

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Olga Yamilova

PhD Program: Materials Science and Engineering

Title of Thesis: Revealing electrochemical degradation pathways in complex lead halides and design of stable perovskite solar cells

Supervisor: Professor Keith Stevenson

Name of the Reviewer: Sergey Levchenko

I confirm the absence of any conflict of interest	Date: 19-12-2022
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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

- Brief evaluation of the thesis quality and overall structure of the dissertation.

The thesis presents an experimental study of electrochemical degradation pathways of halide perovskite solar cells. This is a practically important topic, and the candidate uses a series of synthesis and characterization techniques to thoroughly address it. The results of the work are published in three high-level peer-reviewed journals (fourth one is submitted). The thesis is clearly written. Overall, the quality of the thesis is excellent. There are only several minor issues with the thesis text to be addressed (listed below) for better clarity.

- The relevance of the topic of dissertation work to its actual content

The topic is directly related to the actual content.

- The relevance of the methods used in the dissertation

All the used methods are not only relevant but necessary to resolve the complex problem of solar cell degradation.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

The candidate used a systematic approach to reveal mechanisms of electrochemical degradation of halide perovskite solar cells. Not only model systems but also complete solar cells were produced to study the effects of different charge-transfer layers and electrodes on solar-cell stability. Different state-of-the-art microscopy and composition analysis methods were applied to confirm conclusions from several angles. As a result, the conclusions of the paper are very convincing, and the work paves a way towards improving solar-cell stability significantly. In fact, the candidate's research has led to a paradigm shift in the area of solar-cell stability.

- The relevance of the obtained results to applications (if applicable)

The work is directly relevant to applications, namely to solar energy conversion. The results of the work can be directly used to improve solar-cell stability.

- The quality of publications

There are three publications, all in high-level peer-reviewed journals with the lowest impact factor 6.88. A fourth paper has been submitted. The publications are of very high scientific quality, clearly written, and featuring strong conclusions well supported by the measurements.

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

All comments/questions below are meant to be addressed directly by changing thesis text, unless a discussion is needed.

“what allows this technology to be considered as a strong competitor” -> “which allows this technology...”

“The most classical perovskite material” -> “A prototypical perovskite material”

“crystals with a perovskite structure have a very low concentration of traps (~1010 cm³ for CH₃NH₃PbI₃)”
– some typos here

“Here the FF is a fill factor of the solar cell. Determined as the relation” -> “Here the FF is a fill factor of the solar cell, determined as the relation”

“In ideal situation the curve should fill the 100% of the area,” – clarify which area

“but in real life the decrease in blue area usually caused by front surface recombination, decrease in red area by low diffusion length and reduced absorption of long-wavelength photons.” -> “but in real life the decrease in blue area is usually caused by front surface recombination, while the decrease in the red area is caused by low diffusion length and reduced absorption of long-wavelength photons.”; I guess you mean blue and red light, this needs a clarification

“cadmium-tellurate” -> “cadmium telluride”

“And brightest representatives of third generation photovoltaics such as dye-sensitized, organic and quantum-dot solar cells has always been” -> “... have always been...”

“on pair with” -> “on par with”

“ion migration can easily proceed during the voltage applying” -> “ion migration can easily proceed during the voltage application”

“All perovskite solutions for further experiments were prepared according to the” – unfinished sentence; I guess, a paragraph on preparation methods is missing

“Nevertheless, according to the XDR measurements of the films, they fully correspond to the required materials” – clarify what XDR is; did you mean XRD?

“The experiments performed with the lateral two-terminal devices allowed us to reveal the important degradation pathway occurring in the perovskite films under applied electric bias.” – repeat here which exactly pathway was revealed

“Figure 14. Cyclic voltammograms for 0.1 M solution of NaClO₄ in DMF as illustration of the DMF electrochemical stability window” – please show the stability window in the figure, otherwise it is not easy to see for a non-specialist

“at the applied voltage 1 V/μm” – the units are not voltage; are you talking about field? clarify this in the text, also in Figure 16

“The process of electrochemical doping can be referred as the accumulation of charge carriers or defects in the material” -> “The electrochemical doping is due to accumulation of charge carriers or defects in the material”

“which will correspond to the Q – limit accumulated charge that material could sustain” -> “which will correspond to maximum accumulated charge Q that material could sustain”

“So this confirms the applicability of the degradation pathway we defined earlier with reduction at the cathode to all hybrid perovskites.” – remind the reader which pathway you mean

“But, according to all obtained data, Cs_{0.15}FA_{0.85}PbI₃ is to be considered the most stable perovskite material.” – can you explain why?

“J-V evolution examples for all systems are given on the Figure A4 in Supplementary materials.” – better to write “in Appendix A”.

“It widely known that” -> “It is widely known that”

“Based on the presented scientific findings, important guidelines for charge-transport material design for stable PSCs should be established.” -> “Based on the presented scientific findings, important guidelines for charge-transport material design for stable PSCs **are** established.”

“Herein, we revealed for the first time a comprehensive mechanism of poorly investigated electrochemical decomposition” -> “Herein, we revealed for the first time a comprehensive mechanism of **previously** poorly investigated electrochemical decomposition”

unsignificant -> insignificant

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