

Fabrication of 3-Dimensional LiMn_2O_4 Thin Film

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3-Dimensionally ordered macroporous LiMn_2O_4 thin film was prepared by a sol-gel and dip coating method on Pt/Ti/SiO₂/Si substrate. An opal structure consisting of mono dispersed polystyrene beads (300 nm) was used as a template. After solution containing Mn and Li precursors was coated on the template-deposited substrate, the template and organic materials in the precursors was removed by calcination at 400 °C. And then the 3-dimensional LiMn_2O_4 thin film with spinel structure was fabricated by heat treatment at 700 °C. The structural and electrochemical property was investigated by XRD, SEM and charge-discharge cyclers.

Key Words: 3-D microbattery, Sol-gel, Template, LiMn_2O_4 , Thin film

Introduction

The miniaturization of electrical, mechanical, and optical systems using microelectromechanical system (MEMS) technologies has provided systems and devices with a total volume on the order of at most a few tens of μm^3 . These MEMS systems and devices need similarly miniaturized power sources. The 3 dimensional thin film micro-battery has considered promising candidate as power source for MEMS devices.¹⁻⁴ The miniaturization of three-dimensional architectures of electrodes is the prospect of achieving high power density from maintaining a short ion diffusion length between anode and cathode.¹ Moreover, it is clear that macroporous structure of electrodes offer improved charge-discharge kinetics owing to their huge surface area for faradaic reaction, as well as the added freedom for volume change that accompanies lithium-ion intercalation and deintercalation.^{1,5}

One of the most critical processes for 3-dimensional battery design is fabrication of periodically ordered macroporous structure of electrode material. The open volume of macroporous structure is available to be filled with a second phase, for example an infiltrated electrolyte or even an opposing electrode structure forming a true 3-dimensional battery assembly. Herein, we fabricated LiMn_2O_4 thin film with 3-dimensionally ordered macroporous structure as a cathode for 3-dimensional micro-battery. Various deposition techniques such as CVD, RF-sputtering, PLD, and sol-gel have been used to fabricate three-dimensional architecture.⁶⁻⁹ In this work, polystyrene microsphere beads were used as a template to form 3-dimensional structure, and sol-gel method was adopted to prepare LiMn_2O_4 thin film. The electrochemical and structural property of 3 dimensional LiMn_2O_4 -electrode was investigated using cyclers, SEM and XRD.

Experimental

A polystyrene template was used to develop the ordered macroporous network for the electrode. An aqueous suspension (1 wt%) of polystyrene microspheres (300 nm) was ultra-

sonically dispersed in deionized water, and then they was coated and dried on a Pt/Ti/SiO₂/Si substrate by dip coating method. The sol for the thin film deposition was made by mixing precursors and solvents. The precursor materials were manganese(III) acetylacetonate [$\text{Mn}(\text{CH}_3\text{CO}-\text{CHCOCH}_3)_3$] and lithium acetylacetonate [$\text{LiCH}_3\text{CO}-\text{CHCOCH}_3$]. Each precursor concentration was controlled to adjust the ratio of Li : Mn = 1 : 2. 1-Butanol and acetic acid was used as solvents. The solution (0.4 M) was stirred with a magnetic stirrer for 10h, and passed through a 0.2 μm filter prior to use. Subsequently it was dripped by pipet onto template-deposited substrate and dried at room temperature. The deposited film was calcinated at 400 °C for 30 min to remove polystyrene template and organic materials of precursors. And then the film was annealed at 700 °C for 10 min, 30 min, and 60 min using a furnace in air condition for crystallization.

The analysis of the phases in the films was carried out by X-ray diffractometer (Philips) with monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Film morphology was observed by FE-SEM. For the electrochemical measurements, the LiMn_2O_4 thin film was placed in an open beaker cell containing 1M LiClO_4 in propylene carbonate (PC), lithium foil counter and reference electrodes, and was located inside an Ar-atmosphere glove box. Charge-discharge tests were controlled with a galvanostatic test system (Wonatech).

Results and Discussion

Surface morphology and structure of 3-dimensional LiMn_2O_4 thin film. Fig. 1a shows FE-SEM images of as-deposited polystyrene template. It is presenting that polystyrene template was successfully coated as a monolayer on the substrate, which is important factor for fabricating uniform 3-dimensional thin film electrode. It seems that polystyrene beads was dispersed and attached with hexagonal close-packing structure on the surface of substrate. The template layer has a good adhesive property sufficient for the subsequent permeation of the precursor solution. In the image of template film coated by precursor solution (Fig. 1b), 3 dimensional architecture seems

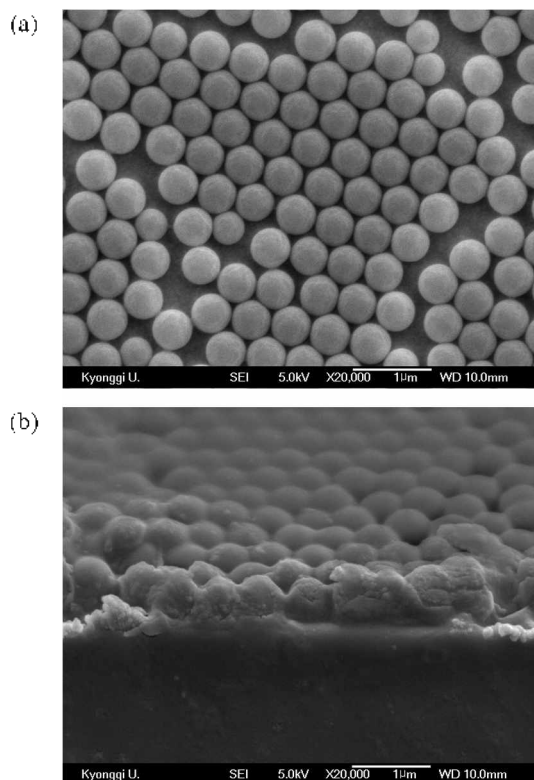


Figure 1. FE-SEM images of template-deposited substrate. (a) top view; (b) cross-sectional image after coating of precursor solution.

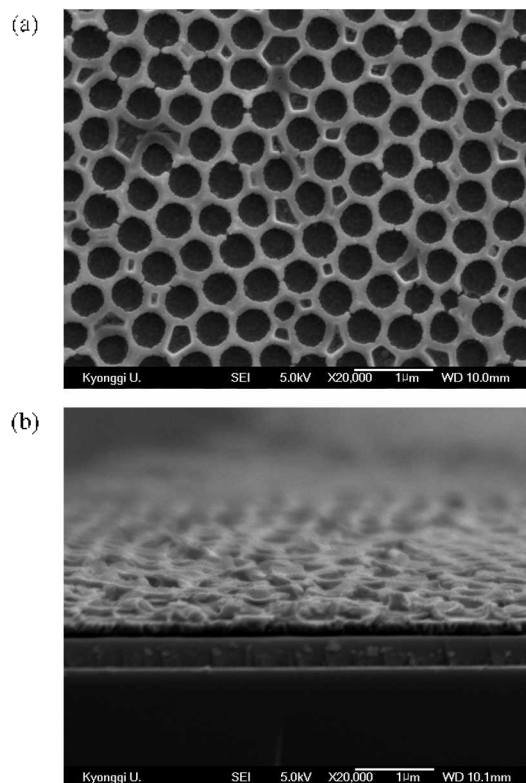


Figure 2. FE-SEM images of 3-dimensional Li-Mn-O precursor film after calcination at 400 °C for 30 min. (a) top view; (b) cross-sectional image

to be remained after Li-Mn-O film deposition. Fig. 2 displays FE-SEM images 3-dimensional thin film after calcination at 400 °C for removing template and organic materials of precursor. It is confirmed that the uniform void was formed on the film due to removing of template. 3-Dimensional macroporous film was composed of spherical voids of the inverse-opal geometry. Its interconnected wall structure can provide a continuous electronic conduction and diffusion path way of lithium ions. Moreover, high surface area of 3-dimensional electrode is readily and uniformly accessible to the electrolyte, which results in high power battery system.

The phase of 3-dimensional LiMn_2O_4 thin film after annealing was investigated by XRD analysis. Fig. 3a shows XRD patterns of precursor film calcinated at 400 °C for 30 min without annealing process. In the pattern, no diffraction peak was detected except peaks for Pt and silicon. High background indicating residual organic material, which can be formed from precursors or polystyrene template, was barely observed in the diffraction pattern. The film was annealed at 700 °C for 10 min, 30 min and 60 min in air condition, respectively, for crystallization using furnace. As shown in Fig. 3b, 3c, and 3d, several diffraction peaks was appeared, indicating crystalline was formed on annealing process. The peaks located at $2\theta = 18.64^\circ$, 36.13° , and 44.10° correspond to the (111), (311), and (400) diffraction reflections of typical spinel LiMn_2O_4 lattice (JCPDS 89-0118). The observed peaks became sharper, i.e., the crystallinity of film seems to be better, with increasing the annealing time. However, the longer annealing time may lead to weakness of adhesion of

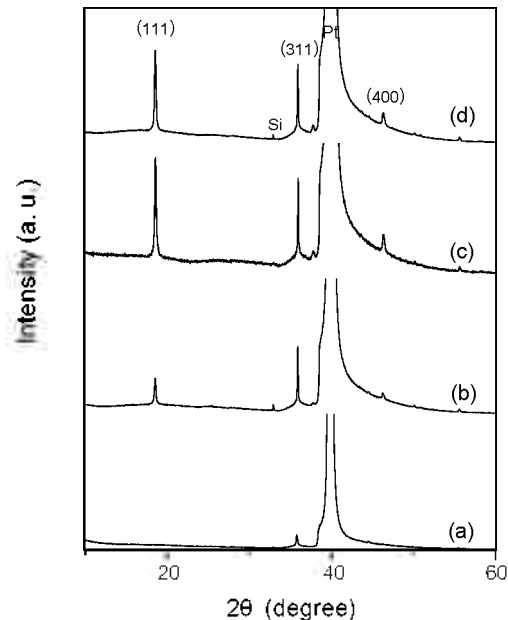


Figure 3. XRD patterns of 3-dimensional LiMn_2O_4 thin film. (a) calcinated at 400 °C for 30 min.; (b) annealed at 700 °C for 10 min. after calcinations; (c) annealed at 700 °C for 30 min. after calcinations; (d) annealed at 700 °C for 60 min. after calcinations.

3-dimensional film on the substrate. The anxiety about adhesion of 3-dimensional film was confirmed by FE-SEM image of the 3-dimensional LiMn_2O_4 thin film. Fig. 4. presents the cross-sectional images of LiMn_2O_4 thin film after annealing at 700 °C. The sample annealed for 10 min. is showing good

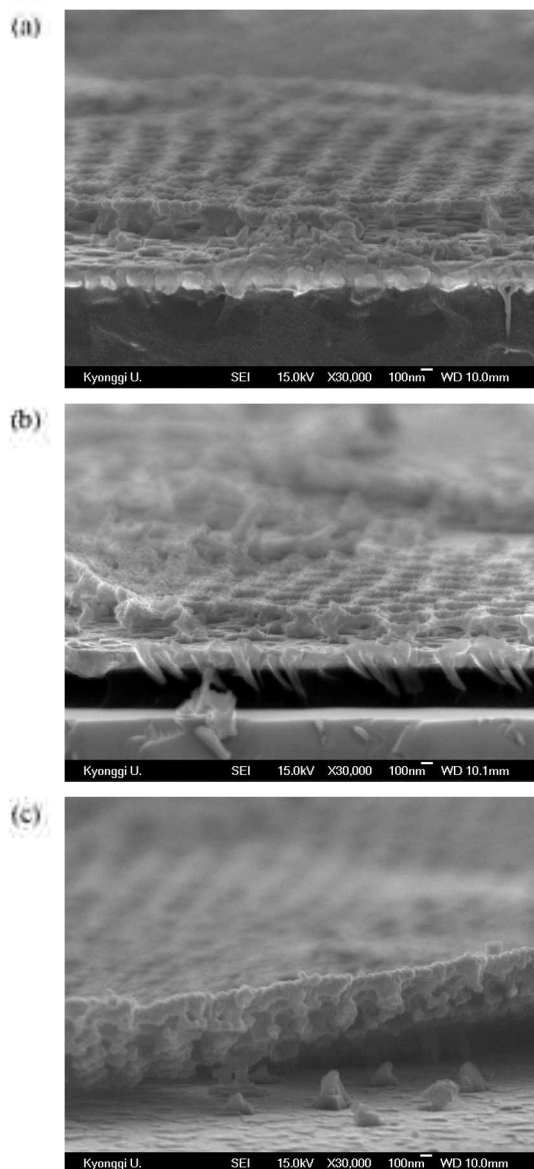


Figure 4. FE-SEM images of 3-dimensional LiMn_2O_4 thin film (cross-section). (a) annealed at 700 °C for 10 min.; (b) annealed at 700 °C for 30 min.; (c) annealed at 700 °C for 60 min.

adhesion between 3-dimensional LiMn_2O_4 thin film and substrate (Fig. 4a). However, as the increase of annealing time to 30 min. and 60 min. (Fig. 4b and 4c), the film seems to be peeled off from the substrate. The long annealing time could induce densification of film due to kinds of sintering process.

As the increase of density, the film may shrink from the initial shape, which could lead exfoliation of film from the substrate. Moreover, the difference of thermal expansion coefficient between LiMn_2O_4 film and substrate may weaken the adhesion of film on the substrate. Thus, in the annealing process using furnace system, long annealing time was not good for stable 3-dimensional architecture. This may be improved by adopting other annealing system, which can effectively form the phase of the LiMn_2O_4 film within a few minutes without sintering process, and/or other substrate with similar thermal expansion coefficient of LiMn_2O_4 film.

Electrochemical characterization of 3-dimensional LiMn_2O_4

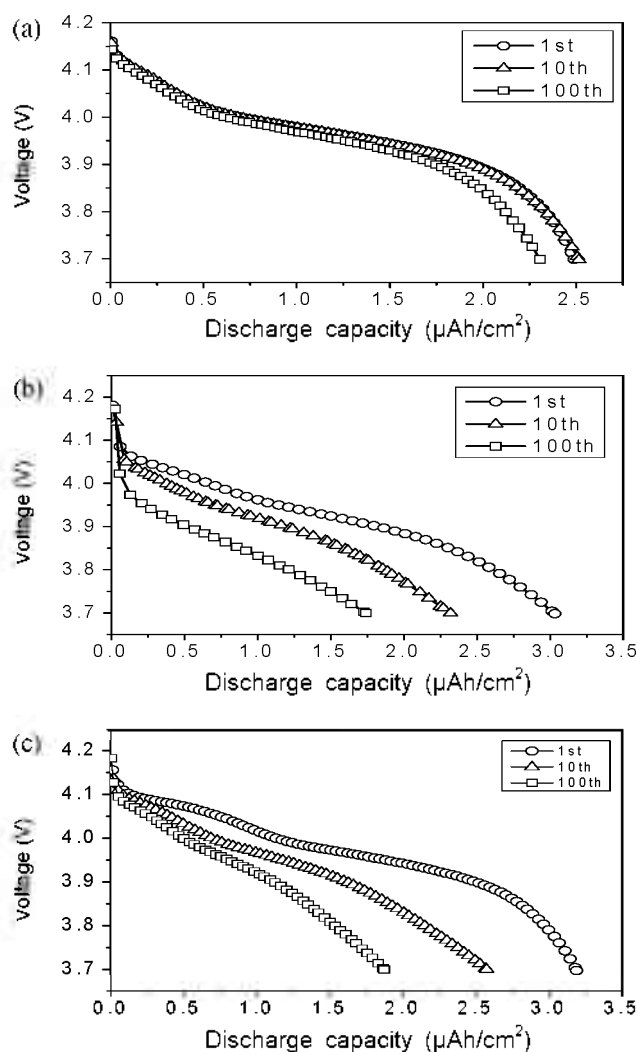


Figure 5. Discharge profiles of 3-dimensional LiMn_2O_4 thin film electrode (current density = 100 nAhcm^{-2}), (a) annealed at 700 °C for 10 min.; (b) annealed at 700 °C for 30 min.; (c) annealed at 700 °C for 60 min.

thin film electrode. Fig. 5 shows discharge curves of 3-dimensional LiMn_2O_4 thin film electrodes annealed at 700 °C for the different times. It was measured with current density of 100 nAhcm^{-2} in the voltage range of 4.3 - 3.7 V. The initial discharge capacities were 2.5 μAhcm^{-2} , 3.0 μAhcm^{-2} , and 3.3 μAhcm^{-2} for annealed 10 min, 30 min, and 60 min, respectively. The longer annealing time, the higher the initial discharge capacity of 3-dimensional LiMn_2O_4 thin film is. This is due to the better crystallinity of film annealed longer time. However, the discharge capacity of the sample annealed for 30 and 60 min. was rapidly dropped during cycling process. As shown in Fig 5b and 5c, 10th and 100th discharge profiles of the sample annealed for 30 and 60 min was markedly deteriorated when they compared with initial discharge curves. While, the sample annealed for 10 min. is showing better cycle life (Fig. 5a).

The cyclic performance of 3-dimensional LiMn_2O_4 thin film electrodes during 100 cycles was displayed in Fig. 6. The test condition is the same as mentioned in Fig. 5. The discharge capacity of the sample annealed at 700 °C for 10

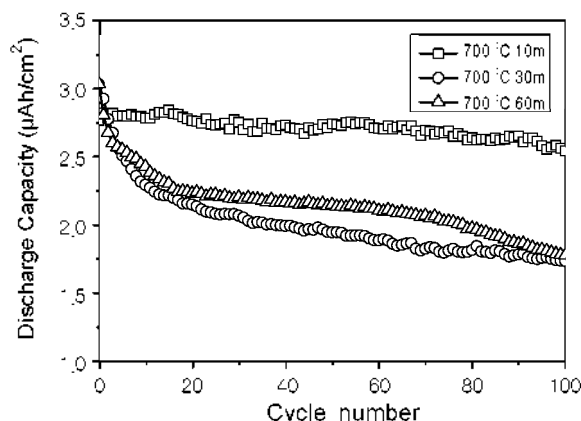


Figure 6. Cycle performance of 3-dimensional LiMn_2O_4 thin film electrode.

min was $2.76 \mu\text{Ahcm}^{-2}$ at the 1st cycle and $2.54 \mu\text{Ahcm}^{-2}$ at the 100th cycle, where the capacity retention was 92%. However, capacity retention of the sample annealed for 30 min. and 60 min presented only ~57% at the 100th cycle. It is showing that the sample annealed for 10 min. has a better cyclic performance than other samples annealed longer time. The crystallinity and initial discharge capacity of 3-dimensional LiMn_2O_4 film can be improved by increasing of annealing time. Nevertheless, the film adhesion was deteriorated due to the stress induced by the difference of thermal expansion coefficient between LiMn_2O_4 thin film and substrate, as confirmed in Fig. 4.¹⁰⁻¹² The degradation of cyclic performances of the films annealed for 30 and 60 min. is likely due to peeling off the film from the substrate during cycling process. 3-Dimensional architecture of the film may be so delicate that the careful controlling of heating condition may need to prepare stable structure. However, stable cyclic property of the film annealed for 10 min. provides a promising possibility of 3-dimensional macroporous electrode system using a polystyrene template.

Conclusion

3-Dimensional LiMn_2O_4 thin film electrode was fabricated with assemble of sol-gel and dip-coating method on Pt/Ti/SiO₂/Si substrate. A polystyrene template was used to develop

the ordered macroporous network for the electrode. The XRD analysis confirmed well-crystallized LiMn_2O_4 spinel lattice. The 3-dimensional macroporous film was composed of spherical voids of the inverse-opal geometry. And its interconnected wall structure can provide a continuous electronic conduction and diffusion path way of lithium ions. The 3-dimensional electrode annealed at 700 °C for 10 min., 30 min., and 60 min. delivered discharge capacities of $2.5 \mu\text{Ahcm}^{-2}$, $3.0 \mu\text{Ahcm}^{-2}$, and $3.3 \mu\text{Ahcm}^{-2}$, respectively. Although longer annealing time of the film seemed to deteriorate cyclic performances due to the stress induced by the difference of thermal expansion coefficient between LiMn_2O_4 thin film and substrate, the sample annealed at 700 °C for 10 min. showed stable cycle life.

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