Short communication

Numerical simulation of lead-acid batteries using Keller–Box method

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Abstract

In this paper, the Keller–Box method has been applied to the coupled one-dimensional electrochemical transport equations in order to simulate lead-acid batteries numerically. The advantages and disadvantages of this method have been discussed. The results indicate that the Keller–Box method is a suitable method for integration of electrochemical transport equations both in integrated and multi-region formulation. The boundary conditions and interface conditions (in the case of multi-region approach) can be implemented easily and require no special routine (for off-diagonal terms). In addition, the effect of acid concentration dependency of open circuit voltage has also been investigated.
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Keywords: Electrochemical transport equations; Computational fluid dynamics; Keller–Box method; Open circuit voltage

1. Introduction

Computational fluid dynamics (CFD) can be used to solve the governing equations of battery dynamics. This makes significant progress toward an insightful understanding of battery performance and detailed characteristics of its behavior. To have a good understanding of battery performance, different design parameters of the lead-acid batteries should be analyzed. Traditionally, these design parameters are evaluated experimentally which is time consuming and costly. Numerical simulation of the battery is an alternative to evaluate the battery performance and optimizing the design parameters. Another advantage of the CFD modeling is that it can be used as a virtual model for battery with which the necessary parameters for dynamic modeling must be obtained. In this method, the partial differential system of equations governing the behavior of the battery dynamics is solved numerically using advanced CFD techniques.

The governing equations of the battery dynamics [1] have been developed in different forms. Gu et al. [6] proposed a multi-region system of equations to simulate the battery dynamics. In this model, each region was studied separately, i.e. for each region (Fig. 1) a system of transport equations was given. To relate the regions at their common boundaries, a set of interface conditions was also proposed. This system of equations was solved numerically with finite-difference method. To

keep second-order accuracy at interfaces, off-diagonal elements appear in the dicretized system of equations destroying the tridiagonal nature of the resulting matrix. Fan and White [2] proposed an auxiliary routine called MBAND to treat the off-diagonal elements without losing the second-order accuracy.

Later, Gu et al. [7] introduced an integrated formulation for battery dynamics. In this approach, the whole battery was considered as a model volume and the transport equations were derived for the whole cell volume. With this formulation, the interface condition is no longer necessary. The proposed system of equations was solved numerically by means of finite-volume method.

In this study, the Keller–Box method is used for numerical integration of transport equations of battery dynamics. This method can be implemented on both approaches. The Keller–Box method is an implicit method which is second-order accurate in both time and space. Since only two points are involved in discretization, a nonuniform grid can be used without any difficulty. In addition, the Keller–Box method works both with the unknown functions and their derivatives at each grid point simultaneously. This property would ease numerical formulation as well as implementation of boundary conditions and interface conditions (if any). The disadvantage of the method is the size of coefficient matrix increases due to introducing the derivatives as unknowns which increases the computational cost. But, once the solution is obtained, the derivatives of unknown functions are available and no new further formulation is needed to obtain the derivatives from the unknown functions as is done in the other numerical methods. The results are compared with

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Nomenclature

a	coefficient
A	specific electroactive area ($cm^2\,cm^{-3}$)
c	acid concentration ($mol\,cm^{-3}$)
D	diffusion coefficient ($cm^2\,s^{-1}$)
F	Faraday constant, $96,487\,C\,mol^{-1}$
I	applied current density ($A\,cm^{-2}$)
j	transfer current density ($A\,cm^{-2}$)
k	conductivity of liquid ($S\,cm^{-1}$)
m	molality of the acid ($mol\,kg^{-1}$)
t	time (s)

Greek letters

ε	porosity
σ	conductivity of solid matrix ($S\,cm^{-1}$)
ϕ	electric potential (V)

Subscripts and superscripts

D	pertinent to diffusion
eff	effective, corrected for tortuosity
ex	exponent in the effective property
l	liquid solution
o	initial value
s	solid phase

the results of previous investigators. Furthermore, the effect of acid concentration dependency of open circuit potential on cell voltage and acid consumption is studied.

1.1. Governing equations

A typical lead-acid cell is shown schematically in Fig. 1 and consists of the following regions: a lead-grid collector at $x=0$ which is at the center of the positive electrode; a positive PbO_2 electrode; electrolyte reservoir; a porous separator; a negative Pb electrode; finally, a lead-grid collector at $x=l$ which is at the center of the negative electrode. The positive and negative electrodes
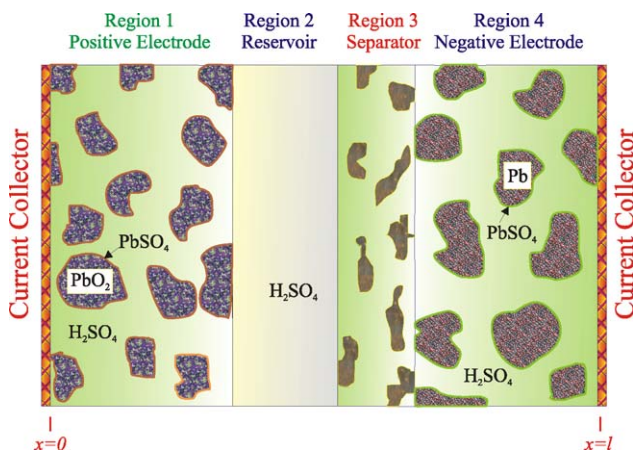

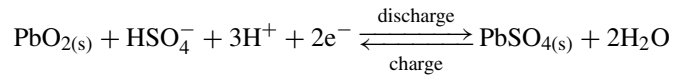Fig. 1. Schematic illustration of a lead-acid cell.
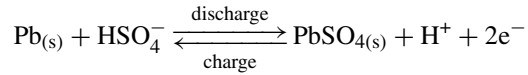
Table 1
Governing equations of the battery dynamics

Conservation of charge in solid	$\nabla \cdot (\sigma^{eff}\nabla\phi_s) - Aj = 0$
Conservation of charge in liquid	$\nabla \cdot (k^{eff}\nabla\phi_l) + \nabla \cdot (k_D^{eff}\nabla(\ln c)) + Aj = 0$
Species conservation	$\frac{\partial(\varepsilon c)}{\partial t} = \nabla \cdot (D^{eff}\nabla c) + a_2\frac{Aj}{2F}$

consist of porous solid matrices whose pores are flooded by a binary sulfuric acid, H_2SO_4. The model is assumed to be one-dimensional perpendicular to the face of the electrode. During charge and discharge, the following electrochemical reactions occur in the positive and negative electrodes:

PbO_2 electrode:

$$PbO_{2(s)} + HSO_4^- + 3H^+ + 2e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} PbSO_{4(s)} + 2H_2O$$

Pb electrode:

$$Pb_{(s)} + HSO_4^- \underset{charge}{\overset{discharge}{\rightleftarrows}} PbSO_{4(s)} + H^+ + 2e^-$$

The governing equations with one-dimensional assumption are summarized in Table 1. In these equations, the effective properties, i.e. σ^{eff}, k^{eff} and k_D^{eff}, are corrected to account for electrode porosity as follows:

$$\sigma^{eff} = \sigma(1-\varepsilon)^{ex}, \qquad k^{eff} = k\varepsilon^{ex}, \qquad k_D^{eff} = k_D\varepsilon^{ex} \qquad (1)$$

where $(1-\varepsilon)$ is the volume fraction of conducting solid matrix.

Details of the governing equations can be found in [7] except that the equilibrium potential ΔU_{PbO_2} (at $25\,°C$) is also added to the model from an empirical equation presented by Bode [8].

$$\Delta U_{PbO_2} = 1.9228 + 0.147519 \log(m) + 0.063552 \log^2(m)$$
$$+ 0.073772 \log^3(m) + 0.033612 \log^4(m) \qquad (2)$$

where m is the molality of the sulfuric acid. Another empirical equation based on literature data at $25\,°C$ is used to relate concentration, c, to molality, m

$$m = 1.00322 \times 10^3 c + 3.55 \times 10^4 c^2 + 2.17 \times 10^6 c^3$$
$$+ 2.06 \times 10^8 c^4 \qquad (3)$$

1.2. Initial/boundary conditions

To solve the system of equations, initial and boundary conditions for the primary variables are necessary. The initial condition for acid concentration is $c=c_o$. Two approaches can be taken to find the initial conditions for potential in solid and liquid which are:

(1) Solve the first two steady equations given in Table 1 with constant $c=c_o$.
(2) Solve the whole system with a very small time step, i.e. 10^{-4} s.

The appropriate boundary conditions at $x = 0$ and l for c and ϕ_l are $\frac{\partial c}{\partial x} = \frac{\partial \phi_l}{\partial x} = 0$; the boundary condition for potential in solid is $\phi_s = 0$ or V for a given voltage, or $-\sigma^{\text{eff}} \frac{\partial \phi_s}{\partial x} = I$ for a prescribed current density. Positive values of I refer to charging, whereas negative values of I denote discharging.

2. Numerical procedure

To solve the system of equations by the Keller–Box method, it should be first converted into a system of first-order partial differential equations [3]. The details of the Keller–Box method can be found in standard CFD books and have been applied frequently in boundary layer theory [4]. By defining $\frac{\partial \phi_s}{\partial x} = u$, $\frac{\partial \phi_l}{\partial x} = v$ and $\frac{\partial c}{\partial x} = w$ and substituting into the system of equations, one can obtain:

$$\begin{cases} \dfrac{\partial(\sigma^{\text{eff}} u)}{\partial x} = +Aj \\[2mm] \dfrac{\partial \phi_s}{\partial x} = u \\[2mm] \dfrac{\partial(k^{\text{eff}} v)}{\partial x} = -Aj - \dfrac{\partial}{\partial x}\left(\dfrac{k_D^{\text{eff}} w}{c}\right) \\[2mm] \dfrac{\partial \phi_l}{\partial x} = v \\[2mm] \varepsilon \dfrac{\partial c}{\partial t} = \dfrac{\partial(D^{\text{eff}} w)}{\partial x} + (a_2 - a_1 c)\dfrac{Aj}{2F} \\[2mm] \dfrac{\partial c}{\partial x} = w \end{cases} \tag{4}$$

where c, ϕ_s and ϕ_l, related by the well-known Butler–Volmer equation:

$$j = i_o \left(\frac{c}{c_{\text{ref}}}\right)^\gamma \left\{ \exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(\frac{-\alpha_c F}{RT}\eta\right) \right\}$$

and overpotential η is defined as $\eta = \phi_s - \phi_l - \Delta U_{\text{PbO}_2}$ for positive electrode and $\eta = \phi_s - \phi_l$ for negative electrode, where ΔU_{PbO_2} is open circuit potential. The system of Eq. (4) together with proper initial and boundary conditions mentioned above makes a complete set of equations. To solve this system of equations, it should be linearized and iteratively solved (for example, using Newton iteration).

The transport equations for potentials in solid and liquid are elliptic partial differential equations (PDE). Mathematically, an elliptic PDE with Newman type of boundary conditions in all of the boundaries of domain has a unique solution if: (a) it satisfies the compatibility equation and (b) at least one value is known inside the domain.

Compatibility equation in battery dynamics is interpreted as the conservation of charge. It means that the amount of charge that enters the cell at one electrode should leave the cell at the other electrode. To have a unique solution, one should specify a value for potential in one point; for example, $\phi_s = 0$ at the center of the positive electrode. Then, ϕ_l at the center of positive electrode can be obtained using compatibility equation [5]. All the potentials then are calculated related to this reference potential. Without this reference point, a unique solution cannot be obtained.
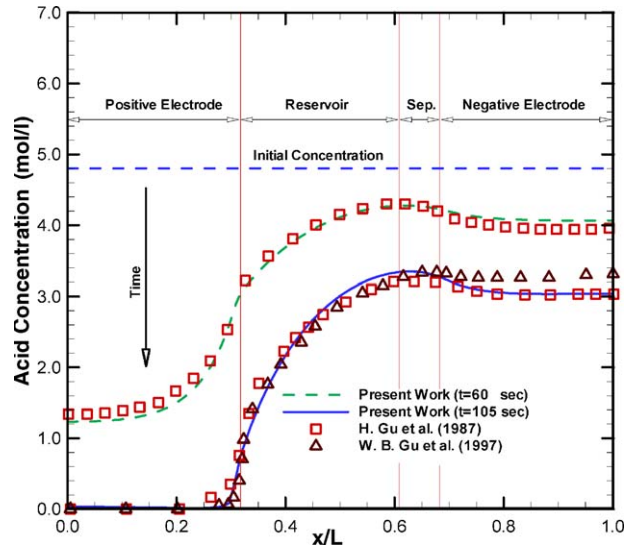

Fig. 2. Distribution of acid concentration across the cell during discharge.

3. Results

The system of governing equations has been solved using the Keller–Box method. To verify the above-mentioned procedure, the discharge problem of a lead-acid battery has been simulated. This sample has been studied by Gu et al. [6] and reproduced by Gu et al. [7]. All the necessary parameters are the same as the ones used by Gu et al. [7].

In Fig. 2, the variations of acid concentration in time levels 0, 60 and 105 s are shown. The figure indicates that the results of present simulation agree well with the previous studies [6,7]. As it can be seen, when the cell reaches cut-off voltage (i.e. $t = 105$ s), the acid is totally consumed in positive electrode. But in the negative electrode, the acid is not totally consumed which means the negative electrode is overdesigned.

Fig. 3 shows the variations of charge across the electrode at different times. The results show that during the battery
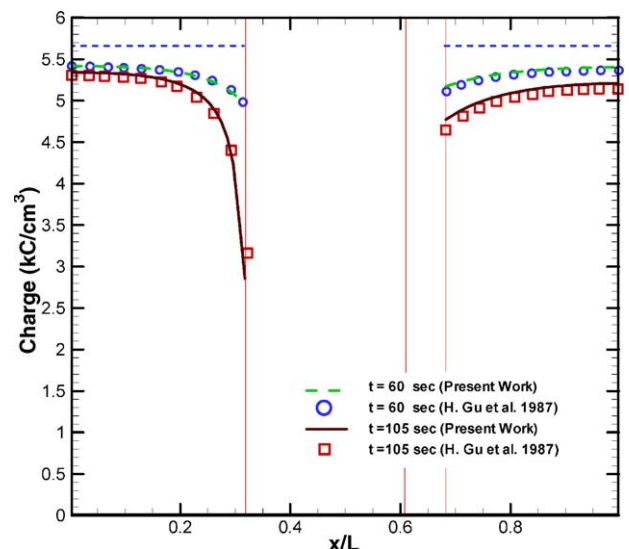

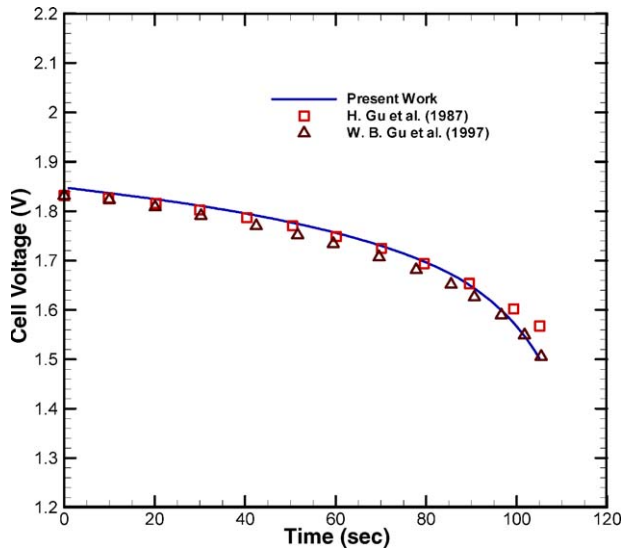Fig. 3. Distribution of charge across the cell during discharge.

Fig. 4. Voltage of the cell during discharge.

Fig. 6. Effect of modeling the open circuit potential on acid concentration using Bode relation.

discharge, the amount of charge in both electrodes decreases. But at the end of discharge, the electrodes still have a lot of charge which means these electrodes are not fully utilized.

Fig. 4 shows the simulated voltage of the battery cell versus time. The results of the present work match very well with the results of the other researchers [6,7].

In the previous works [6,7], the open circuit potential (ΔU_{PbO_2}) was taken to be constant. To get a more accurate simulation, the effect of acid concentration dependency of ΔU_{PbO_2} is considered by introducing Bode relation [8] into the code. Fig. 5 shows the comparison between the two results. As it can be seen, by considering the effect of acid concentration dependency of the open circuit potential, the voltage of the cell drops faster and cut-off voltage occurs at approximately 90 s instead of 105 s.

Fig. 6 shows the acid concentration profile in both cases. At the end of discharge, the acid is not totally consumed in both
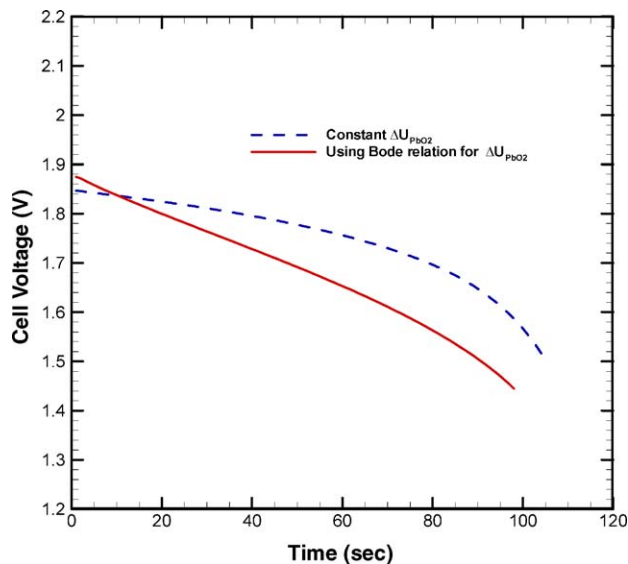
electrodes (comparing to the first simulation) and it means that both electrodes are overdesigned.

4. Conclusions

The system of transport equations of battery dynamic has been solved numerically using the Keller–Box method. The results indicate that the Keller–Box method is a suitable method for integration of electrochemical transport equations both in integrated and multi-region formulation. The boundary conditions and interface conditions (in the case of multi-region approach) can be implemented easily and require no special routine. The developed computer code is capable of simulating lead-acid batteries. Comparisons were made between the simulation results and the results of other researchers. Good agreement was obtained and in addition, the effect of acid concentration dependency of open circuit voltage was also investigated.

Fig. 5. Effect of modeling the open circuit potential on cell voltage using Bode relation.

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