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The electrical and electrochemical properties of an amorphous thin-film lithium electrolyte, lithium phosphorous oxynitride (Lipon), have been studied with an emphasis on the stability window vs. lithium metal and the behavior of the Li/Lipon interface. The ionic conductivity of Lipon exhibits Arrhenius behavior over the temperature range investigated, -26°C to 140 °C, with a conductivity of 1.7×10^{-6} S/cm at 25 °C and an activation energy of $E_a = 0.50 \pm 0.01$ eV. A stability window of 5.5 V was observed with respect to a Li^+/Li reference, and no detectable reaction or degradation was evident at the Li/Lipon interface upon lithium cycling.

INTRODUCTION

Many solid-state lithium electrolytes have been proposed and studied with the goal of developing an all-solid-state lithium battery. An ideal lithium electrolyte should have good lithium ion conductivity with $t_+=1$, but, more importantly, should be stable in contact with lithium metal at potentials from 0 to 5 V. Among various types of solid-state electrolytes, solid polymer electrolytes have attracted considerable attention (1). However, these materials typically react with lithium metal, resulting in the formation of a passive layer at the interface (2–5). This interface reaction impairs the performance and long-term stability of a lithium battery (2). Once assembled into a cell, the electrolyte is constantly under a d.c. bias that equals the cell voltage, and therefore, an acceptable electrolyte must be stable under this d.c. bias. For high voltage cathodes, such as $LiMn_2O_4$ and $LiCoO_2$, this means that the electrolyte must have a stability window on the order of 5 V.

Recently (6), a new Li ion conducting ceramic thin film, lithium phosphorous oxynitride (Lipon), was developed at Oak Ridge National Laboratory and has been successfully incorporated into rechargeable thin-film lithium batteries (7). This amorphous material has a typical composition of $Li_{3.3}PO_{3.8}N_{0.22}$ and an ionic conductivity of about 2×10^{-6} S/cm at room temperature. Rechargeable thin-film lithium batteries fabricated with the Lipon electrolyte have shown excellent cycling performance as well as a long shelf lifetime. (7) While the objective of our earlier research was to synthesize a thin film lithium electrolyte with a satisfactory stability and conductivity (6), the reason for the extraordinary electrochemical stability of Lipon is not yet fully understood. The purpose of the present study was to further our understanding of the electrical and electrochemical properties of lithium phosphorus oxynitride thin films.

EXPERIMENTAL DETAILS

Lipon thin films were deposited at room temperature by r.f. magnetron sputtering of a Li_3PO_4 target in pure N_2, whereas Li_3PO_4 thin films were deposited by sputtering a Li_3PO_4 target in a 3:2 Ar:O_2 mixture (6). For the a.c. impedance measurements Pt/Lipon/Pt sandwich structures were fabricated on alumina substrates with a typical Lipon thickness of 1 µm and a junction area of 2 × 2 mm^2. The Pt electrodes were deposited by d.c. magnetron sputtering of a metal target in Ar. Structures of Pt/Lipon/Li and Li/Lipon/Li also were constructed for a.c. impedance characterization. The top lithium film was deposited by thermal evaporation (7) of lithium metal in a Ta crucible, and a piece of lithium foil was used as the substrate for the Li/Lipon/Li structure. Symmetric Lipon/Pt/Lipon/Pt/Lipon structures were fabricated on alumina substrates for slow-scan current-potential (IV) measurements. The top and bottom Lipon films served as buffer layers to isolate the electrodes from the ambient atmosphere and from the substrate respectively. Three-electrode cells were constructed by interruping the growth of the inner Lipon film to deposit a 3-µm-thick, 1.5 × 5 mm^2 Li strip. The counter electrode was a 3-µm-thick Li film which was covered with a top Lipon buffer layer to complete the structure:Lipon/Li/Lipon/Li/Lipon/Pt/Lipon. Both lithium electrodes extended over Ni films for electrical contact. The distance between the inner Li reference electrode and the working electrode was about 5000 Å. Similar structures also were constructed with Li_3PO_4 for comparison.

Impedance spectra were measured at temperatures from -26 to 300°C over a frequency range from 0.1 Hz to 10 MHz using a Solartron 1250 frequency analyzer and an HP 3577A network analyzer. For high-temperature measurements the specimen was placed on a heated stage inside an O-ring sealed box. For low-temperature measurements the specimen was attached to electrical leads and sealed in a glass jar filled with Ar. The jar was then partially immersed into either ice water for 0°C or a mixture of carbon tetrachloride and dry ice for -26 °C. The IV curves were recorded with a Solartron 1286 Electrochemical Interface and a Keithley 617 electrometer. A voltage scan rate of 1 mV/sec was used throughout the experiment. The IV scan was stopped at selected stages for impedance characterization.

RESULTS AND DISCUSSION

The Lipon/lithium Interface

Representative impedance spectra of a Lipon film between a pair of Pt electrodes and between Li and Pt electrodes are shown in Fig. 1(a) and 1(b) respectively. Both spectra are characteristic of a single-phase ionic conductor with blocking electrodes (8). It is evident by comparing the results in Fig. 1(a) and 1(b) that there is no detectable interface reaction between lithium and Lipon.

Impedance studies also were conducted on the Li/Lipon/Li-foil structure. The impedance spectrum of the Li/Lipon/Li-foil structure remained virtually unchanged after about 0.5 µm- and 1.5 µm-thick lithium was passed from the top lithium film to the Li-foil and from the Li-foil to the top lithium film, respectively, at rates ranging from 10 to

400 μA/cm^2. This result shows that not only is Lipon stable in contact with lithium, but it also has the mechanical strength to accommodate the stress caused by volume changes associated with lithium stripping and plating.

Ionic Conductivity

Arrhenius plots for two Lipon films with different thicknesses and for a Li_3PO_4 film are shown in Fig. 2. The ionic conductivity was 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 measured impedance by selecting the value of Re(Z) at the frequency at which -Im(Z) goes through a local minimum. The breaks in the plots above ~140°C are artifacts caused by the decrease in the resistance of the electrolyte below the resistance of the electrical leads and contacts. The solid line in Fig. 2 is the result of a least-squares fit of the Arrhenius equation $\sigma T = B\exp(-E_a/kT)$ to the experimental data within the linear region. The fit for the Lipon film yielded an ionic conductivity of 1.7×10^{-6} S/cm at 25°C, a pre-exponential term $B = 2.04 \times 10^5$ Scm^{-1}K, and an activation energy $E_a = 0.50 \pm 0.01$ eV. The fit for the Li_3PO_4 film yielded an ionic conductivity of 8.4×10^{-8} S/cm at 25 °C, a pre-exponential term $B = 1.20 \times 10^6$ Scm^{-1}K, and an activation energy $E_a = 0.63 \pm 0.03$ eV. It is evident that N incorporation into the Li_3PO_4 structure increased the ionic conductivity. This was attributed to an increase in the Li^+ mobility brought about by cross-linking the orthophosphate glass through >N- bonds (6).

Stability Range and Electrode Reactions

The electrochemical stability range of Lipon was studied with a combination of slow IV scans and a.c. impedance spectroscopy. The impedance spectra of a Pt/Lipon/Pt junction as a function of the voltage applied during an IV scan are shown in Fig. 3. It is evident that the Lipon film retained its single-phase behavior up to 5 V. At about 5.5 V, a new feature appeared the impedance spectra (Fig. 3c) between 10 and10^3 Hz indicating the formation of a second phase. This feature became the prominent component in the spectra when decomposition of the film started at about 6 V. Impedance measurements also were made as a function of the elapsed time at bias voltages near the decomposition potential. From results shown in Fig. 3b, it is evident that applying a 5 V bias across a Pt/Lipon/Pt junction for up to 1 h did not change the impedance spectra, whereas increasing the bias to 5.5 V induced the formation of a second phase right away.

The resistances the Lipon film (open symbols) and the second phase (solid symbols) as a function of the applied voltage are shown in Fig. 4. It is evident that, within the accuracy of the impedance measurement, the resistance of the Lipon layer remained unchanged throughout the voltage range, indicating that the second phase formation is localized at the Pt/Lipon interface. The constancy of the Lipon resistance also indicates that only a small fraction of the film was decomposed; therefore, the reactive layer is very thin and has a very low conductivity. From the figure, the onset voltage for the second phase formation, i.e. electrolyte decomposition, is about 5.5 V. Similar experiments on Pt/Li_3PO_4/Pt junctions indicated that the onset voltage for second phase formation is about 6 V.

The stability window of Lipon was investigated using a three electrode cell in which the inner lithium strip was the reference electrode, the top lithium film was the counter electrode, and the Pt film was the working electrode. Anodic and cathodic IV scans of a cell are shown in Fig. 5. In the cathodic scan, the current increased significantly as the potential of the Pt film approached that of the lithium reference electrode and lithium metal was deposited onto the Pt film. In the anodic scan, the initial potential corresponded to the OCV of the cell. As the potential was swept positively, the anodic current gradually increased. Potential excursions beyond 5.5 V resulted in the formation of a resistive junction. However, subsequent cycles did not indicate complete passivation of the electrode. The current features below 5.5 V on the anodic scan did not result in the formation of a resistive junction seen above 5.5 V. A stability window of 5.5±0.2 V can be deduced by extrapolating the boundaries of the cathodic and anodic curves as indicated in Fig. 5 (9). This value is consistent with the results of the impedance measurements in Fig. 4 which show that the onset voltage for a second phase formation is about 5.5 V. The result is also consistent with our observations that thin film lithium cells with $LiMn_2O_4$ cathodes can be cycled at voltages up to 5.3 V with no apparent degradation of the Lipon electrolyte (7).

Similar experiments on the three-electrode cells with Li_3PO_4 indicate a stability window of 3.5±0.1 V, with the anodic and cathodic limits of stability at 3.5 and 0 V, respectively, vs. Li^+/Li. Unlike the case with Lipon, this value is inconsistent with the results of the impedance measurements which show that the onset voltage for a second phase formation is about 6 V in a $Pt/Li_3PO_4/Pt$ junction. Further investigations are being conducted to address this disparity.

During the anodic scan of both the symmetric Lipon and Li_3PO_4 cells, gas bubbles were observed at the electrolyte/Pt interface around 6 V. The nature of this electrode reaction is not certain, but we speculate that it involves the cleavage of P-O bonds, forming P-O-P chains, and generating O_2 gas. One possible reaction for the Li_3PO_4 films is:

$$2\,Li_3PO_4 = Li_4P_2O_7 + 1/2\,O_2 + 2\,Li^+ + 2\,e^- .$$

CONCLUSIONS

Amorphous lithium phosphorus oxynitride (Lipon) thin films exhibit Arrhenius behavior at temperatures from -26 to 140°C, with a conductivity of 1.7×10^{-6} S/cm at 25 °C and an activation energy of $E_a = 0.50 \pm 0.01$ eV. The electrochemical stability window of Lipon was found to be 5.5±0.2 V at room temperature, with anodic and cathodic limits of 5.5 and 0 V, respectively, vs. a Li reference electrode. No degradation of the Li-Lipon interface or the Lipon film were detected before and after cycling lithium through the Li/Lipon/Li cell. This result indicates that not only is Lipon stable in contact with lithium at high cell voltages, but also has the mechanical strength to accommodate the stress caused by volume change associated with the lithium stripping and plating.

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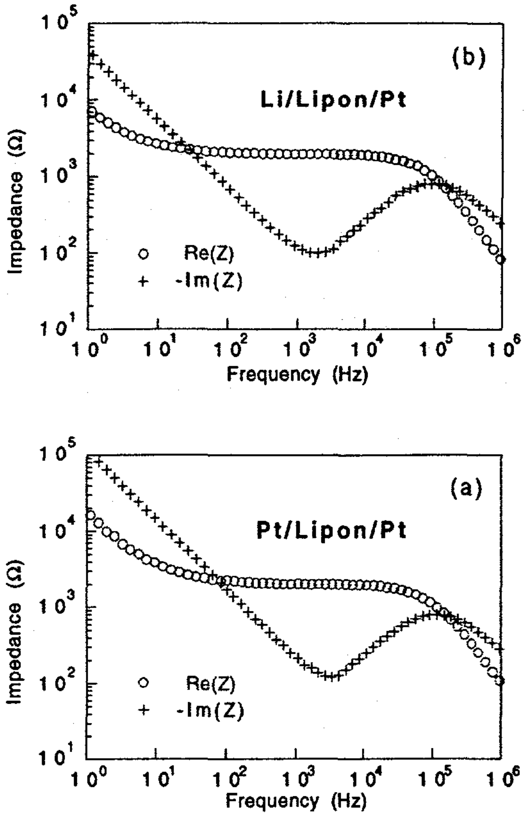

Fig. 1 Impedance spectra of Lipon between (a) a pair of Pt electrodes, (b) a lithium and Pt electrode.

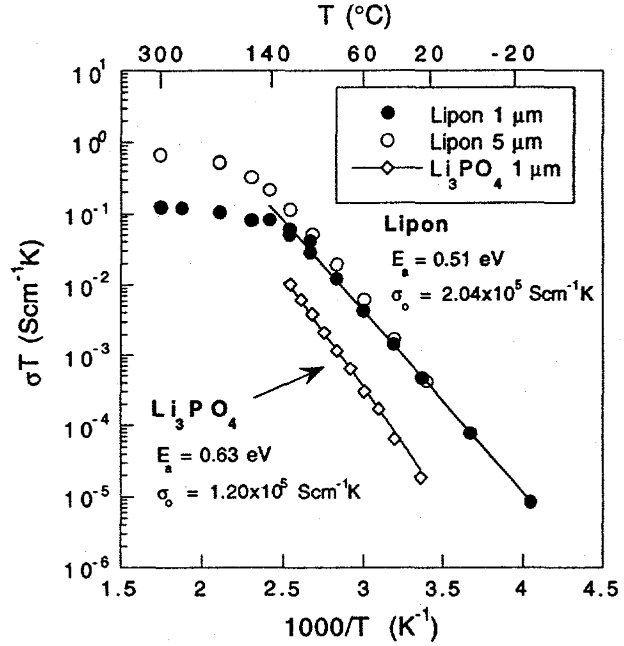

Fig. 2 Arrhenius plot of the ionic conductivity of Lipon vs. temperature.

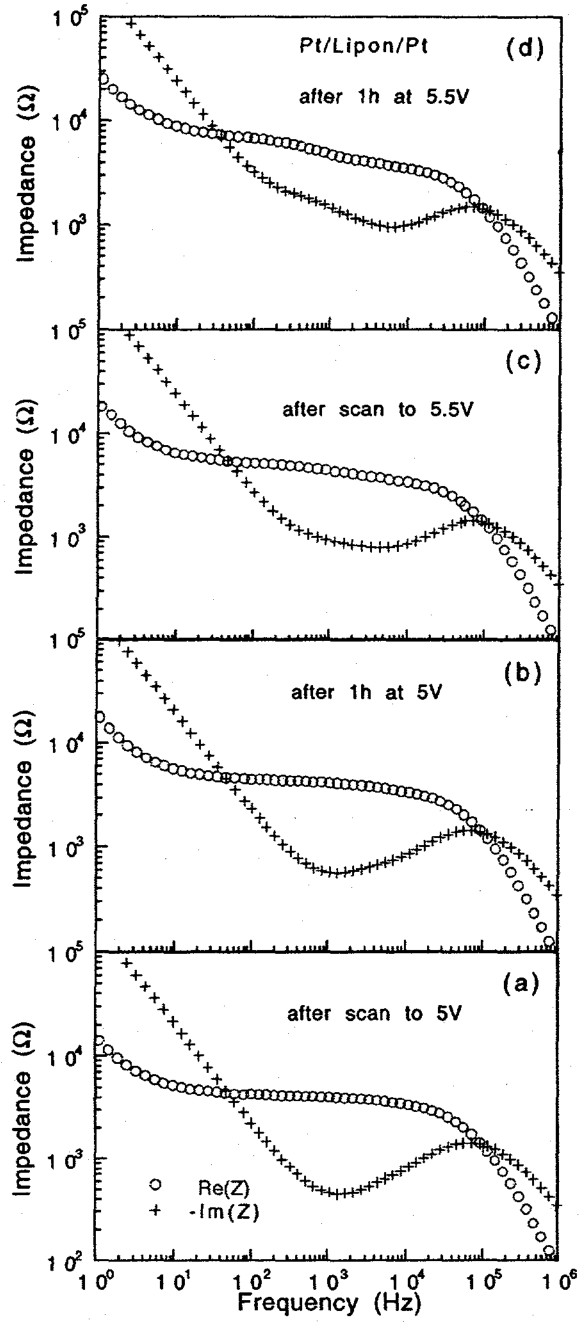

Fig. 3 Impedance spectra of Lipon between a pair of Pt electrodes after scan to (a) 5 V, (b) 1h at 5 V, (c) 5.5 V, and (d) 1h at 5.5 V. The scan rate was 1mV/second.

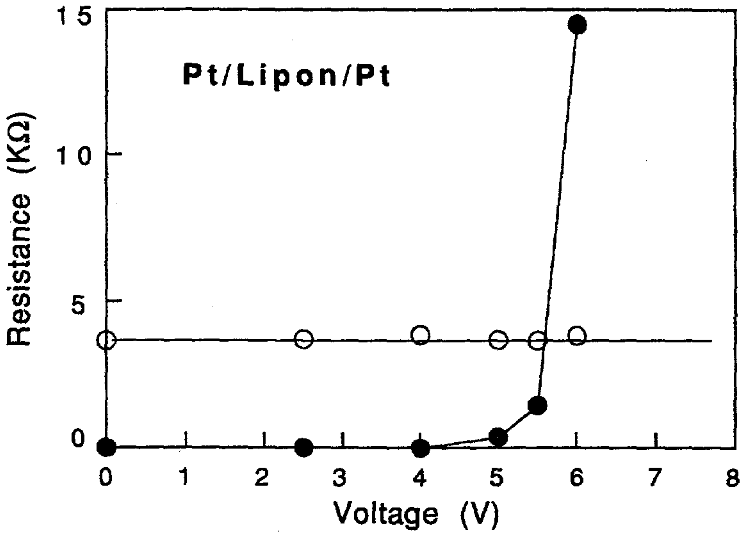

Fig. 4 Resistance of the Lipon layer (open symbols) and the second phase (solid symbols), respectively, as a function of the applied voltage. The solid lines are visual aids.

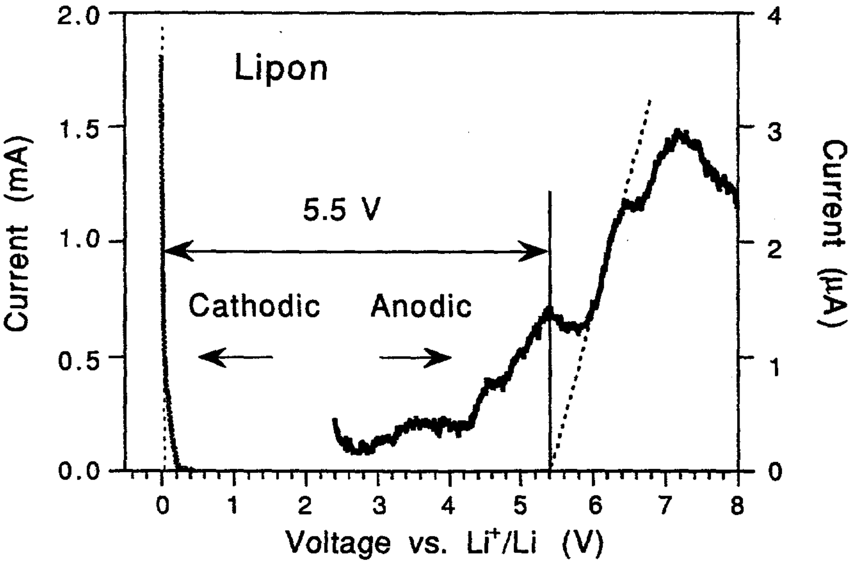

Fig. 5 Current-potential curves of a Lipon/Pt half cell with respect to the Li^+/Li reference. The scan rate was 1mV/s.