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Full Length Article

Carbon-silicon composite anode electrodes modified with MWCNT for high energy battery applications

H. Akbulut *, D. Nalci, A. Guler, S. Duman, M.O. Guler

Sakarya University, Engineering Faculty, Dept. of Metallurgical & Materials Engineering, 54187 Sakarya, Turkey

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ABSTRACT

In this study, we comparatively study the electrochemical characteristics of Si, Si-C and vacuum-assisted filtration fabrication of a novel free-standing Si@C/Mutli Wall Carbon Nanotubes (MWCNT) nanocomposite. The surfaces of the as-received Si nanaoparticles were coated with an amorphous carbon layer and homogenously anchored onto the surfaces of as-received MWCNTs by a simple vacuum filtration method. The samples were then analyzed with field emission scanning electron microscopy and X-ray diffraction (XRD) methods. Si@C/MWCNT samples have shown a stable capacity of 1290 mA h g^{-1} after 200 cycles. The results have proven that MWCNT's large surface area, highly conductive network which can provide good contact between Si@C nanoparticles, tolerating large volume change sand suppressing aggregation of Si@C nanoparticles during charge/discharge processes. Such a comparison between the performances of carbon-MWCNT-metal materials is reasonably envisaged not only to be useful for understanding the individual contribution from MWCNT and metal but also to form a fundamental basis for energy storage applications. Free-standing Si-C/MWCNT nano paper has been successfully obtained by a facile vacuum filtration method.

1. Introduction

After introducing into the market in 1990 by Sony, Lithium ion batteries (LIBs) have dominated the almost all kinds of rechargeable equipment due to their superior energy density and long cyclic life [1,2]. However with the increment of global requirements and mobility needs, there is big bottleneck in the LIBs in terms of energy density, safety with improved service life. It is well known that the anode electrodes determines the total performance of the batteries [3,4]. The increasing demand of global communities for enhanced LIBs, Si has become a popular anode candidate due to its unique theoretical capacity (4.200 mA h/g, lithiated to $Li_{4.4}Si$) [5]. At the same time, Si is world's second most abundant element and harmless to the environment. It should also be noted that the semiconductor industry has significantly developed high technology facilities processing many forms of Si with reasonable prices [6,7].

Nonetheless, there are still some disadvantages for the practical applications of Si as anode electrode, including lower electric conductivity and large volumetric changes (about %300) during the electrochemical processes, which result in fast capacity fading and poor rate capability [8]. In addition, larger expansion and contraction during the lithiation/delithiation processes ruins the solid electrolyte interphase (SEI) passivation layer on the surface of Si, which will result in a low Coulombic efficiency [9]. Consequently, aggregation results in pulsing Si nanoparticles and loss the contact with current collector, resulting a rapid diminish in the battery performance [10]. In order to solve these problems, carbon based buffering matrices could be used as a protecting matrix. Literature studies on Si-C in the form of unique architectures such as "Core-shell" or "Yolk-shell" has significantly improved the electrochemical properties of LIBs [11,12]. In addition, multiwall carbon nanotube (MWCNT) reinforcement as a buffering layer has also improved the electrochemical properties of Si based electrodes [13]. Reducing the particle size to nano scale and reinforcing with a conductive carbon layer as a novel composite architecture has proven to be an effective solution for electrochemically Si anodes [14].

In order to solve problems originated from volume variations of Si during cycling, novel electrode architectures has been suggested by researchers such as nano sized and nano composite based on MWCNTs. MWCNT based paper-like structures, namely known as buckypapers has gain much interests in the field of filtration, catalysts and energy storage applications [15–17]. Single-walled CNTs [18,19], double-walled CNTs [20] and multi-walled CNTs

* Corresponding author.
E-mail address: akbulut@sakarya.edu.tr (H. Akbulut).

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(MWCNTs) [21] could be used to prepare buckypapers. The intrinsic features such as high electrical conductivities, mechanical properties and high surface area are mostly depend on the type of the nanotubes or whether any kind of binder is used or not. It is also reported that the buckypapers based on MWCNTs could provide a buffering matrix for electrode materials suffering from volumetric variations during the alloying-dealloying processes during the electrochemical processes [22].

All of these advantages make silicon and MWCNT composite a very promising electrode anode materials. In addition to carbon coating, it is also possible to obtain robust and flexible both anode and cathode electrodes by using MWCNT nano structures [23,24]. Moreover, the free-standing composite electrodes with three-dimensional (3D) structure have attracted considerable attention, and at the electrode, the binder and the current collector are rendered unnecessary, increased the specific capacity of LIBs [25,26].

Herein is reported that we comparatively study the electrochemical characteristics of Si, Si@C and vacuum-assisted filtration fabrication of a novel free-standing MWCNT/Si@C nano composite. Si@C nanoparticles were designed in the form of "Yolk-shell" architecture. In this architecture, Si nanoparticles were the "Yolk" while an amorphous carbon layer as around the Si nanoparticles was the "Shell". There are numerous advantages of "Yolk-shell" structure such as providing a freestanding architecture while the controlled space between the Si nanoparticles and the carbon shell allows for the Si nanoparticles expanding during the alloying without hampering the carbon shell. In addition to yolk-shell architecture, the intrinsic properties of MWCNT having large surface area, highly conductive network which can provide good contact between Si–C nanoparticles, tolerating large volume change sand suppressing aggregation of Si@C nanoparticles during charge/discharge processes. Free-standing MWCNT/Si@C nano paper has been successfully obtained by a facile vacuum filtration method.

2. Experimental details

2.1. Preparation of "Yok-Shell" Si nanoparticles

The as-received Si nano particles were used as the core and subjected to the following coating process with silica using the hydrolysis of Tetraethyl orthosilicate (TEOS-Sigma Aldrich reagent). In order to determine the conditions for the formation of uniform silica shells, the concentration of TEOS and reaction pH were varied in some limited range. In a typical coating process, a weighed amount of Si nano particles (150 mg) were dispersed in a solution containing ethanol (240 mL) and bidistilled water (60 mL) by ultrasonication for 80 min. Silica source solution prepared separately by dissolving TEOS (4 mL) into ethanol solution (30 mL) was then mixed with the suspension containing Si nano particles under vigorous stirring. In the mixing process, the mole concentration of TEOS was varied in the range of 0.04–3.0 M and the pHs of the mixed solutions were adjusted to 5 or 11 by adding ammonium hydroxide (NH_4OH). The mixed solution was then refluxed at room temperature 12 h with continuous stirring to induce homogeneous and dense SiO_2 layers on Si surfaces. Then the reaction products were separated by centrifugation, washed thoroughly with ethanol aqueous solution to remove any extraneous species, and dried under vacuum for 12 h.

450 g glucose, 150 g Si nanoparticles were dispersed in 150 mL bidistilled and poured into a Teflon reaction container. Si nanoparticles were then hydrothermally carburized by using a microwave labstation (Milestone ROTOSYNTH). The system was heated from 20 °C to 85 °C at 22 °C min^{-1}, then from 85 °C to 145 °C at 7 °C min^{-1}, and from 145 °C to 225 °C at 14 °C min^{-1}, finally an isotherm was held at 180 °C for 2 h. Among microwave irradiation the temperature was controlled by a thermocouple placed in a reference container. The reactor was then cooled to room temperature after the carburization process, and the carbonized material was filtered through a polyvinylidene fluoride (PVDF) filter (0.45 μm, Millipore) using a mechanical vacuum pump and then rinsed with bidistilled water until reaching a neutral pH. The resulting material was dried under vacuum at 40 °C for 12 h. A typical free-standing anode electrode production method is given in Fig. 1.

The as-synthesized Si@SiO_2@C composite structure has also been subjected to etching process in order to remove the sacrificial SiO_2 layer over the surfaces of Si particles. In typical etching process, 50 mg Si@SiO_2@C is added into a solution containing 15 mL HF (Merck) and 35 mL bidistilled water under vigorous mixing conditions for 1 h. The solid product was then rinsed with ethanol until a pH value of 5 is obtained through centrifuging. The solid products were dried under the vacuum at 60 °C for 12 h and Si@C yolk-shell structure is obtained.

In order to specify the amount of C content in the yolk-shell Si@C composite structure, samples are carefully weighed before TEOS coating and after HF etching process. 150 mg nano Si particles were before starting the TEOS coating and HF etching processes. 151.5234 mg of Si@C composite electrodes were obtained after HF etching process, clearly indicating that a C loading of 1.005% is obtained.

2.2. Preparation of MWCNT buckypaper

MWCNTs used in this study in provided by Arry International Co., Ltd., Germany. No further purification or doping has been applied to MWCNTs by the supplier. The length and the diameter of the MWCNTs were 50 nm and 1 μm, respectively. The purity of the MWCNTs were more than 95%, while impurity contents such as metal catalyst, amorphous carbon and ash were less than 5 wt.% according to the supplier specifications. Before producing the buckypapers, MWCNTs are purified and functionalized as a specified recipe. Amorphous carbon content is removed by heating the MWCNTs at 350 °C for 8 h. Heat-treated product was then magnetically stirred at 140 °C for 4 h in a nitric acid solution in order to remove the metal catalysts. Finally, modified MWCNTs are chemically oxidized in a solution, containing H_2SO_4 and HNO_3 acids at a ratio of 3:1 for 3 h. The chemically oxidized MWCNTs were used to prepare freestanding buckypapers. In a typical process, 600 mg functionalized MWCNTs and 300 mg Si@C nanoparticles are dispersed in bidistilled water containing 50 mg sodium dodecyl sulphate (SDS, Sigma Aldrich) and ultrasonicated for 2 h. The suspended product was then vacuum filtrated by a metal mask covering on a sheet of filter paper (Millipore 47 mm nitrocellulose filter paper) as shown in Fig. 2. The product was then sucked by a vacuum force and solution part of the mixture was went through the pores of filter paper, while the solid MWCNTs and Si@C nanoparticles were trapped onto the surfaces of the filter paper. The buckypapers were then peeled-off from paper and dried in a vacuum oven at 60 °C for 12 h. Hence, the MWCNT reinforced electrodes could be fabricated on the paper, as shown in Fig. 2. The loading content of Si@C in the MWCNT/Si@C electrode is calculated as 4.278 in mg/cm^2.

2.3. Characterization

The phase compositions of the as-synthesized Si based electrode materials were characterized by X-ray diffraction (XRD) (Rigaku D/MAX 2000 with thin film attachment) with Cu Kα radiation. The surface morphology was also further conducted to analyze by Field Emission Scanning Electron microscopy (FEI Quanta Q400) and Transmission Electron Microscopy (Jeol TEM-ARM 200 FEG UHR-Transmission Electron Microscope).