COLD NEUTRON DEPTH PROFILING OF LITHIUM BATTERY MATERIALS

As part of a continuing collaboration between NIST and Tufts University, we have employed cold neutron depth profiling (NDP) to measure elemental concentrations versus depth for several lithium ion battery materials. One goal is to rationally design the thermo-mechanical properties of amorphous lithium phosphorous oxynitride (lipon, a solid ionic conductor), particularly the thermal stress (thermal expansion coefficient). A part of this study is to relate the resulting thermal stress to starting composition and temperature of evaporant, and of the composition and pressure of the background gas during deposition. We are also studying $LiCoO_2$ films (a material that can be used as an electrode in batteries) to determine if the ion beam assisted deposition process used has the capability of controlling not only the degree of crystallinity and orientation of crystallites, but also of the Li/Co ratio.

The NIST cold neutron depth profiling instrument and technique have been described previously [1]. The technique of neutron depth profiling (NDP) permits the determination of depth profiles in thin films up to a few micrometers for several light elements. The most readily analyzed elements are lithium, nitrogen, and boron. We have previously reported measurement of lithium mobility in electrochromic devices [2]. The lithium depth profiles are based on the measurement of the energy of alpha particles and/or tritons from the $^6Li(n,\alpha)^3H$ reaction. Nitrogen depth profiles are based on the measurement of the energy of protons from the $^{14}N(n,p)^{14}C$ reaction. Samples are placed in a beam of cold neutrons, and the emerging particles are intercepted by surface barrier detectors that measure their number and energy. Comparing the emission intensity with that of a known standard leads to quantitative determination of the lithium and nitrogen concentrations. Moreover, the emitted charged particles lose energy as they exit the film; this energy loss provides a direct measurement of the depth of the originating lithium nucleus. A great advantage of the NDP technique is that it is non-destructive, which allows repeated observations of the concentrations under different conditions. When combined with other techniques, e.g., activation analysis, ratios to other constituents can be determined.
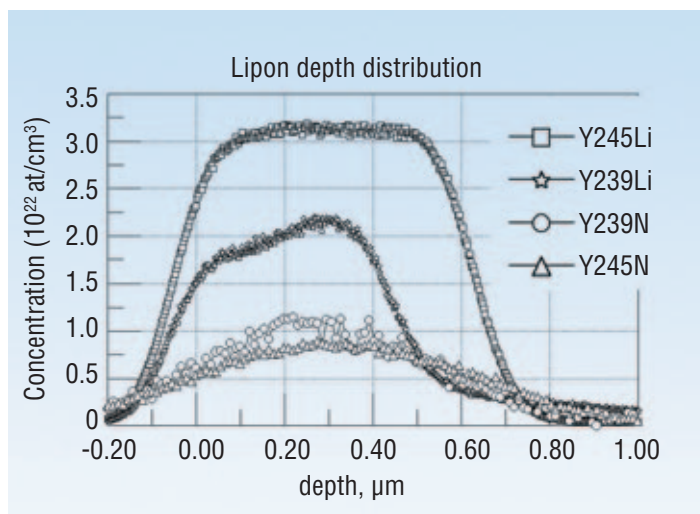

FIGURE 1. Depth profiles of lithium and nitrogen for two different lipon samples.

Table I

Sample	Li/N Ratio	Thickness, μm
Y243	4.46	0.7
Y232	4.39	1.5
Y239	1.63	0.4
Y245	3.1	0.6

Figure 1 gives an example of profiling results using the NDP technique. Shown here are profiles for two lipon samples manufactured under different conditions. The elemental concentrations in atoms/cm³ are presented as a function of depth. Because the alpha particle loses energy at a greater rate than the proton, the resolution for the lithium profile is better than that for nitrogen. One observes that the sample Y245 has a much more uniform distribution of lithium than sample Y239. By integrating the areas under the curves, one obtains the total concentration of lithium and nitrogen, respectively, and therefore the ratio of the two in the sample. Table I gives measured lithium/nitrogen ratios thus obtained and the corresponding thicknesses of four lipon samples.
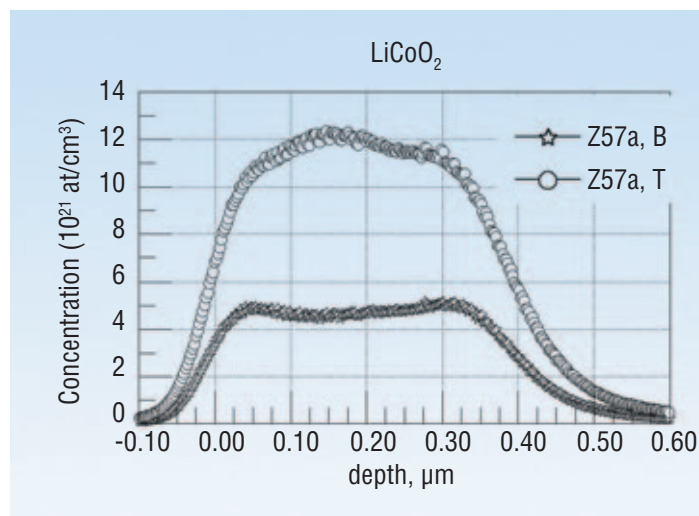
G.P. Lamaze, H.H. Chen-Mayer, and D.A. Becker
Chemical Science and Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899-8395

F. Vereda, A. Gerouki, N. Clay, P. Zerigian, T. Haas, and R.B. Goldner
Electro-Optics Technology Center
Tufts University
Medford, MA 02155

FIGURE 2. Typical lithium depth profiles of two LiCoO$_2$ samples.

Table II

Sample	Lithium (at/cm^2)	Cobalt (at/cm^2)	Li/Co Ratio	Ratio Uncertainty (%)(1σ)
Z57a,T	4.9×10^{17}	7.0×10^{17}	.70	3.5
Z57a,B	2.2×10^{17}	7.0×10^{17}	.31	3.5
Z57b,T	4.8×10^{17}	7.0×10^{17}	.68	3.5
Z57b,B	1.9×10^{17}	7.0×10^{17}	.27	3.5
Z59	9.4×10^{17}	7.6×10^{17}	1.25	3.5

To obtain information on other isotopes that are not measurable by NDP, a combination of techniques is employed. In the following example the ratio of lithium to cobalt in two thin film LiCoO$_2$ samples is determined. The lithium concentration is determined by NDP, as described above; and the cobalt concentration is determined by instrumental neutron activation analysis (INAA). Figure 2 gives lithium depth distributions from NDP measurement for two thin films of LiCoO$_2$. The integral under the curves gives the total amount of lithium in the film. After the depth distributions

were obtained, the samples were encapsulated in polyethylene "rabbits" for irradiation in the core of the NIST reactor. The total cobalt concentration was then determined by INAA in which the ^{60}Co gamma decay intensity was measured and compared with a standard. Table II gives the lithium and cobalt atom area density obtained from NDP and INAA respectively, as well as the lithium/cobalt atom ratios for these and other samples. The INAA technique does not provide any depth information, so that the ratio values listed in the table are for the average over the entire depth.

To summarize, depth profiles of two different lithium ion battery materials have been measured. For the lipon sample, profiles were obtained for lithium and nitrogen as well as the total quantity of each of these elements in the film. To date, an insufficient number of samples have been measured to obtain a good correlation with the physical properties of the films. We are also investigating the possibilities of measuring Li/P ratios of both starting materials and resulting films by combining NDP with RNAA for phosphorous.

For the lithium cobalt oxide sample, the NDP technique was combined with INAA to determine the ratio of lithium to cobalt in the samples. Although further work is needed to better quantify the relative evaporation rates of lithium and cobalt, it has been demonstrated that the measured Li/Co ratio varies in direct proportion to the relative evaporation rates of lithium and cobalt, as anticipated. Furthermore, the results indicate that the Li/Co ratio can be controllably varied from being less than one to greater than one.

REFERENCES

[1] R. G. Downing, G. P. Lamaze, J. K. Langland, and S. T. Hwang, NIST Journal of Research. **98,** 109(1993).

[2] G. P. Lamaze, H. H. Chen-Mayer, A. Gerouki, and R. B. Goldner, Surf. Interface Anal. **29,** 637 (2000).