Energy Proceedings
Vol 43, 2024

ISSN 2004-2965

In-situ Observation of Crack Initiation and Propagation in the NCM811 Cathode particles

Yiming Yao[1,2], Ying Chen[1*], Weiling Luan[1*], Hailong Li[2]

1 Key Laboratory of Advanced Battery Systems and Safety (CPCIF), School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai, 200237, China

2 School of Business, Society and Engineering, Mälardalen University, Västerås, 72123, Sweden
(*Weiling Luan: luan@ecust.edu.cn; *Ying Chen: yingchen96@ecust.edu.cn)

ABSTRACT

Layered nickel-rich oxide $LiNi_xCo_yMn_{1-x-y}O_2$ ($0.6 \leqslant x<1$) is a highly promising positive electrode material. However, the cycling stability of nickel-rich positive electrode materials is limited by particle fracture and a series of side reactions. A comprehensive understanding of particle cracking mechanisms is paramount for material optimization, but crack initiation and propagation have received limited research attention. This paper uses a quasi in-situ SEM observation method and an in-situ optical microscopy observation method to observe crack evolution in real time. The results show rapid cracking behavior under hazardous operating conditions and cracking during cycling under mild conditions. Center cracks and surface cracks are observed during cycling. The observation methods and these insights into the crack behavior offer theoretical guidance for the structural engineering of NCM cathode particles.

Keywords: NCM cathode particle, crack, quasi in-situ SEM, in-situ optical microscopy, prolonged cycling

NONMENCLATURE

Abbreviations

NCM	$LiNi_xCo_yMn_{1-x-y}O_2$
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
FIB	Focused Ion beam

1. INTRODUCTION

Layered nickel-rich oxide $LiNi_xCo_yMn_{1-x-y}O_2$ ($0.6 \leqslant x<1$) is a highly promising positive electrode material due to its high specific capacity, high output voltage, and relatively low cost[1]. However, the cycling stability of nickel-rich positive electrode materials is limited by material degradation. Particle fracture and a series of side reactions caused by it are the primary factors affecting battery capacity decay[2].

The reasons for stress generation in NCM cathode materials can be summarized into three aspects: 1) Various types of defects exist at the atomic scale. Defect-induced rock-salt phase structures can lead to mismatch stress[3]. 2) At the particle scale, the anisotropic volume expansion and contraction result in stress accumulation[4,5]. 3) At the secondary particle scale, the uneven lithium concentration distribution will generate a diffusion-induced stress field[6].

Internal stress in NCM cathode materials induces cracks at micro-defects and grain boundaries. The fracture behavior of NCM cathode particles can be divided into intergranular and intragranular cracks[7]. The operating conditions are the external driving force for particle fracture, which include charge/discharge rate, cutoff voltage, temperature, and cycle number. Wang et al.[8] compared NCM811 cathodes cycled for 50 cycles at different cutoff voltages. Tian et al.[9] distinguished open cracks that extend to the surface and enclosed cracks inside the particles using Nano-CT. However, few studies have described the crack initiation and propagation process in NCM cathode particles during battery operation.

Ex-situ characterization methods necessitate disassembling the battery, so in-situ imaging techniques are pivotal for obtaining insights into the morphological changes of active materials. Three-dimensional X-ray imaging technology represents the optimal means for non-destructively monitoring the internal crack paths within particles[10]. However, the high testing costs and

---

This is a paper for 15th International Conference on Applied Energy (ICAE2023), Dec. 3-7, 2023, Doha, Qatar.

relatively low temporal resolution hinder its application as a research tool. In-situ AFM[11] and in-situ SEM[12] can provide real-time monitoring of the evolution of morphology change. Although both methods offer high spatial resolution, their imaging principles and operating environments limit their suitability for prolonged cycling.

In this study, We employ a quasi-situ observation method based on FIB/SEM to monitor the evolution of cracks within the cross-section of a single particle. The coin cell with a glass window is devised. By combining the single-particle cross-section observation method with the in-situ coin cell, real-time monitoring of the morphology of NCM cathode particles during prolonged cycling can be achieved through optical microscopy.

2. MATERIAL AND METHODS

2.1 Preparation of Electrodes and coin cells

The NCM electrode is manufactured from a surly with the mass ratio of 8:1:1, graphite as active materials, acetylene black as the conductive agent, and polyvinylidene fluoride as the binder. The polished slurry is evenly coated on the aluminium current collector. CR2016 cells and in-situ coin cells with the working electrode of NCM and counter electrode of sufficient Li plate, infiltrated with 1.0 M LiPF6 in EC: DEC: EMC = 1:1:1 Wt%, are assembled in glove box in argon atmosphere.

2.2 Coin cell electrochemical test

The electrochemical tests are carried out on a battery testing system (CT-4008T, Neware Technology Co., Ltd.) at a constant temperature of 25±0.1℃. The NCM811 half-cells are pre-cycled in the voltage rage from 3.0 V to 4.3 V with a C-rate of 0.1 C for cell activation. The cells are deliberately driven to harsh conditions for the single cycle test to induce crack behavior of active particle.

2.3 Quasi-situ SEM observation of NCM particles

We adopted a quasi-in-situ experimental method[13]. First, a small part of the circular electrode is cut off to obtain a straight edge, and select an angle. Three NCM particles are selected in the observation area and processed by FIB to obtain hemispherical particles. Then, the electrodes are assembled into CR2016 coin cells for cycling. At the end of the charging stage, the cells are disassembled, and the electrodes are took out for re-observation of the designated area. This process is repeated to capture the morphology of the particles after the discharging stage.

Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

2.4 In-situ optical microscope observation of NCM particles

The quasi in-situ SEM observation method cannot achieve real-time monitoring. We have devised an in-situ coin cell shown in Figure 1. The cell is designed with a hole in the casing, and glass is installed within the casing. An in-situ coin cell is assembled, the aluminum current collector is positioned snugly against one side of the negative electrode casing. Micropore is integrated into the aluminum current collector, enabling direct observation of the active layer within the micropore region through the glass window.

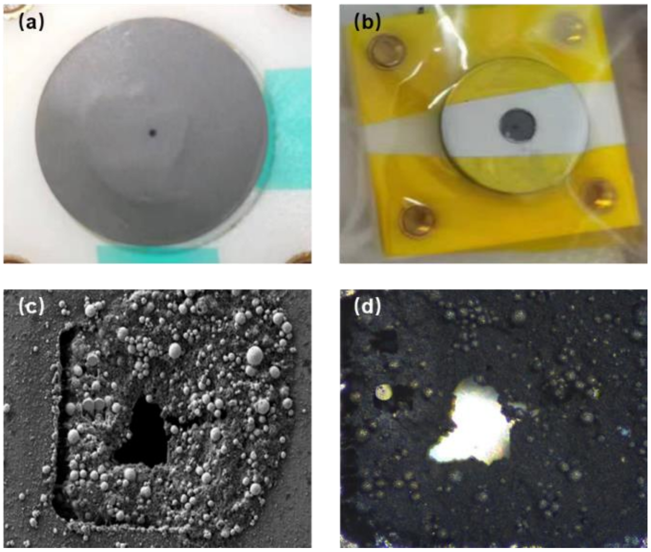

Fig. 1. (a) Micropores on the back of the current collector (b) Observation surface of the in-situ coin cell (c) Activity layer of the microporous region (d) Particle Cross-section particle observed by optical microscope

3. RESULTS AND DISCUSSION

To observe Crack initiation and propagation during the charging and discharging process, quasi in-situ SEM is conducted, shown in Figure 2. Under normal operating conditions at 0.5C and 4.25 V, there is no significant change in the morphology of cross-section particles during charging. After discharging, partial grain boundaries of primary particles are widened. It is indicated that the connection between primary particles becomes weak. Microcracks occur during the charging process under high voltage conditions at 0.5C and 4.9 V. After discharging, the microcracks develop into a main crack that almost runs through the particle, and a high density of microcracks is initiated. Under fast charging conditions at 6C and 4.25V, a significant crack can be observed at the center of the particle. Unlike the high voltage condition, main cracks close during the discharge process. The single-cycle observation shows that high voltage and high rate are harmful conditions for particle structure. The different evolution process is due to the different generation mechanism of diffusion-induced stress under different operating conditions.

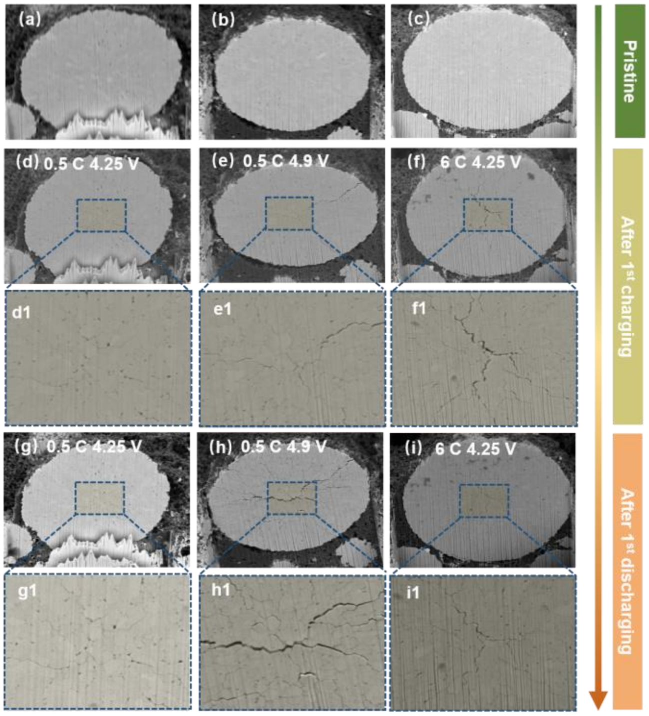

Fig. 2. Crack initiation and propagation during charging and discharging process (a)(d)(g) Normal condtion ; (b)(e)(h) High voltage condition; (c)(f)(i) High rate condition

Figure 3 illustrates the initiation and propagation of cracks in NCM particles during cycling at a 1C rate.

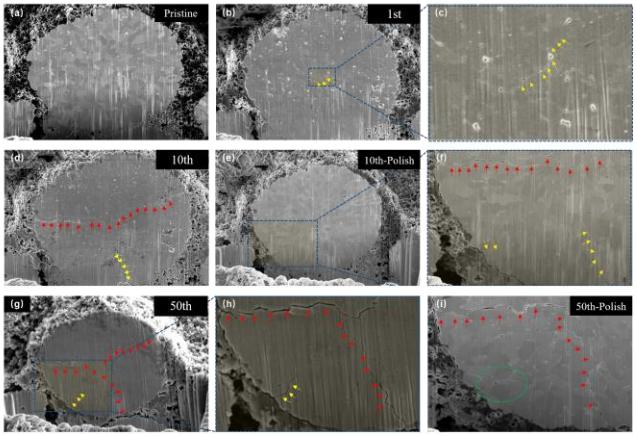

Fig. 3. Crack initiation and propagation during prolonged 1C cycling

Under severe operating conditions, NCM cathode particles often exhibit severe cracking at the beginning of the cycling process. When conditions are relatively mild, NCM cathode particles endure a certain degree of cyclic loading. The damage to NCM cathode particles accumulates continuously throughout the cycling process until particle fracture occurs. Figure 4 illustrates the initiation and propagation of cracks in NCM particles during cycling at a 1C rate.

After the first cycle, only a microcrack is present at the center of the particle. As cycling progresses, this central crack extends into a distinct main crack, and cracks start to initiate at the surface of the particle. The cracks at the surface of the particle propagate towards the center and intersect with the primary crack.

In order to achieve real-time observation of the crack evolution process in NCM cathode particles, we conducted in-situ optical microscopy observations. Although some spatial resolution is sacrificed, the entire crack evolution process could be documented. Figure 4 presents the observation results based on in-situ optical microscopy. The primary crack at the center of the particle and the cracks propagating inward from the surface of the particle can be clearly discerned.

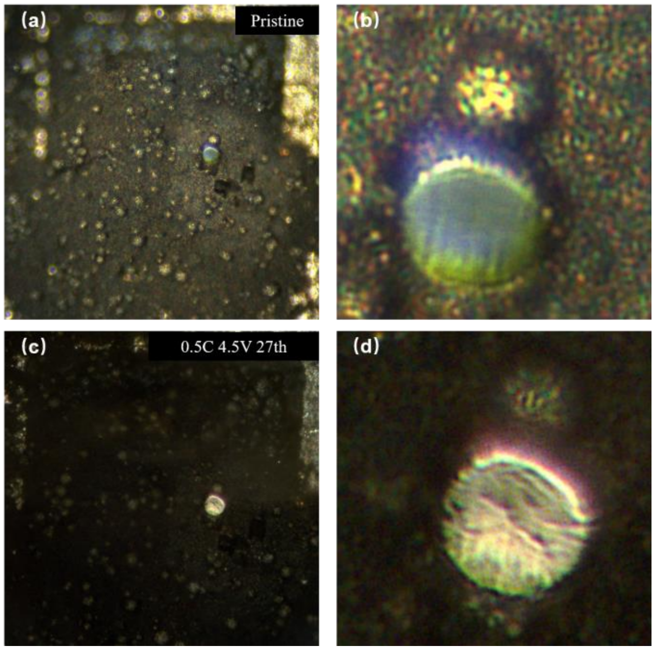

Fig. 4. In-situ optical microscopy observation of NCM cathode particle

4. CONCLUSIONS

This paper studies the crack initiation and propagation in the NCM811 cathode particle by in-situ observation methods. Quasi in-situ SEM observation shows severe cracking at the beginning of the cycling process under hazardous operating conditions, and cracks accumulate during prolonged cycling under mild conditions. The divergent paths of crack propagation signify variations in the driving forces behind crack initiation. The distribution of stress fields determines the characteristics of cracks. Under the condition of high cut-off voltage, anisotropic volume changes more severely. Under the high rate condition, the uneven diffusion of lithium-ion leads to the difference in lithium-ion concentration, which produces tensile and compressive stress. The cracks from the surface exhibit nearly complete radial propagation, implying their origin from stress concentration due to localized loading on the particle surface. In addition, an in-situ optical microscopy observation method has been proposed, which achieves real-time observation of crack initiation and propagation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support from the China Scholarship Council, the National Natural Science Foundation of China (52375144 and 52205153), the foundation by China Postdoctoral Science Foundation (2022M721138 and 2023T160216) during the course of this work.

DECLARATION OF INTEREST STATEMENT

I declare that none of the authors involved above have known competing financial interests or personal relationships. It is unlikely to affect the work reported in this article. All authors read and approved the final manuscript.

REFERENCE

[1] Jamil S, Wang G, Fasehullah M, Xu M. Challenges and prospects of nickel-rich layered oxide cathode material. J Alloy Compd 2022;909:164727.

[2] Li J, Zhou Z, Luo Z, He Z, Zheng J, Li Y, Mao J, Dai K. Microcrack generation and modification of Ni-rich cathodes for Li-ion batteries: A review. Sustain Mater Techno 2021;29:e00305.

[3] De Vasconcelos LS, Xu R, Xu Z, Zhang J, Sharma N, Shah SR, Han J, He X, Wu X, Sun H. Chemomechanics of rechargeable batteries: status, theories, and perspectives. Chem Rev 2022;122:13043-13107.

[4] Kondrakov AO, Schmidt A, Xu J, Geßwein H, Mönig R, Hartmann P, Janek J. Anisotropic lattice strain and mechanical degradation of high-and low-nickel NCM cathode materials for Li-ion batteries. J Phys Chem C 2017;121:3286-3294.

[5] Lee SY, Park GS, Jung C, Ko DS, Park SY, Kim HG, Hong SH, Zhu Y, Kim M. Revisiting primary particles in layered lithium transition-metal oxides and their impact on structural degradation. Adv Sci 2019;6:1800843.

[6] Xia S, Mu L, Xu Z, Wang J, Wei C, Liu L, Pianetta P, Zhao K, Yu X, Lin F. Chemomechanical interplay of layered cathode materials undergoing fast charging in lithium batteries. Nano Energy 2018;53:753-762.

[7] Yan P, Zheng J, Gu M, Xiao J, Zhang JG, Wang CM. Intragranular cracking as a critical barrier for high-voltage usage of layer-structured cathode for lithium-ion batteries. Nat Commun 2017;8:14101.

[8] Wang L, Su Q, Han B, Shi W, Du G, Wang Y, Li H, Gu L, Zhao W, Ding S. Unraveling the degradation mechanism of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ at the high cut-off voltage for lithium ion batteries. J Energy Chem 2023;77:428-437.

[9] Tian F, Ben L, Yu H, Ji H, Zhao W, Monteiro R, Ribas RM, Zhu Y, Huang X. Understanding high-temperature cycling-induced crack evolution and associated atomic-scale structure in a Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ layered cathode material. Nano Energy 2022;98:107222.

[10] Mao Y, Wang X, Xia S, Zhang K, Wei C, Bak S, Shadike Z, Liu X, Yang Y, Xu R. High-voltage charging-induced strain, heterogeneity, and micro-cracks in secondary particles of a nickel-rich layered cathode material. Adv Funct Mater 2019;29:1900247.

[11] Hu J, Li L, Hu E, Chae S, Jia H, Liu T, Wu B, Bi Y, Amine K, Wang C. Mesoscale-architecture-based crack evolution dictating cycling stability of advanced lithium ion batteries. Nano Energy 2021;79:105420.

[12] Cheng X, Li Y, Cao T, Wu R, Wang M, Liu H, Liu X, Lu J, Zhang Y. Real-time observation of chemomechanical breakdown in a layered nickel-rich oxide cathode realized by in situ scanning electron microscopy. ACS Energy Lett 2021;6:1703-1710.

[13] Wu H, Qin C, Wang K, Han X, Sui M, Yan P. Revealing two distinctive intergranular cracking mechanisms of Ni-rich layered cathode by cross-sectional scanning electron microscopy. J Power Sources 2021;503:230066.