Colloidal processing of Li$_2$S–P$_2$S$_5$ films fabricated via electrophoretic deposition methods and their characterization as a solid electrolyte for all solid state lithium ion batteries

Shota AZUMA*, Kota AIYAMA*, Go KAWAMURA*, Hiroyuki MUTO**, Takanori MIZUSHIMA*, Tetsuo UCHIKOSHI*** and Atsunori MATSUDA**

Department of Environmental and Life Sciences, Toyohashi University of Technology, Toyohashi, Aichi 441–8580, Japan
*Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441–8580, Japan
**Institute of Liberal Arts and Science, Toyohashi University of Technology, Toyohashi, Aichi 441–8580, Japan
***National Institute for Materials Science, Tsukuba, Ibaraki 305–0047, Japan

Li$_2$S–P$_2$S$_5$ (LPS) film was prepared using colloidal process by employing electrophoretic deposition (EPD) technique followed by warm pressing for advanced processing of all-solid-state lithium ion battery. LPS precursor film with positive surface charge was obtained from its suspension that was synthesized by liquid-phase shaking method. The homogeneous film with thickness of 10–100 μm was controllably prepared. Resulted LPS film exhibited high conductivity (1.98 × 10$^{-4}$ S·cm$^{-1}$) at ambient temperature and significantly low activation energy (16.6 kJ mol$^{-1}$) compared with conventional LPS materials. Thus, good solid–solid interfacial contact can be obtained in the sulﬁde-based ionic conductor by employing EPD process followed by warm pressing.

Key-words : All-solid-state lithium ion battery, Sulfide solid electrolyte, Electrophoretic deposition, Colloidal process, Ion transfer in grain boundary

1. Introduction

Lithium ion batteries (LIBs) possess high voltage and high energy density and are valuable for portable devices as reliable power sources. Research activities of LIBs with high capacity, by upscaling and enhancing energy density, has increased dramatically in recent year due to expanding applications especially in electric-automobile and smart-grid systems.

Nearly all commercially available LIBs utilize liquid electrolytes as the medium for ion transport. These devices are capable of impressive performance but are inherently dangerous due to the flammability of the electrolytes used and the potential for environmental harm resulting from accidental leakage. These points necessitate special safety precautions in device packaging. All-solid-state LIBs, in which liquid organic electrolytes are replaced with solid-state-inorganic electrolytes, are expected to be the optimal rechargeable batteries for next generation because of their higher energy density, cycle stability and ignition safety. As solid electrolytes for novel solid-state LIBs, the sulfide-based lithium ion conductors are highly promising due to their high conductivities, single-ion conductive properties and non-flammability. Mizuno et al. fabricated novel sulfide lithium-ion conducting materials, as Li$_2$S–P$_2$S$_5$ (LPS), with high conductivity at ambient temperature by a mechanical milling method. Conventionally, mechanical milling is employed for preparing solid electrolytes, as mixtures of active materials and electrode conductive materials. However, by mechanical milling, it is difficult to control the distribution of the components in the mixture. In addition, mechanical milling method is not suitable for practical industrial manufacturing application because it is a time-consuming and energy consuming process. Thus, development of novel methods for preparation LPS that would involve short time and energy consumption with wide versatility in its application is required.

We previously reported that a suspension of LPS precursor (LPS-p) was successfully prepared using liquid-phase shaking (LS) method. In this method, LPS is obtained within a relatively short time and with low energy consumption, using LPS-p suspension in ester solvents. Moreover, LS method is suitable for preparing homogeneous electrolytes, mixtures and composite layers based on its feature of dispersing components into the liquid phase. Process/method to obtain electrolytes or composite layers directly from the suspensions is necessary to achieve above mentioned advantages, in a simple process to achieve advanced film morphology control. Previously, LPS-p was recovered as powder from suspensions, and along electrolyte with composite were fabricated via solid phase in this current LPS method. Briefly, application of LPS-p suspension directly into colloidal processing was not developed yet.

Electrophoretic deposition (EPD) is an important technology for colloidal coating processes. Under the influence of electric field, the charged colloids or particles suspended or dispersed in a fluid are directed towards and deposited onto oppositely charged electrodes. In other words, any materials can be deposited on any charged substrates by EPD if a surface charge can be generated on the material dispersed in a solvent. EPD technique with a wide range of novel application has recently gained increasing interest in the processing of advanced ceramic materials and coatings both in academia and the industrial sector. This is because of not only the high usage versatility with different materials and...
combinations but also because of its cost-effectiveness and simple apparatus requirement. Furthermore, morphology and microstructure of obtained films can be controlled easily by controlling the processing conditions such as strength of electric field, applied time, wave shape, dispersion state, and sequence of deposition. Numerous applications of EPD have been developed for the fabrication of ceramics, including the preparation of coatings, fiber-reinforced composites, laminated materials, porous membranes, stepwise functionally graded materials and continuously graded materials. LPS films with desired morphology and microstructure as mentioned above could be obtained via colloidal processing of LPS particles by EPD. Incidentally, LPS cannot be dispersed in polar solvents such as water and alcohol, which are the common dispersion media in EPD due to the high reactivity of LPS with polar media. Hence, LPS processing by EPD is limited to only in non-polar solvents. On the other hand, generating surface charge on polar materials such as LPS in non-polar solvents is very challenging. For these reasons, there is a need to research into the possibility of preparing LPS via EPD in non-polar solvents.

In this study, LPS films were prepared via EPD from suspension of LPS-p fabricated by LS method as a novel colloidal process and the characteristics of the films as a lithium ion conductor were evaluated.

2. Experimental

Li$_2$S and P$_2$S$_5$ were purchased from Mitsuwa and Merck respectively. Ethyl propionate (EP) and 3A molecular sieves were obtained from Sigma-Aldrich. EP was dehydrated by 3A molecular sieves before used. Li$_2$S (0.3827 g), P$_2$S$_5$ (0.6173 g) [molar ratio Li$_2$S:P$_2$S$_5$ = 3:1], EP (10 mL) and zirconia balls (diameter 4 mm, about 32 g) were mixed and shaken at an amplitude of about 1 cm at 1500 rpm in a dry Ar atmosphere at 30°C for 6 h. The obtained suspension of LPS-p was diluted 10 times with EP and used as the deposition bath in an EPD process. As a reference, pelletized LPS was prepared by EPD with the same condition mentioned above; employment of two specimens is to prevent the short circuit between SUS plugs due to very thin LPS film obtained after pressing process that are mentioned as follow. Thermal aging of the resultant LPS-p films was carried out via two ways; treated by conventional condition denoted above; warm pressed at 220°C with the pressure of 30 MPa under air pressure for 1 h before conventional aging. All film specimens were uniaxial-pressed using SUS plugs, which play roles as presser and electrode, at the pressure of 330 MPa for 1 min followed by thermal aging treatment. By employing the cells prepared according to above mentioned procedure, the ionic conductivity was evaluated using an AC impedance measurement analyzer (SI1260, Solatron) from 1 MHz to 10 Hz in a dry Ar flow atmosphere. As a reference, pelletized LPS was prepared by pressing of LPS powder (80 mg) obtained from LS method at the pressure of 330 MPa.

3. Result and discussion

Figure 2 illustrates the photographs of the (a) LPS-M and (b) LPS-p suspensions. The sediment of LPS-M in EP was observed shortly after sonication. It is well known that polar-matters such as LPS can’t be dispersed in non-polar solvent such as EP because of their non-affinity. On the other hand, the freshly prepared LPS-p precursor suspension after sonication was stable for several hours which indicated that LPS-p precursor possess dispersibility in EP without any treatment or additives. This stability may be originated from the structure of LPS-p precursor.
which contained both LPS and EP in its structure. It is also confirmed that LPS-p powder obtained after drying at elevated temperature, i.e., 170°C, could not be re-dispersed into EP solvent, similar to the result from LPS-M. Thus, direct application of the as-prepared suspension holds higher possibility of achieving EPD and the procedure is also simple. Figure 3 shows the current curves obtained from different suspensions under constant applied voltage (100 V/0.5 cm) between ITO substrates for 60 s. Almost no current was observed in EP without LPS and LPS-p when voltage was applied as EP is non-polar and not included any polar-matters. By contrast, high current density was observed in EP suspended with LPS-p in the process. It means that LPS-p exhibits ionic dissociation in EP, and dispersion of LPS-p in EP is caused by electrostatic repulsion; charge of LPS-p can be characterized as positive according to the particle deposition observation on the cathode. Moreover, as typical behavior of EPD, decreasing current density induced by film deposition was confirmed in EP including LPS-p. Small and flat current density curve was obtained in the case of the EP with LPS-M, and obvious deposition of LPS-M did not occur, indicating that LPS-M produced less surface charging than LPS-p. The low current density may be caused by electrophoresis of impurities.

The LPS-p film was formed on cathode by EPD under applied voltage (100 V/0.5 cm) between ITO substrates for 20 s as shown in Fig. 4(a). The film was formed homogeneously with deposition of plate-like particles as observed in SEM image of film surface [Fig. 4(b)]. There is no marked agglomeration of deposited particles in the surface SEM image. On the contrary, deposited particles were well dispersed in micro-scale and constructed of mesoporous-like structure. The same structure was distributed homogeneously in the overall cross-sectional direction of as-prepared EPD film with the thickness of several 10–100 μm [Fig. 4(c)]. The film formed with particles while maintaining good dispersibility is suggesting that the well-dispersed state of LPS-p suspension has been retained during the process. One of the typical features of EPD method is that the film thickness can be controlled easily by varying EPD conditions such as applied time of electric field. We investigated the dependence of film thickness on applied time under applying constant current density of 5.0 μA cm⁻². Average film thicknesses are noted nearly at each plot.

Fig. 2. Photographs of EP suspended with (a) LPS-M and (b) LPS-p.

Fig. 3. Current curves in various suspensions under applied constant voltage of 100 V between ITO substrates separated by a distance of 0.5 cm.

Fig. 4. (a) Photograph of LPS-p deposited cathode ITO substrate and its SEM images in (b) surface and (c) fracture cross-section. Film was fabricated by applied 100 V/0.5 cm between ITO substrates for 20 s.

Fig. 5. Dependence of amount of deposition weight of LPS-p film on processing time under applied constant current density of 5.0 μA cm⁻².
varies linearly with increasing applied time under constant applied current as fixed current; fixed current means controlling amounts of migrated particles. It was found that LPS-p film with desired film thickness can be fabricated by EPD process.

In order to determine the structure of deposited particles on the cathode, XRD measurement of the powder consisting of deposited particles [Fig. 6a’]) was carried out in suspension as a reference [Fig. 6a]). The deposited particles had the same crystal structure with dispersed particles. Thus, dispersed particle was deposited onto cathode without any chemical change in EPD process. We previously reported that particles of LPS precursor were converted to LPS particles with high ionic conductivity by the similar process with our previous report.

Conventional aged LPS pellet 3.26 45.5
LPS pellet with W.P. 2.02 31.5
EPD film without W.P. 0.18 42.5
EPD film with W.P. 1.98 16.6

The Li ion conductivity of EPD film was evaluated by AC impedance measurement under various temperatures. Figure 8 illustrated Arrhenius plots of EPD films and pelletized LPS powders; pelletized specimens were prepared using conventional method for reference. Parameters obtained from Fig. 8 are indicated in Table 1. EPD film deposited on Al substrate after conventional aging showed lower room temperature conductivity $\sigma_{25}$ ($1.8 \times 10^{-4} \text{Sc m}^{-1}$) than conventional LPS pellet ($3.4 \times 10^{-4} \text{Sc m}^{-1}$). The deposited particles have been already identified as same as pelletized LPS specimen. In other words, the lower conductivity can be ascribed to the film morphology rather than properties of deposited particles. In fact, from the SEM observation of deposited film, Figs. 4(b) and 4(c) the film shows porous structure which is not suitable for ion conduction. Thus LPS film was treated by warm pressing at 220°C in order to obtain higher conductivity. EPD film with warm pressing (220°C, 30 MPa, 1 h) showed comparable conductivity ($1.9 \times 10^{-4} \text{Sc m}^{-1}$) at ambient temperature to pelletized LPS powder fabricated from LS method. Therefore warm pressed EPD film can be utilized as Li ion conductor material which possess sufficient high conductivity. Moreover, the LPS film has a remarkable lower activation energy $E_a$ ($16.6 \text{kJ mol}^{-1}$) compared with LPS film without warm pressing ($42.5 \text{kJ mol}^{-1}$) and pelletized LPS ($45.5 \text{kJ mol}^{-1}$). Although the similar trend is found in pelletized specimen with the warm pressed LPS-p powder, pelletized LPS-p powder indicates a comparatively small change of $E_a$ ($31.6 \text{kJ mol}^{-1}$). The warming pressing effect of LPS-p is insufficient to explain the significance of $E_a$ reduction in LPS-film with warm pressing.

We have further examined the effect of warming pressing of LPS film by XRD and Raman spectroscopy. The XRD patterns are shown in Fig. 9 before and after aging by vacuum heating or warming pressing of LPS-p film. A broad pattern was observed in the film aged by warm pressing, which is different from the specimen dried at 170°C under vacuum indicating that amorphous-like structure was formed by warm pressing. On the other hand, no peak change that is attributed to PS$_4$$_2^2$ was observed in Raman spectra, before and after each heat treatment (Fig. 10).

Table 1. Parameters of ion conduction obtained from Fig. 8

| Sample                        | $\sigma_{25}/10^4 \text{Sc m}^{-1}$ | $E_a/\text{kJ mol}^{-1}$ |
|-------------------------------|------------------------------------|--------------------------|
| Convent. LPS pellet           | 3.26                               | 45.5                     |
| LPS pellet with W.P.          | 2.02                               | 31.5                     |
| EPD film without W.P.         | 0.18                               | 42.5                     |
| EPD film with W.P.            | 1.98                               | 16.6                     |

Fig. 6. XRD patterns of deposited particles prepared by EPD (100 V/0.5 cm) (a’) before and (b’) after aging by heat treatment (170°C, approximately –100 kPa for 2 h). Dispersed particles recovered from suspension (a’) before and (b’) after aging by heat treatment are for reference.

Fig. 7. Raman spectra of deposited particles prepared by EPD (100 V/0.5 cm) (a’) before and (b’) after aging by heat treatment (170°C, about –100 kPa, for 2 h). Dispersed particles recovered from suspension (a’) before and (b’) after aging by heat treatment are for reference.

Fig. 8. Dependence of ion conductivity in LPS film and pelletized LPS powder with/without warm pressing (W.P.) on temperature.

Fig. 9. XRD patterns of deposited particles prepared by EPD (100 V/0.5 cm) (a’) before and (b’) after aging by heat treatment (170°C, approximately –100 kPa for 2 h), Dispersed particles recovered from suspension (a’) before and (b’) after aging by heat treatment are for reference.
to these results, there is difference of structural regularity of PS\textsubscript{43} without chemical change between vacuum heating and warm pressing of LPS-p. The above observations were found equivalently in primal LPS-p powder without obvious difference. Reduced $E_a$ in pelletized or deposited LPS-p treated with warm pressing was probably caused due to crystallographic disorder of PS\textsubscript{43} in the amorphous structure. Even though, large difference in $E_a$ between EPD film and pellet has not been clarified in terms of thermostatics.

Next argument concerns the kinetics of lithium ion at the interfacial boundary in specimens based on electrochemical impedance spectroscopy. Figure 11 is Cole–Cole plots of pelletized LPS powder with/without warm pressing. The reduced diameter of semicircle (approx. 1.7 times) and increased characteristic frequency were observed (2.26 to 2.84 MHz) in spectrum of the specimen treated by warm pressing. These results indicate decreasing interfacial resistance due to grain boundary etc.; it is speculated effect of the disappearance of grain boundary in specimen is caused by amorphous structure. Figure 12(a) shows Cole–Cole plots of EPD film with/without warm pressing; (b) is magnified figure of (a) for EPD film with warm pressing. EPD film without warm pressing is inappropriate as ion conductor due to its too large resistance. In contrast, as shown in Figs. 12(a) and 12(b), interfacial resistance in EPD film with warm pressing treatment was significantly decreased (approx. 80 times) and resulted resistance was equivalent to that of pelletized powder with warm pressing. Similarly, the characteristic frequency (2.84 MHz) is corresponding to the one of pelletized specimen with warm pressing, suggesting that EPD film with warm pressing was also affected by amorphous structure similarly. Additionally, the unclear semicircle compared with other spectra was recorded. It indicates that interfacial resistance range of higher frequency was decreased. In fact, at end of the semicircle, the frequency of EPD film with warm pressing was significantly increased (567.9 kHz) compared with other specimens (below 28.4 kHz). This character is not found in any other specimens. This result shows that upon reaching diffusion-limited access in EPD film, warm pressing could accelerate the ion transport at the boundaries. As a consequence, much lower $E_a$ in EPD film with warm pressing is assumed to be associated with not only crystallographic effect but also accelerated interfacial ion transport as the kinetic effect.

The question we have here is why the specific kinetic effect appeared in only EPD film treated by warm pressing. It may be caused by the morphology of particles in as-deposited EPD film. Already described at the explanation of SEM images, LPS-p particles were deposited as uniform and porous film without obvious agglomeration. Because of porous structure, the as-prepared film showed poor ion conductivity owing to small contact area among particles. However, this film is being expected to be the precursor of dense film formation. Generally, small particles such as the dispersed particle employed in current work are easily sintered. Thus, the improved interfacial properties were achieved due to
the formation of dense ion conductor prepared by warm pressing EPD film. According to above explanation, dense materials formation with good solid–solid interface contact can be achieved via EPD with suitable heat treatment.

4. Conclusion

This study focused on fabricating LPS film using EPD technique followed by warm pressing. The EPD film consisted of LPS-p was obtained successfully from as-prepared suspension of LPS-p after shaking process in LS method. Based on characterization, dispersed LPS-p was deposited on electrode without any chemical change under applied electric fields and the resulted film exhibited homogeneously distributed morphology throughout the film. LPS film obtained via warm pressing also exhibited high conductivity with remarkably lower activation energy compared with conventional LPS materials. The formation of good contact at grain boundary is suggested from the comparison of AC-impedance measurement.

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