OURNALOF

Ceramic Processing Research

Improvement of cycle performance of all-solid-state lithium ion batteries with clustered composite electrodes using PTFE powder

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Cycle performance is a technical challenge for the all-solid-state lithium ion battery because of contact loss between the active materials and solid electrolytes. Providing an intimate adhesive contact between solid electrolyte and active materials might be the most effective and practical solution. To address this issue, we added PTFE powder to the composite cathode in order to create good conducting paths for Li ions and electrons of the lithium batteries. We show the PTFE added composite cathode has significantly better cycle performance. Electrochemical impedance spectroscopy suggests that the charge transfer resistance increased as the amount of PTFE powder increased. On the other hand, differential capacity vs. voltage profiles showed that polarization of the composite cathode was suppressed as cycle number increased in the PTFE added composites. A preliminary model is suggested to guide future development of the microstructure in all-solid-state batteries.

Key words: All-solid-state lithium ion battery, Solid electrolyte, Cycle performance, PTFE powder, Composite cathode.

Introduction

Recently, electric vehicles (EV) have received considerable attention due to environmental issues such as the regulation of CO₂ emissions. Lithium ion batteries have been used as advanced power sources because of high specific energy and specific power [1]. However, safety concerns regarding the flammable organic liquid electrolyte are still a big challenge for lithium ion batteries especially in large-scale applications such as EVs. In this respect, all-solid-state lithium ion batteries with inorganic solid electrolytes are regarded as an excellent solution to safety issues [2-5]. In particular, sulfide electrolytes in the $Li_2S-P_2S_5$ system are highly promising as the solid electrolytes because of high lithium ion conductivities of about 10^{-3} S cm⁻¹ and wide electrochemical potential windows for the all-solid-state battery system [6, 7].

Compared to cells using the liquid electrolyte, it is more difficult to form the interfacial area between cathode and solid electrolyte in all-solid-state cells [8, 9]. Therefore, it is critical to form adhesive, high interfacial area solid-solid interfaces for lithium ion and electron conducting paths. However, a major obstacle is the expansion and contraction of the active materials, which cause contact loss between the active materials and electrolytes [10].

Therefore, a favorable interfacial contact area between the solid constituent particles should be

maintained to improve cycle performance of the allsolid-state lithium batteries. In this respect, a polymeric binder in the composite cathode can provide an intimate adhesive contact among the solid constituent particles and can improve the cell performances.

In this study, the composite cathodes were fabricated by adding Polytetrafluoroethylene (PTFE) binder to provide good conducting paths for Li ions and electrons of the lithium batteries. The composite cathodes were prepared by using planetary ball milling to achieve a favorable contact between the particles.

Experimental

The solid electrolyte in this work is the $78Li_2S \cdot 22P_2S_5$ glass-ceramics prepared using a previously reported mechanical milling process with subsequent heat treatment [11, 12]. Briefly, reagent-grade Li₂S (99.9%, Alfa) and P₂S₅ (99%, Aldrich) starting materials were mixed in the appropriate molar ratios. The mixture was then mechanically milled at 520 rpm for 25 hrs using a high energy planetary ball mill (Pulverisette 7, Fritsch) with milling cycles of 40 min and rests for 20 min. The lithium ion conductivity of the glass-ceramics was 1 x 10^{-3} S cm⁻¹ at 25 °C.

Composite electrodes were prepared by mixing the coated $LiCoO_2$ particles, prior to preparing the cells the surface of the $LiCoO_2$ (LCO) active material was coated with $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) using our previously reported sol-gel method [13]. The 78Li₂S·22P₂S₅ solid electrolyte, Super P carbon (Timcal) and PTFE powder (Aldrich) using a planetary ball milling with weight ratio of 69 : 29 : 2. The concentration of PTFE in the composite

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cathodes was varied from 0 to 6 wt%, which will be referred to as PTFE0 to PTFE6 in the text. The microstructures of the all-solid-state composite electrodes with different ratio of binder additives were observed by using scanning electron microscopy (SEM, Jeol JCM-5700). To fabricate all-solid-state cells, 78Li₂S·22P₂S₅ glass-ceramics powders and indium foil (99.9975%, Alfa Aesar) were used as solid electrolytes and the anode layers, respectively. To make the complete cells, 15 mg of the composite cathode mixture, 150 mg of the 78Li₂S·22P₂S₅ glass-ceramics powder and indium foil (0.1 mm) were cold-pressed together under 4 metric tons in a 16 mm diameter mold. The obtained threelayer pellets were packaged in a 2032-type coin cell for electrochemical measurements. All processes were performed in a dry, Ar-filled glove box ([H₂O] < 1 ppm). All the cells were galvanostatically charged and discharged using a charge/discharge measurement device (TOSCAT-3100, Toyo system) at room temperature [14].

The charge/discharge performance was evaluated under a constant current density of 0.06 mA cm^{-2} and cut off voltages of 1.88 and 3.68 V vs. Li-In. For measurements of rate capability, the discharge current density was gradually changed every 5 cycles from 0.05 C to 2 C. Electrochemical impedance spectroscopy of the obtained cells were performed using an impedance analyzer (Wonatech, Zive-mp5) in the frequency range from 0.1 Hz to 1 MHz after charging to 3.68 V.

Results and Discussion

SEM images in Fig. 1 show the morphologies of the all-solid-state composite cathodes. Fig. 1(a) and (c) show the morphology of PTFE0 and (b), (d) the PTFE4 sample. The top row of images are lower magnification showing the particles of the composite cathode. The solid electrolyte and the cathode active material are not well adhered to each other in the absence of the PTFE



Fig. 1. SEM images of the composite cathodes (a), (c) PTFE0 and (b), (d)PTFE4.



Fig. 2. Charge-discharge curves of all-solid-state cells with different amounts of PTFE in the composite cathode. Measurements were made at room temperature at 0.05C charge and discharge rate with cut off voltages of 1.9-3.68 V (vs. Li-In).



Fig. 3. Cycle performance of all-solid-state cells with different amounts of PTFE in the composite cathode. Measurements were made at room temperature at 0.05C charge and discharge rate with cut off voltages of 1.9-3.68 V (vs. Li-In).

powder Fig. 1(a,c). In contrast, the surface of the solid electrolyte are well bonded to the surface of $LiCoO_2$ active particles in the PTFE4 sample Fig 1(b,d). Hence, the addition of PTFE powder brings the $LiCoO_2$ and solid electrolyte particles into closer contact. PTFE2 to PTFE6 samples were expected to improve the overall electrochemical performance.

Fig. 2 shows the first charge/discharge curves of allsolid-state $In/LiCoO_2$ cells using the composite cathodes with different PTFE amounts. PTFE0 sample has the maximum value of 152.2 mAh/g. On the other hand, PTFE2 to PTFE6 samples showed a non-linear decrease in the discharge capacity as the PTFE increases: PTFE2 (148.2 mAh/g), PTFE4 (142.4 mAh/ g), and PTFE6 (133.4 mAh/g). Increasing the amount of PTFE seems to increase the interfacial chargetransfer resistance between solid electrolyte and cathode.

Fig. 3 shows the cycle performance of all-solid-state cells using the composite cathodes with different PTFE

amounts. The sample with no PTFE (PTFE0) showed significant loss of capacity after the 23rd cycle. This poor cycle performance is attributable to reduction of mechanical strength and excess strain at the solid-solid interfaces during large volume expansion and phase transition of LiCoO₂ particles [10]. In contrast, PTFE2 sample showed better cycle performance than PTFE0 sample, which was maintained until the 35th cycle. Further addition of PTFE (PTFE4 and PTFE6) enabled cycling beyond 45 cycles. Thus, we can conclude that more than 2% weight PTFE addition is necessary for effective binding of the solid-solid interface. Despite the good cycling performance however, the PTFE6 sample exhibited $\sim 25\%$ lower capacity than the PTFE4 sample. PTFE4 showed the best compromise yielding a higher discharge capacity of 128 mAh/g and a capacity retention of 90% beyond the 45th cycle in the all-solid-state cells. Therefore, Fig. 2 and Fig. 3 showed the importance of the trade-off between cycle performance and discharge capacity in the presence of PTFE.

To understand the effect of PTFE addition on interfacial resistance, electrochemical impedance of the all-solid-state cells were measured. Electrochemical impedance spectroscopy gives information on the resistance of lithium ions through the interface. Fig. 4 shows electrochemical impedance plots for all-solidstate cells using the composite positive electrode with different PTFE amounts after charging to 3.68 V (vs. Li-In) at a current density of 0.06 mAcm⁻² in the frequency region of $1 \sim 1.3 \, 103 \, \text{Hz}$. The resistance components are attributed to the charge-transfer resistance at the interface between the sulfide based solid electrolyte and the cathode materials. The calculated charge-transfer resistance of the all-solidstate cells are: PTFE0 (58.8 Ω cm²), PTFE2 (62.4 Ω cm²), PTFE4 (75.4 Ω cm²) and PTFE6 (81.6 Ω cm²). Thus, the trade-off between connectivity (Fig. 1, 3) and transfer resistance (Fig. 2, 4) confirm that an optimal amount of PTFE is needed for maximum overall battery performance.

Fig. 5 shows the differential capacity (dQ/dV) vs. voltage profiles of the all-solid-state cells with various amounts of PTFE at the 1st and 35th cycles. Shifting and broadening of the major redox peaks were observed in the potential range of 3.3-3.4 V. All cells show a similar cathodic peak potential of approximately 3.33 V in the first cycle, while a notable difference occurs after 35 cycles. Although continuous cycling causes the cathodic peaks of all the cells to shift to a higher potential, the potential shifts of all-solid-state cells with PTFE4 sample is evidently limited after 35 cycles to only 11mV. In contrast, the cathodic peak potential of



Fig. 4. Electrochemical impedance spectra of batteries with different amounts of PTFE in the composite cathode. Measurements were made at room temperature after 0.05C charge with cut off voltages of 3.68 V (vs. Li-In).



Fig. 5. Differential capacity (dQ/dV) vs. voltage profiles of allsolid-state cells with different amounts of PTFE in the composite cathode at the 1st and 35th cycles.



Fig. 6. Schematic model of the microstructure binder's interaction with the active materials and solid electrolytes.

the all-solid-state cell with PTFE6 shifted to a higher value. These results show that electrode polarization is reduced in all-solid-state cells with PTFE added samples, which demonstrates better reversibility of the charge and discharge cycle.

The schematic drawing in Fig. 6 illustrates the PTFE interaction between the active materials and solid electrolytes during charge-discharge cycling. Repeated volumetric expansion and contraction of the active particles occurs as the lithium ions move into and out of the lattice. Over time this results in capacity loss due to the breaking of contact with the solid electrolyte as represented in the schematic. However, when PTFE is added, the solid electrolyte and the cathode active particles are more effectively bound together and show much less capacity loss during cycling as demonstrated in Fig. 4 and 5.

Conclusions

The addition of PTFE to composite cathodes provide for a more intimate and adhesive contact among the solid constituent particles. Improved contact between active materials and solid electrolytes are a promising contribution to the development of advanced all-solidstate lithium secondary batteries. In this work, we demonstrated that the PTFE additive ensures good binding during the expansion and contraction of the active material during the repeated charge-discharge cycling. Further, we showed that the optimal amount of PTFE is around 4% by weight providing the best compromise between effective binding of solid electrolytes to active material and limited charge transfer resistance.

Acknowledgments

This work was supported by the Dual Use Technology Program of the Institute of Civil Military Technology Cooperation granted financial resources from the Ministry of Trade, Industry & Energy and Defense Acquisition Program Administration (17-CM-EN-11).

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