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Submitted to ACS Nano

February 2017

Center for Functional Nanomaterials
Brookhaven National Laboratory

U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (SC-22)

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Operando Grazing Incidence Small Angle X-Ray Scattering/X-Ray Diffraction of Model Ordered Mesoporous Lithium Ion Batteries Anodes

Sarang M. Bhaway¹, Zhe Qiang¹, Yanfeng Xia², Xuhui Xia¹, Byeongdu Lee³, Kevin G. Yager⁴, Lihua Zhang⁴, Kim Kisslinger⁴, Yu-Ming Chen², Kewei Liu², Yu Zhu², Bryan D. Vogt¹*

¹Department of Polymer Engineering, University of Akron, Akron OH 44325 United States
²Department of Polymer Science, University of Akron, Akron OH 44325 United States
³X-ray Science Division, Advanced Photon Source, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439 United States
⁴Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States

KEYWORDS: cooperative assembly, nanoporous, metal oxide anode

ABSTRACT: Emergent lithium ion batteries commonly rely on nanostructuring of the active electrode materials to decrease the Li⁺ ion diffusion path length and to accommodate the strains associated with the insertion and de-insertion of Li⁺, but in many cases these nanostructures evolve during electrochemical charging-discharging. This change in the nanostructure can
adversely impact performance, and challenges remain regarding how to control these changes from the perspective of morphological design. In order to address these questions, *operando* grazing-incidence small-angle x-ray scattering and x-ray diffraction (GISAXS/GIXD) were used to assess the structural evolution of a family of model ordered mesoporous NiCo$_2$O$_4$ anode films during battery operation. The pore dimensions were systematically varied and appear to impact the stability of the ordered nanostructure during the cycling. For the anodes with small mesopores ($\approx$ 9 nm), the ordered nanostructure collapses during the first 2 charge-discharge cycles, as determined from GISAXS. This collapse is accompanied by irreversible Li ion insertion within the oxide framework, determined from GIXD and irreversible capacity loss. Conversely, anodes with larger ordered mesopores (17–28 nm) mostly maintained their nanostructure through the first 2 cycles with reversible Li ion insertion. During the 2$^{nd}$ cycle, there was a small additional deformation of the mesostructure. This preservation of the ordered structure lead to significant improvement in capacity retention during these first two cycles; however, a gradual loss in the ordered nanostructure from continuing deformation of the ordered structure during additional charge-discharge cycles leads to capacity decay in battery performance. These multiscale *operando* measurements provide insight into how changes at the atomic scale (lithium insertion and de-insertion) are translated to the nanostructure during battery operation. Moreover, small changes in the nanostructure can build up to significant morphological transformations that adversely impact battery performance through multiple charge-discharge cycles.

Rapid advancements in mobile electronics and electric vehicles have been enabled by the performance of lithium ion batteries (LIB). However, future advancements in this battery technology are limited by the low theoretical capacity of standard graphite based anodes (372
mAh/g), which has led to significant efforts in developing alternate anode materials that possess significantly higher discharge capacities. Conversion (such as metal oxides or mixed-metal oxides) and alloying (such as Si or Ge) charge storage mechanisms tend to enhance the capability of Li ion storage in comparison to intercalation mechanisms such as those associated with graphite anodes, but also lead to larger volumetric changes upon cycling that can cause pulverization of the anode and loss of performance. Engineering of the anodes, through introduction of pores or other nanostructuring, can improve the cycle stability, but this improved cycle stability appears to be strongly dependent on the details of the nanoarchitecture. Intriguingly, some recent reports have illustrated that the nanostructure can be significantly changed after extended cycling without necessarily losing performance.

One challenge with quantifying these nanostructure changes is the complexity of the initial morphology for many high performance anodes, especially with the need for dense nanostructures to maximize the power and energy capabilities. Block copolymer templating offers a convenient strategy to generate a periodic nanostructure that can be more directly interrogated to quantify these changes on charge-discharge cycling. Moreover, these templated materials can provide enhanced charge storage capabilities, but the performance depends on the mesopore wall thickness, mesopore geometry and pore length. Despite the significant efforts towards the fabrication of anodes with high energy density, there are no clear rules for designing the morphology of these materials in order to produce high initial capacity and low capacity fade on cycling. This problem becomes more complex by the evolution in the nanostructure of many anodes as well as the nature of the solid electrolyte interface (SEI) layer. It is even more challenging to identify the dynamic morphological changes occurring during battery operation to gain insights into electrochemical charge storage processes.
Measurements of individual model nanowires by in situ TEM have identified the dramatic dimension changes for alloying anodes, but these isolated nanowires do not, in general, provide information about how the aggregate in a full cell would respond due to the interactions between the nanowires themselves as well as other components in an active anode (e.g., carbon black and polymer binder). Similarly, the atomic scale changes associated with the incorporation of Li\(^+\) can be readily assessed in a full cell using x-ray diffraction or x-ray absorption spectroscopy, but the larger mesoscale changes that accompany these atomic perturbations cannot be resolved with these techniques. An additional challenge with operando characterization is the inherent heterogeneity of electrodes, which leads to local hot spots that are intrinsic to most electrode designs. Thus, local operando measurements, such as TEM, may not be representative of the whole electrode if one of these hot spots is measured.

Small-angle x-ray scattering (SAXS) probes the average nanostructure to potentially circumvent challenges posed by the local nature of TEM to ensure that the heterogeneity of the electrodes does not impact the conclusions drawn from the operando measurements. Recently, ordered mesoporous metal oxide anodes were characterized by operando SAXS during lithiation and de-lithiation processes. The ordered structure provides a clean fingerprint based on the correlation of the ordered structure to elucidate nanostructural changes during battery operation. For a common nanostructure via hard templating (KIT-6), the mesostructural changes during one charge-discharge cycle were found to apparently be dependent on the charge storage mechanism of the active material. Intercalation with titanium dioxide exhibited reversible nanostructure changes, while the nanostructure was significantly distorted after a single charge-discharge when using mesoporous cobalt oxide (conversion) anodes and the ordered nanostructure was completely lost for a mesoporous tin oxide (alloying) anode as determined from operando SAXS
measurements.\textsuperscript{32} However as the wall thickness/pore size is invariant, it is not clear if these differences in the stability of the nanostructure through a single discharge-charge cycle are an intrinsic issue or directly related to the sizes selected for the nanostructural engineering. Moreover, a single discharge-charge cycle limits insight into if these changes continue through additional cycles to allow the evolution of structure to be predicted.

Here, we seek to address these questions about the impact of the nanopore size on the structural changes of a single conversion-type material,\textsuperscript{33,34} ordered mesoporous nickel cobaltite (NiCo$_2$O$_4$), over multiple charge-discharge cycles. Model anodes based on mesoporous NiCo$_2$O$_4$ thin films on gold coated substrate provide a more homogenous anode due to the avoidance of binders and carbon black and better contact of the active material with the current collector to avoid one of the possible artifacts (local hot spots in the electrode) that can impact the conclusions obtained with \textit{operando} measurements for batteries.\textsuperscript{35} Simultaneous \textit{operando} grazing-incidence small-angle x-ray scattering (GISAXS) and grazing-incidence x-ray diffraction (GIXD) are used to elucidate multiscale (atomic and nano-scale) structural evolution during discharge-charge cycles (Figure S1). GISAXS measures the distortion of ordered mesostructure with the cyclic effects dependent on the initial nanostructure. Interestingly, the loss of order of the NiCo$_2$O$_4$ mesostructure occurs simultaneously with irreversible electrochemical reactions where Li$_2$O and metallic Co remain on discharge. The extent of these irreversible electrochemical reactions is dependent on the mesostructure where the larger pores (and thicker walls) lead to less distortion of the mesostructure and less formation of irreversible Li$_2$O. These anodes with improved structural stability exhibit improved charge-discharge cycle stability. This work illustrates that there is likely an optimal pore size of mesoporous lithium ion
battery electrodes, while the decrease in the capacity during charge-discharge cycling can be correlated with a simultaneous loss of nanostructure and irreversible electrochemical reactions.

**RESULTS AND DISCUSSION**

![Figure 1](image)

**Figure 1.** AFM micrographs illustrating the surface morphology of ordered mesoporous NiCo$_2$O$_4$ films prior to galvanostatic cycling: (A) m-NC28 (B) m-NC16 and (C) m-NC9 films. The variation in pore size is due to a change in the degree of polymerization of the hydrophobic segment of the block copolymer template.

Figure 1 illustrates the surface morphology of poly[methoxy poly(ethylene glycol)methacrylate]-block-poly(butyl acrylate) (PMPEGMA-b-PBA, Figure S2) templated porous m-NCx films that are approximately 90 nm thick. The three block copolymer templates differed only by the degree of polymerization of the hydrophobic PBA segment (Figure S3), which changes the size of the mesopores. The mesoporous NiCo$_2$O$_4$ templated by the largest block copolymer template ($M_w = 10.1 \times 10^4$ g/mol) (Figure 1A) leads to an average pore width of $28 \pm 3.2$ nm with short range local ordering of the mesopores. The ordering is improved using the intermediate molecular weight template ($M_w = 5.9 \times 10^4$ g/mol) (Figure 1B,) with larger grains from AFM images and a decrease in the average pore width to $16 \pm 2.8$ nm. The surface morphology of the film templated by the smallest block copolymer ($M_w = 3.7 \times 10^4$ g/mol)
(Figure 1C) is significantly different with small NiCo$_2$O$_4$ nanoparticles (~5 nm) across the surface. Based on the AFM micrographs, the average pore width of the smallest block copolymer templated mesoporous NiCo$_2$O$_4$ is estimated to be $9 \pm 5.5$ nm. The nomenclature for these mesoporous NiCo$_2$O$_4$ thin film anodes is m-NC$x$, where “m” stands for mesoporous, “NC” stands for nickel-cobalt mixed metal oxide, and “x” denotes the average pore width of the templated oxide thin film in nm determined from AFM images. The fast fourier transform (FFT) of the micrographs (insets in Figure 1) provide a measure of correlations in the surface morphology. For the samples with a clear ordered structure from the real space images, a narrow ring is observed with average center-to-center distance of $48.5 \pm 2.5$ nm for m-NC28 and $26.5 \pm 1.5$ nm for m-NC16 respectively. For m-NC9, the FFT is a very broad ring associated with a poorly ordered nanostructure with an average spacing of ~15 nm. (m-NC9), but this quantification is challenged by the irregular shape of the pores. Ellipsometric porosimetry provides an independent measure for the pore dimensions. Assuming uniaxial contraction and ellipsical pore shape, the lateral mesopore dimensions (14.1 nm for m-NC9, 17.4 nm for m-NC16, 26.3 nm for m-NC28) determined using ellipsometric porosity (Figure S4) agree well with the AFM micrographs. This variation in pore sizes from approximately 9 nm to 28 nm is difficult to obtain with commercial block copolymers/surfactants or hard templates such as KIT-6$_{36,37}$ or SBA-15$_{38,39}$ which enables a systematic investigation into the role of pore size on structural changes during charging-discharging. Based on the average pore width and average center-to-center distance between pores determined from FFT of AFM micrographs, the wall thickness decreases from 20.5 nm (m-NC28) to 10.5 nm (m-NC16) to 6 nm (m-NC9), concurrent with the pore size. The block copolymer selection also impacts the surface area (92.8 m$^2$/cm$^3$ (m-NC9), 78.7 m$^2$/cm$^3$ (m-NC16), and 51.9 m$^2$/cm$^3$ (m-NC28)) and porosity (45.6 % (m-NC9),
51.9 % (m-NC16), and 43.8 % (m-NC28)) of these mesoporous films as determined from the ellipsometric data (see SI for details).

The well-defined mesostructure of these NiCo$_2$O$_4$ materials facilitate the quantification of the changes during battery operation using a custom-designed lithium ion cell (Figure S1) that uses a tube in a tube window design to provide Ar purge around the electrolyte. The O$_2$ and H$_2$O from the ambient atmosphere can permeate through the Kapton windows to oxidize the electrodes or electrolyte. The annular region of the tube in tube window is continuously purged with Ar to sweep away the O$_2$ and H$_2$O before it can reach the electrodes and electrolyte, which are held within the inner Kapton window. Figure 2 illustrates the scattering profiles obtained from operando GISAXS and GIXD of m-NC9 during galvanostatic cycling between 0.2-3V vs Li/Li$^+$. The 1-D GISAXS profile for the m-NC9 anode (Figure 2A) prior to galvanostatic cycling exhibits two peaks; the primary peak is centered around $q_x \approx 0.044$ Å$^{-1}$ ($d$-spacing = 14.2 nm) and a weak second-order peak is at $q_x \approx 0.068$ Å$^{-1}$. These scattering profiles are line cuts around $q_z = 0$ (through plane direction) as the ordered nanostructure contracts significantly through the thickness direction during calcination, which leads to anisotropy in the scattering patterns. The $d$-spacing of primary scattering peak (14.2 nm) agrees with the average center-to-center distance (15 nm) between mesopores determined from AFM micrographs (Figure 1C). As shown in Figure 2A, a plateau-like feature in the voltage profile is clear at approximately 0.92 V (with small inflection at around 2.1 V and 1.5 V) on initial discharging of the m-NC9 anode. This discharge behavior is consistent with conversion-type charge storage in NiCo$_2$O$_4$ anodes for lithium ion battery$^{33,40}$ corresponding to the reduction of NiCo$_2$O$_4$ to metallic Ni and Co with the corresponding formation of Li$_2$O. After this initial discharge, the m-NC9 anode is then subsequently charged (blue), discharged (green) and re-charged (black). The discharge capacities
associated with the thin film m-NC9 anode are estimated as 3692 mAh/g for the initial discharge, 881 mAh/g for the 1st cycle, and 766 mAh/g for the 2nd cycle. It should be noted that the theoretical capacity for NiCo$_2$O$_4$ is 890 mAh/g,$^{33}$ so the initial discharge capacity is dominated by irreversible events, likely the SEI formation. As these anodes are nanoporous thin films, high surface area is likely leads to high electron transference through the SEI formation as has been reported previously for NiCo$_2$O$_4$ nanosheets.$^{41}$ Additionally, the details of the nanostructured surface can also dramatically impact the SEI formation on similar metal oxides.$^{42}$ After the initial discharge, the capacity from this m-NC9 anode is less than the theoretical capacity for NiCo$_2$O$_4$.

Qualitatively from the GISAXS profiles in Figure 2A, the primary peak remains well resolved through the initial discharge and 1st charge with a slight shift in the peak position (red and blue curves). However, the weak second-order peak associated with mesopore geometry almost completely disappears by the end of the 1st charge. The loss of the higher-order peak indicates loss in the long-range correlations. During these successive lithiation and de-lithiation segments, the intensity of primary scattering peak is found to significantly reduce (Figure S6A). This is most evident during the 1st discharge (green curves) where the primary peak is initially well resolved, but after the discharge this peak has evolved to a weak shoulder. The decrease in the peak intensity can be partially attributed to a decrease in scattering contrast. There are two potential sources for the reduced contrast: local densification associated with the solid electrolyte interface (SEI) formation on the mesopore walls to increase the local electron density of the mesopores and the incorporation of Li into the NiCo$_2$O$_4$, which acts to dramatically reduce the electron density. This later effect likely dominates for the decreased contrast in the system as the maximum change in electron density associated the SEI is significantly smaller than for the addition of Li into the NiCo$_2$O$_4$. However, primary scattering peak broadens in addition to the
decrease in intensity, which indicates some degradation in the extent of ordering. On re-charging (black curves), the primary peak does not recover in intensity or breadth, which indicates an irreversible loss in the ordering of the mesostructure.

**Figure 2.** (A) 1D (in plane) *operando* GISAXS profiles from galvanostatic cycling of m-NC9 film anode. The scattering curves are vertically offset for clarity. The corresponding voltage profile is color coded to the same charge and discharge cycle examined by GISAXS. The capacity is shown as the total energy driven through the system to clearly illustrate the path during the measurements. (B) Quantitative analysis of change in *d*-spacing of m-NC9 from GISAXS during successive lithiation and de-lithiation.
Quantitative analysis of the primary peak from GISAXS illustrates the breathing of the mesostructure during the lithiation and de-lithiation process (Figure 2B). During the initial discharge cycle (lithiation segment, red curve), the in-plane $d$-spacing increases from 14.2 nm to 14.5 nm. While the redox conversion reaction should cause volumetric expansion of the NiCo$_2$O$_4$ framework, in this case, the insertion of Li$^+$ into the oxide acts to also deform the entire mesostructure in the plane of the supported film (non-uniaxial deformation). This suggests that the stresses associated with the insertion and de-insertion of Li$^+$ are larger than those encountered during the initial calcination of most ordered mesoporous metal oxide films. During the 1st charge cycle (de-lithiation, blue curve), the in-plane $d$-spacing decreases reversibly from 14.5 nm back to 14.2 nm as the Li$^+$ ions are extracted from the mesoporous framework. On the subsequent lithiation of m-NC9 anode (1st discharge cycle, green curve), the $d$-spacing increases to 14.5 nm at the end of the discharge, which indicates a reversible expansion-contraction experienced by m-NC9 framework in the plane of the film through the 1st complete charge-discharge cycle. However, by the end of 2nd charge (de-lithiation, black curve), the primary scattering peak originating from m-NC9 mesostructure almost disappears. This loss in the scattering peak suggests a collapse of mesoporous morphology in the m-NC9 anode. Quantitative analysis of the primary peak after 2nd de-lithiation segment indicates almost 8.5% volume expansion of the m-NC9 framework after re-charging in comparison to the initial mesostructure.

The loss of correlations between mesopores can be further quantified by examination of the full width half maximum (FWHM) of the primary scattering peak (Figure S5). The FWHM of the primary peak centered at $q_x \approx 0.044$ Å$^{-1}$ is 0.0115 Å$^{-1}$ prior to galvanostatically cycling of the m-NC9 anode. This FWHM does not significantly change during the initial discharge (lithiation).
However, on successive cycling, the FWHM of primary scattering peak monotonically increases from 0.013 Å⁻¹ (1ˢᵗ de-lithiation segment) to 0.016 Å⁻¹ (2ⁿᵈ lithiation segment) to 0.0205 Å⁻¹ at the end of the 2ⁿᵈ de-lithiation segment. The uncertainty associated with determination of FWHM also increases upon successive cycling as the intensity of primary scattering peak reduces significantly. Nonetheless, this large increase in the FWHM suggests a reduction in the structural coherence length, and is thus consistent with the decay in the order of the mesostructure inferred from the decreased intensity of the primary peak (Figure S5). The initial distortion of the NiCo₂O₄ mesostructure is consistent with a prior report examining an ordered mesoporous Co₃O₄ anode templated by KIT-6 (pore size ~ 5 nm) after the initial discharge and a single charge.³² However, this work demonstrates the continual deterioration of the mesostructure on a second discharge-charge cycle.

As the metal nitrate-citric acid method tends to yield a nanoporous framework of m-NCx anode composed of NiCo₂O₄ nanoparticles,⁶ ⁴³ the high-q region of GISAXS spectra can be fit to a spheroid form factor to gain insights into evolution of NiCo₂O₄ nanoparticle size during galvanostatic cycling (Figure S6A). As these high q analyses used only in-plane data (qₓ), the nanoparticle sizes reported are for the in-plane direction only, but it is assumed that the nanoparticles will be isotropically distributed in the framework such that these sizes should describe the average dimensions of the nanoparticles. Prior to galvanostatic cycling, the average diameter of NiCo₂O₄ nanoparticles in m-NC9 anode is 3.3 nm. During the 1ˢᵗ lithiation segment (initial discharge cycle), nanoparticles grow in size due to Li⁺ ion insertion and redox conversion reactions. At a potential of 0.96 V, the nanoparticle size increased to 3.8 nm, corresponding to a volume expansion of 45% (Figure S6B). At the end of the initial discharge, the nanoparticles have grown by 85% of their initial volume (4.05 nm), which is similar to the theoretical volume
expansion (~100%) expected during electrochemical insertion of 8 Li\textsuperscript{+} ions.\textsuperscript{45} Despite this large expansion of nanoparticles, the ordered mesoporous lattice swells by less than 10 % (Figure 2B) as the porosity accommodates the volume expansion of the mesopore framework consisting of many nanoparticles. However, this nanoparticle-expansion phenomenon contributes towards significant distortion of mesopore geometry, initially leading to a decrease in intensity of 2\textsuperscript{nd} ordering peak. On reversing the electrochemical redox reactions, Li\textsuperscript{+} ion de-insertion leads to a slight contraction in the nanoparticle size to 3.75 nm by the end of the 1\textsuperscript{st} charge cycle, which is 45 % larger than its initial volume. This behavior is counter to the \textit{d}-spacing (Figure 2B) where the mesostructure returns to its initial dimensions at the end of the 1\textsuperscript{st} charge cycle. At the end of the 2\textsuperscript{nd} charge cycle, the average nanoparticle size returns to 3.8 nm, while the ordered lattice becomes larger (Figure 2B), which suggests that there is a cascade of processes that lead to the translation of atomic scale changes to larger length scales. These structural changes potentially impact the electrochemical performance as determined from the voltage profiles obtained during the \textit{operando} measurement with the capacity decreasing from 881 mAh/g at the end of 1\textsuperscript{st} cycle to 766 mAh/g in the 2\textsuperscript{nd} cycle.
Figure 3. (A) 1-D *operando* GIXD profiles from galvanostatic cycling of m-NC9 film anode. Magnified micrographs of the GIXD spectra in the range of (B) $q = 2.3$ Å⁻¹ to 3.2 Å⁻¹ and (C) $q = 4.0$ Å⁻¹ to 4.7 Å⁻¹. Note the shift in diffraction peaks during lithiation to smaller $q$ associated with the increase in crystal lattice spacing. The color scheme is selected to match that for the galvanostatic data shown in Figure 1: initial discharge (red), 1ˢᵗ charge (blue), 1ˢᵗ discharge (green), and 2ⁿᵈ charge (black). The potential for select GIXD profiles are listed to the right of the curves for guidance.

In order to better understand the structural changes at the atomic scale and its correspondence with battery performance, the crystal structure of the mesoporous NiCo₂O₄ thin films during galvanostatic cycling were elucidated using *operando* grazing incidence x-ray diffraction (GIXD) (Figure 3) that were measured simultaneously with the GISAXS data (Figure 2). The 2D GIXD profiles were symmetric, so the intensities are the azimuthally averaged and reported as a function of $q$ (no directionality). The GIXD profiles prior to battery operation exhibit distinct peaks that can be indexed to (220), (311), (222), (400), (422), (511) and (440) crystal planes (Figure 3A) of Fd-3m spinel phase of NiCo₂O₄ (PDF card no. 01-073-1702). Applying the
Scherrer equation\(^{46}\) to the most intense (311) diffraction peak \((q = 2.56 \text{ Å}^{-1})\), the average NiCo\(_2\)O\(_4\) crystal size is 2.8 nm, which is similar to the particle size (3.3 nm) determined from GISAXS analysis. During initial discharge process, Li\(^+\) ion insertion with conversion reactions\(^{33}\) occur that increases the distance between NiCo\(_2\)O\(_4\) crystal planes to shift the (400) and (440) diffraction peaks to lower \(q\) (Figure 3B and 3C). However, the (311) diffraction peak does not shift to lower \(q\) as this plane has been shown to not be expanded during the initial Li\(^+\) insertion.\(^{48}\) There is an apparent slight shift of this peak position to higher \(q\) as the intensity of the (311) peak decreases rapidly, which may be associated with the reduction of the trivalent Ni and Co to their divalent state during the 1\(^{st}\) step of the conversion reaction.\(^{49}\) Concurrently, the intensity of diffraction peaks associated with spinel crystal structure of NiCo\(_2\)O\(_4\) decreases due to the reduction of NiCo\(_2\)O\(_4\) to metallic Ni (PDF card no. 01-070-0989) and Co (PDF card no. 00-001-1259) that gives rise to a diffraction peak at \(q = 3.12 \text{ Å}^{-1}\) corresponding to their (111) planes. An additional peak at \(q = 4.42 \text{ Å}^{-1}\) develops associated with the (311) plane of Li\(_2\)O. On re-charging of the m-NC9 anode (de-lithiation), only weak diffraction peaks associated with (400) and (440) planes of Co\(_3\)O\(_4\) and NiO can be observed, suggesting formation of amorphous products upon de-lithiation as has been reported previously for other conversion-type metal oxide anodes.\(^{50,51}\)

Due to the limited crystallinity, the charge product cannot be unambiguously identified from GIXD. Oxidation state of Ni and Co after the first charge was compared to that for the pristine m-NC9 films using x-ray photoelectron spectroscopy (XPS, Figure S7). There is a slight decrease in the fraction of trivalent Ni and Co after the re-charge, which is consistent with prior XANES investigations of the NiCo\(_2\)O\(_4\).\(^{48}\) This irreversibility in oxidation state agrees with non-recovered irreversible capacity during subsequent discharge for NiCo\(_2\)O\(_4\). The XPS data provides some information about the local environment that can provide some differentiation of
amorphous cobalt oxide and nickel oxide from amorphous NiCo$_2$O$_4$. The shifts in the peak positions in XPS in the charged state correspond well to those of NiO and Co$_3$O$_4$, which suggests phase separation of the Ni and Co during discharge to produce a mixture of oxides on subsequent charging. Additionally, the XPS demonstrates some metallic Ni and Co remaining in the charge product.

The persistence of diffraction peaks associated with metallic Ni, Co and Li$_2$O at the full charged state suggests the irreversible formation of Li$_2$O. These irreversible reactions are thought to occur predominately at the electrochemical interface.\textsuperscript{52} The distinct diffraction peaks arising from (111), (220) and (311) planes of Li$_2$O (PDF card no. 01-080-4679) at $q = 2.28$ Å$^{-1}$, $q = 3.71$ Å$^{-1}$ and $q = 4.42$ Å$^{-1}$ are suggestive of well-defined Li$_2$O crystals in the m-NC9 anode after 2 cycles of operation. The irreversible incorporation of Li$_2$O within the nanoparticle framework is consistent with the increase in the particle size through the cycling (Figure S6). The low electron density of Li$_2$O is closer to the electrolyte than the NiCo$_2$O$_4$, so the build-up of Li$_2$O on the surface of the nanoparticles would not lead to the conclusion of an increased size of the nanoparticles, thus the Li$_2$O is likely incorporated within the nanoparticles that comprise the mesoporous framework. The change in crystal structure of the framework appears to be correlated with the mesostructure evolution where the loss of ordered mesoporous structure in m-NC9 anode occurs during the simultaneous volumetric distortion of the mesostructure, amorphization of the framework nanoparticles, and irreversible electrochemical reactions that lead to residual metallic Co and Ni as well as crystalline Li$_2$O.
Figure 4. (A) Dark-field cross-sectional TEM image and (B) high resolution TEM micrograph of m-NC9 thin film anode after 2 galvanostatic discharge-charge cycles. The loss of the ordered mesostructure is clear with nanoparticles remaining in the film. (C) STEM (Scanning transmission electron microscopy) image of m-NC9 and (D) combined elemental (Ni (red), Co (green), O (magenta) and C (blue)) color map of corresponding region illustrating the potential phase separation of Co and Ni into nanoparticles

To corroborate loss of ordered porous structure upon galvanostatic cycling of m-NC9 anode, cross-sectional transmission electron microscopy (TEM) micrographs were obtained after 2 cycles. TEM micrographs of the m-NC9 prior to cycling are shown in Figure S8A. Initially, m-NC9 is highly porous, but lacking long range order. As can be seen in Figure 4A, m-NC9 anode
possesses some distorted mesopores after 2 charge-discharge cycles, but there are also regions with high pore density (Figure 2B) and limited porosity with some large pores (Figure 2C). This heterogeneity in the mesostructure is consistent with the loss of the correlation peak in the GISAXS (Figure 2A) profiles upon successive cycling. Examination of the film with high resolution TEM (Figure 4B) indicate that the oxide framework consists of $3.4 \pm 0.3$ nm nanoparticles that are surrounded by a low Z coating, which is likely to be the solid electrolyte interface (SEI). Further evidence for this morphology can be obtained from scanning transmission electron microscopy (Figure 4C) where a few large distorted pores can be seen with bright spots corresponding to high Z atoms. Elemental mapping (Figure 4D and S9) indicates a partial segregation of the Co with Ni tending to surround the Co, which may be further evidence of the irreversible formation of metallic Co and Ni as Ni tends to surface segregate. This elemental mapping also suggests that the amorphous charge product is likely to be separate phases of cobalt and nickel oxides, not amorphous NiCo$_2$O$_4$, from the segregation of Co and Ni. Additionally, the presence of carbon (C) in the anodic film after 2 cycles confirms the formation of SEI and this layer tends to be segregated to the surface of the mesopore voids. This SEI layer will modestly contribute towards the reduction in scattering intensity in the GISAXS profiles. Irrespective, the microscopy confirms the loss of the ordered mesostructure of the m-NC9 anode after 2 lithiation/de-lithiation segments.
Figure 5. *operando* GISAXS profiles during galvanostatic cycling of (A) m-NC16 and (B) m-NC28 thin film anodes. (C) Change in d-spacing of m-NC16 and m-NC28 anodes based on analysis of primary scattering peak. 1-D *operando* GIXD profiles from galvanostatic cycling of (D) m-NC16 and (E) m-NC28 film anodes. The same color scheme is used throughout: initial discharge (red), 1st charge (blue), 1st discharge (green), 2nd charge (black), and 2nd discharge (grey).
Analogous mesoporous NiCo$_2$O$_4$ with larger pores (m-NC16 and m-NC28) enable understanding the impact of mesopore dimensions on mesostructure evolution during battery operation assessed by combining the operando GISAXS and GIXD measurements during galvanostatic cycling (Figure 5). Prior to the initial discharge, 1-D GISAXS profiles for m-NC16 and m-NC28 anodes demonstrate a well-defined primary peak at $q_x \approx 0.0236 \text{ Å}^{-1}$ ($d$-spacing = 26.6 nm) and $q_x \approx 0.0128 \text{ Å}^{-1}$ ($d$-spacing = 49.1 nm) and a second order peak at $q_x \approx 0.0394 \text{ Å}^{-1}$ ($d$-spacing = 15.9 nm) and $q_x \approx 0.0216 \text{ Å}^{-1}$ ($d$-spacing = 29.1 nm), respectively. The improved resolution of the second order peak for m-NC16 and m-NC28 in comparison to m-NC9 is consistent with the more ordered surface morphology from AFM (Figure 1). The galvanostatic charge-discharge voltage profiles of m-NC16 and m-NC28 anodes exhibit multiple redox plateaus as expected for NiCo$_2$O$_4$ (Figure S10), similar to the m-NC9 anode. Analysis of primary diffraction peak indicates significant reduction in primary peak intensity during the initial discharge segment, which is likely primarily associated with the reduction in the contrast from the formation of Li$_2$O to reduce the electron density of the mesoporous framework (Figure S11). The primary diffraction peak in the GISAXS profiles of m-NC16 and m-NC28 indicates breathing of the mesostructure during the lithiation and de-lithiation process (Figure 4C). At the end of initial discharge cycle (lithiation segment, red curve), the $d$-spacing is found to increase from 26.6 nm to 27.1 nm (m-NC16) and from 49.1 nm to 49.8 nm (m-NC28), respectively. Upon de-lithiation ($1^{st}$ charge segment, blue curve), the $d$-spacing is found to decrease back to 26.6 nm (m-NC16) and 49.2 nm (m-NC28) respectively associated with the volumetric contraction of the oxide framework. Unlike m-NC9 anode, quantitative analysis of primary scattering peak obtained from GISAXS profiles of m-NC16 and m-NC28 indicates a reversible increase and decrease in $d$-spacing during the 2nd lithiation/de-lithiation segments (Figure 5C). The
mesoporous structure is retained for these two mesoporous films after 2 cycles of operation. However, the intensity of the 2\textsuperscript{nd} order peak reduces during the cycling process for m-NC16 and m-NC28 anode, indicating distortion of spherical mesopore geometry and loss of pore ordering upon successive cycling. The mesostructure dimensions appear to be a critical factor in the evolution of ordered porous structure during galvanostatic cycling of metal oxide anodes, suggesting that larger nanopores might be desired for preserving the nanostructure in these electrodes.

GISAXS also enables particle size analysis during battery operation from the high $q$ data. There is 78\% and 89\% volumetric expansion of nanoparticles during the initial discharge/lithiation cycle (Figure S6) for m-NC16 and m-NC28 anode, respectively. On de-lithiation, nanoparticles making up the framework of m-NC16 and m-NC28 anodes shrink to 37\% and 23\% their lithiated volume, respectively (Figure S6), as opposed to 45\% for the m-NC9 anode. This difference in the reversibility of the nanoparticle size suggests that the Li\textsuperscript{+} insertion is more reversible in larger nanoparticles as this change in size for m-NC9 appears correlated with irreversible formation of Li\textsubscript{2}O. The \textit{operando} GISAXS profiles and particle size analysis suggests that larger mesostructures with $d_{\text{pore}} > 15$ nm can maintain their nanostructured architecture better than smaller mesoporous of m-NC9 ($d_{\text{pore}} \sim 9$ nm), which collapse in the first 2 cycles of battery operation (Figure 2A). The improved stability of the mesostructure appears to be correlated with electrochemical performance as the discharge capacities in the 1\textsuperscript{st} cycle for m-NC28 and m-NC16 (1272 mAh/g and 941 mAh/g) exceed that of m-NC9 (881 mAh/g) as the pore size increases. The higher discharge capacity exhibited by m-NC28 as compared to m-NC9 anode, despite the higher initial specific surface area of m-NC9 (92.8 m\textsuperscript{2}/cm\textsuperscript{3} (m-NC9) and 51.9 m\textsuperscript{2}/cm\textsuperscript{3} (m-NC28), (Figure S4) indicates the importance of retaining the mesopore morphology
to facilitate reversible insertion/de-insertion of Li\textsuperscript{+} ions through redox reactions for a starting anode material of NiCo\textsubscript{2}O\textsubscript{4}.

\textit{Operando} grazing incidence x-ray diffraction (GIXD) provides insight into atomic scale changes in the crystalline structure of m-NC16 and m-NC28 (Figure 5D and 5E). Both m-NC16 and m-NC28 initially consist of the same \textit{Fd}-3\textit{m} spinel phase of NiCo\textsubscript{2}O\textsubscript{4} (PDF card no. 01-073-1702) as discussed previously for m-NC9. During the initial discharge, the (400) and (440) diffraction peaks shift to lower \( q \) due to increase in lattice spacing associated with Li\textsuperscript{+} ion insertion. Similar to the m-NC9 anode, the intensity of (311) diffraction peak monotonically decreases indicating the reduction of NiCo\textsubscript{2}O\textsubscript{4} with metallic Ni and Co formed as evidenced by the (111) diffraction peak that grows at \( q = 3.12 \ \text{Å}^{-1} \). The diffraction peaks associated with spinel NiCo\textsubscript{2}O\textsubscript{4} do not re-emerge on de-lithiation of m-NC16 and m-NC28 anodes, corresponding to the formation of primarily amorphous reaction products as was found previously for m-NC9. The small diffraction peak at \( q = 4.42 \ \text{Å}^{-1} \) corresponds to Li\textsubscript{2}O formation and is present throughout successive de-lithiation/lithiation cycles, indicating some irreversibility. This behavior is consistent with the nanoparticle size analysis (Figure S6), which indicated particles possess an increased volume upon de-lithiation. However, unlike m-NC9 anode, the diffraction profiles do not exhibit well defined peaks from the (111) and (220) crystal planes of Li\textsubscript{2}O upon successive galvanostatic cycling, which suggests that the Li\textsubscript{2}O is not as well developed in these larger nanoparticles. Elemental mapping by STEM suggest potential phase separation of the Ni and Co in these mesoporous films as well after cycling (Figures S12 and S13), which leads to discrete oxides (nickel oxide and cobalt oxide) as the charge product.
**Figure 6.** Cross-sectional TEM micrographs of (A,B) m-NC16 and (C,D) m-NC28 thin film anode illustrating the distorted spherical mesopores on galvanostatic cycling.

*ex situ* TEM after galvanostatic cycling (Figure 6) illustrates the cross-section of m-NC16 and m-NC28 anodes to confirm the conclusions from the *operando* GISAXS measurements. Both m-NC16 and m-NC28 anodes exhibit a porous matrix consisting of NiCo$_2$O$_4$ nanoparticles (6 nm-12 nm) with distorted ordered mesopores. A distribution of mesopore size varying from 6 nm to 21 nm (Figure 6B and 6C) in the TEM micrographs is present, but the local ordering of the framework could lead to a broad primary peak in the GISAXS spectra. The poor long-range ordering of these mesopores is consistent with the GISAXS profiles that indicated significant distortion of mesostructure during the galvanostatic cycling process. Based on these *operando* GISAXS study and *ex-situ* TEM micrographs, the m-NC16 and m-NC28 anodes undergo
distortion in morphology during the cycling process, but the nanoporous structures are still partially maintained. This result is in contrast to the near complete collapse of the nanoporous structure of m-NC9 and suggests that below a critical pore dimension (~9 nm) and pore wall thickness (~6 nm), the stresses developed in NiCo$_2$O$_4$ framework due to lithium insertion/de-insertion could lead to collapse of the ordered mesoporous structure during the initial battery cycling. These data also suggest that there is some critical size for single component nanostructures to be stable during battery operation, at least for conversion-based materials, below which the nanostructure will collapse.

In the end, the most critical factor is if the changes in the nanostructure can be correlated with the battery performance. For NiCo$_2$O$_4$ examined here, the stability of the nanostructure appears to be directly correlated with the charge storage performance through the first 2 charge-discharge cycles. To understand the longer term cycling performance, m-NC28 and m-NC9 anodes were subjected to ex-situ galvanostatic cycling at a constant current density of 600 mA/g (Figure 7). Mesoporous m-NC28 and m-NC9 anodes provide high discharge capacities of 1170 mAh/g and 772 mAh/g in the first cycle, but the storage capacity drops in both cases on successive cycles. However, m-NC9 more drastically loses its charge storage capabilities to 245 mAh/g after the 2$^{nd}$ cycle and only 201 mAh/g in the 5$^{th}$ cycle, corresponding to capacity retention of only 26%. This severe capacity fade of m-NC9 anode in the first few cycles is consistent with the loss of ordered porous structure and irreversible electrochemical reactions determined from GISAXS/GIXD (Figure 2). m-NC9 essentially behaves as a non-porous bulk NiCo$_2$O$_4$ anode after the 2$^{nd}$ cycle, which primarily explains the drop in specific capacity. The specific discharge capacity of m-NC9 continues to fade to 115 mAh/g at the end of 30 cycles (15% capacity retention).
Figure 7. Capacity and columbic efficiency of m-NC28 (●) and m-NC9 (▲) anodes at a current density of 600 mAh/g during Galvanostatic cycling.

The capacity fade of m-NC28, is more gradual with specific capacities of 754 mAh/g in the 2\textsuperscript{nd} cycle and 482 mAh/g in the 5\textsuperscript{th} cycle (41% capacity retention), which are significantly higher than for the m-NC9 anode. The retention of mesoporous morphology is not complete and some distortion still occurs (Figure 4), which may be responsible for the continual capacity fading. After 30 cycles, the discharge capacity decreased to 182 mAh/g for the m-NC28 anode (15.5% capacity retention) and the ex-situ GISAXS measurements indicate loss of ordered mesostructure after 30 cycles of operation (Figure S14). This result clearly demonstrates an apparent relationship between the retention of the ordered structures and capacity; the stability of the morphology depends on the size of the nanostructure. It is also important to note that sum of small changes in the nanostructure due to stresses associated with the charge-discharge over multiple cycles can lead to significant re-arrangement of the morphology. Thus, conclusions drawn from operando measurements during a single charge-discharge must be carefully...
considered. *operando* GISAXS/GIXD measurements have been used to correlate evolution of mesostructure and charge storage performance in a model lithium ion battery.

**CONCLUSION**

In this *operando* measurement study, we demonstrate that the evolution of metal oxide anode mesostructure during battery operation is greatly affected by the initial mesopore dimensions. Complementary GISAXS and GIXD probing of mesostructure and crystal structure changes illustrates that NiCo$_2$O$_4$ anodes possessing mesopores smaller than 10 nm collapse during the first 2 cycles of operation with irreversible electrochemical reactions. The loss of mesostructure is accompanied by substantial capacity fade (85%). Conversely, ordered mesoporous metal oxide anodes possessing larger pore dimensions exhibit less distortion of the mesostructure and remain porous through the first 2 charge-discharge cycles. This structural retention appears correlated with the improvement in cycling performance in a lithium ion battery. These complementary *operando* GISAXS and GIXD studies begin to provide a mechanistic understanding of structural evolution during electrochemical cycling and provide a route to start to develop design principles for fabrication of high energy density oxide anodes that exhibit improved cycling stability in lithium ion batteries. We believe this study can be further extended to gain fundamental insights into reinforcement provided by carbon through ALD or other conformal coating methods on the ordered nanostructure.

**MATERIALS AND METHODS**

*Materials:* Nickel (II) nitrate hexahydrate (puriss. p.a., ≥ 98.5%), cobalt (II) nitrate tetrahydrate (reagent grade, 98 %), citric acid (ACS reagent, ≥ 99.5%), ethanol (ACS reagent, ≥
99.5% (200 proof, absolute), tetrahydrofuran (THF) (ACS reagent, ≥ 99.0%, 250 ppm BHT as inhibitor), mercaptosuccinic acid (97%), methoxy poly(ethylene glycol) methacrylate (PMPEGMA, 475 g mol⁻¹), butyl acrylate (>99%), N,N-dimethylformamide (DMF) (anhydrous, 99.8%), and hexane (anhydrous, 95%) were purchased from Sigma-Aldrich and used as received. 2,2’-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized following prior literature reports. Deuterated chloroform (CDCl₃) (Cambridge Isotope Laboratories, Inc.) was used as received as solvent for NMR.

For battery testing, lithium hexafluorophosphate (LiPF₆) in ethylene carbonate: dimethyl carbonate (EC: DMC) 1:1 (v/v) was purchased from BASF Battery Materials. Lithium metal foil (0.25 mm thickness) was used as the reference and counter electrode.

Preparation of mesoporous NiCo₂O₄ thin film anodes: A thin gold layer (~ 50 nm) was sputter-coated on sapphire substrate (0.375” diameter, 0.02” thickness, Esco Optics) for the conductive current collector. The gold-coated sapphire substrates were immersed in 10 mM ethanoic mercaptosuccinic acid for 24 h and subsequently rinsed by ethanol multiple times and dried using a nitrogen gas stream. This treatment improves the wetting of the solution used to fabricate the mesoporous thin films.

Mesoporous NiCo₂O₄ thin films were prepared using block copolymer micelle templating protocols as described elsewhere. The use of PMPEGMA-b-PBA as the structure directing and templating agent led to pore sizes varying between 9 nm and 26 nm by varying the molecular weight from 37 kg•mol⁻¹ to 59 kg•mol⁻¹ to 101 kg•mol⁻¹. The PMPEGMA-b-PBA were synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization following protocols described elsewhere. In a typical synthesis, thin films were fabricated by
first mixing 0.147 g of Ni(NO$_3$)$_2$•6H$_2$O and 0.285 g of Co(NO$_3$)$_2$•6H$_2$O with 0.143 g of citric acid in 0.77 g ethanol. This mixture was stirred in a vortex mixer for 1 h at 22 °C. In a separate vial, 0.254 g of PMPEGMA-b-PBA was dissolved in 2.28 g of THF and stirred at 400 rpm for 1 h. The ethanoic solution of metal nitrates and citric acid was then added dropwise to the PMPEGMA-b-PBA/THF solution and stirred for another 1 h to obtain a dark red solution. Table 1 provides the compositions utilized to fabricate m-NC9, m-NC16 and m-NC28. The molecular weight of the PMPEGMA-b-PBA was 37 kg/mol, 59 kg/mol, and 101 kg/mol for m-NC9, m-NC16 and m-NC28, respectively.

**Table 1.** Chemical compositions utilized for fabrication of m-NCx thin film anodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni(NO$_3$)$_2$•6H$_2$O (g)</th>
<th>Co(NO$_3$)$_2$•6H$_2$O (g)</th>
<th>Citric acid (g)</th>
<th>PMPEGMA-b-PBA (g)</th>
<th>Ethanol (g)</th>
<th>THF (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-NC9</td>
<td>0.147</td>
<td>0.285</td>
<td>0.143</td>
<td>0.254</td>
<td>0.77</td>
<td>2.28</td>
</tr>
<tr>
<td>m-NC16</td>
<td>0.172</td>
<td>0.345</td>
<td>0.176</td>
<td>0.275</td>
<td>0.86</td>
<td>2.46</td>
</tr>
<tr>
<td>m-NC28</td>
<td>0.137</td>
<td>0.266</td>
<td>0.134</td>
<td>0.257</td>
<td>0.79</td>
<td>2.27</td>
</tr>
</tbody>
</table>

The gold coated substrates were dip coated into these solutions at 1 mm/s at relative humidity of 30% to 40% to fabricate the film anodes. The cast films were dried at room temperature for 15 min followed by calcination in preheated muffle furnace (Ney Vulcan 3-130) at 225 °C for 1 h to produce micelle templated metal carbonates. These NiCo$_2$(CO$_3$)$_3$ films were passively cooled down to room temperature, followed by heating at 365 °C for 30 min to fabricate the final oxides, m-NCx.
Mesoporous NiCo$_2$O$_4$ characterization: Thermogravimetric analysis (TGA, Thermal Analysis Q50) was used to determine the decomposition temperature of the PMPEGMA-b-PBA templates and the temperatures for NiCo$_2$(CO$_3$)$_3$ and NiCo$_2$O$_4$ formation as shown in Figure S15. Powders of the nickel nitrate, cobalt nitrate and citric acid were prepared from drying solutions of metal nitrate and citric acid in ethanol / THF mixture at 50 °C for 10 h. TGA measurements on this powder was performed using a constant air purge and heating rate of 5 °C/min. Spectroscopic ellipsometry (M-2000, J. A. Woollam) in the wavelength range of 350–1100 nm was used to determine the thickness of the m-NCx films. The optical properties were modeled using Gaussian and Lorentz oscillators (GenOsc model) in WVase software (J. A. Woollam). The porosity and pore size distribution of m-NCx thin film anodes were estimated from ellipsometric porosimetry (EP)$^{57}$ using ethanol as the probe solvent. The Kelvin equation was applied to the adsorption isotherm to determine the pore size distribution.$^{58}$ Based on EP data, the volume of solvent adsorbed at saturation was used to estimate the porosity. The surface morphology was investigated prior to and after galvanostatic cycling using atomic force microscopy (AFM, Dimension ICON, Veeco). Cross-sectional HRTEM image were acquired on JEOL2100F HRTEM at 200kV. STEM and elemental mapping were performed on Hitachi 2700C with accelerating voltage at 200kV. We employed the focused ion beam (FIB) in situ lift-out technique using FEI Helios 600 dual beam FIB to prepare the TEM thin-film samples.

operando synchrotron GISAXS/GIXD characterization: Grazing incidence small angle X-ray scattering (GISAXS) and grazing incidence X-ray diffraction (GIXD) were performed simultaneously at the 12-ID-B beamline of Advanced Photon Source (APS) at Argonne National Laboratory (ANL) to monitor changes in m-NCx structure during battery operation. Galvanostatic cycling was carried out in a custom-designed lithium ion cell consisting of a
polyimide tube window (inner diameter = 0.3937"; thickness = 0.00787") to allow x-rays to penetrate onto the thin film anodes (Figure S1). A second, larger tube was used to generate an annular region for an Ar purge to prevent O₂ and H₂O from reaching the electrodes and electrolyte. An incident X-ray beam of energy 14 keV (wavelength = 0.0918 nm) and beam size of 250 µm was used. The scattering data were collected using a Pilatus detector with sample to detector distance (SDD) fixed at 1922 mm for GISAXS and 176 mm for GIXD. All samples were measured at incident angle of 0.18°, which is above the critical angle of the NiCo₂O₄ thin film sample (0.159° at 14.0 keV). The 2-dimensional scattering patterns obtained from GISAXS were processed using the Irena software package⁵⁹ to obtain the one-dimensional (1D) line-cuts profiles in the form of the Intensity vs qₓ.

The GISAXS data were quantitatively analyzed in the high-q region. The scattered intensity at high q should arise from the NiCo₂O₄ nanoparticles that comprise the mesoporous framework in these thin films. The scattering intensity, I(q), was expressed using standard decoupling approximation for analysis of nanoparticles as I(q) = N(Δρ)²F(q)S(q).⁶⁰,⁶¹,⁶² where q is the momentum transfer vector defined as q = (4π/λ) sin θ, N is the particle number density, Δρ is the electronic density contrast, λ is the x-ray wavelength, θ is one half of the scattering angle, F(q) is the form factor and S(q) is the structure factor. The shape, size and polydispersity of NiCo₂O₄ nanoparticles is described by F(q), which S(q) describes the positional correlation between particles. As the nanoparticles are randomly distributed in the framework and quite polydisperse, the structure factor was assumed to be essentially invariant in the high q limit (e.g., S(q)=1).⁶¹ With this assumption, the scattering at high q can be approximated as I(q) = K·F(q), where K is a constant. Based on TEM micrographs, the NiCo₂O₄ nanoparticles were almost spherical and thus the form factor for spheres was used to account for the nanoparticle
shape in fitting the high $q$ data. A Schulz-Zimm distribution function was used to describe the nanoparticle sizes. The scattering data was fit to this model using Modeling II tool in Irena software package.\textsuperscript{59} For GIXD, the background scattering contributions from LiPF$_6$ in EC/DMC electrolyte and gold coated sapphire substrate was subtracted from the diffraction patterns of m-NCx. The 2D diffraction data was azimuthally averaged to generate the 1D GIXD profiles. The average crystal size of m-NCx was estimated applying the Scherrer equation\textsuperscript{46} to the most intense diffraction peak and assuming $\beta = 0.9$.

**Electrochemical characterization of m-NCx thin film anodes:** The fabricated m-NCx films were tested as binder-free anodes in the custom-designed lithium ion cell that enabled the *operando* x-ray measurements. The average NiCo$_2$O$_4$ mass loading was \textasciitilde 500 mg/m$^2$. Galvanostatic measurements used 1M LiPF$_6$ in EC/DMC (1:1 v/v) as the electrolyte with Li metal foil as the counter and reference electrode. A battery tester (BST8-WA, MTI) was used for constant current density charge-discharge between 0.2V-3.0V vs Li/Li$^+$. All anodes were subjected to an initial galvanostatic discharge at 300 mA/g, while a current density of 600 mA/g was utilized in subsequent cycles. To prevent oxidation of the Li cathode, Ar was flowed across the custom-designed cell during battery operation. *Ex-situ* long-term cycling tests were performed in an Ar glovebox with O$_2$ and H$_2$O <0.5 ppm.

**Supporting Information.** Design of custom-designed lithium ion cell body, Chemical structures of MPEGMA, butyl acrylate, 4-cyanopentanoic acid dithiobenzoate (CPADB) RAFT agent, GPC traces of PMPEGMA-b-PBA templates, TGA traces indicating formation of NiCo$_2$(CO$_3$)$_y$ and NiCo$_2$O$_4$, ellipsometric porosimetry and t-plots analysis, *in-situ* nanoparticle size analysis of m-NC9, m-NC16 and m-NC28 anodes, mapping of peak intensity and FWHM of m-NC9, m-NC16 and m-NC28 anodes, cross-sectional TEM micrographs of m-NC9, m-NC16 and m-NC28
anodes, charge-discharge profiles of m-NC16 and m-NC28 anodes, ex-situ GISAXS micrographs of m-NC28 anode after 30 cycles of operation are included in the Supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

**Corresponding Author**

*B.D.V: vogt@uakron.edu*

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**ACKNOWLEDGMENT**

This work has been partial supported by the National Science Foundation under grant CBET-1336057. The authors express their gratitude to Min Gao at Kent State University for assistance with obtaining TEM images of the initial (uncycled) samples. The TEM data were obtained at the (cryo) TEM facility at the Liquid Crystal Institute, Kent State University, supported by the Ohio Research Scholars Program *Research Cluster on Surfaces in Advanced Materials*. The authors thank Dr. Pattarasai Tangvijitsakul and Dr. Mark Soucek for their synthesis and characterization of the PMPEGMA-\(b\)-PBA block copolymer template. This research used JEOL2100F HRTEM and Hitachi2700C STEM of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704. Preliminary GISAXS measurements were performed using X9 beamline of National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic
Energy Sciences, under Contract DE-AC02-98CH10886. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

REFERENCES


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*In-operando* GISAXS

*In-operando* GIXD