

## Batteries, an Overview and Outlook

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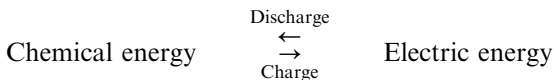
### 15.1 TERMS, DEFINITIONS, AND CHARACTERIZING MARKS

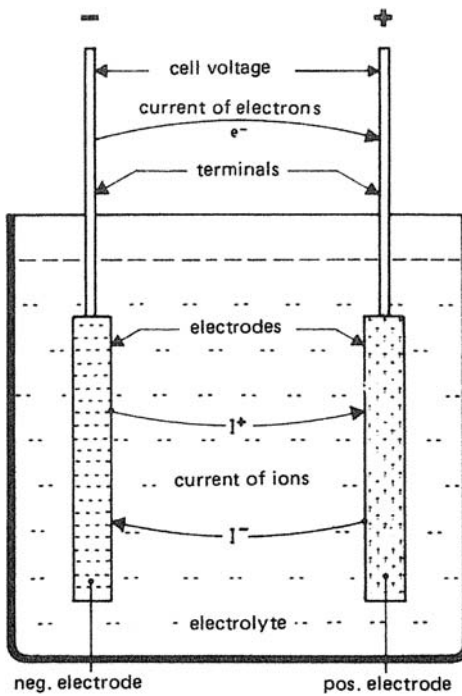
Some terms, which will be repeated throughout this book, shall be defined more precisely:

- “Portable batteries” are understood to be all kinds of electrochemical energy-storing devices used in portable appliances regardless of whether they are rechargeable or not.
- Non-rechargeable batteries are called primary cells (batteries) or dry cells (batteries).
- Rechargeable batteries are called secondary batteries or accumulators.
- Also the terms “galvanic primary” and “galvanic secondary” cells are common.

According to the electromotive series of the elements there are innumerable pairs which will yield electrochemical energy accumulators. For instance, take a metal and a metallic oxide and immerse them in a liquid electrolyte. These are the main parts of a cell as [Figure 15.1](#) demonstrates.

All batteries are chemical energy-storage devices and they are energy converters. A primary cell releases chemical energy while being discharged. Secondary cells have a reversible energy conversion characteristic:





**Figure 15.1** Scheme of an electrochemical cell.

Preconditions for the adoption of a storage system are its stable long-term durability, a reasonable voltage range, cheap raw materials, as well as controllable substances regarding production techniques, and also a regard for possible environmental damage.

The nominal voltage is a value that characterizes the system:

$$U_n = f(\text{system})$$

The off-load voltage is dependent on the system and temperature:

$$U_o = f(\text{system}, \delta)$$

and is calculable.

The discharge voltage is dependent on the current:

$$U_D = f(\text{system}, \delta, I_D)$$

For secondary cells the charging voltage is dependent on the current:

$$U_L = f(\text{system}, \delta, I_L)$$

The capacity of a battery is dependent on the system, the temperature, and the discharge voltage:

$$C = f(\text{system}, \delta, I_D, U_s)$$

**Table 15.1** Survey of different primary systems, listed by nature of their electrolytes.

| Electrolytes                                       |                                                        |                                                                     |                                              |                                                                                        |
|----------------------------------------------------|--------------------------------------------------------|---------------------------------------------------------------------|----------------------------------------------|----------------------------------------------------------------------------------------|
| Liquid                                             |                                                        | Nonliquid                                                           |                                              |                                                                                        |
| Low acidic                                         | Alcalic                                                | Organic                                                             | Inorganic                                    | Solid                                                                                  |
| MnO <sub>2</sub> /Zn<br>(NH <sub>4</sub> cl)       | MnO <sub>2</sub> /Zn<br>HgO/Zn<br>Ag <sub>2</sub> O/Zn | MnO <sub>2</sub> /Li<br>CF <sub>x</sub> /Li<br>CrO <sub>x</sub> /Li | SOCl <sub>2</sub> /Li<br>SO <sub>2</sub> /Li | I <sub>2</sub> /Li<br>(P2VP)<br>PbI <sub>2</sub> /Li                                   |
| MnO <sub>2</sub> /Zn<br>(ZnCl <sub>2</sub> )       | AgO/Zn<br>Luft/Zn<br>Ni/Zn                             | CuS/Li<br>CuS/Li<br>FeS <sub>2</sub> /Li                            |                                              | LiI(Al <sub>2</sub> O <sub>3</sub> )<br>PbS/Li<br>LiI(Al <sub>2</sub> O <sub>3</sub> ) |
| Air/Zn<br>(NH <sub>4</sub> Cl)                     | HgO/Cd                                                 | Bi <sub>2</sub> O <sub>3</sub> /Li                                  |                                              |                                                                                        |
| Air/Zn<br>(MgCl <sub>2</sub> , MnCl <sub>2</sub> ) |                                                        | CdO/Li                                                              |                                              |                                                                                        |

Apart from the desired main chemical reactions, every electrochemical system is strained by secondary reactions (oxidation and corrosion), which cause a self-discharge; these are system- and temperature-specific.

The multitude of combinations of materials suitable for the electrode, especially metal oxides of higher energy densities and their combination with an abundance of different materials, cannot be treated here. For this reason Table 15.1 shows a survey of the most important substances presently used for anodes, cathodes, and electrolytes. Specialists for every profile of demand can be generated from combinations of this table, where the IEC and DIN standards define primarily the outer shape, so in international commerce interchangeability is guaranteed.

This applies to the same extent for secondary cells, which in small units are also used in many appliances. Table 15.2 shows a survey of the most important presently used main substances for the positive and negative electrodes and electrolytes.

There are several parameters relevant for describing the properties of batteries, such as:

- Capacity, energy content, on-load voltage range.
- Performance, energy density per volume and weight.
- Power density per volume and weight.

**Table 15.2** Survey of secondary cells for portable batteries.

| Positive electrode | Elelectrolyte                                     | Negative electrode |
|--------------------|---------------------------------------------------|--------------------|
| PbO <sub>2</sub>   | H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O | Pb                 |
| NiOOH              | KOH + H <sub>2</sub> O                            | Cd                 |
| Ag <sub>2</sub> O  | NaOH + H <sub>2</sub> O                           | Fe                 |
| HgO                |                                                   | Zn                 |
| O <sub>2</sub>     |                                                   | C                  |

- Internal resistance, storage life, self-discharge rate.
- Temperature resistibility, mechanic stability.
- Leak safeness, reliability, dimensional stability.
- Contact certainty, price-efficiency ratio.

For secondary batteries there are in addition the following relevant parameters: Wh efficiency factor Ah efficiency factor, rechargeability, and others. Especially important for the portable battery is its energy density per volume and weight.

Of all primary systems the Leclanché system has the lowest and the lithium, as well as the alkaline zinc/air system, the highest energy density. The rechargeable batteries are still inferior to the Leclanché system in this regard, but this is compensated by the possibility of some 100 to 1000 recharges apart from some other properties, such as the high current discharge ability.

Fresh primary cells and secondary batteries when charged have an open voltage close to the nominal voltage dependent on the electrochemical system. This voltage decreases during discharge via the average discharge voltage to the end voltage (see Table 15.3). Also the nominal voltage of the different electrochemical systems is different (see Table 15.3).

Significant for portable batteries is the representable energy density per volume in practice. Table 15.4 gives a survey on the ranges of energy densities per volume of primary and secondary systems, as they are at present available as single cells or batteries consisting of several cells. It is understandable that these values are much lower than the theoretical calculated ones, because the total amount of active material can not be converted into the discharge condition; while discharge increases the internal resistance of the active material results in a lower useful voltage.

Furthermore it has to be mentioned that the practically achievable energy density of course is lower than the theoretically calculated value because of nonactive parts needed for a technically usable system such as containers, seals, separators, and supporting frames. Also the active material of the electrode chemicals only is usable to the point of a suitable end-discharge voltage.

**Table 15.3** Voltage behavior of battery systems.

| Electrochemical system     | Nominal voltage<br>Volts | Average<br>calculated<br>discharge<br>voltage<br>Volts | Cutoff<br>voltage<br>advised<br>Volts | Allowed<br>Volts | Remarks      |
|----------------------------|--------------------------|--------------------------------------------------------|---------------------------------------|------------------|--------------|
| Leclanché (normal)         | 1.5                      | 1.2                                                    | 0.9                                   | 0.75             | Primary cell |
| Alkaline-Manganese         | 1.5                      | 1.2                                                    | 0.9                                   | 0.75             | Primary cell |
| Mercury-Zinc               | 1.35                     | 1.2                                                    | 0.9                                   | 0.9              | Primary cell |
| Silveroxide-Zinc           | 1.55                     | 1.4                                                    | 0.9                                   | 0.9              | Primary cell |
| Air-Zinc                   | 1.4                      | 1.15                                                   | 0.9                                   | 0.9              | Primary cell |
| Manganese dioxide-Lithium  | 3.0                      | 2.4                                                    | 1.8                                   | 1.5              | Primary cell |
| Nickel-Cadmium (gas-tight) | 1.2                      | 1.2                                                    | 1.0                                   | 0.75             | Accumulator  |
| Lead (maintenance-free)    | 2.0                      | 1.9                                                    | 1.7                                   | 1.6              | Accumulator  |

**Table 15.4** Ranges of the energy density per cm<sup>3</sup> of marketed electrochemical systems.

| Electrochemical system                | Nominal voltage V | Energy density mWh/ccm | Remarks                                                        |
|---------------------------------------|-------------------|------------------------|----------------------------------------------------------------|
| Carbon/Zinc<br>Leclanche system       | 1.5               | 120–190                | Primary cell as<br>button, cylindric,<br>or prismatic cell     |
| Carbon/Zinc<br>alkaline               | 1.5               | 200–300                | Primary cell as<br>button, cylindric,<br>or prismatic cell     |
| Zinc/Mercury oxide                    | 1.35              | 400–520                | Primary battery in<br>button cell design                       |
| Zinc/Silver oxide<br>valency: 1 or 2  | 1.55              | 350–650                | Primary battery in<br>button cell design                       |
| Air/Zinc with acidic<br>electrolyte   | 1.45              | 200–300                | Primary battery in<br>cylindric design                         |
| Air/Zinc with<br>alkaline electrolyte | 1.4               | 650–800                | Primary battery in<br>button design                            |
| Lithium/Manganese<br>dioxide          | 3.0               | 500–800                | Primary battery<br>button and<br>cylindric cell                |
| Nickel/Cadmium                        | 1.2               | 40–80                  | Accumulator;<br>button, cylindric,<br>and prismatic<br>designs |
| Lead/Lead dioxide                     | 2.0               | 50–100                 | Accumulator;<br>cylindric and<br>prismatic designs             |

## 15.2 CONSTRUCTION, SIZES, AND MARKING

### 15.2.1 Construction

Primary and secondary batteries are produced in different designs; mainly the following can be distinguished:

- Round or cylindrical cells.
- Button-type cells.
- Prismatic cells and batteries.
- Foil-type cells.
- Special designs for civil and military use.

Very popular are five standard sizes of cylindrical cells as listed in [Table 15.5](#). Inside the same outer shape very different constructions are hidden, e.g. as shown in [Figure 15.2](#). [Figure 15.3](#) shows the construction of a primary button cell. [Figure 15.4](#) shows the construction of a zinc/air button cell. [Figure 15.5](#) shows the construction of a lithium/manganese dioxide button cell; and [Figure 15.6](#) the construction of cylindrical cells of the same system. [Figure 15.7](#) shows the section of a lithium/chromium oxide cylindrical cell with molded electrodes. [Figure 15.8](#) shows the

**Table 15.5** Sizes and IEC designation of the most popular cylindrical cells.

| Type   | Code IEC | Code ANSI | Size Dia. × h (mm) |
|--------|----------|-----------|--------------------|
| Mono   | R 20     | D         | 34.2 × 61.5        |
| Baby   | R 14     | C         | 26.2 × 50          |
| Mignon | R 6      | AA        | 14.5 × 50.5        |
| Lady   | R 1      | N         | 12 × 30            |
| Micro  | R 03     | AAA       | 10.5 × 44.5        |

construction of a nickel/cadmium button cell with so-called “mass electrodes”. [Figure 15.9](#) shows the construction of a cylindrical nickel/cadmium cell with rolled sintered electrodes.

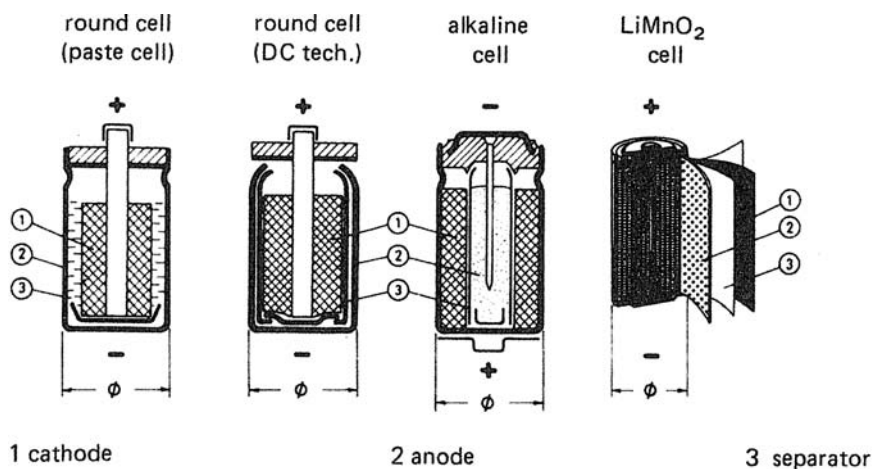
One of the most popular prismatic batteries is the so-called “9-V transistor battery” with the IEC designation 6 F 22, available as Leclanché type and alkaline type as well as a rechargeable nickel/cadmium battery. [Figure 15.10](#) shows a drawing and the dimensions.

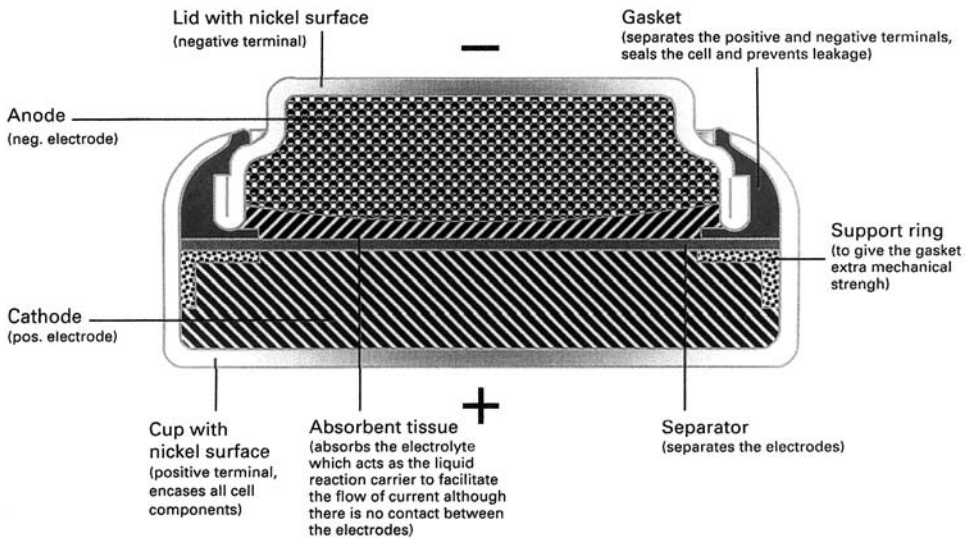
Small portable maintenance-free valve-regulated lead-acid batteries (VRLA) with immobilized electrolyte are available as well in cylindrical as in prismatic design.

[Figure 15.11](#) shows the section of such cell in maintenance-free design and [Figure 15.12](#) a cylindrical cell (Gates).

### 15.2.2 The IEC Designation System for Primary Batteries Defined in IEC Standard 60 086 1

The designation system for primary batteries and cells gives the following information.

**Figure 15.2** Comparison of different cell construction of cylindrical cells.

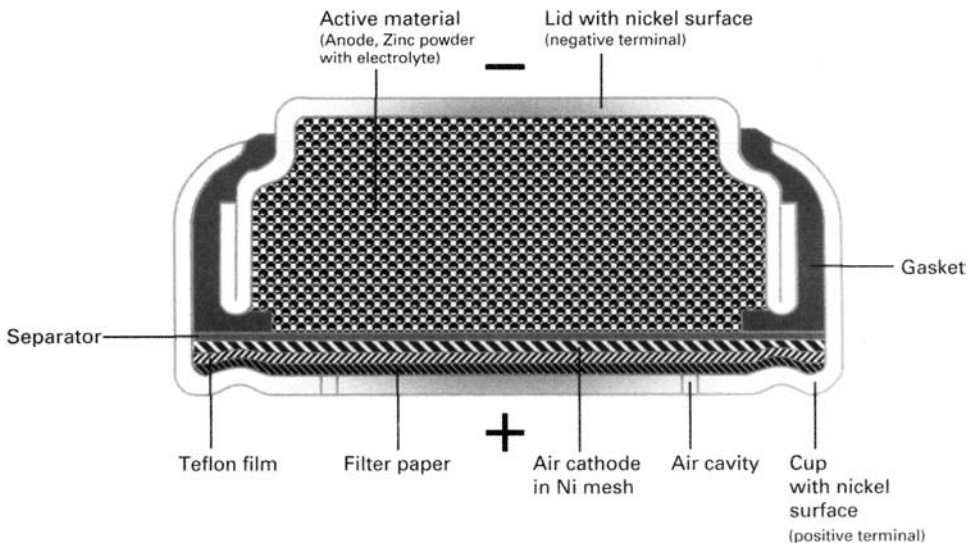


**Figure 15.3** Section through a button cell.

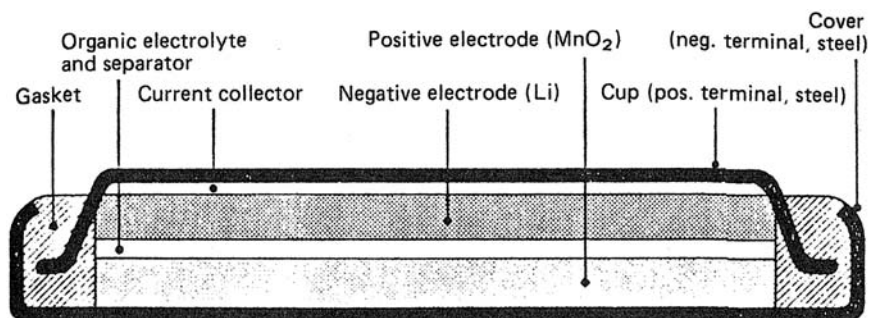
#### 15.2.2.1 Construction

The letters R, S, and F preceding a number mean:

- R = cylindrical cell or button cell.
- S = prismatic cell.
- F = flat cell.



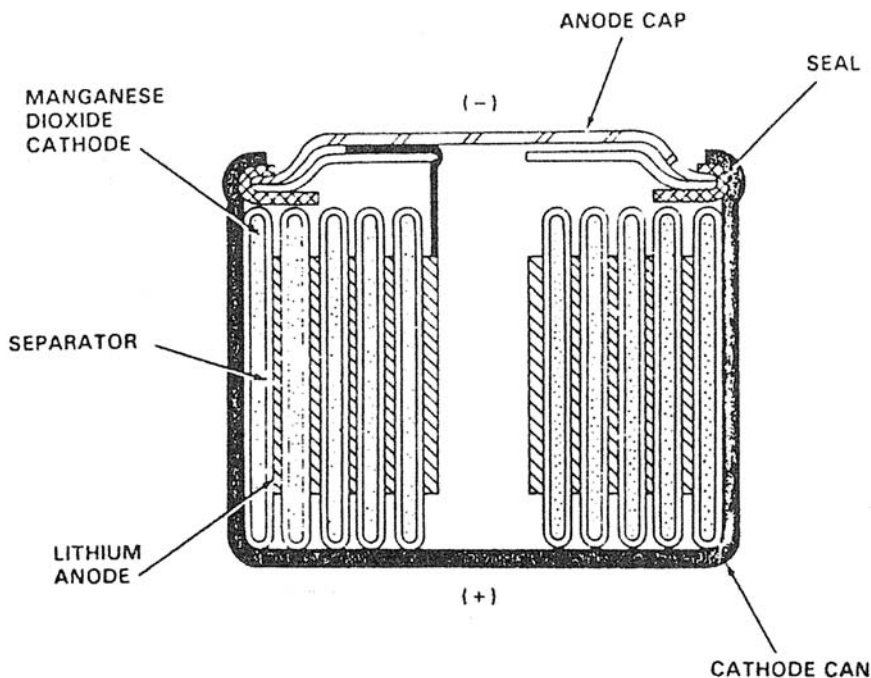
**Figure 15.4** Section through a zinc/air button cell.



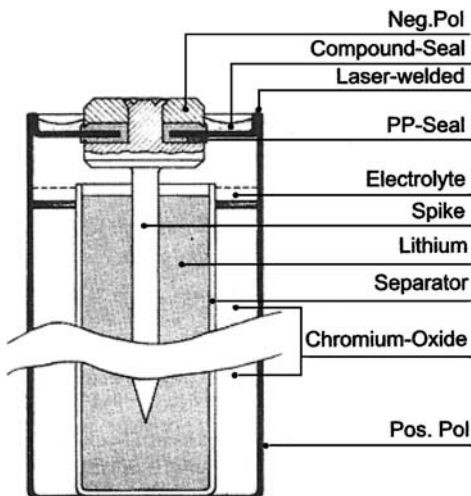
**Figure 15.5** Section through a lithium/manganese dioxide button cell.

### 15.2.2.2 Dimensions

A designation number is distributed to cells and batteries laid down in data sheets of the IEC standard 60 086-2. This standard defines as well the dimensions and their tolerances. *Example: R 20 is the well-known mono cell, or D cell.*



**Figure 15.6** Section through a lithium/manganese dioxide cylindrical cell with rolled electrodes.



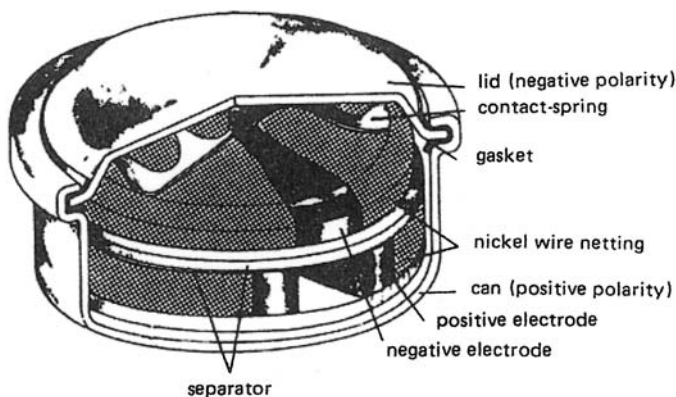
**Figure 15.7** Section of a lithium/chromium oxide cylindrical cell.

### 15.2.2.3: Electrochemical System

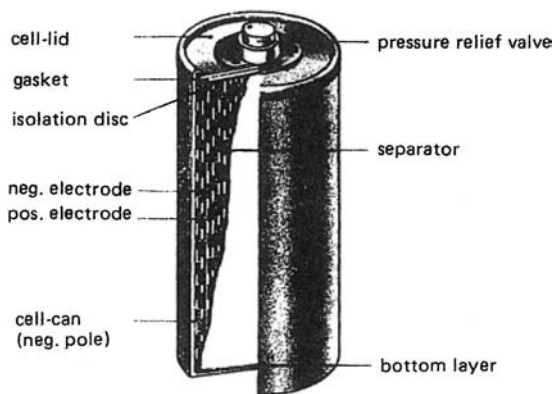
A letter preceding the letters R, S, and F characterizes the electrochemical system (see [Table 15.6](#)). Normal Leclanché types do not have such an additional letter. *Examples: R 20 = mono cell (D cell) Leclanché; LR20 = mono cell (D cell) alkaline.*

Further letters are reserved to describe the following systems:

- BR: carbon monofluorid/lithium
- VL: vanadium pentoxide/lithium
- GR: copper oxide/lithium
- CL: carbon/lithium (rechargeable)
- H: nickel/metal hydride (rechargeable)



**Figure 15.8** Section through a nickel/cadmium button cell with “mass electrodes”.



**Figure 15.9** Section showing the construction of a cylindrical cell with positive and negative sintered electrodes.

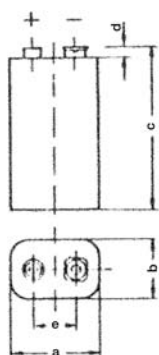
**Note:** The letter K always indicates a nickel/cadmium cell or a battery conforming to the specifications of IEC Standard 60285, sealed nickel/cadmium cylindrical rechargeable single cell.

#### 15.2.2.4 Number of Cells in Series

A number preceding the designation, e.g. 3, means, that three cells are connected in series. *Example: 3 R 20 = battery of three mono cells connected in series.*

#### 15.2.2.5 Number of Cells in Parallel

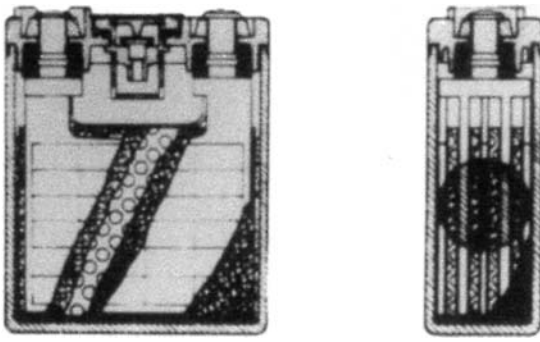
A number connected to the designation at the end by a hyphen, e.g. -3, means that three cells are connected in parallel. *Example: R 20-3 = three mono cells connected in parallel.*



**Dimensions (mm)**

|   | VARTA     | IEC       |
|---|-----------|-----------|
| a | 26,5-2    | 26,5-2    |
| b | 17,5-2    | 17,5-2    |
| c | 48,5-2    | 48,5-2    |
| d | 2,5±1     | —         |
| e | 12,7±0,25 | 12,7±0,25 |
| f |           |           |
| g |           |           |

**Figure 15.10** Dimensions of the battery IEC 6 F22 (9-V transistor battery).

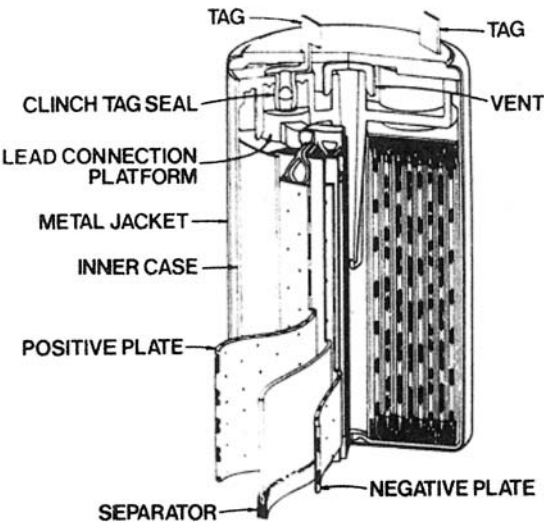


**Figure 15.11** Principle design of a prismatic VRLA cell.

### 15.3 THE ALKALINE MANGANESE CELL

The birthyear of the alkaline manganese cell was 1945 but it was not until 1960 that it was successfully introduced to the market. The most common design is the round cell; here the user has many different designs to choose from, as in the field of Leclanché cells in Western Europe alone about 20 manufacturers of batteries in the sizes mono, baby, and mignon, and so on offer their products, not counting the hundreds of trademarks.

In all about 200 trademarks are registered. Apart from this, alkaline cells are offered in four different classes. The manufacturers attempt to make these classes differentiable by using certain labels, but a uniform designation has not been introduced. As has already been mentioned, choosing a product is a complex problem, with the consumer mainly making a decision on the brand and price.



**Figure 15.12** Principle of a cylindrical VRLA cell (Design of Gates, United States).

**Table 15.6** IEC designation letters for electrochemical systems.

| Letter | Positive electrode                 | Electrolyte                 | Negative electrode | Nominal voltage (V) |
|--------|------------------------------------|-----------------------------|--------------------|---------------------|
| —      | Manganese dioxide                  | Sal ammoniac, Zinc chloride | Zinc               | 1.5                 |
| A      | Oxygen                             | Sal Ammoniac, Zinc chloride | Zinc               | 1.4                 |
| B      | Carbon monofluoride                | Organic electrolyte         | Lithium            | 3                   |
| C      | Manganese dioxide                  | Organic electrolyte         | Lithium            | 3                   |
| L      | Manganese dioxide                  | Alkaline electrolyte        | Zinc               | 1.45                |
| M      | Mercury oxide                      | Alkaline electrolyte        | Zinc               | 1.35                |
| N      | Mercury oxide + Manganese dioxide  | Alkaline electrolyte        | Zinc               | 1.4                 |
| P      | Oxygen                             | Alkaline electrolyte        | Zinc               | 1.4                 |
| S      | Silver oxide $\text{Ag}_2\text{O}$ | Alkaline electrolyte        | Zinc               | 1.5                 |
| T      | Silver oxide $\text{AgO}$          | Alkaline electrolyte        | Zinc               | 1.55                |

Concerning alkaline manganese cells the problem is far smaller, as only about ten manufacturers worldwide offer such batteries, all fitting in one class, mostly directly distributed by the manufacturers.

## 15.4 REGENERATION/RECHARGING

Regeneration of primary cells is generally not advisable. There is a danger of an augmented inner pressure which can lead to a leakage or explosion. Regeneration should especially not be taken into consideration with mercury oxide, alkaline manganese, and silver oxide batteries due to the mentioned risk of explosion.

**Note:** Several manufacturers have developed rechargeable alkaline manganese and silver oxide batteries and development is still going on but a broad presentation seems to be uneconomic at present; but these developments may gain importance in connection with solar cells for power supply of electric consumers with low power demand.

## 15.5 A NEW GENERATION OF BATTERIES: LITHIUM PRIMARY BATTERIES

Lithium cells and batteries have been subject of great interest by the consumer side. What kind of system is the right one, what are its advantages and disadvantages? These and other questions are often asked. The user's strong interest is understandable as the following advantages are presented:

- High energy density per volume weight.
- High voltage.
- Superior ability for a long storage time.
- Very low self-discharge rates.

- Good discharge, performance even at low temperatures.
- Also employable at high temperatures.
- Cheap.

What of the above is true? What are the disadvantages? How is the lithium system to be classified in relation to the other primary systems?

First of all it must be pointed out that every primary battery is a "specialist". A universal cell or system which is equally favorable for all applications is not existent. This is understandable regarding the variety of requirements that have to be met:

- High energy and power density.
- Stable discharge voltage.
- Wide temperature range for use and storage.
- Not harmful to the environment.
- Size and weight according to IEC or DIN standards.
- Easy manufacturability construction.
- Low material costs.
- Shock resistant, rugged design.
- Safety against leakage.
- Safety while in use and recharging.

Out of the multitude of possible choices the chemical periodic system of elements offers, the developer always had an eye on lithium and its feasibility as negative electrode. Lithium is the lightest of all metals in the periodic system of elements. In the last few decades a variety of publications and patents concerning different combinations of electrochemical elements with lithium in the negative electrode has been made. Prototypes of cells with liquid and solid electrolytes, with organic compounds and with dry electrolytes, and also models as fill-up elements or models that can be thermally activated, have been built. Many of these are listed products now with growing sales figures.

Some engineers have been keen on the idea of combining cells with water as electrolyte, but a general utilization of the principle has of course not been taken into consideration due to the brisance of the involved reactions.

The technicians have always been well aware of the problems not only in finding a suitable positive electrode, but also in dealing with this available and therefore not-too-precious element. Lithium reacts with humidity, especially with water, and has its melting point at 180°C. Apart from this, the fact that perchlorates and hydrides of lithium are poisonous and must be coped with.

The following rough classification of the electrochemical elements with lithium can be made:

1. Lithium cells with molten salts for electrolytes (e.g. lithium chloride).
2. Lithium cells with inorganic salts with an organic solution as electrolyte (e.g.  $\text{LiClO}_4$  with the solution of propylene carbonate).
3. Lithium cells with inorganic, aprotic (=nonaqueous) liquids for electrolyte (e.g. sulfur oxide-dichloride  $\text{SOCl}_2$ ).
4. Lithium cells with solid electrolyte (e.g. lithium iodide).

Advantages:

- High voltage rating 1.7–3.6 V.
- High energy density 500–800 mWh/ccm and 150–500 mWh/g.
- Wide temperature range – 55 to 75°C.
- High storage life up to 10 years.
- Very small self-discharge less than 1% p.a.

Disadvantages:

- Relatively high inner resistance (about 50–100 times higher than in so-called conventional systems).
- Relatively small power density.
- Danger of a short-circuit explosion (only wrapped cells).
- Relatively expensive production methods in dry atmosphere, relative humidity less than 1%.
- High requirement for seals.

For more about lithium cells and batteries see Chapter 4 of Volume II, Portable Batteries.

## 15.6 OUTLOOK

New user profiles have been generated through the known turbulent development on the electronics sector, as for instance an electronic watch with an analog display has a power consumption of only 0.3 microamps. This makes a theoretical lifespan of 5 or more years possible with the presently realizable energy density no matter whether lithium or conventional cells are used. Accommodation of the systems is necessary as the power consumption is of the size of parasite side-effects such as self-discharge, especially the longer lifespan sets high requirements for the seals to be met (possible but at greater expense: glass seals).

Design of watches has called for extremely thin batteries; the same goes for pocket calculators. After some efforts the manufacturers managed to meet this demand and have followed this trend. Independent from the developers' challenge, as shown by these examples, new profiles of demand can be listed and must be considered with new solutions. For this incitement, such as demands from the appliance industry, but also basic research and development, the need to make a system ready for marketing is necessary (e.g. solid electrolytes instead of liquid electrolytes).

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