

# Preparation of carbon-coated Sn powders and their loading onto graphite flakes for lithium ion secondary battery

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## Abstract

Carbon-coated Sn powders were prepared from the powder mixtures of thermoplastic precursor PVA, SnO<sub>2</sub> and MgO. The characterization of composite powders synthesized was carried out by XRD, TG, TEM, SEM and anodic performance measurement. SnO<sub>2</sub> was reduced to metallic Sn by heating with PVA, and its particle size in carbon shell was around 30–100 nm. MgO existence hindered the agglomeration of molten metallic Sn and made the dispersion of metallic Sn as fine particles possible. They showed high anodic performance in lithium ion batteries; high charge capacity as 500 mAh g<sup>-1</sup> even after tenth cycle and stable cyclic performance. The spaces left in carbon shell by MgO after its dissolution were supposed to absorb a large volume expansion of Sn metal particle by Li alloying during discharging. When carbon-coated Sn loaded onto graphite flakes, metallic tin contributed to the increase in capacity.

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## 1. Introduction

The development in lithium ion rechargeable batteries has helped to make various modern electronic devices lighter and smaller. Now their higher power, better performance and longer life are strongly desired. Commercial cells have been developed by selecting suitable electrode materials, either LiCoO<sub>2</sub> or LiMn<sub>2</sub>O<sub>4</sub> for the cathode and graphite for the anode, where the intercalation and deintercalation processes of lithium ions were known to be fundamental electrochemical reactions [1–4].

For the anode, various types of carbon materials were used: a wide range of carbon materials from low-temperature carbons with amorphous structure to well-crystallized natural graphite [5], surface modified carbons [6] and carbon nanotubes [7]. Instead of carbon materials, metal oxides and metal alloys also have been investigated; for example, MnV<sub>2</sub>O<sub>6</sub> possessing brannerite-type structure [8,9], silicon–carbon alloy [10] and

metallic tin mixed in carbon materials [11,12]. Tin, Sn, was one of the materials, which attracted attention, mainly because of its large theoretical capacity of 990 mAh g<sup>-1</sup>, but it shows marked volume expansion when it is alloyed with lithium in the electrode of lithium ion rechargeable batteries. In order to prevent volume expansion, various preparation and dispersing processes of fine Sn particles were tried [11–14].

Carbon coating through a simple process, i.e., heat treatment of a mechanical mixture of a ceramic powder with a carbon precursor in inert atmosphere, has been successfully applied on various ceramics, such as different aluminum oxides, magnesium oxide, titanium oxide, various iron oxides, nickel oxide, natural graphite, ceramic tiles, etc., and also aluminum plate of which surface was electrochemically oxidized [15–25]. The particles of oxides of typical elements, Al and Mg, were covered by thin carbon layers and kept in separated particles, no aggregation, if the mixing ratio of carbon precursor was selected appropriately [15]. In the cases of transition elements, Fe and Ni, their oxides were reduced to metals through the interaction with coated carbon, resulting in carbon-coated metal particles, and graphite crystals were formed at a temperature of 900–1100 °C by the catalytic

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action of transition metals formed [18,19]. Carbon-coated TiO<sub>2</sub> having anatase type structure was prepared through this process and found to have various advantages as photocatalysts, suppression of the phase transformation to rutile, high adsorptivity, high crystallinity of anatase phase which was found to be advantageous for water purification, etc. [20–23]. Partial reduction of substrate TiO<sub>2</sub>–Ti<sub>4</sub>O<sub>7</sub> was also observed [24]. Carbon coating of natural graphite flakes was found to improve the anodic performance in lithium ion rechargeable batteries [25]. Most of carbons thus coated on ceramic particles were found to be porous, which was confirmed by dissolving out MgO substrate with diluted sulfuric acid [26,27].

In the present work, the carbon-coated Sn particles were prepared from the mixture of tin oxide with poly(vinyl alcohol) by the same procedure as carbon coating described above, in order to study their performance in lithium ion secondary batteries. The loading of these carbon-coated Sn particles onto graphite flakes was also carried out in order to increase the capacity in lithium ion batteries.

## 2. Experimental

### 2.1. Preparation of carbon-coated Sn powders

Ceramic powders as carbon coating substrate, mixtures of SnO<sub>2</sub> and MgO were used. SnO<sub>2</sub> powder (reagent grade) had the particle size of about 200 nm, and MgO powder (reagent grade) had the particle size of about 100 nm and the BET surface area of 3 m<sup>2</sup> g<sup>-1</sup>. Carbon precursors used in the present study were poly(vinyl alcohol) (PVA) and natural graphite. These four powders, SnO<sub>2</sub>, MgO, PVA and graphite, were mechanically mixed in an agate mortar in different ratios and then heated in a flow of argon at a temperature of 700–900 °C for 1 h. Heating rate to the programmed temperature was 5 °C min<sup>-1</sup> and a flow rate of Ar gas was 60 mL min<sup>-1</sup>.

After heat treatment, black powders were always obtained. During this heat treatment, SnO<sub>2</sub> was found to be reduced to metal, but no change was observed in MgO. Therefore, metallic Sn and MgO particles were supposed to be coated by carbon, as in our previous papers used TiO<sub>2</sub> and MgO ceramic substrates [18,23]. From these carbon-coated Sn/MgO powders thus prepared, MgO was dissolved out by using 1 mol L<sup>-1</sup> HCl and carbon-coated Sn powders were obtained. The samples obtained were examined by X-ray powder diffraction (XRD: Rigaku RINT-2500) with Cu K $\alpha$  radiation. Morphology of the particles was observed under scanning electron microscope with the acceleration voltage of 1.0 kV (FE-SEM: JEOL JSM-6355F) and transmission electron microscope with the acceleration voltage of 200 kV (TEM: JEOL JEM-2010). The content of carbon was determined from the ignition loss of the sample heated at 800 °C for 1 h in air in a TGA apparatus and that of tin was calculated from the weight of the residue by taking into account of the fact that the metallic tin was changed to SnO<sub>2</sub>. The thickness of carbon layer was very difficult to be determined and so the carbon content was used as a measure of the thickness of carbon layer: the larger the carbon content the larger the thickness of the carbon larger.

### 2.2. Anodic performance for lithium ion secondary battery

The electrode to determine anodic performance was prepared by mixing the sample powder with acetylene black as an electrical conductor and polyvinylidene difluoride (PVDF) as a binder in a mass ratio of 80:10:10, and by pasting the mixture on a thin film of Ni. Li metal was used as counter electrode. The electrolyte solution was the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in equal volume ratio, in which 1 mol L<sup>-1</sup> LiPF<sub>6</sub> was dissolved. The electrochemical performance was measured in the potential range of 0.0–2.0 V with a current density of 50 mA g<sup>-1</sup> at room temperature in a glove

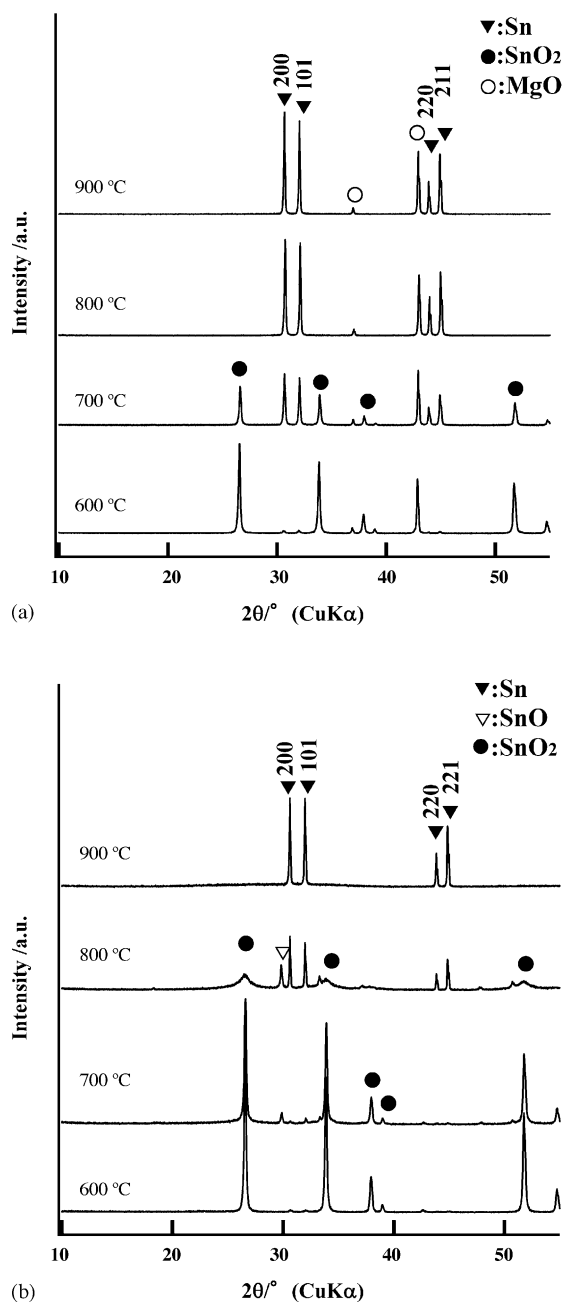


Fig. 1. Changes in X-ray diffraction pattern of the powder mixture of PVA and SnO<sub>2</sub> in mass ratio of 50 and 50 with heat treatment temperature in Ar flow before (a) and after (b) washing out of MgO.

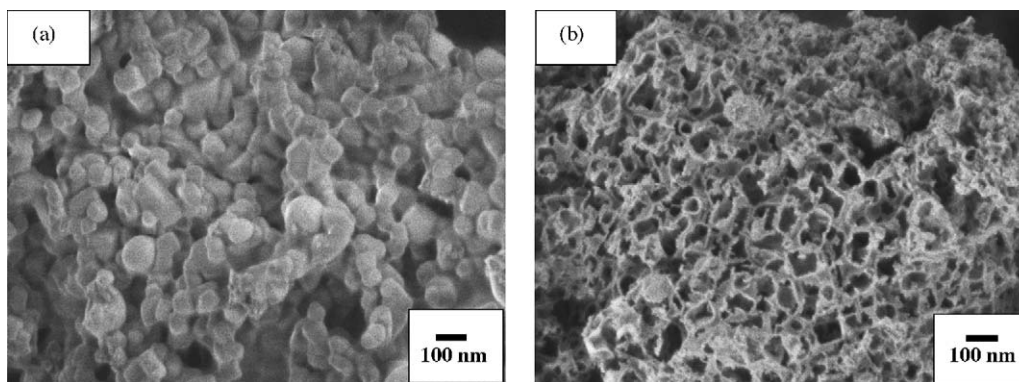


Fig. 2. SEM images of the products heated at 900 °C with or without MgO coexistence. (a) Heat treated without and (b) with MgO.

box filled with high purity He. Charge and discharge cycles were performed up to 20th. Discharge and charge capacities were determined as the electric quantities used for the intercalation and deintercalation of lithium ions, respectively, at the potential range between 0.0 and 2.0 V. In the present work, the notation of anode was used for the electrode consisting of sample carbons, even though it worked as cathode by coupling with lithium metal as counter electrode, because the words of anode and cathode were premised being used in the actual batteries.

### 3. Results and discussion

#### 3.1. Carbon-coated Sn powders

Tin oxide ( $\text{SnO}_2$ ), was found to be reduced to metallic tin (Sn), by heating with PVA above 800 °C, as shown in Fig. 1(a). Tin metal was melted under these temperatures and agglomerated to large particles, most of which were separated from carbon formed by the pyrolysis of PVA, as shown in Fig. 2(a), because the melting temperature of tin metal was about 230 °C. Sometimes, large particles of tin with metallic luster were observed even by naked eyes. Under the coexistence of MgO powder, however, carbon-coated tin was found to be successfully prepared without marked agglomeration by the heat treatment above 800 °C. The formation of metallic Sn was clearly shown in X-ray diffraction pattern after dissolving out of MgO (Fig. 1(b)) and small Sn particles were recognized in the pores left by MgO after its dissolution under SEM (Fig. 2(b)). Before dissolution of MgO by HCl, only metallic Sn and MgO were detected after 800 °C treatment (Fig. 1(a)), but after dissolution broad peaks for  $\text{SnO}_2$  and also a peak for SnO were observed, suggesting that the reduction of  $\text{SnO}_2$  was not yet completed by the heat treatment at 800 °C for 1 h. On the samples heated up to 900 °C, no SnO and  $\text{SnO}_2$  were detected even after washing by HCl. These powders obtained after carbonization of PVA were perfectly black, both silver metallic particles of Sn and white particles of MgO being not observed. From SEM images like Fig. 2(a), the thickness of carbon shells, which was left by MgO particles after its dissolution [27], was supposed to be few nanometers, but it was difficult to be determined accurately.

When the powders obtained above 800 °C was washed by either sulfuric or acetic acid in order to dissolve out of MgO, a part of metallic tin was found to be oxidized to either SnO or  $\text{SnO}_2$ . However, MgO was able to dissolved out with  $1 \text{ mol L}^{-1}$  HCl without any oxidation of metallic tin, as shown in Fig. 1(b).

In order to demonstrate the effectiveness of mixing of MgO, XRD patterns of carbon-coated Sn powders are shown in Fig. 3, which were prepared from the mixtures with different PVA/MgO/ $\text{SnO}_2$  ratios at 900 °C, by keeping the ratio of PVA to total oxides (MgO +  $\text{SnO}_2$ ) constant and then MgO in the carbonized samples was dissolved out by diluted HCl. TEM images of Sn particles in three samples used in Fig. 3 are shown in Fig. 4(a–c).

Only metallic tin can be identified and its diffraction peaks are sharpened with decreasing MgO/ $\text{SnO}_2$  ratio, as shown by enlarged 220 line around 45° in  $2\theta$  in Fig. 3. The crystallite size determined from the line broadening of 220 line in XRD pattern was 150, 45 and 35 nm with changing PVA/MgO/ $\text{SnO}_2$  ratio of 10/2/8, 10/5/5 and 10/8/2, respectively. The particle sizes of Sn

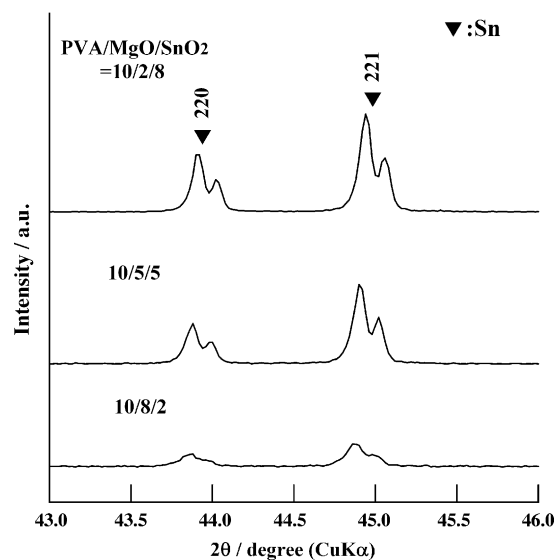


Fig. 3. XRD patterns of powder the mixture of MgO and  $\text{SnO}_2$  in various mass ratios on constant PVA amount with heat treatment at 900 °C in Ar flow after washing out of MgO.

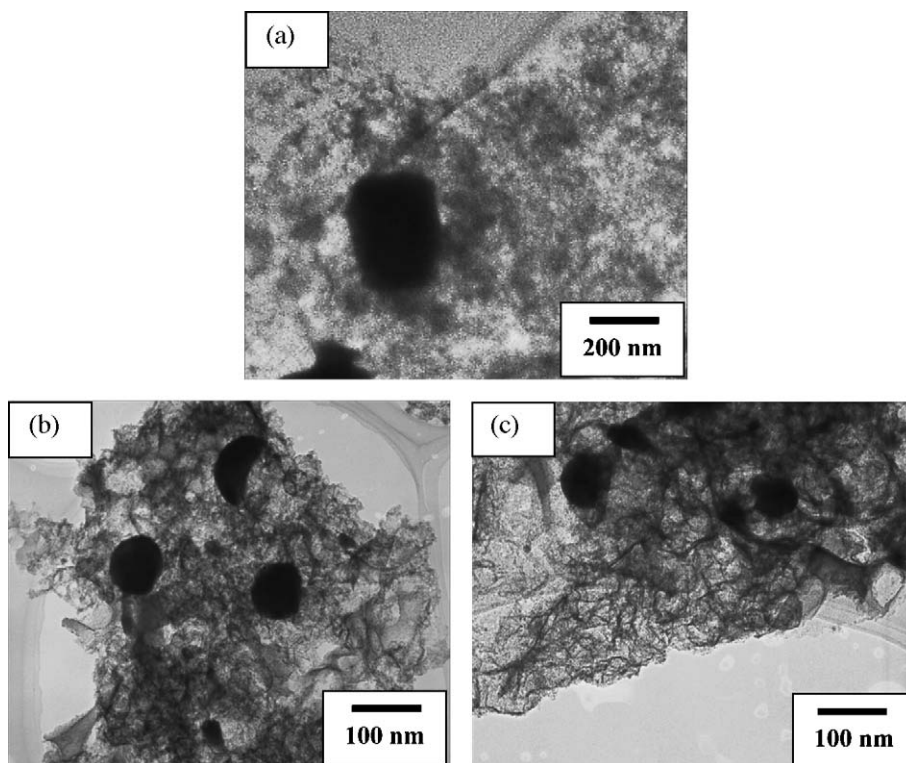


Fig. 4. TEM images of carbon-coated metallic Sn particles with mixture of PVA/MgO/SnO<sub>2</sub> = 10/2/8 (a), 10/5/5 (b) and 10/8/2 (c).

observed in TEM images in Fig. 4(a–c) for these three samples agree roughly with those determined from XRD. In these three samples prepared from PVA/MgO/SnO<sub>2</sub> of 10/2/8, 10/5/5 and 10/8/2, the content of metallic Sn was 96, 80 and 75 mass%, respectively.

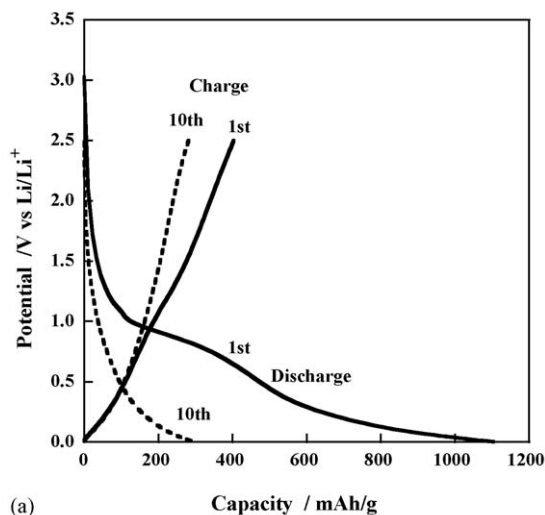
The present results showed that, by the coexistence of MgO with SnO<sub>2</sub>, carbon-coated Sn powders could be prepared, avoiding the agglomeration of molten Sn metal, at a temperature above 800 °C. MgO particles were assumed to play a following role during high temperature treatment; molten Sn formed by the reduction of SnO<sub>2</sub> through the reaction with coated carbon was kept on the surface of MgO particles due to its wettability, which made difficult for molten Sn to flow and coagulate with each other. Without MgO, molten Sn could be easily coagulated with each other to large particles because of its poor-wettability to carbon. In our previous paper [27], MgO particles were experimentally shown to be covered by carbon formed from PVA at high temperatures. When relative amount of MgO to SnO<sub>2</sub> was small, such as MgO/SnO<sub>2</sub> = 2/8, MgO surface might not be enough to keep molten metallic tin formed, and as a consequence molten tin tended to coagulate into large particles. On the other hand, when ratio was MgO/SnO<sub>2</sub> = 8/2, small metallic tin particles were obtained because molten tin was quickly wetted on MgO surface and hindered its agglomeration.

### 3.2. Anodic performance of carbon-coated Sn

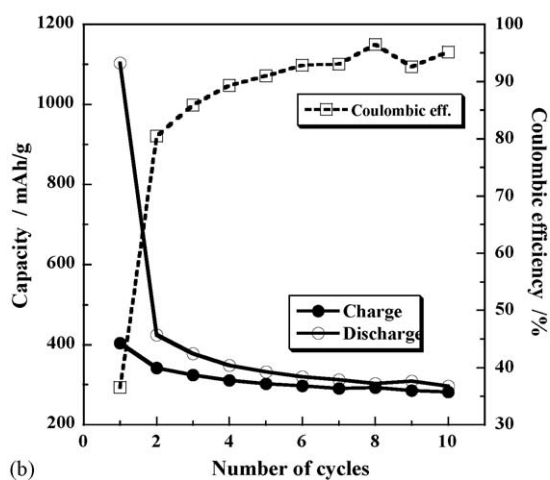
In Fig. 5(a), discharge–charge curves for first and tenth cycles are shown on the carbon prepared from the mixture of

PVA with MgO in the ratio of 10/5 at 900 °C, the procedure being exact by the same as that for the preparation of carbon-coated Sn. Cyclic performance in discharge–charge capacities and Coulombic efficiency with cycling are shown in Fig. 5(b). Performance of this carbon was very similar to those reported on low-temperature treated carbons in other reports, gradual increase in potential with charging [28]. However, charge capacity decreases with cycling, but saturates quickly. It is worthwhile to point out that it gives relatively high capacity saturated, about 300 mAh g<sup>-1</sup> in the potential range of 0.0–2.0 V, about 200 mAh g<sup>-1</sup> in 0.0–1.0 V. Coulombic efficiency increases gradually with cycle and reaches only about 95%. The carbon powder thus prepared, i.e., carbonization with MgO powder, was found to be microporous [27].

In Fig. 6(a and b), discharge–charge curves and cyclic performance are shown, respectively, for the carbon-coated Sn powders prepared from the mixture of PVA/MgO/SnO<sub>2</sub> ratio of 10/5/5 at 800 °C. In Fig. 7(a and b), discharge–charge curves and cyclic performance, respectively, on the sample prepared from the same mixture at 900 °C are shown. All carbon-coated Sn samples showed a plateau at around 1.0 V in the first cycle of discharging, which was also observed on the carbon powder without Sn and was known to be due to the formation of solid/electrolyte interfaces and resulted in irreversible capacity. For carbon-coated Sn, a plateau at around 0.5 V was also observed, as shown in Figs. 6(a) and 7(a), which was not observed on the carbon samples without Sn. After second cycle, discharge capacity tends to approach charge capacity and to decrease gradually with increasing cycle number. The

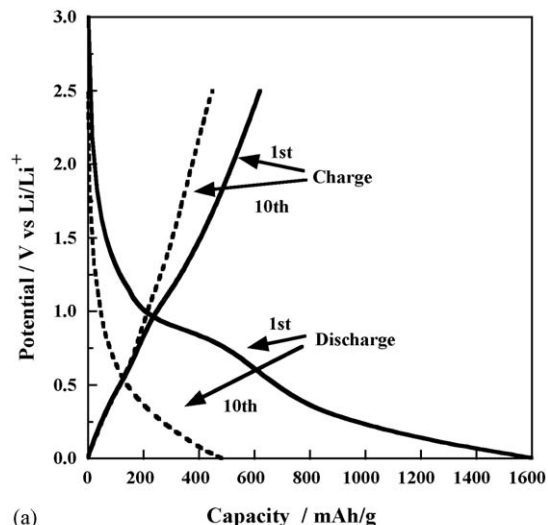


(a)

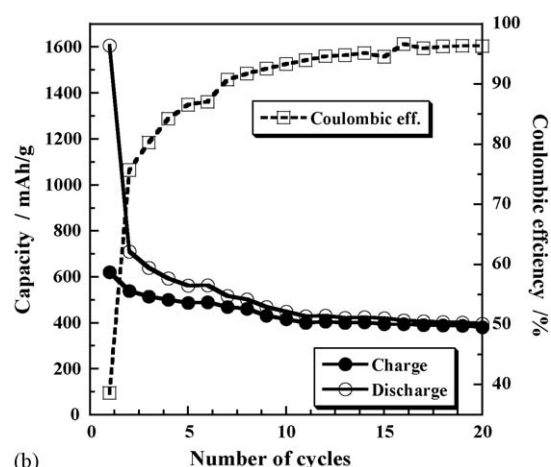


(b)

Fig. 5. Discharge–charge curves (a) and cyclic performance (b) for the carbon powder prepared from the mixture of PVA/MgO in 10/5 mass ratio at 900 °C.



(a)



(b)

Fig. 6. Discharge–charge curves (a) and cyclic performance (b) for the powder of carbon-coated Sn prepared from the mixture of PVA/MgO/SnO<sub>2</sub> in 10/5/5 mass ratio at 800 °C.

decrease in discharge capacity was found to be mainly due to the decrease in capacity for the plateau at around 0.5 V, as shown by the charge curves of first and tenth cycle in Figs. 6(a) and 7(a). Coulombic efficiency for two samples of carbon-coated Sn increases rapidly at second cycle and then gradually with increasing cycle number, tending to saturate to about 97% (Figs. 6(a) and 7(a)). High irreversible capacity and low Coulombic efficiency at the first discharge–charge cycle on the sample prepared at 800 °C (Fig. 6) may be due to small amount of SnO<sub>2</sub> or SnO remained, as shown in Fig. 1(b), due to incomplete reduction of SnO<sub>2</sub>. The sample prepared at 900 °C had much smaller irreversible capacity than that at 800 °C, about 550 mAh g<sup>-1</sup> for the former and about 1000 mAh g<sup>-1</sup> for the latter (Figs. 7(b) and 6(b)).

The comparison among the discharge–charge performances between carbon and carbon-coated Sn powders prepared in the same procedure shows that the carbon-coated Sn gives higher capacity saturated, though it takes more cycling to reach the saturation; about 500 mAh g<sup>-1</sup> for carbon-coated Sn with the total Sn content of 75 mass%, but about 300 mAh g<sup>-1</sup> for the carbon without Sn. It has to be pointed out here that the cyclic perfor-

mance observed on the present carbon-coated Sn powders did not show any marked degradation, as reported in tin metal anode [14]. This high performance of carbon-coated Sn powders was supposed to be due to the presence of open spaces neighboring to metallic Sn in carbon shell, which was formed by dissolving out of MgO particles. These spaces are assumed to absorb a large volume expansion due to alloying of Li into Sn metal during discharging.

In Fig. 8, cyclic performance is shown for the carbon-coated Sn powders prepared from the mixtures of three different PVA/MgO/SnO<sub>2</sub> ratios, of which XRD patterns and TEM images of tin particles are shown in Figs. 3 and 4, respectively. This result shows that it is important to disperse fine particles of metallic Sn to get high capacity and high Coulombic efficiency, the sample prepared with PVA/MgO/SnO<sub>2</sub> of 10/2/8 giving much small capacity and Coulombic efficiency than that with 10/8/2. The sample prepared with PVA/MgO/SnO<sub>2</sub> of 10/5/5 has a little smaller capacity but more stable with cycling and a little higher Coulombic efficiency than that with 10/8/2.

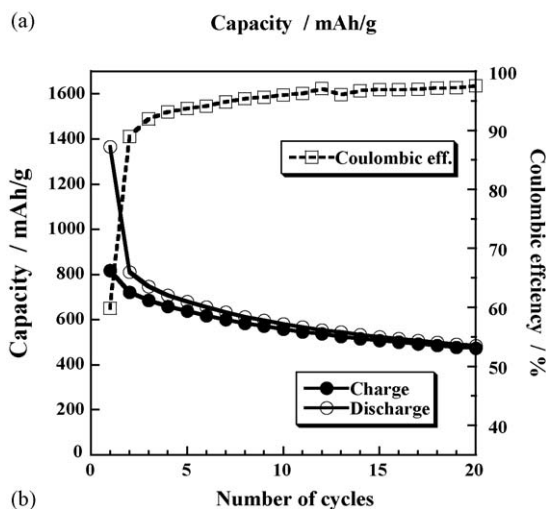
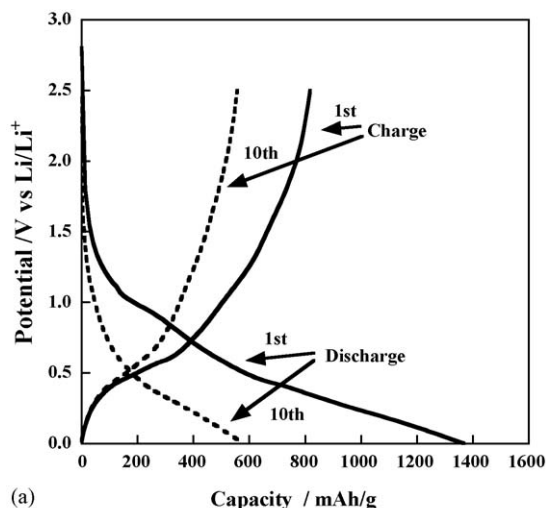


Fig. 7. Discharge–charge curves (a) and cyclic performance (b) for the powder of carbon-coated Sn prepared from the mixture of PVA/MgO/SnO<sub>2</sub> in 10/5/5 mass ratio at 900 °C.

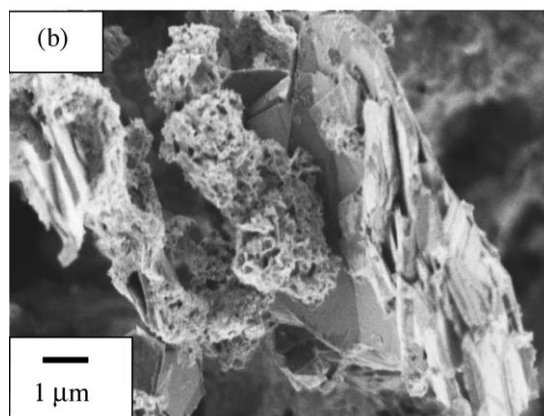
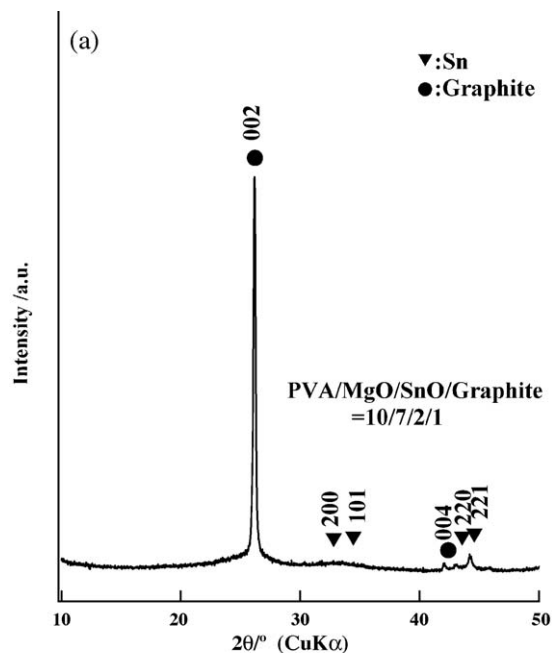


Fig. 9. XRD pattern (a) and SEM image (b) of graphite loaded by carbon-coated Sn.

### 3.3. Graphite flakes loaded by carbon-coated Sn

Loading of carbon-coated Sn onto graphite flakes (carbon-coated Sn/graphite) was performed by heating the powder mixtures of PVA, MgO, SnO<sub>2</sub> and natural graphite in the mixing ratio of 10/7/2/1 in mass. XRD pattern and its SEM image of the powder obtained after heat treatment at 900 °C and then dissolving out of MgO are shown in Fig. 9(a and b), respectively. In XRD pattern, diffraction peaks for metallic Sn are observed, though very weak, because 002 peak for graphite is so strong. SEM image, however, proves clearly the coexistence of carbon-coated Sn with graphite flakes.

In Fig. 10(a and b), discharge–charge curves and cyclic performance, respectively, are compared for graphite with and without loading of carbon-coated Sn. On carbon-coated Sn/graphite sample, faint plateau at around 0.5 V is seen, in addition to the plateau at around 0.2 V due to graphite flakes. Although carbon-coated Sn/graphite gives Coulombic efficiency less than graphite, it gives about 1.5 times larger capacity than graphite.

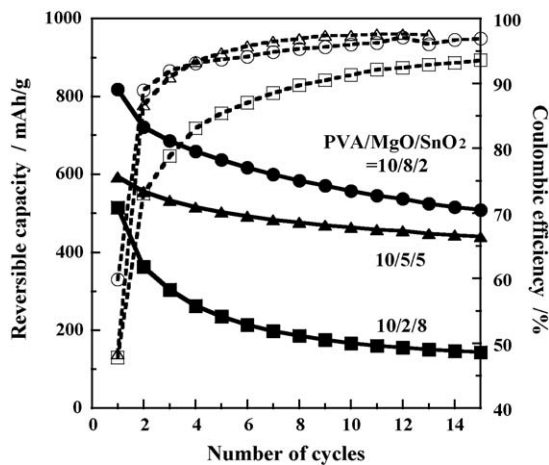


Fig. 8. Changes of discharge capacity and Coulombic efficiency with cycling for the carbon powders prepared from the mixture of PVA/MgO/SnO in 10/2/8, 10/5/5 and 10/8/2 mass ratio at 900 °C.

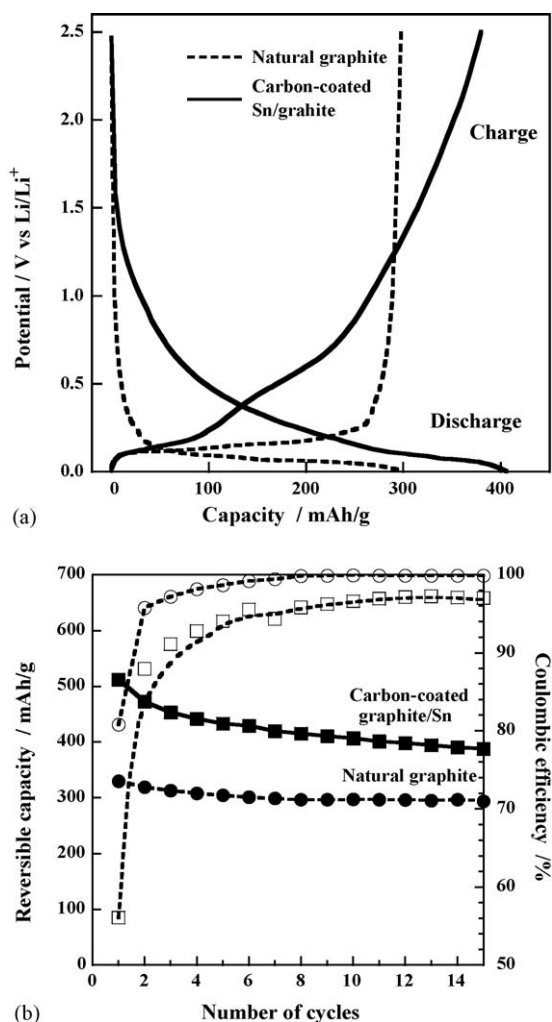


Fig. 10. Discharge–charge curves (a) and cyclic performance (b) for graphite with and without loading of carbon-coated Sn.

This proves that carbon-coated fine particles of metallic Sn have certain contribution to the increase in capacity.

#### 4. Conclusion

Carbon-coated Sn powders were successfully prepared from the powder mixtures of thermoplastic precursor PVA,  $\text{SnO}_2$  and MgO. The presence of MgO particles was found to be effective to avoid the agglomeration of molten Sn metal at high temperatures and also to leave open spaces neighboring to Sn metal particles in carbon shell which could absorb a large volume expansion due to alloying of Li. Therefore, a high charge capacity and high discharge–charge cyclicability were successfully added to carbon electrode. The carbon-coated Sn was demonstrated to be able to load onto graphite flakes through a simple process; mechanical mixing of PVA, MgO and  $\text{SnO}_2$  with graphite flakes, heating in inert atmosphere at  $900^\circ\text{C}$  and then washing out of MgO using 1 M HCl. The composites of carbon-coated Sn/graphite gave high discharge capacity and stable cyclic performance.

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