



Activated Flake Graphite Coated with Pyrolysis Carbon as Promising Anode for Lithium Storage



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ARTICLE INFO

Article history:

Received 2 December 2015

Received in revised form 2 March 2016

Accepted 2 March 2016

Available online 4 March 2016

Keywords:

Flake graphite
pyrolysis carbon
KOH activation
lithium-storage

ABSTRACT

A facile route to improve the lithium-storage properties of flake graphite (FG) is proposed through coating pyrolysis carbon from polyvinylidene fluoride (PVDF) assisted by KOH activation. The interplanar distance between the graphene sheets of activated PVDF/FG is enlarged, effectively suppressing the electrode deformation during lithium (de)-intercalation. More edge and porous structures of PVDF/FG arising from KOH activation on graphite flakes contribute to improved electron and ion transport, leading to great improvement in its rate and cycling performances. The initial specific capacity of the activated PVDF/FG is 476.6 mAh g⁻¹ at 50 mA g⁻¹ and when the current increases to 1000 mA g⁻¹, the value still retains 142.6 mAh g⁻¹.

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1. Introduction

Currently the lithium-ion battery, one kind of rechargeable solid-state batteries, has been a common technology of choice for portable electronics and electric vehicles mainly on account of its high-energy density. In order to ensure a long lifespan, a high electrode integrity of a battery is needed after a number of charge-discharge cycles, especially under large current densities [1]. As a result of the well-defined layered structure for lithium intercalation, low operating potential and remarkable interfacial stability, graphite has been the dominant anode material in today's commercial lithium-ion batteries [2,3]. However, a passivating solid electrolyte interface (SEI) layer typically can be formed and stabilize on the external surface of graphite in a battery during the first few charge-discharge cycles, which can prevent the undesirable side-reactions such as the co-intercalation of solvent molecules between the graphene layers, as well as the caused gas evolution, but also can inevitably give rise to some capacity loss [4]. It is of particular importance to protect the graphite anode from solvate intercalation and decomposition, meanwhile, decrease the irreversible capacity arising from SEI film. The surface coating on graphite with carbon has been reported to be an effective technique to realize the two aims simultaneously [4,5].

Flake graphite (FG) is the most geologically common variety of natural graphite when compared with other types of natural graphite, including blocky and amorphous graphite, which are distinguished by the different morphologies of crystals. Generally, FG can be obtained in either metamorphic or igneous geologic environments, and nowadays, there are large deposits of FG having been mined in many places of the world. In most instances, FG has distinctly flaky or platy morphology regardless of particle size though all kinds of graphite almost have flaky morphology on some level. Even the FG has been claimed as a promising candidate for the anode material in lithium-ion batteries [6,7], there are still fewer literatures reporting the satisfactory performances for lithium storage. Yoshio et al. concluded that the raw natural FG should be rolled into spheres by impacting milling and then coated with carbon by thermal vapor decomposition in order to enhance its electrochemical properties [7]. Lin et al. reported that the natural FG could be modified by a complicated process to increase the interlayer distance and get a porous structure aiming to the remarkable improvement in specific capacity [6]. On account of the high anisotropy of FG, its wider dimensions in the parallel directions but thinner dimensions in the perpendicular direction to the basal plane are comparably obvious [7]. As a consequence, it is difficult to get thin and uniform electrode slice on the current collector, and its high orientation would allow the basal plane expose towards the current flow direction while the edge plane is vertical to the flow. Since the transportation of electron and lithium ion occurs mainly via the edge plane [7–10], the rate

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capacity of FG in a lithium-ion battery may not give a satisfactory performance due to the insufficient utilization of edge structures.

To tailor the textural properties and structures of carbon materials including graphite, the chemical activation by using KOH as activating reagent is promising because of its low activation temperature and high yield. Wang et al. have summarized KOH activation mechanisms on carbons, as well as the corresponding characteristics and performances, pointing out that the properties of the activated products depended on not only the synthesis parameters, but also the different carbon sources [11]. In the present work, a facile method is proposed for the activation of polyvinylidene fluoride (PVDF)/FG by KOH, as it can not only produce pyrolysis carbon coated on the graphite surface, but also break the arrangement of graphite flakes, creating more edge and porous structures, which are beneficial for the improvement of lithium-storage properties.

2. Experimental Section

At first, 0.5 g PVDF was dissolved into N-methyl-2-pyrrolidone (NMP) solvent to get a homogeneous sol. Then 0.5 g FG purchased from Alfa Aesar was directly poured into the above sol and milled together by grinding manually in an agate mortar to make the graphite uniformly dispersed. Then, the FG/PVDF composite precursor was activated by KOH with a mass ratio of 1:6.5 in a furnace flowing with Nitrogen atmosphere under 600 °C for 1 h to get the activated pyrolysis carbon-coating flake graphite (Activated PVDF/FG). For comparison, 0.5 g FG and 0.5 g PVDF were separately activated by KOH under the same conditions to obtain the corresponding samples, namely activated FG and activated PVDF, respectively. Subsequently, the as-prepared samples were washed by distilled water and collected by pumping filtration repeatedly

till the pH of the filtrate was neutral, followed by drying at 60 °C in an oven.

The crystallographic structure of the as prepared materials was studied by X-ray powder diffraction (XRD) using a Bruker D8 diffractometer with monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), and the diffraction data was recorded in the 2θ range of 10–80°. The particle morphology of the composite was investigated by a FEI Quanta 200 scanning electron microscopy (SEM) and JEOL 2010F transmission electron microscopy (TEM). XPS was performed on VG-Microtech Multilab electron spectrometer.

The working electrode was fabricated with the active material, acetylene black, and binder (Polyvinylidene Fluoride, PVDF) in a weight ratio of 8:1:1 by using NMP as solvent and a copper foil as current collector ($\sim 1.7 \text{ mg cm}^{-2}$), followed by drying in vacuum at 110 °C for 24 h. The R2016 coin cell was assembled in an argon-filled glove box using metallic lithium as the counter electrode with a Celgard 2500 membrane as separator. The electrolyte was 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) (v/v/v, 1/1/1). Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling tests were carried out in a setting voltage range by using an electrochemical workstation (CHI660C) and a CT2001A LAND battery tester, respectively. Electrochemical impedance spectroscopy (EIS) was studied using a Zahner IM6e working station with the amplitude of 5 mV in the frequency range from 1 MHz to 10 mHz.

3. Results and Discussions

For crystallography study, the XRD patterns of as-prepared activated PVDF/FG, FG and activated PVDF have been shown in

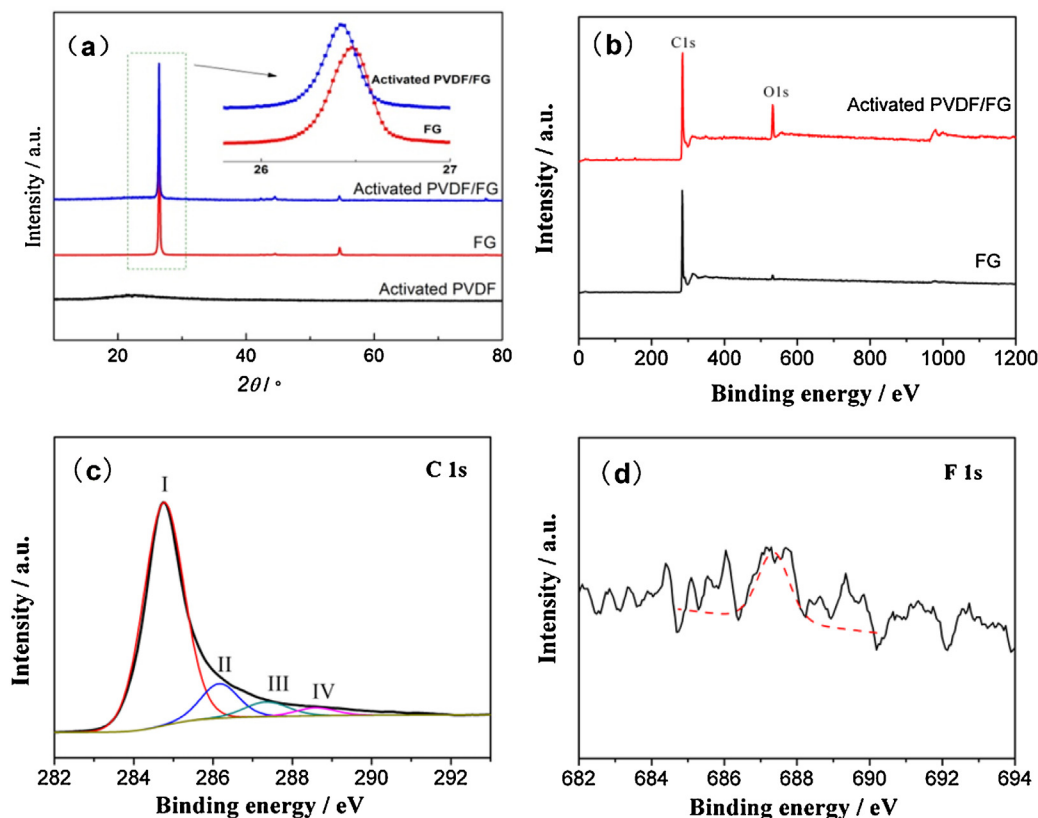


Fig. 1. (a) XRD patterns of activated PVDF/FG, FG and activated PVDF, and the insert is magnified patterns around (0 0 2) peak. (b) The survey scan of activated PVDF/FG and FG. (c) C 1s and (d) F 1s core level XPS spectrum of activated PVDF/FG.

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