5.16. Study of the lead-acid battery.

Purpose

In this experiment you will determine the different efficiencies of a lead-acid battery. You wil measure the change of the cell-potential in time and the change of the density of the electrolyte in time, and from the measured values you can calculate both the coulombic efficiency and the energetic efficiency.

Background

An electrochemical power source or battery is a device which enables the energy liberated in a chemical reaction to be converted directly into electricity.

Batteries fulfill two main functions:

1. They are portable sources of electric power;

2. They are used to store the electrical energy.

In the practice the words cell and battery mean closed electrochemical power sources. The primary cell or battery is a system whose useful life is ended once its reactants have been consumed by the discharge process. But the secondary battery is capable of being charged or recharged when its reactants have been used up. The spontaneous electrochemical reaction can be reversed by passing current through the cell in the opposite direction to that of cell discharge. It means the secondary battery might be considered as an electrochemical energy storage unit. (Sometimes other terms are used to describe this type of system, e. g. accumulator, storage battery and so on .)

A cell may be characterised in terms as follows:

1. Available capacity;

2. Available energy;

3. The power it can deliver.

The theoretical capacity of a cell may be calculated as

$$Q_T = x \left(n \cdot F \right) \tag{1}$$

where x is the theoretical number of moles of reaction associated with the complete discharge of the cell.

The practical capacity, Q_p , is the actual number of ampere hours delivered. Generally the Q_p is lower than Q_T . The rated capacity is the practical capacity of a cell which has been discharged under prescribed conditions until the cell-voltage has fallen to a pre-selected cut-off voltage.

The ability of a cell to accept charge or be recharged is measured in terms of the capacity and energy efficiencies of the charge/discharge cycle.

The capacity or ampere-hour efficiency of a cell cycled under stated conditions of rate and depth is defined as

$$\eta_{Q} = \frac{\int_{0}^{t} i_{dis} \cdot dt}{\int_{0}^{t} i_{ch} \cdot dt}$$
(2)

where i_{dis} and i_{ch} refer to the currents flowing during discharge and charge respectively.

The overall cycle energy efficiency is:

$$\eta_{Wh} = \frac{\int_{0}^{t} E_{dis} \cdot \dot{i}_{dis} \cdot dt}{\int_{0}^{t} E_{ch} \cdot \dot{i}_{ch} \cdot dt}$$
(3)

where E_{dis} and E_{ch} mean the cell voltage during discharge and charge respectively.

One fo the most wide-spread primary battery is the Leclanche cell. This may be written as:

$$Zn_{(s)} | ZnCl_{2(aq)}, NH_4Cl_{(aq)} | MnO_{2(s)}, C_{(s)}$$
 (4)

and its open circuit voltage is in the range 1,55 - 1,74 V. The discharge mechanism of the Leclanche-cell is complex and not all the details are yet full understood.

The basic process consists of oxidation of zinc at the anode to form zinc ions in solution:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$$
(5)

together with the reduction of Mn(IV) to Mn(III) at the cathode, e.g.:

$$2 H_2O + 2 MnO_{2(s)} + 2e \rightarrow Mn_2O_{3(s)} + H_2O + 2 OH_{(aq)}$$
 (6)

The principal overall cell reaction can therefore be summarised as

$$Zn_{(s)} + 2 MnO_{2(s)} + 2 NH_4Cl_{(aq)} \rightarrow Zn(NH_3)_{2(s)} + Mn_2O_{3(s)} + H_2O$$
 (7)

A typical composition of electrolyte in this cell is 28 $\%~NH_4Cl$ and 16 $\%~ZnCl_2$ in aqueous solution.

There are some other possibilities to constuct primary cells. For example the zincmercury oxide cell is often used as "miniature" or "button" cell in watches, photographic apparatus, and other miniature electronic devices.(This cells have a height of less then 5mm.) The favourable features of this cells are the following: high volumetric capacity (Ah/dm^3) , relatively unaffected by current drain, good discharge characteristic.

The cell composition is as follows:

$$Zn_{(s)} | ZnO_{(s)} | KOH_{(aq)} | HgO_{(s)}, C_{(s)}$$

$$(8)$$

The anodic reaction may be written as:

$$Zn_{(s)} + 2 OH_{(aq)} \rightarrow ZnO_{(s)}$$
⁽⁹⁾

and the cathodic reaction is

$$HgO_{(s)} + H_2O_{(l)} + 2 e \rightarrow Hg_{(l)} + 2 OH_{(aq)}$$
 (10)

so the overall cell reaction is:

$$Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$$
 (11)

The mercury cells have practical specific capacites of up to 400 Ah/dm^3 and specific energies of 550 Wh/dm³. Their discharge characteristics are very good, nearly independent of load over a wide range (see Fig. 1.)

From the "accumulators" or secondery batteries the lead-acid cell is the most used. The first one was constructed by Gaston Plante in 1859. Today more than one hundred million lead-acid battery are manufactured in every year.

The lead-acid cell can be represented schematically as having a negative electrode of porous lead (lead sponge) and a positive electrode of lead dioxide, PbO_2 , both immersed in an aqueous solution of sulphuric acid:

$$Pb_{(s)} | PbSO_{4(s)} | H_2SO_{4(aq)} | PbSO_{4(s)} | PbO_{2(s)} | Pb_{(s)}$$
(12)

The overall electrochemical process can be written by the equation:

$$Pb_{(s)} + PbO_{2(s)} + 2 H_2SO_{4(aq)} \qquad \Leftrightarrow \qquad 2 PbSO_{4(s)} + 2 H_2O_{(l)} \qquad (13)$$

$$\leftarrow charge$$

When the cell is discharged, the H_2SO_4 is consumed and the Water is formed. It means that the electrolyte composition and the density change from about 40 % by weight of H_2SO_4 (1,30 kg/dm3) at full charge (with an associated Opened Circuit

Voltage of 2,15 V at 25 $^{\rm O}$ C) to about 16 % by wight of H₂SO₄ (1,10 kg/dm3) when fully discharged (with an OCV of 1,98 V).

The electochemical reactions at the positive electrode are usually expressed:

$$PbO_{2(s)} + 4 H^{+}_{(aq)} + SO_{4}^{2-}_{(aq)} + 2 e \Leftrightarrow PbSO_{4(s)} + 2 H_{2}O_{(l)}$$
(14)

$$\leftarrow charge$$

and at the negative electrode:

$$Pb_{(s)} + SO_4^{2^-}(aq) \qquad \begin{array}{c} \text{discharge} \rightarrow \\ \Leftrightarrow & SO_4^{2^-}(aq) + 2 e \\ \leftarrow \text{charge} \end{array} \qquad (15)$$

Because the PbO_2 and $PbSO_4$ are in solid state, their activity are constant, so the potential of cell reaction in lead-acid batteries is:

$$E_{cell} = \frac{RT}{2F} \ln K + \frac{RT}{F} \ln \frac{a_{H_2S O_4}}{a_{H_2O}}$$
(16)

From the Eq. 16. you can see that the E_{cell} is larger if the concentration of sulphuric acid is larger. But the conductivity of the sulphuric acid solution has a maximum value at about 25 - 30 % by wight of H₂SO₄, therefore the generally used concentration in the lead-acid batteries are in this intreval.

During working of the lead-acid battery water is forming, the conductivity of the electrolyte is decreasing by the dilution, the activity of water is increasing, so the E_{cell} is decreasing.

Because of the dependence of E_{cell} on the density of sulphuric acid solution, if you measure the density of electrolyte, you can get information of the charged or discharged state of the battery.

Procedure

The first step of this experiment is the discharging of the battery.

1. Constuct the discharging circuit (see Fig.2.). Be careful! The discharging current must not flow through any wires of the voltmeter!

2. Set the previously given discharging current value with the variable load resistance. The potential of the positive electrode is measured by comparison of the potential of cadmium-electrode (so called cadmium-potential in the practice of battery-technique)

The density of the electrolyte is measured by the refractometer. During the discharge the cell voltage, the potential of the positive electrode (cadmium-potential) and the density of sulphuric acid are measured at every 5-th minutes. From time to time

control the discharge current, and if it is necessary, correct it. Continue the discharge until the cell potential rapidly decreases (overdischarge).

3. Construct the charging circuit (see Fig. 3.) and repeat the step 2.

Continue the charging until the evolution of gas begins (overcharging).

The recommended discharging and charging current values are in thr 0,6 - 1,0 A interval. The current must be I < 1,2 A.

The circuit automatically will be opened if the cell potential decreases under 1,6 V.

Calculation

1. Plot the cell potential vs. time, the positive electrode potential vs. time and the density vs. time diagrams.

2. Calculate the ampere hour efficiency from the Eq. 17.

$$\boldsymbol{\eta}_{Ah} = \frac{\int_{1}^{t_2} \boldsymbol{I}_{dis} \cdot dt}{\int_{1}^{t_2} \boldsymbol{I}_{ch} \cdot dt}$$
(17)

where t_1 and t_2 just as t'_1 and t'_2 mean the limits of integrals. We must choose this values so that the state of the battery must be the same at the starting of the discharging (t_1) and the end of the charging (t'_2) just as at the end of the discharging (t_2) and the starting of the discharging (t'_1)

This values can be determined from the density of acid (ρ) vs. time curves namely the values of time which belong to the same densities of acid, the states of the battery are the same.

It means, you must look for the maximum time interval on the graph of ρ vs. time in which the density values are both on the charging and the discharging curves. In that case if the charging current and discharging current were constants during the process, you can use a simple equation:

$$\eta_{Ah} = \frac{I_{dis}(t_2 - t_1)}{I_{ch}(t_2 - t_1)}$$
(18)

[It means, we choosed the limits of integrals so that $\rho(t_1) = \rho(t'_2)$ and $\rho(t_2) = \rho(t'_1)$]

The energy efficiency is calculated by the following equation:

$$\boldsymbol{\eta}_{Wh} = \frac{\int_{1}^{t_2} \boldsymbol{I}_{dis} \cdot \boldsymbol{U}_{dis} \cdot dt}{\int_{1}^{t_2} \int_{1}^{t_2} \boldsymbol{I}_{ch} \cdot \boldsymbol{U}_{ch} \cdot dt}$$
(19)

where U_{dis} and U_{ch} are the cell potentials at the discharging and the charging process. Because the value of I_{dis} and I_{ch} were constant, we can simply the Eq.19.

$$\eta_{Wh} = \frac{I_{dis} \int_{t_1}^{t_2} U_{dis} \cdot dt}{I_{ch} \int_{t_1}^{t_2} U_{ch} \cdot dt}$$
(20)

In that case, when the values I_{dis} and I_{ch} are constants and equal to each other, the Eq. 19. will be more simply:

$$\boldsymbol{\eta}_{Wh} = \frac{\int_{1}^{t_2} \boldsymbol{U}_{dis} \cdot dt}{\int_{1}^{t_2} \boldsymbol{U}_{ch} \cdot dt}$$
(21)

The values of integrals you can calculate with the numerical method.

Graphs, results, data to be reported

- 1. Cell potential vs. t diagrams.
- 2. Positive electrode potential vs. t diagrams.
- 3. Density of acid vs. t diagrams.
- 4. Ampere-hour efficiency.
- 5. Energy efficiency.

Supplement

Recommended readings:

From the book "Modern batteries" written by C.A. Wincent:

4.4. chapter (Iron-nickel cells)

8. chapter (secondary hybrid cells).



Fig. 1

The scheme of the discharging current circuit of lead-acid battery.

A - ammeter; V - galvanometer; K - measure switch; R - variable load resistance; B and C - the electrodes of lead-acid battery; D - cadmium electrode or some other refernce electrode for measuring the positive electrode potential; E - density meter.



Fig. 2.

The scheme of the charging current circuit of lead-acid battery.

T - power source with variable voltage; (the other notations mean the same as on the Fig. 1.).