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Hierarchical NiMoO$_4$ nanowire arrays supported on macroporous graphene foam as binder-free 3D anodes for high-performance lithium storage

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A novel three-dimensional (3D) NiMoO$_4$ nanowire arrays (NWAs) grown directly onto the surface of the macroporous graphene foams (GF) with robust adhesion were synthesized via a facile chemical vapor deposition (CVD) and subsequent hydrothermal route. The as-prepared NiMoO$_4$ nanowires composed of ultra-small nanoparticles (~5 nm) with diameter of 70–150 nm and several micrometers in length. Such as-grown NiMoO$_4$ NWAs/3DGF composites are then evaluated as monolithic electrodes for lithium-ion batteries (LIBs) without the need of binders or metal-based current collectors. Benefiting from the unique three-dimensional arrayed architecture and characteristics with a high specific surface area and more active sites which facilitate fast electron and ionic transport within the electrode, the NiMoO$_4$ NWAs/GF composites deliver a high reversible specific capacity of 1088.02 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$ and 867.86 mAh g$^{-1}$ after 150 cycles (79.77% retention of the second cycle), and excellent rate capability. With the advantages of excellent electrochemical performance and facile synthesis method, the NiMoO$_4$ nanowire arrays supported on 3DGF exhibit great potential as an anode material for LIBs.

Introduction

Rechargeable lithium-ion batteries (LIBs) are widely recognized as the choice of power sources for a wide range of applications, such as portable electronic devices, electrical/hybrid vehicles, implantable medical devices and storage devices of renewable energy.$^{1-3}$ However, current commercial graphite anodes with limited specific capacity (372 mAh g$^{-1}$) and low power density give rise to a very limited energy output for LIBs.$^{4,5}$ Therefore, considerable efforts have been dedicated to explore alternative anode materials based on alloying or conversion reactions with higher reversibility and rate capacities, as well as long-term cyclic stability.$^{6-8}$

Transition metal molybdates, such as cobalt molybdates and nickel molybdates have been considered the promising candidates because the transition-metal centers for most of them possess multiple accessible valence states, which would enable a variety of reversible redox activity and reversibility, and thus generate high lithium storage properties for LIBs.$^{9-11}$ Particularly, their mixed-oxide forms exhibit far better electrochemical performance than monometallic component oxides due to the enhanced electrochemical reversibility and conductivity.$^{12-14}$ Despite these distinct advantages, transition metal oxides still suffer from kinetic problems derived from their intrinsic low electrical conductivity and slow solid-state diffusion of Li ions, as well as the concomitant volume expansion/contraction caused pulverization of electrode materials, which significantly limits its practical application in high performance LIBs.$^{15-16}$ Until now, the reported transition metal molybdates-based electrodes have been usually made by a traditional slurry-coating technique, where the involved binder has greatly decreased the electrical conductivity of the active materials, hindering the fast electron transport required by excellent cycling ability and rate capability.$^{10-11,15}$ In addition to alternative electrode materials, the rational design and fabrication of binder-free electrode architectures is also regarded as effective strategy to improve the performance for LIBs.

As an important class of nanostructures, self-supported nanowire arrays architecture grown directly on the conducting substrates has become a very promising material for nano-devices and very large-scale integrated circuits manufacturing.$^{17,18}$ Such an additive/binder-free electrode architectures can avoid the “dead surface” in traditional slurry-derived electrodes, which eliminates the need for binders and conducting additive, and then increases the
mass energy density of the batteries. Moreover, the self-supported nanowire arrays architecture provides numerous conducting channels for electron transport to the current collector, which benefit for high efficiency of ion and electron transports in the electrodes and across the electrode/electrolyte interface, therefore improving the lithium storage performance potentially.

For various conductive substrates, especially 3D graphene foam (GF) assembled by two-dimensional (2D) graphene nanosheets exhibit continuously interconnected macroporous structures, low mass density, high specific surface area, excellent electrical conductivity, which can serve as robust matrix for loading electroactive materials for improving electrochemical performance of the electrode materials. The 3D graphene matrices not only provide a conductive network for fast ion and electron transport, increase the electrolyte/electrode contact area, and maximize the utilization of active materials, but also can act as a volume buffer to absorb the internal stress due to the combination of 3D porous structures and the excellent intrinsic properties of graphene. Recently, using porous Ni foam as a template in the CVD process is an effective way to produce seamless 3DGF with high conductivity comparable to other 3D carbonaceous materials, which would facilitate the fast mass and electron transport between the active materials and current collectors in electrochemical energy storage.

Herein, we demonstrate a simple approach to fabricate 3D hierarchical NiMoO$_4$ nanowire arrays directly grown on a graphene foam (denoted as NiMoO$_4$ NWAs/3DGF) via a simple chemical vapor deposition (CVD) and subsequent hydrothermal route. The nanowires are composed of ultra-small nanoparticles (~5 nm) and further self-assembled into a hierarchical structure. When applied directly as anode for LIBs without any binders and conductive additives, the NiMoO$_4$ NWAs/3DGF electrode exhibited high lithium-storage capacity and impressive rate capability due to the unique hierarchical nanowire arrays and macroporous architecture with high electrolyte/electrode contact area, fast ion and electron transfer, and good strain accommodation.

**Experimental**

**Synthesis of NiMoO$_4$ NWAs/GF composites**

_Growth of the 3DGF:_ Nickel foams (NF, Changsha Lyrun New Material Co., Ltd, China) with an areal density of ~0.038g cm$^{-2}$ and a porosity of ~97.3% were used as 3D templates for the growth of GF by chemical vapor deposition (CVD). Briefly, prior to deposition, nickel foam cut into piece with the size of 2 cm×4 cm was degreased with acetone, etched with 1M HCl solution for 10 min, then washed by deionized water and ethanol for 10 min with sonication, respectively. After dried with nitrogen gas, the nickel foams were placed in the center of a quartz tube in a horizontal tube furnace (OTF-1200X), and samples were heated to 1050 $^\circ$C in 50 min under an Ar (50 sccm.) and H$_2$ (20 sccm.) flow. The temperature was maintained for 30 min to reduce the formation of oxides on the surface of the nickel foams. A CH$_4$ gas (5 sccm.) was then flowed for 120 min with the same amounts of Ar and H$_2$. Following the synthesis, the CH$_4$ gas was turned off and the samples were rapidly cooled to room temperature under a constant flow of Ar (50 sccm.) and H$_2$ (20 sccm.). After the growth, the resulting graphene@Ni foam structure was etched in 2M Fe(NO$_3$)$_3$ solution at 80°C for 12 hours to dissolve the nickel framework. Finally, free-standing 3DGF was obtained after washed with DI water and alcohol.

_Synthesis NiMoO$_4$ NWAs/GF composites:_ The NiMoO$_4$ NWAs/GF composites were synthesized via a facile hydrothermal approach and the subsequent thermal annealing in Ar atmosphere. In a typical experiment, 3 mmol of NiCl$_2$·6H$_2$O and 3 mmol of Na$_2$MoO$_4$·7H$_2$O were dissolved successively in 90 mL deionized water with magnetic stirring at room temperature. After 10 min, the homogeneous solution was transferred to a 100 mL Teflon-lined autoclave with two pieces of the as-prepared 3DGF immersed into the reaction solution. The autoclave was sealed and maintained at 150 $^\circ$C for 6 h, and then cooled down to room temperature. The Ni-Mo-precursors grown on 3DGF was removed, rinsed with distilled water several times, and dried in air at 60 $^\circ$C. Finally, the NiMo-precursors/3DGF composites further annealed under the protection of argon gas at 300°C for 2 h to obtain the NiMoO$_4$ NWAs/GF composites. For the comparison, NiMoO$_4$ nanowires powders were prepared by the same process only without adding the substrate of graphene foam.

**Characterization**

The phase composition and crystallographic structures of the samples were directly examined by using X-ray diffraction system (XRD, Rigaku D/max 2200PC) with Cu Kα radiation (λ=0.15418 nm). Morphology and crystalline structure of the samples were characterized with a JEOL JSM-7500F field-emission scanning electron microscope (SEM) and a JEOL JEM-2100F transmission electron microscope (TEM). For the TEM observations, the NiMoO$_4$ NWAs/3DGF composites were subjected to strong ultrasonication to detach the NiMoO$_4$ nanowires from the GF. The surface elemental composition analysis of the samples was performed by a JEOL JSM-7500F with energy dispersive X-ray spectroscopy (EDS) attachment. The specific surface area was determined by measuring N$_2$ adsorption-desorption isotherms using an ASAP-2010 surface area analyzer at 77 K.

**Electrochemical Measurements**

The CR2025-type coin cells were assembled in an Ar-filled glovebox, in which oxygen and water contents were less than 1 ppm. The as-prepared NiMoO$_4$ NWAs/GF composites were punched in the form of 12 mm diameter disks, and then used directly as the working electrode without any conductive additive or polymer binders. In order to reduce the mass uncertainty of the electrodes, the as-prepared 3DGF and NiMoO$_4$ NWAs/3DGF composites were punched in the form of 12 mm diameter disks, and then used directly as the working electrode without any conductive additive and polymer binder. Then, we took 10 pieces of samples (3DGF and NiMoO$_4$ NWAs/3DGF composites, respectively) and weighed them together. The specific mass loading of the active material (NiMoO$_4$) for the testing electrodes was about ~1.0 mg cm$^{-2}$, estimated by weighing the graphene foam before and after the loading of NiMoO$_4$ NWAs. The metallic lithium circular foil was used as both the counter electrode and the reference electrode, a microporous
polypropylene membrane (Celgard 2400) served as the separator. The electrolyte consisted of 1 M LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). In a control experiment, the NiMoO$_4$ nanowires powder electrode were prepared by mixing 80 wt.% active material, 10 wt.% conducting carbon black, and 10 wt.% polyvinylidene fluoride binder in N-methyl-2-pyrrolidone. The homogeneous slurries were then pasted on copper current collector and dried under vacuum at 60 °C for 12 h. Before the electrochemical measurements, the assembled cells were aged in the glovebox for 10 h.

Galvanostatic charge-discharge and cyclic voltammetry (CV) measurements were conducted using a LAND CT2001A battery-testing instrument and a multichannel Arbin Instruments BT2000 (USA) unit in the voltage range of 0.005-3.0 V at room temperature (25±1°C). Electrochemical impedance spectroscopy (EIS) measurements were performed using a PARSTRAT 2273 electrochemical measurement system by employing an ac voltage of 5 mV amplitude in the frequency range from 100 kHz to 0.01 Hz.

**Results and discussion**

The fabrication process of the NiMoO$_4$ NWAs supported onto the skeleton of graphene foam is schematically depicted in Scheme 1. Two main steps are required for the entire fabrication process. Firstly, 3D macroporous graphene networks was grown on the scaffold of Ni foam via a chemical vapor deposition (CVD) method and then Ni skeleton was etched away by a Fe(NO$_3$)$_3$ solution to leave from the free-standing 3DGF. Secondly, the raw materials reacted under hydrothermal conditions and formed NiMo-precursors (NiMoO$_{x}$-xH$_2$O) grown directly onto the surface of graphene foam. And then the NiMo-precursors was thermally decomposed to NiMoO$_4$ nanowire arrays supported on the graphene foam under the protection of argon gas, which can be described by the simple dehydration reaction.

The crystallographic structure and phase purity of the samples were examined by powder X-ray diffraction (XRD). As shown in Fig. 1a, the XRD patterns of as-grown graphene foam show two significant diffraction peaks at 20 = 26.5 and 54.6°, which were attributed to the (002) and (004) reflections of graphitic carbon (JCPDS 75-1621), respectively. The sharp peak at 26.5° indicates high crystallinity and an interlayer space of ca. 0.34 nm. The high crystalline structure of graphene is favorable for the ion diffusion and electron transfer. Apart from the characteristic peaks from graphene foam substrate, all other diffraction peaks originating from the NiMoO$_4$ NWAs/3DGF composites are well indexed to the standard XRD pattern of monoclinic NiMoO$_4$. (b) Nitrogen adsorption-desorption isotherm of NiMoO$_4$ NWAs/3DGF composites and inset shows the corresponding BJH pore size distribution plots.

![Scheme 1](image)

**Scheme 1.** Schematic representation of the fabrication process of NiMoO$_4$ NWAs onto skeleton of 3D macroporous graphene foam.
nanoparticles within a single NiMoO$_4$ nanowire, while the macropores and some of the large mesopores come from the void spaces between the NiMoO$_4$ nanowire and 3DGF. The specific surface areas were calculated from the Brunauer-Emmett-Teller (BET) method and the pore size distributions (PSD) were obtained by means of the Barrett-Joyner-Halenda (BJH) equation using the adsorption isotherm branch. The corresponding BET specific surface areas of NiMoO$_4$ NWAs/3DGF composites is calculated to be 70.83 m$^2$ g$^{-1}$. The pore size distribution curves of NiMoO$_4$ NWAs/3DGF composites is also shown in inset of Fig. 1h, and the average pore size in NiMoO$_4$ NWAs is in the range of 5-11 nm. The high specific surface area of NiMoO$_4$ NWAs/3DGF composites with massive mesopores and macropores, which is capable of providing sufficient electrode/electrolyte interfaces and increasing the number of reversible redox reaction sites, leads to high electrochemical capacity of the electrode material.$^{32}$

The morphology and microstructure of the as-prepared samples were investigated by field-emission scanning electron microscopy (SEM). Fig. 2a shows the optical images of the as-prepared 3DGF and NiMoO$_4$ NWAs/3DGF composites. After removal of the Ni template, the color of the nickel foam changed from shiny white to dark gray (Fig. 2a) after the CVD process, suggesting the graphene sheets successfully replicates the 3D macroporous network structure of Ni foam without collapsing and cracking. It can be seen that the 3DGF surface completely turned into light green after the growth of NiMoO$_4$ NWAs. As shown in Fig. S2a and b, the intact 3D network structure and smooth graphene skeleton with continuous macropores of hundreds of micrometers are clearly observed. The intrinsic grains and wrinkles of graphene sheets were well remained without any observable crack or break, indicating a continuous network of graphene. SEM images in Fig. S2d show that the foams are built from corrugated hollow micro-tubes to form a 3D interconnected architecture. It can be seen that the graphene micro-tube is in diameters of 30-50 μm, with thin layer graphene sheet as the wall of the micro-tube. Furthermore, it can be observed that the inner wall of graphene micro-tube seems flat, while the outside surface of the graphene micro-tube is rugged, which is consistent with the observations of Fig. S2c. Fig. 2b-e show the typical SEM images of the NiMoO$_4$ nanowires supported on 3DGF at different magnifications. It can be seen that the surface of the GF was fully covered by the grass-like NiMoO$_4$ nanowires with lengths of several micrometers. From a closer view in Fig. 2c-e, the NiMoO$_4$ nanowires has a sharp tip and the diameter of the nanowire is in the range of 70-150 nm. The composition of the as-prepared products was confirmed by EDS analysis. It is clear that there is no Ni element in the 3DGF, which indicates that nickel has been completely dissolved (Fig. S3 Supporting Information). As shown in Fig. 2f, the EDS spectrum verifies the composition of NiMoO$_4$ NWAs/3DGF composites to be Ni, Mo, O and C elements, arising from the carbon substrate can be found in this spectrum. In strong contrast, in the absence of GF, the exact same synthesis process produced NiMoO$_4$ nanowires of about 100-300 nm in diameter (Fig. S4 Supporting Information), which is several two folds thicker and aggregate severely than the nanowires in the NiMoO$_4$ NWAs/3DGF composites. The NiMoO$_4$ nanowire arrays are densely grown on 3D macroporous graphene foam with highly open space between nanowires which facilitate the electrolyte penetration into the inner region of the electrode, increase the utilization of the active materials, and accommodate volume expansion upon Li insertion. Furthermore, the direct growing of nanowires can ensure good mechanical adhesion and electrical connection to the current collector, avoid the use of polymer binders and conducting additives which generally increase the series resistance and the deterioration of specific capacity during redox reactions.

Further insight into the detailed microstructure of the nanowire in NiMoO$_4$ NWAs/3DGF composites is demonstrated by TEM. Fig. 3a is a typical TEM image of an individual NiMoO$_4$ nanowire scraped off from graphene foam, confirming their needle-like nanostructures. The NiMoO$_4$ nanowires with diameter of 70-150 nm and length up to several micrometers can be seen clearly, which are in good agreement with the SEM observations. The high-resolution TEM (HRTEM) image of the middle region shown in Fig. 3b further reveals that the NiMoO$_4$ nanowire with a rough surface was composed of lots of crystalline NiMoO$_4$ nanoparticles with a size of ca. 5 nm. Besides, irregular pores with an average size of 5-11 nm are numerous disturbed in the NiMoO$_4$ nanowire. As reported in the literatures,$^{37}$ the crystal growth mechanism of “oriented attachment” and “self-assembly” could be proposed to demonstrate the complicated nano-architecture process. The oriented attachment mechanism describes the spontaneous self-organization.
of adjacent particles, followed by the joining of these particles at a planar interface. The process is particularly relevant in the nanocrystalline regime, where bonding between the particles reduces overall energy by removing surface energy associated with unsatisfied bonds. In addition, the formation of the mesopores probably results from the successive release and loss of water molecules during the thermal decomposition of the precursors. The existence of pores in nanowires could benefit Li ion diffusion in the nanowires, providing larger contact areas with electrolyte, buffer the strain induced by the volume change, and enhance the electrochemical performance of the electrode. The high-resolution TEM (HRTEM) image in Fig. 3c reveals the interplanar spacing of 0.27 nm, corresponding to the (222) planes of NiMoO$_4$. In addition, the selected-area electron diffraction (SAED) pattern of the NiMoO$_4$ nanowire (Fig. 3d) shows a well-defined lattice, indicating their crystalline characteristics. The crystal growth mechanism of “oriented attachment” and “self-assembly” were proposed to demonstrate the complicated nano-architecture process. In the our reaction, the 3DGF were used as the “substrate”, which can guide the NiMoO$_4$ self-assembling growth in aqueous solution without surfactant and stabilizers. Then the “oriented attachment” can guide the nanoparticles oriented growth. Meanwhile, the similar phenomena can be commonly observed in NiMoO$_4$-based materials.

To further investigate the elemental composition and valence state of the as-prepared NiMoO$_4$ NWAs/3DGF composites, X-ray photoelectron spectroscopy (XPS) measurements were carried out. Fig. 4a presents the initial five consecutive cyclic voltammogram (CV) curves of the NiMoO$_4$ NWAs/3DGF electrode at a scanning rate of 0.1 mV s$^{-1}$ in the voltage window of 0.001-3.0 V. In the first cathodic scan, the two well-defined reduction peaks at around 0.58 V and 1.26 V can be corresponded to the irreversible electrochemical reduction of NiMoO$_4$ to metallic Mo and Ni, as well as the decomposition of organic electrolyte to form a solid-electrolyte interface (SEI) layer at the electrode/electrolyte interphase. Meanwhile, the two anodic peaks at around 1.34 and 1.68 V can be attributed to the oxidation of Ni to Ni$^{2+}$ and Mo to Mo$^{6+}$, respectively. In the second and subsequent cycles, two cathodic peaks located at 0.58 V and 1.26 V are shifted to 0.61 and 1.40 V, which are induced by the reversible reductive reaction of MoO$_3$ and NiO to Mo and Ni metal, respectively. It is noteworthy that the peak intensity and integral areas are almost identical from the second cycle to the fifth cycle, suggesting the good reversibility and stable...
The cycle stability and rate capability of 3DGF supported NiMoO₄ NWAs electrode and conventional NiMoO₄ nanowires electrode were investigated by galvanostatic discharge and charge measurements with various applied currents. Fig. 5c compares the cycling performance of the NiMoO₄ NWAs electrode with conventionally prepared electrode from casting NiMoO₄ nanowires based slurry on a copper current collector at a current density of 200 mA g⁻¹ at room temperature. It can be seen that the NiMoO₄ NWAs electrode shows significantly improved capacities in comparison with the conventional NiMoO₄ nanowires electrode. The capacity of the conventional NiMoO₄ nanowires electrode drops rapidly to below 590 mAh g⁻¹ after 40 cycles. In contrast, the NiMoO₄ NWAs electrode shows superior cycling performance, delivering a high reversible capacity of 867.86 mAh g⁻¹ after 150 cycles, which is about 79.77% of the reversible capacity in the second cycle. Compared to the conventional traditional slurry-coating electrode, the integrated and binder-free NiMoO₄ NWAs electrode not only avoid the use of a polymer binder and conductive additives in the preparation process of traditional slurry electrode, but also reduce the electron transfer distance and ion diffusion path obviously, and as a result, the reversible capacity especially high rate capacity can be improved. Meanwhile, the traditional slurry-derived electrode used for electrochemical evaluation seriously limits the reversibility of the electroactive NiMoO₄ because of the increased “dead surface”. Compared with other reported NiMoO₄-based materials, such as Nanocrystalline NiMoO₄ thin film (148 mA h g⁻¹ after 40 cycles), Ni₄C₁₀MoO₁₄ nanowire (520 mA h g⁻¹ at current density of 196 mA g⁻¹ after 20 cycles), and NiMoO₄ NSs/Ni foam (680 mA h g⁻¹ after 150 cycles), the NiMoO₄ NWAs electrode possesses much higher capacities and better cyclability obviously.

The rate performance of LIB anodes is highly crucial especially for high-power applications in power grids and electric vehicles. To further investigate the rate performance of the NiMoO₄@3DGF and conventional NiMoO₄ nanowires electrodes, we tested the rate performance at various current densities ranging from 200 to 3200 mA g⁻¹, which are shown in Fig. 5d. All specific reversible capacity results of the NiMoO₄@3DGF electrode fall moderately with increasing current density, and the composite electrode capacity is higher than that of the NiMoO₄ nanowires electrode in each sweep speed. Even when the current density was as high as 3200 mA g⁻¹, a capacity of around 770 mA h g⁻¹ was still available, which is higher than the theoretical capacity of the graphite anode of 372 mA h g⁻¹. More importantly, after the high rate discharge-charge cycles, a discharge capacity of about 915 mA h g⁻¹ could be resumed and maintained for another 10 cycles without obvious decay when the current density was 200 mA g⁻¹ again. The superior rate capability of the NiMoO₄@3DGF electrode is mainly attributed to the direct coupling of the active material onto the current collector thereby greatly enhancing the charge transfer properties. However, for the conventional NiMoO₄ nanowires electrode, an obvious drop in capacity is observed from the rate capability curve. This finding also corroborates the enhanced charge transfer obtained by direct coupling of NiMoO₄ nanowires on the 3DGF with highly electrical conductivity.

To further understand the electrochemical performance characteristics, we resorted to electrochemical impedance spectra (EIS) carried out at open circuit potential with an ac voltage of 5 mV amplitude in the frequency range from 100 kHz to 0.01 Hz. Fig. 6a demonstrates that the Nyquist plots of the NiMoO₄@3DGF and the NiMoO₄ nanowires electrode fall moderately with increasing frequency, which is in agreement with the reduced charge transfer distance and ion diffusion path. Optical images of the NiMoO₄@3DGF and the NiMoO₄ nanowires electrode are shown in Fig. 6b and 6c, respectively. The NiMoO₄@3DGF electrode shows significantly improved capacities in comparison with the conventional NiMoO₄ nanowires electrode. The capacity of the conventional NiMoO₄ nanowires electrode drops rapidly to below 590 mAh g⁻¹ after 40 cycles. In contrast, the NiMoO₄ NWAs electrode shows superior cycling performance, delivering a high reversible capacity of 867.86 mAh g⁻¹ after 150 cycles, which is about 79.77% of the reversible capacity in the second cycle. Compared to the conventional traditional slurry-coating electrode, the integrated and binder-free NiMoO₄ NWAs electrode not only avoid the use of a polymer binder and conductive additives in the preparation process of traditional slurry electrode, but also reduce the electron transfer distance and ion diffusion path obviously, and as a result, the reversible capacity especially high rate capacity can be improved. Meanwhile, the traditional slurry-derived electrode used for electrochemical evaluation seriously limits the reversibility of the electroactive NiMoO₄ because of the increased “dead surface”. Compared with other reported NiMoO₄-based materials, such as Nanocrystalline NiMoO₄ thin film (148 mA h g⁻¹ after 40 cycles), Ni₄C₁₀MoO₁₄ nanowire (520 mA h g⁻¹ at current density of 196 mA g⁻¹ after 20 cycles), and NiMoO₄ NSs/Ni foam (680 mA h g⁻¹ after 150 cycles), the NiMoO₄ NWAs electrode possesses much higher capacities and better cyclability obviously.

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shows the Nyquist plots of the NiMoO$_4$ NWAs/3DGF and conventional NiMoO$_4$ nanowire arrays electrodes and the fitted equivalent circuit. As shown in Fig. 6a, the Nyquist plots consist of one depressed semicircle at high-medium frequency and a sloping line at low frequency. The EIS data were fitted based on an equivalent circuit model consisting of ohmic resistance of the electrolyte and cell components ($R_\text{e}$), SEI layer resistance ($R_\text{i}$), dielectric relaxation capacitance (CPE$_i$), charge-transfer resistance at the interface between the electrode and electrolyte ($R_\text{ct}$), double-layer capacitance (CPE$_dl$), and Warburg diffusion impedance ($Z_\text{w}$), and the result is shown in Fig. 6a. The observed single semicircle is related to the combination of the surface film and charge-transfer resistance $R_{\text{(film)}}$. The fitted results reveal that the NiMoO$_4$ NWAs/3DGF electrode shows a much smaller $R_{\text{(film)}}$ (48.36 $\Omega$) as compared to that of the NiMoO$_4$ nanowire electrode (99.46 $\Omega$). suggesting that the nanosheets possess a more stable surface film (including the SEI layer) and faster charge-transfer process. To recap, the results clearly demonstrate that the NiMoO$_4$ NWAs/3DGF electrode display favorable charge-transfer kinetics and much faster electron transport, and thus exhibit the dramatically enhanced lithium storage performance.

We believe that these excellent electrochemical performances can be attributed to the rationally designed nanoarchitectures of the NiMoO$_4$ NWAs/3DGF composites. Firstly, the nanowire arrays grow directly on conductive substrates to form integrated electrode, which is regarded as beneficial to improve the electric connection between the active material and current collector, and reduce the “dead volume” and resistance possibly caused by the polymer binder. Secondly, the 3D macroporous graphene networks with high conductivity and high specific surface area are served as a double highway for electron transfer and electrolyte ions to access into the electrode interior easily, which contribute to the much improved reversible capacities and rate capabilities. Thirdly, the open space between nanowires provides large electrolyte/electrode contact area and effective electrolyte-accessible channels for ion transportation, and shortens the distance for lithium ion diffusion, which is beneficial to enhance the reaction kinetics of electrode at different rates. Therefore, the as-prepared NiMoO$_4$ nanowire arrays supported on 3DGF present a promising high performance anode system for advanced lithium-ion batteries.

**Conclusions**

In summary, self-supported NiMoO$_4$ nanowire arrays have been grown on 3D conductive graphene foams through a facile hydrothermal route together with a post-annealing treatment. These self-supported, additive-free, unique NiMoO$_4$ NWAs/3DGF composites exhibits enhanced electrochemical cycling stability and rate capability compared to the conventional NiMoO$_4$ nanowires electrode. The dramatic improvement in the LIBs performance can be ascribed to the advantages endowed by the well-ordered nanowire arrays grown directly onto the surface of macroporous graphene foams, large interfacial area for lithium insertion/extraction, and reduced ion diffusion pathways.

**Acknowledgements**

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51271012) and Innovation Foundation of Beihang University for PhD Graduates. The authors thank the Analysis and Testing Center of the School of Materials Science and Engineering of Beihang University for support.

**Notes and references**
