


Facile Fabricated of CNT Based Free-Standing Electrode with Cotton Carbon for Flexible Lithium-Ion Batteries

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Abstract: Flexible lithium ion batteries (FLIBs) are considered as potential application in the next 20 years for wearable devices and internet of things. However, it is a rough road to commercial preparation of flexible electrodes due to the complicated experimental process and expensive cost. Herein, a facile fabricated strategy, filtration, is applied to disperse active materials LiFePO₄ in conductive flexible network (LFP/CNTs/cotton) as a free-standing cathode for FLIBs. The fabricated free-standing LFP/CNTs/cotton electrode holds promising electrochemical stability, which still has a high capacity of 120 mAh/g at a current density of 2000 mA/g for 900 cycles. In addition, this method can be easily replicated for the flexibility of other powder active materials. This study is of great significance for the industrialization of the flexible electrode and exhibiting great potential in high-performance flexibility energy-related systems.

Keywords: free-standing; flexible batteries; high stability.

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1. Introduction

With the advent of the 5G era, flexible lithium ion batteries (FLIBs) with excellent electrochemical performance and mechanical properties play a vital role in the application fields of intelligent and portable micro-devices such as flexible ultrasonic

communication, medical flexible sensors, software robots and even multi-flexible technologies like smart driving, etc.[1-4] However, the stable and regular work of flexible batteries in a natural surrounding is a headache for many scientific



researchers. In the bending process, it is necessary not only to ensure that the electrode without fracture but also to pledge that the active material does not peel-off from the collector, which can not be guaranteed by the traditional coating method to prepare the electrode sheet. So far, many researchers have taken different measures to replace the traditional collector system to prepare flexible electrodes, such as paper electrodes[5], metal foil electrodes[6], polymer electrodes[7], fabric electrodes[8], and carbon-based graphene (rGO) or carbon nanotubes (CNTs) electrodes[9,10]. Although these strategies have enhanced flexibility of electrodes, to some extent, improving the electrochemical working stability of flexible battery.

Generally, the electrochemical stability of flexible materials is a great challenge. Carbon-based flexible electrodes, especially CNTs-based flexible electrodes are still the most potential due to the easy route to preparation, rich active sites brought by large specific surface area, and light weight[11].

However, it does not require additional processing for preparing flexible electrodes, despite the cost of CNTs is slightly higher, so in general, the fabrication of CNTs-based flexible electrodes with a high cost-performance. It is currently the most flexible electrode with commercial potential. More than that, many of the fabrications of flexible electrodes are to prepare flexible anode electrodes, such as SnO₂[12], Si/C[13]. On the other hand, a few of the preparation methods or techniques for

flexible cathode electrodes cannot be used for the preparation of flexible anode electrodes or others cathode, such as LiFePO₄[14]. In terms of performance, although the electrochemical performance of rGO-based flexible batteries is considerable, it has a great relationship with the purity, the number of layers and the number of oxygen-containing functional groups, which puts forward strict requirements for graphene, both in terms of cost and preparation operation, leading to the increases of research risk. However, as a carbon-based flexible electrode, the degree of commercialization of CNTs is much better than that of rGO, it has great prospects for development.

At present, many researchers have reported on the preparation methods of carbon nanotube-based flexible electrodes, including in situ growth of active materials[15], electrospinning[16], hydrothermal[17] and filtration[18]. Nevertheless, this requires harsh preparation conditions and additional raw materials.

In this paper, we have reported for the first time to use cotton carbon to enhance the hydrophilicity of CNTs and to form interwoven networks. Besides, the co-operation of conductive cotton carbon and carbon nanotubes makes the prepared flexible electrode have favorable flexibility and high electrochemical stability.

2. Materials and Methods

2.1. Materials.

Lithium iron phosphate (LiFePO₄, P198-S13) was purchased from Shenzhen Kejing Star Technology Co., Ltd. Sodium Lauryl Sulfate (SDS, 99%) was purchased from Aladdin Chemical Co., Ltd. carbon nanotube (CNTs, XFM31) was acquired from Nanjing Xianfeng Nanotechnology Co., Ltd. Cotton carbon (Prepared by annealing the degreasing cotton in inert atmosphere).

2.2. Fabrication of LFP/CNTs/cotton.

The 20 mg CNTs, 0.05g SDS were dispersed in 50 mL distilled (DI) water, after ultrasonic 20 min, the mixture was filtered in a nylon filter by a sand-cored funnel and washed with DI water until not observed visible bubbles, the first carbon film was finished. And then, 60 mg cotton carbon, 60 mg CNTs, 0.3g SDS and 20 mg SDS were dispersed in

150 mL DI water for ultrasonic 4h, after ultrasonic dispersion, the mixture was poured into a sand core funnel for filtration, and a film was deposited on the CNTs film. Finally, washed with DI water and tearing the film after drying at the 60 °C oven.

2.3. Characterization.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out on a field emission SU-8000 microscope.

2.4. Electrochemical performance measurements.

Coin cells (type: 2025) was assembled in an Ar-filled glovebox. Adopting LFP/CNTs/cotton as cathodes, lithium foils as anode, and microporous polypropylene membranes as separators. The electrolyte is 1M LiPF₆ in EC:DEC (1:1, v/v). Galvanostatic charge/discharge measurements

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were performed on a LAND CT-2001A battery testing system (Wuhan, China) in the voltage window of 2.35–4.2 V and 2.0–4.0 V at ambient temperature. Cyclic voltammetry (CV)

was recorded on an Autolab PGSTAT204 electrochemical workstation.

Electrochemical impedance spectroscopies (EIS) were performed in the frequency range of 100 kHz to 0.01 Hz.

3. Results and Discussion

The surface morphology of LFP/CNTs/cotton was studied using the SEM (Fig. 1(a-b)). Unlike the powdered electrode material, the free-standing electrode of LFP/CNTs/cotton was full of intertwined CNTs network while hardly observed the LFP particles, which is fundamental to maintain the LFP/CNTs/cotton flexible without any powder dropping or breaking. From the mapping images of LFP/CNTs/cotton, the element of C, Fe, O and P are detected, which confirmed the existing of LFP,

and from the contour of the mapping image can be proved the elements uniform distribution of LFP/CNTs/cotton. Fig. 1(c) exhibits the photo of LFP/CNTs/cotton electrode. The LFP/CNTs/cotton cathode has excellent flexibility despite no binder and additional assistance. Furthermore, the thickness of this cathode is only 0.26 mm, which provides a powerful possibility making the thickness of whole flexible battery devices no more than 1 mm.

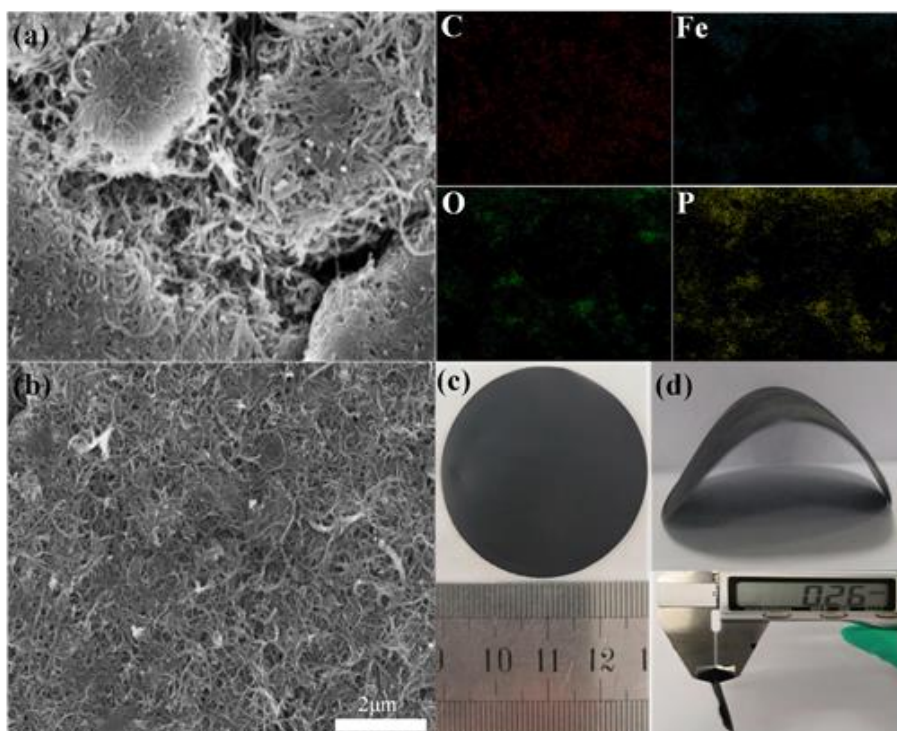


Figure 1. (a) SEM images of LFP/CNTs/cotton and EDS mapping images of C, Fe, O and P. (b) low rate SEM image of LFP/CNTs/cotton. (c) LFP/CNTs/cotton electrode's photo and (d) thickness.

Assembling LFP/CNTs/cotton flexible cathode into a lithium ion cell demonstrates excellent electrochemical performance. As shown in Fig. 2(a), the rate and capacity performance of LFP/CNTs/cotton has a great boost than prepared by conventional coating method, and there is still 120 mAh/g specific capacity at 2 A/g, while the

traditional LFP capacity attenuation is 80 mAh/g. The platform of charge-discharge curve can be clearly observed from Fig. 2(b), as the current density increases, the polarization is not more seriously affected. Even the current density arrived at 1 A/g, the platform is still not affected too much, indicating that the interface impedance is low

between the first layer CNTs substrate and the second film, and overall shows good conductivity. While the current density continues to increase to 2 A/g, affected by reaction kinetics, the platform begins to shift to high and low voltage, which is due to the serious polarization phenomenon, but - remains a specific capacity of 120 mAh/g. From the

CV curve of Fig. 2(c) can be clearly observed, with the increase of sweep speed, the shape of redox peak gradually becomes larger, but the peak type is basically maintained, which also indirectly confirms the good electronic conductivity and ion transport of LFP/CNTs/cotton flexible electrode.

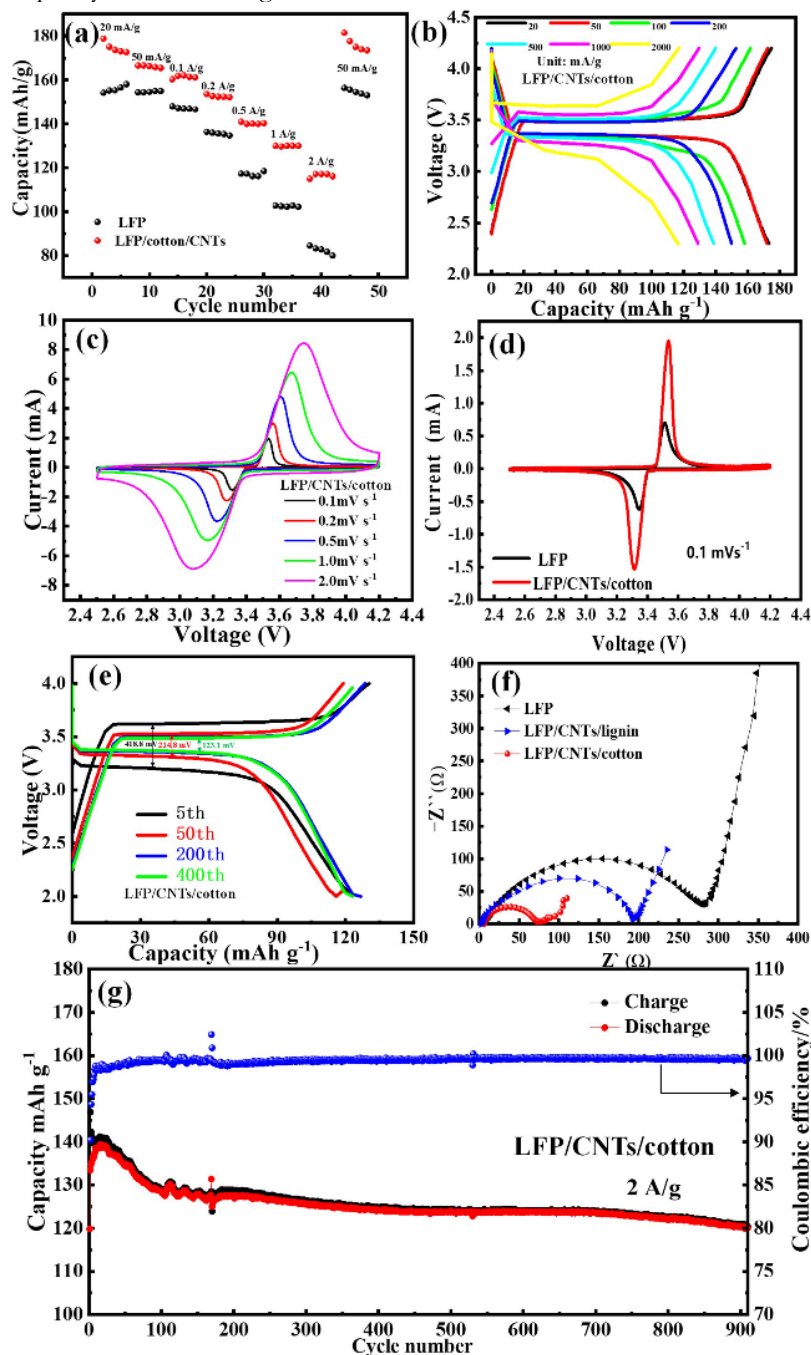


Figure 2. (a) Rate performance of LFP/CNTs/cotton. (b) Charge/discharge curves of LFP/CNTs/cotton with different current density. (c) CV curves of LFP/CNTs/cotton with different scan rates. (d) CV curves of LFP/CNTs/cotton and LFP at 0.1mV/s. (e) Charge/discharge curves of LFP/CNTs/cotton with different cycles. (f) Nyquist plots of LFP/CNTs/cotton, LFP/CNTs/lignin and LFP. (g) Cycling stability of the LFP/CNTs/cotton free-standing cathode at 2A/g.



From the comparison of the CV curves of LFP/CNTs/cotton and LFP in Fig. 2(d), it is intuitively observed that the pair of redox peaks of LFP/CNTs/cotton is significantly larger than that of traditional LFP, which provides a direct explanation for the higher capacity than LFP. Perhaps attribute to the sizeable specific surface area of LFP/CNTs/cotton, the porous structure of CNTs and cotton can also undergo partial Li^+ intercalation and deintercalation reactions, resulting in a significantly higher actual capacity than traditional LFP electrodes. In addition, it is further found that the pair of redox peaks of LFP/CNTs/cotton are much sharper than LFP, confirming that the overall conductivity of LFP/CNTs/cotton is superior to traditional LFP. This is also confirmed from the EIS map of Fig. 2(f), the traditional LFP impedance is about 300 ohms. The self-supporting electrode prepared with lignin instead of cotton is 200, while the impedance of LFP/CNTs/cotton is only 75, which directly indicates that LFP/CNTs/cotton has good conductivity. In addition, LFP/CNTs/cotton are also subjected to a long cycle life at high current density. Fig.2 (g) illustrates that the cycle in the first 200 laps is particularly unstable, the capacity first increases and then decreases sharply, and after 200 laps the capacity rises again in a cliff-like manner, and then start a stable cycle. What makes this phenomenon is that may be due to the activation of LFP/CNTs/cotton at high current density, CNTs and cotton allow ion insertion and extraction, at the initial stage of charge and discharge, the large specific surface area provides more lithium storage sites, it shows that the capacity of the first 10 laps

increases, but the polarization is serious. When the polarization is serious to a certain extent, because the long length aspect ratio of the CNTs is relatively long, it will cause much Li^+ embedded in the CNTs too late to be fully deintercalated and enter the anode electrode before they are discharged. At the end, the result is much Li^+ always trapped in the hole of the CNTs. The macroscopic performance is that the capacity drops sharply. But with the charge/discharge continuing, the polarization begins to balance, at this time, the intercalation and deintercalation of Li^+ begin to stabilize. When the cycle reaches about 200 cycles, the internal electric field reaches equilibrium, Li^+ begins to completely intercalate and deintercalate, and the capacity rises sharply, keeping the cycle stabilizes. This phenomenon can be better explained by the charge and discharge curve in Fig. 2(e). The polarization phenomenon at the beginning cycle of fifth is serious, and the distance between the charging platform and the discharge platform is 418.8 mV. By the 50th cycle, the polarization effect is significantly weakened, and the platform interval is 214.8 mV, when it circulates to 200 circles, the internal electric field has reached equilibrium and the polarization phenomenon gradually disappears, which platform spacing is only 123.1 mV and has been maintained at 123.1 mV. In addition, the new charge/discharge internal environment that achieves the new balance system, which exhibits good cycle stability, with a stable cycle of more than 900 cycles, and the coulomb efficiency and capacity has not greatly attenuated. All in all, the rate performance of LFP/CNTs/cotton electrodes and the cycle stability at high rates are very excellent.

4. Conclusions

In this paper, we designed and facile constructed free-standing LFP/CNTs/cotton flexible electrode as cathode for FLIBs. By a simple filter method to accomplish the fabrication of flexible electrode. Cotton carbon with a tubular structure similar to carbon nanotubes, the interaction between cotton carbon and CNTs not only enhances the ability of CNTs to disperse in aqueous solution, but also enhances the overall mechanical properties of the electrode. Meanwhile,

since no binder is used, this greatly improves the loading of the active material and enhances the overall conductivity of the flexible electrode. As a result, LFP/CNTs/cotton exhibit favorable capacity, reliable rate performance and promising cycling stability. Moreover, this facile strategy of fabricated flexible electrodes can be easily replicated for the preparation of flexible anode electrodes and other various types of powder materials flexible.

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Conflicts of Interest

The authors declare no conflict of interest.

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