Electrochemical Insertion and Extraction of Lithium Ion at Uniform Nanosized $Li_{4/3}Ti_{5/3}O_4$ Particles Prepared by a Spray Pyrolysis Method

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Nanosized particles of spinel $Li_{4/3}Ti_{5/3}O_4$ were prepared at 673 K by an electrospray pyrolysis method for the first time. TEM observation clarified that the resultant particles were fairly uniform and that the particle sizes were ca. 12 nm with well-defined crystal form. Cyclic voltammetry gave very sharp and symmetrical redox peaks at around 1.56 V vs Li/Li^+ due to the insertion and extraction of lithium ion at the nanosized $Li_{4/3}Ti_{5/3}O_4$. These results indicate that the apparent fast diffusion of lithium ion can be attained by using uniform nanosized particles.

Introduction

Nanometer-size particles have attracted much attention for achieving a dramatic improvement in electronic devices or opening a new frontier in nanotechnology. In addition, recent rapid development of polymer electrolyte membrane fuel cells has been achieved by employing nanosized catalysts of Pt and Ru. The nanosized particles affect the performance of catalysts, optics, batteries, etc., and therefore uniform nanosized particles are essential for the basic understanding of the particle-size effects on the performance.[1−3]

The use of nanosized particles is very available in lithium-ion batteries for use in hybrid electric vehicles (HEV), which drastically decreases environmental burden caused by the emission of CO_2. Rapid charge and discharge reactions are required when lithium-ion batteries are used for high-power application. To enhance the charge and discharge reactions, lithium-ion diffusion through the active materials must be very fast, and therefore, granulated particles of battery active materials (ca., 10−20 μm) are usually used to shorten the diffusion paths of lithium ion through the active materials in the commercial lithium-ion batteries. In lithium-ion batteries for high-power use, further decrease in the particle sizes of active materials is very essential to obtain apparent high lithium-ion diffusion. Nanoparticles of electroactive materials provide a large surface area, and therefore charge-transfer resistances at electrode/electrolyte interface can be effectively decreased. Further, nanosized particles with a narrow size distribution are also required in lithium-ion batteries for high-power use in order to obtain homogeneous current distribution in the electrode.

There are a variety of lithium-ion insertion materials such as transition-metal oxide and chalcogenide.[4] Among them, spinel $Li_{4/3}Ti_{5/3}O_4$ shows minimal variation of the cubic unit cell during the electrochemical insertion/extraction of lithium ion.[5] $Li_{4/3}Ti_{5/3}O_4$ accommodates 1 equiv of lithium per formula unit, which takes place at an extremely constant potential of about 1.56 V vs Li/Li^+.[6] The phase composition during insertion/extraction of lithium ion has also been studied by X-ray and neutron diffraction analysis and was revealed to be two phase, with differences only in the lithium-ion sublattices.[5,7,8]

Various synthesis methods, such as chemical vapor deposition, pulsed laser ablation, spray pyrolysis, sol−gel, and hydrothermal, have been so far employed to synthesize nanosized particles.[9−12] Electrospray deposition is one of the spray pyrolysis methods to produce nanosized materials by pyrolyzing fine droplets with a narrow size distribution, which are produced by applying high dc voltage to the spray.[13,14] Furthermore, the resulting particles can be directly deposited on a substrate due to a spray method.

In this paper, we prepared uniform nanosized particles of spinel $Li_{4/3}Ti_{5/3}O_4$ on Pt by electrospray depositon for the first time. The electrochemical properties of the nanosized particles were studied in lithium-ion insertion/extraction reactions by cyclic voltammetry.

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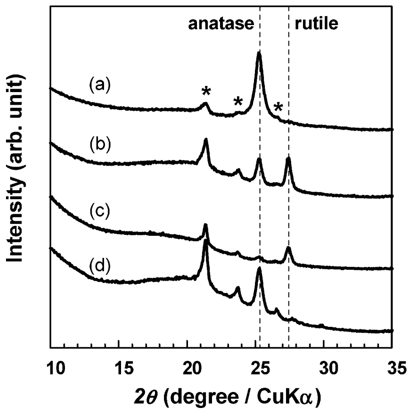

Figure 1. XRD patterns of TiO_2 particles prepared at (a) 573 K, (b) 673 K, (c) 773 K by electrospray pyrolysis, and (d) 673 K by spray pyrolysis.

Experimental Section

Materials. A starting solution of 2-propanol (IPA) containing 10^{-3} mol dm^{-3} titanium tetraisopropoxide ($Ti(OC_3H_7)_4$) was used. Another solution was 10^{-3} mol dm^{-3} each of $Ti(OC_3H_7)_4$ and lithium acetonate ($Li(CH_3COO)$) dissolved in IPA.

Synthesis. The electrospray setup used in this study was similar to that described in the literature.[15] The solution was flowed at 1.0 sccm (cm^3/min) through a nozzle at which a dc voltage of +7.0 kV was applied. The resulting droplets were pyrolyzed at temperature between 573 and 773 K in a tubular furnace and deposited on a Pt substrate.

Characterization. The deposits on Pt were characterized by X-ray diffraction (XRD). The resultant powders were subjected to ultrasonic agitation in ethanol, and then the particles were deposited on Au microgrids to observe their morphology and microstructure by transmission electron microscopy (TEM). Electrochemical properties were studied by cyclic voltammetry at a sweep rate of 0.1 mV s^{-1} using a three-electrode cell. The working electrode was the particles deposited on Pt. Lithium metal was used for both counter and reference electrodes. A liquid electrolyte of 1 mol dm^{-3} $LiClO_4$ dissolved in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume) was used. Unless otherwise stated, the potential is given vs Li/Li$^+$. All experiments were conducted under an argon atmosphere with a dew point below −60 °C.

We first prepared TiO_2 nanoparticles by an electrospray pyrolysis method to show its superiority as compared with a conventional spray method, and then spinel $Li_{4/3}Ti_{5/3}O_4$ was prepared.

Results and Discussion

Figure 1 shows XRD patterns of the particles obtained at 673 K from a starting solution of $Ti(OC_3H_7)_4$ in IPA. The peaks at 2θ angles of 25.3° and 27.4° correspond to the (101) diffraction line of anatase phase and the (110) of rutile phase, respectively. The peaks at 21.4°, 23.8°, and 26.6° were assigned to diffraction lines of clay used to fix the substrate on the sample stage. TiO_2 with anatase structure was obtained at 573 K. The amount of anatase phase decreased with an increase in the reaction temperature, and rutile phase gradually increased up to 773 K as alternated. Rutile phase was obtained at 673 K by an electrospray pyrolysis method, while not formed by a spray method without applied voltage at identical temperature. These results indicate that oxide particles can be synthesized by electrospray pyrolysis at lower temperature than that needed for conventional spray pyrolysis.

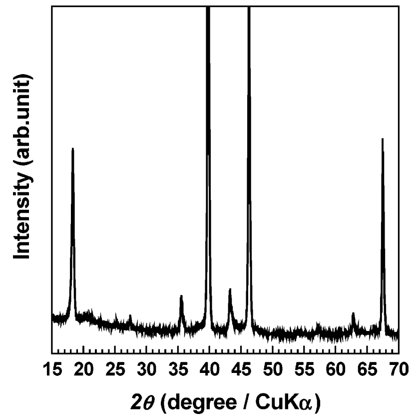

Figure 2. XRD patterns of $Li_{4/3}Ti_{5/3}O_4$ particles prepared at 673 K by electrospray pyrolysis.

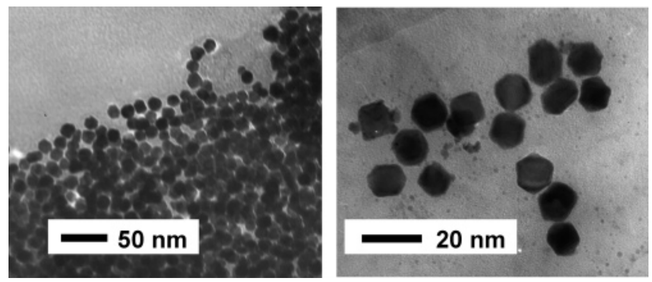

Figure 3. (a) Low-magnification and (b) high-magnification TEM images of $Li_{4/3}Ti_{5/3}O_4$ particles prepared at 673 K by electrospray pyrolysis.

Figure 2 shows XRD patterns of the samples prepared at 673 K by electrospray pyrolysis using a solution of $Ti(OC_3H_7)_4$ and $LiOC_3H_7$ dissolved in IPA. The peaks at 2θ angles of 18.3°, 35.6°, 43.2°, 57.2°, and 62.9° were indexed as the (111), (311), (400), (333), and (440) reflections of $Li_{4/3}Ti_{5/3}O_4$, respectively. Very small peaks were observed at 25.3° and 27.4°, indicating that the resultant particles contained trace amounts of TiO_2. Other peaks at 39.9°, 46.3°, and 67.5° were assigned to diffraction lines of Pt.

Figure 3 shows TEM images of $Li_{4/3}Ti_{5/3}O_4$ particles prepared at 673 K by electrospray pyrolysis. Fairly uniform particles were observed, and their size was ca. 12 nm. Since a distinct crystal form, i.e., hexagon or regular tetragon, was clearly observed, the $Li_{4/3}Ti_{5/3}O_4$ particles were highly crystallized. In an electrospray technique, droplets with a narrow size distribution can be created, and therefore uniform-size particles seem to be formed.[14]

Figure 4 shows cyclic voltammograms of $Li_{4/3}Ti_{5/3}O_4$ particles prepared by electrospray pyrolysis. Very sharp and symmetrical redox peaks were observed at around 1.56 V due to the insertion and extraction of lithium ion at $Li_{4/3}Ti_{5/3}O_4$.[6] The peak separation was about 25 mV, which was much smaller than those reported in the literature.[16,17] The voltammogram seemed to show a similar behavior to the redox reactions of an adsorbate; i.e., oxidation and reduction peaks are symmetrical. The diffusion of lithium ion through active electrode materials is well-known to be

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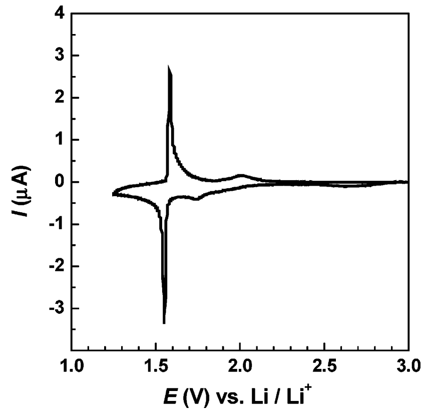

Figure 4. Cyclic voltammograms of $Li_{4/3}Ti_{5/3}O_4$ particles in 1 mol dm^{-3} $LiClO_4$/EC+DEC. Scan rate was 0.1 mV s^{-1}.

slow.[18] The use of large particles or thick films of active materials, which have long diffusion paths of lithium ion, gives diffusional behavior of lithium ion through the active materials, and therefore broad redox peaks due to the insertion and extraction of lithium ion should be observed in cyclic voltammograms.[19] In this work, electroactive species were deposited on Pt and their size was uniformly very small. Based on the area of the reduction peak in the cyclic voltammogram and the particle size of ca. 12 nm, the thickness of the deposit on Pt was roughly estimated to be around two- or three-particle layer. Hence, the influence of diffusional behavior of lithium ion through the $Li_{4/3}Ti_{5/3}O_4$ particles were apparently suppressed, and sharp redox peaks were observed in the cyclic voltammogram. The peaks at around 1.85 V were broad, and the peak separation in potential was very large. This behavior was characteristic of the insertion and extraction of lithium ion at anatase TiO_2, which is in good agreement with the XRD pattern shown in Figure 2.[17]

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Conclusion

Rutile TiO_2 particles were formed at 673 K by electrospray pyrolysis, while not obtained by conventional spray pyrolysis at identical temperature. These results indicate that oxide particles can be synthesized by electrospray pyrolysis at lower temperature than that needed for spray pyrolysis. Spinel $Li_{4/3}Ti_{5/3}O_4$ particles prepared by an electrospray pyrolysis method had a fairly uniform particle size of around 12 nm and a distinct crystal form. Cyclic voltammetry gave very sharp and symmetrical redox peaks at around 1.56 V vs Li/Li^+ due to the insertion and extraction of lithium ion at $Li_{4/3}Ti_{5/3}O_4$. These results indicate that the apparent fast diffusion of lithium ion can be attained by using nanosized particles. The use of nanosized particles containing short diffusion paths for lithium ion should improve the rate performance of lithium-ion batteries and is currently under investigation. The present results will inspire intensive studies on the particle-size effect in various disciplines by using uniform nanosized particles with a well-defined particle size.

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