Electrochemistry Communications 46 (2014) 52–55

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Building ultrastable carbon nanotube/vanadium oxide electrodes via a crosslinking strategy

Xilai Jia [a,b], Ranran Wang [c], Zheng Chen [c], Hang Yu [c], Fei Wei [a,*], Yunfeng Lu [c,*]

[a] Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[b] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing 102249, China
[c] Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095, USA

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 30 May 2014
Accepted 2 June 2014
Available online 10 June 2014

Keywords:
Lithium-ion battery
Carbon nanotube
Crosslinking strategy
Stable electrode

ABSTRACT

Reliability of electron and ion transport pathways is one of the most essential criteria that govern cycling stability of lithium-ion battery devices. Herein, crosslinked CNT/V_2O_5 composite electrodes were fabricated using a chemical coupling method between their interfacial contacts. The crosslinked electrodes show a mechanical strength of ~4.8 MPa, and have stable performance during long-term charge–discharge cycles. The results suggest the importance of forming a crosslinked structure to enhance electrode stability.

1. Introduction

High-performance energy storage devices, such as lithium-ion batteries and supercapacitors, are essential for a broad range of applications. Such devices rely on effective transport of electrons and ions during their charge and discharge processes, where energy is reversely transformed as chemical energy and electric energy, respectively [1]. Reliability of such transport pathways is therefore one of the most essential criteria that governs the device cycling stability.

Traditionally, the electron-transport pathways are constructed by mixing active electrode materials with conducting agents and polymeric binders [2]. Such an approach utilizes a significant amount of inert components inevitably compromising the device's energy density. Moreover, the mechanical stress that may be generated due to large volume change of active materials during charge–discharge process may destroy the electron-conductive pathways, resulting poor stability. Alternatively, binder-free electrodes have been proposed [3], mostly with active materials directly incorporated into conducting agents. Such electrodes could achieve improved transport kinetics; however, the reliability may need further engineering for better cycling stability.

Herein, we report the construction of highly robust binder-free electrodes via a crosslinking strategy between carbon nanotubes (CNTs) and oxide nanowires. Nanowires of vanadium oxide (V_2O_5) were used as the model system. Besides their high aspect ratios, V_2O_5 nanowires also possess high theoretical capacity and can be synthesized at low cost [4,5]. Fig. 1a illustrates the structure of such electrodes. Experimentally, functionalized CNTs and V_2O_5 nanowires were dispersed in chloroform forming a homogeneous dispersion. Coupling agent of 3-(triethoxysilyl) propyl isocyanate (TPI) was then added to initiate crosslinking bridge between CNTs and nanowires. Subsequent hydrolysis and condensation reactions of TPI with the surface hydroxyl groups on the nanowires, as well as the reactions between the isocyanate constituents between the CNTs and nanowires, are expected to lead to the formation of crosslinked CNT/nanowire networks. A following filtration process enables the formation of robust yet flexible nanocomposite electrodes. Such interpenetrating network structure creates interconnected porous channels for effective ion-transport, while the crosslinked interfacial contacts within CNT/nanowires enable stable electron-conductivity. Note that flexible electrodes were reported by a physical mixing of CNTs with nanowires [6]. Nevertheless, to the best of knowledge, this is the first demonstration of building crosslinked networks of CNTs and nanowires towards highly stable binder-free electrodes.

2. Experimental

V_2O_5 nanowires were synthesized using a reported hydrothermal approach [7]. The product was washed and then dried by freeze-drying. Pristine CNTs were purified using 18 wt.% HCl and 20 wt.% HF solution alternatively. Then, they were oxidized using HNO_3 solution at 60 °C for 1 h. Next, 16 mg of as-obtained CNTs was dispersed in

---

* Corresponding authors. Tel.: +86 10 62785464; fax: +86 10 62772051.
E-mail addresses: wf-dce@tsinghua.edu.cn (F. Wei), luucla@ucla.edu (Y. Lu).

http://dx.doi.org/10.1016/j.elecom.2014.06.003

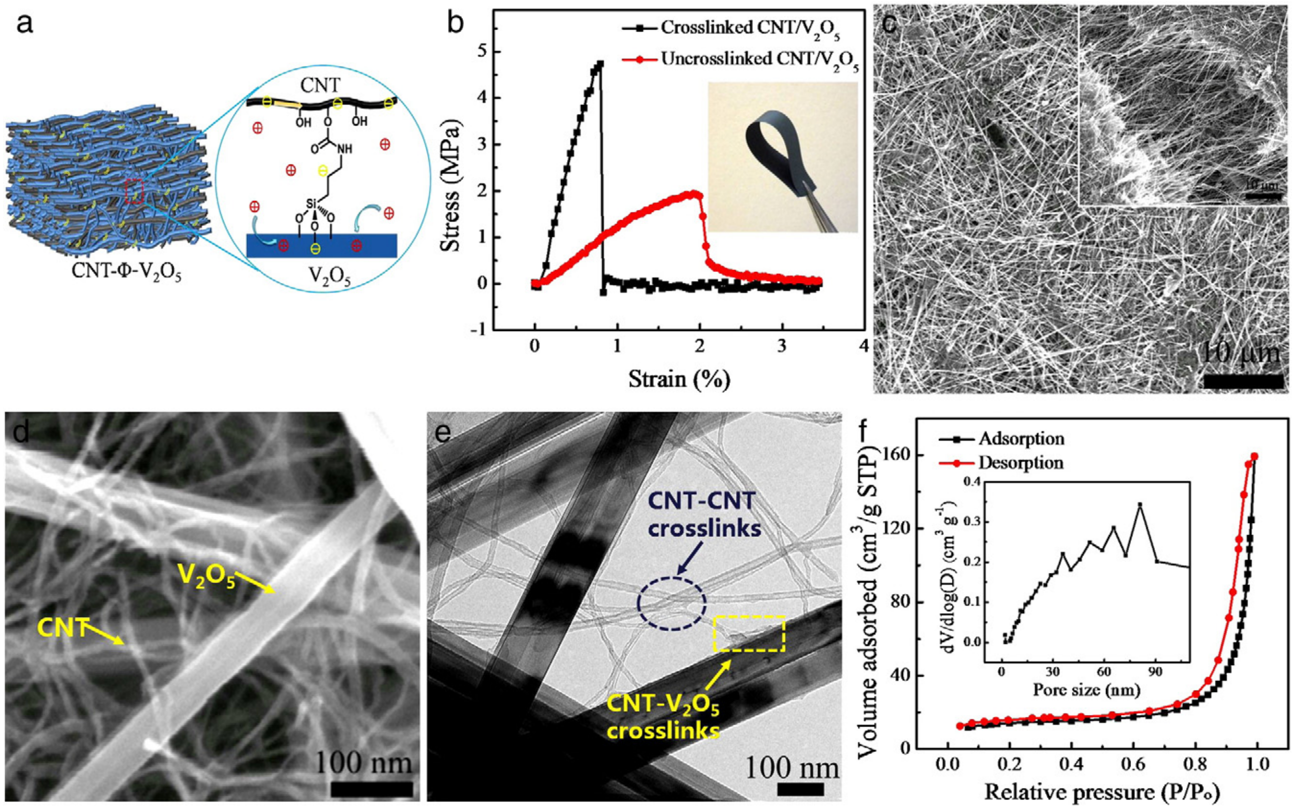

Fig. 1. (a) Schematic structure of crosslinked CNT/V_2O_5 electrodes. (b) Mechanical strength comparison of crosslinked and uncrosslinked electrodes. (c, d) SEM and (e) TEM images and (f) nitrogen isotherms of crosslinked electrodes.

chloroform, to which 48 mg of V_2O_5 nanowires and 160 μL of TPI were added. After stirring, the mixture was placed in an oven at 60 °C for 2 days. The obtained product was filtrated and free-standing films were formed. Finally, they were dried at 150 °C under a pressure of 0.5 MPa. Uncrosslinked CNT/V_2O_5 electrodes were fabricated using an identical process without TPI.

Fourier transform infrared spectrum (FTIR) was performed using a Nicolet 6700 spectrometer. The surface composition of crosslinked composite was analyzed by X-ray photoelectron spectroscopy (XPS) with a PHI 3057 spectrometer using Mg–K X-rays. Composite morphology was characterized using scanning electron microscopy (SEM, JSM-6700) and transmission electron microscope (TEM, FT12) instruments. Nitrogen-sorption isotherms were measured with a Micromeritics ASAP 2020 analyzer. Mechanical tests were conducted on INSTRON 5564 at 2.0 mm/min. Thermogravimetric analysis (TGA) was measured on TGA/DSC1 STAR^e system under oxygen at 10 °C/min.

The electrochemical measurements were tested on a Solartron 1860/1287 Electrochemical Interface. The electrolyte solution was 1 mol/L $LiClO_4$ in propylene carbonate solution. Metallic lithium was used as the counter electrode. Cyclic voltammetry (CV) measurement was carried out in half-cells (2016-type coin cells) between voltage limits of 1.8–4.0 V. The charge/discharge measurements were carried out by LAND CT2000 at different current densities.

3. Results and discussion

The crosslinked network structure endows the electrodes with excellent mechanical strength. In Fig. 1b, the strength of the crosslinked electrode is improved to ~4.8 MPa, and the modulus approaches ~500 MPa. For comparison, uncrosslinked electrodes exhibit a lower strength (~1.9 MPa) and lower modulus (~100 MPa). The improved strength suggests that the crosslinking has occurred. Such robust electrodes (inset of Fig. 1b) offer potential applications in flexible energy-storage devices [3]. SEM images of the surface (Fig. 1c) and peeled-off (inset of Fig. 1c) morphology of the crosslinked electrode reveal a highly entangled network. Fig. 1d shows the enlarged SEM image of the composite, indicating that CNTs and nanowires are intimately intertwined. TEM image (Fig. 1e) further confirms its intimate interfacial contacts through coupled crosslinks. Interconnected CNTs and nanowires of high-aspect-ratios are clearly observed. Fig. 1f shows that the crosslinked electrodes have a porous structure with surface areas of ~70 $m^2\ g^{-1}$ and broad pore sizes of 10–100 nm (inset of Fig. 1f). Such pore structure facilitates ion transport, a key factor affecting electrode's rate performance.

FTIR and XPS characterizations further confirm the formation of crosslinked CNT/V_2O_5 composites. FTIR spectra (Fig. 2a) of the composites exhibit $-CH_2$ stretching at 2918 and 2849 cm^{-1} and Si–O stretching at 1088 cm^{-1}, indicating that TPI is successfully coupled within the composites. Fig. 2b shows the survey-scan XPS spectrum of crosslinked electrodes. The C1s core-level spectra (Fig. 2c) can be deconvoluted into four peaks at 284.6, 285.2, 286.3 and 289.0 eV, respectively. The dominant peaks at 284.6 and 285.2 eV are ascribed to sp^2- and sp^3-hybridized carbon atoms from CNTs. The peak at 286.3 eV is assigned to carbon atoms coordinated to an oxygen atom as in phenols or ethers (C–O), while the small peak at 289.0 eV is attributed to the presence of carbonyl (C=O) groups, which bridge the coupling agents. Fig. 2d shows the core level binding energy for V2p peaks, where vanadium 2p 3/2 and 2p 1/2 are observed at 517.2 and 524.5 eV, respectively, agreeing well with those of V^{5+} in V_2O_5. The corresponding O1s spectrum is deconvoluted into four peaks (Fig. 2e). The peak position at 530.0 eV is attributed to O (1 s) of V_2O_5. Peaks at 531.4 and 532.5 eV are assigned to C–O and Si–O bonds, respectively, which indicates the existence of coupling reaction. Combining the electron microscopic observation with XPS and FTIR observation, it is reasonable to conclude the formation of crosslinked network composites. Moreover, the elemental composition (CNTs: 23 wt.%, V_2O_5: 71 wt.%, TPI: 6 wt.%) of the crosslinked electrodes was determined by TGA (Fig. 2f).