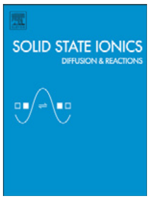
Solid State Ionics 198 (2011) 22–25

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Electrochemical properties of thin TiO_2 electrode on $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ solid electrolyte

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ARTICLE INFO

Article history:
Received 4 March 2011
Received in revised form 7 July 2011
Accepted 7 July 2011
Available online 17 August 2011

Keywords:
All-solid-state battery
Sol–gel method
Thin film battery
Lithium battery

ABSTRACT

A fabrication of all-solid-state thin-film rechargeable lithium ion batteries by sol–gel method is expected to achieve both the simplification and cost reduction for fabrication process. TiO_2 thin film electrode was prepared by PVP (polyvinylpyrrolidone) sol–gel method combined with spin-coating on $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) solid electrolyte which has wide electrochemical window. The thin film was composed of anatase TiO_2 that is the most active phase for Li insertion and extraction and contacted well with LAGP substrate. In the cyclic voltammogram, a redox couple was observed at 1.8 V vs. Li/Li^+ assigned to Li insertion/extraction into/from anatase TiO_2, indicating that the thin film worked as electrode for lithium battery. The charge and discharge test in various charge and discharge rates revealed that the discharge process (delithiation) is thought to be faster than charge process (lithiation). It is attested that the sol–gel process, which derives both simplification and cost reduction for fabrication process, can be applied to thin film battery using LAGP solid electrolyte.

1. Introduction

All-solid-state thin-film rechargeable lithium ion batteries have received considerable attention as the suitable power sources for some specialized applications, such as smart cards, implantable medical devices, and microelectromechanical systems [1–6]. The thin film rechargeable lithium batteries composed of thin-film electrodes and solid electrolytes have been extensively studied and have acquired great development.

In the fabrication process of these film batteries, thin films of electrodes, solid electrolyte, and current collectors are sequentially piled-up on a substrate using different kinds of vapor deposition techniques such as pulsed laser deposition, r.f. magnetron sputtering, and vacuum evaporation [7–12]. For the practical application of thin-film batteries, the fabrication process is desirable to be simplified as much as possible. One of the effective methods to overcome the above problem will be the use of the sol–gel method combined with spin coating method. Using the sol–gel method and spin coating method, fabrication of thin film electrode does not require vacuum condition, leading to achieve both the simplification and cost reduction for fabrication process.

We have succeeded on fabrication of $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ thin film electrode on $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) NASICON-type solid electrolyte by PVP (polyvinylpyrrolidone) sol–gel method and proof their good electrochemical properties [13,14]. However, electrochemical window of LATP electrolyte is limited by facile reduction of Ti^{4+} and this provides restrict application of the LATP [15–18] because the narrow window conducts to low energy and power densities of batteries.

$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) solid electrolyte is a member of Li ion conductive ceramics with NASION type structure. The total ionic conductivity of LAGP is 4.2×10^{-3} S cm^{-1} [19], which is comparable with LATP. Moreover, the LAGP has an advantage for the electrochemical window because Ge^{4+} is insensitive to reduction in contrast with Ti^{4+} [20]. Therefore, the all-solid-state thin-film rechargeable lithium ion batteries using LAGP electrolyte prepared by the sol–gel method are expected to not only provide high energy and powder densities, but also achieve both the simplification and cost reduction for fabrication process.

In this paper, we report fabrication of anatase TiO_2 thin film anode on the LAGP electrolyte by the PVP sol–gel method and its electrochemical properties.

2. Experimental

LAGP plate ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$) with 300 μm thickness was supplied from OHRA Inc. and used without any further treatment. The Li ion conductivity of the LAGP was measured with an impedance analyzer (YHP4192-A, Yokogawa) ranging from 5 Hz to 13 MHz at room temperature. For impedance analysis of the LAGP, both faces of the LAGP plate were sputtered with gold as ionically blocking electrodes.

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doi:10.1016/j.ssi.2011.07.003

TiO_2 thin film electrode was prepared by PVP sol–gel method. The Ti–O sol composed of $(CH_3)_2CHO)_4Ti$:PVP:CH_3COOH:i-C_3H_7OH in molar ratio of 1:1:12:20 was spin-coated under a rotation speed of 3000 rpm, in order to prepare Ti–O gel film on the LAGP plate. The gel film was converted to TiO_2 thin film by heating at 600 °C for 5 min. This process was repeated five times. Finally, the thin film was heated at 600 °C for 30 min. A weight of prepared TiO_2 thin film was measured by microbalance carefully.

Morphology of the prepared TiO_2 thin film was observed by scanning electron microscope (SEM, JSM-5310, JEOL). The characterization of prepared thin film was carried out by Raman spectroscopy (NRS-1000, Jasco) with 532 nm radiation.

Electrochemical measurements were performed using two electrode configuration. The working electrode was TiO_2 coated on LAGP solid electrolyte. In order to obtain electrical contact from TiO_2 surface, Au thin film was fabricated on TiO_2 surface by the dc sputtering method. Lithium metal was used for counter electrode as well as reference electrode. In order to avoid undesirable reaction between LAGP solid electrolyte and lithium metal, Li ion-loaded poly methyl methacrylate (PMMA) gel-polymer electrolyte was used as a buffer layer. The PMMA gel-polymer electrolyte was prepared by thermal polymerization. Methyl methacrylate monomer (MMA) containing ethylene glycol dimethacrylate (EGMA) as crosslinking agent was polymerized in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) containing 1 mol dm^{-3} $LiClO_4$. Azobisisobutyronitrile (AIBN) was used as polymerization initiator. The mixed weight ratio of MMA, EGMA, AIBN, and the mixed solvent was 1:0.05:0.02:2.87. The polymerization was carried out in inert atmosphere at 80 °C for 1 h. The thickness of the PMMA gel-polymer was 300 μm and its conductivity was ca. 1×10^{-3} S cm^{-1} at room temperature [14].

Cyclic voltammetry was also performed at a scan rate of 1 mV s^{-1} in a potential range from 1.5 to 2.5 V vs. Li/Li^+. This potential range was decided by electrochemical window of LAGP electrolyte. The LAGP was not stable below 1.5 V vs. Li/Li^+. A charge and discharge cycle test was also conducted to evaluate an electrochemical performance of the prepared TiO_2 thin film under galvanostatic conditions by using the same cell configuration. The charge (lithiation of TiO_2) and discharge (delithiation of TiO_2) currents were changed from 0.1 to 5 C. Cut off voltages were 1.5 and 2.5 V at charge and discharge processes, respectively. All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

3. Results

Fig. 1 shows the complex impedance plot of the Au/LAGP/Au. A semicircle in a frequency range 3 MHz to 25 kHz, which was attributed to the Li^+ ion conduction in the grain boundary of the LAGP and Warburg-type impedance were observed. This Warburg-type tail at low frequencies corresponds to a usual behavior of ionically conductive materials with ionically blocking electrodes [21]. The contribution of the Li^+ ion conduction in the crystal grain appeared in a higher frequency range than 3 MHz. The total resistance (R_t) was estimated to 220 Ω cm^2 by equivalent circuit of $(R_bQ_b)(R_{gb}Q_{gb})(Q_{el})$ (where R is the resistance, Q is the constant phase element, and the subscripts g, gb, and el refer to the grain, grain boundary, and electrode) [22]. The total Li^+ ion conductivity of the LAGP was estimated to 1.4×10^{-4} S cm^{-1} at room temperature from the total resistance (220 Ω cm^2) and thickness of LAGP (300 μm) using an equation shown below

$$\sigma(\mathrm{S/cm}) = \frac{t}{R_t}$$

where σ, R_t and t mean total conductivity, total resistance and thickness of LAGP, respectively.

The Raman spectra of anatase TiO_2 fabricated on Au substrate, LAGP substrate, and TiO_2/LAGP are revealed in Fig. 2. Four Raman bands were detected at 396, 462, 517, and 640 cm^{-1} in the spectrum of TiO_2/LAGP. It is obvious that the band at 462 cm^{-1} was assigned to LAGP substrate by comparison with Raman spectrum of LAGP itself. The other bands were attributed to B_{1g}, A_{1g}, and E_g bands of anatase TiO_2, respectively [23]. Other phases such as rutile TiO_2, which were the most possible impurities, were not detected in the prepared TiO_2 thin film.

Fig. 3 displays the SEM images of the TiO_2 thin film prepared on the LAGP substrate. The surface of the thin film was very smooth and no cracks were observed. The thickness of the thin film was estimated to be 0.6 μm from the cross-sectional view. The thin film contacted well with LAGP substrate and no void between them was observed.

Fig. 4 shows a cyclic voltammogram of the TiO_2 prepared on the LAGP solid electrolyte. An anodic peak was observed around at 2.1 V vs. Li/Li^+ and a cathodic peak was confirmed at 1.6 V. This is attributed to Li insertion/extraction into/from anatase TiO_2 [24] although some deviation from intrinsic redox potential of TiO_2 (1.8 V) was observed. The reversible electrochemical behavior suggested that the Li ion transfer between TiO_2 and LAGP took place reversibly.

Charge and discharge curves of TiO_2 thin film on LAGP substrate are revealed in Fig. 5. A potential plateau around 1.8 V in the charge and discharge curves was ascribed to intrinsic redox potential of anatase TiO_2. In the first cycle, irreversible capacity corresponds to irreversible

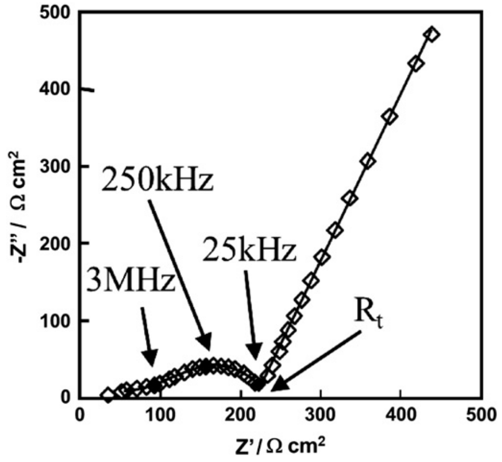

Fig. 1. Complex impedance plot of Au/LAGP/Au.

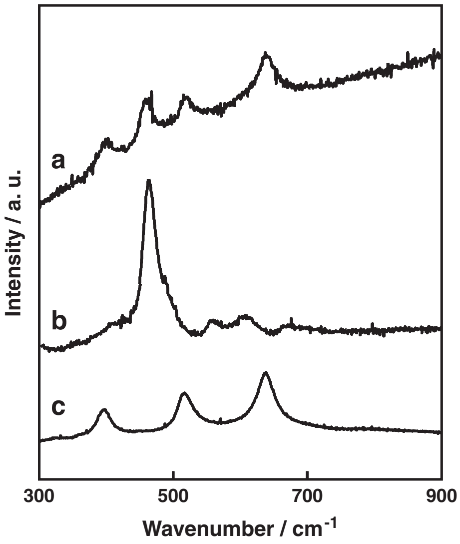

Fig. 2. Raman spectra of (a) TiO_2/LAGP, (b) LAGP, and (c) anatase TiO_2.