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To cite this article: Norihiro Togasaki et al 2023 J. Electrochem. Soc. 170 050519

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# Utilization Ratio of Active Materials in All-Solid-State Batteries Examined Using Electrochemical Impedance Analysis with the Transmission Line Model

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In all-solid-state batteries (ASSB), increasing the thickness of electrodes is essential for increasing the energy density. However, this limits the C-rate performance, particularly for electrodes with a large volume fraction of active materials (AMs), transport of ions in the electrode is hindered, leading to poor utilization of AMs in ASSBs. To accelerate the development of ASSBs, it is highly desirable to develop analytical methods for understanding the utilization of AMs in thick electrodes. In this paper, we propose a novel impedance analysis method using the transmission line model (TLM) for estimating the utilization of AMs in an electrode in terms of effective electrode thickness. In the TLM model, electrode thickness is treated as a variable instead of a fixed parameter in the conventional sequence. Hence, the modified C-rate performance considering the TLM-calculated thickness reflects the effective electrode thickness, suggesting the calculated electrode thickness reflects the effective electrode thickness. This indicates effective utilization of AMs for electrochemical reactions. We also demonstrate the versatility of this method by using different electrode specifications.

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Manuscript submitted March 8, 2023; revised manuscript received April 26, 2023. Published May 16, 2023.

Supplementary material for this article is available online

All-solid-state batteries (ASSB) incorporating inorganic solid electrolytes (SE) are one of the most promising types of battery because of their high safety without the use of flammable liquid electrolytes (LE).<sup>1–4</sup> While many efforts have been made to develop ASSBs, there are still some hurdles that need to be overcome before practical application.

One of the critical issues is the trade-off between energy density and power density, called C-rate performance. To facilitate the mass transport of Li<sup>+</sup> ions in the electrode, in ASSBs, active materials (AM) are typically mixed with SEs to form composite electrodes, whereas in liquid-based batteries, the LE easily infiltrates the electrode and provides a good liquid/solid interface for electrochemical reactions. Theoretically, a high volume fraction of AM in the composite electrode contributes to increased cell energy density; however, it limits the ionic conductivity in the electrode, owing to the small volume fraction of SEs,<sup>5</sup> Tan et al. reported that reducing the volume fraction of SE in the composite electrode reduces the utilization of AMs, owing to the poor percolation of SE throughout the electrode.<sup>6</sup> The low utilization of AMs leads to a significant deterioration in C-rate performance because the AMs, which are electrochemically active in the electrode, are exposed to a current density that is higher than intended.<sup>7</sup>

Alternatively, increasing the thickness of electrodes, which minimizes the relative volume of inactive components (e.g., current collector, tab, and cell exterior) in the cell is another way to increase cell energy density, but it also limits the C-rate performance. Kato et al. achieved a gravimetric energy density of 180 Wh kg<sup>-1</sup> and a volumetric energy density of 450 Wh l<sup>-1</sup> using a 600  $\mu$ m-thick electrode with an AM volume fraction of ~40 vol%.<sup>8</sup> In such thick electrodes, the ionic conductivity of the composite electrode plays a key role in determining the C-rate performance. Indeed, by exploiting the high ionic conductivity of Li<sub>10</sub>GP<sub>2</sub>S<sub>12</sub> (bulk ionic conductivity is 3.2 mS cm<sup>-1</sup>) as the composite agent in the electrode, the C-rate performance is demonstrated to be considerably

greater than that using  $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$  (bulk ionic conductivity is 0.28 mS cm<sup>-1</sup>). A similar phenomenon indicating the degradation of C-rate performance with the use of thick electrodes (~258  $\mu$ m) has also been observed in liquid-based batteries.<sup>9</sup>

To evaluate the C-rate performance of lithium-ion batteries (LIB), galvanostatic rate capability tests (GRCT) are typically conducted. In GRCTs, battery cells are charged at a low C-rate (e. g., 0.1 C) under a constant current-constant voltage (CC - CV) protocol followed by discharging at various C-rates under the CC protocol until the voltage reaches the low cutoff voltage. As this sequence is typically repeated several times to ensure statistical accuracy, it takes several weeks or over a month, which is a major drawback of this test.<sup>7,10</sup> To decrease the measurement time, chronoamperometry was developed by Heubner et al.<sup>10</sup> In this method, the cells are charged under the CC - CV protocol as in GRCTs, but the cells are discharged under constant voltage. The CV on discharging is set to a low cutoff voltage for the battery cell and the rate capability is estimated by analyzing the current transition during discharge. Yanev et al. successfully evaluated the C-rate characteristics of ASSBs by using this sequence, leading to a reduction in measurement time to less than one-tenth that of the GRCT sequence.<sup>7</sup> Nevertheless, faster analytical methods for evaluating the rate capability are still highly desired in order to accelerate the development of ASSBs.

Electrochemical impedance spectroscopy (EIS), which can divide complicated electrochemical reactions into fundamental electrochemical processes based on their characteristic time constants, is widely used as an analytical tool for LIBs.<sup>11,12</sup> In our previous studies, we have successfully predicted the steep capacity decay of LIBs caused by overcharge<sup>13,14</sup> or by overdischarge<sup>15</sup> via the tracking of the impedance signals of each fundamental process during cycling. EIS analysis also provides beneficial information for diagnosing the state-of-charge misalignment of modules.<sup>16</sup> In these studies, we analyzed the impedance spectra using Randles-type equivalent circuit because the commercialized LIBs that we used showed homogeneous electrochemical reactions throughout the electrode ( $\cong 60 \,\mu$ m thickness) with LE systems. On the other hand, if reactions in the electrode are inhomogeneous, the obtained



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Figure 1. Charge curves of ASSB half-cells with cathode thicknesses of (a) 30  $\mu$ m, (b) 60  $\mu$ m, and (c) 90  $\mu$ m for C-rates of 0.1–6.0 C. (d) The C-rate capability results.

impedance spectra should be analyzed by transmission line models (TLM) in order to avoid misinterpretation for the results.<sup>17</sup> Unlike Randles-type equivalent circuit, TLMs which incorporates the normalized resistances of Li ion and electron transport through in the electrode thickness direction provides some useful information regarding the reaction distribution in the depth direction of electrodes in LIBs.<sup>11,12,17,18</sup> Recently, EIS analysis with TLM has been extended to ASSBs which incorporate composite electrodes.<sup>19–21</sup> Because the C-rate capability of ASSBs is strongly related to the utilization of AMs in the composite electrode, it is crucial to understand the effective utilization of AMs (or effective electrode thickness) in electrochemical reactions in order to deduce C-rate characteristics.

In this study, we propose a novel impedance analysis using a TLM to estimate the effective electrode thickness for electrochemical reactions and to deduce the C-rate performance of ASSBs. While the electrode thickness is generally treated as a fixed value in a TLM, we treat it as a variable parameter in this study. As a result, the electrode thickness calculated by the TLM is confirmed to reflect the utilization of AMs in the composite electrode, which corresponds to the C-rate capability test results. We also demonstrate the versatility of this method by using different electrode specifications.

### Experimental

To understand the effect of cathode thickness on the C-rate performance, we prepared three types of ASSB half-cells with different cathode thicknesses:  $30 \,\mu\text{m}$  (9.4 mg cm<sup>-2</sup>),  $60 \,\mu\text{m}$  (19.4 mg cm<sup>-2</sup>), and  $90 \,\mu\text{m}$  (29.6 mg cm<sup>-2</sup>). Figure S1 shows cross-sectional scanning electron microscopy (SEM) images of these

electrodes. The cathode was composed of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (NCM523, Sumitomo Metal Mining), an argyrodite-structured SE (Mitsui Mining & Smelting), and additives (such as a binder and an electrical conductive agent) at a volume ratio of 65:30:5. The surface of the NCM523 particles was coated with an ~2 nm-thick LiNbO<sub>3</sub>, which reduced the space charge layer and inhibited the chemical reactions occurring between NCM523 and SE.<sup>22</sup> The Li-In alloy, which was prepared by stacking three layers of In foil (300  $\mu$ m)/Li foil (200  $\mu$ m)/In foil (100  $\mu$ m), was used as an anode material. The cathode and anode were separated by the argyrodite-structured SE (~600  $\mu$ m thickness). More details of material specifications are mentioned elsewhere.<sup>23–25</sup> In this manuscript, the description of cell voltage is revised from "V vs In-Li" to "V vs Li/Li<sup>+</sup>" by considering the flat potential plateau at 0.62 V vs Li/Li<sup>+</sup> of the Li-In alloy.<sup>26,27</sup>

After assembling the ASSB half-cells, we carried out charge –discharge tests for three cycles within the voltage range of 3.0 - 4.4 V using the CC – CV protocol; the charge and discharge load currents are 0.1 C with a termination current of 0.01 C. We define the current at 1 C-rate from the result of the charging capacity obtained at the initial cycle by considering the AM loading amount of the cathode and its specific capacity (204 mAh g<sup>-1</sup>). The cathode capacities of the ASSB half-cells with cathode thicknesses of  $30 \ \mu\text{m}$ ,  $60 \ \mu\text{m}$ , and  $90 \ \mu\text{m}$  within the voltage range of  $3.0 \ V-4.4 \ V$  (vs Li/Li<sup>+</sup>) are 1.24 mAh, 2.58 mAh, and 3.93 mAh, respectively. After cycling, the C-rate capability tests for charging within the voltage range of  $3.0 - 4.4 \ V$  were conducted under the CC protocol at a C-rate of  $0.1 - 6.0 \ C$ . Before the test, the half-cells were discharged to  $3.0 \ V$  using at the CC – CV protocol (CC =  $0.1 \ C \ CV^{-1} = 0.01 \ C$ ). All the cycling tests in this study were performed at 25 °C.



**Figure 2.** Nyquist plots of the ASSB half-cells with cathode thicknesses of (a) 30  $\mu$ m, (b) 60  $\mu$ m, and (c) 90  $\mu$ m at DoD 0% (4.4 V Li/Li<sup>+</sup>). Impedance was measured within the frequency range of 100 kHz to 1 mHz under an atmospheric temperature of 25 °C.

Impedance spectra of the battery cells were measured using a potentiostat system (VMP-300, BioLogic) at the open-circuit voltage, with an AC signal of 10 mV (zero to peak) in a frequency range of 100 kHz to 1 mHz at -5 °C, 5 °C, 15 °C, and 25 °C. The cell voltage for the impedance measurements was set to 4.4 V with a 0% depth of discharge (DoD). Data fitting was performed using the Microsoft Excel Solver package until the minimum error was obtained. This was achieved by minimizing the sum of all differences between the acquired experimental complex impedance data and the calculated impedances from the equivalent circuit using the fitted parameters at each frequency; this method was similar to that detailed in our previous studies.<sup>13–16</sup> To identify the frequency response of each fundamental electrochemical process, distribution of relaxation times (DRT) analysis was performed on the obtained impedance spectra using commercial software (Z-Assist, TOYO Corporation).

#### **Results and Discussion**

Figures 1a-1c show the voltage curves during charging at C-rates of 0.1 - 6.0 C using the ASSB half-cells with varying cathode thicknesses of (a)  $30 \,\mu\text{m}$ , (b)  $60 \,\mu\text{m}$ , and (c)  $90 \,\mu\text{m}$ . Regardless of the cathode thickness, at a low C-rate of 0.1 C, the charging capacity is  $\sim 180$  mAh g<sup>-1</sup>, which is close to the theoretical capacity of NCM523 between 3.0 V and 4.4 V.<sup>28</sup> With the increase in the C-rate, the capacity of each ASSB half-cell decreases in a similar manner, and the capacity at each C-rate is quite different; the thicker the cathode in the ASSB, the lower the charging capacity. Generally, with the increase in the C-rate, the mass and chargetransport limitations increase, resulting in a high overpotential and reaching a cut-off voltage before attaining a theoretical capacity.<sup>7</sup> In this study, we adopted a volume ratio of SE in the cathode of 30 vol % for the evaluation of a cathode with a high energy density. The SE volume ratio herein is considerably less than the typically reported value of  $\geq 50 \text{ vol}\%$ , <sup>5,29–33</sup> leading to a poor ionic conductivity of 0.06 mS cm<sup>-1</sup> for the cathode (Fig. S2), which is much lower than that of the bulk ( $\sim 2 \text{ mS cm}^{-1}$ ).<sup>34</sup> We speculate that such severe mass- and charge-transport limitations may occur in our cathodes as the cathode thickness increases.

Internal resistance in the cell affects the C-rate characteristics; hence, we performed EIS measurements on ASSB half-cells. Figure 2 shows the Nyquist plots of the ASSB half-cells with different cathode thicknesses. In all cases, two semi-circles are observed with a slope of 45° in the high-frequency region (>5 kHz). Semicircles obtained for the cathode thickness of 30  $\mu$ m are relatively larger than those obtained for cathode thicknesses of 60  $\mu$ m and 90  $\mu$ m. Since all three ASSB half-cells consist of identical cathodes and anodes except for the cathode thickness, similar electrochemical reactions at each frequency response should be observed. Therefore, the observed difference in the impedance is thought to be due to the difference in the reaction volume of the cathode; the reaction volume of the ASSB with a cathode thickness of 30  $\mu$ m or 90  $\mu$ m, resulting in a higher impedance response per unit area ( $\Omega$  cm<sup>2</sup>).

In contrast, this hypothesis is not applicable to the impedance spectra of ASSBs with a cathode thickness between 60  $\mu$ m and 90  $\mu$ m; the semicircles of these two ASSBs are mostly identical, while the cathode thickness is different. The identical sizes of the semicircles indicate that similar amounts of cathode AM contribute to the charge-transfer reactions. Therefore, this phenomenon implies that the utilization ratio of AM for electrochemical reactions with the 90- $\mu$ m cathode thickness is less than that for the reactions with the 60- $\mu$ m cathode thickness. Further discussion is provided in the following section.

In several cases, the fundamental electrochemical processes in the lithium-ion cells are observed in a similar frequency domain, which are overlapped with each other at around room temperature:<sup>14,35,36</sup> hence, there is a potential risk of misinterpretation of the impedance behavior of each process. According to previous studies investigating the impedance of ASSB half-cells anode/SE/layered with Li-In transition-oxide cathode systems,<sup>24,25,29,37</sup> the ASSB half-cells in this study should exhibit at least three fundamental electrochemical processes, namely the charge-transfer reactions of Li-In and NCM523 and the reaction through the LiNbO<sub>3</sub> layer on NCM523. In order to separate the fundamental electrochemical processes in the Nyquist plots, impedance measurements at different atmospheric temperatures are reported to be effective for liquid-based batteries.<sup>14</sup> This separation is due to the difference in activation energies of each fundamental process. However, when the activation energies of each fundamental process are mostly identical, this approach does not work well for impedance analysis. That is, the number of semicircles does not change even when the impedance measurement is conducted



**Figure 3.** DRTs of the ASSB half-cells with cathode thicknesses of (a) 30  $\mu$ m, (b) 60  $\mu$ m, and (c) 90  $\mu$ m at DoD 0% (4.4 V Li/Li<sup>+</sup>) under an atmospheric temperature of 25 °C. The analyzed frequency range is 4.3 kHz to 0.6 Hz, corresponding to the appearance of capacitive semicircles, in order to identify the fundamental electrochemical processes in the cell.

at different temperatures in the current ASSB half-cell systems (Fig. S3a).

DRT analysis, which utilizes the relationship between the impedance spectrum and the distribution of relaxation times, is a powerful tool for separating complex impedance spectra.<sup>38–41</sup> Pang et al. successfully separated the fundamental processes in the ASSB system of Li/LIPON/LiCoO<sub>2</sub>.<sup>42</sup> Figure 3 shows the DRTs analyzed via impedance spectra obtained from ASSBs with different cathode thicknesses. The results clearly reveal three fundamental processes in each ASSB half-cell and similar apex frequencies regardless of the cathode thickness; the apex frequencies in the low-, middle-, and high-frequency regions are  $\sim 10$  Hz,  $\sim 100$  Hz, and  $\sim 1$  kHz, respectively. The fundamental process in the low-frequency region  $(\sim 10 \text{ Hz})$  may be attributed to the reaction of the Li-In anode because it typically appears at around a few hertz.<sup>29,37,43</sup> The impedance spectra from a symmetrical cell of the Li-In alloy also support this presumption (Fig. S4). The other two fundamental processes in the middle- and high-frequency regions may be related to the reactions on the cathode. From the impedance analysis using a

similar cathode AM of NCM523 with a LiNbO<sub>3</sub> layer reported by Morino et al.,<sup>24,25</sup> the fundamental processes in the middle-( $\sim$ 100 Hz) and high-frequency regions ( $\sim$ 1 kHz) are attributed to the charge-transfer reactions of NCM523 and reactions related to the LiNbO<sub>3</sub> layer, both of which appear at approximately a dozen hertz and kilohertz, respectively. The identification of each fundamental electrochemical process was also discussed and verified by the results of activation energy shown in Fig. S3b.

Based on the apex frequencies obtained from DRT analysis, we performed data fitting of the Nyquist plots in Fig. 2. A slope of  $45^{\circ}$  in the high-frequency region (>5 kHz) is a typical behavior for the distribution of electrochemical reactions is in the depth direction of the electrode.<sup>11,18,19</sup> We analyzed the Nyquist plots using a TLM, which can express the reaction distribution of the electrode in the depth direction. Figure 4a shows the equivalent circuit used in this study. For electrochemical reactions in the ASSB half-cells, the equivalent circuit comprises three regions, corresponding to the anode of the Li-In alloy, the SE, and the cathode of LiNbO<sub>3</sub>-coated NCM523, which are connected in series. Because the distribution of

the reactions in the cathode should be in the depth direction, we applied a TLM for reactions regarding NCM523 and a LiNbO<sub>3</sub> layer. To fit the compressed semicircles in the Nyquist plot, a constant-phase element (CPE) is utilized to express the interfacial capacitance of each fundamental process. R corresponds to resistance;  $R_{Li-In}$ ,  $R_{SE}$ ,  $R_{NCM}$ , and  $R_{LiNbO3}$  represent the charge-transfer resistance of Li-In, ionic resistance of SE, charge-transfer resistance of NCM523, and film resistance of each fundamental electro-chemical process by the following equation:

$$\mathbf{C} = T^{1/p} \mathbf{R}^{(1-p)/p},$$

where T and p are the CPE constant and CPE exponent, respectively. R in the equation corresponds to resistance (R<sub>Li-In</sub> for anode, R<sub>NCM</sub> for NCM523 cathode, and  $R_{LiNbO3}$  for LiNbO<sub>3</sub> layer on the cathode), which are connected in parallel to CPE (CPE<sub>Li-In</sub> for anode, CPE<sub>NCM</sub> for NCM523 cathode, and CPE<sub>LiNbO3</sub> for LiNbO<sub>3</sub> layer on the cathode). Rion in the TLM region represents the ionic resistivity of the composite cathode. Theoretically, the Nyquist plot at high frequencies on the real axis shifts toward the right if the electron resistance of the cathode is significantly large when thick electrodes are used.<sup>19</sup> However, such impedance behavior is not observed in our half-cells as shown in Fig. 2. Therefore, we disregard the electron resistance of the cathode in this study. At the end of the equivalent circuit, an additional CPE<sub>Diff</sub> is utilized to represent the impedance of the diffusion area for fitting analysis (however, analysis of the diffusion area in the impedance spectra is beyond the scope of this study). For SE resistance, Gaberscek et al. reported non-active ions in the electrolyte should be taken into account in the equivalent circuit<sup>44–46</sup> because those represent larger transport number than Li ions<sup>47</sup> and significantly contribute to the ionic transport between the electrodes in the case of LIBs with LE. On the other hand, we adopted R<sub>SE</sub> as a single resistive element in this study on the basis of the premise the  $Li^+$  transport number of  $\cong 1$  in the ASSB systems as the similar manner in some literatures.<sup>8,21,4</sup>

Figures 4b-4i show the fitting results of each component in the equivalent circuit. For the impedance fitting, we employed two different methods. One is a typical method in which the parameters of electrode thickness and ionic resistivity ( $R_{ion}$ ) in the TLM model are fixed; we set the cathode thickness to 30  $\mu$ m, 60  $\mu$ m, and 90  $\mu$ m and the ionic resistivity to 16,666  $\Omega$  cm for data fitting. The other method involves the treatment of the parameters as variable parameters. Fitting results and their fitting errors plotted as a function of the input frequency signals are shown in Figs. S5a-i.

For the reaction of the Li-In anode, there is no significant difference between the fitting sequences. The apex frequency, charge-transfer resistance, and interfacial capacitance at each cathode thickness are similar in different fitting sequences, suggesting that the fitting results of the Li-In anode are not affected by the fitting sequence of the cathode. The corresponding values are calculated to be 5–15 Hz, 13–17  $\Omega$  cm<sup>2</sup>, and 0.8–2.4 mF cm<sup>-2</sup>, which are similar to those reported previously for reactions of the Li-In anode.<sup>29,37,43</sup>

A notable difference in the fitting sequence is observed in the cathode reactions. While the apex frequencies of the charge-transfer reaction of NCM and the reaction through the LiNbO<sub>3</sub> layer are identical (Figs. 4d and 4f), the resistances of  $R_{CT-NCM}$  and  $R_{f-LiNbO3}$  as a function of the cathode thickness are different (Figs. 4e and 4g). Overall, the charge-transfer resistance of NCM523 and the film resistance of LiNbO<sub>3</sub> decrease with the increasing cathode thickness. However, the charge-transfer resistance of NCM523 and the film resistance of LiNbO<sub>3</sub> are markedly different, particularly in the large cathode thickness region ( $\geq 60 \ \mu$ m); those values obtained by the fitting sequence, where the ionic conductivity of the cathode and the cathode thickness are treated as variable parameters are greater those obtained by the conventional fitting sequence. An opposite behavior is observed for the interfacial capacitances of  $C_{NCM}$  and  $C_{LiNbO3}$  (Figs. 4e and 4g). When the

ionic resistivity of the cathode and the cathode thickness are treated as variable parameters, the interfacial capacitances of  $C_{\rm NCM}$  and  $C_{\rm LiNbO3}$  become lower than those obtained by the conventional fitting sequence. These opposing behaviors of  $R_{\rm CT-NCM}$ ,  $C_{\rm NCM}$ ,  $R_{\rm f-LiNbO3}$ , and  $C_{\rm LiNbO3}$  account for the unchanged constant apex frequencies in the charge-transfer reaction of NCM and the reaction through the LiNbO<sub>3</sub> layer.

When ionic resistivity and cathode thickness are treated as variable parameters, these values are calculated by data fitting. Figures 4h and 4i show the fitting results for the calculated ionic conductivity of the cathode and cathode thickness. The ionic resistivity does not change from the experimental result shown in Fig. S2, which is a reasonable result because of its intrinsic property of the material. This suggests the ionic conductivity of the cathode doesn't affect the fitting results if it is treated as a variable parameter. A remarkable difference is observed for the cathode thickness: the calculated cathode thickness is much smaller than designed cathode thickness and the difference between the calculated thickness and designed thickness is observed to be higher when the designed cathode thickness is higher. The calculated thicknesses are 25.1  $\mu$ m, 32.3  $\mu$ m, and 34.8  $\mu$ m at the designed thicknesses of 30  $\mu$ m, 60  $\mu$ m, and 90  $\mu$ m, respectively. Interestingly, the calculated thickness values between the designed cathode thicknesses of 60  $\mu$ m and 90  $\mu$ m are almost identical, indicating that the resistance and interfacial capacitance of the cathode with a thickness of 60  $\mu$ m are similar to those with a thickness of 90  $\mu$ m, as shown in Figs. 4e and 4g. It is also observed that the charge-transfer resistance of NCM or film resistance of LiNbO3 decreases as increasing the calculated cathode thickness, vice versa for the interfacial capacitance of NCM or LiNbO3. (Fig. S6) Regardless of the fitting sequences, the fitting errors calculated using the equivalent circuit in Fig. 4a are typically less than 0.3% over the entire frequency range (Fig. S5g), however, fitting errors in the frequency range in between 10 kHz and 1 kHz with fixed parameters were larger than those with variable parameters (depicted with dotted square in Fig. S5g). In principle, the parameter of electrode thickness affects the length of a 45° slop in the high-frequency region of Nyquist plots, that is, the length of a  $45^{\circ}$  slop in the high-frequency region becomes larger as increasing electrode thickness.<sup>19,21</sup> Therefore, when the impedance fitting is conducted with the fixed parameter of electrode thickness, the fitted plots corresponding to the high-frequency region appear to be different from the experimental results, (see Figs. S5h and i) which may suggest that the impedance fitting with a variable parameter of electrode thickness provide reasonable fitting results. If the calculated thicknesses represent the active thickness of the cathode composite for electrochemical reactions, the AM of 83.7%  $(=25.1 \ \mu m/30 \ \mu m)$  for 30  $\mu m$ , 53.8%  $(=32.3 \ \mu m/60 \ \mu m)$  for 60  $\mu m$ , and 38.7% (=34.8  $\mu$ m/90  $\mu$ m) for 90  $\mu$ m in the cathode composite are electrochemically active, respectively.

In the TLM, the units of  $R_{NCM}$  and  $R_{LiNbO3}$  are [ $\Omega$  cm<sup>3</sup>], and the units of  $C_{NCM}$  and  $C_{LiNO3}$  are [F cm<sup>-3</sup>].<sup>19</sup> To obtain the resistance as in units of [ $\Omega$  cm<sup>2</sup>] and the capacitance in units of [F cm<sup>-2</sup>], the units of [ $\Omega$  cm<sup>3</sup>] should be divided by the cathode thickness, while the unit of [F cm<sup>-3</sup>] should be multiplied by the cathode thickness. Therefore, when the active cathode thickness for electrochemical reactions (or the utilization of AMs in the cathode) is less than the designed thicknesses of 30  $\mu$ m, 60  $\mu$ m, or 90  $\mu$ m (Fig. S1), the resultant resistance in [ $\Omega$  cm<sup>2</sup>] is greater than the results from the conventional fitting sequence, while the results shown in Figs. 4e and 4g.

As Fig. 1 shows, the C-rate performance of the ASSB half-cells deteriorates with increasing cathode thickness. In other words, the utilization ratio of the cathode AMs in the thick electrode is less than that in the thin electrode, even in the case of identical C-rates obtained by the C-rate capability test of the ASSB half-cells. If the utilization ratio of the cathode AMs is not considered in the C-rate capability test, the obtained data could be misinterpreted because AMs, which are electrochemically active in the electrode, are



Figure 4. (a) Equivalent circuit used to analyze the impedance spectra of ASSB half-cells with cathode thicknesses of 30  $\mu$ m, 60  $\mu$ m, and 90  $\mu$ m. R<sub>SE</sub>: resistance of the solid electrolyte; R<sub>Li-In</sub> and R<sub>NCM</sub>: charge-transfer resistances of the Li-In anode and NCM523 cathode, respectively; CPE<sub>Li-In</sub> and CPE<sub>NCM</sub>, constant-phase elements of the anode and cathode electrode surfaces, respectively; R<sub>LiNbO3</sub> and CPE<sub>LiNbO3</sub>, film resistance and constant-phase element of LiNbO<sub>3</sub>, respectively; Rion, ionic resistivity of the cathode. Fitting results of the apex frequencies for the reactions in (b) Li-In, (d) NCM, and (f) LiNbO3. The charge-transfer resistance and interfacial capacitance of (c) Li-In, (e) NCM, and film resistance of (g) LiNbO<sub>3</sub>. Fitting results of the (h) ionic resistivity of the cathode and (i) cathode thickness.

exposed to a current density that is higher than intended. Therefore, the C-rate should be defined based on the amount of cathode AMs which effectively function for electrochemical reactions. Based on

the results of the impedance fitting analysis for the calculated thickness, we defined the "effective C-rate" at the C-rate for ASSB half-cells according to the equation:



Figure 5. Modified C-rate performance of the ASSB half-cells with cathode thicknesses of 30 µm, 60 µm, and 90 µm.

Fable I.	Effective	C-rates	based o	on the	calculated	cathode	thickness	from	modified	TLM fitting	ζ.
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		C-rate [C]						
		0.1	0.2	0.5	1.0	2.0	3.0	4.0
Designed cathode thickness	gned cathode thickness Calculated cathode thickness Effective C							
30 µm	25.1 μm	0.12	0.24	0.60	1.20	2.39	3.59	4.79
$60 \ \mu m$	32.2 µm	0.19	0.37	0.93	1.86	3.71	5.57	7.42
90 µm	$34.8 \ \mu \mathrm{m}$	0.26	0.52	1.29	2.59	5.17	7.76	10.34

Effective C - rate[C] = C - rate [C] 
$$\times \frac{Designed \ thickness \ [\mu m]}{Calculated \ thickness \ [\mu m]}$$

where "C-rate" in the right side of the equation represents the value derived from the designed cathode thickness, that is, the "C-rate" is 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, 3.0 C, or 4.0 C. The obtained results are summarized in Table I. Since the calculated thicknesses are always smaller than the designed thicknesses, the greater value of "effective C-rate" compared to "C-rate" demonstrates a current density that is higher than intended.

Figure 5 shows the modified C-rate performances of the ASSB half-cells with different cathode thicknesses of 30  $\mu$ m, 60  $\mu$ m, and 90  $\mu$ m. Regardless of the designed cathode thickness, the effective C-rate performance of each ASSB half-cell exhibits identical behavior: the charge capacities at a low C-rate approach asymptotically to the theoretical value of ~190 mAh g<sup>-1</sup> at a low C-rate of  $\cong 0.1$  C in NCM523 systems, and two-stage capacity fading is observed before or after ~2 C. Significant drops in capacity from a certain C-rate have typically been reported in other ASSBs with different cathode AMs, i.e., lithium cobalt oxide, lithium nickel manganese cobalt oxide, lithium manganese oxide, and lithium nickel cobalt aluminum oxide.<sup>7,29</sup> Zhang et al. reported the inflection point in such two stage capacity fading shifts to be low C-rate as decreasing the volume fraction of SE in the cathode composite.<sup>29</sup>

an insufficient ionic paths around AM in the cathode composite may be a reason for the observed two capacity decay. If the entire AM in the cathode reacts uniformly at each cathode thickness, then the C-rate capability results should be identical regardless of the designed cathode thickness because the current density per unit volume in the cathode is identical regardless of the cathode thickness. However, the reality is quite different, as shown in Figs. 1a-1(c). The results in Fig. 5 clearly show that the C-rate performances for the ASSB halfcells with different designed cathode thicknesses are mostly identical to each other provided the modified C-rate is set by considering the electrode thickness calculated using TLM fitting. In summary, the cathode thickness calculated by the TLM fitting sequence with variable parameters illustrates the effective cathode thickness (or the effective utilization of the cathode AMs), which contributes to the electrochemical reactions. To confirm the versatility of this fitting sequence, we prepared an additional ASSB half-cell with a cathode thickness of 60  $\mu$ m; however, its impedance is different from that in the main manuscript (Fig. S7). This case also confirms that an identical C-rate capability is obtained even when the battery specification is different (Fig. S7d).

To accelerate the development of ASSBs, it is critically important to obtain quantitative information regarding the utilization ratio of the electrode-active material and subsequently conduct experimental modification. To this end, we established an innovative analytical sequence to understand the AM utilization ratio using the TLM by focusing on the fact that the impedance spectra do not change above a certain electrode thickness. The impedance signals which appear in the high-frequency region with a slope of 45° involve the information of electrode thickness.<sup>49,50</sup> This innovative analytical sequence using such a high-frequency region is considered to be a useful tool for rapid exploration of the C-rate performance of ASSBs. Further analysis in terms of using different cathode materials (i.e.  $LiCoO_2$ ) and solid electrolyte (i.e.  $Li_{10}GP_2S_{12}$ ) is ongoing in current research to confirm the versatility of the present impedance analytical method.

#### Conclusions

This study demonstrated for the first time the fitting results for a transmission line model (TLM) with electrode thickness as the variable parameter to estimate the effective electrode thickness for electrochemical reactions in all-solid-state batteries (ASSBs) cells. In the case of high volume fraction of AM in the cathode, the impedance spectra barely changed above a certain electrode thickness because the utilization ratio of AMs for electrochemical reactions decreases as electrode thickness increases. Since the trend of C-rate capability is unchanged under a predetermined electrode composition, the proposed fitting sequence facilitates exploration of the C-rate capability of ASSB; that is, when the calculated electrode thickness is close to the designed electrode thickness, a good C-rate capability of the cell is expected. We hope this innovative fitting sequence will contribute to the development of ASSB technology.

#### Acknowledgments

The authors express gratitude to Dr. Mikinari Shimada and Dr. Takuhiro Mivuki at the Consortium of Lithium-Ion Battery Technology and Evaluation Center (LIBTEC) for their fruitful discussions regarding impedance results. This study was supported by the "Development of Fundamental Technologies for All Solid State Battery applied to Electric Vehicles" project (SOLiD-EV, JPNP18003) commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

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