Electrochemical performance of an all-solid-state lithium ion battery with a binder-free lamellar LiVO₃ active material layer prepared by liquefaction approach

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A B S T R A C T

Newly designed binder-free lamellar LiVO₃ (LVO) active material layer with superior charge-discharge cycle properties was developed by liquefaction approach. The LVO cathode was fabricated by coating the aqueous cathode slurry containing the liquefied LVO on the Al foil and dried at low temperature below 150 °C. The liquefied LVO High adhesion between the lamellar LVO and Al foil was observed. It was demonstrated that can be formed freely to fit on the shape of an application object by liquefying the LVO. The lamellar LVO cathode exhibited the first charge and discharge capacities as high as the design capacity, and the first coulomb efficiency was approximately 100%. The crystallinity of the LVO decreased with increasing the depth of discharge on the first discharge process. On the other hand, no deterioration of the charge and discharge capacities was confirmed during the charge-discharge cycle test of 50 cycles. From the comparison between the lamellar LVO cathode and the conventional cathode with the LVO particles, the superior cycle properties were attributed to the lamellar structure of the LVO.

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1. Introduction

In order to enhance the safety of Li ion batteries (LIBs), advanced research and development on all-solid-state LIBs were actively promoted. All-solid-state LIBs with a nonflammable solid electrolyte exhibit higher safety compared to LIBs with a flammable organic electrolyte solution. In addition, the all-solid state LIBs will realize a high energy density by application of bi-polar structure [1].

Bulk-type all-solid-state LIBs with active material particles and solid electrolyte possesses a high energy capacity relative to thin film-type all-solid-state LIBs which are formed via spattering process. An active material layer for bulk-type all-solid-state LiB consist of active material particles, solid electrolyte, and electron conductive materials. One of challenges is the improvement of interfacial contact among solid materials in an active material layer for improving the cycle properties and charge-discharge capacities.

Sulfur-based electrolytes such as Li_4GeS_4-Li_3PS_4 [2], Li_2S-P_2S_5 [3], Li_2S–SiS_2–Li_xMO_y (M = Si, P, Ge) [4] are promising materials for all-solid-state LIBs because of their high lithium ion conductivity ($>1.0 \times 10^{-3}$ S cm^{-1} at room temperature) and a high flexibility. But

then, these sulfide electrolytes are unstable in the ambient atmosphere and emit toxic gas when they react with moisture.

Oxide electrolyte is safety but their oxide materials have low flexibility. Li_3BO_3 [5] and Li_3BO_3-Li_2SO_4 glass-ceramics [6] have been suggested as electrolytes in an active materials layer to improve the interfacial contact among solid materials.

On the other hand, although there are many researches on the morphology of active materials in the liquid electrolyte-based LIBs field [7–13], research on morphology of active materials has not been reported so far in the all-solid-state LIBs field.

Recently, we have developed the low temperature fabrication process of the $LiCoO_2$-$LiVO_3$ composite electrode using the deliquescent $LiVO_3$ (LVO) for all-solid-state LIBs [14]. The LVO is reportedly a candidate for active material [13,15–19], morphology of LVO particles [13], structural analysis [15–17], synthesis condition [18–19]. In addition, it has been reported that the LVO cathode exhibit high capacity (275.6 mAh g^{-1}) with excellent cycling stability by designing the morphology of the LVO particles [13]. We focus on its deliquescent property as a new approach for designing the morphology of the LVO. The dense $LiCoO_2$-$LiVO_3$ composite electrode was fabricated by applying the mixture of the $LiCoO_2$ (LCO) active material particles and the liquefied LVO to Al foil and subsequent drying it at 150 °C. The LVO functioned as a lithium ion conductive path in the LCO-LVO composite electrode.

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In this paper, The LVO was used as a cathode active material for all-solid-state LIBs, and the LVO active material layer was fabricated by applying the liquefied LVO to Al foil without a binder. The morphology, the charge-discharge cycle properties, and the change in the crystallite structure of the LVO active material layer during cycle test were investigated.

2. Experimental

2.1. Preparation of LiVO$_3$ powder and LiVO$_3$ aqueous solution

The LVO powder was prepared via conventional solid state reaction. Li$_2$CO$_3$ and V$_2$O$_5$ in a mole ratio of 1:1 were uniformly mixed using mortar and pestle. The mixture was heated at 650 °C in air for 10 h. The product with light green in color, was grounded using mortar and pestle again. The obtained LVO powder was dissolved in pure water and N-methylpyrrolidone (NMP) was added to the LVO aqueous solution.

2.2. Preparation of LiVO$_3$ electrode

The LVO electrode was prepared by conventional blade coating method. The slurry consisting of 0.7 g LVO aqueous solution and 0.01 g of Ketjen Black EC 300 J (KB) as electron conductive materials was coated on Al foil, where the gap of used blade was 100 μm. The slurry-coated Al foil was dried in an oven at 150 °C for 6 h, and then pressed under a pressure of 40 MPa. For comparison, the LVO electrode with the LVO active material particles was prepared by the same manner except the slurry composition. The slurry consisted of the LVO powder (0.6 g), 13 wt.% Polyvinylidene difluoride (PVdF) binder solution (1.66 g), and KB powder (0.01 g).

2.3. Morphology and crystallite structure analysis

The morphology of the LVO electrode was observed using scanning electron microscopy (SEM, Hitachi S-4800) with an energy dispersive X-ray spectroscopy (EDX, Horiba EX-350). The crystallite structures of the LVO powder and the LVO electrodes were characterized by X-ray diffraction (XRD) measurement using Cu-Kα irradiation.

2.4. Electrochemical measurements

The prepared-LVO electrode (10 mm in diameter), Li foil, and polyethylene oxide (PEO) polymer membrane with Lithium Bis (trifluoromethanesulfonyl) imide (Li-TFSI) were used as a cathode, anode, and solid electrolyte layer. These specimens are assembled and put into a stainless steel cell in Ar-filled glove box. Li ion diffusion coefficient was measured by cyclic voltammetry (CV), where the scan rate of 0.25, 0.50, 0.75, and 1.00 mV s^{-1}, and applied potential was between 4.3 V and 1.0 V. The charge-discharge tests were performed at 25 °C under current constant condition with 7.4 μA, corresponding to C/25, design capacity of 150 mAh g^{-1} using a potentio-galvanostat (Solartron, 1480). Although the theoretical capacity of the LVO is 253 mAh g^{-1} (LiVO$_3$ + Li$^+$ + e- ⇔ Li$_2$VO$_3$), deterioration of the LVO active materials layer is accelerated by when charging and discharging the LVO to the theoretical value expansion and contraction of the LVO increases. In all-solid-state LIBs field, the influence of degradation due to cracks of the LVO is larger than that of the liquid-based LIBs field for the cycle properties. Thus, the design capacity was set lower than the theoretical capacity.

The internal resistance of the cell on the charge-discharge cycle test was analyzed by use of frequency response analyzer (Solartron, FRA 1252A) with the frequency ranging from 0.1 Hz to 0.3 MHz with the amplitude of 10 mV.
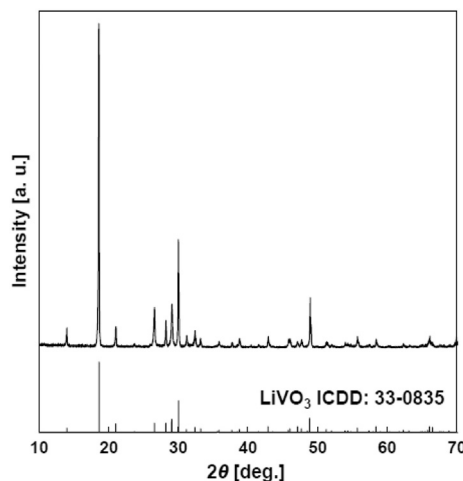

Fig. 1. XRD pattern of the prepared powder sample.

3. Results and discussion

The X-ray diffraction pattern for the obtained LVO powder is shown in Fig. 1. The XRD pattern of the obtained powder coincides with the LVO of the ICDD card No. 33-0835 with monoclinic C2/c space group without impurity. The image of the liquefied LVO is shown in Fig. 2. The LVO aqueous solution was clear greenish yellow. These results agreed with the finding of our latest research [14].

Fig. 3 shows the cross-sectional SEM images and energy dispersive X-ray analysis (EDX) mapping images of the LVO cathode fabricated by applying the mixture of the LVO aqueous solution and KB carbon powder to Al foil. The LVO active materials layer formed as a lamellar structure, and high adhesion between the LVO active materials and Al foil was also observed (Fig. 3a, b). It is essential to dissolve the LVO in order to conveniently form this structure under the temperature as low as 150 °C. Hereafter, the fabricated cathode was expressed as "the lamellar LVO". In Fig. 3c, lots of lineal void is clearly observed, which was probably formed when the NMP solvent was vapored in the drying process of the LVO slurry. However, the isolation of the LVO active materials is inhibited by dense connection among the LVO active materials in the lamellar structure. Fig. 3d shows the EDX mappings (V, O, C, Al) of

Fig. 2. The image of the LiVO$_3$ dissolved in aqueous-organic mixed solvent.