

CHAPTER 14

Catalysis and Inhibition by Thin Layers

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14.1 INTRODUCTION

Many thin film electrodes have been in common use in electrochemical science and technology for many decades now. Battery electrodes based on oxides such as PbO_2 , MnO_2 and nickel oxides were used as anode materials in electrochemical synthesis as well as O_2 evolution electrodes in electrometallurgical operations. Pt black is another example of active thin deposited film electrode that is widely employed in standard electrode potential and conductivity measurements. However, thin film electrodes as a class owe their existence to the development and successful technological application of $\text{TiO}_2/\text{RuO}_2$ mixed oxide electrode in the chlor-alkali industry in the early seventies. Many of the rare earth metal oxides and other types of oxide electrodes received great attention as electrocatalysts for many technologically important reactions such as Cl_2 and O_2 evolution and O_2 reduction. Very rapid progress is noticed in the understanding and interpretations of electrocatalytic properties of these electrode materials.

The different types of chemically-, thermally- or electro-chemically prepared metal oxide electrodes mentioned above have at least one important common feature. These electrode films are good electronic conductors. In the middle and late seventies, the polymer films containing redox centres that can serve as electron carriers were developed and investigated for their electrochemical behaviour. In the early eighties, electronically conducting polymers were developed. The electrochemical behaviours of even passive oxide films are now investigated.

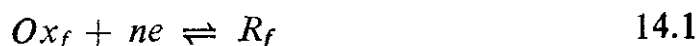
The electrochemical preparation and characterization of all these types of thin films have been extensively discussed in Chapters 8 and 10 respectively. This chapter mainly concentrates on the catalytic and inhibitive properties of these thin films, and it starts with the model of redox catalysis in thin films. As will be seen this apparently simple 'redox catalysis' takes a very complicated shape when treating it in a 'thin three dimensional film' (Section 14.2.1). This model is so much involved that at present no solution exists except for the steady state (Section 14.3.2). Important concepts are introduced such as electrochemically active surface area and acid-base catalysis. A brief discussion in the field of catalysis and inhibition by different types of thin films will also be presented (Section 14.4).

14.2 THE MODEL

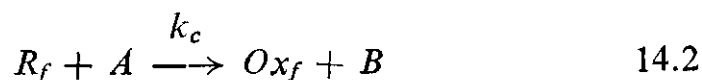
14.2.1 REDOX CATALYSIS IN THIN FILMS

The concept of the electrode surface acting as an oxidizing or reducing agent is in fact a very old concept in electrochemistry. In the early stages of development of electro-organic chemistry, for example, it was believed that all the electrodes generate nascent oxygen at the anode end and nascent hydrogen at the cathode end as the oxidizing and reducing agents respectively. These nascent reagents were believed to oxidize or reduce all the organic compounds in subsequent steps. Direct electron transfer between the reactants and electrode surface has been established in a number of cases. However, there is again an interest in the redox catalysis by surface-bound redox couples. Some new evidences collected in the past few years even suggest that many conventional metal oxide electrodes in fact function as redox electrodes. What a cyclic turn of events in the development of the concept of electrocatalysis and redox catalysis! (See Sections 14.4.2 and 14.4.3).

Now one may consider the model for redox catalysis on a thin film. The simplest model would be to consider a thin redox layer as a composite of a number of monolayers of surface-bound Ox species [1]. Also assume that these Ox species (Ox_f) would undergo reversible charge transfer at the surface.



The reduced R species in the film can catalyse the reduction of another substrate A into B .



Now the rate of irreversible chemical reaction would be given by

$$V_2 = k_c \cdot C_{Rf} \cdot C_A \quad 14.3$$

When the charge transfer is reversible, there are only two ways for increasing the redox catalytic rate. One is to increase the temperature which is a trivial one. One can increase the concentration of catalyst Ox or R in the film. Hence one would expect the redox catalysis to proceed efficiently as the thickness of the film increases.

The voltammetric response for such a single rate process (*rds* equation 14.2) can be easily simulated as discussed in Section 14.3.2.

The above model however is too simple to be real. In fact, a large number of rate processes are involved in this case. One can actually picture an electrode/redox film/electrolyte interface as represented in Fig. 14.1. The number of processes and rate parameters that describe these processes in this figure are also listed. Each of these component processes and their combined influence have been exhaustively treated in literature [2–6]. In the present context however only a brief and qualitative discussion is offered of this intricate phenomena.

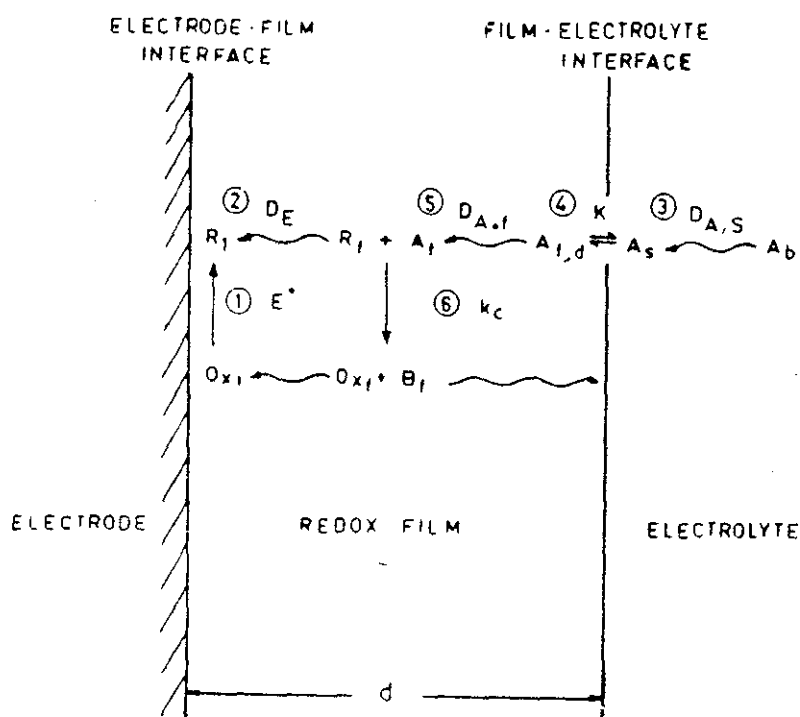


Fig. 14.1 Schematic representation of the phenomenological steps in the catalysis on redox modified electrodes (See text for symbols and details).

The electron transfer from the electrode surface (equation 14.1) is the starting point. One can assume that this is a perfectly reversible reaction since the selection of the redox couple is at one's control and a fast redox couple can always be selected to ensure better catalytic influence. However it must be remembered that the surface electron transfer can proceed only between the electrode surface and the first layer of fixed redox centres.

The electron transfer between successive layers should proceed only by an electron exchange between R species of first layer (R_1 for example) and Ox species of next layer (Ox_2 for example)



Chapter 10 has extensively treated this 'electron hopping' between redox layers. It is also indicated there that the overall electron transport process can be considered as a diffusional process with an electron diffusion coefficient D_E completely describing the transport rate. The redox site concentration effect on D_E and the overall redox catalysis itself have received considerable attention [7].

For a redox catalysis to occur, the R layers that slowly spread towards the solution side of the interface must meet the substrate A species on their path. The substrate molecules however must come from the bulk of the electrolyte solution. In the electrolyte solution, one can describe the transport of A by a diffusion coefficient $D_{A,s}$.

Once the substrate reaches the surface, it will be partitioned between the film and the solution side of the interface. This can be described by a partition function K .

The transport of A in the film should be much more difficult when compared with the diffusion in solution. If the electrocatalysis is to occur in the film, the substrate species should possess a reasonably large substrate diffusion coefficient in the film $D_{A,f}$.

All the above processes ensure the redox reaction (equation 14.2) to occur in the film. This reaction rate is controlled by the intensive variable k_e . Depending upon the relative values of D_E , $D_{A,f}$ and $D_{A,s}$ the redox catalytic reaction can occur either in the bulk or near the surface. However, it is generally assumed that k_C , the rate constant is independent of the plane at which the catalytic process takes place. There is however some minor variations in the mathematical approach to the problem (compare ref. 5 and 6 for example).

Now one can list the parameters that completely describe the redox catalysis in a thin film as follows:

$$E^0, n, D_E, D_{A,s}, D_{A,f}, K \text{ and } k_e$$

A long list indeed. It is quite obvious that as the number of components increases the mathematical analysis and even a qualitative physical representation of any multicomponent system becomes more and more difficult. This is why one tries to introduce as many

simplifying assumptions as possible in the model. A few assumptions have already been mentioned. One assumed reversible electron transfer at the interface. At the limiting or peak current region, the catalytic current will not depend on electron transfer kinetics. Electron transport is described as a simple diffusion process, overlooking all the inherent assumptions involved in it (see Chapter 10). It is assumed that k_c is independent of the plane of redox catalysis. Even with these assumptions the analysis will still be difficult [6]. Some more assumptions can be proposed. One can assume that mass transfer effects are absent in the electrolyte solution. This can be ensured to some extent by taking a high concentration of substrate in the electrolyte medium.

However, with these assumptions, one certainly has a manageable situation. The limiting catalytic current will now depend only on three rate processes, the electron transport (D_E), the substrate transport (D_A, f) and the redox catalytic reaction (k_c). Even under this condition, the complete mathematical solution and the methods for evaluating the rate parameters are available only for steady state technique such as *RDE* voltammetry and polarography (Section 14.3.2). The voltammetric methodology for transient techniques are yet to be developed. It was however decided to discuss the redox catalytic model and methods developed for the steady state techniques as they are available for a few reasons. Because of the more involved and slow nature of the process, *RDE* method is generally sufficient and is widely used for the study of this process and so a discussion becomes relevant. Many of the conclusions derived from these methodologies are qualitatively related to the LSV and CV results and hence qualitatively both the techniques can be employed for the study of redox catalysis using these methods. The most important reason for dealing with this overall process is to show the types of complexities encountered and the simplifying assumptions made to overcome these complexities in system analysis. In this sense among the faradaic processes involved in electrochemistry, redox catalysis in films is probably the most complicated one at the phenomenological level. One faces many problems here. But one does move ahead by constructing the most trivial models and improving upon them by successive improvements.

Interestingly enough, the redox catalysis in thin films itself may turn out to be just one of academic interest (Section 14.4.1). The

oxide based surface catalytic systems may still be technologically more important for a few decades to come. But still, the model building at this level can improve one's physical understanding of many electrochemical processes and increase one's capability to deal with them mathematically.

14.2.2 ACTIVE SURFACE AREA

In the discussions on redox catalysis on thin films, one has assumed that the thin film itself consists of finite monolayers of uniform composition. The overall film geometry is hence considered to be uniform. This is certainly an ideal situation. The film can contain a lot of nonuniform features including rough surface structures which will be listed separately (Section 14.2.4). However, the surface of the film is not intentionally made rough in this type of film formation process. Since the redox catalysis reaction itself takes place in the whole film region, rough surface formation is not required in this type of thin films.

However, in the development of many other oxide catalysts for effecting technology-oriented problems, one usually employs electrodes that possess fairly good electronic conductivity. In these cases the electron transport in the film is essentially much faster than the electron-hopping mechanism considered above. So the electron transfer reactions essentially take place at the surface of the electrode. Since these electrodes are required to catalyse fairly slow electron transfer reactions involving adsorption of intermediate species, the surface area becomes an important parameter for achieving very high charge transfer rate. As discussed later (Section 14.4.2), thin film oxide electrodes can now be prepared, which have good mechanical stability and an actual surface area which is around 100 times the geometric surface area. In the development of new thin film electrodes and evaluating their long-term use, it is necessary to develop effective methods for assessing the real or electrochemically active surface area of such electrodes. As discussed shortly (Section 14.3.1) cyclic voltammetric method of measuring the total charge of an electrode surface process is used as an effective method for evaluating this surface area.

One should not conclude that electrocatalysis is achieved only by increasing the real surface area of three-dimensional oxide electrodes.

The emphasis here is that the real area effect can be a cause for current enhancement. This factor should be taken into consideration before assessing the intrinsic catalytic property of an electrode. For example, if one can have an assessment of the catalytic current values (for Cl_2 evolution under identical conditions for example) of an electrode material whose active surface area can be systematically varied and independently measured, one can plot the catalytic current versus active surface area. If this plot shows a perfectly linear relation, the apparent catalytic efficiency is due to surface area effect. If the catalytic efficiency shows positive deviations from unit slope of this graph, one can conclude that additional catalytic effects are involved. References to some systematic investigations are made later (Section 14.4.2).

Surface area effects and additional electrocatalytic effects must also operate in the active electrode materials used as cathodes. Pt deposited films, electrodes made of Raney Ni for electrohydrogenation and noble metal deposited graphite electrodes are examples of this type. However, systematic investigations of these electrodes are not very extensive.

14.2.3 CATALYSIS BY CONDUCTING METAL OXIDES

Most of the thin film electrodes, other than chemically modified electrodes, employed as electrocatalysts today are rare earth and transition metal oxide electrodes. Any metal oxide that is stable in the electrolyte medium of interest and can show good electronic conductivity, can be evaluated for its electrocatalytic properties. This actually gives a vast scope for applied research on evaluating different systems for their electrocatalytic applications. And this has led to the development of this field as an empirical science. Efforts to understand the cause of the electrocatalytic or inhibitive behaviour of different oxide electrodes to different electrochemical reaction of interest are too little when compared with the technological evaluations as seen later (Section (14.4)).

Now what can be the physicochemical basis for electrocatalysis on metal oxide electrodes. There were some initial efforts to find correlations on the basis of intermediate adsorption (Section 14.4.2) as was done for hydrogen evolution on metal electrodes (Chapter 12). The adsorption site on an oxide surface is not at all well-defined as

the adsorption site of a metal electrode [8]. The electrocatalytic behaviour of any 'oxide' cannot be directly related to the property of the 'metal' surface such as the free energy of adsorption on a metal.

Two basic properties of the oxides seem to be quite important in understanding their electrocatalytic behaviour; their acid-base and redox characteristics. Consider any metal oxide $M-OH$ for which the two following reactions can be assumed to take place.



Reaction 14.5 is an acid-base equilibrium and reaction 14.6 is a redox equilibrium. Practically all the metal oxide electrodes that show some electrocatalytic property worth the name, can exist in multivalent state and can show pH dependent acid-base properties. These two pH dependent and electrode potential dependent equilibria should certainly exert profound influence on the electrocatalytic behaviour of the metallic oxides.

The influence of redox behaviour of the metallic oxides on their electrocatalytic properties is already being recognized in the literature. Some new thrust is noted in this direction over the past few years as discussed later (Sections 14.4.2 and 14.4.3). The influence of the acid-base property of the oxides is revealing itself in some studies. However, there is some obvious inconsistency between the acid-base property on electrocatalysis. For example, Cl^- , a base is the reacting species in the Cl_2 evolution reaction. One would expect an acidic oxide surface to catalyze this reaction so that the electrocatalysis would be predominant at low pH. However, the practical observation is found to be exactly the opposite. The Cl_2 evolution reaction on TiO_2/RuO_2 electrodes show a reaction order of -1 with respect to H^+ ion concentration (Section 14.4.2). However, this obvious inconsistency would be removed if one assumes that the *electrocatalytic behaviour of metal oxides depend on the acidity or nucleophilicity of the central metal ion* rather than the acidity of the oxide phase as such. As shown later (Section 14.4.2) this view consistently explains the overall electrocatalytic behaviour of metal oxides in general.

It is once again emphasised that the acid-base catalysis proposed here is only a hypothetical statement. This is directly related to the

same type of concept introduced in the last chapter. More detailed analysis of this view is necessary.

14.2.4 FILM STRUCTURE AND FILM DEFECTS

The development as well as scientific understanding of electrocatalysis depends very much on proper characterization of thin film structure and the defects present on the film. The voltammetric characterization of different types of films has been considered in Chapter 10, and so also the various types of porous and compact, homogeneous and heterogeneous, conducting and insulating, organic and inorganic films and their characterization. However even a systematic classification of the thin film formation and growth processes in electrochemistry are yet to be achieved [9]. A few thin film features that specifically influence the electron transfer on the film surface are listed out in qualitative terms here which should give some guidelines regarding the strategies to be adopted in the development of new catalytic film electrodes.

The surface roughness in detail has been discussed in Section 14.2.2. In redox catalytic electrodes, there is an attempt to construct surfaces with low roughness factor. In oxide catalytic electrodes, the roughness factors are intentionally kept high.

The bulk phase in the thin film itself needs not always be uniform. In the mixed oxide electrodes, there can be regions where single oxide phases can predominate. In the redox polymer electrodes there can be regions where the hydrophobic polymer film or redox centres predominantly exist. This is especially true when perfluoro sulphonic acid (Nafion *R*) based membranes are present. These membranes contain hydrophilic ionic regions embedded in a highly hydrophobic polymeric network. This type of network is in fact responsible for some interesting electrocatalytic properties.

The solvent dependent properties of the thin films can also be very different. Inorganic thin films can show solubility and film dissolution depending on the polarity and pH of medium. The polymer films can show different levels of swelling properties in different solvents. Films that exhibit very high swelling behaviour cannot exhibit long-term stability. In fact this is one of the important causes for the instability of most of the redox polymer films.

Under the experimental conditions employed in the preparations of the thin films, one cannot ensure total compactness of the films. This is not desirable either, since one needs pores and channels through which substrate, solvent, protons and anions should move in the film. Inorganic films can usually contain three-dimensional cracks. All the films also contain pores of different sizes and structures. These voids in the films should however be carefully controlled since they can modify the catalytic properties substantially.

Another possibility is the existence of multilayers in the thin film structure itself. The intentional construction of redox bilayers is mentioned in Chapter 10. These layers are not meant for electrocatalysis and hence need not be treated here. In the case of inorganic films the region that exists near the solution side would usually be more hydrated when compared with the anhydrous film region near the electrode surface. Rare earth metal oxide electrodes are usually coated on Ti base electrode. TiO_2 as such is a highly insulating barrier film. Growth of this type of film is an important technical problem in oxide coated electrodes. Methods to overcome this problem are available.

It is beyond the scope of the present work to deal with all these film-structure related problems in detail. But one should certainly keep in mind these problems when dealing with thin film electrodes. Quantitative characterization of all these features of each electrode is still a dream to be fulfilled by future effort. But qualitative characterization and control of most of these problems are now quite possible.

14.3 THE METHOD

14.3.1 VOLTAMMETRY FOR THE MEASUREMENT OF ACTIVE SURFACE AREA

Although many methods such as gas phase N_2 adsorption and zinc ion adsorption from solution are available for surface area measurements, the electrochemical method is more relevant, straightforward and easy for obtaining the electrochemically active surface area of the electrodes. The basic assumption of the method is that the active sites for the electrochemical process can undergo a redox change [10, 11]. Since all the oxides that are employed as electrocatalysts can exhibit multiple oxidation states, this assumption is essentially valid.

The method of obtaining the voltammogram is essentially similar to method described for surface redox processes. Some oxides such as $\text{Ni(OH)}_2/\text{NiOOH}$ would show sharp voltammetric oxidation and reduction peaks which can be integrated to obtain the electrochemically active surface charge. Other oxides such as $\text{Ru}_2\text{O}_3/\text{RuO}_2$, $\text{IrOOH}/\text{IrO}_2$ couples and oxidized carbon surfaces would contain redox couples with different closely spaced redox potentials. The voltammograms of such systems would be rather broad and would not show sharp voltammetric peaks [12, 13]. However one can still record the voltammograms in between H_2 evolution and O_2 evolution region for these electrodes. The integration of these voltammograms would again correspond to an electrochemically active surface area. Some typical voltammograms and the analytical approaches are discussed in detail in Chapter 10.

Now, the electrochemical charge measured in this way gives a direct measure of real surface area. One can evaluate electrodes prepared under different conditions for real surface area and electrochemical activity. Some typical case studies of the electrocatalytic activity by this method are discussed later (Section 14.4.2).

14.3.2 VOLTAMMETRY FOR REDOX CATALYSIS ON UNIFORM FILMS

As mentioned earlier (Section 14.2.1) the first model considered for voltammetric investigations of redox catalysis on thin film assumed that all the processes other than the redox catalytic reaction (equation 14.2) are very fast. The voltammetric analysis of this multilayer model is extremely simple since it contains only one rate process. The voltammetric simulation results [1] discussed in Section 13.3 for monolayer redox catalysis is directly applicable to the present multilayer model as well. The dimensionless parameter λ_s in Fig. 13.1 contains a parameter l which is the number of monolayers. If $l = 1$, the model corresponds to the monolayer system discussed in Section 13.3. If l is greater than 1, it corresponds to the multilayer redox catalysis model. Large values of l play the same role as large values of k_c would play in the extent of redox catalysis. This model simply predicts that as the number of redox layers increases, the catalytic efficiency of the electrode would also increase.

The above predictions are too simple to be true. The electron transport and the substrate transport processes are too slow processes to be neglected in any redox catalytic model

on thin films. The model may however be applicable for extremely thin films containing very few monolayers of redox centres. No specific range of applicability of this model has been suggested by experimental verification.

The redox catalysis in thin films is mainly controlled by three rate processes. The electron diffusion (D_E), the substrate diffusion ($D_{A,f}$) and chemical reaction (k_c) as discussed in Section 14.2.1. The voltammetric responses for this model under steady state conditions have been solved in great detail [2-6]. In the present work, a recent discussion [5] which clearly relates to these three rate parameters into dimensionless quantities, is presented.

The limiting current density for electron transport (i_E), substrate transport (i_S) and chemical reaction (i_k) controlled processes are given by equations 14.7 to 14.9 under steady state polarization conditions.

$$i_E = \frac{F \cdot \tau_{Ox}^0 \cdot D_B}{d^2} \quad 14.7$$

$$i_S = \frac{FC_A^0 K D_{A,f}}{d} \quad 14.8$$

$$i_k = FC_A^0 \mu_{Ox}^0 \cdot K \cdot k_c \quad 14.9$$

In these equations τ_{Ox}^0 is the total film concentration of redox species, C_A^0 is the bulk concentration of the substrate in solution and d is the thickness of the film. All the other parameters have been defined earlier (Fig. 14.1 and Section 14.2.1).

Two dimensionless parameters i_E/i_k and i_S/i_k are defined from these expressions. The overall electrochemical behaviour can be described using these two dimensionless parameters, as represented in Fig. 14.2. The figure shows the regions where the overall process is controlled by electron transport (E), substrate transport (S), and chemical reaction kinetics (R). The regions where combined effects (SR , ER etc) of two processes are to be expected are also indicated.

The actual experimental approach for decoupling these effects and evaluating the rate parameters in RDE voltammetry are discussed in detail [2-6] and some experimental case studies are also cited [6]. However, these methods have not received wider application. The simple single rate control model [1] discussed earlier is more widely employed in practice. Although this method lacks descriptive accuracy, it still gives a practical assessment of overall catalytic efficiency of each electrode, which is after all what is essentially required in practice.

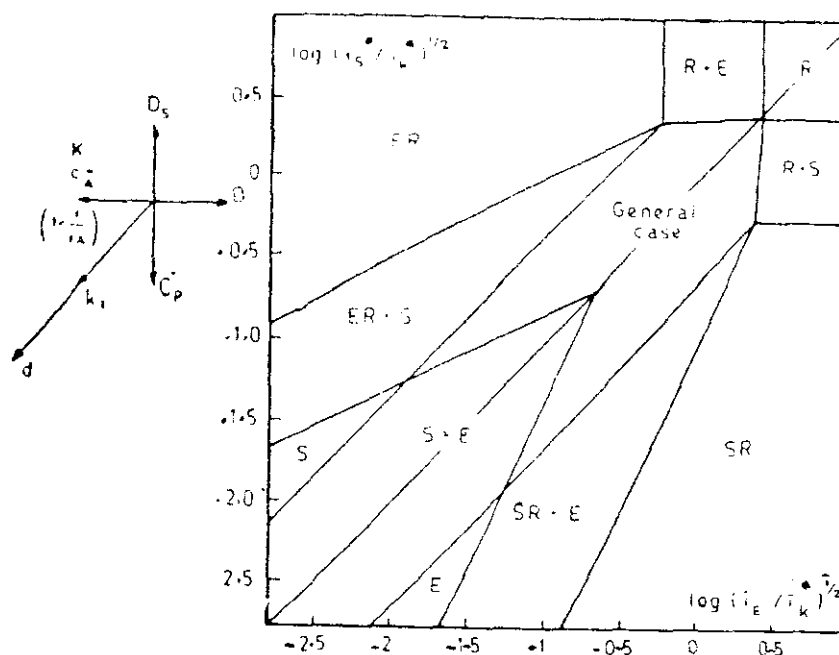


Fig. 14.2 Kinetic zone diagram. The boundary lines are based on a 5 per cent accuracy of measurement of the catalytic plateau current in *RDE* voltammetry.
[From CP Andreux, JM Dumas-Bouchat and JM Saveant, *J Electroanal Chem* 169 (1984) 9]

14.4 THE PROCESS

14.4.1 REDOX CATALYSIS BY CHEMICAL MODIFICATION

One of the primary objectives of developing chemically modified electrodes was to employ them in redox catalysis. Very early investigations in this area reported the redox catalysis of both simple electron transfer reactions and inner sphere reactions [14-16]. Comprehensive reviews on the earlier works on redox catalysis by polymer modified electrodes are already available [6, 17, 18]. Hence only a brief outline with some recently reported examples are presented here.

Many investigations essentially concentrate on the redox catalysis of outer sphere electron transfer reactions by organic [19, 20] and inorganic [21] redox catalysts. Since the E° values of the redox couple and the substrate couple are well-defined and well-known, it is quite easy to follow the catalytic pathway. Figure 14.3 for example illustrates the redox catalytic property of a polymer film containing two different surface-bound redox couple, namely a dialkyl bipyridium ($\text{BPy}^{2+}/\text{BPy}^+$) and ferricyanide/ferrocyanide (FRO/FRI) redox couple. The cyclic

voltammogram at the more negative potential region corresponds to $\text{BPy}^{2+}/\text{BPy}^+$ redox couple [22]. The $\text{Ru}(\text{NH}_3)_6^{3+}$ species is electrocatalytically reduced only at the potential region corresponding to $\text{BPy}^{2+}/\text{BPy}^+$ redox couple (Fig. 14.3.a). On the other hand, addition

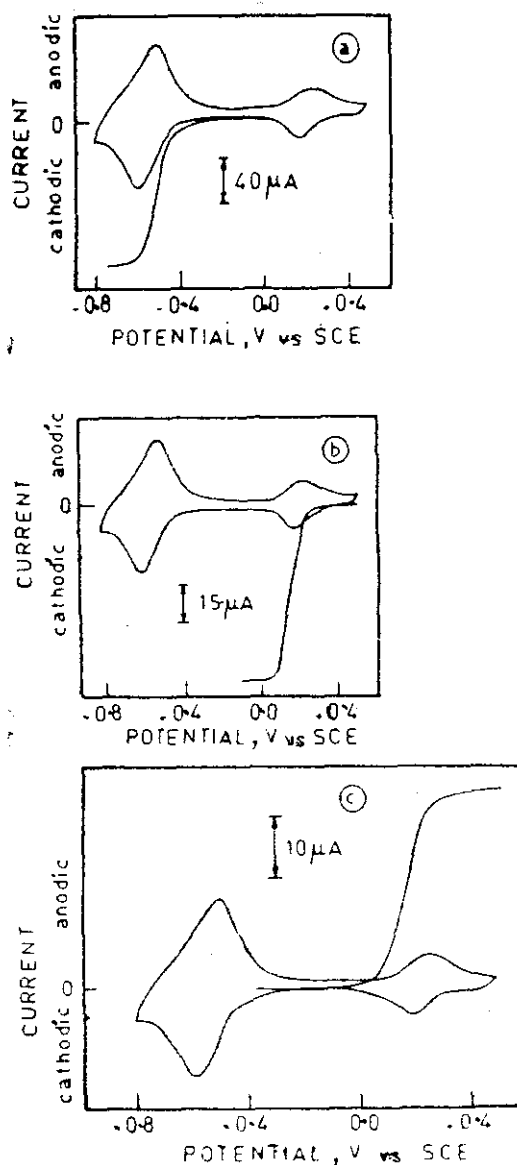


Fig. 14.3 Cyclic voltammogram of Pt/dialkyl bipyridinium^{2+/1+} polymer electrode with electrostatically bound $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl in the absence and in the presence of (a) 4.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$, sweep rate 20 mVs^{-1} (b) 4.0 mM $\text{Fe}(\text{CN})_6^{3-}$, sweep rate 100 mVs^{-1} , and (c) 4.0 mM $\text{Fe}(\text{CN})_6^{3-}$, sweep rate 100 mVs^{-1} [From NS Lewis and MS Wrighton, *J Phys Chem* 88 (1984) 2009]

of ferricyanide (Fig. 14.3.b) and ferrocyanide (Fig. 14.3.c) alone shows enhanced cathodic and anodic currents in the potential region of FRO/FRI couple. The latter results again confirm the established fact (Chapter 10) that the attached redox couples have properties very similar to the solvent soluble redox couple.

O₂ reduction reaction is once again one of the extensively investigated reactions on redox modified polymer film electrode. Various redox catalyst-incorporated polymer films such as anthraquinone [23], prussian blue [24], phthalocyanin [25], tetraphenyl porphyrin [26] and other inorganic complex [27] films were extensively investigated for their electrocatalytic properties. Cyclic voltammetric methods for film characterization and *RDE* voltammetric methods for evaluating overall redox catalysis are invariably employed. However, almost all these redox catalysts reduce O₂ to the H₂O₂ stage only. Complete reduction to H₂O by redox polymer films is yet to be achieved. Many of the polymer cross-linkings are susceptible to high swelling rates in aqueous electrolytes which subsequently lead to film rupture. Perfluoro ion exchange membranes as a class are comparatively more stable in aqueous conditions. The sulphonic acid anions can easily retain cationic redox couples. Such redox couples attached membranes have been extensively investigated for their electrocatalytic activities in both outer sphere electron transfer [28] and O₂ reduction reactions [29-31]. One of the important causes of limited success of this electrode is the inherent heterogeneity of the film. The membrane film essentially contains hydrophilic island regions containing high concentrations of redox couples separated by hydrophobic perfluorocarbon networks. The electron transport between such redox catalyst-containing islands is a very slow process. Some other redox carriers consisting of smaller size redox couples are employed for charge transport between the islands [31]. It is indeed possible to quantitatively evaluate the intricate processes of this type involving two redox couples and a substrate to be catalytically reduced.

Redox polymer modified electrodes cannot catalyze H₂ evolution. But one can deposit Pt group metals on redox polymer films and achieve such electrocatalysis [32]. One may question the need for coating the electrode with a polymer film and then activating it by depositing another metal on it. But such studies [32, 33] should be considered as model systems for the modification of semiconductor electrodes (Chapter 16) where the polymer film is coated to prevent

the photo-dissolution of the surface and further metal deposit is used to achieve electrocatalysis.

14.4.2 ACID-BASE CATALYSIS BY CONDUCTING METAL OXIDES

Table 14.1 presents a typical list of metal oxide-coated electrodes used in the electrocatalytic reactions [34]. These electrodes are generally good electronic conductors and hence the charge transfer

Table 14.1

Classification of redox electrodes in terms of
solubility of redox states in 1M H_2SO_4

Category	Red	Ox
Both states insoluble	Pt	$\text{PtO}, \text{Pt}_2\text{O}_3$
	Ru_2O_3	RuO_2
	MnOOH	MnO_2
	Cr_2O_3	CrO_2
	V_2O_3	VO_2
	PbSO_4	PbO_2
Only Ox state insoluble	FeO	$\text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3$
	NiO	Ni_2O_3
	CrO	Cr_2O_3
	VO	V_2O_3
	PbO	PbO_2 (in HClO_4)
Only Red state insoluble	RuO_2	$\text{RuO}_3, \text{RuO}_4$
	Ir_2O_3	IrO_2
	Cr_2O_3	CrO_3
	MoO_2	MoO_3
	VO_2	V_2O_5

From ref [34]

reactions occur mainly at the oxide-electrolyte interface (Section 14.2.2). However as the Table reveals almost all the metal oxides used can exist in different redox states and the oxides can be classified into three major groups depending on the solubility of the oxides.

In a general sense, the oxides whose oxidized as well as the reduced states are quite stable may serve as an acid-base type of catalyst depending on the acid-base character of the central metal ion. This class of electrodes is more commonly employed in the electrocatalysis of small inorganic molecular processes such as Cl_2 or O_2 evolution and O_2 reduction. The oxides that show unstable or reactive oxidized states serve as redox catalysts for oxidation and those with reactive reduced states as redox catalysts for reduction reactions. There can be a lot of overlap in this classification. NiO/NiOOH system for example is investigated for O_2 evolution as well as redox catalytic oxidations. However, for the sake of convenience, this type of overview is taken as a basis for classification of oxide-based electrocatalysis in this and subsequent sections.

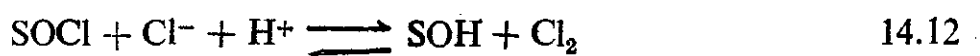
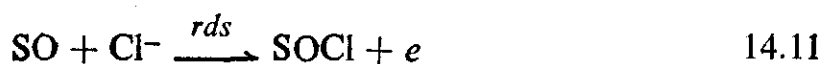
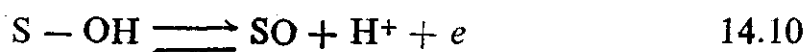
O_2 evolution and Cl_2 evolution are the two most predominant electrochemical reactions investigated on oxide electrodes. Both O_2 evolution [35, 36] and Cl_2 evolution [37, 38] have been thoroughly reviewed several times with special reference to oxide electrodes. The kinetic and mechanistic aspects of Cl_2 and O_2 reactions have a lot of similarity among them. This concept is clearly brought out again in two excellent reviews [8, 39]. Hence in the present section an overview is presented with the main emphasis on the understanding of the catalytic activity of the oxides.

Following the success of an intermediate adsorption model in correlating the electrocatalytic behaviour of different metals in hydrogen evolution reactions, similar efforts were made to understand O_2 evolution electrocatalysis on the basis of oxygen adsorption free energy on the metal surfaces [40]. The early linear correlations of these types were later questioned [8]. A catalytic reaction is not being dealt with on a metal surface but rather on an oxide surface. And hence the metal-oxygen bond formation cannot give a direct idea of the electrocatalytic behaviour of the oxide surface. Some careful analysis of Cl_2 evolution on Pt surface in CF_3COOH medium clearly establishes the catalytic behaviour of Pt metal and its oxides. Cl_2 evolution reaction rate in anhydrous CF_3COOH is rather slow. But the rate increases substantially in the presence of traces of water when an

oxide layer is formed on Pt. The intermediate Cl radical is too strongly held on Pt when compared with PtOH and hence the faster rate on oxide films [41, 42]. Hence any electrocatalytic correlations should be traced from the properties of metal oxides rather than from metals themselves.

As indicated earlier (Section 14.2.2), one must first evaluate the true surface area of the oxide electrodes before attempting to correlate their electrocatalytic behaviour [12, 13]. Since practically all the oxides exhibit multiple redox states, the oxide formation charge q gives a direct measure of the active surface area. Figure 14.4, for example presents the surface charge versus O_2 evolution rate on Co_3O_4 (Fig. 14.4.a) and IrO_2 (Fig. 14.4.b) electrodes prepared at different heat treatment temperatures leading to different active surface areas. Co_3O_4 electrode shows catalytic activity directly in proportion to the active surface area increase. IrO_2 electrodes show some additional catalytic transformations at high temperatures [39, 43]. This type of study enables one to choose appropriate conditions for comparing different electrode materials.

Extensive experimental work on the electrocatalytic Cl_2 evolution [12, 44] and O_2 evolution reactions on different oxide materials such as $NiCo_2O_4$ [45, 46], RuO_2/TiO_2 [13, 47], and RuO_2/IrO_2 [48] have been reported recently. A historic view of the studies relating to reaction kinetics may be obtained from the recent reviews [35, 39]. A real breakthrough in the mechanism determination however came from some recent investigation. The similarity in the kinetic parameters between O_2 and Cl_2 evolution reactions led to the suggestion [35] that oxide surface oxidation is involved in both the rate processes. The pH-dependence of the rate of Cl_2 evolution [12, 49, 50] and the pH dependent properties of oxide electrodes on O_2 evolution reactions [13, 49–53] further substantiate this viewpoint. The presently accepted mechanism for Cl_2 evolution on oxide electrodes may be represented as



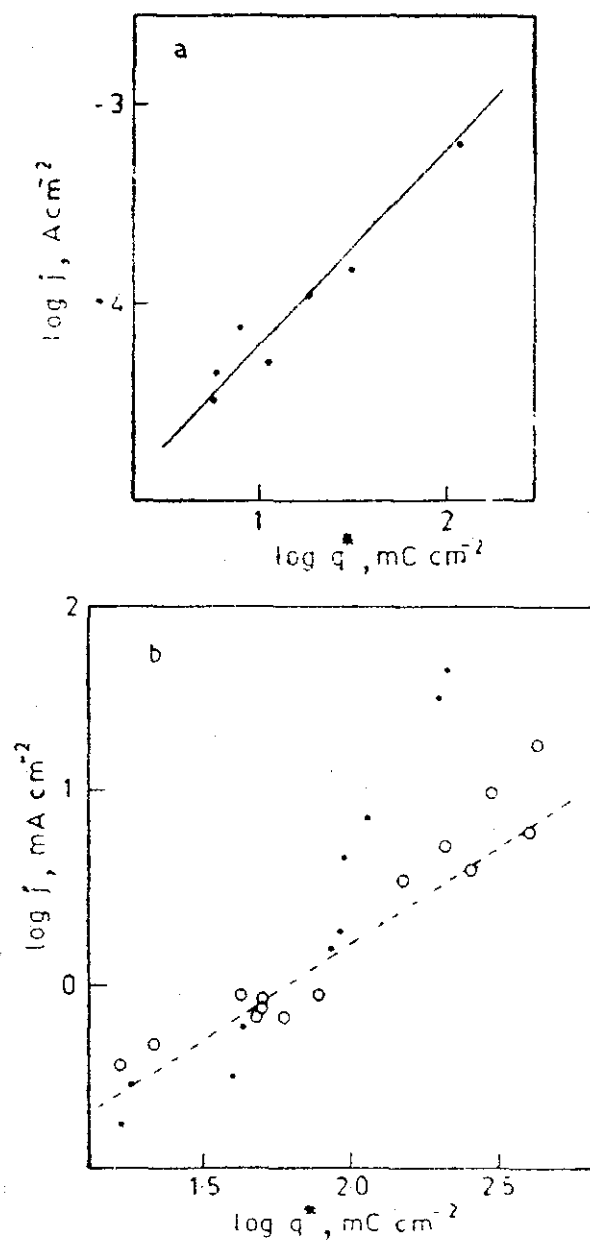
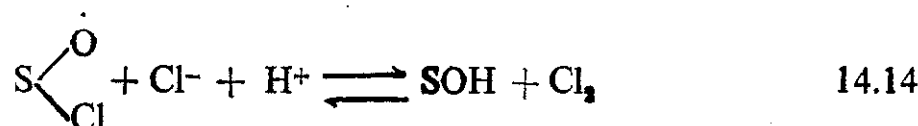
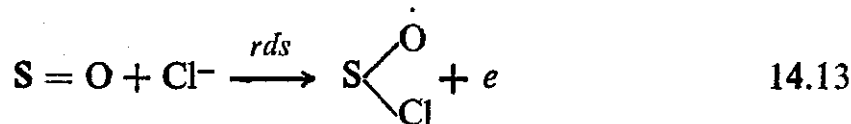


Fig. 14.4 Electrocatalytic activity of (a) Co_3O_4 electrode and (b) Ti/IrO_2 electrode in O_2 evolution from alkaline solution as a function of surface charge q^* corresponding to electrochemical active surface area.

[From S Trasatti, *Electrochim Acta* 29 (1984) 1503]

The pre-equilibrium 14.10 is essentially an electrochemical surface oxidation process. For a base like Cl^- , one would expect that a protonated or reduced SOH species would serve as a better interacting system and hence a better electrocatalyst. However, if one assumes

the interaction of Cl^- with the central metal atom, an oxidized metal ion should be a better catalyst. One can in fact write equations 14.11 and 14.12 as follows:



The last step may consist of many simpler steps. However, since this step follows *rds*, these simpler steps cannot be evaluated in detail, even if they do exist.

Similar mechanism for O_2 evolution can be written as well. The close similarity between the mechanism of O_2 and Cl_2 evolution is supported by the parallel relation between the electrocatalysis of different oxides for these two reactions [8, 39]. Figure 14.5 shows such a correlation. There are certainly many more questions to be answered regarding these important reactions. However, the studies

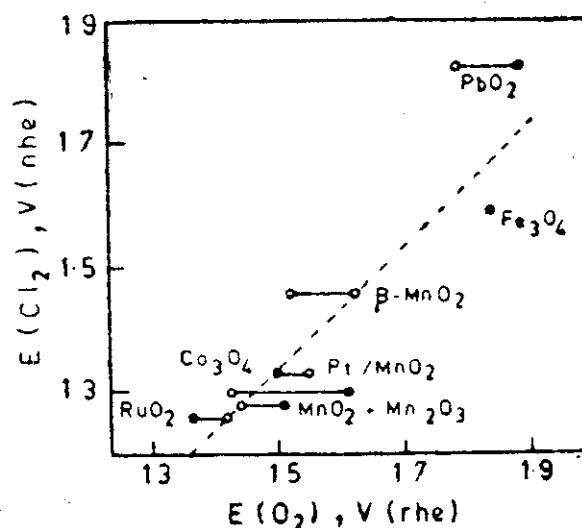


Fig. 14.5 Plot of the potential for Cl_2 against potential for O_2 evolution at the same current density for a number of oxides in (o) alkaline and (.) acidic solutions.

[From S Trasatti, *Electrochim Acta* 29 (1984) 1503]

made so far lead to the belief that theory of electrocatalysis on metal oxides would reach a stage soon when it can '*predict*' rather than '*explain*' the catalytic behaviour.

Oxide electrodes are also employed as O_2 reduction catalysts. But the theory of these catalytic systems are yet to pick up. One can observe the O_2 reduction catalysis on a lanthanum barium manganate electrode in Fig. 14.6 [54]. But the reduction potentials achieved are still far from satisfactory. Overvoltages in the order of 500 mV are still needed for this reduction. These systems are yet to advance in both theoretical understanding and technological application. But it is worthwhile looking at the acid-base properties of these oxides to find answers to the catalytic behaviour of these oxide electrodes as well.

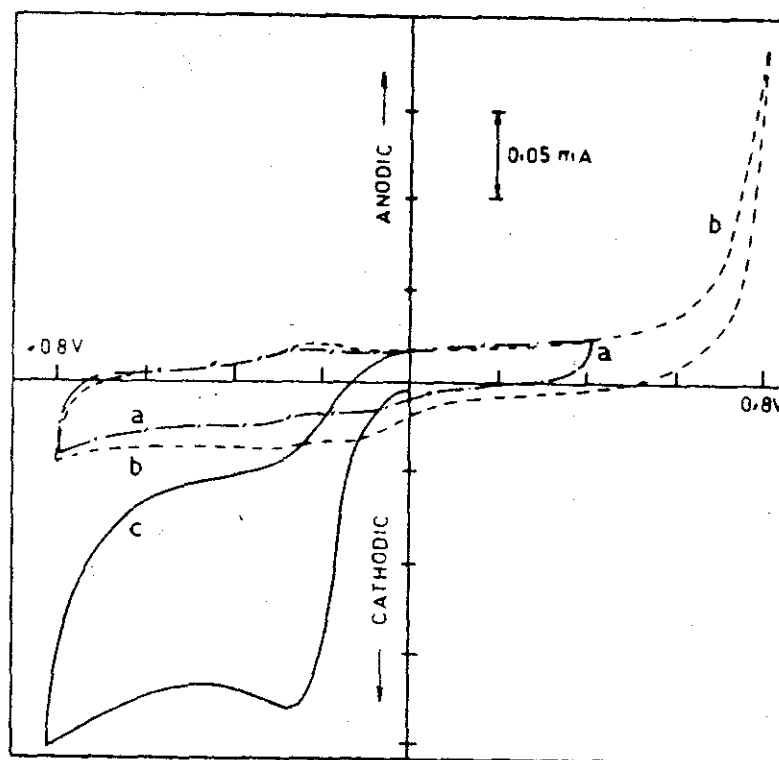


Fig. 14.6 Cyclic voltammograms of $La_{0.5}Ba_{0.5}MnO_3$ in the absence of (a, b) and in presence of saturated O_2 in 1.0 M KOH solution. Sweep rate 10 mV s^{-1}

[I Arul Raj, K Venkateswara Rao and VK Venkatesan, Proc Symp Interactions at Electrode-Electrolyte Interfaces, IIT Madras, India (1982) paper. K.1]

14.4.3 REDOX CATALYSIS BY CONDUCTING METAL OXIDES

The idea that all the electrodes function by generating oxidizing and reducing agents was proposed in the nineteenth century [55]. It is now very clear that in many cases this cannot be true. However, at least in the case of oxide electrodes which can serve as a very good reactive chemical oxidizing agent, this classical concept should hold good. In the case of Ni, Ag and Cu oxides there is strong evidence for the operation of such a reaction mechanism [56, 57]. NiO on anodic polarization, for example, can form a very reactive NiOOH film [56–59]. This higher oxide is a very reactive oxidizing agent towards aliphatic and aromatic alcohols and amines. Extensive voltammetric as well as preparative work has substantiated the redox catalytic function of these metal oxides generated electrochemically on the metal surface during the oxidation of organic compounds.

PbO₂ film electrode is a good example of a thin film electrode that is in use in the electrochemical industry for a very long time. It is well-known that PbO₂ is a good oxidizing agent. It can, for example, oxidize benzene to quinone in strong H₂SO₄, converting itself to PbSO₄ in the process [60]. Electrochemical regeneration of PbO₂ from PbSO₄ is another well-known process. Some recent voltammetric investigations on this electrode [61] also support the operation of redox catalytic mechanism on this electrode.

Recently a wide variety of redox catalytic metal oxides were coated and evaluated for their redox catalytic properties on Ti substrate electrodes [34, 62–64]. These electrodes include Cr₂O₃ [34, 62] and PbO₂ [63, 64] coatings for electrocatalytic oxidations and V₂O₃ and TiO₂ [63, 64] coatings for electrocatalytic reductions. These electrodes are prepared by thermal decomposition method which is very similar to the popular Ti/RuO₂ oxide electrode fabrication [43]. The redox catalytic behaviour of the electrodes are also found to be fairly good. Figure 14.7 for example presents the cyclic voltammograms showing the redox catalytic oxidation of different aliphatic alcohols on Ti/Cr₂O₃ electrode. The Cr³⁺ oxide is probably oxidized to Cr⁶⁺ type which serves as the oxidizing agent.

One should remember that the electrocatalytic reaction on electronically conducting metal oxides always proceed at the oxide-electrolyte interface. Being a surface redox catalytic reaction, the surface area of the electrode is an important factor in the overall elec-

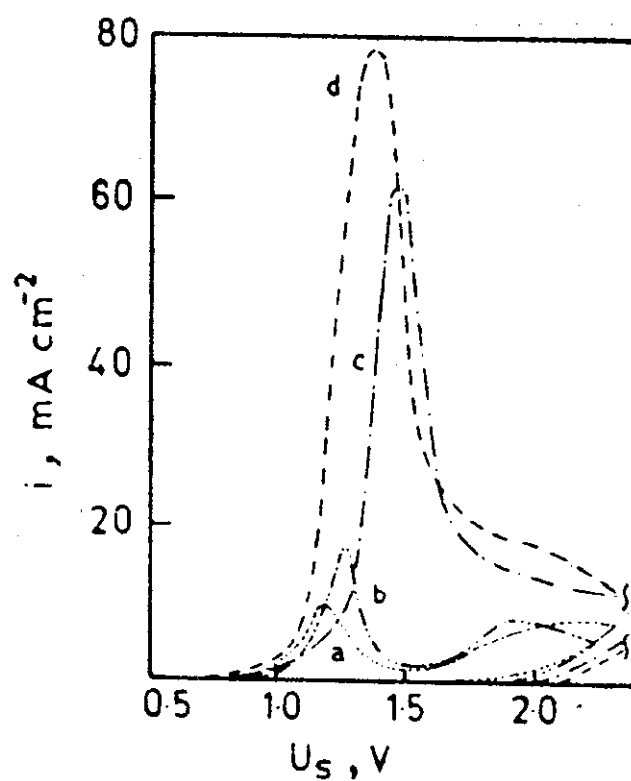


Fig. 14.7 Voltammograms for standard $\text{Ti/Cr}_2\text{O}_3$ electrode in presence of 1.0 M oxidizable substances in 1 M sulphuric acid. Sweep rate 5 mV s^{-1} (a) base curve, (b) methoxy propionitrile, (c) tetrahydro furane, and (d) isopropanol.

[From F Beck and H Schulz, *Electrochim Acta* 29 (1984) 1569]

trocatalytic response. Hence the thin film oxide electrodes mentioned above [34, 60-64] should offer better overall electron transfer rate when compared with *in situ* oxidized plain metal electrodes [56-59]. But even for the thin film oxides the redox catalysis is still a surface process and the concentration of the redox catalyst would be too low to show overall catalytic efficiency [1]. Hence these types of heterogeneous redox catalytic electrodes can operate only at rather low current densities.

One of the important differences between the acid-base and redox catalysis by metal oxide electrodes (Sections 14.4.2 and 14.4.3) is the overall electrocatalysis rate. Cl_2 and O_2 evolution on catalytic metal oxides are exceptionally fast reactions when compared with the reactions considered in this section. This is in fact the main reason for considering the two classes separately here assuming distinct pathways for each class, in spite of the fact that both the reaction mechanisms

involve higher oxidation states of metals. There is need for evaluating these concepts in great detail.

14.4.4 CHEMICAL REACTIONS ASSOCIATED WITH CHARGE TRANSFER ON CONDUCTING OXIDE ELECTRODES

The surface of an electrode should also exert substantial influence on the chemical reactions associated with charge transfer reaction such as dimerization, further oxidation or nucleophilic or electrophilic substitution. These subsequent reactions substantially influence the product selectively and product distribution in electro-organic synthesis. The anodic oxidation of fatty acid anions (carboxylates) is a classical example. On Pt electrode, the decarboxylated alkyl radicals dimerize whereas on carbon electrodes the alkyl radical undergoes further oxidation to carbonium ion and hence monomeric products result. The exact cause for this classical selective process is still an open question. It is suggested that strong chemisorbed layer on Pt inhibits further oxidation of alkyl radicals thus favouring dimerization at the outer Helmholtz plane on this electrode [65].

If this explanation is correct, one would also expect higher dimerization rate for other organic molecules that can exhibit chemisorption on Pt when compared with carbon. But exactly an opposite trend is noticed in the electrochemical oxidation of azide [66, 67] and styrene [68]. For these reactants dimerization is predominant on carbon when compared with Pt. Carbon electrodes containing oxide layers also favour dimerization of carbonyl compound when compared with Hg electrodes [69]. In the opinion of the present authors a simple chemisorption concept [65] cannot explain such a product distribution.

In these cases one should note that the —COO^- oxidation takes place at much more positive potentials when compared with the other processes [66-68]. The difference in the behaviour of Pt and carbon should probably be traced in the difference in the acid-base properties of these two electrodes in these potential regions. More experimental data on the influence of oxide electrodes on chemical reactions are required for further analysis of mechanistic pathways involved.

14.4.5 ELECTROCATALYSIS BY CONDUCTING POLYMERS

Conducting polymers (Chapter 10) offer one of the attractive applications in the field of constructing extremely light weight batteries. However they are sufficiently electronically conducting and so it should naturally be possible to carry out solution-phase oxidations and reductions at the conducting polymer-electrolyte interface. In recent years, quite a large number of reports on the electrocatalytic behaviour of these films are being noticed. Electrocatalytic oxidation of hydroquinone on polypyrrole, poly *n*-methyl pyrrole [70] and poly pyrrole benzene sulphonate [71] films, oxidation of ascorbic acid on polypyrrole [72] and other polymer gels [73], oxidation of carboxylate on polypyrrole [74] and electrocatalytic oxidations on polycarbazole electrodes [75] are typical examples. Some typical cathodic reductions such as O₂ reduction [76] and nitrobenzene reduction [77] have also received some attention.

The nature of the electrocatalytic influence, however, is not clearly known. Interestingly all the conducting polymers essentially contain a basic hetero-atom such as nitrogen or oxygen in the aromatic ring. The basis of this hetero-atom seems to be important in determining the catalytic behaviour. Polypyrrole for example shows catalytic behaviour which is qualitatively better than poly *n*-methyl pyrrole. There is however need for more systematic investigation. Another point of interest is the region where electron transfer takes place. In spite of better electronic conductivity than the redox polymers, the former films are also porous and hence can allow reactant movement into the film. The charge transfer can hence take place within the film matrix as well. The overall charge transfer rate in electrocatalytic reactions seems to depend on the thickness of the polymer film [76] lending support to this view. This aspect also needs further investigation.

The electrocatalytic behaviour of the conducting polymer can be substantially improved by incorporating redox catalysts [78] or catalytic metal particles [79] into the film. Figure 14.8 for example shows the electrocatalytic oxidation of H₂ on Pt-loaded conducting polypyrrole film. The diffusion controlled oxidation of H₂ occurs with much higher overvoltage on other Pt loaded conducting polymer films including poly-*n*-methyl pyrrole [80]. Although the relevance of such modification after modification may not be clear in the present

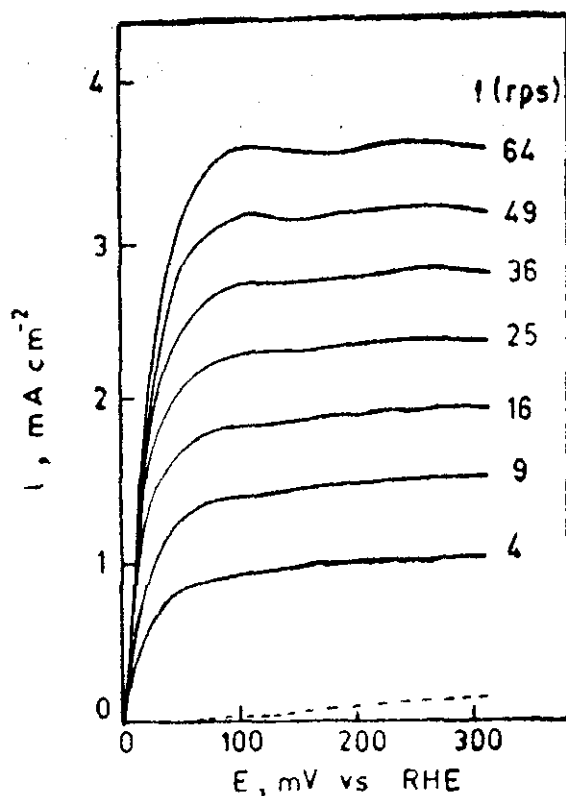


Fig. 14.8 RDE voltammograms of polypyrrole electrode with $40 \mu\text{g cm}^{-2}$ of Pt loading in $0.5 \text{ M H}_2\text{SO}_4$ saturated with H_2 . Sweep rate 10 mV s^{-1} . Dashed line shows, voltammogram in polypyrrole without Pt loading. [From FTA Vork, LJJ Janssen and E Barendrecht, *Electrochim Acta* 31 (1986) 1569]

context, it is quite relevant in protecting the semiconductor surfaces against photo-dissolution and simultaneously serving as a catalyst in photo-electron transfer (Chapter 16).

14.4.6 ELECTRON TRANSFER AND PASSIVE FILMS

Electrode surfaces covered with passive films would not allow electron transfer at the film-electrolyte interface. However, the electroactive reactant can move through the film to reach the metal surface and undergo electron transfer. This type of behaviour can be used to study the structure and structural defects of the passive films. Figure 14.9 for example shows the voltammograms of ferrocyanide oxidation on $\gamma\text{-FeOOH}$ films of different thicknesses on another substrate electrode [81]. The oxidation current for ferrocyanide system is found to decrease with the thickness of the film. This is due to the transport limitation of the reactant through the film. OH^- and H^+

ions move through the film much more conveniently in that oxide growth and reduction on an Au substrate containing γ -FeOOH are not retarded by the thickness of the film [82].

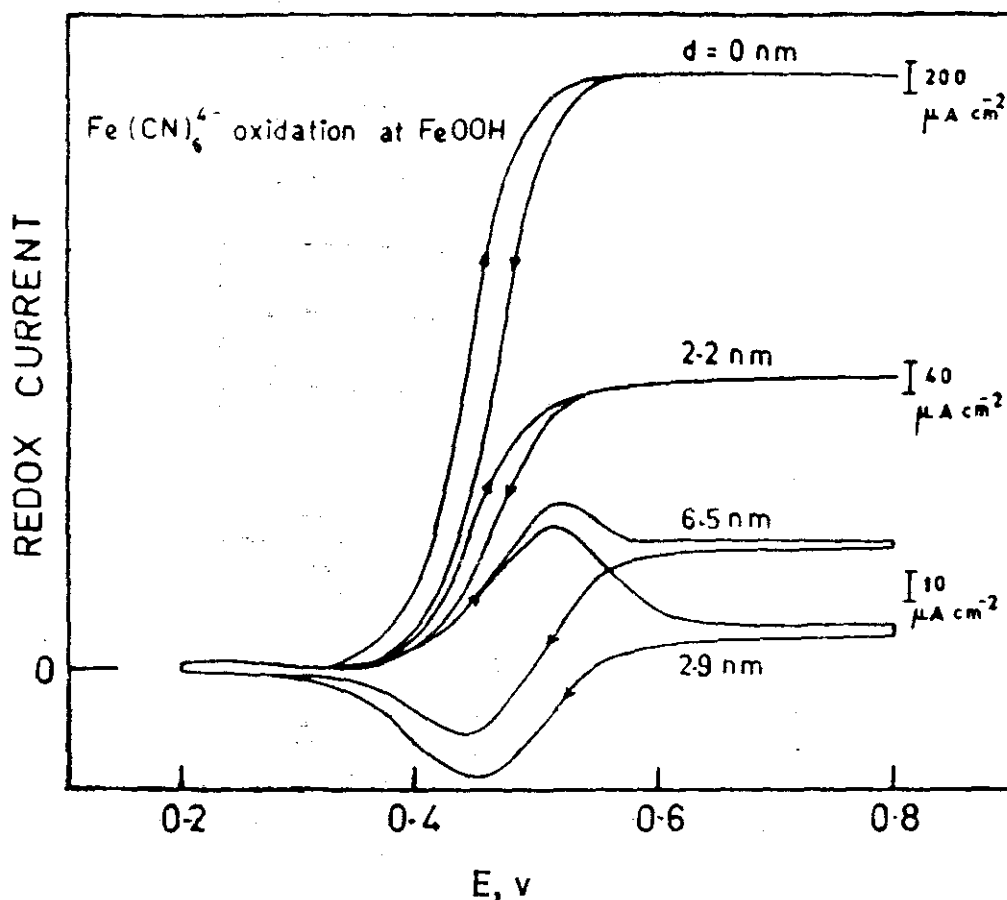


Fig. 14.9 Voltammograms for the oxidation of 50 mM ferrocyanide at FeOOH films of various film thickness values d (mentioned in graph) on a gold base electrode. Sweep rate 10 mV s^{-1} .

[From U Stimming, *J Electroanal Chem* 136 (1982) 345]

Electron transfer through the compact passive films is a much more difficult process. The charge transfer is assumed to proceed through a dual barrier [83] consisting of the passive film and the double layer. Different mechanisms, including quantum-mechanical tunnelling, through the film are proposed to explain the transport behaviour. A brief section on this topic is available in a general review on passive films [84].

14.5 ANALYTICAL APPLICATIONS AND SCOPE

Some redox modified electrodes mentioned above can find analytical applications in organic chemistry as well as molecular biology.

Electroanalysis of ascorbic acid and carboxylates mentioned earlier (Sec. 14.4.5) may be cited as examples of this type. The application of voltammetry for the evaluation of active surface area of oxide electrodes has been discussed. It should however be accepted that voltammetry on thin film electrodes is mainly aimed at electrocatalytic investigations rather than analytical applications.

Finally, one should admit that all types of thin film electrodes have not been dealt with in detail. Electrocatalysis on active metal deposited electrodes such as Pt-black, Raney nickel and other noble metal deposits did not receive the type of attention they deserve. This is primarily because not enough basic voltammetric investigations on this system are available at present. Another topic, of course, is the electrocatalysis on porous and flow-through electrodes. The basic understanding on the redox behaviour of these electrodes themselves is still not comprehensively understood (Chapter 10). Hence the basic investigations on the electrocatalytic behaviour of these electrodes should come mainly from future research efforts. Some new electrode materials such as tungsten-molybdenum carbide [85] are being developed for electrocatalytic applications. These electrodes will receive greater attention in future.

In this part (Part D, Chapters 11–14) one has tried to develop the studies on surface effects in solution phase processes in a systematic fashion. This is an area that is of interest in electrochemical synthesis, electrometallurgy, electroplating and almost any other branch in electrochemistry. There is potential for fast developments in this area provided a clear conceptual view of electrocatalysis emerges.

So far (Chapters 3 to 14) the interfacial charge transfer has been considered with the electrode potential as the predominant energy input. There is another interesting and exciting new energy input which has received greater attention over the past few years—the photon. The interaction of photonics, electronics and ionics is discussed in the next two chapters of the new part (Part E) on photoelectrochemistry.

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