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Synthesis of Fe_3O_4/C composite microspheres for a high performance lithium-ion battery anode

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HIGHLIGHTS

- ► We prepare Fe_3O_4/C composite microspheres containing high content of Fe_3O_4.
- ► We examine the electrochemical performances depending on the particle morphologies.
- ► Our particle structure effectively suppresses the aggregation of Fe_3O_4 nanoparticles.
- ► Surface modified-Fe_3O_4 nanoparticles can be uniformly embedded in carbon matrix.

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ABSTRACT

Fe_3O_4/carbon (Fe_3O_4/C) composite microspheres with a high content of Fe_3O_4 nanoparticles as an active material are prepared by suspension polymerization and heat treatment. A significant difference is observed in the morphology of the Fe_3O_4/C composite microspheres with the introduction of different amounts of Fe_3O_4 nanoparticles. The morphological and structural differences of the Fe_3O_4/C composite microspheres are characterized by focused ion beam cross-section, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction analysis. Thermogravimetric analysis is conducted to measure the amount of Fe_3O_4 nanoparticles introduced into a carbon matrix. We fix two samples with Fe_3O_4 contents of 72 wt.% and 98 wt.%, respectively. Fe_3O_4/C composite microspheres containing 72 wt.% Fe_3O_4 nanoparticles show much higher capacity retention with an excellent columbic efficiency of 99% at every cycle in comparison with that of the Fe_3O_4/C composite microspheres containing 98 wt.% Fe_3O_4 nanoparticles when used as anodes for LIBs. These results indicate that the particle morphology and weight ratio of incorporated Fe_3O_4 to carbon matrix affects the electrochemical performance of Li-ion cells.

1. Introduction

Graphite is currently used commercially as the anode active material for lithium-ion batteries (LIBs) because of its good cycling stability and high columbic efficiency. However, the low intrinsic specific capacity and low energy density of LIBs cannot satisfy the needs of future applications such as electric devices and vehicles with high power requirements [1]. In the past few years, various materials have been studied as potential anode alternatives for LIBs [2–6]. Among these alternatives, transition metal oxides (MO) have been developed for use in novel anodes because they have a high specific capacity from the conversion mechanism without an intercalation reaction. Magnetite (Fe_3O_4) anodes have attracted great attention for next-generation LIBs because of their much higher theoretical capacity (927 mAh g^{-1}) than that of conventional graphite anodes (372 mAh g^{-1}), low cost, increased safety, and environmental benignity [7,8]. Unfortunately, Fe_3O_4 anodes also display poor cycling performance, especially at high rates, because the repeated volume change of Fe_3O_4 anodes during lithiation/delithiation breaks down the electrical conduction of electrodes [7,9]. Nano-sized Fe_3O_4 powder has recently been employed in anodes to accommodate volume variation and improve rate capability by increasing active reaction sites [8,10–14]. However, they show large irreversible capacity at the first cycle and gradual capacity fading during continuous cycling due to electrolyte decomposition and nanoparticle aggregation during the Li-ion reaction.

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Many research groups have prepared Fe_3O_4/amorphous carbon composite materials that have shown improved electrochemical performance [7–9,15–17].

We prepared Fe_3O_4/C composite microspheres with a high Fe_3O_4 nanoparticle content as an active material and evaluated them as anode material for high performance LIBs. The Fe_3O_4 nanoparticles were synthesized by a co-precipitation method, and a large amount of Fe_3O_4 nanoparticles could be introduced into the poly(acrylonitrile-co-3-(trimethoxysilyl)propyl methacrylate) (poly(AN-co-TMSPM)) matrix by suspension polymerization, which had different morphologies depending on the weight ratio of Fe_3O_4 nanoparticles to polymer matrix. After heat treatment, a black powder was obtained which was used as the anode electrode in coin-type cells. The electrochemical performance of the Fe_3O_4/C composite microspheres was evaluated, and the Fe_3O_4/C composite microspheres containing 72 wt.% Fe_3O_4 nanoparticles showed a high reversible capacity of 500 mAh g^{-1} at 1 C with an excellent columbic efficiency of 99% even after 300 cycles.

2. Experimental

2.1. Materials

Acrylonitrile (AN, JUNSEI, Chuo-ku, Tokyo, Japan), 2,2′-azobis-(2,4-dimethylvaleronitrile) (ADVN, Waco Chemical Co., Dalton, GA, United States), 3-(trimethoxysilyl)propyl methacrylate (TMSPM, 98%, ALDRICH Chemical Co., Milwaukee, WI, United States), Methylene Chloride (MC, DAEJUNG Chemicals & Metals Co., Siheung Si, Gyeonggi-do, Korea), Poly(vinyl alcohol) (PVA, avg. Mw. 85,000–124,000, 87–89% hydrolyzed, Sigma ALDRICH Chemical Co., Milwaukee, WI, United States), Di-2-ethylhexyl sodium sulfosuccinate (Aerosol® OT, Wako Chemical, Dalton, GA, United States), Iron (III) Chloride, Anhydrous ($FeCl_3$, Showa), Iron (II) Chloride Tetrahydrate ($FeCl_2 \cdot 4H_2O$, Wako), and Citric Acid (CA, S.P.C GR Reagent, SAMCHUN PURE CHEMICAL INDUSTRIES LTD) were used as received.

2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared with citric acid by co-precipitation of a $FeCl_2$ and $FeCl_3$ (1:2 M ratio) salt solution by the addition of NH_4OH [18]. In a typical synthesis, 0.86 g of $FeCl_2$ and 2.35 g of $FeCl_3$ were dissolved in 40 mL of DI water in a four-neck flask equipped with a condenser and nitrogen inlet system with constant mechanical stirring at 400 rpm at 80 °C. 10 mL of NH_4OH was then slowly added to the salt solution and heated for 30 min. Afterward, 2 mL of water containing 1 g of citric acid was added into the reactor and heated to 95 °C with additional stirring for 90 min. When the above procedure was finished, the reaction mixture was cooled to room temperature under nitrogen injection. The black precipitates were separated and rinsed magnetically about three times with DI water, and dialysis was conducted over approximately 72 h by the periodic exchange of DI water. Very fine Fe_3O_4 nanoparticles were obtained after freeze-drying.

2.3. Preparation of Fe_3O_4/C composite microsphere

First, 2 g of TMSPM and 0.5 g or 1.0 g Fe_3O_4 nanoparticles were put into a 250 mL four-neck glass reactor containing 30 g of methylene chloride (MC). To disperse the aggregated nanoparticles in the mixture, the reactor was sonicated on ice for 1 h. 10 g of acrylonitrile (AN) containing 0.1 g of ADVN was then added into the reactor, and immersed in a 55 °C pre-heated oil bath equipped with a nitrogen inlet system and condenser. After constant stirring at 300 rpm for 2 h, the polymerized mixture was dripped slowly into the polymeric solution, which contained 500 mL of PVA 2 wt.% and Aerosol OT 1 wt.%, and stirred vigorously at ambient temperature for 12 h. The resultant precipitates were washed with DI water and freeze-dried. Dried particles were heated to 670 °C at 5 °C min^{-1} and maintained for 3 h at 670 °C under nitrogen atmosphere.

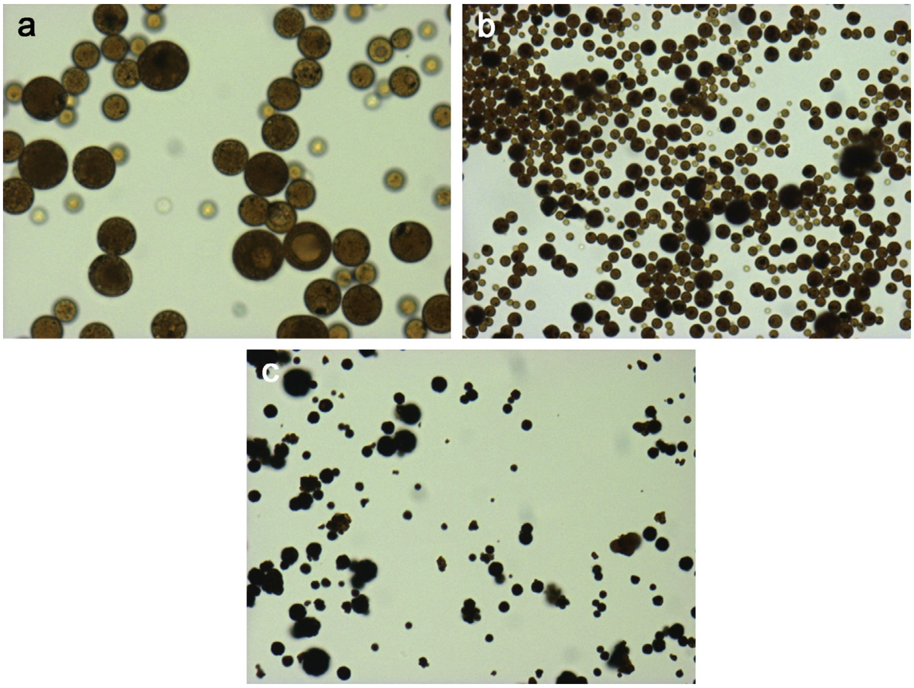

Fig. 1. OM images of (a) S1001, (b) S1005 and (c) S1010 stabilized in water containing PVA and Aerosol OT.