

Three-dimensional investigation of cycling-induced microstructural changes in lithium-ion battery cathodes using focused ion beam/scanning electron microscopy

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Abstract

For vehicle electrification, one of the biggest issues for lithium ion batteries is cycle life.

Within this context, the mechanisms at the source of capacity degradation during cycling

are not yet to be fully understood. In this work, we use state-of-the-art FIB-SEM serial

sectioning and imaging techniques to determine the effect of cycling on lithium-ion battery

cathodes. The three-dimensional (3D) microstructural study was performed on both pristine

and cycled $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) and $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13})\text{O}_2$ (HE-NMC)

cathodes. The spatial distribution of active material, carbon-doped binder and pore spaces

were successfully reconstructed by appropriate image processing. Comparisons of NMC

and HE-NMC cathodes after different number of cycles showed only minor increases in the

number of smaller active particles, possibly negligible, considering the intrinsic

microstructure variation within the cathodes. However, the connectivity between carbon-

doped binder additives and active particles in NMC and HE-NMC cathodes, assessed using

a “neighbor counting” method, showed an appreciable decrease after cycling which

indicates a detachment of carbon-doped binder from active particles. This significant

cycling-induced detachment effect between the two phases (e.g., ~22% for HE-NMC) could indicate a loss in electrical connectivity, which may partially explain the capacity fade in the cells.

Keywords: Lithium-ion battery, Focused ion beam tomography, 3D reconstruction, Cathode, Microstructure evolution

1. Introduction

Lithium-ion batteries are promising energy storage systems with high energy density, power density, long cycle life, and have found widespread use in electronic devices and electric vehicles. Nevertheless, advanced automotive electrification is requiring even greater capacity, longer cycle life and lower cost cathode materials. The necessity for such materials has therefore become one of the most important tasks in lithium-ion battery research. LiCoO_2 is a well-known cathode material that has been widely used in commercial markets [1–3]. However, because of its high cost and poor thermal stability, a variety of elements, such as Ni, Mn, and Al [4–7], are used to replace or partially substitute for Co. One family of such substitutions is $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC in short), which belongs to $\bar{R}3m$ crystalline structure and provides both high capacity (~200 mAh/g cycled between 2.5-4.7V) and good thermal stability [8–10]. By partially replacing Co^{3+} with Ni^{2+} and Mn^{4+} , the structural stability of NMC is enhanced, and the cost is greatly reduced due to cheaper price of Ni and Mn compared to Co. Recently, Li-rich layered materials $\text{Li}_{1+x}\text{TM}_{1-x}\text{O}_2$, where the transition metals (TM) can also be Mn, Ni, and Co, etc. have attracted great interest due to their enhanced capacity, over 250 mAh/g when charged above 4.6V, concomitant with oxygen release at 4.4-4.6V [11–13].

However, the layered transition metal oxide cathode materials exhibit structural transformations into spinel or rock-salt structures and electrode–electrolyte side reactions during cycling that can lead to the deterioration of the batteries performance [14-18]. Furthermore, negative electrodes are known to suffer structural changes during Li^+ intercalation/de-intercalation upon cycling, which induce local stresses and lead to microstructure degradation of the electrode. The volumetric changes of graphite (~13%) and more substantially in Si (~300%) anodes have been observed during charge and discharge [19,20]. While the smaller volume changes of the cathode materials are less well recognized, they may turn out to be significant[21].

Although 2D imaging has revealed some evidence of electrode integrity loss [22,23], it is clear that 3D imaging is necessary to provide a complete geometric evolution of the cathode microstructure upon cycling. Focused ion beam in combination with scanning electron microscopy (FIB-SEM) and X-ray tomography techniques are widely used for three-dimensional (3D) reconstruction of energy materials and enable quantitative assessment on their complex microstructures. The 3D structure of electrodes in lithium-ion batteries have been successfully reconstructed and a number of geometric parameters—volume fraction, surface area, particle size distribution and tortuosity have been extensively analyzed [24-38]. X-ray tomography is a non-destructive method which has been applied to a variety of electrode materials to capture their microstructure details [24–31]. With X-ray tomography, the 3D microstructure of graphite and tin (II) oxide negative electrodes were successfully reconstructed and the geometric parameters were analyzed [24,25]. Heat generation was simulated based on the 3D microstructure of the LiCoO_2 cathode acquired

by X-ray nano-computed tomography by Zhu et al. [26]. By tuning the X-ray energies appropriately, an optimum contrast for the cathode active materials $\text{LiCoO}_2/\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ could be achieved [27]. However, one disadvantage of this method is the difficulty of distinguishing the carbon-doped binder from the pore space due to the small particle size and the low X-ray absorbance of the binder phase. Recently, Thiele et al. managed to insert the carbon-binder domain of LiCoO_2 cathode by combining statistical modeling with X-ray tomography [28], but to obtain a complete 3D dataset including all the three phases with good spatial resolution remains a major challenge for X-ray tomography. Additional FIB-SEM 2D information was still needed for creating a complete 3D hierarchical reconstruction of the cathode [29].

With the total volume sampling and higher spatial resolution, the reconstruction of lithium-ion battery electrodes with the FIB-SEM technique has been reported by several groups [32–38]. Using a dual beam FIB-SEM, one can obtain a slice spacing of less than 20 nm—this value is comparable with the pixel resolution of the 2D cross-section plane [39]. In previous work, Ender et al. have successfully reconstructed the LiFePO_4 cathode structure in 3D and carried out some detailed calculations on the microstructure parameters including particle size distribution and tortuosity [32,33]. The 3D microstructure of LiCoO_2 cathode has also been widely studied using FIB-SEM. Wang et al. [34] calculated the tortuosity based on an actual 3D structure while the internal cracks and grain boundaries of LiCoO_2 active particle were discovered, and the influence of these features on batteries' performance was studied by Wilson et al. [35]. Whilst there are many detailed structural

studies of different cathodes, the correlation between 3D microstructural changes and electrochemical cycling remains comparatively unexplored for cathode materials.

Here, we present a semi-quantitative study of structural evolution occurring in the cathodes of lithium-ion batteries following electrochemical cycling. A commercial NMC cathode was successfully reconstructed in 3D using the FIB-SEM technique to resolve each of the three phases: active material, carbon-doped binder additives, and pore spaces of a cathode without any epoxy infiltration. In most cases, the usual approach to prepare FIB sample is to vacuum infiltrate the electrode with epoxy resin and extract the active material phase from the acquired SEM images with almost no contrast between the carbon-binder and the epoxy filled pores [29,30]. Although it has been reported that a better contrast between binder phase and pores can be achieved using silicone resin [27], small features of the binder matrix and pore spaces may be smeared or destroyed by resin infiltration. In our work, a segmentation algorithm was developed to apply refined threshold values and gradient analysis to the 2D images thereby avoiding the need for epoxy infiltration. Furthermore, a lab-scale HE-NMC cathode was studied using FIB-SEM 3D reconstruction. The geometric parameters including volume fraction and particle size distribution were quantitatively analyzed for cycled material. A “neighbor counting” method was used to evaluate the structural changes related to the connectivity of the active material and binder matrix three-dimensionally, thus, providing a three dimensional insight into the battery degradation and a correlation with microstructural changes.

2. Experimental methods

2.1 Sample preparation

A commercial HKE-IMP-0660J0 battery (HECO, Shanghai, China) with $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) as the active material was studied. The battery was fully discharged, then disassembled and dried in a glove box. The NMC cathode sheet was cut into small circular pieces and constructed into coin cells with Li metal as the anode and LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC 1:1-v/v) as the electrolyte, the half-cells were then subjected to 20 and 50 electrochemical cycles, respectively (Supplementary Fig. S1). The cells were then disassembled and dried in the glove box. Note that the NMC cathode taken from a commercial battery may have undergone a few pre-cycles from battery manufacturer. In the following discussion, we refer the coin cell made with the commercial NMC cathode before cycling as a “pristine” sample, which relates to the NMC cathode before the cyclic test in a half-cell. In the following study, we use the microstructure observed in the pristine NMC sample as a starting point (with pre-existing features generated from pre-cycles) in contrast to the sample after cycling test.

The lab-scale $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.56}\text{Co}_{0.13})\text{O}_2$ (HE-NMC) cathode material was synthesized using the co-precipitation method. The transition metal acetates: $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot x\text{H}_2\text{O}$ (99+%, Alfa Aesar), $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot x\text{H}_2\text{O}$ (99+%, Arcros Organics), and $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot x\text{H}_2\text{O}$ (99+%, Alfa Aesar) were dissolved in de-ionized water and added to a solution of KOH (0.1M) to form the mixed transition metal hydroxide precipitate. The precipitate was filtered and washed with de-ionized water to remove the residual KOH and then dried overnight at 100°C . The dried product was mixed with a 3% excess lithium hydroxide and heated for 24 hours in air at 900°C .

The HE-NMC cathode was prepared with 80% HE-NMC active material, 10% super

carbon and 10% PVDF polymer. The HE-NMC cathodes were constructed into half cells with 1M LiPF₆ EC/DMC (1:2-v/v) as electrolyte and subjected to 1 and 50 electrochemical cycles, respectively (Supplementary Fig. S2). The cells were then disassembled and dried in a glove box. All the cathode samples were positioned on the SEM stages using conducting carbon tape, with silver paste applied at the edge to enhance the conductivity.

2.2 FIB-SEM microscopy

The samples were serial-sectioned and imaged with a Zeiss NVision 40 dual beam FIB-SEM equipped with a gallium (Ga) ion beam source and a Schottky Field Emission Gun (FEG). In general, the samples were milled by a high-energy Ga ion beam and a series of cross-sectional SEM images were acquired with the electron beam. Then, the sliced images were converted into a 3D dataset and analyzed. A tungsten (W) coating was deposited on top of the region of interest (ROI) to protect the sample's intrinsic surface morphology from high-energy Ga ions and reduce curtaining effects on the sectioned face. Fig. 1 (a) shows an SEM image of a NMC cathode after serial sectioning. As the duration time of the serial sectioning process is strongly dependent on the intensity of the ion beam used for milling (faster milling uses higher current), and the quality of the section is affected by the ion beam size, a relatively small ion beam current (1.5nA at 30KeV) was selected to mill and polish the cutting surface, in order to produce an ideal surface flatness with a reasonable time duration.

Because the incident electron beam does not scan the sectioned surface normal to the sectioning plane due to the intrinsic angle between the electron beam column and the ion beam column (54° from the electron beam and parallel to the surface), the apparent tilt (36°)

of the image was compensated by software before image collection, as shown in the schematic diagram in Fig. 1 (b). Also due to the geometry of the ion and electron beam columns with respect to the sample surface, an apparent image drift is generated with each slice. This effect was corrected by software using reference markers as the images will appear to shift upwards during serial sectioning. Markers were also used to calibrate and adjust slight drifts in the horizontal direction (on the image plane). The sampling of the acquired SEM images is 1024×768 pixels with the pixel sizes of approximately 25 nm (for NMC cathode) and 35 nm (for HE-NMC cathode), while the spacing between each slice were 50 nm (for NMC cathode) and 70 nm (for HE-NMC cathode), respectively. A larger pixel size was chosen for HE-NMC cathode due to the larger size of the HE-NMC secondary particles compared with regular NMC. These imaging and sectioning parameters were selected to be consistent with the sampling needed to represent, with fidelity and given the time constraints of the sectioning work of a representative volume, the various components of the cathode (the features in NMC particles were consistently detected at the resolution provided by the SEM), so as to provide reasonably accurate 3D reconstruction. For the NMC cathode samples, 300 consecutive cross-section images were obtained from a volume of $\sim 5100 \mu\text{m}^3$, and 280 cross-section images were obtained from the HE-NMC cathode samples corresponding to a volume of $\sim 11800 \mu\text{m}^3$. The total 3D sampling volume is evaluated to be sufficient for this study as it yields the measured volume fraction consistent with the predetermined volume fraction of the cathode (see details in Supplementary materials).

For large scale sectioning and comparative purposes, an ion beam cross-section polisher (JEOL IB-09010CP) was also used to prepare the 2D cross-sections of the pristine

and cycled NMC cathodes. The sample was mounted on a Mo block and a thin layer of Au was deposited on the sample surface with physical vapor deposition by Ar ion sputtering. The sample was then milled by the cross-section polisher with an Ar ion beam at 5 keV.

2.3 Image segmentation

Before the raw 2D image dataset can be analyzed in a meaningful and systematic manner, the images must be digitally segmented into three distinct phases: (i) active material (AM), (ii) carbon-doped binder (CB), and (iii) pore spaces which are filled with electrolyte during operation. The term “carbon-doped binder” indicates the additive mixture of conductive agent (carbon black) and polymer binder (PVDF). Usually, the carbon black is mixed with PVDF to bind active particles together and enhance the conductivity of electrode, so they are defined as one phase of additives under segmentation. The epoxy infiltration is avoided in this work, so that the sample preparation is less invasive. The 3D reconstruction process is illustrated with our lab-scale NMC cathode as shown in Fig. 2. The in-house segmentation algorithm is based on thresholding and gradient analysis implemented in MATLAB utilizing the IMAGE PROCESSING toolbox. The key aspects of the electrode microstructure from SEM images that facilitate a reliable semi-autonomous segmentation are: (i) the separation in grey-scales of the different phases – the AM phase with lighter gray, the CB phase typically in medium gray, and pore spaces appearing as darkest features, and; (ii) the distinctive vertical grooves on the active material that are caused by the FIB and general milling process. Despite minor artifacts which can be subsequently corrected afterwards, we were able to obtain good accuracy by carefully controlling the various parameters that characterize the weighting between grey-scale thresholds and analysis of

gradient values in an automated fashion. The systematic error arising from the image processing step is estimated by comparing the experimental volume fraction deduced by our algorithm with the expected volume fraction of a lab-made NMC cathode with known composition (based on weight ratio of AM, carbon black, and PVDF). A comparison of the measurements and expected values leads to a small systematic error of less than 2%. Fig. 2 (a) shows an example of a series of raw 2D images of a lab-scale NMC cathode, and the corresponding segmented images are shown in Fig. 2 (b). A 3D image of the reconstructed cathode volume using the segmented images is shown in Fig. 2 (c) with: (i) AM in white; (ii) CB in yellow; and (iii) pore spaces in transparent. Separate 3D structures revealing the spatial distribution of the active material (NMC particles) and binder phases are shown in Fig. 2 (d) and (e). These 3D rendered volumes show that the structure of these components is sufficiently well represented and can be subsequently used to calculate the volume of the particles and in any further modeling work aimed at predicting the transport properties of the cathodes.

2.4 Neighbor Counting Method

In order to assess the evolution of the relative positions of the important phases, we quantified the segmented structure with a “neighbor counting” method. This approach provides statistical analysis to assess the degree of connectivity between the surface of active particles and binder matrix. A “neighbor counting” algorithm was used to scan along each row of pixels (for a 2D image) or each row and column of voxels (for the 3D structure) in the directions parallel to the separator and current collector of the segmented dataset. The number of occurrences of a pixel or voxel of AM being in direct contact with CB were

counted. More precisely, this technique computes the proportion of the AM surface that is adjacent to the binder matrix as a function of depth into the cathode (i.e., in the direction perpendicular to separator and current collector).

3. Results and discussion

3.1 $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC) cathode

Fig. 3 (a) shows a top-view SEM image of the NMC cathode before cycling. The NMC cathode has a relative smooth surface where the active particles were tightly embedded in the CB matrix. However, some cracks were observed in the large secondary NMC particles of the pristine sample, as shown in Fig.3 (b). This is consistent with the expectation that the calendaring process could lead to particle fracture due to the high pressure applied to the cathode [40]. The presence of these cracks in the particles could enhance the Li diffusion, and thus improve the cycling kinetics, but would also generate more exposed surface area for the side reactions with electrolyte [29].

Fig. 3 (c) shows a cross-sectional SEM image of the NMC cathode after 20 cycles. We note that large gaps have formed inside the cathode, separating the active particles and binder, as highlighted with red arrows. This will be discussed below. In addition, cracks inside the secondary active particles are also observed in the cycled NMC cathode, and appear similar to those observed in the pristine sample. However, it is difficult to ascertain, from visual inspection alone, whether there are more fractured particles after electrochemical cycling. Fig. 3 (d) and (e) show the 3D reconstructions of the AM and CB phases of the pristine NMC cathode. Based on the reconstructed 3D structure, the volume

fraction of the three phases in the cathode was calculated as: (i) 69% active material; (ii) 24% carbon-doped binder; and (iii) 7% pore spaces. The result shows that the majority of the cathode volume is occupied by the active material which would be beneficial in achieving a high battery capacity.

In order to quantify the structural observations, particle size distribution analysis was performed on the segmented 3D dataset, and is shown in Fig. 4 (a). The particle size was specified based on volume rather than diameter due to the irregular non-spherical shapes of NMC secondary particles. Because the sample contains both small fractured particles and large secondary ones, the particle size variation is large. Thus, the particle size distribution of active particles was calculated with different volume ranges, that is, the number of particles belonging to a given volume “bin” was counted. This should provide a general idea of the proportion of particles belonging to different size ranges. As shown in Fig. 4 (a), the majority of NMC particles have sizes below $10 \mu\text{m}^3$ and there are fewer large secondary particles with sizes above $100 \mu\text{m}^3$. It is reasonable to expect few large particles due to the limited sampling volume. Compared with pristine NMC cathode, the cycled NMC cathode shows a small increase in the number of particles with smaller sizes (typically less than $1 \mu\text{m}^3$), indicating that there might be large particles fractured into small ones. It has been reported that the internal cracks may promote the particle fracture [35], so the cracks being observed from the pristine sample may contribute to the particle size change. However, local variations in the distribution of the AM phase cannot be ignored for the assessment of particle sizes, and the slight increase being observed in this comparison could be due to a combination factors, including the electrochemical cycling and sample inhomogeneity [41].

From the comparison of pristine and cycled NMC cathodes, large gaps between active particles and binder are clearly visible from 2D cross-sectional images of the electrode after 20 cycles. To evaluate the connectivity between the CB phase and active particles, we performed an analysis based on the “neighbor counting” method to the segmented 3D dataset of the NMC cathodes at different cyclic numbers in order to extract the probability of carbon-doped binder being adjacent to the active particles (PBA) as a function of depth into the cathode. Comparing the pristine and cycled NMC cathodes, there is an obvious decrease in PBA of the whole sample with the increase number of cycles, as shown in Fig. 4 (b). Each data point represents the probability of CB being in contact with active particle surface of each slice perpendicular to the depth of the 3D structure. The x-axis is the distance of each slice from the sample surface (close to the separator) in units of pixels, each pixel corresponding to the slice thickness (35 nm), as shown in the schematic diagram in Fig. 4(b). From the “neighbor counting” analysis, the average PBA of the pristine sample is around 0.54 and decreases to 0.48 after 20 cycles, thus an 11% loss in connectivity between AM and CB in the NMC cathode is observed after 20 cycles. We note that the value of the average PBA, e.g. 0.54, means 54% of the AM surface is in contact with the CB phase within the 3D volume. Moreover, the average PBA shows a further decrease to 0.43 when the cathode was subjected to additional cycling (50 cycles), the sample thus exhibits a 20% loss of AM/CB connection after 50 cycles. The results therefore indicate that the connectivity between AM and CB decreases with the increase number of cycles, where a cycling-induced detachment between the two phases was observed. However, local variations needs to be considered in order to assess the PBA changes.

To evaluate the influence of local microstructural variations and to validate the data obtained from 3D volumes, large cross-sectional images of the pristine and cycled NMC cathodes, with the depth covering the full cathode thickness and width of around 1 mm, were prepared using ion beam cross-section polishing. Three different locations were selected from each of the two samples, and a series of SEM images were collected at each location along the depth of the cathode.

Fig. 5 (a) and (b) are the large 2D cross-section images taken at one location within the pristine and 20 cycles NMC cathodes. As shown in Fig. 5 (c) and (d), the PBA of the pristine NMC cathode has a relatively uniform distribution along the depth of the cathode indicating there is good contact between the AM and CB phases. Compared with the pristine sample, the contact area of the active particle and binder of the cycled NMC cathode decreased at some localized positions after electrochemical cycling where the PBA almost reached zero, and the average PBA dropped from 0.57 in the pristine state to 0.47 in the cathode after 20 cycles. The detachment of the CB phase from the active particle surface was revealed from the segmented 2D slice of the NMC cathode after 20 cycles, where a 17.5% decrease in PBA is detected, and this is consistent with the measurements in other locations of the cathode (Supplementary Table 1). Based on the 3D and 2D “neighbor counting” results, the detachment between CB and AM appears to be prevalent in the NMC cathode after electrochemical cycling. We suggest that the origins of the binder detachment could be: (i) the volume expansion and contraction of the active particles induced stresses [42], and (ii) the local volume change of the anode which could influence indirectly the cathode structure especially the porous binder matrix.

Since the CB phase contains carbon black additive in order to enhance the electrical conductivity of the cathode, our results thus suggest that the detachment between the conductive CB phase and active particles will reduce the efficiency of electrons transport from the active particle (where Li^+ intercalation/deintercalation happens) to the current collector, in other words, it becomes increasingly difficult for electrons to connect from the active particles through the conductive CB network to the current collector. This effect could therefore contribute to the degradation of the battery performance after cycling (Supplementary Fig. S1). As shown in the results above, when the cell is suffering larger capacity loss from longer term cycling, from 20 cycles to 50 cycles, the cathode also loses AM/CB connectivity as indicated by the decreased average PBA values from 20 cycles to 50 cycles. The PBA loss as a function of cycle numbers therefore provides direct experimental evidence that the detachment effect correlates with the capacity loss. While we cannot exclusively attribute the cause-effect link between the PBA drop and the capacity loss at this point, the unambiguous drop of PBA evidenced from our measurements needs to be considered as a possible factor in the performance degradation, together with other known effects such as solid electrolyte interface (SEI) formation [43], and structure distortion of active materials [14-16]. Furthermore, electrical conductivity calculation of the cathode based on this observed microstructural evolution has also been determined and will be published elsewhere.

3.2. $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.56}\text{Co}_{0.13})\text{O}_2$ (HE-NMC) cathode

Fig. 6 (a) shows a top-view SEM image of the single cycle HE-NMC cathode. In addition to the very large secondary particles, there are numerous significantly smaller

primary HE-NMC particles embedded in the binder matrix with diameters in the order of hundreds of nanometers. Compared with the NMC cathode studied above, the HE-NMC active material has smaller primary particle sizes and these are less compact. The representative 2D cross-section images of the 1 and 50 cycles HE-NMC cathodes are shown in Fig. 6 (b) and (c). In each 2D SEM cross-sectional image, the irregular shaped HE-NMC active particles are clearly visible in light grey intensity, while the CB phase appears in medium contrast as compared to the pores, which are seen as the darkest features. While the HE-NMC secondary particles have much smaller grains and pores, compared to the cracks existing in the NMC secondary particles, the pores distributed inside the HE-NMC particles appear to be poorly connected to the surface. This may limit electrolyte penetration within the HE-NMC secondary particles. The 3D reconstruction of active particles of the HE-NMC is shown in Fig. 6 (d), the active material phase is composed of a variety of irregular shapes of small and very large particles. The corresponding carbon-doped binder phase is shown in Fig. 6 (e).

As observed from the cross-sectional images, the size distribution of the HE-NMC active particles is broad, from submicron primary particles to large secondary ones. Fig. 7(a) shows the comparison of the particle size distributions of HE-NMC samples at 1 and 50 cycles. The majority of particles are below $1 \mu\text{m}^3$ and about 40% of the particles are hundreds of nanometers in diameter. Only a few large secondary particles are found contributing to less than 10% of the total distribution. The existence of a large fraction of small particles in the electrode has important implications on its performance. The specific surface area of the active material will be dramatically increased, thus facilitating

electrode/electrolyte side reactions which adversely impact the battery capacity and lifetime (the cycling performance of the HE-NMC cathode is shown in Supplementary Fig. S2). After 50 cycles, there is an increase in the fraction of small particles (volume $< 0.5\mu\text{m}^3$). The medium sized particles thus appear to have fractured into small ones. However, yet again, local variation of the AM phase distribution has to be taken into account for the observed particle size changes.

The “neighbor counting” method was applied to the segmented 3D dataset of HE-NMC cathodes with different cycle numbers, and the PBA was calculated through the depth of the electrode, Fig. 7(b). Similar to the NMC samples, the PBA was calculated for each slice parallel to the separator and current collector across the depth of cathode. The averaged PBA of HE-NMC samples decreased from 0.60 at the first cycle to 0.46 after another 49 cycles. The 50 cycles HE-NMC electrode therefore shows a 22.5% decrease in AM and CB contact which is consistent with the PBA analysis on the NMC cathode. We note, however, that the cells were specifically cycled in harsh conditions over a large voltage window (2.0 V ~ 4.6 V) resulting in a dramatic ~ 45% loss in capacity (Supplementary Fig. S2). The significant PBA decrease is yet again correlated with the observed capacity loss, although we cannot entirely exclude other possible factors evolving in parallel (e. g. SEI formation). The PBA analysis of the HE-NMC electrode indicates that there would be a loss of electrical conductivity as a consequence of the detachment between the conductive binder matrix and active particles.

4. Conclusions

The 3D reconstruction of two types of lithium-ion battery cathode microstructures,

NMC and HE-NMC, after different electrochemical cycling states were achieved using FIB-SEM combined with a refined segmentation algorithm without any epoxy resin infiltration. The particle size distribution analysis from the 3D reconstruction shows that the active particles in the NMC and HE-NMC cathodes exhibit no significant changes from the different cycling states. Measurements of the connectivity between active particles and binder phase of NMC cathode after electrochemical cycling were also carried out in order to assess the PBA, calculated with a “neighbor counting” method from 3D dataset. The results show significant decreases in PBA during cycling which reveal the loss of connectivity between the conductive CB and active particles. We noted a correlation between the drop in average PBA, indicative of detachment between the AM and CB phases, and cell capacity loss with increased number of cycles. Furthermore, detachment between the CB phase and AM is also discovered from the lab-made HE-NMC cathode after 50 cycles. These results thus suggest that the cycling-induced AM/CB detachment is a common trend regardless of the way that electrode is manufactured. In general, our findings show that the loss of electrical connectivity of the cathode, as inferred from the detachment between the phases, is one of the challenges in achieving and maintaining the high capacity and stable cycling performance of lithium-ion batteries.

Acknowledgments

This work is supported by a NSERC-Automotive Partnership Canada grant with General Motors. The electron microscopy characterization was carried out at the Canadian Centre for Electron Microscopy, a national facility supported by NSERC, the Canada Foundation for Innovation (via the MSI program) and McMaster University.

References

- [1] J.N. Reimers, J.R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2–8.
- [2] H. Xia, L. Lu, Y.S. Meng, G. Ceder, *J. Electrochem. Soc.* 154 (2007) A337–A342.
- [3] D.R. Diercks, M. Musselman, A. Morgenstern, T. Wilson, M. Kumar, K. Smith, M. Kawase, B.P. Gorman, M. Eberhart, C.E. Packard, *J. Electrochem. Soc.* 161 (2014) F3039–F3045.
- [4] D.P. Abraham, R.D. Twisten, M. Balasubramanian, I. Petrov, J. McBreen, K. Amine, *Electrochem. Commun.* 4 (2002) 620–625.
- [5] H. Liu, C.R. Fell, K. An, L. Cai, Y.S. Meng, *J. Power Sources.* 240 (2013) 772–778.
- [6] S.H. Kang, J. Kim, M.E. Stoll, D. Abraham, Y.K. Sun, K. Amine, *J. Power Sources.* 112 (2002) 41–48.
- [7] M.W. Jang, H.G. Jung, B. Scrosati, Y.K. Sun, *J. Power Sources.* 220 (2012) 354–359.
- [8] N. Yabuuchi, T. Ohzuku, *J. Power Sources.* 119-121 (2003) 171–174.
- [9] I. Belharouak, Y.K. Sun, J. Liu, K. Amine, *J. Power Sources.* 123 (2003) 247–252.
- [10] Y. Koyama, I. Tanaka, H. Adachi, Y. Makimura, T. Ohzuku, *J. Power Sources.* 119-121 (2003) 644–648.
- [11] M. Gu, A. Genc, I. Belharouak, D. Wang, K. Amine, S. Thevuthasan, D.R. Baer, J.G. Zhang, N.D. Browning, J. Liu, C. Wang, *Chem. Mater.* 25 (2013) 2319-2326.
- [12] J. Zheng, M. Gu, J. Xiao, P. Zuo, C. Wang, J.G. Zhang, *Nano Lett.* 13 (2013) 3824–3830.
- [13] G.A. Elia, J. Wang, D. Bresser, J. Li, B. Scrosati, S. Passerini, J. Hassoun, *ACS Appl. Mater. Interfaces*, 6 (2014) 12956-12961.
- [14] B. Xu, C.R. Fell, M. Chi, Y.S. Meng, *Energy Environ. Sci.* 4 (2011) 2223–2233.
- [15] F. Lin, I.M. Markus, D. Nordlund, T.C. Weng, M.D. Asta, H.L. Xin, M.M. Doeff, *Nat. Commun.* 5 (2014) 3529.

- [16] A. Boulineau, L. Simonin, J.F. Colin, C. Bourbon, S. Patoux, *Nano Lett.* 13 (2013) 3857–3863.
- [17] L. Terborg, S. Weber, F. Blaske, S. Passerini, M. Winter, U. Karst, S. Nowak, *J. Power Sources* 242 (2013) 832–837.
- [18] Y. Koyama, H. Arai, I. Tanaka, Y. Uchimoto, Z. Ogumi, *Chem. Mater.* 24 (2012) 3886–3894.
- [19] Y. Qi, S.J. Harris, *J. Electrochem. Soc.* 157 (2010) A741–A747.
- [20] D. Larcher, S. Beattie, M. Morcrette, K. Edström, J.C. Jumas, J.M. Tarascon, *J. Mater. Chem.* 17 (2007) 3759–3772.
- [21] D.S. Eastwood, V. Yufit, J. Gelb, A. Gu, R.S. Bradley, S.J. Harris, D.J.L. Brett, N.P. Brandon, P.D. Lee, P.J. Withers, P.R. Shearing, *Adv. Energy Mater.* 4 (2014) 1300506.
- [22] J. P. Maranchi, A. F. Hepp, A. G. Evans, N. T. Nuhfer, P. N. Kumta, *J. Electrochem. Soc.* 153 (2006) A1246–A1253.
- [23] J. Chen, J. Liu, Y. Qi, T. Sun, X. Li, *J. Electrochem. Soc.* 160 (2013) A1502–A1509.
- [24] M. Ebner, F. Marone, M. Stampanoni, V. Wood, *Science*, 342 (2013) 716–720.
- [25] P.R. Shearing, L.E. Howard, P.S. Jørgensen, N.P. Brandon, S.J. Harris, *Electrochem. Commun.* 12 (2010) 374–377.
- [26] B. Yan, C. Lim, L. Yin, L. Zhu, *Electrochim. Acta.* 100 (2013) 171–179.
- [27] Y.K. Chen-Wiegart, Z. Liu, K.T. Faber, S.A. Barnett, J. Wang, *Electrochem. Commun.* 28 (2013) 127–130.
- [28] F. Tariq, V. Yufit, M. Kishimoto, P.R. Shearing, S. Menkin, D. Golodnitsky, J. Gelb, E. Peled, N.P. Brandon, *J. Power Sources.* 248 (2014) 1014–1020.
- [29] J. Gonzalez, K. Sun, M. Huang, J. Lambros, S. Dillon, I. Chasiotis, *J. Power Sources.* 269 (2014) 334–343.

- [30] L. Zielke, T. Hutzenlaub, D.R. Wheeler, I. Manke, Y. Arlt, N. Paust, R. Zengerle, S. Thiele, *Adv. Energy Mater.* 4 (2014) 1301617.
- [31] L. Zielke, T. Hutzenlaub, D.R. Wheeler, C.W. Chao, I. Manke, A. Hilger, N. Paust, R. Zengerle, S. Thiele, *Adv. Energy Mater.* 4 (2014) 1401612.
- [32] M. Ender, J. Joos, T. Carraro, E. Ivers-Tiffée, *Electrochem. Commun.* 13 (2011) 166–168.
- [33] M. Ender, J. Joos, T. Carraro, E. Ivers-Tiffée, *J. Electrochem. Soc.* 159 (2012) A972–A980.
- [34] Y.K. Chen-Wiegart, R. DeMike, C. Erdonmez, K. Thornton, S.A. Barnett, J. Wang, *J. Power Sources.* 249 (2014) 349–356.
- [35] J.R. Wilson, J.S. Cronin, S. a. Barnett, S.J. Harris, *J. Power Sources.* 196 (2011) 3443–3447.
- [36] Z. Liu, J. Scott Cronin, Y.K. Chen-Wiegart, J.R. Wilson, K.J. Yakal-Kremiski, J. Wang, K.T. Faber, S.A. Barnett, *J. Power Sources.* 227 (2013) 267–274.
- [37] D.E. Stephenson, B.C. Walker, C.B. Skelton, E.P. Gorzkowski, D.J. Rowenhorst, D.R. Wheeler, *J. Electrochem. Soc.* 158 (2011) A781–A789.
- [38] A. Gully, H. Liu, S. Srinivasan, A.K. Sethurajan, S. Schougaard, B. Protas, *J. Electrochem. Soc.* 161 (2014) E3066–E3077.
- [39] L. Holzer, B. Muench, M. Wegmann, P. Gasser, R.J. Flatt, *J. Am. Ceram. Soc.* 89 (2006) 2577–2585.
- [40] C.W. Wang, Y.B. Yi, A.M. Sastry, J. Shim, K.A. Striebel, *J. Electrochem. Soc.* 151 (2004) A1489–A1498.
- [41] D. Kehrwald, P.R. Shearing, N.P. Brandon, P.K. Sinha, S.J. Harris, *J. Electrochem. Soc.* 158 (2011) A1393–A1399.
- [42] M. Balasubramanian, X. Sun, X.Q. Yang, J. McBreen, *J. Power Sources* 92(2001) 1–8.

[43] P. Verma, P. Maire, P. Novak, *Electrochem. Acta.* 55 (2010) 6332-6341.