THE LITHIUM-ION BATTERY MODELING CHALLENGE:

By Donald J. Docimo,
Mohammad Ghanaatpishe,
Michael J. Rothenberger,
Christopher D. Rahn,
and Hosam K. Fathy
Pennsylvania State University

A DYNAMIC SYSTEMS AND CONTROL PERSPECTIVE

Electrochemical batteries are central to the portable consumer electronics market. They power critical biomedical devices such as cardiac pacemakers. They help improve the fuel economy, performance, and emissions characteristics of hybrid electric vehicles by enabling regenerative braking, component right-sizing, and optimal power management. They have the potential to lessen the variability of large data centers' electric power demand through *peak shaving* and *valley filling*. In the electricity market, they are gaining attention as means for addressing the intermittencies associated with renewable generation from photovoltaics and wind power plants.

Batteries are challenged by competing energy storage technologies. This competition can be appealing for business, as in the case of heavy vehicles potentially benefiting from hydraulic hybrid powertrains. To remain commercially viable, batteries must compete with rival technologies on multiple fronts/metrics. These include monetary/societal/environmental cost, safety, efficiency, longevity, scalability, and specific power/energy. Today, we have a large portfolio of battery chemistries, each of which is a tradeoff among the above criteria. This portfolio can be subdivided into *primary* versus *secondary* batteries. Primary batteries are intended for single-use applications as they release energy through an irreversible chemical reaction. The lithium-iodine battery found in cardiac pacemakers is an example: it gradually releases energy over a period of years, after which it must be surgically replaced. Secondary batteries are rechargeable. They release energy through a reversible chemical reaction. Examples include lead-acid, nickel-metal-hydride, and lithium-ion batteries.

LITHIUM-ION BATTERIES: INTERNAL STRUCTURE AND OPERATION

Much of the progress in secondary battery technology has been driven by applications requiring mobility, such as portable electronics and transportation. The need for mobility creates impetus for higher *specific power/energy* (i.e., higher rated power/energy per unit mass). Lithium's position on the periodic table makes it light and highly reactive. Thanks to these two properties, lithium-ion batteries provide an attractive combination of specific power and specific energy. This is illustrated by the *Ragone plot* in **Figure 1**.

To construct a lithium-ion battery, one needs positive and negative electrodes, as shown in **Figure 2**. Each electrode contains active material particles, brought together into a porous mix using a binder, and infused with an electrolytic solution or gel. A porous separator allows the electrodes to exchange lithium ions through the solution. Electrons cannot travel through this separator, and must go through the electrodes' metallic current collectors plus outside circuitry to travel from one electrode to another. The negative electrode's active material is often a carbon substance, such as graphite. Popular choices of active positive electrode materials include lithium iron phosphate (LFP), lithium cobalt oxide (LCO), and lithium manganese oxide (LMO)[1].

Regardless of the choice of electrode materials, the basic principles of lithium-ion battery operation are the same. Lithium can reside in *interstitial sites* within the crystal structures of both electrodes, but has a higher affinity for the positive electrode. During battery charging, external current pulls electrons from the positive electrode and injects them into the negative electrode. External work is done on the battery, since current is forced uphill against an electric potential. Inside the battery, energy is stored through the transfer of ions to the negative electrode, for which they have less affinity. Lithium's journey during this charging process proceeds as follows. Solid-state diffusion transfers lithium from interstitial sites inside the positive electrode's active material crystals to the surfaces of these crystals. A *de-intercalation* reaction then transfers lithium ions from the positive electrode crystals to the electrolyte. The ions diffuse within the electrolyte, through the separator, and into the negative electrode. An *intercalation* reaction transfers lithium into the crystal structure of the negative electrode's active material. Finally, lithium diffuses within the negative electrode's crystal structure and settles within its interstitial sites. Separating lithium ions from electrons in the positive electrode is an *oxidation* process. Re-uniting them in the negative electrode is a *reduction* process. This oxidation-reduction reaction stores energy in the battery. Should the external power source be replaced by a load, the lithium ions will trace the journey backwards, releasing energy to the load.

This description raises a few important questions. *What role does instrumentation and control have in improving battery performance, safety, and health? To what extent are electrochemistry-based models important for battery management? What are the underlying physics in lithium-ion batteries, and how does one model them? What insights can*
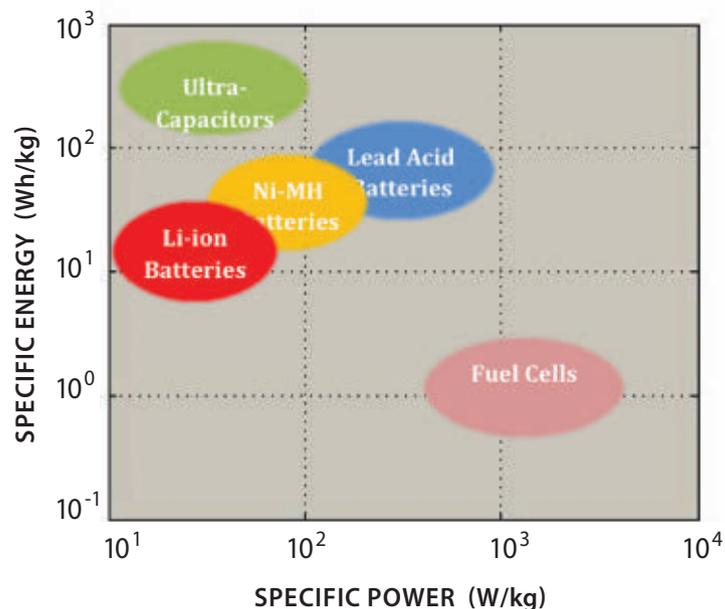

FIGURE 1 Ragone plot showing specific power vs. specific energy for different battery chemistries, in comparison to fuel cells and ultra-capacitors.

one gain from electrochemistry-based models regarding battery behavior in the time/frequency domain? How easy is it to obtain lithium-ion battery parameter values from experimental data? Finally, what role can education and outreach play in lithium-ion battery modeling and control? The remainder of this article is an attempt to examine these questions from a high-level vantage point, with the scientific literature serving as a guiding light.

HOW DO LITHIUM-ION BATTERIES AGE, DEGRADE, AND FAIL?

It would be ideal to maximize a lithium-ion battery's power and energy through cycles of deep charge/discharge at a high current over a broad temperature range. This is crucial for applications such as electrified transportation, as in a hybrid car's resilience to both Arizona summers and Alaskan winters. But this ideal temperature-blind, deep, and aggressive battery charging/discharging is difficult to achieve for at least three reasons:

■ Aggressive battery use may not be efficient. The higher currents result in larger dissipative losses which diminish efficiency.

■ The tradeoff between a battery's useful power and energy capacity is partly the result of internal diffusion dynamics. When a lithium-ion battery is charged or discharged at high currents, lithium ions do not have sufficient time to spread evenly throughout its electrolyte and crystal structure. Substantial lithium concentration gradients build inside the battery and cause it to appear "full" or "empty" prematurely from an input-output perspective, as terminal voltages hit their upper and lower bounds more quickly than during less aggressive operation. In order to prevent battery damage, charging or discharging prematurely
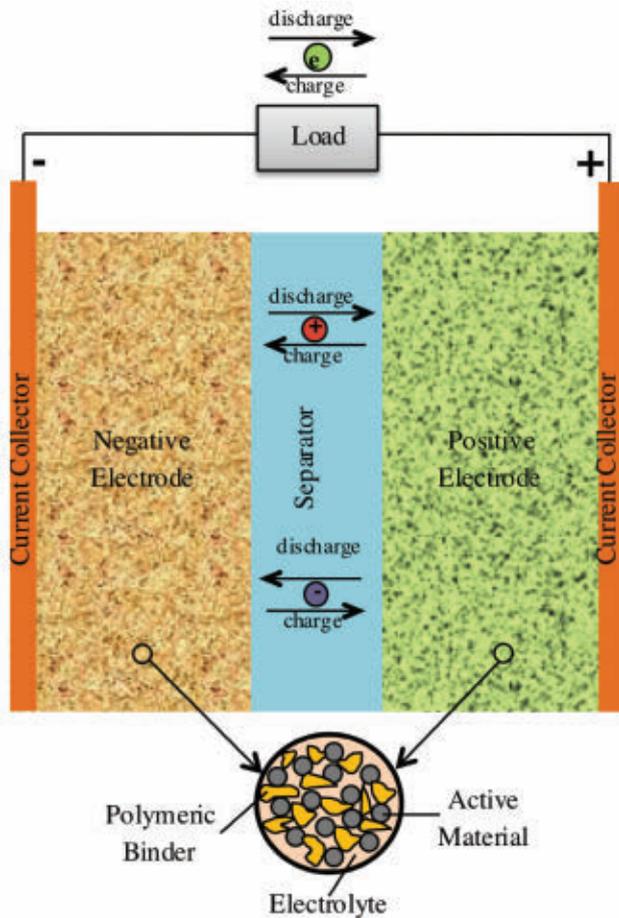
FIGURE 2 Internal structure of a lithium-ion battery.

must then be curtailed. This results in the *Peukert effect*, where larger battery charge/discharge currents diminish useful capacity.

■ Aggressive use of a lithium-ion battery can also reduce the life of its useful power, as it accelerates aging and degradation.

Lithium-ion battery control is an exercise in degradation constraint management. It helps to have a physical understanding of how lithium-ion batteries age and degrade in order to achieve this control. Although surveys of battery degradation exist [1–4], the goal here is to provide an introduction to four damaging phenomena: solid electrolyte interphase growth, dendrite growth, mechanical fatigue, and thermal runaway.

Damage Mechanism #1: SEI Layer Growth

The *solid electrolyte interphase* (SEI) is a protective layer that coats the negative electrode's active material particles as soon as they come in contact with the electrolyte. The degree to which lithium-ion batteries contain SEI layers is chemistry-dependent, and our discussion here focuses on batteries where carbon is the active negative electrode material. The presence of an SEI layer is desirable in moderation: the SEI layer coats the negative electrode particles and protects them from further reaction with the electrolyte. Moreover, the SEI layer allows lithium ions to travel between the electrolyte and negative electrode particles during battery charging and discharging. Over the lifetime of the

battery, the SEI layer tends to grow, consuming lithium ions in an irreversible manner and reducing the battery's ability to store charge and energy. This results in visible *capacity fade*. In addition, the growth of the SEI layer can contribute to the battery's *power fade,* which results from growing internal resistance that diminishes the its ability to provide high levels of power. SEI layer growth continues throughout the life of lithium-ion batteries with carbon-based negative electrodes—even while unused batteries are sitting in storage—and greatly affects battery longevity. Limiting SEI layer growth can be key to prolonging lithium-ion battery life. From a control-theoretic perspective, this growth can be limited by managing the input variables contributing to it in addition to the battery state. It is especially important to note the acceleration of SEI layer growth at higher *states of charge* (SOCs), during faster charging, and at elevated temperatures.

Damage Mechanism #2: Lithium Plating

Lithium plating is a damage phenomenon that occurs when metallic lithium precipitates on the surfaces of a battery's active negative electrode particles. Lithium plating can be very damaging, especially when the precipitated metallic lithium forms dendrites that pierce the battery's separator, thereby creating an internal short circuit. To understand the main cause of lithium plating, consider the following hypothetical experiment. Imagine creating a lithium-ion battery with a very small amount of metallic lithium buried inside the separator. This lithium deposit is called a third electrode. One can hypothetically connect this third electrode to an external current source or sink. Depending on whether that source/sink provides positive or negative current, the third electrode could either release lithium ions into the electrolyte
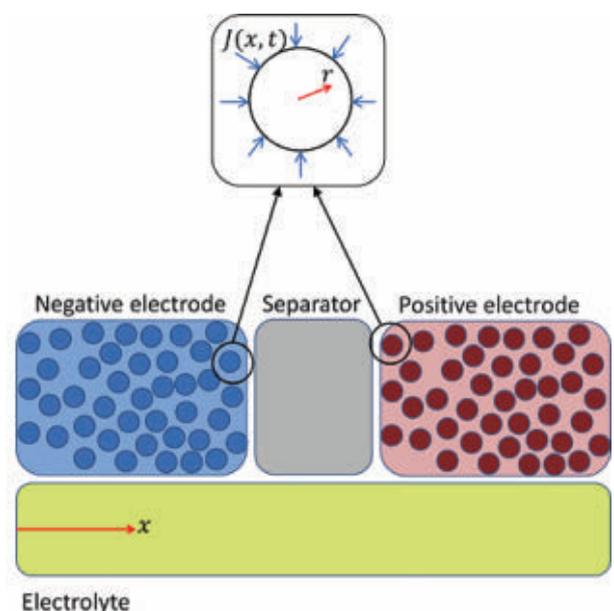
FIGURE 3
Schematic of the DFN lithium-ion battery model.

solution or gain lithium from the solution. This explains the battery community's convention of referring to this electrode as the Li\Li+ electrode: it is an electrode that represents the ionization and precipitation of pure lithium. In our hypothetical experiment, we will not utilize this third electrode for battery charging or discharging. Instead, we will use it as a reference electrode, and measure different battery potentials relative to it. One quickly discovers through this experiment that carbon-based negative electrodes in lithium-ion batteries operate at potentials very close to zero relative to Li\Li+ reference electrodes. This is especially true at high overall battery states of charge. Because of this fact, lithium-ion batteries with carbon-based negative electrodes tend to be quite vulnerable to lithium plating. Plating is particularly likely to occur when one attempts to exceed the physical limitations on intercalation rates in the negative electrode: in that scenario, lithium begins to plate the surfaces of negative electrode particles instead of intercalating into the particles. The achievable intercalation rate in a battery electrode is temperature-dependent: lower temperatures translate to slower intercalation rates. This explains the fact that lithium plating is particularly worrisome when batteries are operated at low temperatures.

Damage Mechanism #3: Mechanical Degradation

Inserting lithium into the interstitial sites in an electrode can cause the electrode to expand in volume, and removing ions can cause it to shrink. The process of charging and discharging a lithium-ion battery therefore creates cycling mechanical stresses that can induce mechanical fatigue. Deep charge/discharge cycles produce larger swings in internal battery stress with cycling, thereby resulting in higher levels of mechanical degradation. The way in which a battery is used therefore has a significant impact on the degree to which it degrades mechanically. Compared to plug-in electric vehicles, for instance, the fact that hybrid electric vehicles cycle their batteries over much narrower ranges of state of charge is attractive from a mechanical degradation perspective.

Damage Mechanism #4: Thermal Runaway

Most battery degradation mechanisms, such as SEI layer growth, progress slowly over years of battery life and thousands of battery charge/discharge cycles. Thermal runaway is an exception. As its name suggests, this is a phenomenon where battery temperature rises in a very rapid manner, leading to catastrophic failure. Thermal runaway typically begins in an already-overheated battery: one whose temperature has risen above roughly 90°C, perhaps because of an internal short circuit. From that point onwards, the battery experiences a sequence of exothermic damage reactions. If these reactions generate heat faster than the battery

can dissipate it, internal battery temperature rises to the point of catastrophic failure. The thermal runaway of one cell in a battery pack could potentially trigger a domino cascade of thermal runaways in neighboring cells. The degree to which this occurs in practice depends on the care taken in overall battery pack construction, design, and thermal management.

Thermal runaway can be catastrophic, but is often a manifestation of underlying damage mechanisms, and involves cascading stages of battery failure. Instrumentation, estimation, and control technologies may perhaps be able to: *(1)* lessen the likelihood of thermal runaway by monitoring and controlling the factors leading to it (e.g., cell temperature); *(2)* detect the inception of thermal runaway early enough to be able to at least manage the resulting damage.

ELECTROCHEMICAL MODEL-BASED LITHIUM-ION BATTERY MANAGEMENT

There is growing evidence in the literature suggesting that model-based battery management grounded in the fundamentals of electrochemistry can help expand the envelope of lithium-ion battery performance, efficiency, longevity, and perhaps even safety. A recent study by Rahimian *et al.*, suggests that one can tailor a battery's charge/discharge trajectory to prolong useful life by up to 29% without compromising performance[5]. Research by Smith and Wang suggests that electrochemical model-based health management can potentially improve useful lithium-ion battery power density by as much as 50% without compromising longevity[6]. Research by Bashash *et al.* suggests that there is an opportunity to achieve a Pareto-optimal tradeoff between overall energy cost and long-term SEI growth in plug-in hybrid electric vehicle (PHEV) battery packs by optimizing the timing and rate with which PHEVs charge their battery packs with grid electricity[7]. Boovagaravan *et al.* and Methekar *et al.* provide an elegant physical explanation for why model-based battery management can potentially help expand the envelope of lithium-ion battery performance[8,9]. Specifically, they use electrochemistry-based battery simulations to suggest that optimal battery charging/discharging utilizes active battery electrode materials more effectively than traditional battery cycles. An experimental study by Zhang presents the finding that the shape of a lithium-ion battery's charge/discharge cycle does indeed have a significant impact on internal degradation via impedance growth, even if the time-averaged charge/discharge current is held constant[10]. Model-based lithium-ion battery management is clearly an unfolding research topic, with much need for additional study and discovery. However, the emerging literature in this field appears to lend credence to the exciting conclusion that model-based estimation and control, grounded in the fundamentals of electrochemistry, can perhaps lead to substantial improvements in lithium-ion battery performance, efficiency, longevity, and safety.

There is a sharp distinction between this research and the traditional battery management system (BMS) design mindset. In a traditional BMS, strict safety limits are imposed on battery current, SOC, voltage, and temperature. There is freedom to operate the battery within these safety limits. In sharp contrast, the model-based battery control literature attempts to minimize battery degradation and damage by managing the internal battery state variables contributing to degrada-

tion and damage, rather than imposing ad-hoc limits on measured battery input/output variables. Implicit in this literature is the belief that this electrochemistry-based approach leads to less conservative and better-optimized battery management. Understanding the electrochemical processes occurring inside lithium-ion batteries is of great importance, and necessary in order to model these processes, and train new generations of engineers on how to use them for monitoring and control.

MODELING THE DYNAMICS OF A LITHIUM-ION BATTERY

The literature presents a large family of lithium-ion battery models, with varying degrees of fidelity and complexity. Some of these models abstract a lithium-ion battery into an equivalent circuit, while other models express battery dynamics using coupled algebraic and differential equations grounded in the discipline of electrochemistry. The mindsets behind these models are very different: equivalent circuit modeling tends to emphasize simplicity, and often involves fitting low-order approximations to empirically-measured input/output battery behavior. Electrochemical modeling, in contrast, tends to emphasize predictive ability, and focuses on describing a battery's underlying physics. This difference in mindset can be misleading: it can potentially exaggerate the contrasts between equivalent circuit models and electrochemical models. One goal of this article is to emphasize the commonalities between equivalent circuit and electrochemical battery models, particularly the degree to which both reflect the fundamental physical processes inside a lithium-ion battery.

Much of the literature on lithium-ion battery modeling has roots in the seminal work of Doyle, Fuller, and Newman (DFN)[11]. **Figure 3** provides a schematic representation of the DFN model's structure. The model describes the evolution of two quantities inside a battery: *electric potential*, ϕ, and the *volumetric concentration of lithium ions, c*. The model idealizes the active electrode material inside the battery as an infinite assortment of homogeneous spherical particles, distributed evenly across the thickness of the battery. There are two spatial axes in this model: an *r* axis representing radial distance inside the battery's spherical particles, and an *x* axis representing distance perpendicular to the battery's electrode layers. This choice of axes reflects the fact that variations in ion concentrations and electric potentials tend to be relatively small along the length and width of the electrode layers. DFN model construction is a three-step process:

■ STEP 1 Modeling potential distributions using Ohm's law

Elementary circuits textbooks present a lumped-parameter version of Ohm's law, $V = IR$, with V being the voltage across a resistor, I being the current through it, and R beings its resistance. If the resistor has a uniform cross-section, then its resistance can be expressed in terms of its cross-section area, A_r, effective conductivity, σ, and length. Here we are interested in an infinitesimal resistor of vanishingly small length δx. The voltage V, in this case, is the difference in potential, ϕ, between the two ends of the resistor, and the current, I, flows in the positive x-direction. Applying Ohm's law gives:

FIGURE 4
Sketch of lithium-ion battery EIS plot.

$$\phi(x + \delta x) - \phi(x) = -I \frac{\delta x}{\sigma A_r} \qquad \textbf{1}$$

Rearranging the above equation and taking the limit as $\delta x \longrightarrow 0$ results in the following differential equation:

$$\sigma \frac{\partial \phi}{\partial x} = -I \frac{\delta x}{\sigma A_r} \qquad \textbf{2}$$

Equation 2 assumes that the same current that enters the resistor at location x leaves the resistor at location $x + \delta x$. If the above resistor represents, say, one of the solid electrodes of a lithium-ion battery, then this assumption is not true. Current travels along the x-axis in the electrode, but additional current also enters the electrode via intercalation from the electrolyte. If the intercalation current density (i.e., intercalation current per unit volume) is J, then the following equation enforces conservation of charge:

$$I(x + \delta x) - I(x) = J A_r \delta x \qquad \textbf{3}$$

Rearranging **Equation 3** and taking the limit as $\delta x \longrightarrow 0$ gives:

$$J A_r = \frac{\partial I}{\partial x} = \frac{\partial}{\partial x} \left(-\sigma A_r \frac{\partial \phi}{\partial x} \right) \qquad \textbf{4}$$

Finally, canceling the area A_r from both sides of **Equation 4** yields Ohm's law as it applies to the solid material of a lithium-ion battery electrode:

$$J + \frac{\partial}{\partial x} \left(-\sigma A_r \frac{\partial \phi}{\partial x} \right) \qquad \textbf{5}$$

The above derivation can be used to relate solution-phase potential gradients to intercalation current density, with only two minor changes. First, one must change the sign associated with intercalation current density, J, to ensure conservation of charge between the electrodes and electrolyte. Second, one must also account for the impact of lithium ion concentration gradients on solution-phase potentials: a phenomenon known as *concentration polarization*.

■ STEP 2 Modeling concentration dynamics using Fick's law

During charging and discharging, the electrodes of a lithium-ion battery exchange ions via diffusion. Fick's law of diffusion—analogous to the law of conduction heat transfer—states that diffusion proceeds opposite to concentration gradients. For a prismatic medium of cross-sectional area A, Ficks's law states that the total ion flow rate, Q, is related to concentration gradient, $\frac{\partial c}{\partial x}$, as follows:

$$ Q = -AD\,\frac{\partial c}{\partial x} \qquad\qquad 6 $$

The quantity D represents diffusivity. Treating diffusivity as a constant parameter furnishes a linear diffusion model. This can lead to some inaccuracy if the underlying diffusion dynamics are nonlinear. Additional modeling complexities arise when solid-state lithium ion diffusion induces a crystal structure phase change: a phenomenon that occurs in lithium iron phosphate electrodes.

Using Fick's law of diffusion to model battery dynamics involves imposing an ion conservation law, analogous to Equation 3. Consider, for example, an element of the electrolyte of infinitesimal thickness δx. Diffusion causes lithium ions to enter this infinitesimal element at a rate equal to $Q(x) - Q(x+\delta x)$. Moreover, if the volumetric intercalation current density is J, then ions leave this electrolyte element at a rate $JA\delta x\,\frac{(1-t^+)}{F}$. The constants t^+ and F are a *transference number* and Faraday's number, respectively. Dividing intercalation current by Faraday's number converts it to an ionic transfer rate. Furthermore, multiplying by $(1-t^+)$ accounts for the fraction of intercalation current transmitted via lithium ions. Altogether, the net rate at which lithium ions enter this infinitesimal electrolyte element equals the rate of charge accumulation within the element, i.e.:

$$ Q(x) - Q(x+\delta x) - \frac{J(1-t)A\delta x}{F} = \frac{\partial}{\partial t}\left[\varepsilon c A \delta x\right] \quad 7 $$

The symbol ε in the previous equation represents battery porosity: a quantity that is important because the electrolyte only occupies the pores within a lithium-ion battery. Substituting Equation 6 into Equation 7 and taking the limit as $\delta x \longrightarrow 0$ gives:

$$ \nabla.\left(D\nabla.c\right) - \frac{J(1-t)}{F} = \varepsilon\,\frac{\partial c}{\partial t} \qquad 8 $$

Equation 8 is Fick's law of diffusion, written specifically for the electrolyte in a lithium-ion battery. This is a partial differential equation which, when discretized in space, yields state equations for solution-phase ion concentrations as state variables. The "driving force" in this PDE is intercalation current density. A similar derivation, omitted for brevity, yields a partial differential equation for ion concentration dynamics over the spherical coordinate system for the active electrode particles.

■ STEP 3 Modeling intercalation using the Butler-Volmer equation

Intercalation current density appears in all of the above battery model derivations. Intercalation is a chemical reaction, driven by a difference in potential between the solution and solid phases in a lithium-ion battery. Depending on lithium ion concentration at the surface of a given solid particle, there is an *equilibrium potential U_{ref}* at which intercalation and de-intercalation reactions occur at equal rates, denoted as i_o. When the potential difference between the solid and solution phases equals that equilibrium potential, there is no net transfer of charge via intercalation. Suppose we increase the difference between solution-phase and solid-phase potentials relative to this equilibrium, by some *overpotential η*. This overpotential will accelerate the intercalation reaction by the factor $e^{\frac{\alpha F}{RT}\eta}$, where F is Faraday's number, R is the ideal gas constant, T is absolute temperature, and α is a constant known as a charge transfer coefficient. Furthermore, de-intercalation slows down by the factor $e^{-\frac{(1-\alpha)F}{RT}\eta}$. The end result is that the *net intercalation rate* grows to some nonzero value, J, governed by the *Butler-Volmer equation*:

$$ J = i_o\left(e^{\frac{\alpha F}{RT}\eta} - e^{-\frac{(1-\alpha)F}{RT}\eta}\right) \qquad 8 $$

Overpotential, in the Butler-Volmer law, is the difference between solution-phase and solid-phase potential computed relative to equilibrium:

$$ \eta = \phi_{solution} - \phi_{solid} - U_{ref} \qquad 9 $$

The Butler-Volmer equation is central to the DFN battery model. It couples all the other major elements of the model, bringing together the phenomena of solid- and solution-phase diffusion and Ohmic resistance into an integrated whole. To complete the DFN model, one needs to incorporate boundary conditions representing the fact that potential gradient is zero at interfaces where current is zero (e.g., the interface between the solid electrode and separator), and is proportional to total battery current at the interface with external circuitry. Furthermore, modeling the thermal dynamics of the battery requires additional equations capturing reversible and irreversible heat generation, thermal energy storage, heat transfer, and the dependence of battery parameters such as diffusivities and equilibrium reaction rates on temperature.

THE NEED FOR CONTROL-ORIENTED LITHIUM-ION BATTERY MODELING

From a control-theoretic perspective, the DFN battery model is very complex. It captures the evolution of battery state variables as a function of time, transverse distance within the battery material (x axis), and radial distance within the battery particles (r axis). It consists of coupled ordinary differential equations, partial differential equations, and algebraic constraints. Reasonable discretizations of the DFN model can yield thousands of lumped-parameter differential algebraic equations (DAEs).

The scientific community has been actively developing different tools for balancing the fidelity and complexity of electrochemical battery models such as the DFN model. Examples of these tools include the use of orthogonal collocation methods, proper orthogonal decomposition, pole residue grouping, and Padé approximation to reduce the number of state variables needed to model battery dynamics[1]. These model reduction techniques are valuable, but it is equally important to build an intuitive understanding of which electrochemical phenomena are important to model for different battery operating conditions. Towards this goal, consider the problem of extracting appropriate simplifications of the DFN model for different battery *C-rates*. A battery's C-rate is defined as its charge/discharge current, in Amperes, divided by its charge capacity in Ampere-hours. A 1-C charge rate, for instance, represents an attempt to charge the battery in exactly 1 hour, whereas a 2-C charge rate represents an attempt to charge it in 30 minutes. The question, here, is: *which components of the DFN model are important at different C-rates?* Examining the literature reveals the following insights:

■ At extremely slow C-rates measuring less than C/100, the relationship between state of charge and open-circuit voltage defined battery behavior. The corresponding relationship in the DFN model is between solid-phase ion concentrations and equilibrium potential, U_{ref}, for each of the two electrodes.

■ As C-rates increase to roughly 1-C, the battery's Ohmic resistance and solid-phase diffusion dynamics become more important. This motivates the literature's development of the single-particle model: a simplification of the DFN model where solution-phase ion concentration is assumed to be constant. By neglecting spatial variations in solution concentration, the single particle model is able to: *(1)* represent each battery electrode by a single spherical diffusion particle (hence the model's name), *(2)* eliminate the need for solving Fick's law of diffusion for the solution, *(3)* replace Ohm's law for both the solid and electrolytic media by lumped equivalent resistors.

■ At C-rates higher than 1-C, the need for the DFN model to fully incorporate thermal behavior increases substantially.

LITHIUM-ION BATTERY BEHAVIOR IN THE FREQUENCY DOMAIN

When developing physics-based battery models such as the DFN model, electrochemists are typically looking to capture battery behavior over a reasonable range of frequencies, for a broad range of charge/discharge currents and temperatures. The need for accurate models of frequency-domain battery behavior motivates *electrochemical impedance spectroscopy* (EIS): the process of measuring and plotting the complex impedance of a battery for different excitation current frequencies. An EIS plot is essentially a Nyquist plot, with one small caveat: while the real axis represents battery resistance, the imaginary axis represents imaginary battery impedance multiplied by -1. An EIS plot of an RC circuit, for instance, lies in the first quadrant of the complex

ABOUT THE AUTHORS

Donald Docimo is a doctoral student in the Department of Mechanical and Nuclear Engineering at the Pennsylvania State University. He earned a B.S. in mechanical engineering from the College of New Jersey in 2012. His research focuses on modeling and control, currently applied to lithium-ion battery systems and smart grid applications.

Mohammad Ghanaatpishe received the B.Sc. degree in mechanical engineering from the Sharif University of Technology, Tehran, Iran, in 2012. He is currently working toward the Ph.D. degree in Mechanical Engineering at the Pennsylvania State University. His research interests include optimal control, modeling, and system identification.

Michael Rothenberger is a doctoral student in the Mechanical and Nuclear Engineering Department at the Pennsylvania State University. He received his B.S. and M.S. degrees from Penn State in 2010 and 2012, respectively. He is currently researching lithium-ion battery diagnostics for hybrid electric and electric vehicle applications.

Christopher D. Rahn obtained his Ph.D. from the University of California, Berkeley in 1992 and is currently a Professor of Mechanical Engineering, Director of the Mechatronics Research Laboratory, and Co-Director of the Battery and Energy Storage Technology Center at The Pennsylvania State University. His research on the modeling, analysis, design, and control of mechatronic systems has resulted in three books, over one hundred and fifty refereed publications, and several patents. He is a Fellow of the American Society of Mechanical Engineers.

Hosam K. Fathy earned his B.Sc., M.S., and Ph.D. degrees, all in Mechanical Engineering, from the American University in Cairo (1997), Kansas State University (1999), and University of Michigan (2003). His research focuses on the reduced-order modeling and optimal control of energy storage and management systems. He is a 2014 NSF CAREER award recipient.

plane. EIS plots are an excellent means for emphasizing the connections, as opposed to contrasts, between electrochemistry-based and equivalent circuit battery modeling.

Figure 4 presents a sketch of a lithium-ion battery's EIS plot. As battery excitation frequency increases from zero to infinity, one traces this EIS plot from the top right corner to the bottom left. The DFN model excels at matching the low-frequency portion of this plot. At very low frequencies, the battery acts as a pure integrator. The battery's output voltage at these frequencies is a function of state of charge, which is proportional to the integral of input current. The DFN model represents this fact through the static relationship between electrode equilibrium potentials and solid-phase ion concentrations. The EIS plot shows this integral behavior by curving upwards to become almost vertical at frequencies in the sub-mHz range. As excitation frequency increases, diffusion dynamics become relatively important. Consider Fick's law of diffusion for a spherical solid electrode particle. Fick's law can be discretized spatially to furnish a set of lumped-parameter state-space equations that physically represent cascades of resistive-capacitive dynamics. The corresponding EIS plot curves with frequency such that its slope approaches 45°. This model-based insight is typically visible in an EIS plot, particularly as frequency increases from the mHz range to the Hz range. At higher excitation frequencies, the interfaces between the electrode particles, electrolyte, and current collectors become more important to model. Phenomena such as the double-layer capacitance of the SEI layer, the charge transfer resistance of the SEI layer, and the impedance of the passivation film at the heart of the SEI begin to reveal their own RC dynamics at the battery's input/output ports. We did not incorporate these RC dynamics in the DFN model presented here, but this can be done fairly easily, pushing the model's bandwidth to the neighborhood of 100Hz. As excitation frequencies push into the kHz range, inductive phenomena and *skin effects* come into play, causing the EIS plot to drop into the fourth quadrant.

CONCLUDING REMARKS

The overarching messages of this article have been that: *(1) Lithium-ion batteries have a key role to play in mobile energy storage. (2) One can potentially expand the envelope of lithium-ion battery performance, efficiency, safety, and longevity by using fundamental electrochemistry-based models for battery control. (3) There are clear tradeoffs between battery model fidelity and complexity, and a significant literature addressing these tradeoffs. (4) Electrochemistry-based battery models can be effective at capturing frequency-domain battery dynamics, especially at lower frequencies. When they are examined in this light, the commonalities between them and equivalent-circuit models become more visible.*

We refer in the title of this article to the lithium-ion battery modeling *challenge*. Constructing lithium-ion battery models certainly takes effort, and so does reducing these models for control design purposes. One important open challenge in lithium-ion battery modeling is the matching of sophisticated battery models to experimental data. Fortunately, with full charge/discharge, duty cycle, and EIS testing there is considerable input/output data available for validation. Half-cell testing or insertion of a third reference electrode in a feul cell can separate the contributions of the negative and positive electrodes, and researchers are pursuing other novel technologies for in-cell instrumentation and measurement. Most importantly, there is a need to educate the next generation so that they can contribute to the community's growing efforts to tackle the lithium-ion battery modeling challenge. ■

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