

## A LITTLE RETROSPECTION

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In the life of a scientific worker, there are certain milestones at which it is necessary to stop for a while, think about one's own work, evaluate its results, and prepare a plan for the future. On such occasions, one mostly has an unpleasant feeling that time passes too rapidly, while the results of one's own research activity are very modest.

One such milestone is the completion of the tenth volume of our journal. On this occasion, its editors asked their coworkers to consider which problems in the field of power sources had been satisfactorily solved, which problems should be studied in the near future, and what should be the role of our journal during these future investigations.

If we think about research activity in the field of galvanic power sources during the existence of our journal, we conclude that the development of semihydrophobic, carbon-based air cathodes and lithium primary cells with aprotic electrolyte have made the greatest progress.

With air cathodes in alkaline electrolyte, the current-carrying capability has, in the past decade, been raised to hundreds of mA/cm<sup>2</sup> at room temperature, while their lifetime has reached several thousand hours of continuous operation. This is doubtless the result of investigations having been directed not only towards the catalysis of the oxygen reduction, but also towards the transport problems, especially in the gas-filled pores of the air cathodes. A tendency towards a simultaneous solution of both these problems has become increasingly apparent: not only to find the most efficient catalyst, but also to incorporate it within the porous structure of the cathode. The problem of the stability of the catalyst and of the three-phase interface has been satisfactorily solved: the minimization of the peroxide concentration in the pores being considered as most important from this point of view.

With oxygen and air cathodes operating in acidic media and based on active carbon, significant progress has been achieved by using organic N<sub>4</sub> macrocyclic catalysts, which have resulted in an increased lifetime of these electrodes. A high-temperature treatment of the N<sub>4</sub> macrocyclic catalyst-carbon support system yielded surprisingly favourable results. The reason for this stabilization effect, which was discovered by accident, has not been satisfactorily explained. Its principle probably consists in a lucky combination of the earlier discovered catalytic effect of the complex of nitrogen groups with a central metal atom, especially Fe or Co, with a new carbon phase formed at 600 - 800 °C. The latter is apparently due to the thermal decomposition of the original organic N<sub>4</sub> macrocycle. This new carbon phase

has doubtless the advantage of being hydrophobic, similar to the observation made by Kordesch during the activation of carbon in a carbon dioxide atmosphere in the presence of spinels (Boudoird's equilibrium,  $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ ).

With regard to the bifunctional oxygen electrode in alkaline medium, significant progress has also been achieved during recent years, although the cycle life of this electrode is, as yet, insufficient for practical applications in secondary metal-air cells. It seems that the main problem consists of a decision whether it is preferable to develop an efficient and stable catalyst both for the anodic and the cathodic reactions at the oxygen electrode, or to construct the electrode in such a manner that these reactions proceed on different reaction sites.

Quite exceptional success has been achieved in the case of primary lithium cells with an aprotic electrolyte. Various kinds of cathode make it possible to choose a suitable terminal voltage for the cell, and are also decisive for the type of practical application. All types of lithium cells have one feature in common, namely, that they were brought to the market exceptionally quickly and contribute significantly to the fact that the power sources industry has succeeded in keeping pace with the high speed of progress, especially in the field of microelectronics. Thus, a source of energy was developed which has an extremely high storage and service life even under extreme temperature conditions. Scientists have succeeded also in quickly developing the techniques of electrochemical measurements under strictly nonaqueous conditions. Last, but not least, the lithium cells have the merit of saving the prestige of electrical power sources, which suffered somewhat from the fact that fuel cells could not be introduced into genuine common practice. Thus, a modern attractive theme is offered to the young generation of electrochemists, which was not previously the case in other battery domains.

Hopeful results have also been obtained from investigations of the iron electrode for use in alkaline accumulators, although no agreement has been arrived at between various working groups as to the optimum construction of the electrode and the influence of admixtures of certain metal or ions on its electrochemical parameters. There is a real hope that this electrode will, to a large extent, soon replace the cadmium electrode, especially in the case of batteries used for traction.

On the other hand, no significant progress has been achieved in the field of rechargeable zinc electrodes. A partial success has been the suppression of the formation of dendrites; however, this was achieved at the expense of either a lower utilization of the active zinc material during discharge or of a more complicated charging process. Thus, the development of this electrode finished in a blind alley. Further, various electrolyte admixtures or various separator materials brought only small improvements, and their favourable effect usually decreases during cycling. Still less successful were attempts to suppress undesirable shape changes in the zinc electrodes during cycling; obviously, we must reconcile this with the fact that the zincate ion enriched electrolyte has a higher density, and it therefore accumulates preferentially

at the bottom of the cell, resulting in non-uniform distribution of the charging current over the electrode surface.

In basic research on electrode reactions and materials, many optical methods have been used with success. However, the results were often incompatible with those of electrochemical measurements. This seems mostly to be caused by the circumstance that different kinds of measurements are carried out by different workers or teams, whose specialization adds to the difficulties in finding correlations of interest. An analogous situation exists in the computerization of electrochemical measurements, where much remains to be done in order that the new technique shall serve the purpose of research.

In respect of the fields of further intense study, we would mention those tasks, the realization of which on an industrial scale would appear to be most hopeful.

The alkaline-air electrodes are nowadays only suitable for applications where the idle period, or storage, is not extended, otherwise the catholyte undergoes carbonization and dehydration. Therefore, it is necessary to develop membranes selective for oxygen and impermeable to carbon dioxide. Provided that the latter is more or less completely eliminated from the cell, a necessary prerequisite is, of course, a sufficiently high rate of oxygen transport through the membrane. This would allow use of the outstanding results achieved recently with finely porous, completely hydrophobic, and often electrically conductive porous layers, through which oxygen is transported to the three-phase interface, mainly by Knudsen diffusion.

A further study of the principle of the high-temperature stabilization of the organic  $N_4$  macrocycles as catalysts for oxygen reduction in both alkaline and acidic media would doubtless aid the choice of suitable catalysts for deposition on a suitable carbon support. The main point is that the air electrode should contain a continuous network of microelectrodes represented by catalytically active particles contacting both gas and electrolyte.

In this connection, by analogy with the successful accomplishment of a store of international common samples of manganese dioxide, an attractive possibility appears to be the establishment of a similar store of active carbon samples. This would enable scientists to judge or to compare the properties of different catalysts and, moreover, the quality of the porous structure of the air electrodes, from the point of view of mass transport, in a more objective manner.

We now wish to emphasize a problem which is common to the research and development of power sources. In our opinion it is desirable that teams of specialists be formed to concentrate either on oriented basic research or on so-called applied research. In a number of countries in the "fuel cell era", various functional models were designed and constructed at basic research institutions; these models were, however, a great departure from basic research as well as from practical applications, having one feature in common, namely, the high costs of their construction, maintenance, and operation. Many of these models still "decorate" a number of laboratories throughout

the world. Hence, it is desirable on the one hand to improve the coordination of research work carried out by differently oriented teams, and on the other hand to organize collaboration between different laboratories with regard to the principal "reaction scheme": research → development → production.

From an industrial point of view, the nickel oxide electrode appears to be important since it is economically attractive by comparison with the silver electrode. In our opinion, it is necessary to investigate the volume changes of this electrode more closely during cycling with the object of keeping it within acceptable limits. The active component of this electrode has been used as an "activating" admixture in cadmium and iron electrodes, although the principle of its action has not been satisfactorily elucidated.

Studies concerning the influence of admixtures on the behaviour of iron, cadmium, and other accumulator electrodes, and the problems of charge transfer between the current collector and the active mass (*i.e.*, the semiconductor) are rather rare in the literature. This may be due to the fact that the solution of these problems requires special techniques and materials (working with extremely pure materials, study of the Schottky junction, techniques of semiconductors and their doping), for which purpose there is a lack of specialists in most electrochemical laboratories. Collaboration between different laboratories in this field would represent only an emergency solution; the formation of a single team of corresponding specialists joined by a single unifying idea would doubtless achieve the goal more rapidly. From such research results could be expected that would not only remove the existing controversies as to the positive, zero, or negative effect of certain admixtures, but would also be of a considerable practical or technological significance.

These are a few comments and suggestions on research activity into galvanic power sources. As to our journal, it may be said without hesitation that it has proved its merit. It has united workers from different countries into a kind of large family.

The scientific contents of our journal should, in the future, be directed more towards clearly defined long-term research programs, such as new organic electrode materials (polyacetylene, etc.). Publications of a technological character will, of course, often meet with problems of secrecy, *e.g.*, in cases of new methods of electrode preparation. Nevertheless, it would be desirable for such publications to appear much more frequently in our journal.

In conclusion, we wish an optimistic outlook and good fortune to all specialists during their often very tedious work in the field of batteries.