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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: Jian-Feng Li

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 08-09-2022**

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

This doctoral thesis by SERGEI V. POROKHIN reports that Ca-doped Ni-Fe-based perovskite obtained by spray pyrolysis competes with a high specific surface area by a modified USP method, and then systematically evaluated the OER activity, morphology, and crystal structure of various LCFNs. The differences in OER performance of LCFN5 m and LCFN5 ms are discussed in further detail, and it is concluded that immersion in 1 M NaOH promotes the formation of surface monolayer oxides. Finally, the impure effect of Fe in the electrolyte is also explored, and it is concluded that the presence of Fe stabilizes the active sites in the (oxy)hydroxide and prevents deep structural changes by forming a stable interface with the perovskite catalyst. The thesis is of high quality and with clear motivation. The overall structure of the dissertation is reasonable, systematic and logical. The relevant research content and methods fit the thesis theme. In addition, this thesis has excellent scientific significance for developing new OER catalysts. Based on the above research, the author has published some high-quality papers, such as in *ACS Catalysis*. Nevertheless, some issues are still to be addressed during the thesis defense.

1. The surface charge density of Ni^{3+}/Ni^{4+} redox increases by ca. 5 times after the LCFN5_m sample was kept in the PTFE cell for 48 hours in 1M NaOH. The same phenomenon is observed on LCFN5_m-based electrodes with different total mass loadings. The author thought such an increase in the charge density would imply a surface reconstruction process, but does not explain why. If this is due to the dissolution/deposition, the roughness is increased by a factor of 5. In other words, is it reasonable to substantially increase the roughness of nanocatalysts by soaking alone?
2. From Figure 3 and Figure 14, we understand that samples prepared by ultrasonic spray pyrolysis (USP) have poor homogeneity and whether this difference affects the performance.
3. In Figure 25a, is the difference in an activity primarily due to the specific surface area? What would happen if the current density was normalized using BET?
4. In Figure 26, in addition to the peak current increase, there is another reduction peak located at 1.35 V. What reaction might this peak be? Furthermore, no corresponding oxidation peaks were observed, perhaps further careful inspection of the CVs is required.
5. In the XPS chapter, Figure 30, it is recommended to first perform peak fitting processing before determining valence and composition. In view of XPS's test error, it may not be rigorous to determine the formation of (oxy)hydroxides on the surface of LCNF5_m S through the weak changes of O1s and Ni2p.
6. When discussing the effect of Fe impureness, Figure 38a, whether the Fe content in the 1M NaOH solution was first determined by ICP.
7. There are some mistakes in the text, such as on Page 90, "(b) - total loading 59.5 μg cm^{-2}/30 wt.% oxide:70 wt.% VC)."; Page 92 "…after soaking in alkaline solution for 4 weeks, without polarization)."

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*