



Short communication

Water-stable lithium anode with $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3\text{-TiO}_2$ sheet prepared by tape casting method for lithium-air batteriesMing Zhang^{a,b}, Keita Takahashi^b, Ichiro Uechi^b, Yasuo Takeda^b, Osamu Yamamoto^{b,*}, Dongmin Im^c, Dong-Jonne Lee^c, Bo Chi^a, Jian Pu^a, Jian Li^a, Nobuyuki Imanishi^b^aSchool of Materials Science and Engineering, State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China^bDepartment of Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan^cSamsung Advanced Institute of Technology, Samsung Electronics, Yongin, Gyeonggi 446-712, Republic of Korea

H I G H L I G H T S

- ▶ $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$ (LAGP)–5 wt.% TiO_2 lithium ion-conducting solid electrolyte sheets were prepared by a tape casting method.
- ▶ The composite sheet of LAGP and epoxy resin (about 4 wt.%) was water impermeable.
- ▶ The electrical conductivity of the composite sheet was $4.19 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C.
- ▶ The $\text{Li}/\text{PEO}_{18}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{composite}$ sheet was successfully operated as a lithium electrode in a saturated LiCl aqueous solution.

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A $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$ (LAGP) sheet was prepared using a tape casting method with a fine LAGP powder prepared from a sol–gel precursor. The addition of nanosize TiO_2 as a sintering additive was effective to enhance the ionic conductivity of the tape-cast sheet. The highest electrical conductivity of $8.37 \times 10^{-4} \text{ S cm}^{-1}$ was observed for the tape-cast LAGP sheet with 5 wt.% TiO_2 at 25 °C. A hybrid sheet of the tape-cast LAGP and epoxy resin was water impermeable. The electrical conductivity of the water impermeable hybrid sheet with ca. 4% epoxy resin was $4.19 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C. The three-point bending strength of the LAGP–5 wt.% TiO_2 –epoxy resin hybrid sheet was 111 N mm^{-2} , which is comparable with a $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{P}_{3-y}\text{Si}_y\text{O}$ glass ceramic plate. The $\text{Li}/\text{PEO}_{18}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{LAGP}$ –5 wt.% TiO_2 –epoxy sheet was successfully operated as a lithium electrode in saturated LiCl aqueous solution.

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1. Introduction

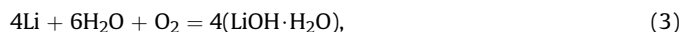
Lithium-air rechargeable batteries have theoretically higher energy density than lithium ion batteries, and are therefore attracting increased attention as possible power sources for electric vehicles [1–4]. Two types of lithium-air batteries have been developed; aqueous and non-aqueous systems. The non-aqueous system consists of a lithium electrode, a non-aqueous electrolyte, and an air electrode, and are based on two possible reactions [5]:



and



Reaction (1) is reversible, but reaction (2) is irreversible. In the aqueous system, the lithium electrode is protected by a water-stable lithium ion-conducting solid electrolyte, and the cell reaction is [6]:



where water in the electrolyte is involved in the cell reaction. The calculated energy densities including oxygen are 3460 Wh kg^{-1} for reaction (1) using an open circuit voltage (OCV) of 2.96 V, and 1910 Wh kg^{-1} for reaction (3) using an OCV of 3.0 V. The non-aqueous system has higher energy density than the aqueous

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system, but it has some serious problems, including high polarization for the charge and discharge processes, electrolyte decomposition, and contamination by moisture in the air. These problems could be overcome for the aqueous system. The most important issue for the aqueous system is to develop a water-stable lithium electrode, because lithium reacts severely with water and should be covered with a water-stable lithium conducting solid electrolyte. Recently, Visco et al. [7] proposed a water-stable lithium metal electrode protected by a NASICON-type water-stable lithium ion-conducting glass ceramic of $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{P}_{4-y}\text{Si}_y\text{O}_{12}$. (LATP). The discharge product of the aqueous lithium-air system is LiOH, and the LiOH is saturated to approximately 5% discharge depth, because of the solubility limit of LiOH in water at room temperature is ca. 5 mol L^{-1} . LATP is unstable in concentrated LiOH aqueous solution, but Imanishi et al. found that LATP is stable in an aqueous solution saturated with LiOH and LiCl [8]. Therefore, LATP could be used as the protective layer of a lithium metal electrode for lithium-air batteries with a LiCl saturated aqueous solution. The LATP glass ceramic, which is supplied by Ohara Co., Japan, had a high lithium ion conductivity of $3.5 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The glass ceramic was prepared by quenching from the melt and crystallized at high temperature. This glass ceramic is expensive and the sizes are limited. We have previously reported that $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ge}_{1.6}(\text{PO}_4)_3$ (LAGP) is stable in an aqueous solution saturated with LiOH and LiCl, and the electrical conductivity is higher than that of $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ [9]. LAGP is the other candidate for the protective layer of the water-stable lithium metal electrode. In this study, we have prepared LAGP thin sheet by the tape casting method, which is suitable for the production of large sized thin sheets. The electrical conductivity, mechanical properties, and water permeability of a hybrid sheet prepared with epoxy resin and the tape-cast sheets were examined. In addition, the stability and charge–discharge performance of the $\text{Li}/\text{PEO}_{18}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}-10\% \text{ BaTiO}_3/\text{LAGP}-\text{epoxy}$ hybrid sheet/saturated LiCl aqueous solution/Pt cell were examined. LAGP is unstable in contact with lithium metal; therefore, the polyethylene oxide (PEO)-based polymer electrolyte was used as an interlayer between Li and LAGP.

2. Experimental

The NASICON-type LAGP powder was prepared using a precursor prepared by the sol–gel method with citric acid, as reported previously [9]. Stoichiometric amounts of $\text{Ge}(\text{OC}_2\text{H}_5)_4$ (Aldrich), chemical grade LiNO_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in a 0.2 M aqueous solution of citric acid and stirred continuously with a magnetic stirrer to obtain a homogeneous solution. A certain volume of ethylene glycol [citric acid:ethylene glycol molar ratio = 1:1, (citric acid + ethylene glycol):(Li⁺ + Al³⁺ + Ge⁴⁺) molar ratio = 4:1] was added to the mixed solution to prevent the formation of hard agglomerates and promote polyesterification and polycondensation. The mixed solution was kept at 80 °C during the sol–gel preparation process. After a homogeneous solution was formed, the gel was kept at 170 °C for 1 day to allow the evaporation of water and to promote esterification and polymerization, and the gel was then heated at 500 °C for 4 h. The powder obtained was uniformly ground to a fine powder with an agate mortar and pestle before sintering at 800 °C for 5 h to complete the chemical reaction.

Stoichiometric amounts of LAGP powder made by sol–gel method, and TiO_2 (Aldrich), GeO_2 (Aldrich), or ZrO_2 (Tosoh) fine powders were dispersed in ethanol and toluene mixed solution (3:7 volume ratio) using Menhaden fish oil (2 wt.% to LAGP) as a dispersant. The mixed slurry was then ball milled with ZrO_2 balls for 24 h using high energy mechanical milling (HEMM; Fritsch Planetary Micro Mill). A certain amount of poly(vinyl butyral) (Aldrich, Butvar B-98, 7 wt.% to LAGP) as a binder and butyl benzyl

phthalate (7 wt.% to LAGP) as a plasticizer were then added into the mixed slurry and ball milled using HEMM for another 24 h. The slurry was defoamed for 3 min using a planetary vacuum mixer (Thinky, Japan) before casting to remove air bubbles. Tape casting was performed on a silicon coated polyethylene substrate foil using double blades with gap heights of 700 and 400 μm . The casting speed was constant at 60 cm min^{-1} . After tape casting, the green sheets were left to dry at room temperature for 24 h. The green sheet was cut into small pieces of $1.2-1.5 \text{ cm} \times 1.2-1.5 \text{ cm}$. Three green sheets were hot pressed together at 90 °C for 10 min and then sintered at 900 °C in air.

The LAGP and epoxy resin hybrid sheets were prepared by dropping a mixed dilute solution of 1,3-phenylenediamine (1 mol L^{-1}) and 2,2-bis(4-glycidioxyphenyl)propane (2 mol L^{-1}) in tetrahydrofuran on the surface of LAGP sheet. The LAGP sheets with the epoxy resin solution were kept in vacuum for several minutes to allow the solution to penetrate into the pores of the LAGP sheets. The hybrid sheets were then placed into an oven at 80 °C for 2 h and then at 150 °C for 24 h to allow evaporation of the solvent and to promote polymerization.

The crystal structure of the samples was analyzed using X-ray diffraction (Rigaku RINT-2500) with $\text{Cu K}\alpha$ radiation in the 2θ range from 10 to 90° at a scanning step rate of $0.02^\circ \text{ s}^{-1}$. Impedance measurements of the LAGP–epoxy resin hybrid sheet with gold electrodes sputtered on both surfaces were conducted using an impedance analyzer (Solartron 1260) in the temperature range from 20 to 80 °C and in the frequency range of 0.01 Hz–1 MHz. The impedance profiles were analyzed using a nonlinear instant fit program in the Z-View software. The hybrid sheets were immersed in an aqueous solution with saturated LiOH and LiCl at 60 °C for one week to test their stability. The LAGP sheets were then washed with distilled water and dried in a vacuum oven at 110 °C for 5 h before measuring the electrical conductivity and XRD patterns. The epoxy resin content in the samples was estimated from the weight loss measured by thermogravimetric analysis (TGA; Rigaku Thermoplus TG8120). The three-point bending strength of the LAGP sheet was measured using Shimadzu EZ-S 500 N at room temperature.

The water permeation test was performed using an H-type cell with saturated LiCl aqueous solution on one side and distilled water on the other. The LAGP sheet was packed using a plastic film. The package was then evacuated and heat-sealed apart from a hole with a 6 mm diameter on the LAGP sheet. The water permeation speed through the LAGP sheet was estimated from the change of the chloride ion content in the distilled water over time, measured using a chorine meter (Kasahara Chemical Instruments).

The lithium ion-conducting polymer membrane of $\text{PEO}_{18}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI)–10% BaTiO_3 was prepared using a previously reported casting technique [10]. A certain amount of PEO (Aldrich, average molecular weight 6×10^5) powder and lithium salt of LiTFSI (Aldrich) with Li/O = 1/18 were dissolved in a certain volume of acetonitrile. 10 wt.% nanosize BaTiO_3 particles of (100 nm particle size, Sakai Chemical Industry) were added to the solution as the filler. The solution was stirred at room temperature for 24 h in an Ar-filled dry glove box. The homogeneous slurry was then cast into a clean Teflon dish. The acetonitrile solvent was allowed to evaporate slowly in an Ar-filled dry glove box for 24 h, and then dried at 110 °C for 24 h under vacuum. The water-stable lithium anode was assembled by laminating lithium metal, $\text{PEO}_{18}\text{LiTFSI}-10 \text{ wt.}\% \text{ BaTiO}_3$ and the LAGP–epoxy resin hybrid sheets in a plastic package, leaving a circular window of 6 mm in diameter. Nickel foil was used as the anodic current collector. The stability and electrochemical performance of the water-stable lithium electrode were examined using a beaker-type cell of $\text{Li}/\text{PEO}_{18}\text{LiTFSI}-10 \text{ wt.}\% \text{ BaTiO}_3/\text{LAGP}-\text{epoxy}/\text{LiCl}$ saturated aqueous solution/Pt, air at 60 °C.

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