



Improved rate capability of lithium-ion batteries with Ag nanoparticles deposited onto silicon/carbon composite microspheres as an anode material

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ABSTRACT

Ag-deposited silicon/carbon (Ag/Si/C) composite microspheres were synthesized and evaluated as an anode material for lithium-ion batteries (LIBs). The Si/poly(AN-co-TMSPM) composite microspheres were prepared through suspension polymerization and were decorated with Ag nanoparticles by a wet chemical method in an aqueous AgNO₃ solution. Ag nanoparticles remained on the surface of the Si/carbon (Si/C) composite microspheres even after heat treatment at high temperatures. The Si/C and Ag/Si/C composite microspheres were characterized by scanning electron microscopy, focused ion beam-scanning electron microscopy, and X-ray diffraction. The electrochemical performance of the Ag/Si/C composite electrode was compared to that of the Si/C composite electrodes using electrochemical impedance spectroscopy, constant current charging and discharging, and cycling performance at various cycling rates. The Ag/Si/C composite microspheres exhibited a higher specific capacity and better rate capability at the various current rates from C/10 to 5C than those of the Si/C composite electrode without Ag nanoparticles when they were used as the anode material in LIBs. These results suggest that the surface deposition with Ag nanoparticles contributes to the charge-transfer kinetics of the Si/C composite electrode.

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1. Introduction

Graphite has been used as an anode material for lithium-ion batteries (LIBs) for decades due to its excellent behavior during continuous charge/discharge cycles [1–3]. However, since its low theoretical capacity (372 mAh g⁻¹) is insufficient for high energy applications, alternative anode materials such as silicon (Si), tin (Sn), aluminum (Al), and antimony (Sb) have all been investigated for their potential to improve the energy density of LIBs [4–6]. Among these materials, silicon has attracted much attention as a promising anode material through the formation Li_{4.4}Si alloys due to its much higher theoretical specific capacity (4200 mAh g⁻¹) than graphite [7,8]. However, lithium/silicon alloys experience huge changes in volume, which results in poor cyclability because of the strong physical stresses on the crystallites [9]. To resolve this problem, many groups have investigated silicon-based composite anodes consisting of active silicon and amorphous carbon phases, such as amorphous carbon-coated Si composites [10,11], carbon coated Si-graphite composite anodes [12], Si/disordered carbon composite anodes [13–15], and core-shell Si/carbon nanocomposites [16]. Our research group synthesized multi-core/shell structured Si/C microspheres for use with high performance anodes, in which nanosized

silicon particles are embedded in amorphous carbon microspheres. The amorphous carbon phase prevents changes in the volume of the silicon nanoparticles during the lithiation and de-lithiation processes, thus improving cyclability [17]. Although the Si/carbon composite anodes showed better cycling performance than pure Si anodes, these composite anodes have the drawback of severe capacity fading at high current densities.

In this study, Ag-deposited Si/poly(AN-co-TMSPM) multi-core/shell microspheres were synthesized by suspension polymerization and a wet chemical method using aqueous silver nitrate (AgNO₃) and hydrazine as a reducing agent. Decorated Ag nanoparticles remained on the surface of the Si/C composite microspheres even after heat treatment. The composite microspheres were used as anodes in a lithium-ion battery, which exhibited better rate capability compared to the Si/C composite microspheres. The deposited Ag nanoparticles on their surface reduce the charge-transfer resistance during the charging and discharging processes.

2. Experimental

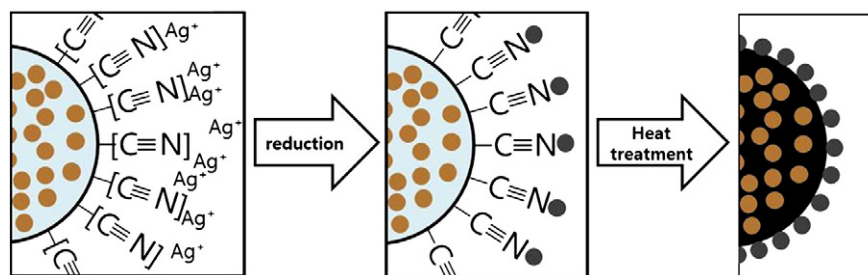
2.1. Materials

Hydrazine, monohydrate (NH₂NH₂·H₂O, JUNSEI, Chuo-ku, Tokyo, Japan), silver nitrate (99.999%, Aldrich Chemical Co., Milwaukee, WI, United States), acrylonitrile (AN, JUNSEI, Chuo-ku, Tokyo, Japan), 3-(trimethoxysilyl)propyl methacrylate (TMSPM, 98%, Aldrich Chemical

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Scheme 1. Schematic illustration of the formation process of Ag nanoparticles on the surface of Si/P(AN-co-TMSPM) composites.

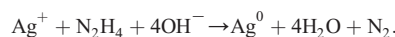
Co., Milwaukee, WI, United States), 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN, Wako), divinylbenzene (DVB, isomer mixture; 55%, Aldrich Chemical Co., Milwaukee, WI, United States, Wako Chemical, Dalton, GA, United States), methylene chloride (MC, Dae-Jung Chemicals & Metals Co., Siheung Si, Gyeonggi-do, Korea), silicon powder (Si, crystalline, APS $\leq 50\text{ nm}$, laser synthesized from vapor phase, Alfa Aesar), sodium dioctyl sulfosuccinate (Aerosol-OT (AOT)), and polyvinyl alcohol (PVA, MW = $8.8\text{--}9.2 \cdot 10^4\text{ g mol}^{-1}$, Aldrich Chemical Co., Milwaukee, WI, United States) were used as received.

2.2. Synthesis of silicon/poly(AN-co-TMSPM) composite microspheres

Solution polymerization and the O/W system for Si/poly(AN-co-TMSPM) composite microspheres were employed as described previously [17]. Monomer mixtures of AN (8 g), TMSPM (2 g), ADVN (0.1 g), and the cross-linking agent DVB (0.01 g) were dissolved in MC (15 g). Silicon nanopowders (1 g) were dispersed in this solution with mechanical stirring and sonication. The mixture was then heated in a 250-mL glass reactor equipped with a reflux condenser and a mechanical stirrer operated at a speed of 300 rpm for 1.5 h at 50 °C. After that, the polymeric solution containing the Si nanoparticles was added dropwise into 4 wt.% PVA aqueous solution containing AOT (0.1 wt.%). MC was evaporated from the mixture with vigorous stirring (200 rpm) over 12 h at room temperature. For purification, the Si/poly(AN-co-TMSPM) composite microspheres were sieved through a strainer with a mesh size of 10 μm . Purification was repeated five times using distilled water (DI water). The brown powders were dried in a vacuum oven at room temperature.

2.3. Synthesis of Ag-deposited silicon/carbon multi core-shell composite microspheres

The as-prepared Si/poly(AN-co-TMSPM) composite microspheres were dispersed in an aqueous AgNO_3 solution (0.05 wt.%) over 1 h with mechanical stirring. An aqueous hydrazine solution (0.06 wt.%) was then added to the mixture of Si/poly(AN-co-TMSPM) composite microspheres and stirred for 30 min. Functional affinity between the nitrile group of the PAN and silver ions promotes random deposition of silver nanoparticles onto the surface of the composite microspheres [18], as illustrated in Scheme 1. The chemical reaction of Ag nanoparticle synthesis using hydrazine oxidation is as follows:



Ag-deposited Si/poly(AN-co-TMSPM) composite microspheres were washed several times using DI water and dried in a vacuum oven at room temperature. Dark-brown colored powders were heated at 750 °C and maintained for 3 h under an Ar/H_2 atmosphere.

2.4. Characterization of Ag-deposited silicon/carbon multi core-shell composite microspheres

The Si/C and Ag/Si/C composite microspheres were characterized using X-ray diffraction (XRD, Rigaku, C/MAX 2500) and

thermogravimetric analysis (TGA, TG209F3, NETZSCH). In order to estimate the ratio of Si to amorphous carbon, the Si/C composite microspheres and Ag nanoparticles were measured by TGA under air atmosphere. Their morphologies were confirmed by scanning electron

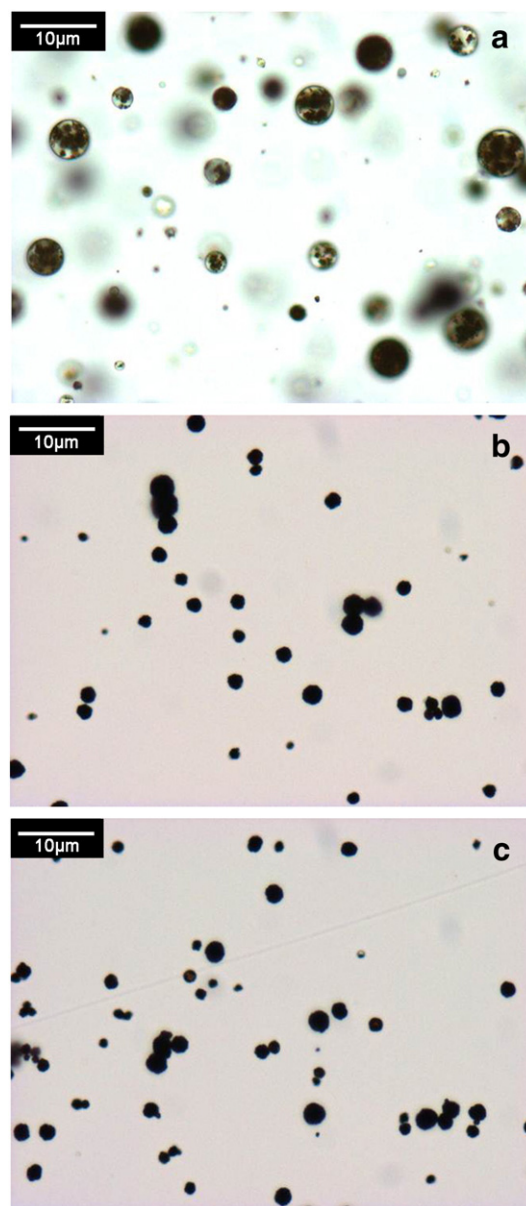


Fig. 1. OM image of (a) droplets containing Si nanoparticles, AN, TMSPM, and MC during suspension polymerization; (b) Si/Poly(AN-co-TMSPM) composite microspheres; and (c) Ag/Si/Poly(AN-co-TMSPM) composite microspheres after evaporation of MC.

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