Parameters inference and model reduction for the Single-Particle Model of Li ion cells*.

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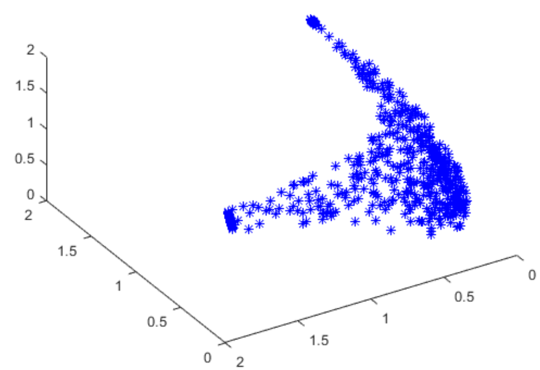


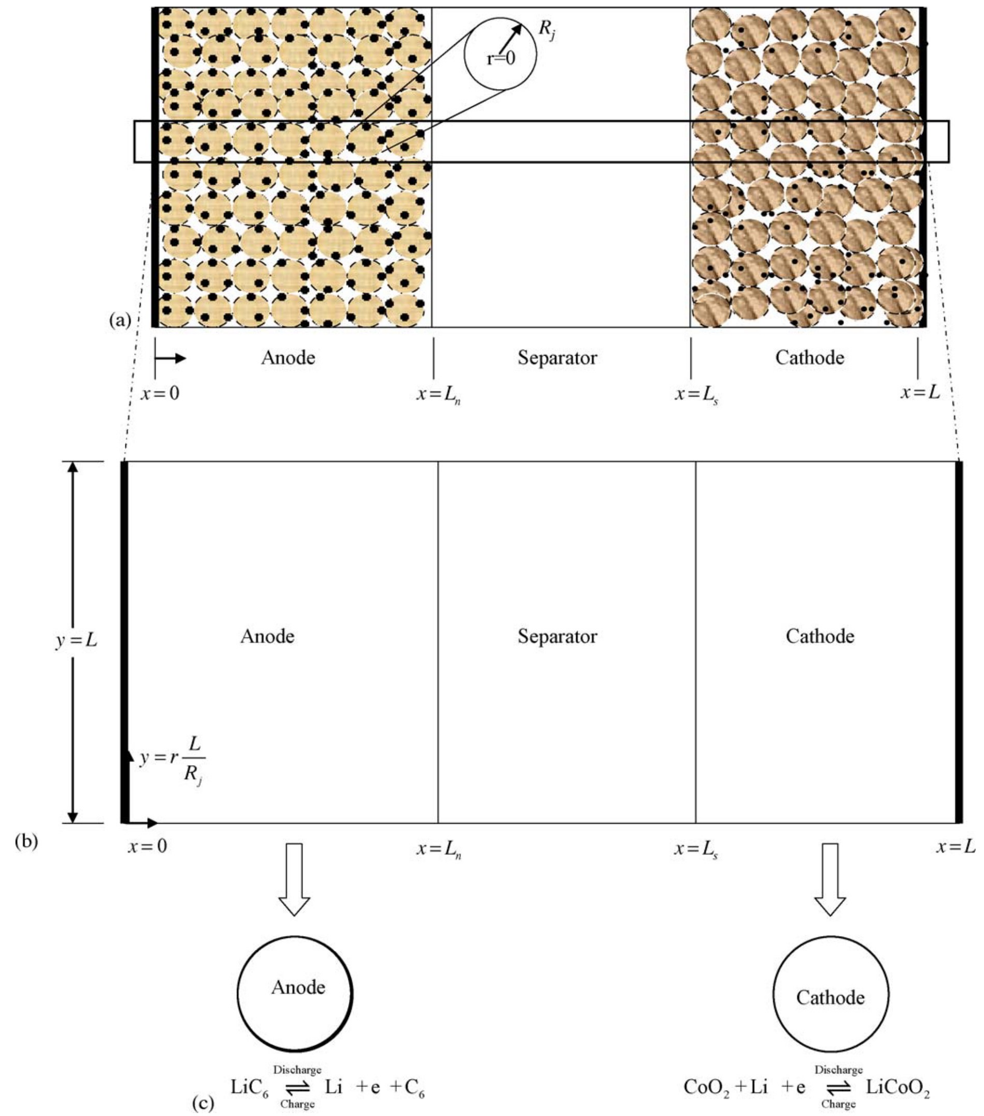
*M. Khasin, C. S. Kulkarni, K. Goebel, Parameters inference and model reduction for the Single-Particle Model of Li ion cells, https://arxiv.org/abs/1912.05807

Outline

- **Battery Models:** 1. predicting performance (e.g., SOC); 2. Physical state characterization (SOH)
- **1 does not imply 2:** e.g. data-driven models
- **Physics-based models**: inference of parameters provide physical state characterization
- **Single-particle Model (SPM)**: high efficiency and reasonable fidelity
- **A fundamental limitation on SOH characterization:** The best-fit values of the parameters are not necessarily physically meaningful
- **What meaningful information about the battery SOH can a SPM provide and how to obtain this information?**

Single Particle Model (SPM)*

- ***Assumptions:***
  - Electrolyte state is uniform
  - Solid phase potential is uniform
  - Solid electrodes particles are spherical and of the same size in a given electrode.
  - Solid particles form a connected cluster
  - Solid diffusivity is constant



*S. Santhanagopalan, Q. Guo, P. Ramadass, and R. E. White. Review of models for predicting the cycling performance of lithium ion batteries. Journal of Power Sources, 156:620628, 2006.

SPM. Parameters

$$V(t) = \Delta\phi_c(l_c,t) - \Delta\phi_a(l_a,t)$$

$$= \Delta\phi_c^{eq}(\bar{\theta}_c^{(0)}) - \Delta\phi_a^{eq}(\bar{\theta}_a^{(0)}) - I_a\,(r_a + r_c) + \frac{2k_B T}{e}\ln\left(\frac{\chi_c^{(0)} + \sqrt{(\chi_c^{(0)})^2+1}}{\chi_a^{(0)} + \sqrt{(\chi_a^{(0)})^2+1}}\right)$$

$$\chi_i^{(0)}(\bar{\theta}_i) = \frac{I_i}{\tilde{I}_i\left(\theta_i^{(0)}\right)^{\frac{1}{2}}\left(1-\theta_i^{(0)}\right)^{\frac{1}{2}}}, \quad \tilde{I}_i \equiv \frac{3Al_i(1-\epsilon_i)k_i c_e^{\frac{1}{2}}}{R_i},$$

$$I_a = -I_c, \quad |I_i| = I, \quad I_a > 0 \quad for \quad discharge,$$

$$\theta_a = \bar{\theta}_a\Theta_a^*, \quad \theta_c = 1 - \bar{\theta}_c\,(1-\Theta_c^*)\,,$$

$$\boxed{Parameters\ (5):\ r = r_a + r_c,\ \tilde{I}_i,\ \Theta_i^*;\ i = a, c,}$$

$$\bar{\theta}_i(t) = 1 - \mathcal{L}^{-1}\left[\frac{\mathrm{sign}(I_i)\mathcal{L}\left[\bar{\zeta}_i(t')\right]}{\sqrt{s}\tanh\sqrt{s}-1}\right]\left(\frac{t}{\tau_i}\right),$$

$$\bar{\zeta}_i(t/\tau_i) = \frac{I_i(t)}{I'_{i,eff}}, \quad I'_{i,eff} \equiv \frac{3eN_{Li,i}}{\tau_i}, \quad \tau_i = \frac{R_i^2}{D_i},$$

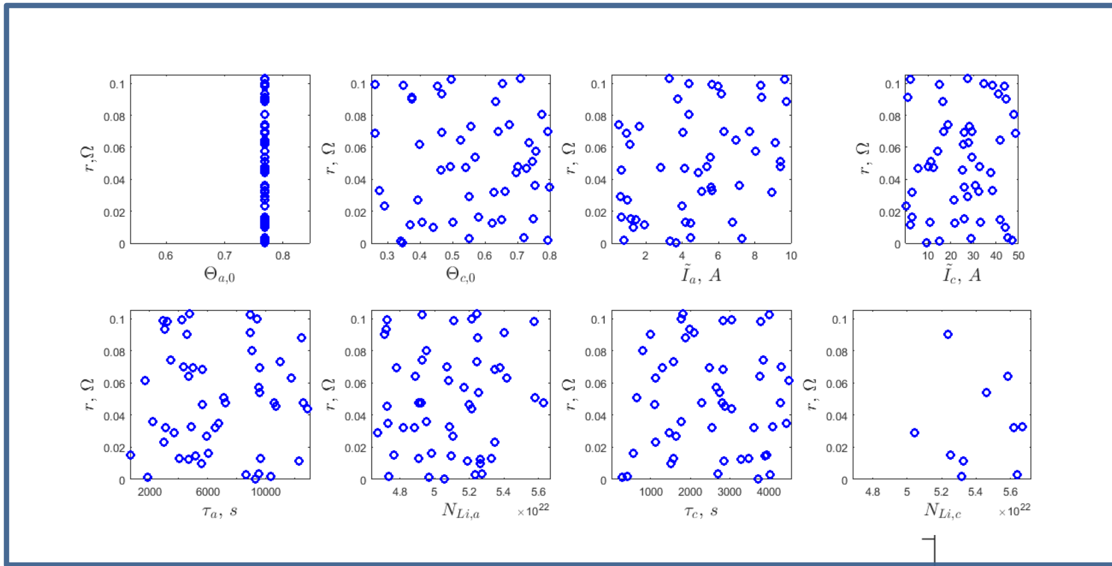
$$N_{Li,a} = M_{Li,a}\Theta_a^*, \quad N_{Li,c} = M_{Li,c}\,(1-\Theta_c^*), \quad M_{Li,i} = \frac{4}{3}\pi R_i^3 K_i m_i.$$

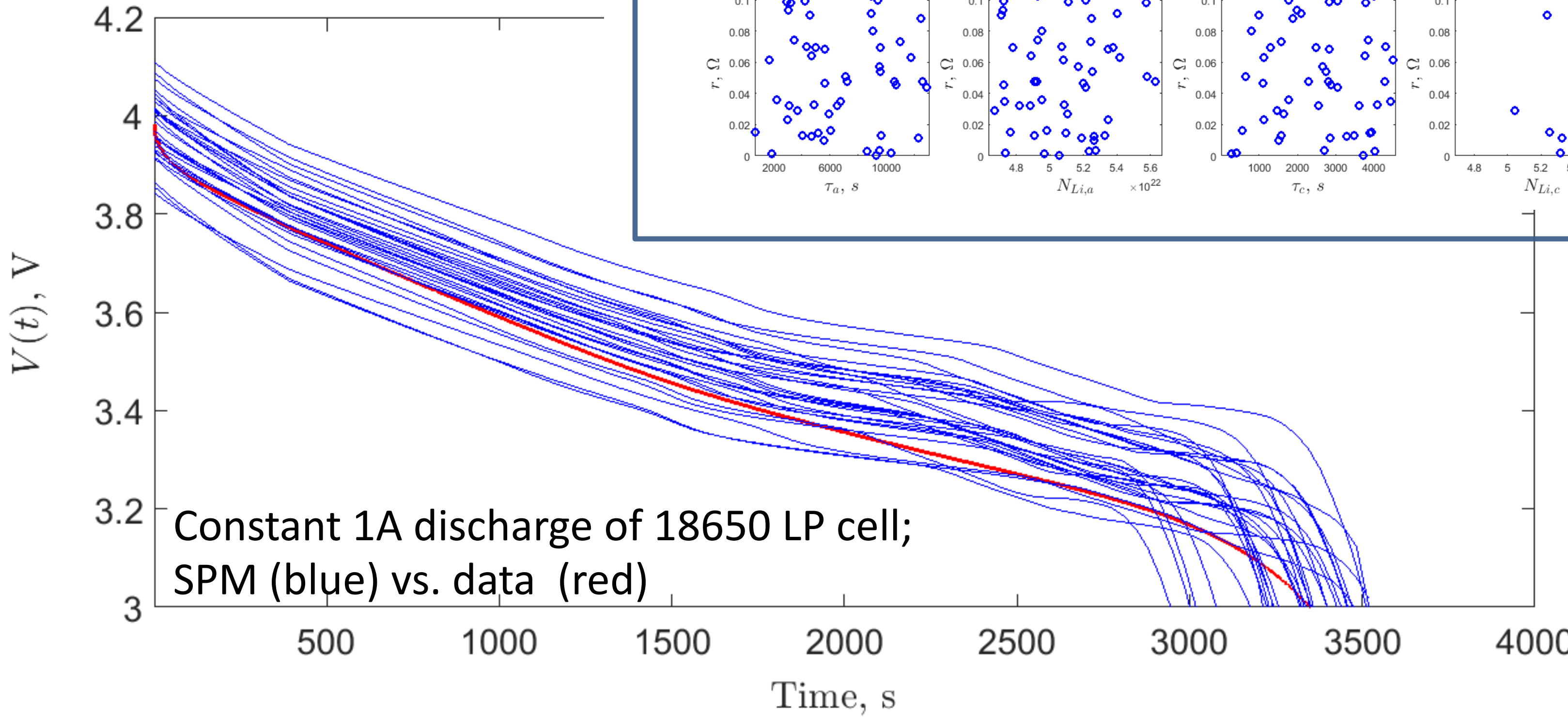
$$\boxed{Parameters\ (4):\ \tau_i,\ N_{Li,i};\ i = a, c,}$$

- $N = 9$ "microscopic" parameters
- Cathode and anode OCPs
- **The goal: to infer as many parameters as possible from the cycling data, based on the SPM, for given OCPs**

“Emergent behavior” of a Li ion battery

- Values of $N = 9$ parameters are randomly picked over admissible region
- The corresponding SPM predictions are plotted below

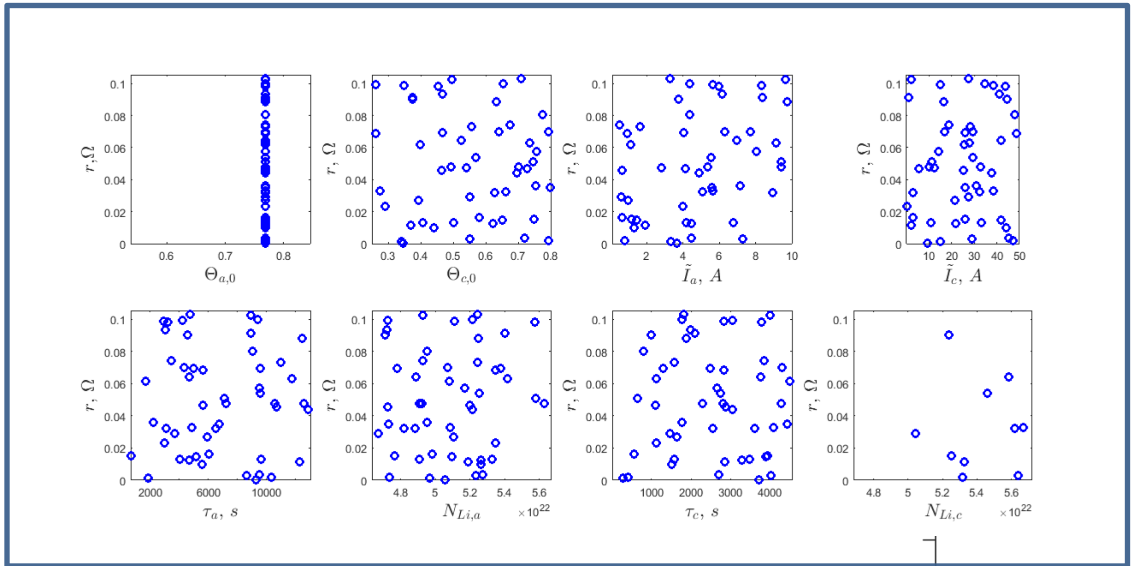


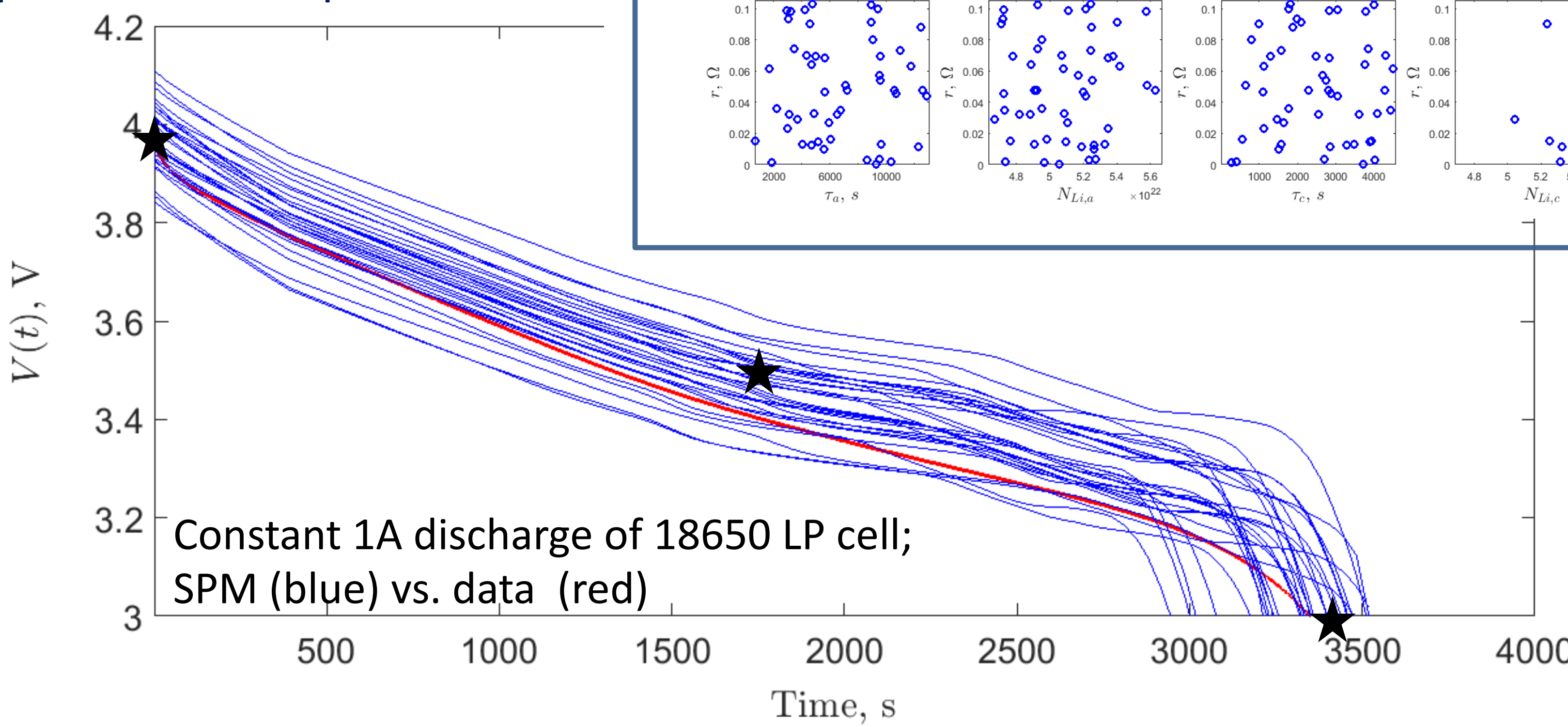


- Discharge curves are “simple”= emergent behavior of the Li ion cell
- Simple=the curves can be parametrized by few parameters $M < N = 9$

“Emergent behavior” of a Li ion battery

- Values of $N = 9$ parameters are randomly picked over admissible region
- The corresponding SPM predictions are plotted below





- For example, fixing $M = 3$ data points (stars in the figure) will severely constrain variability of the discharge curves

Best-fit manifold (BFM)

Generic subset $\mathcal{M}$ of data points $x_m, \quad m = 1, \ldots, M < N$

Cost function for the fit obtains its minimum at $p^*_{\mathcal{M}}$

$$C(\mathbf{p})|_{\mathcal{M}} = \sum_{x_m \in \mathcal{M}} [f_m(\mathbf{p})|_{\mathcal{M}} - x_m]^2$$

Best-fit Manifold is the set of parametric values p, such that

$$f_m(\mathbf{p})|_{\mathcal{M}} = f_m(\mathbf{p}^*_{\mathcal{M}})|_{\mathcal{M}}, \quad m = 1, 2, \ldots, M < N$$

- BFM is defined by values of *M* stiff parameters
- BFM is parameterized by *N-M* sloppy parameters
- Sloppy Models* have *M<<N*
- The dependence of the BFM on the choice of $\mathcal{M}$ is weak

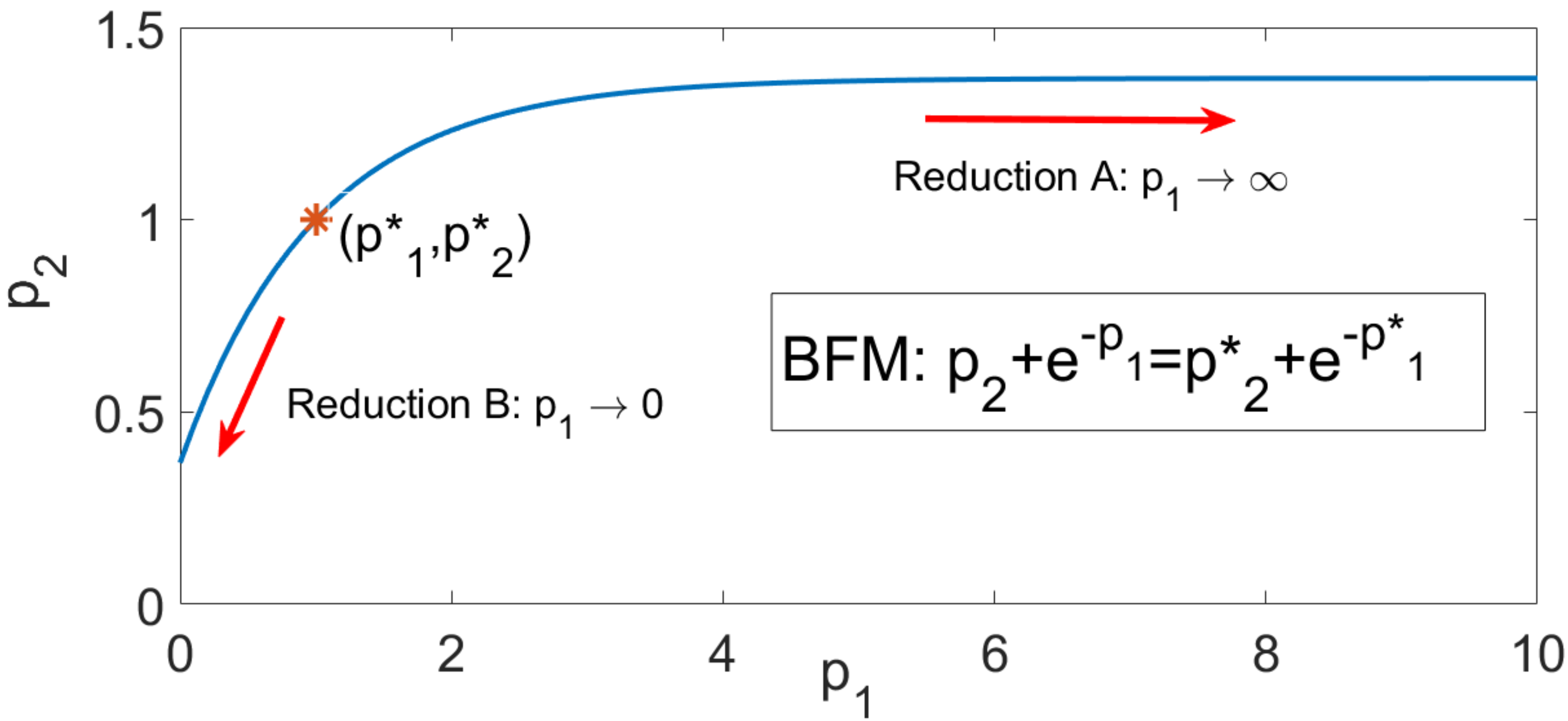
*Perspective: Sloppiness and emergent theories in physics, biology, and beyond, M. K. Transtrum, et al, J. Chem. Phys. 143, 010901 (2015)

Consequences of the “sloppiness” of SPM

- Only a few stiff parameters $M \ll N$ of the battery can be inferred from the SPM
- The stiff parameters are generally not the original (“microscopic”) parameters of the SPM
- The stiff parameters can be recovered using the model reduction by moving on the BFM towards limiting values of its parameters*

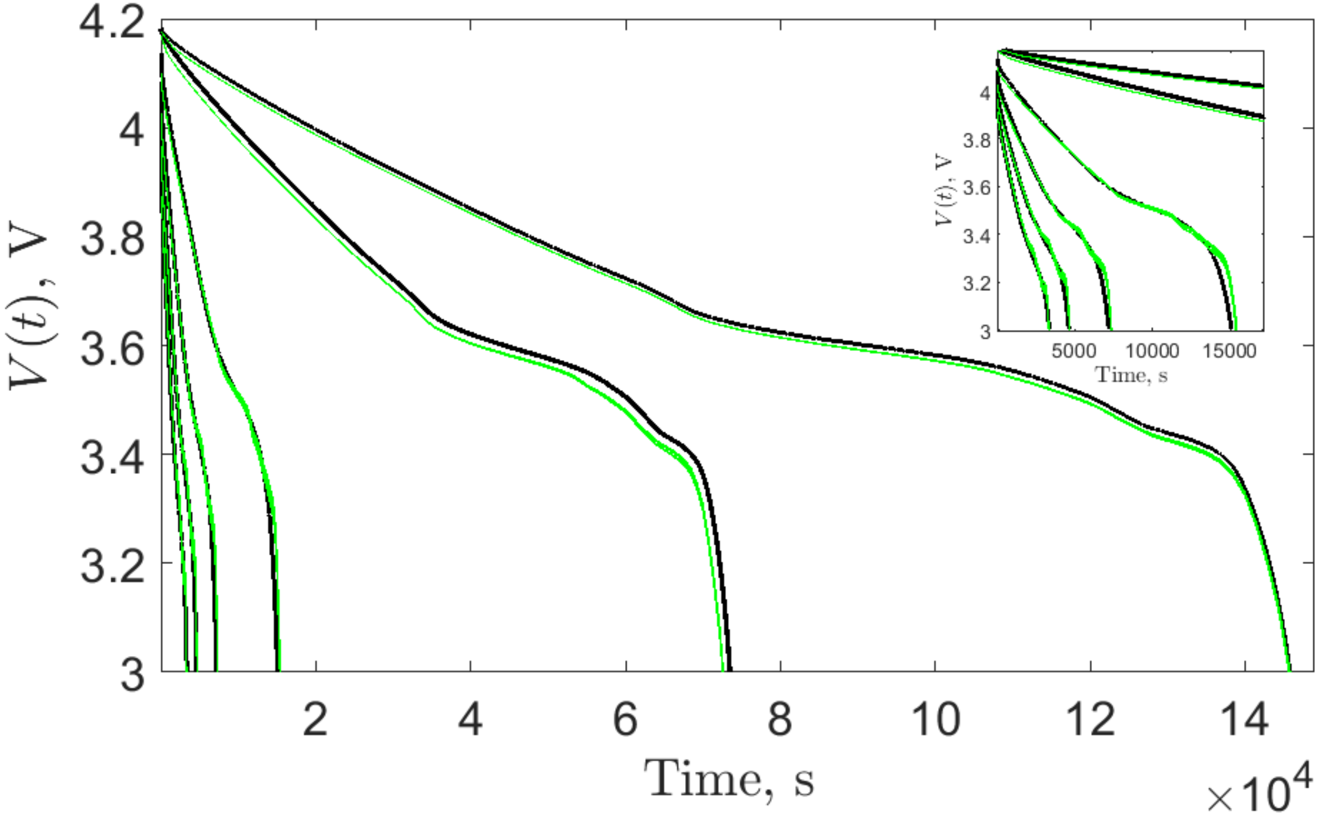
M. K. Transtrum and P. Qiu. Model reduction by manifold boundaries. Physical Review Letters, 113:098701, 2014.

A toy model of Model Reduction.



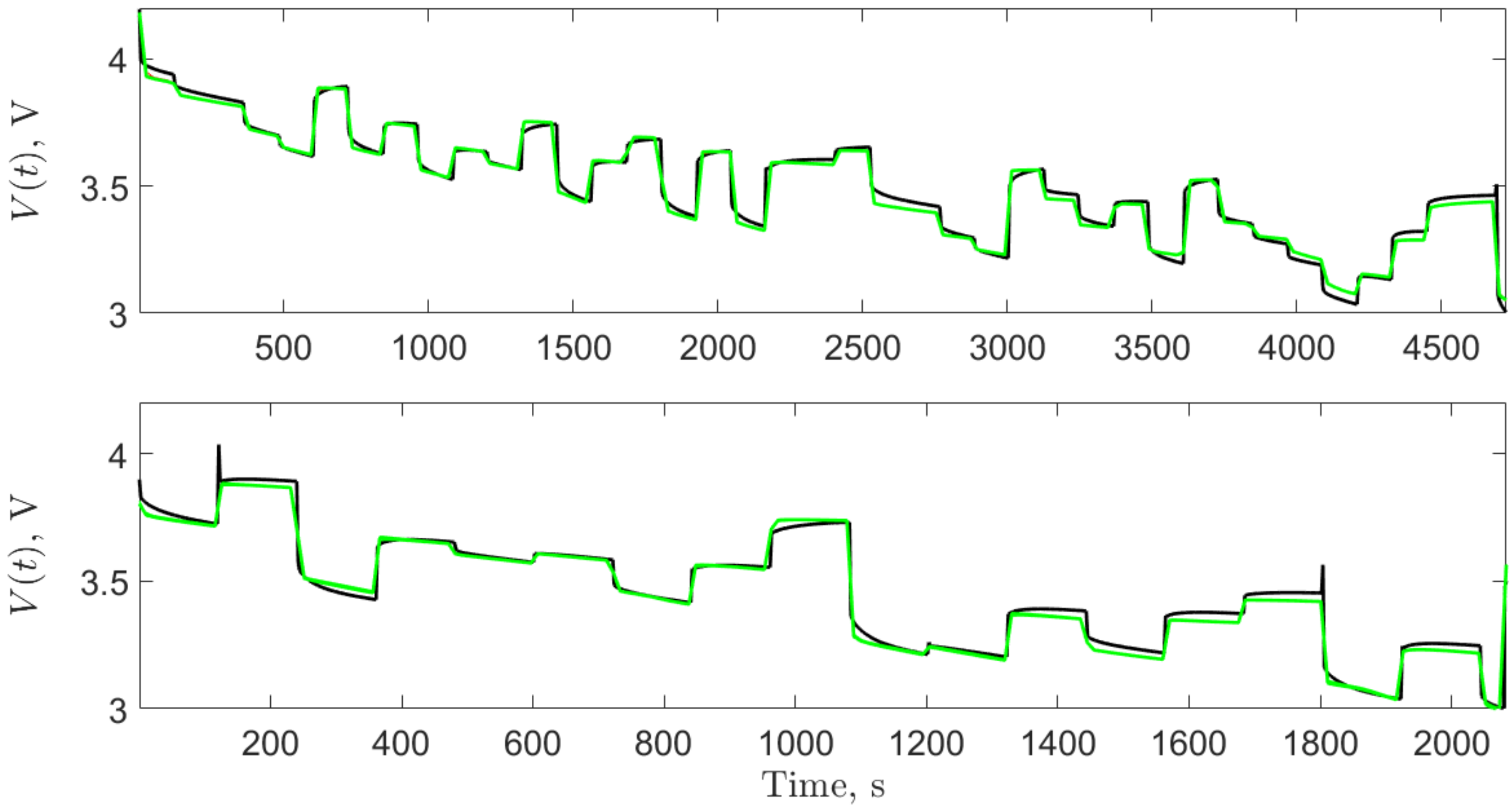
- Reduction A: $p_1 \to \infty \Rightarrow p_2 \to p_2^* + e^{-p_1^*}$
- Reduction B: $p_1 \to 0 \Rightarrow p_2 \to p_2^* + e^{-p_1^*} - 1$
- The limiting values of p_2 are *nonlinear functions* of the values of original parameters p_1^*, p_2^*

SPM fit to constant discharge data: 18650 LP



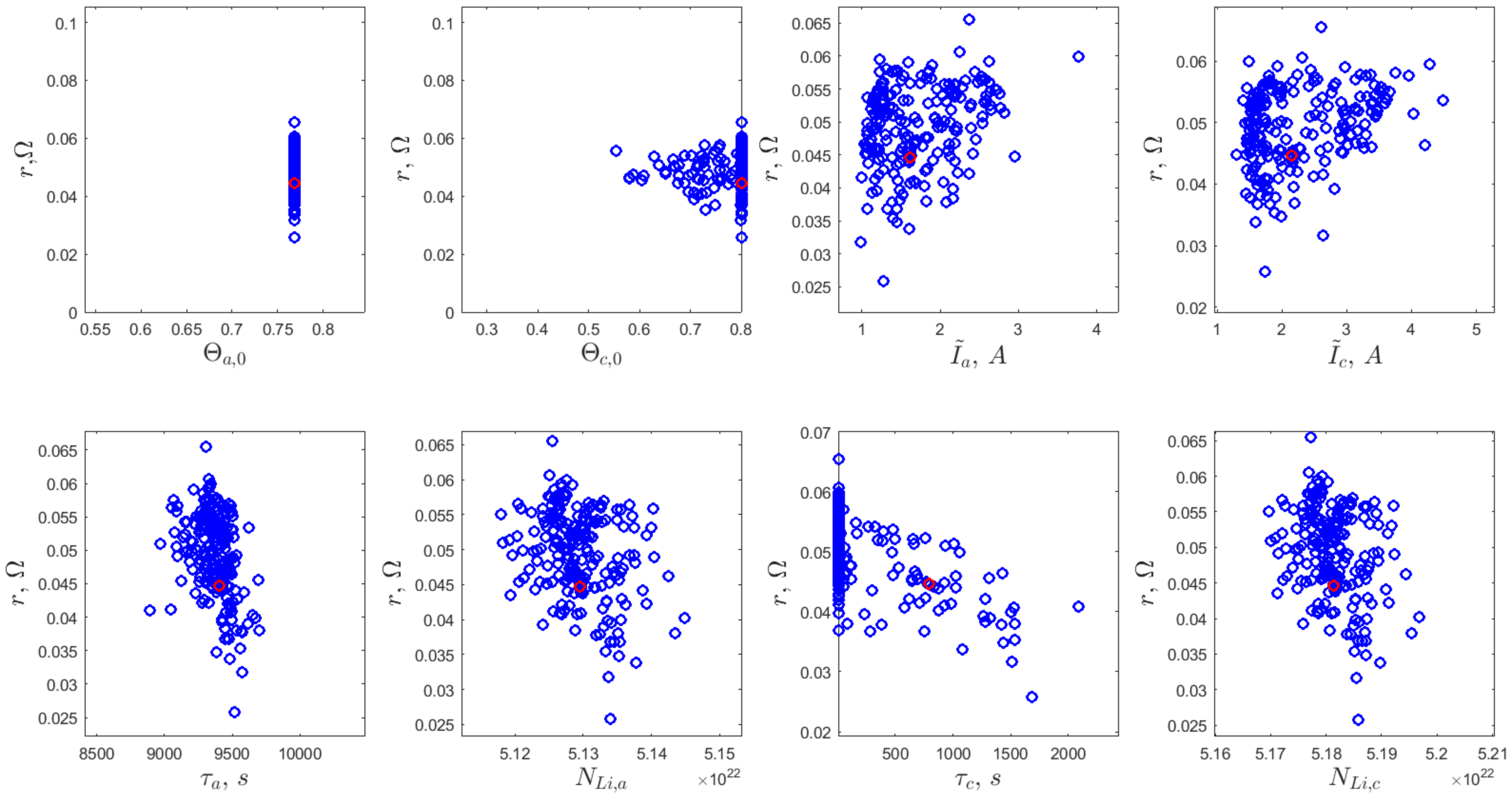
- Discharge data (**black**: discharge currents $I = 2.0, 1.5, 1.0, 0.5, 0.055$A);
- Parameters fit to data subset (training data): e.g., $I = 2.0, 1.0, 0.055$A;
- Ensemble of 20 predictions: $RMSE|_{tr} < 1.02\min(RMSE|_{tr})$ (**green**);
- $\min(RMSE|_{tr}) \approx 20mV$: 2% of the total voltage drop;
- $RMSE = 25mV$ (2.5%);
- Computation time per discharge: 0.1s.

SPM fit to random pulses: $\max(I) < 2A$



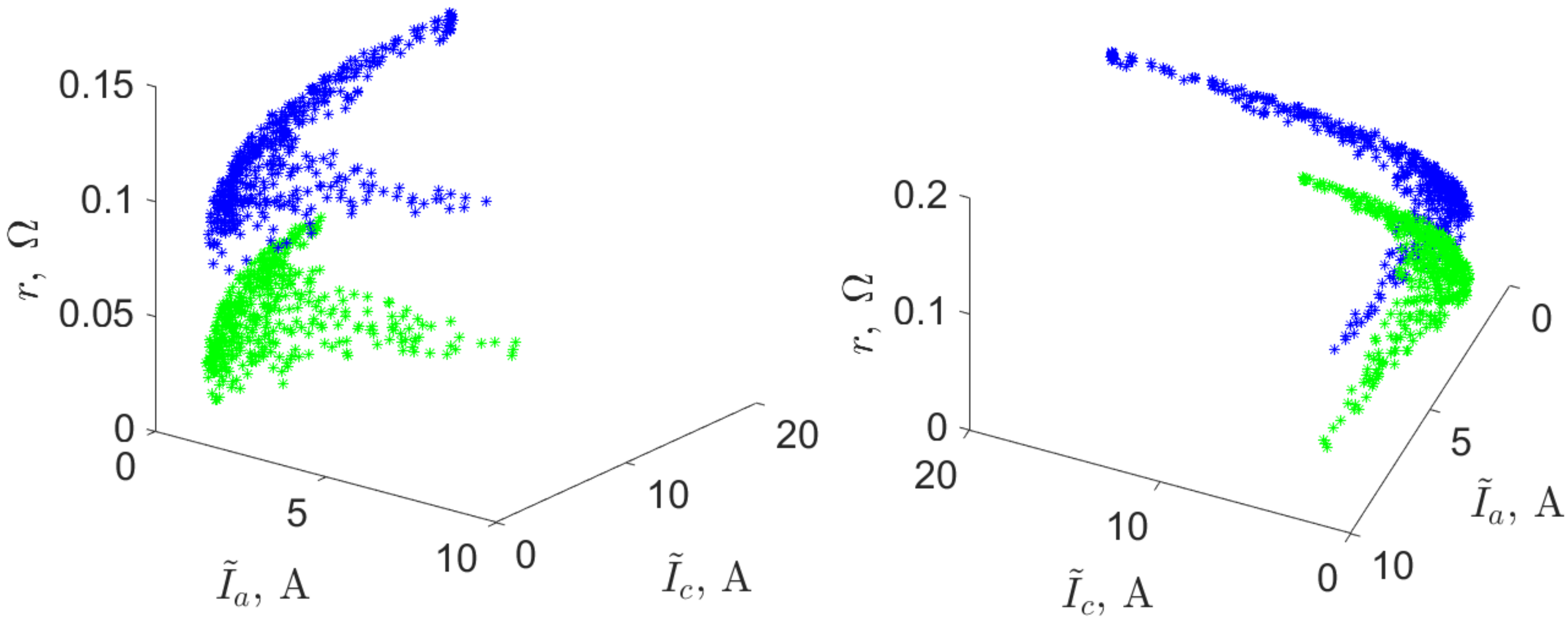
- Discharge data (**black**)
- Ensemble of 20 predictions: $RMSE|_{tr} < 1.02\min(RMSE|_{tr})$ (**green**);
- $\min(RMSE|_{tr}) \approx 20mV$: 2% of the total voltage drop;
- $RMSE = 20mV\ (2.0\%)$;
- Computation time per discharge: ~30s

Mapping out the BFM.



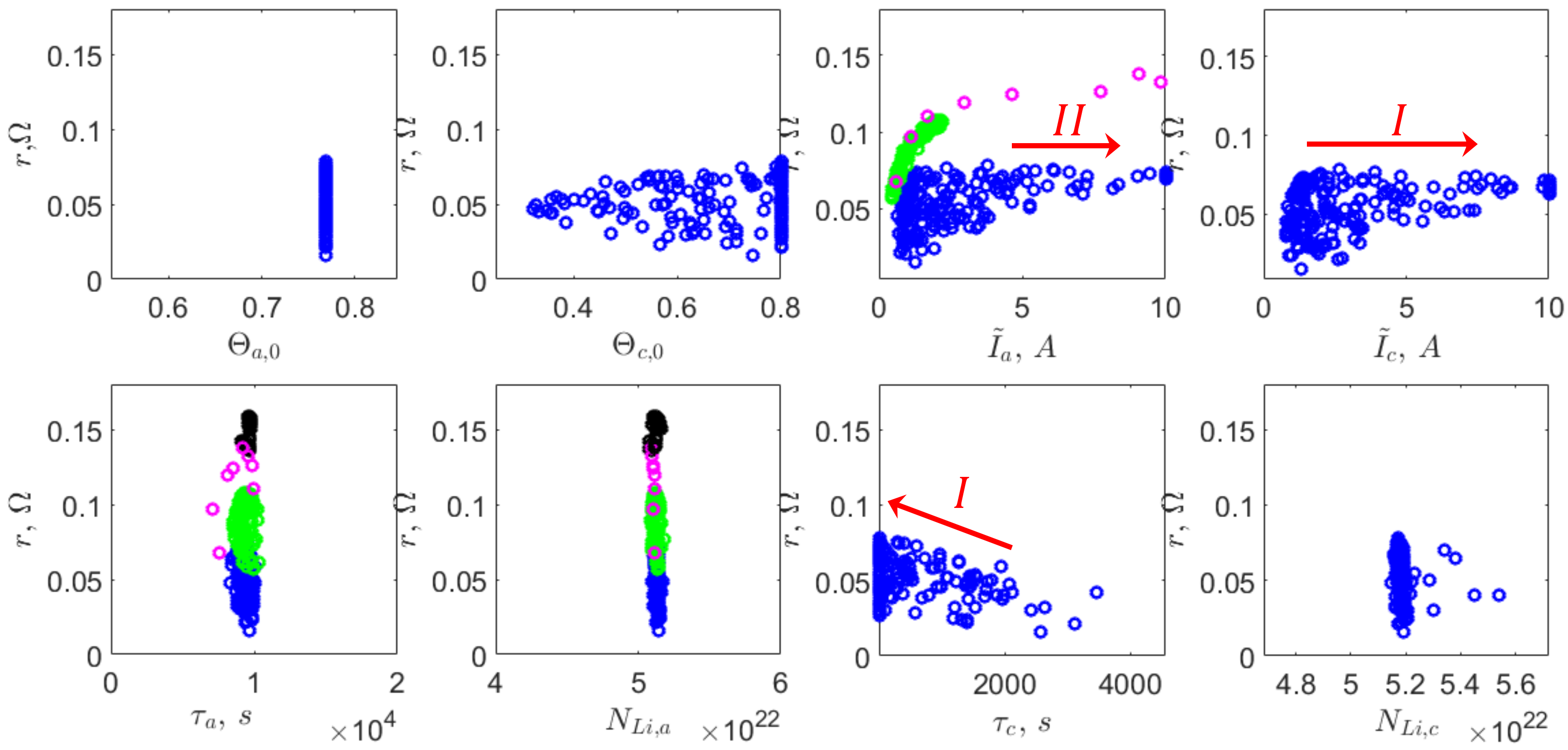
- Ensemble of 100 predictions: $RMSE|_{tr} \approx 1.02\min(RMSE|_{tr})$ (**blue**)
- $\min(RMSE|_{tr}) \approx 20mV$: 2% of the total voltage drop (red);
- The accuracy of the SPM is essentially identical for all the points
- However - large variations in the parametric values

Projection of the BFM on the $(\tilde{I}_a, \tilde{I}_c, r)$ subspace



- Early-life (green) vs. middle-life (blue) 18650 LP cells;
- Ensemble of parametric values with $RMSE|_{tr} < 1.1\min(RMSE|_{tr})$
- The BFM projection is seen to be quasi-2D: $f(\tilde{I}_a \tilde{I}_c, r) = f(\tilde{I}_a^*, \tilde{I}_c^*, r^*)$, i.e., a single stiff variable;
- The stiff variable is a function of $f(\tilde{I}_a^*, \tilde{I}_c^*, r^*)$;
- Ageing affects the value of the stiff parameter through the function $f(\tilde{I}_a^*, \tilde{I}_c^*, r^*)$.

SPM reduction



- Reduction $I : \tilde{I}_c \rightarrow \infty, \tau_c \rightarrow 0; BFM \rightarrow 1D$ (green dots)
- Reduction $II: \tau_c \rightarrow 0; BFM \rightarrow 0D$ (black dots)

Reduced Model I

$$V(t) = \Delta\overline{\phi_c^{eq}}(t) - \Delta\phi_a^{eq}(\bar{\theta}_a) - I_a\left(r_a + r_c\right)$$

$$-\frac{2k_BT}{e}\ln\left(\chi_a + \sqrt{(\chi_a)^2+1}\right),$$

$$\Delta\overline{\phi_c^{eq}}(t) \equiv U_{OCP}(y(t)) + \Delta\phi_a^{eq}(y(t)),$$

$$y(t) = 1 - \int_0^t \frac{I_a(t')dt'}{eN_{Li,a}},$$

$$\chi_a(\bar{\theta}_a) = \frac{I_a}{\tilde{I}_a\left(\theta_a\right)^{\frac{1}{2}}\left(1-\theta_a\right)^{\frac{1}{2}}},$$

$$I_a > 0 \quad for \quad discharge, \quad \theta_a = \bar{\theta}_a\Theta_{a,0},$$

$$Parameters\ (3):\ r = r_a + r_c,\ \tilde{I}_a,\ \Theta_{a,0},$$

$$\bar{\theta}_a(t) = 1 - \mathcal{L}^{-1}\left[\frac{\mathrm{sign}(I_a)\mathcal{L}\left[\bar{\zeta}_a(t')\right]}{\sqrt{s}\coth\sqrt{s}-1}\right]\left(\frac{t}{\tau_a}\right)$$

$$\bar{\zeta}_a(t/\tau_a) = \frac{I(t)\tau_a}{3eN_{Li,a}},$$

$$Parameters\ (2):\ \tau_a,\ N_{Li,a};$$

- 5 parameters are left: 3 stiff, 1 sloppy and 1 (Θ_a) fixed by the given anode OCP
- Cathode properties enter through the renormalized 1-D BFM in the $(\widetilde{I}_a^*, r^*)$ parametric subspace and the cathode OCP

Reduced Model II

$$V(t) = \Delta\overline{\phi_c^{eq}}(t) - \Delta\phi_a^{eq}(\bar{\theta}_a) - I_a\left(r_a + r_c\right)$$

$$\Delta\overline{\phi_c^{eq}}(t) \equiv U_{OCP}(y(t)) + \Delta\phi_a^{eq}(y(t)),$$

$$y(t) = 1 - \int_0^t \frac{I_a(t')dt'}{eN_{Li,a}},$$

$$Parameters\ (1):\ \ r = r_a + r_c,$$

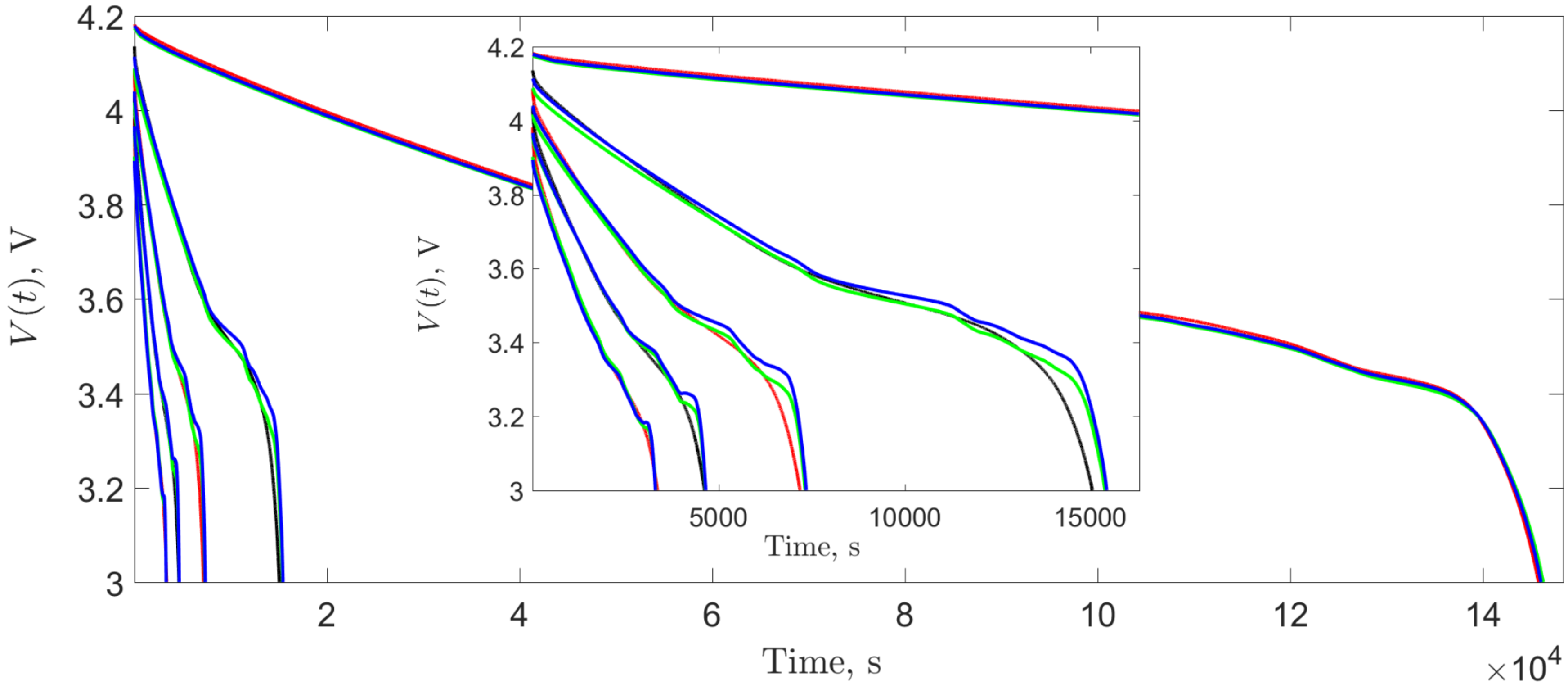
$$\bar{\theta}_a(t) = 1 - \mathcal{L}^{-1}\left[\frac{\mathrm{sign}(I_a)\mathcal{L}\left[\bar{\zeta}_a(t')\right]}{\sqrt{s}\coth\sqrt{s} - 1}\right]\left(\frac{t}{\tau_a}\right)$$

$$\bar{\zeta}_a(t/\tau_a) = \frac{I(t)\tau_a}{3eN_{Li,a}},$$

$$Parameters\ (2):\ \ \tau_a,\ \ N_{Li,a};$$

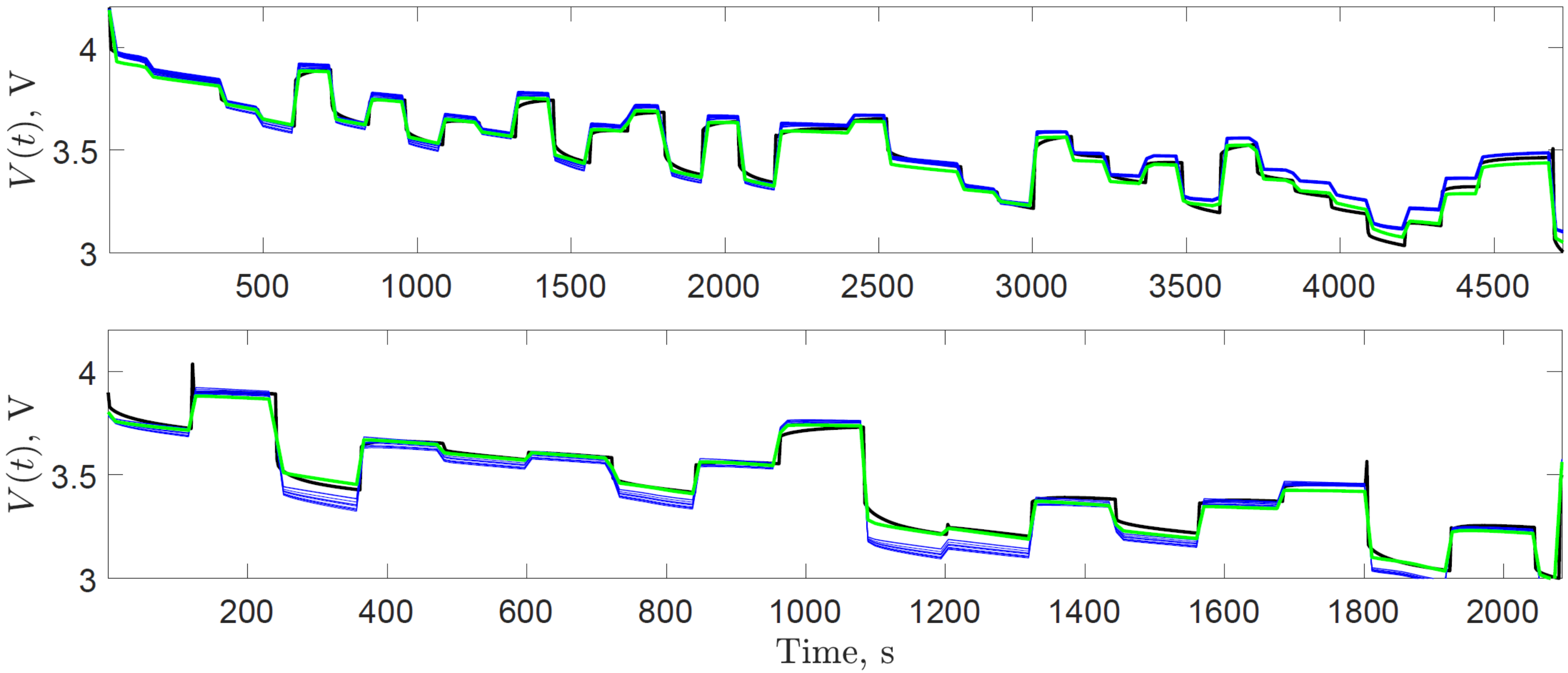
- 3 parameters are left (all stiff!):
  1. $N_{Li,a}$ -number of Li ions
  2. τ_a -anode diffusion time
  3. r -effective Ohmic resistance
- r is renormalized by "interaction" with parameters $\tilde{I}_a$ and $\tilde{I}_c$ through the reduction: the best-fit value of *r* is a function of $\tilde{I}_a^*, \tilde{I}_c^*, r^*$

Reduced Models. Comparison



- Reduced Model I (green) vs. Reduced Model II blue; 20 predictions sampled from the respective BFMs
- Both RM I (RMSE 2.5%) and RM II (RMSE 3.2%) perform fairly well

Reduced Models. Comparison



- Reduced Model II (blue) vs. full SPM (green); 20 predictions sampled from the respective BFMs
- Performance of the Reduced Model II is fair (RMSE 3.5% and 5% for the two pulses; compared to 2% for the SPM)

Conclusions

- SPM of Li ion battery is "sloppy"
- Only 3 ("stiff") parameters of the battery can be determined based on the SPM and cycling data:

    1. *Number of available Li ions (original parameter)*
    2. *Diffusion time of the anode (original parameter)*
    3. *Effective Ohmic resistance (a function of the original parameters $f(\tilde{I}_a^*, \tilde{I}_c^*, r^*)$)*

- SPM can be systematically reduced to a model with 3 stiff effective parameters with an insignificant reduction of accuracy
- Fully reduced model provides values of the stiff parameters, which characterize the battery's SOH
- Characterization of the SOH based on the SPM and cycling data is unavailable in terms of the original ("microscopic") parameters
- Ageing was found to affect all three stiff parameters
- The presented model-reduction approach should be applicable to other multi-parametric models of the battery cycling behavior

References:

- *M. Khasin, C. S. Kulkarni, K. Goebel, Parameters inference and model reduction for the Single-Particle Model of Li ion cells, https://arxiv.org/abs/1912.05807