Li-Ion Battery State of Health Electrothermal Model

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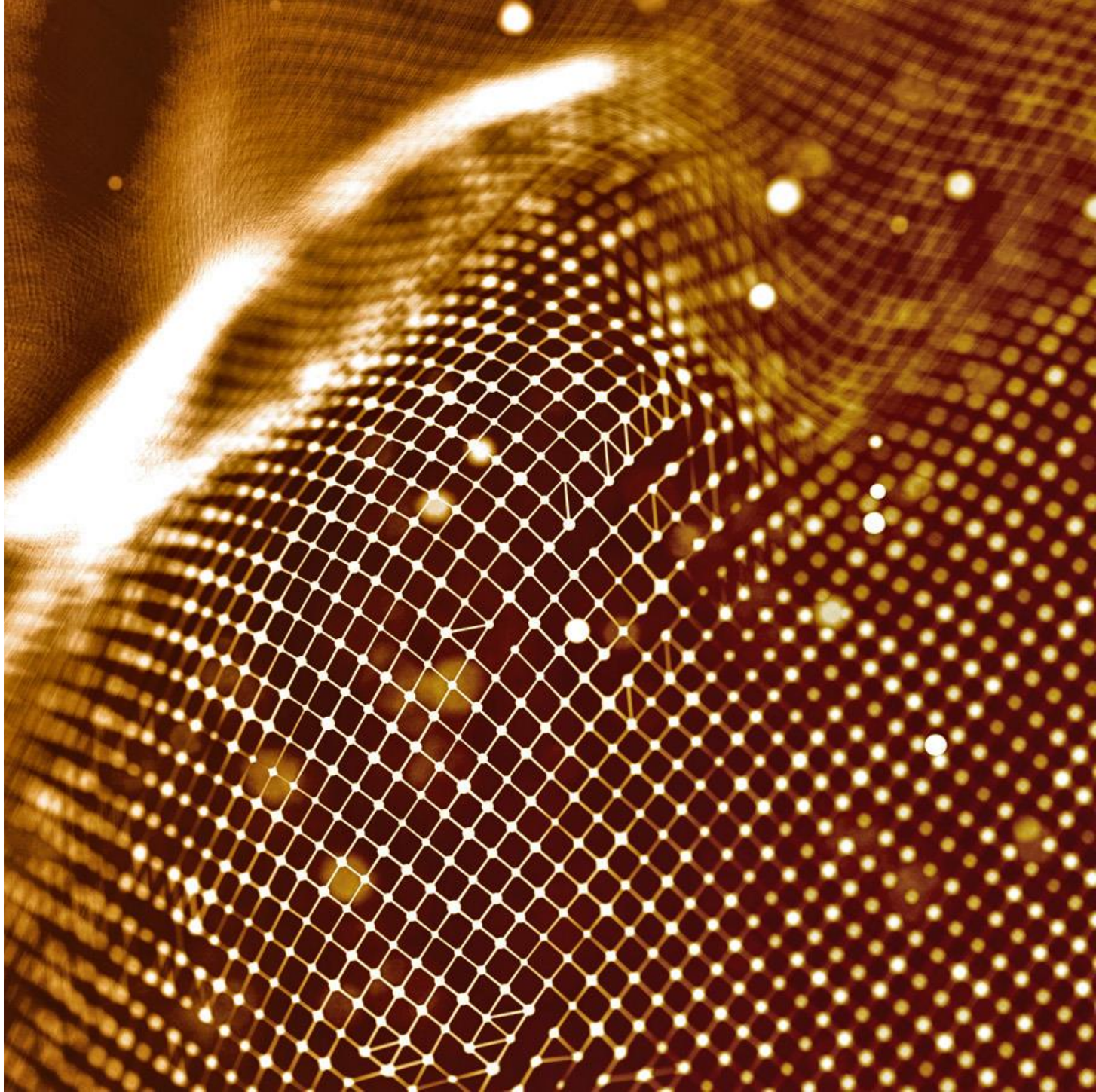
PNNL is operated by Battelle for the U.S. Department of Energy



Project Overview

Project Objectives

- Develop an electrothermal physics-based bottom-up model that predicts battery performance and degradation
- Develop a statistics-based top down model to predict battery performance and degradation, using insights from the bottom up model
- Identify the most important design and operating parameters that affect battery state of health
- Incorporate results into BSET to increase net benefits

Project Importance

- Multiple degradation mechanisms have been addressed in the electrothermal model
- Enables reliable prediction of battery performance degradation, which is critical to deployment in the grid
- Enables deployment of thermal and battery management strategies to optimize battery throughput
- Enhances battery safety by reliable prediction of battery internal temperature under various operating conditions

Project Relevance to US DOE-OE's Core Mission

- Global physics-based model provides high-level insights, helping enhance reliability of chemistry-specific models
- 0-d physics-based model provides further insights into specific degradation mechanisms further strengthening model fidelity
- Top Down model strengthened by Physics-Based Model findings for reliable degradation prediction using machine learning
- Enhances renewables penetration in the grid by deployment of reliable battery energy storage systems
- Improves grid resiliency and flexibility

Project Team

Pacific Northwest NATIONAL LABORATORY

Dr. Vilayanur Viswanathan	Modeling Strategies Lead
Alasdair Crawford	Battery Modeling
Dr. Daiwon Choi	Materials
Dr. Di Wu	BSET
Dr. Jan Alam	Power Systems
Patrick Balducci	Project Manager
David Reed	Project Manager
Vincent Sprenkle	Program Manager

External collaborators

Prof. Venkat Subramanian	University of Texas, Austin
Maitri Uppaluri	Graduate Student, University of Texas, Austin
Johan Sunqvist	COMSOL, Inc.

Project Metrics and Milestones

Milestones	Associated Tasks
Complete thermal coupling with Multi-Physics electrochemical model	1. Added SEI cracking and degradative effect of cathode dissolution on solid electrolyte interphase formation 2. Used literature parameter values for Global model for all chemistries 3. Global model for all chemistries used for selection of initial parameter values for single chemistry models 4. Verified approach with 0-d model 5. Validate with in-house data
Validate results with top down model and incorporate results of top down model into BSET	1. Update top down model with machine learning using in-house data for multiple chemistries using findings from Multi-Physics model 2. Develop a linear model to be fed into BSET
Publish and present results	

Project Metrics

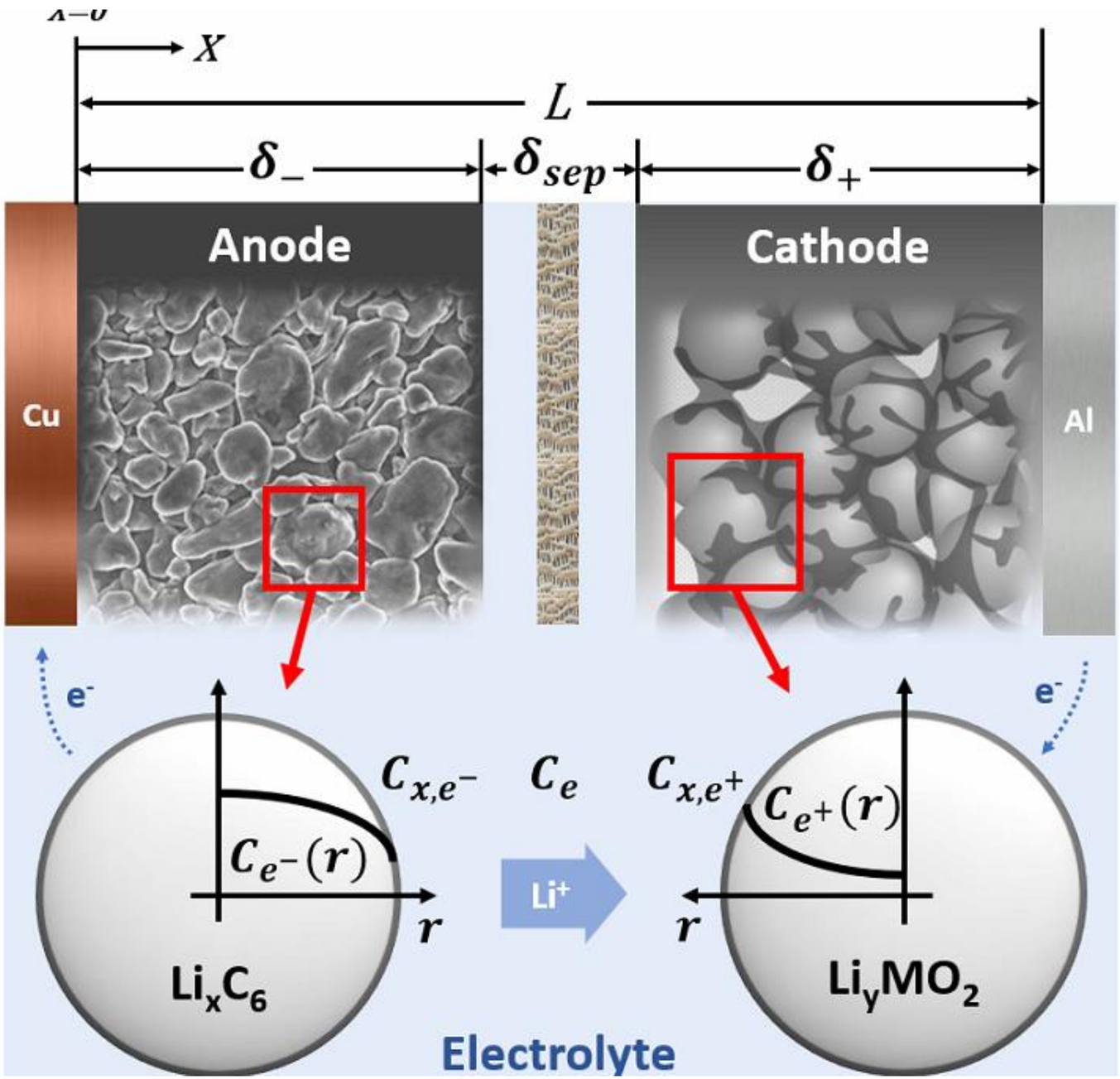
- Model uniqueness – Global model enables high level understanding of degradation mechanism and provides input to single chemistry model
- Model reliability – predicts capacity loss with RMSE of 1% after 500 cycles
- Enable 10 to 20% increased increase in renewables penetration due to increased reliability Battery Energy Storage
- Enable safe operation of battery storage

Challenges/Gaps

- Input parameters in the literature have a wide range
  - Extracting above parameters by optimization results in multiple combinations
    - Use combination of global model, chemistry-specific model and 0d model to overcome above limitation
- Computational time massive bottleneck for complicated models – need to identify most important mechanisms/interactions to model and most important parameters to optimize
- Not all degradation mechanisms considered
  - Solid electrolyte interphase (SEI) formation
  - SEI layer fracture
  - Lithium plating
    - Overestimates SEI formation
  - Graphite stress-related cracking
  - Cathode dissolution and its effect on SEI formation rate
  - Thermal coupling with all of above degradation mechanisms included

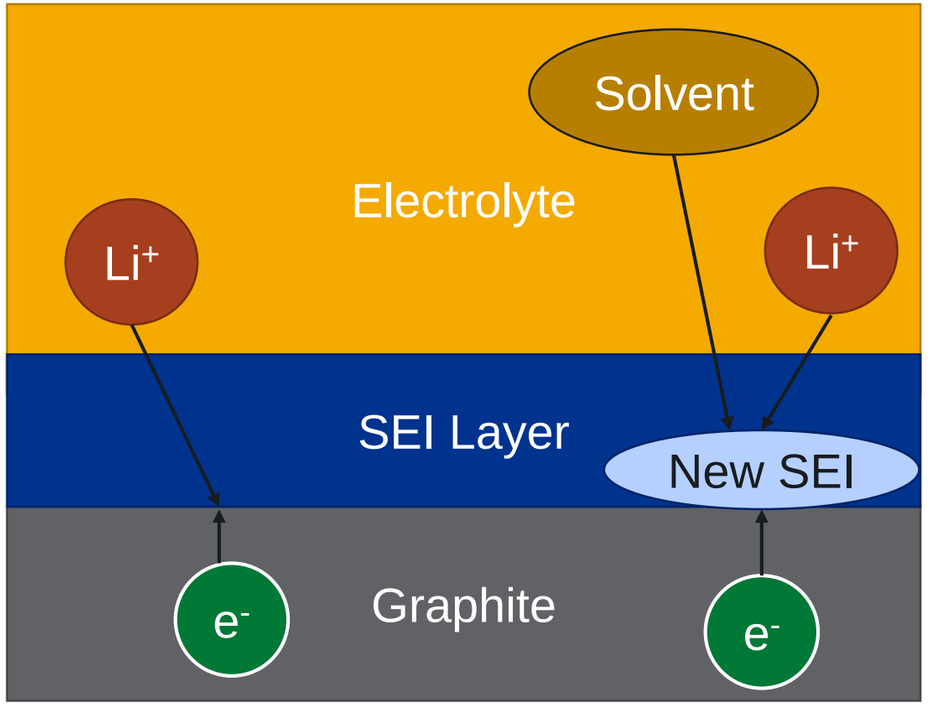
Electrothermal Model

- Modeling uses COMSOL finite element analysis software
- Newman's pseudo 2d model is foundation
- Degradation mechanisms modeled include
  - Li lost to SEI layer formation (uncracked and cracked)
  - Cathode dissolution
  - Graphite lost to mechanical stress
- Modeled heat generation and its interaction with the chemistry



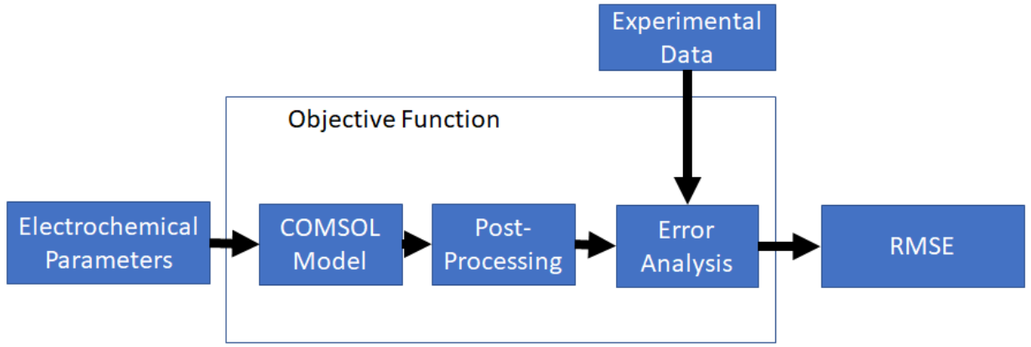
SEI Formation

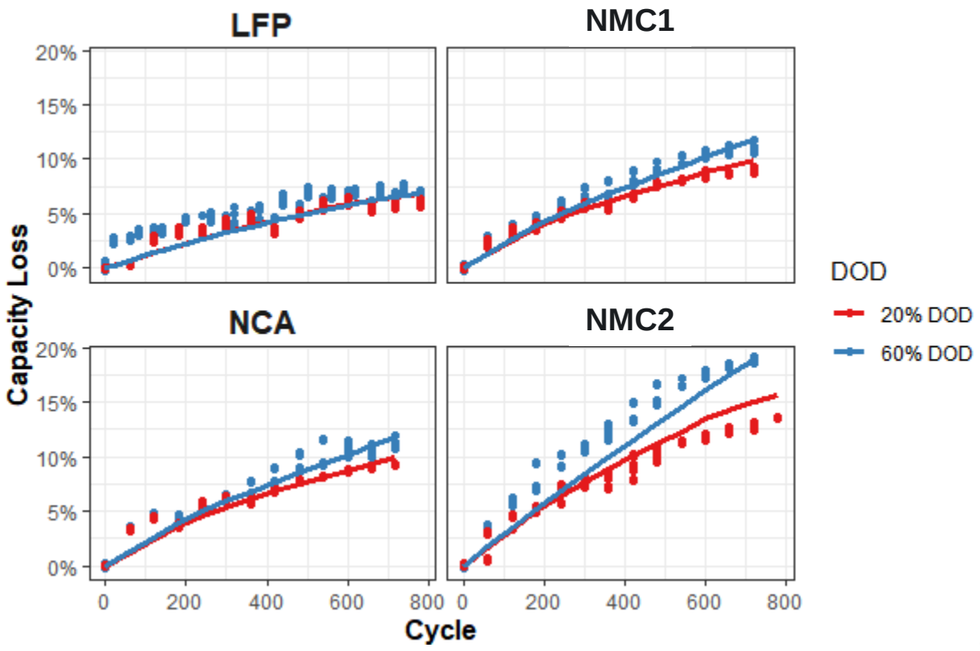
- SEI (solid electrolyte interphase) Layer formation is primary mechanism of capacity loss, lithium at the anode reacts with solvent to produce SEI. Capacity is lost from loss of lithium to SEI and increased internal resistance from SEI.
- Diffusion through SEI layer limits rate of SEI formation
- Graphite expands and contracts while charging and discharging, this cracks the SEI layer and speeds up formation
- Nickel dissolved in the cathode makes its way over and speeds up reaction



Model Validation Individual Chemistries

- Literature values for electrochemical parameters such as SEI formation current density, overpotential, solvent diffusion through SEI layer, SEI cracking rate, all vary over several orders of magnitude in literature – so we optimize to fit data. This allows us to get a good fit

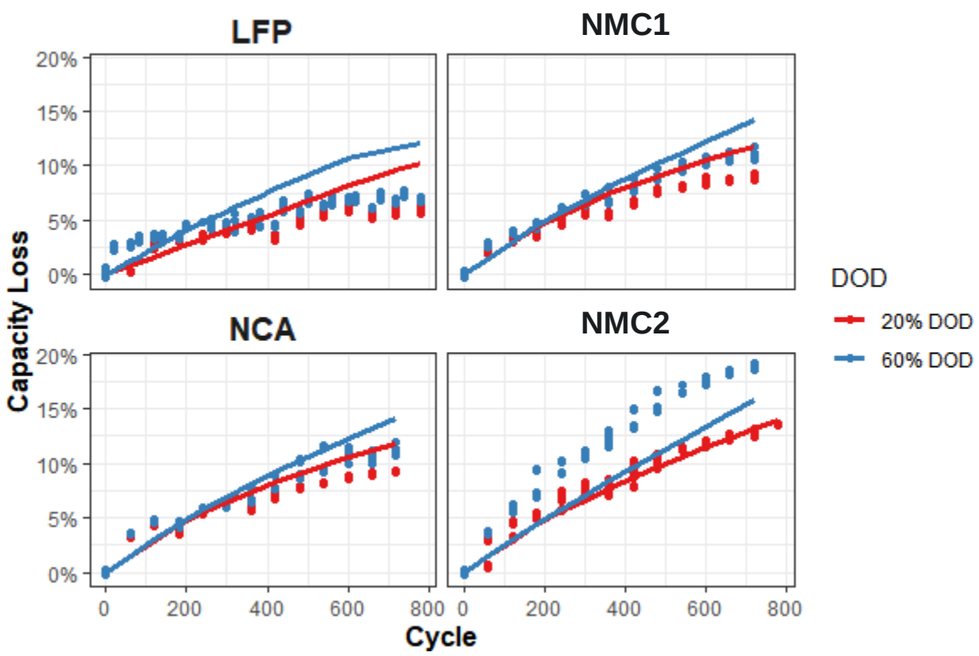




Capacity degradation data and model for cells doing peak shaving from 80-60% SOC (20% DOD) and 80-20% SOC (60% DOD)

Model Validation All Chemistries

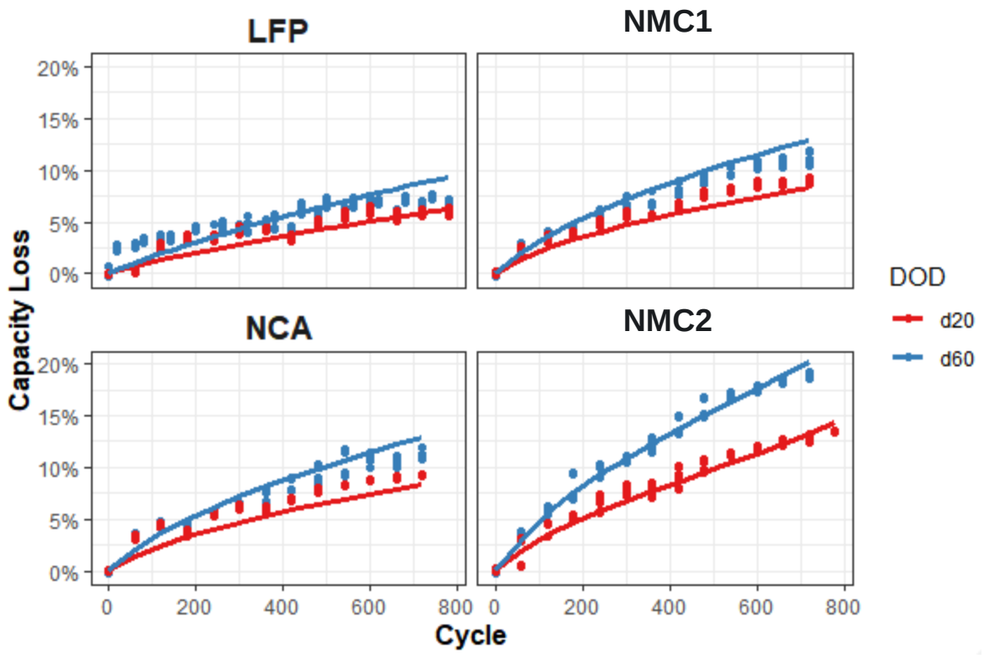
- Most models in literature use previous approach to fit one chemistry at a time – however since all chemistries have the same graphite anode, they should have the same graphite electrochemical parameters.
- Run optimization with this requirement. Cathode dissolution potential and effect of dissolved nickel stays the same but each chemistry has its own cathode dissolution rate.
- Fit is worse and shows room for improvement



Capacity degradation data and model for cells doing peak shaving from 80-60% SOC (20% DOD) and 80-20% SOC (60% DOD)

Model Validation 0D

- COMSOL model takes 1 hour per iteration – can take weeks to test hypothesises especially with high dimensional optimization.
- Build simplified 0D model – model electrochemical reactions very simply, ignore current distribution over thickness, heat generation, concentration inside particle. Calculate lithium lost. This gives a model that can simulate peak shaving test in 1 second instead of 1 hour – thousands of times faster
- Use the all chemistries approach – same graphite parameters - to see if our approach in COMSOL is mathematically feasible
- We can get a good fit with this model – suggests bottleneck with COMSOL model is computational time from model complexity.



Capacity degradation data and model for cells doing peak shaving from 80-60% SOC (20% DOD) and 80-20% SOC (60% DOD)

Top Down Modeling

- Several duty cycles were performed in house – baseline, peak shaving, frequency regulation, electric vehicle. Each service performed at various SOC and DOD. 3 cells per experiment. Total of 13 duty cycles over 4 chemistries with 3 cells each, 156 cells.
- A statistical model was built to predict battery performance based on its history – current, voltage, and interaction

$$\frac{dCaploss}{dt} = f(V, I, SOC)$$

- Model was evaluated based on out of sample error
- Insights from the bottom up model such as SEI cracking were incorporated

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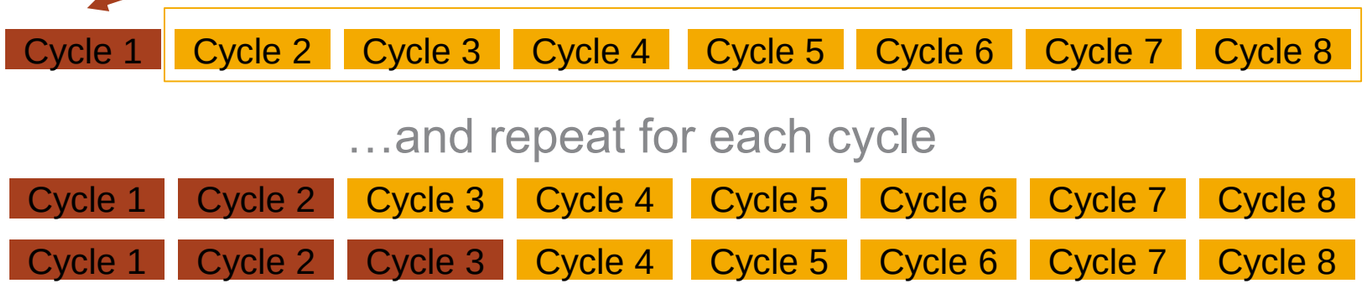
For this cycle, build model on
this data to predict this performance



…and repeat for each cycle

Top Down Modeling Results

- Final model:

Quadratic in current

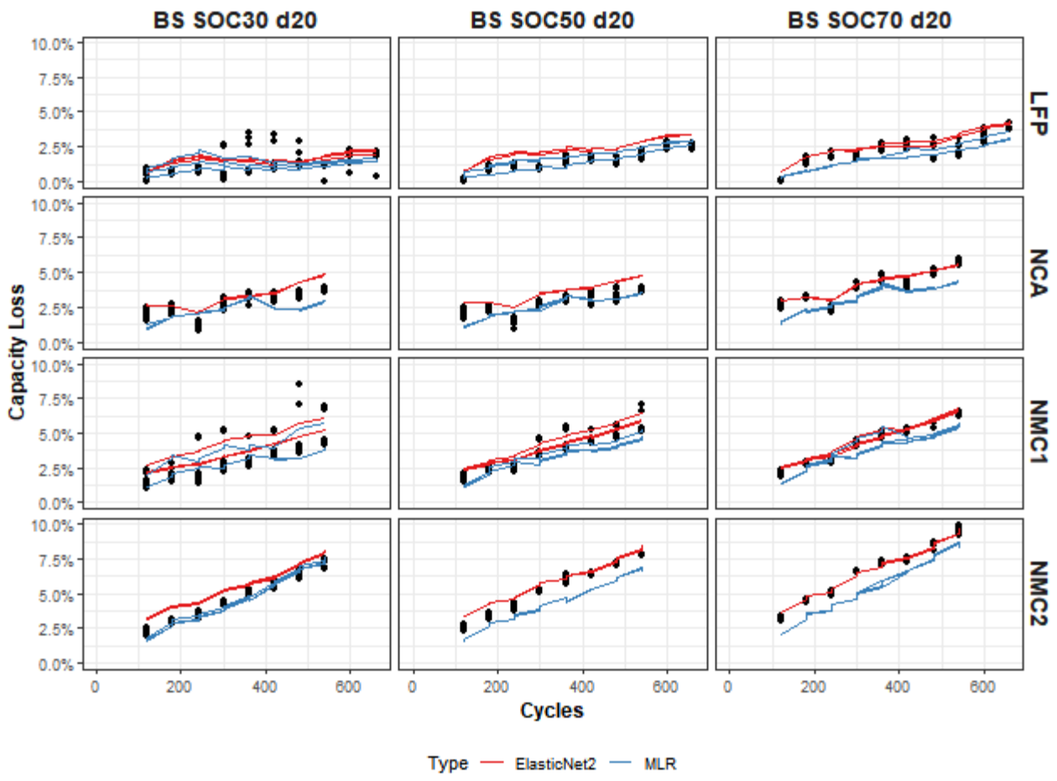
Cubic in voltage

Interaction with current and rate of graphite expansion

$$\frac{dCaploss}{dt} \sim \boxed{(I + I^2)} \times \boxed{(V + V^2 + V^3)} + \boxed{I\frac{dvol}{dc_{Li}}(SOC) + I\frac{d^2vol}{dc_{Li}^2}(SOC)}$$

- Model evaluated predicting 60 through 300 cycles ahead

- Tested both multilinear regression and elasticnet algorithm – reduced RMSE by 1/3 with elasticnet suggesting overfitting issues



Top Down Modeling EPRI Collaboration

- EPRI Collaboration – EPRI shares standardized data from ESS and analysis techniques and insight, PNNL produces predictive capacity degradation models
- ESS included both Li-Ion and flow system
- Very similar methodology – use battery's history to predict its performance in future cycles
- Challenge - harder to evaluate ESS performance vs single cell performance. Degradation still detected.

Mean and RMS out of sample error for predicting an Li Ion System performance using various techniques

Looking Forward

Research Accomplishments:

- Reliable battery state of health model developed for single cell (one pair of electrode)
- Incorporates various degradation mechanisms

Next Steps:

- Determine effect of plated lithium on tortuosity of SEI layer and electronic percolation within SEI layer
- How does this affect SEI formation rate?
- Model pouch (multi-electrode cell) and cylindrical cells
- Model multi-cell modules
- Use tertiary current distribution to get mass transfer related effects
- Use measurable parameters alone for Top Down Model
- Apply 0d model to more duty cycles

Acknowledgments

Dr. Imre Gyuk, DOE – Office of Electricity

Mission – to ensure a resilient, reliable, and flexible electricity system through research, partnerships, facilitation, modeling and analytics, and emergency preparedness.

https://www.energy.gov/oe/activities/technology-development/energy-storage

Q/A and Further Information

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https://energystorage.pnnl.gov/