



Electron beam modification of anode materials for high-rate lithium ion batteries



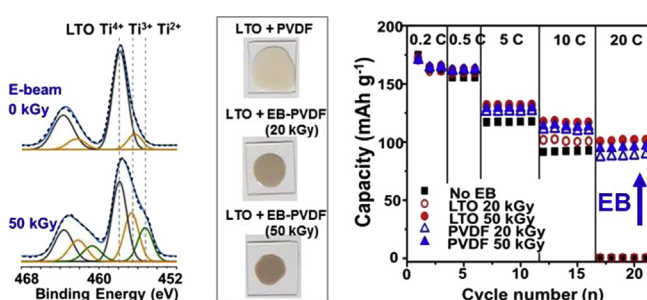
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HIGHLIGHTS

- The rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode was increased by a simple electron-beam (EB) irradiation.
- EB irradiation changed the properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and PVDF.
- The electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was enhanced by Ti^{3+} formation.
- More conjugated structure could be formed in EB-PVDF by the dehydrofluorination.
- Mixing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and PVDF using ball-milling caused the further dehydrofluorination.

GRAPHICAL ABSTRACT



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ABSTRACT

The rate capability of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)-based anode in a lithium ion battery can be easily improved by electron beam (EB) irradiation without the need for complicated synthetic procedures. The electrode prepared with EB-irradiated LTO at a 50 kGy dose has an enhanced rate capability while retaining a discharge capacity of 100 mAh g⁻¹, even at the 20 C-rate. The effect of EB irradiation on the properties of the anode materials (i.e., LTO, poly(vinylidene fluoride) (PVDF), super P carbon) is examined in detail through systematic experiments. Both LTO and PVDF are affected by EB irradiation and dependent on the exposed electron dose, but super P is affected negligibly. EB irradiation partially reduces LTO with forming Ti^{x+} ($2 < x < 4$) which is attributed to the enhanced electrical conductivity. EB irradiation causes dehydrofluorination and cross-linking in PVDF, resulting in the formation of carbon–carbon double bonds. The conjugated structure of PVDF is formed by the further dehydrofluorination during mixing with LTO via ball-milling, and this is accelerated in the presence of EB-PVDF. This conjugated structure enhances the electrical conductivity and is responsible for the improved rate capability.

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1. Introduction

Lithium ion batteries (LIBs) are widely used as the main power sources in small electronic devices and are now being extended to larger applications, such as portable power tools, hybrid electric vehicles (HEVs), and electric vehicles (EVs), because of their high energy densities [1,2]. For HEV and EV applications in particular,

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which require rapid charge–discharge and good safety levels, battery electrodes must be capable of working at a high rate while maintaining excellent capacity and cycling stability. Graphitic carbon has been widely employed as an anode material for commercial LIBs because of its high electrical conductivity and low cost. However, graphite carbons demonstrate poor rate performance induced by their low Li-ion diffusion coefficient. In addition, their low lithiation potentials (below 0.2 V versus Li^+/Li) close to the lithium plating voltage could cause safety issues [3,4]. In the search for safe materials with good rate capabilities and excellent cycle stability, the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been extensively studied as an alternative anode material for LIBs and has several inherent advantages [5–7]. It has good reversibility and structural stability with an almost negligible volume change during the Li^+ insertion and extraction processes. Moreover, LTO exhibits flat discharge and charge plateaus at approximately 1.55 V versus Li^+/Li , which safely avoids solid-electrolyte interphase (SEI) formation, which indicates the decomposition of metallic lithium and electrolytes. However, despite the advantages of LTO, its low electronic conductivity and slow Li-ion diffusion still limit its application as an anode material. Overcoming these drawbacks has typically been approached in two ways. The LTO can be modified to enhance its electronic conductivity through doping with metal (or nonmetal) ions or by applying the conductive species to the LTO [3,8]. The other approach involves the synthesis of nanostructured materials with various morphologies to shorten the diffusion length of the Li ions [2,6,9]. However, previous efforts have primarily focused on the modification (or synthesis) of LTO through chemical routes that involve several sequences and complicated procedures, which limit its application to large-scale production of commercial LIBs. Additionally, these nano-sized materials have restricted use in industrial processes because of their low density and high cost.

Electron beam (EB) irradiation has several advantages in the modification of the surface of organic and inorganic materials [10]. (i) The sample can be irradiated at atmospheric pressure regardless of the status of the sample (i.e., surface roughness, phase). (ii) It does not require the removal of residues as in liquid-phase treatment. (iii) It can be easily adapted to the industrial scale because it is a conventional treatment. Surface morphology, oxidation states, optical properties, and electrochemical properties can be modified by EB irradiation [10–12]. For example, Endo et al. reported the effects of EB irradiation on the performance of carbon anodes for LIBs and attributed the performance enhancement to the surface structure change in the carbon materials and the degradation of the poly(vinylidene fluoride) (PVDF) binder by the EB irradiation [10]. The degradation of the PVDF binder could affect electrode performance because it is related to the binder content in the bulk material and at the electrolyte interface [13]. Turbostratic component formation from the amorphous carbon due to EB irradiation further enhances electrode performance [10]. By contrast, Kim et al. found that the electrochemical performance of a V_2O_5 thin film [11] is enhanced by EB irradiation because of the increased surface area and crystallinity and change in oxidation states. However, changes in material properties caused by EB irradiation were not significant, and the electrochemical properties were measured for a $\text{V}_2\text{O}_5/\text{ITO}$ glass electrode in an aqueous electrolyte without other components (e.g., PVDF binder, super P carbon additive). To the best of our knowledge, an EB-irradiated LTO-based anode that contains LTO, PVDF, and super P together has never been reported.

Here, we demonstrate that the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)-based anodes can be improved by EB irradiation without complicated chemical synthesis procedures. We investigated the effect of EB irradiation on the rate capability by EB irradiation i) of an electrode coated with an LTO, PVDF, and super P slurry mixture and ii) of individual component powders. For the EB-irradiated

electrode, the LTO, PVDF, and super P were irradiated together in a single mixture. In contrast, the individually EB-irradiated component powders were mixed with other non-irradiated components, and the mixture was coated onto Al foil. The electrochemical properties of the EB-irradiated electrodes were investigated, and the effects of EB irradiation on the properties of each component were also examined by characterization of the EB-irradiated materials.

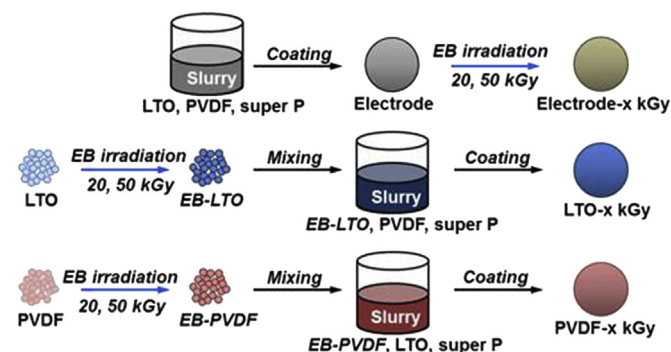
2. Experimental section

2.1. Preparation of electrodes

The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) samples were prepared by a solid-state method from a mixture of Li_2CO_3 (99%, JUNSEI) and TiO_2 (99%, Rutile, JUNSEI). Excessive Li_2CO_3 (3 wt.%) was provided to compensate for the loss of Li during synthesis. The precursors were ball-milled (100 rpm) in an acetone solution for 24 h and dried at 100 °C for 24 h. The dried precursor mixture was then calcined at 850 °C for 36 h in air to obtain LTO. The samples were then cooled to room temperature and ground. A slurry was prepared by mixing LTO (as the active material), a super P carbon-conducting additive, and a PVDF (Aldrich) binder at a weight ratio of 80:12:8, respectively, in an *n*-methyl pyrrolidone (NMP, JUNSEI) solvent with ball milling for 24 h at 100 rpm. The prepared slurry was coated onto aluminum foil (UACJ Foil Co.), dried at 110 °C in a vacuum oven for 12 h and then pressed into a final thickness of 50–60 μm . After drying was completed, the dried slurry was cut into sections with 14-mm diameters to obtain neat LTO electrodes. The samples were irradiated with an electron beam (EB) using an electron beam accelerator (ELV-0.5, BINP, Russia) with 20- and 50-kGy irradiation doses by controlling the beam current, and the EB was extracted by a potential of 0.7 MeV applied between the electron source and the sample target at room temperature. The speed of the conveyor was 1.83 m/min for all samples, which resulted in identical exposure times of a few seconds. The slurry-coated electrodes and the LTO and PVDF powders were separately irradiated by the EB. The EB-irradiated slurry-coated electrodes were dried at 110 °C in a vacuum oven for 12 h before coin-cell assembly. The EB-irradiated LTO (or PVDF) powders were mixed with non-irradiated components using the slurry preparation method mentioned above. For example, the EB-irradiated LTO powder was mixed with non-irradiated PVDF and super P using ball milling, and the electrode preparation method was the same as that of the non-irradiated sample (Scheme 1).

2.2. Characterization of materials

The crystal structures of the anode materials were studied using



Scheme 1. Schematic illustration of the process for the sample preparation.

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