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ARTICLE TYPE

A Flexible and Binder-free Reduced Graphene Oxide/ $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ Composite Electrode for High-performance Sodium Ion Batteries

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A novel, flexible and binder-free reduced graphene oxide/ $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ composite electrode (GNNM) is fabricated simply. Reduced graphene oxide (RGO) establishes stably electric conductive structures in the GNNM electrode. The prepared GNNM electrode delivers 86 mAh/g at 0.1C rate, and the capacity retention reaches 68.4% at 10C rate. The discharge capacity of GNNM electrode at 1C rate can reach 80 mAh/g after 200 cycles.

Energy storage devices employing abundant, affordable and environmentally friendly materials are highly concerned. The sodium resource is the 4th most abundant element and the second-lightest and smallest alkali metal next to lithium. Sodium ion battery (SIB) has similar ion intercalation/ deintercalation properties and similar redox potential to Lithium ion battery (LIB).¹⁻³ And SIB has become a promising electrochemical energy storage devices with low-cost and eco-friendly.^{4,5} Many sodium-based materials, such as Na_xMnO_2 ,⁶ Na_xCoO_2 ,⁷ $\text{P}_2\text{-Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$,⁸ $\text{Na}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$,⁹ $\text{Na}_4\text{Mn}_9\text{O}_{18}$,¹⁰ NaFePO_4 ,¹¹ Na_xVO_2 ,¹² $\text{Na}_4\text{Fe}(\text{CN})_6/\text{C}$ composite and $\text{P}_2\text{-Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ have been developed as cathode materials for SIB application.^{13,14} Recently, the electrochemical property of $\text{P}_2\text{-Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ cathode material in different potential ranges was investigated, and it showed excellent cycling stability with reversible capacity of 77 mAh g⁻¹ (1C) between 2.0V to 4.0V.¹⁵ It only could reach its theoretical capacity at lower rate of 0.05C between 2.0~4.0V, and cycling stability in 1.6~3.8 V was not as excellent as that in 2.0~4.0V. The poor electrical conductivity of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ limits its application. Many treatments of active materials especially liking carbon coating have been developed.¹⁶ Graphene has excellent physical properties with high electrical conductivity, and has been applied to LIB and Supercapacitors.^{17,18} But the effect of graphene on the electrical performances of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ has not been reported.

On the other hand, polyvinylidene fluoride (PVDF) has been widely used as binder in the electrode fabrication during commercial batteries manufacture process. But the binder will decrease the electrical conductivity. Herein, a novel, flexible and binder-free reduced graphene oxide/ $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (GNNM) composite electrode was fabricated. Reduced graphene oxide (RGO) was prepared by the reduction of graphene oxide synthesized by a modified Hummer's method.¹⁹ RGO was characterized by an atomic force microscope (AFM) and X-ray

photoelectron spectroscopy (XPS). Fig.1a presents the AFM morphological image and the corresponding cross section analysis of RGO. The thickness of RGO is approximately 0.7nm and matches well with the reported value in the literature,²⁰ indicating that a single layer RGO sheet has been fabricated successfully. Fig. 1b shows XPS survey spectrum of RGO. The residual oxygen functionalities were detected on the sample. Deconvolution reveals the presence of C-C (284.8eV), C-O (286.2eV) and C=O (287.8eV) species. The oxygen/carbon atomic (O/C) ratio of RGO is 9.2%, suggesting this sample is highly reduced graphene oxide.²¹ Fig.2a shows fabricating process of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ materials and GNNM electrode. New sol-gel method based on agarose was applied to synthesis nano-sized $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ materials (See S1 of ESI). For preparation of GNNM electrode, 30wt% RGO and 70wt% $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ materials were ultrasonic dispersed in ethanol solution and then vacuum filtrated to obtain GNNM electrode (See S1 of ESI).

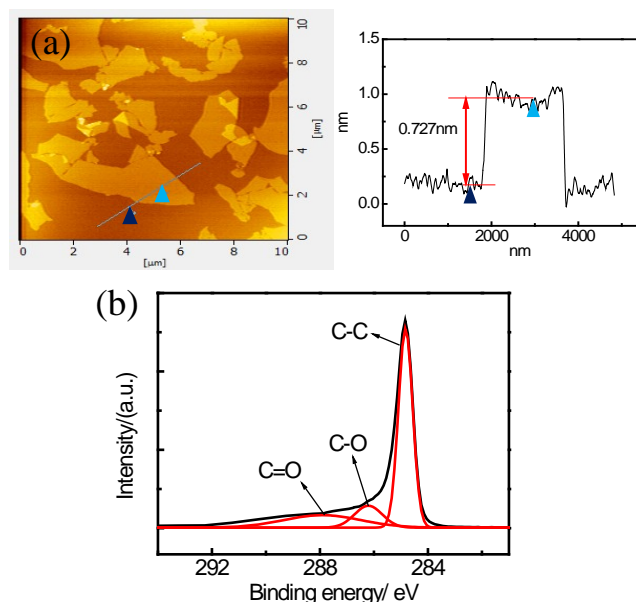


Fig.1 (a) Tapping mode AFM image and the corresponding cross section analysis of RGO; (b) XPS C 1s spectrum of RGO.

Fig.2b shows XRD patterns of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ material and GNNM electrode. The peaks of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ are well consistent with standard $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ pattern expect two

inconspicuous peaks of unknown phases. A broad diffraction peak of GNNM electrode at about 25 degree corresponds to the average d-spacing of RGO layers.²² From thermogravimetric analysis (TGA), the content of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ in the composite electrode is 69.8%, which is kept consist with our designs (See S2 of ESI).

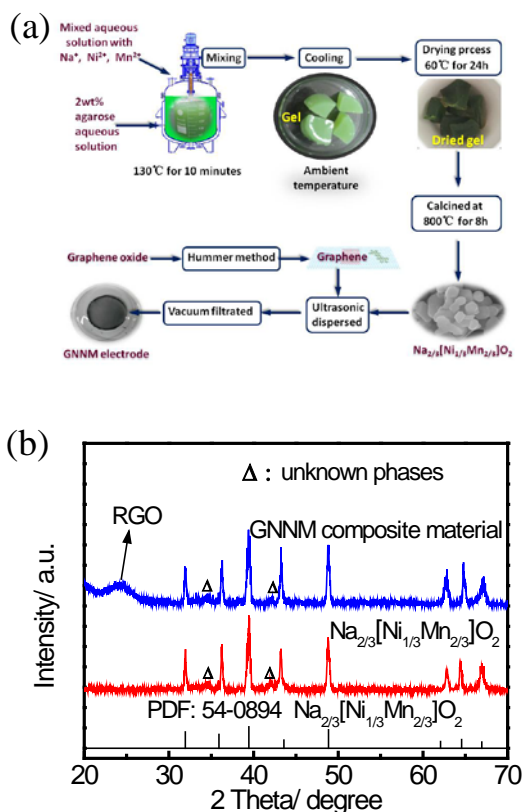


Fig.2 (a) Schematic of fabricating process of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ materials and GNNM electrode. (b) X-ray diffraction patterns of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and GNNM electrode.

SEM image of GNNM electrode is depicted in Fig.3a. It can be seen, the prepared $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ particles reach about 300 nm diameters and are encompassed by RGO well. In our work, the fabrication processes of GNNM electrode only need ultrasonic dispersion and vacuum filtration. During vacuum filtration of mixed ethanol solution, $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ particles will be wrapped up by RGO layer by layer, as shown in Fig.3b. From the view of the edge, RGO tends to stack disorderly to form electrical conductive structure rather than order stacking liking graphene paper (See S3 of ESI). It may due to that $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ partials are much larger than the gap distance of RGO sheet and cannot be embedded into the gap effectively.

Compared with normal electrode used in batteries, the prepared GNNM electrode is totally binder-free and flexible and strong enough for folding and punching without cracking, as shown in Fig. 4. More importantly, the prepared GNNM electrode is stably in the 1.0 M $\text{NaClO}_4/\text{EC}+\text{PC}$ (1:1, v/v) electrolyte. After one month sorted in this electrolyte, it can be found that no decomposition is appeared (See S4 of ESI). These indicate that the strong connection between RGO and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ partials is formed by the π - π bonds of RGO.

In order to evaluate the electrochemical performances of GNNM electrode, CR2016 coin cells were assembled with Na metal as counter electrode. A normal electrode composited of 70% $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$, 15% Super P and 15% PVDF was prepared and tested in the same condition for comparison. Fig. 5a shows the charge/discharge curves of GNNM electrode at different rates. According to $1/3 \text{ Na}^+$ of $\text{P2-Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ per unit reversibly extracted and inserted between 2.0V to 4.0V, the theoretical capacity of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ can be calculated to be 86.3 mAh/g. In our results, GNNM electrode delivers 86 mAh/g at 8.63 mA/g (0.1C), which is approaching the theoretical capacity. The charge/discharge profiles of GNNM electrode and normal electrode at 1C rate are illustrated in Fig. 5b, and their coulomb efficiencies of both electrodes reach about 99% in the first cycle. On account of the high electrical conductive structure constructed by RGO, GNNM electrode displays 83 mAh/g discharge capacity, while only 76 mAh/g for normal electrode.

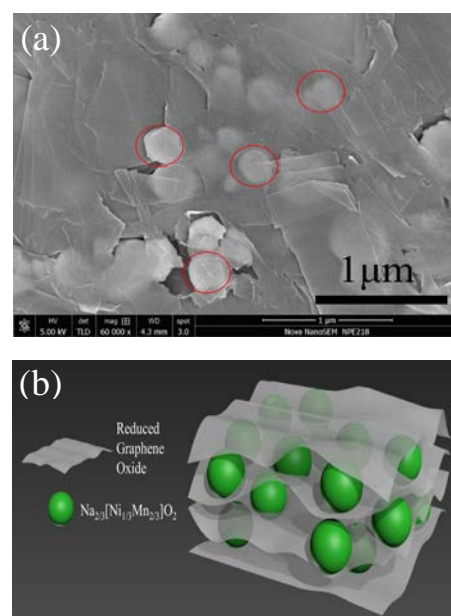


Fig.3 (a) SEM image of GNNM electrode; (b) Schematic of GNNM electrode.

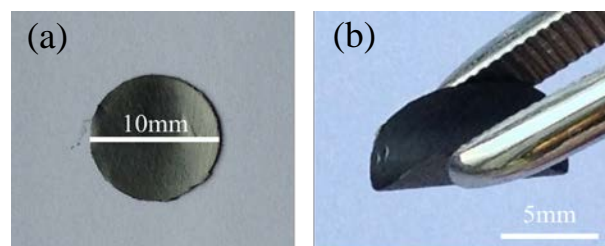


Fig.4 (a) Front view and (b) Side view of flexible and binder-free GNNM electrode.

Fig. 6a shows the rate performances of GNNM electrode and normal electrode. With increasing charge/discharge rate, big distinctions of discharge capacity between GNNM and normal electrode are performed. When both electrodes are charged/discharged under as high as 10C rate, compared with 0.1C rate, capacity retention of GNNM electrode reaches 68.4%, as well as only 54.5% for normal electrode.

As we all know, the rate performances of the cell are related with the electrode resistance directly, and the conductivity of electrode can be measured by four probes method. The thickness, area and quality of electrode are three important factors which influence on measuring results. But in our experiments, it is hard to control these three factors of GNNM electrode and normal electrode to keep consistent simultaneously. Therefore, the resistances of both electrodes were measured directly by using multi-functional ammeter and normalized to per active materials. The specific resistance of normal electrode is $15 \Omega/\text{mg}$ and about 7.5 times larger than GNNM electrode ($2 \Omega/\text{mg}$). We further investigated electrochemical impedance spectra (EIS) on the GNNM electrode and normal electrode after three cycles. As shown in the Nyquist plots (Fig. 6b), the charge transfer resistance of GNNM electrode markedly decreased compared with normal electrode. These results indicate that the introduced RGO can reduce the resistance of the electrode and more high performance battery can be attained. Meanwhile, the ionic conductivity of GNNM electrode and normal electrode were also a little different. That maybe due to that the PVDF in the normal electrode would limit the fast transfer of Na ion and thus change the ion conductivity (See S5 of ESI).

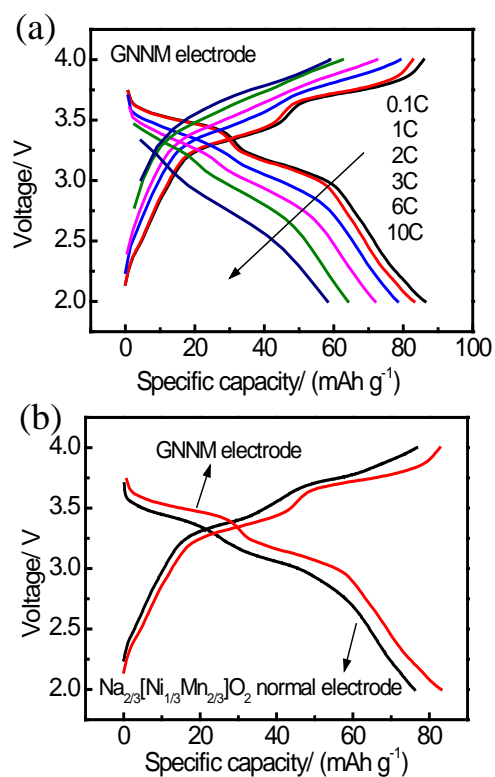


Fig.5 (a) The galvanostatic charge–discharge profiles of GNNM electrode at different rates; (b) The first galvanostatic charge–discharge profiles of GNNM electrode and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ normal electrode.

Moreover, the cycle performances of the prepared GNNM electrode and normal electrode were also investigated at charge/discharge of 1C rate. Fig. 6c shows the coulombic efficiencies (CE) and cycle performances of the GNNM electrode and the normal electrode at 1C rate. The CE of both electrodes reached from 99% to 99.8% and kept stable upon cycling. The

normal electrode shows excellent cycle performances as well as GNNM electrode. The small particle sizes of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and strong connections between RGO and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ may be important factors. The discharge capacity of GNNM electrode at 1C rate can reach 80 mAh/g after 200 cycles, indicating the prepared GNNM electrode to be a promising electrode for SIB application.

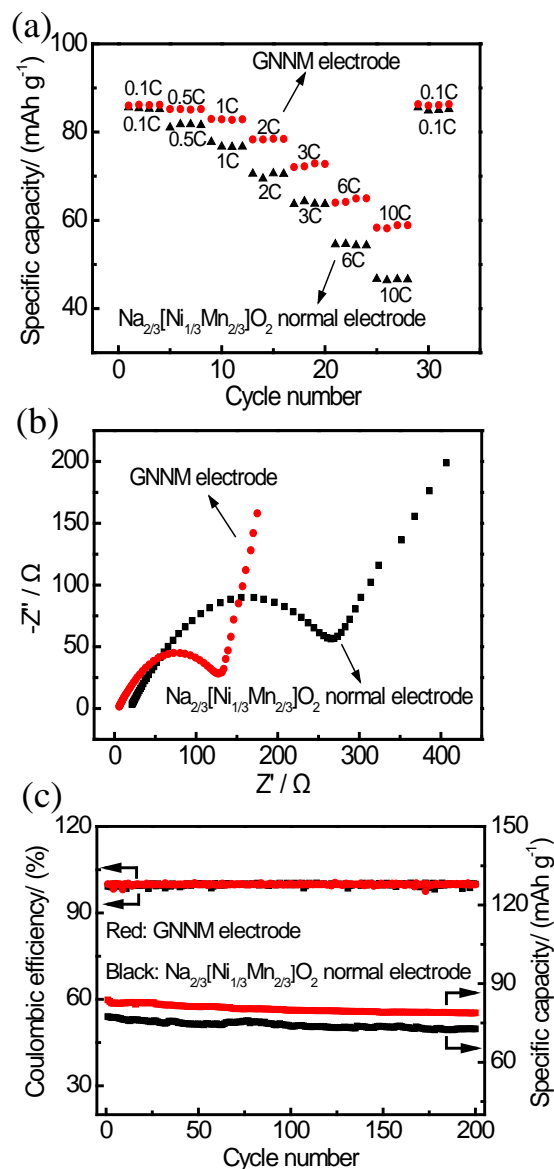


Fig.6 (a) Rate capabilities of GNNM electrode and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ normal electrode at different rates; (b) The Nyquist plots of GNNM electrode and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ normal electrode charge/discharge after 3 cycles; (c) Coulombic efficiencies and cyclic performances of GNNM electrode and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ normal electrode at 1C rate.

In summary, a novel, flexible and binder-free GNNM electrode has been successfully prepared by simple ultrasonic dispersion and vacuum filtration. The π - π bonds of RGO promise the strong connection between RGO and $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ particles. Compared with normal electrode preparation process, the improved electrical conductivity of GNNM electrode may be a result of the binder-free and the excellent physical properties of

RGO. Without employing a metal current collector or a polymeric binder, GNNM electrode delivers specific capacity of 83 mAh/g at 1C rate and is close to the theoretical capacity of $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}]\text{O}_2$. Furthermore, 68.4% capacity retention of the prepared GNNM electrode can still be maintained at 10C rate. The excellent cycle performances are also presented that after 200 cycles with the specific capacity of 80 mAh/g. The GNNM electrode reported in this work demonstrates a new electrode design and preparation process for enhancing the rate performances, and it can be applied as a novel electrode assembly for developing high power density sodium ion battery.

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Notes and References

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