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Designing SnO_x/C films via co-sputtering as anodes for all-solid-state batteries

Seyong Park [a], Kang Soo Lee [a,b], Young Soo Yoon [c,*]

[a] Department of Nano Science and Technology, Gachon University, Gyeonggi-do, 13120, Republic of Korea
[b] Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea
[c] Department of Chemical & Biological Engineering, Gachon University, Gyeonggi-do, 13120, Republic of Korea

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ABSTRACT

SnO_x/C composite thin films were deposited on stainless steel disc substrates by radio frequency magnetron co-sputtering. SnO_x/C thin film anode samples with different tin oxide and carbon ratios were electrochemically investigated. Samples with high carbon composition showed high capacity retention and stability compared to SnO_2-only thin film anodes. The film with high carbon content delivered an initial discharge capacity of 8990 mA h cm^{-3} at a current density of 150 μA cm^{-2}. In the rate capability test from 50 to 500 μA cm^{-2}, the last cycle showed 58% of the 1st cycle capacity, while the other samples retained below 50% of the initial capacity. These results indicate that carbon in the thin films resulted in electric conductivity and acted as a buffer for the detrimental tin oxide volume expansion. Consequently, co-sputtering of tin oxide and carbon opens up the possibility of non-lithium anode materials. Moreover, these SnO_x/C thin films can be applied as high-performance anode materials for all-solid-state batteries.

1. Introduction

For the last couple of decades, lithium-ion batteries have been used as power sources for many applications, including portable devices, and mobile phones [1–4]. Recently, lithium-ion batteries have been applied to micro-electro-mechanical systems (MEMS), for which micro-energy storage systems are imperative. Thin film lithium ion batteries can satisfy the size and capacity requirements for these systems [5].

Finding stable electrode materials for thin film lithium-ion batteries is one of the key issues still needing extensive research. As an anode material, lithium is widely used in thin film form. This is due to the high electrical conductivity (1.1×10^7 S m^{-1}) of lithium, high theoretical charge capacity (3840 mAh g^{-1}), and most importantly, an almost infinite lithium source compared to a thin film cathode. Lithium, however, has a major chemical stability problem, i.e., high moisture reactivity. Therefore, lithium electrodes must be fabricated and used only in specific environments such as argon-filled glove boxes. Furthermore, dendrites form after repeated charging and discharging inside metal lithium anodes, a process that eventually causes failure by short circuiting [6]. These are inherent disadvantages of lithium metal anodes, disadvantages that are unlikely to be solved [7]. Thus, metal oxide anode materials, which are easier to handle under more moderate conditions, are being investigated. These materials include TiO_2, SnO_2, SnO, SiO, GeO_2, CuO, and NiO [8–14]. Among these candidates, tin oxide (SnO_2) possesses desirable properties that make it likely to be a new generation anode material. SnO_2 has a higher theoretical capacity (800 mAh g^{-1}) as compared to other metal oxides such as TiO_2, LTO, CuO, and etc [15–17]. SnO_2 has a lower specific capacity than silicon (4200 mAh g^{-1}), but it has a lower active voltage of approximately 0.3 V as compared to that (>0.5 V) for silicon [18]. Therefore, SnO_2 has much more potential applicability than other metal oxide anode materials.

Like any other metal oxide anode, tin oxide also suffers from pulverization problems due to volume changes during lithium intercalation and deintercalation. Pulverization induces irreversible capacity and decreasing cyclic capacity, a result mainly due to loss of active material during volume change [19] and peeling off of active material from the current collector [7]. Many studies have attempted to solve these problems by introducing nanocomposites [18], nanorods [20], nanoneedles [21], nanoribbons [8], nanoflowers [10], nanocrystals [22], and other related strategies.

On promising approach to improve electrochemical performance is to use composite anode materials containing tin oxide. A few examples of this approach exist: SnO_2/C nanocomposites fabricated using a sol-gel method [18]; SnO/TiO_2 nanotubes constructed using electrochemical deposition [23]; SnO/carbon nanofiber anodes with a reversible capacity of ~250 mA h g^{-1} in the range 0.1–1.0 V [24]; and $SnO(V_2O_3)_x$ (x = 0, 0.25, and 0.5) material fabricated by high-energy ball milling from SnO and V_2O_3/VO [25]. Among various types of composite anodes, thin film anodes have excellent volume expansion resistance and electrical conductivity because of their two dimensional structure. In this study, we deposited SnO_x/C films via co-sputtering, therefore using carbon to

* Corresponding author.
E-mail address: benedicto@gachon.ac.kr (Y.S. Yoon).

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Table 1
The r.f. magnetron sputtering conditions and thicknesses of Sn/C thin films.

Sample name	SnO_2 input power (W)	C input power (W)	Deposition time (min)	Thickness (nm)
(a) Sn_{15}	15	–	90	310
(b) $Sn_{15}C_{100}$	15	100	60	340
(c) $Sn_{15}C_{150}$	15	150	60	290
(d) C_{150}	–	150	100	280

provide a buffering effect to reduce pulverization during charging/discharging.

Thin film anodes with low volume expansion were fabricated with a co-sputtering method using tin oxide and carbon targets, which can give atom homogeneity and free spaces in the thin films. Additionally, this co-sputtering method is simple and requires no post process. The influence of the carbon ratio in the SnO_x/C composite thin films was studied to find a possible candidate composite anode for an all-solid-state battery.

2. Experimental procedure

2.1. Materials and preparation

The tin oxide (Sigma-Aldrich, 325 mesh, 99.9% purity) and carbon (Sigma-Aldrich, 325 mesh, 99.999% purity) targets were synthesized by a solid-state method. Tin oxide or carbon powder was ball-milled for 24 h with zirconia balls to produce a fine powder. Sputtering targets

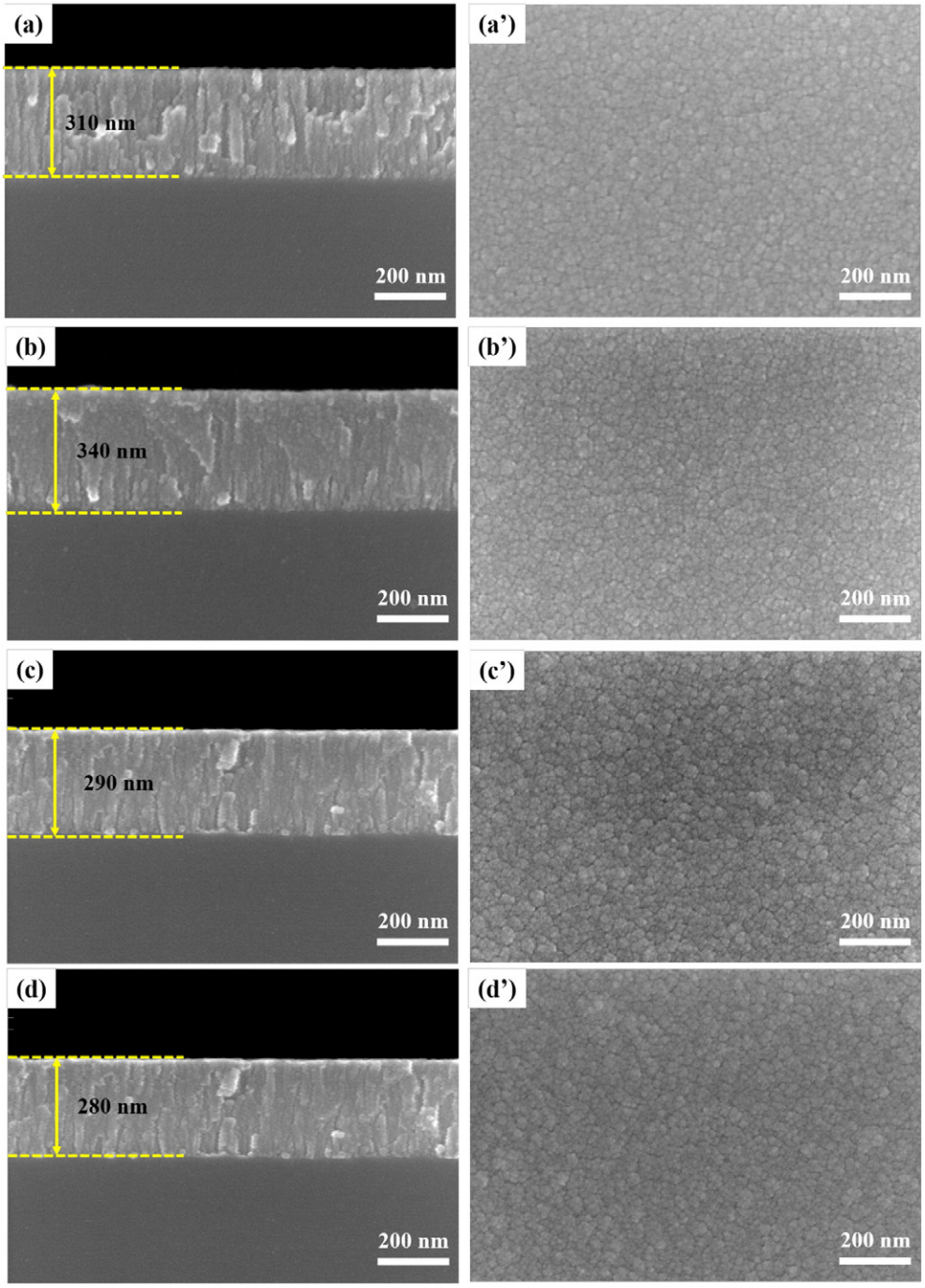

Fig. 1. SEM images of cross sections and surfaces of (a,a′) Sn_{15}, (b,b′) $Sn_{15}C_{100}$, (c,c′) $Sn_{15}C_{150}$, and (d,d′) C_{150}.