Microband-Array Electrode Technique for the Detection of Reaction Distributions in the Depth Direction of Composite Electrodes for the All-Solid-State Lithium-Ion Batteries

Masanobu Chiku,* Keiichiro Ota, Eiji Higuchi, and Hiroshi Inoue

ABSTRACT: There are several problems left to be solved for the practical use of an all-solid-state lithium-ion battery (ASSLIB) such as the inhomogeneous reaction of active materials due to the intermittent ion/electron conduction pathway. In this study, a triple-microband electrode was embedded in the composite positive electrode of ASSLIB for the direct measurement of the reaction distribution of active materials. We found that the balance of the ionic/electronic conductivity of the composite electrode determines the reaction distribution in the depth direction of the composite electrode. Moreover, the active material was utilized equally even in the composite electrode, which has balanced ionic/electric conductivity and 300 μm thickness.

INTRODUCTION

The introduction of low-emission vehicles is a key for the reduction of greenhouse gas emission, which is a solution to global warming.1 Lithium-ion batteries (LIBs) are important power sources for electric vehicles (EVs) because of their high power and energy density;2–6 nevertheless, further improvement in battery performance is necessary to have the cruising range of an EV comparable to a classical gasoline-powered vehicle.5,7–10 In general, conventional LIBs consist of layered transition metal oxides as a positive electrode material, graphite as a negative electrode material, and flammable organic liquid as an electrolyte, therefore LIB-powered EVs have the risk of fatal explosion in a car accident. Various types of novel rechargeable batteries have been developed to overcome these problems.11 Among them, all-solid-state LIBs (ASSLIBs) are one of the most promising batteries for use in EVs12 because they use a nonflammable solid electrolyte (SE), which can decrease the possibility for the explosion of a damaged rechargeable battery. Moreover, SE may inhibit lithium dendrite formation, leading to the use of lithium metal as a negative electrode material.13

There are several problems left to be solved for the practical application of ASSLIBs, especially their poor high-rate capability due to high interfacial resistance between an active material and SE.14 LiNbO₃ coating on active material particles is a key technology to decrease interfacial resistance between SE and the active material, leading to the enhanced rate capability of ASSLIBs. Meanwhile, organic liquid electrolytes easily permeate porous composite electrodes and provide good electrolyte/electrode interfaces in conventional LIBs; however, SE and active material particles in ASSLIB form point-to-point contact interfaces. Hence, intermittent electron and ion conductive networks in an ASSLIB account for low utilization of the active material and significant capacity loss.15–17

Research with various spectroscopic methods and mathematical-model simulations has been conducted to understand the distribution of the depth of discharge (DOD) for each active material particle in composite electrodes of LIBs with a liquid electrolyte and provided useful findings to improve performance by tuning parameters such as porosity, thickness, and particle size;18–22 nevertheless, there are a limited number of
In this paper, we demonstrate a simple technique with a novel microband-array electrode (MBAE) to evaluate the distribution of the DOD in a composite positive electrode for ASSLIBs. For this purpose, a triple-microband electrode, which consists of three individually addressable parallel electrodes, each 2.5 mm wide, 5 µm thick, and separated 50 µm from each other, was embedded in the composite positive electrode of the ASSLIB, and open-circuit potentials (OCPs) after charge/discharge tests were measured at three different depths from a current collector with the microband electrodes to discuss the inhomogeneity of the progress of DOD. DOD distribution in composite electrodes becomes rapidly homogeneous because of the migration of Li ions after the charge/discharge process. Our techniques have an advantage for the rapid measurement compared with spectroscopy with synchrotron radiation; therefore, we successfully detected the reaction distribution in the composite electrode, which becomes rapidly homogeneous in several minutes. Depth-directional OCP distribution curves for the composite positive electrode with different ionic and electronic conductivities are investigated to figure out how those parameters influence reaction distribution in the composite positive electrode. Thus, the current method will accelerate further development of ASSLIBs and provide a guideline for tuning the composite electrode parameters.

## RESULTS AND DISCUSSION

Figure 1A shows a schematic image of a cross-sectional view of the MBAE. Microband electrodes were in contact with the composite electrode with 200 µm × 2.5 mm size rectangular area. Figure 1B shows a SEM image of the cross-sectional view of the MBAE embedded in the composite positive electrode. The thickness of the pristine Kapton film was 50 µm; however, the Ni foils were aligned at regular intervals of 77 µm, the total thickness of the MBAE was 230 µm because the cross section of the positive electrode expanded during the cutting procedure, and Ni foils separated from the Kapton films. Figure S1 shows the SEM image of the cross section of the composite electrode, and its thickness was 300 µm.

Electronic (σ_e) and ionic (σ_i) conductivities of NMC-50, NMC-60, NMC-75, and NMC-80 were measured by the AC impedance method in Figure S2. Conductivities determined by a DC polarization method and AC impedance method were summarized in Table S1 and show almost the same values. σ_e and σ_i values of NMC-50, NMC-60, NMC-75, and NMC-80 determined by the DC polarization method were indicated in Figure 2. NMC-50 showed the highest ionic conductivity (8.3 × 10^{-5} S cm^{-1}) and the lowest electronic conductivity (2.8 × 10^{-6} S cm^{-1}) because of the largest amount of SE; on the other hand, NMC-80 showed the poorest ionic conductivity (3.4 × 10^{-6} S cm^{-1}) and relatively high electronic conductivity (1.4 × 10^{-5} S cm^{-1}) owing to the lowest amount of SE. These features were in good agreement with the result reported by Siroma et al.16

Figure S2 shows the potential changes of the current collector and the microband electrodes in the batteries with each NMC-50, NMC-60, NMC-75, and NMC-80 during the charge/discharge cycle. Each microband electrode had different potentials at the start of the first charging and converged into the same potential at the end of the first charging. The electrode potential of the microband electrode was started at the same potential during the first discharging, while it was distributed at the end of discharge. This tendency of the potential distribution in the composite electrode reflected several differences accompanying the balance of the ionic/electronic conductivity of the composite electrode. However, the rapid change of the electrode potential around the end of discharging makes it difficult to observe the constant trend of the microband electrode potential. Therefore, we tried to observe the trend of microband electrode potential after the charging and discharging. Figure S3 shows the OCP change after the end of charge/discharge in the cell with NMC-50. The OCP immediately after the discharging was undergoing significant changes. Therefore, we had to set waiting time for
measurement; however, active materials are electrically connected to each other, and OCP becomes homogeneous after a long time. We decided to take the OCP with one minute waiting time because it was long enough to take saturated OCP and rapid enough to take OCP before becoming homogeneous.

Figure 3A,B shows depth profiles of potential after charging and discharging for NMC-50, NMC-60, NMC-75, and NMC-80, respectively. All potentials are given against the potential of the current collector. The depth profile of potential after charging was even with the four composite positive electrodes, indicating that in each composite electrode, the whole active material was equally charged because the electric conductivity of NMC increased with the degree of charge. On the other hand, the depth profiles of potential after discharging were significantly different from those after charging (Figure 3B). The potential significantly changed with an increase in the distance from the current collector in the composite electrode; moreover, the depth profile was strongly dependent on the NMC content of the composite electrode. For the NMC-50 and NMC-60 electrodes with a higher ionic conductivity, the potential rose as the distance from the current collector increased, whereas for the NMC-80 electrode with a lower ionic conductivity, it decreased. Such different trends of depth profiles after discharging can be caused by local variation of DOD in the composite electrodes. For the NMC-50 and NMC-60 electrodes with a lower electronic conductivity, the supply of electrons from the current collector to the NMC bulk in the composite electrode becomes a bottleneck in discharging, and consequently, the active material near the current collector is discharged deeper than that near the SE layer. On the other hand, for the NMC-80 electrode with a lower ionic conductivity, the supply of Li\(^+\) ions to the current collector from the SE layer becomes a rate-limiting process of discharging, and consequently, the active material around the SE layer is discharged deeper than that near the current collector. Moreover, the depth profile of the potential for the NMC-75 electrode was almost flat. This can be also explained by the same mechanism as mentioned above. For the NMC-75 electrode, the electrons and Li\(^+\) ions can be supplied at a similar rate because electronic and ionic conductivities (\(\sigma_e 1.5 \times 10^{-5} \text{ S cm}^{-1}; \sigma_i 9.5 \times 10^{-6} \text{ S cm}^{-1}\)) are nearly equal, and consequently, the whole active material in the composite electrode is equally utilized.

The balance of ionic and electronic conductivity is also the key factor for the discharging capacity of ASSLIBs. Figure 3C shows the discharging capacity for the first discharging of the cells with NMC-50, NMC-60, NMC-75, and NMC-80. The discharge capacity decreased with an increase in the NMC content because the utilization of NMC is strongly influenced by the contact area of the NMC and SE; however, NMC-75 showed an exceptionally large discharge capacity because it has balanced ionic and electric conductivities. Figure 3D shows the discharging capacity calculated with the weight of the positive electrode, and NMC-75 showed the largest discharging capacity because of its high NMC content and utilization. 

The same phenomena in the case of porous electrodes in liquid electrolytes have been reported.\(^{21-25}\) Therefore, it is concluded that the rate-limiting process during the discharge process was strongly influenced by the balance of ionic and electronic conductivities of composite electrodes. Thickness (300 \(\mu\)m) of each composite electrode used in this study is larger than that of conventional positive electrodes for LIBs whose thickness is ca. 100 \(\mu\)m. The thickness of the composite electrode is important to improve the energy density of an ASSLIB cell. The current MBAE technique to give a depth profile of DOD has revealed the possibility for the use of a 300 \(\mu\)m thick electrode, which has balanced ionic and electronic conductivities, for the high energy density ASSLIB cell.

### EXPERIMENTAL SECTION

A LiPS\(_4\) glass solid electrolyte was prepared from Li\(_2\)S (99.98%, Sigma-Aldrich) and P\(_2\)S\(_5\) (92%, Kanto Chemical) powders by a mechanochemical method. The mixture of the starting materials and 400 numbers of ZrO\(_2\) beads with a size of 4 mm were put into a ZrO\(_2\) pot under an Ar atmosphere, and the mechanical milling was carried out at a rotational speed of 560 rpm for 12 h.

Li\(_2\)SO\(_4\)-coated Li\(_{1-x}\)Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) (NMC) particles whose mean size is ca. 15 \(\mu\)m were used as an active material for the composite positive electrode. Composite electrodes with different weight ratios of NMC to SE were prepared by mixing them on a mortar and pelleting to form a 10 mm diameter coin structure by pressing 405 MPa for 5 min in a polycarbonate tube using a pair of stainless-steel sticks. The resultant composite electrodes were named as NMC-50 (NMC/SE = 50:50), NMC-60 (NMC/SE = 60:40), NMC-75 (NMC/SE = 75:25), and NMC-80 (NMC/SE = 80:20). An ion-blocking cell for the measurement of electron conductivity was prepared by sandwiching NMC-50, NMC-60, NMC-75, or NMC-80 between two stainless-steel (SUS) rod current collectors. An electron-blocking cell for the measurement of ion conductivity was prepared by sandwiching NMC-50, NMC-60, NMC-75, or NMC-80 with SE pellets by pressing SE powder under 405 MPa for 5 min in a polycarbonate tube using a pair of stainless-steel sticks; after that, Li metal was attached to the surface of both SE pellets, and finally, the electron-blocking cell was sandwiched with SUS rod current collectors. Electronic and ionic conductivities were estimated by measuring the average value of the current.
for a DC polarization of 10 mV for 10 s. AC impedance measurement for the detection of electronic and ionic conductivity was investigated with the method using a transmission-line model according to Siroma et al.\textsuperscript{16}

An MBAE consists of three Ni foils (50 mm $\times$ 4 mm, thickness of 5 $\mu$m, Nilaco) and four Kapton films (thickness of 50 $\mu$m, Nilaco), which are alternately stacked. Polyethylene films were inserted between Ni foils and Kapton films and used for sticking them by heating on a hot plate at 220 °C. MBAE was glued with insulating epoxy resin to the stainless-steel rod, which works as a current collector because MBAE is electrically independent with electrochemical measurement devices. Distance between Ni foil electrodes was measured by scanning electron microscopy (SEM; VE-9800, KEYENCE) after the pelleting procedure mentioned below.

The mixtures of NMC and SE powders with different weight ratios as the composite electrode material were put into a polycarbonate cylinder. The amount of the mixtures was varied from ca. 40 to 80 mg to keep the thickness of the electrode at ca. 300 $\mu$m. The mixtures were pressed under 20 MPa with a pair of SUS rods, one of which was glued to the MBAE on the face in contact for the mixture; therefore, the MBAE was embedded into the composite electrode. One of the SUS rods, which does not have the MBAE, was temporally removed, and the whole cell was pressed again under 405 MPa. After that, an In foil was attached to the SE to employ as a negative electrode. All operations were carried out in an Ar-filled glovebox.

Charge–discharge testing at 78.5 $\mu$A (0.1 mA cm$^{-2}$) was carried out with the galvanostatic charge–discharge unit (HJ1001 SD8, Hokuto Denko) in a voltage range of 1.9–3.8 V at room temperature. The potentials at three Ni foil electrodes (Ni1, Ni2, and Ni3) with different depths and the current collector of the composite positive electrode were measured at 1 min after the end of charging or discharging with a potential data logger (GL240, Graphtec) to obtain potential profiles in the depth direction of the composite electrode.

### ASSOCIATED CONTENT

- Supporting Information
- Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00949.

- SEM image of the cross section of the composite electrode, the charge/discharge curves, and Cottrell plots (PDF)

### AUTHOR INFORMATION

#### Corresponding Author

Masanobu Chiku — Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan; orcid.org/0000-0002-2156-1785; Email: chiku@chem.osakafu-u.ac.jp

#### Authors

Keiichiro Ota — Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

Eiji Higuchi — Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The research was financially supported by the Japan Science and Technology Agency (JST), Advanced Low Carbon Technology Research and Development Program (ALCA), and Specially Promoted Research for Innovative Next Generation Batteries (SPRING) Project, Grant Number JPMJAL1301, Japan.

### REFERENCES

1. Tollefsen, J. C. Industry: Charging up the future. Nature 2008, 456, 436–440.
2. Lu, J.; Chen, Z.; Ma, Z.; Pan, F.; Curtiss, L. A.; Amine, K. The role of nanotechnology in the development of battery materials for electric vehicles. Nat. Nanotechnol. 2016, 11, 1031–1038.
3. Armand, M.; Tarascon, J.-M. Building better batteries. Nature 2008, 451, 652–657.
4. Nishi, Y. Lithium ion secondary batteries: past 10 years and the future. J. Power Sources 2001, 100, 101–106.
5. Scrosati, B. Challenge of portable power. Nature 1995, 373, 557–558.
6. Ozawa, K. Lithium-ion rechargeable batteries with LiCoO$_2$ and carbon electrodes: the LiCoO$_2$/C system. Solid State Ionics 1994, 69, 212–221.
7. Goodenough, J. B.; Kim, Y. Challenges for rechargeable Li batteries. Chem. Mater. 2010, 22, 587–603.
8. Smith, K.; Wang, C.-Y. Power and thermal characterization of a lithium-ion battery pack for hybrid-electric vehicles. J. Power Sources 2006, 160, 662–673.
9. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. Energy Environ. Sci. 2011, 4, 3243–3262.
10. Lu, L.; Han, X.; Li, J.; Hua, J.; Ouyang, M. A review on the key issues for lithium-ion battery management in electric vehicles. J. Power Sources 2013, 226, 272–288.
11. Khaligh, A.; Li, Z. Battery, Ultracapacitor, Fuel Cell, and Hybrid Energy Storage System for Electric, Fuel Cell, and Plug-In Hybrid Electric Vehicles: State of the Art. IEEE Trans. Veh. Technol. 2010, 59, 2806–2814.
12. Smith, K.; Wang, C.-Y. Solid-state diffusion limitations on pulse operation of a lithium ion cell for hybrid electric vehicles. J. Power Sources 2006, 161, 628–639.
13. Takada, K.; Aotani, N.; Iwamoto, K.; Kondo, S. Solid state lithium battery with oxysulfide glass. Solid State Ionics 1996, 86-88, 877–882.
14. Sumita, M.; Tanaka, Y.; Ikeda, M.; Ohno, T. Charged and Discharged States of Cathode/Sulfide Electrolyte Interfaces in All-Solid-State Lithium Ion Batteries. J. Phys. Chem. C 2016, 120, 13332–13339.
15. Machida, N.; Maeda, H.; Peng, H.; Shigematsu, T. All-Solid-State Lithium Battery with $\text{LiCoO}_2$/$\text{NiS}_2$O$_5$ Fine Powder as Cathode Materials with an Amorphous Sulfide Electrolyte. J. Electrochem. Soc. 2002, 149, A688–A693.
16. Siroma, Z.; Sato, T.; Takeuchi, T.; Nagai, R.; Ota, A.; Ioroi, T. AC impedance analysis of ionic and electronic conductivities in electrode mixture layers for an all-solid-state lithium-ion battery. J. Power Sources 2016, 316, 215–223.
(17) Doyle, M.; Fuller, T. F.; Newman, J. Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell. J. Electrochem. Soc. 1993, 140, 1526–1533.
(18) Wang, M.; Li, J.; He, X.; Wu, H.; Wan, C. The effect of local current density on electrode design for lithium-ion batteries. J. Power Sources 2012, 207, 127–133.
(19) Zhao, R.; Liu, J.; Gu, J. The effects of electrode thickness on the electrochemical and thermal characteristics of lithium ion battery. Appl. Energy 2015, 139, 220–229.
(20) Smith, K. A.; Rahn, C. D.; Wang, C. Y. Control oriented 1D electrochemical model of lithium ion battery. Energy Convers. Manage. 2007, 48, 2565–2578.
(21) Orisaka, Y.; Gogyo, Y.; Yamashige, H.; Katayama, M.; Chen, K.; Mori, T.; Yamamoto, K.; Masese, T.; Inada, Y.; Ohta, T.; Siroma, Z.; Kato, S.; Kinoshita, H.; Arai, H.; Ogumi, Z.; Uchimoto, Y. Ionic Conduction in Lithium Ion Battery Composite Electrode Governs Cross-sectional Reaction Distribution. Sci. Rep. 2016, 6, 26382.
(22) Kitada, K.; Maruyama, H.; Fukuda, K.; Arai, H.; Uchimoto, Y.; Ogumi, Z.; Matsubara, E. Factors determining the packing-limitation of active materials in the composite electrode of lithium-ion batteries. J. Power Sources 2016, 301, 11–17.
(23) Chen, K.; Shinjo, S.; Sakuda, A.; Yamamoto, K.; Uchiyama, T.; Kuratani, K.; Takeuchi, T.; Orikasa, Y.; Hayashi, A.; Tatsumisago, M.; Kimura, Y.; Nakamura, T.; Amezawa, K.; Uchimoto, Y. Morphological Effect on Reaction Distribution Influenced by Binder Materials in Composite Electrodes for Sheet-type All-Solid-State Lithium-Ion Batteries with the Sulfide-based Solid Electrolyte. J. Phys. Chem. C 2019, 123, 3292–3298.
(24) Murayama, H.; Kitada, K.; Fukuda, K.; Mitsui, A.; Ohara, K.; Arai, H.; Uchimoto, Y.; Ogumi, Z.; Matsubara, E. Spectroscopic X-ray Diffraction for Microfocus Inspection of Li-ion Batteries. J. Phys. Chem. C 2014, 118, 20750–20755.
(25) Strobridge, F. C.; Orvananos, B.; Croft, M.; Yu, H.-C.; Robert, R.; Liu, H.; Zhong, Z.; Connolley, T.; Drakopoulos, M.; Thornton, K.; Grey, C. P. Mapping the Inhomogeneous Electrochemical Reaction Through Porous LiFePO4-Electrodes in a Standard Coin Cell Battery. Chem. Mater. 2015, 27, 2374–2386.