Lecture 13

Influence of electrode material composition on self-discharge of lead-acid battery

Goal of the Lecture

The goal of this lecture is to analyze how the thermodynamics, kinetics, phase transformations, and electrode material composition of lead–acid batteries contribute to discharge behavior under high load, low load, and zero-current (self-discharge) conditions. Using a COMSOL-based lead–acid battery model, students will understand how electrode composition controls side reactions, porosity changes, gas evolution, and overall battery ageing mechanisms.

Lecture Objectives

By the end of this lecture, students will be able to:

1. ***Explain** the main electrochemical reactions in PbO_2 and Pb electrodes and their dependence on electrolyte concentration.*
2. ***Analyze** high-rate, low-rate, and open-circuit behavior using a multiphysics lead–acid model.*
3. ***Describe** self-discharge mechanisms driven by electrode composition, porosity evolution, and gas evolution.*
4. ***Interpret** how concentration-dependent material properties (e.g., electrolyte conductivity, diffusion coefficient) influence battery performance.*
5. ***Evaluate** modelling outputs such as voltage relaxation, SOC decay, and equilibrium potential shifts to determine long-term stability.*

Lead-acid batteries are widely used as starter batteries for traction applications, such as for cars and trucks. The reason for this wide usage of lead-acid batteries is their low cost in. combination with their performance robustness for a broad range of operating conditions. However, one drawback of this battery type is that the inherent thermodynamics of the battery chemistry causes the battery to self-discharge over time.

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Below we will discuss a lead-acid battery model which explains behaviour of battery at high (1200 A) and low (3 A) discharge rates, and the long-term self discharge behavior with no applied external current (0 A).

Figure 1 shows the 1D model geometry. There are four domains: the positive porous electrode, the reservoir, the separator, and the negative porous electrode. The model uses the Lead-Acid Battery interface for solving for the following unknown variables: ϕ_s - the electronic potential; ϕ_l - the ionic potential; ε - the porosity (electrolyte volume fraction) of the porous electrodes, and c - the electrolyte concentration.

Figure 1. Modeled geometry. The model is in 1D in the x direction.

The outer boundary of the negative electrode is grounded and a discharge current is applied to the positive end terminal.

Three different discharge currents are simulated in three separate studies. The first study performs a C/20-discharge — a constant current in order to obtain a full discharge in 20 hours, followed by a one hour relaxation period at zero external load. The second study simulates a high load 20C-discharge during 1 minute. In the third study the external load is set to zero and the simulation time is extended to one year to study the self-discharge behavior [1].

The main electrode reaction in the positive (PbO2) electrode during discharge is following:

$$PbO_2(s) + HSO_4^- + 3H^+ + 3e^- = PbSO_4(s) + H_2O$$

The equilibrium potential of the electrode depends on the electrolyte concentration as shown in Figure 2.

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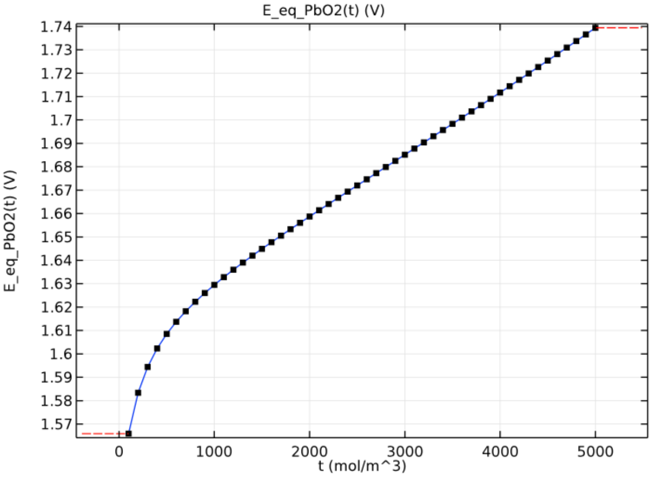

Figure 2. Equilibrium potential of the PbO_2 reaction as a function of electrolyte concentration in the positive electrode.

The combination of an aqueous solution and a high potential results in oxygen gas evolution at the positive electrode according to:

$$H_2O = \frac{1}{2} O_2(gas) + 2H^+ + 2e^-$$

The main discharge reaction for the negative (Pb) electrode is:

$$Pb(s) + HSO_4^- = PbSO_4(s) + H^+ + 2e^-$$

with a equilibrium potential that depends on the electrolyte concentration as shown in Figure 3.

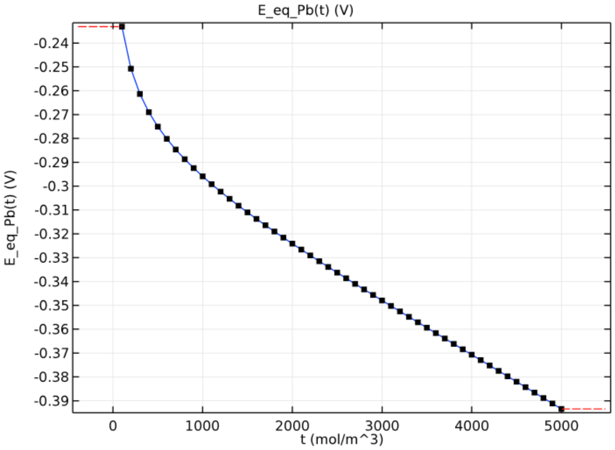

Figure 3. Equilibrium potential of the Pb reaction as a function of electrolyte concentration in the negative electrode.

This dependence of the equilibrium potential on the electrolyte concentration, for both discharge reactions, is present in [2].

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The low operating potential of the negative electrode results in hydrogen evolution according to:

$$2H^+ + 2\ e^- = H_2(\text{gaseous}) \qquad E_0=0V$$

For the gas evolution reaction, Butler-Volmer type kinetic expressions are used. For the main discharge reactions the default discharge reactions of the Lead-Acid Battery interface (in COMSOL Multiphysics) are used.

The electrolyte diffusion coefficient and the electrolyte conductivity vary with the concentration according to Figure 4 and Figure 5, respectively.

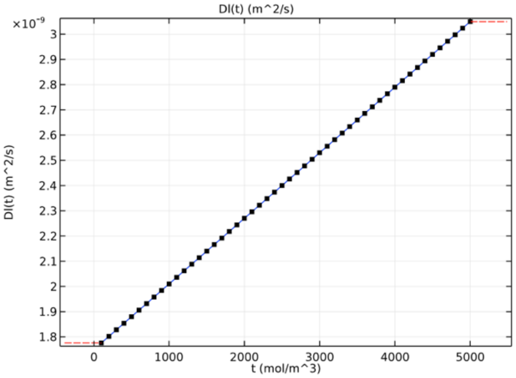

Figure 4. Electrolyte diffusion coefficient as a function of electrolyte concentration.

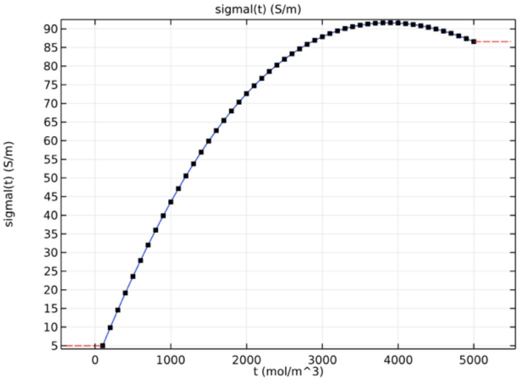

Figure 5. Electrolyte conductivity as a function of electrolyte concentration.

Figure 6 shows the polarization plot of the cell. At the shut-off of the current the cell voltage first rises swiftly due to the sudden absence of activation and resistive losses, but after this the potential continues to rise slightly during a relaxation period.

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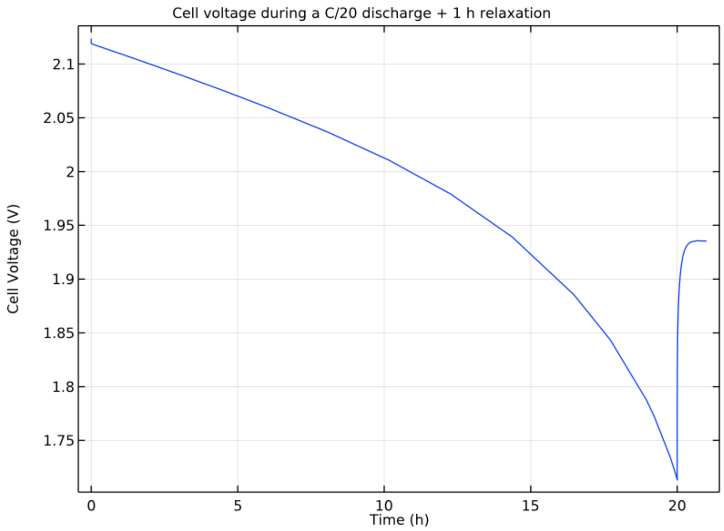

Figure 6. Cell voltage versus time for a C/20 discharge + 1-hour resting period.

Figure 7 compares the discharge curves of the three simulations on a log t scale. The 20C cell voltage is much lower than the C/20 curve due to higher internal resistive and activation losses.

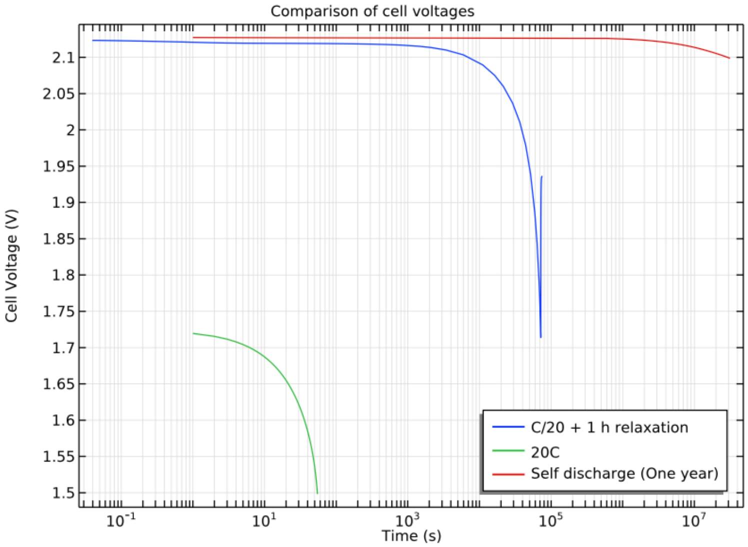

Figure 7. Discharge curves (cell voltage versus time) for the three simulations.

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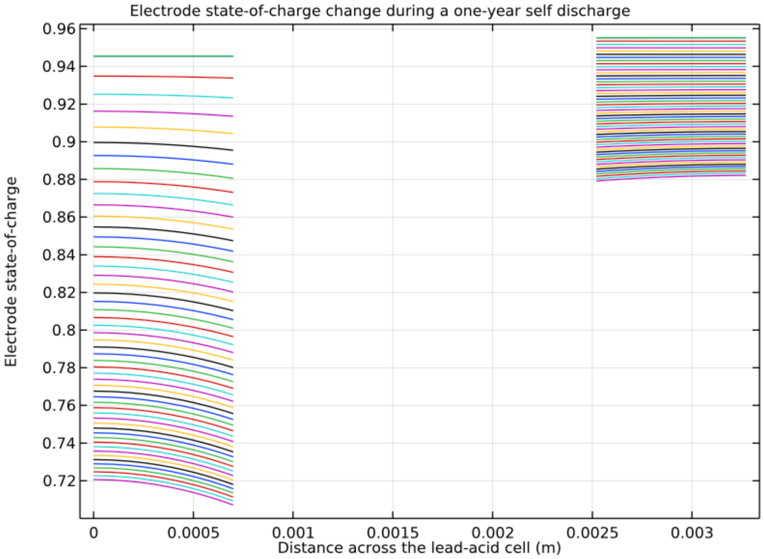

Figure 8. State-of-charge during the one-year self-discharge simulation.

The self-discharge curve indicates a moderate cell voltage drop after a year, Figure 8 shows that the state-of-charge of the positive electrode has decreased by over 25% during the same period.

Questions for Self-Examination

1. What thermodynamic and kinetic factors contribute to self-discharge in lead–acid batteries?
2. Why do concentration-dependent equilibrium potentials (positive and negative electrodes) influence long-term open-circuit voltage?
3. Explain why PbO_2 is more susceptible to side oxidation reactions than Pb.
4. What roles do H_2 and O_2 gas evolution play in long-term capacity loss?
5. Why does the state-of-charge decrease even at zero external current?
6. How do porosity changes in the positive and negative electrodes affect diffusion and reaction rates?
7. What are the key differences between C/20 and 20C discharge curves?
8. Why does voltage increase immediately after stopping current in the C/20 experiment?

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Self-Study Assignment
Assignment Title:

COMSOL Simulation of High-Rate, Low-Rate, and Zero-Current Self-Discharge Behavior in a Lead–Acid Battery

Objective:
To simulate three discharge scenarios (C/20, 20C, and open-circuit self-discharge) using the Lead–Acid Battery interface in COMSOL Multiphysics and analyze how electrode composition and electrolyte concentration dependence influence battery voltage, SOC, and ageing behavior.

Tasks

1. Model Setup

- Use the COMSOL Application Library model:
  Lead-Acid Battery, 1D (Batteries & Fuel Cells Module).
- Keep the default four-domain layout:
  - Positive porous electrode
  - Electrolyte reservoir
  - Separator
  - Negative porous electrode

Solve for:

- Electronic potential (ϕ_s)
- Ionic potential (ϕ_l)
- Porosity $\varepsilon(x,t)$
- Electrolyte concentration $c(x,t)$

2. Define Operating Conditions

Perform three separate studies:

1. **Low-rate discharge (C/20)**
   - Constant current for ~20 hours
   - 1-hour relaxation at 0 A
2. **High-rate discharge (20C)**
   - Large current for ~1 minute
3. **Self-discharge simulation**
   - Zero external current ($I = 0$)

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  - Simulation time: up to 1 year
  - Observe SOC decay and voltage changes

3. Material Composition Effects
Modify model parameters:

- **Electrode porosity** (initial ε_0)
- **Pb and PbO_2 kinetic constants for main reactions**
- **Gas-evolution kinetics**
- **Electrolyte conductivity c-dependent functions**

Perform sensitivity analysis for:

- Porosity (±30%)
- Exchange current density (i_0) variations
- Gas evolution rate variations

4. Output Plots
Generate:

1. **Voltage vs time** for all three scenarios
2. **Equilibrium potentials** vs electrolyte concentration (reproduce behavior of Figures 2 & 3)
3. **Electrolyte diffusion coefficient and conductivity** vs concentration (Figures 4 & 5)
4. **State-of-charge decay** for self-discharge
5. **Porosity evolution** in electrodes
6. **Gas evolution distribution** (if using side reactions)

5. Interpretation
Discuss:

- Why high-rate discharge produces much lower terminal voltages.
- Mechanisms of voltage rebound during relaxation.
- Why SOC decreases by >25% over a year under open-circuit conditions.
- How concentration-dependent properties accelerate self-discharge.
- Impact of porosity degradation and $PbSO_4$ layer formation.

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Learning Outcomes

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 4: Describe the key structures and performance criteria of chemical and electrochemical energy storage systems.	**ID 4.2:** Explain the influence of material composition and electrochemical deposition mechanisms on self-discharge and capacity loss.	Students will analyze how electrode composition and side reactions influence self-discharge in lead–acid batteries.

References

1. M. Cugnet, S. Laruelle, S. Grugeon, B. Sahut, J. Sabatier, J.M. Tarascon, and A. Oustaloup, “A Mathematical Model for the Simulation of New and Aged Automotive Lead-Acid Batteries,” J. Electrochemical Soc., vol. 156, pp. A974–A985, 2009.
2. COMSOL Multiphysics. Application Library path: Batteries_and_Fuel_Cells_ Module/Batteries,General/pb_acid_battery_1d

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