



Short communication

# Fabrication of all-solid-state rechargeable lithium-ion battery using mille-feuille structure of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$

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## ABSTRACT

A mille-feuille structure, which comprises both sides of dense layer are sandwiched by porous layers, is one of the promising structures for 3-dimensional (3D) all-solid-state battery. The porous layers should have 3-dimensionally ordered macroporous structure to obtain large contact area between electrolyte and electrode.  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  (LLT) solid electrolyte with the mille-feuille structure was fabricated by the suspension filtration method. The dense layer was sintered well, no grain boundary was observed. The porous layers contacted well with dense layer. Thicknesses of dense and porous layers were 30 and 26  $\mu\text{m}$ , respectively. To check compatibility of the mille-feuille LLT with all-solid-state Li ion battery, chronopotentiometry of symmetric cell with  $\text{LiMn}_2\text{O}_4$ /mille-feuille LLT/ $\text{LiMn}_2\text{O}_4$  configuration was measured. Charge and discharge currents were clearly observed, indicating that the cell was successfully operated.

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## 1. Introduction

Rechargeable lithium ion battery has been widely used in many kinds of electronic devices due to its high energy density [1]. One of the current problems should be overcome is safety issue caused by usage of flammable organic electrolytes [2]. Therefore, all-solid-state battery composed of non-flammable ceramic electrolyte has come into the spot light. However, it has been insisted so far that poor contact between solid electrolyte and solid electrode increases internal impedance of the battery and conducts to inferior performance [3].

To improve the performance of the all-solid-state battery, 3D configuration has been proposed [4]. The 3D structure can enlarge the contact area between solid electrolyte and electrode, resulting in better performance. Some of 3D structures such as honeycomb-type [3] and interdigitated array structure [5,6] have been reported so far. We have proposed a novel electrode system with three-dimensional ordered macroporous structure (3DOM) [7]. This is made up of inverse-opal structure which has quite high porosity as well as 70%. This makes us image to gain large contact area between solid electrolyte and solid electrode if the pores were filled by active material. Recently, we have succeeded on fabrication of  $\text{LiMn}_2\text{O}_4$ /3DOM  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  (LLT) electrode by a colloidal crystal templating method and a sol-gel process and the electrode demonstrated the volumetric capacity of  $220 \text{ mAh cm}^{-3}$ , which was

comparable to a volumetric capacity of  $\text{LiMn}_2\text{O}_4$  electrode used in a Li-ion battery with liquid electrolyte [8]. Additionally, we have succeeded on 2 layer configuration of LLT which is 3DOM layer on dense layer.

For application of the 3DOM electrode to practical all-solid-state battery, one of the promising structures is a mille-feuille structure which is composed of dense layer having the 3DOM layer on both sides (Fig. 1). By filling electrode material in the pores of the 3DOM layer, the all-solid-state battery can be fabricated easily. In this structure, an interface between the 3DOM and dense layers must be sintered well to reduce internal resistance. Therefore, calcination after formation of framework of the mille-feuille structure from raw material powder is thought to be better way than calcination after accumulation of each sintered layer.

In this paper, we report fabrication of a novel 3D battery with the mille-feuille structure. By using a suspension filtration method with monodispersed polystyrene and LLT powder, solid electrolyte with mille-feuille structure was successfully prepared. And compatibility of the novel 3D battery with all-solid-state Li ion battery was tested.

## 2. Experimental

$\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  (LLT) solid electrolyte powder was prepared by a sol-gel method according to our previous paper [8]. The Li-La-Ti-O sol as a precursor of LLT was prepared from  $\text{CH}_3\text{COOLi}$ ,  $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5\text{H}_2\text{O}$ ,  $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ,  $\text{CH}_3\text{COOH}$ ,  $i\text{-C}_3\text{H}_7\text{OH}$ , and  $\text{H}_2\text{O}$  in molar ratios of 0.35:0.55:1:10:20:140. The sol was dried at  $80^\circ\text{C}$  overnight and then calcined at  $450^\circ\text{C}$  for 1 h to obtain

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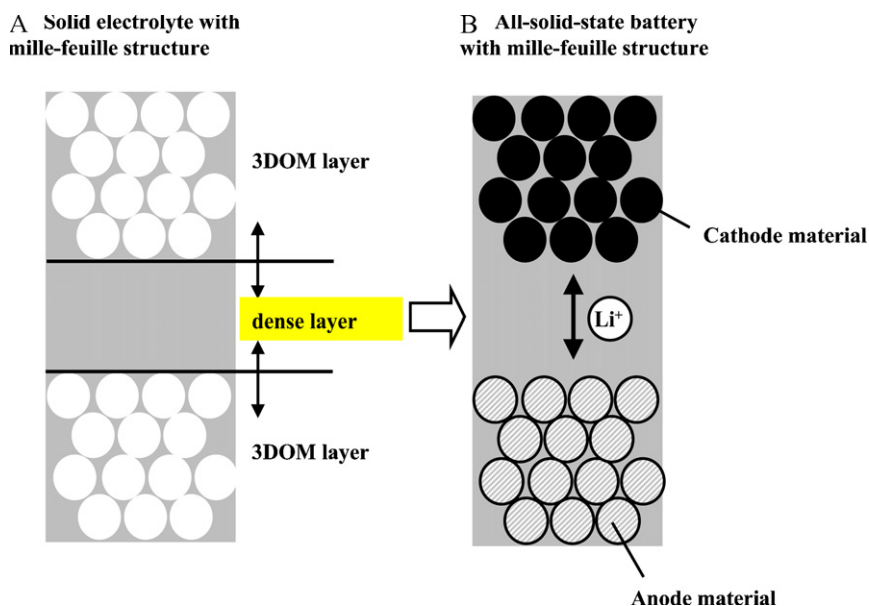
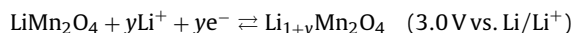
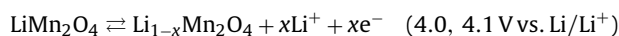


Fig. 1. Schematic illustration of a concept of all-solid-state battery with the mille-feuille structure.

amorphous LLT powder. The mille-feuille LLT was prepared by the suspension filtration method [9]. For preparation of 3DOM porous layer, an ethanol suspension composed of LLT powder and monodispersed polystyrene (PS) beads with 3  $\mu\text{m}$  in diameter (MAGSPHERE Inc.) was filtered under a small pressure difference of 5 kPa using a PTFE filter with 18 mm diameter and pore size of 100 nm (ADVANTEC). Then, LLT powder suspended in ethanol was filtered to prepare the dense layer. Finally, the suspension of LLT and PS beads was filtered again. Obtained composite membrane was calcined at 450  $^{\circ}\text{C}$  for 1 h to remove PS template and then 1100  $^{\circ}\text{C}$  for 10 h. Morphology of the mille-feuille LLT was observed by a mean of scanning electron microscope (SEM, JEOL) and crystalline phases were identified by X-ray diffraction (XRD, RINT-Ultima, Rigaku) with Cu K $\alpha$  radiation.

To evaluate the performance of the all-solid-state battery,  $\text{LiMn}_2\text{O}_4$  was filled into the pores of both 3DOM layers. Although different active materials should be filled into each 3DOM layer,  $\text{LiMn}_2\text{O}_4$  was filled into both 3DOM layers to simplify experimental procedure in this paper.

$\text{LiMn}_2\text{O}_4$  shows discharge curve with three plateaus at 3.0, 4.0, and 4.1 V vs.  $\text{Li}/\text{Li}^+$  [10,11], thus,  $\text{LiMn}_2\text{O}_4$  can work as both cathode and anode. The plateau corresponding to 4.0, and 4.1 V is due to insertion/extraction of  $\text{Li}^+$  into/from cubic spinel  $\text{LiMn}_2\text{O}_4$ , respectively. On the other hand, another plateau at 3.0 V involves a phase change between cubic and tetragonal phases. These reactions are described as below [10,11]:



Therefore, all-solid-state battery of  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  can work as the rechargeable battery and expected operation voltage is about 1.0 V.

Impregnation of  $\text{LiMn}_2\text{O}_4$  into pores of the 3DOM layer was performed by the solvent substitution method using sodium dodecyl sulfate (SDS) solution and  $\text{Li-Mn-O}$  sol [8]. The  $\text{Li-Mn-O}$  sol as a precursor of  $\text{LiMn}_2\text{O}_4$  was prepared from  $\text{CH}_3\text{COOLi}$ ,

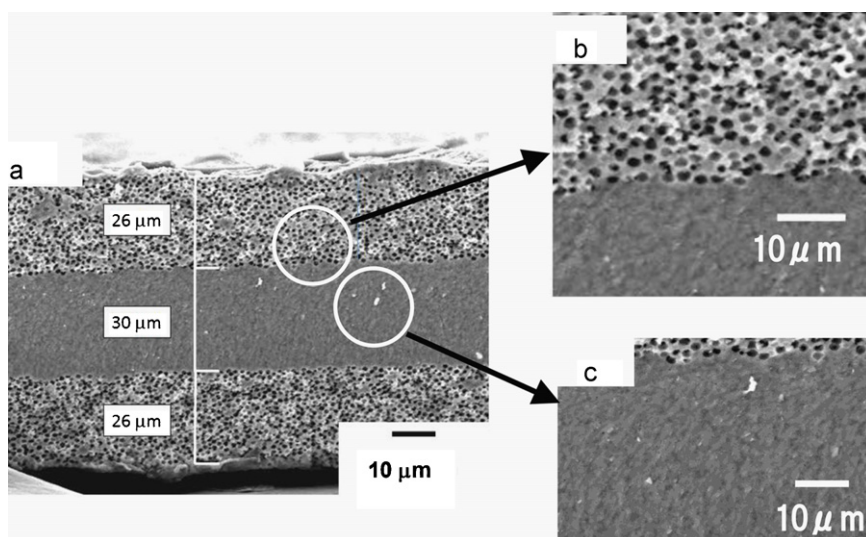


Fig. 2. SEM images of the LLT solid electrolyte with mille-feuille structure. (a) Whole cross-section, (b) magnified image of porous layer, and (c) magnified image of dense layer.

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $i\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{H}_2\text{O}$  (molar ratio = 1.1:2:20:40:70). The pores in the 3DOM layer were filled with 0.02 wt% SDS solution. Then mille-feuille LLT filled with the SDS solution was immersed in the precursor sol for 1 h and dried at  $70^\circ\text{C}$  for 10 min followed by calcination at  $450^\circ\text{C}$  for 1 h. This procedure was repeated 4 times and finally the mille-feuille LLT with Li–Mn–O was calcined at  $700^\circ\text{C}$  for 1 h to obtain a symmetric cell with  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$ .

The symmetric cell with  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  was evaluated by chronopotentiometry using ALS-660B (BAS Inc.) under current density of  $100\text{--}400\text{ nA cm}^{-2}$ . To ensure electronic contact, Au thin film was sputtered on the surface of both 3DOM layers.

### 3. Results

Fig. 2 shows the SEM images of LLT solid electrolyte with mille-feuille structure. It is clearly confirmed that dense layer was sandwiched by porous layers. Thicknesses of dense and both porous layers were 30 and  $26\text{ }\mu\text{m}$ , respectively (Fig. 2(a)), which were consistent with those expected from the amount of LLT powder in the suspension. This means the thicknesses of dense and porous layers can be controlled. Pore diameter of the porous layers was about  $2.0\text{ }\mu\text{m}$ , which is a little smaller than that of PS template ( $3\text{ }\mu\text{m}$ ) due to shrinkage of the PS template during

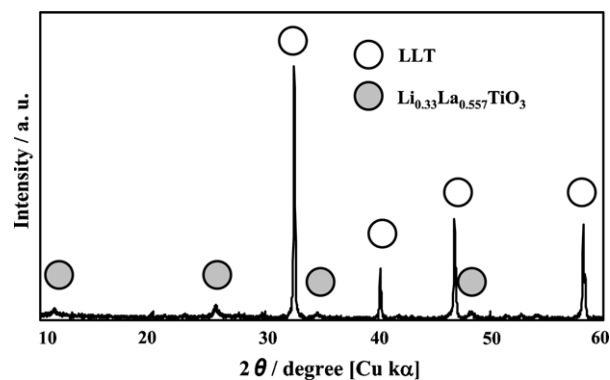


Fig. 3. XRD pattern of the LLT solid electrolyte with mille-feuille structure.

calcination (Fig. 2(b)). The dense layer was sintered well and no grain boundary was observed (Fig. 2(c)). It seems that the dense layer can separate each porous layer completely and prevent from making electrical short circuit when both porous layers were filled by electrode active materials. Both porous layers contacted well with dense layer and no gap existed. Therefore, Li ion moving in LLT of the porous layer can go into the dense layer easily, conducting lowering of impedance of cell. XRD pattern of the LLT solid electrolyte with mille-feuille structure was depicted in

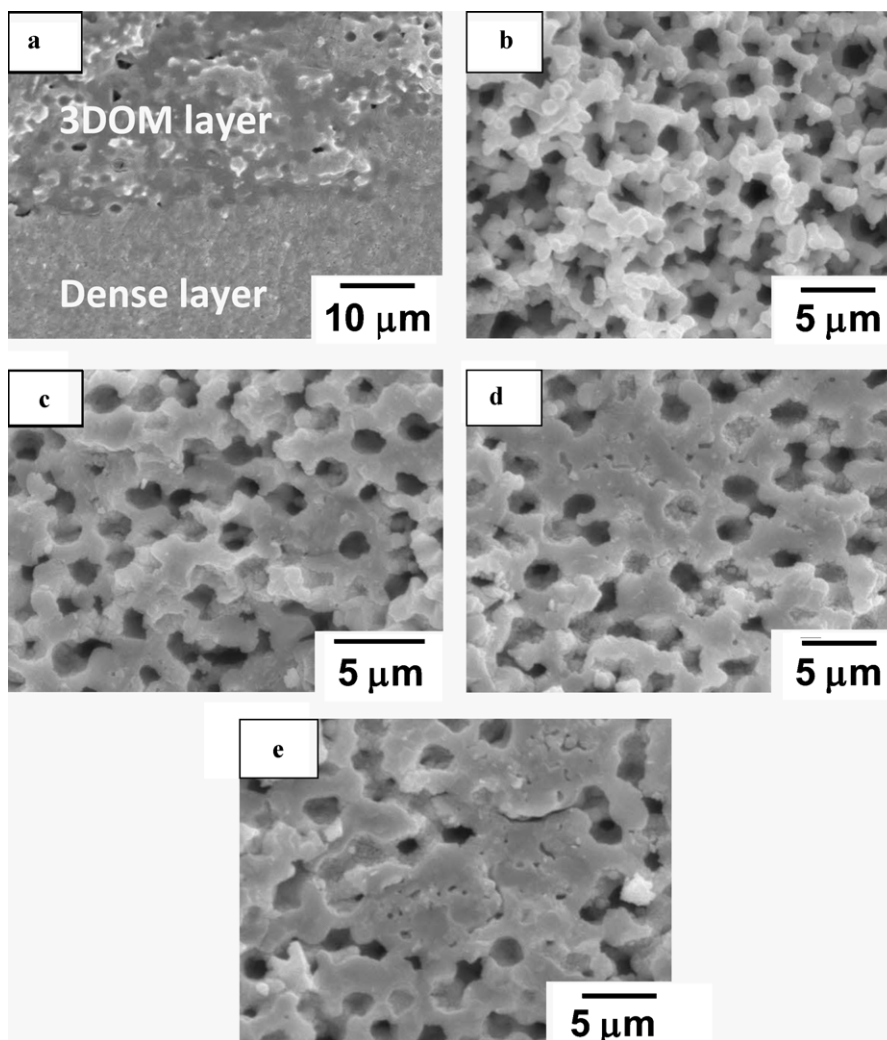


Fig. 4. SEM images of porous layer at each step of impregnation of precursor sol for  $\text{LiMn}_2\text{O}_4$  by the solvent substitution method. (a) After gelation, (b) impregnation of Li–Mn–O sol once, (c) twice, (d) three times, and (e) four times.

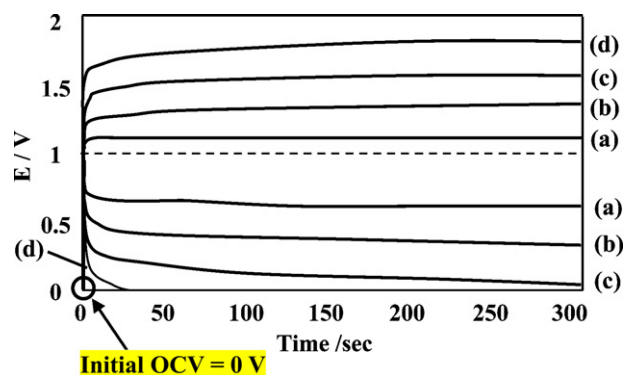


Fig. 5. Chronopotentiograms of the symmetric cell of  $\text{LiMn}_2\text{O}_4/\text{LLT}/\text{LiMn}_2\text{O}_4$  obtained under different current densities. (a)  $100 \text{ nA cm}^{-2}$ , (b)  $200 \text{ nA cm}^{-2}$ , (c),  $300 \text{ nA cm}^{-2}$ , and (d)  $400 \text{ nA cm}^{-2}$ .

Fig. 3. Sharp diffraction peaks were assigned to  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  and broad diffraction peaks ascribed to  $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$  were observed as well. We have obtained similar diffraction pattern in the LLT with honeycomb structure, whose Li ion conductivity was  $1.1 \times 10^{-3} \text{ S cm}^{-1}$  [3]. Therefore, dense layer in the mille-feuille LLT is expected to possess comparable Li ion conductivity.

Active material,  $\text{LiMn}_2\text{O}_4$  was impregnated into both porous layers. As mentioned above, each porous layer should be filled by different active materials, however, purpose of the test was that the compatibility of the mille-feuille structure with 3D all-solid-state battery was examined. Therefore, same active material was impregnated into both porous layers. Cross-sectional SEM images at each impregnation step were displayed in Fig. 4. After gelation of precursor sol (Fig. 4(a)), it was confirmed that the gel reached at dense layer. By using the solvent substitution method, precursor sol of  $\text{LiMn}_2\text{O}_4$  was impregnated into pores near dense layer. However, some voids were still observed after calcination at  $450^\circ\text{C}$  (Fig. 4(b)). This is due to a large amount of solvents contained in the Li–Mn–O sol. With repeating the impregnation procedure, amount of the  $\text{LiMn}_2\text{O}_4$  in the pores increased.

In order to investigate the potential use of the mille-feuille LLT as the all-solid-state battery, chronopotentiometry was carried out by using the symmetric electrochemical cell with  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  configuration. Fig. 5 shows chronopotentiograms of the  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  cell at various current densities. Initial OCV (open circuit potential) of the cell was 0 V. With charging at  $100 \text{ nA cm}^{-2}$ , cell voltage went up to 1.1 V. The OCV was 0.8 V after charging. The overpotentials for insertion/extraction of  $\text{Li}^+$  into/from  $\text{LiMn}_2\text{O}_4$  were increased with current density. The chronopotentiograms of the symmetrical cell should be mirrored relationship at 1.0 V. However, obtained chronopotentiograms were not symmetrical. That is because the porous structure and filling ratio and condition of the  $\text{LiMn}_2\text{O}_4$  were not completely symmetric. Although not symmetric, charge and discharge currents were clearly observed, indicating that successful operation of the symmetric cell with  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  configuration was verified.

#### 4. Discussion

In this paper, we proposed a novel structure for 3D battery which is the mille-feuille structure. The mille-feuille LLT was fabricated by the suspension filtration method and it was confirmed that the all-solid-state battery with mille-feuille LLT electrolyte was operated successfully. However, operated current density was low, a few hundred nanoampere.

One of the reasons of such low performance is attributed to thickness of the dense layer. The thickness of dense layer in this

experiment was  $30 \mu\text{m}$ . This thick dense layer provides long Li ion diffusion path and improves impedance of the cell. Thinner dense layer should be used, but mechanical strength of the mille-feuille structure would diminish with decrease of thickness of the dense layer. Additionally, thin dense layer may not be able to separate both porous layers completely and make a short circuit. Therefore, exploration of optimum thickness satisfying these requirements is needed.

Moreover, a regularity of the porous layer was not good in this experiment as shown in Fig. 2(b). This irregularity leads to uneven current distribution in the cell. This was because condensation of the suspension took place during filtration. The stability of suspension should be improved by using different media, small particle of LLT, and so on. If the porous layer with high regularity could be prepared, the contact area between electrolyte and electrode would be enlarged, resulting in lowering internal impedance.

The last point is impregnation of active material. As shown in Fig. 4(e), some voids were observed in the active material. These voids collapsed electronic conductive path in the active material and some of the active materials did not concern with electrode reaction. In the case of 3DOM LLT electrode, the Li–Mn–O sol could be impregnated from every direction, but the active material sol could be impregnated from only one direction, opposite side of dense layer. Therefore, some modifications of the solvent substitution method are required.

Some problems are still remained, but it was verified that the mille-feuille structure was one of the promising structures of the 3D battery. To further improve the cell performance, some trial is already launched in our laboratory. The results will be reported.

#### 5. Conclusion

A novel 3-dimensional battery with a mille-feuille structure was fabricated by suspension filtration method using  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  (LLT) solid electrolyte. Both porous layers had three-dimensionally ordered macroporous (3DOM) structure, which is expected to diminish internal impedance due to enlargement of contact area between electrode and electrolyte. The dense layer and both porous layers were sintered well each other, completely unified mille-feuille structure was obtained. Chronopotentiograms of symmetrical cell of  $\text{LiMn}_2\text{O}_4/\text{mille-feuille LLT}/\text{LiMn}_2\text{O}_4$  configuration clearly showed charge and discharge currents, indicating that the cell worked as a rechargeable battery. However, the current density was still low, possible reasons would be thickness of dense layer, regularity of porous layer, and lack of amount of impregnated active material. Some problems are still remained, but it was verified that the mille-feuille structure was one of the promising structures of the 3D battery.

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