



Short communication

Compatibility of LiCoO_2 and LiMn_2O_4 cathode materials for $\text{Li}_{0.55}\text{La}_{0.35}\text{TiO}_3$ electrolyte to fabricate all-solid-state lithium battery

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ARTICLE INFO

Article history:

Received 13 January 2010

Received in revised form 23 February 2010

Accepted 2 March 2010

Available online 19 March 2010

Keywords:

All-solid-state Li ion battery

3-D battery

Sol-gel method

ABSTRACT

In order to improve performance of all-solid-state lithium ion battery with honeycomb structure, a compatibility of two commonly used cathode materials, LiCoO_2 and LiMn_2O_4 , to $\text{Li}_{0.55}\text{La}_{0.35}\text{TiO}_3$ (LLT) solid electrolyte was studied. LiCoO_2 /honeycomb LLT and LiMn_2O_4 /honeycomb LLT half cells were fabricated by the impregnation of mixture of the cathode material with its precursor sol into honeycomb holes followed by the calcination. Impurity phases were observed at interface between LiCoO_2 and honeycomb LLT, while no impurity phase was confirmed in the case of LiMn_2O_4 . In half cell test, the LiMn_2O_4 /honeycomb LLT cell showed about 6 times larger discharge capacity than the LiCoO_2 /honeycomb LLT cell, because of high internal resistance of the LiCoO_2 /honeycomb LLT cell caused by the impurity phases. It can be said that the formation of low resistance interface at active material/electrolyte is one of the most important key to improve performance of the all-solid-state battery. Using LiMn_2O_4 instead of LiCoO_2 , better interface between cathode material and LLT was obtained.

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1. Introduction

The present commercially available lithium ion batteries contain flammable organic liquid electrolyte, which are major safety concern [1]. To avoid this problem, all-solid-state lithium batteries with non-flammable solid electrolyte have been strongly required [2–4]. They are usually composed of thin layers of cathode, solid electrolyte, and anode to compensate low Li ion conductivity of the solid electrolyte [5,6]. This two dimensional (2D) configuration can give low internal resistance of cell caused by short lithium ion path in the thin electrolyte. However, in this 2D configuration, capacity is quite low and practical current is also low, since such thin electrode cannot support plenty amount of active materials. Three-dimensional (3D) design of the batteries has been suggested to overcome this problem and provide both high current density and capacity [7–9]. We have tried to fabricate the 3D design all-solid-state lithium battery using $\text{Li}_{0.55}\text{La}_{0.35}\text{TiO}_3$ (LLT) electrolyte with honeycomb structure which possesses microsized holes on the both sides of a membrane. Such honeycomb structure is expected to be able to equip plenty amount of the active materials in their holes, leading to the high capacity. Moreover, a high current density would be also achieved by constructing thin walls between the holes. We have found that it is possible to prepare well-contacted

electrode with the honeycomb electrolyte by the impregnation of active material powder with its precursor sol into the honeycomb holes. Finally, the prepared LiCoO_2 /honeycomb LLT/ $\text{Li}_4\text{Mn}_5\text{O}_{12}$ cell can be operated successfully [10]. However, discharge capacity of the cell is only $7.3 \mu\text{A h cm}^{-2}$ and must be improved for practical use. AC impedance measurements have revealed internal resistances of LiCoO_2 /honeycomb LLT and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ /honeycomb LLT half cells were 27 and $4 \text{ k}\Omega \text{ cm}^2$, respectively. Hence, it is concluded that the internal resistance of the LiCoO_2 /honeycomb LLT is one of the reasons of such low capacity of the 3D battery. Liao et al. studied on stability between the LLT solid electrolyte and three kinds of commonly used cathode materials (LiNiO_2 , LiCoO_2 and LiMn_2O_4) during annealing of mixture of the LLT powder and each cathode material powder [11]. They have reported LiMn_2O_4 was the most stable among them. It is anticipated that the LiMn_2O_4 may exhibit better performance than the LiCoO_2 . However, studying on direct comparison of electrochemical properties of LiCoO_2 /LLT with LiMn_2O_4 /LLT half cells has not been appeared yet. Consequently, this study is focused on difference of the electrochemical properties between LiCoO_2 /LLT and LiMn_2O_4 /LLT half cells in order to fabricate better all-solid-state battery.

2. Experimental

LLT ($\text{Li}_{0.55}\text{La}_{0.35}\text{TiO}_3$) was used as a solid electrolyte material. A half honeycomb structure with 400 holes ($180 \mu\text{m} \times 180 \mu\text{m} \times 180 \mu\text{m}$) on one side of the LLT membrane supplied from the NGK Insulators, LTD., was used in this

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research. Gaps between the holes were 80 μm . Li ion conductivity of the LLT was $1.1 \times 10^{-3} \text{ S cm}^{-1}$ [10].

Two kinds of cathode materials (LiCoO_2 and LiMn_2O_4) were prepared by sol–gel method. Preparation of LiCoO_2 was already reported in our previous paper [10]. Precursor sol for LiMn_2O_4 was prepared from CH_3COOLi , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $i\text{-C}_3\text{H}_7\text{OH}$, CH_3COOH , and H_2O (molar ratio = 1.1:2:20:40:70) [12]. The sol was dried at 100°C for 20 h in air to convert to gel and calcined at 450°C for 5 h. The obtained powder was grinded in a mortar and then calcined at 700°C for 5 h.

To evaluate the performance of prepared LiMn_2O_4 powder, a galvanostatic charge/discharge test was performed. A mixture of the LiMn_2O_4 powder, Ketjen black, and polyvinylidene difluoride (PVdF) in the weight ratio of 80:10:10 was coated on Al current collector as a composite electrode. The electrode (14 mm diameter) was put into a coin cell 2032 with ethylenecarbonate (EC) and dimethylcarbonate (DEC) (volume ratio = 1:1) containing $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ as an electrolyte and with Li metal as a negative electrode. The charge/discharge test of the coin cell was performed at 0.1 C using battery charge/discharge unit (HJ1001SM8A, Hokuto Denko Co.) and cut-off voltages were 4.3 and 3.5 V vs. Li/Li^+ for charge and discharge, respectively.

To test the compatibility of the cathode materials to the LLT electrolyte, a half cell composed of LiCoO_2 or LiMn_2O_4 /honeycomb LLT was fabricated. By contact with Li metal negative electrode, electronic conductivity of LLT is strongly enhanced due to Ti^{4+} reduction [2]. To avoid enhancement of the electronic conductivity of the LLT electrolyte, polymethylmethacrylate (PMMA) gel electrolyte was settled between Li metal and LLT as a buffer layer. The PMMA gel was prepared by the polymerization of a mixture of methylmethacrylate monomer, ethylene glycol dimethacrylate, azobisisobutyronitrile, and $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ (in EC:DEC = 1:1 vol.) with the weight ratio = 1:0.05:0.02:2.87 [13]. The PMMA gel electrolyte with 300 μm thickness was used in all of experiments. To construct cathode, a mixture of the cathode material powder with its precursor sol was impregnated into the honeycomb holes under reduced pressure [10]. Then, the mixture in the honeycomb holes was dried at 100°C for 30 min followed by calcination at 450°C for 30 min. This process was repeated three times to improve the amount of cathode material. After the impregnation, the honeycomb LLT was calcined for 10 h at 800 and 700°C for LiCoO_2 and LiMn_2O_4 , respectively. Loadings of the active materials were calculated from difference in weight of the honeycomb LLT between before and after impregnation. Before electrochemical measurements, Au thin film was deposited on cathode face by DC-sputtering method to decrease electronic resistance between the cathode and a current collector.

Morphologies of the LiMn_2O_4 particle and cross-section of the half cells were observed by scanning electron microscope (SEM, JEOL Co.). Crystalline phases were identified by X-ray diffraction (XRD, RINT-Ultima, Rigaku) with $\text{Cu K}\alpha$ radiation. The electrochemical performance of the half cells was evaluated by the galvanostatic charge/discharge test with same procedure as the coin cell. Internal resistances of the half cells were measured by AC impedance method conducted by SI 1260 impedance/gain-phase analyzer (Solartron analytical) using as-prepared cells at OCV. Data was collected in the range of 0.01–100 kHz. All of electrochemical experiments were performed in Ar atmosphere at 30°C .

3. Results

3.1. Performance of cathode materials prepared by sol–gel method

Characterization and evaluation of LiCoO_2 powder prepared by the sol–gel method have been already reported in our pre-

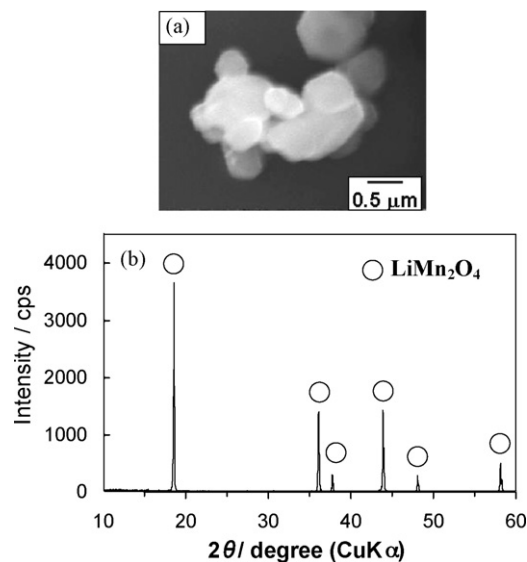


Fig. 1. SEM image (a) and XRD pattern (b) of LiMn_2O_4 powder prepared by the sol–gel method.

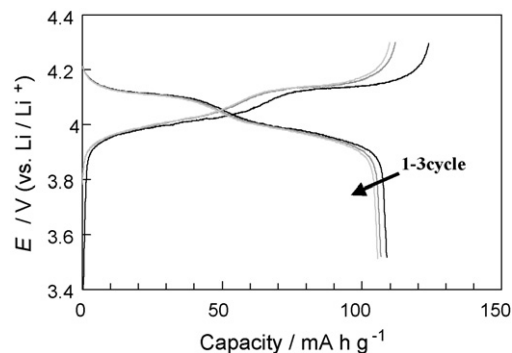


Fig. 2. Charge/discharge curve of the LiMn_2O_4 powder using 1 M LiClO_4 in EC:DEC = 1:1 vol.% measured at 0.1 C.

vious paper [10]. Briefly, particle size was about $0.6 \mu\text{m}$ and discharge capacity was 138 mA h g^{-1} , 98.6% of theoretical capacity (140 mA h g^{-1} [14]). In the case of LiMn_2O_4 , small particles (about $0.7 \mu\text{m}$) were obtained as shown in Fig. 1(a). All of diffraction peaks in a XRD pattern (Fig. 1(b)) were attributed to LiMn_2O_4 with spinel structure and no impurity phase was observed. To evaluate electrochemical performance of the obtained LiMn_2O_4 powder, the galvanostatic charge and discharge test was performed at 0.1 C (Fig. 2). The discharge capacity of LiMn_2O_4 was 109 mA h g^{-1} , 73.6% of theoretical one (148 mA h g^{-1} [15]), indicating that the powder had plenty of discharge capacity.

The obtained LiMn_2O_4 was enough small compared with the holes of honeycomb LLT ($180 \mu\text{m}$) and exhibited high discharge capacity as well as LiCoO_2 , concluding that appropriate powder to impregnate into the honeycomb holes were prepared.

3.2. Evaluation of LiCoO_2 and LiMn_2O_4 electrode in the hole of honeycomb LLT

In previous paper, we reported the impregnation of the mixture of the active material powder with its precursor sol was very efficient way to reduce internal resistance of electrode [10]. This method was applied to fabricate the LiMn_2O_4 /honeycomb LLT as well as LiCoO_2 /honeycomb LLT half cells. Fig. 3 shows cross-sectional SEM images of the honeycomb LLT after the impregnation of the cathode materials. In both cases, the cathode materials dis-

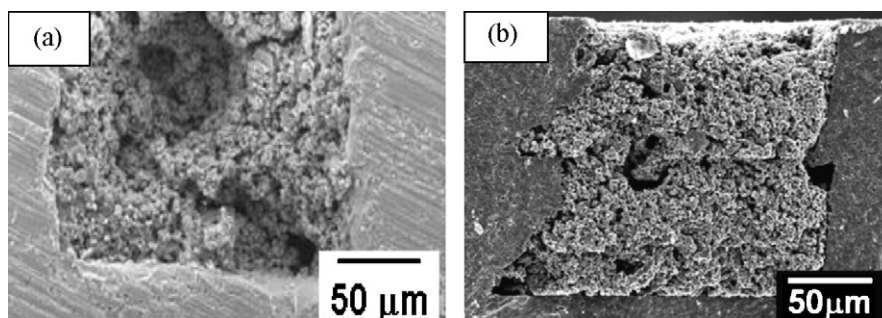


Fig. 3. Cross-sectional SEM images of LiCoO₂/honeycomb LLT (a) and LiMn₂O₄/honeycomb LLT (b) impregnated by a mixture of powder with its precursor sol followed by calcination at 700 and 800 °C for LiCoO₂ and LiMn₂O₄, respectively.

tributed whole holes and were filled almost completely in the honeycomb holes. Additionally, no large gap between LLT and cathode materials was observed in Fig. 3(a) and (b), indicating that both the cathode materials contacted well with the LLT electrolyte. There is no doubt that this impregnation method is also useful for the LiMn₂O₄. XRD patterns of the LiCoO₂/honeycomb LLT and the LiMn₂O₄/honeycomb LLT are shown in Fig. 4. In the case of LiCoO₂/honeycomb LLT, clear diffraction peaks of LiCoO₂ and LLT were observed (Fig. 4(a)), but simultaneously peaks at $2\theta = 37^\circ$ and 29° were attributed to Co₃O₄ and La₂Ti₂O₇, respectively. Liao et al. reported that only diffraction peaks of β -LLT was appeared as impurity after the calcination of mixture of the LLT powder with the LiCoO₂ powder at 800 °C for 2 h [11]. This discrepancy might result from difference of LLT electrolyte since they used the LLT powder. Additionally, the diffraction peaks of Li_{0.33}La_{0.557}TiO₃ were also observed in Fig. 4(a). This is because of the impurity, which the honeycomb LLT contains originally [10]. In the case of LiMn₂O₄/honeycomb LLT, all diffraction peaks were assigned to LiMn₂O₄, LLT, and Li_{0.33}La_{0.557}TiO₃ and no impurity phase were observed.

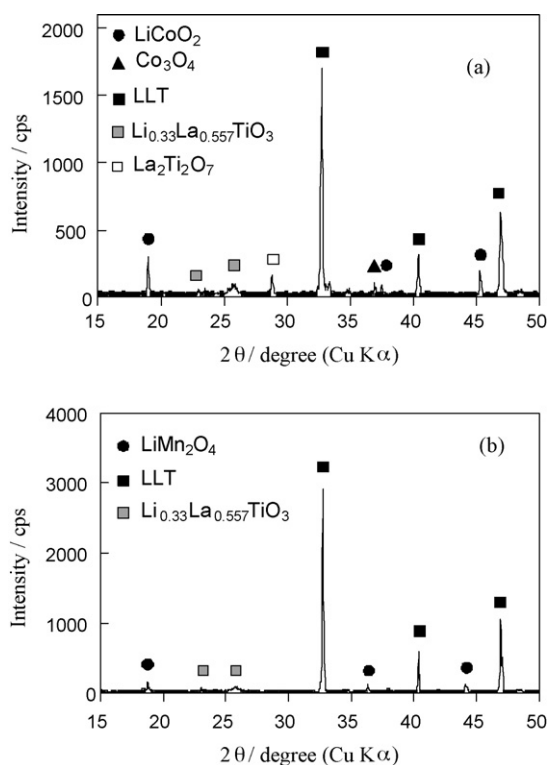


Fig. 4. XRD patterns of the LiCoO₂/honeycomb LLT (a) and the LiMn₂O₄/honeycomb LLT (b) impregnated by a mixture of powder with its precursor sol followed by calcination at 700 and 800 °C for LiCoO₂ and LiMn₂O₄, respectively.

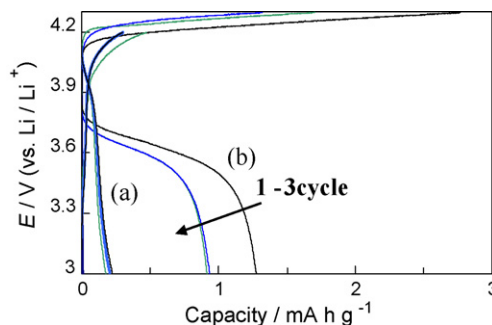


Fig. 5. Charge/discharge curves of the LiCoO₂/honeycomb LLT/PMMA/Li metal (a) and the LiMn₂O₄/honeycomb LLT/PMMA/Li metal cells (b).

Electrochemical properties of the prepared electrodes were evaluated by the charge/discharge test and the AC impedance method. Fig. 5 reveals charge/discharge curves of the LiCoO₂/honeycomb LLT and the LiMn₂O₄/honeycomb LLT half cells. The discharge capacity of the LiCoO₂/honeycomb LLT half cell was estimated to be 0.22 mA h g⁻¹-LiCoO₂. On the other hand, the discharge capacity of the LiMn₂O₄/honeycomb LLT was about 6 times larger than LiCoO₂/honeycomb LLT, 1.27 mA h g⁻¹-LiMn₂O₄. This difference of cell performance may be explained by the formation of the impurity phase in the LiCoO₂/honeycomb LLT, as shown in Fig. 4. The impurity phases such as Co₃O₄ and La₂Ti₂O₇ would work as resistance layer. In fact, the AC impedance measurements (Fig. 6) showed clearly that the internal resistance of the LiMn₂O₄/honeycomb LLT (3200 Ω cm²) was much lower than that of the LiCoO₂/honeycomb LLT cell (27 kΩ cm²).

4. Discussion

The compatibility of two commonly used cathode materials, LiCoO₂ and LiMn₂O₄, to LLT solid electrolyte was tested to improve cathode performance of the 3D battery with honeycomb structure. The discharge capacities of LiCoO₂/honeycomb LLT and LiMn₂O₄/honeycomb LLT were 0.22 and 1.27 mA h g⁻¹, respectively. The AC impedance measurement demonstrated LiMn₂O₄/honeycomb LLT had much lower internal resistance than LiCoO₂/honeycomb LLT as shown in Fig. 6.

By the impregnation of mixture of the cathode material with its precursor sol, both cathode materials can be distributed well into the honeycomb holes, and their contact qualities to the solid electrolyte may not be so different. Probably, electrochemical interface between the solid active material and the solid electrolyte may be similar, each other. Hence, the electrode area cannot explain difference of the discharge capacity. On the other hand, XRD measurement provided different patterns among two kinds of active material. In the case of LiCoO₂/LLT honeycomb, formation of Co₃O₄ and La₂Ti₂O₇ was confirmed. In this study, the LiCoO₂ powder was

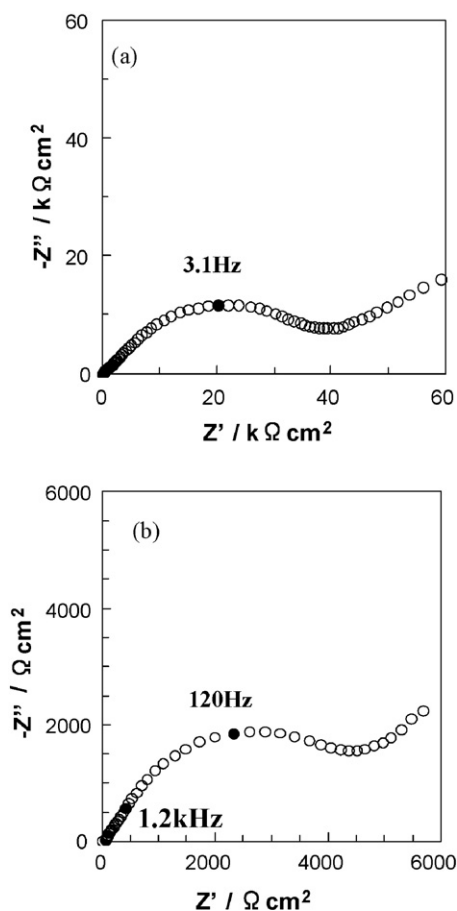


Fig. 6. Complex impedance plots of the LiCoO₂/honeycomb LLT/PMMA/Li metal (a) and the LiMn₂O₄/honeycomb LLT/PMMA/Li metal cells (b).

prepared by the calcination of the precursor sol at 800 °C [10]. The honeycomb LLT was sintered at 1165 °C for 4 h prior to use. Both LiCoO₂ powder and LLT electrolyte would be stable during the calcination at 800 °C, if they did not contact each other. The XRD pattern showed only Li loss phases of LiCoO₂ and LLT, and no Co-Ti containing compounds were detected. Both LiCoO₂ and LLT may act as enhancer promoting Li loss each other. Therefore, these impurities were produced at interface of LiCoO₂/LLT. In the case of LiMn₂O₄, only LiMn₂O₄, LLT and Li_{0.33}La_{0.557}TiO₃, which is originally included as the impurity in the LLT, were observed from its XRD pattern. From the comparison of these two kinds of half cells, it can be considered that the impurity phases like Co₃O₄ and La₂Ti₂O₇ formed at the interface may have high resistance against Li ion conduction and may account for the lower discharge capacity of the LiCoO₂/honeycomb LLT. However, some impurities which could not be detected by XRD due to low concentration and/or crystallinity may be formed at LiMn₂O₄/LLT interface. The impurities at LiMn₂O₄/LLT interface were thought to possess less resistance than that of LiCoO₂. These results imply clearly that the formation of low resistance interface at active material/electrolyte is one of the most important key to improve performance of the all-solid-state battery and better interface can be constructed using LiMn₂O₄ instead of LiCoO₂. Therefore, it is concluded that the LiMn₂O₄ was more suitable cathode material than LiCoO₂. It is expected that the all-solid-state battery composed of LiMn₂O₄/honeycomb LLT/Li₄Mn₅O₁₂ would exhibit better performance than LiCoO₂/honeycomb LLT/Li₄Mn₅O₁₂ we fabricated before [10].

In Fig. 6, appeared semicircle in LiMn₂O₄ was much smaller than that of LiCoO₂. Origin of the semicircle was deduced to be resistance at grain boundary of LiMn₂O₄ and/or at LiMn₂O₄/LLT interface. The grain boundary of LiMn₂O₄ seemed similar to LiCoO₂ in SEM images. Thus, the semicircle may be mainly attributed to the resistance at LiMn₂O₄/LLT interface. However, it is thought that charge transfer resistance is affected by state of charge (SOC). The AC impedance measurement should be performed under stable SOC, but the cells could not achieve to stable SOC during three charge/discharge cycles.

The discharge capacity of LiMn₂O₄/honeycomb LLT was still not enough, 1.27 mA h g⁻¹. This indicated that only 0.9% of impregnated LiMn₂O₄ contributed to the discharge reaction. Further research on the optimization of the impregnation condition (sol composition, particle size, and so on) and exploration of more suitable cathode materials are required to improve the performance. Another reason of the low capacity would be a long Li ion path. The hole size and wall thickness of the honeycomb electrolyte used in this research were 180 and 80 μm, respectively. The Li ion existing at center of the hole has to transport long way until the electrolyte, additionally, has to move at least another 80 μm in the electrolyte. This long path would derive high internal resistance.

The formation of low resistance interface of the active material and solid electrolyte is definitely important, but the optimization of the 3D structure of electrolyte must be needed as well. The fabrication and evaluation of the all-solid-state 3D battery with LiMn₂O₄ cathode, Li₄Mn₅O₁₂ anode and honeycomb LLT electrolyte and optimization of electrode preparation including exploration of more suitable cathode materials are underway simultaneously. Results will be reported in due course.

5. Conclusions

A compatibility of two cathode materials, LiCoO₂ and LiMn₂O₄, to LLT (Li_{0.55}La_{0.35}TiO₃) solid electrolyte with honeycomb structure was studied. XRD pattern of the LiMn₂O₄/honeycomb LLT exhibited that no impurity phase was observed. On the other hand, the impurity phase produced at interface of LiCoO₂/honeycomb LLT increased internal resistance. Moreover, the discharge capacity of LiMn₂O₄/honeycomb LLT half cell was about 6 times larger than that of LiCoO₂/honeycomb LLT cell. From these results, it can be said that the formation of low resistance interface at active material/electrolyte is one of the most important key to improve performance of the all-solid-state battery. Using LiMn₂O₄ instead of LiCoO₂, better interface between cathode material and LLT was obtained. It is expected that the all-solid-state battery composed of LiMn₂O₄/honeycomb LLT/Li₄Mn₅O₁₂ would be better performance than LiCoO₂/honeycomb LLT/Li₄Mn₅O₁₂ that we fabricated before. However, only 0.9% of the impregnated LiMn₂O₄ contributed to the discharge reaction in the LiMn₂O₄/honeycomb LLT half cell. To achieve further improvement of the performance, optimizations of electrode and electrolyte structure are required strongly.

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