[62] do Prado T.M., Machado S.A.S. (2016). Spectroelectrochemical study of salicylate in alkaline medium. Journal of Solid State Electrochemistry, 20, 2569–2574.

[63] Xie Y., Li D., Jin B. (2016). In situ FT-IR spectroelectrochemical study of the reduction of 1,4-dinitrobenzene in room-temperature ionic liquids. Journal of Electroanalytical Chemistry, 774, 1–6.

[64] Roznyatovskaya N., Noack J., Fühl M., Pinkwart K., Tübke J. (2016). Towards an all-vanadium redox-flow battery electrolyte: electrooxidation of V(III) in V(IV)/V(III) redox couple. Electrochimica Acta, 211, 926–932.

[65] Izquierdo J., Mizaikoff B., Kranz C. (2016). Surface-enhanced infrared spectroscopy on boron-doped diamond modified with gold nanoparticles for spectroelectrochemical analysis. Physica Status Solidi A, 213, 2056–2062.

[66] Grayburn R.A., Dowsett M.G., Sabbe P.J., Wermeille D., Anjos J.A., Flexer V., De Keersmaecker M., Wildermeersch D., Adriaens A. (2016). SR-XRD in situ monitoring of copper-IUD corrosion in simulated uterine fluid using a portable spectroelectrochemical cell. Bioelectrochemistry, 110, 41–45.

[67] Kim Y., Kim E., Clavier G., Audebert P. (2006). New tetrazine-based fluoroelectrochromic window; modulation of the fluorescence through applied potential. Chemical Communications, 3612–3614

[68] Quinton C., Alain-Rizzo V., Dumas-Verdes C., Miomandre F., Clavier G., Audebert P. (2014). Redox- and Protonation-Induced Fluorescence Switch in a New Triphenylamine with Six Stable Active or Non-Active Forms. Chemistry A European Journal, 21, 2230.