Fe$_2$(MoO$_4$)$_3$ nanoparticle-anchored MoO$_3$ nanowires: strong coupling via the reverse diffusion of heteroatoms and largely enhanced lithium storage properties†

Yeping Song,$^{ab}$ Hai Wang,*$^{ab}$ Zihua Li,$^a$ Naiqing Ye,$^a$ Linjiang Wang$^{ab}$ and Yong Liu$^c$

A novel hierarchical heterostructured Fe$_2$(MoO$_4$)$_3$@MoO$_3$ (FM) nanowire is developed by mild hydrothermal treatment of precursor MoO$_3$ nanobelts with only the assistance of FeCl$_3$·6H$_2$O combined with the heat treatment. Subsequently, a model of reverse heteroatoms diffusion is proposed to describe the formation of FM nanowires. Further, it is found that the heteroatoms diffusion and facet-selective growth of Fe$_2$(MoO$_4$)$_3$ on MoO$_3$ nanobelts brought about the change of MoO$_3$ morphology from nanobelts to nanowires, and Fe$_2$(MoO$_4$)$_3$ nanoparticles are firmly anchored onto MoO$_3$ nanowires. When tested as LIBs anodes, compared to pristine MoO$_3$ nanobelts, high reversible lithium storage capacities of the anodes are obtained from novel FM nanowires. The FM nanowire electrode obtained at 500 °C (FM-500) exhibits superior reversible capacity of 585 mA h g$^{-1}$ retained at a current density of 100 mA g$^{-1}$ after 100 cycles, and 518 mA h g$^{-1}$ retained after 100 cycles at 200 mA g$^{-1}$. The distinct electrochemical activity of the Fe$_2$(MoO$_4$)$_3$ nanoparticles probably activates the irreversible capacity of the MoO$_3$ nanobelts. Moreover, the amorphous layer and structure stability of heterojunction electrodes are also beneficial for charge storage, electron transfer and lithium ion diffusion during the charge–discharge process.

Introduction

The design and rational synthesis of electrode materials with high energy density, high rate capability, and good cyclability for lithium-ion batteries (LIBs) has been a hot topic. Compared with commercial graphite anodes with a specific capacity of 372 mA h g$^{-1}$, MoO$_3$ has long been considered as an attractive anode material for LIBs, due to its relatively high theoretical capacity of 1111 mA h g$^{-1}$. However, its practical applications are still hindered by its relatively low specific capacities and rate properties that are caused by poor intrinsic ionic and electronic conductivity.$^{1-3}$ Designing MoO$_3$ nanobelts has been demonstrated to be an effective solution to overcome the aforementioned obstacles. Recent studies in these areas have revealed that fabricating a conducting layer on the surface of MoO$_3$ nanobelts, employing carbon-coating, graphene and using lithiation technologies et al. are several ideal strategies to enhance the electrochemical performance of 1D MoO$_3$ nanobelts.$^{4-7}$ But still, the performance of MoO$_3$ nanobelt-based anodes are not very satisfactory, especially the decay of capacity with long-term cycling.

NASICON-structured Fe$_2$(MoO$_4$)$_3$ has been identified as a potential candidate for either sodium or lithium storage due to its cheap, non-toxic of iron and its open three dimensions framework.$^{8,9}$ However, the lack of direct Fe–Fe or Fe–O–Fe interaction results in its poor electronic conductivity, low rate capability and bad cyclability despite good lithium ion conduction in the Nasicon-based frameworks.

Recently, numerous studies have been taken to fabricate heterogeneous metal oxides as promising anode materials for LIBs due to their higher energy density and longer cycle life.$^{1,4-6,10,11}$ From the technological viewpoint, the composites may offer novel applications since they could take advantage of the synergistic effects between different constituent phases. To date, tremendous efforts have been devoted to choosing suitable LIBs materials and their assemblies in appropriate hierarchical heterostructures with smart composition and nanosized building blocks to achieve better performance, such as, α-Fe$_2$O$_3$@SnO$_2$ core–shell nanorattles,$^{12}$ SnO$_2$@MoO$_3$ core–shell nanobelts,$^5$ SnO$_2$@WO$_3$ core–shell nanorods,$^{1,14}$ SnO$_2$@ZnWO$_4$ core–shell nanorods,$^{15}$ NiFe$_2$O$_4$@Fe$_2$O$_3$ nanorods,$^{16}$ etc. However, the lack of direct Fe–Fe or Fe–O–Fe interaction results in its poor electronic conductivity, low rate capability and bad cyclability despite good lithium ion conduction in the Nasicon-based frameworks.
ion and electron transfer, thus leading to superior lithium-ion storage performance. For example, Fe₄O₆@SnO₂,¹⁷,¹⁸ Fe₂O₃@MnO₂,¹⁹ SnO₂@WO₃,¹⁵ SnO₂@MoO₃,⁵ Co₃O₄@Fe₃O₄,²⁰ etc. hierarchical heterostructures composites with good contact between two materials showed high electrochemical performance for Li-ion batteries. It seems that epitaxial growth and heterogeneous nucleation may be a more attractive way for building an idea interface. Nevertheless, the match of crystal lattice is a basic requirement, which greatly limits the choice of materials. Therefore, building new interface model is highly desired and important for the applications of LIBs.

Here, we present an alternative route by constructing novel hybrid metal oxide core–shell nanowires for LIBs. This unique designed electrode has the following advantages. First, both the core and shell metal oxides materials are good LIBs electrode materials (e.g., MoO₃, Fe₂(MoO₄)₃). Second, compared with the previous fabricated heterogeneous metal oxides, the way of Fe₂(MoO₄)₃ nanoparticles firmly anchored onto the MoO₃ nanobelts via the reverse diffusion of heteroatoms is mechanically stable and favourable especially for the cycling performance during charge–discharge process at high current densities. Third, the connection between (101)MoO₃ and (202)Fe₂(MoO₄)₃ leads to a continuous interface, which is beneficial for the transfer of the charge carriers. For this electrode design, not only all the desired functions of each constituent can be utilized effectively, but also a strong synergistic effect can be realized. Further, the interface relationship between MoO₃ and Fe₂(MoO₄)₃ would be clarified. To prove this concept, we choose MoO₃ and Fe₂(MoO₄)₃ as the model shell and core materials, respectively. It is found that, the FM-500 hybrid nanowires exhibit a high specific capacity of more than 3-fold compared with pristine MoO₃ nanobelts, according to the good cycle performance of 585 mA h g⁻¹ after 100 cycles and remarkable rate capability at a current density of 100 mA g⁻¹.

**Experimental**

**Materials synthesis**

All chemical reagents were commercial products used without further purification. Firstly, MoO₃ nanobelts were prepared via a facile hydrothermal approach, according to reported studies.²¹ Typically, 1 g of ammonium molybdate was dissolved in 30 mL of deionized water under continuous stirring. After 30 min, 6 mL of HNO₃ was added to the beaker dropwisely and stirred for another 30 min. The homogeneous suspension was formed. Then the resulting suspension was transferred to a Teflon-lined autoclave with a capacity of 50 mL and then kept inside an electric oven at 180 °C for 24 h. The as-prepared MoO₃ nanobelts powder was collected by filtration and thoroughly washed with deionized water and ethanol for several times and finally dried in air.

The fabrication of the Fe₂(MoO₄)₃@MoO₃ nanowires was carried out by a soaking hydrothermal process combined with post-heating treatment. Scheme 1 illustrates the formation process of the Fe₂(MoO₄)₃@MoO₃ nanowires. In a typical synthesis, first, 0.6 g of FeCl₃·6H₂O was added into 60 mL deionized water, and 0.2 g of as-prepared MoO₃ powder was subsequently added into the above solution with magnetic stirring for 1 h. Then, the suspension was transferred to a 100 mL autoclave at 90 °C for 6 h. The hydrothermal sample was centrifuged and washed using deionized water and ethanol for several times, and dried under vacuum. Finally, the as-obtained sample is calcined at 500 °C (denoted as Fe₂(MoO₄)₃@MoO₃-500, FM-500) and 600 °C for 2 h (denoted as Fe₂(MoO₄)₃@MoO₃-600, FM-600), respectively. To investigate the formation process of final Fe₂(MoO₄)₃@MoO₃ nanowires, the samples after the hydrothermal treatment of MoO₃ nanobelts-soaked with FeCl₃·6H₂O solution are annealed at 200 °C (denoted as MoO₃-200) and 400 °C (denoted as Fe₂(MoO₄)₃-400) for 2 h, respectively.

**Characterization**

The crystal structure was performed by X-ray diffraction (XRD) analysis with a PANalytical X’Pert spectrometer using Cu Kα radiation with wavelength of 0.15405 nm. The surface morphologies of the samples were studied using a JEOL JSM6300 (Tokyo, Japan) field emission scanning electron microscope (FESEM). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEM-2010F electron microscope (JEOJ, Japan) operating at 200 kV. The specific surface area and the pore size distribution (BJH method, desorption branch) were determined by nitrogen adsorption–desorption isotherms (Micromeritics, ASAP 2010). TG and DSC analysis of the samples were conducted on TGA 2050 thermogravimeter with a heating rate of 10 °C min⁻¹ in air.

![Scheme 1](image-url)
Electrochemical measurements
The electrochemical performance of as-prepared samples was tested by employing CR2032-type coin cells at room temperature. The working electrode included active material, acetylene black and PVDF in a 50:30:20 weight ratio. For electrochemical characterization, electrodes were prepared on aluminium foil (0.2 mm thick) as a current collector. A circular Al foil of area 1 cm$^2$ was cleaned with detergent. Coating were repeated to get the required loading level (2–3 mg) of the active material. A Celgard 3400 membrane was used as a separator and 1.0 M LiPF$_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 volume, Novolyte Technologies, USA) was used as the electrolyte. The cell was made in an argon-filled glovebox. The charge–discharge cycling performance and cyclic voltammetry (CV) (0.01–3.0 V, 0.2 mV s$^{-1}$) were carried out at room temperature by using a battery testing system (NEWARE) at different current rates with a voltage window of 0.01–3.0 V and using an electrochemical workstation (CHI 860 D, Beijing), respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed at frequencies from $10^{-2}$ to $10^5$ Hz.

Results and discussion
The temperature-controlled XRD patterns of the samples obtained at various reaction stages, with MoO$_3$ nanobelts as the precursors, are shown in Fig. 1. For the samples at annealing temperature 200, 400 °C, only the orthorhombic MoO$_3$ phase (JCPDS card no. 89-7112) was found. When the reaction temperature was increased to 500 °C, the monoclinic Fe$_2$(MoO$_4$)$_3$ phase (JCPDS card no. 72-0935) was formed and increased continuously in crystallinity at 600 °C. Surprisingly, we noticed that the MoO$_3$ (060) diffraction peak was shift slightly towards higher angles (the inset of Fig. 1) with the increase of annealing temperature (before 400 °C) in the sample. Subsequently, the (060) diffraction peak began to shift slightly towards lower angles. Since Mo atom will migrate from MoO$_3$ to unknown Fe source to form Fe$_2$(MoO$_4$)$_3$ phase, the Fe-doped MoO$_3$ will lead to the increase of d (060). Therefore, we reasonably assume that the Mo atoms first began to migrate into the Fe sources and the Fe$_2$(MoO$_4$)$_3$ began to nucleate before 400 °C and crystallize after 400 °C. After that, the Fe atoms were diffused into MoO$_3$ crystal lattice to balance the change of interplanar spacing of (060).

To clarify the chemical reactions of the FM-500 nanowires that occur at the different reaction stages, TG-DSC analysis of the sample before calcination was carried out in air to find a suitable temperature program for obtaining FM nanowires. TG-DSC recorded in air with a heating rate of 10 °C min$^{-1}$ is illustrated in Fig. S1.† The details of the TG-DSC curve in the first temperature region are attributed to the loss of physisorbed water at about 136 °C. The second main weight loss corresponds to the decomposition of Fe(OH)$_3$.23,24 The specific process of the hydrolysis of FeCl$_3$·6H$_2$O in aqueous solution into Fe(OH)$_3$ will be discussed in the latter section. The results show that Fe(OH)$_3$ began to decompose into Fe$_2$O$_3$ at about 363 °C. At about 500 °C in the TG-DSC curve, there is an endothermic peak, which corresponds to the formation of new phase Fe$_2$(MoO$_4$)$_3$. The result is consistent with the XRD results. After 500 °C, there is no obvious mass loss. This indicates that the sample reaches constant weight.

Fig. 2 shows the FESEM images of the samples at various reaction stages. The microstructure of the pre-synthesized MoO$_3$ nanobelts precursors were almost identical compared with previously reported MoO$_3$ nanobelts (Fig. 2a and b). When the reaction proceeded to 500 °C, many Fe$_2$(MoO$_4$)$_3$ particles were unevenly precipitated on the surfaces of the 1D MoO$_3$ nanowires (Fig. 2c and d). As the reaction temperature was increased to 600 °C, the sample FM-600 images are almost similar to that of sample FM-500, except for slight changes observed from Fig. 2e and f.

To explore how the Fe$_2$(MoO$_4$)$_3$ phase couples with the MoO$_3$ nanobelts, TEM observations of the FM-500 and FM-600 samples were conducted, respectively, as presented in Fig. 3 and S2.† Fig. 3a and b show a segment of FM-500 sample. To investigate the junction between MoO$_3$ and Fe$_2$(MoO$_4$)$_3$, HRTEM observation was performed on the FM-500 nanowires (Fig. 3c). It is apparent that Fe$_2$(MoO$_4$)$_3$ is continuously grown with MoO$_3$ and it forms a distinguished interface boundary (Fig. 3a and b). The HRTEM image on the interface between the nanowires and the nanoparticles is shown as Fig. 3c. The visible lattice fringes with d spacings of 0.381 and 0.388 nm, correspond to the (101) planes of MoO$_3$ and the (202) planes of Fe$_2$(MoO$_4$)$_3$, respectively, indicating the nanowires elongate along the [010] direction of MoO$_3$ and the lateral facet belongs to the {101} facets of MoO$_3$ nanobelts. The most clear lattice fringes for the Fe$_2$(MoO$_4$)$_3$ are from the (202) planes, which parallel to the (101) plane of MoO$_3$. Based on the results and the
crystal knowledge of Fe₂(MoO₄)₃, the planes parallel to the {101} planes of MoO₃ can be formed as the requirements of crystal lattice match. The lattice mismatches between (101)MoO₃ and (202)Fe₂(MoO₄)₃ are ca. 1.84% \((\frac{0.388}{0.381}/0.381 \times 100\%)\), which is small enough to be tolerated for the epitaxial growth of Fe₂(MoO₄)₃. Significantly, the connection between (101)MoO₃ and (202)Fe₂(MoO₄)₃ leads to a less-defective and abrupt interface, as revealed in Fig. 3c, which is beneficial for the transfer of the charge carriers. The SAED pattern for FM-500 is consistent with the single-crystalline structures of both the MoO₃ (yellow dots) and Fe₂(MoO₄)₃ phases (red dots) (Fig. 3d). Fig. S3a† is a scanning TEM (STEM) image of FM-500 nanowires and Fig. S3b–d† show corresponding EDX elemental mapping of Fe, Mo and O, respectively. It is noticeable that O and Fe elements distribute in both the core area and the shell area. Specially, the Fe element maps from EDX further confirm the Fe elements existence within nanowires. Further, the orientation relationship between MoO₃ nanowires and Fe₂(MoO₄)₃ nanoparticles, as shown in Fig. 4. It should be noted that the lateral facet belongs to the \{100\} faces of conventional of the MoO₃ according to the literature presented method.¹¹,²⁵–²⁹ Surprisingly, it is found that the lateral facet occurs change from \{100\} to \{101\} as Fe₂(MoO₄)₃ nanoparticles were formed. It is found that the morphology of MoO₃ changes from nanobelts to nanowires due to the heteroatoms diffusion and facet-selective growth of Fe₂(MoO₄)₃ on MoO₃ nanobelts.

Interestingly, for the sample FM-600, the increase of the diffusion rate with the assistant of increased temperature also leads to the appearance of some hollow hierarchical heterostructures, as shown in Fig. S2.† For this case, by choosing the proper diffusion pairs, such as Fe and Mo, the discrepancy in diffusion rates of the two components could be utilized to generate interior voids based on mechanisms similar to the nanoscale Kirkendall effect.³⁰ Based on the XRD, FESEM and TEM analyses stated above, the formation process of the hierarchically assembled FM-500 nanowires is concluded, as illustrated in Scheme 2. First, the MoO₃ nanobelts were coated by FeCl₃·6H₂O colloid nanoparticles via the soaking process, which were then further converted to amorphous Fe(OH)₃ during the hydrolysis process.
of FeCl$_3$·6H$_2$O (eqn (1)), forming the Fe(OH)$_3$@MoO$_3$ hierarchical nanostructure (step 1).

$$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{HCl} + 3\text{H}_2\text{O} \quad (1)$$

As the reaction temperature is further increased (low than 500 °C), the Fe(OH)$_3$ nanoparticles on the surface of MoO$_3$ nanobelts will aggregate and transform into Fe$_2$O$_3$ particles (eqn (2)), forming the Fe$_2$O$_3$@MoO$_3$ hierarchical nanostructure (step 2).

$$2\text{Fe(OH)}_3 = \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (2)$$

As the product is thermally treated at 500 °C, MoO$_3$ will fuse together with the Fe$_2$O$_3$ particles, and the reaction (eqn (3)) occurs between them, accompanied with the initial nucleation of Fe$_2$(MoO$_4$)$_3$ (step 3).

$$\text{Fe}_2\text{O}_3 + 3\text{MoO}_3 = \text{Fe}_2(\text{MoO}_4)_3 \quad (3)$$

With continuous reverse heteroatoms diffusion, it is reasonable to assume that MoO$_3$ nanobelts may form a hollow structure, which may be due to the diffusion of Mo atoms into the Fe$_2$O$_3$ shell layers to eliminate the MoO$_3$ nanobelts. Our assumption is further confirmed by TEM measurements of FM-600 (Fig. S2†). As expected, the hollow structure of the FM-600 is observed, as evidenced by the red arrows in Fig. S2a.† The morphology evolution process of MoO$_3$ nanobelts is illustrated in Scheme S1.†

Chen et al. reported the production of such hybrid structures and porous homogenous material Fe$_2$(MoO$_4$)$_3$ nanorods, in pursuit of enhanced ethanol sensing properties. However, it is not clear whether this unique structure is suitable for LIBs application.$^{31,32}$ To explore the potential application of the FM-500 nanowires electrodes in LIBs, we investigated their electrochemical performance. Fig. 5 shows the galvanostatic discharge–charge voltage profiles of the three samples cycled at different rates in the voltage range of 0.01–3.0 V vs. Li/Li$^+$. Both the two FM nanowires samples show a high initial specific capacity of 1574 and 1413 mA h g$^{-1}$ at the current density of 50 mA g$^{-1}$ for FM-500 and FM-600 nanowires, respectively. The results indicate the superiority of FM hierarchical nanostructures as potential high-performance anode materials for Li ion batteries. Among the three samples, the FM-500 nanowires electrode shows the best rate performance. Even at a high rate of 500 mA g$^{-1}$, it can still deliver a capacity of ca. 1270 mA h g$^{-1}$, while the MoO$_3$ and the FM-600 only deliver a capacity of ca. 910 and ca. 1010 mA h g$^{-1}$, respectively. For clarity, the 1st discharge curves of the three samples and their corresponding $dQ/dV$ profiles are shown in Fig. S4.† Clearly, based on the voltage plateaus at ca. 0.5 V for the three samples, it is found that the voltage plateaus of MF-500 and MF-600 are higher than that of the MoO$_3$ nanobelts, which is due to higher Fe$^{2+}$/Fe$^{3+}$ redox levels relative to the Li/Li$^+$ redox level.$^8$ The significance of elevated voltage plateau is that it can reduce the discharge electrode polarization. Based on the above consideration, for individual MoO$_3$ and Fe$_2$(MoO$_4$)$_3$, the synergistic effect is very obvious. For example, for MoO$_3$, Fe$_2$(MoO$_4$)$_3$ can help to decrease the polarization phenomenon during the charge–discharge process due to the increase of the voltage plateau. Moreover, it can roughen the surface of the MoO$_3$ nanobelts and provide the electrochemical reaction sites. While for Fe$_2$(MoO$_4$)$_3$, 1D MoO$_3$ nanowires are a fast electron transport carrier. Additionally, the formed amorphous layer during the process of the heteroatoms reverse diffusion also helps to increase extra lithium-storage capacity and increase the lithium-ion diffusion capacity. It can be proposed that the amorphous layer surface may be rich in Mo, which may be in octahedral coordination surrounded by six oxygen atoms.$^{33,34}$

Compared to MoO$_3$ nanobelts, the FM hierarchical nanostructure displays superior cycling performance. For example,
for FM-500, it can deliver stable discharge and charge capacities of ca. 585 and 580 mA h g\(^{-1}\), respectively, after 100 cycles at the current density of 100 mA g\(^{-1}\), as shown in Fig. 6a, whereas for the FM-600, under the identical conditions, it just delivers discharge and charge capacities of 519 and 517 mA h g\(^{-1}\), respectively (Fig. 6a). Although the capacities decrease with increasing current density, the FM-500 nanowires still show a high capacity with excellent capacity retention even at the 200 mA g\(^{-1}\) (Fig. S5). Moreover, it is worthy of noticing that the capacity of FM first increased and then decreased with the increasing number of cycles, as shown in Fig. 6a and S5. Anomalous behaviors have been reported in previous reports. Two factors may be attributed to this phenomenon: (1) the Fe\(_2\)(MoO\(_4\))\(_3\) nanoparticles have transformed into metastable lithiated orthorhombic Li\(_x\)Fe\(_2\)(MoO\(_4\))\(_3\) as the lithium ions insert in the first discharge process, while the deconstruction of the crystal Fe\(_2\)(MoO\(_4\))\(_3\) electrodes will synergistically affect the lithium storage of MoO\(_3\) nanowires and cause capacity fading at the early stage; (2) just as mentioned above, the remaining unused active materials would be further pulverized into finer Mo nanoclusters, which continually increases active sites as the lithium ions insert, resulting in an increased capacity with the increasing number of cycles. It can be predicted that if more cycles are applied in the cycling performance for FM, the capacity will reach a maximum and then drop, due to the full usage of active materials and the decreasing conductivity upon later cycling. The unique structure effectively enhanced lithium-ion storage capacity and improved storage kinetics, particularly at higher current density.

The rate performance of MoO\(_3\) nanobelts and FM is also tested to study the fast discharge behaviour. As shown in Fig. 6b, the discharge rates are increased successively from 50 to 500 mA g\(^{-1}\) for each 5 cycles. For the FM, as shown in Fig. 6b, the average discharge capacities for each 5 cycles at 50, 100 and 200 mA g\(^{-1}\) are ca. 1045, 708 and 558 mA h g\(^{-1}\), respectively. At a high rate of 500 mA g\(^{-1}\), it can still deliver a discharge capacity of ca. 423 mA h g\(^{-1}\). More surprisingly, the intercalation capability of FM-500 nanowires is over 3-fold than individual MoO\(_3\) nanobelts in practical scenario. Moreover, the FM-500 exhibits a superior rate performance in comparison with FM-600.

Monoclinic Fe\(_2\)(MoO\(_4\))\(_3\) can theoretically accommodate up to 8 Li atoms via intercalation reaction leading to a capacity contribution of 364 mA h g\(^{-1}\) which is lower than theoretical capacity of MoO\(_3\). According to the traditional calculation method, the theoretical reversible capacity of FM composites should be 364–1111 mA h g\(^{-1}\). However, the experimental reversible capacity of FM-500 nanowires is about 3 times higher than the MoO\(_3\) nanobelts, as shown in Fig. 6a and S5. From the comparison of FM-500 nanowires, FM-600 and MoO\(_3\) nanobelts microstructure, it is found that the FM-500 exhibited a higher specific surface area and abundant mesoporous features as a result of surface coarse treatment by the facet-selective nucleation and growth of Fe\(_2\)(MoO\(_4\))\(_3\) nanoparticles based on the Nitrogen adsorption and desorption isotherms and pore-size distribution curves (Fig. S7 and Table S1). No doubt, the features increase the electrochemical active sites of MoO\(_3\). As shown in Fig. S6, a ca. 10 nm thick amorphous surface layer was extended around the interface and Fe\(_2\)(MoO\(_4\))\(_3\), which can effectively hinder the side reaction between the active material and organic electrolyte cause capacity fading and safety issues.

To help understand the different lithium-storage behaviors, the lithium-ion diffusion and electron transport of the FM-500 and FM-600 are depicted in Fig. 6c and d. It is well known that 1D nanowires have attracted considerable interest and have been used in LIBs due to their unusual mechanical and electrical performance. Obviously, compared to the rapid electron transport channel in FM-500 nanowires (Fig. 6c), FM-600 exhibits the random network at the grain boundaries, thus leading to discontinuous electron transport (Fig. 6d). This difference between the nanowires and nanoparticles on the electrochemical properties will be disclosed in the following discussion.

The electrochemical activity of the prepared FM electrodes was evaluated in an electrochemical measurement system and compared with that of MoO\(_3\) nanobelts. Cyclic voltammetry (CV) results which recorded at a scan rate of 0.2 mV s\(^{-1}\) within the potential window of 0.01–3.0 V vs. Li/Li\(^+\) is shown in Fig. 7. Obviously, FM-500 has a larger curve area and higher redox peak current than other samples, suggesting that FM-500 has the highest capacity and the fastest kinetics for Li ion insertion–extraction. The higher electrochemical activity of FM-500 nanowires may be attributed to the Fe\(_2\)(MoO\(_4\))\(_3\) modification of MoO\(_3\) nanowires surface and the stable interface structure.

FM-500 is used as an example to explain the electrochemical process. All of these peaks originate from the phase transitions between Li\(_x\)Fe\(_2\)(MoO\(_4\))\(_3\) components with different x values (0 < x < 2). Compared with CV curves of individual MoO\(_3\) nanobelts, there are one extra oxidation peak and two reduction
FM-500 nanowires electrode at a current density of 100 mA g
transport behavior.

Fig. 7 Cyclic voltammogram curves of (a) the MoO3 nanobelts electrode, (b) FM-500 nanowire electrode, (c) FM-600 electrode scanned at 0.2 mV s\(^{-1}\). (d) Nyquist plots of the three electrodes. The inset shows the equivalent circuit.

peaks. The extra oxidation peaks around 1.6 V correspond to the removal of the first Li in Li\(_2\)Fe\(_2\)(MoO\(_4\))\(_3\), since there is an ordered Li\(_2\)Fe\(_2\)(MoO\(_4\))\(_3\) phase. The extra two reduction peaks located at ca. 0.6, 1.6 V. The peak ca. 0.6 V may result from the reduction of Li\(_2\)Fe\(_2\)(MoO\(_4\))\(_3\), associated with the Fe\(^{2+}/Fe^{3+}\) redox couple, which shifts to ca. 0.7 V from the second cycle. The peak ca. 1.6 V is ascribed to the formation of a solid electrolyte interface (SEI) layer on the electrode surface, which disappears from the second cycle. In the anodic polarization process, a broad peak centered at 1.6 V is obtained in the first and successive cycles, which is ascribed to the oxidation of Fe\(^{2+}/Fe^{3+}\) For FM-500 and F-600 electrodes, besides the first cycle, the following cycles display overlapped curves, indicating the high reversibility and stability of electrodes reaction, as shown in Fig. 7b and c.

To evaluate the electrode kinetic behaviour of the MoO3 nanobelts, FM-500 nanowires and FM-600, electrochemical impedance spectroscopy (EIS) measurements were carried out. The Nyquist plots of the three electrodes are shown in Fig. 7d. In Table S2,† the FM-500 electrode shows a much lower charge-transfer resistance than that of the pristine MoO3 nanobelts and FM-600 based on the equivalent circuit presented in the inset of Fig. 7d. Obviously, the \(R_{ct}\) is much smaller for the FM-500 nanowires electrode (ca. 68.8 \(\Omega\)) than the MoO3 nanobelts electrode (ca. 245.5 \(\Omega\)) and FM-600 electrode (ca. 128.7 \(\Omega\)), which are attributed to the backbone MoO3 nanowires in FM-500 nanowires with good conductivity and efficient electron transport behavior. Fig. S8† shows the charge-discharge voltage profiles for the first three charge-discharge cycles of the FM-500 nanobelts electrode at a current density of 100 mA g\(^{-1}\). There are three voltage plateaus observed in the discharge process, which are in accordance with the redox peaks in CV curves (Fig. 7b). Additionally, as shown in Fig. 7d, FM-500 nanowires have a obvious larger slope than the MoO3 nanobelts and FM-600, which means that the FM-500 nanowires have faster lithium-ion diffusion rates, indicating that the Fe\(_2\)(MoO\(_4\))\(_3\) nanoparticles and amorphous layer are beneficial to improve the reaction kinetics. Furthermore, the exchange current density \((i^0 = RT/nF\alpha\beta\gamma\delta)\) of the FM-500 nanowires cell was higher than those of the pristine MoO3 nanobelts and FM-600, indicating an increase in the electrochemical active sites surface area of FM-500 nanowires due to the mesoporous features of the FM-500 nanowires. On the basis of the above analyses, the outstanding electrochemical performances of FM-500 nanowires at both low and large current densities should be ascribed to the following points: (1) the continuous interfaces formed during Fe\(_2\)(MoO\(_4\))\(_3\) growth can increase the surface area and mesoporous volume that is favorable to the electrolyte diffusion; (2) the 1D structure can not only provide more sites for the adsorption of lithium ions, but also facilitate their fast intercalation and deintercalation of active species; (3) the amorphous layer directly formed on the surface of the Fe\(_2\)(MoO\(_4\))\(_3\) nanoparticles is favorable for lithium-ion diffusion and extra storage; (4) superior to MoO3 nanobelts, the strongly coupled Fe\(_2\)(MoO\(_4\))\(_3\)/MoO3 may synergistically enhance the electrochemical properties, such as electrical or ionic conductivity, reversible capacity, and mechanical stability. Thus, the novel FM-500 nanowires show great promise as anodes for LIBs.

Conclusions

In summary, for the first time FM-500 nanowires, as novel anode materials for LIBs, have been demonstrated in this study. The Fe\(_2\)(MoO\(_4\))\(_3\) nanoparticles were tightly anchored onto the surface of MoO3 nanobelts via a heteroatom diffusion method. Importantly, a conceptually straightforward approach is developed to further enhance lithium storage capacity by introducing ternary oxide and binary oxide via a heteroatom diffusion. It may also be extended to other anode and cathode materials, such as Fe\(_2\)TiO\(_4\)/Fe\(_2\)O\(_3\), Mn\(_2\)TiO\(_4\)/TiO\(_2\), NiTiO\(_3\)/TiO\(_2\) et al. These important findings could open up new opportunities for the design of novel electrodes in constructing high-performance energy storage devices.

Acknowledgements

This research was supported by the National Nature Science Foundations of China (no. 51462007, 41272064, 51272294), Guangxi Natural Science Foundation (no. 2014GXNSFAA18349) and the National Basic Research Program of China (Grant 2012CB933704).

Notes and references

