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Amorphous $LiCoO_2$–Li_2SO_4 active materials: Potential positive electrodes for bulk-type all-oxide solid-state lithium batteries with high energy density

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HIGHLIGHTS

- Amorphous $LiCoO_2$–Li_2SO_4 positive electrodes are prepared via mechanochemistry.
- All-oxide solid-state lithium cells with the electrode operated at 3.3 V vs. Li.
- The 150 μm-thick electrode without any conductive additives is utilized.

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ABSTRACT

Newly amorphous $Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$ ($xLiCoO_2\cdot(100\text{-}x)Li_2SO_4$ (mol%)) positive electrode active materials are synthesized using mechanochemical techniques. SEM observation indicates that average radii of the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ ($80LiCoO_2\cdot 20Li_2SO_4$ (mol%)) particles are about 3 μm. HR-TEM images indicate that the particles comprise nano-crystalline and amorphous phases. The crystalline phase is attributable to cubic $LiCoO_2$ phase. These active materials exhibit a high electronic conductivity of around 10^{-5}–10^{-1} S cm^{-1} and an ionic conductivity of around 10^{-7}–10^{-6} S cm^{-1} at room temperature. Bulk-type all-oxide solid-state cells (Li–In alloy/Li_3BO_3-based glass-ceramic electrolyte/amorphous $Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$) are fabricated by pressing at room temperature without high temperature sintering. Although the cell with the milled $LiCoO_2$ shows no capacity, the cell using the $Li_{1.2}Co_{0.8}S_{0.2}O_{2.4}$ electrode with no conductive components (*ca.* 150 μm thickness) operates as a secondary battery at 100 °C, with an average discharge potential of 3.3 V (vs. Li^+/Li) and discharge capacity of 163°mAh°g^{-1}. A positive electrode with large amounts of active materials is suitable for achieving high energy density in all-solid-state batteries. These newly synthesized amorphous $Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$ electrodes with ionic and electronic conductivities and good processability meet that demand.

1. Introduction

Lithium cobalt oxide ($LiCoO_2$) was first reported as an insertion positive electrode material in 1980 [1]. In 1991, Li-ion batteries (LIB) were commercialized by Sony Corp. Today, intercalated lithium transition metal oxide positive electrode materials (e.g., $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$) are used in conventional lithium ion batteries [1–3]. The lithium excess layered Li_2MO_3 (M = Mn, Ru, Ir) family has attracted great attention recently because of their cationic (M^{4+}/M^{5+}) and anionic (O^{2-}/O_2^{n-}) redox activities [4,5]. Moreover, lithium-excess layered rock-salt type positive electrode materials (e.g. Li_2MnO_3–$LiMeO_2$ (M = Co, Ni, Mn)) have attracted much attention because of their high operating voltage (>3.5 V vs. Li^+/Li in average) and high capacity (>230°mAh°g^{-1}) [6,7].

To the present day, cation disordered materials have been disregarded for use as electrode active materials because of their poor electrochemical performances [8–10]. Dahn et al. reported mechanochemical synthesis of $LiMO_2$ (M = Ti, Mn, Fe, Co, Ni) electrode materials and described their electrochemical investigation of these materials [10]. $LiCoO_2$ and $LiNiO_2$ active materials with the

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layered rock-salt structure were mechanically milled, which transformed their structure to a disordered rock-salt structure in which the transition metal and lithium ions were ordered randomly in cation sites. The milled materials showed poor electrochemical performance as positive electrodes in lithium batteries.

More recently, Ceder et al. reported the potential of lithium-excess cation disordered rock-salt type oxide electrode materials such as $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ [11]. In the cation disordered materials without lithium excess, lithium diffusion tends to be suppressed based on their structure. However, in the lithium excess disordered materials, the diffusion can be facile because of percolation of a certain type of active diffusion channels: the 0-transition metal percolation channel. According to this theory, lithium-excess disordered materials exhibit excellent electrochemical performances [12–14]. Moreover, Li_3NbO_4-based active materials with disordered rock-salt structure also have shown excellent electrochemical performances with high capacity (>300°mAh°g^{-1}) [15]. These lithium-excess cation disordered rock-salt type active materials are therefore favorable positive electrode materials for use in next-generation lithium batteries.

For large-scale energy storage devices such as smart grids and electric vehicles, LIBs have been used preferentially because of their high energy density [16]. In large-scale use, battery safety is of paramount importance because risks of fire and explosion become greater from the increased the amounts of flammable organic liquid electrolytes contained in LIBs. To increase battery safety and reliability, solidification of the batteries is the ultimate goal [17]. Replacement of flammable liquid electrolytes with non-flammable inorganic solid electrolytes is expected to increase battery safety dramatically.

For commercial use of all-solid-state batteries, energy density enhancement is strongly desired. Many types of all-solid-state batteries using sulfide and oxide electrolytes have been reported, showing high cycle stability [18–20]. All-solid-state cells reported so far comprise composite electrodes and solid electrolytes. Because a composite electrode is a mixture of active materials, solid electrolytes and conductive additives, the capacity per unit of the total weight of the battery necessarily decreases with increased weight of electrolytes and additives. To increase the battery energy density, an increase of active materials contents must be achieved.

Sabi et al. reported fabrication of thin film type all-solid-state batteries using a sputtering technique [21]. Amorphous positive electrode active materials $Li_xM_yPO_z$ (M = Ni, Ci, Co, Mn, Au, Ag, Pd) were prepared from metal, metal oxide or lithium metal oxide, and lithium ortho-phosphate using the sputtering method. Thin-film type all-solid-state batteries (Cu–Ti/LiPON glass/$Li_xM_yPO_z$) showed the large capacity (330°mAh°g^{-1}) with the relatively high average discharge potential (*ca.* 3 V vs. Li^+/Li), good cycle performance, and high rate capability. Nevertheless, it is difficult to apply thin-film batteries to large-scale energy systems because of the limited loading amounts of the active material. We have therefore specifically examined the preparation of amorphous oxide electrode particles suitable for bulk-type all-solid-state battery with high energy density.

This report describes the mechanochemical synthesis of the amorphous active materials in the $LiCoO_2$–Li_2SO_4 system, and the fabrication of bulk-type all-solid state batteries. $LiCoO_2$ was chosen as the active material. Li_2SO_4 was chosen as the low melting oxide material (T_m = 823 °C). The use of Li_2SO_4 improves electrode formability because of its low melting property [22]. As described above, Dahn et al. reported that hexagonal $LiCoO_2$ transforms to cubic $LiCoO_2$ during ball milling, and that the cubic $LiCoO_2$ shows poor electrochemical performance [10]. Combination with Li_2SO_4 might increase lithium diffusion channels in $LiCoO_2$-based active materials because the conductivity of the Li_3BO_3 electrolytes increases with the addition of Li_2SO_4 [22]. Vitrification of the $LiCoO_2$–Li_2SO_4 system is expected to provide positive electrode materials with both high formability and high ionic conductivity. Bulk-type all-oxide solid-state cells using amorphous $LiCoO_2$–Li_2SO_4 active materials were fabricated. Then their electrochemical performances were evaluated.

2. Experimental

2.1. Synthesis

Starting materials were $LiCoO_2$ (>99%, Nippon Chemical industrial Co. Ltd.) and $Li_2SO_4 \cdot H_2O$ (99.9%, Wako Pure Chemical Inds. Ltd.). First, Li_2SO_4 crystal was obtained by heat treatment of $Li_2SO_4 \cdot H_2O$ at 300 °C for 3 h in dry Ar atmosphere. Positive electrode active materials of $Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$ ($xLiCoO_2 \cdot (100\text{-}x)Li_2SO_4$) ($x$ = 60, 70, 80, 90, 100 mol%) were prepared by mechanical milling (Pulverisette 7; Fritsch GmbH). A mixture of the crystals of $LiCoO_2$ and Li_2SO_4 was put into a 45 ml zirconia pot with 160 balls (5 mm diameter), and milled at the rotating speed of 370 rpm with the milling period of time for 50 h. All processes were conducted in a dry Ar atmosphere.

Additionally, $33Li_3BO_3 \cdot 33Li_2SO_4 \cdot 33Li_2CO_3$ (mol%) glass electrolyte was also prepared using mechanical milling [23]. A mixture of the crystals of Li_3BO_3, Li_2SO_4, and Li_2CO_3 was put into a zirconia pot and was milled for 90 h to form the $33Li_3BO_3 \cdot 33Li_2SO_4 \cdot 33Li_2CO_3$ glass. This glass electrolyte exhibited an excellent formation property at room temperature. The electrolyte pellet prepared by cold-pressing at 720 MPa showed the packing density of about 90%, which is comparable to that of the sulfide electrolytes [24]. Achieving a large contact area between active materials and solid electrolytes is important. The glass electrolyte has a suitable formability. In addition, this glass electrolyte presents the conductivity of 3.8×10^{-7} S cm^{-1} at room temperature. By crystallization of the glass at 260 °C, a metastable phase was precipitated. The conductivity increased to 1.8×10^{-6} S cm^{-1} at room temperature. Because of the excellent formability and relatively high conductivity, the $33Li_3BO_3 \cdot 33Li_2SO_4 \cdot 33Li_2CO_3$ glass-ceramic electrolyte is used as a solid electrolyte in this study.

2.2. Characterization

X-ray diffraction (XRD) measurements (CuKα) were conducted using a diffractometer (Ultima IV; Rigaku Corp.). The morphology of the prepared samples was observed using a field emission scanning electron microscope (FE-SEM, SU8220; Hitachi High-Technologies Corp.) and a high-resolution transmission electron microscope (HR-TEM, JEM-2100F; JEOL). Densities of the milled powders were measured using a gas pycnometer (AccuPycII1340; Shimadzu Corp.) placed in an Ar-filled glove box.

Electronic and ionic conductivities were measured for the pelletized samples pressed under 720 MPa. The pellet diameter and thickness were, respectively, 10 mm and about 0.5 mm. Then stainless steel disks were attached to the pellets as current collectors. Then, the electronic conductivities were measured for the pellets (Stainless-steel (SS)/$Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$/SS) using AC impedance and DC polarization methods. To evaluate lithium ion conductivities of the $Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$ active materials, the other three layer pellets (Li_3PS_4 glass/$Li_{2\text{-}x/100}Co_{x/100}S_{1\text{-}x/100}O_{4\text{-}x/50}$/$Li_3PS_4$ glass) were obtained by pressing at room temperature. The Li_3PS_4 glass as a lithium ion conductor was used as an electron blocking layer. Li metal foils were attached to both sides of the pellet. The five layer pellets (Li metal/Li_3PS_4 glass/$xLiCoO_2 \cdot (100\text{-}x)Li_2SO_4$/$Li_3PS_4$ glass/Li metal) were sandwiched between stainless steel disks. These prepared cells were sealed in a