# Battery modeling and analytics spanning multiple chemistries and technologies

Anirban Roy, PhD

# Key Experiences

| Organization | Topic | Chemistry/technology |
|---|---|---|
| AMBRI | Accurate quantification of open circuit voltage | Liquid metal<br>Ca anode, Sb cathode |
| | Equivalent circuit modeling and optimization | |
| | COMSOL Multiphysics electrical system modeling | Liquid metal<br>SS-304 plates |
| GoVidYouth Inc | Identification of degradation mechanisms in lead acid batteries | Flooded tubular lead-acid |
| | Pack-to-cell current deconvolution and integrating with single particle model | Li-ion (graphite-NCA) |
| Nanodian Inc | Modeling surface layer concentrations in bulk and nanosized LMO cathodes | Li-ion (graphite-LMO) |
| | NSF grant writing | |
| Miscellaneous | A data-driven approach to predict SoC using cycling data | Li-ion (graphite-$LiCOO_2$) |

# My journey till today

**9** Ambri
Equivalent circuit optimization
Accurate OCV test
COMSOL modeling

**8** GoVidYouth
Single particle modeling
data analytics for lead-acid batteries
equivalent circuit modeling

**6,7** Consultant, MOEV, Nanodian
Single particle modeling


**1** BE ChemE, VIT, Pune

**4** PDF, UH
Motor vehicle emissions,fleet electrification

**2** MTech EnvE, IIT Kanpur
*Modeling of titania nanoparticle formation, coagulation and sintering*

**5** ARE, CARB
Real-world big data analytics for construction eqpt

**3** PhD MechE/EnvE, CMU
Numerical air quality modeling
Air quality impacts of transportation and energy development

# Accurate characterization of open circuit voltage in Ca-Sb liquid metal batteries

Ambri

# Pulse tests: accurate OCV representation

| SoC | Resting time |
|---|---|
| >70% | 45 minutes |
| 40%<SoC≤70% | 3 hrs |
| 30%<SoC≤40% | 8 hrs |
| ≤30% | 3 hrs |

**Why not a standard HPPC test?**

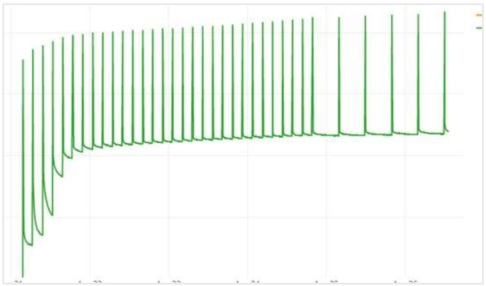
- Covers only discharge
  - no accountability for hysteresis
- Too fast C-rates
  - our chemistry accepts only ≤ C/4
- 10% granularity
  - higher resolution can throw more light on physics

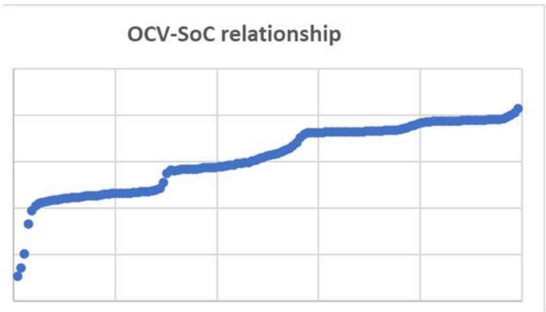
**Previous GITT tests**

- showed marked variability in OCV-SoC relationship
- Coarse time resolution employed through GITT tests unable to capture early transient phenomena
  - E.g. charge transfer

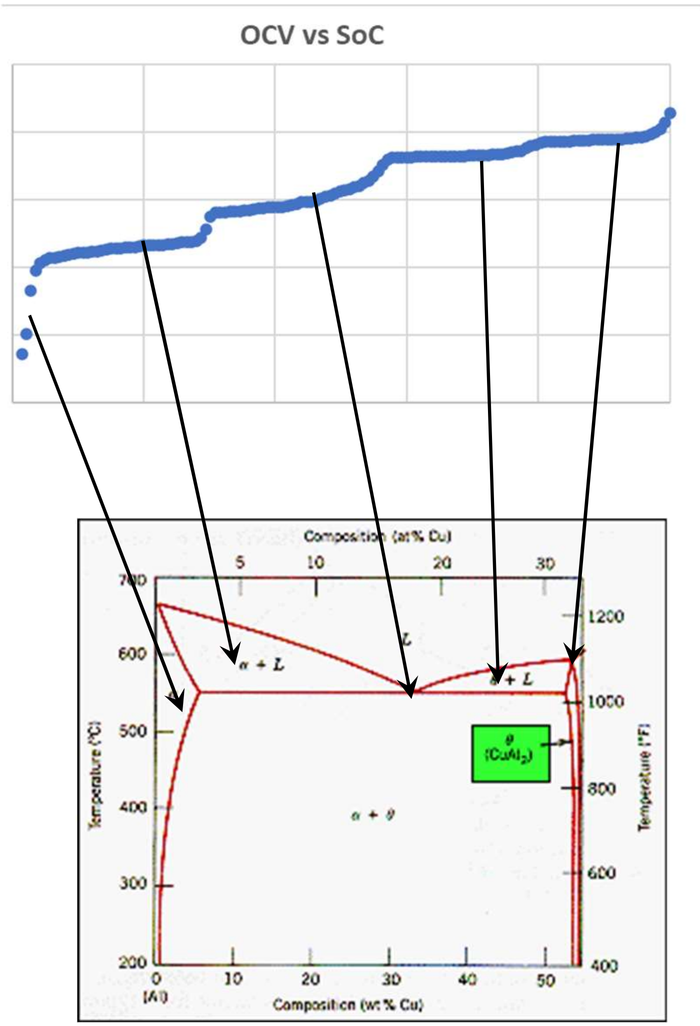
**New approach**

- Cycling between 0.6V and 1.2 V @C/4
- Removes 1% SoC every pulse
- Resting period characterized by SoC value
- Time resolution of 1 second during pulsing to accurately capture trends





# OCV-SoC relationship  and hypothesis




**Beginning kink in OCV curve describes concentration polarization in surface layer of a fully loaded cathode at start of charging**

**End kink in curve describes limiting reactant situation in the cathode**

- Phase diagram for $CuAl_2$ used as a surrogate
  - Newhouse (2014) indicates intermetallic behaviour is also common for intercalating liquid metal electrodes
- The Newhouse study was for liquid-liquid Mg-Sb electrodes
  - Feasibility for solid Sb sys  tem?

***Newhouse, 2014***

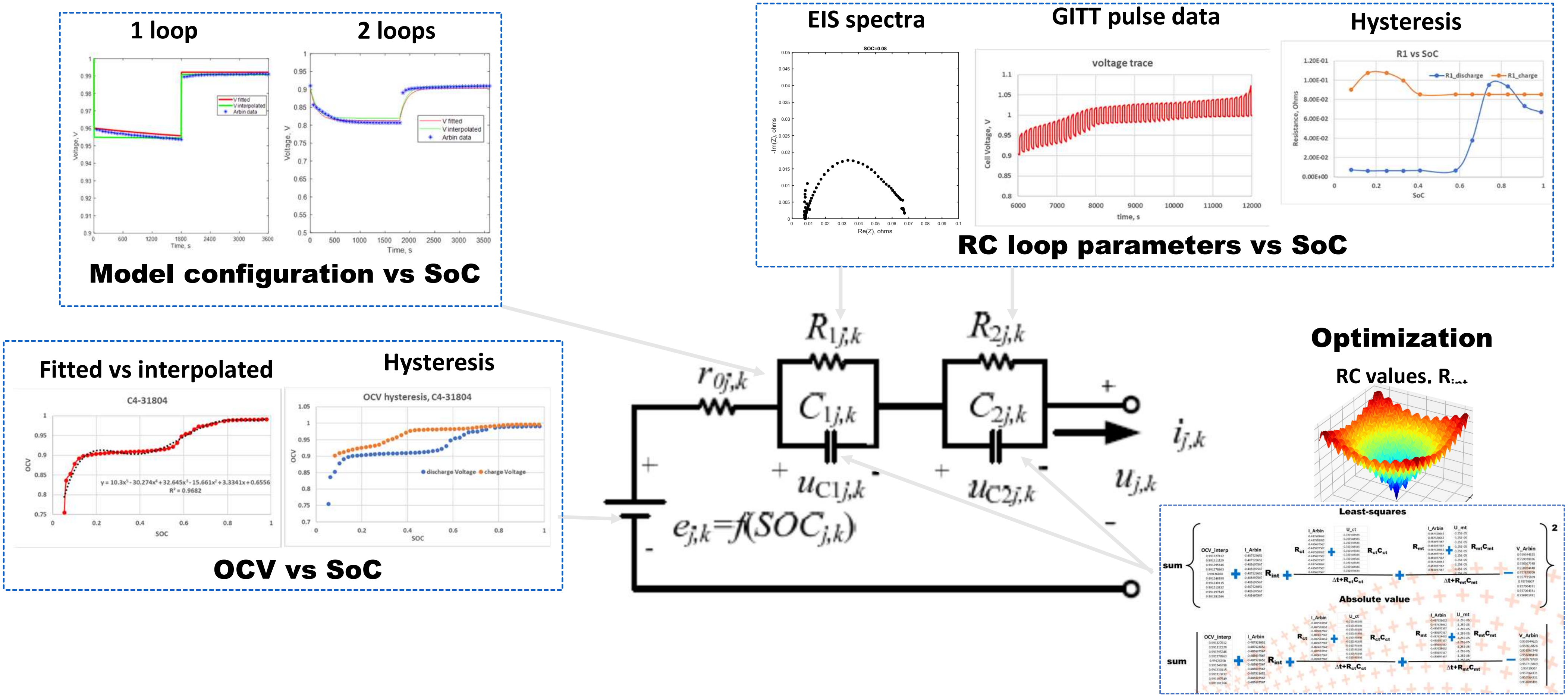
***Callister and Wiley, 1994***

# Optimization of RC parameters in liquid metal batteries using pulse testing data

# Motivation

- Approach hitherto used for lead-acid and lithium-ion batteries
  - Not implemented yet for liquid-metal chemistries
    - Complex Multiphysics
      - Not easily represented in standard physics-based e.g. PnD models
- Change in loop parameters and internal resistance with cycle/time
  - -> pointer towards state of health
    - Help to identify specific failure mechanisms

# Data sources and modeling approaches in a nutshell



# Approach

**Initialize**

**SoC lower limit = 0**

**SoC lower limit**

**SoC higher limit = SoC lower limit + ΔSoC**

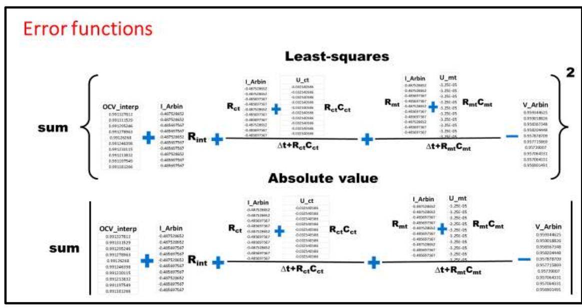
**Extract SoC interval specific pulse data**

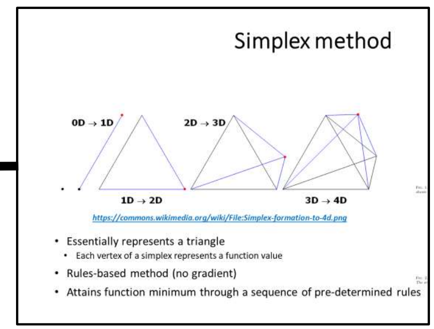
**Use MATLAB ndgrid to generate initial guesses for RCs and $R_{int}$**

**Use MATLAB fminsearch to estimate fitting error**

***Root mean square***

***Absolute value***




**Choose RCs and $R_{int}$ based on lowest error**

**SoC lower limit = SoC higher limit**

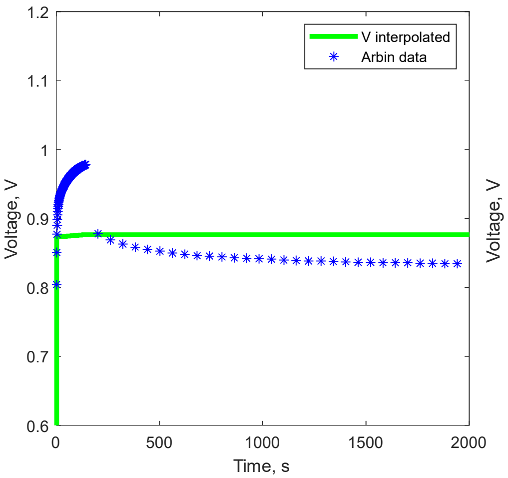
**SoC higher limit = SoC higher limit + ΔSoC**

**SoC=1.0?**

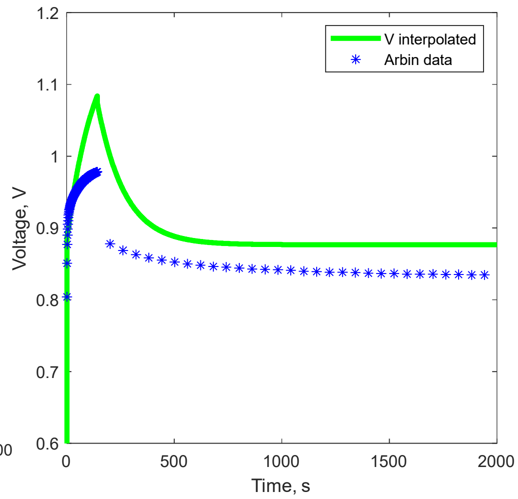
**End**

# Effect of initial coordinates, least squares

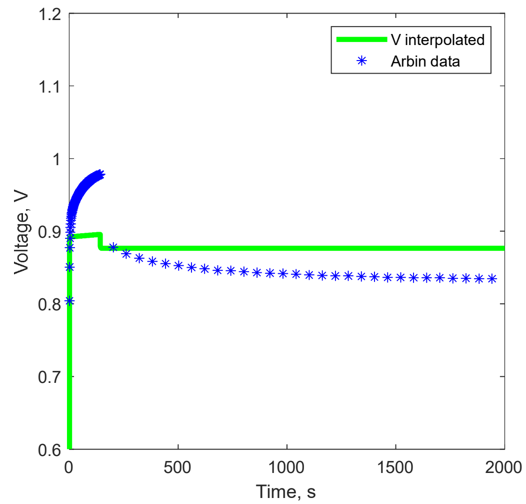
**scale =10**



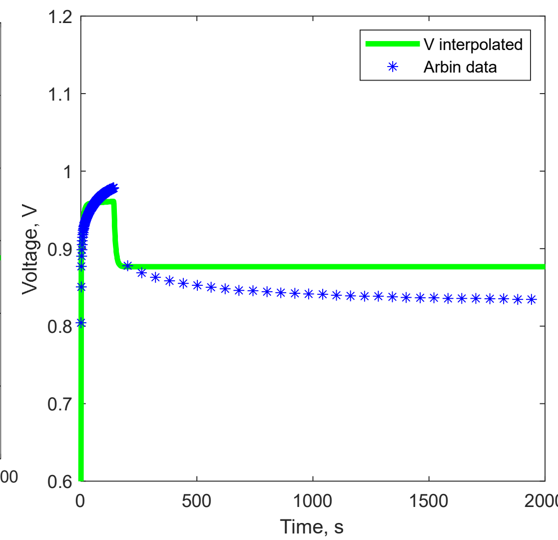

**scale =2**




**scale =1**

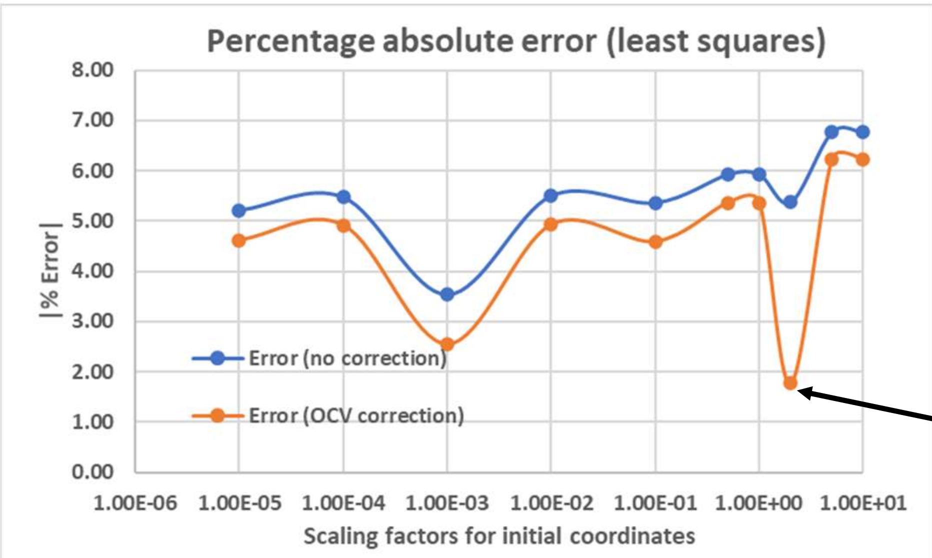


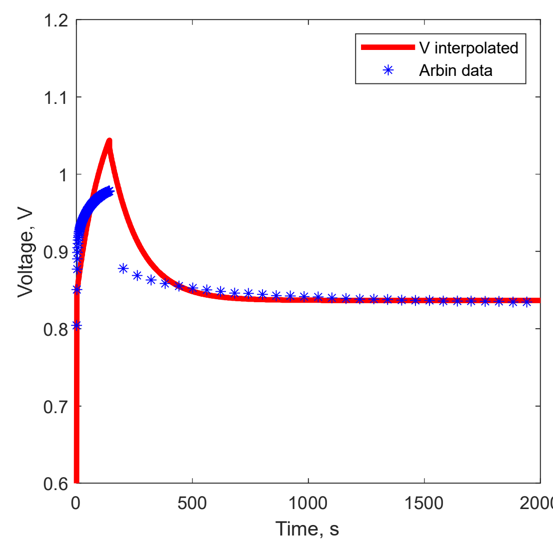

**scale =$10^{-3}$**



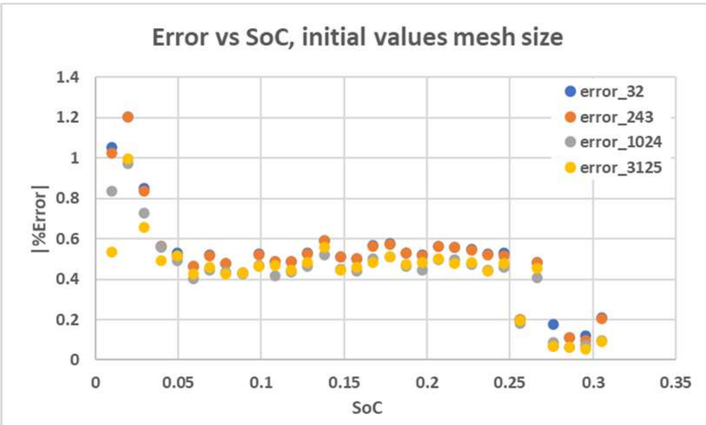

- Initial guess
  - $R_{ct}$ = 8.9x$10^{-5}$ Ω, $C_{ct}$ = 208F
  - $R_{mt}$ =3.4x$10^{-3}$ Ω, $C_{mt}$ = 7700F
  - Scale represents the number used to multiply this initial value
- Plots presented show effect of scaling initial coordinates
  - Results plotted only uptil 2000 seconds to magnify “action”

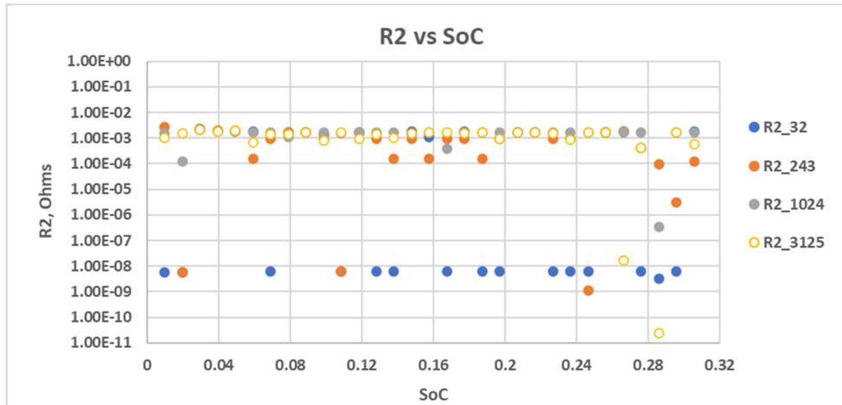
# Variation of fitting error with scaling factors



# Effect of initial value mesh space, least squares



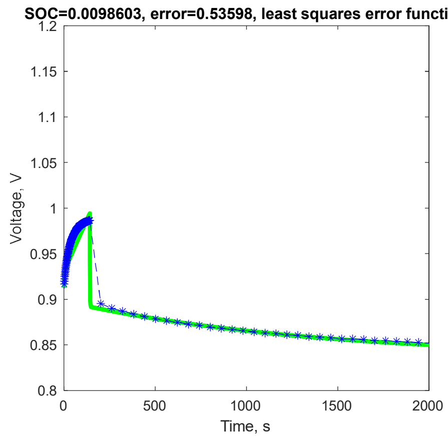



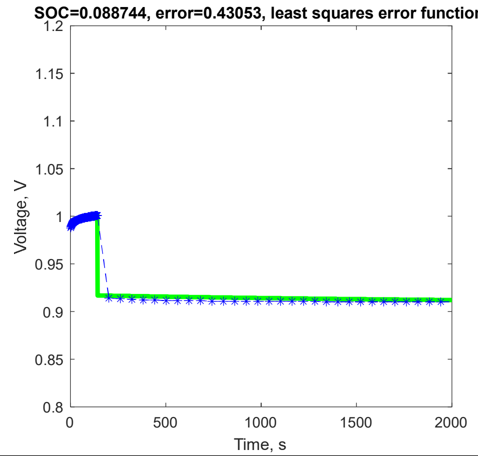

- Initial guess
  - $R_{ct}$ = 8.9x$10^{-5}$ Ω, $C_{ct}$ = 208F
  - $R_{mt}$ =3.4x$10^{-3}$ Ω, $C_{mt}$ = 7700F
- Scaling factors used to multiply first guess
- Range from $10^{-6}$ to $10^{3}$ divided into N points
- 5-D grid: $R_{mt}$, $C_{mt}$, $R_{ct}$, $C_{ct}$, $R_{int}$
- Granularity: $N^5$
- No appreciable change in error

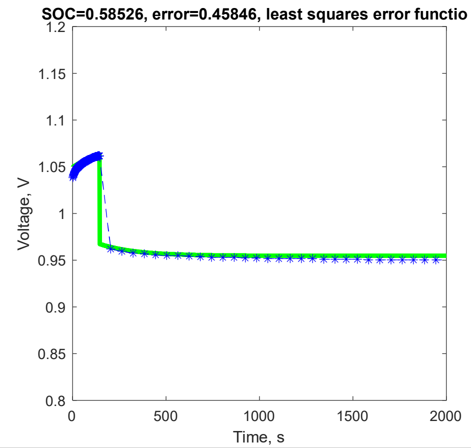
| Number of points N | Number of mesh elements $N^5$ | Run-time (minutes) |
|---|---|---|
| 2 | 32 | 2.75 |
| 3 | 243 | 10.75 |
| 4 | 1024 | 27.95 |
| 5 | 3125 | 87.33 |

# Least squares vs absolute value, sample results wrt SoC

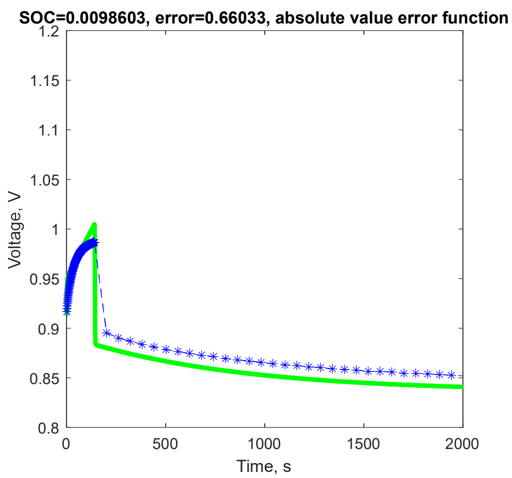
**Least squares**

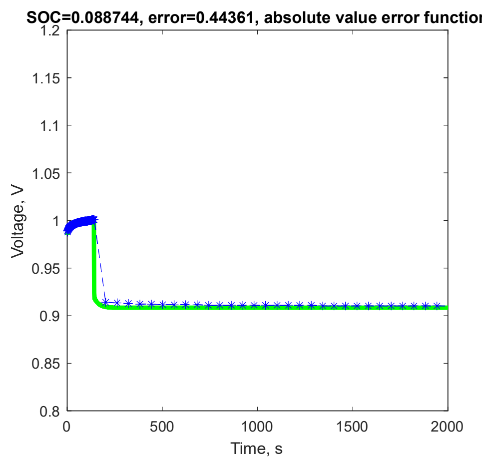


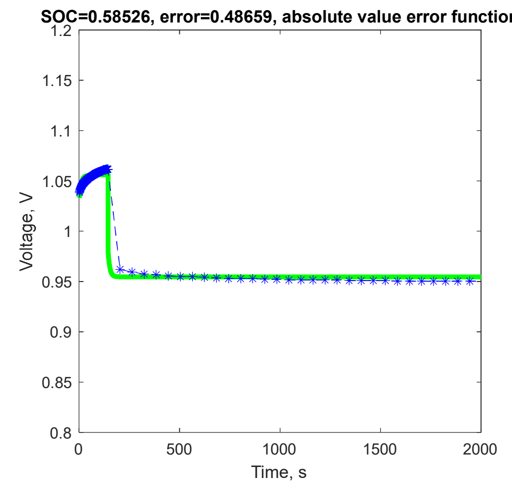



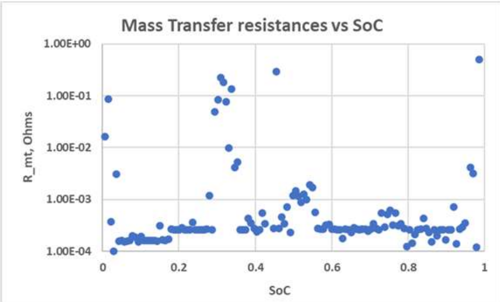

**Absolute value**

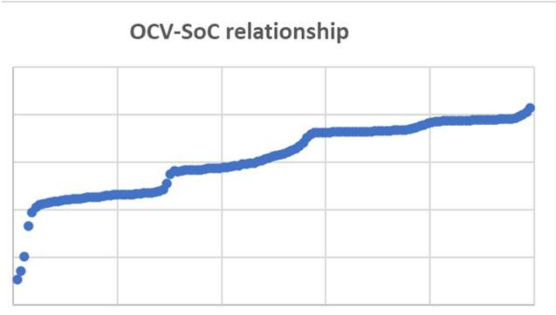


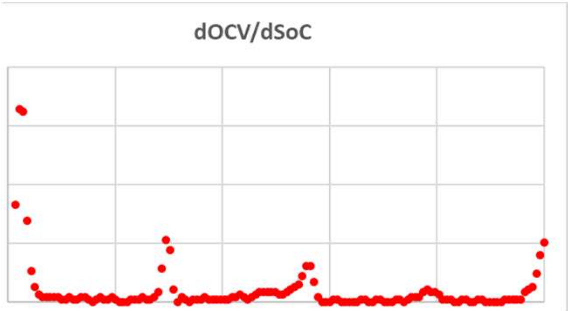



# Insights provided by a 1% SoC resolution



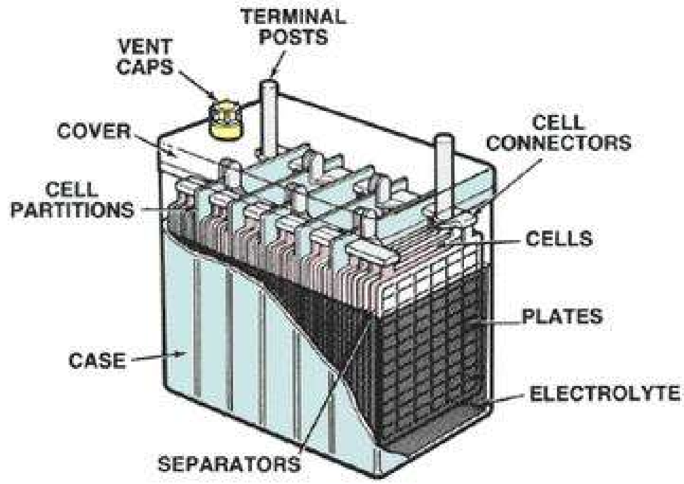




- Mass transfer resistances highest in regions OCV curve not approximately flat
- These are regions where OCV is dictated primarily by diffusion
  - -> there is no phase change
  - Concentration polarization is prevalent inside cathode
- Phase change regions involve minimal diffusion
  - Only associated with surface growth/dissolution of new phase particles
  - Characteristic response time and voltage drop << concentration polarization
  - Changes with thickness of mass transfer boundary layer outside nanoparticles

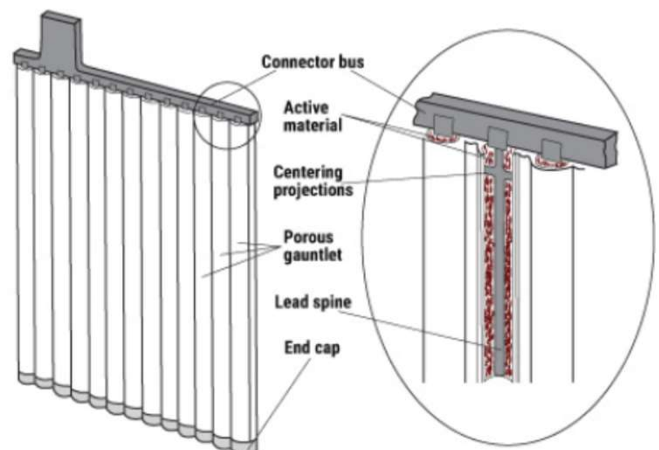
  - **Change of OCV slope happens actually much before the linear region**
  - **-> real physical phenomena, NOT outlier**
    - **Computed resistance trend phenomena unseen by available instrumentation**
      - **->helpful for SoH apps**

# Analyzing degradation mechanisms in lead-acid batteries

# Overview


- Used for propulsion in 3-wheelers in India
- Light-duty transport
- Similar duty to golf-carts
- Flooded tubular architecture
  - Battery infilled with electrolyte
  - Active material coated around tubular spine
    - Secured with “gauntlet”



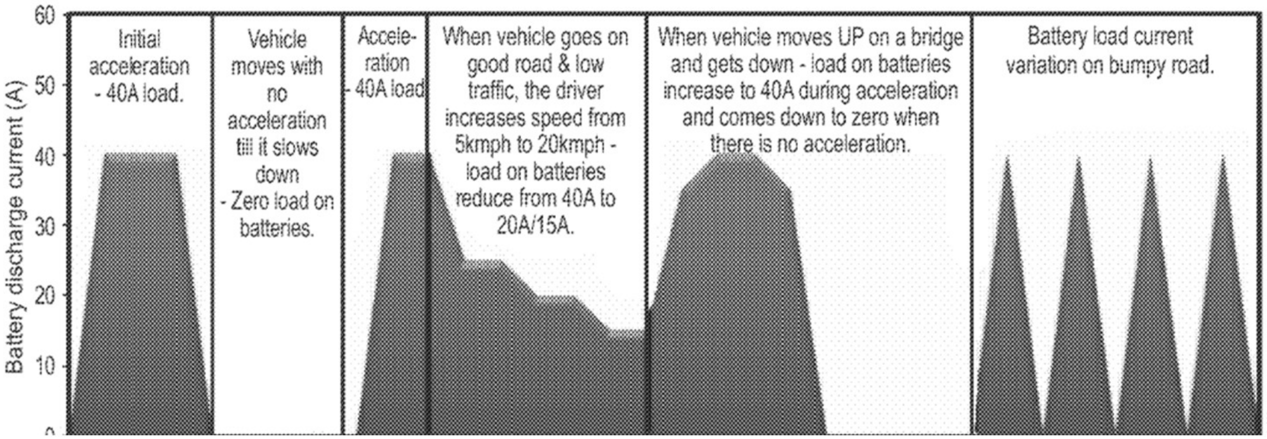
# Corrosion mechanisms in lead-acid batteries

| Mechanisms | Effects |
|---|---|
| **Hydrolysis/Water loss/Water splitting** | Reaction causes loss of charge, increasing probability of sulfation |
| **Sulfation** | Growth of $PBSO_4$ crystals reduces capacity and increases resistance |
| **Corrosion** | Reduces contact between active material and current collector |
| **Stratification** | Heavier sulfuric acid settles  down to bottom, causing inhomogeineity in discharge |
| **Shedding** | Swelling and shrinkage of electrode active material causes disengagement, potential to short-circuit |

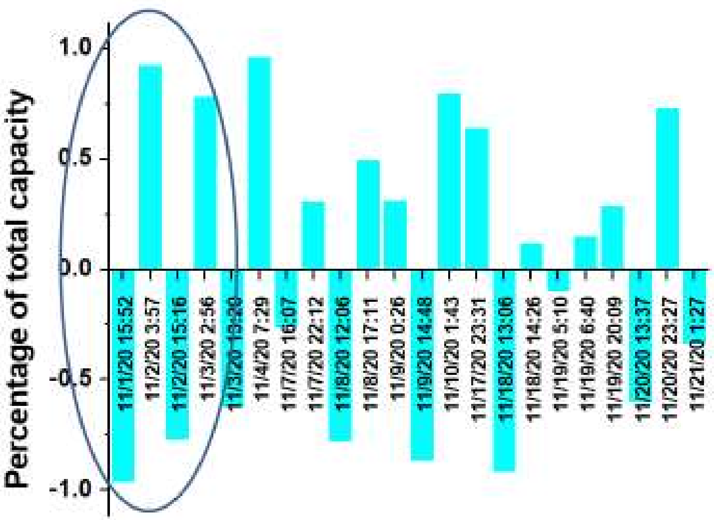
- Batteries fail in 6 months
- What is the key degradation mechanism?

***Bindner et al., 2005*;**
***Gandhi, 2020*.**

# What do the field data tell us?



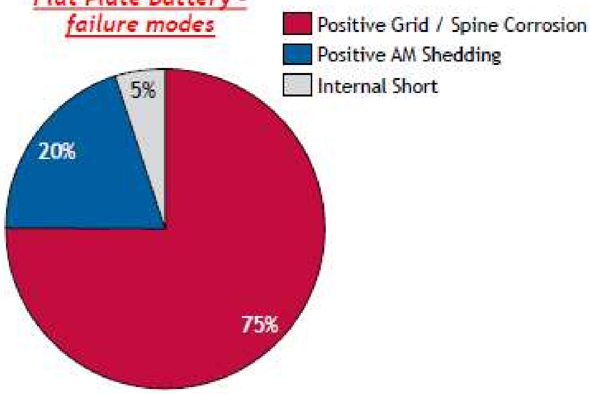

- Bumpy ride
  - Loosening of active material
- High SoC/DoD change multiple times in a day
  - Fatigue -> loosening of active material
- Potential to shed?



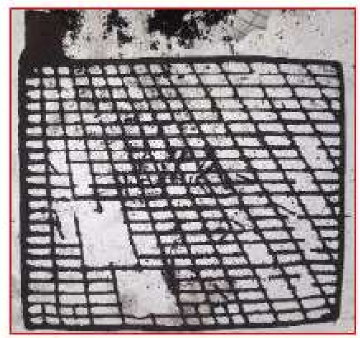

***Mittal et al., 2017***

# Industry findings

*Flat Plate Battery - failure modes*




*Flat Plate Battery - Positive Grid Corrosion*



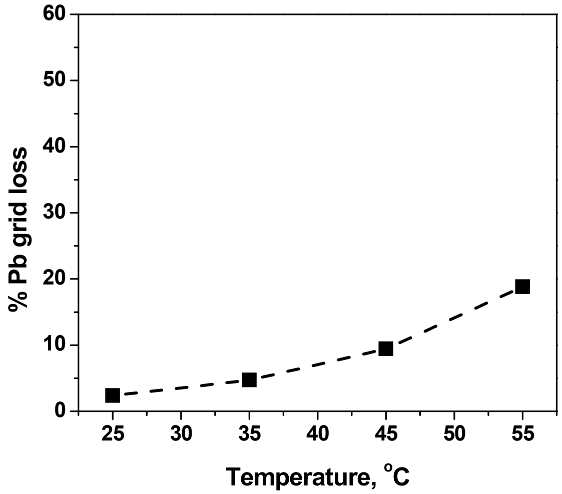
*Tubular Battery - Spine Corrosion*

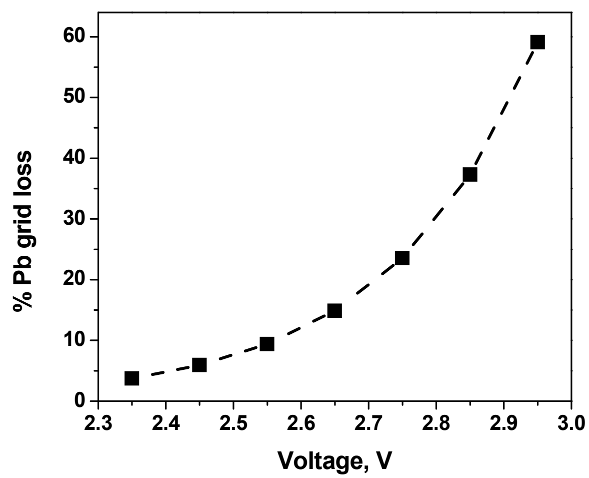
*Source: Cut Open analysis of field return batteries (4 to 6 months)*

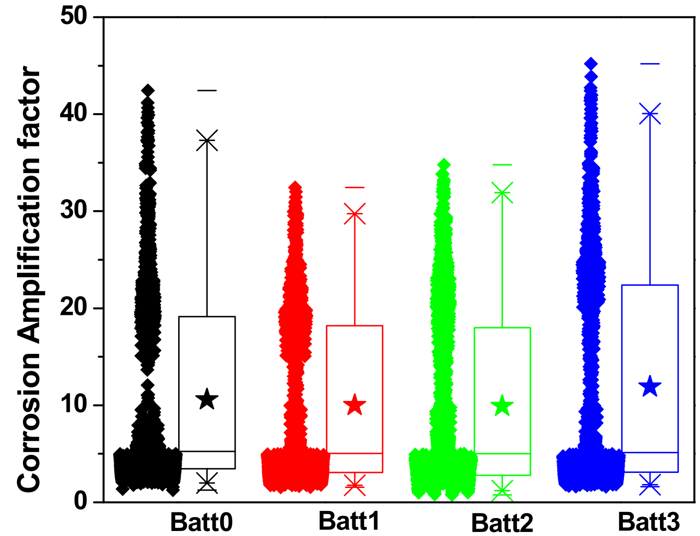
- ❑ Field failure batteries under warranty claim (4 to 6 months service) in E-Rickshaw application were collected and cut-opened (flat plate ~40 nos. and tubular ~10 nos.) to understand failure modes
- ❑ Irrespective of the battery design, positive electrode corrosion is the major failure mode

- Tubular battery: 14 out of 20 spines eaten away
- 9 out of 14 corroded spines are reduced >50% in length

# Effects of temperature and voltage on corrosion



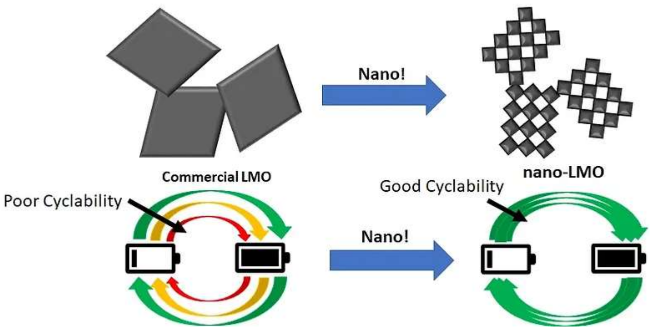



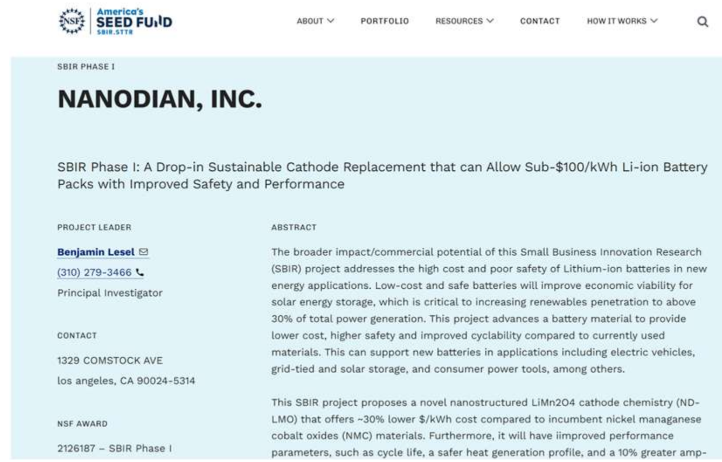

- Assumptions
  - Temperature variation studied at float voltage = 2.25V
  - Voltage variation studied at temperature = 298 K
  - Assumed 10 active hrs/day
- Temperature effects constrained to <20% degradation/yr, voltage up to 60%
  - Temperature dependence an exponent of 2,
  - voltage that of 10

- $Amplification\ Factor = 10^{\frac{Overvoltage}{500}} \times 2^{\frac{Battery\ Temperature}{10}}$
- Overvoltage = voltage-open circuit voltage (2.07 V)
- Combined effects of temperature and voltage
- Average amplification ~10 (wrt value at 0 overvoltage and 298K)

# Single particle modeling of pseudocapacitive LMO cathodes

# Overview



SBIR PHASE I

NANODIAN, INC.

SBIR Phase I: A Drop-in Sustainable Cathode Replacement that can Allow Sub-$100/kWh Li-ion Battery Packs with Improved Safety and Performance

PROJECT LEADER

Benjamin Lesel

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Principal Investigator

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NSF AWARD

2126187 – SBIR Phase I

ABSTRACT

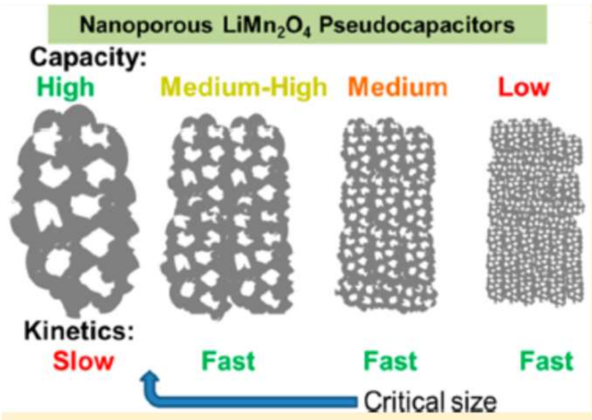
The broader impact/commercial potential of this Small Business Innovation Research (SBIR) project addresses the high cost and poor safety of Lithium-ion batteries in new energy applications. Low-cost and safe batteries will improve economic viability for solar energy storage, which is critical to increasing renewables penetration to above 30% of total power generation. This project advances a battery material to provide lower cost, higher safety and improved cyclability compared to currently used materials. This can support new batteries in applications including electric vehicles, grid-tied and solar storage, and consumer power tools, among others.

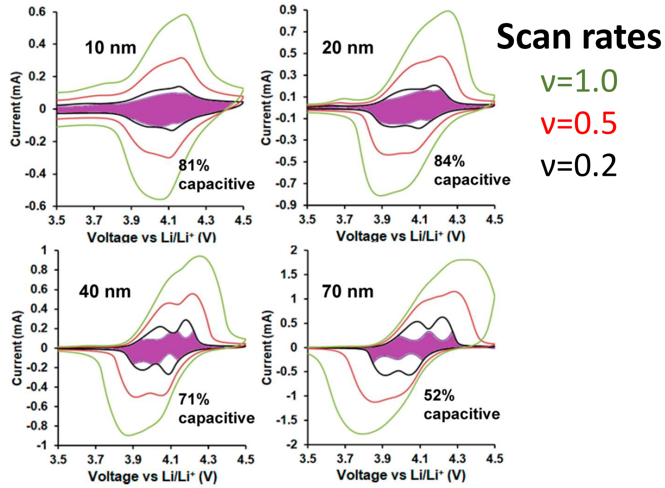
This SBIR project proposes a novel nanostructured LiMn2O4 cathode chemistry (ND-LMO) that offers ~30% lower $/kWh cost compared to incumbent nickel managanese cobalt oxides (NMC) materials. Furthermore, it will have iimproved performance parameters, such as cycle life, a safer heat generation profile, and a 10% greater amp-

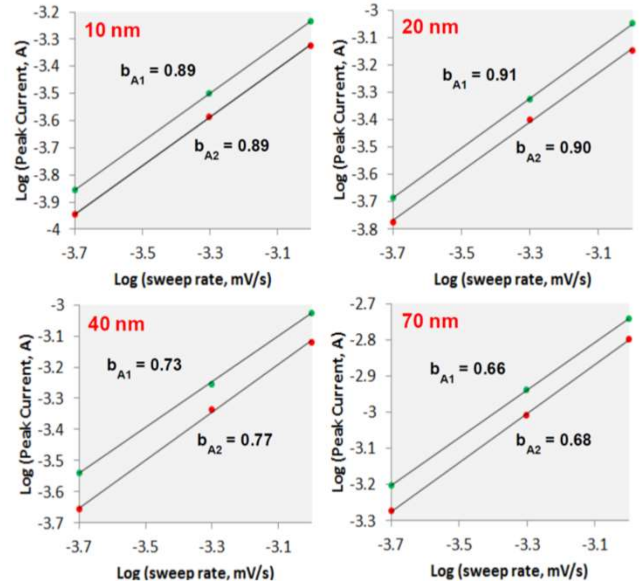
- Bulk (~µm) LMO particles e.g. Nissan Leaf
  - Phase change on intercalation
    - Particle swelling -> CEI rupture -> Mn leaching -> anode poison
- Nanodian technology
  - Nanosized LMO particles
    - Phase change suppressed by Kelvin effect
    - Functionalized surface reduces leaching

[https://www.nanodian.com/technology](https://www.nanodian.com/technology)
[https://seedfund.nsf.gov/awardees/history/details/?company=nanodian-inc](https://seedfund.nsf.gov/awardees/history/details/?company=nanodian-inc)

# Pseudocapacitive phenomena

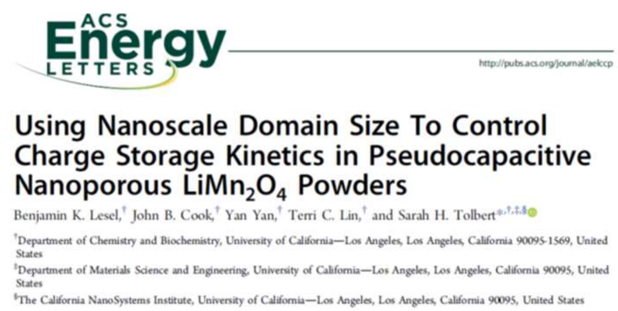



$$i_{Total}(V) = k_{capacitive}\nu + k_{diffusive}\nu^{1/2}$$

- Synonym for fast-diffusion
- Similar length scales as capacitance
- No gradients inside particle
- Critical particle threshold
  - Every electrode particle exhibits a mixture
    - Proportion dependent upon particle size


ACS Energy Letters
http://pubs.acs.org/journal/aelccp

Using Nanoscale Domain Size To Control Charge Storage Kinetics in Pseudocapacitive Nanoporous $LiMn_2O_4$ Powders

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# Objectives, assumptions and equations

## Goals

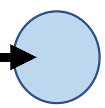
- Model lithium concentrations in cathode, layer-by-layer
- Demonstrate faster responses in pseudocapacitive system

## Model configurations

- 5 um diameter for bulk, 40 nm for pseudocapacitive LMO particle
- C/30 rate
- Diffusivity value $10^{-14}$ $m^2s^{-1}$

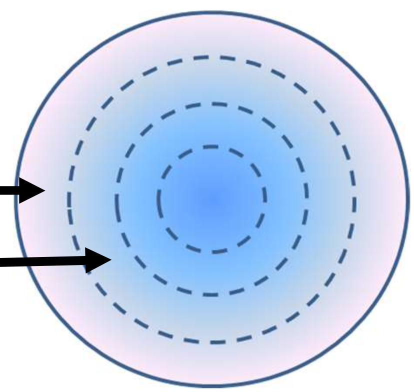
## Pseudocapacitance

- $\frac{\partial C_{S,interface}}{\partial t} = -J_{PC}\frac{3}{R}$

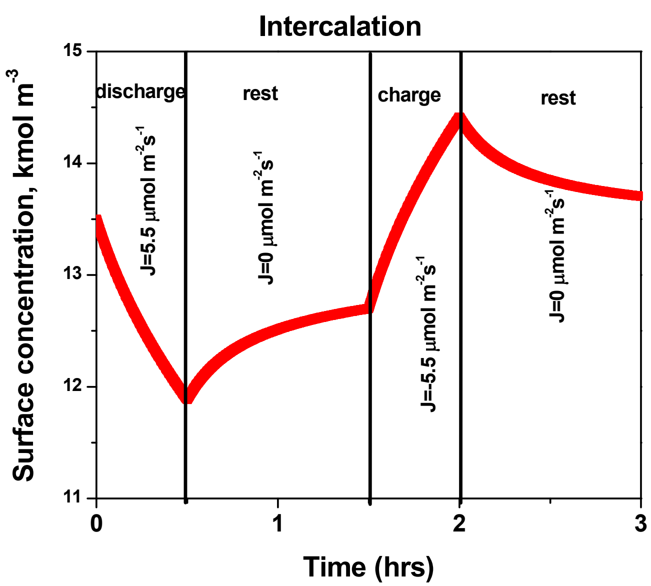


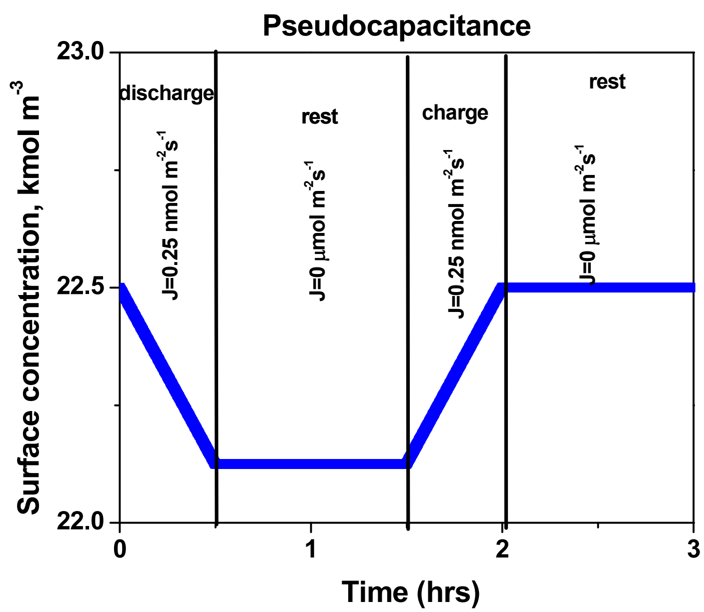
## Intercalation

- $\frac{\partial C_{S,interface}}{\partial t} = -D\frac{\partial}{\partial r}\left(\frac{\partial C_s}{\partial r}\right) - J_{PC}\frac{3}{R}$
- $\frac{\partial C_{S,interior}}{\partial t} = -D\frac{\partial}{\partial r}\left(\frac{\partial C_s}{\partial r}\right)$



# Surface concentrations

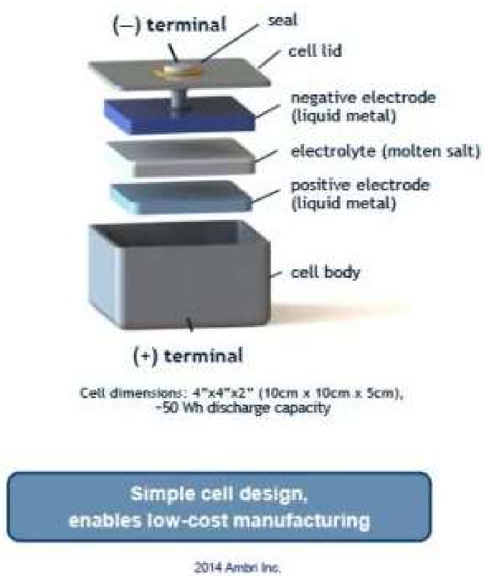



- Cathode particle discharge (0-0.5 hrs) = battery charging, vice versa.
- Diffusion process has intraparticle relaxation timescale.
- Response in pseudocapacitance is crisper with no relaxation.
- Also 100% capacity utilizable in pseudocapacitance – notice larger initial values)
- Applicable to high power density applications e.g. EVTOL

# Identification of optimum negative current collector geometry through COMSOL modeling

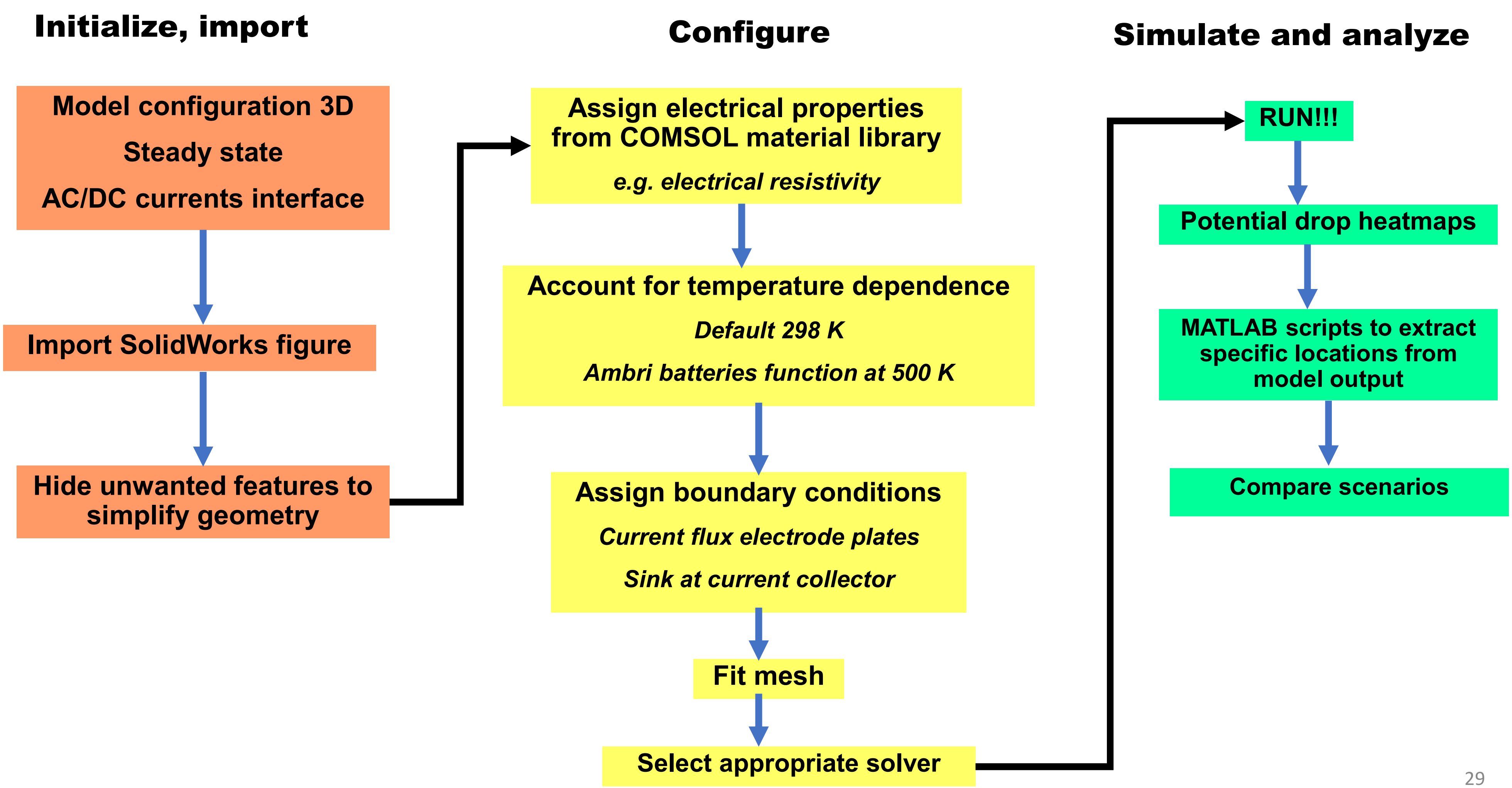
# Overview



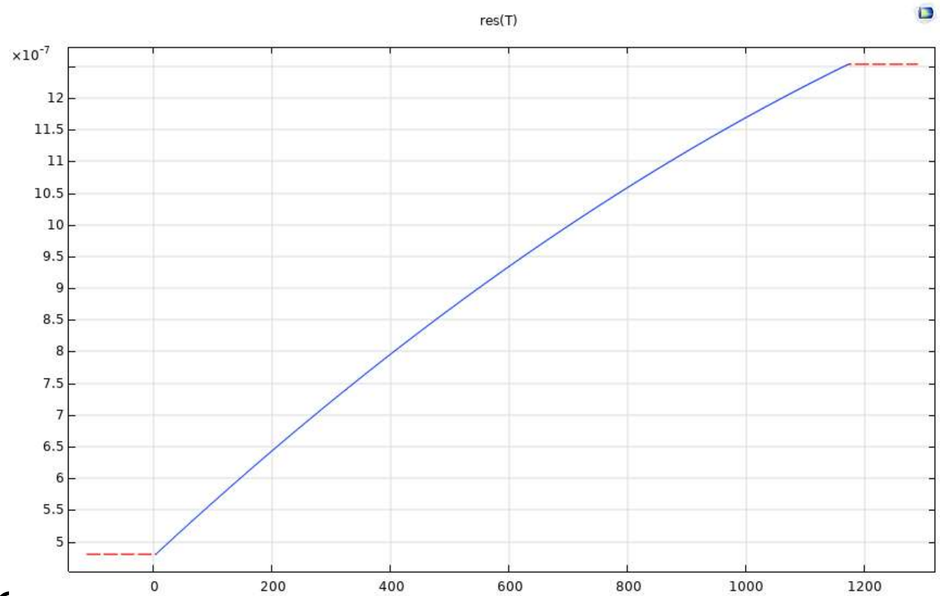


- Negative current collector is flush with the seal
- Exact proposed locations of a 2-seal system are proprietary information

# Step-by-step procedure, run across multiple geometries

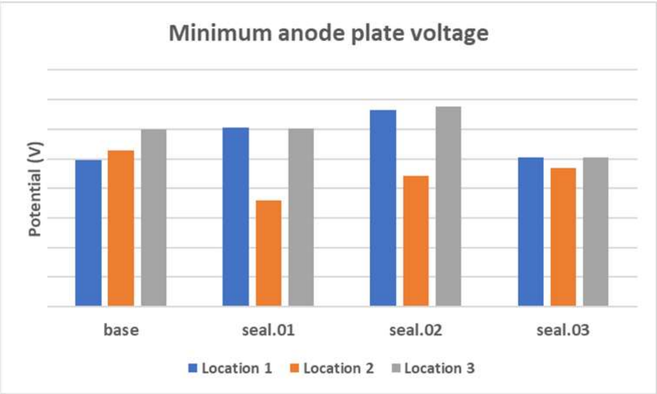


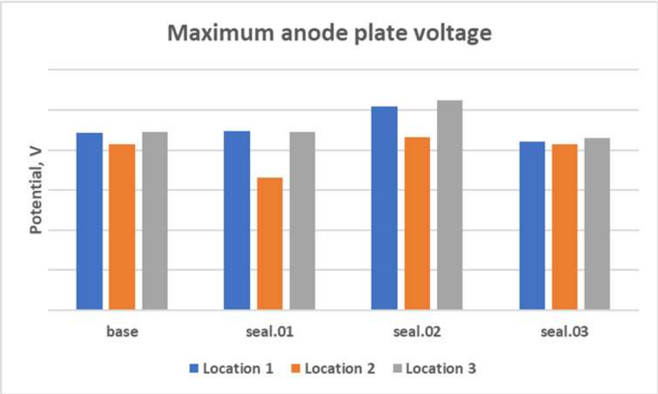
# Accounting for temperature dependence

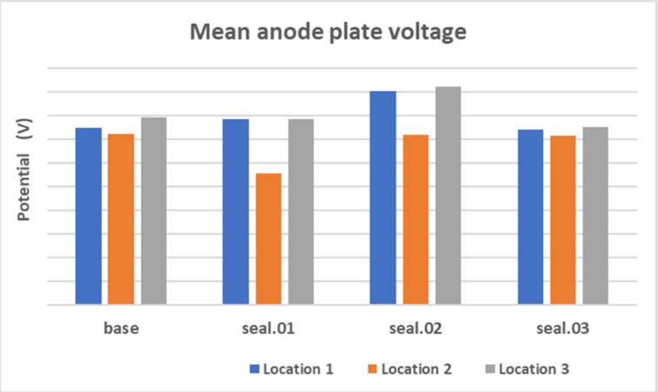



- T=293 K default in COMSOL
- Battery operation is at 773 K
- Imperative to identify how voltage drop changes with temperature
- Simulations carries out at i=7500 A $m^{-2}$ (144 A)
  - Geometric dimensions are in meters and potential drop in volts (V)

# Plate-level statistics

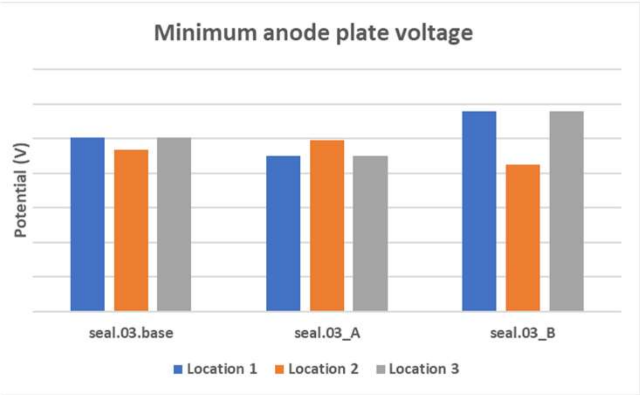


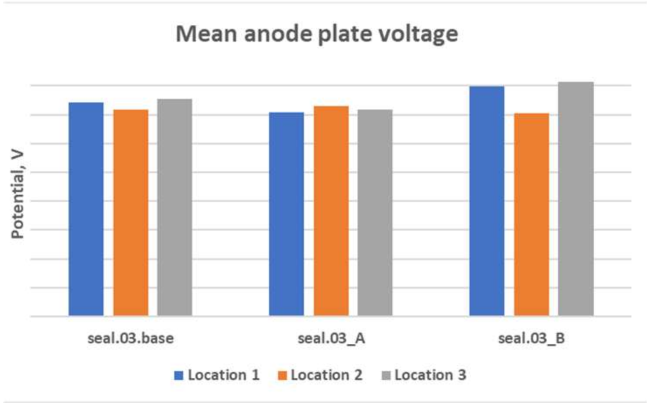



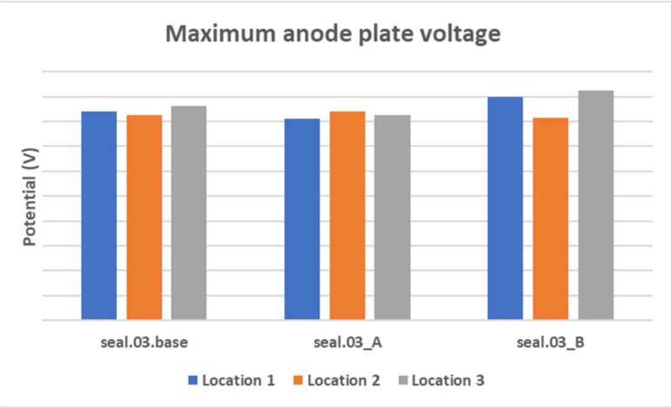




**Seal.03 shows highest uniformity in voltage**

# Statistics by location

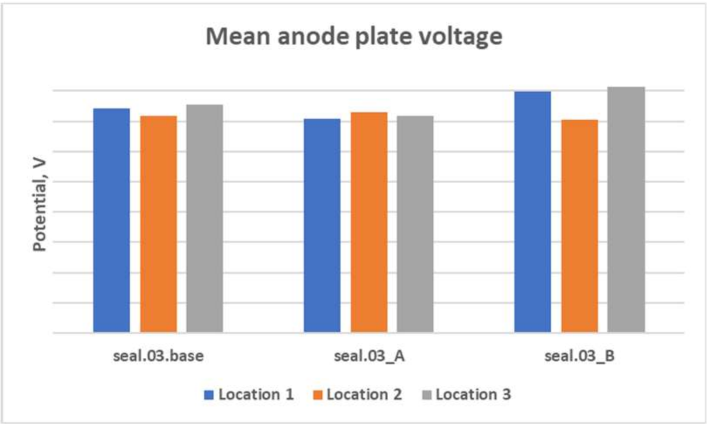


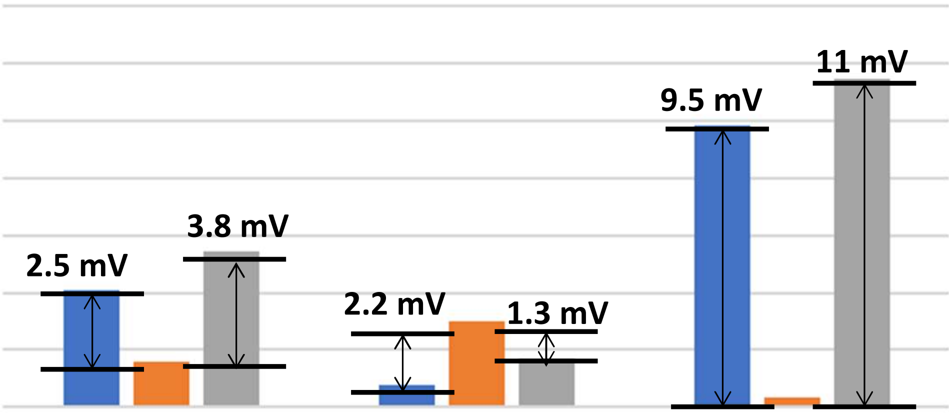




- Base and spacing design A show highest uniformity in voltage
  - Shows slightly lower values around outside anode plates due to proximity to ground
- Spacing design B shows highest voltages but also highest non-uniformity
  - Lowest voltage around central plate – attributed to ground proximity

# Choosing a finalist based on differences vs central location



# A data-driven approach to predict SoC in a non-lithium chemistry battery

# Data driven approaches

- Commonly used predictors
  - Current (I)
  - Voltage (V)
  - Temperature (T)
  - SoC at previous time step

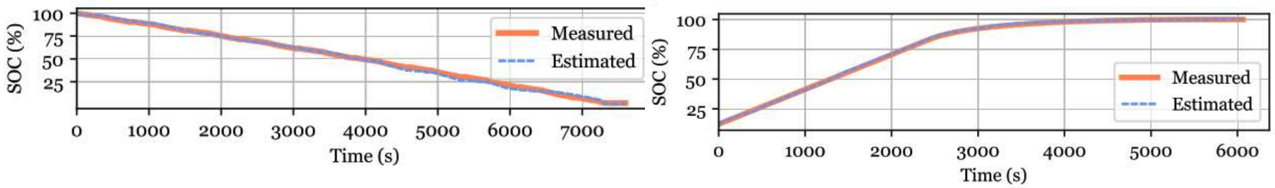
**Commonly used techniques**

- Linear approximations
  - Multilinear regression
  - Piecewise linear regression
- Nonlinear approximations
  - Neural networks
  - Support Vector Machines
  - Random Forest

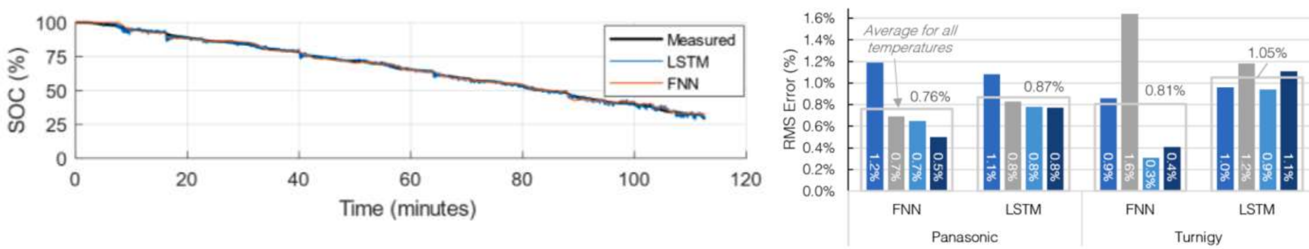
$$\boldsymbol{SoC = f(p_1, p_2 \ldots p_n)}$$

# Proof of concept: literature

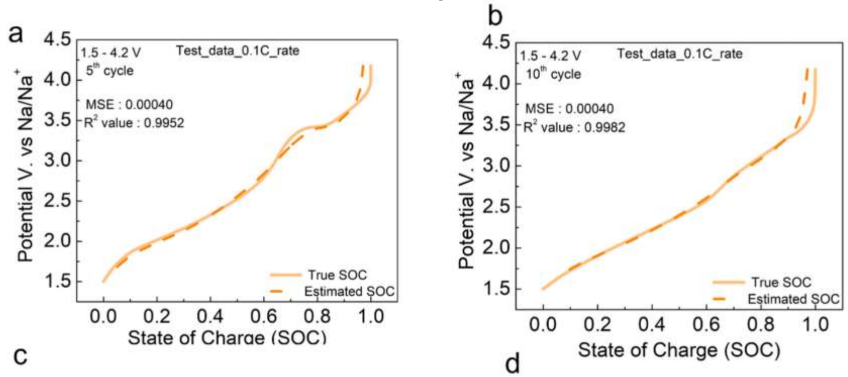
**Chemali et al., J.Power.Sources. Deep MLP, Li-ion**




**Vidal et al., J.Power.Sources. Recurrent (LSTM) vs deep MLP, Li-ion**




**Darbar and Bhattacharya, MLP, Li-ion, Na-ion**




**Li et al., IJDSN, 1-layer MLP, Li-ion**

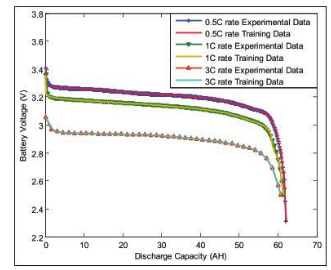



**Figure 2.** Measured and training values of discharge capacity under different ratios.

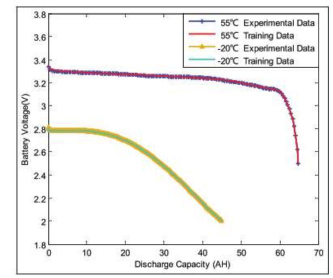



**Figure 3.** Measured and training values of discharge capacity under different temperatures.

**Wong et al., GoodIT, RNN, Li-ion**

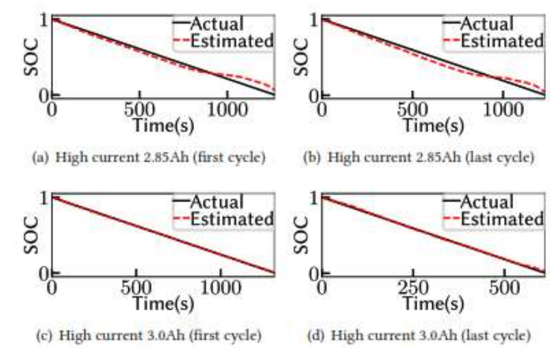



**Figure 5: UNIBO dataset SOC estimation results (high current)**

# Neural network configuration

**How do layers connect?**

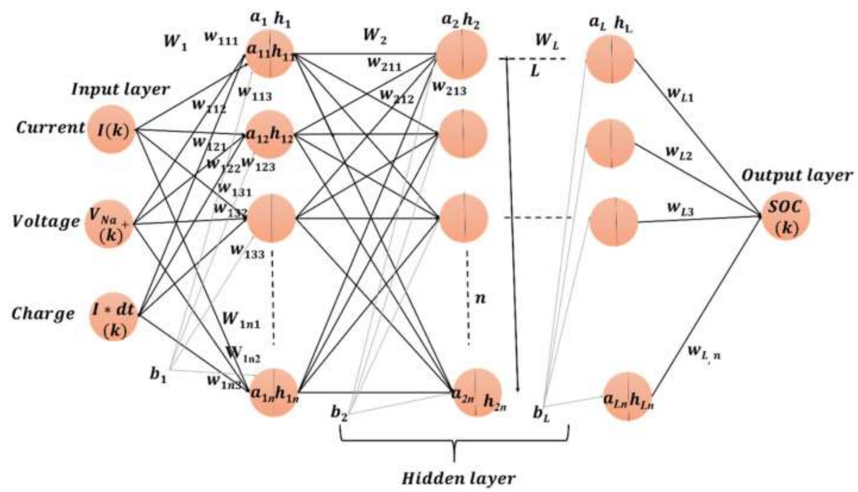
- Only one connection between successive layers
- Interconnection between successive layers
- Output feedbacks into memory

**Standardization**

- Feature scaling
- Mean normalization

**Number of neurons and layers**

- Single layer
- Multilayer



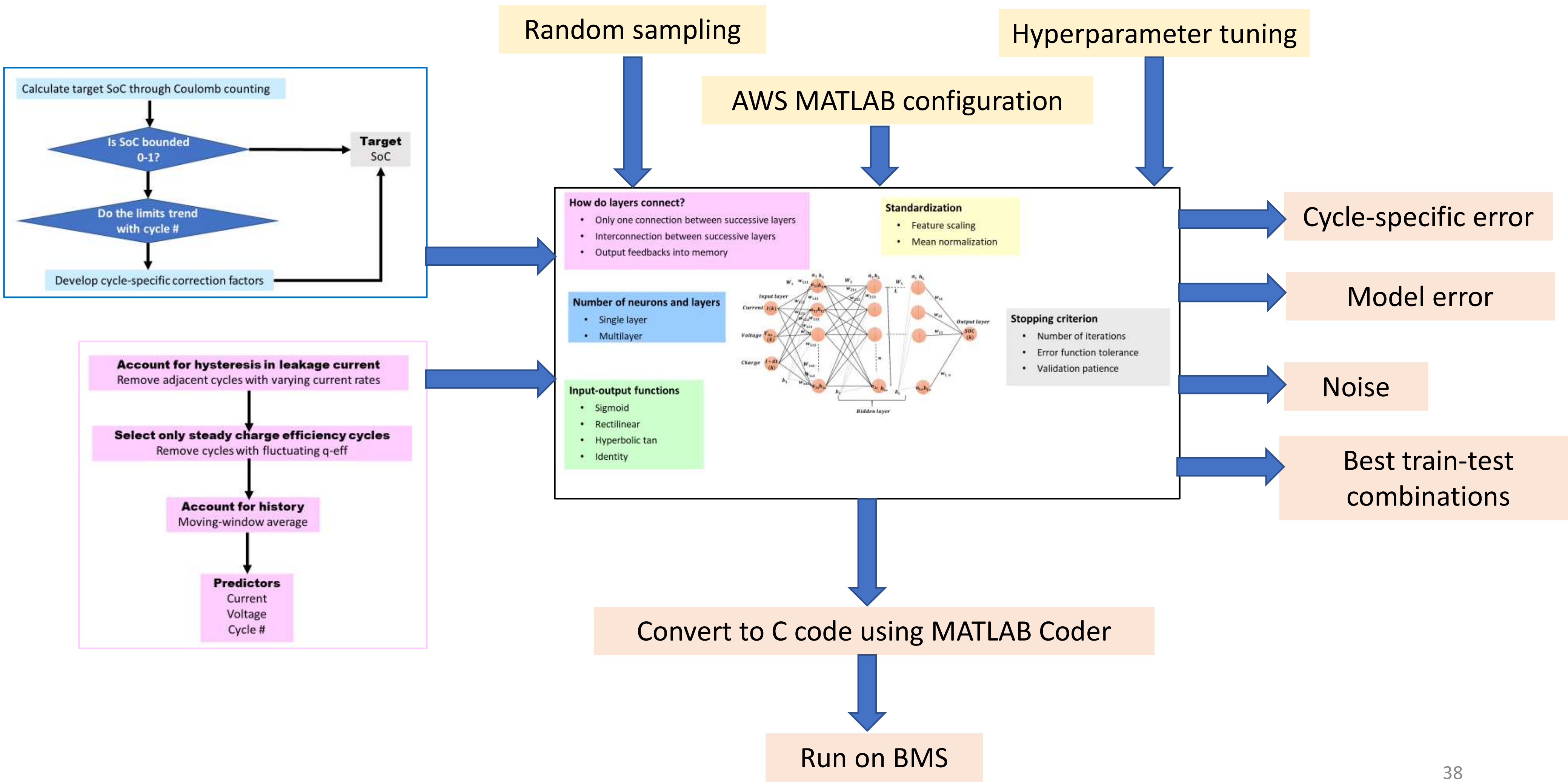

**Stopping criterion**

- Number of iterations
- Error function tolerance
- Validation patience

**Input-output functions**

- Sigmoid
- Rectilinear
- Hyperbolic tan
- Identity

# Modeling SoC



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