ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Molybdenum carbide embedded in carbon nanofiber as a 3D flexible anode with superior stability and high-rate performance for Li-ion batteries

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ARTICLE INFO

Keywords:
Molybdenum carbide
Carbon nanofiber
Electrospinning
Stability
High-rate performance
Li-ion batteries

ABSTRACT

The fabrication process and material design of flexible lithium-ion batteries (LIBs) are essential in flexible portable devices. In particular, the carbon nanofiber (CNF)-based active anodes with flexibility synthesized using an electrospinning technique showed fairly stable cycling performance in the LIBs. In this study, we synthesized the molybdenum carbide (MoC) embedded in CNFs as an anode for LIBs (MoC/CNF) using an electrospinning technique with amorphous Mo precursor and polyacrylonitrile as the molybdenum and carbon sources, respectively, and using a heating process under an N_2 atmosphere. The as-prepared flexible MoC/CNF showed a 3D porous structure consisting of crystalline MoC and amorphous CNF. MoC/CNF, directly utilized as an active electrode without binder, conductor, or current collector, exhibited superior LIB performance, i.e. high capacity, cyclability, and high-rate properties. In particular, at a considerably high charge/discharge rate of 10 A g^{-1}, the specific capacity of MoC/CNF (109 mAh g^{-1}) was significantly higher than that of pure CNF electrode (3 mAh g^{-1}).

1. Introduction

Recently, for batteries as portable power sources, high capacity, flexibility, and small volume are needed because of the rapid growth of electronic devices such as the smart watch and flexible display [1–5]. In particular, the fabrication process and material design of flexible lithium-ion batteries (LIBs) are essential for the flexible portable devices [6–10]. According to many studies, to design flexible LIBs, thin-film electrodes and solid-state electrolytes for thin-film batteries (TFBs) have been fabricated using various methods such as sputtering deposition and evaporation [11–14]. Furthermore, the flexible electrodes consisting of graphene, carbon nanofiber (CNF), and carbon nanotube (CNT) have been intensively studied [15–21]. The CNF-based composite anodes synthesized using an electrospinning technique showed fairly stable cycling performance in LIBs [22–27].

Especially, transition metal carbides (TMCs) such as tungsten carbide, vanadium carbide, and molybdenum carbide exhibited a metallic structure of the metal host lattice with interstitial voids filled with carbon atoms, representing excellent mechanical, chemical, and thermal properties [28,34,35]. Among these TMCs, molybdenum carbide (MoC) with superior chemical stability and high electrical conductivity can be a promising candidate of the CNF-based composite structure for LIBs [29–33]. Yu et al. reported that the MoC@C core@shell nanostructure anode showed a discharge capacity of 664 mAh g^{-1} at a current density of 200 mA g^{-1} [34]. Moreover, Li et al. proposed the nanocomposite structure of MoC on porous graphitic carbon for LIBs with a discharge capacity of 742 mAh g^{-1} at a current density of 200 mA g^{-1} and high-rate performance due to a high electrical conductivity of MoC [35].

In this study, we proposed the molybdenum carbide (MoC) embedded in CNFs as an anode for LIBs (denoted as MoC/CNF). The 3D flexible MoC/CNF was fabricated using an electrospinning technique with amorphous Mo precursor and polyacrylonitrile (PAN) as molybdenum and carbon sources, respectively, with the heating process under an N_2 atmosphere. In particular, the as-prepared MoC/CNF could be directly utilized as an active electrode without a binder such as polyvinylidene difluoride (PVDF), conductor such as carbon black powder, or current collector such as a copper foil. The structure of the electrode was characterized using an X-ray diffraction (XRD) method and Raman spectroscopy. The morphology, structure, and elemental distribution of the electrodes before and after the cycling test for LIBs were confirmed using field-emission scanning electron microscopy (FE-

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https://doi.org/10.1016/j.ceramint.2018.01.237
Received 7 December 2017; Received in revised form 26 January 2018; Accepted 28 January 2018
0272-8842/ © 2018 Published by Elsevier Ltd.

Please cite this article as: Lee, G.-H., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.01.237

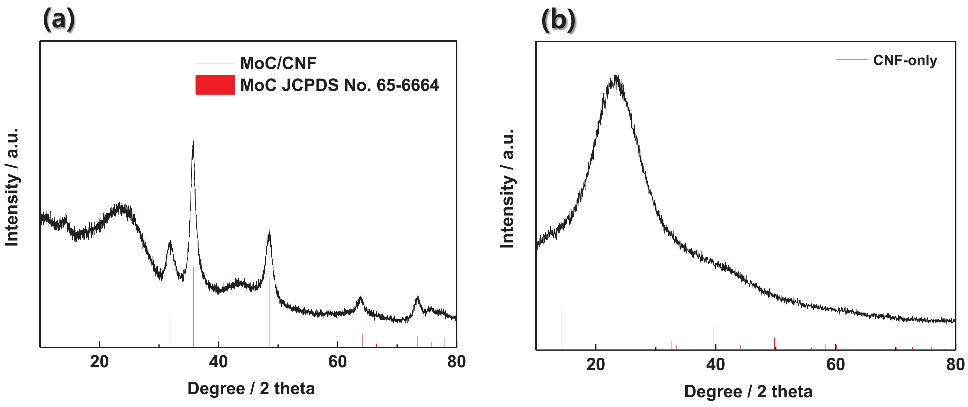

Fig. 1. XRD patterns of (a) MoC/CNF and (b) CNF-only synthesized via an electrospinning technique and heating process.

SEM), field-emission transmission electron microscopy (FE-TEM), and energy dispersive spectrometer (EDS). The electrochemical performance of the coin cells assembled with the as-prepared electrodes was then evaluated.

2. Experimental

2.1. Synthesis of MoC/CNF composite

The MoC/CNF was fabricated using an electrospinning technique with amorphous MoS_2 precursor and polyacrylonitrile (PAN) as the molybdenum and carbon sources, respectively, and a heating process under an N_2 atmosphere. The amorphous MoS_2 precursor was prepared by mixing ammonium molybdate (0.88 g, $(NH_4)_2MoO_4$, Sigma Aldrich) and sodium sulphide nonahydrate (2.64 g, $Na_2S{\cdot}9H_2O$, Sigma Aldrich) dissolved in 0.8 M·HCl (100 mL) at 80 °C for 30 min and adding hydroxylamine hydrochloride (0.7 g, $NH_2OH{\cdot}HCl$, Sigma Aldrich) with continuous mixing at 80 °C for 1 h. The as-prepared MoS_2 (1 g), PAN (4 g, MW = 150,000, Sigma Aldrich), and N,N-dimethylformamide (40 g, DMF > 99.8% purity, Sigma Aldrich) were homogeneously mixed using a paste mixer. The mixed solution was electrospun on an Al foil as a collector surface at a distance of 20 cm under an applied voltage of 20 kV with an injection rate of 10 μL min^{-1}. The as-electrospun sample was heated at 250 °C for 3 h under an air atmosphere to remove the impurities and then heated at 800 °C for 3 h under an N_2 atmosphere (MoC/CNF). In addition, the sample was prepared using an electrospinning technique with the mixed solution of PAN (4 g) and DMF (40 g) and heating process following the same procedure as that for MoC/CNF (denoted as CNF-only).

2.2. Materials characterization

The crystal structure of the samples was characterized using a Bruker X-ray diffractometer (D2 Phase System, Cu K_α source of λ = 0.15418 nm) with an accelerating voltage of 30 kV and a working current of 10 mA. The morphology, structure, and elemental distribution of the electrodes were confirmed using FE-SEM (JEOL, JSM-7001M), FE-TEM (Tecnai G2 F30), and an energy dispersive spectrometer (EDS). The crystal structure of the electrodes was analyzed using Raman spectroscopy (Horiba Jobin Yvon, LabRam Aramis) with a yttrium aluminum garnet (YAG) laser of λ = 532 nm. Thermogravimetric analysis (TGA, TA Instrument, SDT Q600) of the electrodes was conducted to compare the relative elemental amount in the temperature range of from 25 to 700 °C under an air atmosphere. The specific surface area was measured using an N_2 adsorption analyzer (Micromeritics, ASAP 2020).

2.3. Electrochemical characterization

To characterize the electrochemical performance of the electrodes as anodes, the coin-type cells (size 2032, Hoshen Corporation) were assembled in an Ar-filled glove box (< 5 ppm H_2O and Ar). A Li foil and porous polyethylene were used as a counter electrode and separator, respectively. 1.1 M $LiPF_6$ dissolved in ethylene carbonate (EC): dimethyl carbonate (DEC) = 1:1 vol% was used as the electrolyte. The charging/discharging test was performed using a multi-channel battery tester (WBCS3000L, Wonatech Co.). The cycle performance of the cells was evaluated at current densities of 500 and 2000 mA g^{-1} for 300 cycles. The high-rate performance of the cells was compared with varying current densities from 0.1 to 10 A g^{-1}. Cyclic voltammograms (CVs) of the electrodes were obtained in the potential range of 0.0 − 3.0 V at a scan rate of 0.2 mV s^{-1}. Electrochemical impedance spectroscopy (EIS, Eco Chemie, AUTOLAB) analysis was conducted at an applied voltage of 5 mV in the frequency range of 10 mHz to 100 kHz.

3. Results and discussion

Fig. 1(a) and (b) show the XRD patterns of the as-electrospun MoC/CNF and CNF-only, respectively. MoC/CNF exhibited XRD peaks corresponding to the (001), (100), (101), and (110) planes of molybdenum carbide (γ-MoC, space group of $P\bar{6}m2$) at 31.83°, 35.74°, 48.60°, and 64.22°, respectively. MoC/CNF also exhibited the (002) of amorphous carbon at ~ 26°, demonstrating that the amorphous MoS_2 precursor and PAN as molybdenum and carbon sources, respectively, could be transformed into crystalline MoC and amorphous carbon phases, respectively, via a heating process at 800 °C under an N_2 atmosphere. On the other hand, CNF-only electrospun with PAN as the carbon source exhibited broad XRD peaks associated with an amorphous carbon structure. Furthermore, the Raman spectra of MoC/CNF and CNF-only indicates the formation of an amorphous carbon structure, i.e. a relatively high intensity ratio of the D- to G-band, which is in agreement with the XRD results (Fig. 2). In particular, the I_D/I_G ratios of MoC/CNF and CNF-only were 1.01 and 1.11, respectively, which the relatively low

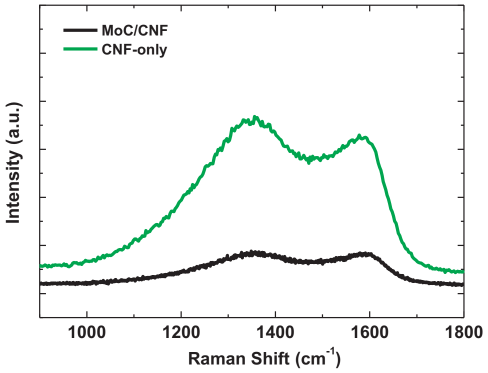

Fig. 2. Raman spectra of the as-prepared MoC/CNF and CNF-only.

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