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Electrochemical performance of the graphene/Y_2O_3/$LiMn_2O_4$ hybrid as cathode for lithium-ion battery

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ABSTRACT

The graphene/Y_2O_3/$LiMn_2O_4$ hybrid wrapped the Y_2O_3 coated $LiMn_2O_4$ microsphere with graphene nanosheet was firstly synthesized. The structure and performance of the pristine $LiMn_2O_4$, Y_2O_3/$LiMn_2O_4$, graphene/$LiMn_2O_4$ and graphene/Y_2O_3/$LiMn_2O_4$ composites had been characterized by powder X-ray diffraction (XRD), energy dispersive analysis spectroscopy (EDAS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), galvanostatic charge–discharge, cyclic voltammetry (CV) and impedance spectroscopy (EIS). The results exhibited that the addition of graphene and Y_2O_3 did not change the bulk structure of $LiMn_2O_4$. The graphene/Y_2O_3/$LiMn_2O_4$ hybrid showed an initial discharge capacity of 129.3 mAh g^{-1}, and the excellent capacity retention was still as high as 89.3% even after 500 cycles at a rate of 1 C and at an elevated temperature 55 °C. Meanwhile, it delivered a high capacity of 90.0 mA h g^{-1} even at 30 C. These remarkable enhancements indicated that coating Y_2O_3 and then wrapping graphene on the quasi-spherical surface of $LiMn_2O_4$ was an effective way to simultaneously improve the cycling stability and the rate performance of $LiMn_2O_4$. The Y_2O_3 coating could be accounted for the improved cycling performance by suppressing Mn^{3+} dissolution, and the graphene could enhance the conductivity of $LiMn_2O_4$ and thus improved the high rate capability.

1. Introduction

Lithium-ion battery has been considered as the most promising alternative environmentally friendly energy because of the global warming and the exhaustion of fossil fuels. Over the past decades, lithium-ion batteries have been applied as an essential electric source for portable electronic device [1–3]. Moreover, they have also been expected to be used in high power fields such as electric and hybrid vehicles. However, the power density and cycle life of lithium ion batteries are still too low to support these industrial needs. To meet such a demand, the rate capability and cycling stability of lithium ion batteries must be improved.

$LiMn_2O_4$ with a spinel structure is one of the most promising cathode materials due to its good intrinsic characteristics, such as high energy density, low cost and environmental friendliness [4,5]. However, $LiMn_2O_4$ electrodes in the 4 V (versus Li/Li^+) region suffer from severe capacity fading, especially at elevated temperature [6–10]. The reason for capacity fading is mainly ascribed to the Mn^{3+} dissolution occurred by the corrosive reaction between $LiMn_2O_4$ and electrolyte during cycling. Therefore, many researchers have attempted to improve cycling performance under the high temperature by a coating layer that would reduce the direct contact area of $LiMn_2O_4$/electrolyte interface thus decrease the dissolution of manganese effectively [11–14]. In previous reports, metal oxide, ceramic oxide, phosphates and fluoride, are usually prepared as the coating layer on the surface of the cathode materials. Whereas, the majority of these covering materials are electrochemically inactive, which leads to the composite materials generally suffering from the poor rate performances [15–18]. Sen Zhao et al. [14] have reported that the 3.0 wt.% YPO_4-coated $LiMn_2O_4$ exhibits the good cycling performance. The initial capacity is about 110.0 mAh g^{-1} and still retains 84.1% after 200 cycles at 0.2 C at room temperature. But, it only delivers about 85.0 mAh g^{-1} when the rate turns to 1 C. Thus, the improvement of the high rate capability is intensively appealed. Many efforts have been made to improve the rate capability [19]. Qu et al. have synthesized the porous $LiMn_2O_4$, which consists of nanograins by using polystyrene as template, and obtained the discharge capacity of 118 mAh g^{-1} at 10 A g^{-1} using 0.5 mol L^{-1} Li_2SO_4 aqueous solution as the electrolyte [20].

Recently, graphene and its composites have been extensively investigated due to their extraordinary electrical behavior, stable chemical property and high specific surface area [21–25]. And it also shows the great potential in lithium ion battery applications. Lately, Jiang et al. have synthesized and investigated graphene-wrapped lithium-excess layered (Li_2MnO_3·$LiMO_2$) hybrid materials

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with directly adding $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ into a graphene suspension. The composites show a discharge capacity of 50.2 mAh g^{-1} even at a very high rate of 12 C [26]. Another report by Rao et al. describes the improvement of the rate performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-graphene composites. At the rate of 5 C, the composites reveal a discharge capacity of 158.4 mAh g^{-1}, while that of the pure $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is 138.1 mAh g^{-1}. However, there are no significant improvement in cycling performance, because the hybrid materials do not retain the original morphology (particles aggregating with each other with addition of graphene) and the entire surface cannot be completely coated by the graphene, thereby the result only has made a limited enhancement in electrochemical properties.

To take advantages of the admirable properties of graphene and metal-oxides, herein the spherical spinel $LiMn_2O_4$ synthesized by precipitation method is used as the substrate material, and is prepared further the graphene/Y_2O_3/$LiMn_2O_4$ composites. The physical and electrochemical properties of graphene/Y_2O_3/$LiMn_2O_4$ are studied in detail.

2. Experimental

2.1. Preparation of the spherical spinel $LiMn_2O_4$

$MnCO_3$ is firstly synthesized by the co-precipitation method as the precursor. An aqueous solution of $MnSO_4$ with a concentration of 1.6 mol L^{-1} is pumped into a continuously stirred tank reactor. At the same time, a 1.6 mol L^{-1} Na_2CO_3 solution (aq) and the desired amount of NH_4OH solution (aq) as the chelating agent are also separately fed into the reactor. The obtained spherical $MnCO_3$ precursor is then filtered, washed and dried at 80 °C. Then the as-prepared powder and an appropriate amount of Li_2CO_3 are mixed homogeneously and calcined at 750 °C for 20 h to obtain the spherical spinel $LiMn_2O_4$ (denoted by LMO).

2.2. Synthesis of the Y_2O_3-coated $LiMn_2O_4$

The Y_2O_3-coated spherical $LiMn_2O_4$ (denoted by Y/LMO) are prepared via precipitation method. $Y(NO_3)_3{\cdot}6H_2O$ are dissolved in distilled water and the solution is adjusted to pH about 9.0 by aqueous buffer solution of $NH_4Cl/NH_3{\cdot}H_2O$ with stirring. Subsequently, the as-prepared $LiMn_2O_4$ powders is added to the solution with vigorous stirring for 2 h, sonicated for 2 h to obtain a suspension then filtered and washed to obtain a black deposit, finally evaporate at 80 °C. The obtained coated $LiMn_2O_4$ powder is heated at 550 °C for 5 h.

2.3. Preparation of graphene/Y_2O_3/$LiMn_2O_4$ composites

Graphene oxide (GO) is prepared using the modified Hummers method and the details can be found in the literature [27–29]. Then, the as-synthesized Y/LMO powder is mixed with graphene oxide aqueous suspension at room temperature with moderate stirring. The mixture is subsequently dried overnight at 90 °C and then annealed at 600 °C in Ar atmosphere for 5 h. The as prepared composites are denoted by Y/LMO/G.

Fig. 1 illustrates the preparation process of the Y/LMO/G composites. First of all, the Y_2O_3-coated spherical $LiMn_2O_4$ are prepared via a precipitation method and subsequent heat-treatment at 550 °C for 5 h in air. And then, the Y/LMO/G composites are prepared via mixing aqueous suspension of the as-prepared Y/LMO particles and GO nanosheets with sonicating and stirring. As GO nanosheets are highly hydrophilic and easy dispersed, herein we do not use graphene nanosheets [30]. The Y/LMO/GO composites are then converted to Y/LMO/G through annealed at 600 °C in Ar atmosphere for 5 h. Moreover, the graphene nanosheets can not cover the entire surface of the $LiMn_2O_4$ sphere due to the different size between the spherical $LiMn_2O_4$ and graphene nanosheets. Thus, it may only wrap on the surface of microsphere in the form of pieces. Finally, the equally distributed modified spherical spinel $LiMn_2O_4$ particles which have retained the original morphology of LMO are successfully obtained.

2.4. Physical characterizations

The phase identification of the samples is performed with a diffractometer (D/Max-3C, Rigaku, Japan) using Cu Kα radiation (λ = 1.54178 Å) and a graphite monochromator at 36 kV, 20 mA. The scanning rate is 8 min^{-1} and the scanning range of diffraction angle (2θ) is $10° \leqslant 2\theta \leqslant 80°$. Energy dispersive analysis spectroscopy (EDAS) is used to approximately determine the element content of powders. The morphology of the sample is observed using scanning electron microscopy (SEM, JEOL JSM-5600LV) and high resolution transmission electron microscopy (HRTEM, JEOL JEM 2010).

2.5. Electrochemical characterizations

To fabricate the positive electrode, the as-prepared materials are mixed with acetylene black, graphite and polyvinylidene fluoride (80:5:5:10) in N-methylpyrrolidinone. The obtained slurry is coated onto Al foil and roll-pressed. The loading mass of the active material of electrode is 4–5 mg per cm^2. The electrodes are dried overnight at 120 °C in a vacuum before use. Preliminary cell tests are done with a 2025 coin-type cell using Li metal as the anode and a Celgard 2400 as the separator. The electrolyte is a 1 mol L^{-1} $LiPF_6$ solution in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, v/v). The charge–discharge measurements are carried out on a Neware battery test system BTS-XWJ-6.44S-00052 (Newell, Shenzhen, China). The electrochemical impedance spectroscopy (EIS) is conducted on three-electrode system with lithium metal as the counter and reference electrodes by using a VersaSTAT3 electrochemical workstation (Princeton, America). A perturbation voltage of 5 mV and frequency range from 50 kHz to 10 mHz were employed.

3. Results and discussion

Fig. 2 shows the XRD patterns of LMO, Y/LMO, LMO/G and Y/LMO/G composites. All the reflections reveal the cubic spinel structure with a space group of F$d3m$, excepting the broad peak centered at $2\theta = 22.2°$, which is at a slightly lower angle than the peak for bulk graphite (centered at $2\theta = 26.5°$) and can be assigned to the graphene sheets (Fig. 2a and b) [31]. It indicates that the GO nanosheets are reduced to graphene nanosheets and partially re-

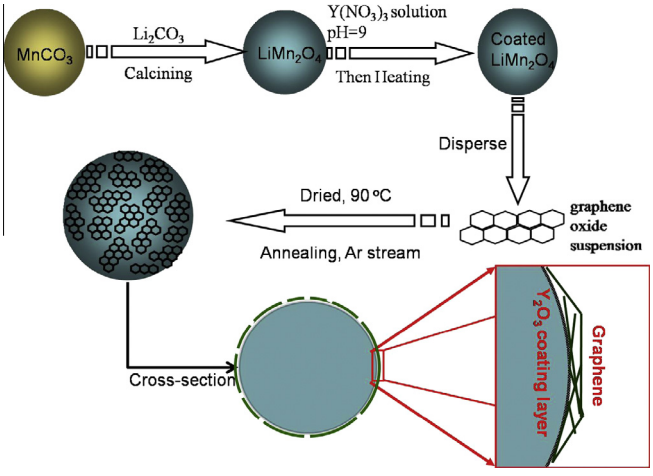

Fig. 1. Schematic diagram of the formation process of Y/LMO/G.

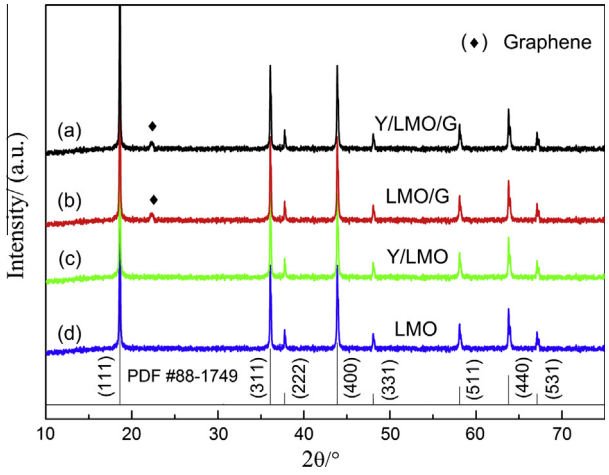

Fig. 2. XRD patterns of LMO, Y/LMO, LMO/G and Y/LMO/G.