

Thesis Changes Log

Name of Candidate: Aleksandr Kurilovich

PhD Program: Materials Science and Engineering

Title of Thesis: Oxygen Reduction Reaction Mechanism on Metal Oxide/Carbon Composite Materials

Supervisor: Prof. Keith Stevenson

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

In respond to Prof. E. Antipov review

- *Obviously that (La,Sr)CoO₃ is not very stable in alkaline media, therefore testing of its stability would be useful*
The discussion on LSCO stability was added in p. 91-92. The additional references were included in the Bibliography section: “The simulation of the ORR mechanism requires the experimental data for the materials which are stable within the experimental setup. Otherwise, the degradation processes should be directly taken into consideration by the model. For these reasons, the data for the LCO and LSCO64 perovskite materials are used in simulations. LCO is shown to be stable at the potentials above 0.4 V vs RHE, where ORR and HPRR/HPOR are studied [60], [81]. Despite LSCO64 has lower bulk stability than LCO [219], which is correlated with the more negative free energy change for the lattice oxygen vacancy formation [214], rather low O vacancy concentration in LSCO64 [214], [220] and the use of fresh electrodes at each ORR and HPRR/HPOR RDE experiments suggest that the catalytic degradation process (if present) is slow during the experiments and does not notably change the results.”
- *The chapter 2.1.2.2.3. describing transition metal oxides as electrocatalysts for the ORR is too short (about 1 page) and does not give an important information about recent progress in this field. Moreover, a chemical formula of the pyrochlore La₂Zr₂O_{7-δ} looks wrong, and this insulating material cannot be considered as a highly active electrocatalyst for the ORR. It would be better if this chapter will list more materials have been actively studied, and a brief comparison of their properties will be presented aiming to explain why the particular Mn- and Co-based materials have been chosen for the experimental part of the thesis*
The chapter 2.1.2.2.3 was expanded to provide a better description of the actively studied materials for ORR and the explanation for the model system choice: “Opposite to acidic media, some of the non-noble transition metal oxides are stable in alkaline media at the potentials where ORR occurs. Many of them are highly active for ORR demonstrating the activity close to the one of Pt-based commercial catalysts. However, their relatively low electrical conductivities necessitate the use of conductive support, generally manifested through mixing with high-surface-area carbons. It significantly complicates the analysis and comparison of the intrinsic catalytic activities of different TMO catalysts, as the type and amount of the carbon support, catalyst synthesis and electrode preparation routines, and possible cathodic degradation significantly influences the overall ORR activity [60], [61]. The most widely studied materials are based on spinels, perovskites, and other oxides (Mn-based).”

Pure spinels are relatively inert for ORR. However, they demonstrate an excellent catalytic activity for ORR within the spinel/carbon composite materials. It is further enhanced by the N-doping of carbon component and the presence of strong coupling between the spinel and carbon components (i.e. if the spinel nanoparticles are directly grown on carbon instead of physical mixing) [7], [62], [63]. The additional synergistic effects from strong coupling and ORR activity of carbon (or N-doped carbon) components further challenge the ORR mechanistic studies on these materials. Regarding the spinel component, the most active materials are based on Co_3O_4 [64], Mn_3O_4 [62], and Fe_3O_4 [63]. They can be further optimized, e.g. Mn-substituted MnCoO_4 spinel has higher catalytic activity than Co_3O_4 on the same carbon component [65], while $\text{Mn}_x\text{Cu}_{1-x}\text{Mn}_2\text{O}_4$ compounds with both Mn and Cu atoms demonstrate the highest catalytic activity [66]. These materials show $\sim 4e^-$ reduction of oxygen with $<10\%$ HO_2^- yield and onset potential almost identical to the one for Pt/C, thereby being a promising alternative for ORR in alkaline media.

Perovskites, with the general formula $\text{ABO}_{3\pm\delta}$, where A is a large alkali-earth or rare-earth element and B is a transition metal, are an appealing model system because the physico-chemical and electronic properties of these materials can be easily tuned through substitution into the A and B sites, as well as through the formation of oxygen vacancies. For the initial optimization of site A, the La-based perovskites demonstrated the highest catalytic activity for ORR within the LnMnO_3 series (Ln = La, Pr, Nd, Sm, Gd, Y, Dy, Yb) [67]. As for the site B, Mn [68], [69], Co [70], [71], and Ni-based [53], [72] perovskites generally provide the highest catalytic activities for ORR. The reported results are highly dependent on the perovskite electrodes preparation method and the methodology of their studies, often being controversial. For example, within the LaBO_3 (B = Ni, Co, Mn, Ni, Fe, Cr) bulk perovskites without the conductive additives, the LaCoO_3 exhibits the highest catalytic activity for ORR [71]. In contrast, the Co-based perovskites show the lower catalytic activity for ORR than the Mn-based ones [73]. Therefore, the mechanistic studies of ORR on perovskite materials require the self-consistent experimental dataset to evaluate and decouple the factors influencing the overall ORR activity.

Many other Mn oxides are active for ORR in alkaline media [74]. Their performance was shown to be connected with the experimentally observed [75] Mn(III)/Mn(IV) surface redox process, with the Mn(III) being the active site for ORR [76]. Mao et. al [77] demonstrated the Nafion-modified Mn /Au electrodes to follow the sequence $\text{Mn}_5\text{O}_8 < \text{Mn}_3\text{O}_4 < \text{Mn}_2\text{O}_3 < \text{MnOOH}$ for ORR activity. Cheng et. al [78] reported catalytic performance of MnO_2 polymorphs to follow the sequence $\alpha\text{-MnO}_2 > \beta\text{-MnO}_2 > \gamma\text{-MnO}_2$. Ryabova et. al [79] showed an excellent activity of $\alpha\text{-Mn}_2\text{O}_3$ (byxbyite) for ORR, being the highest within the series of studied Mn oxides: $\alpha\text{-Mn}_2\text{O}_3$ (byxbyite) $>$ $\beta\text{-MnO}_2$ (pyrolusite) $>$ Mn_3O_4 (spinel) $>$ $\gamma\text{-MnOOH}$ (manganite). The opposite trend was observed for HO_2^- yields and the limiting currents for the $2e^-$ reduction of HO_2^- on these materials. The amount and consistency of these experimental findings make them a good model system to obtain further insights on the ORR mechanism with respect to the TMO component.”

Additionally, p. 29: “Therefore, further insights for the ORR mechanism and the catalytic activity trends for the TMO/C components require the self-consistent dataset (i.e. the same electrode composition, mass loadings, methodology of experimental measurements, etc.). The $\alpha\text{-Mn}_2\text{O}_3$ -...- $\gamma\text{-MnOOH}$ series [79] can be used to study the ORR mechanism with respect to the TMO component due to the pronounced difference in ORR and HO_2^- reduction and availability of high-quality experimental data. The influence of the carbon type (including the N-doping effects) can be probed on LaCoO_3/C materials, which are stable above 0.4 V vs. RHE [81], provide flexibility in further modification of their properties, and exhibit the synergy for ORR within the composite.”

The references were included in the Bibliography section.

- *It would be beneficial for the thesis to make a general discussion of the ORR reaction on studied materials and compare own data with the literature ones. In present form the thesis looks like a number of independent parts while all of them are focused on the ORR.*

The general comparison of the studied ORR mechanisms with the literature data was added in p. 144: “The obtained mechanistic insights for ORR on the TMO/C composite materials are in a good agreement with the reported literature data. Indeed the probed inner-sphere mechanisms for ORR on Mn_2O_3 , MnOOH , and LSCO are excessively applied to explain the origins of the catalytic activity trends for the TMO materials [68], [72], [73], [199], [226], [227]. The alternative outer-sphere ORR mechanism on Mn_2O_3 and MnOOH is supported by the computational studies of ORR on Pt and Au

in alkaline media [205], [206]. The concept of oxygen spillover is well known in literature for the composite catalytic materials [228], [236]. It worth noting that it calls for an additional verification for LSCO/NC. The effective ORR mechanisms on CNTs, used to study the inverse uncertainty propagation, can be linked with the previously reported one-electron mechanisms [39], [51], [52] within the quasi-equilibrium and almost-empty surface approximations.”

- *MnOOH is not a simple oxide, it is oxide-hydroxide or oxohydroxide*
The correction was added to the title of Chapter 3

In respond to Prof. S. Fedotov review

- *The Candidate did not mention who performed the synthesis of different materials in all parts of the work.*
This information was added in the 3.1.1, 4.1.1, 5.1.2, and 6.1.1 sections.
- *The manuscript contains some technical misprints (the title of Chapter 4 on p. 74 has an error in the formula) and some grammatical incorrections (e.g. informal reduced forms of auxiliaries like “won’t” (p. 41), “doesn’t” (p. 52) or incorrect use of tenses)*
The technical misprints and grammatical mistakes were corrected.
- *The most significant comment concerns the Chapters 2, 3, and 4 which lack logical connectivity both among them and with the following Chapters 5 and 6. From the first sight they might even look like unrelated parts of different research. The Candidate is encouraged to add more “glue” between the parts during the presentation to show the integrity of the work in whole and significance of each part in particular in addressing the problem posed.*
- The connection between the chapters 2-6 was improved by expanding the introduction parts of chapters 3-6 and chapters 2.1.2.2.3, 2.1.3, and 7.

In respond to Prof. S. Levchenko review

- *"It can be seen that molecular oxygen is relatively weakly adsorbed at the model surfaces, with the Mn-OO distance being 1.96 -2.05 Å" -report adsorption energies in a separate table; I don't think one can judge the strength of adsorption from the distances*
The additional table 3.2 with calculated adsorbates bonding energies was added on p. 62
The sentence was clarified “The molecular oxygen is relatively weakly adsorbed on the model surfaces (see Table 3.2). The Mn-Oo distance for adsorbed oxygen is in the range of 1.96 – 2.05 Å.”
- *"The active centers, which are assigned to the closest Mn atoms, are marked in Figure 3.2."; it is very hard to see the marks, please improve*
The marks in figure 3.2 were improved.
- *Eq. 2.27 does not make any sense*
Please, note that the Eq. 2.27 represents the formal representation of the elementary step with summation over the reactants ($\alpha_{ij} < 0$) and the products ($\alpha_{ij} < 0$) in the left- and right-hand parts respectively
- *Eq. 2.30 is wrong*
- *Eq. 2.28 -notation \hat{X} appears suddenly, as well as the capital J index"*
- *The latter is determined from the \hat{X}^0 , which provide the equilibrium by setting all r_i to zero simultaneously" - \hat{X}^0 is not defined before, perhaps a typo*
This part of the thesis was reorganized to clarify these points
- *Tell if long-range van der Waals interaction contributions were taken into account; discuss how this would affect Fig. 3.5 and other results*
The information and discussion were added to the text on p. 60. “The long-range van der Waals interactions were not taken into account within the framework of periodic DFT. Different approaches exist to incorporate them, though they have their own shortcomings [186], [187]. They

require an excessive testing for the studied system which is beyond the scope of this work. However, one might expect that the introduction of the long range interactions would stabilize the ORR intermediates on the electrode surface ca. 0.1-0.2eV [188]. The relative change in binding energies is lower than for the absolute values. Therefore, one can believe that it would not qualitatively change the results presented in this chapter.”

- *Describe how magnetization of the surfaces was treated (collinear, non-collinear), what spin configuration was obtained (anti-ferromagnetic, ferromagnetic?)*

The description was added to the thesis on p. 59:

“Collinear spin-polarized periodic DFT calculations were performed using the VASP program package [184] with PAW [185] pseudopotentials and the RPBE-GGA functional [134]. The 3d4s(ZVAL=7), 2s2p(ZVAL=6), and 1s(ZVAL=1) electrons were treated as valence ones for the Mn, O, and H, respectively.”

and

“The ferromagnetic ground state was obtained for α -Mn₂O₃, which coincides with the results reported by Franchini et. al. [189]. The ferromagnetic ground state for γ -MnOOH was calculated. The optimized bulk structures were then used to construct the surfaces with the ferromagnetic spin configuration. The more detailed calculations of the α -Mn₂O₃ ground state magnetic structure require the DFT+U formalism, which was not adopted in calculations due to the reasons discussed below.”

- Multiple clarifications and corrections were added throughout the thesis according to all the remaining reviewer’s comments. The additional references were incorporated into the Bibliography section.

In respond to Prof. C. McCrory review

- *The first page of the chapter (pg 13) is largely arguing for the increased use of renewable energy which requires new energy storage technologies...not necessarily energy conversion technologies like fuel cells. The actual argument for fuel cell development – increased conversion efficiency decreases CO₂ and other emissions per mile – is relegated only 7 lines on pages 13-14. I suggest the student consider slightly reframing their first few pages of Chapter 1 to emphasize the importance of efficient conversion technologies for transport as means of lowering CO₂ emissions.*

This part of the thesis was reframed according to the reviewer’s comment (p. 13): “CO₂ emission should be reduced to less than 20 Gt by 2030 in order to prevent the major negative climate changes [2]. The temporal decrease by 8% is observed in CO₂ emissions due to the ~4-6% lowered energy demand compared with 2019 because of the pandemic situation in the world. It is correlated with the decrease in the coal, oil, and natural gas consumption by 8, 5, and 2% respectively (Q1 2020 vs. Q1 2019). However, the long term trends for energy demand growth are unlikely to change. The transport applications have a huge share of ~30% for global CO₂ emissions [3]. Therefore, a special effort should be made to replace the combustion engine-based technology with more environmentally friendly alternatives. The low-temperature fuel cell technology [4], typically operating on hydrogen fuel, can be used to address this problem. It provides the generation of the electric energy with high efficiency of 40-80% and the lower or absent emission of hazardous substances, such as SO₂, NO_x, CO, and CO₂, being compared with the combustion engines operating on the fossil fuels. CO₂ is generated in the full lifecycle of hydrogen production/consumption, as it is mainly produced from the fossil fuels. However, its amount is significantly lower than that for production/combustion lifecycle of gasoline, diesel, and natural gas fuels [5]. Nevertheless, the further optimization of fuel cell efficiency is required, as it indirectly reduces the amount of generated CO₂ per mile through the lowered consumption of hydrogen fuel.”

- *In the final paragraph of the chapter, I suggest the student conclude a final statement that explains “why” or “how” the research presented in this thesis will tie into the stated goal of decreasing CO₂ emissions. This chapter could use additional English-language proofreading.*

The grammar corrections were introduced. The final statement was added: “Its quantitative treatment is crucial to determine the level of insights that can be experimentally verified, thus providing better coupling of the methods within the multiscale modeling approach. These results should facilitate further search for more active and cost-efficient ORR catalysts, which would enhance the

performance of related energy storage and conversion devices. It should help to solve the problem of huge CO₂ emissions from the transport applications, as efficient low-temperature fuel cells should reduce the hydrogen consumption per mile and thus the overall CO₂ generation.”

- *The student might consider including a schematic figure highlighting the MEA and GDL components in a fuel cell, either as a standalone figure or incorporated with labels into figure 2.1*
The labels were incorporated into the figure 2.1 in accordance with the reviewer’s comment.
- *The student should be careful to be consistent with a nomenclature, though. For instance, the student defines two specific pathways for the ORR: the “Direct 4-electron pathway” and the “Peroxide pathway” (or “2e-+2e-” pathway). However, in the text the student refers to undefined pathways including the “pseudo 4e- pathway” and the “peroxide-mediated or dual path mechanism”. The student should be careful of this not only here, but throughout the thesis (Chapters 3-6) to avoid ambiguity*
The consistency of the nomenclature was improved throughout the thesis.
- *It would be helpful for the student to include the figure of the experimentally-observed kinetically-limited HPRR for MnOOH indicated in the text on pg 67. I believe this may have been shown in the manuscript from which this chapter was derived, but not included in the chapter itself. It might be helpful to the reader to take the section of the manuscript on prior results that was not included in the thesis and incorporate it into Chapter 3 (to motivate the study) or into Chapter 2 (to provide greater context)*
The figure 3.2 with the prior results was included in the Chapter 3.
- *These chapters are taken substantively from published manuscripts. The only minor comment I might suggest is expanded introductions to put into better context how the individual chapters relate to each other and the overall theme of the thesis*
The introduction parts of Chapters 3-6 were expanded to provide a better connection between them.

In respond to Prof. T. Kallio review

- No comments for consideration