Short Communication

A novel, non-destructive method for the prediction of the state-of-charge of maintenance-free lead/acid batteries from galvanostatic transients

M.P. Vinod, K. Vijayamohanan

Materials Chemistry Division, National Chemical Laboratory, Poona 411 008, India

Abstract

A direct determination of the uncompensated resistance of a porous $Pb/PbSO_4$ electrode, as promoted by variation in the state-of-charge (SOC), has been obtained by comparing the theoretical potential–time transients with experimental data. This method is non-evasive and can be useful in predicting the SOC of maintenance-free batteries.

1. Introduction

A maintenance-free lead/acid battery [1–4], as the name indicates, should be capable of long-term silent operation in a permanent location. As a consequence, qualities such as long life, stable characteristics, low self-discharge rates and high efficiency must be incorporated into the cell design. Although lead/acid batteries with immobilized electrolyte, with or without gas-recombination catalysts, have been used increasingly in maintenance-free applications, their large-scale implementation has been hindered to a certain extent by uncertainties in the determination of the state-of-charge (SOC). The SOC of a battery indicates the ratio of residual capacity at a given instant to the maximum available capacity. A sound knowledge of the SOC is especially significant for maintenance-free systems in rural applications (such as storage of solar energy) where a change in the SOC due to progressive self-discharge limits the efficacy of the system. Hence, an accurate and non-evasive method of determining the SOC is highly desirable for large-scale applications. Furthermore, a knowledge of the SOC can be extremely useful in predicting the residual capacity and, more significantly, it can help to increase the cycle life by proper control of the degree of charge and the depth-of-discharge.

The present methods for determination of the SOC [5] suffer from the following limitations. Density measurements are crude and do not reflect the SOC accurately; they can predict the SOC to only within about 10% over the useful portion of the discharge curve. In addition, the density of acid inside the pores is often drastically different to that in the bulk of the solution [6], and the use of gelled electrolytes and hermetically sealed units preclude the application of density measurements for measuring the SOC. Impedance methods require sophisticated instruments and are too complicated to apply on a routine basis. Moreover, the interpretation is ambiguous as the behaviour of porous electrodes often cannot be represented by any unique equivalent circuit of passive elements [7,8]. Conventional internal-resistance measurements using large current are proven to give inaccurate results as the pores of the electrodes have several resistive and reactive components, some of which may be time-dependent and, thereby, may cause non-stationary behaviour [8]. More importantly, a change of composition during these tests is often responsible for large errors. Lastly, the prediction of the SOC on the basis of equilibrium values of open-circuit voltage is more relevant for negative-limited cells and difficulties arise due to significant battery-to-battery variations. The preferred SOC measuring test should be fast, simple to use and should not cause any change in the fundamental parameters of

the electrochemical system, i.e., it should permit well-defined and verifiable criteria for the non-evasive aspects to be set out both at the beginning and during the test.

In this communication, a novel non-destructive method to predict the SOC of maintenance-free lead/acid batteries is derived from the galvanostatic transients in the linear polarization domain. More specifically, these transients have been analysed quantitatively by considering the charge transfer and ohmic contribution of the Pb/PbSO$_4$ reaction and the irreversible charge-transfer kinetics of the hydrogen-evolution reaction (HER). The slopes of these transients are correlated with SOC. This technique is of marked importance for evaluating the variation in SOC due to progressive self-discharge during the operation of maintenance-free batteries.

2. Experimental

The experimental details are similar to those described earlier [9]. In brief, negative-limited cells were assembled, with an excess of sulfuric acid (4.8 M) electrolyte, by placing a counter electrode (PbO$_2$) on either side of the working electrode (Pb/PbSO$_4$), along with a Hg/Hg$_2$SO$_4$, H$_2$SO$_4$ (4.8 M) reference electrode. A Luggin capillary tip was employed close to the working electrode in order to minimize the uncompensated resistance. All potentials reported in this study were measured at 25 ± 1 °C with an accuracy of ± 1 mV by connecting a buffer amplifier with unity gain and high input impedance (10^{13} Ω) between the reference and the working electrodes.

After a few initial conditioning cycles (charging at $C/10$ and discharging at $C/8$) to get stable capacity, all the cells were given the same amount of overcharge (20%), kept at open circuit for 30 min, and polarized with appropriate current densities so that the steady state could be obtained within a few minutes. This steady-state current was then interrupted and the relaxation to open-circuit potential was monitored till attainment of the original value. These experiments were repeated at various SOC values (viz., 1, 0.8, 0.5, 0.2 and 0.05) by using the same current densities. Studies were also conducted with an immobilized electrolyte that was prepared by mixing a thixotropic agent with the sulfuric acid [10,11].

3. Results and discussion

By consideration of the various electrochemical reactions that occur at a Pb/PbSO$_4$ electrode, the build-up and decay transients in the linear polarization domain can be expressed as [9,12]:

$$I = -C(dE/dt) - f(E - E_{Pb}{}^r)(\tau I_{0, Pb} + \alpha_H Q) + Q \qquad (1)$$

where E_{Pb} is the reversible potential, Q and τ are constants given by:

$$Q = I_{0, H} \exp[-\alpha_H f(E_{Pb}{}^r - E_H{}^r)] \qquad (2)$$

$$\tau = (\alpha_{Pb} + \beta_{Pb}) \qquad (3)$$

C is the double-layer capacitance, $E_H{}^r$ is the reversible potential for H$^+$/H, R_0 is the uncompensated resistance, $I_{0, Pb}$ and $I_{0, H}$ are the exchange-current densities of the lead-electrode reaction and hydrogen-evolution reactions, respectively; α_{Pb}, β_{Pb} and α_H are the apparent transfer coefficients of the associated reactions, and f is equal to nF/RT with n as the number of electrons involved in the respective rate-determining steps.

The major assumptions involved in deriving the above equations are that diffusional polarization is negligible and the magnitude of the electrode polarization is very much less than $1/f$, and both these can be satisfied by judicious selection of the accessible experimental conditions. Although, in principle, there can be a diffusional polarization contribution from the oxygen-reduction reaction (especially in maintenance-free batteries with glass-fibre separators or in a stirred cell with oxygen evolution from PbO$_2$ electrodes) this can be neglected as the exchange current is much smaller than $I_{0, Pb}$.

A lead electrode in sulfuric acid at open circuit undergoes corrosion and is usually covered by a passive film of PbSO$_4$, even at the highest SOC that is accessible experimentally. In addition, corrosion also causes gas bubbles (formed as a result of a parasitic hydrogen-evolution reaction) to become attached to the electrode surface to varying degrees that depend on the SOC and the composition of the electrolyte. These offer an ohmic resistance to an unknown extent and cannot be compensated by using a reference electrode, since the latter has to be located away from the apparent surface of the lead electrode. These two contributions, together with those from the electrolyte and separator, contribute to the total ohmic component of polarization in Eq. (1) as $E + IR_0$. This uncompensated resistance, R_0, not only causes an error in the observed electrode potential, E, but also the error cannot be corrected due to the fact that R_0 is not known.

Indirect potentiostatic feedback techniques are often proposed to compensate for R_0 by a trial-and-error method. Nevertheless, these cannot be considered reliable since positive feedback-induced oscillations make the result ambiguous. More importantly, since current is not a controlled parameter in a potentiostatic mode of operation, surge currents at least in the beginning (close to a ms) could alter the composition and R_0 of the surface layer. A formal correction for the potential drop across the uncompensated resistance may be introduced into Eq. (1) by replacing E with $E + IR_0$.

Hence,

$$I = -Cd(E + IR_0)/dt$$

$$-f(E - E_{Pb}{}^r + IR_0)(\tau I_{0, Pb} + \alpha_H Q) + Q \tag{4}$$

For porous battery electrodes, R_0 can be considered as a function of the SOC. The value increases continuously with the ohmic resistance of accumulated $PbSO_4$ in the pores. In several practical systems, this is known to limit the discharge behaviour of battery electrodes [13]. Quantitative models based on pore-plugging confirm the crucial role of this parameter for high-rate applications [14]. This is especially important with immobilized systems for maintenance-free applications in which a key parameter to be optimized is the ohmic drop due to the SOC variation as a result of self-discharge. Assuming R_0 is not a function of potential, potential–time transients for a given SOC can be written as:

$$I = -C/(1 + KR_0)(dE/dt)$$

$$-K(E - E_{Pb}{}^r)/(1 + KR_0) + Q/(1 + KR_0) \tag{5}$$

where K is a constant given by $f(\tau I_{0, Pb} + \alpha_H Q)$. During the build-up and subsequent decay of polarization on open circuit, $I = 0$, therefore:

$$-C/(1 + KR_0)(dE'/dt)$$

$$-K(E' - E_{Pb}{}^r)/(1 + KR_0) + Q/(1 + KR_0) = 0 \tag{6}$$

the prime (') indicates, for clarity, the quantity measured under open-circuit conditions. In the absence of concentration polarization, the faradaic current I in Eqs. (5) and (6) depends only on the electrode potential with every given instant of time; similarly the double-layer capacitance C depends only on the electrode potential prevailing at the given instant. Let a particular value of electrode potential, E^*, be chosen on both the build-up and decay transients, then:

$$I^* = -C(E^*)/(1 + KR_0)(dE/dt)_E.$$

$$-K(E - E_{Pb}{}^r)/(1 + KR_0) + Q/(1 + KR_0) \tag{7}$$

$$-C(E^*)/(1 + KR_0)(dE'/dt)_E.$$

$$-K(E' - E_{Pb}{}^r)/(1 + KR_0) + Q/(1 + KR_0) = 0 \tag{8}$$

These equations may be solved to get $C/(1 + KR_0)$ values; R_0 can be calculated by using the slopes and intercepts of the dE/dt plot against $E - E_{Pb}{}^r$ at various C values and the reported values of $I_{0, H}$ and $I_{0, Pb}$ on a porous lead electrode [15]. The validity of these equations has been confirmed earlier by the expected linear plots at both high and low SOC values [9].

Typical potential–time transients at SOC = 0.8 are shown in Figs. 1 and 2 for gelled and non-gelled electrolytes, respectively. The potential tends to reach the steady-state value asymptotically with time. The
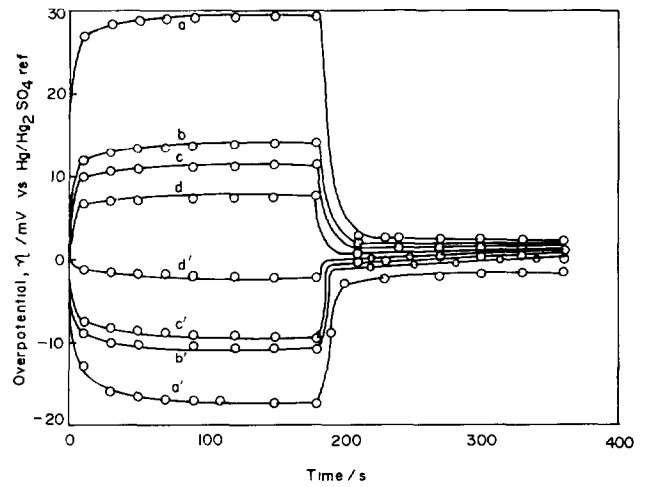

Fig. 1. Galvanostatic potential–time transients at various current densities for non-gelled electrolyte at SOC = 0.8; (a), (b), (c) and (d) correspond to anodic and (a'), (b'), (c') and (d') to cathodic currents at 60, 45, 30 and 15 μA cm^{-2}.
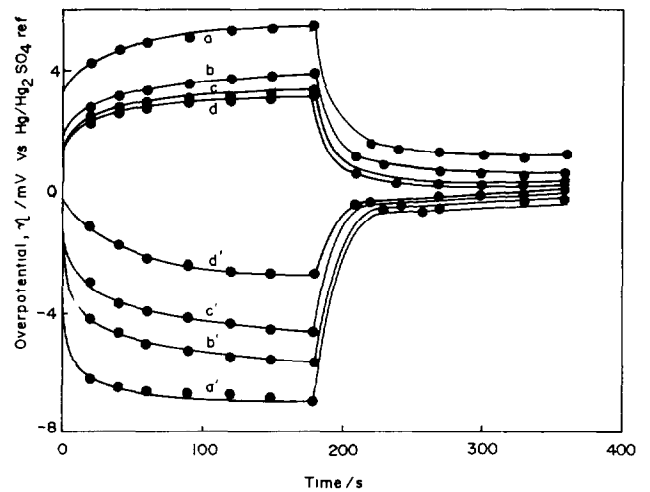

Fig. 2 Galvanostatic potential–time transients at various current densities for gelled electrolyte at SOC = 0.8; (a), (b), (c) and (d) correspond to anodic and (a'), (b'), (c') and (d') to cathodic currents at 60, 45, 30 and 15 μA cm^{-2}.

latter increases with increase in the deviation from equilibrium. In addition, the build-up and decay patterns are much steeper for the gelled electrolyte. This may be attributed to the increased hindrance of mass transfer that is caused by the presence of an interpenetrating network of polysilicic acid gel. Although Figs. 1 and 2 are only representative examples, both these trends are fairly general for potential–time transients taken at all other SOC values.

Figs. 3 and 4 show the uncompensated resistance versus SOC curves derived from the data for prior anodic and cathodic potential–time transients (Figs. 1 and 2), respectively. For the purpose of comparison, values for immobilized electrolyte are also included. The variation of R_0 generally reflects the change in the concentration of the electrolyte with SOC and/or the accompanying change in the ohmic resistance of the
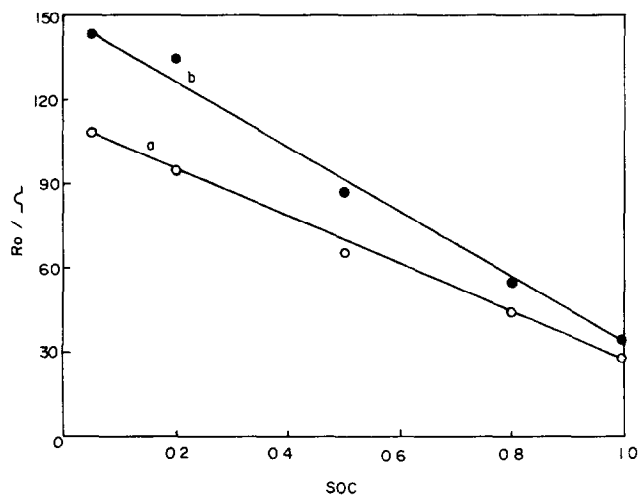
Fig. 3. Variation of R_0 with SOC derived from data of a prior anodic polarization: (a) non-gelled electrolyte, and (b) immobilized electrolyte.
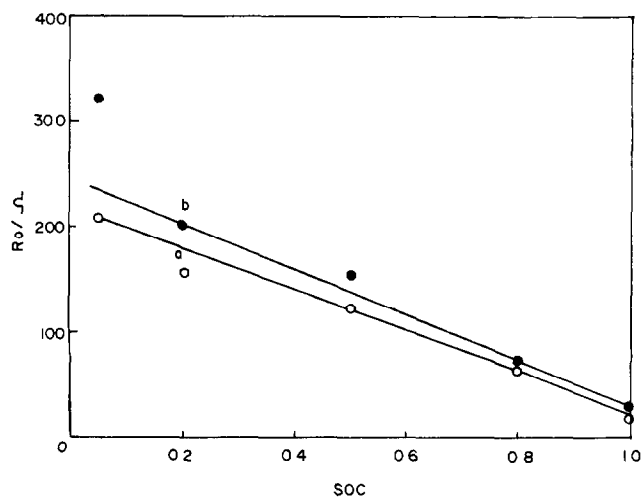

Fig 4 Variation of R_0 with SOC derived from the data of a prior cathodic polarization: (a) non-gelled electrolyte, and (b) immobilized electrolyte.

active materials. In sharp contrast with the cathodic case, the anodic case shows a large variation at extremely low SOC values since the amount of insoluble $PbSO_4$ that is accumulated in the pores of the electrode is large. As the SOC increases, the density of acid in the pores increases and, consequently, the resistance decreases. This explanation may be further supported by the enhanced effect in immobilized electrolyte. In addition, similar behaviour is generally observed for the variation of acid density with SOC [16].

Linearity over a range of SOC values from 0.2 to 0.8 confirms that the above resistance is actually the ohmic part of the internal resistance and has no contribution from the charge-transfer component, R_{ct}, as shown by the separation of the two terms in Eq. (5). Furthermore, the variation of charge-transfer resistance with SOC can be appreciated from the relation with

the exchange current, viz., $R_{ct} = RT/nFI_{0,\,Pb}$. As $I_{0,\,Pb}$ is proportional to $C_0^{1-\alpha}$ and C_R^{α}, where C_0 and C_R refer to the concentrations of active materials[1], the SOC can be considered to be non-linear with respect to charge-transfer resistance. More specifically, an approximate functional dependence of the form

$$R_{ct} \propto \frac{1}{SOC(1\text{-}SOC)^{1/2}}$$

can be obtained from the additional assumption of α being 0.5.

One of the significant features of the above data is that the variation of the uncompensated resistance is almost linear with SOC, especially if the latter is not very small. Thus, the method can be used to measure the SOC of lead/acid batteries by simply measuring the uncompensated resistance. The prediction of SOC is generally considered as one of the basic requirements for large-scale applications of maintenance-free lead/acid batteries. As a design implication, it can be seen that the rapid fall of R_0 at a low SOC in the anodic case is more important for normal operation, namely discharge. Improvement of this design aspect is very useful, especially for pulsed and high-rate applications.

4. Conclusion

The present study demonstrates that there is a systematic variation of the galvanostatic transient pattern with SOC of maintenance-free lead/acid batteries. A quantitative analysis of this phenomenon provides a useful non-destructive method for the determination of the SOC of maintenance-free lead/acid batteries. The technique is especially significant for immobilized or hermetically sealed systems.

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