

Dear Editor and Reviewer,

We would thank you for the careful reading and the constructive comments on our manuscript. In the following we address all points of the reviewer. Besides, we have carefully checked through the whole manuscript and the changes in the revised manuscript are marked by "track changes" function in word document.

Reply to Reviewers' questions**Reviewer 1#****Comments:**

1. A lot of good work has been described in this paper. However, to make it more appealing to readers the authors need to highlight the significance of the work more in the abstract and in the introduction section.

Reply:

Thank you for your good suggestion. We highlight the following two significance of the work.

(1) This manuscript has presented fluent experimental demonstrations in the structural, optical, morphological, and electrochemical properties of SnO_x thin films as an anode used for thin film lithium ion batteries. And the regularly changed performance has a strong correlation with the film composition. It is known that magnetron sputtering is a technique for preparation of thin film based on gas discharge. The instability of reactive magnetron sputtering mainly originates the unstable oxidation of metal targets by the active species in mixture atmosphere. Therefore, the sputtering mode would lie in a spontaneous conversion between the metal and oxide sputtering mode when the oxygen partial pressure increases gradually ^[S1], then a transition state in film composition is formed. In order to calculate the stoichiometry of an oxide film correctly, the obtained O/Sn atomic ratios has been calibrated by the results of Ar⁺ etching, average Sn cation valence ^[S2] and SnO₂ standard material.

(2) In multiple papers found in literature ^[S3–S5], the role of work function (WF) of the anode material over the performance of the Li-ion device is explored. I cannot find

any paper that relates the WF of SnO_x films with the device performance and I think this paper would benefit from the exploration of this aspect. WF is critical for understanding the field–emission property of a material, and is usually defined as the energy required taking away one electron from the Fermi level (F). If the vacuum level is V, thus, WF = V–F. Therefore, it is potentially able to express the capability of electron loss from the surface of SnO_x. With the aid of WF concept, the chemical stability of SnO_x immersed in the electrolyte can be evaluated and the process of the detailed redox reaction between SnO_x and the electrolyte could be further predicted or understood. Generally, WF values could be simulated by density functional theory (DFT) or measured by the valence band (VB) spectra, which is usually measured by the ultraviolet photoelectron spectroscopy (UPS) with a He lamp (21.22 eV), and Alessandro et al. ^[S6] introduce the WF calculation procedures using the equation (S.1). The stoichiometry dependence of WF in some metal oxide films has been depicted, for instance, the WF would increase from 4.3 eV of the pure vanadium to ~7 eV in stoichiometric V₂O₅ ^[S7].

$$WF = h\nu_{He} - BE_{so} \quad (S.1)$$

Where the $h\nu_{He}$ =21.22 eV, BE_{so} is the binding energy corresponding to the secondary electron onset.

New Reference

- [S1] Safi, I. Recent aspects concerning DC reactive magnetron sputtering of thin films: a review. *Surface and Coatings Technology* 2000, 127(2–3), 203–218.
- [S2] Silversmit, G.; Depla, D.; Poelman, H.; et al. Determination of the V2p XPS binding energies for different vanadium oxidation states (V⁵⁺ to V⁰⁺). *Journal of Electron Spectroscopy and Related Phenomena* 2004, 135, 167–175.
- [S3] Gao, Y.; Wang, Z.; Chen, L. Work function, a new viewpoint to understand the electrolyte/electrode interface reaction. *J. Mater. Chem. A* 2015, 46, 1–20.
- [S4] Cherkashinin, G.; Hausbrand, R.; Jaegermann, W. Performance of Li–ion batteries: contribution of electronic factors to the battery voltage. *Journal of the Electrochemical Society* 2019, 166(3), A5308–A5312.
- [S5] Ane, E.; Stephan, L. K.; Oleksandr, B.; et al. Work function evolution in Li anode processing. *Adv. Energy Mater.* 2020, 10(24), 1–9.
- [S6] Alessandro, D.; Cinzia, C.; Monica, S.; et al. Interplay among work function, electronic structure and stoichiometry in nanostructured VO_x films. *Physical Chemistry Chemical Physics* 2020, 11, 1–9.

[S7] Li, D.; Tong, C.; Ji, W.; et al. Vanadium oxide post-treatment for enhanced photovoltage of printable perovskite solar cells. ACS Sustain. Chem. Eng. 2019, 7, 2619–2625.

List of changes

General:

1. Paper structure:

We specify the film preparation and XPS measurement conditions in the experimental section.

2. Figures:

Fig. 4(f) in manuscript is replaced by the calibrated data. Furthermore, three figures are added to illustrate the accuracy of O:Sn atomic ratios in the revised support information.

3. References:

We add five new references and their locations in the revised manuscript are rearranged and marked.

Title:

4. Line 7:

Remove the number from the affiliation because all authors are from same institute.

Abstract:

5. Line 10~20:

Six positions are need to be modified.

(1) The term of “non-stoichiometry SnO₂” is replaced by “Sn oxides” in line 10.

(2) We add the exact experiment name and pressure condition in line 11, “pulse direct current reactive magnetron sputtering (pDC-RMS), at 0.3 Pa”.

(3) The phrase of “measurement results” is replaced by “characterization” in line 13.

(4) The phrase “and more” take the place of “et al” in original manuscript to make the description sound fluent in line 14.

(5) The word “morphology” is more accurate than “topography” to describe film surface. And we use the work “transitioned” to describe the surface involution in line

15.

(6) We correct the film composition information first. Then add a sentence “and the oxidation degree was further calibrated by average valence method and SnO₂ standard material” to explain the correction method between the line 18 to line 20.

Introduction:

6. 1st paragraph, line 26~41:

Five improper language applications are revised.

(1) The word “during” is more suitable than “after” in line 30.

(2) The word “but” is not the written pattern and we replace it with “however” in line 33.

(3) We add a new word “would” to make the sentence read fluently in line 35.

(4) The word “however” is replaced by “on the contrary” in line 38 to avoid duplication.

(5) The word “exhibit” seems more accurate than “behave” in the sentence in line 39.

7. 2nd paragraph, line 42~56:

(1) The original first sentence in line 43~43 is combined into “SnO_x nanofilm ... and could be fabricated by many ways,”.

(2) We add definite article before “film thickness” in line 47.

(3) We add one paragraph depicting the advantages of reactive magnetron sputtering in line 47.

(4) The term “at a fixed working pressure” is added to eliminate doubts from readers in line 51.

(5) The sentence in line 55 “and showing a performance evolution when the...” is revised to “and introducing a gradual evolution when the...”.

8. 3rd paragraph, line 57~62:

(1) There two “hence” in this paragraph, the first “hence” in line 57 is replaced by “In this paper”, the second “hence” in line 59 is replaced by “later”.

(2) The term of “especially work function” is added in line 58 to supplement the new characterization content.

(3) The improper expression of “a better understanding that the influence of...” in line 61 is revised to “a better understanding of the O:Sn atomic ratio effect”.

Experimental

9. 1st paragraph, line 64~71:

We add the important sample information at the end of this paragraph; the samples to be tested possess the same thickness of ~130 nm. This could eliminate the reader's question about whether the film thickness is the same during characterization.

10. 2nd paragraph, line 72~88:

(1) The sentence in the experimental part should use normal past tense, hence, the word “are” in line 81 is replaced by “were”.

(2) The detailed methods and conditions for XPS test and analysis are introduced in line 83~88. Original information about XPS measurement has been deleted, the revised information provides the accurate information for the XPS measurement.

11. 3rd paragraph, line 89~102:

(1) We add “on Cu foil” after SnO_x film in line 89 to point out the samples tested in this part becomes different.

(2) We delete the extra term “performed with” in line 102.

Results and Discussion

12. 1st paragraph in 3.1 basic physical properties of the SnO_x films, line 105~124:

(1) One sentence “MA is a technique ... from metallic target ^[24]” is introduced in line 105~106 to express the importance of partial pressure.

(2) The specific condition “at a fixed working pressure” is added after Ar/O₂ flow ratios in line 107, and this could convert the influence of oxygen partial pressure to that of Ar/O₂ flow ratios.

(3) The phrase of “which is because” in line 114 is replaced by “the reason is”.

(4) The preposition “with” is more accurate than “under” in line 118.

(5) We simplify the term of “the high metallic Sn content” into “the metal deposition mode” in line 121.

(6) One sentence “(Ar/O₂=24/6), namely, a transition state lies between the metal and oxide sputtering mode” is added in line 122 to explain the transition state.

13. 2nd paragraph in 3.1 basic physical properties of the SnO_x films, line 125~136:

(1) The specific condition “but possessing similar thickness of ~130 nm” is added in line 126 to point out the samples performing characterizations have the approximate

thickness.

(2) The informal word “but” is replaced by “whereas” in line 127.

(3) Some words in the original sentence “The phenomenon of ... O₂ flow ratios is small [25, 26]” are arranged into “The blue shift phenomenon of absorption edge occurs with low O₂ flow ratios is small” in line 134~135.

(4) The term of “doping energy levels in the” is arranged before Sn oxides in line 136.

14. 3rd paragraph in 3.1 basic physical properties of the SnO_x films, line 137~155:

(1) The phrase “can be” is replaced by “is” directly in line 140.

(2) The original sentence “and the grain size is calculated in ...” is simplified to “and its grain size is calculated in ...” in line 143.

(3) The word “hence” is replaced by “next” in line 145.

(4) The term “crystal materials” sounds more fluent in the line 155.

15. 4th paragraph in 3.1 basic physical properties of the SnO_x films, line 160~177:

(1) The word “morphology” is better than “topography” in line 161 and 167 for expressing film surface.

(2) The inappropriate expression “regular spherical shape” is revised to “sphere-like shape” in line 162.

(3) The original sentence “these particles are further ... in Fig. S1” in line 165~166 is revised to “these particles are proved to be composed of metallic Sn by the EDS information in Fig. S1”.

(4) The original sentence in line 172~174 shows a wrong message, and it is corrected as following “But for the films deposited with relatively high O₂ flow ratios, the sputtered Sn particles are quickly oxidized and the Sn–O bonds are formed, therefore, these films exhibit ...”.

16. 5th paragraph in 3.1 basic physical properties of the SnO_x films, line 182~202:

(1) The term “For the films after performing cycling” is added in line 182.

(2) The word “occurring” is added in line 186 to make sentence easy to understand.

(3) Two terms “one kind of crack” and “the other kind of crack” are added in line 187 and 189 separately to clearly indicate two types of cracks.

(4) The word “information” is added after EDS in line 197.

(5) The original sentence “there are almost no other kind of elements detected in ...” in line 199 is revised to “there is no other kind of elements detected in ...”

17. 6th paragraph in 3.1 basic physical properties of the SnO_x films, line 203~233:

- (1) The long sentence in line 204~205 is divided into two parts. And the term “It demonstrates” is added.
- (2) The original sentence “which is consistent with the evolution of surface morphology” in line 208 is deleted.
- (3) The important information “the fitting results of periodic oscillation curve” is added in line 209.
- (4) The original sentence “the fitting thickness is close to the values measured by cross-section SEM images” in line 214 is simplified into “the fitting thickness is close to the actual thickness of 130 nm”.
- (5) The word “lastly” is added in line 217.
- (6) The word “furthermore” in line 218 is deleted.
- (7) The sentence “In the end, ... do not reach 100% close packing state” in line 227~230 is revised to “In the end, the values of film density are summarized in Fig. 3(h), they are always less than the corresponding density of bulk material. For example, the density of the Sn film deposited at Ar/O₂=30/0 is smaller than 7.29 g/cm³ of the bulk metallic Sn, this is because the films deposited with MS method could not reach 100% close packing state”.
- (8) The last sentence in line 231~233 is also revised to “The deposited films belong to Sn oxides with oxygen vacancy and the actual densities of the films deposited at various O₂ flow ratios are lower than the theoretical density”.

18. 1st paragraph in 3.2 composition of the SnO_x films, line 240~260:

- (1) The content in line 240~245 is simplified into one sentence “The types of elements contained in the SnO_x films are determined to be C, Sn and O according to the survey spectrum shown in Fig. S6.”.
- (2) The content in line 246~247 is simplified into “Then the Sn 3d spectrum are presented in Fig. 4(a), the Sn 3d core level peak is composed of double peaks”.
- (3) The term of “by the way” is added in line 259.

19. 2nd paragraph in 3.2 composition of the SnO_x films, line 261~276:

- (1) The term of “curves of” in line 262 is replaced by “peak in”.
- (2) The sentence of “the following conclusions are obtained:” is added in line 165.
- (3) The phrase of “chemical states of” in line 270 is deleted.

(4) The phrase of “deposition Ar/O₂ condition” is replaced by “Ar/O₂ atmosphere”.

20. 3rd paragraph in 3.2 composition of the SnO_x films, line 277~289:

(1) The term of “all components” is added in line 284.

(2) The word “moreover” is more suitable than “furthermore” in line 285.

(3) New sentence “Hence, we add Ar⁺ etching experiment^[51] and the XPS spectra of SnO₂ standard material to calibrate the O:Sn atomic ratios, as shown in Fig. S8~S9.” is added in line 289 to provide the ancillary information.

21. 4th paragraph in 3.2 composition of the SnO_x films, line 290~300:

New sentence “The VB spectra could also be used to analyze the work function, Fig. S10 shows two corresponding curves.” is added in line 297~298.

22. Caption of Figure 4, line 303~304:

New caption of “(f) Summary of the O:Sn atomic ratios and average Sn cation valence” replace the old caption in line 303~304.

23. 5th paragraph in 3.2 composition of the SnO_x films, line 305~325:

(1) The corresponding works are introduced in line 305~306, namely, one sentence of “The related literatures^[56, 57] have introduced the calculating procedures by the atomic sensitivity factor (ASF), for instance, Kwoha et al.^[58] calculate the relative O:Sn concentration in SnO₂ films based on the ASF.” is added.

(2) The word “furthermore” is replaced by “next” in line 311.

(3) The word “oxide” is replaced by “detected oxygen component” in line 315.

(4) The term “the introduced reactive” is added in line 322.

24. 6th paragraph in 3.2 composition of the SnO_x films, line 327~328:

New content “Where the $n_{\text{Sn}}/n_{\text{O}}$ represents the atomic ratio, the letter I stand for intensity of the photoelectron (namely, refers to the peak area of a characteristic peak), which has a linear relationship with the atomic concentration in the sample, and the ASF values for Sn and O are confirmed to be 4.095, 0.711 separately according to the library of ASF in XPS apparatus.” is used to explain the formula (1.1) in line 327~328.

25. 1st paragraph in 3.3 electrochemical performance of the SnO_x films, line 330~340:

(1) The word “composition” is replaced by “atomic ratios” in line 331.

(2) New words “occurring”, “this indicates” are added in line 336.

26. 2nd paragraph in 3.3 electrochemical performance of the SnO_x films, line 341~354:

(1) The word “exhibites” is replaced by “exibiting” in line 342.

(2) The term “as shown” is replaced by “just like” in line 343.

27. 3rd paragraph in 3.3 electrochemical performance of the SnO_x films, line 355~381:

(1) The term “in the SnO_x electrodes” is deleted in line 356.

(2) The term “as shown in Fig. 2” is deleted in line 374.

(3) The sentence “derived from the polymerization of solvent molecules in the electrolyte solution” in line 377 is deleted.

(4) The sentence in line 378~380 is arranged into “While in the following oxidation process, the intensity of three peaks remains unchanged except for the intensity of the oxidation peak positioned at 0.62 V.”.

28. 4th paragraph in 3.3 electrochemical performance of the SnO_x films, line 388~405:

(1) The term “O₂ flow ratios increase” is replaced by “oxidation degree” in line 393.

(2) The sentence in line 393~395 is revised to “This position corresponds to the formation of SEI layer in SnO_x material and is very different from that in Sn material. The metallic Sn provides a high ...”.

(3) The word “is” is replaced by “has been” in line 396.

(4) The wrong expression of “the numbers of cycles” is replaced by “cycle numbers” in line 398.

(5) The last sentence in line 403~405 is revised to “this view has been proved by the Mössbauer spectroscopy^[45, 65] and could be used to explain why the first discharge capacity of SnO_x is higher than the theoretical capacity”.

29. 5th paragraph in 3.3 electrochemical performance of the SnO_x films, line 409~419:

(1) The term “react on the surface od SnO_x” in line 413 is replaced by “react at the interface of SnO_x/electrode”.

(2) The word “lastly” is replaced by “next” in line 415.

30. 6th paragraph in 3.3 electrochemical performance of the SnO_x films, line 420~436:

- (1) The term “during first cycle process” is deleted in line 431.
- (2) The word “namely” is added in line 435.

31. 7th paragraph in 3.3 electrochemical performance of the SnO_x films, line 437~455:

The term “close to the stoichiometry SnO_2 ” in line 449 is deleted.

32. 8th paragraph in 3.3 electrochemical performance of the SnO_x films, line 459~475:

The term “the formation of” in line 465 is deleted.

33. 9th paragraph in 3.3 electrochemical performance of the SnO_x films, line 476~496:

- (1) The word “but” in line 483 is replaced by “however”.
- (2) The term “is typically regarded as a complete SnO_2 and” in line 495 is deleted.

34. 10th paragraph in 3.3 electrochemical performance of the SnO_x films, line 499~519:

- (1) We use the term “semicircle” uniformly to describe impedance spectroscopy.
- (2) The content “electrochemical activity”, “but the pure Sn material ... contact loss” in line 518~519 is deleted.

Conclusions:

35. Line 524~536:

- (1) The word “decomposition” is replaced by “deconvolution” in line 528.
- (2) The word “occur” is replaced by “appear” in line 530.
- (3) The sentence “Third, ... conversion + alloying” in line 531~532 is revised to “Third, it is the increase of oxidation degree within the SnO_x films that determines the reaction transition from "single alloying" to "conversion + alloying" mode”.
- (4) The content “must be present to” in line 533 is deleted.

Supplementary materials:

36. Line 537~544:

New descriptions of three figures are added in line 544.