Part E

PHOTOELECTROCHEMISTRY

CHAPTER 15

Molecular Photo-Excitation

15.1   INTRODUCTION

In the last three parts (Chapters 3 to 14) a variety of interfacial dynamic processes have been considered quite extensively. But all those processes were brought about predominantly by just one single driving force, namely, electrode potential. There is another energy input that is avilable free of cost on the surface of the earth, the solar energy in the form of photons of different energy contents or frequencies. How does the photonic excitation at the electrode-electrolyte interface influence electron transfer process? Can one synthesize electrochemicals or produce electrical energy by effectively utilizing the abundant photonic energy quantas? This is the major concern of photoelectrochemistry which is the subject matter in this part (Chapters 15 and 16).

Photoelectrochemistry just remained as an academic science up to the late sixties and even in the early seventies. A few lucid treatments on semiconductor photoelectrochemistry were available [1-3]. The spectroscopic properties of redox molecules received attention because of their potential use in enhancing the understanding of the electrochemical behaviour of molecules [4-6]. The potential application of both these processes were very strongly felt when the energy crisis struck the globe suddenly in the early seventies. Even today the photoelectrochemical processes have not made a, substantial impact on the electrochemical technology. Photovoltaic cells containing solid electrolytes and compound semiconductors seem to be the only technology that has seen the market place. But there is certainly very great promise for the future. This hope has sustained a continuing research in this field all over the world. This is evident from the regular flow of conference proceedings in different aspects of photoelectrochemistry [7-13]. At least three recent books deal with the recent developments in a comprehensive manner [14-16]. Two collective volumes containing excellent review articles [17, 18] and the recent literature surveys [19-20] may be cited. One can easily state that this is the fastest growing branch of electrochemistry today.

Since voltammetric methods are also used extensively in photoelectrochemistry, it was felt that it should certainly find a place in this monograph. However, there are certainly a number of problems in selecting material from a recently born, fast growing, extensive literature. One cannot attempt a comprehensive survey of all the

latest developments. One's efforts would be just to develop the elementary concepts in the field and illustrate them with sufficient examples so that the reader can approach any recent literature that is relevant with sufficient confidence.

Photons can obviously excite both the components of the electrode-electrolyte interface. The electrode can be a metal, semiconductor, passivating oxide film or even some organic insulator film. The electrolyte species may be an organic, inorganic or organometallic species dissolved in the electrolyte solutions of varying composition or preferably adsorbed on the electrode surface. Instead of conventional cells containing two electrodes in an electrolyte medium, one may employ microheterogeneous systems where small conducting particles would contain both anodic and cathodic regions [17]. The overall anodic and cathodic photoelectrochemical reactions will proceed in a mixed potential process pattern (Chapter 12) on each heterogeneous particulate system producing the desired chemical products (say H_2 and O_2 from water). The individual anodic and cathodic processes are similar to the electrochemical processes at single electrode-electrolyte interfaces and hence can be subjected to voltammetric investigations.

There are similarities in the photo-excitation of electrode surface and molecular species and the associated processes after this central action in photoelectrochemistry. This is the reason for simultaneous treatment of both the processes in most of the literature [1-3, 7-20]. However, it is still worthwhile treating them separately for the sake of clarity and convenience. Hence the processes involving molecular photo-excitation shall be treated here and photo-excitation of electrodes shall be reserved for the next chapter.

After a brief introduction of molecular photo-excitation, the reactivities of the excited electronic states with special reference to their electron transfer properties are treated which are of primary interest in electrochemistry. Analogy and differences between electron transfer brought out by electrode potential and photo-excitation are clearly brought out. In the methodology Section (15.3), the voltammetric methods employed in spectroelectrochemistry and photoelectrochemistry are discussed in some detail. Illustrative examples of electrochemical processes and analytical applications are treated subsequently.

15.2 THE MODEL

15.2.1 MOLECULAR PHOTO-EXCITATION

It is well-known that molecules of all kinds contain different rotational, vibrational and electronic energy levels that give rise to well-defined spectra for each molecular species. In spectroelectrochemistry, use of these spectroscopic properties of the molecules is made to understand their electrochemical behaviour ingreater detail. Although a good understanding of molecular spectroscopy is quite essential for spectroelectrochemical studies, it is felt that it is neither possible nor necessary to introduce it here because of the extensive use of this technique by almost every practising electrochemist. Some good text book on spectroscopy may however be consulted, if necessary [21-23].

Photo-excitations at the molecular electronic level however produce electrons with much higher energy that can lead to a variety of irreversible chemical changes. This type of electronic excitation is the basic phenomena in all photochemical processes [24-26] and the newly developing area of photo-electrochemistry. Even here one cannot however describe all aspects of molecular photo-excitation and the subsequent processes. However for the sake of continuity and introducing some of the terminologies that are often found in the photoelectrochemical literature, very briefly the optoelectronic processes associated with molecular photo-excitation are introduced.

Figure 15.1 is a typical schematic representation of processes involved in molecular photo-excitation. It shows three allowed and two forbidden excited states for the molecular species to note all possible transitions. Table 15.1 contains the optical processes mentioned in Fig. 15.1 with their typical half-life values. The time scales involved in photon absorption (10^{-15} s) and internal conversion ($10^{-14} - 10^{-13}$ s) are very fast processes when compared with typical time scales in volved in electron transfer ($10^{-10} - 10^{-5}$ s) reactions. Hence in most of the electron transfer reactions, the molecular species of the lowest allowed transition states of the photo-excited molecule would participate. However, in some inorganic molecular processes intersystem crossing (singlet to triplet for example) can be very fast and so the lowest forbidden state of the photo-excited species can also participate in electron transfer. Any excited molecular species that

Table 15.1

Time scales of different photo-excitation processes in liquids

Symbols	Process	Time (s)
A	Absorption	10^{-15}
F	Fluorescence	$10^{-9} - 10^{-5}$
P	Phosphorescence	$10^{-5} - 10^{-3}$
IC	Internal conversion	$10^{-14} - 10^{-3}$
ISC	Intersystem crossing	10^{-6}
	Bimolecular redox reactions	$10^{-10} - 10^{-5}$

shows fairly long shelf-life period can involve in photochemical change, energy transfer or electron transfer reactions [27]. The first which may lead to the photodegradation of the molecular species itself would not be of interest in electrochemistry. This type of process however is the widely investigated one in photochemistry proper [24-26]. The second process energy transfer does not produce any chemical change. The molecule simply exchanges energy with the surroundings and goes to the ground state. This type of process is mainly responsible for low photoefficiencies in photochemical as well as photoelectrochemical processes. This energy transfer can be even more important in electrochemistry where heterogeneous solid surfaces (electrodes) can very well be involved in the energy transfer. Finally one can always envisage a faster electron transfer reaction from an excited molecule when compared with the ground state of the same molecular species. This important process is the desired one in electrochemistry.

If one considers all the possibilities offered by the photo-excitations represented in Fig. 15.1 one would in essence assume that a number of excited molecular states with different excitation energies can undergo photoelectron transfer or photoredox reactions with other molecules. However, the fast internal conversions make it possible to simply assume a single excited state for electron transfer reactions.
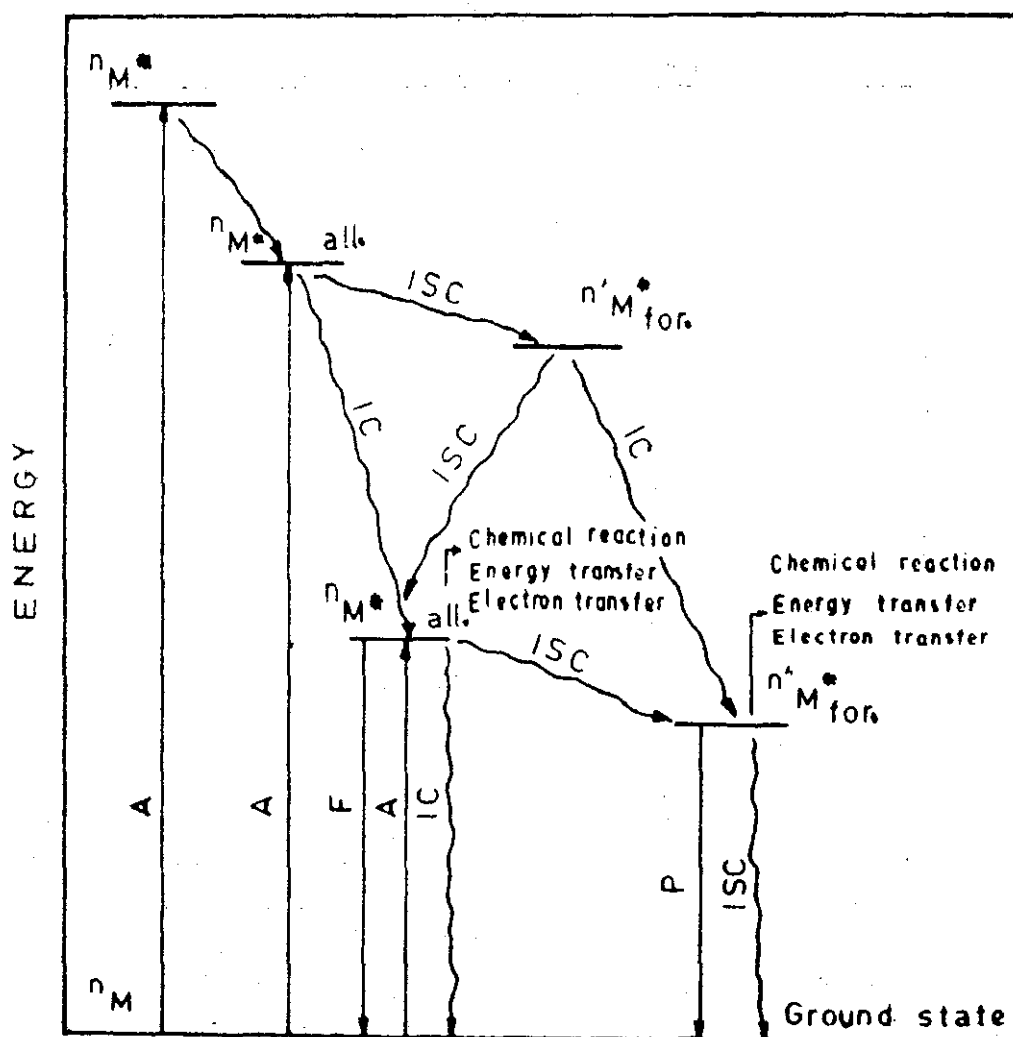
Fig. 15.1   Energy level diagram and photo-excited state processes
for a molecule, n_M = molecular state of spin multi-
plicity n; $n \neq n$; all = allowed state, for = forbid-
den state. See Table 15.1 for explanation of photo-
processes (other symbols in figure) and time scale.

This is the basis for indicating only one excited state for any photo-
chemical system in the literature. The same procedure is adopted
in the subsequent sections. However, when analyzing experimental
results, one should always remember that more than one excited
state can participate in the process although the relative contri-
butions from individual components may be very different.

15.2.2   PHOTOCHEMICAL VERSUS ELECTROCHEMICAL EXCITATION

Now consider an organic molecule whose highest occupied molecular
orbital energy level (bonding molecular orbital, M_b), and the lowest

unoccupied molecular energy level (antibonding molecular orbital, M_a) are denoted in Fig. 15.2. In the ground state, two electrons occupy the M_b level (Fig. 15.2.a). Now what happens to the molecule during photochemical and electrochemical excitation?
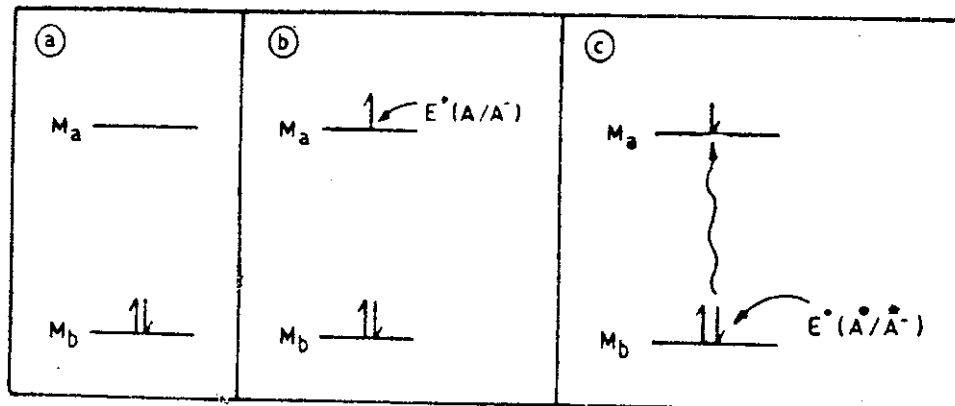
Fig. 15.2   Energy levels and redox potentials of ground and excited states. (a) Ground level, (b) addition of a new electron to the ground state electrochemically, (c) addition of a new electron to the excited molecule.

One can, for example, add an electron to the molecule by applying sufficiently negative potential on an electrode surface near the molecule. This new electron will now occupy the unoccupied M_a level (Fig. 15.2.b). However, if one excites the electron from the ground state of the molecule by photons of sufficient energy, one of the M_b level electron itself is excited to the M_a level. Hence the new electron may be added to Ma level itself (Fig. 15.2c). This is the main difference between the electrochemistry of molecular ground state and photo-excited state.

In ths energy diagrams of the type shown in Fig. 15.1 and Fig. 15.2, the top portions correspond to loosely held electrons which can serve as reducing agents. The bottom regions correspond to strongly held electronic levels which can serve as strong oxidizing agents (if the energy levels are empty). The standard electrode potentials of the molecules also would follow a parallel pattern. The top level would correspond to highly negative values of E^o and the bottom level correspond to positive E^o values.

Now again consider the E^o values of ground and excited molecular states. The E^o value of A/A^- couple would be around the M_a energy level which would be highly negative (The level would not be exactly equal to spectroscopic M_a level because of the

solvation energy difference between A and A^-. But one will neglect such effects here). However, in an excited molecule one can add the electron in the bonding energy level itself (Fig. 15.2.b and c). The redox potential of the excited state E^o (A^*/A^{*-}) would hence be much more positive when compared with the ground state E^o (A/A^-). The difference would approximately correspond to the energy difference between M_a and M_b levels.

The same type of situation arises in the electrochemical oxidation of A to A^+ as well. In the oxidation of ground state, the electron from the M_b level has to be removed which will be more positive. In the photo-excited state, one can remove the electron from the M_a level itself which will be much more negative. The difference between E^o (A^*/A^{*+}) and E^o (A/A^+) would again correspond to ΔE ($M_a - M_b$).

The above concept is so basic to photoelectrochemistry that it is worthwhile repeating it from another angle. In electrochemistry one can generate an anion radical (A^-) or a cation radical from a neutral molecule at sufficiently negative or positive potentials respectively. But a photo-chemically excited neutral molecule itself serves as a powerful oxidizing or reducing agent at the same time. The oxidizing power of the excited molecule arises because of the vacancy in the bonding orbital. The reducing power arises because of the excited electron in the antibonding molecular orbital. The photon thus serves as a catalytic source to improve the oxidizing and reducing power of the molecular species.

The next question is how do we tap this improved reactivity of the excited state in electrochemistry? This is achieved by effective electron transfer at the electrode-catalyte interface. This important question is taken up in the next section.

15.2.3   ELECTRON TRANSFER : METALS AND SEMICONDUCTORS

In electrochemistry, one deals with a single form of energy (electric energy) and electrodes which possess metallic conductivity. The Fermi level of these electrodes could always be raised or lowered by increasing the electrode potential in the negative or positive direction respectively. But in photoelectrochemistry, one is dealing with two forms of energies, namely electrical and photonic. Moreover the photoexcited states are always very reactive and so the direction of charge transfer is mainly decided by the energy

levels of the molecules and the electrodes in the photo-excited states. Hence a good understanding of the structure and method of construction of the energy level diagrams at the electrode-electrolyte interface are quite important for a good grasp of photoelectrochemistry. Let us briefly consider these energy level diagrams and their electrochemical consequences in this section.

The Fermi energy level of a metal under open circuit condition can be easily obtained from the literature. This is directly related to the work function of metals (see Table 1.1). The Fermi level of a semiconductor electrode can also be measured by the potential dependence of photovoltage measurement [1] or capacitance measurements [20]. Knowing the E_F and the absorption spectrum of the semiconductor material, constructing the energy level diagram of the electrode under open circuit condition is quite simple. The energy levels of the molecules can also be easily established. The E° value or the redox potential energy level of the ground state is evaluated by simple voltammetric measurements on any metal electrode. This coupled with the absorption spectral data enables the fixation of the excited state energy levels. We shall discuss some examples of these types of measurements in Section 15.4.3. Studies of this type enable us to construct the characteristic energy level diagrams shown in Fig. 15.3. Now, how do these diagrams help to predict the photoelectron transfer rate?

Two important guidelines should be kept in mind when one employs the energy level diagrams. *The direction of charge transfer* always follows the direction of greater stability for the electric charge involved. The electron in the energy level diagrams for example will always move downwards. The holes or positive charges would always move upwards. Secondly, *the extent of charge transfer* will always depend on the closeness of the energy levels involved in the charge transfer reaction. If the energy levels are equal, for example, the charge exchange between the states would be maximum.

Using these two rules one can try to predict the direction and extent of charge flow in Fig. 15.3. The excited states of the molecules near the metal electrode (Fig. 15.3.a) lie above the Fermi level of the metal and the ground state lies below it. Hence the electron transfer in both directions is possible. But the metal Fermi level lies closer to the ground state molecular level. Hence electron
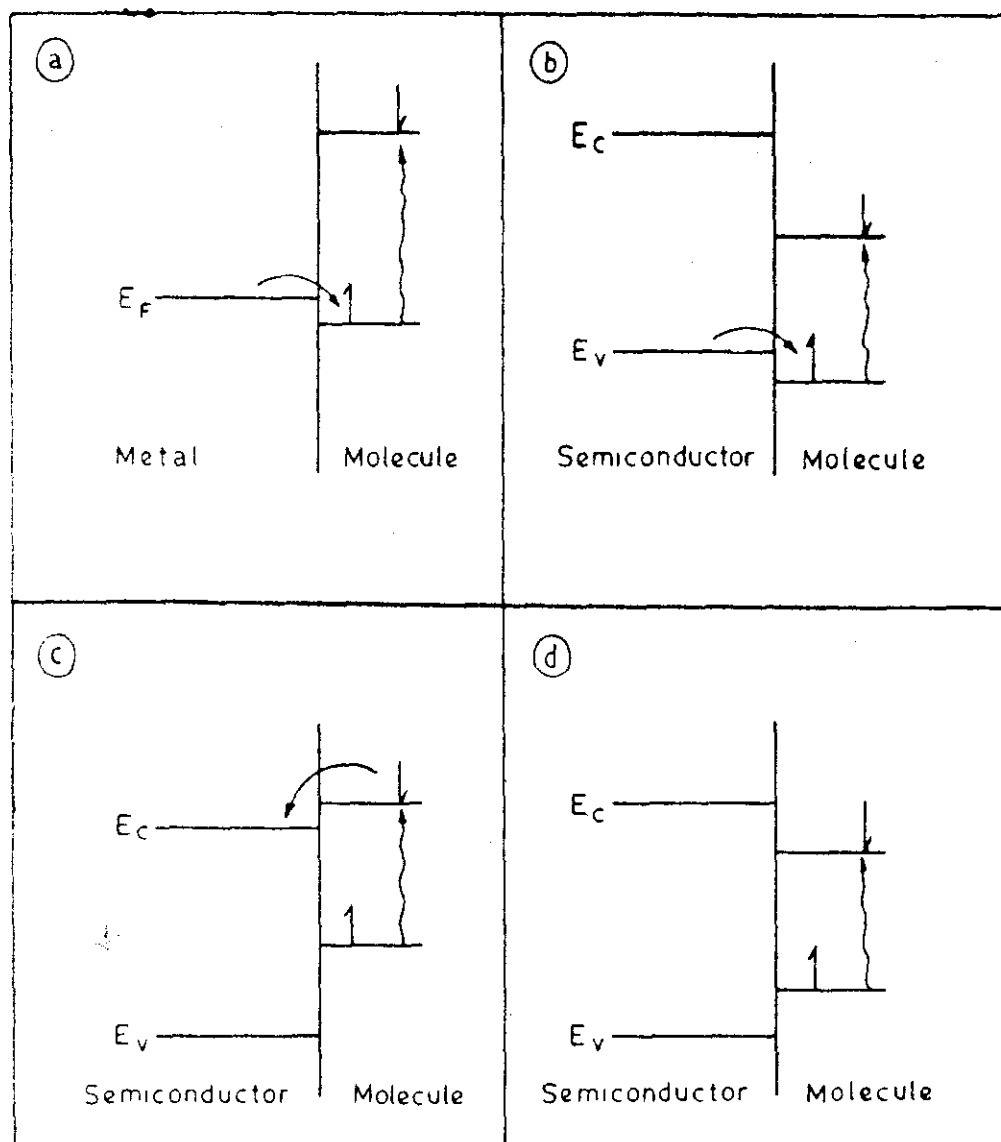
Fig. 15.3   Electron transfer between electrode-photo excited molecule inter-
face. (a) metal-molecular system. Molecular reduction more
probable. (b)-(d) semiconductor-molecule system (b) reduction of
molecule (c) oxidation of molecule (d) no redox process is
possible.

transfer from the metal to the electrolyte species is more probable.

Similarly on the semiconductor electrode/molecule interface
represented by Fig. 15.3.b, the reduction of the molecular species
is more probable. In the situation of Fig. 15.3.c, however, the
excited state lies above and closer to the conduction band of the
semiconductor. In this case, therefore, one would predict oxidation
of the molecular species. These examples clearly indicate that one
can induce either electrochemical oxidation or reduction of a
molecule by choosing the right type of electrode and the molecular

species of desired interfacial energy levels and inducing photo-excitation.

Now, what will happen in the case represented by Fig. 15.3.d? Both the ground and excited state of the molecule lie in between the E_C and E_V levels of the semiconductor. Such molecular species will not undergo electron transfer (unless some semiconductor photo-excitation of surface states are involved which are treated in Chapter 16). This is the typical spectroelectrochemical situation which can be contrasted with the photo-electrochemical situations considered in Fig. 15.3.a to Fig. 15.3.c. In photoelectrochemistry one deals with photochemical absorptions that can cause charge transfer. In spectroelectrochemistry one deals with photochemical absorptions that have (or that are assumed to have) no effect on interfacial charge transfer. The former is closer to photochemistry while the latter is essentially spectroscopy. These two methodologies are discussed in greater detail (Section 15.3) after considering another important aspect, that of the redox chemistry of photo-excited states.

15.2.4 REDOX REACTIONS OF EXCITED STATES

It has already been noticed that the molecules that should be of use in photoelectrochemistry should fulfil some stringent requirements. They should absorb and emit photons without decomposition (Section 15.4.1). They should serve as a good electron transfer system (Section 15.4.2). They should possess M_b and M_a energy levels that would suit the electron transfer in the desired direction (Section 15.4.3). In addition, they should absorb photons from the wavelength region where solar energy is predominantly available. It is not at all easy to find molecules that would simultaneously fulfil all these requirements. Only a selected few high molecular weight organic molecules and inorganic transition metal redox couples can be of use in such photo-excitation processes (See 15.4). In such a situation naturally the ultimate interest is not to generate the oxidized or reduced form of the molecule through photo-excitation, but rather to use it as the mediator for achieving many other overall redox reactions. It is once again necessary that the energy levels should be favourable for the redox reaction. Briefly these requisite conditions are considered here.

Consider the photosensitive A adsorbed on the electrode surface with energy levels represented in Fig. 15.4.a. Now let one add R with energy level (E^o value of Ox/R couple) in between the mole-
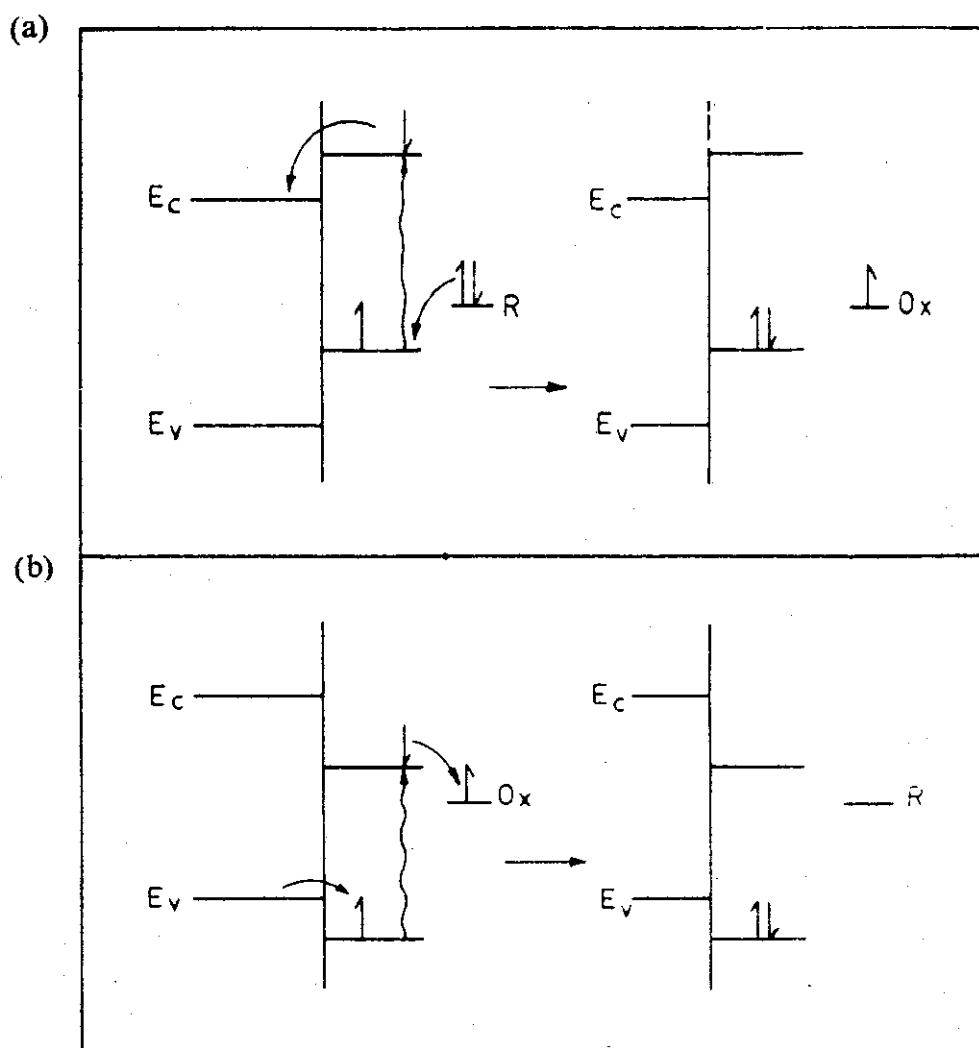

Fig. 15.4   Photoredox catalysis. (a) Oxidation of R. (b) Reduction of Ox.

cular energy levels. The excited electron can flow into the conduction band of semiconductor and the R species can simultaneously be transferred to the ground state of the absorbed species A. In this cycle R is oxidized to Ox and A is ready for another photo-excitation. Another photon absorption will oxidize another R species and the chain of events would continue. Similarly a reduction process of the molecule Ox to R can proceed as represented in Fig. 15.4.b. The electron is now transferred from the E_v of metal to M_b of A, gets excited to M_a of A and then drops on Ox and reduces it to R. This is the general principle behind sustained

photoredox catalysis. In the photochemical jargon, this is called supersensitization.

Photoredox catalytic systems adsorbed on electrodes are usually employed to oxidize or reduce small molecular species present in solution. Decomposition of H_2O into H_2 and O_2 by achieving photoreduction at the cathode or photo-oxidation at the anode or photoprocesses at both the electrodes may be cited as an example. Such processes are usually called photo-electrolytic or photo-electrosynthetic processes. Alternatively, one and the same Ox/R couple can be used in the overall electrode reactions at both the electrodes. A photosensitized cathode for example can reduce Ox to R. The R species can be oxidized on another photosensitized anode. The Fe-Thionine system is a good example of this type. In such cells, there is no net chemical change but electron flow through the external circuit is achieved. Such photochemical energy conversion processes are called photogalvanic processes. Examples of both types of processes are considered in Sections 15.4.4 and 15.4.5. However, basic processes involved are quite identical insofar as single electrode-electrolyte interfaces are concerned.

Even the limited discussion of the energy requirements for photo-excited electron transfer in this section would clearly indicate the stringent requirements for a successful development of a photoelectrochemical process. It is therefore no wonder that most of the photoelectrochemical processes investigated at present (including semiconductor photo-excitation discussed in the next chapter) do not lead to economically viable quantum efficiencies. However, for a new field that has received keen attention only in the past ten years, this is not a disappointing situation at all. There seems to be a fairly good comprehension of the molecular processes involved now. There is certainly great hope for a successful future which will sustain the present tempo and enthusiasm in the field.

15.3 THE METHOD

As mentioned earlier, molecular photo-excitation is used for analysis of the molecules or inducing electron transfer of the molecules. In the models section, the latter aspect was considered because it involved some new concepts at that level. The spectroelectrochemistry, on the other hand, is conceptually quite simple. Only the

well-known spectroscopic properties of molecular species are involved. However, the measurement of spectroscopic properties of an electrode-electrolyte interface involves considerable developmental efforts at the methodological level. This section therefore concentrates on the spectroelectrochemical methods in some detail.

15.3.1   SPECTROELECTROCHEMISTRY—A GENERAL OVERVIEW

The measurement of current, potential, time and charge under controlled conditions has remained as the predominant method for the investigation of the dynamic processes at the electrode-electrolyte interfaces for many decades now. However, the inadequacy of depending solely on electrical measurements for all the changes in the molecular species and electrode surface was also felt and discussed extensively. In recent years, a host of newer spectroelectrochemical methods for the investigation of electrode-electrolyte interface have been developed. At least one book [4] and a major portion of another book [28] have been completely devoted to these methods. One comprehensive review [29] and two lucid discussions [30, 31] on many spectroelectrochemical aspects are also available. It is indeed quite impossible to deal with all these aspects in the present context. There will therefore be a restriction to a brief listing of some more popular methods, the experimental approaches adopted and the advantage of the methods. The main emphasis will be on the resemblance and comparative advantages and limitations of spectroelectrochemical techniques when compared with the voltammetric techniques discussed so far.

Optical [32] and electron microscopy [33] are indeed extensively used to study the electrode surfaces after surface processes occur on them. The photoelectron spectroscopy and Auger electron spectroscopy [34, 35] are even more powerful in the sense that they can establish even minor changes of surface chemical composition. However, these techniques can be used only after taking out the electrode from the electrochemical cell. Such removal of the electrode from the electrolyte environment can cause substantial surface reconstruction (Chapter 7). This is the reason for more serious efforts to standardize *in situ* spectroelectrochemical techniques.

The most direct and simple way of introducing spectroscopy into

electrochemical investigations is of course introducing optically transparent electrodes (OTE). By constructing a suitable cell with proper optical windows and optically transparent electrodes, one can carry out absorption spectroscopy experiments under voltammetric conditions. This method naturally has grown much faster than many other spectroelectrochemical techniques [5, 6]. In the next section some recent developments in this field are considered as illustrative examples of spectroelectrochemical methods (Section 15.3.2).

One can use optically transparent electrodes in the total internal reflection mode [36]. Application of OTEs in the transmission [5, 6] or total internal reflection [36] mode generally enables one to investigate the optical or spectroscopic properties of molecular species in the diffusion layer of the electrolyte solution, although there are some subtle differences among them.

In electrochemistry, one employs non-transparent electrode materials as a rule. One can employ specular reflectance spectroscopy [37] in the UV-visible region to investigate the interfacial properties on such electrode surfaces. These techniques provide more information on the modifications near the electrode surface (oxide formation, for example). Although many molecules including the solvent of the electrolyte would show absorption in infra-red region, special construction efforts still enable one to obtain the reflection spectroscopy of the electrode surface in this region [38].

Raman scattering of molecular species produces very weak signals in the electrolyte solutions. But one can employ laser beams and also take advantage of the resonance in the Raman signal. This laser resonance Raman spectroscopy can offer accurate information regarding the small molecular species adsorption on electrodes [39]. Recently it was found that some active surfaces like Ag produce a very good signal enhancement. This surface enhanced Raman scattering is one of the active areas of spectroelectrochemical research in recent times [39].

Although the construction of cell, electrode preparation, optical windows and many other practical aspects of the *in-situ* spectro-electrochemical techniques discussed so far are quite different, the basic methodology adopted in system excitation and response measurement are the same in all these techniques. There are basically two modes for exciting the electrode-electrolyte interface, the electrode potential and photons of different wavelengths. One can keep either

one of them constant and vary the other. One can conveniently get two responses of this photoelectrochemical excitation, the current and absorbance. We can also retain both the excitation inputs at a constant level and measure absorbance or current as a function of time. All these variables offer essentially six spectroelectrochemical measurement techniques (Table 15.2). The two measured parameters involved in spectroelectrochemistry, the absorbance and current are in fact closely related in a subtle way. The absorbance measures the amount of spectroscopically active species present at any time t. This quantity is similar to the total charge consumed q in an electrochemical reaction. Just as the differential $dq/dt = i$ gives the rate of charge transfer, the differential absorbance with respect to time gives the rate of formation or consumption of molecular species. The differential absorptivity versus potential curves would hence be quite identical to the typical cyclic voltammetric curves discussed so far under otherwise identical experimental conditions (Section 15.3.2). This is the last experimental method cited in Table 15.2.

Now one may have a quick look at the individual methods used in spectroelectrochemistry. Spectroscopy at constant electrode potential is the most direct method from spectroscopic viewpoint. Recording the spectra at different electrode potentials would show a regular and continuous decrease in the absorbance of the reactant consumed at the interface and increase in the absorbance of the products formed. Alternatively the wavelength of the absorbance maxima of one of the products formed can be fixed in the process and the absorbance at this wavelength as the function of applied electrode potential can be measured. This voltabsorptometry is one of the closest neighbours of the voltammetric technique discussed throughout this monograph. Derivative cyclic voltabsorptometry is the direct differential form of this technique (see previous paragraph).

Keeping the input conditions intact in the two aforementioned experiments, if one measures the photocurrent response instead of absorbance of the molecules, one obtains two new methods namely photocurrent spectroscopy and photocurrent voltammetry (Table 15.2). The measurement of the dark current as background is always necessary in these methods to ensure proper interpretation of experimental methods.

There is one important difference between the measurement of absorbance and photocurrent. In spectroelectrochemical conditions,

Table 15.2

Measurement modes employed in spectroelectrochemistry

No	Potential Input	Optical Input	Time	Absorbance	Current	Differential absorbance	Technique
1	Constant	Varying	...	measured	...	...	Spectroscopy at constant E
2	Varying E	Constant	$E = f(t)$	measured	...	...	Voltabsorptometry
3	Constant	Varying	...	...	measured	...	Photocurrent spectroscopy
4	Varying E	Constant	$E = f(t)$	...	measured	...	Photocurrent voltammetry
5	Constant	Constant	Varying	measured	...	...	Chronoabsorpto-metry
6	Constant	Constant	Varying	...	measured	...	Absorptive chronoamperometry
7	Varying E	Constant	$E = f(t)$	...	...	measured	Derivative cyclic voltabsorptometry

the photocurrent in presence and in the absence of photoexcitation should be the same. This is the important criterion for establishing that the photochemical changes are not involved in the investigation. In contrast, if any significant variation of current on photo-excitation is observed one should realize that one is working in the photoelectrochemical domain. Other than this subtle basic difference, all the methodologies developed in spectroelectrochemistry can in principle be employed in the photoelectrochemical investigations.

One can also maintain both the excitation signals at constant values and measure the time dependence of absorbance or photocurrent. Although these techniques are not quite similar to the voltammetric techniques, they form the basis for the latter, and the quantitative analysis of the time-response analysis is much more straightforward and convenient.

In addition to the absorbance signal which has been discussed so far, one can also consider any other photochemical property of the molecule for analysis on similar lines. The electrogenerated chemiluminescence is a typical example [40]. The luminescence can be measured as a function of all these properties. One can also employ a plain polarized light for *in situ* measurement and evaluate the phase shift Δ and electric field component ψ of the emerging light. This powerful technique, ellipsometry, is in use in the field of *in situ* electrochemical surface studies for a very long period now [41, 42].

The general discussion presented here should not lead one to think that all the spectroelectrochemical measurements are usually employed in the seven modes mentioned in Table 15.2. Neither is it meant that all the modes for any specific spectrochemical method have been theoretically and experimentally comprehensively treated. Only the modes of measurements generally employed are listed. It is true that most of the modes are generally in use in the transmission spectroscopy at OTEs. This is the reason for selecting this method for a more detailed consideration as an illustrative example in the next section.

A general discussion on spectroelectrochemical techniques would not be complete without a note on electron-spin-resonance. A radical formation in electrolyte solution can be established beyond doubt using this technique. For stable radicals, the electrolyte can be transferred to ESR set-up before measurements are made.

Methods for obtaining ESR signals of shortlived intermediate have also been developed [43]. This method is commonly employed only at constant potential conditions because of the inherent nature of the ESR signal. The time dependence of the ESR response and rate evaluation however are possible.

15.3.2 VOLTABSORPTOMETRY ON OPTICALLY TRANSPARENT ELECTRODES

Already two excellent reviews covering the spectroelectrochemistry on OTEs have been cited [5, 6]. This section will just present a brief introduction to the subject with emphasis on some recent developments.

An ideal optically transparent electrode should not absorb light at any light frequencies so that it does not in anyway interfere with the spectroscopic phenomena under investigation. SnO_2 and In_2O_3 materials coated on glass plates by conventional methods are the best choice from this viewpoint. From the point of view of electrochemistry (background current, potential window etc.) Pt, Au and Hg thin films coated on quartz materials are also frequently employed. Optical transparency may be achieved by employing minigrid type of electrodes having a few hundred grid wires per cm length. Pt, Au and Ni electrodes of this type can be fabricated. Although edge effects and non-linear diffusion effects will be present in these electrodes, these effects have been shown to be unimportant at fairly longer time scales and slower sweep rates. Reticulated vitreous carbon is another high porosity electrode which can be employed as an OTE.

One can essentially employ OTEs in two different cell configurations during spectroelectrochemical measurements. Thin layer cells containing OTE at one side of the cell [44] employs finite diffusion layer of solution (Chapter 10). OTE cells employing semi-infinite linear diffusion conditions (Chapters 3 to 5) were also introduced almost at the same time [45]. Both the methods are quite complementary to each other and each of these techniques will be discussed briefly.

a) *OTTLE cells*

Optically transparent thin layer electrochemical cells are usually called OTTLE cells. The construction of these cells as well as their

operations are similar to those of the conventional thin layer voltammetric cells discussed earlier (Chapters 2 and 10). However, the thickness of the thin solution layer in OTTLE cells will be about 50-200 μm, somewhat thicker than conventional thin layer cells. This would require a fairly longer time for the equilibration as well as completion of electrolysis at each potential. However, this thickness ensures higher absorption levels which ensure good response signal.

The longer time requirement of thin layer cells is essentially one of the advantages of these types of cells. Spectrochemical response of an electrochemical reaction is sought mostly when fast electrochemical responses are not obtained. The absorbance of a molecule can be measured at large time intervals if only the intermediates or products are quite stable. Voltabsorptometry is thus mainly used in the study of redox properties of biological molecules as illustrated later.

b) *OTE response under semi-infinite linear diffusion conditions*

OTEs can also be used in the conventional fashion containing a semi-infinite diffusion layer at the electrode-electrolyte interface. One cannot employ very slow sweep rates since connective diffusion effects and time-dependency of absorbance can complicate quantitative treatments. However, this method is particulary suited for the investigation of faster reactions and charge transfer involving unstable intermediates (Chapter 5). The voltabsorptometry also has a specific advantage over voltammetry in the sense that the former response does not contain a double layer charging component usually associated with the latter. For handling electrodes with surface modifications of different types again this type of cell set up is more convenient.

Quantitative treatments of interfacial processes were mainly developed for constant potential voltabsorptometry. However, the quantitative theory for cyclic voltabsorptometry was developed recently [6, 46]. This study also brought out the morphological similarity between cyclic voltammetry and voltabsorptometry recognized much earlier [47]. In Fig. 15.5, for example, one notices the CV, voltabsorptometry and derivative cyclic voltabsorptometry of tri-para anisidine on an OTE [46]. This figure shows the continuing rise

in the absorbance during the reverse sweep as well, until the electro-chemical reaction itself is driven in the opposite direction.

0·20 mA
0·050 AU
3·0 X 10⁻⁴ AU/mV

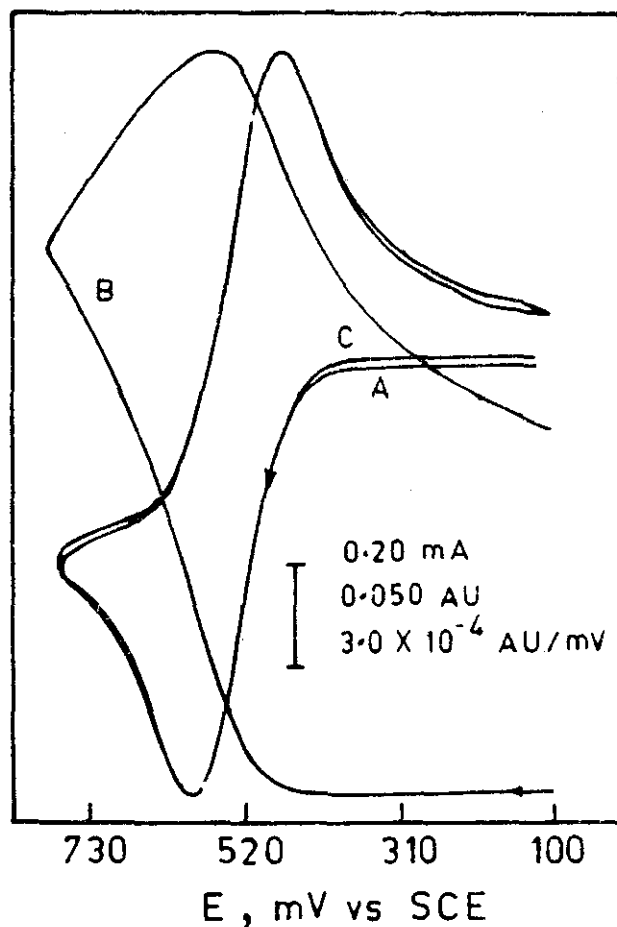730   520   310   100

E , mV vs SCE

Fig. 15.5 Simultaneously acquired (A) current-potential, (B) absorbance potential, and (C) differential absorbance potentials for tri para anisylamine at a Pt OTE in acetonitrile
0.1M TEAP at V = 551 mV s⁻¹.

[From EE Bancroft, JS Sidwell and HN Blount Anal Chem 53 (1981) 1390]

There are some specific advantageous features in the derivative cyclic voltabsorptometry as well. The molar absorbance can be differentiated with respect to the applied potential or time. The dA/dt (where A is the absorbance) would give a voltabsorptogram which will be similar in all sense to the CV curves. However, one can also obtain the differential with respect to potential E. The response would then have some novel features. For a typical simple electron transfer reaction 15.1, for example, the dA/dE is given by equation 15.2 [6, 46]

$$Ox + ne \rightleftharpoons R \qquad\qquad 15.1$$

$$\frac{dA_R}{dE} = \beta \, n^{1/2} \, \epsilon_R \, D_{Ox}^{1/2} \, C_{Ox} \, v^{-1/2} \qquad\qquad 15.2$$

where $\beta = -0.8810 \, mV^{-1/2}$, ϵ_R is the absorption coefficient of R and v is the sweep rate in $mV \, s^{-1}$. All other symbols have their usual meaning. It may be noted that the measured derivative decreases with sweep rate rather than increase with $v^{1/2}$, as in the case of cyclic voltammetry. This difference can in fact be much more important than meets the eye. In the redox catalytic EC reaction, for example, one will observe CV peaks even at pure kinetic controlled conditions where only an S-shaped wave will be obtained in conventional CV (Fig. 15.6). This type of differences may be favourably exploited in the analysis of more complicated systems.
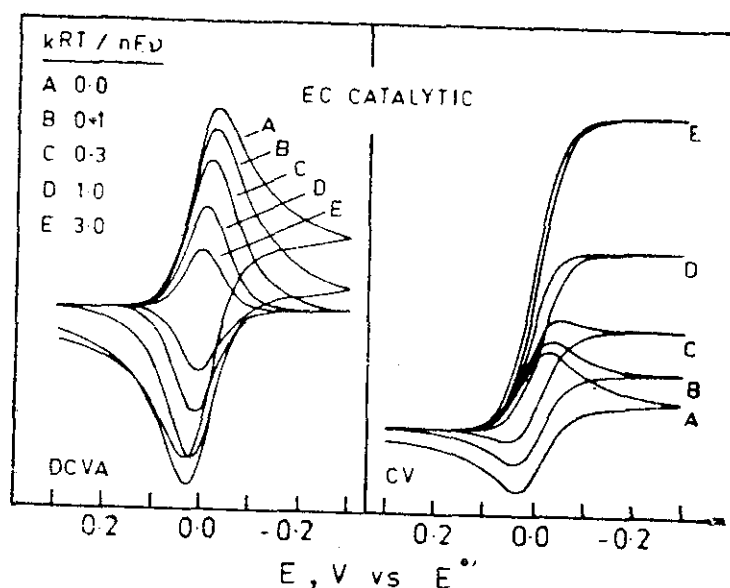

Fig. 15.6 Digitally simulated derivative sweep cyclic voltabsorpto-
metric (DCVA) and CV responses for first order redox
catalytic mechanism as a function of the dimensionless
kinetic parameter kRT/nFV

[From WR Heineman, FM Hawkridge and HG N Blount,
Electroanal Chem 13 (1984) 1]

As discussed in Section 15.3.1, voltabsorptometry is extensively used in the investigation of many other reflectance measurements as well. The derivative cyclic voltabsorptometry however is quite

new in the field and may be extended to other techniques in the near future.

15.4 THE PROCESS

It is obvious from the above discussions that the present chapter is a combination of two distinct areas of research, namely spectro scopy and electrochemistry. In this section, the use of spectroscopy for understanding electrochemical processes is considered first (Section 15.4.1). Quite often, electrochemistry also comes to the aid of the studies on optical properties of molecules (Section 15.4.2). Investigation of redox properties of ground state and excited properties of molecules is the vital area for successful application of molecular photo-excitation in electrochemistry (Section 15.4.3). After considering some specific examples in this area the applications of molecular photo-excitation on metal (Section 15.4.4) and semiconductor electrodes are treated.

15.4.1 SPECTROSCOPIC STUDIES OF ELECTROCHEMICAL PROCESSES

Spectroscopic analysis of electroactive species has become an integral part of electrochemical experiments in the investigation of many organic [48] and biologically important [49] molecules. Present day understanding of the redox properties of biological molecules [50, 51] has come mainly from spectroelectrochemical investigations of this type.

In addition to identification of the intermediates and products of electrochemical reactions by controlled potential spectroscopy, one can also employ these methods for evaluating some of the thermodynamic and kinetic parameters of these electrochemical systems. Consider the Nernst equation describing the electrochemical equilibrium of reaction 15.1:

$$E_{eq} = E^o + 2.303 \frac{RT}{nF} \log \frac{a_{ox}}{a_R} \qquad 15.3$$

Now if the electrode potential is held on either side of E^o and the absorbance of Ox and R is independently measured one can construct a plot of E_{eq} versus $\log a_{ox}/a_R$ quite easily. This would straightaway give two important parameters E^o and n value of the

electrode process. The only requirement for the application of this method is that both Ox and R should be stable. The charge transfer rate as such need not be fast since the potential can be held for a long enough time at any value until equilibrium is established. In fact, E^o and n values of redox couples that do not even give a good voltammetric curve have been determined by this method [5, 6].

The above potentiometric spectroscopy can be employed to estimate n and E^o values of bioredox systems that do not get reduced directly on the electrode surface. For example, one can employ a redox couple Ox/R to mediate electron transfer between redox couple A/B according to the following reaction scheme:

$$Ox + ne \rightleftharpoons R \qquad\qquad 15.1$$

$$A + R \rightleftharpoons B + Ox \qquad\qquad 15.4$$

If these two reactions are held at equilibrium, the E_{eq} is defined by both the redox couples and is given by

$$E_{eq} = E^o_{Ox/R} + \frac{2.303\,RT}{nF}\log\frac{a_{Ox}}{a_R}$$

$$= E^o_{A/B} + \frac{2.303\,RT}{nF}\log\frac{a_A}{a_B} \qquad\qquad 15.5$$

If one can get the absorbance of species A and B, the same method can be adopted for evaluation of $E^o_{A/B}$ of the redox couple that is not directly reduced on the electrode surface. A large number of biological molecules have been subjected to this type of analysis and the equilibrium parameters evaluated (See Table 3 in ref. 6).

Some rather concealed information in a voltammetric experiment can be decoupled by a simple voltabsorptometric experiment under identical conditions. Figure 15.7, for example, shows the voltammetry and voltabsorptometry of vitamin B_{12}. The voltammogram shows a single two-electron reduction wave. But voltabsorptometric curve shows the rise and fall in absorbance distinctly indicating two one-electron intermediates. The E^o values of both the one-electron steps were identified from this experiment [52]. Spectroelectrochemical literature contains a number of illustrative examples of this type in the study of solution phase redox equilibrium, chemical equilibrium (stability constant) and chemical reaction kinetics associated with charge transfer [5, 6].

In contrast to transmission spectroscopic techniques, voltab-sorptometry using ellipsometry and specular reflectance spectro-
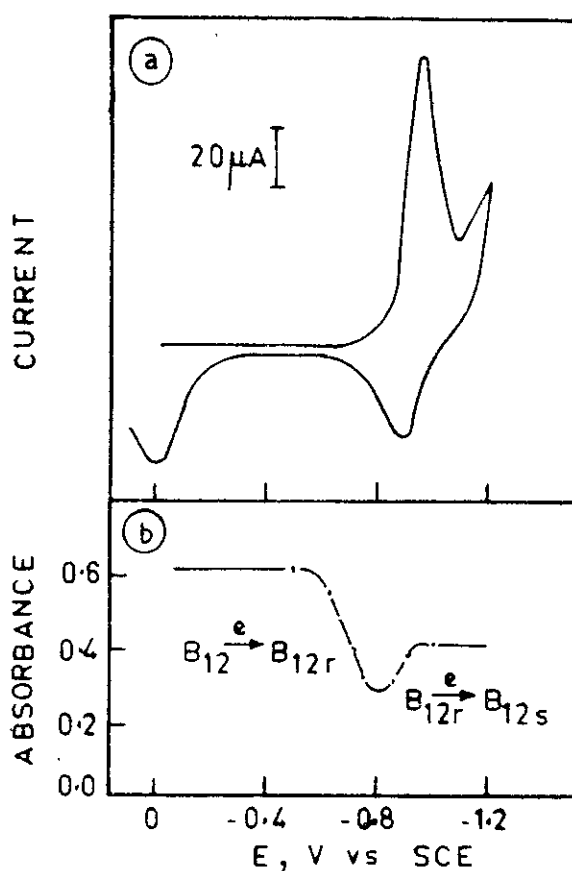

Fig. 15.7   (a) Voltammetry of 1 mM vitamin B_{12}; Britton-Robinson buffer of pH 6.86 in 0.5M Na_2SO_4 on Hg-Au mingrid OTTle. (b) Plot of absorbance at 368 nm vs potential obtained from constant potential spectroscopic data.

[From KA Robinson, E Itabashi and HB Mark, Jr. Inorg Chem 21 (1982) 3571].

scopy are found to be more useful in surface studies. Figure 15.8, for example, shows the reflectance spectra of Pt electrode in the presence and in the absence of O_2. One finds that the reflectivity variation is related to the oxide formation process on Pt (Chapter 7). The response does not depend on O_2 reduction process, thus enabling one to distinguish the surface process from the total voltammetric response [53].

15.4.2 ELECTROCHEMICAL STUDIES OF SPECTROSCOPIC PROCESSES

Spectroelectrochemical techniques find applications in the spectroscopic investigations of a number of newly formed electrochemical systems. The spectroscopic properties of the dicationic species of aniline [48] and methyl viologen radical cationic species [54] may be cited as examples.
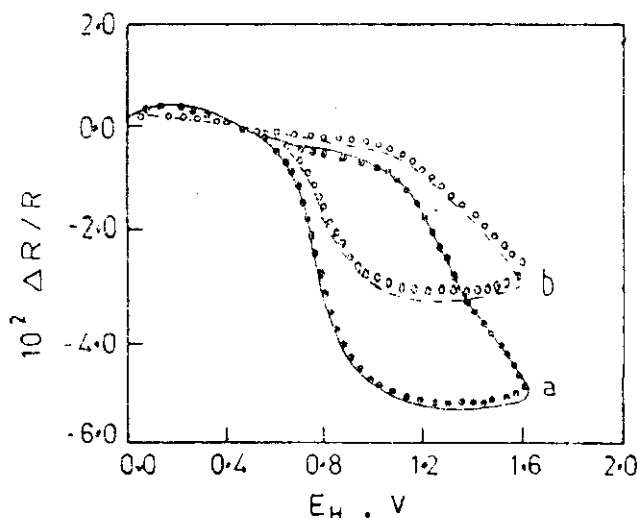
Fig. 15.8   Reflectance change versus potential for parallel (a) and perpendicular (b) polarizations of a platinum electrode in 1.0M $HClO_4$ in Ar saturated (curves) and O_2 saturated (points) solutions; sweep rate 20 mV s^{-1}.

[From JDE McIntyre and Dm Kolb in Symp Faraday Soc 4 (1970) 99].

Many organic molecules based on phthalocyanines [55] and alkyl viologens [56, 57] and other large π electron systems can show different colours at the oxidized and reduced states. These molecular systems are widely investigated for their possible electrochromic applications in electronic display devices. Electrochemical investigations including cyclic voltammetry can be conveniently employed to evaluate these systems in the electrolyte solutions [56] as well as surface modified [57] states. The delay time, the reversibility, the cycle life and many other properties relevant to optical applications can be evaluated quickly using cyclic voltammetry.

Many organic and inorganic redox systems can exhibit multiple redox states. An aromatic hydrocarbon such as anthracene for

example can form radical anion (An⁻) and cation (An⁺) at extreme negative and positive potentials. One can allow these two reactive species to interact directly by switching the electrode potential quickly from extreme negative to positive potential. What happens now is :

$$An^- + An^+ \rightleftharpoons An^* + An \qquad 15.6$$

The high energy reaction will generate an excited molecular state. Electrochemistry is extensively used to study the fate of the electro-generated excited states of these organic molecules by tracing their voltammetric as well as luminescence characteristics [40]. The spectroelectrochemistry of these species is also studied using thin layer cell arrangements [58]. The energy levels of excited molecules [59], the transitions between singlet-triplet states and many other consequences relevant to spectroscopy and photoelectrochemistry are obtained from these investigations. Recently, it has been established that excited luminescent states can be generated by redox catalytic processes. The voltammogram as well as voltage-luminescence relation of rubrene generated using $S_2O_8^{2-}$ redox catalysis for example is presented in Fig. 5.9. The direct correlation between the measured electrochemical and photoresponse is clearly noticed in this figure [60]. One can also modulate the fluorescence of the molecular species electrochemically [61].

Studies on these electrogenerated chemiluminescence and other related aspects essentially provided information on spectroscopic interest alone in the early stages [40]. However, they are also found to be of help in better understanding of electrochemical processes. In one recent study, for example, luminescence has been employed for probing the charge transport through thin polymer film at the electrode-electrolyte interface [62].

15.4.3 ELECTROCHEMISTRY OF GROUND AND EXCITED STATES OF MOLECULES

The energy levels of the ground and excited states of molecules are very important in deciding the success of a photogalvanic or photosynthetic process (Section 15.2). Hence, cyclic voltammetry and spectroscopic techniques are employed in a combined manner to evaluate the redox potentials of the ground and excited states,
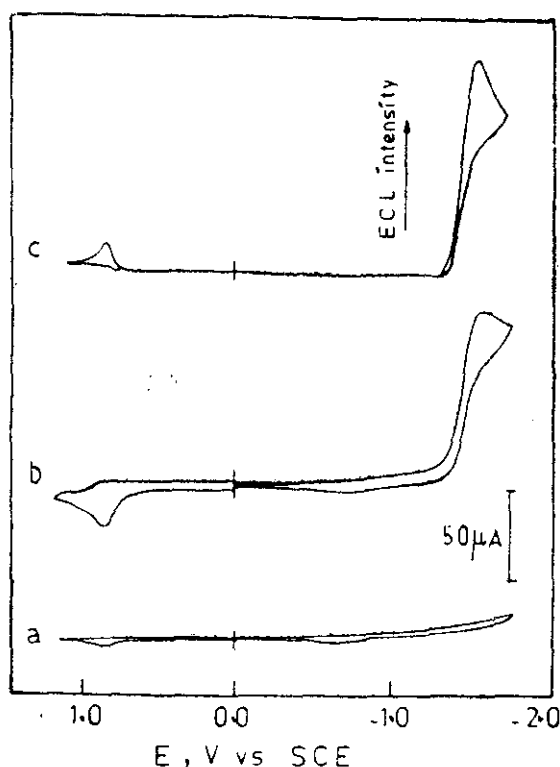
Fig. 15.9   Cyclic voltammograms (0.1 Vs^{-1}) at a Pt disk electrode in 2:1 acetonitrile-benzene (v/v) containing (a) 0.1M TBA BF$_4$ and 20 mM (TBA)$_2$S$_2$O$_8$; (b) solution in (a) with 1.0 mM rubrene; (c) relative ECL intensity vs potential for solution (b).

[From WG Becker, HS Seung and AJ Bard, J Electroanal Chem 167 (1984) 127].

the stability of the excited state, the energy transfers in the excited state and the suitability of solvent-supporting electrolyte system for the use of a specific photoredox system in the medium. Although many studies of this type form part of the photoelectrochemical interfacial study (Sections 15.4.4 and 15.4.5) some independent evaluation of these properties are also available.
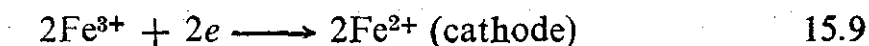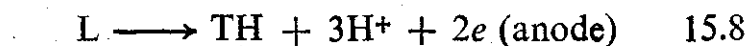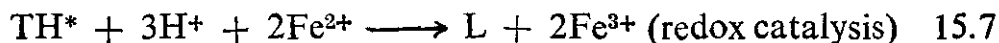
Most of the new photoredox systems investigated for this type of application are the alkyl viologens mentioned above and some Ruthenium and other Platinum group metal complexes [63–65]. The Co (III) complexes of the biological cyanocobalamine type [66] are also investigated. Manganese porpyrin type of complexes involved in photosynthesis [67] are another group of complexes that receive active consideration [68]. Photoelectrochemical characterization of metal complexes formed as thin stacked films [69] is also reported.

One would certainly hope that the basic studies on new systems involving photoredox states would continue to evaluate and pinpoint efficient ones for photoelectrochemical applications considered in the next two sections.

15.4.4 PHOTO-EXCITED ELECTRON TRANSFER ON METALS

Photosynthesis, the most important chemical process for human survival is a process that proceeds through molecular photo-excitation and photoredox catalysis. However, the efforts to duplicate this process remains to be a very challenging one before the scientific community [70]. Construction of photogalvanic and photoelectrolysis cells using molecular photo-excitation should certainly be considered as an effort in this direction. In fact, efforts have been made to attach chlorophyll itself on to the electrode surface and its electron transfer properties have been investigated [71] just as other photo-excitable systems [72]. In this section just the efforts in the development of photogalvanic and photoelectrosynthesis cells are illustrated with two typical examples.

Among the handful of photogalvanic systems investigated on metal electrodes [73], the Fe (III)-thionine system has received greater attention. In this cell, the thionine-coated electrode serves as the photoanode and another electrode serves as cathode. The photo-excited thionine (TH) is reduced to Leucothionine (L) by the Fe^{2+} ions present in solution. The Leucothionine is oxidized at the metal electrode where it is attached and the Fe^{3+} is reduced back to Fe^{2+} at the cathode. The cycle of events continue producing electricity in the external circuit [74, 75]

$$TH^* + 3H^+ + 2Fe^{2+} \longrightarrow L + 2Fe^{3+} \text{ (redox catalysis)} \quad 15.7$$

$$L \longrightarrow TH + 3H^+ + 2e \text{ (anode)} \quad 15.8$$

$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+} \text{ (cathode)} \quad 15.9$$

One important technical problem here is that the Fe^{3+} generated near the photosensitive surface should not get reduced there itself electrochemically. Figure 15.10 shows that this problem is solved quite easily. The presence of the thionine film slows down the electroreduction of Fe^{3+} ions on this surface. However, many other

problems associated with molecular photoexcitation still remain and the quantum efficiency is still very low [74, 75].
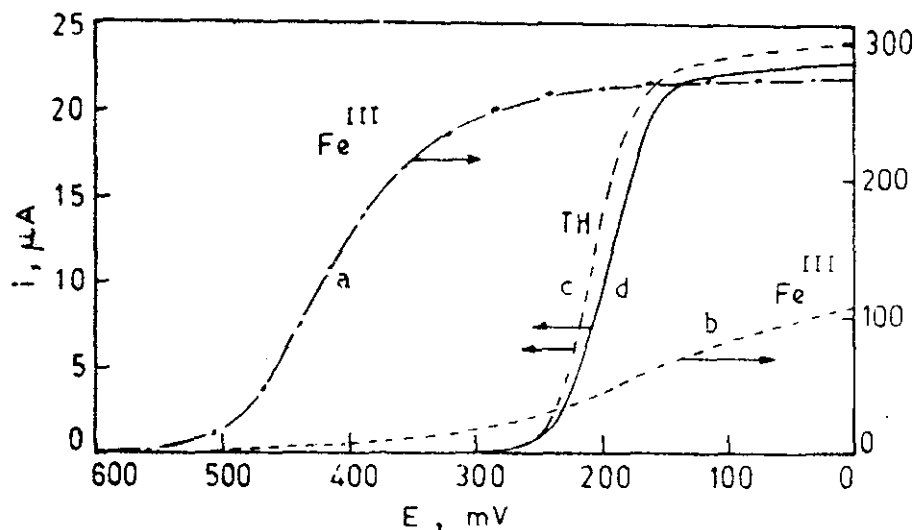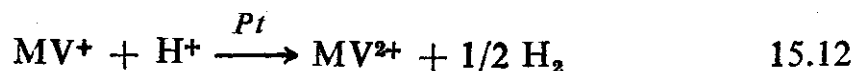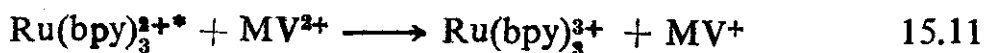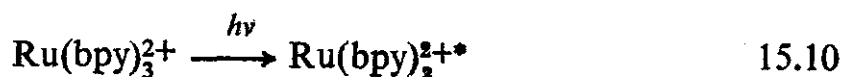

Fig. 15.10   Current-voltage curves for the reduction of Fe^{3+} (right hand scale) and thionine (left hand scale) on clean (a and c) and thionine coated (b and d) electrodes.

[From WJ Albery, PN Bartlett, JP Davies, AW Fowler, AR Hillman and FS Bachiller, Farad Discuss. Chem Soc 70 (1980) 342]

As a typical example of photoelectrosynthesis cell, one can consider the photogeneration of hydrogen [76]. This is achieved by photo-excitation of $Ru(bpy)_3^{2+}$ system and two subsequent redox reactions *via* methyl viologen (MV^{2+})

$$Ru(bpy)_3^{2+} \xrightarrow{\ h\nu\ } Ru(bpy)_3^{2+*} \qquad\qquad 15.10$$

$$Ru(bpy)_3^{2+*} + MV^{2+} \longrightarrow Ru(bpy)_3^{3+} + MV^{+} \qquad 15.11$$

$$MV^{+} + H^{+} \xrightarrow{\ Pt\ } MV^{2+} + 1/2\ H_2 \qquad\qquad 15.12$$

At the other electrode, O_2 evolution takes place. Photochemical conversion efficiency in this type of system is also very low.

There is a basic difference between metals and semiconductors (Section 15.2.3). There is practically no difference between the energy level where an electron is added or removed in a metal. Therefore the pobability of forward and reverse electron transfer reaction with a molecular species is quite high unless the electrode itself is strongly polarized with high overvoltages. In photoelectrochemistry,

one would not like to spend electrical energy in this fashion and hence the quantum efficiencies are bound to be low. However, because of the simplicity of dealing with metals when compared with semiconductors, this mode of photoelectrochemical conversion is still being continuously investigated.

15.4.5 PHOTO-EXCITED ELECTRON TRANSFER ON SEMICONDUCTORS

The energy levels where the electron is received and donated (valence and conduction bands respectively) on the semiconductor electrodes are quite different. Moreover, the depletion layer present on the semiconductor (see next chapter for more details) ensures preferential charge-movement in one direction (say electrode to electrolyte) when compared with the other. These two aspects ensure a better chance of success for photo-excited electron transfer on a semiconductor electrode. This is the reason for more extensive research in this field on semiconductor electrode.

SnO_2 electrodes modified with the Rhodamine B system is probably the first example of surface modified photo-excited electron transfer [77, 78], although other solution phase photo-processes were reported earlier [20]. Hydroquinone oxidation for example was achieved on Rhodamine B modified electrodes [77, 78]. Although other semiconductor electrodes such as n-type TiO_2 are also investigated [79], SnO_2 still remains the electrode of choice due to its optical transmission properties and very good electronic conductivity. A wide variety of photo-excitable molecules such as Ruthenium bipyridyl [79, 80], Viologens [80], Phthalocyanines [81], erythrosine [82] and even high molecular weight hydrocarbons such as anthracenes [83] are being investigated for their electron transfer properties and as redox catalytic properties. Even polypyrrole films [84] have been investigated for their photocurrent generating properties.

15.5 ANALYTICAL APPLICATIONS AND SCOPE

The quantum efficiencies of a number of dye-sensitized electrode systems are still around 1 per cent. But this fact need not discourage the new entrants into this field. For example, in some recent studies on crystalline $MoSe_2$, WS_2, WSe_2 electrodes, an infra-red dye is found to transfer 0.8 to 1.0 electron for each photon absorbed by the mole-

cules [85, 86]. This is indeed a very good efficiency. This type of investigation gives hope that once well-defined interfaces are constructed and major causes of quenching eliminated, molecular photo-excitation can become a major source of photoelectrochemical energy conversion.

The analytical applications of molecular photo-excitation have already been discussed extensively. Evaluation of electrochemical properties of biological molecules on the one hand and the interfacial structural changes of the electrodes on the other would continue to benefit from the fast growth in different areas of spectro-electrochemistry.

Although the electrochemistry of molecular photo-excitation has grown substantially as seen in this chapter, photo-excitation of electrodes, especially semiconductors, has seen a much faster and more successful growth. These studies seem to offer much more tangible results in the area of photoelectrochemical energy conversion in the foreseeable future. These fascinating and promising aspects of semiconductor photo-excitations are considered in the next chapter.

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