

A Survey of Long-Term Health Modeling, Estimation, and Control of Lithium-Ion Batteries: Challenges and Opportunities

Kelsey B. Hatzell, Aabhas Sharma, and Hosam K. Fathy

Abstract—This paper reviews the literature on Lithium-ion battery characterization, control, and optimization. The paper examines the primary degradation processes in cycled cells, then proceeds to the challenges associated with controlling these processes. One key challenge is the multiplicity of complex phenomena contributing to battery aging, and the failure of most empirical battery health models to account for this multiplicity. This creates a need for identifying how batteries fail, and developing control-oriented fundamental models of their failure: a task that requires tight integration of experimental characterization techniques, system identification, and electrochemistry-based battery modeling and simulation. The paper provides an overview of battery degradation mechanisms and reactions, and the various methods used to characterize these reactions. We also highlight the battery control strategies currently in use, and the potential for long-term battery health improvements using model-based degradation control.

I. INTRODUCTION

This paper surveys the literature on characterizing, modeling, and controlling Lithium-ion batteries (LIBs), and emphasizes open research areas in the onboard estimation and management of battery State of Health (SoH). The paper is motivated by the rapid pace of ongoing innovation in LIB materials and chemistries, and the resulting gains in battery power and energy density, cost effectiveness, and long-term durability [1], [2]. The paper adopts the key conjecture that to eke out the best performance and useful life from a novel LIB, one must account for its aging and degradation in onboard control design [3]. This justifies the paper's focus on two primary areas: the modeling and experimental characterization of battery degradation [4], [5], and the optimal control of battery functions in onboard applications. The paper begins with a description of the electrochemical working principles of LIBs. Next, we review the mechanisms and reactions that cause failure, and the methods used to characterize these reactions. We highlight the useful information and fundamental models that can be obtained from this experimental characterization. Finally, the paper concludes with a review of efforts to develop optimal charging strategies for battery health as well as onboard battery health estimation algorithms. This survey highlights the key conclusion that while the scientific community has made significant strides in LIB health characterization and modeling, there is still a need for research on the electrochemistry-based estimation and control of battery health.

Hatzell and Sharma are graduate students and Fathy is an assistant professor in Mechanical and Nuclear Engineering at the Pennsylvania State University. Emails: (kbh5081, axs5358, hkf2)@psu.edu.

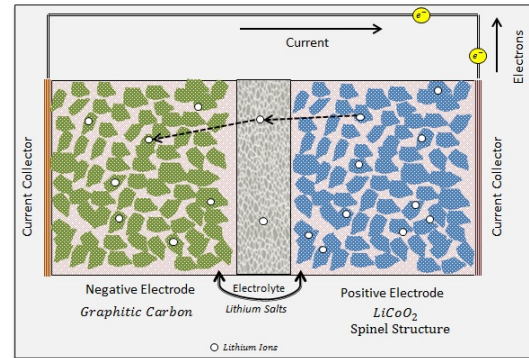
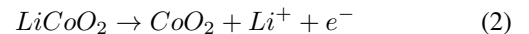


Fig. 1. Lithium Ion Dynamics.

II. LITHIUM ION BATTERY OPERATION

Figure 1 illustrates the charging of a Lithium-ion cell. The cell contains a positive electrode (cathode) and a negative electrode (anode). The flow of electrons is generated by redox reactions. An oxidation half-reaction at the anode releases electrons, and a reduction half-reaction at the cathode accepts and stores these electrons. One example of these oxidation-reduction reactions, for the charging of a battery with a graphite anode and Lithium-Cobalt-Oxide cathode, is:



A porous separator prohibits the direct exchange of electrons between the anode and cathode, forcing the electrons through external circuitry. This produces useful work because of the Lithium ions' higher affinity for the cathode material. The ions travel into and out of interstitial sites in the anode and cathode crystal structures via intercalation, and an electrolyte facilitates their diffusion between the electrodes.

III. DEGRADATION IN LITHIUM ION BATTERIES

Lithium-ion batteries degrade due to several complex and intertwined processes that occur at similar time scales, which makes it difficult to decipher exactly how LIBs fail [6]. From an input-output perspective, one can quantify cell degradation in terms of capacity fade and power fade. Capacity fade is the loss of battery charge/discharge capacity over time [7], whereas power fade is the deterioration in a battery's ability to absorb and deliver electrical power, and is directly related to internal impedance rise [8]. This section surveys some

key mechanisms for LIB power and capacity fade, including Solid Electrolyte Interphase (SEI) growth, dendrite formation [9], [10], [11], lithium plating [12], thermal aging, and mechanical degradation. These aging effects are described in detail in [13], [6]. The following subsections provide a brief introduction to each of these mechanisms, and discuss the potential use of battery control to decelerate them.

A. Solid Electrolyte Interphase Growth

The solid electrolyte interphase (SEI) is a layer that forms on the surface of electrode particles during charging, especially when the electrode and electrolyte first chemically react. It protects the electrode from further reaction with the electrolyte while still permitting Lithium ion transport between the two [14], [15]. Furthermore, it both consumes cyclable Lithium ions and impedes their transport as it grows, thereby contributing substantially to both power and capacity fade [15]. Researchers describe the SEI as a multilayered “mosaic of microphases” produced by film formation, dissolution, redeposition, and decomposition [15], [16]. The first layer is thin and compact, and the second is a more porous and open layer that stifles the transport of lithium ions. The literature presents several models of SEI growth [17], [18], [15], [16], [19]. Peled et al., for instance, model the SEI layers as four RC circuits in series with Warburg impedance [15], while Ramadass et al. use a first-principles model for SEI growth via continuous solvent reduction during charging [17].

Modeling the physics of SEI growth can be a key prerequisite to controlling this growth. Safari et al. pursue this problem by developing a single-particle multimodal battery model based on dilute solution theory, and capturing minor species transport across the SEI layer, capacity loss, and SEI porosity growth [20]. Safari et al. use this model to analyze capacity fade during battery cycling and storage, and conclude that SEI porosity is a particularly critical parameter in describing SEI properties and capacity fade in LIB cells [20]. Molecular and atomistic models provide additional insights into the microscale reactions that cause SEI growth and battery degradation. Bedrov et al. use molecular dynamic simulations to explore the reduction of the ethylene carbonate electrolyte in the presence of common electrolyte additives such as Vinylene Carbonate (VC) [21]. Their findings show that ethylene carbonate radicals react differently in the presence of VC, and do not always form SEI products, e.g., lithium ethylene dicarbonate. This work supports Aurbach’s characterization of VC as a desirable additive due to decreased impedance in the cathode [22]. In summary, aggressive research is furnishing models at various scales of SEI growth, but much work remains in the areas of both validating these models and using them for battery health management and control.

B. Thermal Degradation

Temperature dynamics affect Lithium-ion batteries in at least two critical ways. First, the performance and long-term aging dynamics of LIBs are highly temperature-dependent.

Second, the rates at which battery reactions occur tend to grow exponentially with temperature, while passive heat transfer typically only grows linearly. The net result is that at high enough temperatures, LIBs are vulnerable to thermal runaway, defined as “the self-sustaining increase in cell heat as various components react exothermically” [23]. This is especially critical in delithiated carbon-based electrodes, which are highly oxidizing and therefore more likely to react with the electrolyte [24]. Researchers are actively exploring alternative electrolytes [25], [26], electrode materials [27], [28], [29], [26], and cell designs in order to reduce battery vulnerability to thermal runaway [30], [31]. Our focus here is on an equally valuable path for preventing thermal runaway, namely, the modeling and control of temperature dynamics.

1) **Thermal Models:** To model the temperature dynamics of a battery, one should ideally model: (i) the generation and accumulation of heat inside the battery, (ii) heat transfer between the battery and its surroundings, and (iii) the dependence of battery processes and reactions on temperature. Pals et al. address these challenges by combining energy balance equations [32] with a model of battery electrochemistry [33] to obtain a one-dimensional model of LIB thermal behavior during discharge. Capturing the effect of temperature on the rates of different battery reactions is critical in such a model. Gu et al. address this challenge using a coupled thermo-electrochemical model that uses the Arrhenius equation to capture the temperature dependence of battery parameters [34]:

$$\Phi = \Phi_{ref} \exp \left[\frac{E_{act,\Phi}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (3)$$

As LIB technology migrates from the portable electronics domain to larger-scale transportation applications, the need increases for models of temperature distribution within large battery packs. Smith and Wang underscore this need in their development of a one-dimensional lumped thermal model accounting for ohmic heating, contact resistance, heat generation, and convective heat dissipation within a battery pack [35]. Their findings show that ohmic heating dominates other heating mechanisms within the entire pack, and at the upper end of the temperature range of 52 °C a forced air convection cooling system is necessary [35]. This research highlights the continuing need for models that can predict temperature distributions within potentially heterogeneous large-scale battery packs, while remaining simple enough for the design of temperature control systems.

2) **Temperature Control:** Lithium-ion batteries must operate within a narrow temperature range for performance, efficiency, and health. Generally, this desired temperature range is between -30°C and 52°C [36]. Temperatures below -30°C cause diffusion and intercalation dynamics to slow down, thereby increasing cell impedance considerably [37]. Battery storage above 60°C exhibits significantly more capacity loss than storage at lower temperatures [38], [39], and at temperatures exceeding 85°C the SEI layer decomposes and can cause rapid degradation and thermal runaway [40]. Onboard control systems are necessary to measure heat generation,

run convection cooling systems, and maintain a uniform temperature range among battery cells.

Battery temperature control systems are either passive or active. Passive thermal management methods include the use of phase changing materials [41], [42], [43]. These materials absorb energy or heat emitted by the battery during discharge and store it as latent heat. When the battery cools down, the heat returns to the battery: a process that fundamentally amounts to built-in temperature feedback control. Active methods for temperature control usually make use of convective cooling. Schmitz et al. examine several coolant choices for cylindrical cells, and show that aqueous propylene glycol can be an attractive choice compared to both forced air and dimethyl polysiloxane, a popular commercial coolant [44]. Research also suggests that reciprocating air flow systems are favorable when compared with unidirectional systems [45]. Thermal management is especially important for battery pack performance, and ultimately to prevent aging. Work to develop comprehensive thermal management systems requires both model development and advanced control strategies that cater to a broad range of usage cycles and environments.

C. Mechanical Degradation

The insertion and removal of Lithium ions creates mechanical stresses within intercalation electrodes. These stresses cause the porous solid electrode particles to change in volume, which can cause loss of electrical contact within a battery cell. Moreover, extreme stresses can induce electrode fracture, and repeated stresses can induce fatigue. These factors limit the permissible rates of ion insertion and removal in LIBs, and therefore the permissible currents that health-conscious control systems can apply to LIBs. Christensen et al. study the mechanical stresses induced by LIB charging and discharging by combining a porous electrode model with a diffusion-induced stress model [46], [47], [48]. This study shows that pressure diffusion has little effect on the voltage response of a system exhibiting small volume expansion, but does play an important role in the stress response. Additional work focuses on understanding the critical rate of charging and the size of active material to stifle fractures within the electrode. Zhao et al., for example, develop a method of comparing lithium ion distributions and stress exhibited at different discharge rates, and show that when the maximum energy release is smaller than the fracture energy, cracks do not advance [49]. Furthermore, Zhang et al. study the interplay between thermal- and stress-induced failures, and show that ellipsoidal electrode particles with larger aspect ratios are less vulnerable to such failures than spherical particles [50]. From a control systems perspective, the ability to model mechanical battery failure is a critical step towards designing controllers capable of delaying the onset of such failure: a research goal that remains relatively unexplored.

D. Dendrite and Moss Formation

A critical disadvantage of carbon-based LIB anodes is the fact that they operate at voltages conducive to the deposition

of metallic Lithium. As one cycles a LIB, this deposition leads to dendrite or moss formation on the negative electrode. Moss is a thick layer of deposited Lithium that forms at lower current densities and becomes more compact with cycling, while dendrites form at higher current densities and are characterized as sharper protrusions that run the risk of puncturing the separator and causing thermal runaway [51]. Both mechanisms are associated with accelerated capacity fade [51], and their prevention via battery control is hence very desirable. Until recently, models of dendrite formation have been based on qualitative data obtained from scanning electron microscopy, while quantitative data were hard to acquire. Bhattacharyya et al. made major strides in developing quantitative relationships when they used Li Nuclear Magnetic Resonance spectroscopy while cycling a cell [52]. *In situ* tests carried out with cycling were found to be capable of monitoring growth of lithium deposited structures. Data from these tests are relatively young, but are invaluable for better health modeling and control.

IV. BATTERY CHARACTERIZATION TECHNIQUES

Previous sections of this paper provide a panoramic view of multiple LIB aging mechanisms. This section studies the problem of characterizing and distinguishing between these mechanisms experimentally. We focus on electrochemical impedance spectroscopy (EIS): the nondestructive measurement of a battery's internal impedance as a function of frequency (typically in the mHz-kHz range), for a given state of charge and temperature [53], [37]. Put simply, EIS refers to the experimental determination of a battery cell's Nyquist plot, the most common sign convention being that discharge current is the input, terminal voltage is the output, and capacitive effects therefore correspond to positive phase angles. Impedance spectroscopy is a powerful diagnostic tool because: (i) battery impedance increases with aging, and (ii) different battery dynamics tend to affect different frequency ranges on the EIS plot. Figure 2 illustrates this using an EIS sketch where: (i) inductive effects in the battery wiring and porous structure are prominent at high frequencies (bottom left), (ii) impedance becomes purely Ohmic (i.e., resistive) as frequency decreases, and (iii) capacitive effects become important at even lower frequencies [54], [53], [37]. EIS plots often exhibit two resistive-capacitive (RC) "lobes", one corresponding to the resistance and capacitance of the SEI, and one corresponding to charge transfer resistance and double-layer capacitance effects inside the battery cell. When only one lobe is apparent, it encompasses all of these RC effects simultaneously [55]. The lowest-frequency portion of an EIS plot corresponds to ion diffusion dynamics in both the electrodes and electrolyte.

There are several important battery parameters that can be extracted from an EIS plot. First, a transition is sometimes visible at very low frequencies (top right) where the plot's angle changes from approximately 45° to 90° , indicating a switch from semi-infinite diffusion to finite-length diffusion [55], [56]. Knowledge of this transition frequency, ω_t ,

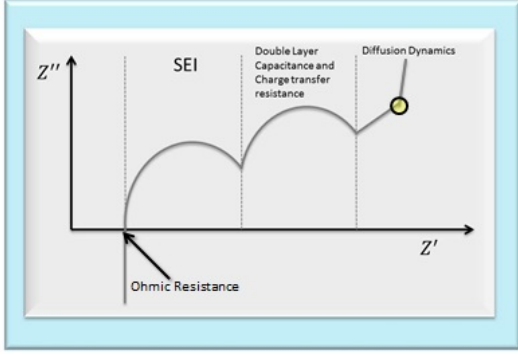


Fig. 2. Regions of an EIS Plot

allows one to calculate the diffusion coefficient, $D_{1,j}$, for given material through the following relationship [57]:

$$\omega_t \approx \frac{D_{1,j}}{\ell^2} \quad (4)$$

where ℓ^2 is the finite diffusion length, or the mean radius of an electrode particle [56]. Second, it is possible to fit simple and accurate equivalent circuit models to a battery's EIS plot. The parameters of these models correspond to the effective resistances and capacitances of physical constituents of the battery, such as the SEI layer and electrode particles [58]. This means that EIS can be a very powerful control-oriented battery diagnostics and forensics tool, allowing control engineers to create empirical maps relating a battery's operating parameters (e.g., current, voltage, state of charge, and temperature) to changes in the battery's various internal impedance effects over time. Zhang et al., for example, use three-electrode EIS to study the cycling degradation in a battery with a Lithium-Iron-Phosphate ($LiFePO_4$) cathode [55]. Their work reveals that the negative electrode contributes little to overall cell aging, and furthermore shows that impedance rise is mainly associated with the midfrequency arc of the EIS plot [55]. These insights highlight the power of impedance spectroscopy as a tool for characterizing battery dynamics, understanding how these dynamics change with aging, and - most importantly - creating control-oriented models of such aging. Impedance spectroscopy is already a standard tool in electrochemistry, but it remains relatively under-utilized as a tool for control-oriented battery modeling, battery diagnostics, and battery health-conscious control design.

V. BATTERY HEALTH MODELING, ESTIMATION, AND CONTROL

Previous sections of this paper survey the fundamental phenomena behind battery charging, discharging and aging, and furthermore highlight the use of EIS for battery characterization. Our goal in this section is to survey existing research on the modeling, estimation, and control of battery dynamics. A key goal of this survey is to highlight the degree to which bridging the current gap between the battery electrochemistry and control literatures can furnish novel

control systems capable of prolonging battery life. We survey the control-oriented battery modeling literature, examine the problems of battery charge and health estimation, and conclude with an examination of two battery control problems: charge profile optimization and cell-to-cell balancing.

A. Control-Oriented Battery Modeling

To optimize a battery's performance, efficiency, and health, one needs to develop models of its charge, temperature, and degradation dynamics. These models should ideally capture the spatio-temporal variations in battery state variables such as ion concentration and temperature, since even a localized spike in these variables can trigger accelerated damage through mechanisms such as dendrite formation or thermal runaway. The literature provides fundamental electrochemistry-based models of LIB dynamics [33], [59], [18]. These models typically consist of coupled ordinary and partial differential equations. The computational costs associated with these models can be prohibitive for both onboard estimation and control applications and offline parameter identification and control optimization studies.

The literature presents several methods for reducing the complexity of electrochemical battery models to make them more suitable for control design. These methods typically address one or more of the following four root causes for electrochemical battery model complexity. First, diffusion effects in the electrolyte can induce significant variations in ion concentration and electric potential over the thickness of a battery cell. For small charge/discharge rates, one can reasonably neglect these electrolyte diffusion effects and represent each electrode by a single aggregated solid particle. This furnishes much-simplified "single-particle" battery models that are valid for relatively small charge/discharge rates. A second cause for battery model complexity is the fact that the governing equations for intercalation and potential distribution cause these models to have a nonzero index. Forman et al. address this challenge by quasi-linearizing the algebraic constraints governing intercalation and potential distribution [60]. The third computational challenge is perhaps the most well-studied in the literature: reasonable discretizations of electrochemical LIB models can easily furnish thousands of state equations, most of them associated with ion diffusion in the solid electrode particles. The literature presents several approaches for addressing this problem. Wang et al., for instance, solve the solid diffusion sub-model using a volume-averaging technique that approximates the concentration of Lithium ions within the electrode particles by a parabolic function. This reduces the diffusion partial differential equation to two differential algebraic equations [61], [62]. The integral describing the volume-averaged concentration is:

$$c_{s,avg} = \frac{1}{V} \int_0^{R_p} c_s dV \quad (5)$$

Subramanian et al. extend this method and consider both constant pore wall flux [63] and time-dependent pore wall flux boundary conditions [64]. Finally, one can also simplify

a battery's spherical diffusion model by recognizing that it corresponds to the following transcendental transfer function, presented by Jacobsen and West [65]:

$$\frac{C_{s,e}(s)}{J^{Li}(s)} = \frac{1}{a_s F} \left(\frac{R_s}{D_s} \right) \left[\frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right] \quad (6)$$

$$\beta = R_s \sqrt{\frac{s}{D_s}} \quad (7)$$

Smith et al. decompose this transfer function into a pole/residue series, then apply residue grouping to obtain a reduced spherical diffusion model with improved overall speed and numerical stability [66]. Smith et al. use this model in conjunction with Kalman filtering to estimate battery states and explore the model's operating limits. Their work shows that a linear filter based on the above simplified diffusion model works well for a battery operating between 30%-70% state of charge [67]. Furthermore, Forman et al. also simplify the above spherical diffusion transfer function using analytic Padé approximation. They show that a second-order Padé approximation of the above transcendental transfer function provides comparable accuracy to a 100th order finite difference model [60]. These studies highlight the degree to which the community has studied reduced-order models of spherical diffusion in solid battery electrodes. The final - and perhaps most important - LIB model reduction challenge remains comparatively unexplored. Specifically, LIB models are complex not only because of the complexity of the individual submodels representing different battery phenomena, but also because of the complex interactions between these submodels. The problem of applying rigorous combined model order and index reduction to a full electrochemical battery model remains relatively unexplored and very promising. Evidence of the importance of tackling this problem comes from Cai and White's application of proper orthogonal decomposition (POD) to an entire electrochemistry-based LIB model, which furnishes a reduced model seven times as fast as the full battery model with little loss of accuracy [68].

B. Battery Charge and Health Estimation

To control LIB charging and discharging in a health-conscious manner, one needs to estimate battery State of Charge (SoC) and State of Health (SoH) online. This section reviews the techniques employed for battery SoC and SoH estimation. It focuses on electric and hybrid electric vehicle applications where current demands are typically greater (in terms of both magnitude and rate of change) than in portable electronic systems. This more aggressive battery use increases the need for SoC/SoH estimation to ensure efficiency, avoid overcharge/overdischarge, and facilitate condition-based maintenance [69]. We begin with a very brief discussion of SoC estimation, then focus on the relatively less-explored SoH estimation problem.

1) *State of Charge (SoC) Estimation:* State of charge estimation is a relatively well-explored research problem. Much of the SoC estimation literature explores the use of linear equivalent circuit models in conjunction with either

open-loop estimation methods (e.g., Coulomb counting) or closed-loop methods (e.g., Kalman filtering) to determine state of charge from input current and terminal voltage measurements [70], [71], [72], [73]. This approach is reasonable for portable electronics, but faces two challenges in the context of electrified vehicles. First, rapid improvements in automotive battery materials are furnishing new LIBs with both reduced self-discharge and flatter characteristic curves relating open-circuit potential to state of charge. One negative consequence of these improvements is the fact that state of charge is less observable/detectable for these newer batteries compared to their predecessors. One promising solution to this problem is to build SoC estimators that capitalize on fundamental nonlinearities in battery dynamics by using the relationship between a battery's SoC and electrochemical impedance plot as a foundation for SoC estimation [74], [75], [75]. The second SoC estimation challenge associated with electrified vehicle applications is the fact that the large battery currents seen in such applications tend to excite complex dynamics that equivalent circuit models typically do not capture (e.g., finite- and infinite-dimensional diffusion dynamics, etc.). This motivates the ongoing research in the literature on battery SoC estimation using reduced-order electrochemistry-based battery models, which in turn motivates the ongoing research on electrochemical battery model reduction [76], [77], [3], [78].

2) *State of Health (SoH) Estimation:* Compared to SoC estimation, the equally important battery health estimation problem remains relatively unexplored. At least four challenges make SoH estimation a very difficult problem. The first challenge in the multiplicity of SoH definitions in the literature. Thanks to this multiplicity, different SoH estimators in the literature tackle problems as disparate as estimation the charge capacity of a battery using open-loop Coulomb counting versus estimating internal resistance and open-circuit voltage versus amount of charge stored in a given battery cell for different levels of aging [79], [80]. The second challenge is the paucity of control-oriented battery health-predicting models that can serve as the "plant models" in feedback algorithms for SoH estimation. Saha et al. address this challenge by using experimental battery testing data to construct predictive aging models that serve as the "plant models" within a battery prognostics and diagnostics algorithm based on particle filtering and relevance vector machines [81], [82], [83]. This work by Saha et al. highlights the third challenge in battery SoH estimation, namely, the need for control-oriented electrochemistry-based battery degradation models that can be used to provide greater predictiveness within battery health estimation, prognostics, and diagnostics algorithms. Finally, perhaps the largest challenge in battery SoH estimation is *identifiability*. Specifically, the fact that different battery aging dynamics are complex, intertwined, and similar in their time constants means that it is fundamentally very difficult to estimate the progress of different battery aging effects online using voltage, current, and temperature measurements. This, in turn, makes it very challenging to estimate the health of LIBs online, predict

their death, and control them in a manner that postpones such death. Battery identifiability remains a very open research area whose exploration can shed light on the extremely important question of what additional sensors - beyond terminal current, temperature, and voltage - provide the best means for onboard battery health prognostics, diagnostics, and control.

C. Optimal Battery Charging

Modeling and estimating battery health is an important first step towards the ultimate goal of controlling batteries in a manner that maximizes performance and efficiency, and - perhaps most importantly - prolongs useful life. One of the most central elements of traditional battery management systems (BMSs) is the basic constant-current, constant-voltage (CCCV) charging/discharging circuit. This is a circuit that charges or discharges a given battery cell or string of cells at some user-dictated current until a maximum or minimum voltage is reached, then switches to constant-voltage charging/discharging until battery current drops to a predefined “small” value. The CCCV protocol is cheap and easy to implement using power electronics, but a growing body of research suggests that it may not be optimal for battery efficiency or health [3], [84]. Zhang et al., for instance, compare the battery life cycle implications of constant-power/constant-voltage (CPCV) and multi-stage constant-current/constant-voltage (MCCCV) protocols to the CCCV protocol [85]. They find that at low charging rates, constant current limits capacity fade the most, while at a higher charge rate of 1C constant power yields the least capacity fade. The results of this study support the notion that cycle life is affected significantly by charging protocol, and under different operating conditions different charging protocols may be optimal.

Given the above insights, it is not surprising that several researchers are aggressively pursuing the basic but critical question of: *what is the “best” way to charge/discharge a lithium-ion battery?* Boovaragavan et al., for instance, solve a dynamic optimization problem with the objective of maximizing battery depth of discharge [86]. They find that the optimal control policy can better utilize the active electrode material during discharge than the standard constant current control protocol. Methekar et al. also use a dynamic optimization method to find a charging profile that maximizes the energy storage capacity within a given cell. They use a reformulated, control-oriented battery model for this optimization exercise [87], and find that using the optimized charging profile a battery can store significantly more energy than using a normal charging pattern [88]. Rahimian et al. also use dynamic optimization to find a charging profile that maximizes battery life, and find that a computer-simulated cell’s life can be extended by 29% using the optimized charging pattern [89]. Finally, Klein et al. develop open- and closed-loop strategies to charge a battery pack with the intent of limiting degradation. They use a full physics-based battery model in this optimization, and impose constraints on the amount of charge stored in the battery and

the current available from it. They also apply a temperature constraint and a constraint on side reaction overpotential that limits Lithium deposition in the battery. They solve this problem using both offline trajectory optimization and online nonlinear model predictive control (NMPC) and find that these two strategies give comparable results [90].

D. Cell Equalization

When battery cells are assembled into strings, modules, and packs, manufacturing variations and differences in initial states of charge and health can cause them to experience drastically different operating conditions. Degraded batteries with lower energy capacities, for example, will experience larger SoC swings for the same input current profiles, thereby potentially degrading faster than their healthier counterparts. This motivates *cell-to-cell*, *string-to-string*, and *module-to-module balancing* as an essential function in modern battery management systems. Balancing is a very mature research area, and the literature already proposes both passive and active solutions to the balancing problem [91]. Kimball et al., for instance, develop a switched-capacitor converter to maintain SoC between adjacent cells. Baughman et al. introduce a balancing circuit similar to Kimball et al.’s in its use of capacitive shuttling, but with a double-tiered structure that decreases overall cell equalization time compared to single-tiered systems [92]. Finally, the literature also introduces modularized balancing systems that enable balancing over a number of distinct battery modules [93]. The fundamental premise behind these balancing circuits is the idea that forcing the states of charge of all battery cells in a pack to march in lockstep helps prevent rapid unequal degradation. While this premise has some appeal, recent research by Moura et al. suggests that deliberately controlling different cell strings and modules in a battery pack to follow different charge trajectories may have substantial health benefits, thereby opening the door to a fresh research perspective on “equalization” [94].

VI. CONCLUSIONS

This paper examines the problem of controlling Lithium-ion batteries in a health-conscious manner. This is a very challenging problem because batteries degrade through several complex and intertwined phenomena with similar time constants: a fact that leads to a fundamental “identifiability problem”. Impedance spectroscopy provides a very promising tool for battery health model identification, and also for online health estimation, prognostics, and diagnostics. Furthermore, while the electrochemistry literature provides excellent fundamental models of battery dynamics and degradation, there is still a need for the integrated order/index reduction of these models: a critical prerequisite to their use for online SoH estimation. Finally, health-conscious battery control is an extremely promising research area, especially if the community sheds the constraints imposed by “traditional” battery control solutions, such as CCCV charging/discharging and strict cell-to-cell balancing.

REFERENCES

- [1] J. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, no. 6861, pp. 359–367, 2001.
- [2] M. Armand and J. Tarascon, "Building better batteries," *Nature*, vol. 451, no. 7179, pp. 652–657, 2008.
- [3] N. Chaturvedi, R. Klein, J. Christensen, J. Ahmed, and A. Kojic, "Algorithms for advanced battery-management systems," *Control Systems Magazine, IEEE*, vol. 30, no. 3, pp. 49–68, 2010.
- [4] G. Sarre, P. Blanchard, and M. Broussely, "Aging of lithium-ion batteries," *Journal of power sources*, vol. 127, no. 1–2, pp. 65–71, 2004.
- [5] E. Wood, M. Alexander, and T. Bradley, "Investigation of battery end-of-life conditions for plug-in hybrid electric vehicles," *Journal of Power Sources*, 2011.
- [6] J. Vetter, P. Novak, M. Wagner, C. Veit, K. Moller, J. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche, "Ageing mechanisms in lithium-ion batteries," *Journal of power sources*, vol. 147, no. 1–2, pp. 269–281, 2005.
- [7] R. Spotnitz, "Simulation of capacity fade in lithium-ion batteries," *Journal of power sources*, vol. 113, no. 1, pp. 72–80, 2003.
- [8] K. Amine, C. Chen, J. Liu, M. Hammond, A. Jansen, D. Dees, I. Bloom, D. Vissers, and G. Henriksen, "Factors responsible for impedance rise in high power lithium ion batteries," *Journal of power sources*, vol. 97, pp. 684–687, 2001.
- [9] P. Verma, P. Maire, and P. Novák, "A review of the features and analyses of the solid electrolyte interphase in li-ion batteries," *Electrochimica Acta*, vol. 55, no. 22, pp. 6332–6341, 2010.
- [10] W. McKinnon and R. Haering, "Modern aspects in electrochemistry," vol. 15, 1987.
- [11] T. Tatsuma, M. Taguchi, and N. Oyama, "Inhibition effect of covalently cross-linked gel electrolytes on lithium dendrite formation," *Electrochimica acta*, vol. 46, no. 8, pp. 1201–1205, 2001.
- [12] M. Ecker, S. Kábitz, J. Gerschler, and D. Sauer, "Modeling of lithium plating in lithium-ion batteries," ECS, 2010.
- [13] P. Arora, R. White, and M. Doyle, "Capacity fade mechanisms and side reactions in lithium-ion batteries," *Journal of the Electrochemical Society*, vol. 145, p. 3647, 1998.
- [14] E. Peled, D. Golodnitsky, A. Ulus, and V. Yufit, "Effect of carbon substrate on sei composition and morphology," *Electrochimica acta*, vol. 50, no. 2–3, pp. 391–395, 2004.
- [15] E. Peled and D. Golodnitsky, "SEI on lithium, graphite, disordered carbons and tin-based alloys," *Lithium-ion batteries: solid-electrolyte interphase*, p. 1, 2004.
- [16] K. Tasaki, A. Goldberg, J. Lian, M. Walker, A. Timmons, and S. Harris, "Solubility of lithium salts formed on the lithium-ion battery negative electrode surface in organic solvents," *Journal of The Electrochemical Society*, vol. 156, p. A1019, 2009.
- [17] P. Ramadass, B. Haran, P. Gomadam, R. White, and B. Popov, "Development of first principles capacity fade model for li-ion cells," *Journal of the Electrochemical Society*, vol. 151, p. A196, 2004.
- [18] R. Darling and J. Newman, "Modeling side reactions in composite limno electrodes," *Journal of The Electrochemical Society*, vol. 145, p. 990, 1998.
- [19] P. Ramadass, B. Haran, R. White, and B. Popov, "Mathematical modeling of the capacity fade of li-ion cells," *Journal of power sources*, vol. 123, no. 2, pp. 230–240, 2003.
- [20] M. Safari, M. Morcrette, A. Teyssot, and C. Delacourt, "Multimodal physics-based aging model for life prediction of li-ion batteries," *Journal of the Electrochemical Society*, vol. 156, p. A145, 2009.
- [21] D. Bedrov, G. Smith, and A. Van Duin, "A quantum chemistry and reactive (reaxff) molecular dynamics simulations study of mechanisms of sei formation in lithium-ion batteries," ECS, 2010.
- [22] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, and U. Heider, "On the use of vinylene carbonate (vc) as an additive to electrolyte solutions for li-ion batteries," *Electrochimica acta*, vol. 47, no. 9, pp. 1423–1439, 2002.
- [23] H. Maleki, S. Al Hallaj, J. Selman, R. Dinwiddie, and H. Wang, "Thermal properties of lithium-ion battery and components," *Journal of the Electrochemical Society*, vol. 146, p. 947, 1999.
- [24] G. Chen and T. Richardson, "Thermal instability of olivine-type LiMnPO₄ cathodes," *Journal of Power Sources*, vol. 195, no. 4, pp. 1221–1224, 2010.
- [25] D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J. Gnanaraj, and H. Kim, "Design of electrolyte solutions for li and li-ion batteries: a review," *Electrochimica acta*, vol. 50, no. 2–3, pp. 247–254, 2004.
- [26] B. Scrosati, "Recent advances in lithium ion battery materials," *Electrochimica Acta*, vol. 45, no. 15–16, pp. 2461–2466, 2000.
- [27] Y. Baba, S. Okada, and J. Yamaki, "Thermal stability of lixcoo₂ cathode for lithium ion battery," *Solid State Ionics*, vol. 148, no. 3–4, pp. 311–316, 2002.
- [28] D. MacNeil, Z. Lu, Z. Chen, and J. Dahn, "A comparison of the electrode/electrolyte reaction at elevated temperatures for various li-ion battery cathodes," *Journal of power sources*, vol. 108, no. 1–2, pp. 8–14, 2002.
- [29] H. Yang, H. Bang, K. Amine, and J. Prakash, "Investigations of the exothermic reactions of natural graphite anode for li-ion batteries during thermal runaway," *Journal of the Electrochemical Society*, vol. 152, p. A73, 2005.
- [30] D. Linden and T. Reddy, "Handbook of batteries," *New York*.
- [31] S. Al Hallaj, H. Maleki, J. Hong, and J. Selman, "Thermal modeling and design considerations of lithium-ion batteries," *Journal of power sources*, vol. 83, no. 1–2, pp. 1–8, 1999.
- [32] D. Bernardi, E. Pawlikowski, and J. Newman, "A general energy balance for battery systems," *Journal of the Electrochemical Society*, vol. 132, p. 5, 1985.
- [33] M. Doyle, T. Fuller, and J. Newman, "Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell," *Journal of the Electrochemical Society*, vol. 140, p. 1526, 1993.
- [34] W. Gu and C. Wang, "Thermal-electrochemical modeling of battery systems," *Journal of the Electrochemical Society*, vol. 147, no. 8, pp. 2910–2922, 2000.
- [35] K. Smith and C. Wang, "Power and thermal characterization of a lithium-ion battery pack for hybrid-electric vehicles," *Journal of power sources*, vol. 160, no. 1, pp. 662–673, 2006.
- [36] "Freedomcar battery test manual," vol. Rev. 3, 2003.
- [37] D. Andre, M. Meiler, K. Steiner, C. Wimmer, T. Soczka-Guth, and D. Sauer, "Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy i. experimental investigation," *Journal of Power Sources*, 2011.
- [38] G. Ehrlich, "Handbook of batteries," 2002.
- [39] K. Amine, J. Liu, and I. Belharouak, "High-temperature storage and cycling of c-lifepo₄/graphite li-ion cells," *Electrochemistry communications*, vol. 7, no. 7, pp. 669–673, 2005.
- [40] H. Yang, S. Amiruddin, H. Bang, Y. Sun, and J. Prakash, "A review of li-ion cell chemistries and their potential use in hybrid electric vehicles," *Journal of Industrial and Engineering Chemistry*, vol. 12, no. 1, pp. 12–38, 2006.
- [41] S. Al-Hallaj *et al.*, "Novel pcm thermal management makes li-ion batteries a viable option for high power applications," *Battery Power Products and Technology Magazine*, 2004.
- [42] S. Al Hallaj and J. Selman, "A novel thermal management system for electric vehicle batteries using phase-change material," *Journal of the Electrochemical Society*, vol. 147, p. 3231, 2000.
- [43] R. Kizilel, R. Sabbah, J. Selman, and S. Al-Hallaj, "An alternative cooling system to enhance the safety of li-ion battery packs," *Journal of Power Sources*, vol. 194, no. 2, pp. 1105–1112, 2009.
- [44] I. Schmitz, "Thermal modeling of automotive lithium ion cells using the finite elements method in modelica," 2009.
- [45] R. Mahamud and C. Park, "Reciprocating air flow for li-ion battery thermal management to improve temperature uniformity," *Journal of Power Sources*, 2011.
- [46] J. Christensen and J. Newman, "Stress generation and fracture in lithium insertion materials," *Journal of Solid State Electrochemistry*, vol. 10, no. 5, pp. 293–319, 2006.
- [47] J. Christensen, J. Newman, "A mathematical model of stress generation and fracture in lithium manganese oxide," *Journal of the Electrochemical Society*, vol. 153, p. A1019, 2006.
- [48] J. Christensen, "Modeling diffusion-induced stress in li-ion cells with porous electrodes," *Journal of the Electrochemical Society*, vol. 157, p. A366, 2010.
- [49] K. Zhao, M. Pharr, J. Vlassak, and Z. Suo, "Fracture of electrodes in lithium-ion batteries caused by fast charging," *Journal of Applied Physics*, vol. 108, p. 073517, 2010.
- [50] X. Zhang, A. Sastry, and W. Shyy, "Intercalation-induced stress and heat generation within single lithium-ion battery cathode particles," *Journal of the Electrochemical Society*, vol. 155, p. A542, 2008.

- [51] F. Orsini, A. Du Pasquier, B. Beaudoin, J. Tarascon, M. Trentin, N. Langenhuisen, E. De Beer, and P. Notten, "In situ scanning electron microscopy (sem) observation of interfaces within plastic lithium batteries," *Journal of power sources*, vol. 76, no. 1, pp. 19–29, 1998.
- [52] R. Bhattacharyya, B. Key, H. Chen, A. Best, A. Hollenkamp, and C. Grey, "In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries," *Nature Materials*, vol. 9, no. 6, pp. 504–510, 2010.
- [53] A. Lasia, "Electrochemical impedance spectroscopy and its applications," *Modern aspects of electrochemistry*, vol. 32, pp. 143–248, 1999.
- [54] J. Goodenough, "Design considerations," *Solid State Ionics*, vol. 69, no. 3–4, pp. 184–198, 1994.
- [55] Y. Zhang and C. Wang, "Cycle-life characterization of automotive lithium-ion batteries with linio cathode," *Journal of the Electrochemical Society*, vol. 156, p. A527, 2009.
- [56] M. Thomas, P. Bruce, and J. Goodenough, "Lithium mobility in the layered oxide $\text{Li}_1\text{-xcoo}_2$," *Solid State Ionics*, vol. 17, no. 1, pp. 13–19, 1985.
- [57] A. Vaccaro, T. Palanisamy, R. Kerr, and J. Maloy, "Electrochemical investigations of alkali-metal intercalation reactions in tis: Chronoamperometric determination of mass and charge transport properties of liquid electrolyte systems," *Journal of The Electrochemical Society*, vol. 129, p. 682, 1982.
- [58] D. Andre, M. Meiler, K. Steiner, H. Walz, T. Soczka-Guth, and D. Sauer, "Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy ii. modelling," *Journal of Power Sources*, 2010.
- [59] T. Fuller, M. Doyle, and J. Newman, "Simulation and optimization of the dual lithium ion insertion cell," *Journal of the Electrochemical Society*, vol. 141, p. 1, 1994.
- [60] J. Forman, S. Bashash, H. Fathy, and J. Stein, "Reduction of an electrochemistry-based li-ion battery health degradation model via constraint linearization and padé approximation," *preperation for submission to Journal of the Electrochemical Society*.
- [61] C. Wang, W. Gu, and B. Liaw, "Micro-macroscopic coupled modeling of batteries and fuel cells: Part 1. model development," *J. Electrochem. Soc.*, vol. 145, no. 10, pp. 3407–3417, 1998.
- [62] W. Gu, C. Wang, and B. Liaw, "Micro-macroscopic coupled modeling of batteries and fuel cells: Part 2. application to nickel-cadmium and nickel-metal hybrid cells," *J. Electrochem. Soc.*, 1998.
- [63] V. Subramanian, J. Ritter, and R. White, "Approximate solutions for galvanostatic discharge of spherical particles i. constant diffusion coefficient," *Journal of the Electrochemical Society*, vol. 148, p. E444, 2001.
- [64] V. Subramanian, V. Diwakar, and D. Tapriyal, "Efficient macro-micro scale coupled modeling of batteries," *Journal of The Electrochemical Society*, vol. 152, p. A2002, 2005.
- [65] T. Jacobsen and K. West, "Diffusion impedance in planar, cylindrical and spherical symmetry," *Electrochimica acta*, vol. 40, no. 2, pp. 255–262, 1995.
- [66] K. Smith, C. Rahn, and C. Wang, "Model order reduction of 1d diffusion systems via residue grouping," *Journal of Dynamic Systems, Measurement, and Control*, vol. 130, p. 011012, 2008.
- [67] C. Smith, K.A. Rahn and C. Wang, "Model-based electrochemical estimation and constraint management for pulse operation of lithium ion batteries," *Control Systems Technology, IEEE Transactions*, vol. 18, no. 3, pp. 654–663, 2010.
- [68] L. Cai and R. White, "Reduction of model order based on proper orthogonal decomposition for lithium-ion battery simulations," *Journal of the Electrochemical Society*, vol. 156, p. A154, 2009.
- [69] J. Zhang and J. Lee, "A review on prognostics and health monitoring of li-ion battery," *Journal of Power Sources*, 2011.
- [70] F. Codeca, S. Savaresi, and G. Rizzoni, "On battery state of charge estimation: A new mixed algorithm," in *Control Applications, 2008. CCA 2008. IEEE International Conference on*. IEEE, 2008, pp. 102–107.
- [71] G. Plett, "Extended kalman filtering for battery management systems of lipb-based hev battery packs:: Part 1. background," *Journal of Power sources*, vol. 134, no. 2, pp. 252–261, 2004.
- [72] —, "Extended kalman filtering for battery management systems of lipb-based hev battery packs:: Part 2. modeling and identification," *Journal of power sources*, vol. 134, no. 2, pp. 262–276, 2004.
- [73] —, "Extended kalman filtering for battery management systems of lipb-based hev battery packs-part 3. state and parameter estimation," *Journal of Power sources*, vol. 134, no. 2, pp. 277–292, 2004.
- [74] J. Kozlowski, C. Byington, A. Garga, M. Watson, and T. Hay, "Model-based predictive diagnostics for electrochemical energy sources," in *Aerospace Conference, 2001, IEEE Proceedings.*, vol. 6. IEEE, 2001, pp. 3149–3164.
- [75] A. Salkind, C. Fennie, P. Singh, T. Atwater, and D. Reisner, "Determination of state-of-charge and state-of-health of batteries by fuzzy logic methodology," *Journal of Power Sources*, vol. 80, no. 1–2, pp. 293–300, 1999.
- [76] D. Di Domenico, G. Fiengo, and A. Stefanopoulou, "Lithium-ion battery state of charge estimation with a kalman filter based on an electrochemical model," in *Control Applications, 2008. CCA 2008. IEEE International Conference on*. IEEE, 2008, pp. 702–707.
- [77] C. Speltino, D. Di Domenico, A. Stefanopoulou, and G. Fiengo, "Experimental identification and validation of an electrochemical model of a lithium-ion battery," in *Proceedings of 2009 IEEE European Control Conference*, 2009.
- [78] R. Klein, N. Chaturvedi, J. Christensen, J. Ahmed, R. Findeisen, and A. Kojic, "State estimation of a reduced electrochemical model of a lithium-ion battery," in *American Control Conference (ACC), 2010*. IEEE, 2010, pp. 6618–6623.
- [79] K. Ng, C. Moo, Y. Chen, and Y. Hsieh, "Enhanced coulomb counting method for estimating state-of-charge and state-of-health of lithium-ion batteries," *Applied Energy*, vol. 86, no. 9, pp. 1506–1511, 2009.
- [80] Y. Chiang, W. Sean, and J. Ke, "Online estimation of internal resistance and open-circuit voltage of lithium-ion batteries in electric vehicles," *Journal of Power Sources*, 2011.
- [81] B. Saha, K. Goebel, S. Poll, and J. Christophersen, "Prognostics methods for battery health monitoring using a bayesian framework," *Instrumentation and Measurement, IEEE Transactions on*, vol. 58, no. 2, pp. 291–296, 2009.
- [82] B. Saha and K. Goebel, "Modeling li-ion battery capacity depletion in a particle filtering framework," in *Proceedings of the annual conference of the prognostics and health management society*, 2009.
- [83] B. Saha, K. Goebel, S. Poll, and J. Christophersen, "An integrated approach to battery health monitoring using bayesian regression and state estimation," in *Autotestcon, 2007 IEEE*. IEEE, 2007, pp. 646–653.
- [84] M. Sternad, M. Cifrain, D. Watzenig, G. Brasseur, and M. Winter, "Condition monitoring of lithium-ion batteries for electric and hybrid electric vehicles," *e & i Elektrotechnik und Informationstechnik*, vol. 126, no. 5, pp. 186–193, 2009.
- [85] S. Zhang, "The effect of the charging protocol on the cycle life of a li-ion battery," *Journal of power sources*, vol. 161, no. 2, pp. 1385–1391, 2006.
- [86] V. Boovaragavan and V. Subramanian, "Evaluation of optimal discharge current profile for planar electrodes to maximize the utilization," *Journal of Power Sources*, vol. 173, no. 2, pp. 1006–1011, 2007.
- [87] V. Subramanian, V. Boovaragavan, V. Ramadesigan, and M. Arabandi, "Mathematical model reformulation for lithium-ion battery simulations: Galvanostatic boundary conditions," *Journal of The Electrochemical Society*, vol. 156, p. A260, 2009.
- [88] R. Methekar, V. Ramadesigan, R. Braatz, and V. Subramanian, "Optimum charging profile for lithium-ion batteries to maximize energy storage and utilization," *ECS Trans*, vol. 25, no. 35, pp. 139–146, 2010.
- [89] S. Rahimian, S. Rayman, and R. White, "Maximizing the life of a lithium-ion cell by optimization of charging rates," *Journal of The Electrochemical Society*, vol. 157, p. A1302, 2010.
- [90] R. Klein, N. Chaturvedi, J. Christensen, J. Ahmed, R. Findeisen, and A. Kojic, "Optimal charging strategies in lithium-ion battery," in *American Control Conference (ACC), 2011*. IEEE, 2011, pp. 382–387.
- [91] J. Kimball, B. Kuhn, and P. Krein, "Increased performance of battery packs by active equalization," in *Vehicle Power and Propulsion Conference, 2007. VPPC 2007. IEEE*. IEEE, 2007, pp. 323–327.
- [92] A. Baughman and M. Ferdowsi, "Double-tiered switched-capacitor battery charge equalization technique," *Industrial Electronics, IEEE Transactions on*, vol. 55, no. 6, pp. 2277–2285, 2008.
- [93] H. Park, C. Kim, C. Kim, G. Moon, and J. Lee, "A modularized charge equalizer for an hev lithium-ion battery string," *Industrial Electronics, IEEE Transactions on*, vol. 56, no. 5, pp. 1464–1476, 2009.
- [94] S. Moura, J. Forman, S. Bashash, J. Stein, and H. Fathy, "Optimal control of film growth in lithium-ion battery packs via relay switches," *Industrial Electronics, IEEE Transactions on*, no. 99, pp. 1–1, 2009.