Thesis Changes Log

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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: Prof. Keith Stevenson

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

I am grateful to the Jury Members for their positive feedback and useful comments. I am happy to address the comments and questions in this document and in the revised version of the Thesis.

Response to Prof. Evgeniy Antipov

P. 20. The statement "Perovskite is a type of crystal with a cubic structure and orthorhombic, tetragonal or trigonal symmetry" is not correct and should be corrected.

The passage about perovskite structure was rephrased correctly in the Literature review part in a revised version.

P.26 kW/h – should be corrected

The misprint is corrected to the kW·h

P.35 What does it mean "Nevertheless, according to the XDR measurements of the films, they fully correspond to the required materials"? If XDR means X-ray powder diffraction, the experimental data should be presented in the thesis to prove this statement. How the compositions of the anion-deficient perovskites ($Cs_{0.125}FA_{0.875}PbBr_{0.375}I_{2.625}$ and $Cs_{0.12}FA_{0.8}PbI_{2.92}$) were determined? Please, provide the reliable own or literature data confirming the anion deficiency in these perovskites.

The abbreviation of X-ray diffraction was corrected and XRD data for all eight obtained perovskite materials was added to the Supplementary Materials. I would like to note that all materials were prepared according to the literature sources added to the Table 1 in Experimental section of revised Thesis and XRD analysis only confirms their correspondence to the literature and the purity of desired phase. Chemical formulas written here do not represent exact composition of each material, but correspond to the initial ratios of precursors in prepared solutions. There is undoubtedly a deviation of real compositions from the formulas, but according to the literature sources it is not significant enough to disrupt our comparative analysis.

P.38 What does it mean "NiO_x and CuO_x"? P. 68. What does "NiO_x system" on P. 68 means?

During the preparation of thin films of corresponding oxides for perovskite photovoltaics according to the long established in the literature methods and procedures we get the complicated mixture of oxides with metals in several oxidation states. This way of naming these charge-transport layers is already a term established in the

literature. And the phrase NiO_x system was rewritten as NiO_x-based system, which means the perovskite solar cell with NiO_x as hole-transport material.

Fig.13. ToF-SIMS chemical maps show the distribution of different ions in the cells. The most remarkable changes were revealed at the maps of $CH_3NH_3^+$ cations while the changes for the other ions are much less. Please, provide an explanation what are the probable products of the perovskite degradation when positively charged ions are deintercalated from the perovskite structure to the PEDOT:PSS hole selective layer with the formation of methylammonium salt of polystyrene sulfonic acid.

According to our assumption, during the electrochemical degradation we most likely have a two-component process including the reduction of methylammonium cation into the methylamine and hydrogen which easily reacts with PEDOT:PSS or can intercalate into the fullerene derivative charge-transport layer. And simultaneously we also have an oxidation of iodide anions and formation of molecular iodine, which can also participate in various reactions, including reaction with the top electrode metal, fullerene derivatives, hydrogen and methylamine. And we also will have the lead remaining in the initial perovskite layer in the form of lead iodine, metallic lead or even lead complexes. This corresponds to the mechanism of photoinduced degradation of perovskite solar cells.

P. 54 Why "The oxidation of I^- with formation of I_2 seems to be reversible"? The probable formation of polyiodides does not prove the reversibility of the redox process.

With this phrase we wanted to emphasize the potential of this reaction to be reversible because I_2 seems to remain in the perovskite layer after oxidation and thus it can be potentially returned back into the perovskite structure if we manage to: first, create proper charge-transport layers that will prevent iodine from undesirable reactions with other components of solar cell; and second, create the way to shift the equilibrium between the perovskite and its degradation products to the perovskite side. The phrase was corrected to avoid further misunderstandings.

P. 60 What does it mean "Nevertheless Cs^+ cations partially migrate from anode to the cathode, leading to the chemical shift in the structure"? P. 65 What does it mean "Also, excess of PbI_2 in the chemical structure"? P.65. What does it mean "…chemical structure of perovskite material influences the stability of bulk material"?

All phrases were corrected to avoid the misunderstanding and incorrect terminology.

Response to Prof. Stanislav Fedotov

What is the x value in $MAPbI_xCl_{3-x}$

The preparation of thin films of $MAPbI_xCl_{3-x}$ perovskite material goes according to the long established in the literature. The exact composition is uncertain because the process includes a lot of unreacted excess of precursors. This way of naming this perovskite material is already a term established in the literature. The main point is to get the correct phase according to the XRD data without any impurities.

What is the new phase observed by AFM for $MAPbI_3$ lateral devices? Can it be detected somehow?

Unfortunately we were not able to determine this new phase because of too low amount of material we did not have an access to any microscopy sensitive enough when this experiment was provided. We could only assume this new particles to be the product of iodine reaction with either gold electrodes, either other iodides with formation of polyiodides. Now we consider the further investigation of these particles with ultra-high resolution EDX.

Shouldn't it be Pb^{2+} for ToF-SIMS analysis instead of Pb^+?

No, ToF-SIMS analysis measures exactly the amount of Pb^+

On page 67 the timestep is 50 h, while it is 20 h above. How do you choose this parameter?

Usually this is a matter of empirical experience and choice of the parameter depending on the situation. Usually at the beginning of degradation process measurements provided more often to catch important starting processes (like burn-in effect) and then pauses between tests become larger. Also measurements of lateral two-electrode devices should be provided more often because bulk material degrades faster (at least in this case) than assembled solar cell.

Also all noted by **Prof. Stanislav Fedotov** grammar and technical misprints were addressed in the revised version of the Thesis.

Response to Prof. Sergey Levchenko

"But, according to all obtained data, $Cs_{0.15}FA_{0.85}PbI_3$ is to be considered the most stable perovskite material." – can you explain why?

Compared to its less stable competitors ($MA_{0.15}Cs_{0.1}FA_{0.75}PbI_3$, $MAPbI_3$, $Cs_{0.125}FA_{0.875}PbBr_{0.375}I_{2.625}$ and $CsPbI_2Br$) $Cs_{0.15}FA_{0.85}PbI_3$, does not have the small, mobile and highly volatile MA^+ cation, only larger FA^+ and inorganic Cs^+. This factor slows down the degradation process related to the reduction of organic cations. Another important point is that iodide anions in $Cs_{0.15}FA_{0.85}PbI_3$ are not partially substituted by bromine, as it is in $Cs_{0.125}FA_{0.875}PbBr_{0.375}I_{2.625}$ and $CsPbI_2Br$. Mixture of two anions is frequently reported to be the cause of phase segregation under photoinduced degradation, so it is possible that similar effects could happen during the electrochemical degradation.

Also all noted by **Prof. Sergey Levchenko** grammar and technical misprints were addressed in the revised version of the Thesis.

Response to Prof. Jovana Milic

In the introduction, it is pointed out that "the only remaining obstacles is a short lifetime of devices under realistic operating conditions". This claim is made once more in the next chapter, providing more information from the literature reports. While instability is indeed one of the most pressing challenges, there are others that remain towards practical applications of these materials and devices. In particular, this refers to the toxicity of lead-based components, which is not relevant to this particular thesis. The candidate should however revise the statement to point at the instabilities as "one of the most important obstacles" rather than "the only ones".

The passage about perovskite instability as "the only problem" was rephrased correctly in a revised version of Thesis.

In the experimental section, the preparation procedures are outlined for different perovskite compositions. This involves different (anti)solvents and annealing temperature conditions without information about the basis for these experimental details. Even though some of these aspects are further discussed in the other sections, the candidate should briefly comment on whether these are optimized conditions or those based on literature reports and provide the corresponding literature (e.g., in Table 2). Similarly, the candidate should briefly comment on the reasons behind the selection of specific solar cell architectures in the first two studies.

Regarding the perovskite compositions: all used recipes for perovskite thin film preparation were taken from the literature sources with minor corrections (adjustment of the process to the local working conditions). All references are included in the Table 1. PSCs for experiments at first stage and for the testing of various hole-transport materials were assembled in a conventional p-i-n configuration because this structure permitted the largest variability in used HTMs. It also helps to avoid large J-V curve hysteresis, which we consider as a significant factor since large hysteresis exhibits presence of additional polarization effects able to affect the experiment. In the second part of the work for testing various perovskite materials the n-i-p device configuration was chosen because of the difficulties in optimizing the manufacturing process of solar cells with various active layers. Out of all tested device architectures only this one allowed us to make devices with all desired perovskite materials of sufficient quality and starting efficiency not less than 15% for hybrid

systems and not less than 10% for CsPbI$_2$Br and MAPbI$_x$Cl$_{3-x}$. To investigate the influence of electron-transport materials and top metal electrodes we decided to shift from the p-i-n to the n-i-p configuration for the best variability in both type of desired materials with sufficient starting efficiencies. Regarding the point of results interpretation we think that all these experiments can be looked at separately, since in every experiment it was a comparative analysis inside the closed group of materials.

In the discussion of results, the candidate points at the reaction of iodine with "virtually all iodides to form polyiodides" under experimental conditions, which can be misleading as it is not specifically put into context with respect to experimental evidence. It is important to note that iodine could engage in other reactions at the contacts and its volatility could also contribute to degradation. Similarly, the reduction of ammonium cations is implied and it is important to put these conclusions into context with respect to experimental evidence and discuss briefly whether there are other reactivities that could be considered.

Of course, the formation of polyiodides is not the only possible degradation process. Formation of volatile iodine vapor which leaves the perovskite film and even can react with gold electrodes should also be considered under applied electric field. And in solar cells this molecular iodine can react with other components of the device, for example fullerene derivatives of even the backside of top silver electrodes. There is also a possibility of other products formation from organic components beside the methylamine and hydrogen, which we were unable to detect with ToF-SIMS. But nevertheless, while the iodine could be trapped within the device, the latter is too mobile to be captured in the reaction zone e.g. by adjacent layers. Therefore, the reduction of organic cations should be considered as the most important and virtually irreversible electrochemical process affecting severely the stability of the perovskite films.

Finally, in the third part of the study, the normalized PCEs should include a comment on the range of values of initial PCEs in the caption or the Appendix for clarity and comparison with other devices.

The required information is indeed needed and it was added in corresponding parts of the revised Thesis text.

In terms of language, the thesis is very well written, clear and coherent. On a minor note, the candidate refers to "iodine ions" where iodide might be more appropriate. Also, there is a reference to perovskite materials "recommending themselves" (page 35) and their sustainability (page 65) which could be revised as it might not reflect the intended meaning.
Moreover, in terms of the thesis format, the candidate should ensure the appropriate use of formulae and units (i.e., applying subscripts or superscripts, such as on page 37/41, where some of them are not formatted), the use of space between the unit and the value (e.g., page 38), and a consistent use of units of time (s/min/h). Finally, even though the candidate introduces abbreviations at the beginning, it might be helpful to also introduce them upon first use as well.

Thank you for your comments, all inconveniences were addressed in the revised version of the Thesis.

Response to Prof. Annie Ng

Page 18: "The only remaining obstacle is a short lifetime of the devices under realistic operating conditions." Please note that short lifetime is not the only remaining obstacle. Please revise this statement.

The statement was revised.

Chapter 1 Introduction: "Unfortunately, among all aforementioned factors the bias-induced degradation processes remain the least elucidated." is the last sentence. However, no further information was introduced related to this work. It is better to elaborate further the motivation of this work and briefly introduce the designed experiments and related information.

The completion of Chapter 1 was revised and new information added.

The 1-page Chapter 3 Research objectives is a separated chapter, which can be combined with Chapter 1 "Introduction".

I am really sorry for the caused inconvenience, but this separate chapter and its form are a part of requirements.

Please explain clearly about the stability and device lifetime of CsPbI₂Br. Some phrases on this topic were misleading. If it is the factor of thickness, the experiment should exclude this uncertainty by preparing the same thickness for all kind of perovskites (e.g. all of them around 200 nm or 400 nm depending on the preparation technique). The aim of this experiment is to compare the perovskite with different compositions. Therefore, thickness should be the same for fair comparison.

Initially, we considered the fully inorganic CsPbI₂Br as a very promising candidate for long-living devices, because it does not contain any organic components prone to reduction process, but even first experiments demonstrated its comparatively low stability. Besides, we were not able to perform PL mapping for CsPbI₂Br because this material was the only one who could not sustain the transportation between the glovebox and measurement device. Even encapsulated lateral devices immediately degraded after getting into ambient atmosphere, starting from edges of the film. The poor performance of this material during first tests in lateral devices was supported by the low thickness of the photoactive film in assembled solar cells, which is unfortunately around 200 nm for CsPbI₂Br because of its processing method, while for other materials thickness is around 400 nm. Unfortunately, we could not increase its thickness because of phase instability. But from the other hand our ultimate goal here could be named as to compare the stability of devices at their most efficient architecture. Of course, we can reduce the thickness of all other perovskite materials in solar cells, but it won't be their optimal working conditions for real-life applications.

In the chapter of conclusion, please suggest the potential methods and materials selection for achieving good stability and lifetimes of perovskite solar cells based on the findings in this thesis work.

It was revealed that the most important factors for improving the solar cell stability are enhanced V_{OC} and FF of complete device, chemical inertness of adjacent charge-transport material (for example polymers or carbon-based materials) and its solvent towards perovskite (toluene, chlorobenzene), insolubility of CTLs in solvents for perovskite materials, formation of tight flawless films and finally the high thickness of perovskite layer. These conclusions can serve as material selection criteria for enhancement of perovskite solar cell stability. We also think that method of measuring PCE(t) of solar cells described in this Thesis can be widely applied for the analysis of PSC stability because of its flexibility and easy variation of parameters.

Response to Dr. Danila Saranin

Provide the additional comments on the motivation of using different device architectures (p-i-n and n-i-p) in different chapters. This makes the interpretation of the obtained results a bit more complex.

PSCs for experiments at first stage and for the testing of various hole-transport materials were assembled in a conventional p-i-n configuration because this structure permitted the largest variability in used HTMs. It also helps to avoid large J-V curve hysteresis, which we consider as a significant factor since large hysteresis exhibits presence of additional polarization effects able to affect the experiment. In the second part of the work for testing various perovskite materials the n-i-p device configuration was chosen because of the difficulties in optimizing the manufacturing process of solar cells with various active layers. Out of all tested device architectures only this one allowed us to make devices with all desired perovskite materials of sufficient quality and starting efficiency not less than 15% for hybrid systems and not less than 10% for CsPbI₂Br and MAPbI$_x$Cl$_{3-x}$. To investigate the influence of electron-transport materials and top metal electrodes we decided to shift from the p-i-n to the n-i-p configuration for the best variability in both type of desired materials with sufficient starting efficiencies. Regarding the point of results interpretation we think that all these experiments can be looked at separately, since in every experiment it was a comparative analysis inside the closed group of materials.

You describe the data for the process of electrochemical doping with simple charge-current dependance. The specific conductivity and/or the difference in dielectric constants values could give an impact on the process of the current flow. It is necessary to consider the differences between the set of the transport properties to make the logical conclusion.

We agree that additional measurements is necessary for the deep understanding of the process of current increasing in the beginning of biasing process. My goal over using a simple charge-current dependance was a trial to make a rough estimation for preliminary comparison of the materials. Of course, in real life the full combination of effects of dielectric constant change with time, specific conductivity and others. Nevertheless, even our rough calculations allowed us to correctly define the leaders and outsiders in terms of stability and probably proved their applicability.

The evolution of normalized PCE on Fig 22a has a sharp difference between the configuration of the devices based on organic/inorganic HTLs. The reasons of the different behavior at the starting testing period require additional comments and interpretation.

Actually, I could not say that the difference is sharp. Of course, it can be misleading from the figure, but in the text, it was mentioned, that starting voltage was set as 0.7 V and then it was increased every 50 hours by 0.1 V up to 1 V, then the voltage was increased every 50 hours by 0.2 V up to 2.2 V. Applying bias from 0.7 to 0.9 V did not induce any changes in the device performance regardless the hole-selective material. So, it can be said that their initial behaviour was rather similar and flat. The difference appeared only when some of the configurations reached their threshold point, which according to our conclusion is equal or near the V_{OC} of the device.

The integration of large Rb ions into crystal lattice of hybrid halide perovskite creates some doubts. Probably some comments on this point.

If I remember correctly from the publication of [Turren-Cruz, S.-H.; Hagfeldt, A.; Saliba, M. Methylammonium-free, high-performance and stable perovskite solar cells on a planar architecture. *Science* **2018**, 362, 449–453] the size of Rb^+ cation is smaller than the one for the Cs^+ and thus it can integrate into the lattice of hybrid perovskites quite well and even improve device characteristics and stability, which was confirmed not only by this Thesis, but also by various publications on related topic.

The choice of proper chemically stable electrodes is well established topic in wafer and thin-film solar cells. The interpretation of results in the third part of the work requires the comments for the choice of metal contacts used in the research work.

We decided to compare various metals for the top electrode, since the only metal we used in all previous experiments with solar cells was silver, as one of the most widespread and commonly used electrodes in solar energy generation industry. While considering almost all our available metals, we also hoped that we will be able to correlate the obtained results for top electrodes with some of the characteristics of all metals, but unfortunately, we were not able to define any dependences and so we assume that this matter requires additional long-term investigations, broadening the list of top electrode materials with other materials like carbon, carbon nano-tubes, ITO and etc. The only obvious conclusion could be made for now is that the gold electrodes demonstrate the best stability due to the low reactivity towards iodine.