

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Sergei Porokhin

PhD Program: Materials Science and Engineering

Title of Thesis: Perovskite mixed oxides as catalysts of oxygen evolution reaction

Supervisor: Professor Artem Abakumov

Co-supervisor: Assistant Professor Victoria Nikitina

Name of the Reviewer: Daniil Itkis

I confirm the absence of any conflict of interest

(Alternatively, Reviewer can formulate a possible conflict)

Date: 13-09-2022

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 thesis is well written and has a classic structure – it is divided into three main parts including literature survey, methodology and discussion of the results. The text is easy to read and navigate through. The literature survey gives a comprehensive picture on what is happening in the field. Non-precious catalysts for OER are a hot topic nowadays as the IrO₂ catalysts, often used a benchmark in this field, are quite expensive, while the OER efficiency is crucial for overall efficiency of hydrogen production by water splitting (HER itself contributes much less to the total overpotential). The topic reflects the contents of the work; however, it is stated in quite general way.

The work is performed according to high scientific standards, the results are novel. The set of experimental analytical tools used by the author seems reasonable.

There are two publications by the author which are related to the thesis. One paper is published in a high-level journal ACS Catalysis, while other one is published in Q2 journal, what is somewhat less than I would expect from thesis made at Skoltech. At the same time, scope of work is enough wide.

Although the work gives a positive impression there are several questions and comments, which should be addressed by the author during his defense:

1. In my view, one of the most important conclusions is that the increased (or even record) OER activity is promoted by the formation of Ni_{0.5}Fe_{0.5}O_x(OH)_{2-x} thin layer on the perovskite. This conclusion is drawn from the data obtained by the set of analytical techniques. However, HREM and XPS should be the most indicative in the case. At the same time the author states that such a layer can be hardly seen in the micrographs. Maybe the best observation is given in fig. 41 and corresponding discussion explains the cation ratio 1:1 for the oxyhydroxide layer. In this figure we can see that the thickness of this amorphous layer is somewhat in the range of 1-2 nm. At the same time XPS, which is probably the best tool for monitoring surface chemistry, shows nearly no difference between the pristine sample and the sample soaked in NaOH. The differences in Ni 2*p*, Fe 2*p* and even in O 1*s* are really very small, while XPS is very sensitive to changes at the very surface (electron yield falls very quickly with depth and although the signal is collected from 5-10 nm (for AlKalpha source), first few nm give much higher contribution). Aren't the spectra shown in fig. 30 just the spectra of surface contaminants rather than of the layer of interest? Were any efforts put into surface cleaning or preparation?
2. One more technical point on the photoemission spectra. The high-res spectra are not presented in a good way. First, fair practice is to show the binding energy axis reversed (historical custom). Second, the deconvolution into components along with the component parameter should be always given. Third, it is not clear what do "main peak" and "satellite" labels mean. Also, it is useful to give the pass energies of electron analyzer along with other experimental parameter in Experimental (Methodology) section
3. The element concentrations derived from XPS data (table 11) indirectly show that surface contamination is strong. At the same time is it a good idea to calculate the concentrations using lab X-ray source, which probes different elements from different depth especially for the case of analysis of surface layer?
4. The author claims that the preference of Ca²⁺ as a dopant over Sr²⁺ is driven by ambiguous stability of strontium-substituted perovskites, which were studied before by other groups. Why was the stability expected to be higher for calcium-containing compounds? It would be also interesting to understand, why charge compensation due to Ca²⁺ is mainly reached by Ni oxidation state change rather than equal contributions from Ni and Fe.

5. The author says that the hollow microsphere morphology is "unique". What advantages does it give in terms of OER activity? Is the internal surface of the hollow spheres wetted by the electrolyte? Is there any ionomer inside?
6. How ozone for synthesis was generated and how its flow rate was controlled? What is the reasoning for selecting ozone instead of simple increase in partial oxygen pressure?
7. Was the oxygen non-stoichiometry analyzed for LCFN5 sample? From the text I got an impression that LCFN3 and LCFN5 has small non-stoichiometry index, while it reached 0.1 for LCFN5_m. If so, isn't it surprising that employment of more oxidative atmosphere results in lower oxygen content?
8. On p.88 the author sums up previous discussion and concludes that increase in OER activity is due to the "surface reconstruction and an increase in active surface area". ECSA grows up 5 times due to the surface modification according to the area of the CV peak attributed to Ni redox at the surface. Is the author sure that these currents cannot be ascribed to redox in the bulk or surface layer of a certain thickness?
9. There are also some minor technical points (e.g. «18.2 MOhm» instead of «18.2 MOhms*cm» on p.58, low-quality (low resolution, grey background) figures with EDX signal profiles) and few mistypes.

Provisional Recommendation

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

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