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**PROPERTIES OF VACUUM DEPOSITED THIN FILMS OF  
LITHIUM PHOSPHOROUS OXYNITRIDE (Lipon) WITH AN  
EXPANDED COMPOSITION RANGE**

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**Technical Abstract:**

Thin films of an amorphous, solid-state, lithium electrolyte, referred to as "Lipon," were first synthesized and characterized at ORNL in 1991. This material is typically prepared by magnetron sputtering in a nitrogen plasma, which allows nitrogen atoms to substitute for part of the oxygen ions of  $\text{Li}_3\text{PO}_4$ . Lipon is the key component in the successful fabrication of ORNL's rechargeable thin film microbatteries. Cymbet and several other US Companies have licensed this technology for commercialization. Optimizing the properties of the Lipon material, particularly the lithium ion conductivity, is extremely important, yet only a limited range of compositions had been explored prior to this program. The goal of this CRADA was to develop new methods to prepare Lipon over an extended composition range and to determine if the film properties might be significantly improved beyond those previously reported by incorporating a larger N component into the film.

Cymbet and ORNL investigated different deposition processes for the Lipon thin films. Cymbet's advanced deposition process not only achieved a higher deposition rate, but also permitted independent control the O and N flux to the surface of the growing film. ORNL experimented with several modified sputtering techniques and found that by using sector sputter targets, composed of  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_3\text{N}$  ceramic disks, thin Lipon films could be produced over an expanded composition range.

The resulting Lipon films were characterized by electrical impedance, infrared spectroscopy, and several complementary analytical techniques to determine the composition. When additional N plus Li are incorporated into the Lipon film, the lithium conductivity was generally degraded. However, the addition of N accompanied by a slight loss of Li gave an increase in the conductivity. Although the improvement in the conductivity was only very modest and was a disappointing conclusion of this study, forcing a higher N content in the Lipon may alleviate some of the run-to-run variations in the Lipon quality that have been problematical for years.

**Statement of Objectives:**

The common objective for both participants of this crada was to synthesize and characterize lipon thin films with nitrogen and lithium concentrations in excess of typical compositions currently used at ORNL. This was accomplished. Although the results were disappointing for the commercial applications of Lipon, a broader understanding of the effects of composition and structural relaxation on the lithium conductivity was gained. In addition, Cymbet has demonstrated that Lipon films of good quality can be deposited by a more economical and practical high-deposition rate process.

The second objective for ORNL researchers was to investigate the oxygen-nitrogen equilibrium for the lipon films during film deposition. Little progress was made on this challenging undertaking to develop new approaches to monitor and control the oxygen partial pressure within the plasma. Such a project would be worthy of additional effort in the future. If successful it might advance our ability to reproducibly control the film stoichiometry for a variety of thin film materials.

**Project Duration:** 12 months, April 1, 2001 to March 30, 2002. Later extended to November 17, 2003

### **Benefits to the Funding DOE Office's Mission**

Lipon is being used by a number of companies and research groups as the solid electrolyte for thin film batteries and electrochromic devices. In addition, Lipon is being used as a protective layer at the electrode interfaces for larger batteries. Despite this wide acceptance, there are still many properties of the Lipon material that are still poorly characterized and poorly understood.

Although this research did not lead to any tremendous improvements in the Lipon properties, it did answer the nagging question concerning the effect of still greater nitrogen addition to the composition. With a fairly simple alteration in the deposition process, the expanded composition range has been explored, hopefully alleviating the need for more elaborate and costly deposition processes to investigate this phase region in the future. The results also provided additional evidence that the network or chain formation by the phosphate groups plays an essential role in providing an environment for the ready mobility of the lithium ions.

The use of  $\text{Li}_3\text{N}$  as an oxygen + lithium getter may be a simple addition to the deposition target to help ensure the optimum composition and maximum conductivity under the widest range of processing conditions. This may prove a useful technique for a great number of researchers and production engineers who are actively using Lipon in their studies or device fabrication.

### **Technical Discussion of Work Performed by All Parties:**

#### *1. Work performed at ORNL*

Lipon films were deposited using RF magnetron sputtering processes with a variety of standard and modified sputter sources (targets) with the goal of enhancing the nitrogen concentration relative to the oxygen content. A variety of substrates, alumina, graphite, and NaCl, were used for each deposition run in order to characterize the ionic conductivity, composition, and infrared absorption for nominally the same film, referred to as "sister" films. The most challenging aspect of the work was determining the composition with sufficient accuracy.

Several attempts to reduce the background level of oxygen proved unsuccessful indicating that this approach would require heroic efforts to realize a higher N/O ratio in our films. A more efficient alternative route to achieving a N-rich Lipon composition, was to boost the N content at the source by codeposition of  $\text{Li}_3\text{PO}_4$  along with  $\text{Li}_3\text{N}$ .  $\text{Li}_3\text{N}$  sputter targets and small disks used for preparing sectioned targets were prepared from  $\text{Li}_3\text{N}$  powder by pressing and sintering under a  $\text{N}_2$  atmosphere. This was necessary to minimize the reaction to form the more stable lithium oxide or lithium hydroxide.

In initial experiments, two to five small disks of  $\text{Li}_3\text{N}$  (1cm dia. X 1 mm thick) were arranged on the surface of the  $\text{Li}_3\text{PO}_4$  target. Because of the circular magnetic field of the magnetron source, sputter targets do not erode evenly, but form a circular erosion groove. Sputtering of the  $\text{Li}_3\text{N}$  disks lead to a deep erosion groove across the  $\text{Li}_3\text{N}$  disks, while material accumulated on the

surfaces away from the erosion ring. This gave the insight that ultimately proved successful in expanding the composition window. When Li<sub>3</sub>N was added to the target within the erosion groove, the film composition was effectively doped with N and Li. Alternately, when Li<sub>3</sub>N was added to the unsputtered edges and central areas of the target, it functioned as an effective getter for oxygen yielding higher N/O ratios, without the addition of additional Li to the film composition. These trends were confirmed by analysis of the film compositions. We believe that this is the *first demonstration where a “getter” material was used to adjust the composition of a sputtered film.*

Determining the film composition required coordination of several analytical techniques (edx, rbs, icp) and careful consideration of the sources of systematic error and uncertainty in each. Trends in the results were clearly distinguished, despite rather large uncertainties in the composition of each film. Results demonstrated a previously unappreciated complication. Comparison of the film compositions for sister films on the alumina versus graphite substrates suggests that *Li may be adsorbed into the graphite substrate during the Lipon deposition.* This is consistent with other recent investigations in our laboratory and the mechanism is still not fully understood. The magnitude of the lithium insertion in the graphite varies from run to run. When the Lipon films are subsequently dissolved from the graphite substrates for icp analysis, in severe cases the top surface of the graphite disintegrates as the Li dissolves from the carbon. This realization greatly limits the useful information that was gained from analysis of the films on graphite, though comparison of the edx and rbs results added confidence that the edx determination of the N/O ratio was accurate.

The range of film compositions obtained with the Li<sub>3</sub>PO<sub>4</sub> + Li<sub>3</sub>N sectioned targets are illustrated by the table. These compositions represent the *extremes* observed in this study; a number of samples fall within these ranges.

	Typical Li <sub>3</sub> PO <sub>4</sub> film deposited with no source of N*	Typical Lipon film deposited in N <sub>2</sub> plasma	Lipon film deposited with max. Li <sub>3</sub> N dopant	Lipon film deposited with max. Li <sub>3</sub> N getter
Composition	Li <sub>2.9</sub> PO <sub>3.9</sub>	Li <sub>2.9</sub> PO <sub>2.9</sub> N <sub>0.7</sub>	Li <sub>4.2</sub> PO <sub>2.8</sub> N <sub>1.2</sub>	Li <sub>2.5</sub> PO <sub>2.4</sub> N <sub>0.9</sub>
Conductivity (S/cm)	7 X 10 <sup>-8</sup>	1.2 X 10 <sup>-6</sup>	4.1 x 10 <sup>-7</sup>	2.4 X 10 <sup>-6</sup>
Activation Energy (eV)	0.67	0.54	0.58	0.48

\* From earlier work.

With the Li<sub>3</sub>N arranged within the target erosion groove, films were deposited with a much higher N content compensated by added lithium. The high lithium content limits the cross links formed between the oxynitride phosphate groups. The composition in the table suggests that most of the phosphate groups are isolated “ortho” (PO<sub>3</sub>N)<sup>-4</sup> groups. Alternatively, with Li<sub>3</sub>N arranged in positions to act as an oxygen getter at the Li<sub>3</sub>PO<sub>4</sub> target surface, an increasing amount of N substitutes for the oxygen in the film, but it is now compensated by oxygen vacancies forming cross links between oxynitride phosphate groups. Linked phosphate groups

form the pyro ( $\text{P}_2\text{O}_7$ )<sup>-4</sup> group and longer “meta” chains or rings. The composition in the table suggests an average chain length of 6 phosphate groups. The effect of the  $\text{Li}_3\text{N}$  getter just continues the trend reported many years ago by Bates and Dudney for films deposited from  $\text{Li}_3\text{PO}_4$  targets sputtered in plasmas with an increasing  $\text{N}_2$  to Ar gas ratio. That is, the enhanced conductivity and improved chemical stability of the films is attributed to the greater crosslinked structure achieved by the nitrogen substitution and is accompanied by a decrease in the activation energy for the ion conduction. It seems unlikely that further chain formation, beyond an average of 6 units achieved in this study, would lead to any additional increase in the lithium ion mobility.

Overall, although significantly higher nitrogen content has been achieved in the Lipon films, the effect on the lithium ion conductivity was far more modest than we hoped to see. In many cases the conductivity degraded with the higher N content, while only a modest enhancement was seen for several films with lower Li contents. It should be noted that plots of the film conductivity versus compositional atomic ratios, including  $(\text{O}+\text{N})/\text{P}$ ,  $\text{O}/\text{N}$ , and  $\text{Li}/\text{P}$ , have a great deal of scatter, so *the trends are not as well behaved as suggested by the extremes listed in the table*. The highest conductivities and lowest activation energies reported previously in the literature for Lipon deposited with the normal  $\text{N}_2$  plasma process, from ORNL work as well as other researchers, are  $2 \times 10^{-6}$  S/cm and 0.54 eV. Although this work does not offer opportunities for greatly improving the lithium conductivity in the Lipon films, perhaps *the  $\text{Li}_3\text{N}$  getter technique would be useful to ensure that a maximum conductivity is indeed achieved from run-to-run*.

Comparable enhancements of the lithium conductivity has been achieved by a post deposition anneal of the films. This effect has been known at ORNL for a number of years and is now part of our protocol for preparing Lipon films in thin film batteries. The heat treatment is typically a brief 10 minute soak in a 250°C oven. For all films prepared in this study, regardless of the composition and as deposited conductivity, *the lithium conductivity increased by a factor of 1.4 to 2 times when briefly annealed at 250°C*. Presumably this is due to a relaxation of the structure, allowing more optimal sites for the lithium to form in the relaxed amorphous phosphate structure. Infrared absorption spectra for the Lipon films on NaCl substrates were recorded for films before and again after the 250°C anneals to investigate this effect. The changes in the P-O vibrational modes due to the heat treatment are only very small shift to higher energy and have not been fully analyzed. On the other hand, the formation of carbonate groups, presumably as  $\text{Li}_2\text{CO}_3$ , upon anneal in air is clearly evident in the infrared results. Annealing in oxygen, nitrogen or argon gas was equally effective in relaxing the Lipon structure, yet prevented this carbonate formation. Although it is not clear if the carbonate formation is either detrimental or beneficial for the thin film lithium battery application, prevention may allow both the temperature and duration of the temperature treatment to be extended. This should be investigated further using a structural probe that is more sensitive to changes of the Lipon structure, especially the Li ion environment. Such an investigation may suggest a more effective way to enhance the lithium ion conductivity in the electrolyte film.

## *2. Work performed at Cymbet*

Installation of the equipment for Cymbet's proprietary film deposition process was unexpectedly delayed beyond the initiation date of this CRADA program. Because of this, initial work was preformed using standard sputtering techniques comparable to those used at ORNL.

Initial Lipon films were deposited onto silicon wafers with an insulating surface oxide film. Achieving good Lipon films on silicon substrates which are free of flaws that result in electrical shorts either across the Lipon film or across the insulating oxide film to the silicon is quite challenging. Eventually, Cymbet did deposit Lipon films with lithium ion conductivities comparable to those achieved on alumina substrates at ORNL. An interesting interaction was observed between adjacent conductivity electrodes on the Lipon films. This may be due to lithium insertion into the  $\text{SiO}_2$  surface during the Lipon deposition, effectively reducing the resistance between the metal contacts. In addition, Cymbet confirmed the effect of the  $250^\circ\text{C}$  heat treatment on the conductivity of their Lipon films, and report a slow increase in the Lipon film resistance, if not stored under dry Argon conditions. This is likely due to the carbonate reaction.

Concerning the influence of an enhance nitrogen content in the Lipon film and other process variations, Cymbet observed as is discussed above, that most changes lead to a deterioration of the conductivity, rather than an improvement.

## *3. Joint Work*

Although a number of Lipon and also  $\text{LiCoO}_2$  film samples were exchanged between ORNL and Cymbet during the course of this CRADA, the disappointing results for the enhanced lithium conductivity did not inspire the active collaboration that was anticipated.

### **Plans for Future Collaborations**

Plans at this time include providing assistance with fabrication of Li anode thin film batteries and/or hosting researchers from Cymbet to evaluate batteries with Li anodes. These will be used as bench mark for their Li-ion battery deposition experiments. Other than providing occasional assistance or advice, we have no plans to pursue more extensive collaborative work at this time.

### **Conclusions**

Increasing the nitrogen concentration in the Lipon thin film via substitution for oxygen ions of the phosphate groups resulted in an extended chain or network formation. This gave a modest enhancement in the lithium ion conductivity and a lower activation energy for the ion mobility compared with typical Lipon properties reported earlier. On the other hand, when the increasing nitrogen concentration is compensated by additional lithium ions, there is a detrimental effect on the conductivity and an increase in the activation energy. These two cases were achieved using  $\text{Li}_3\text{N}$  pellets as either a getter at the sputter target, or as a dopant. Because the influence of the nitrogen content on the Lipon films was minimal, the more elaborate efforts to control and monitor the oxygen and nitrogen partial pressures in the plasma environment were abandoned.

Additional results were obtained concerning the influence of the high temperature anneal on the Lipon property. The ion conductivity for Lipon films of all compositions was significantly enhanced when annealed for a brief time at 250°C. If annealed in the presence of carbon dioxide, a reaction layer of  $\text{Li}_2\text{CO}_3$  forms at the surface.

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