Coupled Mechanical and Electrochemical Analyses of Three-Dimensional Reconstructed LiFePO₄ by Focused Ion Beam/Scanning Electron Microscopy in Lithium-Ion Batteries

Limited lifetime and performance degradation in lithium ion batteries in electrical vehicles and power tools resulting from various interrelated processes is still a challenging obstacle [1]. Typically, these phenomena are more serious under specific conditions such as higher discharging rates (C-rates) and longer cycling life [2]. One of the main reasons for battery degradation is the large mechanical stress resulting from volume expansion (or contraction) during the (dis)charging processes. It is well known that stress-induced fractures degrade the performance of lithium ion cells, as evidenced by the observation of fractured surfaces in postmortem analysis of batteries [3]. Moreover, Xu and Zhao [4] reported that the insertion of lithium is blocked by the high local compressive stress, and finally, results in significant reduction of the effective capacity. Lu et al. [5] also confirmed by theoretical and experimental analyses that mechanical stress plays an important role in voltage hysteresis in lithium ion batteries. It is, therefore, very important to analyze electrochemical degradation due to mechanical stresses.

As LiFePO₄ cells are discharged, both lithium intercalation at the cathode–electrolyte interface and diffusion inside the cathode can result in diffusion-induced stress. Early stage studies analyzed diffusion-induced stresses in cathode materials based on simple geometries such as spheres, spheroids, cylinders, and disks by using Newman’s pseudo-two-dimensional (2D) model, while recognizing that stress development has a major impact on the performance of lithium ion batteries. However, there were still limitations when simple geometries were used because they failed to predict the phenomena relating to the inhomogeneous natures of the electrode microstructures [6]. Currently, more studies are focusing on realistic microstructures of electrodes to investigate diffusion-induced stress. Mendoza et al. [6] investigated the mechanical and electrochemical responses of a LiCoO₂ cathode during charging. They reported mechanisms of stress generation and the effect of charge rate on capacity fade. Stress generation in LiCoO₂ [6], LiMn₂O₄ [7], and nickel-manganese-cobalt [8] has also been investigated using realistic microstructures.

Three-dimensional (3D) characterization methods such as focused ion beam-scanning electron microscopy (FIB-SEM) and...
X-ray computed micro/nanotomography have been commonly used to quantify electrode microstructural parameters including grain size, phase volume, surface area, phase connectivity, and tortuosity [9]. Ender et al. [10] first presented a 3D reconstructed LiFePO₄ model obtained by FIB/SEM tomography. Based on the reconstructed figures, they analyzed microstructural features such as active surface areas, particle size distribution, porosity, and tortuosity of the pore phase for both LiFePO₄ and carbon black. Moreover, detailed structural degradation of LiFePO₄ was investigated by using low voltage FIB/SEM [11]. Biton et al. developed a new methodology via contrast enhancement for 3D imaging of LiFePO₄ [11]. Nanoscale X-ray computed tomography data have been utilized for a 3D microstructure of LiFePO₄ to investigate the distribution of lithium ion concentration inside LiFePO₄ during discharging [12]. Kashkooli et al. [12] demonstrated that their electrochemical results from the reconstructed geometry were in good agreement with experimental measurements. However, we could only uncover one published study focusing on investigating stress generation within the 2D microstructure of LiFePO₄ [3]. Nevertheless, a complete study of the 3D electrode microstructure is required to better understand the coupled mechanical and electrochemical effects in lithium ion batteries.

A multiscale multiphysics finite element model consisting of one-dimensional electrochemistry, 2D axis symmetry heat generation, 2D mass transport, and 2D solid mechanics was previously established to investigate thermal- and diffusion-induced stresses in the reconstructed porous microstructures of commercial LiFePO₄ batteries [3]. Specifically, with the 2D model, we could investigate the effects of lithium ion concentration and stress in the cathode with complicated geometry such as at concave and/or convex corners and particle connecting areas. Moreover, it was confirmed that a strong relationship existed between mechanical stresses and capacity loss in lithium ion batteries. However, our previous model had several limitations, such as one-dimensional electrochemistry and the assumption that 2D solid mechanics behave exactly the same throughout the depth of the battery (i.e., along the z-axis). We realized that a three-dimensional fully coupled finite element model is essential to better study performance degradation in lithium ion batteries.

The current study is intended to demonstrate a methodology for using FIB/SEM to generate a 3D reconstructed microstructure through the conjunction of simulations for electrochemistry and solid mechanics to better understand the battery system. This paper presents an improved 3D fully coupled electrochemical-mechanical model, which is crucial for establishing the relationship between electrochemical performance and mechanical stresses. Specifically, our primary focus was on the effects of complicated structure on mechanical stresses and the prediction of particle crack initiation in LiFePO₄ cells.

2 Methods

2.1 Construction of the Microstructure. The LiFePO₄ sample for microscopy was prepared according to the study published by Kim and Huang [3]. Briefly, FIB/SEM imaging was carried out using FEI Quanta 3D FEG (FIB-SEM) at the NC State Analytical Instrument Facility (AIF, Raleigh, NC). As shown in Fig. 1(a), the sample stage was tilted to 52° deg and the FIB was perpendicular to the sample, which allowed cross-sectional micromilling. To focus on the region of interest, each side of the region of interest was milled by the FIB. For more detailed particle configuration, a sector of 2.5 × 2.5 μm² with higher magnification (>15,000×) was used. The pixel size of the scanning electron microscopy (SEM) images was 4.06 nm. Since a polyvinylidene difluoride (PVDF) binder was likely to be an ultrathin layer below the resolution, which made it difficult to distinguish from the LiFePO₄ cathode using SEM [9], carbon black and the PVDF binder were not considered in this study. Figure 1(b) presents a stack of over 50 SEM images. The smoothing and edge finding processes in the ImageJ analysis software (National Institute of Health, Bethesda, MD) were conducted to determine the boundary between the electrolyte and the electrode. Moreover, binary images were produced based on a threshold prior to the 3D reconstruction process. Based on the set of cross-sectional images, a 3D microstructure was also generated in ImageJ and exported in Standard Tessellation Language (STL) format, which allows the files to be imported into COMSOL MULTIPHYSICS (Fig. 1(c)). Since a 3D microstructure with 1.5 × 1.5 × 0.1 μm³ was computationally expensive to reduce the computation time, the geometry was partitioned to a final size of 0.8 × 0.8 × 0.1 μm³, which was shown in shaded region in Fig. 1(c). The imported 3D microstructure was combined with a 100 nm thick electrolyte domain. Current density was applied to the left side of the half-cell domain (i.e., the current collector) and the ground was set on the right side of the electrolyte (Fig. 1(d)). The mesh was generated via COMSOL MULTIPHYSICS and the mesh size was optimized using a standard finite element model procedure based on convergence [6]. The maximal and minimal sizes of the generated mesh were 9.16 nm and 1.65 nm, respectively.

2.2 Mathematical Model. This section summarizes the equations for electrochemistry and solid mechanics for both the electrodes and electrolyte, including elastic strain and diffusion induced strain during repeated charging–discharging cycles (Table 1). Diffusion induced strain was observed to be over an order of magnitude larger than thermal strain based on our previous work [3]. Thus, in the current study, we only focused on diffusion induced strain in cathode particles. To represent phase transformation between LiFePO₄ and FePO₄, concentration-dependent material properties were incorporated into the material property [K], such as the Poisson’s ratio and Young’s modulus described in Table 2, and were defined as $K(x) = \text{DoD}/[K_{\text{FePO}_4}^0 + (1 - \text{DoD})/K_{\text{LiFePO}_4}^0]$. DoD was calculated by the following equation:

$$\text{DoD} = \frac{\sum_{i=1}^{n} C_i V_i}{\sum_{i=1}^{n} C_{\text{max}} V_i}$$

(1)

where $V$ and $n$ indicated the volume of the 3D ten-node tetrahedral mesh and the total number of meshes, respectively. $C_{\text{max}}$ indicates the maximum concentration at the cathode [15].

Total polarization and over potential were calculated to quantify electrochemical battery degradation. The total polarization was defined as the difference between the open circuit voltage and the cell voltage as described by the following equation:
properties for solid mechanics were used in this study. Moreover, all directions. Thus, by adopting this same idea, isotropic material randomly so that macroscopic elastic properties were almost equal in of the crystalline and grain microstructures were distributed ran-

Table 2 summarizes the material properties used in this work

<table>
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<tr>
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<th>Type</th>
<th>Description</th>
<th>Equations</th>
<th>#</th>
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<td>Mass transport</td>
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<td>Charge balance</td>
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<td>c</td>
</tr>
<tr>
<td></td>
<td>Mass transport</td>
<td></td>
<td>$J_i = -D_i \nabla \epsilon_i + \frac{i_{oc}}{F}$</td>
<td>d</td>
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| Interface         | Electro-chemical kinetics | \begin{align*} \eta_{oc} &= \eta_0 \left(\exp\left(\frac{\alpha_F \eta}{RT}\right) - \exp\left(\frac{-\alpha_F \eta}{RT}\right)\right) \\
\eta &= \eta_0 \left(1 + \frac{\alpha_F \eta}{RT}\right) - \eta_0 \left(1 + \frac{\alpha_F \eta}{RT}\right) \end{align*} | e   |
| Solid mechanics   | Total strain       |                   | $\epsilon_t = \epsilon_{tot} + \epsilon_{diff}$ | f   |

where $\eta = \phi_\epsilon - \phi_l - E_{eq}$

Table 2 summarizes the material properties used in this work

<table>
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<th>Description</th>
<th>Equations</th>
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<td>Maximum concentration ($c_{i,max}$)</td>
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<td>Diffusion coefficient ($D_i$)</td>
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<td>$7 \times 10^{-18}$</td>
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<td>Solid mechanics</td>
<td>Young’s modulus</td>
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<td>FePO$_4$</td>
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<td>FePO$_4$</td>
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respectively. The plateau during the discharging process was observed around 3.4 V. Total discharging times for 0.6 C, 1.2 C, and 2 C were 6000 s, 2868 s, and 1589 s, respectively. To compare the predicted capacity of the models at different C-rates, a 100% capacity was used for the 0.6 C model for relative comparison. We observed that the capacity of the cathode under 0.6 C, 1.2 C, and 2 C were 100%, 95.6%, and 88.3%, respectively. We hypothesized that the capacity fade was caused by higher stress in the electrode based on our previous work, thus we further investigated the electrochemical and mechanical behaviors in the half cell system.

Because the lithium ion concentration gradient induces mismatched strains and generates mechanical stresses [17,18], we investigated the concentration distribution in the microstructure of the electrode (Fig. 1(d)).

2.3 Model Parameters Table 2 summarizes the material properties used in this model. From Zhu et al. [16,17], the orientation of the crystalline and grain microstructures were distributed randomly so that macroscopic elastic properties were almost equal in all directions. Thus, by adopting this same idea, isotropic material properties for solid mechanics were used in this study. Moreover, current density was set as $-24$ A/m$^2$, $-50$ A/m$^2$, and $-70$ A/m$^2$ to represent 0.6 C, 1.2 C, and 2 C, respectively, and were applied on the left side of the electrode (Fig. 1(d)).

3 Results

Figure 2 shows the electrical potential curves for the LiFePO$_4$ during the discharging process at three different C-rates. The upper and lower potential limits were 3.8 V and 2.0 V, respectively.
LiFePO₄. In Fig. 3, P₁, P₂, and P₃ indicate the region near the separator, at the middle of the cathode, and the region near the current collector, respectively. As discharge proceeded, the cathode was lithiated along the direction from the separator to the current collector (as shown by a black arrow in Figs. 3(a)–3(e)). At 5400 s (i.e., at the depth of discharge (DoD) of 0.9 at 0.6 C), the surface of the electrode was fully saturated (Fig. 3(e)). Even though the cathode surface was fully saturated, the region inside the particle was not saturated, as shown in Fig. 3(f). The particle in the middle of the cathode (marked as A) has a higher concentration than the particle near the current collector (marked as B) (Fig. 3(f)). Moreover, we could also confirm that lithium ions diffused from outside toward the inside, as indicated by the white arrow.

The lithium ion concentration variations, ranging from 2000 mol/m³ to 22,800 mol/m³ under the three C-rates shown in Fig. 4, had demonstrated drastic differences upon discharging in the region near the separator (P₁), as compared to the one near the current collector (P₃). In this study, we used the slopes of the curves in Fig. 4 to present the concentration gradient. As many studies have demonstrated that a higher lithium ion concentration gradient would result in higher stress [2,3,18,19], our results in Fig. 4 may be used to explain why cracks were generally observed near the separator in cathode materials [13]. It was observed that higher C-rate resulted in higher concentration gradients at both P₁ and P₃, whereas lithium-ion concentration changed gradually at lower C-rate. By comparing P₁, P₂, and P₃ under each C-rate, lithium ion concentration in the region near the separator increased and saturated in the early stages of discharging, whereas lithium ion concentration at the region near the current collector increased and saturated at the end of discharging. Interestingly, different phenomena were observed at P₂: before DoD = 0.37 (Fig. 4), the concentration gradient at lower C-rate was steeper than that at higher C-rate. After DoD = 0.37, this trend was reversed. In spite of different C-rates, each DoD moves the same amount of lithium across the electrode. In other words, only a small portion of the electrode had a relatively higher lithium ion fraction at higher C-rate. On the other hand, at lower C-rates, a larger portion of the electrode was discharged with a relative lower lithium ion fraction. Thus, we concluded that at the same DoD, higher C-rate could possibly result in a more inhomogeneous lithium ion concentration distribution.
energy was also measured by the overpotential as shown in barrier between the electrode and the electrolyte. The activation
intercalation onto the surface, which was essential to overcome the energy mainly caused by the additional energy during lithium intercalation.

Polarization peaks in Fig. 5 confirmed that the activation polarization had occurred at the beginning and at the later stages of discharging, respectively. It was concluded that the activation polarization had occurred at the beginning and at the later stages of discharging process under different C-rates. We noted two total polarization peaks in Fig. 5(a): the first peak and second peak occurred at the beginning and at the later stages of discharging, respectively. It was concluded that the activation polarization had caused the first peak. That is, the activation polarization was mainly caused by the additional energy during lithium intercalation onto the surface, which was essential to overcome the energy barrier between the electrode and the electrolyte. The activation energy was also measured by the overpotential as shown in Fig. 5(b). Higher overpotential at P1 under three C-rates was also observed at the beginning of discharging. However, the total polarization reached the maximum values at DoD = 0.86 for all C-rates (Fig. 5(a)). The largest total polarization at the end of discharging was mainly caused by the lithium ion concentration polarization (i.e., the second peak). As shown in Fig. 5(e), most regions of the cathode had reached the maximum concentration prior to DoD = 0.86 (at 5400 s), which is when the exchange current density dramatically decreased. This phenomenon could also be verified by Eq. (f) in Table 1, where the decreased exchange current density resulted in limited mass transport in the electrode and correspondingly higher polarization occurred. The results indicate that lithium ion concentration polarization was much higher than the activation polarization during the whole discharging process. Moreover, higher temperature gradients observed at the early stage and at the end of discharging process, as compared to our previous work [21], can also be explained by Fig. 5(a) in the current study, where higher total polarization and higher temperature gradients occurred at the same DoD (i.e., 0.86). Figure 5(b) provided over-potential evolutions for P1, P2, and P3 during discharging. Higher overpotential was observed under higher C-rate at all points (shown in red). Moreover, for all C-rates, P1, P2, and P3 showed higher overpotential around DoD = 0.2, 0.55, and 0.85, respectively. The results also suggested that lithium intercalation causes higher overpotential at specific DoDs (i.e., 0.2, 0.55, and 0.85). A detailed overpotential distribution is shown in Figs. 6(a)–6(c).

Figure 6 shows the normalized concentration gradient, overpotential, and von Mises stress distribution across the electrode at different DoDs (i.e., 0.25, 0.5, and 0.75) at 0.6 C. In Fig. 6(d), an extremely high concentration gradient was observed in the connecting area near the separator. It was caused by the larger surface area exposed to electrolyte as compared to other regions. In spite of higher concentration gradients at this area, the von Mises stress did not show a significantly higher value. Rather, higher von Mises stress was observed in the center of the particle. From Fig. 6(b), stresses were accumulated inside the particle and were released as discharging proceeded, as shown in Fig. 6(i). Figure 6 suggests that the highest von Mises stress was consistently observed at the same location where the highest normalized concentration gradient and overpotential occurred, except in the connecting area between the particles. This can be explained by the fact that the overpotential and diffusion induced stress both have direct relations to the concentration. It suggested a strong coupling between the mechanical behavior and diffusion in the electrode.

Figure 7 shows the maximum von Mises stress evolution across the cathode during discharging at different C-rates. As expected, higher stress was observed at higher C-rate. Moreover, as C-rate decreased, von Mises stress variation was less significant except at the very beginning and the end of discharging. In other words, the von Mises stress plateaus observed at 0.2 C and 0.6 C, and the plateau region became narrower as C-rate increased. For example, at 0.2 C, plateaus were observed between DoD = 0.2 and DoD = 0.8, but no plateaus were observed at 1.2 C and 2.0 C. Moreover, under high C-rate (i.e., 2.0 C), von Mises stress drastically increased from the early stage of discharging until DoD = 0.5. A similar trend was also reported in LiCoO2 by Mendosa et al. [22]. Additionally, Fig. 7 showed that with higher C-rate, the maximum stress occurred earlier in the discharging process.

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process (i.e., at lower DoD). Figure 7 also shows that the normal-
ized maximum von Mises stresses were 0.29, 0.45, 0.79, and 1.0
for 0.2 C, 0.6 C, 1.2 C, and 2.0 C, respectively. In the previous
study with core–shell models for cathode materials, it was
reported that peak stresses generally occurred when the surface
concentration reached saturation [20]. However, the model with
3D reconstructed microstructure in the current study demonstrates
that there was no direct relationship between mechanical stress
and surface saturation. As shown in Fig. 4, we observed that the
surface of the whole electrode was saturated around a depth of
discharge of 0.9 for all C-rates. However, the mechanical stress
variation after the depth of discharge of 0.9 was not significant.
When the cathode surface was fully saturated, the inside of the
particle was not fully lithiated at the end of the discharging pro-
cess. Thus, we concluded that the mechanical effect of li-
thium intercalation at the cathode–electrolyte interface was a
critical factor, as compared to the mechanical stress due to lithium
diffusion inside cathode materials.

4 Conclusions

This study was motivated by the fact that stress-induced frac-
tures can degrade the performance of lithium ion cells. To reveal
the relationship between diffusion-induced stress and electro-
chemical degradation, we developed a three-dimensional finite
element model incorporating 3D electrochemical and mechanical
analysis in COMSOL MULTIPHYSICS. The microstructure of LiFePO4
was reconstructed based on a 2D FIB-SEM technique. The multi-
physics models developed in this study demonstrated 88.3% of
capacity fade at 2 C, which may be explained by higher concen-
tration gradients as compared to lower C-rates. The concentration
distribution in the cathode was also presented, and it provided
insight toward microstructural effects on electrochemical phe-
nomena. Further, the peak total polarization under each C-rate
was observed at the DoD where the higher temperature gradient
had also been observed in our previous experiment. At different
locations, one of the critical degradation factors (overpotential)
indicated that lithium intercalation at the electrode–electrolyte
interface causes higher overpotential at specific DoDs. From
the maximum normalized von Mises stress variation, higher C-rates
showed peak stress, whereas lower C-rates showed stress plateaus
within a specific range of DoDs. Finally, the regions where higher
mechanical stress was observed were consistent with the regions
where higher overpotential and higher concentration gradients
also occurred. We believe that our results may be
helpful for understanding particle crack initiation in cathode
materials.

Further work extending this study should include mechanical
interactions between adjacent particles by including carbon black
and PVDF binder in a larger region of interest. Specifically, a
modified Butler–Volmer equation for electrochemical kinetics,
which accounts for the influence of mechanical stress resulting
from electrochemical reactions, will be adopted. It will clearly reveal whether there is a direct relationship between elec-
trochemical degradations and mechanical stresses. Moreover,
since the anode, made of materials such as silicon or graphite,
showed significantly larger volume expansion during electro-
chemical cycling, a model combining the anode and cathode
based on 3D reconstruction will be investigated. We believe it
will provide better insight into mechanical stresses in lithium ion
cells.

Nomenclature

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<th>Symbol</th>
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<tr>
<td>a, c, l</td>
<td>anode, cathode, electrolyte</td>
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<tr>
<td>C</td>
<td>concentration</td>
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<tr>
<td>D</td>
<td>diffusivity</td>
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<td>( E_{\text{eq}} )</td>
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