



Regular article

Effects of phase assemblage and microstructure-type for Sn/intermetallic 'composite' films on stress developments and cyclic stability upon lithiation/delithiation



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ABSTRACT

Annealing treatment of as-deposited β -Sn film on Cu resulted in the development of 'composite' film comprised of Sn-Cu intermetallic phases (Cu_3Sn and Cu_6Sn_5) surrounding 'percolating' network of β -Sn, all underneath a thin continuous β -Sn layer. Such phase assemblage and microstructure-type resulted in significantly improved mechanical integrity upon lithiation/delithiation; and accordingly very stable Li-capacity retention with continued electrochemical cycling. *In-situ* monitoring of the stress developments during lithiation/delithiation indicated that the presence of intermetallic 'buffer' phase(s) results in ~ 3 times lower stress magnitudes compared to 'pure' Sn upon 'full' lithiation, along with absence of signature for mechanical degradation in the stress-time profiles.

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Sn, as possible alternative to graphitic carbon as anode material for Li-ion batteries, has considerable advantages owing to the nearly three times greater specific Li-capacities (*i.e.*, ~ 994 mAh/g for Sn, as compared to ~ 372 mAh/g for graphite) and improved safety aspects, especially at the higher discharge/charge rates [1–3]. However, poor cycle life due to stress induced fracture/disintegration, arising from enormous volume expansion/contraction (up to $\sim 300\%$) during repeated lithiation/delithiation cycles, is the major bottleneck towards the usage of Sn as anode material [1–5]. Among the various possible means for improving the cyclic stability of Sn-based electrodes, usages of Sn-Cu intermetallic (especially, Cu_6Sn_5 and sometimes Cu_3Sn , in the place of Sn) have been envisaged [6–14], where it is often believed that the 'inactive' Cu may act as 'buffer' towards the stress developments.

However, direct use of such intermetallics alone do not offer considerable advantages since the theoretical Li-capacity of Cu_6Sn_5 (*viz.*, ~ 300 mAh/g; with ~ 200 – 250 mAh/g usually achieved) is lesser even compared to graphitic carbon, with Cu_3Sn being interestingly reported to be 'inactive' against lithiation at room temperature [11,12]. Furthermore, the insulating natures of such intermetallics [15] are not expected to offer any advantage towards the rate capability, as well. In this context, Cu_3Sn (resistivity ~ 8.8 $\mu\Omega$ cm) fairs slightly better as compared to Cu_6Sn_5 (resistivity ~ 17.5 $\mu\Omega$ cm) [16]. Accordingly, it is not surprising that the best reported performance to-date with such intermetallic-based electrodes, even in the case of composite with Sn (*i.e.*, Sn/

Cu_6Sn_5) [6–14], has not been more than ~ 450 mAh/g (delithiation capacity; after 20 cycles), considering no contribution from any other material and reversibility (*i.e.*, Coulombic Efficiency) within acceptable range. Additionally, truly significant improvement has also not been reported for cyclic stability, either.

Against these backdrops we report here the development of Sn/Sn-Cu based 'composite' thin film electrodes, having desired microstructure-type, *via* simple annealing treatment of as-deposited Sn on Cu. As will be presented in the following, such electrodes, without any binder/conducting additive, resulted in stable cyclic performance and superior Li-capacity retention, which may be comparable to the best (if not the best) achieved to-date with Sn/Sn-intermetallic based electrodes. Furthermore, the simple thin film electrode architecture also allowed monitoring of the in-plane stress developments *in-situ* during electrochemical lithiation/delithiation (for the first time with Sn/intermetallic electrodes); throwing some valuable insights into the suppressed mechanical degradation and significantly improved cyclic stability for such electrodes (developed *via* simple heat treatment), as compared to the pure (as-deposited) Sn electrodes.

Phase pure β -Sn films (see inset of Fig. 1a) were deposited on Cu foil (~ 30 μm thick), as well as on ~ 100 nm thick Cu-coated quartz wafer (diameter ~ 2.5 cm, thickness ~ 0.5 mm; for aiding stress measurements), *via* e-beam evaporation at pressure of 10^{-6} mbar using 99.99% pure Sn target (similar to our previously published work [5]). In order to form the Cu-Sn intermetallic phase, the as-deposited films were heat treated at 250 $^\circ\text{C}$ for 2 h in Ar atmosphere. Such heat treatment resulted in the formation of Cu_3Sn and Cu_6Sn_5 as the intermetallic phases (due to

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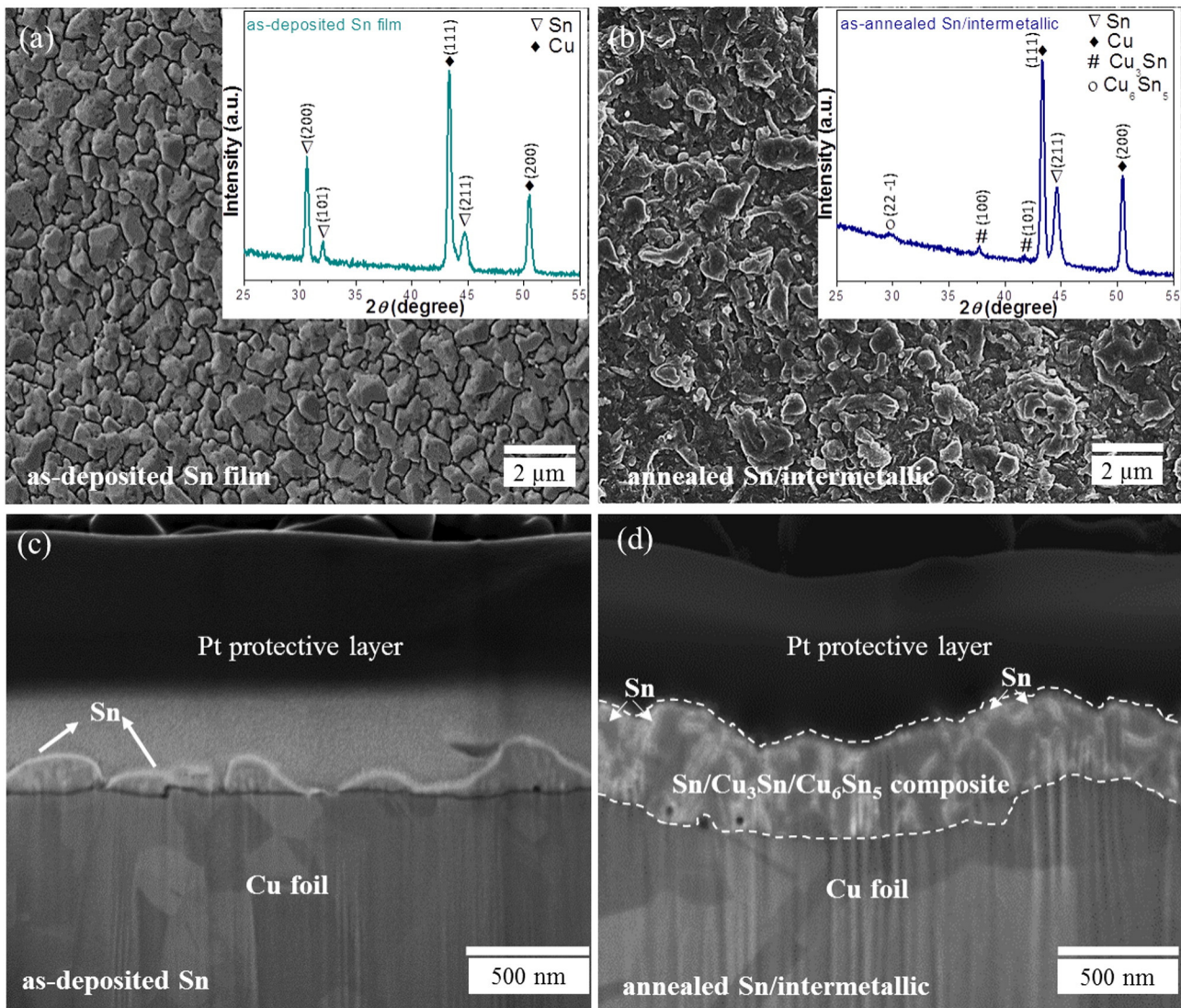


Fig. 1. Representative FEG-SEM images, along with the corresponding GI X-ray diffraction patterns (obtained at GI of 1°) as insets, obtained with the (a) as-deposited Sn films and (b) annealed Sn/Sn-Cu intermetallic 'composite' films on Cu foils. The representative cross-section images, obtained using dual-beam FIB/SEM, for the corresponding films are also shown in (c) and (d), respectively.

reaction with the Cu foil underneath), which co-existed with the 'unreacted' β -Sn (see inset of Fig. 1b). In the as-recorded Glancing Incidence (GI) XRD patterns (compare insets of Figs. 1a and b), even though the maximum intensity was recorded for the Sn (200) peak before annealing (*i.e.*, for as-deposited Sn), the Sn (211) peak, which was the second most intense peak in the former, became the most intense peak upon annealing [along with disappearance of the Sn (200) peak]. Even though this points towards a possible change in preferred orientation upon annealing (and formation of the intermetallic phases), the present observations just based on GI-XRD patterns on thin films may not be considered as definite proof for the same (further investigations on this aspect and its possible influences are presently underway; but beyond the scope of the present letter).

Top view SEM images (using JEOL-JSM7600F) indicate nearly uniform coverage for both the as-deposited (*i.e.*, β -Sn; Fig. 1a) and annealed (*i.e.*, β -Sn/intermetallic; Fig. 1b) films. Cross-section images obtained with dual-beam FIB/SEM (AurigaTM Compact; Carl Zeiss) show the individual grains for phase pure β -Sn (thickness up to ~ 200 nm) on Cu foil for the as-deposited film (Fig. 1c) (as is usually observed for vapor deposited Sn). By contrast, a more uniform 'composite' layer of ~ 350 nm in thickness, based on β -Sn (brighter contrast) and the Sn-Cu intermetallic phases (darker contrast) could be seen in the case of

the annealed film (Fig. 1d). The overall volume fraction for the intermetallic regions, as estimated *via* standard stereological method; *viz.*, by superimposing very fine grid and estimating the fraction of the total points lying on the darker region, is ~ 0.6 . Among the intermetallics, estimation based on the integrated intensity ratios between the strongest peaks for the two intermetallics in the GI-XRD pattern (inset of Fig. 1b) [*i.e.*, for Cu_3Sn (100) and Cu_6Sn_5 (22-1); normalized by the corresponding structure, multiplicity and Lorentz-polarization factors] suggests nearly equal volume fraction (*Vf*) for both the intermetallic phases (*i.e.*, $Vf_{\text{Cu}_6\text{Sn}_5}/Vf_{\text{Cu}_3\text{Sn}} \sim 1.1$). However, it may be reiterated here that such estimation may not be true representation of the volume fractions since the as-recorded X-ray diffraction pattern are GI-XRDs obtained with films (and not powder XRD). Additionally, the contrasts in the cross-section SEM images (as in Fig. 1b) could not clearly distinguish between Cu_6Sn_5 and Cu_3Sn .

The more notable observations are that the Sn itself forms a very thin, nearly continuous layer on the top, with the mixture of the phases (*i.e.*, Sn/ Cu_3Sn / Cu_6Sn_5) underneath it, extending till the pure (unreacted) Cu current collector. More importantly, the conducting Sn phase forms a sort of 'percolating' network, connecting the top of the electrode (*i.e.*, the continuous thin Sn layer) to the Cu current collector below. To the best of our knowledge, such microstructure-type, which

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