Interpretation using Multi-Physics Simulation of Rechargeable Battery Electrolyte Gelation Process by Electron Beam Irradiation

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1. Introduction

Historically, the interaction of radiation with polymers was often viewed in terms of degradation. However, recently, there has been a significant increase in studies exploring the use of radiation in polymer synthesis techniques like graft copolymerization and cross-linking [1].

Rechargeable batteries are garnering increasing interest as an eco-friendly power solution for transportation, presenting notable benefits in the quest for carbon neutrality compared to conventional fossil fuels. When it comes to automobiles, the risk of severe accidents escalates, and this risk is particularly pronounced for electric vehicles due to the potential for fire hazards resulting from Li-based rechargeable batteries [2].

Given that the liquid electrolyte within these batteries is flammable, solidifying the electrolyte with a polymer matrix emerges as a strategy to avert drastic failures in the event of an accident [3]. While traditional thermal-setting methods for gelation can take around an hour, thus increasing production costs, gelation via electron beam irradiation can be achieved in a mere 30 seconds.

This indicates that the fabrication process utilizing electron beam irradiation for the gelation of polymer matrix-based electrolytes has the potential for much higher productivity [4].

This study aimed to combine electron beam transport modeling and thermal analysis for a multi-physics simulation of the cross-linking process in a secondary cell system. The goal was to determine optimal process conditions, and the simulation processes closely collaborated with experimental research.

2. Experimental Background

In this section, fundamental information about the batteries used in these experiments is described.

2.1 Coin-cell Battery

Coin-cell batteries were used for laboratory-scale production. The battery has a diameter of 20mm and a height of 3.229mm. Further details regarding the battery can be found in Table I.

Table I: Dimension and materials of the coin-cell battery

Component	Thickness	Outer Diameter	Inner Diameter	Material
Cap (1)	0.250 mm	18.5 mm	17.2 mm	SUS 316L
Cap (2)	0.250 mm	16.5 mm	15.8 mm	SUS 316L
Spring	0.722 mm	14.5 mm	10.5 mm	SUS 316L
Spacer	1 mm	16.0 mm	-	SUS 316L
Lithium	1 mm	16.0 mm	-	Lithium metal
Gasket	2.4mm	19.0 mm	17.0 mm	Poly
Separator	15μm	18.0 mm	-	Poly
Electrode	50μm	14.0 mm	-	NCM811, CB, PVDF, Al foil
Case	0.250 mm	20.0 mm	19.5 mm	SUS 316L

A novel electrolyte composition used for this study was 1M LiTFSI in EC/EMC (85%) and ETPTA (15%) and the electrolyte filled inside the battery.

2.2 Experiment Environment

The experiment was conducted with a 2.5 MeV electron beam and batteries that were exposed to absorbed doses of 10kGy, 20kGy, and 30kGy, respectively. The absorbed dose increased proportionally with the number of turns of the rail. The electron irradiation zone was positioned 35 cm above the rail on which the battery was placed. The velocity of the rail was 0.283 m/s. The electron beam area measured 7.5 cm in width and 150 cm in length.

2.3 Thermal Property

The performance of a battery is determined by its electrode material and electrolyte [5]. In this study, a new composition of electrode material and electrolyte was used, and its thermal properties were measured for the use of thermal analysis in COMSOL Multi-physics.

Table Ⅱ: Thermal properties of electrode and electrolyte

Thermal Property	Electrode	Electrolyte
Density [kg/m³]	1848	1211
Heat Capacity [J/(kg·K)]	768	1552
Thermal Conductivity [W/(m·K)]	83.7	0.145

3. Simulation Methodology

To model the gelation of the electrolyte inside the secondary cell using electron irradiation, we followed a two-step process. Firstly, we modeled the situation where the battery is irradiated with electrons using a GEANT4-simulation tool kit. Secondly, we performed a thermal analysis in COMSOL Multi-physics using the results from the first step.

3.1 Electron Beam Irradiation Simulation

The GEANT4 particle simulation toolkit is popularly used in various communities. GEANT4 is developed in an object-oriented environment and has great flexibility [6]. Using Geant4, this study aimed to simulate the electron beam irradiation process. From experimental data, the electron beam energy was set to 2.5MeV, and positioned 35cm above the battery. To take this geometry, the control volume (world in Geant4) size is made of a 50cm×50cm×50cm box. It is shown in Fig. 1.

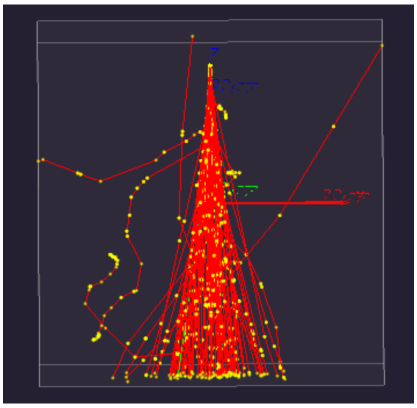

Fig. 1. Electron beam irradiation simulation using GEANT4

Through Geant4, we achieved the average value of deposit energy per initial electron. The absorbed dose of the battery was set to 10kGy as an experiment.

As the heat source is the primary parameter for thermal analysis of the battery, the correlation between the average value of deposit energy per initial electron and absorbed dose, deposited energy under 10kGy is calculated.

Finally, we determined the heat source of the battery by using GEANT4 under the electron irradiation process.

3.2 Thermal Analysis

Simulating the gelation process and conducting thermal analysis are crucial for several reasons beyond mere process optimization.

Firstly, they ensure quality control and consistency, enabling the identification of potential issues early in the manufacturing process to maintain product quality uniformly. Understanding the behavior of materials during gelation under different conditions is vital for material selection, setting process parameters, and potentially developing new materials or processes. This also leads to significant reductions in production costs and time.

Safety assessment is another critical aspect, especially for batteries where enhanced safety can be achieved through solid electrolytes [7]. Thermal analysis helps predict temperature increases during the process, allowing for appropriate safety measures. Lastly, optimizing manufacturing processes minimizes environmental impacts by reducing unnecessary energy consumption, aligning with sustainable manufacturing practices.

The energy deposited in the components that compose the coin-cell is the final result of the electron irradiation simulation using GEANT4. Each component's deposited energy was converted into heat source value to perform thermal analysis.

In COMSOL Multiphysics, the thermal analysis was performed using the 'Heat Transfer in Solids and Fluids' module. As the coin-cell battery is cylindrical, it was generated using 2D axis symmetry geometry. Fig. 2 below shows half of the 2D cross-section of a coin-cell battery and the blue region is the electrolyte.

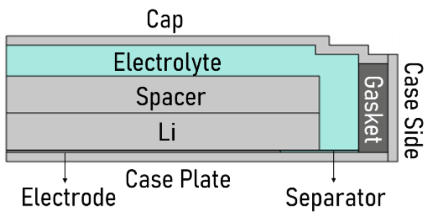

Fig. 2. Schematic of a coin-cell battery's 2D axis geometry in COMSOL Multiphysics

Thermal analysis is performed using the governing equations (1), (2) and (3). The initial temperature was assumed to be 298.15K. The heat transfer coefficient in the irradiation facility is not able to be measured. Therefore, this study assumed 3 values to see the temperature behavior when heat transfer coefficient (h) is 10, 15, 20 W/m^2-K.

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \boldsymbol{u} \cdot \nabla T + \nabla \cdot \boldsymbol{q} = Q \cdots (1)$$

$$\boldsymbol{q} = -k \nabla T \cdots (2)$$

$$-\boldsymbol{n} \cdot \boldsymbol{q} = h(T_{ext} - T) \cdots (3)$$

It was assumed that the heat generation is valid only during the time of irradiation with electron beams. Thus, the analysis was conducted in two steps. During the radiation exposure time of 5.294s, the analysis was performed by inputting the Q value for each component from Eq. (1). For subsequent times, the analysis proceeded under the condition that there was no heat generation.

4. Result

After 5.294 seconds, it was observed that the temperature reached its peak at 313K. This is illustrated in Fig. 3, and it was also confirmed that this outcome does not vary with changes in the h value.

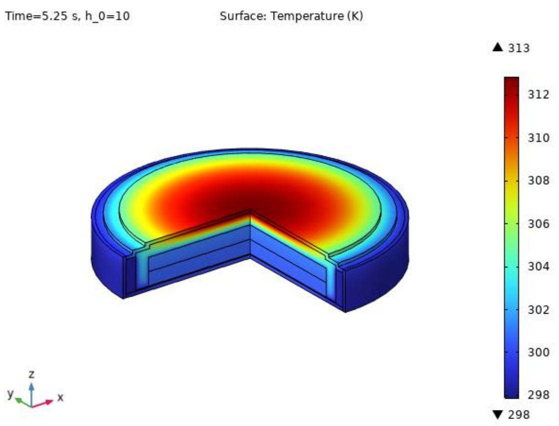

Fig. 3. Spatial distribution of temperature at 5.294 s with convective heat transfer coefficient, h = 10 W/m^2-K.

After 5.294 seconds, heat equation in Eq. (1) was solved with assumption Q=0 (no heat generation) and it converged to the stationary state. In thermal analysis, distinct approaches yield different results. The stationary case, assuming an infinite timespan, attained a stable temperature of 293K, irrespective of variations in the heat transfer coefficient (h).

Conversely, the time-dependent analysis, conducted over a span of 200 seconds, demonstrated a dynamic behavior where the temperature reverted to the initial value of 298K after approximately 145 seconds when h=10 W/m^2-K.

A key factor in time dependent analysis, the heat transfer coefficient h, influenced the rate at which equilibrium was achieved. Notably, in the time-dependent scenario, a higher h value of 20 W/m^2-K resulted in a faster return to the initial temperature, taking about 115 seconds. This confirms that an increased h value accelerates the thermal response of the system to reach the initial state.

5. Conclusion

It was observed that the peak temperature of 313K was reached immediately after the radiation exposure time at 5.294 seconds, and this was found to be unaffected by the heat transfer coefficient. The equilibrium temperature of 293K was determined under the assumption of an infinite timespan for the stationary analysis. In contrast, during the time-dependent analysis, it was observed that the time required to reach the initial temperature decreased as the heat transfer coefficient (h) increased.

Additionally, this investigation encompasses not only thermal analysis but also simulations of the cross-linking gelation process utilizing a phase-field methodology. Subsequent stages of this research will delve into the liquid-gel phase transition during gelation, coupled with a comprehensive multi-physics thermal analysis to accommodate the variances in thermal properties between liquids and gels.

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