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To cite this article: Lin Li *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **772** 012040

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Synthesize of NiMoO₄/Reduced Graphene Oxide Composite as High Capacity Anode Material for Lithium Ion Batteries

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Abstract. NiMoO₄/Reduced graphene oxide (NiMoO₄/rGO) composites material was prepared by a hydrothermal method. When used as a anode material for lithium-ion batteries, the NiMoO₄/rGO composites show superior rate capability and excellent cycling stability. A reversible capacity of approximately 808 mAh g⁻¹ is retained even after 100 cycles at 100 mA g⁻¹. It is believed that the surface modification by graphene nanosheets contribute to the improved kinetics of lithium-ion diffusion, excellent structural stability and superior electrochemical performance.

1. Introduction

Lithium-ion batteries (LIBs) have become the most widely used energy storage systems for portable electronic devices such as laptops, mobile phones, medical microelectronic devices, and electrical vehicles due to their many outstanding features, including high energy density, no memory effect, low maintenance, and little self-discharge [1, 2]. However, the growing requirements for better LIBs requires constant innovation, in terms of improved safety, longer lifetime, smaller size, lighter weight, and lower cost [3]. Transition metal molybdates can be considered as prospective anode materials due to the ability of the metal ions to exist in several oxidation states in these oxides, ranging from 3+ to 6+ for Mo and reversibly reacting with Li delivering high capacity, at potentials lower than 2 V. Molybdenum can form stable oxides with many metals with stoichiometry, MMoO₄, where M = Co, Zn, Mn, Cu, Ni, Mg, Pb, Ca, Fe, Cd [4]. NiMoO₄ have gradually been considered as promising effective and scalable alternatives to the commercial graphite anode for LIBs in view of their excellent electrochemical performance, low-cost, environment benignity and abundance. Most importantly, NiMoO₄ has been reported to demonstrate better performance than single-component metal oxides due to its multiple feasible oxidation states, large cell parameters and comparative higher electrical conductivity (10⁻⁶ S cm⁻¹) [5]. In this work, we have prepared NiMoO₄ and NiMoO₄/rGO composites using the hydrothermal method. When the prepared materials were evaluated as anode for lithium ion batteries, they shows good electrochemical performance, in terms of rate capability, and cycling stability.

2. Experimental

All chemicals were of analytical grade and were used without further purification. GO was made using a modified Hummers method. In a typical experiment, 3 mmol of NiCl₂ 6H₂O and 3 mmol of



$\text{Na}_2\text{MoO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved successively in 40 mL GO solution (1 mL g^{-1}) with magnetic stirring at room temperature. After treating the above mixture at 180°C for 12 h in a 50 mL Teflon-lined stainless steel autoclave, it was cooled to room temperature. The product was collected, washed with deionized water and absolute ethanol, and dried in air at 80°C . For comparison, NiMoO_4 sample was also synthesized via the same procedure without the addition of GO.

Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. TEM images were taken on a JEOL JEM-2100F microscope. XPS measurements were performed on a KRATOS XSAM800 X-ray photoelectron spectrometer with a Mg K α excitation source (1253.6 eV).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 mol L^{-1} $\text{LiPF}_6/(\text{EC})$ and (DEC) (1:1). Charge-discharge tests were carried out at different current densities in the range of 0.01 V to 3.0 V. Electrochemical impedance spectroscopy (EIS) experiments were conducted in the frequency range of 0.01-100 kHz on a CHI 600A electrochemical analyzer.

3. Results and discussion

Fig. 1a illustrates the XRD patterns of the NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$ samples. All diffraction lines can be indexed to the monoclinic NiMoO_4 , according to the standard XRD data file (JCPDS file no. 12-0348). No peaks of impurities can be detected from the XRD pattern. The chemical composition and the oxidation state of the as-prepared $\text{NiMoO}_4/\text{rGO}$ composites are identified from XPS measurements and the typical survey spectra are given in Fig. 1. As shown in Fig. 1b, the observed peaks correspond to Ni 2p, Mo 3d, C 1s, and O 1s confirm the presence of Ni, Mo, C and O elements within the as-prepared $\text{NiMoO}_4/\text{rGO}$ composites, and the absence of other impurities. The peaks located at 878.6, 871.8, 860.4, and 853.9 eV identified with the binding energy of Ni 2p $_{1/2}$ and 2p $_{3/2}$. The peaks appearing at 235.2 and 232.1 eV are attributable to the binding energy of Mo 3d $_{3/2}$ and Mo 3d $_{5/2}$. The O 1s orbital spectrum exhibiting a broad peak at 530.7 eV can be fitted by oxygen in the metal–oxygen bonds (Fig. 1e). Moreover, the C 1s orbital spectrum (Fig. 1f) at 284.8 eV further confirmed the existence of the rGO.

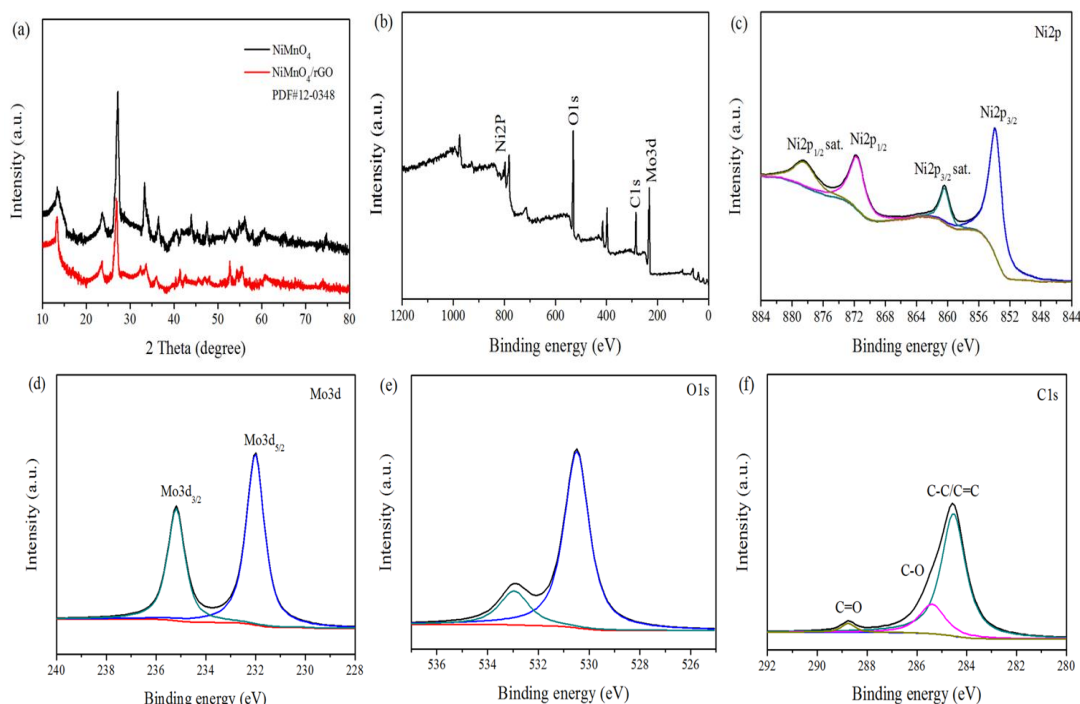


Figure 1. (a) XRD patterns of the NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$; XPS spectra of (b) survey spectrum, (c) Ni 2p, (d) Mo 3d, (e) O 1s, and (f) C 1s for the $\text{NiMoO}_4/\text{rGO}$ composites.

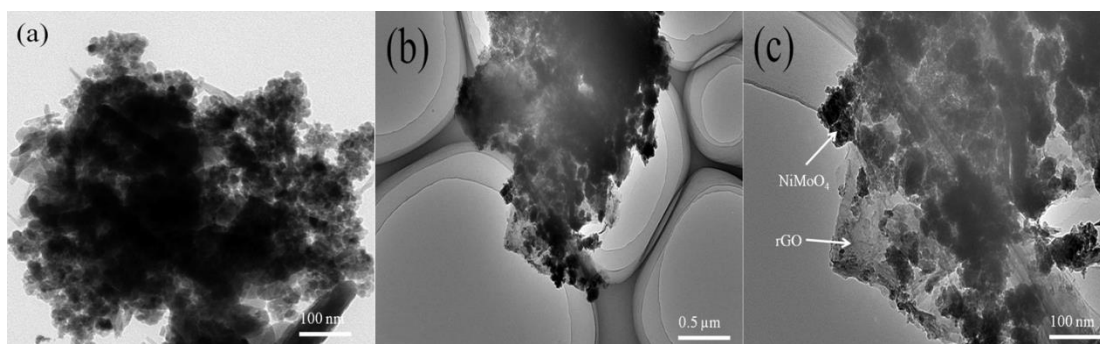


Figure 2. Typical TEM images the (a) NiMoO_4 and (b, c) $\text{NiMoO}_4/\text{rGO}$ composites.

The surface morphological features of the NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$ were investigated by TEM. As shown in Fig.2, they are all composed of non-uniform particles with different sizes. From Fig. 2a, it can be observed that the particles of the bare NiMoO_4 sample was agglomerated with the particles sized with ca. 20–100 nm. As shown in Fig. 2b and c, the surfaces of the NiMoO_4 were coated with graphene layers. Obviously, the NiMoO_4 of the $\text{NiMoO}_4/\text{rGO}$ sample maintained the identical size and morphology with NiMoO_4 , and the rGO layers are tightly anchored on the surface of the NiMoO_4 to form a composite structure. Such hybrid materials can effectively reduce the volume expansion during the lithiation and delithiation processes owing to their better mechanical strength.

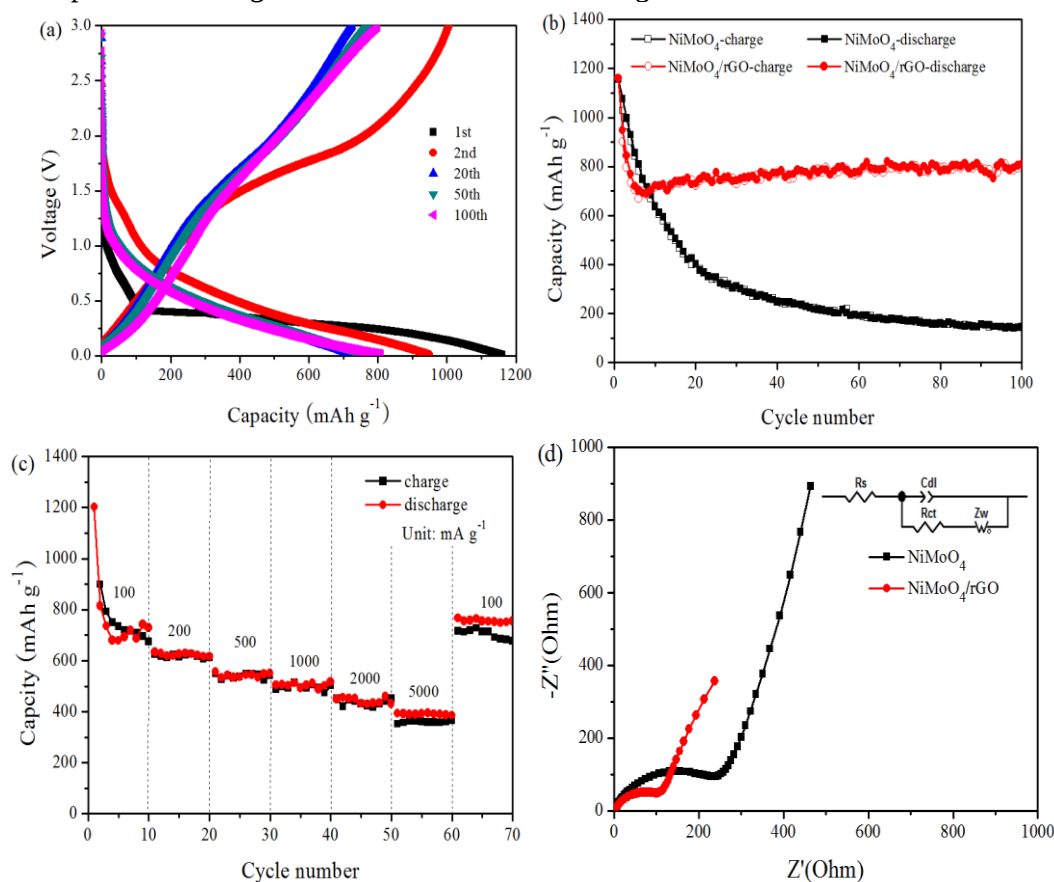


Figure 3. (a) Typical discharge/charge curves of $\text{NiMoO}_4/\text{rGO}$, (b) cycling performance of the NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$ electrodes, (c) cycling performance of the NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$ electrodes at various current densities, (d) EIS of NiMoO_4 and $\text{NiMoO}_4/\text{rGO}$.

Fig. 3a, b illustrates the electrochemical performance of all the NiMoO₄ samples as anode materials for rechargeable lithium batteries at a current density of 100 mA g⁻¹ in a potential window between 0.01 and 3.0 V (versus Li⁺/Li). The specific capacity of the NiMoO₄ showed an obvious decrease with cycling, from 1157 mAh g⁻¹ for the first cycle to 146 mAh g⁻¹ for the 100th cycle, whereas the NiMoO₄/rGO delivers a larger initial capacity of 1160 mAh/g and a high reversible capacity of 808 mAh g⁻¹ after 100 cycles, which is much higher than what was reported for pure NiMoO₄ samples. The excess capacities could be associated with the decomposition of the electrolyte at low voltages generating a solid electrolyte interphase (SEI) layer and the further lithium storage by interfacial charging at the metal/Li₂O interface. It is obvious that the NiMoO₄/rGO electrode shows much improved cycling performance with higher specific capacities at the same cycle with the same current density, as compared with the other samples, which may be attributed its bigger porous structure. To better understand the electrochemical behavior of the NiMoO₄/rGO electrode, we also investigated its rate performance as shown in Fig.3c. The cell shows good rate capability with average discharge capacity of 1203, 634, 557, 505, 449, and 393 mAh g⁻¹ when the current density increased stepwise to 100, 200, 500, 1000, 2000, and 5000 mA g⁻¹, respectively. Upon altering the current density back to 100 mA g⁻¹, an average discharge capacity as high as 766 mAh g⁻¹ could be recovered. These results demonstrate that the NiMoO₄/rGO electrode has great potential as high-rate anode material in lithium-ion batteries. To reveal the superior electrochemical performance of NiMoO₄/rGO compared with NiMoO₄ for lithium energy storage, the charge-transfer resistance was tested by EIS over the frequency domain from 0.01 Hz to 100 kHz (Fig.3d). The result showed that the resistance of the NiMoO₄/rGO electrode was 105 Ω, which is lower than that of pure NiMoO₄ (237 Ω). So, NiMoO₄/rGO shows better conductivity than NiMoO₄, that is, the NiMoO₄/rGO electrode has accommodated the high current density during the cycles. It is why NiMoO₄/rGO has a better cycling stability than NiMoO₄.

4. Conclusion

Herein, the NiMoO₄/rGO composites anode material was prepared by a hydrothermal method. When used as a anode material for lithium-ion batteries, the NiMoO₄/rGO composites show superior rate capability and excellent cycling stability. A reversible capacity of approximately 808 mAh g⁻¹ is retained even after 100 cycles at 100 mA g⁻¹, approximately 88.3% of the initial discharge capacity. It is believed that the surface modification by graphene nanosheets contribute to the improved kinetics of lithium-ion diffusion, excellent structural stability and superior electrochemical performance.

Acknowledgments

This work was financially supported by the joint science and technology funds of the Guizhou Provincial Education Department (No. KY [2014] 322 and KY [2018] 031).

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