

A Double Carbon Synthesis for Si-Ti Composite Anode Materials for Li-ion Batteries

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Abstract

A Si-Ti composite prepared by high energy mechanical ball milling and subsequent pyrolysis was investigated as an anode material for Li-ion batteries. High energy mechanical ball milling was initially used to control the Si-Ti particle size, and then carbon was added to the Si-Ti and again mixed by milling. Electrochemical characterization of the composite synthesized from Si, Ti, mesocarbon microbeads, and polyvinyl pyrrolidone shows that the first discharge and charge capacities were 612 and 516 mA h g⁻¹, respectively, and that 81% of the initial charge capacity of 495 mA h g⁻¹ was maintained for up to 30 cycles. The high electrochemical performance was attributed to the controlled Si crystallite morphology, the presence of titanium silicide phases, and the double treated carbon process that minimized the volume expansion associated with the Li-Si alloying reaction during cycling

Keywords: Li-ion battery, Anode, Silicide, Composite, Carbon coating

INTRODUCTION

As the development of portable electronic devices accelerates and the production of electric vehicles and energy storage systems expands, the importance of Li-ion battery performance increases. With a surge in Li-ion battery applications, the demand for enhanced battery performance, including higher energy density, higher power density, greater stability, and longer life cycle, is essential [1]. Because enhanced battery performance requires improvements to commercial cathode materials, typically LiCoO₂ (LCO), researchers have investigated variations in LCO compositions, including LiNi_xCo_yMn_zO₂ (NCM) and LiNi_xCo_yAl_zO₂ (NCA) [2]. However, advanced anode materials with properties exceeding those of graphite have not yet been developed in the battery industry.

In the search for a new anode material, silicon is an attractive material because of its high theoretical capacity compared to graphite [3]. Unfortunately, excessive volume expansion during the charge-discharge process causes a loss of electrical contact between the active material and the current collector, resulting in a poor life cycle [4]. To overcome the drawbacks, researchers have investigated metal silicide and carbon as buffering matrix materials at the active-inactive battery

interface [5,6]. The metal silicide is an important material used in heating elements, thermoelectric conversion, mechanically structured materials, and microelectronic devices [7]. Because metal silicides have good mechanical and electrical properties compared to metal oxides, research is being conducted on them as a buffer layer in the Li-ion charge-discharge process of a Li-ion battery [8].

In addition, the soft structure and a high electrical conductivity of materials such as pyrolysed carbon, graphite, CNT, and graphene make it capable of reacting with Li ions [9-11]. For this reason, many studies of carbonaceous materials for Li-alloy anodes have been carried out because of the attractive electrical conductivity and mechanical stability. In terms of improving the electrochemical performance, carbon-containing anode materials exhibit superior properties to other matrix materials and they alleviate the volume expansion of the Li alloy [12]. Carbonaceous materials are also being applied not only as simple coatings on the alloy materials but also in studies involving size and shape control of active materials.

In this study, we report on the processing of a novel anode material, Si-Ti/MCMB (mesocarbon microbeads) with polyvinyl pyrrolidone (PVP), prepared by a two-step process of high energy mechanical ball-milling (HEMM) and subsequent pyrolysis. The two step HEMM process controls the Si-Ti crystallinity and mixes the Si-Ti/MCMB composite. Pyrolysing PVP results in a carbon coating on the Si-Ti/MCMB composite. The motivation of this research is the possibility of a double carbon treatment method for synthesizing Li-Si alloy anode materials and its potential for improving electrochemical properties.

EXPERIMENTAL PROCEDURES

A Si-Ti/MCMB with PVP was prepared by the following procedure. To control the crystallinity, Si (>99%, Kojundo Chemical Lab, Japan) and Ti (>99%, Kojundo Chemical Lab, Japan) powders and ball mill media were placed in a hardened steel jar with a ball to powder weight ratio of 20:1 under an Ar-atmosphere, and then milled using a high-energy ball mill at 500 rpm for 12 h. The crushed composite product was ground, and particles with a mesh size of less than 200 were used. To synthesize the Si-Ti/MCMB composite, the milled Si-Ti powder and mesocarbon microbeads (MCMB, 10–28, Osaka Gas Co., Japan) with a mass ratio of 1:1 were mixed by HEMM

in an argon-filled hardened steel vial at a rotational speed of 500 rpm for 1 h. Finally, to prepare a double carbon treatment, the as-synthesized Si-Ti/MCMB composite was mixed with polyvinyl pyrrolidone (PVP, $[-C_6H_9NO-]_n$, Aldrich, USA) in the mortar and then subsequently pyrolysed at 900 °C for 1 h.

Phase analysis of the synthesized samples was performed using a MacScience M18XHF-SRA X-ray diffractometer (XRD) with Cu K α radiation. The morphology and microstructure were examined by JEOL JXA-8900R scanning electron microscopy (SEM). Electrodes for electrochemical evaluation were prepared by mixing 70 wt.% carbon black (Super C65, 15 wt.%) as a conducting agent and 15 wt.% poly(vinylidene fluoride) dissolved in N-methylpyrrolidone as a binder to form a slurry. The slurry was coated onto a Cu foil, which was subsequently pressed and dried at 120 °C for 2 h in a vacuum. CR2032-type coin cells were assembled using polypropylene (Celgard 2400) as a separator, Li metal foil as counter and reference electrodes, and 1 M LiPF $_6$ in ethylene carbonate/diethyl carbonate (1:1, v/v, PanaxEtec) as an electrolyte. Galvanostatic cycling was performed at a constant current density of 100 mA g $^{-1}$ in a potential window of 0.0–1.5 V vs. Li $^+$ /Li.

RESULTS AND DISCUSSION

The XRD patterns of the as-received Si-Ti, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite powders are shown in Fig. 1. The reflections for the Si-Ti composite could be indexed based on cubic Si (JCPDS No. 80-0018), hexagonal Ti (JCPDS No. 44-1294), and hexagonal Si $_3$ Ti $_5$ (JCPDS No. 29-1362). This finding confirms the presence of three crystalline phases, including Si $_3$ Ti $_5$ which originated from the alloying reaction between Si and Ti during the HEMM process. The broad diffraction peaks indicated a low degree of crystallinity. The Si-Ti/MCMB composite shows a sharp carbon peak at 28° related to the MCMB (111) plane. In contrast, after pyrolysis of PVP, the reflection of Ti eventually disappeared and a Si $_2$ Ti phase was formed, while the remaining Si, graphite, and Si $_3$ Ti $_5$ remained. No peaks corresponding to carbon from PVP could be detected due to its amorphous nature.

Fig. 2 presents SEM images of the Si-Ti, Si-Ti/MCMB, and Si-Ti/MCMB with PVP composites and their corresponding particle morphologies. The Si-Ti composite particles are agglomerated and are <1 μ m after ball milling for 12 h. In the case of the Si-Ti/MCMB composite (shown in Fig. 2(b)), the Si-Ti particles are attached to the partially broken MCMB particles. Fig. 2(c) shows the as-synthesized Si-Ti/MCMB with PVP in which the pyrolysed carbon is dispersed on the Si-Ti/MCMB composite.

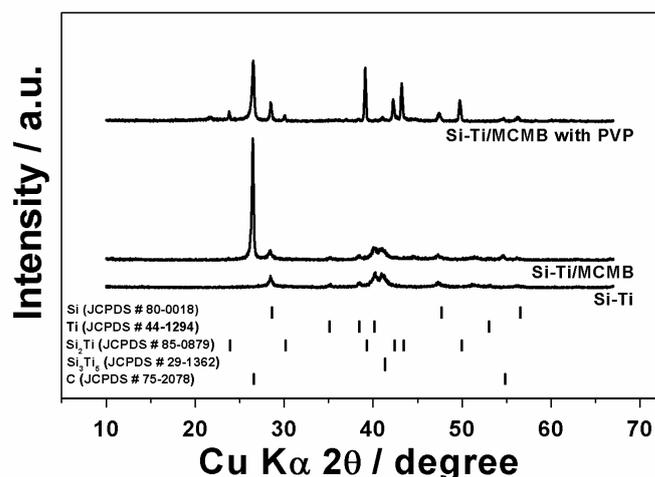


Figure 1: X-ray diffraction patterns of Si-Ti composite, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite.

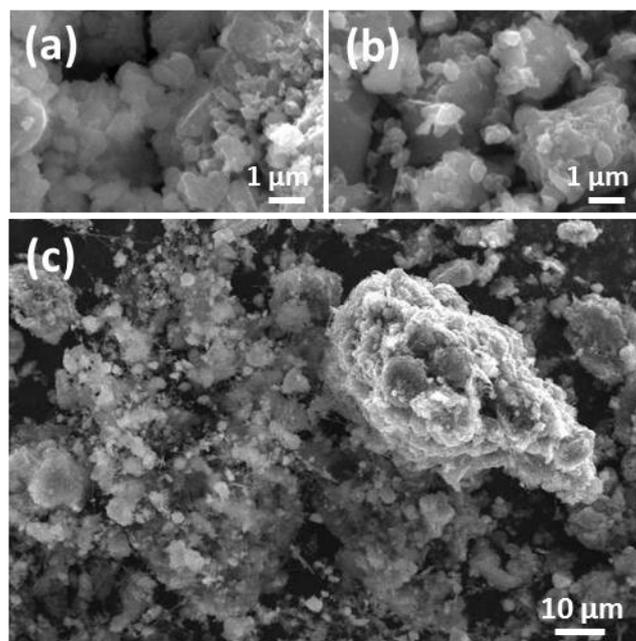


Figure 2: SEM images of (a) Si-Ti composite, (b) Si-Ti/MCMB composite, and (c) Si-Ti/MCMB with PVP composite.

To evaluate the double carbon treated Si-Ti composite as an anode material, the Si-Ti, the Si-Ti/MCMB, and the Si-Ti/MCMB with PVP composites were evaluated by electrochemical testing between 0.0 and 1.5 V at a constant current of 100 mA g $^{-1}$, as shown in Fig. 3. The first discharge capacities of the Si-Ti, Si-Ti/MCMB, and Si-Ti/MCMB with PVP composites are 1721, 981 and 612 mAh g $^{-1}$, respectively. This corresponds to an initial cycling efficiency of 91, 82, and 84%, respectively.

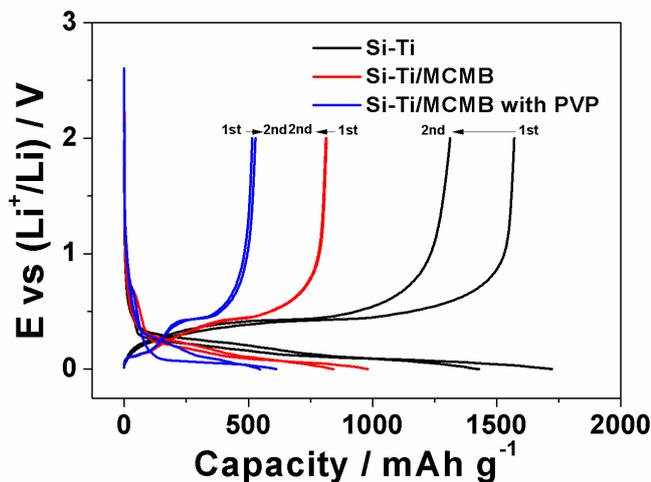


Figure 3: The first and second voltage profiles of Si-Ti composite, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite.

The HEMM process can crush powders, blend material, and synthesize compounds [13]. In this system, the size of the Si particles was reduced, Si-Ti alloy particles were occurred, and Si-Ti was mixed with MCMB by ball milling process. Polymer decomposition during pyrolysis results in the development of carbon on the composite sample. Consequently, the capacity values continuously decreased as the amount of processing increased, but capacity retentions were gradually more stable. The stability is likely a result of the diminished volume change during cycling and the enhanced electrical contact between particles and the current collector.

Fig. 4 exhibits differential capacity plots (DCPs) of the Si-Ti composite, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite samples at the first cycle. The DCP of Si-Ti composite features characteristic voltage plateaus during the discharge process at 0.21 and 0.09 V. The cathodic peaks correspond to the Li-Si alloying reaction with Li, because the Si-Ti crystal structure lacks suitable tunnels for Li-ion diffusion. The anodic peak for the Li-Si dealloying reaction is evident at 0.426 V during the charging process. On the other hand, the Si-Ti/MCMB composite shows new cathodic peaks at 0.06 and 0.08 V, and anodic peaks at 0.11 and 0.16 V corresponding to the reaction of MCMB with Li. The Li-Si alloying reaction is slightly shifted and occurred near 0.21 and 0.07 V due to the overpotential caused by MCMB. Anodic peaks also present a similar shift to higher voltages. The reduction of peak intensities at these positions is due to increasing ball milling time for mixing with MCMB. In the case of the Si-Ti/MCMB with PVP composite, peaks like those in the Si-Ti/MCMB composite occurred during cycling, except with slight shifts due to the overvoltage caused by pyrolysed carbon.

The cycle performances of the Si-Ti, Si-Ti/MCMB, and Si-Ti/MCMB with PVP composites are shown in Fig. 5. The Si-Ti composite presents a poor capacity retention at increasing

cycling due to the huge volume expansion from the Li-Si alloying reaction. The cycle performance of Si-Ti/MCMB composite is more stable than the Si-Ti composite. The MCMB acts as an effective buffering matrix and alleviates volume change, and acts as a connection material between the active material and the current collector to offer electrical conductivity. Unlike the other composites, the cycle performance of Si-Ti/MCMB with PVP composite shows a high reversible capacity and improved cycle performance, and 81% of its initial capacity of 612 mA h g^{-1} is retained after 30 cycles. This enhancement of capacity retention is probably due to the double treated carbon process providing a structural matrix that buffers against the volume expansion-contraction and provides a necessary electronic conduction pathway.

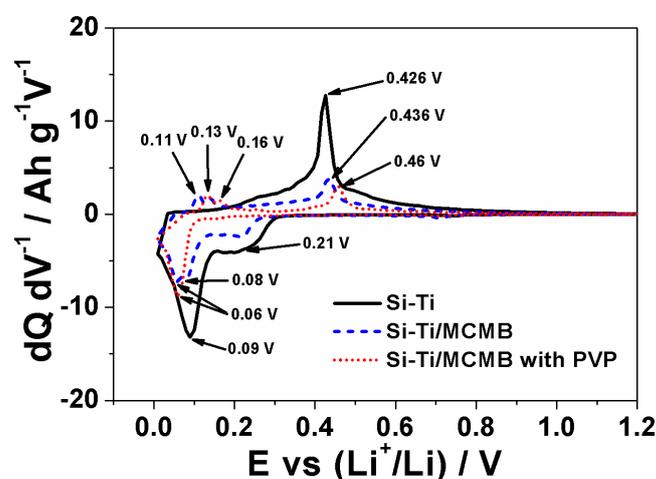


Figure 4: Differential capacity plots of Si-Ti composite, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite.

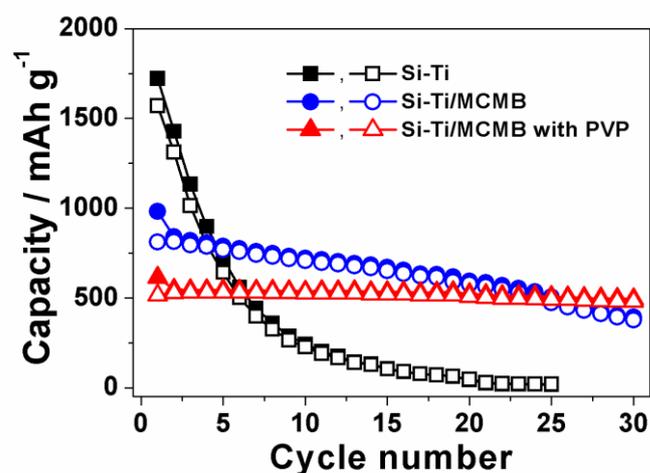


Figure 5: Cycling performances of Si-Ti composite, Si-Ti/MCMB composite, and Si-Ti/MCMB with PVP composite.

CONCLUSION

A double treated carbon process was used to fabricate a Si-Ti/MCMB with PVP composite material, and the composite was investigated as an anode material for Li-ion battery applications. The Si-Ti/MCMB with PVP composite exhibited high reversible capacity, excellent cycle life, and effective electron transport. This superior electrochemical performance resulted from the reduced Si crystallite size and the conductive carbon matrix, which alleviated mechanical strain and provided an efficient network for electron transfer. This work emphasizes the potential of a double treated carbon process, which significantly affects the electrochemical performance for Li-alloy materials.

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