Optimization of Pulse Shape Discrimination for Enhanced Neutron Depth Profiling in Solid State Electrolytes

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1. Introduction

All-solid-state lithium-ion batteries are garnering attention for their high energy density and safety, with the solid-state-electrolyte (SSE) playing a crucial role in battery performance. During charging and discharging, the transportation of lithium ions in the solid electrolyte can lead to dendrite formation and aging, potentially resulting in reduced energy efficiency and shorter lifespan. Hence, it is essential to evaluate the distribution of lithium within the SSE to address these issues [1].

Neutron Depth Profiling (NDP) is recognized as a feasible technique for evaluating lithium distribution in solid electrolytes. NDP is a non-destructive analysis technique that measures the residual energy of charged particles emitted by neutron capture reactions, thereby enabling precise in situ depth profiling of the element [2][3][4]. The large thermal neutron capture cross-section of ^{6}Li (940 barns) makes it suitable for NDP analysis.

$$^6\mathrm{Li} + \mathrm{n} \rightarrow {}^4\mathrm{H}\ (2055\ \mathrm{keV}) + {}^3\mathrm{H}\ (2727\ \mathrm{keV})$$

For NDP analysis applied to $Li_{6.5}La_3Zr_{1.5}Ta_{0.6}O_{12}$ (LLZTO) SSE, lithium depth profiling is feasible up to tens of micrometers with depth resolutions in the hundreds of nanometers. The alpha particles emitted from neutron capture reaction from ^{6}Li have a higher stopping power than tritons, resulting in superior depth resolution. Conversely, due to their lower stopping power, tritons enable the analysis of deeper regions. For thick LLZTO electrolytes, triton analysis is pivotal in assessing lithium distribution at deeper depths, which is essential for evaluating the performance and safety of solid electrolytes.

Korea Atomic Energy Research Institute (KAERI) has established an NDP system utilizing a cold neutron source (~4 meV) with a flux of 1.80 x 10^8 $cm^{-2}s^{-1}$ generated by the HANARO research reactor. However, in the KAERI-NDP system, the beta and gamma rays emitted from the neutron activation of surrounding materials result in a high background in the low energy region. The presence of background signals in the low-energy region tends to degrade the accuracy of LLZTO analysis as depth increases. Therefore, reducing the background signals in the KAERI-NDP system could decrease the uncertainty in quantitative analysis. Although background signals can be evaluated and subtracted post-measurement, this process is time-consuming. The need to consider variations in experimental conditions, such as reactor power, leads to increased uncertainty in the analysis. Furthermore, a method for removing background signals during operand NDP analysis of SSE is essential. This study aims to apply Pulse Shape Discrimination (PSD) via the rise time method to remove background signals during NDP analysis. It evaluates optimal PSD parameters, performance, and cut criteria for PSD parameters [5][6][7].

2. Materials and Methods

During the 108-1 operation cycle of HANARO, the silicon-charged particle detector of the NDP system was utilized to measure the background and LLZTO in the NDP chamber. During measurements, the reactor power was maintained at 27 MW, and the NDP chamber was kept in a vacuum. Pulses corresponding to LLZTO and background were acquired using a DT5781 digitizer (100 MS/s, 14-bit resolution, Caen), which was connected to the pre-amplifier coupled with the Si detector.

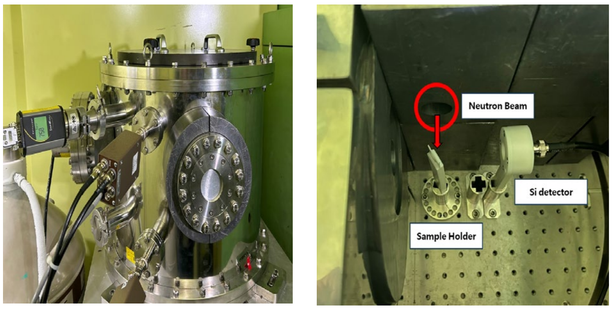

Fig. 1. (Right) KAERI-NDP system. (Left) The interior structure of the KAERI-NDP chamber.

The time interval between samples of the pulses was 10 ns, acquiring 2000 samples per pulse. In the pre-processing stage of the acquired pulses, a low-pass filter was applied to remove high-frequency noise, and the filtered signals were normalized. Among the available PSD methods in the time domain, the rise time method was applied to the pre-processed pulses, thereby setting the rise time as a PSD parameter. PSD performance was assessed using the Figure of Merit (FOM), calculated after Gaussian fitting of the rise time distributions for triton and background. A higher FOM indicates better signal discrimination, and the optimal FOM was evaluated after optimizing the rise time. Under optimized

FOM conditions, rise time cut criteria were evaluated to enhance PSD efficiency, employing the F-measure as the evaluation function. A value of the F-measure closer to 1 indicates improved discrimination between signals.

$$\text{FOM} = \frac{|\mu_{LLZO} - \mu_{Background}|}{FWHM_{LLZO} + FWHM_{Background}}$$

$$\text{Precision} = \frac{True\ positive}{True\ positive + False\ positive}$$

$$\text{Recall} = \frac{True\ positive}{True\ positive + False\ Negaitve}$$

$$\text{F-measure} = \frac{2 * Recall * Precision}{Recall + Precision}$$

3. Result and Discussion

The optimization of various PSD parameters acquired based on the rise time method is shown in Figure 1 (left). Figure 1 (right) shows the variation in the FOM values when varying the conditions for rise time calculation. Also, Figure 2 (left) shows the FOM results of the PSD analysis, where the optimized FOM value reached 1.056. This optimization was achieved by setting the upper and lower fractions of the maximum amplitude at 55% and 25% during rise time calculation. Clear separation is possible between background and LLZTO signals in the high-energy region, as shown in Figure 1 (right).

In contrast, the contamination of the signals makes discrimination challenging in the low-energy region. The F-measure evaluation method was introduced to improve PSD efficiency to determine the optimal rise time cut criteria. Figure 2 (right) shows the analysis results, where the optimal F-measure value of 0.934 corresponded to a rise time cut criterion of 31 ns. At this criterion, the corresponding significance level for Type 1 error was determined to be 7.5%. The results of this study indicate that applying and optimizing PSD techniques in KAERI-NDP analysis of LLZTO can significantly reduce uncertainty in the analysis by removing background noise. Furthermore, this improvement is expected to contribute substantially to the precise analysis and application of materials like LLZTO.

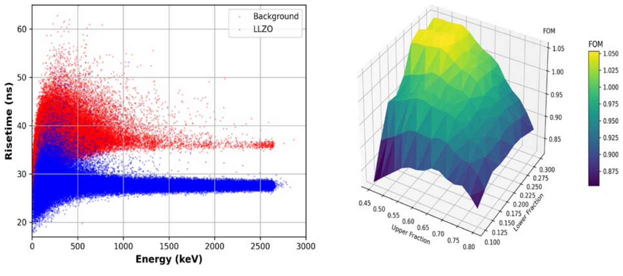

Fig. 2. (Right) PSD plot of LLZTO and background and (Left) FOM values at various parameters.

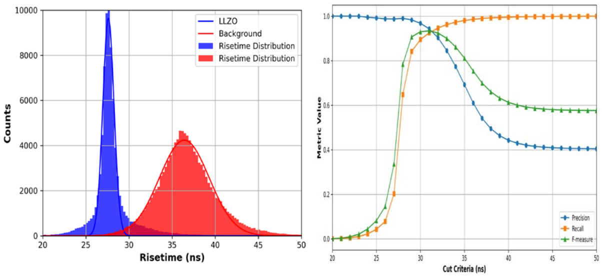

Fig. 3. (Right) Rise time distribution and optimized FOM. (Left) Evaluation functions at various cut criteria.

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