

# NUMERICAL SIMULATION OF ACID STRATIFICATION IN LEAD-ACID BATTERIES

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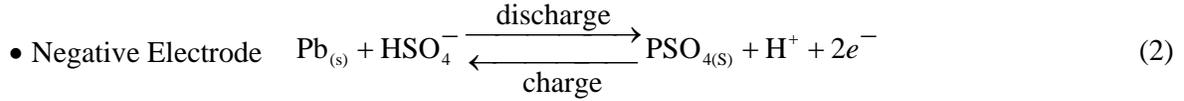
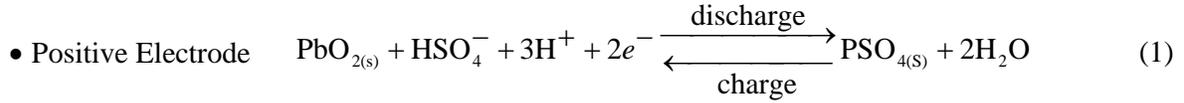
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## Introduction

A typical lead-acid cell without separator is shown schematically in Figure 1 which consists of the following regions: a lead-grid collector at  $x=0$ ; a positive  $PbO_2$  electrode; electrolyte reservoir negative  $Pb$  electrode; and finally, a lead-grid collector at  $x=l$ . During charge and discharge, the following electrochemical reactions



According to the main electrochemical reactions of lead-acid batteries, sulfuric acid is produced and consumed in the positive and negative electrodes during charge and discharge. However, the rate of production and consumption in positive electrode is much faster than the negative electrode, due to its faster reaction rate. This fact, results to a non-uniform acid concentration across the cell width as can be seen in Figure 2. Considering the charge process, acid is produced in electrodes, which sinks under the action of gravity force, since the acid close to the electrode surfaces is more concentrated and heavier. The diluted lighter acid at the center of reservoir rises according to the continuity law. The whole process leads to movement of the acid and makes a free convection which is one of the main mechanisms of mass transfer. The free convection plays an important role in generation of acid stratification which in turn results in non-uniform cell reactions and electrode utilization. This phenomenon reduces the performance and thus, the life-time of the battery.

To numerically investigate the acid stratification, electrochemical governing equations of the battery dynamics should be coupled with the equations of conservation of mass and momentum. Alavyoon et al. [1] studied this phenomenon experimentally and theoretically. Gu et al. [2] introduced a complete set of equations required to simulate the acid stratification. This article is basically based on the same principles of ref [2] with minor modifications.

## Mathematical Modeling

In flooded lead-acid batteries, only main reactions (equations (1) and (2)) exist and all the side reactions are neglected. The governing equations of the flooded lead-acid battery are introduced in [2] and the final equations are summarized in Table 1. These equations construct a closed system to obtain the main primitive variables i.e. 1) potential distribution in solid electrode  $\varphi_s$ , 2) potential distribution in electrolyte  $\varphi_l$ , 3) acid concentration  $c$ , 4) velocity vector  $\vec{v}$  and 5) pressure distribution  $p$ . The definition of the terms and equations are fully detailed in [2-4].

As it can be seen, convection is one of the mechanisms of mass transport (Eq. (5)) and the acid concentration is the only source of acid movement in momentum equation (Eq. (6)). In this equation, the term  $\beta(c - c_0)$  is the driving force for the natural free convection in the reservoir.

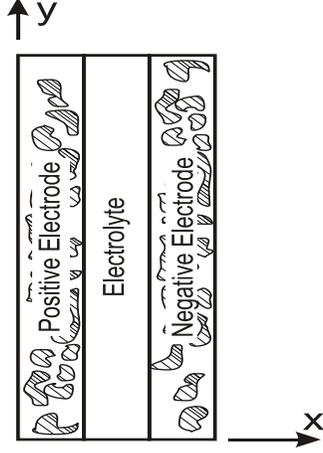


Figure 1: Schematic illustration of the model.

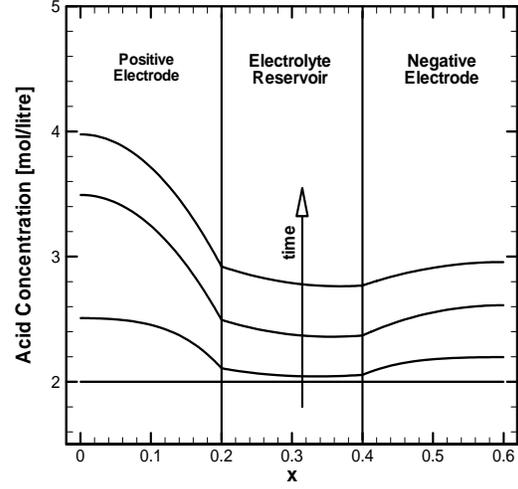


Figure 2: A typical acid concentration during charge.

Table 1: Governing equations of flooded lead-acid battery.

Conservation of Charge in Electrode	$\nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) - Aj = 0$	(3)
Conservation of Charge in Electrolyte	$\nabla \cdot (k^{\text{eff}} \nabla \phi_l) + \nabla \cdot (k_D^{\text{eff}} \nabla (\ln c)) + Aj = 0$	(4)
Conservation of Species	$\frac{\partial(\varepsilon c)}{\partial t} + \vec{v} \cdot \nabla c = \nabla \cdot (D^{\text{eff}} \nabla c) + a_2 \frac{Aj}{2F}$	(5)
Conservation of Linear Momentum	$\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} = -\frac{1}{\rho} \nabla p + \nabla \cdot (\nu \nabla \vec{v}) + g[1 + \beta(c - c_0)] + \frac{\nu}{K} (\varepsilon \vec{v})$	(6)
Conservation of Mass	$\nabla \cdot \vec{v} = 0$	(7)

Wherever, the concentration is less than the reference concentration (i.e.  $c_0$ ) this term will be negative and forces the adjacent electrolyte to move upward and wherever acid concentration is less than the reference, this term will be positive and forces the adjacent electrolyte to sink downward. Therefore, the coupling between the electrochemical and fluid dynamic governing equations is via the acid concentration gradient. If the mass and momentum conservation equations are omitted from the model, the acid will be stagnant and convection will not exist. The resulting model will not be able to predict the stratification of acid.

## Numerical Simulation

To numerically solve the governing equations, they should be discretized into a computational domain. In this study, the Semi Implicit Method for Pressure Linked Equation (SIMPLE) introduced by Patankar [5] is used. A non-uniform computational grid is generated to reduce the computational cost and improve the accuracy where the gradients of variables are higher.

## Results

To illustrate the capability of the model on capturing the acid stratification, a slow charge experiment is simulated. The experiment is carried on by Alavyoon et al. [1], in which a lead-acid cell is charged in a 2 M sulfuric acid with a constant current of 9.4334 mA/cm<sup>2</sup>. Both electrodes have a thickness of 0.2 cm and are 0.2 cm apart. The height of the electrodes is 3.2 cm and no separator exists. The plates were discharged in a 5M sulfuric acid with a constant current of 9.434 mA/cm<sup>2</sup> until the cell reaches the cut-off voltage 1.5 V. Then the electrodes were put in a 2 M sulfuric acid for 48 hours to insure that the concentration becomes uniform throughout the cell width.

During the discharge process, some properties such as acid concentration, porosity, SoC, etc., are not constant and vary across the cell. During the rest process, acid concentration becomes uniform across the cell because of diffusion. Other parameters, however, remain the same. In the

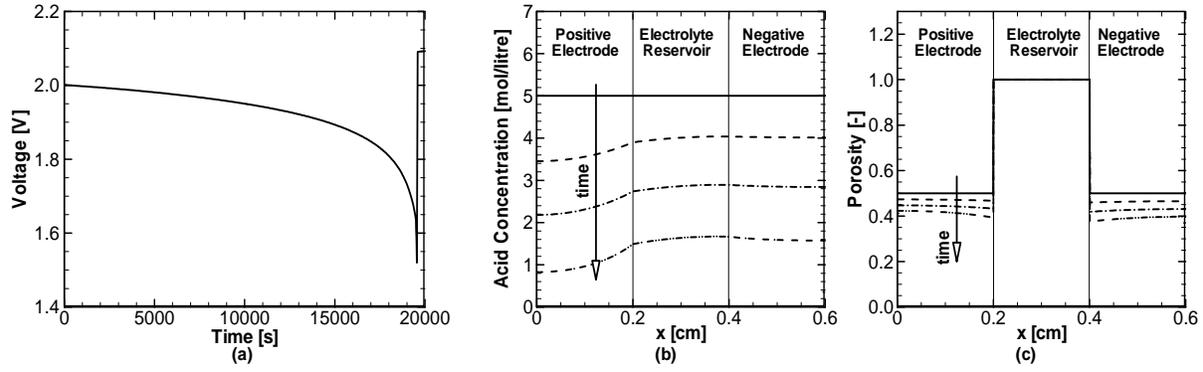


Figure 3: Discharge process, (a) Voltage vs. time, (b) acid concentration variation, (c) variation of SoC, (d) variation of porosity at time levels  $t=0, 5000, 10000, 15000$  and  $19600$  s.

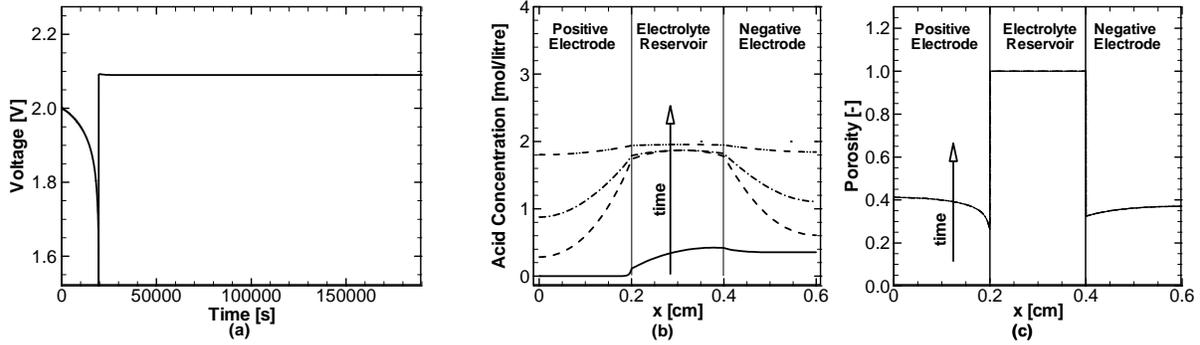


Figure 4: Rest process, (a) Voltage vs. time, (b) variation of acid concentration, (c) variation of SoC, (d) variation of porosity at time levels  $t=1960, 20100, 21000, 25000$  and  $192000$  [s].

present study, the whole preparation process is simulated with a one-dimensional model. The one-dimensional model can be obtained by neglecting the fluid dynamic equations [4]. Figure 3 shows the voltage variation vs. time and acid concentration and porosity gradients during discharge at different time levels. Figure 4 shows the same parameters during the rest process. The initial conditions for charge process are taken as that in Figure 4 for two-dimensional charge simulation.

Figures 5 and 6 show the velocity vectors and acid concentration contours at time levels 15 min and 30 min respectively. From the figures, one can see that as it was expected, the electrolyte sinks near the electrode surfaces and moves upward in the middle of the reservoir. This movement develops the convection mechanism of mass transfer as it can be seen (Figure 5(b) and 6(b)) flattens the concentration gradient in the electrolyte reservoir. The velocity profile after 15 min charging at the half height of the cell is shown in Figure 7 compared with the experimental data [1]. This figure shows that the result of the present model has a good agreement with the experiment. Figure 8 shows the acid concentration gradient at the same cross section compared with acid concentration gradient obtained from one-dimensional code which neglects the electrolyte movement. As it can be seen, the velocity profile (Figure 7) influences the concentration profile and almost has made it flattened across the reservoir.

## Discussion

In this article, the effect of electrolyte movement on acid stratification was studied. This has been performed by coupling the fluid flow governing equations (Navier-Stokes equations) and electrochemical equations. The results show that free convection results in convective mass transfer and plays an important role in acid stratification. In this study, the whole preparation process for two-dimensional computation was also simulated which shows the capability of the current model for simulation of discharge, rest and charge processes.

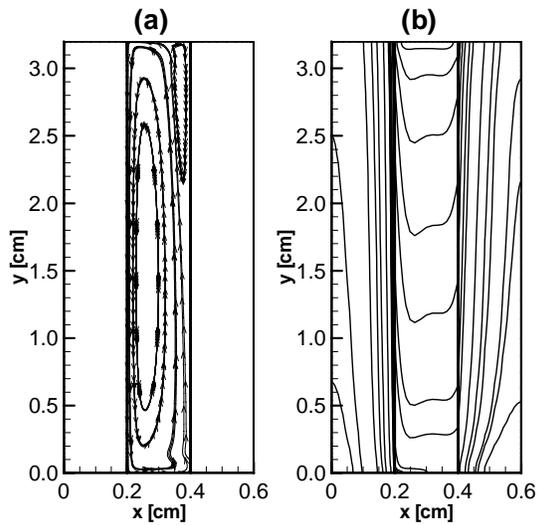


Figure 5: Simulation results at  $t=15$  min (a) Velocity vectors and (b) acid concentration contours.

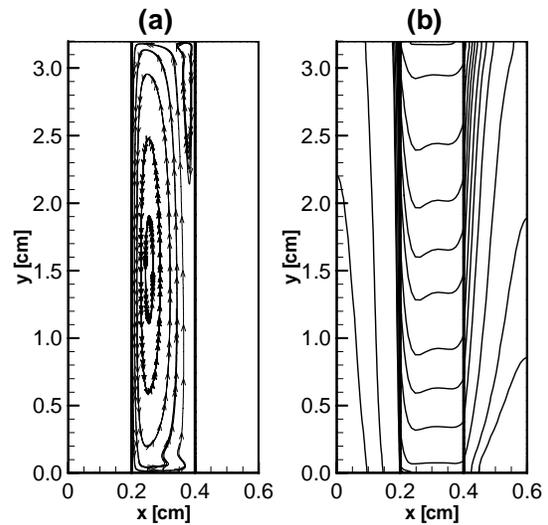


Figure 6: Simulation results at  $t=30$  min (a) Velocity vectors and (b) acid concentration contours.

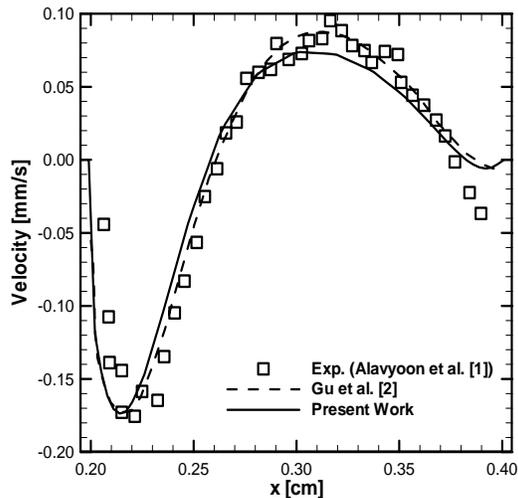


Figure 7: Comparison of velocity profile with experiment after 15 min at the height of 1.6 cm.

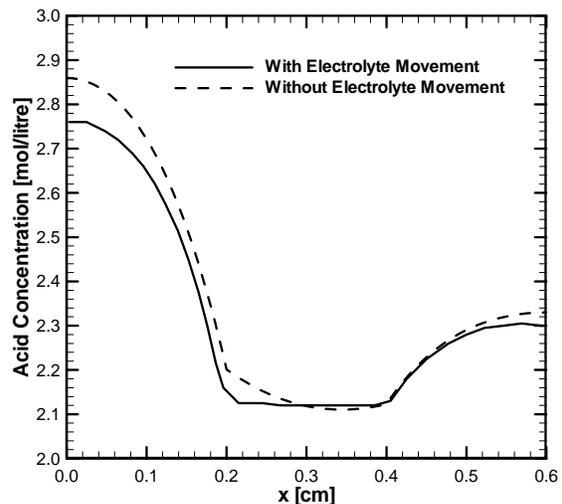


Figure 8: Comparison of acid concentration gradient with and without electrolyte movement.

### Acknowledgement

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