

# Effect of Conductive Carbon Morphology on the Cycling Performance of Dry-Processed Cathode with High Mass Loading for Lithium-Ion Batteries

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The solvent-free dry processing of electrodes is highly desirable to reduce the manufacturing cost of lithium-ion batteries (LIBs) and increase the active mass loading in the electrode. The drying process is based on the fibrillation of the polytetrafluoroethylene binder induced by shear force. This technique offers the advantage of uniformly dispersing the active material and conductive carbon without binder migration, thereby facilitating the fabrication of thick electrode with high mass loading. In this study, we explored the influence of conductive carbon morphology on the cycling performance of dry-processed LiNi<sub>0.82</sub>Co<sub>0.10</sub>Mn<sub>0.08</sub>O<sub>2</sub> (NCM) cathodes. In contrast to Super P, which provided electronic pathways through point-contact, the fibrous structure of the vapor-grown carbon fibers (VGCFs) promoted line-contact, ensuring long and less-torturous electronic pathways and enhanced utilization of active materials. Consequently, the cathode employing fibrous VGCFs achieved higher electrical conductivity, resulting in enhanced electrochemical performance. The dry-processed NCM cathode employing VGCF with an areal capacity of 8.5 mAh cm<sup>-2</sup> delivered a high discharge capacity of 212 mAh g<sup>-1</sup> with good capacity retention. X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy were conducted to investigate the degradation behavior of the high-mass-loaded cathodes with two different conductive carbons.

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Lithium-ion batteries (LIBs), which provide sustainable and ecofriendly transportation solutions, are experiencing remarkable growth owing to the rapid expansion of the electric-vehicle market.<sup>1-3</sup> Despite being recognized as clean energy-storage devices, LIBs have not yet provided an ideal solution for sustainable energy storage systems, which can be ascribed to the environmental issues associated with the emission of toxic and volatile organic solvents during cathode fabrication. The cathode used in LIBs is usually fabricated by wet slurry process using N-methyl-2-pyrrolidone solvent that is toxic and environmentally harmful.<sup>4–7</sup> In addition, the active mass loading in the electrode cannot be increased due to the migration of conductive carbon and binder during solvent drying in the wet slurry process.<sup>8</sup> To address these issues, solventfree dry processes that can improve the uniformity and thickness of electrode has garnered growing interest. The dry process eliminates the three-stage process of coating, drying, and solvent recovery in electrode fabrication, reducing the cost and energy consumption. Moreover, the active mass loading can be increased without increasing the resistance in the electrode owing to the inhibited migration of conductive carbon and binder, thereby increasing the energy density.<sup>12–14</sup>

The dry process relies on the fibrillation of polytetrafluoroethylene (PTFE) induced by shear force, facilitating the binding of active materials and conductive agents.<sup>15–17</sup> In thick electrodes prepared by dry process, active materials often experience irregular utilization, resulting in more heterogeneous electrochemical reactions within the electrode and rapid deterioration of electrochemical performance compared to thin electrodes. Accordingly, establishing homogeneous and long-range electron pathways in thick electrodes is very important for ensuring the good cycling performance of LIBs, highlighting the crucial role of conductive carbon in dry-processed electrodes.<sup>18–23</sup>

In this study, we investigated the influence of two conductive carbons on the electrochemical performance of dry-processed  $LiN_{0.82}Co_{0.10}Mn_{0.08}O_2$  (NCM) cathode with high mass loading. To focus on the morphology of conductive carbon, Super-P with powder shape and vapor-grown carbon fiber (VGCF) with fibrous morphology were used in fabricating the dry-processed cathode. Our

results revealed that VGCF formed well-distributed conductive networks through line-contact in the cathode, leading to superior cycling performance compared with the cathode employing Super-P carbon. The degradation of the electrochemical performance in highmass-loaded cathodes with two different conductive carbons was investigated by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

#### **Experimental Methods**

*Materials.*—Polycrystalline NCM with a small particle size ( $d_{50}$ : 4 µm, L&F Co., Ltd.), Super-P (MTI Korea), VGCF (Sigma-Aldrich), and PTFE (Solvay) were vacuum dried at 100 °C for 12 h prior to use. The liquid electrolyte, supplied by the Dongwha Electrolyte Co., Ltd., was composed of 0.6 M lithium difluoro (oxalato)borate and 0.6 M lithium tetrafluoroborate in a solvent mixture of diethyl carbonate and fluoroethylene carbonate at a volume ratio of 2:1. lithium metal (thickness: 200 µm, Honjo Metal Co., Ltd.) pressed onto a copper current collector was used as the anode. A polyethylene separator (SKIET) was vacuum dried at 90 °C for 12 h before use.

*Electrode preparation and cell assembly.*—The cathode for the solvent-free dry process was prepared by mixing NCM, conductive carbon (VGCF or Super-P), and PTFE at a mass ratio of 94:5:1, respectively. The cathode fabrication process consisted of three steps. First, the NCM and conductive carbon were mixed in a mortar for 10 min. Second, PTFE was added to the mortar and kneaded for 10 min under a shear force, thereby forming a dry dough. Finally, a freestanding cathode film was fabricated. The dry dough was calendered to achieve the target thickness. To facilitate the adhesion between the freestanding cathode and the Al current collector, we coated the primer composed of binder and conductive agent onto the Al foil. Subsequently, we roll-pressed the cathode onto the primercoated Al current collector several times, and the resulting cathode was dried in a vacuum oven at 100 °C for 12 h. After vacuum drying, the cathode with a mass loading of  $40 \text{ mg cm}^{-2}$  was obtained. The Li/NCM cell was fabricated by stacking the lithium anode, polyethylene separator, and NCM cathode in a coin cell and injecting liquid electrolyte. All electrode preparation and cell assembly



processes were performed inside an argon-filled glove box (MBRAUN).

Characterization and electrochemical measurements.—The morphology of the electrodes was analyzed using field-emission SEM (FE-SEM; Verios G4) with energy-dispersive X-ray spectroscopy (EDS). The cross sections of the samples were polished using a cross-section polisher (IB-19510CP, JEOL). High-resolution TEM (HR-TEM, JEOL, JEM 2100 F) was used to examine the morphology of the cathodes processed using a focused-ion beam (FIB, Scios, FEI). The electronic conductivity of the cathodes was measured using a four-point probe (CMT-100S, AIT). XRD was performed to investigate the crystal structure of the cathode active material. XPS (K-alpha+, Thermo Fisher Scientific) was used to examine the chemical composition of the surface layer on the electrode. Electrochemical impedance spectroscopy was carried out using an impedance analyzer (CHI660d, CH Instruments) in the frequency range from 0.01 Hz to 1 MHz with an amplitude of 5 mV. Cycling test of the Li/NCM cell was conducted in the voltage range of 3.0-4.3 V using a battery cycler (WBS3000, WonA Tech) at 25 ° C. After two preconditioning cycles at a rate of 0.1 C, the cell was repeatedly charged at 0.2 C and discharged at 0.5 C, respectively.

### **Results and Discussion**

Figure S1 shows the morphologies of the conductive carbon materials (Super-P and VGCF) used in this study. Super-P and VGCF have powdery and fibrous morphologies, respectively. Figures 1a and 1b present the cross-sectional SEM images of the dry-processed NCM cathodes prepared with Super-P and VGCF, respectively. The low-magnification SEM images are also shown in Fig. S2. The porosity of the obtained electrodes was 13.4% for NCM cathode with Super-P (denoted as NCM-SP) and 12.9% for the NCM cathode with VGCF (denoted as NCM-CF), respectively. We investigated the dispersion of components (active material, conductive carbon, PTFE binder) in dry-processed electrode by EDS mapping images. The analysis was performed on the upper and

lower sides of the NCM-SP and NCM-CF, respectively, and the results are presented in Fig. S3. It was confirmed that the elements (Ni in active material, C in conductive carbon and PTFE binder, F in PTFE binder) were evenly distributed. When comparing the carbon content in the upper and lower sides of the electrodes, the values at the upper and lower sides of the NCM-SP were 5.03 and 4.98 wt%, and the values of the NCM-CF were 4.96% and 5.05 wt%, respectively. These results suggest that active materials and conductive carbon are uniformly dispersed without migration and well bound by fibrillated PTFE binder in the electrode despite their large thickness ( $\sim 180 \,\mu$ m). The powder-like morphology of Super-P exhibits point-contacts with active materials, providing short electron pathways within the electrode that can electrically connect nearby active materials, as schematically illustrated in Fig. 1c. In contrast, the fibrous morphology of VGCF enables the formation of extended electron pathways through line-contact with the active materials, resulting in facile electron transfer to a wide range of active materials, as schematically presented in Fig. 1d. Because of their fibrous structure, several active materials are in simultaneous contact with a single carbon fiber, unlike the restricted contact in cathode employing particulate Super-P carbon. The electronic conductivities of the electrodes were measured by four-probe method to confirm these assumptions: the results are shown in Fig. S4. Regardless of the active mass loading in the electrodes, the NCM-CF exhibited notably higher electronic conductivities than NCM-SP. When the mass loading was doubled, the electronic conductivity of NCM-SP was considerably decreased from 1.4 to 0.6 S cm<sup>-1</sup>. In contrast, NCM-CF had almost similar electronic conductivity even at high loading  $(3.7 \text{ S cm}^{-1})$  as that at low loading  $(4.2 \text{ S cm}^{-1})$ . These results can be ascribed to the formation of extended and long-range electronic pathways in the presence of VGCF, even at high active mass loadings.

The Li/NCM cells were initially subjected to two preconditioning cycles at 25 °C. As shown in Fig. S5a, the two cells initially delivered similar discharge capacity ( $\sim$ 212 mAh g<sup>-1</sup>), corresponding to a high areal capacity of 8.5 mAh cm<sup>-2</sup>. Figures 2a and 2b show the galvanostatic charge–discharge curves of the cells



Figure 1. Cross-sectional scanning electron microscopy (SEM) images of dry-processed cathodes prepared with (a) Super-P and (b) VGCF. Schematic of the electron pathways in the dry-processed NCM cathodes employing (c) Super-P and (d) VGCF.



Figure 2. Voltage profiles of the cells assembled with dry-processed (a) NCM-SP and (b) NCM-CF cathodes. (c) Discharge capacities of the cells as a function of the cycle number. (d) Discharge curves of the Li/NCM-CF cell at different current densities and (e) rate capability of the cells with NCM-SP and NCM-CF cathodes.

with NCM-SP and NCM-CF, respectively. The cell with NCM-CF exhibits more stable cycling characteristics without large increase in the overpotential with cycling, compared to the cell with NCM-SP. As a result, the NCM-CF cell exhibited higher capacity retention than the NCM-SP cell, as depicted in Fig. 2c. The rate capability of the Li/NCM cell was evaluated by measuring the discharge capacity at current densities ranging of  $0.8-16.0 \text{ mA cm}^{-2}$ . A current density of  $8.0 \text{ mA cm}^{-2}$  corresponds to a rate of approximately 1.0 C. The cells were charged at the same current density of  $0.8 \text{ mA cm}^{-2}$  during charging process and discharge five times at each current density during discharging. The initial discharge curves of the cells with NCM-CF and NCM-SP at each current density are shown in

Figs. 2d and S5b, respectively. The discharge capacities at different current densities are compared in Fig. 2e. At low current densities ( $\sim 1.6 \text{ mA cm}^{-2}$ ), no significant difference in discharge capacities are noted for the two cells. The difference in the discharge capacities of the two cells increased with further increase in the current density. Choi et al. reported that 1D carbon materials had higher crystallinity than 0D carbon materials.<sup>21</sup> According to their work, the Ni-rich cathodes prepared with highly crystalline 1D conductive carbon showed superior cycling stability and rate performance in sulfide-based all-solid-state batteries compared to 0D conductive carbon (carbon black) with low crystallinity. This is because the use of 1D carbon materials enhances the electrical conductivity of the

electrode, thereby reducing polarization and interfacial resistances in the electrodes. Accordingly, the superior high-rate performance of the NCM-CF cell can be ascribed to the high electronic conductivity of the NCM-CF cathode, which arises from the formation of extensive and uniform electronic conduction pathways by VGCF, as previously mentioned.

The cycling behavior of the two cells with different conducting carbons was elucidated by plotting the differential capacity (dQ/dV) curves with cycling, as presented in Figs. 3a and 3b. In the voltage range of 3.0–4.3 V, the dQ/dV curves exhibited a series of redox peaks corresponding to phase transitions that occur during delithiation and lithiation. These redox peaks can be attributed to the transformation of the original layered structure phase (H1) to monoclinic (M) and two other hexagonal phases (H2 and H3).<sup>24–28</sup> As the cycle progressed, the peak intensities of NCM-SP are remarkably decreased and the peaks are considerably shifted, indicating an increase in the irreversible phase transitions of the cathode active materials with cycling. These irreversible phase transitions are the primary reasons for capacity fading during repeated cycling. In contrast, the dQ/dV curves in the NCM-CF cell are stable without a noticeable peak shift or reduction in peak intensity, implying less degradation of the cathode active materials. Figures 3c and 3d present the electrochemical impedance spectra of the Li/NCM cells employing Super-P and VGCF, respectively,



Figure 3. dQ/dV plots of cells assembled with (a) NCM-SP and (b) NCM-CF cathodes with cycling. AC impedance spectra of the cells assembled with (c) NCM-SP and (d) NCM-CF cathodes, which were obtained after preconditioning and 100th cycles. (e) Equivalent circuit for fitting the AC impedance data and (f) variation of resistances with cycling in the cells with NCM-SP and NCM-CF cathodes.

obtained after the first preconditioning and 100 cycles. We performed fitting of the impedance data by using the equivalent circuit in Fig. 3e, and the results are shown in Fig. 3f. In the equivalent circuit,  $R_b$  is the bulk resistance of electrolyte,  $R_f$  is the resistance associated with the surface film formed on the electrode, and  $R_{ct}$  is the charge transfer resistance at the electrode-electrolyte interface. As shown in Fig. 3f, the two cells exhibited similar resistances after the initial preconditioning cycle. After 100 cycles, the interfacial resistances ( $R_f$  and  $R_{ct}$ ) were remarkably increased. It should be noted that the increase in the interfacial resistances during cycling was much higher in NCM-SP than NCM-CF, indicating more degradation of the active material in the NCM-SP cell than that in NCM-CF cell.

The cross-sectional morphologies of the cathodes were analyzed before and after cycling; the resulting SEM images at different magnifications are shown in Figs. 4 and S6. NCM-CF exhibited fewer microcracks within the active material than NCM-SP after 100 cycles, suggesting that NCM-CF maintained the secondary particle structure of the active materials during repeated cycles. The restricted electronic conduction pathways in the thick NCM-SP cathode led to nonuniformity in the extent of lithiation/de-lithiation across the NCM particles during cycling.<sup>29,30</sup> This resulted in anisotropic volume changes and large strains of secondary NCM particles, accelerating the microcracking of the cathode active materials.<sup>31–33</sup> The formation of microcracks in NCM-SP causes electrolyte penetration into the particles; thus, the newly exposed surfaces are susceptible to side reactions with electrolyte, thereby degrading the cycling performance with repeated cycling.

XRD analysis was conducted to elucidate the degradation of the active material. The distinct separation between the (006)/(102) and (108)/(110) peaks in the XRD patterns of the pristine NCM confirms a well-defined hexagonal structure (Fig. 5a).<sup>34</sup> However, the XRD pattern of NCM-SP after 100 cycles showed broader and shifted

peaks compared with those of pristine NCM, implying the structural instability and gradual degradation of the active material during cycling.<sup>35</sup> In contrast, NCM-CF maintained sharp diffraction peaks and distinct splitting of the (006)/(102) and (108)/(110) peaks after cycling, similar to those in pristine NCM. This result suggests that active materials in the NCM-CF maintained its initial layered crystalline structure without any noticeable structural deterioration during cycling. The nickel valence states and oxygen bonds in the cycled NCM cathodes were investigated using XPS. As shown in Fig. 5b, the Ni 2p spectrum split into two main peaks in the  $2p_{3/2}$ region, indicating that the valence states of nickel are  $Ni^{2+}$  and  $Ni^{3+}$ .  $Ni^{2+}/(Ni^{2+}+Ni^{3+})$  was determined to compare the degree of cation mixing.<sup>36–38</sup> According to the XPS results, NCM-CF has a  $Ni^{2+}/(Ni^{2+}+Ni^{3+})$  value of 0.58, which is lower than 0.68 that of NCM-SP (0.56), indicating a lower degree of cation mixing (Li<sup>+</sup>/Ni<sup>2+</sup>) in NCM-cf Fig. 5c shows the O 1s spectra of the pristine and cycled NCM cathodes. NCM-CF exhibits a higher intensity of the M-O peak at 529.0 eV, suggesting that a thin cathode-electrolyte interphase (CEI) was formed on the cathode surface. The peaks corresponding to RO-Li (531.4 eV) and  $C=O/Li_2CO_3$  (532.3 eV) result from the reductive decomposition of the liquid electrolyte.<sup>39</sup> These peaks have lower intensities for NCM-CF than for NCM-SP. These results suggest the presence of less detrimental side reactions between the active materials and electrolyte in NCM-CF, forming a thinner CEI on the cathode.<sup>40</sup> This presumption was confirmed by TEM analysis of NCM-SP and NCM-CF after 100 cycles. As depicted in Fig. S7, the NCM-CF showed a thinner CEI layer ( $\sim 2.8$  nm) than NCM-SP ( $\sim 7.5$  nm).

The extent of the surface degradation was elucidated by TEM of the cathode samples before and after cycling after FIB milling, as shown in Fig. S8. As presented in Fig. 6a, the pristine NCM particle exhibited a layered structure. However, the layered structure was degraded, and many NiO-like rock-salt structures were formed in the



Figure 4. Cross-sectional SEM images of NCM-SP (a) before and (b) after 100 cycles. Cross-sectional SEM images of NCM-CF (c) before and (d) after 100 cycles.



Figure 5. (a) X-ray diffraction (XRD) patterns of pristine NCM, NCM-SP, and NCM-CF with partially magnified plot of (006)/(102) and (108)/(110) peaks obtained after 100 cycles. (b) Ni 2p and (c) O 1 s X-ray photoelectron spectroscopy (XPS) spectra of pristine NCM, NCM-SP, and NCM-CF after 100 cycles.

active material after 100 cycles. As depicted in Fig. 6c, NCM-CF has a thin (~6 nm) rock-salt layer on the surface with well-retained lattice fringes in the inner regions. In contrast, NCM-SP has a thicker (~12 nm) rock-salt layer on its surface (Fig. 6b), indicating the higher degree of cation mixing than that in NCM-cf This phase transformation is attributed to the reduction of the highly reactive Ni<sup>4+</sup> species to Ni<sup>3+</sup> and Ni<sup>2+</sup> in the de-lithiated state of NCM. Ni<sup>2+</sup> ions with ionic radii similar to those of Li<sup>+</sup> ions result in undesirable Li<sup>+</sup>/Ni<sup>2+</sup> cation mixing in the lithium-ion channels within the crystal structure, inducing structural disorder and negatively affecting the cycling stability.<sup>41,42</sup> Furthermore, the Ni<sup>2+</sup> ions in the rock-salt phase originating from the reduction of Ni<sup>4+</sup> ions are accompanied by an increase in the electrode impedance and dissolution in the electrolyte, thereby deteriorating the structural stability.

The influence of Ni<sup>2+</sup> ions dissolved from the cathode was investigated through the XPS and SEM of the cycled lithium anode.

As shown in Fig. 7a, the peak intensity of Ni<sup>2+</sup> was lower in the cycled NCM-CF, indicating the mitigated dissolution of Ni<sup>2+</sup> ions in NCM-cf Moreover, the Ni content was measured after 100 cycles by inductively coupled plasma-mass spectrometry (ICP-MS). ICM-MS results revealed that the Ni content was higher in the NCM-SP (30.8 ppm) than NCM-CF (21.8 ppm), which was consistent with XPS results. Figure 7b shows the surface SEM images of the pristine and cycled lithium anodes. The lithium electrode cycled in the NCM-CF cell shows compact and dense morphologies of the deposited lithium, which is beneficial for suppressing the dendrite growth and improving the interfacial stability of lithium metal. In contrast, the lithium electrode cycled in the NCM-SP cell exhibits a rough and dendritic surface morphology. The nickel ions dissolved from the cathode were deposited on the lithium anode and reduced to nickel metal. The nickel formed on the lithium anode catalyzes the decomposition of the liquid electrolyte, leading to nonuniform



Figure 6. High resolution transmission electron microscopy (HR-TEM) images and corresponding selected area electron diffraction (SAED) patterns of (a) pristine NCM, (b) NCM-SP, and (c) NCM-CF after 100 cycles.

lithium morphologies and deteriorated the cell performance.<sup>43,44</sup> In addition, the depletion of surface lithium due to low coulombic efficiency in the NCM-SP would be attributed to the rough and dendritic surface morphology of Li anode.

## Conclusions

In this study, we investigated the effect of conductive carbon morphology on the electrochemical performance of the dry-processed NCM cathode with a high mass loading  $(40 \text{ mg cm}^{-2},$ 

 ${\sim}8.5~{\rm mAh}~{\rm cm}^{-2})$  to achieve high energy density. Fibrous VGCF formed the extended electronic pathways through line-contacts with active materials, resulting in the facile electron transfer to the active materials even in the thick electrode ( ${\sim}180~{\mu}{\rm m}$ ). Such an efficient electronic conduction ensured the uniform and high utilization of the active material, thereby suppressing the degradation of the active materials. Consequently, the dry-processed NCM-CF cathode exhibited better cycling stability and rate capability than the NCM-SP cathode. Our results provide guidelines for fabricating dry-processed electrodes with high mass loadings to enhance the energy density of LIBs.



Figure 7. (a) Ni 2p XPS spectra of pristine lithium and lithium anodes from cells employing NCM-SP and NCM-CF after 100 cycles. (b) Surface SEM images of pristine lithium and lithium anodes from the cells with NCM-SP and NCM-CF after 100 cycles.

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