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Abstract

Ternary transition metal oxides (TMOs) have attracted considerable attention for rechargeable batteries because of their fascinating properties. However, the unsatisfactory electrochemical performance originating from the poor intrinsic electronic conductivity and inferior structural stability impedes their practical applications. Here, the novel hierarchical porous NiO/ β -NiMoO₄ heterostructure is fabricated, and exhibits high reversible capacity, superior rate capability, and excellent cycling stability in Li-ion batteries (LIBs), which is much better than the corresponding single-phase NiMoO₄ and NiO materials. The significantly enhanced electrochemical properties can be attributed to its superior structural characteristics, including the large surface area, abundant pores, fast charge transfer, and catalytic effect of the intermediate product of metallic nickel. The NiO/ β -NiMoO₄ heterostructure delivers a high capacity of 1314 mAh g⁻¹ at 0.2 A g⁻¹ after 100 cycles. Furthermore, even after 400 cycles at 1 A g⁻¹, the reversible capacity remains at around 500 mAh g⁻¹. These results indicate that the NiO/ β -NiMoO₄ heterostructure shows great potential as an anode material for high-performance LIBs.

Keywords

superior, heterostructure, nio/b-nimoo₄, porous, lithium, hierarchical, material, anode, storage

Disciplines

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Hierarchical Porous NiO/ β -NiMoO₄ Heterostructure as Superior Anode Material for Lithium Storage

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Ternary transition metal oxides (TMOs) have attracted considerable attention for rechargeable batteries because of their fascinating properties. However, the unsatisfactory electrochemical performance originating from the poor intrinsic electronic conductivity and inferior structural stability impedes their practical applications. Here, the novel hierarchical porous NiO/ β -NiMoO₄ heterostructure is fabricated, and exhibits high reversible capacity, superior rate capability, and excellent cycling stability in Li-ion batteries (LIBs), which is much better than the corresponding single-phase NiMoO₄ and NiO materials. The significantly enhanced electrochemical properties can be attributed to its superior structural characteristics, including the large surface area, abundant pores, fast charge transfer, and catalytic effect of the intermediate product of metallic nickel. The NiO/ β -NiMoO₄ heterostructure delivers a high capacity of 1314 mA h g⁻¹ at 0.2 A g⁻¹ after 100 cycles. Furthermore, even after 400 cycles at 1 A g⁻¹, the reversible capacity remains at around 500 mA h g⁻¹. These results indicate that the NiO/ β -NiMoO₄ heterostructure shows great potential as an anode material for high-performance LIBs.

Introduction

High-performance rechargeable Li-ion batteries (LIBs) are gradually becoming indispensable units in portable commercialized electronics, electric vehicles, and renewable energy storage systems.^[1,2] Nevertheless, the conventional LIBs based on the prevailing carbon-based intercalation materials are already reaching their energy capacity limits. Hence, tremendous efforts have been devoted to exploring novel anode materials with higher energy densities, sustainable lifespans, cost-effec-

tiveness, and safe working potentials, to make these materials applicable for the advanced LIBs required to meet the ever-growing demands for electrical applications.^[3–5]

Ternary transition metal oxides (TMOs) are emerging as promising candidate electrode materials for high-energy LIBs owing to their distinctive properties.^[6,7] It has been widely demonstrated that TMOs generally exhibit superior reversible capacity, good structural stability, and high electronic conductivity. Specifically, the synergetic effects associated with their complex chemical compositions typically contribute to remarkable electrochemical activities and high specific capacities, and the multiple valences of the cations are beneficial for achieving more versatile redox reactions.^[8,9] More importantly, because of the lower activation energy for electron transfer between different cations, they normally possess higher electrical conductivities than their corresponding binary metal oxide counterparts.^[10] Among various potential TMOs, spinel-structure nickel molybdate (NiMoO₄) has been regarded as an attractive material in view of its high theoretical capacity (about 984 mA h g⁻¹), good electrical conductivity, environmental friendliness, and low cost.^[11,12] At atmospheric pressure, there are two phases of NiMoO₄ both with a monoclinic structure: α -NiMoO₄ (low-temperature stable phase) and β -NiMoO₄ (high-temperature stable phase). The most striking difference between those two polymorphs is the coordination of the Mo⁶⁺ ions, with pseudo-octahedral coordination in the α -NiMoO₄ phase and distorted tetrahedral coordination in the β -NiMoO₄ phase.^[13] Generally, β -NiMoO₄ has a higher intrinsic conductivity and reactivity than α -NiMoO₄,^[14] but it is very difficult to prepare and maintain. In addition, NiMoO₄ electrode materials suffer from some drawbacks such as the huge volume change and low electrochemical reversibility, leading to inferior elec-

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trochemical performance.^[15,16] Therefore, the rational design and facile synthesis of β -NiMoO₄ materials for high-energy LIBs remains a significant challenge.

Constructing heterostructures by combining active materials with metal oxides or sulfides has proven to be an effective way to conquer the abovementioned obstacles.^[17,18] It is believed that such constructed heterostructures usually enable abundant electrochemical active sites, short ion diffusion paths, and good structural stability originating from the synergistic effect of different components, and therefore exhibit better electrochemical performances.^[19] For example, Yuan et al. developed hierarchical mesoporous ZnO/ZnFe₂O₄ sub-microcubes, which exhibited better electrochemical Li-storage properties than the single-phase ZnFe₂O₄, owing to the striking synergistic effect between the bicomponent active, well-dispersed ZnO and ZFO phases at the nanoscale.^[20] Mai et al. found that hierarchical MnMoO₄/CoMoO₄ heterostructured nanowires showed enhanced specific capacitance and reversibility compared with the MnMoO₄ and CoMoO₄ electrodes.^[21] Similarly, other hybrid heterostructures such as ZnCo₂O₄/NiO core/shell nanowires,^[22] NiO-Co₃O₄ nanoplates,^[23] CoO/CoFe₂O₄ nanocomposites,^[24] and CoMoO₄/Co₃O₄ composites^[25] have been employed as LIB electrodes and demonstrated improved reversible capacity and cycling performance.

Besides the favorable components, the structure also plays an important role in determining the electrochemical properties of the developed electrode materials. It is considered that the hierarchical architectures constructed from 2D building blocks possess superior structural characteristics with large specific surface areas, more accessible pores, and high structural stabilities, making them promising candidates for energy-related applications.^[26] Undoubtedly, the large specific surface would provide rich Li-storage active sites, and the generated numerous pores may offer additional space to accommodate the volume expansion, consequently maintaining the structural stability and electrode integrity. Lou et al. synthesized the hierarchical tubular structure of Co-Mn mixed metal oxides, manifesting excellent electrochemical properties upon employment as electrodes in Li-ion batteries and hybrid supercapacitors.^[27] A hierarchical fascicular structure of Zn₂GeO₄ anode obtained through a wet chemistry method also exhibited remarkable Li-ion storage performance, as the hierarchical structure could alleviate the volume changes and retain the whole configuration, and the small building units enlarged the electrode/electrolyte contact area and constructed an integrated interlaced conductive network.^[28]

Herein, we have designed and constructed a novel hierarchical porous NiO/ β -NiMoO₄ (NNMO) heterostructure through a facile hydrothermal technique followed by a calcination process. Interestingly, the NiO phases in the NNMO heterostructure could be regarded as a multifunctional layer, which can not only contribute to the high theoretical capacity, but also function as a mechanical buffer to alleviate the huge volume changes in the NiMoO₄ matrix, thus offering high capacity and good structural stability. Furthermore, the generated metallic nickel (Ni) nanoparticles from the lithiation reaction of NiO nanosheets with Li are able to promote the reversible decom-

position of Li₂O during the delithiation process, leading to a high initial Coulombic efficiency and enhanced reversible capacity of the NiMoO₄. In addition, the abundant pores produced from the surface interconnected nanosheets and the self-assembled microspheres with hierarchical structure provide more space to relieve the induced stress during the lithiation/delithiation processes and preserve the structural integrity. As expected, the as-prepared NiO/ β -NiMoO₄ heterostructured anode exhibited much better electrochemical Li storage properties than its single-phase NiO or NiMoO₄ counterparts. Such a significantly enhanced electrochemical performance can be attributed to its superior structural characteristics achieved by rational structure engineering of the electrode.

Results and Discussion

The synthesis of the hierarchical porous NiO/ β -NiMoO₄ (NNMO) heterostructure through a novel and facile strategy is illustrated in Scheme 1. First, appropriate proportions of Ni²⁺ and MoO₄²⁻ precursors were mixed homogeneously into deionized water under magnetic stirring for a certain time, so that the acetate could be adsorbed on the surface of MoO₄²⁻ by electrostatic interaction, and subsequently, the NNMO was obtained by oxidation of the as-prepared precursor mixture at 550 °C under an oxygen atmosphere. For further comparison, single-phase NiO (NO) and NiMoO₄ (NMO) were also fabricated through similar processes, but with different precursors chosen.

Scheme 1. Schematic illustration of the novel hierarchical porous NiO/ β -NiMoO₄ (NNMO) heterostructure prepared through a facile hydrothermal method followed by a calcination process.

The purity and crystal structure of the fabricated samples were analyzed by powder X-ray diffraction (XRD). The XRD patterns in Figure 1a confirm that the as-prepared NNMO materials are composed of pure β -phase NiMoO₄ (JCPDS Card No. 12-0348) and cubic bunsenite NiO (JCPDS Card No. 47-1049), indicating the coexistence of pure β -NiMoO₄ and NiO phases in the obtained NNMO composite. Furthermore, the formation of the cubic NiO phase in the hybrid heterostructure is revealed by the diffraction peaks centered at 37.25°, 43.28°, and 62.89°, corresponding to the (111), (200), and (220) crystal planes, respectively. The remarkable diffraction peak at the value of 26.65° can be indexed to the characteristic (220) planes of β -NiMoO₄, suggesting the high purity of the β -phase NiMoO₄,

Figure 1. a) General XRD pattern of as-prepared NNMO; b) N₂ adsorption/desorption isotherms (inset: comparison of the specific surface areas of NO, NMO, and NNMO); and c) pore-size distributions of the three samples.

without any trace/residual of the α -phase.^[29] As shown in Figure S1a (Supporting Information), the diffraction patterns of the prepared single-phase NO are well matched with those of pure NiO (JCPDS Card No. 47-1049), whereas all the diffraction peaks in Figure S1b (Supporting Information) can be assigned to the pure monoclinic α -NiMoO₄ (JCPDS Card No. 33-0948). Notably, no diffraction peaks can be indexed to β -phase NiMoO₄.

N₂ adsorption/desorption measurements were performed to analyze the physical properties of the obtained samples (Figure 1b,c). As presented in Figure 1b, the isotherm curves of all three samples show distinct type IV adsorption isotherms with H1-type hysteresis loops within a relative pressure P/P_0 range from 0.05 to 0.95 in the desorption isotherm, implying the existence of numerous pores. On the basis of the BET method analysis, it was found that the NNMO has a much larger specific surface area of 23.20 m²g⁻¹, with a total pore volume of 2.4 cm³g⁻¹, compared with the single-phase NO (10.45 m²g⁻¹) and NMO (18.40 m²g⁻¹) (inset in Figure 1b). Accordingly, the BJH pore-size distribution profiles derived from the adsorption branches of the isotherms were also calculated and are shown in Figure 1c. The pore-size distribution curves for NNMO reveal that most of the pores range between 20 and 50 nm, markedly confirming the existence of a kind of mesoporous nanostructure. In addition, the narrow pore-size distributions of NO and NMO show that the numerous pores are mainly macropores. Impressively, the unique structural features, including the high specific surface area and abundant porous structure of the NNMO heterostructure, will not only provide many electroactive sites, a large electrode/electrolyte contact area, and easy electrolyte access, but will also accommodate the huge volume changes of the electrode during repeated lithiation/delithiation processes,^[8,30,31] thus making it extremely beneficial for high-rate performance and long cycle stability for Li-ion storage.

The chemical states and elemental composition of the as-synthesized sample were further characterized by X-ray photoelectron spectroscopy (XPS). As displayed in Figure 2a, the whole survey scan of the NNMO primarily demonstrates the presence of the elements Ni, Mo, and O. The high-resolution spectrum of Ni2p (Figure 2b) can be deconvoluted into two

main peaks by using the Gaussian fitting method, with the binding energies centered at 855.9 and 873.8 eV, corresponding to two spin-orbit doublets (Ni2p_{3/2} and Ni2p_{1/2}) and two weak shake-up satellite peaks of nickel located at 861.5 and 880.1 eV, respectively.^[32,33] The spin-energy separation of 17.9 eV is characteristic of the presence of Ni²⁺.^[34] On the other hand, the binding energies of Mo3d_{5/2} and Mo3d_{3/2} (Figure 2c) are located at 232.0 and 235.1 eV, respectively. The binding energies and energy separation (3.1 eV) are characteristics of the Mo⁶⁺ oxidation state in NiMoO₄.^[35] Figure 2d clearly shows the high-resolution spectrum in the O1s region, which consists of a main peak located at 531.7 eV coupled with a shoulder at 532.7 eV. Therefore, the XPS results indicate the presence of both β -NiMoO₄ and NiO in the composite, which is consistent with the XRD result (Figure 1a).

The detailed morphology and microstructure of the as-prepared hierarchical porous NiO/ β -NiMoO₄ heterostructure were investigated by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Figure 3a and b show representative SEM images of the NNMO at low and high magnification, respectively. It can be seen that the NNMO shows typical hierarchical porous microspheres, constructed from a large number of nanosheets with a thickness of 10–20 nm. Moreover, close observation reveals that there are numerous nanopores generated on the nanosheets (Figure 3b) and the assembled nanosheets also form abundant large pores, which is also consistent with the BET results. The TEM images further confirm the hierarchical porous structure of the NNMO sample (Figure 3c,d). The pores could promote electrolyte access to the interior portion of the material and offer enough additional space to accommodate the volume changes of the electrodes, thus improving electrochemical performance for Li-ion storage. Furthermore, the marked interplanar distances in the high-resolution TEM image are 0.336 and 0.241 nm (Figure 3e), corresponding to the (220) and (111) lattice planes of β -NiMoO₄ and NiO, respectively, certifying the presence of the two phases in the composite. More interestingly, the β -NiMoO₄ and NiO nanosheets are in tight contact with each other and form the heterostructure, which may promote rapid ion/electron transfer.^[18] In addition, the introduced NiO phase could function as the buffer layer to accommodate

Figure 2. a) XPS survey spectrum, b) high-resolution Ni2p spectrum, c) Mo3d spectrum, and d) O 1s region of the obtained NNMO material.

Figure 3. a,b) Representative SEM images at different magnifications of NNMO; c–e) TEM and HRTEM images of as-prepared NNMO; f) SAED pattern; and g–j) corresponding EDS elemental mapping images of the NNMO material.

the volume expansion and effectively maintain the structural integrity and stability. In the selected area electron diffraction (SAED) pattern of the NNMO (Figure 3 f), the diffraction rings can be assigned to the (111), (200), (220), and (222) planes of the NiO phase, as well as to the (220) planes of β -NiMoO₄, respectively, which also indicates the coexistence of the two phases in the NNMO composite. This novel architecture and its composition were further researched by the corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping images (Figure 3 g–j), which confirm the presence of Ni, Mo, and O elements in the NNMO. Moreover, the Ni, Mo, and O elements are distributed homogeneously in the entire microsphere, indicating the intimate contact between the two components and the formation of heterostructures. On the contrary, the SEM images of the NO (Figure S2 a,b in the Supporting Information) show networks constructed from many disor-

dered and aggregated rods. The length of the rods is between one and tens of micrometers. Figure S2 c,d further reveals the general microsphere architecture of α -phase NiMoO₄ with average diameters of several micrometers. Although the morphologies of α -phase and β -phase NiMoO₄ are quite similar, without the introduced NiO phase, the nanosheets of the NMO microsphere aggregate severely, resulting in fewer pores and inferior structural stability.

For further investigation of the electrochemical behavior of the synthesized materials for Li-ion batteries, cyclic voltammetry (CV) measurements were conducted. Figure 4 a shows the first five consecutive CV curves of the NNMO electrode recorded at a scan rate of 0.1 mV s⁻¹ in the potential range 0.01–3.00 V versus Li/Li⁺. It is evident that from the second to the fifth cycles, these CV profiles overlap well, implying good reversibility and cycling stability of the NNMO electrode during

Figure 4. Electrochemical evaluation of NNMO, showing: a) cyclic voltammograms for the first five cycles from 0.01 to 3.00 V; b) galvanostatic charge/discharge voltage profiles versus capacity of NNMO electrode for selected cycles at a current rate of 0.2 A g⁻¹; c) cycling performances of the obtained NO, NMO, and NNMO electrodes at 0.2 A g⁻¹ and Coulombic efficiency of the NNMO electrode at 0.2 A g⁻¹; d) rate performances of the three electrodes at varying current rates of 0.2, 0.5, 1, 2, 5, and 0.2 A g⁻¹; and e) long-term cycling performance at 1 A g⁻¹ of the obtained NNMO electrode and the corresponding Coulombic efficiency.

electrochemical reactions. In the first cycle, two intense reduction peaks in the cathodic scan occur at around 0.59 and 0.42 V, corresponding to the initial reduction of β -NiMoO₄ to Ni and Mo ($\text{NiMoO}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow \text{Ni} + \text{Mo} + 4\text{Li}_2\text{O}$) and NiO to Ni ($\text{NiO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Ni} + \text{Li}_2\text{O}$), combined with the formation of amorphous Li₂O and SEI layers.^[16,36,37] Meanwhile, the broad peaks in the voltage range from 1.4 to 1.8 V can be ascribed to the oxidation process of Mo to Mo⁶⁺ ($\text{Mo} + 3\text{Li}_2\text{O} \rightarrow \text{MoO}_3 + 6\text{Li}^+ + 6\text{e}^-$),^[38] whereas the oxidation of metallic Ni to NiO_x contributes to the anodic peak located at approximately 1.83 V.^[39] In subsequent cycles, the different reduction/oxidation peak pairs of 0.75/1.45 V and 1.42/1.79 V are reversible because of the Li insertion/extraction process with MoO₃.^[39,40] Notably, an anodic peak near 2.25 V is observed in the NNMO electrode, owing to the conversion reaction of Ni to NiO ($\text{Ni} + \text{Li}_2\text{O} \rightarrow \text{NiO} + 2\text{Li}^+ + 2\text{e}^-$).^[36] On the other hand, the CV curves of NO and NMO electrodes show different behavior from that of the NNMO electrode. In the first cathodic process of the NO electrode, two sharp peaks are observed clearly at 0.437 and 0.398 V, respectively, attributed to the reduction reactions of NiO and the formation of amorphous Li₂O, as well as a partially irreversible SEI layer. The oxidation of metallic Ni to NiO contributes to the anodic peak located at approximately 2.26 V, whereas the anodic peaks located at about 1.805 V are attributed to the formation of Mo (Figure S3 in the Supporting Information).

Figure 4b shows the typical galvanostatic discharge/charge voltage profiles of the NNMO anode from 0.01 to 3.0 V at a current density of 0.2 Ag⁻¹. In the first cycle, the NNMO electrode delivered an initial discharge capacity of 1538 mAh g⁻¹ and charge capacity of 1282 mAh g⁻¹, corresponding to an initial Coulombic efficiency (ICE) of 83%, which is higher than those of the NO (80%) and NMO electrodes (78%) (Figure S4 in the Supporting Information), demonstrating the high reversibility and good stability of the NNMO electrode during the electrochemical reactions. The higher reversible capacity of the NNMO can be explained by the further delithiation reaction observed above 2.0 V (Figure 4a), which is attributed to the catalytic behavior of the metallic nickel nanocrystals and its unique porous hierarchical structure that can shorten ion diffusion pathways.^[41] Furthermore, the NNMO anode exhibited excellent cycling stability. As shown in Figure 4c, the NNMO electrode delivered an initial reversible capacity of 1282 mAh g⁻¹, which then increased gradually to 1314 mAh g⁻¹, with a Coulombic efficiency of nearly 100% after 100 cycles. The feature of increased capacity after the initial cycle is not surprising for a metal-oxide-based material, as it is always ascribed to the reversible growth of polymeric gel-like layers and capacitive interface storage including electric double layer capacitance, as well as an activation process in the nanostructures.^[37] On the contrary, rapid capacity fading and inferior capacity retention are clearly observed in the NO and NMO materials. The high electrochemical reversibility and good cycling stability of the NNMO material may be attributed to the following factors: 1) the Ni nanocrystals generated in situ from the NiO phase could function as a direct catalyst for the reversible decomposition of intermediate Li₂O and the oxidation of metallic Ni and

Mo from β -NiMoO₄; 2) the NiO nanosheets can act as a mechanical buffer to stabilize the NiMoO₄ phase effectively, thus reducing the self-agglomeration of NiMoO₄ nanosheets and maintaining good structural stability; 3) the unique hierarchical porous architecture constructed from the small nanosheets will provide more active sites for Li⁺ storage, short ion diffusion pathways, and abundant additional space to release the internal stress induced by volume changes during the discharge/charge process.

Additionally, the NNMO electrode also exhibited a remarkable rate capability at different current densities. As seen from Figure 4d, the NNMO electrode is capable of delivering specific capacities of 1360, 1003, 631, 469, and 308 mAh g⁻¹ at current densities of 0.2, 0.5, 1.0, 3.0, and 5.0 Ag⁻¹, respectively. More importantly, the capacity can recover to the initial value (about 1339 mAh g⁻¹) upon returning the current rate back to 0.2 Ag⁻¹ after 60 cycles, indicating the excellent rate capability and good reversibility of the NNMO electrode. On the contrary, both the NO and the NMO electrodes show far inferior capacity retention and severe capacity decay between current densities of 1 and 5 Ag⁻¹. The excellent rate capability can be attributed to the synergistic effects of the binary composition and the short lithium diffusion distance in the porous hierarchical NNMO heterostructure. The long cycling performance is also an important parameter for batteries in practical applications. Hence, we further examined the long-term cycling property of the NNMO electrode at a high current density of 1 Ag⁻¹ (Figure 4e). After 400 cycles, the NNMO anode still retained a high reversible capacity of around 500 mAh g⁻¹, and the average Coulombic efficiency was close to 100%. More importantly, the NNMO electrode can maintain its hierarchical porous structure after long-term cycling, demonstrating its good structural stability. The superior structural characteristics, such as the 2D building blocks, large surface area, and abundant pores enable its good structural integrity (Figure S5 in the Supporting Information).

To reveal the boosted charge-transfer behavior in the NNMO heterostructure, we also investigated the kinetic differences of lithium ion diffusion in these anodes. As shown in Figure 5a,b, the NNMO sample exhibits larger peak intensities and smaller polarization at all scan rates, indicating the greatly enhanced electrochemical kinetics in the NNMO electrode, which are favorable for achieving better rate capability. Furthermore, the significantly promoted charge-transfer process in the NNMO heterostructure can also be proved by the higher diffusion coefficient of Li⁺ compared with that of the NMO sample (Figure 5c). Meanwhile, EIS measurements were conducted to research the kinetic differences between various electrodes (Figure S6 in the Supporting Information). Note that the diameter of the semicircle in the high-to-medium-frequency region for the NNMO electrode is much smaller than those for the NMO and NO electrodes, demonstrating the highly improved electron/ion transport dynamic in the heterostructure of the NNMO sample.^[42,43]

Figure 5. CV curves at different scan rates for LIB cells with a) NNMO and b) NMO materials, and c) the linear relationship between the peak current (i_p) and the square root of the scan rate ($\bar{v}^{1/2}$) for NNMO electrode.

Conclusion

In summary, we have developed a facile strategy for the synthesis of a novel hierarchical porous NiO/ β -NiMoO₄ heterostructure constructed from small nanosheets, featuring a large surface area, short ion-diffusion paths, and good structural stability. By means of synergistically active ternary metal oxides, boosted charge-transfer dynamics, and enhanced electrochemical reversibility, the NNMO heterostructure achieved a high reversible capacity, good rate capability, and superior long-term cyclability for Li-ion batteries. Our material design strategy presented here could be a promising approach for the design of novel heterostructure nanomaterials for high-performance rechargeable batteries.

Experimental Section

Synthesis of hierarchical porous NiO/ β -NiMoO₄ heterostructure

In a typical synthesis process, nickel acetate tetrahydrate (2 mmol, 0.4978 g) and sodium molybdate dehydrate (1 mmol, 0.3629 g) with a Ni/Mo molar ratio of 2:1 were slowly added into deionized water (30 mL) under magnetic stirring for 30 min to form a transparent solution. The resultant solution was then transferred to a 50 mL Teflon-lined autoclave, and was kept in an oven at 180 °C for 12 h. After the hydrothermal reaction, the obtained green product was separated by centrifugation and washed several times with deionized water and ethanol. The resultant composite was then dried at 80 °C overnight, followed by heating in a tube furnace under an

oxygen atmosphere at 550 °C for 2 h with a ramp rate of 2 °C min⁻¹, yielding the hierarchical NNMO electrode with a Ni/Mo ratio of 2.3:1, as determined by inductively coupled plasma (ICP) (Table S1 in the Supporting Information).

Synthesis of single-phase NiO (NO) material

The synthesis process was similar to that for NNMO. First, nickel chloride hexahydrate (1.2 mmol, 0.2852 g), urea (3 mmol, 0.1802 g), and cetyltrimethyl ammonium bromide (CTAB, 0.33 mmol, 0.12 g) were added into deionized water (30 mL) under magnetic stirring for 30 min to form a transparent solution. Then, the above solution was transferred to a 50 mL Teflon-lined autoclave and kept in an oven at 180 °C for 12 h. The obtained slurry was centrifuged, washed with deionized water, and then dried at 80 °C for 24 h. After thermal oxidation at 550 °C for 2 h with a ramp rate of 2 °C min⁻¹, the single-phase NiO material was obtained.

Synthesis of single-phase α -NiMoO₄ (NMO) material

In a typical procedure, nickel chloride hexahydrate (1.3 mmol, 0.3090 g) and sodium molybdate dehydrate (1.3 mmol, 0.3527 g) with a Ni/Mo molar ratio of 1:1 were added into a given amount (30 mL) of distilled water. The resulting solution was then transferred into a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. After cooling to room temperature, the slurry was washed several times with deionized water and dried at 80 °C for 24 h in an oven. Finally, the dried material, which had a green color, was thermally treated at 550 °C for 2 h in a tube furnace under an oxygen atmosphere to yield the α -NiMoO₄.

Material characterization

The crystalline structure of the materials was investigated by X-ray diffraction (XRD, Bruker AXS, D8 diffractometer) with $\text{CuK}\alpha$ radiation at a scanning rate of 1° min^{-1} . The morphology and energy dispersive spectroscopy (EDS) mapping of the as-prepared products were observed by scanning electron microscopy (SEM; JEOL JSM, 6510 V), and the details of the crystal structure were further examined by transmission electron microscopy (TEM; FEI TF20). X-ray photoelectron spectroscopy (XPS) was then conducted on an ESCALAB 250XI photoelectron spectrometer using monochromatic $\text{AlK}\alpha$ radiation under vacuum at 2×10^{-6} Pa. All of the binding energies are referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The actual contents of Ni and Mo elements were measured by inductively coupled plasma (ICP) emission spectroscopy using a PerkinElmer Optimal 8000 instrument (detection limit: 0.01 ppm for Ni, 0.01 ppm for Mo). Specific surface areas and pore-size distributions were also obtained from N_2 adsorption/desorption isotherms recorded at 77 K with a Micromeritics ASAP 2020 porosimeter. Prior to surface area measurements, the samples were dried under vacuum at 393 K for 8 h. The surface area was computed using the Brunauer–Emmett–Teller (BET) method, and the pore-size distribution was calculated in accordance with the Barrett–Joyner–Halenda (BJH) method.

Electrochemical measurements

Electrochemical tests were conducted on CR2025 coin-type cells, which were assembled in an Ar-filled glovebox. The working electrodes were prepared by mixing the active materials, Super P, and Na-carboxymethyl cellulose (CMC) in the weight ratio 60:30:10. The mixture was then pasted on Cu foil, dried at 80°C for 12 h in a vacuum oven, and pressed at 300 kg cm^{-2} . The mass loading of the materials on individual electrodes was approximately 1.15 mg cm^{-2} . Electrochemical measurements were performed using two-electrode coin cells with Li metal as the counter and reference electrode and Celgard (product 2300) film as the separator. The electrolyte consisted of a solution of 1 M LiPF_6 in ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1:1:1, v/v/v). Electrochemical impedance spectroscopy and cyclic voltammetry were conducted on a CHI 660E electrochemical workstation at different scan rates. The cells were galvanostatically charged/discharged in the voltage range 0.01–3.00 V versus Li/Li^+ at different current densities on a Land CT2001A battery tester.

The Li-ion diffusion coefficient (D_{Li^+}) was calculated on the basis of the Randles–Sevcik Equation (described previously^[3]), as given in Equation (1), in which i_p is the peak current (A), n is the number of transferred electrons, D_{Li^+} is the diffusion coefficient of Li ions ($\text{cm}^2 \text{ s}^{-1}$), S is the electrode surface area ($S = 70.85 \text{ cm}^2$), C is the concentration of Li^+ in the electrolyte, and $\bar{\nu}$ is the potential scan rate (V s^{-1}).

$$i_p = (2.69 \times 10^5) n^{3/2} S D^{1/2} C \bar{\nu}^{1/2} \quad (1)$$

As the electrodes were prepared and tested by the same procedure, the Randles–Sevcik equation could be simplified further, as given in Equation (2), in which A is supposed to be a constant and $AD^{1/2}$ is defined as the apparent diffusion coefficient of Li^+ in the coin cells, which can be calculated by fitting the linear curves.

$$i_p = AD^{1/2} \bar{\nu}^{1/2} \quad (2)$$

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Conflict of interest

The authors declare no conflict of interest.

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