



Rice paper-derived 3D-porous carbon films for lithium-ion batteries

L.C. Zhang, Z. Hu, L. Wang, F. Teng, Y. Yu, C.H. Chen*

CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Anhui, Hefei 230026, China

ARTICLE INFO

Article history:

Received 25 October 2012

Received in revised form

13 November 2012

Accepted 14 November 2012

Available online 23 November 2012

Keywords:

Rice paper

Carbon film

Free-standing

Separator

Lithium-ion battery

ABSTRACT

Rice paper (RP) is thermally carbonized in nitrogen to prepare three-dimensionally porous carbon films, which are used for the first time as both a free-standing active anode material and a current collector of a cathode (LiFePO₄ here) for lithium-ion batteries. The latter is fabricated through a one-step co-sintering of a Li–Fe–P–O precursor top layer supported on the rice paper. The rate and cycling performances of both these electrodes are found to be rather good or even better than the traditional electrodes due to the three-dimensionally porous structure of the RP-derived carbon. We also design and fabricate an RP-based full cell constructed with the above mentioned anode and cathode together with an RP membrane as the separator. Without using traditional metallic current collectors and separator membranes, such a cell exhibits reversible cycling performance.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

With ever increasing care for global environment and energy sources, materials derived from eco-friendly and renewable biological materials are attracting extensive attentions, especially in the field of lithium-ion batteries. For example, people have tried prepared binders or active anode materials from bio-materials such as cellulose fibers, pig bones or bio-minerals from the jaws of a marine bloodworm [1–3]. As a biomaterial, a rice paper (RP) is a kind of non-woven fibrous membrane which is made from some certain plants such as bamboo. It can also be used in our previous study as the separator in the lithium-ion cells which show good electrochemical performance [4].

On the other hand, as the most widely used anode materials for lithium-ion batteries, carbonaceous substances can be either crystalline graphite or amorphous hard carbons. As reported in literature [5–8], compared with the graphite anode, a hard carbon can exhibit comparable cycling performance, higher BET surface and better rate performance. Also, due to the high electronic conductivity of carbon, some groups have used graphene or carbon papers made of carbon nanotubes as the current collectors of electrodes [9–14], which may introduce more flexibility and avoid using traditionally metal foils. It is reasonable to use a hard carbon as an alternative.

In this study, we carbonize the RP to obtain a hard carbon film, or RP-derived carbon (RPC) film, and use it as a free-standing anode

for lithium-ion cell. Meanwhile, the RPC is also used as the current collector of a cathode (LiFePO₄ here). Furthermore, we combine all of RP-derived anode, cathode and separator together in one full cell and characterize its electrochemical properties. Because the fabrication of such a full cell can be completed in one step, this novel-constructed cell may be put into some potential applications.

2. Experimental

2.1. Synthesis of the RP-derived carbon (RPC)

A commercial RP membrane (Taoji Rice Paper Co., Anhui) was purchased and stored in a drier (Dry-498XE, Ace Dragon Co.) at room temperature and under a relative humidity of less than 5%. The RP membrane was punched into discs with a diameter of 14 mm, which were heated and carbonized at 630 °C for 5 h in a pure nitrogen atmosphere to obtain discs of the RPC, which could be used directly as an active anode electrode for lithium-ion batteries as schematically shown in Fig. 1a.

For comparison, a commercial graphite powder (ATL, Guangzhou) was made into a traditional anode electrode laminate on a copper foil, i.e. graphite@Cu. The composition of the electrode was 90 wt% graphite and 10 wt% poly(vinylidene difluoride) (PVDF).

2.2. Synthesis of in situ produced LiFePO₄@C laminate

Stoichiometric amounts of lithium carbonate (Li₂CO₃), monoammonium phosphate (NH₄H₂PO₄), and iron oxide (Fe₂O₃) with a molar ratio Li:Fe:P = 1:1:1 were mixed in a ball-milling jar.

* Corresponding author. Tel.: +86 551 3606971.

E-mail address: cchchen@ustc.edu.cn (C.H. Chen).

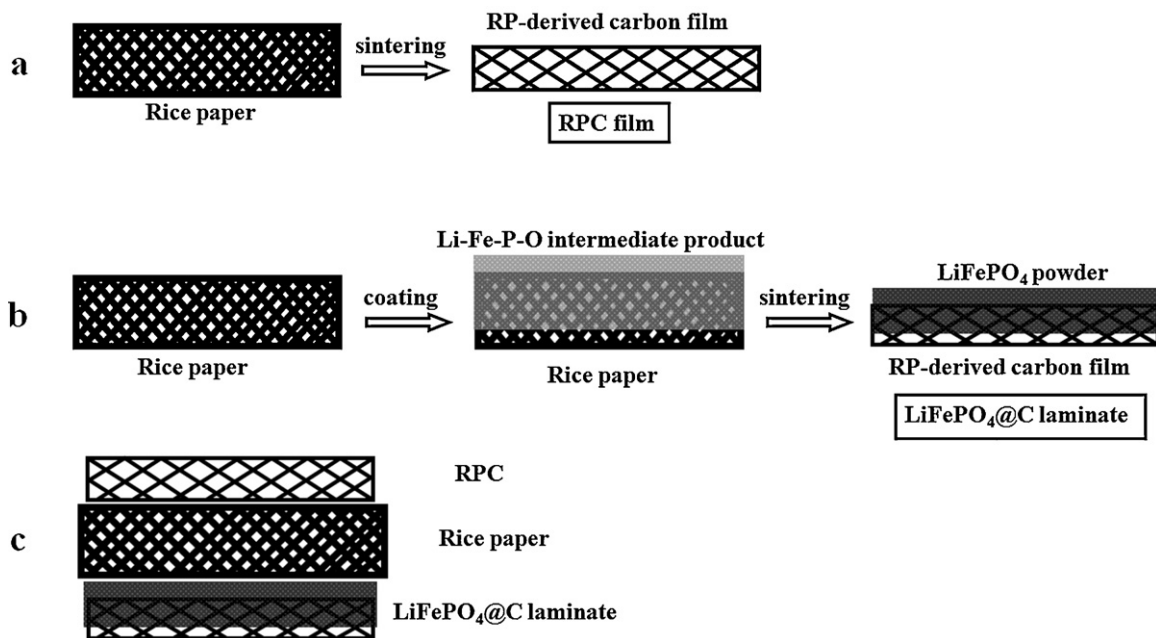


Fig. 1. The schematic illustration of RPC synthesis via RP carbonization (a) and LiFePO₄@C laminate by a one-step co-sintering process (b), and a RP-based full cell assembly (c).

Then some glucose as a carbon source was added into the jar. The mass of glucose was 15% that of the target product LiFePO₄. Then the mixture was ball-milled for 24 h with acetone as the dispersant. Subsequently, the obtained mixture was dried at 120 °C and calcined at 350 °C in a pure nitrogen atmosphere for 10 h. After being grinded, this calcined Li–Fe–P–O intermediate product powder was mixed with PVDF in a mass ratio of 92:8 with N-methyl pyrrolidone (NMP) as the dispersant to obtain a slurry. Then the slurry was coated on the RP membrane with a doctor-blade method to form a thick film. Due to the 3-dimensionally porous structure of the RP, some portion of the slurry can permeate into the RP membrane through its pores and along its fibers. Thanks to the presence of the binder PVDF, the coating layer was adhered tightly with the RP membrane. After drying in an oven at 120 °C, the thick film supported on the RP membrane was punched into round discs with a diameter of 14 mm. Then these discs were sintered at 630 °C for 5 h in nitrogen atmosphere to form an in situ produced LiFePO₄@C laminate (Fig. 1b). Thus, through above one-step co-sintering process, the calcined Li–Fe–P–O intermediate product was converted to a well-crystallized LiFePO₄ powder, meanwhile the RP membrane was converted to a carbon fibrous film.

For comparison, part of the intermediate product powder was sintered alone at 630 °C for 5 h in nitrogen atmosphere directly to synthesize a LiFePO₄ powder. Then a traditional LiFePO₄ electrode laminate on an aluminum foil, i.e. LiFePO₄@Al, was prepared. The composition of the electrode was 84 wt% LiFePO₄, 8 wt% acetylene black and 8 wt% PVDF.

2.3. Electrochemical measurements and structural analyses

The coin-type half cells (CR2032 size) were assembled in an argon-filled glove box with above electrode laminates as working electrodes, Li metal as the counter electrode, and 1 M LiPF₆ in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1, w/w) as the electrolyte. The separators were either a layer of Celgard 2400 membrane or the RP membrane. The schematic illustration of a RP-based full cell assembly is shown in Fig. 1c. The cells were tested on a multi-channel battery test system (NEWARE BTS-610) with

galvanostatic charge and discharge in different selected voltage ranges.

The microstructures of the RPC and the LiFePO₄@C laminate were observed under a scanning electron microscope (SEM, JSM-6390LA and SIRION200). The specific surface areas of the graphite, RP membrane and the RPC were measured on a BET analyzer (Beckman coulter, SA3100).

The structures and compositions of the RPC and the LiFePO₄@C laminate samples were characterized by X-ray diffraction (XRD, Philips X'Pert Pro Super). The diffraction patterns were recorded at room temperature in the 2θ range from 10° to 70° using Cu Kα radiation.

3. Results and discussion

3.1. RPC film

Fig. 2 presents the SEM images of the surface and cross-section morphologies of the RP and the RPC film. It can be seen that the RP membrane is consisted of interweaved tortuous cellulose fibers with diameters of 5–20 μm (Fig. 2a). The thickness of the RP membrane is about 111 μm (Fig. 2b). A large number of pores and three-dimensionally interweaved fibrous structure can provide a huge contact area with the later-put intermediate Li–Fe–P–O top layer. After the heat-treatment, the RPC film consists of carbon fibers with smaller diameters and larger pores compared with the RP membrane due to the pyrolysis of the bio-cellulose in nitrogen (Fig. 2c). Meanwhile, the RPC film becomes 62 μm in thickness (Fig. 2d), which is thinner than its starting material RP membrane. Fig. 2e shows the SEM image of the cross section of a carbon fiber in the RPC film and there are many fine nanopores even in a single fiber which can significantly increase the specific surface area and work as pathways for the ions when it is used as an electrode in a lithium cell.

The XRD pattern of the RPC film is shown in Fig. 3. The broad peaks at about 23° and 44° correspond to the (002) and (100) diffraction peaks of graphite, which suggest that the RPC is composed of amorphous carbon or a poorly graphitized structure [1]. Fig. 4 shows the nitrogen sorption isotherm of the RPC film and the

Download English Version:

<https://daneshyari.com/en/article/187604>

Download Persian Version:

<https://daneshyari.com/article/187604>

[Daneshyari.com](https://daneshyari.com)