Fabrication of Thin LiMn$_2$O$_4$ Electrode on the Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ Solid Electrolyte by a Sol-Gel Method

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ABSTRACT: In order to fabricate a thin film battery made up of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) solid electrolyte and LiMn$_2$O$_4$ cathode, the PVP (poly vinylpyrrolidone) sol-gel method combined with spin-coating method is applied. From XRD and Raman spectrum, it is confirmed that LiMn$_2$O$_4$ thin film is successfully prepared on the LAGP, although some defects can be observed in the thin film. A cyclic voltammogram of the thin film reveals clear redox peaks corresponding to Mn$^{3+/4+}$ in the LiMn$_2$O$_4$, implying possible application of the PVP sol-gel method combined with spin-coating to the thin film battery preparation. The discharge capacity of the film is 42 mA h g$^{-1}$ at 0.1 C.

Keywords: Thin film battery, Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ Solid electrolyte, All-solid-state battery, Sol-gel method

1. Introduction

All-solid-state lithium ion batteries are expected as a next generation lithium ion battery because of their safety, reliability, long life and incombustibility [1]. Particularly, ceramic electrolytes have been paid much attention owing to high durability against high temperature operation. Of many candidates of the ceramics electrolytes, L$_{0.33}$Li$_{0.55}$TiO$_3$ (LLT) with perovskite structure [2, 3] and Li$_{1+x}$Al$_{1-x}$Ti$_2$O$_4$ (LATP) with NASICON-type structure [4-8] have been studied in many groups due to their high ionic conductivities ($\sim$10$^{-3}$ S cm$^{-1}$).

In recent years, trends toward miniaturizing electronic devices have raised demands for small power sources [9]. Therefore, the thin film rechargeable lithium batteries composed of thin film electrodes and solid electrolytes with high energy and power densities have been extensively studied and have acquired a great progress.

Dokko et. al. [10,11] studied on a fabrication of the thin film electrode on thin film solid electrolyte by a sol-gel method combined with spin-coating method. They succeeded in fabrication of Li$_4$Ti$_5$O$_{12}$ thin films on LATP by the PVP (poly-vinylpyrrolidone) sol-gel method and the thin film revealed charge and discharge behaviors at its intrinsic redox potentials. However, narrow electrochemical window of the LATP solid electrolyte due to facile Ti$^{4+}$ reduction at 2.4 V vs. Li/Li$^+$ leads to a limited operation voltage, resulting in limited power densities of the battery [12].

Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) solid electrolyte is a member of Li ion conductive ceramics with NASICON type structure. The total ionic conductivities of LAGP is reported to 4.2×10$^{-5}$ S cm$^{-1}$ [13], which is comparable to LATP. The LAGP showed a reduction peak at 0.8 V vs. Li/Li$^+$ in a cyclic volummetry and was not decomposed until 7 V [14]. Therefore, the LAGP has an advantage for the electrochemical window since Ge$^{4+}$ is insensitive to reduction compared with Ti$^{4+}$ [15]. Therefore, thin film based micro-batteries with the LAGP electrolyte is expected to be able to be operated at high voltage, leading to high energy and power densities of the batteries.

In this paper, a fabrication of LiMn$_2$O$_4$ thin film cathode on the LAGP electrolyte by the PVP sol-gel method combined with spin-coating and its electrochemical properties as rechargeable lithium batteries are reported.

2. Experimental

LAGP plate with 300 µm thickness was supplied from Ohara Inc and used as the solid electrolyte. The Li ion conductivity of the LAGP plate was reported to 1.4×10$^{-4}$ S cm$^{-1}$ [16]. LiMn$_2$O$_4$ thin film was prepared on the LAGP plate by the PVP sol-gel method [17, 18]. A molar composition of the precursor sol for LiMn$_2$O$_4$ was Li(CH$_3$COO)$_2$:Mn(CH$_3$COO)$_2$:4H$_2$O:PVP:CH$_3$COOH:ti-C$_3$H$_7$OH:H$_2$O = 1.1:2.2:20:40:50. The sol was supplied for the spin coating as a coating solution for LiMn$_2$O$_4$ films. Spin coating was conducted on the LAGP substrate under a rotation speed of 3000 rpm in order to prepare a gel film.

This gel film was converted to ceramic thin film by heating at temperature of 600 °C in air for 20 min. The gel film reacted with the LAGP substrate over 700 °C. Therefore, the heating temperature of 600 °C was selected in this research. Both spin coating and heating processes were repeated 5 times to obtain the LiMn$_2$O$_4$ film with enough thickness for electrochemical measurements. Morphology of prepared LiMn$_2$O$_4$ thin film was observed by scanning electron microscope (SEM, JEOL). The prepared thin film was characterized by X-ray diffraction (XRD, Rigaku) with Cu ka radiation and Raman spectroscopy (JASCO) with laser radiation of 532 nm.

Electrochemical measurements were performed using two electrode configuration composed of LiMn$_2$O$_4$ cathode coated on the LAGP plate and Li metal as anode.
and reference electrodes. In order to avoid undesirable reaction between LAGP and Li metal, Li ion-loaded polymethyl methacrylate (PMMA) gel-polymer electrolyte was used as a buffer layer [19]. The thickness of the PMMA gel-polymer was 300 µm and its Li ion conductivity was ca. 1×10⁻³ S cm⁻¹ at room temperature. Cyclic voltammetry (CV) was performed using a potentiostat (HSV-100, Hokuto Denko) at a scan rate of 1.0 mV s⁻¹ and potential range of 3.5-4.3 V vs. Li/Li⁺. The galvanostatic charge and discharge test was conducted by an automatic discharge and charge equipment (HJR-110mSM6, Hokuto Denko). The charge and discharge currents were 3.5 µA cm⁻² (0.1C). Cut-off voltages were 4.3 and 3.5 V for charge and discharge processes, respectively. All electrochemical experiments were performed in an argon-filled glove box at room temperature.

3. Results and discussion

Figure 1 shows XRD patterns of LiMn₂O₄ thin film on the LAGP electrolyte. A small peak due to a diffraction of (111) plane in LiMn₂O₄ spinel structure was observed at 2θ = 18.6°. Very small peaks of (311) and (400) planes of LiMn₂O₄ were also observed at 36.0° and 43.8°, respectively. The peak at 20.3° could not be assigned because of a smallness of the peak. MnO₂ formation is thought a possible reason for the peak. All other peaks were assigned to LAGP substrate. Raman spectra of LiMn₂O₄ thin film and LAGP substrate were revealed in Figure 2. Four peaks were confirmed at 488, 593, 627 and 650 cm⁻¹ in the Raman spectrum of LiMn₂O₄ thin film on the LAGP (fig. 2(a)).

According to Julien et al. [20], LiMn₂O₄ thin film has five Raman active modes. The vibration band at around 627 cm⁻¹ is related to symmetric stretching A₁g of the Mn-O bands in MnO₆ octahedron. The vibration bands at around 593 and 488 cm⁻¹ would be ascribed to symmetric stretching F₂g(3) and F₂g(2), respectively, of the Li-O bands in the LiO₄ tetrahedron. The band at around 650 cm⁻¹, is assigned to asymmetric stretching A₂u of the Mn-O bands in MnO₆ octahedron, should be inactive in Raman spectra of species showing the high symmetry O₇h. However, distortions of this local symmetry, caused by defect formation and so on, may activate the stretching (A₂u) [21]. The Raman band at 380 cm⁻¹ assigned to F₂g(1) was buried in noise of spectrum and could not be clearly observed.

Surface and cross-sectional SEM images of LiMn₂O₄ thin film on the LAGP substrate were displayed in fig. 3. A surface of the thin film with submicron roughness was observed (Figure 3a). The precursor sol for LiMn₂O₄ contained CH₃COOLi, Mn(CH₃COO)₂ and PVP. After gelation, they still remained in the gel. In following calcination, they decomposed to H₂O, CO₂ and LiMn₂O₄. The gas generation would produce pores and surface roughness [11]. From cross-sectional SEM image (Figure 3b), thickness of the thin film was estimated to be about 0.8 µm.

**Figure 1**: XRD patterns of (a) LiMn₂O₄ thin film on the LAGP, (b) LAGP electrolyte, and (c) the standard peaks of LiMn₂O₄ (PDF 00-035-0782)

**Figure 2**: Four peaks were confirmed at 488, 593, 627 and 650 cm⁻¹ in the Raman spectrum of LiMn₂O₄ thin film on the LAGP (fig. 2(a)).
Figure 2: Raman spectra of (a) LiMn$_2$O$_4$ thin film on the LAGP and (b) LAGP electrolyte

Figure 3: SEM images of (a) surface and (b) cross-section of LiMn$_2$O$_4$ thin film prepared on the LAGP substrate
Electrochemical properties of the thin film were evaluated by means of cyclic voltammetry and galvanostatic charge/discharge test. Figure 4 shows cyclic voltammogram of LiMn$_2$O$_4$ thin film on the LAGP solid electrolyte measured at scan rate of 1.0 mV s$^{-1}$. In the anode scan, clear two peaks at 4.0 and 4.2 V vs. Li/Li$^+$ was observed. This electrochemical reaction was led by the oxidative state changing of manganese corresponding to Mn$^{3+}$/Mn$^{4+}$ in the LiMn$_2$O$_4$. In the cathode scan, two reduction peaks, which are attributed to reductive state changing of manganese in the LiMn$_2$O$_4$, were observed. These results indicate that LiMn$_2$O$_4$ thin film worked as cathode for all-solid-state lithium rechargeable batteries.

The galvanostatic charge/discharge test of the LiMn$_2$O$_4$ thin film was performed at 0.1 C (Figure 5). Two potential plateaus at 4.0 and 4.1 V vs. Li/Li$^+$ corresponding to redox Mn$^{3+}$/Mn$^{4+}$ in the LiMn$_2$O$_4$ thin film were clearly observed as shown in fig. 4. A large irreversible capacity in the first cycle is thought to be a decomposition of impurity phase in the LiMn$_2$O$_4$ thin film and/or at the interface between the thin film and LAGP solid electrolyte and a delamination of a part of the LiMn$_2$O$_4$ thin film due to a volume change upon cycling. The discharge capacity of the LiMn$_2$O$_4$ thin film was 42 mA h g$^{-1}$, which is 28% of its theoretical capacity (148 mA h g$^{-1}$) [22]. After the first cycle, reversible charge/discharge behavior was observed and coulomb efficiency was over 90%.

As supported by XRD (Figure 1) and Raman (Figure 2) characterizations, LiMn$_2$O$_4$ was successfully prepared on the LAGP solid electrolyte by the PVP sol-gel method combined with spin-coating method. In the galvanostatic charge/discharge test, two clear potential plateaus at 4.0 and 4.1 V vs. Li/Li$^+$ corresponding to the intrinsic redox potential of Mn$^{3+}$/Mn$^{4+}$ in the LiMn$_2$O$_4$, convincing us that the LiMn$_2$O$_4$ thin film worked as cathode of lithium batteries. However, the discharge capacity was not high enough. It was considered that some part of the thin film would be electrically isolated due to porous nature of the film and a volume change upon cycling which causes a contact loss between the thin film and electrode as shown in Figure 3.

Additionally, impurity phase would form at the interface between cathode and solid electrolyte and restrict smooth electrochemical reaction. This could be overcome by optimization of the preparation procedure such as usage of minimum amounts of solvent and lowering calcination temperature. This attempt is underway. New findings will be reported in due course.

Figure 4: Cyclic voltammogram of LiMn$_2$O$_4$ thin film on the LAGP solid electrolyte at scan rate of 1 mV s$^{-1}$
4. Conclusion

The electrochemical solid-solid interface between LiMn$_2$O$_4$ and LAGP was successfully fabricated by the PVP sol-gel method combined with spin-coating method. Clear redox behavior of prepared LiMn$_2$O$_4$ thin film on the LAGP solid electrolyte was confirmed, implying that application of the combined method to fabrication of thin film batteries is possible. However, the discharge capacity was smaller than theoretical one due to porous nature of the film. Further efforts are required to optimize the fabrication process.

References


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