

Two-dimensional graphitic carbon-nitride (g-C₃N₄)-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathodes for high-energy-density and long-life lithium batteries

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April 26, 2024

Abstract

High-capacity nickel-rich layered oxides are promising cathode materials for high-energy-density lithium batteries. However, the poor structural stability and severe side reactions at the electrode/electrolyte interface result in unsatisfactory cycle performance. Herein, the thin layer of two-dimensional (2D) graphitic carbon-nitride (g-C₃N₄) is uniformly coated on the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (denoted as NCM811@CN) using a facile chemical vaporization-assisted synthesis method. As an ideal protective layer, the g-C₃N₄ layer effectively avoids direct contact between the NCM811 cathode and the electrolyte, preventing harmful side reactions and inhibiting secondary crystal cracking. Moreover, the unique nano-pore structure and abundant nitrogen vacancy edges in g-C₃N₄ facilitate the adsorption and diffusion of lithium ions, which enhances the lithium deintercalation/intercalation kinetics of the NCM811 cathode. As a result, the NCM811@CN-3wt% cathode exhibits 161.3 mAh g⁻¹ and capacity retention of 84.6% at 0.5 C and 55 °C after 400 cycles and 95.7 mAh g⁻¹ at 10 C, which is greatly superior to the uncoated NCM811 (i.e. 129.3 mAh g⁻¹ and capacity retention of 67.4% at 0.5 C and 55 °C after 220 cycles and 28.8 mAh g⁻¹ at 10 C). The improved cycle performance of the NCM811@CN-3wt% cathode is also applicable to solid-liquid-hybrid cells composed of PVDF:LLZTO electrolyte membranes, which show 163.8 mAh g⁻¹ and the capacity retention of 88.1% at 0.1 C and 30 °C after 200 cycles and 95.3 mAh g⁻¹ at 1 C.

1. Introduction

The development of portable electronics and electric vehicles has stimulated a huge demand for rechargeable lithium batteries because of their high energy density and high safety requirements.^[1] To continuously improve the energy density of lithium batteries, various cathode and anode materials with high specific capacities have been explored. Among them, Ni-rich layered transition metal oxide LiNi_xCo_yMn_zO₂ (NCM, x + y + z = 1) has become a key cathode material to be developed for applications with its reasonable cost and high practical energy density.^[2,3] However, several problems still need to be overcome to meet practical demands, including insufficient cycling stability and poor rate ability. These problems all stem from Li⁺/Ni²⁺ cation mixing, poor structural stability, and harmful side reactions at the electrode/electrolyte interface.^[4-6] Surface side reactions might cause a significant increase in interfacial resistance as well as severe dissolution of transition metals, especially at high temperatures and increased anodic cut-off voltage.^[7-9] Therefore, side reactions at the electrode/electrolyte interface remain the limiting factor for performance.

Protective particle coatings, mainly including metal oxides,^[10-13] oxide solid electrolytes,^[14-16] phosphates,^[6,17,18] fluorides,^[19-22] or graphene,^[23-25] were widely utilized to address these problems. For example, Xu et al.^[26] used Al₂O₃ and Zhou et al.^[10] utilized ZnO. In recent years, two-dimensional (2D) materials, such as graphene and boron nitride, were used as electrode coating materials due to their high specific surface area, and adjustable physicochemical properties,^[27] which could

significantly enhance the electrochemical performance of cathode materials. However, ex-situ-added 2D materials tended to restack and aggregate in the cathode, which seriously slowed down the lithium-ion transport rate and reduced the active surface of the active materials.^[28,29] Moreover, commonly used 2D materials often exhibited poor lithium-ion conductivity, which hindered the effective transfer of lithium ions inside the cathode. Selecting the 2D material with excellent lithium conductivity and achieving its uniform coating on the surface of cathode particles is crucial for improving the electrochemical performance of the cathode. g-C₃N₄ consists of a continuous 3-s triazine ring (C₆N₇) as the basic unit and is thought to possess a two-dimensional layered structure similar to graphene.^[30] C and N atoms are sp²-hybridised, forming a highly delocalised p-conjugated system.^[31] The unique nano-pore structure and abundant nitrogen vacancy edges in g-C₃N₄ facilitate the adsorption and diffusion of lithium ions.^[32,33] Moreover, the mild synthesis conditions make it suitable for uniform in-situ coating of matrix electrode materials. Therefore, the utilization of 2D thin-layer g-C₃N₄ for uniform coating of NCM cathode particles is expected to suppress side reactions at the cathode/electrolyte interface without affecting the lithium-ion transport, thereby improving the electrochemical performance of NCM cathodes.

Herein, g-C₃N₄-coated LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂(NCM811@CN) is constructed to alleviate the side reaction and improve the cycle performance. The g-C₃N₄ coating effectively inhibits structural degradation and intergranular cracks. Meanwhile, strong chemical bonds form between g-C₃N₄ and the NCM cathode due to the unsaturated bonds on the surface of g-C₃N₄,^[34,35] which not only improves the interface stability and accelerates the interfacial Li⁺ diffusion but also avoids the direct contact between the cathode and the electrolyte, suppressing the side reactions. Benefiting from the above advantages, the optimized NCM811@CN-3wt% cathode exhibits better rate capability and cycling stability than the uncoated NCM811 in both conventional liquid and solid-liquid-hybrid electrolyte-based cells. This work sparks new ideas on constructing ultra-thin interface layers with excellent comprehensive performance for high-nickel ternary-metal oxide cathodes.

2. Results and Discussion

A Simple and extensible chemical vaporization-assisted synthesis method was executed to uniformly cover the 2D g-C₃N₄-thin layer on NCM811 using dicyandiamide as the precursor at 500 °C (**Figure 1a**). Rietveld refinement shows that the diffraction peaks of both NCM811 and NCM811@CN-3wt% have α-NaFeO₂ layered structure (space group: R-3m), with no additional peaks from related impurities (**Figure 1b and 1c**). As the relative amount of g-C₃N₄ increases above 10 wt%, the peaks of g-C₃N₄ can be observed, as shown in **Figure S1**. **Table S1** shows the Li⁺/Ni²⁺ cation mixing of NCM811@CN-3wt% is slightly reduced, which is due to the formation of strong chemical bonds between the unsaturated bonds on the surface of g-C₃N₄ and the NCM oxide cathode.^[34,35] The reduction of Li⁺/Ni²⁺ disorder should be consistent with the improved structural stability. Based on the TGA analysis, the coating amount of NCM811@CN-3wt% was determined (**Figure 1d**). g-C₃N₄ coated on the surface of NCM811 particles decomposes at 600 °C, and the mass loss of NCM811@CN-3wt% is about 3.31 wt%. As shown in **Figure 1e**, except for that of pristine NCM811, the Fourier transform infrared spectrometer (FT-IR) curves of NCM811@CN-3wt% and g-C₃N₄ show characteristic peaks corresponding to the triazine unit (810 cm⁻¹) as well as the C-N heterocycle (1200-1700 cm⁻¹). This result indicates that g-C₃N₄ is successfully coated.

The surface chemical and valence states of NCM811 and NCM811@CN-3wt% were determined by X-ray photoelectron spectroscopy (XPS). The N 1s of NCM811@CN-3wt% show three peaks at 397.55 eV, 398.52 eV, and 401.25 eV, respectively corresponding to C-N-C/C-N=C, N-(C)₃ and C-N-H in g-C₃N₄ (**Figure 1f**). Meanwhile, two unique peaks can be found in C 1s of NCM811@CN-3wt% at 287.18 eV and 288.78 eV, corresponding to N-(C)₃ and N-C-N/N-C=N, respectively (**Figure 1g**). In contrast, the spectrum of NCM811 does not display N 1s peaks and the unique N-(C)₃ and N-C-N/N-C=N in C 1s peaks. This result demonstrates the existence of the g-C₃N₄ coating on NCM811. The relative intensity of Ni³⁺ for NCM811@CN-3wt% is greater than that of uncoated NCM811, as shown in **Figure S2a**. In addition, C 1s of the NCM811 and NCM811@CN-3wt% exhibit two peaks at 283.86 eV and 288.78 eV, belonging to hydrocarbon and the Li₂CO₃/LiOH, which are mostly probably generated from exposure in air. Compared with NCM811, the relative intensity of Li₂CO₃/LiOH on the surface of NCM811@CN-3wt% decreases from

29.80% to 19.34% (Figure 1g). O 1s further indicates that the relative of Li_2CO_3 decreases after $\text{g-C}_3\text{N}_4$ modification (**Figure S2b**), in agreement with improvement of NCM811 surface stability by $\text{g-C}_3\text{N}_4$ coating.

The morphologies of NCM811 and NCM811@CN-3wt% were observed using scanning electron microscopy (SEM), as shown in **Figure 2**. All the samples exhibit spherical morphology with a particle size of approximately 13 μm , aggregated from parent crystal particles. Compared to NCM811 (**Figure 2a and 2b**), the surface of NCM811@CN-3wt% exhibits a relatively fuzzy roughness, which suggests that it contains a thin coating layer (**Figure 2d and 2e**). The chemical composition of its coating is examined by EDS-mappings, and the elements Ni, Co, Mn, O, and N are uniformly distributed on the surface of NCM811@CN-3wt%, confirming the uniform coverage of $\text{g-C}_3\text{N}_4$ (**Figure S3**). Transmission electron microscopy (TEM) further revealed the surface/interfacial structures of NCM811 and NCM811@CN-3wt%. As a result, it is observed that the NCM811 particles in NCM811@CN-3wt% are uniformly encapsulated by a crystalline coating of approximately 7 nm (**Figure 2e and 2f**). Meanwhile, the relatively smooth surface of the original NCM811 can be found in **Figure 2c**. According to the TEM-EDS spectra (**Figure 2g**), the Ni, Co, Mn, O, and N elements of NCM811@CN-3wt% remain uniformly distributed.

The cycling performance of NCM811 and the $\text{g-C}_3\text{N}_4$ -coated ones are evaluated at 1 C and the voltage range of 3-4.3 V, as shown in **Figure 3a and Figure S4**. The NCM811@CN-3wt% cathodes show the best performance of NCM811@CN with different CN content. After 300 cycles, the reversible capacity of NCM811@CN-3wt% cathodes remains 150.6 mAh g^{-1} with a capacity retention of 81.8% at 30 °C. In contrast, the NCM811 specific capacity decreases to 114.1 mAh g^{-1} after 300 cycles with 62.1% capacity retention. Furthermore, the uncoated NCM811 exhibits severe voltage decay during cycling. It can be found in **Figure 3b and 3c** that the NCM811 discharge voltage decreases by 284 mV from the 1st to the 300th, whereas the NCM811@CN-3wt% decreases by only 98 mV in the first 300 cycles, indicating the improvement effect of $\text{g-C}_3\text{N}_4$ coating on mitigation voltage degradation. A key issue facing Ni-rich cathodes is that charge and discharge at elevated temperatures accelerate the decomposition of LiPF_6 , which leads to severe side reactions on the cathode surface. Therefore, the electrochemical stability of NCM811 and NCM811@CN-3wt% is comparatively studied at 55 °C. **Figure S5** displays the charge-discharge characteristic curves of NCM811 and NCM811@CN-3wt% in the 3 V to 4.3 V range at 0.5 C and 55 °C. **Figure 3d** shows the specific capacity of NCM811@CN-3wt% after 400 cycles is 161.3 mAh g^{-1} and the capacity retention of 84.6%. After 220 cycles, the specific capacity of NCM811 is only 129.3 mAh g^{-1} with 67.4% capacity retention. Another issue with Ni-rich cathodes is that increased charge voltage causes irreversible phase transition, thereby deteriorating the cycle performance. **Figure 3g** shows that the capacity of the NCM811 cathode degrades rapidly within the voltage range of 3-4.5 V at 0.5 C, only retaining 165.6 mAh g^{-1} and 74.8% capacity retention after 200 cycles (**Figure S7a**). In contrast, the NCM811@CN-3wt% cathode still shows the ideal specific capacity as high as 195.2 mAh g^{-1} and 88.6% capacity retention after 200 cycles (**Figure S7b**). Furthermore, when the loading mass of the cathode increases, the capacity of NCM811 decreases rapidly, and the capacity retention rate after 100 cycles is only 75.1%, while the capacity retention rate of NCM811@CN-3wt% maintains 82.1% (**Figure S8**). **Figure 3h and Figure S6** display the rate capability of NCM811 and the $\text{g-C}_3\text{N}_4$ -coated ones, tested from 1 C to 10 C between 3-4.3 V, then followed by switching to 0.5 C for 165 cycles. Notably, the $\text{g-C}_3\text{N}_4$ -coated NCM811 cathodes have a higher specific capacity than the uncoated NCM811. This difference becomes more pronounced as the density of the current increases. Meanwhile, the NCM811@CN-3wt% cathode exhibits a specific capacity of 119.2 mAh g^{-1} at 5 C and 95.7 mAh g^{-1} at 10 C, which is superior to that of the NCM811 cathode (99.5 mAh g^{-1} at 5 C and 30.1 mAh g^{-1} at 10 C), owing to the interfacial stabilization of the $\text{g-C}_3\text{N}_4$ coating facilitating the diffusion of lithium ions. Furthermore, when switching to 0.5 C for cycling, the specific capacity of the NCM811@CN-3wt% cathode is as high as 180.1 mAh g^{-1} after 165 cycles with 95.2% capacity retention. Whereas the capacity of the NCM811 cathode decreases to 119.8 mAh g^{-1} after 165 cycles with a capacity retention of 65.2%.

The equivalent differential capacity (dQ dV^{-1}) curves of NCM811 and NCM811@CN-3wt% are detailed to investigate the electrochemical behaviors associated with phase transition during long cycling between 3-4.3 V and 3-4.5 V, the results being shown in **Figure 3e and 3f**, and **Figure S7c and S7d**. NCM811 and NCM811@CN-3wt% undergo the same phase transition (H1-M-H2-H3). The H2-H3 phase transition causes

the crystal structure to shrink sharply along the c-axis, resulting in uneven stress distribution and local stress concentration, thus forming microcracks. The peak intensity of the unfavorable H2-H3 phase transition in NCM811@CN-3wt% is smaller than that in NCM811. Compared with NCM811@CN-3wt%, the redox of three pairs peaks of NCM811 undergo a larger shift from the 2nd to 200th cycle, indicating that the g-C₃N₄ coating reduces the degree of polarisation and improves the reversibility of the H2-H3 phase transition. These results indicate that the NCM811@CN-3wt% cathodes have better cycle performance than NCM811, which can be attributed to the reduction of side reactions as well as the improvement of crystallinity stability.

To understand how the g-C₃N₄ modification improves the cycling capability and structural stability, in-situ XRD measurements were carried out during lithiation/delithiation processes of NCM811, NCM811@CN-3wt% at 0.1 C in the voltage region from 3 V to 4.3 V. As previously reported hexagonal the LiCoO₂, the peak shift of (003) indicates the change in the lattice parameter of c, while (101) represents changes in a and b.^[36,37] Although NCM811 and NCM811@CN-3wt% have similar crystal structures, significant differences in the crystalline phase evolution of the cells during charging and discharging can be observed in **Figure 4a and 4b**. The (003) peak of NCM811 indicates a greater variation of 0.98deg than that of NCM811@CN-3wt% (i.e. 0.82deg). The different evolutionary behavior of the (003) peaks during charging and discharging shows that the volume change of NCM811 is larger than that of NCM811@CN-3wt%. It is known that the large volume change causes irreversible phase transition and layered structure collapse, especially in the case of elevated temperatures and increased cut-off voltages. Therefore, the above results clearly indicate that the modification of g-C₃N₄ is related to suppression of the lattice distortion and stabilization of the crystal structure.

The de-/lithiation kinetics of the cathodes investigated by cyclic voltammetry (CV) in the voltage of 3-4.3 V at the scan speeds from 0.1 to 0.5 mV s⁻¹ are shown in **Figure 4c and 4d**. Both cathodes undergo a series of phase transitions, which are consistent with the dQ dV⁻¹ curves. As the scanning speed increases, the redox potential of NCM811 shifts in a greater extent than that of NCM811@CN-3wt% does. **Figure S9a** displays the CV curves of NCM811 and NCM811@CN-3wt% at 0.5 mV s⁻¹. The potential difference between the oxidation and reduction peaks of NCM811 (i.e., $\Delta E = 0.15$ V) is much greater than that of NCM811@CN-3wt% (i.e., $\Delta E = 0.07$ V), indicating that the g-C₃N₄ coating helps to reduce the polarization. Meanwhile, the redox coupling becomes more sensitive, indicating that the electrochemical reaction is faster. The lithium-ion diffusion coefficient is calculated by the Randles-Sevcik formula based on the relationship between the maximum current intensity and the square root of the scan rate (**Figure 4e**).^[38,39] As a result, NCM811@CN-3wt% shows the high apparent lithium-ion coefficients of 2.07×10^{-6} cm² s⁻¹ and 4.67×10^{-7} cm² s⁻¹ for the delithiation and lithiation process, respectively. The lithium-ion diffusion coefficient of NCM811@CN-3wt% is approximately a factor of two greater than that of NCM811 (**Figure S9b**). This indicates that the g-C₃N₄ coating helps to increase the adsorption and diffusion of lithium ions, in agreement with the fact that the NCM811@CN-3wt% anode has excellent rate capability.

To understand how the g-C₃N₄ coating on the surface of NCM811 particles affects the interfacial characteristics and thus optimizes the cycle performance, EIS studies were performed and the results are shown in **Figure 5a-c**. The EIS data can be quantitatively analysed by fitting the spectra to the corresponding equivalent circuit model as shown in **Figure S10**. The fitting results are shown in **Figure 5c**. Notably, the charge transfer resistance (R_{ct}) of the exposed NCM811 cathode increased significantly from 92.3 Ω in the 2nd to 646.4 Ω after 300 cycles. In contrast, the R_{ct} for NCM811@CN-3wt% cathode is only increased from 50.7 Ω to 259.4 Ω (after 300 cycles). This is due to the accumulation of side reactions during long-term cycling, leading to surface passivation and increased impedance. This indicates that such problem can be effectively solved by the g-C₃N₄ coating modification. In addition, the change of surface film resistance (R_f) further confirms this result. By comparison, changes of R_f and R_{ct} for NCM811@CN-3wt% are smaller than that for NCM811 during 300 cycles. Importantly, R_f of NCM811 changes with cycling, while it remains nearly constant for NCM811@CN-3wt% (**Figure 5c**). This indicates that NCM811@CN-3wt% forms the more stable interface during cycles with the help of the g-C₃N₄ coating.

The surface chemistry of NCM811 and NCM811@CN-3wt% was determined by XPS analysis. As shown

in **Figure 5d**, the peaks at 285.8 eV and 288.5 eV on the C 1s spectrum can be attributed to ethers and carbonates, which are derived from the decomposition of electrolytes. Notably, the peak intensities of carbon oxides in NCM811@CN-3wt% are smaller than that of NCM811, which indicates that the electrolyte decomposition on the surface of the g-C₃N₄-coated cathode is less. For the F 1s spectrum shown in **Figure 5e**, the peaks at 685.00 eV and 687.10 eV are LiF and Li_xPO_yF_z (i.e., hydrolysis products of LiPF₆), respectively. The weaker peak intensities of LiF and Li_xPO_yF_z on NCM811@CN-3wt% compared to NCM811 implies that the g-C₃N₄ coating attenuates the dissolution of actives and decomposition of LiPF₆. The improved stability of surface is also verified by the M-O bonds in the O 1s spectra with the higher intensity for NCM811@CN-3wt% than that of NCM811 (**Figure 5f**). Moreover, the analysis of N 1s shows that Li₃N and LiN_xO_y with the high ionic conductivity appear on NCM811@CN-3wt%. g-C₃N₄ is reduced to inorganic with high ionic conductivity, which further confirms that the g-C₃N₄ coating contributes to the increase of lithium-ion adsorption and diffusion (**Figure S11**). The cross-section SEM images of NCM811 and NCM811@CN-3wt% are shown in **Figure 5h and 5j**. The NCM811 shows obvious cracks from center to surface, while the NCM811@CN-3wt% exhibits no obvious microcracks. Such microcracks can lead to electrolyte infiltration, which can lead to side reactions. The secondary microspheres of NCM811@CN-3wt% are well preserved without apparent cracks, as can be seen in **Figure 5g and 5i**, and **Figure S12**, verifying that the g-C₃N₄ coating can effectively inhibit the generation of microcracks. The above results indicate that NCM811@CN-3wt% has excellent interfacial, structural, and mechanical stability, which contributes to its excellent electrochemical performance and long-term cycle life.

To enhance the safety of lithium batteries and evaluate the compatibility of g-C₃N₄ coated NCM811 with solid-state electrolyte systems, the PVDF:LLZTO membranes with small amount of ionic liquid as the wetting materials for cathode/electrolyte interfaces have been used for the solid-state-hybrid Li batteries. Meanwhile, a series of characterization and electrochemical tests on PVDF:LLZTO electrolytes are carried out. The particle sizes of LLZTO, i.e., D10, D50, and D90 are 0.096 μm, 0.302 μm, and 0.636 μm, respectively (**Figure S13a**). The thickness of the PVDF:LLZTO electrolyte membranes is approximately 50 μm (**Figure S13b**). The small thickness endows the PVDF:LLZTO membranes with excellent flexibility, as shown in the inset of **Figure S13b**. PVDF:LLZTO membranes show the dense arrangement of small grains, which form the continuous texture (**Figure S13c**). The electrochemical window for measuring the PVDF:LLZTO electrolyte using linear scanning voltammetry (LSV) is approximately 4.8 V, as shown in **Figure S13d**. The Li-ion conductivities of PVDF:LLZTO at 30 °C and 45 °C are 1.19×10⁻⁴ S cm⁻¹ and 2.18×10⁻⁴ S cm⁻¹, respectively (**Figure S13e**). The Li-ion transference number (*t*_{Li⁺}) of PVDF:LLZTO is approximately 0.32 (**Figure S13f**). The symmetric battery composed of Li|PVDF:LLZTO|Li is cycled stably for more than 4000 hours at 30 °C, 0.1 mA cm⁻² and 0.1 mAh cm⁻², as shown in **Figure S14a**. Increasing the current density to 0.2 mA cm⁻² led to stable operation for over 700 hours, as shown in **Figure S14b**.

The NCM811|PVDF:LLZTO|Li and NCM811@CN-3wt%|PVDF:LLZTO|Li cells are investigated, the results of which are shown in **Figure 6a**. **Figure 6b** shows the rate performance. When the current density increases from 0.1 C to 1 C, the capacity of the NCM811@CN-3wt% changes from 188.9 mAh g⁻¹ to 95.3 mAh g⁻¹, whereas the capacity of the NCM811 changed from 182.9 mAh g⁻¹ to only 34.7 mAh g⁻¹. **Figure 6c** illustrates the cycle performance of NCM811 and NCM811@CN-3wt% under 0.1 C between 3–4.3 V at 30 °C. The reversible capacity of NCM811@CN-3wt% is still 163.8 mAh g⁻¹ after 200 cycles with a capacity retention of 88.1%, as shown in **Figure 6d**. In contrast, the specific capacity of NCM811 decreases to 130.7 mAh g⁻¹ after 200 cycles with 71.8% capacity retention, as shown in **Figure 6e**. **Figure 6f** shows the cycle performance at the elevated temperature of 45 °C. The capacity of NCM811 capacity is reduced from 189.6 mAh g⁻¹ to 131.7 mAh g⁻¹ after 200 cycles with a capacity retention of 69.5% (**Figure 6g**). Nevertheless, the NCM811@CN-3wt% capacity drops from 189.6 mAh g⁻¹ to 159.5 mAh g⁻¹ with 84.2% capacity retention (**Figure 6h**). These results indicate that g-C₃N₄ coating is also beneficial to the cycle performance of lithium batteries with solid-state-hybrid electrolytes.

A comparison of cycle performance between this work and other coated NCM cathodes for liquid and solid-liquid-hybrid cells has been summarized in **Table S2 and Table S3**. This comparison confirms that the prepared material has better cycle performance than other coated NCM cathodes for liquid and solid-liquid

hybrid batteries.

3. Conclusion

2D g-C₃N₄ coating on NCM811 has been achieved by in-situ surface engineering. The g-C₃N₄-coated NCM811 contributes to the formation of a thin and homogeneous cathode/electrolyte interface, thereby greatly reducing adverse side reactions. Structural stability is improved and no micro-cracking occurs after long-term cycling. Furthermore, the g-C₃N₄ coating promotes lithium ion transport and improves reaction kinetics. As a result, the NCM811@CN-3wt% cathode displays 161.3 mAh g⁻¹ and capacity retention of 84.6% at 0.5 C and 55 °C after 400 cycles and 95.7 mAh g⁻¹ at 10 C, much better than NCM811 (i.e. 129.3 mAh g⁻¹ and capacity retention of 67.4% at 0.5 C and 55 °C after 220 cycles and 28.8 mAh g⁻¹ at 10 C). The performance improvement of the NCM811@CN-3wt% cathode is also applicable to solid-liquid-hybrid electrolyte systems composed of PVDF:LLZTO with ionic-liquid electrolytes, which show 163.8 mAh g⁻¹ and the capacity retention of 88.1% at 0.1 C and 30 °C after 200 cycles and 95.3 mAh g⁻¹ at 1 C. This work sparks new ideas on constructing the interface layers with excellent comprehensive performance for high-nickel ternary metal oxide cathodes.

4. Experimental Section

4.1. Synthesis of g-C₃N₄ coating on NCM811. A series of dicyandiamides corresponding to 1 wt%, 2 wt%, 3 wt%, and 4 wt% of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (denoted as NCM811) were dissolved in 50 mL of anhydrous ethanol. Subsequently, 3 g of commercial NCM811 cathode was added to each solution and ball milled for 12 hours at a 10:1 ball-to-powder ratio and 100 rpm. Finally, the mixture was dried at 80 °C for 12 h and calcined under Ar at 500°C for 1 h to synthesize g-C₃N₄-coated NCM811 samples (denoted as NCM811@CN-1wt% for 1 wt%, NCM811@CN-2wt% for 2 wt%, NCM811@CN-3wt% for 3 wt%, and NCM811@CN-4wt% for 4 wt%, respectively).

4.2. Fabrication of PVDF:LLZTO electrolytes. The fabrication process of the electrolyte was carried out in a dry room (dew point of -40 °C). Typically, 600 mg polyvinylidene fluoride (PVDF) and 600 mg Lithium bis((trifluoromethyl)sulfonyl)azanide (LiTFSI) were dissolved in 6 mL Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) dispersed N,N-Dimethylformamide (DMF) solvent and mixed for 12 h to obtain a uniform slurry (Content of LLZTO is 15 wt%). Afterwards, the slurry was scraped onto the surface of the glass plate with a scraper and vacuum dried at 80 deg C for 24 h. The PVDF:LLZTO electrolyte membranes were obtained when the temperature was reduced to room temperature.

4.3. Electrode Preparation. The composite electrodes were fabricated by using NCM811 and g-C₃N₄-modified NCM811 as active material (80 wt%), PVDF as the adhesive (10 wt%), and super-p (10 wt%) as a conductive agent. The homogeneous paste was applied to the Al foil and then vacuum-dried overnight at 80 degC to remove residual solvents. The mass loading of NCM811 and NCM811@CN was ~2.0 mg cm⁻². Moreover, NCM811 and NCM811@CN cathodes were also prepared using the same method, with a mass loading of up to ~7.5 mg cm⁻².

4.4. Battery assembly. For electrochemical characterization, CR2032 button cells were assembled in a glove box filled with argon (O₂ < 0.1 ppm, H₂O < 0.1 ppm). Li metal anodes and 1 M LiPF₆ in EC/DEC (1:1 in volume) were used as the counter electrodes and electrolytes, respectively. The electrolyte was infiltrated into a single-layer Polypropylene (PP) membrane, serving as the separator. For solid-liquid-hybrid batteries, Li metal anodes and PVDF:LLZTO electrolyte membranes were used as the counter electrodes and electrolytes, respectively. 1.5 μL cm⁻² 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM-TFSI) ionic liquid as the wetting materials for cathode/electrolyte interfaces. Li/Li symmetric cells were assembled by sandwiching the electrolyte membranes between two pieces of Li foils.

4.5. Materials characterization. The crystalline structure was analysed in the 2θ range of 10°-80° by smartlab SE X-ray diffractometer (XRD) using Cu-Kα. The microstructure and morphology were characterized by transmission electron microscopy (TEM, JEM-2100F) and scanning electron microscopy (SEM, Hitachi, FE-SU4800). The particle size distribution was analysed using a (Brookhaven Zeta Plus) laser

particle size analyser. Fourier transform infrared spectroscopy (FTIR, Necchi X70) was used to analyse the composition of the samples. Thermogravimetric analysis (TGA) (TA, SDT-650) was performed in an argon atmosphere in the range of 25-900 °C. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to characterize the surface chemical environment of materials.

4.6. Electrochemical Analysis. The battery charge-discharge experiments were performed at various rates using the NETWARE (CT-4008Tn) battery analyser. Cyclic voltammetry (CV, 0.1 mV s⁻¹-0.5 mV s⁻¹ and 3-4.3 V) characterization was performed using a CHI660E electrochemical workstation, while the electrochemical workstation in Princeton, NJ, USA, was used to acquire electrochemical impedance spectra (EIS, frequency 100,000-0.1 Hz, signal amplitude 5 mV). The electrochemical window of the PVDF:LLZTO electrolyte was tested between 0 and 6 V by linear sweep voltammetry (LSV, 1 mV s⁻¹) and the lithium-ion mobility number (t_{Li^+}) was measured by direct current (DC) polarization of Li/Li symmetric batteries with a polarization voltage of 10 mV using an electrochemical workstation (in Princeton, NJ, USA).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Key R&D Program of China (Grant No.2023YFB2503900), National Natural Science Foundation of China (Grant No. 52372203), National Natural Science Foundation of China (Grant No. 52202259) and the Shandong Province Natural Science Foundation (ZR2022QE093).

Received: (will be filled in by the editorial staff) Revised: (will be filled in by the editorial staff) Published online: (will be filled in by the editorial staff)

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