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Regular Article

Preparation and characterization of flexible lithium iron phosphate/graphene/cellulose electrode for lithium ion batteries

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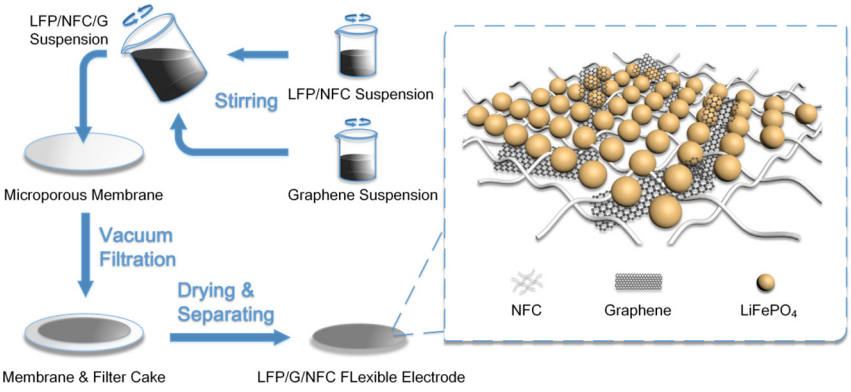
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a free-standing flexible composite electrode was prepared by vacuum filtration method with $LiFePO_4$, graphene and nanofibrillated cellulose (NFC). Compared with the pure $LiFePO_4$ electrode, the resulting flexible composite ($LiFePO_4$/graphene/NFC) electrode showed excellent mechanical flexibility, and possessed an enhanced initial discharge capacity of 151 mA h/g (0.1 C) and a good capacity retention rate with only 5% loss after 60 cycles due to suitable electrolyte wettability at the interface. Furthermore, the NFC and graphene formed a three-dimensional conductive framework, which provided high-speed electron conduction in the composite and reduced electrode polarization during charging-discharging processes. Moreover, the composite electrode could endure bending tests up to 1000 times, highlighting preferable mechanical strength and durability. These results demonstrated that the as-fabricated electrodes could be applied as flexible electrodes with an embedded power supply.

1. Introduction

Over the past decade, with the rapidly-growing demand for wearable devices [1,2], flexible displays [3] and interconnection devices for Internet of Things [4], extensive interest in flexible electronics has developed [5,6]. As the most promising energy supply of flexible electronics, Li-ion batteries (LIBs) need to meet higher demands such as flexibility, light weight, low cost and excellent mechanical properties [7–9]. One of the challenges is to replace metal current collectors and polymeric binders, which can impede

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electrode performance and are unable to withstand the daily-repeated deformation.

To date, academia has put great effort toward preparation of flexible electrodes for LIBs. Paper [10], textile [11] and other organic substrates [12–14] are becoming potential components for flexible electrodes due to their intrinsically good flexibility and high surface area, but their poor electronic conductivity has limited further application. Thus, the highly conductive carbon-based low-dimensional materials such as carbon nanotubes and graphene have been introduced into the preparation of flexible LIBs electrodes [15–25]. Cheng et al. [17] fabricated a $LiFePO_4$/graphene foam electrode by chemical vapor-deposition (CVD) with a high specific capacity of 98 mA h/g at 50 C. Zhou et al. [22] prepared AlF_3-coated $LiCoO_2$/multiwall carbon nanotube electrode by atomic layer deposition (ALD) and the electrode exhibited a high LCO loading of 20 mg/cm^2 with excellent flexibility and low surface resistivity. However, the preparation procedures like CVD, ALD and anodic electro-polymerization [23] are relatively complicated, costly and difficult for mass production.

Nanofibrillated cellulose (NFC), a highly fibrillated colloid fiber with good dispensability and stability, has been widely used as suspending and thickening agent mixing with other materials [26–28]. Jabbour et al. [26] used NFC as binders for the aqueous processing of flexible electrodes for Li-ion batteries, and the resulting graphite/NFC anode showed good flexibility and cycling performances. Wang et al. [27] prepared Si anodes using cladophora nanocellulose in the process, and the specific capacity of the flexible Si/CNT/CNC anode was up to 800 mA h/g. Thus, NFC is of great potential in the preparation of composite electrode materials.

In this paper, by utilizing NFC as the mechanical support and graphene as the conductive assistant, a flexible $LiFePO_4$/-graphene/NFC electrode is prepared by a facile vacuum filtration process. The as-fabricated flexible electrode is suitable as a scalable embedded power supply and easily scale-up manufacturing because of their good electrochemical performance, excellent mechanical properties, low cost and environmental compatibility.

2. Experimental

2.1. Materials preparation

$LiFePO_4$ was synthesized by carbothermic reduction method as described below. Stoichiometric Fe_2O_3, $NH_4H_2PO_4$, Li_2CO_3 and acetylene black were mixed and ball-milled in ethanol medium at 250 rpm for 10 h and then dried at 60 °C. The obtained precursor was heated at 350 °C for 6 h and subsequently sintered at 700 °C for 10 h under a nitrogen atmosphere. The $LiFePO_4$ powder was collected after cooling down.

As illustrated in Fig. 1, the flexible $LiFePO_4$/graphene/NFC (LFP/G/NFC) composite electrode was prepared by vacuum filtration method with a mass ratio of 85:5:10 for $LiFePO_4$, graphene and NFC, respectively. Graphene and NFC used in this work were provided by Suzhou Hengqiu and Ningbo ATMK, respectively. 0.25 g NFC (0.02 g dry weight) was firstly dispersed in 150 ml ethanol and stirred for 2 h, then 0.17 g $LiFePO_4$ prepared was subsequently added and agitated for another 3 h. Simultaneously, 0.01 g graphene with ethyl cellulose as the surfactant, was sonicated for 4 h to form a uniform dispersion in 50 ml ethanol. After mixed with the $LiFePO_4$/NFC slurry, the graphene suspension was continuously stirred for 6 h to obtain the electrode dispersion. The resulting dispersion was vacuum filtered through an organic microporous membrane (0.22 μm pore size, Tianjin Jinteng) and the self-supporting flexible LFP/G/NFC electrode was obtained from the filter cake after drying in vacuo at 150 °C for 12 h and finally separated from the membrane.

2.2. Measurements

The structure and morphology of the samples were characterized by X-ray diffraction (XRD, Shimadzu DX2700) using Cu K_α radiation, Raman spectroscopy (Renishaw inVia), and scanning electron microscopy (SEM, JEOL JSM-6490L).Electrochemical performances of the samples were evaluated by CR2032 two-electrode cells with the prepared flexible electrode as cathode, lithium metal as anode, Celgard 2600 as separator, and 1 M $LiPF_6$ (dissolved in ethylene carbonate/ dimethyl carbonate/ diethyl carbonate with 1:1:1 vol ratio) as the electrolyte. The half cells were assembled in a glove box under an argon atmosphere. The galvanostatic charge-discharge performance of the cells were performed between 2.2–4.2 V using a NEWARE BST-8 electrochemical test instrument at room temperature. Electrochemical impedance spectroscopy (EIS) tests were carried out with a CHI-660 C electrochemical workstation between 0.01–100 kHz with an amplitude of 5 mV, and the cells were charged/discharged to the potential plateau at about 3.4 V before the test. The ion diffusion coefficient was calculated according to $D_{Li} = 0.5(R \cdot T/S \cdot n^2 \cdot F^2 \cdot C \cdot \sigma)^2$ and $Z' = R_{ct} + R_S + \sigma \cdot \omega^{-\frac{1}{2}}$, where R the molar gas constant, T the thermodynamic temperature, S the area of the electrode, F the Faraday constant, C the concentration of Li^+ in the material, σ the Warburg resistance, ω the corresponding frequency in the test.

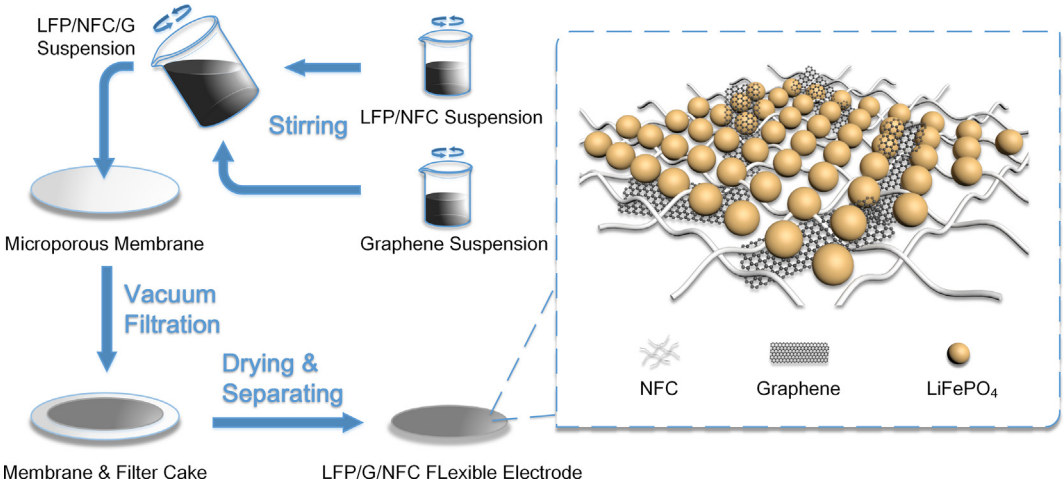

Fig. 1. Schematic illustration of the preparation procedure and the structure of flexible LFP/G/NFC electrode.