Analysis of depth profile of Lithium in Solid State Electrolyte using Geant4

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1. Introduction

The recent surge in the demand for lithium-ion batteries highlights the criticality of understanding their core components.

Among the many features of the lithium-ion battery, electrolyte behavior can significantly influence the overall battery performance, especially regarding safety and efficiency. In particular, the behavior of lithium ions within the next-generation solid-state electrolytes plays a pivotal role in assessing battery safety and performance. Neutron Depth Profiling (NDP) analysis of solid-state electrolytes (SSE) has been recognized as a potential method in electrolyte evaluation. NDP is a non-destructive analytical method that assesses the depth distribution of elements by analyzing the residual energy of charged particles produced by neutron capture reactions [1]. Lithium has a large thermal neutron cross-section (940 b), making it suitable for NDP analysis of SSE.

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

Transport of Ions in Matter (TRIM) [2] and Geant4 simulation tools for NDP analysis were adopted in this study. Prior to the actual NDP analysis of SSE of Li ion battery, it is essential to validate the accuracy of the NDP analysis applying Geant4 [3].

Since Geant4 utilizes suitable stopping power data for calculating the residual energy of charged particles, it is applied for NDP analysis of SSE. We analyzed the depth of lithium based on the results from TRIM and Geant4, both widely used Monte Carlo simulation tools for analyzing the residual energy of charged particles.

2. Materials and Methods

2.1 Geant4 Setup

The Lithium Lanthanum Zirconium Oxide (LLZO, $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$) cell geometry is modeled in TRIM and Geant4 simulation. The LLZO based battery cell configuration consists of 20 μm LLZO, 0.2 μm Cu cathode and 7.5 μm Kapton film affixed on the LLZO sequentially. The Kapton film is fabricated on the top layer to block the produced alpha particle [4]. In this study, we applied the Geant4 simulation tool to model NDP system of LLZO. The detector was positioned parallel to the cell, facing the cell directly. For defining the source term, a thermal neutron source (0.025 eV) was oriented to impinge on the cell at an angle of 45 degrees. Charged particles generated within LLZO traverse multiple layers before eventually escaping the surface for detection. The G4SDParticleFilter was applied to detector to ensure that only charged particles are scored. The residual energy of the charged particles was calculated based on the energy deposited by the charged particles in the detector. QGSP_BIC_HP was applied as the physics model due to neutron source below 20 MeV. EM standard physic under QGSP_BIC_HP was utilized to calculate the residual energy of charged particles.

2.2 Energy-Depth Calibration

To model geometry in the TRIM simulation, several depths were set to determine relationship between depth and residual energy of escaping triton. All other parameters remaining consistent with those of Geant4.

We calculated the mean residual energy of escaped charged particles for each determined depth. Then, the relationship between residual energy and depth was derived and analyzed using a fitting equation.

3. Result and Discussion

The residual energy calculated from the TRIM simulation and the depth of LLZO cell were fit via quadratic equation. The fitting parameters and the corresponding fitted figure can be found in Table 1 and Figure 1, respectively.

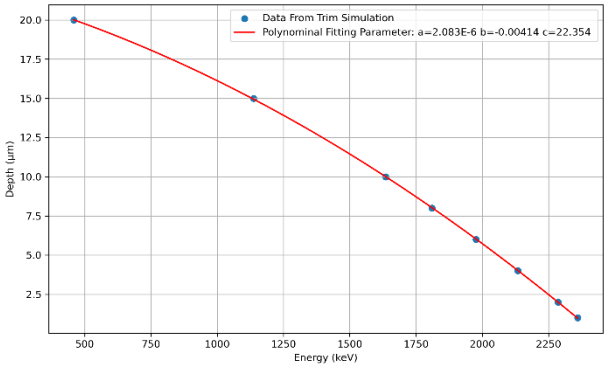

Fig. 1. Fitted energy-depth from TRIM simulation.

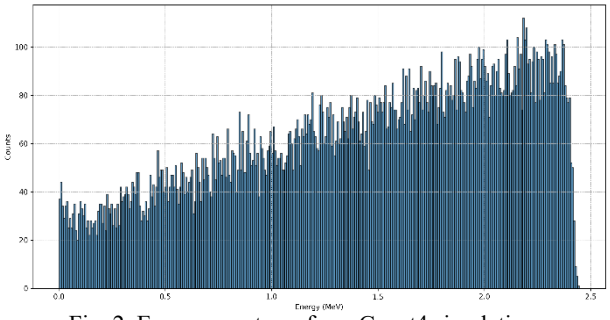

Fig. 2. Energy spectrum from Geant4 simulation

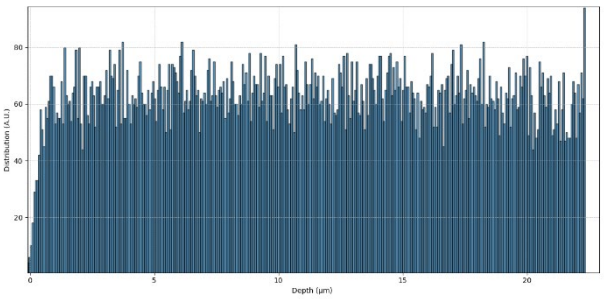

Fig. 3. Depth distribution of Li in LLZO

Figure 2 and 3 shows the energy spectrum obtained through Geant4 simulation and the distribution of lithium in LLZO when the energy is converted to depth, respectively. Figure 2 shows the energy spectrum without considering the energy-broadening effect.
In NDP analysis, as the depth from the sample surface increases, the width of the detected particle's energy distribution also expands correspondingly due to energy-broadening (e.g., energy straggling and multiple small-angle scatterings). Therefore, the energy-broadening leads broader energy spectrum with distinct edges [5]. Consequently, inaccuracies arise when converting the spectrum to depth distribution without considering energy broadening. As shown in Figure 3, this can overestimate the depth of Li. Since the coefficient of quadratic term is significant and simulates LLZO with uniform distribution of Li, the gradient observed in Figure 2 is eliminated upon this energy-to-depth conversion. Again, the energy-broadening leads to an overestimation of Li's depth.

In this work, we analyzed the energy spectrum and the distribution of Lithium within LLZO using TRIM and Geant4. In future work, energy-broadening effects should be considered to increase the accuracy of depth conversion processes.

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