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Short communication

Improved electrochemical performance of lithium iron phosphate in situ coated with hierarchical porous nitrogen-doped graphene-like membrane

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HIGHLIGHTS

- LFP in situ coated with HPNGM is successfully synthesized.
- The HPNGM increases the electrons and Li^+ diffusion rate.
- The hierarchical porous structure favors the electrolyte access to active material.
- The composite exhibits excellent rate capability and cycling stability.

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ABSTRACT

$LiFePO_4$ in situ coated with hierarchical porous nitrogen-doped graphene-like membrane (HPNGM) composite derived from a electrospun polymer membrane (EPM) precursor has been achieved for the first time. The N-doped graphene-like membrane which is in situ coating on $LiFePO_4$ can provide a highly conductive layer, and the hierarchical porous structure facilitates Li^+ transfer. The composite exhibits a high reversible capacity (171 mAh g^{-1} at 0.1 C), excellent high-rate capability and cycling stability. In addition to construct the traditional structure of nanofiber or nanowire, the EPM can also form graphene-like structure after annealing, which is a new application in constructing sheet structure by electrospinning.

1. Introduction

Carbon coating is the most effective and facile way for improving the conductivity of $LiFePO_4$ (LFP) [1,2]. Besides, an in situ grown carbon coating is more advantageous for limiting the LFP particle growth, which can improve the electrochemical performance of the cathode [3]. Graphene has aroused intense research interest in energy-related applications, owing to its high surface area, extraordinary in-plane electrical conductivity, excellent tensile modulus, and mechanical durability [4]. Especially, the nitrogen-doped graphene, which could further enhance the electronic conductivity, might be a suitable material for lithium-ion batteries (LIBs) [5]. However, few reports describe a simple method to synthesis LFP in situ coated with nitrogen-doped graphene composite, as graphene is generally prepared from graphite via exfoliation, and its two-dimensional sheet structure resists to wrap the particle surface of the cathode materials tightly. Therefore, graphene-like coatings or nitrogen-doped graphene-like coatings have been proposed and developed for advanced LIBs [6,7]. Mi et al. developed a carbon-thermal method to coat Si nanoparticles with nitrogen-doped graphene-like nanosheets derived from a liquid acrylonitrile homopolymer (LPAN) precursor [6]. Zhou et al. constructed a novel graphene-like membrane using liquid-polyacrylonitrile (LPAN) as the carbon source to in situ coat

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$LiMn_2O_4$ [3]. Associating with the improved electric conductivity of LFP, it is desirable to create a hierarchical porous carbon matrix for LFP particles that allows efficient percolation of the electrolyte through the electrode, facilitates Li^+ transfer, favors the electrolyte access to active material via the pores, then makes efficient use of the electrode material [8].

Electrospinning is an inexpensive, simple, and versatile technique to prepare one-dimensional nanofibers or nanowires [9]. However, HPNGM produced by combination of electrospinning and low temperature hydrothermal technique is quite rare. Herein, for the first time, a simple and novel strategy to in situ coat LFP with HPNGM using a EPM precursor is reported. The sample shows initial discharge capacity of 171 mAh g^{-1} at 0.1 C and excellent rate capability. Moreover, it displays superior long-term cycling stability at high current density of 10 C, attaining a discharge capacity of 80 mAh g^{-1} for up to 300 cycles.

2. Experimental

2.1. Synthesis

Polyvinylpyrrolidone (PVP, $M_w = 1300000$) was purchased from Aladdin Reagent Company. All the other reagents were AR grade and provided by commercial suppliers, and used without further purification.

A typical synthesis for the HPNGM precursor is as follows: The EPM was prepared from electrospinning solutions of 0.7 g urea, 8.6 g N,N-dimethylformamide (DMF), and 1.4 g PVP. The solution was fed through a syringe with a stainless steel spinneret. A voltage of 18 kV was applied to the spinneret. A piece of graphite paper was used as the collector. 0.5202 g of $CH_3COOLi{\cdot}2H_2O$, 0.576 g of H_3PO_4 (85%) solution and 2.02 g of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in distilled water with molar ratios of 1.02:1:1. 2% excess Li was used to supplement the volatilization of Li at high temperature. After stirring for 10 min, 0.264 g ascorbic acid was added under stirring for 30 min. Followed by addition of 0.3 g EPM, the reaction mixture was transferred into a 80 mL polytetrafluoroethylene (Teflon)-lined stainless-steel autoclave and kept in an electric oven at 80 °C for 4 h, the precursor was obtained. Finally, the composite was obtained by annealing the as-prepared precursor at 350 °C for 6h, then 700 °C for 8 h under 5 vol % H_2/Ar atmosphere. For comparison, a control experiment was also carried out to prepare LFP/C, here, as the carbon source, PVP polymer was not be electrospun.

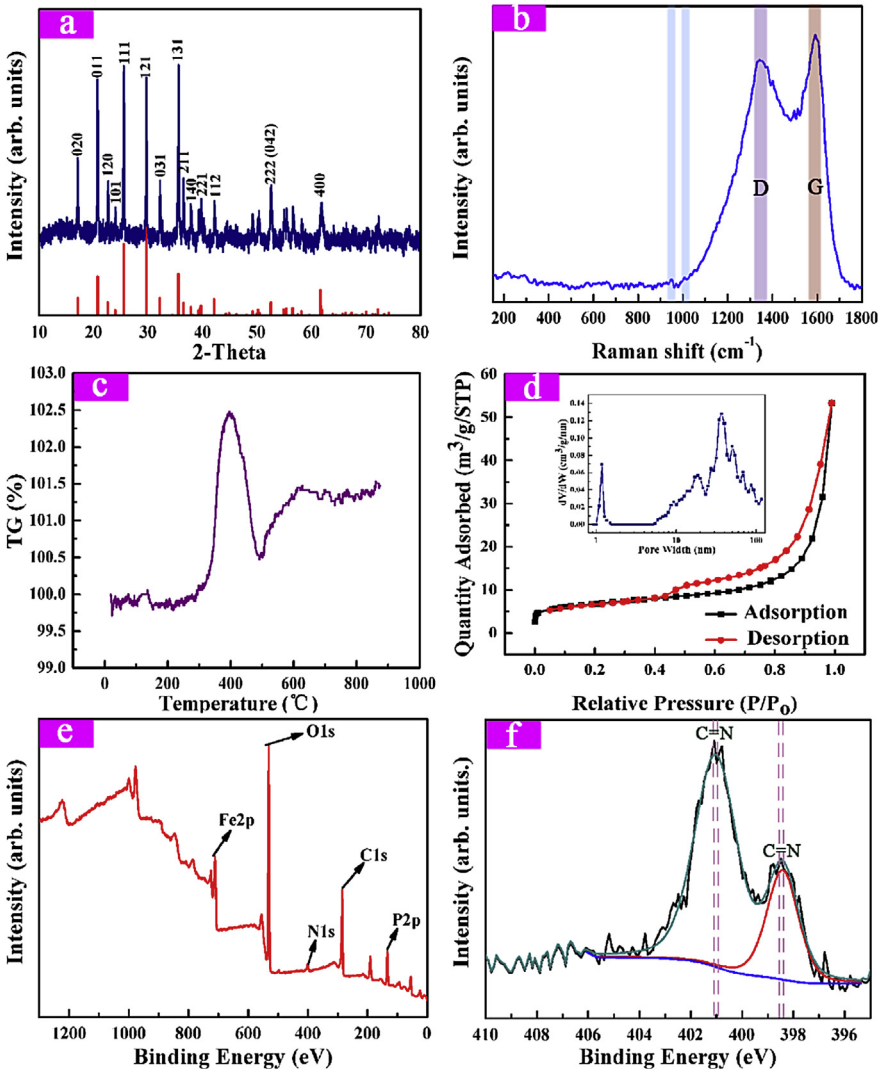

Fig. 1. The coated LFP composite: (a) XRD pattern; (b) Raman spectrum; (c) TGA analysis; (d) The N_2 adsorption/desorption isotherms and pore size distribution; (e) XPS survey; (f) High resolution XPS spectrum of N 1s.