Alkali ions pre-intercalation and reduced graphene coating of MnO₂ for high-capacity Li-ion battery

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Abstract—MnO₂ is considered to be a prospective material for lithium-ion batteries anode. However, in practical applications, MnO₂ has shortcomings such as low conductivity, large volume change and high charge transfer resistance, which seriously hinder its commercial application. In this work, MnO₂ are pre-intercalated with various alkali cations (Na^+, or NH_4^+) and coating with reduced graphene oxide through electrodeposition which designed for LIBs to improve its electrochemical behavior and understand the effect of cations and coating. It demonstrates that alkali cations can affect the growth morphology and electrochemical performance of MnO₂, and graphene can improve electrical conductivity. Due to the advantages of its structure, $MnO_2\&NH_4^+@rGO$ shows high capacity, rate performance (640 mAh g^{-1}) and a long lifetime in lithium-ion batteries.

1. Introduction

Due to the increasingly prominent energy and greenhouse gas issues, people's demand for energy storage equipment is increasing. Lithium-ion batteries (LIBs) have received widespread attention from people which has been widely used because of its high energy density and a long lifetime during cycles [1–3]. However, the energy density of lithium batteries is gradually unable to meet the growing demand of people. One of the important factors affecting the energy density of batteries is the anode material. One of the most important anode materials is the graphite, which was used for most lithium batteries, but shows a theoretical specific capacity of about 350 mAh g^{-1}, this specific capacity is not meet commercialization requirements [4, 5]. MnO₂ is considered a promising material as an anode material for lithium-ion batteries, which due to its high theoretical capacity (1230 mAh g^{-1}), abundant Resources, and low oxidation /reduction potential.

However, the practical application of MnO₂ in Li-ion batteries still faces many problems and challenges. MnO₂ is easily soluble in electrolytes and shows low conductivity, which will lead to low material utilization and low mass specific capacity. In addition, some studies have shown that the traditional preparation of MnO₂ electrode usually need conductive agents and adhesives, which not only does not contribute to the electrode

capacity, but also increases the electrode volume. The electrodeposition method has advantages such as rapid synthesis, low cost, and simple operation. And the materials prepared by the electrodeposition method are mostly nanostructures. Many researchers used electrodeposition methods to prepare manganese dioxide, which typically exhibited a higher specific capacitance. However, although manganese dioxide prepared by electrodeposition has high capacitance, its cycling performance is often unsatisfactory due to Jahn-Teller effect. Although many research works were proposed to improve the energy density and lifetime of manganese dioxide electrodes. However, it is often difficult to solve both specific capacity and cycle stability problems simultaneously with simple processes.

Herein, we propose a facile electrodeposition method to enable high capacity MnO₂ anode. MnO₂ are pre-intercalated with various alkali cations (Na^+, or NH_4^+) and coating with reduced graphene oxide through electrodeposition which designed for LIBs to improve its rate performance, structural and electrochemical cycling stability and understand the effect of cations and coating.

2. Experimental details

All MnO₂ electrodeposition experiments were conducted using electrochemical workstation (CHI 660e), with the Ag/AgCl as the reference, and Ni foam as the working electrode. MnO₂ electrode was prepared in 0.1 M

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Manganese acetate solution at a constant potential of 0.7 V last about 1 min. $MnO_2\&Na^+@rGO$ and $MnO_2\&NH_4^+@rGO$ were prepared by electrodeposition in a mix solution of 0.06 M $Mn(CH_3COO)_2$ and 1mM Na_2SO_4 or CH_3COONH_4 at a potential of 0.6 V for 1min firstly. Then, $MnO_2\&Na^+@rGO$ and $MnO_2\&NH_4^+@rGO$ were deposited at a constant potential of -1.4 V vs. Ag/AgCl with graphene oxide solution as the precursor [6].

All the structures of MnO_2 were observed by SEM. Both of the Cyclic Voltammetry (CV) and

Electrochemical Impedance Spectroscopy (EIS) tests were performed using electrochemical workstation (CHI 660e). To estimate the Electrochemical properties of MnO_2, CR2032 cells were assembled using Li metal as the anode. All the electrochemical performance of the half cells were estimated with a potential range from 0.01 to 3.0 V using LAND battery system.
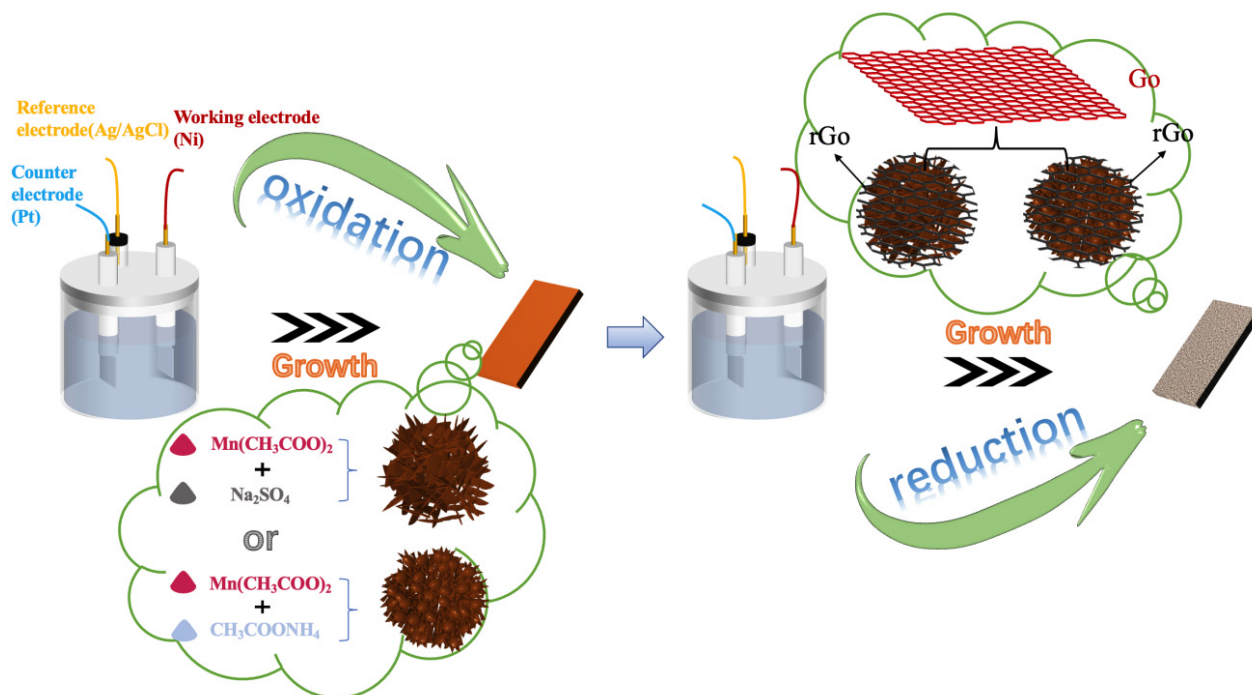
3. Results and Discussion

Fig.1 The schematic diagram of MnO_2 construction

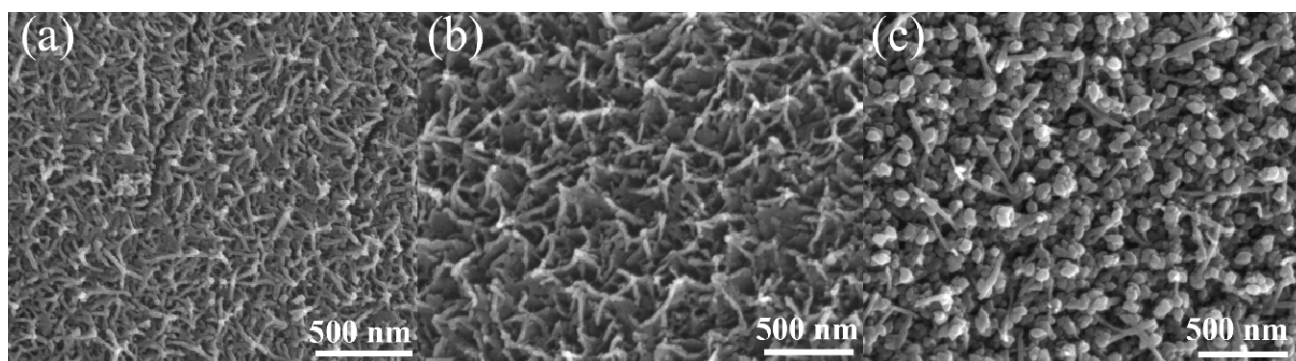Fig. 1 illustrates our method to synthesize MnO_2 through a simple electrodeposition method.

Fig.2 The SEM images. (a) bare MnO_2, (b) $MnO_2\&Na^+@rGO$ and (c) $MnO_2\&NH_4^+@rGO$.

Fig. 2 displays the SEM images of bare MnO_2, $MnO_2\&Na^+@rGO$ and $MnO_2\&NH_4^+@rGO$. It can be clearly seen that the pre intercalation of cations will significantly change the morphology and structure of MnO_2. The surface of bare MnO_2 is relatively dense,

which is not advantageous to the transmission and electrons move. $MnO_2\&Na^+@rGO$ shows 3D network structure, interconnected and porous manganese dioxide can increase the contact area with the solution, ensuring rapid electron transmission. $MnO_2\&NH_4^+@rGO$ exhibits

a fine nanorod structure, which is far from MnO_2 and $MnO_2\&Na^+@rGO$. The structure which with a larger specific surface area is conducive to rapid electron and ion transfer, which is conducive to improving the kinetics of electrochemical reactions. Pre intercalation of Alkali ions can increase the layer spacing of manganese dioxide and broaden the ion channel which is conductive to the improvement of MnO_2 electrochemistry.

In order to assess the electrochemical properties of all MnO_2, CR2032 coin cells were assembles using Li metal as the anode. Fig.3(a) shows the EIS spectrum of different MnO_2 cells. $MnO_2\&NH_4^+@rGO$ displays a lower resistance and confirm the effectiveness of the alkali cations pre intercalation and rGO coating. The rate electrochemical performance of different cells is displayed in Fig. 3(b), $MnO_2\&Na^+@rGO$ and $MnO_2\&NH_4^+@rGO$ exhibit a high specific capacity than bare MnO_2. $MnO_2\&NH_4^+@rGO$ shows the high capacity of 640 mAh g^{-1} at 0.2 A g^{-1}, which is almost 2 times than that of bare MnO_2 (350 mAh g^{-1}). In addition, even at a high current density of 5 A g^{-1}, $MnO_2\&NH_4^+@rGO$

exhibits a capacity of about 300 mAh g^{-1}, bare MnO2 shows 50 mAh g^{-1} only. The good rate performance of $MnO_2\&NH_4^+@rGO$ proved the superiority of the structure. It is worth noting that in ammonium ions, nitrogen has a strong negative charge, which facilitates the rapid migration and movement of cations in MnO_2 which can improve the electrochemical performance. However, due to the electrostatic force, Na ions have a certain degree of repulsion with cations. In the subsequent cycles, all cells show an increased specific capacity, which is due to the activation process and generations of some polymers. this phenomenon was observed in many transition metal oxides report [7]. As shown in Fig. 3(c), $MnO_2\&NH_4^+@rGO$ shows the highest capacity than bare MnO_2 and $MnO_2\&Na^+@rGO$, which is consistent with the pervious analysis. Benefitting from the enhanced electrochemical process, $MnO_2\&NH_4^+@rGO$ displays a good specific capacity of about 640 mAh g^{-1} after 200 cycles at the current of 0.2 A g^{-1}.
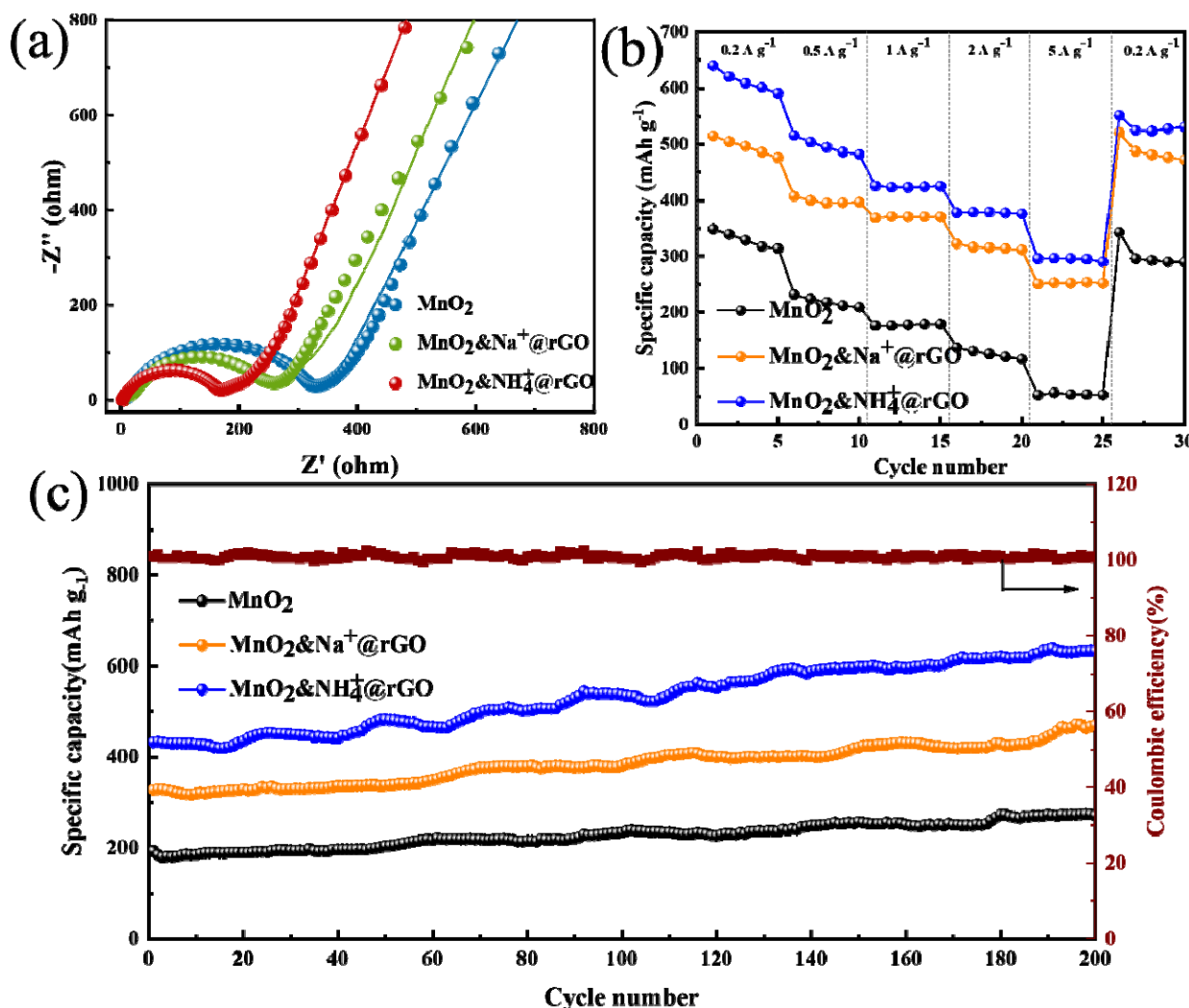

Fig.3 Electrochemical performance of MnO_2, $MnO_2\&Na^+@rGO$ and $MnO_2\&NH_4^+@rGO$.cells. (a) EIS spectrum. (b) Rate performance. (c) Cycle performance.

4. Conclusion

In summary, MnO_2 are pre-intercalated with various alkali cations (Na^+, or NH_4^+) and coating with reduced graphene oxide through electrodeposition which designed for LIBs to improve its electrochemical behavior and understand the effect of cations and coating. SEM results shows that alkali cations can affect the growth morphology of MnO_2, increase the specific surface area and improve the contact between electrode materials and electrolytes. EIS results shows that pre-intercalated cations and graphene coating can improve the electrical conductivity, lower the charge resistance. Due to the advantages of its structure, $MnO_2\&NH_4^+@rGO$ shows the highest rate performance (of about 640 mAh g^{-1}), and a long cycle lifetime in lithium-ion battery. This work may provide a promising design idea for lithium-ion battery anodes.

Acknowledgments

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