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Preparation and Characterisation of Silicon/Carbon Nanotube Composite Electrodes for Li-Ion Battery Systems

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Silicon powders and different amounts of multiwalled carbon nanotube were mechanically alloyed in polyacrylonitrile solution via high speed planetary ball milling. Produced composite was characterised via X-ray diffraction pattern, scanning electron microscopy, energy dispersive spectroscopy and thermogravimetric analysis.

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1. Introduction

Nowadays lithium-ion batteries represent the system of choice for energy intense mobile application such as smart phones, laptops and other consumer electronic devices. Presently graphite or other carbonaceous materials are the most common active masses for negative electrodes in lithium-ion batteries [1]. However, the theoretical gravimetric capacities of these materials are limited (372 mAh g^{-1} , LiC_6). Therefore, silicon and silicon containing compounds are attractive candidates due to their high theoretical specific capacities (4200 mAh/g , $\text{Li}_{22}\text{Si}_5$) [2].

A crucial problem with a view to Si-based anode implementation is its volume expansion of up to 400% at full lithiation. There are several ways to overcome this problem, such as decreasing particle-size, using composites with active and inactive matrixes as well as use of different binders [3]. Among them, Si-carbon composite anodes with carbon nanomaterials demonstrated very promising performances [4]. Although carbon nanotubes (CNTs) in general, as reported in the literature are known to exhibit a higher reversible capacity than graphite, a high irreversible loss and a large voltage hysteresis are commonly observed in the cycling performances of CNTs, which greatly limit their use as an anode material in Li-ion batteries.

Nevertheless, CNTs prove to be a better choice as a matrix material for Li-ion anodes due to their excellent physical properties including superior mechanical strength and electrical conductivity in comparison to any of the existing materials systems [5].

In this study silicon powders and multiwalled CNTs (MWCNTs) were mechanically alloyed using planetary ball mill and dispersing of MWCNTs were characterised by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analyses. Furthermore, thermogravimetric analysis (TGA) was performed to determine silicon content in composite structure.

2. Experimental methods

MWCNT used in this study has diameter of 50–100 nm and length of 10 μm . MWCNTs were purified in nitric

acid solution for 12 h before mixing with silicon powders. Silicon powder used in this study was of purity 99.5% and 130 nm in size. Silicon powders and MWCNTs mechanically alloyed for 1 h using 80 ml stainless steel bowl and 5 mm balls by planetary ball mill (Fritsch, Pulverisette 7) and ball to powder weight ratio was 10:1. To investigate dispersing activity of MWCNTs in composite, different amounts of MWCNTs were selected to produce Si/MWCNT composite. Polyacrylonitrile (PAN) solution was used for mechanical alloying of Si/MWCNT composite and PAN solution was prepared with dissolving of 0.6 g PAN in 10 ml *N*-methyl-2-pyrrolidinone (NMP). Amount of PAN was kept constant at all composites. In order to investigate the PAN effect, silicon powders were mixed with PAN solution at the same conditions. Si/PAN and two types of Si/MWCNT composites were produced and these composites were labelled as SP, SC1 and SC2 type composites, respectively, in this study.

The mechanical alloying process parameter of samples are shown in Table. Mixing of powders and adding of PAN solution were carried out in argon filled glove box. After the alloying of powders, the powders were dried at 150°C for 10 h and then isothermally annealed at 800°C heating rate 5°C min⁻¹ for 4 h to decompose of PAN to PAN-based carbon in flowing argon gas medium. Phase constituents of powders were recorded on a Rigaku Dmax 2200 XRD analyser using Cu K_α radiation. Composite surface morphologies were observed with JEOL 6060 LV SEM equipped with an energy dispersive X-ray spectroscopy (EDS). To investigate PAN decomposition temperature and silicon content in carbonised composites, TGA was performed in argon and air atmosphere, respectively.

TABLE

Mechanical alloying parameters for producing silicon/MWCNT composite.

Composition of starting material [wt%]	Samples	Milling speed [rpm]
70 Si-30 PAN	SP	700
10 MWCNT-60 Si-30 PAN	SC1	700
20 MWCNT-50 Si-30 PAN	SC2	700

3. Results and discussion

In order to identify weight loss of PAN, TGA has been performed for pure-PAN in argon environment. Furthermore, TGA has been performed for SC1 and SC2 types composites in air to determine the content of silicon in composites in Fig. 1. TGA results of PAN shows a significant weight loss (73 wt%) at 800 °C which corresponds to decomposition of PAN to form PAN-based carbon in Fig. 1a [6]. TGA results of carbonized SC1 and SC2 type composites demonstrate that SC1 type composite contains 75 wt% silicon and SC2 type composite contains 65 wt% silicon in Fig. 1b. The weight increase after 700 °C in the TGA curves of SC1 and SC2 type composites is due to the oxidation of Si in air above 700 °C [4].

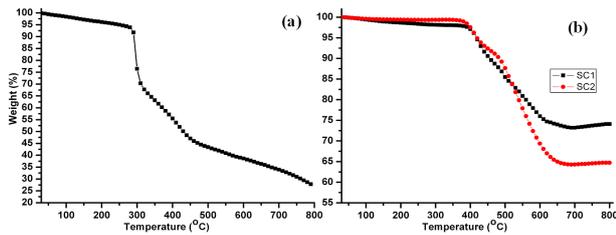


Fig. 1. TGA curves of (a) the pure PAN conducted in high purity argon, (b) the carbonized Si/MWCNT composite in air.

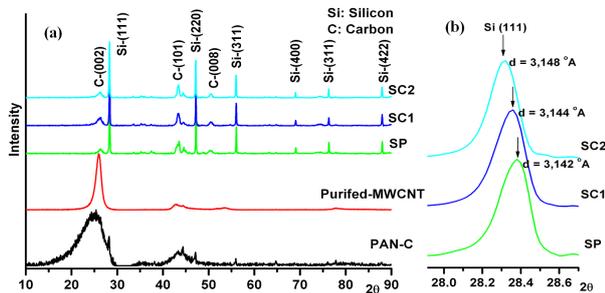


Fig. 2. XRD results of (a) PAN-based carbon, purified-MWCNT, SP type composite, SC1 type composite and SC2 type composite and (b) low angle XRD results from (111) plane.

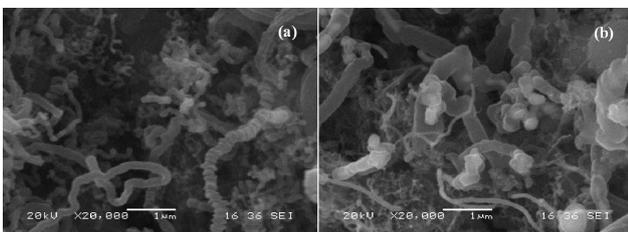


Fig. 3. High magnification SEM images of (a) SC1 type composite, (b) SC2 type composite surface morphology.

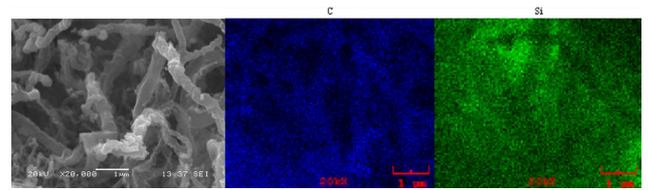


Fig. 4. EDS elemental map of SC1 type composite (C — carbon, Si — silicon).

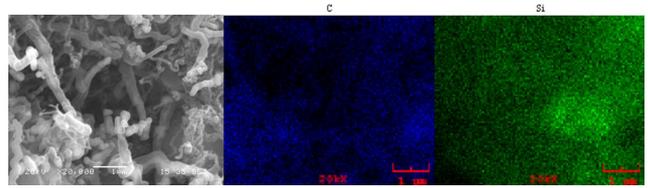


Fig. 5. EDS elemental map of SC2 type composite (C — carbon, Si — silicon).

Figure 2 shows XRD patterns of PAN-based carbon (PAN-C), purified-MWCNT, SP, SC1 and SC2 type composites. On the other hand, Fig. 2 shows changing of silicon highest plane (111) with increasing amount of MWCNT. When XRD patterns of PAN-C was investigated, it was clearly seen that PAN-C has almost amorphous crystal structure, however, there are some crystalline peaks at 2θ values between 40° – 50° and these peaks were detected as carbon phases in SP type composite (Fig. 2a). When amount of MWCNT is increased, carbon peaks reflection intensity in SC1 and SC2 type composites do not change due to the high amorphous structure of CNT (Fig. 2a) [7]. Dominant reflection peak of silicon plane (111) is shown in Fig. 2b and it is clearly seen that highest silicon reflection peak is shifted towards to the lower 2θ values and this plane spacing increases from 3.142 Å to 3.148 Å which attribute lattice strain [8] of silicon structure with increasing amount of MWCNT.

Furthermore, silicon carbide which has an inactive behaviour with lithium [9] is not detected in composite constituents. Figure 3 shows SEM micrographs of SC1 and SC2 type composites. Figure 3a and b demonstrates SC1 and SC2 type composites surface morphologies, respectively. In SC1 type composite, silicon particles are observed as settled on MWCNTs surface. In SC2 type composite, it is interesting to note that silicon particles appear as strongly coating on MWCNTs surface. As mentioned before, silicon structure indicates lattice strain with increasing amount of MWCNT, so it is possible to say lattice parameter of silicon particles change and coat on MWCNT surface with increasing amount of MWCNT. In order to investigate of silicon and MWCNT distribution behaviour in SC1 and SC2 types composites, EDS elemental map analysis was performed for composites.

Figure 4 and Fig. 5 demonstrate EDS elemental map analysis of SC1 and SC2 type composites, respectively. EDS elemental map analysis shows MWCNTs and silicon

particles homogeneously distributed in composite structure.

4. Conclusions

Silicon powders and MWCNTs are successfully mechanically alloyed using planetary ball mill. Silicon particles and MWCNTs are homogeneously distributed in composite structures. When amount of MWCNTs is increased, silicon particles show lattice strain and tended to coat on MWCNTs surface.

Acknowledgments

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