

MULTI-SCALE MODELING AND OPTIMIZATION OF STRUCTURALLY INTEGRATED LITHIUM-ION BATTERIES

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1 Introduction

Batteries play an increasingly important role for a broad range of technologies. Applications range from powering small wireless sensors and smart phones to storing larger amount of energy for electric cars and providing buffers for wind farms and photovoltaic plants. There is a growing demand for more reliable, higher energy density, longer lifetime, batteries. Conventionally, batteries are designed to provide a single function: to store energy. The battery cell is shielded from mechanical loads by enclosure in a stiff containment and the integration of batteries into structural components, subsystems, and devices is mainly driven by thermal management requirements. However, for a broad range of applications, such as aircraft and cars, a multi-functional battery design with load-bearing capabilities is a promising concept to reduce the weight and increase the payload capacity of the overall system [1].

In this paper we are concerned with modeling and designing multi-functional batteries, focusing on the fundamental interactions between electrochemical and structural performance of Lithium ion (Li^+) batteries. This class of batteries features among the highest theoretical energy storage density, but is plagued with significantly shorter lifetimes when compared to other battery chemistries. The performance and degradation of Li^+ batteries strongly depend on both electrochemical and mechanical phenomena which are strongly coupled. In particular these coupling phenomena need to be considered when integrating Li^+ batteries into structural composites.

Rechargeable batteries consist of anodic and cathodic electrodes and current collectors, as shown in Fig. 1. A separator prevents contact of the electrodes. When the battery is discharged, lithium

(Li) in the anode is oxidized into Li^+ and electrons. The electrons flow through the external circuit to the cathode while the ions enter the electrolyte and are carried by diffusion and migration to the cathode, where they are reduced. This process is reversed when the battery is charged.

In Li^+ batteries, the electrodes are composed of porous active insertion compounds, binders, and conductive additives, with a solid or gel-like (liquid) electrolyte filling the pores. The active material particles swell upon Li^+ intercalation. Depending on the material, this swelling can range from 6.5% for Mn_2O_4 cathode material to 300% to 400% for Si anode materials and leads to stresses in both the active material particle as well as the entire battery cell. The stresses can lead to cracking of the electrode particles which may cause parts of the cracked particles to be electrically and ionically isolated and thus may lead to capacity fade.

Two distinct length scales can be identified at which phenomena relevant for the electrochemical and mechanical performance of a battery cell occur. The transport of ions and electrons across the electrodes and separator are macroscopic, likewise the mechanical deformation of the battery cell. The

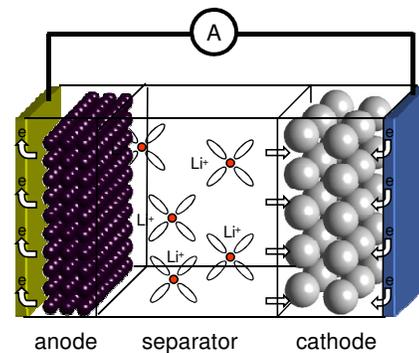


Figure 1: Battery cell.

characteristic length scale is at the order of $100\mu m$. The macroscopic phenomena are strongly interconnected with the response of a single active material particle. Micro-scale phenomena include the transport of Li across the particle surface and within the particle as well as its mechanical deformation. The characteristic microscopic length scale depends on the particle size and ranges from a few nano meters up to $\sim 10\mu m$.

In this paper we present a multi-scale modeling and analysis approach for predicting the behavior of structurally integrated batteries. We embed this approach into a design optimization framework to study the optimal layout of electrodes. The optimization studies allow assessing the trade-off between mechanical and electro-chemical performance.

2 Multi-scale modeling

The behavior of Li^+ batteries is an interesting multi-scale, multi-physics problem involving nonlinear transient coupled electrochemical and mechanical phenomena at macro and micro scales. Owing to the wide range of characteristic lengths at which these phenomena occur ($10^{-9} - 10^{-4} m$) directly resolving all length scales leads to an impractically large computational burden. Instead, we use a multi-scale modeling approach [2] and assume a separation of length scales between macro and micro scales. For the class of problems considered in this study, a separation of time scales is not necessary as Li transport occur at similar paces at both the macro- and micro-scale.

Our approach extends the electrochemical battery model developed by Doyle *et al.* [3] which uses porous electrode theory to account for micro-scale effects. At the macro-scale, Li^+ transport, electric potentials, and mechanical deformations across the entire battery cell are considered. We extend this macro-scale model to account for elastic and inelastic deformations due to external mechanical loads and electrochemical eigenstrains. At the micro-scale, the response of a single electrode particle is considered. Here we adopt the coupled stress-diffusion model of Zhang *et al.* [4], account for electrochemical surface reactions, and include surface stress effects. As we will show later, classical continuum mechanical models suggest that particle stresses due to Li intercalation decrease as

the size of the particle decreases. Surface stress effects need to be considered when optimizing the size of electrode particles in order to avoid non-physical solutions for particle sizes at the order of nano-meters. Meso-scale homogenization methods are used to account for the interactions between the particles and bridge macro and micro scales. We model macro- and micro-scale phenomena using a multi-scale finite element approach which is described in detail in Golmon *et al.* [5].

3 Design optimization framework

Improved performance of the battery can be achieved by altering the design and discharge parameters of the battery. Manipulation of macro-scale parameters such as the discharge rate, electrode thickness, and porosity, as well as micro-scale parameters such as the size and shape of the particles in the electrode can affect the overall behavior of the battery and the level of the internal stresses. Because the battery problem involves multiple length scales and the interaction of transient multi-physics phenomena, designing by intuition is difficult. Therefore we have developed a computational design optimization approach which combines the multi-scale finite element battery cell model described above with mathematical optimization schemes to drive the cell design [6].

Much of the previous work on optimization of batteries has focused on battery pack design, considering thermal and power management [7,8]. To enhance the battery performance at the cell level, Battery cell design was considered for example in [9,10,11]. All of the above design studies rely primarily on intuition, experience, and parameter sweeps but do not employ a formal design optimization approach, capable of handling large numbers of constraints and design variables.

In this study we apply a computational framework for optimizing the transient, nonlinear behavior of structurally integrated batteries in order to improve the electrochemical and mechanical performance by manipulating a potentially large number of macroscopic and microscopic design parameters [6]. In the following we demonstrate the capabilities of our optimization framework to find the optimal porosity and particle size distributions in functionally graded electrodes. This design optimization problem is solved by a nonlinear programming method. This method requires the

gradients of the objective and constraints with respect to the design variables. The numerical and computational complexity of the battery cell model necessitates the use of analytical sensitivities. To accommodate a large number of optimization variables we employ an adjoint sensitivity analysis approach. Details regarding the formulation and solution techniques, in particular the adjoint sensitivity analysis method, are provided in [6].

4 Example

We demonstrate the potential of the proposed optimization framework for improving the electrochemical and mechanical performance of Li battery electrodes. Specifically, we seek to find optimal electrode designs to maximize the capacity of a battery cell while constraining the stresses during discharge by manipulating both the local porosities and particle radii. The particle stress is a micro-scale design criterion, while the capacity is macro-scale. The design variables of the local porosities and particle radii were chosen due to their previously shown effect on particle stresses [5,12]. The design configuration assumes a 90 minute galvanostatic discharge of a cell at a constant current of 12.1 A/m^2 . To simplify the problem, we model a Li half cell which includes a porous cathode and Li foil anode, modeled through boundary conditions on the macro-scale Li^+ concentration and potential fields [5]. The cathode is Mn_2O_4 , and the electrolyte is $\text{PEO-LiCF}_3\text{SO}_3$. The thicknesses of separator and cathode are $50 \mu\text{m}$ and $100 \mu\text{m}$, respectively. The reader is referred to [6] for details on the material parameters. The problem is discretized in time using $N_t = 270$ time steps and spatially using 20 elements along the separator, 40 elements along the cathode, and 20 elements in each micro-scale problem. Two-point Gauss integration is used at the macro-scale which results in $N_m = 80$ micro-scale problems. In total, there are 244 macro-scale state variables and 8320 micro-scale state variables. Studies were performed to ensure mesh and time convergence.

4.1 Formulation of optimization problem

The battery potential at the end of a galvanostatic discharge for a set period of time is directly related to the usable capacity of the battery: the greater the potential, the greater the usable capacity of the battery.

First we illustrate the influence of porosity on the electrochemical and mechanical response of the battery cell by considering an electrode with spatially uniform porosity and micro-scale particles of constant radius $R_s = 5 \mu\text{m}$. As seen in Fig. 2, uniformly varying the porosity strongly influences the discharge behavior of the battery: high porosities result in a lower capacity and a quick discharge to the cutoff potential, i.e. the lower bound of the battery potential for operation. Low porosities allow for a greater overall volume of active material and yield a higher capacity, resulting in a close to constant potential during the 90 minutes discharge period.

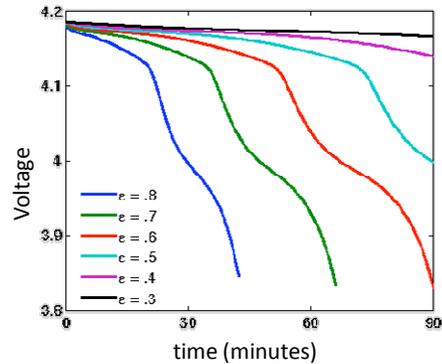


Figure 2: Discharge behavior in dependence of porosity.

Fig. 3 shows the relationship between the maximum tangential particle stress and the battery potential at 90 minutes as a function of a spatially uniform porosity. The end potential is highest with low porosities, while increasing the porosity leads to lower potentials. For constant porosities above $\epsilon = 0.6$, the battery reaches the cutoff potential in less than 90 minutes. However, small and large porosities lead to higher stresses, which are generated by a high Li flux into the particles.

The electrochemical and mechanical performance of Li^+ batteries is also affected by the size of the micro-scale particles. For uniform particle radius and porosity distributions across the electrode, Fig. 4 illustrates the influence of different particle radii on the battery potential as a function of time. This plot suggests that, in general, smaller particle radii improve the usable capacity. However, as seen in Fig. 5, stresses increase significantly for nano-size particles due to surface stress effects. For larger

particles, the intercalation of Li into the particle is diffusion limited and the resulting concentration gradient causes mismatch strains and stresses, owing to the stress-diffusion coupling. This effect increases with increasing particle size.

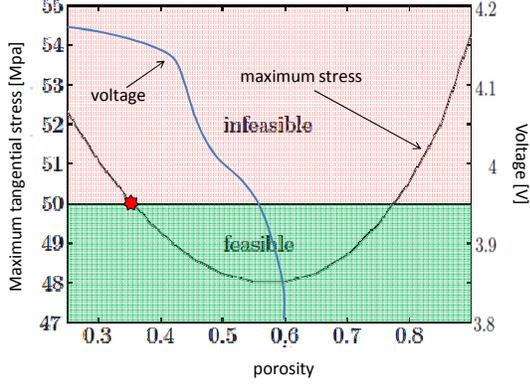


Figure 3: Maximum tangential particle stress and battery voltage in dependence of porosity.

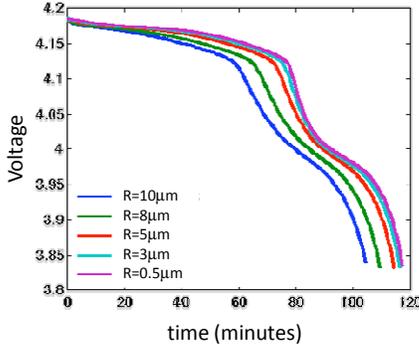


Figure 4: Discharge behavior in dependence of particle size.

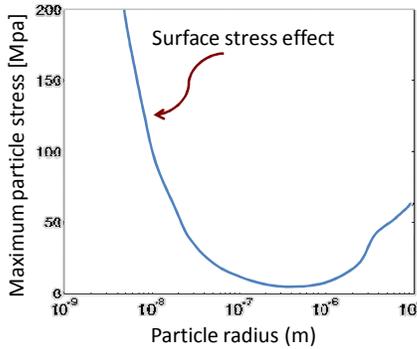


Figure 5: Maximum tangential particle stress in dependence of particle size.

After having illustrated the influence of porosity and particle size on the electrochemical and mechanical response of a battery cell, we now study the effects of spatially varying porosity and particle size distributions by maximizing the battery potential at the end of the galvanostatic discharge while constraining the maximum tensile tangential stress, $\sigma_{T,i}$, observed in a particle over the discharge period. To obtain a well posed and differentiable optimization problem, this design problem is formulated as follows:

$$\begin{aligned} \min_s \quad & -\phi(t_{N_t}) + \gamma \|\nabla \varepsilon\|_2 \\ \tilde{\sigma}_{T,i} - \sigma_{max} \leq 0 \quad & i = 1:N_m \end{aligned} \quad (1)$$

with

$$\begin{aligned} \tilde{\sigma}_{T,i} = \frac{1}{\beta} \ln \sum_t \sum_r \exp(\beta \sigma_{T,t,r,i}) \\ t = 1:N_t, r = 0:R_s \end{aligned} \quad (2)$$

The term, $\gamma \|\nabla \varepsilon\|_2$, regularizes the objective function by suppressing oscillations in the porosity distribution due to low local sensitivities; γ is chosen to keep this term below approximately 0.001% of the objective. To reduce the number of stress constraints we approximate the maximum particle stress, $\sigma_{T,i}$, by the Kreisselmeier-Steinhauser (KS) function. Using 40 finite elements along the cathode with elementwise constant porosity and 80 micro-scale problem with individual particle radii results in 120 design variables. The local porosities are varied between 0.1 and 0.9 and the particle radii between 1 nm and 10 μm . The KS stress constraint is imposed for each micro-scale problem resulting in 80 inequality constraints. The maximum feasible stress, σ_{max} , is set to 50MPa. The design optimization problem is solved using the Globally-Convergent Method of Moving Asymptotes (GCMMA) of Svanberg [13].

4.2 Optimization results

The optimization problem is initialized with particles of radius $R_s = 500 \text{ nm}$ and a porosity distribution that linearly decreases towards the cathodic current collector. The value for the initial

particle radius corresponds to the region of lowest stresses in Fig. 5. The linear porosity sweep allows for greater Li^+ diffusion into the electrolyte and ensures that the initial configuration is sensitive to all porosity variables.

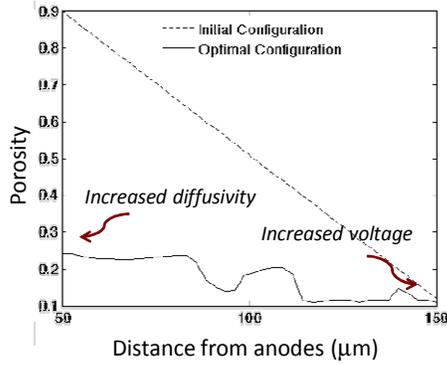


Figure 6: Initial and optimized porosity distributions.

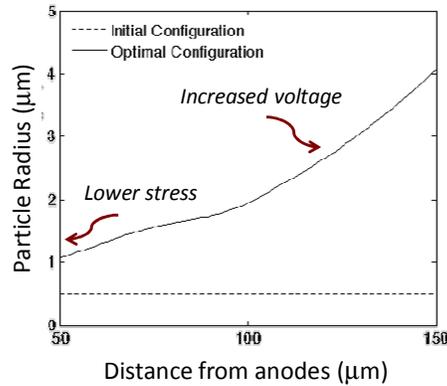


Figure 7: Initial and optimized distribution of particle radii.

Figure 6 and 7 show the initial and optimal porosity and particle radii distributions. The initial configuration has an end potential of 4.1255 V while the optimal configuration has an end potential of 4.1789 V. This value is higher than what can be achieved with uniform porosity and particle radii distributions. The initial configuration has a maximum stress of approximately 5MPa while in the optimal configuration the maximum stress is approximately 9MPa; both values are well below the constraint level of 50 MPa.

The optimal design has low porosities throughout the cathode which allows for higher theoretical and usable capacity. The optimal design uses small particle radii to decrease the stress levels in the front

of the electrode where the highest Li fluxes into the particles occur. The larger particle sizes at the back of the electrode result in a decreased rate of Li insertion into the particles which helps to maintain a higher battery potential. Because large particles are diffusion limited, the Li concentration at the particle surface remains high, decreasing the rate of Li insertion. At the front of the cathode, the porosity is higher which allows for greater Li^+ diffusion through the electrolyte. As seen in Fig. 8, the initial design utilizes the entire cathode, with Li uptake occurring throughout the electrode. The optimal design pushes the majority of the Li uptake to the front half of the cathode. The optimal design does not see a significant increase in the Li concentration in the cathode particles in the back half of the electrode, maintaining a high potential. In this region, the regularization term dominates the objective as porosities smaller than $\epsilon=0.15$ have little influence on the battery potential.

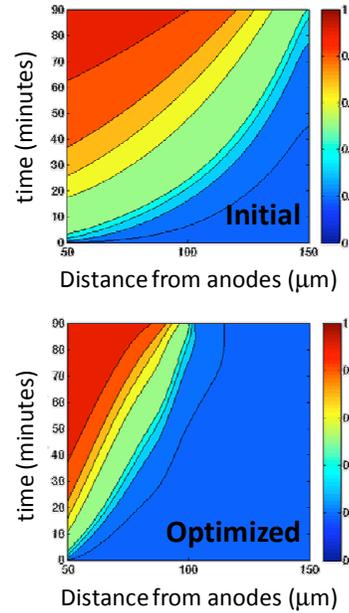


Figure 8: Li concentration in electrolyte for initial and optimized electrode designs.

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