Sb$_2$MoO$_6$ Decorated on Graphene as an Anode Material for Lithium/Sodium-Ion Batteries

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Abstract. The ternary materials have attracted wide attention owing to the synergistic effect and multi-component flexibility. Herein, Sb$_2$MoO$_6$ decorated on graphene (Sb$_2$MoO$_6$/RGO) is synthesized and proved to be a novel anode material for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs). Benefiting from the conductive networks of graphene and the synergistic effect between two metal elements, Sb$_2$MoO$_6$/RGO shows the improved electrochemical performance, including a high reversible capacity of 967.2 mAh g$^{-1}$ for LIBs and 349.4 mAh g$^{-1}$ for SIBs at 100 mA g$^{-1}$, an excellent cycle performance of 606.8 mAh g$^{-1}$ for LIBs after 55 cycles and 264.9 mAh g$^{-1}$ for SIBs after 100 cycles at 100 mA g$^{-1}$. Therefore, Sb$_2$MoO$_6$/RGO has a wide application prospect for both the LIBs and SIBs.

1. Introduction

In view of the increasingly scarce natural resources and serious energy problems, more excellent energy storage devices need to be discovered and exploited [1]. Meanwhile, lithium-ion batteries (LIBs) have been applied to small portable devices owing to the environmentally friendly and high energy density [2]. Unfortunately, the development of LIBs is also limited, which cannot meet the needs of large-scale power grids because of their high cost and poor cycle life [3]. Sodium-ion batteries (SIBs), as an alternative of LIBs, have been widely researched due to the similar electrochemical properties and a wealth of sodium resources [4]. Unfortunately, the large-scale application of SIBs is still limited by the important performance metrics (include cycle lifetime and power density). To extend the application area and enhance the electrochemical performance of LIBs/SIBs, it is urgent to develop a potential anode material, especially with low cost and high performance.

Among a lot of anode materials, Sb-based materials have caused high concern owing to their low-cost, higher capacity, and environmentally friendly [5,6]. However, poor conductivity and large volume change will affect their electrochemical performance, that is, this leads to the slower electronic/ionic transmission speed and the pulverization and agglomeration of particles during cycling [7,8]. The most promising strategy is to combine advanced carbon materials with these Sb-based materials, which can conquer the above problems [9]. Graphene has been confirmed to be a promising matrix due to its exceptional mechanical properties, excellent electronic conductivity, and large surface area [10-12]. Therefore, the introduction of graphene can enhance the conductivity and alleviate the volume expansion of particles [13,14]. Actually, the construction of Sb-based ternary materials is also an effective strategy, which can demonstrate good electrochemical behaviors [15,16]. More importantly, compared with single metal oxides, the bimetallic compositions show the superior electrochemical activity via the synergy between two metal elements [17,18]. Moreover, the second
inert metal can act as a buffer matrix, which can effectively buffer the volume change [19]. As a typical ternary oxide, the layered structure of Sb$_2$MoO$_6$ consists of \{Sb$_2$O$_2$\}$^{2n+}$ and \{MoO$_4$\}$^{2n-}$, which could exhibit remarkable physical properties (include pyroelectricity and piezoelectricity) [20]. Thus, it is quite interesting to explore Sb$_2$MoO$_6$/RGO composites and study their lithium/sodium-ion storage performance.

Herein, using a simple hydrothermal method, Sb$_2$MoO$_6$ particles decorated on graphene (Sb$_2$MoO$_6$/RGO) was successfully prepared, which is served as anode material for LIBs/SIBs. The Sb$_2$MoO$_6$/RGO shows extraordinary electrochemical performance for LIBs (high reversible capacity of 967.2 mAh g$^{-1}$ and a remarkable cycle performance of 606.8 mAh g$^{-1}$ after 55 cycles at 100 mA g$^{-1}$). Meanwhile, The Sb$_2$MoO$_6$/RGO also shows extraordinary electrochemical performance for SIBs (high reversible capacity of 349.4 mAh g$^{-1}$ and an excellent cycle performance of 264.9 mAh g$^{-1}$ after 100 cycles at 100 mA g$^{-1}$).

2. Experimental Section

2.1. Synthesis of Sb$_2$MoO$_6$/RGO

Typically, 0.2 g Na$_2$MoO$_4$ was dissolved in 20 mL GO aqueous solution (2.5 mg/mL) and then SbCl$_3$ ethanol solution (0.3711 g SbCl$_3$ in 10 mL ethanol) was moved into the solution under vigorously stirring for 10 min. Subsequently, the mixture solution was moved into a Teflon-lined autoclave, which was heated at 180 °C for 24 h. At last, the resulting products (denoted as Sb$_2$MoO$_6$/RGO) were washed and centrifugated and then freeze-dried.

2.2. Electrochemical Measurements

The working electrode was constructed by the acetylene black, polyvinylidene fluoride (PVDF), and active materials with the weight ratio 10:10:80. The homogenous slurry was prepared in N-methyl-2-pyrrolidone (NMP) and spread on the Cu foil. The working electrode was dried at 100 °C for 12 h. The assembly process of the coin cell (CR2025) was performed in the Ar-filled glovebox. LIBs were assembled using the as-prepared anode, 1 M LiPF$_6$ in EC/DMC/EMC (1:1:1 Vol%) as the electrolyte, Celgard 2400 as the separator, and lithium metal foil as the counter electrode. SIBs were assembled using the as-prepared anode, 1 M NaClO$_4$ in EC/DEC (1:1 Vol%) with FEC (5 Vol%) as the electrolyte, sodium metal foil as the counter electrode, and glass fiber as the separator. The active materials on the electrode are about 0.6-0.8 mg.

3. Results and Discussion

Figure 1 illustrates the preparation process for Sb$_2$MoO$_6$/RGO composite, in which Sb$_2$MoO$_6$/RGO is synthesized by a hydrothermal method. First, Na$_2$MoO$_4$ and SbCl$_3$ ethanol solution are successively dissolved in GO aqueous solution under vigorously stirring. At the end of the hydrothermal method, it can easily obtain the Sb$_2$MoO$_6$/RGO composite. In conclusion, the Sb$_2$MoO$_6$/RGO composite is directly synthesized by the common raw materials and a facile hydrothermal method could be used to provide the low-cost and eco-friendly anode material.

![Figure 1. Schematic for the formation of Sb$_2$MoO$_6$/RGO.](image)
The crystal structure and phase purity are observed using X-ray diffraction (XRD) pattern. As shown in Figure 2, the diffraction peaks can be well indexed to the Sb$_2$MoO$_6$ (PDF No. 33-1491) without extra peaks. The above results confirm that the Sb$_2$MoO$_6$ particles have good crystallinity and high purity.

![Figure 2. XRD pattern of Sb$_2$MoO$_6$/RGO.](image)

To analyze the detailed microstructure and morphologies of Sb$_2$MoO$_6$/RGO, scanning electron microscopy (SEM) is investigated. The low-resolution SEM image shows the two-dimensional (2D) thin graphene sheets (Figure 3a). The high-resolution SEM image of Sb$_2$MoO$_6$/RGO is shown in Figure 3b. The Sb$_2$MoO$_6$ particles are decorated on graphene sheets without aggregation. The combination of Sb$_2$MoO$_6$ particles and graphene can enhance the conductivity and alleviate the volume expansion of particles.

![Figure 3. (a) Low and (b) high-resolution SEM images of Sb$_2$MoO$_6$/RGO.](image)

To analyze the Li-storage mechanism of Sb$_2$MoO$_6$/RGO, the Li$^+$ half cells coupled with lithium foil are assembled. The discharge/charge curves of Sb$_2$MoO$_6$/RGO at 100 mA g$^{-1}$ are tested (Figure 4a). In the initial cycle, two potential plateaus can be clearly observed. The obvious plateau at about 1.65 V can be observed and disappears in the following cycles, which can be attributed to the irreversible dissolution of Sb$_2$MoO$_6$ and the formation of the solid electrolyte interface (SEI) layer [20]. The plateau at 0.8 V is assigned to the following reversible Sb-Li alloying reaction, which is holding steady in the subsequent cycles. Furthermore, the Sb$_2$MoO$_6$/RGO delivers initial discharge/charge capacities of 1201.4/967.2 mAh g$^{-1}$ and high Coulombic efficiency (CE) of 80.5%. Nevertheless, the capacities show a slight decay and the Sb$_2$MoO$_6$/RGO delivers the discharge/charge capacities of 1000/976 mAh g$^{-1}$ in the 2nd cycle. In the 10th cycle, the Sb$_2$MoO$_6$/RGO shows the high and stable discharge/charge capacities of 933.7/913.2 mAh g$^{-1}$, demonstrating the well Li-storage performance. In the subsequent cycles, the discharge/charge curves show similar shapes, indicating the well reversible electrochemical process. The cycle performance of Sb$_2$MoO$_6$/RGO at 100 mA g$^{-1}$ is exhibited (Figure 4b), the Sb$_2$MoO$_6$/RGO delivers the high reversible capacity of 606.8 mAh g$^{-1}$ after 55 cycles with the capacity retention of 62.7%. Interestingly, the initial CE is 80.5% due to the formation of the irreversible SEI layer. Subsequently, CE of Sb$_2$MoO$_6$/RGO gradually rises and then up to 97.6% after 2 cycles. Meanwhile, the CE can remain more than 93% throughout the 55 cycles.
To analyze the Na-storage mechanism of Sb$_2$MoO$_6$/RGO, the Na$^+$ half cells coupled with sodium foil are assembled. The discharge/charge curves of Sb$_2$MoO$_6$/RGO are shown in Figure 5a at 100 mA g$^{-1}$. Two potential plateaus at about 1 V and 0.5 V can be clearly observed in the initial cycle, which can be assigned to the irreversible dissolution of Sb$_2$MoO$_6$, the formation of the SEI layer, and Sb-Na alloying reaction, respectively. Furthermore, the initial discharge/charge capacities of Sb$_2$MoO$_6$/RGO are approximately 660.4/349.4 mAh g$^{-1}$ with the initial CE of 52.9%. Subsequently, in the 2nd cycle, the Sb$_2$MoO$_6$/RGO delivers the discharge/charge capacities of 382.3/379.3 mAh g$^{-1}$. It is important to note that the Sb$_2$MoO$_6$/RGO shows the high and stable discharge/charge capacities of 409/398.1 mAh g$^{-1}$ in the 10th cycle, indicating the reversible Na-storage behavior during cycling. As shown in Figure 5b, the cycle performances of Sb$_2$MoO$_6$/RGO at 100 mA g$^{-1}$ are tested. Sb$_2$MoO$_6$/RGO delivers a high reversible capacity of 264.9 mAh g$^{-1}$ with a high capacity retention of 75.8% after 100 cycles. While the initial CE for the Sb$_2$MoO$_6$/RGO is 52.9%, the CE of the Sb$_2$MoO$_6$/RGO shows the slight fade in the second cycle and can remain more than 97% throughout the 100 cycles.

4. Conclusions
In summary, the Sb$_2$MoO$_6$ decorated on graphene (Sb$_2$MoO$_6$/RGO) is successfully synthesized using a hydrothermal treatment method. The bimetallic-based ternary materials can show good electrochemical activity owing to the synergistic effect of two metal elements. Meanwhile, the combined graphene with the Sb-based materials can avoid the volume change and agglomeration of Sb$_2$MoO$_6$ particles. Overall, based on the above electrochemical characterization, Sb$_2$MoO$_6$/RGO exhibits excellent electrochemical performance as the anode material for LIBs/SIBs.
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