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Enhancing electrochemical performance of silicon anodes by dispersing MWCNTs using planetary ball milling

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ABSTRACT

Three different types of silicon/MWCNTs composite electrodes were prepared with dispersing different amount of MWCNT (10 wt.%, 30 wt.%, 50 wt.%) by high energy mechanical milling method. Surface morphology of produced electrodes characterized by scanning electron microscopy, and X-ray diffraction analysis was carried out to investigate nanocomposite constituents of produced electrodes. Discharge capacity of produced Si/MWCNT nanocomposite electrodes cyclically tested and resistivity of electrodes was studied by EIS. Furthermore, cyclic voltammetry analyse was performed to investigate lithium insertion and extraction reactions between electrode and electrolyte. Eventually, silicon/MWCNT composite electrodes containing 50 wt.% MWCNT demonstrated best stable capacity retention and 750 mAh/g discharge capacity was obtained after 30 cycles in this composite. This study proved that CNT improves interphase electronic contact between current collector and active material and also prevents pulverization of the electrode.

1. Introduction

The development of next-generation energy storage devices with high power and high-energy density is the key to the success of electric and hybrid-electric vehicles (EVs and HEVs, respectively), which are expected to at least partially replace conventional vehicles and help solve the problems of air pollution and climate change. These energy storage technologies will rely on innovative materials science, i.e. developing electrode materials capable of being charged and discharged at high-current rates [1]. Lithium-ion rechargeable battery is a highly attractive power source among commercial rechargeable batteries because of its high-current density, high specific energy density and superior cycle characteristics [2]. At the present time, the most widely used anode material is graphite; whose theoretical capacity is only 372 mAh g^{-1} in commercial lithium-ion batteries. However, graphite has some disadvantage such as its capacity obviously insufficient and its energy density rather low (508 mAh cc^{-1}). Compared with graphite, elemental materials that can alloy with lithium, such as Si (4200 mAh g^{-1}), Sn (994 mAh g^{-1}) and Sb (660 mAh g^{-1}), are promising alternative candidates due to their markedly higher capacities [3]. In these candidates, silicon has highest theoretical capacity; nevertheless, silicon anode cannot use as practical application due to its low intrinsic conductivity, poor cycling stability during the insertion and extraction of Li over cell cycling, which consequently leads to the pulverization of the active mass particles, hence permanent capacity fading [4]. Therefore, the main issue on the improvement of the Si cycle performance is how to overcome the volume change and to reinforce Si to prevent pulverization [5] numerous ideas have been suggested to minimize the volume change and to increase the electrical conductivity of silicon. Several remarkable approaches are the use of nanometer sized silicon and preparation of composites with carbon materials such as amorphous carbon, disordered carbon, graphane, carbon fibre and carbon nanotube [6–10]. CNTs have been demonstrated to exhibit high electric conductivity and good mechanical properties. Furthermore, CNTs are also chemically stable and have very large accessible surface area [11]. Recently, great efforts have been devoted to synthesizing Si/CNT composites, aiming to take both advantages of CNT and Si to develop anode materials with high-performance [4].

In this study, it is aimed to enhance electrochemical performance of the silicon anode with producing Si/MWCNT composite electrodes. Although there are some investigations on the CNT reinforced silicon anode materials for Li-ion batteries, effect of the amount of CNT on the electrochemical response of silicon anodes is not well understood. It is considered in this work to obtain a nanocomposite structure, tailoring electrode expansion, preventing pulverization of silicon active material and improving electrical conductivity with creating a network with carbon nanotubes and homogenously distribute silicon particles on the CNT network by HEMM method. The HEMM parameters were projected in such a way that a thin shell structure to provide on the CNT surfaces.

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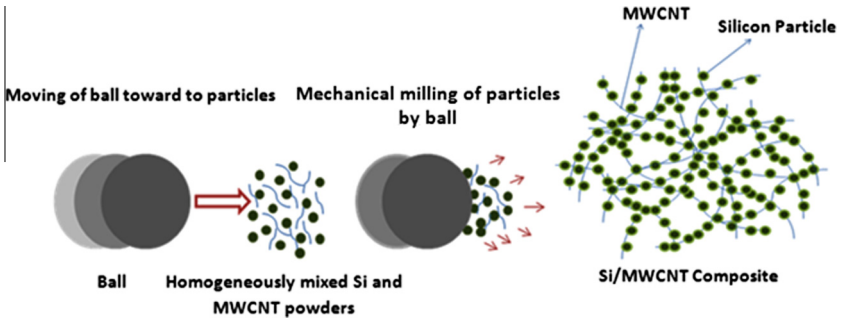


Fig. 1. Schematic illustration of the projected nanocomposite structure.

Structure of the intended Si/MWCNT composite electrode structure is schematically shown in Fig. 1. Therefore, it is targeted to compensate the volume increase aroused from lithium alloying during charging.

2. Experimental methods

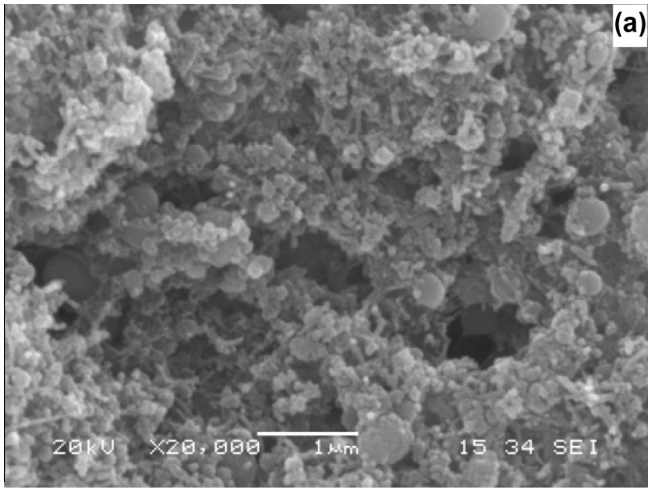
MWCNT (purity 95%, diameter 50–100 nm) used as reinforcing material for producing Si/MWCNT composites, in this study, supplied from Arry Nano. In order to purification, MWCNTs were stirred in HNO3 for 12 h, and then they were washed with water and dried overnight in an oven. Silicon particles (purity 99.5%, 130 nm in size) supplied from Nanostructured & Amorphous Materials Inc.. Three different types of Si/MWCNT composite electrodes were prepared with dispersing different amount of carbon nanotubes. These three different types of Si/MWCNT composite electrodes were produced at three steps. In the first step, silicon particles and purified MWCNTs were added in NMP (*N*-Methy-2-Pyrrolidinone) solution in argon filled glove box and then mixed via ultrasonic homogenisator for providing homogenously dispersing of silicon particles and MWCNTs in NMP solution for 30 min. In the second step, subsequently, this suspension charged to bowl and mechanically milled for 1 h at 500 rpm with using planetary ball mill (Fritsch P7) in argon inert gas medium to achieve mechanical alloying between silicon particles and MWCNTs. For mechanical alloying process, 80 ml stainless steel bowl and 5 mm stainless steel balls were used and ball to powder weight ratio was chosen 10:1. In the last step, PVDF (Polyvinylidene Fluoride) binder dissolved in NMP solution added to suspension and stirred with a magnetic stirrer. Obtained mixture was cast on a copper foil, pasted with doctor blade, dried at 120 °C a vacuum oven for 12 h and then sample on copper foil cut by cutter disc and used as an electrode. Furthermore, in order to compare the effect of MWCNT on the silicon electrode, also unreinforced pure-silicon electrode was prepared at same conditions. Prepared different type composite electrodes with their codes and mechanical alloying parameter are shown in Table 1.

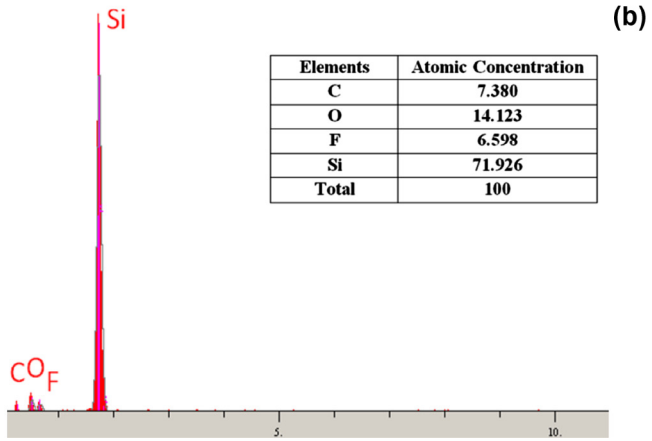
Prepared electrodes were characterized by scanning electron microscopy (SEM) facilities to reveal the surface morphology and dispersion of MWCNTs and silicon particles in composite electrodes. Energy dispersive spectroscopy (EDS) conducted to understand the elemental surface composition of composite electrodes. X-ray diffraction patterns (XRD) of Si/MWCNT composite electrodes were carried out to investigate phase constituents of produced electrodes.

Coin type CR2016 test cells were assembled in argon filled glove box, the prepared electrodes were used as working electrode, Li foil used as counter electrode, 1M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte. The working and counter electrodes were separated with polypropylene (PP) separator. Charge–discharge characteristics of electrodes were tested between 0.05 V and 1.5 V at a constant current of 200 mA g^{-1} (C/20). Cyclic

Table 1
Mechanical alloying parameters and sample codes of produced electrodes.

Composition of starting material (wt.%)	Samples	Milling speed (rpm)
Silicon powders	Unreinforced Si	500
10 MWCNT-90 Si	SC1	500
30 MWCNT-70 Si	SC2	500
50 MWCNT-50 Si	SC3	500





Elements	Atomic Concentration
C	7.380
O	14.123
F	6.598
Si	71.926
Total	100

Fig. 2. SEM images of (a) unreinforced silicon electrode, and (b) EDS spectra of unreinforced silicon electrode.