BATTERIES AND THEIR CHEMISTRY

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Contents

Summary

In this chapter batteries are studied. They are devices converting chemical energy to electrical energy. Primary batteries were defined as a source of electrical energy when they are in a charged state. When they use all of their energy, they cannot be used

again. Secondary or storage batteries can be recharged to their original state after they are discharged. Thus secondary batteries can be used repeatedly.

The chemical changes, which take place during the discharge of a primary cell and various storage batteries, were investigated. The focus of the study was on secondary batteries in load leveling in electric utility systems and the use of storage batteries in electric vehicles.

Various types of storage batteries and their chemistry were covered. Lead-acid, nickel-cadmium, nickel-metal hydride, lithium-ion, lithium-polymer, zinc-air, zinc-bromine, and sodium sulfur batteries were presented. Their chemistry was studied during charge and discharge operations. For battery storage systems a general overview was given. Some existing operating systems were presented.

Electric vehicles are the driving force on the battery research in recent years. Currently the most common battery being used is the lead-acid battery. Nickel-metal hydride seems to be the most promising battery to meet the requirements of electrical vehicles for the near future.

1. Introduction

A battery is a device that converts chemical energy into electrical energy. This is done by means of an electro-chemical oxidation - reduction reaction of its active materials. This process involves the transfer of electrons from one material to another through an electric circuit. An oxidation-reduction reaction is defined as a reaction in which electrons are transferred. Oxidation means loss of electrons. Reduction is the process of accepting electrons.

The basic electrochemical unit is the "cell". A battery of any number of cells is used depending on the desired output voltage. In modern usage a battery may refer to just one cell or a group of cells.

1.1 Types of Batteries

There are two types of batteries, primary batteries and secondary or storage batteries. Primary batteries can provide only one continuous or intermittent discharge. Bringing together individual chemical components and assembling the battery in a charged state forms a primary battery. In the process of discharge these components are irreversibly changed and electrical energy is obtained from chemical energy. Primary batteries cannot be re-charged. Primary batteries are used as a source of dc (direct current) power for everyday items such as flashlights and transistor radios.

A secondary or storage battery is made of several chemical and elemental materials. These materials change during charging and discharging and this change is reversible. After the battery has discharged, it is brought back to a charged state, by causing the current to flow back through the battery in the opposite direction. The electrodes are thus returned to approximately their original state. The most common battery of this type is a lead- (sulfuric) acid battery. Secondary batteries are used as a source of dc power when the battery is the main source of power and many discharge and charge cycles are required, such as electrical vehicles, mine locomotives, submarines, or stand-by power required such as telephone exchange and emergency lighting. They are often used to supply large, short time repetitive power requirements such as car and airplane batteries. They are also used for load leveling of an electric power supply network.

1.2 Cell Structure

A cell generally has two conducting electrodes, one positive and one negative, and an electrolyte. One electrode must be an electron donor (anode), and the other an electron receiver (cathode). Anode is the negative electrode and the cathode is the positive electrode. Zinc has been the most common anode, although the most effective anodes are alkali metals such as lithium and sodium. The most effective cathodes are fluorine, chlorine, oxygen, sulfur and metal oxides. The electrolyte must have ionic conductivity. The majority of electrolytes are in liquid form.

1.2.1 Operation of a Primary Cell

To understand how a battery operates, it is easiest to look at a common primary cell. The most familiar primary cell is the Leclanché cell. It is also called "zinc-carbon dry cell". It is used for flashlights and portable radios. The negative electrode is zinc and the positive electrode is a graphite rod surrounded by a densely packed layer of graphite and manganese dioxide. The electrolyte is a moist powder containing zinc chloride. The discharge operation can be represented schematically as in Figure 1
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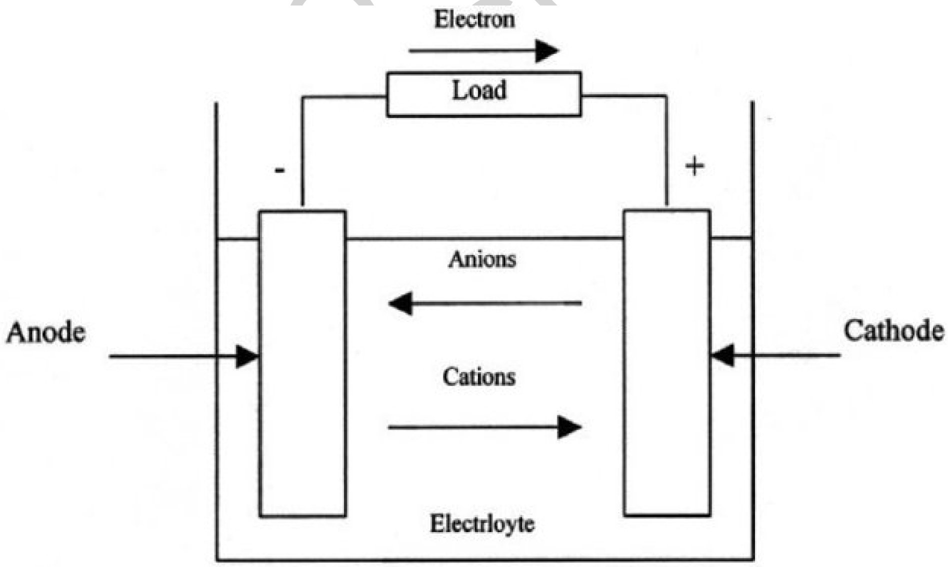

Figure 1: Electrochemical operation of a cell (discharge).

The load outside the cell provides a path for electrons to flow from anode to cathode. This flow of electrons causes the anode to be oxidized and the cathode to be reduced. Inside the cell, in the electrolyte, anions (negative ions) flow to the anode and cations (positive ions) flow to the cathode. The discharge reaction can be written for Leclanchè battery as follows:

Negative electrode oxidation (production of electrons)

$$Zn \rightarrow Zn^{2+} + 2e^{-} \qquad (1)$$

Positive electrode reduction (gain of electrons)

$$2MnO_2 + 2NH_4^{+} + 2e^{-} \rightarrow Mn_2O_3 + 2NH_3 + H_2O \qquad (2)$$

The overall reaction is

$$Zn + 2MnO_2 + 2NH_4^{+} \rightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O \qquad (3)$$

A fresh zinc-carbon dry cell generates a potential difference of 1.5 V. Once this type of battery has been discharged, it cannot be charged and used again.

1.2.2. Charge and Discharge of Secondary Batteries

Secondary batteries are different because the process can be reversed and the battery can be used again. In secondary batteries the electrodes can be regenerated after depletion. An external source of potential is applied across them to reverse the direction of current flow through the cell. The process of returning them to their original state is called charging. To charge (or recharge) a run-down secondary battery the voltage of the external source must be larger than that of the battery in its original state and opposite in polarity.

Consider the lead-acid battery during charging and discharging. The negative electrode is lead (Pb) and positive electrode is lead dioxide (PbO_2). The electrolyte is a sulfuric acid solution. The discharge operation can be represented schematically as in Figure 1. When the external circuit is completed, electrons are released from the anode to the external circuit and the resulting Pb^{2+} ions precipitate on the electrode as insoluble lead sulfate. At the cathode, electrons from the external circuit reduce PbO_2 to water and Pb^{2+} ions, which also precipitate as $PbSO_4$ on that electrode. The discharge reaction can be written as follows:

Negative electrode: oxidation (loss of electrons)

$$Pb \rightarrow Pb^{2+} + 2e^{-} \qquad (4)$$

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \qquad (5)$$

Positive electrode: reduction (gain of electrons)

$$PbO_2 + 4H^{+} + 2e^{-} \rightarrow Pb^{2+} + 2H_2O \qquad (6)$$

$$Pb^{2+} + SO_4^{2-} \rightarrow Pb\ SO_4 \qquad (7)$$

Overall reaction can be expressed as follows:

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2Pb\ SO_4 + 2H_2O \quad (8)$$

Similarly charging of the battery can be represented schematically as in Figure 2.

The electron flow is from the positive electrode to the negative electrode during the charging operation. The reactions are

Negative electrode:

$$Pb^{2+} + 2e^- \rightarrow Pb \quad (9)$$

$$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-} \quad (10)$$

Positive electrode:

$$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^- \quad (11)$$

$$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-} \quad (12)$$

Overall reaction

$$2Pb\ SO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2\ SO_4 \quad (13)$$

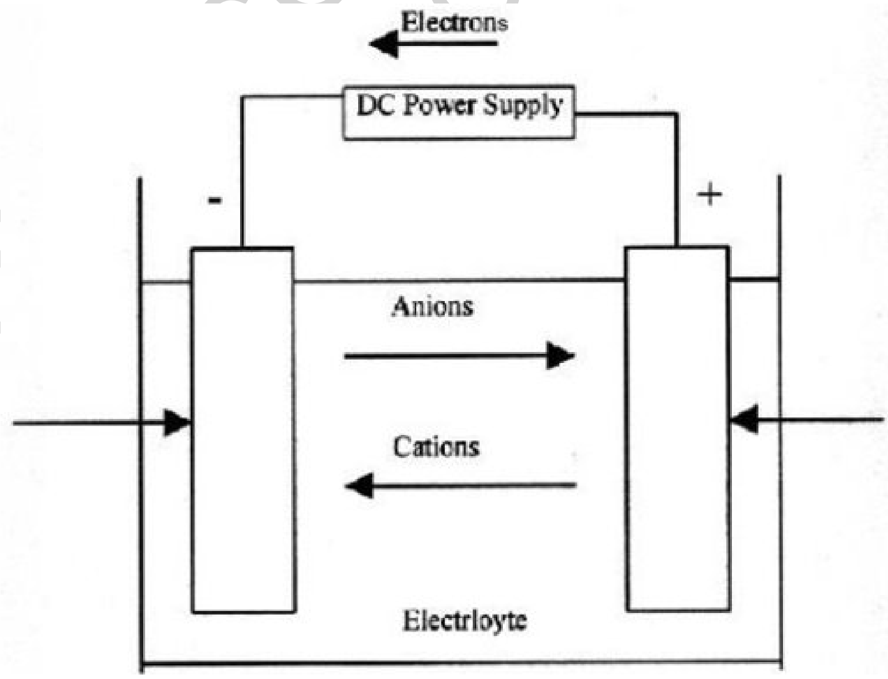

Figure 2. Electrochemical operation of cell (charge).

1.3 Capacity

The total quantity of charges involved in the electrochemical reaction determines the capacity of a battery and is measured in terms of ampere-hours (Ah). The ampere-hour capacity is a function of active materials in the battery.

The capacity of a battery is also expressed on energy basis by multiplying ampere-hours by the voltage of the battery. Specific energy is defined as the amount of energy a battery stores per unit mass at a specified discharge rate; also called gravimetric energy density. It is usually measured in watt hours per kilogram (Wh kg^{-1}). Similarly the ampere hour or watt hour capacity on a volume basis can be calculated. Energy density is defined as the amount of energy a battery can deliver per unit volume at a specified discharge rate; also called volumetric energy density, it is usually measured in watt hours per liter (Wh L^{-1}). Another concept used in connection with capacity is specific power. It is the power a battery can deliver per unit mass at a specified state of charge usually 20 percent. It is also called gravimetric power density. It is usually measured in watts per kilogram (W kg^{-1}). Similarly power density is the amount of power a battery can deliver per unit volume at a specified state of charge - usually 20 percent. It is also called volumetric power density and is usually measured in watts per liter. (W L^{-1}).

Another term related to the capacity of a battery is discharge rate. It is expressed as C/X discharge rate. It means the current that would completely discharge a fully charged battery in X hours. For example, a battery with a total capacity of 120 ampere hours has a C/3 discharge rate of 40 amperes.

Table 1 shows several materials used in the batteries with their specific energies.

Battery	Nominal Cell Voltage (V)	Commercial Specific Energy (Wh kg^{-1})
Lead Acid	2.0	15-35
Nickel Cadmium	1.2	40-60
Nickel Metal Hydride	1.2	60

Table 1. Potential and Specific Energies of Several Batteries.

1.4 Scope of the work

The emphasis of this chapter will be on the secondary battery. The use of storage batteries for load leveling in electric utility systems to meet peak power demands will be covered. Another area of use of secondary batteries is the electric vehicle.

2. Secondary Batteries

The electric utility industry needs energy storage systems. The reason for this need is the variation of electric power usage by the customers. Most of the power demands are periodic, but the cycle time may vary in length. The annual variation is usually handled by the scheduling of outage of the equipment and maintenance during low-demand duration. The daily and weekly changes of the demand are the most important, because of the magnitude of the power variations that may occur in less than one hour. The electric power utilities meet the power demand using a combination of three power sources. The base load generation (approximately 45 percent of the peak power) is provided by relatively efficient, large coal or nuclear power plants that operate around the clock. The intermediate load, (approximately 40 percent of the peak power), is furnished by older less efficient plants. These intermediate units are cycled in and out of service as power demand changes from 45 to 85 percent of peak demands. The peak 15 percent of the power is delivered by gas turbines. The gas turbines require costly and special fuels, and need high expenditures for maintenance.

An ideal solution to this problem would be to provide all the systems' energy requirements with base load plants operating at full capacity (corresponding to the annual average load), and use energy storage systems that could absorb extra energy developed during periods of less demand and deliver it back to the system during periods of excess demand. Pumped hydroelectric storage systems have been used for this application, although there are relatively few areas where conditions are suitable for this type of storage. Using secondary batteries to store energy is an alternative solution. Batteries would allow a very efficient energy transfer and modular construction. Figure 3 shows the typical impact that storage could have on utility operations. The top part indicates the weekly variation in the power demand and the distribution of base, intermediate, and peaking capacity to satisfy the demand. The lower parts show how the power demand can be met without the use of peaking generating equipment, by increasing the base load capacity and adding energy storage.

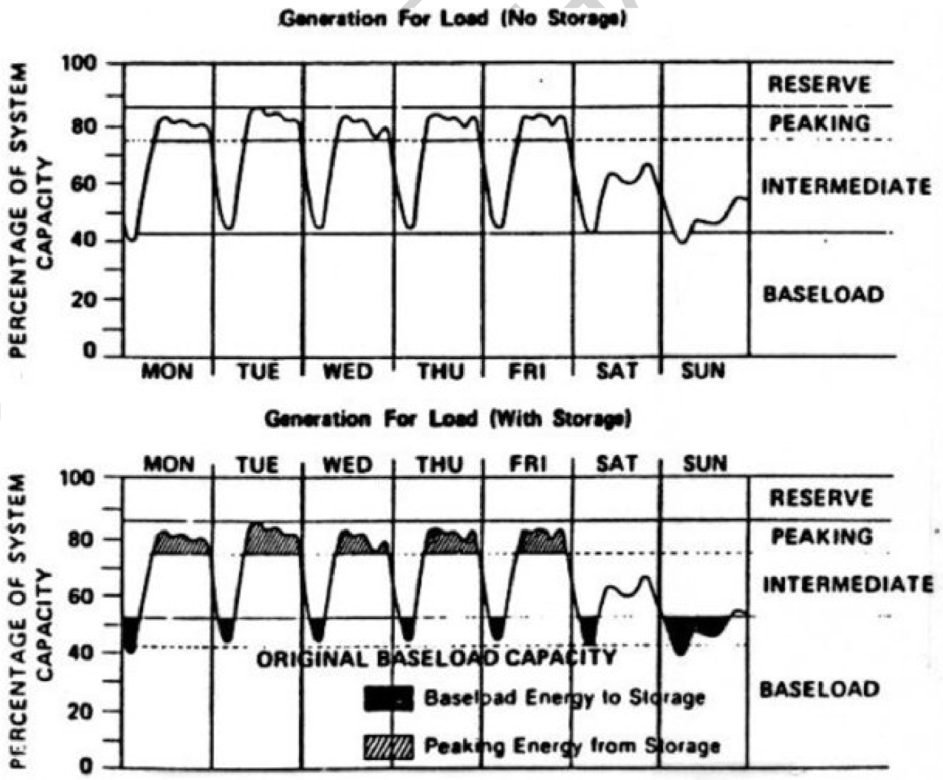

Figure 3. Typical weekly load curve of an electric utility

Despite an interest in electric propulsion for environmental reasons, electrical vehicles have been slow coming into the market. The unavailability of suitable batteries has slowed the development and commercial acceptance of electric vehicles. Up to a few years ago, most of them used lead acid batteries. The energy stored per unit mass is low in a lead acid battery, which limits the range of electric vehicles less than 150 km. The energy content of gasoline is approximately 12 000 Wh kg^{-1}. Regular lead acid batteries can store 30 Wh/kg as can be seen from Table 1. This is a big difference. Specific energy has, therefore, been the concern for electric vehicle batteries.

There are many types of batteries having a higher specific energy than lead acid. But all cost more, some do not perform as well, and some have safety and environmental risks. A big problem in battery research is that the characteristics of a battery are interdependent. That is, energy performance, power performance and lifetime of a battery can have an inverse effect on each other. Increase in one will result in one or both others to decrease. Use of thinner electrodes to improve the power performance of a battery lowers both energy density and life expectancy.

Electric vehicles require improved or advanced rechargeable batteries. Commercially available batteries cannot meet the requirements. There is an on-going need for conventional battery technology with improved performance and advanced battery technology with high energy and power densities, low cost, safety features and minimal maintenance.

Various battery chemistries and technologies are being investigated and developed to meet the required characteristics. These works can be categorized as follows:

- Short term activities to enhance the performance of existing technologies for use within the near future.
- Midterm activities to finalize the development of advanced battery technologies that are not on the market yet. They hopefully can be introduced to the market within 5-10 years.
- Long-term activities to develop new electrochemical systems which need significant advancement before commercialization.

The trouble with batteries is that they store less energy per unit weight or volume than users would like. There are two reasons for this. The first is the active material of the battery makes up only a fraction of its mass. The rest of the material adds weight but no energy. The second problem is the active material has low energy to weight ratio.

In order to solve the first problem, new designs were applied to lead-acid batteries. They have improved over the past few decades when the industry switched from heavy hard rubber cases to lighter plastic ones.

To solve the second problem scientists searched for an element with high electrochemical potential but with low equivalent weight. This led scientists to lithium - the lightest and most reactive of metals. Research is being conducted on lithium based batteries.In order to understand the options available for electric utility usage and for electric vehicles, the various types of batteries will be discussed.

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Bibliography

Cultu, M. (1988) Energy Storage Systems In Operation, Energy Storage Systems: Fundamentals and Applications, 225-248. [This paper presents pumped hydro-storage and battery storage systems.]

Hunt, G.L. (1998) The Great Battery Search, IEEE Spectrum, November 1998, 21-28. [This presents the battery search for practical electric vehicles.]

Linden, David (1995) Handbook of Batteries, McGraw Hill Publishing [This presents a detailed description of the electrochemistry and design of different types of primary and storage batteries.]

Ovshinsky, S.R., Fetcenko M.A., Ross J. (1993) A Nickel-Metal Hydride Battery for Electric Vehicles, IEEE Spectrum April 1993, 176^{-1}81. [A scientific review of the chemistry and physics of the nickel-metal hydride battery is presented in this paper.]

Oxtoby, D.W., Nachtrieb, N.H. (1990) Principles of Modern Chemistry, Saunders College Publishing [This presents college chemistry material.]

Riezenman, Michael J. (1995) The Search for Better Batteries, IEEE Spectrum, May 1995, 51-56. [Paper discusses promising advanced batteries and explores their chances of success.]

Stempel, R.C., Ovshinsky, S.R., Gifford, P.R., Corrigan, D.A. (1998) Nickel-Metal Hydride: Ready to Serve, IEEE Spectrum November 1988, 29-34. [This presents the progress of nickel metal-hydride battery in the electric vehicle application.]

Biographical Sketch

Mehmet Cultu received his BSEE and MSEE from Middle East Technical University (METU) of Ankara, Turkey, and his Ph.D. in Electrical Engineering from Northwestern University, Evanston, Illinois USA. He taught in METU during 1973^{-1}978. He has been with Gannon University since 1978 and Chairman of the Electrical Engineering Department since 1994. In 1984, he received the IEEE Outstanding Student Branch Counselor Award. He was a consultant at General Electric Company on AC drives during 1988-89. His fields of interest include power system engineering, electrical energy storage, electrical circuits, and electrical machines. He is a Professional Engineer in the Commonwealth of Pennsylvania, USA. Dr. Cultu is a senior member of IEEE and a member of the American Society for Engineering Education.