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Potential of Mesoporous SnO_2 as Anode Materials for Rechargeable Lithium-ion Batteries

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Many kinds of carbon materials are now widely used as an active anode material for rechargeable lithium-ion secondary batteries. However, Sn-based materials are superior to carbon materials from the viewpoint of discharge capacity. The aim of the present study is to investigate the potential of mesoporous SnO_2 (m-SnO_2) -based materials as anode. Effects of heat treatment conditions and doping of foreign metals on the anodic performance have been investigated.

m-SnO_2 was prepared by using $SnCl_2 \cdot 2H_2O$ as a Sn-source and a triblock copolymer (P123, $EO_{20}PO_{70}$-EO_{20}) as a surfactant in a manner similar to that reported previously.[1)] The m-SnO_2 powder was then thermally treated under different conditions, as summarized in Table 1. m-SnO_2 doped with 50 mol% Fe and Cu, which are referred as to SF and SC, respectively, were also prepared and then subjected to heat treatments (see Table 2). Charge-discharge characteristics of these anode materials were measured by employing a Li counter electrode.

Figure 1 shows variations in discharge capacity of the lithium cells consisting of m-SnO_2-based anodes with the cycle number. Characterization of the anode materials and cycle performance are summarized in Table 1. The cell with S1 anode (S1 cell) showed a discharge capacity of ca. 557 mAh g^{-1} at the first cycle, but its cycle performance needed to be modified, i.e. the capacity decreased to 159 mAh g^{-1} after 20 cycles. Although the S3 cell showed the highest discharge capacity, its cycle performance was again insufficient. Among the cells tested, the S5 cell showed the highest efficiency after 20 cycles. Since the S5 anode material was black in color, some residual carbonaceous materials might remain in the mesoporous structure. The highest efficiency may arise from such residual carbonaceous materials in the case of the S5 cell.

When doped m-SnO_2 was heat treated in air, both the initial discharge capacity and the efficiency after 20 cycles decreased by the doping (see the results shown in Fig. 2 and Table 2). However, treatment in H_2 atmosphere resulted in the improvement of efficiency for both the SF and SC cells. Nevertheless, among the cells tested, the S5 cell was revealed to have relatively high capacity at the first cycle and the highest cycle efficiency.

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1) T. Hyodo, N. Nishida, Y. Shimizu, M. Egashira, *Sens. & Actuators B*, **83**, 209 (2002).

Table 1 Preperation conditions and characterization of m-SnO_2-based materials.

Sample No.	Urea	Calcination conditions	Crystal phase	Specific surface area ($m^2 g^{-1}$)	Cycle capacity (mA h g^{-1}) 1st	20th	Efficiency* (%)
S1	○	Air, 300°C, 5 h	SnO	52.3	557	159	28.6
S2	○	Ar, 300°C, 5 h	SnO	59.2	705	165	23.4
S3	○	H_2, 300°C, 5 h	SnO	22.0	776	111	14.3
S4	○	Ar, 500°C, 5 h	SnO_2	49.3	529	27	5.1
S5	×	Ar, 500°C, 5 h	SnO_2	53.1	622	303	48.8

*Efficiency = (Cap_{20} / Cap_1) × 100

Table 2 Preperation conditions and characterization of doped-m-SnO_2-based materials.

Sample No.	Urea	Calcination conditions	Crystal phase	Specific surface area ($m^2 g^{-1}$)	Cycle capacity (mA h g^{-1}) 1st	20th	Efficiency* (%)
S1	○	Air, 300°C, 5 h	SnO	52.3	557	159	28.6
SF1	○	Air, 300°C, 5 h	SnO_2	145.6	468	110	23.5
SF2	○	H_2, 300°C, 5 h	Sn, SnO, SnO_2	83.4	452	157	34.7
SC1	○	Air, 300°C, 5 h	SnO_2	144.1	406	53	13.0
SC2	○	H_2, 300°C, 5 h	Cu_6Sn_5, Sn	40.2	489	224	45.8

*Efficiency = (Cap_{20} / Cap_1) × 100

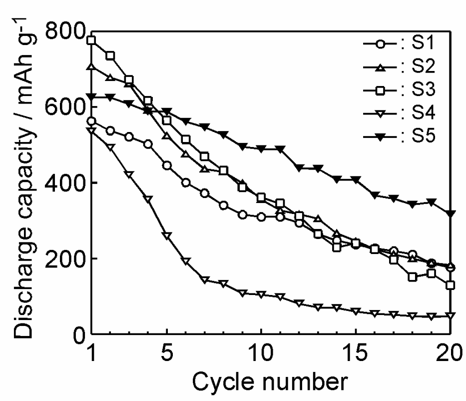

Fig. 1 Cycle performance of m-SnO_2-based anodes.

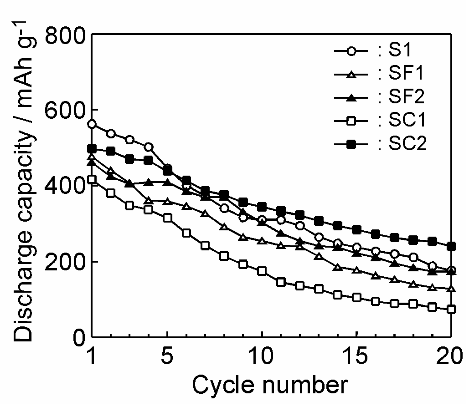

Fig. 2 Cycle performance of doped-m-SnO_2-based anodes.