Improvement of the Anode Properties of Lithium-Ion Batteries for SiO\textsubscript{x} with a Third Element

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ABSTRACT: Silicon oxide (SiO\textsubscript{x}) has been placed into practical use as an anode active material for next-generation Li-ion batteries because it has a higher theoretical capacity than graphite anodes. However, the synthesis method is typically vapor deposition, which is expensive, and the poor electron conductivity of SiO\textsubscript{x} restricts high performance. In this study, we prepared M/SiO\textsubscript{x} active materials consisting of SiO\textsubscript{x} and a third element (M = Al, B, Sn) using a low-cost mechanical milling (MM) method and investigated their electrode properties as Li-ion battery anodes. Also, the authors added a third element to improve the conductivity of the SiO\textsubscript{x} matrix. Al, B, and Sn were selected as elements that do not form a compound with Si, exist as a simple substance, and can be dispersed in SiO\textsubscript{x}. As a result, we confirmed that SiO\textsubscript{x} has a nanostructure of nanocrystalline Si dispersed in an amorphous-like SiO\textsubscript{x} matrix and that the third element M exists not in the nanocrystalline Si but in the SiO\textsubscript{x} matrix. The electron conductivity of SiO\textsubscript{x} was improved by the addition of B and Sn. However, it was not improved by the addition of Al. This is because Al\textsubscript{2}O\textsubscript{3} was formed in the insulator due to the oxidization of Al. The charge–discharge cycle tests revealed that the cycle life was improved from 170 cycles to 330 or 360 cycles with the addition of B or Sn, respectively. The improvement in electron conductivity is assumed to make it possible for SiO\textsubscript{x} to react with Li ions more uniformly and form a structure that can avoid the concentration of stress due to the volume changes of Si, thereby suppressing the electrode disintegration.

1. INTRODUCTION

Lithium-ion batteries have been used in many types of devices, such as power supplies for laptop computers, because they are lighter and have a higher energy density than other secondary batteries. In recent years, owing to the demands of the higher performance of portable electronic devices and the electrification of automobiles, there has been a strong demand for energy densities higher than those exhibited by conventional materials. Therefore, it is necessary to further increase the capacities of the cathode and anode materials.

Currently, graphite is used as the anode material, and its initial capacity reversibility has reached 90% or higher. In addition, it has excellent cycle properties because the volume change during charge–discharge is small. However, its theoretical capacity is only 372 mA h g\textsuperscript{-1}, and it is not expected to exceed this theoretical capacity.

Therefore, Si is an attractive active material as an anode for lithium-ion batteries because it is the same group 14 element as graphite and repeatedly alloyed and dealloyed reversibly with lithium ions. Si is an indispensable material for increasing capacity because it has a theoretical capacity (3600 mA h g\textsuperscript{-1}) that is nearly 10 times that of graphite. However, the smooth redox reaction of alloying and dealloying with lithium ions cannot be performed because the electron conductivity of Si is low, and the diffusion of lithium ions is slow. Additionally, it causes a large volumetric change of approximately 380% during lithiation and delithiation, and the stress generated at that time causes cracks in the Si particles, causing the particles to fall out of the current collector. As a result, a rapid capacity decrease occurs because the contact between the active material, surrounding Si particles, and conductive material is interrupted; the Si particles are electrically isolated, and they are not involved in the subsequent charge–discharge reaction.

To address this problem, various approaches have been carried out.\textsuperscript{1–20} For example, it has been reported that the yield stress exceeds the stress generated during charging by setting the Si crystallite size to 10 nm or less so that the cracking of Si particles is suppressed and the cycle properties are improved. In addition, it has been reported that the cracking of Si particles can be suppressed and the cycle properties can be improved by reducing the Si particle size to 150 nm or less.\textsuperscript{21}

As a result of such various developments, in recent years, SiO\textsubscript{x} has been installed in the anode material for Li-ion
batteries of electric vehicles because it enables a longer driving range. SiO$_2$ has a higher capacity than the current graphite. SiO$_2$ is a mixed phase consisting of Si and SiO$_2$. Our group has previously revealed that SiO$_2$ is an amorphous material composed of a three-dimensional SiO$_4$ tetrahedral network similar to silica (SiO$_2$) glass and metallic Si clusters and that the Si clusters are finely dispersed in the SiO$_2$ matrices. Therefore, the SiO$_2$ matrix is considered to exhibit better cycle properties than Si alone by relaxing the stress due to volume expansion during charge and discharge of Si.

However, the capacity reduction of SiO$_2$ during the charge—discharge cycle is remarkable compared to that of graphite. It is expected that the mixing ratio of SiO$_2$ to graphite tends to increase because further increases in the driving range and extension of battery life are required. Therefore, it is necessary to improve the anode properties of SiO$_2$.

The main efforts to improve the anode properties of SiO$_2$ have involved improving Si particles and imparting conductivity. Meanwhile, there are no reports that focus on the properties of a SiO$_2$ amorphous matrix with a third element. Therefore, the authors developed a new approach to improve the anode properties of SiO$_2$ by improving the poor electron conductivity of the SiO$_2$ matrix.

![Figure 1](image1.png)

**Figure 1.** Schematic illustration of the target SiO$_2$ structure.

Silicon oxides prepared using the mechanical milling method showed irregular shapes. Therefore, it can be considered that the influence of the third element on the size and shape of the secondary particles was small. Subsequently, the shapes of the primary particles could not be clearly confirmed. Therefore, the primary particles are expected to have mixed on a scale smaller than several hundred nanometers.

### 2. RESULTS AND DISCUSSION

#### 2.1. Observation of Powder Shape

**Figure 2** shows the scanning electron microscopy (SEM) images of SiO$_2$ and M/SiO$_2$ powders prepared using the mechanical milling method. In each case, secondary particles with a size of approximately 5 μm were observed. The secondary particles showed irregular shapes. Therefore, it can be considered that the influence of the third element on the size and shape of the secondary particles was small. Subsequently, the shapes of the primary particles could not be clearly confirmed. Therefore, the primary particles are expected to have mixed on a scale smaller than several hundred nanometers.

**Figure 2.** SEM images of milled SiO$_2$ and M/SiO$_2$ (M = Al, B, Sn).

#### 2.2. Structural Analysis of Powder

There was concern that each raw material would react or that the third element would dissolve in Si because of the high energy when the balls collide with each other in the powder prepared using mechanical milling. First, we checked whether the prepared material had a target structure (**Figure 1**). It has a structure of cluster-shaped Si dispersed in a SiO$_2$ matrix in which the third element (Al, B, Sn) is dispersed.

**Figure 3a** shows the X-ray diffraction (XRD) patterns of the SiO$_2$ and M/SiO$_2$ powders prepared using mechanical milling.
The Si diffraction peaks of (111), (220), and (311) were observed for all of the powders. The crystallite size of these Si was calculated from the Scherrer equation and was found to be approximately 8–12 nm. In contrast, the diffraction peak of SiO$_2$ did not appear. This is probably because SiO$_2$ became amorphous-like owing to the high-energy milling of the mechanical milling.

Regarding the third element, the diffraction peaks of elemental substances, derivative compounds, oxides, etc. were not confirmed. First, we investigated the Si diffraction peak of (111) at approximately 28° that the third element was not dissolved in Si to disperse the third element in the SiO$_2$ matrix. Figure 3b shows the X-ray diffraction pattern in the range of 25–32° of SiO$_2$ and M/SiO$_2$ (M = Al, B, Sn) powders. If the third element is dissolved in Si, the crystal lattice of Si should expand or contract and the diffraction peak should shift to the low- or high-angle side. However, by comparing the powder with and without the addition of the third element, it was found that the position of the Si diffraction peak (111) at approximately 28° did not change at all. Thus, it is considered...
that the third element was not dissolved in Si, but it became amorphous and existed in the SiO$_2$ matrix as intended.

From these results, it was confirmed that the powder with the third element prepared using mechanical milling was composed of amorphous-like SiO$_2$ and nanocrystalline Si, and the third element was not present in Si.

Furthermore, the structures of the prepared powders were analyzed. Figure 4a shows a low-magnification bright-field image of the edge of the SiO$_2$ particles using transmission electron microscopy. It is considered that the black spot-like part in the particle is Si and the gray area is SiO$_2$. It was found that Si and SiO$_2$ were finely pulverized after the mechanical milling treatment and Si formed a structure dispersed in the SiO$_2$ matrix. Figure 4b shows a high-magnification bright-field image and electron diffraction of a SiO$_2$ powder using transmission electron microscopy. Most of the gray areas, except the black spots, showed a halo pattern. It was considered that the areas were amorphous Si oxide because energy-dispersive X-ray spectroscopy (EDS) analysis of the part revealed that Si comprised 78 wt %, while O comprised 22 wt %. On the other hand, black spot-like parts of red dashed line part (1) was confirmed to be elemental Si using electron diffraction. It was also found that the size of the Si microcrystals was approximately 10 nm. These results support the structure in which fine Si is dispersed in an amorphous SiO$_2$ matrix, as predicted based on XRD results.

Similarly, we found that the black spot-like part of red dashed line parts (2) and (3) of the powders with third elements Al (Figure 4c) and Sn (Figure 4d) was elemental Si using electron diffraction. It was also found that the size of the Si microcrystals was approximately 10 nm. Meanwhile, there was a difference in the amorphous SiO$_2$ matrix, which was confirmed in the SiO$_2$ particles. EDS analysis of these areas revealed compositions of Si 73 wt %, O 24 wt %, and Al 1.8 wt % for the Al/SiO$_2$ powder, and Si 72 wt %, O 23 wt %, and Sn 2.1 wt % for the Sn/SiO$_2$ powder. Therefore, it is highly possible that the added third element is dispersed in the amorphous SiO$_2$ matrix.

The distribution of the third element was confirmed from the bright-field image and the EDS mapping images of Al, B, and Sn of the M/SiO$_2$ particles in Figure 5. In the case of the powder with Al or Sn, elemental Al and Sn in microcrystals, such as Si, that were confirmed in Figure 4b–d were not confirmed, and it was found that Al and Sn were uniformly dispersed throughout the powder. Meanwhile, with respect to the powder with B, B was dispersed throughout the powder, but some large particles of approximately 1 μm were confirmed. It is presumed that the mechanical milling power was insufficient under the same mechanical milling conditions because B (Mohs hardness 9.5) is harder than Al (Mohs hardness 2.9) and Sn (Mohs hardness 1.8).

Figure 6 shows the measurement results of the electrical resistivity of the pressed M/SiO$_2$ powder. It was confirmed that the addition of B or Sn improved the electron conductivity by nearly an order of magnitude compared to the powder without the addition of the third element. On the other hand, the electron conductivity of the powder with Al did not improve because the electrical resistivity was equivalent to that of SiO$_2$.

The reaction Gibbs energies ($\Delta G^\circ$) of Al$_2$O$_3$, B$_2$O$_3$, and SnO$_2$ are −594.61, 181.25, and 340.93 kJ mol$^{-1}$, respectively.

$$3\text{SiO}_2 + 4\text{Al} \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3$$

$$3\text{SiO}_2 + 4\text{B} \rightarrow 3\text{Si} + 2\text{B}_2\text{O}_3$$

$$\text{SiO}_2 + \text{Sn} \rightarrow \text{Si} + \text{SnO}_2$$
In the case of the powder with B and Sn, $\Delta G^\circ$ was a positive value, and it can be found that the presence of SiO$_2$ was more stable than that of B$_2$O$_3$ and SnO$_2$. Meanwhile, in the case of the powder with Al, $\Delta G^\circ$ was negative, and it can be found that the presence of Al$_2$O$_3$ was thermodynamically more stable than SiO$_2$. Therefore, it is presumed that Al$_2$O$_3$ which is an insulator, was formed because the oxidation reaction proceeded during sample preparation.

From these results, it is inferred that B and Sn may have been dissolved in the SiO$_2$ matrix during the mechanical milling method.

2.3. Charge–Discharge Properties. Figure 7 shows the dependence of the discharge capacity of M/SiO$_2$ ($M = \text{Al, B, Sn}$) electrodes on cycle number in 1 M LiTFSA/PC solution with a charge capacity limit of 1000 mA h g(Si)$^{-1}$ (the result of Si alone electrode is also shown).

![Figure 7. Dependence of the discharge capacity of M/SiO$_2$ ($M = \text{Al, B, Sn}$) electrodes on cycle number in 1 M LiTFSA/PC solution with a charge capacity limit of 1000 mA h g(Si)$^{-1}$ (the result of Si alone electrode is also shown).]

Sn) electrodes on the cycle number in 1 M lithium bis(trifluoromethanesulfonyl)amide (LiTFSA)/propylene carbonate (PC) solution with a charge capacity limit of 1000 mA h g(Si)$^{-1}$ (the result of Si alone electrode is also shown).

To determine the reason for the improvement of the electrode properties as described above, an active material consisting only of a matrix was prepared and the electrode reaction was investigated. In addition, in the M/SiO$_2$ samples, the reactivity with lithium ions due to the addition of the third element was investigated. In other words, to investigate how much lithium ions are occluded, we decided to conduct a test to examine the amount of lithium ions reacted without capacity regulation. Figure 8a shows the dependence of the discharge capacity of SiO$_2$ and M/SiO$_2$ ($M = \text{Al, B, Sn}$) electrodes on cycle number in 1 M LiTFSA/PC at 0.38 A g$^{-1}$. The temperature and potential range for testing were set to 303 K and 0.005–2.000 V vs Li$^+/\text{Li}$, respectively. It was found that the electrodes with B and Sn showed higher capacities than those of SiO$_2$ without the addition of the third element. Originally, SiO$_2$ hardly reacted with Li ions and did not exhibit Li storage properties. However, it has recently been reported that, when SiO$_2$ becomes amorphous, the reaction

$$5\text{SiO}_2 + 4\text{Li}^+ + 4e^- \rightarrow 2\text{Li}_2\text{Si}_5\text{O}_3 + \text{Si}$$

proceeds, and it is possible to form silicon and lithium silicate ($\text{Li}_5\text{Si}_4\text{O}_{12}$), due to lithium-ion activity. 27 The authors confirmed from Figures 3 and 4 that SiO$_2$ is amorphous. In addition, the charge–discharge curves and dQ/dV curves after 10 cycles were newly investigated for SiO$_2$ and M/SiO$_2$ ($M = \text{Al, B, Sn}$) electrodes. As a result, it was found that the Si single-phase peak was observed even though these were matrix-only electrodes. In particular, it appears clearly near 0.5 V on the discharge side. This also suggests that reaction 1 is progressing. Therefore, in this study, it is considered that SiO$_2$ which became amorphous after mechanical milling, showed charge–discharge capacity. Furthermore, it is considered that the electrode with B and Sn showed higher capacity than the SiO$_2$ electrode because the reactivity with the lithium ions in the matrix was improved by the solid dissolution of B and Sn in the SiO$_2$ matrix and the uniform dispersion of B and Sn (Figure 8b). Meanwhile, it is considered that Al was oxidized and formed amorphous Al$_2$O$_3$, and it is dispersed in SiO$_2$ because the electron conductivity of Al/SiO$_2$ is equivalent to that of SiO$_2$. Therefore, it is presumed that the capacity of the Al/SiO$_2$ electrode did not increase because the reactivity with lithium ions could not be improved and reaction 1 was not promoted.

From these results, we consider the mechanism of extending the life of the cycle properties by adding B and Sn to SiO$_2$. Figure 9 shows a schematic illustration of the M/SiO$_2$ ($M = \text{B, Sn}$) performance improvement mechanism. Si exhibits the following two-step lithium alloying reaction during charging. 28–31 If reaction 3 progresses, the electrode will collapse because the volume change (380%) due to the formation of Li$_{1.75}\text{Si}$ in reaction 3 is larger than the volume change (240%) due to the formation of Li$_{2.00}\text{Si}$ in reaction 2 ("a" in a-Si and a-Li$_{2.00}\text{Si}$ means amorphous, and "c" in c-Li$_{1.75}\text{Si}$ means crystalline).

$$\text{a-Si} + 2\text{Li}^+ + 2e^- \rightarrow \text{a-Li}_2\text{Si}_{0.00} \quad (2)$$

$$\text{a-Li}_2\text{Si}_{0.00} + 1.75\text{Li}^+ + 1.75e^- \rightarrow \text{c-Li}_1\text{.75}\text{Si} \quad (3)$$

In the case of a charge capacity limit of 1000 mA h g$^{-1}$, it is considered that lithium alloying of Si occurs locally because the electrodes without the addition of the third element or with the addition of Al have low reactivity with lithium ions in the SiO$_2$ matrix. As a result, Lili$_{1.75}\text{Si}$, which has a large volume...
change, was formed, which is thought to have caused electrode collapse and capacitance decline. Meanwhile, in the case of the electrode with B or Sn, the electron conductivity was improved, and the lithium-ion reactivity of the SiO2 matrix was increased. Thus, Si in the entire active material phase can easily react with lithium ions more uniformly. Therefore, it was possible to suppress the formation of Li2.00Si, which has a small volume change. Therefore, it is considered that the electrode with B or Sn improved the cycle properties because the stress due to the volume expansion of Si was difficult to concentrate during charging, and the damage to the electrodes was relatively small and the electrode collapse could be suppressed.

3. CONCLUSIONS

In this study, we prepared an active material (M/SiOx) with a third element (M = Al, B, Sn) in SiOx using a mechanical milling method and investigated the anode properties of Li-ion batteries. We confirmed that the structure of SiOx consists of nanocrystalline Si dispersed in an amorpha-like SiO2 matrix, and a third element is present in the SiO2 matrix but not in the nanocrystalline Si. The electron conductivities of B/SiOx and Sn/SiOx were higher than that of SiOx. Meanwhile, the electron conductivity of Al/SiOx was not higher than that of SiOx. This is because Al2O3 was formed in the insulator due to the oxidization of Al. In the cycle properties test conducted with a charge (Li storage) capacity limit of 1000 mA h g⁻¹, it was found that the cycle life was improved from 170 cycles to 330 or 360 cycles in the powder with B or Sn, respectively. When SiOx becomes amorphous, the reaction SiO2 + 4Li⁺ + 4e⁻ → 2Li2Si2O5 + Si (1) proceeds, and it is possible to form silicon and lithium silicate (Li2Si2O5), due to lithium-ion activity. The electron conductivity was improved because they were present in the matrix and B or Sn was dispersed in the SiO2 matrix. Therefore, it is considered that this is because SiO2 reacts uniformly with lithium ions due to the improvement of electron conductivity so that the stress due to the volume change of Si is difficult to concentrate and the destruction of the electrode is reduced.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation.

4.1.1. Preparation of SiOx and M/SiOx (M = Al, B, Sn) Powder.

Normal Si powder was prepared using a mass-produced gas-atomizing device. A flake-shaped Si raw material (purity 98.7%) of approximately 10–20 mm was placed in a crucible with pores of φ2.5 mm at the bottom of the crucible and heated and melted in a dry argon gas atmosphere using a high-frequency induction melting furnace. The molten metal was then discharged at 1823 K. N2 gas was sprayed on the molten metal at the part directly below the pores, and it was solidified at a cooling rate of approximately 10⁵–2 K s⁻¹. As a result, a gas-atomized Si powder was obtained. This powder was classified using a sieve with an opening of 300 μm.

To prepare the SiOx powder, a mixture of the above-mentioned gas-atomized Si powder and commercially available SiO2 powder (Kojundo Chemical Lab. Co. Ltd., purity 99.9%) was placed in an austenite-based stainless steel vessel together with high-carbon chromium-bearing steel (C 1%, Cr 1%) balls (φ19 mm) with a Si:SiO2 weight ratio of 54:46. The amount of each powder was 32.4 g for the Si powder and 27.6 g for the SiO2 powder. The weight of each ball was 12 kg. The weight ratio of the active material to the balls was 1:200.

To prepare the M/SiOx powder, a mixture of the above-mentioned gas-atomized Si powder and commercially available SiO2 powder and the third element M (Al: purity 99.9%, Kojundo Chemical Lab. Co. Ltd., B: purity 99.9%, Kojundo Chemical Lab. Co. Ltd., Sn: purity 99.0%, Kojundo Chemical Lab. Co. Ltd.) was placed in an austenite-based stainless steel vessel together with high-carbon chromium-bearing steel balls with a Si:SiO2:M weight ratio of 54:46:46.
ratio of 52:45:3. The amount of each powder was 31.4 g for Si powder and 26.8 g for SiO2 powder and 1.8 g for M (Al, B, Sn) powder. The weight of each ball was 12 kg.

These vessels were sealed, the interior was evacuated to a pressure of 0.1 MPa, and dry argon gas was sealed through gas replacement. The vessel was set in a vibrating ball mill device (MB-1 type manufactured by Chuo KakoKik Co. Ltd.). After 50.4 ks of mechanical milling treatment under the specified conditions (amplitude: ± 4 mm, frequency: 1200 rpm), the number of balls was increased, the weight ratio of the active materials to the balls was 1:300, and the mechanical milling was repeated for 50.4 ks.

The obtained mechanical milling powder was adjusted to a particle size of 10 μm or less due to collisions between powders in a 0.7 MPa N2 gas stream using a jet mill device (Co-Jet manufactured by SEISHIN ENTERPRISE Co. Ltd.) to crush the agglomerated powder. The target powder was obtained using this process.

4.1.2. Preparation of M/SiO2 and SiO2 Powder. For comparison, the same powder preparation was performed by adding only SiO2 and the third element M, without adding the gas-atomized Si powder. Consequently, the change in the properties (reactivity with lithium ions) of the SiO2 matrix due to the presence of the third element M was investigated.

Commercially available SiO2 powder was weighed and placed in a zirconia vessel filled with φ5 mm zirconia balls. Additionally, SiO2 powder and the third element powder (Al powder: purity 99.9% FUJIFILM Wako Pure Chemical Corporation, B powder: purity 99.0% FUJIFILM Wako Pure Chemical Corporation, Sn powder: purity 99.9%, 325 mesh RARE METALLIC Co., Ltd.) were placed in a zirconia vessel together with φ5 mm zirconia balls with a SiO2:M weight ratio of 94:6 (powder: 1.5 g, ball: 100 g).

The vessel was then sealed and set in the Premium Line planetary ball mill device (PL-7 type). Each powder was subjected to a mechanical milling treatment (SiO2: 7.2 ks, Al/SiO2: 14.4 ks, B/SiO2: 7.2 ks, Sn/SiO2: 7.2 ks) at 380 rpm to obtain the target powder.

4.2. Analysis of the Obtained Sample. The Si crystallite sizes of the prepared SiOx and M/SiO2 powders were measured using X-ray diffraction (XRD, RINT-2500, Rigaku Corporation, Cu Kα, 50 kV, 200 mA, 4° min−1, 20–60°).

The morphologies of the powders were observed using a scanning electron microscope (JSM-6490LV, 5 kV, JEOL Ltd.). In addition, the prepared powders were attached to conductive tape for observation.

The size and dispersibility of nanocrystalline Si and the third elements were observed using a transmission electron microscope (JEM-F200, 200 kV, JEOL Ltd.). The preparation of the observation samples is described below. First, the prepared powder was embedded in a conductive thermosetting resin. Subsequently, a carbon-protective film was deposited on the sample surface. Finally, these samples were cut to a size of approximately 10 μm × 10 μm × thickness 100 nm using a high-performance focused ion beam device (M14050, Mo mesh; Hitachi High-Tech Corporation) and used as an observation sample.

The electron conductivity of the obtained powder was evaluated using a powder resistivity measuring unit (MCP-PDS1, Nittosako Analytech Co. Ltd., four-probe device). Approximately 3 g of the prepared powder was placed in a sample holder of φ10 mm and compressed to a maximum of 64 MPa to measure the volumetric electron conductivity.

4.3. Electrode Fabrication. SiOx, M/SiO2 powder, SiOx, and M/SiO2 powder were each mixed with acetylene black, carboxymethyl cellulose, and styrene-butadiene rubber at a weight ratio of 70:15:10:5 using a kneading machine. These were then applied on a Cu foil with a coating amount of approximately 1.0 mg cm−2 to obtain a mixture electrode.

4.4. Cell Assembly and Charge–Discharge Tests. For the charge–discharge test, a 2032-type coin was constructed, composed of the above electrode as the working electrode, a Li metal sheet as the counter electrode, and a glass fiber filter as the separator. Lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) dissolved in propylene carbonate (PC) was used at the concentration of 1 M. Cell assembly and electrolyte preparation were conducted in an Ar-filled glovebox (Miwa MFG, DBO-2.5LNKP-TS) with an oxygen content less than 1 ppm and dew point below 173 K. Also, the authors want to show that this material can be used in cold climates. Therefore, it is evaluated on a PC (MP 223 K), which has a lower melting point than EC (MP 311 K) and is hard to freeze.

Regarding the SiOx and M/SiO2 electrodes, galvanostatic charge–discharge cycling tests were performed using an electrochemical measurement system in the potential range of 0.005–2.000 V vs Li+/Li. In addition, the current density and measurement temperature were set to 1.60–1.93 A g−1 (1C) and 303 K, respectively. Electrochemical measurements were performed with a charge limit of 1000 mA h g−1. In this study, we considered it to be a mixture of Si and SiO2 and treated SiO2 as being inactive with lithium ions. The theoretical capacitance was calculated assuming that only Si reacted with lithium ions. The maximum alloying composition in this case was calculated to be Li2Si4. In this case, the theoretical capacity of each powder was calculated to be 1931 mA h g−1 for SiO2, 1890 mA h g−1 for Al/SiO2, 1860 mA h g−1 for B/SiO2, and 1890 mA h g−1 for Sn/SiO2. Regarding SiO2 and M/SiO2 electrodes, galvanostatic charge–discharge tests were performed with a potential range of 0.005–2.000 V vs Li+/Li, a current density of 0.38 A g−1, and a measurement temperature of 303 K.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05689.

Charge–discharge curves and dQ/dV plots (PDF)

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ACS Omega 2022, 7, 1223–1231
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The manuscript was written through contributions of all authors.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was partially supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant nos. 19H02817, 19K05649, and 20H03099).

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