A novel graphene modified $LiMnPO_4$ as a performance-improved cathode material for lithium-ion batteries

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A novel graphene-modified $LiMnPO_4$ composite as a performance-improved cathode material for lithium-ion batteries has been prepared with LiH_2PO_4, $Mn(CH_3COO)_2{\cdot}4H_2O$, and graphite oxide (GO) suspension by spray-drying method. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and galvanostatic charge–discharge tests are applied to characterize these materials. The structure analysis shows that $LiMnPO_4$ sheets with width of 100–200 nm and thickness of 20–30 nm are attached to the graphene sheets in pieces. The graphene sheets with good electrical conductivity serve as a conducting network for fast electron transfer between the active materials and charge collector, as well as buffered spaces to accommodate the volume expansion/contraction during the discharge/charge process. The electrochemical tests show that the composite cathode material could deliver a capacity of 105.1 mAh/g at 0.05 C in the voltage range of 2.5–4.4 V. Moreover, the cells showed fair good cycle ability over 50 cycles.

I. INTRODUCTION

Recently, olivine structure lithium transition-metal phosphates $LiMPO_4$ (M = Fe, Mn, Co, Ni) has become a research topic as a new type of potential cathode material for next generation of lithium-ion batteries due to their high energy capacity, nontoxicity, low cost and high electrochemical, and thermal stabilities.[1–3] Among the reported lithium metal phosphate cathode materials, the voltages of $LiCoPO_4$ and $LiNiPO_4$ materials are 4.9 V and 5.1 V (versus Li^+/Li) respectively, beyond the stable electrochemical windows of present electrolytes,[4] thus developing $LiMnPO_4$ (4.1 V versus Li^+/Li) seems to be more promising. $LiMnPO_4$ is less studied compared with $LiFePO_4$, although it exhibits a higher operating voltage (4.1 V) and a larger theoretical energy density (684 Wh/kg) than those of $LiFePO_4$.[5]

However, the fatal flaw of $LiMnPO_4$ material is inherently low ionic and electronic conductivities, which render it difficult to achieve excellent electrochemical activity.[4] Additionally, possible key rate limiting factors, such as passivation phenomenon upon delithiation, Jahn–Teller anisotropic lattice distortion in Mn^{3+}, interface strain due to the large volume change between $LiMnPO_4$ and $MnPO_4$, and the metastable nature of the delithiated $MnPO_4$ phase, were suggested causes and are still under debate.

Inspired by the previous research on $LiFePO_4$, the strategies include carbon coating,[6] particle size reduction,[7–9] and cation doping.[10–13] Among them, the particle size reduction and the carbon-coated $LiMnPO_4$ are main methods. In spite of those tremendous efforts, the electrochemical performance of $LiMnPO_4$ prepared is not sufficient for application to commercial cells. Especially, large polarization during charging has been a significant problem for achieving reasonable rate. For $LiMnPO_4$ cathode material, crystallinity is as important as particle size, but widely known nanomaterial synthesis methods are generally designed for liquid-phase routes to avoid grain growth and agglomeration, which may lead to Mn^{2+} disorder on the Li^+ sites in $LiMnPO_4$ and thus limit the electrochemical activity. Additionally, high-potential cathode materials require a higher sintering temperature to form a more thermodynamically stable structure with stronger bonding. Therefore, a relatively low-temperature route to obtain well-dispersed uniform nanoparticles with good crystallinity is vital for $LiMnPO_4$ synthesis.

Recently, graphene has shown great potential in Li ion battery application. Improvement on specific capacity and

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cycling stability of $LiFePO_4$ and metal oxide anode materials was reported when modified by graphene.[14–16] Our group have also successfully prepared only graphene-modified $Li_3V_2(PO_4)_3$ composite by spray-drying process with an improved electrochemical performance.[17] Here, it should also be ascribed to the high conductivity and structural flexibility of graphene sheets, which are much better than that of pyrolytic carbon.

In this paper, we report on the preparation of a novel graphene-modified $LiMnPO_4$ composite by spray-drying process. Compared with other methods, spray-drying technology is well known to be an attractive route to synthesize fine homogeneous and multicomponent powders with high yield, high crystallinity, at the same time with low cost and energy-consuming.[18] In this composite, the $LiMnPO_4$ sheets are attached to the graphene sheets in pieces. First, graphene sheets serve as a conducting network for fast electron transfer between the active materials and charge collector. Second, they provide buffered spaces to accommodate the volume expansion/contraction during the discharge/charge process. The graphene-modified $LiMnPO_4$ composite shows high specific capacity and excellent cycling stability.

II. EXPERIMENTAL

The nanostructured pure phase $LiMnPO_4$ was synthesized using the polyol synthesis reported in previous paper.[3] All chemicals were of analytical grade (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and used directly without any purification. First, 0.06 mol manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$) was dissolved into 30 mL deionized water and poured into a three-neck round-bottom flask containing 200 mL diethylene glycol (DEG). This mixed solution was vigorously stirred and heated to 100 °C, kept for 1 h, and then 30 mL of 2 mol/L lithium dihydrogen phosphate (LiH_2PO_4) aqueous solution was dropped into this system at a speed of 1 mL/min. Then, the above suspension was kept for another 4 h at this temperature. After cooling down to room temperature, the $LiMnPO_4$ material was separated by centrifugation and washed three times with ethanol to remove the residual DEG and organic remnants. Finally, the achieved material was dried in an oven in air at 120 °C overnight. To maintain platelet-structural $LiMnPO_4$ material, 0.095 g polystyrene was dissolved into 10 mL acetone and then 1 g $LiMnPO_4$ was added to the above solution. After ultrasonically exposed for 1 h and dried at 60 °C overnight, the achieved precursor was ground for 20 min and heated to 450 °C at a rate of 5 °C/min for 4 h under N_2 atmosphere to form carbon coated $LiMnPO_4$ material (denoted by $LiMnPO_4$/C).

Graphite oxide (GO) sheets were prepared from natural graphite powder via a modified Hummer's method as described in our previous work.[19,20] Typically, graphite powder (3 g) was put into an 80 °C solution of concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). The mixture was kept at 80 °C for 4 h and then cooled to room temperature, diluted with deionized water (DI, 0.5 L), and left overnight. The mixture was centrifuged, washed with DI water, and dried. The preoxidized graphite was further oxidized in concentrated H_2SO_4 (120 mL) and $KMnO_4$ (15 g) for 2 h under stirring and ice bath. Then, the mixture was diluted with DI water (250 mL) in an ice bath to keep the temperature below 50 °C for 2 h and further diluted with DI water (700 mL); 30% H_2O_2 (20 mL) was then added to the mixture, and a brilliant yellow product was formed. The product was centrifuged and washed with 1:10 HCl (1 L) aqueous solution and DI water (1 L) to remove the metal ions and acid. At last, the suspension was centrifuged at 4000 rpm for 15 min to remove the few layers GO. The concentration of the resultant GO suspension was determined by determining the concentration of GO in the slurry. A known amount of the slurry was dried over P_2O_5 for 1 week in a vacuum desiccator. From the weight of the dry GO product, the concentration of GO in the slurry was found to be about 3 mg/mL.

The graphene-modified $LiMnPO_4$ composite was prepared with $LiMnPO_4$/C and GO suspension by spray-drying and annealing processes. First, the above-mentioned $LiMnPO_4$/C was dissolved into 170 mL GO suspension under continued stirring. After stirred for 1 h at room temperature, the achieved mixture was ultrasonically exposed for 10 min, and then spray-dried at 200 °C to form a solid composite. The solid composite was heated to 550 °C at a rate of 5 °C/min for 4 h under N_2 atmosphere to form the active cathode material [denoted by $LiMnPO_4$/(G + C)], the carbon content was controlled to be ~15 wt%.

The morphology and microstructure of obtained products were characterized by x-ray power diffraction (XRD, Rigaku D/max-2500, Rigaku Co., Japan, Cu K_α radiation, $\lambda = 1.50405$ Å), field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Ltd., Tokyo, Japan), and transmission electron microscopy (TEM, JEOL 200CX, JEOL Ltd., Tokyo, Japan) in the Instrumental Analysis and Research Center, Shanghai University. The carbon contents in the final cathode materials were determined by Carbon & Sulfur Determinator (CS444LSc).

The electrochemical test of the obtained composites was carried out in 2016 coin-type cells. The working electrodes were prepared by mixing 85 wt% active materials, 10 wt% acetylene black, and 5 wt% polytetrafluoroethylene (PTFE). The lithium metal foil was used as the anode, whereas the electrolyte was a solution of 1 M $LiPF_6$ in dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by weight). The coin-cells were assembled in an argon-filled glove box and tested on a LAND CT2001A cell test system (Wuhan, China) with galvanostatic charge and discharge in the voltage range of 2.5–4.4 V under different current densities at room temperature.

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III. RESULTS AND DISCUSSIONS

Figure 1 shows x-ray diffraction patterns of (a) pure phase $LiMnPO_4$, (b) $LiMnPO_4$/C, and (c) $LiMnPO_4$/(G + C) composites. From the XRD patterns, the olivine-type $LiMnPO_4$ phase is formed devoid of any impurity. No featured peaks of other possible impurities such as Li_3PO_4 (JCPDS 25–1030), $Mn_2P_2O_7$ (JCPDS 35–1497), and MnO (JCPDS 78–424) are observed. All patterns are identified as well-crystallized olivine orthorhombic structures with space group of *Pnma*. (JCPDS No.: 01-072-7844). Carbon is not detected based on XRD analysis, which indicates that the residual carbon is an amorphous structure and/or the thickness of the residual carbon layer on the particles is too thin to be detected by the powder XRD.[21] No evidence of diffraction peaks for graphene in the $LiMnPO_4$/(G + C) composite is detected [Fig. 1(c)], which may be that the regular lamellar structure of the graphene has been broken in the as-prepared composite, forming exfoliated monolayer graphene sheets.[12] Moreover, the polystyrene or GO aqueous solution in the preparing process does not influence the structure of $LiMnPO_4$.

Figure 2 shows SEM micrographs of (a) pure phase $LiMnPO_4$, (b) $LiMnPO_4$/C, and (c) $LiMnPO_4$/(G + C) composites. The SEM observation of Fig. 2(a) shows that the pure phase $LiMnPO_4$ material processes a platelet structure with a width of 0.5–1 μm and a thickness of 20–30 nm. Figure 2(b) shows that the width of platelet-structural $LiMnPO_4$ reduces to about 200 nm after carbon coating, it may be that the $LiMnPO_4$ sheets smash to pieces during the process of ultrasonic or high temperature sintering. As can be seen from Figs. 2(c) and 2(d), through spray-drying and annealing processes, the flexible graphene sheets are formed with a width of ~1 μm and interweave with $LiMnPO_4$ sheets, generating a novel $LiMnPO_4$/(G + C) composite in pieces. Moreover, there are no existing individual or conglomerate $LiMnPO_4$ sheets in the composite.

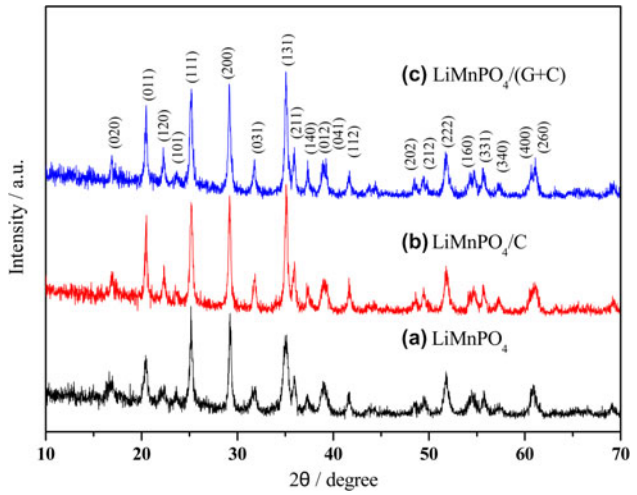


FIG. 1. X-ray diffraction patterns of (a) pure phase $LiMnPO_4$, (b) $LiMnPO_4$/C, and (c) $LiMnPO_4$/(G + C) composites.

To further investigate the morphology and microstructure of $LiMnPO_4$/(G + C) composite, the TEM characterization was performed and the result is shown in Fig. 3. It can be obviously seen that the forming flexible graphene sheets interweave with $LiMnPO_4$ sheets with a width of 100–200 nm. On one hand, the pyrolytic carbon coating on the surface of $LiMnPO_4$ sheets could limit the growth or gathering, prevent regathering of $LiMnPO_4$ sheets caused by volume shrinking and expanding in the charge–discharge process. On the other hand, the graphene with high conductivity and excellent mechanical properties contacts tightly with $LiMnPO_4$ sheets, acting as the electronic conducting skeleton of the composite.[22]

Figure 4 shows the initial charge–discharge curves of $LiMnPO_4$/C and $LiMnPO_4$/(G + C) composites at 0.05 C rate in the voltage range of 2.5–4.4 V. These samples exhibit a reversible plateau around 4.1 V versus Li/Li^+, which is the typical redox potential of Mn(II)↔Mn(III) in olivine manganese phosphate. The difference between charge and discharge voltage plateaus for the $LiMnPO_4$/(G + C) is smaller than $LiMnPO_4$/C, indicating lower polarization for the $LiMnPO_4$/(G + C) sample. Furthermore, the discharge curve of $LiMnPO_4$/(G + C) composite is more flattened than that of $LiMnPO_4$/C, which means energy can be used more effectively in $LiMnPO_4$/(G + C) composite.[23] The initial discharge specific capacity of $LiMnPO_4$/(G + C) is 105.1 mAh/g, whereas the $LiMnPO_4$/C delivers an initial discharge capacity of 60.1 mAh/g, and the first coulombic efficiencies are 94.1% and 82.8%, respectively. Similar to the previous reports,[7–9] the reversible capacity of the prepared $LiMnPO_4$ is much lower than its theoretical value (171 mAh/g), even though a low charge–discharge rate was applied. This limited capacity is the result of extremely low intrinsic electronic conductivity and slow lithium diffusion kinetics within the $LiMnPO_4$ grains.[4]

The charge–discharge curves of (a) $LiMnPO_4$/C and (b) $LiMnPO_4$/(G + C) composites at different discharge rates in the voltage range of 2.5–4.4 V are shown in Fig. 5. The cells were charged at 0.1 C rate between 2.5 and 4.4 V before each discharge and then were discharged at rates ranging from 0.1 to 1 C except when charged and discharged at the same rate of 0.05 C. The capacity of $LiMnPO_4$/(G + C) decreases from 105.1 to 60.2 mAh/g by increasing the discharge rates from 0.05 to 1 C, which can be ascribed to the Li^+ diffusion in the interface between $LiMnPO_4$ and $MnPO_4$.[23] Apparently, the rate performance and charge-discharge efficiency of $LiMnPO_4$/(G + C) increase dramatically with low content of graphene nanosheets. The confinement effect and excellent electron conductivity of graphene sheet obviously play an important role. First, compared with $LiMnPO_4$/C, the smaller $LiMnPO_4$ sheets in size in $LiMnPO_4$/(G + C) with high surface area

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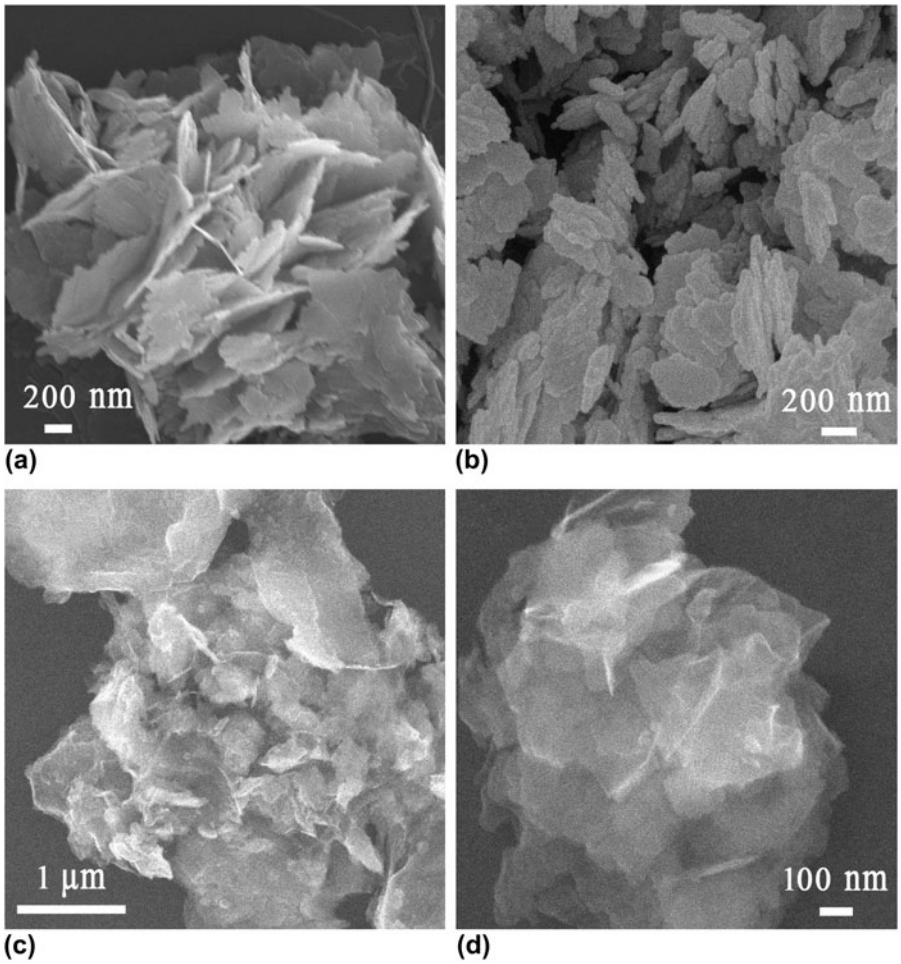


FIG. 2. SEM micrographs of (a) pure phase $LiMnPO_4$, (b) $LiMnPO_4$/C, and (c, d) $LiMnPO_4$/(G + C) composites.

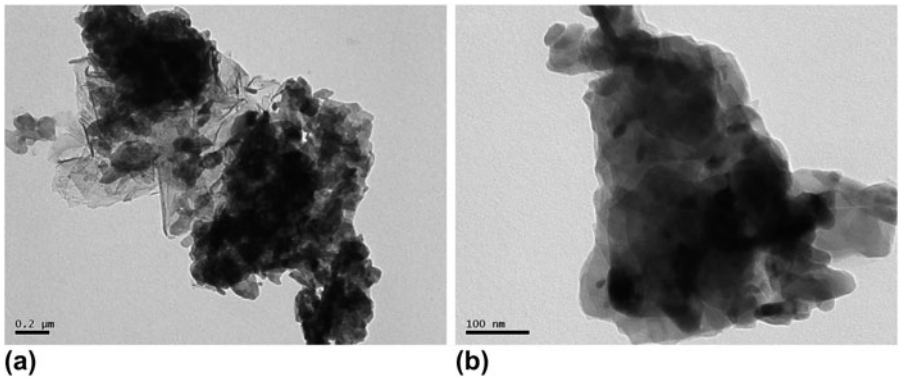


FIG. 3. TEM images of $LiMnPO_4$/(G + C) composite.

yield a decrease in the Li ion concentration and electron transport length and may ease the strain associated with the two-phase boundary of $LiMnPO_4$ and $MnPO_4$. Second, the graphene nanosheets act as conducting routes between the $LiMnPO_4$ sheets and the contact resistance is reduced.[24] It is also able to accommodate the strain induced by volume change of $LiMnPO_4$ and maintain the integrity of the electrode during charge/discharge, which is responsible for the good cycling stability and rate capability.

Figure 6 shows the cycling performances of $LiMnPO_4$/C and $LiMnPO_4$/(G + C) composites at 0.05 C rate in the voltage range of 2.5–4.4 V. For $LiMnPO_4$/C, the discharge specific capacity fades gradually down to 46.4 mAh/g after 50 cycles with a capacity retention of only 75.4%.

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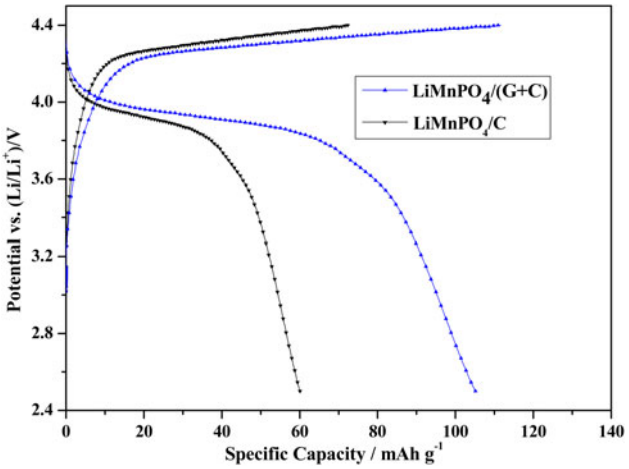


FIG. 4. The initial charge–discharge curves of $LiMnPO_4$/C and $LiMnPO_4$/(G + C) composites at 0.05 C rate in the voltage range of 2.5–4.4 V.

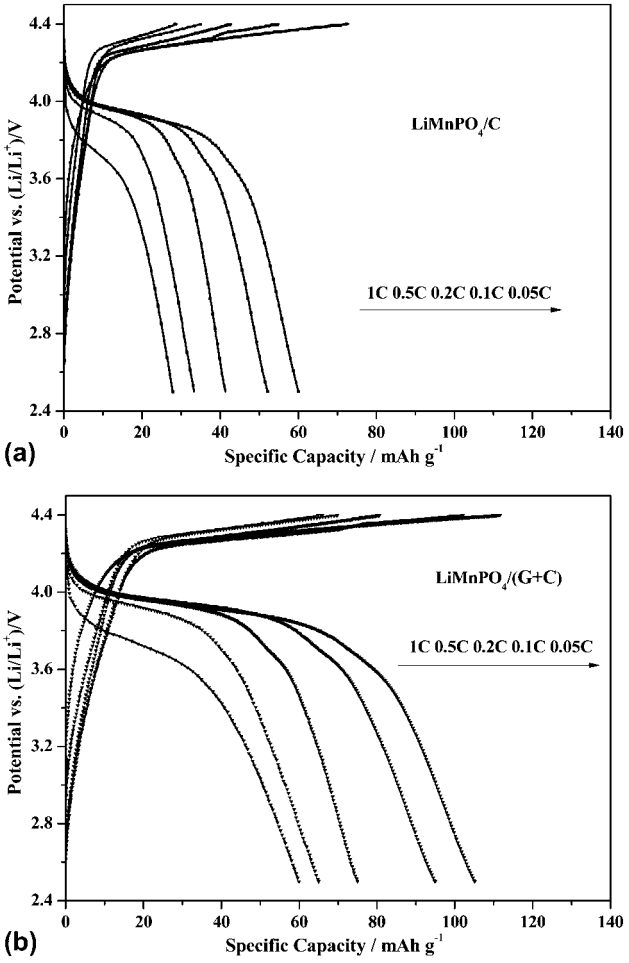


FIG. 5. The charge–discharge curves of (a) $LiMnPO_4$/C and (b) $LiMnPO_4$/(G + C) composites at different discharge rates in the voltage range of 2.5–4.4 V.

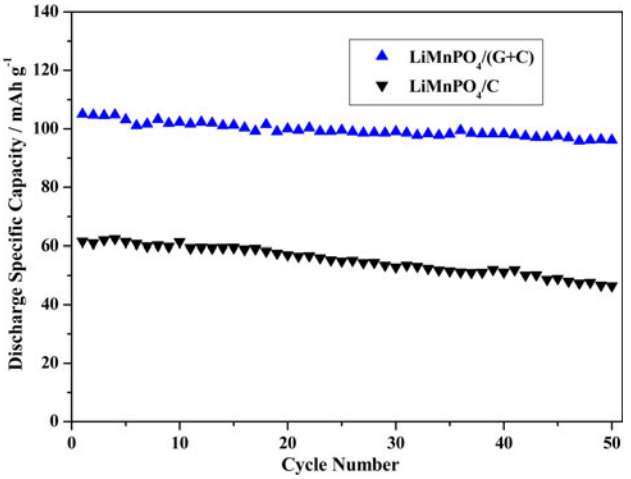


FIG. 6. The cycling performances of $LiMnPO_4$/C and $LiMnPO_4$/(G + C) composites at 0.05 C rate in the voltage range of 2.5–4.4 V.

In contrast, the $LiMnPO_4$/(G + C) shows much better cycling stability with a capacity retention of 91.4%. Similar to the above analysis, it could be ascribed to the $LiMnPO_4$/(G + C) composite in pieces providing buffered spaces to accommodate the volume expansion/contraction during discharge/charge process and promises the cyclical stability.

IV. CONCLUSIONS

In summary, we have successfully prepared a novel graphene-modified $LiMnPO_4$ composite as a performance-improved cathode material for lithium-ion batteries with LiH_2PO_4, $Mn(CH_3COO)_2{\cdot}4H_2O$, and GO suspension by spray-drying method and annealing processes. The graphene nanosheets are used as scaffolds for fast electron transfer between the active materials and charge collector, as well as buffered spaces to accommodate the volume expansion/contraction during discharge/charge process. The discharge capacity of the $LiMnPO_4$/(G + C) composite could achieve 105.1 mAh/g in the voltage range of 2.5–4.4 V at 0.05 C discharge rate, with faint capacity decay after 50 cycles.

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