

the methods available at present for the determination of the isotopic composition of microamounts of water are insufficiently accurate⁵.

We also synthesised [¹⁸O] deuterium peroxide D₂¹⁸O₂. For this purpose, mixed D₂O and H₂¹⁸O vapours with the composition 35.6 at. % of deuterium and 1.19 at. % ¹⁸O were subjected to the action of the glow discharge in the apparatus shown in Fig. 1. The resulting peroxide contained 26% of active oxygen and 1.26 at. % ¹⁸O, *i. e.* there was an enrichment.

SUMMARY

An effective laboratory method has been developed for the preparation of [¹⁸O] hydrogen peroxide from the vapour of [¹⁸O] water dissociated in a glow discharge. The method differs from those used previously in that the [¹⁸O] peroxide is very pure and not only does the entire heavy oxygen isotope present in the initial water pass to the peroxide but the latter is actually somewhat enriched in ¹⁸O.

The method also has the advantage that, depending on the energy of the discharge and the flow rate of the water vapour, it is possible to obtain hydrogen [¹⁸O] peroxide solutions at concentrations ranging from 1 to 50 wt. %. In the case of 5–7% solutions the yield is 1 g h⁻¹, calculated as 100% H₂¹⁸O₂. Using the same apparatus, the H₂¹⁸O₂ synthesised in the discharge concentrated to 90 wt. %.

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Received 30th May 1963

U. D. C. 541.13

INCLUSION OF ALKALI METALS IN ELECTRODES, INVESTIGATED BY MEANS OF POTENTIAL-TIME CURVES

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When electrodes are cathodically polarised in solutions containing alkali-metal cations, the latter may at the appropriate potentials, react with the metal of the cathode

to form solid alloys or intermetallic compounds on the surface¹⁻³. The inclusion of an alkali metal with formation of an intermetallic compound affects the electrochemical behaviour of the electrode. The difficulty of investigating such systems is that the compounds are unstable, and when polarisation ceases are rapidly decomposed by water with the evolution of hydrogen. Ordinary analytical methods cannot, therefore, be used. Even electron microscopy reveals only disintegration of the electrode surface resulting from decomposition of the compound³.

In the present work potential-time ($\varphi-t$) curves have been used to study the compounds formed with the alkali metals.

EXPERIMENTAL

Measurements were made on silver, lead, zinc, and cadmium cathodes in solutions of LiOH, NaOH, KOH, and CsOH.

Before experiments were undertaken, special attention was paid to the purity of the solution. Salts of "chemically pure" quality were recrystallised twice and ignited. Solutions were made up with twice distilled water. The aqueous alkalis were purified by electrolysis at 0.05–0.2 A cm⁻² for 3–5 d, the cell used for this purpose having the catholyte separated from the anolyte by a glass filter. The anode was of platinum, and the cathode of the metal on which the $\varphi-t$ curves were to be obtained. The cells were mainly of Jena or No. 23 glass. In order to demonstrate the absence of any effect due to impurities extracted from the glass, some of the experiments were made in a Teflon cell with solutions which had been purified in Teflon and the results compared.

Anolyte and catholyte in the cell were separated by a trap, and a platinum anode was used. A voltage was applied to the test electrode in advance, so that the electrode was cathodically polarised at the instant of contact with the solution. The electrode potential was measured relative to a mercuric oxide electrode in the same solution, and converted to the normal hydrogen scale. Experiments were carried out in an atmosphere of hydrogen. The silver electrodes were made from a metal containing a maximum impurity content of 0.001%. Before an experiment the electrode was etched in concentrated nitric acid, and cleaned with moistened fine glass powder. Metal of SV quality was used for the lead electrode, whose surface was cleaned with a stainless steel blade. Cadmium electrodes were made from spectroscopically pure metal and from metal of "analytical reagent" quality. Before an experiment the surface was cleaned with glass powder. Zinc electrodes were made from samples of the metal of 99.995% and 99.9995% purity, and before an experiment the surface was cleaned with glass powder or the sharp edge of a glass plate.

The electrode was placed in the aqueous alkali saturated with hydrogen, and subjected to preliminary cathodic polarisation in a stream of hydrogen. At a definite instant the cathodic current was replaced by an anodic current, and the strength of the current could be changed at the same time. When cathodic polarisation for a short period was required, an electronic time relay† was used, which

† The relay circuit was suggested by L. L. Knots and the relay was constructed by V. V. Kushnev, to both of whom we express our deep gratitude.

automatically switched from cathodic to anodic current after a specified interval, the changeover time not exceeding 0.01 s. The duration of polarisation was fixed by means of an electrical timer. The circuit of the relay is shown in Fig. 1.

An experiment was begun with preliminary cathodic polarisation of the electrode at -1.2 V for 1 h, until the surface had been completely reduced. Then a high negative potential, at which appreciable inclusion of the alkali metal would occur, *i.e.* from -1.5 to -2.0 V, was applied for a definite time, varying between 0.05 s and 2 h. When the specified time had elapsed, an anodic current was passed through, the variation of electrode potential with time (φ - t curve) was recorded by means of an oscillograph of type ENO-1. The direction of the current was then changed again, and the cathodic φ - t curve determined.

The examples of anodic and cathodic potential-time curves for silver, cadmium, lead, and zinc in 1 N lithium hydroxide solution illustrated in Fig. 2 clearly show arrests in the fall and rise in potential. The potential of the anodic arrests varies linearly with the logarithm of the anodic

current density. The presence of arrests on the cathodic curves is associated with the formation of intermetallic compounds, and their presence on the anodic curves with decomposition of such compounds. The equilibrium potentials of the compounds lie between the potentials at which cathodic and anodic arrests begin. Table 1 gives the measured potentials of cathodic and anodic arrests in 1 N LiOH (at 0.001 A cm^{-2}), and the resulting calculated equilibrium potentials of the intermetallic compounds formed by lithium with silver, cadmium, lead, and zinc.

In the case of zinc the anodic arrest corresponding to the cathodic arrest at -1.45 V has superimposed on it another arrest representing the anodic dissolution of zinc. It is therefore difficult to find the exact potential of this anodic arrest, and Table 1 gives its approximate value.

Two or three arrests may be observed on the anodic curves (Figs. 3 and 4), which indicates that more than one intermetallic compound may be obtained on cathodic polarisation. Table 2 gives the potentials of these plateaux on the anodic φ - t curves in 10 N KOH.

Under our conditions the anodic arrests in the vicinity of -1.3 V (Table 1) are the easiest to reproduce. Other anodic arrests are less reproducible, and in general we have not yet been able to obtain the corresponding arrests on the cathodic curves. Probably these compounds are more difficult to produce or may not be obtained depending

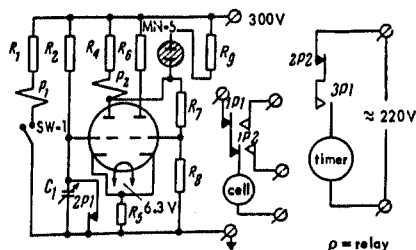


Fig. 1. Circuit of timing relay.

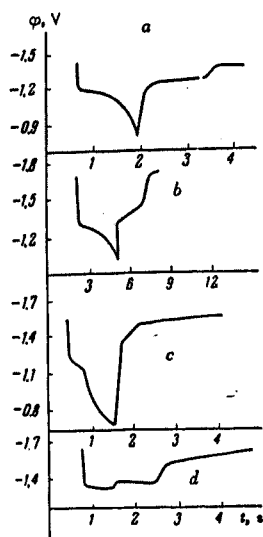


Fig. 2. Anodic and cathodic potential-time curves obtained in 1 N LiOH at: a) Ag, $i_a = 0.005$ and $i_c = 0.0021$ A cm^{-2} ; b) Cd, 0.00065 and 0.00046; c) Pb, 0.0008 and 0.0008; d) Zn, 0 and 0.0019 A cm^{-2} .

TABLE 1.

Potential	Ag	Cd	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)

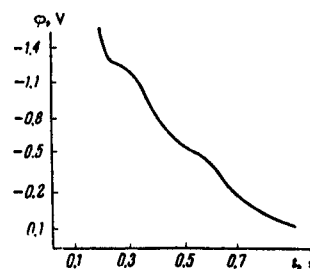


Fig. 3. Anodic potential-time curve at Ag in 1 N KOH, $i_a = 8 \times 10^{-5}$ A cm^{-2} .

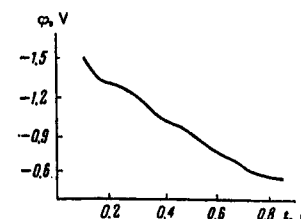


Fig. 4. Anodic potential-time curve at Pb in 1 N KOH, $i_a = 4 \times 10^{-5}$ A cm^{-2} .

TABLE 2.

Arrest	Cd	Ag	Pb
I	-1.5	-1.4	-1.4
II	-1.4	-1.1	-1.05
III	-1.05		

on unnoticed changes in the experimental conditions. Henceforward we shall be discussing only the main anodic arrests, which are readily reproducible and for which the corresponding cathodic arrests have been obtained.

If the intermetallic compounds which are formed are assumed to contain one atom of lithium per molecule, we can calculate from their equilibrium potentials the free energies of these compounds $F_{\text{LiM}_n}^\circ$ and the free energies of the processes involved in their formation ΔF° by the reactions

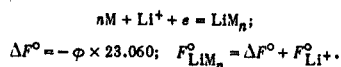


Table 3 gives the free energies of lithium compounds calculated in this way, with data for NaHg_3 and NaHg_2 as comparison.

Formation of an intermetallic compound is influenced by the state of the electrode surface. Under some conditions inclusion apparently does not occur, and we observe no arrests on the charging curves, whereas under other conditions the arrests are short, and sometimes sloping. And, finally, long clear plateaux may be obtained, associated with the presence of a very large amount of intermetallic compound. It may be supposed that active sites must be present on the cathode surface for inclusion of alkali metal into the metal of the electrode. Defects in the crystal lattice, for example, may provide such sites.

Production of an active surface may be favoured, for example, by preliminary anodic etching of the cathode surface. Therefore curves with a clearer anodic arrest are obtained on cadmium which has been anodically etched in concentrated aqueous H_3PO_4 than on the unetched metal. The length of the arrest on the curves in Fig. 5 corresponds to anodic decomposition of the same amount of substance, but on the etched electrode (curve 1) the plateau is almost horizontal, whereas on the unetched electrode (curve 2) it is sloping and has been displaced to more positive potentials.

Surface activation occurs also on strong cathodic polarisation. This is evident from the fact that, on a fresh electrode which has been freed from oxides by weak cathodic polarisation (at -1.2 V), it is practically impossible to obtain a cathodic arrest at potentials at which the shape of the φ - t curves has not yet been affected by hydrogen evolution. After passage of a large cathodic current, however, the potential of hydrogen evolution becomes

TABLE 3.

Composition	φ°	$\sqrt{F^\circ}$	$F_{\text{LiM}_n}^\circ$	Composition	φ°	ΔF°	$F_{\text{LiM}_n}^\circ$
LiAg_n	-1.29	30	-40	LiZn_n	(-1.4)	(32)	(-38)
LiCd_n	-1.33	30.5	-39.5	NaHg_3	-1.92	44.2	-18.35
LiPb_n	-1.34	31	-39	NaHg_2	-2.0	46	-16.48

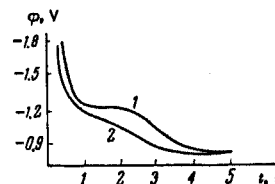


Fig. 5. Anodic potential-time curves for $i_a = 5 \times 10^{-5} \text{ A cm}^{-2}$ at cadmium which has been: 1) etched; 2) not etched.

slowly more negative (over a period of minutes or tens of minutes). During this time an intermetallic compound gradually accumulates on the electrode, as is evident from the appearance of a plateau on the subsequent anodic curve. If the compound which has accumulated is removed from the electrode by passage of an anodic current, and then a cathodic current is immediately passed through again, the second penetration of alkali metal is considerably more rapid and occurs at a potential which is hundred of millivolts less negative. The cathodic curve then shows distinct arrests. This active state of the surface is not maintained for very long. If the electrode is left without current for some time, subsequent formation of intermetallic compound again takes place only with a very high overpotential. The structure of the electrode surface retains for some time the "memory", as it were, that an intermetallic compound had previously been present. It must be noted that, even on an active electrode, an extremely limited quantity of intermetallic compound is formed near its equilibrium potential. It may be assumed that compound formation takes place only on part of the surface, and that on another part it takes place at more negative potentials. This is evident from the fact that the cathodic arrests in 1 N alkali are usually shorter than the subsequent anodic arrests.

Further confirmation that cathodic polarisation definitely activates the electrode surface is the experimental observation that the variation in cathodic current with time at constant potential is initially slower than it is later (Fig. 6).

Lithium shows the greatest capacity for inclusion in the electrodes investigated. Anodic and cathodic arrests can be observed also in NaOH solutions. In KOH and CsOH under the same conditions, a clear cathodic arrest is not obtained at all, and an anodic arrest is observed only after cathodic polarisation at a high potential (between -1.7 and -2.0 V). This is probably associated with a difference in the size of the unhydrated ions.

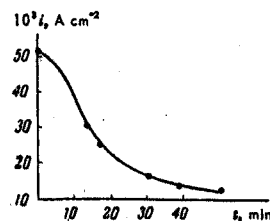


Fig. 6. Time variation in rate of hydrogen evolution at Ag in 1 N KOH at a constant potential of -1.4 V.

In contrast to the cathodic arrests, anodic arrests are always observed after sufficiently prolonged cathodic polarisation on silver, cadmium, and lead, and with all the cations investigated — Li^+ , Na^+ , K^+ , and Cs^+ . The length of the anodic arrests can vary greatly depending on the duration of the preliminary cathodic polarisation, when the quantity of electricity Q_c which has passed through exceeds by several orders of magnitude the quantity Q_a corresponding to the length of the anodic arrest. Table 4 shows the dependence of Q_a on Q_c for Cd in 10 N KOH.

The amount of compound formed depends on the concentration of the solution. After prolonged cathodic polarisation in 10 N KOH the length of the anodic arrest on cadmium reaches 0.001 C cm^{-2} , which corresponds to a quantity of intermetallic compound decomposed of $10^{-8} \text{ g-equiv. cm}^{-2}$. In 1 N KOH solutions the length of the anodic arrest changes little with increase in the cathodic quantity of electricity Q_c , and corresponds to the decomposition of about $6 \times 10^{-10} \text{ g-equiv. cm}^{-2}$ based on the apparent surface (see Table 5).

If it is supposed that, over the range of potentials investigated, one atom of alkali metal is combined with more than one atom of the electrode metal in the intermetallic compounds, and that the true electrode surface exceeds the apparent surface by factors of 2–3, the quantity of compound which undergoes anodic decomposition, $6 \times 10^{-10} \text{ g-equiv. cm}^{-2}$, can be regarded in the case of 1 N alkali as corresponding in order of magnitude to a monolayer. The intermetallic compounds which is formed can be obtained more rapidly with 10 N KOH than in the case of 1 N alkali.

On cathodic polarisation, compounds may also be expected between the electrode metal and hydrogen, and the possibility of hydride formation under such conditions has been discussed in several papers⁵. Cathodic formation of surface hydrides may, perhaps, take place on such metals as iron and nickel, which are distinguished by the ability to adsorb hydrogen strongly. However, hydrides have not been obtained with zinc, cadmium, and lead. Such metals, which show a high overpotential of hydrogen evolution, adsorb, like mercury, very little atomic hydrogen on their surface⁶. In this case the cathodic formation of hydrides in appreciable quantities is improbable, and in amounts of the order of a monolayer is excluded.

On the other hand, intermetallic compounds formed by Pb, Zn, Cd, and Ag with alkali metals are well known. They are readily obtained by chemical means or by electrolysis in melts or non-aqueous solutions. Smith noted

TABLE 4.

$Q_c, \text{C cm}^{-2}$	$Q_a, \text{C cm}^{-2}$
20	$1.5 \cdot 10^{-4}$
400	$9 \cdot 10^{-4}$
700	$1.3 \cdot 10^{-3}$

TABLE 5. Cadmium in 1 N KOH; $i_c = 1.5 \times 10^{-3} - 2 \times 10^{-4} \text{ A cm}^{-2}$, $i_a = 3 \times 10^{-5} \text{ A cm}^{-2}$.

$Q_c, \text{C cm}^{-2}$ (preliminary)	0.0003	0.006	0.13	0.3	2	9	40
$Q_a, \text{C cm}^{-2}$	$2 \cdot 10^{-8}$	$4 \cdot 10^{-8}$	$3 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	$7 \cdot 10^{-8}$	$7 \cdot 10^{-8}$

TABLE 6.

Cation	Li^+	Na^+	K^+	Rb^+	Cs^+
ϕ°	-3.045	-2.7	-2.92	-2.92	-3.0
$E_{1/2}$ in 0.1 N $\text{N}(\text{CH}_3)_4\text{OH}$	-2.02	-1.80	-1.88	-1.78	-1.85

long ago⁷ the poor solubility of potassium in molten zinc, and concluded that on cooling the chemical compound KZn_{12} is formed. Later work⁸ indicates the composition KZn_{13} . Zinc also forms compounds — LiZn , $\text{Li}_{12}\text{Zn}_{13}$, and NaZn_{13} — with lithium and with sodium. Silver forms compounds with sodium and several modifications of the compound LiAg . In the case of lead several compounds are known with lithium, sodium, and potassium — $\text{Li}_{10}\text{Pb}_3$, LiPb , Na_3Pb_4 , Na_4Pb , NaPb_3 , K_2Pb , and KPb_4 .⁹

Because of the evolution of hydrogen in aqueous solutions, the potentials which are in practice reached at the highest cathodic current densities (about -2.0 V s.c.e.) are still almost 1 V more positive than the equilibrium potential of, for example, potassium. But intermetallic compounds having a low proportion of alkali metal can be obtained electrochemically even in aqueous solutions, thanks to their large negative free energies of formation. This phenomenon is utilised in the manufacture of alkalis with a mercury electrode. As the concentration of sodium in the mercury increases, the cathode potential shifts in a negative direction to -1.8 to -2.0 V.¹⁰ This latter range of potentials corresponds to the equilibrium potentials of the amalgams, which vary with the concentrations of solution and of amalgam and the nature of the alkali metal. The formation of intermetallic compounds and their solutions in mercury explains also the difference between the standard potentials of the metals and the half-wave potentials, which is especially marked with the alkali metals¹¹ (Table 6).

With solid electrodes, in contrast to amalgams, diffusion of the resulting compound into the interior of the electrode is difficult. Furthermore, the kinetic stability of these compounds varies greatly, and many of them are unstable towards water. It must be recalled for comparison that several amalgams, too, are very unstable. Thus those of lithium are decomposed by water 1000 times as rapidly as sodium and potassium amalgams, the corresponding factor for the very rapidly decomposed magnesium amalgams being 10 000.¹²

SUMMARY

1. Oscillographic anodic and cathodic potential-time curves have been recorded at silver, cadmium, lead, and zinc electrodes in solutions of lithium, sodium, potassium, and caesium hydroxides. The curves show arrests in the change in potentials, corresponding to the cathodic formation and anodic decomposition of several intermetallic compounds of the above metals with the alkali metals.
2. Equilibrium potentials have been determined and free energies calculated for the compounds.
3. The rate of the cathodic formation of intermetallic compounds depends greatly on the state of the electrode surface.

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Received 1st June 1963

U.D.C. 541.13

KINETICS OF SOME HETEROGENEOUS REACTIONS AT A SEMICONDUCTOR-ELECTROLYTE INTERFACE

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Much work has recently been done on the kinetics of heterogeneous redox reactions at a semiconductor-electrolyte solution interface¹. Most theoretical work on the kinetics of electrode processes is based on the formulae of the theory of absolute reaction rates². The application of this theory to electron-transfer reactions needs justification. A quantum-mechanical calculation of the probability of an elementary act of ion discharge at an electrode³ has been based on the hypothesis that electron transfer between an ion in an electrolyte solution and an electrode can be regarded as a radiationless electron jump. This theory has subsequently been applied to the kinetics of several electrochemical redox reactions on metals⁴ and semiconductors⁵. The latter paper considered an idealised case in which the whole potential drop was concentrated in the semiconductor. In the present paper we discard this hypothesis, and regard the potential as falling in both semiconductor

and electrolyte. Formulae will be obtained below for the equilibrium potential, the exchange current, and the polarisation characteristic of several systems.

General Kinetic Relations

Let us consider the elementary act of discharge of an ion A^{2+} in the electrolyte:



As shown previously^{3,6}, the energy of the system fluctuates about an equilibrium value I . It is easy to show that the values of I for the initial and final states in reaction (1) can be determined from the respective formulae

$$I_s = -\epsilon_1 + 2e\varphi(x) - \alpha_2, \quad (2)$$

$$I_f = \epsilon_f - U_0 - e\varphi_n + 3e\varphi(x) - \alpha_3, \quad (3)$$

where ϵ_1 is the energy of ionisation of A^{2+} (in the gas phase), α the energy of hydration, $\varphi(x)$ the potential at the position occupied by the ion, and φ_n the internal (voltaic) potential of the semiconductor. The significance of ϵ_f and U_0 is clear from the diagram.

The current flowing through the system can be written in the form

$$i = i_{ns} - i_{sn} = (i_{ns}^e + i_{ns}^p) - (i_{sn}^e + i_{sn}^p), \quad (4)$$

where i_{ns} is the current flowing from the semiconductor to the solution (i.e. associated with transfer of an electron from A^{2+} to the semiconductor), while i_{sn} is the reverse current; the superscripts e and p indicate whether the electrons belong to the conduction band or the valency band respectively:

$$i_{ns} = e \int_0 c_2(x) dx \int W_{sf}(x) [1 - n(\epsilon_f)] \rho_f d\epsilon_f, \quad (5)$$

$$i_{sn} = e \int_0 c_3(x) dx \int W_{fs}(x) n(\epsilon_f) \rho_f d\epsilon_f, \quad (6)$$

$c_2(x)$ and $c_3(x)$ being the concentrations of A^{2+} and A^{3+} ions in the electrolyte distant x from the electrode, $n(\epsilon_f)$ the Fermi partition function, ρ_f the density of levels in the semiconductor, and W_{sf} the probability of electron transfer from the ion A^{2+} to the semiconductor. In the theory of radiationless electron transitions it is shown that the probability of the reverse transfer W_{fs} is linked with W_{sf} by the relation⁶

$$W_{fs} = W_{sf} \exp \left\{ \frac{I_f - I_s}{kT} \right\}. \quad (7)$$

