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Electrochemical performance of Si-multiwall carbon nanotube nanocomposite anode synthesized by thermal plasma

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ABSTRACT

Lithium-ion (Li-ion) batteries are widely used in electric devices and vehicles. Silicon is a promising material for the anode of Li-ion battery due to high theoretical specific capacity. However, it shows large volume changes during charge–discharge cycles leading to the pulverization of electrode. In order to improve such disadvantage, a multiwall carbon nanotube (MWCNT) has been used with silicon as composite material. In this work, Si-MWCNT nanocomposite was prepared in thermal plasma by attaching silicon nanoparticles to MWCNT column. Electrochemical tests for raw materials and synthesized nanocomposites were carried out. The discharge capacities of silicon, MWCNT, synthesized nanocomposites collected from a reaction tube, and a chamber were 4000, 310, 200, and 1447 mAh/g, respectively.

1. Introduction

Lithium-ion (Li-ion) battery, which is one of secondary batteries, has been developed as a promising rechargeable power storage system because of its excellent characteristics such as high energy density and low self-discharge [1,2]. As a result, Li-ion batteries are widely used in electric devices and vehicles devices [3]. Recently, many researches are attempted to increase the storage capacity and cycling life time of Li-ion battery by changing anode materials. Silicon is widely used as anode material due to its high theoretical specific capacity of 4200 mAh/g, which is corresponding to the $Li_{22}Si_5$. Silicon-based electrodes, however, have enormous volume expansion up to 300% during charging and discharging cycle leading to electrode pulverization and poor capacity retention [4,5].

In order to overcome such problem, carbon materials are incorporated into the anode as a form of Si-carbon composite. The Si-carbon composite has good properties of high electronic conductivity, low-voltage range, and uniform cycle performance [6]. Especially, carbon nanotubes (CNTs) are suitable for the electrode of Li-ion batteries because of the high specific capacity of ~470 mAh/g compared with other carbon materials such as the graphite anode of 372 mAh/g. In addition, CNTs have unique cylindrical structure, which controls the swell of silicon nanoparticles due to the high tensile strength CNT [7,8]. Furthermore, CNTs can diffuse lithium ions into stable sites leading to high lithium capacity and can support silicon particles to reduce the pulverization of electrode. According to the number of graphene sheets, CNTs are divided into a single-walled carbon nanotube (SWCNT) and a multiwalled carbon nanotube (MWCNT), which consists of a single rolled sheet and multiple rolled sheets, respectively. The MWCNT is suitable to transfer charges compared with SWCNT because it has large amount of graphitic tubes that hold a lot of defects of stable sites for silicon particles in various size [9].

Si-MWCNT nanocomposite has been synthesized by pyrolysis, chemical vapor deposition, and sol-gel methods, which require several process steps [10–12]. On the other hand, thermal plasma has been applied for synthesizing nanomaterials in a single process step by high temperature and rapid quenching [13]. In addition, thermal plasma method is environmentally clean process for synthesizing Si-MWCNT nanocomposite because it does not require pretreatment and additional chemicals except Si powder leading to a low contamination. Therefore, a low contamination in Si-MWCNT nanocomposite product is achievable by using thermal plasma synthesis method. Moreover, the size and the content of Si nanoparticles in Si-MWCNT nanocomposite are controllable by manipulating operation condition.

In this work, Si-MWCNT nanocomposite was synthesized by a non-transferred direct current (DC) arc plasma system using a micro-sized silicon powder and a commercial MWCNT. This study was focused on to evaluate the electrochemical performance of synthesized Si-MWCNT nanocomposite. The chemical bonding change of product was confirmed by X-ray diffractometry with CuK_α source (XRD, DMAX-2500, Rigaku Co.). Size distributions and morphologies of raw materials and products were observed by field emission scanning electron microscopy at 15 kV (FE-SEM, S-4300, Hitachi Co.). In addition, electrochemical performance tests for raw materials and synthesized Si-MWCNT nanocomposites were conducted to compare their capacities.

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2. Experiment

2.1. Synthesis of Si-MWCNT nanocomposite

Fig. 1 shows the schematic diagram of the non-transferred DC thermal plasma system to prepare Si-MWCNT nanocomposite. The system consists of a power supply for generating thermal plasma, a DC plasma torch, two powder feeders, and a water-cooled reaction tube and a chamber. The powder feeder 1 (MF, Technoserve, Japan) was used to carry micro-sized silicon powder (99%, Aldrich, USA), which was injected into the plasma core at anode region, while the powder feeder 2 (PFV-100, TEKNA, Canada) was used to supply MWCNT (~95 wt. %, Hanwha Chemical, Korea), which was injected into the peripheral region of plasma flame at the entrance of the reaction tube. Silicon powder injected into the inside of the plasma torch was completely evaporated to form nanoparticles. On the other hand, MWCNT injected into the relatively low temperature region maintains its original structure well without chemical and physical changes.

The experimental conditions are summarized in Table 1. Because Si-MWCNT nanocomposite was well synthesized at a relatively high power in our previous study, the input power was fixed at 12.4 kW in the present work. The reaction tube and the chamber were purged by argon gas at 20 L/min before plasma generation to avoid the oxidation of product. All experiments were operated at atmospheric pressure during system operation for 20 min. Flow rates of argon used for plasma forming gas, and Si carrier gas and MWCNT carrier gas were maintained at 15 L/min, 7 L/min, and 7 L/min, respectively. In such condition, feed rates of silicon powder and MWCNT were measured at 0.10 g/min and 0.25 g/min, respectively. After the synthesis experiment, products were collected from the reaction tube and the chamber. The chemical bonding of raw materials and products was investigated by XRD. In addition, the sizes and the morphology were confirmed by an FE-SEM.

2.2. Electrochemical characterization

The electrochemical performances of silicon powder, MWCNT, and synthesized nanocomposites collected from the reaction tube and the chamber were analyzed after fabricating test samples with Swagelok-type cells. Each sample was mixed with activated charcoal and polyvinylidene fluoride used as binder material at the mass ration of 3:1:1. The mixture was dissolved in an excessive *N*-methylpyrrolidone solution to form slurry. Then the slurry was coated on a Cu collector, which is punched to circular shape with 12 mm in diameter, and dried at 60 °C for 2 h. Lithium metal was cut to circular shape with 11 mm in diameter, and it used as a counterelectrode. In addition, a Cu emitter was punched to circular shape with 12 mm in diameter. For the preparation of electrolyte, 1 mol of $LiPF_6$ was dissolved in the mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate at the same volume faction. The working electrode and the counterelectrode were separated by glass microfiber filters punched to 12 mm in diameter. The assembly process of test cells was carried in an inert Ar atmosphere using a glove box to prevent moisture and oxidation. The image of cell assembly is shown in Fig. 2. The charge–discharge cycling was performed in the voltage range from 0.01 to 1.5 V at the current density of 100 mA/g.

Table 1
Experimental condition for the synthesis of Si-MWCNT nanocomposites by thermal plasma process.

Power (kW)		12.4
Feed rate of feedstock (g/min)	Si	0.1
	MWCNT	0.25
Mass ratio of feedstock (Si/MWCNT)		0.4
Injection position	Si	Torch
	MWCNT	Reaction tube
Plasma gas(L/min)		Ar 15
Carrier gas (L/min)		Ar 7 (Si and MWCNT, respectively)

3. Results and discussion

Fig. 3 exhibits XRD patterns of raw materials of the silicon powder and the commercial MWCNT. It is observed that silicon peaks at the 28.4°, 47.0°, 56.0°, 59.0°, 76.5°, and 88.0° corresponding cubic structure in Fig. 3(a), while carbon peaks at 26.5° and 42.3° indicate graphitic

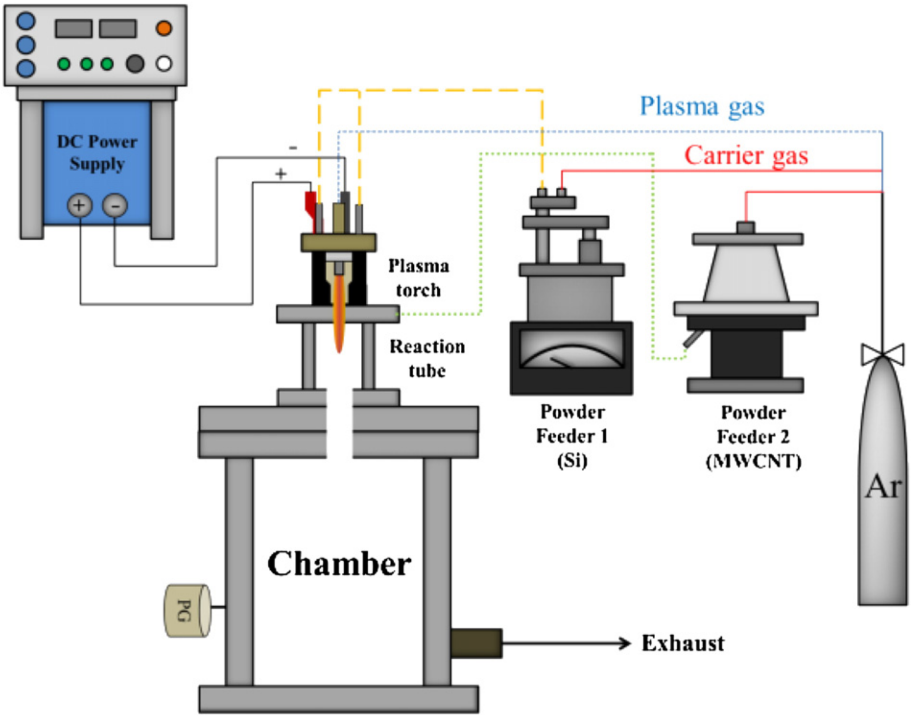

Fig. 1. Schematic diagram of the non-transferred thermal plasma system to synthesize Si-MWCNT nanocomposite.