Investigation of Electrochemical Performance Enhancement in Electron Beam-Irradiated Battery Cathodes

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1. Introduction

With the increasing demand for batteries, the development of high-capacity and fast-charging batteries has become essential. While silicon-based anode materials can provide capacities exceeding 2000 mAh/g, cathode materials are limited to less than 280 mAh/g, which constrains the overall capacity improvement of batteries. If the capacity limitation of cathode materials cannot be overcome, achieving high-energy-density batteries will be challenging, directly impacting the driving range of electric vehicles (EVs) and the energy storage efficiency of energy storage systems (ESS) [1].

Moreover, for fast charging and discharging, lithium-ion diffusion within the cathode material must be rapid. However, conventional cathode materials have limited lithium-ion diffusion rates, leading to increased side reactions on the electrode surface during rapid charge/discharge cycles, ultimately causing performance degradation. To enhance the capacity of cathode materials, increasing the nickel content has been a common approach. However, as the nickel content increases, the structural stability of the cathode deteriorates, necessitating doping and coating strategies to improve stability. Nevertheless, these methods only enhance material stability without significantly increasing capacity [2].

In this study, we aim to overcome the limitations of conventional cathode materials by employing electron beam irradiation to introduce oxygen vacancies in the cathode material, thereby generating additional lithium-active regions. Additionally, we enhance electrical conductivity and increase the specific surface area by inducing conjugation bonding in the conductive material. Furthermore, cross-linking in the binder is utilized to improve the structural stability of the cathode, ultimately enhancing the performance and stability of the material.

2. Method

2.1 Fabrication of Cathode

Commercial LCO was used as the active material, Super P as the conductive additive, and PVDF as the binder. The ratio of active material, conductive additive, and binder was set to 8:1:1, forming a slurry. The slurry was uniformly coated onto an aluminum current collector using a doctor blade and subsequently dried in an oven at 80°C for 12 hours. The thickness of the fabricated electrode was approximately 10–15 μm.

2.2 Electron Beam Irradiation

Electron beam irradiation was performed using a 50 keV electron beam system available in our laboratory and a 2 MeV electron beam system at EB-Tech. The irradiation was applied to the fabricated cathode, conductive additive, and LCO cathode material. The cathode electrode was irradiated using the 50 keV system, while the conductive additive and LCO cathode material were irradiated separately with different doses using the 2 MeV electron beam system.

2.3 Electrochemical measurements

To evaluate the electrochemical performance of the electron beam-irradiated LCO-based cathode, CR2032 coin cells were assembled. The working electrode was the prepared cathode with a diameter of 15 mm, while lithium metal (300 μm in thickness, 16 mm in diameter) served as both the counter and reference electrode. The electrodes were separated by a polypropylene separator (Celgard PP2075) with a diameter of 19 mm. The coin cells were filled with an electrolyte solution containing $LiPF_6$ in EC/DMC/EMC and were assembled in an argon atmosphere. The rate capability of the electrodes was measured within a potential range of 3.0–4.2 V (vs. Li/Li^+) using an electrochemical testing system (WBCS3000Le32, WonATech, Seoul, Korea).

3. Result and Discussion

After irradiating the LCO-based cathode with a 50 keV electron beam, a half-cell was fabricated to evaluate the difference in electrochemical performance before and after irradiation through rate capability measurements. Fig. 1 shows the rate capability results of

the LCO-based cathode before and after electron beam irradiation.

The sample irradiated for 6 hours exhibited a difference of approximately 8 mAh/g at 0.5 C-rate (full charge/discharge in 2 hours) compared to the non-irradiated sample. However, this variation falls within the error range of the cell fabrication process, and thus, it cannot be concluded that the performance change was caused by electron beam irradiation. Based on these results, it was confirmed that 50 keV electron beam irradiation does not significantly affect the performance of LCO-based cathodes.

Additionally, although the 50 keV electron beam was expected to influence the binder and carbon-based conductive additive, the current experimental conditions indicate that it does not have a significant impact on electrochemical performance.

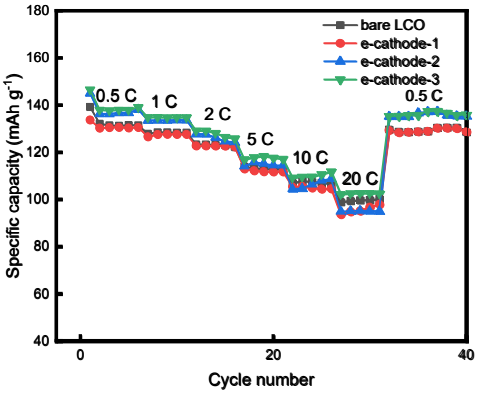

Fig. 1 Rate capability performance of LCO-based cathodes irradiated with 50 keV electron beam at different doses.

To induce changes in LCO and the conductive additive, electron beam irradiation with higher energy was applied. When LCO cathode material and carbon-based conductive additives are irradiated with an electron beam of energy higher than 50 keV, significant material changes can occur. Therefore, 2 MeV electron beam irradiation was performed on LCO cathode material and the conductive additive, and each was subsequently used to fabricate cathodes for rate capability measurements.

Fig. 2 presents the rate capability performance of LCO-based cathodes irradiated with a 2 MeV electron beam. The results indicate that the performance change before and after irradiation was negligible. Although it was initially expected that high-energy electron beams would generate oxygen vacancies in LCO, the energy of the electron beam was insufficient to break the bonding between metal and oxygen. Consequently, oxygen vacancies were not formed, leading to no significant change in electrochemical performance.

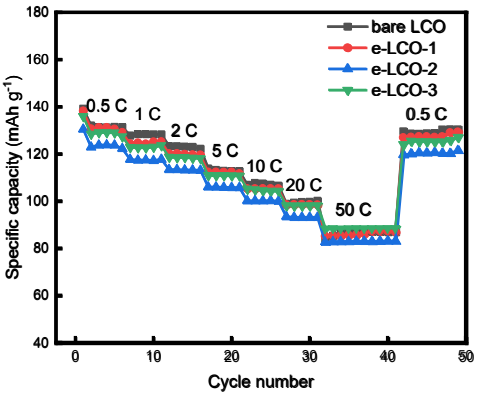

Fig. 2 Rate capability performance of cathodes fabricated with 2 MeV electron beam-irradiated LCO at different doses.

Fig. 3 presents the rate capability performance of cathodes fabricated using electron beam-irradiated conductive additives and non-irradiated LCO. A comparison of pre- and post-irradiation performance shows that the cathode sample containing conductive additives irradiated for 40 minutes exhibited an approximately 15 mAh/g increase in capacity compared to the bare sample. Additionally, the irradiated sample demonstrated relatively superior capacity retention at high charge/discharge rates.

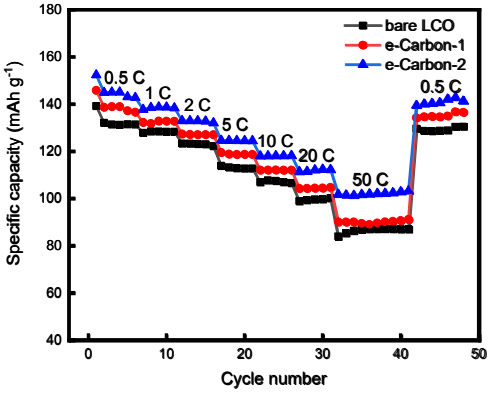

Fig. 3 Rate capability performance of cathodes fabricated with 2 MeV electron beam-irradiated conductive additives at different doses.

The increase in capacity can be explained using Fig. 4 and Table 1. As shown in Fig. 4, the intensity of the C-H bonding peak decreases as the electron beam irradiation time increases, indicating that the C-H bonds on the conductive additive surface are being broken due to irradiation.

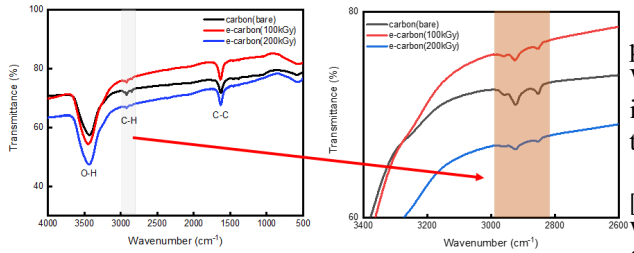

Fig. 4 FT-IR spectrum of conductive additives irradiated with 2 MeV electron beam.

Table 1 shows the BET(Brunauer-Emmett-Teller) surface area measurements for each sample. The results indicate that the surface area increases with longer irradiation times. This increase is attributed to the breaking of C-H bonds on the conductive additive surface, which causes hydrogen (H) to be released as H_2 gas, leading to the formation of pores on the surface. The enhanced surface area contributes to the overall capacity improvement of the cathode.

	bare cathode (m^2 g^{-1})	e-Carbon-1 (m^2 g^{-1})	e-Carbon-2 (m^2 g^{-1})
BET Surface Area	56.3	60.38	63.2

Table 1 BET surface area measurement results of conductive additives irradiated with 2 MeV electron beam.

4. Conclusion

This study investigated the effects of electron beam irradiation on LCO-based cathodes, binder and carbon-based conductive additives. 50 keV electron beam irradiation showed no significant impact on the electrochemical performance of LCO-based cathodes. Additionally, 2 MeV electron beam irradiation did not induce noticeable changes in LCO, likely due to insufficient energy to generate oxygen vacancies.

However, when 2 MeV electron beam irradiation was applied to the conductive additive, a 15 mAh/g capacity increase was observed, along with improved capacity retention at high charge/discharge rates. FT-IR analysis confirmed the reduction of C-H bonds, and BET surface area measurements showed increased porosity, which enhanced electrode-electrolyte interactions.

These results suggest that while electron beam irradiation does not significantly modify LCO, it can effectively enhance the properties of conductive additives, offering a potential strategy for improving cathode performance.

REFERENCES

List and number all bibliographical references in 9-point Times, single-spaced, at the end of your paper. When referenced in the text, enclose the citation number in square brackets, for example [1]. It is recommended that the number of references does not exceed five.

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