

## CHAPTER 13

# Catalysis and Inhibition by Monolayers

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### 13.1 INTRODUCTION

In the last two chapters, the surface effects have been discussed on electron transfer reactions. Although an attempt was made to confine oneself to electrode surfaces of metals and carbon *without any intentional modifications*, one did encounter some *inherent interfacial structural changes* and their influence on charge transfer. The solvent layer on the electrode surface can be affected by chemisorption. Anions, cations and neutral organic molecules can adsorb on electrode surfaces and influence electrode processes. Impurities can block the electron transfer rate. The electrode pretreatment and activation can cause changes in surface chemistry itself and this would subsequently cause changes in electron transfer rate (Chapters 11 and 12).

Electrode processes are essentially surface processes. Hence one can catalyse or inhibit any electrode reaction by intentionally modifying the electrode surface. The methods of formation of monolayers and thin films on electrode surfaces have been discussed in Chapters 7 and 8. The main objective of formation (Chapters 7 and 8) and characterization (Chapters 9 and 10) of these modified surfaces is to exploit them to catalyse or inhibit the reactions of interest in electrochemistry. Also the influence of monolayer oxide/hydroxide films on noble metals in the electrocatalytic oxidation of hydrogen and organic compounds have been discussed in the last chapter. In this and the subsequent chapter, the effects of different monolayers and three dimensional layers on electron transfer processes respectively, are discussed.

The electrocatalytic influence of chemically synthesized or tailor-made monolayers have received considerable attention in recent years. Electrocatalysis by redox monolayers or chemically modified electrodes has been an active field of research for over a decade now and has been reviewed from time to time [1-4]. Electrocatalysis by adatom monolayers or underpotential deposits continues to be an active area of research [5-7]. The chemistry of carbon surfaces, its oxidation and the resulting catalytic influence is also receiving considerable attention [8, 9]. However, most of these works attempt to answer the 'how' side of the story, namely, how to prepare and characterize the surface and how to measure and achieve electrocatalysis. The answer to the 'why' side of the story



oxidizing agent would function as an electron acceptor from the substrate in solution. But apart from these electron transfer reagents one can also attach some electron-sharing reagents or Lewis acids and bases on to the electrode surface. A surface acid would interact with electron-rich base in solution and a surface base would share its electrons with a Lewis acid in solution. One can also assume that some surface species would function neither as acid-base nor as redox reagents. On the basis of decreasing electron donating capacity, one can put these five classes of surface-bound species in the following order:

Reducing agent

Base

Neutral molecular species

Acid

Oxidizing agent

It may be possible to consider many chemical, electrochemical, biochemical and photochemical process mechanisms and reactivity correlations on this general basis. However, one confines oneself to surface functional groups from the electrochemical viewpoint alone. Even here, the redox catalysts and their catalytic influences are very similar to the homogeneous solution phase processes discussed in Chapter 5. The neutral molecular entities generally exhibit an inhibitive effect on all electrode processes and hence need no further discussion here. Hence there will be emphasis on the surface acid-base functional groups alone in greater detail here.

Any component in the electrolyte can interact with the electrode surface and form an acid-base couple (Table 13.1). Depending on the nature of the electrode material, water itself can show acid-base properties. Gold, for example, would show a low water chemisorption when compared with gallium. Hence on Ga, the  $H_2O$  would polarize to form  $Ga-HO^{\delta-} \dots H^{\delta+}$  type of species with some acidic properties. On Au this effect would be absent. Similarly, specifically adsorbed metal cations would function as acid groups although we cannot specify a corresponding conjugate base on the electrode surface. Tetra-alkyl-ammonium cations, however, can serve as acids and bases. Specifically adsorbed anions are probably the best known chemical catalysts on electrode surfaces (Chapter 11). A little recollection would reveal that they catalyse mostly acids ( $H_2$  evolution)

and cationic species (metal deposition). From the present viewpoint, they are effective surface bases.

**Table 13.1**  
**Surface acid-base functional groups**  
**Classifications and some typical examples**

Model	Acid	Conjugate base
Solvent chemisorption	$S-H_2O...H^+$	$S-H_2O$
Specific adsorption	$S-M^{n+}$	...
	$S-NR_4^+$	$S-NR_3$
	...	$S-Cl, S-Br, S-I$
Underpotential deposits	$S-M$	...
Oxidized metals	$M-O...H^+$	$M=O$
Oxidized carbon	$S-COOH$	$S-COO^-$
	$S-OH$ (phenolic)	$S-O^-$
	$S=O...H^+$	$S=O$ (Carbonyl)
Polyelectrolytes, membranes	$-SO_3H$	$-SO_3^-$
	$-NR_3^+$	$-NR_2$
	$S-M_xO_yH$	$S-M_xO_y^-$
Conducting polymers	$Poly-NH^+$	$Poly-N$

S refers to substrate atom except in  $-SO_3H, -SO_3^-$  couple where it refers to sulphur.

One can also chemically synthesize surface acids and bases. In underpotential deposition, if one deposits a base metal (electron donor Pb, Tl, Cd) on a noble metal (Pt, Au, Ag), the monolayer would electronically interact with the noble metal surface and in this process would attain a small positive polarization. Hence these underpotential deposits would certainly function as acids. Again, one cannot define a conjugate base for this system. The oxides on metals

can function as acids or bases depending on their chemical nature and oxidation states of the metal species. Oxidized carbon may contain many acid-base couples such as carboxylic acids, phenolic groups and carbonyl groups.

The three-dimensional films on electrode surfaces may also contain such acid-base functional groups. Coated rare earth metal oxides are good examples of these types of electrodes. Polyelectrolyte materials contain functional groups such as  $-\text{SO}_3\text{H}$  and  $-\text{NR}_2$  groups that can function as acid-base catalysts. Hetero polyacids such as tungstic acid and tungsto-molybdic acids can also function as acid-base catalysts when attached to electrode surfaces [12, 13]. The conducting polymer films also contain hetero atoms that can show acid-base properties. Although these three-dimensional films possess certain distinct additional model features which need separate consideration (in the next chapter), the basic classification and acid-base catalytic features are not at all different in all these surface acid-base groups.

Three important facts regarding the identification and classification of surface functional groups should however be mentioned here. For those functional groups for which both acidic and basic forms exist, the acid-base property of the functional group can be varied by varying the pH of the medium. One and the same functional group ( $-\text{COOH}$  for example) can serve as an acid as well as base ( $-\text{COO}^-$ ) depending on the pH of the medium and  $\text{pK}_a$  value of the acid. The medium effects such as complex formation, solvation etc. may also effect acid-base property as well as acid-base catalysis.

In addition to medium, the electrode potential can also modify the acid-base character of electrode surface functional groups. The electrode potential can change the concentration of the surface functional group as in the case of specific adsorption and *upd* formation and dissolution; it can also change the oxidation state of the species ( $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$  for example); it can even change an acid into another base as in the case of phenolic group oxidation (phenolic OH is an acid, but the oxidation product quinone is a base). Hence, while investigating the electrocatalytic influence, one should consider both the medium and electric field effects when deciding about the nature of the surface functional group.

The above discussion itself points to the third aspect. A particular species can function either as a redox catalyst or as an acid-base

catalyst. For example, quinone/hydroquinone couple is a popular redox catalysis. But they can also function as acids and bases. In general, if the redox couple attached to the surface shows distinct redox wave and the electrocatalytic reaction also proceeds around the same electrode potential of the redox couple, one can assume that it is proceeding in redox pathway. But even this evidence cannot completely rule out the chemical catalytic pathway as will become evident later (Sections 13.2.3 and 13.4.1) This fact again emphasizes the similarities and relevance of redox catalysis as well as surface acid-base catalysis as a generally mutually related process rather than as distinct unrelated entities.

### 13.2.2 SURFACE ACID-BASE CATALYSIS

Acid-base catalysis is a well-known concept in chemistry. The study of homogeneous acid-base catalysis [14, 15] has recently been extended to the heterogeneous surface processes such as heterogeneous oxide surfaces [16] and enzyme catalysis [17]. One may assume that similar catalytic influence is exerted by the surface functional groups in the electrochemical process as well.

If the nature of the surface functional group and its relative acidity are properly understood, the prediction of its catalytic influence on any specific reactant is a straightforward question. An acidic surface group would facilitate the electron transfer of a base (negatively charged or negatively polarized reactant) and a basic surface functional group would facilitate the electron transfer of an acid (positively charged or positively polarized reactant). One can also generalize that acidic functional groups would facilitate reduction processes and the basic functional groups would facilitate oxidation processes (similar to the solution phase protonation effect for example). Exception to this latter statement however is possible. One may for example encounter electrode processes that are both acid and base catalysed just as the general acid-base catalysis encountered in homogeneous acid-base catalysis.

As shown later (Sections 13.4.3 to 13.4.5), a number of individual experimental works carried out on independent surface functional groups are found to fit very well in this generalized mechanistic schemes. The present model thus seems to bring out a uniformity among the different modes of surface modifications. The similarity in

electrocatalytic behaviour of specifically adsorbed cations, underpotential deposits, carboxylic acids, sulphonic acids and polyelectrolytes is certainly a very interesting observation that requires further systematic evaluation. However, it should be admitted that what is proposed here is only an hypothesis that requires further investigation at different levels. One can outline here some of the lines of approach for further work in this direction.

Specific experimental work designed to verify the acid-base catalysis concept is the first requirement. Specific catalysis of acidic reactants by surface bases and basic reactants by surface acids may be verified. For surface functional groups that can exist in conjugate pairs, one can evaluate the pH dependence of catalytic influence.

Correlations between catalytic efficiency and acid-strength of the surface functional groups can be evaluated. These correlation attempts can be at the level of single class of surface functional groups (say *upd* of different base metals on a single noble metal) in the initial stages of analysis. However, the ultimate goal should be to establish a general acid-base strength and catalytic efficiency correlation. Such correlations can be the basis for *a priori* predictions of catalytic efficiencies.

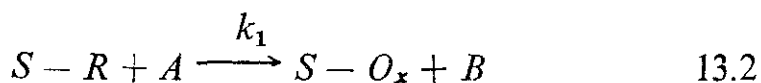
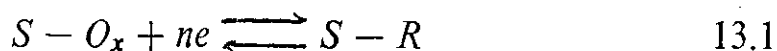
Quantitative evaluations of the catalytic efficiencies and the related rate parameters can be the next objective. Based on these data, one may attempt to understand the nature of catalytic influence of the catalysts. It may be possible to predict whether the catalysis is due to enthalpic or entropy factor, or whether the catalyst influences the reactant state or activated transition state. Some of these objectives may appear somewhat speculative at the present juncture. However, this is certainly inevitable when attempting to unify the catalytic influence of such a wide variety of surface functional groups (Table 13.1). It should also be stated that most of these objectives can be fulfilled in a realistic time frame with proper experimental as well as theoretical effort.

### 13.2 3 SURFACE REDOX CATALYSIS

Compared with other surface functional groups and their electrocatalytic influence, the redox catalysis is more straightforward, at least in the model level. One can describe a surface redox catalytic process in terms that are very similar to the homogeneous redox

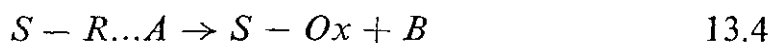


catalysis discussed in Chapter 5. The overall process is considered as a coupling of an electrochemical reaction 13.1 and a redox reaction 13.2.



The major difference is the appearance of surface-bound redox couple and hence surface concentration  $\tau_{Ox}$  and  $\tau_R$  in the rate expressions for reaction 13.2. The mass transfer effect for  $Ox$  and  $R$  species need not be considered since they are totally surface bound. The mass transfer effect of the substrate couple  $A, B$  should however be considered. The voltammetric method for this model of redox catalysis is simple and straightforward as discussed subsequently (Section 13.3.1).

However, one cannot assume that all the surface redox catalytic processes would follow the simple catalytic sequence described above. In fact, the most important and successful redox catalysis of  $O_2$  reduction does not follow this sequence at all (Section 13.4.1). The catalyst seems to form a fairly stable intermediate which undergoes further chemical or electrochemical reaction to give the final product. This type of catalysis is usually termed as chemical redox catalysis. For a one-electron overall substrate reduction, one can formally write



The equilibrium property of reaction 13.3 can now have a substantial influence on the overall redox catalytic rate. For an overall  $4e, O_2$  reduction, one can think of more involved reaction sequence. Hence redox catalytic reactions of this type are generally not subjected to complete quantitative evaluation by cyclic voltammetric method. Some general comparison of catalytic efficiencies are however certainly possible (Sections 13.3.1 and 13.4.1).

### 13.3 THE METHOD

The voltammetric methods for studying the acid-base type of catalysis and the redox catalysis are quite different. In the acid-base catalysis,

the overall electron transfer reaction is considered as a single step process. Hence a single reversible, quasi-reversible or irreversible response is obtained which can be analysed for apparent charge transfer parameters such as  $k_h^o, app$  and  $\alpha n_a, app$  using the methods discussed in Chapter 4. The influence of the surface structure on these parameters can lead to further evaluation of catalysis. In this regard, the evaluation of rate parameters is possible only for simple single step process (see Chapter 11). For more involved processes where the surface coverage itself may vary during the electron transfer and processes involving adsorbed intermediates, cyclic voltammetry can serve only as a qualitative tool (Chapter 12). In these circumstances other methods also cannot be of great help.

### 13.3.1 VOLTAMMETRY OF REDOX CATALYSIS BY MONOLAYERS

The voltammetric method for evaluating the redox catalytic process is very similar to the homogeneous case discussed in Chapter 5. Consider the reaction scheme involving equations 13.1 and 13.2. In the absence of substrate molecule  $A$ , the surface redox couple will give a redox voltammogram similar to the ones discussed in Chapter 10. When the substrate is added, the voltammetric response will vary depending on the rate constant  $k_1$  of reaction 13.2. If  $k_1$  is small, an  $S$ -shaped polarographic wave will be observed very close to the  $E^o$  value of the reversible redox couple  $Ox/R$ . If the rate constant  $k_1$  is higher, the limiting current wave will be replaced by a voltammetric peak and the peak potential would appear at more positive potential regions.

Quantitatively [18], the voltammetric behaviour depends on the dimensional parameter  $\lambda_s$ , which is defined by equation 13.5

$$\lambda_s = \frac{k_1 l \mu^o}{(nfvD_A)^{1/2}} \quad 13.5$$

In this expression  $l$  is the number of redox layers on the electrode surface (for the monolayer considered here  $l = 1$ ),  $\tau^o$  is the surface concentration of the redox species which can be estimated in the absence of  $A$  and other terms have their usual meaning. The shapes of the voltammograms for different values of  $\lambda_s$  are presented in Fig. 13.1.a. The current function  $\psi$  in this figure is given by equation 13.6.

$$\psi_s = \frac{i_c}{FAC_A^0 (fvD_A)^{1/2}} \quad 13.6$$

Quantitative evaluation of rate constants can be achieved by measuring the catalytic current (and hence evaluating  $\psi$ ) and the catalytic peak potential shift and then using these values for getting  $\lambda_s$  from Fig. 13.1.b and Fig. 13.1.c respectively.

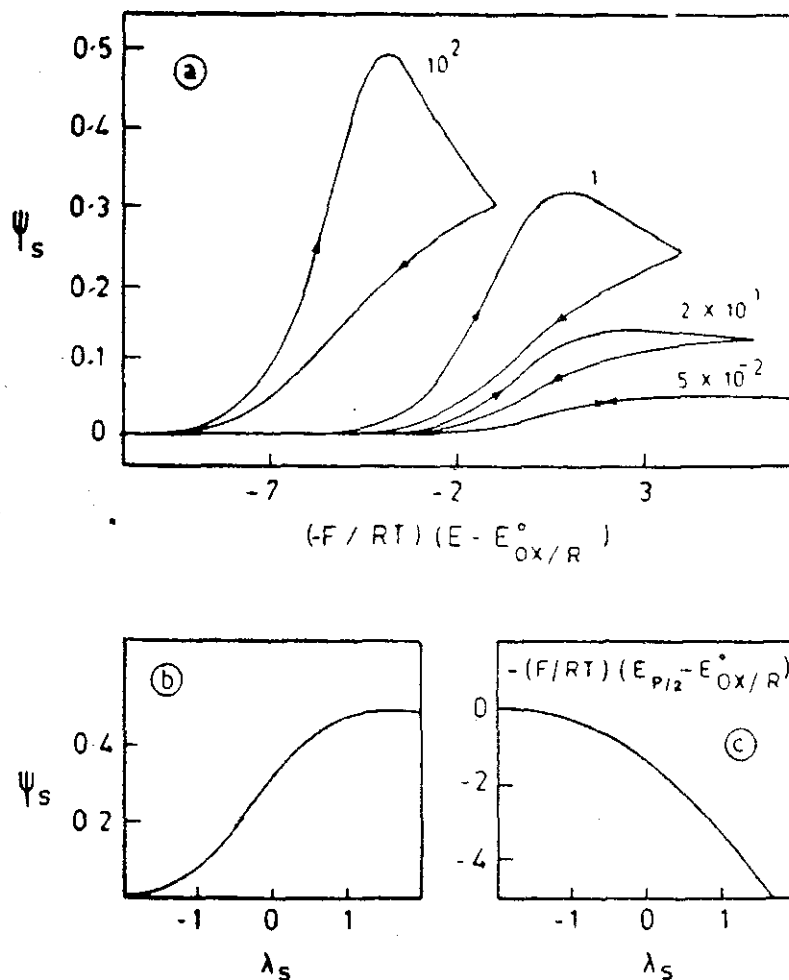


Fig. 13.1 Voltammetric shapes, (a) Peak current, and (b) peak potential, (c) characteristics of the catalytic waves in surface redox catalysis. The numbers on the voltammograms are the values of the dimensionless parameter  $\lambda_s$ . See text for  $\lambda_s$  and  $\psi$  values.

[From C P Andreux and J M Saveant, J Electroanal Chem 93 (1978) 163]

For achieving the reduction of  $A$  as in the case considered above, the  $E_{A/B}^{\circ}$  of the substrate should be more positive to the  $E_{ox/R}^{\circ}$  of the redox couple. For achieving a catalytic oxidation, the  $E_{A/B}^{\circ}$  must be

more negative than the  $E_{Ox/R}^{\circ}$ . This criteria is required to ensure the thermodynamic feasibility of reaction 13.2. If the formal potential of both the redox catalytic couple and the substrate couple are close to each other, the redox catalysis can be achieved in both directions. This type of redox catalysis is very useful in the study of redox behaviour of biological molecules.

The voltammetric method described above is developed under the assumption that equation 13.1 is a perfectly reversible electrochemical process. In surface redox catalysis, only such reversible redox couples are widely employed. However, one may use quasi-reversible or even irreversible redox catalysts. Although quantitatively there can be some differences, the redox catalytic wave would still show qualitative responses similar to Fig. 13.1. The same considerations also apply when chemical redox catalysis (reaction scheme involving equations 13.1, 13.3 and 13.4) is involved. Hence the relative increase in peak current when compared with the peak current of the redox couple ( $Ox/R$ ) and relative catalytic shift of the peak potential can always give a qualitative idea of a catalytic efficiency of a redox catalytic surface process.

### 13.4 THE PROCESS

Surface modification for electrocatalysis is one of the fast growing areas in electrochemical research. Each branch in this area such as redox modified electrodes, heat treated redox modifications, enzyme modified electrodes, underpotential deposits and modifying carbon surfaces is being pursued with great vigour for obtaining good electrocatalytic and electroanalytical applications. It is impossible to review all these developments comprehensively. Hence only the types of research work that are currently in progress are outlined in this field. Also the formation and redox behaviour of these monolayer surfaces are not treated as these had been the topic of discussion in Chapters 7 and 9 respectively. Straightaway this chapter shall deal with redox catalysis (Sections 13.4.1 and 13.4.2) and the surface acid-base catalysis (Sections 13.4.3 to 13.4.6) with ample references for further study.

#### 13.4.1 REDOX CATALYSIS OF ELECTROCHEMICAL REACTIONS

Redox pathways offer an excellent route for catalysing important electrochemical reactions [19], if only they can be constructed in a

stable electroactive form. Efforts are in progress to construct and characterize chemically modified electrodes with a wide variety of organic compounds, inorganic complexes and organometallics that can function as good redox catalysts [1-4]. Figure. 13.2 shows the mode of redox catalysis by these electrodes in electrocatalytic reduction (Fig. 13.2.a) and oxidation (Fig. 13.2.b). Because the redox catalyst is strongly held to the electrode surface, the redox couple does not mix with the substrate reactant and product. This is a very important advantage when compared with homogeneous redox catalysis. This is certainly the main cause for looking for electrosynthetic applications of these electrodes [1-4].

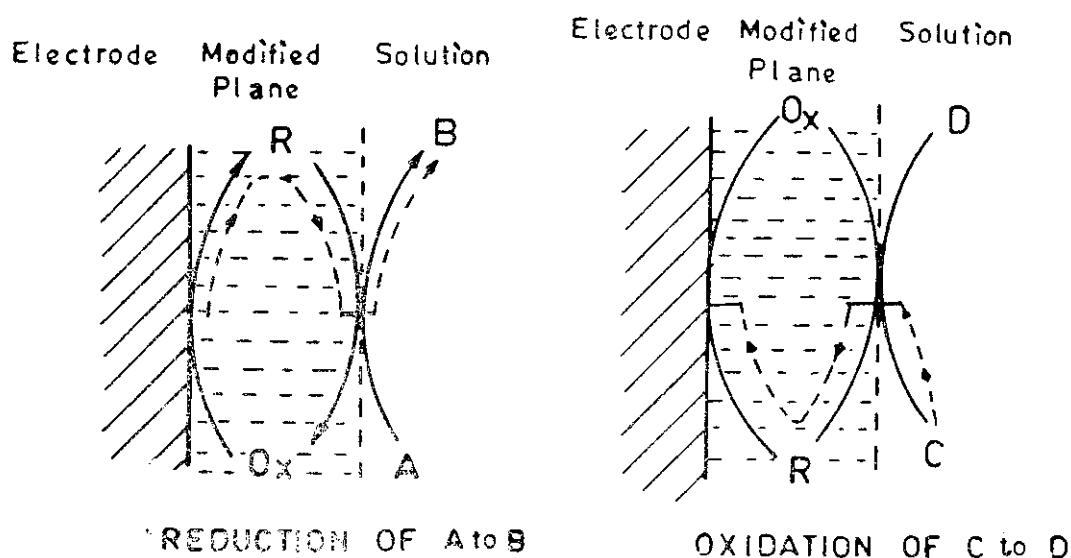


Fig. 13.2 Catalysis of electron transfer by surface redox modified electrodes. Full arrows indicate the changes occurring in the molecular species. Dashed arrows indicate the electron flow.

[From M Noel, PN Anantharaman and HVK Udupa, Trans SAEST 15 (1980) 49.]

A typical application of redox electrode in electro-organic synthesis is in the reduction of alkyl halides [20, 21]. Figures. 13.3 a and 13.3 b for example show the redox behaviour of porphyrin redox catalyst attached to carbon electrodes. The reduction of alkyl bromide  $\text{PhCH Br CH}_2\text{Br}$  occurs around  $-1.4\text{ V}$  on naked carbon electrode (Fig. 13.3c). But on redox modified carbon electrode, the compound is reduced around  $-0.8\text{ V}$  itself (Fig. 13.3.d) through the mediation of the

catalyst. The catalytic potential shift is thus as high as 0.6V. Similar electrocatalysis is also noted in the oxidation of aromatic compounds [21] and reduction of  $\text{CO}_2$  [22] and many other compounds [1-4, 23].

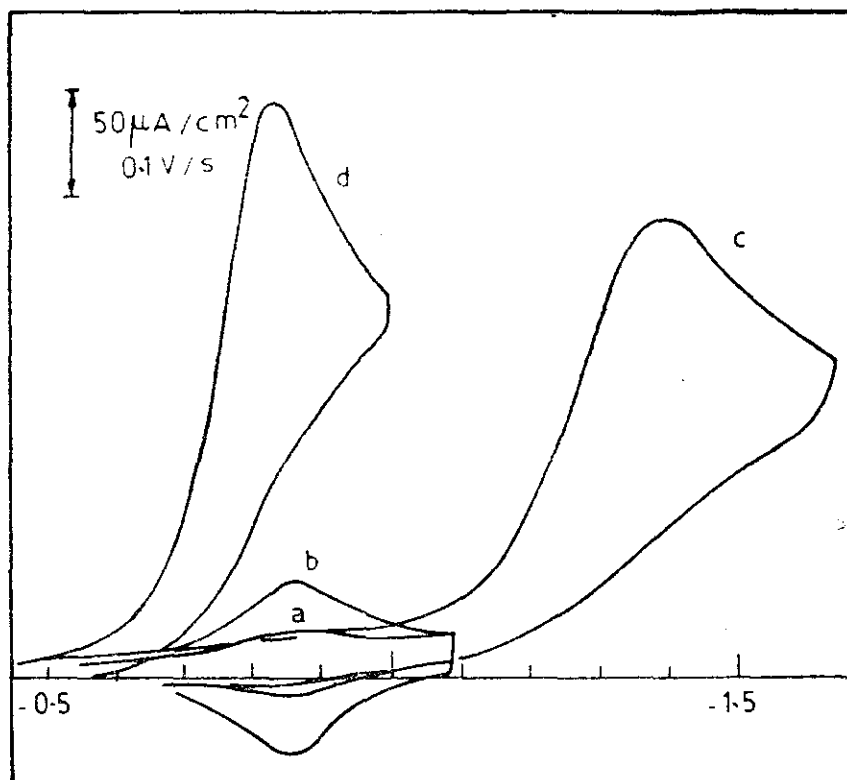


Fig. 13.3 Cyclic voltammetric curves of  $5 \times 10^{-11}$  (a), and  $11 \times 10^{-10}$  mole  $\text{cm}^{-2}$  of tetra (p-aminophenyl) porphyrin attached to GC electrode. Voltammograms of  $\text{PhCHBrCH}_2\text{Br}$  on naked GC (c), and on modified GC corresponding to curve b (d) are also given in figure.

[From R W Murray, *Phil Trans R Soc Lond A* 302 (1981) 253]

Among the catalytic applications investigated on chemically modified electrodes,  $\text{O}_2$  reduction is the most comprehensively investigated one. Many organo-metallic redox couples are good catalysts of  $\text{O}_2$  reduction to  $\text{H}_2\text{O}_2$  [24-26]. However, a real breakthrough in the direct reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$  was achieved (Fig. 13.4) when two cobalt (III) tetraphenyl porphyrin entities were end-connected by an organic entity to provide a critical distance between the two Co (III) entities [27]. The dioxygen chemically interacted with the two metal centres to form  $\text{Co}^{n+}\text{-O-O-Co}^{n+}$  type of linkage which facilitates its

complete reduction to  $\text{H}_2\text{O}$ . The effect of different modifications in the porphyrin rings, their linkage, the metal ion centres and their catalytic influences have been comprehensively investigated [27-32]. As a result of these investigations, it is possible to reduce  $\text{O}_2$  to  $\text{H}_2\text{O}$  using redox catalytic system at least as efficiently as it is done now on Pt electrodes [27-33]. The only limiting factor that stands in the practical application of these electrodes is the instability of these electrodes over long periods under practical conditions. However, efforts are still on to overcome this difficulty.

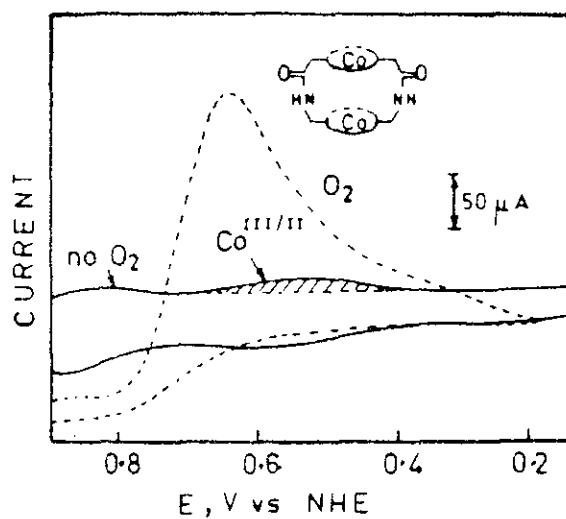


Fig. 13.4 Cyclic voltammograms of graphite electrode coated with the dimer of Co (III) tetraphenyl porphyrin complex in the absence and in the presence of oxygen. Supporting electrolyte 0.5M  $\text{CF}_3\text{COOH}$ . Potential scan rate  $50\text{ mV s}^{-1}$ .

[From JP Collman, P Denisevich, Y Konai, M Marrocco, C Koval and FC Anson, *J Am Chem Soc* 102 (1980) 6027]

It has been shown in many recent investigations [34] that the macrocyclic complexes attached to the carbon electrodes by the above procedures at  $500^\circ\text{C}$  and above still show some good electrocatalytic activity towards  $\text{O}_2$  reduction. The complexes cannot remain intact after such severe heat treatment. But one can assume the presence of  $\text{Co}^{n+}$  or similar  $\text{M}^{n+}$  catalyst ion on the electrode surface and the interatomic distances between these ions formed from the same binuclear complex can also remain constant. The fact that these metal ions still exhibit catalytic effect in spite of their loss of redox behaviour (due to the destruction of the complex structure) suggests that they

behave as acidic centres catalysing the same electron transfer reaction. These catalysts which promise to show very good long term stability as well as catalysis, also seem to establish the direct linkage between the chemical redox catalysis and acid-base catalysis of electrochemical reactions.

#### 13.4.2 REDOX CATALYSIS OF ELECTROBIOCHEMICAL REACTIONS

Many important biochemical processes are essentially redox reactions which can be studied at the electrode surfaces. However, these biological molecules are comparatively bigger and so easily block the electrode surface or undergo very slow electron-transfer at the electrode surfaces due to the orientational problems of the big molecules. Redox modified electrodes can eliminate these difficulties. This is why these electrodes are being actively investigated for electrochemical applications [1-4, 23, 35, 36].

Redox modified electrodes can be used for catalytically oxidizing ascorbic acid [37] and NADH [38] for example. Quite large molecules like horse heart cytochrome-*C* can be oxidatively or reductively catalysed [39, 40] by choosing proper redox couple. In addition to conventional redox couples like methyl viologens and ferrocenes [39, 40], even organic compounds like purines [41] can be used as promoters for these reactions.

For achieving electrobiocatalysis, redox modifications are not always necessary. 4-4' bipyridyls for example serve as good catalysts for the catalytic oxidation of a variety of organic compounds [42-44]. The process involved is certainly not redox catalysis. This should be considered as surface acid-base catalysis according to the present definition since it is known that the bipyridyls are good bases that can interact with acidic reaction centres and promote electron transfer. Redox modified electrodes can also catalyse very large biological entities like proteins [44] and enzymes [45]. However a more interesting development is the immobilization of enzymes themselves on electrode surfaces. Such enzyme modified electrodes themselves have been comprehensively reviewed [35]. One can visualise two possibilities. Some immobilized enzymes can actually catalyse direct electrochemical oxidation or reduction at the electrode surface [46, 47]. Since enzymes themselves do not behave as redox catalysts, such catalytic influence should be ascribed to surface-acid-



base catalytic property of the enzyme. Secondly the enzyme can serve as a support where a chemical redox reaction can proceed just as in the case of biological systems. Glucose can for example get oxidized to gluconic acid in the presence of the enzyme glucose oxidase [48]. In this process,  $O_2$  present in solution is reduced to  $H_2O_2$ , thus  $O_2/H_2O_2$  couple serving as a redox mediator in this case. One can sense the concentration of glucose by evaluating the amount of  $H_2O_2$  produced by voltammetric or amperometric method. Active research work is in progress in this type of electrobiocatalytic processes for achieving better understanding and for developing analytical tools for electrobiochemistry itself.

### 13.4.3 ACID-BASE CATALYSIS OF SIMPLE ELECTRON TRANSFER REACTIONS

It has been seen that the *upd* monolayers possess a small net positive charge on the adatoms and hence should be considered as acids (Section 13.2.1). Hence these layers should not show any catalytic effect on positively charged redox couples. This is found to be the case in many simple electron transfer reactions of positively charged redox couples [49, 50]. However, this should not lead to the conclusion that these *upd* systems have no catalytic effect on simple electron transfer reactions [7]. In fact a very good catalytic effect of *upd* layers was found in the cases of quinone/hydroquinone couple [51, 52] which can specifically interact with these layers. The catalytic effect seems to be even more predominant in the case of negatively charged electroactive species.  $IO_3^-$  [53],  $Cr_2O_7^{2-}$  and  $S_2O_8^{2-}$  [54] are some examples where very good catalytic effect due to *upd* systems are observed. Figure 13.5 for example shows that a positive catalytic shift amounting to as much as 500 mV is observed in the electrochemical reduction of  $S_2O_8^{2-}$  on Pb adsorbed Pt electrode when compared with bare Pt electrode. These experiments certainly point to the importance of working at the acid-base nature of the surface modifications on their acid-base catalytic effect.

Some effects of oxidized carbon surfaces on simple electron transfer reactions have been discussed (Section 11.4). It is interesting to view the oxidized carbon surface as a carbon surface containing acidic functional group. This would explain the electro-reduction of oxalate and citrate complexes of iron (negatively charged) in acidic medium

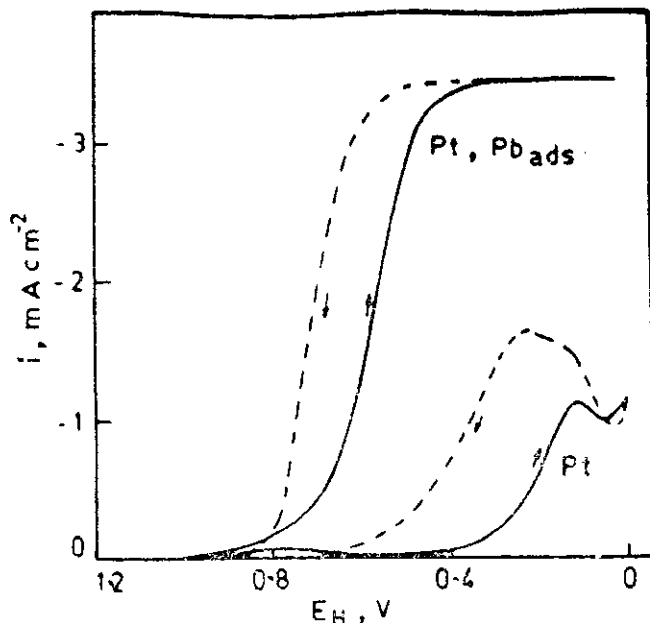


Fig. 13.5 Voltammetric curve for  $2 \times 10^{-3} \text{M K}_2\text{S}_2\text{O}_8$  reduction and rotating Pt disc electrode in  $0.5 \text{M HClO}_4$  in the absence (a) and in the presence of  $10^{-3} \text{M Pb}(\text{ClO}_4)_2$ . Rotation frequency  $f = 50 \text{ Hz}$ . Scan rate  $200 \text{ mVs}^{-1}$ . [From G Kokkinidis and D Sazoa, *J Electroanal Chem* 237 (1987) 137]

alone where carbon surface would possess acidic properties [55]. The pH dependence of charge transfer rate constant of ferricyanide/ferrocyanide redox couple on GC electrode when compared with the rate-independence on Pt electrode [56] can be understood on this basis. The acidic surface functional groups allow the radical ions to come closer and thus enable faster dimerization of the one-electron reduction intermediates of carbonyl compounds [57]. More detailed investigations on these phenomena however are needed.

#### 13.4.4 ACID-BASE CATALYSIS OF $\text{O}_2$ REDUCTION REACTIONS

$\text{O}_2$  reduction is once again the most thoroughly investigated reaction on *upd* surfaces. Extensive research work on electrocatalytic  $\text{O}_2$  reduction in alkaline [5] and acidic [7] media have been carried out and these works have been comprehensively reviewed [5–7]. It is well-known that  $\text{O}_2$  undergoes direct electro-reduction to  $\text{H}_2\text{O}$  only on Pt, some Pt group metals and on silver electrodes. In these electrodes, *upd* has a negative effect on electrocatalysis. However on gold [58–62]

and glassy carbon [63] electrodes where  $O_2$  undergoes a two-step pathway involving  $H_2O_2$  intermediate, the underpotential deposits of Tl, Cd, Pb and Bi show positive catalytic effect, both in alkaline [58, 59] and in acid [60–63] media. Apart from Pt, Ag, Au and carbon surfaces that have received wider attention, Ru [64] and Cu [65] electrodes have also attracted some attention. The overall result however is the same. *Upd* metals show electrocatalysis wherever  $H_2O_2$  intermediate formation is observed on bare electrode surfaces.

A typical ring disc electrode voltammogram of  $O_2$  reduction on gold electrode in the presence of Pb *upd* is presented in Fig. 13.6 [66]. One may notice that the ring current due to  $H_2O_2$  formed on the disc electrode is reduced substantially in the presence of *upd* Pb

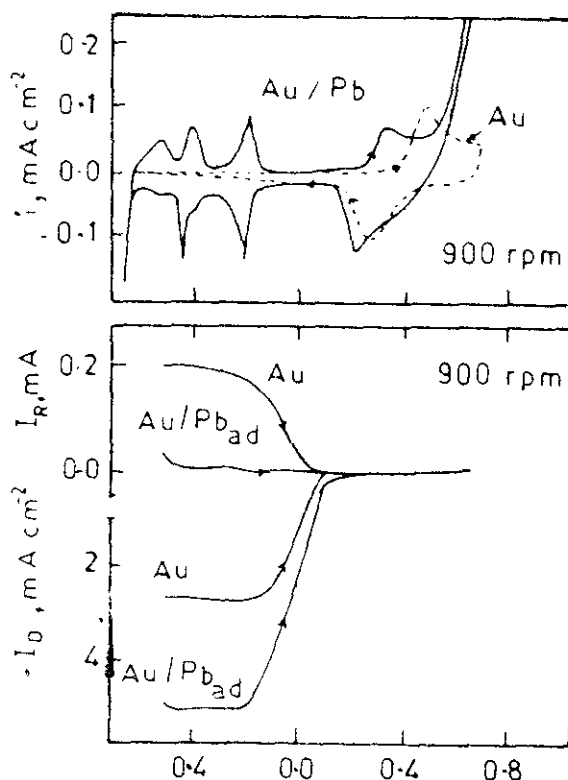


Fig. 13.6 Ring-disc voltammograms of  $O_2$  reduction and Au and Au with Pb adsorbate in 1M NaOH containing  $1 \times 10^{-3}$  M  $HPBO_2^-$ . Ring potential 0.3V. Sweep rate  $50 \text{ mV s}^{-1}$ . The upper curves represent the *upd* Pb formation on Au.  $I_R$ -ring current and  $I_D$ -disc current.

[From RR Adzic, AV Tripkovic and NM Markovic, *J Electroanal Chem* 114 (1980) 21]

adatoms. The disc current due to direct reduction of  $O_2$  to  $H_2O$  is also found to increase.

How can one explain this type of catalytic influence? Many explanations are offered. Improved hydrophilicity, improved  $M-O-O-M'$  type of linkage in the presence of adatom  $M'$  and even redox catalysis by adatom [67] are suggested as possible explanations [5-7]. However, if one considers the adatoms as positively polarized acidic catalytic centres one can visualize that  $O_2^-$  radical anion as well as  $O_2^{2-}$  dianion would interact with these catalytic metal centres and retain the  $H_2O_2$  intermediates on the electrode surface itself for further reduction. This type of catalytic influence is further supported by the fact that  $Tl^+$  cations, even at potentials where *upd* formation would not have been initiated, still shows electrocatalytic influence on  $O_2$  reduction [5].

$O_2$  reduction is also catalysed by oxidized electrode surfaces [34, 68]. In Chapter 12, the catalysis of  $O_2$  reduction on an oxidized carbon surface has been seen (Section 12.4.6 and Fig. 12.10). This catalytic effect can be explained on the basis of catalytic acidic centres on the oxidized carbon surfaces. The catalytic influence of polyelectrolytes [12, 13] on  $O_2$  reduction is possibly due to this effect.

#### 13.4.5 INHIBITION OF ELECTRODE PROCESSES BY MONOLAYERS

If a surface modification neither produces redox centres, nor acid-base centres they are likely to show inhibitive effects on electrode reaction. This is quite similar to the blocking effect of the adsorbed molecular species (Chapter 11). Typical examples of covalent modifications of this type are the silinated electrode surfaces (electrode surface covered by  $Si-OH$  or  $-Si-O-$  type of bonds) before the attachment of redox couples [69-71]. These electrodes invariably show an inhibitive effect on simple electron-transfer processes. Even in this case, there seems to be some electrostatic influence of the acid-base type. The silinated surface for example shows greater inhibitive effect on positively charged redox couples like  $Ru(III)$  bipyridyls. A negatively charged redox couple such as ferricyanide/ferrocyanide is comparatively less affected [71].

The monolayer forming metals such as  $Tl$ ,  $Cd$ ,  $Pb$  and  $Bi$  belong to high hydrogen overvoltage group when compared with the substrate

metals like Pt, Au, Ag and copper. Hence the underpotential depositions in all these cases are expected to inhibit hydrogen evolution reaction. This is found to be the case in all the *upd* systems investigated [5–7]. Typical inhibitive effect of Tl *upd* layer on two crystal planes of Ag single crystal are presented in Fig. 13.7 [72]. The inhibition of hydrogen evolution (Fig. 13.7 a) is found to correlate very well with voltammetric pattern of monolayer formation (Fig. 13.7 b).

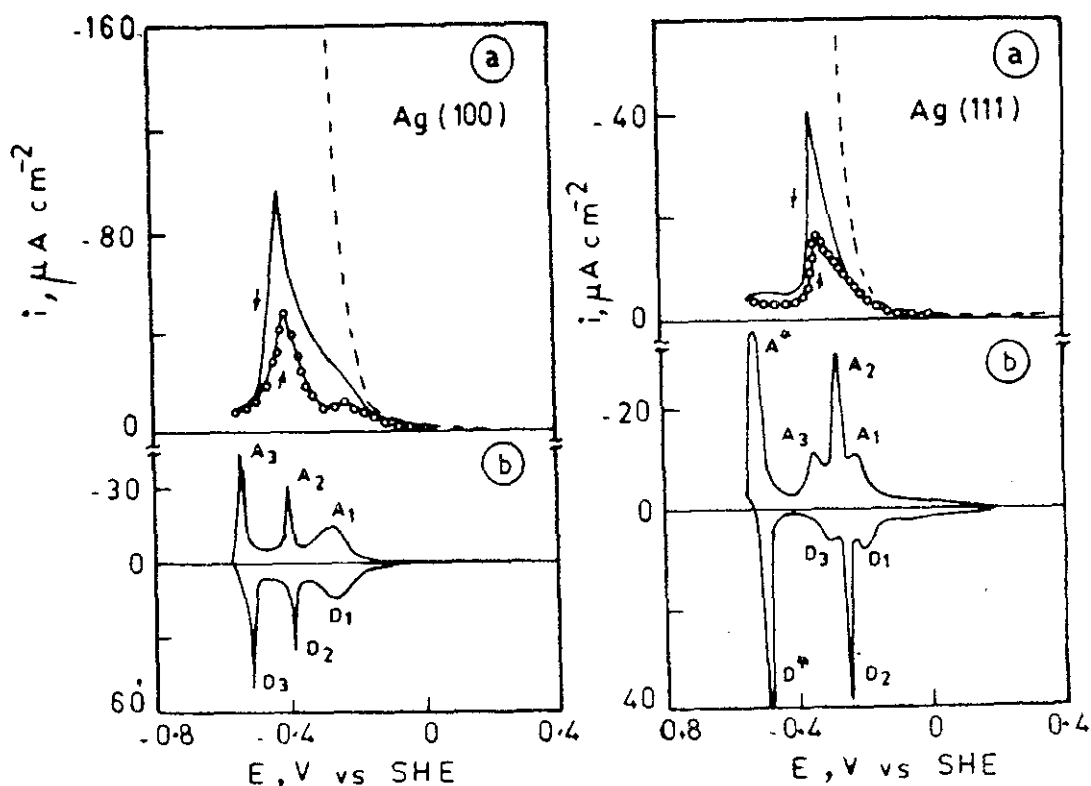


Fig. 13.7 (a) Hydrogen evolution on Ag (100) and Ag (111) in 0.5M  $\text{NaClO}_4 + 0.5\text{M HClO}_4$  without (---) and with Tl adatoms. Polarization in anodic (o-o-o) and cathodic (---) directions.

(b) *Upd* of Tl formation in 0.5M  $\text{NaClO}_4 + 10^{-3} \text{HClO}_4$  under otherwise identical conditions.

[From AM Abd, E Halim, K Jutner and WJ Lorenz, *J Electroanal Chem* 106 (1980) 193].

Although the nature of the monolayer atoms explains the inhibitive effect, interestingly from the acid-base catalytic viewpoint acidic *upd* monolayers are expected to show an inhibitive effect on the acidic reactant, such as  $\text{H}^+$  ion. It is possible to evaluate the sites

occupied by each adatom on a substrate by evaluating the quantity of adatoms adsorbed and their relative inhibition of  $H_2$  evolution reaction [73].

*Upd* layers are also found to have some partial inhibitive effect on aromatic nitrocompounds [74]. Aromatic nitrocompound reduction is found to stop at  $4e$  stage to phenyl hydroxylamine ( $\phi$  NHOH) on *upd* surfaces [74]. The exact cause of this behaviour requires further investigation. However from acid-base catalysis viewpoint one is tempted to speculate that in acid medium,  $\phi N^+H_2OH$  species is formed which is inhibited by the acidic *upd* layer.

#### 13.4.6 INHIBITION OF POISON FORMATION BY MONOLAYERS

$H_2$  evolution and oxidations of small organic molecules proceed by intermediate adsorption on electrode surfaces (Chapter 12). However, while *upd* layers inhibit  $H_2$  evolution reaction, they catalyse small organic molecule oxidation when the surface coverage by these *upd* adatoms is small. This type of catalysis was noticed in HCOOH oxidation for the first time [75]. Subsequently this reaction has been comprehensively investigated under different experimental conditions [76–79]. Figure 13.8 for example shows the electrocatalytic effect of Pb *upd* layer on the three single crystal planes of Pt electrode.

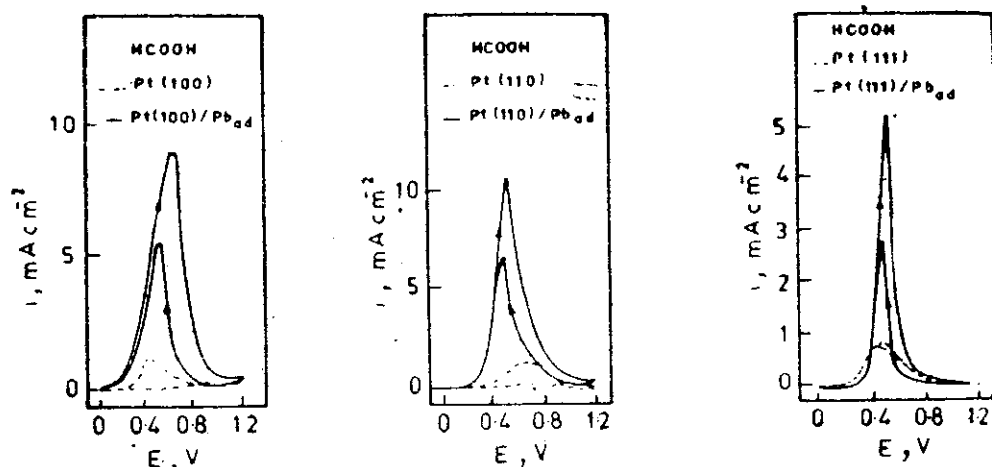
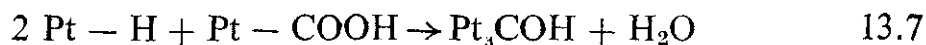


Fig. 13.8. Oxidation of HCOOH (0.26 M) on single crystal platinum in  $HClO_4$  acid without (---) and with (—) Pb adatoms;  $1 \times 10^{-3} M Pb^{2+}$  in electrolyte; Sweep rate  $50\ mV\ s^{-1}$ .

[From RR Adzic, AV Tripkovic and NM Markovic, *J Electroanal Chem* 150 (1983) 79]

Comprehensive investigations on this and other small organic molecule oxidations have led to the conclusion that the catalytic effect in these cases is actually due to the inhibition of poison formation on these electrodes. In the case of formic acid oxidation for example the poison (Pt-COH) formation should proceed *via* two Pt-H and one Pt-COOH adsorption centres.



This is essentially a reaction between three adjacent reactant sites. If one can randomly place Tl or Pb adatoms on Pt sites, they inhibit this type of three-centre or multicentre interactions required for poison formation. A general discussion on these catalytic effects is also available [80].

Electrocatalytic effects of *upd* on the oxidation of molecules of fairly large size such as glucose [81-83] and other monosaccharides [84] are being investigated. They do give catalytic oxidations in the presence of *upd* layers. But the relative increase in the catalytic response is not quite high. The mechanism of the overall oxidation process is not very clear. But complete oxidation of these molecules to CO<sub>2</sub> under these experimental conditions is certainly unlikely.

### 13.5 ANALYTICAL APPLICATIONS AND SCOPE

Although the surface modifications are attempted for electrocatalytic applications, these electrodes are now finding immediate applications in electroanalysis. This is especially true in the case of redox modified electrodes. Bioanalytical applications are very promising. These electrodes can be employed for the determination of many molecular entities, co-enzymes and even proteins. Both *in vitro* and *in vivo* analysis should become possible in the near future. Among synthetic applications, O<sub>2</sub> reduction by redox catalysis as well as catalysis by *upd* metals seem to offer considerable promise.

The main difficulty with regard to the application of monolayer modified electrodes treated here concerns their long term stability. Most of the redox modifications become unstable over long periods of time. *Upd* electrodes can be produced by *in situ* addition of adatom forming cations in very low concentrations. This method works very well under voltammetric experimental situations. But in long-term polarizations, the deposition can cross monolayer levels.

The bulk deposits certainly would not be expected to show high catalytic effects. Taking out the *upd* electrode also may not ensure the stability of catalytic monolayers intact. The successful technological applications of these electrodes would depend on overcoming these crucial problems.

It is in this sense that the investigations on the acid-base catalysis receive utmost importance. If this type of behaviour is indeed established to be the causes of electrocatalysis, one can fabricate electrodes containing very strong acidic and basic catalytic centres which can be stable under trying conditions. Further work on these lines is indeed highly promising.

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