All-Solid-State Lithium-Ion Battery using $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ Electrolyte

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Abstract

Oxide-based all-solid-state lithium-ion battery is prepared by a conventional sintering process, thanks to the intrinsic low melting point of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$. A well-defined interface between LiCoO_2 and $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ was confirmed without any traces of impurities. Li ion reversibly (de-)intercalated from/into LiCoO_2 at initial charge-discharge process when the charge capacity was limited to 120 mAh g^{-1} . The capacity degradation after subsequent cycling was suppressed by further limitation of the charging capacity. However, capacity fade could still be confirmed after 20 cycles albeit the capacity was limited at 60 mAh g^{-1} . This study suggests large repetitive expansion-contraction of the electrode during cycling as a possible cause of fatigue failure of the electrode/oxide electrolyte interface.

Keywords: All-solid-state Li-ion battery, $\text{Li}_2\text{CO}_3\text{-Li}_3\text{BO}_3$, Solid electrolyte, Li ion conductor

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1. Introduction

Oxides are generally non-flammable, durable and non-toxic materials; high safety and reliability in a battery system is assured by the use of oxide as an electrolyte instead of the highly-reactive non-aqueous liquid. Indeed, a μAh – mAh class thin-film Li-ion battery has been commercialized as an energy storage part of medical micro devices and microelectronic devices, in which electrode and electrolyte thin films are stacked by deposition techniques.[1,2] To develop a several-hundred mAh class all-solid-state lithium-ion battery (hereafter denoted as ASS-LIB) for applications such as electric vehicles, the thicknesses of stacked electrode and electrolyte layers need to be curtailed to several ten to hundred μm order. This can be achieved through powder technology. In ASS-LIB, the desirable electrolyte/electrolyte and electrode/electrolyte interfaces should be prepared by a simple powder sintering process, which confers good contact at the atomic scale for the fast Li-ion transfer, and also produces little ion-blocking impurities.[3] Well-known lithium-ion conductive oxides based on the garnet [4], perovskite [5,6] and NASICON-type [7] structures possess high bulk conductivities of over $10^{-4} \text{ S cm}^{-1}$; however, these oxides required sintering at high temperature beyond 1000°C to facilitate good contact with the electrodes by a simple powder sintering process. In addition, most electrode materials such as layered or spinel oxides produce

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3 impurities after sintering [8,9]. To address these issues, several routes to obtain the
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6 desirable interface have been recently suggested for assembling ASS-LIB: 1) the use of
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9 other Li-ion conductive oxides as alternative electrolyte-body materials or interfacial
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12 additives, which could be processed at low temperature [10,11], 2) the choice of
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15 thermally stable electrodes on contact with electrolyte [12], and/or 3) the use of
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18 distinctive processing methods [12-14]. In spite of all these approaches, the
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21 electrochemical performance metrics of ASS-LIB assembled by powder sintering
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24 processes was not necessarily satisfactory. The solid-state battery system has been
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27 plagued with many problems, which have encumbered its commercial realization.[15]
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31 Nonetheless efforts to improve the electrochemical performance of ASS-LIB have been
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34 thwarted, considering that the problems reported occur cumulatively.
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38 Although the Li-ion conductivity of Li_2CO_3 was extremely low (about $10^{-12} \text{ S cm}^{-1}$
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41 at room temperature),[16] the ion-blocking impurities were hardly formed at the
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44 electrode/ Li_2CO_3 electrolyte interface since Li_2CO_3 could be sintered at lower
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47 temperatures below 700 °C. $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$, which is isostructural with Li_2CO_3 , is also a
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50 Li-ion conductive oxide [16]. According to the literature, the Li-ion conductivity was
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53 enhanced dramatically from 10^{-7} to $10^{-3} \text{ S cm}^{-1}$ at 200 °C as x in $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ changes
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56 from 0 to 0.25 [16]. In the present paper, we assembled ASS-LIB by using
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3 $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ as electrolyte-body material, and investigated the electrochemical
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6 properties in this simple battery in the quest to propose the origin for the improved
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9 cyclability.
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11 12 13 14 15 16 **2. Experimental**

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19 $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$) was synthesized *via* a conventional solid-state
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21 reaction, in which Li_2CO_3 (99.99%, Kojundo Chemical Laboratory), $\text{LiOH}\cdot\text{H}_2\text{O}$ (99.0%,
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23 Kojundo Chemical Laboratory) and H_3BO_3 (99.5%, Wako Pure Chemical Industries)
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25 were used as the starting materials. The required amount of each starting material was
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28 ground and heated at 600 °C for 10 h in air. The obtained powder was cold-pressed into
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31 a pellet and re-heated at 650 °C for 10 h in air twice. Powder XRD patterns of the
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34 synthesized product were collected on a RINT-TTR diffractometer using Cu $K\alpha$
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37 radiation. All the XRD analyses were carried out in the Bragg-Brentano geometry mode.
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41 For ion conductivity measurements, the prepared $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$) were
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44 firstly put in a 80 mL ZrO_2 cap with five of 5 mm ZrO_2 disks, and was pulverized by
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47 disk mill (Ito Seisakusho, MC-4A). The samples were then pressed into pellets (10 mm
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50 in diameter) and sintered at 660 °C for 2 h in air, and both sides were polished and
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53 coated with gold (*via* sputtering) as blocking electrodes. AC impedance profile was
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collected using a frequency response analyzer (Solartron, 1260) over a frequency range of 1 Hz – 30 MHz at 30 °C and 120 °C.

Composite electrode powder was prepared from a mixture of 70 wt% LiCoO_2 (Nippon Chemical Industrial, Average particle size; $D(50) = 9.4 \mu\text{m}$) and 30 wt% $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte. 10 mg of the composite electrode powder was placed on 40 mg of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ powder as electrolyte separator, and a pressure of 850 MPa was applied using a uniaxial pressing machine to obtain disks with an outside diameter of 10 mm. The prepared $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte disk was sintered at 660 °C for 2 h in air, and the composite electrode side was coated with gold *via* sputtering. Note that the melting point of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ is 708 °C. Lithium foil was used as a reference/counter electrode. A poly(ethylene oxide)(PEO)-based polymer electrolyte film (Daiso, $\text{LiTFSA}/\text{EO} = 0.06$) was inserted between the lithium foil and the $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte separator to reduce the interfacial resistance with adhesion as possible. Electrochemical charge-discharge test was performed at a constant current of $32 \mu\text{A cm}^{-2}$ or $64 \mu\text{A cm}^{-2}$ (3.6 mA g^{-1} or 7.1 mA g^{-1} of LiCoO_2) at 120 °C (Solartron, 1470E+1255B). The electrochemical AC impedance measurement (Frequency range; 0.1 Hz – 10 kHz) was also done after the end of each charge process. *Ex-situ* Powder XRD patterns were conducted for the disk

samples of as-prepared and those after electrochemical tests. The cross-section of the samples was conducted by mounting the samples on carbon tape. Samples for microscope were then cut out from the carbon tape through ion-milling. A field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-5500LV) was used to observe the cross-section of the samples.

3. Results and Discussion

The powder XRD patterns of as-synthesized $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$) are shown in Fig. 1. All the observed diffraction peaks of $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ could be indexed in the monoclinic phase (space group: $C2/c$) [16] without any other impurities as well as those of Li_2CO_3 ; BO_3^{3-} ion substitutes for CO_3^{2-} ion with the introduction of interstitial Li ion in monoclinic structure based on the following Kröger-Vink notation:

At $x \geq 0.4$, an unknown impurity which had similar diffraction peaks as Li_3BO_3 or $\text{Li}_4\text{B}_2\text{O}_7$ phases appeared as well as $\text{Li}_{2+x-\delta}\text{C}_{1-x+\delta}\text{B}_{x-\delta}\text{O}_3$ solid solution. The lattice parameters and volumes of $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3$) were estimated using CellRef program [17], which are summarized in Table 1. The variation of estimated lattice parameters was in the line with reported literature values [16]. A large expansion

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3 along c axis with the increase of x value result in the formation of interstitial Li ion as
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6 has been discussed in the literature [16]. The relative densities of pellets for ion
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9 conductivity measurements were controlled by the sintering temperature (660 °C) and
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12 dwell time (2h), and were over 90%. Total Li-ion conductivities for $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x =$
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15 0.1, 0.2, 0.3) determined from the onsets of deformed semi-circles were respectively 3.6
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17 $\times 10^{-7} \text{ S cm}^{-1}$, $6.5 \times 10^{-7} \text{ S cm}^{-1}$ and $4.6 \times 10^{-7} \text{ S cm}^{-1}$ at 30 °C, which were
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22 hundred-thousand-fold of that for Li_3BO_3 . This result suggests that the interstitial Li ion
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25 introduced by substituting BO_3^{3-} ion contributes to the Li-ion transfer in the monoclinic
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28 structure and/or grain-boundary. $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$, which exhibits maximum conductivity
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31 in the present paper, was used to assemble the ASS-LIB. Note that the total ion
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35 conductivities of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ was $7.3 \times 10^{-5} \text{ S cm}^{-1}$ at 120 °C.
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41 $\text{LiCoO}_2\text{-Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte disk is shown in
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44 Fig. 2 (b). LiCoO_2 (grey color) was surrounded by $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ (black color) melted
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47 under heat treatment, and a well-defined interface could be confirmed without impurity
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50 phases or voids. As further shown in Fig. 3 (c), no impurity peak was observed in the
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53 powder XRD pattern of the $\text{LiCoO}_2\text{-Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode except for the
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56 original patterns of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ (Fig. 3 (a)) and LiCoO_2 (Fig. 3 (b)). The thickness of
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the total disk and composite electrode part were about 330 μm and 50 μm , respectively.

At the first electrochemical test of the ASS-LIB, the electrolyte side of $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte was in direct contact with lithium foil or indium foil as reference/counter electrode. This ASS-LIB exhibits reversible capacities during charge-discharge process without the chemical reduction of the electrolyte, but has low reproducibility of charge-discharge profile, which can be attributed to a considerable resistance measured by AC impedance analyzer. Thus, the polymer electrolyte film was inserted between lithium foil and $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte in order to assess the electrochemical behavior in $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode accurately. Fig. 4 shows the initial electrochemical charge-discharge profile of ASS-LIB ($\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte/polymer electrolyte/Li foil) at a constant current of 32 $\mu\text{A cm}^{-2}$ (3.6 mA g^{-1} of LiCoO_2) at 120 $^\circ\text{C}$. The charge capacity was limited to 120 mAh g^{-1} . The ASS-LIB shows an initial charge-discharge profile which is similar to the liquid electrolyte case [18], and the discharge capacity is 97 mAh g^{-1} . The circles in Fig. 4 indicate the various charge/discharge states. The 003 diffraction peaks of LiCoO_2 measured from the *ex-situ* powder XRD patterns for samples subjected to varying degrees of electrochemical reaction clearly visualize the changes along *c* axis

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3 during charge or discharge process, as shown in Fig. 5(a). The changes along c axis
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6 relate to the (de-)intercalating amount of Li ion from/into LiCoO_2 . Fig. 5(b) shows the
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9 changes of the lattice parameters c of $\text{Li}_{1-y}\text{CoO}_2$ in ASS-LIB as well as those in
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12 liquid-electrolyte cells operated previously [18]. It can be assumed that the applied total
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15 current was consumed by the (de-)intercalation from/into LiCoO_2 in liquid electrolyte
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18 case since a constant current rate of $C/40$ (about $42 \mu\text{A cm}^{-2}$) was slow enough [18]. The
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21 degree of the lattice parameters c change during charge process in ASS-LIB is close to
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24 that in liquid electrolyte case. Furthermore, the 003 diffraction peak shifted back to the
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27 initial position of LiCoO_2 after the discharge process. Therefore, Li ion reversibly
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30 (de-)intercalated from/into LiCoO_2 at initial charge-discharge when a charge capacity
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33 was limited to 120 mAh g^{-1} . An irreversible shift of the 003 diffraction peak after
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36 discharge process was observed with the charge capacity of 160 mAh g^{-1} . Note that the
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39 discharge capacity of ASS-LIB is only 97 mAh g^{-1} , although Li ion reversibly
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42 intercalated into LiCoO_2 at initial discharge. After a long period ($\sim 10\text{h}$) of the charged
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45 ASS-LIB, the open-circuit potential decreased due to the leak current of electrolyte at
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53 The cycle dependence of the charge-discharge profiles was examined in ASS-LIB as
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56 shown in Fig. 6. The large capacity degradation during cycling could be confirmed
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when a charge capacity was limited to 120 mAh g⁻¹ (Fig. 6(d)). A possible cause for the degradation is the mismatch of y value in Li_{1-y}CoO₂ after cycling, because an irreversible capacity has been already observed at the initial cycle and intercalated Li ion was limited by same charge capacity during cycling. However, the aforementioned *ex-situ* powder XRD measurements suggest that Li ion removed from Li_{1-y}CoO₂ intercalates back to the structure after discharge process. Thus, the mismatch of y value in Li_{1-y}CoO₂ is not the origin of the degradation. The fracture at the electrode/electrolyte interface upon expansion-contraction of electrode is another possibility for the degradation during (dis-)charging. Fig. 7 shows the polished cross-sectional SEM image of the composite electrode part of ASS-LIB after 5 cycles (Charge capacity limited to 120 mAh g⁻¹). A significant void (black) was observed between LiCoO₂ (light grey) and Li_{2.2}C_{0.8}B_{0.2}O₃ (dark grey). This result indicates that the repetitive electrode expansion-contraction can affect the degradation even though the change of lattice parameter c is just 2.1 % after a charging capacity until 120 mAh g⁻¹. To confirm the effect of the repetitive electrode expansion-contraction on the cyclability, the charge-discharge profiles was also measured at different charge capacity ranges: 60 mAh g⁻¹ (Fig. 6(a)), 80 mAh g⁻¹ (Fig. 6(b)), 100 mAh g⁻¹ (Fig. 6(c)). The capacity degradation was suppressed on further limiting of the charge capacity since the cyclical

expansion-contraction change decreased. After 20 cycles, the degradation could be observed even at a charging capacity until 60 mAh g⁻¹. Fig. 8 shows the impedance plots of ASS-LIB after the charge process at each cycle. The deformed semi-circle represents the combination of resistances for grain-boundary and charge-transfer reaction, since the observed frequency range was 0.1 Hz – 10 kHz. The total resistance after initial charge process estimated from the semi-circle had small variation (450 – 700 Ω) among Fig. 8 (a)-(d) because the distribution of LiCoO₂ and Li_{2.2}C_{0.8}B_{0.2}O₃ in the composite electrode was inhomogeneous. However, this resistance variation had an insignificant effect on the charge-discharge profile since a current rate of 64 μA cm⁻² was small enough. The resistance did not change too much after 5 cycles when the charge capacity was limited to 100 mAh g⁻¹, but the non-negligible resistance increase could be observed after 3 cycles when the charge capacity was limited 120 mAh g⁻¹. These results further revealed that the repetitive electrode expansion-contraction is one of the key factors behind the capacity degradation in oxide-based ASS-LIB. Note that the variation of the resistance for charge-transfer reaction at each charge capacity was negligible, which could be confirmed by the impedance plots during the initial charge process. Considering the capacity degradation, there is need to discuss whether the interfacial side reaction at high voltage contributes to the resistance increase. However,

the reason behind the resistance increase after 3 cycles is difficult to explain from this reason, since no new $\text{LiCoO}_2/\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ interface would be formed once the side reactions occur in this solid electrolyte / electrode in contrast to liquid electrolyte / electrode case.

In summary, the fatigue failure of the electrode/oxide electrolyte interface caused by repetitive electrode expansion-contraction significantly affects the capacity degradation of oxide-based ASS-LIB at 120 °C. From the literature, the lattice parameter c and volume of LiCoO_2 expands by 0.13 % and 0.10 % at an operating temperature of 120 °C compared to operation at 27 °C, respectively [19]. This is an indistinctive difference on the fully lithiated LiCoO_2 . On the contrary, the lattice parameter c of the delithiated $\text{Li}_{1-x}\text{CoO}_2$ (corresponding to a charging capacity of 60 mAh g⁻¹) expands by 1.0 % upon Li ion de-intercalation at 27 °C. Upon delithiation at 120 °C, the difference in volume change in $\text{Li}_{1-x}\text{CoO}_2$ is also expected to be negligible, as is the case with the fully lithiated LiCoO_2 . Therefore, the volume change during delithiation at 120 °C should, more or less, be the same to that at 25 °C. This means that the capacity degradation observed at 120 °C should also be expected to occur at 25 °C. The control of the lattice expansion and contraction of electrodes through limiting the charging

capacity is a feasible strategy to improve cyclability; nonetheless, this strategy cannot sufficiently suppress the capacity fade after 20 cycles and thus cannot provide a large capacity and energy density. In liquid electrolytes, LiCoO_2 exhibits a stable and reversible capacity of over 150 mAh/g after prolonged cycling. Therefore, other strategies are necessary to reinforce(strengthen) interfacial adhesion which is adversely weakened by the lattice expansion and contraction. For instance, the use of an electrolyte possessing plastic property [10], and/or the use of an electrode possessing small lattice expansion-contraction during electrochemical cycling [12] or with small grain size would be effective strategies to improve the cyclability of oxide-based ASS-LIB.

Conclusion

A well-defined interface between LiCoO_2 and electrolyte without any impurity could be formed *via* a conventional sintering process by using $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ with low melting point as electrolyte. Reversibly capacity of LiCoO_2 obtained in ASS-LIB at 120 °C, that is, the ion conductivity of $10^{-5} \text{ S cm}^{-1}$ order is required in electrolyte at least for measuring the charge-discharge profile similar to liquid electrolyte case. Although the conductivity of $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ was low around room temperature, it can be used as

the interfacial additive for connecting electrode/high conductive electrolyte interface for ASS-LIB.

The effect of electrode lattice expansion-contraction on the capacity degradation was discussed by a combination of electrochemical (dis)charge tests, AC impedance spectroscopy and the polished cross-sectional SEM image. This study highlights that the control of the interfacial adhesion caused by the lattice expansion-contraction of electrodes is crucial to developing oxide-based ASS-LIB for large scale application exhibiting high safety and reliability.

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Table 1 Lattice parameters and volumes of $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3$) estimated from powder XRD patterns

	lattice parameter				volume
	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$\beta / ^\circ$	$V / \text{\AA}^3$
Li_2CO_3	8.3572	4.9747	6.1941	114.72	233.92
$\text{Li}_{2.1}\text{C}_{0.9}\text{B}_{0.1}\text{O}_3$	8.3779	4.9559	6.2715	114.63	236.69
$\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$	8.3980	4.9363	6.3416	114.70	238.83
$\text{Li}_{2.3}\text{C}_{0.7}\text{B}_{0.3}\text{O}_3$	8.4037	4.9349	6.3925	114.75	240.76

Figure captions

Fig. 1

Powder X-ray diffraction patterns of $\text{Li}_{2+x}\text{C}_{1-x}\text{B}_x\text{O}_3$; (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, and (d) $x = 0.3$.

Fig. 2

(a) SEM image of LiCoO_2 electrode used in present paper. (b) Polished cross-sectional SEM image of electrode part in $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte disk after sintering at 650 °C for 2 h.

Fig. 3

Powder X-ray diffraction patterns of (a) $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$, (b) LiCoO_2 , and (c) $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode (weight ratio; 1 : 1) after sintering at 650 °C for 2h.

Fig. 4

Initial electrochemical charge-discharge profile of $\text{LiCoO}_2\text{--Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ composite electrode/ $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte/polymer electrolyte/Li foil battery at a constant current of 32 $\mu\text{A cm}^{-2}$ (3.6 mA g^{-1} of LiCoO_2) at 120 °C. The charge capacity was limited to 120 mAh g^{-1} . The circles indicate points where the electrochemical measurements were halted during charge-discharge process in order conduct XRD measurements.

Fig. 5

(a) *Ex situ* powder X-ray diffraction patterns of electrochemical samples halted during the charge process in ASS-LIB. The charging capacity is (i) 0 mA h g⁻¹, (ii) 20 mA h g⁻¹, (iii) 40 mA h g⁻¹ (iv) 60 mA h g⁻¹, (v) 80 mA h g⁻¹, (vi) 100 mA h g⁻¹ and (vii) 120 mA h g⁻¹. (viii) *Ex situ* powder X-ray diffraction patterns of samples halted after the discharge process. (b) Lattice parameter *c* of LiCoO₂ at each electrochemical sample.

Fig. 6

Electrochemical charge-discharge profile of LiCoO₂-Li_{2.2}C_{0.8}B_{0.2}O₃ composite electrode/Li_{2.2}C_{0.8}B_{0.2}O₃ electrolyte/polymer electrolyte/Li foil battery cycled under 20 cycles at a constant current of 64 μA cm⁻² (7.1 mA g⁻¹ of LiCoO₂) at 120 °C. Charge capacity limited to: (a) 60 mAh g⁻¹, (b) 80 mAh g⁻¹, (c) 100 mAh g⁻¹, (d) 120 mAh g⁻¹.

Fig. 7

Polished cross-sectional SEM image of the composite electrode part of ASS-LIB after 5 cycles (Charge capacity limited to 120 mAh g⁻¹).

Fig. 8

Impedance plots of ASS-LIB after charge process at each cycle. Charge capacity limited to: (a) 60 mAh g⁻¹, (b) 80 mAh g⁻¹, (c) 100 mAh g⁻¹, (d) 120 mAh g⁻¹.

Figure 1 (T. Okumura *et al.*)

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Figure 6 (T. Okumura *et al.*)

Figure 7 (T. Okumura *et al.*)

Figure 8 (T. Okumura *et al.*)