Grain boundaries contribute to highly efficient lithium-ion transport in advanced LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ secondary sphere with compact structure

Cheng Liu#, Heyi Xia#, Yinpeng Wei#, Jiabin Ma, Lin Gan, Feiyu Kang, Yan-Bing He

Shenzhen Geim Graphene Center, Institute of Materials Research (iMR), Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, P.R. China

Correspondence
Yan-Bing He and Lin Gan, Shenzhen Geim Graphene Center, Institute of Materials Research (iMR), Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P.R. China.
Email: he.yanbing@sz.tsinghua.edu.cn; lgan@sz.tsinghua.edu.cn

# These authors contributed equally to this work.

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Abstract
LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) secondary particles with high tap density have a great potential for high volumetric energy density lithium (Li)-ion power battery. However, the ionic conductivity mechanism of NCA with compact structure is still a suspense, especially the function of grain boundaries. Herein, we systematically investigate the Li-ion transport behavior in both the primitive NCA (PNCA) secondary sphere densely grown by single-crystal primary grains and ball-milled NCA (MNCA) nanosized particle to reveal the role of grain boundaries for Li-ion transport. The PNCA and MNCA have comparable Li-ion diffusion coefficients and rate performance. Moreover, the graphene nanosheet conductive additive only mildly affects the Li-ion diffusion in PNCA cathode, while which severely blocks the Li-ion transport in MNCA cathode. Through high-resolution transmission electron microscopy and electron energy loss spectroscopy, we clearly observe Li-ion depletion at lower state of charge (SOC) and Li-ion aggregation at high SOC along the grain boundaries of PNCA secondary particles during high-rate lithiation process. The grain boundaries can construct an interconnected Li-ion transport network for highly efficient Li-ion transport, which contributes to excellent high-rate performance of compact PNCA secondary particles. These findings present new strategy and deep insight in designing compact materials with excellent high-rate performance.

Keywords
compact structure, grain boundaries, graphene nanosheet, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, lithium-ion transport

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1 | INTRODUCTION

In recent years, the application realm of lithium-ion batteries (LIBs) has expanded from mobile terminals to electric vehicles/plug-in hybrid electric vehicles (EV/PHEV), and stationary energy storage.1,2 To meet the requirement of high power and energy densities in EVs, cathode materials for next-generation LIBs should fulfill the properties such as higher energy density, longer cycle life, and better safety performance.3 Conventional layered structure LiCoO$_2$ is not suitable for large-scale applications in EV/PHEV due to its poor safety performance and a relatively small amount of capacity (up to 160 mAh g$^{-1}$).4 LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA), as one of the most widely studied Ni-rich materials, has been commercialized because of its high capacity (200 mAh g$^{-1}$), long-term cycle life, and low cost.5,6

It is of great significance to improve the Li-ion diffusion ability in cathode materials of power LIBs. It is widely established that the diffusion of Li-ion in the layered structure occurs along with a two-dimensional (2D) interstitial space, which is considered as a pathway for higher Li-ion mobility.7 Conventional layered structural LiCoO$_2$ consists of micron-sized single crystal particles with higher Li-ion diffusion ability and therefore presents good rate capability. NCA cathode materials are commonly prepared by a co-precipitation method, which exhibits a morphology of spherical secondary particles densely grown by many single-crystal primary grains with different orientations.8,9 However, since the densely compacted structure almost does not contain pores, it is difficult for the electrolyte to enter into the interior area of dense NCA, thus making the Li-ion diffusion more difficult. Nevertheless, NCA usually presents much better performance than LiCoO$_2$ at high discharge rate, indicating excellent ionic conductivity of NCA.10

It should be noticed that the secondary particle structure of NCA contains abundant grain boundaries between primary particles, which is quite distinct from LiCoO$_2$ single particles.11,12 The more densely the primary particles grown together, the higher the grain boundary density is in NCA secondary particle. Therefore, the grain boundaries presumably play a significant role in ion transportation in compact NCA.

Many reports have reported that the interface design is an effective way to control the characteristics of ionic and electronic transportation.13–21 Like the solid-liquid interfaces, the solid-solid interfaces have the same substantial effect on ion storage and transportation.22–26 Grain boundaries, which are observed in a broad class of materials, are known to have novel physical properties.27,28 Plenty of lattice distortion occurs at the grain boundaries, therefore providing more active sites for ion storage and transportation.29–31 Meanwhile, the ion transport rate along the grain boundaries has been investigated and modified to reveal the ion transport mechanism and construct highly efficient ion transport pathway.32–36

For instance, Yan et al.37 infused the grain boundaries of nickel-rich layered cathode secondary particles with a solid electrolyte (Li$_3$PO$_4$), which could act as a fast channel for Li-ion transportation to dramatically enhance the capacity retention and voltage stability of the cathode. Zhu et al.38 employed the conductive atomic force microscopy technique to study the local Li-ion diffusion induced conductance change in Li$_x$CoO$_2$ nanograins, discovering that the grain boundaries have a low diffusion energy barrier and provide a fast Li diffusion pathway. Gong et al.39 reported a method for in-situ atomic-scale observation of electrochemical delithiated LiCoO$_2$ working in all-solid-state battery. The pristine single-crystal LiCoO$_2$ became nanosized polycrystals connected by coherent twin boundaries and antiphase domain boundaries after high voltage delithiation, both of which can promote the extraction of Li-ions.

From the reports mentioned above, it is found that the grain boundary and modification can distinctly improve the electrochemical performance of electrode materials. Nevertheless, the mechanism of Li-ion transportation at the grain boundary of secondary particles of the electrode remains unclear. In addition, a real-space observation of the Li-ion at the grain boundaries is of great significance for completely understanding the detailed process of how the grain boundaries transport Li-ions. The NCA secondary particle with a compact structure contains affluent grain boundaries. It is urgent to reveal the ionic transportation mechanism of the NCA particle with the densely compacted secondary structure as well as how to form the conductive network during the Li intercalation reaction for enriching the ionic transportation theory of cathode materials. It is well-known that the graphene nanosheet (GN) has very high electronic conductivity. When the GN is used as a conductive additive in the cathode, the electronic conductivity of the electrode can be significantly improved even using much less amount of GN.40,41 Additionally, it was found that the GN in cathode would block the transportation of Li-ion in nanosized LiFePO$_4$ cathode, which is called steric effect that results in the decrease of power density.42,43 Nevertheless, the hindering effect is not found in LiCoO$_2$ cathode due to its micro-sized single crystal structure.44 Therefore, it is considerably significant to investigate whether there is a steric effect when the GN is applied in compact NCA secondary particle electrode, which can give a convincing evidence to illustrate the Li-ion transportation role of grain boundaries in compact NCA secondary particle.

In this work, we systematically investigate the Li-ion transportation behavior of the primitive NCA secondary spheres (PNCA) with densely compacted structure and...
fragmentized ball-milled NCA (MNCA) particles with single nanosized particles. Interestingly, the PNCA and MNCA have comparable Li-ion diffusion coefficients and high-rate performance (Figures 1A and 1B). Moreover, the GN conductive additive was also introduced to prove the importance of grain boundaries on Li-ion transportation. When the GN was added into the cathodes, the Li-ion transport mechanism was different in PNCA and MNCA. In PNCA, the GN can only cover a part of the particle, so the Li-ion in the electrolyte can enter into the particles by the uncovered area and transport through the grain boundaries network (Figure 1C). In MNCA, since the GN wraps lots of grains, the Li-ion of these grains cannot penetrate through the GN, and these encapsulated particles can hardly be charged/discharged (Figure 1D). It is found that the Li-ion diffusion in PNCA is mildly affected by the GN, while the transportation of Li-ion in fragmentized MNCA is severely blocked due to severe steric effect (Figures 1C and 1D). The grain boundaries are quite beneficial for Li-ion long-range and fast transportation in compact PNCA. Furthermore, using high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS), we clearly observe Li-ion depletion at lower state of charge (SOC) and Li-ion aggregation at high SOC along the grain boundaries of PNCA secondary particles during high rate lithiation process. A highly efficient and interconnected Li-ion transportation network is formed at abundant grain boundaries of compact NCA during high-rate lithiation. This work demonstrates that the grain boundaries in the compact structure of NCA can serve as a fast Li-ion transport network for achieving high-rate performance, which also provides a novel insight to construct highly efficient Li-ion transport pathway in compact electrode materials with high volumetric energy density.

2 | METHODS

Ball-milled NCA (MNCA) particles were prepared as follows: primitive NCA particles (purchased from Shenzhen Battery Technological Co., LTD) was ground by ball milling in ethanol for 2 h using a planetary ball mill apparatus and then dried at 80 °C to get MNCA. The crystallographic characteristics of PNCA and MNCA particles were measured by X-ray diffraction (XRD) by Rigaku D/max 2500/PC using Cu Kα radiation with λ = 1.5418 Å. The XRD results were refined by Rietveld methods using Topas version 5 program. The morphologies were characterized using a field emission scanning electron microscope (FE-SEM, HITACHI S4800) at 5 kV. HRTEM and EELS elemental mapping images were acquired on FEI Tecnai G² F30 300 kV field-emission TEM. The EELS mapping was recorded under scanning transmission electron microscope (STEM) mode by collecting L2,3-edge of Ni and K-edge of Li simultaneously. The samples for cross-sectional SEM observation, HRTEM, and EELS characterization were prepared by a focused ion beam (FIB) (Leica EM RES 102). The coin half-cell was transferred to an argon-filled glove box to be disassembled, and cathode is taken out. After that, we washed the cycled cathode using dimethyl carbonate (DMC) to eliminate the residual lithium salt. Then, the NCA powder was gently abraded from the current collector. Next, the NCA particles were cut with an FIB for characterization. The particle size distribution was measured by a laser particle size analyzer (Mastersizer 2000Hydro2000MU). The cycled NCA electrodes were recorded with Fourier transform infrared spectroscopy (FTIR) (Nicolet iS10) at ambient temperature. The nitrogen adsorption/desorption isotherms were obtained at 77 K by using an automated adsorption apparatus (Micromeritics ASAP 2020). The surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation. The pore size distribution was calculated from the adsorption branch of the isotherms based on the Barrett–Joyner–Halenda model.

Electrochemical measurements were carried out by using CR2032-type coin half-cells assembled in an Ar-filled glove box. The NCA electrodes were prepared by mixing the active material with Super-P/GN, polyvinylidene fluoride in an N-methyl-pyrrolidone (NMP) solution. The GN sheets were prepared using a vacuum-promoted low-temperature exfoliation of graphite oxide approach. Before added to the slurry, GN was suspended in NMP and...
ultrasonicated for 2 h. The as-prepared cathode was rolled before cell assembly. For the half-cells, metallic lithium was used as the anode, a microporous polyethylene membrane (Celgard 2500) was served as the separator, and the 1 M LiPF₆ solution in a 1 M mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (volume ratio: 1:1:1) was used as the electrolyte. The assembled half cells were galvanostatically cycled between 2.7 and 4.3 V (on a Land 2001A battery testing system) at different current densities (1 C = 180 mA g⁻¹). The electrochemical impedance spectra (EIS) of electrodes after charging to various SOC were obtained on a VMP3 multichannel electrochemical station in the frequency range of 10⁻² - 10⁵ Hz with a perturbation of 5 mV. Cyclic voltammogram (CV) were examined using the VMP3 multichannel electrochemical station at a scan rate of 0.1 mV s⁻¹ in the range of 2.7-4.3 V. For the galvanostatic intermittent titration technique (GITT) tests, the batteries were charged and discharged at a current of 0.1C for 1 h and followed by open-circuit relaxation for 4 h.

3 | RESULTS AND DISCUSSION

The PNCA are secondary spheres with the average size of 10 μm composed of densely packed primary NCA nanograins with a size of 200–500 nm (Figures 2A and 2B), while the MNCA prepared by ball milling of PNCA are fragmentized NCA particles with only a few primary grains sticking together (Figures 2C and 2D). Thus, the MNCA has a shortened Li-ion diffusion path, which should possess an improved rate performance. According to the nitrogen adsorption/desorption isotherms (Figure S1B), the BET-specific surface areas of PNCA and MNCA are 2.77 and 4.79 m² g⁻¹, respectively, and their corresponding pore volumes are 0.00842 and 0.0222 cm³ g⁻¹ (Figure S1A).
These small BET surface areas and pore volumes demonstrate very dense structures with nearly no pores inside the NCA secondary particles even after the ball milling process, which results in very high tap densities (2.64 g cm–3 of PNCA and 1.97 g cm–3 of MNCA).

The SEM image of the cross-sectional PNCA in Figure 2E further reveals that the PNCA is a compact structure composed of densely primary particles. In HRTEM image of Figure 2F and 2G, two grains grow closely, and no crack or hole exists at the grain boundaries. Therefore, the electrolyte is unlikely to penetrate through the grain boundaries. The considerable difference of morphology and structure between PNCA and MNCA suggests their quite different grain boundaries densities. With more grains densely packed together, the PNCA are thought to have more grain boundaries than MNCA particles. A cross-sectional PNCA sample with a thickness of tens of nanometer was prepared by FIB for TEM observation (Figure 2F), which clearly presents the existence of grain boundaries between intimately contacted primary particles. The corresponding selected area electron diffraction pattern in the inset shows that the primary NCA particles exhibit a hexagonal lattice along [4 5 1] and [2 2 1] zone axis. HRTEM image (Figure 2G) indicates the existence of high angle grain boundaries, with the interface parallel to [012]. In addition, the coherent twin boundaries with the interface along [102] planes can also be found (Figure S2A). Defects such as distortions can be observed at the grain boundaries (Figures S2C and S2D). These results actively demonstrate that the PNCA contain numbers of different type grain boundaries. Figures 2H and 2I show the XRD patterns and Rietveld refinement of PNCA and MNCA samples, and all the diffraction lines can be indexed as a hexagonal lattice of a-NaFeO2 structure with R3m space group. There is no apparent structural difference between PNCA and MNCA particles, meaning that the ball milling process did not change the grain structure. In addition, the PNCA and MNCA particles after 300 cycles at 1C also present similar XRD patterns and maintain hexagonal lattice of a-NaFeO2 structure (Figure S3), indicating that both PNCA and MNCA particles present well structure stability during long cycling.

The electrochemical properties of the PNCA and MNCA were evaluated using half-coin cells (Figures 3A and 3B). The specific capacity of PNCA is 188.3 mAh g–1 at 0.2 C, which is larger than that of MNCA (169.3 mAh g–1). The 1st coulombic efficiency of PNCA and MNCA at 0.2 C is 89.7% and 83.4%, respectively. MNCA has larger-specific surface areas that are contacted with the electrolyte compared with PNCA, making it more difficult to activate the initial structural phase and requiring more Li-ion to form a cathode electrolyte interphase (CEI) film. Therefore, MNCA showed higher irreversible capacity and lower-specific capacity. The charge and discharge profiles also indicate that the MNCA has larger polarization than PNCA (Figure S4). The relatively lower 1st coulombic efficiency and larger polarization of MNCA may be attributed to its increased specific surface areas, making it more difficult to activate the initial structural phase transformation and requiring more Li to form a CEI film.45 The CV results in Figure S5 could also demonstrate this behavior. In the 1st oxidation (delithiation) process, a prominent anodic peak is seen at 3.925 V for PNCA and 3.981 V for MNCA, which is much larger than that in the following cycles due to the activation of the NCA. It is reported that the 1st charge of NCA is a combination of an irreversible two-phase transformation and a reversible solid solution reaction mechanism.46 In addition, the initial fully lithiated phase (Rh1) is a semiconductor material with poor Li-ion mobility.47,48 Therefore, a large overpotential is required to extract the Li-ions from the NCA that is corresponding to a transformation from the initial phase (Rh1) to a second rhombohedral phase (Rh2). The Rh2 has a larger c lattice parameter and smaller a lattice parameter compared to Rh1, which leads to faster Li-ion mobility and increased electrical conductivity. However, the Rh1 state cannot be formed again when discharged, which is the reason for the capacity loss in the 1st cycle. Since the MNCA has larger-specific surface area than PNCA, which results in more transformations from Rh1 to Rh2, higher irreversible capacity, lower coulombic efficiency and specific capacity of MNCA.

However, the MNCA possesses higher capacity retention of 88% after 100 cycles compared to 77.8% of PNCA. This could be due to the larger volume expansion during the cycling of PNCA that induces the cracks of PNCA secondary particles along grain boundaries, which deteriorates the cycling performance.49,50 Although the PNCA presents a higher-specific capacity than MNCA, they have similar high-rate performance. The PNCA and MNCA delivers 99 mAh g–1 and 92.5 mAh g–1 at 10 C, respectively (Figure 3B). It is easily understood that the MNCA with smaller particles has shortened Li-ion diffusion distance, and the MNCA particle contacts with the electrolyte more easily, which leads to excellent high-rate performance. However, for the PNCA with densely compact structure, it is difficult for the electrolyte to enter the dense NCA, which will make the Li-ion diffusion more difficult inside the dense NCA sphere. From Figures 2E and 2F, we have found that the PNCA contains abundant grain boundaries between primary particles. Therefore, grain boundaries may play a significant role in ion transportation to achieve a comparatively high-rate performance in compact PNCA.

To understand ionic transport mechanism of grain boundaries, the EIS of the PNCA and MNCA cathodes at various SOC after 0.1 C and 10 C charging were measured.
FIGURE 3  Electrochemical performance of PNCA and MNCA: (A) Cyclic performance at 1 C after three cycles at 0.2 C for activation, (B) specific capacities at different rates; R ct of PNCA and MNCA electrodes after delithiation to various SOC using (C) 0.1 C and (D) 10 C. (E) The Li-ion diffusion coefficients calculated from the GITT curves of PNCA and MNCA as a function of voltage during the discharge (lithiation) process. Cyclic performance and rate performance of (F and G) PNCA and (H and I) MNCA with different conductive additives (0.5GN, 1GN, 2GN, 3GN) (Figure S6). It should be noted that the cells have been cycled three times at 0.1 C before the 10 C-EIS tests. The Nyquist plots display two semicircles in the high-frequency region and medium-frequency region with a straight line in the low-frequency region. The obtained charge transfer resistance (R ct) and cathode electrolyte interface resistance (R SEI) are shown in Figures 3C and 3D and Figure S8, respectively. It is seen that during the initial stage of delithiation from 0% to 10% SOC at 0.1 C, the R SEI increases to a certain value (Figure S8A), indicating formation of the CEI film. It is well-known that the high operating voltage charged cathode with catalytic properties would oxidize the carbonate solvents and decompose the lithium salt to produce a CEI layer, which increases the R ct and deteriorates the performance of battery.51,52 This can be proved by the morphologies and FTIR of the PNCA and MNCA electrodes after 300 cycles at 1 C (Figure S9 and S10), which present more formation of Li2CO3 on cycled MNCA electrode in CEI film (Figure S10). Thus, more side reactions of MNCA occur with the electrolyte due to its larger-specific surface, which leads to the much larger R CEI and R ct of MNCA than PNCA at both 0.1 C and 10 C. In addition, according to the reaction mechanism of NCA from Rh1 to Rh2, the main phase at early stage of delithiation is Rh1, which possesses poor electronic and ionic conductivity,46 also resulting in larger R SEI and R ct of NCA at 10% SOC. With the SOC increasing from 10% to 40% SOC, the R SEI remains unchanged while the R ct drops fast. During this stage, the transformation from Rh1 to Rh2 is almost completed. The newly formed R2 phase has an increased interlayer distance to facilitate Li-ion diffusion, and an increased Ni4++ ion concentration also increases the electronic conductivity,47 which leads to the larger decrease of R ct from 20% SOC. Furthermore, the PNCA and MNCA electrodes during 10 C charging presents similar change properties with SOC compared with that of 0.1 C results (Figures S6C and S6D), but the R ct, R SEI and D Li are all smaller than that of 0.1 C. Thus, the high rate
delithiation for NCA results in the obvious decrease of $R_{ct}$ and $R_{SEI}$.

We also investigated the diffusion coefficients of Li-ion ($D_{Li}^+$) calculated by GITT curves (Figures S11A and S11B), which shows that the diffusion of Li-ion in PNCA is faster than in MNCA during discharge (Figure 3E) and charge process (Figure S11C). The GITT results are well consistent with the result of EIS. This quite extraordinary and interesting result suggests that the Li-ions easily transport into and outside the dense PNCA during high-rate cycling. The grain boundaries of layered structure act like superionic Li-ion conductor, which play a significant role for highly efficient Li-ion transportation.\(^{35}\) In the initial delithiation stage of NCA, the grain boundary regions may be preferentially delithiated and transformed to Rh2, creating a highly efficient electronic and ionic conducting network throughout the grain boundaries, which results in the smaller $R_{ct}$ and higher $D_{Li}$ of PNCA. After 40% SOC, the delithiation of Rh2 proceeds via a solid solution mechanism that creates more phase boundaries and better 3D ion transport network, which leads to the much smaller $R_{ct}$, $R_{SEI}$, and larger $D_{Li}$ of PNCA than MNCA. These results give strong evidence that the grain boundaries in PNCA possess the excellent ability to transport Li-ion.

GN is a typical 2D material with excellent electron conductivity.\(^{53}\) When GN is used as a conductive additive, all the particles of electrodes can be well connected, which diminishes the difference of electronic conductivity between PNCA and MNCA electrodes to further reveal the effect of grain boundaries. We prepared the GN cells with GN content increasing from 0.5 to 3 wt% and a reference cell containing 4 wt% SP (Figures 3F–3I). The GN is a micro-size 2D layer structure (Figure S12). Figure 3F presents the cycling performance of PNCA cathodes at 1 C with different contents of GN and SP. It is obvious that when the GN content is less than 2 wt%, the cells present poor cycling performance compared with that using SP additive. This is because the electron conduction is not matched with the ion conduction. When the GN content is higher than 2 wt%, the cycling performance of PNCA is comparable with that using 4% SP additive, indicating that the GN is more efficient to build an electronic conductive network than SP when acting as conductive additives in NCA cathode. The quite smaller resistance of cell with GN content higher than 2 wt% also proves this result (Figure S13). However, although the cycling performance of PNCA is improved at high GN content, the rate performance exhibits completely different results. When GN used as the conductive additive in the cathode, the GN will wrap around PNCA and MNCA particles, as shown in Figure 4. Since Li-ion cannot penetrate through the GN, Li-ion has to bypass the GN, which greatly increases the Li-ion transport distance. When cycling at high rate, the Li-ion sluggish transport cannot match with the rapid transport of electrons, which results in almost no capacity. As shown in Figure 3G, the rate performance of PNCA drops obviously compared with SP additive above 1 C even the GN content reaches 3 wt%, indicating that the steric effect of GN
exists in PNCA cathode. This is because that the GN wraps the part surface of PNCA particles (Figures 4B and 4C), which blocks the Li-ion transportation between PNCA particles. Surprisingly, when the GN additives are added in the MNCA cathode, the steric effect becomes more severe. The MNCA cannot deliver capacity even cycled at 0.5 C, which can only deliver small capacity when cycled at 0.2 C, and GN content is more than 2 wt% (Figures 3H and S1). Considering that the GN additives have diminished the difference of electronic conductivity, the only reason causing this result is their different ionic conductivity. The GN additives with much larger size than MNCA wraps the most of the MNCA (Figures 4E and 4F), which may cut off the long-range Li-ion transport channels inside MNCA cathode, resulting in extremely low discharge capacity. Whereas, the part of the surface of PNCA without covered by GN can freely exchange Li ions with electrolyte, whose grain boundaries can construct highly efficient and long-range Li-ion transport channels and network, which contribute to the much higher rate and cycling performance of PNCA than MNCA cathode using GN.

To further reveal the role of grain boundaries for Li-ion transport in the densely compact NCA, the element distributions and chemical state of Li/Ni around the grain boundaries were investigated by EELS spectrum imaging of Li-K edge and Ni-L edge in STEM (Figure 5). Two cross-sectional samples of the PNCA electrodes discharged to 30% SOC (the early stage of lithiation) and 100% SOC (fully lithiated) at 10 C, respectively, were prepared by FIB. For the PNCA at 30% SOC (Figures 5A–5D and Figures S14E-S14H), EELS spectrum imaging of Li and Ni shows much lower Li/Ni atomic ratios at the grain boundary, indicating that the grain boundary is Li-ion deficient (Figure S15). When the PNCA comes to a deeper Li-ion insertion...
at 100% SOC (Figures S5E–5H and Figures S14A–S14D), the Li/Ni ratio at the boundary substantially increased compared to the PNCA at 30% SOC and even shows Li enrichment at boundaries (Figures S5H and S16A–S16D). Figure S1 compares the Li-K EELS spectra at the grain boundaries of the PNCA at 30% and 100% SOC. The Li-K edge locates at the energy loss of ca. 60 eV (before the Ni-M edge), and the intensity ratio of Li-K edge to Ni-M edge at the grain boundary substantially increased in the 100% SOC sample compared to that in the 30% SOC sample. We further found that the near edge fine structure of Li-K edge and Ni-L edge at the grain boundary also differ from those in the bulk region (Figures S3 and 5K, respectively), both shift to lower energies compared to those in the bulk region, suggesting a different chemical environment likely associated with the low coordination of metal ions at the boundary. These results suggest that the grain boundaries provide a comparably Li-ion diffusion pathway during the (de)lithiation processes. At the early stage of lithiation (30% SOC), the crystal structure of PNCA shows a larger c lattice parameter and smaller a lattice parameter, indicating a larger Li slab spacing, which lowers the activation energy barrier for Li-ion motion. Therefore, the Li-ion at the grain boundary diffuses more easily into the interior of the grain, leading to the Li-deficient phenomenon at this stage. When the PNCA is fully lithiated to 100% SOC, the subsurface area of grain is mostly recovered to the original layered structure, leading to lower conductivity. As a result, the Li-ion transports and accumulates at the grain boundary. Therefore, the grain boundary serves as a Li-ion transport network between electrolyte and grains of PNCA. These results illustrate that the grain boundaries in PNCA have a great ability to transport Li-ion during high rate lithiation. The highly efficient Li-ion transport properties of grain boundaries in compact electrode materials give an inspiration for all-solid-state batteries design strategy. As we all know, a main problem prohibiting the development of all-solid-state batteries is the solid-to-solid contact interface. The grain boundaries can achieve tightly contact between two solid phases and construct a high efficient Li-ion transport network, which is important for all-solid-state batteries.

4 | CONCLUSIONS

In summary, the Li-ion transportation behavior between the primitive NCA secondary particles (PNCA) with densely compacted secondary structure and fragmentized ball-milled NCA (MNCA) nanosized particles were systematically investigated. The PNCA and MNCA have comparable Li-ion diffusion coefficients and high-rate performance. Moreover, the GN conductive additive mildly affects the Li-ion diffusion in PNCA, while severely blocked the Li-ion transport in fragmentized MNCA, illustrating that the grain boundaries are quite beneficial for Li-ion long-range and fast transportation in compact PNCA secondary particles. Furthermore, employing STEM-EELS characterization, we observe the Li-ion concentration increase process at the grain boundary during high rate lithiation, proving that an interconnected and highly efficient Li-ion transportation network is formed at grain boundary of compact NCA. This work demonstrates that the grain boundaries in the compact structure of NCA can serve as a fast Li-ion transportation network for achieving excellent rate performance of high volumetric energy density Li-ion power battery. Especially, the solid/solid interface ion transport network by grain boundary can also give some design inspiration for all-solid-state Li batteries.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Yan-Bing He https://orcid.org/0000-0001-5787-5498

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of the article.

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