

Jury Member Report – Doctor of Philosophy thesis.


Name of Candidate: Aleksandr Kurilovich

PhD Program: Materials Science and Engineering

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

Supervisor: Professor Keith Stevenson

Name of the Reviewer:

I confirm the absence of any conflict of interest	Signature:  (Sergey Levchenko) Date: 01-09-2020
---	---

Reviewer's Report
<ul style="list-style-type: none">• Brief evaluation of the thesis quality and overall structure of the dissertation. <p>The thesis is generally well-written and has a clear structure. The scientific quality is very good. The English is not grammatically correct and therefore not easy to understand in some places, but there is nothing that could prevent overall understanding. One general drawback is that it is sometimes unclear what was done by the defender, and what not, although in some places it is stated explicitly. For example, I could not tell if the defender did microkinetic modelling in all projects or only in part.</p>• The relevance of the topic of dissertation work to its actual content <p>The topic of dissertation is directly related to its content.</p>• The relevance of the methods used in the dissertation <p>The methods, in particular experimental data analysis, ab initio calculations, and microkinetic modelling, are an important part of the study. Some details on the ab initio calculations are missing, but this does not undermine the relevance of the methodology.</p>

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

The high scientific significance of the results is best demonstrated by the high level of publications with the defender's contributions. Understanding mechanisms of complex electrocatalytic reactions is a challenging task, and the work of the candidate is an important step both towards this understanding and to the development of methodology that allows us to achieve it.

- The relevance of the obtained results to applications (if applicable)

The obtained results are directly relevant to applications, namely finding better materials for electrolyzers and fuel cells.

- The quality of publications

The defender lists four publications, two of which are first-author (one is just submitted). Judging by the already published work, its scientific quality is excellent. The work combines experiment, modeling, and data analysis, and the contribution of the candidate is an important part of the overall success.

The summary of issues to be addressed before/during the thesis defense

All comments are recommended to be addressed by modifying directly the text of the thesis, unless an explicit answer is requested or a comment is unclear.

"periodical" -> "periodic"

"The accuracy of this type of calculations is generally higher than that of the periodical DFT methods." - Clarify what you mean. Cluster models suffer from the artificial border effects.

"within the such called multiscale modeling approach" -> "within the multiscale modeling approach"

"complex electrocatalytic reactions mechanism" -> "complex electrocatalytic reaction mechanisms"

"as well as the constraints the experimental data may introduce to the ab initio calculations through the MF-MKM" - not clear what you mean by constraints; do you mean "bias"?

"oxidation of the fuel at the cathode" - anode

"are also can be used" - either "are also used" or "can also be used"

"The combination of RRDE experimental data for Pt/VACNF in H₂SO₄ and HClO₄, elementary step models based on previous experimental findings[33]–[35] and microkinetic modeling was shown that" -> "... has shown that"

check Eqs. 2.6 and 2.8, looks like they are imbalanced

"Various ORR mechanisms suggested for different carbon materials" -> "Various ORR mechanisms were suggested for different carbon materials"

Eq. 2.20 - looks like a typo: "O_{2 0ads}"

"are reactant/product species and correspondent stoichiometric numbers" - "corresponding"

Eq. 2.27 does not make any sense

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

Eq. 2.30 is wrong

"are coefficients, which dimensionality depends on" -> "are coefficients, whose dimensionality depends on"

"specie" -> "species" (specie has a different meaning)

"are also depend on the space coordinates" - "also depend" or "are also dependent"

"It brings the necessity for either to use of advanced methods" - "for either use" or "to either use"

"assuming that the later one is governing" - latter, not later

"One can make right the part of ODEs system non-autonomous by addition following ODE" - badly written sentence, please clarify

RLS - abbreviation was never defined

"Therefore, the methods for the direct solution of the Schrodinger equation" - clarify in the text which methods you imply here

"The computational cost is gradually decreased due to the use of 3-dimensional electronic density instead of 3N-dimensional wave functions." - "gradually" is not appropriate here; "dramatically" or "significantly" would be better

"which shows that the ground state energy is the unique function of the electronic density" - "functionAL"

"In practice, electronic density is calculated from wave functions using the Kohn-Sham equations" - "from one-electron wave functions"

"interacting energy between each electron and the collection of the atomic nuclei" - "interaction energy..."

"The exchange-correlation potential is treated as the exchange potential of the spatially uniform electron gas." - not only "the exchange potential of the spatially uniform electron gas", but also correlation

"led to the development of the Volcano plot" - "volcano plot" (small letter)

"any random variable can be approximated by with required precision by PCE" - redundant "by"

"The problem is, that the will be never enough experimental data" - "that THERE will never be enough"

"Therefore, the inverse problem may become the ill-posed" - "may become ill-posed" (no "the")

" It can be explained the principles of MCMC sampling based on commonly used the Metropolis algorithm" -> "The principles of MCMC can be explained based on the commonly used Metropolis algorithm"

"MCMC methods require burn-in to reach the equilibrium distribution," - explain the term "burn-in" in the text

" TPE is also advantageous for the excessive parameters" - TPE was not defined in the text

"2.3. Outline" - clarify outline of what; of Chapter 3?

"of the conventional ab initio thermodynamic approach" - "thermodynamicS approach"

"the probability of the outer-sphere ORR mechanism is elucidated" - maybe "the relevance of the outer-sphere ORR mechanism"?

"Spin-polarized periodical DFT calculations were performed using the VASP program package [172] with PAW [173] pseudopotentials" - describe details on pseudopotentials (which orbitals were pseudized and which not

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

describe which bulk phase of Mn₂O₃ was used to construct surfaces and why

tell if long-range van der Waals interaction contributions were taken into account; discuss how this would effect Fig. 3.5 and other results

"However, this potential shift is not sufficient to cancel out the pronounced difference in the oxides' electrochemical activities" - maybe "However, this potential shift is not sufficient to explain the pronounced difference ..."?

"(which is the inevitable assumption on the current stage)" - clarify why

"Zero-point energy (ZPE) and entropic corrections (TS)" - clarify that this does not include configurational entropy; also mention that the pV term was neglected

"Table 3.1 ZPE and TS corrections for the reaction intermediates" - write for which temperature these data were obtained

Eq. 3.5: explain where the number 4.92 eV comes from

Eq. 3.5: explain what index "l" means in $G_{\text{O}_2}(\text{l})$; how then $G_{\text{O}_2}(\text{g})$ is determined

"The clusters were constructed using the geometry of Mn₂O₃ (111) and MnOOH (110) surfaces optimized at the periodical DFT calculations" - "optimized using periodic DFT"

"One can see the additional details on the model parameters and equations in Supplementary information [182]" - there should be no supplementary information in thesis; include the supplementary information explicitly, e.g. as an appendix

"The later decreases at lower catalyst loadings" - "The latter"

Figure 3.2, panel a: why there is H at the surface of Mn₂O₃? how its coverage was determined

"The active centers, which are assigned to the closest Mn atoms, are marked in the Figure." -> "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

Table 3.2: some text is subscripted; explain in the caption what this means (if it is not a typo, I guess it is not)

"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

"Instead, the MnOOH (110) and Mn₂O₃ (111) surfaces were used at 0.5 ML OHads and 0.5 ML Oads coverages and computed the free energy diagrams" -> "Instead, the MnOOH (110) and Mn₂O₃ (111) surfaces were used at 0.5 ML OHads and 0.5 ML Oads coverages, and the free energy diagrams were computed"

"The hypothesis of the outer-sphere ORR mechanism should be also elucidated due to the low adsorption energies of O₂ on both MnOOH (-0.03 eV) and Mn₂O₃ (0.07 eV)

obtained from the periodic DFT calculations." - clarify the sentence, the wording is confusing ("should be elucidated due to")

"can then be adsorbed Mn active site" -> "can then be adsorbed on Mn active site"

"Then the origin in the catalytic activity difference" -> "Then the origin OF the catalytic activity difference"

"The presence of O-terminated Mn active sites showed the repulsion effect only in vertical(2) geometry" - clarify what is "repulsion effect"

"while the MnOOH ($\kappa \sim 10^{-2}$) for all O₂ orientations." -> while for the MnOOH $\kappa \sim 10^{-2}$ for all O₂ orientations."

"The results of MF-MKM, obtained out by A. Bonenfant" - "obtained by"

"It was shown that periodical DFT calculations within the conventional thermodynamic approach cannot account for the differences between Mn₂O₃ and MnOOH" - clarify this statement; would periodic hybrid functional DFT be sufficient? or is it because of the need to calculate charged systems?

"Instead, it provided the optimized surface geometry, which was used for the activation barriers calculations of the likely elementary steps." - clarify this, e.g.: "Instead, it provided the optimized surface geometry, which was used for the calculations of activation barriers for the likely elementary steps using cluster models."

"7) The reduction of the adsorbed oxygen into the HO₂-/oxidation of adsorbed oxygen into the HO₂-" - the reverse reaction is not described correctly

Chapter 4: clarify what was done by YOU

"ORR and HPRR/HPOR were calculated as:" - ""ORR and HPRR/HPOR currents ..." ?

"Therefore, it should be possible to access independently the diversity of the experimental base and detailing it provides on the macroscale level" - bad English, clarify the sentence

"the ORR on Multiwalled carbon nanotubes" - "multiwalled"

"Then the Mean squared error" - "mean"

Figure 5.4: specify units for the y axis, explain the meaning of the value 3.1×10^{-2} on the plot, explain the meaning of the word "geom" at the bottom right corner

"by the introduction of HPRR/HPOR data It is still low corresponding to the" - period is missing after "data"

"Even the relatively low increase of threshold value" - clarify what "threshold value" is

"which is accessible by the current methods of inverse uncertainty propagation quantification methods" - redundant word "methods"

"arising from the accuracy of methods and correspondent approximations" - "corresponding"

"It worth noting that this work serves as the first step to better couple the experimental and macroscale modeling parts through the quantitative inverse uncertainty propagation treatment" -> "It is worth noting that this work serves as the first step towards better coupling of the experiment and macroscale modeling through the quantitative inverse uncertainty propagation treatment"

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