Thesis Changes Log

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PhD Program: Materials Science and Engineering

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

Supervisor: Prof. Artem Abakumov **Co-advisor:** Assistant Prof. Victoria Nikitina

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

Response to Prof. Antipov.
Dear Prof. Antipov,
Thank you for your attention to my thesis, below you will find answers to your comments.

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.
Answer: The paragraph has been rewritten, see page 49. “Such a chemical formula is widely used in the literature, this designation is used for simplicity, because water molecules and alkali ions can intercalate into the (oxy)hydroxide, making it difficult to determine the exact composition. A more accurate representation to take into account the variable stoichiometry of the compound would be γ-$NiOOH_xA_y{*}z(H_2O)$ (where A - alkali metal cations and the nickel oxidation state reaches +3.66 when $x = 0$, $y = 0.33$, $z = 1$)”.

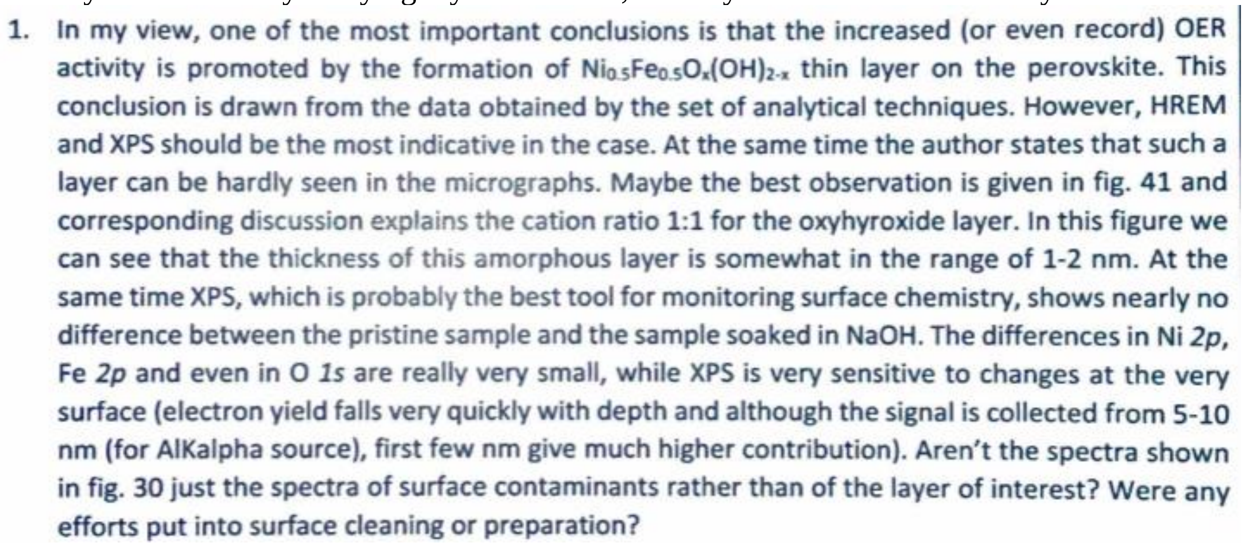
2. What was the reason to use ozone instead of oxygen as an oxidizer for the annealing at high temperature (850 ^{o}C) (p. 59)? Such treatment is usually made at much lower temperature thus preventing rapid ozone decomposition.
Answer: Ozone generation was chosen initially as a safer alternative to oxygen to be applied under the laboratory conditions. We assumed that the oxidizing medium together with an organic additive during pyrolysis would affect the morphology of the particles, and as a simple and affordable solution, it was decided to use a household ozone generator to create an appropriate atmosphere. We suggest that using oxygen instead of an ozone should probably have the same effect during spray pyrolysis.

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.
Answer: Sentence was corrected «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 there are impurity diffraction peaks.»

Response to Dr. Itkis.

Dear Dr. Itkis,

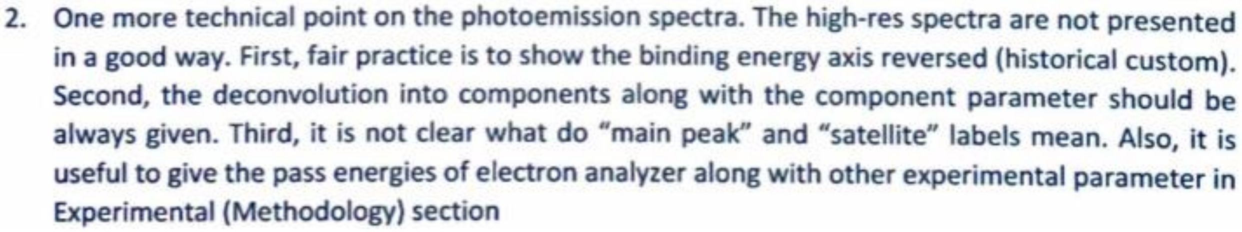
Thank you for carefully studying my dissertation, below you will find answers to your comments.



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 oxyhyroxide 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 *2p*, Fe *2p* and even in O *1s* 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?

Answer: The thickness of the (oxy)hydroxide layer depends on the treatment procedure. The (oxy)hydroxide layer shown in Fig.41 refers to a sample LCFN5_m that was analyzed after long-term constant current tests in an electrolyte with additional 1 ppm Fe. On this sample, which showed record OER activity, we were able to visualize the active layer. TEM images where the active layer was not resolved refer to the samples that were measured under different conditions and without introducing additional Fe ions into the electrolyte. Moreover, we deliberately used the lowest loading in the last electrochemical experiment for TEM (Fig. 41), so that all particles were wetted and a smaller amount of Nafion, in order to avoid such picture as in Fig. 34.

We did not use preliminary special cleaning of samples for electrochemical studies, so the XPS spectra were taken for the samples without additional surface cleaning. We pursued the goal of studying the state of the surface under conditions similar to those that were when the sample was soaked in a Teflon cell. And, indeed, the surface contamination factor does not allow us to directly compare elemental composition of these two samples, however, using the literature data on minor variations in high-resolution spectra for Ni2p and O1s in combination with the behavior of redox peaks on CV and data from ICP-AES/MS on the dissolution of terminal layers, allowed us to suggest what was happening to the surface.



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

Answer: The high-resolution spectra have been changed (Fig.20). Pass energies have been added to the methodology section.

We did not perform peak deconvolutions, because Ni cation XPS spectra fitting as well as XPS spectra fitting for other 3d element cations are very complex and include multiple components (doi:10.1016/j.susc.2006.01.041) [1]. Additional complications give us some uncertainty in component positions and component half-widths, for example differential charging effect. As for terminology "main peak" and "satellite", it was taken from the same article. However we added the positions of interested peaks and labeled them as "a" and "b", which corresponds to the position in the NIST database, see page 99.

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?

Answer: We tried to analyze the samples by XPS in a state close to that in the electrochemical experiment with soaking. Indeed, surface contamination skews the concentration data, and therefore we use a comprehensive analysis and literature data to make conclusions.

4. The author claims that the preference of Ca^{2+} as a dopant over Sr^{2+} 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 Ca^{2+} is mainly reached by Ni oxidation state change rather than equal contributions from Ni and Fe.

Answer: “The Sr for La substitution shifts the 2*p*-band center even closer to the Fermi level that can lead to enhanced cation leaching and surface amorphization (doi:10.1021/acs.jpcc.8b01397) [2], while the position of the 2*p*-band center in the Ca-substituted perovskites provides an optimal compromise between the stability and catalytic activity” (page 108). So, initially, we thought that due to the different electronic structure, Ca-doped samples would have better stability, but as it turned out later, the presence of impurity Fe ions is a decisive stability factor. From this point of view, Ca or Sr impurities determine the rate (and probably depth) of surface restructuring, which accommodates the formation (oxy)hydroxide surface layer. This restructured layer interacts with trace amounts of Fe ions in the electrolyte, which determine the stability of the composition due to the continuous formation of dynamically stable active centers. It is likely that Sr doping will increase the rate of restructuring (compared to Ca), and higher concentrations of Fe ions in the electrolyte will be required for dynamic stability.

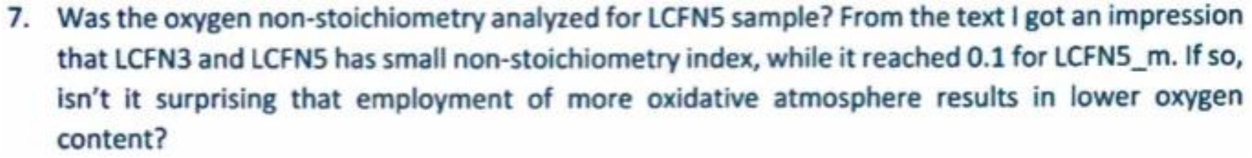
In ref. (doi.org/10.1021/acsami.8b19592) [3] it was shown that for $La_{1-x}Sr_xFeO_{3-\delta}$ iron in the B-site causes the perovskite to preferentially form oxygen vacancies (δ) rather than oxidizing the iron center because of the difficulty in oxidizing Fe^{3+}. In our case, it seems that in the perovskite structure it is easier to stabilize nickel with a higher degree of oxidation compared to iron; moreover, in ref. (doi.org/10.1038/s41467-018-05600-y) [4] in a sample with the RP structure, but with the same ratio of Fe and Ni $La_{0.5}Sr_{1.5}Ni_{0.3}Fe_{0.7}O_{4\pm\delta}$, the nickel oxidation state was estimated as +3.82, and for Fe as +3.58, which is consistent with our results.

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 the any ionomer inside?

Answer: Unique morphology means a different morphology (hollow sphere with pores confirmed on TEM) compared to solid dense particles. In terms of OER, we have a larger surface area with a larger number of catalytic sites. From our data, we see that LCFN5 and LCFN5_m has the same BET-normalized current density or the same active site density Fig.25, p.88), where a reaction can occur. This allows us to conclude, that the inner surface is wetted in the same way (pore diameter according to BET analysis up to 140 nm, which is consistent with TEM) as the outer surface in the case of a solid dense particle. Since in our experiments the ionomer was added to the ink, and not separately (on the dried catalyst thin film on the electrode), it should be evenly distributed over the entire area of the particles.

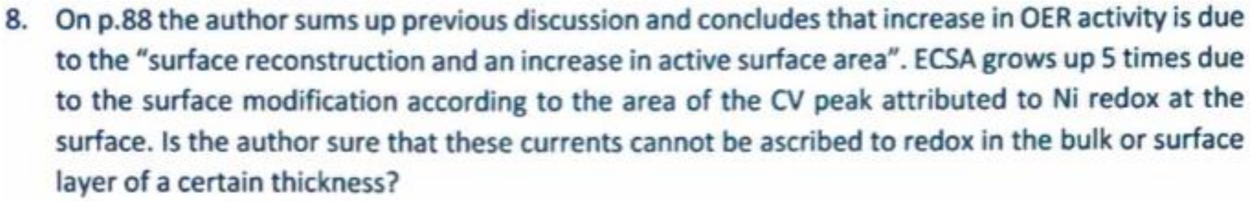
6. How ozone for synthesis was generated and how its flow rate was controlled? What is the reasoning for selecting ozone instead of simple increase in partial oxygen pressure?

Answer: Ozone is produced by a household ozone generator with the constant ozone flow rate of 400 mg h^{-1}, (taken from the device passport). Ozone generation was used instead of oxygen stream due to better compliance with laboratory safety protocols.



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?**

Answer: Oxygen non-stoichiometry was analyzed only for sample LCFN5_m, as the sample that showed the most homogeneous distribution of elements and the highest electrocatalytic activity. We did not analyze the oxygen non-stoichiometry of the LCFN3 and LCFN5 samples due to the presence of impurities. In the case of an oxidizing atmosphere, we assume that this atmosphere allows us to burn organics, which, when burned, creates a porous structure, however, after spray pyrolysis, all samples were annealed in air to crystallize, and we can speculate that during this procedure, the difference in oxygen could potentially be reduced between samples.



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?**

Answer: In the case of the porous structure of the samples and the structure of layered hydroxides (from the literature, layered nickel oxyhydroxide compounds are capable of embedding alkali ions and water molecules, thus being electrochemically active not only on the surface, but also in the bulk), we can indeed interpret the area of the redox peak on CV as referring to a layer of certain thickness. However, the electrochemical surface area estimation (ECSA) approach, which is related to the number of available redox active sites, is still a very convenient tool to draw correlations on the electrocatalytic activity trends and is widely used in the literature (e.g. ref. [5] 10.1016/j.jelechem.2020.114246)

9. Mistypes were corrected and Figures 28,30,33 where changed.

1. Grosvenor, A.P.; Biesinger, M.C.; Smart, R.S.C.; McIntyre, N.S. New interpretations of XPS spectra of nickel metal and oxides. *Surf. Sci.* **2006**, *600*, 1771–1779, doi:10.1016/j.susc.2006.01.041.
2. Han, B.; Grimaud, A.; Giordano, L.; Hong, W.T.; Diaz-Morales, O.; Yueh-Lin, L.; Hwang, J.; Charles, N.; Stoerzinger, K.A.; Yang, W.; et al. Iron-Based Perovskites for Catalyzing Oxygen Evolution Reaction. *J. Phys. Chem. C* **2018**, *122*, 8445–8454, doi:10.1021/acs.jpcc.8b01397.
3. Alexander, C.T.; Mefford, J.T.; Saunders, J.; Forslund, R.P.; Johnston, K.P.; Stevenson, K.J. Anion-Based Pseudocapacitance of the Perovskite Library La 1- x Sr x BO 3-δ (B = Fe, Mn, Co). *ACS Appl. Mater. Interfaces* **2019**, *11*, 5084–5094, doi:10.1021/acsami.8b19592.
4. Forslund, R.P.; Hardin, W.G.; Rong, X.; Abakumov, A.M.; Filimonov, D.; Alexander, C.T.; Mefford, J.T.; Iyer, H.; Kolpak, A.M.; Johnston, K.P.; et al. Exceptional electrocatalytic oxygen evolution via tunable charge transfer interactions in La0.5Sr1.5Ni1−xFexO4±δ Ruddlesden-Popper oxides. *Nat. Commun.* **2018**, *9*, 3150, doi:10.1038/s41467-018-05600-y.
5. Cossar, E.; Houache, M.S.E.; Zhang, Z.; Baranova, E.A. Comparison of electrochemical active surface area methods for various nickel nanostructures. *J. Electroanal. Chem.* **2020**, *870*, 114246, doi:10.1016/j.jelechem.2020.114246.

Response to Prof. Jian-Feng Li.

Dear Prof. Jian-Feng Li,

Thank you for your careful consideration of my dissertation and questions, below you will find the answers to them.

1 The surface charge density of Ni3+/Ni4+ 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?
Answer: We have not systematically studied the relationship between the increase in roughness during soaking and during cycling. However, we can note that if the transformation rate of surface layers into (oxy)hydroxide is associated with the rate of leaching cations, then during cycling this process should occurs faster than during simple soaking. In our case, the increase in roughness was achieved in a combined mode: first, the sample was cycled 5 times (see Fig.25b,26a,b) then the potentiostat was turned off and the sample was left to soak in the cell.

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.
Answer: The inhomogeneity of the LCFN3 and LCFN5 samples is indeed visible on the EDX map and their Tafel slope is higher than that of the LCFN5_m sample, indicating slower kinetics with a less uniform distribution of elements.

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?
Answer: The currents at 1.61 V normalized to specific area (Figure 25c) for the LCFN5 and LCFN5_m are very close within the measurement error (ca. 1.0 and 0.85 mA cm^{-2}_{oxide}, respectively), which shows that the intrinsic activity does not depend strongly on the morphology. However, the samples have different Tafel slopes, which is noticeably lower for the LCFN5_m sample, which can thus be considered more active. The difference in Tafel slopes might be related to catalyst/VC distribution effects, as discussed on page 90-91.

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.
Answer: This tiny peak is shifted to less positive potential values and appears as a shoulder during the cathodic sweep. It can be associated with two crystallographic varieties of NiOOH. Thus, this transition can be characterized as γ-NiOOH to β-NiOOH (doi:10.1016/0013-4686(86)80087-1). We do not observe the corresponding peaks of oxidation due to the OER onset overlapping.

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.
Answer: In the XPS analysis, we did not extract the valence state of Ni, the conclusions about the nickel valence were made after iodometric titration and Mössbauer spectroscopy. We absolutely agree, that the conclusion about the formation of (oxy)hydroxide cannot be drawn only from weak changes in O1s and Ni2p, so we also used additional ICP and CV data for analysis.

6. When discussing the effect of Fe impureness, Figure 38a, whether the Fe content in the 1M NaOH solution was first determined by ICP.
Answer: We measured the initial amount of Fe ions in aqueous 50 wt.% solution of NaOH (Sigma-Aldrich) by ICP-AES and observed 1200 µg L^{-1} concentration that corresponds to 63.4 µg L^{-1} (~0.063 ppm) in the as-prepared pristine 1M NaOH electrolyte. Therefore, 1 ppm of Fe is a

significant addition which substantially improves the OER activity. This is discussed on p. 113 of the thesis.

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).”
Answer: Extra hyphen and parenthesis removed from image description.

Response to Prof. Levchenko.
Dear Prof. Levchenko,
Thank you for your attention to my thesis, below you will find answers to your comments.

“the only concern is that the personal contribution of the candidate is not clearly outlined.”
Answer on comment: The section “The PhD candidate contribution” was added.

1.Minor comments: "and it does not depend on how weak or strong these two intermediate species bind with O*." - I guess you meant M* instead of O*
Answer: Thank you for comment, I have modified the text to clarify the meaning of sentence. “and it does not depend on where the binding energy of O* level is located relative to OH* or OOH*”

2.Figure 10 caption - explain the meaning of red, green, and blue circles, squares and arrows
Answer: The description for the picture has been added, see page 53.
“The circles represent the same area on the particle after different processing. The red square in “f” means the area that is zoomed in and pasted in the corner in the same figure. Figure “g” shows the same area for the cycled sample, but the zoomed area from the square is shown separately for illustration “h”. The arrows point to the oxygen vacancies in the crystal structure”

3."Since Fe greatly slows down the leaching of other metal cations during OER [121] and affects the surface restructuring itself: with a sufficient amount of Fe, a dynamic active layer is formed and the surface layer of the initial catalyst completes the restructuring, whereas with a lack of Fe a dynamic layer is not formed, provoking further leaching and the growth of an amorphous layer on the surface of the perovskite." - a very long and incorrectly structured sentence
Answer: Sentence modified “Previously, it was reported that Fe greatly slows down the leaching of other metal cations during OER [121], which affects the restructuring of the surface itself. With a sufficient amount of Fe, a dynamic active layer is formed and the rearrangement of the surface layer of the initial catalyst is completed. Whereas, when Fe is absent, the dynamic layer is not formed, which provokes further leaching and the growth of an amorphous layer on the perovskite surface.”

4. The U values of 4.0 eV and 6.2 eV were used for Fe and Ni, respectively." - explain why these particular values of U were chosen
Answer: In the methodological part, the description has been added, see page 68.
“The value are chosen based on refs. http://dx.doi.org/10.1063/1.4887802 and http://dx.doi.org/10.1016/j.commatsci.2011.02.023, respectively. These U values reproduce electronic structure in good agreement with previous theoretical methods and experiment. In particular, the chosen U value for Fe reproduces experimental band gap and local magnetic moment of Fe in LaFeO3. The chosen U value for Ni is very close to the self-consistent U value of 5.8 eV in LaNiO3. The slightly larger value used in our study is to due to reasons of compatibility with our previous calculations. Overall, the U=6.2 eV is used for Ni-based oxides in Materials Project, which we also adopt in most of our calculations.”

5."this position is in the range of binding energy (BE) of Fe3O4. Fe2O3 and FeOOH which can be found in National Institute of Standards and Metrology (NIST) references" - I guess the dot after Fe3O4 should be a comma
Answer: This typo was corrected.

6."Additionally, the NaOH soaking reduces the high of most prominent C1s peak" - the height?
Answer: This typo was corrected.

7. We used pseudocubic cells with 40 atoms for both structures and adopted experimental lattice vectors" - write which lattice vectors were used
Answer: a_1 = [7.733, -0.01, -0.032], a_2 = [-0.022, 7.733, -0.032], a_3 = [0.0, 0.0, 7.733]. see page 107.

8. The DOS at Fermi level is predominantly of p-type, showing the formation of an electron hole in the oxygen 2p orbital" - please clarify this part in the text; p-type is related to semiconductors, but here you have no band gap; also, it is unclear, how the PDOS can show "formation of an electron hole in the oxygen 2p orbital"
Answer: We modified sentence on p.108: “The DOS at Fermi level comes predominantly from O 2p orbitals. The partial filling of O 2p states shows that LFN can be considered as an O 2p metal with holes in the valence band practically not associated with Ni ions. This is in line with earlier LDA+U results obtained for nickelates”.

9. the partial replacement of La with Ca results in concurrent oxidation of Fe, Ni and O, causing the following changes (Figure 36b): (i) downshift of the Fermi level" - explain what was the reference energy level with respect to which the Fermi level was downshifted
Answer: Sentence modified “partial replacement of La with Ca results in concurrent oxidation of Fe, Ni and O, causing the following changes (Figure 36b): (i) diminishing of PDOS at the Fermi level, (ii) downshift of the Fermi level relative to the O *2p*-band center (dashed vertical line),”

10. "The two latter changes can be attributed to the increase of the La0.6Ca0.4Fe0.7Ni0.3O2.9 catalytic activity" - maybe like this: "The two latter changes can explain the higher catalytic activity of La0.6Ca0.4Fe0.7Ni0.3O2.9."; otherwise it sounds awkward
Answer: The sentence was rewrite: The two latter changes can explain the higher catalytic activity of $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$

11. "which in result has" -> "which results in" Answer: Corrected.

12. "when the rate of cation leaching can be incomparable with the rate of redeposition" - "incomparable" does not fit well here, perhaps you want to say "can exceed"
Answer: Corrected.

Response to Prof. Tsybulya.
Dear Prof. Tsybulya, I express my gratitude for the attention paid to the work.
No corrections were requested by this Jury Member.

Response to Prof. Nuraje.
Dear Prof. Nuraje, I express my gratitude for the attention paid to the work.
No corrections were requested by this Jury Member.