

Cold neutron depth profiling of lithium-ion battery materials

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Abstract

We report the characterization of two thin-film battery materials using neutron techniques. Neutron depth profiling (NDP) has been employed to determine the distribution of lithium and nitrogen simultaneously in lithium phosphorous oxynitride (LiPON) deposited by ion beam assisted deposition (IBAD). The depth profiles are based on the measurement of the energy of the charged particle products from the ${}^6\text{Li}(n,\alpha){}^3\text{H}$ and ${}^{14}\text{N}(n,p){}^{14}\text{C}$ reactions for lithium and nitrogen, respectively. Lithium at the level of 10^{22} atoms/cm³ and N of 10^{21} atoms/cm³, distributed in the film thickness on the order of 1 μm , have been determined. This information provides insights into nitrogen incorporation and lithium concentration in the films under various fabrication conditions. NDP of lithium has also been performed on IBAD LiCoO₂ films, in conjunction with instrumental neutron activation analysis (INAA) to determine the cobalt concentration. The Li/Co ratio thus obtained serves as an ex situ control for the thin-film evaporation process. The non-destructive nature of the neutron techniques is especially suitable for repeated analysis of these materials and for actual working devices.

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1. Introduction

We have employed cold neutron depth profiling (NDP) to measure elemental concentrations and spatial distributions for two different lithium-ion battery materials. One goal of our ongoing research program was an attempt to modify the thermo-mechanical properties, especially the thermal expansion coefficient, of amorphous lithium phosphorous oxynitride (LiPON), a solid ionic conductor [1,2], in order to reduce the thermal stress in the films [3]. The use of these techniques can help us relate the microscopic composition parameters to the resulting stress, and hence to deposition parameters, such as the starting composition and temperature of evaporant, the ion gun anode current and voltage, and the composition and pressure of the background gas during deposition. We have also studied LiCoO₂ films (a widely used cathode material in lithium-ion batteries) to determine if the ion beam assisted deposition (IBAD) process being used has the capability of controlling the Li/Co ratio as well as the degree of crystallinity and orientation of crystallites.

2. Experimental

LiPON films were prepared by a nitrogen ion beam assisted deposition process as described previously [3]. Basically, the process consists of the thermal evaporation of Li₃PO₄ (purchased from Alpha Aesar¹) using a resistance-heated tungsten boat, and the simultaneous bombardment of the substrates with nitrogen ions provided by a Commonwealth Mark I ion gun. LiPON films were deposited on Corning #2947 glass substrates. The LiCoO₂ films were deposited by a process described elsewhere [4]. Separately controlled sources were used for each element. Cobalt was thermally evaporated with an electron beam system (Airco-Temescal electron beam gun and an IVI power supply and sweeper). Lithium was also thermally evaporated from a capped graphitic carbon container, the cap of which had a small (ca. 1 mm diameter) centrally located aperture; the carbon container was snugly fit into an alumina crucible, and

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment are necessarily the best available for the purpose.

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the two were heated by a Mathis tantalum resistance heater. A Commonwealth Mark I End Hall ion beam gun supplied oxygen ions. The evaporation rates of the Co and Li sources were monitored with water-cooled quartz crystal thickness monitors (Inficon).

The substrates for both the LiPON and the LiCoO₂ depositions were mounted on holders on a planetary system that was mechanically rotated and each holder revolved to obtain films of uniform thickness. No intentional heating except radiant heating from the sources was used. A Gould or a DekTak profilometer was used to determine the heights of steps resulting from cover glass masking of 1 mm thick microscope glass slides. Densities were estimated by using the mass change measured by an Inficon quartz crystal thickness monitor.

The NIST cold neutron depth profiling instrument and technique have been described earlier [5]. The technique of neutron depth profiling permits the analysis of depth profiles in films up to a thickness of 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 [6]. The lithium depth profiles are based on the measurement of the energy of alpha particles and/or tritons from the ⁶Li(n,α)³H reaction. Nitrogen depth profiles are based on the measurement of the energy of protons from the ¹⁴N(n,p)¹⁴C reaction. Samples are placed in a beam of cold neutrons that induce the capture reactions, and the intensity and energy of the emitted charged particles are measured by

surface barrier detectors. Comparing the emission intensity with that of a known standard leads to the quantitative determination of the lithium and nitrogen concentrations. The emitted particles lose energy as they exit the film; this energy loss provides a direct measurement of the depth of the originating nucleus. The stopping power is a function of the elements in the matrix and their atom density. If either the density of the material or the thickness in linear dimensions is known, then the depth distribution can also be calculated in linear dimensions. An example will be given in the results section. The NDP technique is non-destructive, which allows repeated determinations of the concentrations under different conditions.

3. Results

Tables 1 and 2 provide summary descriptions of the deposition parameters and operating conditions used in the deposition of the LiPON films being studied. We also include some measured and derived results, such as film thicknesses, conductivities and deposition rates. The first set of LiPON samples was produced at various deposition rates. Fig. 1a gives the depth distribution of lithium atoms in a thin LiPON sample. Sample LiPON2 was determined to have an area density of 0.76×10^{18} atoms/cm² of LiPON. From profilometry measurements, the thickness of the film is 0.7 μm; this permits a calculation of the density of 2.36 g/cm³ and a replot of the data in linear

Table 1
N/Li ratios, residual stress and Li-ion conductivity measured in four LiPON films, with corresponding deposition parameters of those films

Sample	Thickness (μm)	Atom ratio [N]/[Li]	Anode current (A)/voltage (V)	Rate (Å/s)	Fresh source?	Continuous/intermittent (maximum T (°C) ^a)	Residual stress (MPa)	Conductivity (S/cm)
LiPON1	0.55	0.61 ± 0.03 ^b	0.98/110	0.80	No	Continuous (204)	130	8.9 × 10 ^{-8b}
LiPON2	0.7	0.32 ± 0.02	0.88–0.98/77	1.5 ^c	Yes	Intermittent (100)	70	1.3 × 10 ⁻⁷
LiPON3	1.0	0.18 ± 0.01	0.98/135	10.3	Yes	Continuous (220)	185	1.1 × 10 ^{-6d}
LiPON4	1.0	0.17 ± 0.01	0.98/170	10.1	Yes	Continuous (239)	230 ^e	1.4 × 10 ^{-6d}

^a A chromel–alumel thermocouple embedded in a carbon block was used to monitor the temperature. Its reading was considered the highest attainable temperature for the samples.

^b Very low rates have usually resulted in low Li concentration and small Li-ion conductivity.

^c For sample LiPON2, a low rate was achieved by placing an aperture over the source. For sample LiPON1, the low rate was achieved simply by controlling the current through the boat. This means that the temperature of the source was higher for LiPON2 than it was for LiPON1.

^d Higher rates resulted in higher conductivity. For sample LiPON2 the effective rate was low, but the temperature of the boat was high. The conductivity is even higher if the deposition is continuous. That was the case for samples LiPON3 and LiPON4.

^e Note that residual stress is mostly of thermal origin. The deposition that reached the highest temperature was also the one that gave the highest residual stress. The purpose of the intermittent depositions was to control the stress of the films.

Table 2
N and Li concentrations for two IBAD LiPON films made with two different ion gun anode currents

Sample	Anode current (A)	Thickness (μm)	[Li] (cm ⁻³)	[N] (cm ⁻³)	[N]/[Li]
LiPON5	0.30	1.12	2.60 × 10 ²²	2.87 × 10 ²¹	0.11 ± 0.01
LiPON6	0.98 ^a	1.18	2.31 × 10 ²²	4.42 × 10 ²¹	0.19 ± 0.01

Rest of deposition parameters were kept fixed. Deposition rate was approximately 9 Å/s.

^a Maximum available anode current.

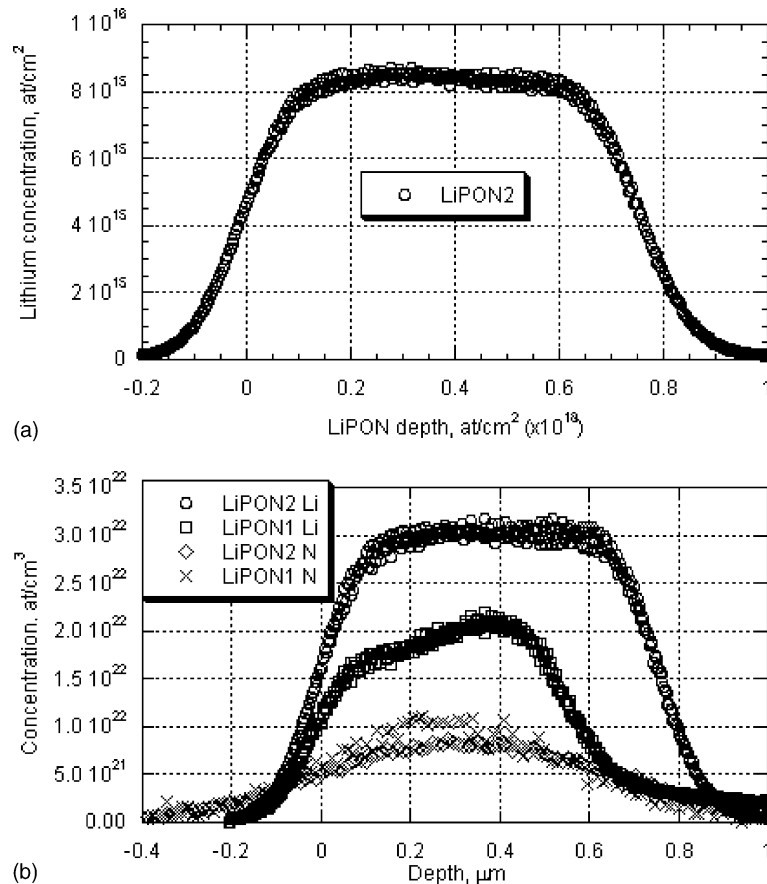


Fig. 1. (a) Depth profile of lithium in sample LiPON2 to establish the thickness in atoms/cm². This result with the total film thickness generates the depth scale in microns. (b) Depth profiles of lithium and nitrogen for two different samples, LiPON1 and LiPON2.

dimensions. Fig. 1b compares this sample with another made under different conditions. Additionally, the nitrogen distributions of these samples are also shown. 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. Sample LiPON2 has a much more uniform distribution of lithium than sample LiPON1. By integrating the areas under the curves, one obtains the total concentration of lithium and nitrogen, respectively. Table 1 presents measured lithium/nitrogen ratios and the corresponding thickness of four LiPON samples measured by NDP. The stated uncertainties of the atom ratios are $\pm 1\sigma$. Regarding the lithium depth profiles of LiPON films obtained by NDP, it can be seen in both Fig. 1b and Table 1, that the Li concentration of sample LiPON1 is remarkably lower than in the other films. This coincides with the fact that sample LiPON1 was deposited at the slowest rate (0.9 Å/s) we have employed for LiPON production in our laboratory, and the fact that the source had been used in previous runs. The results to date suggest that slow deposition rates result in increased Li deficiency, either because of the relatively low temperature of the source, and/or a larger arrival ratio of N ions to evaporated Li₃PO₄. Furthermore, for the sake of

reproducibility, we are currently using fresh Li₃PO₄ sources in all of our depositions.

For the second set of LiPON samples the depositions were made at a constant rate, but at different gun currents. The NDP technique provides an accurate measurement of the lithium and nitrogen concentrations of atoms per unit area. Table 2 shows the concentration (calculated as the area concentration divided by the thickness measured with the profilometer) of two LiPON films. The only difference between the films in samples LiPON5 and LiPON6 was the anode current of the ion gun during the deposition. It can be seen that a higher anode current, which is proportional to the actual density flow of ions, results in a higher nitrogen content and therefore a greater [N]/[Li] ratio, as expected. The uncertainties (1σ) for the lithium and nitrogen concentrations are ± 2 and $\pm 5\%$, respectively, and thus less than $\pm 6\%$ for the ratio uncertainty.

Taking a [Li]/[P] value of 2.7, which is a typical value obtained for our films by means of inductively coupled plasma (ICP) spectroscopy, and using the NDP [N]/[Li] ratio of 0.19, the formula factor for N would be approximately 0.5. That is, the composition of sample LiPON6 would be approximately Li_{2.7}PO_xN_{0.5}. This nitrogen concentration is as high as the highest reported by Yu et al. [2] or Roh et al. [7] for their sputtered LiPON films. However, it is

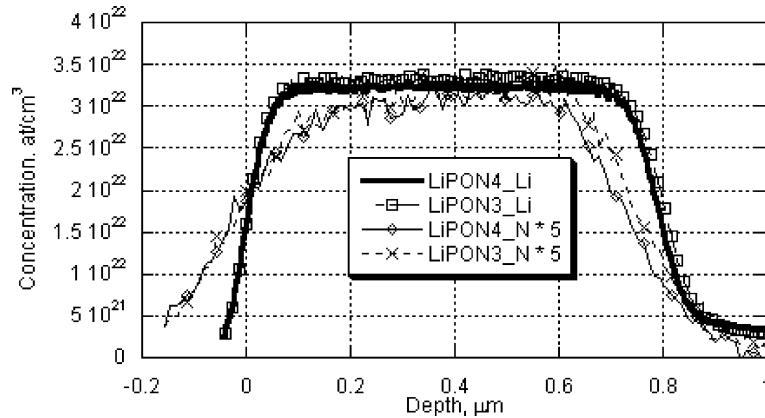


Fig. 2. Lithium and nitrogen depth distributions for LiPON3 and LiPON4 films. Nitrogen concentration values are multiplied by 5 for ease of comparison.

not clear if all this nitrogen enters the films as active monatomic nitrogen (active in the sense that the nitrogen bonds to phosphorous atoms and alters the structure of the starting Li_3PO_4), or if trapped diatomic nitrogen is also present. ^{15}N and ^{31}P NMR studies are under way to try to resolve this matter.

Shown in Fig. 2 are the lithium and nitrogen depth profiles of two LiPON films, for which the only difference between their depositions was the ion gun anode voltage; it was 135 V for LiPON3 and 170 V for LiPON4 (cf. Table 1). The anode current was 0.98 A in both depositions, the deposition rate was approximately 10 \AA/s and both films were $1.0 \text{ }\mu\text{m}$ thick. The NDP analysis did not reveal any significant differences between their concentration profiles for either Li or N, even though the films exhibited different Li-ion conductivities ($1.1 \times 10^{-6} \text{ S/cm}$ for LiPON3 and $1.4 \times 10^{-6} \text{ S/cm}$ for LiPON4) and residual stress (185 MPa for LiPON3 and 230 MPa for LiPON4, tensile in both cases). A possible explanation could be the way in which nitrogen incorporated into the films, either as

trapped molecular nitrogen, or chemically as monatomic nitrogen.

Even though lithium concentrations were sub-stoichiometric (as has been observed previously when Li_3PO_4 was nitrated [8]), using high deposition rates ($10\text{--}20 \text{ \AA/s}$) and fresh sources for each deposition can minimize lithium deficiency. It should be noted that in addition to minimizing the lithium deficiency, the use of higher rates and fresh sources has led to films that exhibit very uniform lithium profiles (as illustrated in Fig. 2). In addition, lithium vacancies caused by nitridation have been pointed out as one of the reasons why nitrogen incorporation leads to higher lithium mobility and therefore higher lithium-ion conductivity [8].

To obtain information on other elements that were not measurable by NDP, a combination of techniques was employed. In two thin-film LiCoO_2 samples, the lithium concentration was determined by NDP, as described above; and the cobalt concentration was determined by instrumental neutron activation analysis (INAA). Fig. 3 gives lithium

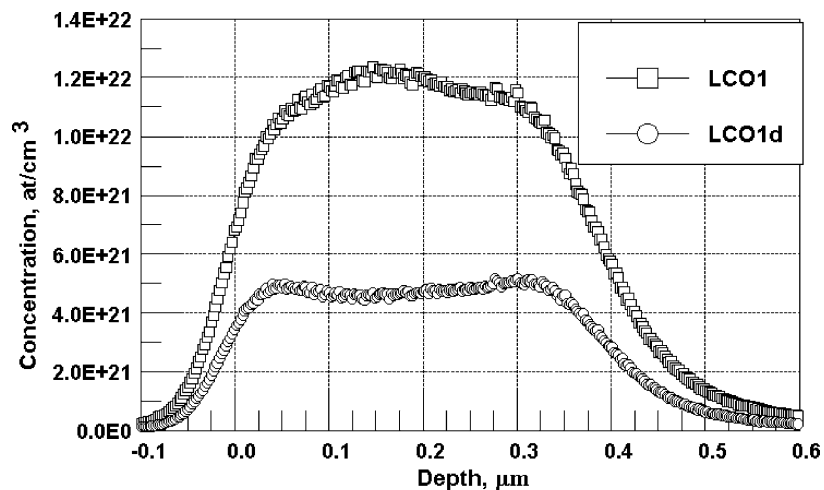


Fig. 3. Lithium depth profiles of two LiCoO_2 samples. Lithium had been extracted from sample LCO1d during coulometric titration experiments. Sample LCO1 was as deposited. Note the non-uniform profiles, which we attribute to loss of control of the lithium source as a result of excess heating during the deposition of a quartz crystal thickness monitor used to determine the lithium evaporation rate.

Table 3
Li/Co ratios for three samples of IBAD Li_xCoO_2

Sample	Lithium (atoms/cm ²)	Cobalt (atoms/cm ²)	Li/Co ratio	Ratio uncertainty (%) (1σ)
LCO1	4.9×10^{17}	7.0×10^{17}	0.70	3.5
LCO1d	2.2×10^{17}	7.0×10^{17}	0.31	3.5
LCO2	4.8×10^{17}	7.0×10^{17}	0.68	3.5
LCO2d	1.9×10^{17}	7.0×10^{17}	0.27	3.5
LCO3	9.4×10^{17}	7.6×10^{17}	1.25	3.5

Samples LCO1 and LCO2 were made in the same run. LCO1d and LCO2d refer to two pieces of LCO1 and LCO2 that were delithiated during coulometric titration experiments.

depth distributions for two thin films of LiCoO_2 . 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 3 gives the lithium/cobalt atom ratios for these and other samples. The INAA technique does not provide any depth information, so that the ratios obtained are averages over the entire depth.

Two sister LiCoO_2 samples (LCO1 and LCO2) from the same run were studied. Lithium had been extracted from one half of each of the samples (LCO1d and LCO2d, where ‘d’ at the end of the sample name stands for ‘delithiated’) during coulometric titration experiments. These were carried out in an argon atmosphere, using a 1 M lithium perchlorate in propylene carbonate electrolyte, and lithium metal strips as reference and counter electrodes. The other half of each sample remained as deposited (LCO1 and LCO2). The measured Li/Co ratios confirmed the lithium extraction. Table 3 also contains information regarding sample LCO3 (run code Z59). Due to the position of the thickness monitor crystals in the chamber, and to instabilities during the deposition process, we were unable to estimate a value for the Li to Co deposition rates ratio. However, it can be said that on average the Li to Co deposition rate was relatively higher for Z59 (sample LCO3) than it was for Z57 (samples LCO1 and LCO2).

4. Summary

Depth profiles of two different lithium-ion battery materials have been measured. For LiPON samples, profiles were obtained for lithium and nitrogen as well as the total concentration of each of these elements in the film. The data support the conclusion that the IBAD process is quite capable of giving consistent and constant lithium and nitrogen incorporation in the growing LiPON films. They also show that the IBAD technique used for the deposition of these LiPON films allows the incorporation of nitrogen in concentrations that can exceed those reported for sputtered films [2,7]. In contrast to the constancy of the lithium and nitrogen concentrations in LiPON, the non-uniformity of the

lithium-ion distribution in LCO was critical in demonstrating the lack of consistent control and constant lithium incorporation in the lithium cobalt oxide. This was a very useful observation which has led to modification of the deposition system and further attempts to improve the control of the separate lithium and cobalt sources in that IBAD process.

For lithium cobalt oxide samples, the NDP technique was also combined with INAA to determine the ratio of lithium to cobalt in the samples. Although further research is needed for better in situ control of the relative average 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 NDP and INAA measurements made on films from several different depositions show that the Li/Co ratio can be varied from less than to greater than one; therefore, with better control of the evaporation rates, one should be able to deposit LiCoO_2 films having any of a wide range of Li stoichiometries by the multi-source IBAD process being developed.

In conclusion, the NDP technique has proven to be valuable; first, because it provided depth profiles of Li and N concentrations in LiPON films, and of Li concentrations in LiCoO_2 films. The importance of this capability relies on the fact that the IBAD of both LiPON and LiCoO_2 can lead to undesirable variations in the composition of the films along their thickness. In the case of the LiPON deposition, preferential evaporation of the Li_3PO_4 source could lead to changes in time of the composition of the vapor phase and therefore of the films. In the case of the LiCoO_2 , this could happen because of poor control of any one of the sources especially of the Li and/or Co sources. This occurred during the deposition of LCO1 and resulted in the non-uniform profile seen in Fig. 3. Despite the non-uniform Li profile for LCO1, the data presented in Table 3 for LCO3 indicates that with the IBAD process one might be able to deposit LiCoO_2 films with excess lithium—with Li/Co as high as approximately 1.25.

The second important attribute of the NDP technique compared to other analytical methods is the fact that it is non-destructive. This is useful for the study of films which are used in active devices, since it allows measurements of the same area of the sample when in different states (e.g. for

a battery in any state of charge). This second attribute of the profiling capability of nuclear profiling methods has been shown in previous work regarding thin-film electrochromic window devices [6,9].

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