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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Sergei V. Porokhin

PhD Program: Materials Science and Engineering

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

Supervisor: Professor Artem M. Abakumov

Co-supervisor: Assistant Professor Viktoria A. Nikitina

Name of the Reviewer: Professor Evgeny Antipov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 10-09-2022**

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 entitled “Perovskite mixed oxides as catalysts of oxygen evolution reaction” by Sergei Porokhin is devoted to synthesis and characterization of perovskites in the La-Ca-Fe-Ni-O system for oxygen evolution reaction. This work represents an important and original contribution to the field of electrocatalysis and materials science since it provides valuable insights into characterization and electrochemical properties of prospective Fe-Ni based perovskites, that could serve as anode materials in electrolyzers.

The thesis is well structured and organized, it includes one introductory chapter, the chapter presenting literature overview, the two main chapters: methodology, results and discussion; and a concluding chapter summarizing main important outcomes of the research. The chapter 2 contains a general overview of the literature, which briefly describes the current situation regarding hydrogen economy and the prospects for using hydrogen generated by electrolysis. The review considers various types of electrolyzers and catalysts, also provides information about the OER descriptors that are used to predict electrocatalytic performance and additionally pays special attention to surface transformations during the OER. Based on literature review the author formulated the goal of the present study: to evaluate the electrocatalytic properties of NiFe- based perovskites with heterovalent substitution of La^{3+} by Ca^{2+}, because this system is not well studied and these materials can be very promising for commercial use as an OER catalyst.

The methodology part describes the synthesis and utilized methods of analysis. The overall level of materials characterization is very impressive. Advanced material characterization techniques: X-ray powder diffraction, surface area analysis, electrochemical techniques including galvanostatic/potentiostatic cycling, cyclic voltammetry, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, inductively coupled plasma mass spectroscopy/atomic emission spectroscopy, electron microscopy and density functional theory calculations were used to validate the results and provide detailed information on the structure and related changes during and after the OER.

The chapter "Results and discussion" contains an in-depth multi-faceted characterization of Ni-Fe based perovskite electrocatalysts. The chapter "Conclusions" combines key achievements and results of the work. As illustrative and supporting materials the thesis contains 45 figures and 12 tables; the bibliography list consists of more than 150 references.

The results presented in the thesis have a significant scientific novelty:

1. It was shown that Ca doping results in an enhancement of the perovskite materials performance in OER, which correlates with a decrease in the oxygen vacancy formation energies for Ca-doped samples.

2. It was found that $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$ material with hollow spherical particle morphology and soaked in 1M NaOH demonstrated record specific and mass activities in OER.

3. It was established that the enhanced OER activity of these perovskite materials is caused by the formation of catalytically active mixed(oxy)hydroxide layer on the surface of the perovskite structure.

4. It was shown that the presence of Fe in the electrolyte stabilizes the dynamically active OER sites in (oxy)hydroxides, which ensures the stability of the electrocatalyst during oxygen evolution.

As a whole, Sergei Porokhin's dissertation is a complete reliable study representing a solution of an important problem: development of highly active and stable catalysts for oxygen evolution reaction.

The two papers (published in the Q1 journals) reflect the main results of the thesis. In all of them Sergei Porokhin is the first author. The results from the PhD thesis were presented at 7 national and international conferences.

The results of the research represent a significant practical importance because the studied materials demonstrate impressive electrocatalytic properties competing with the best catalysts among perovskites and iridium oxides for OER. The obtained results are important for the next step of development of an electrolysis cell prototype and potential commercial use.

The dissertation of Sergei Porokhin is a complete research which meets the requirements for awarding a PhD degree according to the criteria of relevance, scientific novelty and reliability of the conclusions.

The following remarks can be made on the content of the thesis:

1. What does it mean "With an increase in the potential, β-NiOOH can transform into the γ-NiOOH (different in the amount of water and cations), where the nickel oxidation state is +3.5–3.7"(p.48)"? The chemical formula should be changed.

2. What was the reason to use ozone instead of oxygen as an oxidizer for the annealing at high temperature (850 ^{O}C) (p. 59)? Such treatment is usually made at much lower temperature thus preventing rapid ozone decomposition.

3) The sentence "All diffraction peaks in PXRD pattern of the sample annealed at 800 ^{O}C correspond to the perovskite structure, while for the samples prepared at 600 ^{O}C and lower annealing temperatures (p. 69)" should be corrected.

These remarks do not reduce the significance of the obtained results and do not affect the overall very positive evaluation of Sergei Porokhin's dissertation. This thesis represents a significant step in understanding of the origin of the electrocatalytic behavior of perovskite materials in OER. Sergei Porokhin deserves to be awarded a PhD degree.

Provisional Recommendation
X *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*