

Electronic Supplementary Material (ESI) for Chemical Communications

Enhanced Charge-Discharge Properties of SnO₂ Nanocrystallites in Confined Carbon Nanospace

Shinji Oro, Koki Urita and Isamu Moriguchi*

Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-
8521, JAPAN

Supplementary Materials

Experimental details

Fig. S1 XRD patterns of samples.

Fig. S2 SEM images of (a) C45, (b) SnO₂/C45-vap, and (c) the surface of a SnO₂/C45-vap electrode pressed with PVdF.

Fig. S3 Initial charge-discharge curves of SnO₂/C120 samples and SnO₂·AB.

Fig. S4 Initial charge-discharge curves and cycle performance of CXs.

Fig. S5 Change of Coulombic efficiency with cycling.

Fig. S6 Rate capability of SnO₂·AB and SnO₂/C120-vap.

Fig. S7 Cycle performance of SnO₂/C18-vap up to 100 cycles.

Experimental details

Synthesis: A porous carbon with an average pore diameter (X) of 120 nm, 45 nm or 18 nm, which was denoted as CX , was obtained by a silica opal template process as previously reported.²² SnO_2 -embedded porous carbon composites (SnO_2/CX s) were synthesized by following two methods: (1) mixing of CX with a SnO_2 sol in a solution, (2) introduction of SnCl_2 vapor and conversion into SnO_2 in CX . As for the method (1), a $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ sol was first prepared by dropwise addition of aqueous NH_4OH to aqueous SnCl_2 under stirring until the pH reached at 9.7, washing with pure water and drying at room temperature for overnight. The obtained gel was dissolved in ethanol and was mixed under sonication for 6 h with C120, of which mixing ratio was $\text{SnO}_2 \cdot n\text{H}_2\text{O}/\text{C120} = 85/15$ by weight. The filtrated material was heated at 120 °C for 2 h. On the other hand, the method (2) was carried out by heating a mixture of SnCl_2 and CX with the weight ratio of $\text{SnCl}_2 / CX = 85/15$ in a sealed tube at 320 °C for 25 h. The CX used was preheated at 120 °C for 2 h under vacuum to remove adsorbed water. 400 mg of the mixed sample obtained above was dispersed in 600 mL of pure water and was filtered off to remove unreacted SnCl_2 , and then was dried in *vacuo* for overnight. SnO_2 powder were also synthesized by heating the $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ sol at 500 °C for 2 h in an O_2 atmosphere.

Instrumental Analysis: X-ray diffraction (XRD) patterns of samples were obtained on a Rigaku RINT-2200 diffractometer using $\text{Cu K}\alpha$ radiation. The SnO_2 content in samples was estimated by thermogravimetric analysis (TGA, SEIKO Instrument Inc, TG/DTA7300). The specific surface area was determined by α_s -plot analysis from the N_2 adsorption isotherm (BEL Japan Inc, BELSORP-max). The morphology of samples was observed by transmission electron microscopy (TEM, JEOL JEM-2010UHR) and scanning electron microscopy (SEM, JEOL JSM-7500FAM). Electrochemical charge-discharge curves were measured on an electrochemical analyzer (Hokuto Denko, HJ-SM8) using a beaker-type three-electrode cell with metallic Li as a counter and reference electrode at room temperature. The electrolyte

used was a 1.0 mol dm^{-3} solution of LiPF_6 in ethylene carbonate/dimethyl carbonate (1/1 by volume). A mixture of SnO_2/CX sample and poly(vinylidene difluoride) (PVdF) with the weight ratio of 90 : 1 were pressed on Ni mesh, and then were used as working electrodes. For the SnO_2 powder, 10 wt% of acetylene black (AB) was mixed as a conductive additive in the preparation of working electrode ($\text{SnO}_2 : \text{AB} : \text{PVdF} = 80 : 10 : 10$ by weight). To minimize the effect of IR drop associated with the electrolyte resistance, the tip of a capillary in connection to the reference electrode was placed as close as possible to the working electrode. A constant current (CC) mode charging-discharging was carried out at the current density of 50 mA g^{-1} in the potential range of $0.01 \text{ V} - 2.0 \text{ V}$ vs. Li^+/Li after the initial discharging from open circuit voltage to 0.01 V . Rate capability was evaluated in the range of $50 - 1000 \text{ mAh g}^{-1}$. Cyclic voltammetry (CV) was carried out on a potentiostat/galvanostat (Solartron Analytical Inc. S1287) at a scan rate of 0.2 mV/s in the potential range of $0.01 - 3.0 \text{ V}$ vs. Li^+/Li . Rate

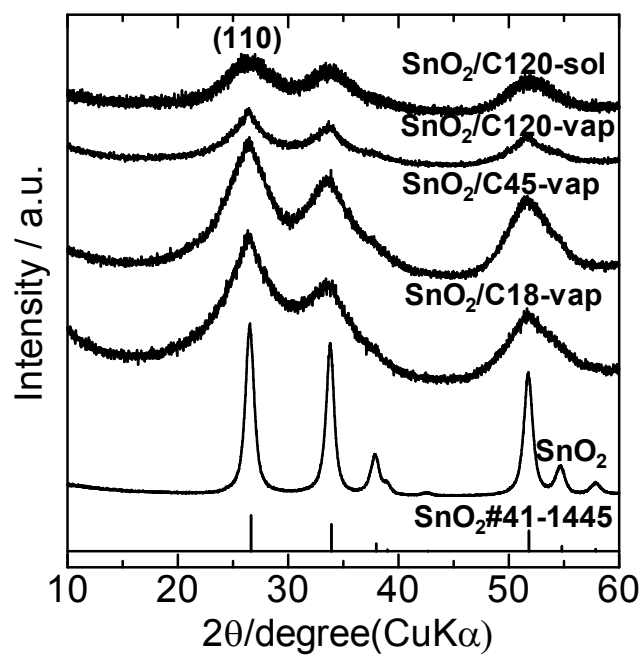


Fig. S1 XRD patterns of the samples.

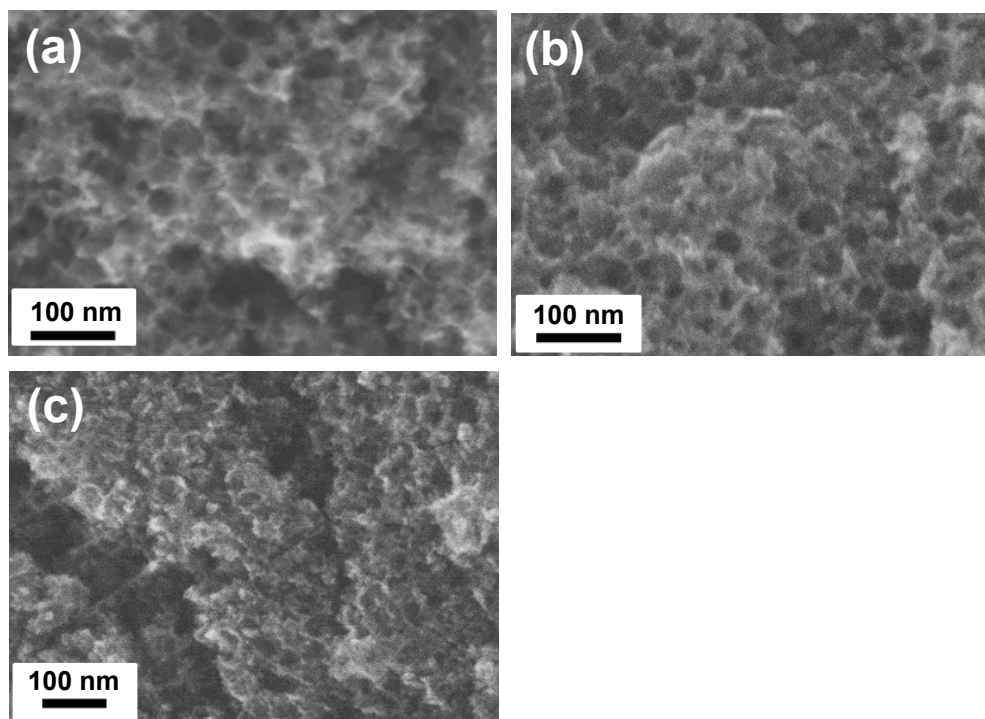


Fig. S2 SEM images of (a) C45, (b) SnO₂/C45-vap, and (c) the surface of a SnO₂/C45-vap electrode pressed with PVdF.

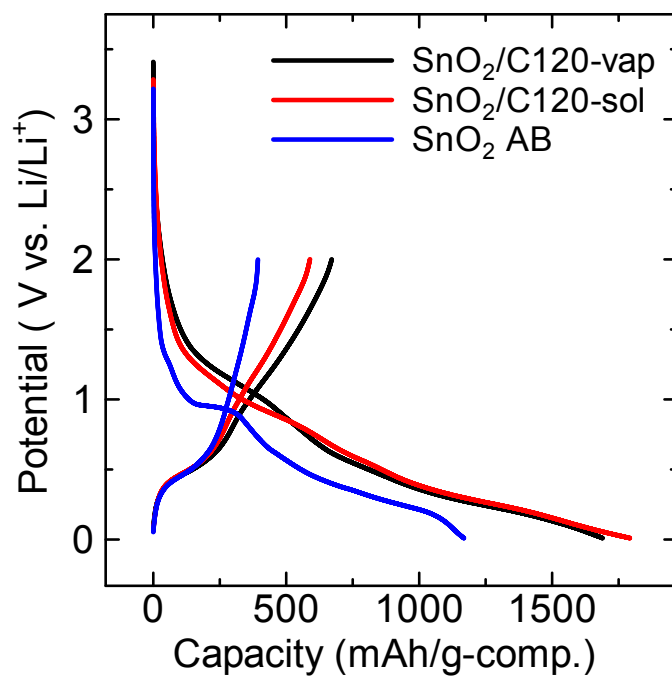


Fig. S3 Initial charge-discharge curves of SnO₂/C120 samples and SnO₂·AB.

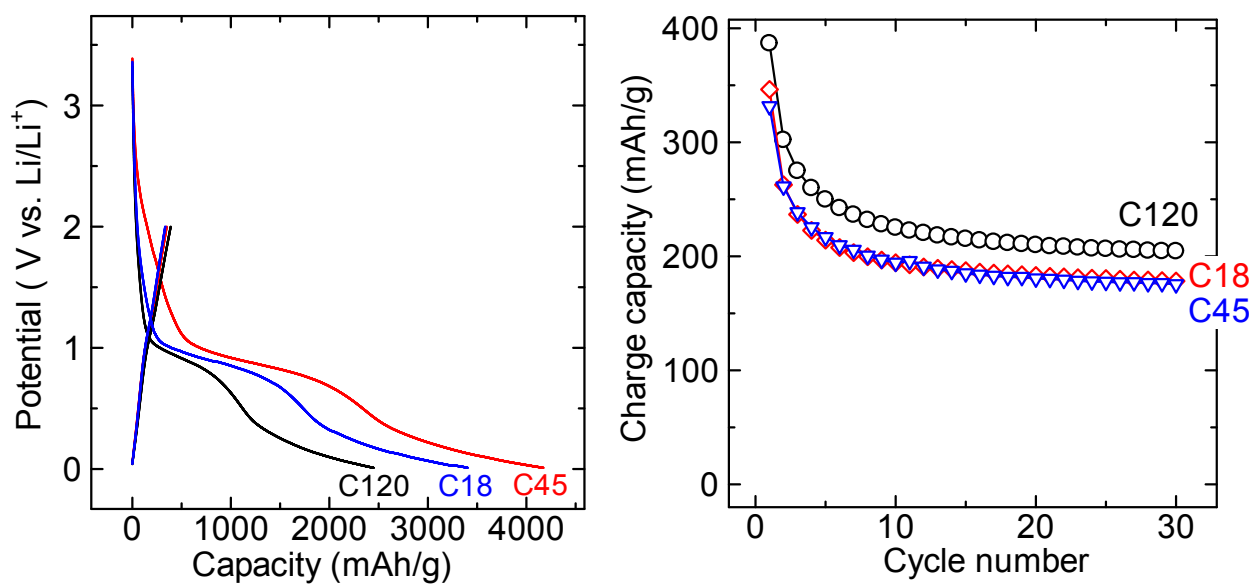


Fig. S4 Initial charge-discharge curves and cycle performance of CXs.

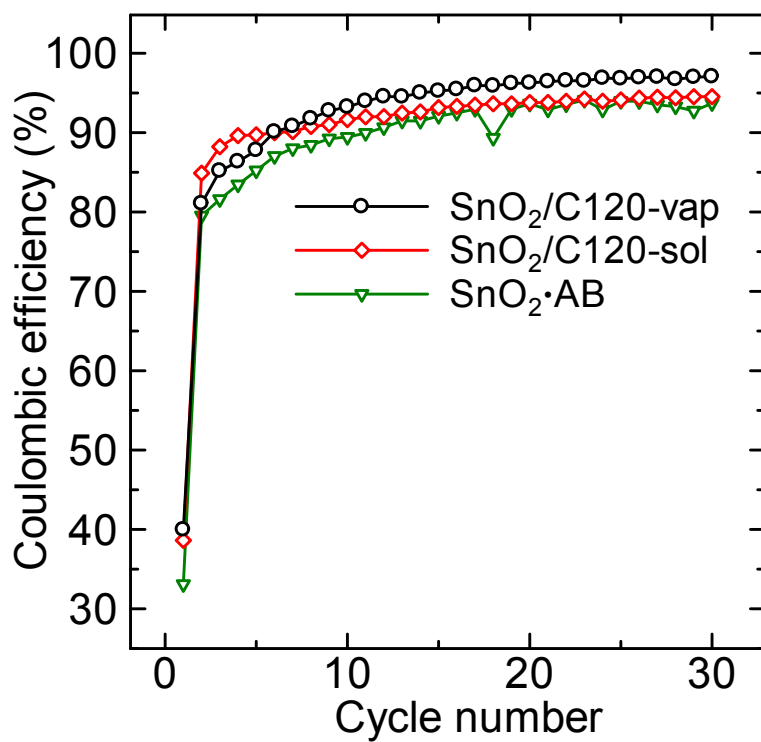


Fig. S5 Change of Coulombic efficiency with cycling.

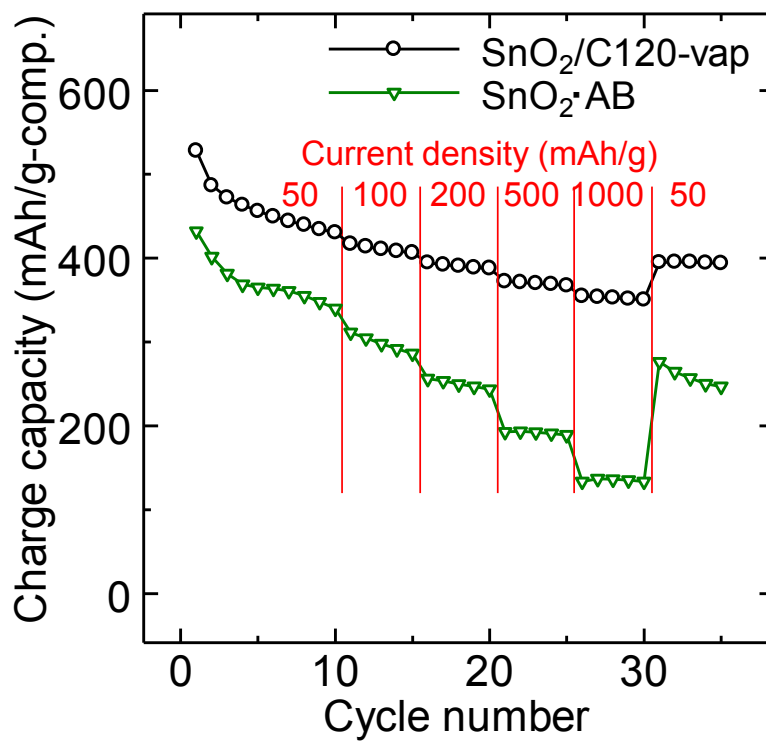


Fig. S6 Rate capability of SnO₂·AB and SnO₂/C120-vap.

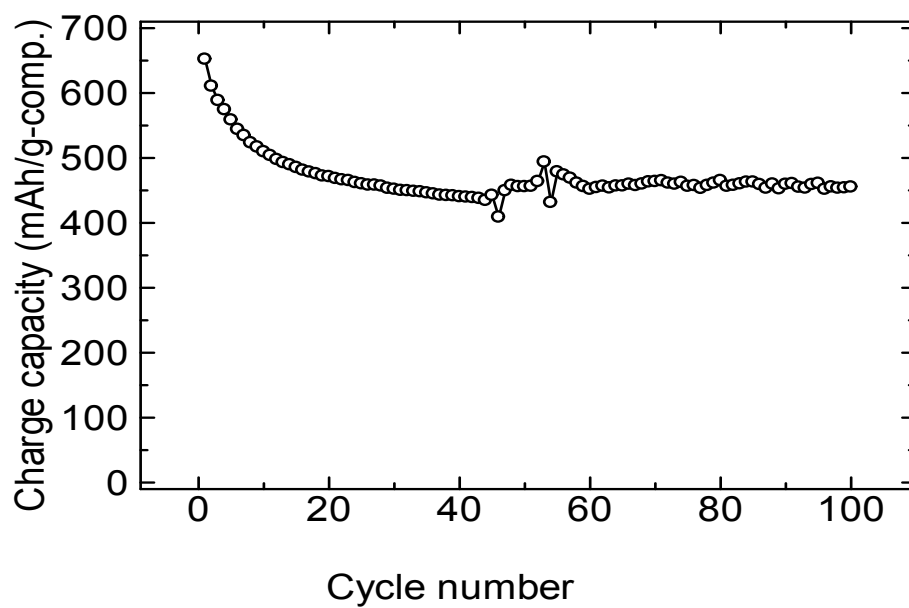


Fig. S7 Cycle performance of SnO₂/C18-vap up to 100 cycles.