Final Report
Modeling and Control of Electrochemical Power Sources
June 2016 – June 2021
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This grant was concerned primarily with physics-based modeling of secondary Li-ion batteries, with several objectives in mind:

1. Develop and validate a predictive understanding of battery electrochemistry,
2. Extract locally linear state-space models from large physical models,
3. Incorporate state-space models into model-predictive control.

The following paragraphs summarize the technical approach and results. Details are documented in archival publications.

Physics-based modeling followed several complementary routes. One aspect of the research was concerned with the chemistry of batteries based on lithium-titanate anodes and lithium-iron-phosphate cathodes. These relatively low-voltage batteries offer some potential advantages, such as being inherently safe and long cycle life. However, the phase-transformation electrodes behave quite differently from more traditional intercalation electrodes. For example, the terminal voltage is not a monotonic function of state-of-charge, as is the case for typical intercalation electrodes. This means that battery state-of-charge cannot be determined simply by measuring voltage. Thus, there are practical consequences for battery-management-system design. Results of the lithium-iron-phosphate cathode chemistry were published in three papers [1-3].

The electrode electrochemistry and Li transport are embedded into pseudo-two-dimensional (P2D) models that can predict cell behaviors, including charge and discharge polarization (i.e., voltage versus state of charge) under different operating conditions (e.g., temperature) and at different rates. The P2D models, first conceptualized by Newman in 1993, are widely used in battery research [4]. Broadly speaking, such models can be tuned to represent polarization behaviors accurately. However, as discussed subsequently, it is difficult to simultaneously represent electrochemical impedance spectra (EIS) accurately.

The P2D models represent the behavior of a small physical domain (tens of microns) that spans from the anode current collector to the cathode current collector. However, such models cannot model a full battery, such as an 18650-format cell. The Battery Design Studio (BDS) software (Siemens, CD-Adapco) is designed to embed multiple P2D models into a full-battery model. Our experience is that the BDS approach works well to predict measured polarization behavior. However, simultaneously predicting EIS response has proven difficult, and perhaps not possible. In fact, we spent about one year in trying, with very little success, to predict accurate EIS with the BDS model.

We find that tuning a P2D model (i.e., fitting numerous physical and chemical parameters) to predict polarization data is relatively straightforward. However, finding a *unique* set of physical parameters is very difficult. A correct model, with associated physical parameters, *must* predict both polarization and impedance spectra simultaneously. With this challenge in mind, we set out to develop new computational algorithms to efficiently extra impedance spectra from physical models such as P2D.

Any physical model (including battery models) can be conceptualized in a state-space form. That is, the rate of change of state variables is a function of the state variables themselves (e.g., temperatures, Li-ion concentrations, …) and any actuation (e.g., charge rate). Further, observables (e.g., terminal voltage) are also functions of the state and actuation. State-space models are locally linear at some operating condition. In principle, a state-space model can be extracted from a full physical model by differentiating the physics model, producing four Jacobian matrices. Although this approach is possible, it can be difficult to implement. Also, one must have access to the source code and know how to accomplish the linearization. As an alternative, state-space models can be obtained using the results of simulating the system with an appropriately broad-band input, such as a pseudo-random binary sequence (PRBS). The challenge for this method is the wide range of time constants that characterize battery behavior, necessitating the appropriate combination of multiple experiments at different sampling rates. We have successfully implemented this approach, enabling the highly efficient extraction of a state-space model from a physical model [3-4].

Having a physically based state-space model in hand opens several avenues of investigation. One avenue is to extract the impedance spectra (EIS), which is accomplished by a sequence of complex matrix algebraic operations [3-4]. This approach enables a thread from physics-based model to the EIS. One way to take advantage of this capability is to connect the EIS to battery characteristics such as state of charge and state of health [2,5]. We note that alternative, and widely practiced, approaches such as equivalent-circuit analysis cannot clearly establish the links between independently measured physical properties and features in the complex impedance.

A state-space model extracted directly from the physical model can be large, meaning that the locally linear Jacobian matrices can be very large. A typical P2D model usually leads to Jacobian matrices that are on the order of 1000 x 1000. Although good representations of the model's dynamic behavior, such state-space models are too large to be run in real time on embedded microprocessors within battery management systems. Thus, there is a need to develop significantly reduced, but still accurate, state-space models. We have implemented the needed state-space reduction algorithms and validated their accuracy.

Reduced-order state-space models can be run in real time and incorporated into model-predictive control algorithms (MPC). This approach enables the incorporation of physical knowledge into feedback control algorithms. Of course, batteries, and the physical models, are highly nonlinear. However, the state-space models are locally linear. Thus, a *gain-scheduling* algorithm was developed to bridge between locally linear state-space models as the battery operating conditions and state-of-charge vary.

Model-predictive control is a feedback control algorithm that has some especially valuable properties. The control actuation depends on measurements from sensors (e.g., measured terminal voltage), but interprets the sensors with knowledge of the physical dynamics via a real-time state-space model. MPC also enables the imposition of constraints, which is not possible with more-traditional control algorithms such as PID. Moreover, MPC enables sensor inferences to predict unmeasurable behaviors. For example, using measured temperature and voltage, an MPC algorithm can be developed to predict and avoid deleterious Li plating or dendrite growth [6].

An important element of our physics-based modeling research is concerned with chemo-mechanical behaviors. As electrode particles intercalate Li, the atomic-scale lattice dimensions can change greatly and anisotropically. The three-dimensional electrode-scale shrinking and swelling can cause damage, including particle decohesion or fracture that degrades the battery performance. Two papers document this research, one on graphite anodes [8] and the other on NMC cathodes [9].

Early in this project, some of the research was concerned with fuel cells. However, because of ONR interests, the focus shifted to being dominantly on secondary batteries. Nevertheless, there is a great deal of synergy in the underpinning mathematical and control aspects of these different electrochemical power sources.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The objective of this proposal is to develop and apply physically based models that bridge from fundamental chemistry, electrochemistry, and transport to system-level applications. Although the fundamental research and physics-based modeling has very broad applicability, the programmatic focus is on applications that assist the development and deployment of relatively small electrochemical power sources, such as for unmanned undersea vehicles (UUVs). The scope emphasizes, but is not limited to, secondary (rechargeable) batteries, fuel cells, and supporting technology. Fundamental physical and chemical models provide the quantitative insight that is needed for effective system design and development. However, the predictive ability of these models depends on numerous physical and chemical properties and parameters that may not be readily available. One objective of the present proposal is to develop the needed macroscale properties from more fundamental analysis at the microscale. In addition to physics-based modeling, the proposed effort develops strategies to incorporate physical knowledge into real-time control decisions. Full physical models (e.g., Li-ion battery packs) can be very large and require substantial computational resources for solution. However, for control purposes such large models can be systematically reduced to linear, low-order, state-space models. The state-space models play important roles in assisting the interpretation of measured electrochemical impedance spectra, in evaluating the system state of health, and in implementing real-time model-predictive control (MPC).

15. SUBJECT TERMS
Li-ion batteries, Physic-based modeling, Model-predictive control

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