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(Review)

## THE FIRST JAPAN-USSR SEMINAR ON ELECTROCHEMISTRY<sup>\*)</sup>

— General Discussion —

By

A. MATSUDA<sup>\*\*)</sup>

(Received October 25, 1974)

The first JAPAN-USSR seminar on electrochemistry was held in Tokyo from the 7th to the 10th, October 1974, in cooperation of the electrochemists of the two countries, on the subject "Thermodynamical and molecular approach to the electrified interphases and electrode processes". In the final session of this seminar three topics on the basic problems of electrochemistry were taken up for discussion, the first one is the mechanism of the establishment of the electrode potential, the second one is the theoretical and experimental treatment of the electron transfer process and the third one is the new instrumentation for the molecular approach to the electrified interphases and the elementary acts of the electrode processes.

Very much interesting and valuable comments on these subjects were made from the modern and historical aspects of electrochemistry by Prof. FRUMKIN and other Soviet and Japanese electrochemists who participated in this seminar. These comments will be reported in this review article following the original representation as far as possible<sup>\*)</sup>.

One of the most basic problems of electrochemistry is on the mechanism of the setting up of the electrode potential. How can it be established in the electrochemical systems? To say nothing of the Nernst equation in the reversible system, two fundamental conceptions have been developed to answer this question, the charging up of the electric double layer at the metal-solution interface and the electronic work function of the electrode. In this respect Prof. FRUMKIN pointed out in his report at this seminar

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<sup>\*)</sup> The contents were reproduced from the tape record by Dr. K. KUNIMATSU of the Research Institute for Catalysis and Dr. T. SASAKI of the Faculty of Engineering, Hokkaido University.

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A. MATSUDA

the important role of the specific orientation of the solvent molecule on the electrode surface in the establishment of the electrode potential, comparing the charge density *vs.* potential curves between the gallium and mercury electrodes. The general discussion started with the remark of Prof. FRUMKIN on the establishment of the electrode potential.

Prof. A. FRUMKIN: —

"I should say something about the establishment of the electrode potential. I should remember there have been two approaches in the history of electrochemistry and until now perhaps the question is not finally settled. The first approach goes back to Nernst. Nernst considered the establishment of the electrode potential as a result of one process, the ionization of the electrode metal or the backward process of the discharge of the ions in the solution.

In our first paper or in others the idea was used which I think was that of RIDEAL and BOWDEN in the early thirties. We considered the establishment of the potential at the platinum hydrogen electrode under potentials between the reversible hydrogen and the reversible oxygen potentials as a result of accumulation on the platinum surface of dipoles formed by Pt-H or Pt-O bonds. Of course, as the potential changes the number of such bonds changes and so the potential is realized. This was the problem which occupied me since the early beginning of my studies in this field and which occupied me during the last years still.

I will try to show some different ways. Both approaches, if they are used without consideration of the existence of two simultaneous possibilities, cannot give correct results. First of course it is easy to show that the establishment of the potential is caused also by the specific adsorption or by the orientation of solvent molecules, this was the start of the work I have done, and it was shown later by the existence of a difference in point of zero charge between different metals which is partly related to the potential difference between two metal-metal interface. This was the thing which Nernst completely neglected and which plays a definite role in the interpretation of electrochemical phenomena and I must say until now very much practical use of this potential difference has not been done. We have tried to show in some cases that it is necessary to take into account, for instance, in our study of thallium amalgams, but there was not much done in this direction.

What is about the orientation of solvent dipoles? Especially during the last perhaps ten years much work has been done in our country and

*The First JAPAN-USSR Seminar on Electrochemistry*

in Italy by TRASATTI. This line of research of TRASATTI and ours is in many respects similar and too there are some differences in the interpretation of what is adsorbed. The difference refers to the case of d-metals. In the case of sp-metals the interpretation of TRASATTI and ours practically coincides. Well, perhaps sometimes different words are used but the mathematical relations and the physical meaning are very similar.

As to the case of the orientation of water and other molecules on the surface of d-metals there is difference in approach which is connected with the different evaluation of the experimental material. Well, I make a more severe choice, I would say, when TRASATTI and I think those what we call d-metals. The available experimental material is not yet sufficient to draw the conclusion which TRASATTI draws. This is now some polemic which is not yet readily published, but the exchange of letters in something between TRASATTI and myself on this question will be published later, because I think TRASATTI uses the experimental material for d-metals which is not perhaps so good as it should be for the building up of a theory.

Now in connection with what I am speaking about and the paper of Prof. KITA which was given yesterday I should draw your attention to one point. When we make classification of the reactions on metals we must be very careful. For instance, according to Prof. KITA gold is one which belongs to the category of d-metals. Now, Prof. TRASATTI quite from the beginning pretended that gold behaves specifically as sp-metals and at the beginning I was against it. But in this case I had to state that TRASATTI was right, because metallic gold is really not a d-metal, in gold compounds gold becomes a d-metal. When we have metallic gold it does not behave as d-metal as far as the double layer structure is considered, for instance, the orientation of water molecules with the oxygen towards the metal is typical or qualitatively typical for d-metals and it is not adsorbed at the gold electrode interface and in that respect gold behaves like mercury or even perhaps the orientation is still less pronounced than in the case of mercury. I showed in my paper drawn that gold was quite at the beginning of the series of metals in which come mercury, cadmium, gallium and sp-metals which by behavior little by little approach the behavior of d-metals. So one must be very careful when we classify the difference in groups because using different choice of the experimental material we can show quite different classification which depends very much on the author.

Now, this dipole approach which goes back to RIDEAL and the time of early thirties was used recently again by BOCKRIS who tried to show that the behavior of the platinum electrode in the oxygen region can be

## A. MATSUDA

interpreted simply as the accumulation of the oxygen dipoles and I already said in connection with the discussion which followed the paper of Prof. TAKAMURA that this approach leads to contradiction with thermodynamics. You cannot refer the building up of an electrode potential only to the accumulation of oriented dipoles. You have not enough variables such as to find equilibrium conditions in that case. So you must always consider both possible mechanisms, surface dipoles and surface adsorption phenomena and also ionization processes. In some cases one proper phenomenon is the most important and in other cases another one, but always you must consider that both exist.

Now the problem which interested us, not personally myself, in Moscow last years was the theory of the surface layer of the platinum group metals. We have very strongly pronounced phenomena of adsorption of hydrogen or of oxygen or of both perhaps together. We tried first of all to develop a thermodynamical treatment which would be equivalent to the theory of the ideal polarized mercury electrode which was developed well at the beginning by the work of KOENIG, directed by LANGE and finally by GRAHAME and which for a certain time dominated completely modern electrochemistry. Of course the theory of the ideal polarized electrode is a very elegant theory but it is, I think, rather strange feature of this period of the development of electrochemistry that the whole treatment of the double layer problem was based on the electrode which is in the usual sense of the word not an electrode at all, because it was the fundamental assumption that there was no possible electrochemical reaction occurs at this interface. Now this is not an electrode. This is some different body in the electrolyte solution and of course we should consider how to change the theory so that you could adapt to the real electrode, I mean the electrode at which electrode reactions can occur. If you look at the wrong use given by MOHILNER quite recently on the double layer structure in the series edited by BARLOW, you see that on the basis of simple small correction of the theory given by GRAHAME the problem cannot be solved and I think we give a much better solution, of course the question is still discussed in the literature. We had quite an argument recently with SCHULTZ and VETTER, but finally they had to state that at least in one respect they had been wrong. At any rate this is a question which is still debated and which PARSONS described as controversial. Well, I hope this will be finally settled and I think the theory which have been worked out by PETRY and DAMASKIN in Moscow will be accepted by everybody.

Now, I think it is practically all what I can say, but we see all effects

*The First JAPAN-USSR Seminar on Electrochemistry*

must be considered, ionization, adsorption of ions, adsorption of neutral molecules, orientation of surface surfactants adsorbed from the solution, orientation of solvent dipoles, VOLTA potential difference at the interface between two metals, dipole effect caused by adsorption of atoms of hydrogen or oxygen perhaps other atoms too and the different state of charge transfer between adsorbed particles and the electrode. This is an very interesting problem.

LORENTZ in East Germany was the first one to draw attention to this problem and I think this is a great merit of LORENTZ, although the first treatment which has been given by LORENTZ was not correct in all respects. It was criticized by DAMASKIN, but I think we have now especially thanks to the work done in Moscow by GRAFOV and PEKKAR which comes to some agreement with LORENTZ. But we have to distinguish between two approaches to the treatment of charge transfer, one is which is based on the molecular picture and must assume a definite model of the electrode which is always something hypothetical but is very interesting and very important, and the other is some definitions of the charge transfer which can be given on the basis of thermodynamic relations using either GIBBS thermodynamics or thermodynamics of irreversible processes which is given by ONSAGER relations. This was done recently by GRAFOV and leads to the same result. Well, in the paper which will be published soon this question is treated again and I will try PETRY and DAMASKIN to give final comparison between different approaches to the theory of charge transfer which is also an important factor in the establishment of the electrode potential.

How and to what degree an adsorbed ion begin to behave like an atom? How this problem can be treated? As I already stated there are two possible approaches which lead to different mathematical expressions which have also a different physical meaning. This is, I think, an important electrochemical problem but I shall not dwell further on it because it was not considered in this seminar, well, might come back to it after two years in Moscow until when our last paper on this subject will be published. Well, a very long paper of PETRY and myself is also in course of publication in *Electrochimica Acta*, which gives the review of all the work we have done on the platinum hydrogen system. There are also some considerations concerning the charge transfer but not in detail.

Well, this is what I could say to this part of the discussion. I should like to say a few words later about instrumentation."

A. MATSUDA

Prof. TAMAMUSHI: —

"I would like to ask Prof. FRUMKIN one question on the role of point of zero charge in the kinetic theory of the charge transfer processes. In many cases when we analyze the irreversible process, the hydrogen scale is used as the reference potential. If you use the zero charge potential instead of the hydrogen scale, is there any merit or advantage of this scale?"

Prof. FRUMKIN: —

"Well, I understand the question in the following way whether we should abandon the usual way of presenting the electrochemical data referred to the standard hydrogen potential or express everything in the rational scale as it was called by GRAHAME, or reduced scale as it was called by ANTROPOV and for some period proposed also by BOCKRIS.

I think we should keep the use of the method which is used, because if we use the rational scale we must introduce a correction for the work function of the electrode, because in that case we neglect that the extraction of the electron from the electrode to the solution at the point of zero charge requires different work.

There was a period when BOCKRIS advocated that he could use the *p.z.c.* scale or the rational scale, because at the point of zero charge every metal is in the same condition. This is not correct. It is the same condition so far as adsorption from the solution is considered, but it is not in the same condition with respect to the extraction of the electron from the metal.

The most important agent in any electrochemical processes is the electron. It should not be forgotten. The work necessary to extract electron from metal into the solution is equal for all metals not at the potential of zero charge but at any equal potential measured against any standard electrode. I should say this is a fundamental law. This can be directly shown without introduction of any clever concept like the electrochemical potential so simply by considering the equilibrium of two electrodes in a solution. And keep it in mind that equilibrium must suffer to any possible processes and we can assume always the electronic conduction of the solution, when you see at once that the work of extracting electron from the metal into solution at equal potential must be independent of the metal nature. Well, I am very proud I have said it already in 1939 although nobody paid any attention to it, this was not a paper, say, this was a footnote of the famous HORIUTI and POLANYI paper. This shows you clearly that you must use the standard scale and not the rational or the ANTROPOVSKY.

If the drop of potential in the diffuse double layer cannot be neglected,

*The First JAPAN-USSR Seminar on Electrochemistry*

of course, you must apply the double layer correction because what I have said concerning the electronic structure refers only to a point into the solution which is the outside the limit of the diffuse double layer, and if you enter the limit of the diffuse double layer everything already changes and this was shown clearly in the excellent paper of PLESKOV and I very greatly admire his work.

So I can quite clearly state my opinion that this is internationally accepted now. You should use the standard hydrogen electrode scale and apply the double layer correction when necessary and when possible.

You should not forget that the point of zero charge exists, but should not shift from this way of treating the experimental data to the idea of preparing all processes to the point of zero charge. It was proposed especially by ANTROPOV. ANTROPOV wrote a book which was published in New Delhi when he was in India for three years Null point and Electrochemical Kinetics which I think something like that, but this idea is not correct. I mean you should always think about the point of zero charge concept, but you must not forget that not everything can be in similar terms treated on the basis of this concept.

If you do so as BOCKRIS has done in some period of his work, if you try to introduce a correction of the work function, I mean the work function of the extraction of the electron into the solution at *p.z.c.*, you come back to the standard hydrogen scale, so this compensates. This is published in 64 or 65, I think. I published a paper in a Journal of Electrochemistry on the subject and nearly at the same time Parsons published one somewhat earlier. There was a paper in Russian published by TEMKIN and myself on the same point in Russian Journal of Physical Chemistry and this was already expressed in the foot note of HORIUTI and POLANYI paper. So I mentioned it in Hokkaido just to quote once more Prof. HORIUTI."

Prof. V. S. KRYLOV reported on a role of the micropotential in ionic mass transfer controlled processes in this seminar. The discrete nature of an ionic charge in the solution side of the electric double layer was taken into consideration in his theory. In connection with his work Prof. KRYLOV gave us an elementary lecture in this session on some fundamental concepts of the micropotential in the double layer resulted from the discreteness of the charge in the double layer.

Prof. V. S. KRYLOV: —

"When we consider the discrete nature of an ionic charge in some solvent we have to take into account the situation which takes place when

A. MATSUDA

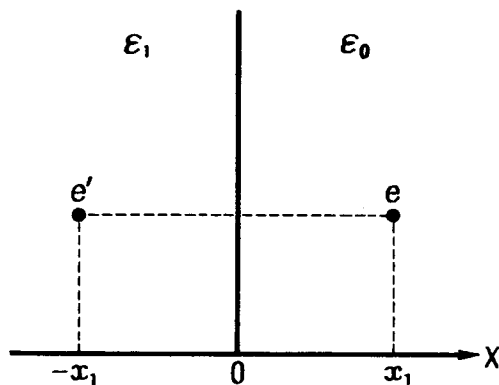


Fig. 1.

we have two continuum dielectric media, for example, one has the dielectric permittivity  $\epsilon_1$  and the other  $\epsilon_0$ . Let us suppose that a discrete charge  $e$  is located in one medium at  $x_1$  near the boundary between these two media (Fig. 1). In order to take into account the interaction of this charge with the boundary between the two media, one can imagine that there is another so-called image charge in the other medium located just on the same distance from the boundary as the charge  $e$ . But the value of this image charge  $e'$  depends on the relation between these dielectric permittivities, and is given by a well known formula,

$$e' = \frac{\epsilon_0 - \epsilon_1}{\epsilon_0 + \epsilon_1} e. \quad (1)$$

In the limiting case where one of the two media with the permittivity  $\epsilon_1$  is a metal and the other is an electrolyte solution,  $\epsilon_1$  approaches infinity. So there will be an image charge of the opposite sign and of the same value as  $e$ . What does it mean? It means that the discrete charge  $e$  will be attracted to the boundary by the image force.

In an electrochemical system where we have a metal adjacent to the electrolyte solution, the dielectric properties of the solvent near the metal surface are quite different from the dielectric properties of the solvent in the bulk of the solution due to several causes, for example, the dielectric saturation of water molecules, the specific adsorption of the solvent molecule as it takes place on gallium-water solution boundary and the adsorption of some organic substances in the solution. So we can imagine that there is some region just near this boundary which has another dielectric permittivity compared with the bulk phase. It means that in the case of very close approximation, we can consider the solution as the dielectric continuum but

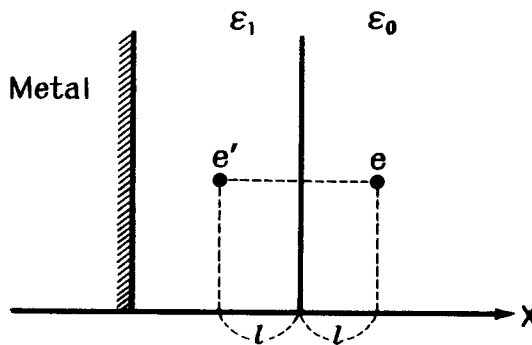


Fig. 2.

with the different permittivities,  $\epsilon_1$  and  $\epsilon_0$ , where  $\epsilon_0$  is the value in the bulk of the solution (Fig. 2).

If an ionic charge  $e$  is located very far from the boundary region, it will feel mainly metal, because the metal occupies all the space to the left and the dielectric interlayer is very thin compared with such a great bulk of space. So the charge  $e$  will feel mainly metal and consequently it will be attracted to the metal-solution boundary and if I draw the electrostatic potential energy of this ion with respect to the distance from the metal surface, the potential energy will be negative due to attraction.

When the charge  $e$  goes toward the boundary it begins to be sensitive to the dielectric interlayer and the image charge  $e'$  will be induced in the compact layer, the value of which is given by Eq. 1. Usually  $\epsilon_1$  is less than  $\epsilon_0$  and  $\epsilon_0$  may have the value about 80 in an aqueous solution. According to the differential capacity data  $\epsilon_1$  may have the value between 3 and 10. So there must be the image charge of the same sign as  $e$ , as seen from Eq. 1, which generates the additional force for the discrete ionic charge  $e$ . When  $e'$  is of the same sign with  $e$  there must be repulsion, not attraction, between  $e'$  and  $e$ . It follows that there must be some critical distance from the metal where the potential energy curve changes its sign from negative to positive.

In the vicinity of the boundary between the compact part and the diffuse part of the electric double layer the potential energy in this approximation must be very large and positive. It means in rather concentrated solution where the probability to find any ion near the interphase is quite high, all ionic species will be in average repulsed from the boundary and this is quite an opposite effect compared with the effect created by the image force in metal.

## A. MATSUDA

There must be complication in the interpretation of the electrochemical data because of this well known fact, which was mentioned for the first time in 1939 in the paper of JOFA and FRUMKIN who found that there is a negative adsorption near the point of zero charge in a very concentrated solution about 10 mol/l. This effect of the repulsion of an ion in the metal-solution interphase was interpreted afterward in the framework of such approximation. The difference in the dielectric permittivity is the main reason for the negative adsorption.

The same consideration must be applied to the ionic mass transfer problems, because it is the same situation as the equilibrium state. When the ionic species moves from the bulk of the solution toward the electrode, it feels firstly metal when it is far from the interphase, but secondly it begins to feel the dielectric interlayer and the change of the sign of the potential energy curve can create some effect which must be reflected on the curve of the diffusional current *vs.* potential of the electrode. Really I showed four years ago, for example, the limiting diffusional flux as a function of the potential decrease with the increasing potential of the metal.

Now, the problem is to construct such a picture of the dielectric behavior of the metal-solution interphase which reflects the real metal-solution interphase as far as possible. In my opinion in order to construct a good model, one must use the experimental data which enable to find the most characteristic parameters of this model, and if the theory is sound, these parameters should have some reasonable values, for example, the thickness of the compact layer must not exceed four or five angstroms and the dielectric permittivity, the effective permittivity, must correspond to the differential capacity data. It must be about 6 or 10, not more.

Well, I cannot now dwell on your attention more, but I think our theoretical papers which will be published in the Russian Journal *Elektrokhimiya* will give you some impression about this problem in the future."

The kinetic theory of the charge transfer process in homogeneous polar solutions has been constructed on the basis of quantum mechanics by the theoretical group of Soviet Union, Prof. DOGONADZE, Prof. KUZNETSOV *et al.* and this theory has recently been extended to the processes in the heterogeneous electrochemical systems. Some papers on the theoretical and experimental treatment of the elementary act of the charge transfer process were also reported in this seminar. Prof. KRISHTALIK made comprehensive comments on this topic.

*The First JAPAN-USSR Seminar on Electrochemistry*

Prof. KRISHTALIK: —

"I think it is not necessary for me and Prof. KUZNETSOV to repeat our papers. I would like to say something about the elementary act of the charge transfer reaction which is connected with a problem of electrochemistry of solvated electrons. An interesting paper on this topic was presented by Dr. KANZAKI and Prof. AOYAGI in this seminar, and we discussed on details of experiment. We are now fully convinced that there are no any considerable differences between the experimental data of KANZAKI and ours, and some differences are due to the difference in experimental conditions.

The works in Japan and USSR are in many respects complementary for each other because here the most attention was paid to the anodic process and in our first paper the most attention was paid to the cathodic process, so both groups gave first approach to rather full picture of the problem.

I would like to say some words about two points. The first is the anodic process. It was shown by Dr. KANZAKI that in the anodic oxidation of the solvated electron there were two polarographic waves in sodium ion contained solutions. Such a curve can be shown in a potentiodynamic method. We have obtained the same form of the curve. But in lithium-contained solutions we have obtained only one wave and only one limiting current. In the papers of Tokyo group this first wave was interpreted as either a kinetic limiting current or a limiting current of the dissociation of an ionic pair of sodium-solvated electron. I think the idea that it is a limiting current of dissociation may be true.

Now we can interpret these phenomena more precisely on the basis of the spectroscopic investigation of these solutions. We can show that in the presence of sodium ion there are, of course, some ionic pairs, but the ionic pairs have not very different spectral form from that of the solvated electron obtained by irradiation of pure solvent. In the presence of sodium ion the spectrum has a second maximum shifted a little due to the ionic pair formation. It means that there is a second species in sodium solutions which is absent in lithium solutions. So it was shown that these species corresponded to an equilibrium between sodium ion and two solvated electrons and the bielectron form was stabilized due to the interaction with cation. The solvated lithium cation cannot stabilize this bielectron and so we have not such species in the lithium solution.

This was also studied by different methods, spectroscopic and E.S.R. methods. The rate constant of the process of association was measured in radiation chemical experiments, and from spectroscopic data we obtained

## A. MATSUDA

the equilibrium constant, so we can calculate the rate constant for the dissociation process. In an electrochemical experiment we can calculate the rate constant of the dissociation process. The two quite independent methods gave the coinciding quantity. So I think it is now confirmed that this is the process of slow dissociation, *i.e.* it is a current limited by the slow dissociation rate of the bielectron. In the lithium solution we have not the bielectron, then we have not any limiting current of such a nature. Now we can see that the anodic process is not so simple, *i.e.* there are two possibilities of the reaction of the bielectron and the reaction of monoelectron at the electrode.

Let us now talk something about the cathodic process. At the beginning of our work we thought about the cathodic generation of solvated electron as a possibly simplest electrochemical process. But, besides the complication due to the formation of some more complex particles, which is not very important because it can be taken into account, there exist some possibilities for the cathodic generation of the solvated electron which do not exist in any other electrochemical processes.

Any electrochemical process consists of some charge transfer, for instance, some electron from metal on some particles in a oxidized state to form some reduced states. In any charge transfer process we have the elementary act which is a transfer of charge from the electrode into some localized states immediately near the electrode. Such a process is possible also for the electron, of course, with forming some solvated electron. It means that we have an electron which goes into a cavity forming some surroundings from dipole molecules. But the electron is so light that it can propagate as a quasi free particle. As a way, it can leave the electrode and propagate for some distances as a quite delocalized particle and after that due to the interaction with solvent it reorganizes the solvent molecules slowly step by step and then it is localized.

In this case, we have the competition between two possible ways. One is the usual electrochemical process of charge transfer into a delocalized state and the other is the process of formation of delocalized electron with subsequent localization. We were able to show that we could obtain under some conditions both of these processes. We could obtain the process of thermal emission of electron which means the process of emission of the electron as a delocalized quasi free particle. This process corresponds to the Tafel line with a slope of 55 mV. In other conditions, we cannot obtain such a thermal process because of some difficulties connected with the diffusion limitation, but we can obtain some Tafel lines with a slope

about  $2RT/F$  which corresponds to the usual electrochemical processes.

On this thermal process there is a small negligible influence of some double layer structure which was shown, for instance, for photoemission in a paper of Prof. PLESKOV. Photoemission is very low sensitive to the structure of the double layer except some special cases. Here is the same circumstances in the thermal emission, because the wave length of the thermally emitted electrons corresponding to the energy of the order of  $kT$  is very large, about  $60 \text{ \AA}$ , so it is larger than any region in which the double layer structure changes. The electrochemical process is very sensitive to all the influences of the double layer structure and so on.

I would like to show you one slide which shows the Tafel line for the thermal emission of electron. You can see the different points which correspond to different solutions, lithium or sodium solutions and to different metals, copper or platinum or cadmium. You can see that the process is independent of the nature of cations and metals. This corresponds quite well to what mentioned Prof. FRUMKIN today, *i.e.*, the work function for electron to go into solution at the same potential is independent on the electrode nature. The polarization curves with other slope in this Figure correspond to the hydrogen evolution at the same solvent on the different metals. There is a large distance between these two groups of the polarization curves which is larger than 1.5 V.

Fig. 3 shows that the solvated electron cannot be the intermediate of the usual process of the hydrogen evolution. Some years ago, the idea that the reducing particle in all electrochemical reduction processes is the solvated

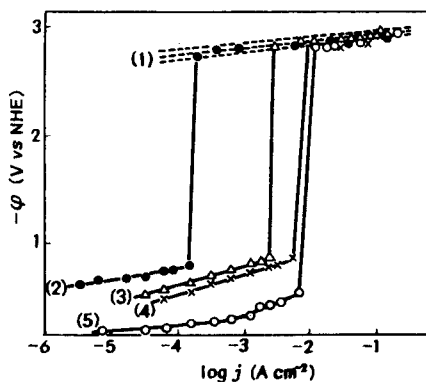


Fig. 3. Dependence of the electrode potential on the current density in 0.2M LiCl HMPA solution on Cu (1-4) and Pt (5); curve (1) in pure LiCl solution, curves (2-5) in LiCl solution including HCl respectively 0.09 mol/l (2), 0.15 mol/l (3), 0.24 mol/l (4), 0.20 mol/l (5).

## A. MATSUDA

electron was very actively discussed, *i.e.*, the first step is the generation of the solvated electron and then it reacts with solvent molecules. You can see that it is improbable for most processes, because the generation of solvated electrons demands much higher potential than the potential at which the process proceeds usually. Well, this is all what I could say about the electrochemistry of the solvated electron."

Prof. N. TANAKA: —

"I would like to ask Prof. FRUMKIN two general questions. In most cases I have used a slowly dropping mercury electrode in the kinetic studies of the electrode processes, because it is very difficult to have a constant surface condition in the case of solid electrodes. A dropping mercury electrode is superior to a hanging mercury electrode which is easily deteriorated with surface active substances in solution, and I prefer a slowly dropping mercury electrode to a usual one because the usual dropping mercury electrode has not enough drop time to obtain constant surface area.

Now, my first question is how to standardize the surface condition when we use solid electrodes to obtain kinetic parameters, I mean, the rate constant and the transfer coefficient. The second question is on the dependence of the transfer coefficient on the electrode potential. Both are the complicated problems for the determination of the kinetic parameters. I would like to hear the opinion of the Russian delegates on these problems."

Prof. A. FRUMKIN: —

"Well, first of all I think we should start more wise use of solid electrodes because there are problems in electrochemical kinetics concerning the mechanism of the electrode process which cannot be solved so long as you use the electrode of one metal. Well, I'll give you one example which we met practically.

When you try to solve the question what is the charge of the reactant particle in the case of the electroreduction of anions, which was very much discussed in the literatures by Gierst, by us or others, in the recent analysis which is not yet published but soon will appear in Jour. of Electrochemistry, we can show this question cannot be solved so long as you work only with mercury. You can attempt to solve this question only if you compare the behaviors of different electrodes.

Now, if you start to use different electrodes, the choice of liquid metals is rather limited because there are mercury and gallium as well as gallium alloys and amalgams. Gallium is in many respects interesting but not very

*The First JAPAN-USSR Seminar on Electrochemistry*

convenient electrode because it is very easily oxidized. So we are interested in the use of solid electrodes.

How can you control the state of the solid electrode to be sure at least you have reproducible results, and how can you obtain the electrode in a good state? There are two different questions.

I think the most unambiguous method of control is to take a set of differential capacity *vs.* potential curves at different concentrations of the supporting electrolyte. When there is a normal set of curves, which can be shown primarily in our work in Moscow and later perhaps in work of Grahame, and if you get a similar set of curves, there is a definite relation between the capacity at a higher electrolyte concentration and at a lower electrolyte concentration which was established by the work done in Moscow and by Grahame. Then you can be sure that the electrode really has a clean surface which can be used for any measurements. Of course, in many cases it becomes spoiled during the reaction. You cannot help it. You must simply renew it.

There are different methods. You can scrape the electrode as proposed by Eyring. This is a practically easily realized method. Some similar work was done by Tomashova in Moscow but you must not forget that the scraped electrode in its behavior is markedly different from a smooth electrode. So you cannot identify the results of the scraped electrode as the results of smooth electrode.

The best method, but it cannot be used in all cases, is to get a monocrystalline face just by splitting the monocrystal but this work is limited in number of metals. In the case of zinc, of course, you have a wonderful (0001) face which is a perfect face. It works absolutely well. It has a coefficient of flexuosity very close to unity, not perhaps 1 but 1.05 or something like that. It is very good and very easily obtainable but there was only limited number. You can split also the bismuth crystal. We have done some work on such faces. Probably some are true but this has not yet been investigated.

If you cannot obtain such a face by splitting, you can in many cases obtain by chemical or electropolishing the surface and by reducing the oxide layer but very carefully. There has been tendency in the electrochemical work to all polarize in the cathodic region assuming that the strong cathodic polarization is something very good to obtain a clean surface. It is wrong, because when you go over a certain limit you introduce foreign metal cations into the electrode, there are very much data investigated by Kabanov in Moscow, and instead of oxide layer you get contamination of sodium atom

## A. MATSUDA

or something like that. To what extent? That depends on the material, well, we have no general rules presently.

But in many cases how can you control? You can control it just by taking again good differential capacity *vs.* potential curves at low supporting electrolyte concentration. Very extensive work in this direction has been done by the Group of Dr. LEIKIS at the Institute of Electrochemistry. We have a quite program of the point of zero charge in our country. When she started studying silver, new or old data obtained in USA, in our country and elsewhere were all related to oxidized surfaces. So she started to polarize cathodically, but she soon saw that she got electrodes which were absolutely useless. Then she started to work out conditions at which you remove the oxide layer. This must be done rather in acid solution even if you have to work afterwards in alkaline solutions. You had better remove the oxide layer in acid solution, then you substitute acid one to alkaline one under control of the cathodic potential and you will take differential capacity *vs.* potential curves, then you see that you have a good surface.

Of course, there are some definite cases where splendid surface have been obtained by Burgarian electrochemists. They worked out a method of growing in a capillary a dislocation free metallic surface with a definite crystallographic index. At first it was a quartz capillary and now it is a teflon capillary. We had a cubic face and a octahedral face.

Somewhat later French people in the Laboratoire d'Electrolyse du C.N.R.S. which is directed by Prof. BONNEMAY, lady Antoinet Hamelin started also work on silver and now I am very glad I can show you that they obtained also good results; not first results obtained with monocrystalline face, first was the work which has been done by Burgarian electrochemists and us. We obtained for the first time data for (1110) face of a dodecahedron. Now we have data for three different faces of silver monocrystal and for polycrystalline silver which are absolutely reproducible.

But this I mean you must find out a good method in each case. I must state that there are many cases for published modern work from people who have not realized this. I would give you now an example, a series of papers of HAMPSON and others published in England, I think in Middlesex. We have quite a polemic about cadmium. So LEIKIS group published papers on the cadmium electrode, and HAMPSON's group wrote: We don't believe you can obtain such data with cadmium electrode. So I wrote a letter to Parsons and he apologized it was published in his absence. But when they published a paper LEIKIS and others were to explain, I mean: you must work out a method, you cannot use the first method which you have read

*The First JAPAN-USSR Seminar on Electrochemistry*

in the literature about electropolishing. Because if you electropolish using, for instance, cyanide solution, it is impossible to get rid of the cyanide groups from the metal surface. So this is an experimental work which must be done in case to find out a good method.

Now you see how to seal which method is a good one. Well we might say, the method is a good one which gives a point of zero charge which you like to know. No, that is not so, not the point of zero charge but a series of differential capacity *vs.* potential curves which correspond to a reasonable structure of the electric double layer. The point of zero charge is afterwards some product of this work and this is not a criterion. The criterion is the dependence of the concentration which semi-quantitatively corresponds to the theory of the double layer. I said semi-quantitatively because in the theory enters a constant about which we are not sure. This is a dielectric constant of the liquid or the water in the diffuse double layer. Well, Grahame assumed that it has always the bulk value 81 at room temperature. Now we are not quite sure about it. It appears that it can deviate somewhat in this respect. But this is not very important, because at any rate the shape and relative position of this curve do not depend very much on the numerical value of this constant. So you can see always whether you got a good electrode. We can say HAMPSON didn't get a good electrode. Really if you would obtain such results elsewhere published for many metals, we could say we have not yet worked out the method to get a good electrode.

Well, let us quote other work, but HACKERMAN's work on solid electrodes. He was also one of the first to do the measurement on solid electrodes, I can say this result cannot be used. You see from the relative position of the curves those measurements were not correct. It is very easy to obtain with solid electrodes quite wrong data because of course solid surface is very much easy to contaminate and it is difficult to get rid of contamination as a mercury drop. This is quite clear but it is possible to do this. But it requires some work.

Now, there is one case where it is very easy to obtain an absolutely reproducible solid electrode. That is when this electrode has a large surface. In that case it is quite easy to get it clean. So platinized platinum or other platinum group metals are quite easily obtained, at least absolutely reproducible if you use some standard method of depositing platinum black. It is important. The method must be a standard one. You can get absolutely reproducible surface after you get forward and backward from anodic to cathodic potential quite a plenty of times, and it changes only very slowly

## A. MATSUDA

and you can check it from time to time. That is, I should say, as good as a mercury electrode, although it has quite different property of course, but this is because it has a very large surface.

Now, what I think must be kept in mind in the work with solid electrodes is the purity of water. This is a difficult problem too, because I think in the most work the difficulty of removing organic impurities from water is very much underestimated. This is quite a problem because when you take up water you add sodium-permanganate and distil it twice or three times, but you don't get water free of organic contamination. It can be shown that you must use more elaborate method. Some have been proposed in Moscow and some by Conway. We have not yet compared both methods but I think this gives identical results. I think Conway's method is a good one too, but we haven't used other method. At any rate you must control it and you must get rid of organic contaminations.

The simplest way to control is by measuring the polarographic maximum of the second kind. It is very sensitive to organic contaminations and the method is very easy to handle and doesn't require any special apparatus. This is described in the literature and for details you can look at the work of Nikolaevna Fedrovich which was published in Soviet Electrochemistry.

So, of course, the requirement is becoming more and more strict. I mean it is becoming more difficult to work. Fourty years ago very good electromhemical investigation was very easily done and now it requires much more work but we can't help it."

In this seminar three papers were reported on the rototing ring-disk electrode, the first is the theoretical one of Prof. V. Ju. FILINOVSKY\*) on the application of the rotating disk and ring-disk electrodes to the analysis of kinetics of electrochemical processes on solid electrodes, the second one is on the electrochemical reduction of oxygen at oxide electrodes by Prof. SHUMILOVA\*) and the third is on the theory of hydrodynamic voltammetry by Prof. H. MATSUDA. Prof. V. FILINOVSKY and Prof. H. MATSUDA made adequate comments on this topic in this session.

Prof. V. Ju. FILINOVSKY : —

"I have no special comments to my report and to the paper of Prof. SHUMILOVA. But I want to emphasize that in my report I tried to show

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\*) The papers of Professors A. N. FRUMKIN *et al.*, V. Ju. FILINOVSKY, and N. A. SHUMILOVA *et al.* read in this Seminar were published in the Journal of the Electrochemical Society of Japan "Denki Kagaku", Vol. 43, No. 1 (1975), and others in this Journal Vol. 22, No. 2 (1974).

*The First JAPAN-USSR Seminar on Electrochemistry*

the new theoretical method for the investigation of the mechanism and kinetics of the electrochemical transformations and the publication of the asymptotical method for this purpose. For instance, the dependence of the current density on the rotating speed of the electrode in the case of disk system and also for the case of ring-disk electrode system. This method gives us some possibility for the determination of the rate constant of the multi-stage electrode processes. This is my first comment.

The second one is the comment to the contribution by Prof. H. MATSUDA. I think this paper is very fruitful and interesting for the people who work with the rotating disk and ring-disk system, because it is an attempt to find the analytical expression for the efficiency coefficient in the double electrode system. On the meeting we tried to criticize the paper of Prof. MATSUDA, but I think it is on the question which we have ourselves, because it is a very difficult mathematical problem to give the answer for this problem.

I want to emphasize also that in our book on the monograph on the rotating disk electrode by Prof. PLESKOV and myself I tried to treat this problem only in the simplified manner to get some simplified expression for the efficiency coefficient. I am very glad that our simplified form of this dependence is the same as the exact expressions of Prof. MATSUDA."

Prof. H. MATSUDA : —

"As you know, the rotating disk electrode is widely used in many laboratories. I cannot say everything about the rotating disk and ring-disk electrodes, but in connection with the paper of Prof. FILINOVSKY I would like to say only about a new cell in hydrodynamic voltammetry which we have recently constructed and examined the behavior of the diffusion current in this new system.

Sometimes we encounter the situation in which it is better to do all experiments in a completely closed cell. In the case of a rotating disk or ring-disk electrode, however, it is difficult to close completely the cell, because we have some moving parts which are connected with the outside of the cell. So we have constructed a new type of cell which is just the inverse of the rotating disk electrode. In the case of the rotating disk electrode the electrode is rotating in a stationary solution, but in our cell the solution is rotating and the disk electrode is stationary. The rotation of the solution is produced by a rotator driven by a rotating magnet.

We derived for this case some theoretical equations of the diffusion current and examined the behavior of this diffusion current. The theory

## A. MATSUDA

predicts us that the current distribution in this case is different from that of the rotating disk electrode which have a uniform distribution, but if we integrate this current distribution over the electrode surface we have just completely the same equation as in the case of the rotating disk system. The numerical constant is different between the rotating disk and stationary disk electrodes. Now we are going to improve this cell design to construct with all glass."

Another new instrumentation reported in this seminar was on the effect of light on the elementary act of the electrode processes. There are two cases of the light effect on the electrode processes. The one is the photo-excitation of the electronic state of an electrode metal as reported by Prof. PLESKOV in his paper on the photoemission of electrons into electrolytes from solid metals with poor hydrogen adsorption properties, and the other is the photo-excitation of a reacting particle in the solution side, for instance, as reported by Prof. K. HONDA in his work on the electrochemical photo-cell constructed with semiconductor electrodes.

Prof. K. HONDA : —

"There are two cases of the excitation by light, *i.e.*, the excitation of the electrode material itself and the excitation of the chemical species in the solution. We can cite, for instance, the spectral sensitization of the electrode processes with semiconductor which I talked for very short time in my paper. The works in this direction were done already by Prof. GERISCHER, Prof. HAUFÉ and other investigators in Germany and USA.

The excitation of chemical species in the solution is the work originally carried out by Prof. LABINOVITCH. This work is now very widely undertaken in USA from the standpoint of energy conversion. This field of work is called in terms of photogalvanic cell. I would like to cite only one example of this type of photogalvanic cell which uses methylene blue or cyanine redox couple with the iron redox couple. This was of course originally reported by Prof. LABINOVITCH, but I think actually there is a considerable improvement of this kind of cell, and now in USA, they say, the life time of such photogalvanic cell is so long that it works at least one half year or more. But I am sorry I cannot say for the details about this.

Can I profit this occasion to ask some questions to Prof. PLESKOV? The question is that can you obtain a very good coincidence between the zero charge potential which is obtained from the ordinary method and that obtained from your method using the photoemission current. Is it possible

*The First JAPAN-USSR Seminar on Electrochemistry*

to apply your method to measure the flat band potential of the semiconductor electrode?

Prof. Yu. V. PLESKOV: —

"So far the photoemission method has been restricted mainly to the metal electrodes. Only a small amount of work has been done for the semiconductor photoemitter. I think this method is very little adjusted now to measure the flat band potential. But there is no need, I think, to apply this method to measure the flat band potential of semiconductors. Because there are number of other methods just good for this purpose.

I think the photomission method is quite good adjusted to measure some electrochemical kinetics on metals especially for some stable and non-stable intermediates of the electrochemical reactions. Choosing special type of scavengers of hydrated or solvated electrons it is possible to produce some new species in the solution layer adjacent to the photoelectrode surface which can be investigated by the photoemission method as intermediates of the electrochemical reactions, say, atomic hydrogen, some organic species and so on".

Prof. A. FRUMKIN: —

"I should like to draw your attention to the point. The validity of the slow discharge theory has been, well I should say perhaps in the case of mercury, finally demonstrated by photoelectroemission work. Because what remained not quite clear for the second step of the reaction when you have slow discharge mechanism, this was cleared by photoelectrical measurements.

So I think I would like to say, some Japanese electrochemists should not spend so much time in trying to show that the slow discharge theory cannot be applied to any electrode reaction. I think this will be a hopeless attempt and we had better work together on the perfection of this theory."