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The effect of grid configurations on potential and current density distributions in positive plate of lead–acid battery via numerical modeling

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ABSTRACT

During the last decades, huge efforts have been made to enhance the efficiency as well as performance of lead–acid batteries. The configuration of grid wires plays an important role in minimizing the ohmic drop and hence, improving its current collecting ability. In the current study, numerical methods have been employed to investigate the effects of grid configuration on the performance of a positive electrode in lead–acid batteries. Potential and current density distributions have been modeled through grid wires, active material and adjacent electrolyte to the surface of each grid. The modeling results are consistent with experimental findings in the literature saying that the optimized diagonal design for grid configuration provides lower total grid weight as well as enhanced current collecting role comparing to other designs such as, conventional, diagonal and expanded metal. This confirms that numerical modeling is a fast, inexpensive and effective method for optimization of the battery grid configuration.

1. Introduction

During the last decade, huge efforts have been made to enhance efficiency and performance of lead–acid batteries, i.e. incorporating promising alloying elements including Ca, Sn, Ag, into the grid alloy, optimizing the grid configuration and applying additives to both active material and battery electrolyte [1–5].

Each grid of SLI (starting, lighting, and ignition) battery is usually made of two compartments; first, a rectangular frame surrounded a network of wires and second, a lug on top of the frame basically used for carrying the current in or out of the plate. During the discharge or charge process, electric current generated or applied moves through both lug and grid wires in opposite directions [6]. While the battery grid is mainly a precursor for the active material and absorbent for mechanical stress specially caused by external forces or volume changes of active mass during cycling, it is also responsible for current distribution through the plate [7].

In industrial scale, grids are usually manufactured via two different methods named as casting and expanded metal. While first method uses casted lead-alloy frame as a precursor for active material, expanded metal method employs a different idea. In this method, a strip of lead alloy sheet is subjected to pressure in guillotine fashion between slitting and stretching dies leading to a mesh-like plate with polygonal paste-retaining cells [7].

The configuration of grid wires plays an important role in minimizing the ohmic drop which could lead to uniform current distribution through the electrode. Such design could also introduce more reaction sites on the electrode [6,8].

Even though several attempts have been made to investigate the role of grid configuration on its potential and current density distributions, the effects of electrolyte and active material on these issues are not fully considered [6,9,10]. Numerical methods could help simulate the effects of such parameters on the battery performance instead of time consuming experimental studies [8]. In the present study, the potential and current density distributions have been modeled via numerical methods to study the effect of grid configuration on the performance of a positive electrode in lead–acid batteries. The effects of both electrolyte and active material have been also taken into account.

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2. Theory

The molar flux of a charged species (j) in an electrolyte arises from three transport mechanisms, i.e. migration, diffusion and convection.

$$N_j = -z_j \mu_j F C_j \nabla \Phi - D_j \nabla C_j + C_j \nu \quad (1)$$

where Nj is ionic flux, z_j charge, μ_j ionic electrochemical mobility, F is the Faraday's constant, C_j concentration, Φ electrostatic potential outside the electric double layer, D_j diffusion coefficient, ν bulk average fluid velocity, and ∇ differential operator, respectively. The total ionic current density (i) is given by assigning the charge to flux of each species and summing over all species:

$$i = F \sum_j z_j N_j \quad (2)$$

Substituting Eq. (2) into (1),

$$i = -F^2 \nabla \Phi \sum_j z_j^2 \mu_j C_j - F \sum_j z_j D_j \nabla C_j + F \nu \sum_j z_j C_j \quad (3)$$

The condition of electroneutrality in solution implies:

$$\sum_j z_j C_i = 0 \quad (4)$$

Therefore, the last term of Eq. (3) is zero. Considering no ionic concentration gradients in the electrolyte, Eq. (3) becomes ohm's law for ion transport in electrolytes:

$$i = \sigma \nabla \Phi \quad (5)$$

where σ is the specific electrolyte conductivity given by

$$\sigma = -F^2 \sum_j z_j^2 \mu_j C_j \quad (6)$$

In case when there is no homogenous reaction in the electrolyte involving the ionic species or its net effect is zero, we can say:

$$\tilde{N} i = 0 \quad (7)$$

From Eq. (5), one can say:

$$\nabla i = \sigma \nabla^2 \Phi \quad (8)$$

which results in the Laplace equation,

$$\nabla^2 \Phi = 0 \quad (9)$$

The overall overpotential at the electrode is also given by:

$$\eta = E - E_e - \Phi \quad (10)$$

where E is the electrode potential and E_e denotes the thermodynamic equilibrium potential.

In case of no ionic concentration gradient in the electrolyte of an electrochemical cell and perfectly reversible faradic reactions, the mass transport and kinetic limitations are negligible, respectively. In such condition, which the overpotential is associated with the ohmic drop, the Laplace equation can be solved by implementing following boundary conditions. At insulator boundary:

$$\nabla \Phi = 0 \quad (11)$$

and potential in the solution adjacent to the electrode is equal to the potential on the electronic conductor:

$$\Phi_0 + \Phi_m = \text{constant} \quad (12)$$

During charge and discharge process at positive electrodes of lead–acid batteries, the following electrochemical reaction takes place in forward and backward directions, respectively:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \leftrightarrow PbSO_2 + 2H_2O \quad (13)$$

The equilibrium potential of the half-cell results in:

$$E_{e,PbO_2/PbSO_4} = 1.683 - 0.118\text{pH} + 0.029 \log a_{SO_4^{2-}} \quad (14)$$

An important parameter in designing battery plates is known to be

$$\alpha = W_g/(W_g + W_{am}) \quad (15)$$

where W_g is grid weight and W_{am} is the weight of active mass. The value of this ratio varies between 0.35 and 0.60. Since the plate capacity depends on its available active mass, the tendency is to minimize the value of α [7,11].

The conductivities of lead and lead oxide (PbO_2) are much higher than that of lead sulfate [12]. Hence, when PbO_2 converts to $PbSO_4$ during the discharge mode (cf. Eq. (13)), ohmic resistance of active material increases. Although employing additives, such as active carbon, titanium oxide and graphite, can improve conductivity of the active materials [11,13], it seems that some modifications in grid design could also solve the problem. For example, reduction in the mesh size of each grid could lead to more uniform potential and current density distribution through the grid [11]. It is worth mentioning that even though any decrease in mesh dimensions of a grid could lower its active mass consumption, smaller meshes would increase total grid weight hence the costs [11].

Since more currents are carried by wires near the lug in comparison to other parts of the grid, resistance characteristics of the grid can be improved by increasing the number of vertical wires as well as skewed ones. However, the former method could increase consumed lead and hence raise the grid weight. Therefore, the factor α increases which is not desirable [7]. Thus, a compromise has to be made between Pb consumption and grid design to lower plate resistivity without significant weight increase.

3. Model

Based on the theory explained in Section 2 and with the help of Comsol software, a 3D numerical model has been developed to investigate the potential and current density distribution of four different grid configurations. Fig. 1a shows the conventional grid configuration consisting of interconnected vertical and horizontal ribs surrounded by a rectangular frame with a lug located on the top right corner of the frame. Rectangular-like configuration of second grid, shown in Fig. 1b, consists of parallel horizontal ribs which are crossed by a series of skewed ribs headed toward the lug. Fig. 1c demonstrates configuration of the expanded metal grid. This grid comprises of a reticulated pattern of thin lead wires encompassed by a rectangular frame. It is worth mentioning that for the sake of better current collection, upper and lower edges of the frame are considered to be thicker than side edges in the latter configuration. It is assumed that dimensions of the frame, location and dimensions of the lug as well as thickness of the wires are similar in all cases. Table 1 shows specifications of three modeled grids, i.e. conventional, diagonal and expanded metal grids. In order to find the mass of each grid and its associated active material, their calculated volumes using modeling data has been multiplied by the densities of lead and lead oxide, respectively.

The existence of various materials in the different parts of the grids, i.e. grid alloy, active material and electrolyte, could severely

Table 1
Grid specifications as well as their design parameter.

Grid name	Grid weight (g)	Active mass weight (g)	Grid surface (cm^2)	α
Conventional	130.41	232.59	289.50	0.359
Diagonal	130.52	232.40	297.50	0.359
Expanded metal	130.29	232.68	256.60	0.358