具备高首周库仑效率的高性能锂离子电池 负极材料Li₂Ni₂(MoO₄)₃@C的制备

张建银*.^{1.2} 刘浩浩^{1.2} 史笑笑^{1.2} (¹山西师范大学现代文理学院,临汾 041000) (²山西师范大学化学与材料科学学院,临汾 041004)

摘要:采用常规的固相反应法结合机械球磨制备了含碳质量分数23.7%的Li₂Ni₂(MoO₄)₃@C复合材料,并应用于锂离子电池负极。与纯Li₂Ni₂(MoO₄)₃相比,Li₂Ni₂(MoO₄)₃@C具有优异的电化学性能,在电流密度为200 mA·g⁻¹时,50周循环后,可逆容量高达845 mAh·g⁻¹。值得注意的是,Li₂Ni₂(MoO₄)₃@C的首周库仑效率高达85%。此外,运用循环伏安法对Li₂Ni₂(MoO₄)₃@C复合物存储锂行为进行了初步探索。

关键词:Li₂Ni₂(MoO₄)₃;固相合成反应;负极材料;锂离子电池;高首周库仑效率 中图分类号:O611.3;O611.4 文献标识码:A 文章编号:1001-4861(2021)10-1862-09 DOI:10.11862/CJIC.2021.205

Preparation of Li₂Ni₂(MoO₄)₃@C Composite as High-Performance Anode Material for Lithium-Ion Batteries with High Initial Coulombic Efficiency

ZHANG Jian-Yin^{*,1,2} LIU Hao-Hao^{1,2} SHI Xiao-Xiao^{1,2}

(¹Modern College of Humanities and Sciences, Shanxi Normal University, Linfen, Shanxi 041000, China) (²School of Chemical and Material Science, Shanxi Normal University, Linfen, Shanxi 041004, China)

Abstract: Herein, $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C composite with mass ratio of 23.7% of carbon was prepared using conventional solid-state method combined with mechanical ball milling and first investigated as the new anode of lithium-ion batteries. Compared with pure $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$, $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C presented an outstanding electrochemical performance, where a high reversible capacity of 845 mAh·g⁻¹ can be acquired at a current density of 200 mA·g⁻¹ after 50 cycles. It's worth noting that $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C delivered high initial coulombic efficiency of 85%. Moreover, the lithium intercalation/de-intercalation behavior of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C was preliminarily investigated by cyclic voltammetry.

Keywords: Li₂Ni₂(MoO₄)₃; solid state synthesis; anode material; lithium-ion batteries; high initial coulombic efficiency

Lithium-ion batteries (LIBs), one of the most promising energy storage devices, have been extensively used in many fields, such as electronic vehicles and portable devices^[1-2]. At present, graphite is mainly used to the commercial anode material for LIBs with a theoretical capacity of 372 mAh·g^{-1[3]}. With the growing demand for various electronic products, new anode materials with admirable properties that contain high capacity and safety performance are required. Among those alternative graphite materials, Mo-based bimetallic oxides (such as Li₂MoO₄, FeMoO₄, Bi₂MoO₆, and Cr₃Mo₂O₁₂), as conversion reaction materials, benefiting from the high capacity delivered due to the multielectron transfer during the lithiation/delithiation pro-

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^{*}通信联系人。E-mail:jyzhang@sxnu.edu.cn

cess, have been investigated intensively for lithium-ion battery anodes^[4-7]. However, the inherent low electrical conductivity of these materials and the structural instability during the reaction process shackle its practical application.

In the past ten or twenty years, Na-super-ionicconductor (NASICON) framework-type lithiated bimetallic oxides, such as Li₃Fe(MoO₄)₃, Li₂Co₂(MoO₄)₃, Li₂FeSiO₄, and Li₃V(MoO₄)₃, have been systematically studied as cathode materials, and it has been found that they have excellent electrochemical properties, which are mainly attributed to their three-dimensional framework structure with the coordination between different metals and many lithium ion channels during the charge/discharge process^[8-9]. In recent years, many studies have proved that the above cathode materials can be applied as excellent anode materials for LIBs^[10-11]. For example, Chen et al. prepared a pure Li₃Fe(MoO₄)₃ with micro-nanoporous structure. Electrochemical test showed that the charge capacity was 622 mAh·g⁻¹ after 450 cycles at a current density of 100 mA·g^{-1[10]}. In 2004, Quaternary lithium nickel molybdenum oxide, Li2Ni2(MoO4)3, was first reported by Prabaharan as a novel cathode material for rechargeable lithium batteries^[12]. The reversible intercalation capacity of $Li_2Ni_2(MoO_4)_3$ was 115 mAh $\cdot g^{-1}$ in the voltage range of 1.5 to 4.9 V. When Ni²⁺ and Mo⁶⁺ are completely reduced to the corresponding metallic elementals, it can be expected that Li₂Ni₂(MoO₄)₃ has a high theoretical specific capacity (965 mAh \cdot g⁻¹). As far as we know, there is no research on $Li_2Ni_2(MoO_4)_3$ as anode material for LIBs. Therefore, it is of great significance to develop high performance anode materials

based on $Li_2Ni_2(MoO_4)_3$.

Herein, $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C composite was successfully synthesized via a simple method using the conventional solid - state process combined with ball milling technique. When first applied as anode material for LIBs, it showed high delithium capacity with high initial coulombic efficiency (85%). Meanwhile, Li_2Ni_2 (MoO₄)₃@C electrode also showed excellent cycling and rate performance, which is attributed to that the addition of carbon not only improves the electrical conductivity of the material, but also as a buffer medium alleviates the large volume changes in the process of charge and discharge. In addition, the lithium storage mechanism of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C was preliminarily explored by cyclic voltammetry (CV).

1 Experimental

1.1 Material synthesis

First, Li₂CO₃, Ni(NO₃)₂ · 6H₂O, and (NH₄)₆Mo₇O₂₄ · 4H₂O were adequately ground in an agate mortar for 30 min with a molar ratio of n_{Li} : n_{Ni} : n_{Mo} being 2:2:3, and the mixture was heated in air at 300 °C for 10 h and then at 550 °C for 24 h to obtain a pure phase of Li₂Ni₂(MoO₄)₃. Next, Li₂Ni₂(MoO₄)₃@C was synthesized by planetary ball milling (QM-3SP04, Nanjing NanDa Instrument Plant, China) at 400 r · min⁻¹ for 12 h. The mass ratio of Li₂Ni₂(MoO₄)₃ to Ketjen Black (ECP -600JD, Lion Corporation) was 8:2. The mass ratio of grinding balls to the material was set as 40:1. For comparison, pure Li₂Ni₂(MoO₄)₃ without added Ketjen Black was also ball - milled under the same condition. The synthesis schematic diagram of Li₂Ni₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃@C is shown in Fig.1.



Fig.1 Synthesis schematic diagram of Li2Ni2(MoO4)3@C

1.2 Material characterization

The crystalline structure of the materials was

investigated using X-ray diffractometer (XRD, Ultima \overline{W}) with Cu $K\alpha$ radiation (λ =0.154 nm) at 40 kV and

40 mA in a scanning range of $10^{\circ} \sim 80^{\circ}$ (2 θ). The surface morphologies were observed by scanning electron microscopy (SEM, JSM-7500F) working at 10 kV and transmission electron microscopy (TEM, JEM-2100F) operated at 200 kV. Thermogravimetric analysis (TG, DTG-60H) was carried out under air atmosphere with a temperature ramp of 10 °C ·min⁻¹. The surface valence states of the samples were researched by X-ray photoelectron spectroscopy (XPS, PHI - 5000 Versa Probe) with Al K α radiation (λ =0.835 nm).

1.3 Electrochemical measurements

The electrochemical performance of $Li_2Ni_2(MoO_4)_3$ and $Li_2Ni_2(MoO_4)_3$ @C was evaluated by a 2016 - type coin cell assembled in a MBRAUN glove box filled high-purity argon gas. The working electrode consisted of $Li_2Ni_2(MoO_4)_3$ (or $Li_2Ni_2(MoO_4)_3$ @C), carbon powder (Super p) and adhesive (polyvinylidene fluoride) (mass ratio of 8:1:1). Li foil and Celgard-2400 membrane were served as counter electrode and separators, respectively. The electrolyte was constituted by 1.0 mol·L⁻¹ LiPF₆ dissolved in ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and ethylene carbonate (EC) (volume ratio: 1:1:1). The CV and electrochemical impedance spectroscopy (EIS) of the as - prepared samples were performed on an electrochemical workstation (CHI660e, Chenhua Instrument Co., Ltd., Shanghai, China). Constant current discharge - charge tests were completed at a NEWAR CT3008 battery system.

2 Results and discussion

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The XRD patterns of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ and $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C are displayed in Fig. 2a. For comparison, Fig. S1 (Supporting information) illustrates the XRD pattern of ball-milled $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$. All the peak positions are well indexed as PDF card (PDF No.70-0452, an orthorhombic structure with space group *Pmcn*), indicating that the samples form a well single - phase crystalline structure. In addition, the characteristic dif-



fraction peaks of carbon are not found, demonstrating it exists as an amorphous state in Li₂Ni₂(MoO₄)₃@C composite after ball milling^[13]. In contrast to pristine Li₂Ni₂ (MoO₄)₃, the broadening of some diffraction peaks observed in Li₂Ni₂(MoO₄)₃@C can be attributed to particle refinement after ball milling^[14], which is shown in the SEM measuring results below. Fig. 2b presents the crystal structure of Li₂Ni₂(MoO₄)₃ as determined by the Diamond software, where the figure exhibits a threedimensional framework. What matters is that the open frame structure may allow Li⁺ to move into and out of the structure easily^[5]. In order to obtain accurate structural information, Rietveld refinements of XRD profiles of the as-synthesized samples were performed by the GSAS software. As shown in Fig.2c and 2d, the calculated results are in good agreement with the experimental XRD patterns. R_{p} and R_{wp} are collectively referred to

as reliability factors, representing profile factor and weighted profile factor, respectively. The Rietveld refinements are credible only if R_p and R_{wp} values are both under $15\%^{[15]}$. For Li₂Ni₂(MoO₄)₃, the refinement terminates with R_p =3.2% and R_{wp} =4.5%. The corresponding lattice parameters were calculated to be a= 1.040 69(8) nm, b=1.749 83(1) nm, c=0.507 89(4) nm, and V=0.924 89(2) nm³. These values are very close to standard data (a=1.042 nm, b=1.752 nm, c=0.507 nm), which also corresponds with the conclusion drawn by the above XRD. The detailed structural parameters of Li₂Ni₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃@C acquired from the refinement results are summarized in Table 1.

The morphology of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ prepared by solid state synthesis was revealed by SEM, as shown in Fig. 3a. It is obvious that the sample shows irregular sintered block shape. When $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ was milled

Table 1 XRD refinement results of as-prepared samples

Sample	Space group	<i>a /</i> nm	<i>b</i> / nm	<i>c</i> / nm	<i>α=β=γ</i> / (°)	V / nm^3
Standard	Pmcn	1.042	1.752	0.507	90	0.926 83
${\rm Li}_2{\rm Ni}_2({\rm MoO}_4)_3$	Pmcn	1.040 69(8)	1.749 83(1)	0.507 89(4)	90	0.924 89(2)
Li ₂ Ni ₂ (MoO ₄) ₃ @C	Pmcn	1.047 95(3)	1.762 31(5)	0.511 22(1)	90	0.930 13(5)



Inset in (a) and (b): powder sample images

Fig.3 SEM images of (a) Li₂Ni₂(MoO₄)₃ and (b) Li₂Ni₂(MoO₄)₃@C; (c) TEM image and (d) HRTEM image of Li₂Ni₂(MoO₄)₃@C

with Ketjen Black (Fig. 3b), it displayed irregular agglomeration. It can be seen that the particle sizes of most of Li₂Ni₂(MoO₄)₃@C were smaller than that of pure Li₂Ni₂(MoO₄)₃ after ball milling. The average particle size was roughly calculated by Image-Pro software from SEM images. The sizes of Li₂Ni₂(MoO₄)₃ and Li₂Ni₂ $(MoO_4)_3$ @C were ~0.31 and ~0.15 μ m, respectively. Further, among various strategies to improve electrochemical behavior, reducing the particle size is an effective method to shorten the diffusion path of ions for LIBs^[16]. Digital photographs of Li₂Ni₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃@C are displayed in the upper right corners of Fig. 3a and 3b. Li₂Ni₂(MoO₄)₃@C powder was black in sharp contrast with the yellow Li₂Ni₂(MoO₄)₃ powder, which demonstrates that Li₂Ni₂(MoO₄)₃ particles have become a composite with carbon. Fig.3c presents the TEM image of Li₂Ni₂(MoO₄)₃@C, where the size of the particles was about 145 nm. The particle size is basically consistent with the SEM measurement result. High-resolution TEM (HRTEM) image (Fig. 3d) exhibited a 0.246 nm lattice spacing corresponding to the (161) plane of Li₂Ni₂(MoO₄)₃. The perfect lattice fringe indicates the excellent crystal structure of Li₂Ni₂ $(MoO_4)_3$, which is essential for the high-performance anodes of LIBs.

The TG curve of Li2Ni2(MoO4)3@C composite under air atmosphere is shown in Fig. 4a. The weight percentage of Li₂Ni₂(MoO₄)₃ in the composite was 76.3% at 800 °C, which is roughly the same as the feed ratio before ball-milling. The electronic state of different elements of Li₂Ni₂(MoO₄)₃@C was verified by XPS, as presented in Fig. 4b~4f. The survey spectrum (Fig.4b) exhibits the existence of Li, Ni, Mo, and O, as well as C from the composite material and the reference electrode. The binding energy observed near 56 eV is in line with the Li1s XPS spectrum (Fig.4c)^[12]. As shown in Fig. 4d, the two peaks located at 856.1 and 873.4 eV can be ascribed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, representative of the presence of Ni^{2+[17]}. And there are two satellite peaks with binding energies at 878.8 and 860.9 eV (Fig. 4d). The binding energies of two peaks existed at 232.4 and 235.5 eV are assigned to $Mo3d_{5/2}$ and $Mo3d_{3/2}$, respectively, which corresponds to the characteristic of Mo^{6+} as depicted in Fig.4e^[18]. The O1s XPS spectrum for Li₂Ni₂(MoO₄)₃@C shows two peaks with binding energies at 530.4 and 532.5 eV, which is attributed to the lattice oxygen and chemisorbed oxygen, respectively (Fig.4f)^[8].

The lithium intercalation/de-intercalation behavior of pure Li₂Ni₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃@C composite was studied by CV and galvanostatic chargedischarge cycling. Fig. 5a shows the first three CV curves of Li2Ni2(MoO4)3@C electrode for LIBs in the voltage range of 0.02~3.0 V (vs Li⁺/Li) at the scan rate of 0.1 mV \cdot s⁻¹, which is similar to that of NiMoO₄ anodes^[19]. The initial cathodic scan displays three reduction peaks at 1.46, 0.70, and 0.17 V. The peak at 1.46 V involves an irreversible transition, possibly due to the insertion of Li⁺ into the Li₂Ni₂(MoO₄)₃. This phenomenon also appears in another molybdenum-based material^[5,10-11]. The other two peaks correspond to the transformation of Mo⁶⁺ to Mo and Ni²⁺ to Ni, accompanied by the formation of solid electrolyte interface (SEI) film on the electrode surface. When the scanning direction was reversed, the anodic peak at 1.38 V can be related to the oxidation of Mo to Mo⁴⁺, while the peak located 1.80 V represents the overlapping peaks of Mo⁴⁺ to Mo⁶⁺ and Ni to Ni^{2+[19]}. It can be visibly seen from the second cycle that three reduction peaks appeared (1.50, 0.64, and 0.15 V). Among them, the peaks located at 1.50 and 0.15 V may be attributed to the multi - step reduction of Mo⁶⁺ to Mo^[10]. Another reduction peak at 0.64 V can be related to the reduction of Ni²⁺ to Ni^[20]. Meanwhile, two peaks at 1.38 and 1.80 V are shown in the anodic process, which is basically consistent with the initial anodic scans. During the scanning process, the changes in the redox potential of Ni²⁺ and Mo⁶⁺ are related to the existence of the polyanion $(MoO_4)^{2-}$ in the main frame structure^[21]. Clearly, the CV curves of Li2Ni2(MoO4)3@C after the first cycle overlap better than that of pure Li₂Ni₂(MoO₄)₃ (Fig. 5b), indicating that the former has superior reversibility as an anode material. In short, the reaction processes are as follows:

$$\begin{array}{l} \mathrm{Li}_{2}\mathrm{Ni}_{2}(\mathrm{MoO}_{4})_{3} + x\mathrm{Li}^{+} + x\mathrm{e}^{-} \rightarrow \\ \mathrm{Li}_{2+x}\mathrm{Ni}_{2}(\mathrm{MoO}_{4})_{3} \ (0 < x \leq 2) \end{array} \tag{1}$$



Fig.4 (a) TG curve of Li₂Ni₂(MoO₄)₃@C in an air atmosphere; XPS spectra of Li₂Ni₂(MoO₄)₃@C:
(b) survey spectrum, (c) Li1s, (d) Ni2p, (e) Mo3d, and (f) O1s

$$\mathrm{Li}_{2+x}\mathrm{Ni}_{2}(\mathrm{MoO}_{4})_{3} + (22-x)\mathrm{Li}^{+} + (22-x)\mathrm{e}^{-} \rightarrow$$

$$12Li_2O+2Ni+3Mo$$
 (2)

$$\text{Li}_2\text{O}+\text{Ni} \rightleftharpoons \text{NiO}+2\text{Li}^++2\text{e}^-$$
 (3)

$$3\text{Li}_2\text{O}+\text{Mo} \rightleftharpoons \text{MoO}_3+6\text{Li}^++6\text{e}^-$$
 (4)

Fig. 5c presents the charge/discharge curves of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C electrode for the 1st, 2nd, and 50th cycles at 200 mA·g⁻¹. During the first discharge process, three voltage platforms were recorded, which was also in line with the CV results (Fig. 5a). First, a short platform located at 1.5 V (86 mAh·g⁻¹), which corre-

sponded to the intercalation of 2Li^+ into $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3^{[21]}$. When the discharge voltage was below 1 V, the two voltage platforms contribute a capacity sum of 930 mAh \cdot g⁻¹ (21Li⁺), which is involved in the decomposition of $\text{Li}_{2+x}\text{Ni}_2(\text{MoO}_4)_3$ to produce Ni and Mo as well as the formation of SEI film. It is worth noting that the polarization of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C between the discharge platform and the charging platform is smaller than that of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ (Fig. 5d), indicating that its kinetic characteristics are better than that of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$.



Fig.5 CV profiles of (a) Li₂Ni₂(MoO₄)₃@C and (b) Li₂Ni₂(MoO₄)₃ at scan rate of 0.1 mV • s⁻¹; Discharge/charge curves of (c) Li₂Ni₂(MoO₄)₃@C and (d) Li₂Ni₂(MoO₄)₃ at 200 mA • g⁻¹

The improved kinetics of $Li_2Ni_2(MoO_4)_3@C$ can be attributed to the higher electrical conductivity and Li^+ ion diffusivity^[22-23].

The comparative cycling performance of Li₂Ni₂ (MoO₄)₃ and Li₂Ni₂(MoO₄)₃@C composite electrodes at a current density of 200 mA \cdot g⁻¹ is shown in Fig.6a. For Li₂Ni₂(MoO₄)₃@C electrode, the initial discharge and charge capacities were 1 131 and 961 mAh \cdot g⁻¹, respectively, corresponding to the initial columbic efficiency of 85%. It should be noted that such a high coulomb efficiency is very competitive in reported anode materials, which is of great importance for practical applications^[11]. Li₂Ni₂(MoO₄)₃@C delivered a charge capacity of 845 mAh \cdot g⁻¹ after 50 cycles and exhibited excellent capacity retention (87.5% of the initial capacity). In contrast, pure Li₂Ni₂(MoO₄)₃ remained at 95 mAh \cdot g⁻¹ and the capacity retention was only 12.6%. In addition, the cycle properties of ball-milled Li₂Ni₂(MoO₄)₃ without adding Ketjen Black were also characterized under the same condition. As shown in Fig.S2, the reversible capacity of ball-milled Li₂Ni₂(MoO₄)₃ was only 135 mAh·g⁻¹ after 50 discharge-charge cycles. This significantly enhanced electrochemical performance is mainly attributed to the fact that Ketjen Black in $Li_2Ni_2(MoO_4)_3$ @C composite protect the electrode from collapse due to volume expansion/contraction during Li^+ insertion/extraction process, thus improving the electrode stability^[22].

To verify practicality, the rate capabilities of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ and $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C electrodes were also studied at different current densities, as shown in Fig. 6b. $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C electrode showed a superior rate performance with the specific discharge capacity of approximately 936, 876, 760, and 551 mAh·g⁻¹ at 200, 400, 800, and 1 600 mA·g⁻¹, respectively. After 40 cycles, when the current density was restored to 200 mA·g⁻¹, the specific discharge capacity could recover to ~811 mAh·g⁻¹, which is 86% of the first stage capacity. By contrast, $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ only returned to 32% under the same conditions, indicating that $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C possesses a good structural stability under the large current density changes.



Fig.6 (a) Cycling performance at 200 mA \cdot g⁻¹ and (b) rate performance of as-prepared samples

In order to further investigate the reasons for the improved electrochemical properties, comparative alternating current (AC) impedance spectroscopy analyses were performed after the rate performance cycles. There are a semicircle and a sloping line in the Nyquist plot that was fitted using the equivalent circuit acquired by Z-view software (Fig.7a). In the equivalent circuit, R_s , R_{ct} , CPE and Z_w stand for ohmic resistance of electrolyte and contact resistance, resistance of charge transfer, double layer capacitance, and Warburg impedance controlled by diffusion, respectively^[24]. The diffusion coefficient of lithium ions (D_{Li}) was calculated according to the following equation^[25-26]:

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$$D_{\rm Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 c^2 \sigma^2}$$
(5)

Where R, T, A, n, F, c, and σ represent gas constant, absolute temperature, surface area of the anode, num-

ber of electrons per molecule during oxidization, Faraday constant, concentration of lithium-ion and Warburg factor, respectively. The σ is relative with Z':

$$Z' = R_{\rm s} + R_{\rm cl} + \sigma \omega^{-1/2} \tag{6}$$

Fig. 7b presents the linear fitting of Z' vs $\omega^{-1/2}$, from which the slope σ can be derived. Based on Eq.5, it is possible to calculate D_{Li} of the samples using the σ value. The fitting results of resistance and the values of D_{Li} are tabulated in Table 2. It is obvious that the R_{s} and R_{ct} for Li₂Ni₂(MoO₄)₃@C electrode are smaller than those of pure Li₂Ni₂(MoO₄)₃ electrode, demonstrating that Li₂Ni₂(MoO₄)₃@C electrode possesses a more stable surface film and a faster charge transfer process. In addition, the D_{Li} values of Li₂Ni₂(MoO₄)₃@C and Li₂Ni₂ (MoO₄)₃ indicate that the electrochemical kinetics for Li₂Ni₂(MoO₄)₃@C is easier with Li⁺ insertion/extraction than Li₂Ni₂(MoO₄)₃, which also verifies the enhance-



Fig.7 (a) EIS spectra of $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ and $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ @C (Inset: simulated equivalent circuit); (b) Relationship between Z' and the square root of frequency ($\omega^{-1/2}$) in the low frequency region

Table 2	Fitted imped	ance parameters	s of Li ₂ Ni ₂ (Mo	$O_4)_3 @C$ and	l Li ₂ Ni ₂ (MoC) ₄) ₃
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Sample	$R_{ m s}$ / Ω	$R_{ m ct}$ / Ω	$D_{\rm Li} / ({\rm cm}^2 {\cdot}{\rm s}^{-1})$
Li2Ni2(MoO4)3@C	8.21	241.9	5.36×10 ⁻¹³
${\rm Li}_2{\rm Ni}_2({\rm MoO}_4)_3$	10.21	300.2	3.48×10 ⁻¹³

ment of lithium storage performance of Li₂Ni₂(MoO₄)₃ @C after compounding with carbon.

3 Conclusions

In summary, Li₂Ni₂(MoO₄)₃@C composite was synthesized using solid-state reaction combined with ball milling and researched as novel anode material for LIBs. In contrast to Li₂Ni₂(MoO₄)₃, Li₂Ni₂(MoO₄)₃@C composite exhibited competitive rate performance and cyclic stability. Moreover, Li₂Ni₂(MoO₄)₃@C provided a discharge capacity of 861 mAh·g⁻¹ after 50 cycles at 200 $mA \cdot g^{-1}$ and delivered high initial coulombic efficiency of 85%. The excellent electrochemical performance is due to the reduction of particle size after ball milling, and more importantly, the carbon matrix of Li₂Ni₂(MoO₄)₃@C composite can improve electrode conductivity, buffer massive volume changes, and raise reaction kinetics. All the results highlight that Li₂Ni₂ (MoO₄)₃@C would become a promising candidate for new anode materials of LIBs.

Supporting information is available at http://www.wjhxxb.cn

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