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Enhanced Electrochemical Performance of Lithium Iron(II) Phosphate Modified Cooperatively via Chemically Reduced Graphene Oxide and Polyaniline

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ABSTRACT

It is essential to improve the electron and lithium ion conductivities of Lithium iron(II) phosphate ($LiFePO_4$) used as a cathode material for lithium-ion batteries. In the work, we designed and fabricated a series of composites of $LiFePO_4$ modified cooperatively with chemically reduced graphene oxide (RGO) and polyaniline. It was demonstrated that the composites have a three dimensional network structures in which the CRGO and the polyaniline were intertwined and coated uniformly on the surface of $LiFePO_4$. Comparably, as cathode for lithium-ion batteries, the as-prepared composites showed better electrochemical performances than the bare $LiFePO_4$ and the $LiFePO_4$ modified simply with CRGO or polyaniline alone. The elaboration of the underneath mechanism on the pronounced electrochemical properties of the composites was also attempted and discussed.

1. Introduction

As one of the most promising cathode materials for lithium-ion batteries (LIBs), lithium iron(II) phosphate ($LiFePO_4$) assuming olivine crystal structure has attracted much attention owing mainly to the high operating voltage ~3.4 V (vs Li/Li^+), acceptable theoretical capacity (~170 mA h g^{-1}), good structural and cycling stabilities.[1,2,3] However, the bare $LiFePO_4$ shows poor rate capability because of its intrinsically low electronic conductivity (~10^{-1} S cm^{-1}) and Li^+ diffusivity (~10^{-14} cm^2 s^{-1}). [4,5] Therefore, incredible efforts have been devoted to improve the electron and Li^+ conductivities, and, thus, to increase the electrochemical performances of $LiFePO_4$ as cathode mainly by coating physically and/or chemically a thin layer of conductive carbon or derivatives on it.[6,7,8]

Graphene and chemically reduced graphene oxide (CRGO) sheets, owing to the unique electronic conjugate state within the basal plane and also the single atomic layered morphology, have superior electronic mobility (200000 $cm^2 Vs^{-1}$) and lithium ion diffusivity (~10^{-7} to 10^{-6} S cm^{-1}), large surface area (2630 m^2 g^{-1}), and decent thermal and chemical stability. [9,10,11] Thus, the grapheme, and derivatives, such as CRGO, have been demonstrated as one of optimal materials to modify the electrode materials, including $LiFePO_4$.[12] Conversely, the grapheme or CRGO sheets aggregate usually during the processing and storage. Therefore, it is hard to control the distribution of the graphene or CRGO sheets within the as-prepared composites of $LiFePO_4$ and graphene or CRGO, which may deadly affect the electrochemical performances of the composites as cathode.[13] To overcome this obstacle, the composites with high graphene contents are usually manufactured, but this decreases certainly gravimetric/volumetric energy density of the cathode, and may also rises the cost. [14,15,16] Besides the graphene and CRGO, graphitized carbon black, more recently, the conductive polymers, such as polyaniline (PANI), have also been utilized as additives to modify the $LiFePO_4$, and it has been illustrated that the electrochemical properties of the composite of $LiFePO_4$ and PANI are better than the bare $LiFePO_4$. [17,18,19,20] For instance, the $LiFePO_4$/PANI (7 %, in mass) composite showed specific capacity of 120 mAh g^{-1} when the charge/discharge current rate at 10C, which is much higher than that of bare $LiFePO_4$, 86 mAh g^{-1}.[18] Additionally, electrochemical properties of PANI can be tuned simply by oxidation or protonation.[21,22] Many researches showed also that the PANI can mediate the polarity difference between the cathode materials and the electrolyte, promoting electrolyte permeation into the surface of the cathode materials, and hence enhancing Li^+ insertion/extraction during a charge/discharge process.[19] However, due to low solubility in most solvents and immiscibility of PANI with $LiFePO_4$, the preparation of $LiFePO_4$ coated uniformly with PANI is laborious and often time-consuming.

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It was well known that the aniline can be polymerized thorough oxidization under an acidic condition using a variety of oxidants. On the other hand, graphene oxide (GO) sheets can be chemically reduced into CRGO via certain reductants including aniline.[23] Based on these, in this work, we intend to prepare $LiFePO_4$/CRGO/PANI composites using bare $LiFePO_4$, GO, and aniline as raw materials through the *in situ* redox reaction between GO and aniline. As will be shown, the redox reaction between GO and aniline can take place instantly in the mixture at room temperature. The as-generated CRGO and PANI could be coated uniformly on the $LiFePO_4$ particles. The electrochemical measurement showed that even with low contents of CRGO and PANI within the composites, the rate capability and cycling stability of $LiFePO_4$ can be improved readily.

2. Experimental

$LiFePO_4$ crystalline powder was purchased from Jinli Company Ltd. (Hebei, China). GO was prepared from graphite powder through a modified Hummers method that we described previously. [24,25] $LiFePO_4$/ CRGO /PANI composites were prepared through *in situ* redox reaction of GO and aniline in the aqueous suspension of $LiFePO_4$. Briefly, in a typical experiment, 2 gram of $LiFePO_4$ and 0.01 gram of GO were mixed in 200 ml H_2O, then, aniline and diluted HCl was added into the mixture and to keep the final concentrations of aniline and HCl less than 0.3 and 0.27 M, respectively, and the mixed solution was stirred for 10 min. The powder product was separated from reaction mixture by filtration, washed thoroughly with deionized water, and finally dried in vacuum at 110 °C.

The morphology of powders was examined using Ultra 55 field emission-scanning electron microscopic (FE-SEM) (Zeiss, Germany) and AXIS Ultra DLD X-ray photoelectron spectroscopy (XPS) (Kratos Analytical, UK). Raman spectra were recorded on an Invia/Reflrx Lasser Micro-Raman spectroscope (Renishaw, England) with an excitation laser beam wavelength of 514 nm. Electrochemical measurements were carried out between 2.5 and 4.2 V vs Li^+/Li^0 on CR2032 coin cells. Within the coin cells, the as-prepared $LiFePO_4$/CRGO/PANI composite mixed with carbon black and PTFE (80:10:10, in weight) was used as the cathodes; metallic lithium foil was used as the counter and reference electrodes; a Celgard 2032 membrane was served as separator; the electrolyte was 1 mol/L $LiPF_6$ in a 1:1 mixture solvent of ethylene carbonate and diethyl carbonate (EC/DEC).

The galvanostatic charge/discharge curves were recorded on a LAND CT2001A electrochemical workstation (Wuhan, China). The cyclic voltammograms (CV) were obtained from 2.5 to 4.2 V at a scanning rate of 0.1 mV s^{-1}. The potential static step charge measurement were performed by charging at +500 mV potential steps for 800 s, and the electrochemical impedance spectroscopy (EIS) was carried out by applying a perturbation voltage of 5 mV in a frequency range of 10 m Hz to 100 KHz using an electrochemical working station (PGSTAT 302N) (Merohm, Switzerland).

3. Results and discussion

Fig. 1a and b show the FE-SEM images of $LiFePO_4$ particles, GO and aniline as-prepared $LiFePO_4$/CRGO/PANI composite, respectively. It can be seen clearly within the composite the $LiFePO_4$

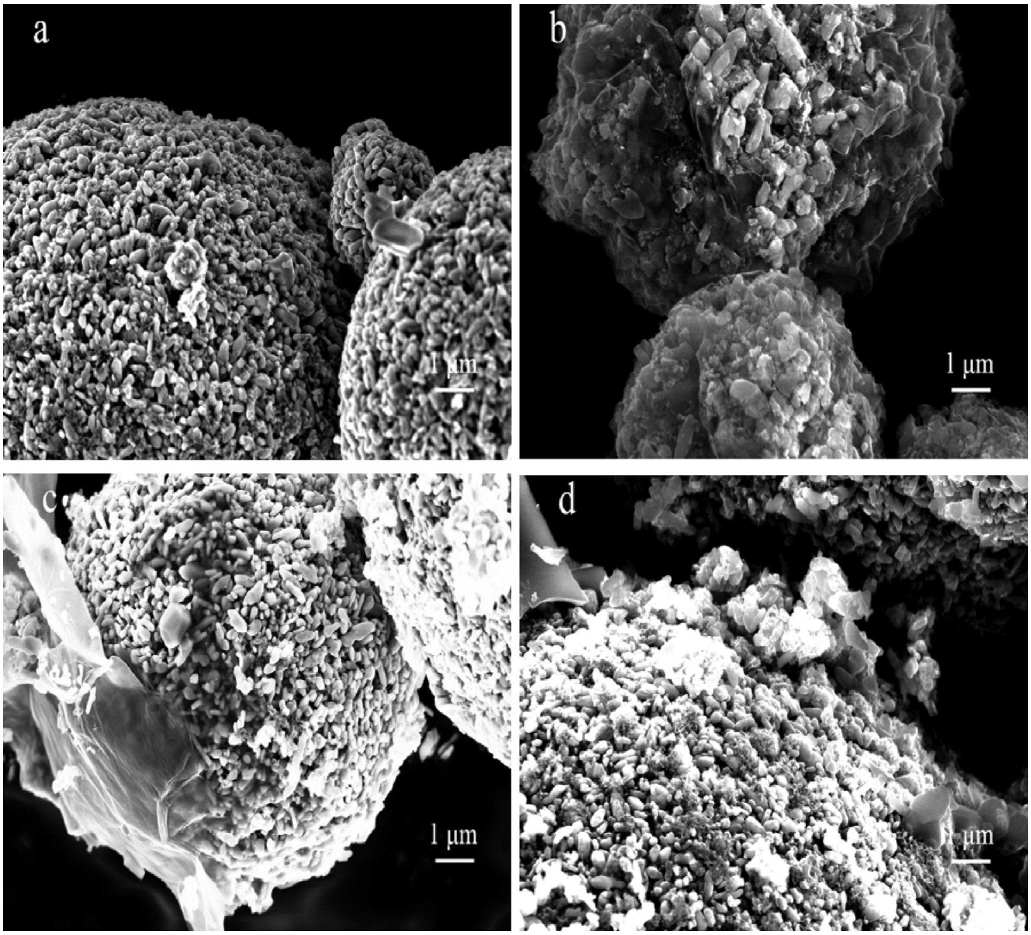

Fig. 1. FE-SEM images of (a) $LiFePO_4$, (b) $LiFePO_4$/CRGO/PANI (1/0.005/0.15), (c) $LiFePO_4$/CRGO, and (d) $LiFePO_4$/ PANI, respectively.