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REVIEWS OF APPLIED ELECTROCHEMISTRY 9

Electrocatalysis: present and future

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The development of electrocatalytic materials and our knowledge of the factors which determine catalytic activity are reviewed. To the present, the main aim has been to produce electrocatalysts which minimize overpotentials, particularly for gas evolving or consuming electrode reactions. In the future, however, materials which optimize the selectivity of more complex reactions may increase in importance. It must be recognized that the development of electrocatalysts has been essentially empirical and there remains a gulf between those who develop electrode materials and those who seek to understand the physical chemistry of electrocatalysis.

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1. Introduction

The end of a year which has seen two large conferences [1, 2] devoted to electrocatalysis seems an appropriate time to reassess the role of electrocatalysis within electrochemical technology and to ask a number of questions. Where and why do we need new electrocatalysts? To what extent do we understand the relationship between catalyst composition and its activity for various reactions? Do we understand the mechanisms by which the successful electrocatalysts operate? How might we design and/or develop better electrocatalysts? Hence this review is my personal attempt to answer some of these questions and to define a way in which the subject should develop in the coming years.

First, I should define what I mean by electrocatalysis. This is necessary because the boundaries of the topic are diffuse; to some people, it is uncertain whether for a simple reversible electron transfer involving solution-free species an electrode such as mercury should be regarded as an electrocatalyst or whether catalysis by solution-free species (i.e. indirect electrode processes, e.g. the catalysis by Cl^- or Br^- of the anodic oxidation of propylene to propylene oxide or the oxidation of a toluene to a benzaldehyde via electron transfer from Mn^{2+} or Ce^{3+}) should be included. I take a narrower view and consider electrocatalysis to be the acceleration of a particular electrode reaction by the appropriate choice of electrode material. Such a definition implies a key role for adsorbed intermediates and that, at some electrodes, the reaction will occur only slowly (i.e. at high overpotentials) or not at all.

2. The need for electrocatalysts

The need for electrocatalytic materials is most obvious in the large, energy intensive electrolytic processes where the cost of electric power is a dominant factor in determining process economics. The prime example is the chlor-alkali industry which, worldwide, consumes in the order of 10^{11} kWh/year of electric power and where the cost of electricity is typically 30% of the total production cost. However, the same discussion would be appropriate to other systems (e.g. aluminium extraction, large scale water electrolysis, large battery systems for load levelling or energy storage, fuel cells). The energy consumption of an electrolytic cell is proportional to its voltage, V, which is given by an equation of the type

$$V = \Delta E_e - \eta_A + \eta_C - IR \qquad (1)$$

where ΔE_e is the difference between the equilibrium electrode potentials for the two electrode reactions, η_A and η_C are the overpotentials at the anode and cathode respectively (both will increase the numerical value of the negative cell voltage) and the IR term expresses the Ohm's

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law losses through the electrolyte and other current-carrying cell components. Here, electrocatalysis is the science of minimizing the overpotential terms, each given by a Tafel equation

$$|\eta| = \frac{2.3RT}{\alpha nF} \log (I/I_0) \qquad (2)$$

Hence it can be seen that a good catalyst will have a high exchange current density, I_0, and/or a low Tafel slope, $2.3RT/\alpha nF$. Clearly from Equation 1, it will be most important to minimize η when these terms are significant compared to ΔE_e and the IR term. This is most likely for intensively engineered systems using media of high conductivity; again chlor-alkali is the obvious example where the use of concentrated brine, low resistance cell components and narrow interelectrode gap cells combine to minimize the IR term. Of course, the cell voltage is a strong function of current density and in large scale processes the operating current density will be determined by a trade-off between the use of energy (helped by a low I) and the costs resulting from the initial investment for cells (lowered by the use of a high I).

Electrocatalysis may also have an important role in electrolytic processes where energy consumption may not be an important factor in the overall economics of the process. For example, in few electroorganic processes is energy consumption a particularly important factor [3]. For medium tonnage processes, the initial investment in cells and the cost of product isolation may well predominate. Both these factors may be helped by the use of a high current density and it is probably quite acceptable to take the large current density even at the cost of a substantial overpotential. Clearly this requires different modes of catalysis and, from the viewpoint of electrode materials, the main requirements are stability and, perhaps, the ability to inhibit unwanted side reactions. On the other hand, for special applications and fine chemicals, the major factor determining the process economics may be the selectivity of the process because of the high cost of starting materials and the cost of removing unwanted side products. Again electrocatalysis has a role to play. The electrochemical reduction of an organic molecule, A, can, in general, occur by three types of mechanism

(a) by direct electron transfer

$$A + e^- \rightarrow A^{-\cdot} \xrightarrow{2H^+ + e^-} AH_2 \qquad (3)$$

(b) by an indirect process involving an inorganic intermediate

$$M^{n+} + e^- \rightarrow M^{(n-1)+} \qquad (4)$$

$$2M^{(n-1)+} + 2H^+ + A \rightarrow 2M^{n+} + AH_2 \qquad (5)$$

(c) by an electrocatalytic route

$$2H^+ + 2M + 2e^- \rightarrow 2M\text{–}H \qquad (6)$$

$$2M\text{–}H + A_{ADS} \rightarrow 2M + AH_2 \qquad (7)$$

The last route offers much, largely unexplored, scope for the design of electrode materials which will give great selectivity, even stereoselectivity for a range of organic transformations. Such materials inevitably also give a bonus in terms of a reduction of overpotential since they operate close to the reversible hydrogen potential, maybe 1–2 V less negative than that required for routes of Type a. Parallel thought for transformations other than hydrogenations has led to initiatives to develop oxide electrodes and a variety of chemically modified electrodes [4, 5]. Again the main objective is unusual selectivity which might be used in sensors or synthesis.

An essential property of any practical electrode is stability at an acceptable cost. But corrosion of electrode materials in use and/or on open circuit is a widespread and difficult problem and the stability of the electrodes, even the counter-electrode, commonly determines the cell operating parameters. Because of the great stability of some electrocatalytic electrodes, particularly the DSA (see later), it is becoming common to use such materials even where no special catalytic activity is shown or needed. Hence one should bear in mind a need to seek materials which are simply inert. Certainly many modern engineering concepts have put greater strain on the electrode materials and, for example, in organic electrosynthesis the advantages of undivided cells is well accepted. Here, the common need is for materials to operate as counter-electrodes, evolving O_2 or H_2, without poisoning by components of the electrolyte or oxidizing or reducing the products. Again the overpotential may be quite unimportant.

3. Factors determining catalytic activity

The ultimate goal must be to select and/or design catalysts for each electrode reaction from a knowledge of the chemical and structural properties of potential catalyst materials. Unfortunately we remain far from this point, and this may explain why the last extensive discussion of the design of electrocatalysts of which I am aware was published as long ago as 1969 [6]. (Very recently Conway *et al.* [7] have edited a book containing relevant material.) On the other hand, it is not difficult to set out the factors which must be important in relating activity to composition and structure and this is done below.

Firstly, however, it should be recognized that electrocatalysts, whether they are in the form of

(a) metals, e.g. Pt, Ir, Ni
(b) alloys, e.g. PtSn, NiMo
(c) semiconductors, particularly oxides, e.g. RuO_2, $Ni(OH)_2$ and mixed oxides, e.g. spinels, perovskites and bronzes, or
(d) complexes, e.g. metal phthalocyanines and porphyrins

are almost always based on transition metal atoms or ions and it therefore seems likely that the design of the catalyst requires the placing of the transition metal in a matrix which optimizes the various factors discussed below, e.g. unpaired electron density and the spacing of transition metal centres. In just a few examples, e.g. SnPt, the two components of the catalyst have been chosen to perform different roles; SnPt has been studied as a catalyst for methanol oxidation [8, 9] and the choice of alloy was based on the concept that the organic molecule would adsorb on the Pt and oxygen more readily on the Sn.

3.1. *Chemical composition of the catalyst*

The dependence of electrocatalysis on the adsorption of intermediates has already been emphasized. An example is the hydrogen evolution reaction which is generally agreed to occur by the reaction

$$M + H^+ + e^- \rightarrow M\text{–}H \qquad (8)$$

followed by either

$$2M\text{–}H \rightarrow 2M + H_2 \qquad (9)$$

or

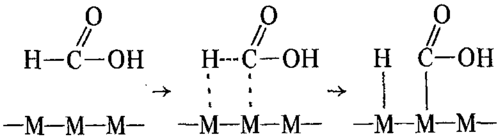
$$M\text{–}H + H^+ + e^- \rightarrow M + H_2 \qquad (10)$$

depending on the nature of the surface site, M. But in both cases, the formation of the adsorbed hydrogen atom creates an alternative, low activation energy pathway between proton and hydrogen gas and hence an enhancement of rate.

The predominance of transition metal species in electrocatalysts arises because of their unpaired *d*-electrons and unfilled *d*-orbitals which are available for forming bonds with adsorbates. It is to be expected that the free energy of adsorption will depend strongly on the number of unpaired *d*-electrons per metal atom and also on their energy levels, and, hence, both on the choice of transition metal and its detailed environment. In the limit, the surroundings (i.e. the adjacent metal atoms in a metal or alloy, the ligands to a metal complex or the oxide ions in an ionic lattice) and the adsorbate may be considered as ligands to the central transition metal ion acting as the catalyst centre, and the surroundings will moderate all the properties of the metal–adsorbate bond.

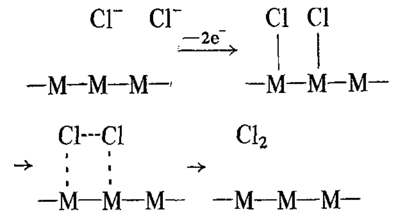
It should be noted that electrocatalytic reactions (of which sequences (8 + 9) and (8 + 10) are typical) will normally involve both the formation and cleavage of the metal–adsorbate bond. As a result the most effective catalysis will be observed when the bond is of intermediate strength – too low a free energy of adsorption will lead to insufficient coverage by adsorbate for it to be an effective catalyst while too high a free energy of adsorption will cause the rate of the cleavage step to become too low. This dependence of the rate of such catalytic sequences was recognized by Parsons [10] when he introduced the Volcano curve into the discussion of the hydrogen evolution reaction. An alternative mechanism for achieving effective catalysis is possible if the properties of the catalyst centre can change during the reaction sequence leading to a weakening of the metal–adsorbate bond. A change of oxidation state is the most obvious such change within an electrocatalyst.

In addition to these electronic factors, the geometric arrangement of catalyst centres is also important. All electrocatalytic reactions involve the cleavage or formation of bonds and it is likely that the rate of such processes will be substantially increased if they can occur as concerted reactions. For example, the oxidation of formic acid occurs via initial cleavage of the C–H bond [11] and it will clearly be advantageous if the bonds between the hydrogen atom and the surface, and the organic fragment and the surface can form as the C–H bond is broken, i.e.



(11)

A similar mechanism can be written for the chlorine evolution reaction where the concerted step could be the formation of the Cl–Cl bond i.e.



(12)

All such reactions depend on the correct spacing of the adsorption sites. A geometric requirement can also be placed on the surface by the adsorption of large molecules which need to interact with more than one surface site before a heterogeneous chemical reaction can occur. Such molecules might include aromatic hydrocarbons and butadienes.

The influence of the geometric arrangement of surface atoms on catalytic activity is well illustrated by studies on single crystal metal surfaces. Cyclic voltammograms for both proton reduction [12–14] and formic acid oxidation [15] are quite different on the various single crystal faces of Pt. Fig. 1 shows the curves for formic acid on three single crystal faces of Pt when the potential scans are commenced from a negative limit in the hydrogen adsorption regions. It can be seen that the responses for the Pt(100), Pt(110) and Pt(111) faces are quite different: at Pt(100), no oxidation is seen on the forward sweep but a peak occurs on the reverse; at Pt(110), a high current density peak is seen commencing at 0.66 V and a lower peak on the reverse; while at Pt(111), the current density for the oxidation is lower but the response is similar on forward and reverse scans and oxidation commences at the low value of + 0.25 V. It can also be seen that the *I–E* curve at polycrystalline Pt can be simulated by addition of the responses at the three faces.

While the geometric and electronic factors are not completely separable since one clearly affects the other, together they largely determine the relationship between catalytic activity and chemical composition.

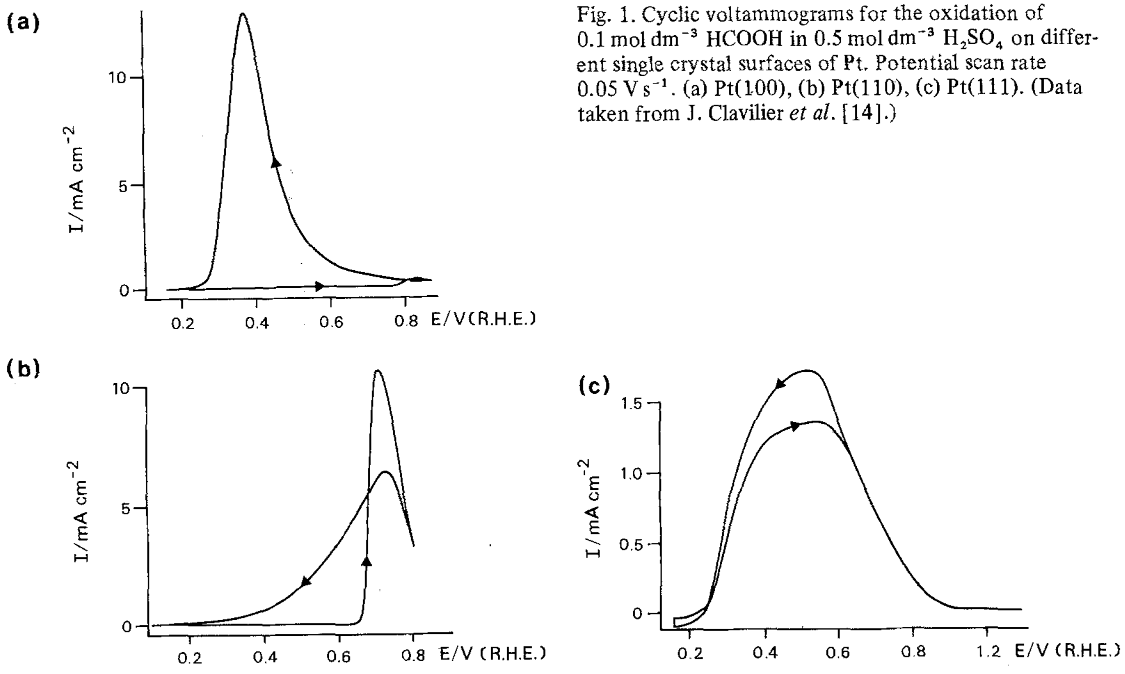


Fig. 1. Cyclic voltammograms for the oxidation of 0.1 mol dm^{-3} HCOOH in 0.5 mol dm^{-3} H_2SO_4 on different single crystal surfaces of Pt. Potential scan rate 0.05 V s^{-1}. (a) Pt(100), (b) Pt(110), (c) Pt(111). (Data taken from J. Clavilier *et al.* [14].)

3.2. *Real surface area*

Unlike mass transport controlled currents which reflect only the apparent geometric area of the electrode (provided the rugosity of the surface is small compared to the diffusion layer thickness), currents which depend on the rate of heterogeneous chemical reactions will scale with the real surface area of the electrode. Hence the current density for an electrocatalytic reaction can be increased by deliberately creating a rough surface; preparing a high surface area form of the electrocatalyst is part of the technology of manufacturing practical electrodes, see Section 5.

3.3. *The catalyst support*

Commonly electrocatalysts are expensive and are therefore prepared either in the form of small particles dispersed on a cheaper substrate or as a thin layer, again, on a support. The substrate must, of course, be a good electronic conductor and stable to corrosion in the electrolyte. Typically, it is a steel, titanium or a carbon. It is well known in gas phase catalysis that the support influences the activity of a catalyst but the parallel effects in electrocatalysis have been less widely studied. There is, however, much evidence that the form and pretreatment of carbons can determine the activity of an electrocatalyst [16] while a more extreme example is provided by the different activity to both hydrogen adsorption and formic acid oxidation of small Pt deposits on Au and vitreous carbon [17].

3.4. *Catalyst structure on an atomic scale*

There is also much, although rather fragmented, evidence to confirm that electrocatalytic activity is dependent on the structure of the catalyst close to the atomic scale. For example, factors such as the size and shape of small centres, the presence of grain boundaries, lattice defects and special sites, e.g. kinks, edges or screw dislocations, can all be important.

These effects are well illustrated by studies of the hydrogen evolution reaction on freshly deposited ruthenium metal [18, 19]. At mercury [18], it can be shown by potential step experiments that, over a range of potentials, only a single monolayer of ruthenium is deposited and that while the growth of the monolayer is accompanied by strong hydrogen evolution, the completed monolayer is only a very poor catalyst. This suggests the model shown in Fig. 2a where the catalytic sites for hydrogen evolution are the step sites at the perimeters of the growing islands of the Ru monolayer; the ratio of the activity of these perimeter sites to those on the top of the monolayer is of the order of 10^7. In contrast, on a vitreous carbon surface [19], Ru electrodeposits as hemispheres which grow three dimensionally. Again, the deposition is accompanied by hydrogen evolution but analysis of the potential step data clearly shows that there is a delay before gas evolution commences. This led to the model of Fig. 2b which assumes that small Ru centres are unable to catalyse hydrogen evolution and a critical diameter of approximately 15–20 nm is necessary before proton reduction becomes possible. The explanation of this size effect is uncertain: it could be electronic in origin but it is also possible that the density of some type of site, e.g. step sites increases as the centres grow.

The importance of special lattice sites may also be a contributor to the differences seen between single crystal electrodes [12–15].

3.5. *Selective poisoning*

Again, for a concept which is totally accepted in gas phase catalysis selective poisoning has had little impact on electrocatalysis. There has been little success in modifying surfaces so as to increase activity or selectivity by adsorbing a component of the electrolyte. An encouraging exception is the effect of metal adatoms (e.g. Pb, Tl or Bi) on the oxidation of formic acid on Pt surfaces [20–22]. It is found that a Pt surface fully covered by Pb adatoms is totally inactive for formic acid oxidation while a clean Pt surface, although initially active, is quickly poisoned by the formation of strongly adsorbed carbon fragments (identified by IR to be adsorbed CO [23]) and the current density drops to a very low value. In contrast, a Pt surface approximately half covered by Pb is very active and, moreover, maintains its activity. The accepted mechanism for the anodic oxidation of formic acid is [11]

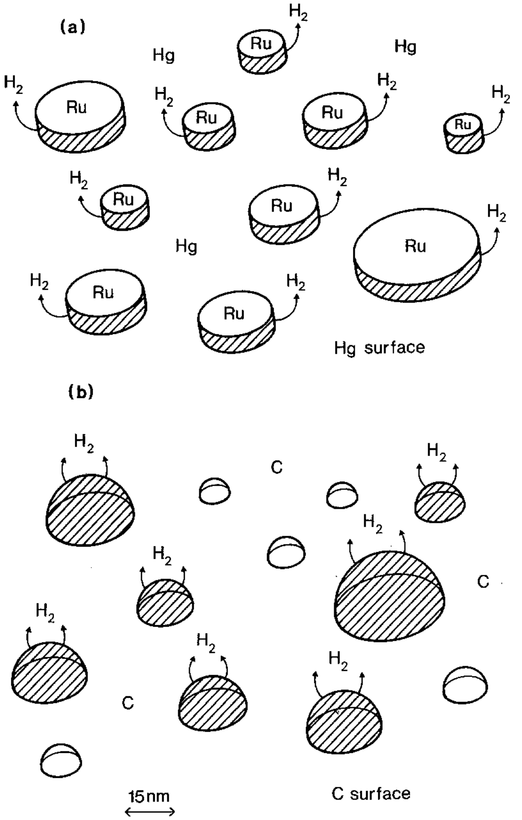


Fig. 2. Models for the H_2 evolution on Ru centres growing cathodically on (a) Hg and (b) C, from acid Ru^{3+} solution. Only the shaded areas are active for H_2 evolution. Note: on Hg the centres grow in only 2 dimensions, on vitreous C as hemispheres.

$$HCOOH + 2Pt \xrightarrow{r.d.s.} Pt\text{-}H + Pt\text{-}COOH \quad (13)$$

$$Pt\text{-}H - e^- \xrightarrow{fast} H^+ + Pt \quad (14)$$

$$Pt\text{-}COOH - e^- \xrightarrow{fast} H^+ + CO_2 + Pt \quad (15)$$

with the poison being formed by competing reactions of the adsorbed intermediates (r.d.s. is rate determining step). The explanation of the long term activity of the Pb/Pt surface lies in the conclusion that the surface poison must be formed in a reaction which requires more than two adjacent Pt atoms. The Pb adatoms, which are known to each interact with two Pt atoms, are distributed over the Pt surface in such a way that for a surface where $\theta_{Pb} = 0.5$ (see Fig. 3) there are many sites with two adjacent Pt atoms for the essential step (Reaction 13) to occur but very few sites where there are three or more adjacent Pt atoms where unwanted side reactions which poison can take place.

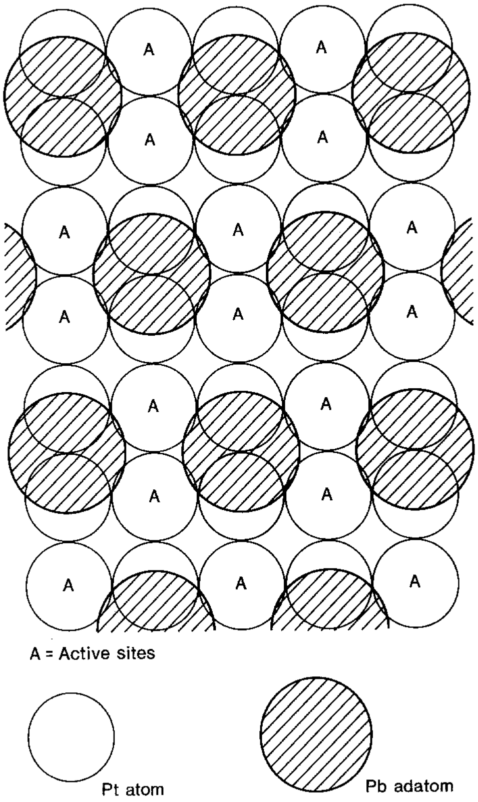


Fig. 3. A model for a Pt surface half covered by Pb adatoms. Each Pb adatom interacts with two 2Pt atoms leaving an active surface not able to form poison in the oxidation of HCOOH in acid solution.

4. Techniques for the study of electrocatalysis

The classical technique for investigating electrocatalytic reactions, the interpretation of steady-state *I–E* data in terms of Tafel slope and reaction orders [24], remains the most reliable, general method for obtaining an insight into the mechanisms by which they occur.

Other electrochemical techniques such as the measurement of capacitance, cyclic voltammetry and potential step methods can provide very detailed information about the surface of the catalyst in the electrolyte and also about the changes in the surface which occur with potential. On the other hand, information about reaction intermediates and the mechanism of electrocatalytic reactions is more difficult to obtain. The Southampton group have sought with some success

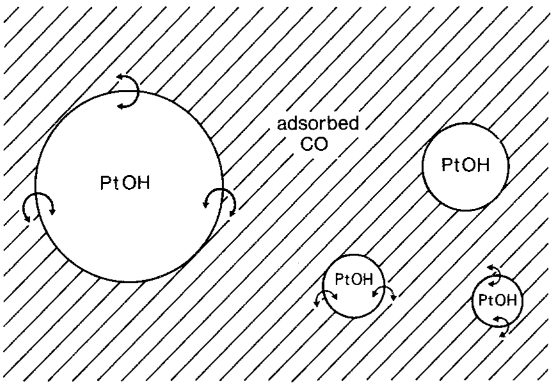


Fig. 4. Model for the oxidation of a monolayer of CO on Pt. Medium 1 mol dm^{-3} $HClO_4$. ↷ indicates typical sites where reaction between CO and PtOH occurs, leading by oxidation of Pt sites formed to expansion of PtOH islands.

to use the detailed analysis of *I–t* transients from potential step methods; one technique involves the study of the catalytic reaction at growing centres of the catalyst and the evolution of hydrogen at ruthenium is an example of this procedure. There are, however, other situations where transient analysis can be fruitful and lead to an insight into the molecular organization during electrocatalysis. For example, the oxidation of carbon monoxide adsorbed onto Pt has long been known to occur by a chemical reaction with a platinum oxide formed on the surface. By analysis of *I–t* transients, however, it can be shown [25] that a monolayer of adsorbed carbon monoxide is oxidized by a mechanism initiated by nucleation of the platinum oxide phase. The platinum oxide then grows as a monolayer but the growth of the monolayer occurs by a reaction between the oxide and carbon monoxide as they occur at adjacent surface sites i.e. at the perimeter of the islands of the platinum oxide phase. This mechanism is illustrated in Fig. 4 and by the equations

$$\mathrm{Pt} + \mathrm{H_2O} - e^- \rightarrow \mathrm{Pt{-}OH} + \mathrm{H^+} \qquad (16)$$

$$\mathrm{Pt{-}OH} + \mathrm{Pt{-}CO} - e^- \xrightarrow[\text{at perimeter of Pt–OH islands}]{\text{r.d.s.}} 2\mathrm{Pt} + \mathrm{CO_2} + \mathrm{H^+} \qquad (17)$$

$$2\mathrm{Pt} + 2\mathrm{H_2O} - 2e^- \rightarrow 2\mathrm{Pt{-}OH} + 2\mathrm{H^+} \qquad (18)$$

Much has been written [26–29] about *in situ* and *ex situ* spectroscopic techniques (see Table 1) for the study of electrode/electrolyte interfaces. There is no doubt that these methods contribute much to our knowledge of the composition and structure of the catalyst in the electrolyte but the information they have produced about reaction mechanisms remains limited. Despite the great advances which have been made with these techniques, it remains impossible to make measurements on the short timescale essential to identify intermediates in reactions which occur at practical current densities or to obtain the resolution necessary to distinguish similar intermediates in complex mechanisms, e.g. the oxidation of methanol. IR probably remains the most promising method; it has been applied to both the oxidation of organic fuels [23] and the hydrogen evolution reaction [30]. In the former case, while it leads to convincing conclusions concerning the nature of

Table 1. Spectroscopic methods for the study of electrode/electrolyte interfaces

In situ	Ex situ
UV–visible reflectance spectroscopy	X-ray photoelectron spectroscopy (XPS)
IR reflectance spectroscopy	UV–photoelectron spectroscopy (UPS)
Raman vibrational spectroscopy	Auger spectroscopy
Transmission spectroscopy using optically transparent electrodes	Electron energy loss spectroscopy
Ellipsometry as a spectroscopic tool	Low energy electron diffraction (LEED)
Mössbauer spectroscopy	Reflectance high energy electron diffraction (RHEED)
Electron spin resonance	Ion scattering spectroscopy
Photoelectrochemistry	
Acoustoelectrochemical methods	
X-ray diffraction	
Surface-plasmon spectroscopy	
NMR-broadline and high resolution spectroscopy	
Extended X-ray absorption fine structure (EXAFS)	

the poison it cannot yet be used to identify reaction intermediates. Finally, the contribution of scanning electron microscopy to our knowledge of the structure of surfaces cannot be overemphasized.

5. The design of practical electrodes

The first essential of a practical electrode is a high activity for the desired reaction which is stable over a long period of time. This will generally mean the ability to deliver a current density of 0.1–1.0 A cm^{-2} at an acceptable overpotential (in an energy conscious environment, maybe < 100 mV) and this performance must be maintained for the service interval of the cell, usually more than a year. The main factors likely to lead to loss of activity are

(a) mechanical erosion or damage during servicing and handling
(b) corrosion in the electrolysis medium either when the cell is on load or standing on open circuit
(c) poisoning either by side reactions or adsorption of an impurity from the electrolysis medium
(d) recrystallization of the surface leading to a substantial loss in surface area; such changes are much accelerated by cycling the electrode through changes in oxidation state

Each of these factors will need to be tested before a new electrode material will be accepted for use in a commercial cell house.

It will also be necessary for the electrode material to show the desired selectivity. Moreover, in practice, it may be essential for this selectivity to be based on favourable kinetics rather than thermodynamics. For example, the anode in a chlor-alkali cell is expected to evolve 100% chlorine and any oxygen evolved represents a safety hazard as well as a loss in current efficiency. The equilibrium potential of the H_2O/O_2 and the Cl^-/Cl_2 couples at pH 4 (a typical pH for the anolyte of a chlor-alkali cell) are, however, + 0.99 and + 1.36 V, respectively. Hence it can be seen that oxygen is thermodynamically the preferred reaction and one is dependent on the anode being a good catalyst for chlorine but an inhibitor of oxygen evolution.

It was noted above that it will be advantageous for the catalyst to be used in a high surface area form. In any case, catalysts are usually expensive materials and are therefore used as a coating on a cheaper substrate. Hence the coatings are manufactured by techniques such as spray coating followed by thermal decomposition or electrodeposition, under conditions which produce a high surface area deposit. In some cases the surface roughness is enhanced further by codepositing a material which can later be leached out of the catalyst. Platinum remains an excellent catalyst for many reactions but it is seldom used because of its cost and much research effort has gone into finding alternative materials or using Pt in a highly dispersed form so that the Pt loading of the final electrode is less than 1 mg cm^{-2}.

Many useful electrocatalytic reactions involve a gaseous reactant or product and the overall design of the electrode must take this into account. When it is the electroactive species which is the gas, the electrode is normally a porous structure with the gas entering from the side away from the electrolyte. The porous electrode is made by compressing onto a conducting grid a mixture of the catalyst, a conducting powder (normally some form of carbon) and perhaps a hydrophobic material (e.g. PTFE). The gas is then passed over the back of the electrode so that a three-phase interface between gas, electrolyte and catalyst is formed within the pores. Recent gas electrodes are duplex structures with a more porous layer on the gas side and a less porous layer containing the catalyst on the electrolyte side; such structures make it easier to control the three-phase interface where all the electrochemical reaction occurs. In gas evolving systems the electrode is commonly macro-shaped in such a way that the gas is rapidly passed out of the interelectrode gap (where it increases the resistance of the cell) into a space behind the gas evolving electrode. Fig. 5 shows one design of such an electrode. In addition the electrode coating may contain a component to reduce the extent to which small bubbles stick to the surface.

6. Some electrocatalytic reactions

6.1. *Chlorine evolution*

Anode materials for chlorine evolution have been particularly well described in several chapters in two conference books [31, 32] and three recent

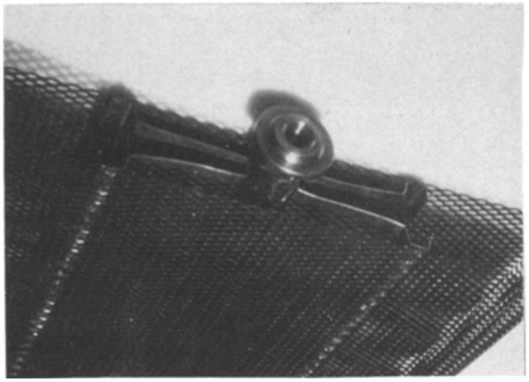


Fig. 5. Diamond Shamrock dimensionally stable anodes for a diaphragm Cl_2–NaOH cell. Note the complex shape which allows Cl_2 gas to pass out of interelectrode gap. (Photograph supplied by Diamond Shamrock Inc.)

reviews [33–35]. Even so, the spectacular success of the RuO_2 coatings on Ti, universally known as dimensionally stable anodes (DSA), make them an essential element of any review on applied electrocatalysis. These electrodes, separately developed by Beer and Cotton during the early 1960s, are prepared by thermal decomposition of $RuCl_3$ solutions sprayed onto the Ti substrate. Their performance was so outstanding, that during a ten year period, almost all the graphite anodes in the chlor-alkali industry were replaced by them. Now improved DSA are available and slightly different coatings will be used in mercury, diaphragm and membrane cells. Typical performance will be a current density of up to 1.5 A cm^{-2} at an overpotential of 10–40 mV and a coating lifetime of several years (this compares with 500 mV at a lower current density and a continuous wear rate of 5 g C per ton Cl_2 for graphite anodes). In addition to the much superior catalytic properties of the DSA, it is their stability and the consequent flexibility of cell design including much reduced and constant interelectrode gaps which have produced very large energy savings.

In retrospect, the success of catalytic chlorine electrodes is not surprising. The overpotential for chlorine evolution can be low at many materials while the kinetics of oxygen evolution are notoriously poor. The key property of the DSA was their stability to corrosion. It is therefore interesting to note that similar performances have been claimed for other oxide materials, namely cobalt spinels (e.g. $Zn_xCo_{3-x}O_4$ containing ZrO_2 to increase surface area) [36] and palladium oxide [37].

6.2. *Hydrogen evolution*

The hydrogen evolution reaction is probably the most studied of electrode processes and the mechanism and kinetics of the reaction at many cathode materials have been elucidated [38, 39]. In electrochemical technology, the greatest interest in this reaction is with an alkaline catholyte and, until recently, the electrode material was always steel or occasionally nickel despite an overpotential of over 300 mV at practical current densities. It

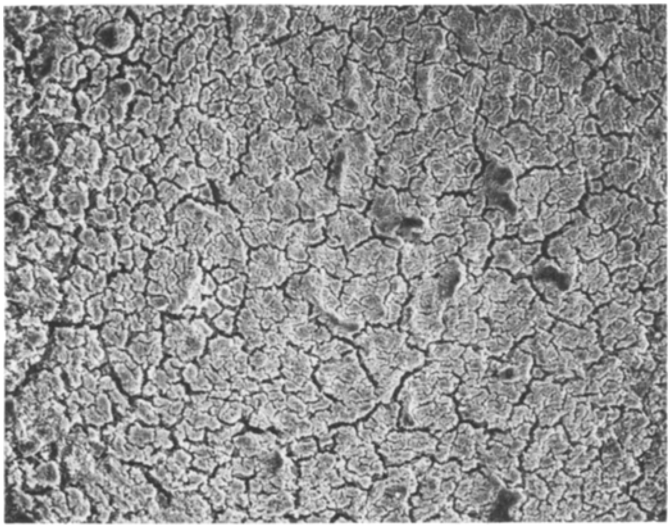


Fig. 6. Scanning electron micrograph of NiMo catalytic cathodes for H_2 evolution. (Photograph supplied by BP Ltd.)

had long been recognized that Pt metals would give a better performance but such metals were considered too expensive. With the increase in energy prices, there has been an interest in cheaper but good catalysts for application in both chlorine and water electrolysis cells. Initial attempts concentrated on the preparation of high surface area Ni deposits either directly or by coating steel with a mixture of NiAl or NiZn; in the alkaline electrolysis medium the Al and Zn dissolve leaving a form of Raney nickel [40]. Later it was found that some nickel and cobalt alloys, e.g. NiMo [41–43], prepared either by spray coating and thermal decomposition followed by treatment with hydrogen gas or by electrodeposition, showed much higher activity and overpotentials of around 60 mV for a current density of 0.25 A cm^{-2} have been reported. In these cases, the Mo remains in the surface and the catalytic activity is thought to be due to the presence of the alloy. Several cathode coatings are either available or in the late stages of development but there remains doubts about their long term stability in practice and there is uncertainty as to whether such coatings will have the success of DSA.

6.3. *The oxygen electrode*

There is technological interest in oxygen evolution (both as a generator of pure gas and life support atmospheres and as a counter-electrode reaction for many reduction processes), and in oxygen reduction (as a low potential cathode in chlor-alkali cells, for fuel cells and batteries, and as a counter-electrode for other oxidations). The overall reaction is

$$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O \qquad (19)$$

with a formal potential of + 1.23 V at pH 0. This is clearly a multistep process and certainly the reduction is further complicated by reaction routes where hydrogen peroxide is an intermediate or even a final product. Because of the complexity of the reaction and difficulties in the formation and breaking of the O–O bond, the kinetics of both oxygen evolution and reduction are very poor at almost all electrode materials. The choice of catalysts is further restricted by the problems of corrosion at the potentials where these reactions take place. Our knowledge of the oxygen electrode has been reviewed [27, 44, 45].

At the present time, the electrode materials which are commonly used as anodes for oxygen evolution are lead dioxide (sometimes containing another metal such as Ag) or even steel although this may lead to an overpotential of more than 0.5 V. Better materials are becoming available, for example, some semiconducting oxides (e.g. $NiCo_2O_4$) [46] work reasonably in alkaline solution while for acid solution RuO_2/Ir coatings on Ti [47, 48] are probably the best available giving 100 mA cm^{-2} at about 250 mV overpotential. For oxygen reduction the most practical catalyst remains Pt; indeed, dispersed Pt on C electrodes with Pt loadings as low as a few mg cm^{-1}, manufactured using special techniques for creating small crystallites, are currently on test in a pilot scale chlor-alkali plant [49]. In the laboratory there is interest in both metal oxide catalysts [50, 51] and transition metal macrocycles (e.g. Fe or Co phthalocyanines and porphyrins) [27, 45]. The macrocyclic species can be quite good catalysts but there are problems over long term stability. Moreover, it has been found that heat treatment to 950° C of the metal macrocycles adsorbed on carbon greatly enhances the catalytic activity of the surface [27, 45, 52] and since such strong heat treatment must destroy the metal complex, the nature of the catalyst is presently unclear. There is also great interest in dimeric, cofacial prophyrins [53] where it should be possible to control both the electronic environment of the two metal centres via ligand substituents and, separately, the M–M distance and thus ability of the oxygen molecule to bond to both metal centres. Such complexes could provide a way to readily cleave the O–O bond and hence be good catalysts. Early indications are that the species are good catalysts but the resulting electrodes are not yet very stable.

6.4. *Fuel cell anode reactions*

The original concept of the fuel cell was that it would convert a primary fuel, methanol or better a hydrocarbon, and air directly into electrical energy. In the absence of potential catalysts for such anode reactions, fuel cell technology has concentrated on the development of cells where the anode fuel is H_2 or $H_2 + CO$. Two types of system are under development.

(a) Cells where the electrolyte is concentrated phosphoric acid at about 200° C. In such cells both electrodes are Teflon-bonded gas diffusion electrodes with dispersed Pt as the catalyst and the hydrogen feed to the anode must be free of CO and SO_2. Typically such cells give 200 mA cm^{-2} at a cell voltage of 0.67 V (cf. reversible cell potential 1.16 V) but such a performance was considered sufficient to allow the building of a 4.8 MW fuel cell in New York City.

(b) Cells where the electrolyte is a mixture of molten carbonates at 650° C. At this high temperature it is possible to use nickel electrodes and to feed the anode a gas mixture of $CO + H_2$. The cell voltage can be as high as 0.9 V at 150 mA cm^{-2}.

Both cells suffer from the problem that to use a primary fuel, the cell must be combined with a catalytic reactor to produce the cell feed. This increases greatly the complexity of the engineering and reduces the overall energy efficiency of, say, oil to electricity, to about 40%.

The development of catalysts for primary organic fuel oxidation is presently becalmed. Materials studied so far suffer from both low activity and poisoning problems. The use of metal adatoms (see Section 3.5) to protect the surface from poisoning reactions may point the way to overcoming one of the problems. To produce higher activity catalysts we need to understand how to promote reactions of the type:

$$CH_3OH + 2Pt \rightarrow Pt\text{–}H + Pt\text{–}CH_2OH \qquad (20)$$

In the last two decades there has been little progress towards such materials.

6.5. *The reduction of carbon dioxide*

The cathodic reduction of carbon dioxide is an interesting reaction; carbon dioxide is cheap and under some conditions its reduction can lead to formic acid, oxalic acid, methane and, potentially, other molecules such as methanol and glycollic acid. The reaction has, however, two problems: i. the current density is limited by the low solubility of free CO_2 in many media and the slow dehydration of bicarbonate in water, ii. the potential at which the reduction occurs is very negative to the reversible potential. Both are under attack with some success. A recent patent [54] has reported the use of a gas feed electrode for the reaction in aqueous solution and claimed a 70% current efficiency for formic acid at a current density of 150 mA cm^{-2}. The reduction in the overpotential is being tackled by the use of transition metal complexes (e.g. $Fe_4S_4(SPh)_4^{3-}$ and Co(Salen)) [55, 56]. As yet the complexes are usually free in the electrolyte, but substantial reductions in overpotential can be achieved.

6.6. *The hydrogenation of organic molecules*

At the turn of the century, many cathodic reductions were written as occurring via atomic hydrogen formed by the initial reduction of water. Later studies showed that this formulism was incorrect and, in general, the initial step was addition of an electron to the molecule. Even so, it is clear that at cathode materials where there is a substantial coverage by adsorbed hydrogen and where organic molecules are likely to adsorb, catalytic hydrogenation is possible. Indeed, through the years there have been many examples of such reactions including some of clear interest in synthesis, for example, the hydrogenation of functional groups [57], benzene rings of aromatic molecules [58] and steroids [59]. Such reactions have been reported at high surface area Pt, Pd, Rh and Ni cathodes and in some cases, e.g. the reduction of phenol to cyclohexanol [58], the reactions go much better at one metal. Moreover, the hydrogenation of phenol shows a support effect [58], Pt on C being a much better cathode than Pt on Pt. The selectivity of such hydrogenations also depends strongly on the electrolysis conditions the ratio of ethylbenzene to 1-phenylethanol from the reduction of acetophenone at Pt/Pt is highest in almost anhydrous ethanol and in the absence of cations added to the acid. On the other hand, current density and the choice and strength of acid had little effect [60]. In contrast, however, the hydrogenation of phenol at Rh/C has been shown to be adversely affected by the addition of methanol to the aqueous acid.

Hence it can be seen that interesting synthetic reactions are possible and the yield of desired product can be optimized empirically. Moreover, the current density need not be particularly low. On the other hand, we have little understanding of the physical chemistry of such systems (the present status has also been summarized by Beck [61]), the factors which determine the choice of electrode material, current density and other electrolysis conditions. Therefore we need a thorough, in-depth study of several of these systems so that our choices may be made on a rational basis.

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