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Fabrication of a deliquescent-$LiVO_3$ and $LiCoO_2$ composite electrode for a recoverable all-solid-state lithium ion battery and its electrochemical performance

Taigo Onodera *, Jun Kawaji, Tadashi Fujieda, Takashi Naito

Research and Development Group, Hitachi, Ltd., 7-1-1 Omika, Hitachi, Ibaraki 319-1292, Japan

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ABSTRACT

The entirely-new concept of forming cathode for all solid state Li ion batteries was advocated. Deliquescent-$LiVO_3$ (LVO) was used as an Li ion conductor in a $LiCoO_2$ (LCO) based cathode. LVO is soluble in water and recrystallizes by drying the LVO aqueous solution. An LVO–LCO composite electrode was easily prepared by coating the mixed slurry of LCO powder and LVO aqueous solution on an Al foil and drying it at 150 °C. Cross-sectional SEM images revealed that the deliquescent LVO intruded the vacancy formed among the LCO particles in the composite electrode. The LVO exhibited Li conductivity and functioned as Li conductive paths among the LCO particles. Superior electrochemical performances of LVO–LCO composite electrode were exhibited by the charge/discharge test and electrochemical impedance spectroscopy (EIS). These performances are attributed to the increase in contact area among the LCO particles and that between cathode electrode and solid electrolyte due to a use of the LVO electrolyte binder. Moreover, a recovery of the discharge capacity was demonstrated by dissolving the LVO in LVO–LCO composite electrode again after the charge/discharge cycle test. In conclusion, the LVO for an electrolyte binder possesses a tremendous advantage in simplification of making an electrode process and forming Li ion conductive paths at the interface among different materials.

1. Introduction

Lithium ion battery (LIB) is widely used such as in mobile phone, large scale power source, electric vehicle, and other power supply. For further increase in the LIB use, some properties, such as energy density, cost, and safety, are required. An all-solid-state LIB containing a solid electrolyte is a candidate to solve the safety problem because of its non-flammability. In addition, the all-solid state LIB will realize a high energy density by application of bi-polar structure.

All-solid-state LIB is classified into two types according to the difference of solid electrolyte; the first type contains a sulfuric compound as electrolyte [1–5] and the second type a metal oxide as electrolyte [6–8]. Glasses and glass-ceramics as sulfide electrolytes have been reported such as $Li_2S–SiS_2–Li_xMO_y$ (M = Si, P, Ge) [5] and $Li_4GeS_4–Li_3PS_4$ [1]. They possess a high lithium ion conductivity ($>1.0 \times 10^{-3}$ S cm^{-1}) and a high flexibility, and they are the promising materials for all-solid-state LIB. But then, these sulfide electrolytes are unstable in the ambient atmosphere and emit toxic gas when the sulfide electrolytes react with moisture. On the other hand, the second type, metal-oxide-based electrolyte, has some advantages in terms of stability relative to the first type because of no toxic gas, high chemical stability, and thermal stability. Consequently, high lithium ion conductive materials have been studied such as ($Li_{4-2x}Zn_xGeO_4$ ($0 \leqq x \leqq 1$)) [6], $Li_7La_3Zr_2O_{12}$ (LLZO) [7], and $Li_5La_3M_2O_{12}$ (M = Nb, Ta) [8]. Lithium ion conductivity of these materials ranged from 10^{-4} to 10^{-3} S cm^{-1}, and these materials are expected to next generation electrolyte. However, these materials are completely unfit for the improvement of low contact among active material particles and solid electrolytes due to their high melting points, resulting in a higher interfacial resistance. Recently, Li_3BO_3 (LBO) has been reported as a cathode electrolyte to increase the contact area among the LLZO based solid electrolyte and cathode active materials [9]. The melting point of LBO is approximately 700 °C, and which has a lower temperature compared with LLZO. The melted LBO effectively intrudes the vacancy among the oxide based particles by heating the sample at the temperature higher than 700 °C, and forms a proper solid–solid interface, enabling charge/discharge reaction in LBO based cathode. Though, this material and the cathode preparation condition are hard to be applicable to a conventional LIB fabrication process, where the collective layer was aluminum foil with a melting point at 660 °C. It is hoped that the melting point of cathode electrolyte will be lower than 660 °C.

Vanadium oxides are well known as electrode material such as $LiVO_2$ [10], LiV_2O_5 [11–14], Li_3VO_8 [15–17], and $LiVO_3$ [18–20]. $LiVO_3$ (LVO) has been considered to be one of candidates for active material. Among them, LVO is a deliquescent material, and the deliquescence of LVO has never been focused before.

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* Corresponding author.

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Fig. 1. The images of LVO before and after liquefaction.

In this research, we have focused on the deliquescence of LVO and successfully improve the contact area in cathode by filling the deliquescent LVO intruding into the boundary among the active material particles. LVO was used as a cathode electrolyte binder and was filled between $LiCoO_2$ (LCO) active material particles and between LCO and solid electrolyte. The importance of Li ion conductive path in LCO based cathode electrode for the all solid state LIB was investigated by the comparison between LVO electrolyte binder and polyvinylidene difluoride (PVdF) nonconductive binder. In addition, the recovery of degraded discharge capacity during the charge/discharge cycle test of the cell (with the LVO–LCO composite electrode) was investigated.

2. Experimental

2.1. Preparation of LVO powder and LVO electrolyte binder solution

$LiVO_3$ (LVO) powder was synthesized by the conventional solid state reaction method. Li_2CO_3 and V_2O_5 in a mole ratio of 1:1 were mixed using mortar and pestle for 20 min. The mixture was calcined at 650 °C in air for 10 h. The product with dark green in color was grounded using mortar and pestle again. The LVO electrolyte binder solution was prepared as follows: 2.0 g of LVO powder was dissolved in 2.0 g of pure water for a day, 3.0 g of N-methylpyrrolidone (NMP) was added to the aqueous solution, and the solution was homogeneously mixed. Fig. 1 shows the LVO before and after liquefaction. The LVO electrolyte binder solution was clear greenish yellow.

2.2. Preparation of LVO and LCO–LVO composite electrode

LVO electrode for cyclic voltammetry measurement was prepared by a blade coating method. The slurry consisting of 0.7 g LVO electrolyte binder solution and 0.01 g of Ketjen Black EC 300J as an electron conductive material was coated on Al foil using a blade with a gap of

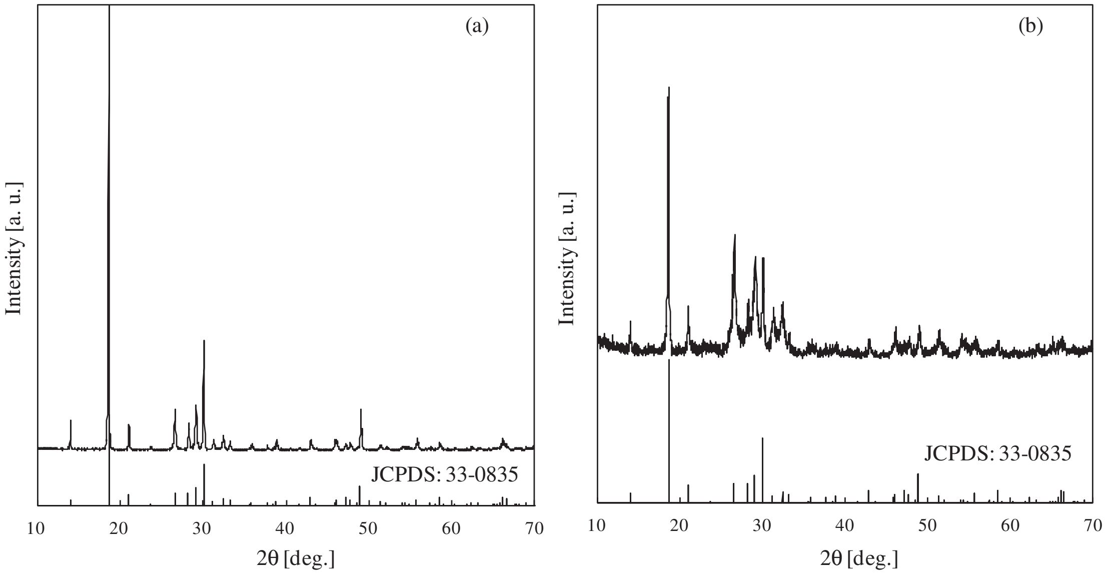

Fig. 2. XRD patterns of the synthesized $LiVO_3$: (a) as made $LiVO_3$, (b) $LiVO_3$ obtained by drying the $LiVO_3$ electrolyte binder solution.

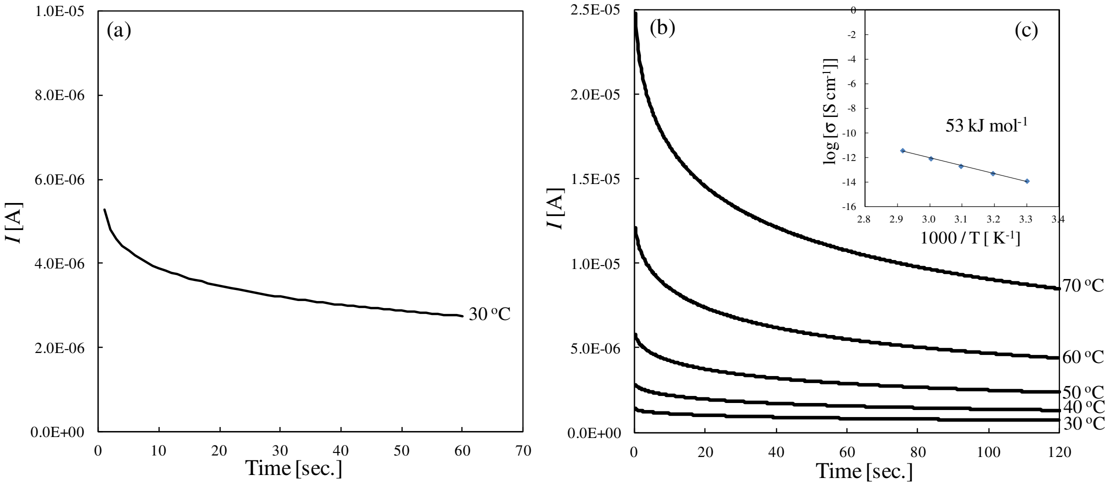

Fig. 3. DC current curves of each blocking cell: (a) Li ion blocking cell, (b) electron blocking cell, (c) Arrhenius plot of Li ion conductivity with different temperature conditions.