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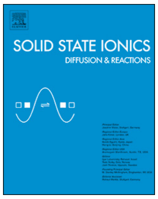

Characterization of thin film $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ electrolyte for all-solid-state Li-ion batteries

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ABSTRACT

Since addition of Al in $Li_{0.5}La_{0.5}TiO_3$ has enhanced ionic conductivity in bulk materials, it is important to apply this material on all solid state thin film batteries. Because some of the good ionic conductors such as Lithium Phosphorus Oxynitride (LiPON) are sensitive to oxygen and moisture and their application is limited, so amorphous $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ (LLTAlO) is a most promising candidate because of its stability. In this study, the crystalline LLTAlO targets were prepared changing the amount of x content by conventional solid state reactions. Using these targets, lithium lanthanum titanium oxide (LLTO) thin film electrolytes were deposited on ITO/SLG substrates by radio frequency magnetron sputtering system in Ar atmosphere. The structural and compositional properties of targets and thin films were characterized by SEM, XRD, Raman spectroscopy and XPS. It was found that all targets are crystalline while the thin films are amorphous. To understand the effect of Al doping on ionic conductivity, electrical measurements were done at room temperature by AC impedance spectroscopy forming ITO/LLTAlO/Al structure like capacitor. Highest ionic conductivity result, 0.96×10^{-6} S·cm^{-1}, is obtained from the nominal thin film composition of $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ ($x = 0.05$) at room temperature measurements. Heat treatment is also conducted to investigate to understand its effect on ionic conductivity and the structure of the thin films. It is found that ionic conductivity enhances with annealing. Also, temperature dependent ionic conductivity measurements from 298 K to 385 K are taken in order to evaluate activation energy for Li-ion conduction.

1. Introduction

Due to the increasing demand of energy sources, it is crucial to develop energy storage technology in a way that the environment is protected and give response to demands of today's living standards like higher energy density, longer lifespan, lightweight and flexible designs [1]. All solid state batteries have attracted much attention to bring solutions for new improvements. Commonly used liquid electrolytes have begun to fail because of some safety concerns like leakage and pollution, although they serve high ionic conductivity at room temperature [2]. On the other side, lithium ion conducting solid electrolytes have received substantial interest because of their significant advantages such as thermal stability, resistance to shocks and vibrations, and miniaturization capability [3].

Especially by the thin film applications of all solid state batteries, it is possible to provide higher volumetric and gravimetric energy densities [4,5]. Electrolyte layer, which is the main focus in this study, is responsible for the ionic conduction from anode to cathode regions during charge and discharge cycle of a battery. This phenomenon has crucial importance to determine system performance in terms of charge/discharge rate, power density and efficiency [6].

The first compound of this solid electrolyte family of $Li_{3x}La_{(2/3)-x}TiO_3$ was synthesized by Belous et al. [7] and their outstanding room temperature lithium conductivity enhanced by Inaguma et al. [8] with highest ionic conductivity 10^{-3} S/cm up to that date. Since then, much attention has been paid to ABO_3 perovskite type $Li_{3x}La_{(2/3)-x}TiO_3$ (LLTO) compound and its structurally related modifications to enhance its ionic conductivity. The reason for this high ionic conduction is explained by the presence of vacancies on A-site of the lattice which allows Li^+ to move freely through the vacant sites of the ABO_3 perovskite LLTO structure [9]. Furthermore, it is found that perovskite structure can tolerate having different valence states on A-site and B-site and this enables to develop substitutional structure modifications like Al substitution for Ti to increase ionic conductivity like in our research topic. In the study of Morata-Orrantia et al. [10], $La_{2/3}Li_xTi_{1-x}Al_xO_3$ was examined as bulk structure with compositions of x

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and the highest ionic conductivity was calculated as 7.6×10^{-5} S·cm^{-1} at room temperature, which proved that Al substitution have positive effect on ionic conduction up to some level. During the intercalation process, a reduction of Ti^{4+} to Ti^{3+} at low potentials causes short circuit by the electronic conduction [11]. So with the light of this knowledge, it is necessary to prevent reduction. Therefore, substitution of Al for Ti becomes our focus in this research [12]. Besides, lower effective ionic radii of Al^{3+} ($r_{Al}{}^{3+} = 0.53$ Å) compared to Ti^{4+} ($r_{Ti}{}^{4+} = 0.605$ Å) enables less reduction by Al substitution [13]. Furthermore, different composition-structure and ionic conductivity properties of LLTO were studied by Youmbi et al. [14] and found that $Li_{0.5}La_{0.5}TiO_3$ composition has the highest ionic conductivity as 1.7×10^{-3} S·cm^{-1} among $Li_{0.34}La_{0.51}TiO_{2.94}$, $Li_{0.27}La_{0.59}TiO_3$, $Li_{0.34}La_{0.56}TiO_3$ (cubic), $Li_{0.34}La_{0.56}TiO_3$ (tetragonal), $Li_{0.10}La_{0.63}TiO_3$ compositions.

As a result, $Li_{0.5}La_{0.5}TiO_3$ composition is chosen as our starting material, later by aluminum substitution $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ samples were synthesized with different x compositions (x = 0.01, 0.05, 0.10, 0.15). The powders were prepared after some steps of conventional solid state reactions, and then they were pressed in a Cu-base plate in order to form a ceramic powder target for the RF magnetron sputtering process. $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ (LLTAlO) thin films were grown on indium tin oxide (ITO)/Soda lime glass (SLG) substrate under pure Ar atmosphere. ITO/SLG, which were grown and improved by our group [15,16], were preferred as a substrate to obtain contact from the back side of the thin film electrolyte for the impedance measurements to determine ionic conductivities. Ionic conductivity of samples was determined using probe station. Furthermore, to explain the relationship between the ionic conduction and the structure of the thin films, SEM, XRD, Raman and XPS analysis were realized for the structural characterizations. In the present study, Al doped LLTO thin film growth is the first study according to the best of our knowledge.

2. Experimental

2.1. Target preparation

The $Li_{0.5}La_{0.5}TiO_3$ pure and doped targets were prepared by conventional solid state reaction from stoichiometric amounts of Li_2CO_3 (Sigma Aldrich, 99.997%), La_2O_3 (Sigma Aldrich, 99.999%), and TiO_2 (Sigma Aldrich, > 99.5%) powders. The batch of powders was mixed by using agate and pestle for 6 h in order to obtain homogeneous mixture for the calcination process. Then, the stoichiometric mixture of the powder was put in alumina crucible boat and calcinated 3 times at 1200 °C in air for 6 h. During these treatments CO_2 gas was released. After every step of calcination, powder was grinded. Finally, the calcinated batch was poured in a 2 inch circular Cu base plate ground and pressed with a cylindrical button at 5 MPa and sintered at 600 °C for 1 h in air to have compact and solid mass form for sputtering process. In addition, for Al doping, Al_2O_3 (Sigma Aldrich, 99.99%) powder was added to mixed powder after the second and third calcination was performed again at 1200 °C for 6 h in air [17] for various stoichiometric Al doped LLTO targets. The produced LLTO targets were placed into the sputter gun of the vacuum chamber pumped by turbomolecular pump to grow LLTO thin films using RF magnetron sputtering technique.

2.2. Thin film deposition by RF magnetron sputtering technique

Through RF-magnetron sputtering method, thin films were deposited under high vacuum on SLG and ITO/SLG substrates. The sputtering was done using the pure and Al doped LLTO targets. Before deposition, the substrates were cleaned in ultrasonic cleaner with ethyl alcohol and de-ionized water, respectively, for 5 min. When the vacuum chamber was evacuated down to low 10^{-6} Torr, 5 min pre-sputtering of LLTO and LLTAlO target, and later 60 min deposition was carried out under 50 sccm Ar atmosphere. The working gas pressure, the distance between the target and substrate, and the sputtering power were 4.78 mTorr, 13 cm, and 96 W, respectively. The film thicknesses were measured as 120 nm by profilometer. LLTO and LLTAlO films were also subjected to annealing process at temperatures 100, 200, 300, and 400 °C for 2 h in air ambient to observe the effect of annealing treatment on the structure and ionic conductivity of the solid state electrolyte.

2.3. Characterization

The crystallinity of the various composition targets and the thin films were determined by X-ray diffraction method using X'Pert Pro diffractometers with Cu K_α X-ray radiation wavelength of 1.54 Å over the angular range $20^\circ < 2\theta < 80^\circ$ with a 0.0334° step. The surface morphology of the thin films with various Al_2O_3 content was determined by scanning electron microscopy (SEM) using Philips XL 30SFEG operated at 3.0 kV using TLD detector. Confocal Raman spectroscopy setup (Scientific Instruments) with Argon laser having 488 nm excitation wavelength with 600 grating was used to determine the vibrational peaks of $Li_{0.5}La_{0.5}TiO_3$ and $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ targets with various x content.

X-ray photoelectron spectroscopy (XPS) analyses were performed using a SPECS Phoibos 150 3D-DLD system with using Mg K_α radiation ($h\nu = 1254$ eV) operated at 200 W, 1.5 kV. The high resolution scans of each element in $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ were conducted at 30 eV pass energy with a scan rate of 0.1 eV/s and the dwell time of 1 s. The spectra were calibrated with respect to C 1s at 284.6 eV which is the characteristic of aromatic/aliphatic carbons.

In order to evaluate ionic conductivities of the thin films on ITO/SLG, Al was evaporated on the upper side of the thin films via Leybold UNIVEX thermal evaporation device by using a shadow mask. Aim of the mask usage was to create contact areas for the ionic conductivity calculations. Janis Probe Station was used to take contacts from ITO on the back side and Al on the top. Impedance measurements were performed at controlled temperatures within the frequency range from 0.1 Hz to 200 kHz with IM 3590 HIOKI impedance analyzer.

3. Results and discussion

3.1. Characterization of the targets and $Li_{0.5}La_{0.5}Ti_{1-x}Al_xO_3$ thin films

The surface morphology and the microstructure of thin films were characterized by SEM. Fig. 1(a) shows the morphology of the ITO surfaces on SLG substrate. The image shows grain structure as seen most of the ITO studies [15]. In Fig. 1(b), the undoped LLTO film surface can be seen. It is understand that the grown films follow similar surface morphology of the underlayer ITO surface. SEM images of thin films deposited with different Al substitution were also presented in Fig. 1(c), (d), (e) and (f). It can be observed that LLTAlO thin films have also similar grain size with ITO film. It is found that the all coated surfaces have the same morphology with ITO surfaces showing that the Al substitution does not affect the morphology of the grown films on ITO.

X-ray diffraction (XRD) analysis for the crystallographic characterization of the targets and produced thin films were done to determine the perovskite LLTAlO structure. In Fig. 2, all the diffraction peaks of the targets, at 2θ = 29.3°, 32.8°, 40.3°, 47.0°, 58.4°, 68.6° and 78.1° correspond to planes (101), (110), (112), (200), (212), (220) and (310) that can be ascribed to the reflections of $LiLaTiO_3$ crystalline phase [18], which confirms that the fabrication process conducted in this work is appropriate with those reported in related literature results [19].

The thin films of LLTO and LLTAlO deposited on ITO/SLG substrates do not show any crystalline peaks of LLTO target. Thin films are amorphous, since peaks observed in Fig. 3 belong to ITO/SLG substrate. When the peaks of ITO substrate are investigated, there is a broad peak