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Effect of Si addition to thin-film SnO_2 microbattery anodes on cycling performance

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Abstract

Thin-film SnO_2 and Si-doped SnO_2 microbattery anodes are deposited on a Mo/Si substrate by e-beam evaporator at room temperature. The deposited film are characterized by energy dispersion X-ray spectroscopy (EDS), X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Constant-current galvanostatic charge–discharge tests of half cells are performed. Both the SnO_2 film consist of short-range ordered small grains (nano-scale) and exhibit good ability to and extract Li^+ ions. Electrochemical cycling performance is dependent on the cut-off voltage. Tin oxide film anodes which are cycled in the voltage range 0.1–0.8 V show the highest reversible capacity (302 μA h/cm^2 μm for Si-doped film; 200 μA h/cm^2 μm for pure SnO_2 film) and the longest cycle-life. Its a papers that Si plays an important role as a glass former element in the Li–Si–O network by suppressing the growth of Sn grains, reducing the surface roughness, and enhancing film adhesion. Thus, Si-doped films are strong candidates for microbattery anodes with improved electrochemical cycling performance.

Keywords: Anode film; Tin oxide; Surface roughness; Cut-off voltage; Microbattery; Silicon-doping

1. Introduction

In recent years, electronic devices have been considerably improved in terms of memory capacity and power efficiency. With respect to the physical dimension of power source, however, the improvement appears to be not enough. Further miniaturization of electronic devices is, thus being delayed. One of the power sources — the rechargeable thin-film microbattery — has attracted considerable attention as an independent power supply for micromachines and as a back-up for electronic circuits [1,2]. Tin oxide has been shown [3,4] to be a promising anode material since its theoretical volumetric capacity is four times lager and its gravimetric capacity is twice as large as those of carbon-based materials [3,4].

Tin oxide thin-films have been prepared by various methods such as sputtering [4], spray method [5], CVD [6], and e-beam evaporator [7]. With respect to cycling performance, however, the formation of metallic Sn and Li_2O occurs during the first cycle and substantial irreversibility and large volume differences between the Li–Sn and the Sn phase on further cycling induce cracking and crumbling of the inherent structure [8]. The resulting large capacity loss of the cell is attributed to poor adhesion of the film to the substrate, and density differences which cause a change in surface roughness [6,7].

To improve the surface roughness, to achieve better cycling performance, this work reports the effect of Si addition to SnO_2 anodes. The Si-doped SnO_2 and pure SnO_2 thin-films are prepared by an e-beam evaporator at room temperature without post thermal treatment for application in a rocking-chair Li-ion microbattery. The electrochemical cycling characteristics of both film are compared by applying various cut-off voltage ranges.

2. Experimental

A thin-film of molybdenum (2500 Å) served as a current collector and was deposited on a B-doped p-type Si(1 0 0) substrate by radio frequency (rf) magnetron sputtering with a rf power of 400 W in 5 mTorr at room temperature.

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Nanocrystalline SnO_2 and Si-doped SnO_2 films were deposited on the Mo/Si substrate by an e-beam evaporator from SnO_2 and a powder and a powder mixture of 95 mol% SnO_2 and 5 mol% Si with a purity of 99.95% (Cerac Co.), respectively. The film thickness was controlled by the evaporation time and measured by using a surface profilometer. Qualitative analysis of the composition of the films was conducted by means of energy dispersion X-ray spectroscopy (EDS). The phase composition and the structure of the deposited films were investigated by X-ray diffraction (XRD) using Cu Kα radiation and by transmission electron microscopy (TEM), respectively. The surface morphology and surface roughness of the films were characterized by field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM), respectively. Half-cells were assembled with Li foil (Cyprus) as the counter and reference electrodes, and 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) as an electrolyte. The cells were used to evaluate the charge–discharge performance of the oxide and Si-doped tin oxide film anodes. The galvanostatic charge–discharge tests (WBCS3000) were performed with a constant current of 100 μm/cm^2 μm in various potential ranges (i.e. 0.1–2.0, 0.1–1.5, 0.1–1.0, and 0.1–0.8 V versus Li/Li$^+$).

3. Results and discussion

Electron diffraction (ED) patterns of the SnO_2 and Si-doped SnO_2 films were obtained by TEM and are shown in Fig. 1. Both films have an ill-defined structure and short range record small grains. The broad rings imply that both films also contain amorphous phases. The XRD patterns of the SnO_2 and Si-doped SnO_2 films are presented in Fig. 2. Two major peaks corresponding to SnO and SnO_2 appear in both films. The board peaks are typical of an amorphous structure, which is good agreement with the ED patterns. The formation of a SnO phase is due to oxygen-deficiency deposition by evaporating oxide compounds [7]. Field-emission scanning electron micrographs of the SnO_2 and Si-doped SnO_2 films are shown in Fig. 3. Both films show ill-defined and featureless images, a similar observation has been reported by Nam et al. [7].

The discharge capacity of pure SnO_2 and Si-doped SnO_2 film electrodes as a function of cycle number are given in Fig. 4(a) and (b), respectively. Both electrodes were cycled at a constant current density of 100 μA/cm^2 and over various cut-off voltage ranges. After 300 cycles of pure SnO_2, the highest discharge capacity, viz. 200 μA h/cm^2 μm, was obtained with the cut-off voltage range 0.1–0.8 V (Fig. 4(a)). This capacity was maintained for more than 150 cycles. The highest capacity (320 μA h/cm^2 μm) of Si-doped SnO_2 was also found in the voltage range 0.1–0.8 V and this value was maintained for over 250 cycles (Fig. 4(b)). It is apparent that cycling performance is significantly improved by reducing the voltage range from 0.1–2.0 to 0.1–0.8 V. Similar results have been reported by Courtney and Dahn [9]. The charge–discharge capacities of the SnO_2 and Si-doped SnO_2 film electrodes on the first, second, and thirtieth cycles are shown in Fig. 5(a) and (b), respectively.

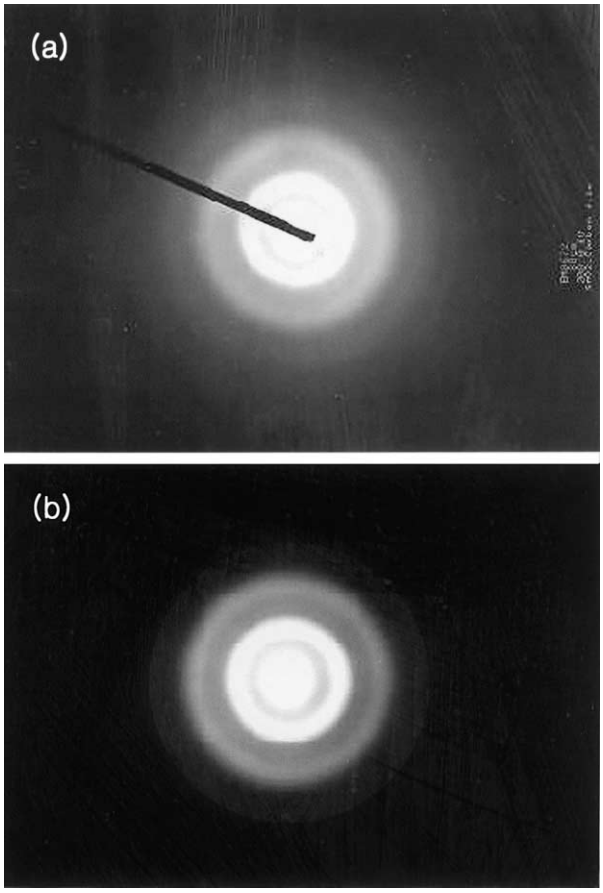

Fig. 1. ED patterns of (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films.

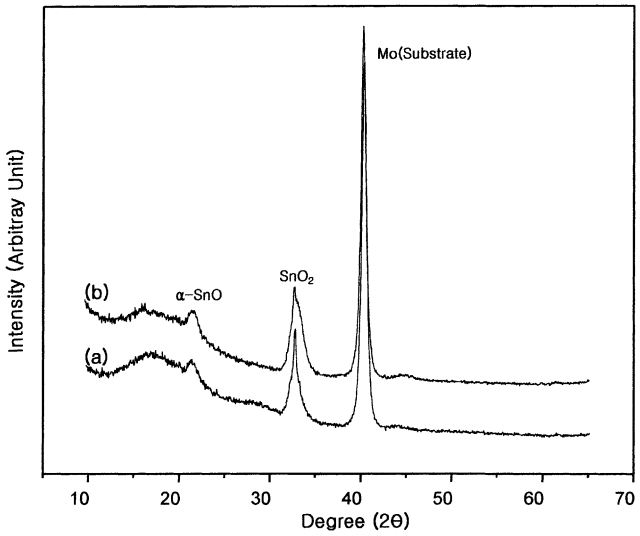

Fig. 2. XRD patterns of (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films.

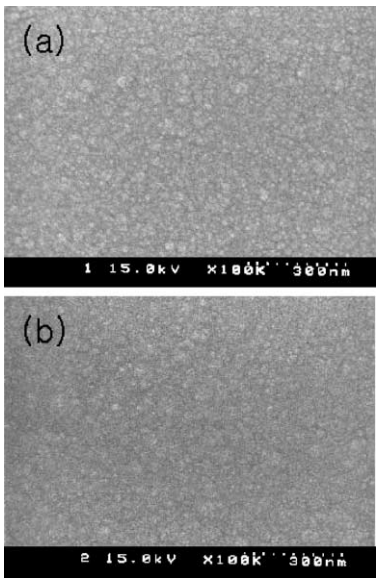

Fig. 3. FESEM images of (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films.

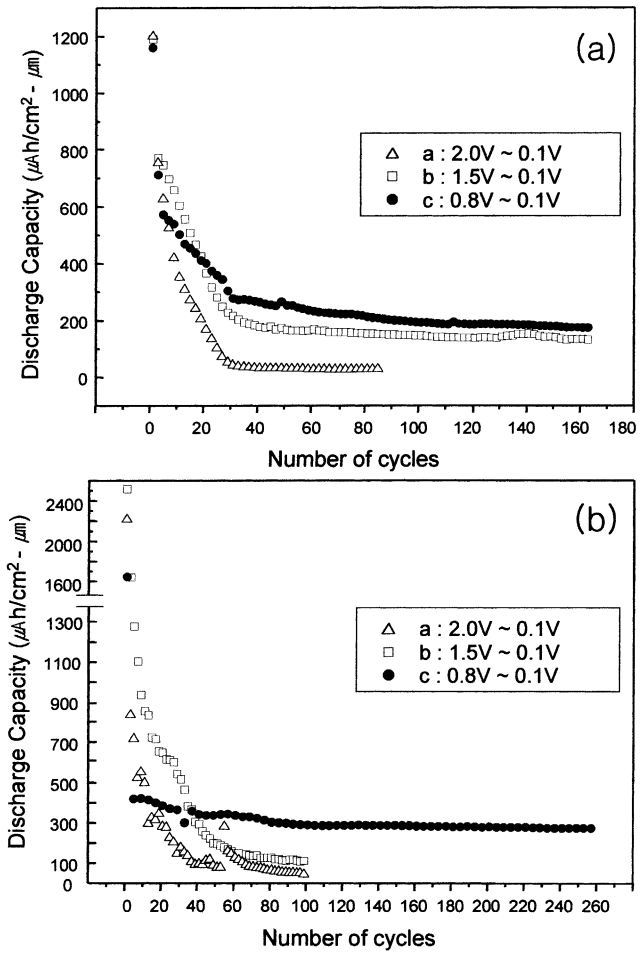

Fig. 4. Discharge capacity vs. cycling performance for (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films.

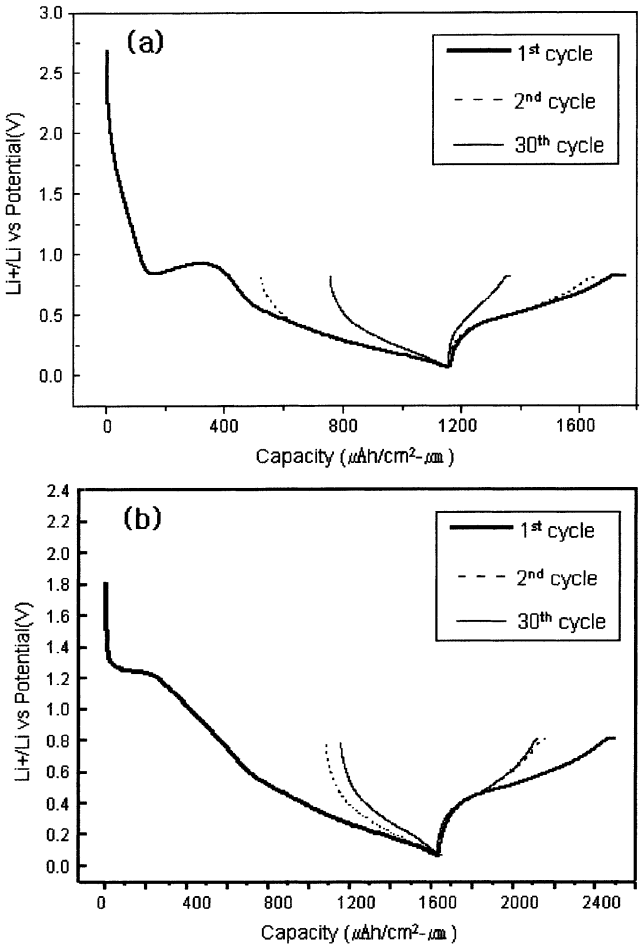

Fig. 5. Charge–discharge curves of (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films cycled in the voltage range 0.1–0.8 V.

The cut-off voltage range for both electrodes was fixed at 0.1–8 V. In the case of SnO_2 film electrode, the initial irreversible plateau was observed at 0.85 V. On the other hand, the Si-doped SnO_2 film electrode showed shorter plateau near 1.2 V and higher first discharge capacity (1620 μA h/cm^2 μm) was obtained. Both electrodes have a gradual capacity loss and good retention of reversible capacity over 200 cycles.

To investigate the effect of cut-off voltage range on the electrochemical performance, FESEM and AFM analyses of pure SnO_2 films which were cycled in different cut-off voltage ranges were obtained, see Fig. 6. It is seen that reducing the voltage range from 0.1–2.0 to 0.1–0.8 V decreased the root mean square (RMS) roughness from 0.335 to 0.192 μm. The resulting high surface roughness is one of the main factors for promoting the capacity loss shown in Fig. 4(a). The surface morphologies of bare SnO_2 films cycled in three cut-off voltage range are shown in Fig. 6(d)–(f). Fig. 6(d) shows the formation of large cracks of about 1 μm in width. These are due to the density difference between tin oxides, metallic Sn and Li alloy

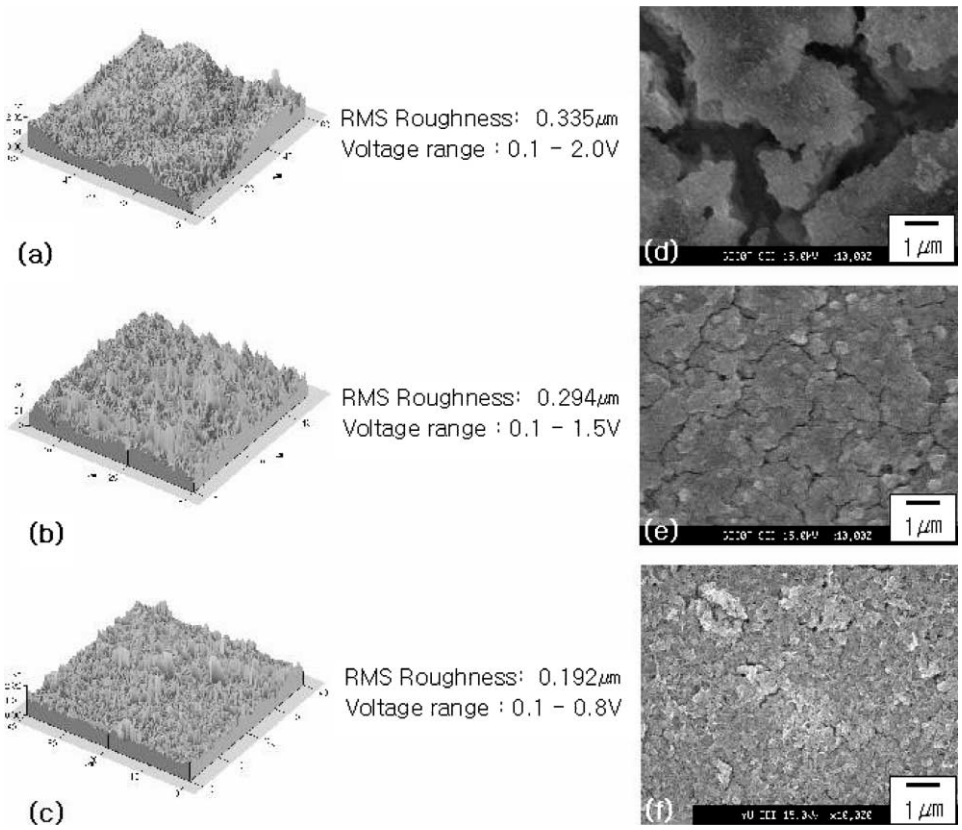

Fig. 6. AFM images ((a)–(c)) and FESEM images ((d)–(f)) of undoped SnO_2 thin-films e cycled in three different voltage ranges.

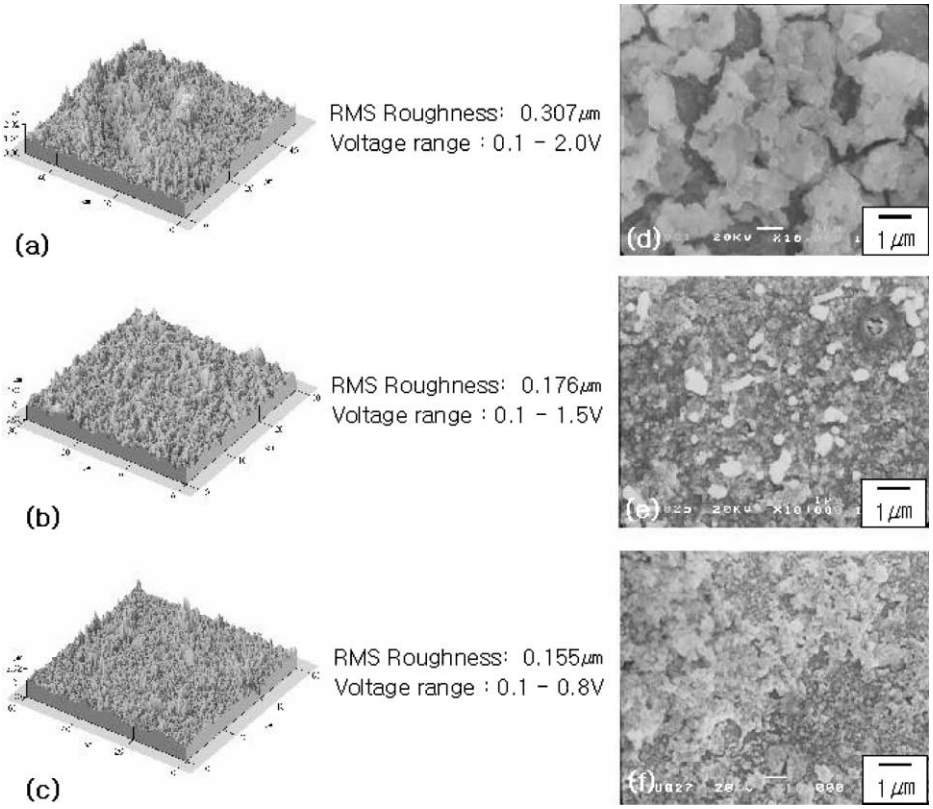

Fig. 7. AFM images ((a)–(c)) and FESEM images ((d)–(f)) of Si-doped SnO_2 thin-films cycled in three different voltage ranges.

phases. Fig. 6(e) shows a film which has been subjected to 160 cycles in the voltage range 0.1–1.5 V. There is less formation of cracks, and the cracks are smaller, i.e. less than 0.1 μm. A further reduction in cracking was found in the voltage range 0.1–0.8 V, as shown in Fig. 6(f). These results clearly explain that the reduced microcracks and decreased surface roughness are strongly associated with the cycling performance and capacity retention. Surface image of Si-doped SnO_2 films cycled in various voltage ranges are also presented in Fig. 7. The films show a similar trend in morphology to the pure SnO_2 films, but the surface roughness and the cracks are significantly reduced. The RMS value for the Si-doped SnO_2 film cycled in the voltage range 0.1–2.0 V is almost twice as high at that cycled in the voltage range 0.1–0.8 V. The FESEM images are shown in Fig. 7(d)–(f). These are for much denser structures. It is concluded that a RMS value of less than 0.15 μm is the optimum condition to give a tin-based anode which show good stability on cycling.

The structural modification of electrodes after cycling was examined by TEM. Low-resolution image of pure SnO_2 and Si-doped SnO_2 films after 200 and 300 cycles over a fixed voltage range 0.1–0.8 V as shown in Fig. 8(a) and (b), respectively, EDS results confirm that the dark regions shown in Fig. 8 are composed almost of tin and the grey areas consists of tin and oxygen. Patterns obtained by selected-area electron diffraction of several dark parts exhibit the tetragonal cell structure of tin ($a = 5.83$ Å, $c = 3.18$ Å). This finding agrees with that of Retoux et al. [10]. In Fig. 8(b), doped Si was detected in the grey parts, which indicates the formation of a Li–O–Si network. The Si-doped SnO_2 film has tin particles with an average size of 150 nm, while bare SnO_2 film has larger tin particles of size near 200 nm and also in a more aggregated form. The average size of tin particles in Si-doped SnO_2 film after 300 cycles is almost equivalent to those in a pure SnO_2 film which has been cycled only once. Rapid loss in capacity and poor cycling performance can, thus be explained by aggregation of the tin, which causes a volume expansion between other phases. Therefore, the rapid cell failure of the undoped tin oxide film is due to the growth of tin particles and aggregation of tin grains. In conclusion, Si plays an important role as a glass former for the Li–Si–O network by suppressing the growth of tin grains and reducing the surface roughness.

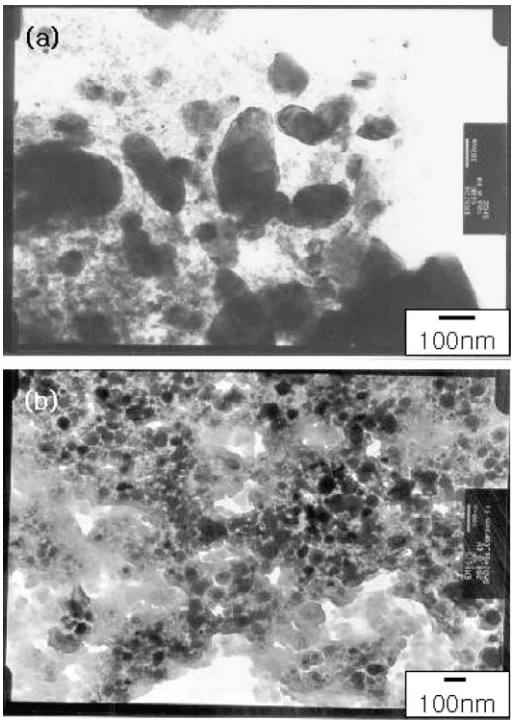

Fig. 8. TEM images of (a) undoped SnO_2 and (b) Si-doped SnO_2 thin-films cycled in voltage range 0.1–0.8 V.

4. Conclusions

The Si-doped SnO_2 and pure SnO_2 thin-film electrodes for application as microbattery anodes have been deposited on a Mo/Si substrate by an e-beam evaporator and compared in terms of electrochemical cycling performance as a function of the range of cut-off voltage. Film electrodes cycled in the voltage range 0.1–0.8 V show the highest reversible capacity (320 μA h/cm^2 μm for Si-doped film and 200 μA h/cm^2 μm for bare SnO_2 film) and longest cycle-life. This behavior is due to a reduction in surface roughness, which causes better cycling performance and reversible capacity retention. Doping Si (5 mol%) into SnO_2 effectively reduce the surface surface roughness by more than 20% after cycling and increases the reversible capacity by about up to 30% and the cycle-life by a factor of two. Doped Si, thus plays an important role as a glass former element for the Li–Si–O network by suppressing the growth of tin grains and reducing the surface roughness. The doped electrode is a candidate for microbattery anodes which have better electrochemical performance.

Acknowledgements

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