

# Modelling and simulation of lead-acid battery charging

Henry A. Catherino <sup>a,\*</sup>, Joseph F. Burgel <sup>a</sup>, Andrew Rusek <sup>b</sup>, Fred Feres <sup>c</sup>

<sup>a</sup> US Army Tank, Automotive and Armaments Command, Warren, MI 48397-5000, USA

<sup>b</sup> Electrical and Systems Engineering Department, Oakland University, Rochester, MI 48063, USA

<sup>c</sup> Exide Corporation, 2750 Auburn Road, Auburn Hills, MI 48321-4410, USA

Received 8 November 1998; accepted 19 November 1998

## Abstract

The renewed interest by the US Army in lead-acid SLI battery charging was spurred by the recent shift to Army-wide use of ‘maintenance free’ batteries. Although the use of calcium-grid construction reduces the need for periodic water additions, using battery maintainers for extended float charging may cause an even greater problem. By charging at constant voltage, the batteries can slowly lose water if the charging is performed in the absence of suitable temperature compensation. This uncontrolled water loss is of particular significance in those batteries that do not permit access to the electrolyte. In this study, charging curves measured at constant current were obtained over a range of temperatures. The curves were modelled analytically by combining the individual effects of battery charging and gassing. The modelled results were compared with the actual measurements. The model is given as a semi-empirical equation in closed form. With this equation, the response surface is displayed graphically to visualize the effect of changes in critical variables. The results of the investigation will help determine the best charging conditions for the regular and float charging modes in order to deliver the maximum charge without excessive gassing. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lead-acid batteries; Maintenance free; Mathematical modelling; Charging techniques

## 1. Introduction

The change to use of maintenance-free lead acid batteries by the US Army has revitalized an interest in the gas evolution taking place in these batteries. The maintenance requirements associated with these ‘maintenance-free’ batteries have raised a number of questions especially at their operational temperature extremes. The objective of this paper is to model the charging process together with the overcharging associated with gassing. One of the goals of this study was to observe the convergence of the gassing curve with the charging process. In this way, we sought to analytically examine the data to show the effect of elevated temperatures on the convergence of the two processes. The modelling and simulation showed that this hypothesis was essentially incorrect. However, it resulted in a better phenomenological understanding of the underlying effects.

The analytical approach described here is of a general nature and can be applied to batteries other than those of the lead-acid flavor.

## 2. The model

The model of the charging of a lead-acid battery that includes over-charging or gas generation can be established in the following manner. The equation for the charging of a discharged battery can be approximated in the semi-empirical form:

$$E = a + b \ln \frac{Q - it}{it} \quad (1)$$

$Q$  is the capacity of the battery,  $it$  is the charge passed to the battery and  $a$  and  $b$  are empirically determined constants. This general form is that of the Nernst Equation without assigning the theoretical quantities to the constants.

The effect of gassing can be superimposed by adding a component that simulates the gassing process. In this case, a form of the Tafel equation will be used.

$$E = c + d \ln i \quad (2)$$

The constants  $c$  and  $d$  shall remain as empirical constants.

Both the Nernst and the Tafel equations have substantial theoretical support [1]. They have been used here as a means for fitting the observed data and, at the same time,

\* Corresponding author

for generating values of the constants for other studies.

Since the gassing and the charging are coupled, the sum of the two individual components can be set equal to the total applied current ( $I$ ):

$$I = i(\text{charging}) + i(\text{gassing}) \quad (3)$$

For the purposes of this model, the charging shall be defined as taking place at constant current. The first tendency is to solve Eqs. (1)–(3) simultaneously for  $E$  as a function of  $t$ . This approach is clumsy because the solution does not appear in closed form. It is possible to solve these equations iteratively but the process is numerically tedious. A better approach is to solve the equation using  $t$  as the dependent variable. Then a closed form solution results.

$$t = \frac{Q}{\left(I - \exp\left[\frac{E-c}{d}\right]\right)\left(1 + \exp\left[\frac{E-a}{b}\right]\right)} \quad (4)$$

This is a better form because it makes the computer simulations far more efficient.

### 3. Fitting data to the model

As a first step, the constants  $a$  and  $b$  can be estimated as a first approximation from the foot of the  $E$  vs.  $t$  charging curve where  $Q \gg it$ . These values serve as a seed for the iterations that follow. Having estimated  $a$ ,  $b$ , and  $Q$ ,  $c$  and  $d$  can be obtained using regression techniques. This is not particularly easy to see at this point. To do this, one needs to solve explicitly for either  $c$  or  $d$ . For example, solving Eq. (4) for  $c$  gives:

$$c = -\ln\left(\frac{-Q + It + It \exp\left(\frac{E-a}{b}\right)}{t\left(1 + \exp\left(\frac{E-a}{b}\right)\right)}\right)d + E \quad (5)$$

This equation is in the form:

$$c = dx + y \quad (6)$$

where  $y$  is  $E$  and  $x$  is computed from the previously obtained values of  $a$ ,  $b$ ,  $E$  and  $Q$ . So solving for  $y$ :

$$y = -dx + c \quad (7)$$

The values of  $c$  and  $d$  can be obtained using a simple linear regression of data taken from  $E$  vs.  $t$  data from constant current charging.

As an additional iterative step to ensure goodness of fit,  $a$  and  $b$  can be re-estimated using data from the entire charging curve using the same technique. This refines the estimate because the earlier estimate used only the foot of the charging curve. The domain of the available data is

now significantly larger. That is, since  $c$  and  $d$  have been estimated,  $a$  and  $b$  can be re-estimated because:

$$a = -\ln\left(-\frac{-Q + It - t \exp\left(-\frac{E-c}{d}\right)}{t\left(I - \exp\left(\frac{E-c}{d}\right)\right)}\right)b + E \quad (8)$$

In the same manner described above,  $a$  and  $b$  are estimated by regression techniques. The processes can be repeated to watch convergence. Usually, a single iteration is sufficient.

### 4. Experimental

A set of experiments was performed to determine the constants required for the simulation. Four military-grade batteries were used. Two, designated as 6TL, and two, designated as 6TLFP were used. The former batteries are a mixed calcium-alloy (the negative grid) and 2.5% anti-mimony-alloy grid (the positive grid) design known as ‘reduced-maintenance’ batteries. The latter use all calcium-alloy grids and are popularly designated as ‘maintenance-free’ batteries. The batteries were put into a repeated cycling protocol involving: (1) a charged stand, (2) a constant current 25 A discharge to 10.5 V, (3) a constant current charge at 4 A to approximately 130% of its capacity, (4) a constant current discharge at 25 A to 10.5 V, (5) a constant current charge at 8 A to approximately 130% of its capacity, and (6) a return to is charge stand condition. This sequence was repeated at 150°F (65.6°C), 130°F (54.4°C), 110°F (43.3°C), 90.0°F (32.2°C), 70.0°F (21.1°C), 40.0°F (4.4°C), 20.0°F (−6.7°C), 0.0°F (17.8°C), −20.0°F (−28.9°C) and −40.0°F (−40.0°C). The data was acquired using a computer-controlled data acquisition system. This same computer controlled the operation of a battery cycling system in concert with an environmental chamber. Distilled water was added as needed to keep the battery plates submerged in the electrolyte.

### 5. Discussion

Although the collected data was rather extensive, a comparison of the measured data with the model is shown in Fig. 1. The plot shows the consequence of charging a lead-acid battery into overcharge such that it is gassing freely.

The axes are reversed for the sake of convenience, so the independent variable is shown on the ordinate axis.

By regressing the constants as a function of temperature and charging current, a response surface (shown in Fig. 2) was generated in 3D showing the composite relationships between ampere-hours of charge as a function of temperature in degrees Fahrenheit and of battery voltage. The surface shows the charging step followed by the develop-

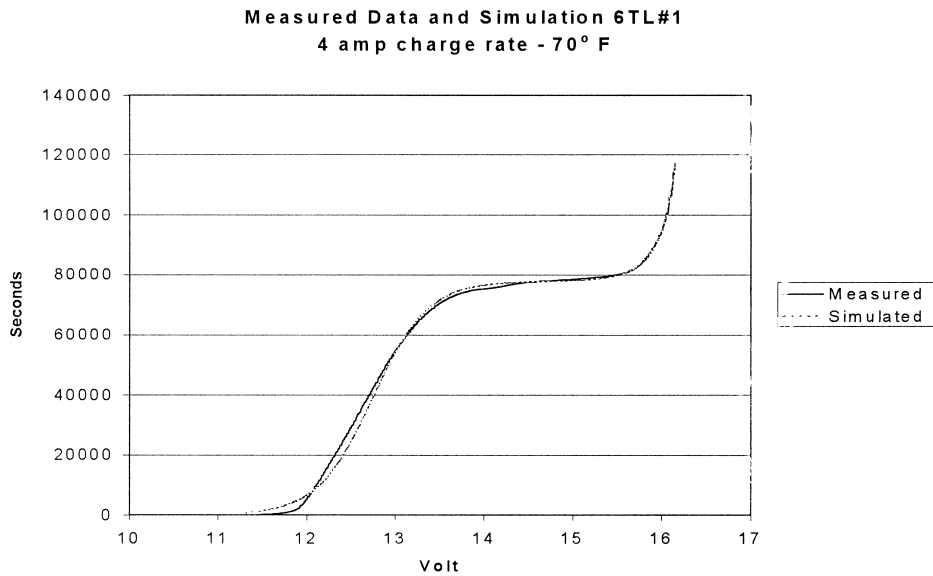


Fig. 1. Simulation compared to actual data.

ment of the gassing process. The gas evolution process tries to converge with the charging process at higher temperatures. However, a clearly developed plateau remains, isolating the two processes.

The simulation provided the Tafel parameters for the gas evolution process. A knowledge of these parameters allows an estimation of the gassing contribution associated with the gas evolution process at any particular applied voltage. For example, at 150°F (65.6°C), the steady state gas evolution rate at 14.25 V is equivalent to 0.5 mA for a 6TLFP battery. An attempt to directly verify this under the same environmental conditions showed that the steady state charging current was about 0.5 A. That is, it was

three orders of magnitude larger than predicted from the normal gassing process. This was an unexpected outcome.

As a check, a fully charged battery was subjected to a 150°F environment with an applied voltage set at 14.25. The integrated  $i-t$  curve (the applied charge) corresponded within experimental error to the stoichiometric decrease in the battery mass. The calculated mass loss assumed the electrolysis of water. The mass loss was then recovered by adding water to the battery.

The original objective of the study was not achieved. Initially, the gassing process was anticipated to converge with the charging process and this did not occur. However, the actual gassing does occur but in excess of that ex-

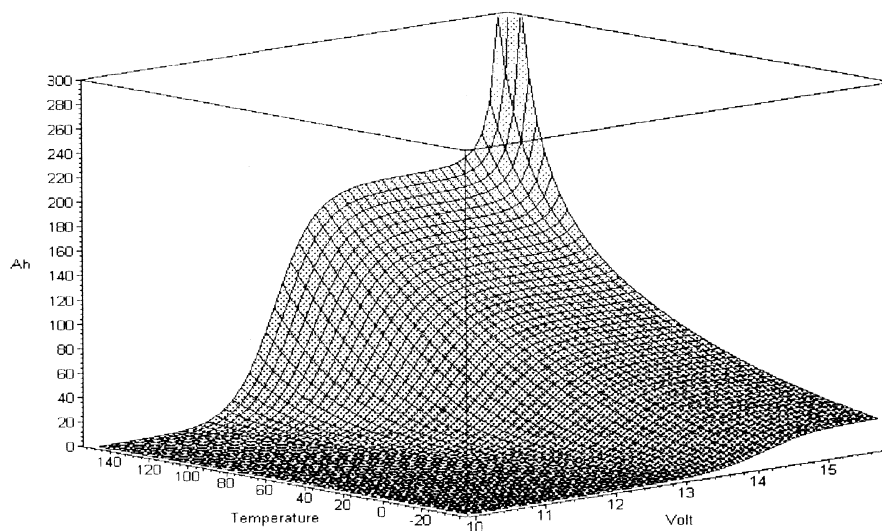


Fig. 2. Simulated response of a 6TLFP battery to constant current charging at 4 A.

pected from the normal gas evolution process at the electrode surface. This leads one to formulate the hypothesis that the prevailing gas evolution process is of a kinetic nature and quite independent of the 'normal' gas evolution process that is characteristic of the electrode system. The inference is that the kinetic gas evolution process is being catalyzed by contaminants naturally occurring in the system. In fact, this behaviour is well known and considerable data exists consistent with this view. An early review of this was presented by Vinal [2]. This constant voltage electrolysis has been the matter of considerable study by battery manufacturers.

Considerable data has been collected by Exide on the dependence of the steady state current and the actual gas evolved as a function of temperature and applied voltage for lead acid batteries during overcharge. This data reveals the functional dependence of these parameters. An examination of this data revealed that the results could be correlated by noting that the observed current fit the linear model:

$$\ln I = a + bE + cT + d[\%Sb] \quad (9)$$

The domains of the independent variables were as follows: for  $E$ —[13.2, 15.60], for  $T$ —[32°F (0°C), 140°F(60°C)] and for %Sb—the alloy composition—[0, 2.6%].

An important inference that stands out as the result of this study is that an extremely low self-discharge rate for

lead-acid batteries is a distinct possibility. This is consistent with the observations of battery manufacturers who produce lead-acid batteries under highly controlled conditions.

## 6. Conclusions

(1) A general method for modelling the constant current charging curve of a battery was developed. Although the model was applied to the lead-acid battery in particular, the model appears to be generally applicable to other electrochemical systems.

(2) The gas evolution process occurring at a constant applied voltage appears as a kinetically controlled gas evolution step. It is independent of the normally occurring gas evolution process on the electrode surface appearing at higher voltages.

(3) The kinetic gassing process appears to behave in accordance with the form:

$$I = d' \exp(bT) \exp(cE) \exp(d[\%Sb]) \quad (10)$$

within the domains of  $t$ ,  $E$  and %Sb that were studied.

## References

- [1] K.J. Vetter, *Electrochemical Kinetics*, Academic Press, 1967.
- [2] G.W. Vinal, *Storage Batteries*, Wiley, 1965.