One-Dimensional Modeling of Lead-Acid Batteries Using CFD

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Why Modeling?

- Deliverable Energy (kWh)
- Deliverable Power (W)
- Deliverable Charge (Ah)
- SOC
- Voltage
- Current
- Time
- Temperature
- Load Prediction
- Age, Condition
Methods of Modeling

- Dynamic Modeling
  - Based on equivalent circuit
  - Dynamic behavior of Battery
  - Requires many experimental data
  - Simulation of *TIME* dependant variables

- CFD Modeling
  - Stands for *Computational Fluid Dynamics*
  - Solving transport equations numerically
  - Simulation of battery in *TIME* and *SPACE*
  - CFD can provide *INPUTS* for dynamic modeling
  - Investigating the effect of different parameters on battery performance
Lead-Acid Battery Model

Region 1: Positive Electrode
Region 2: Reservoir
Region 3: Separator
Region 4: Negative Electrode

$\text{PbO}_2$
$\text{H}_2\text{SO}_4$
$\text{PbSO}_4$
$\text{Pb}$
$\text{H}_2\text{SO}_4$
History

• Hirman Gu et al. (1987)
  – Transport equations in each region
  – Requires matching conditions at boundaries
  – Off-diagonal blocks at boundaries
  – Using a special routine for off-diagonal blocks
  – Finite Difference Method

• W. B. Gu et al. (1997)
  – Integrated coupled electrochemical model
  – No need for matching conditions at boundaries
  – Finite Volume Method
Lead-Acid Battery Model

Region 1: Positive Electrode
Region 2: Reservoir
Region 3: Separator
Region 4: Negative Electrode

$x=0$

Current Collector

$\text{PbSO}_4$

$\text{PbO}_2$

$\text{H}_2\text{SO}_4$

$\text{Pb}$

$\text{PbSO}_4$

$\text{H}_2\text{SO}_4$

Current Collector

$x=l$
History

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  – Transport eqs. in each region
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The diagram illustrates the structure of a lead-acid battery model. It consists of four regions:

- **Region 1**: Positive Electrode, containing PbO₂, and H₂SO₄
- **Region 2**: Reservoir, containing H₂SO₄
- **Region 3**: Separator, containing PbSO₄
- **Region 4**: Negative Electrode, containing Pb and PbSO₄

The battery is divided into two sections by the separator, labeled with x=0 and x=l, indicating the boundaries between the regions.
History

• Hirman Gu et al. (1987)
  – Transport eqs. in each region
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Coupled Electrochemical and Transport Processes in Lead-Acid Batteries

– Conservation of Charge in Solid
\[ \nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) - A j = 0 \]

– Conservation of Charge in Liquid
\[ \nabla \cdot (k^{\text{eff}} \nabla \phi_l) + \nabla \cdot (k^{\text{eff}} D \nabla (\ln c)) + A j = 0 \]

– Species (ionic) Conservation
\[ \frac{\partial (\epsilon c)}{\partial t} + v \cdot \nabla c = \nabla \cdot (D^{\text{eff}} \nabla c) + a_2 \frac{A j}{2 F} \]

– Conservation of Momentum
\[ \frac{\partial v}{\partial t} + v \cdot \nabla v = -\frac{1}{\rho} \nabla p + \nabla \cdot (\nu \nabla v) + g[1 + \beta(c - c_o)] + \frac{\nu}{K}(\epsilon v) \]

– Conservation of Mass
\[ \nabla \cdot v = 0 \]
One-Dimensional Assumptions

- Conservation of Charge in Solid
  \[ \nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) - Aj = 0 \]

- Conservation of Charge in Liquid
  \[ \nabla \cdot (k^{\text{eff}} \nabla \phi_l) + \nabla \cdot (k_D^{\text{eff}} \nabla (\ln c)) + Aj = 0 \]

- Species (ionic) Conservation
  \[ \frac{\partial (\epsilon c)}{\partial t} + v \cdot \nabla c = \nabla \cdot (D^{\text{eff}} \nabla c) + a_2 \frac{Aj}{2F} \]

- Conservation of Momentum
  \[ \frac{\partial v}{\partial t} + v \cdot \nabla v = \frac{1}{\rho} \nabla p + \nabla \cdot (\nu \nabla v) + g[1 + \beta(c - c_0)] + \frac{\nu}{K}(c\nu) \]

- Conservation of Mass
  \[ \nabla \cdot v = 0 \]
Governing Equations (1-D)

- Conservation of Charge in Solid

\[
\frac{\partial}{\partial x} \left( \sigma \frac{\partial \phi_s}{\partial x} \right) = +A_j
\]

- Conservation of Charge in Liquid

\[
\frac{\partial}{\partial x} \left( k \frac{\partial \phi_l}{\partial x} \right) = -A_j - \frac{\partial}{\partial x} \left( \frac{k}{c} \frac{\partial c}{\partial x} \right)
\]

- Species (ionic) Conservation

\[
\epsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) + a_2 \frac{A_j}{2F} - c \frac{\partial \epsilon}{\partial t}
\]
Boundary Conditions

- Potential in Solid

\[ \phi_s = 0, \quad V \quad \text{or} \quad -\sigma^{\text{eff}} \frac{\partial \phi_s}{\partial x} = I \]

- Potential in Liquid

\[ \frac{\partial \phi_l}{\partial x} = 0 \]

- Acid Concentration

\[ \frac{\partial c}{\partial x} = 0 \]
Initial Conditions

- Initial acid concentration
  \[ c = c_0 \]
- Initial potential in solid and liquid
  1. Solve steady state equations.
     \[
     \frac{\partial}{\partial x} \left( \sigma \frac{\partial \phi_s}{\partial x} \right) = +A_j \quad \text{and} \quad \frac{\partial}{\partial x} \left( k \frac{\partial \phi_l}{\partial x} \right) = -A_j - \frac{\partial}{\partial x} \left( \frac{k}{c} \frac{\partial c}{\partial x} \right)
     \]
  2. Solve the whole system up to a small time step (i.e. $10^{-4}$ sec.)
Numerical Difficulties

• All equations are highly non-linear
• Non-linear source terms

\[ j = i_o \left( \frac{c}{c_{ref}} \right)^\gamma \left\{ \exp \left( \frac{\alpha_a F}{RT} (\phi_s - \phi_l - \Delta U_{PbO_2}) \right) - \exp \left( \frac{\alpha_c F}{RT} (\phi_s - \phi_l - \Delta U_{PbO_2}) \right) \right\} \]

• The system of equations is highly stiff
• All equations are highly coupled together
• All boundary conditions are of Newman type (singularity occurs)
Numerical Scheme

• Method of use: Keller-Box
• Specifications
  – Delta formulation
  – Implicit
  – 2\textsuperscript{nd}-order accurate in TIME and SPACE
• Advantages
  – Calculation of the functions and their derivative simultaneously
  – Leads to a block tridiagonal matrix
  – Can be used on nonuniform grid
  – Large band of stability
  – Ease of programming
Numerical Procedure

- Convert the system to first order system of Equations
- Linearization of the system
- Solve the system iteratively using Newton’s iteration method
Converting to 1-st order System

- Defining

\[ \frac{\partial \phi_s}{\partial x} = u \]
\[ \frac{\partial \phi_l}{\partial x} = v \]
\[ \frac{\partial c}{\partial x} = w \]
The System of Equations

- We have

\[
\begin{align*}
\frac{\partial (\sigma_{\text{eff}} u)}{\partial x} &= + A j \\
\frac{\partial \phi_s}{\partial x} &= u \\
\frac{\partial (k_{\text{eff}} v)}{\partial x} &= - A j - \frac{\partial}{\partial x} \left( \frac{k w}{c} \right) \\
\frac{\partial \phi_l}{\partial x} &= v \\
\frac{\partial c}{\partial c} &= \frac{\partial (D_{\text{eff}} w)}{\partial x} + (a_2 - a_1 c) \frac{A j}{2F} \\
\frac{\partial c}{\partial x} &= w
\end{align*}
\]
Discretization

• Time independent equations are differenced at location \( i-1/2 \) and time level \( n \)

\[
\frac{\partial \Psi}{\partial x} \bigg|_{i-1/2}^n = \frac{\Psi_i^n - \Psi_{i-1}^n}{\Delta x_i}
\]

• Time dependent equations are differenced at location \( i-1/2 \) and time level \( n-1/2 \)
Block tridiagonal system

\[
\begin{bmatrix}
[B][C] \\
[A][B][C] \\
[A][B]
\end{bmatrix}

\begin{bmatrix}
[X_1] \\
[X_2] \\
[X_3] \\
\vdots \\
[X_n]
\end{bmatrix}

= \begin{bmatrix}
[RHS_1] \\
[RHS_2] \\
[RHS_3] \\
\vdots \\
[RHS_n]
\end{bmatrix}

\begin{bmatrix}
\delta \
\delta \phi_s \\
\delta \frac{\partial \phi_s}{\partial x} \\
\delta \phi_i \\
\delta \frac{\partial \phi_i}{\partial x} \\
\delta c \\
\delta \frac{\partial c}{\partial x}
\end{bmatrix}

=X_n
Simulated Sample

• H. Gu et al. (1987)
  – Discharge ($I=-340$ mA)
Potential in Liquid

![Graph showing potential in liquid](image-url)
Potential in Solid

![Graph showing potential distribution in a solid model. The x-axis represents the distance from the positive electrode to the negative electrode, while the y-axis represents the potential difference. The graph includes time markers at 1 sec, 50 sec, 75 sec, and 105 sec, showing the potential distribution at these times.]
Simulated Acid Concentration

![Graph of simulated acid concentration over time and position. The graph shows the concentration profile with distinct sections labeled as Positive Electrode, Reservoir, Separation, and Negative Electrode. Initial concentration is indicated by a dashed line. The x-axis represents position (x/L), and the y-axis represents acid concentration (mol/l). Different markers and lines represent data from the present work and previous studies by H. Gu et al. (1987) and W. B. Gu et al. (1997).]
Charge in Battery

Charge (kC/cm³)

\[ \frac{x}{L} \]

- \[ t = 60 \text{ sec (Present Work)} \]
- \[ t = 60 \text{ sec (H. Gu et al. 1987)} \]
- \[ t = 105 \text{ sec (Present Work)} \]
- \[ t = 105 \text{ sec (H. Gu et al. 1987)} \]
Simulated Cell Voltage

![Graph showing simulated cell voltage over time with data points and comparisons to previous work by H. Gu et al. (1987) and W. B. Gu et al. (1997).]
Effect of over potential on cell voltage

Constant $\Delta U_{\text{PbO}_2}$

Using Bode relation for $\Delta U_{\text{PbO}_2}$

![Graph showing the effect of over potential on cell voltage](image-url)
Effect of over potential (Acid Concentration)

- Positive Electrode
- Reservoir
- Sep.
- Negative Electrode
- Initial Concentration
- Time

Acid Concentration (mol/l)

- Constant $\Delta U_{\text{PbO}_2}$
- Using Bode relation for $\Delta U_{\text{PbO}_2}$
Conclusions

• Transport equations of battery are solved using Keller-Box method
• The results show good agreement with previous calculations
• This model can be used for simulation and design of batteries
  – The model costs less compared to experiment
  – Modeling is much faster than experiment
Future works

- Simulating more complicated models including other phenomena
  - Oxygen evolution in VRLA
  - Coupling energy equation for investigating the effect of temperature on battery behavior
- Simulation of two-dimensional model
- Obtaining necessary parameters for dynamic modeling
Thanks