**Electrode morphology in all-solid-state lithium secondary batteries consisting of
LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and Li₂S–P₂S₅ solid electrolytes**

Atsushi Sakuda, Tomonari Takeuchi, Hironori Kobayashi

Corresponding Author: Dr. Atsushi Sakuda, Ph.D.

Authors' Institution: National Institute of Advanced Industrial Science and Technology (AIST)

Abstract

The effect of the particle sizes of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and Li₂S–P₂S₅ solid electrolytes (SEs) on the electrode morphology was investigated. Smaller-sized SE particles were advantageous in fabricating dense and homogeneous electrode layers with an effective lithium-ion conduction pathway and a large electrode–electrolyte interfacial contact area because of the unique mechanical properties of sulfide-based SEs. The homogeneous distribution of the SE is also effective in the suppression of cracking and fracturing of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ because of the favorable mechanical properties of the sulfide-based SEs. The capacity of the all-solid-state cells under high-rate operation was thus remarkably improved.

Introduction

All-solid-state lithium secondary batteries with sulfide-based solid electrolytes (SEs) are expected to serve as next-generation batteries on the road to attaining improved safety, long cycle and calendar life, and high energy density.

The selection of the composite electrode is one of the most important factors to improve the battery performance of all-solid-state batteries. The following criteria should lead to better electrode performance: (i) low-resistance electrode–SE interface, (ii) homogeneous lithium-ion and electron conduction pathway with high packing density (small porosity), (iii) suppression of damage to the electrode active materials during processing, (iv) higher electrode active material content, and (v) use of electrode active materials with small volume change during charging and discharging. Obviously, the use of a highly conducting SE and large-capacity electrode active materials are the most important factors.

Lithium–nickel–cobalt–manganese oxide ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; NCM), which was developed by Ohzuku *et al.*, is a promising electrode active material [1,2]. Among the many advantages of NCM, the large capacity, long cycle life, and small volume change during charging and discharging are especially attractive for all-solid-state batteries because of the importance of retaining the favorable solid–solid contact between the electrode and electrolyte. Some studies on all-solid-state batteries using NCM and sulfide-based solid electrodes have been reported, and the potential of NCM as a standard electrode for all-solid-state batteries has been demonstrated [3–5]. The

improvement of the energy density is an important challenge in all-solid-state batteries. The first requirement is the increase of the active materials ratio in the composite electrode. Although the weight ratio of the active material composition is 40–70 % in the majority of studies on bulk-type all-solid-state batteries [3–5], over 70 wt.% is required for the positive composite electrode to design all-solid-state batteries with a high energy density of 200–250 Wh kg⁻¹. Designing a favorable solid–solid interface between the electrode active material and SE particles is important to achieve a larger capacity, high power, and long cycle life.

The sulfide-based SEs exhibit the unique mechanical property that dense compacts are formable by pressing the powder at room temperature [6]. This property yields the formation of a desirable composite electrode layer with intimate contact between the electrode and electrolyte using only room-temperature pressing of the composite electrode powder consisting of the electrode and SE particles.

To construct a favorable composite electrode layer with a large active material ratio, the morphology of the SEs is also important. It has been reported that the LiCoO₂ electrode particles coated with the Li₂S–P₂S₅ SE yields a favorable electrode layer with an effective lithium-ion conduction pathway as well as intimate contact between the electrode and SE [6–9]. From the industrial standpoint, a more convenient process to achieve such a favorable electrode is desired; the advantages of the use of smaller-sized SE particles are reported in several patents [10, 11]. However,

a detailed investigation of the electrode layer has not been conducted.

Scanning electron microscopy (SEM) observation of the cross section is a powerful approach to obtain information about the electrode layer. For instance, the distribution of the electrode and SE particles can be investigated by cross-sectional SEM examination [6].

In this study, we investigated the electrode morphology, such as the distribution of NCM and the SE using cross-sectional SEM examination. The effects of the particles sizes of NCM and the SE on the electrode morphology and electrode performance are also reported.

Experimental

Commercial NCM particles with average sizes of approximately 9 μm (NCM-9 μm) and 5 μm (NCM-5 μm) were used as electrode active materials. The specific capacities of both NCM-9 μm and NCM-5 μm were confirmed to be the same using the cells with liquid electrolytes. The oxide coatings have been reported to be effective in achieving a low-resistance interface in a positive electrode using 4 V-class oxide electrodes [4,5, 12–15]. Thus, the NCM particles were coated with LiNbO_3 in advance. The LiNbO_3 coatings were formed by spray coating of an ethanol solution of lithium and niobium double ethoxide on NCM particles using tumbling fluidized bed granulating-coating machines (MP-01, Powrex) and heating at 400 $^{\circ}\text{C}$ for 30 min under oxygen flow. More details are provided in a previous report [13]. We have confirmed that most of the particle surface is covered with LiNbO_3 . The estimated thickness of the LiNbO_3 coating is less than 10 nm.

The 75Li₂S·25P₂S₅ (mol%) glassy SE was selected as the most typical sulfide-based SE. The SE was prepared by mechanical milling from crystalline Li₂S (Mitsuwa Chemicals) and P₂S₅ (Aldrich). Heptane was used as the solvent for wet ball milling. Zirconia pots (500 mL) with 1 kg of zirconia balls (4 mm in diameter) were used. The starting materials were weighed in an Ar-filled glove box and milled using air sealing pots for 20 h. The smaller-sized SE particles were prepared by pulverizing SE in heptane using small zirconia balls (0.1 mm in diameter) and dibutyl ether as a dispersant [16]. The lithium-ion conductivity of the powder-compressed pellet of the as-prepared SE and smaller-sized SE particles exhibited almost the same value of approximately $4 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C. The grain boundary resistance is not a dominant resistance component in the compressed pellets of Li₂S–P₂S₅ glasses. Thus, the resistance of the SE layer does not increase by pulverizing the SE. The particle size distribution was measured using a laser diffraction and scattering method (AEROTRAC SPR, model 7340, Nikkiso, Japan).

All-solid-state cells were constructed as follows. The NCM and SE with a weight ratio of 75:25 were mixed for 1 min using a vortex mixer (IKA® Lab Dancer test tube shakers) via a dry process to prepare the positive composite electrode. The use of the vortex mixer was effective in improving the electrode performance and reproducibility. A lithium–indium alloy was used as the counter electrode. Bilayer pellets ($\phi=10 \text{ mm}$) consisting of the positive composite electrodes (10 mg) and the SE (80 mg) were obtained by pressing under 330 MPa at room temperature; indium foil ($t=$

0.1, $\phi=9$ mm, 46.5 mg) and a piece of lithium (0.8 mg) were then attached to the bilayer pellets by pressing under 100 MPa. The reproducibility of the charge–discharge measurements was improved with the addition of a small amount of lithium to indium. The pellets were pressed using two stainless steel rods; the stainless steel rods were used as current collectors for both the positive and negative electrodes. All the processes for preparing all-solid-state cells were performed in an Ar-filled glove box ($[\text{H}_2\text{O}] < 1$ ppm).

Cross-sections of the all-solid-state cells for SEM observation were prepared using an *Ar ion beam* cross-section polisher (CP; IB-9020CP, JEOL) with an air-sealing holder to avoid the explosion of air on the prepared cross section. The samples were placed in the Ar-filled glove box and transferred to the CP using the air-sealing holder and milled for approximately 2 h. The used acceleration voltage and Ar gas pressure were 6 kV and 3×10^{-3} Pa, respectively. During the Ar ion milling, the stage was rocked $\pm 30^\circ$ to prevent beam striations and ensure uniform etching of the composite materials. Then, the obtained cross-section samples were transferred to the glove box and placed in the transfer vessel for SEM observation. The examination was performed using an SEM (JEOL JSM-6510A). The charge–discharge performances were evaluated at 30°C.

Results and discussion

Figure 1a–d show the particle size distribution of the NCM and SE particles used in this study, which were measured using laser diffraction and scattering methods. The average particle sizes of

the value at 50% cumulative population (d_{50}) of NCM-9 μm , NCM-5 μm , as-prepared SE, and smaller-sized SE particles were 9.4, 5.3, 16, and 3.8 μm , respectively. The as-prepared SE and smaller-sized SE particles are described as a SE-16 μm and SE-4 μm hereafter. Figure 1e–h present SEM images of the respective samples. The particle sizes of the SEM images are consistent with the particle size distribution results. The particle size of the SE particles is dramatically decreased by pulverizing; disk-shaped smaller-sized particles are obtained.

Figure 2 presents SEM images and energy-dispersive X-ray spectroscopy (EDX) elemental mappings for oxygen (O) and sulfur (S) of cross-sections of the positive electrode layer. An electrode using NCM- $X\mu\text{m}$ and SE- $Y\mu\text{m}$ is described as NCM- $X\mu\text{m}$ /SE- $Y\mu\text{m}$ hereafter. The EDX elemental mappings of O and S show the distribution of NCM and the SE, respectively.

NCM and the SE are disproportionately located in the electrode layer using SE-16 μm (Figure 2a and 2c) because a large amount of large SE particles is present in the electrode. However, the NCM and SE are homogeneously located in the electrode layer using SE-4 μm (Figure 2b and 2d) because of the use of smaller-sized SE particles. The particle volume is roughly proportional to the cube of the particle diameter or radius; the roughly estimated average volume of SE-16 μm is more than 50 times larger than that of SE-4 μm . That is, the particle volume and number of particles of SE-4 μm are approximately 1/50 times smaller and 50 times larger than those of SE-16 μm , which should yield a homogeneous distribution of SE particles.

The SE images indicate that the void volume in the electrode using SE-4 μ m is smaller than that using SE-16 μ m. Similarly, a homogeneous SE layer is also achieved using smaller-sized SE particles in addition to the homogeneous electrode layer. The highly dense electrode layer and SE layer can be achieved using smaller-sized SE particles. The SEM images also reveal that NCM particles are dispersed in the SE matrix. A research group at Osaka Prefecture University reported that sulfide-based SEs can undergo room-temperature pressure sintering, and an effective lithium-ion conduction pathway can be formed by coating LiCoO₂ particles with SE using pulsed laser deposition (PLD) [6–9] and solution processing [17]. The electrode morphologies of the cells using smaller-sized SE particles are similar to those prepared using SE-coated electrode particles. This result suggests that a favorable lithium-ion conduction pathway is able to be formed using smaller-sized SE particles as well as SE coatings formed on electrode particles because the particle size reduction of SE improves the homogeneity of the NCM and SE particles in the composite electrode powder. The smaller-sized SE particles would be industrially more useful than SE coatings prepared using PLD.

The ratio of the particle diameters of SE and NCM (D_{SE}/D_{NCM} ratio) is also important to design a favorable electrode layer. The large D_{SE}/D_{NCM} ratio causes an inhomogeneously distributed electrode layer. At least, D_{SE} should be smaller than D_{NCM} to prepare a relatively homogeneous electrode layer. The D_{SE}/D_{NCM} ratio would become more important in improving the energy density

of the batteries because a favorable electrode/electrolyte contact area should be designed with a small volume ratio of the SE.

In the composite electrode layer with SE-16 μm , the cracking and fracturing of NCM are observed in some particles, as shown in Figure 2e. The cracking is dramatically decreased when using SE-4 μm instead of SE-16 μm (Figure 2f). Cracks are mainly observed where two NCM particles are in direct contact; cracking is rarely observed at the interface between NCM and the SE. At the interface between two NCM particles, a relatively large stress concentration develops owing to the high-pressure compression because NCM is a typical brittle material. However, the stress concentration is suppressed at the interface between NCM and the SE because SE particles deform by compression at a high pressure and have a lower elastic modulus of approximately 20 GPa [6, 18]. The highly dispersed SE particles are effective in suppressing damage to the electrode active materials, which becomes more significant in the composite electrode with higher NCM ratio.

Figure 3 presents the charge–discharge curves of the all-solid-state cells measured using constant current (CC) mode at a current density of 0.064 mA cm⁻², which corresponds to 6.7 mA g⁻¹-NCM and an approximate C/20 rate. The cutoff voltage is 3.7 and 2.5 V vs. a Li–In counter electrode, which corresponds to 4.3 and 3.1 V, respectively, vs. Li/Li⁺ [19]. All the cells exhibit initial charging capacities of 160–180 mAh g⁻¹. After the first charging, stable discharging and charging are confirmed with capacities of approximately 140–150 mAh g⁻¹. No remarkable

difference between the particle sizes of NCM and the SE is observed during the charging and discharging at a low current density of 0.064 mA cm^{-2} . As observed in the SEM images in Figure 2, the dense and homogeneous electrode layer can be formed using smaller-sized SE particles. During low-current-density operation, there is little difference in the electrode performance between the homogeneous and inhomogeneous electrode layer. Both the cells with an inhomogeneous electrode layer ((a) NCM-9 μm /SE-16 μm and (c) NCM-5 μm /SE-16 μm) and those with a homogeneous electrode layer ((b) NCM-9 μm /SE-4 μm and (d) NCM-5 μm /SE-4 μm) exhibit high capacity. This result suggests that the lithium-ion conduction pathway and electrode–electrolyte interfacial contact area of the electrode layer of the all-solid-state cells prepared with SE-16 μm are sufficient under low-current-density operation.

Figure 4 a-d presents the charge–discharge curves of the all-solid-state cells under a higher current density measured using the constant current and constant voltage (CCCV) mode for charging and the CC mode for discharging. The current density used for charging and discharging was 0.64 mA cm^{-2} , which corresponds to 67 mA g^{-1} -NCM and an approximate C/2 rate.

The initial discharge capacities of (a) NCM-9 μm /SE-16 μm , (b) NCM-9 μm /SE-4 μm , (c) NCM-5 μm /SE-16 μm , and (d) NCM-5 μm /SE-4 μm are 109, 117, 122, and 126 mAh g^{-1} , respectively. The reversible capacities of the cells using SE-4 μm are larger than those using SE-16 μm . Similarly, the reversible capacities of the all-solid-state cells using NCM-5 μm are larger than those using

NCM-9 μm . Figure 4e compares the rate performance of NCM-5 μm /SE-16 μm and NCM-5 μm /SE-4 μm . At high current densities, the cell prepared using the smaller-sized SE exhibited larger capacities than that prepared using the larger SE particles. Figure 4f shows their charge–discharge curves under the current density of 2.6 mA cm⁻² (2C rate). At a high current density, the higher discharge voltage is observed in the cell using smaller-sized SE particles, indicating that the smaller resistance in the composite electrode layer is achieved by using smaller-sized SE particles. The all-solid-state cells using smaller-sized SE particles exhibit better performance for the high-rate operation. This result suggests that designing a homogeneous electrode layer using smaller-sized SE particles is effective in improving electrode performance for high-rate operation.

Conclusion

The electrode and SE were inhomogeneously distributed in the electrode layers of all-solid-state cells prepared using a SE with a larger particle size. The electrode and SE were homogeneously distributed in the electrode layer using smaller-sized SE particles. The homogeneity of the electrode was more strongly related to the size of the SE particles than that of the electrode materials. Cracking and fracturing of the electrode particles were mainly observed where the electrode particles were in direct contact. The cracking and fracturing were suppressed by using the smaller-sized SE

particles because of the homogeneous distribution of SE particles. The all-solid-state cells were charged and discharged with high capacities of 140–150 mAh g⁻¹ at a low current density of 0.064 mA cm⁻²; no significant difference was observed between the particle sizes of the NCM and SE. At high current densities, the cells prepared using the smaller NCM and SE exhibited larger capacities and higher voltage discharging than those prepared using the larger NCM and SE particles; this suggests that the improvement of homogeneity in the electrode using smaller-sized SE particles is an effective approach to improve the electrode performance of all-solid-state batteries.

Although we selected NCM as a typical electrode active material in this study, the mechanical properties of electrode materials differ for each material. The process used to prepare the electrode layer also affects the electrode morphology and performance. Thus, the electrode morphology prepared using various materials and processes should be investigated in detail in a future study to achieve a highly designed electrode layer.

Acknowledgments

This research was financially supported by the Japan Science and Technology Agency (JST), Advanced Low Carbon Technology Research and Development, Specially Promoted Research for Innovative Next-Generation Batteries (ALCA-SPRING).

References

- [1] T. Ohzuku, Y. Makimura, *Chem. Lett.*, **30** (2001) 642.
- [2] N. Yabuuchi, T. Ohzuku, *J. Power Sources*, **119–121** (2003) 171–174.
- [3] H. Kitauro, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Electrochim. Acta*, **55** (2010) 8821–8828.
- [4] N. Machida, J. Kashiwagi, M. Naito, T. Shigematsu, *Solid State Ionics*, **225** (2012) 354–358.
- [5] K. Okada, N. Machida, M. Naito, T. Shigematsu, S. Ito, S. Fujiki, M. Nakano, Y. Aihara, *Solid State Ionics*, **255** (2014) 120–127.
- [6] A. Sakuda, A. Hayashi, M. Tatsumisago, *Sci. Rep.*, **3** (2013) 2261.
- [7] A. Sakuda, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, *Electrochem. Solid-State Lett.*, **13**(6) (2010) A73–A75.
- [8] A. Sakuda, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, *J. Power Sources*, **196** (2011) 6735–6741.
- [9] Y. Ito, A. Sakuda, T. Ohtomo, A. Hayashi, M. Tatsumisago, *Electrochemistry*, **82**(7) (2014) 591–594.
- [10] K. Iwamoto, N. Aotani, K. Takada, S. Kondo, *JP patent* 8-195219 A.
- [11] T. Koga, H. Hasegawa, K. Sugiura, K. Omori, *WO patent* WO2013/073035.
- [12] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, *Adv. Mater.*, **18** (2006) 2226.
- [13] N. Ohta, K. Takada, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada, T. Sasaki,

Electrochem. Commun., **9** (2007) 1486.

[14] A. Sakuda, H. Kitaura, A. Hayashi, K. Tadanaga, M. Tatsumisago, *Electrochem. Solid-State Lett.*, **11** (2008) A1.

[15] A. Sakuda, A. Hayashi M. Tatsumisago, *Chem. Mater.*, **22** (2010) 949.

[16] K. Sugiura, M. Ohashi, *WO patent* WO2013/073035.

[17] S. Teragawa, K. Aso, K. Tadanaga, A. Hayashi, M. Tatsumisago, *J. Mater. Chem. A*, **2** (2014) 5095.

[18] A. Sakuda, A. Hayashi, Y. Takigawa, K. Higashi, M. Tatsumisago. *J. Ceram. Soc. Jpn*, **121**(11) (2013) 946–949.

[19] K. Takada, N. Aotani, K. Iwamoto, S. Kondo, *Solid State Ionics*, **86–88** (1996) 877–882.

Figure captions

Figure 1 Particle size distribution measured by laser diffraction and scattering methods (a–d) and SEM images of (e–h) NCM-9 μ m (a, e), NCM-5 μ m (b, f), SE-16 μ m (c, g), and SE-4 μ m (d, h).

Figure 2 SEM images and EDX elemental mappings for O and S of cross-section of positive electrode layer of NCM-9 μ m/SE-16 μ m (a), NCM-9 μ m/SE-4 μ m (b), NCM-5 μ m/SE-16 μ m (c), and NCM-5 μ m/SE-4 μ m (d). *Magnified SEM images of NCM-9 μ m/SE-16 μ m (e) and NCM-9 μ m/SE-4 μ m (f) are also shown.*

Figure 3 Charge–discharge curves of the all-solid-state cells at a current density of 0.064 mA cm^{-2} (approximately C/20 rate) at 30°C : (a) NCM-9 μm /SE-16 μm , (b) NCM-9 μm /SE-4 μm , (c) NCM-5 μm /SE-16 μm , and (d) NCM-5 μm /SE-4 μm .

Figure 4 Charge–discharge curves of the all-solid-state cells at a current density of 0.64 mA cm^{-2} (approximately C/2 rate) at 30°C : (a) NCM-9 μm /SE-16 μm , (b) NCM-9 μm /SE-4 μm , (c) NCM-5 μm /SE-16 μm , and (d) NCM-5 μm /SE-4 μm . (e) Rate performance of NCM-5 μm /SE-16 μm and NCM-5 μm /SE-4 μm . (f) Comparison of charge–discharge curves of NCM-5 μm /SE-16 μm and NCM-5 μm /SE-4 μm under the current density of 2.6 mA cm^{-2} (2C rate).

Fig. 1

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 2

Fig. 3

Fig. 4