Reduction of external pressure on all-solid-state battery using SnO2-embedded porous carbon by CNT assistance

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Abstract
All-solid-state batteries (ASSBs) using non-flammable inorganic solid electrolyte are expected as a safety energy storage system that exhibits a high energy density. Since external pressure is required to maintain stable interface between active materials and solid electrolyte, the pressure applicable system make the cell modules larger and heavier, and it prevents the practical realization. In the present study, an ASSB system reduced external pressure was achieved by using single-walled carbon nanotube (SWCNT) assistance. The ASSB electrode mixed with SWCNTs showed high capacity and stable cycle performance even under a coind-type cell without additional external pressure which is conventionally used on an organic liquid electrolyte system. The unique characters of SWCNT which is high electrical conductivity and self-supporting force are effective to reduce external pressure of ASSBs. This result opens a new route to design a downsized battery cell.

KEYWORDS
all-solid-state batteries, external pressure, porous carbons, single walled carbon nanotubes, SnO2

1 | INTRODUCTION

An all-solid-state battery (ASSB) using solid electrolytes (SEs) has been expected to achieve enough performance for the application to electronic devices such as an electric vehicle. In the bulk type ASSB system, the ionic conduction between active material and SE is limited to the solid-solid interface. The charge-discharge process enable to be performed under highly dense electrode with high mechanical cell construction. Although alloying/dealloying reaction and conversion reaction on active materials such as SnO2 and Si show high theoretical capacity compared with existing carbon electrodes in Li ion battery system, the mechanical construction is necessary to maintain the Li ion conductive interfaces due to the large volume change during charge-discharge reactions. The pressure induced cell systems is impractical to apply them to electronic devices because it makes the cell larger and heavier. In order to realize high capacity and stable charge-discharge reaction on ASSBs, it is important to design stable electrode structure even under the volume changing without the excessive cell construction. Recently, we have reported that SnO2 nanoparticles embedded nanoporous carbon (SnO2/PC) shows high capacity and stable cycle stability in the ASSB system using a sulfide based solid electrolyte(SE), The carbon pores...
played an important role as a buffer space for volume expansion of SnO$_2$, and the performance of SnO$_2$/PC was improved compared with a mixture of SnO$_2$ and conductive carbon. The SnO$_2$/PC electrode is expected stably to work without high external pressure because the system does not require the direct contact between SnO$_2$ and SE. However, our previous study mentioned that the cell performance is still decreased with lower external pressure. In this study, we achieved an ASSB cell system using the SnO$_2$/PC electrode which shows high capacity and stable cycle performance under practical external pressure by applying single walled carbon nanotubes (SWCNTs). Here we note that multi-walled carbon nanotube assumes to be unsuitable as a binder due to the rigid and inflexible structure. Since SWCNTs show high electronic conductivity and the structure with the diameter of a few nm and the length of $\mu$m order forms a flexible and self-supporting structure without binder,$^{10,11}$ it has been considered as electrode and current corrector for battery application.$^{[12–14]}$ The SWCNT is expected to act as an electrical conductor and a binder between SnO$_2$/PC and SE.

SnO$_2$/PC with the average pore size of 140 nm was synthesized by a silica-colloidal templating method. The detail method and structural characterization are shown in our previous study.$^{[15,16]}$ The SnO$_2$ nanocrystals with the crystallite size from 3 to 5 nm loaded into pores of PC were confirmed by X-ray diffraction (XRD) measurement and high-resolution transmission electron microscopy (HR-TEM) observation (Figure S1 in the Supporting Information). Since the volume of SnO$_2$ is theoretically expands to 4.1 times against pristine SnO$_2$ by the full lithiation process of both conversion and alloying reactions, the loading amount of SnO$_2$ in SnO$_2$/PC was set to 75 wt%. The loading rate corresponds to 25 vol% against the total pore volume, whose value shows maximum electrochemical performance on the ASSB system.$^{[9]}$

The SnO$_2$/PC-CNT was formed a self-supporting sheet by mixing with only 2.9 wt% of SWCNT (Figure S2 in the Supporting Information). The detail morphology of a SnO$_2$/PC, a SnO$_2$/PC and SWCNT mixture (SnO$_2$/PC-CNT), and those mixtures with SE (SnO$_2$/PC//SE, SnO$_2$/PC-CNT//SE) was directly observed by scanning electron microscopy (SEM: JEOL JSM-7500FAM)(Figure S3). The porous structure of SnO$_2$/PC derived from SiO$_2$ template particles is confirmed before (Figure. S3a) and after (Figure. S3b) mixing with SWCNT. The diameter of SWCNT bundles is less than 500 nm. After mixing with SE (Figure. S3c and d), the porous structures are still maintained and each component seems to be mixed well; SWCNTs were loaded not only on SnO$_2$/PC but also SE. The composite structure that SWCNT partially covers SnO$_2$/PC is important for Li ion conduction which directly passes through the interface between SnO$_2$/PC and SE.

Figure 1 shows charge-discharge curves of SnO$_2$/PC//SE and SnO$_2$/PC-CNT//SE at 1, 2, 3, 10, 50, and 100th cycles under the external pressure of 3.5, 6.3, and 9.1 MPa. The large irreversible capacity at an initial cycle seems to stem from oxygen functional groups on porous carbons.$^{[9]}$ SnO$_2$/PC-CNT//SE showed higher capacity compared with that of the SnO$_2$/PC//SE cell at all the external pressures. The SnO$_2$/PC-CNT//SE even under the external pressure of 3.1 MPa is comparable performance to the SnO$_2$/PC//SE at 9.1 MPa. In SnO$_2$/PC//SE, the charge capacities derived from the dealloying reaction (0–0.9 V vs. Li) and the conversion reaction (0.9–2 V vs. Li) of SnO$_2$ with Li ion$^{[8]}$ are confirmed as shown in Figure 1A and dQ/dV plot (Figure S4 in the Supporting information). The charge-discharge capacity strongly depends on the external pressure. The capacity is increased with the increase of external pressure. In SnO$_2$/PC-CNT//SE, the both electrochemical reaction of conversion reaction and dealloying reaction are clearly confirmed as well as SnO$_2$/PC//SE at 9.1 MPa. The reactivities of SnO$_2$ particles with Li ions on the charge-discharge process are enhanced by SWCNT addition even at low external pressure.

Figure 2 shows the cycle performance of samples. In SnO$_2$/PC//SE, the initial Li extraction capacity measured under 3.5 MPa is 136 mAh g$^{-1}$, and the capacity is gradually increased to around 300 mAh g$^{-1}$ with cycling. The initial improvement of the charge capacity suggests that the outspread of Li ion conduction path from the pore entrance to inside of porous carbon. Since the irreversible capacity is expected to be increased by the spread of conduction area on carbon surface, the coulombic efficiency is low until 60 cycle. After that, the conduction path effectively work to improve the coulombic efficiency (Figure S5 in the Supporting Information). In SnO$_2$/PC-CNT//SE, the charge capacity measured at 3.5 MPa shows 755 mAh g$^{-1}$, which is obviously higher value compared with SnO$_2$/PC//SE. After 250 cycles, the capacity is 613 mAh g$^{-1}$; 81% of the initial charge capacity is maintained even after 250 cycles. The capacity is slightly increased with cycling unlike SnO$_2$/PC//SE. Since capacity does not increase at the initial cycle, the Li ion conduction path seems to easily form at an initial lithiation process. The charge capacity of SnO$_2$/PC-CNT//SE measured at 3.5 MPa is higher than that of SnO$_2$/PC//SE measured at any external pressure. A stable charge-discharge performance was confirmed on SnO$_2$/PC-CNT//SE under practical external pressure of 1 MPa by two spring washers for CR2032 coin cell. Although the capacity slightly decreases with cycling, the initial charge capacity reaches at 755 mAh g$^{-1}$ which is almost same as that of the cell under 3.5 MPa. The coulombic efficiency of SnO$_2$/PC-CNT//SE hardly depends on the external pressure and is drastically higher than that of SnO$_2$/PC//SE through initial several 10 cycle (Figure S5 in
FIGURE 1 Charge-discharge curves during the initial three cycles of (A, C, E) SnO$_2$/PC//SE and (B, D) SnO$_2$/PC-CNT//SE. The external pressure during charge-discharge cycle was (A, B) 3.5 MPa, (C, D) 6.3 MPa, (E) 9.1 MPa, respectively.

The stable charging and discharging reactions are achieved even under the practical external pressure by SWCNTs. It clearly indicates that the addition of SWCNT is effective to reduce external pressure.

Figure 3 shows the electronic conductivity of SnO$_2$/PC//SE and SnO$_2$/PC-CNT//SE at each external pressure. The electronic conductivity of SnO$_2$/PC-CNT//SE is from 24 to 37 times higher than that of SnO$_2$/PC//SE. The value is dramatically increased with only 2.9 wt% addition of the SWCNT, whose electronic conductivity on sheet form was reported at 200 to 300 S cm$^{-1}$ in a performance table. The SWCNT obviously plays a role to improve the electronic conductivity. On the other hand, the electronic conductivities of both samples are hardly depended on the external pressure. The improvement in charge-discharge capacity at higher external pressure seems not to stem from the electronic conductivity. Since the capacity of SnO$_2$/PC//SE is decreased with the decrease in external pressure, the dense contact between porous carbon including SnO$_2$ and SE should be...
important for Li ion conduction into the pores. In the case of SnO2/PC-CNT//SE, the capacity is maintained around 90% between the pressure of 6.3 and 3.5 MPa; the contact might be improved by SWCNT addition even under lower external pressure. Mixing of SWCNT to electrode assists to maintain good contact between SnO2/PC and SE same as increasing external pressure. It is considered that the SWCNT acts as binder in the SnO2/PC and SE mixture.

In summary, The ASSB using SnO2/PC-CNT showed high capacity at low external pressure as well as the cell without SWCNT addition at high external pressure. The addition of SWCNT into SnO2/PC and SE mixture is effective to decrease in the external pressure of ASSB system using sulfide based solid electrolyte. This simple removal method of external pressure represents a promising strategy for designing the ASSB cell.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis of SnO2/PC-CNT

SWCNT (ZEONANO SG101) used as an additive was provided from Zeon Nano Technology Co., Ltd. The SnO2/PC-CNT was obtained by a vacuum filtration of ethanol dispersion of SnO2/PC (11.73 mg) and CNT (0.35 mg).

2.2 | Structural characterization

A XRD pattern of SnO2/PC was obtained on a Rigaku MiniFlex 600 diffractometer equipped with Cu Kα. The loading state of SnO2 nanoparticles in the porous carbon was directly observed by HR-TEM (ARM-200CF, JEOL). The SnO2 loading amount of SnO2/PC was confirmed by thermogravimetric analysis (TGA: TG/DTA7300, SEIKO Instrument Inc.) and N2 adsorption isotherm at 77 K (BELSORP-mini, MicrotracBEL Co. Ltd.).

2.3 | Electrochemical measurements

A LiIn alloy set as a counter electrode was prepared by pressing a stacked Li foil (8 mm in diameter and 0.1 mm in thickness) and In foil (10 mm in diameter and 0.1 mm in thickness) at 70 MPa for 7 minutes at room temperature. A glassy SE was prepared by ball-milling of 10 wt% LiI and 90 wt% of 75Li2S-25P2S5 (mol%) at 370 rpm for 40 hours, and then heating at 583 K for 2 hours in vacuum. The SnO2/PC-CNT was mixed with the SE in a mortar, and then sonicated in heptane. The working electrode of mixture of SnO2/PC and SE (SnO2/PC//SE) was gotten by evaporation of heptane under vacuum at room temperature. All procedures using SE were performed in an Ar-filled glovebox. We also prepared an electrode of mixture of SnO2/PC and SE (SnO2/PC//SE) by similar method for comparison. Constant current charge-discharge test was performed on a Swagelok-type two-electrode ASSB cell. The SE powder (135 mg) was pressed in a polycarbonate tube with a diameter of 13 mm by two stainless rods to make a SE layer. SnO2/PC//SE or SnO2/PC-CNT//SE (2–3 mg) was put on the one side of the SE layer. The LiIn alloy was put on the other side of SE layer as a counter electrode. These stacked layers were sandwiched by two stainless rods, and finally pressed at 300 MPa for 5 minutes by using a uniaxial oil hydraulic press. The external pressure of ASSB cell was set to 3.5, 6.3, and 9.1 MPa by using a vise for charge-discharge measurements, and practical external pressure of 1 MPa by two spring washers for CR2032 coin cell, which is widely used in the liquid electrolyte battery systems. The charge-discharge test (HJ-SD8, Hokuto Denko) was performed on
the specific current of 300 mA g\(^{-1}\) based on the weight of SnO\(_2\)/PC and on the potential range of -0.61 to 1.38 V versus LiIn, corresponding to 0.01 to 2 V versus Li, at the room temperature. The electronic conductivity of working electrode layers was evaluated from a direct current resistance (DCR) measurement at the external pressure from 0.84 to 9.1 MPa. The working electrode material (SnO\(_2\)/PC//SE, SnO\(_2\)/PC-CNT//SE) was pressed at 300 MPa for 5 minutes in a polycarbonate tube by two stainless rods. The electronic resistance of the working electrode layer was calculated from the current at the applied voltage of 0.1 V (detail calculation in Supporting Information). The external pressure was controlled by shrinking a spring.

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**DATA AVAILABILITY STATEMENT**

Research data are not shared.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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