第15卷 第2,3期 广东有色金属学报 Vol. 15, No. 2,3
2005年9月 JOURNAL OF GUANGDONG NON-FERROUS METALS Sep 2005

Article ID: 1003−7837(2005)02,03−0462−05

Fabrication and electrochemical properties study of LiSiPON electrolyte films

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Abstract: The LiSiPON electrolyte films were prepared by magnetron sputtering method with different N_2 working pressure. The structure, morphology, composition and the relationship between ionic conductivity and N content were studied in detail. The result showed that N content in the films depended on N_2 partial pressure. With the N_2 partial pressure increasing, N content increased firstly and gained a maximum values then decreased. N content in the LiSiPON films affected the ionic conductivity of the films. The ionic conductivity of the films increased with the N content increasing, and could reach a maximum value 10.4×10^{-6} S/cm.

Key words: N content; ionic conductivity; LiSiPON; electrolyte; thin film

CLC number: TM 911.4 **Document code**: A

1 Introduction

Solid electrolyte films have been attracted much attention in their application to electronic devices, high power density batteries due to their higher ionic conductivity, lower electronic conductivity and lower activation energy[1,2]. Li-ion conducting, inorganic, solid electrolyte films have been used for fabricating all-solid-state thin film lithium batteries and several kinds of materials for electrolyte films have been studied nowadays.

Kanehori[3] reported the fabrication of all-solid-state thin film lithium batteries using $Li_{3.6}Si_{0.6}P_{0.4}O_4$ film as electrolyte film. Levasseur[4] and Creus[5] studied the Li_2O-B_2O_3-Li_2SO_4 and Li_2S-SiS_2-P_2S_4 electrolyte thin film respectively, and used them for fabricating all-solid-state thin film lithium batteries successfully. Bates[6] made use of $Li_{3.3}PO_{3.9}N_{0.17}$ (LiPON) as electrolyte film and fabricated several kinds of all-solid-state thin film lithium batteries, such as Li/LiPON/$LiCoO_2$ and Li/LiPON/V_2O_5. Liu[7] deposited LiPON electrolyte thin films by nitrogen plasma-assisted deposition coupled with electron-beam reactive evaporated Li_3PO_4 and prepared a new all-solid-state thin film lithium battery of Li/LiPON/$Ag_{0.5}V_2O_5$. Lee[8,9] investigated the Li;SiPON electrolyte thin films with different composition and fabricated a lithium battery of $LiCoO_2$/LiSiPON/$Si_{0.7}V_{0.3}$.

LiSiPON solid electrolyte thin films attracted much attention as a new kind of electrolyte material due to its higher ionic conductivity and perfect electrochemical stability[9]. However, there are few reports a-

Received date: 2005−06−23

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bout the fabrication and electrochemical behavior study of LiSiPON solid electrolyte thin films. Therefore, there are much works to investigate the electrochemical characteristic of LiSiPON solid electrolyte films. In this paper, we report the preparation of LiSiPON electrolyte films with magnetron sputtering method by adjusting process parameters and investigate the relationship between ionic conductivity of LiSiPON films and different N_2 working pressure.

2 Experimental

LiSiPON electrolyte thin films were deposited by magnetron sputtering method with different N_2 working pressure. The target for LiSiPON electrolyte was made by cold pressing then sintering the mixture comprising a lithium phosphate/lithium silicate, $0.6Li_3PO_4 \cdot 0.4Li_2SiO_3$ at 1050℃ for 5 h in air. The diameter of sputtering target is about 60 mm. In the depositing procedure, the distance between the target and substrates, depositing power and substrate temperature were fixed at 60 mm, 130 W and ambient temperature, respectively. The working gas is pure N_2(99.99%) and the gas flow was 20 cm^3/min。 The relationship between N content and ionic conductivity of LiSiPON electrolyte films was investigated in detail by controlling the N_2 working pressure (from 0.13 Pa to1.6 Pa) during depositing process.

For measurement of the lithium ionic conductivity of LiSiPON electrolyte, Pt/LiSiPON/Pt sandwich structure was made on silicon substrate with a typical thickness of 1.0μm and area of 0.08 cm^2. The ac impedance measurement to determine ionic conductivity was carried out with EG&G M388 (Model 273A) electrochemical impedance analysis system in the range from 1 Hz to 100 kHz at room temperature.

The structures of $0.6Li_3PO_4 \cdot 0.4Li_2SiO_3$ target and LiSiPON electrolyte films were studied with X-ray diffraction (XRD, Rigaku, Japan). The compositions of LiSiPON electrolyte films were determined with X-ray photoelectron spectroscopy (XPS, MkII, VG). The thickness of the films was measured with an Alpha-Step profilometer (Sloan dektak II).

3 Results and discussion

Fig. 1 showed the SEM image of as-deposited LiSiPON electrolyte films. We can see that the surface of electrolyte film is very smoothing and fine, and no defects such as grain agglomeration, pinhole and crack. For electrolyte thin films, this kind of surface is very important because the surface roughness influenced the ionic conductivity of electrolyte films and cycling behavior of solid state thin film batteries.

The X-ray diffraction pattern of $0.6Li_3PO_4 \cdot 0.4Li_2SiO_3$ target prepared by heating the mixture was shown in Fig. 2. The (a) curve in Fig. 2 showed that $0.6Li_3PO_4 \cdot 0.4Li_2SiO_3$ target was composed of the γ-Li_3PO_4 and Li_2SO_3 phases[10]. The (b) curve of Fig. 2 was the XRD pattern of LiSiPON thin film prepared by magnetron sputtering method and it has no diffraction peaks, which showed that LiSiPON thin film was typical amorphous structure. For LiSiPON electrolyte films, the amorphous structure has more vacancies for the moving and conducting of lithium ion thus the activation energy for lithium ion moving reduced. Therefore, the ionic conductivity of amorphous LiSiPON electrolyte films is much higher than that of the crystalline electrolyte films.

A typical integral XPS spectrum of the as-deposited LiSiPON film is presented in Fig. 3. There is an intense peak of N 1s, indicating nitrogen has been incorporated into the structure of Li_3PO_4. According to the XPS data, it can be calculated the stoichiometric composition and N content of the LiSiPON films. The results were shown in Table 1. The N content of LiSiPON film, 8.8%, is much small when the N_2 working pressure was 0.13 Pa. With the increasing of N_2 working pressure, N content also increased and

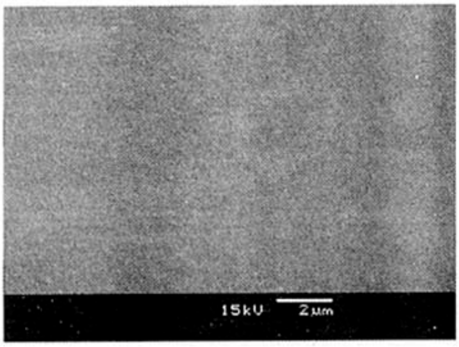

Fig. 1 SEM image of the LiSiPON electrolyte thin film

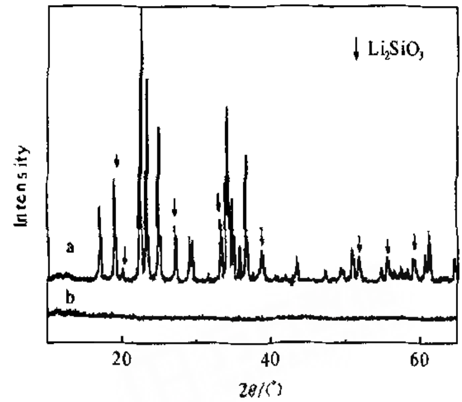

Fig. 2 XRD patterns of 0. 6Li_3PO_4 • 0. 4Li_2SiO_3 target (a) and LiSiPON electrolyte thin film (b)

reached a maximum value, 15. 1%, under the N_2 working pressure of 0. 53 Pa. However, when the N_2 working pressure is above 0. 53 Pa, the N content become small not large. It's only 5. 1% when the N_2 working pressure is 1. 6 Pa. Therefore, LiSiPON electrolyte films with different N content can be prepared by adjusting N_2 working pressure.

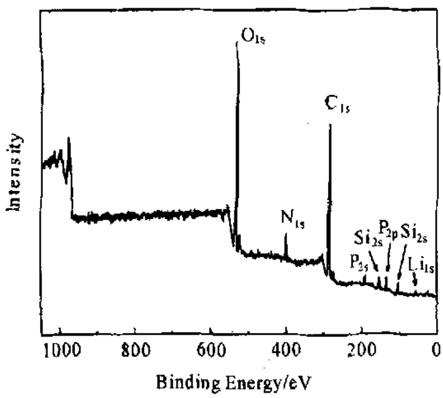

Fig. 3 XPS spectrum of LiSiPON electrolyte thin film

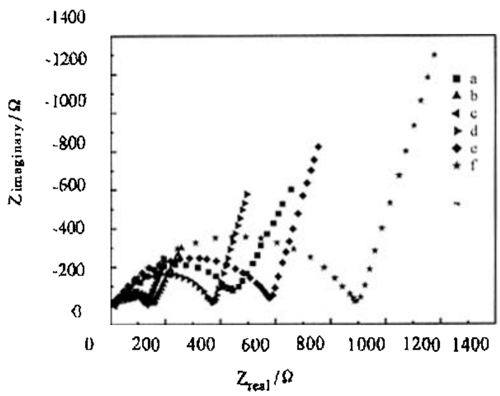

Fig. 4 AC impedance spectra of the LiSiPON electrolyte films

AC impedance spectrums of the LiSiPON electrolyte films measured at room temperature (about 23℃) were shown in Fig. 4. The impedance spectrum consists of a high frequency semi-circle and a low frequency inclined line. The high frequency semi-circle can be regard as the bulk LiSiPON thin film and the inclined line comes from the blocking electrode system of the Pt/electrolyte/Pt sandwich structure and the gradient is ascribed to the interfacial roughness between electrolyte thin film and Pt electrodes. The influence of grain boundaries on the conductivity was not observed from Fig. 4, which showed that the thin film is of amorphous structure. The DC impedance of LiSiPON film was determined by selecting the Z_{real} value at the frequency at which $Z_{imaginary}$ goes through a local minimum, and the ionic conductivity can be calculated from $\sigma^{DC} = (d/A)/R$, where d is the thickness of the film, A is the area of the metal contact, and R is the resistance determined from the complex impedance plots. The resistance and ionic conductivity of the LiSiPON films are listed in Table 1.

Table 1 Chemical composition, N content and ionic conductivity of LiSiPON electrolyte films

Samples	N_2 pressure /Pa	N content /%(atom fraction)	Composition	Resistance /Ω	Ionic conductivity /($\times 10^{-6}$ S · cm^{-1})
a	0.13	8.8	$Li_{2.3}Si_{0.28}P_{1.0}O_{2.5}N_{0.59}$	434.7	2.88
b	0.40	13.6	$Li_{2.5}Si_{0.31}P_{1.0}O_{1.7}N_{0.87}$	145.4	8.61
c	0.53	15.1	$Li_{2.7}Si_{0.45}P_{1.0}O_{1.6}N_{1.01}$	120.4	10.4
d	1.0	9.5	$Li_{2.5}Si_{0.41}P_{1.0}O_{2.2}N_{0.64}$	362.9	3.45
e	1.3	7.7	$Li_{2.1}Si_{0.33}P_{1.0}O_{2.3}N_{0.48}$	566.5	2.21
f	1.6	5.1	$Li_{2.6}Si_{0.37}P_{1.0}O_{2.4}N_{0.34}$	875.5	1.43

Fig. 5 showed the relationship between N_2 partial pressure and ionic conductivity of LiSiPON films. The ionic conductivity of LiSiPON film deposited with 0.13 Pa of N_2 working pressure is very small, only 2.88×10^{-6} S/cm. The ionic conductivity of the films increased with the increasing of N_2 working pressure and reached a maximum value, 10.4×10^{-6} S/cm, when the N_2 working pressure is 0.53 Pa. However, the ionic conductivity reduced gradually when the N_2 working pressure above 0.53 Pa. It's about 1.43×10^{-6} S/cm at the 1.6 Pa of N_2 pressure. In view of the influence of N_2 partial pressure on the N content of the films, the factor affecting the ionic conductivity is the N content. The film has more N atoms, the ionic conductivity larger. When the N_2 pressure is 0.53 Pa, both the value of N content and the ionic conductivity are the largest. The reason may be that the N atoms were substituted for oxygen atoms of Li_3PO_4 molecule framework thus a great deal of interconnection formed, which was favorable for the lithium ion crossing and moving.

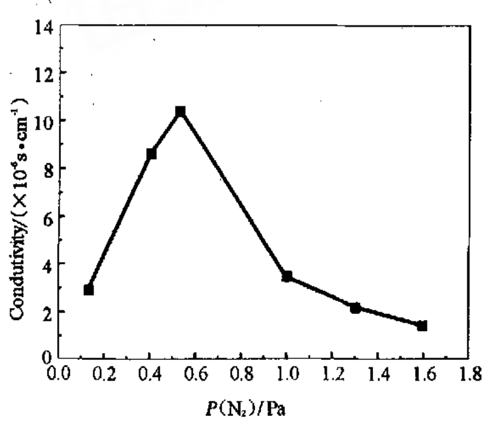

Fig. 5 Relationship between N_2 working pressure and ionic conductivity of LiSiPON

4 Conclusion

The LiSiPON electrolyte thin films with different N content can be prepared with magnetron sputtering method by controlling N_2 working pressure. The N content affected the ionic conductivity of the films remarkably. With the increasing of N_2 working pressure, N content of the films increased and also the ionic conductivity. When the N_2 working pressure is 0.53 Pa, the value of the N content of the film approaches 15.1%, and the ionic conductivity also get its maximum value, 10.4×10^{-6} S/cm. However, the N content and the ionic conductivity decreased gradually when the N_2 working pressure is above 0.53 Pa.

References

[1] Bates J B, Gruzalski G R, Dudney N J, *et al*. Rechargeable thin-film lithium batteries[J]. Solid State Ionics, 1994, 70—71: 619.

[2] Balkanski M. Solid-state microbatteries for electronics in the 21st century[J]. Solar Energy Materials & Solar Cells, 2000, 62: 21—35.

[3] Kanehori K, Malsumoto K, Miyauchi K, *et al*. Thin film solid electrolyte and its application to secondary lithium cell[J]. Solid State Ioncis, 1983, 9—10: 1445—1448.

[4] Levasseur A, Kbala M, Hagenmuller P, *et al*. Elaboration and characterization of lithium conducting thin film glasses[J]. Solid State Ioncis, 1983, 9−10: 1439−1444.

[5] Creus R, Sarradin J, Astier R, *et al*. The use of ionic and mixed conductive glasses in microbatteries[J]. Mater Sci Eng, 1989, B3: 109−112.

[6] Bates J B, Dudney N J, Gruzalski G R, *et al*. Electrical properties of amorphous lithium electrolyte films[J]. Solid State Ionics, 1992, 53−56: 647−654.

[7] Liu W Y, Fu Z W, Qin Q Z. Studies on lithium phosphorous oxynitride electrolyte thin film sand a new all-solid-state thin film lithium battery[J]. Acta Chimica Sinica, 2004, 62: 2223−2227.

[8] Lee S J, Baik H K, Lee S M. An all-solid-state thin film battery using LiSiPON electrolyte and Si-V negative electrode films[J]. Electrochemistry Communications, 2003, 5: 32−35.

[9] Lee S J, Bae J H, Lee H W, *et al*. Electrical conductivity in Li-Si-P-O-N oxynitride thin-films[J]. J Power Sources, 2003, 123: 61−64.

[10] Reculeau E, Elfakir A, Quarton M. Caractérisation et prévision structurale d'une nouvelle variété de Li_3PO_4[J]. J Solid State Chem, 1989, 79: 205−211.