# ELECTRODE PROCESSES IN NEW ELECTROCHEMICAL SOURCES OF CURRENT

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In recent years there has been an appreciable increase in the volume of research work in one of the important branches of applied chemistry—in the field of electrochemical sources of current: galvanic cells and storage cells. This is due to the ever-increasing use of such current sources in the national economy, e.g., in transportation, in aviation, as power supply for portable radio apparatus and other means of communication, etc. The general development of technique led to intensification of the demands made on current sources—demands which essentially amount to an increase in the electrical characteristics, improvement of the working capacity at various temperatures, and mitigation of self-discharge.

The widely-used types of chemical sources of current, manufactured by industry, e.g., lead-acid storage batteries, alkaline cadmium-nickel storage batteries, and primary cells of the manganese system (Léclanche type) proved unable to satisfy these growing demands in a number of cases. Therefore, research on other electrochemical systems, on which chemical sources of current might be based, was very important. This research has led to the invention of new types of primary and storage cells in several countries in the last few years. Among these new types, which already have acquired practical importance, silver-zinc storage cells must be mentioned first. These storage cells have 5-6 times the capacity of lead storage cells of the same weight and, besides, permit discharges of much higher current strength. Further, mention must be made of mercuric oxide cells, which permit a relatively large amount of capacity to be concentrated in a very small volume, water-filling magnesium batteries (using cuprous chloride as the positive electrode), which have good characteristics at low ambient temperatures, and others. The long-known, so-called air-depolarization cells also are promising from the technical and economic point of view.

Progress recently made in the field of chemical sources of current is based to a considerable degree on extensive electrochemical investigations, on work in the determination of the electrochemical properties of various substances, and on the study of electrode reaction mechanisms.

In this brief report it is impossible to give a complete review of electrochemical work in the field of current sources, done in recent years. This report aims only at a brief account of certain questions connected with the course of electrochemical reactions at the electrodes of the new types of storage and primary cells and to show the connection of the given questions with the general properties of the current sources.

One of the important parameters of a chemical source of current, which determines its practical utility to a great extent, is the rate of its self-discharge. If such trivial, nonelectrochemical phenomena as, for instance, the presence of an internal short-circuit, or drying out or other changes in the electrolyte are disregarded, the main cause of the self-discharge of current sources is the electrochemical self-discharge of the individual electrodes.

The phenomenon of electrochemical self-discharge of the individual electrodes is mainly characteristic of the negative electrodes of many types of chemical sources of current, although self-discharge of the positive electrode also is sometimes possible. Numerous investigations were devoted to the dissolving of metals in solutions, with hydrogen evolution—notwithstanding the fact that these reactions have been known a long time and, it would seem, have been throughly studied. It is quite obvious that in those types of chemical sources of current, in which impure materials are used, the rate of self-discharge of the negative electrode is determined to a great degree by the effect of inclusions—local cells on the surface of the dissolving metal. On the other hand, however,

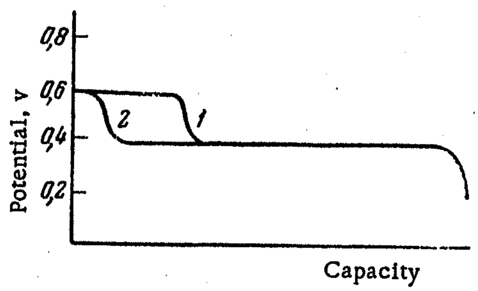

Fig. 1. Discharge curves of the silver electrode. 1) Freshly charged; 2) within several hours after charging. The potential of approximately 0.6 v corresponds to AgO, and that of approximately 0.4 v to $Ag_2O$

a number of cases have recently come to light, in which the rate of self-discharge is determined by the kinetics of hydrogen evolution not at inclusions with diminished overvoltage, but at the surface of the pure, dissolving metal. Thus in these cases the process of self-solution of the metal must be regarded as a group of concurrent cathodic and anodic reactions which statistically are not separated in space. This was shown, in particular, in the well-known work by Ya. M. Kolotyrkin on the self-solution of spongy lead—the negative electrode of the lead storage cell. In recent years similar conclusions have been reached for another type of electrode used in chemical sources of current, namely, the pure zinc electrode in alkaline solutions. It follows from this work that the regularities of hydrogen overvoltage quantitatively determine the rate of self-solution.

Hence, the great importance of the theory of hydrogen overvoltage in the analysis of phenomena of self-discharge of the negative electrode becomes understandable. By the way, it must be noted that in chemical sources of current, as a rule, metals with high hydrogen overvoltage, such as zinc, lead, and cadmium are used. The development of ideas concerning the mechanism of the reaction of hydrogen evolution on such metals and the effect of solution composition on the kinetics of this reaction, by Soviet electrochemists under the direction of Academician A. N. Frumkin, had a great effect on the formation of our theoretical concepts on self-solution reactions and in a number of cases made it possible to work out a method of mitigating the self-solution of the negative electrode. The best-known example is the theoretically-predicted effect of surface-active cations, which in acid solution diminish the self-solution of such metals as zinc, etc., several-fold as a result of an increase in the hydrogen overvoltage. Practical use of such additives was made in the work of A. K. Lorents et.al.

In determining the mechanism of action of various surface-active substances on electrode processes in chemical sources of current, it is essential to know the zero charge potentials of the electrode materials in the working solutions. For instance, B. N. Kabanov and others determined the zero charge potentials of lead and lead dioxide in concentrated solutions of sulfuric acid.

Self-discharge of the positive electrode is observed much less often. Self-discharge of the active material —usually reduction of a higher oxide—just be accompanied by a concurrent anodic reaction. If the positive potential is high enough, this reaction is anodic evolution of oxygen. However, owing to the high overvoltage of this reaction for the oxides usually employed in chemical sources of current, it proceeds exceptionally slowly.

The frequently-encountered cases of reduction of the active material of the positive electrode and simultaneous oxidation or destruction of extraneous substances, such as, for instance, the material of the separator, case, terminals, etc., are of practical and theoretical interest.

The case of the concurrent electrochemical reaction, taking place in the active mass of the positive electrode of the silver-zinc storage cell, is interesting. In the discharged condition the active mass consists of a mixture of metallic silver, argentous oxide, and argentic oxide. Argentous and argentic oxides are electrochemically active and take part in the discharge reaction. As I. Kh. Zeilikman showed, the higher oxide is electrochemically reduced to the lower by metallic silver on contact with the electrolyte within the active mass:

$$Ag + AgO \rightarrow Ag_2O$$

Since the product (argentous oxide) formed in this reaction also is electrochemically active, the capacity of the electrode is not decreased as a result of this "self-discharge," the only change being in its working potential (Fig. 1).

Increase in the use coefficients of active masses, or, in other words, increase in the capacity or electrical energy of chemical sources of current, is often closely connected with detailed analysis of electrode passivation (where the term "passivation" means any retardation or complete cessation of the main current-generating reaction).

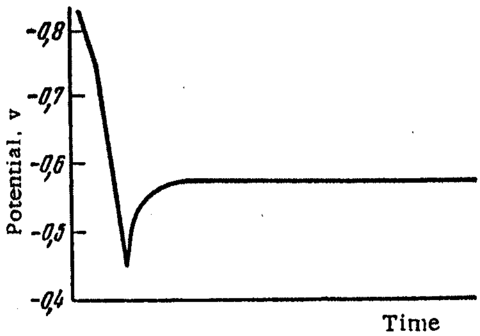

Fig. 2. Passivation of zinc in acid solution at -20°. Current density 10 ma/cm².

In chemical sources of current various cases of passivation both of negative and of positive electrodes are observed. The most important case is the behavior of the zinc electrode in alkaline solutions. An electrode of this type is used in cupric oxide and mercuric oxide cells, air-depolarization cells, and silver-zinc storage cells. Passivation of the zinc electrode sharply decreases the capacity of these cells at low temperatures. Z. A. Iofa and co-workers carried out a number of important works in the study of this phenomenon.

A characteristic peculiarity in the functioning of the zinc electrode in alkaline solutions consists in the formation of rather thick layers of zinc hydroxide on its surface, which acquire all the properties of phase layers. Depending on the solution composition, temperature, and current density, oxides of different modifications are formed. But, as follows the analysis of numerous experimental data, these rather thick zinc hydroxide layers are not the cause of electrode passivation. Obviously passivation is connected with the electrochemical action of very thin oxide films which do not always bear a phase character and are formed in the process of discharge of the zinc electrode, independently of the thick hydroxide layers. In connection with this, mention may be made of the interesting observations, carried out a few years ago by T. G. Lyapuntsova, on the passivation of the zinc electrode at reduced temperatures in sulfuric acid solutions. In these solutions, in which the formation of oxide phases or other insoluble surface compounds is obviously excluded, a well-defined, short-lived passivation of the zinc is observed under certain conditions, which is evinced by a brief, pronounced potential shift in the positive direction. On further anodic polarization the potential again acquires a more negative stationary value (Fig. 2). Such a brief potential shift indicates the possibility of sharp inhibition of the ionization of zinc in acid solutions under the influence of thin oxide layers.

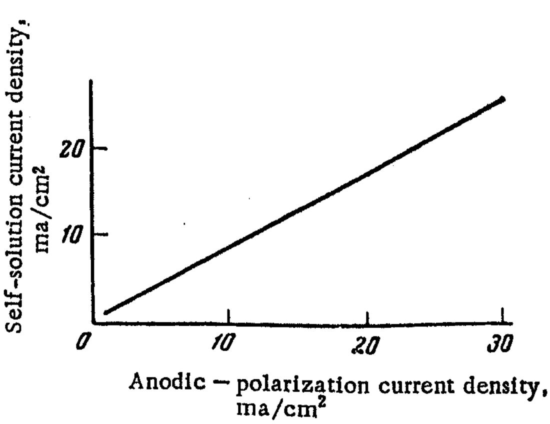

Fig. 3. Self-solution of the magnesium electrode in neutral solutions with respect to the anodic polarization current density.

A similar phenomenon is sometimes observed in certain types of manganese cells with neutral-salt electrolytes. In the arts this phenomenon has come to be called "voltage creep."

The effect of oxide layers is manifested much less often with such metals as magnesium and aluminum than with zinc. The first of these metals in particular — magnesium — is becoming ever more important as a negative electrode material for chemical sources of current, which functions in neutral, saline electrolytes. Owing to its greater negative potential and lower equivalent weight, cells with a magnesium electrode have higher voltage and energy content than similar cells using other metals. Together with this, however, these cells have an essential shortcoming — self-solution of the magnesium, which ensues when anodic polarization is present and is accompanied by hydrogen evolution. This phenomenon, which is well-known in the literature as the negative difference effect, is very pronounced with magnesium; as the anodic current density increases and the potential shifts in the positive direction, the rate of self-solution of the magnesium increases, being always proportional to the current density (Fig. 3). Thus, the use coefficient of magnesium is independent of the current and has a practically constant value equal to 50-70%.

The investigations, conducted recently by D. V. Kokoulina and B. N. Kabanov confirmed the previously suggested idea that the ionization of magnesium proceeds partly through intermediate formation of univalent magnesium ions. These ions, withdrawing to a certain distance from the electrode surface and being strong reducing agents, liberate hydrogen from the water, being themselves oxidized to the bivalent state.

In recent years numerous investigations of the possibility of using iron as the negative electrode in chemical sources of current with an alkaline electrolyte have been conducted. The problem presented by the use of iron in alkaline iron-nickel storage cells has long been known. The iron electrode, which has sufficiently good polarization characteristics, also has a great shortcoming—rapid self-discharge in the charged condition. Self-solution of the charged iron electrode proceeds relatively rapidly, and attempts at decreasing this rate by using various inhibitors have been without result up to now. A somewhat different situation exists in the case of the iron electrode in single-action galvanic cells. As the investigations of R. Kh. Burshtein showed, the reduced iron electrode can be passivated by air under certain conditions. The rate of self-solution of such a passivated electrode in solution is low; on the other hand, such a semipassive state does not hinder the main current-generating reaction of anodic oxidation of iron in the course of operation of the cell. Later it was shown, by work done at the All-Union Scientific-Research Institute of Current Sources, that other types of semipassive iron electrodes also could be used in cells. The outcome of all this work was the development of a new type of cell with an iron negative electrode and an air-depolarized positive electrode. The invention of this iron-air cell solves the old problem in the field of chemical sources of current, of making an inexpensive cell working on the process of oxidation of iron by air, without using scarce materials.

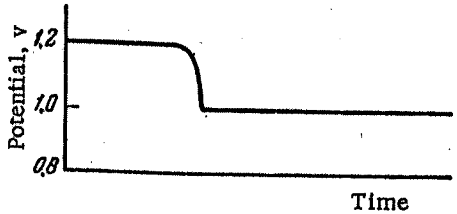

Fig. 4. Curve of the relation between the potential of the carbon electrode and time with cathodic polarization in chromic acid solution.

Passivation in chemical sources of current is observed not only in anodic, but also in cathodic processes, i.e., at the positive electrode of a discharging cell. Phenomena occurring at the positive electrode of an old type of chemical source of current—a cell in which the positive electrode consists of a carbon plate immersed in concentrated chromic acid solution, and the negative electrode is zinc. The cathodic reaction at the positive electrode consists in the reduction of the sexivalent chromium in the chromic acid anion to the trivalent chromium cation. This reduction proceeds quite rapidly, and the overvoltage of the reaction is small. Frequently during the reduction process, however, the reaction is sharply, suddenly retarded, and the overvoltage spasmodically increases to several tenths of a volt (Fig. 4). It was shown by the investigations of G. V. Shteinberg that this abrupt retardation of the process is due to extremely slight changes in the state of the carbon electrode surface and not to the formation of relatively thick phase films of a mixed salt of tri- and sexivalent chromium, as had been assumed earlier.

In conclusion I would like to dwell further on one unique type of chemical source of current, in which diffusion-type electrodes are used. The principle of these electrodes consists in the following: the electrolyte solution is in contact with a porous, chemically inert electrode-terminal made of carbon or porous metal. Through the electrode an electrochemically active substance—an oxidizing agent for the positive electrode and a reducing agent for the negative—continuously diffuses or is driven; the substance enters into electrochemical reaction at the surface of the inert electrode. A very simple, long-known electrode of this type is the air-depolarization electrode, based on continuous diffusion of atmospheric oxygen through carbon electrode and reduction of the oxygen at the three-phase interface.

The principle of the diffusion electrode is used also in various types of thermal cells with gaseous active substances. An obvious case of such a cell is the oxygen-hydrogen cell invented by Bacon in very recent years. This is based on porous nickel electrodes with pores of a certain size, which are in contact with an alkaline electrolyte, through which, at a pressure of several tens of atmospheres and an elevated temperature (200°), is steadily passed gaseous oxygen and hydrogen, respectively, for the positive and negative electrodes. With a steady influx of fresh active substances and removal of reaction products, such electrodes have a long working life.

In the last few years in our country N. S. Lidorenko and co-workers conducted research in the development of diffusion electrodes of another type, with which not gaseous, but liquid active substances are used. Such an electrode can be realized, in particular, by driving nitric acid under pressure through a porous carbon electrode. Owing to the high electrochemical activity of nitric acid, such an electrode has a relatively low overvoltage even at high current densities. This electrode can function for a long time with a continuous supply of nitric

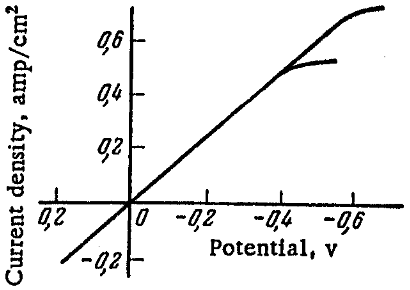

Fig. 5. Curve of the relation between the potential and the current density in the cathodic reduction of trivalent iron at a diffusion electrode.

acid without passivation. Similarly, negative electrodes for current sources can be made, with which solutions of reducing agents, such as, e.g., formalin, solutions of alkali metal sulfides, hydrazine hydrate, etc., are used. With the appropriate choice of carbon or metallic porous electrode for use with the stated substances, continuous operation at high current densities also can be realized. In contrast to the Bacon thermocell, diffusion electrodes with liquid active substances can function without the use of elevated temperatures or high pressures.

As the investigations conducted by I. A. Zaidenman showed, the mechanism of operation of liquid diffusion electrodes has a number of interesting peculiarities. One of them consists in the fact that under certain conditions the curve of dependence of the electrode potential on the current density is linear up to polarization levels of several tenths of a volt (sometimes, even up to one volt; Fig. 5). With ordinary nonporous electrodes, as is generally known, the length of the straight-line portion of the polarization curve is not greater than about 25 mv. As was shown by a mathematical analysis based on the laws of convective diffusion, the linear dependence of the diffusion electrode is due to the specific distribution of current density within the electrode, which is determined by ohmic losses and concentration gradients of the electrolyte in the pores. The slope of the straight line depends on the electrode structure and the kinetics of the electrode reaction.

In many of the examples mentioned in the present paper the solution of practical problems was the result of complex experimental and theoretical electrochemical investigations. In turn, the invention of new types of current sources and the practical problems arising in this case will lead to quite a number of new electrochemical investigations and will act as a stimulus for the further development of electrochemical science.