

Si/Mo/MWCNT Nanocomposites for Lithium Ion Battery Applications

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In this study, silicon/multi-wall carbon nanotube (Si/MWCNT) and silicon/molybdenum/multi-wall carbon nanotube (Si/Mo/MWCNT) composites were produced by high speed planetary ball milling. Produced Si/MWCNT composite containing 50 wt.% Si and 50 wt.% MWCNT and dispersing different amount of molybdenum nanopowders (1 wt.%, 3 wt.% and 5 wt.%) Si/Mo/MWCNT composites were produced by high speed planetary ball milling. Surface morphology of produced composite electrodes was characterized using scanning electron microscopy (SEM) and EDS dot-map analyze was performed to investigate dispersion of MWCNT and molybdenum powders in the composite structure. X-ray diffraction (XRD) technique was carried out to investigate structure of produced Si/Mo/MWCNT composites. Electrochemical performance of the electrodes were tested between 50 mV and 1.5 V in CR2016 test cell.

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1. Introduction

Among the various available storage technologies, lithium ion batteries (LIBs) currently represent the state-of-the-art technology in small rechargeable batteries, power sources for mobile communication devices, portable electronic devices, and electric vehicles, due to offer the largest energy density and output voltage among the other rechargeable battery technologies [1]. At the present time, the most widely used anode material is graphite; whose theoretical capacity is only 372 mA h g^{-1} in commercial lithium-ion batteries, which is obviously insufficient for future energy storage applications [2]. Among several alternative (Si, Sn, Sb, Al etc.) anode materials, silicon has emerged as one of the most promising anode material due to its ultrahigh theoretical capacity (4200 mA h g^{-1}) and low discharge potential [3]. However, a large volume change ($> 300\%$) during the discharge and charge processes could lead to severe pulverization, cracking, and then a rapid capacity fading. In order to overcome the capacity fading, various silicon based nanocomposites have been reported with using active phases such as CNT, Graphene and CNF and inactive phases such as Cu, Ni, Mo and Cr etc. [4, 5]. In the present work, Silicon/Mo/MWCNT nanocomposite electrodes were produced by mechanical alloying of silicon, molybdenum and MWCNTs via high energy mechanical milling method. In order to investigate the effect of Mo content on the electrochemical performance of the electrodes, content of Mo was altered in the composite structure. It is aimed to contribute the electrochemical performance of the anodes by increasing both conductiv-

ity and stress relaxation provided with Mo nano powders and MWCNTs.

2. Experimental details

MWCNTs (purity 95%, diameter 50–100 nm) used as reinforcing material for producing Si/MWCNT composites, in this study, supplied from ArryNano. In order to purification, MWCNTs were stirred in HNO_3 for 12 hours, and then they were washed with distilled water and dried overnight in an oven. Silicon particles (purity 99.9%, 130 nm in size) supplied from Nanostructured Amorphous Materials Three different types of Si/Mo/MWCNT composites were produced with dispersing different amount of molybdenum nano powders (1 wt.%, 3 wt.% and 5 wt.%). The starting materials, mechanical alloying parameters and produced composite electrodes with their codes is shown in Table. For producing Si/Mo/MWCNT composite powders, firstly MWCNTs were homogenously distributed in 15 ml N-Methyl-2-Pyrrolidione (NMP) solution by ultrasonic homogenizer for 30 min to prevent agglomeration of MWCNTs in composite materials. In the second step, silicon and Mo powders added in MWCNT suspension and charged to bowl for mechanical alloying process. For mechanical alloying process, 80 ml stainless steel bowl and 5 mm balls were used and ball to powder weight ratio was chosen as 10:1. In the last step, silicon and molybdenum powders were mechanically milled in MWCNT suspension to provide mechanical locking of silicon and molybdenum with MWCNT. 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 and dried at 120°C in a vacuum oven for 12 hours to obtain about $200 \mu\text{m}$ thick active layer on the copper foil. Sample on copper foil cut by cutter disc and used as an electrode. Surface morphology and structure of produced

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Silicon/Mo/MWCNT composite powders were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) technique. For electrochemical characterization of the electrodes, Coin type CR2016 test cells were assembled in an argon filled glove box. The prepared electrodes were used as working electrode, Li foil used as counter electrode and 1M LiPF₆ 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 were obtained at 25 °C between 50 mV and 1.5 V at a constant current of 200 mA/g. Moreover, cycleability of the electrodes were also tested at 35 °C and 50 °C.

Mechanical alloying parameters and sample codes of produced electrodes TABLE

| Composition of starting material [wt.%] | Samples | Milling speed [rpm] |
|---|-----------------|---------------------|
| Silicon powders | Unreinforced Si | 500 |
| 50 MWCNT-50 Si | SC50 | 500 |
| 50 MWCNT - 1 Mo - 49 Si | SM1C50 | 500 |
| 50 MWCNT - 3 Mo - 47 Si | SM3C50 | 500 |
| 50 MWCNT - 5 Mo - 45 Si | SM5C50 | 500 |

3. Results and discussion

Figure 1 shows the surface morphologies and EDS spectra of Si/Mo/MWCNT composite electrodes containing different content of Mo powders. Figure 1a shows surface morphology, EDS spectra and EDS dot-mapping of SM1C50 composite electrode. Figure 1b shows surface morphology, EDS spectra and EDS dot-mapping of SM3C50 composite electrode. Figure 1c shows surface morphology, EDS spectra and EDS dot-mapping of SM5C50 composite electrode. It can be seen from the EDS dot-mapping of the nanocomposite electrodes from the Fig. 1; when Mo content is increased in the composite structures, slight aggregation of Mo nanopowders were observed. Although slight aggregation of the Mo nanopowders was observed, MWCNTs were distributed homogeneously throughout the nanocomposite electrodes. Figure 2 shows XRD patterns of unreinforced silicon and Si/Mo/MWCNT composites containing different amount of Monano powders. The reflection peak of the Mo was not observed on the XRD patterns due to less amount of Mo content in composite structure. However, increasing content of Mo in the nanocomposite structure leads to decreasing intensity of silicon main peaks (111), (220) and (311) [4] probably due to covering surface of the silicon by Mo.

The cyclic voltammetry curves of Si/Mo/MWCNT composite is shown in Fig. 3a. The cyclic voltammetry curve of Si/Mo/MWCNT composite electrode clearly shows peaks corresponding to insertion and extraction of Li ions. In the first cathodic sweep of CV curves, the peak between 0.6 V and 0.8 V appeared during the first cycle of CV curves is due to decomposition of the electrolyte caused an irreversible reaction for the SEI (solid

electrolyte interface) formation. During the second cycle, the peak at 0.15 V, which is not observed at the first cycle, indicates the crystal-to-amorphous transition of silicon. In the anodic sweep of the CV curves, the peak around 0.2 V shows the lithium extraction between graphene layers of MWCNT and de-alloying reaction of silicon with lithium observed between 0.3 V and 0.6 V [2].

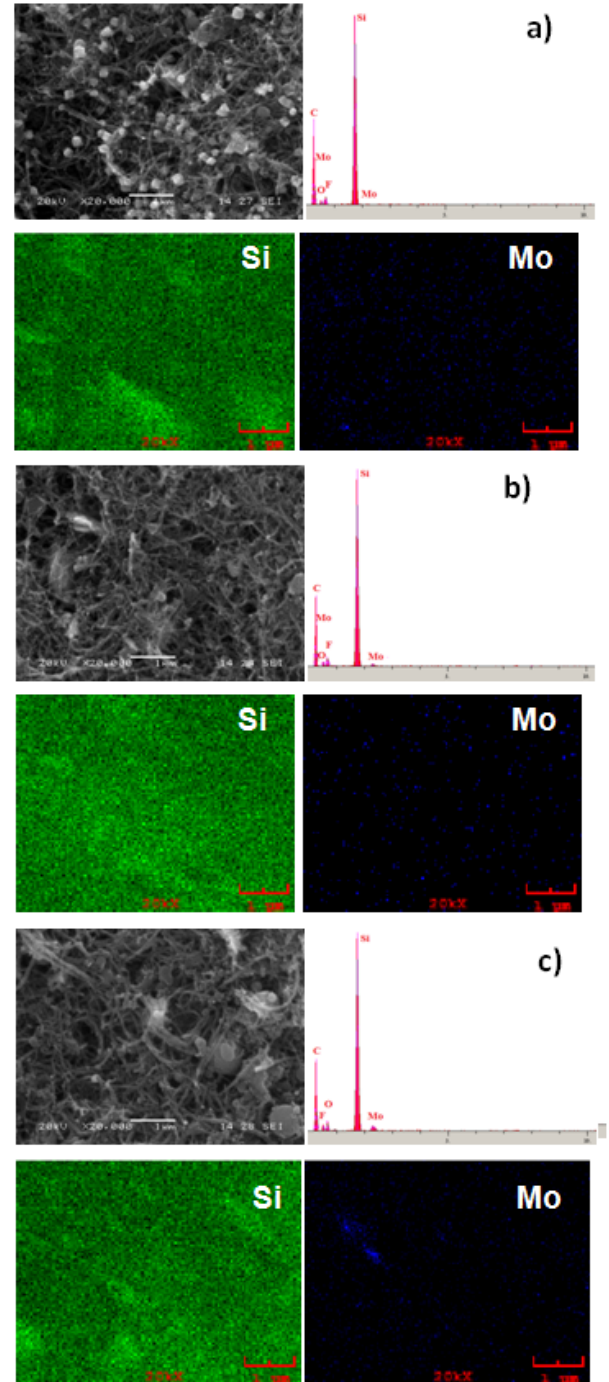


Fig. 1. SEM image, EDS spectra and EDS dot-mapping of a) SiM1C50, b) SiM3C50 and c) SiM5C50 nanocomposite electrodes.

Figure 3b shows electrochemical cycling test of the SC50, SM1C50, SM3C50 and SM5C50 nanocomposite electrodes. When the electrochemical cycling test of the electrodes is carefully investigated, it is seen that increasing content of Mo in the composite electrodes leads to capacity increment during 30 cycles due to conductive and inactive buffer agent effect of Mo nanopowders [6].

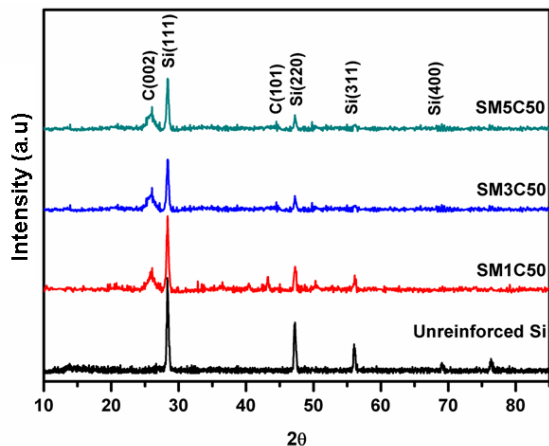


Fig. 2. XRD patterns of unreinforced Si, SM1C50, SM3C50 and SM5C50 nanocomposites.

In Fig. 3b, SC50 nanocomposite electrode shows 767 mA h g^{-1} discharge capacity and when the Mo content is increased to 5 wt.% in the nanocomposite, the electrode shows 1035 mA h g^{-1} discharge capacity. By dispersing Mo in the nanocomposite, 268 mA h g^{-1} discharge capacity increment was obtained against SC50 nanocomposite electrode. Among the produced electrodes, the SM5C50 electrode was selected to investigate for further characterization. Therefore, electrochemical performance of the SM5C50 nanocomposite electrode was tested at different medium temperatures and is shown in Fig. 4.

It is well known that increasing temperature cause easier decomposition of the electrolyte in the cell. It is seen from Fig. 4 that when the medium temperature is increased, capacity of the SM5C50 electrode was rapidly lose and the electrode shows 935 mA h g^{-1} and 672 mA h g^{-1} discharge capacity at 35°C and 50°C after 30 cycles, respectively.

4. Conclusion

Si/Mo/MWCNT composite electrodes were successfully produced by high speed planetary ball milling. When Mo content is increased in the composite structure, Mo powders shows slight agglomeration, but CNTs distributed homogeneously and create a conductive network. The best performance among the nanocomposite electrodes obtained from the SM5C50 nanocomposite electrode indicated 1035 mA h g^{-1} discharge capacity after 30 cycles. Moreover, SM5C50 nanocomposite electrode

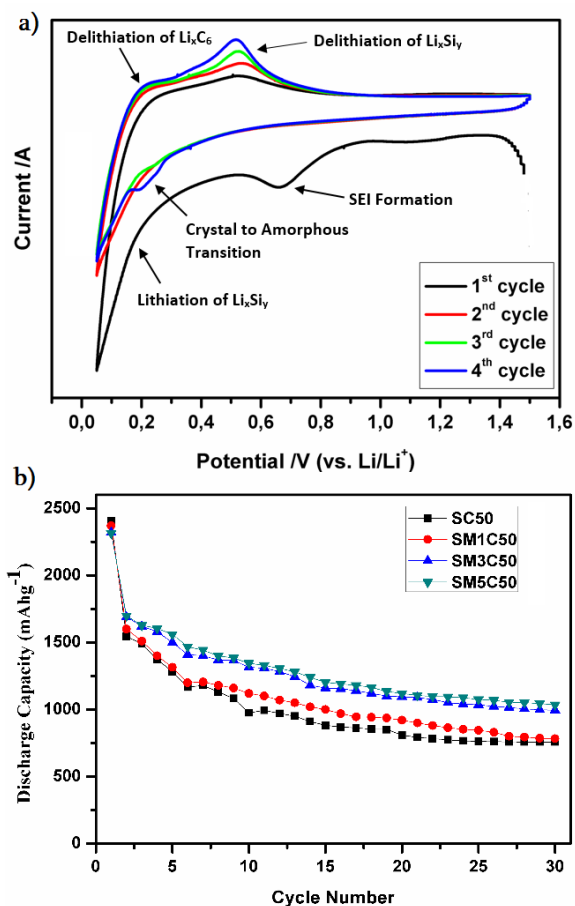


Fig. 3. a) Cyclic voltammetry curve of produced Si/Mo/MWCNT composite electrode and b) electrochemical cycling test of SC50, SM1C50, SM3C50 and SM5C50 composite electrodes.

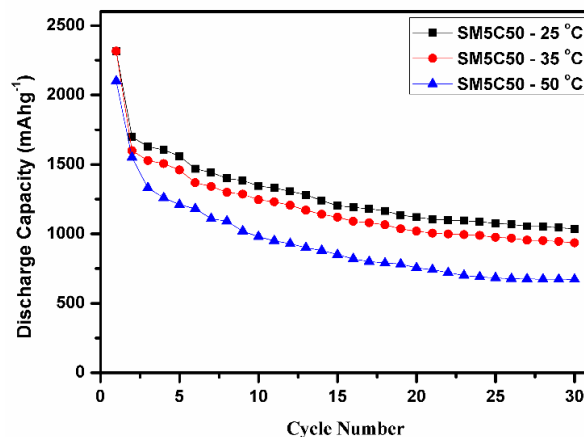


Fig. 4. Electrochemical cycling test of SM5C50 nanocomposite electrodes tested at different temperature.

exhibited 935 mA h g^{-1} and 672 mA h g^{-1} discharge capacity after 30 cycles at 35°C and 50°C , respectively.

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