



AC impedance analysis of NCM523 composite electrodes in all-solid-state three electrode cells and their degradation behavior

Goro Fukunishi^a, Mayu Tabuchi^a, Atsunori Ikezawa^{a,b}, Takeyoshi Okajima^{a,b},
Fusao Kitamura^{a,b}, Kota Suzuki^b, Masaaki Hirayama^{a,b}, Ryoji Kanno^b, Hajime Arai^{a,b,*}

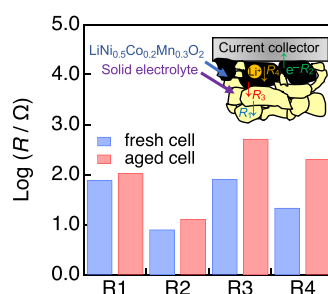
^a School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502, Japan

^b All-Solid-State Battery Center, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

HIGHLIGHTS

- AC impedance of NCM523 electrodes is analyzed with all-solid-state three-electrode cells.
- Several NCM523 impedance components are identified and assigned to elemental processes.
- Activation energies of these processes are evaluated.
- Cycling durability tests cause impedance increase particularly in charge transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical analysis offers useful information to understand the behavior of electrochemical systems including lithium-ion batteries and to take measures for their improvement. In this study, we report AC impedance analysis of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) composite electrodes in all-solid-state three-electrode cells using glass-ceramic $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$ (LPSE) or crystalline $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) electrolytes to evaluate the rate-limiting processes in NCM523 electrodes and their variations after the charge-discharge cycles. Besides the lithium-ion transfer resistance in the electrolyte layer (i), electron transfer resistance between NCM523 composite electrode and current collector (ii), charge transfer resistance between NCM523 and solid electrolyte (iii), component that has been unidentified (iv), and lithium-ion diffusion resistance in NCM523 particles as Warburg impedance (v) are observed. The activation energies of (iii) are relatively low compared to those in liquid electrolyte systems. After the charge-discharge cycle tests, the impedance of the NCM523 electrode using both LPSE and LPSCl electrolytes shows a significant increase in (iii). On the other hand, the LPSE system exhibits larger increase in (iv) and fine voids in NCM523 secondary particles more than those in the LPSCl system, showing that (iv) can be attributed to the charge transfer resistance between NCM523 primary particles.

* Corresponding author. School of Materials and Chemical Technology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502, Japan.
E-mail address: arai.h.af@m.titech.ac.jp (H. Arai).

1. Introduction

Lithium-ion batteries (LIBs) are the most widespread rechargeable batteries [1,2] because of their high reversibility (high coulombic efficiency) and long cycle life. LiCoO_2 [3,4], which has a layered rock salt structure and is an intercalation-type electrode, was first applied as a positive electrode material of LIBs owing to its high operating potential and cycling stability. However, the use of cobalt has been a problem because of its high cost. Subsequently, lithium nickel-cobalt-manganese oxides (NCM) have been developed [5,6] to increase the capacity and reduce the amount of cobalt use. Currently, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) is widely used as a positive electrode material.

Electrochemical impedance spectroscopy (EIS) has been applied to the study of NCM523 and other lithium-ion battery positive electrode materials [7–14]. EIS is a technique to quantitatively evaluate the rate-limiting processes of LIB electrode reactions that directly affect the charge-discharge characteristics. Previous studies have clarified that the dominant resistance in NCM523 electrodes in the liquid-type electrolytes is the charge transfer resistance at the electrolyte|active material interface [10], which mainly involves the solvation/desolvation process of lithium ions in conventional liquid-LIBs [11]. Other impedance components have also been clarified, such as the electronic resistance at the current collector|NCM electrode interface [12] and the Li diffusion in the NCM particles [13,14]. It has also been reported that the charge transfer resistance increases during the charge-discharge cycle tests [14,15]. Many analytical methods have been applied to investigate the physicochemical cause of the increased charge transfer resistance during cycle tests, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). These studies have suggested that the increase in the charge transfer impedance can be ascribed to the formation of a surface layer [11], elution of transition metals into the electrolyte [16,17], and particle cracking [18,19].

Recently, significant interests have emerged in all-solid-state lithium-ion batteries (ASS-LIBs) that are expected to have high power characteristics and high safety standards [20,21], and NCM523 is again a candidate as a positive electrode material of ASS-LIBs [22]. However, there are many factors in ASS-LIBs that are different from those in conventional liquid electrolyte systems. For example, no solvation/desolvation is involved in the charge transfer process, and crosstalk reactions of transition metals to the counter electrode could be well suppressed in ASS-LIBs. On the other hand, resistances related to the space charge layer formed at solid electrolyte|active material interface [23] can be significant. In order to reduce the resistance, LiNbO_3 coating [24–26] is applied to the surface of active material particles. Furthermore, the contact area between the solid electrolyte and solid electrode materials is limited in ASS-LIBs, and thus a large amount of solid electrolyte is used in the composite electrode to decrease the weight and volume energy density of the cell. The cycle life is also affected by the insufficient contact between the solid electrolyte and solid electrode materials. EIS is useful to understand the behavior of the components of ASS-LIBs and to take measures for solving these issues. For effective EIS measurements, three-electrode cell setup is critical in ASS-LIB systems as well as in the conventional liquid electrolyte LIB systems [27]. Actually, the influence of the Li-In counter electrode on the impedance is significant, showing the necessity to use three-electrode cells for adequately measure the impedance of the working electrodes [27].

In this study, we fabricated ASS-LIBs three-electrode cells, measured the impedance of the NCM523 electrode, and quantitatively evaluated the impedance components to estimate the activation energies of the corresponding electrode processes. Furthermore, we conducted charge-discharge cycle tests and compared the impedance responses before and after the cycling tests to identify what process the most significantly affects the cell deterioration. We used two types of electrolytes for the

degradation tests, glass-ceramic $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiI}$ (LPSI) and crystalline $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI), and analyzed the effects of solid electrolytes on the degradation.

2. Experimental

2.1. Materials

NCM523 powder coated with LiNbO_3 (basically $D_{50} = 5.0$ and occasionally $11.2 \mu\text{m}$, Sumitomo Metal Mining) was used as active material for working electrode. Glass-ceramic LPSI ($D_{50} = 5.0 \mu\text{m}$, $\sigma_{\text{ion}} = 2.6 \text{ mS cm}^{-1}$, Idemitsu Kosan) or argyrodite-type LPSCI ($D_{50} = 0.66 \mu\text{m}$, $\sigma_{\text{ion}} = 1.8 \text{ mS cm}^{-1}$, Mitsui Metal & Mining) was used as the solid electrolyte. The weight ratios of the working electrode of LPSI and LPSCI systems were NCM523: LPSI: VGCF = 49 : 43: 8.0 wt % and NCM523: LPSCI: VGCF = 69 : 26: 5.0 wt %, respectively. These optimized mixing ratios were determined with the preliminary tests. These powders were mixed using a milling pot (ANZ-10S0, Nitto Kagaku) to make the composite electrodes. The kind of solid electrolyte used in the composite electrode was the same as that of the electrolyte (separator) layer. As the reference electrode active material, black powder of partially reduced lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (R-LTO) was obtained using the synthetic method previously reported [27]. A mesh-type reference electrode of R-LTO was made by coating the slurry of R-LTO on nickel mesh current sheets (3Ni7-3/0, Taiyo Wire Cloth, aperture ratio: 90–91%, thickness: 0.08 mm, ϕ : 9.0 mm) as shown in the previous report [27]. The mesh-type R-LTO reference electrode has a universal design without solid electrolytes so that it can be applied to both LPSI and LPSCI systems without modification. The Li-In counter electrode was prepared by pressing pieces of indium foil ($\phi = 10.0 \text{ mm}$, 0.05 mm thick, Niraco) and lithium foil ($\phi = 5.0 \text{ mm}$, 0.1 mm thick, Honjo Metal).

2.2. Cell fabrication

The all-solid-state three-electrode cells were prepared as shown in the previous report [27]. The R-LTO mesh reference electrode was sandwiched between two solid electrolyte layers of 1.3 and 1.0 mm thick above and below the reference electrode, respectively, and set in a poly (ethylene terephthalate) tube (ϕ : 10.0 mm). The Li-In counter and NCM523 composite (6.0 mg, ca. 7.6 mg/cm^2) working electrodes were placed above and below the solid electrolyte layer containing the reference electrode, respectively, and the entire assembly was pressed at 110 MPa to fabricate the cell. The whole cell was placed in Ar-filled polystyrene container, and electrochemical measurements were performed through the terminals attached to the container. The cell fabrication process, including cell-sealing in the airtight container, was performed in a glove box filled with Ar atmosphere (dew point $< -80^\circ\text{C}$, oxygen concentration $< 5 \text{ ppm}$). Symmetric cells were fabricated by sandwiching the NCM523 composites between two aluminum current collectors and pressuring at 150 MPa in hollow cylindrical containers.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a multi-channel electrochemical system (VSP-300, BioLogic). The C-rate was calculated based on the nominal capacity of NCM523 of 160 mA h g^{-1} . The cutoff potential of the working electrode was set at 0.85–2.65 V (2.40–4.20 V vs. Li/Li^+). At first, we conducted cycling tests at 0.10C for three cycles to observe the initial behavior. After that, the EIS measurements were sequentially employed. The AC amplitude and the frequency range of EIS were set at 10 mV and 7.0 MHz–5.0 mHz, respectively. The state of charge (SoC) of the NCM523 electrode was defined with the charge capacity at 0.10C. The temperature of the cell was controlled by a constant temperature oven (SH-222, Espec).

The curve fitting of the measured impedance was employed with the

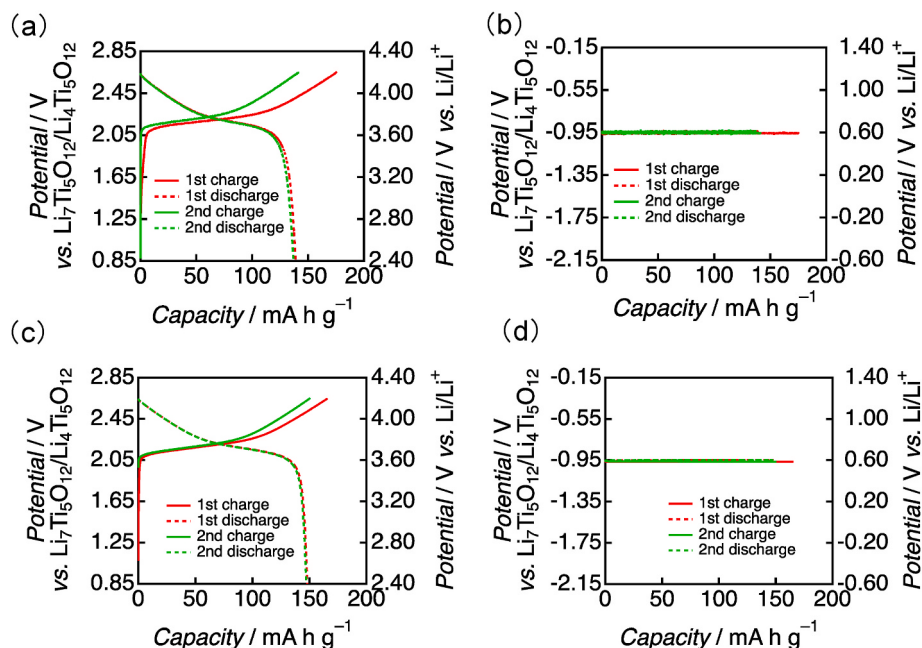


Fig. 1. Charge-discharge curves of (a) NCM523, (b) Li-In electrodes in LPSI systems and those of (c) NCM523, (d) Li-In electrodes in LPSCI systems, both at 0.10C rate.

software Z-View (Scribner) based on the equivalent circuit shown later. The distribution of relaxation times (DRT) analysis [28,29] was occasionally performed to separate several electrode processes. Inductive components at high-frequency regions were subtracted by curve fittings prior to the DRT analysis. The analyzed data was proven to satisfy the Kramers-Kronig (K-K) equation by using the software for K-K transformation (Lin-KK tools, Karlsruhe Institute of Technology [30]), and residuals were less than 0.40 (See Fig. S1 and Fig. S2). The data were then imported into the DRT analysis software (Z-assist, TOYO Corp.). The impedance curve fitting based on the DRT result was performed with the following procedure. First, the time constants obtained from the

DRT analysis were fixed and the other parameters were refined. Then, all the valuable parameters in the equivalent circuit were refined to obtain adequate and optimal curve fitting.

The repeated charge-discharge cycle (durability) tests were conducted at 1.0C rate for 50 cycles at 333 K. In addition, the state of health of the cell was evaluated by 0.10C charging and discharging at 298 K before and after the durability test.

2.4. SEM-EDX observation

The fully charged electrode pellets from the three-electrode cells

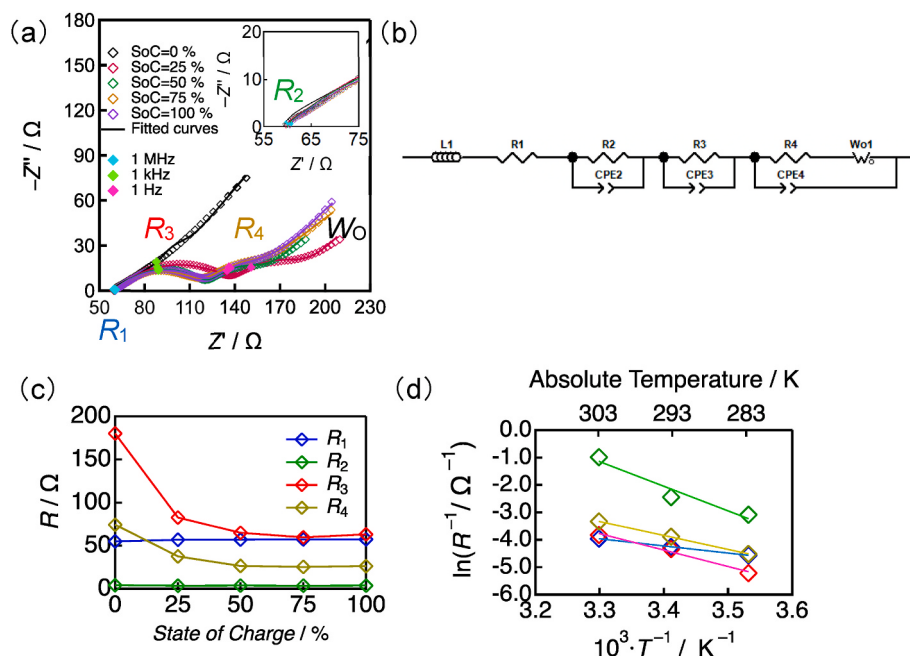


Fig. 2. (a) Nyquist plots of NCM523 impedance in various SoCs at 298 K with experimental data (dots) and fitted curves (solid lines), (b) equivalent circuit used for the analysis, (c) obtained resistance values R_1 , R_2 , R_3 , and R_4 at various SoCs, and (d) Arrhenius plots for R_1 , R_2 , R_3 , and R_4 (at SoC = 100%).

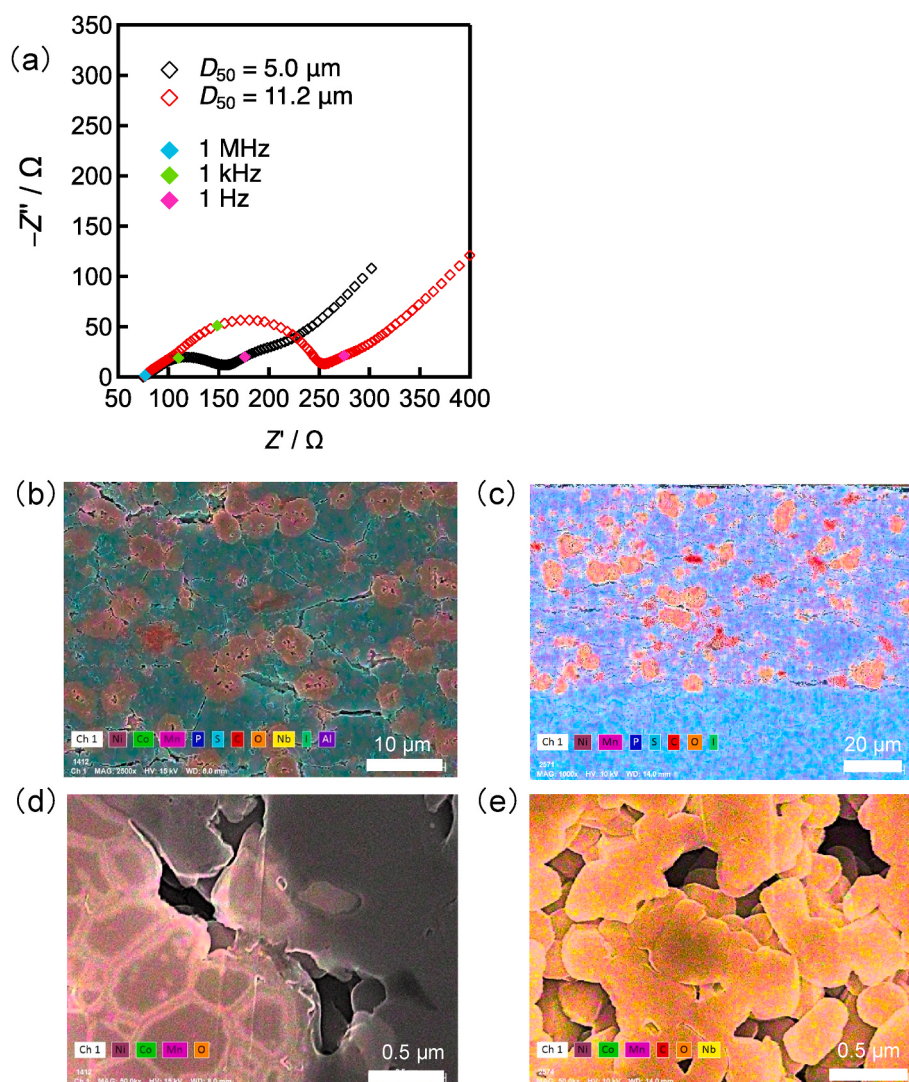


Fig. 3. (a) Nyquist plots of NCM523 ($D_{50} = 5.0$ and $11.2 \mu\text{m}$), (b), (c) cross-sectional SEM images and EDX-mappings of NCM523 composite electrodes ($\times 2500$), and (d), (e) those of NCM523 secondary particles ($\times 50,000$). (b) and (d) correspond to NCM523 with $D_{50} = 5.0 \mu\text{m}$ while (c) and (e) correspond to that with $D_{50} = 11.2 \mu\text{m}$.

were dismantled, cut with a variable angle slicer (SliceMaster HW-1S, JASCO), and then sectioned using an ion milling device (IM-4000, Hitachi High-Tech). The electrodes were simultaneously observed by field emission (FE)-SEM (Regulus 8230, Hitachi High-Tech) and energy dispersive X-ray (EDX) (FlatQUAD, Bruker) analyzer. Image processing software Image-J was used to estimate the contact area between the solid electrolyte and active material particles [31].

3. Results and discussion

3.1. Separation of cell components to unipolar components with three-electrode configuration

The charge-discharge measurements of the NCM523 half-cell were performed to confirm the validity of the R-LTO reference electrode and the charge-discharge characteristics of the three-electrode cells. Fig. 1(a) and (b) show the charge-discharge curves of the NCM523 working electrode and Li-In counter electrode in LPSI, while Fig. 1(c) and (d) show those in LPSCI. Assuming that the potential of the R-LTO reference electrode is $1.55 \text{ V vs. Li/Li}^+$ [32,33], the plateau potentials of the NCM523 and Li-In electrodes are ca. 3.7 and $0.6 \text{ V vs. Li/Li}^+$, which agree with those in the liquid electrolyte systems [5,6,34]. This result

confirms that the R-LTO reference electrode works as a $\text{Li}_7\text{Ti}_5\text{O}_{12}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ redox couple. Furthermore, the charge-discharge capacities of $140\text{--}150 \text{ mA h g}^{-1}$ are comparable to those of two-electrode ASS-LIB cells with NCM523 positive electrodes in the previous report [35], indicating no negative effect of the reference electrode on the intrinsic charge-discharge characteristics.

Fig. S3 shows the Nyquist plots of the impedance spectra in the fully charged states at 283, 293, and 303 K. The combined impedances of NCM523 and Li-In electrodes measured with the R-LTO reference electrode agree well with the cell impedances measured in the two electrode configurations (NCM523 vs. Li-In) in the frequency ranges below 1 MHz. This indicates that the R-LTO reference electrode can reasonably separate the impedance components of the NCM523 and Li-In electrodes below 1 MHz. It should be noted that the cell impedance (in the two-cell configuration) is significantly different from the impedance of NCM523, indicating that the three-electrode configuration with the reference electrode is crucial for the impedance analysis of NCM523 in all-solid-state systems.

3.2. Analysis of NCM523 electrode processes through impedance spectra

The impedance of the NCM523 electrodes was analyzed under

several conditions to clarify the reaction processes in the electrodes. Fig. 2(a) shows the Nyquist plots of the impedance spectra measured at different SoCs (0, 25, 50, 75, 100%) at 298 K in the LPSI systems. The profile consists of the following five components: (i) resistance R_1 at around 1 MHz shown as an intercept, without SoC dependency, (ii) a small semicircle R_2 at around 1 MHz without SoC dependency, (iii) a large semicircle R_3 at around 1 kHz with SoC dependency, (iv) a semicircle R_4 at around 1 Hz with relatively small SoC dependency, and (v) an SoC dependent linear region W_0 in the frequency range below 1 Hz. The relatively small SoC dependency of R_4 is possibly due to the overlaps of components (iii), (iv), and (v). The shape of the impedance spectra is similar to that of the LiCoO₂ electrode, except that R_4 is absent in LiCoO₂ [27].

The spectra were analyzed using the equivalent circuit shown in Fig. 2(b). The fitted curves shown in Fig. 2(a) as solid lines adequately reproduce the experimental data. The fitted R_1 , R_2 , R_3 , and R_4 values at various SoCs are plotted in Fig. 2(c), showing clear potential (SoC) dependence in R_3 . Subsequently, the measurements were employed at various temperatures to obtain the Arrhenius plots shown in Fig. 2(d). The apparent activation energies for R_1 , R_2 , R_3 , and R_4 are 24 ± 1 , 70 ± 20 , 49 ± 6 , and 42 ± 1 kJ mol⁻¹, respectively.

The activation energy of R_1 (ca. 24 kJ mol⁻¹) is roughly consistent with that of the ionic resistance of the LPSI electrolyte [36]. Therefore, R_1 is assigned to the component caused by the ion transport in the solid electrolyte layer between the reference and working electrodes. The absolute R_1 value of 55 Ω is indeed close to the geometrically estimated value of 49 Ω , considering that the conductivity of LPSI is 2.6 mS cm⁻¹, the geometric area 0.79 cm², and the thickness of the solid electrolyte layer between the reference and working electrodes 1.0 mm.

R_2 can be ascribed to the electron transfer resistance at the interface between the composite electrode and current collector. This was verified by measuring the impedance of symmetric cells consisting of an NCM523 composite layer sandwiched between two aluminum current collectors as shown in Fig. S4(a). There are two kinds of electron transfer resistance there, that within the composite bulk (R_{bulk}) and that between the composite and the current collectors of both sides ($R_{\text{interface}}$). When the thickness (or the amount in the same cylinder) of the composite is increased, only R_{bulk} increases whereas $R_{\text{interface}}$ is kept constant. The experimentally obtained EIS spectra are shown in Fig. S4(b). There appear two semicircles in the 1 MHz and 1 Hz ranges, which is similar to the previous report [22], and only the latter increased with increasing the amount of the composite. Therefore, the high and low frequency semicircles can be attributed to $R_{\text{interface}}$ and R_{bulk} , respectively. The low frequency semicircle starts as a straight line with an angle of 45° on its high frequency side and closes on its low frequency side, which is in accordance with the diffusion of electron in the mixed conductors. The obtained electronic resistances (the intercepts on the low frequency side) are plotted against the amount of the composite as shown in Fig. S4(c), with the slope corresponding to R_{bulk} . The extrapolated intercept at NCM mass = 0, excluding the contribution of the bulk, is $R_{\text{interface}}$ and the value was 7.9 Ω . Then the one side of $R_{\text{interface}}$ is ca. 4 Ω and this is the same order as R_2 . Considering the frequency range of $R_{\text{interface}}$ of about 1 MHz being similar to that of R_2 , R_2 can be attributed to the electronic resistance at the Al current collector|NCM523 interface. In liquid electrolyte LIBs, a small semicircle at around 1 MHz has also been attributed to the electronic resistance at the interface between the active material and current collector, whereas the activation energy is estimated to be ca. 4 kJ mol⁻¹ [37,38]. The much larger activation energy (ca. 70 kJ mol⁻¹) obtained here is presumably due to the LiNbO₃ coating on the surface of NCM523 particles in the all-solid-state system. Note that this large activation value does not come from the nature of the solid electrolyte composite because the electrolytes are essentially electronically insulating and do not contribute to the electron transfer at the interface.

R_3 is considered to be the charge transfer resistance at the interface between NCM523 and the solid electrolyte, as the SoC dependence is

very similar to that reported for the liquid electrolyte systems [15]. It is noteworthy that the activation energy of R_3 (49 kJ mol⁻¹) is smaller than that reported for the liquid electrolyte systems (59–71 kJ mol⁻¹) [39]. This can be ascribed to the lithium-ion solvation/desolvation process significantly affecting the charge transfer at the interface in the liquid system [10], leading to the low activation energy in the all-solid-state system [40] without the solvation/desolvation process.

To prove that R_3 is derived from the interface phenomenon (charge transfer), we performed experiments using the NCM523 samples with different particle sizes of $D_{50} = 5.0$ μm and $D_{50} = 11.2$ μm . The representative Nyquist plots at 293 K are shown in Fig. 3(a), and the refined parameters at 283 K, 293 K, and 303 K are shown in Table S1. Table S1 shows that the ratios of R_3 for $D_{50} = 5.0$ μm to R_3 for $D_{50} = 11.2$ μm , R_3 ($D_{50} = 5.0$ μm)/ R_3 ($D_{50} = 11.2$ μm), are about 0.5, while the time constants are nearly unchanged. Here we assume that the active material particles with volumetric density d (g cm⁻³) are spherical with a radius of r . For a fixed active electrode mass M (g), the following equations hold:

$$\text{Volume of an individual particle : } V_i = \frac{4\pi r^3}{3} \quad (1)$$

$$\text{Volume of the whole particles : } V_w = \frac{M}{d} \quad (2)$$

$$\text{Number of the particles in the mass } M : N = V_w \div V_i = \frac{3M}{4\pi dr^3} \quad (3)$$

$$\text{Surface area of the whole particles : } S_w = 4\pi r^2 \times N = \frac{3M}{dr} \quad (4)$$

Therefore, for a fixed mass ratio in a composite electrode, the total surface area of the active material particles is inversely proportional to the radius r . If these particles are completely immersed in the electrolyte, the contacting area should also be inversely proportional to the radius of r . In our case, the contacting area ratio $S_{(D_{50}=5.0 \mu\text{m})}/S_{(D_{50}=11.2 \mu\text{m})}$ is calculated to be 2.4. Moreover, the graphical analysis of the cross-sectional SEM images (Fig. 3(b) and (c)) using Image-J software shows that the ratio of contacting area $S_{(D_{50}=5.0 \mu\text{m})}/S_{(D_{50}=11.2 \mu\text{m})}$ is 2.0, which is in good agreement with the calculated value of 2.4. Considering the interface resistance value is inversely proportional to the surface area, the reciprocal of the estimated contacting area ratio, 0.42 or 0.50, can be used as the estimated ratio of R_3 ($D_{50}=5.0 \mu\text{m}$)/ R_3 ($D_{50}=11.2 \mu\text{m}$). This is nearly the same as the experimentally obtained ratio R_3 ($D_{50}=5.0 \mu\text{m}$)/ R_3 ($D_{50}=11.2 \mu\text{m}$) from the EIS measurements of 0.5. Accordingly, we conclude that R_3 is the resistance associated with charge transfer at the interface of NCM523|solid electrolyte. The result also suggests the uniform physical contact between the active electrode and solid electrolyte particles.

R_4 is a component that has not been isolated in the previous studies. The existence of R_4 is apparent when the three-electrode cell is applied to separate the Li-In component, which significantly affects the low-frequency behavior. R_4 appearing in the frequency range close to R_3 suggests that this process is also related to the charge transfer, but not that at the interface between the electrode and the electrolyte. The R_4 values for NCM523 with $D_{50} = 11.2$ μm were 2–3 times larger than that of NCM523 with $D_{50} = 5.0$ μm . The SEM images at high magnification (Fig. 3(d) and (e)) indicate that there are grain boundaries between the primary particles within the NCM523 secondary particles in both samples, and voids are more apparent for the sample with $D_{50} = 11.2$ μm . This suggests that R_4 is assignable to the charge transfer resistance within the secondary particles of NCM523. Other experimental results to support this hypothesis are shown in the next section.

Consequently, five components are identified in the NCM523 impedance in the LPSI electrolyte systems: R_1 as the ionic transport resistance in the solid electrolyte layer between the reference and working electrodes, R_2 as the electronic resistance at the Al current collector|NCM523 interface, R_3 as the charge transfer resistance at the NCM523|LPSI interface, R_4 possibly as the charge transfer resistance

Table 1

Activation energy in LPSI and LPSCI systems before and after charge-discharge cycle test (SoC = 100%).

	LPSI		LPSCI	
	before	after	before	after
$E_a (R_1 \text{ or } R_1 + R_1') / \text{kJ mol}^{-1}$	24 ± 1	26 ± 4	40 ± 2	36 ± 5
$E_a (R_2) / \text{kJ mol}^{-1}$	70 ± 20	41 ± 8	60 ± 10	43 ± 6
$E_a (R_3) / \text{kJ mol}^{-1}$	49 ± 6	54 ± 1	50 ± 2	63 ± 5
$E_a (R_4) / \text{kJ mol}^{-1}$	42 ± 1	64 ± 4	50 ± 3	56 ± 1

between primary particles within the NCM523 secondary particles, and W_o as the Warburg impedance showing the ion transportation in the NCM523 particles.

The behavior in the LPSCI electrolyte systems was similarly examined as shown in Fig. S3 (d-g). When the LPSCI electrolyte is applied, the intercept component R_1 accompanies a semicircle ($R_1'//CPE$ in the

equivalent circuit) in the 1 MHz range. A similar semicircle is also observed for the Li-In counter electrode component, suggesting that this is caused by the nature of the LPSCI electrolyte. The Arrhenius plot of the sum of R_1 and R_1' gave the activation energy of 40 kJ mol^{-1} (Table 1, before), which is consistent with the value reported for ionic conduction in LPSCI [41]. The reason why the capacitive components appear in the LPSCI electrolyte can be expressed as follows. The Young's modulus of LPSCI (22.1) lower than that of LPSI (30) [42] implies that the adhesions between LPSCI particles are less sufficient than those between LPSI particles, leading to void formation to generate capacitive components in the impedance. The R_2 component was nearly undetectable in the LPSCI system because it is sandwiched between the 1 MHz semicircle described above and the 1 kHz semicircle caused by the charge transfer process. In addition, the boundary between R_3 and R_4 is relatively unclear compared to that in the LPSI system. Here we performed DRT analysis to clearly separate these components. As shown in Fig. S2

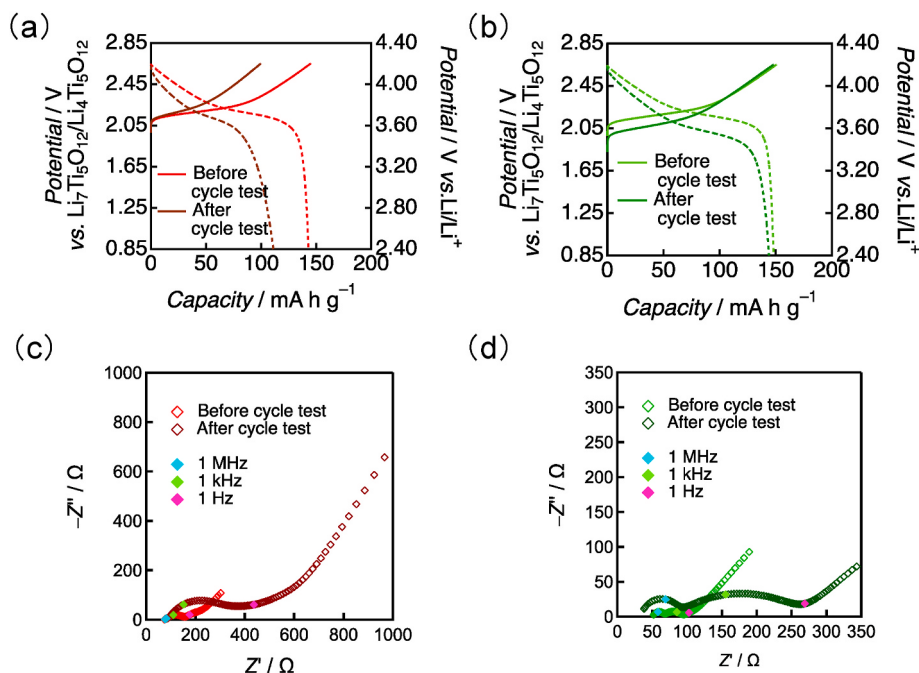


Fig. 4. (a), (b) Charge-discharge curves at 0.10C rates and (c), (d) Nyquist plots of NCM523 before and after charge-discharge cycle (durability) tests. (a), (c) correspond to the data obtained in the LPSI system while (b), (d) correspond to those obtained in the LPSCI system.

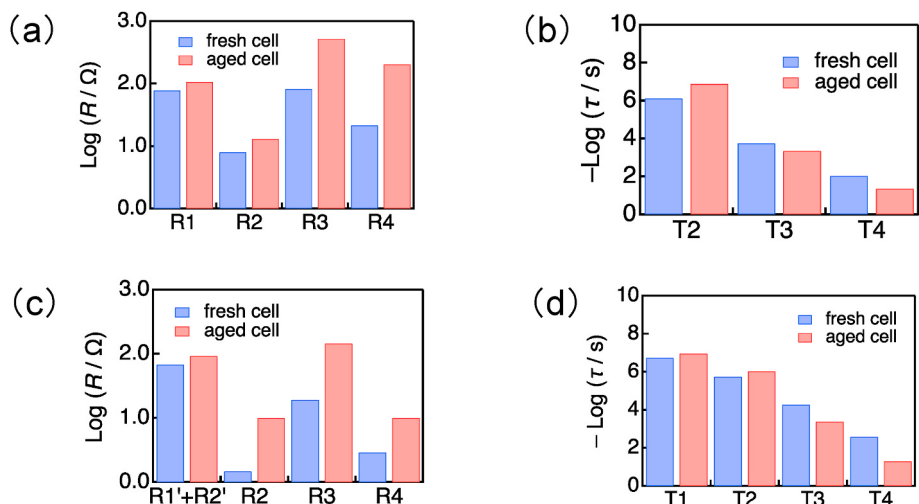


Fig. 5. Comparisons of fitting parameters at logarithmic scale in (a,b) LPSI and (c,d) LPSCI systems; (a,c) resistance; (b,d) time constant.

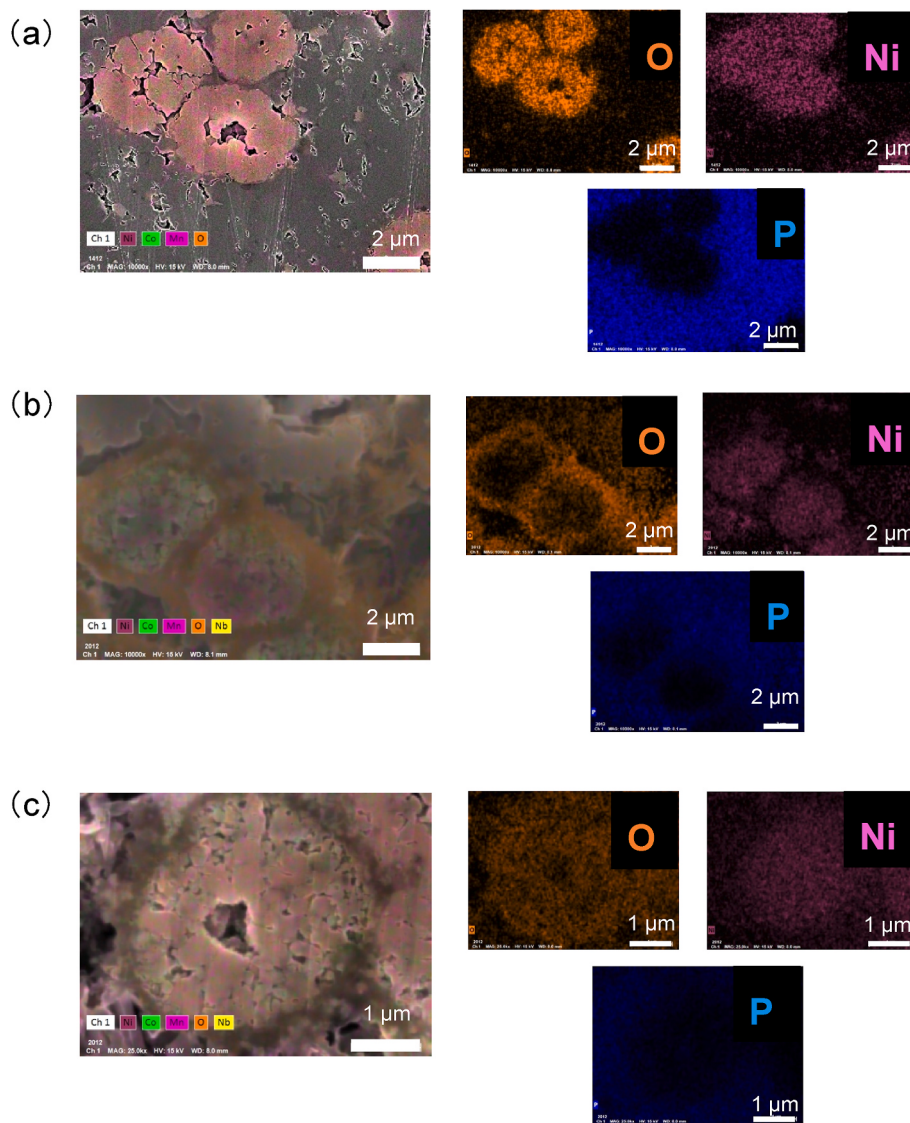


Fig. 6. Cross-sectional SEM images and EDX-mappings of the inside of NCM523 electrode layer in LPSI system (a) before and (b) after cycle tests ($\times 10,000$), and (c) overall image of NCM523 secondary particles after cycle tests ($\times 25,000$), together with Ni, O, and P element mapping.

(before), the independent components of R_2 to R_4 are confirmed by using $\lambda = 8.5 \times 10^{-4}$ as the regularization parameter. Finally, the Arrhenius plots were also made for the LPSCI system, and the comparison of the activation energies with the LPSI system is summarized in Table 1 (before), showing good agreement in the two systems except for the electrolyte behavior itself ($E_a(R_1)$). The activation energy of R_3 is about 50 kJ mol^{-1} for both LPSI and LPSCI, which is lower than that of the liquid electrolyte systems [10], indicating the solvation-free nature of the solid electrolyte systems.

3.3. Degradation caused by repeated charge-discharge

The repeated charge-discharge (durability) tests were performed at 333 K, at 1.0C for 50 cycles, to clarify the degradation mechanisms of NCM523 in ASS-LIBs. Fig. 4(a) shows the 0.1C charge-discharge curves of the NCM523 electrode at 298 K before and after the durability tests in the LPSI system, while Fig. 4(b) shows those in the LPSCI system. While the discharge potential drop was observed after the durability tests in both the LPSI and LPSCI systems, the charge-discharge capacity was nearly kept in the LPSCI system, which is in contrast to the significant decrease in the LPSI system. These results suggest that the overpotential increased in both systems, possibly due to reaction inhomogeneity

caused by the resistance increase, whereas the amount of effective active material decreased only in the LPSI system.

In order to investigate the causes of these changes, we compared the impedance of NCM523 in the fully charged states before and after the durability tests. The Kramers-Kronig residuals within ± 0.4 (Figs. S1 and S2) suggest the stability of the reference electrodes during the durability tests. The Nyquist plots in the LPSI and LPSCI systems are shown in Fig. 4 (c) and (d), respectively. Since the boundary between R_3 and R_4 is unclear after the durability tests in both systems, we applied the DRT analysis as in the previous section. We were able to confirm the independent components of R_2 , R_3 and R_4 , by applying adequate regularization parameters (LPSI system in Fig. S1: $\lambda = 6.0 \times 10^{-2}$, LPSCI system in Fig. S2: $\lambda = 8.5 \times 10^{-4}$). The resistance and time constant values obtained by the curve fitting are shown in Fig. 5. In the LPSI system, there were insignificant changes in R_1 and R_2 , whereas R_3 drastically increased (6 times larger) during the durability tests. These results suggest that the chemical composition at the interface or the contact area between the NCM523 and electrolyte particles changed. In addition, the resistance of R_4 significantly increased (9 times) throughout the cycle test. In the LPSCI system, the growth of R_3 and R_4 during the durability test significantly affects the whole EIS signal. The increase in R_3 in the LPSCI system was the same as that in the LPSI system, while the

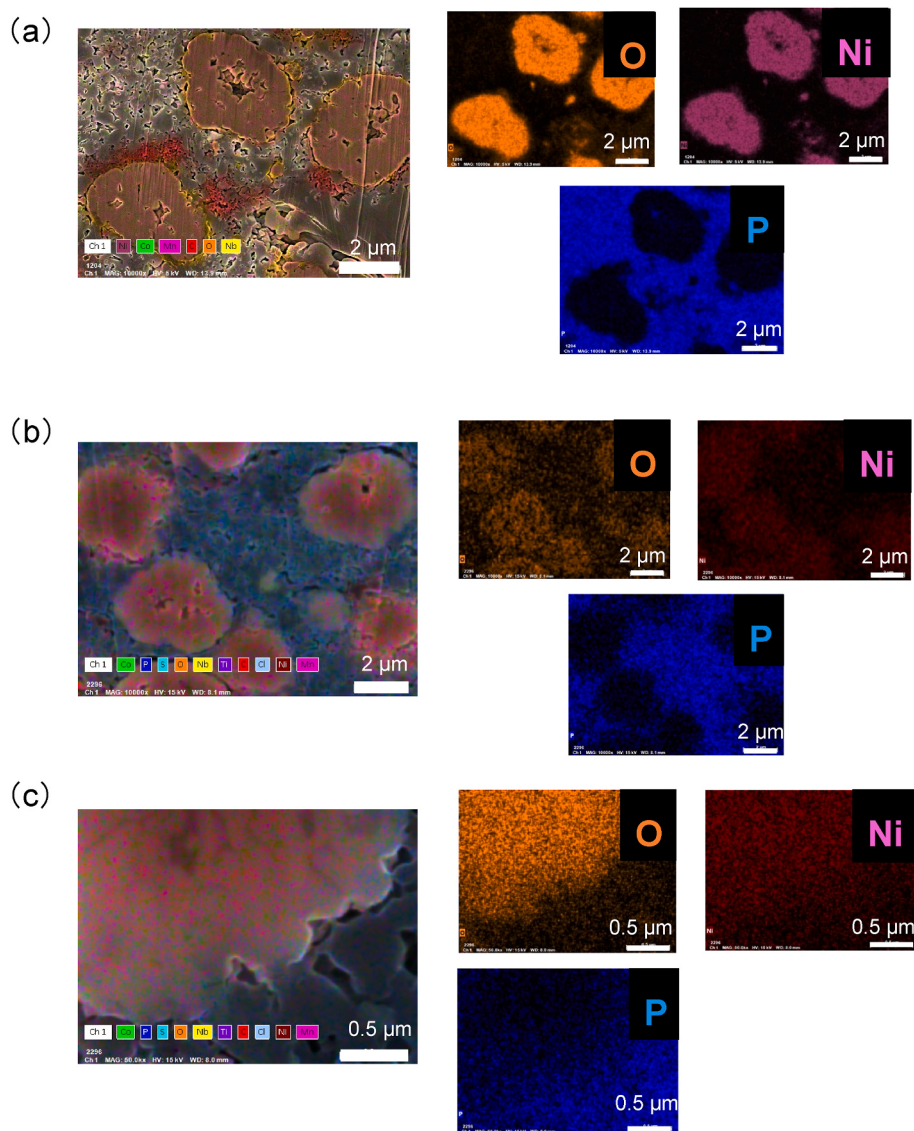


Fig. 7. Cross-sectional SEM images and EDX-mappings of the inside of NCM523 electrode layer in LPSCI system (a) before and (b) after cycle tests ($\times 10,000$), and (c) overall image of NCM523 secondary particles after cycle tests ($\times 50,000$), together with Ni, O, and P element mapping.

increase in R_4 in the LPSCI system was much suppressed.

As for the activation energies of the various components, $E_a(R_1)$ and $E_a(R_2)$ remained almost unchanged, while $E_a(R_3)$ increased after the cycle test (Table 1). This suggests that the nature of the interface between the electrolyte and active material was altered with degradation. On the other hand, the apparent activation energy $E_a(R_4)$ increased in the LPSI system more than that in the LPSCI system.

The FE-SEM/EDX observation was then conducted to investigate these changes from the viewpoint of the electrode morphology. The SEM images with the EDX elemental mappings obtained for the LPSI and LPSCI systems are shown in Figs. 6 and 7, respectively. In both systems, the migration of O atoms from the active material to the solid electrolyte was observed, which has been previously reported in ASS-LIBs with sulfide solid electrolytes [43,44]. In addition, there are deposit layers (2 μm in thickness) that contain O and P elements around the secondary particles after the durability test in the LPSI system, whereas such layers were not apparent in the LPSCI system. If these layers are chemically formed resistive compounds, the increase in R_3 would be more significant in the LPSI system than in the LPSCI system. On the other hand, if insulative layers completely cover the active material to make the particle inactive, such dead particles probably have no contribution to the

charge transfer process. This could explain the large capacity decrease in the LPSI system. Furthermore, apart from the original large voids, there were fine voids inside the NCM523 secondary particles in the LPSI system more than in the LPSCI system, which is probably caused by particle cracking during the repeated cycling. Considering that the increase of R_4 was much large in the LPSI system, it is suggested that R_4 is a resistance associated with charge transfer between primary particles (within NCM523 secondary particles) and the generated voids are harmful for the charge transfer resistance between the primary particles. The activation energy corresponding to R_4 increased after the durability test, suggesting that there were some chemical changes. Figs. 6 and 7 show that the element distribution in the primary particles, particularly that of oxygen, changes during the durability tests, in addition to their isolation. Accordingly, the crack formation and the element distribution change in the NCM523 secondary particles seem to result in the increase of R_4 and $E_a(R_4)$, respectively, leading to the capacity decrease. It is unclear at the moment why the kind of the electrolyte affects the physical characteristics of the active material, and further study is needed to clarify this point as well as to reinforce the R_4 assignment.

In summary, the impedance measurements and morphological observations suggest two degradation processes. One is the oxygen

migration to cause chemical composition change in the active material and sulfide solid electrolyte, which seems to be responsible for the increases of R_3 . The other one is the void formation seen in the LPSI system that causes the increase in R_4 and the diffusion-related resistance. Accordingly, stable interface design to suppress the former, which results in the increase in the overpotential, and robust electrode material particles to suppress the latter, which results in the capacity loss, are essential to improve the durability in ASS-LIBs.

4. Conclusion

By using all-solid-state three-electrode cells, the impedance components of the NCM523 electrode and the Li-In electrode were successfully separated in both LPSI and LPSCI electrolyte systems, which allows the adequate and detailed analysis of impedance spectra of NCM523. Five components are identified in the NCM523 impedance: R_1 as the ionic transport resistance in the solid electrolyte layer between the reference and working electrodes, R_2 as the electronic resistance at the Al current collector|NCM523 interface, R_3 as the charge transfer resistance at the NCM523|electrolyte interface, R_4 as the charge transfer resistance between primary particles within the NCM523 secondary particles, and W_o as the Warburg impedance showing the ion transportation in the NCM523 particles. The DRT analysis is effective to separate these components to design appropriate equivalent circuits. During repeated cycling, the main cause of the degradation is the increase in R_3 . The SEM/EDX observation suggests that this arises from the side reaction at the active material|solid electrolyte interface. Void formation by particle cracking also affects the increase in R_4 , that leads to the capacity loss particularly seen in the LPSI electrolyte systems. Such quantitative analysis of impedance spectra using the three-electrode cell is essential for degradation diagnosis for ASS-LIBs.

CRedit authorship contribution statement

Goro Fukunishi: Formal analysis, Methodology, Conceptualization, Data curation, Investigation, Visualization, Writing – original draft. **Mayu Tabuchi:** Investigation, Methodology, Data curation, Visualization. **Atsunori Ikezawa:** Methodology, Data curation, Supervision, Writing – review & editing. **Takeyoshi Okajima:** Supervision, Writing – review & editing. **Fusao Kitamura:** Supervision, Writing – review & editing. **Kota Suzuki:** Supervision, Resources, Writing – review & editing. **Masaaki Hirayama:** Supervision, Resources, Writing – review & editing. **Ryoji Kanno:** Project administration, Supervision, Resources, Writing – review & editing. **Hajime Arai:** Conceptualization, Methodology, Data curation, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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