

REVIEW  
**A primer on electrocatalysis**

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*Abstract:* A short review of the development and achievement of electrocatalysis in the last 50 years is given. The need for the knowledge of the reaction mechanism and position of the rate determining step for rational choice of catalyst is particularly stressed. Fundamental aspects of electrocatalysis are elaborated in more detail on the examples of electrochemically important reactions of hydrogen evolution and oxygen reduction, as well on the reaction of electrochemical oxidation of organic fuels (*e.g.*, methanol).

*Keywords:* electrocatalysis, intermediates, adsorption, hydrogen evolution, oxygen reduction, fuel cells.

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1. OBJECTIVES OF THE PAPER

It is undeniable that electrocatalysis is a very important subject. This is not only for the obvious situations, for example, increasing the amount of energy obtained

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from a fuel cell, –but also for every kind of electrochemical reaction which is going to be developed industrially, because the cost of producing a certain amount of a substance is simply proportional to the total amount of electricity which is needed, and this depends upon the overpotentials at the electrode–solution interfaces.

There is no doubt that everybody in the field would agree that the oxygen reduction reaction is more important than any other in respect to electrocatalysis. This is because it gives rise to the principal overpotential in fuel cells and fuel cells are in a stage of rapid development so that anything related to increasing the efficiency of them is economically important.

Just to show the tremendous savings which could be obtained by improved electrocatalysis of the oxygen reduction reaction (and any corresponding one with the same types of  $i_0$ ) let us start with a familiar equation, derived from Tafel's Law, and say that the change in overpotential at a given current density in the irreversible region with two different  $i_0$ 's are given (roughly of course) by:

$$\Delta\eta = 2 \frac{RT}{F} \ln \frac{(i_0)_1}{(i_0)_2}$$

There is only one assumption in this equation and that is that this value for  $\alpha$  in the relevant Tafel equation for the reaction is about one-half, which is a widely observed value (though for certain rate determining steps, it may indeed be substantially increased, thus reducing the overpotential).

Now, the order of magnitude for the  $i_0$  of the oxygen reduction reaction at room temperatures is  $10^{-10}$  to  $10^{-5}$  A cm<sup>-2</sup> so that were we able to increase the exchange current density, by means of electrocatalysis from  $10^{-10}$  A cm<sup>-2</sup> to  $10^{-5}$  A cm<sup>-2</sup>, then the lessening of overpotential (see Eq. (1)) would be about 0.6 V.

One immediately appreciates the large increase in the efficiency of conversion in fuel cells (more than 30 %) which this implies. Catalysts which increase the exchange current density for the oxygen reduction reaction at room temperature to the extent of  $10^5$  times are not yet known but the point of the present article is to explain how they may be approached and fuel cell efficiencies brought up toward 80 %.

Incidentally, the paper is for the electrochemists who already knows the field, but is entering into the subfield of electrocatalysis. Hence, it is a heuristic article and is not intended for the expert in the electrocatalytic field.

## 2. THE NEED TO THINK OUT EACH CASE ANEW RATHER THAN LOOKING FOR "A GOOD CATALYST"

Of course, everybody knows that 'platinum is a good catalyst' and this phrase has often given rise to the impression that one has to look for a substance which will be, in a universal way, 'a good catalyst'. There are several reasons why platinum has been brought out and focused upon and two of them are that it is an easily available substance which can catalyze substances at highly anodic potentials without being decomposed. In this sense, it has wide applicability. Indeed, one of

the difficulties in finding other catalysts, better than platinum, is that, although one might make theoretical calculations which would indicate a given substance to be a better catalyst than platinum it may not withstand the anodic potentials which are often met in, *e.g.*, the reduction of oxygen and undergo decomposition itself, thus making it impractical to use.

One of the properties of platinum, – its stability under anodic potential, – parallels its thermal stability as is shown in the following table (*cf.* Table I)<sup>1</sup> shows that there are five metals which have a melting point lower than that of platinum (for which the melting points is 1770 °C) and five metals the melting point of which is higher than that of platinum. One would immediately expect that among the latter group, the electrocatalysis might be better than that on platinum for some reaction involving a rate-determining proton transfer and this indeed does occur with ruthenium and ruthenium oxide in oxygen reduction. The material melting points higher than Ru are rarely met materials and have not been examined for their catalytic properties.

TABLE I. Melting points of some refractory elements<sup>1</sup>

Lower m.p. than Pt	°C		Higher m.p. than Pt	°C
Lanthanum	920		Rhodium	1996
Gold	1003	Platinum	Ruthenium	2427
Palladium	1550	= 1770 °C	Iridium	2454
Tantalum	1695		Osmium	2700
Lutechium	1760		Tungsten	3380

It is easy to demonstrate quite dramatically why each case should be looked on anew. For example, let us take the hydrogen evolution reaction for which we have been receiving reliable data for sixty years. One finds here<sup>2</sup> that there are a number of metals in which the reduction of  $H_3O^+$  increases in rate, at a given potential, if the bonding strength of the adsorbed hydrogen to the catalysts (all 'soft' metals) *increases*, but yet is low compared with that on the transition metals.

On the other hand, on a group of metals, particularly the transition metals, the trend goes in the other directions: as the bond strength of H to the catalyst gets greater, the reaction rate gets slower (hence, the volcano type relation between  $\log i_0$  and the bond strength). Obviously, here, the rate determining step for the hydrogen evolution reaction has changed from that on the soft metals where it is proton discharge onto surfaces on which the H atom concentration is low to that on the hard transition metals where it is electrochemical desorption by the discharge of protons onto adsorbed hydrogen which (because of the higher bond strength) covers the surface to a high degree.

Therefore, looking for catalysts to evolve hydrogen on the soft metals and looking for catalysts evolve hydrogen on the transition metals in an entirely different thing, dif-

ferent trends are present (although the reaction is the same), and one will end up with quite different catalysts for an optimal performance in this well known reaction.<sup>3</sup>

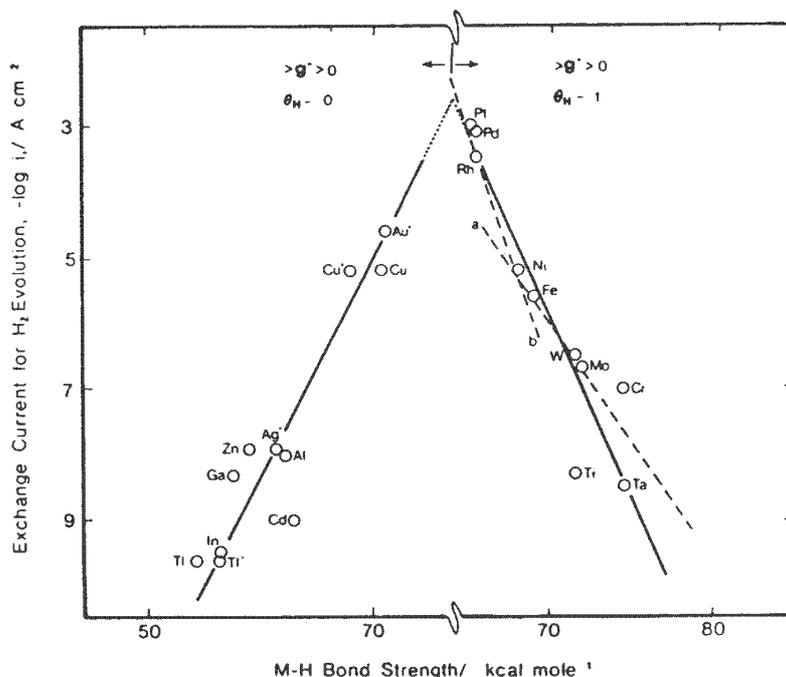


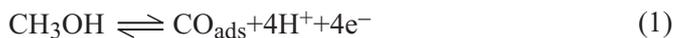
Fig. 1. A plot of exchange current density for hydrogen evolution reactions vs. M-H bonding strength.<sup>3</sup>

### 3. RATE DETERMINING STEP

#### 3.1. Need to evaluate the rate determining step in multi-step reactions

Confusion originating in the 1960's, affected electrochemistry in the last few decades because so many fundamental electrochemists used the relatively rare one step redox reaction of the type  $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ . Such reactions do not involve electrocatalysis because they are simply electron transfer reactions at the interface and the properties of intermediates and their bonding to the surface do not come in. In fact, it has been shown<sup>4</sup> that the energy of activation of these simple reactions on noble metals is independent of the work function of these metals.<sup>5</sup>

The majority of practical electrode reactions (for example, the oxidation of methanol) involves several steps. A typical example for methanol would be:



The question here then, – vital to know before one can *start* thinking of the electrocatalyst, – is which is the rate determining step? If one knows that (and only if one knows it) then one can change the properties of the surface so that this particular step in the consecutive sequence, reaction 3 in the above sequence,<sup>6</sup> is optimized in its rate (which, then, will accelerate the rate of the overall reaction).

### 3.2. A difficulty of rate determining steps in more complex reactions

As the number of consecutive steps in an overall reactions increases exceeds three (it may go to much more, *e.g.*, six or seven consecutive steps) the difficulty of determining the rate determining step increases. For example, let us look at the possible rate determining steps (with preceding quasi-equilibrium steps where present) for the oxidation of propane on platinum in phosphoric acid at temperatures between 80 °C and 150 °C.<sup>7</sup>

TABLE II. Nine possible rate determining steps (with preceding quasi-equilibrium steps where present for the oxidation of propane on platinum in phosphoric acid. 80 °C to 150 °C and 300 to 500 mV (Reversible Hydrogen Scale)<sup>7</sup>

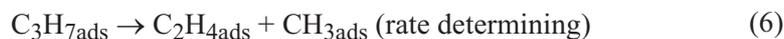
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1. $C_3H_{8soln} \rightarrow C_3H_{7ads} + H^+ + e^-$
2. $C_3H_8 \rightleftharpoons C_3H_{7ads} + H^+ + e^-$ $C_3H_{7ads} \rightarrow C_3H_{6ads} + H^+ + e^-$
3. $C_3H_8 \rightleftharpoons C_3H_{7ads} + H^+ + e^-$ $C_3H_{7ads} \rightarrow C_3H_{6ads} + H^+$
4. $C_3H_8 \rightleftharpoons C_3H_{7ads} + H^+ + e^-$ $C_3H_{7ads} \rightarrow C_2H_{4ads} + CH_{3ads}$
5. $C_3H_8 \rightarrow C_3H_{6ads} + 2H^+ + 2e^-$
6. $C_3H_8 \rightleftharpoons C_3H_{8ads}$ $C_3H_{8ads} \rightarrow C_3H_{7ads} + H^+ + e^-$
7. $C_3H_8 \rightleftharpoons C_3H_{7ads} + H^+ + e^-$ $H_2O \rightleftharpoons OH_{ads} + H^+ + e^-$ $C_3H_{7ads} + OH_{ads} \rightarrow C_3H_7OH_{ads}$
8. $C_3H_8 \rightleftharpoons C_3H_7 + H^+ + e^-$ $C_3H_7 + H_2O_{soln} \rightarrow C_2H_4OH_{ads} + CH_{3ads} + H^+ + e^-$
9. $C_3H_8 \rightleftharpoons C_3H_{7ads} + H^+ + e^-$ $C_3H_7 \rightleftharpoons C_3H_{6ads} + H^+ + e^-$ $C_3H_{6ads} + H_2O_{soln} \rightarrow C_3H_7OH_{ads}$

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In fact, in these more complex cases, there is a lack of certainty in the rate determining step until one takes into account other things, for example, the energy involved in the various possible stages, that one can come to a conclusion.

The conclusion with propane oxidation is that the rate determining step involves some carbon–carbon bond breaking and that it is a chemical reaction so that the first two steps are:



Another difficulty with rate determining steps comes in reaction which have many steps, let us say more than six. This occurs often in biochemical situations and the heat of activation for the various successive steps comes rather close together. If the difference is less than, say, 10 kJ/mol, then it becomes questionable to what extent the reaction is controlled in rate by *one* step because the situation is that more than one step gives more or less the same resistance to the reactions progress and this has to be allowed for in constructing the optimal catalyst.

### 3.3 To what extent is the finding of a rate determining step vital in advancing towards new catalysts

The reason is that if one does not know a rate determining step of the reaction which determines the overall rate, then how is one to design the surface so that the energy of activation of the individual reaction which is rate controlling for the whole reaction can be optimized to maximum velocity?

There is a further complication with rate determining steps in that although one may start off with a reaction and using certain catalysts (inevitably, platinum to start with) determine the rate determining step, then of course if that is made sufficiently fast, another reaction will become the rate determining step and it is that reaction which must be allowed for in the design of catalysts.

## 4. THE COMMENCEMENT OF RATIONAL THINKING ABOUT ELECTROCATALYSIS

Although Bowden and Rideal<sup>8</sup> are the true originators of studies of rates on a series of different materials, it was Horiuti and Polanyi<sup>9</sup> who wrote for the first time a paper which began the *theory* of electrocatalysis.

They considered the hydrogen evolution reaction and drew curves (Fig. 2) for the potential energy–distance variation in respect to the proton and its oscillations with oxygen atom in the initial state. On the other side, they drew the potential energy curves for the hydrogen–metal interaction, *i.e.*, the final state.

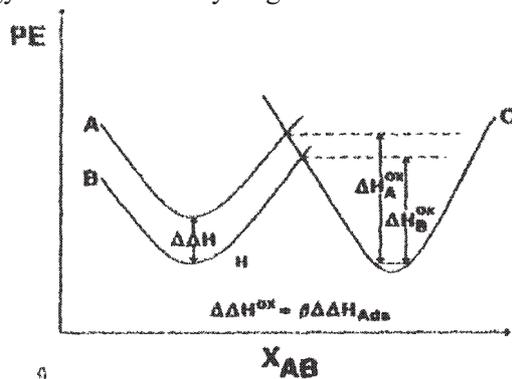


Fig. 2. The effect of the variation of the  $\Delta\Delta H$  (change of the enthalpy of adsorption of  $\text{H}_{\text{ads}}$  from metal A to a strongly adsorbing metal B) on the potential energy–distance diagram.<sup>9</sup>

Of course, when these two curves intersect, one can obtain a calculation of the heat of activation for the forward reaction (assuming proton discharge is the rate-determining step). Horiuti and Polanyi pointed out, that in this case, with the assumption of a mechanism involving proton discharge, then it would be an improvement if the change of catalyst were in the direction of increasing hydrogen–metal bond strengths (Fig. 2).<sup>9</sup>

#### 4.1. The term "electrocatalysis"

Reaction rates varied with the different electrodes (*i.e.*, catalysts) which Bowden and Rideal used in their classic study of reaction rates, but they did not feature this, for example, they did not extrapolate the overpotential–log *i*-lines to a specific representative potential and then find the relative rates of the reaction at this potential on a number of metals. They always looked at the overpotential alone and the relative *rates* of the reaction was not discussed (although implied). It was Agar<sup>10</sup> in 1947 who introduced the idea of exchange current density and focused for the first time upon *rates* at a fixed potential with the potential as something controlling the rate.

Even then the word "electrocatalysis" was not introduced by Grubb until 1963 when he introduced the term in fuel cell work.

### 5. WHAT ARE SOME OF THE METHODS FOR INVESTIGATING A MECHANISM AND FOR DETERMINING A RATE DETERMINING STEP?

Some of them are given in Table III.

TABLE III. Some methods for the determination of the mechanism (including the rds) of electrode reactions

Method	Type of information
Rate at constant pressure and temperatures as a function of overpotential	Tafel constants $\partial \ln i / \partial \eta$ may give the rds, particularly for hydrogen evolution
Rate at constant potential and pressure as a function of temperature	Gives $\Delta H_{ox}$ . Eliminates rds's with significantly higher $\Delta H_{ox}$ 's
Rotating disk with ring	Identifies and determines certain kinds intermediates and the mechanism which involves them
Ellipsometry and ellipsometric spectroscopy	Used spectroscopically, determines valence state, <i>etc.</i> , of surface atoms. Faster in data processing time than FTIR. An under-developed technique
Impedance (real and imaginary) as a function of $\omega$ (the applied AC frequency)	Can isolate $\omega$ ranges in which impedance of one branch of a circuit dominates. Computer simulation allows determination of various <i>R</i> 's in circuit from the impedances. A step with an <i>R</i> at least 10 times greater than any other in the sequence is the rds

TABLE III. Continued

Method	Type of information
Fourier transform infrared spectroscopy (FTIR)	Can lead to identification of intermediate radicals present on the electrode surface. Such information distinguishes path and rds
Comparison of rate of reaction containing H and one or more of its isotopes	Highly diagnostic for reactions involving protons
STM and AFM	Can observe surface terrain at 1–2 nm definition; occasionally atoms resolution, in solution. AFM particularly useful in observation of biosurfaces
Computer applications	Can be programmed to recognize patterns of behavior characteristic of certain mechanism sequences, computer simulation is vital in, <i>e.g.</i> , impedance spectroscopy.

Of course, not all these methods need be used in a given case, it depends on how the determination of the mechanism the reaction turns out. There are occasionally situations, particularly with the hydrogen evolution reaction,<sup>12</sup> where a single measurement, for example, the measurement of the separation factor between hydrogen and tritium as a function of potential, will give rise to the determination of the rds (rate determining step).

#### 6. A NEEDED CHOICE

At what potential shall one compare the rates of a reaction on various catalysts? The generally accepted answer to this question is to compare them all at the reversible potential, *i.e.*, namely compare their various  $i_0$ 's. This is all very well for a reaction which is to be treated academically and theoretically, but the electrochemical engineer needs a different criterion. He is usually trying to work at the maximum possible rate, – the limiting current, – and he wants to know what is the overpotential (the energy loss) at this point. Of course, as all the reactions have different limiting currents, it is not very helpful to choose the overpotential at the potential of the rds and so electrochemical engineers who wish to compare the efficiency of various metal catalysts in reducing the overpotential (hence the cost of the reaction) often take the current density at 1 milliamper per square cm, a medium current density, where the Tafel lines are relatively straight and continuous so that comparing the overpotential reached at this current density may be the best indicator of electrocatalysis on various surfaces. The electrochemical engineer would like to see a minimum overpotential at this representative current density: his product will then be at minimum cost. (The implicit assumption here is that the reaction concerned gives the same Tafel constant  $b$  for different catalysts).

#### 7. OTHER MATTERS TO BE TAKEN CARE OF IN ELECTROCATALYTIC WORK

This article is a primer and not a study in depth so I am not going to give a great deal of detail in the following matters, but there is no doubt that they all come into studies of electrocatalysis.

(1) *Single crystals*. Until the 1980's it was thought acceptable to work on poly crystals. After all, they are the cheapest, but gradually people began to look at the electrochemical reaction rates on various faces of single crystals, and it became clear that, indeed, the reaction rate varies considerably on the different faces for the same metal and therefore it is important to give the electrocatalytic rate not only on, *e.g.*, molybdenum, but on certain crystal faces ((011) or (101) for example) of the metal.

This greatly increases the expense of the experimental work and some people argue that it is useless from the industrial point of view because industrialists are always going to use poly crystals. This is a point of controversy. Ideally, in the future, the electrochemical engineer will use the fastest crystal face for the given reaction.

(2) *Spectroscopic aspects*. Until the 1980's *in situ* spectroscopic measurements were not of great use in electrochemical measurements, but work done with FTIR measurements at Texas A&M University in particular<sup>13</sup> has turned out to be often quite informative. For example, one can determine the intermediate radicals in an electrochemical reaction and the way in which they change with potential.

Thus, in methanol oxidation, it has been shown by Chandrasekharen *et al.*<sup>6</sup> that the variation of an adsorbed CO radical (at least in the steady state measurements) is an important part of the mechanism in methanol oxidation and this helps, – of course with the help of indications from other methods, – to identify the rate determining step.

(3) *Scanning, tunneling microscopy*. This relatively recent tool does enable one to actually (at least with certain metals) see atoms on the surface of crystals.<sup>13</sup> It is not yet clear how this determines the mechanism, but it is certainly a hopeful point for the future when we may be able to obtain pictures in real-time of atoms on the surface and, perhaps further into the future, put this kind of information to work in directly observing a pathway on an electrode surface.

(4) *Ellipsometric spectroscopy*. One of the techniques which electrochemists use primarily for looking at oxide films, is a technique called ellipsometry. It is called this because it deals in the elliptical properties of polarized light. The description of the mechanism is rather lengthy but suffice to say that, although hitherto it has been mainly used for the examination of oxide films, it can also be used to look at radicals on the surface, and using various wave lengths, obtain their spectroscopy,<sup>14</sup> and hence identify them.

Such measurements are highly sensitive to mono-layers and provide data in time ranges much less than those in, say, FTIR.

## 8. PURIFICATION OF THE SOLUTION

This is another controversial matter. A certain group of electrochemists will insist that purification of the solution must be followed through to a high degree, because organic trace impurities are always present in unpurified aqueous solutions,

and tend to compete with the reaction under examination so that the mechanism determination necessary prior to catalyst choice becomes obscured (and the presence of different impurities in different originating waters means irreproducibility, lab to lab). The effect of impurity adsorption on the catalyst may cause difficulty. All this is worse if the reaction is to be carried out at very low current density, for here reaction of the impurity may compete with the reaction under examination.

There are two arguments against working in super pure solutions. The first is to say that there is no chance of getting anything like the degree of purification used in some academic measurements when the final product is used in industry. The other objection refers to a technique known as cyclic voltammetry, in which the rate of reaction is measured on a continuously changing potential. In this case the whole measurement can be over in seconds and under these circumstances, so it is claimed, the adsorption of impurities on the surface of the metal does not have time to take place.

I think there is a difficulty in the latter argument because if one has to examine an electrode reaction with the idea that it could be useful on a large scale, then one certainly has to examine it in the steady state, not in a transient state, which is the state referred to in potentiometry. In fact, in the cyclic voltammogram or potentiometric measurement, it is unlikely that the various intermediates obtain the same degree of coverage – or intensity of occupation of the metal – as they do in the steady state. It could even be that this "halfway house" of a measurement which occurs in potentiometry, gives indications which lead to different mechanism conclusions than one would have if one stuck to steady state measurements. However, the cyclic voltammetric or moving potential measurements are so much easier to make than other types of transient measurements.

This is something which has to be discussed, but, at least in my view, an electrocatalytic reaction which has been looked at only from the point of view of potentiometry runs the danger of giving rise to a mechanism of the rate determining step which may not be the one to which the reaction settles down in the steady state.<sup>15</sup>

What sort of measurement should one use then? I advocate using constant potential measurements. One chooses, say, ten different potentials starting near to the reversible potential and going up by several tenths of volts or even more at each potential making  $i-t$  measurements until one is near the limiting current. Here again there is much to be said about for how long one should measure the reaction because if one measures it for too long a time, then one runs into the trouble of concentration polarization which will make the current decrease with  $t^{1/2}$  at constant potential.

#### 9. THE IMPORTANCE OF LOWERING TAFEL'S $b$ CONSTANT

If one looks at Tafel lines, one sees that many of them have a characteristic slope which is given in the equations by  $2RT/F$  and in fact  $\frac{d\eta}{d\log i}$  is about 0.12 at room temperature.

However, this is by no means the only case and there are well-known reactions which have a slope of  $2RT/3F$ , and some reactions which have a slope of  $RT/2F$  (0.029 on a log scale or four times less than the usual value).

Now trivial calculations will show that the smaller Tafel slope, the better, because, – for the electrochemical engineer – a large overpotential is expensive. A large current density with the smallest overpotential (*i.e.*, the best electrocatalysis) is best.

It is important, therefore, in electrocatalytic studies not only to aim at the largest  $i_0$  but also the smallest value of  $b$ , mechanism which has a minimal Tafel slope. There is no analogue of this in gas catalysis.

#### 10. SOME IDEAS FOR THE FUTURE

One may mention here some ideas which are in an early stage of development.

(1) Use of various types of solvent. Of course the activation energy of an electrochemical reaction depends not only upon the interaction of the reaction with electrode surface, but also with the solvent. It is the energy of activation that we want to minimize and therefore if one can find a solvent from which the reaction has a faster rate (all other circumstances being the same), one has achieved electrocatalysis though not by means of conventional methods.

A good example of this is use of trifluoromethane sulphonic acid, as a solvent in oxygen reduction which was,<sup>16</sup> shown to give a faster reduction of oxygen compared with phosphoric acid.

(2) Heat pulses. Here the idea is to make the electrode pulsed in such a way that its temperature is momentarily raised to a very high degree, well above the boiling point of water, and then, diminish it before the boiling point of the solution is reached. If the solution is flowed over the electrode, the time at which the electrode can remain above the boiling point may be very significant.

(3) Cleaning surfaces from sludge buildup. In the oxidation of methanol, in particular, one of the troubles is that as time goes on the surface gradually gets covered with polymer-type substances which do not take part in the reaction but simply block the surface. Obviously this greatly decreases the electrocatalytic value of the situation and must be controlled. There are ideas about this, one of them is that electrodes should be pulsed potentially at intervals into a high anodic value, thus burning off the polymer. In practice these intervals are lengthy, minutes and not seconds.

(4) Lastly, I would like to introduce the idea of patch alloys.<sup>17</sup> Thus this idea is at the present time hypothetical but one can imagine a consecutive series of reactions:



*etc.*, and one can start off by imagining it is the  $A \rightarrow B$  reaction which is rate determining.

Well, under these circumstances a certain kind of patch on the surface is designed so that it catalyzes this  $A \rightarrow B$  reaction to run at high velocity (followed by the rest of

the consecutive sequences) is needed. If one applies this, of course another step in the consecutive series on the surface will become rate determining because the first one is now going quickly. For simplicity, let us assume that the next one is  $B \rightarrow C$ .

It is clear that if one knows what this reaction is, one can design a surface, using patch alloys, which contains patches of materials which will optimize the rate of  $B \rightarrow C$ .

One then comes to  $C \rightarrow D$  as the rate determining step, and, the procedure is now obvious: new alloying materials should be introduced in patches to optimize that reaction.

The concept here is that these patches shall be put in multi-form, *i.e.*, thousands of them in different situations on the surface of the electrode, and the reaction will seek out, if surface diffusion is fast, those of the electrode which have a suitably fast character for the given step.

A most important aspect comes out of these considerations: Each of these step has a different  $b$  value in Tafel's equation and in a series of reactions which involve charge transfer, it turns out that as one goes along a consecutive series, the reactions have an always lesser  $b$ , so thus the ideal state would be that, *e.g.*, after three or four steps (not all of them should be charge transfer) one has got to a  $b$  value with a rate determining step which is as low as  $RT/2F$ ; or even lower. This would be an ideal solution because now the overpotential which has been developed at a given current density would be very low, and the reaction hence carried out economically.

#### 11. EVENTUAL AIM

The eventual aim of electrocatalysis is: To be able to run reactions at their limiting currents as near as possible to the reversible potential, say, less than 0.1 V. We are far from this at the moment, but then, we do very little fundamental work on electrocatalysis, so if we change the attitude here and then apply new ideas, one may eventually go towards the ideal electrochemical reaction happening very near to the reversible value.<sup>17</sup>

#### ИЗВОД

#### ОСНОВИ ЕЛЕКТРОКАТАЛИЗЕ

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Дат је кратак приказ развој и достигнућа електрокатализе у протеклих 50 година. Указано је на значај познавања механизма посматране реакције и положаја спорог ступња у реакцији за рационалан избор катализатора. Фундаментални аспекти електролизе детаљније су приказани на примерима електрохемијски значајних реакција издвајања водоника, редукције кисеоника, као и реакције електрохемијске оксидације органских горива (нпр. метанола).

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