Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

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 Borzenko

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

Date of Thesis Defense: 09 October 2018

Name of the Reviewer: Mykhaylo Lototskyy

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 01-09-2018**

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 PhD thesis under evaluation deals with the application of "low-temperature" metal hydrides (MH) on the basis of AB5-type intermetallic alloys for safe low-pressure storage of hydrogen (H2) and its supply, in small-to-medium scale energy systems which use Low Temperature Proton Exchange Membrane Fuel Cells (LT PEMFC). Accordingly, the structure of the thesis includes; (i) a detailed consideration of the state of the art in energy storage technologies including the ones based on H2 fuel cells for the power generation and MH for the storage of the H2 fuel (chapter 1), (ii) experimental studies of the integration of MH with low- (chapter 2) and medium-power (chapters 4-5) LT PEMFC systems supplemented by (iii) methodological description (approach and its implementation; chapter 3) and (iv) economic estimations for the implementation of the suggested concept (chapter 6). The logical structure and the content of the thesis is undoubtly relevant to its topic; the applied modelling and experimental methods are typical for the development and integration of LT PEMFC Balance-of-Plant (BoP) components reported in the literature; also practiced by the reviewer's team.

On the basis of analysis of literature data and results of the experimental studies, the PhD candidate has made a conclusion about feasibility of the integration of MH in the BoP systems of the small- (~200 W) and medium-scale (~ 1kW) LT PEMFC stacks utilizing waste heat generated during their operation, as well as has suggested a concept of medium-to-large scale (30 kW) fuel cell energy system comprising MH based H2 storage and supply component. The conclusions have been supported by the experimental data about performance of the selected AB5-type MH alloys, as well as behaviour of the developed MH reactors integrated with LT PEMFC. Importantly, that the content of the thesis would help a reader to evaluate in more details application potential of MH in H2 fuel cell power systems including outlining the most promising niche applications. Thus, this PhD study (including publications of the results in high-impact international journals) makes a noticeable contribution in the international development of MH based BoP components of hydrogen fuel cell power systems.

At the same time, the reviewer has the following comments to the actual content of the thesis:

1. 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.
2. 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
3. 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
4. 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)

5. 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
    b. Page 42 "*systemization* of hydrogen atoms by the formation of hydride" – "*systemization*" should be replaced by **ordering**
    c. Same page "presence of *voids in the IMC*" – better to say "**interstitials in the crystal structure of**…"
    d. 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).
    e. Page 44: "When *hydrogen* decomposes…" – most probably, the author meant "**metal hydride**"
    f. Page 47 "…the *low conductivity* of a solid state MH…" – low **thermal** conductivity, it is important
    g. 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*
    h. Pages 54, 86: "…MPa (*excessive*)" – commonly used term is **gage** pressure
    i. Page 56: ""…a *low pressure* was supplied to…" – low **H2** pressure
    j. 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.
    k. 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.
    l. Page 96: "*waste* electrical energy", better to say **excessive**
    m. 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
    n. Page 104: "or *12 ... 13* norm l / kg" – **120…130**
    o. Section 5.5, first sentence: "The concept described in this *paper*…" – **thesis** or **chapter**

The numerous comments above do not concern overall value of the candidate's work which can be, in general, evaluated positively. The candidate, Aliya Glagoleva, deserves awarding her the PhD degree. However, before the submission to formal thesis defence, the thesis should be revised to address my comments

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*