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Jury Member Report – Doctor of Philosophy thesis.

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: Professor Alexander Korsunsky
Co-supervisor: Alexey Salimon, Senior Research Engineer

Name of the Reviewer: Dr. Petr Prikhodchenko

I confirm the absence of any conflict of interest	**Date: 26-05-2023**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The development of nanostructured silicon-based materials from siliceous precursors is highly relevant to modern technology and has a wide range of potential applications. This area of research holds promise for enhancing the performance of electronic devices, as well as improving energy storage systems and catalytic process efficiency. Despite the significant amount of research already conducted, further study is required to fully address the challenges associated with material production and enhancing performance through detailed analysis of specific synthesis conditions. This research proposes opportunities to produce nanostructured silicon-based materials with a wide range of functional properties through a simple, environmentally friendly, and cost-effective method.

The thesis represents a 118-page report which has typical structure and is divided into several logically arranged chapters. These include an abstract, introduction, materials and methods, results and discussion, conclusions, and a bibliography list (153 titles). The thesis includes 8 tables and 40 figures. The dissertation is done at a high level, using modern research methods, clear structure, and logic, and contains conclusions and practical recommendations. Thesis demonstrates a possibility to synthesize nanocrystalline Si-based materials different morphology and their modification by using complex of synthetic techniques like as magnesiothermic reduction reaction and sol-gel method. The influence of a complex of factors on the structure and properties of the final material has been studied in detail.

In the abstract, the relevance of the topic of the dissertation work is substantiated, goals and objectives are formulated, an assessment of the scientific novelty of the obtained results and their practical significance is given.

The introduction delivers the background by describing the present studies of Si-O system, recently reported nanostructuring approaches and the significance of this processing route for silicon-based materials in energy related applications. Methods and approaches for the synthesis of nanostructured Si-based materials are presented. Much attention is paid to the influence of the type of initial silicon oxide, its pre-treatment (mechanical and thermal treatments). A separate section of the introduction is devoted to the study of the metallothermic reduction reaction and the effect of synthesis conditions, such as reaction time and temperature, heating rate, ratio of reagents, homogeneity of the reaction mass, on the parameters of the final material - Si.

The second chapter (Materials and Methods) outlines the experimental approaches used in the work - synthetic procedures and methods used to determine the structure, composition, morphology and properties of synthesized materials and parameters of the used equipment.

In the third chapter "Results and Discussions" the main experimental results of the research are presented, their interpretation is proposed, a correlation with literature data is made, and a generalization is carried out in the form of a holistic picture of the influence of many factors on the morphology and properties of the final silicon-based materials. In particularly, the present study considered the effects of thermally induced phase transformations in the Si-O system on the synthesis via the magnesiothermic reduction reaction and properties of silicon-based nanomaterials in the form of powders and porous consolidates. Thermal treatment of diatom-derived silica precursors has significant effects on the powder characteristics of recovered silicon product. The results of the study of the original silicon oxide and pure silicon in the composition of the anode in a half-cell with lithium counter electrode are presented. The author extends this approach to obtain nanostructured silicon coatings as nanoflakes formed on silicon wafer.

The use of sol-gel method in combination with a metallothermic reduction reaction allowed to modify the silicon-wafer, forming on its textured surface porous and continuous a-C carbon thin films. This, in turn,

had a positive effect on the optical properties of the material. The porous and continuous a-C modified surface showed a steadier absorption than c-Si and textured Si surfaces. The development of such low cost and facile textured surfaces is crucial for optimizing the light-matter interaction of optical devices and the results captured in this work adds up to the existing progress made so far in this area. The conclusions compactly and clearly present the main results of the research.

Thus, the proposed approach to the synthesis of silicon-based nanostructured materials and the achieved properties of the obtained materials can be qualified as a scientific novelty that is of fundamental and applied importance and shows that the work is important for the development of the subject area.

The main results of the research have been published in peer-reviewed scientific journals indexed in the Web of Science and Scopus databases.

The dissertation ready for defense in its current form. I only have a few superficial comments at this point:

1. Thermal analysis of magnesiothermic reduction of silica precursors at different heating rates (5 and 10 C/min) presented on Fig. 16. The author postulates that an increase in the heating rate affects the values exothermic peak temperatures, in particularly at 10C/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 a 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.

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 it is to evaluate and compare the values of the specific electrochemical capacity of an anode of such composition?

3. The electrochemical performance of anodes based on silicon and silicon oxide is presented. It might be good to compare of specific capacities with available in literature data for analog materials.

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.

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.

6. Using the sol-gel method, a solid material (PAN/silica) was obtained and further processed to form a porous carbon membrane. "An aqueous solution of TEOS was prepared by mixing the precursor with 0.024 M hydrochloric acid (HCl) in a ratio of 6:2.3." Why is such a large excess of hydrochloric acid used? Usually, a small amount of HCl, which plays the role of a catalyst, is sufficient for such process.

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 "In 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.

Summarizing, the scientific work is done at a high level, using modern research methods, clear structure, and logic, and contains conclusions and practical recommendations. It is ready to be defended. Patrick Aggrey has done original work and addresses many challenges of this field. The obtained results have great practical potential. He deserves to be awarded a PhD degree.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*