A BRIEF REVIEW OF PROGRESS IN ELECTROCHEMICAL POWER SOURCES

FU-YING PAN

Tianjin Institute of Power Sources, P.O. Box 277, Tianjin 300381 (The People's Republic of China)

Since the late 1880s, the field of application of primary and secondary batteries has been gradually expanded, yet only a few types of batteries existed in the years before World War II. The main types available on the market were Leclanché dry cells, lead/acid and alkaline nickel/cadmium storage batteries, and a limited number of zinc/air cells. Up to the present, these batteries are still considered to be the most popular types, a situation which has arisen as a result of the steady improvement in their characteristics.

The heavy, intermittent discharge life of R20 flashlight dry cells was 250 min in 1930, 839 min in 1947 [1], 1250 min in 1970 [2], and attained an average of 1400 min in 1980. Their average storage life has been advanced from 12 months to around 2½ years. These improvements were obtained both by adopting synthetic MnO_2, acetylene black, and paper lining construction and by using better top-sealing techniques.

Performance improvements were also gained with lead storage batteries by introducing low antimony content (or Pb–Ca–Sn) alloys as grid metals, by adding beneficial additives to the active material, by adopting new assembly designs, and by using plastic instead of hard rubber containers. For instance, the specific energy of SLI batteries was raised from 34.4 to 46 W h kg^{-1} at the 10 h rate, the low-temperature cranking ability progressed greatly, and the cycle life of maintenance-free batteries under refined charging processes is being extended.

The specific energy of nickel/cadmium batteries has also been raised significantly from 15 to 26 W h kg^{-1} for the pocket type to 20 - 36 W h kg^{-1} for the sintered type. Furthermore, the light weight, hermetically sealed spacecraft type has reached a peak of 55 W h kg^{-1} [3].

Batteries, whose developments should match those taking place rapidly in electronics, rockets, ballistic missiles, space technology and portable appliances, now have to operate more reliably and reproducibly over a wider temperature range, have to discharge at higher power, and have to provide greater energy density and longer storage life. Conventional batteries were found inadequate for these services. Through decades of vigorous research and development work, many new battery systems have been developed to attain these performance goals.

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By altering the electrolyte of conventional electrode couples and by changing their reaction mechanism, new systems of higher performance have been developed, such as the alkaline MnO_2/Zn cell [4] and the reserve primary cell of Pb/PbO_2 with $HClO_4$ (or H_2BF_4 or H_2SiF_6) as electrolyte. By using higher energy density cathodic active materials and by raising the degree of utilization of the active material, zinc/mercuric oxide cells and zinc/silver oxide cells were introduced. These are powerful cells among the electrochemical systems.

Fuel cells, with a continuous supply of active materials and removal of reaction products, can generate higher electric power for a longer period. In the early 1960s, the H_2/O_2 fuel cell was the main powerpack used in spacecraft. Recent fuel cell development programs are turning towards terrestrial use as stationary power units, but there are several inherent problems, economical and technical, yet to be solved before large-scale production can be realized.

Based upon the advanced technology of gas-diffusion electrodes, which was achieved in developing fuel cells, a variety of new cells, such as zinc (or iron)/air, nickel/hydrogen, etc., have been created; their specific energy being relatively higher.

Many newly developed ordnance systems require batteries of large power, small volume, high strength and long shelf-life, but conventional cell systems can hardly meet these requirements. Reserve type batteries have been developed. Reserve batteries can be activated for immediate use automatically or manually. Thermal batteries and reserve zinc/silver oxide, zinc/chromic acid and magnesium/silver chloride batteries are of this category.

The use of alkali-metal anodes has led to the development of non-aqueous and solid electrolyte batteries, based on lithium, sodium, and various other cathode active materials. Systems such as Li/$SOCl_2$, Li/MnO_2, Li/FeS_2, and Na/S all possess suitable characteristics for many present-day applications.

During the last four decades, the significant improvements made in the characteristics of conventional batteries, together with the development of new cell types, have satisfied the requirements of different applications in various fields.

In the future, batteries will still maintain their role in portable power sources in the various fields of technological society. Continuous effort to further improve existing cells must still be emphasized. The characteristics of non-aqueous electrolyte lithium cells and their safety problem must be solved.

The development of high energy storage batteries for motive power and load levelling is anxiously awaited. Lithium storage batteries and batteries with liquid and gas reactants, such as Zn/Cl_2, Zn/Br_2 and metal/air cells are primary candidates for consideration in this area.

The research and development work on fuel cells with gas-diffusion electrodes is worth continuing for application at local, small power stations. There are many problems yet to be solved to achieve suitable inexpensive and durable catalysts, long operating life, and low cost. The chemically regenerative redox systems could provide a satisfactory fuel cell and avoid many difficult problems existing in gas-electrode fuel cells. Although the redox system itself may introduce some extra problems, such as difficulties in control and the selection of an adequate ion-exchange membrane, such systems are expected to be low in cost and promising.

The steady progress of microelectronics requires reliable back-up power to safeguard stored information and to allow operation during primary power failure; they need batteries with long operating life, low self-discharge, high energy density, no electrolyte leakage, and good performance at low temperatures. Solid-electrolyte batteries possess most of these criteria and are potentially the most suitable for such applications. To date, miniature, solid-electrolyte batteries are still at the development stage and many difficulties are yet to be overcome. Further research and development should be carried out on these systems in the coming years.

References

1 G. W. Vinal, *Primary Batteries*, Wiley, New York, 1951, p. 114.
2 K. Takahoshi, S. Yoshazawa and A. Kogawa, in Helen M. Joseph (ed.), *Electrochemistry of MnO_2 and Manganese Dioxide Batteries in Japan*, Vol. 1, Electrochem. Soc. Jpn., Cleveland, OH, 1971, p. 171.
3 E. S. Can, *Proc. 25th Power Sources Conf., May, 1972*, PSC Publ., Red Bank, NJ, p. 57.
4 J. P. Gabano, B. Morignat and J. F. Laurent, in D. H. Collins (ed.), *Power Sources 1966*, Pergamon Press, Oxford, 1967, p. 49.