

Short communication

## Electrical conductivity in Li–Si–P–O–N oxynitride thin-films

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### Abstract

Nitrogen-incorporated lithium silicophosphate (LiSiPON) thin-film electrolytes, which contain two glass-forming elements, are fabricated by sputtering from a  $(1-x)\text{Li}_3\text{PO}_4 \cdot x\text{Li}_2\text{SiO}_3$  target in a nitrogen reactive plasma. The results of impedance measurements show that the activation energy for conduction decreases as the Si content increases, which leads to an increase in the ionic conductivity of the films. It is suggested that these improvements in the electrical properties of the films are due to the combined effect of the mixed former and nitrogen incorporation. It appears that the decomposition potential of the electrolyte film in contact with Pt is about 5.5 V.

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**Keywords:** Solid-state electrolyte; Thin-film electrolyte; Lithium microbattery; Ion conductivity

### 1. Introduction

Li-ion conducting, inorganic, solid electrolyte films have attracted much attention in their application to thin-film, rechargeable, lithium microbatteries. The microbattery is fabricated by depositing thin-layers of the cell components, i.e. cathode, electrolyte, anode, and current-collectors. As an electrolyte, amorphous glassy thin-films of sulfides [1], oxides [2,3], or oxynitrides [4,5] have been extensively investigated because of their ease of fabrication and ability to be prepared in wide range of compositions. An ideal solid electrolyte requires high ionic conductivity, low electronic conductivity, good thermal stability, and resistance to dielectric breakdown at the voltages at which the batteries operate. Intensive studies have been performed to meet these requirements through various methods.

It has been reported that the use of two glass formers leads to conductivity enhancement due to the mixed former effect. For example, glasses of the  $\text{Li}_4\text{SiO}_4\text{--Li}_3\text{BO}_3$  system show improved conductivities compared with those of the end members, as expected from the Vegard interpretation [6,7]. Similarly, when Si is incorporated in  $\text{Li}_2\text{O--P}_2\text{O}_5$  films, large conductivity increases are also observed [8,9]. By contrast, amorphous electrolyte films in the  $\text{Li}_2\text{O--SiO}_2\text{--P}_2\text{O}_5$  system have not sufficient ionic conductivities and stabilities for Li microbattery systems [4].

Incorporating nitrogen into the oxide network is another approach. For example, in Lipon electrolyte films, which are deposited by sputtering  $\text{Li}_3\text{PO}_4$  in  $\text{N}_2$ , the incorporation of nitrogen appears to change the distribution of the phosphate anion chains and form nitrogen cross-linked structures. This results in an increase in conductivity due to an increase in the mobility of the  $\text{Li}^+$  ions and an improvement electrochemical stability [4,5].

To increase the ionic conductivity and to enlarge the electrochemical stability window as an electrolyte for solid-state, thin-film, lithium batteries, this study attempts to combine the above approaches, viz. the mixed former effect and nitrogen incorporation. In our previous report [10], it was shown that an all-solid-state  $\text{Si}_{0.7}\text{V}_{0.3}/\text{Li}_{1.9}\text{Si}_{0.28}\text{O}_{1.1}\text{N}_{1.0}/\text{LiCoO}_2$  cell operates mainly between 3.5 and 3.0 V, and that nitrogen-incorporated lithium silicophosphate is a promising electrolyte for thin-film batteries [10]. In this investigation, a series of nitrogen-incorporated  $\text{Li}_2\text{O--P}_2\text{O}_5\text{--SiO}_2$ , amorphous, thin-film electrolytes are prepared, and their electrical properties examined for battery application. The film composition are investigated for  $\text{Si:P} < 0.5$ , since for a higher Si:P ratio the  $\text{Li}_2\text{O--P}_2\text{O}_5\text{--SiO}_2$  system appears to show the phase separation in as-deposited films [3,9].

### 2. Experimental

The nitrogen-incorporated lithium silicophosphate (for simplicity, referred to as LiSiPON) films were deposited by RF-magnetron sputtering of single targets in pure  $\text{N}_2$ . The

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targets were prepared by cold pressing and then sintering mixtures at 1050 °C in air. The starting mixture comprised lithium phosphate and lithium silicate represented by the general formula  $(1-x)\text{Li}_3\text{PO}_4 \cdot x\text{Li}_2\text{SiO}_3$ , in which  $x = 0.1, 0.2, 0.3$  and  $0.4$ . The sample for each compositions is represented by A, B, C and D, respectively. Initially, the chamber was evacuated to a vacuum of  $2 \times 10^{-6}$  torr and then films were deposited in a carrier gas ambient ( $\text{N}_2$ ) at a sputtering pressure of  $5 \times 10^{-3}$  torr. The substrates were water-cooled to prevent elevation of the substrate temperature and rotated for homogeneous deposition during the sputtering process.

The compositions of the electrolyte films were determined from Rump simulation of the spectra from Rutherford backscattering spectrometry (RBS). The time-of-flight method of the elastic recoil detection (TOF-ERD) technique using a high-energy Cl ion incident beam was used to quantify the Li content. The crystallographic structure was analyzed by X-ray diffraction using Cu  $K\alpha$  radiation.

For ac impedance measurements, Pt|electrolyte|Pt sandwich structures were fabricated on alumina substrates with a typical electrolyte thickness of 1  $\mu\text{m}$ . The platinum electrode layers of  $\sim 2000$  Å thick were deposited by dc magnetron sputtering of a Pt target in Ar. Impedance measurements to determine ion conductivities were made at frequencies from 1 Hz to 1 MHz and at temperatures from 25 to 110 °C. Electrochemical stability was determined by means of linear sweep voltammetry at a scan rate of 1  $\text{mV s}^{-1}$ .

### 3. Results and discussion

The X-ray diffraction patterns of sputtering targets prepared by heating the cold-pressed mixtures are given in Fig. 1.  $\text{Li}_3\text{PO}_4$  is known to transform to a  $\gamma\text{-Li}_3\text{PO}_4$  structure above 520 °C [11]. The patterns reveal that the sputtering targets were composed of the  $\gamma\text{-Li}_3\text{PO}_4$  and the  $\text{Li}_2\text{SiO}_3$  phases. As the  $\text{Li}_2\text{SiO}_3$  content in the starting mixture increases, only the relative intensity from each constituent

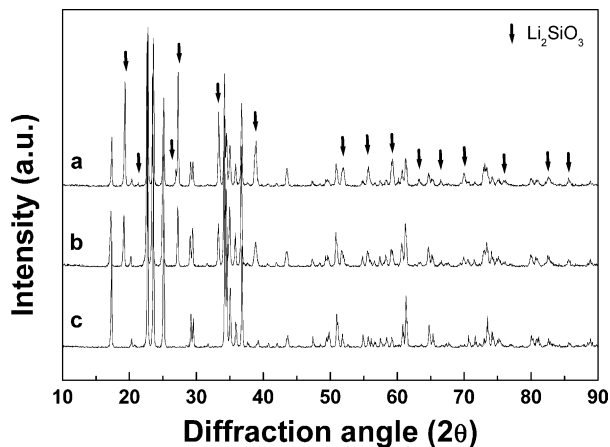


Fig. 1. X-ray diffraction patterns for sputtering targets and high-temperature phase of  $\text{Li}_3\text{PO}_4$ : (a) sample D; (b) sample B; (c)  $\gamma\text{-Li}_3\text{PO}_4$ .

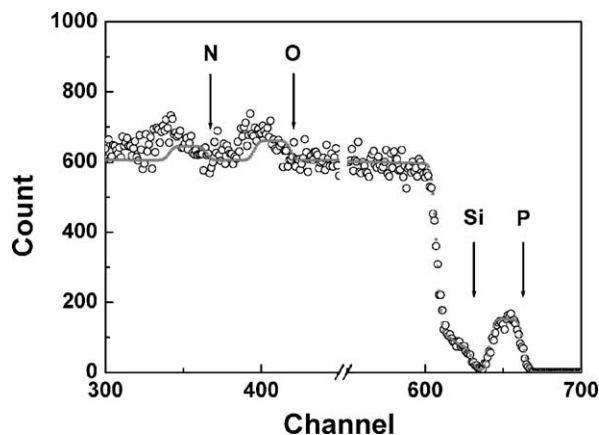


Fig. 2. The RBS spectrum of as-deposited  $\text{Li}_{2.9}\text{Si}_{0.35}\text{P}_{1.0}\text{O}_{1.5}\text{N}_{1.26}$  film.

phase is varied without any evidence of the formation of a third phase.

The RBS spectrum of the as-deposited film on a Si substrate from a  $0.6\text{Li}_3\text{PO}_4 \cdot 0.4\text{Li}_2\text{SiO}_3$  target is shown in Fig. 2. The open circles are the measured data and the solid line is the calculated backscattering by the Rump simulation program. The simulation curve suggests that only one layer with a uniform concentration profile of Li, P, O and N along a depth direction from the surface exists in the as-deposited film. The same trend for Li is determined by TOF-ERD analysis. This indicates that the steady-state deposition condition is maintained during deposition in all the samples investigated. The compositions of the films determined by RBS and TOF-ERD are listed in Table 1. X-ray diffraction measurements show that all the as deposited films are in the amorphous state.

Complex impedance spectra of the electrolyte films have been examined as a function of composition. The Nyquist plots are presented in Fig. 3. Each plot is composed of a semicircle and characteristic capacitive spike. The spike comes from the blocking electrode system of the Pt|electrolyte|Pt sandwich structure. This spike is somewhat inclined. It seems to be due to the interfacial roughness, given that the Pt and electrolyte layers are deposited on rough, sintered, alumina substrates. The bulk resistances are measured from the intercept of the low-frequency end of the semi-circle with the real axis of the complex impedance plot. The conductivity is determined using  $\sigma = (d/A)/R$ , where  $d$  is the film thickness,  $A$  the area of the metal contact, and  $R$  the film resistance determined from the complex

Table 1  
Compositions of electrolyte films

Sample	$(1-x)\text{Li}_3\text{PO}_4 \cdot x\text{Li}_2\text{SiO}_3$	Composition
A	$x = 0.1$	$\text{Li}_{2.3}\text{Si}_{0.2}\text{P}_{1.0}\text{O}_{1.4}\text{N}_{1.1}$
B	$x = 0.2$	$\text{Li}_{1.9}\text{Si}_{0.28}\text{P}_{1.0}\text{O}_{1.1}\text{N}_{1.0}$
C	$x = 0.3$	$\text{Li}_{2.9}\text{Si}_{0.35}\text{P}_{1.0}\text{O}_{1.5}\text{N}_{1.26}$
D	$x = 0.4$	$\text{Li}_{2.9}\text{Si}_{0.45}\text{P}_{1.0}\text{O}_{1.6}\text{N}_{1.3}$

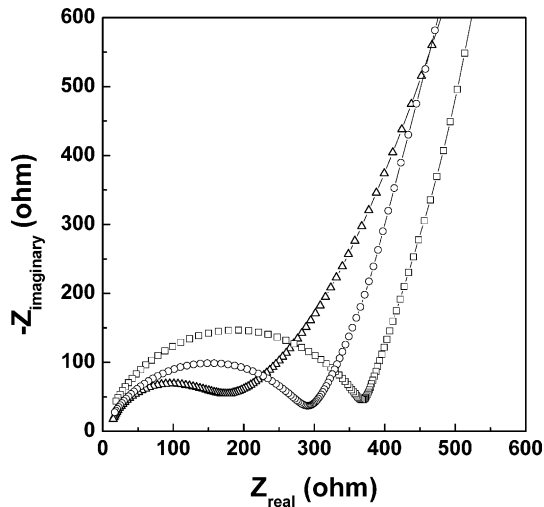


Fig. 3. Complex impedance spectra of Pt|LiSiPON|Pt cells at 27 °C for sample A ( $\square$ ), sample B ( $\circ$ ), sample D ( $\Delta$ ).

impedance plots. As the Si:P ratio increases, the bulk resistance value decreases, which leads to an increase in conductivity, as shown in Fig. 4. The conductivity approaches  $1.24 \times 10^{-5}$  S cm, when the Si:P ratio reaches 3.5.

To determine the activation energy for ionic conduction, the conductivity has been obtained from impedance plots measured at various temperatures, see Fig. 5. The conductivity,  $\sigma$ , obeys the Arrhenius equation, i.e.

$$\sigma T = A_0 \exp(E/kT)$$

where  $T$  is the absolute temperature;  $A_0$  the pre-exponential factor;  $E$  the activation energy for conduction;  $k$  the gas constant. Given the linear relationship, it is concluded that a consistent mechanism is responsible for ion transport over the temperature range investigated. The conductivity at room temperature and the activation energy for conduction of the LiSiPON films determined from Figs. 4 and 5 are summarized in Table 2. Data for lithium silicophosphate and Lipon films are also given for comparison [4]. The electrical properties of the LiSiPON films are superior to those of lithium

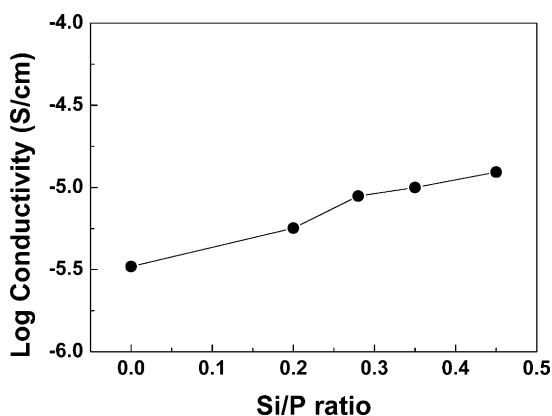


Fig. 4. Ionic conductivity of LiSiPON film electrolyte at 27 °C as function of Si:P ratio.

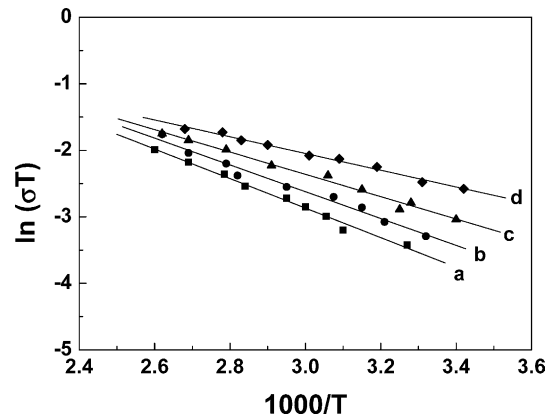


Fig. 5. Arrhenius plots of conductivities of LiSiPON thin-film electrolytes: (a) sample A; (b) sample B; (c) sample C; (d) sample D.

Table 2

Room temperature ionic conductivity of electrolyte and its activation energy for conduction

Sample	Conductivity ( $\times 10^{-6}$ S cm $^{-1}$ at RT) <sup>a</sup>	Activation energy (KJ mol $^{-1}$ )
A	5.65	48.2
B	8.86	47.37
C	10.00	47
D	12.40	46.2
LIPON	3.3	52.06 [3]
Lithium silicophosphate	0.2	54.95 [3]

<sup>a</sup> RT: room temperature.

silicophosphate. This suggests that the incorporation of nitrogen into the  $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$  system leads to the large increase in conductivity and the decrease in the activation energy. The addition of a  $\text{SiO}_2$  co-glass former may also enhance the conductivity in the nitrogen-incorporated lithium phosphate glasses, as in the case of  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2$  system [8,9], though the reason is not clear at this stage because detailed structural analysis has yet to be undertaken.

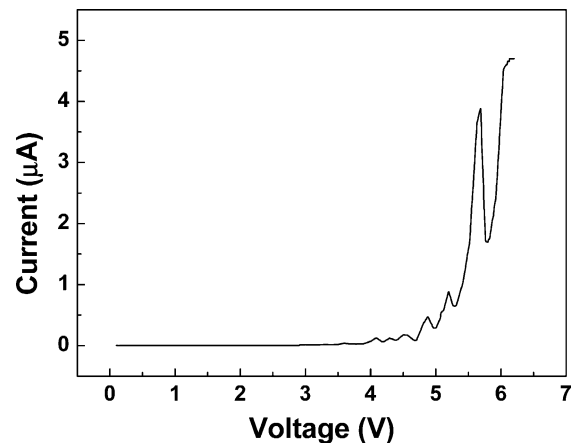


Fig. 6. Linear sweep voltammogram of Pt|LiSiPON|Pt cell (scan rate:  $1 \text{ mV s}^{-1}$ ).

The linear sweep voltammogram for the Pt|LiSiPON|Pt cell up to 6.2 V is shown in Fig. 6. The current increases dramatically when the voltage across the junction exceeds 5.5 V. This indicates that the decomposition potential of LiSiPON film in contact with Pt is about 5.5 V.

From the above results, the combination approach of the mixed former effect and nitrogen incorporation is believed to be effective in increasing the ionic conductivity of the glass thin-film electrolyte. Therefore, further studies to determine the structure and to interpret the transport mechanism are necessary.

#### 4. Conclusion

Nitrogen-incorporated, lithium silicophosphate, thin-film electrolytes are fabricated by sputtering from a  $x\text{Li}_3\text{PO}_4 \cdot (1-x)\text{Li}_2\text{SiO}_3$  target in a nitrogen reactive plasma. Nitrogen incorporation improves the conductivity of the  $\text{Li}_2\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$  system. As the Si:P ratio increases in the LiSiPON film, the activation energy for conduction decreases, which leads to an increase in electrical conductivity. The conductivity approaches  $1.24 \times 10^{-5} \text{ S cm}^{-1}$ . The electrolyte film is electrochemically stable up to 5.5 V. It appears that lithium silicon phosphorus oxynitride is a promising electrolyte for all-solid-state, thin-film, lithium-ion batteries.

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