U.S.–CHINA CLEAN ENERGY RESEARCH CENTER
中美清洁能源研究中心
www.cerc-cvc.research.umich.edu
www.cerc-cvc.com

WITH FUNDING PROVIDED BY:
U.S. DEPARTMENT OF ENERGY
CHINA MoST
AND BY U.S. and CHINA INDUSTRIAL PARTNERS

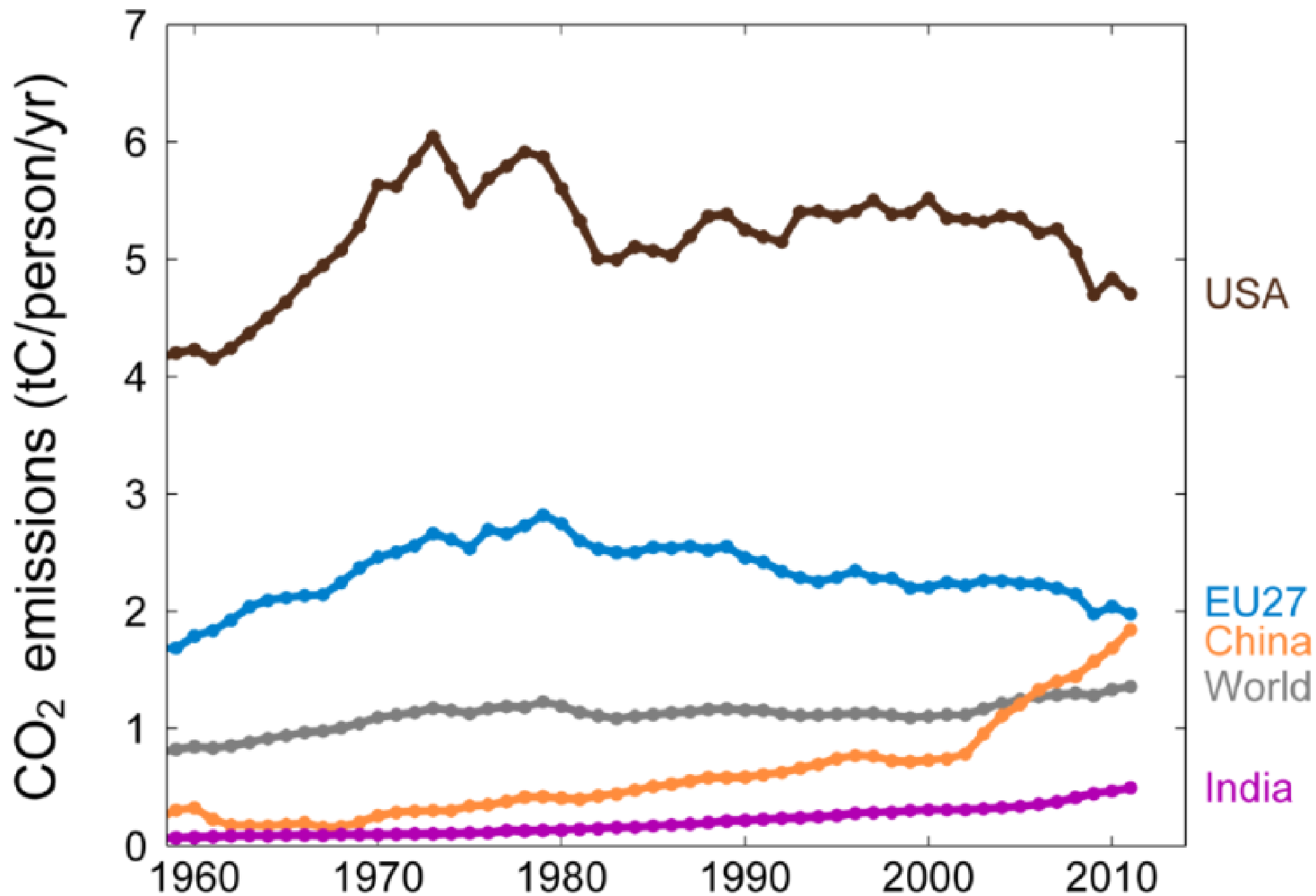
Selected US CERC-CVC Research on Improving Battery Safety and Reliability

美国CERC-CVC提高电池安全性和可靠性的研究

Huei Peng – US Director of CERC-Clean Vehicle Consortium, University of Michigan
彭晖，美方主任, 美国密歇根大学

Top four emitters in 2011 covered 62% of global emissions

China (28%), United States (16%), EU27 (11%), India (7%)



Plots from Global Carbon Project report 2012

Seven Joint Clean Energy Initiatives (2009)

- Electric Vehicles Initiative
- Energy Efficiency Action Plan
- Renewable Energy Partnership
- 21st Century Coal
- Shale Gas Resource Initiative
- Energy Cooperation Program
- U.S.-China Clean Energy Research Center

US-China Strategic Forum on Clean Energy Cooperation, January 18, 2011

Clean Vehicles

Building Energy

Clean Coal

Academic & National Lab Partners

U.S.

China

Industrial Partners

U.S.

Ford · DELPHI · DENSO · EATON

TOYOTA · HONDA · pjm · TE connectivity · Aramco Services Company

China

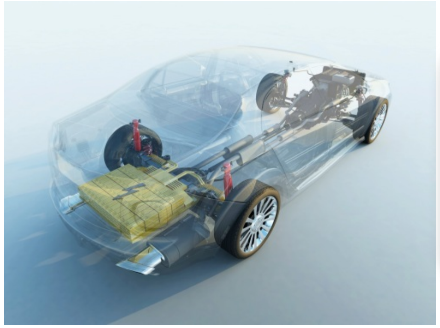
SAIC · GEELY · JAC · CAERI · CATARC

LISHEN · Potevio · ECTEK · KeyPower 科易动力

Research Thrust Areas

1. Advanced Batteries and Energy Conversion

2. Advanced Biofuels, Clean Combustion and APU



3. Vehicle Electrification

4. Lightweight Structures

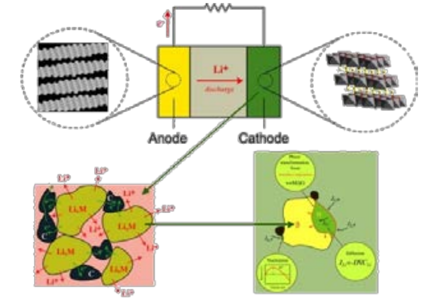
5. Vehicle-Grid Integration

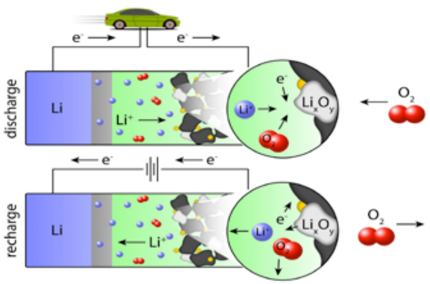
6. Energy Systems Analysis Technology Roadmaps and Policies

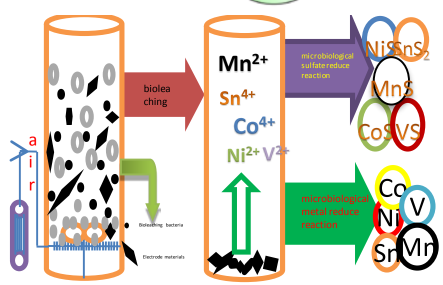
源研究中心

www.cerc-cvc.research.umich.edu

- **Degradation**: Combine modeling and advanced characterization to understand degradation mechanisms in Li-ion batteries.
- **Modeling, Controls, and Implementation**: To extend battery life, develop battery management systems with on-board balancing technologies. Review protocols for battery testing & safety. Explore pathways for reuse & recycling of batteries.
- **New Chemistries**: Advance Li-air and Li-sulfur chemistries towards commercial viability by revealing limiting phenomena and developing materials/architectures that overcome these obstacles.



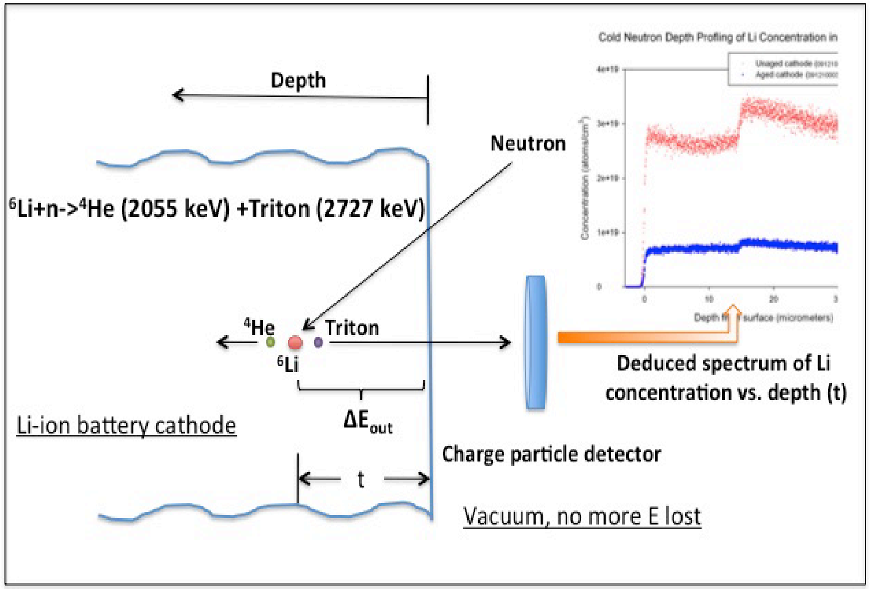


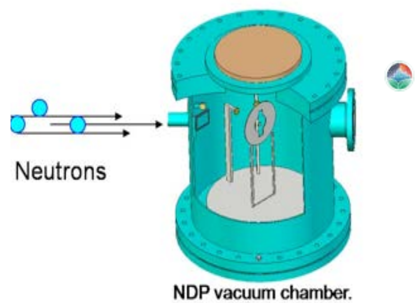


Degradation Babu (OSU) Bhushan (OSU) Conlisk (OSU) Cao & Canova (OSU) Daniel (ORNL) Leung (Sandia) Amine (ANL)	**Degradation** Qiu (THU)
Modeling & Controls Bernstein & Stein (UM)	**Modeling & Controls** Lu (THU)
Protocols, Recycling Bloom, Gaines, Sullivan (ANL)	**Protocols, Recycling** Hua (THU)
New Chemistries Siegel (UM) Van der Ven (UM) Shao-Horn (MIT) Ceder (MIT)	**New Chemistries** Wu (BIT) Kang (THU) Qui (THU) He (THU)

Three Highlighted Projects

- NDP Measurement Techniques for Improved Electrochemical Performance and Aging Models of Li-ion Batteries (Canavo, Cao, Nagpure)
- Data-Based Techniques for Battery-Health Prediction (Stein, Bernstein, Ersal)
- Battery State of Health Estimation Based on Incremental Capacity Analysis (Sun and Peng)

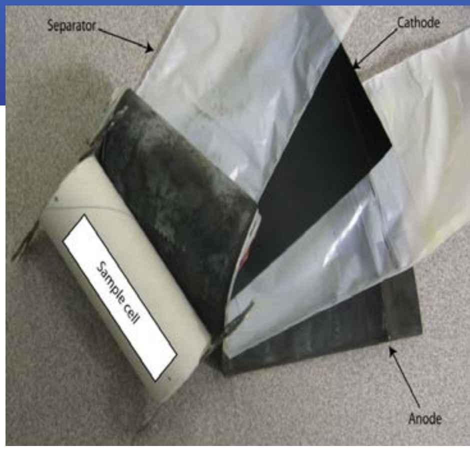


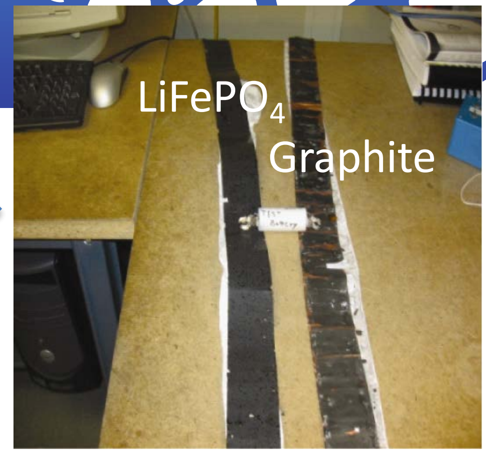


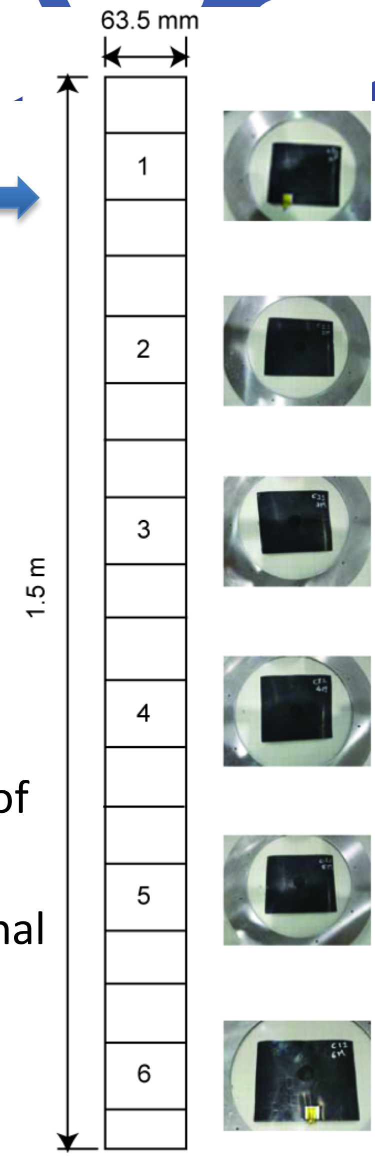
- Sample is bombarded with a low energy neutrons (energy ~ 0.025 eV);
- Difference between the residual energy of the particle emerging from the surface and energy of the particle at its origin is measured;
- Relate to the depth of the reacting lithium atom and Li concentration.

Advantages:

- Li cross-section for NDP is 940 barn (1 barn = 10^{-24} cm^2), one of the largest among the light elements.
- Direct quantitative measurement of lithium concentration possible.
- Depth resolution of 100 nm possible.
- Non-destructive sample preparation necessary.
- Technique is well known and largely applied for ***ex-situ*** characterization of Li-ion cells.



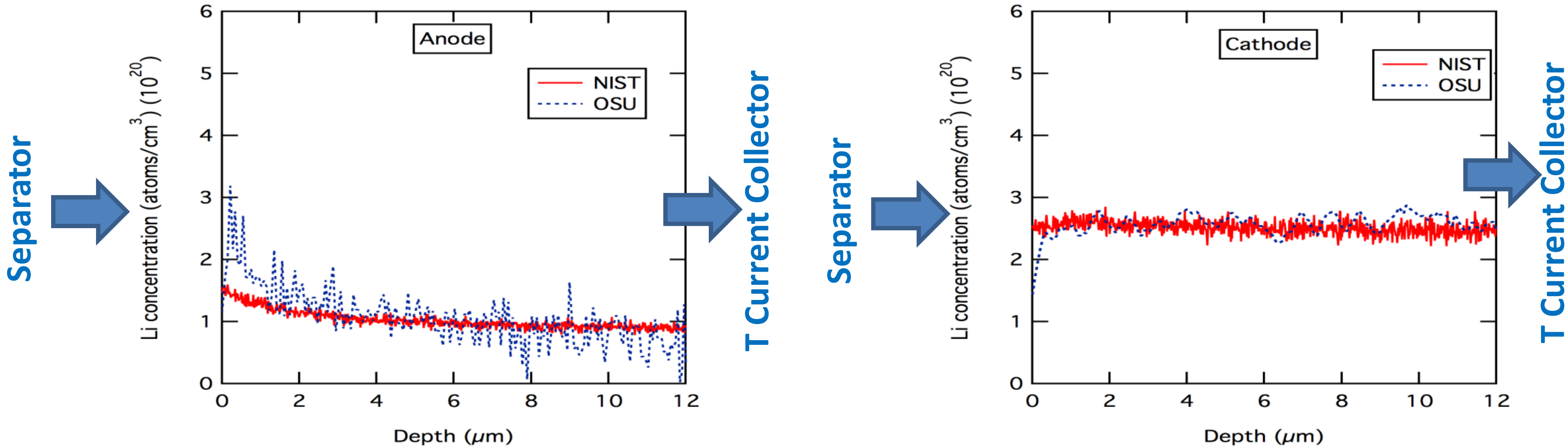




Cells	C-rate	SOC	Temperature (°C)	Ah Removed
C0	unaged	-	-	0
C2-1-1	2	0-10%	55	5830
C4-1-1	4	0-10%	55	5540
C7-3-1	~7	68% ±7%	45	3441

- The NDP facility at OSU was benchmarked by conducting measurements of the Li concentration in electrodes harvested from aged cells.
- The same samples were previously tested at the NDP facility at the National Institute of Standards (NIST).
- OSU-NDP facility has low thermal neutron flux (8.5 x 10^6 n/cm^2 s) as compared to NIST facility (1.2 x 10^9 n/cm^2 s), but has an improved acquisition system with solid state energy detectors.

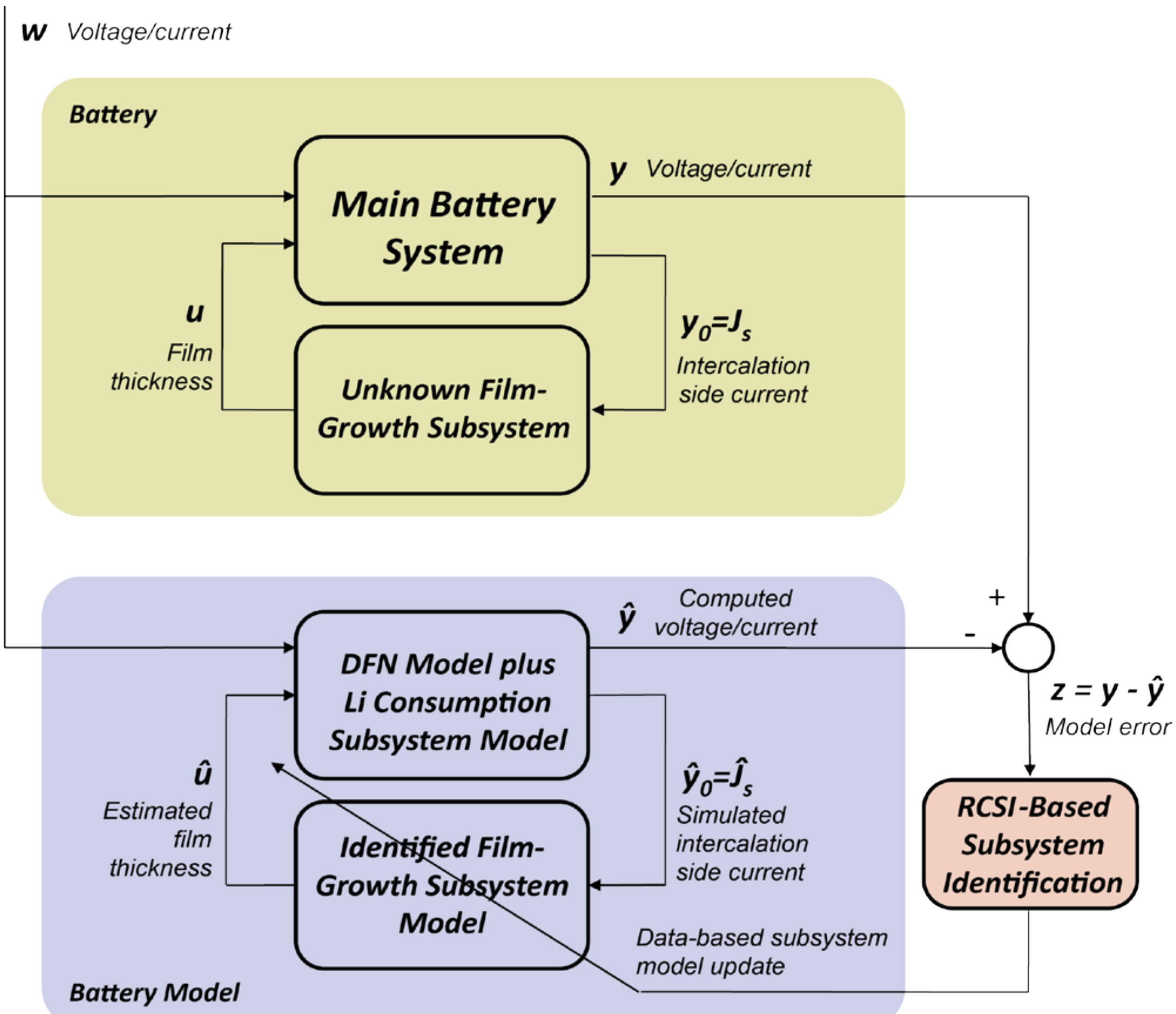
Example: Comparison of NDP Results for OSU and NIST Facility



- The profiles match in terms of shape, concentration, and depth values. Difference in the profiles close to the surface (first few nanometers) is caused by error in aligning the zero depth with the first channel in the detector.
- Even though there is significant difference in the count rate at NIST and at OSU due to the difference in the available neutron flux, the eight solid state detectors at OSU provide significant number of counts to establish accurate concentration profiles along the depth of the samples.
- Analysis is currently being repeated for all samples tested at NIST.

Future Outlook

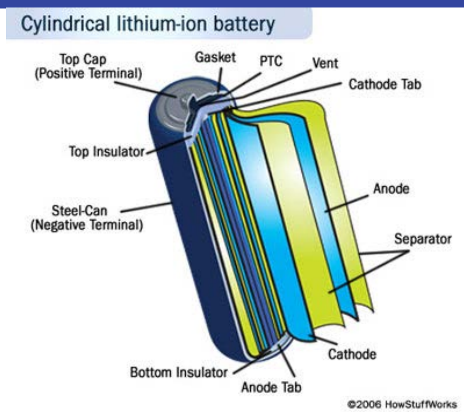
- Continued improvement of the facility will enable in-situ testing not in vacuum
- Full calibration against NIST test results
- Validate prototype cells by comparing against conventional half-cell;
- Use experimental results to improve Li-ion electrochemical models.

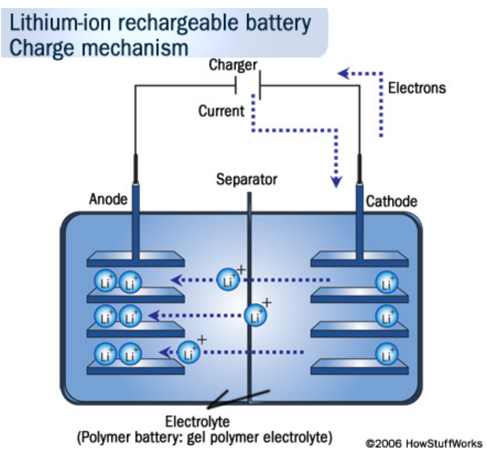


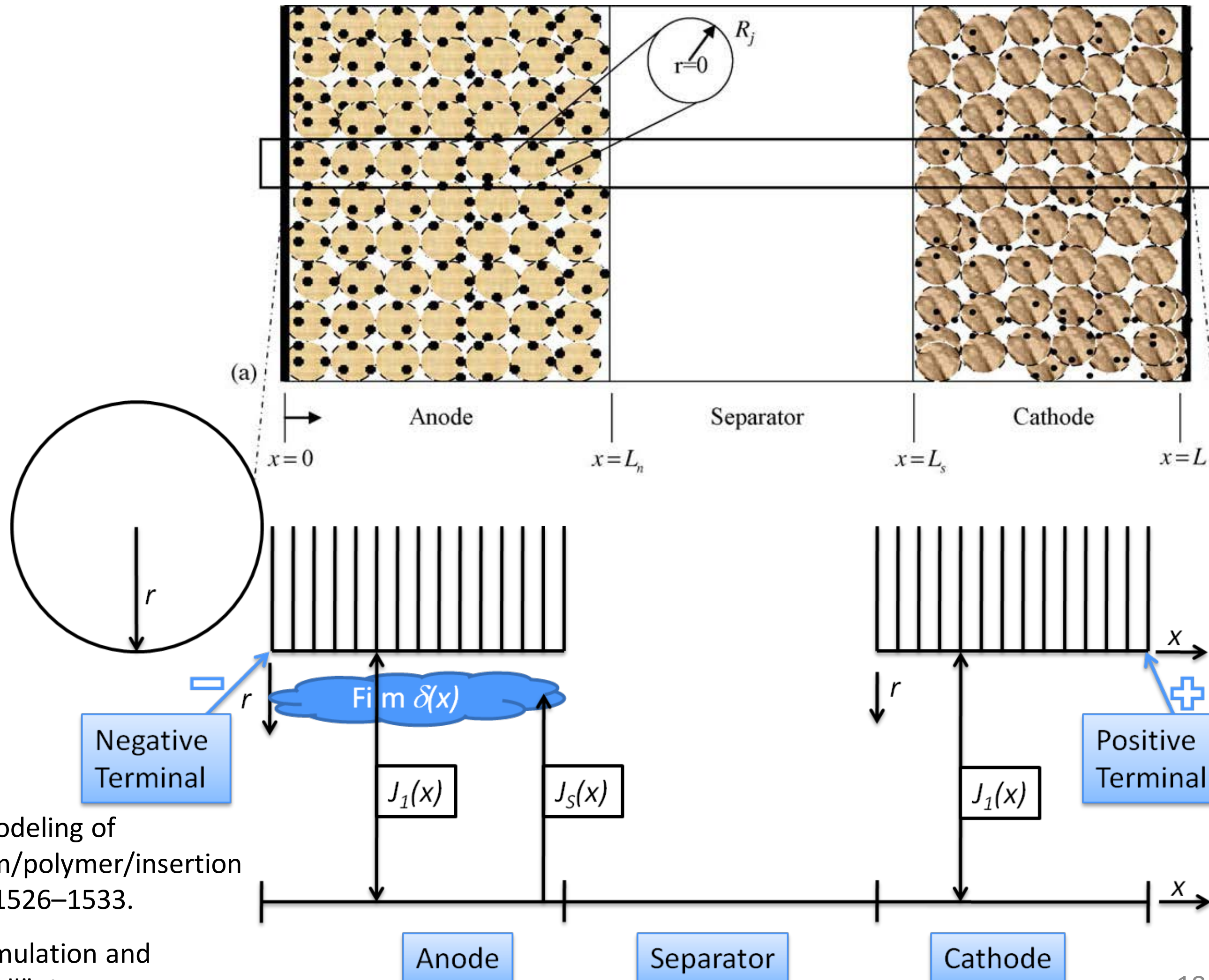
RCSI is a technique for data-based modeling that can identify a dynamic subsystem whose inputs and outputs are not measured.

RCSI is based on RCAC (Retrospective Cost Based Adaptive Control) Technique

The Main System Model: The Doyle-Fuller-Newman Model

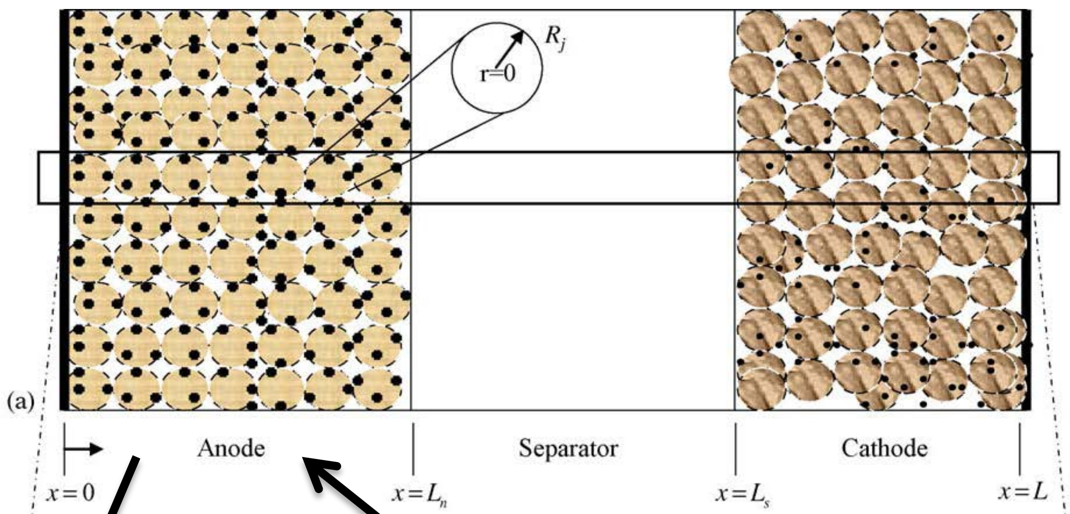






Doyle, M., Fuller, T., and Newman, J., 1993. "Modeling of galvanostaic charge and discharge of the lithium/polymer/insertion cell". *J. Electrochemical Society*, 140, June, pp. 1526–1533.

Fuller, T., Doyle, M., and Newman, J., 1994. "Simulation and optimization of the dual lithium ion insertion cell". *J. Electrochemical Society*, 141, January, pp. 1–10.



Side Reaction Intercalation Current J_s

$$J_s = -i_{0,s} a_n e^{\left(-\frac{\alpha_c F}{RT}\eta_s\right)}$$

Resistive Film δ_{film}

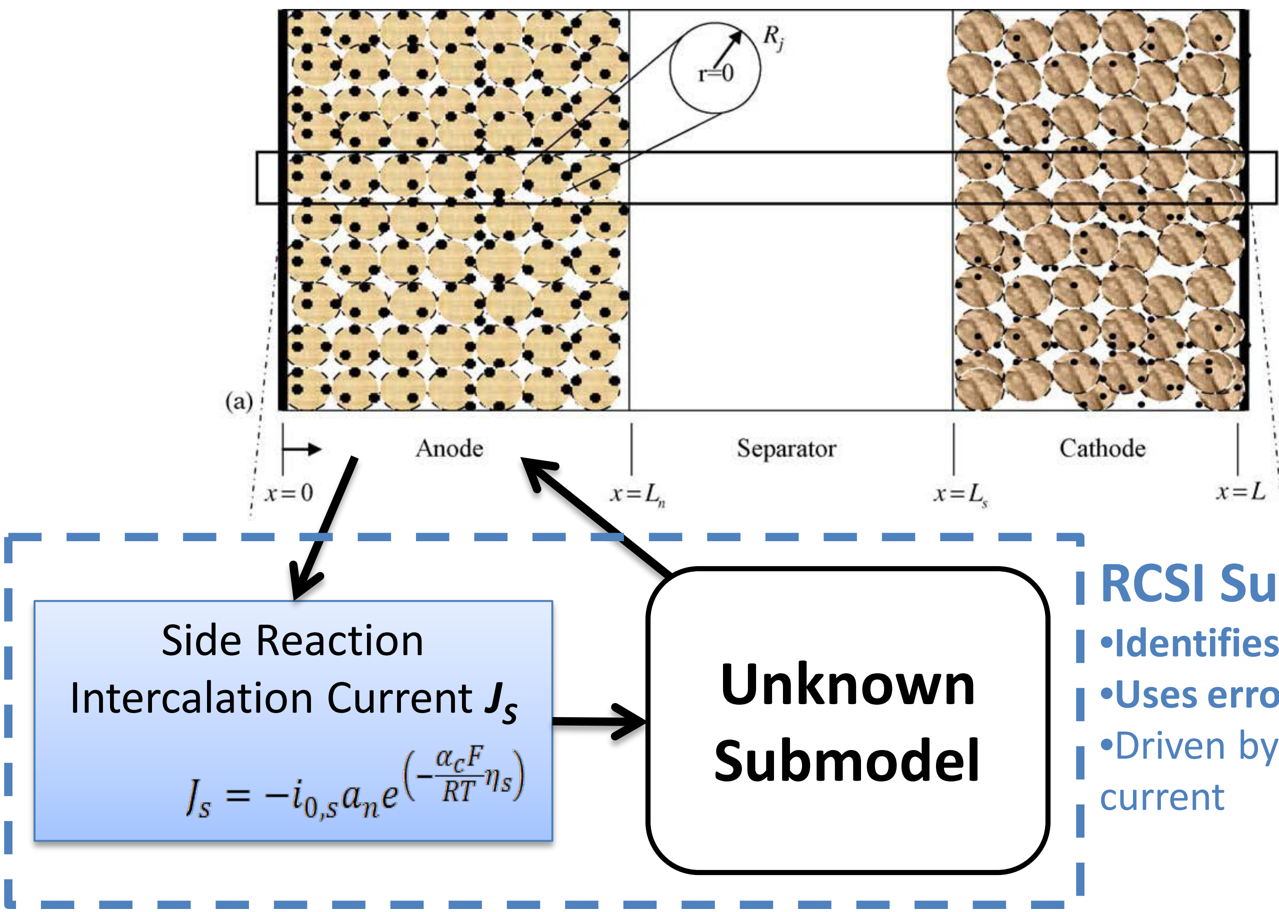
$$\frac{\partial \delta_{film}}{\partial t} = -\frac{J_s M_P}{a_n \rho_P F}$$

$$R_{film} = R_{SEI} + \frac{\delta_{film}}{K_P}$$

Ramadass *et al.* Health Model

- **Power Fade** through increased resistance
- **Capacity fade** through consumed Li-ions
- Driven by side reaction intercalation current

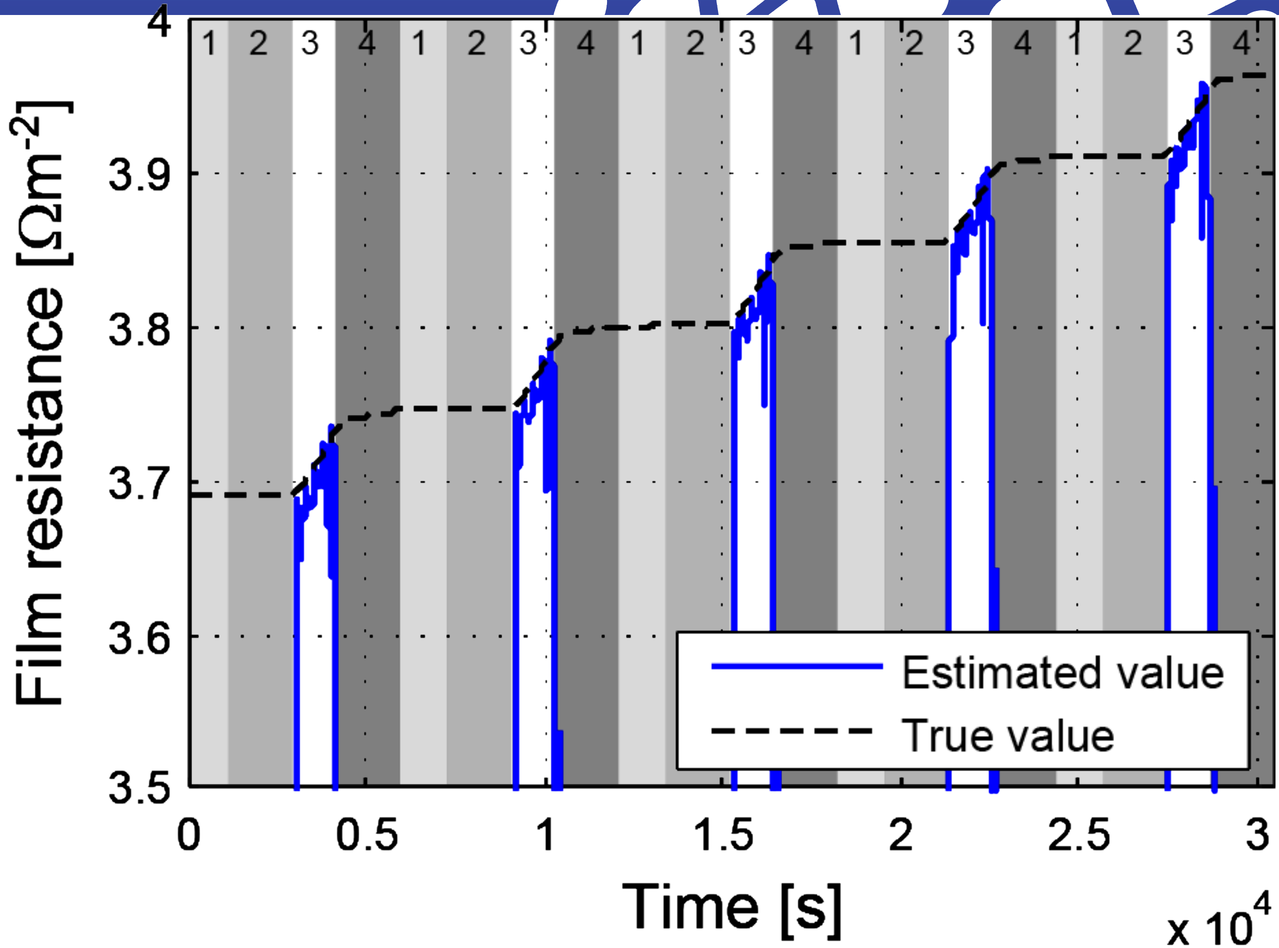
Ramadass, P., Haran, B., Gomadam, P. M., White, R., and Popov, B. N., 2004. "Development of first principles capacity fade model for Li-ion cells", *J. Electrochemical Society*, 151(2), January, pp. A196–A203.



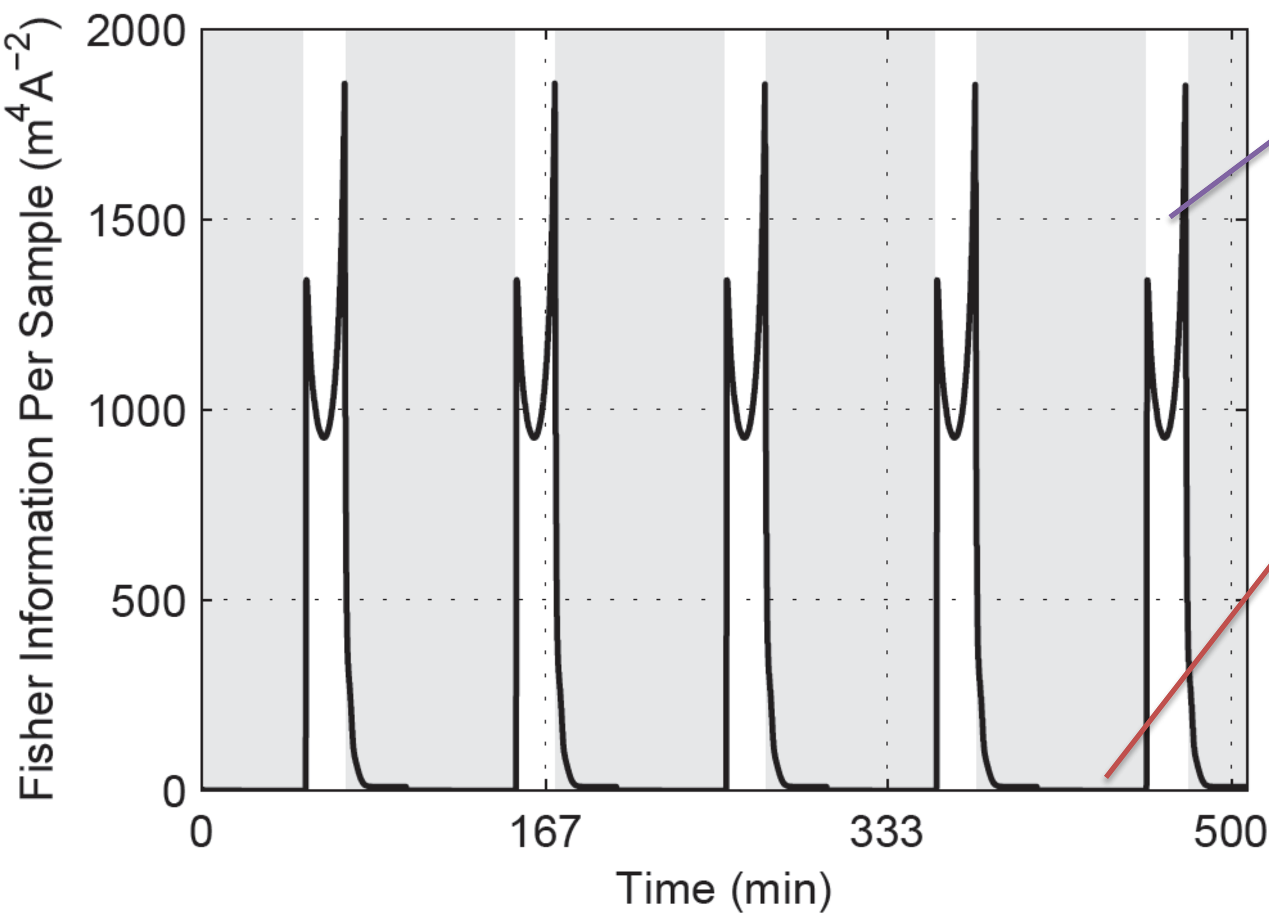
RCSI Submodel Identification

- **Identifies submodel and state**
- **Uses error signals to tune submodel**
- Driven by side reaction intercalation current

Ramadass, P., Haran, B., Gomadam, P. M., White, R., and Popov, B. N., 2004. "Development of first principles capacity fade model for Li-ion cells", *J. Electrochemical Society*, 151(2), January, pp. A196–A203.



1: CC discharge
2: CV discharge
3: CC charge
4: CV charge



WHITE REGIONS: Data contains enough information for identification

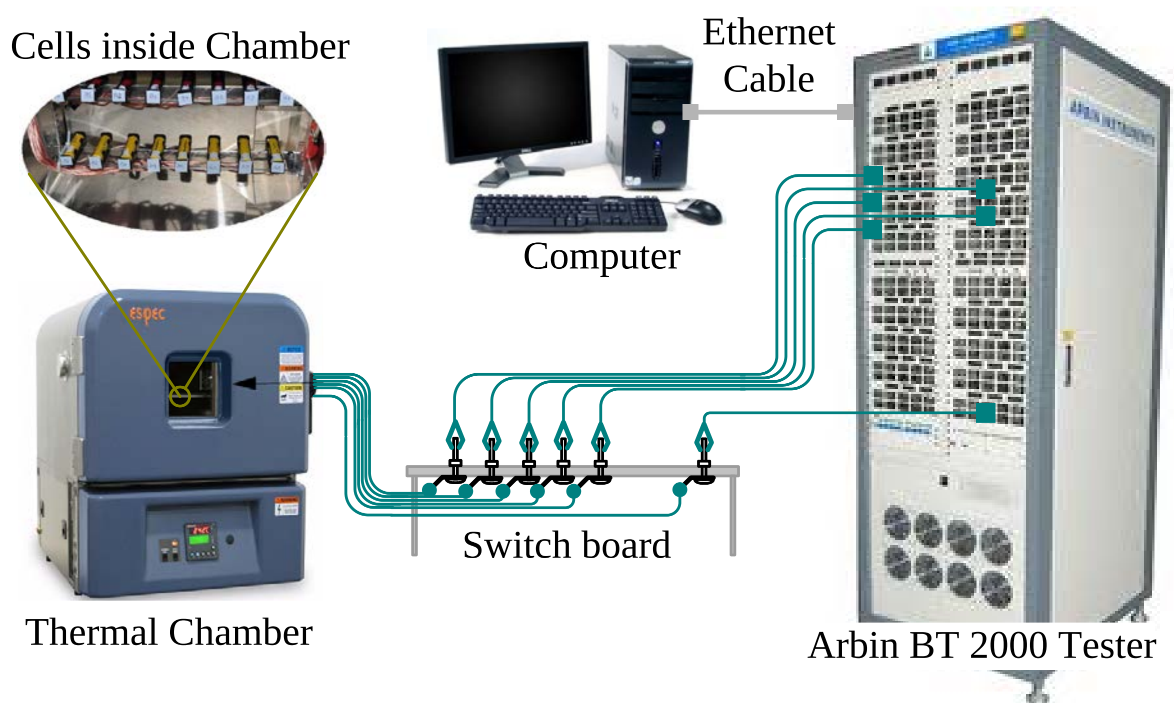
GRAY REGIONS: Data does not contain enough information for identification

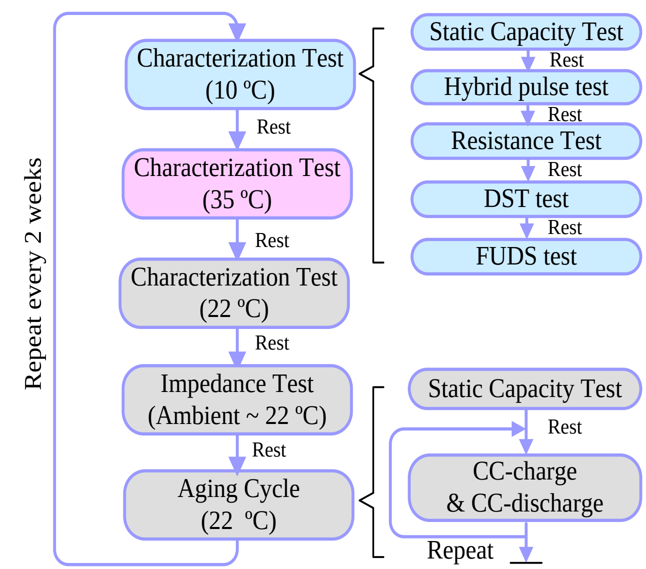
RCSI works well during the constant current charging phase, because this is the only phase where battery SoH is identifiable.

Experiment Setup

Spec for Li FePO4 cells (APR18650M1) manufactured by A123 Systems.

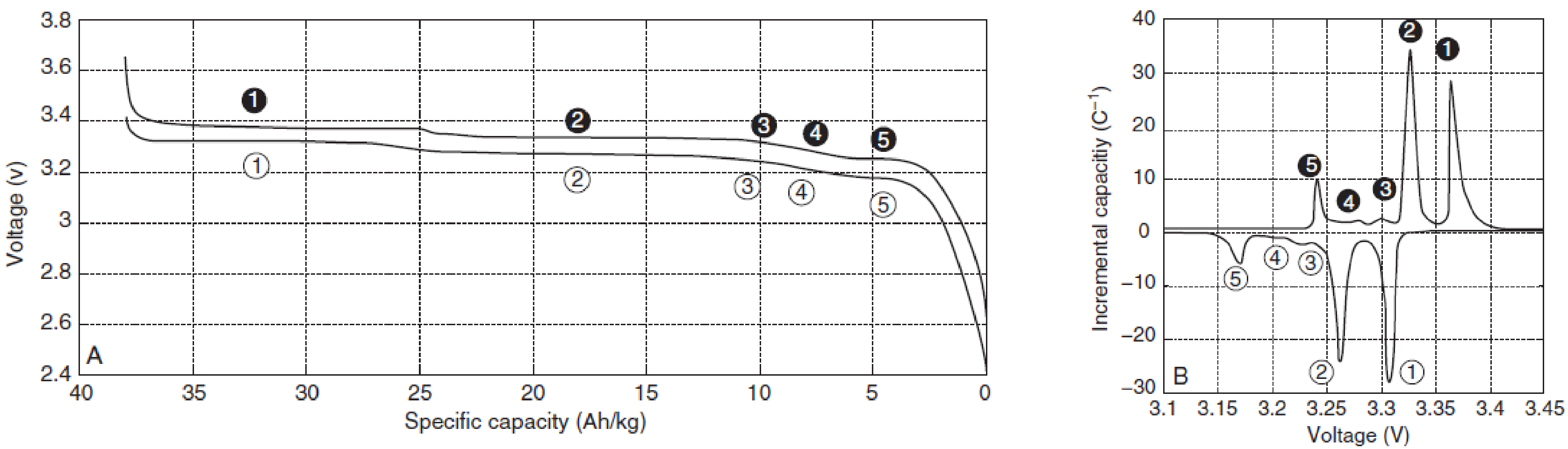
Typical Capacity	1.1Ah
Nominal Voltage	3.3V
Constant Voltage	Charging Voltage 3.7V
Power	3000W/Kg, 5800W/L





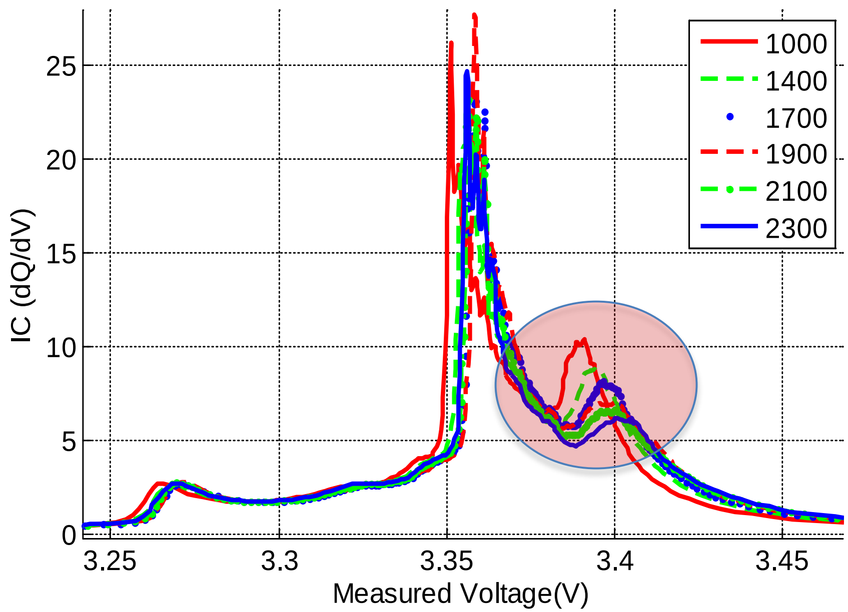
1. X. Hu, S. Li, and H. Peng. "A comparative study of equivalent circuit models for li-ion batteries." *J. Power Sources,* 198:359–367, 2012.

- Transforms plateaus on V-Q curve into identifiable peaks on incremental capacity curve (dQ/dV)
- Reflects the staging phenomena in lithium intercalation process
- Amplified sensitivity

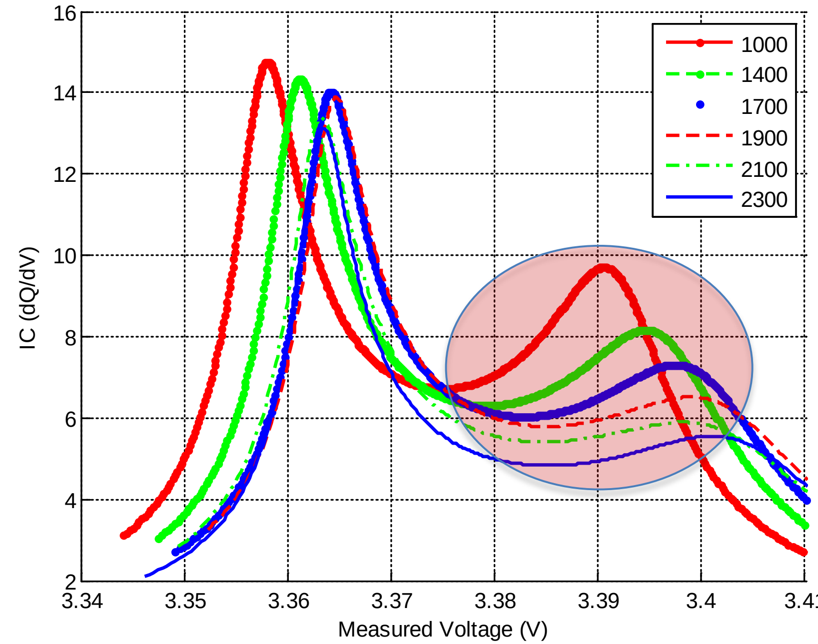


1. M. Dubarry, B.Y. Liaw, "Identify capacity fading mechanism in a commercial LiFePO4 cell", *J. Power Sources* 194:541–549,2009.

- Full charging/discharging V-Q curves not available in real-life operation
- ICA performed with partially charging data
  - Numerical derivative
  - Polynomial curve fitting (5th order)



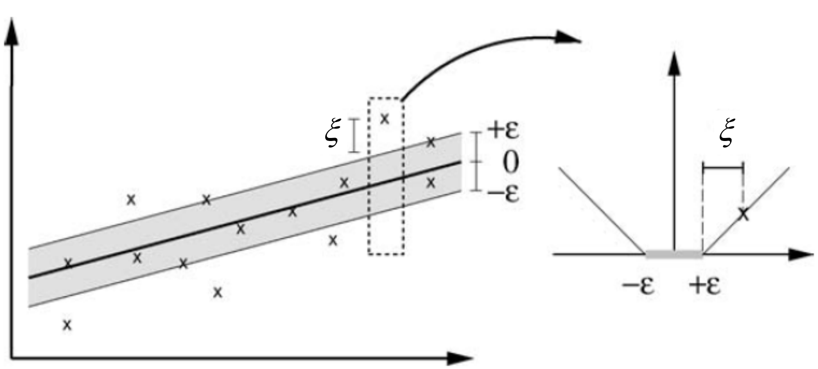
Results by numerical derivative



Results by polynomial curve fitting

1. C. Weng, Y. Cui, J. Sun, and H. Peng. "On-board state of health monitoring of lithium-ion batteries using incremental capacity analysis with support vector regression." *J. Power Sources,* 235:36–44, 2013.

- Numerical Derivative
  - Applicable to data set at any capacity range
  - Computationally expensive
  - Resulting curves are noisy
- Polynomial Curve Fitting
  - Smooth and suitable for quantitative analysis
  - Efficient identification algorithm is readily available
  - Highly sensitive to the selection of data set
- A more robust and flexible method is needed



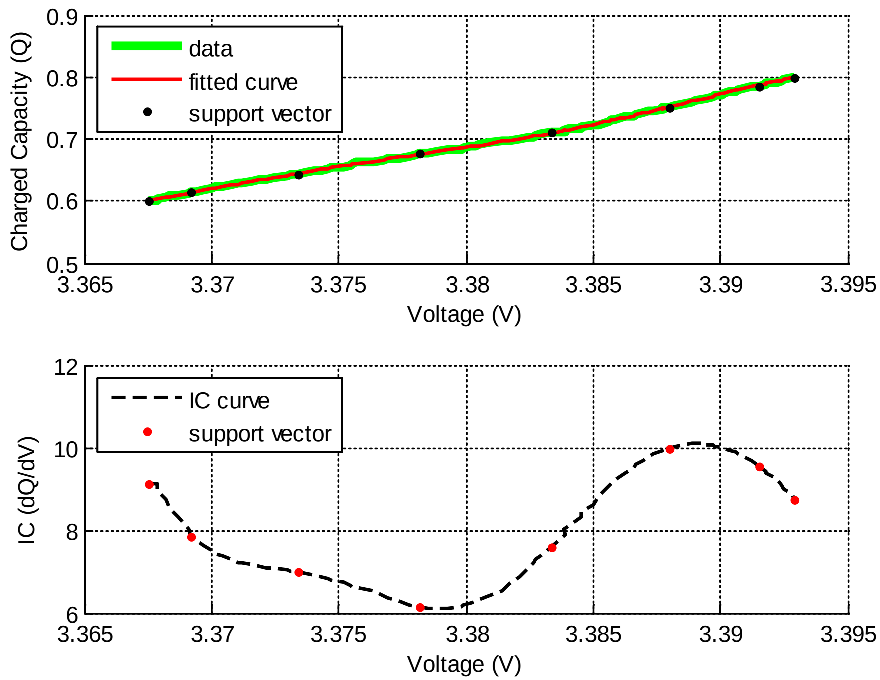
- SVR Basics:
  - Phenomenological and data driven
  - Model derived through an optimization process
  - Non-parametric function estimation
  - Excellent approximation and generalization capabilities
  - Low sparsity and model complexity

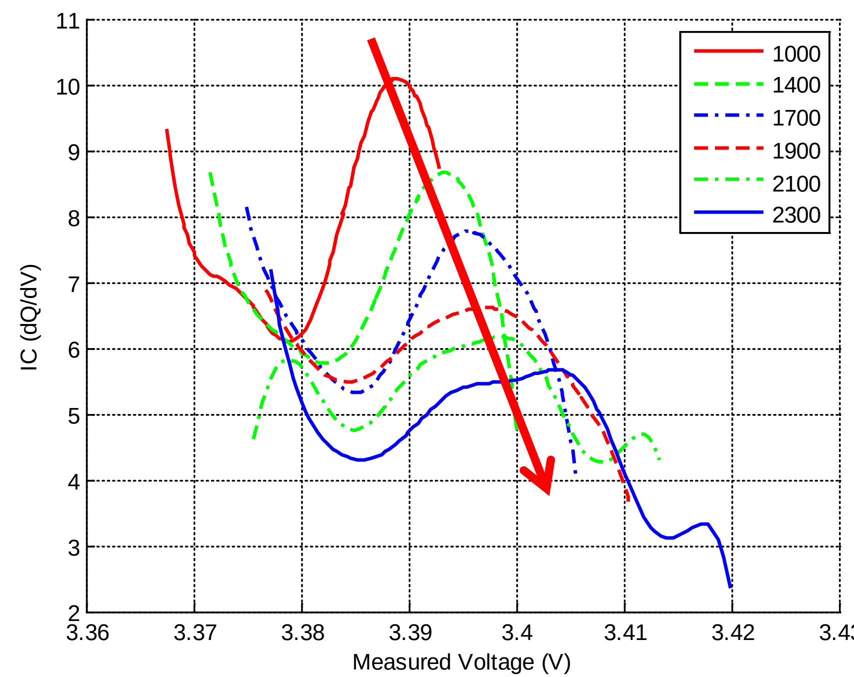
$$f(x_n) = \sum_{i=1}^{N} \beta_i k(x_i, x_n)$$

$$\text{minmize } \frac{1}{2}\|\boldsymbol{\beta}\|_1 + w\sum_{n=1}^{N}\xi_n,$$

$$\text{subject to } \begin{cases} y_n - \sum_{i=1}^{N}\beta_i k(x_i, x_n) \le \varepsilon + \xi_n \\ \sum_{i=1}^{N}\beta_i k(x_i, x_n) - y_n \le \varepsilon + \xi_n \\ \xi_n \ge 0 \end{cases}$$

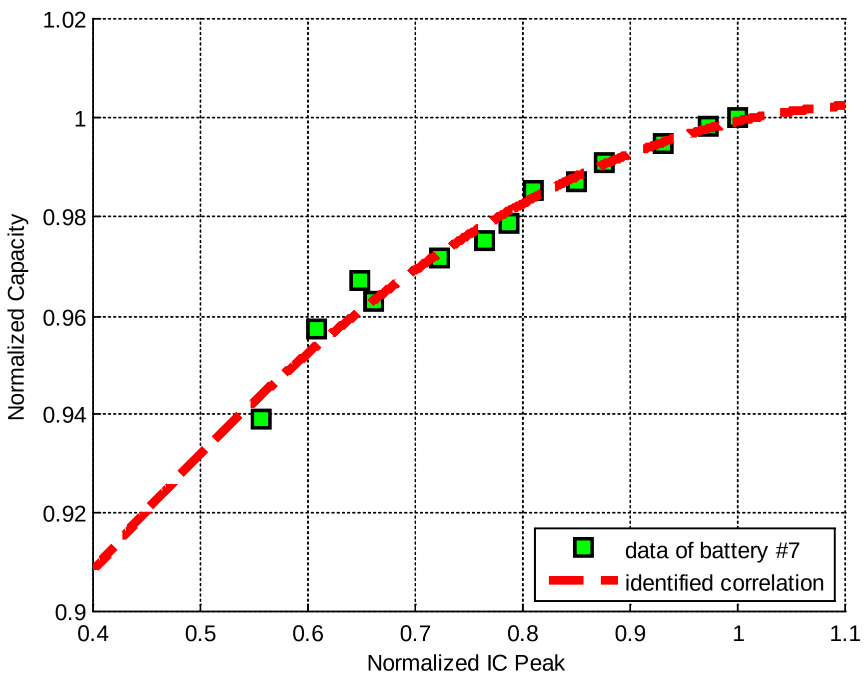
- Apply the SVR algorithm iteratively as battery ages
- Robust in effective aging signature extraction



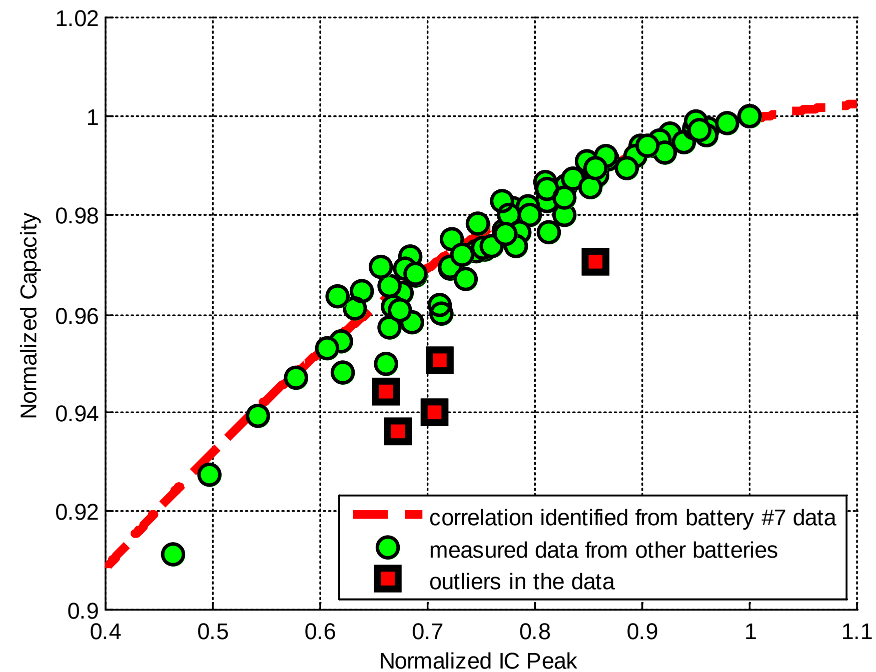


1. C. Weng, Y. Cui, J. Sun, and H. Peng. "On-board state of health monitoring of lithium-ion batteries using incremental capacity analysis with support vector regression." *J. Power Sources,* 235:36–44, 2013.

- The SVR model built upon the data from one single cell is able to predict the capacity fading of 7 other cells with less than1% error.



Correlation identified from cell #7



Used for capacity fading prediction of other cells

- CERC-CVC is a US-China collaborative team with capabilities to address a broad range of battery-related R&D:
  - Near term: Safety, implementation, degradation, system modeling, controls
  - Future: New chemistries
- Responsive to industrial inputs and needs

3rd CERC-CVC annual meeting on August 19-20 2013 in Beijing!