Optimal Input Design for Parameter Identification in an Electrochemical Li-ion Battery Model

Saehong Park, Dylan Kato, Zach Gima, Reinhardt Klein, Scott Moura

Abstract—We consider the problem of optimally designing an excitation input for parameter identification of an electrochemical Li-ion battery model. The optimized input is obtained by solving a relaxed, convex knapsack problem. In contrast to performing parameter identification with standard test cycles, we consider the problem as designing an optimal input trajectory that maximizes parameter identifiability. Specifically, we analytically derive sensitivity equations for the electrochemical model. This approach enables parameter sensitivity analysis and optimal parameter fitting via a gradient-based algorithm. The simulation results show that the optimized inputs achieve faster parameter identification compared to standard test cycles and tighten the parameter estimation confidence intervals.

Keywords—*Electrochemical Model, Sensitivity Analysis, System Identification, Input Design, Levenberg-Marquardt*

I. INTRODUCTION

Batteries are a key enabling technology behind electrified transportation, portable consumer electronics, and more. To enhance the safety and performance of these devices, one must understand their electrochemical behavior, particularly in extreme operating conditions. To this end, battery systems researchers are deeply interested in mathematical electrochemical models. An experimentally validated model can be used for design purposes or online battery management systems (BMS) [1], [2]. Identifying the unknown model parameters, however, is challenging for multiple reasons. First, battery cell manufacturers do not disclose this information on data sheets. Second, one can only measure voltage, current, and temperature - at best. Third, characterizing certain properties, e.g. diffusivities, requires destructive testing. Finally, the model parameters are nonlinear with respect to the measured signals, and the dynamics are governed by coupled nonlinear partial differential-algebraic equations.

In BMS research, battery models can be categorized into two groups: equivalent circuit models (ECMs), and electrochemical models. ECMs represent the input-output behavior using circuit elements, such as resistors and capacitors. However, ECMs do not directly capture the physical phenomena inside the battery, such as lithium transport, solid-electrolyte interphase dynamics, and degradation mechanisms. Electrochemical models directly incorporate diffusion, intercalation, and electrochemical kinetics. Although these models can accurately explain the internal behavior of the battery, their mathematical structure is relatively complicated, which motivates the active sub-field of electrochemical model

Saehong Park, Dylan Kato, Zach Gima, and Scott Moura are with the Energy, Controls and Applications Lab (eCAL) at the University of California, Berkeley, CA 94720, USA (E-mail: {sspark, dkkato, ztakeo, smoura}@berkeley.edu)

Reinhardt Klein is with Robert Bosch LLC, Research and Technology Center, Palo Alto, CA 94304 USA (E-mail: reinhardt.klein@us.bosch.com)

reduction. Several important innovations in electrochemical model reduction include the single particle model [3]–[5], quasilinearization with Padé approximation [6], spectral methods [7], residue grouping [8] and more.

Non-invasive parameter identification of electrochemical models has become an emergent research topic, due to interests in electrochemical models for simulation, analysis, and control purpose. The authors in [9], propose parameter identification via Fisher information analysis and a grouping strategy, applied to an extended single particle model. Parameter optimization is performed using nonlinear least squares. In contrast, [10] identifies the parameters via an all-in-one approach from driving cycle data using a genetic algorithm. They validate the identified parameter values with experiments and perform Fisher information analysis *ex post factor*. Similarly, [11] uses a multi-objective genetic algorithm for parameter identification. They use terminal voltage and surface temperature curves as identification objectives. Rather than identify all the parameters, some researchers focus on identifying specific subsets of parameters, such as battery health-related or kinetic parameters. For example, [11] mainly target the physical parameters, such as diffusion coefficients, and activation energies. [12] focuses on the the electrochemical parameters that govern power and capacity prediction, as well as their temperature dependence under a variety of charge sustaining and depleting experiments. In [13], the parameter estimation for kinetic parameters and sensitivity analysis via analysis of variance for nonlinear models is proposed.

Most existing literature on battery parameter identification focuses on parameter fitting, namely, matching model output to experimental data. However, it is unclear if the experimentally data is "sufficiently rich" to identify the parameters. A small set of publications in the battery parameter identification literature deal with this problem by formulating an input trajectory optimization problem [14], [15]. This work optimizes the amplitude and frequency of a sinusoidal input signal to maximize the Fisher information matrix, in some sense, for an ECM and single particle model. One could exploit a series of inputs that excite specific parameter sensitivity, however, collecting the required data from experiments can be cost intensive. The motivating question is: which inputs should be considered to maximize parameter identifiability in a systematic way? In addition, the estimated parameters should be characterized by confidence intervals. These question motivate *optimal experimental design* (OED), which provides an important link between experimental design and modeling [16]. In this paper, we propose an electrochemical model-based optimal experiment design framework that yields parameter estimates and confidence intervals. Instead of formulating a nonlinear trajectory
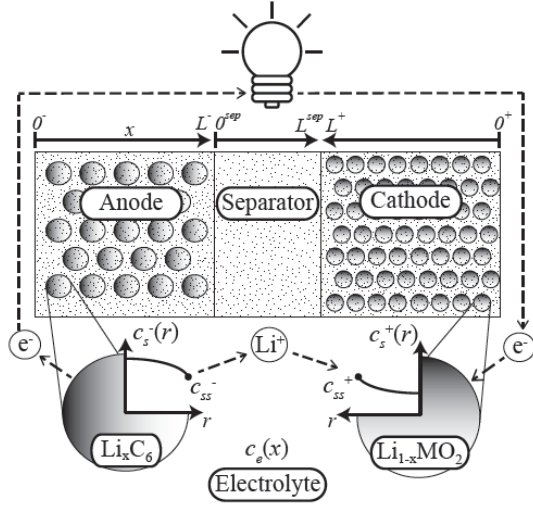
Figure 1: Schematic of the first-principle electrochemical model, called pseudo two-dimensional model (P2D model).

optimization problem, we propose a convex input selection problem. We summarize our key contributions as follows.

First, a sensitivity analysis for the full-order electrochemical model is executed, by analytically deriving the sensitivity differential algebraic equations. To the best of authors' knowledge, an analytic sensitivity analysis for all the electrochemical parameters has never been executed before. We place emphasis on this sensitivity analysis, as it plays a crucial role in computing the Fisher information matrix, and the parameter estimation algorithm. Secondly, we formulate an optimal experimental design via convex optimization. Rather than solving a large-scale nonlinear optimal control problem, we propose a (relaxed) "knapsack problem" where the optimal inputs are selected from a discrete set. Lastly, we estimate the parameters and their confidence intervals via nonlinear least squares with the Levenberg-Marquardt algorithm [17].

The paper is organized as follows. Section II briefly presents the electrochemical Li-ion battery model. Section III details the parameter identification framework. Section IV presents simulation results with visual examples. In Section V, we summarize our work and provide perspectives on future work.

II. ELECTROCHEMICAL BATTERY MODEL

In this section we describe the electrochemical model considered in the paper. It consists of two electrically separated porous electrodes and a separator, as shown in Fig. 1. The lithium ions are transported by a diffusion process inside the active particles along the r-axis in the solid phase. They traverse the particle-electrolyte interface via Butler-Volmer kinetics. The ions dissolved in the electrolyte pass through the separator to the opposite electrode along the x-axis. The diffusion, intercalation, and electrochemical kinetics account for the internal battery dynamics expressed by a combination of partial differential equations (PDEs) and ordinary differential equations (ODEs). The state variables are lithium concentration in the solid $c_s^{\pm}(x,r,t)$, lithium concentration in the electrolyte $c_e(x,t)$, solid electric potential $\phi_s^{\pm}(x,t)$, electrolyte electric potential $\phi_e(x,t)$, ionic

current in the electrolyte $i_e^{\pm}(x,t)$, and molar ion fluxes between electrodes and electrolyte $j_n^{\pm}(x,t)$. We summarize the governing equations for $j \in \{-, \text{sep}, +\}$,

$$\frac{\partial c_s^{\pm}}{\partial t}(x,r,t) = \frac{1}{r^2}\frac{\partial}{\partial r}\left[D_s^{\pm}r^2\frac{\partial c_s^{\pm}}{\partial r}(x,r,t)\right], \quad (1)$$

$$\varepsilon_e^j\frac{\partial c_e^j}{\partial t}(x,t) = \frac{\partial}{\partial x}\left[D_e^{\text{eff}}(c_e^j)\frac{\partial c_e^j}{\partial x}(x,t) + \frac{1-t_c^0}{F}i_e^j(x,t)\right], \quad (2)$$

$$\sigma^{\text{eff},\pm}\cdot\frac{\partial \phi_s^{\pm}}{\partial x}(x,t) = i_e^{\pm}(x,t) - I(t), \quad (3)$$

$$\kappa^{\text{eff}}(c_e)\cdot\frac{\partial \phi_e}{\partial x}(x,t) = -i_e^{\pm}(x,t) + \kappa^{\text{eff}}(c_e)\frac{2RT}{F}(1-t_c^0)$$
$$\times\left(1 + \frac{d\ln f_{c/a}}{d\ln c_e}(x,t)\right)\frac{\partial \ln c_e}{\partial x}(x,t), \quad (4)$$

$$\frac{\partial i_e^{\pm}}{\partial x}(x,t) = a_s^{\pm}Fj_n^{\pm}(x,t), \quad (5)$$

$$j_n^{\pm}(x,t) = \frac{1}{F}i_0^{\pm}(x,t)\left[e^{\frac{\alpha_a F}{RT}\eta^{\pm}(x,t)} - e^{-\frac{\alpha_c F}{RT}\eta^{\pm}(x,t)}\right], \quad (6)$$

where $t \in \mathbb{R}_+$ represents time. Some parameters, such as $D_e, \kappa, f_{c/a}$ are functions of the states, $c_e(x,t)$. $D_e^{\text{eff}} = D_e(c_e)\cdot(\varepsilon_e^j)^{\text{brug}}$, $\sigma^{\text{eff}} = \sigma\cdot(\varepsilon_s^j+\varepsilon_f^j)^{\text{brug}}$, $\kappa^{\text{eff}} = \kappa(c_e)\cdot(\varepsilon_e^j)^{\text{brug}}$ are the effective electrolyte diffusivity, effective solid conductivity, and effective electrolyte conductivity given by the Bruggeman relationship. In (6), the exchange current density $i_0^{\pm}(x,t)$ and over-potential $\eta^{\pm}(x,t)$ are expressed:

$$i_0^{\pm}(x,t) = k^{\pm}\left[c_{ss}^{\pm}(x,t)\right]^{\alpha_c}\left[c_e(x,t)\left(c_{s,\max}^{\pm} - c_{ss}^{\pm}(x,t)\right)\right]^{\alpha_a}, \quad (7)$$

$$\eta^{\pm}(x,t) = \phi_s^{\pm}(x,t) - \phi_e(x,t) - U^{\pm}(c_{ss}^{\pm}(x,t))$$
$$- FR_f^{\pm}j_n^{\pm}(x,t), \quad (8)$$

where c_{ss} is the solid phase surface concentration $c_{ss}^{\pm}(x,t) = c_s^{\pm}(x,R_s^{\pm},t)$, $U^{\pm}$ is the open-circuit potential, and $c_{s,\max}^{\pm}$ is the maximum possible concentration in the solid phase.

A complete exposition on the model equations and boundary conditions can be found in [1]. The input to the model is the applied current density $I(t)$ [A/m^2], and the output is the voltage measured across the current collectors:

$$V(t) = \phi_s^+(0^+,t) - \phi_s^-(0^-,t) + R_cI(t). \quad (9)$$

In contrast to an ECM, which has a limited ability to interpret internal battery dynamics, the electrochemical model has parameters that directly explain physical phenomenon inside the battery. Note that some of the parameters are measurable by disassembling the cell, such as geometric parameters, while other parameters are not directly measurable and change over time. These fixed and internal model parameters are listed separately in Table I-II.

Symbol	Description [SI units]
L^-	Thickness of negative electrode [m]
L^{sep}	Thickness of separator [m]
L^+	Thickness of positive electrode [m]
A	Electrode current collector area [m^2]

Table I: Fixed geometric parameters.

Symbol	Description [SI units]
D_s^-	Solid-phase diffusion coefficients [m^2/sec]
D_s^+	Solid-phase diffusion coefficients [m^2/sec]
R_s^-	Solid-phase particle radii [m]
R_s^+	Solid-phase particle radii [m]
σ^-	Solid-phase conductivity [$\Omega^{-1}m^{-1}$]
σ^+	Solid-phase conductivity [$\Omega^{-1}m^{-1}$]
$D_e(\cdot)$	Electrolyte diffusion coefficient [m^2/sec]
ϵ_e^-	Electrolyte volume fraction [-]
ϵ_e^{sep}	Electrolyte volume fraction [-]
ϵ_e^+	Electrolyte volume fraction [-]
$\kappa(\cdot)$	Electrolyte conductivity [Ω m]
t_c^0	Transference number [-]
$\frac{d \ln f_{c/a}}{d \ln c_e}(\cdot)$	Activity coefficient [-]
k^-	Kinetic rate constants [(A/m^2)(m^3/mol)$^{(1+\alpha)}$]
k^+	Kinetic rate constants [(A/m^2)(m^3/mol)$^{(1+\alpha)}$]
R_f^-	Film resistance [Ω m^2]
R_f^+	Film resistance [Ω m^2]
c_{e_0}	Initial Li-ion concentration in electrolyte [mol/m^3]

Table II: Electrochemical model parameters.

DAE Variables	P2D Variables
$\mathbf{x}$	c_s^-, c_s^+, c_e
$\mathbf{z}$	$\phi_s^-, \phi_s^+, i_e^-, i_e^+, \phi_e, j_n^-, j_p^+$
u	I
$\boldsymbol{\theta}$	Parameters in Table II

Table III: DAE notations for electrochemical model.

For the subsequent sections, we use the notation in Table III to describe the general dynamic system model and parameter identification framework. In this context, we can formulate the system model as a system of differential algebraic equations (DAEs):

$$\dot{\mathbf{x}} = \boldsymbol{f}(\mathbf{x}, \mathbf{z}, u, \boldsymbol{\theta}), \quad \mathbf{x}(t_0) = \mathbf{x_0}, \tag{10}$$

$$0 = \boldsymbol{g}(\mathbf{x}, \mathbf{z}, u, \boldsymbol{\theta}), \quad \mathbf{z}(t_0) = \mathbf{z_0}, \tag{11}$$

$$\mathbf{y} = \boldsymbol{h}(\mathbf{x}, \mathbf{z}, u, \boldsymbol{\theta}), \tag{12}$$

III. PARAMETER IDENTIFICATION FRAMEWORK

A. Sensitivity Analysis

Sensitivity analysis is used to understand how a model's output depends on variations in the parameter values [18]. Based on nominal parameter values, local sensitivity analysis measures the effects that small changes in the parameters have on the output. For continuous dynamic systems, the local sensitivities are defined as the first-order partial derivatives of the system output with respect to the parameters. In this section, we briefly introduce how to derive local sensitivities in dynamical system described in (10)-(12) and develop this approach toward parameter estimation framework via Fisher information.

Let us define sensitivity variables as follows:

$$S_\mathbf{x} = \frac{\partial \mathbf{x}}{\partial \boldsymbol{\theta}}, \quad S_\mathbf{z} = \frac{\partial \mathbf{z}}{\partial \boldsymbol{\theta}}, \quad S_\mathbf{y} = \frac{\partial \mathbf{y}}{\partial \boldsymbol{\theta}}, \tag{13}$$

$S_\mathbf{x}, S_\mathbf{z}, S_\mathbf{y}$ are sensitivity matrices where the i, j matrix element is defined as the partial derivative of the i-th state to the j-th parameter:

$$s_{i,j}(t) = \frac{\partial x_i(t)}{\partial \theta_j}. \tag{14}$$

Then, we can derive the sensitivity differential algebraic equations (SDAEs):

$$\dot{S}_\mathbf{x} = \frac{\partial \boldsymbol{f}}{\partial \mathbf{x}} S_\mathbf{x} + \frac{\partial \boldsymbol{f}}{\partial \mathbf{z}} S_\mathbf{z} + \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{\theta}}, \quad S_\mathbf{x}(0) = S_{\mathbf{x}0} \tag{15}$$

$$0 = \frac{\partial \boldsymbol{g}}{\partial \mathbf{x}} S_\mathbf{x} + \frac{\partial \boldsymbol{g}}{\partial \mathbf{z}} S_\mathbf{z} + \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{\theta}}, \quad S_\mathbf{z}(0) = S_{\mathbf{z}0} \tag{16}$$

$$S_\mathbf{y} = \frac{\partial \boldsymbol{h}}{\partial \mathbf{x}} S_\mathbf{x} + \frac{\partial \boldsymbol{h}}{\partial \mathbf{z}} S_\mathbf{z} + \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{\theta}}. \tag{17}$$

The advantage of SDAEs is that they provide a fundamental mathematical computation of the sensitivities, compared to a perturbation method where sensitivity is obtained by perturbing each parameter slightly and calculating the output difference with respect to nominal parameters. Note that SDAEs are linear time-varying DAEs, where the Jacobians are computed at each time step. In particular, we use CasADi [19], which efficiently computes the first and second-order derivatives. In this work, the battery model DAEs and its SDAEs are simulated by using the IDAS integrator provided by SUNDIALS via the CasADi interface.

B. Parameter Grouping

In this section, we introduce the methodology of parameter grouping for parameter identification. It is well known that the entire electrochemical parameter vector $\boldsymbol{\theta}$ is weakly identifiable from the measured output, since the system is nonlinear in the parameters. This is mainly due to linear dependence between the parameter sensitivity vectors [9]. Therefore, it is necessary to analyze the linear dependency among electrochemical parameters, and rank/organize them into groups to avoid linear dependence during the parameter identification process. For parameter grouping, we first perform sensitivity analysis across a library of input values. The input library includes a variety of profiles, including (i) pulses, (ii) sinusoids, and (iii) driving cycles. A normalization is applied to each category to fairly evaluate candidate profiles. In this work, a total of 738 profiles across these three input categories were analyzed. Across all categories, profiles have been normalized to 1 Ah of charge processed in both charge and discharge cases.

After calculating the sensitivities via the process in Section III-A, we apply the Gram-Schmidt process on $S_\mathbf{y}^T S_\mathbf{y}$ to reveal the sensitivity ranking and linear dependence. Figure 2 visualizes the average sensitivity magnitudes via Graham-Schmidt orthonormalization over 738 profiles.

Based on this sensitivity analysis, we group the parameters based on their orthogonalized sensitivity magnitude. The resultant groups are shown in Table IV. The criteria for classification is determined by the frequency of times each parameter is ranked in the top or bottom in each subgroup of the input library. For instance, Group 1 parameters positioned the highest rank for all subgroups, while Group 4 parameters are the lowest rank in this analysis.

C. Optimal Experiment Design

In statistical experiment design, the amount of the information about parameters $\boldsymbol{\theta}$ contained in the observation $\mathbf{y}$ from an experiment is calculated by the Fisher information matrix, $\boldsymbol{F}$ [20]. The Fisher information matrix is defined as:

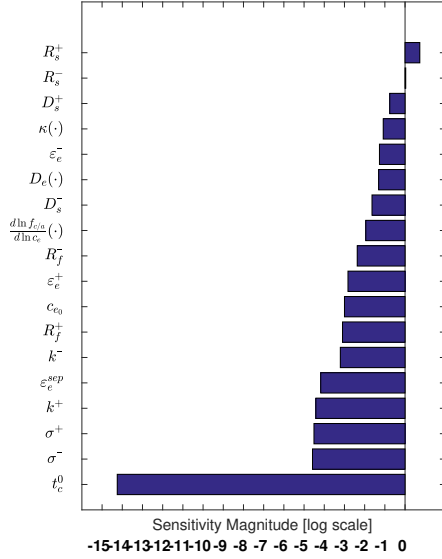$$\boldsymbol{F} = \int_0^{t_f} S_\mathbf{y}^T(t) Q(t)^{-1} S_\mathbf{y}(t) \, dt, \tag{18}$$

Figure 2: The mean of orthogonalized sensitivity magnitudes in the input library.

Group 1	Group 2	Group 3	Group 4
R_s^-	D_s^-	R_f^-	σ^-
R_s^+	D_s^+	k^-	σ^+
-	ε_e^-	ε_e^+	ε_e^{sep}
-	$\kappa(\cdot)$	c_{e_0}	k^+
-	$D_e(\cdot)$	R_f^+	t_c^0
-	$\frac{\mathrm{d}\ln f_{c/a}}{\mathrm{d}\ln c_e}(\cdot)$		

Table IV: The result of electrochemical parameters grouping.

where $t \in [0, t_f]$, and $Q(t)$ is the covariance matrix of the measurement error. Since the true parameters $\boldsymbol{\theta}^*$ are unknown, the sensitivity is calculated at nominal parameter values θ_0. The deviation of the parameter estimates from their true values can be expressed as the covariance matrix Σ. According to the Cramer-Rao bound [21], the inverse of the Fisher information matrix provides a lower bound on $\Sigma \geq \boldsymbol{F}^{-1}$,

Our objective is to find inputs that minimize the lower bound of the parameter estimation error, thus improving the parameter estimation quality. To optimize the amount of information, a proper scalarization of F should be considered, namely,

D-optimality : $\min \det(\boldsymbol{F}^{-1})$
A-optimality : $\min \mathrm{tr}(\boldsymbol{F}^{-1})$
E-optimality : $\min \lambda_{\max}(\boldsymbol{F})$

D. Optimal Experiment Design via Convex Programming

We formulate a procedure to optimize experiment design to produce inputs that are *maximally informative* for parameter estimation. To bypass the challenge of solving a large-scale nonlinear optimal control problem, we pursue a different approach. Specifically, we seek the combination of inputs from an input library which maximizes the Fisher information matrix. This process yields a convex optimization program, which can be rapidly solved via computationally efficient open-source solvers, such as cvx [22].

Suppose we have a set of L experimental inputs $u_i(t), i = 1, 2, \cdots, L$. Given any input profile $u_i(t)$, we obtain a corresponding sensitivity vector $S_{\mathbf{y},i}(t)$ by solving (10)-(12) and (15)-(17) simultaneously. The basic idea is that

we can select M inputs from a large fixed set of L inputs. Amongst these L inputs $u_i(t), i = 1, 2, \ldots, l$, we select M inputs that are maximally informative as measured by the Fisher information matrix, F. Let m_j denote the number of experiments with index number j that are executed from the input library. Then, the total number of experiments is

$$m_1 + m_2 + \ldots + m_l = M \qquad (19)$$

We can then rewrite the Fisher information matrix as:

$$\boldsymbol{F} = \sum_{i=1}^{L} m_i S_{\mathbf{y},i}^T Q_i^{-1} S_{\mathbf{y},i}. \qquad (20)$$

We now formulate a combinatorial optimization problem to maximize $\boldsymbol{F}$:

$$\underset{m_i}{\text{minimize}} \quad \det\left(\sum_{i=1}^{l} m_i S_{\mathbf{y},i}^T Q_i^{-1} S_{\mathbf{y},i}\right)^{-1}, \qquad (21)$$

$$\text{subject to} \quad m_i \geq 0, \quad m_1 + \ldots + m_l = M, \qquad (22)$$

$$m_i \in \mathbb{Z}. \qquad (23)$$

This problem is an integer program, where the optimal number of experiments m_i is the solution. In addition, large-scale combinatorial problems are NP-hard. So, in this work, we relax the last integer constraint (23), yielding a relaxed optimization problem that is convex. Let $\eta_i = m_i/M$ be the fraction of experiment type i to execute. Then the Fisher information (20) can be re-written as

$$\boldsymbol{F} = M \sum_{i=1}^{L} \eta_i S_{\mathbf{y},i}^T S_{\mathbf{y},i}, \qquad (24)$$

where $\eta \in \mathbb{R}^L$, $\mathbb{1}^T \eta = 1$. Thus, our ultimate convex optimal experiment design problem is:

$$\underset{\eta}{\text{minimize}} \quad \log \det\left(\sum_{i=1}^{L} \eta_i S_{\mathbf{y},i}^T S_{\mathbf{y},i}\right)^{-1} \qquad (25)$$

$$\text{subject to} \quad \eta \succeq 0, \quad \mathbb{1}^T \eta = 1 \qquad (26)$$

E. Optimal Parameter Fitting via Nonlinear Least Squares

After obtaining experiment data, we now seek to optimally fit the parameters. The optimization problem for parameter identification can be formulated as a nonlinear least squares problem:

$$\underset{\hat{\boldsymbol{\theta}}}{\text{minimize}} \quad \sum_{i=1}^{M} \sum_{t=1}^{t_f} \frac{\mathbf{y}_i(t) - \hat{\mathbf{y}}_i(t; \hat{\boldsymbol{\theta}})}{\sigma_{\mathbf{y}_i}^2}, \qquad (27)$$

where M is the number of optimized input profiles from OED, and $\sigma_{\mathbf{y}_i}^2$ is the measurement variance for input profile i. The Levenberg-Marquardt algorithm is used to update the parameters $\hat{\boldsymbol{\theta}}$ iteratively to solve the nonlinear optimization problem (27). This algorithm adaptively updates the parameter estimates via a hybridization of the gradient descent update and the Gauss-Newton update [23]:

$$\left[\mathbf{J}^T \mathbf{W} \mathbf{J} + \gamma \mathrm{diag}(\mathbf{J}^T \mathbf{W} \mathbf{J})\right] \Delta \boldsymbol{\theta} = \mathbf{J}^T \mathbf{W}(\mathbf{y} - \hat{\mathbf{y}}), \qquad (28)$$

where $\mathbf{J} = \partial \hat{\mathbf{y}} / \partial \hat{\boldsymbol{\theta}}$, the local sensitivity of the output $\hat{\mathbf{y}}$, and $\mathbf{W}$ is the inverse of the measurement error covariance

matrix, $\mathbf{W} = Q^{-1}$. The value of γ weighs gradient descent update against Gauss-Newton update. Conveniently, the Levenberg-Marquardt algorithm utilizes the Jacobians already computed in the sensitivity analysis in Section III-B.

After optimally fitting the parameters, estimation error statistics are calculated according to

$$\rho_{\boldsymbol{\theta}} = \mathbf{J}^T \mathbf{W} \mathbf{J}, \tag{29}$$

$$\sigma_{\boldsymbol{\theta}} = \sqrt{\mathrm{diag}[\mathbf{J}^T \mathbf{W} \mathbf{J}]^{-1}}, \tag{30}$$

where ρ is the parameter covariance matrix, and σ is the standard parameter error. Lastly, confidence intervals for the parameter estimates are calculated as follows:

$$\hat{\boldsymbol{\theta}} - \boldsymbol{t}_{(1-0.05,n)} \frac{\sigma_{\boldsymbol{\theta}}}{\sqrt{n}} \leq \boldsymbol{\theta}^* \leq \hat{\boldsymbol{\theta}} + \boldsymbol{t}_{(1-0.05,n)} \frac{\sigma_{\boldsymbol{\theta}}}{\sqrt{n}}, \tag{31}$$

where n is the number of observations, and $\boldsymbol{t}$ is the upper critical value for the t-distribution with $n-1$ freedom.

## IV. Simulation Results

A. Optimal Input Validation

First we compute the sensitivity trajectories for each input in the library described in Section III-B by exploiting parallel computing. After running optimal experiment design via convex programming, we obtain a series of optimal inputs. In order to examine the identifiability of the inputs, we plot the L_2 norm of the model error with respect to parameter estimates, for instance $\theta_1 = (R_s^- - \underline{R_s^-})/(\overline{R_s^-} - \underline{R_s^-})$ and $\theta_2 = (R_s^+ - \underline{R_s^+})/(\overline{R_s^+} - \underline{R_s^+})$ plotted in Fig. 3a, 3b for the optimized and standard input cycles, respectively.

Note the optimal input profile has a more pronounced bowl shape, while the pulse input has flatter shape. By appropriately optimizing the input, we can improve the convergence rate of the parameter estimation process. For example, if we start our initial guess around $\hat{\theta} = (0.25, 0.25)$, then the optimal input yields estimates that converge to the optimal points in just five iterations, while the non-optimized input does not converge clearly. Although this example is specific to R_s^-, R_s^+, pulse inputs and a selected optimized input, the observed trend is consistent when comparing optimized and standard input cycles across the electrochemical parameters.

B. Parameter Identification Validation

Next, we compare the parameter estimation performance for optimized versus standard inputs. In this scenario, we assume the true parameter values are known. We perturb four parameters, $R_s^\pm, R_f^\pm$, from their true values and attempt to estimate them. Note that parameters are selected from different groups, namely, $R_s^\pm$ are in Group 1, and $R_f^\pm$ are located in Group 3. The convex OED program generates optimal input sequences that maximize parameter identifiability. To test if our optimal input profiles outperform other simple inputs, a 1C discharge/charge profile is chosen for comparison. The simulation results are summarized in Table V-VI.

The results indicate that the optimal input sequences provide more accurate parameter estimates and tighter confidence intervals than the 1C charge/discharge cycle. Note the estimated value for R_f^- still exhibits non-trivial error. This is expected, since R_f^- is weakly identifiable from voltage, as demonstrated by the sensitivity analysis in Fig. 2. A consequence of achieving lower parameter estimation error
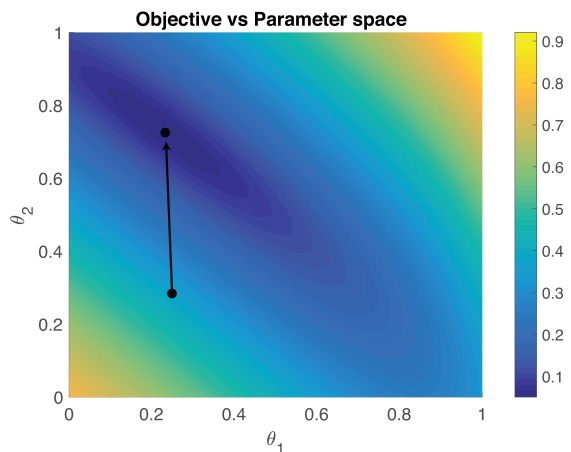
(a) Optimal input profile
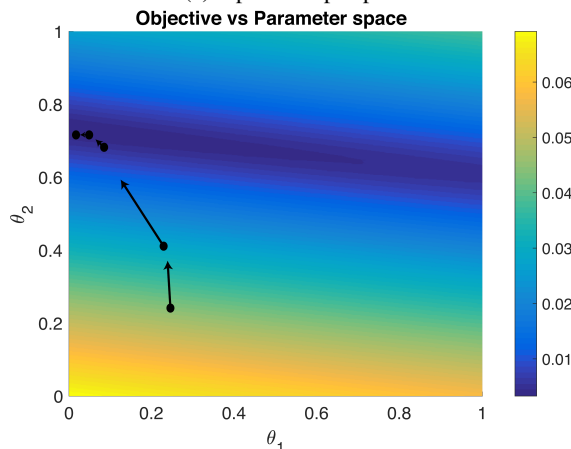
(b) Standard input profile

Figure 3: L2 norm of model error $\|\mathbf{y}^* - \mathbf{y}(\theta_1, \theta_2)\|$ for a pulse input. The points indicate parameter estimates every 5 iterations during the parameter estimation process. Parameter values are normalized by Min/Max scaling.

Parameter	Estimated Value	True Value	95% C.I.
R_s^- [m]	11.4561E-06	10.9E-06	± 3.18864E-07
R_s^+ [m]	9.69823E-06	10.9E-06	± 2.49251E-07
R_f^- [Ω]	8.35184E-04	5.0E-04	± 4.70283E-04
R_f^+ [Ω]	1.00000E-03	1.0E-03	± 9.01101E-04

Table V: Estimated values of the parameters and the corresponding confidence intervals using optimal input profiles.

Parameter	Estimated Value	True Value	95% C.I.
R_s^- [m]	12.4151E-06	10.9E-06	± 2.05626E-06
R_s^+ [m]	8.97366E-06	10.9E-06	± 1.15361E-06
R_f^- [Ω]	1.00000E-03	5.0E-04	± 6.02711E-04
R_f^+ [Ω]	1.00000E-03	1.0E-03	± 2.73964E-03

Table VI: Estimated values of the parameters and the corresponding confidence intervals using 1C Charge-Discharge input.

increases voltage prediction accuracy for input cycles that are different from those used for identification. In contrast, incorrect parameter estimates from non-optimized inputs may yield poor prediction accuracy for different inputs from those used for identification. So, it is necessary to design optimal inputs that improves parameter estimation performance.

V. CONCLUSION

This paper addresses optimal experiment design for parameter identification of an electrochemical Li-ion battery model. Sensitivity analysis is explored to understand each electrochemical parameter's identifiability. We observe that each parameter has different levels of identifiablity, which motivate a parameter grouping strategy. Optimal inputs for the parameter groups are designed to maximize (a scalarization of) the Fisher information matrix. We propose an input selection problem via convex programming. Once the optimal input profiles are designed, the Levenberg-Marquardt algorithm is used to solve a nonlinear least square problem for optimal parameter fitting. In order to test our proposed framework, we simulate the overall process using a model-to-model comparison. These results demonstrate how optimized inputs enhance identifiability and ultimately yield data that improves parameter estimation performance. On-going work involves validating our proposed parameter estimation framework with experimental data, thermal dynamics, and various types of Li-ion batteries.

REFERENCES

[1] N. A. Chaturvedi, R. Klein, J. Christensen, J. Ahmed, and A. Kojic, "Algorithms for advanced battery-management systems", *IEEE Control Systems*, vol. 30, no. 3, pp. 49–68, Jun. 2010.

[2] R. Klein, N. A. Chaturvedi, J. Christensen, J. Ahmed, R. Findeisen, and A. Kojic, "Electrochemical model based observer design for a lithium-ion battery", *IEEE Transactions on Control Systems Technology*, vol. 21, no. 2, pp. 289–301, 2013.

[3] S. Santhanagopalan and R. E. White, "Online estimation of the state of charge of a lithium ion cell", *Journal of Power Sources*, vol. 161, no. 2, pp. 1346–1355, 2006.

[4] D. Di Domenico, A. Stefanopoulou, and G. Fiengo, "Lithium-Ion Battery State of Charge and Critical Surface Charge Estimation Using an Electrochemical Model-Based Extended Kalman Filter", *Journal of Dynamic Systems, Measurement, and Control*, vol. 132, no. 6, p. 061 302, 2010.

[5] S. Park, D. Zhang, and S. Moura, "Hybrid electrochemical modeling with recurrent neural networks for li-ion batteries", in *American Control Conference (ACC), 2017*, IEEE, 2017, pp. 3777–3782.

[6] J. C. Forman, S. Bashash, J. L. Stein, and H. K. Fathy, "Reduction of an electrochemistry-based li-ion battery model via quasi-linearization and pade approximation", *Journal of the Electrochemical Society*, vol. 158, no. 2, A93–A101, 2011.

[7] A. M. Bizeray, S. Zhao, S. R. Duncan, and D. A. Howey, "Lithium-ion battery thermal-electrochemical model-based state estimation using orthogonal collocation and a modified extended Kalman filter", *Journal of Power Sources*, vol. 296, pp. 400–412, 2015.

[8] K. A. Smith, C. D. Rahn, and C.-Y. Wang, "Model Order Reduction of 1D Diffusion Systems Via Residue Grouping", *Journal of Dynamic Systems, Measurement, and Control*, vol. 130, no. 1, p. 011 012, 2008.

[9] A. P. Schmidt, M. Bitzer, Á. W. Imre, and L. Guzzella, "Experiment-driven electrochemical modeling and systematic parameterization for a lithium-ion battery cell", *Journal of Power Sources*, vol. 195, no. 15, pp. 5071–5080, 2010.

[10] J. C. Forman, S. J. Moura, J. L. Stein, and H. K. Fathy, "Genetic identification and fisher identifiability analysis of the Doyle-Fuller-Newman model from experimental cycling of a LiFePO 4 cell", *Journal of Power Sources*, pp. 263–275, 2012.

[11] L. Zhang, L. Wang, G. Hinds, C. Lyu, J. Zheng, and J. Li, "Multi-objective optimization of lithium-ion battery model using genetic algorithm approach", *Journal of Power Sources*, pp. 367–378, 2014.

[12] J. Marcicki, M. Canova, A. T. Conlisk, and G. Rizzoni, "Design and parametrization analysis of a reduced-order electrochemical model of graphite/LiFePO4 cells for SOC/SOH estimation", *Journal of Power Sources*, vol. 237, pp. 310–324, 2013.

[13] J. Vazquez-Arenas, L. E. Gimenez, M. Fowler, T. Han, and S. K. Chen, "A rapid estimation and sensitivity analysis of parameters describing the behavior of commercial Li-ion batteries including thermal analysis", *Energy Conversion and Management*, pp. 472–482, 2014.

[14] M. J. Rothenberger, J. Anstrom, S. Brennan, and H. K. Fathy, "Maximizing Parameter Identifiability of an Equivalent-Circuit Battery Model Using Optimal Periodic Input Shaping", in *2014 ASME Dynamic Systems and Control Conference*, 2014, V001T19A004.

[15] J. Liu, M. Rothenberger, S. Mendoza, P. Mishra, Y.-s. Jung, and H. K. Fathy, "Can an Identifiability-Optimizing Test Protocol Improve the Robustness of Subsequent Health-Conscious Lithium-ion Battery Control? An Illustrative Case Study", *2016 American Control Conference*, no. ii, pp. 6320–6325, 2016.

[16] G. Franceschini and S. Macchietto, "Model-based design of experiments for parameter precision: State of the art", *Chemical Engineering Science*, vol. 63, no. 19, pp. 4846–4872, 2008.

[17] K. Madsen, H. B. Nielsen, and O. Tingleff, "Methods for non-linear least squares problems", 2004.

[18] H. Yue, M. Brown, F. He, J. Jia, and D. B. Kell, "Sensitivity analysis and robust experimental design of a signal transduction pathway system", *International Journal of Chemical Kinetics*, vol. 40, no. 11, pp. 730–741, 2008.

[19] J. Andersson, "A General-Purpose Software Framework for Dynamic Optimization", PhD thesis, Arenberg Doctoral School, KU Leuven, Oct. 2013.

[20] E. Walter and L. Pronzato, *Identification of parametric models from experimental data*. Springer Verlag, 1997.

[21] T. M. Cover and J. A. Thomas, *Elements of information theory*. John Wiley & Sons, 2012.

[22] M. Grant and S. Boyd, *CVX: Matlab software for disciplined convex programming, version 2.1*, http://cvxr.com/cvx, Mar. 2014.

[23] K. Levenberg, "A method for the solution of certain non-linear problems in least squares", *Quarterly of applied mathematics*, vol. 2, no. 2, pp. 164–168, 1944.