Hierarchically Micro/Nanostructured Current Collectors Induced by Ultrafast Femtosecond Laser Strategy for High-Performance Lithium-ion Batteries

Yaya Wang, Zexu Zhao, Jiang Zhong, Tao Wang, Lei Wang, Hanjiao Xu, Jinhui Cao, Jinhao Li, Guanhua Zhang, Huilong Fei, and Jian Zhu*

1. Introduction

Among existing energy storage systems, lithium-ion batteries (LIBs) stand out in portable electronic products and large-sized electric devices due to their high energy density.[11–4] Nevertheless, the limited cycle life makes LIBs difficult to meet the ever-increasing demands of current long-cycle and high-energy-density energy storage devices. Generally, a complete lithium-ion battery system consists of battery shell, dual electrodes, porous separator, current collectors, and electrolyte.[5] Numerous reports have focused on the development of novel structured electrode materials,[6–8] high-performance electrolyte and separator materials,[9–13] However, the current collectors, as an important factor responsible for supporting the entire electrode and bridging the internal and external circuits, can affect battery performance, yet, are not receiving sufficient attentions.[14–16]

Aluminum (Al) and copper (Cu) foils are commonly used as current collectors for commercial LIBs on account of their high electric conductivity, moderate chemical/electrochemical stability, and cost-effectiveness.[17,18] A typical slurry casting method is massively adopted to fabricate an electrode pole piece, where the slurry composed of active material, conductive additive, and polymer binder is uniformly cast on the surface of current collectors.[19,20] However, when using the slurry casting method, the relatively smooth surface of commercial current collectors will lead to weak bonding strength and increased interface contact resistance between the active materials and Al/Cu foil, triggering poor structural integrity of the whole electrodes, insufficient electronic conduction, and further battery degradation during charge/discharge process.[21–23] Therefore, the surface morphology of Al/Cu foils, the electrochemical contact, and bonding strength between current collectors and active materials are widely recognized as key factors to affect the cycle performance of LIBs.[24,25] In this regard, surface treatment has emerged as a promising strategy to improve the overall performance of LIBs, such as creating embossed/porous aluminum through the anodization process and electrochemical etching process,[26,27] employing a coating treatment,[28–30] constructing microcrystalline Cu foil through ultrasonic peening technique and orthogonal plowing/extrusion (PE) machining,[31,32] as well as other

Commercial Cu and Al current collectors for lithium-ion batteries (LIBs) possess high electrical conductivity, suitable chemical and electrochemical stability. However, the relatively flat surface of traditional current collectors causes weak bonding strength and poor electrochemical contact between current collectors and electrode materials, resulting in potential detachment of active materials and rapid capacity degradation during extended cycling. Here, we report an ultrafast femtosecond laser strategy to manufacture hierarchical micro/nanostructures on commercial Al and Cu foils as current collectors for high-performance LIBs. The hierarchically micro/nanostructured current collectors (HMNCCs) with high surface area and roughness offer strong adhesion to active materials, fast electronic delivery of entire electrodes, significantly improving reversible capacities and cyclic stability of HMNCCs based LIBs. Consequently, LiNi0.5Co0.2Mn0.3O2 (NCM523) cathode with Al HMNCC generated a high reversible capacity after 200 cycles (25% higher than that of cathode with Al CC). Besides, graphite anode with Cu HMNCC also maintained prominent reversible capacity even after 600 cycles. Moreover, the full cell assembled by graphite anode with Cu HMNCC and NCM523 cathode with Al HMNCC achieved high reversible capacity and remarkable cycling stability under industrial-grade mass loading. This study provides promising candidate for achieving high-performance LIBs current collectors.

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Al/Cu foils with different surface textures. Nevertheless, the intrinsic complexity and time-consumption of these existing methods bring about huge barrier for large-scale application, which is undesirable for rechargeable commercial batteries. Here, a facile and ultrafast femtosecond laser strategy was proposed to customize the surface structure of Al/Cu current collectors (CCs) to enhance the electrochemical performance of LIBs. The hierarchically micro/nanostructured current collectors (HMNCCs) were tailored by simply optimizing the process parameters including some excellent features as follows: i) greatly improved charge-transport efficiency, strong bonding strength, and superior contact wettability between HMNCCs and active materials; ii) the durable structural flexibility of large-scale and high-yield preparations. Remarkably, NCM523 cathode with Al HMNCC and graphite anode with Cu HMNCC displayed outstanding cycling stability and rate capacity. Moreover, the obtained full battery composed of NCM523 cathode with Al HMNCC and graphite anode with Cu HMNCC with industrial-grade mass loading also exhibited excellent cycling performance at different voltage windows.

2. Results and Discussion

2.1. Preparation and Characterization of Al HMNCCs and Cu HMNCCs

Figure 1a illustrates the schematic diagram for the synthetic process of Al HMNCC and Cu HMNCC by an ultrafast femtosecond laser interference patterning process. Whereafter, the laser-treated Al/Cu HMNCCs are applied as current collectors for lithium-ion full batteries. In this approach, the commercial Al and Cu CCs with a thickness of about 12 μm are selected as substrates. The HMNCCs with hierarchical micro/nanostructures are constructed, a beam of femtosecond laser periodically scanning in the horizontal and vertical directions by the typical line-by-line. This customized micro/nanostructures characteristic can effectively offer fast charge transport, strong bonding strength, and superior contact wettability between HMNCCs and active materials, thus boosting the reversible capacities and cycling performance of electrodes for both half and full cells. Under adjustable power and scanning speed of laser beam, Al HMNCCs and Cu HMNCCs with different hierarchical micro/nanostructures can be realized (Figure 1b–g). Obviously, commercial Al/Cu CCs show a nearly smooth surface without obvious micro/nanostructures, which makes them difficult to grip active materials firmly on the surface of current collector, thus resulting in the potential detachment of active materials during the long-term cycling (Figure 1b and e). Driven by the femtosecond laser, regular zebra-like patterns with a scan pitch of 30 μm can be observed (Figure 1c, Al HMNCC-1), which is consistent with the preset space between two laser scans. The evenly distributed dark stripes are not ablated by the laser, as shown in the red box. The gray stripes are the products of periodic burning by the laser, and the selected yellow square area is enlarged to become a rough wavy surface. The size of the micro/nanopores between two wavy lines ranges from 50 to 500 nm. When the laser is periodically scanned in the typical line-by-line in the horizontal and vertical directions, the gray stripes become rough net-like structures (Figure 1d, Al HMNCC-2). The dark black part in the red area is still consistent with Al CC, while the yellow area is laser-ablated areas with regular and rough micro/nanostructures in the enlarged illustration. The gray area exhibits a more exquisite structure in nanoscale with diameter of 20–500 nm. These structural units of the hierarchical micro/nanostructures and “pits” may be originated from the unstable capillary wave of the smelting and evaporation upon the ultrahigh energy of the pulsed laser. The small pits inside the rough net-like structure also greatly increase the surface area and trap polymeric binders and carbon black (CB) nanoparticles tightly as “pitfalls” and further prevent the active materials from falling off during extended cycling.

Besides, Cu CC possesses random shapes and dimensions ranging from 1 to 2 μm (Figure 1e). When the laser is applied to the surface of Cu foil, the similar rough zebra-like and net-like structures with hierarchical micro/nanostructures are observed, as revealed in Figure 1f and g. This phenomenon also shows the universality and practicality of ultrafast femtosecond laser strategy. Notably, the whole synthetic process of Al/Cu HMNCCs can be completed within 5 min, indicating the femtosecond laser strategy is facile, time-efficient, cost-effective with great potentials for large-scale manufacture. In fact, two or more polygon scanners with scanning speeds up to a few hundred meters per second can be used to increase the existing processing speed by hundreds of times to achieve practical production application (Figure S1).

Furthermore, the corresponding optical photographs at different states are displayed in Figure S2, in which the silver-gray areas are caused by laser energy, implying the change of surface structures. The macrostructures were well retained for Al HMNCC-1, Al HMNCC-2, Cu HMNCC-1 and Cu HMNCC-2. However, huge wrinkles would appear on the Al/Cu foil after further increasing laser power, severely damaging the structures and mechanical properties of collectors. After coating the corresponding NCM523 and graphite onto the Al/Cu HMNCCs, uniformly dispersed and well-structured electrodes can be obtained (Figure S3). Additionally, X-ray diffraction (XRD) patterns in Figure S4 declares almost the same crystal structures of various Al CCs or Cu CCs. Therefore, Al HMNCC-1, Al HMNCC-2, Cu HMNCC-1, and Cu HMNCC-2 are mainly investigated.

Physical properties such as continuous structural integrity and tensile strength of current collectors are indispensable in the electrode manufacturing process. Figure S5 demonstrates the tensile strengths with Al HMNCCs and Cu HMNCCs. Apparently, tensile strengths and thicknesses of current collectors hardly change before and after femtosecond laser treatment, indicating excellent mechanical strength and structural integrity. The surface roughness is further explored by the 3D images of surface profile analysis in Figure 2a. The high roughness reflects the strong binding force with active material. 3D image of Al CC is consistent with the SEM, showing a relatively smooth surface without any pits, hills, valleys, or waves. However, Al HMNCC-1 and Al HMNCC-2 display waves and grid surface. The average surface roughness (Ra) of Al CC and Al HMNCC-1 is 252.2 and 291.7 nm, respectively. More importantly, the Ra value of Al HMNCC-2 even reaches 466.9 nm. The contrast between Cu CC and Cu HMNCCs is also obvious, and Cu HMNCC-2 exhibits the highest surface roughness of 484.5 nm.

Based on the surface structure, the laser-treated samples can also show different adhesion properties to the coated slurry. As shown in Figure 2b, the contact angles of Al CC, Al HMNCC-1, and Al HMNCC-2 are 38.8°, 30.1°, and 10.4°, respectively. The Cu HMNCC-1 and Cu HMNCC-2 also produce low contact angles of 38° and 33.9°, respectively. This multifunction structure allows the slurry to be homogeneously distributed within the micro/nanopores, thereby ensuring the
maximum utilization of the selected active materials. The cross-sectional morphologies of Al/Cu HMNCCs combined with NCM523 and graphite electrode materials are carefully characterized. A huge gap between the active materials and Al/Cu CC was found (Figure 2c and f), which may trigger shedding during cycling, resulting in poor electrochemical performance. These cracks would cause weak bonding strength and slow charge transport between CCs and active materials. NCM523 is in close contact with Al HMNCCs and completely covers the substrate, which is better than that with Al CC (Figure 2d and e). As the surface roughness increases, the combination of NCM523 and Al HMNCC-2 becomes tighter, which can help to reduce the interface resistance and prevent the electrode capacity from declining. For the graphite anodes, the same satisfactory results are also obtained in Figure 2g and h. According to the above analysis, the highly improved roughness and wettability will enhance the bonding strength and charge transport between active materials and current collector, thereby obtaining excellent electrochemical performance.

### 2.2. Electrochemical Performance of Al HMNCCs

To clarify the structural advantages of Al HMNCCs, the as-prepared Al HMNCCs with different structures were employed as current collectors with NCM523 as cathode material to explore lithium storage performance. Figure 3a shows the CV curves of Al HMNCC-2 electrode based on NCM523 cathode with a scan rate of 0.2 mV s⁻¹. Obviously, a pair of redox peaks in the voltage range of 2.8–4.35 V is mainly contributed to the redox reactions of Ni²⁺/Ni⁴⁺ and Co³⁺/Co⁴⁺ during cycling, while Mn⁴⁺ does not undergo a valence state change to ensure the stability of the metal-oxide lattice. During the following cycles, the well-overlapping CV curves reveal high electrochemical reversibility and excellent cycle stability. Meanwhile, the galvanostatic charge/discharge profiles of Al CC and Al HMNCCs at 0.5 C (1 C = 160 mA g⁻¹) in the first cycle are shown in Figure 3b, in which the cells are pre-cycled for the activation at the current rate from 0.02 C to 0.5 C with the voltage gradually rising from 2.8 to 4.35 V. An obvious charging platform is located at 3.9 V and a discharging platform at 3.7 V in the initial cycle, corresponding to typical electrochemical behavior of NCM523. The Al CC, Al HMNCC-1, and Al HMNCC-2 supported cells deliver reversible discharge capacities of 147.6, 148, and 150.2 mAh g⁻¹ at a current density of 0.5 C in the first cycle. Figure 3c illustrates galvanostatic charge/discharge profiles tested on NCM523 with Al HMNCC-2 at 0.5 C for a certain number of cycles and the charge/discharge platforms shift after the cycling process. The galvanostatic charge/discharge profiles of Al CC and Al HMNCC-1 at 0.5 C are shown in Figure 3e. Evidently, the Al HMNCC-2-based half-cell reveals the highest reversible capacity after 200 cycles with the capacity retention of 74.4%, while Al HMNCC-1 exhibits a lower capacity retention of 64.2%. For comparison, the capacity retention rate of Al CC is only 56.7% after 200 cycles (Figure 3f). Figure S7 indicates SEM images of Al HMNCC-1 and Al HMNCC-2 electrodes before and after cycles. It can be clearly seen that the NCM523 particles are still in a tightly packed state in two electrodes without structure pulverization after cycles, thus confirming the stability of electrodes. This phenomenon preliminarily clarifies that the introduction of micro/nanostructures is conducive to cycling performance of current collector.

Meanwhile, the favorable performances of Al HMNCC-2 are further amplified in the rate capability. As shown in Figure 3f, the capacities of the half-cells based on these three samples are almost the same under small current rate, but when the current rate increases to 5 C, the Al HMNCC-2 delivers the highest reversible capacities of 60.1 mAh g⁻¹. By contrast, Al CC shows the lowest capacity of 22 mAh g⁻¹ at 5 C among the obtained samples. Impressively, when the current rate is restored to 0.2 C, the capacity of cathode with Al HMNCC-2 can recover back to 158.7 mAh g⁻¹ with only 2% loss compared with the capacity of 168.2 mAh g⁻¹. To further explore the rate performances of Al HMNCC-2, the charge/discharge profiles at different rates are exhibited in Figure 3g. Apparently, the charge/discharge platform of cathode with Al HMNCC-2 shortens with the sharp increase of current density. In addition, electrochemical impedance spectroscopy (EIS) is used to further discuss the resistance of the obtained materials before cycling. Figure 3h reveals that the EIS of the three electrodes include the semicircular feature in the high-frequency region and the tilt feature in the low-frequency region as well as the equivalent circuit, where Rₑ and Rₛ represent ohmic resistance and charge-transfer impedance, respectively. The Rₑ of cathode with Al HMNCC-2 exhibits the lowest value (161.4 Ω) from ZView software fitting compared to that with...
Al HMNCC-1 (291.3 $\Omega$) and Al CC (394.7 $\Omega$), as shown in Figure S8. Cathode with Al HMNCC-2 confirms the lowest interface impedance and fast electron transfer characteristics. These results are in good agreement with the optimal roughness and contact wettability described of Al HMNCC-2. Thus, the Al HMNCC-2 is more favorable as current collector for LIBs.

2.3. Electrochemical Performance of Cu HMNCCs

Considering the universality of femtosecond lasers, the Cu HMNCCs have also been adopted to deeply understand the Li-storage mechanism. Half-cell was assembled with graphite as anode and Cu HMNCCs as current collectors. Firstly, the CV curves in Figure 4a are employed to evaluate the electrochemical reactivity of graphite on Cu HMNCC-2 at a scan rate of 0.5 mV s$^{-1}$ within the voltage window of 0.01–2 V. A redox peak at 0.35 V can be observed in sample corresponding to the Li$^+$ insertion. In the next two cycles, the 0.49 V peak almost disappeared due to the formation of SEI. Figure 4b and Figure S9 explain the selected galvanostatic discharge/charge profiles of graphite anodes with Cu CC and Cu HMNCCs at 0.2 C (1 C = 372 mA g$^{-1}$), respectively. The initial discharge capacity of anode with Cu HMNCC-2 is about 504.8 mAh g$^{-1}$, which is higher than that with Cu HMNCC-1 (410.4 mAh g$^{-1}$) and Cu CC (408.1 mAh g$^{-1}$). Even after 250 cycles, anode with Cu HMNCC-2 still retains the highest capacity of 385.4 mAh g$^{-1}$ (Figure 4c). The higher reversible capacity of Cu HMNCC-2 should be attributed to hierarchically micro/nanostructures within the current collector. The rate performance of anodes with Cu CC and Cu HMNCCs is demonstrated in Figure 4e. The discharge capacity of graphite anode with Cu HMNCC-2 reaches up to 428.4, 381.9, 304.7, 272.9, 186.2, 104.2, and 75.2 mAh g$^{-1}$ at current rate of 0.1, 0.2, 0.6, 1, 2, 3, and 4 C, respectively. When the current rate is set back to 0.1 C, the discharge capacity recovers to 443.9 mAh g$^{-1}$, which is still much higher than that with Cu CC (387.3 mAh g$^{-1}$) and Cu HMNCC-1 (410.2 mAh g$^{-1}$). Additionally, the discharge/charge curves of graphite anode with Cu HMNCC-2 at various current rates exhibit similar slope behavior (Figure 4d).

Long-term cycling capabilities are crucial for the durability. To this end, we compared the long-term cycling capabilities at a high current density of 1 C in Figure 4f. Anodes with the Cu HMNCC-2 and Cu HMNCC-1 maintain ultrahigh reversible capacities of 342.1 mAh g$^{-1}$ and 313.8 mAh g$^{-1}$ even after 600 cycles, respectively. However, the capacity of anode with Cu CC reduces to 265.9 mAh g$^{-1}$. As shown in Figure S10, the SEM images of Cu HMNCC-1 and Cu HMNCC-2 after cycles also maintain a tightly embedded state without structural pulverization, thus confirming the stability of the electrode. Figure 4g presents the electrochemical impedance spectra of anodes on the various Cu current collectors and the equivalent circuit. As shown in Figure S11, the $R_{ct}$ of electrode with Cu HMNCC-2 exhibits the lowest value (182.1 $\Omega$) from ZView software fitting compared with Cu HMNCC-1 (231.8 $\Omega$) and Cu CC (425.9 $\Omega$), indicating the lowest electrical resistance. Therefore, the enhanced electrochemical performance confirms the advantage of Cu HMNCC-2 obtained by laser treatment.

2.4. Electrochemical Performance of Full Battery with Al HMNCC-2 and Cu HMNCC-2

To demonstrate the practical application of Al HMNCC-2 and Cu HMNCC-2 for high-performance LIBs, NCM523 cathode and graphite anode with Al or Cu HMNCCs was assembled into full cell (NCM523@Al HMNCC-2)G@Cu HMNCC-2). Both NCM523 and graphite possess a commercial loading of approach 18 and 10 mg cm$^{-2}$, respectively. Simultaneously, full cell assembled with NCM523@Al CC and graphite@Cu CC was used as a comparison. The battery capacity is calculated based on the mass of graphite anode (1 C = 340 mA g$^{-1}$). Figure 5a shows galvanostatic discharge/charge profiles of NCM523@Al HMNCC-2‖G@Cu HMNCC-2 at 0.5 C with the voltage window of 2.8–4.35 V, which is more stable than that of NCM523@Al CCG@Cu CC in Figure S12. The cycling performance is carried out at 0.5 C after initial ten cycles at 0.2 C, NCM523@Al HMNCC-2‖G@Cu HMNCC-2 maintains 74.7% of initial capacity after 200 cycles in the voltage window of 2.8–4.35 V, whereas NCM523@Al CCG@Cu CC retains only 63.5% of initial capacity (Figure 5b). Specifically, NCM523@Al HMNCC-2‖G@Cu HMNCC-2 can provide a higher reversible capacity of 227.8 mAh g$^{-1}$, which is 1.47 times of NCM523@Al CCG@Cu CC (154.8 mAh g$^{-1}$). The rate performance is tested at various current rates from 0.1 to 2 C. When the
current rate rises to 2 C, the capacity of NCM523@Al CC||G@Cu CC suddenly drops to 32.8 mAh g\(^{-1}\), while NCM523@Al HMNCC-2||G@Cu HMNCC-2 can still reach 87.8 mAh g\(^{-1}\). The typical Nyquist plots and equivalent circuit diagram in Figure 5e and Figure S13 show that NCM523@Al HMNCC-2||G@Cu HMNCC-2 (\(R_{\text{ct}} = 216.7 \ \Omega\)) exhibits a much lower \(R_{\text{ct}}\) value compared with NCM523@Al CC||G@Cu CC (\(R_{\text{ct}} = 333.1 \ \Omega\)). When the voltage window is adjusted to 2.8–4.2 V, excellent long-term cycling performance can be still maintained after continuous 300 cycles (Figure 5f). More importantly, we also test the pouch cell with electrode thickness of \(\sim 60 \ \mu\text{m}\) and acquire satisfactory cycle performance with high average Coulombic efficiency of 99.5%, which is comparable to cycle performance of coin full cell. (Figure S14). Such superior electrochemical performance of NCM523@Al HMNCC-2||G@Cu HMNCC-2 can be attributed to the hierarchical micro/nanostructures, which increase the mechanical adhesion and electron transport between HMNCCs and active materials (Figure S15). Besides, the COMSOL Multiphysics was also carried out to verify the electrode kinetics of lithium-ion batteries. As shown in Figure S16, it should be pointed out that lithium-ion concentration distribution on the surface of porous electrode coated with active material is almost the same as that of the flat electrode, but the porous electrode presents higher current density than that of flat electrodes, indicating faster ion movement. Generally, uniform lithium-ion concentration on the surface of porous electrode coated with active material and current density distribution in electric field can induce the matching reaction velocity and similar diffusion rate, thereby leading to outstanding cyclic stability.

3. Conclusion

In summary, we report a facile, efficient and low-cost strategy to fabricate Al HMNCCs and Cu HMNCCs for high-performance lithium-ion batteries. The unique hierarchical micro/nanostructures with high surface area and roughness endow strong bonding strength and reduced interface resistance between HMNCCs and active materials, thus resulting in prominent reversible capacities and
cycle stability both in half and full batteries. Based on these advantages, NCM523 cathode with Al HMNCC-2 delivers a high discharge capacity after 200 cycles, which is 25% higher than that of cathode with Al CC. Graphite anode with Cu HMNCC-2 maintains prominent excellent long-cycle performance over 600 cycles. Moreover, the NCM523@Al HMNCC-2/G@Cu HMNCC-2 full cell also displays excellent cyclic stability and rate performance. Simultaneously, the facile synthetic routes provide inspiration for the design of advanced current collectors for the development of next-generation high-performance lithium-ion batteries.

4. Experimental Section

Formation of Direct Laser-assisted Surface Structures: Commercial Al foil with thickness of 12 µm (Shenzhen MTI Co., Ltd.) was selected as the positive current collector. The purchased Al current collector was named as Al CC, which was thoroughly cleaned by ethanol and flattened by mechanical external force before surface treatment. A coherent femtosecond laser-treated aluminum with hierarchically micro/nanostructures current collector was named as Al HMNCC. The laser beam was focused using a galvanometer scanner (IntelliSCAN III14, SCANLAB, Germany) with a 160 mm F-Theta objective, and the patterning process was performed by typical line-by-line laser scanning in the horizontal and vertical directions. In the experiments, the fixed pulse duration was set to 250 fs and other detailed laser process parameters was summarized in Table S1. The samples obtained with different parameters are named Al HMNCC-1 and Al HMNCC-2, respectively.

Commercial Cu foil with thickness of 12 µm (Shenzhen MTI Co., Ltd.) was chosen as the current collector for negative electrode. The purchased Cu current collector and femtosecond laser-treated Cu current collector with hierarchically micro/nanostructures were named as Cu CC and Cu HMNCC, respectively. The manufacturing process of micro/nanostructures surface is similar to that of Al CC, except that the laser parameters are changed. The samples obtained with different parameters are named Cu HMNCC-1 and Cu HMNCC-2 (Table S1), respectively.

Materials Characterization: The morphology and microstructure of Al CC and Cu CC before and after different laser parameters treatment were characterized by scanning electron microscope (Hitachi S-480, Zeiss, Germany). X-ray diffraction (XRD) patterns were conducted on a XRD-6100 spectrometer with Cu-Kα radiation (Shimadzu, Japan). The surface flatness and roughness of Al HMNCC and Cu HMNCC was obtained using 3D optical surface profiler (Wyko...
NT9100). The wettability of Al HMNCC and Cu HMNCC surface was acquired using an optical contact angle measuring device. The tensile strength measurements of the samples were determined by an intelligent electronic tensile testing machine (XWL-H TSL-1002).

**Electrochemical Measurements:** In order to test the electrochemical performance of current collectors, 2032-type half-cells were assembled in an argon-filled glove box (H₂O < 0.5 ppm, O₂ < 0.5 ppm). The pure Li foil and Celgard 2400 polypropylene membrane were used as the counter/reference electrode and separator, respectively. LiNi₀.₅Co₀.₂Mn₀.₃O₂ (NCM523) with the high capacity and chemically stable graphite (G) were selected as the positive and negative materials, respectively. To maintain consistency with commercial battery performance, the electrolyte is selected from commercial electrolytes. The main component is 1 M LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC) (v:v = 1:1) with 1 wt% VC, which was provided by Guangdong Tianfeng Material Co., Ltd. All the batteries were measured on a LAND-CT2001A cell test system (LANDTE Co., China) at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were conducted on an IVIUM electrochemical workstation (Ver- tex One. EIS) over a frequency range of 0.01 Hz to 100 kHz.

For fabrication of cathode, NCM523, conductive carbon black (super P), and polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) solvent at a ratio of 90:5:5, followed by magnetic stirring for 24 h to obtain a homogeneous slurry. The produced slurry was then coated onto Al CC and Al HMNCC and dried at 80 °C under vacuum for 24 h to form NCM523@Al HMNCC. The NCM523 loading on the cathode was approximately 1–2 mg cm⁻². The charge-discharge experiments and cyclic voltammetry (CV) analyses were carried out in the range of 2.8–4.35 V with scanning speed of 0.2 mV s⁻¹. For the fabrication of anode, graphite powder, conductive carbon black (super P), and carboxyl methylated cellulose (CMC) were mixed in a ratio of 80:10:10 with the solution of ethanol and H₂O as solvents, followed by magnetic stirring for 24 h to obtain homogeneous slurry. The resultant slurry was then coated onto Cu CC and Cu HMNCC and dried at 80 °C under vacuum for 24 h to form G@Cu HMNCC. The graphite active material content was about 0.5–1 mg cm⁻². The charge-discharge experiments and CV analyses were carried out in the range of 0–2 V with scanning speed of 0.5 mV s⁻¹.

In order to highlight the electrochemical advantages of Al HMNCC and Cu HMNCC, the NCM523@Al HMNCC cathode and G@Cu HMNCC anode were used to assemble CR2032 full cell. As comparison, NCM523@Al CC cathode and G@Cu CC anode were also assembled into the same cell. The mass loading of NCM523 and graphite were about 18 and 10 mg cm⁻², respectively. The charge/discharge tests were...
completed on a LAND-CT2001A cell test system (LANDTE Co., China) in the voltage range of 2.8–4.35 V and 2.8–4.2 V.

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

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

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[1] M. Li, J. Lu, Z. W. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561.
[2] L. Xiao, Z. Qin, J. Y. Yi, H. Y. Dong, J. P. Liu, J. Energy Chem. 2020, 51, 216.
[3] M. Zhang, J. Zhong, W. Q. Kong, L. Wang, T. Wang, H. L. Fei, H. Y. Luo, J. Zhu, J. W. Wu, B. A. Lu, Energy Environ. Mater. 2020. https://doi.org/10.1002/eem2.12086.
[4] H. Tan, X. Z. Yu, K. Huang, J. X. Zhong, B. A. Lu, J. Energy Chem. 2020, 51, 388.
[5] J. M. Jiang, P. Nie, B. Ding, Y. D. Zhang, G. Y. Xu, L. Y. Wu, H. Dou, X. G. Zhang, J. Mater. Chem. A 2017, 5, 23283.
[6] Q. Y. Gui, L. X. Wu, Y. Y. Li, J. P. Liu, Adv. Sci. 2019, 6, 1802067.
[7] J. W. Han, H. Li, D. B. Kong, C. Zhang, Y. Tao, H. Li, L. Q. Chen, Q.-H. Yang, ACS Energy Lett. 2020, 5, 1986.
[8] L. Xiao, J. Y. Yi, Z. K. Kou, E. Li, B. H. Deng, J. Wang, J. P. Liu, Small Methods 2020, 4, 1900619.
[9] S. Li, S.-Q. Zhang, L. Shen, Q. Liu, J.-B. Ma, W. Lv, Y.-B. He, Q.-H. Yang, Adv. Sci. 2020, 7, 1900388.
[10] J. F. Tan, J. P. Liu, Energy Environ. Mater. 2020. https://doi.org/10.1002/eem2.12125.
[11] R. Z. Li, X. Ba, H. F. Zhang, P. Xu, Y. Y. Li, C. W. Cheng, J. P. Liu, Adv. Funct. Mater. 2018, 28, 1800497.
[12] C. Zhang, L. Shen, J. Q. Shen, F. Liu, G. Chen, R. Tao, S. X. Ma, Y. T. Peng, Y. F. Lu, Adv. Mater. 2019, 31, 1808338.
[13] Z. F. Liu, Y. J. Jiang, Q. M. Hu, S. T. Guo, L. Yu, Q. Li, Q. Liu, X. L. Hu, Energy Environ. Mater. 2020. https://doi.org/10.1002/eem2.12129.
[14] Y. Q. Lan, W. J. Yao, X. L. He, T. Y. Song, Y. B. Tang, Angew. Chem. Int. Ed. 2020, 59, 9255.
[15] H. J. Xu, L. Wang, J. Zhong, T. Wang, J. H. Cao, Y. Y. Wang, X. Q. Li, H. L. Fei, J. Zhu, X. D. Duan, Energy Environ. Mater. 2020, 3, 177.
[16] Y. Y. Wang, Z. X. Zhao, W. Zeng, X. B. Liu, L. Wang, J. Zhu, B. A. Lu, J. Energy Chem. 2021, 58, 292.
[17] S. Jin, Y. Jiang, H. X. Ji, Y. Yu, Adv. Mater. 2018, 30, 1802014.
[18] P. C. Zhu, D. Gastol, J. Marshall, R. Sommerville, V. Goodship, E. Kendrick, J. Power Sources. 2021, 485, 229321.
[19] M. Lin, D. L. Cheng, J. W. Liu, L. Z. Ouyang, R. Z. Hu, J. Liu, L. C. Yang, M. Zhu, Energy Environ. Mater. 2020. https://doi.org/10.1002/eem2.12136.
[20] C. F. Shen, X. Fang, M. Y. Ge, A. Y. Zhang, Y. H. Liu, Y. Q. Ma, M. Mecklenburg, X. Nie, C. W. Zhou, ACS Nano 2018, 12, 6280.
[21] Y. Yang, W. Yuan, X. Q. Zhang, Y. Z. Ke, Z. Q. Qiu, J. Luo, Y. Tang, C. Wang, Y. H. Yuan, Y. Huang, Appl. Energy 2020, 276, 115464.
[22] M. Wang, A. V. Le, D. J. Noelle, Y. Shi, S. Meng, Y. Qiao, J. Power Sources 2017, 349, 84.
[23] B. H. Deng, H. Y. Dong, T. Y. Lei, N. Yue, L. Xiao, J. P. Jin, Sci. China Mater. 2020, 63, 492.
[24] N. X. Zhang, Y. J. Zheng, A. Trifonova, W. Pfieger, J. Appl. Electrochem. 2017, 47, 829.
[25] M. Z. Wang, H. Yang, K. X. Wang, S. L. Chen, H. N. Ci, L. R. Shi, J. Y. Shan, S. P. Xu, Q. C. Wu, C. Z. Wang, M. Tang, P. Gao, Z. F. Liu, H. L. Peng, Nano Lett. 2020, 20, 2175.
[26] C. U. Jeong, S.-Y. Lee, J. Kim, K. Y. Cho, S. Yoon, J. Power Sources 2018, 398, 193.
[27] D.-Y. Shin, D.-H. Park, H.-J. Ahn, Appl. Surf. Sci. 2019, 475, 519.
[28] M. Z. Wang, M. Tang, S. L. Chen, H. N. Ci, K. X. Wang, L. R. Shi, L. Lin, H. Y. Ren, J. Y. Shan, P. Gao, Z. F. Liu, H. L. Peng, Adv. Mater. 2017, 29, 1703882.
[29] X. X. Li, L. J. Wang, C. F. Li, B. K. Chen, Q. Zhao, G. Q. Zhang, J. Power Sources 2016, 308, 65.
[30] K. X. Wang, C. Z. Wang, H. Yang, X. B. Wang, F. Cao, Q. C. Wu, H. L. Peng, Nano Res. 1948, 2020, 13.
[31] Z. Xiao, J. Chen, J. Liu, T. X. Liang, Y. Xu, C. J. Zhu, S. W. Zhong, J. Power Sources 2019, 438, 226973.
[32] W. Yuan, B. Y. Pan, Z. Q. Qiu, Z. M. Peng, Y. T. Ye, Y. Huang, H. L. Huang, Y. Tang, ACS Sustainable Chem. Eng. 2019, 7, 12910.
[33] H. Abe, M. Kubota, M. Nemoto, Y. Masuda, Y. Tanaka, H. Munakata, K. Kanamura, J. Power Sources 2016, 334, 38.
[34] J. M. Jiang, P. Nie, B. Ding, W. X. Wu, Z. Chang, Y. T. Wu, H. Dou, X. G. Zhang, J. Power Sources Interfaces. 2016, 8, 30926.
[35] T. T. Xia, T. X. Liang, Z. Xiao, J. Chen, J. Liu, S. W. Zhong, J. Alloys Compd. 2020, 830, 154682.
[36] J. I. Rosales, G. W. Marshall, S. J. Marshall, L. G. Watanabe, M. Toledano, M. A. Cabrerizo, R. Osorio, J. Dent. Res. 1999, 78, 1554.
[37] J. Wojciechowski, L. Kolanowski, A. Bund, G. Lota, J. Power Sources 2017, 368, 18.
[38] L. C. Wang, L. Li, X. X. Zhang, F. Wu, R. J. Chen, ACS Appl. Mater. Interfaces 2018, 10, 32120.
[39] B. Y. Hou, G. R. Li, X. P. Gao, J. Mater. Chem. A 2016, 4, 7689.
[40] Z. Q. Chen, C. Y. Liu, G. Y. Sun, X. B. Kong, S. B. Lai, J. Y. Li, R. Zhou, J. Wang, J. B. Zhao, ACS Appl. Mater. Interfaces 2018, 10, 25454.