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Spinel $Li_4Ti_5O_{12}$ Nanowires for High-Rate Li-Ion Intercalation Electrode

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A large quantity of spinel $Li_4Ti_5O_{12}$ nanowires was prepared by firing a mixture of $TiO_2 \cdot 1.25H_2O$ nanowires and Li acetates at 800°C for 3 h. The spinel nanowire had a diameter of 150 nm, which was similar to that of $TiO_2 \cdot H_2O$ nanowire. The Brunauer-Emmett-Teller (BET) surface area of the spinel wire was 38 m^2/g, which was seven times higher than that of fine particles, which had a BET surface area of only 4.6 m^2/g. The first discharge capacity was 165 mAh/g at a 0.1 C rate and 93% capacity was retained even after a 10 C rate. We believe that these results were associated with a more active surface in the nanowires which facilitated faster lithium diffusion due to shorter pathways.
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The structure of spinel $Li_4Ti_5O_{12}([Li_{1+x}]_{8a}[Li_{1/3}Ti_{5/3}]_{16d}O_4)$ consists of a cubic close packed oxygen array in which the lithium ions are located at the 8a tetragonal sites, while the titanium and part of lithium ions are located at the 16d octahedral sites of a cubic unit cell with space group *Fd*3*m*.[1-7] In spinel $Li_4Ti_5O_{12}$, the $[Li_{1/3}Ti_{5/3}]O_4$ framework provides a three-dimensional network of channels for fast lithium-ion diffusion, and Li-ion diffusion coefficients of the as-prepared spinel powder are generally about 10^{-6} cm^2/s measured by using a neutron radiography.[8] Furthermore, the spinel shows a slight volume expansion even after full lithium intercalation.[4] Accordingly, good reversibility and the ability to resist structural change (zero-strain insertion material) during lithium inter/deintercalation make it an attractive anode for high rate battery applications. Also of importance are a high surface area and few side reactions with electrolytes related to the irreversible capacity.

In this regard, significant effort has recently been devoted to producing smaller particles that have a more active surface available for lithium insertion, which should facilitate faster lithium diffusion owing to their shorter pathways. In the case of TiO_2 (B) or TiO_2 nanoparticles and nanowires, even though the first reversible capacity was >200 mAh/g, the capacity retention was below 50% at a 5 C rate.[9,10] On the other hand, $Li_4Ti_5O_{12}$ nanoparticles revealed 70% capacity retention at a 10 C rate, but no information was provided on particle size or Brunauer-Emmett-Teller (BET) surface area.[11] Haung et al. reported that Ag-doped $Li_4Ti_5O_{12}$ particles showed ~165 mAh/g between 2 and 1 V at a 0.1 C rate but showed a rapid decrease in capacity to ~100 mAh/g at 4 C rate cycling.[12] Sosensen et al. prepared macroporous $Li_4Ti_5O_{12}$ spinel using a polymer template method with a different pore volume fraction, and the first discharge capacity was 167 mAh/g at 0.0625 mA/cm^2 (=0.12 C), but the capacity faded to 155 mAh/g at 0.63 mA/cm^2.[13] On the other hand, a thin film-type nanocrystalline spinel with a thickness of 2–6 μm showed an excellent rate capability compared to the composite spinels, out to a 250 C rate.[14]

Until now, many studies have focused on improving the high rate characteristics by pursuing zero and 1D TiO_2 particles, rods, and wires,[15-20] but a $Li_4Ti_5O_{12}$ spinel with a 1D nanostructure is rare. Even though Li et al. reported a spinel nanowire by ion-exchange with lithium, followed by firing at 500°C, the capacity retention at only 1 C, compared with 0.2 C, was 70%.[21] In this study, we report the large quantity synthesis of 1D-$Li_4Ti_5O_{12}$ nanowires, which have an exceptionally high capacity retention of 93% even at 10 C (6 min for lithium intercalation) rate cycling, and hence is expected be more suitable for Li-ion batteries for high rate applications.

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Experimental

$TiO_2 \cdot 1.25H_2O$ nanowires were prepared by using commercially available rutile TiO_2 powders (99.9%, Junsei Chem.) with a primary particle size of 1 μm. Ten grams of TiO_2 powders were mixed with 140 mL of 10 M NaOH solution, and sonicated for 30 min, followed by treating the mixture at 150°C in a Teflon-lined autoclave for 24 h. After the treatment, the powders were filtered and washed with a 0.2 M HNO_3 solution for 30 min at pH 2. The final product was oven dried at 100°C. For preparing spinel $Li_4Ti_5O_{12}$ nanorods, 6 g of TiO_2 nanowires were vigorously mixed with 70 mL of ethanol in which 8 g of lithium acetate was previously dissolved. Finally, the solution was oven dried at 100°C. The dried powders were fired at 800°C for 3 h and quenched to room temperature. To prepare fine spinel powder, rutile TiO_2 (average particle size was 0.3 μm) and Li acetate was thoroughly mixed in the 60 mL of ethanol solvent and dried at 100°C for 7 h. The dried product was heated at 800°C for 3 h, followed by slow cooling to room temperature.

High-resolution transmission electron microscopy (HRTEM) samples were prepared by the evaporation of the nanowires in acetone or hexane on carbon-coated copper grids. The field-emission electron microscope was a JEOL 2000F operating at 200 kV. Powder X-ray diffraction measurements were carried out using a Rigaku DMax/2000PC with a Cu-target tube. The nitrogen adsorption isotherms were obtained with Micrometrics ASAP 2020 system, and the samples were degassed for 24 h at 150°C before the measurements.

The cathodes for the battery test cells were made of the nanowires materials, Super P carbon black, and polyvinylidene fluoride (PVDF) binder (Solef) in a weight ratio of 90:5:5. The slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone (NMP) (Aldrich) solution of PVDF, carbon black, and the cathode material. The coin-type half cells (2016R size), prepared in a helium-filled glove box, contained a cathode, a Li metal anode, a microporous polyethylene separator, and an electrolyte solution of 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %) (Cheil Industries, Korea).

Results and Discussion

Figure 1 shows the XRD patterns of $TiO_2 \cdot 1.25H_2O$ and $Li_4Ti_5O_{12}$ nanowires compared with fine powders prepared from rutile TiO_2 and Li acetate at 800°C for 5 h. Our $TiO_2 \cdot 1.25H_2O$ sample is neither rutile nor anatase TiO_2 phases. However, the XRD pattern of the $TiO_2 \cdot 1.25H_2O$ phase was identical to that reported by Lan et al.[22] XRD patterns of the $TiO_2 \cdot 1.25H_2O$ phase is similar to those of alkali or hydrate titanates, which possess monoclinic phase (*C*2/*m*).[23,24] The spinel nanowires had a lattice constant of a = 8.3546(2) Å with a space group of *Fd*3*m*. Figure 2 shows scan-

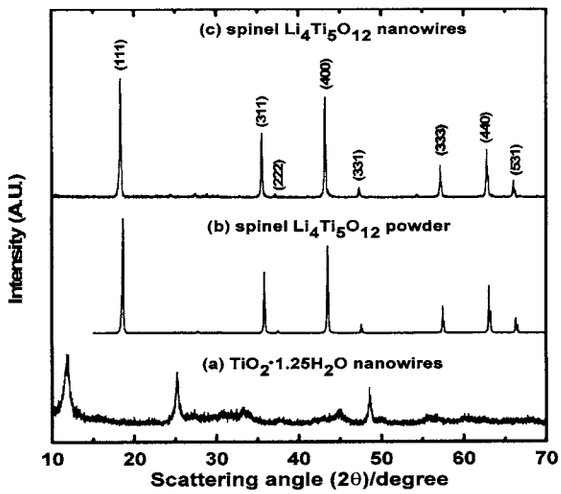

Figure 1. XRD patterns of $TiO_2 \cdot 1.25H_2O$ nanowires, fine powders, and $Li_4Ti_5O_{12}$ nanowires.

ning electron microscopy (SEM) and TEM images of the $TiO_2 \cdot 1.25H_2O$ (Fig. 2a and b and $Li_4Ti_5O_{12}$ nanowires (Fig. 2c-e), and it can be seen that the initial morphology was maintained (~150 nm diam) even after the lithium reaction. In addition, the TEM image of expanded spinel nanowires clearly shows the lattice image of the {111} plane, corresponding to a *d* spacing distance 0.48 nm (Fig. 2e). Preservation of original $TiO_2 \cdot 1.25H_2O$ morphology even after 800°C heating is believed to be related with sample preparation method. In our case, the mixture of $TiO_2 \cdot 1.25H_2O$ and Li precursor was heated to 800°C within 1 h and maintained at this temperature for 3 h, followed by quenching it to room temperature. Upon prolonged annealing beyond 3 h at 800°C, the nanowire morphology was found to be almost disappeared.

The BET surface area of the spinel nanowires was 38 m^2/g, but that of the ultrafine $Li_4Ti_5O_{12}$ powders (particle size was ~0.7 μm) prepared using TiO_2 nanoparticles using the same synthesis method was only 4.6 m^2/g. The nitrogen adsorption and desorption isotherm of the nanowires showed a typical hysteresis for the nanowires with an absence of pores, demonstrating the formation of a nanostructured material with an enhanced surface area (Fig. 3)

The highlight of the $Li_4Ti_5O_{12}$ nanowires was their electrochemical properties at high rates. In particular, they possessed an especially high rate capability because the BET surface area was 7–8 times higher than the fine powder due to the remarkably enhanced lithium-ion reaction sites. Figure 4a shows the voltage profiles of the spinel nanowires between 1 and 2.5 V at a rate of 0.1 C (=16 mA/g). The reversible first discharge capacity was 165 mAh/g, and no capacity fading was observed out to 30 cycles. Figure 4b shows rate capabilities of the sample between 1 and 2.5 V at rates of 0.5, 1, 5, and 10 C with a fixed charge rate of 0.1 C. The first capacity at 0.5 C was identical to that at 0.1 C, but there was a slow capacity fading with increasing current. At 5 and 10 C (=1600 mA/g) rates, the capacity retention was 95 and 93%, showing 157 and 155 mAh/g, respectively. This result was comparable with TiO_2-B and TiO_2 nanomaterials, which also showed excellent

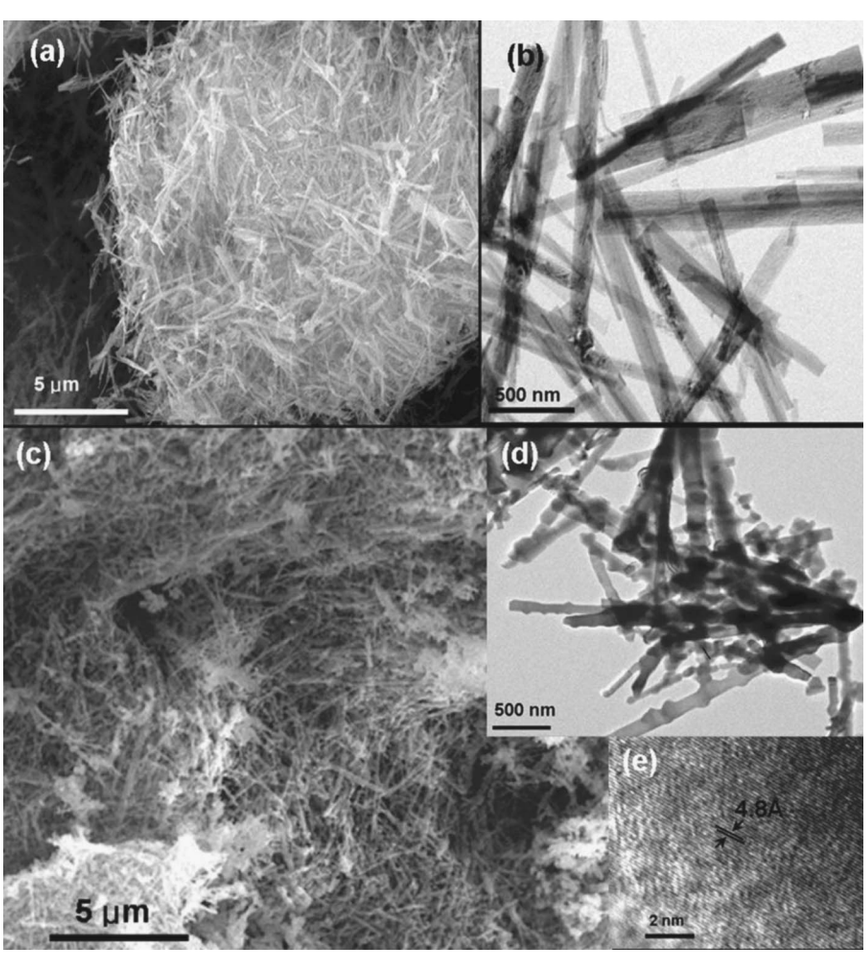

Figure 2. (a) SEM and (b) TEM images of $TiO_2 \cdot 1.25H_2O$ nanowires. (c) SEM and (d) TEM images of $Li_4Ti_5O_{12}$ nanowires. (e) High-resolution TEM image of the $Li_4Ti_5O_{12}$ nanowires shown in (d).

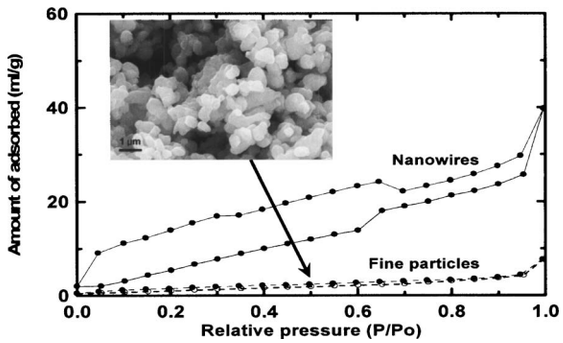

Figure 3. Nitrogen adsorption-desorption isotherms of $Li_4Ti_5O_{12}$ nanowires and fine particles. The samples were outgassed overnight at 150°C prior to analysis. Inset: An SEM image of the fine $Li_4Ti_5O_{12}$ particles.

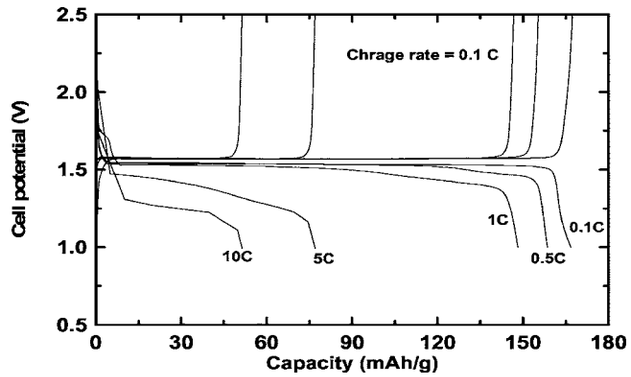

Figure 5. Rate capability test of the ultrafine $Li_4Ti_5O_{12}$ particles at different C rates (0.5, 1, 5, and 10 C). The charge rate was fixed at 0.1 C (=16 mA/g).

capacity retention at higher C rates.[9,10] Li et al. reported that hydrothermally lithium ion exchanged lithium titantate nanowires has the diameter of ~80–100 nm.[21] However, even after annealing at 500°C, its original wire diameter appears to be almost preserved, showing ~100 nm. The BET surface area of the lithium titanate nanowires prepared at 120°C was 126.7 g/m^2, but its value after annealing at 500°C was not provided. Thus, we cannot find any direct comparison of our result with Li's work. However, slow potential drop at the end of discharge is quite different to the spinel prepared above 800°C like ours that shows the rapid potential drop.

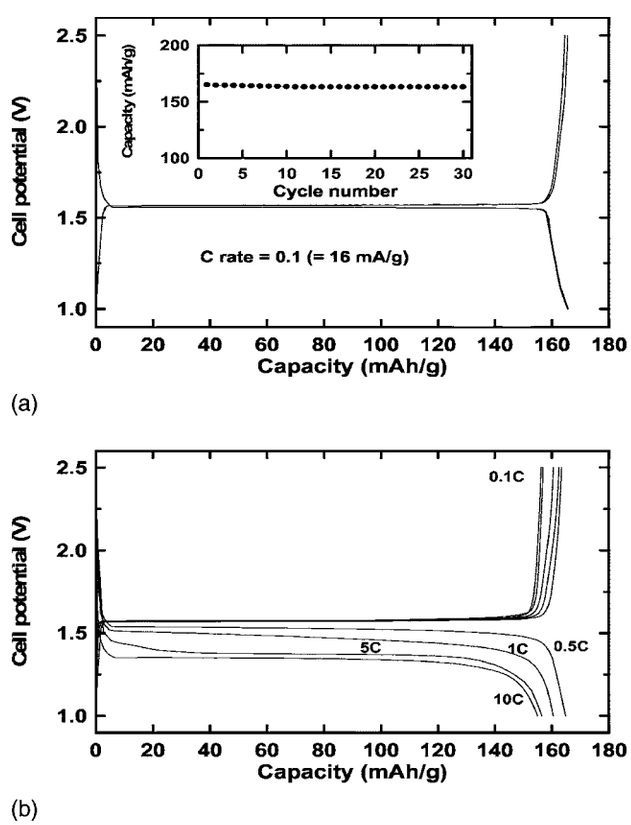

Figure 4. Voltage profiles of (a) $Li_4Ti_5O_{12}$ nanowires in a coin-type half cell and discharge capacity as a function of cycle number and (b) rate capability test of the $Li_4Ti_5O_{12}$ nanowires at different C rates (0.5, 1, 5 and 10 C). The charge rate was fixed at 0.1 C (=16 mA/g).

This phenomenon may be related to the partial structural disorder due to the low temperature annealing, resulting in decreased rate capability, compared with our result.

For comparison, fine $Li_4Ti_5O_{12}$ particles (average particle size was 0.7 μm) with a BET surface area of 4.6 m^2/g were also prepared, incorporated into an identical composite electrode, and cycled under identical condition to that of the nanowires (Fig. 5). Unlike the wires, the particles exhibited rapid capacity fading at higher C rates, with only 77 and 51 mAh/g at 5 and 10 C rates, respectively. The result was far inferior to that of the nanorods, and the capacity retention of the ultrafine particles decreased by 49% and 59% at 5 and 10 C rates, respectively, compared to the nanowires. The electrode density of the spinel nanorods was 2.8 g/cm^3 while that of the ultrafine particles was 1.5 g/cm^3, and therefore the volumetric density of the nanorods and the ultrafine particles were estimated to be 464 and 250 mAh/cm^3, respectively. Finally, we prepared spinel nanoparticles according to the synthetic procedure reported by Kavan et al.,[14] but, due to an excessively high BET surface area, over 20 wt % binder and 20 wt % carbon black were required. This meant a large decrease in electrode density, and only 1 g/cm^3 was obtained, which is 2.8 times smaller than the nanowires.

In conclusion, the large scale production of one-dimensional $Li_4Ti_5O_{12}$ nanowires was achieved by firing a mixture of Li acetate and TiO_2 nanowires. The spinel nanowires demonstrated superior rate capability even at a 10 C rate, and unlike other nanostructure materials, they retained over 93% capacity.

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