Identification of Dominant Mechanisms for Capacity Fade of Lithium-Ion Batteries


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Motivation

Electrochemical power sources are expected to play a vital role in future applications of automobiles, power storage, military, mobile applications, and space. Lithium-ion chemistry has been identified as the preferred candidate for high-power/high-energy secondary batteries and commercial batteries of up to 75 Ah have been manufactured. Applications for batteries range from implantable cardiovascular defibrillators (ICDs) operating at 10 µA current to hybrid vehicles requiring pulses of 100 A.

Introduction

Lithium-ion battery, chemistry and reactions

LiCoO₂ \rightarrow Li⁺ + CoO₂⁻ + xLi⁺ + xe⁻

xLi⁺ + xe⁻ + 6C \rightarrow Li₄C₆

Modeling Approaches

Improper Utilization

Capacity Fade

Optimal Design

Parameter Estimation

Model Refinement

- Based on combination of various applied mathematics techniques including order reduction, exact solution of dynamic equations, dimensionless analysis, perturbation, novel symbolic solutions, etc.
- Guided by numerical and experimental experiences.
- Yields models that are accurate and efficient (CPU time < 100 milliseconds).

Transport Models

35 PDEs (400 DAEs)

Predict process and internal variables accurately, no trial by parameter estimation and optimization.

Empirical-circuit Models

Real time prediction of process variables. Fails (or wrong prediction) at many operating conditions, can't predict capacity fade leads to under-utilization.

Stochastic Models

Behavior in nanoscale, microscale should be observable. Cannot be coupled with transport models to observe variations. Too slow.

Stochastic Models

Unknown input model is not ideal for parameter variables accurately.

Predicts process and internal variables accurately. Good initial guess is needed.

Transport Models

10 PDEs (480 DAEs).

Yields models that are accurate and efficient (CPU time < 100 milliseconds).

Guided by numerical and experimental experiences.

Dimensionless analysis, perturbation, novel symbolic solutions, etc.

including order reduction, exact solution of large matrix equations, polynomial chaos expansions.

Transport Models

Motivation

Nonlinear Estimation Results (Jacobian based)

Bayesian Estimation Results

Parameter Estimation - Techniques

Gauss Newton Method

- Based on Jacobian calculation
- Iterative procedure
- Good initial guess is needed

Bayesian Estimation

- No need for Jacobian
- Uncertainty analysis – Markov Chain Monte Carlo method, polynomial chaos expansions

Mathematical Modeling of Capacity Fade

- Side Reactions: Represented by additional kinetic expressions, SEI layer growth: Rate of film resistance increase
- Tracking parameters with cycles (Discrete Empirical Approach)
- Track the variations in kinetic and transport parameters with cycle number

Capacity Fade Mechanisms

Composite negative electrode (Anode) - Separator - Composite positive electrode (Cathode)

Active Material (Li₄C₆)

Cu current collector

Al current collector

Electrolyte

Active material (LiMO₂)

Filler, Binder & Electrolyte

Li₄C₆ + CoO₂ - e⁻ → Li⁺ + CoO₂⁻ + xLi⁺ + xe⁻

Electrolyte decomposition (Reduction consuming salt)

and solvent species

Reversibility and Irreversible Self Discharge due to Superplastic Oxidation, etc.

Interfacial film formation.

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Nonlinear Estimation Results (Jacobian based)

Capacity fade for Quallion cells

Bayesian Estimation Results

Capacity fade prediction for Quallion data

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