Referee report on the doctoral thesis "Investigation of magnetron sputtered Pt-CeO_2 thin film catalyst for fuel cell applications" by Mgr. Mykhailo Vorokhta

The submitted doctoral thesis is a case study of the morphology of Pt-doped CeO_2 films proposed as a cost efficient substitute material in a proton exchange membrane fuel cells. The reported results provide technological solution to a high catalytic activity at a lower noble metal loading of the electrode catalysts.

The author claims that the choice of substrate and preparation method impacts the composition and morphology of the Pt-CeO_2 films. In particular, author demonstrated that a highly porous Pt-Ce-O mixed oxide can be obtained by means of magnetron sputtering onto carbon substrates. The factors influencing growth and composition of the Pt-CeO_2 deposits were systematically investigated.

The thesis starts with a brief introduction and concise description of the experimental techniques and equipment. That is being followed by the results that are partitioned into five sections.
In the Section 5.1, the author discusses composition of Pt-Ce-O mixed oxide on silicon wafer. In the Section 5.2, the growth of highly porous mixed oxide films on carbon nanotubes is demonstrated. In the same section, author offers several hypotheses on the causes of the high porosity of the mixed oxide; those are properly addressed in the following Sections 5.3-5.5.
Finally, the results are summarized. The summary provides important information required for the development of the next generation materials for fuel cells application.

The author has demonstrated ability to conduct a high-quality experimental work. He reports his results in clear, well-structured communication. The part of the reported results has been published in recognized journals.
Thereby, I state that in my opinion the presented dissertation fulfill the requirements for the doctoral degree. Therefore I recommend the dissertation committee to award Mgr. Mykhailo Vorokhta the title of Doctor of Philosophy (Ph.D.).

Regarding the content of the Thesis I have following questions arranged in the order of descending importance as follows.

1) Page 31. Table 5.1.1. The intensity ratios between the spectral components in Ce 3d spectrum, $f^0(Ce^{4+})/f^1(Ce^{4+})$ and $f^0(Ce^{4+})/f^2(Ce^{4+})$, depends on the amount of Pt dispersed in CeO_2. The observed phenomenon is elucidated by a substitution of some Ce^{4+} cations by Pt^{4+} on the page 36.

   The given explanation is not comprehensive.

2) Pages 36-37. Figure 5.1.5. The author suggests the model of Pt-CeO_2 deposit that contains ions of Ce^{4+}, Ce^{3+}, Pt^{4+}, O^{2-}, as well as oxygen vacancies. It is mentioned that this model explains reduction of cerium cations upon doping cerium dioxide with Pt ions.

   Since Pt^{4+} is in the same oxidation state as Ce^{4+}, the reason for the reduction of cerium cations and creation of oxygen vacancies in the mixed oxide is not obvious.

3) Page 47. Author suggests that Pt atoms segregate on the surface of the porous film and stay there in Pt^{2+} or metallic state.

   What is the mechanism of suggested Pt segregation? Is this a migration of an oxygen vacancy to the surface that leads to oxidation of Pt^{2+} to Pt^{4+} in the bulk during the mixed oxide growth?

4) Page 47. Author suggests that Ce^{3+} interacts strongly with Pt^{2+} cations forming Pt-O-Ce bonds on the surface of the reduced cerium oxide.

   It is not clear how these two ions interact and what is the resulting oxidation state of Pt and Ce in the mentioned "Pt-O-Ce" bond?

5) Page 28. "Minimizing X-ray exposure time at the fixed point on the sample was important to prevent the X-ray damage …"

   What was the result of the X-ray damage on the samples and how it was minimized?

6) Page 54. It is mentioned that the particles impinging the substrate during magnetron sputtering are mainly neutral Ce, O, and Pt atoms.

   It is hard to believe that atoms are not ionized under the deposition conditions.

7) Page 67. Silicon oxide shows partial reduction.

   How the reduction of silicon oxide was determined?

Less important comments:

1) Figure 2.2.2. Inconsistent labeling of the f^1 (Ce^{4+}) and f^2 (Ce^{4+}) features in Ce 3d spectrum with the rest of the spectra.
2) Figure 3.1.1. The black balls "A" are not explained.
3) Page 26. … Al $K\alpha_{1,2}$ anode… should be … Al $K\alpha_{1,2}$ line …
4) Page 42, line 4: reference to Fig. 5.1.5(a) is wrong. The text refers to Fig. 5.1.3(a).
5) Page 67, line 13: reference to Fig. 5.3.2 is wrong. The text refers to Fig. 5.4.2.
6) Page 70. Figure 5.5.2. The fitting of Ce 3d spectra is low quality.

Erlangen, 23.05. 2013

Mgr. Yaroslava Lykhach, PhD.