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Thesis Changes Log

Name of Candidate: Patrick Aggrey

PhD Program: Materials Science and Engineering

Title of Thesis: Nanoscale Phase Separation And Transformations In The Silicon-Oxygen And Related Systems

Supervisor: Prof. Alexander M. Korsunsky

The thesis document includes the following changes in answer to the external review process.

Professor Aksyonov Dmitry

1. "drew on a wide range of characterization techniques" what do you mean here? Please be more specific
   Thank you very much for this comment. This statement talks about several characterization techniques used for structure and property studies of the material in this work. The abstract did not provide specific names because of the numerous techniques used.

2. "opened the possibilities for producing nanostructured silicon materials with a vast range of functionalities in a facile, eco-friendly and cost-effective way … a vast range of functionalities". What possibilities do you mean? What is the vast range of functionalities? Please be more specific.
   Thank you very much for this comment. The vast range of possibilities covers battery anodes, optical devices, gas sensing, and photocatalyst

3. it is mentioned that "certain shortcomings and challenges are encountered in the nanostructuring of materials ...". Do you mean the challenges with the process of nanostructuring or problems with nanostructured materials? Should be clarified.
   Thank you very much for this comment. This statement has been rectified.

4. What was the partial pressure of oxygen during calcination and roasting?
   Thank you very much for this comment. The partial pressure of oxygen during roasting was 212.28mbar and 361.11mbar as calculated using data from literature.

5. Why the temperature of 1100 C and time of 4 hours were used for calcination and roasting?
   Thank you very much for this comment. The temperature and time chosen for the heat treatments were done so to prevent significant damage to the nanoporous network of the diatom-derived silica frustules. This has been provided in the revise Thesis

6. First and second paragraphs of Section "2.4.2 In situ formed Silicon nanoflakes" should be moved to introduction or results

Thank you very much for this comment. This has been resolved.

7. It should be clarified what silica powders (pristine of after roasted) were used to create coatings
   Thank you very much for this comment. This has been corrected in the revised Thesis.

8. In section 2.8 Electrode Preparation and Electrochemical Measurement it is stated "All measurements were carried out at a constant temperature of 20 °C." How did you control the temperature?
   Thank you very much for this comment. This has been corrected in the revised Thesis.

9. "When tested as anode materials, the calcined diatom-derived silica powder showed the best discharge capacity of 550mAhg -1 amongst the three silica types (380mAhg -1 for roasted and 175mAhg -1 for the pristine powders)." Why did the calcined samples show the highest capacity? How does it compare to other silica materials obtained in literature?
   Thank you very much for this comment. This has been corrected.

10. In Section 3.1.1 Modifications in Color, Particle and Crystallite Sizes - you present analysis of chemical composition. Please mention this in the title.
    Thank you very much for this comment. This has been corrected.

11. "It is evident from this study that particle size reduction is an effective tool to improve electrochemical performance in devices" Here this statement was not proved yet or do you mean literature data?. Reformulate.
    Thank you very much for this comment. This has been corrected in the revised Thesis.

12. "In this work, the calcined and roasted diatom-derived silica powders had crystallite sizes of 8.58 nm and 11.44 nm respectively for the main cristobalite phase as shown in Table 4." Clarify how the size of crystallites was determined? The fact that cristobalite is the main phase is shown only in the next section. Please correct.
    Thank you very much for this comment. This has been revised.

13. "The limited flow of oxygen (argon environment) appears to not only limit coloration but is equally suitable for obtaining small cristobalite crystallites." Why are you interested in a limited air flow? The size of crystallites during roasting is only slightly larger.
    Thank you very much for this comment. The limited flow of oxygen was explored to understand the role of heating environments on the powder characteristics and initial colour changes suggested significant effects of the heating environment.

14. Figure 12. What is the space group of cristobalite phase? Is it alpha-phase or beta phase? Please clarify in the text and in the caption
    Thank you very much for this comment. The main phase after the thermally-induced phase transformation was α-cristobalite with space group $P4_12_12$

15. Figure 17. The capacity of heat treated sample is increasing each cycle. Why? The currently given explanation should be expanded and requires clarification about the mechanism of electrochemical milling.
    Thank you very much for this comment. The revised Thesis contains further discussion of the electrochemical results.

16. What is the coulombic efficiency? It should be provided.
    Thank you very much for this comment. The revised Thesis contains information about the coulombic efficiency of the anodes.

17. Figure 17. What is the electrochemical reaction taking place here? What are the discharge products? Is there any O2 gas formation upon discharge? Do you consider insulating SiO2 as a viable anode material?
    Thank you very much for this comment. The revised Thesis contains details of the electrochemical reactions taking place. From extensive literature search, there is no formation of O2 upon discharge. Yes, insulating SiO2 could be viable anode considering it offers quite high theoretical capacity and offers better structural stability when compared to Si.

18. A summary for Section 3.1 is required. What are the advantages and disadvantages of each heat treatrement? What are the main differences between them in terms of microstructure, composition and properties?
    Thank you very much for this comment. The revised Thesis includes a summary of this section.

19. Why XRD in Fig 12a and Fig19a are strongly different?
    Thank you very much for this comment. I completely agree with you. Although the XRD patterns look different from first glance, they all show a broad hallow which is characteristic of the main amorphous phase, Opal. The difference is due to the difference in size representation of the patterns. Thank you.

20. Figure 22. Why only five cycles are provided?
    Thank you very much for this comment. The number of cycles was increased and new results provided in the revised Thesis.

21. In section 3.3.5 Optical Properties of Silicon nanoflakes - “The silicon nanoflakes suppressed light reflection to less than 15% in the infrared region compared to the 45% light reflection from the c-Si wafer surface.” Is it for pristine or roasted SiO2 powder? How does it compare to black silicon?
    Thank you very much for this comment. This has been provided in the revised Thesis

22. A summary for Section 3.2 is required.
    Thank you very much for this comment. The summary has been provided.

23. “results could help provide guidelines for selecting the most ideal precursor diatom derived silica for the synthesis of silicon based materials for energy related applications.” Can you formulate these guidelines here?
    Thank you very much for this comment. The guidelines have been provided in the concluding statement for the silica and silicon anodes

24. “possessed very intricate details of the precursor diatomite powder to some extent” Can you be more specific?
    Thank you very much for this comment. The intricate details correspond to the nanoporous network which could only be found in diatom-derived silica

25. “A preliminary adhesion scratch test also confirmed a good bonding of the silicon nanoflakes to the surface of the substrate silicon wafer.”

Thank you very much for this comment. This preliminary test confirmed good adhesion of the textured Si coating to the underlying substrate

26. Figures: - Improve the quality of Fig. 9 and 10. The y axis label is hardly visible. - Improve Fig 14. The figures are compressed along the horizontal line. Looks strange. - Improve Fig 16 and Fig 17. figures have different size. Looks inaccurate - improve Figure 31, b and c are blurred
    Thank you very much for this comment. These changes have been made

Prof Petr Prikhodchenko

1. Thermal analysis of magnesiothermic reduction of silica precursors at different heating rates (5C/min and 10C/min) presented or. Fig. 16. The author postulates that an increase in the heating rate affects the values exothermic peak temperatures, in particularly at l0C/min, all the silica-reduction reactions had exothermic peaks at lower temperatures compared to reactions at 5C/min. Did the author consider the possibility of hardware measurement error when changing the heating rate? Since it is known that for slower heating rates, data resolution (e.g., accuracy of temperatures reported) is increased, but the sensitivity (e.g., the sharpness of the peaks) of the heat measurement is lower, especially for smaller sample masses. For higher heating rates, resolution is lost, but sensitivity is increased.
    Thank you very much for this comment. This is actually an important aspect of the thermal studies that has already been considered in post-Thesis research. As far as this work is concerned, hardware measurement errors were not taken into consideration. Different heating rates were used just to confirm if different on-set temperatures were dependent on the ramp rate. In current on-going experiments, heating rate at 10C/min was used. It must also be mentioned that the measurements were performed in the same crucible but sequentially.
2. The composition of the slurry in the preparation of electrodes based on silicon and silicon oxide in this work is 50% active material, 35% active carbon (carbon black), and 15% binder (PVDF). What is the reason for using such a relatively small load of active material in the anode composition? And how fair is it to evaluate and compare the values of the specific electrochemical capacity of an anode of such composition?
    Thank you very much for this comment. The protocol used for preparing the silica based anode was taken from literature for preliminary studies of their electrochemical performance. Such high carbon black content was used because the silica powders were not carbon coated. Future studies aims at reducing the carbon black content and increase silica significantly.

3. The electrochemical performance of anodes based on silicon and silicon oxide is presented. It might be good to compare specific capacities with in literature data for analog materials.
    Thank you very much for this comment. This has been corrected in the revised Thesis.

4. Figure 21 shows the Raman spectra of silicon powders obtained by reduction of untreated and treated silicon oxide. On the spectrum of silicon obtained by the reduction of silicon oxide heated in air, the main peak has a shoulder. How to explain it? At the same time, this sample is positioned as silicon with higher crystallinity and purity.
    Thank you for bringing my attention to this. As far as the purity of elemental silicon is concerned, the Raman peak position reveals much more information. The width of the Raman peak provides information about the structure (amorphous, crystalline or semi-

crystalline). The shoulder could account for the micro-crystalline silicon in this silicon type.

5. Figure 31b,c is of poor quality and in this condition does not carry any information about the surface morphology. In addition, there is no dimensional scale, which makes it difficult to evaluate.
   Thank you very much for this comment. This has been corrected.

6. Using the sol-gel method, a solid material (PAN/silica) was obtained and further processed to 1 form a porous carbor1 membrane. "An aqueous solution of TEOS was prepared by mixing the precursor with 0.024 M hydrochloric acid (HCI) in a ratio of 6:2.3." Why is such a large excess of hydrochloric acid used? Usually a small amount of HCI, which plays the role of a catalyst, is sufficient for such process.
   Thank you very much for this comment. That is very true. This protocol was adopted from literature to explore the creation of porous amorphous carbon coating. I totally agree that a small amount of HCl is sufficient for this purpose.

7. There are typos, and some inaccuracies in the figures design, in particularly, 1) Figures 17 and 22 show charge-discharge curves. The X scale is signed as "Capacity, mAh/g", it would be more correct to indicate as specific capacity. 2.) Page 73 - repeated sentence "ln equation 7, T is the crystallite size, K is a constant (0.9), λ is the wavelength of the x-ray source, β is the FWHM and θ is the Bragg angle" 3) No scale bar on SEM and optical images –Fig 34 and Fig 31
   Thank you very much for this comment. These issues have been resolved in the revised Thesis.

Professor Maria Kandyla

1. In Section 2.2, Heat Treatments, maybe the differences between calcination and roasting can be clarified by describing in more detail each method.
   Thank you very much for this comment. The revised Thesis includes more details about the heat treatment procedures

2. In chapter 3, Fig. 12a, the signature of opal must be explained in the text right above the Figure because only the quartz peaks are denoted in Fig. 12a
   Thank you very much for this comment. This has been corrected in the revised Thesis

3. What is the broad peak at low angles in chapter 3, Fig. 19, last row?
   Thank you very much for this comment. The broad peak seen in Fig. 19 is contribution from the XRD sample holder.

4. In chapter 3, Fig. 22b, from what type of silica is the anode derived? Pristine, roasted, or calcined?
   Thank you very much for this comment. The silicon anode was derived from the calcined powder due to its superior powder properties.

5. In Fig. 23b, the reference must be provided.
   Thank you very much for this comment. The figure was changed and reference provided.

6. At the top of p. 84, where the doping results of Si nanoflakes are discusses: what were the electric properties of the original Si substrate, was it n or p doped and how much?
   Thank you very much for this comment. The original Si substrate was an n-doped Si

substrate.

7. In Fig. 34, scale bars are missing.
   Thank you very much for this comment. This has been corrected in the revised Thesis.

Professor Mailis Sakellaris

1. There should be a section where the advancement of the state of the art should be made clear. Although there are elements in the thesis where the advancement of knowledge is indicated, it is my opinion that there should be a clear statement of purpose regarding the particular areas where this work makes a clear contribution.
   Thank you very much for this comment. The Thesis has been revised with a clear statement outlining the clear contribution of this work.

2. A second point is related to continuity of this work in the form of an outlook section, which is currently missing.
   Thank you very much for this comment. The revised Thesis includes a chapter dedicated the continuity of this work.

3. Finally, due to the extremely applied nature of this work and its relevance to production, I believe that any statements regarding the cost efficiency should be substantiated by some elementary cost analysis in comparison with mainstream analogues
   Thank you very much for this comment. The revised Thesis provides some concept of the cost comparison with regards to the complexity of procedures and laboratory equipment needed for the approach outline here and conventional methods

4. There are very few minor typos and omissions, like missing scale bars in figure 34 and terminology inconsistencies such as EDX vs EDS. A careful review of the manuscript should be performed for the final version.
   Thank you very much for this comment. These corrections have been made.

Professor Henni Ouerdane

1. Chapter 3, Results and Discussion, is quite bulky and could easily be split into two different chapters given the number of results, which deal with various aspects and properties of the materials; but this depends on how the candidate wants to construct his narrative. Chapter 2 is on the contrary quite short considering the all techniques and materials discussed. It appears as an imbalance in the writing of the thesis.
   Thank you very much for this comment. I completely agree. The Thesis structure has been revised. The revised Thesis comprises 7 Chapters.

2. Note that a similar comment might be made for the Introduction Chapter, which could be split into two parts: one that ends at section 1.2 Overall Aims of the Thesis, and the rest which can constitute a literature review chapter. But again, it is a matter of editorial choice made by the author.
   Thank you very much for this comment. I completely agree. The Thesis structure has been revised.

3. The Conclusion chapter provides a good recap of the work and ending with the list of outcomes as the take-home message is fine. However, this does not quite mirror the

"general questions" listed in the Introduction, section 1.2. A clearer or more direct link between the outcomes and the questions would be good.

Thank you very much for this comment. The list of outcomes covers the second part of the Thesis which focused on textured Si nanostructures and bi-layer Si/a-C nanocomposite coating. A direct link between the outcomes and questions are provided in the first part of the conclusions with revisions.

Professor Dong LIU

1. The author should check and revise the manuscript carefully. Page 38, Line 1: "Fig 4" should be "Figure 4". Page 56, Figure 8: b and c do not have ")". The figures in the thesis should be presented properly, not be stretched, such as Figures 5, 7, 14, 32.

   Thank you very much for bringing my attention to this. All changes have be made

2. The nano/microstructures of silicon affect their light absorption. Do these nano/microstructures of silicon influence their band structures?

   Thank you very much for this question. Yes, the nanostructures influenced the optical band energy to some extent and this has been provided in the revised Thesis.