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Low-temperature synthesis of $LiMnPO_4$/RGO cathode material with excellent voltage platform and cycle performance

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A B S T R A C T

Pure and well-crystallized $LiMnPO_4$/reduced graphene oxide (RGO) nanopowders are synthesized by adding a small amount glucose and graphene oxide simultaneously in dimethyl sulfoxide (DMSO)/H_2O, under constant atmospheric pressure and at low-temperature (108 °C). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that the addition of different amounts of graphene oxide can significantly affect the particle size and morphology of $LiMnPO_4$/RGO composites. With small amounts of graphene oxide (1 and 3 wt.%), the small $LiMnPO_4$ particles are wrapped in RGO, in a cocoon-like structure. This special morphology can be maintained after a rapid carbon coating treatment at high temperature. Electrochemical studies show that these cocoon-like C-LiMnPO4/G nanocomposites not only have a higher discharge specific capacity, but also show improved high voltage platform and high rate cycle performance. When the added graphene oxide is 3%, the specific capacity of C-$LiMnPO_4$/G nanocomposite is 160.8 mAh g^{-1} at 0.05 C, the discharge capacity in the area of more than 4.0 V is up to 115 mAh g^{-1}, accounting for 70% of the total discharge capacity. The proposed C-$LiMnPO_4$/G nanocomposites also exhibit an outstanding high rate capability, where the discharge specific capacity at 1C can reach to 99.6 mAh g^{-1} and after 1000 cycles at 5 C, it still has 83% of capacity retention.

1. Introduction

At present, olivine-type polyanionic compounds such as $LiMPO_4$ (M = Fe, Mn, Ni and Co) have attracted increasing attention as powerful cathode materials for lithium ion batteries, due to their good structure and chemical stability [1,2]. Compared with $LiFePO_4$, $LiMnPO_4$ is a more interesting material because of its redox potential (4.1 V vs. Li/Li^+) which shows 0.7 V higher than that of $LiFePO_4$, and is still within the stable electrochemical window of currently used liquid electrolytes. Meanwhile, $LiMnPO_4$ also has a much higher theoretical energy density than $LiFePO_4$, 701 Wh $kg^{-1} = 171$ mAh $g^{-1} \times 4.1$ V vs. 586 Wh $kg^{-1} = 170$ mAh $g^{-1} \times 3.45$ V; this plays an important role for applications in electric cars. In addition, $LiMnPO_4$ has other important properties; in fact it can be produced using abundant and low cost raw materials, it is environmental friendly, it has good structural stability, wide chemical compatibility, and it is safe to use; because of all this, it is considered the most promising cathode material for Li batteries [3–5].

Nevertheless, $LiMnPO_4$ has a very poor electronic conductivity and Li^+ diffusion coefficient, which make it an insulator material [6], with poor electrochemical activity [7]. To improve $LiFePO_4$ performance, different methods were developed which can increase the ion diffusion coefficient and the electron conductivity; these include carbon coating on the surface of nanoparticles, bulk phase element doping, nanocrystallization of material particles [8–13]. These improvements are mostly focused on the enhancement of the discharge capacity at low rates. Less investigation was performed, however, on the performances of the discharge of high voltage platform and of the high rate discharges; consequently some materials have a higher specific capacity at low rate, but the platform performance at high voltage is poor [14–19] .For examples, Chen et al. [20] synthesized CeO_2-modified $LiMnPO_4$/C composites by solvothermal method at 190 °C for 24 h, and then calcined at 550 °C for 3 h under dynamic argon atmosphere, the discharge capacity of the prepared composites was about 60 mAh g^{-1} above 4.0 V high voltage. Zhu et al. [21] used $Mn(CH_3COO)_2 \cdot 4H_2O$ and LiH_2PO_4 as the raw material, synthesized $LiMnPO_4$ in diethylene glycol solution keeping 3 h in the

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temperature of 160 °C. $LiMnPO_4/C$ composites were prepared using planetary ball-milling of the $LiMnPO_4$ powders with 20 wt.% carbon black; they can deliver a discharge capacity of 129 mAh g^{-1} at 0.05 C, but at more than 4.0 V high voltage discharge area, the discharge capacity of the material was very low, about less 30 mAh g^{-1}. Dai et al. [22] studied the impact of the rate properties of LMP, when doped with different proportions of vanadium. A series of $LiMn_{1-x}V_xPO_4/C$ ($0 < x < 0.075$) samples were synthesized via an improved solid-state method. Results showed that the $LiMn_{0.075}V_{0.025}PO_4/C$ exhibited the highest discharge capacity of 108 mAh g^{-1}at 0.2 C for the first cycle; for over 4.0 V high voltage discharge area, however, the discharge capacity of the material was still too low, about less than 40 mAh g^{-1}.

Guo et al. [23] synthesized the plate-like $LiMnPO_4$ material by a solvothermal method. After a high temperature carbon treatment, at over 4.0 V high voltage discharge area, the discharge platform of C- $LiMnPO_4$ was relatively good. Coating with too much carbon (weight ratio of $LiMnPO_4$/glucose is 2:1) would greatly reduce the amount of active material and, hence, reduce the volume ratio of energy of the electrode. Meanwhile, the solvent thermal conditions at high temperature and high pressure were quite harsh.

As it is well-known, graphene has good electrical conductivity and chemical and mechanical stability; literature showed that it can improve the electrochemical performance of $LiMPO_4$ cathode materials [24–27]. Zong et al. [28] synthesized $LiMnPO_4$-C/Acetylene black (AB) and $LiMnPO_4$-C/graphenes by solvothermal method. The samples had a capacity of 134 mAh g^{-1} and 139 mAh g^{-1} at 0.05 C, respectively. The retention of discharge capacity maintained 90% and 94% of the initial values after 40 cycles. When the discharge ratio was increased to 0.5 C and 1.0 C, the discharge capacities of $LiMnPO_4$-C/Acetylene black were 92 mAh $g^{-1}$and 60 mAh g^{-1}, but that of $LiMnPO_4$-C/graphenes still could be as high as 125 mAh $g^{-1}$and 119 mAh g^{-1}. These data confirm that the electric capacity and cycle performance of $LiMnPO_4$ samples improved substantially with the addition of graphene. Despite this, however, the discharge voltage platform was still not ideal; in fact at over 4.0 V high voltage discharge area, the discharge capacity of the material was about less than 40 mAh g^{-1}, accounting for only 30% of the total capacity. To take advantage of the 4.1 V vs. Li/Li^+ redox potential of $LiMnPO_4$, further improvements in the performance of the materials are needed. These can be achieved by optimizing the size of the nanoparticle and their structural morphology, and by optimizing the preparation of $LiMnPO_4$/graphene composites. An effective improvement of the electrical conductivity of the particle will enhance the material's discharge platform, taking full advantage of its high energy density.

In our previous work, our team had synthesized sphere-like $LiFePO_4/C$ nanocomposites with particle sizes of about 100–300 nm via a solution-phase method. The synthesized $LiFePO_4/C$ sample showed excellent rate and cycle performances [29,30]. Based on our previous works, we added glucose as additive in dimethyl sulfoxide solvent; the glycoside formed during the reaction acted as a surfactant and led to the successful preparation of hollow spindle $LiMnPO_4$ particles [31]. The discharge capacity was 161.8 mAh g^{-1}mAh g^{-1} at 0.05 C. To further improve the high voltage platform performance, the high rate performance and the electrical conductivity between the particles, we also added different mass fraction of graphene oxide in the solution, together with the glucose. The results showed that nano $LiMnPO_4$/RGO was synthesized after the reaction. With the graphene oxide ratios of 1%, 3%, the materials have a cocoon-like morphology, with the surface of the particles completely wrapped up by soft graphene fold layer.

Nano C-$LiMnPO_4$/G composite was then produced after a rapid high temperature carbon treatment. This kind of composite with special morphological structure had excellent conductive network structure, produced by the close contact of $LiMnPO_4$ particles with amorphous carbon and graphene layers; this will greatly improve the high voltage platform performance and the high rate cycle performance of the material. This proposed method is based on a simple and facile procedure, using cheap raw materials and under mild reaction conditions (no high temperatures or pressure need to be employed). This method can also be applied in the preparation of other olivine structure for lithium ion battery materials, it has therefore great application prospects.

2. Experimental section

2.1. Synthesis of graphene oxide

Graphene oxide (GO) was prepared by an improved Hummers method [32]: 1.0 g graphite were added to 100 ml concentrated H_2SO_4 (98%). 4.5 g of $KMnO_4$ and 0.5 g of $NaNO_3$ were slowly added into the above solution, which was magnetically stirred in an ice bath for 10 min. The mixture continued to be stirred for 3 days at room temperature. Subsequently, water was added dropwise to the mixture under vigorous stirring, and the stirring was continued until the solution was cooled to room temperature. 15 ml of H_2O_2 solution (30 wt.%) and 200 ml of water were added dropwise under vigorous stirring for another 2 h. Then, the resulting graphite oxide suspension was washed 3 times with HCl (0.5 M), and washed repeatedly with distilled water, until the solution pH keep a constant value of about 5.0. The sol was scattered to H_2O again. After ultrasound treatment, the complete delamination of graphite oxide was achieved.

2.2. Synthesis of samples

The synthesizing procedure of sample $LiMnPO_4$/RGO is shown in Fig.S1 (See Supplementary materials); the process is based on our previous work to prepare $LiMnPO_4$ [31].

Deionized water and DMSO ($V_{H2O} = V_{DMSO} = 25$ ml) were mixed in a three neck round bottom flask. 5% glucose was slowly added to the above solution. The DMSO-H_2O solution with glucose was vigorously stirred and heated to 108 °C for 2 h, then cooled to room temperature. This is named Solution A.

Solution B was obtained by dissolving 0.05 mol of manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$, 99%) and 3.42 ml of phosphoric acid (H_3PO_4, 85%) into the solution A under constant stirring, for 1 h at 50 °C. Then, 6.3545 g of lithium hydroxide ($LiOH{\cdot}H_2O$, 99%) were slowly added into the Solution B. The final concentration of lithium hydroxide was 1.5 mol L^{-1}. The reaction solution was heated at 108 °C for 2 h under nitrogen atmosphere, cooled to room temperature, and stored overnight. The $LiMnPO_4$ material (named LMP) was obtained by precipitation; the precipitate was washed several times with deionized water and ethanol and dried overnight in an oven at 60 °C.

To facilitate the measurement and guarantee the repeatability of experiments, experiments according to the theoretical production of $LiMnPO_4$ were performed adding different amounts of GO to the reaction system; more specifically, solution with GO concentrations of 1 wt.%, 3 wt.%, 5 wt.% and 7 wt.% were prepared. The corresponding samples obtained by liquid phase reaction were denoted as LMP/RGO (1 wt.%), LMP/RGO (3 wt.%), LMP/RGO (5 wt.%), and LMP/RGO (7 wt.%).

The C-$LiMnPO_4$/G was synthesized via the following steps; samples LMP, LMP/RGO(1 wt.%), LMP/RGO(3 wt.%), LMP/RGO(5 wt.%) and LMP/RGO(7 wt.%) were milled with 10% of glucose. The milled powder was collected in boat shape alumina crucible and then heated at 650 °C for 4 h in an atmosphere of (N_2:H_2 = 95:5) in a tube furnace, and then cooled to room temperature. The resulting product was named as C-LMP, C-LMP/G(-1), C-LMP/G(-3), C-LMP/G