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# Electrode Behaviour of a Suspension of Insoluble Material

M.R.Dausheva and O.A.Songina

The electrochemical behaviour of suspensions of insoluble materials at different electrodes is discussed, with special emphasis on recent studies of the adhesion of particles of a suspension to the surface of the dropping mercury electrode and of the rotating amalgamated disk electrode. 89 references.

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## I. INTRODUCTION

Processes in which electron transfer involves insoluble materials (in addition to the electrode metal and the electrolyte) have recently attracted a great deal of attention among electrochemists. We can distinguish three separate cases[1]:

1. The electrode is made of an insoluble compound (single crystal, pressed powder, solidified melt); electron transfer takes place between the electrolyte and the insoluble substance.

2. A metallic electrode is covered with a film of an insoluble substance (for example, an oxide film); in this case electron transfer takes place between the electrolyte, the insoluble substance, and the electrode metal.

3. The insoluble substance is present in suspension in the electrolyte; electron transfer between the insoluble substance and the electrolyte can occur either directly or through dissociation of the substance into electrochemically active ions.

Cases 1 and 2 have been fully investigated in theoretical electrochemistry, and are widely used in practice (for example, in accumulators, cells, and rectifiers). On the other hand, relatively little work has been done on the electrochemical behaviour of suspensions (case 3), largely because of the difficulties arising in studies of heterogeneous systems. If these difficulties could be overcome, new prospects would be created in theoretical and in applied electrochemistry. This review attempts to systematise existing data on the electrochemical behaviour of suspensions.

## II. MECHANISMS OF ELECTROCHEMICAL REACTIONS INVOLVING SUSPENSIONS

Most of the published papers on the electrochemical behaviour of suspensions† relate to their reduction. We shall therefore discuss the mechanisms by which suspensions can be electrochemically reduced. However, the same mechanisms can be invoked, in general, for the oxidation of suspensions.

The following mechanisms are possible for the electrode reactions of suspensions.

Mechanism I is an electronic mechanism, involving direct discharge of the solid particle

for salts

$$[M^{n+} + n\,A^-] + ne \rightarrow M + n\,A^- \qquad (1)$$

for oxides

$$\left[M^{n+} + \frac{n}{2}\,O^{2-}\right] + ne + \frac{n}{2}\,H^+ \rightarrow M + \frac{n}{2}\,OH^- \qquad (1')$$

In the case of reduction of oxides the process has been termed[2] electronic–protonic.

Eqns. (1) and (1′) give only a very general description of the process. The detailed discussions of reduction processes found in the literature on oxide electrodes are beyond the scope of the present review. However, we can state that the mechanisms considered for oxide electrodes[2,3] are also applicable, in general, to the discharge of particles of a suspension in contact with the electrode surface.

Mechanism II. An intermediate (X) formed at the electrode during the process takes part in the electron transfer:

for salts

$$[M^{n+} + n\,A^-] + n\,X \rightarrow M + n\,X^+ + n\,A^- \qquad (2)$$

for oxides

$$\left[M^{n+} + \frac{n}{2}\,O^{2-}\right] + n\,X + n\,H^+ \rightarrow M + n\,X^+ + \frac{n}{2}\,H_2O \qquad (2')$$

Mechanism III. The particle of insoluble substance decomposes into ions; the metal ions or the anions are discharged at the electrode:

for salts

$$[M^{n+} + n\,A^-] \rightarrow M^{n+} + n\,A^- \qquad (3)$$

for oxides

$$\left[M^{n+} + \frac{n}{2}\,O^{2-}\right] + n\,H^+ \rightarrow M^{n+} + \frac{n}{2}\,H_2O \qquad (3')$$

$$M^{n+} + ne \rightarrow M \qquad (3'')$$

† The term "suspension" is used to denote unstable, coarsely dispersed systems (particle size $\gg 1\ \mu m$), in contrast to colloids which are stable for very long periods.

Evidently, the decomposition of the particles into ions is determined (for an insoluble substance) by the solubility product of the compound and by the nature of the electrolyte.

Thus, direct electrochemical discharge of an insoluble substance at an electrode occurs only by mechanism I.

It is often difficult to identify the discharge mechanism for the particles of a suspension, and as a result different interpretations of a given process are sometimes found. Thus, the debate on the mechanism of reduction of manganese and tungsten oxide suspensions is well known[4-7]. Kobozev[4,5] states that tungstic oxide is reduced by free hydrogen atoms when hydrogen is evolved at a high-overvoltage cathode (such as lead); on a low-overvoltage (platinum) cathode the reduction involves excited hydrogen molecules (mechanism II). According to Kobozev, manganese dioxide is not reduced at either cathode in spite of its good electrical conductivity. Bagotskii and coworkers[6], and also Lukovtsev[7], prefer mechanism I, and state that tungsten trioxide and manganese dioxide are reduced at high-overvoltage cathodes (mercury, or amalgamated copper) without involving any form of active hydrogen whatsoever: by direct electron transfer, or (in the case of manganese dioxide) by interaction with the mercury of the electrode.

The difficulty of identifying the electrochemical reaction mechanism of a suspension stems from the large number of factors which can influence the electrochemical reduction or oxidation of a suspension: electrode material, electrolyte composition, current density, electrical conductivity of the solid phase, solubility product of the suspended phase, the contact between the solid phase and the electrode, etc.[3,8-11].

It is usually assumed that an electronic discharge mechanism must be involved in the reduction of compounds possessing an appreciable electrical conductivity ($10^{-2}$–$10^{-5}$ ohm$^{-1}$ cm$^{-1}$). Poor conductors, on the other hand, are reduced by mechanisms II and III. Evidently, depending on the electrolysis conditions, the process can occur by several mechanisms, but one mechanism usually predominates. For example, the decomposition of particles of an insoluble substance (mechanism III) is accompanied to a greater or lesser extent, depending on the solubility product and on the nature of the electrolyte, by processes which involve the first two mechanisms.

## III. BEHAVIOUR OF SUSPENSIONS OF INSOLUBLE SUBSTANCES DURING ELECTROLYSIS

Most of the work on the electrolysis of suspensions has been concerned with their reduction on platinum electrodes. The first publication on this topic was due to Fischbeck[12], who studied the reduction of powdered metal oxides, sulphides, and halides at a platinum cathode in sulphuric acid solutions. Many workers have shown[13-21] that silver halides are easily reduced at a platinum electrode, the silver being deposited on the cathode as a metallic sponge with a very good current yield. The reduction of silver chloride occurs mainly in the solid phase[14-18], i.e. by mechanism I; however, mechanism III can occur at low current densities[8]. Suspensions of lead halides are also easily reduced[14-21]. In a potassium chloride solution they are reduced by direct electron transfer from the electrode (mechanism I), but Sancelme[22] suggests that atomic hydrogen is involved in the reduction of lead halides (mechanism II).

The medium plays a very important role in the reduction of suspensions. Cupric oxide, cuprous oxide, and copper hydroxide are fully reduced to metallic copper only in sufficiently acid solutions. In dilute acids, and also in alkalis, the reduction is slow and does not go beyond a mixture of metallic copper and cuprous oxide[8,10]. Evidently, reduction in acid solutions is assisted by partial dissolution of the oxides (mechanism III). Lead sulphate[19,21] is not easily reduced at a platinum electrode in dilute neutral solutions, and is entirely unaffected in solutions of sulphuric acid. This is thought to be due to the poor electrical conductivity of lead sulphate; furthermore, the dissociation of lead sulphate into ions is hindered in sulphuric acid solutions, and reduction by mechanism III is impossible. Thus, lead sulphate is easily reduced in solutions of hydrochloric acid, sodium carbonate, and sodium hydroxide in which it is partly soluble. Lead phosphate, chlorophosphate, and chromate also can be reduced only in electrolytes in which they are appreciably soluble[19]. Vanadium pentoxide is smoothly reduced to vanadium in dilute sulphuric acid solutions[22]. The hydroxides of tervalent iron and nickel[23] are reduced to the hydroxides of the bivalent metals in neutral solutions. A suspension of $\alpha$-$Fe_2O_3$ is reduced to the metal in a concentrated sodium chloride solution, mainly by the action of atomic hydrogen but with a contribution by the electronic mechanism[24].

Platinum is not the only electrode metal on which the reduction of suspensions of insoluble compounds has been investigated. As stated above, some workers have used a mercury cathode[7] and cathodes of amalgamated lead[5] and copper[7]. The reduction of lead, copper, cadmium, zinc, and titanium oxides at a lead cathode has also been studied[25]. A lead cathode has been used to reduce the sulphides and other salts of various metals[26,27]; a silver cathode has been used to reduce a suspension of silver suboxide[28]. Vrebosch and Tiggelen[20] studied the reduction of silver halides and of copper sulphide suspended in dilute solutions of sodium chloride and sulphuric acid, using silver and copper electrodes respectively. It can be seen from the "potential–time" curves for a mixture of silver chloride, bromide, and iodide that the processes corresponding to the reduction of each halide can be resolved in time[20]. The reduction of copper sulphide at a copper electrode in dilute sulphuric acid goes as far as metallic copper, and is accompanied by the evolution of hydrogen and hydrogen sulphide[20]. The reduction of a suspension of cupric and cuprous oxide[8] at a copper cathode in 0.1 *N* sodium hydroxide proceeds mainly by direct electron transfer:

$$CuO + 2e \rightarrow Cu + O^{2-} \quad (4)$$

$$Cu_2O + 2e \rightarrow 2Cu + O^{2-} \quad (4')$$

$$O^{2-} + H_2O \rightarrow 2OH^- \quad (4'')$$

The reduction of cupric and cuprous oxide begins at potentials more negative than the theoretical values by 338 and 616 mV respectively, indicating the presence of a slow step (overvoltage). The authors[8] suggest that reduction by hydrogen adsorbed on the electrode also occurs, but to a smaller extent:

$$H_2O + M + e \rightarrow MH_{ads} + OH^- \quad (5)$$

$$CuO + 2MH_{ads} \rightarrow Cu + H_2O + 2M \quad (5')$$

The symbol M denotes the electrode metal.

The reduction of cupric hydroxide on a copper cathode is attended by a very large overvoltage, and occurs at a

potential 954 mV more negative than the theoretical value[8]. It is concluded that the reduction of cupric hydroxide has a greater dependence on the participation of adsorbed hydrogen than does the reduction of the copper oxides:

$$Cu(OH)_2 + 2MH_{ads} \rightarrow Cu + 2H_2O + 2M \quad (6)$$

With the hydroxide, however, dissociation is possible, and the reaction proceeds partially through the reduction of copper ions:

$$Cu(OH)_2 \rightarrow Cu^{2+} + 2OH^- \quad (6')$$

$$Cu^{2+} + 2e \rightarrow Cu \quad (6'')$$

In the above examples the intermediate (X) which is formed at the electrode and reacts chemically with the insoluble substance is hydrogen. However, this role can be played by other substances, for example metal ions which can exist in two valency states. Addition of such ions to the electrolyte is suggested[29] as a means of increasing the rate of the electrochemical reduction of suspensions of insoluble compounds. For example, suspensions of bismuth oxide and cuprous chloride are reduced electrolytically at a lead cathode in the presence of quadrivalent titanium:

$$Ti^{4+} + e \rightarrow Ti^{3+} \quad (7)$$

$$Bi_2O_3 + 6Ti^{3+} + 6H^+ \rightarrow 2Bi + 6Ti^{4+} + 3H_2O \quad (7')$$

$$CuCl + Ti^{3+} + H^+ \rightarrow Cu + Ti^{4+} + HCl \quad (7'')$$

Some electrochemical studies of the anodic oxidation of suspensions have also been reported. A suspension of arsenious oxide is oxidised to arsenic acid[30]; manganous hydroxide, formed by mixing solutions of manganous sulphate and ammonia, is oxidised to manganese dioxide at an iron anode[31]; manganous carbonate in a sodium chloride solution is also oxidised to manganese dioxide[32]. The oxidation of suspensions of bivalent nickel and cobalt hydroxides and of lead oxide on graphite in sodium chloride solutions[29] involves the chlorine formed at the anode, and the oxidation products are tervalent nickel and cobalt hydroxides and lead dioxide.

Only a few individual papers have dealt with the practical applications of the electrolysis of suspensions. The process has been used as a preparative method for manganese dioxide[31,32], and to convert sparingly soluble compounds into a soluble form[10,22]. The work[33-35] on the production of pure metals directly from their ores could have great practical importance. One of these papers[35] deals with the electrochemical "extraction" of lead compounds. The lead ore, suspended in a chlorate solution, is introduced into the anode compartment of the electrolytic cell and vigorously stirred throughout the reaction. The lead gradually goes into solution, is transferred to the cathode compartment, and is deposited as a sponge on the lead cathode in 86–90% yield. Electrolysis of a suspension of galena in a mixed melt of potassium and sodium chloride yields[33,34] the metal at the (molten lead) cathode and sulphur at the anode. A technical process for the continuous electrolysis of lead concentrates in fused salts could be based on this experiment. The yield of lead is 96–97%, and the purity of the deposited metal is 99.8–99.9%.

Several workers[36-38] have begun to use the suspended electrode method for studies of catalysts. A conventional electrode of the pressed catalyst acts as a current carrier and a carrier of catalytic activity at the same time: by using a suspension of the catalyst these two functions can be separated. The method has been used to study the anodic behaviour of a suspension of Raney-nickel in a sodium hydroxide solution on platinum and gold electrodes, and the cathodic behaviour of a suspension of aluminium oxide (carrier) with additions of silver (catalyst).[36] When the catalyst contacts the electrode, hydrogen is oxidised in the anodic process and oxygen is reduced in the cathodic process. The method has been recommended for studying the oxidation of organic compounds in fuel cells[36]. The electrolytic oxidation of hydrogen and methanol has been studied[37] by the suspended electrode method, using suspensions of platinised and nickel-coated carbon, and Raney-nickel. The effectiveness of catalysts for the porous diffusion electrode of a fuel cell[38] has been assessed by using suspended electrodes of platinum black and Adams' catalyst (finely divided $PtO_2$). With these suspended electrodes the material in suspension does not react electrochemically at the electrode, and therefore work in this area falls outside the scope of the present review.

Suspensions of sparingly soluble compounds can be reduced by cementation with liquid amalgams[39-41] as well as by electrolysis. When a suspension is stirred with an amalgam the metal from the compound in suspension goes into the mercury, from which it can be extracted by shaking the resulting amalgam with a solution of mercurous nitrate. The liquid amalgam can be brought into intimate contact with the particles, and the electrochemical reaction is therefore favoured. The cementation reaction, which takes place at high negative mixed potentials, is accompanied by hydrogen evolution. Hence, there is a possibility that the reduction of suspensions of sparingly soluble compounds by cementation with amalgams will occur by mechanism II (with participation of the evolved hydrogen) as well as by an electronic mechanism. It has been shown[40] that the behaviour of suspensions in this respect is fully consistent with the electrochemical theory of cementation processes[42]. The cementation method is used mainly to separate precipitates and to convert insoluble into soluble compounds. Thus, cementation with zinc amalgam[39] has been used analytically to separate lead sulphate quantitatively from barium sulphate, and cementation with sodium amalgam has been used to bring into solution heavy metal chlorides, sulphates[40], and carbonates[41].

## IV. ELECTROCHEMICAL BEHAVIOUR OF SUSPENSIONS ON SOLID MICRO-ELECTRODES UNDER AMPEROMETRIC TITRATION CONDITIONS

The reduction or oxidation of insoluble substances at an electrode is often encountered in amperometric titrations by the precipitation method[43-51]. The precipitate formed during the titration is sometimes reduced or oxidised at the platinum microelectrode either directly (by contact between the particles and the electrode) or by partial dissolution of the precipitate (if its solubility product is not too small). As a result, the equivalence point on the titration curves becomes ill-defined, and precision is lost. Because of this problem, special electrochemical studies of suspended precipitates with platinum microelectrodes have been undertaken.

Songina and Zakharov[43] made a detailed study of the reduction and oxidation of mercuric iodide precipitates in 1 M sulphuric acid. The oxidation and reduction polarograms of mercury iodide show clearly defined limiting current plateaux: the reduction begins at +0.3 V and the

oxidation at +1.0 V (relative to the mercury/iodide electrode). Because of the very low solubility product of mercuric iodide ($5 \times 10^{-29}$), it has been suggested that the reduction and oxidation of this compound proceed by the electronic mechanism

$$HgI_2 + 2e \rightarrow Hg + 2I^- \quad (8)$$

$$HgI_2 - 2e \rightarrow Hg^{2+} + I_2 \quad (8')$$

By comparing the polarograms for the reduction of mercuric ions and for the oxidation of iodide ions with those for the oxidation and reduction of a suspension of mercuric iodide it can be shown that the reduction potential of the suspension is 0.4 V more negative, and the oxidation potential 0.4 V more positive, than the corresponding potentials for the mercuric and iodide ions respectively. It is concluded that sharp titration curves can be obtained by carefully setting the potential at a value where neither oxidation nor reduction of the precipitate can occur.

Detailed studies have been reported also of the reduction of silver halide[45-47] and of silver and mercury molybdate and tungstate suspensions[48-51].

The reduction of a sparingly soluble precipitate of silver chloride was used as the basis of an original method for the amperometric titration of iodide in the presence of chloride by a solution of silver nitrate[52]. Particles of silver chloride are formed after the end-point of the titration of the iodide ions: their reduction (at a graphite electrode maintained at a potential of +0.38 V relative to another graphite electrode coated with silver) produces a sharp increase in current.

## V. ELECTROCHEMICAL BEHAVIOUR OF SUSPENSIONS ON MERCURY MICRO-ELECTRODES

Micka and Kalvoda's papers on the reduction of suspensions of sparingly soluble compounds (termed "insoluble depolarisers") by classical[53-55] and by oscillographic polarographic methods[56,57] began to appear in the 1950's. Micka used a dropping mercury electrode and conventional polarographic base electrolytes (solutions of sulphuric acid, salts, etc.). The polarograms of his stirred suspensions usually showed a current step over a well defined potential region[53,55], accompanied by sharp current fluctuations associated with the irregular collisions of the solid particles against the electrode (Fig. 1). At more negative potentials the current falls back to the background value. The polarogram plotted without stirring is indistinguishable from the polarogram for the base electrolyte, because the precipitate settles and cannot contact the dropping mercury electrode. The peak height and the frequency of the current fluctuations increase with the rate of stirring and with the number of solid particles in suspension. Micka examined suspensions of several dozen sparingly soluble compounds (sulphides, oxides, chlorides, elemental sulphur, etc.[55]), and determined the potentials corresponding to the maxima in their reduction polarograms.

Kalvoda studied the reduction of suspensions by Heyrovsky and Foreit's oscillographic polarography method[56,57]. He plotted $dE/dt = f(E)$ curves for single-sweep and repeated-sweep polarisations of the dropping electrode. Lobes were found in the oscillograms (Fig. 2) at potentials close to those of the maxima obtained by Micka using classical polarography[55]. By comparing the oscillograms given by single-sweep and multiple-sweep polarisations, Kalvoda concluded that in many cases the direct reduction of solid particles is accompanied by reactions involving the products of interactions between the particles and the electrolyte. For example, suspensions of sulphides and elemental sulphur in acid solutions give an additional peak on the polarogram, corresponding to electronic processes involving the $SH^-$ ions formed at the electrode, and the oscillograms of many substances show additional peaks due to the reduction of metal ions produced by the partial dissolution of the solid particles or to chemical reaction of the sulphide with mercury ions produced by dissolution of the mercury electrode under anodic polarisation:

$$MS + Hg^{2+} \rightarrow M^{2+} + HgS \quad (9)$$

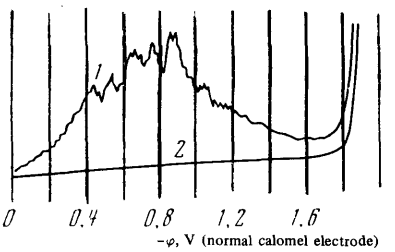



**Figure 1.** Polarograms obtained with a carbon suspension (20 mg) in a 1 M $NH_4Cl$ base electrolyte (5 ml) using a dropping mercury electrode: 1) stirred, 2) unstirred (from Ref. 53).

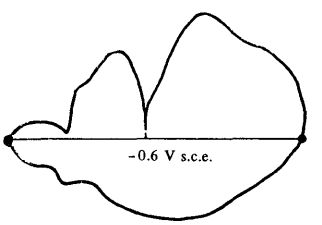



**Figure 2.** Oscillographic polarogram of a suspension of AgI in 0.5 M KCl, measured with a dropping mercury electrode[56].

Kalvoda points out that the electrochemical behaviour of suspensions of sparingly soluble compounds can be predicted from a knowledge of the position of the metallic component in the electrochemical series: the more noble the metal, the more easily are its sparingly soluble compounds reduced. For example, suspensions of copper, mercury, silver, etc. compounds are easily reduced. Conversely, suspensions of the insoluble compounds of metals such as calcium and magnesium are not reduced at all.

Micka made a detailed study[54,58] of the reduction at a dropping mercury electrode of suspensions of sulphides

of the iron-group metals ($Fe_2S_3$, FeS, CoS, NiS). The reduction polarograms obtained in the presence of ammonium salts have a sharp current maximum (peak) at potentials 1.5–1.7 V more negative than the normal calomel electrode. The following mechanism is proposed[54,58]:

$$MS + 2e \rightarrow M + S^{2-} \quad (10)$$

$$S^{2-} + 2\,NH_4^+ \rightarrow H_2S + 2NH_3 \quad (10')$$

$$M + H_2S \rightarrow MS + H_2 \quad (10'')$$

There are serious objections to this mechanism, since reactions (10′) and (10″) are impossible under these conditions. Firstly, the reaction between sulphide ions and ammonium ions in aqueous solution should lead to the formation of ammonium sulphide: this, being the salt of a weak acid and a weak base, should be almost completely hydrolysed with formation of $SH^-$ ions and ammonium hydroxide. Secondly, it is hard to accept the oxidation of a metal on the surface of the electrode at a fairly negative potential by hydrogen ions from hydrogen sulphide. Alternative mechanisms, suggested by Micka, seem more convincing: 1) since metals of the iron group are insoluble in mercury, the metal atoms formed by reaction (10) do not penetrate into the mercury but remain on the electrode surface, and the reduction of hydrogen takes place on the metal rather than on mercury, i.e. at a lower overvoltage; 2) as a result of the relatively high electrical conductivity of the heavy metal sulphides the particles of the suspension acquire the potential of the electrode when they collide with its surface, and the hydrogen is reduced at a lower overvoltage.

The catalytic evolution of hydrogen at a dropping mercury electrode in the presence of suspensions of semiconductors‡ was studied by Japanese workers[59] in a 1 M $NH_4Cl$ base electrolyte. The aim of this work was to correlate the properties of the semiconductor (Si, Ge, P, As, Sb, CdSb, CdTe, $Sb_2S_3$, ZnS, Bi, S, Se, Te, PbS, $Bi_2Te_3$, InAs) with the shape of the polarogram. As with the sulphides of the iron group[54], the polarograms of suspensions of semiconductor catalysts have a current maximum at a potential more negative than −1.0 V. The height of the maximum depends on the electrophysical properties of the semiconductor and on the concentration of the suspension. The potential of the maximum depends on the width of the forbidden gap of the semiconductor. Electrolysis on the macro scale has shown[59] that a semiconductor suspension lowers the overvoltage for hydrogen evolution. A possible mechanism is the following[59]:

$$\underset{\text{on electrode}}{(\text{Catalyst}) + NH_4^+} \rightarrow \underset{\text{on electrode}}{(\text{Catalyst})H^+} + NH_3 \quad (11)$$

$$\underset{\text{on electrode}}{2(\text{Catalyst})H^+} + 2e \rightarrow \underset{\text{on electrode}}{2(\text{Catalyst})} + H_2 \quad (11')$$

The particle itself is not reduced. An analogous mechanism has been proposed[60] for cobalt sulphide. It should be noted, however, that with sulphide suspensions one must consider, in addition to catalytic hydrogen evolution (for sulphides of the iron group[54,60] metals) and to direct reduction of the solid particles of the suspension (for sulphides of metals such as copper, mercury, etc.[55]), also the reduction of the mercury sulphide film formed at the surface of the mercury drop by the sulphide and hydrogen sulphide ions present in these suspensions. The formation and the reduction of such a film in solutions containing $S^{2-}$ and $SH^-$ ions and a suspension of elementary sulphur has been discussed by Kiselev and Zhdanov[61–64].

‡ The term "semiconductor" is used[59] in the wider sense to include electrical insulators.

## VI. MECHANISM OF THE ATTACHMENT OF SUSPENDED PARTICLES TO THE ELECTRODE SURFACE

The reduction of insoluble substances at a dropping mercury electrode in a well defined potential region (Fig. 1) is ascribed by Micka to the existence of adsorption forces between the electrode and the solid particles at these potentials[53]. At very negative potentials repulsive forces arise, and the current falls off[65]: this conclusion is reached from the work of Voropaeva and coworkers[66], who measured the repulsive forces between two crossed wires (gold and platinum) in various electrolytes as a function of the potential of the wires, and found that the force is a minimum at a definite potential.

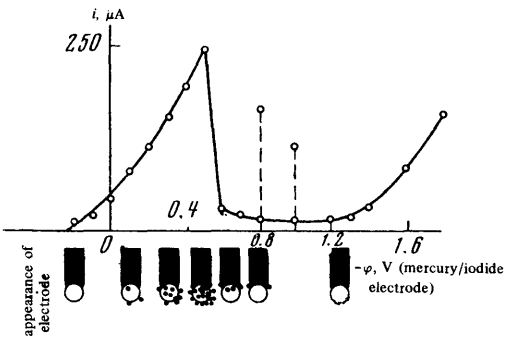



**Figure 3.** Reduction polarogram of a suspension of $Hg_2I_2$ (0.01 mole litre$^{-1}$) in 0.1 M $KNO_3$, measured[67] with a "hanging mercury drop" electrode and a mercury/iodide reference electrode.

Measurements of the polarographic reduction[67] of insoluble halide and mercury oxide suspensions with a "hanging mercury drop" electrode have shown that an increasing proportion of the particles becomes attached to the electrode surface as the cathodic polarisation is increased to −(0.4–0.5) V relative to the mercury–iodide electrode, but at −(0.5–0.6) V the particles are strongly repelled (Fig. 3). The maximum current in the polarogram corresponds to the maximum number of particles attached to the surface, and the decrease in current corresponds to expulsion of the particles: in other words, the polarographic currents of the suspension are related to the attachment of particles to the electrode surface and to their subsequent reduction. The potential region corresponding to the current maximum extends on either side of the zero-charge potential ($\varphi_{\epsilon=0}$). Electrocapillarity measurements by the mercury drop time method[68] in suspensions of mercury oxides and halides have confirmed that the potential of the current peak is close to the potential of the maximum on the electrocapillarity curve, i.e. to the zero-charge potential.

Jones and Kaye[69] also stressed the significance of $\varphi_{\epsilon=0}$ in their work on the reduction of suspensions of various carbons on mercury-pool and hanging-mercury-drop electrodes. They ascribe the current maximum on the reduction polarograms of their suspensions to the damping of the motion of the mercury surface near the zero-charge potential, which enables the particles to come into contact

with the mercury surface, rather than to attraction of the particles by the surface: as the potential deviates from $\varphi_{\epsilon=0}$ in either direction, the surface of the mercury and the adjacent layer of electrolyte experience violent motions (as in the case of polarographic maxima of the first kind) which destroy the contact between the particles and the surface. However, it is difficult to reconcile this explanation with the absence of a reduction current at high cathodic polarisations even when intensive stirring is applied to increase the frequency of collisions between the particles and the electrode[53,67]. The loss of the contact between the particles of the suspension and the surface of the electrode at potentials well removed from $\varphi_{\epsilon=0}$ has also been pointed out by other workers[70].

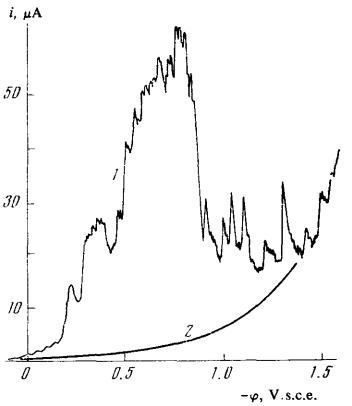



**Figure 4.** 1) polarogram obtained with a dropping mercury electrode in a suspension of positive oxidised carbon (10 mg) in a 1 M $HClO_4$ base electrolyte (25 ml), deaerated and stirred; 2) polarogram of the base electrolyte (from Ref. 71).

Stirred suspensions of activated oxidised carbons give rise to large polarographic currents, due to the reduction of oxygen-containing surface groups (Fig. 4)[71]. If these suspensions (which are relatively stable, and settle very slowly[72]) are left unstirred, their polarograms lose all the reduction peaks and become identical to the polarogram of the base electrolyte (curves *1* and *2* of Fig. 5). In the presence of molecular oxygen the polarogram develops a reproducible maximum in the region of the oxygen reduction wave at potentials which include the point of zero charge (curve *4* of Fig. 5). The current maximum is due to the reduction of molecular oxygen on the electrode surface, enhanced by the attachment of carbon particles[71,73]. The shape of polarograms for suspensions of active carbons, measured in the presence and in the absence of oxygen, indicates that the particles in unstirred suspensions are not reduced although they adhere to the surface of the electrode at potentials near $\varphi_{\epsilon=0}$. A similar phenomenon was reported by Micka[65], who found that particles at rest on the mercury surface are not reduced.

These phenomena, and the link between $\varphi_{\epsilon=0}$ and the degree of adhesion, are convincingly explained by some observations of Frumkin[74,75] on the relative stabilities of liquid films of different thickness, which are determined by the relationship between the surface tension and the thickness of the layer[74]. When the layer of liquid between a gas bubble and the solid surface is made progressively thinner, a critical thickness is reached beyond which instability sets in. The liquid layer is disrupted, and the bubble can attach itself to the surface, but a very thin film of liquid nevertheless remains between the bubble and the surface. In the case of a metallic surface the adhesion depends on the potential[75]: for example, the attachment of a hydrogen bubble to a mercury surface is instantaneous at the zero-charge potential, because the liquid layer of electrolyte becomes labile in the absence of charge and is easily disrupted by the approaching bubble. As the potential moves away from $\varphi_{\epsilon=0}$ the liquid layers are stabilised by the electrical double layer, and the attachment of the bubbles becomes slower[75]. The surface tension of the layer of electrolyte between the bubble and the electrode (and therefore also the force needed to separate the layer) is proportional to the square of the potential difference between the metal and the solution. Hence, the wettability of the metal by the liquid increases as the potential departs from the point of zero charge, and the angle of contact observed after the attachment of a bubble decreases[76]. The bubble is held in contact with the electrode surface by capillarity forces acting on the perimeter of the area of contact.

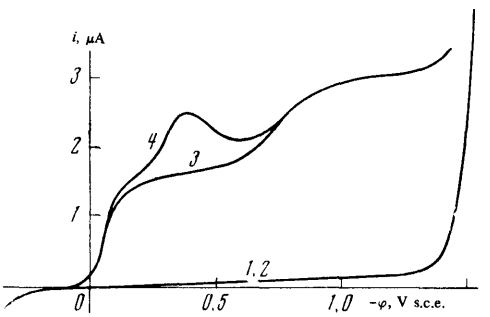



**Figure 5.** Polarograms measured in 1 M $KNO_3$ with a dropping mercury electrode: 1) without oxygen or carbon (base electrolyte only), 2) without atmospheric oxygen but in the presence of a suspension of positive oxidised carbon (10 mg in 25 ml); 3) in the presence of atmospheric oxygen but without carbon; 4) in the presence of atmospheric oxygen and a suspension of positive oxidised carbon (10 mg $ml^{-1}$) (from Ref. 71).

The adhesion phenomenon has been studied also for mercury droplets on glass[77]. The force of attraction between the mercury and the glass surface varies with the potential of the mercury in much the same way as the adhesive force of gas bubbles.

In the case of suspensions, the layer of liquid between particle surface and electrode surface behaves very probably as described above. Thus, the fact that the solid particles become attached to the electrode surface only in a well defined region of potentials can be ascribed to the disruption of labile layers of electrolyte near the zero-charge potential.

By comparing the peak potentials in the polarograms for positive and negative oxidised carbon suspensions[73]

we conclude that the electrostatic effect of the charges on the particles is negligibly small: with a negative carbon the adhesion of the particles reaches a maximum at a charge on the mercury surface slightly more positive (no more than 0.07 V) than with a positive carbon, but the region of adhesion is the same for the two carbons [−(0.3–0.6) V relative to the saturated calomel electrode]. This suggests that the adhesion results primarily from the ready disruption of electrolyte layers in the region of $\varphi_{\epsilon=0}$, rather than from interaction between the charges on the electrode surface and on the particles of the suspension.

In contrast to other types of attachment to an electrode (for example, the interaction of freshly precipitated particles with an electrode, due to the influence of their surface charges), the attachment of particles at potentials close to the point of zero charge may be termed electrocapillary attachment.

The exaltation of the reduction current of dissolved oxygen in the presence of a carbon suspension[71] can be used as a measure of the degree of attachment of the particles to the surface of a dropping mercury electrode as a function of the experimental conditions. The method has been used to demonstrate the dependence of electrocapillary attachment on the amount of carbon in suspension (the "concentration" of the suspension) and on the height of the mercury column ($h$).[71] By increasing the "concentration" of the suspension we can increase the number of particles attached to the electrode surface, and thus obtain enhanced reduction currents of dissolved oxygen in the potential region which favours attachment of the particles. However, since the drop has a limited surface area, there is a critical "concentration" beyond which further increase has no effect on the oxygen reduction current. The dependence of electrocapillary attachment on $h$ has the characteristic form of slow adsorption processes, in which the maximum in the first oxygen wave is suppressed. This dependence also can be easily explained by invoking the analogy between the adhesion of bubbles and the adhesion of solid particles to the electrode surface. For a bubble of a given size we can define an "induction period": the time for the disruption of the layer of electrolyte between the bubble and the electrode surface immediately before the bubble becomes attached[75]. Evidently, this definition applies also to the particles of a suspension. For low values of $h$ the life time of the drop ($\tau$) is greater than the "induction period", and particles can adhere to the surface of the drop until the drop becomes detached. As $h$ increases the drop time of the mercury decreases, and only those particles whose size corresponds to an "induction period" smaller than $\tau$ can become attached. Lastly, at large values of $h$ attachment is impossible because $\tau$ is smaller than the "induction period" of even the smallest particles.

Decreasing the concentration of the base electrolyte increases the exaltation of the oxygen reduction current in the presence of a carbon suspension, i.e. it increases the electrocapillary attachment of the carbon particles to the electrode[73]. This effect arises from the increased diffuseness of the double layer, i.e. from the increased double layer thickness: theory predicts[75] that under these conditions the stability of the layers of electrolyte adjacent to the electrode should decrease, and hence the attachment of particles should be enhanced.

Assuming (by analogy with the case of a bubble) that a very thin layer of electrolyte remains between the electrode surface and the particle attached to it, it is easy to see why adsorbed oxygen in unstirred carbon suspensions is not reduced at the electrode (see curve *2* of Fig. 5), in spite of the attachment of particles to the electrode[71]. When the suspension is stirred, however, the layers of electrolyte between electrode and attached particles become even thinner, and may disappear completely, thus allowing the reduction of the oxygen bound to the carbon (see Fig. 4). Frumkin has pointed out[74] that stable layers can become unstable under the influence of quite small external disturbances. If we assume that even the thinnest layers of electrolyte can prevent the reduction of a solid particle at the electrode, we must conclude (from the fact that large currents are observed in stirred but not in unstirred suspensions) that neither the complete disruption of the electrolyte film nor the direct reduction of a particle can be excluded in the case of stirred suspensions.

At potentials too negative to permit electrocapillary attachment the reduction of solid particles of polarographically active suspensions such as mercury halides is suppressed even with vigorous stirring, in spite of the collisions between the particles and the electrode[67]. However, for small negative excursions from the region of attachment potentials [−(0.7–0.9) V s.c.e.] the particles colliding with the electrode squeeze the layer of electrolyte adjacent to the electrode to a very small thickness, or even disrupt it completely, and can be reduced without attachment. Hence, on stirring, the potential region where reduction can occur is shifted towards values more negative than the region of electrocapillary attachment [−(0.3–0.6) V]. For example, a carbon suspension in a neutral base electrolyte gives a current peak at −0.8 V when stirred. In the light of this discussion, the high negative peak potentials observed in the reduction polarograms of other insoluble substances[55] should cause no surprise. Some of the more energetic particles can "puncture" the layer of electrolyte at still more negative potentials, as shown by the sharp and random current surges observed in the polarogram[67].

Summing up, the behaviour of suspensions of insoluble substances at a dropping mercury electrode may be described by the following steps: 1) breakdown of the layer of electrolyte adjacent to the electrode as the particle approaches the surface; 2) attachment of the particle to the electrode surface under the influence of capillarity forces; 3) discharge of the solid particle at the electrode.

As shown above, the second step may be absent, and discharge without attachment can occur if the particle collides with the electrode surface with sufficient energy to disrupt the boundary layer of electrolyte. The third step also is not invariably observed, but only occurs at sufficiently negative potentials.

It is interesting to note that freshly precipitated iron, cobalt, and nickel sulphides (in the form of a very slight turbidity) are not polarographically active[54]. A reduction current appears only when the colloidal sulphide begins to coagulate, i.e. when the particles begin to grow. The lack of electrochemical activity of a freshly precipitated compound (silver bromide) was pointed out also by Bowers and Kolthoff[78]. Most probably, particles of typically colloidal dimensions ($0.1 < r < 1\ \mu m$) such as those of a freshly formed turbidity cannot become attached to the electrode and be reduced because their kinetic energy is insufficient to overcome the disjoining influence of the layer adjacent to the electrode surface. (Deryagin[79] discusses the relationship between the size of colloidal particles and the repulsive forces acting on the particles. It may be assumed that the size of the particle influences also its interaction with the electrode surface.) Reduction currents at a dropping mercury electrode are sometimes

observed in colloidal systems, but they are not usually associated with the direct reduction of the particles. For example, the current in finely divided carbon suspensions[80,81] arises from the reduction of quinoid groups transferred to the solution from the surface of the carbon particles. In transparent colloidal solutions of iron hydroxide (particle radius $< 0.1$ μm) a reduction wave is observed[82] rather than a maximum. Evidently, the reduction of these colloidal solutions is governed by the same diffusion laws as the reduction of ions in true solutions.

Pairs of maxima have been observed in the reduction polarograms of mixtures (HgS and PbS[53], HgS and FeS[54]). However, the appearance of two current maxima does not necessarily imply that the potential of maximum attachment is different for the two kinds of particle. The particles of the two compounds adhere to the electrode over a wide range of potential, which includes the zero-charge potential, but only the mercury sulphide particles can be reduced at low negative potentials. At the same time, the film of mercury sulphide[61,62] formed on the electrode because of the presence of sulphide ions in the suspension is also reduced. At more negative potentials the reduction of the PbS and FeS particles can take place—or catalytic hydrogen evolution in the presence of FeS—and the second maximum is formed, followed by a decrease in current due to the loss of adhesion at sufficiently negative potentials.

A pair of maxima is observed also in the reduction polarograms of suspensions of manganese dioxide, plotted with a dropping mercury electrode in solutions of sulphuric acid and ammonium sulphate: the first maximum occurs at +0.1–(–0.2) V s.c.e., the second at much more negative potentials [–(1.3–1.4) V][65]. Their origin is not discussed[65], but it is assumed that solid particles are reduced in both cases (to give manganese ions of different valencies). However, the first maximum is more likely to be due to the reduction of mercury ions, formed by the direct oxidation of the metallic mercury of the electrode by particles of adhering manganese dioxide. (A weak electrocapillary attachment can be expected even at the potentials of the first maximum, since they are not too far removed from $\varphi_{\epsilon=0}$.) We have shown[83] that mercury ions can be formed in the presence of an oxidising agent. The fall in current after the first peak can be ascribed to the inhibiting effect of the increasingly cathodic potential on the reaction between the manganese dioxide and the mercury. Reduction of $MnO_2$ occurs at high negative potentials (second peak). Although the electrocapillary attachment is not very strong at these potentials, the particles colliding with the electrode can overcome the disjoining effect of the interfacial layer of electrolyte and remain briefly in contact with the electrode. The reduction process is accompanied by catalytic hydrogen evolution[65], made possible by the decreased overvoltage on the $MnO_2$ particles.

A second maximum at very cathodic potentials(–1.2 V relative to the normal calomel electrode) has been observed also in the reduction polarograms of heat-treated silver carbonate[84]. This maximum is ascribed to the formation of a new form of silver carbonate with a high density of lattice defects; it is not very sharply defined, and consists of a collection of current surges probably associated with particularly energetic collisions outside the region of electrocapillary attachment.

Thus we may conclude that particles of a suspension of insoluble material are reduced at a dropping mercury electrode by virtue of the electrocapillary attachment of the particles to the electrode in the region of potentials around $\varphi_{\epsilon=0}$, or by collisions between the particles and the electrode at potentials not too far removed from this value. The following conditions are necessary: 1) the reduction potential of the insoluble substance must not be more negative than the region of potentials at which attachment occurs: 2) the particle size of the suspension must be greater than average colloidal dimensions ($r > 1$ μm), i.e. the suspensions must be coarsely disperse according to the conventional classification used in colloidal chemistry: 3) stirring (not necessarily vigorous) of the suspension is essential.

In all the work discussed above stirring was produced by a stream of inert gas or by a magnetic stirrer. However, the random collisions of the particles with the electrode produce irregular current surges, and therefore the polarograms are not easy to reproduce. A novel design of polarographic cell has been proposed[85] with the aim of providing a more regular stream of particles colliding with the electrode: a stream of gas, supplied at a constant flow rate, induces circulation of the solution towards the electrode, also at a constant rate. External means of ensuring regular drop detachment are provided. A cell of this design was used to measure the rate of dissolution of lead salts in various media, but the results were disappointing[85]. Evidently, an even flow of particles towards the electrode had not been achieved.

## VII. BEHAVIOUR OF SUSPENSIONS ON AN AMALGAMATED ROTATING-DISK ELECTRODE

An even flow of the particles of a suspension towards the electrode can be achieved only by using a rotating disk electrode. Suspensions of activated oxidised carbon[86,87] and of insoluble mercury halides[88] have been studied on an amalgamated rotating-disk electrode. Strong attachment of the particles to the electrodes is again observed in the potential region corresponding to the point of zero charge of mercury. However, the region of electrocapillary attachment is much broader with the rotating disk electrode than with the dropping mercury electrode, and can extend over 1.0–1.1 V. This is because the layers of electrolyte between the solid particles and the electrode surface are more easily disrupted when the electrode is a rotating disk, which produces a very energetic flow of particles, and adhesion becomes possible at potentials quite far removed from $\varphi_{\epsilon=0}$. Carbon particles attached to the electrode[86] are retained even when the potential is moved still further from $\varphi_{\epsilon=0}$: down to potentials of –(1.7–1.9) V s.c.e. At still more cathodic potentials the particles are eventually detached. Thus, with carbon suspensions the amalgamated electrode is covered with particles over a range of potentials extending over almost 2 volts.

In the polarisation curves given by suspensions of oxidised carbons the reduction current is directly proportional to potential over a wide range of potentials. This current is due to the reduction of oxygen groups on the surface of carbon particles attached to the electrode (Fig. 6). The steeper increase in current which sets in at –(1.0–1.2) V in neutral and in alkaline solutions, and at –(0.7–0.8) V in acid solutions, is due to the evolution of hydrogen on the surface of the particles, since the hydrogen overvoltage on carbon is lower than on mercury. The polarograms for the neutral and the alkaline electrolyte show a steep fall in current at –(1.7–1.9) V, due to the detachment of the carbon particles. In acid solutions the detachment potential is not reached because hydrogen evolution begins at lower voltages. (Note that detachment is not observed

with the dropping mercury electrode, discussed in Section VI, because the surface of that electrode is constantly renewed.) The detachment is the result of the enhanced disjoining action of the interfacial layer of electrolyte at potentials sufficiently far removed from $\varphi_{\epsilon=0}$. The reduction currents of attached particles are independent of the rate of rotation of the electrode, but they show a slight increase with the "concentration" of the suspension. The detachment potential of the particles, on the other hand, depends on the rate of rotation of the electrode ($\omega$): the greater $\omega$, the more readily are the particles detached, evidently because of the centrifugal forces acting on them[86].

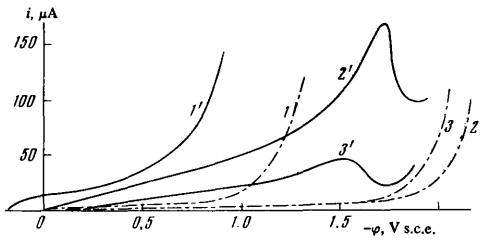



**Figure 6.** Polarisation curves measured with an amalgamated rotating-disk electrode in 0.1 M solutions of $HClO_4$ (*1*, *1'*), KCl (*2*, *2'*), and KOH (*3*, *3'*) in an argon atmosphere without (*1*, *2*, *3*) and with (*1'*, *2'*, *3'*) a suspension of positive oxidised carbon; $\omega$ = 3890 revolutions $min^{-1}$ (from Ref. 86).

In the course of studies of carbon suspensions it was realised that information could be obtained on a number of electrochemical processes (such as the reduction of dissolved molecular oxygen and hydrogen peroxide[86,87]) which can occur on the surface of carbon particles attached to the electrode. By making a number of simplifying assumptions, the degree of screening ($\theta$) of the surface of the amalgamated electrode by the carbon particles could be calculated[86]: it was found to be independent of the rate of rotation of the electrode, but slightly dependent on pH ($\theta$ = 0.4 in alkaline electrolyte and 0.5 in a neutral electrolyte). In acid solutions $\theta$ cannot be evaluated, but it is reasonable to assume an even higher screening because the reduction currents in acids are higher than in alkalies by a factor of 2–4.

The reduction currents on a rotating amalgamated electrode of suspensions of mercury halides are an order of magnitude greater than the reduction currents of carbon suspensions on the same electrode, since the whole of the attached particle is reduced, and not just the oxidised surface groups[88]:

$$Hg_2Br_2 + 2e \rightarrow 2Hg + 2Br^- \qquad (12)$$

Thus, under reducing conditions the particles of mercury halide attached to a rotating amalgamated electrode are continually disappearing, and the electrode surface is continually restored: this is shown in the polarograms by periodic negative current surges. Hence, the steep fall in the polarographic current (Fig. 7) is not due to the detachment of particles, but to the weakening of the electrocapillary attraction effect as the potential swings beyond $\varphi_{\epsilon=0}$. Increasing the speed of rotation of the electrode strengthens the onrush of the particles towards the surface, and helps them to overcome the disjoining effect of the interfacial layers of electrolyte at more negative potentials, thus causing a shift of the sharp drop in current towards more negative potentials.

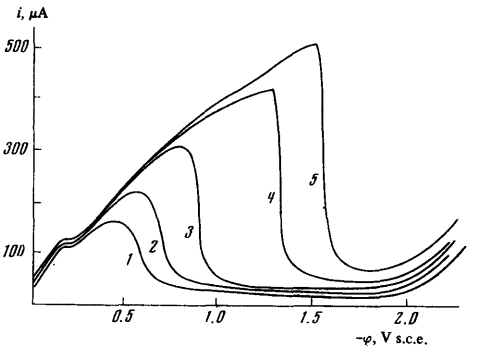



**Figure 7.** Polarisation curves for the reduction of a suspension of $Hg_2Br_2$ (0.05 mole $litre^{-1}$) in 0.1 M $Na_2SO_4$ on an amalgamated rotating-disk electrode: 1) $\omega$ = 1030, 2) 1970, 3) 3890, 4) 5700, 5) 7660 revolutions $min^{-1}$ (from Ref. 88). Periodic current surges are not shown.

The fact that the suspensions do not give a reduction current at high negative potentials, in spite of the very vigorous stirring and of the powerful collisions of the particles with the surface of the disk electrode, is further proof of the reality of the attachment of particles to the surface of a mercury or amalgamated electrode at potentials close to $\varphi_{\epsilon=0}$, and strengthens our conclusion that direct reduction of the solid particles of a suspension under polarographic conditions can occur, in general, only if the particles are attached to the surface of the electrode.

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Our recent study of mercury halide suspensions on a solid (rotating) disk electrode[89] has shown that the particles of coarse suspensions do not adhere to the surface of a solid electrode. Accordingly, no reduction currents are produced by the particles of these suspensions. Most probably, the electrocapillary attachment of solid particles to an electrode surface is possible only when the surface is liquid (as in the case of the dropping mercury electrode or the amalgamated electrode), i.e. mobile and capable of sufficient deformation to produce the angle of contact at the three-phase boundary (electrode–electrolyte–particle) needed to accommodate the capillarity forces which hold the particle to the electrode surface. Frumkin[77] has invoked deformation of the surface of a liquid electrode in his discussion of the attachment of gas bubbles and of glass surfaces to mercury. It should be noted that small, colloidal particles were always present in the coarse suspensions of mercury halides used in our work with a rotating electrode. These particles are reduced at a platinum electrode (see Section IV): they can reach the electrode surface by diffusion, and furthermore these very small particles are subject to forces of adhesion (but not electrocapillary attraction) to the electrode by virtue of their roughness and of their surface charge.

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Kirov State University of Kazakhstan,
Alma-Ata