Coulombic efficiency of lead/acid batteries, particularly in remote-area power-supply (RAPS) systems*

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Abstract

This paper investigates the effect of charging regimes and battery designs — and the combined effects of the two parameters — on the overall coulombic efficiency of lead/acid batteries operating in RAPS systems. Under such service, it is highly desirable to achieve a good match between the energy source and the battery characteristics in order to achieve optimum coulombic efficiency at a given state-of-charge of the battery

Introduction

Lead/acid batteries are commonly classified into three usage areas
(i) automotive;
(ii) motive power (traction);
(iii) stationary.
In latter years, with the growth of the RAPS market worldwide, and particularly with the diversity of energy sources available for recharging batteries in these situations, the traditional classification of 'stationary' in terms of a battery's operating condition is no longer closely definable. In many systems, the duty could best be described as a 'hybrid' of both 'motive power' and 'stationary' where deep cycling, fast and slow recharging, and floating are all components of the battery's operating conditions.
It is the main purpose of this paper to review and report on charging regimes, battery designs, and the interaction of the two, as they affect the overall coulombic (A h) efficiency of batteries operating in RAPS applications over a full discharge/recharge cycle
There are three different efficiency factors that can be applied to batteries, namely:
(i) coulombic (A h);
(ii) voltaic (V);
(iii) energy (W h)
The energy efficiency is the product of the first two factors. While the efficiency of energy storage (and it's retrieval) is of prime importance, involving

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as it does charge and voltage factors, the emphasis here will be on the charge or coulombic component The overall coulombic efficiency of a battery is determined by factors that operate on both the discharge and the recharge stages of the cycle

Discharge

The relationship between the obtained capacity as a function of the discharge current has been discussed in detail in a previous paper [1] Briefly, it was concluded that the capacity is a logarithmic function of the 'normalised' discharge current Mathematically.

$$C_x = \left\{ 1 - k \, \log\left(\frac{I_x}{I_r}\right) \right\} C_r \tag{1}$$

where C_x is the capacity to be calculated at current I_x The reference capacity is C_r and corresponds to a discharge current of I_r 'k' is the battery performance constant

During the discharge of a battery no charge is actually 'lost', but rather is 'unavailable'. The coulombic efficiency of a battery during discharge is 100% The total amount of useful charge available during discharge is, however, limited by the rate and temperature described by eqn. (1) If a battery reaches the end of its discharge at a rate I_{d1} some portion of the 'unavailable capacity' can be obtained if the battery is further discharged at a rate I_{d2} which is much less than I_{d1} A number of methods are available (e g , SBA6000) that allow the system designer to size the battery installation correctly provided the load profile is known and relatively constant Hence, the state-of-charge (SOC) of the system battery can easily be calculated at any point during the discharge period irrespective of the complexity of the load profile. The calculation of the true SOC during a complex recharge pattern is much more difficult. Later in this paper, a method to achieve this calculation will be presented

Recharge

As opposed to the discharge part of the cycle, during any practical recharge of a battery there are inevitably more ampere-hours required to reach 100% SOC than were obtained during discharge, regardless of the discharge duration The recharge efficiency factor can be defined as

$$\epsilon = \frac{\displaystyle\int_0^{t_d} I_d \, dt}{\displaystyle\int_0^{t_c} I_c \, dt} \tag{2}$$

where I_c, t_c relate to the charging current, time; I_d, t_d relate to the discharge current, time Factors that determine the efficiency include

(i) depth of previous discharge,
(ii) battery temperature,
(iii) recharge parameter (current, voltage, time)

In the simplest case, where a battery is recharged at constant current, the recharge process can be broken down into three separate regions [2]

efficient $\epsilon \approx 100\%$
mixed $\epsilon \approx 50-100\%$
inefficient $\epsilon < 50\%$

Generally, the 'efficient' region is where the SOC of the battery is below 70–75% and the voltage is less than 2.3 V/cell. The time to reach 70–75% SOC obviously depends on the initial SOC after the previous discharge

The following, second region of the recharge is 'mixed', not only because lead sulphate is converting to lead and lead dioxide, but also because the cell voltages are in the region of 2.3–2.4 V and water is being electrochemically decomposed into hydrogen and oxygen. As this stage progresses with time, a greater and greater proportion of the current flowing through the cell is generating gas rather than causing useful active material conversion At any time, the efficiency in this region can be defined as.

$$\epsilon = \frac{I_a}{I_c} \tag{3}$$

where $I_c = I_a + I_g$; I_a and I_g are the active-material conversion and gas-generating currents, respectively

When the SOC has reached about 90%, the efficiency becomes progressively poorer, until at 100% SOC the recharge efficiency has, by definition, become zero (and all the current is being used to produce gas and overcharge corrosion of the positive grids). Depending on the value of the current, cell voltages as high as 2.7 V/cell are possible [3]

Apart from the externally imposed current and the cell temperature, the factors that have a major effect on the 'mixed' and, to a lesser degree, the 'inefficient' regions are:

(i) grid alloy composition;
(ii) additives in the negative paste;
(iii) recharge current density (A m^{-2}),
(iv) battery age,
(v) previous morphological changes in the paste and/or the grid/active-material interface.

To investigate the recharge efficiency of cells under various conditions further, it is necessary to consider methods and techniques that allow its measurement.

Charge acceptance

In many battery standards it is common to incorporate a 'charge acceptance' test Briefly, this test usually consists of discharging a battery to 50–70% SOC, reducing the temperature to 0 °C then, after applying a constant potential of 2.4 V/cell, recording the charging current that flows into the battery after an interval of 10 min The larger the current the better The charge-acceptance value is a good indicator of the proportion of charge that can be replaced in the battery during the 'efficient' region, as opposed to the following regions of the recharge scheme

Differential recharge efficiency

The differential recharge efficiency (ϵ_s) is the instantaneous efficiency at a particular SOC, S, under the conditions of the experiment. It is obviously a function of the particular SOC at which it is measured. The procedure for its determination is as follows.

(i) Discharge the battery to an SOC of $(S_1 - 5)$% at I_d to voltage cut-off of V_d volts.

(ii) Recharge the battery under specified conditions of current and temperature until it reaches an SOC of $(S_1 + 5)$%, theoretically

(iii) Discharge the battery again at I_d to the same cut-off voltage V_d (theoretically 10% change in SOC or C_{120})

(iv) Compute the ratio Q_d/Q_c as above.

Integral recharge efficiency

The integrated recharge efficiency, ϵ', is the efficiency that applies over the interval between the S_1 and S_2 states-of-charge. If the difference between S_1 and S_2 is very small, then $\epsilon' = \epsilon_s$ The procedure for its determination is as follows.

(i) Discharge the battery to a known DOD

(ii) Recharge the battery under specified conditions of constant current and temperature until it is 100% SOC.

(iii) Compute the ratio Q_d/Q_c where Q_d and Q_c are the charges (coulombic) associated with the discharge and recharge portion of the test

There is a relationship between the integrated and differential efficiencies that can be deduced theoretically.

Consider a battery in a state-of-charge S_1 being recharged to a state-of-charge S_2 where S_1 and S_2 are expressed as a fraction of the total slow-rate capacity of the battery, say C_{120}. If the recharge current I_c is constant for a total time t_c, and the process is completely efficient then:

$$I_c t_c = (S_2 - S_1)C_{120} \tag{4}$$

If the average efficiency is ϵ', then:

$$\epsilon' I_c t_c = (S_2 - S_1) C_{120} \tag{5}$$

From the definitions of the two efficiencies,

$$\epsilon' = \frac{\displaystyle\int_{S_1}^{S_2} \epsilon_s \, ds}{(S_1 - S_2)} \tag{6}$$

$$\int_{S_1}^{S_2} \epsilon_s \, ds = \frac{(S_2 - S_1)^2 C_{120}}{I_c t_c} \tag{7}$$

In general, the integral $\int_{S_1}^{S_2} \epsilon_s \, ds$ is not known and depends on conditions such as rate (I_c) and temperature From measurements made using a variety of methods, and in conformance with the concept of three regions of varying efficiency, we have deduced an empirical mathematical relationship that shows $\int \epsilon_s \, ds$ as a function of S (the SOC) with the battery capacity and charge rate as variables and two recharge constants that depend on the temperature and the battery construction This relationship is

$$\epsilon_s = 1 - \exp(B(S - 1)) \tag{8}$$

where

$$B = \frac{b}{(n + c)} \tag{9}$$

and

$$n = \frac{I_c}{C_{120}} \times 120 \tag{10}$$

In the above eqns : I_c is the recharge current, b, c are recharge constants depending upon battery construction, S is the SOC expressed as a decimal Hence, in principle, using eqns. (5) and (7), the value of ϵ' can be calculated over any chosen interval of SOC $S_1 \to S_2$. Alternatively, given an initial state-of-charge, S_1, a charge current, I_c, and a time, t_c, the finally attained SOC, S_2, can be calculated by finding the value of the upper limit of the integral that makes eqn (7) true

This latter ability is particularly valuable as it is possible to estimate available battery capacity at any discharge rate and at any point in time given the previous history of time and current on both charge and discharge using eqns (7) and (1)

Effect of battery design parameters on charge acceptance

The limiting factors of charge acceptance are usually
(i) amount and type of low-temperature additives in the negative plate;
(ii) composition of the grid alloy,

(iii) total surface area of the plates;

(iv) nature of the lead sulphate covering the plates.

Low-temperature additives are present in negative plates to lower the polarization of these plates during discharge at low temperatures and, hence, make the discharge more efficient Unfortunately, unless properly purified [4] and used in an appropriate quantity relative to the battery application, the additives can exert a deleterious effect on the recharge efficiency of the cell

It is well known [5] that the presence of certain alloying elements, particularly antimony, in grids can cause the onset of gassing at voltages lower than optimal for recharging batteries. We have recently shown [6] that the gassing rate, particularly in the case of the negative grids, is not only influenced by the amount of antimony present but also by its disposition in the microstructure of the alloy. This latter factor can be controlled to some extent by modification to the casting process such that at the same potential the gassing rate is only one-third to one-half of the original. The gassing rate of a modified alloy in a positive grid is virtually unaltered It appears that the rate is determined by the PbO_2/O_2 overpotential, at least when the grids or plates are new We have evidence to show that the rate of antimony released out of the positive mass and into the electrolyte will be lowered, hence the battery should maintain its lowered on-charge gassing rate for a longer period than in the unmodified case

For a given C_{120} it is beneficial to maximise the total plate area so that the recharge *current density* is minimized This, in turn, decreases the plate polarization and, therefore, the gas losses in the 'mixed' region.

Lead sulphate crystals that are present in plates, especially in low states of charge, can cause blocking and blinding of pores and active material surfaces This gives rise to excessive on-charge polarization and poor efficiency The severity of these problems can be controlled by limiting the cycle depth, careful selection of plate additives, and prompt recharging whenever possible

Conclusions

Various recharge strategies can, and are, used in RAPS systems to obtain improvements in recharge efficiency and to reduce the amount of damage that can result from either over- or under-charging cells These strategies include current-limiting, and voltage-limiting, multiple-stage recharging, with or without temperature compensation Nevertheless, such methods can only define an envelope of 'permissible operation' for both the system and the cells in order to achieve the dual goals of recharge and minimal damage (cell life). As the availability of a recharge source in terms of current, maximum voltage, and duration is usually stochastic in nature, especially in the case of PV and wind systems, it is highly desirable to match the source and cell characteristics as closely as possible in the interests of coulombic efficiency for a given state-of-charge

Methods of measuring and calculating battery efficiency in RAPS systems can be utilized for the purposes of cell design and system management

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