

Three dimensionally ordered composite solid materials for all solid-state rechargeable lithium batteries

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Abstract

Three dimensionally ordered macroporous membrane of a Li-ion conductive ceramic, Li–La–Ti–O (LLT), for all solid-state rechargeable lithium battery was prepared using colloidal templating process combined with sol–gel method. An opal structure consisting of mono-dispersed polystyrene beads (470 nm in diameter) was used as a template. The preparation conditions of LLT membrane were optimized to obtain a relatively large size porous membrane. The LLT calcinated at 600 °C was amorphous, and its Li-ion conductivity was 10^{-5} S cm⁻¹ at room temperature. The composite electrodes of LLT–Li₄Ti₅O₁₂ and LLT–LiMn₂O₄ were successfully prepared by sol–gel process.

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1. Introduction

1.1. All solid-state rechargeable lithium batteries

Rechargeable lithium batteries have been widely used in various kinds of electronic devices. One of remaining problems is a safety issue of battery, especially in the course of overcharging state. This is due to flammable organic electrolyte and active cathode or anode materials. In order to realize a perfect safety even at high temperature, organic electrolyte may be replaced by solid electrolyte system. As solid electrolyte systems, polymer or ceramic electrolytes will be utilized in rechargeable lithium batteries. In fact, there are many excellent reports on all solid-state rechargeable lithium ion batteries using polymer and ceramic electrolytes [1–5]. In a sense of non-flammable electrolyte, ceramic electrolytes may have an advantage. So far, some researchers have investigated on application of ceramic solid electrolyte to rechargeable lithium batteries. However, one big problem has been claimed, that is poor contact between

solid electrolyte and active material. The poor contact increases the charge transfer resistance and cell impedance. In other words, the electrochemical interface in the electrode system used in all solid-state rechargeable lithium batteries should be enlarged to realize a high electrode performance.

1.2. Design of novel electrode system

In the present paper, a new electrode system for all solid-state rechargeable lithium battery is proposed. A three dimensionally ordered macroporous (3DOM) solid electrolyte was prepared to fabricate electrodes used in all solid-state rechargeable lithium batteries. Using 3DOM electrolyte, a new all solid-state electrode system can be prepared with a high contact area between active materials and electrolyte. This type of electrode will reduce the internal resistance of the all solid-state electrode system. First of all, 3DOM lithium conductive ceramic has to be prepared. Many kinds of lithium ion conductive materials have been proposed. Some of materials have high lithium ion conductivity (higher than 10^{-3} S cm⁻¹). In this study, lithium ion conductive oxide with perovskite structure, Li_{0.35}La_{0.55}TiO₃, was adopted as porous solid electrolyte matrix [6–8]. 3DOM matrix was

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prepared by using colloidal templating process with sol–gel process [9–13]. Three dimensionally ordered mono-dispersed spherical colloidal particles were used as a template to prepare an inverse opal structure. This is a well-known method for 3DOM materials. Composite electrodes consisting of 3DOM LLT and battery active materials such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiMn_2O_4 were also prepared via sol–gel process [14,15].

2. Materials and methods

2.1. Fabrication of 3DOM Li-ion conductive ceramic

Mono-dispersed polystyrene beads (PSB) were used as a template material to prepare 3DOM structure. The arrangement of PSB was performed by a filtration of suspension containing PSB. The filter was hydrophilic poly-tetrafluoroethylene with diameter of 18 mm and pore size of $0.1\ \mu\text{m}$ (ADVANTEC). PSB (470 nm in diameter, Seradyn Inc.) suspended in ethanol was applied to the filtration process. The PSB suspension ($2\ \text{mg mL}^{-1}$) of 20 mL was filtrated. The beads were accumulated on a filter under a small pressure difference of 5 kPa. Fig. 1 shows a scanning electron micrograph of an opal structure consists of PSBs. The opal structure has a free space between beads, which is ideally 26% in volume. The thickness of the prepared agglomerate of beads was $200\ \mu\text{m}$.

The Li–La–Ti–O (LLT) sol was put into the free space of PSB template by a filtration. The LLT sol was prepared as follows: 2-propanol, acetic acid and titanium tetraisopropoxide were mixed. Then, lithium acetate and lanthanum acetate were dissolved into water. These two solutions were mixed to be LLT sol. The molar ratio of lithium acetate, lanthanum acetate, titanium tetraisopropoxide, 2-propanol, acetic acid and water was 0.35:0.55:1:20:10:140. The prepared sol of 2 mL was filled into the void of PSB template by a filtration under a small pressure difference (2 kPa) at $40\ ^\circ\text{C}$, and the sol

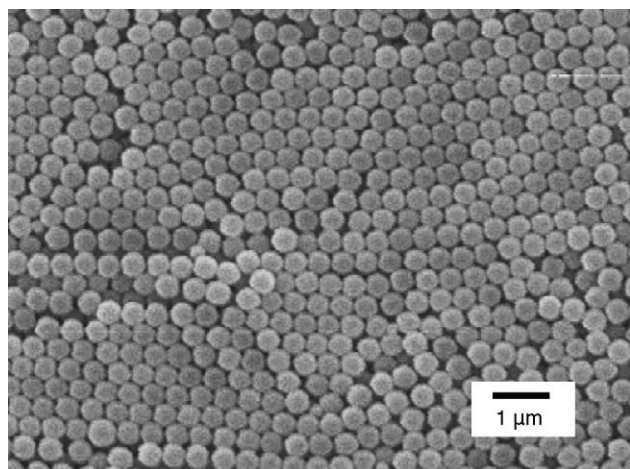


Fig. 1. SEM image of an opal structure consisting of polystyrene beads.

converted to gel simultaneously. This sol injection process was repeated four times to fill out the all free space. After the gelation, the composite membrane was removed from the filter. In order to remove PSBs, this composite was heated at $450\ ^\circ\text{C}$ in air for 1 h. Further, heat-treatment at higher temperature ($600\text{--}1200\ ^\circ\text{C}$) was conducted to improve its Li^+ ion conductivity and mechanical strength.

The prepared porous materials were observed with a scanning electron microscope (SEM, JED-2100, JEOL Co.), and analyzed with X-ray diffraction (XRD, RINT-UltimaII, Rigaku Co.). The conductivity of the porous material was measured with impedance analyzer (YP4192-A, Yokogawa). In order to measure the conductivity, silver paste was used to obtain electrical contact from the sample.

2.2. Injection of active materials into 3DOM solid electrolytes

Composite electrodes consisting of 3DOM LLT and active materials were prepared via sol–gel process. A sol of Li–Ti–O as a precursor for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared from lithium acetate, titanium tetraisopropoxide, 2-propanol and acetic acid. An optimized molar ratio of these starting compounds was 4:5:100:60 [14]. A precursor solution for LiMn_2O_4 was prepared from lithium acetate, manganese acetate, 2-propanol, acetic acid, water and poly-vinyl pyrrolidone (PVP, molecular weight: 55,000) [15]. A molar ratio of the starting material in the precursor was 1:2:40:20:50:2. The precursors were injected into the 3DOM LLT using vacuum impregnation. After gelation of the precursors, the obtained composites between 3DOM LLT and the gels were calcinated at $600\ ^\circ\text{C}$ in air for 1 h.



Fig. 2. Photograph of three dimensionally ordered macroporous Li–La–Ti–O ceramic calcinated at $600\ ^\circ\text{C}$.

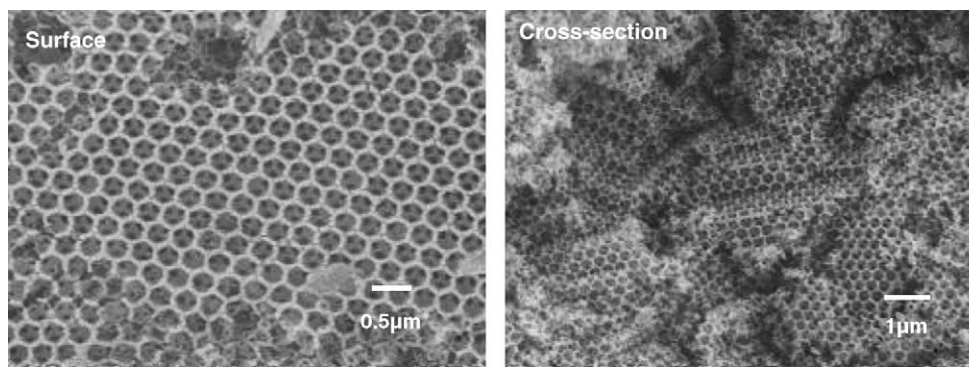


Fig. 3. SEM images of three dimensionally ordered macroporous Li-La-Ti-O ceramic calcinated at 600 °C.

3. Results and discussion

3.1. 3DOM Li-ion conductive ceramic

Fig. 2 shows the photograph of LLT porous membrane calcinated at 600 °C. The membrane size was about 5 mm and the thickness was 100 μm. During the gelation and drying of the LLT precursor, the composite membrane of PSB and LLT gel broke into small pieces because of mechanical stress and poor mechanical strength. The SEM images of 3DOM LLT were shown in Fig. 3. From these images, it was found that the prepared membrane had 3DOM structure and the pore size was about 400 nm, which was close to the size of PSB, and each pore was interconnected by small holes. An ordered macroporous structure was sustained even after heat-treatment at 600 °C. However, the 3DOM LLT calcinated at 600 °C was amorphous. In fact, no peaks were observed in the XRD pattern, as shown in Fig. 4. In general, a crystalline LLT with perovskite structure can be prepared by heat-treatment at higher than 1000 °C. However, the heat-treatment temperature higher than 700 °C decreased the ordering of pores in the membrane and weakened the mechanical strength of the macroporous LLT. The sintering of LLT at 1000 °C was carried out to crystallize the LLT, and the Bragg peaks originated from the perovskite structure were observed in the XRD pattern (not shown

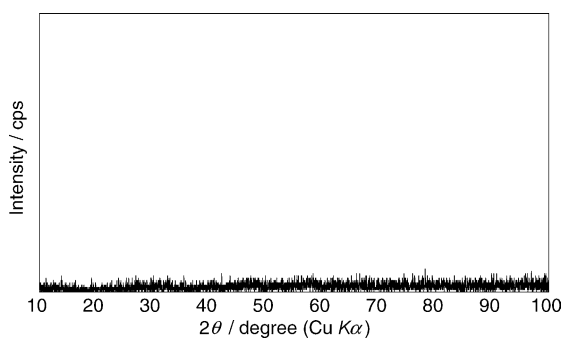


Fig. 4. XRD pattern of three dimensionally ordered macroporous Li-La-Ti-O ceramic calcinated at 600 °C.

here), although the obtained LLT was broke into tiny pieces, and the ordering structure of the pores completely vanished.

Fig. 5 shows the Cole–Cole plots of 3DOM LLT calcinated at 600 °C. From the impedance measurement, its ionic conductivity was estimated to be 10^{-5} S cm^{-1} . The conductivity was calculated based on an assumption that the porosity of the 3DOM membrane was 74%. This conductivity was lower than that of crystallized LLT reported by Inaguma and Itoh [7]. This is due to an amorphous nature of the sample. To achieve the enough high conductivity (10^{-3} S cm^{-1}) at room temperature for practical use in batteries, crystallization of the LLT membrane may be needed.

3.2. Composite of 3DOM LLT and active materials

The injections of battery active materials into the 3DOM amorphous LLT were demonstrated. The SEM images of the composites of LLT– $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LLT– LiMn_2O_4 are shown in Fig. 6(a and b), respectively. It was confirmed that both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiMn_2O_4 were injected into the pores of the membrane properly. Fig. 7 shows the XRD patterns of the composite materials. It was recognized that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiMn_2O_4 were crystallized in the pores.

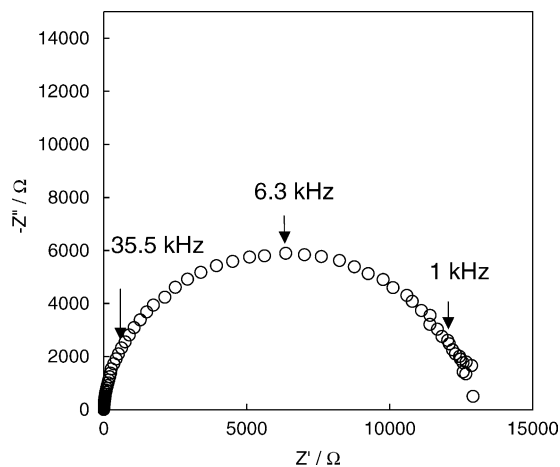


Fig. 5. Cole–Cole plot of three dimensionally ordered macroporous Li-La-Ti-O ceramic membrane prepared by calcination at 600 °C.

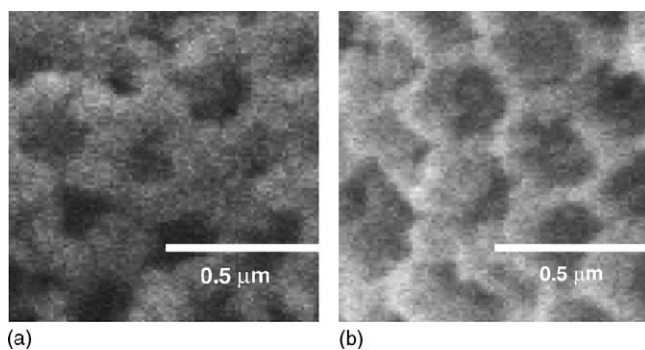


Fig. 6. SEM images of composites between LLT– $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and LLT– LiMn_2O_4 (b).

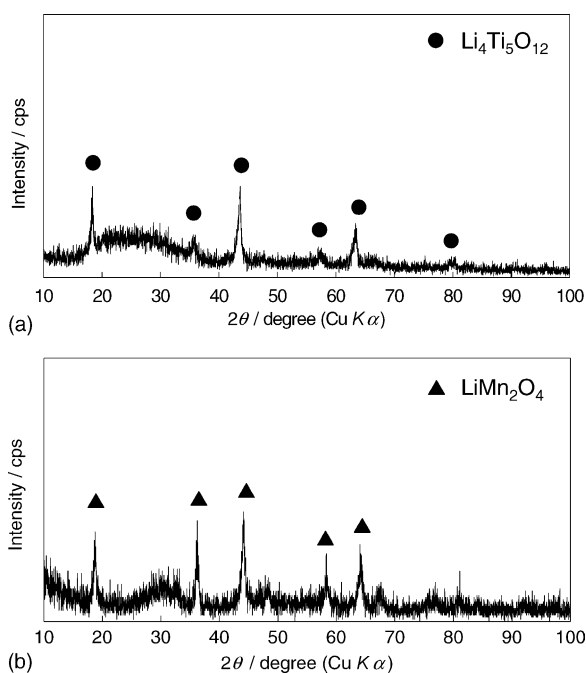


Fig. 7. XRD patterns of composites between LLT– $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) and LLT– LiMn_2O_4 (b).

4. Conclusions

A novel design of electrode system for all solid-state rechargeable lithium battery was proposed. 3DOM LLT membrane was prepared using colloidal templating process combined with sol–gel method. The preparation conditions were optimized to obtain an adequate size of the membrane for practical use. The LLT with 3DOM structure calcinated at 600°C was amorphous, and its conductivity was $10^{-5} \text{ S cm}^{-1}$ at room temperature. Further efforts are needed to prepare 3DOM solid electrolyte membrane with high conductivity. The composites of LLT– $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LLT– LiMn_2O_4 were successfully prepared by sol–gel process. The electrochemical characterizations of the composite electrodes are now underway, and it will be reported in due course.

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