

THE INFLUENCE OF TEMPERATURE ON THE DISCHARGE CAPACITY OF POSITIVE LEAD-ACID BATTERY PLATES. THEORY AND EXPERIMENTS

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Summary

A theoretical expression has been derived for the dependence of the discharge capacity, C , of the positive plate of the lead-acid battery, on the temperature, T , in the form

$$\ln C/dT = (k - 1)(\ln \kappa /dT + 1/T),$$

where k is the coefficient of Peukert's equation and κ is the specific conductivity of the electrolyte. This formula was confirmed by measurements on SLI battery positive plates.

List of symbols

a_{\pm}	Mean molal activity of H_2SO_4 (mol/kg)
A	Geometric surface area of both sides of positive plate (cm^2)
c_a^*	Bulk concentration of H_2SO_4 (mol/cm^3)
C	Discharge capacity (A h)
d	Half-thickness of positive plate (cm)
D_1, D_2	Diffusion coefficients of H_3^+ and HSO_4^- ions in the pores
D_{10}, D_{20}	Values of D_1 and D_2 at a reference concentration
f_p	Tortuosity factor of electrode pores
F	Faraday's constant, 96 487 C/mol
i_0	Exchange current density for reduction of PbO_2 (A/cm^2)
I	Discharge current density (A/cm^2)
I/I_a	Criterion defined as $dI/c_a^*(D_{10} + D_{20})F$
I_0/I_a	Criterion defined as $d^2i_0S/c_a^*(D_{10} + D_{20})F$
k	Coefficient of Peukert's equation
K	Criterion defined as $c_a^*(V_4 - V_3)$
S	Specific surface area of positive plate (cm^2/cm^3)

t	Time from the beginning of discharge (s)
t_d	Discharge time (s)
t_1^0	Transference number of H^+ ions
T	Absolute temperature (K)
V_3, V_4	Molar volumes of PbO_2 and $PbSO_4$, respectively (cm^3/mol)
γ_{\pm}	Mean molal activity coefficient of H_2SO_4
ϑ	Temperature ($^{\circ}C$)
κ	Electrolytic conductivity ($\Omega^{-1} cm^{-1}$)
τ	Dimensionless time equal to $t(D_{10} + D_{20})/2d^2$
τ_d	Dimensionless discharge time equal to $t_d(D_{10} + D_{20})/2d^2$

Introduction

As far as we are aware, no theoretical formula for the dependence of the discharge capacity of the lead-acid battery has been given in the literature. This dependence is experimentally well known, and the question is whether the drop in the discharge capacity at low temperatures is due only to the decreasing conductivity of the electrolyte or whether there are any other causes of this behaviour. The answer can be relatively simply derived from the theory of the lead-acid accumulator developed earlier [1], as will be shown below.

Theory

We shall consider the positive plate, since it frequently limits the discharge capacity of the lead-acid battery. The basic equations describing its behaviour [1] depend on four auxiliary functions $\psi_i(u)$ ($i = 1 - 4$), and three criteria, I_0/I_d , I/I_d , and K . If the temperature changes, all these functions and criteria will also change, but to a different extent. We shall consider these changes in turn.

The auxiliary functions $\psi_i(u)$ involve the transference number, t_1^0 , of hydrogen ions, the mean molal activity, a_{\pm} , of H_2SO_4 , and the diffusion coefficients of hydrogen ions, D_1 , and HSO_4^- ions, D_2 , divided by their sum at an arbitrarily chosen reference concentration, $D_{10} + D_{20}$. The dependence of t_1^0 on the temperature is negligible, the mean value of $t_1^0(25^{\circ}C)/t_1^0(0^{\circ}C)$ in the interval 0.05 - 5.0 mol/kg being 0.973 ± 0.006 [2]. From the mean molal activity coefficient, γ_{\pm} , data of Gardner and coworkers [3] it follows that $\gamma_{\pm}(25^{\circ}C)/\gamma_{\pm}(0^{\circ}C) = 0.778 \pm 0.040$ in the interval 0.1 - 5.0 mol/kg; and since the auxiliary functions involve the logarithmic derivative of γ_{\pm} with respect to concentration, it is obvious that the change of this quantity with temperature can be neglected. It is also obvious that the ratios $D_1/(D_{10} + D_{20})$ and $D_2/(D_{10} + D_{20})$ involved in the auxiliary functions are insensitive to temperature changes, especially if the reference concentration corresponding to D_{10} and D_{20} is chosen close to the actual concentration of the electrolyte, i.e., about 5 mol/dm³.

Thus, the solution of the differential equations describing the processes in the positive plate depends on the temperature only through the above mentioned criteria I_0/I_d and I/I_d (since K is a constant related to the bulk concentration of H_2SO_4 and the molar volumes of PbO_2 and $PbSO_4$). The former, which is proportional to the exchange current density, has been shown to influence only the calculated polarization of the electrode [4], and this only slightly. The latter criterion is defined as

$$I/I_d = dI/c_a^*(D_{10} + D_{20})F, \quad (1)$$

and it determines the course of the calculated characteristics in dimensionless coordinates; d denotes plate thickness $\times 0.5$ (cm), c_a^* the bulk concentration of the acid (mol/cm³), and F is Faraday's constant (96 487 C/mol). The dimensionless time is defined as

$$\tau = t(D_{10} + D_{20})/2d^2, \quad (2)$$

where t (s) denotes time from the beginning of the discharge. The value of t at the end of the discharge will be denoted as t_d . Both theory [1] and experiments lead to the following approximate relation between I and t_d :

$$t_d = \text{const.} |I|^{-k}, \quad (3)$$

which is known as Peukert's equation.

The dependence of the discharge capacity, C , on the temperature can now be derived as follows: Assuming that all the quantities in eqns. (1) - (3) are known for a given lead-acid cell at 20 °C, we want to determine the discharge time $t_d(\vartheta)$ corresponding to another temperature, ϑ . As mentioned above, the calculated characteristics depend under these conditions only on the parameter I/I_d . A change in temperature results in a change in the diffusion coefficients D_{10} and D_{20} . If we now replace the current density I by another one, I' , so that

$$I/(D_{10} + D_{20}) = I'/[D_{10}(\vartheta) + D_{20}(\vartheta)], \quad (4)$$

then the criterion I/I_d and the calculated characteristics together with eqn. (3) remain the same, hence, also the dimensionless discharge time, τ_d , remains the same:

$$\tau_d = t_d(D_{10} + D_{20})/2d^2 = t'_d [D_{10}(\vartheta) + D_{20}(\vartheta)]/2d^2. \quad (5)$$

Here t'_d is the discharge time corresponding to the current density I' and the temperature ϑ . However, we want to know the discharge time $t_d(\vartheta)$ corresponding to the original current density I and temperature ϑ : Equation (3) gives

$$t'_d |I'|^k = t_d(\vartheta) |I|^k = \text{const.} \quad (6)$$

By eliminating t'_d and I' from eqns. (4) - (6), we obtain for the discharge capacity, $C(I, \vartheta) = |I|t_d(\vartheta)A$, where A is the geometric surface area of the plate (both sides), the expression

$$C(I, \vartheta) = C(I) \left(\frac{D_{10}(\vartheta) + D_{20}(\vartheta)}{D_{10} + D_{20}} \right)^{k-1} \quad (7)$$

where $C(I) = |I|t_d A$ is the capacity at the chosen reference temperature, 20 °C.

The diffusion coefficients D_i and D_{i0} ($i = 1, 2$) can be calculated [5] as $RTt_i^0 \kappa / c_a F^2 f_p$, where t_i^0 denotes the transference number of the i -th ion, κ the electrolytic conductivity, and f_p the tortuosity factor of electrode pores. Hence, eqn. (7) gives the final formula

$$C(I, T) = C(I) \left(\frac{T \kappa(T)}{T_0 \kappa(T_0)} \right)^{k-1}, \quad (8)$$

where $T_0 = 293.15$ K (the reference temperature) and $T = \vartheta + 273.15$ K. Accordingly, the temperature coefficient of the discharge capacity is given as

$$\frac{d \ln C}{dT} = (k - 1) \left(\frac{d \ln \kappa}{dT} + \frac{1}{T} \right). \quad (9)$$

We will consider a positive plate which is discharged in an excess of sulphuric acid solution of 1.28 g/cm³ density (37% H₂SO₄). The temperature dependence of the conductivity of 35% H₂SO₄ can be expressed [6] as

$$\kappa = \kappa_0 (1 + 0.0250\vartheta - 0.0000193\vartheta^2) \quad (10)$$

for $0 \leq \vartheta \leq 70$ °C. Values of κ at temperatures from 0 to -50 °C were tabulated by Gerzhberg *et al.* [7]; their data for 35.3% H₂SO₄ (except for the value at 0 °C, 0.4781 Ω⁻¹ cm⁻¹, which is obviously too low) can be expressed by the following regression polynomial:

$$\kappa = 0.4953(1 + 0.02539\vartheta + 0.0001638\vartheta^2) \quad (11)$$

for $-2 \geq \vartheta \geq -50$ °C (standard deviation 0.0038). In the range $0 \geq \vartheta \geq -50$ °C, this polynomial fits, within several percent, the diagram published by Garrett and Woodruff [8].

Calculated values of $d \ln \kappa / dT$ and $d \ln C / dT$ are given in Table 1, where the theoretical value of $k = 1.547$, calculated for the positive plate [1], was used. It is seen that the temperature coefficient of capacity increases markedly with decreasing temperature.

Experimental

To check the theory, experiments were undertaken on commercial dry charged positive plates of dimensions 14.3 × 12.6 cm, thickness 0.2 cm, and nominal capacity 12.5 A h (at 20 h discharge rate). They were assembled in cells consisting of two negative plates and one positive plate in an excess of electrolyte (about 37% H₂SO₄ of 1.28 g/cm³ density). After soaking with the electrolyte for 2 h, they were subjected to four cycles (charging at 1.25 A, discharge at 0.625 A) to develop their full capacity. Finally, the cells were

TABLE 1

The temperature coefficients of the conductivity of 35% H₂SO₄ and of the discharge capacity according to eqn. (9); κ according to eqns. (10) and (11)

ϑ (°C)	κ	κT	$d \ln \kappa / dT$	$d \ln C / dT$
50	1.0905	352.4	0.0105	0.0074
40	0.9753	305.4	0.0119	0.0083
30	0.8582	260.2	0.0138	0.0094
20	0.7391	216.7	0.0162	0.0107
10	0.6182	175.0	0.0197	0.0127
0	0.4953	135.3	0.0250	0.0157
-10	0.3777	99.4	0.0290	0.0179
-20	0.2762	69.9	0.0338	0.0206
-30	0.1910	46.5	0.0403	0.0243
-40	0.1221	28.5	0.0498	0.0296
-50	0.0693	15.5	0.0644	0.0377

brought to different temperatures in a refrigerator or a water bath (-20, -10, 0, 20, and 40 °C) and their discharge capacities were measured at a current density of 20 mA/cm² (7.7 A per plate). The cell voltage and the potential of the positive electrode against a calomel reference electrode were measured and plotted against time to give the discharge $E-t$ curves. The discharge time was defined by the attainment of the final cell voltage of 1.7 V. The value of C was expressed in A h/kg of dry, charged active mass, whose average quantity was 120.6 ± 1.9 g per plate. Each measurement was repeated with two different plates, and a mean value of the capacity was taken which differed from the experimental values by only 1 - 2 percent.

Results and discussion

According to eqn. (8), a plot of $\log C$ against $\log(T\kappa)$ should give a straight line with a slope equal to $k - 1$. This is actually the case, as seen from Fig. 1; the experimental points were fitted to a regression line corresponding to the equation

$$\log C = 0.5026 \log(T\kappa) + 0.7079 \quad (12)$$

(coefficient of determination $r^2 = 0.9844$), whence $k = 1.5026$. The theoretical value was calculated [1] as $k = 1.547$, whereas the value fitting the experimental dependence of the discharge time on current density in ref. 1 is 1.276. Since eqn. (8) is only approximate, the agreement with experiments can be considered as satisfactory.

Figure 2 was derived from the dependence of the capacity on the temperature published by Bode [9]. These data were obtained with a commercial type 100 A h battery, where our assumption of a constant electrolyte concentration during discharge does not apply. However, at high discharge

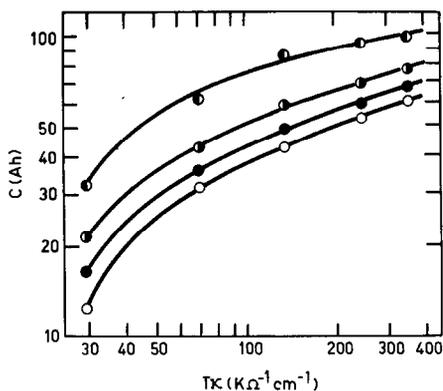
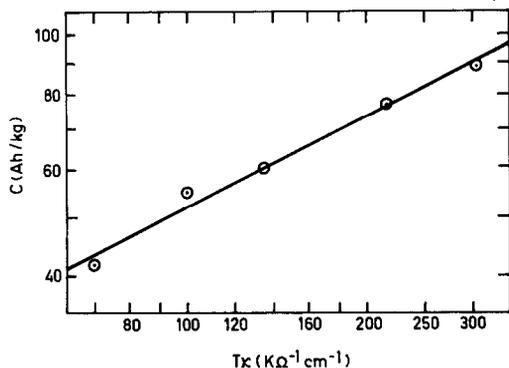


Fig. 1. Dependence of the discharge capacity C (A h/kg) of the positive plate on the product of absolute temperature and conductivity, Tk ($K \cdot \Omega^{-1} \text{ cm}^{-1}$) in logarithmic coordinates.

Fig. 2. Dependence of the discharge capacity C (A h) of a lead-acid battery on the product of absolute temperature and conductivity Tk ($K \cdot \Omega^{-1} \text{ cm}^{-1}$) in logarithmic coordinates. Data for a 100 A h battery at discharge currents of \bullet , 20 A; \circ , 100 A; \ominus , 200 A; \odot , 300 A. Data from Bode [9].

rates the concentration of the electrolyte between the plates changes relatively little [4], hence the curve corresponding to the highest discharge current (300 A) should be in reasonable agreement with the theory, eqn. (8). The point at the extreme left corresponds to a temperature of -40°C , and it can be assumed that at such a low temperature the cell capacity is no longer limited by the positive plates, but rather by the negative plates. The four remaining points correspond to temperatures of -20 , 0 , 27 , and 50°C ; the respective capacities are 31.3, 43.2, 53.5, and 60.9 A h. These can be fitted by a regression line given as

$$\log C = 0.408 \log(Tk) + 0.751, \quad (13)$$

which is close to eqn. (12). If the curves corresponding to 200 and 100 A discharge currents are treated analogously (the points at -40°C being omitted), the slopes of the regression lines are 0.385 and 0.359 (additive constants 0.857 and 0.984), respectively. With decreasing discharge rate, the concentration changes of the acid between the plates become more pronounced [4] so that the curve for 20 A in Fig. 2 shows the greatest deviation from a straight line.

To determine the temperature coefficient of the capacity at 300 A discharge current from the four mentioned points, values of $\ln C$ were fitted with a third-order interpolation polynomial, which was differentiated to give $d \ln C / dT$ equal to 0.0055, 0.0064, 0.0116, and 0.0213 at 40, 20, 0, and -20°C , respectively. This compares well with the data in Table 1. Thus, the experimental results of Bode [9] are in reasonable agreement with the theoretical expectation.

According to the International Electrochemical Commission [9], the dependence of the capacity on the temperature can, in a limited interval, be expressed as

$$C(\vartheta) = C(\vartheta_0)[1 + 0.008(\vartheta - \vartheta_0)], \quad (14)$$

where $\vartheta_0 = 30^\circ\text{C}$. From this formula we obtain $\text{dln}C/\text{d}\vartheta = \text{dln}C/\text{d}T = 0.008$, in good agreement with the theoretical value (Table 1) of 0.0094 at 30°C .

Further tests over a wide range of discharge currents are being carried out and the results of these tests will be published later.

Conclusions

The theory of the positive plate of the lead–acid battery [1] and the assumption that the diffusion coefficient of sulphuric acid is proportional to Tk are, of course, approximate. Hence, eqn. (8) is also approximate. Nevertheless, we feel that for the first time the dependence of the discharge capacity of the positive plate of the lead–acid cell has been theoretically elucidated.

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