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Numerical Simulation of Intragranular and Intergranular Crack in NCM Polycrystalline Particles Under Different Operating Conditions

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ABSTRACT

The $LiNi_xCo_yMn_zO_2$ (NCM, x+y+z=1) cathode materials for lithium-ion batteries (LIBs), are at the forefront of advancements in various emerging technologies within the power and energy storage sectors. However, the diffusion-induced stresses resulting from lithium-ion intercalation and deintercalation can lead to mechanical damage in NCM polycrystalline particles and consequently impact the overall battery cycle life. This study employs finite element simulations and experiments to investigate the initiation and evolution of intragranular and intergranular cracks in NCM polycrystalline particles under different charging-discharging conditions. This work contributes to a deeper understanding of the mechanical responses of NCM materials within LIBs, it highlights the potential for optimizing battery cycling conditions to mitigate crack-related degradation, thereby extending the lifespan of lithium-ion batteries in practical applications.

Keywords: lithium-ion batteries, NCM polycrystalline particles, intragranular and intergranular crack

NONMENCLATURE

Abbreviations	
NCM	$LiNi_xCo_yMn_zO_2$
NCM811	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$
PVDF	polyvinylidene fluoride

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in both portable electronics and electric vehicles (EVs) owing to their high energy densities, environmental benignity, and low cost [1]. The $LiNi_xCo_yMn_zO_2$ (NCM, x+y+z=1) is one of the most widely used cathode materials of Li-ion battery, due to its high energy density and cost effectiveness [2,3].

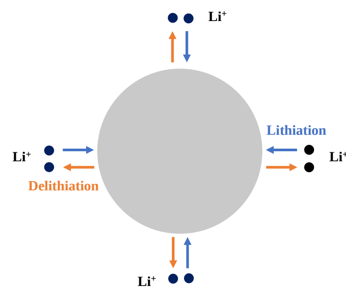

Fig. 1. NCM polycrystalline particle model during lithiation and delithiation process

Under the influence of mechanical-electrochemical multi-physical fields, the mechanical stability of the NCM cathode materials is disrupted, which causes particle damage such as Intragranular and Intergranular cracking and significantly affects the performance of the battery [4,5]. Currently, the demand for high energy density and fast charging of Li-ion batteries, exposes the active particles to extreme electrochemical conditions such as high voltage and high Li-ion flux. But extreme conditions mean more diverse damage forms and more complex damage mechanisms. At present, damage studies on polycrystalline NCM active particles focus on intergranular cracking. However, intragranular cracking are also important damage forms under extreme working conditions, and this is ignored in the existing studies.

2. NUMERICLA METHOD AND EXPERIMENTS

2.1 Numerical method

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For the NCM polycrystalline particle (Fig. 1), two-dimensional geometric structure model with simplified cylindrical models with assumed plane strain was conducted, due to the circular disks cross-section geometry of the secondary particles [2]. The hexagonal shape of the primary particles was used in the proposed geometric model, and randomly distributed in the secondary particle [6,7].

For the lithium-ion intercalation and deintercalation during charging and discharging process, lithium-ion diffusion-induced stresses were simulated with analogy to thermal stress [8,9]. And cohesive-zone elements were used in primary particles and grain boundaries between primary particles for the analysis of cracking process.

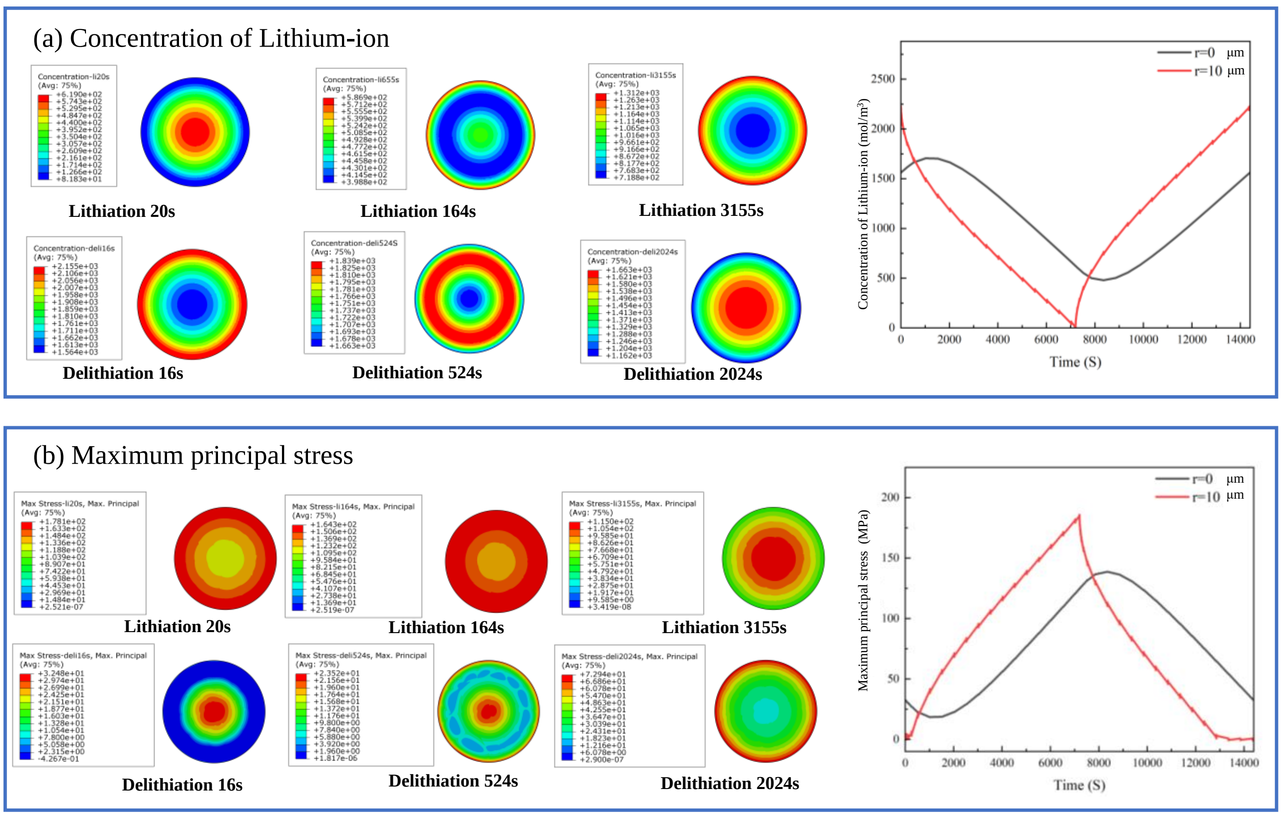

Fig. 2. Concentration of lithium-ion and maximum principal stress during intercalation and deintercalation process

2.2 *Experimental analysis*

The NCM electrode is manufactured from a surly with the mass ratio of 8:1:1, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) powder as active materials, super p carbon black as the conductive agent, and polyvinylidene fluoride (PVDF) as the binder. The CR2016 coin cell was assembled in an Ar-filled glove box with oxygen and water contents of less than 0.1 ppm.

The electrochemical tests were carried out on a battery testing system at room temperature. The NCM811 half-cells were pre-cycled in the voltage rage from 2.8 V to 4.25 V with a C-rate of 0.1 C for cell activation. Cycle conditions include different voltage range (2.8-4.9 V) and different rates (0.5C-6C).

3. *RESULT AND DISCUSSION*

3.1 *Diffusion-induced stress*

Based on the model depicted in the Fig.2, lithium-ion concentration and maximum principal stress are obtained. At the end of lithium intercalation, the maximum stress occurs at the center of the particle, whereas after lithium deintercalation, the maximum stress is observed at the particle's edge. A clear comparison of these two sets of results reveals that the change in lithium-ion concentration at the particle's center exhibits a noticeable lag, indicating a corresponding hysteresis in the stress variation. After lithium deintercalation, the maximum principal stress within the particle reaches its peak value.

3.2 *Crack initiation and propagation process*

The simulation compared three scenarios involving different charge/discharge rates and cut-off voltages: 0.5C/4.25V, 0.5C/4.9V, and 6C/4.25V, and the results are presented in Fig. 3.

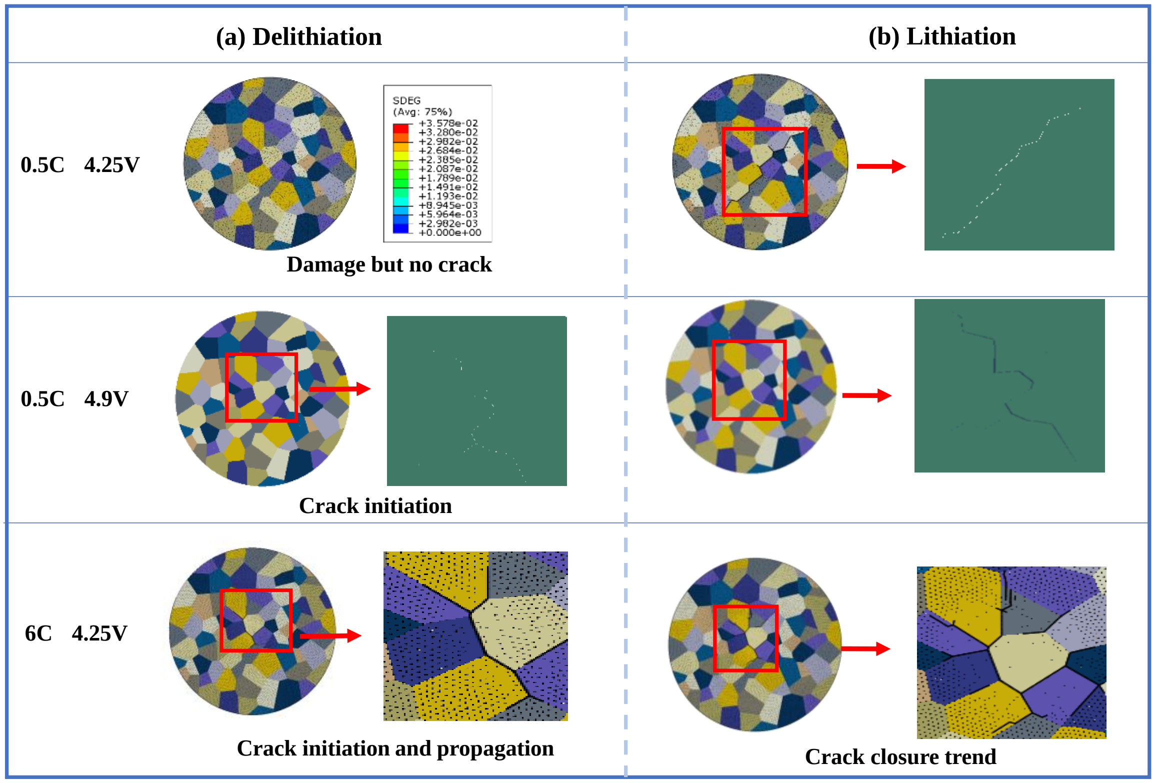

Fig. 3. Crack initiation and propagation under various charging-discharging conditions

At normal condition (0.5C/4.25V), damage was observed within the particle after lithium deintercalation, but no cracks initiated. Small cracks did appear at the center of the particle after lithium intercalation. At low charge/discharge rates and high cut-off voltage (0.5C/4.9V), cracks initiated at the center of the particle after the lithium deintercalation process concluded, and during lithium intercalation, these cracks continued to propagate outward. At high charge/discharge rates and low cut-off voltage (6C/4.25V), significant cracks formed at the center during lithium deintercalation. During lithium intercalation, these cracks rapidly extended and produced noticeable intragranular cracks.

This phenomenon can be explained as follows: during the lithiation phase, the central region experiences the maximum tensile stress, causing cracks to initiate and propagate from the center under sustained tensile stress. However, as the material enters the delithiation phase in the subsequent cycle, the edges of the particles experience tensile stress, expanding outward and simultaneously compressing the interior of the particles. The central region of the particle gradually experiences compressive stress, leading to the closure of cracks. However, this closure at this stage does not imply the restoration of the particle's damage. The magnitude of the bonding force between primary particles due to the cracks has been significantly affected. Therefore, during the lithiation phase of the second cycle, these cracks reopen under tensile stress.

3.3 Intergranular and intragranular cracking

In addition to intergranular cracks at the grain boundaries, the primary particles that make up the NCM polycrystalline particles also develop cracks and are also part of the rapid cracking (Fig. 4). High cut-off voltages lead to crack in the primary particles, and as the charging voltage rises, the intragranular crack of the primary particles becomes more significant.

Intergranular cracks are more prone to occur due to the combined action of tensile and shear stresses, primarily influenced by internal tensile stresses arising from crystalline structure changes in primary grains and shear stresses caused by volume variations in neighboring primary grains due to their anisotropy. While intergranular cracks are more likely to form, stress concentration along the tips of these cracks can trigger the initiation and propagation of intragranular cracks. However, the initiation and propagation of intragranular cracks are not solely dependent on this effect. Microcracks may also form within primary grains, eventually developing into intragranular cracks that either remain within the grain or extend to the edges as transgranular cracks. We believe that the initiation of intragranular cracks is mostly induced by tensile stress.

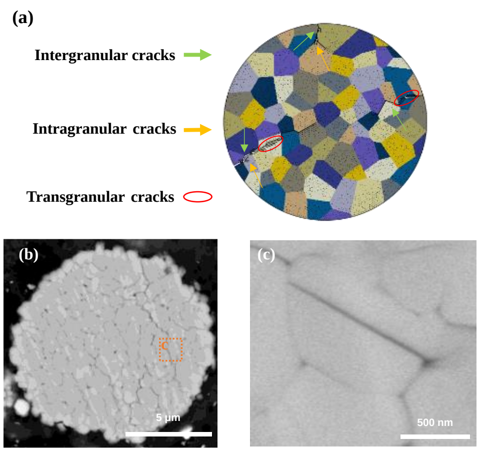

Fig. 4. Intergranular and intragranular cracks (a)numerical result (b)experimental observation (c) logical marked region of (b)

4. CONCLUSIONS

Through numerical simulations and experimental analysis, conditions for intragranular and intergranular cracks propagate and crack closure occurs are identified. The study sheds light on the complex mechanical behaviors of NCM polycrystalline particles subjected to various charge/discharge rates and cutoff voltages. This work contributes to a deeper understanding of the mechanical responses of NCM materials within LIBs, offering critical knowledge for the development of safer and more durable battery technologies. Additionally, it highlights the potential for optimizing battery cycling conditions to mitigate crack-related degradation, thereby extending the lifespan of lithium-ion batteries in practical applications.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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