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ELECTROCHEMICAL IMPLANTATION OF ALKALI METALS

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I. INTRODUCTION

The alkali metals are deposited on cathodes at potentials so negative that hydrogen evolution makes them inaccessible in aqueous solutions, even when the electrodes consist of metals with a high hydrogen overvoltage such as lead or mercury. The highest potentials attainable under ordinary experimental conditions are more positive than the equilibrium potentials of the alkali metals by about 1 V. However, if liquid mercury is used as cathode, the alkali metals can be discharged at not too negative potentials because the discharge potential is shifted towards more positive values. This phenomenon is well known, and has been used in industry for a long time and has been investigated by physical chemists for over a hundred years. The cause of this shift is the strong chemical interaction between the alkali metals and mercury, with formation of amalgams. Electrolysis of aqueous solutions has produced amalgams not only of the alkali and alkaline earth metals, but also of ammonium and of some organic cations such as tetramethylammonium [1,2].

The large free energy change accompanying amalgam formation is the basic factor which enables alkali metal ions to be discharged on mercury from aqueous solutions. The high hydrogen overvoltage of mercury, which increases the fraction of the current carried by alkali metal deposition, and the rapid convective transport of the alkali metal towards the deeper layers of the liquid cathode (coupled with the high rate of formation of the amalgam), favour the discharge of alkali metal cations and enable the process to be used in practice. For this reason, the process has effectively been studied only at a liquid mercury cathode.

Numerous experimental studies have shown that the rate of discharge of alkali metal ions on mercury is very high[3-9]. Only recently have such measurements been made possible by the use of the Faradaic impedance[10] and the Faradaic rectification method[11]. Exchange current densities of the alkali metal ions have been found to be of the order of 0.1–0.2 A cm^{-2} on these amalgams.

II. THERMODYNAMIC POSSIBILITY OF DISCHARGING ALKALI METAL IONS

Strong chemical interactions with alkali metals are not an exclusive property of mercury. It is well known that the alkali metals, which occupy the first subgroup of the Periodic Table, react energetically with many elements, the reactivity increasing with increasing non-metallic character of the elements in question. We must remember that the overriding factor in the formation of intermetallic compounds is not, in general, the energy of interaction between the atoms involved in compound formation, but other factors such as the dimensional relationship between the reacting atoms or the concentration of free electrons in the resulting metallic compound. However, if the atoms from which the compound is formed show a strong interaction (as in the case of gold and an alkali metal) this interaction is found, as a rule, to be the major factor which determines the structure and properties of the intermetallic compound[12]. This accounts for the formation of stable intermetallic compounds, similar to amalgams in their properties, between the alkali metals and many other metals.

The behaviour of atoms towards compound formation can be characterised, for example, by the Pauling electronegativity concept[13]. The greater the electronegativity difference between two atoms, the more strongly the atoms will interact, and the greater the percentage ionicity of the resulting bond. Electronegativity values, taken from Ref. 14, are listed in Table 1. Most of these values were obtained by thermochemical methods.

It is evident from the table that the electronegativity of mercury is no greater than that of many other metals. Therefore, these metals should interact with the alkali metals at least as strongly as mercury.

TABLE 1.

Elements	Li	Na	K	Rb	Cs	Cu	Ag	Au	Zn	Cd
Electronegativity	0.95	0.9	0.8	0.8	0.75	1.8	1.9	2.3	1.6	1.7
Elements	Hg	Sn^{2+}	Sn^{4+}	Pb^{2+}	Pb^{4+}	Bi				
Electronegativity	1.8	1.7	1.8	1.6	1.8	1.8				

TABLE 2.

	Cd	Sn	Pb	Zn
Na	1.4	1.2	1.5	1
K	1.8	1.2	1.5	1.1

Many experimental investigations have been aimed at the interactions between alkali metals and other metals. They include measurements of the e.m.f. of a cell consisting of an alloy of the alkali metal and of one of the components of this alloy. However, this work was done mostly at high temperatures, above the melting point of the alloys. Hauffe and Vierk[15,16], and also Alabyshev, Morachevskii, and others[17-20], examined a large group of metals (Cd, Tl, Hg, Sn, Pb, etc.). Their experimental results indicate that at temperatures of 300–600° some of the metals (e.g. Cd, Tl) react with the alkali metals more strongly than does mercury, whilst others (e.g. Sn, Pb) show an interaction comparable to that of mercury or somewhat weaker. In order to extrapolate from these experimental data to the interaction at room temperature, we must know the temperature variation of the specific heats of the alloys. No such data are available at the present time. It must also be remembered that compounds which would form at room temperature may dissociate at higher temperatures. Hence, no firm conclusions as to the likely value of the interaction energy between these metals at room temperature can be drawn from these and other similar investigations.

Two series of relatively old papers (by the schools of Haber[21,22] and Kremann[23-29]) are concerned with studies of the potentials of alloys of the alkali metals. The work was carried out in solutions of electrolytes in organic solvents at room temperature and below. The results of these two series of papers are in good agreement, but the measurements of Kremann and his coworkers are the more accurate, and include a greater variety of metals. Some of the results obtained by Kremann's school are reproduced in Table 2, which lists the potentials of the most noble of the intermetallic compounds examined by those workers. The potentials are referred to the pure alkali metal, and are therefore equivalent to the maximum positive shift of the potential for cathodic deposition of the alkali metal on the particular electrode.

The table shows that the discharge potential of Na and K on Sn, Pb, Zn, and Cd electrodes is lowered by more than 1 V, which suggests that the deposition of alkali metals from aqueous solutions on these electrodes is apparently quite feasible.

Thus, we may conclude from these data that mercury has no thermodynamic advantage over a number of other metals. The discharge of alkali metal ions from aqueous solutions can be expected to occur also on other metals under suitable conditions.

III. EXPLANATION OF SOME OBSCURE PHENOMENA BY MEANS OF THE IMPLANTATION CONCEPT

Until quite recently, there had been no experimental papers giving a direct demonstration of the possibility of discharging alkali metal ions on solid electrodes from aqueous solutions. There was some indirect evidence, however, that the process should be possible. Some

remarkable electrochemical phenomena have been observed during cathodic polarisation of solid electrodes in aqueous solutions containing alkali metal ions. A satisfactory explanation of these phenomena necessitates the assumption that the alkali atoms can be implanted into solid electrodes. The deposition of alkali metals on solid metal electrodes with formation of intermetallic compounds accompanied by penetration of the alkali metal into the bulk of the electrode has been termed[30] electrochemical implantation of alkali metals.

At the turn of the century Bredig and Haber[31,32] discovered and investigated the cathodic disintegration of lead, tin, mercury, thallium, and bismuth. They showed that the process can be reproduced satisfactorily only if the electrolyte contains alkali metal ions. In all cases, loosening of the electrode occurs before disintegration. The cathodic disintegration of lead and tin was later examined in more detail by Haber and Sack[21], and by Sack[22]. These workers explained the phenomenon by postulating the possibility of discharge of alkali metal ions at the electrode, but their discussion of the mechanism of this process is rather superficial.

After the work of Haber and Sack, not a single paper on the cathodic disintegration of lead appeared for almost half a century, and it was not until 1953 that Salzberg[33-35] again investigated the features of this process. He also found that cathodic disintegration proceeds stably and reproducibly only when alkali metal cations are present in solution, but he was unable to give the correct explanation of the phenomenon. Angerstein[36] showed that the disintegration of lead in acids, observed in some experiments both by Haber's school and by Salzberg, is due to the presence of alkali metal impurities in the solution.

Kabanov and his coworkers[37-39] observed the cathodic superactivation of aluminium and magnesium in alkalis, and explained it by assuming cathodic formation of a surface compound of Al or Mg with an alkali metal. This hypothesis was based on the dependence of superactivation upon the nature of the cation (from lithium to tetramethylammonium). In their study of the electrolytic reduction of acetone in alkaline solutions, Antropov and his coworkers[40] observed anomalous current yields on a number of solid cathodes. The anomalies were similar to those resulting from the use of amalgam cathodes. To explain their results, the authors suggested that intermetallic compounds are formed between an alkali metal and the cathode metal when lead, tin, zinc, and cadmium electrodes are cathodically polarised.

Turomshina and Stender[41] studied the electrodeposition of zinc from sulphuric acid solutions, and found that the current efficiency of zinc deposition drops when alkali metal ions are present in solution. They ascribe this behaviour to incipient co-deposition of alkali metal ion with the zinc ions†, with formation of the appropriate intermetallic compounds.

There are many reports of unexplained phenomena, noticed during measurements of the hydrogen overvoltage of various metals: slow changes in overvoltage with time, hysteresis, abnormally high slopes of the linear plots of overvoltage against the logarithm of current density[42-45]. The absolute values of the overvoltage (or the rates of hydrogen evolution at a given potential) in alkaline solutions are often very sensitive to elusive differences in experimental conditions. These surprising phenomena have not always been described in the published papers (unless of course they had a direct bearing on the main topic of the paper) because they were thought to arise from trivial, random causes. In some cases these phenomena are explicitly ascribed to the influence of random factors[43-45]. Thus, Kaptsan and Iofa have retracted the electrochemical mechanism of decomposition of amalgams[46] put forward in their previous papers, believing it to be due to random factors, and early measurements of the hydrogen overvoltage of mercury and of dilute amalgams in alkaline solutions have recently been re-examined[47-49], but no explanation has been given why the difficulties encountered in alkalis do not arise to the same extent when working in acid solutions. In some cases the change of overvoltage with time is explained by postulating the formation of surface hydrides.

The idea of alkali metal implantation was first put forward a few years ago[30] to explain the very startling hydrogen overvoltage curves obtained for zinc in alkalis. The explanation was later extended to other cases of hydrogen evolution on solid metals in alkaline solutions.

The shape of the plot of hydrogen evolution potential against the logarithm of current density is very sensitive to the conditions of measurement. Under certain conditions we find satisfactorily reproducible linear plots with a slope of 0.11–0.12 V. The requirements are that the cathodic potential of the electrode is not allowed to exceed a certain value, and that the measurements are made in a sufficiently short time. When the curve is plotted slowly, the potential begins to increase with time upon reaching a certain value (Fig. 1). After a few tens of minutes the electrode potential has shifted by 0.2–0.3 V in the negative direction. After this cathodic polarisation the slope of the curve is very much higher, and hysteresis is observed. If the curve is now plotted in the reverse direction (from high towards low polarisations), the potential is found to decrease with time at constant current when the polarisation of the electrode has been reduced by a sufficient amount.

We put forward the hypothesis that the time variation of the hydrogen evolution potential is associated with the formation (by implantation) or with the decomposition at the cathode surface of intermetallic compounds formed by the cathode metal with alkali metal atoms. The hydrogen overvoltage at the surface of these compounds is higher, as a rule, than on the pure metal (probably because of the lower hydrogen adsorption energy). The properties of the intermetallic compounds formed depend on the nature of the cation. Thus, the hydrogen overvoltage in alkalis is a

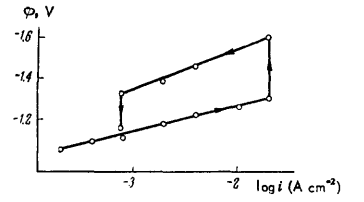


Fig. 1. Polarisation curves for hydrogen evolution on silver in 1 *N* NaOH.

† Since co-deposition of alkali metal ions with zinc ions is involved, rather than penetration of the alkali metal into the zinc cathode, this phenomenon is of minor relevance to our problem.

function of the nature of the alkali metal cation. The overvoltage increases with increasing ionic radius of the non-hydrated cation. After strong cathodic prepolarisation, the potential of the silver electrode at a current density of 10^{-2} A cm^{-2} corresponds to -1.42, -1.54, -1.56, -1.68, and -1.72 V for the cations Li^+, Na^+, K^+, Cs^+, and $(CH_3)_4N^+$ respectively.

The observed dependence of hydrogen overvoltage upon the nature of the cation can be explained in terms of the variation of the adsorption properties of the intermetallic compounds towards hydrogen atoms when the cation is varied.

On the other hand, the implantation of the alkali metal is easier and faster, the smaller the intrinsic ionic radius, i.e. the faster the diffusion of the cation into the electrode metal. For this reason, lithium is implanted faster than any other alkali metal, and the lithium intermetallic compounds decompose more rapidly than others. This conclusion was drawn from measurements of the time needed to establish a constant electrode potential in hydrogen evolution experiments. The time was found to be shorter for the cations of smaller radius.

Recently, the structural changes of the surface of silver and zinc electrodes have been examined by electron microscopy after cathodic polarisation in solutions containing alkali metal ions[30,50]. Fig. 2 shows the structure of a silver electrode surface after weak polarisation lasting 3 h, Fig. 3 shows the same surface after strong polarisation. It is easy to see that strong polarisation causes loosening of the electrode surface. Similar changes take place on the surface of strongly polarised zinc electrodes. It was interesting to find that silver electrodes are embrittled only when their surface is etched in concentrated HNO_3 before polarisation. Electrodes whose surface has been cleaned with glass powder or mechanically polished before polarisation are not loosened under these conditions.

To detect structural changes in the deeper layers of the electrode, electron diffraction studies were made on silver films prepared by vacuum evaporation and cathodically polarised in a solution of sodium sulphate. It was found

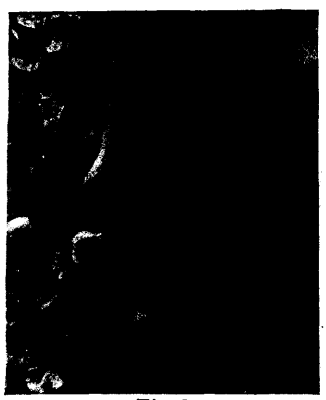


Fig. 2.

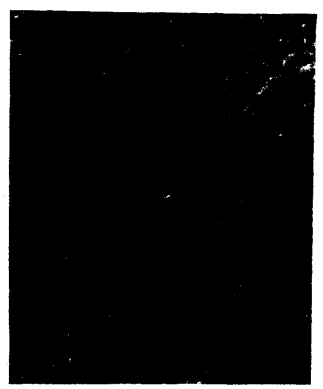


Fig. 3.

Figs. 2 and 3. Electron micrographs (×15 000) of the surface of a silver electrode after polarisation in 1 *N* NaOH:
Fig. 2 — at φ = -1.1 V relative to the normal hydrogen electrode (n.h.e.); Fig. 3 — at φ = -1.5 V (n.h.e.).

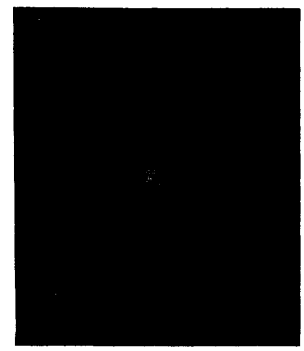


Fig. 4.

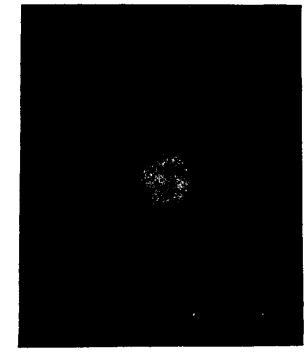


Fig. 5.

Figs. 4 and 5. Electron diffraction pattern of a thin silver film after polarisation in 1 *N* Na_2SO_4:
Fig. 4 — at φ = -1.1 V (n.h.e.); Fig. 5 — at φ = -1.4 V (n.h.e.).

that weakly polarised films give a fairly sharp electron diffraction pattern with narrow lines (Fig. 4). After strong cathodic polarisation the lines become diffuse (Fig. 5), showing that the films tend towards an amorphous structure as a result of polarisation.

Thus the implantation of alkali metals causes both loosening of the electrode surface and also, in some cases, a structural change in a layer adjacent to the surface. This phenomenon should no longer be ignored by electrochemists working with alkaline solutions.

However, none of these explanations was entirely satisfactory, because the implantation process itself was not understood owing to the many and serious contradictions. The most important one is the sharp difference between the small experimentally observed rate of penetration of the alkali metal and the large rates expected from various theoretical considerations and obtained experimentally for the amalgam formation process. Before attempting to explain this difference, we shall deal with the methods for investigating the implantation of alkali metals into solid metallic electrodes, and with the experiments on which was based the assertion that alkali metal implantation is possible.

IV. EXPERIMENTAL STUDY OF IMPLANTATION

The electrochemical membrane method[50] is one of the techniques which have been applied to the study of alkali metal implantation into electrodes.

In this method the alkali metal is passed through a zinc foil membrane, polarised on one side. Double electrochemical cells are used, similar to the cells used in electrochemical studies of hydrogen diffusion through a metallic membrane (Fig. 6). On one side of the membrane the alkaline solution is placed, and cathodic polarisation is applied for a long time at various current densities, and on the other side is placed a dilute solution of K_2SO_4, and the pH of this solution is monitored. The results of diffusion measurements of lithium, potassium, caesium, and tetramethylammonium ions through a membrane 30 μm thick indicate that the rate of implantation of the first two ions is in inverse proportion to the crystallographic radius of the ions, whereas caesium and tetramethylammonium ions

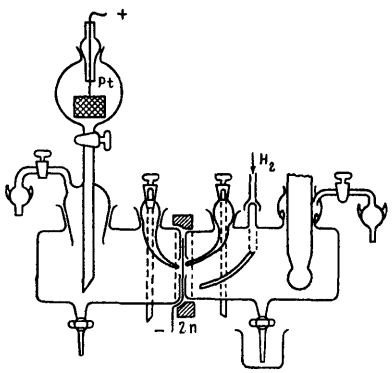


Fig. 6. Cell for measuring the diffusion of an alkali metal through a zinc membrane.

do not in fact diffuse through the membrane. These results are in qualitative agreement with the measurements of the rate of implantation of various ions from the time needed to establish a constant hydrogen evolution potential[42].

The diffusion coefficient of potassium through the zinc membrane was evaluated from the measured time dependence of the rate of diffusion, and found to be of the same order of magnitude as the coefficient for the self-diffusion of zinc along crystal grain boundaries.

The variation of the rate of implantation with electrode potential was investigated in the particular case of penetration of potassium into zinc. In Fig. 7 the polarisation potential of the membrane is plotted horizontally, and the logarithm of the amount of potassium diffusing through the membrane in 22 h is plotted vertically. The membrane thickness was 20 μm. It can be seen that the rate of implantation increases exponentially with increasing membrane potential. A negative shift in membrane potential of 0.35 V raises the implantation rate by nearly a factor of 100.

Implantation is a complicated, inadequately investigated type of diffusion: it involves reactive diffusion, during which the diffusing substance interacts with the medium. In particular, nothing is known about the difference between bulk and grain-boundary reactive diffusion of the alkali metals in other metals. It is known, however,[51,52]

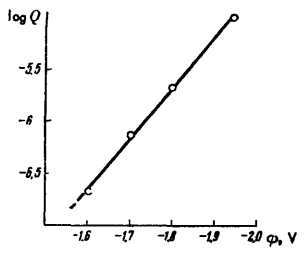


Fig. 7. Variation of the amount (Q) of potassium diffusing in 22 h through a zinc membrane 20 μm thick with polarisation potential of the membrane in 1 N KOH.

that the rate of bulk self-diffusion in zinc at room temperature is smaller by a factor of about 5×10^5 than the rate of boundary self-diffusion. Most often, the bulk and boundary heterodiffusion rates differ by at least as much as the rates of self-diffusion, since the difference is caused primarily by the difference in structure between the crystal grain boundaries and the bulk phase. Therefore, the transport of the alkali metal through the membrane at room temperature can be expected to occur exclusively along crystal grain boundaries. Thus, when comparing measurements of the rate of implantation by diffusion of alkali metal ions through a membrane with measurements based on the time needed to reach a steady potential during hydrogen evolution, it is important to remember that diffusion measurements characterise only the rate of penetration at the outcrop of grain boundaries on the electrode surface. Since the grain boundaries occupy only a small fraction of the electrode surface, clearly, this process cannot give rise to a significant increase in hydrogen overvoltage. The coverage of the whole surface of the electrode by the intermetallic compound and the consequent establishment of a high hydrogen overvoltage arise from penetration of the alkali metal into the surface of the crystal grains (albeit to a very small depth). The rates of these two penetration processes are expected to be vastly different.

The experiments show that loosening of the surface takes place during the actual polarisation. This makes it very difficult to analyse the results of hydrogen overvoltage measurements on solid electrodes, if the solutions contain alkali metal cations, since at least two opposing factors are always operative. On the one hand, the formation of an intermetallic compound raises the electrode potential at constant current density, and, on the other hand, the loosening of the electrode surface lowers the hydrogen overvoltage. There have been reports of a decrease (rather than an increase) of potential resulting from implantation, and the process responsible for this change in potential could not be unambiguously identified. In any case, we cannot exclude the possibility of the hydrogen overvoltage at some intermetallic compounds being lower (rather than higher) than at the pure metal.

The direct study of the implantation process and the study of the properties of the resulting intermetallic compounds meet with a host of difficulties. We must first of all point out that cathodic implantation of an alkali metal in aqueous solutions is invariably accompanied by hydrogen evolution, the rate of the latter process being higher than that of the former by several orders of magnitude. Yet another difficulty attending the study of these systems is the fact that the compounds which are formed are often unstable, and are rapidly attacked by water when the electrode polarisation is removed. For this reason, they cannot be studied by conventional analytical methods. The most appropriate method for the purpose has been found to be one based on oscillographic recording of $\varphi-t$ (potential–time) curves, or charging curves[53].

The $\varphi-t$ curve allows the change in electrode potential to be monitored after an interruption or a reversal of the current. From the type of curve obtained, one can deduce whether or not a certain process operates at the electrode in a given potential region.

It was found that, when a $\varphi-t$ curve is measured without preliminary cathodic polarisation of the electrode in alkaline solutions, the potential suffers a steep, monotonic change, and the electrode capacity calculated from

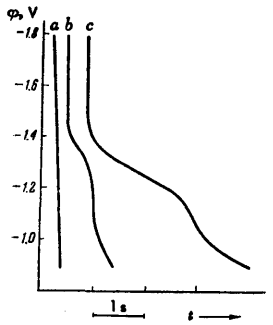


Fig. 8. Anodic potential–time curves for Pb in 1 *N* NaOH; $i_a = 5 \times 10^{-5}$ A cm^{-2}: *a*) t_c = 1 min; *b*) t_c = 15 min; *c*) t_c = 30 min

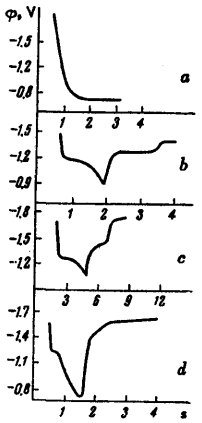


Fig. 9. Anodic and cathodic potential–time curves in 1 *N* LiOH after polarisation at φ_c = -1.6 V: *a*) Cd, t_c = 1 min; *b*), *c*), and *d*) Ag, Cd, Pb, t_c = 30 min.

this curve is equal to the double-layer capacity. If, however, the electrode is cathodically polarised during 30 min in the alkaline solution at a potential of, say, -1.6 V, before plotting the φ–t curve, an arrest is observed on the anodic φ–t curve (Fig. 8). If the cathodic polarisation is once again applied, it is possible to observe a curve for the growth of cathodic polarisation which also has a plateau (potential arrest). Typical anodic and cathodic φ–t curves are shown in Fig. 9: the arrests in the fall and in the growth of potential are clearly visible. Arrests on the cathodic φ–t curves are normally ascribed to the formation of intermetallic compounds, whereas arrests on the anodic curves are ascribed to their decomposition. From the position of the arrests, we can determine an important characteristic of the intermetallic compounds: their equilibrium potential. The equilibrium potential values are intermediate between those corresponding to the onset of the anodic and of the cathodic arrests. Table 3 lists the measured potentials of the arrests, and the equilibrium potentials of the intermetallic compounds of silver, cadmium, lead, and zinc with lithium[53].

TABLE 3.

Potential	Ag	Cb	Pb	Zn
Cathodic arrest	−1.30	−1.40	−1.40	−1.45
Anodic arrest	−1.28	−1.27	−1.28	(−1.35)
Equilibrium	−1.29	−1.33	−1.34	(−1.40)

The presence of arrests on the φ–t curves is indisputable evidence that electrochemical processes occur at the electrode when these potentials are reached. It remains to be proved, however, that these processes are in fact the formation and decomposition of intermetallic compounds, and that the equilibrium potentials observed are those of the intermetallic compounds. Charging curves alone are not enough to justify this assertion. Cathodic polarisation may be expected to give rise also to compound formation between the electrode metal and hydrogen (hydrides)[54].

On metals (such as iron and nickel) which show a strong tendency to adsorb hydrogen, electrochemical formation of surface hydrides is a definite possibility. However, zinc, cadmium, and lead are metals for which no hydrides are known. Metals from which hydrogen is evolved with a large overvoltage, such as mercury, are known to adsorb very small amounts of atomic hydrogen on their surface[55]. Cathodic formation of hydrides in appreciable quantities is unlikely in this case, and amounts of the order of a monolayer are out of the question. Conversely, intermetallic compounds of lead, zinc, cadmium, and silver with alkali metals are well known, and can be prepared chemically or by electrolysis in molten salts with liquid cathodes.

A direct proof that these arrests are associated with the formation and decomposition of intermetallic compounds was obtained by comparing the equilibrium potentials calculated from the arrests with the potentials of genuine intermetallic compounds, prepared by fusing the elements together. This test was applied to a number of compounds, both in aqueous and in non-aqueous solutions. It was found, for example, that the equilibrium potential of $NaPb_3$ prepared by fusing lead with sodium is the same as the equilibrium potential read off the charging curve of lead in a solution of NaOH. Thus the identity of intermetallic compounds obtained by thermal synthesis with those formed by cathodic polarisation was demonstrated.

Anodic curves sometimes show two or three arrests instead of a single one. This indicates that several intermetallic compounds of different composition can be obtained on the electrode under cathodic polarisation.

Assuming that each molecule of the resulting intermetallic compound contains one alkali metal atom, and knowing the standard potentials of the compounds, we can calculate their standard free energies ΔG° of formation by the implantation reaction

$$nM + Li^+ + e = LiM_n$$

and the free energy of these compounds.

TABLE 4.

Composition	φ°	ΔG°	$G^\circ_{LiM_n}$	Composition	φ°	ΔG°	$G^\circ_{LiM_n}$
$LiAg_n$	−1.29	30	−40	$LiZn_n$	(−1.4)	(32)	−38
$LiCd_n$	−1.33	30.5	−39.5	$NaHg_8$	−1.92	44.2	−18.35
$LiPb_n$	−1.34	31	−39	$NaHg_8$	−2.0	46	−16.48

Table 4 lists the free energies of the lithium compounds calculated in this way; for comparison, the values for $NaHg_5$ and $NaHg_2$ are also given.

V. MECHANISM OF IMPLANTATION

1. Implantation Overvoltage

Despite the conclusive evidence discussed above for the existence of alkali metal implantation into solid electrodes in aqueous solutions, all attempts at explaining the behaviour of electrodes in alkalis in terms of implantation failed until the inconsistencies mentioned above (mostly concerning the high implantation overvoltage) were overcome. It was difficult to visualise the cause of the high overvoltage for the deposition of alkali metals, since these metals are deposited on mercury cathodes in alkaline chloride solutions with negligible overvoltage, and they are deposited even more readily in melts. Table 4 shows that implantation into solid metals gives rise to compounds which are more stable than the alkali metal amalgams. Thus we can expect the electrochemical stage of the implantation reaction to proceed at least as fast as the electrochemical amalgam formation reaction. But if implantation into solid metals is fast and exceeds (as in the case of mercury) the rate of hydrogen evolution, we would expect not one monolayer but 10^5 or more monolayers to form in 30–60 min. Furthermore, when the cathodic polarisation is lowered the compound decomposes very rapidly (hundreds of thousands of times faster than implantation into the pure metal).

Using the observed increase of hydrogen overvoltage with time, we can obtain some information on the rate of the cathodic implantation reaction. If we assume that the achievement of a limiting hydrogen overvoltage denotes the completion of a monolayer of the compound, we can evaluate the mean rate of implantation on a fresh electrode. Clearly, this calculation can give no more than the order of magnitude of the reaction rate. The hydrogen overvoltage of lead in 1 *N* CsOH reaches a limiting value after 60 min cathodic polarisation (Fig. 10). The extrapolated mean current density of alkali metal implantation into pure lead at φ = -1.3 V is of the order of 10^{-10} A cm^{-2}. This means that implantation proceeds with an extremely high overvoltage. The fact that, after brief cathodic polarisation of the electrode, the anodic oscillographic charging curve does not show an arrest is further evidence of the slowness of implantation. An anodic arrest can be observed only after lengthy cathodic polarisation (30 min, say)[53,56].

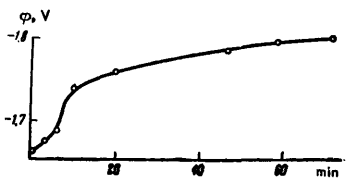


Fig. 10. Growth of the hydrogen overvoltage of lead in 1 *N* CsOH at constant current density $i_c = 3 \times 10^{-3}$ A cm^{-2}.

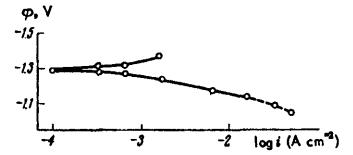


Fig. 11. Polarisation curve for the decomposition of an intermetallic compound, measured for a prepared alloy in 1 *N* NaOH.

The plot of overvoltage curves (φ–log i) is one of the methods used in electrochemistry to measure reaction rates. For the alkali metal implantation reaction, these curves were plotted using the lead–sodium compound obtained by thermal synthesis (Fig. 11). The exchange current of sodium over the alloy was found to be of the order of 10^{-3} A cm^{-2}.

For an electrode of pure metallic cadmium, the variation with potential of the rate of the anodic decomposition of the intermetallic compound produced by previous cathodic polarisation was measured from a series of anodic charging curves, taken over a range of anodic current densities between 10^{-4} and 10^{-2} A cm^{-2}. The potential of the anodic arrest varied with anodic current density. These results were used to construct a φ–log i curve for the reaction at a cadmium electrode (Fig. 12). The exchange current was again found to be $\sim 10^{-3}$ A cm^{-2}.

Thus, even allowing for the very rough approximation made in the estimation of the rate of the implantation reaction on lead, we can say that the rates of implantation into a fresh lead electrode and into cathodically polarised lead or an alloy of lead with sodium differ very substantially (by approximately seven orders of magnitude).

We concluded earlier, on the basis of published data, that from the point of view of thermodynamics and of electrochemical kinetics mercury should be in no way superior to a number of other metals. It seems reasonable to suppose that the major obstacle to the rapid deposition of alkali metals on solid electrodes is the structural difference between liquid and solid metals. Thus, when alkali metal ions are discharged at a liquid mercury cathode the free volume which exists between atoms in the liquid ensures that the penetration of the alkali metal ions into the cathode is unhindered. Solid metals (lead, silver, zinc, etc.) are composed of closely packed atoms. All the intermetallic compounds which they form with alkali metals are of the substitutional type. Diffusion in these metals and in the intermetallic compounds occurs by exchange between a metal atom and a vacancy in the crystal lattice.



Fig. 12. Polarisation curve for the decomposition of an intermetallic compound, measured for cadmium in 1 *N* NaOH.

Therefore, the diffusion of an alkali metal into the bulk of a solid electrode can only occur by the vacancy mechanism [56].

On the other hand, if we assume, as is often done, that the interaction energy of an ion in the metal with its surroundings is proportional to the coordination number of the ion, it turns out that the most energetically favourable process is the transition of the alkali metal ion undergoing discharge to a vacancy on the electrode surface, since its coordination number then takes the value 9. For comparison we might point out that the coordination number of an ion falling on the plane surface of the electrode is 3, and the coordination number of an ion falling onto the edge of a step (incomplete crystal plane) or of a screw dislocation is 5 or 6. Since the equilibrium potentials of the alkali metals are approximately 1.5 V more negative than the electrode potential during implantation of alkali metals, it is evident that any alkali metal ion falling on the plane surface of the solid electrode will have a higher probability of going back into the solution than of remaining on the electrode surface or of diffusing along the surface until it meets a site where the number of bonds between the ion and the atoms of the electrode is a maximum. Such a site, as was said above, is a surface vacancy. Of course, there is a finite probability that an alkali metal ion falling on a vacancy will also go back into the solution, but the average residence time of the ion on the electrode will be greater the stronger the binding to the electrode. Therefore, an ion falling on a vacancy has the highest probability of exchanging places with another vacancy diffusing outwards from the bulk of the electrode, thus penetrating further into the electrode, instead of going back into the solution.

We have already remarked that the electrochemical stage of the implantation reaction should be a fast one, and cannot therefore determine the rate of the overall reaction. It follows that, even at potentials slightly more negative than the equilibrium potential of the intermetallic compound, all the vacancies present at the electrode surface should be occupied by the alkali metal. Hence, the phenomena taking place at a solid electrode undergoing alkali metal ion implantation are determined by the interplay of two factors. On the one hand, we have the increased concentration of the alkali metal in the surface layer of the electrode due to ion implantation. The rate of this process is determined by the number of vacancies at the electrode surface, which may depend (as we shall see below) on the potential of the electrode. On the other hand, we have the diffusion of alkali metal to the interior of the electrode at a rate which can be very sensitive to the structure of the electrode. Therefore, the course of the overall process of alkali metal implantation is determined (unlike the course of the majority of electrochemical reactions) not only by processes taking place at the electrode surface itself but also (and to a considerable extent) by the structural peculiarities of the electrode metal. As long as the rate of diffusion of the alkali metal towards the interior of the electrode remains smaller than the rate of implantation into the surface, the concentration of alkali metal in the surface layer of the electrode will increase. At first, a solid solution of the intermetallic compound in the electrode metal is formed, and later, when the concentration of alkali metal reaches a value corresponding to the composition of the intermetallic compound, reorganisation of the crystal lattice occurs at a definite rate. With further increase in concentration, a solid solution of the alkali metal (or of a compound richer in the alkali metal) in the intermetallic compound first formed is obtained. In time, the alkali metal diffuses to the interior of the electrode, and the thickness of the layer of intermetallic compound increases [50].

2. Loosening and Disintegration of Cathodes

The well-known phenomenon of cathodic loosening and disintegration of metals is intimately associated with diffusion of an alkali metal into the bulk of the electrode. The mechanism responsible for surface loosening of electrodes during implantation is not completely understood. Some authors believe the loosening to result from decomposition of an intermetallic compound formed at the surface [21,22,30,36,50]. Decomposition of the compound present in intercrystalline layers probably plays an important part. It is possible that the compound decomposes as a result of changing polarisation conditions at a given locality on the electrode, for example, by the formation of a hydrogen bubble which screens the surface. A significant accumulation of alkali metal must obviously be present in the surface layer of the electrode to produce loosening. This can happen if the alkali metal penetrating into the electrode cannot reach the interior rapidly enough. Disintegration is possibly connected with the fact that implantation occurs mainly along grain boundaries. If the rapid penetration of alkali metal gives rise to stresses tending to weaken the mutual binding of the grains, separate grains of the metal can break loose and float away with hydrogen bubbles.

Silver electrodes which have been mechanically polished or cleaned with glass powder have a surface layer of heavily deformed metal (cold working) showing enhanced permeability towards diffusion processes. The alkali metal rapidly penetrates to the interior of the electrode, the surface layer cannot become supersaturated with alkali metal, and as a result the electrode does not disintegrate. Etching the electrode in HNO_3 dissolves the cold-worked layer, and the electrode disintegrates upon subsequent cathodic polarisation.

Since all the surface vacancies are occupied by the alkali metal even at potentials very little different from the equilibrium potential for the implantation reaction, the observed relationship between the rate of implantation and potential suggests that the concentration of vacancies at the electrode surface increases with increasing potential. Polukarov [57] tried to explain the dependence of the structural peculiarities of the metallic electrode on the electrode potential by suggesting that the change in surface tension of the metal with potential is responsible for the variation with potential of the rate of disappearance of defects in the electrolytic deposit. Similar ideas were used to explain the implantation process [50]. The energy of formation of vacancies depends on the surface tension of the metal, and the relationship can be taken to be linear to a first approximation. The lower the surface tension, the lower will be the energy of formation of vacancies. According to the laws of electrocapillarity, an increase in cathodic potential lowers the surface tension of the electrode metal, lowers the energy of formation of vacancies, raises the surface concentration of vacancies, and therefore increases the rate of implantation. This explanation of the potential dependence of the rate of implantation cannot, of course, be advanced as the only possible one, since it must be remembered that in aqueous solutions a much more intensive process — hydrogen evolution — occurs

in parallel with the implantation of alkali metal and can also affect the energy of formation of vacancies.

The conversion of deposited silver films into an amorphous state by cathodic polarisation in a solution containing alkali metal ions, mentioned above, can be ascribed to the excess of vacancies left behind when alkali metal is implanted and subsequently diffuses outwards.

The number of vacancies at the surface is a function of their rate of formation and of their rate of arrival from the underlying layers of the metal. Lead, unlike silver, has a low melting point and a relatively large self-diffusion coefficient, which allows recrystallisation to occur at room temperature. A concentration of vacancies in excess of the thermodynamic equilibrium value is therefore unlikely to exist at room temperature within the crystal grains of a lead electrode. The main sources of vacancies in this case are the surface, the grain boundaries, and the dislocations.

As we have already pointed out, progressive coverage of the electrode surface by a layer of intermetallic compound is accompanied by an increase in hydrogen overvoltage. The overvoltage reaches its limiting value, in all probability, when the surface is completely covered. Upon further polarisation the layer of intermetallic compound on the electrode surface gradually thickens, whilst at the same time the compound penetrates more rapidly into the core of the electrode along grain boundaries. If during cathodic polarisation the intermetallic compound was formed not merely as a surface monatomic layer, but was allowed to penetrate to the adjacent layer of the metal, and was then decomposed at the surface by passing anodic current, a vastly increased number of vacancies will appear not only at the surface, but also in a small volume immediately below the surface (mainly along grain boundaries and near the intermetallic phase remaining undecomposed below the surface). Such an electrode is said to be "worked". Its high vacancy concentration facilitates the discharge of alkali metal cations with formation of an intermetallic compound, and increases the rate of diffusion. As a result, the overall rate of the process is increased by several orders of magnitude [56].

The electrode can retain its "worked" condition for only a limited time, until the excess vacancies have diffused to the sites which act as sinks for vacancies. Thereafter, the electrode regains the properties characteristic of the pure metal rather than of the compound, and the rate of the process once again becomes very small.

The following experiments confirm the mechanism described for the implantation process. An electrode was polarised for 90 min, and its anodic φ–t curve was recorded. Without delay, the electrode was again cathodically polarised for 0.5 s and the anodic polarisation curve was again recorded, followed by further brief cathodic polarisation and so on. It was found that after the 90 min polarisation it was possible to plot a number of anodic curves in succession, showing a gradual decrease in the length of the potential arrest, by applying brief periods of cathodic polarisation. The explanation of this is that the rate of diffusion of sodium from the bulk of the electrode is not high enough to give rise to a single large arrest at φ = = -1.3 V for the particular anodic current density employed. However, the layer of compound on the surface can become partly reduced after 0.5 s cathodic polarisation, due to the discharge of sodium ions and to the diffusion of sodium from the interior. After 20 min cathodic polarisation, only one anodic arrest can be detected, and the next anodic charging curve does not show any potential arrest. This indicates that even after 20 min a sufficiently thick layer of intermetallic compound has not had time to form.

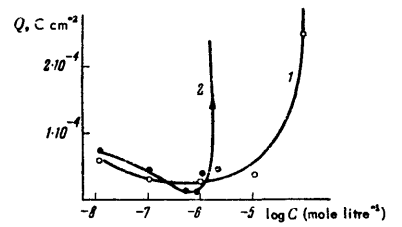


Fig. 13. Variation of the length of the anodic arrest with concentration of As_2O_3 (1) and HgO (2) in 1 *N* NaOH.

The anodic decomposition of the resulting intermetallic compound is characterised by the diffusion of sodium atoms from the interior of the electrode to the surface through a layer of intermetallic compound, both for a "worked" lead electrode and for an electrode of the intermetallic compound, prepared by alloying in a separate experiment. We have already pointed out that this type of diffusion should be much faster than the diffusion of the same atoms in the pure electrode metal. The experimental results show that, in fact, on a fresh lead electrode (but not on the alloy) the cathodic formation of intermetallic compound is slower by several orders of magnitude than the anodic decomposition of the intermetallic compound formed by cathodic polarisation. Similar results have been obtained with other electrode metals and other alkali metals [56].

These experiments made it clear that "equilibrium" vacancies, generated at the surface of a metallic electrode or diffusing from the bulk, can give rise to implantation but only at extremely low rates, typically 10^{-10} A cm^{-2} for the case of lead. Implantation can occur at appreciable rates only in the presence of a number of vacancies greatly in excess of the "equilibrium" concentration, supplied to the surface from the deeper layers of the electrode. Hence, the essential characteristic of the implantation process is rate control by the state of the metal in the bulk (but close to the surface), a situation not often found in electrochemistry. Of course, factors affecting only the state of the surface can play a part in this case also. However, their effect is incomparably smaller than the effect of structural changes in the bulk of the electrode. Anodic polishing and etching activate the surface and significantly assist implantation. The rate is affected also by the presence of arsenic, mercury, and tellurium on the electrode surface, the effect being a function of the concentration of these elements in solution. At concentrations of 10^{-8}–10^{-6} M, these impurities inhibit implantation, but when present in greater amounts they assist the process by being co-deposited with the alkali metal (Fig. 13).

Thus, the rate of implantation of an alkali metal into an electrode is determined by the concentration of defects in the bulk of the cathode metal, whilst factors affecting only the electrode surface, such as adsorption of poisons, polishing, and etching, have a vastly smaller effect on the rate of the process [56].

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We may conclude as follows. Electrochemists working at the turn of the century suggested that implantation of alkali metals into electrode metals can occur in aqueous solutions, but they were unable to demonstrate the phenomenon experimentally, and the majority of electrochemists rejected the suggestion. In later years there were occasional indications of the reality of alkali metal implantation, since a number of phenomena observed during cathodic polarisation with alkali metal cations in the solution could not otherwise be explained. These included the cathodic disintegration of metals, the cathodic superactivation of aluminium and magnesium in alkalis, the anomalous behaviour of lead, tin, zinc, and cadmium electrodes during cathodic reduction of acetone, anomalies in hydrogen overvoltage in alkalis, certain phenomena in electroplating, and others. Many departures from the expected behaviour for cathodic processes in alkaline and in neutral solutions were disguised by introducing empirical coefficients, and practical methods of preparation of electrodes failed to attract the attention of electrochemical analysts, for example. Of course, a related phenomenon can often accompany implantation in analytical electrochemistry, in electro-hydrometallurgy, and in electroplating; the co-deposition of alkali metals with other metals such as Zn, Pb, Cd, Ag, and others. However, the most striking feature of implantation — an extremely high initial overvoltage — does not manifest itself. This overvoltage is responsible for the apparent lack of reproducibility of the phenomenon, which compelled most electrochemists of the first half of the present century to abandon their attempts to substantiate the idea of cathodic formation of intermetallic compounds between alkali metals and various electrode metals, and to establish its mechanism. Haber and others tried to investigate this phenomenon 60 years ago, but they did not progress far towards an explanation of the mechanism. In very recent years considerable progress has been made in this direction, and the remarkable features of alkali metal implantation into electrodes have been revealed and explained to some extent; we owe this to the rapid developments in electrochemistry, to the very high level reached by the theory of electrochemistry and of electrochemical methods (due in large measure to the fundamental researches of A. N. Frumkin), and lastly to progress in solid state physics.

It now remains to develop in more detail and to substantiate the theory of electrochemical implantation, and to broaden its experimental foundations.

We cannot exclude the possibility that this process takes place also on metals of Group VIII, say, although hardly any intermetallic compounds have so far been reported between these metals and alkali or alkaline-earth metals.

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BARRIERLESS ELECTRODE PROCESSES

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The slow discharge theory, developed and substantiated by the work of Frumkin and his school, satisfactorily describes the basic features of a large number of electrochemical processes (see, for example, Ref. 1). The concepts which had been originally used to describe the discharge of hydrogen ions were shown to be widely applicable to all types of reaction, such as the electrochemical desorption of adsorbed hydrogen, the reduction of anions and neutral molecules, etc. In recent years it has been shown that the basic ideas of the slow discharge theory imply the existence (in a few limiting cases) of new types of electrode reactions showing a number of interesting features [2-4]. The present review article aims to discuss these limiting cases.

The most distinguishing feature of electrochemical reactions is the variation of their activation energy with potential: as the electrode departs from its equilibrium potential in the cathodic (or the anodic) direction, the activation energy of the corresponding electrode process decreases. This behaviour is most conveniently described by the relation

$$A = A_0 - \alpha\eta F, \qquad (1)$$

where A is the activation energy at an overvoltage η (real activation energy values [5] will be used throughout), and A_0 is the activation energy at the equilibrium potential. The transfer coefficient α is found experimentally to be constant over a range of potentials, and its value is often close to 1/2.

If the activation energy of the forward reaction decreases with increase of overvoltage, the activation energy for the reverse reaction must increase

$$A' = A_0' + \beta\eta F. \qquad (2)$$

It can be shown thermodynamically† that at a given potential $\alpha + \beta = 1$.

Relationships involving activation energy values are conveniently visualised with the help of a potential energy diagram. Fig. 1 shows a cross-section of the potential energy surface along the reaction coordinate. Curve *2* corresponds to a higher potential than curve *1*. Since the energy of the activated transition state increases more slowly with potential than does the energy of the initial state, the difference between the two, i.e. the activation energy, decreases.

Consider a discharge reaction (cathodic, say). Since its activation energy is finite at any given potential, and since it decreases with increase of overvoltage, it must ultimately tend to zero at a high enough overvoltage. Under these conditions the reaction rate will be a maximum, and further increase in potential will not affect the current. In other words, for a non-activated process such as this we can write $\alpha = 0$. But for the reverse ionisation reaction we find $\beta = 1$ at these potentials. The potential curves for this case are shown in Fig. 1 as curves *3* and *4* .

Imagine now that the overvoltage is decreased. This raises the activation energy for discharge, but at the same time the activation energy for ionisation is lowered. At a sufficiently low cathodic (i.e. at a sufficiently high anodic) potential the activation energy vanishes. Under these conditions $\beta = 0$ and $\alpha = 1$. The shape of the corresponding potential energy diagram is shown by curves *5* and *6* of Fig. 1.

Unlike non-activated processes, the processes for which $\alpha = 1$ (or $\beta = 1$) require a considerable activation energy. However, and in contrast to normal discharge processes, this activation energy is equal to the heat of the fundamental reaction step, and the activation energy for the reverse processes is zero‡. On a potential diagram this process does not show the familiar hump of the

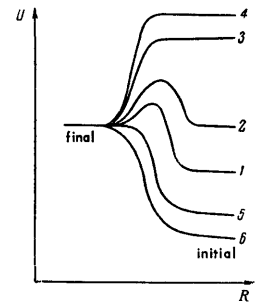


Fig. 1. Potential energy diagram for normal (curves 1 and 2), non-activated (curves 3 and 4), and barrierless discharge (curves 5 and 6).

† We are confining the discussion to one-electron processes.

‡ We must stress once again that we are considering the real activation energy, so that the heat of the fundamental step is a real heat, i.e. a quantity which does not include the latent equilibrium heat of the overall electrode process. We could have based the whole discussion on ideal activation energies, but this would not affect the results.