CHEMICAL SOURCES OF CURRENT:

DISCUSSION

The Role of Barium Sulfate in the Negative Plates of Lead Storage Batteries by Ya. B. Kasparov, E. G. Yampol'skaya, and B. N. Kabanov

N. F. Razina. As V. V. Stender has repeatedly stated, the problem of "the insoluble anode" is now important in the field of nonferrous metallurgy. A successful solution to this problem may be provided by anodes of electrically conducting oxides, such as PbO_2 and MnO_2, deposited anodically as dense films, either on a metallic or nonconducting base. Great interest therefore attaches to research on the precipitation of conducting oxides in connection with chemical sources of current.

Theoretical questions are also very important. If B. N. Kabanov is right in supposing that the corrosion of a lead anode is due to oxidation of lead by oxygen penetrating the PbO_2 layer, then a stable oxide electrode can only be obtained by deposition on a nonmetallic base, as done by us, or by deposition on a noble metal.

The Growth of Zinc Dendrites in Some Swelling Polymers by T. A. Kryukova

V. N. Flërov. I would now like to say a few words with respect to the sprouting of growths through the film. T. A. Kryukova's experiments on films were carried out under conditions somewhat different to those prevailing in storage batteries. However, her results are still of considerable interest in this connection. Why do these growths form, and how can their appearance be prevented? It would appear that the phenomenon is analogous to the cathodic process in zincate baths. N. T. Kudryavtsev established that addition of tin to a zincate bath electrolyte prevented the formation of such growths on the cathode. André stated, in his patent, that addition of 10-15% of metallic tin to the zinc electrode of a zinc-silver storage battery increased its life to 300 cycles.

T. A. Kryukova made the interesting observation that the sprouting of zinc growths through the film was retarded by raising the temperature. N. T. Kudryavtsev's experiments showed that the same was true for zincate baths, where raising the temperature may completely eliminate cathode growths. This similar behavior obviously deserves attention.

N. S. Lidorenko. T. A. Kryukova has discussed the mechanism of sprouting of zinc dendrites through polymers. But she has not stated that this phenomenon completely determines the life of a zinc-silver storage battery. Its life is determined by a number of factors. Suppose that there are four polymer films, existing in the swollen state, between the positive and negative electrodes of the battery. We have investigated the durabilities of the separate films as a function of their position between the electrodes. During the cyclic process of charging and discharging, the film strength is reduced not only near the positive electrode or by the oxidizing agents which are formed in the solution at the positive electrode. The films begin to break down at both the positive and negative electrodes. They last longest in the mean position. Kryukova stated that, by adding surfactants, she could control the form of the zinc crystals on the electrode and make the zinc precipitate looser, and, consequently, create more favorable conditions for the separator. The conclusions from her observations are very positive in this respect. The influence of surfactants is a well known factor in electrocrystallization. The choice of polymer must also be considered. There are polymers through whose films the zinc can sprout very rapidly, within a few seconds; there are other polymers containing substances which impede the formation of needle-like dendrites. The crystals growing through the latter adopt a sponge-like shape, growing uniformly over their whole front, and their penetration time is considerably increased, so that the cell life is increased proportionately. With regard to the swelling of the films in alkali, it should be noted that it has not yet been possible to eliminate the swelling by compression between the electrodes—at any rate in our experiments. Swelling of the negative electrode can be reduced by firmer compression in the electrode package.

The Effects of Ageing Processes on the Operation of Alkali-Zinc Batteries by V. N. Flërov

S. A. Gantman. I was very interested in the paper by V. N. Flërov. The method of approach used with this electrode should be carried further. In particular, as Flërov points out, an investigation should be made of the use of lithium as an additive with the zinc-silver storage battery. On the other hand, it would also be desirable to reconsider our conclusions with respect to this additive in copper oxide electrodes. On the basis of O. V. Gornostaleva's work, we added hydrated lithium oxide to an alkaline electrolyte with the object of improving the copper oxide electrode performance at low temperatures. However, there was no improvement. It follows, from Flërov's work, that lithium addition may improve performance at high, but not at low temperatures, and this may prove significant in the case of the zinc-silver storage battery, where the temperature can be very high at times. For the copper oxide electrode, attention must be payed to SiO_2 as additive. This may be of interest, since the electrode is only used as a primary element.

I have never studied films, but would like to draw attention to the statement, in Zhumo's paper, that Fe_2O_3 and Fe_3O_4 are used as additives in the zinc-silver storage battery to improve the working of the silver electrode. In this way, it is possible to increase the life to 1000 cycles, with a 50% reduction in capacity. If this is so, trivalent iron must appear in the electrolyte, but T. A. Kryukova maintains that the latter is not permissible because a film will grow.

V. N. Flërov. For the last two years we have been concerned with the problem of the insoluble zinc electrode. I would like to refer to the very interesting problem of the ageing of the active material of such an electrode. I emphasize, in the paper, that our results and views on the ageing of zincate solutions are probably applicable to a wider set of conditions than were investigated. Thus, in our view, the same considerations apply to the zinc electrode of an alkaline zinc storage battery. The capacity of this electrode falls with use. This is clearly due to some ageing process of the active material. It is known that zinc hydroxide can exist in several modifications. It may be supposed that the hydroxide is converted to a less active form during the charging process. Retardation of the hydroxide ageing should produce a retardation in the drop of electrode capacity.

In this connection, there is considerable interest in the retardation of the ageing of zincate solutions brought about by the addition of silicic acid and lithium compounds. We checked the effects of these additives on the operation of the reversible zinc electrode. Its characteristics were adversely affected in that the charging reaction was made more difficult. In the case of lithium as additive, our experimental evidence was too little to give a complete picture. At least, no negative effect was shown by the additive. However, it is reported that lithium compounds are added to zinc-silver storage batteries in American factories, with the object of retarding the ageing of the zinc electrode active material.

Z. A. Ioffa. Apart from the ageing process of the cell electrolyte, there are a number of other factors which control the passivation of the zinc anode in the operation of a galvanic cell. In pure alkali, or in alkali containing zincate, at any high current density exceeding a certain critical value, the zinc anode becomes passive after a definite time, and there is a linear relation between the logarithm of this time and the logarithm of the anode current density used. This process is controlled by diffusion; it is necessary that sufficient time should elapse, at any given current density, for the neighborhood of the electrode to become supersaturated with zincate, so that zinc hydroxide or oxide can precipitate to form a thin passifying film.

In the case of galvanic cells, the normal current density at the zinc electrode is considerably less than the critical value. For this reason, with a constant electrolyte composition, and thanks to diffusion, no supersaturation occurs in the neighborhood of one electrode. Working on the above basis, it should take a very long time to produce passivation. However, the electrolyte composition changes during operation of the cell; the curve for the accumulation of zinc with time has a maximum, which is higher the greater the current concentration and the lower the temperature. There are three processes occurring here — accumulation of zinc, precipitation of hydroxide, and ageing of the solution. The two latter lead to a decrease in zincate concentration in the saturated solution.

In order to prevent passivation, it is very important to control the processes so that the rate of ageing is greater than the rate of zincate accumulation. Flërov's investigation, described above, is undoubtedly of great interest in this connection.

However, it is also necessary to consider electrode processes, as well as those occurring in the bulk of the solution. Experiments in our laboratory, and the work of Z. A. Nikitina in the All-Union Scientific Research Institute for Current Sources, have shown that it is a definite form of hydroxide, primarily rhombic, which is responsible for the passivation of the zinc anode in a battery. It is, therefore, very important to create conditions which will prevent deposition of this form of hydroxide on the electrode. Changes in the metal composition, such as alloying the zinc with lead or amalgamating its surface, are known to affect passivation during operation of the cell. Thus, in considering passivation of a zinc anode, we must take into account the processes occurring in the bulk of the solution and at the electrode. Simultaneous consideration of these processes may give a key to the understanding of the anode process in an alkaline zinc battery, and to the prevention of zinc passivation.

The Iron-Carbon Cell by N. A. Shurmovskaya and R. Kh. Burshtein

S. A. Gantman. In the last few years, at the All-Union Scientific Research Institute for Current Sources, we have made some progress toward the practical development of iron-carbon cells. The material used for the iron electrode is a spongy iron produced by the Sulinsk Metallurgical Plant. Activation of this spongy iron, i.e., removal of the passifying film, is done by etching. A thickened electrolyte has been developed. The thickening agent is quick lime, which has the advantage over such materials as starch and flour that it is not decomposed by the hydrogen peroxide formed at the carbon electrode during operation of the cell.

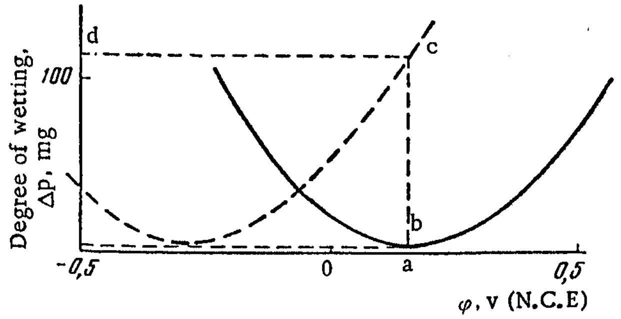
An important consideration in the practical performance of iron-carbon cells is our use of horizontally disposed electrodes and of a number of auxiliary components of the same construction. In practice we have encountered a whole series of problems, not altogether the same as those which we have heard about from N. A. Shurmovskaya and R. Kh. Burshtein. In particular, the following should be noted about iron electrodes. No auxiliary passivation was required when the Sulinsk spongy iron was reduced with a nitrogen-hydrogen mixture and cooled to room temperature in a stream of the same gas mixture. The electrodes lasted for a satisfactory time, as the result of the oxide film which formed at room temperature.

Shurmovskaya and Burshtein believe that there is an oxide film on the iron electrode, because it does not discharge itself. This may be true, but the method used to demonstrate it – removal of the film by cathodic polarization, after which there is a great increase in gas evolution – is unsound. If the spongy iron is activated by removing the film by cathodic polarization, then it has a very high self-discharge. However, if the same iron is activated by etching, then it remains active and hardly discharges itself for a year or longer. It appears that the above authors did not study the work of T. E. Usanov, who showed that even partial cathodic polarization of an iron electrode increased its self-discharge. In general, thermally reduced iron has less tendency to self-discharge than cathodically reduced iron.

As regards the carbon electrode, there is no reason for doubting that Shurmovskaya and Burshtein, using their proposed technique of a rubber adhesive as binder, obtained with more highly dispersed carbon an electrode of longer life and lower permeability. But this method is not universal. When we tried out a carbon, ground to approximately the same degree of dispersion as that used by the above authors, and made up the carbon electrode according to the technique proposed by V. S. Daniel'-Bek, we obtained the opposite result. The electrode with fine pores, made up from the ground up carbon, had a shorter life than that made up from normal carbon. Also, when we took another grade ("clarifying") of carbon for preparing the electrode, it was found to be considerably less hydrophobic. Thus, with other methods of preparing the carbon electrode, porosity is not the deciding matter. It is also necessary to consider the state of the carbon surface and the character of its oxides.

F. R. Yuppets. Research on a carbon electrode with air as depolarizer has been carried out in the All-Union Scientific Research Institute for Current Sources and affiliated organizations. Products of the electro-carbon industry were used for this purpose. Various carbonaceous starting materials were tried, particularly different forms of carbon black, similar to those produced industrially. Mixing, pressing, and baking were performed in accordance with current production technology for the manufacture of electro-carbon products. Gas carbon was found to be the starting material. The work showed that it was possible to prepare a carbon electrode, for use with air as depolarizer, which had high mechanical strength and good electrochemical characteristics. Special experiments established that the electrochemical characteristics of the carbon electrode, with air as depolarizer, could be considerably improved by addition of catalysts, which enabled the load to be increased from 3-4 ma/cm^2 to 5-7 ma/cm^2 of apparent surface.

Carbon electrodes, from different materials and of different porosity, baked in a reducing atmosphere of CO (i.e. under the conditions for electro-carbon manufacture), and then rendered hydrophobic with a solution of paraffin in gasoline, did not wet for a long time. Electrodes from the same carbons, which had been oxidized with air or at high temperature and then rendered hydrophobic in the same way, wetted very quickly, even if a large amount of paraffin was used in the solution for treatment. This phenomenon was checked with a large number of electrodes, and it was established that the character of a carbon surface with respect to wetting by alkali solution could be altered by such treatment an indefinite number of times. These experiments indicated that the wetting of a carbon electrode was a function of the oxygen content of its surface. According to the work of N. A. Shilov and his school, the above phenomenon can be explained by the existence of basic and acid surface oxides. We succeeded in obtaining carbon electrodes, for use with air as depolarizer, which were not wetted by alkali solution for a long time, and these were tested in a large number of iron-carbon and carbon-zinc cells. The figure reproduced from the work of R. Kh. Burshtein and I. E. Veselovskaya, shows the relation between the degree of wetting and the potential of a carbon electrode.



Relation between the degree of wetting and the potential of an unoxidized and an oxidized electrode.

It is clear from the figure (and there is no doubt about this) that the relation between degree of wetting and electrode potential is expressed by a parabolic curve, and that the wetting minimum (point b) lies at the potential for zero charge on the carbon electrode, which, in alkaline solution with air as depolarizer, is + 0.15 v (vs S.C.E.). In the case shown, the potential for zero charge coincides with the potential of the quiescent carbon electrode (point a).

According to N. A. Shurmovskaya and R. Kh. Burshtein, the potential for zero charge on the carbon electrode shifts in the negative direction when the surface is oxidized. Suppose that the potential for zero charge of an oxidized electrode is - 0.3 v. The parabolic relation between degree of wetting and potential is preserved, but the quiescent potential in the given alkaline solution is + 0.15 v as before (point c). It naturally follows from the figure that the wetting of such a carbon electrode will be considerable (ordinate d), since, in this case, the potential for zero charge of the electrode and the quiescent potential do not coincide. We therefore conclude that, when investigating the wetting of a carbon electrode with air as depolarizer, the most important factor to consider is the state of oxidation of the surface, and not the pore size.

A. P. Ksenofontov. For three years our industry has been producing air depolarized cells, with an alkaline electrolyte and carbon and zinc electrodes. However, there are still a large number of problems in the production of these cells, particularly regarding the positive electrode. For example, the method recommended for determining the carbon quality (the iodine method) is unsatisfactory. Carbon electrodes with the same electrochemical characteristics can be obtained from carbons with different activities towards iodine. To assist normal production, it is desirable that a new method should be developed for determining the quality of the carbon used for electrode manufacture.

The problem of grinding the carbon, and the effects of grinding on the wettability and electrochemical characteristics of the positive electrode, are of great industrial interest. The recommendations, given in the paper by N. A. Shurmovskaya and R. Kh. Burshtein, were tried out with production samples in the Ural Battery Plant. The results obtained agreed entirely with those given in the paper, and enabled us to reconsider the question of grinding the carbon. Until recently, we used a carbon passing through a 1 x 1 mm mesh sieve. We now use a finer carbon fraction. The cells produced from this show less wetting and have better electrochemical characteristics.

The new technique for preparing carbon electrodes, developed by F. R. Yuppets, is of special interest to manufacturers. The present technology is unsatisfactory, because of its low productivity and the use of large amounts of organic solvents — gasoline, etc.

R. Kh. Burshtein. As stated in our paper, there are now a number of methods available for producing semipassive iron, including the one described by S. A. Gantman. In this case, the thin oxide film dissolves when the iron electrode is immersed in acid; but a thin oxide film reforms instantaneously when the iron electrode is exposed to air, for example, while it is being transferred from acid to alkali. The existence of an oxide film on the surface is revealed if polarization curves are recorded in terms of current and of gas, as described in the paper.

As regards the autodissolution of thermally reduced iron which has not been in contact with the atmosphere, it is clear from the paper that it dissolves ten times as fast as iron covered with an oxide film. The thermally reduced iron, used by Gantman and also by T. E. Usanov, was coated with an oxide film, since it had always been allowed to come into contact with atmospheric air. According to our ideas, removal of this film by cathodic polarization should lead to an increase in the rate of autodissolution. Progress has been made in the practical use of the iron-carbon cell at the All-Union Scientific Research Institute for Current Sources. It may be pointed out, however, that Gantman's method of obtaining semipassive iron does not permit the iron electrodes to be stored for any length of time in air without electrolyte, since they become passive and then require additional treatment to convert them back to the semipassive condition.

It seems to me that there is something wrong with the views expressed about the paper dealing with the effect of structure on the operation of a carbon electrode with air as depolarizer. Indeed, there is also some literature data on gaseous electrodes which shows that, by creating the correct structure, it is possible to obtain carbon electrodes which operate well at current densities exceeding 100 ma/cm². The effect of pore radius on electrode wetting may be expressed by the following formula:

$$p = -\frac{2\sigma \cos \theta}{r}.$$

This shows that the pressure required to drive liquid into the pores of a non-wettable alkaline electrode is inversely proportional to the pore radius. Liquid penetration is easy if the pores are wide, but difficult if they are narrow. The best indication of the correctness of these conclusions is that A. P. Ksenofontov obtained reduced wetting and improved electrochemical characteristics, under factory conditions, after grinding up the carbon.

The results obtained with the baked type of electrode confirm the views set out in the paper. The unfavorable effect of grinding the carbon on the operation of the VD electrode, prepared by the method of V. S. Daniel'-Bek (see Gantman's contribution), is a result of the fact that this electrode (Fig. 4, curve 6 of paper) in general had few narrow pores, and these were blocked with vinyl chloride resin. Grinding the carbon increased the number of narrow pores and reduced the number of wide ones. The number of pores blocked by vinyl chloride resin therefore increased, the total porosity dropped, and the electrochemical characteristics were impaired.

I consider it unsound to ignore the effects of pore diameter on the operation of gas electrodes, since the electrochemical characteristics of such electrodes are determined by their structures.