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Freestanding silicon/carbon nanofibers composite membrane as a flexible anode for Li-Ion battery

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HIGHLIGHTS

- The composite membrane is obtained by electrospinning and chemical vapor deposition.
- The novel composite membrane is prepared for the flexible anode in LIBs.
- High capacity and good cyclability are achieved as the novel composite anode.

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ABSTRACT

A flexible freestanding Si/Carbon nanofibers composite membrane with high mechanical strength is prepared by electrospinning and chemical vapor deposition techniques. The physical characteristics of Si/Carbon nanofibers are characterized by scanning electron microscopy, thermo-gravimetric analysis, X-ray diffraction and transmission electron microscopy. The electrochemical performances are investigated by galvanostatic charge-discharge tests and cyclic voltammograms. Carbon nanofibers matrix shows uniform diameter, smooth surface and three dimensional network structures. Si shell with a thickness of 50 nm is uniformly deposited on the surface of carbon nanofibers. The as-synthesized Si/Carbon nanofibers anode delivers 1310 mAh g^{-1} at 2nd cycle and the loss rate of capacity per cycle is as lower as 0.0703% from 2nd to 480^{th} cycles, which exhibits excellent electrochemical performance. It demonstrates that the structure of three dimensional network membrane that has played an important role in alleviating volume expansion-contraction of Si-based anodes during charge-discharge process.

1. Introduction

The lithium-ion batteries (LIBs) as a kind of commercialized rechargeable batteries have been widely applied in portable electronic products [1–6]. However, the main bottleneck including the energy density, power density and cycle performance have seriously inhibited the development of high performance LIBs [7–9]. The commercial graphite anode of LIBs has already approached its theoretical capacity limit of C_6Li (372 mAh g^{-1}) [10]. It is an urgent task to explore new anode electrode with high capacity and power density in order to meet the ever-growing requirements of next-generation LIBs [11,12]. Si was considered as one of the most promising anode materials because of its high theoretical specific capacity of 4200 mAh g^{-1} (close to ten times that of the graphite anode [13,14]. However, the implementation of Si material for LIBS application has been greatly hampered by the large volume expansion (300%) and low electric conductivity [15–17]. In order to improve the electrochemical performance, a design of nanostructure included silicon nanotubes [18], silicon nanowires [19], silicon nanowalls [20] and nanosized porous silicon materials [21–23] have been widely suggested. But nanostructured Si is liable to aggregate, and results in the ineffectiveness of electronic transport pathways [24]. Thus, an effective method was proposed to reduce the side reaction and volume expansion by forming composite materials of the high electric conductive and Si nanoparticles [25]. For example, Si/C composites [26–28], Si/carbon pyrolysis [29,30] and amorphous Si/C thin film [31] have reported to exhibit excellent lithium storage performance. Many efforts have been made by researchers to gain improvement of capacity and cyclability. However, the traditional synthesizing approaches of Si-based composite electrodes could decrease the gravimetric and volumetric energy densities because of the introduction of polymer binders [32]. Besides, these complex preparation methods are difficult to large-scale production and low economic benefits for

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commercialization.

Recently, some considerable attention have been focused on three-dimensional (3D) porous materials as promising new anode materials for LIBs [33,34]. As is well known, the carbon nanofiber (CNF) membrane has some merits as follows: (1) the 3D network structure of fiber morphology can ensure a larger wetting area of the material for the electrolyte with a higher rate of liquid retention, (2) CNF membrane is used as a flexible freestanding substrate, which can improve electron conductivity of Si materials and provide a rapid path for the lithium ions and electrons transfer.

Herein, the flexible freestanding Si/CNFs composite membrane is obtained through the electrospinning combined with chemical vapor deposition technique. The composite membrane can be directly used as electrode material without adding conductive additive and additional binder. It avoids complex process of mixing and coating. The Si/CNFs composite membrane can be arbitrarily bent and folded, showing good flexibility and high mechanical strength. These advantages endow the Si/CNFs anode as an outstanding lithium storage performance.

2. Experimental section

2.1. Materials preparation

Si/CNFs composite membranes were prepared by the combination of electrospinning and chemical vapor deposition technique. Typical synthesis process of the Si/CNFs composite membranes can be described as follows. Firstly, 1.0 g polyacrylonitrile (PAN, $M_w = 150000\ \mathrm{g\,mol^{-1}}$) was dispersed in 9.0 g N, N-dimethyl formamide solvent with vigorous magnetic stirring at 70 °C for 12 h. The high voltage power supply of the electrostatic spinning was pre-heated for half an hour in advance, and the spinning liquid was poured in the syringe. The PAN membrane was obtained under a voltage of 18 kV. At the same time, the glass panel was used as a collector, which placed 10 cm below the needle. Subsequently, the PAN fiber membrane was dried in a vacuum oven for 24 h at 60 °C. Finally, the as-spun nanofiber membrane was pre-oxidized at 180 °C for 2 h in air and then carbonized at 900 °C for 2 h in Ar atmosphere (heating rate: 10 °C $\mathrm{min^{-1}}$). The pre-oxidation process can improve the degree of crystallization of PAN-nanofibers.

Si grown on the CNF membranes was finished via chemical vapor deposition where silane gas (SiH_4) was used as the Si precursor. Eventually, the Si/CNFs composite membranes were obtained at 490 °C.

2.2. Materials characterization

The morphologies and structures of Si/CNFs composite membranes were investigated by JSM-6610A scanning electron microscope (SEM) and JEM-2100 transmission electron microscopy (TEM). The crystallographic structures of the composite membranes were determined with X-ray diffractometer (XRD, German D/max-2550, CuKα, λ = 1.5418 Å). The relative contents of Si and CNFs in the composite membrane were calculated by using thermo-gravimetric (TG) analyzer TGA Q50.

2.3. Electrochemical measurement

Electrochemical performances of the as-synthesized Si/CNFs composite membranes were performed by galvanostatic charge and discharge measurements in LIR2016 coin cells. The cells were assembled via using resultant Si/CNFs composite membrane was cut into a size of 1 × 1 $\mathrm{cm^2}$ as working electrode, lithium foil as the reference electrode and counter electrode with water and oxygen ratio lower than 1 ppm. In this process, the Celgard 2400 standard membrane was treated as the separator. 1M $LiPF_6$ dissolved in the organic solvents of ethylene carbonate and dimethyl carbonate (volume ratio 1:1) as electrolyte. A slurry electrode were prepared where pure Si nanoparticles as an active material (70 wt%), polyvinylidene fluoride as a binder (20 wt%), carbon black as a conducting agent (10 wt%). The slurry was dried for 24 h at 80 °C under vacuum to get rid of the residual solvent completely. Generally, the loading mass of Si electrode was about 0.76 mg $\mathrm{cm^{-2}}$. Galvanostatic charge/discharge testing on BTS-5V 10 mA electrochemical workstation. The cyclic voltammetry (CV) was tested in CHI-604e electrochemical workstation at a scan rate of 0.1 mV $\mathrm{s^{-1}}$.

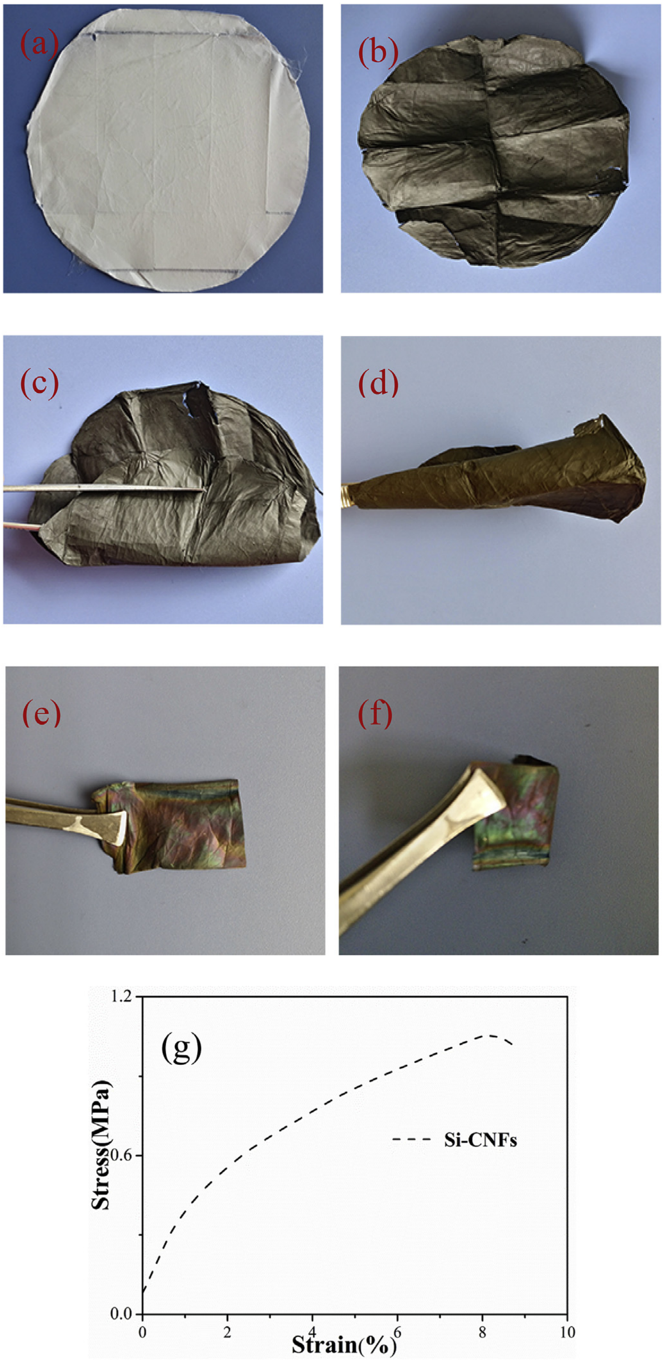

Fig. 1. Physical images of (a) PAN nanofiber membrane, (b) CNF membrane, (c and d) CNF membrane after bent or folded to 180° and 360°, (e) Si/CNFs composite membrane, (f) Si/CNFs composite membrane after benting to 180°, and (g) the tensile stress-strain curve of Si/CNFs composite membrane.