

# Li–V–Si–O thin film electrolyte for all-solid-state Li-ion battery

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## Abstract

Ultraviolet (355 nm) reactive pulsed laser deposition (PLD) using a mixture of  $\text{Li}_2\text{CO}_3$ ,  $\text{V}_2\text{O}_5$  and  $\text{SiO}_2$  as a target was employed to prepare Li–V–Si–O thin film electrolyte in  $\text{O}_2$  gas ambient for all-solid-state Li-ion battery. The morphology and structure of Li–V–Si–O thin films were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques, and the properties of thin films strongly depend on the substrate temperature. A dense and smooth Li–V–Si–O thin film without pinholes and cracks was obtained at substrate temperature of 300 °C. The ionic conductivity of this thin film electrolyte was determined by AC impedance measurement, and an ionic conductivity was estimated to be  $3.98 \times 10^{-7}$  S/cm at 25 °C with conductivity activation energy of 0.55 eV. In addition, the ionic transference number was measured by Wagner's DC polarization technique and the cyclic voltammetric measurement was performed to investigate the electrochemical stability of the thin film electrolyte.

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## 1. Introduction

The miniaturization of electronic devices has resulted in very low current and power requirements for many applications. Microenergy sources such as thin-film energy storage devices must be developed to drive these micro-electronic devices. A thin film Li-ion battery is one of the options for satisfying these demands. Generally, the thin film Li-ion battery consists of intercalation compounds for both positive and negative thin film electrodes as well as a thin film solid electrolyte. The development of high quality thin film electrolytes will make it possible to fabricate the all-solid-state Li-ion battery with high electrochemical performance.

Lithium ion conductors are promising electrolyte material for all-solid-state Li-ion battery and have been widely studied in recent years [1–3]. Among them, the glassy lithium phosphorus oxynitride (LIPON) thin film electrolyte has been used in these batteries because it is stable in contact with metallic lithium and has an acceptable conductivity in thin film form [4]. Besides LIPON,  $\text{Li}_2\text{O–V}_2\text{O}_5\text{–SiO}_2$  thin films as solid electrolyte have been investigated by Ohtsuka and co-workers [5–7] because these films are not only a chemically stable solid state ionic conductor but also exhibit high lithium ion conductivity at room temper-

ature. They fabricated  $\text{Li}_2\text{O–V}_2\text{O}_5\text{–SiO}_2$  thin films fabricated by radio frequency (rf) magnetron sputtering method and found that the film exhibits the ionic conductivity of  $1.0 \times 10^{-6}$  S/cm at room temperature with a conductivity activation energy of 0.50 eV. Using this  $\text{Li}_2\text{O–V}_2\text{O}_5\text{–SiO}_2$  thin film as solid-state electrolyte and both metallic lithium and  $\text{MoO}_{3-x}$  films used as anode and cathode materials, they prepared an all-solid-state thin film battery, exhibiting good electrochemical performance and the solid electrolyte film was stable in contact with metallic Li thin film anode.

To our knowledge, there is no report on fabricating Li–V–Si–O thin films by pulsed laser deposition (PLD). This method has been successfully used for preparing thin film electrodes, such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{V}_2\text{O}_5$  [8–10]. We have also employed this method for preparing the thin films of the transition metal oxides, such as  $\text{Ta}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ , metallic silver doped  $\text{V}_2\text{O}_5$  and tin-based composite oxide (TCO) with good electrical and electrochemical properties [11–15]. Recently, LIPON thin film electrolyte with high ionic conductivity has been successfully fabricated in our laboratory [16].

In this work, we employed the reactive pulse laser ablation method to fabricate Li–V–Si–O thin films in an ambient  $\text{O}_2$  gas. The dependence of the ionic conductivity, structure and morphology of thin films on the deposition conditions was investigated. Electrochemical measurements were performed to examine the ionic conductivity, ionic transference number, activation energy and electrochemical window of

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the Li–V–Si–O films. We hope to explore the application of PLD technique to fabricating Li–V–Si–O film electrolyte for all-solid-state thin film Li-ion batteries.

## 2. Experimental

The experimental set-up for the fabrication of Li–V–Si–O thin films by reactive PLD method has been described elsewhere [17]. Briefly, a stainless steel vacuum chamber equipped with a rotating holder for the Li–V–Si–O target was used for thin film deposition. 355 nm laser beam provided by the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics, GCR-190) was focused and irradiated onto a rotating target at an incidence angle of 45°. The laser energy was measured by a power meter with a pyroelectric detector. The repetition rate was 10 Hz with a pulsed width of 6 ns, and the laser fluence was 1.2 J/cm<sup>2</sup>. Two different substrates, Si wafer and Al-coated glass sheet were used in our experiments. The substrate was placed at a distance of 4 cm away from the target, and can be heated by an electrical resistance heater. Before deposition, the reactive chamber was evacuated to high vacuum and then introduced O<sub>2</sub> (99.2%) gas with a needle valve. The film deposition was carried out with a continuous flow of the O<sub>2</sub> gas, and the ambient gas pressure was maintained at 50 mTorr. The structure of the thin film was analyzed by X-ray diffraction (XRD) with a Rigata/max-C diffractometer (Cu K $\alpha$  radiation source,  $\lambda = 1.5406 \text{ \AA}$ ). A Cambridge S-360 scanning electron microscopy (SEM) was used to characterize the morphology and measure the thickness of the thin film. Ionic conductivity of the Li–V–Si–O thin film electrolyte was obtained from an AC impedance measurement of Al/Li–V–Si–O/Al sandwich structure on Al-coated glass substrate, and this type of sandwich structure has been described elsewhere [4]. AC impedance measurements were performed using a CHI 660 electrochemical station at frequencies from 1 Hz to 100 kHz at different temperature. The ionic transference number was measured using the Wagner's DC polarization technique. Cyclic voltammetry was performed to examine the electrochemical stability of the thin film electrolyte.

The Li–V–Si–O target was prepared by mixing the starting materials of Li<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> powders with a chemical composition ratio of Li<sub>6.16</sub>V<sub>0.61</sub>Si<sub>0.39</sub>O<sub>5.36</sub>. The mixture was heated at 700 °C for 12 h in order to convert Li<sub>2</sub>CO<sub>3</sub> to Li<sub>2</sub>O, then the mixture calcinated at 1000 °C for 12 h to prepare a solid solution by a conventional solid-state reaction. The resulting sample was milled into powder and was compressed into a 13-mm diameter pellet followed by 700 °C for 24 h.

## 3. Results and discussion

The morphology and structure of Li–V–Si–O thin films prepared by PLD were investigated by SEM and XRD. The

surface morphology of the films deposited on Si wafer at different substrate temperatures are shown in Fig. 1. It can be seen that the Li–V–Si–O thin film prepared at substrate temperature of 100 °C seems to be rough, loose and porous, however, the film prepared at substrate temperature of 300 °C is very smooth and dense without any pinholes and cracks. Fig. 1(c) presents the film prepared at higher substrate temperature of 400 °C in which a dense film is observed but the presence of coagulated particles on the surface makes the film surface rough. The cross-sectional view shown in Fig. 1(d) demonstrates that the thin film deposited at 300 °C is well adherent to the substrate surface with a uniform thickness.

X-ray diffraction patterns of the Li–V–Si–O films prepared at different substrate temperatures are shown in Fig. 2. It shows that there is no diffraction peaks observed for the films prepared at lower substrate temperatures (25 and 100 °C). However, a broad hump appears for the films prepared at higher substrate temperatures (200, 300, and 400 °C) and its intensity increases with the increasing of the substrate temperature. This evidence indicates that the thin films prepared at lower substrate temperatures exhibit an amorphous structure and gradually transform into partial crystalline with increasing the substrate temperature. But the micro-structure of the thin film may still be a amorphous at higher substrate temperature because only a broad hump without sharp peaks is observed. This amorphous Li–V–Si–O film results in high ion conductivity, since the Li ion conductivity for the amorphous phase is orders of magnitude higher than that of the crystalline phase for many solid-state Li ionic conductors [1].

A typical AC impedance spectrum of Li–V–Si–O thin film between a pair of Al electrodes is shown in Fig. 3. The impedance is characteristic of a thin film conducting dielectric with a single bulk relaxation process and blocking (Al/Li–V–Si–O) electrodes [18]. The ionic conductivity  $\sigma$  of Li–V–Si–O film prepared by PLD can be obtained by the following equation [4]:

$$\sigma = \frac{d}{RA} \quad (1)$$

where  $d$  is the thin film thickness,  $A$  is the area of the Al contact, and  $R$  is the film resistance, which can be obtained from the measured impedance by selecting the value of the real part  $\text{Re}(Z)$  at the frequency at which the imaginary part  $\text{Im}(Z)$  goes through a local minimum. It should be pointed out that the measured resistances of the deposited Li–V–Si–O film at four different sections are nearly the same, indicating that the uniformity of film is fairly well.

In addition, AC impedance technique has been widely used to separate the contribution of the bulk and grain boundaries to the overall resistance. The Nyquist AC impedance spectrum of the Li–V–Si–O film prepared at 300 °C is shown in Fig. 4. It can be seen that impedance spectrum consists of high frequency semi-circle, caused by bulk Li–V–Si–O film and low frequency inclined line ascribed to the interfaces

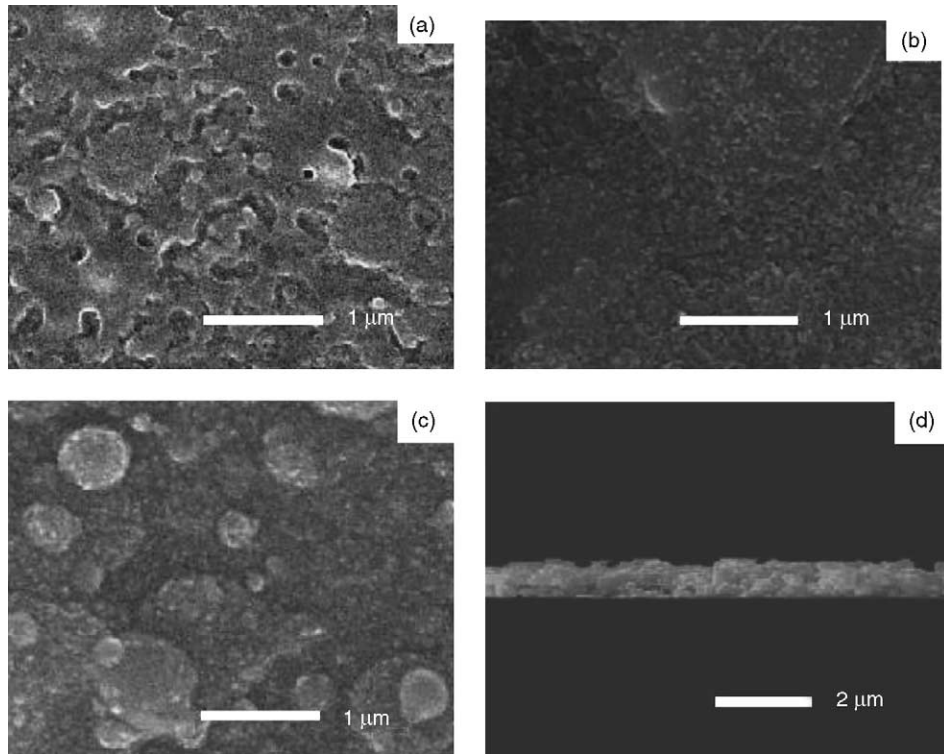


Fig. 1. Surface morphology of Li-V-Si-O films deposited on Si wafer at substrate temperatures of (a) 100°C, (b) 300°C, (c) 400°C, and (d) a cross-sectional view at 300°C.

between film and adjacent Al electrodes. However, our experimental results show that the influence of grain boundaries on the conductivity even for the films prepared at higher substrate temperature cannot be observed. One of the reasons

could be the amorphous phase of Li-V-Si-O film prepared by PLD. We employed the equivalent circuit as shown in the inset of Fig. 4 for the interpretation of the impedance analysis data. The combination  $C_C-R_{ion}-C_C$  corresponds to a

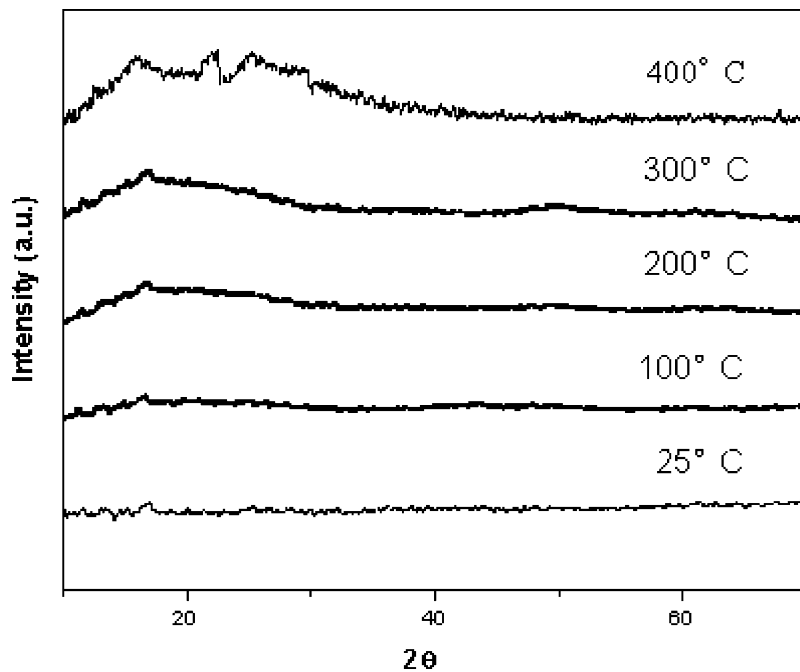


Fig. 2. X-ray diffraction patterns of the Li-V-Si-O films prepared at different substrate temperatures.

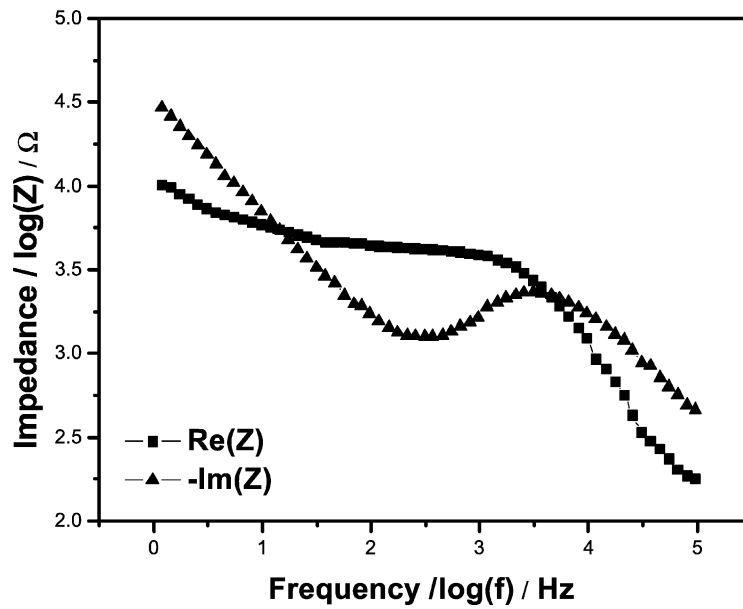


Fig. 3. Impedance spectrum of Li–V–Si–O thin film between a pair of Al electrodes.

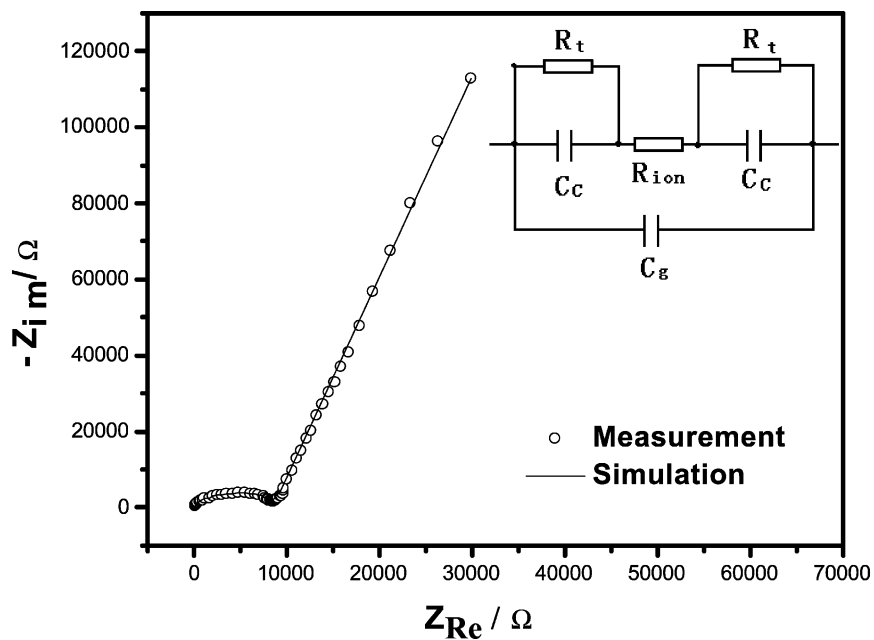


Fig. 4. The Nyquist AC impedance spectrum of the Li–V–Si–O film prepared at substrate temperature of 300 °C. Inset: the electrical equivalent circuit.

pure ion conductor with perfectly blocking electrodes. Practically, charge carriers pass through the sample/electrode interface, and it should be taken into account by the two parallel resistance  $R_t$  and  $C_g$  [19]. As shown in Fig. 4, AC impedance spectrum of the  $\text{Li}_2\text{O-V}_2\text{O}_5\text{-SiO}_2$  film can be well fitted using above-mentioned equivalent circuit.

The substrate temperature is an important experimental condition for the fabrication of Li–V–Si–O film during PLD. The influence of the substrate temperature on the film ionic conductivity is presented in Table 1. It shows that the ionic conductivity increases with increasing the substrate temper-

Table 1

The influence of the substrate temperature on ionic conductivity and ion transference number of Li–V–Si–O thin films

Substrate temperature (°C)	Thin film thickness (μm)	Resistance (Ω)	Ionic conductivity (S/cm)	Ion transference number (%)
25	1.5	$10^{5.1}$	$10^{-7.25}$	99.91
100	1.7	$10^{4.7}$	$10^{-7.07}$	99.97
200	1.4	$10^{4.3}$	$10^{-6.76}$	99.99
300	1.6	$10^{4.0}$	$10^{-6.40}$	99.99
400	1.7	$10^{4.0}$	$10^{-6.37}$	99.99

ature in the range of 25–400 °C. It is well known that PLD is experimentally simple but the mechanisms of laser–target interaction and film growth are very complex. The ablated species impinging onto the substrate need a certain time for surface diffusion and incorporation at proper sites. Surface diffusion is a thermally activated process, and the film structure could become denser with the increasing of substrate temperature. This expected result has been confirmed by our SEM measurements shown in Fig. 1. The dense film will result in a high ion conductivity for many solid-state Li ionic conductors. Aono et al. [20,21] have studied the Li ionic conductor based on lithium titanium phosphate and pointed out that the ionic conductivity enhancement resulted mainly from densification of the sample. In order to prepare an all-solid-state Li-ion battery, it is necessary to deposit a solid thin film electrolyte on an electrochemical active thin film. The deposition of thin film electrolyte at high substrate temperature is not suitable, since the two films may react and/or be separated because of their different expansion coefficient. According to our SEM and ionic conductivity results, it is reasonable to suggest the Li–V–Si–O film prepared at a substrate temperature of 300 °C.

The ionic transference number  $t_{\text{ion}}$  has been measured from the plot of polarization current versus time using the following equation [22]:

$$t_{\text{ion}} = \frac{I_i - I_f}{I_f} \quad (2)$$

where  $I_i$  is the initial current and  $I_f$  is the final residual current. Fig. 5 presents a plot of polarization current versus time for the Li–V–Si–O thin film, and the measured transference numbers for all the samples prepared at different substrate temperatures were found to be close to unity (see Table 1), indicating that these electrolyte thin films are ionic conduc-

tors. The electronic conductivities of the thin films are estimated to be in the range of  $10^{-11}$  to  $10^{-12}$  S/cm. This means that the charge transport is mainly due to  $\text{Li}^+$  ion transfer whereas the electronic contribution to the charge transport can be negligible.

The ionic conductivity of Li–V–Si–O thin film prepared at a substrate temperature of 300 °C was measured at different ambient temperature ( $T$ ). A plot of  $\log(\sigma T)$  against  $10^3/T$  is shown in Fig. 6 in the temperature range of 25–200 °C. The data can be simulated by Arrhenius relation [19]:

$$\sigma = \left(\frac{\sigma_0}{T}\right) \exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

where  $\sigma_0$  is the pre-exponential factor,  $T$  is the absolute temperature,  $k$  is the Boltzmann constant and  $E_a$  is the conductivity activation energy for the migration of  $\text{Li}^+$  ions. As shown in Fig. 6, the temperature dependence of the film conductivity exhibits the Arrhenius relation. Thus, our result also indicates that the electronic conductivity of thin film can be negligible. The conductivity activation energy of the thin film was estimated to be 0.55 eV from the slope of the straight line in Fig. 6. The value is slightly greater than that of  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{SiO}_2$  solid solution reported by Ohtsuka. The reason may be due to  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{SiO}_2$  solid solution is denser than Li–V–Si–O thin film and lithium ions in the film cannot migrate as easily as those in the solid solution.

Cyclic voltammetric measurement was performed to examine the electrochemical stability of the thin film. Two blocking Al electrodes were used as the anode and cathode, respectively. Fig. 7 shows the cyclic voltamogram with a scan rate of 10 mV/s for the Li–V–Si–O film prepared at a substrate temperature of 300 °C. Cathodic and anodic currents resulted from the electrolyte decomposition were not

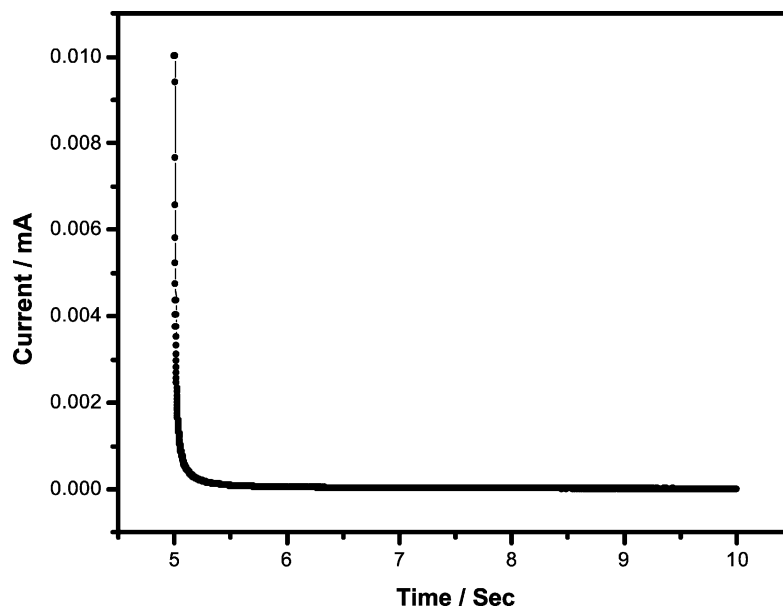


Fig. 5. Polarization current as a function of time for Li–V–Si–O thin film.

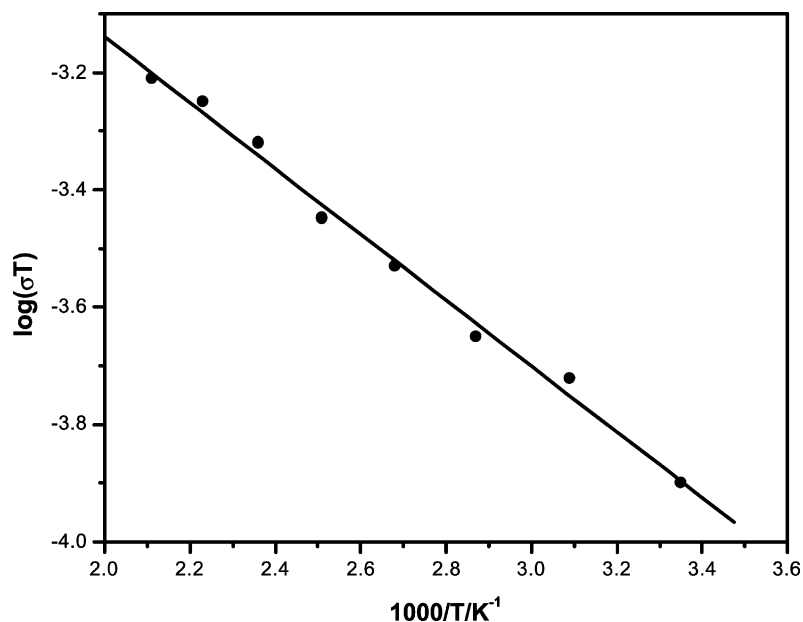


Fig. 6. Variation of  $\log(\sigma T)$  vs.  $10^3/T$  for Li-V-Si-O film prepared at substrate temperature of 300 °C.

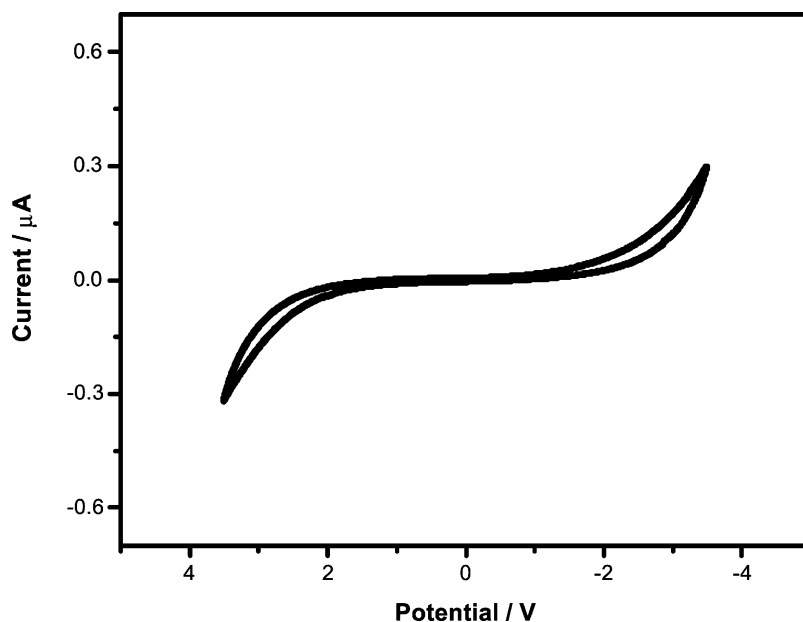


Fig. 7. Cyclic voltammogram with a scanning rate of 10 mV/s for the Li-V-Si-O film prepared at a substrate temperature of 300 °C.

observed in the potential range of  $-1.75$  to  $+1.75$  V, suggesting that this electrolyte thin film exhibits an electrochemical window at least more than 3.5 V. The electrochemical window of Li-V-Si-O thin film electrolyte seems to be narrow comparing with the LIPON film electrolyte reported by Bates from ORNL. However, if appropriate electrode materials are chosen to make a thin film battery with a voltage lower than 3.5 V such as Li/Li-V-Si-O/MoO<sub>3-x</sub> cell [7], this solid electrolyte can be used in the all-solid-state battery.

#### 4. Conclusions

Ultraviolet (355 nm) PLD was employed to prepare Li-V-Si-O thin film electrolyte for the first time. The properties of thin films strongly depend on the substrate temperature in deposition. A dense, smooth and uniform thickness Li-V-Si-O thin film without pinholes and cracks was obtained at a substrate temperature of 300 °C. In this condition, the prepared thin film exhibits an ionic conductivity of  $3.98 \times 10^{-7}$  S/cm at 25 °C with conductivity

activation energy of 0.55 eV, and a electrochemical window of 3.5 V is found in the Al/Li<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>/Al sandwich structure. In addition, the thin film electrolyte possesses high ionic transference number ( $t_{\text{ion}} > 99.9\%$ ) indicating that the electronic conductivity can be negligible. Our results demonstrate that Li–V–Si–O thin film electrolyte could be used as a solid state Li-ion electrolyte for the fabrication of all-solid-state thin film rechargeable Li-ion batteries.

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