Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Aliya Glagoleva

PhD Program: Materials Science and Engineering

Title of Thesis: Development of kW Scale Hydrogen Energy Storage System

Supervisor: Prof. Keith Stevenson

Co-advisor: Dr. Vasily I. Borzenko

Chair of PhD defense Jury: Prof. Alexei Buchachenko ***Email***: *a.buchachenko@skoltech.ru*

Date of Thesis Defense: 09 October 2018

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

Thesis Changes in answer to the external Jury Members comments and suggestions.

1. Answers to the comments of Professor Darius Milčius

*C1: Talking about solid state hydrogen storage materials two dimensions were in use. For example, page 36: "…10 ÷ 13% **(mass)**"; but in the page 40 "…**%wt**", page 39 "…1 to 2**% by weight**". Would be useful to unify it.*

The dimensions were unified.

C2: Page 54 "…Fig. 2.9c" is mentioned. It must be properly checked.

The Figures and the Tables have been made as hyperlinks throughout the text and properly checked.

C3: References [123] and [141] were the same.

Corrected.

2. Answers to the comments of Victor Zaichenko, D.Sci, Joint Institute for High Temperatures of RAS

C1: An interesting next step might include choosing an existing model and comparing the outcomes of the model with experimental investigations. However, the candidate shall be awarded PhD degree regardless of the addition.
Additionally, minor mistakes and typos should be addressed before final submission.

We have already made some significant steps towards modeling the system. However, this work was not added to the thesis due to a large number of aspects that had already been covered.

3. Answers to the comments of Dmitry Dunikov, PhD, Joint Institute for High Temperatures of RAS

C1: For example tables 1 and 2 are presented as pictures, there are some misprints and so on. The work *has to be proof red.*

Both tables have been worked upon and changed. The misprints were eliminated, and the work has been checked for mistakes, typos, errors. The text had intense proofreading to eliminate language imperfections.

4. **Answers to the comments of Professor Mykhaylo Lototskyy, University of the Western Cape**

C1: The work on the development of MH reactors lacks a study related to the modelling of heat‑ and‑ mass transfer and experimental verification of the models by separate experiments on their H2 charge and discharge. The main outcome from these studies would be in the time dependencies of the charge / discharge flow rates at various operating conditions including temperatures and flow rates of a heat transfer fluid.

My colleagues and I carried out the work on hydrogen charge and discharge modeling, however, it was not added to the thesis as the outcomes of the modeling would not influence the goal and outcomes. The modeling was carried out with the purpose of designing the next system of 30 kW power level, utilizing the proposed concept with a need for an optimized heat transfer carrier. Additionally, the model was already tested on multiple reactors (including the one described in the thesis) and the outcomes published in the multiple articles* and dissertations**. However, complying with the current suggestion, an additional subsection was added where an introduced reactor is used for experimental verification tests for two kinetics models.

*Dmitry V. Blinov, Vasily I. Borzenko, Dmitry O. Dunikov, Ivan A. Romanov. Experimental investigations and a simple balance model of a metal hydride reactor. International journal of hydrogen energy 39 (2014) 19361-19368
** V. Borzenko, «The reserch of processes, design and development of a metal hydride system for storage and purification of hydrogen for the power plants based on the 1kW PEM FC», Dissertation, [in Russian] (2012)

C2: Though the literature review mainly covers details of the topic, on the opinion of the reviewer, some extra sources related to the integration of MH with fuel cells should be also considered (could be added to section 1.8. State of the art in MH reactors):

a. Applied Energy 88 (2011) 4517–4526
b. Applied Energy 109 (2013) 60‑66
c. Journal of Alloys and Compounds 645 (2015) S329–S333
d. International Journal of Emerging Electric Power Systems 17(1) (2016) 59–67
e. Nature Reviews: Materials 2 (2016) 16091
f. Progress in Natural Science: Materials International 27 (2017) 3–20

A separate subsection 1.8.1 was added to the thesis that includes the outcomes and examples of FC and MH integration from all the mentioned articles, [164-169] in the list of references.

C3: Literature review; section 1.7.3. Chemical methods of hydrogen storage – Liquid Organic Hydrogen Carriers (LOHC) should be considered in addition; this field recently attracts attention of many researchers, see e.g. Journal of Power Sources 396 (2018) 803–823

The subsection 1.7.3 now has a separate introduction of the LOHCs technology from an abovementioned paper and four other articles.

C4: When discussing element doping / substitution in AB5‑type intermetallides (section 1.7.4, page 43), the author writes that the doping is done "...in order to increase the ability to absorb hydrogen, ...". First of all, the doping is carried out to tune thermodynamic properties of the AB5‑H2 system. For example, Ce reduces stability of the MH (increase of plateau pressure / decrease of temperature; Al, Mn – increase the stability)

The clarification and examples were added.

C5. Technical and terminology inconsistencies:
a. It is stated in the first paragraph of section 1.7.1 "Figure 2 presents a comparative analysis of the mass

content and bulk density for hydrogen storage in cylinders of various types". No such figure presented

The final version of submission had no such reference and figure; the mentioned inconsistency has been resolved earlier.

*b. Page 42 "systemization of hydrogen atoms by the formation of hydride" – "systemization" should be replaced by **ordering***

The term was replaced.

c. Page 43: "The typical representatives of the AB2 alloy are the so−called Laves phases: ZnFe2, ...". The Laves phase ZnFe2 does not exist (most probably, the author meant ZrFe2). Better illustration of the Laves phases which form MH and have practical importance is TiMn(2±x).

The typo was corrected, and TiMn(2±x) was added to the list of Laves phases.

*d. Page 44: "When hydrogen decomposes..." – most probably, the author meant "**metal hydride**" Page 47 "...the low conductivity of a solid state MH..." – low **thermal** conductivity, it is important*

Both clarifications and corrections were implemented.

*e. Table 2.3: LaNi5 is specified as "MH reactor metallic alloy type". Since the author uses substituted LaNi5 and refers to the type, it is better to specify **AB5** instead of LaNi5*

The AB5 type was added.

*f. Pages 54, 86: "...MPa (excessive)" – commonly used term is **gage** pressure*

The term was corrected.

g. Page 56: ""...a low pressure was supplied to..." – low **H2** pressure

Corrected.

*h. Page 73: "during the FC's temporary fault" – it is better to say "**when the FC is out of operation**". Power supply from a battery is normally needed for the periods of the fuel cell start−up, this is not failure. Also, the battery is needed to compensate peaks of the power consumption which exceed the maximum fuel cell power.*

The phrase was clarified and corrected. The term "fault" here was used to describe unexpected shutdowns of the FC, which normally lead to the greater demand from the battery rather than a smooth start-up procedure.

i. Page 85: "Peaks on the graph are connected with the volatile rise of the heating agent temperature". Most probably, the author meant periodic pressure drops (figure 4.7). Their appearance is typical for the operation of fuel cells at temperatures below 100 °C; actually, these are H2 purging impulses which are necessary to remove excessive water from the fuel cell.

The explanation was added to the paragraph.

*j. Page 96: "waste electrical energy", better to say **excessive***

Corrected.

k. Page 97: "moisture can irreversibly affect metallic alloy" – please, give the reference or illustrate this statement by own experimental data. On the opinion of the reviewer, the effect of water vapours on the hydrogen sorption performance of AB5−type alloys is not so dramatic

The phrase was eliminated to avoid dramatic formulation.

*l. Page 104: "or 12 ... 13 norm l / kg" – **120...130***

m. Corrected.

*n. Section 5.5, first sentence: "The concept described in this paper..." – **thesis** or **chapter***

Corrected.

However, before the submission to formal thesis defence, the thesis should be revised to address my comments

All comments were addressed.

5. Answers to the comments of Professor Alexei Buchachenko, Skoltech (Chairman)

C1: Chapter 1 of the Thesis presents the overview of the known energy storage technologies, their advantages, drawbacks and relevant applications. The author tried to be as broad as possible in considering various energy storage options. This demonstrates deep knowledge and understanding, but, from the viewpoint of Thesis structure, poor relevance of this review to the research performed is a weak point of the Thesis presentation (see below).

Alas, the composition and logic of the written presentation are not so bright. To me, the main weakness is the introductory chapter 1. First, combination of very general overview of energy storage technologies and very specific case of Batamai village is confusing.

As for the introductory chapter 1, the logic is the following: the chapter starts with introducing a great variety of ES technologies and functions with a note on latest developments in the field from the systematic point of view. Then continues with a techno-economic comparison of different ES technologies and concludes that a case-based approach is necessary. As a system engineer, I could not avoid techno-economic comparison of different technologies; it is necessary to further argument choice of technology. Even though it seems rather general, it is a starting point for each system to be built. After concluding that a case is necessary to determine a suitable technology, a case of a small village was presented with following sections of chapter 1 proposing an ES technology feasible for this case (and villages like the one presented) and introduce state-of-the-art in the chosen technology. The chapter concludes with the formulation of the goals of the research. To avoid further confusion, a figure one representing the structure of the thesis was added to the introduction section.

C2: Only very basic information is given on the second important component of the proposed technology, proton-exchange membrane fuel cell (PEM FC). From an engineering viewpoint, however, it can be justified by the use of commercially available cell, a kind of "black box" device.

Yes, since the fuel cell was a commercial piece and no particular work was done on the internal process of it, the topic of fuel cells was not included in the literature review. It was also done to keep the thesis focused.

C3: Chapter 2 describes the first prototype system, so-called H2Bio, which uses 175W commercial PEM FC (sometimes 200W power is referred to in the Thesis).

The manufacturer of the commercial PEM FC has a licensed name E-200 Hoppecke. However, the maximum power output is 175W only. A number 200 was referred to in this thesis to determine the class of the FC (power level) rather than indicate actual maximum power output. 175W was used to determine the latter. However, the author agrees with the reviewer that a feeling of inconsistency occurred thus the power output was changed to actual 175W along the text.

C4: Chapter 3 introduces the methodology for simulating the performance of the different batteries that accounts, among other factors, empirical description of efficiency function and degradation. Though the approach developed is efficient, economic and reliable, connection of this chapter to the mainstream of the Thesis research does not seem clear enough.

The connection of this chapter to the mainstream of the Thesis research was cleared by adding clarifications in the Conclusions section of Chapter 2 and by adding an introductory paragraph answering to the current Reviewer's concern.

C5: Also, simulating and characterizing lead-acid, NiMH, NiCD and Li-ion batteries the authors did not make any comment on the novelty of the results (even in connection with the data presented in the chapter 1 as overview, Tables 1.1, 1.2).

The novelty of the results was presented in connection with Tables 1 and 2 as well as the primary description of the batteries at the beginning of Chapter 3 was made by a previously described overview from the Chapter 1.

C6: In addition, implications of the results to integrated MH-FC system are limited by the conjecture that back-up battery should be maintained at highest possible state of the charge and thus should be charged whenever external load permits. I consider proposed battery simulation methodology as important and useful research result, but the author may wish either to put it into the Thesis context more logically or present it as an Appendix.

Even though the difference in the outcomes cannot be considered as significant for the coupled operation with the FC for the specific case described in this thesis, the smoothness of the response to the operating regimes, the recovery dynamics of these batteries and other experimentally obtained results make a sufficient contribution to the current theoretical basis of the battery technical characteristics comparison (Tables 1 and 2). The simulation testbed and methodology described in this thesis provide a valuable contribution to the process of energy storage system design that was previously limited by theoretical comparison. Thus the author of this Thesis finds it as a valuable contribution to the Energy System design, which is generally the main scope and framework of this thesis.

In response to the concerns of the Reviewer, I added multiple clarifications to the text and the conclusions section of this thesis.

C7: The chapter 4 showed that heat generated should be enough to maintain hydrogen regeneration of the MH reactor. While this important result is well justified, the choice of reactor is not clear. On the one hand, 1000 l MH reactor suggested for integration in the H2Smart system (chapter 5) is mentioned. On the other, experiments were made with the larger "semi-commercial" reactor. Moreover, air heating was used despite both reactors are designed for water cooling/heating.

The term semi-commercial was used to describe a self-made reactor of JIHT RAS that is used for commercial realization on the market. The term was corrected in the thesis. In chapter 4, the 1000l reactor was used for integration experiments with 1kW PEM FC as these are the components of the future H2Smart system. At the same time, a bigger 13m3 reactor was used to perform a qualitative simulation of the desorption process under an artificially created airflow. It is a so-called "bottom line" experiment that helped qualitatively assess the possibility of utilizing excessive heat from the FC. Since this concept was not straightforward and the positive outcome was not guaranteed the author chose available reactors, which happened to be water heated/cooled, as no air heated/cooled reactors exist on the market/in the lab. The author followed the logic that if these qualitative experiments and created systems will work for water heated/cooled reactors (with the need to cool and heat water left in the system), then a specifically designed air cooled/heated reactor will be able to function too. This approach avoids an expensive need for creating an air-cooled reactor prior to proving the possibility of a positive outcome. To avoid confusion, the experiments with 1000l reactor were eliminated from the Chapter.

C8: Did the Thesis suggest air-cooled reactor concept despite the problem of water accumulation noted? Does the air-based system indeed "shows promising future", as concluded? And if yes, why this technology was not further explored?

I am afraid I need to clarify this question. In both concepts hydrogen accumulation happens in MH, the question is only in the heat carrier supplied to the reactor. Of course, water is a more efficient heat carrier than air. However, hot water is an external heat carrier that needs to be supplied to the system when hot air is already there in the system in the form of excessive air coming from the FC. Using excessive heat from the FC makes the system autonomous thus current Thesis suggests using it for H2Smart. Exploiting excessive heat from the FC is indeed helpful and necessary for the future systems.
Future steps, such as creating an air-heated reactor and introducing a thermosyphon concept with additionally choosing a more efficient heat carrier, lie outside of the current Thesis due to already exceeding a recommended volume.
All of the clarifications were added throughout the text to avoid further confusion.

C9: In Chapter 5, the system description and demonstration of its function are convincing enough to be taken as the "proof-of-the-concept". However, analysis of the working regimes and flows looks rather brief, at least, much less detail is given than for the first H2Bio prototype.

The following working regimes were added to the chapter: FC and MH integration (4 working regimes of such integration), electrolyser fueling the MH with hydrogen, multiple whole-system running experiments.

C10: Indeed, there is a kind of logical break in coming to case of Yakutian Batamai village considered as a documented example of small-scale isolated energy grid with integrated solar-battery storage technology.

How does the author see her technology? As the general solution? But little practical alternatives of the similar scale are considered for comparison. As a specific solutions to Batamai-like village?

These two paragraphs mention the same issue of Batamai village. In section 1.5, a case of a small village in Yakutia is presented as a reference and a real pilot settlement for the introduction of RES with real load data and solar power output, however, current thesis and research is dedicated for the development of a technology feasible for application in many villages like the one presented. The author also kept in mind the modular design of the system to be suitable for the variety of different settlements. Multiple clarifications throughout the text were added to avoid further confusion. Practical alternatives were discussed in chapters one and six during the technical and economic comparison. More attention was added to these discussions in the text.

C11: Chapter 6 indeed proves the benefits of the proposed system in this case, but may be even more precise connections, like account for ambient temperature and humidity regimes and supply limitations, are crucial?

Just like all of the other practical alternatives to the proposed technology, current systems are considered to be used in a heated box/building. Technical requirements for the additional water supply include a connection to a general water system in the city. Researching the solution for installation outside in Northern regions is a promising topic. However, it is a wide field of research that would require a separate additional (if not bigger) time to conclude it. Thus it is outside of the scope of the current research.

C12: Also, the review by Chen et al. [21] is used as the main source of overview of storage technology. Are there significant post-2009 achievements in this rapidly developing field?

Currently, there are few publications, introducing the variety of ES technologies and its technical (and somewhat economic) comparison. These are Ibrahim et al. (2008), Chen et al. (2009) and Huggins (2010); all of them formed the basis of the first subsections of the literature review introducing the great spectrum of ES technologies. Other authors in the later years reviewed only part of the spectrum, narrowing down to one aspect, for example, ES for wind power applications Diaz-Gonzales (2012), electricity storage Brunet (2013), phase change materials Cabeza (2011). Later reviews became even more specific, for example, Li-ion batteries for automobile applications by Stan (2014), UK distribution grids demonstration by Lyons (2015) from our partner laboratory, life-cycle costs of different ES technologies by Zakeri (2015), and, of course, multiple publications on optimization techniques, such as Ho et al (2016).

So technically the review from 2009 might seem outdated, but current reviews are narrowed down to a specific topic rather than provide an overview. The author finds the first three papers as a solid basis for the first sections of chapter 1. However, multiple additional sources from 2016-2018 were added to provide more up-to-date information.

Ibrahim H, Ilinca A, Perron J. Energy storage systems—characteristics and comparisons. Renew Sustain Energy Rev 2008;12:1221–50.
Chen H, Cong TN, Yang W, Tan C, Li Y, Ding Y. Progress in electrical energy storage system: a critical review. Progress Nat Sci 2009;19:291–312.
Huggins R. Energy storage. Stanford, California, USA: Springer Science & Business Media; 2010.
Díaz-González F, Sumper A, Gomis-Bellmunt O, Villafáfila-Robles R. A review of energy storage technologies for wind power applications. Renew Sustain Energy Rev 2012;16:2154–71.
Brunet Y. Energy storage. London SW19 4EU UK: John Wiley & Sons; 2013.
Cabeza LF, Castell A, Barreneche C, De Gracia A, Fernández A. Materials used as PCM in thermal energy storage in buildings: a review. Renew Sustain Energy Rev 2011;15:1675–95.
Stan A-I, Swierczynski M, Stroe D-I, Teodorescu R, Andreasen SJ. Lithium ion battery chemistries from renewable energy storage to automotive and back-up power applications—An overview. Optimization of Electrical and Electronic Equipment (OPTIM) International Conference on: IEEE. p. 713-720.
Niaz S, Manzoor T, Pandith AH. Hydrogen storage: materials, methods and perspectives. Renew Sustain Energy Rev 2015;50:457–69.
Lyons P, Wade N, Jiang T, Taylor P, Hashiesh F, Michel M, et al. Design and analysis of electrical energy storage demonstration projects on UK distribution networks. Appl Energy 2015;137:677–91.

Zakeri B, Syri S. Electrical energy storage systems: a comparative life cycle cost analysis. Renew Sustain Energy Rev 2015;42:569–96.
Ho WS, Macchietto S, Lim JS, Hashim H, Muis ZA, Liu WH. Optimal scheduling of energy storage for renewable energy distributed energy generation system. Renew Sustain Energy Rev 2016;58:1100–7.

C13: Second, the review of MH hydrogen storage technologies, though generally relevant, is poorly used in the main text. I think the author should be more precise in fitting introductory to the context of her research.

The PCT diagrams, IMC, doping, and other connections have been introduced in the text.

C14: Presentation of the research part looks complete and justified, but suffers a bit from the lack of logical connections. Special attention should be paid for the problems pointed above for chapters 3 and 4. Other minor imperfections can be noted.

The structure of the thesis has been added to the introduction section that clarifies the logic of the narrative. Also, the conclusions section of chapter two has been widened to explain the connection to all the chapters of the thesis. Additionally, chapters 3, 4, and 5 start with an explanation and connection to previous chapters to create an understanding of the logic of the dissertation.

C15: And of course the text requires intent proofreading. There are multiple errors in referencing tables and figures, misprints and some language imperfections. The list of references should be properly formatted.

The errors with referencing tables and figures have been eliminated by introducing a hyperlink/cross-reference throughout the text. The text had intense proofreading to eliminate language imperfections. The list of references was properly formatted.

I would like to thank all of the Jury Committee members for their time and effort that they invested in the improvement of my work.

Aliya Glagoleva (Khayrullina)