38

ELECTROCHEMICAL OXIDATION OF ALCOHOLS

A. N. FRUMKIN

U.S.S.R. Institute of Electrochemistry of the Academy of Sciences and Moscow State University, Moscow

I MUST first apologize for the fact that the subject of the paper has been changed. It was originally intended that Prof. Burshtein from the Institute of Electrochemistry, Moscow, would speak about the oxidation of hydrocarbons, but she was not well and could not come to Brighton.

I do not propose, however, to present her paper which has been distributed. I thought it would be more interesting if I say something about the work on the oxidation of alcohols which was carried out in my laboratory at the Moscow State University by O. Petry, B. Podlovchenko and Hira Lal.

Another point I wish to make is that this is what is called fundamental work. It concerns the mechanism of the processes which occur, or might occur, in fuel cells, but I shall not speak directly about fuel cells.

First a few words about our experimental methods. We have used different methods, including triangular and linear voltage pulse methods, but most of our experiments were carried out by a method which many of the people present at this Conference would probably consider rather primitive. We simply took a heavily platinized platinum electrode with a few square centimetres of apparent surface, which was introduced into the solution. If the electrode is prepolarized to 500 mV, referring to the hydrogen electrode in the same solution, and alcohol is introduced into the solution (0·1 N H_2SO_4), the potential shifts to the negative and we obtain two kinds of curves (Fig. 1) representing the dependence of the potential on time.

In the case of methanol, the potential shifts steadily towards the negative until it approaches a value of about 85 mV. If methyl alcohol is introduced at a lower potential, at say 50 mV, then nothing happens at all, the potential is not affected.

If we take another alcohol, for example, butyl alcohol, then we have the same shift to the negative, but the potential goes through a minimum and approaches afterwards a steady value which in this case is somewhere near 140 mV. If these higher alcohols are introduced at say 50 mV then we observe a shift in the potential to the anodic side. The cathodic shift has been already observed by many people and also explained in different ways.

We have been specially interested in why this anodic shift occurs. In this potential region some gas evolution is observed which also has been noted already by other people. The explanation given was that hydrogen displaced from the electrode surface by alcohol is evolved. Now this apparently is thermodynamically impossible at this potential. So we collected some of the gas and analysed it and found that it was a mixture of hydrocarbons. Let us give you an example of some of the results of the analysis. In the case of propyl alcohol introduced at an initial potential of 64 mV, the analysis showed that the gas contained 19 per cent of ethane, 76 per cent of propane and 4 per cent of butane. When butyl alcohol was introduced at a potential of 41 mV the gas contained < 1 per cent of methane, < 1 per cent ethane, 23 per cent propane and 76 per cent butane. When butyl alcohol was introduced at

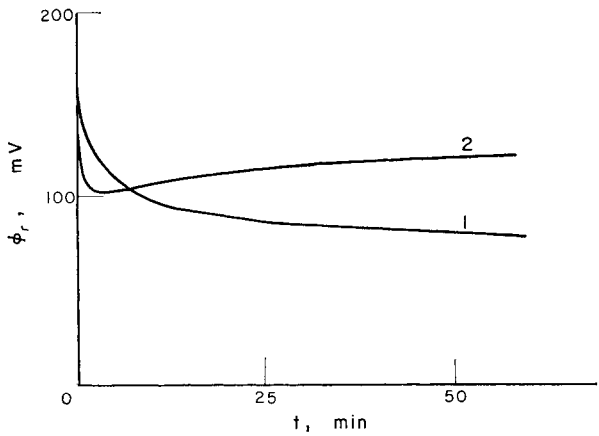

FIG. 1. Shift of the potential of a platinized platinum electrode after the introduction of CH_3OH at 500 mV (1) and of C_4H_9OH at 200 mV (2) in 0·1 N H_2SO_4. Concentration of alcohols—0·5 M.

500 mV, the gas contained 2 per cent ethane, 69 per cent propane and 28 per cent butane. This shows that there was a far-reaching hydrogenation of the alcohols. Further there was a considerable splitting of the molecules as some ethane and methane were formed from the butyl alcohol and very large amounts of propane. In the case where butyl alcohol was introduced at 500 mV, propane was the most important product. We also found some polymerization products as under certain conditions butane was formed from propyl alcohol. The results obtained show that the final product depends on the potential at which the alcohol is introduced into the aqueous solution.

The other thing which can be investigated is the organic residue firmly adsorbed on the electrode, which is formed a certain time after the alcohol has been introduced into the aqueous solution (0·1 N H_2SO_4 or 0·1 N KOH).

This was done in the following way. We simply washed the electrode with a solution of the electrolyte from which oxygen was very carefully removed. As the electrode was washed the potential shifted a little bit. After 8–9 washings the point was reached when the residue could not be further removed, which was controlled by the absence of a change of the anodic charging curve on further washing. After that we could study the electrode by a variety of methods, for instance, by polarizing it anodically. Some charging curves obtained are given in Fig. 2. They show the relation between the amount of electricity passed through the electrode and the potential under conditions of a slow change of the latter.

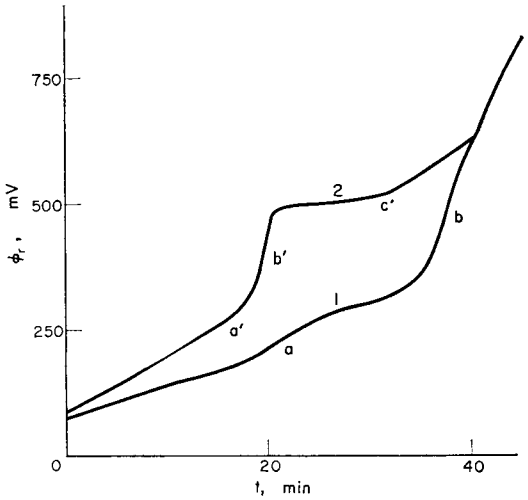

FIG. 2. Anodic charging curves of a platinized platinum electrode in 0·1 N H_2SO_4 (1) and in 0·1 N H_2SO_4 (2) in the presence of chemisorbed methanol. The methanol was introduced at 500 mV; concentration —0·5 M. Current density 10^{-4} A/cm², apparent electrode surface 2 cm². a, a'—hydrogen arrests; b, b'—double layer regions; c'—organic residue oxidation arrest.

With a platinum electrode in sulphuric acid, the first part of the curve is due to the removal of adsorbed hydrogen, the second is what we call the double layer region, and after this the oxidation starts. After some methyl alcohol had been brought into contact with the electrode, which had been previously freed from hydrogen by prepolarization, the hydrogen arrest appears again. The double layer region is followed by a plateau at which the organic substances are oxidized. From the length of the hydrogen arrest and from the length of this plateau some conclusions can be drawn about the nature of these residues. If these measurements are made at different current densities, polarization curves which have the normal form of a Tafel line with some definite slope are obtained.

Now let us present a few results which we have obtained in this way. In the case of methyl alcohol the chemical composition of the residue was something like COH. This means that three hydrogen atoms were split from the methyl alcohol molecule. It was interesting to conjecture what influence this residue had on the process occurring at the electrode. It could play a double role. Firstly, it could be considered as an intermediate which was oxidized at an oxidation rate which determines the overall rate of the process. This possibility was checked in the following way. If the Tafel line obtained in a methyl alcohol solution is compared with the Tafel line obtained with the residue, you find that the overvoltage in the second case is only about 40 mV higher than in the first case. As a first approximation, therefore, it can be stated that the rate of oxidation of dissolved methyl alcohol is determined by the removal of this firmly bound substance, although actually the process in the solution was a little bit faster. Probably adsorbed molecules are partly involved which were not so firmly bound as the residue obtained by our method.

With other alcohols the difference was larger. It amounted to 100 mV with butyl alcohol and to 200 mV with formic acid, so that in the case of formic acid you cannot assume that the firmly bound residue is the intermediate. It must be some other adsorbed form which is not so firmly bound to the electrode.

Another aspect is that the formation of this residue poisons the electrode and prevents the oxidation of the dissolved alcohol. From the rate of decrease of the potential of the electrode upon addition of the alcohol to the solution and from the capacity of the electrode you can determine the oxidation rate on a clean electrode. We have also used other methods; all of them give the same result which is rather astonishing. Thus we found that at a potential of 800 mV on a surface in a steady state condition, as compared with a clean surface, the rate of oxidation of methyl alcohol is decreased by the presence of the adsorbed firmly bound film by a factor of 2·5. At 400 mV, which is a potential which would be of practical interest, however, the decrease of the rate of the process which occurs on a clean electrode amounts to 10^4-fold.

This residue is therefore the substance which prevents the electrode from functioning in the desired way, and its study appears to be a rather important problem.

I would like to say finally a few words on what we have done with other catalysts. At Moscow State University during the last 3 years much work has been done in studying the catalytic activity of ruthenium. We thought it would be interesting to try ruthenium instead of platinum as a catalyst for the electrochemical oxidation of methanol and to try also palladium. We did not, however, get interesting results with palladium.

The experiments with ruthenium were carried out with ruthenium electrolytically deposited from a solution of the salt $K_2Ru(NO)Cl_5$.

Ruthenium turned out to be catalytically very inactive in the oxidation of methanol. But when we made alloys by simultaneous deposition of platinum and ruthenium we found that mixtures which contained about 10 per cent or less of ruthenium behaved in an interesting way (similar results concerning the platinum–ruthenium system have been quoted by Bockris and Wroblowa). Namely, such mixtures were about 100 times as active as pure platinum. The overvoltage decreased by about 200 mV. Moreover, the electrochemical behaviour was in some respects different from the behaviour of platinum. If you try to work out the kinetic mechanism for the oxidation of methyl alcohol it is rather difficult to succeed. If you assume that the first step is controlled by an electronic transfer the rate should be in the first approximation pH independent when studied at constant potential referred to the normal hydrogen electrode. This is not the case as the reaction is pH dependent.

If you assume that the first step in the reaction is the splitting of hydrogen atoms from the molecule, or that the reaction involves adsorbed OH, as is assumed for other reactions for instance by Bockris, then the rate should be pH independent if measured at constant potential with reference to the hydrogen electrode in the same solution. Actually the reaction rate changes in a rather complicated way with the pH, which is different at different current densities. We worked quite a time with this reaction but I must say we could not give a good kinetic scheme.

With regard to these mixed deposits, we have not done much work on this yet, but we can give some preliminary results. With reference to a hydrogen electrode in the same solution, the reaction rate is practically pH independent. There is another fact which might in time perhaps give an explanation of this, namely, that the bond strength of the metal hydrogen bond in the case of platinum, as is well known, is strongly dependent on the pH, but on these mixed platinum–ruthenium deposits it is practically pH independent.

The higher activity of these deposits is also shown by another fact. As I have already mentioned, in the case of platinum you reach a stationary potential of about 85 mV after the introduction of methanol in the solution. In the case of the platinum–ruthenium deposits after the introduction of methyl alcohol at molar concentration you reach a potential of only 30 mV which comes quite close to the reversible hydrogen electrode.

For further details see the following papers:

1. Frumkin, A. and Podlovchenko, B. *Doklady Akad. Nauk SSSR*, **150**, 349 (1963).
2. Podlovchenko, B., Petry, O. and Frumkin, A. *Doklady Akad. Nauk SSSR*, **153**, 379 (1963).
3. Podlovchenko, B. and Jofa, Z. *Zhurn. phys. Khim.* **38**, 211 (1964).
4. Podlovchenko, B. and Gorgonova, E. *Doklady Akad. Nauk SSSR*, **156**, 673 (1964).
5. Lal, Hira, Petry, O. and Podlovchenko, B. *Doklady Akad. Nauk SSSR*, **158**, 1416 (1964).

6. PETRY, O. *Doklady Akad. Nauk SSSR*, **160**, N4 (1965).
7. PODLOVCHENKO, B. *Electrokhimya*, N1 (1965).
8. LAL, HIRA, PETRY, O. and PODLOVCHENKO, B. *Electrokhimya*, N3 (1965).

DISCUSSION

W. VIELSTICH (*University of Bonn, Germany*): I understand the investigation of methanol and alcohols in general referred to acid solutions. In alkaline solutions of course formate is definitely formed, and so I think the COH compound does not occur there, but in acid solutions do you think that formaldehyde and formic acid are not formed as intermediate products as has been shown by analysis by American workers and also by Bloch? Does the factor of 100 for the platinum–ruthenium mixture refer to a clean surface or to a poisoned surface? In other words, could you indicate the difference between platinized platinum and the platinum–ruthenium couple on a clean surface without poisoning?

A. N. FRUMKIN: We have carried out experiments in both acid and alkaline solutions, but not so many in alkaline ones. In alkaline solutions also you get both arrests, so there is a residue on the surface, the composition of which is probably the same at least as when the residue is formed on open circuit. Regarding the formation of the intermediates I think that in the course of a steady oxidation reaction at sufficiently high concentrations of methanol there is an exchange between the adsorbed substance and the bulk of the solution so what you observe in the bulk of the solution are in a certain sense signals of what happens on the interface.

My quantitative data refer to the surface in the steady state condition, that is to the poisoned surface. We have no comparative results for unpoisoned surfaces.

K. R. WILLIAMS (*Shell Research Ltd.*): I wonder whether Professor Frumkin would care to comment on the relative " free areas " on his electrodes. Has he observed any differences in the " free areas ", i.e. unpoisoned sites, on the surface of platinum as compared with the platinum–ruthenium or ruthenium alloy in the steady state oxidation by methyl alcohol?

A. N. FRUMKIN: I cannot give you an answer because we have not worked this out yet. There is a certain difficulty with some of these alloys. With platinum we can have a good insight into the behaviour of the electrode surface because it has a well-pronounced hydrogen arrest on the charging curve. When you wish to know something about the electrode surface you start by measuring this arrest, as it is known from our work and the work done by the German School in Munich. The arrest on the charging curves of ruthenium is unfortunately not as well pronounced as the one previously described. The hydrogen region merges continuously with the oxygen region. So we don't know exactly how many hydrogen atoms are on the ruthenium surface. It appears that the saturation with hydrogen atoms is smaller and that the oxygen atoms appear at a lower anodic potential than in the case of platinum. I think that the surface chemistry of the platinum and ruthenium system should be investigated in more detail.

G. W. WALKIDEN (*International Nickel Co. (Mond.) Ltd.*): Can Professor Frumkin give any indication of the structure of the platinum–ruthenium deposits? Were these alloys or simply mixtures?

A. N. FRUMKIN: They were obtained by simultaneous deposition of both metals. It was at any rate a very intimate mixture and chemically an extremely stable one, very much more stable than pure platinum. Actually the difficult problem for us was to analyse the deposits. We tried it but gave it up. What we did was to use radioactive ruthenium and to measure the radioactivity of the electrodes to have an idea of the composition. It turned out that the platinum–ruthenium ratio in the deposit is not materially different from the platinum–ruthenium ratio in the solution. This certainly does not point to compound formation.

N. E. BAGSHAW (*Chloride Technical Services Ltd.*): Did Professor Frumkin investigate different compositions of the platinum–ruthenium electrodeposit?

A. N. FRUMKIN: Yes, we tried out different compositions, 5 per cent, 10 per cent, 23 per cent and 40 per cent. We found a flat maximum of activity in the region of 10 per cent. This is in agreement with what is known in the literature about the catalytic activity of platinum–ruthenium alloys in gas reactions.

W. BETHERIDGE (*International Nickel Co. (Mond) Ltd.*): May I ask Professor Frumkin the nature of the platinum electrolyte which was mixed with ruthenium nitroso chloride to produce the alloy deposits?

A. N. FRUMKIN: The usual platinum hexachloro 2-, of course without lead addition.

M. BARAK (*Chloride Technical Services Ltd.*): I have a question concerning the relation between adsorption of the species on the surface and the straight electron transfer reaction which could take place as an alternative. In one case one might get a substance such as methanol breaking down into two radicals before the electron transfer reaction takes place. In the other case, a direct electron transfer might take place from a reaction in which the substance breaks by a different route. This could affect the relationship between the type of substrate used and the catalyst because the substrate may be a substance which has very highly adsorptive properties, whereas the catalyst may be a material providing the greatest activity for the straightforward electron transfer reaction. My question, therefore, is this. Has Professor Frumkin any decided views on which of these two functions is more important and, if so, whether one is in effect more rate-determining than the other?

A. N. FRUMKIN: First of all, of course, we looked for direct electron transfer reaction. You could suppose that the reaction we have been studying is electron transfer controlled because you get normal Tafel slopes, characteristic of such a reaction. However, you can get normal Tafel slopes if the first rate-controlling step is a chemical step as well. It is therefore difficult to draw a conclusion about the mechanism from determining the Tafel slope. This is possible in the case of a homogeneous surface at low coverage, but in the case of a non-homogeneous surface and at high coverage it is easy to show that you can get a normal Tafel slope assuming that the first step is, for example, a dehydrogenation step. I think under conditions which correspond to the changes of the potential which I described, the process is really controlled by the dehydrogenation. It is possible, however, that at higher positive potentials the first step is not a dehydrogenation, but as Bockris assumes a reaction with some form of adsorbed OH. In the steady state conditions the reaction rate is probably controlled by the removal of the firmly adsorbed residues. I do not think that the splitting of the molecule into two organic radicals plays a great role here. I think what is important at not too high an anodic polarization is the splitting off of hydrogen atoms. Of course, various reactions can occur in the condensed layer of adsorbed radicals. We do not know at the present moment much about this. Certainly the reaction mechanism is rather a complex one and one must try to use very different methods in studying it.