Lecture #12 Modeling of Chemical Power Sources: Lead-Acid and Lithium-Ion Batteries

Goal

This lecture introduces students to the modeling of two major classes of chemical power sources—lead-acid batteries and lithium-ion batteries. We focus on electrochemical reaction mechanisms, mass transport, charge-transfer kinetics, and governing equations required to simulate charge–discharge behavior, performance limits, and degradation pathways.

Chemical power sources, such as lead-acid and lithium-ion batteries, are widely used for energy storage in applications ranging from portable electronics to electric vehicles and grid stabilization. Accurate modeling of these systems is essential for optimizing their performance, lifetime, and safety.

This lecture focuses on modeling the electrochemical processes in lead-acid and lithium-ion batteries, including charge-discharge dynamics, mass transport, and reaction kinetics.

Lead-Acid Batteries

Lead-acid batteries are one of the oldest and most established battery technologies. They consist of lead dioxide (PbO_2) as the positive electrode, sponge lead (Pb) as the negative electrode, and sulfuric acid (H_2SO_4) as the electrolyte.

The main reactions during discharge are:

• At the positive electrode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
• At the negative electrode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Modeling focuses on the balance of species in the electrolyte and electrodes, described by:

$$\partial C/\partial t = \nabla \cdot (D_{eff} \nabla C) + R(C)$$

Where C is the concentration of species, D_eff is the effective diffusion coefficient, and R(C) is the reaction rate.

Lithium-Ion Batteries

Lithium-ion batteries are the dominant technology for portable electronics and electric vehicles due to their high energy density and long cycle life. They consist of a graphite negative electrode, a lithium metal oxide positive electrode (e.g., $LiCoO_2$), and a liquid electrolyte containing lithium salts.

The main reactions during discharge are:

- At the positive electrode: $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
- At the negative electrode: $xLi^+ + xe^- + C_6 \rightarrow Li_xC_6$

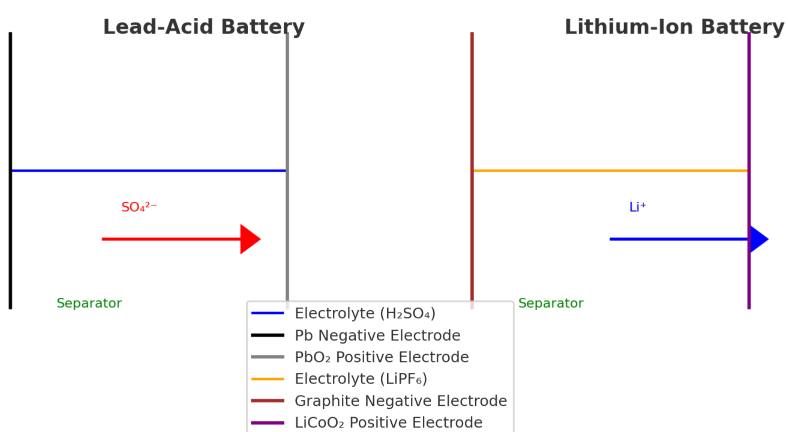
Modeling involves solving coupled equations for lithium ion diffusion, charge transfer, and potential distribution, such as:

$$\partial C\_Li^+/\partial t = \nabla \cdot (D\_Li^+ \nabla C\_Li^+)$$

$$i = i_0 [\exp(\alpha F\eta/RT) - \exp(-\beta F\eta/RT)]$$

Where η is the overpotential, and i_0 is the exchange current density.

Illustration: Lead-Acid and Lithium-Ion Battery Schematic



The above schematic compares the structures of lead-acid and lithium-ion batteries. Note the differences in electrode materials, electrolyte compositions, and ion transport mechanisms.

Example Problem

Consider a lithium-ion battery with a graphite electrode and a lithium cobalt oxide cathode. The diffusion coefficient of lithium ions in the electrolyte is 10^{-6} cm^2/s, and the reaction rate constant is 0.1 s^{-1}. Calculate the concentration profile of lithium ions during discharge.

Conclusion

Modeling chemical power sources involves understanding the coupled electrochemical, transport, and kinetic processes that occur in the system. Lead-acid batteries rely on well-understood reactions and diffusion in aqueous electrolytes, while lithium-ion batteries involve more complex intercalation and ion transport mechanisms.

These models are crucial for designing better batteries, improving energy efficiency, and extending cycle life.

Learning Outcomes

By the end of this lecture, students will be able to:
1. Explain the fundamental electrochemical reactions in lead-acid and lithium-ion batteries (related to LO 4, ID 4.4–4.6).
2. Describe mass transport processes and effective diffusion in porous battery electrodes (related to LO 4, ID 4.5–4.6).
3. Formulate governing equations for concentration, potential, and current distribution during charge–discharge cycles (related to LO 4, ID 4.4–4.5).

Questions and Self-Study Assignments

1. Write the discharge reactions for lead-acid and lithium-ion batteries and compare their mechanisms.
2. Define the effective diffusion coefficient and explain why it is needed for battery modeling.

3. Derive the mass balance equation for sulfate ions in a lead-acid battery.
4. Explain how solid-state diffusion in Li-ion particles affects rate capability.
5. Using the Butler–Volmer equation, describe how the overpotential changes at high discharge currents.
6. Read a recent (≤3 years) research article on Li-ion or Pb-acid modeling. Summarize:
- equations used
- assumptions in the model
- key findings

References

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2. Pryor, R.W. Multiphysics Modeling Using COMSOL 5 and MATLAB. Mercury Learning, 2015. Modeling electrochemical systems, porous electrodes, battery simulations in COMSOL.
3. Pereira, A.C.; Inacio, M.; Pereira, H.; Paiva, I. Modelling in Science and Engineering: A Brief Introduction to COMSOL Multiphysics 5. 2019.