



Short communication

A novel structure of ceramics electrolyte for future lithium battery

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ABSTRACT

In order to fabricate large scale all-solid-state Li battery, we suggested a novel structure of solid electrolyte, which is composed of porous electrolyte supported by honeycomb-type electrolyte. A possibility of fabrication of the honeycomb-supported porous electrolyte and a compatibility of this structure with all-solid-state battery were examined using LLT ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) solid electrolyte which is one of the anticipated solid electrolytes due to its high Li ion conductivity. A porous layer membrane with 3 dimensionally ordered (3DOM) macroporous structure was prepared by a colloidal crystal templating method. The porous honeycomb was fabricated by pushing the membrane into holes of honeycomb using a needle followed by calcination. The 3DOM membrane and honeycomb electrolyte were sintered well each other. After filling the 3DOM pores with LiMn_2O_4 cathode material, the compatibility of this novel porous honeycomb electrolyte with all-solid-state battery was examined. The LiMn_2O_4 /porous honeycomb cell clearly demonstrated charge and discharge behaviors, indicating the porous honeycomb structure can be applied to the all-solid-state battery. The discharge capacity was 71 mA h g^{-1} (1.3 mA h cm^{-2}) at 30°C .

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1. Introduction

Current economic activity due to mankind has consumed vast energy and we have encountered energy problem. Recovery of energy from brake (regenerative brake) in automobile is recognized as one of the provisions. However, power supplies using the regenerative brake are not stable and very difficult to effective use.

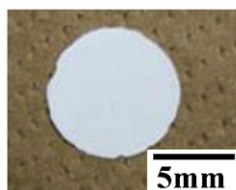
Rechargeable batteries can store energy recovered by the regenerative brake. Therefore, the batteries are expected as a key component for effective use of the recovered energy. Among many kinds of rechargeable batteries, lithium battery has been much attention due to its high energy and power densities. The lithium battery with organic electrolyte has been mainly used for small electronic device such as laptop computer and mobile phone so far. At moment, application of lithium battery to electric vehicle and hybrid car is being challenged by many groups [1–3]. In this application, a large scale battery is required, however, dangerousness such as explosion of flammable organic electrolyte also increase with size of battery. All-solid-state Li battery with non-flammable ceramic electrolyte has been expected as a novel type lithium battery for next generation because of its ultimate safety [4–6]. One of the problems of all-solid-state battery is poor contact between

solid electrolyte and electrode material [7,8]. In order to solve this problem, we have proposed the solid electrolyte with three dimensionally ordered macroporous (3DOM) structure [9,10]. This porous structure is possible to enlarge a contact area between solid electrolyte and electrode, leading to low internal resistance. The 3DOM porous solid electrolyte has been prepared by a colloidal crystal templating method followed by calcination process [11]. A shortcoming of this method has been very difficult to prepare large 3DOM porous solid electrolyte because the porous electrolyte was easy to be broken due to internal stress during the calcination [12] (Fig. 1(a)). This issue has given us a hardship for practical use of the porous electrolyte. To overcome this issue, we suggest Multi-Scale-Bottom-Up (MSBU) technique, i.e. fabrication of large scale battery due to connection of small size of porous electrolytes. It is expected that various scale batteries from a few mm to sub-ten cm scale can be fabricated using this technique. To make the connection of small porous layers, honeycomb type solid electrolyte was selected. Fabricating the porous electrolyte in honeycomb holes allows us to produce various scale batteries with porous structure (Fig. 1(b)). The honeycomb electrolyte works as framework for the porous electrolyte.

The purpose of this work is exploration of a possibility of fabrication of the porous electrolyte supported by honeycomb electrolyte and proof of which this structure can really be applied to all-solid-state battery or not. The LLT ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) solid electrolyte, which is one of the promising solid electrolytes due to its high Li

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(a) 3DOM electrolyte prepared by colloidal crystal templating method



(b) Honeycomb electrolyte with porous layer in the hole

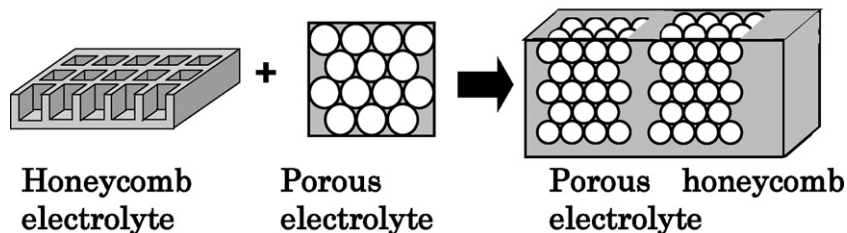


Fig. 1. (a) Photograph of 3DOM electrolyte prepared by colloidal crystal templating method. (b) Schematic illustration of composite electrolyte of 3DOM and honeycomb structures for large scale battery.

ion conductivity (about $1 \times 10^{-3} \text{ S cm}^{-1}$) [13,14], was used in this work.

2. Experimental

LLT ($\text{Li}_{0.55}\text{La}_{0.35}\text{TiO}_3$) solid electrolyte with honeycomb structures supplied from NGK Insulators LTD was used in this work. The honeycomb electrolyte ($5 \text{ mm} \times 5 \text{ mm} \times 260 \mu\text{m}$) had 400 holes ($180 \mu\text{m} \times 180 \mu\text{m} \times 180 \mu\text{m}$) on one side of LLT membrane and the other side did not possess any hole. The honeycomb wall thickness was $80 \mu\text{m}$ [7,8] (Fig. 2). These hole and wall sizes are limited by current ceramics production process.

3DOM LLT membrane was prepared by a colloidal crystal templating method [15]. Monodispersed polystyrene (PS) beads with $3 \mu\text{m}$ in diameter (MAGSPHERE Inc.) used as a template were dispersed in ethanol and filtered under a small pressure difference of 5 kPa using a PTFE filter with 18 mm in diameter and pore size of 100 nm (ADVANTEC). After interconnection of the PS template by heat treatment at 110°C for 1 h , precursor sol for LLT composed of CH_3COOLi , $\text{La}(\text{CH}_3\text{COO})_3 \cdot 1.5\text{H}_2\text{O}$, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, CH_3COOH , $i\text{-C}_3\text{H}_7\text{OH}$, and H_2O in molar ratio of $0.35:0.55:1:20:10:50$ was put into voids of the template. After gelation at 80°C , gel-PS composite was calcined at 1165°C for 2 h . Prepared 3DOM LLT membrane was pushed into the holes of honeycomb by a needle and then honeycomb-3DOM membrane composite was sintered each other at 1165°C for 2 h in air.

A preparation of LiMn_2O_4 cathode was performed by a solvent substitution method [16]. A precursor sol for LiMn_2O_4 was composed of $\text{Li}(\text{CH}_3\text{COO})$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 2-propanol, CH_3COOH and H_2O in molar ratio of $1.1:2:20:40:70$. Before impregnation of the precursor sol, the pore of porous honeycomb electrolyte was filled with 0.02 M sodium dodecyl sulfate (SDS) solution. Then, the solid electrolyte filled with SDS solution was immersed in the precursor sol for 1 h to substitute the sol into the pores. After the immersion, porous honeycomb LLT was lifted up from the sol solution, and the Li-Mn-O sol in the pores was converted to gel at 60°C . The LLT-gel composite was calcined at 450°C for 30 min . Since the Li-Mn-O gel contains a large amount of solvent and

organic compounds, some voids still remain as results of evaporation of the solvent and decomposition of organic species during the heat treatment. In order to increase the filling ratio of active material in the pore of 3DOM solid electrolyte, the impregnation of Li-Mn-O sol and the following calcination was repeated four times and filling ratio reached around at 70% . Finally, the composite was calcined at 700°C for 10 h .

To examine electrochemical property, Li ion-loaded polymethylmethacrylate (Li-PMMA) gel electrolyte was set between Li metal and LLT as a buffer layer to avoid enhancement of the electronic conductivity of the LLT electrolyte due to reduction of Ti^{4+} by Li metal [4]. The Li-PMMA gel was prepared by a polymerization of a mixture of methylmethacrylate monomer, ethylene glycol dimethacrylate, azobisisobutyronitrile, and 1 mol dm^{-3} LiClO_4 (in ethylenecarbonate (EC): diethylcarbonate (DEC) = $1:1$ of weight ratio) with a weight ratio = $1:0.05:0.02:2.87$ [17]. The Li-PMMA gel electrolyte with $300 \mu\text{m}$ thickness was used in all of experiments.

An observation of morphology of solid electrolyte was performed by a scanning electron microscope (SEM, JEOL Co.). Crystalline phases of porous honeycomb LLT were identified with a mean of an X-ray diffractometer (XRD, RINT-Ultima, Rigaku) with $\text{Cu K}\alpha$ radiation. Internal resistances of fabricated LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li cell was measured by the AC impedance method with SI 1260 impedance/gain-phase analyzer (Solartron analytical) using as-prepared cells at OCV. Data was collected at $\pm 5 \text{ mV}$ voltage signal in a frequency range of $0.01\text{--}100 \text{ kHz}$. In cathode side, Au was sputtered to ensure electrical contact between Al current collector and LiMn_2O_4 . In anode side, Cu current collector was put on the Li foil. Galvanostatic charge/discharge test was performed by using battery charge/discharge unit (HJ1001SM8A, Hokuto Denko Co.) under constant current conditions. All electrochemical experiments were performed in Ar atmosphere at 30°C .

3. Results

SEM image of the prepared membrane was shown in Fig. 3. It was clearly observed that the membrane has regularly opened pores

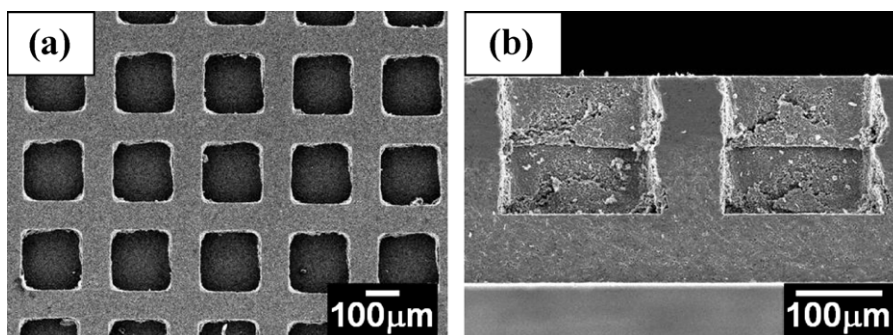


Fig. 2. SEM images of honeycomb LLT electrolyte used in this work. (a) Surface image. (b) Cross-sectional image.

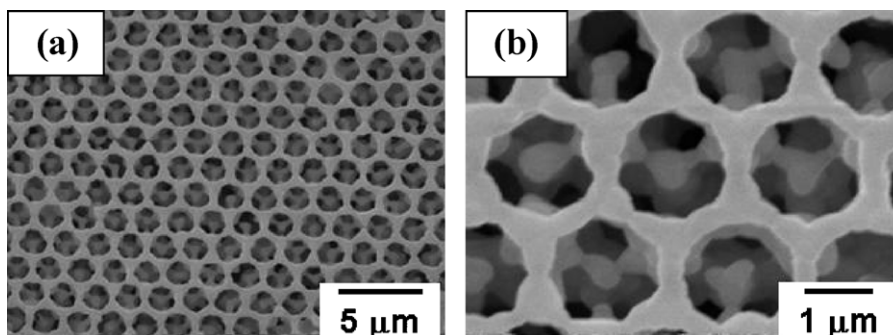


Fig. 3. SEM images of 3DOM LLT membrane prepared by the colloidal crystal templating method.

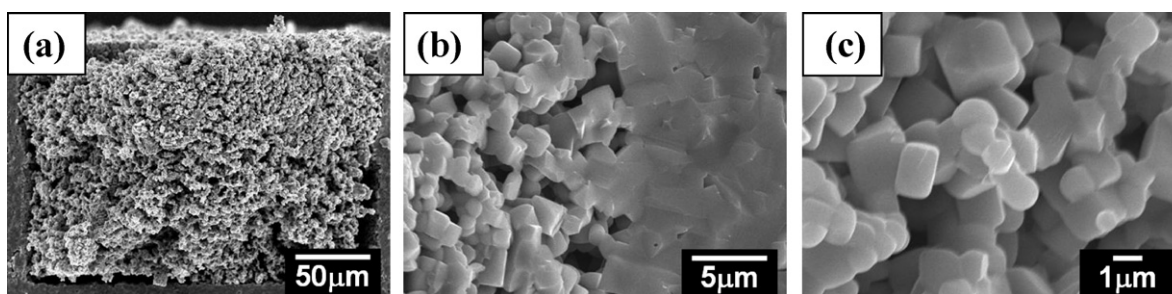


Fig. 4. Cross-sectional SEM image of porous honeycomb LLT electrolyte. (a) Whole cross-section. (b) Magnified image near boundary between porous layer and honeycomb framework. (c) Magnified image of porous layer.

and the pores 3 dimensionally interconnected each other. Pore size of the membrane was about $1.2 \mu\text{m}$, which was smaller than diameter of polystyrene template due to shrinkage of the template during the calcination. It was concluded that 3DOM membrane was successfully prepared.

The 3DOM membrane was pushed into holes of honeycomb electrolyte by a needle and then honeycomb-3DOM membrane composite was sintered each other at 1165°C for 2 h in air. Fig. 4 displays cross-sectional SEM images of honeycomb LLT electrolyte with porous layer. The honeycomb hole was filled with the membrane (Fig. 4(a)). In magnified image near interface at porous layer and honeycomb hole (Fig. 4(b)), it was confirmed that the porous layer sintered well with honeycomb framework. No boundary between porous layer and honeycomb electrolytes was observed. Although regularity of the porous structure seems to be lost a little probably during being pushed by needle (Fig. 4(c)), it was expected that large contact area between electrode material and solid electrolyte would be obtained. XRD pattern of the porous honeycomb electrolyte is represented in Fig. 5. Diffraction peaks of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ were observed as well as those of LLT. The $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ is originally contained in LLT honeycomb [7,8]. Therefore, it is concluded

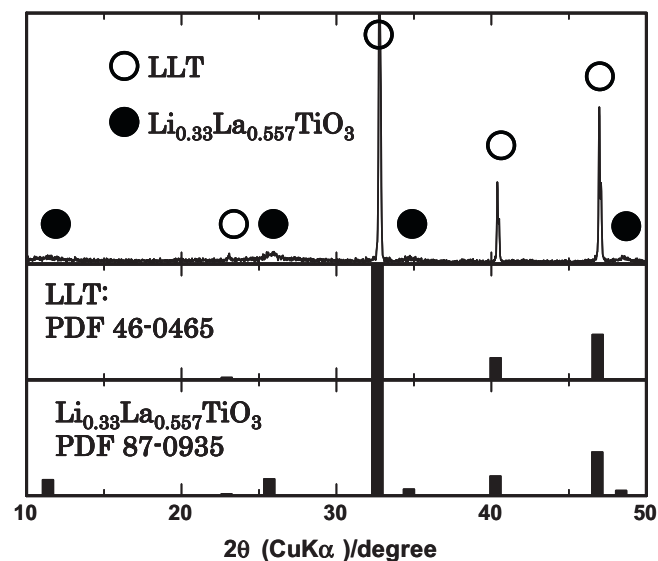


Fig. 5. XRD pattern of porous honeycomb LLT electrolyte.

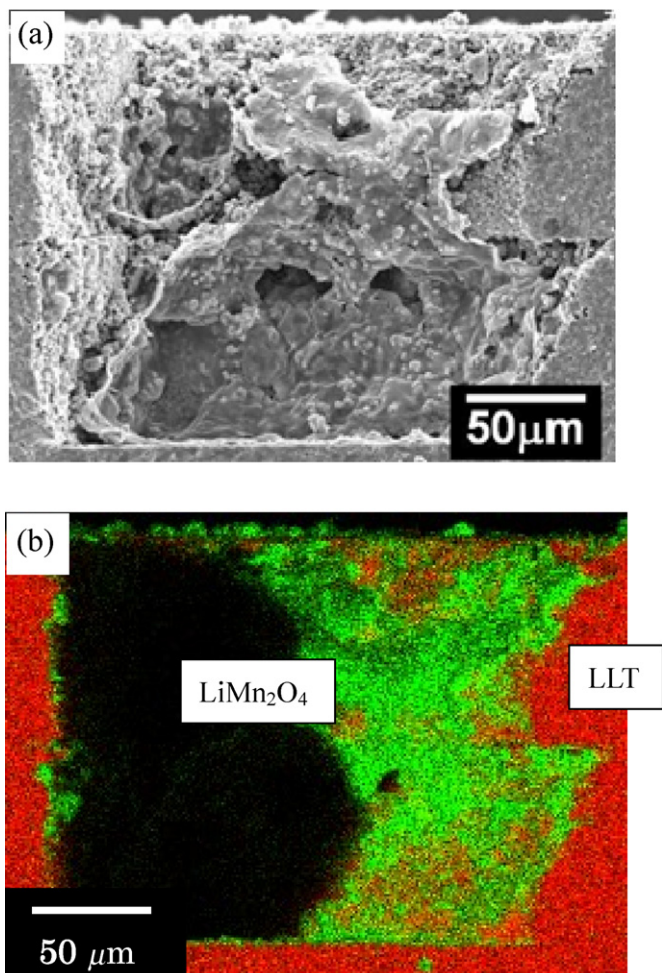


Fig. 6. (a) Cross-sectional SEM image and (b) EDS mapping of porous honeycomb LLT electrolyte after filling LiMn_2O_4 . In the mapping, green and red mean Mn and Ti, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

that porous honeycomb LLT electrolyte was successfully fabricated.

To check compatibility of fabricated novel electrolyte with all-solid-state battery, precursor sol of LiMn_2O_4 cathode material was impregnated into honeycomb holes using the solvent substitution method like our previous paper [16]. Cross-sectional SEM image and EDS mapping of porous honeycomb with LiMn_2O_4 cathode is revealed in Fig. 6(a) and (b), respectively. In the EDS mapping, a signal from Mn (green) was detected whole porous layer. The LiMn_2O_4 cathode reached until bottom of honeycomb hole, indicating that pores in the porous layer interconnected each other. Therefore, cathode material in the porous layer could also contact each other and thus Li ion and electron transport paths were thought to be successfully created. Lack of signal in left side of porous layer was caused by peeling of the active materials when the porous honeycomb electrolyte with the active materials was cracked by hand to observe the cross-section.

Fig. 7 shows a comparison of complex impedance plot of LiMn_2O_4 /porous honeycomb LLT/polymethylmethacrylate (Li-PMMA) gel electrolyte/Li with LiMn_2O_4 /honeycomb LLT/Li-PMMA/Li cell [18]. In both cases, two semicircles in the high frequency region and Warburg-type impedance in the low frequency region were observed. We have observed a semicircle at 1.2 kHz in the complex impedance plot of Li metal/Li-PMMA/honeycomb LLT/Li-PMMA/Li metal cell as shown in triangle

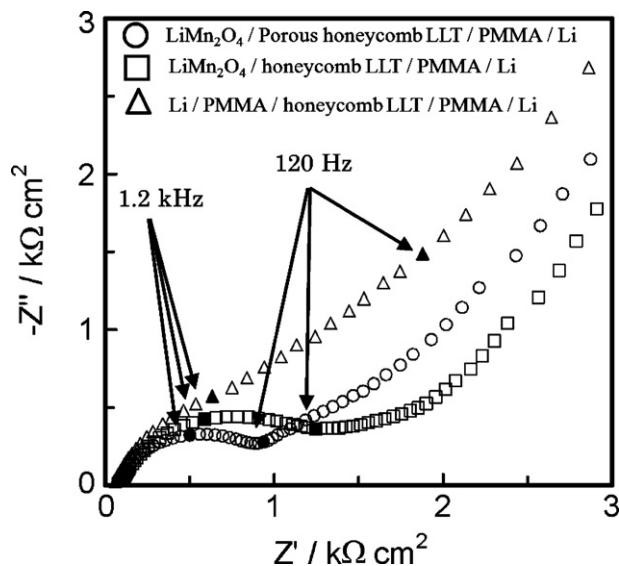


Fig. 7. Complex impedance plots of Li/Li-PMMA/honeycomb LLT/Li-PMMA/Li, LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li, and LiMn_2O_4 /honeycomb LLT/Li-PMMA/Li cells.

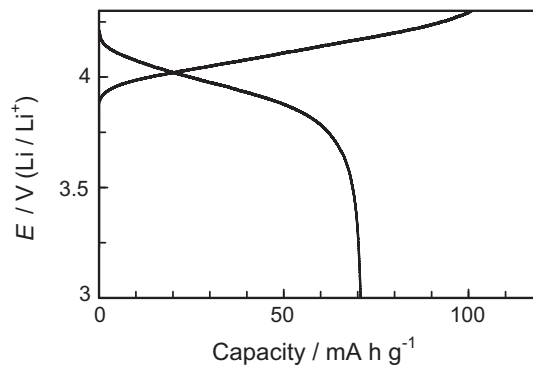


Fig. 8. Charge and discharge curves of LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li cell measured at $12.5 \mu\text{A cm}^{-2}$ (0.01C) at 30°C .

plot in Fig. 7. Therefore, it can be stated that the semicircle at 1.2 kHz represents resistances of both LLT and Li-PMMA gel electrolytes including Li ion transfer at interfaces of LLT/Li-PMMA and Li-PMMA/Li metal anode. Another semicircle at 120 Hz was attributed to Li ion transfer at solid–solid interface at LiMn_2O_4 /honeycomb LLT. This semicircle of porous honeycomb electrolyte was much smaller than that of honeycomb electrolyte due to large contact area between solid electrolyte and electrode. Consequently, whole resistance of LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li was smaller than that of LiMn_2O_4 /honeycomb LLT/Li-PMMA/Li cell. It is expected that LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li cell could work as a rechargeable battery because we clearly observed charge/discharge behavior of LiMn_2O_4 /honeycomb LLT/Li-PMMA/Li cell [18].

Fig. 8 depicts charge and discharge curves of LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li cell. As expected from the impedance plot, it was clearly observed a plateau around at 4.0 V vs Li/Li⁺, which corresponds to intrinsic redox voltage of LiMn_2O_4 and the discharge capacity was 71 mA h g^{-1} (1.3 mA h cm^{-2} , $46.3 \text{ mA h cm}^{-3}$).

4. Discussion

In this paper, a possibility of fabrication of porous electrolyte supported by honeycomb electrolyte and compatibility of the

fabricated porous honeycomb electrolyte with all-solid-state battery were examined using LLT electrolyte.

By pushing 3DOM membrane using needle into honeycomb hole followed by calcination, the porous honeycomb LLT electrolyte was prepared. However, regularity of 3DOM pores was lost a little. This would be because small collapse of 3DOM structure occurred during pushing by needle. This process must be modified. By direct preparation of 3DOM layer in the honeycomb holes, for example formation of PS template in the honeycomb holes and then injection of precursor sol for LLT into voids of the template, this problem may be avoided. Although regularity of 3DOM structure was lost a little, pores connected each other. This was proven by contact of LiMn_2O_4 with bottom of honeycomb holes.

Smaller semicircle at frequency of 120 Hz of LiMn_2O_4 /Porous honeycomb LLT/Li-PMMA/Li cell compared with that without porous structure was revealed by the AC impedance measurement. This semicircle was attributed to Li ion transfer at solid–solid interface at LiMn_2O_4 /LLT. The porous structure provided large contact area between LiMn_2O_4 and LLT, leading to decrease the Li ion transfer resistance. It has to be said that the semicircle at 1.2 kHz was almost no difference among the cells. This semicircle contains Li ion transfer resistance in the LLT electrolyte. If the porous layer did not sinter well with honeycomb wall, boundary resistance at porous layer/honeycomb wall would increase and large semicircle at 1.2 kHz should be observed. Therefore, it was thought that the porous layer and honeycomb wall sintered well each other.

The discharge capacity of the LiMn_2O_4 /Porous honeycomb LLT/Li-PMMA/Li cell was 71 mA h g^{-1} , which is 1.7 times larger than LiMn_2O_4 /non-porous honeycomb LLT [18]. The Li metal anode sits on planar surface, so the interface contact area between Li metal and electrolyte was much smaller than that of cathode side. Li metal anode has much larger capacity (about 25 times) than LiMn_2O_4 cathode. Therefore, the lithium metal anode worked better than LiMn_2O_4 even if the contact area was small. This is supported by observation of larger capacity of the porous honeycomb cell compared with non-porous honeycomb cell. If the lithium metal anode decided cell performance, the performances of both cells would be same.

Volumetric capacities of porous and non-porous cells were almost same, 46.3 and $44.4 \text{ mA h cm}^{-3}$, respectively. This was due to a small loading of the active material in the porous honeycomb. An improvement of volumetric capacity would be achieved by optimization of pore diameter in porous layer which allows a larger loading of active material.

However, the discharge capacity of the LiMn_2O_4 /Porous honeycomb LLT/Li-PMMA/Li cell was only 48% of theoretical capacity [19]. This low utility of active material is attributed to three reasons. One is low regularity of porous layer. This low regularity would make uneven current distribution in the porous layer and thus lead to low utility of the active material. Second is no sufficient contact between active material and electrolyte. The filling ratio of active material was about 70%. Although the partial pore filling may necessary to provide breathing room for volume changes of cathode on Li insertion/extraction, the volume change is very small in the case of LiMn_2O_4 . Therefore, electrically isolation of the active material would be more serious problem. Further research on the optimization of the impregnation condition (sol composition, and so on) and exploration of more suitable cathode materials are required for improvement of performance. The last is honeycomb electrolyte used in this research. The hole size and wall thickness of the honeycomb electrolyte were 180 and $80 \mu\text{m}$, respectively. The Li ion has to move at least $80 \mu\text{m}$ in the LLT to reach Li-PMMA gel electrolyte. This long path would derive high internal resistance. Although this size is limited by ceramic process for fabrication of honey-

comb structure at moment, fabrication of honeycomb structure with smaller holes and thin walls may be possible by applying the MEMS (Micro Electro Mechanical Systems) technique. By using the honeycomb electrolyte with small hole size and thin wall, energy and power densities of the cell will improve.

Although some modifications are required to improve cell performance, it is concluded that this porous honeycomb solid electrolyte can be applied to the all-solid-state battery. Further study on electrochemical properties of LiMn_2O_4 /porous honeycomb LLT cell such as rate capability, cycle stability, and so on are being examined now. New findings will be reported.

5. Conclusions

A novel structure of solid electrolyte for practical all-solid-state Li battery was developed by using the Multi-Scale-Bottom-Up technique. This structure involves porous layer supported by honeycomb structure. The porous layer provides large contact area between active material and solid electrolyte. The honeycomb structure gives mechanical strength to porous layer as framework, making us be possible to fabricate all-solid-state battery with the size from a few mm to sub-ten cm. 3DOM membrane prepared by colloid process was pushed by needle into honeycomb hole and calcined. Although regularity of the 3DOM porous structure was lost a little, porous structure could be constructed in the honeycomb holes successfully. The charge/discharge behavior of LiMn_2O_4 /porous honeycomb LLT/Li-PMMA/Li cell was clearly observed. It was proven that this structure can be applied to the all-solid-state battery. In this work, honeycomb electrolyte whose size was $5 \text{ mm} \times 5 \text{ mm} \times 260 \mu\text{m}$, was used. By using large size honeycomb, fabrication of large scale all-solid-state battery would be achieved easily. However, the discharge capacity was still not enough 48% of theoretical capacity of LiMn_2O_4 . This is mainly attributed to less regularity of porous layer and thick wall and large hole size of honeycomb structure which give long Li diffusion path. Although some modifications are required to improve cell performance, this porous honeycomb solid electrolyte would be one of the promising structures for large scale all-solid-state battery.

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