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MECHANICAL DEGRADATION BEHAVIOR OF SINGLE CRYSTAL $LINI_XMN_YCO_ZO_2$ CATHODE IN LI-ION BATTERY BY INDENTATION ANALYSIS

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Abstract

$LiNi_xMn_yCo_zO_2$ (NMC) is among the most promising cathode materials for commercial Li-ion batteries due to its high electrochemical performance. However, NMC composite cathode is still plagued with limited cyclic performance, which is influenced by its structural stability during the cycling process. The cathode, which comprises of the active material, polymeric binder, and porous conductive matrix, often exhibits large structural variation during the electrochemical cycling process. This inevitably increases the challenge of measuring the mechanical properties of the material. Even though single crystal NMC possesses better stability as compared to the polycrystalline NMC, the electrochemical performance degradation of single crystal NMC cathode remains relatively unexplored. Different sample preparation methods are compared systematically in accordance to the previous report, and a new method of sample preparation is proposed. Nanoindentation instrument is used to measure the elastic modulus and hardness of the single crystal NMC particles. The measured elastic modulus and hardness of NMC particles, under different electrochemical environments, are dependent on a large number of nanoindentation experiments and statistical analysis of the result obtained from the carefully prepared samples. The sample preparation method is the key factor that can significantly influence the nanoindentation experiment results of the NMC particles. This work shows that the mechanical properties of the single crystal NMC particles degrade significantly with number of electrochemical cycles. The decreasing elastic modulus with the number of electrochemical cycles can be fitted using a two-parameter logarithm model.

Keywords: single crystal NMC; degradation; elastic modulus; hardness;

electrochemical cycles

1. INTRODUCTION

Layered lithium nickel manganese cobalt oxide, $LiNi_xMn_yCo_zO_2$ (NMC), is considered as one of the most promising materials as the cathode for next-generation Li-ion battery (LIB) due to its high energy density and cost effectiveness [1][2]. Despite the advantages that NMC can potentially bring as the LIB cathode, one of the most critical flaws of NMC is its structural stability. This can influence the cyclic performance of the NMC cathode, which ultimately hinders the mass adoption of NMC in commercial LIB application [3]. As such, one of the major challenges in the development of high performing LIB is to address the mechanical degradation of the material, which demands urgent attention from researchers.

To further enhance the performance of LIB, a deeper understanding behind the fading mechanism of these materials has to be attained. From a multi-physical perspective, the mechanical behaviors of NMC composite cathodes are coupled with their electrochemical performances [4]. During the repeated charge-discharge process, defects such as dislocations, cavities, and cracks may appear throughout the active material. The presence of these defects can also lead to the rupturing of the solid-electrolyte interface (SEI) layer, and even causing the electrodes to be separated from the conductive network [5-6]. The repeated expansion and contraction of NMC particles can induce a mechanical stress within the material, which subsequently leads to the pulverization of the material. Such mechanical degradation in the material can result in the capacity fading of the batteries [7]. In addition, the mechanical properties of cathode are essential input parameters for the further simulation model.

The elastic modulus, E, and hardness, H, of NMC are measured and analyzed using a series of well-designed nanoindentation tests. For the NMC nanoindentation tests, the sample preparation process is critical for achieving high accuracy in the measured results. This is mainly due to the high requirements for the sample flatness and surface roughness. For instance, a set of nanoindentation experiments was performed by K. Zhao research group to study the mechanical properties of the polycrystalline NCM cathode (hierarchical meatball structure). In their work, they studied its individual constituent components[8], single particle for its variation over state of charge and cycle numbers[9], and the influence of electrolyte soaking on conductive matrix with different degrees of porosity [10]. D. Dang et al.[11] studied the fracture behavior of the polycrystalline $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ at both the primary and secondary particle levels. It was suggested that the fracture of the NMC secondary particles were dominated by inter-granular fracture. J. Li et al. [12-13] compared a single-crystal $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) material (~3 μm) with conventional polycrystalline NMC532 material (~10 μm), and it was discovered that the single-crystal NMC532 was able to demonstrate better stability as compared to the polycrystalline NMC532. Even though few papers have reported the elastic modulus and hardness of the NMC, they are mainly for the polycrystalline NCM cathode. This means that the behavior of single crystal NMC electrode remains to be relatively unexplored.

In this work, different sample preparation methods are compared systematically using nanoindentation test, according to the previous report. In addition, we propose a method to measure the elastic modulus and hardness of the single crystal $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) particle with the consideration to the impact of repeated charge-discharge cycles. Furthermore, the experimental data can be fitted to the two-parameter logarithm model. The quantitative variation of the mechanical properties of the single crystal NMC with the number of cycle can provide useful information for the computational modeling of the chemo-mechanical behavior of the batteries. As such, based on this work, we are able to shed some insight in the accumulated damage to the NMC material over cycles.

2. MATERIALS AND METHODS

2.1 Sample preparation

In this work, NMC samples are prepared in three different forms: a) NMC cathode, b) sintered NMC, and c) NMC powder obtained from the cathode.

To prepare the NMC cathode, single-crystal NMC powder (used as received), polyvinylidene fluoride (PVDF), and carbon black (CB), in the weight ratio of 80:10:10, are mixed in N-methylpyrrolidone (NMP). The mixture is grinded until a constant slurry is obtained, and this slurry is then coated onto a Al current collector. The mass loading of the coated NCM523 on the current collector is about 2.7 mg/cm^2. In order to remove the volatile solvent and moisture, the as-coated electrode is dried in a vacuum oven at 120 °C overnight, before storing in an argon-filled glovebox (O_2 and H_2O contents of < 0.5 ppm). Figure 1a shows the scanning electron microscope (SEM) image of the cathode. It can be observed that the microstructure of the cathode consists of irregular single-crystal NMC particles, with an average diameter of ~ 3 μm. Figure 1b shows the transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images of NMC. According to the TEM result, NMC possesses irregular nanoparticle morphology which is consistent with the SEM result. It can be observed from the inset of Figure 1b that the lattice fringes are present in the crystalized structure.

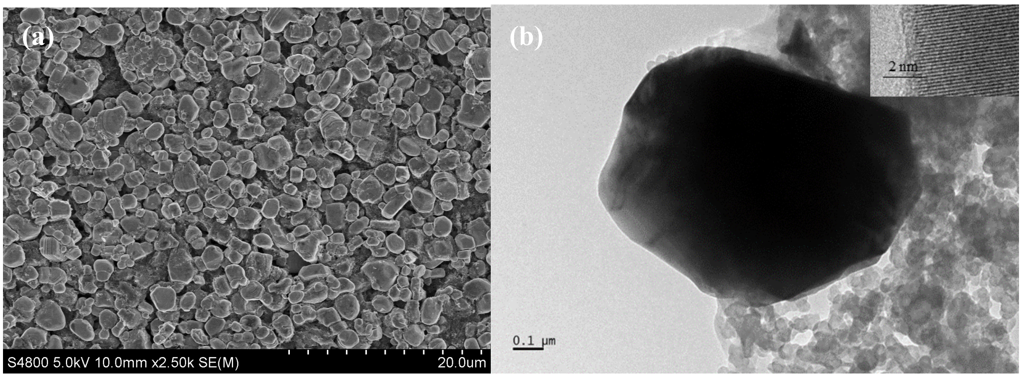


Figure 1: (a) SEM image of the single-crystal NMC532 cathode, and (b) TEM of the single-crystal NMC particle (inset showing the HRTEM image)

After which, the as-fabricated electrode is assembled into a CR-2025 coin cell in the Ar-filled glove box so as to evaluate its electrochemical performance. In the coin cell assembly, NMC is used as the cathode, Li foil is used as the anode, and Celgard-2500 membrane is used as the separator. The electrolyte used in the coin cell is composed of a 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate in the volume ratio of 1:1. To ensure a complete wetting of the electrode by the electrolyte, all assembled cells are left undisturbed overnight before conducting the electrochemical tests.

Cyclic tests are designed to investigate the influence of the cycle number with the mechanical properties of NMC. Land Cell System (CT2001A, Wuhan Jinnuo Electronic Co. Ltd, Wuhan China) is used to study the electrochemical performance of assembled coin cells. The cells are cycled between a potential window of 2.8 and 4.3V (vs. Li/Li+) using a Biologic VSP potentiostat at different current densities. All cells are activated by cycling charging rate of 0.1C, 0.2C, and 0.5C, separately. After the cyclic tests, the post-mortem investigations are carried out. The cycled cathode is carefully removed from the coin cell in an Ar-filled glovebox. The electrode is then washed several times with DMC, and it is later dried in a vacuum oven at room temperature for 3 h.

To prepare the sintered NMC, the as-received NMC powder is firstly milled to ensure uniform particle size. 1g milled NMC powder is then pressed using a die at an applied compressive load of 50 MPa for 10 min. To maintain the disk shape of the compressed powder, the pellet is sintered at 1000 °C for 10 h at a ramping rate of 5°C/min. After that, the pellet is left to cool in the furnace before retrieving.

The pristine NMC, sintered NMC, and cycled NMC samples are cold mounted and polished before the indentation experiments. It should be noted that the polishing process is a vital step in the entire sample preparation, as the surface of the nanoindentation samples should be sufficiently smooth and flat. It is more challenging to achieve good polishing result for the prepared electrode, as compared to the sintered sample and powder sample. For the pristine NMC, the pristine electrode and the powder scraped from the active material layer (consisting of NMC particle, PVDF, and CB) are both studied. As for cycled NMC sample, the powder is collected by scraping the active material from the cycled cathode.

All NMC samples are placed in a cold mounting mold with a diameter of 25 mm. The mounting fluid, consisting of acrylic powder and liquid hardener in a mass ratio of 1:0.8, is prepared. The obtained mounting fluid is then added into the mold to cover the NMC samples. When the hardening process is completed, the casted sample is removed from the mold. The surface of the sample is polished using micro-diamond compounds. Grit sizes of 3 and 1 μm are used for the initial polishing process and then 0.05 μm colloidal silica suspension is applied for the final polishing process. The sample is polished until a mirror-like surface is obtained. After the final polishing process, the as-polished samples are later cleaned with isopropyl alcohol and transferred to the glovebox for nanoindentation test.

The optical microscopic analyses, presented in Fig. 2, show the morphology of the electrode sheet sample, electrode powder sample, and sintered samples after cold mounting and polishing process. The electrode sample, shown in Fig.2a, is prepared from the cathode used in the coin cell. The substrates surrounding the NMC particles are PVDF and CB. As shown in Fig.2b, the electrode sheet sample used in the nanoindentation test requires extremely high flatness, otherwise it can become more challenging to perform the subsequent polishing treatments. Attention is needed to ensure the flatness of the electrode in the cold mounting material. In addition, the surface finishing requirements for the electrode sample are difficult to achieve. The active material layer of the electrode (consisting of NMC particle, PVDF, and CB) could be easily polished off from the current collector (Al foil), while the polished part is necessary for the indentation test. Fig. 2c and Fig. 2d show the powder sample scratched from the cathode and the matrix around the NMC particle, respectively. Fig. 2e and Fig. 2f present the sintered NMC sample after cold mounting and polishing.

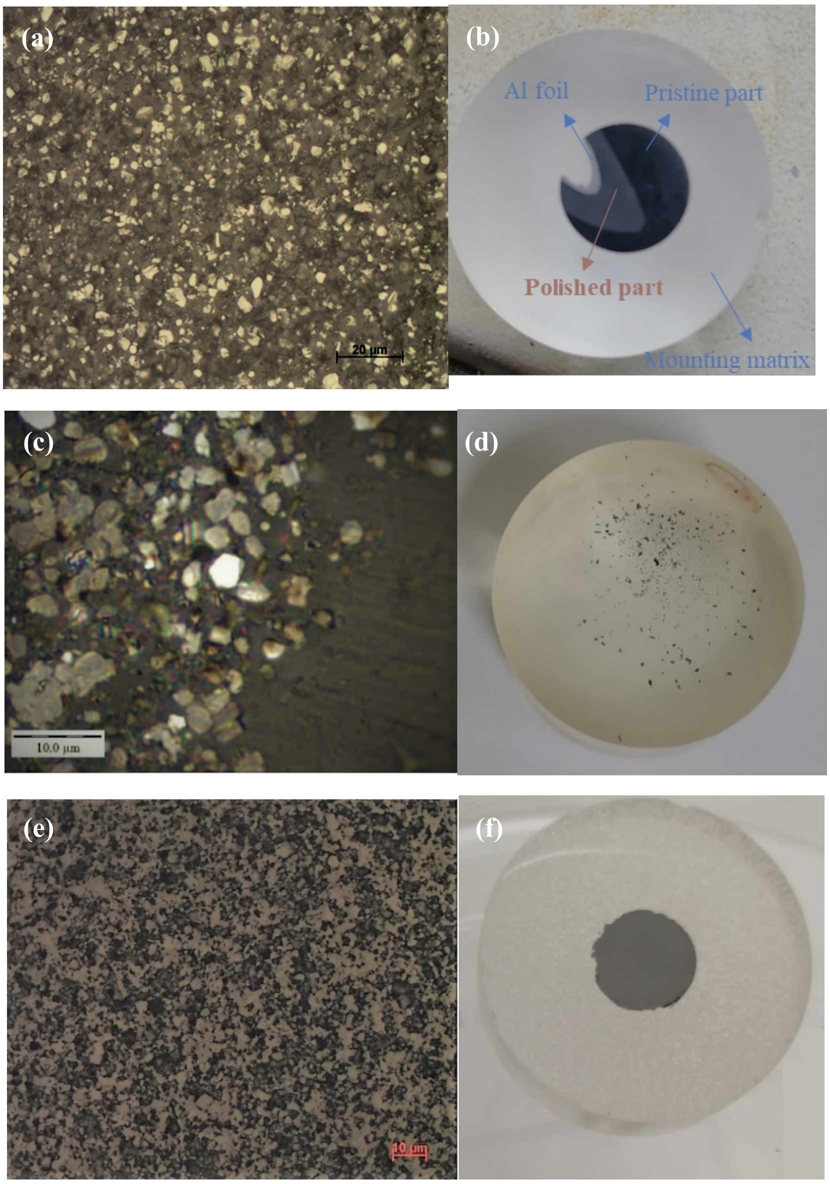


Figure 2: NMC sample after mounting and polishing process. (a) Optical microscopic image of electrode sheet sample, (b) electrode sheet sample for nanoindentation, (c) optical microscopic image of powder sample removed from electrode, (d) cathode powder sample for nanoindentation, (e) optical microscopic image of sintered NMC powder, and (f) sintered NMC sample for nanoindentation

2.2 Nanoindentation measurement

Indentation is one of the major techniques used in the measurement of elastoplastic properties of a material. Such technique can be used when the classical tensile test approach is not feasible, e.g., thin film, very small components, etc. Indentation instrument (Anton Parr NHT3) is used for the measurement of the mechanical properties of NMC samples. Indentation tests are performed using a Berkovich tip according to the Oliver-Pharr method [14]. The indenter is performed under a load control. Poisson ratio of 0.3 is used. To obtain the elastic modulus and hardness of the NMC particles, the particle of interest should be carefully selected and measured. This is due to the possibility of NMC particles buried underneath the cold mounted matrix.

As a result of the non-negligible effect of surface roughness, the experimental accuracy is lower at a low indentation load. On the other hand, a high load may introduce pop-in events such as crack formation or particle sink-in [15]. As such, all tests are performed with appropriate indentation loads under ambient conditions to avoid the generation of noise during the test.

2.3 Material characterization

The microstructure of the NMC is observed under a scanning electron microscope (SEM, T330, JEOL) and transmission electron microscope (TEM, 2100f operated at 200 kV, JOEL). X-ray diffraction (XRD) is recorded using a diffractometer (D-8 Focus, Bruker) with Cu K-alpha radiation in the 2θ range between 12–90° at 100 mA and 40 kV.

3. RESULTS AND DISCUSSION

3.1 Nanoindentation tests of pristine single crystal NMC samples

Factors such as sample preparation methods, substrate surrounding the single crystal NMC particle, nanoindentation load, and the selected particles can significantly influence the experimental results. Thus, in order to systematically compare various sample preparation methods, pristine NMC523 samples (consisting of electrode sheet samples, cathode powder samples and sintered NMC samples) are studied in the nanoindentation test.

According to the previous reports [6-9], sintering method of NMC is used to study the modulus, E, and hardness, H, of pristine NMC particles. Figure 3a shows the elastic modulus, E, and hardness, H, of the NMC particles in the sintered sample (Fig.2e and Fig.2f), under the maximum indentation loads of 3 mN, 5 mN, and 10 mN. The elastic modulus, *E*, and hardness, *H*, measured at 3 mN (226.87±9.35 GPa and 13.9±1.86 GPa, respectively) are higher as compared to the *E* and *H* measured at 5 mN (213.31±18.227 GPa and 12.44±2.27 GPa, respectively). The recorded *E* and *H* at 3 mN are also higher as compared to the *E* and *H* measured at 10 mN (206.19±19.23 GPa and 10.97±2.89 GPa, respectively). In addition, it is noticed that the error bar increases with the increase in the applied load. The reduction in *E* and the increase in error bar at high load may be due to the pop-in events that can occur when a high load is applied to the particles. This is shown by the sudden drop in the load-displacement curve as presented in Fig.3b. The sudden increase in the displacement into the surface can cause an overestimation in the indentation depth and the contact area. This in turn can lead to a lower measured values as compared to the intrinsic values of NMC particles. Figure 4a and 4b show the SEM images of the pristine NMC powder before and after sintering, respectively. It is shown that the surface morphology of the powder is changed after the sintering process. The XRD comparison shown in Fig. 4c reveals no obvious change in the lattice structure after the sintering process.

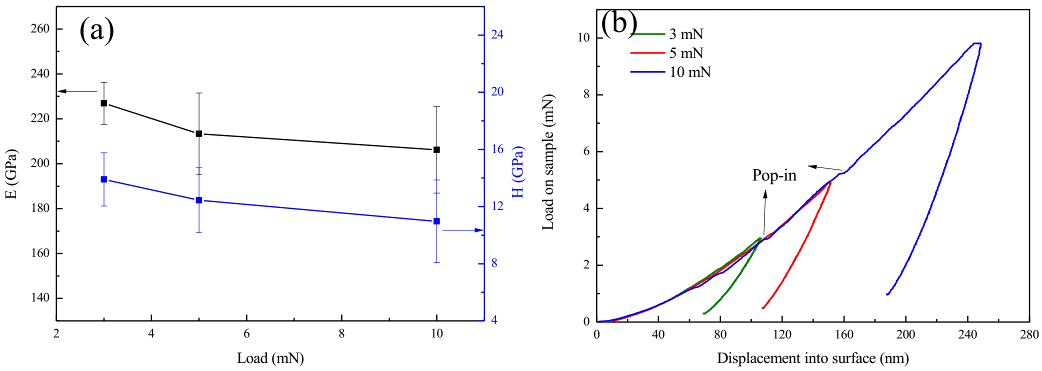
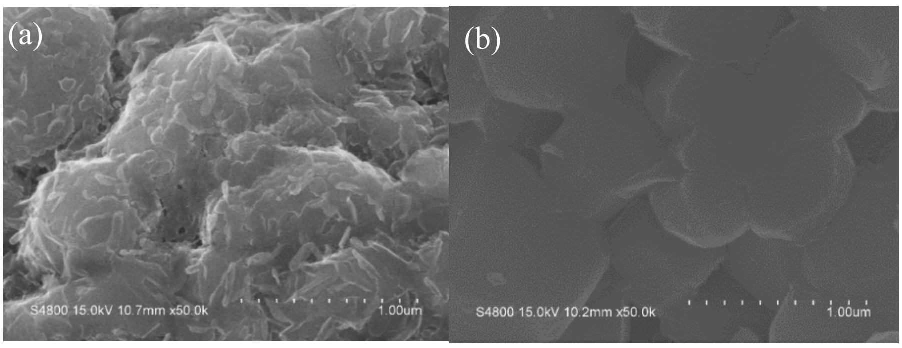


Figure 3: Mechanical characterization of the pristine sintered NMC samples. (a) Elastic modulus, E, and hardness, H, of NMC particles measured under the load of 3 mN, 5 mN, and 10 mN, (b) load-displacement curve of nanoindentation of primary sintered NMC samples under 3 mN, 5 mN, and 10 mN



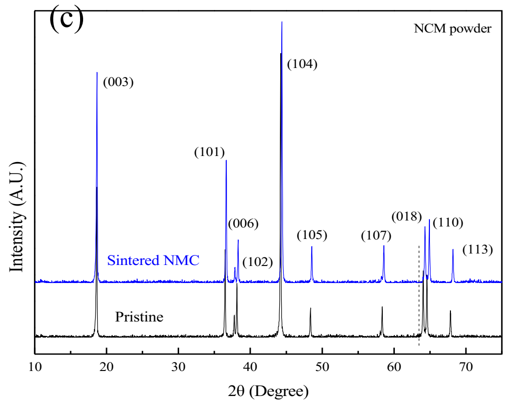
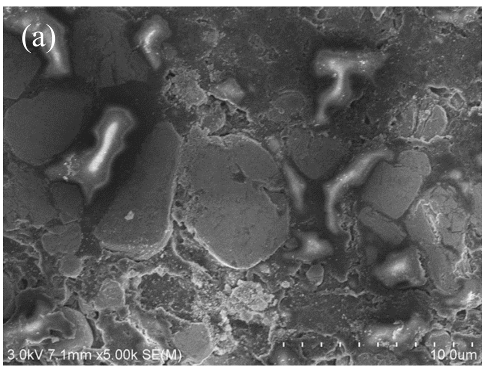


Figure 4: (a) SEM image of the pristine NMC powder before sintering, (b) SEM image of the pristine NMC powder after sintering, and the (c) XRD profiles of NMC powder before and after sintering

To investigate the mechanical properties of the NMC particles in the electrode, cathode sheet samples (Fig.2b) are prepared for the nanoindentation test. The pristine cathode sheet is prepared for the coin cell assembly and it is used in the electrochemical cycling process. Figure 5a shows the SEM image of the polished electrode sheet sample, whereby it can be observed that the NMC particles are embedded in the PVDF and CB matrix, which are included in the electrode preparation. Figure 5b presents the elastic modulus, *E*, and hardness, *H*, of 10 chosen indentation points on the NMC particles of the primary electrode sheet. The average *E* and *H* for NMC (indicated in the red box) are 40 GPa and 2.2 GPa, respectively. The other three points cannot be used since the measured values are greatly affected by the quality of the surface (Fig.2a). Comparing with the mechanical characterization results of NMC particles in the sintered sample, *E* and *H* of the electrode sheet sample are smaller. This result may be due to the sintering process and the presence of different matrix.



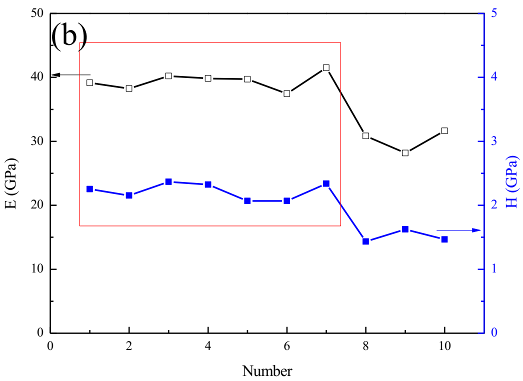
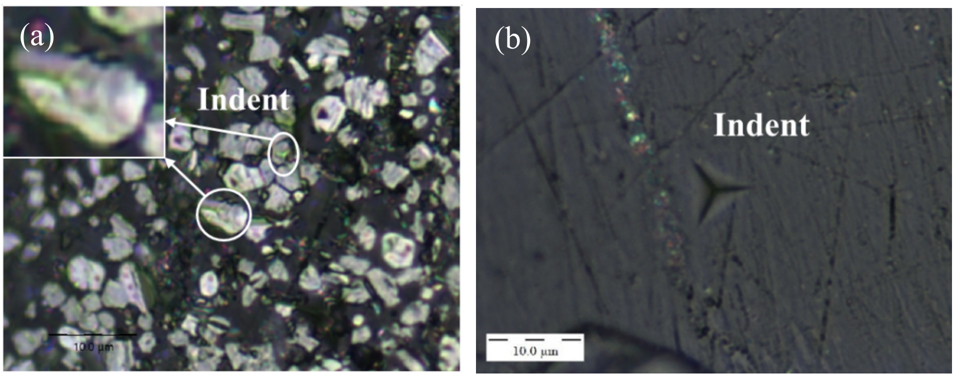


Figure 5: (a) SEM of the electrode sheet sample, (b) elastic modulus, E, and hardness, H, of the NMC particles under 3 mN

It is of great significance to study the mechanical properties of NMC particles in the electrode sheet sample. However, it is more challenging to polish the electrode sheet sample (Fig.2b) as compared to cathode powder sample and sintered NMC sample. This translate to the greater influence of the sample surface roughness on the indentation results. To focus on the NMC particles and to consider the indentation sample preparation process, cathode powder is collected by scraping the electrode (Fig.2c and Fig.2d). Fig. 6a and Fig. 6b show the morphologies of NMC particles and cold mounting matrix of cathode powder sample after nanoindentation test. Each of the NMC particle in the cathode powder sample is surrounded by the cold mounted composite material. Figure 6c shows the load-displacement plot of pristine NMC particles and acrylic mounting matrix in the cathode powder nanoindentation sample at a maximum load of 3 mN, with 10 chosen indentation points. It is worth noting that there is no observable pop-in at this load range. The average elastic modulus, *E*, and hardness, *H*, of NMC particles are 10.5 GPa and 0.46 GPa, respectively. The *E* and *H* values of NMC are higher than those of the acrylic mounting matrix, i.e., *E*=1.77 GPa and *H*=0.095 GPa. The measured results of NMC particles for the electrode powder sample derivate from those of the NMC sintered samples and electrode sheet samples. This derivation can be largely explained by the difference in the matrix surrounding the NMC particles and the changes in the mechanical properties of the surface of NMC after the sintering process.



(c)

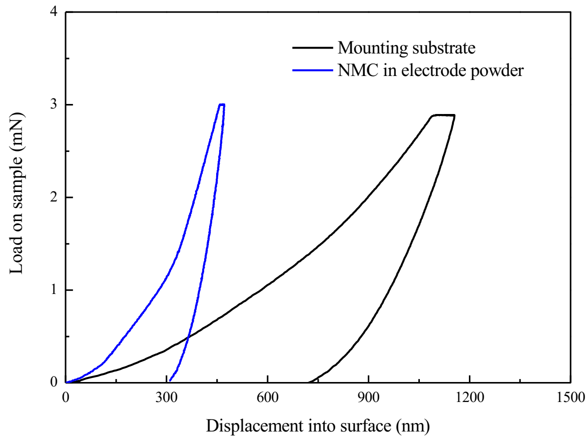


Figure 6: (a) Optical microscopic image of the electrode powder sample, (b) optical microscopic image of the cold mounting material after nanoindentation, and (c) load-displacement curve of nanoindentation of primary NMC particles in cathode powder nanoindentation samples under 3 mN

Substrate effect is one of the leading causes in the nanoindentation tests for NMC523 due to their small particle size (~3 μm). It is worth mentioning that the cathode powder sample could be used to study the influence of the electrochemical cycling process. After the coin cell is disassembled, the electrode is removed. On the other hand, the material obtained from powder sintering method is not available after charge-discharge test. Therefore, in this paper, to study the effect of electrochemical cycles for NMC particles, powder is collected from scraping the electrode.

3.2 The influence of charge-discharge cycles on the mechanical properties of NMC

To study the impact of electrochemical cycles on the mechanical properties of NMC particles, NMC cathode is assembled into a coin cell and it is later electrochemically cycled for a pre-determined number of cycles. After which, nanoindentation tests are performed on the material after specific number of cycles. Figure 7a shows the 1st, 25th, 50th, 75th, and 100th charge-discharge curves of the NMC/Li half-cell, recorded at a charging rate of 1C. It can be observed that the capacity obtained in 1st cycle decays faster as compared to the subsequent cycles. As shown in Fig.7b, the electrochemical properties of cells are consistent with each other and can be prepared for the indentation tests. The capacity retention of cell degrades with the number of cycle, with a ~83.9% capacity retention after 100 cycles. The SEM images presented in the insets of Fig. 7b show that the pristine and cycled NMC particles after 100 cycles, It can be clearly observed that as a result of the lithiation and delithiation process, NMC particles break and cluster together after 100 cycles.

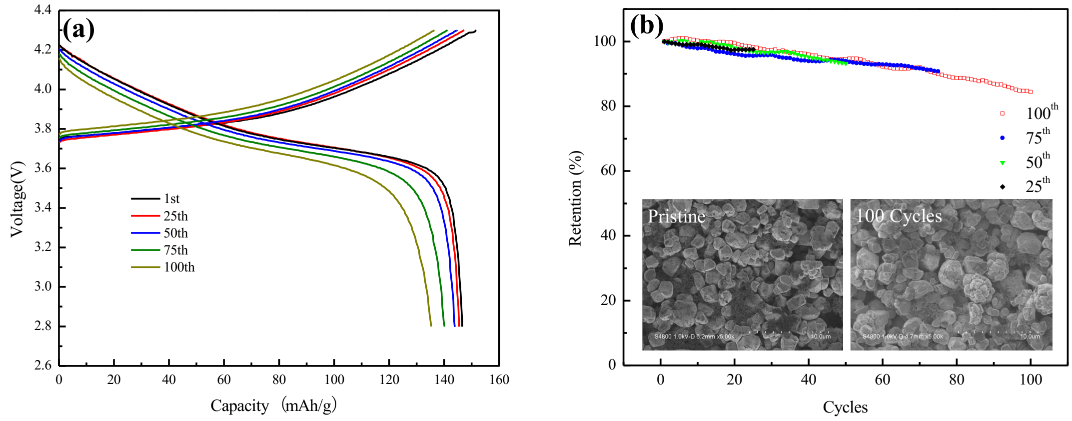


Figure 7: (a) Electrochemical performance of NMC//Li half-cell at the current density of 1C in the 1st, 25th, 50th, 75th, and 100th cycles in the potential window of 2.8-4.3 V, and the (b) capacity decay with the cycle number (insets showing the corresponding SEM images of the pristine NMC cathode and NMC cathode after cycling for 100 cycles)

Figure 8 reveals the degradation of the mechanical properties of NMC particles with the number of cycles. After 100 cycles, the elastic modulus, *E*, and the hardness, *H*, of the fully lithiated NMC particles are reduced to 6.95 ± 0.7 GPa and 0.24 ± 0.03 GPa, respectively. It is interesting to note that E and H decay the fastest after the first cycle. This significant decrease in *E* and *H* of NMC particles may be attributed to the crystallinity loss in NMC after the initial electrochemical cycle [16]. The degradation of mechanical properties with the number of cycles can be explained by the Li^+ insertion-extraction mechanism during the discharge-charge process. Such Li^+ intercalation-deintercalation within the material framework can lead to volume expansion and contraction. This impact is particularly damaging to the material during pro-longed cycling process whereby the material will experience repeated volume expansion and contraction. This repeated volume change can lead to the initiation and propagation of crack, which can ultimately lead to the pulverization of the NMC particles. The accumulation of the microstructural damage in the material caused by the electrochemical cycling process can be observed in the experiment (Fig.7b inset). In fact, the structural damage in the NMC particles may not fully account for the degradation of its mechanical properties with the number of cycles. The lattice distortion and layered structure change caused by cation mixing can also influence the mechanical properties of NMC particles. Specifically, Li^+ is extracted from the lattice of the layered structure, then the transition metal (TM) ion (mainly Ni^{2+}, similar size of Li^+) migrates to the vacant Li site and occupy it. This process contributes to the reduction of elastic modulus, *E*, and hardness, *H*, of the material.

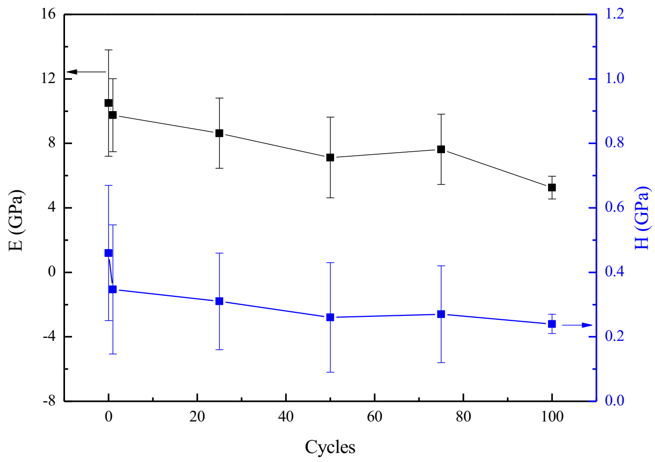


Figure 8: Elastic modulus, E, and hardness, H, of NMC particles with the number of cycles

To reduce the impact of the experimental polishing process and cold mounting matrix on the measured nanoindentation results of the NMC particles, we analyze the relationship between the degradation rate of elastic modulus with the number of charge-discharge cycle, as shown in Fig.9, where E-degradation rate is defined as below:

$$E - \text{degration rate} = (E_0 - E_c)/E_0 \tag{1}$$

where, E_0 represents the elastic modulus of the pristine NMC particles, and E_c is the current measured elastic modulus of NMC particles at certain cycles.

Figure 9 shows that degradation rate of the elastic modulus of NMC, whereby it varies sharply at the beginning of the cycle. The degradation rate then increases gradually with the number of charge-discharge cycle, which is consistent with results shown in Fig.8. We propose the use of two-parameter logarithm model to fit the degradation rate, E, as a function of the cycle number, as presented in the following equation.

$$y = a * ln(x + b) \tag{2}$$

where, y is the degradation rate of the elastic modulus and x is the number of the electrochemical cycle. The parameters a and b are fitting parameters, which are 0.070 and 1.12, respectively. The adj. R-square of the fitting curve is 0.93, which shows that the fitting result is a good match with the experimental data.

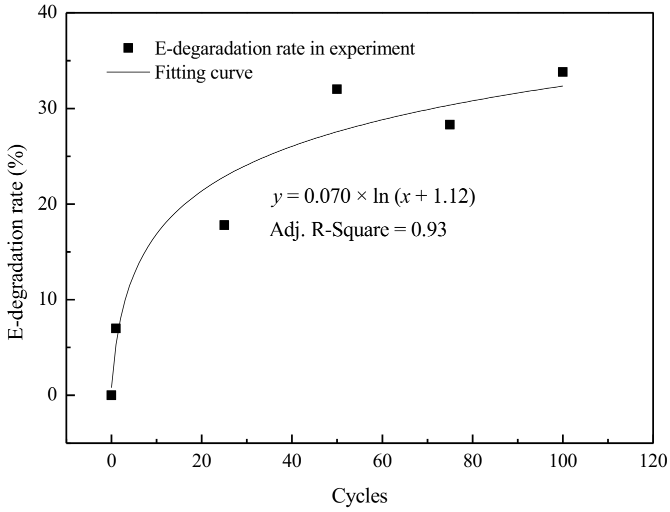


Figure 9: Degradation of elastic modulus determined in the nanoindentation test as a function of cycle number and the fitting curve based on the experimental data

Since the elastic modulus clearly varies during charge-discharge process, elastic modulus that is used in the simulation study should also be considered as a dynamically changing parameter. To study the damage and the stress-strain response of single crystal NMC particles and the lifetime prediction of the LIB, the described fitted equation can be considered as the input parameter for the cycle-dependent elastic modulus in the simulation analysis. Further experimental research at long cycles and various cycle rates to completely understand the mechanical properties degradation is still undergoing.

4. CONCLUSION

The elastic modulus, E, and hardness, H, of the pristine single crystal NMC particles are measured using an nanoindentation instrument, with NMC cathode sheet sample, sintered NMC powder sample, and NMC powder collected from electrode. The influence of the number of charge-discharge cycle on the mechanical properties of NMC particles is also studied. The following conclusions can be made.

1) The cathode powder sample is more suitable for the nanoindentation test as compared to the electrode sheet sample and sintered sample. The measured results may be affected by the sintering process and the matrix surrounding the NMC active material in the nanoindentation sample.

2) The reduction in E and H of the NMC particles with cycle number is mainly due to the accumulation of microstructural damage caused by the repeated electrochemical cycles. E and H decay the fastest during the first cycle, and this may be attributed to the loss in the crystallinity of NMC after the initial electrochemical cycle.

3) The relationship between the degradation rate of elastic modulus with the number of charge-discharge cycle can be well fitted to the two-parameter logarithm model. The dynamically changing degradation rate of elastic modulus can be used as the input parameter in further simulation study of the damage in the material so as to improve the accuracy of the model.

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