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AN ENGINEERING ANALYSIS OF THERMAL PHENOMENA
FOR LEAD-ACID BATTERIES
DURING RECHARGE PROCESSES

by

K. W. Choi and N. P. Yao

MASTER

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Chemical Engineering Division

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NOMENCLATURE

$\hat{C}$	Average specific heat of battery (J/g-K)	$T_{\max}$	Maximum temperature in the battery (K)
C_e	Specific heat of electrolyte (J/g-K)	T^*	Dimensionless temperature $(T - T_0)/T_0$
$\hat{C}_s$	Specific heat of electrode (J/g-K)	U	Velocity of electrolyte in y-direction (cm/sec)
F	Faraday's constant (96479 C/equiv.)	U_0	Circulation velocity of electrolyte (cm/sec)
f	Internal heat production as a function of cell potential, heats of reaction, current density and current efficiency (J/cm ² -sec)	v^*	Dimensionless velocity (U/U_0)
G	Internal heat production per degree Kelvin due to the contribution of current density, current efficiency and specific heats (J/cm ³ -sec-K)	V	Cell potential (volt)
h	Convective heat-transfer coefficient on the battery container surface (J/cm ² -sec-K)	V_r	Volume of reservoir in the battery per unit length (cm ³ /cm)
ΔH_j	Heat of reaction for reaction j (J/mol)	$\bar{V}_i$	Partial molar volume of species i (cm ³ /mol)
i	Apparent current density on the electrode surface (A/cm ²)	W_t	The combined thickness of positive electrode, separator, and negative electrode, (cm)
j	Faradaic current density in the porous electrode (A/cm ²)	W	Dimensionless rate of heat generated, $\dot{q}/k(T_0 - T_c)$
k	Average thermal conductivity of battery (W/cm-K)	x	Distance in x-direction (cm)
k_e	Thermal conductivity of electrolyte (W/cm-K)	x^*	Dimensionless distance in x-direction, x/L_x
k_s	Thermal conductivity of electrode (W/cm-K)	y	Distance in y-direction (cm)
K_e	Electrical conductivity of electrolyte (mho/cm)	y^*	Dimensionless distance in y-direction, y/L_y
K_s	Electrical conductivity of electrode (mho/cm)	Z_i	Charge number of species i
l	One half of the height of the battery (cm)	α_x	Dimensionless group, kL_e/CL_x
L_x	Length of the battery (cm)	α_y	Dimensionless group, kL_e/CL_y
L_y	Height of the battery (cm)	β	Dimensionless group, $\rho_e C_e / C$
L_t	Assigned time period (sec)	ϵ	Infinite small value
M_i	Molecular weight of species i (g/mol)	ϕ	Porosity
n	Number of electron transfers for the reaction on electrode surface	τ	Dimensionless group, $\rho h/k$
n_1	Number of electron transfers on the electrode surface for the cell reaction	τ^*	Dimensionless distance, τ/L_t
n_2	Number of electron transfers on the electrode surface for the gassing reaction	θ	Dimensionless temperature, $(T - T_c)/(T_0 - T_c)$
$\dot{q}$	Rate of heat generated per unit volume (J/cm ³ -sec)	η	Current efficiency
$\dot{q}_e$	Rate of heat generated per unit volume in the electrolyte solution due to ohmic loss (J/cm ³ -sec)	ρ	Density (g/cm ³)
$\dot{q}_s$	Rate of heat generated per unit volume in the electrode due to ohmic loss (J/cm ³ -sec)	ρ_e	Density of electrolyte (g/cm ³)
s_i	Stoichiometric coefficient of species i in electrode reaction	ρ_s	Density of electrode (g/cm ³)
ΔS	Entropy production for reaction (J/mol-K)	τ	Dimensionless time, tk/CL
t	Time (sec)	τ^*	Dimensionless time, tU_0/L_y
t_s	Time period to reach steady state for temperature distribution in the circulation of electrolyte process (sec)	$\dot{q}$	Dimensionless rate of heat generation, $\dot{q}L_y/(\rho_e U_0 (T_0 - T_c))$
t^*	Dimensionless time scale (t/L_t)	η	Surface overvoltage (volt)
T	Temperature (K)	ϵ	Dimensionless group, $\rho_e L_t / \rho C T_0$
T_c	Temperature of coolant (K)	ω	Dimensionless group, $CL_t / \rho C$
T_0	Temperature of environment outside the battery (K)		
T_s	The steady-state temperature at the outlet for the circulation of the electrolyte process (K)		

Subscripts

e	electrolyte
s	electrode
x	x-direction
y	y-direction

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ABSTRACT

Transient thermal phenomena in Pb/PbO_2 (lead-acid) batteries during charging processes have been investigated. Mathematical models have been formulated for the studies of heat transfer behavior across the electrode/electrolyte interface within a porous PbO_2 electrode during charging; thermal behavior and temperature distribution over a lead-acid battery during different charging processes designed for electric-vehicle propulsion application; and cooling methods for lead-acid batteries during recharge cycles. Numerical solutions show that the heat transfer across the solid electrode and the electrolyte within the porous electrode is so fast that their temperatures may be regarded as the same. The results also show that in a lead-acid battery designed for electric-vehicle propulsion, the heat generated in the cell during fast charging processes may cause a noticeable rise of temperature in the cell if the heat is not removed properly. The studies of heat-removal processes indicate that incorporation of cooling tubes within the cell cannot effectively remove the heat being released from the cell. However, the heat may be removed effectively by circulation of electrolyte through the battery. Numerical solutions are provided for the engineering evaluation of heat-removal design during battery cycling processes.

1. INTRODUCTION

In the development of advanced batteries for applications to electric-vehicle propulsion, high energy density, power density, and long cycle life are required. In a highly packed battery composed of modular cells, the amount of heat generated in the cell due to ohmic loss, polarization, and entropy production becomes noticeable during cycling processes. If the internal heat is not removed properly, this will cause a rise of temperature within the cell. The increase of cell temperature may affect the physical and chemical properties of the electrode, electrolyte, and cell components. The charge and discharge characteristics, cell performance, and cell cycle life may also be affected by the variation of temperature. For example, the rise of temperature in lead-acid batteries during the charging process is usually a critical factor that causes the charging current to become unstable. Moreover, the current may rise to the extent that it is out of control, thereby leading to damage of the battery and charging equipment. Also, the electrolyte (sulfuric acid) may become more corrosive at higher temperatures; this may cause a loss of cell capacity and cycle life. It has also been found that the active material (PbO_2) in the positive electrode decomposes to different forms depending on the temperature variation.¹ The thermal effects during cycling processes in lead-acid batteries may be an important factor leading to a gradual loss of capacity of the active material.

In the passage of electrical current from one electrode through the electrolyte to the other electrode, heat is generated in the electrode and the electrolyte due to irreversible ohmic losses. At the electrode/electrolyte interface, the irreversible polarization and the reversible or irreversible entropy production contribute to the heat being generated. The heat-transfer behavior across these mediums and how this heat is removed from inside the battery to the outer atmosphere will be an important consideration in cell performance and cycle life. To achieve the required cell performance and to maintain the energy density and cycle life, an understanding of temperature distribution and heat-transfer behavior within the cell may be helpful in a sophisticated thermal design for removing the internal heat in batteries.

Baker, Gidaspow, and Wason² have examined general thermal behavior in fuel cells and batteries, and the associated mathematical techniques for obtaining analytical solutions for fuel cells and batteries. The analytical method is, however, limited by the characteristics of the mathematical functions and the boundary conditions. In the present analysis, mathematical models were developed for the studies of battery thermal behavior and heat release processes during recharge. Numerical solutions were obtained by use of the finite difference method. Section II elicits the heat-transfer phenomena across the electrode, the electrolyte, and their interface for a porous PbO_2 electrode. Section III describes investigations of the thermal phenomena and temperature distribution during cycling processes for a composite battery designed for electric-vehicle propulsion. Studies of the thermal behavior in lead-acid batteries during charging processes are also given. Section IV examines some design aspects which may be helpful in removing the heat generated in the battery during cycling. Numerical solutions are provided and these are discussed in terms of engineering applications.

II. HEAT TRANSFER ACROSS THE ELECTRODE, THE ELECTROLYTE, AND THEIR INTERFACE

During the charging process of a porous, positive PbO_2 electrode in a lead-acid battery, the electrical current passes through the electrode to the electrolyte, and the electrochemical reaction takes place on the electrode surface. Because of the differences of the ohmic resistivities in the electrolyte and the solid electrode, the amount of heat generated due to the ohmic losses in the two mediums will be different. At the electrode/electrolyte interface, heat is generated owing to the surface polarization and entropy contributions. The temperature distribution over the electrolyte, the electrode, and their interface is affected by the heat transfer behavior across them. This section examines the heat transfer behavior across the electrode and the electrolyte in a porous PbO_2 electrode. A similar procedure may be applied to other systems.

A. Mathematical Treatment

For a porous PbO_2 electrode, the electrode structure may be represented by Fig. 1a. At $x = 0$, there is a backing structure for the electrode. The front of the electrode is represented by $x = L$. The porous electrode may be modified and replaced by a simple fin model as shown in Fig. 1b, with the assumptions that the current density, i , is uniformly distributed

Fig. 1. (a). Schematic Cross Section for a General Porous Electrode
 (b). Schematic Cross Section for a Simplified Porous Electrode
 (c). Cross Section for a Region Across the Electrolyte/Electrode Interface

in y-direction and that the local faradaic current density, j , is uniform in the x-direction on the fin surface. In this case, the heat-transfer behavior across the electrode and electrolyte in a local region, encircled by "c" in Fig. 1b may represent the general thermal behavior in the electrode. The following paragraphs discuss the thermal behavior across the electrode and the electrolyte in the y-direction, as shown in Fig. 1c. For the solid electrode, the governing energy equation may be written as

$$\rho_s \hat{C}_s \frac{\partial T}{\partial t} = k_s \frac{\partial^2 T}{\partial y^2} + \dot{q}_s \quad (1)$$

where ρ_s , $\hat{C}_s$ and k_s are the density, specific heat, and thermal conductivity of the solid electrode, respectively. The heat source ($\dot{q}_s$) in the solid electrode due to electrical dissipation may be expressed as

$$\dot{q}_s = j^2 / K_s \quad (2)$$

where j is the local current density, and K_s is the electrical conductivity of the solid electrode.

For the electrolyte, the governing energy equation is

$$\rho_l \hat{C}_l \frac{\partial T}{\partial t} = k_l \frac{\partial^2 T}{\partial y^2} + \dot{q}_e \quad (3)$$

where ρ_l , $\hat{C}_l$ and k_l are the density, specific heat, and thermal conductivity of the electrolyte, respectively. The heat production per unit volume ($\dot{q}_e$) in the liquid electrolyte from electrical dissipation is expressed as

$$\dot{q}_e = j^2 / K_l \quad (4)$$

where K_l is the electrical conductivity of the electrolyte.

At $y = 0$, the temperature gradient may be regarded as zero because of symmetry in the assumed model. Then the boundary condition may be written as

$$y = 0, \quad \frac{\partial T}{\partial y} = 0 \quad (5)$$

At the interface, $y = y_1$, the rates of heat transfer in both mediums must be conserved. The boundary condition at the interface may be written as

$$y = y_1, \quad -k_s \left(\frac{\partial T}{\partial y} \right)_s = \dot{q}_0 - k_l \left(\frac{\partial T}{\partial y} \right)_l \quad (6)$$

where $(\partial T / \partial y)_s$ and $(\partial T / \partial y)_l$ are the temperature gradients in y -direction in the respective mediums at the interface. The amount of heat generated per unit area at the interface, $\dot{q}_0$, which is contributed by the surface polarization and the entropy production, is expressed as

$$\dot{q}_0 = j\phi - j \frac{T\Delta S}{nF} \quad (7)$$

where ϕ is the surface overvoltage, ΔS is the entropy change of the reaction occurring on the electrode surface, T is absolute temperature in Kelvins, n is the number of electron transfers in the reaction, and F is the Faraday constant.

If the electrolyte solution is stagnant, the temperature gradient in the y -direction at $y = y_2$ may be assumed equal to zero.

$$y = y_2, \quad \frac{\partial T}{\partial y} = 0 \quad (8)$$

The initial temperature profiles across the electrode and electrolyte may be assumed to be the same, that is:

$$t = 0, T = T_0 \quad (9)$$

Equations 1 and 2 have been solved numerically with initial and boundary conditions (Eqs. 5, 6, 8 and 9). The finite difference analogue is used. The Crank-Nicolson implicit technique³ is employed. The numerical solution is obtained by solving the tridiagonal matrix with elimination algorithm. The values of physical parameters and other data for the calculation are listed below.

The positive electrode is composed largely of PbO_2 and PbSO_4 , for which the thermal masses ($\rho_s \hat{C}_s$) are quite similar. They are $2.14 \text{ J/cm}^3\text{-K}$ for PbSO_4 and $2.53 \text{ J/cm}^3\text{-K}$ for PbO_2 . Since the averaged thermal mass is dependent on the states of charging or discharging, for convenience, it is set equal to the value of PbSO_4 . The specific heats of PbO_2 and PbSO_4 for the calculation of thermal masses may be found in the Kaze Laby tables.⁴

Other values are as follows:

$$\begin{aligned} k_s &= 0.005 \text{ W/cm-K (estimated)} \\ \rho_L \hat{C}_L &= 3.81 \text{ J/cm}^3\text{-K for 35.25 wt \% H}_2\text{SO}_4^5 \\ k_L &= 0.005 \text{ W/cm-K for 37 wt \% H}_2\text{SO}_4 \text{ at } 20^\circ\text{C}^b \\ K_s &= 5 \text{ mho/cm}^7 \\ K_L &= 0.812 \text{ mho/cm for 35 wt \% H}_2\text{SO}_4 \text{ at } 25^\circ\text{C}^a \\ j &= 0.4 \text{ mA/cm}^2 \text{ (estimates based on } 20 \text{ mA/cm}^2 \text{ apparent} \\ &\quad \text{current density, } 250 \text{ cm}^2\text{/cm}^3 \text{ active material} \\ &\quad \text{surface area per unit volume, } 0.2 \text{ cm for the} \\ &\quad \text{electrode thickness, and } 0.5 \text{ porosity).} \\ y_1 &= 0.002 \text{ cm (estimated as above).} \\ y_2 &= 0.002 \text{ cm (estimated as above).} \end{aligned}$$

The electrode reaction in the porous PbO_2 electrode during charging and discharging may be expressed as

The entropy change for Eq. 10 is equal to

$$\Delta S = -193.6 \text{ J/mol-K}$$

In the calculation, for simplicity, the heat generated at the interface by polarization is not considered because its contribution amounts to 10% of the entropy heat for a surface overvoltage equal to 30 mV.

B. Results

The numerical solutions for the thermal phenomena across the electrode and the electrolyte are summarized in Fig. 2 and Fig. 3. Figure 2 shows the temperature distribution across the electrode and the electrolyte and their interface at 5.0×10^{-6} sec, and 0.6 sec after passage of current during charging in the PbO_2 electrode. These are given as differences from a reference temperature, T_f . The results show that the temperature profiles across both mediums increase with time. The temperature distribution across the electrode and the electrolyte is not uniform, but the temperature difference is small. Figure 3 shows that the variation of the maximum temperature difference over the two mediums reaches a steady value of less than 10^{-4}°C within a few seconds and maintains this same value for the rest of the cycling period.

Fig. 2. Temperature Distribution Across the Electrode/Electrolyte Interface for a PbO_2 Electrode at 5.0×10^{-6} and 0.6 sec after Passage of Current during Charge (T_f = reference temperature)

For the case of electrolyte flowing through the porous electrode, the temperature just outside the stagnant layer of the electrolyte may be assumed to be constant. The boundary condition at $y = y_2$ may be rewritten as

$$y = y_2, T = T_0 \quad (11)$$

Where T_0 may be any reference temperature.

Fig. 3. Time Variation of the Maximum Temperature Difference Across the Electrode and the Electrolyte for a Local Region in a PbO_2 Electrode During Charge

The numerical results for the case of flowing electrolyte (also shown in Fig. 3) indicate that the maximum temperature difference over the solid and liquid phase is less than $10^{-4}^\circ C$, which reaches a steady value within a few seconds.

C. Discussion

Numerical solutions have shown that the temperature distribution across the electrode, the electrolyte, and the interface during charging in the porous PbO_2 electrode is not the same, but the maximum temperature difference over the two mediums is less than $10^{-4}^\circ C$ and reaches a steady value within a few seconds. From a macroscopic point of view, at any location within the PbO_2 porous electrode, the temperatures of the electrode and the electrolyte may be regarded as the same, within an error of about $10^{-4}^\circ C$ for this case. This result enables us to treat the temperatures of the solid electrode and the electrolyte at any location within the porous electrode as being the same; this simplifies considerably the study of thermal phenomena for composite batteries described below in Section III.

An approximation of the temperature difference between the electrode and electrolyte may be derived from Eq. 6. If there is no heat loss to the environment, the maximum temperature difference between the solid electrode and the electrolyte at any location within the cell may be expressed as

$$(\Delta T)_{\max} = q \frac{\Delta X}{k} \quad (12)$$

where $\dot{q}$ is the amount of heat produced at the interface per unit area, ΔX is the thickness of the stagnant layer of electrolyte, and k is the thermal conductivity of the electrolyte.

For the above calculation,

$$\dot{q} = 1.21 \times 10^{-6} \text{ J/cm}^2\text{-sec}$$

$$\Delta X = 0.003 \text{ cm}$$

$$k = 0.005 \text{ J/sec-cm-K}$$

and

$$(\Delta T)_{\max} = \frac{1.21 \times 10^{-4} \times 0.002}{0.005} = 4.84 \times 10^{-5} \text{ K}$$

This value is in good agreement with the numerical solutions (Figs. 2 and 3) obtained from the model.

III. THERMAL PHENOMENA IN A COMPOSITE LEAD-ACID BATTERY DURING RECHARGE PROCESSES

The solution from the preceding section enables us to treat temperatures of the electrode and the electrolyte at any location as the same. For a composite cell design, following the suggested approximation in previous sections, the positive and negative plates and the separator may be regarded as an entity and their averaged temperature may represent the local temperature, at any location, within an error of less than 0.066°C if the electrode thickness is about 0.25 cm. In this way, for a composite lead-acid battery, the whole cell may be treated as a homogeneous medium with the averaged physical parameters (density, specific heat, thermal conductivity, and electrical conductivity), and the heat generated within the cell due to ohmic loss, polarization, and entropy contribution may be averaged over the battery.

A. Model Development

For a composite battery design, the cell configuration is shown in Fig. 4. The two posts are exposed outside the container at the top, and the electrodes, the electrolyte, and other cell components are within the cell container. The length of the cell is represented by L_x , the height by L_y , and the width by L_z .

In this analysis, only x and y directions are considered. The energy conservation equation for the system may be written as

$$\rho \hat{C} \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + k \frac{\partial^2 T}{\partial y^2} - \rho \hat{C} U \frac{\partial T}{\partial y} + \dot{q} \quad (13)$$

Fig. 4. A Generalized Battery Cell Configuration

where ρ , $\hat{C}$, k are the average density, specific heat, and thermal conductivity of the cell, respectively. They are dependent on the compositions of cell components and may vary with position and time during the cycling process. During overcharge, gas evaluation may enhance the heat transfer rates within the cell. This has been experimentally measured by *Mixon et al.*,⁹ and by *MacMullin et al.*¹⁰ In lead-acid batteries, H_2 and O_2 evolution may occur at the electrodes during charging. The gassing effect on heat transfer may be included in the expression of thermal conductivity. An estimated relation for thermal conductivity dependence on current efficiency during charge in lead-acid batteries is given in the following numerical calculation based on the reported data in Refs. 9 and 10.

The superficial velocity of electrolyte in the y-direction (U) represents the electrolyte movement due to the electrode porosity change from the electrochemical and chemical reactions. The velocity gradient in the y-direction may be written as

$$\frac{\partial U}{\partial y} = - \frac{\partial \epsilon}{\partial t} \quad (14)$$

where ϵ is the average porosity of the electrodes. Generally, the cell reaction may be expressed as

$$\sum_{\text{reactant}} s_i M_i Z_i = \sum_{\text{product}} s_i M_i Z_i \quad (15)$$

where M_i is the symbol representing the chemical formulas of species i , S_i is the stoichiometric coefficient of species i , and Z_i is the charge carried by species i .

The change in porosity with respect to time may be written as

$$\frac{\partial \epsilon}{\partial t} = i \left(\sum_{\text{product}}^{\text{solid phase}} s_i \bar{V}_i - \sum_{\text{reactant}}^{\text{solid phase}} s_i \bar{V}_i \right) / nFW_X \quad (16)$$

where $\bar{V}_i$ is the partial molar volume of species i ; i is the superficial current density over the electrode; n is the electron-transfer number for the cell reaction; and W_X is the thickness across the positive electrode, the negative electrode, and the separator. In Eq. 12, $\dot{q}$ is the rate of heat production per unit volume in the battery, which is a function of cell reaction, temperature, current density, cell resistance, current efficiency, polarization, and cell geometry. Generally, $\dot{q}$ may be written as a combination of functions $f(i, \epsilon, W_t, V, \sum_j \Delta H_j^\circ)$ and $G(i, \epsilon, W_t, \sum_j \Delta C_{p,j})$ as follows:

$$\dot{q} = f \left(i, \epsilon, W_t, V, \sum_j \Delta H_j^\circ \right) + G \left(i, \epsilon, W_t, \sum_j \Delta C_{p,j} \right) (T - T_o) \quad (17)$$

where i is the apparent current density, ϵ is the current efficiency, W_t is the combined thickness of the positive and negative electrodes plus the separator, and V is the cell potential during the cycling process, ΔH_j° is the heat of reaction for reaction j at the reference temperature T_o , and $\Delta C_{p,j}$ is the algebraic sum of the species' partial-molar heat capacities for reaction j . If the major cell reaction and the gas evolution reaction have occurred in the cell, functions f and G may be expressed explicitly by following the approximations:

$$f \left(i, \epsilon, W_t, V, \sum_j \Delta H_j^\circ \right) = \frac{1}{W_t} \left[V - \epsilon \frac{\Delta H_r^\circ}{n_1 F} - (1 - \epsilon) \frac{\Delta H_g^\circ}{n_2 F} \right] \quad (18)$$

and

$$G \left(i, \epsilon, W_t, \sum_j \Delta C_{p,j} \right) = - \frac{1}{W_t} \left[\epsilon \frac{\Delta C_{p,r}}{n_1 F} + (1 - \epsilon) \frac{\Delta C_{p,g}}{n_2 F} \right] \quad (19)$$

where ΔH_r° and ΔH_g° are the heats of reaction for the major cell reaction and the gas evolution reaction, respectively; n_1 and n_2 are the number of charge transfers for the cell and the gas evolution reactions, respectively.

Since the heat transfer between the surface of the battery wall and the outer atmosphere occurs by means of convection, or forced convection if air is circulated to the battery by a fan, the wall temperature of the battery will be a function of time and location. The boundary conditions (B.C.) may be represented by the following equations:

B.C. (1). At $x = 0$, any y ,

$$k \left(\frac{\partial T}{\partial x} \right)_{x=+\delta, y} + k \left(\frac{\partial T}{\partial y} \right)_{x, y+\delta} - k \left(\frac{\partial T}{\partial y} \right)_{x, y-\delta} = h(T_{x,y} - T_o) \quad (20)$$

B.C. (2). At $x = L_x$, any y ,

$$-k \left(\frac{\partial T}{\partial x} \right)_{x=L_x-\delta, y} + k \left(\frac{\partial T}{\partial y} \right)_{x, y+\delta} - k \left(\frac{\partial T}{\partial y} \right)_{x, y-\delta} = h(T_{x,y} - T_o) \quad (21)$$

B.C. (3). At $y = 0$, any x ,

$$k \left(\frac{\partial T}{\partial y} \right)_{x, y=+\delta} - k \left(\frac{\partial T}{\partial x} \right)_{x+\delta, y} + k \left(\frac{\partial T}{\partial x} \right)_{x-\delta, y} = h(T_{x,y} - T_c) \quad (22)$$

and

$$U = 0 \quad (23)$$

where k is the average thermal conductivity of the battery, h is the heat-transfer coefficient from the battery wall to the outer atmosphere, δ is an infinitely small value, and T_o is the outer atmospheric temperature.

At the top of the battery plates (at $y = L_y$), there is an electrolyte reservoir. One may treat this boundary condition in a manner similar to the treatment at the boundary for mass transfer to the electrolyte reservoir by Choi et al.¹¹ This is done by assuming that whenever a net amount of heat goes into the reservoir, the reservoir heats up immediately. The boundary condition at $y = L_y$ may then be written as

B.C. (4). At $y = L_y$, any x

$$\begin{aligned} \rho_l \hat{C}_l \left(\frac{\partial T}{\partial t} \right)_{x,y} &= \\ &- k \left(\frac{\partial T}{\partial y} \right)_{x, y-\delta} + \rho_l \hat{C}_l T_{x,y} U - k \left(\frac{\partial T}{\partial x} \right)_{x-\delta, y} + \left(\frac{\partial T}{\partial x} \right)_{x+\delta, y} \\ &- h(T_{x,y} - T_o) \end{aligned} \quad (24)$$

where V_r is the volume of the reservoir per unit distance in x -direction.

For the initial condition of the battery before charging, it may be assumed that the temperature in the battery is equal to the outer atmospheric temperature. The initial condition is then written as

I.C. At $t = 0$, any x , any y , $T = T_o$ (25)

In order to obtain the numerical solution which may be used in more general engineering applications, dimensionless groups are introduced into the mathematic treatment. Let

$$T^* = (T - T_0)/T_0$$

$$x^* = x/L_x$$

$$y^* = y/L_y$$

$$t^* = t/L_t$$

$$\alpha_x = kL_t/\rho\hat{C}L_x$$

$$\alpha_y = kL_t/\rho\hat{C}L_y$$

$$v^* = UL_t/L_y$$

$$\chi = fL_t/\rho\hat{C}T_0$$

$$\omega = GL_t/\rho\hat{C}$$

where T_0 is the reference temperature in kelvins, which may be assigned as the cell initial temperature, L_x is the length of the cell (cm), L_y is the height of the cell (cm), L_t is the time period for any cycling process. Equations 13, 14, and 16 become

$$\frac{\partial T^*}{\partial t^*} = \alpha_x \frac{\partial^2 T^*}{\partial x^{*2}} + \alpha_y \frac{\partial^2 T^*}{\partial y^{*2}} - U^* \frac{\partial T^*}{\partial y^*} + \chi + \omega T^* \quad (26)$$

$$\frac{\partial U^*}{\partial y^*} = - \frac{\partial \varepsilon}{\partial t^*} \quad (27)$$

and

$$\frac{\partial \varepsilon}{\partial t^*} = 1/L_t \left(\sum_{\text{product}}^{\text{solid phase}} s_i \bar{v}_i - \sum_{\text{reactant}}^{\text{solid phase}} s_i \bar{v}_i \right) / nFw_t \quad (28)$$

The initial and boundary conditions become

$$\text{I.C.} \quad \text{At } t^* = 0, \text{ any } y^*, T^* = 0 \quad (29)$$

$$\text{B.C. (1). At } x^* = 0, \text{ any } y^*,$$

$$\left(\frac{L_y}{L_x} \right) \left(\frac{\partial T^*}{\partial x^*} \right)_{x^*=+\delta, y^*} + \left(\frac{\partial T^*}{\partial y^*} \right)_{x^*, y^*+\delta} - \left(\frac{\partial T^*}{\partial y^*} \right)_{x^*, y^*-\delta} = \frac{hL_y}{k} T^* \quad (30)$$

$$\text{B.C. (2). At } x^* = 1, \text{ any } y^*,$$

$$- \left(\frac{L_y}{L_x} \right) \left(\frac{\partial T^*}{\partial x^*} \right)_{x^*=1-\delta, y^*} + \left(\frac{\partial T^*}{\partial y^*} \right)_{x^*, y^*+\delta} - \left(\frac{\partial T^*}{\partial y^*} \right)_{x^*, y^*-\delta} = \frac{hL_y}{k} T^* \quad (31)$$

B.C. (3). At $y^* = 0$, any x^* ,

$$\left(\frac{L_x}{L_y}\right) \left(\frac{\partial T^*}{\partial y^*}\right)_{x^*, y^*=0} - \left(\frac{\partial T^*}{\partial x^*}\right)_{x^*+\delta, y^*} + \left(\frac{\partial T^*}{\partial x^*}\right)_{x^*-\delta, y^*} = \frac{hL_x}{k} T^* \quad (32)$$

$$U^* = 0 \quad (33)$$

B.C. (4). At $y^* = 1$, any x^* ,

$$\begin{aligned} \left(\frac{\partial T^* v_r / L_y}{\partial t^*}\right)_{x^*, y^*} = & - \frac{kL_t}{\rho_\ell \hat{C}_\ell L_y^2} \left(\frac{\partial T^*}{\partial y^*}\right)_{x^*, y^*} + (1 + T^*) U^* \\ & - \frac{kL_t}{\rho_\ell \hat{C}_\ell L_y L_x} \left(\frac{\partial T^*}{\partial x^*}\right)_{x^*-\delta, y^*} + \frac{kL_t}{\rho_\ell \hat{C}_\ell L_y L_x} \left(\frac{\partial T^*}{\partial x^*}\right)_{x^*+\delta, y^*} - \frac{hL_t}{\rho_\ell \hat{C}_\ell L_y} T^* \end{aligned} \quad (34)$$

B. Numerical Calculations

Equations 26-28 are solved subject to the initial and boundary conditions (Eqs. 29-34). Numerical solutions were obtained by use of a finite difference analogue. The implicit alternating-direction method^{12,13} followed by elimination algorithm are employed. The convergence criterion is that the difference between two successive solutions at all the mesh points be less than 0.001%.

Two kinds of numerical solutions for temperature distributions in batteries are calculated: The first yields generalized dimensionless solutions which may be used for most batteries of similar construction. The second is for a specific lead-acid battery at different cycling processes. The calculation details of the latter are illustrated below:

(1) Calculation for the general dimensionless solution for batteries.

Since the characteristics of cell reactions and cell performance behavior can not be specified by calculation of a general solution for temperature distribution, some simplifications have been made here. The electrolyte movement due to porosity change and the contribution due to species partial molar heat capacities are assumed not to affect the temperature field distribution. Therefore, Eq. 26 may be rearranged as

$$\frac{\partial(T^*/\chi)}{\partial t^*} = \alpha_x \frac{\partial^2(T^*/\chi)}{\partial x^{*2}} + \epsilon_y \frac{\partial^2(T^*/\chi)}{\partial y^{*2}} + 1 \quad (35)$$

for calculation of a general solution. Equation 35 is still subject to the initial condition of Eq. 29 and the boundary conditions Eqs. 30-34. The input data for the calculation are listed as below:

$$h = 3.0 \times 10^{-4} \text{ J/cm}^2\text{-sec K}$$

$$L_x/L_y \geq 2.0$$

$$L_y = 30 \text{ cm}$$

Two different values for the thermal conductivity k are used in the calculations, 0.005 W/cm-K in one, and 0.02 W/cm-K in the other. For a typical lead-acid cell, the average thermal conductivity is about 0.025 W/cm-K. For advanced lead-acid cells with higher specific energy where the grid weight is reduced, the average thermal conductivity is accordingly reduced.

(2) Calculation for the temperature field in a specific lead-acid battery. In this part of the calculation, the cell reaction, the cycling process, and the cell performance may be specified for a lead-acid battery. The lead-acid battery is designed with a capacity of 4 kW-hr, 350 A-hr at a 5-hr discharge rate. The cell dimensions are 60 cm (L) x 30 cm (H) x 30 cm (W) and the energy density is 30 W-hr/kg at the 5-hr rate. The charging processes start after the battery has been discharged to 30, 50 and 80% of its rated capacity and charging is made at different rates. The charging cycle includes two steps. The first step is constant-current charge until the cell potential reaches a specified value, and then the cell potential is maintained the same for the second step of charging. The required data and the physical parameters are specific for the lead-acid cell. Calculation of the characteristic functions f and G (Eqs. 18 and 19) are based on the following:

Cell reaction:

The heat of reaction (ΔH_r) for the above cell reaction varies with time during charge due to the change in sulfuric acid concentration. However for simplicity, a constant value of ΔH_r , based on a specific gravity of 1.1 for the electrolyte is assumed and given as follows:

$$\Delta H_r (298 \text{ K}) = 361570.0 \text{ J/mol}^{14}$$

$$\Delta C_{p,r} (298 \text{ K}) = -47.53 \text{ J/mol-K}^{14}$$

Gas evolution reaction: $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 1/2 \text{O}_2$

$$\Delta H_g (298 \text{ K}) = 285786.6 \text{ J/mol}^{15}$$

$$\Delta C_{p,g} (298 \text{ K}) = -32.89 \text{ J/mol-K}^{16}$$

The average thermal conductivity of the system, k , which includes the correlation due to gassing during charging cycle may be calculated as follows:

$$k = k_o [29.07 (1 - \xi) + 1.0]$$

where k_o is the average thermal conductivity of the system if no gas evolution occurs in the cell. For this calculation,

$$k_o = 0.0255 \text{ W/cm-K (average value for grid, active material, electrolyte, and separator)}$$

$$\rho \hat{C} = 2.80 \text{ J/cm}^3\text{-K (estimated as above)}$$

$$\rho_r C_r = 3.81 \text{ J/cm}^3\text{-K (for sulfuric acid)}$$

$$L_t = 3600 \text{ sec}$$

$$L_x = 60 \text{ cm}$$

$$L_y = 30 \text{ cm}$$

$$T_o = 29.8 \text{ K}$$

$$W_t = 0.5 \text{ cm}$$

$$\frac{V_r}{V_y} = 0.1$$

$$h = 3.763 \times 10^{-4} \text{ J/cm}^2\text{-sec-K (estimated for natural heat convection on flat plate)}$$

During charge, cell potential, cell current, and current efficiency vary with time. Their variations are estimated and given in Figs. 5, 6, and 7.

Fig. 5. Assumed Profiles for Cell Potential, Cell Current, and Current Efficiency During 5-hr Charge

Fig. 6. Assumed Profiles for Cell Potential, Cell Current, and Current Efficiency During the 2.5-hr Charge

C. Results

1. For the Generalized Dimensionless Solution

The numerical solutions for the dimensionless temperature profiles as a function of time and locations are plotted in Fig. 8. The values of thermal conductivity (k) are set equal to 0.005 W/cm-K and 0.02 W/cm-K for the calculations. The temperature variations with time are approximately the same for both values of k . The temperature in the battery center increases more rapidly with time, as expected. The temperatures at the bottom are slightly lower than those at the center due to the heat loss from the wall to the outer atmosphere. At the electrolyte reservoir on the top of the battery places, the temperature rise is the slowest since there is no internal heat source. The rise of the reservoir temperature is due to the heat transfer by conduction and convection from the cell's interior to the electrolyte reservoir. The temperature distribution in the y -direction is almost the same for all x -locations except the region near the side walls of the cell. Figure 9 shows the temperature variation in y -direction at $x/L_x = 1/2$ at the end of the charging for both cases of k . Again, the temperature with a larger value of $k = 0.02$ is more uniform in the y -direction than in the case where $k = 0.005$, as expected.

Fig. 7. Assumed Profiles for Cell Potential, Cell Current, and Current Efficiency During the 1.0-hr Charge

Fig. 8. Variations of Cell Temperature During Charge at Three Locations (reservoir, center, bottom) in the Battery

Fig. 9.

Temperature Distribution Profile
in y-Direction for the Battery
at the End of Charge

2. For a Specific Lead-Acid Battery

The temperature field in a conceptual lead-acid battery has been studied at different charging rates. Figures 10 and 11 show the temperature

Fig. 10. Temperature Variations for the Electrolyte at the Top of Reservoir During the 1-, 2.5- and 5-hr Charge Cycles to Full Capacity

Fig. 11. Temperature Variations at the Center of a Lead-Acid Battery During 1-, 2.5- and 5-hr Charge Cycles to Full Capacity

variation with time for the electrolyte reservoir at the top and the center of the battery during the 5-hr, 2.5-hr, and 1-hr charging process. The cell had been discharged to 30, 50, and 80% of its rated capacity before charge. For all the charging cycles, the cell is charged to its full capacity. The coulombic efficiency is assumed to be 91% for the 5-hr charge, 88% for the 2.5-hr charge, and 85% for the 1-hr charge as indicated in Figs. 5-7.

The results show that the temperatures at the center of the battery rise with time during charging. The temperature in the electrolyte reservoir and the temperature rise are due to heat conduction from the cell interior to the reservoir. For the same charging period, the temperature of the battery center increases proportionally with the charging rates (see Fig. 11). The temperature distribution in the y-direction for all the x-locations is approximately the same except for the region next to the side wall of the cell container. Table 1 shows the temperature distribution in the cell in x and y directions at the end of a 2.5-hr charging process.

Numerical calculations were also carried out for an advanced lead-acid battery which is designed to yield 6.67 kW-hr, 583 A-hr at a 5-hr rate with an energy density of 50 W-hr/kg. The cell has the same geometric dimension as the one discussed above (60 x 30 x 30 cm). The variations of cell potential, cell current, and current efficiency for this calculation are shown in Fig. 12. Figure 13 shows the temperature variation with time at three locations of the cell during 2.0- and 1-hr charging processes. The cell had been discharged to 50% of its rated capacity before charge; 88% coulombic efficiency is assumed for both charging processes. A comparison of the results (Figs. 11-13) show that the temperature at the center of the advanced lead-acid battery is about 27°C, or about 12°C higher than that for

Table 1. Temperature Distribution [$T - T_0(^{\circ}\text{C})$] Over the Lead-Acid Battery at the End of 2.5-hr Charge to Full Cell Capacity

Cell capacity: 4 kW-hr, 350 A-hr for 5-hr rate
 Energy density: 30 W-hr/kg
 Cell dimensions: 60 cm (L) x 30 cm (W) x 30 cm (H)

TOP RESERVOIR

SIDE WALL	9.35	9.07	9.22	9.28	9.30	9.30	9.30	9.28	9.22	9.07	9.35	SIDE WALL
	10.27	10.91	11.15	11.23	11.26	11.26	11.26	11.23	11.15	10.91	10.27	
	11.35	12.31	12.64	12.75	12.79	12.79	12.79	12.75	12.64	12.31	11.35	
	12.22	13.31	13.71	13.84	13.88	13.89	13.88	13.84	13.71	13.31	12.22	
	12.85	13.97	14.41	14.56	14.61	14.62	14.61	14.56	14.41	13.97	12.85	
	13.25	14.38	14.84	15.00	15.05	15.06	15.05	15.00	14.84	14.38	13.25	
	13.45	14.58	15.05	15.22	15.27	15.28	15.27	15.22	15.05	14.58	13.45	
	13.48	14.61	15.08	15.25	15.31	15.32	15.31	15.25	15.08	14.61	13.48	
	13.34	14.47	14.94	15.11	15.17	15.18	15.17	15.11	14.94	14.47	13.34	
	13.02	14.14	14.60	14.78	14.84	14.85	14.84	14.78	14.60	14.14	13.02	
	12.51	13.57	14.03	14.21	14.27	14.28	14.27	14.21	14.03	13.57	12.51	

BOTTOM

the battery with 30 W-hr/kg of energy density for a 2.5-hr charging process. The ratio of the temperatures for both cases is close to their energy-density ratio ($15^{\circ}\text{C}/27^{\circ}\text{C} \approx 30/50$). This is another indication that in the present design, it is difficult to release the heat generated internally during cycling processes by means of conduction from inside the cell to the wall and through the wall to the outer atmosphere.

D. Discussion

The numerical results show that the temperature within the cell increases with time during cycling processes. Because of the air-cooling effect due to natural heat convection occurring on the walls of the cell container, the temperature around the wall is lower than that inside the cell. However, this kind of cooling can not effectively remove the heat from the cell; thus, the cell temperature increases.

The dimensionless solution for temperature fields in batteries may be estimated from Fig. 8 for different cycling rates. For example, from Fig. 8

Fig. 12.

Assumed Profiles for the Cell Potential, Cell Current, and Current Efficiency During 2-hr and 1-hr Charge Cycles for the Advanced Lead-Acid Battery

Fig. 13. Temperature Profiles in the Advanced Lead-Acid Battery During 1-hr and 2-hr Charge Cycles to Full Capacity

(where $k = 0.02$), if the average thermal mass ($\rho\hat{C}$) of the system is $3.0 \text{ J/cm}^3\text{-K}$, the rate of heat production per unit volume ($\dot{q}$) is equal to $10^{-2} \text{ J/cm}^3\text{-sec}$, and the cycling period is of 2-hr duration, then the internal temperature will be 24°C higher by the end of the cycling period. For the same conditions, if the thermal mass of the system is reduced to one-half of the above value (*i.e.*, $\rho\hat{C} = 1.5 \text{ J/cm}^3\text{-K}$), then the temperature rise will be doubled.

The results also show that, for the assumed characteristics of the lead-acid battery, the heat generated internally during charging processes remains in the cell and heats up the cell for the 5-hr, 2.5-hr and 1-hr charging rates (see Figs. 10 and 11). If the total delivered charge is the same, the process with the longest charge time will result in the most uniform temperature distribution within the cell. (Comparison of Figs. 10 and 11.)

The predicted temperature for the advanced lead-acid battery (50 W-hr/kg) may rise by 32°C during a 1.0-hr charge and by 27°C during a 2.0-hr charge. About 50% of cell capacity had been delivered during the 2.0-hr and the 1.0-hr charges. Such temperature rises will be critical to the cell charging process, cell performance, and eventually the cycle life.

In the next section, some possible methods for removing heat from the cell during cycling are discussed. Numerical solutions will be given to aid in evaluations of engineering designs.

IV. HEAT RELEASE PROCESSES FOR BATTERIES DURING CYCLING

In the preceding Section III, numerical solutions showed that the heat generated within a lead-acid battery due to ohmic loss, polarization, and the entropy contribution may cause a significant rise of temperature within the cell during charging unless adequate cooling is provided. During battery recharging, heat may be removed by use of a cooling fan blowing air over the cell container, by inserting cooling tubes within the cell, or by circulating electrolyte through the cell. However, blowing air over the battery container can only increase the convective heat transfer coefficients from the wall to the outer atmosphere, but the heat removal from the cell is limited by the internal heat conduction inside the cell to the wall of container and across the container wall. An approximate calculation based on the previous analysis in Section III is done for the temperature distribution within the cell for the condition of blowing air over the cell container. The convective heat transfer coefficient from the wall to the outer atmosphere is assumed equal to $1.688 \times 10^{-3} \text{ J/cm}^2\text{-sec-K}$, which corresponds to a Reynolds number of about 10^5 for a flat plate. Figure 14 compares the calculated temperature distribution for the same system with and without air blowing. The results show that air blowing has no significant effect on the interior cell temperature; temperatures of the wall and the region near the wall are only slightly lowered.

For the case of inserting cooling tubes within the cell, the basic heat transfer mechanism is similar to the case of blowing air over the battery container. The heat transfer within the cell is governed by conduction. However, the average heat transfer coefficient across the cooling tube may

Fig. 14.

Temperature Distribution Profile in y-Direction at the Ends of Charge Cycles. The cell had been discharged to 50% of its rated capacity before charge. The coulombic efficiencies are assumed to be 88% for the 2-hr charge and 85.1% for the 1-hr charge.

be increased by choosing highly conductive materials, thinner wall thickness, and low coolant temperature.

For the case of circulation of electrolyte through the system, the major heat transfer mechanism is convection, which is considered a more effective means of heat removal than conduction. In this analysis, both case, *i.e.*, cooling tubes and electrolyte circulation, are analyzed. Numerical solutions are also provided for design applications.

A. Analysis of Heat Removal by Use of Cooling Tubes

A schematic of a battery cell with cooling tubes is shown in Fig. 15. The cooling tubes are arranged at the top and the bottom of the cell, where the coolant flows from one end to the other. The heat generated within the cell is transferred by conduction through the cell interior to the cooling tubes and across the cooling tubes walls, and finally is carried away by the coolant.

Fig. 15. Schematic of a Battery Cell with Cooling Tubes

1. Mathematical Treatment

The previous results from Section III show that the temperature distribution in the y-direction is quite similar over the entire x-direction except close to the walls. Therefore, in the following analysis, only the variation in y-direction is considered. The energy equation may be represented as

$$\rho \hat{C} \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial y^2} + \dot{q} \quad (36)$$

where ρ , $\hat{C}$, and k are the density, heat capacity, and thermal conductivity of the system, respectively. The term $\dot{q}$ is the heat source per unit volume inside the cell, which is a function of the cell characteristics, the cell design cycling process, and performance. At $y = 0$ (see Fig. 15), because of symmetry, the temperature gradient is zero. Then

$$y = 0, \quad \frac{\partial T}{\partial y} = 0 \quad (37)$$

At $y = l$, the rate of heat transfer across the boundary is conserved. Then

$$y = l, \quad -k \frac{\partial T}{\partial y} = h(T - T_c) \quad (38)$$

where T_c is the coolant temperature. The average heat transfer coefficient across the cooling tube, h , is finite and dependent on the properties of the cell medium, fluid, and the cooling tube and its geometry. It also depends on the coolant temperature and its physical properties, and the circulation rate of coolant. The magnitude of h may be varied by adjusting these parameters. For an ideal situation of zero heat-transfer resistance across the cooling wall, the temperature at $y = l$ should be equal to the coolant temperature.

The limiting case for zero heat transfer resistance is therefore:

$$y = l, \quad T = T_c \quad (39)$$

The initial conduction may be written as

$$t = 0, \quad \text{any } y, \quad T = T_o \quad (40)$$

where T_o is the initial temperature.

To perform the dimensionless group solution for engineering application, the variables are transformed into the following forms. Let

$$\theta = (T - T_c) / (T_o - T_c)$$

$$\tau = tk / \rho \hat{C} l^2$$

$$\zeta = lh / k$$

$$\eta = y/l$$

$$W = l^2 \dot{q}/k(T_o - T_c)$$

Then Eqs. 36, 37, 38, and 40 become

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \eta^2} + W \quad (41)$$

$$\text{I.C.} \quad \tau = 0 \quad \theta = 1 \quad (42)$$

$$\text{B.C. (1).} \quad \eta = 0 \quad \frac{\partial \theta}{\partial \eta} = 0 \quad (43)$$

$$(2). \quad \eta = 1 \quad \frac{\partial \theta}{\partial \eta} = -\zeta \theta \quad (44)$$

For the limiting case of zero heat transfer resistance across the cooling tube, the boundary condition in Eq. 39 becomes

$$\text{B.C. (2).} \quad \eta = 1 \quad \theta = 0 \quad (45)$$

Equation 41 is solved subject to the initial condition (Eq. 42) and the boundary conditions of Eqs. 43, 44 or 45 by use of the finite difference method. The Crank-Nicolson implicit technique³ followed by elimination algorithm is employed.

2. Results

The dimensionless temperature distribution as a function of time and space is shown in Figs. 16 and 17 for the case of a finite heat transfer

Fig. 16. Transient Temperature Profiles for a Battery with Cooling-Tube Design

Fig. 17. Transient Temperature Profiles for a Battery with Cooling-Tube Design with Zero Heat Transfer Resistance Across the Cooling Tube

coefficient ($lh/k = 20$) and the limiting case of zero heat transfer resistance across the cooling tube (in this case, $y/l = 1$, $T = T_c$) at a specific value of $W = 4$. This is approximately equivalent to a 1-hr charge process to deliver 30% of cell capacity for the lead-acid battery discussed in section III, with a heat-transfer coefficient across the cooling tube of $0.034 \text{ J/cm}^2\text{-sec-K}$ and a 15°C difference between the initial cell temperature and the coolant temperature. Figure 18 shows the temperature distribution profiles for different heat transfer coefficients across the cooling tube at time $\tau = 0.6$ ($kt/\rho\hat{C}l^2 = 0.6$) along with the distribution of the limiting case for $W = 4$. Figures 19 and 20 show the maximum temperature variations with time at different values of W for the case of finite heat transfer coefficient and for the case of zero heat transfer resistance across the cooling tube. The maximum temperature variations with time for different heat transfer coefficients across the cooling tube at a specific value of W are shown in Fig. 21.

For the case of a finite heat transfer coefficient across the cooling tube (for $lh/k = 20$) as shown in Fig. 16, the dimensionless temperature next to the cooling tube dropped from an initial value of 1 to a value of 0.35 as the time-characteristic parameter $kt/\rho\hat{C}l^2$ increased from zero to 0.005. The dimensionless temperature next to the cooling tube then dropped to 0.18 at $kt/\rho\hat{C}l^2 = 0.04$ and changed very little after that. The temperatures in the region away from the cooling tube rose continuously with time. However, the rate of temperature rise did decrease with time. The same trend of behavior is seen for the limiting case of zero heat transfer resistance across the cooling tube ($y/l = 1$, $T = T_c$) (see Fig. 17). Comparison of the

Fig. 18.

Temperature Profiles for a Battery with Cooling-Tube Design at Different Values of Heat-Transfer Resistance Across the Cooling Tube

Fig. 19.

Temperature Variations with Time for a Battery with Cooling-Tube Design at Different Cycling Rates. $T_{\max}$ is the temperature at $y = 0$, (the battery center).

Fig. 20.

Temperature Variations with Time at Different Cycling Rates for a Battery with Cooling-Tube Design. Zero heat-transfer resistance across the cooling tube is assumed. $T_{\max}$ is the temperature at $y = 0$, (the battery center).

Fig. 21.

Temperature Variations with Time for a Battery with Cooling-Tube Design. Different values for the heat transfer resistance across the cooling tube are used for comparison.

two cases (Figs. 16 and 17) shows that even though the heat transfer coefficient varies from a finite value ($lh/k = 20$) to an infinite value (zero heat transfer resistance) across the cooling tube, the temperature at the center ($y = 0$) varies from 2.1 (Fig. 16) to 1.93 (Fig. 17) for $kt/\rho\hat{C}l^2 = 1.0$, which is equivalent to a difference of 1.7°C if $(T_o - T_c) = 10^\circ\text{C}$. From an economical standpoint, the cost for the limiting case of zero heat resistance will be much higher than for the cases of finite heat-transfer resistance across the cooling tube due to the design cost of tubes and pumping cost of coolant circulation. This clearly indicates that the rate of heat being removed inside the cell is limited by the conductive heat mechanism.

This limitation by conduction is also reflected by the small change of $(T - T_c)/(T_o - T_c)$ with different values of lh/k as shown in Fig. 18. The maximum temperature (temperature at the center, $y = 0$) varies with time as cycling continues (see Fig. 19). For smaller values of W ($W \leq 2$), the maximum temperature at $y = 0$ rises with time at the beginning and then decreases slowly with time for the case of $lh/k = 40$ (see Fig. 19) and also the limiting case ($y = l$, $T = T_c$) in Fig. 20. But for values of W greater than 2, the maximum temperature rises with time at the beginning and then increase continuously with time for both cases. The rise of maximum temperature is proportional to the magnitude of W for $W > 2$ (see Figs. 19 and 20). This also implies that the heat generated internally during cycling cannot be removed effectively by using cooling tubes. This conclusion is also reflected in Fig. 21 for different values of heat transfer coefficient across the cooling tubes at a given W ($W = 4$).

Tables 2 and 3 show the temperature distribution as a function of charging process and as a function of different heat transfer coefficients

Table 2. Temperature Variation with Time During a 2-hr Charging Process for the Lead-Acid Battery with a Design Capacity of 6.67 kW-hr, 583 A-hr^a

t , min	$T_{\max} - T_c$, $^\circ\text{C}$	$T_{\max} - T_o$, $^\circ\text{C}$
30	11.64	5.35
60	36.24	10.35
90	39.35	13.46
120	42.19	16.30

^aCalculation is based on data from Fig. 19.

$$T_o - T_c = 25.88^\circ\text{C}$$

$$k = 0.0254 \text{ W/cm-K}$$

$$l = 15 \text{ cm}$$

$$\dot{q} = 1.169 \times 10^{-2} \text{ J/cm}^3\text{-sec}$$

$$\rho\hat{C} = 3.02 \text{ J/cm}^3\text{-K}$$

$$h = 6.77 \times 10^{-2} \text{ J/cm}^3\text{-sec-K}$$

Table 3. Variation of Maximum Cell Temperature with Different Heat Transfer Coefficients Across the Cooling Tube at the End of 2-hr Charging Process for the Lead-Acid Battery^a

$h, \text{J/cm}^2\text{-sec-K}$	$T_{\text{max}} - T_c, ^\circ\text{C}$	$T_{\text{max}} - T_o, ^\circ\text{C}$
13.54×10^{-2}	44.31	18.42
3.385×10^{-2}	42.71	16.85
6.77×10^{-2}	49.19	16.30
limiting case ($y = l, T = T_c$)	49.16	15.27

^aCalculation is based on data from Fig. 21.

$$\tau = 0.2694 \text{ (equivalent to } t = 2 \text{ hr)}$$

for the cooling tubes. The lead-acid battery being examined here is one with a designed capacity of 6.67 kW-hr, 583 A-hr at a 5-hr discharge rate. The charging period is a 2-hr constant current process to deliver 80% of the cell capacity.

B. Analysis of Heat Removal by Electrolyte Circulation During Charge

In the previous section, the results showed that the use of cooling tubes in lead-acid batteries is ineffective in removing internal heat during charge owing to the limiting conductive heat transfer in the cell. In contrast, flowing electrolyte would provide good thermal contact with the electrode and also would remove gaseous products during the charge. Section II showed that the temperatures of the electrolyte and the electrode are almost the same for both stationary and flowing electrolyte conditions. Therefore, the heat within the cell may be effectively removed by circulating the electrolyte.

Consider a battery design with circulating electrolyte to remove heat generated within the battery during charging, as shown in Fig. 22; one end of the battery (*e.g.*, the top) may connect to an electrolyte reservoir outside the battery. The electrolyte can be circulated from the reservoir to a cooling stage C, and then go to the battery, and be collected at the other end. In this way the heat generated in the cell can be removed and the rise of cell temperature minimized. At the same time, other advantages, such as gas removal (if the flow direction is from the bottom to the top) and reduction in concentration polarization can be obtained simultaneously.

1. Mathematical Treatment

The results from Section III showed that the temperatures in the x-direction are quite similar except at the region next to the wall of the container (see Table 1). Therefore, the variation in x-direction is not considered in this treatment. During the process of circulation of electrolyte, the heat conduction will be negligible compared with the heat convection

Fig. 22. General Design for Electrolyte-Circulation Process

in the y -direction. The energy conservation equation in the y -direction may be simplified as follows:

$$\rho \hat{C} \frac{\partial T}{\partial t} = - \rho_{\ell} \hat{C}_{\ell} U_0 \frac{\partial T}{\partial y} + \dot{q} \quad (46)$$

where ρ and $\hat{C}$ are the average density and heat capacity of the battery, respectively; ρ_{ℓ} and $\hat{C}_{\ell}$ are the density and heat capacity of the circulating electrolyte; U_0 is the superficial velocity of the electrolyte in y -direction; and $\dot{q}$ is the rate of heat production, which is dependent on the cycling process and cell performance. The initial and boundary conditions may be written as

$$t = 0, \quad \text{any } y, \quad T = T_0 \quad (47)$$

$$y = 0, \quad t > 0, \quad T = T_c \quad (48)$$

where T_0 is the initial cell temperature. T_c is the temperature of the electrolyte entering the cell.

Let

$$\theta = (T - T_c) / (T_0 - T_c)$$

$$\tau^* = t U_0 / L_y$$

$$y^* = y / L_y$$

$$\beta = \rho_{\ell} \hat{C}_{\ell} / \rho \hat{C}$$

then Eq. 46 becomes

$$\frac{\partial \theta}{\partial \tau^*} = -\beta \frac{\partial \theta}{\partial y^*} + \phi \quad (49)$$

where $\phi = \dot{q}L_y / \rho \hat{C} U_0 (T_0 - T_c)$. (50)

and the initial conditions and boundary conditions, respectively, become

$$\tau^* = 0, \quad \theta = 1 \quad (51)$$

$$y^* = 0, \quad \tau^* > 0 \quad \theta = 0 \quad (52)$$

Numerical solutions were obtained by use of a finite difference analogue, carried out by computer calculation.

2. Results

The temperature distributions over the cell in y -direction at $\tau^* = 0.1, 0.6$ and 1.1 are reported in Figs. 23 and 24 for $\dot{q}L_y / \rho \hat{C} U_0 (T_0 - T_c) = 1.0$ and 2.0 , respectively. For $\dot{q}L_y / \rho \hat{C} U_0 (T_0 - T_c) = 1.0$, this corresponds to a 1-hr charge to 30% of cell capacity for the lead-acid battery discussed in Section III; a circulation rate of 6.8×10^{-3} cm/sec; and a 10°C temperature difference between the initial cell temperature and the electrolyte temperature at the entrance. At the early stage of cycling (τ^* is about 0.1), the temperatures at the region near the electrolyte entrance ($y = 0$) are lower due to the cooling effect of the electrolyte entering from the reservoir. At the region away from the entrance, the temperature is not affected because the electrolyte has not yet reached this region in such a short time period. As time increases (for example, $\tau^* = 0.6$), the region not affected becomes smaller and further away from the entrance. At $\tau^* = 1.0$, the electrolyte leaving the cell at $y = L_y$ will be the electrolyte which entered the cell at $\tau^* = 0$. After $\tau^* = 1.0$, the temperature distribution reaches a steady state, which is maintained for the rest of the charging process. The dashed lines in Figs. 23 and 24 show that the maximum temperature (the temperature of the

Fig. 23. Temperature Profiles for a Battery with Electrolyte-Circulation Design [$\dot{q}L_y / U_0 \rho \hat{C} (T_0 - T_c) = 1.0$]

Fig. 24. Temperature Profiles for a Battery with Electrolyte-Circulation Design
 $[\dot{q}L_y/U_0\rho\hat{C}(T_0 - T_c) = 2.0]$

electrolyte leaving the cell at the outlet $y = L_y$) varies with time during the charging process. The temperature of the electrolyte at the outlet ($y = L_y$) increases with time in the early stage of charging, reaches a maximum, decays to a minimum at about $\tau^* = 1.0$, and maintains the minimum for the rest of the time. Figure 25 shows the variation in outlet temperature (the temperature at $y = L_y$) with time for different values of $\dot{q}L_y/U_0\rho\hat{C}(T_0 - T_c)$. The temperature is proportional to $\dot{q}L_y/U_0\rho\hat{C}(T_0 - T_c)$, which is a combination of the characteristics of the rate of heat generation ($\dot{q}$), the rate of electrolyte circulation (U_0), the geometry of the cell (L_y), the thermal mass of the cell ($\rho\hat{C}$), and the temperature of the electrolyte at the entrance (T_c). If all the conditions are kept the same, increasing the circulation rate will reduce the temperature difference across the cell by the same proportion. The time period to reach a steady temperature profile will also be reduced in the same proportion. Table 4 summarizes the maximum temperatures that occur at the outlet (T_{MAX}), the steady-state temperature at the outlet (T_S), and the time period to reach steady state (t_S), for different circulation rates during a charging cycle. These calculations are based on the lead-acid battery with a design capacity of 6.67 kW-hr, 583 A-hr (at a 5-hr rate), for a charging period of 2 hr at constant current. The amount of charge delivered during the 2-hr period is 80% of the cell capacity.

The results show that the rise of cell temperature for a lead-acid battery during the charging process is reduced significantly by circulation

Fig. 25. Temperature Variations with Time for Battery with Electrolyte-Circulation Design

Table 4. Predicted Temperatures as a Function of Circulation Rates in Lead-Acid Battery during 2-hr Charge. Eighty percent of the cell capacity is delivered to the cell during the charging period.^a

U_o , cm/sec	1.62×10^{-3}	2.324×10^{-2}	4.68×10^{-2}	9.296×10^{-2}	1.859×10^{-1}
$T_{\max} - T_c$, °C	10.6	7.65	6.25	5.6	2.8
$T_s - T_c$, °C	7.35	3.67	1.835	0.92	0.46
$T_s - T_o$, °C	2.35	-1.33	-3.165	-4.08	-4.54
t_s , min	47	23.5	11.75	5.88	2.94

^aCalculations based on the following values:

$$\begin{aligned}
 T_o - T_c &= 5^\circ\text{C} \\
 \dot{q} &= 1.1689 \times 10^{-2} \text{ J/cm}^3\text{-sec} \\
 L &= 30 \text{ cm} \\
 \rho C &= 3.02 \text{ J/cm}^3\text{-K}
 \end{aligned}$$

of electrolyte. For a circulation rate of 2.324×10^{-2} cm/sec and $T_o - T_c = 5^\circ\text{C}$, the maximum rise in temperature during the early stages is about 2.65°C relative to the initial cell temperature, and the steady temperature of the outlet electrolyte is about 1.33°C lower than the initial temperature. The time required to reach steady state in this case is about 23.5 min.

C. Discussion

Designs applicable for internal heat removal by cooling tubes and circulation of electrolyte have been analyzed. The results indicate that the heat generated in the cell during cycling cannot be removed effectively by the use of cooling tubes. As shown in Table 2 for the process using coolant tubes, the coolant temperature is 25.88°C below the cell initial temperature. This means that if cell temperature is 25°C initially, the coolant would have to be kept below 0°C. Table 2 also shows that the cell temperature increases with time during the entire charging process. At the end of the 2-hr process, the temperature at the center of the battery is about 16.3°C higher than its initial value. Since the temperature in the region next to the coolant tube is near the coolant temperature (see Fig. 18), the center temperature of the battery will be about 40°C higher than the cell temperature in the region next to the cooling tube (Table 2). In other words, the temperature difference across the cell for this case is as large as 40°C at the end of the 2-hr charging process.

Comparison of the cooling performance for the processes using cooling tubes and circulation of electrolyte (Tables 2 and 4) shows that the design with electrolyte circulation proves to be the more effective means of cooling. From Table 4, one can see that for $U_0 = 2.324 \times 10^{-2}$ cm/sec and $T_0 - T_c = 5^\circ\text{C}$, the maximum cell temperature at the outlet has risen to about 2.65°C ($7.65 - 5 = 2.65$) relative to the cell initial temperature. This temperature is reduced rapidly to a value that is 1.33°C lower than the initial cell temperature at 23.5 min after the start of charging, and remains at the lower value for the rest of charging. At steady state (after 23.5 min), the temperature difference across the cell is only 3.67°C ($5 - 1.33 = 3.67$). From an economical standpoint, the design of the circulating-electrolyte process is simpler and more effective in removing the internal heat in comparison with the cooling-tube design.

For the design with electrolyte circulation, the temperature profile at steady state may be estimated by omitting the time derivative from Eq. 49 as shown below:

$$-\beta \frac{\partial \theta}{\partial y^*} + \dot{q} L_y / \rho \hat{C} U_0 (T_0 - T_c) = 0 \quad (53)$$

then

$$\theta (\text{at } y^* = 1) = \dot{q} L_y / \beta \rho \hat{C} U_0 (T_0 - T_c) \quad (54)$$

or

$$T (\text{at } y = L_y) = \dot{q} L_y / \beta \rho \hat{C} U_0 + T_c \quad (55)$$

The time period to reach steady state is about

$$t_s \geq L_y / U_0 \quad (56)$$

Equations 55 and 56 as well as Figs. 23, 24 and 25 may be used for a quick design estimation.

V. CONCLUSIONS

The numerical results show that within a porous PbO_2 electrode, the heat transfer across the solid electrode, the liquid electrolyte, and their interface during the charging process is so rapid that the average temperature at any position within the porous electrode may, for practical purposes, represent the temperatures of the electrode and the electrolyte. For the temperature field studies of a composite battery model, the results indicate that the heat generated within the lead-acid battery during charging due to ohmic loss, polarization, and entropy contributions cannot be released effectively to the surrounding; hence the cell experiences a noticeable rise in temperature. Cell cooling by the incorporation of cooling tubes within the cell was shown to be ineffective and, furthermore, may cause a large temperature gradient within the battery. However, cooling by means of electrolyte circulation was shown to be quite effective during the charging process. The cell temperature may be maintained at a desirable level by controlling the rate of electrolyte circulation. A set of numerical solutions has been presented for engineering applications.

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