

11.1 BATTERY CHARACTERISTICS

A certain performance is necessary for a battery to perform satisfactorily in any duty and we therefore need to define characteristics which may be measured and used to judge whether a battery is suitable for a particular application. Moreover, in some cases (e.g. a car traction battery) no battery system presently available has all the essential properties. It is important, therefore, to understand how the characteristics depend on the choice of electrode reactions and on the design of the cell. It will also be clear that the various battery characteristics are not independent of each other and commonly a change of design to improve one will have an adverse effect on another.

11.1.1 Voltage

The terminal voltage of the battery will depend on the free-energy change in the overall cell reaction and, hence, the choice of electrode reactions, the kinetics of the electrode reactions and the cell resistance, i.e.:

$$E_{\text{CELL}} = E_c^C - E_c^A - |\eta_A| - |\eta_C| - iR_{\text{CELL}} \quad (11.1)$$

This equation has been used in other chapters but, in contrast to its application in electrolytic processes, the battery designers' concern is to make the voltage large and positive. Hence, the electrode reactions will be selected so that the active mass at the positive electrode reduces very easily and the active mass at the negative electrode oxidizes readily. Then, the free energy for the overall battery reaction will be large and negative and $E_c^C - E_c^A$ is a high positive quantity. Moreover, both electrode reactions should occur at the required rate without significant overpotentials and the cell should, as always, be designed to minimize

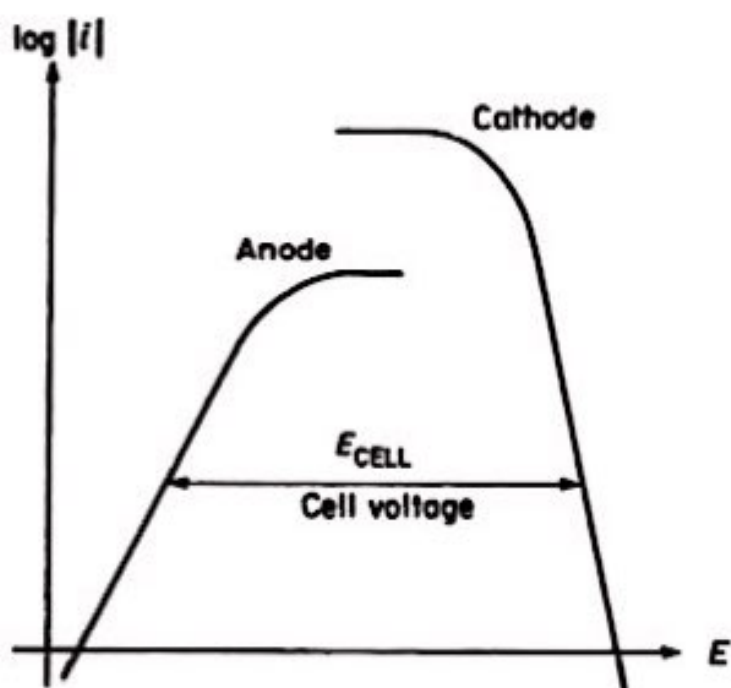


Fig. 11.3 Plot of $\log |i|$ vs. E (vs. a reference electrode) for the cathode and anode of a battery.

to some extent from passivation effects; in this case, however, the passivation overpotential generally decreases when the battery is operating.

Generally, a high cell potential is sought and this is favoured by: (1) the selection of electrode reactions which lead to an overall cell reaction with a high negative free-energy change; (2) electrode reactions without large overpotentials in the range of current to be drawn from the cell (i.e. the electrode reactions should be fast); and (3) designing the cell with a low resistance, i.e. with a high-conductivity electrolyte, low-resistance separator and small interelectrode gap.

11.1.2 Current

Current is a measure of the rate at which the battery is discharging. Current and voltage are, of course, always interlinked (Fig. 11.3) but the ability to deliver a high current without an excessive voltage penalty is dependent on rapid electron-transfer reactions and correct design of the active material to ensure a plentiful supply of electroactive species to the site where electron transfer is occurring. The active material generally behaves as a porous electrode but it should be noted that its composition and structure can change during discharge, e.g. PbO_2 to PbSO_4 during discharge of the lead-acid positive. This involves the conversion of an electronically conducting species to a very poor conductor and, hence, the current which can be drawn from the cell may depend on the state of charge and on the rate at which it has been discharged; both factors will determine the distribution of the PbSO_4 in the porous structure.

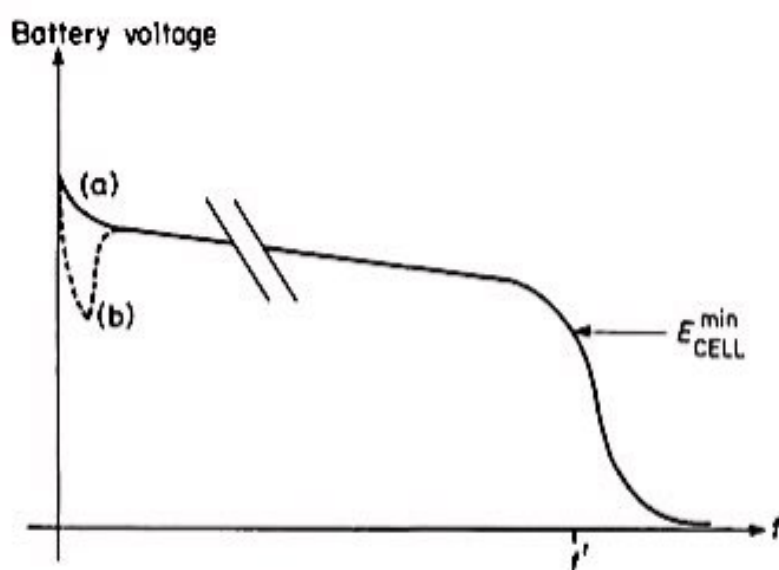


Fig. 11.4 Discharge curves at constant current i for (a) a simple battery and (b) a battery in which one electrode reaction has a nucleation overpotential. t' is the time for the battery voltage to reach a limiting value E_{CELL}^{min} where the cell is no longer useful. The capacity of the battery is then it' .

11.1.3 Capacity

The capacity is the charge that may be obtained from the battery; it is usually quoted in ampere hours and clearly depends on the size of the battery. The nominal capacity of each electrode may be calculated from the weight w of active material via Faraday's law, i.e.:

$$C = wnF/M \quad (11.2)$$

where M is the molar mass of the active material. The capacity of the battery will be determined by the electrode of lowest capacity.

The practical capacity of each electrode and, hence, of the battery, will depend on how much of the active materials can actually be consumed during discharge and this must be determined by experiment. Certainly the capacity will depend on the discharge conditions (e.g. current) and commonly it is measured by monitoring voltage vs. time during a fixed current discharge (Fig. 11.4). The capacity is then it' where t' is the time at the fixed current i for the voltage to reach a value $E_{\text{CELL}}^{\text{min}}$ where the battery is no longer useful. The flatness of the discharge curve (i.e. the variation of the battery voltage during discharge) and the ability of the cell to continue to deliver the expected capacity at increased discharge rates,

11.1.4 Electricity storage density

This is a measure of the charge per unit weight stored in the battery, i.e. it is the capacity per unit weight. Hence, it is measured as in Fig. 11.4 but it applies to the whole battery and hence, the weight is that of the complete battery including electrolyte, current collectors, terminals, the case, etc.

Therefore, a high storage density depends on good battery design (minimizing the weight of all subsidiary elements) and also the correct selection of electrode reactions. The popularity in recent years of lithium anodes is due partly to the low weight of a mole of the metal; 1F of charge is obtained from the dissolution of only 7g of lithium. Of the other possible anode materials, only Al and Mg are comparable – the corresponding weights are 9 and 12 g respectively (cf. Pb 104 g).

For some applications, the battery volume is more important than its weight. Then the electricity storage density and, indeed, energy and power density (sections 11.1.5 and 11.1.6) are normally determined and quoted per unit volume rather than per unit weight.

11.1.5 Energy density

Energy density is the energy obtainable per unit weight of battery, (in, for example, kilowatt hours per kilogram) and is defined by:

$$\text{Energy density} = \frac{it' E_{\text{CELL}}^{\text{ave}}}{w} \quad (11.3)$$

Hence, it is measured by determining the capacity (Fig. 11.4) and noting the average potential during discharge and the total weight of the battery. It depends on the cell voltage (i.e. the choice of electrode reactions) and the factors which determine the storage density.

11.1.6 Power density

Some battery applications require defined capability to deliver power iE_{CELL} per unit weight of battery. This is the power density. The requirement may be for a continuous power density above a certain value or for a high value for a short period, i.e. pulse capability. The power density will decrease during discharge.

11.1.7 Discharge rate

The discharge rate is, as is current, a measure of the rate at which charge is drawn from the cell. It is normally quoted as the C/n or n -hour rate, which is the current to discharge the nominal capacity C of the battery in n hours.

11.1.8 Cycle life

Primary batteries are designed only for a single discharge but a secondary battery is expected to be capable of repetitive charge/discharge cycles. The cycle life is the number of charge/discharge cycles that are possible before failure occurs.

For a secondary battery, it is essential for the discharge/charge cycle to reform the active material in a suitable state for further discharge. The active material must have the correct chemical composition, morphology and distribution in the cell (with respect to current collectors). The cycle life will often depend strongly on the depth of each discharge, attempts to discharge totally the battery often being particularly damaging to the electrodes. The most common forms of failure include: (1) corrosion of the current collectors or contacts; (2) shedding of the active material from the plates; (3) shorting due to dendrites growing between the electrodes; or (4) changes in morphology. The battery may show a gradual decline of performance as it is cycled or the failure can occasionally be quite sudden.

11.1.9 Energy efficiency

With secondary batteries for energy storage on a large scale, the energy efficiency (in per cent) defined by:

$$\% \text{ Energy efficiency} = \frac{\text{energy released on discharge}}{\text{energy required for charge}} \times 100 \quad (11.4)$$

will be important. This will depend on the current efficiency of the electrode processes and the overpotentials involved in both discharge and charge reactions

11.1.10 Behaviour on overcharge

With secondary batteries, it is not always possible to stop charging at exactly the correct moment. If the battery is overcharged, new electrode reactions must occur (e.g. electrolysis of water) and it is important that these reactions do not represent a hazard (e.g. the possibility of fires or explosion) or damage to the active material.

11.1.11 Shelf life

It is essential for most batteries to be stored, sometimes for many years, without self-discharge (i.e. reaction between the anode and cathode active materials or between either and the solvent or electrolyte) or corrosion of current collectors causing a significant loss of performance.

11.1.12 Tolerance to service conditions

The battery duty may require that it provides power continuously, intermittently or at an irregular rate. It may also be expected to perform its duty or be stored under a range of conditions, e.g. a car battery in the USA must operate between temperatures of from -30 to $+50^{\circ}\text{C}$ if it is to be successful in the extreme conditions of winter and summer. The battery may also have to be tolerant to various types of misuse, including occasional shorting, vibration and shock.

11.1.13 Reliability

This is the ability to perform to specification reproducibly and without failure. It will normally be expressed as a failure rate within a given period.

11.1.14 Economic factors

Two factors must be considered: (1) the cost of manufacture; and (2) the cost of servicing during the working life of the battery. Clearly, the components of the battery must be cheap enough for the final product to be competitive (although not all batteries need be cheap – it again depends on the application) and the raw materials must be available on the scale required. In duties which require long service lives, the extent and cost of maintaining the batteries in prime condition will, however, also be important in determining the choice of battery system.