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Enhanced electrochemical performance of surface modified $LiCoO_2$ for all-solid-state lithium batteries

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Abstract

Li_2CO_3-coated $LiCoO_2$ powders are prepared from a lithium hydroxide solution via low-temperature heat treatment and the effects on the electrochemical performance of all-solid-state lithium ion batteries (ASS-LIBs) using Li_2S-P_2S_5 glass-ceramic solid electrolytes are investigated. A combination of X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analyses reveals that the Li_2CO_3 particles on the surface of $LiCoO_2$ particles are formed without significant change in $LiCoO_2$ structure. While the Li_2CO_3 is regarded as an impurity phase in lithium battery systems using liquid electrolytes due to its detrimental effects on electrochemical performance, we show that optimal amounts of Li_2CO_3 coating effectively suppress interfacial side reactions without a significant decrease in interfacial kinetics for all-solid-state lithium battery systems using sulfide solid electrolytes.

Keywords: All-solid-state lithium ion battery; Sulfide solid electrolyte; Surface modification; Lithium carbonate; Interface

1. Introduction

Since the development of solid electrolytes with high lithium ionic conductivity comparable to liquid electrolytes, there have been outstanding technology advances in all-solid-state lithium ion batteries (ASS-LIBs) exhibiting a high safety. In particular, ASS-LIBs utilizing sulfide solid electrolytes with favorable mechanical properties have attracted attention as a promising battery system by combination with conventional oxide cathode materials with superior cyclability. However, interfacial problems resulting in large charge-transfer resistance at the interface between oxide cathode materials and sulfide solid electrolytes arise due to mutual diffusion of component atoms [1,2] or formation of a space-charge layer [3,4]. Thus, inherent interfacial problems need to be overcome to realize ASS-LIBs involving sulfide solid electrolytes.

In order to reduce undesirable interfacial reactions, surface modification of layered lithium transition metal oxide ($LiMO_2$; M = Ni, Mn, and Co) has commonly been conducted [5–7]; this work has revealed that these coating materials can effectively reduce charge-transfer resistance. However, studies on coating materials for composite cathodes in ASS-LIBs involving sulfide solid electrolytes have focused on development of coating materials with higher lithium ionic conductivity [7–9]. Although there is no doubt that coating materials with higher lithium ionic conductivity are helpful in facilitating lithium ion conduction at the interface of the cathode materials (along with the suppression of interfacial side reactions), it is also important to exploit other coating materials besides lithium-conducting metal oxides in order to acquire better understanding of interfacial phenomena and maximize the performance of ASS-LIBs by optimizing the interface between sulfide solid electrolyte and cathode materials.

It is well known that Li_2CO_3, which is commonly formed during the synthesis of $LiCoO_2$ and, therefore, removed from the surface of cathode materials via post treatment [10,11], is not only electrochemically inactive due to poor electronic and ionic conductivity, but also causes gas evolution during battery operation [12] in conventional LIB systems using liquid electrolytes. In contrast to the detrimental effects of Li_2CO_3, it is also one of the inorganic components of solid electrolyte interface (SEI) layers that

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effectively suppresses undesirable interfacial phenomena [13,14]. Compared with organic components of the SEI, the inorganic components are more conductive, resulting in a decrease in impedance per unit thickness. Considering that completely different interfacial mechanisms occur in ASS-LIBs than in conventional LIBs using liquid electrolytes, it is worth investigating the effect of Li_2CO_3 at the interface in ASS-LIBs using sulfide solid electrolytes.

In this respect, lithium carbonate (Li_2CO_3), which has the advantages of low cost and facile coating, was first applied as a new coating material for ASS-LIBs involving sulfide solid electrolytes. In addition, the effect of the Li_2CO_3 coating on the electrochemical properties of ASS-LIBs using sulfide solid electrolytes was examined.

2. Experimental

Li_2CO_3-coated $LiCoO_2$ powders were prepared using an aqueous lithium hydroxide (LiOH) solution. The ratio of LiOH to $LiCoO_2$ was varied to control the coating amount of the Li_2CO_3 on $LiCoO_2$ particles. To prepare the LiOH solution, $LiOH \cdot H_2O$ (> 95% purity, DAEJUNG) was slowly dissolved in distilled water. Subsequently, $LiCoO_2$ powders (99.8% purity, Sigma-Aldrich) were added to the coating solution and were mixed thoroughly for 30 min. After the solution containing the $LiCoO_2$ powders was constantly stirred at 80 °C for 5 h, the slurry was dried in an oven at 150 °C for 12 h and was heated in a furnace at 400 °C under CO_2 for 3 h in order to form a Li_2CO_3 coating on the powder particles. Heat treatments to form the coating layers were performed at a low temperature of 400 °C to avoid formation of a solid solution between the coating medium and the active material. Pristine $LiCoO_2$ powder was also heated under the same conditions without using a coating solution to exclude the effect of heat treatment and clearly compare the effect of the coating. The estimated concentration of Li_2CO_3 on the surface of the $LiCoO_2$ powders was varied from 2 to 8 wt%. The estimated concentration is calculated based on the weight of $LiCoO_2$ powder.

X-ray diffraction measurements were employed to characterize the structure of the Li_2CO_3-coated powders with an X-ray diffractometer (XRD; Ultima IV, Rigaku) using Cu Kα radiation ($\lambda = 1.54178$ Å). XRD data were recorded in the range of $2\theta = 10$–70°. Fourier transform infrared (FTIR) spectra were obtained with a FTIR spectrometer (FT-IR; IRAffinity-1, Shimadzu) in the spectral range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The samples consisted of pellets prepared by pressing a mechanically homogenized mixture of Li_2CO_3-coated $LiCoO_2$ powders with dehydrated KBr. The actual coating amounts of Li_2CO_3 on the surface of the $LiCoO_2$ particles were obtained by thermogravimetric analyses (TGA; SDT Q600, TA Instruments) under flowing dry air at a heating rate of 5 °C min^{-1}. The morphology of Li_2CO_3-coated $LiCoO_2$ powders was analyzed using a field emission scanning electron microscope (FE-SEM; S-4800, Hitachi).

The electrochemical properties of all Li_2CO_3-coated $LiCoO_2$ powders in the ASS cells made using Li_2S–P_2S_5 glass-ceramic solid electrolytes were evaluated by constructing laboratory scale ASS cells assembled in a CR2032-type coin cell. Composite cathodes used as working electrodes were prepared by mixing 64 wt% Li_2CO_3-coated $LiCoO_2$, 34 wt% $78Li_2S \cdot 22P_2S_5$ glass-ceramic solid electrolyte, and 2 wt% Super P carbon. The $78Li_2S \cdot 22P_2S_5$ glass-ceramic powders used as the solid electrolyte were synthesized by high-energy mechanical milling and subsequent heat treatment [15]. The starting materials, i.e., reagent-grade Li_2S (99.9% purity, Alfa Aesar) and P_2S_5 (99% purity, Sigma-Aldrich), were mixed thoroughly at the appropriate molar ratios, and then mechanical milling was performed at 520 rpm for 20 h using a high-energy planetary ball mill (Pulverisette 7, Fritsch). Glass-ceramic powders were prepared from the prepared glass by heat treatment at 230 °C for 3 h in a dry Ar atmosphere. ASS cells were prepared by sequentially stacking and pressing the composite cathode, solid electrolyte powder, and indium foil at a pressure of 290 MPa into a 16-mm-diameter pellet. Carbon nanotube sheet was used as current collector in the ASS cells. All cells were charged and discharged in galvanostatic mode at room temperature using a charge–discharge measurement device (TOSCAT-3100, Toyo System) at room temperature. The charge–discharge performance was evaluated under various current densities from 0.05 C (7.5 mA g^{-1}) to 1 C (150 mA g^{-1}) between 1.9 and 3.63 V (vs. Li-In). Electrochemical impedance spectroscopy measurements of the cells were performed using an impedance analyzer (Solartron 1260) after charging to 3.63 V at 0.05 C (7.5 mA g^{-1}). The obtained impedance profiles were fitted using Z-view software.

3. Results and discussion

XRD patterns of pristine and Li_2CO_3-coated $LiCoO_2$ powders are shown in Fig. 1. All of the fingerprint peaks, namely, (003), (101), (006), (102), (104), (105), (009), (107), (108), and (110) are easily identifiable in the XRD patterns. In particular, the clear splitting of the (006)/(102) and (108)/(110) peaks in all the diffraction patterns indicate that the pristine $LiCoO_2$ powder has a well-defined hexagonal layered structure

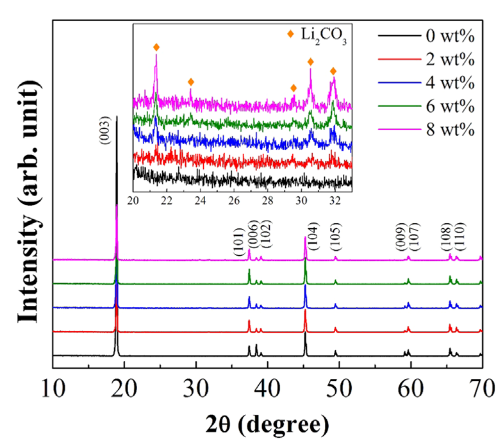

Fig. 1. X-ray diffraction (XRD) patterns of the pristine and Li_2CO_3-coated $LiCoO_2$ powders.