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Unveiling the dimensionality effect of conductive fillers in thick battery electrodes for high-energy storage systems **6**

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ABSTRACT

The applications of lithium-ion batteries are limited, as they cannot fulfill the requirements for high power output and reversible energy storage. The main challenges are centered around developing electrode architectures to produce both high energy and power. As one of the key components, conductive fillers play a vital role in battery electrodes, contributing to the electrical conductivity and shaping electrode structures, which significantly determine the rate capability. In this study, the dimensionality effect of conductive fillers on electrochemical performance is elucidated in thick electrodes for scalable energy storage. In particular, three types of conductive fillers: single-walled carbon nanotubes, graphene nanosheets, and Super P, are studied using commercial $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as the model material. The role of these conductive fillers on electrodes with single-walled carbon nanotubes exhibit superior rate performance owing to both high electrical conductivity and tight wrapping architecture, which was further revealed by various advanced structural and electrochemical characterization. This work demonstrates the dimensionality effect of conductive fillers on both electrochemistry and electrode architecture and highlights the advantages of 1D conductive filler in thick electrodes, which brings new insights in future high energy/power systems.

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I. INTRODUCTION

In recent years, lithium-ion batteries (LIBs) have become the major rechargeable power sources for electric vehicles (EVs) and portable electronic devices.^{1–3} However, applications of LIBs are limited because currently they could not fulfill the requirement for high power output and reversible energy storage.^{4,5} Therefore, challenges still remain for developing novel materials and/or engineering electrode architecture to reach both high energy and power. Approaches for promoting the rate capability of batteries involve a variety of battery components, i.e., active material, electrolyte, conductive filler and binder, means of downsizing the active material to nanoscale,^{6–8} build-ing stable solid-electrolyte interface (SEI),^{9,10} modulating material crystal structure and surface chemistry,^{11,12} and establishing ionically and electronically conducting pathways in the electrode.^{13–15} Ionic conduction, including ion migration in the electrolyte and solid-state diffusion, is always considered as the key factor to the rate capability. While the thick electrode design has been recognized to substantially enhance the energy density, it also suffers from poor Li-ion transport kinetics, resulting in poor material utilization since the Li-ion diffusion in the electrolyte turns out to be the rate-determining step when increasing the electrode thickness.^{16,17} To this end, various techniques have been developed to build vertically aligned channels^{18–20} or create pores with hierarchical sizes²¹ to facilitate ion transport and realize high rate capability in thick electrodes in recent years.

Since electrochemical reactions in the battery consist of various processes with coupled contribution of both Li-ions and electrons, electronic conduction also plays a significant role in the rate capability of batteries.^{22,23} A large number of studies have been focused on developing novel conductive fillers and establishing an interconnected

conducting network in the electrode. Carbon black has been commonly used in commercial batteries because of its high electrical conductivity, low price, and large-quantity production. Additionally, carbon nanotubes (CNTs)²⁴⁻²⁶ and graphene nanosheets (GNs)²⁷⁻ are considered to be promising candidates due to their high electrical conductivity, and their capability in improving electrochemical performance has been verified. Interconnected and conductive scaffolds based on wood template,^{30,31} carbon fiber cloth,³² and reduced graphene oxide (rGO) aerogel¹³ also supply long-range electron transport pathways throughout the electrode. Although a variety of conductive fillers have been extensively developed, the understanding of how the geometry and dimensionality of these fillers affect the electrode conductivity, architecture, and ultimately the electrochemical performance in high-energy storage systems, is still insufficient, despite their considerable significance to advanced battery electrode design. Therefore, understanding the role that a conductive filler plays in a thick electrode is essential, and new insights could be brought toward the high energy/power battery design.

In this study, the dimensionality effects of conductive fillers on both structural and electrochemical properties of thick battery electrodes are systematically investigated. In particular, three types of conductive fillers—single-walled carbon nanotubes (SWCNTs), GNs, and Super P—are studied using LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) as the model material. The effects of these conductive fillers on electrical percolation, electrode architecture, and electrochemical properties of NCM electrodes are illustrated. Impressively, the NCM/SWCNT electrode exhibits the best rate capability owing to the high electrode conductivity and advanced electrode architecture, which have been confirmed by various structural and electrochemical characterization, including electrochemical impendance spectroscopy (EIS), Raman three-dimensional (3D) mapping, and operando X-ray absorption spectroscopy (XAS).

II. RESULTS AND DISCUSSION

NCM electrodes are prepared by a typical slurry-casting method with various conductive fillers (see Sec. IV). GNs and SWCNTs are pre-dispersed with surfactant in water, as shown in the scanning transmission electron microscope (STEM) images in Figs. S1 and S2, respectively, to ensure a homogeneous distribution in the electrode. Figure 1(a) shows the schematic of NCM electrodes with Super P, SWCNTs, and GNs as conductive fillers, respectively. It could be observed that the Super P and NCM particles follow a point-to-point contact mode in the electrode, as shown in the scanning electron microscope (SEM) images in Figs. 1(b) and 1(c). Different from Super



FIG. 1. Electrode architecture of NCM electrodes with various conductive fillers. (a) Schematic of NCM electrodes with Super P, SWCNTs, and GNs as conductive fillers. Topview SEM images of the (b, c) NCM/SP electrode, (d, e) NCM/SWCNT electrode, and (f, g) NCM/GN electrode in different magnifications. In contrast with Super P, SWCNTs wrap closely on the surface of NCM particles and tend to form a conductive coating layer. The wrapping in the NCM/GN electrode is not as uniform as that in the NCM/ SWCNT electrode, potentially due to the stacking of the GNs in the electrode.

P, SWCNTs wrap closely on the surface of NCM particles and form a conductive coating layer because of the high aspect ratio of SWCNTs [Figs. 1(d) and 1(e)]. Networks consisting of interconnected SWCNTs in the interspace of NCM particles can also be observed. Similar to the morphology of the NCM/SWCNT electrode, GNs are attached on the surface of NCM particles. However, the wrapping is not as uniform as that in the NCM/SWCNT electrode, probably resulting from the stacking of GNs in the electrode [Figs. 1(f) and 1(g)]. The observed different electrode structures and contact modes between conductive fillers and active materials potentially bring different effects on the electrochemical performance of thick NCM electrodes.

In the first place, establishing the understanding of how the content and dimensionality of conductive fillers affect the electrical properties of NCM composites is required. Therefore, through-plane conductivities of NCM composite films were measured by a two-point technique and plotted as a function of weight fraction of carbon content, as shown in Fig. 2(a). Figure S3 shows the percolation plot vs volume fraction of carbon content, which has the similar trend to Fig. 2(a). The contents of conductive filler are controlled over the percolation threshold as the electrical percolating network is required in the properly functioning battery electrodes. The measured electrical conductivity is consistent with percolation effects, that is, when an electrically conductive filler is added to an insulating matrix, significant increases in conductivity will occur once the first conducting pathway through the composite is formed. This kind of behavior follows the percolation theory above the percolation threshold:³³

$$\sigma_{\rm c} = \sigma_{\rm f} \left(\frac{\phi - \phi_{\rm c}}{1 - \phi_{\rm c}} \right)^{\rm t},\tag{1}$$

in which σ_c and σ_f are the electrical conductivity of composite and conductive filler, respectively; ϕ_c is the percolation threshold; ϕ is the weight fraction of conductive filler; and t is the percolation exponent. The electrical conductivities of NCM composites are fitted by the percolation theory, as shown in Fig. 2(b). While the measured conductivity for NCM/GN composites follows the percolation theory, neither the NCM/SP nor the NCM/SWCNT composites follow the equation in a high carbon content region. The fitted percolation parameters are shown in Fig. 2(c). The fitted percolation thresholds are 0.16, 0.47, and 0.67 wt. % for the NCM/SWCNT, NCM/GN, and NCM/SP composites, respectively. Since the percolation threshold has positive correlation with the ratio of the smallest to largest dimension of conductive filler,³⁴ SWCNTs with the largest aspect ratio should have the lowest percolation threshold, while isotropic Super P particles have the highest percolation threshold, which are in accord with the fitted result. A similar study using fillers with different dimensionalities has been reported recently,³⁵ though its conclusions are not exactly the same as ours. Although SWCNT composite was still determined to possess the smallest percolation threshold, the composite with carbon black exhibited a smaller percolation threshold compared with the GN sample, as reported in the study. This opposite conclusion may result from different electrode preparation recipes. In our case, polyvinylyrrolidone (PVP) was added to prevent aggregation of GNs, and secondary particle collapse was also inhibited during the electrode preparation process, which makes the most of GNs in the composite and thus lowers the percolation threshold. Compared with NCM/SP composite, composites with SWCNTs and GNs both exhibit smaller percolation exponents, indicating in these two composites, electrical conductivity will increase more rapidly when adding carbon fillers. Another



FIG. 2. Electrical conductivity of NCM composites with carbon fillers of different dimensionalities. (a) Plot of through-plane electrical conductivity vs carbon (i.e., Super P, SWCNT, or GN) content for NCM composites. (b) Conductivity plotted as percolation plots of NCM composites vs carbon weight fraction (ϕ) over the percolation threshold (ϕ_c). (c) Table of the fitted percolation parameters for ϕ_c , percolation parameters for ϕ_c , bercolation exponent (t), and electrical conductivity of conductive filler (σ_t).

Appl. Phys. Rev. 7, 041405 (2020); doi: 10.1063/5.0024123 Published under license by AIP Publishing important parameter is the fitted electrical conductivity, which reveals the intrinsic electrical conductivity of the filler. As shown in Fig. 2(c), SWCNTs exhibit the highest electrical conductivity of 4.43 S m⁻¹, followed by Super P (2.89 S m⁻¹) and GNs (0.16 S m⁻¹). The lowest fitted electrical conductivity of GNs probably results from the remaining oxygen after thermal reduction process. The SEM images of NCM composites with various conductive fillers are shown in Figs. S4–S6 in the supplementary material. It can be observed that with a small amount of conductive filler, the distribution and connection between fillers and active materials inside the electrode are poor, which causes the low electrical conductivity. Therefore, a sufficient amount of conductive filler is essential to the formation of a conductive pathway through the composites, and NCM electrodes with 2 wt. % of conductive fillers are chosen as the model to study the effect of these fillers with various dimensionalities.

To investigate how the dimensionality of conductive fillers affects the electrochemical performance of NCM electrodes, various electrochemical characterizations were conducted on the electrodes with similar carbon contents (~2 wt. %) and areal mass loadings (~15 mg cm⁻²). As shown in CV curves under the scan rate of 0.1 mV s⁻¹, larger peak separations are observed in both NCM/SP and NCM/GN electrodes compared with the NCM/SWCNT electrode, probably resulting from the higher Ohmic resistance in these electrodes. Benefiting from both high electrical conductivity and tight wrapping architecture, the NCM/SWCNT electrode exhibits superior rate capability, delivering capacities of 142, 133, 121, and 101 mAh g⁻¹ at the current rate of 0.2, 0.5, 1, and 2 C, respectively [Fig. 3(b)]. The NCM/ GN electrode also achieves high capacities at low C-rates (e.g., 136 mAh g^{-1} at 0.2 C), however, the capacity drops rapidly when increasing the C-rate, for example, which is only 65 mAh g^{-1} at 2 C [Fig. S7(a) in the supplementary material]. It is possible that the poor rate performance of the NCM/GN electrode results from sluggish lithium ion transport in the electrolyte at high C-rates because GNs will be stacked and block Li-ion transport across the electrode. For the NCM/ SP electrode, it delivers relatively low capacity at $0.2 \text{ C} (131 \text{ mAh g}^{-1})$ compared with the other two electrodes, which could be explained by the poor contact between Super P and NCM particles, resulting in incomplete utilization of active materials [Fig. S7(b) in the supplementary material]. A plot of electrode resistance and conductivity is obtained from the IR drops in the galvanostatic charge/discharge curves, as shown in Fig. 3(c). The calculated conductivity in these electrodes show good agreement with the measured through-plane electrical conductivity, suggesting the significant role that electrical conductivity plays in electrochemical performance of NCM electrodes. Figure 3(d) clearly shows the comparison of rate performances among the electrodes with different fillers. Comparing the rate capability of the NCM/GN and NCM/SP electrodes, higher capacity retention in the NCM/SP electrode can be observed when increasing the C-rate, because the small pores between particles in the NCM/SP electrode can serve as diffusion channels for lithium ions. Impressively, the NCM/SWCNT electrode can also maintain relatively high rate capability when increasing the areal mass loading, with the capacity



FIG. 3. Electrochemical characterization of NCM electrodes. (a) Cyclic voltammetry under the scan rate of 0.1 mV s^{-1} . (b) Galvanostatic charge/discharge curves of NCM electrodes with 2 wt. % SWCNT at different current rates, delivering capacities of 142, 133, 121, and 101 mAh g⁻¹ at specific current rates of 0.2, 0.5, 1, and 2 C, respectively. (c) Plot of resistance and conductivity according to the IR drops in charge/discharge curves. (d) Rate performance and associated coulombic efficiency of NCM electrodes with different conductive fillers (2 wt. %). (e) Plot of specific discharged capacity vs C-Rate of NCM electrodes (2 wt. % SWCNT) with various areal mass loadings. It is visible that the NCM/SWCNT electrode can maintain a relatively high rate capability when increasing the areal mass loading. (f) Rate performance and associated coulombic efficiency of NCM electrodes with different contents of SWCNTs. It can be seen that electrodes with SWCNT content from 0.5 to 2 wt. % exhibit similar rate performance, demonstrating rapid electron transport is guaranteed even with 0.5 wt. % SWCNTs.

retention of 50.3% and 42.4% at 2 C for the electrode with 25 mg cm^{-2} and 31 mg cm^{-2} loading, respectively [Fig. 3(e)]. Through investigating the electrochemical performance of NCM electrodes with the same filler content, SWCNTs are determined to be the best conductive filler to realize a high rate capability of NCM electrodes, as a result of their high electrical conductivity and good wrapping structure.

The electrochemical performance of NCM electrodes with various carbon contents was also investigated to further illustrate the effect of the conductive fillers. Three different filler contents over the percolation threshold were chosen in the percolation plot for each conductive filler, and the rate performance of these electrodes was measured. As shown in Fig. 3(f), electrodes with SWCNT content from 0.5 to 2 wt. % exhibit similar rate performance, demonstrating that rapid electron transport is guaranteed even with 0.5 wt. % SWCNTs. The reason is that the percolation threshold of NCM/SWCNT composites is quite low (0.16 wt. %), therefore a tiny amount of SWCNTs is enough for good electronic conduction. However, with an increase in the content of Super P, obvious improvement of rate capability is observed in the electrode with 5 wt. % Super P, while the enhancement becomes small when keeping increase of the Super P content to 10 wt. % [Fig. S8(a) in the supplementary material]. The enhanced rate capability in these NCM/SP electrodes is due to both increased electrical conductivity with higher filler content [Fig. 2(a)] and sufficient interfacial contact between the Super P and NCM particles (Fig. S4 in the supplementary material). In Fig. S8(b) in the supplementary material, pronounced capacity decline, especially at high C-rates, is observed when reducing the GN content from 2 to 1 wt. %. This performance degradation results from the lowered electrical conductivity and poor utilization of active materials. Therefore, it could be assumed that the electrical conductivity of the electrodes is an important parameter determining the rate performance of NCM electrodes. The influence



EIS was utilized to investigate how the content and dimensionality of conductive fillers affect the electrochemical process in NCM electrodes. Figure 4(a) shows the Nyquist plots of NCM electrodes with 2 wt. % conductive fillers and fitted curves according to the Randles equivalent circuit. The NCM/SWCNT electrode exhibits the smallest series resistance (Rs) of ${\sim}3~\Omega$ cm² compared with NCM/GN and NCM/SP electrodes (~13 Ω cm²), suggesting small Ohmic resistance in this electrode. For the charge-transfer resistance (R_{ct}) , the smallest R_{ct} (~35 Ω cm²) is also observed in the NCM/SWCNT electrode, followed by the NCM/GN electrode (\sim 70 Ω cm²) and the NCM/SP electrode (~91 Ω cm²). Since the measured electrical conductivity of the NCM/GN and NCM/SP composites are close, it is possible that the wrapping structure facilitates the electron transfer in the interface, which reduces the R_{ct} and results in higher specific capacity at low Crate in the NCM/GN electrode. The apparent lithium diffusion coefficient (D_{ion}) can be determined with the following equations:

$$Z_{\rm Re} = R_{\rm s} + R_{\rm ct} + \sigma \omega^{-1/2} \tag{2}$$

$$D_{\rm ion} = \frac{R^2 T^2}{2A^2 n^4 F^4 \sigma^2 C^2},$$
 (3)

in which Z_{Re} is the real part of the Nyquist plot, σ is the Warburg factor, ω is the angular frequency, R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons in the reaction, F is the Faraday constant, and C is the concentration of lithium ion. Plot of Z_{Re} vs $\omega^{-1/2}$ is shown in Fig. 4(b) and Warburg factors can be calculated from the slopes of the fitted lines. The value of C and D_{ion} could refer to lithium ions in the electrolyte or solid phases, depending on the rate-limiting step. For fair comparison, the concentration of lithium ions is chosen as the



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FIG. 4. EIS characterization of the NCM electrodes. (a) Nyquist plots of the NCM electrodes conducted in half-cell (with Li metal as anode). Inset: Randles equivalent circuit for plot fitting. The NCM/ SWCNT electrode exhibits the smallest series resistance compared with NCM/GN and NCM/SP electrodes, suggesting the smallest Ohmic resistance in this electrode. (b) Warburg coefficients derived from the Nyquist plots and (c) associated apparent diffusion coefficients at open circuit voltage. The large differences in Dion is probably caused by different electrode architectures. (d) Charge-transfer resistances of the NCM electrodes with various contents of conductive fillers.

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concentration in the electrolyte ($C = 1 \mod \text{dm}^{-3}$) to determine the apparent diffusion coefficient in all three electrodes. Figure 4(c) shows the calculated D_{ion} for all three kinds of NCM electrodes. The D_{ion} of the NCM/SWCNT electrode is 2.3×10^{-11} cm² s⁻¹, approximately an order of magnitude larger than the Dion of the NCM/GN electrode $(2.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1})$. Considering the active materials used in this study have the same composition and particle size, the large difference in D_{ion} is probably caused by different electrode architectures. The lithium ion diffusion could be blocked by the stacked GNs inside the electrode, which potentially causes the small Dion. This result is consistent with the rate performance of the NCM/GN electrode, in which capacity degrades rapidly at high C-rates because of the sluggish lithium ion transport kinetics. To further understand the effect of conductive filler on the R_{ct}, Nyquist plots of NCM electrodes with various filler contents were measured, as shown in Fig. S9 in the supplementary material, and the R_{ct} of these electrodes were summarized in Fig. 4(d). It can be observed that R_{ct} is dramatically reduced when increasing the GN content, which is in agreement with the improved rate capability of NCM/GN electrodes. Also, for the NCM/SP electrodes, a large decrease in R_{ct} is observed when increasing Super P content to 5 wt. %, and the change of R_{ct} is small in the range from 5 to 10 wt. %, which is also in accord with their electrochemical performance. The smallest R_{ct} is achieved in the 2 wt. % NCM/SWCNT electrode among all these electrodes, which also exhibits the best rate performance.

Raman spectra of the three electrode types are displayed in Fig. S10 in the supplementary material. Bands between 300 and 750 cm⁻ correspond to metal oxygen vibrations, and bands at 1350 and 1590 cm⁻¹ correspond to the D and G modes of the carbon conductive additives.³⁶ For NCM particles [Fig. S10(b) in the supplementary material], two bands can be distinguished at \sim 490 cm⁻¹ and \sim 590 cm⁻¹, which have been previously assigned to the Co-O vibrations and Mn-O vibrations, respectively.37 For the GN sample, the peak located at $\sim 1340 \text{ cm}^{-1}$ represents the D band, which corresponds to the out-of-plane vibrations attributed to the presence of structural defects, while the peak located at $\sim 1590 \,\mathrm{cm}^{-1}$ represents the G band, resulting from the in-plane vibrations of sp² hybridized carbon atoms. Similar peaks are observed in the Super P sample with a relatively smaller I_D/I_G of 0.78 than the GN sample ($I_D/I_G = 0.81$). There is no D band observed in the SWCNT sample, indicating the high crystallinity of SWCNTs. Compared with pristine NCM powder and conductive fillers, no obvious peak shift is observed in any of the three electrode composites, suggesting the chemical interaction between the NCM particle and conductive filler formed during the electrode preparation process is negligible [Fig. S10(a) in the supplementary material]. It is noteworthy that using the same Raman setting parameters, NCM bands can be clearly identified in the NCM/GN and the NCM/SP electrodes; however, the intensity of NCM bands is rather low in the NCM/SWCNT electrode, possibly due to the close wrapping of SWCNTs on the NCM surface and the strong Raman scattering of SWCNTs.

Raman spectroscopy allows for interrogation of materials with both high and low crystallinity, and is sensitive to various metal oxides and carbonaceous materials, which renders capability of probing electrode porosity, tortuosity, and percolation of various materials. 3D confocal Raman mapping of electrodes has been conducted to offer a true chemical view of internal structures and the distribution of carbon fillers within the electrode. The set of spectra was processed using the non-negative matrix factorization (NMF) procedures, and it significantly improved the signal-to-noise ratio of the spectra. From the merged maps shown in Fig. 5, we can clearly observe more pores (empty space) present in the NCM/SWCNT electrode [Fig. 5(b1)], while the 2D GN filler seems to closely wrap the NCM particles [Fig. 5(c1)], as indicated by the highly overlapped blue and red signals. This close contact between active materials and carbon additives is also discernible in the NCM/SWCNT electrode, but is not as strong. The reason is that SWCNTs form interlaced networks in the interspace of NCM particles, which enlarges the porosity of the electrode. For the NCM/SP electrode, separated blue and red signals could be observed, indicating the poor contact between Super P and NCM particles. To further investigate the percolation of different carbon fillers, 2D Raman maps at each electrode depth are summarized in Fig. 5(d). Similar to previous 3D maps, large and deep pores can be clearly identified throughout the $10 \,\mu m$ depth in the NCM/SWCNT electrode, while the close contact between the 2D GN fillers and NCM particles, as indicated by the highly overlapped blue and red signals, seems to only exist on the electrode surface, as a decreasing amount of GNs with the increasing electrode depth was observed. The inhomogeneous distribution of GNs in the electrode could be attributed to the stacking issue of GNs during the electrode preparation process, resulting in relatively poor rate capability among the three electrodes.

The Classical Least Squares (CLS) rendered maps are depicted in Fig. S11 in the supplementary material. In general, these CLS maps agree well with previous NMF maps shown in Fig. 5, where the highest porosity (black region) was observed in the electrode with 1D SWCNT fillers [Fig. S11(b1) in the supplementary material]. The 2D GN fillers are more abundant on the electrode surface [Fig. S11(c1) in the supplementary material], demonstrating the poorest dispersion among the three carbon fillers, which is similar to the NMF 3D map displayed in Fig. 5(c1). Detailed CLS 2D maps demonstrating the distribution of carbon fillers and NCM particles at different electrode depths are displayed in Fig. S12 in the supplementary material. The same conclusion could also be drawn from the energy dispersive spectroscopy (EDS) results. The best percolation in the NCM/SWCNT electrode was also confirmed through analyzing the distribution of carbon element from top view and cross-sectional view SEM images, as shown in Fig. S13 and S14, respectively, in the supplementary material. The NCM/SWCNT electrode shows the most uniformly distributed carbon element and the strongest signal in the entire region, while the carbon distribution is poor in the NCM/SP and NCM/GN electrodes. Overall, the Raman maps provide an effective 3D visualization of the distribution of the active material and conductive additive as well as differences in porosity. These results support the critical role of effective percolation of carbon fillers and electrode porosity critical to the rate capability of the cells.

To further confirm the enhanced electrical percolation and promoted charge transport attributed to the SWCNTs in the NCM electrode, *operando* XAS was employed to probe the dynamic oxidation state change of transition metals (Ni, Co, and Mn) in NCM cells during the electrochemical reaction. With the largest electrical percolation and electrochemical performance differences, NCM/SP and NCM/ SWCNT electrodes were chosen as the representative cases to investigate the structural evolution during electrochemical tests. Figures 6(a) and 6(b) show the XANES spectra at the Ni K-edge collected for NCM/SP and NCM/SWCNT cell, respectively. As discharge occurred,

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FIG. 5. NMF reconstructed Raman mapping of the carbon (blue), NCM (red), and the corresponding overlay map in (a1–a3) NCM/SP, (b1–b3) NCM/SWCNT, and (c1–c3) NCM/GN electrodes with a volume of 60 μ m × 60 μ m × 10 μ m. From the merged maps, more pores (empty space) can be clearly observed in the NCM/SWCNT electrode while the 2D GN filler seems to closely wrap the NCM particles as indicated by the highly overlapped blue and red signals. This close contact between active materials and carbon additives is also discernible in the NCM/SWCNT electrode, but is not as strong. (d) NMF 2D maps showing the distribution of carbon fillers and NCM particles at different electrode depths. Similar to previous 3D maps, large and deep pores can be clearly identified throughout the 10 μ m depth in the NCM/SWCNT electrode, while the close contact between the 2D GN fillers and NCM particles, as indicated by the highly overlapped blue and red signals, seems to only exist on the electrode surface, as a decreasing amount of GNs with the increasing electrode depth was observed.

the Ni edge shifted to lower energy for each cell, suggesting that the nickel is reduced during discharge, which is consistent with lithiation. During charge, the edge shifted to its original position, indicating that the redox of nickel is reversible for both NCM/SP and NCM/SWCNT cells (Figs. S15 and S16 in the supplementary material). A slight shift

to lower energy during discharge was observed at the Co edge while no shift was observed at the Mn edge, which suggests that the majority of the redox activity involves nickel, consistent with prior reports.^{38,39} In the pristine and the charged state, the Ni edge energy is similar for both cell types; however, the shift to lower energy in the discharged



FIG. 6. Structural evolution of NCM during charging/discharging at 1 C probed by operando XAS measurements at the Ni Kedge. (a, b) Ni K-edge XANES of the (a) NCM/SP and (b) NCM/SWCNT cell during lithiation. As discharge occurred, the Ni edge shifted to lower energy for each cell, suggesting that the nickel is reduced during discharge, which is consistent with lithiation. During charge, the edge shifted to its original position, indicating that the redox of nickel is reversible for both NCM/ SP and NCM/SWCNT cells. (c, d) Linear combination fits of the Ni K-edge XANES data collected during (c) discharging and (d) charging. The solid lines represent the percentage of the charged NCM and the dashed lines represent the percentage of the discharged NCM. (e, f) EXAFS of the (e) NCM/SP and (f) NCM/SWCNT cell during lithation/delithiation.

state is more pronounced in the NCM/SWCNT cell compared with the NCM/SP cell, which is consistent with the observed capacity.

Linear combination fitting of the XANES spectra was performed to quantify the differences in edge shift. The two standards used for the fitting analysis were a NCM/SP cell in its fully charged state (C/10, 148 mAh g^{-1}), and a NCM/SP cell in its fully discharged state (C/10, 146 mAh g^{-1}). The two standards were chosen such that the depth of discharge and charge could be evaluated for both of the cells. The results of the Ni edge linear combination fits are shown in Figs. 6(c) and 6(d), and the fits for the Mn and Co edges are shown in Fig. S17 in the supplementary material. Analysis is focused on the shift of Ni edge since nickel contributes to the majority of the capacity in NCM cells. At the end of discharge at a current rate of 1 C, the NCM/SP cell exhibited 33.5(7)% charged NCM character and 66.5(7)% discharged character. This suggests that the discharge leads to significant reduction of the nickel ions, although less reduction compared to the C/10 rate is consistent with the lower delivered capacity at 1 C. At the end of discharge, the NCM/SWCNT cell exhibits significantly more nickel reduction compared to the NCM/SP cell [80.8(7)% discharged character]. Upon charge, the NCM/SWCNT cell reoxidizes Ni to approximately the same state as the NCM/SP cell: 96.7(2)% charged character vs 95.3(2)% charged character, respectively. Similar trends were observed for both the Mn and Co edges (Fig. S17 in the supplementary material).

To gain insights into the local structure evolution during cycling, the extended X-ray absorption fine structure (EXAFS) regions of the XAS spectra were examined. The Ni edge EXAFS is shown in Figs. 6(e) and 6(f), and the Mn and Co edge EXAFS are shown in Fig. S18 in the supplementary material. At the Ni edge, three major peaks are identified in $\chi(R)$ from 0 to 6 Å at ~1.5, ~2.4, and ~5.1 Å. It should be noted that the Fourier transform $\chi(k)$ spectra were not phase corrected, and therefore, interatomic distances will appear contracted in

 $\chi(R)$. The first peak corresponds to the Ni-O correlations in the NiO₆ octahedra, the second peak corresponds to the correlations between Ni and its nearest transition metal neighbors, and the final peak corresponds to Ni and its second nearest neighbors, which are both in the same layer as well as the adjacent layers of the NCM structure. These peaks are consistent with the expected O3-NCM structure that has been previously reported.⁴⁰ During discharge, all of the peaks shift slightly to higher interatomic distance values and shift back upon charge, which is consistent with lengthening of the bonds during lithiation and bond contraction during delithiation. The peaks and shifts noted at the Co and Mn edges exhibit similar features to Ni (Fig. S18 in the supplementary material). However, the lengthening of the M-O bond during lithiation is most pronounced in the Ni EXAFS. This change is reversible, and the position of the recharged M-O peak is essentially identical to the position of the peak prior to discharge. The magnitude of this shift is significantly reduced for the peaks corresponding to Mn-O and Co-O bonds, consistent with the very limited redox that those metals undergo. The Ni-O shift is more pronounced in the NCM/SWCNT cell, which suggests that the NCM/SWCNT cell achieves the higher level of nickel reduction (Fig. S19 in the supplementary material). Taken together, the XANES and EXAFS spectra indicate that the electrodes containing SWCNTs could achieve the higher level of Ni redox activity, which is in good agreement with the observed electrochemical behavior. The findings suggest that the integration of SWCNTs into the NCM electrode facilitate ion and charge transfer, which will lead to higher electrochemical utilization, especially at high rates of (dis)charge.

III. CONCLUSION

To conclude, the dimensionality effect of conductive fillers was comprehensively investigated in NCM thick electrodes with Super P, SWCNTs, and GNs via a variety of electrical, electrochemical, and structural characterization. Different from the point-to-point contact between NCM and Super P particles, both NCM/SWCNT and NCM/ GN electrodes show wrapping structures. In the percolation study, the NCM/SWCNT composite reveals the lowest percolation threshold and the highest electrical conductivity. Impressively, the corresponding electrode exhibits the best rate capability, delivering a capacity of 142 mAh g^{-1} at 0.2 C and maintaining 101 mAh g^{-1} at 2 C, which could be further supported by the smallest fitted Rs and Rct from EIS. Probed by Raman 3D mapping, it is the integration of the largest porosity and highest percolation that ensures the superior electrochemical performance in the NCM/SWCNT electrode. Operando XAS also reveals a more complete material conversion in the NCM/ SWCNT electrode enabled by faster electronic conduction during charging process. This study provides an in-depth understanding of the conductive filler effect on both electrical and structural properties in thick battery electrodes and demonstrates the superiority of 1D SWCNTs as the conductive filler in the electrodes, which provides new insights for the design of electrodes with high energy/power density.

IV. EXPERIMENTAL METHODS

A. Preparation of NCM/SP electrodes

The NCM/SP electrode was fabricated by mixing NCM (LiNi_{1/} $_{3}Co_{1/3}Mn_{1/3}O_{2}$; MTI Corp.) powder, Super P (MTI Corp.), and polyvinylidene fluoride (PVDF; Sigma-Aldrich) with N-Methyl-2-pyrrolidone (NMP) as solvent in the Thinky Mixer for more than 1 h. Afterward, the slurry was cast onto the aluminum foil by a doctor blade and dried in a vacuum oven at 90 °C overnight.

B. Preparation of NCM/SWCNT electrodes

SWCNT dispersion was prepared by mixing SWCNTs (XFNANO, Inc.) and polyvinylyrrolidone (PVP, Mw: ~10000; Sigma-Aldrich) with a mass ratio of 1:1 into de-ionized water. PVP here works as the surface functionalization agent to disperse SWCNTs in water and enables homogeneous distribution of SWCNTs in the electrode. The concentration of the dispersion is 2 mg mL⁻¹. The mixture was probe-sonicated for 2 h under the power of 200 W and a homogeneous SWCNT dispersion was obtained. The NCM/SWCNT electrode was prepared by mixing NCM powder with SWCNT dispersion and grinding manually for 15 min. Ozone treatment was applied to enhance the wettability of Al foil. Next, the slurry was cast onto the treated Al foil using a doctor blade and dried at 60 °C in the open air, followed by vacuum drying at 90 °C overnight.

C. Preparation of NCM/GN electrodes

Graphene oxide (GO) was prepared by the improved Hummer's method, and GNs were obtained by reducing GO powder under Ar/ H₂ (5%) atmosphere at 1000 °C for 1 h with a heating rate of 5 °C/ min. GN dispersion was prepared by mixing GNs and PVP with a mass ratio of 1:1 into de-ionized water. The concentration of the dispersion is 8 mg mL⁻¹. The NCM/GN electrode was prepared by mixing NCM powder, 5 wt. % carboxymethyl cellulose sodium (CMCNa), and GN dispersion grinding manually for 15 min. After that, the slurry was cast onto an ozone-treated Al foil using a doctor blade and dried in the open air, followed by vacuum drying at 90 °C overnight. Unless

otherwise specified, the areal mass loadings of the electrodes are ${\sim}15\,{\rm mg\,cm^{-2}}.$

D. Cell assembly

CR2032 coin cells were assembled inside an Ar-filled glovebox using a metallic Li plate as the anode. Celgard 2320 was used as the separator between the NCM cathode and Li anode. 1.0 M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and dimethylene carbonate (DEC) with the ratio of 1:1 was used as the electrolyte. 60 μ L of electrolyte was used for preparing all coin cells.

E. Electrode characterization

NCM electrode morphology and corresponding elemental mapping were characterized by scanning electron microscopy (SEM; Hitachi S5500). Morphology of SWCNTs and GNs were characterized by scanning transmission electron microscopy (STEM; Hitachi S5500). Through-plane electrical conductivity measurements were carried on a Keithley 2400 source meter using a two-probe technique. All electrochemical characterizations were conducted at room temperature with the electrochemical window 2.8–4.25 V vs Li⁺/Li. Room temperature CV and EIS measurements were conducted on a Bio-Logic potentiostat (VMP3). The frequency range of half-cell tests was from 1 MHz to 0.1 Hz. Galvanostatic charge-discharge curves, rate performance, and cycling stability were measured on a Neware battery tester (BTS 4000).

F. Raman 3D mapping measurements

Raman spectra of the NCM electrodes with different carbon fillers were recorded on a Horiba Scientific XploRA instrument with a 532 nm laser. Wavelength and intensity calibrations were conducted using a silicon standard. Confocal Raman 3D mapping measurements of the various electrodes were conducted using the same grating and objective as those used to collect the individual spectra. The mapped volume (x = 60 μ m, y = 60 μ m, and z = 10 μ m, with z direction being perpendicular to the electrodes) used a 3 μ m step size in the mapping direction. With respect to the 3D map renderings of both NCM and carbon additives, two different multivariate processing procedures including Classical Least Squares (CLS) and non-negative matrix factorization (NMF) were utilized. NMF was selected in favor of the more classical principal component analysis because its non-negativity constraint tends to produce more readily interpretable endmembers for spectroscopic datasets.⁴¹ In the CLS procedure, the 1764 spectra collected for each map were fitted and the NCM and carbon distribution maps were reconstructed based on the spectral weights of pure NCM and each carbon additive, respectively. For the NMF procedure, chemical abundance maps were derived from the integrated intensities of analytically relevant bands in spectra after deconvolution and reconstruction by the trained model. The NMF in this procedure functions as a noise reduction filter and improves the signal-to-noise ratio of the processed spectra.

G. Operando X-ray absorption spectroscopy measurements

X-ray absorption spectroscopy measurements were collected at the Ni edge (8.333 keV), Mn edge (6.539 keV), and Co edge

(7.709 keV) at beamline 7-BM at the National Synchrotron Light Source II at Brookhaven National Laboratory.42,43 To study the NCM materials operando, Li/NCM in situ cells were fabricated using the NCM composite cathodes as described. Prior to beamline measurement, each cell underwent a formation cycle on a Biologic multichannel potentiostat at a rate of C/10; after this formation cycle, the cells were charged at C/10. The cells were brought to the beamline in the charged state and cycled once at 1 C while operando XAS measurements were collected. Each sample was measured in transmission mode and X-ray beam energy calibration was performed with foils of the appropriate metal. Each measurement represents the average of two individual scans; the scans were merged, calibrated, and normalized in the Athena software.44 Linear combination fitting of the X-ray absorption near edge structure spectra was performed in Athena where the spectra were fit with two standards based a NCM pouch cell with Super P at the charged state (C/10) and at the discharged state (C/10).

SUPPLEMENTARY MATERIAL

See the supplementary material for the additional SEM and STEM images, EDS mapping, EIS simulation, charge-discharge profiles, Raman spectra, Raman 2D and 3D mapping, and additional operando XAS profiles.

AUTHORS' CONTRIBUTIONS

G.Y. supervised the project. Z.J., X.Z., and Y.Z. carried out material synthesis and electrode fabrication and measurements. S.K., C.Q., K.T., E.T., D.B., L.W., and A.M. helped with Raman imaging, XANES, and EXAFS characterizations. All authors reviewed the final manuscript.

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DATA AVAILABILITY

The authors declare that all data supporting the findings of this study are included within the paper and its Supplementary Information files. Source data are available from the corresponding author upon reasonable request.

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