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Preparation of Macroporous Li-Ion Conductor Using Colloidal Crystal Templating Method

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Introduction

All solid-state lithium batteries are attractive because of inflammability and applications for electronic devices, medical implant use, *etc.* In order to realize all solid-state lithium batteries, solid electrolytes including polymers and inorganic materials have been studied widely. The $Li_{3x}La_{2/3-x}TiO_3$ (LLT) with perovskite structure has high lithium ion conductivity at room temperature.[1] In addition to the conductivity, a controlling of interface between solid electrolyte and active material is a key issue. The increase of contact area will reduce the interfacial resistance. Three dimensionally ordered macroporous membranes can be prepared using colloidal crystal templating method. We have already reported the fabrication of amorphous LLT using sol-gel process.[2,3] However, the ionic conductivity of non-crystallized LLT was not so high (10^{-5} Scm^{-1}). In this work, the crystallized macroporous LLT was prepared and its properties were evaluated.

Experimental

Monodisperse polystyrene beads (0.47-3.00 μm in diameter) were arranged digestedly by filtration under reduced pressure. This three dimensionally ordered polystyrene was used as a template to prepare porous material. Li-La-Ti-O sol was injected into voids (free space) of ordered polystyrene particles. After drying, polystyrene/Li-La-Ti-O sol composite was obtained. This composite was gelated at 25-40 °C. Then it was heated at 450 °C to remove polystyrene beads and calcinate Li-La-Ti-O gel. Finally, it was annealed at 1000 °C to crystallize macroporous materials. The sol for Li-La-Ti-O was prepared by using CH_3COOLi, $La(CH_3COOH)_3\cdot 1.5H_2O$, $Ti(OCH(CH_3)_2)_4$, CH_3COOH, H_2O and $(CH_3)_2CHOH$, as starting compounds. The molar ratio of Li, La and Ti was 0.35:0.55:1. The prepared porous materials were characterized with SEM, XRD. The ionic conductivity was evaluated by an impedance method.

Results and Discussion

Figure 1 shows the photograph of a prepared LLT membrane. A macroporous disk shape membrane with 10 mm size (50 μm thick) was successfully fabricated. Figure 2 shows a XRD pattern of LLT membrane. It was confirmed that the prepared sample was crystallized. A SEM image of the sample is shown in Fig. 3. The porous structure of the membrane can be observed. This porous LLT was prepared by using polystyrene beads of 3 μm, however, the pore size is about 1 μm. Obviously, the pore shrunk during heat-treatment at high temperature, and three dimensionally ordered structure was not maintained. It is considered that these are caused by the grain growth and crystallization at high temperatures. Actually, the mechanical strength of the membrane was poor. The amount of injected sol might be not enough to fill up all voids of the template. Further optimizations of preparing conditions are needed. The electrochemical measurements are now underway, and these results will be also reported.

References

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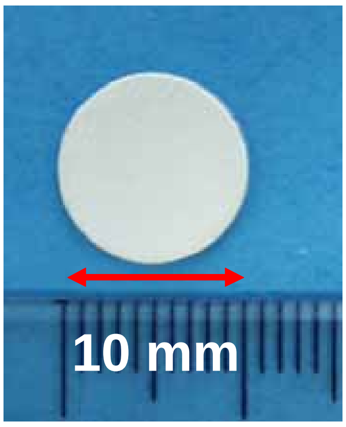

Figure1. Photograph of a $Li_{0.35}La_{0.55}TiO_3$ macroporous membrane heat-treated at 1000°C.

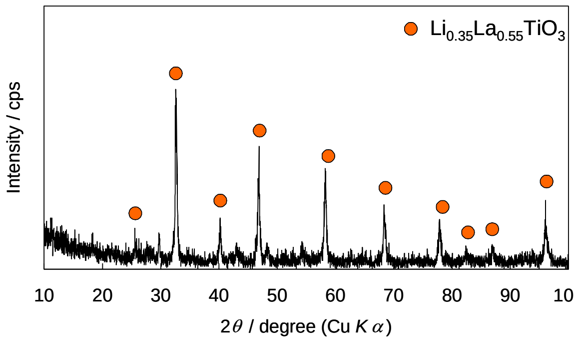

Figure 2. XRD pattern of $Li_{0.35}La_{0.55}TiO_3$ membrane heat-treated at 1000°C..

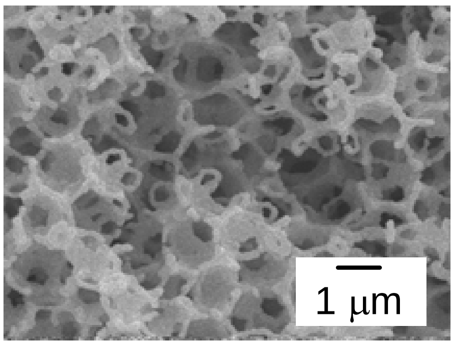

Figure 3. SEM image of $Li_{0.35}La_{0.55}TiO_3$ membrane heat-treated at 1000°C.