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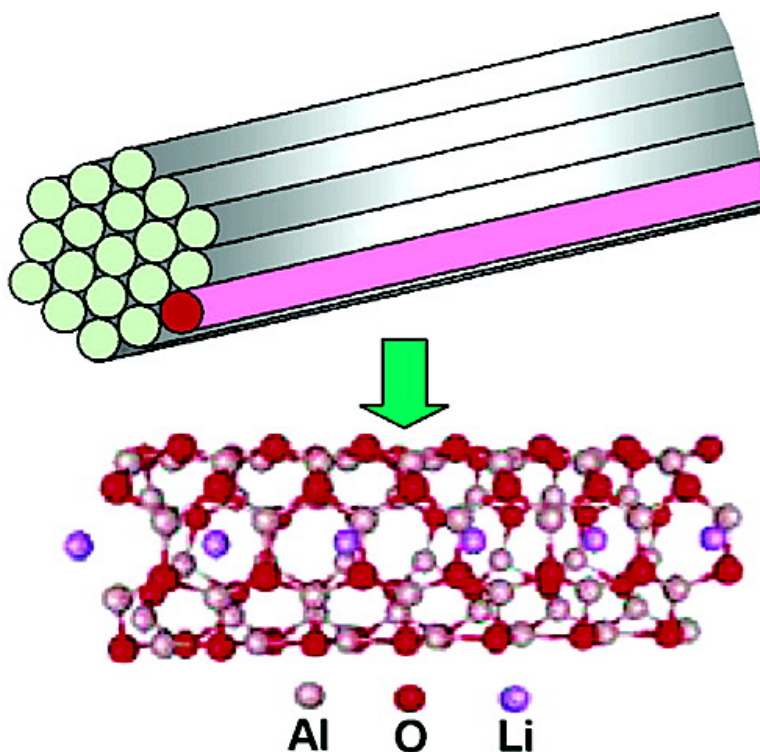
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Alumina Nanotubes Containing Lithium of High Ion Mobility

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The synthesis of nanostructured alumina by the surfactant-templating method is difficult relative to that of silica or titania because hydrolysis rates of alumina precursors (aluminum alkoxides) are too fast.[1] Only the electrochemical anodizing method is known to produce individual and branchy alumina nanotubes.[2] Recently, we reported a general method to synthesize unidirectional alumina nanostructures (nanotubes, nanofibers, and nanorods).[3] The method is a modified surfactant-templating hydrothermal process without the addition of any organic solvents. This synthetic method has been extended in the present Communication to produce crystalline lithium-containing alumina nanotubes, denoted as P-ANT-Li (POSTECH-alumina nanotube containing lithium), and is the first example of the synthesis of thermally stable, crystalline lithium aluminate nanotubes based on the molecular self-assembly of a surfactant and inorganic precursors. The obtained nanotube has an interesting structure unknown thus far for oxide nanotubes: cylindrical bundles (3.6–6.9 nm in diameter and 100–400 nm in length) of lithium aluminate subnanotubules with diameters of 4.8–6.9 Å. These novel nanotubules had walls of crystalline α-LiAlO$_2$ with a honeycomblike Al–O wall-network surrounding a central lithium core that forms a linear array of atoms. The Li ions in this material appeared to be highly mobile at moderate conditions, and thus the material could be a promising candidate as a solid ionic conductor.

The powder X-ray diffraction (XRD) patterns and a low-magnification TEM image for a P-ANT-Li sample, after removal of surfactant by calcination, are displayed in Figure 1.

As a reference, bulk α-LiAlO$_2$ material was prepared by the conventional sol–gel method.[4] The materials show mainly the well-crystallized structure of α-LiAlO$_2$ (Figure 1a, b, and c), a trigonal system (space group $R3m$, subdivision of hexagonal), with three-fold axes along the z-direction. Thus, the sample consists of three-fold coordinated Al–O atoms arranged in a honeycomb network but not in a plane. In this structure, there is no direct interaction between this Al–O lattice and lithium. When the temperature of calcination was increased up to 1273 K, the XRD pattern of P-ANT-Li shows a mixture of the γ-LiAlO$_2$ phase with a nonplanar Li–O–Al hexagonal network of a highly crystalline tetragonal phase of space group $P4_12_12$ and the trigonal α-LiAlO$_2$ phase still remaining (Figure 1d). In TEM images (Figure 1e and f), samples prepared with the surfactant (P-ANT-Li) showed a characteristic fibrous morphology, completely different from the morphology of bulk α-LiAlO$_2$ prepared from the sol–gel method, although both samples showed similar XRD patterns.
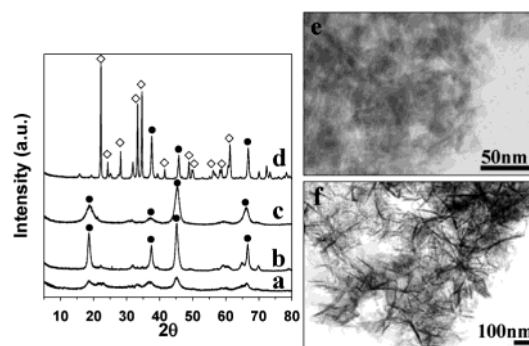
Figure 1. X-ray powder diffraction patterns and TEM images of P-ANT-Li and bulk α-LiAlO$_2$. (a) P-ANT-Li (calcined at 773 K), (b) P-ANT-Li (calcined at 1023 K), (c) bulk α-LiAlO$_2$ (calcined at 773 K), (d) P-ANT-Li (calcined at 1273 K), (●, α-LiAlO$_2$; ◇, γ-LiAlO$_2$), (e) TEM image for bulk α-LiAlO$_2$ (calcined at 773 K), (f) TEM image for P-ANT-Li (calcined at 773 K).
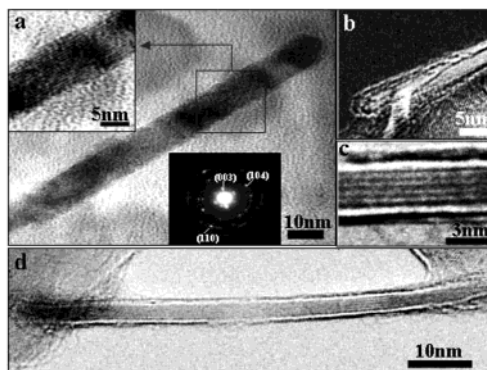
Figure 2. High-resolution TEM images of P-ANT-Li after calcination. (a) P-ANT-Li (calcined at 773 K). Note the fringes due to lithium aluminate tubules of ca. 6.9 Å diameter. (b) The end of a bundle showing many tubules forming the bundle. (c, d) P-ANT-Li (calcined at 1273 K). Now the fringes show a periodicity of 5.4 Å.

The morphology of P-ANT-Li was further characterized using field emission high-resolution transmission electron microscopy (FE-HREM). The P-ANT-Li shows a well-defined tubular structure (Figure 2) with 3.6–6.9 nm diameter and 100–400 nm length. The SAED diffraction (Figure 2a, inset) shows a spot pattern superimposed with a diffuse ring pattern. The single crystal-like spot pattern belongs to hexagonally connected Al, O, and Li networks corresponding to α-LiAlO$_2$. The dark field TEM image corresponding to the spot pattern clearly shows a tubular shape, indicating that the tubes have crystalline walls with α-LiAlO$_2$ structure (see Supporting Information). High-resolution TEM images show that P-ANT-Li is composed of equally spaced fringes without empty cores. The end of a tube in Figure 2b shows actually a bundle of

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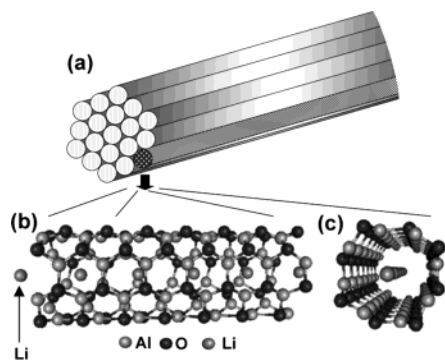
Figure 3. Schematic representation and simulated molecular structure of P-ANT-Li. A bundle (a) is composed of subnanotubules (b, c), whose central lithium core is made of a single-atom array surrounded by an Al–O subnanotube forming overall the lithium aluminate structure.

subnano-size tubules. There was no cap at the end, unlike those of nanotubes of other materials.[5] Hence, unlike most CNTs, there would be no need for a postsynthetic decapping process to utilize the inner space of the nanotubes. A schematic drawing of a bundle is shown in Figure 3a. The overall shape looks like an individual tube, but it is actually a bundle composed of α-LiAlO₂ subnanotubules. Based on XRD patterns of Figure 1b and c, a simulated structure of a single subnanotubule was obtained by energy minimization. As shown in Figure 3b and c, an Al–O wall of a honeycomblike network surrounds a central lithium core that forms a linear array of atoms.

Overall, this bundle of tubules has a lithium aluminate structure in agreement with the XRD patterns and TEM images. This type of well-defined bundles of small tubes has been reported only for carbon nanotubes prepared by an electric-arc technique.[5]

Under conditions employed here to make P-ANT-Li (see Supporting Information), a lamellar liquid-phase crystal phase (L_α) is expected to be formed according to the known phase diagram of the surfactant (CTAB)/water system.[6] It has been established by both theoretical and experimental studies that materials forming a stable layered structure have the potential to form a nanotubular structure.[7-9] The formation of α-lithium aluminate nanotubules in P-ANT-Li might also be related to the layered structure of bulk α-lithium aluminate. At any rate, our procedure of surfactant-driven hydrothermal synthesis provides a single-step, low-temperature route to bundles of lithium aluminate subnanotubules with thermal stability (<1023 K). Thus, it would also allow an easy scale-up unlike rather exotic synthetic methods used to prepare other nanotubes including CNTs.

The characteristics of the lithium ions were investigated by means of ^{7}Li NMR. The fresh P-ANT-Li showed a superposition of the broad and narrow Lorentzian ^{7}Li NMR line shapes (Figure 4a). However, we could remove the narrow line shape by simple evacuation at room temperature leaving only the single broad ^{7}Li NMR line (Figure 4b). Furthermore, one could obtain the same single narrow ^{7}Li MAS NMR spectrum before and after evacuation with a 6 kHz spinning rate (see Supporting Information), suggesting that all lithium ions are in a chemically similar environment in P-ANT-Li. Also, the isotropic chemical shift was found to be independent of temperature with a value of −2 ppm (in reference to a saturated aqueous LiCl solution), which corresponds to cationic Li⁺ ions. From these results, one could conclude that the narrow ^{7}Li NMR peak represents mobile Li⁺ ions inside the nanotube and the broad symmetric peak may be due to the distribution of electric
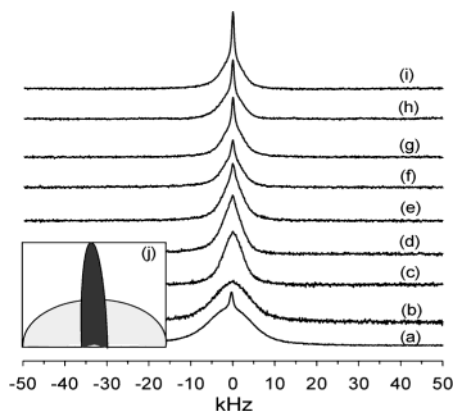
Figure 4. ^{7}Li NMR spectra of P-ANT-Li at various conditions. (a) Fresh sample (calcined at 773 K), (b) after evacuation at 10^{-5} Torr and room temperature, (c) cooling temperature to 223 K, (d) increasing temperature to 253 K, (e) 273 K, (f) 283 K, (g) 303 K, (h) 323 K, (i) 373 K, (j) schematic representation of two types of Li ion mobility.

field gradients associated with quadrupolar interaction between randomly distributed Li and a large number of other nuclei (e.g., ^{27}Al and ^{17}O) outside of the nanotubes.

After evacuation at room temperature, the temperature dependence of the ^{7}Li NMR spectra was followed. The intensity of the narrow NMR line gradually increases, while the broad line decreases with increasing temperatures (Figure 4c−i). The initial state of the lithium distribution was almost recovered by heating the spectra to 283−303 K. The ^{7}Li nuclear spin−lattice relaxation (NSLR) experiment clearly showed the presence of two types of Li motion in P-ANT-Li that give different line shapes as shown in Figure 4j. The fast-relaxing component (the narrow line in static) could be attributed to the mobile Li ion with an estimated T_1 of 0.01 s, while T_1 of the slow component (the broad line in static) was 6.51 s. The successful removal of the narrow ^{7}Li NMR line by the simple evacuation and the confirmation of the mobile Li by the NSLR result demonstrate that the P-ANT-Li would be a good solid ionic conductor working at low temperatures.

Supporting Information Available: Experimental procedures; TEM images; ^{7}Li MAS NMR spectrum (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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