



Degradation Mechanisms and Lifetime Prediction for Lithium-Ion Batteries – A Control Perspective

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Degradation mechanisms and lifetime prediction for lithium-ion batteries – A control perspective

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Abstract—Predictive models of Li-ion battery lifetime must consider a multiplicity of electrochemical, thermal, and mechanical degradation modes experienced by batteries in application environments. To complicate matters, Li-ion batteries can experience different degradation trajectories that depend on storage and cycling history of the application environment. Rates of degradation are controlled by factors such as temperature history, electrochemical operating window, and charge/discharge rate. We present a generalized battery life prognostic model framework for battery systems design and control. The model framework consists of trial functions that are statistically regressed to Li-ion cell life datasets wherein the cells have been aged under different levels of stress. Degradation mechanisms and rate laws dependent on temperature, storage, and cycling condition are regressed to the data, with multiple model hypotheses evaluated and the best model down-selected based on statistics. The resulting life prognostic model, implemented in state variable form, is extensible to arbitrary real-world scenarios. The model is applicable in real-time control algorithms to maximize battery life and performance. We discuss efforts to reduce lifetime prediction error and accommodate its inevitable impact in controller design.

Index Terms—battery, degradation, diagnostics, energy storage, lithium-ion, prognostics

I. EXTENDED ABSTRACT

ELECTROCHEMICAL energy storage is rapidly expanding beyond mobile devices into large-scale grid and automotive applications. Lithium-ion battery production is projected to grow to a \$5 billion business by 2020 [1]. To support this expanded investment, lifetime predictive models are needed that accurately calculate battery excess energy/power needed to meet life requirements [2], perform warranty analyses, and design thermal management systems and onboard control strategies that extend lifetime [3–7].

The goal of a lifetime predictive model is to reproduce device-level capacity fade and resistance growth across the full range of possible storage- and cycle-aging conditions observed in the field and during accelerated aging tests in the laboratory. Model-predicted capacity and resistance

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allow for direct calculation of the device's energy and power [2] over lifetime. The resistance/capacity error between the model and experimental measurement must be minimized because any model uncertainty adds expense to the system due to over-design. The ideal model should have a sound physical basis in the electrochemical literature and be supported by electrochemical diagnostic measurements to provide the widest extensibility of predictions versus tested conditions.

Existing literature related to degradation and lifetime modeling can generally be divided into two categories. In one category, physics-based models are proposed that capture one or two degradation mechanisms and are sometimes validated with a few aging tests. In the other category, lumped statistical models are proposed and fitted to data, sometimes for a wide range of aging tests. These statistical models generally include a mixture of physics-justified surrogate models and semi-empirical mathematical formulas to capture the full behavior of the large dataset [8–10]. There are strong motivators to reduce the empiricism by diagnosing and proposing new mathematical models of physical degradation processes. For lifetime models, reduced empiricism will maximize model extensibility, minimize the expense of aging experiments required to parameterize the model, and provide the proper couplings to model degradation within computer-aided engineering software toolsets for electrochemical cell design [11–14].

Based on experience with multiple Li-ion aging datasets, on the order of five different degradation mechanisms must be included in a model to faithfully reproduce resistance and capacity fade trajectories for a large matrix of some 20–30 aging test conditions. Although it is beyond the scope of this paper to review all of the possible degradation mechanisms in lithium-ion cells, Table 1 presents several broad categories of degradation mechanisms, including their dependence on mechanical-, chemical-, electrochemical-, and thermal-coupled physics.

For lithium-ion chemistries with graphitic negative electrodes, the growth of the solid-electrolyte interphase (SEI) layer is usually a dominant degradation mechanism. SEI layer growth increases the cell's impedance and reduces its capacity as it consumes cycleable lithium from the system. Detailed elementary (electro)chemical reaction models [16] provide a framework for studying the complex SEI formation and growth processes. Simple models of rate-limiting steps in the SEI growth process are available however, and they can accurately reproduce measured performance fade under storage conditions [10,17].

TABLE I
LI-ION BATTERY FAILURE MODES CHARACTERIZED BY THEIR PHYSICS [15]

Mechanical	<ul style="list-style-type: none"> Failure of cell structures and packaging Characterized with mechanical deformation and vibration tests, readily accelerated with magnitude and rapid accumulation of cycles
Chemical	<ul style="list-style-type: none"> Side reactions occurring during rest Rate-dependent on temperature and chemical state Characterized by storage tests, accelerated with elevated temperature, at various chemical states, including full charge/discharge extremes
Electrochemical	<ul style="list-style-type: none"> Side reactions driven by charge rate (sometimes discharge rate) Influenced by electrical cycling on the cell, with rate influenced by temperature-dependent reaction and transport properties Characterized by accelerated cycling in the temperature and potential window exciting the reaction
Electrochemo-mechanical	<ul style="list-style-type: none"> Degradation caused by material expansion/contraction during electrochemical-thermal cycling Influenced by material properties of system, occurrence of phase changes with cycling, packaging, external body forces, charge/discharge rate, temperature, chemical state, and mechanical damage state Characterized by accelerated cycling across a matrix of relevant duty cycles
Thermal coupling	<ul style="list-style-type: none"> Impacting all of the above by accelerating (electro)chemical reaction rates at high temperatures, impeding normal transport/reaction processes at low temperatures, and causing mechanical stresses due to thermal expansion/contraction of cell components Characterized by performing aging tests at 3–5 temperatures including cold and hot extremes

The limiting step of electrolyte solvent diffusion provides a convenient analytical solution whereby capacity fade and resistance growth follow a square-root-of-time trajectory. Fade rate is rapid at beginning of life (BOL), but then gradually slows down. Aside from SEI growth, high-voltage lithium-ion systems may also suffer from electrolyte oxidation at the positive; however, this degradation mechanism is thought to be small for the lower-voltage iron-phosphate positive electrode material.

Although calendar-life models have shown reasonable promise in predicting aging under storage conditions, cycle-life models

have yet to offer any accepted method to predict capacity fade for a wide range of cycling and environmental conditions. Coulombic throughput or energy throughput are sometimes used as proxies to describe mechanical-stress-induced fade and are regressed to experimental capacity data [9,18]. These models can be difficult to extend to a wide range of cycling conditions [19].

Several plausible physical models coupling mechanical stress with electrochemical cycling have been proposed. The mechanism of particle fracture due to diffusion-induced stress of lithium intercalation has been modeled at the particle [20] and electrode length-scales [21]. A coupling between mechanical fracture and electrochemical transport [22] was proposed to capture the impact of stress/fracture on capacity fade. That model suggests that electrochemo-mechanical-driven capacity loss saturates after the first several (dis)charge cycles, in a sort of break-in process. However, some data seem to indicate that a more continuous degradation process evolves throughout life due to

electrochemo-mechanical fatigue [8]. Deshpande et al. proposed a model of electrochemo-mechanical-coupled fatigue wherein diffusion-induced strain at the negative particle surface causes microcracks in the SEI layer, exposing fresh negative surface for new SEI formation [23]. The Deshpande model captures a rapid fade rate at BOL, a decelerating fade rate at middle of life, transitioning to a sudden accelerating fade rate at end of life (EOL).

These various models track capacity fade due to lithium loss, active site damage/loss, or some combination of the two. It is unclear which mechanism is dominant, and in what manner the mechanisms are coupled. Different implications arise depending on which mechanism is assumed to dominate and its coupling with measured capacity. Remaining capacity may track with (i) a summation of calendar and cycling degradation effects [9], (ii) the greater of calendar degradation or cycling degradation [8], or (iii) a multiplicative coupling between calendar and cycling degradation [23]. The proper separation and coupling of calendar- and cycling-driven mechanisms is important to achieve in both life models and aging experiments. Using 6–12 months of data from accelerated aging experiments, a life predictive model needs to accurately extrapolate degradation for the desired 10–15-year lifetime. The model must faithfully reproduce storage degradation, accelerated cycling degradation, and partially accelerated cycling degradation where data are available.

The full presentation briefly reviews three Li-ion battery capacity fade models from the literature, each physically plausible, but with different couplings between calendar and cycling degradation. A generalized model framework is

introduced that captures the major degradation mechanisms from those literature models. A procedure is proposed for down selecting the most statistically relevant life predictive models from multiple hypotheses. The procedure is applied to aging data for the Li-ion graphite/iron-phosphate chemistry, creating a life prognostic model. Two separate control applications are presented that apply similar life prognostic models for other Li-ion chemistries in a hybrid-electric vehicle (HEV) supervisory controller and a plug-in hybrid vehicle (PHEV) active cell balancing system. Goals of those respective control studies are to downsize the HEV battery by 50% and still meet a 10-year lifetime requirement, and to extend the life of the PHEV battery by 20%.

II. REFERENCES

- [1] “Electric Vehicle Batteries, Lithium Ion Batteries for Hybrid, Plug-In Hybrid, and Battery Electric Vehicles: Global Market Analysis and Forecasts,” Navigant Research, 2014.
- [2] “Battery Test Manual for Plug-In Hybrid Electric Vehicles, Revision 3,” Idaho National Laboratory, September, 2014, INL/EXT-14-32849.
- [3] J. Neubauer, E. Wood, “The impact of range anxiety and home, workplace, and public charging infrastructure on simulated battery electric vehicle lifetime utility,” *Journal of Power Sources*, 257, 12–20, 2014.
- [4] K. Smith, E. Wood, S. Santhanagopalan, G.-H. Kim, A. Pesaran, “advanced models and controls for prediction and extension of battery lifetime,” Large Lithium Ion Battery Technology & Application Symposia - Advanced Automotive Battery Conference, 4–6 February 2014, Atlanta, GA.
- [5] A. Hoke, A. Brissette, K. Smith, A. Pratt, D. Maksimovic, “Accounting for lithium-ion battery degradation in electric vehicle charging optimization,” *IEEE J. Pwr. Electronics*, 2, 691-700, 2013.
- [6] R.D. Perkins, A.V. Randall, X. Zhang, G.L. Plett, “Controls oriented reduced order modeling of lithium deposition on overcharge,” *Journal of Power Sources*, 209, 318–325, July 2012.
- [7] A.V. Randall, R.D. Perkins, X. Zhang, G.L. Plett, “Controls oriented reduced order modeling of SEI layer growth,” *Journal of Power Sources*, 209, 282–288, July 2012
- [8] K. Smith, E. Wood, S. Santhanagopalan, G.-H. Kim, J. Neubauer, A. Pesaran. (2013). “Models for battery reliability and lifetime,” Battery Congress, April 15–16, 2013, Troy, MI.
- [9] J. Schmalstieg, S. Kabitz, M. Ecker, D.U. Sauer, “A holistic aging model for $\text{Li}(\text{NiMnCo})\text{O}_2$ based 18650 lithium-ion batteries,” *J. Power Sources* 257, 325–334, 2014.
- [10] M. Safari, C. Deleacourt, “Simulation-based analysis of aging phenomena in a commercial graphite/LiFePO₄ cell,” *J. Echem. Soc.* 158(12), A1436-A1447, 2011.
- [11] G.-H. Kim, K. Smith, K.-J. Lee, S. Santhanagopalan, A. Pesaran, “Multi-domain modeling of lithium-ion batteries encompassing multi-physics in varied length scales,” *J. Electrochem. Soc.* 158(8), A955–A969, 2011.
- [12] K.-J. Lee, K. Smith, A. Pesaran, G.-H. Kim, (2013). “Three dimensional thermal-, electrical-, and electrochemical-coupled model for cylindrical wound large format lithium-ion batteries,” *J. Power Sources*, 241, 20-32, 2013.
- [13] M. Guo, R.E. White, “Mathematical model for a spirally-wound lithium-ion cell,” *J. Power Sources*, 250, 220–235, 2014.
- [14] U.S. Kim, C.B. Shin, C.-S. Kim, *J. Power Sources*, 189, 841, 2009.
- [15] S. Santhanagopalan, K. Smith, J. Neubauer, G.-H. Kim, A. Pesaran, M. Keyser, *Design and Analysis of Large Lithium-Ion Battery Systems*, Artech House, Boston, 2015.
- [16] J. Christensen, J. Newman, “A mathematical model for the lithium-ion negative electrode solid electrolyte interphase,” *J. Echem. Soc.* 151(11), A1977–1988, 2004.
- [17] H.J. Ploehn, R. Premanand, R.E. White, “Solvent diffusion model for aging of lithium-ion battery cells,” *J. Echem. Soc.* 151(3) A456–A462, 2004.
- [18] S.B. Peterson, J. Apt, J.F. Whitacre, “Lithium-ion battery cell degradation resulting from realistic vehicle and vehicle-to-grid utilization,” *J. Power Sources* 195, 2385–2392, 2010.
- [19] J. Wang, P. Liu, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, P. Finamore, “Cycle-life model for graphite-LiFePO₄ cells,” *J. Power Sources* 196, 3942–3948, 2011.
- [20] J. Christensen, J. Newman, “A mathematical model of stress generation and fracture in lithium manganese oxide,” *J. Echem. Soc.*, 153(6), A1019–1030, 2006.
- [21] S. Renganathan, G. Sikha, S. Santhanagopalan, R.E. White, “Theoretical analysis of stresses in a lithium ion cell,” *J. Echem. Soc.*, 157(2), A155–163, 2010.
- [22] K. An, P. Barai, K. Smith, P.P. Mukherjee, “Probing the thermal implications in mechanical degradation of lithium-ion battery electrodes,” *J. Electrochem Soc.* 161(6), A1058–A1070, 2014.
- [23] R. Deshpande, M. Verbrugge, Y.-T. Cheng, J. Wang, P. Liu, “Battery cycle life prediction with coupled chemical degradation and fatigue mechanics,” *J. Electrochem. Soc.* 159(10), A1730–A1738, 2012.