# Energy broadening of neutron depth profiles by thin polyamide films

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## Abstract

A protective covering is often required for neutron depth profiling (NDP) measurements of sensitive materials (e.g., Liion batteries). Addition of this layer can increase NDP profile energy broadening and depth assignment uncertainty. This study evaluates the magnitude of these effects when polyimide films of variable thicknesses are placed over Li-rich solids. Key results include a modeled increase in cold neutron beam attenuation with increased film thickness, a methodology for estimating profile energy broadening using a sigmoidal function, and, when using a thick layer, that the broadening will add uncertainity to the zero-depth position and depth scale assignment.

Keywords Neutron depth profiling · Activation analysis · Energy broadening · Li-ion cells

# Introduction

Neutron Depth Profiling (NDP) is a non-destructive radioanalytical technique that is sensitive to several isotopes, including <sup>6</sup>Li. NDP has become a popular method to measure both static and dynamic <sup>6</sup>Li distributions in Li-ion cells in recent decades [1-6]. Li-ion cells can be run in situ or operando to NDP with the measurement being independent of the chemical state of the isotope. In such NDP cell studies one or more thin (nm's-µm's) outer layers are placed on top of the atmospherically exposed electrode or current collector. The function of these layers is either protectivekeeping the interior material from unwanted atmospheric exposure-and/or functional -working as an electrode or electrochemical contact layer. Addition of these layers can result in a shift of the measured ion(s) energy profile(s) to lower energies and an increase in energy broadening. Such changes may influence data interpretation by increasing uncertainty in the depth dimension.

Two Li containing model materials and a lithiated battery material were measured by NDP with and without polyimide film (Kapton) coverings of variable thicknesses to gain a better understanding of the energy broadening phenomena. Kapton is a common protective layer added to Li-ion cells for NDP experiments [3, 5, 7, 8] with initial presentation of use in [7, 8]. The resulting data and subsequent modeling were analyzed to determine the extent and trends of broadening caused by the addition more Kapton layers (i.e., thicker capping layer) to the Li containing materials. From these results a simple modeling strategy for the observed broadening effects is presented.

# Theory

# NDP

Neutron capture by <sup>6</sup>Li ( $\sigma_0$ , Thermal = 938.5 barns  $\pm$  1.3 barns, 1 barn (b) = 1 × 10<sup>-28</sup> m<sup>2</sup> in Système International units [9]) is the reaction of interest in these cold neutron NDP experiments (Eq. (1)). In this reaction <sup>4</sup>He<sup>2+</sup> (alpha,  $\alpha$ ) and <sup>3</sup>H<sup>+</sup> (triton, <sup>3</sup>H) are produced:

Following emission, energy is lost from these particles (herein referred to as ions). The losses are primarily the result of ion interactions with host material electrons. The  $\alpha$  ions experience a larger stopping force in materials than <sup>3</sup>H ions due to their lower initial emission energy, valence state, and greater mass.



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$$[a] = [b] \frac{\sigma_{0a}}{\sigma_{0b}} \tag{2}$$

where [a] and [b] are the concentrations (atoms cm<sup>-2</sup>) of isotopes a and b being measured in the sample and standard/reference, respectively, and  $\sigma_{0a,b}$  is the thermal neutron cross-sections for the charged-ion emissions.

#### Neutron attenuation correction

Collected spectra need to be adjusted for incident neutron beam attenuation caused by the cover layer(s). Kapton contains, in assumed natural abundances, the neutron absorbing isotopes of <sup>14</sup>N and <sup>2</sup>H. <sup>14</sup>N isotope (stable,  $\approx$  99.6% natural abundance) has a thermal neutron capture cross-section of  $\approx$ 75 mb [10] and <sup>2</sup>H (stable,  $\approx 0.01\%$  natural abundance) has a thermal neutron cross section of  $\approx 0.5$  mb [10, 11]. These cross-sections generally increase with decreasing incident neutron energy (e.g., for "colder" neutrons). The <sup>1</sup>H isotope also has a large neutron scattering cross-section that further attenuates the incident beam. The attenuation of the NIST Neutron Guide-5 (NG-5) cold neutron beam, which has a neutron wavelength spectrum ranging up to 16 Å [12], was estimated from data calculated using values from the ENDF/B-VIII database [13]. Data included in the calculations comprised of absorption, incoherent scattering, and coherent scattering cross-sections for all elements in Kapton using an assumed Kapton density of 1.42 g cm<sup>-3</sup> and a 45° neutron beam incident angle to the surface of the Kapton.

Uncertainty in these calculated values is most likely dominated by the hydrogenous component of the Kapton. At the given wavelengths the absorption cross-sections for H is likely accurate, but the incoherent and coherent scattering cross-sections are most likely underestimated by a few percent. Neutron transmission percentages for each wavelength are presented in Fig. 1 and range from  $\approx 99.9\%$  (7.6 µm Kapton, shorter neutron wavelength) to < 95% (30.4 µm Kapton, longer neutron wavelengths). A color version of this figure is available online. Numerical values and details of their calculations can be found in Supplemental Information (SI) Table 5.

# Spectral interferences

The <sup>14</sup>N(n,p)<sup>14</sup>C reaction is present in the energy regime of neutron depth profiles starting at  $\approx$  584 keV and may overlap with the  $\alpha$  and <sup>3</sup>H reaction products. In this study an overlap was not observed for the discrete profiles (e.g., LiF, battery material ). All curve fitting terminated a minimum of 20 keV above the  $\approx$  584 keV starting point of



**Fig. 1** Incident neutron beam transmission as a function of neutron wavelength and thickness of Kapton capping layer. Data shown in this plot was calculated using an assumed Kapton density of  $1.42 \text{ g cm}^{-3}$  and a  $45^{\circ}$  neutron beam incident angle to the surface of the Kapton. The neutron wavelength range is representative of that found at NCNR NG-5. The 0  $\mu$ m data is not shown. See SI Table 5 for data and notes on these calculations. A color versions of this and all figures are available online

the <sup>14</sup>N reaction profile for the continuous profiles (e.g.,  $LiNbO_3$ ).

# lon energy broadening theory

Energy broadening in NDP data is influenced by system noise, ion energy straggling, multiple small angle scattering, and geometrical acceptance angles [14]. Generally, system noise is additive to energy broadening while energy straggling, scattering, and acceptance angle effects are distributive. It has been previously stated that ion energy broadening in NDP data is dominated by system noise and ion energy straggling depending on the experimental configuration [14, 15]. In this study, the geometry was held constant and has been designed to minimize its effect on energy broadening [16], and the system noise is assumed to be consistent over all experiments. The only varied parameter was the Kapton cover layer thickness. Therefore, the change in magnitude of ion energy broadening in the profiles is assumed to be the result of an increased ion travel path resulting from straggling and multiple scattering events.

Ion energy straggling is the statistical distribution of energies expected for an initially monoenergetic charged ion that has traveled and interacted some distance in a host material. Stated more precisely, it is the second moment of the energy loss distribution from the mean energy loss [17]. When a charged ion moves away from its origin it coulombically interacts with the nuclear and/or electronic properties of the material through which it is traveling. The transport interactions through the Kapton layer(s) are mostly dominated by electronic straggling within the energy range of ions measured in this study (Fig. 2B). Each interaction typically results in the loss of energy and can change the travel direction (by small angle scattering) of a charged ion. These interactions are probabilistic, and therefore, the expected energy of an ion at a given distance is calculated as an energy range. Ion energy straggling can be accounted for in energy broadening calculations using the Bohr (relativistic) model at high ion energies and by the Firsov Model at low ion energies [14, 17, 18].

The stopping force equation (Eq. 3) succinctly describes energy losses for a given material, ion energy and charged ion type. An example curve can be seen in Fig. 2A for a



**Fig.2** A Stopping force curve for Kapton being traversed by a <sup>3</sup>H charged ion with a starting energy of 2727.92 keV. The colored lines mark Kapton thicknesses measured in this study. Other colored lines and numbers denote the approximate change in slope of the stopping force curve as a function of Kapton thickness. The less steep the curve the lower the depth resolution in this region. Literature estimated uncertainty for calculated residual energy values is  $\approx 2\% - 5\%$  at 1 $\sigma$  for ideal systems [17]. **B** Nuclear and electronic stopping force for <sup>3</sup>H in Kapton as a function of Kapton thickness

$$S_{\rm f} = \frac{-\Delta E}{\lambda} \tag{3}$$

A detailed discussion of the stopping force can be found in [17] and will not be reiterated here. What is pertinent to the described research is that the stopping force equation is host material (related to its chemistry, stoichiometry, form, and density) and charge ion (identity, initial energy, and charge state) specific. The stopping force theory for solids predicts that with an increased charged ion pathlength there will be an increase in total energy straggling, and, in turn, an increase in total observed energy broadening. An increase in ion energy broadening suggests an increase in uncertainty of the volumetric concentration of the measured isotope at a given depth.

The projected range and exit energies of ions traveling through a material can be modeled using the Stopping Range Tables (SRT) or Transport of Ions in Matter (TRIM), programs within the Stopping and Range of Ions in Matter (SRIM) software [17]. Only a mean projected ion range is calculated with the SRT calculator due to limitations in the algorithm to accurately predict straggling at low ion energies [19, 20]. TRIM, which takes a more computationally expensive approach, overcomes this limitation by calculating nuclear straggling and scattering at interaction points within the target material for each modeled ion [21, 22]. This results in a more accurate prediction of ion ranges at both high and low energies. It is for this reason that TRIM was predominately utilized in this study. A drawback of both programs is that they model the material(s) the ions are traversing as amorphous [19, 21].

# **Energy broadening modeling**

Changes in energy broadening relative to cover layer thickness was estimated by fitting bounded peak or curve functions to the collected profiles. The sigmoidal function was selected for modeling the high energy edge of the continuous energy profiles (e.g., LiNbO<sub>3</sub>) as it is used to model data when a more specific mathematical function has yet to be defined for a data type [23]. It was also the function with the least number of fit parameters that was applicable to the measured data type. The Weibull function was selected for fitting discrete, peak-shaped profiles (e.g., LiF) as it accounts for the non-normal distribution of the NDP data; in terms of the dominate shape (asymmetric peak) and trailing, low energy tail of the data.

$$y = \frac{a}{1 + e^{-\left(\frac{x - x_0}{\beta}\right)}} \tag{4}$$

$$y = a \left(\frac{c-1}{c}\right)^{\frac{1-c}{c}} \left|\frac{x-x_0}{\beta} + \left(\frac{c-1}{c}\right)^{\frac{1}{c}}\right|^{c-1} e^{\left|\frac{x-x_0}{\beta} + \left(\frac{c-1}{c}\right)^{\frac{1}{c}}\right|^{c} + \frac{c-1}{c}}$$
(5)

Both the Weibull 4-paramter (herein referred to as the Weibull) and sigmoidal equations include a *shape parameter* ( $\beta$ ), that is the slope of the fit models, a *location parameter* ( $x_0$ ), that is related to the center of the higher energy edge of a profile for the sigmoidal fit and the peak center for the Weibull fit, and a *scaler parameter* (a). The shape parameters are pure numbers (i.e., dimensionless) while, and specific to this study, the location parameter and the scaler parameter have units of keV and normalized counts (unitless), respectively. Following from the stopping force theory outlined above, the shape parameter (which follows energy broadening) should change in magnitude as a function of layer thickness and the location parameter (which follows the stopping force of a material) should decrease.

The Weibull function has not been extensively used to model NDP data. Previous studies have utilized several functions within the Pearson family including Gaussians/mixed Gaussian functions to fit or deconvolute peaks in NDP data ([14, 15, 24–28], summary provided in Table 1). Historically, the use of a Gaussian or mixed Gaussian functions have been viewed as poor approximations of the true NDP response profile shapes because NDP profiles are not normally distributed [26, 29]. The use of Pearson family functions to fit depth profiles appears to have some roots in the 1975 dissertation of Hofker on B implantation into Silicon [30]. Utilizing the method of moments, Hofker found that a Pearson IV distribution, with four moments, best described the B implantation profiles-which have a relationship to NDP data through stopping force theory. The four moments calculated were: projected range (mean), standard deviation, skewness, and kurtosis. Of the four moments calculated for the profiles, only the calculated kurtosis values could not be linked with the experimental data as they were "... outside the accuracy limits with which the concentration profiles were measured or the moment are determined ... " [30]. Hofker stated that this occurred because the shape of the predicted tail of the profiles did not fit those calculated by the Pearson IV. The use of the Pearson IV was carried forward to fitting NDP data by Jahnel et al. (working with Biersack, the "godfather" of NDP) in 1981 [27]. However, and also in the 1980's, Winterbon, whose previous work was utilized by Hofker in establishment of the using the Pearson IV function to fit ion implantation data [30], argued that this was the wrong member of the Pearson function family to use in fitting this data type [31]. Winterbon showed that at low energies a variety of Pearson functions could be utilized to fit the data, where at higher energies a Pearson VI function was most appropriate. He explained that using a Pearson IV to fit higher implantation energy data would cause an overestimate of the skewness and other higher moments of the function. This finding was partially supported by the works of Selberherr et al. in 1984, where it was stated that only the Pearson IV and VII distributions should be applied to ion implant data as the physics of implantation were inconsistent with mathematics of the other shapes [32] (note, the Pearson VII distribution is a special case of the type IV). In 1987 Biersack countered this statement by analyzing the semi-infinite moments calculated from Monte Carlo simulations (which are the foundation of the TRIM models used

 Table 1
 Functions used to fit NDP or other types of profiles with associated citations

Fitting function	Paper author	Year published	Citation	Additional comments	
Pearson IV	Hofker	1975	[30]	Suggestion that a 4-moment function best fits ion implant data, but the kurtosis parameter could not be linked with experimental data	
Pearson IV	Jahnel et al	1981	[27]	Used Hofker et al. function to fit NDP data	
Pearson VI, V	Winterbon	1983	[31]	Argued Pearson IV overestimates the tails of the collected distribution because it decreases too slowly at larger implantation depths and because the kurtosis is much larger than published values. Sug- gests a Pearson V could be applied if a single parameter function is preferred	
Pearson IV, VII	Selberherr et al	1984	[32]	Suggests the use of the two negative discriminant functions as they are consistent with the physics of ion implantation	
Pearson I	Biersack	1987	[33, 34]	Used experimental data and Monte Carlo modeling results	
Pearson Family	Ashworth et al	1990	[34]	Choice of function is energy dependent. Infinite moments should be used for higher concentration sample data and semi-infinite moments for lower concentration sample data	
Weibull 4-parameter	Weaver et al	2022	This publication	4-moment, positive function that is related to the Pearson III distribu- tion (aka gamma function)	



Fig. 3 Normalized NDP results for LiF and LiNbO<sub>3</sub> profiles before and after covering with variable thicknesses of a Kapton capping layer (see key in A). A LiF signal count-energy profile with  $\alpha$  profile removed from the "0 µm" (aka non-covered) Kapton sample, and **B** 

in this study) and precise experimental data and showed the best match between data and model could be achieved with a Pearson I (aka *Beta type*) distribution ([33], and as stated in 34). More recently, Ashworth et al. (1990, [34]) have suggested that the choice of a Pearson fitting function is dependent upon the parameters of ion implantation (ion type, energy, angle of implantation, and target material). This finding echo that of Winterbon's from 1981, indicating that the choice of function is related to which region of a material's stopping force curve is being interrogated. This is an important point, as implant profiles are usually created from low energy ions while NDP profiles are derived from higher energy ions; a factor that could affect the shape of a peaked profile.

LiNbO<sub>3</sub> signal count-energy profile. The "\*" in **B** indicates the  $\alpha$  ion profile from the "0.0  $\mu$ m" covered LiNbO<sub>3</sub> sample. This profile was removed from plot (**A**) for clarity

In this study a Weibull 4-parameter distribution is used to fit the LiF NDP sample profiles (See SI Fig. 3). Like the Pearson distributions, the Weibull distribution is nonnormally distributed and has four moments: projected range (mean), standard deviation, skewness, and kurtosis. Additionally, the Pearson VI and IV and Weibull 4- parameters distributions have four parameters: location, scale, shape 1, and shape 2. The location is related to the center position (i.e., mean) of the peak, the scale to the maximum of the peak, shape 1 to the shape of the main peak, and shape 2 to the shape of the trailing tail. Unlike the Pearson functions, an explicit solution cannot be obtained for a Weibull distribution using the method of moments calculation [35]. Therefore, and per the suggestion of Pobočíková et al. in [35], a least-squares method for estimating parameter values for Weibull was employed, and a comparison study to fits with the Pearson IV, VII and Gaussian function to the LiF profiles conducted (see SI Fig. 5 for examples of these fits on LiF covered with 7.6  $\mu$ m of Kapton).

# Experimental

#### NDP

Cold NDP was conducted at the National Institute of Standards and Technology Center for Neutron Research (NCNR), NG-5 [36]. Two model Li materials and one Li-ion battery material were analyzed in this study and their normalized profiles are presented in Figs. 3 and 4A. All materials contain assumed natural abundance amounts of <sup>6</sup>Li ( $\approx 7.59\%$ ). The first model material is a piece of single crystal LiNbO<sub>3</sub> (in-house). This sample was selected as it is thick (several mm) and, as a stochiometric crystal, it yields a uniform, continuous ion energy signal profile within the energy range of the data acquisition system (Fig. 3Bm SI Fig. 1). The second sample is a  $\approx 1.0 \,\mu\text{m}$  thick LiF (Lebow Co.) thin film with a 0.1 µm Parylene backing (Fig. 3A). This sample is used to represent thin Li materials and had a fully visible recoil ion profile within the energy range of the data acquisition system (see SI Fig. 1). An  $\approx$  300 nm Li-alloy thin film was measured as the example battery material (Fig. 4A), and has been previously described in [37]. Individual sheets of 7.6 µm thick Kapton films (Advanced Materials Inc.) were utilized as capping layers.

Only the <sup>3</sup>H ion profiles were analyzed for all measured samples (for example, see Fig. 3A, B). The  $\alpha$  ions were either blocked or shifted to a lower energy for the samples covered with a Kapton film. The  $\alpha$  profiles for the uncovered samples were detected in the observable energy range but were not analyzed (for example see \* profile in Fig. 3B, SI Fig. 1).

Measurements were executed by mounting a sample behind a  $\approx 0.5$  mm thick fluorinated ethylene propylene (Teflon) sheet having a circular aperture of  $\approx 1.0$  mm (diameter) for the Li-alloy sample and  $\approx 3.0$  mm and  $\approx 5.0$  mm for the LiNbO<sub>3</sub> and LiF sample measurements, respectively. Herein reported NDP results are the average distribution of Li from across the surface area of the respective aperture openings. The aperture was affixed to an Al support frame, which was centered and placed facing  $\approx 120$  mm from a circular transmission-type silicon surface barrier detector (Ametek). The reaction product, a charged ion energy spectrum, was processed by a LynxDigital Signal Analyzer (Canberra) using 4096 channels. Data was acquired for  $\approx$ 22 h per aperture defined area for the alloy and 1 h or 4 h per aperture defined area for the LiNbO<sub>3</sub> and LiF samples,



**Fig. 4 A** Li alloy battery material profiles from sample covered with 7.6  $\mu$ m, 15.2  $\mu$ m, and 30.4  $\mu$ m of Kapton. The 22.8  $\mu$ m profile was not collected due to an unplanned reactor outage. **B** Sigmoidal model fit to the front edge of the 7.6  $\mu$ m Kapton covered Li alloy material  $R^2 = 0.999$ 

respectively. Each area analyzed was irradiated at a near constant thermal neutron equivalent fluence rate of  $\approx 1.2 \times 10^9$ neutrons cm<sup>-2</sup> s<sup>-1</sup>. NDP experiments were conducted under high vacuum and near room temperature. The same experimental setup was used to collect background profiles (clean Teflon sheet), and a <sup>10</sup>B concentration reference material (in-house) using the above listed aperture sizes. All profiles were corrected for instrumental deadtime ( $\approx 0.001\%$ ), reactor/beamline related variations in the neutron fluence rate, and background. Concentrations were calculated using the natural abundance of <sup>6</sup>Li (for samples) and <sup>10</sup>B (for the reference material). The normalized and corrected data was binned according to the energy resolution of the NIST NDP system ( $\approx 22$  keV for a 2727 keV <sup>3</sup>H from <sup>6</sup>Li( $n_{cold}$ , <sup>3</sup>H) $\alpha$ at the time of the measurement). Estimated concentration uncertainty is based on experimental counting statistics for each sample and concentration reference material measured.

Uncertainty is reported in the presented plots and tables to one standard deviation unless otherwise stated.

# SRIM modeling

Energy-to-depth modeling was completed in TRIM (SRIM, [17]). These models used a theoretical density of 1.43 g cm<sup>-3</sup> for Kapton ( $C_{22}H_{10}N_2O_5$ ) and 4.65 g cm<sup>-3</sup> for LiNbO<sub>3</sub> (example energy-to-depth model shown in (SI) Fig. 2). A light-element bonding correction to the stopping force of the film(s) was not applied. If implemented using default values in [17], the corrections are estimated to be relatively small (ranging from  $\approx 0.2\%$  at high energies to  $\approx 2\%$  at lower energies) due to the high energy range of the detected ions. The ion energies were calculated for a minimum of ten depths for each sample type. The stopping force curve for <sup>3</sup>H passing through the Kapton was calculated in SRIM using data generated by the SRT program and the above noted density and stoichiometry values in compliment to the TRIM results (SI Fig. 2).

#### **Energy broadening modeling**

Curve and peak model fits to experimental data were completed using fitting algorithms in SigmaPlot 14 [38] or Peak-Fit 14 [39]. The profiles were modeled using a 3—parameter sigmoidal curve (Eq. 4, LiNbO<sub>3</sub>, battery material) or a 4—parameter Weibull peak shape (Eq. 5, LiF). Results are summarized in SI Tables 1–3 and examples of the fits can be found in Figs. 4B and 5A, B and SI Figs. 3, 4, 5. The resulting data was analyzed for trends using dynamic fitting linear regression analysis (SigmaPlot). Values calculated from these analyses are summarized in Table 2 and plots of the data with linear model fits for the modeled compounds can be viewed in Fig. 5C–F.

# **Results and discussion**

## **Evaluation of utilized models**

In general, the quality of the fits (determined by  $R^2$ ) are comparable within uncertainity (±0.004, 1 $\sigma$ ) when the LiF profiles were fit with the Weibull function as opposed to a Pearson IV or VII (see SI Fig. 5). However, high dependencies ( $\approx 0.95$ ) are found for the *c* and  $\beta$  parameters of the Weibull and Pearson fits for all profiles. This suggests that these models are over parameterized for the given data sets. Attempts to fit the experimental data with a lower parameter, non-normal curve type (e.g., Gaussian) results in a similar value for the dependencies, and lower, but not statistically resolved  $R^2$  values. The sigmoidal model produces a good fit with low dependencies (<0.5), suggesting that the correct number of parameters were utilized to model the data (SI Fig. 4, SI Table 1).

## Calculated shape parameters (B)

The shape parameter data sets for the model compounds can be fit with a linear function with  $R^2 > 0.95$  (Fig. 5C, D and Table 2). The calculated slopes for the linear fits are in opposite directions with the  $\beta$  associated with the LiNbO<sub>3</sub> samples becoming more negative with increased Kapton layer thickness and the  $\beta$  associated with the LiF samples becoming more positive under the same conditions. This is expected as the parameters describe different shapesthe sigmoidal fit is for a curve and the Weibull fit is for a peak-and, therefore, do not have to agree in value nor value direction (+ or -). What is important is the change in value magnitude with increasing cover layer thickness. Both data sets show an increase in the  $\beta$  value magnitude as a function of Kapton layer thickness. A visual example of this increase in energy broadening can be seen in Fig. 3A, B (LiF and LiNbO<sub>3</sub> and SI Fig. 3A, D (LiF) for the profiles of a sample with no Kapton capping layer and the sample with 30.4 µm Kapton layer.

## Calculated location parameters (x<sub>0</sub>)

As expected, the calculated  $x_0$  values of both model materials are observed to decrease linearly as a function of added Kapton layers (Fig. 5E, F and Table 2). The y-intercepts calculated from the fits to the location parameter data well predict within uncertainty ( $\pm 2\sigma$ ) the expected surface exit energy of  $\approx 2727$  keV for the <sup>3</sup>H ion from a material, thus providing confidence in the models' accuracy. The calculated  $x_0$  values for each of the LiNbO<sub>3</sub> profiles also agree within uncertainty with the theoretical exit energies of <sup>3</sup>H ions passing through the variable Kapton thicknesses, and provides additional confidence in the use of this model to represent the measured data.

The  $x_0$  parameter is sensitive to variations in the Kapton film thickness and it is known that these films become thinner if stretched. It was therefore necessary to estimate the thickness variation between films. This was achieved by independently measuring four different pieces of Kapton film placed in front of the LiNbO<sub>3</sub> sample. Data collected from each measurement were then fit with the 3-parameter sigmodal curve and the average and standard deviation of the  $x_0$  parameter was calculated. The mean edge position was 2457.56 keV ± 1.35 keV. For this system a 1.35 keV variation is  $\approx \pm 2.0$  nm of Kapton thickness.



**<**Fig. 5 A, B Sigmoidal and Weibull fit models for LiNbO<sub>3</sub> (A) and LiF (B) profiles with no Kapton layers. Additional plots can be found in the SI. C, D Linear fits of calculated shape factors ( $\beta$ ) vs. Kapton layer thicknesses. E, F Linear fits of calculated position factors ( $x_0$ ) vs. Kapton layer thicknesses. Blue, outer lines represent 95% confidence interval (band) for the fits. Uncertainties are estimated from experimental counting statistics (A, B) or model fit calculations (C–F). Some uncertainty ranges may be smaller than displayed data points. (Color figure online)

# **Energy broadening: laboratory experiments**

Increases in energy broadening due to addition of a thicker capping layer can be estimated from the  $\beta$  parameter data collected experimentally for the LiNbO<sub>3</sub>. The LiNbO<sub>3</sub> data is most useful in this assessment as its high energy edge is considered the surface aerial (cm<sup>2</sup>) slice of NDP data, and, therefore, broadening induced here should only be affected by the thickness of the Kapton layer. The LiF data is less useful in this application as the  $\beta$  parameters calculated for the Weibull fit peaks is affected by broadening effects across the whole of the sample, thus convoluting broadening induced by the Kapton with other sample related factors (e.g., sample morphology, changes in chemistry, etc....). The calculated slope for the LiNbO<sub>3</sub>  $\beta$  parameters is—0.35 keV µm<sup>-1</sup>. From this value it is estimated that the front edge of the profile will

**Table 2** Summary of linear fit parameters for calculated shape parameters ( $\beta$ ) vs. Kapton layer thicknesses and calculated location parameters ( $x_0$ ) vs. Kapton layer thicknesses, and calculated energy ranges for exiting <sup>3</sup>H vs. Kapton layer thicknesses. These values describe fits displayed in Fig.5 C-F Uncertainties are calculated from model fits to data sets and are reported to  $1\sigma$ . They are reported under values in ()

Data set	Slope (unitless* or keV $\mu m^{-1}$ )	<i>y-intercept</i> (unit- less* or keV <sup><math>-1</math></sup> )	$R^2$
β			
Model function			
LiNbO <sub>3</sub>	- 0.35	- 6.66	0.95
Sigmoidal	(0.07)	(1.25)	
LiF	2.37	70.48	0.97
Weibull*	(0.35)	(6.41)	
Li alloy	- 0.22	- 4.84	0.997
Sigmoidal	(0.08)	(0.36)	
$x_0$ Model function			
LiNbO <sub>3</sub>	- 40.18	2761.31	0.997
Sigmoidal	(1.60)	(29.22)	
LiF	- 40.70	2725.16	0.998
Weibull*	(1.6776)	(31.23)	
Li alloy	- 42.19	2794.81	0.999
Sigmoidal	(1.77)	(35.71)	

Data and fit models are shown in Fig. 5. \*Note,  $\beta$  are pure numbers (i.e., unitless).

broaden by  $\approx 2.7$  keV following the addition of a 7.6 µm thick Kapton capping layer. While this value is several keV below the resolution of the NDP detector, it is above the energy width of one energy bin,  $\approx 0.7$  keV bin<sup>-1</sup> for the NIST NDP system. This is an important finding because NDP data is first converted on the x-axis from channels to energy bins before the bins are summed to the detector's resolution. This rebinning is sometimes started and centered on the highest energy edge of the ion profile of interest, which is often assigned the zero-depth position for the profile. Adding 7.6 µm of Kapton adds  $\approx 4$  bins (2.7 keV/0.7 keV bin<sup>-1</sup>) of uncertainity to this center/zero-depth position. The number of bins increases with increasing Kapton film thickness with the number growing from  $\approx 4$  bins for addition of 7.6 µm of Kapton.

To summarize, the addition of a thicker Kapton layer increases the uncertainity of the bin in which the true, zerodepth and start of a profile may be set, thus resulting in a greater uncertainity in the profiles depth axis assignment. This result is not particularly important for experiments where thin Kapton layers are used to cap Li samples and where a high energy ion's profile is being analyzed as the added uncertainity in the depth position is well below the resolution of the NDP detector. However, this can become significant and should be considered n situations where thicker Kapton layers are used, as is sometimes required for ultra-high vacuum NDP experiments or on Li-ion cells that contain liquid components, or if higher NDP detector resolutions are utilized. This finding may also be important for thin thicknesses of capping materials of higher density and scattering potential (e.g., Cu, Sn, Al). This is a topic of future research.

## **Energy broadening: modeling and simulations**

Results from the SRT and TRIM simulations are displayed in Figs. 2 and 6, respectively, and listed in SI Table 4 (TRIM only). The SRT calculations enable construction of a stopping force curve for Kapton (Fig. 2A, SI Fig. 2). As stated from above, the stopping force of a material is the force acted upon an energetic charged ion by the material through which it is traveling. This force causes a characteristic loss in charged ion energy. It is also a central calculation utilized during NDP data processing to transform energy profiles to depth profiles. Figure 2A shows the modeled stopping force curve for a <sup>3</sup>H ion traversing Kapton.

It is known that the slope of the stopping force curve for a given energy range is related to the depth resolution of that range [40]. Depth resolution is higher in regions where the stopping force is greatest and is lower where the stopping force is lowest. As seen in Fig. 2A, the steepest slope (highest resolution) was calculated for the 7.6  $\mu$ m thickness of Kapton, followed in descending order by the slopes for the



◄Fig. 6 An increase in exit position ranges (A–E) relates to an increase in exit energy ranges (F) per charge ion stopping theory and as the result of increased Kapton layer thickness. A–E Monte Carlo simulations showing the change in charged ion exit Y and Z exit positions from the Kapton cover. F Range of <sup>3</sup>H exit energies from variable thicknesses of Kapton. 5% uncertainty is based on estimated uncertainty of Monte Carlo simulations

15.2  $\mu$ m, 22.8  $\mu$ m, and 30.4  $\mu$ m (lowest resolution) thicknesses of Kapton. However, accurate value estimation for the amount of energy broadening incurred at each of these points is difficult to determine as the SRT calculations do not include uncertainties—a factor that can be addressed with TRIM.

From the TRIM simulations the range of possible exit energies for an ion traversing variable thicknesses of Kapton is calculated and a value for energy broadening estimated (Fig. 6, SI Fig. 2, SI Table 4). As summarized in Fig. 6F and listed in SI Table 4, increasing the thickness of the Kapton layer results in an increase in possible ion exit energy ranges. That is, energy broadening increases with increasingly thicker modeled Kapton capping layers. This is due to an increase in number of ion/host material atom interactions (e.g., scattering, and straggling events). The rate of energy broadening change is calculated to be about 5.5 keV  $\mu$ m<sup>-1</sup>, which is higher than that calculated from the experimental data based on the  $\beta$  parameter.

The difference between the experimentally calculated energy broadening effect and the TRIM simulation calculated effect may be the result of:

- (1) Inaccuracies in the modeling of Kapton layers due to use of a theoretical density for the Kapton films.
- (2) That in TRIM the detection is assumed to be right next to the surface of the sample and 100% of the ions produced are detected. In a real laboratory setting the detector may be several to 10's of mm away from the sample surface (for an example of a real-world NDP setup see [37]), and may result in a significantly lower number of ions hitting the detector and may affect the range of detected energies.
- (3) The shape parameter of the sigmoidal function not fully or correctly capture the effects of energy broadening.
- (4) That the <sup>3</sup>H ion origin is treated as a point source in the models. In a real laboratory setting the origin would be distributed in 3D and charged ions would be emitted in all directions. This factor may also affect the net number of ions detected.
- (5) Inconsistencies arising from the background correction method. NDP data is often background corrected using experimental results collected from a blank sample—which often is a piece of Teflon or material similar-to-but-not-exactly-the-same as the sample. This

is not a "true" sample blank, but it does represent one component of material that is in the detection range of the NDP detector. For NDP experiments collecting data on a control material is very difficult due to matrix matching. For example, issues can arise as not all lithiated compounds exist or are easily measurable in their non-lithiated or <sup>7</sup>Li-doped form. At energies above  $\geq$ 600 keV such matrix issues may not significantly affect the background profile as most of the signal in this region is generated from electronic noise. However, at lower energies this mismatch in blank to sample chemistry can significantly change the intensity and shape of the background.

Points 2–5 above are topics of current research. However, it is assumed that values estimated from the TRIM models, which are less expensive to acquire in terms of time and resources than the experimental values, could be utilized conservatively to estimate the effects of a capping layer on NDP profiles .

# Application of methods to a real-world-sample

An example of the effect of energy broadening due to the application of capping layers on a real-world system can be seen in the data initially presented in [37] and shown in Fig. 4A. In this study the above outlined methods were employed to estimate how much broadening occurred at the neutron depth profile surface when incremental thicknesses of Kapton protective layers were added on top of a Li alloy battery material. Data was collected from the alloy with 7.6 µm, 15.2 µm, and 30.4 µm thicknesses of Kapton covering. The front edge of each profile was fit with a 3-parameter sigmoidal curve (see Fig. 4B, summarized in SI Table 3), and shape and  $x_0$  parameter values were evaluated against the Kapton layer thickness. Following the above procedure, the data was fit with a linear equation, which was then utilized to predict the  $\beta$  and  $x_0$  parameter of an uncovered Li alloy samples. The results are summarized in SI Table 3.

In general, the changes observed for the LiNbO<sub>3</sub> model data set were also observed for the Li alloy: the  $x_0$  value decreased and the  $\beta$  value increased with increased Kapton thickness. Modeling the linear trends in the calculated  $\beta$  and  $x_0$  results for the Li alloy provided similar slope and y-intercept values as calculated for the LiNbO<sub>3</sub> data set with all results within  $2\sigma$ . Slight differences in modeled values may be due to the presence of a very thin (nm's) Li carbonate layer on the surface of the Li alloy sample as detailed in [37]. These results show the applicability of the above experimental methods in estimating the amount of energy broadening increase following the addition of a thicker, capping layer on top of the Li containing material.

# Other factors and limitations of this work

Other physical factors which contribute to the energy broadening of the profiles and not yet discussed are sample structure, uniformity of sample composition with depth, lateral composition uniformity, porosity, interfacial and surface roughness's, and changes in the charged ions charge state as it passes through the system [17]. These features can be studied by other methods (SEM, TEM, Reflectometry) and their results used to inform NDP results.

Another challenge to processing NDP data arises from the accuracy and precision to which one knows the sample density. This issue was discussed above, however, due to its importance to NDP data processes methods, should be further elucidated. In personal practice of the authors, this value is the least well known for most samples of all parameters input into NDP data analysis calculations and can be the largest source of depth uncertainty (see [41] for an examples). It is therefore often encouraged that NDP data be evaluated when it is expressed in unit of atoms of analyte cm<sup>-2</sup> (i.e., areal density) and not in units of atoms of analyte cm<sup>-3</sup> (i.e., volumetric density) [41] as the data expressed in areal density is not calculated using functions based on estimated sample density values.

# Conclusions

Simple methods for estimating the effects of adding a capping layer (e.g., Kapton) to the surface of an atmospherically sensitive Li containing sample on profile ion energy broadening has been presented. Results on thick (µm's) and thin ( $\approx 1 \ \mu m$ ) model systems indicate, as expected, that energy broadening increases and energy profiles will shift to lower energies as a function of Kapton capping thickness. Incident neutron absorption and scattering and, as a result, neutron beam attenuation, increases relative to capping layer thickness. A decrease in certainty of a zero-depth position assignment was shown to directly relate to increased energy broadening. The magnitude of this effect is below the resolution of NDP detectors for thinner thicknesses of Kapton. The decrease in resolution may have a significant effect on the processing and precise interpretation of samples capped with thicker layers or with other, higher density/scattering materials, such as Cu. Cu is often used as both a protective and functional component of Li-ion cells in NDP experiments. A successful application of described methods to determine energy broadening affects occurring through the capping of a real-world Li-ion sample with Kapton was presented. Several limitations of this study were discussed and outlined as future topics of research including 3D modeling of energy broadening in NDP profiles and expansion of the methods to functional capping materials (e.g., metals) used in Li ion-cell NDP studies.

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