An Overview of Degradation Phenomena Modeling in Lithium-ion Battery Electrodes

Chien-Fan Chen, Pallab Barai, and Partha P. Mukherjee^z

Department of Mechanical Engineering, Texas A&M University, College Station, TX, USA

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^z*Corresponding author:* pmukherjee@tamu.edu

Abstract

The formation of solid electrolyte interphase and diffusion induced microcrack in the lithium-ion battery electrodes are predominant degradation mechanisms, which cause capacity fade and cell impedance rise. Physics-based degradation models reveal new insights and allow fundamental understanding of the transport-chemistry-mechanics interactions. In addition, simulation-based diagnostics (*e.g.* electrochemical impedance spectroscopy, acoustic emission characteristics) can enable virtual probing and interrogation of electrode degradation behavior. This short perspective highlights the recent progress in physics-based degradation modeling and virtual diagnostics in lithium-ion battery electrodes.

Introduction

Life of lithium-ion batteries (LIB) is dictated by the underlying chemo-mechanical degradation mechanisms, such as microcrack formation in the active particles due to the diffusion induced stress generation, [1] and the formation of the solid-electrolyte interphase (SEI) [2-4]. These degradation modes cause capacity fade and impedance rise, thereby affecting the life of LIBs.

During the charging process, the SEI forms as a thin layer (5 nm ~ 300 nm) at the active particle – electrolyte interface.[5] Although the SEI is necessary for preventing undesired reduction and oxidation of the electrode and electrolyte,[6] it also comes with several disadvantages. This chemical degradation mode causes capacity fade due to irreversible consumption of the solvent and active lithium-ions.[7] Moreover, this thin, interfacial layer hinders lithium intercalation, which may increase kinetic resistance.[8]

Mechanical degradation due to diffusion-induced stress (DIS) generation and microcrack formation in LIB electrode active particles also received significant attention in the last few years, as a key degradation mode.[9, 10] Microcracks form when the intercalation induced stress in the active particles exceeds the material fracture threshold. Crack formation and propagation from the particle surface may lead to enhanced SEI formation and concurrent loss of cyclable lithium[11]. Pulverization of active particles may further lead to loss of electrical contact [12].

This review aims to provide a brief overview of the modeling studies related to the mechanical (i.e. microcrack formation) and chemical degradation (i.e. SEI formation) mechanisms, and the corresponding influence on the electrochemical properties and performance decay. A discussion on the simulation-driven diagnostics of the degradation behavior, such as electrochemical impedance spectroscopy and acoustic emission, is also included.

Mathematical Model for the Degradation Phenomena

Solid Electrolyte Interphase

The macroscopic models are useful method to predict the SEI formation, and its influence on the capacity lost [13, 14] and the increase in internal resistance [15]. Figure 1 shows the SEM image of SEI formation on the graphite particle [2]. To date, different degradation models have been developed to predict the SEI formation and its influence. The model development has been focused on the SEI layer structure [16, 17], the thermal effect on the SEI formation [18, 19], the influence of SEI of electrochemical properties [20, 21], and the stress generation inside the SEI layer [22, 23].

In most of the SEI growth model, the SEI layer is treated as a thin layer. However, the growth of SEI and the morphology of SEI layer vary with position and state-of-charge (SOC). Ploehn *et al.* [24] proposed a solvent diffusion model, which assumes that a reactive solvent component diffuses through the SEI and undergoes two-electron reduction at the carbon-SEI interface. This model predicted that the SEI thickness growth is proportional to the square root of time. Li *et al.* [16] studied the formation of SEI in the Graphite/LiFePO₄ batteries, where the SEI layer was assumed to have two layers. The outer SEI layer grows faster than the inner SEI layer, and the formation of SEI is based on electron tunneling. This model also includes the exfoliation of SEI near on the interface between graphite and SEI layer. According to this model, the capacity loss is highly dependent on the SOC due to the electrode potential and the tunneling probability. To study the morphology evolution of the SEI, Guan *et al.* [17] proposed a phase-field method based model. This model can simulate the SEI structure and morphology evolution. From the predicted SEI structure, the model can predict the lithium-ion diffusivity through the compact, porous, and multilayered structure of SEI layer.

To include the influence of temperature on the SEI growth, Liu *et al* [18] and Xie *et al* [19] developed a 1D electrochemical-thermal coupled model, which includes the growth mechanism of the SEI layer and temperature evolution. The influence of temperature is included by using the Arrhenius equation to determine the temperature-dependent properties.

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

From the results of Liu *et al.* [18], the SEI layer thickness grows faster under high temperature operation due to the high side reaction rate and the increase of diffusivity. The results from Xie *et al* [19] shows that high electrolyte salt concentration can stabilize battery performance by compensating the rise of internal resistance due to the consumption of lithium-ion in the electrolyte.

Since the presence of SEI layer can hinder the reaction between electrolyte and active material, there is a potential drop across the SEI layer. To capture the potential drop, Phul *et al.* [20] developed a model, which is able to capture the potential drop according to the diffusion and migration of lithium-ions across the SEI layer. The potential drop from the calculation is fit with the experimental data. From this model, there exists a range of potential drop, which can cause large capacity loss. Besides the prediction of potential drop, Deng *et al.* [21] proposed a phase field model that takes the non-zero charge density into account, which includes the influence of double layer on the SEI formation. In this model, the SEI formation is treated as a phase transformation process, where the SEI phase is transformed to the SEI phase due to the side electrochemical reaction. From this model, the SEI growth was found to be a diffusion-limited process. This study also found that the growth rate of SEI varied with the initial state-of-charge of anode.

According to the experimental study of Mukhopadhyay *et al.* [25], the SEI formation on a thin-film graphite anode causes reversible and irreversible stresses during the SEI formation. The nominal equi-biaxial stress σ_n in the combined graphite/SEI film on the quartz substrate can be calculated from the classical Stoney formula.

$$\sigma_n = \left(\frac{1}{6} \frac{E}{(1-\nu_Q)} \frac{h_Q^2}{h_G} \right) \kappa \quad (2)$$

where κ is the curvature of the plate, E_Q and ν_Q are the Young's modulus and the Poisson's ratio of the quartz substrate, and h_Q and h_G are the thicknesses of the quartz and graphite layers.

To simulate the stress generation in the SEI layer, Rejovitzky *et al.* [22] developed a chemo-mechanical simulation model to predict the SEI growth and the growth stress in the SEI layer. With suitable choices of material parameters, their model can reproduce the experimental results from Mukhopadhyay *et al.* [25]. According to their results, a large non-uniform compressive hoop stress is generated in the SEI layer due to both the lithiation/delithiation of the anode particle and the growth of the SEI layer. Besides the stress generation inside the SEI layer, Laresgoiti *et al.* [23] proposed a model, which predicts the fracture inside the SEI layer. From this model, additional capacity loss during cycling has been found since the fracture in the SEI layer exposes bare active materials to the electrolyte.

Mechanical Damage

For an electrode, possibility of mechanical degradation depends on the maximum amount of diffusion induced stress at the active particles or the particle/additive (or particle/current-collector) interface[26]. If the local stress exceeds the fracture threshold at that point, microcracks will evolve and propagate[27]. Figure 2 shows a representative SEM image of microcracks formed in the graphite active particle[28]. Hence, determination of the magnitude of

stress within the active particle is essential to estimate evolution of mechanical degradation. The pioneering work was conducted by Christensen and Newman, where they looked into the distribution of mechanical stress within carbonaceous anode materials[29]. The presented mathematical model took into consideration the impact of hydrostatic stress and volume expansion during the transport of lithium within spherical active particles. They concluded that carbonaceous anode materials are prone to fracture during high power operations (usually observed in hybrid-electric-vehicles)[29]. This technique has been extended to measure the stress evolution within spherical lithium-manganese-oxide (LMO) cathode materials during two-phase diffusion of lithium[30]. Small volume expansion was considered while estimating transport and mechanical deformation within LMO based active particles. Incorporating formation and movement of dislocations within low volume expansion insertion electrodes, it is possible to reduce the diffusion induced stress experienced during lithiation/delithiation process[31].

The amount of mechanical degradation in intercalation materials is mostly governed by the concentration gradient[27]. Variation in diffusion coefficient with temperature follows the Arrhenius type relation (see Eq. (1)). Reduced diffusivity at lower temperature gives rise to higher concentration gradient, which has the potential to produce enhanced mechanical degradation[32]. Similar to the diffusion coefficient, the fracture threshold parameter and the elastic modulus also vary significantly with temperature. At subzero conditions, graphite anode behaves as a highly brittle material with increased magnitude of elastic modulus, which is prone to rupture. Severe microcracking of the anode has been observed at subzero temperature operation[33]. Ductility of solid materials is also observed to increase at higher temperatures. Hence, negligible mechanical degradation occurs in lithium-ion battery active particles during operation at room temperature[33].

Future lithium-ion batteries are expected to offer higher energy density. Increasing the specific capacity of anode has the potential to achieve that goal. However, high capacity anode materials (such as, silicon, tin, germanium) experience 300% volume expansion during lithiation, which is followed by severe mechanical degradation[34]. Higa and Srinivasan developed a mathematical model to estimate the evolution of mechanical stress within cylindrical silicon active particles under the assumption of elastic deformation[35]. Computational modeling of the two-phase transport of lithium and elastoplastic deformation of silicon active particles has been reported [36]. Concentrated solution theory based lithium transport model coupled with large volume expansion has been developed to study the irreversible changes in atomic structure of silicon during lithiation/delithiation process. This technique permits the creation and destruction of unoccupied silicon lattice sites due to irreversible plastic deformation[37]. Impact of coupled electrical, chemical and mechanical potential on the transport of lithium as well as subsequent mechanical degradation, has been analyzed using a nonlinear finite element based framework[38]. Small strain small displacement based mathematical framework has been developed to study stress generation and delamination experienced by tin micropillars[39] and thin films[26]. They incorporated two-phase diffusion based transport of lithium[26] along with creep deformation of tin active particles[39]. Mathematical models based on large volume expansion and elastoplastic deformation of zinc-oxide nanowires were developed to capture the transport of lithium and subsequent stress generation[40].

Estimation of the magnitude and location of maximum stress gives an idea about whether mechanical degradation is possible within active particles. However, to predict the extent of mechanical damage, evolution of microcracks and propagation of crack fronts must be analyzed. Barai and Mukherjee proposed a lattice spring based computational methodology that is capable

of estimating initiation, nucleation and propagation of microcracks[27]. Small strain small displacement analysis along with single-phase transport of lithium within graphite electrode was assumed in that study. Figure 3(a) demonstrates the evolution of lithium concentration and subsequent mechanical degradation predicted by this technique. An energy based fracture criteria was adopted to initiate microcracks[27]. A safe design (particle size) and operating (C-rate) regime has been demonstrated in Figure 3(c) where minimum microcrack formation occurs. This lattice-spring based technique was later extended to study the impact of operating temperature on mechanical degradation of graphite based anode active particles[32]. By incorporating nonlinear strain-displacement relations, the lattice spring technique has been modified to model the microcrack formation and propagation within high capacity anode materials, which experience severe volume expansion[41]. The governing expression adopted to solve this problem is:

$$\int_{^tV} {}^{t+\Delta t}S_{ij} \delta {}^{t+\Delta t}\epsilon_{ij} d^tV - \int_{^tA} {}^{t+\Delta t}F_i \delta {}^{t+\Delta t}u_i d^tA = {}^{t+\Delta t}R \quad (3)$$

Here, ^tV and ^tA corresponds to the volume at the previous equilibrium configuration, ${}^{t+\Delta t}S_{ij}$ is the 2nd Piola-Kirchhoff stress tensor, ${}^{t+\Delta t}\epsilon_{ij}$ is the Green-Lagrange strain tensor, ${}^{t+\Delta t}F_i$ is the externally applied force, ${}^{t+\Delta t}u_i$ is the displacement and ${}^{t+\Delta t}R$ is the residual (which is usually considered to be zero). Microcrack evolution in silicon active particles during lithiation process has been demonstrated in Figure 3(b). Phase field based computational methodology has been developed that is capable of simulating simultaneously the propagation of crack fronts as well as flow of electrolyte through the spanning cracks[42]. Cohesive zone based electrochemical model has also been proposed to capture the delamination between binder and active particle during lithiation-delithiation process[43].

The mathematical models discussed till now require several mechanical properties as input parameters. Even though some mechanical properties (Young's modulus, shear modulus) of common materials (graphite, silicon, tin) are available in literature, majority of the alloy materials encountered during lithiation are relatively new with unknown properties. Ab-initio calculations using density functional theory (DFT) are useful in estimating the parameters for several new cathode and anode materials[44]. Mechanical properties of lithiated tin and silicon alloy obtained using DFT calculation indicates that, as the amount of lithium increases, Young's modulus decreases along with ductile to brittle transition occurs[45, 46]. Anisotropic and lithium concentration dependent mechanical parameters for lithium-cobalt-oxide have been estimated [47]. Interfacial strengths of silicon/copper and silicon/graphite have been estimated based on first-principle calculations to investigate the mechanical stability of silicon during the lithiation/delithiation process [48, 49]. For materials used in lithium-ion batteries, a comprehensive list of mechanical parameters, as a function SOC, obtained from ab-initio calculations has been reported [44].

Influence of Microstructure

In most of the macrohomogeneous degradation models, simplifying scenarios such as spherical active particles with uniform size through the electrode are considered. The influence of electrode microstructure heterogeneity is expected to play an important role in the degradation phenomena. Recently, Chen *et al.* [15, 50] computationally studied the effect of microstructural variability on the chemical and mechanical degradation in Lithium-ion battery electrodes. For the study of SEI formation, Chen and Mukherjee [15] developed an electrode microstructure-aware model to observe the spatial variation of SEI formation. The essential concept of this model is schematically shown in Figure 4. This study reveals that the SEI growth rate changes with

particle size and morphology, and hence the importance of electrode microstructural variation on the degradation mode. In addition, the resistance increase also corroborates well with the Brunauer–Emmett–Teller (BET) specific surface area of graphite active particle suggested by the experimental results of Martin *et al.* [51]. Chen *et al.* [50] also integrated the diffusion induced damage model with stochastically reconstructed electrode microstructures. Inside the electrode, the microcrack density was observed to vary with particle size, charge/discharge rate and temperature.

A typical electrode microstructure includes not only the active particles, but also conductive additives and binders. Due to the interaction between individual active particles, microstructure significantly impacts the extent of mechanical degradation observed within lithium-ion batteries. Finite element based analysis in mesoscale level indicates that stresses evolve from small-scale particle features and lithium concentration gradients[52]. Taking into consideration the anisotropic swelling of active particles, it has been demonstrated that maximum stress within electrode occurs due to inter-particle interactions[52]. Incorporation of the impact of hydrostatic stress on lithium transport results in significantly smaller magnitude of concentration gradient, and subsequently reduced mechanical degradation[53]. Using the pseudo 2D porous electrode theory model, increased microcrack evolution has been observed within the active particles located close to the separator[12]. An optimal charging protocol has been developed to minimize the intercalation-induced stress within the active materials [54]. Proper distribution of particles within the electrode has the potential to minimize capacity fade induced by mechanical degradation.

Simulation-driven Diagnostics

Electrochemical Impedance Spectroscopy

As mentioned, the SEI thin layer increases the kinetic resistance for electrochemical reaction. To study the variation of internal resistance due to SEI growth, the electrochemical impedance spectroscopy (EIS) is a powerful tool. Meyer *et al.* [55] and Huang *et al.* [56] developed a numerical model, which include the influence of the thickness of SEI layer. The expression of the impedance response is shown below.

$$Y = \frac{1}{Z} = \frac{1}{\frac{R_{ct,1} + \frac{R_{part}}{Y_s}}{1 + j\omega C_{dl,1} \left(R_{ct,1} + \frac{R_{part}}{Y_s} \right)} + R_{film} + \frac{R_{ct,2}}{1 + j\omega R_{ct,2} C_{dl,2}}} + j\omega C_{film}} \quad (4)$$

where $R_{ct,1}$ and R_{part} / Y_s are the charge transfer and diffusion resistance between the solid phase and SEI layer. R_{film} and C_{film} are SEI resistance and capacitance.

This EIS model treats SEI resistance as a layer resistance, and the resistance is a function of film thickness according to the ohm's law. The EIS model proposed by Meyer *et al.* [55] and Huang *et al.* [56] did not include the electrochemical reactions, which cannot capture the impedance variation during cycling. To include the growth of SEI during battery cycling, Xie *et al.* [57] and Chen *et al.* [15] integrated the EIS model with the electrochemical model. The SEI film growth during cycling is coherently coupled with the electrochemical reaction on the interface between active material and electrolyte. With the coupling, the evolution of impedance during battery cycling is observed. The model developed by Chen *et al.* [15] further includes the influence of microstructure on the formation of SEI and its corresponding impedance response. The schematic diagram of the model is as shown in Figure 4. The spatial electrochemical properties distribution, such as SEI thickness, was simulated from mesoscale microstructure-

aware model, and the calculated result was used as inputs to the EIS model. From the results, the electrode resistance contributed by SEI formation is affected by particle morphology, interfacial area, and electrode porosity. Similar to the SEI formation, Chen et al. [50] developed a model, which integrated the diffusion induced damage model and impedance model. This model successfully captured the influence of microcrack on the impedance response. The influence of microcracks is mainly on the solid-phase diffusion resistance and charge transfer resistance.

Acoustic Emission

Acoustic emission (AE) is a useful nondestructive technique for estimating state of health for lithium-ion batteries. Energy gets released during microcrack formation, chemical reaction with lithium or gas evolution, which travels through the cell as a stress wave (as shown in Figure 5(a-d)). The essence of acoustic emission technique is to detect these travelling waves using ultrasound measurement[58]. Depending on the frequency of detected signal, it is possible to determine the mode of degradation. Low frequency signals (20-100kHz) are usually associated with gas generation or SEI formation; whereas, high frequency signals (100-300kHz) are generated because of microcrack nucleation[59]. Acoustic time-of-flight experiment can measure the state-of-charge and state-of-health for any closed battery due to change in density and elastic modulus of cathode and anode materials during charge and discharge process[58]. Acoustic emission technique was first applied on lithium-manganese-oxide cathode active particles to estimate the mechanical degradation during lithiation-delithiation cycles[60]. Evolution of microcracks within silicon active particles has also been detected using AE techniques[61]. For both LMO and silicon, it has been observed that majority of mechanical degradation occurs within the first few cycles, and microcrack evolution saturates after that[60, 61]. A computational technique was developed based on dynamic lattice spring method to simulate

crack formation and strain energy release during lithium transport[62]. The following equation has been solved to obtain the displacement $\{U\}$, velocity $\{\dot{U}\}$ and acceleration $\{\ddot{U}\}$ for each of the nodes in the lattice-spring network:

$$[M]\{\ddot{U}\} + [C]\{\dot{U}\} + [K]\{U\} = \{F\} \quad (5)$$

Here, $[M]$ signifies the mass matrix, $[C]$ indicates the damping matrix, $[K]$ is the stiffness matrix for the dynamic lattice spring network, and $\{F\}$ corresponds to the force vector due to concentration gradient induced load. As demonstrated in Figure 5(e), under the assumption of brittle fragmentation, saturation in microcrack evolution was observed after the first few cycles. By appropriate calibration and usage of AE, it is possible to use this technique for early detection and diagnosis of degradation and safety concerns in lithium-ion batteries under abuse scenarios.

Conclusion & Outlook

This article provides an overview of the modeling of the chemo-mechanical degradation phenomena and highlights some of the recent progress in the simulation-driven degradation diagnostics in lithium-ion battery electrodes. The detrimental effect of SEI and microcrack formation on the capacity fade and impedance rise has been reported from a modeling perspective. The recently reported SEI models provide new insights into the SEI growth and resulting impact on the electrochemical properties and capacity loss. These models reveal that the SEI formation is affected by temperature, state-of-charge, layer morphology, and electrode microstructure. The effects of SEI formation on the potential drop, cell temperature, and stress generation have also been addressed in the recent models. Importance of mechanical degradation in determining the life of lithium-ion batteries has been comprehensively studied using analytical, finite element and lattice spring based models. Two-phase transport of lithium, large

volume expansion and anisotropic swelling during lithiation can be considered as major factors for severe microcrack formation in active particles. Recent developments in the simulation-driven degradation diagnostics (i.e. electrochemical impedance response and acoustic emission) have been highlighted which are expected to provide virtual probing and prognostics of lithium-ion battery life and health.

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In this article, the authors presented a dynamic lattice spring based computational model capable of estimating the acoustic emission spectra observed during mechanical degradation of electrode active particles. This is expected to enable simulation-driven degradation diagnostics in lithium-ion batteries.

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