Highly Cyclable All-Solid-State Battery with Deposition-Type Lithium Metal Anode Based on Thin Carbon Black Layer

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A thin carbon black (CB) layer on a metal current collector is used as a substrate of a deposition-type Li metal anode for a sulfide-based all-solid-state battery (ASSB). In this ASSB, the capacity of the CB layer is set to \( \approx 5\)–10% of the cathode. Therefore, the anode soon overcharges and a large proportion of the Li ions precipitate as Li metal on the anode during the charging process, thus this precipitated Li works as a Li metal anode. This CB-based anode effectively suppresses short circuit of the cell, and an ASSB with this anode has shown an excellent cycle property of over 150 cycles with good capacity retention. From measurements involving cross-sectional scanning electron microscopy, deposited Li metal layer at the CB/Ni interface is observed. It is also found that the addition of metal particles in the CB-based anode drastically improves cell performance by extending the cycle life. An ASSB with an Ag/CB-based anode is operated over 700 cycles at 3 mA cm\(^{-2}\) current density (0.5 C) with a capacity retention of \( \approx 86\% \) after 700 cycles.

1. Introduction

The history of secondary batteries with Li metal anodes, having a high theoretical specific capacity of 3860 mAh g\(^{-1}\) and the most negative electrochemical potential among anode materials, began from the Li/Li\(_2\)TiS\(_2\) system, the cyclable charge–discharge operation of which was confirmed by Whittingham\(^{[1]}\) in 1976. After much effort in developing such batteries, the first portable phone equipped with a Li/MoO\(_2\)-type secondary battery was commercially released in 1988. Soon after its release, however, ignition accidents frequently occurred, and it quickly faded from the market the next year.

Instead of the Li metal anode, various carboneous anodes (the so-called lithium ion batteries [LIBs]) emerged and took over the market. Since then they have been used to power a wide range of portable devices and, in particular, a number of pure electric and plug-in hybrid vehicles. The anode was coupled with a lithium cobalt oxide (LiCoO\(_2\) (LCO)) cathode developed by Mizushima et al.\(^{[2,3]}\). The LCO cathode has a very high redox potential (\( \approx 4\) V) and releases Li ions during charge, which can lithiate the carboneous anode, enabling its use as a Li source during discharge. Since the first product release, the basic concept of the LIB has not been largely altered, and many LIBs still use carboneous anodes, such as graphite, and lithium cobalt oxide cathodes, which include not only LCO but also Li[Ni,Co,Al]O\(_2\) (NCA) and Li[Ni,Co,Mn]O\(_2\) (NCM) cathodes.

The capacities of conventional carbonaceous anodes, however, are approaching their theoretical limits, and the use of Li metal anodes is regaining serious attention regarding secondary LIBs. However, secondary batteries with Li metal anodes have not revived in the market after the fade-out of the early ones. There are two major difficulties in using Li metal anodes: dendrite formation and low coulombic efficiency (CE). Under a typical operating condition of an LIB, Li metal easily grows dendritically on the substrate, leading to poor CE and sometimes short circuit penetrating through the separator and reaching the cathode. It is widely accepted that this short circuit is the reason for the ignition of early secondary batteries with Li metal anodes. Although several approaches have been developed for reducing Li dendrite formation, this phenomenon has not been sufficiently suppressed.

Low CE is induced by not only dendritic growth of the Li metal but also the subsequent destruction and rebuilding of the solid electrolyte interphase (SEI) according to the cycle. When a graphite-based anode is used, liquid electrolyte is electrochemically reduced and forms a stable SEI on the surface, which inhibits the further reduction of the electrolyte. The SEI on a Li metal anode, however, breaks easily and does not stop the reaction of the electrolyte, and the Li metal is exhausted to form a new SEI.
The currently reported CE of a Li metal anode is \( \approx 99\% \) at most, which means the bulk of the Li ions, initially introduced in the cell by the cathode, is consumed within \( \approx 100 \) cycles. The Li foil installed in the anode usually works as a large Li reservoir, but it decreases the energy density and consumption of the electrolyte. In addition, Li foil is not favorable in an actual manufacturing.

To overcome these difficulties, we propose using an all-solid-state battery (ASSB). Among several types of ASSBs, the sulfide type is highly anticipated to realize various commercial products such as batteries for electric vehicles. Therefore, we used sulfide-type ASSBs in this study. One advantage of these ASSBs is that the sulfide SE is usually relatively soft and deformable. It deforms easily to form a densely packed structure only by cold pressing, and the SE particles connect intimately with low grain boundary resistances. Therefore, the sintering process, which is usually essential for oxide-type ASSBs, is not necessary.

Some sulfide SEs are not only stable against both 4-V-class cathodes and Li metal but exhibit an ionic conductivity exceeding 1 mS cm\(^{-1}\). Although this conductivity is lower than that of liquid electrolytes (\( \approx 10 \) mS cm\(^{-1}\)), there is a significant advantage for SEs in that the transport number is unity, i.e., only Li ions contribute to the current flow. Taking into consideration that the transport numbers of many liquid electrolytes are around 0.3–0.5, an ASSB should work as well as conventional LIBs.

However, the interfacial resistivity between the SE and cathode is large, which is believed to be induced through a Schottky barrier at the interface\([7]\) or mutual diffusion of component atoms of the SE and cathode, such as S, P, O, and transition metals, leading to decomposition products forming at the interface.\([8]\) To overcome this difficulty, Ohta et al.\([7]\) interposed an oxide buffer layer, such as Li\(_2\)Ti\(_3\)O\(_4\), at the interface between the active material and SE to shield the SE layer electronically from the high-voltage cathode. The effect of this buffer layer was surprisingly prominent. The interfacial resistivity decreased drastically; finally, the power density of ASSBs became comparable with that of commercial LIBs.\([9]\) This has spurred a vast amount of studies on the improvement of the barrier layer on cathode materials.\([8,10–18]\)

As the SE used in an ASSB is incombustible, using an ASSB reduces the risk of ignition or explosion. Currently, there are numerous efforts to develop ASSBs, particularly regarding electric vehicles. SEs with ionic conductivities exceeding 10 mS cm\(^{-1}\) have recently been reported,\([19–21]\) further accelerating the study of ASSB.

We consider that an ASSB with a Li metal anode is a good combination. SEI from the SE does not form on the anode, and a high CE is expected. Lithium foil is not required for an anode in an ASSB because a Li reservoir is not necessary as the CE is sufficiently high (typically \( > 99.9\% \)). As Li ions are released from the cathode, they can be reduced on the anode and act as a Li metal anode. This can be the ultimate anode (deposition-type Li metal anode) because it enhances the energy density of the cell the most and simplifies the production process as Li foil is not required.

Regarding Li dendrite formation, Monroe and Newman\([22,23]\) once suggested that an SE with a sufficiently high shear modulus, which most inorganic SEs exhibit, may physically suppress Li dendrite growth. However, this idea is no longer accepted because several research groups have recently reported cases in which inorganic SEs paired with a Li metal anode caused short circuit.\([24–28]\) This phenomenon is usually attributed to Li growing on the surface of the SE and propagating through the grain boundaries to the counter electrode. This means that only sufficiently impervious SE layers can physically block the dendritic growth of the Li metal. Only thin-film batteries based on lithium oxynitride (LiPON) film with very small capacities (\( \approx 100 \) \( \mu \)Ah cm\(^{-2}\)) are known to suppress Li dendritic growth.\([29]\) For large-capacity cells (\( \approx 1 \) mAh cm\(^{-2}\)), although many efforts are ongoing,\([26,30,31]\) there is currently no method for effectively suppressing short circuit.

In this study, we used an overcharge-type anode in sulfide-type ASSBs. The anode material, which is composed of carbon black (CB) particles and optionally metal particles, is coated on a current collector using a slurry-coating method. The capacity of the anode is set far less than that of the cathode (5–10\%), so that a large portion of the Li ions precipitate as Li metal on the anode during charge, thus less than that of the cathode. Therefore, we considered it as a deposition-type Li metal anode.

In combination with this anode, we fabricated pocky-type ASSBs (the electrode area is \( \approx 3 \) cm\(^2\)) with Argyrodite-type lithium phosphorus sulfur chloride (Li\(_6\)PS\(_5\)Cl\(_3\)) and Li\(_{0.9}\)Co\(_{0.05}\)Mn\(_{0.05}\)O\(_2\) cathode. The loadings of the cathode and anode were adjusted so that the anode capacity is \( \approx 5–10\% \) of the cathode (Figure S1, Supporting Information). We found that short circuit was effectively suppressed in this type of ASSBs.

We have reported this CB-based overcharge-type anode several times in our patent applications,\([32,33]\) a recent publication,\([34]\] and conferences.\([35,36]\) However, the discussion was limited and they mainly focused on the Ag-added CB-based anode. In this article, we explain various metal/CB-based anodes and their function in more detail and give a scientific explanation to the prodigious property of ASSBs with these anodes.

2. Results

Figure 1a,b shows the charge–discharge curves of ASSBs with an overcharge-type graphite-based anode and an anode without carbon (only Ni current collector) for comparison, respectively. The cycle test was conducted at 0.5 mA cm\(^{-2}\) (\( \approx 0.1 \) C) (CC–CV) for charge and 0.5 mA cm\(^{-2}\) (CC) for discharge between 4.1 and 2.5 V. There is a shoulder both in the charge and discharge curves for the graphite-based cell, but not in the noncarbon cell. Therefore, these shoulders denote the reaction in the graphite-based anode, and the other part represents the deposition and dissolution of Li metal. The CEs for both cells were 67\% and 62\%, respectively. The charge curves at the second cycle became flat and did not rise as the first cycle for both cells, indicating that they short-circuited during the second charge. (We stopped the charge of the graphite-based cell at \( \approx 100 \) mAh g\(_{\text{NCM}}\)\(^{-1}\) because it was clear that this cell had been short-circuited at this moment.) The poor CEs at the first cycle may also be due to the small short circuit during the charge. There may be another explanation about the flattening of the charge curve that it is due to reaction between the cathode and SE. We consider, however, it is not plausible because such a phenomenon was not seen using the CB-based anode as described later. Consequently, we could not find any evidence that the graphite-based anode suppresses short circuit.
Next, we measured an ASSB with the overcharge-type CB-based anode. For this measurement, after 0.5 mA cm\(^{-2}\) charge and discharge, the same as earlier, we continued the cycle test with 0.5 mA cm\(^{-2}\) charge (CC–CV) and 1.67 mA cm\(^{-2}\) (0.33 C) discharge (CC). Figure 2a shows the results. The cell showed excellent cycle performance with no short circuit over 150 cycles. Figure 2b shows the cycle property of the cell. The initial discharge capacity was 166 mAh g\(^{-1}\) (≈4.2 mAh cm\(^{-2}\)), and the capacity retention at the 150th cycle from the second cycle was 87.3%, corresponding to 99.91%/cycle. Apparently, this overcharge-type CB-based anode suppresses short circuit of the cell. The CE maintained at almost 100% until 150 cycles, evidence that short circuit did not occur throughout the 150 cycles.

Figure 3 shows a cross-sectional scanning electron microscopy (SEM) image of the graphite-based ASSB. Figure S2a–d, Supporting Information, represents the atomic distribution maps of C, S, and Ni, respectively, obtained through energy dispersive X-ray spectroscopy (EDX) measurement, and each layer was identified, as shown in Figure 3. The C-rich zone represents the graphite layer and the nonwoven fabric used to make the SE layer self-stand as described in the Experimental Procedures in the Supplemental Information. The S-rich layer represents the sulfide SE, from the SE and cathode layers, but the intensity in the cathode layer is weak because it contains SE of only about 15 wt%. The Ni-rich layer denotes the cathode layer. (Ni current collector was peeled off before SEM observation.) Although Li atoms cannot be detected with EDX, we can identify the Li layer because it appears as a vacant zone in the atomic distribution maps of S, C, Ni, Co, and P. In Figure 3, we see that a Li layer appears between the graphite and SE layers. It is naturally interpreted that the graphite layer, after it is fully lithiated, acts as the substrate of the Li metal growth because it is conductive.

Figure 1. a) Charge–discharge curves of ASSBs with graphite-based anode and b) without it (only current collector).

Figure 2. a) Charge–discharge curves and b) capacity retention and CE of ASSB with CB-based anode.
Figure 4, and S3a–d, Supporting Information, show the SEM and EDX results of the CB-based ASSB. Each layer was assigned in the same manner, as shown in Figure 3. A Li layer formed between the Ni current collector and CB layer. In other words, Li atoms passed through the CB layer and deposited at the interface of the CB layer and current collector. The same phenomenon was also seen when the current collector was stainless steel (SUS) (Figure S3, Supporting Information).

Next, we examined the effect of metal particles in the CB layer on the cell property such as rate capability and cyclability. For this purpose, we chose Ag (Dowa Corp., D_{50} = 60 nm), Zn (Aldrich, D_{50} = 80 nm), Sn (EM Japan, D_{50} = 60–80 nm), Al (New Metals & Chemicals Corp., D_{50} = 40–50 nm), and Ni (EM Japan, D_{50} = 70 nm) particles. We fabricated the metal powder containing anodes by mixing 1 g of metal particles and 3 g of CB with a binder solution to make the slurry. We then obtained metal powder containing CB-based anodes in almost the same process described in the Experimental Procedures in the Supporting Information, but the cathode capacity was slightly larger/C_{25}/C_{0} 2. We used SUS current collectors instead of Ni for this experiment.

Figure 5 shows the rate capabilities of CB-based anodes with and without metal particles. In this measurement, the cells charged at 0.6 mA cm^{-2} (CC–CV) and discharged at 0.6 mA cm^{-2} (first cycle), 2 mA cm^{-2} (second cycle), 3 mA cm^{-2} (third cycle), 4.5 mA cm^{-2} (fourth cycle), and 6 mA cm^{-2} (fifth cycle) (CC). The terminal voltages of the charge and discharge were set at 4.25 and 2.5 V, respectively. The rate capabilities of the Ag/CB- and Ni/CB-based anodes were almost equivalent to that of the pure CB-based anode, but those of the Sn-, Al-, and Zn/CB-based anodes were much less. The result of Zn/CB anode may be exaggerated for about 3% at 6 mA cm^{-2} because the capacity fading of Zn/CB anode is large at early stages, as shown in Figure 6 (=3% within first to fifth cycles, while <0.7% for other metals).

Figure 6 shows the discharge capacities and CEs of the ASSB with the metal/CB-based anode. We conducted a long cycle test with high current density at 3 mA cm^{-2} (0.5 C) with CC mode for both charge and discharge with terminal voltages of 4.25 and 2.5 V, respectively. The ASSBs with the pure CB- and Ni/CB-based anodes quickly short-circuited within a few cycles (not shown in Figure 6), probably because the current density was high. The cells with the Ag-, Zn-, Sn-, and Al/CB-based anodes charged and discharged over much longer cycles. The cells with the Zn-, Sn-, and Al-based anodes charged and discharged over around 400–500 cycles. (We stopped operations before the short circuit.) The CE of the Al cell becomes appreciably less than 100% several times, although the curve of the discharge capacity was very smooth. It soon recovered after several tens of cycles. It is interpreted that a small short circuit occurred due to the Li metal growth in the SE layer during the charge at these cycles, but the short circuit pass from the Li metal growth dissolved during the discharge gradually within the several tens of cycles.

Although the cells with the Sn-, Al-, and Zn/CB-based anodes showed improved cycle lifetimes compared with those with the CB-based anodes, the capacity retentions were poor. On the
contrary, the cell with the Ag/CB-based anode exhibited excellent cycle performance with a capacity retention of 86% at the 700th cycle (99.98%/cycle on average), which corresponds to 80% after 1000 cycles.

3. Discussion

We observed that the deposited Li layer appeared between the CB layer and Ni current collector. This seems unusual because the CB layer is conductive and likely works as a substrate of Li deposition in the same way with the graphite layer.

We interpret this phenomenon as follows. Figure 7a shows a schematic of the ASSB with the CB-based anode at the initial stage of the charge. In this stage, all Li ions are electrochemically reduced and accumulated in the CB layer. As the reaction continues, the reaction potential descends and reaches the Li potential (0 V vs Li⁺/Li). Lithium deposition, however, does not begin right away because of the over potential, and the CB layer continues accumulating Li atoms and oversaturates. If the oversaturated CB particles are energetically unstable, Li metal can precipitate from them. In this case, precipitating in the pores is advantageous because Li does not have to push aside any materials on the CB particles. If the overpotential of the electrochemical deposition of Li metal at the CB/SE interface is sufficiently large, such electrochemical deposition does not occur, and the precipitation of Li metal in the pore proceeds dominantly (Figure 7b). Finally, the pore is totally filled with the precipitated Li metal and overflows to push out the current collector (Figure 7c) probably because the adhesion between the current collector and CB layer is weaker than that of the CB layer and SE layer (Figure S4, Supporting Information). Therefore, only the current collector is pushed out with CB/SE interface adhered.

Unfortunately, we have not got a clear evidence to prove this hypothesis, in particular, if the oversaturation of CB occurs to considerable amount or not, yet. However, a similar phenomenon, where oversaturation leads to a selective growth, is also seen in Vapor-Liquid-Solid (VLS) growth of Si nanowire. In this VLS growth, a gold nanoparticle on a c-Si substrate becomes a liquid droplet of oversaturated Au–Si alloy as the Si deposition proceeds, and Si precipitates epitaxially on the c-Si substrate because it is energetically advantageous, and finally it leads to epitaxial growth of Si nanowire.

On the contrary, the graphite-based anode did not suppress short circuit as did the CB-based anode. The reason is unclear, but we presume as one interpretation that it is because graphite is crystalline. As the arrangement of Li atoms in the crystal is well defined, it may be difficult to accumulate excess Li in the crystal, making overcharge difficult. There is alternative explanation that the graphite particle is too large (D₅₀ = 15 μm). It will be clarified if we do the same experiment using graphite powder whose particle size is as small as that of CB, but we have not obtained such graphite powder yet.

Figure 8a shows a cross-sectional SEM image of the ASSB with the Ag/CB-based anode after the first charge. The deposited Li penetrates the Ag/CB layer, the same as the CB (without Ag) layer. Figure 8b shows the atomic map of Ag for the SEM image. A large proportion of Ag atoms have migrated to the Li layer and dispersed uniformly in the Li layer. This phenomenon strongly supports our hypothesis that Li metal precipitates in the pores among CB particles and moves toward the current collector through the pores. The added Ag particles stick on the surface of the CB particles and form an alloy with Li in the pores during charge, but precipitation of the pure Li metal does not occur during charge because Ag forms a continuous solid solution with Li.

Figure 7. Schematic figures of evolution of ASSB with CB-based anode during charge.
Finally Ag forms a very thin Li–Ag alloy and penetrates the CB layer through the pores among the CB grains. As Ag and Li move together in a form of a Li–Ag alloy, this illuminates the trajectory of Li atoms to the current collector through the CB layer.

Figure 8c,d shows a cross-sectional SEM image and Ag atomic map of the same ASSB after the first discharge. The Li layer has completely disappeared. A small gap is seen between the Ag/CB layer and current collector, which was probably generated while the cell was opened for sample preparation. A large proportion of Ag atoms in the Li layer did not go back in the Ag/CB layer after discharge but formed an Ag layer between the CB layer and current collector. This is probably because the outer pressure on the cell is not enough to push back the Li/Ag alloy into the pores among the CB grains. (It may be verified by charging the cell at much higher outer pressure.) As the Ag atoms do not go back into the pores, it indicates that Li atoms forming a Li/Ag alloy layer between the CB layer and current collector also do not go back into the pores during discharge. The Li atoms enter the CB particles from the interface and diffuse among the CB particles until they reach the CB/SE interface to leave the CB layer with electrochemical oxidation. The Li/Ag alloy layer having formed in the CB/current collector interface becomes Ag rich as the Li atoms leave for the CB layer, finally pure Ag atoms remain at the interface.

Cross-sectional SEM images of the ASSBs with Zn-, Sn-, Al-, and Ni/CB-based anodes after the first charge are shown in Figure S6a, S7a, S8a, and S9a, Supporting Information, and the atomic maps of C, S, and added elements (Zn, Sn, Al, Ni) are shown in Figure S6b–d, S7b–d, S8b–d, and S9b–d, Supporting Information, respectively. Lithium penetration also occurred for the Zn/CB- and Ni/CB-based anodes, but seems to have not for the Sn- and Al-based ones. There is a thin metal/C layer, however, between the Li and SE layers for both Sn- and Al/CB-based anodes, indicating that Li penetrated the CB layer a little and formed a Li layer within the CB layer. Also in the atomic map of C for Zn/CB anode, there is a thin C layer between the Li layer and the current collector, indicating that Ni is inactive to Li and gives no effect to the diffusion of Li in the CB layer. This result where the location of the Li deposition depends on the added metal was reproducible. At this moment, we cannot give a reasonable explanation for it. It may depend not only the added metal particles, but also some experimental conditions such as current density, amount of the added metal particles, thickness of the CB/metal layer, and so on. Further study is necessary to clarify this point. For these cells, dissolution of the metal atoms (Zn, Sn, Al, and Ni) was not observed. This is probably because they do not form a continuous solid solution with Li (Ni does not form alloy with Li), and only the precipitated pure Li metal moves and forms a Li layer in the CB/current collector interface or within the CB layer, and the metal atoms stay at the initial position in the form of Li metal alloy.

We consider it reasonable to attribute the reason that the CB-based anodes inhibit short circuit of the cell to this Li penetration. We presume that this phenomenon separates the electrochemical reaction site and precipitation site. Without the CB
layer, Li ions are electrochemically reduced and concurrently precipitate as Li metal on the current collector. If there is a mound on the deposited Li metal, it strongly attracts surrounding Li ions and induces local growth on it, leading to short circuit. With the overcharged CB layer, however, a Li ion electrochemically reacts at the SE/CB interface but may not precipitate at the same time. It is accumulated once in the CB layer and other Li atom precipitates instead of the incident Li in other place, most likely in the pores among CB grains, as explained earlier. In this case, no electrochemical reaction occurs there, no further Li growth on the deposited Li occurs; therefore, short circuit is suppressed.

Short circuit of the cell is further inhibited largely by adding metal particles (except Ni) to the CB layer. We consider this is because metal particles on the surface of the CB particles make Li deposition (alloying) in the pores easier because the electrochemical potentials of the Li alloying with the metals and subsequent Li precipitation are higher than that of Li deposition on carbon.\footnote{It effectively sends the Li atoms in the CB particles into the pores and keeps the CB particles from too much over-saturation, which probably hampers the further accumulation of Li atoms in the CB particles and leads to precipitation of Li metal at the CB/SE interface, causing short circuit of the cell. Ni particles, on the contrary, do not help send the Li atoms in the CB particles to the pores because it is inert to Li, and they do not contribute to inhibit the short circuit.}

The discharge rate capability of Ag- and Ni/CB-based anodes were almost the same as that of the pure CB-based anode, but Zn-, Sn-, and Al/CB-based anodes became poorer regarding this capability. One possible explanation is that the added metal particles electrochemically reacted with SE and formed an insulative barrier on the CB/SE interface. To confirm this, we conducted impedance measurements. If there is such an insulative barrier, it may produce an additional semicircle in the Cole–Cole plot of the cell. The cells first were charged at 0.6 mA cm$^{-2}$ to 4.25 V, and the impedance measurements were conducted using electrochemical impedance spectroscopy (Autolab, FRA32M) between 1 and 10 MHz. The results for the CB-, Ag/CB-, and Sn/CB-based anodes are shown in Figure S10, Supporting Information. We observed no significant differences among cells, and no additional semicircle appeared for the cells with the Ag- and Sn/CB-based anodes. Therefore, this hypothesis should be rejected. Instead, we consider it is attributed to the diffusion of Li atoms in the CB layer.

As we explained earlier, Li atoms stored in the anode in the form of Li metal during the charge enter the CB particles from the interface between the CB layer and the Li metal layer, and diffuse among them when the cell is discharged. Therefore, a good contact among CB particles is necessary for good discharge. When the CB layer contains Sn, Al, and Zn particles, however, the Li layer forms in the CB layer and damages it. Moreover, Sn, Al, and Zn form an alloy and expand, potentially loosening the contact among CB particles. When the added metal is Ag or Ni, however, a Li layer is formed at the CB/current collector interface, and the CB layer remains almost intact. Although Ag forms a Li/Ag alloy and expands, it flows to the CB/current collector interface and may not disrupt the connections between CB particles. Therefore for the relatively poor capacity retentions of Zn-, Sn-, and Al/CB-based anodes is also explained in the same manner. The CB layers containing these metals degrade according to the formation of a Li layer and the volumetric expansion and contraction of these metal particles. Further study, however, is necessary to elucidate this point.

For Ag, effective short-circuit suppression, good rate capability, and good capacity retention are simultaneously achieved. There may be another explanation for these good properties attributing to the formation of an Ag layer at the CB/current collector interface after discharge. To examine this hypothesis, we deposited a $\approx$200 nm-thick Ag layer on a SUS current collector and coated a CB (without Ag particles) layer on it. We used it as the anode of an ASSB so that an Ag–Li alloy layer would form between the CB layer and current collector during charge and evaluated its performance. We found that the discharge capacity and rate capability were almost the same as that of the Ag/CB-based anode (Figure S11, Supporting Information), but the cell short-circuited within $\approx$10 cycles during the 0.5 C charge–discharge test. (This result was reproducible.) Although it is still not clear if this Ag layer does not have any effect in suppressing short circuit, the main reason for the effective short-circuit suppression with the Ag/CB-based anode should be attributed to the Ag particles in the Ag/CB layer. Although a large proportion of Ag atoms leave the CB/current collector interface during discharge, the residual Ag atoms in the CB layer probably play an important role in suppressing short circuit. At this moment, however, we cannot give a reasonable explanation how the small amount of residual Ag atoms suppresses the short circuit. Further study is necessary to elucidate this point.

4. Conclusion

Thin carbon layers on metal current collectors were examined as deposition-type Li metal anodes for ASSBs. The ASSB with the graphite-based anode soon short-circuited, the same as the anode without a carbon layer (only Ni current collector). On the contrary, the CB-based anode was prodigiously effective in suppressing short circuit of the cell, and the ASSB with this anode was operated over 150 cycles with rather good capacity retention, $\approx$87% at the 150th cycle, without short circuit. From a cross-sectional SEM image, it was observed that Li atoms penetrate the CB layer and precipitate between the current collector and CB layer. The properties of the CB-based anode drastically improved by adding metals, especially Ag particles. The ASSB with the Ag/CB-based anode exhibited excellent cycle performance with a capacity retention of $\approx$86% at the 700th cycle.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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