Journal of Power Sources, 4 (1979) 215 - 226
© Elsevier Sequoia S.A., Lausanne — Printed in the Netherlands

PERFORMANCE LIMITS OF PRIMARY AND SECONDARY BATTERIES*

KARL-JOACHIM EULER

Fachbereich Physik der Gesamthochschule Kassel, Arbeitsgruppe Technische Physik, Heinrich-Plett-Str. 40, D-3500 Kassell (F.R.G.)

(Received June 1, 1979)

Summary

Battery performance is a complicated compromise of many contrary demands in the fields of technology and economics. Further complications are introduced by the need for uniform quality, safe manufacture, etc. Thus, no single property can be regarded in isolation. Also, standards have to be met. A few examples will be given: matching of plates, influence of non-working parts of the surface, influence of porosity, and influence of plate thickness.

Résumé

La performance des piles est un compromis compliqué entre beaucoup de demandes, soit techniques, soit d'économie. De plus, on doit tenir la qualité uniforme, sans réserve. La fabrication doit se dérouler sans difficulté, sans tròp de déchet, etc. Par conséquent, aucune qualité de pile ne peut pas être regardée sans égard pour tous les autres. Aussi, on doit tenir compte des normes. Quelques exemples seront discutés: la balance des électrodes, l'influence de parties mauvaises des plaques, l'influence de la porosité, et l'influence de l'épaisseur des plaques.

Überblick

Das Wort "performance" im technischen Englisch ist schlecht zu übersetzen, am besten noch mit "Leistungsfähigkeit". Bei Batterien ist sie ein komplizierter Kompromiss zwischen vielen sich widersprechenden Forderungen, die sowohl im technischen als auch im wirtschaftlichen Bereich liegen. Erschwerend kommt hinzu, dass die Leistungsfähigkeit gleichmässig und die Fertigung "sicher" sein müssen. Auch die Normen müssen befolgt werden. Einige Beispiele werden behandelt: Abgleich von Elektroden, Einfluss schlechter Platten-Teile, Einfluss der Porosität, und Einfluss der Plattendicke.

---

*Based on a paper presented at the EUCHEM Conference on Solid State Chemistry and Electrochemistry especially with respect to its application to Battery Research, Endorf near Rosenheim/Bavaria, F.R.G., 30 April - 3 May, 1979.

1. Introduction

The principal aim of this paper is to consider a few practical aspects of the performance limitations with respect to batteries. Scientists and engineers not familiar with battery manufacture very often oversimplify the various problems. A frequent error is the treatment in isolation of multiple, interacting, interdependent factors. Therefore, it seems necessary, first of all, to define the word "performance".

In fact, performance is more than just gravimetric energy content and efficiency. A well-designed battery of good performance is a well balanced compromise. Its electric properties [1] are adapted to the main field of application, including standardisation. The number of cell designs has to be kept low. Cells are used in different climates. Environmental behaviour has to be taken into account. The customer expects uniform quality over long periods of manufacture. He identifies with the brand of his choice the impression of a certain behaviour: he can trust, without risk, a good battery with long life.

On the other hand, uniform battery quality must be obtained in large scale manufacture by safe and easily controlled processes. The scrap and rejected batteries or components have to be minimized. Also, the possible expenditure on intermediate and final tests is always limited. Last, but not least, the relation between performance and price must remain reasonable. This becomes more important when considering market competition.

An attempt will be made in this paper to explain a few limiting factors of battery performance, taking four examples. Of course, the factors in question here depend upon the state of battery making technology, which is undergoing continuous development. However, although the principles of interest here have not changed very much during the last years, in some of the figures arbitrary units have been used, as errors in the absolute quantities seemed possible. However, the trends are certainly correct. These trends are well known to most battery manufacturers, but, in general, are not known to most electrochemists.

2. Performance of a single battery

Table 1 gives a few general indications of the complications of compromise and the factors playing a role. The battery has electric properties which, in most cases, depend on power demand, age, history of the battery, temperature, etc. A battery designed for low temperature application may fail very quickly in tropical climates. To avoid a second design, a compromise between electrode activity and shelf life has to be arrived at. Again, the term "life" is complicated. Some batteries release corrosive liquids, explosive or toxic substances, or heat. Finally, a very important role is played by economic considerations. These facts are a complicated web not of fixed numbers, but of functions. Figure 1, taken from ref. 2, indicates the gravimetric energy content of lead–acid, nickel–cadmium and silver–zinc secondary cells

TABLE 1

Performance of a single battery — a compromise of many properties, see [1]

Energy content	volumetric/gravimetric
Capacity	as a function of power
Voltage	flat and steep discharge curves
Internal resistance	interrupted discharge
Temperature range of application	
Shelf life	not activated
Service life	not/partly/fully discharged cycle life floating conditions
Environmental behaviour	toxic dangerous } pollution humidity heat
Economics	price, maintenance, peripheric equipment, efficiency recycling of materials

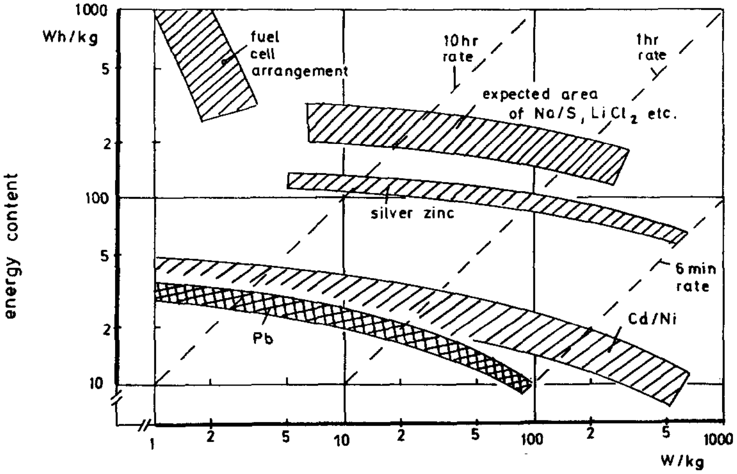

Fig. 1. Gravimetric work-power diagram [2].

at room temperature, depending on the gravimetric power demand during discharge. For comparison, an expected range of energy contents for sodium–sulfur and lithium–chlorine cells is given, and another for fuel cells. However, the latter does not apply to room temperature.

The very important influence of cell design on the matching of an electrochemical system to special applications can be seen in Table 2. The three dry cells are of the same system, zinc/aqueous electrolyte of the com-

TABLE 2

Different D size dry cell designs adapted to specific applications
IEC R 20: 34 mm diameter, 61.5 mm long leak-proof cells, volume 52 cm^3 similar to ref. 3. ●: Optima.

Type		Standard	Radio	Photoflash
E.m.f. (V)		1.60	1.68	1.70
Flash current (A)		6 - 8	5 - 6	12 - 15
Weight (g)		90	95	100
Price (DM)		1.10	1.60	2.-
Flashlight: 5 Ohms	(h)	20	15	24
5 min/d to 0.75 V	(h/DM)	18	9.4	12
Long duration:	(h)	15 000	28 000	25 000
5.000 Ohms, cont., to 0.75 V	(h/DM)	13 600	●17 500	12 500
Photoflash: 1 Ohm, 15 s/min,	(flashes)	400	800	1 200
1 h/d, to 0.75 V	(fl/DM)	360	500	● 600

mon $NH_4Cl/ZnCl_2$ type /manganese dioxide. However, by choice of materials, composition, and design, the standard cell is best suited to the intermittent flashlight test, the radio cell gives the best results at low discharge rates, and the photoflash cell gives about three times more flashes than the standard cell. Each of these special designs, however, is inferior in the other areas of application.

Figure 2 shows a discharge curve, the voltage depending on the relative capacity discharged on different loads [4]. The 20 h curve is fairly flat, resulting in a useful capacity of about 105 A h. If, instead of 5.2 A, we apply a discharge current of 72 A (about a 14 fold increase), the 1 h rate, the useful

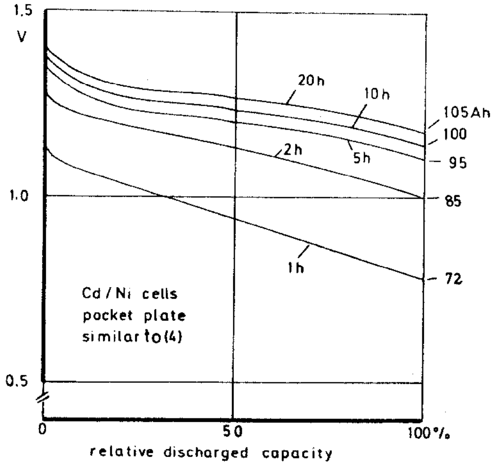

Fig. 2. Cell voltage of Cd–Ni pocket plate cells, similar to ref. 4, during discharge.

capacity is reduced to 72 A h. This may appear to be acceptable, however, the characteristics of the discharge curve have changed severely: the flat 20 h curve has changed its shape into a steeply falling one, discharging at a low cell voltage. It may be mentioned that the simple, low power pocket plate cell considered here, can be easily replaced by high-power cells or sintered plate cells which show flat discharge curves, even under very heavy load. The example given here demonstrates only that a given system has not always the same discharge curve. It may change depending on load and cell design.

A survey of the influence of temperature is given in Table 3. A warm or hot environment results in reduced shelf or service life. In most cases the maximum available power increases with rising temperature, but the detrimental effects of heat always predominate. Adapting cells to high temperature conditions results mostly in a somewhat reduced energy content and a higher price. Batteries today can be used in a fairly wide temperature range, from —40 to +80 °C, not considering cells designed for special extreme applications. Some difficulties exist, not only in a hot, but also in a cold environment. In general, cold batteries exhibit reduced flash current, and therefore reduced useful capacity. Table 3 gives two special effects: the passivation of iron and lead electrodes below 0 °C.

The nominal capacity of a battery is not absolutely fixed. It depends on discharge conditions and on the expected life. The latter is explained in Fig. 3, after ref. 7. If a silver–zinc battery is used for single shot application, as a primary battery, it may have a relative capacity of 100%. The same cell used as a secondary cell has a reduced useful capacity. If a service life of 10 cycles is expected, the permissible depth of discharge still remains at 100%, but if 100 cycles are expected then it is reduced to 50% and for 1 000 cycles to only 10% or less. The coherence between discharge depth and cycle life is well known. If long life is necessary, *e.g.*, in satellites, the battery selection will be changed towards nickel–cadmium cells.

TABLE 3

Influence of temperature range and climate

Warm
Reduced life
    desert: (lead–acid) density reduced from 1.28 to 1.24
        20 h capacity lowered by 15%.
    example: hot sterilization of satellite batteries.
    important: price increases.

Cold
Reduced capacity and yield
    Fe electrodes 20 °C 25% of theory
        0 °C 5% of theory
        —10 °C 0
    Lead–acid batteries are difficult to charge below 0 °C.

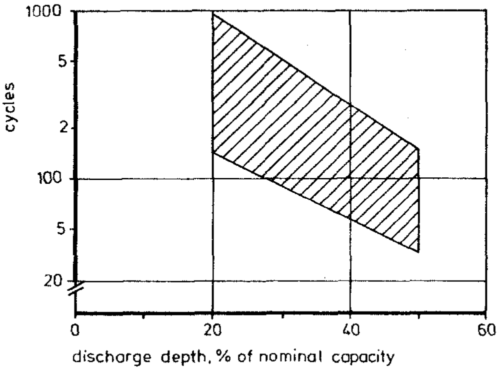

Fig. 3. Cycle life of Zn–Ag secondary cells [7] depending on depth of discharge.

3. Uniform performance

The customer expects uniform performance. Table 4 lists a few additional points of view. It has always to be remembered that with a small profit on large sales, the number of reclaims must be kept as small as possible. The variation of performance must be kept low; uniform production is much more important than exceptionally high energy content, flash current, etc. It is important that the number of early failures is small, because these are always reclaimed. Very often, the manufacturer is asked to guarantee a certain property, which is not within the usual standards. This is quite dangerous, even if the desired property is fulfilled completely. No one knows what will happen tomorrow: a raw material may be replaced by another, similar one or a better manufacturing process will be developed. The standard properties may change. Examples are the internal impedance of dry cells, the number of reactivation cycles of alkaline zinc–manganese dioxide cells, or the inactivated shelf life of lead–acid secondary cells. If these data are guaranteed on the basis of a certain manufacturing situation, the development of new processes and new designs is severely hindered.

In general, uniformity of electrical data decreases with increasing power demand. E.m.f. variations very often occur as a consequence of changed battery raw material, *e.g.*, manganese dioxide or silver oxide. Conducting materials such as graphite, carbon black or nickel flakes have a great influence on the flash current. Every battery material must be replaceable by a similar one from another source. This again is the reason for a reduction of the nominal performance, at least in standards. Some danger always arises with the use of unknown additives, *e.g.*, the organic expanders in lead–acid batteries. These substances work quite well, preventing the recrystallization of spongy lead. Their addition is important for adequate service life. However, it is not known exactly how they work.

Table 5 is concerned with the different types of ageing and failure. Capacity, efficiency, and flash current degrade more or less slowly. If a certain

TABLE 4

The role of uniform performance

- Uniform rather than high
- Few early failures
- No additional guarantee besides standard tests [1]
- Uniformity decreases with increasing current drain
- Every battery material must be replaced by a similar one
- No unknown additives

TABLE 5

Ageing and failure

Degradation	of capacity (A h) of A h efficiency of W h efficiency of flash current (A)
Less important:	of e.m.f. (V)

Failure caused by	results in
Loss of active material Loss of active area (sintering/sulfation) Loss of conductivity Corrosion	capacity fall off R_i, internal resistance, increasing.
Poisoning (Sb)	increase in self discharge decrease in charging efficiency
Bridge forming (dendrites/solder) Separator degradation	short circuit failures

property, *e.g.*, the 5 h rate capacity, falls below a limit which is fixed in the standards, *e.g.*, 65% of the initial nominal value, the natural end of service life of the battery is reached. The rate of degradation of the cell depends on the property under study, on the test procedure, and on the quality of the battery. Chance also plays a certain role: life is always subject to statistical distribution. Loss of active material, loss of active electrode area, loss of conductivity, and corrosion cause increasing internal resistance. Bridge formation or separator degradation cause internal discharge currents, decreased useful capacity, and low voltage. Both may possibly cause sudden failures.

Figure 4 shows failure statistics schematically. The "real" curve (c) is considerably exaggerated. However, a certain small number of early failures always remains. These can be eliminated in several types of cell by artificial

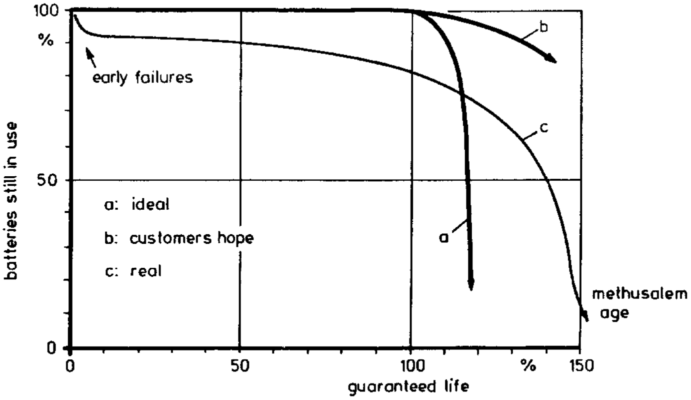

Fig. 4. Schematic of failure statistics: a, ideal; b, customers' hope; c, real.

ageing, but the very important lead–acid secondary cells, and the ordinary dry cells cannot be aged. The guaranteed life is set to a value where the number of reclaims is small. The very old batteries often observed to be still in use, are the happy cases of best maintained, well treated, little used methusalems.

Figure 5 shows the coherence between the absolute value of a battery property, and its variation within a manufacturing series. Ten series of dry cells with the same dimensions, but changed composition and design, have been manufactured. The development goal was a high flash current for a special field of application. As can be easily seen, it was possible to bring up the flash current to about 15 A without increasing the variation. If, however, the flash current was raised to 18 A or more, the uniformity did not remain satisfactory. The final result was that the dry cell had to be replaced by a sealed nickel–cadmium secondary cell of the same size, which had a flash current of >30 A.

4. Examples of performance limiting factors

Table 6 surveys the 4 examples to be treated below. Most of these are unexpected. The *matching* of plates is a difficult task for the battery designer, see Table 7. It can be done exactly for one power demand only and for new cells. Because the battery must fulfill different application demands and because both electrodes are influenced differently by ageing and temperature, the matching is a troublesome procedure requiring great experience.

Each plate, each separator, has both good and bad working areas on its surface. Because the stray angle of the current is small, a bad, or inactive area acts like a shutter for the other electrode. Figure 6 shows the unfavourable

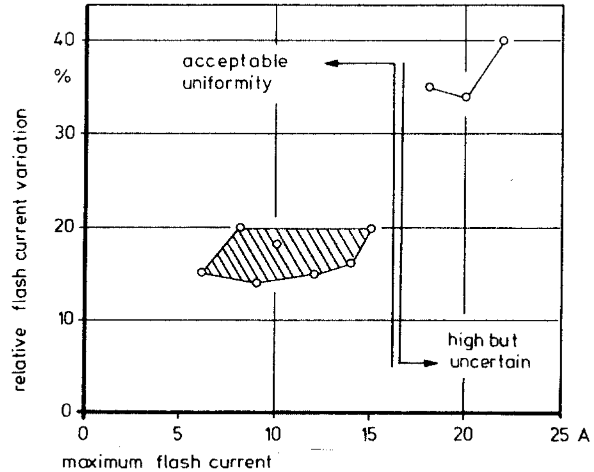

Fig. 5. Dependence of the variation in flash current on its maximum value in D size dry cells. Ten different cell designs.

TABLE 6

Examples of practical battery science

- Matching of plates
- Inactive areas summate
- Influence of porosity (lead–acid)
- Influence of plate thickness on:
  - flash current
  - voltage drop under heavy drain
  - 20 h capacity
  - service life
  - price

TABLE 7

The role of component matching

Positive electrode Negative electrode Amount of electrolyte Separators	have to be matched

to equal capacity at the end of life under lowest temperature and worst discharge conditions

The component degrading most rapidly determines the matching

At the beginning of life better capacity could be achieved if ageing is not considered.

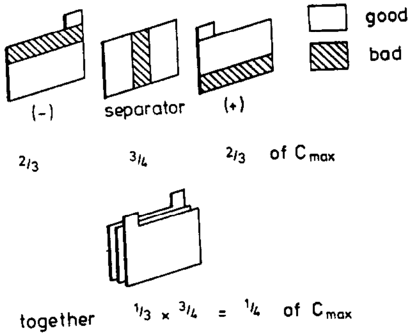

Fig. 6. Summation of additive effect of inactive plate and separator areas.

result. Because the *bad areas* do not coincide, they *add up*. Plate areas which are inactive have been observed [6] by autoradiographic techniques.

Generally, it is believed that increasing the porosity of the active masses in nearly every electrode results in a better faradic yield, increase of flash current, etc. Figure 7 shows that only a small increase is really observed. An increase in the porosity of the active masses in lead and lead dioxide electrodes can be realized by changing the composition of the lead paste [5]. In

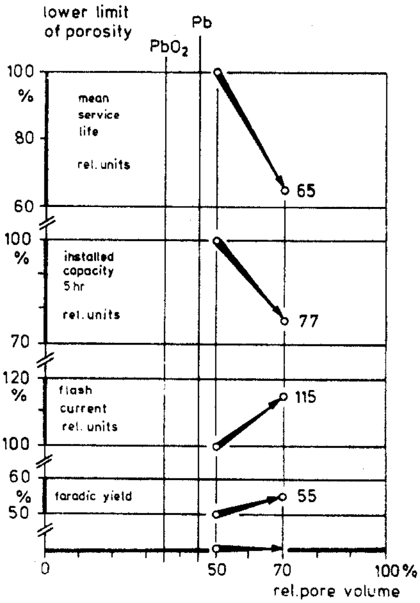

Fig. 7. Influence of mass porosity on mean service life, installed capacity, initial flash current, and initial faradic yield. Lead–acid cell, similar to ref. 5 but simplified. 5 h discharge.

general, the porosity of practical batteries is of the order of 50%. If it is increased from 50 to 70%, the faradic yield increases from 50 to 55% and the flash current from 100 to 115%. However, the installed capacity, *e.g.*, the 5 h capacity, decreases from 100 to 70% and the mean service life decreases from 100 to 65%. Neither reduction can be tolerated. Attempts have been made to improve the preparation of active material by sophisticated milling or atomizing processes or by the incorporation of pore forming components. The possibility cannot be excluded that entirely new processes will result in improved battery materials, but during the last two decades no remarkable progress has been noted.

The last example relates to the influence of plate thickness on several battery properties. With constant cell volume, the plate surface increases with increasing number of plates or with decreasing plate thickness. Since the current demand is distributed over the sum of all plate surfaces, the current density decreases. This again ameliorates the cell characteristics. Figure 8 shows the flash current depending on the number, *n*, of positive plates. The corresponding plate thickness is also indicated. The expected improvement proportional to *n* is limited to plates of more than 1 mm in thickness. With thinner plates, the influence of lugs and connectors as well as plate defects becomes more and more important. Under heavy drain, the increased flash current will improve the discharge curve. Low discharges are not influenced by the elevated flash current. This is confirmed in Fig. 9 which shows the dependence of the 10 h capacity of the cell on the number

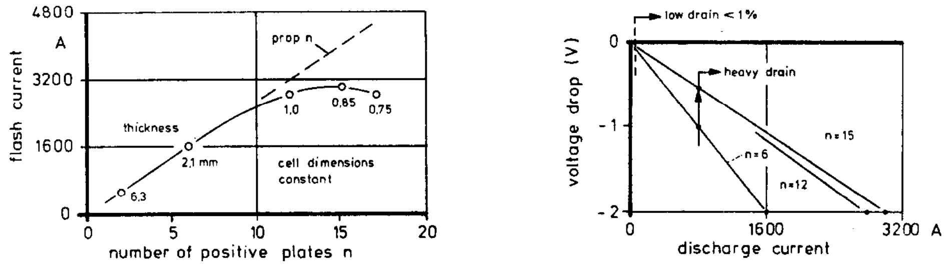

Fig. 8. Influence of the number, *n*, of positive plates on the flash current and voltage drop (simplified). Experimental lead–acid cells of equal size.

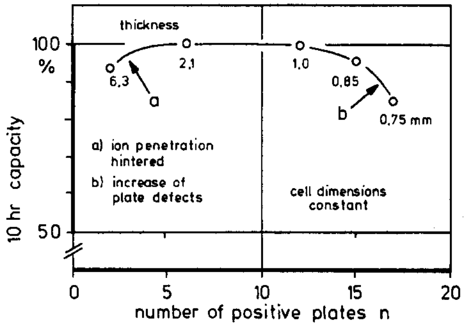

Fig. 9. Influence of the number, *n*, of positive plates on 10 h capacity. Experimental lead–acid cells of equal size. (a) ion penetration hindered; (b) increase of plate defects.

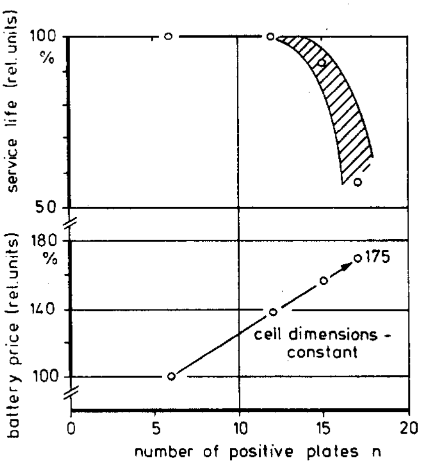

Fig. 10. Influence of the number, *n*, of positive plates on service life and price. Experimental lead–acid cells of equal size.

of plates and their thickness. In very thick plates, ion penetration is hindered (a), whereas in very thin plates frequent structural defects occur (Fig. 9(b)). Both reduce the useful 10 h capacity of the cell. Finally, Fig. 10 relates to service life and price. In very thin plates, the active mass has not sufficient mechanical strength and is soon lost. The battery price increases with the number of plates. Figures 8 - 10 relate to the same cell size and similar design. Again, the possibility that future manufacturing processes may permit the limit of useful plate numbers to be increased cannot be excluded. Today, it can be said, however, that plates below 1 mm in thickness or slightly less exhibit no advantage.

Conclusions

Battery performance is a complex function of several properties, electric characteristics as well as uniformity, environmental behaviour, and economics. Measures taken to improve one of these properties, generally cause deterioration in others. The well balanced compromise is difficult to obtain. This is, however, the real goal of battery design and development. As examples, the matching of positive and negative plates, the additive effects of inactive plate areas, the influence of plate porosity, and the influence of plate thickness are considered. The latter two items are marked by broad maxima. In general, it can be said that the long period of empirical battery research has already resulted in a close approximation to the best obtainable results. Further improvement will become increasingly difficult.

References

1 Anonymous, Vocabulaire Electrotechnique International, group 50, Electrochimie et Electrometallurgie, Genève, 2nd Edn., 1960, pp. 15 - 33. Commission Electrotechnique Internationale, Publication 50 (50).
2 G. Wilke, Denkschrift Elektrofahrzeuge, Franz Steiner-Verlag, Wiesbaden, 1970, p. 87.
3 Anonymous, Varta-Primärbatterien, Technisches Handbuch, Varta Batterie AG, Hannover, 1st Edn., 1973, pp. 34, 111 - 121, 129 - 133.
4 E. Witte, Blei- und Stahlakkumulatoren, Otto Krausskopf-Verlag, Mainz, 3rd Edn., 1967, pp. 90 - 91.
5 H. Bode, Lead-acid Batteries, Wiley, New York, 1977, pp. 274 - 275.
6 H. Bode and K.-J. Euler, Autoradiographische Untersuchungen der Stromverteilung auf Platten von Bleiakkumulatoren I, Electrochim. Acta, 11 (1966) 1 211 - 1 220.
7 G. Seibert, Nickel–Cadmium, Silver–Cadmium and Silver–Zinc Batteries, ESRO SP-49, September, 1969 (Space Power Systems — Engergy Storage), Summer School, Nordwijk, 1968, Vol. 10, pp. 23 - 44.