Structure Evolution from Layered to Spinel during Synthetic Control and Cycling Process of Fe-Containing Li-Rich Cathode Materials for Lithium-Ion Batteries

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Supporting Information

ABSTRACT: As promising cathode materials for lithium-ion batteries (LIBs), Fe-containing Li-rich compounds of Li_{1+x}Fe_{0.1}Ni_{0.15}Mn_{0.55}O_{2-y} (0 ≤ x ≤ 0.3 and 1.9 ≤ y ≤ 2.05) have been successfully synthesized by calcining the spherical precursors with appropriate amounts of lithium carbonate. The structures, morphologies, and chemical states of these compounds are characterized to better understand the corresponding electrochemical performances. With an increase of lithium content, Li_{1+x}Fe_{0.1}Ni_{0.15}Mn_{0.55}O_{2-y} evolves from a complex layered-spinel structure to a layered structure. The lithium content also affects the average size and adhesion of the primary particles. At 0.1 C, sample x = 0.1 shows the highest first charge/discharge specific capacities (338.7 and 254.3 mA h g\(^{-1}\)), the highest first Coulombic efficiency (75.1\%), the lowest first irreversible capacity loss (84.4 mA h g\(^{-1}\)), the highest reversible discharge specific capacity, and good rate capability. Notably, voltage fading can be alleviated through the adjustment of structural features. Such superior electrochemical performances of sample x = 0.1 are ascribed to the hierarchical micro-/nanostructure, the harmonious existence of complex layered-spinel phase, and the low charge-transfer resistance. An integral view of structure evolution from layered to spinel during synthetic control and cycling process is provided to broaden the performance scope of Li−Fe−Ni−Mn−O cathodes for LIBs.

1. INTRODUCTION

A continuously growing population and depletion of traditional fossil fuels have triggered a large demand for alternative energy storage systems with green chemistry, high efficiency, long life, high safety, and low cost.\(^1−3\) Owing to the high energy density and efficient working capability without pollution penalties, lithium-ion batteries (LIBs)\(^4\) have presently occupied a dominant position in consumer electronics.\(^5\) Moreover, LIBs are also considered to be promising to power more challenging fields, such as electric vehicles (EVs) and hybrid EVs (HEVs) for transportation.\(^6−8\) However, the further development of present LIBs is impeded by previous widely studied cathode materials with insufficient specific capacities (<170 mA h g\(^{-1}\)), such as layered LiCoO\(_2\), spinel LiMn\(_2\)O\(_4\), olivine LiFePO\(_4\) and layered LiNi\(_{0.5}\)Mn\(_{0.3}\)Co\(_{0.2}\)O\(_2\).\(^9\) For large-scale applications, the alternative cathode materials have to maintain a comparable performance and low cost by involving manganese, iron, or nickel species rather than the limited cobalt resource in earth.

Among the reported cathode materials, lithium-rich transition-metal oxides represented by the chemical formula \(\text{xLi}_{\text{1−x}}\text{MnO}_2\) (\(0 ≤ \text{x} ≤ 1\)) have attracted significant attention and are considered to be the most promising candidates for high-capacity cathodes of next-generation LIBs.\(^14−19\) Despite some superiorities of these cathodes, several fatal inherent pitfalls still should be overcome to integrate them into commercial use, including the low initial Coulombic efficiency, poor rate capability, and discharge voltage fading. As a primary cause for these drawbacks, the structural instability during the cycling process gives rise to phase transformation from layered to spinel phase.\(^20−23\) Various strategies have been conducted on these Li-rich cathodes, such as structural design, ion doping, and surface coating. Also, considerable improvements have been achieved in reversible capacities and rate performances.\(^24,25\) The design of a hierarchical micro-/nanostructure is demonstrated to be effective to improve lithium storage properties.\(^26\) In addition, the rate capability can be significantly improved by the formation of a complex layered-spinel heterostructure because the three-dimensional (3D) Li\(^+\) diffusion channels provided by the spinel structure could greatly enhance the Li\(^+\) diffusion rate.\(^27\)

In the perspective of cost and raw materials, Fe−Mn metal-based systems would be economically attractive because of their high content of iron and manganese.\(^28−36\) However, as a newly
developing field, the electrochemical performances and stability issues of these systems limit their practical applications. Furthermore, the synthetic process of low-cost-based systems to form the ideal structure is highly complex, involving several intricate steps. The addition of Ni component can effectively improve the average voltage of Fe-containing Li$_2$MnO$_3$. Moreover, the substitution of Co by Fe can also help to mitigate the decrease in the average discharge voltage upon cycling, reported by Nayak et al. Therefore, Li-rich cathodes containing iron and nickel are promising low-cost candidates for commercial LiCoO$_2$. To exploit Li–Fe–Ni–Mn–O compounds with high performance, much efforts have been invested to improve the cycling stability, such as ion doping, surface modification, and stepwise precycling treatments. It is generally known that the morphology and internal crystal structure of the cathode materials play a critical role in Li$^+$ transport conductivity. The effective combination of hierarchical micro-/nanoarchitecture morphology with a well-designed "layered-spinel" integrated structure on these low-cost Li-rich cathodes is still absent. The hierarchical materials can take the merits of both nanomaterials and micromaterials in achieving a shorter Li$^+$ pathway and less superficial side effect. Furthermore, the Li$^+$ diffusion rate can be greatly enhanced owing to the 3D Li$^+$ diffusion channels provided by the spinel structure. Favorable kinetics and good electrochemical capability can be predicted from the hierarchical cathodes with the complex layered-spinel phase.

In this paper, the above well-designed structure was successfully applied on Li$_{1+x}$Fe$_{0.1}$Ni$_{0.15}$Mn$_{0.55}$O$_y$ (0 ≤ x ≤ 0.3 and 1.9 ≤ y ≤ 2.05) compounds without any following modification to achieve good electrochemical performances. The hierarchical micro-/nanoarchitecture morphology was realized by an energy-saving and labor-saving approach (the carbonate coprecipitation method). Scheme 1 shows an illustration for the synthetic process of Li–Fe–Ni–Mn–O compounds with hierarchical micro-/nanostructures. A layered-spinel heterostructure was directly formed through a rational control of the lithium content. The effect of the lithium content was explored on the structure evolution, morphological characteristics, and electrochemical performances of these compounds. An integral mechanism of structure and electrochemical evolution was illustrated to explain the performance scope of these hierarchical Li–Fe–Ni–Mn–O cathode materials.

2. RESULTS AND DISCUSSION

The structural information of the precursor and as-prepared compounds is displayed in Figure 1. The precursor shows a typical hexagonal structure with the space group of R3c, corresponding to MnCO$_3$ rhodochrosite. As for the lithiated compounds, normalized on the basis of the intensity of the (003) reflection, all the main diffraction peaks marked by their number can be indexed to a layered α-NaFeO$_2$-type structure (the space group of R3m). Additional peaks between 20° and 25° are considered as superlattice reflections of the Li$_2$MnO$_3$-like structure (the space group of C2/m). The enlarged graph
of the (003) reflection suggests that sample $x = 0.1$ achieves the highest intensity of the (003) peak. The enlarged graph of the (104) reflection indicates that the increasing lithium content leads to a continuous increase in the (104) d-spacing. In addition, the ratio of $I_{003}/I_{104}$ was calculated and given in Figure 1. The result shows that sample $x = 0.1$ presents the highest value (1.656), indicating the lowest cation disordering. As marked by the pink circles, the observed pores on the surface of the particles are related to the CO$_2$ escape during calcination, which can conduct to electrolyte percolation. However, the detailed morphologies of these lithiated compounds undergo changes with the increase of the lithium content. The average size of the primary grains increases from sample $x = 0$ to $x = 0.3$, indicating that the addition amount of lithium carbonate affects the growth of primary grains during calcination. Unfortunately, the primary particles are observed to be more adhesive to each other when the lithium content reaches higher ($x = 0.2, x = 0.3$), which is not beneficial to lithium diffusion and electrolyte percolation.

As shown in Figure S1, nitrogen adsorption experiments were carried out to examine the pore characteristics of the as-prepared materials. The Brunauer—Emmett—Teller (BET) specific surface area of sample $x = 0.1$ was measured to be the highest ($15.41$ m$^2$ g$^{-1}$) among all the samples. The pore size distribution of sample $x = 0.1$ calculated using the Barrett—Joyner—Halenda method is mainly around 23 nm. Good electrochemical performances of sample $x = 0.1$ are expected from its good hierarchical micro-/nanostructure, small primary grains, high specific surface area, and rational porosity for electrolyte percolation. The following results of electrochemical tests also verify this prediction. Moreover, sample $x = 0.1$ was examined by energy-dispersive X-ray spectroscopy (EDS) to further analyze the element distribution. As presented in Figure 2, except that the Li element cannot be detected by EDS, other elements of Fe, Ni, Mn, and O are all determined. In addition, the even dispersion of these elements in sample $x = 0.1$ is also demonstrated by the corresponding EDS mapping. Elements with uniform distribution have paved the way for good electrochemical performance of this lithiated compound.
Figure 3. (a) TEM image of sample $x = 0.1$, (b) SAED pattern of sample $x = 0.1$, (c) HRTEM image of the layered phase, and (d) HRTEM image of the spinel phase. XPS of (e) Fe 2p, (f) Ni 2p, and (g) Mn 2p on the surface of sample $x = 0.1$.

Figure 4. Charge/discharge curves at 0.1 C and the corresponding differential capacity versus voltage plots ($dQ/dV^{-1}$).
The binding energy of 854.9 eV in Ni 2p3/2 is in good agreement with the valence of Ni 2+ in layered Li1/3Ni2/3Mn2/3O2 compounds. As for Mn 2p3/2 spectra, the binding energy (642.4 eV) fits well with the typical value of Mn3+ ions in manganese-based layered compounds. Therefore, the surface predominant oxidation states of Fe, Ni, and Mn in sample $x = 0.1$ are believed to be +3, +2, and +4, respectively.

Table 1. Charge/Discharge Data of all the Samples at 0.1 C

| sample $x$ | first charge capacity (mA h g$^{-1}$) | first discharge capacity (mA h g$^{-1}$) | first Coulombic efficiency (%) | first irreversible capacity (mA h g$^{-1}$) | discharge capacity at 50th (mA h g$^{-1}$) | discharge capacity retention (%) |
|-----------|-------------------------------------|----------------------------------------|--------------------------------|------------------------------------------|----------------------------------------|---------------------------------|
| $x = 0$   | 312.1                               | 219.7                                  | 70.4                           | 92.4                                    | 168                                    | 76.5                            |
| $x = 0.1$ | 338.7                               | 254.3                                  | 75.1                           | 84.4                                    | 184.4                                  | 72.5                            |
| $x = 0.2$ | 296.6                               | 192.5                                  | 64.9                           | 104.1                                   | 165                                    | 85.7                            |
| $x = 0.3$ | 287                                 | 178.8                                  | 62.3                           | 108.2                                   | 130.5                                  | 73.0                            |

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) are utilized to illustrate the specific structure feature of the remarkable sample $x = 0.1$, and the results are displayed in Figure 3. Figure 3a explicitly exhibits a primary spherical particle with a diameter of 2–3 μm, which is in accordance with that observed in SEM images. The corresponding SAED pattern of the primary particle is shown in Figure 3b. A typical lithium/transition-metal cation ordering in the transition-metal layer with an array of hexagonal symmetry dots is presented to probe the formation of a well-layered structure of the Li-rich material. Meantime, the interplanar spacing of lattice fringe is measured to be 0.44 nm from the HRTEM image in Figure 3c, smaller than a typical value (0.47 nm) of other Li-rich materials without the Fe element, which is ascribed to the different atomic radii of transition metals. Furthermore, as shown in Figure 3d, a small amount of spinel phase can be observed on the edge of the particle between the layered fringes, resulting from the lithium diffusion process during calcination. All these features indicate the formation of a layered-spinel heterostructure in the synthetic process. The observed layered-spinel structure of sample $x = 0.1$ is also well consistent with the result of X-ray diffraction (XRD) pattern.

X-ray photoelectron spectroscopy (XPS) is carried out to confirm the surface chemical states of the component elements in the as-prepared material. Figure 3e–g displays the detailed XPS spectra of Fe 2p, Ni 2p, and Mn 2p on the surface of sample $x = 0.1$. The main peak of Fe 2p3/2 spectra exhibits a binding energy of 711.1 eV, which should be attributed to Fe3+. The binding energy of 854.9 eV in Ni 2p3/2 is in good agreement with the valence of Ni2+ in layered Li1/3Ni2/3Mn2/3O2 compounds. As for Mn 2p3/2 spectra, the binding energy (642.4 eV) fits well with the typical value of Mn3+ ions in manganese-based layered compounds. Therefore, the surface predominant oxidation states of Fe, Ni, and Mn in sample $x = 0.1$ are believed to be +3, +2, and +4, respectively.
Table 1 summarizes the detailed data of charge/discharge specific capacities and first Coulombic efficiency. Among all the samples, sample x = 0.1 delivers the highest first charge/discharge specific capacities (338.7 and 254.3 mA h g⁻¹) and the highest first Coulombic efficiency (75.1%). Also, the first irreversible capacity loss of sample x = 0.1 is 84.4 mA h g⁻¹, which is much lower than the other samples. After 50 cycles, the reversible discharge specific capacity of sample x = 0.1 achieves 184.4 mA h g⁻¹, which is also the highest among all the samples. Sample x = 0.2 shows the best cycle stability with a high-capacity retention of 85.7%, ascribed to its more stable layered structure, which is consistent with the result of structure analysis. In addition, the presence of LiOH phase detected from the XRD patterns in sample x = 0.3 should be responsible for the deterioration of the electrochemical capacities. Furthermore, the issue of discharge voltage fading is still present in all the samples, as observed from the comparison of discharge medium voltage in Figure 5b. The voltage fading phenomenon should be ascribed to the continuous structure transformation from layered to spinel phase, which is well consistent with the analysis of the differential capacity versus voltage plots in Figure 4. Serious voltage fading along cycling is observed in sample x = 0.3, which is related with the undesired impurity phase. Therefore, appropriate lithium content is beneficial for the cycling performance and the alleviation of voltage fading during cycling. Besides, the phenomenon of capacity fading is present in the first 10 cycles for all the samples. The crystallinity of our prepared low-cost Li-rich cathode material containing Fe is not so high as some other Li-rich cathodes without Fe element because of the lower calcination temperature (750 °C). However, experiments on optimizing calcination temperature show that the higher calcination temperature (900 °C) is not beneficial for the electrochemical performances, such as cycling stability and rate capability. In addition, the structure evolution with cycling and discharge voltage fading is also considered to be related with the capacity fading. The migration of transition-metal cations during cycling has also been reported to be responsible for the gradual capacity degradation and potential decay during the cycling of the Li-rich cathode material. To fix transition-metal cations in the parent layered structure, polyanion doping is believed to be effective to maintain the layered structure of the Li-rich cathode material. After considering multifactor comprehensive evaluation, sample x = 0.1 exhibits the best electrochemical performances at 0.1 C, including the high reversible specific capacity and low rate of discharge voltage fading.

Compared with other samples, sample x = 0.1 presents the best rate performance. The rate capability (Figure 6) from 0.5 to 5 C after activation at 0.1 C for three cycles highlights the advantages of its 3D hierarchical structure and complex layered-spinel structure. The charge/discharge curves at 30th and 60th cycles are also shown in the inset of Figure 6. The reversible specific capacities after 30 cycles of sample x = 0.1 are 157.2 mA h g⁻¹ for 0.5 C, 146.5 mA h g⁻¹ for 1 C, 140.8 mA h g⁻¹ for 2 C, and 116.7 mA h g⁻¹ for 5 C. The reversible specific capacities after 60 cycles of sample x = 0.1 are 144.8 mA h g⁻¹ for 0.5 C, 133.4 mA h g⁻¹ for 1 C, 129.9 mA h g⁻¹ for 2 C, and 109.2 mA h g⁻¹ for 5 C. The good rate capability of sample x = 0.1 is related to the fast kinetics of its hierarchical micro-/nanostructure. The 3D Li⁺ diffusion channel can be provided by the spinel phase formed during the synthetic process, thus speeding up the transport of lithium ions.

Figure 6. Rate capability of sample x = 0.1 and the corresponding charge/discharge curves at the 30th cycle and 60th cycle.

Figure 7a–c displays the cyclic voltammetry (CV) curves of the as-prepared samples in the voltage range of 2–4.8 V. Different samples show a similar tendency during the cycling process. During the first charge process, the anodic peak at ~4.0 V is predominantly related to the oxidation from Ni²⁺ to Ni⁴⁺. The anodic peak at 4.6–4.7 V is associated with the extraction of Li₂O from the Li₃MnO₃ component, which is accompanied by the irreversible electrochemical activation reaction. During the first discharge process, the cathodic peak at ~3.8 V is ascribed to the reduction from Ni⁴⁺ to Ni²⁺. The reduction from Mn⁴⁺ to Mn³⁺ is revealed by the cathodic peak at ~3.2 V, and its corresponding oxidation peak of Mn³⁺/Mn⁴⁺ begins to appear in the following two cycles. The absence of the anodic peak of Mn³⁺/Mn⁴⁺ in the first cycle indicates that Mn⁴⁺ in the as-prepared materials is electrochemically inactive. Therefore, the layered structure can be stabilized by the inactive Mn⁴⁺. In addition, the good overlaps of the profiles in the second and third cycles indicate the good electrochemical reversibility of sample x = 0.1.

Electrochemical impedance spectroscopy (EIS) can reveal the kinetics of electrochemical reactions of electrodes. Figure 7d shows the Nyquist plots at open-circuit potential to better understand the superior electrochemical performance of sample x = 0.1. The intercept of the semicircle at the highest frequency with the horizontal axis (Z'') stands for the uncompensated Ohmic resistance (R₀). The impedance spectrum comprises a high-frequency semicircle and a low-frequency slope, which are associated with the charge-transfer resistance (Rct) and Li⁺ diffusion into the bulk material (Warburg impedance, Zw), respectively. By comparing the size of the semicircles, it can be easily found that sample x = 0.1 presents the lowest value of R₀, indicating the best kinetics of electrochemical reactions and thus exhibiting superior rate capability. In addition, there is no significant increase of the Rct value in the EIS curve of sample x = 0.1 after 50 cycles at 0.1 C (Figure S2), indicating a good cycling stability of our prepared material. Differential capacity curves of sample x = 0.1 at different rates are depicted in Figure 7e–h. Phase transformation from layered to spinel phase during cycling can be clearly seen from these profiles. Obviously, the reduction peaks below 3.5 V gradually shift left with the increasing rates, indicating the discharge voltage fading. It is believed that the voltage fading is related with the degree of
polarization at high rate as well as the unexpected phase transformation from layered to spinel. Although voltage fading is observed, the redox of Mn$^{4+}$/Mn$^{3+}$ and Ni$^{4+}$/Ni$^{2+}$ can still be reversible at different rates. In brief, the superior rate capability of sample $x = 0.1$ is ascribed to the stable cycling of Mn$^{4+}$/Mn$^{3+}$ in the 3 V region and Ni$^{4+}$/Ni$^{2+}$ in the 4 V region.

Superior electrochemical performance of sample $x = 0.1$ is attributed to three aspects, as illustrated in Figure 8. First, the stable hierarchical micro-/nanostructure possesses the merits of both micro- and nanosized materials. At high voltage, the electrode polarization is mainly associated with the surficial side reactions between the electrode and the electrolyte. As for our designed hierarchical structure, less surficial side reaction and enough rational porosity for infiltrating liquid electrolyte play important roles in promoting lithium-ion transport and electron transfer. Second, the uniform element distribution probes that the rational cation arrangement can maintain the durability of the layered structure. Meantime, the compact secondary particles can maintain the stability of the hierarchical structure, which can be demonstrated by the SEM images of the electrode after 50 cycles at 0.1 C (Figure S3). The spinel phase generated on the surface of the particles cannot easily extend into the bulk region owing to the closely packed nanoparticles. Thus, the collapse rate of the layered structure can be slowed down, and voltage fading can be alleviated. Third, the harmonious coexistence of layered and spinel phases formed during synthetic control is also an important factor to contribute to the good rate capability. Notably, the spinel phase formed during the synthetic process can provide 3D channels for lithium-ion transport, which is quite different from the spinel-like phase derived from the structure transformation during the cycling process.

Figure 7. CV curves of (a) sample $x = 0$, (b) sample $x = 0.1$, and (c) sample $x = 0.2$ in the first three cycles. (d) Nyquist plots of the as-prepared samples before cycling. (e–h) Differential capacity versus voltage plots (dQ/dV$^{-1}$) of sample $x = 0.1$ at different rates during cycling.
3. CONCLUSIONS

The 3D Li-rich Li$_{1+x}$Fe$_{0.1}$Ni$_{0.15}$Mn$_{0.55}$O$_y$ (0 ≤ x ≤ 0.3 and 1.9 ≤ y ≤ 2.05) cathode materials with a hierarchical micro-/nanostructure have been successfully synthesized through the carbonate coprecipitation method. By optimizing the lithium content, Li$_{1.1}$Fe$_{0.1}$Ni$_{0.15}$Mn$_{0.55}$O$_{1.95}$ with the complex layered-spinel phase delivers high reversible capacity, superior rate capability, and decent suppression of voltage decay. Such superior electrochemical performances benefit from the stable structural and morphological characteristics. The hierarchical micro-/nanostructure takes the advantages of both nano- and microparticles. Uniform element distribution and compact secondary particles with rational porosity can maintain the structural stability and alleviate voltage fading. The complex layered-spinel phase provides a 3D channel for lithium-ion transport and speeds up the electronic transmission, which is beneficial for the good rate capability. In addition, the structure evolution from layered to spinel during synthetic control and cycling process is analyzed emphatically to further interpret the corresponding electrochemical performances. From the view of low cost and environmental friendliness, the hierarchical Li–Fe–Ni–Mn–O compounds with improved electrochemical performances will further become promising cathode materials of LIBs.

4. EXPERIMENTAL SECTION

4.1. Materials Synthesis. The spherical cathode materials were prepared using a carbonate coprecipitation technology, followed by heat treatment. Nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O), manganese sulfate monohydrate (MnSO$_4$·H$_2$O), iron sulfate heptahydrate (FeSO$_4$·7H$_2$O), sodium carbonate (Na$_2$CO$_3$), and ammonium hydroxide (NH$_3$·H$_2$O) were used as starting reagents to prepare the spherical precursor particles. During the reaction, a 2 mol L$^{-1}$ mixed transition-metal solution (Fe/Ni/Mn = 0.1:0.15:0.55) was slowly pumped into a continuously stirred tank reactor at a flow rate of 1 L h$^{-1}$ under a N$_2$ atmosphere. Simultaneously, a 2 mol L$^{-1}$ Na$_2$CO$_3$ solution as a precipitant and a 0.2 mol L$^{-1}$ NH$_3$·H$_2$O solution as a chelating agent were also fed into the reactor to maintain pH inside the reactor at 8.0. The operating temperature (50 °C) and the stirring speed (1000 rpm) of the mixture in the reactor were strictly controlled. The precipitated precursor particles were filtered, washed with deionized water several times, and dried at 120 °C overnight. Afterward, the obtained carbonate precursors were thoroughly mixed with appropriate amounts of lithium carbonate (Li$_2$CO$_3$) by grinding. After that, the mixtures were calcined at 750 °C for 15 h in air and then cooled down to room temperature to form Li$_{1+x}$Fe$_{0.1}$Ni$_{0.15}$Mn$_{0.55}$O$_y$ (x = 0, 0.1, 0.2, and 0.3) cathode materials. To compensate for the possible lithium loss during the high-temperature calcination, a 2% excess of lithium carbonate was used.

4.2. Materials Characterizations. The crystalline phases were identified with XRD (Rigaku Ultima IV-185) using a Cu Kα radiation source. The source tension and current were 40 kV and 40 mA, respectively. Data were acquired with a scanning rate of 2° min$^{-1}$ in the scattering angle (2θ) range of 10°–80°. The particle size, morphology, and element mappings of the prepared powders were observed using a field-emission scanning electron microscopy (FEI, Quanta 200f) with an EDS. The crystal orientation was detected with a TEM (JEM-2100f). The surface chemical state of the as-prepared sample was investigated by XPS (PHI Quantera). The specific surface area

Figure 8. Schematic diagram for superior electrochemical performance.
was measured by the BET method. The nitrogen adsorption measurements were performed on an Autosorb iQ analyzer.

4.3. Electrochemical Measurements. To fabricate the positive electrodes, the as-prepared materials were mixed with acetylene black and polyvinylidene fluoride (8:1:1 by weight) in N-methyl-2-pyrrolidone. The obtained slurry was then cast onto an aluminum foil using a doctor blade and dried overnight at 80 °C in a vacuum oven. The foil coated by the materials was punched out to be circular electrodes with 1.4 cm in diameter and then roll-pressed before use. The electrode loadings were maintained at ~3.0 mg cm⁻². For electrochemical tests, the electrode was assembled into R2025 coin-type cells in an argon-filled glovebox using Li metal as the anode. The electrolyte solution was 1 mol L⁻¹ LiPF₆ in an ethylene carbonate/dimethyl carbonate mixture (1:1 ratio by volume). A Celgard 2400 membrane was used as the separator. The galvanostatic charge/discharge tests were performed using a Land battery test system (Land CT2001A, Wuhan, China) at different current densities from 20 mA g⁻¹ (0.1 C) to 1000 mA g⁻¹ (5 C) in a voltage range of 2–4.8 V (vs. Li⁺/Li). The constant current charge step at 0.1 C was followed by an additional constant voltage charge step until the current density dropped to half of its initial value. The CV experiment was carried out at a scan rate of 0.1 mV s⁻¹ in the range of 2–4.8 V using the CHI660C electrochemical workstation (Chenhua, China). The EIS measurement was carried out using an IM6 electrochemical impedance analyzer with an ac perturbation signal of 5 mV in the frequency range of 10⁵ to 0.01 Hz.

ASSOCIATED CONTENT

Supporting Information
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Notes
The authors declare no competing financial interest.

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Notes

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