Shot Peening on All-solid-state Lithium Metal Battery for High-speed Charging

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Abstract

All-solid-state lithium metal battery is a candidate of the next generation electrical vehicle's battery. However, lithium dendrite generated in the fast charging process penetrates the solid electrolyte layer and breaks the battery with an internal short circuit. With this problem, the charging speed of the all-solid-state lithium metal battery is limited. In this paper, the authors propose and demonstrate a shot peening processing on the solid electrolyte layer surface to increase the charging speed of the all-solid-state lithium metal battery. With the shot peening, crack generation on the solid electrolyte layer can be suppressed with the compressive residual stress, and the lithium dendrite penetration into the solid electrolyte layer should be suppressed. Moreover, the shot peening generates a roughness on the surface of the solid electrolyte layer, and the contact between the solid electrolyte layer to the lithium metal anode would be improved, and the electrochemical reaction should be enhanced. The experimental results show that the shot peening successfully increases the charging speed (critical current density). Moreover, there is a synergistic effect between shot peening and gold thin-film insertion, which is one of the electrochemical performance improvement methods. Shot peening with changing the shot size is also conducted. The results show that there is an optimum shot size that maximizes the charging speed.

Keywords All-solid-state lithium metal battery, shot peening, charging speed, shot size.

Introduction

To reduce the CO_2 emission, gasoline vehicles should be changed to electrical vehicles (EV). However, a conventional EV's cruising distance is only about 400 km and is much shorter than that of a gasoline vehicle (~1000 km) due to lithium-ion batteries' volumetric energy density limitation. Moreover, there is an ignition risk of organic electrolytes in the lithium-ion battery, and some cases are reported of fire accidents of EVs. An all-solid-state lithium-metal battery (ASSLiMB) is proposed to increase the battery volumetric energy density for long cruising distance and as high safety battery [1]. The ASSLiMB's anode is lithium metal, and the energy density is ten times higher than that of a conventional lithium-ion battery anode with graphite. Moreover, the inorganic solid electrolyte (SE) that is fire-resisting material is used as the electrolyte; thus, the ignition risk of the battery is negligibly small [2].

However, the charging speed of conventional ASSLiMB is limited. The reason for the limited charging speed is lithium dendrite. If the ASSLiMB is in high-speed charging (charging under high-current-density condition that exceed a critical current density (CCD)), the lithium dendrite grows into the SE layer that separates the anode and the cathode by developing a clack, and the lithium dendrite connects the anode and cathode, then the battery is in an internal short circuit [3]. For high-speed charging ASSLiMB, the lithium dendrite growth with clack propagation should be suppressed.

Electrochemical performance improvement methods are proposed to increase the charging speed of ASSLiMB [4]. In those methods, thin film (e.g., Au layer by sputtering) is inserted between the SE layer and Li metal anode. Overpotential is suppressed with the thin layer, and homogeneous lithium deposition is induced, and the growth of the lithium dendrite is suppressed, then the charging speed is increased. But, with this electrochemical performance improvement, the charging speed is not enough to use the ASSLiMB as EV's battery, and other methods to increase the charging speed are required.

Shot peening (SP) is one of the methods to suppress the clack generation by compressive residual stress [5-7]. As described above, the lithium dendrite grows in the SE layer by making a clack. If the clack to the SE layer is suppressed, the lithium dendrite growth would be suppressed. Therefore, there is a possibility to increase the charging speed of the ASSLiMB by the SP to the SE layer in ASSLiMB. Moreover, the SP and thin-film insertion method can have a synergetic effect because the dendrite growth suppression mechanism is different.

According to the background mentioned above, in this study, the characteristics of SP processed ASSLiMB is demonstrated with experiments to elucidate the influence of the SP on battery charging speed and electrochemical and mechanical characteristics of the ASSLiMB.

Experimental Methods

To evaluate the influence of SP on the battery performance and the characteristics of lithium batteries with oxide SE, measurements of charging speed, SE surface structure, and SE surface mechanical characteristics are conducted for an oxide SE of $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ [8].

Ga-stabilized oxide SE ($Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$), which is an oxide solid electrolyte with a high ionic conductivity, is used in this study. The starting materials are La_2O_3, ZrO_2, Ga_2O_3, and LiOH. The starting materials are weighed out in their intended stoichiometric proportions together with an excess of 10 wt.% LiOH to compensate for lithium loss during synthesis. The mixed powder of starting materials of 10 g is placed in a zirconia pot (50 ml) with 30 ml hexane and 20 zirconia balls (ϕ 10 mm × 10, ϕ 5 mm × 10). Mechanical milling is conducted using a planetary mill operating at 300 rpm for 2 h. The material is heat-treated at 800 °C in the air for 12 hours at an increase rate of 5 °C/min by an electric furnace with a platinum crucible. The resulting materials are ball-milled with hexane again, following the same procedure as the first ball milling. The resulting materials are dried and pressed into ϕ 5 mm pellets by 150 MPa uniaxial compression. The pellets are set into the platinum crucible and covered by the mother powders. The final sintering step is done in the air in an electric furnace at 1050 °C for 12 hours at an increase rate of 5 °C/min, followed by a decrease rate of 2 °C/min. After sintering, the surface of the sintered pellet is shaped with #1500 sandpaper. The crystal structure of the synthesized pellet is measured by XRD, confirming that the SE is in the cubic garnet phase, which can achieve high ionic conductivity.

The SP is processed on the SE pellet. Al_2O_3 powder is used as the shot, and three grain size (50 μm, 100 μm, and 300 μm) is used to evaluate the influence of the grain size on the SP and battery performance. The shot is propelled to the SE pellet from a gun with high-pressure air. The nozzle diameter of the gun is 2 mm, and the gun inlet air pressure is 0.4 MPa. The distance from the exit of the gun nozzle to the SE pellet is 10 cm. The SP processing time is 10 s on each side of the SE pellet.

To compare the effect of the SP to the electrochemical performance improvement method (thin gold film insertion method between the SE and Li metal) and to investigate the synergistic effect of the SP and the thin-film insertion method, gold thin-film insertion between the lithium metal and the SE was performed by DC sputtering on the SE pellet. The sputtering is processed on the lithium contact area of the SE pellet. The pellet is placed in the DC sputtering system and processed for 4 min in the air with an ion current of 5 mA.

To evaluate the electrode performance, the CCD of a lithium symmetric cell is measured. Lithium metal is attached to both sides of the SE pellet, and the cell was pressurized to 3 MPa with a jig and installed into an airtight container in an argon-filled glove box. The CCD is measured by connecting the symmetric cell to a battery evaluation system. A rectangular current is applied with a 2-hour cycle, and the current density is increased with each cycle to measure the CCD, that is, the current density at which the cell is short-circuited, at 60 °C.

The surface shape of the SE pellet is changed by SP. The surface of SE is an interface of the SE and lithium metal anode and is an electrochemical reaction plane. Therefore, the surface shape of SE has an important role in the interface reaction, so the SE surface 3D structure is observed by a topographic method with reflected-electron SEM images [9]. Four reflected-electron images are obtained with four detectors in the SEM. Because the four detectors are set in different places in the SEM, different shadows can be observed on the reflected-electron images; the shadows contain information about the surface unevenness. The surface 3D structure is obtained with reconstruction software.

SP induces compressive residual stress on the surface of the processed material [5-7]. This compressive residual stress can increase fracture toughness and suppress cracking on the surface and can suppress the growth of the lithium dendrite. To study the change in the fracture toughness, the surface mechanical characteristics of the SE pellet were measured by the indentation system, in which a square indentation is made on the SE pellet with a diamond indenter. At the edge of the square indentation, a crack is generated. The length of the crack depends on the fracture toughness, which can be calculated by the following equation (1) [10].

$$K_c = 0.026\{(E^{1/2}P^{1/2}c)/a^{3/2}\} \tag{1}$$

In equation (1), K_c is the fracture toughness, E is Young's modulus, P is the indenter force, a is the average crack half-length, and c is the average indentation length. Young's modulus E of LLZO (130 GPa) is used for the calculation. The indenter force P is 1 kgf.

Experimental Results

Figure 1 illustrates the CCD of each sample. The CCD of the non-processed sample (non-proc.) is only 0.04mA/cm^2. With gold sputtering, which is an electrochemical performance improvement method, the CCD is increased to 0.38 mA/cm^2 (Au). With the SP with 50 μm grain, the CCD is increased to 0.27mA/cm^2 (S.P. 50 μm). By combining SP and gold sputtering, the CCD is increased to 0.73 mA/cm^2 (S.P. 50 μm + Au). With changing the grain size of the SP, the CCD is changed. With the increase in the grain size to 100 μm, the CCD is increased to 0.76mA/cm2 (S.P. 100 μm + Au). Nevertheless, the CCD is decreased to 0.32 mA/cm^2 with 300 μm grain (S.P. 300 μm + Au).

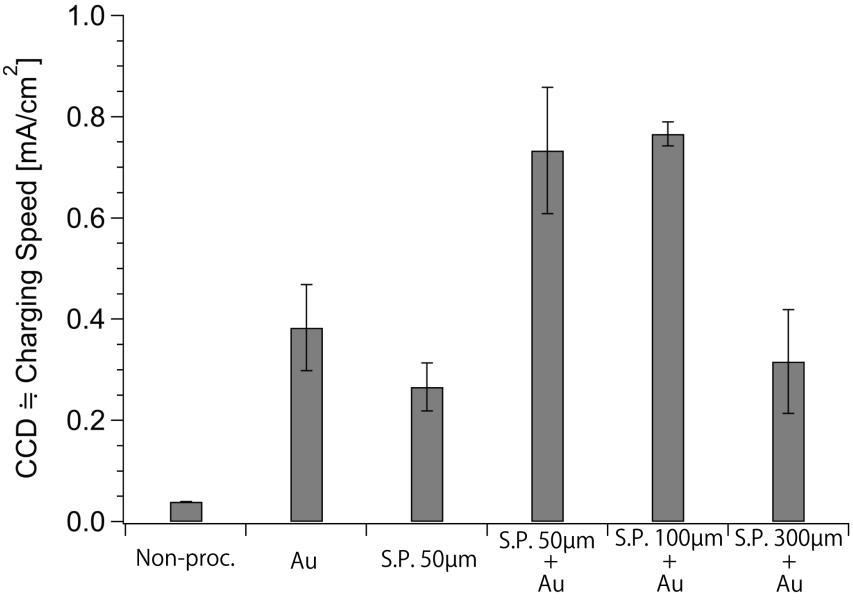

Figure 1. Critical Current Density of each processed samples.

Figure 2 illustrates the surface 3D SEM images of each processed sample. In the non-processed sample (fig.2 (a)) and a sample with gold sputtering (fig.2 (b)), the surface is almost flat. With the SP, surface roughness is generated, and the rough surface is not changed by the gold sputtering after the SP (fig2(c)-(f)). The distance between the bumps and height of the bumps are increased with the increase in the SP grain size.

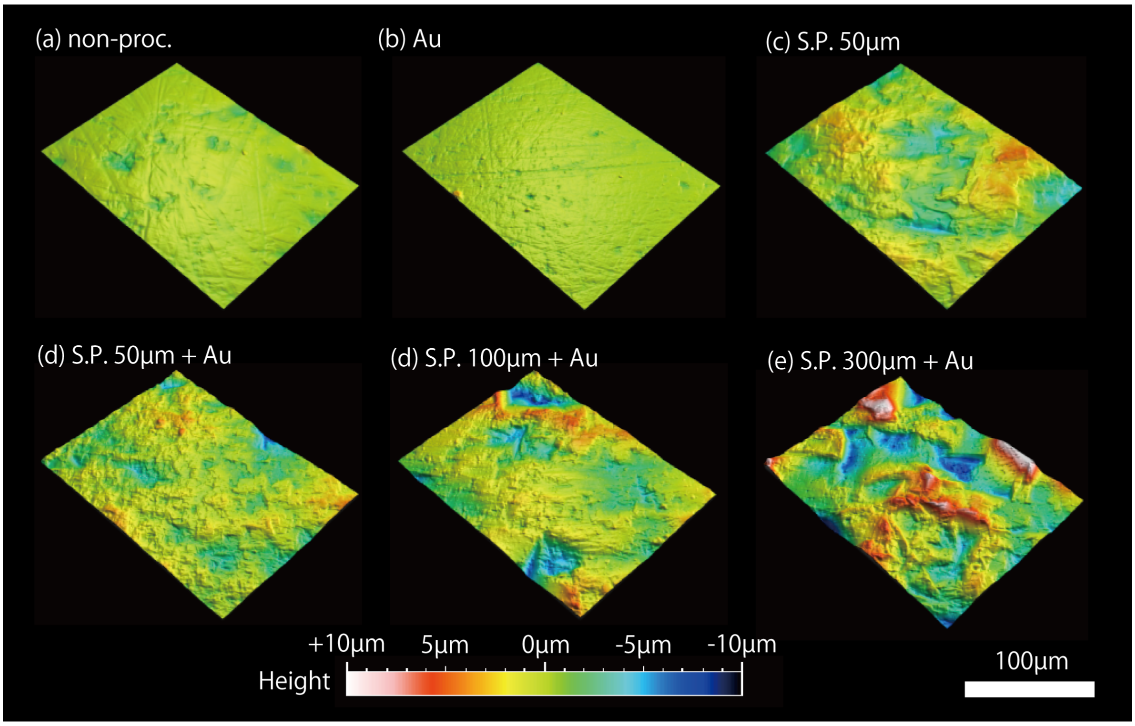

Figure 2. Surface 3D SEM Images of Each Processed Samples (a) non-processed sample, (b) Au sputtering sample, (c) S.P. 50 μm, (d) S.P. 50 μm + Au, (e) S.P. 100 μm + Au, (f) S.P. 300 μm + Au.

Figure 3 shows the fracture toughness of each processed sample. The fracture toughness of the non-SP processed samples (Non-proc. and Au) are around 2.0 MPa･m$^{1/2}$. The fracture toughness is increased by the SP, and 3.0 MPa･m$^{1/2}$ is achieved by the SP with 50 μm grain. The fracture toughness is increased with the increase in the grain size, and fracture toughness is 4.1 MPa･m$^{1/2}$ for 300 μm grain.

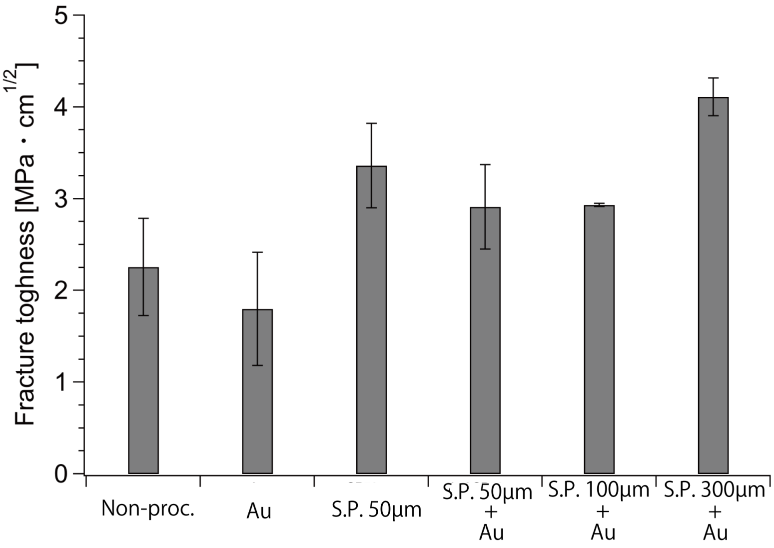

Figure 3. Fracture Toughness of Each Processed Samples.

Discussion

As shown in fig.1, the CCD of the non-processed sample was low. The CCD was increased to 0.38 mA/cm^2 by Au sputtering and to 0.27 mA/cm^2 by SP with 50 μm grain. Therefore, the performance improvement obtained by SP was comparable to conventional thin-film insertion. Moreover, by combining gold sputtering and SP with 50 μm grain, the CCD was increased to 0.73 mA/cm^2. Therefore, SP and gold sputtering can be used together to increase the CCD. With the increase in the grain size from 50 μm to 100 μm, the CCD was increased from 0.73 mA/cm^2 to 0.76 mA/cm^2, but with the increase from 100 μm to 300 μm, the CCD was significantly decreased from 0.76 mA/cm^2 to 0.32 mA/cm^2. Therefore, there is an optimum size of the grain to maximize the CCD.

The surfaces of the non SP processed samples were almost flat (Fig.2 (a),(b)), but surface roughness was made on the SE by SP (Fig2 (c)-(e)). With the increase in the grain size, the distance from top to top of the surface structure was increased, and the height of the structure was also increased. So, the increase of the grain size increases the surface roughness of the SP processed SE. This surface roughness allows mechanical penetration of the solid electrolyte into the lithium metal. This penetration increases the contact between SE and lithium metal anode and enhances the electrochemical reaction and increases the CCD. However, the interface roughness induces inhomogeneous electrochemical reactions and lithium deposition. This inhomogeneous lithium deposition can induce lithium dendrite. As a result of this balance of the enhancement of the electrochemical reaction and lithium dendrite generation, there would be the optimum grain size to maximize the CCD.

The fracture toughness was increased by the SP. This would be because the compressive residual stress is induced around the SE surface. This increase in fracture toughness also can be a reason for the increase of the CCD with the SP. The fracture toughness is slightly decreased by gold sputtering. In the sputtering process, nitrogen plasma is generated around the SE. The plasma is in non-equilibrium condition, and the gas temperature is around room temperature, but the electron temperature is higher than 5000 K. This high-temperature electron increases the processed SE temperature and releases the compressive residual stress, decreasing fracture toughness. The highest fracture toughness is achieved for SP with 300 μm grain. But the highest CCD was achieved for SP with 100 μm. Therefore, the CCD is not simply dependent on the fracture toughness, and the surface shape effect discussed above is also a factor of the CCD.

Conclusions

In this study, the influence of processing by SP to the SE pellet surface on the performance of the lithium metal electrode of an ASSLiB is elucidated by CCD, surface 3D structure, and mechanical strength measurements. The following conclusions can be drawn.

1. By attaching lithium metal to the SE pellet processed by shot peening to form the lithium metal electrode, higher CCD can be obtained than for the electrode formed when using an SE that has not been processed by shot peening. This improvement in performance is comparable to the results obtained with the conventional method of thin gold film insertion. Shot peening can be used in combination with conventional thin gold film insertion; higher electrode performance can be obtained by combining both shot peening and thin gold film insertion than by using either method alone.
2. Shot peening on the surface of the oxide SE pellets generates surface roughness on the pellets. This surface roughness can increase the contact area between the SE and the lithium metal because the surface roughness allows mechanical penetration of the solid electrolyte into the lithium metal.
3. The fracture toughness of the surface of the oxide SE pellet is increased by shot peening, thus suppressing the propagation of the lithium dendrite into the solid electrolyte. This increase in fracture toughness results in the increase in the CCD observed upon shot peening.
4. There is an optimum grain size for shot peening processing to maximize the CCD. In this study, the optimum grain size was 100 μm, and a maximum CCD of 0.76 mA/cm2 was achieved. It is estimated that the shot peening with optimum grain size generates the

optimum roughness on the SE that can enhance the interface electrochemical reaction and does not induce an inhomogeneous electrochemical reaction.

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