Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Thin Film with Inverse Hemispheric Structure

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$\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure was fabricated on a Pt/Ti/SiO₂/Si substrate by the sol-gel and dip coating method for use as an anode for 3-dimensional (3D) thin-film batteries. Polystyrene (PS) beads of 400 nm diameter were used to prepare the template for the inverse hemispheric structure. A coating solution prepared using precursor sources was dropped on the template-deposited substrates, which were then calcinated at 400 °C. The template was removed by calcination, and the inverse hemispheric structure was successfully formed by an annealing process. The cyclic performance during high-rate charge/discharge processes of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film with inverse hemispheric structure was superior to that of the flat $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film.

Key Words: Template, Inverse hemispheric structure, Sol-gel, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Thin film

Introduction

Recently, there has been an increasing demand for on-chip power sources for MEMS (Micro-Electro-Mechanical System) devices. Thin film Li-ion battery (TFLIB) is a promising candidate amongst the several choices for power sources for MEMS devices.¹⁻¹⁰ The thin film Li-ion battery fabricated using only solid-state materials by the thin film process, is a very beneficial type of battery because of its excellent safety and good rechargeability.⁶⁻⁹ However, there are also some limitations caused by the fact that TFLIB uses solid electrolyte, whose ionic conductivity is very low at low temperatures. Therefore, some researchers have suggested the use of 3-dimensional (3D) structured thin film batteries in order to obtain better properties such as higher discharge capacity and superior rate capability.¹⁻⁵ Unfortunately, most of the methods used to fabricate 3D structured TFLIB are too expensive and complicated. However, the sol-gel method used along with a removable template such as that formed with microsphere beads, is a promising process for synthesizing the 3D structured electrode because it is cheap and it easily fabricates the 3D inverse hemispheric structure.⁵

In this study, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure was fabricated by the sol-gel method using 400 nm polystyrene microsphere beads as a monolayer template. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a promising new anode material due to its low cost and good cyclic performance.¹¹⁻¹⁵ Particularly, it is a so-called zero-strain insertion material for application as a negative electrode. Thin film batteries use a solid electrolyte, therefore, the volume change of the electrode during charge and discharge can cause separation on the interfaces of the TFLIB. Since it is known that there is no volume change in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ during cycling, it is very suitable as the material for the anode of the 3D structured thin film battery. In this study, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with inverse hemispheric structure was synthesized and characterized. The macroscopic structure, crystal structure, and the electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode were investigated by SEM, XRD, and the cyclers.

Experimental

Polystyrene beads of diameter 400 nm were used to prepare the template with spontaneously ordered inverse hemispheric void spaces for the electrode. An aqueous suspension (1 wt %) of polystyrene microspheres (400 nm) was ultrasonically dispersed in deionized water, and then it was coated and dried on a Pt/Ti/SiO₂/Si substrate by the dip coating method. The solution for the thin film deposition was made by mixing precursors and solvents. The precursor materials were lithium acetylacetonate [$\text{Li}(\text{C}_5\text{H}_8\text{O}_2)$] (Aldrich, 97%) and titanium(IV) butoxide [$\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$] (Aldrich, 99%). The concentration of each precursor was controlled to adjust the ratio of Li : Ti to 4 : 5. 1-Butanol and acetic acid were used as solvents. The precursors were stirred with a magnetic stirrer for 20 min with 1-butanol, and stirred for an additional 3 h after adding the same volume of acetic acid. The concentration of the solution was controlled

Figure 1. Fabrication process of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure.

to be 0.05 M. The solution was passed through a 0.2 μm filter (Whatman) prior to use. Subsequently, it was dripped by pipette onto a template-deposited substrate and dried at room temperature. The deposited film was heat treated at 120 °C for 30 min and reheated at 400 °C, also for 30 min, to remove organic materials from the precursors and the polystyrene template. Subsequently, the film was annealed for crystallization at 500, 600, 700, and 800 °C for 1 h using a furnace in air atmosphere. All heating rates were 5 °Cmin⁻¹. Figure 1 is a schematic diagram that illustrates the fabrication of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure. A $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with flat surface was also prepared for comparison with that with the inverse hemispheric structure. The same precursor solution mentioned above was dripped on a Pt/Ti/SiO₂/Si substrate and dried at room temperature. The heat treatment following the drying was the same as for the film with the hemispheric structure.

The evaporation temperature of the polystyrene beads and the decomposition temperatures of the precursors were examined by TGA (thermogravimetric analysis, Thermogravimetry Analyzer (TG209F3)). The analysis of the phases in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films was carried out by the X-ray Diffractometer (D/MAX-RC (12 kW), Rigaku) with monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) (angle range : 10° ~ 80°, scan speed : 6° min⁻¹). The film morphology was observed by SEM (scanning electron microscopy, Philips XL30SFEG). For the electrochemical measurements, the inverse hemispheric structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film was placed in an open beaker cell containing 1M LiPF_6 in EC/DEC, a lithium foil counter and reference electrodes, which was located inside an Ar-atmosphere glove box. Charge/discharge tests were controlled with a galvanostatic test system (Wonatech, WBCS3000).

Results and Discussion

Figure 2a shows the SEM image of a template consisting of polystyrene-beads on a Pt/Ti/SiO₂/Si substrate. It appears that the polystyrene beads have been successfully dispersed and are attached to the surface of the substrate as a monolayer with a hexagonal close-packed structure. The monolayer template is a key factor for the fabrication of electrodes with uniform inverse hemispheric structure, because if the polystyrene beads had been deposited as a multilayer, the open volume formed on the template would have been connected in a zig-zag manner rather than perpendicularly. That would have made it very difficult to fill the open volume with electrolyte and thus form the opposite electrode for true 3-dimensional thin film batteries. The coated bead layer has a good adhesive property for the subsequent permeation of the precursor solution. It can be noted in the image of the template film coated by precursor solution (Fig. 2b), that the precursor solution uniformly fills the empty space between the substrate and the template layer. Therefore, it is evident that the inverse hemispheric structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ layer can be spontaneously maintained after the evaporation of the bead template.

To examine the thermal decomposition of polystyrene beads, TGA analysis was performed. The decomposition of polystyrene beads started at around 200 ~ 250 °C, and was completed before the temperature reached 400 °C. There was no gravitational change past 400 °C (not shown in the figures). Consider-

Figure 2. SEM images of (a) the template-deposited substrate; (b) the substrate after precursor solution coating; (c) the Li-Ti-O film calcinated at 400 °C for 30 min ($\times 30,000$); (d) the Li-Ti-O film calcinated at 400 °C for 30 min ($\times 10,000$).

Figure 3. XRD patterns of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes with inverse hemispheric structure.

ing this result, 400 °C was chosen as the calcination temperature for removing the polystyrene beads. Figure 2c and 2d display the SEM images of the Li-Ti-O thin film with inverse hemispheric structure after calcinations at 400 °C for 30 min. It was confirmed that the uniform inverse hemispheric structure was formed on the film on the removal of the template.

XRD analysis was used to investigate the phase of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure after annealing. Figure 3 shows the XRD patterns of the film annealed for crystallization at 500, 600, 700, and 800 °C for 1 h under air atmosphere. Stepped heat treatment was applied in all cases, using a furnace at 400 °C for 30 min for the calcinations. In the diffraction pattern of the film annealed at 500 °C, several diffraction peaks were observed. Among them, the diffraction peak located at $2\theta = 18.3^\circ$ corresponds to the (111) reflection of the typical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure. The (111) reflection becomes higher and sharper as the annealing temperature is increased to 600 °C. Although the peak indicating TiO_2 with anatase structure was also observed, it was confirmed that most of the phase of the

Figure 4. SEM images of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film annealed at (a) 500 °C; (b) 600 °C; (c) 700 °C; and (d) 800 °C, and tilted SEM images of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film annealed at 600 °C (e) $\times 75,000$; and (f) $\times 10,000$.

film annealed at 600 °C had the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure. However at higher temperatures (700 and 800 °C) the observed (111) peak of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure became less pronounced, and finally almost disappeared. The diffraction pattern of the film annealed at 800 °C matches the rutile structure of TiO_2 . This implies that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel were decomposed or changed to the TiO_2 rutile phase at 800 °C. This phase change leads to the macroscopic structural change, that is, the collapse of the inverse hemispheric structure of the electrode. This structural change is shown quite well in Figure 4. The films annealed at 500 and 600 °C acquired inverse hemispherical structures with interconnected pores after annealing (Figs 4a, 4b). The pores were highly ordered, with diameters of approximately 0.5 ~ 0.6 μm , with wall thicknesses between the pores of less than 0.1 μm . However, as annealing temperatures increased (700 °C and 800 °C), the 3-dimensional structure collapsed and finally changed to an almost flat film containing with rod-type crystals, which are probably TiO_2 particles with rutile structure (Fig. 4c, 4d). Therefore, the optimum temperature for crystallization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with inverse hemispheric structure was confirmed to be 600 °C. The tilted SEM image of the film annealed at 600 °C (Fig. 4e, 4f) demonstrate that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure was successfully fabricated at 600 °C.

The cyclic performances of the flat thin film electrode and the inverse hemispheric structured electrode were tested under high rates of charge/discharge. Basically, similar amounts of material of two different films are needed to compare the electrochemical properties. The thickness of the flat thin film electrode was ~100 nm, but it was difficult to measure the exact

Figure 5. Cyclic performances of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric and the flat film structure. (Data shows charge capacity of the sample) (a) 50 μAhcm^{-2} ; (b) 100 μAhcm^{-2}

thickness of the inverse hemispheric structured film. If we could measure the thickness of the 3-dimensional film, it would be almost impossible to know the amount of the electrode material. Thus, in this work, the test was performed with two electrodes with different structures but of similar discharge capacities. The annealing temperature for both samples was 600 °C and the current densities for cycling were 50 μAhcm^{-2} and 100 μAhcm^{-2} in the voltage range of 2.5 - 1.0 V. Because of the very small thicknesses, the current densities can be considered high enough to test rate capability, and cyclic performance under that condition. As shown in Figure 5, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film with inverse hemispheric structure displayed better cyclic performance than the flat film electrode. Figure 6 displays charge profile of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric and the flat film structure at the current density of 100 μAhcm^{-2} . The rapid capacity fading was observed in the flat $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film. However the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure showed stable charge capacity during cycling. This is likely due to the larger reactive surface area of the film with inverse hemispheric structure. Its extended surface area would facilitate access to the electrolyte as well as lithium diffusion during the charge/discharge process, which would enhance the rate capability of the

Figure 6. Charge profiles of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin films at the current density of $100 \mu\text{Ahcm}^{-2}$ (a) flat film structure; (b) inverse hemispheric structure.

electrode and offer good stability during cycling under high charge/discharge rates. In contrast, the flat $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film did not have enough rate capability to react satisfactorily at high charge/discharge rates. Generally, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film has stable cycle life. However, the flat $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film showed rapid capacity drop under high rate conditions due to the damage caused by the high cycling process.¹⁶

Figure 7 displays the SEM image of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film with inverse hemispheric structure after 50 cycles at the current rate of $100 \mu\text{Ahcm}^{-2}$. The inverse hemispheric structure of the film was not changed after 50 high-rate charge/discharge cycles. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a zero-strain insertion material, so the 3-dimensional structure was stable and sustained itself during cycling. This is a very desirable property of the thin film electrode because the thin film battery uses a solid electrolyte. As mentioned earlier, if the volume or the structure of the electrode changes, the interface between the electrode and the solid electrolyte will separate leading to fatal performance degradation of the battery. The inverse hemispheric structured architecture of the film could be so delicate that careful control of the heating conditions may be required in order to achieve a stable structure. However, because of their superior properties such as good rate capability and

Figure 7. SEM images of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric after 50 high-rate charge-discharge cycles. (current rate = $100 \mu\text{Ahcm}^{-2}$)

cyclic stability which can be achieved with cheap and simple processes, thin film electrodes with inverse hemispheric structures fabricated by using polystyrene templates are quite promising.

Conclusion

A $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film electrode with inverse hemispheric structure was fabricated and assembled by the sol-gel and dip-coating method on a Pt/Ti/SiO₂/Si substrate. Polystyrene beads were used as the template to develop the ordered inverse hemispheric structure for the thin film electrode. XRD analysis showed that crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure was formed by the annealing process. The optimum annealing temperature was 600°C for the crystallization of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film with inverse hemispheric structure. The cyclic performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film with inverse hemispheric structure at high charge/discharge rates was more stable than the performance of the flat thin film electrode. The 3-dimensional macroscopic structure was perfectly sustained after 50 high-rate charge/discharge cycles. In view of these results, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film with inverse hemispheric structure synthesized by the sol-gel process is a promising candidate material for the anode of the 3 D thin film batteries.

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