Preparation and performance of novel LLTO thin film electrolytes for thin film lithium batteries

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We prepared a series of lithium lanthanum titanate (LLTO) thin film electrolytes by radio frequency (RF) magnetron sputtering using LLTO targets in a N₂ atmosphere. We also deposited the LLTO thin films in an Ar atmosphere under a same condition as references for comparison. The microstructure morphology and the composition of the thin films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. Results show that the thin film has an amorphous structure with a uniform surface and it is free of pinholes and cracks. Impedance measurements reveal that the ionic conductivity of the electrolytes is beneficial for all solid lithium batteries dependent on the lithium content at room temperature. We found that the amorphous LLTO thin film performs well and it has potential application in microbatteries for use in microelectronic devices.

LLTO thin film electrolytes, RF magnetron sputtering, ionic conductivity, lithium batteries

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Thin film energy storage has attracted much attention recently because of the application of ultra-miniaturization in microelectronic devices such as dynamic random access memory (DRAMs) and implantable medical devices [1–3]. By comparison with other microelectronic sources, thin film lithium batteries can potentially store the most energy applied to microelectronic devices because of their high specific energy, long cycle life, good safety performance and environmental friendliness [4–7].

Solid electrolytes are important components in thin film lithium batteries and the performance of a thin film lithium battery is greatly affected by its solid electrolyte [8,9]. It has been reported that the ionic conductivity of La_{2/3-x}Li_{3-x}TiO₃ ($x=0.11$) is able to reach 10⁻³ S/cm at room temperature, making the study of this kind of electrolyte with high ionic conductivity attractive. Recently, lithium lanthanum

titanate (LLTO) has become a very interesting material [10–12] because it has a high rate of ionic conductivity in the amorphous state. And the amorphous LLTO is one kind of fast ionic conductor [13].

Thin film fabrication can reduce the thickness of the electrolyte layer, resulting in a reduction in the internal resistance of devices. A large surface area is also necessary to achieve a large contact area for a large output current. RF magnetron sputtering is an effective thin film deposition technology for it can be easily used to fabricate large-scale and dense films with outstanding performance [14–16].

In this work, we successfully prepared LLTO thin film electrolytes using RF magnetron sputtering. This constitutes a new chemical composition with an amorphous glassy structure and predominantly ionic conduction. We prepared the nitride LLTO films for the first time with different lithium contents and reported here their effect on structure and ionic conductivity. We also deposited the LLTO thin film in

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an Ar atmosphere in the same condition for comparison. The properties of all thin films were studied and used as a criterion for finding high performance film electrolytes.

1 Experimental

1.1 Preparation of targets

The reagents Li_2CO_3 , La_2O_3 and TiO_2 were mixed in different molar ratios (1.2:1:4, 1.5:1:4, 1.8:1:4, 2:1:4) and they were melted at 700°C for 4 h in an electrical furnace. Then, the mixtures were calcined at 1050, 1100 and 1200°C , respectively, all for 12 h [17]. The obtained ceramic was then ball-milled to obtain a fine powder. Finally, the ultimate powder compound was pressed into a 60 mm diameter thin slice. And the slice was sintered at 1100°C for 5 h. The composition of the LLTO target was $\text{Li}_{0.6}\text{La}_{0.5}\text{TiO}_3$, $\text{Li}_{0.75}\text{La}_{0.5}\text{TiO}_3$, $\text{Li}_{0.9}\text{La}_{0.5}\text{TiO}_3$, $\text{LiLa}_{0.5}\text{TiO}_3$, respectively.

1.2 Deposition of the thin films

The LLTO thin films were deposited on Si-wafer or stainless steel sheet or glass slide which has been sputtered two aluminium (Al) layers to make the LLTO film stuck in the middle, using the target prepared in last step. A working power of 100 W and a room temperature were applied to the target under the purity N_2 atmosphere (purity 99.999%). And the gas pressure was kept at 1 Pa accompanying with the sputtering process lasted for 10 h. Moreover, to guarantee cleanliness, the pressure of the sputtering chamber was lowered to 7.0×10^{-5} Pa before magnetron sputtering.

The thin film electrolytes were fabricated on a Si-wafer to determine their surface morphology and they were also fabricated on a stainless steel sheet to determine their structures, morphologies and compositions. The sandwich structure which was deposited on glass slide was used to measure the ionic conductivity and electrochemical window of LLTO.

For comparison, non-nitrided LLTO thin film electrolytes were prepared in pure Ar atmosphere under the same conditions.

1.3 Characterization of properties

XRD analysis (Rigaku, Japan) was used to determine the crystallinity, crystal parameters and structure of the target and the thin film. The surface morphology was determined using scanning electron microscopy (SEM). And the thickness of the thin film was determined by SEM. The chemical composition of the electrolyte membrane structure was measured using X-ray photoelectron spectroscopy (XPS). Electrochemical impedance spectroscopy and cyclic voltammetry (CV) were carried out using an electrochemical workstation CHI660A in the frequency region from 1 Hz to 100 kHz.

2 Results and discussion

2.1 Morphology and structure of the thin films

As mentioned above, the electrochemical properties of the thin films are related to their microstructures. The surface roughness of the thin film electrolyte directly affects the ionic conductivity of the electrolyte. A film containing cracks would decrease the battery capacity and could even shorten the cycle life of the battery. The surface and cross-sectional view of the LLTO thin film, which was prepared under an Ar atmosphere on a Si-wafer substrate, is shown in Figure 1. In Figure 1(a) and (c), the surface of the film is smooth and it has a noncrystalline structure with no cracks or pinholes. Furthermore, the cross-sectional SEM image of the film (Figure 1(c)) shows that the thickness of the film is about $2.63\text{ }\mu\text{m}$.

Figure 1(b) shows that the surface of the thin film prepared in a N_2 atmosphere is smoother and more uniform with no regular particles or an orderly arrangement by comparing with the film prepared under an Ar atmosphere. The thickness of the film that was prepared under a N_2 atmosphere is about $1.5\text{ }\mu\text{m}$ less than the film prepared under an Ar atmosphere (Figure 1(d)). The results indicate that the choice of synthesis atmosphere is important because it greatly influences the microstructure of the films.

Figure 2(a) shows the XRD pattern of the LLTO target in which the lithium content is 150%. The LLTO target has some sharp diffraction peaks, and these are due to the diffraction of crystalline LLTO. Figure 2(b) shows the XRD pattern of LLTO film. The microcrystalline peaks respectively correspond with the peak of (101) facet (25°) and (110) facet (35°) of LLTO target observed in Figure 1(a). There are no sharp diffraction peaks which are diffracted by crystals in the XRD pattern of LLTO film. As expected, the LLTO thin film electrolyte that was deposited under a N_2 atmosphere onto the stainless steel substrate using the above mentioned target has an amorphous structure. The XRD pattern for the thin film electrolyte only shows sharp peaks from the stainless steel substrate (i.e. 43.582° , 50.791° and 74.697°).

Therefore, an amorphous LLTO thin film was obtained when using the crystalline LLTO target and the RF magnetron sputtering method at a N_2 working pressure of 1 Pa, at room temperature and with an RF power of 100 W.

XPS was used to characterize the chemical nature of thin film electrolytes. Figure 3(a) shows the XPS spectra of the nitride LLTO thin film with the lithium content of 150%. The XPS spectra consist of peaks assigned to Li, La, Ti, O, N and C. $\text{C}1\text{s}$ was used as an internal reference (284.8 eV). An obvious peak around 396.0 eV was observed and this is attributed to the nitrogen incorporation. The composition of the thin films can be calculated using the following equation:

Figure 1 SEM images of the surface (a) and cross-section (c) of the LLTO (lithium content is 150%) thin film prepared under an Ar atmosphere, and the surface (b) and cross-section (d) of the LLTO thin film prepared under a N₂ atmosphere.

Figure 2 XRD patterns of the LLTO (Li_{0.75}La_{0.5}TiO₃) target (a) and the LLTO (Li_{0.75}La_{0.5}TiO₃) thin film (b) prepared under a N₂ atmosphere.

$$C_x = \frac{n_x}{\sum_{i=1}^k n_i} = \frac{I_x/S_x}{\sum_{i=1}^k I_i/S_i}, \quad (1)$$

where n_x is the atomic number density, k is the number of elements detected in the sample, I_x is the photoelectron emission intensity of a specific element x in the XPS survey spectrum and S_x is the atomic sensitivity factor of element x in the sample, as determined from the empirical peak area data [18].

Figure 3(b) illustrates the N 1s XPS spectrum of the thin film. It indicates that the nitrogen is incorporated into the internal structure of the film. There are two asymmetric peaks at 395.4 and 399.8 eV and they can be attributed to two different bonding states of nitrogen atoms [19]. The peak at 395.4 eV represents nitrogen bonds of doubly coordinated nitrogen --N= and the other feeblish peak represents

Figure 3 XPS of the LLTO thin film (a) and the N1s region of the LLTO thin film (b) prepared under a N₂ atmosphere.

triply coordinated nitrogen --N< . This indicates that the nitrogen actually substitutes the partial oxygen during deposition. Hence, --N= and --N< nitrogen atoms replace --O-- and

=O oxygen atoms making for a more cross-linking network in internal structure of the film. This micro-structural modification was considered to be beneficial for the ionic conduction and electrochemical stability of film electrolytes.

2.2 Analysis of impedance properties

Ionic conductivity is a very important parameter for thin film electrolytes and the ionic conductivity of the LLTO films was obtained using the following equation:

$$\sigma = d/(R \cdot A), \quad (2)$$

where d is the thickness of the film, A is SS electrode/electrolyte interface area and R is the resistance of the film that is determined from the measured impedance by selecting the value of Z' when $-Z''$ goes through a local minimum in the electrochemical impedance spectra [20,21].

Impedance spectroscopy was carried out to determine the ionic conductivity using a sandwich structure blocking electrode cell (Al/LLTO/Al). The impedance spectra are typical of dielectric relaxation processes. The impedance spectra of the LLTO thin film electrolytes prepared under N_2 and Ar atmospheres are shown in Figures 4 and 5, respectively. It seems that the spectra are normal alternating current (AC) impedance spectra of electronic conductors with no straight sloping line at the low frequency end.

Figure 4 shows the impedance spectra of the LLTO thin film electrolytes with different lithium content which were prepared under a N_2 atmosphere. We found that an optimal lithium content exists and the highest ionic conductivity was

achieved for a lithium content of 150%.

From Figure 5(a) it is obvious that the LLTO thin film electrolyte that was prepared under an Ar atmosphere is an electronic conductor at lithium content lower than 150%, which is not suitable for solid-state thin film battery electrolytes. However, at lithium content of 150% the ionic conductivity of the thin film electrolyte can reach 10^{-6} S/cm, which is very similar to that reported in the literature [17]. At a lithium content of 180% the ionic conductivity decreased to 3×10^{-7} S/cm. At a lithium content of 200% the battery was shortened. It is obvious from Figure 5(b) that the surface of this film has defects such as cracks and pinholes,

Figure 4 Electrochemical impedance spectroscopy of the LLTO thin films with different lithium content prepared under a N_2 atmosphere.

Figure 5 Electrochemical impedance spectroscopy of the LLTO thin films with different lithium contents prepared under an Ar atmosphere and a SEM image of the surface of the LLTO thin film for a lithium content of 200% prepared under an Ar atmosphere.

which results in its poor electrochemical performance. Comparing with the LLTO films fabricated under an Ar atmosphere, the LLTO films fabricated under a N₂ atmosphere show the nature of the ion conductor in a more wider range of lithium content. The nitride LLTO films have the better combination property than no-nitride LLTO films with an approximate ionic conductivity.

From above results, the LLTO films with 150% lithium content deposited in N₂ or Ar atmosphere both reveal the biggest ionic conductivity. According to the equation, $\sigma = \text{charge density} \times \text{mobility}$, the ionic conductivity is determined by the product of charge density and mobility [22]. Therefore, there are two ways to increase the Li⁺ ionic conductivity of thin films. One is increasing the Li⁺ content to increase the charge carrier density. Another reason for the increase in ionic conductivity is related to the ionic mobility. Especially, in nitride films, N³⁻ substitution of O²⁻ leads to a more reticulated network for the faster ionic mobility. These cross-linking structures create more conduction paths with a lower activation energy and give rise to a notable modification of glass properties. However, when the lithium content overtops the ratio of 150%, the ionic conductivity decreases obviously, and this is due to the ions gather which prevent ionic conduction resulting low charge transport on electrode-electrolyte interface.

Electrochemical stability is also an essential criterion for a solid electrolyte. Figure 6 shows the cyclic voltammogram of the nitride LLTO thin film with lithium content of 150%. The irreversible onset of the current can be defined as the electrolyte breakdown voltage. An obvious current charge occurred above 2.0 V at high voltage and another obvious current charge occurred at -1.5 V at low voltage, this suggests that the film remains stable at high potentials of more than 3.0 V where lithium batteries usually operate. This thin film electrolyte is, therefore, predicted to be a promising candidate for all-solid-state thin film lithium batteries [23]. Another nitride LLTO film with lithium content of 120%

Figure 6 Cyclic voltammogram of the LLTO thin film prepared under a N₂ atmosphere with lithium contents of 120% and 150%.

was used as a comparison, which shows a lower decomposition voltage at 1.2 V at high voltage and its electrochemical stability is worse than the film with lithium content of 150%.

3 Conclusion

A series of LLTO thin film electrolytes were prepared by RF magnetron sputtering using LLTO targets under a pure N₂ atmosphere. Their morphological structures and electrochemical properties were investigated in detail. The results show that the films possess amorphous structures and are smooth, dense and uniform with no cracks or pinholes. Furthermore, the ionic conductivity of the films that were prepared under a N₂ atmosphere can reach 9.4×10^{-7} S/cm at room temperature when the lithium content is 150%. These kinds of electrolytes are close to the film deposited in an Ar atmosphere in morphology and performance. The serious electrolytes have good properties and are promising candidate materials for all solid state thin film lithium batteries.

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