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**DEVELOPMENT OF A LITHIUM MICROBATTERY
PACKAGING TECHNOLOGY
ERKTS01**

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FINAL REPORT
DEVELOPMENT OF A LITHIUM MICROBATTERY
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ABSTRACT

The objective of this joint project between Oak Ridge National Laboratory (ORNL) and Eveready Battery Company (EBC) was to develop a coating process that would protect the lithium anode of thin-film rechargeable lithium batteries from air. Several methods were investigated including metallization of the lithium film, coverage of the lithium anode with the electrolyte, lithium phosphorus oxynitride (Lipon), and other ceramic films, and a multilayer coating consisting of alternating films of parylene and metal and/or ceramic films. The parylene-ceramic or metal multilayer coating was found to be an effective packaging method for thin-film lithium batteries.

BACKGROUND

This project began when it was recognized that rechargeable thin-film lithium batteries developed at EBC and at ORNL required a method for protecting the lithium anode and other components from attack by air before commercialization of either technology could be considered. These cells are fabricated with the lithium anode film on top of a multilayer stack as illustrated in Fig. 1. Because lithium is highly reactive, it was necessary to develop a technique for coating the battery that could protect the lithium anode film from exposure to air and, of course, not react with the lithium.

SUMMARY OF RESULTS

Experimental Procedures

Investigations of the different possible coatings methods were carried out on lithium films deposited onto sodium borosilicate glass slides. In order to avoid the darkening of the glass caused by the formation of color centers on direct exposure to lithium, the slides were first covered with 0.2 μm thick films of lithium phosphorus

Figure 1. Schematic cross section of a thin-film lithium battery.

oxynitride (Lipon) deposited by rf magnetron sputtering of Li_3PO_4 in pure N_2 . This new material discovered at ORNL does not react with lithium and thus provided a protective barrier between the glass slides and the lithium films. Lithium films were deposited by thermal evaporation of Li metal in a vacuum chamber at a pressure of about 10^{-6} Torr. Metal film overlayers were deposited by dc magnetron sputtering or by electron (e-beam) evaporation, and overlayers of the Lipon electrolyte were deposited by the method just described.

A special system was assembled for the deposition of parylene-c and the alternating ceramic or metal layers. It consisted of three interconnected vacuum chambers for: (1) load locking, (2) parylene deposition, and (3) metal or ceramic film deposition. The chambers were separated by gate valves, and each had its own vacuum pump: turbopumps for the load lock and metal/ceramic film chambers and a cold trap backed by a mechanical pump for the parylene chamber. Specimens including single lithium films and thin-film batteries were transported from the controlled atmosphere glove box in a vacuum suitcase and inserted into the load lock chamber. The multilayer structures are denoted below as X/Li/Lipon/S, where X denotes an overlayer on Li, and S denotes the glass substrate.

The films and multilayer structures were examined in optical and scanning electron microscopes before and after exposure to air. In some experiments, the specular reflectivity of the Li/Lipon interface measured with a He-Ne laser and the

resistance of the Li film deposited across two V contacts were monitored continuously as a function of exposure time.

Lithium Metallization

The obvious solution for protecting the lithium anode is to cover it with a metal overlayer that would provide a barrier against penetration of air and water vapor. The metal chosen for this purpose must be one that does not alloy with lithium, such as chromium, nickel, or vanadium. Several attempts were made to cover lithium films with sputter deposited vanadium and electron beam evaporated chromium. Typically, the metal overlayer tended to crack and spall, especially at the edges of the Li film where stress in the overlayer is high. Because Li is ductile while the Cr or V overlayers are brittle, it is not surprising that spalling and cracking usually occurred. In a few instances with both V and Cr, crack-free films were obtained, but the Li film degraded rapidly on exposure to air. On examination by x-ray microanalysis in a scanning electron microscope, we found that the V or Cr was buried under a reaction layer, possibly Li_2CO_3 . We conclude that as a consequence of the rough microstructure, Li atoms diffuse rapidly to the surface through voids in the metal overlayer where they react with water vapor and CO_2 to form Li_2CO_3 . In order to achieve a closer match to the mechanical properties of the lithium, overlayers of Cu and Sn were deposited over the lithium films by evaporation. While the overlayers appeared to be crack free, the lithium films degraded on exposure to air. Direct metallization was abandoned as a possible protective coating method.

Coating Li with Lipon Thin Films

Early attempts to cover the lithium films with the Lipon electrolyte were unsuccessful due to the rough texture of the lithium. After it was found that very smooth lithium films could be deposited by using high deposition rates, $\sim 40 \text{ A/s}$, we succeeded in coating the lithium with a layer of the Lipon electrolyte and with successive layers of SiO_2 /Lipon or metal/Lipon followed by a thick coating of a UV cured epoxy. While investigations supported by another project are still in progress, the results are encouraging. Developing an alternate packaging process that does not require parylene is important in certain cases where it is desirable to avoid coating the entire device with conformal coating.

Li Coverage with Parylene

Parylene is a well-known conformal polymer coating that provides a diffusion barrier to air and water vapor. The molecular structure of parylene C is shown in Fig. 2. The polymer was formed by subliming the dimer at about 150°C in the first section of a two stage furnace and then forming the monomer by heating to 650°C in the second stage. The monomer vapor was pumped into the vacuum chamber maintained at a pressure of 30 mTorr where it condensed on every exposed surface.

Figure 2. Structure of parylene-C polymer.

A Li/Lipon/S test specimen was coated with about 5 μm of parylene. The resistance and reflectivity of the test specimen were measured as a function of exposure time. Degradation of the coated lithium film was noted after about 5 h. This is about 70 times faster than expected, based on the reported diffusion coefficients of air and water vapor through parylene-C. We surmised that pores in the parylene film were responsible for the rapid transport of air and/or water vapor to the lithium films.

Additional test specimens were coated with 5 μm of parylene, and then an 0.5 μm aluminum film was deposited over the parylene. The Al overlapped the underlying Li film by about 50% but did not overlap the parylene which covered the entire surface of the specimen. The lithium films remained essentially unchanged over more than 90% of its area after more than four weeks of exposure to air. For the first three weeks, reaction was noticeable only around the edges of the Li film. After four weeks, some reaction near the center of the film was evident. Graphs of the specular reflectivity from the Li/Lipon interface for the parylene-coated and the Al-parylene coated films are compared in Fig. 3.

Figure 3. Specular reflection from Li/Lipon interface for coverage of Li with parylene alone and with aluminum over parylene.

These results illustrated in Fig. 3 suggest that the thin Al film served to cover many of the pores in the parylene film thus improving the protection. This mechanism is illustrated in Fig. 4.

Figure 4. Schematic drawing of a lithium film covered with a porous thin layer of parylene and a metal film overlayer which closes the pores.

As a test of the ultimate practicality of packaging thin-film lithium batteries with a multilayer coating, numerous cells have been packaged and their performance evaluated. These include several of the EBC batteries that use TiS_2 as

the cathode as well as $\text{Li-V}_2\text{O}_5$ and $\text{Li-LiMn}_2\text{O}_4$ batteries developed at ORNL. Beginning with the Li film, the cells had the construction Li/P/M/P/M/P where P = parylene and M = metal. The metals included V and Ti. In a few instances, the metal layers were replaced with TiO_2 . Typically, the first and second parylene layers were 2 to 5 μm thick while the last layer was 10 to 20 μm thick. The metal and ceramic layers were about 0.05 μm thick.

The packaged cells exhibited months of reliable operation in laboratory air. For many applications, additional protective layers will not be required since the thin film battery will be incorporated into device that will be hermetically sealed with thick coatings or encased in air tight housings. Preliminary results indicate that adding thick layers of a UV curable epoxy over the entire cell can indefinitely extend the operating lifetime in air for those cases in which the battery must remain exposed.

CONCLUSIONS

The objective of this joint project between Oak Ridge National Laboratory (ORNL) and Eveready Battery Company (EBC) to develop a coating process that would protect the lithium anode of thin film rechargeable lithium batteries from air was achieved.

INVENTIONS AND COMMERCIALIZATION

Two patent applications based on work in this project were prepared and submitted to the U. S. Patent Office. The first patent has issued, and the second is awaiting further office action.

1. "Protective Lithium Ion Conducting Ceramic Coating for Lithium Metal Anodes and Associated Method," J. B. Bates, Patent Number 5,314,765.
2. "Packaging Material for Thin-Film Lithium Batteries," J. B. Bates, N. J. Dudney, and K. A. Weatherspoon.

The successful outcome of this project has provided an important step toward commercialization of the thin-film rechargeable lithium battery technology developed at ORNL. License agreements with a consortium of three companies, Teledyne Electronics, Optical Coatings Laboratory Inc., and PRECO have been signed,

and work on developing manufacturing processes is underway. Several additional CRADA projects are in progress for the development of prototype thin-film batteries for specific electronic devices. These include a personal hazardous gas monitor and a transdermal medical device. No future work with EBC is planned as they decided not to pursue commercial development of their thin-film battery.

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