

Referee report on the doctoral thesis “Low Platinum Content Thin Film Catalysts for Hydrogen Proton Exchange Membrane Fuel Cells” by Mgr. Michal Václavů

The submitted doctoral thesis is a study of novel nanostructured Pt-CeO₂ and Pt-Sn-CeO₂ mixed oxides as fuel cell anode catalysts. The thin films are prepared by r.f. magnetron sputtering and demonstrate a high catalytic activity at a low noble metal loading.

The author claims that the high activity of the mixed oxide thin films is related to the presence of ionized platinum in the oxidation state 2⁺.

Moreover, the author prepared sputtered Pt-Co and Pt-Ni mixed alloy cathode catalysts. The factors influencing the mass activity of the sputtered bimetallic alloy catalysts were systematically investigated.

Finally, the performance of a fully functional fuel cell consisting of a Pt-CeO_x anode and a Pt-Co cathode is tested.

The thesis starts with an introduction about fuel cells. It is followed by a description of the experimental techniques and the corresponding equipment for fuel cell testing.

The results are partitioned into three big sections.

In chapter 3.1, the author discusses the composition of Pt-CeO₂ thin films sputtered on double walled carbon nanotubes deposited on a gas diffusion layer (GDL).

In chapter 3.2, the fuel cell performance of sputtered Pt-CeO₂ and Pt-Sn-CeO₂ mixed oxides as anode materials prepared on a bare gas diffusion layer is studied.

The investigated systems revealed a very high specific power with respect to a standard Pt-Ru powder catalyst as a reference anode. The high specific power of the mixed oxides is related to the very low Pt content in the system.

In chapter 3.3, by using a Pt-CeO_x coated nanoGDL as anode material with humidified hydrogen as fuel and oxygen as oxidant, the specific power of the system could be increased even further.

In Section 4.1 and 4.2, the stability of Pt-CeO_x mixed oxides and their interaction with hydrogen and water is studied under UHV conditions and atmospheric pressure. The Pt²⁺ cations present in the systems express a very high stability towards water and hydrogen under UHV conditions. In contrast, under fuel cell conditions at atmospheric pressure, the Pt²⁺ cations are partially reduced to the metallic state with hydrogen whereas they are rather stable while being exposed to water.

In Section 5, the stability and fuel cell performance of sputtered Pt-Co and Pt-Ni bimetallic alloys prepared on a nanoGDL as cathode materials were investigated. The results were compared with a commercially available cathode electrode which is mainly loaded with Pt.

In subsequent fuel cell tests it has been shown, that the prepared bimetallic samples maintain a mass activity which is twice as high if compared to the commercially available cathode electrode.

Finally, the results are briefly summarized. In addition, the summary provides a short outlook on the future research on fuel cell electrodes.

The author has demonstrated the ability to conduct an experimental work and communicate his results. The part of the reported results has been published in recognized journals.

Thereby, I state that in my opinion the presented dissertation fulfills the requirements for the doctoral degree. Therefore, I recommend the dissertation committee to award Mgr. Michal Václavů the title of Ph.D.

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

- 1) Section 3.1: Is the fuel cell performance of the sputtered Pt-CeO₂ thin films dependent on the electronic structure (semiconducting or metallic) of the DWCNTs?
- 2) Section 3.1: Why are the cerium cations in the Pt-CeO₂ thin film highly oxidized, when the working gas during sputtering only consists of Argon?
- 3) Section 3.1.: Where are the Pt²⁺ and Pt⁴⁺ cations stabilized?
- 4) Section 3.2: Fuel cell performance is measured for Pt-CeO₂/GDL, while XPS measurements are conducted on Pt-CeO₂/Si(100). What is the reason for using different substrates?
- 5) Section 4.2: What is the reason for the Pt-CeO₂ mixed oxides being stable with respect to the unstable CeO₂ reference sample? Why is the stoichiometric CeO₂ sample unstable?
- 6) In chapter 4.2, the author is investigating the effect of dry hydrogen with respect to humidified hydrogen on Pt-CeO_x model catalysts. Are these results comparable when the substrate is completely different? C-foil (humidified hydrogen) VS. Si-wafer (dry hydrogen)?

Less important comments:

1. Page 40: Figure 3.2.3 The left and right panel should be switched to fit the text and corresponding legend.
2. Page 47: Is the unfinished summary on purpose?
3. Page 64: "water (middle spectra in figure 4.2.1)" should be "water (bottom spectra in figure 4.2.1)"
4. Page 70: Picture in text without legend is the same as Fig. 3.3.1 on page 44. Please remove.
5. chapter 5: Missing description of Fig. 5.1 a) in the text. Please insert.
6. page 73: What is the binding energy of Co³⁺, as visible in Fig. 5.2? Please mention in text.
7. chapter 5: Why is Fig. 5.4 treated before Fig. 5.3?
8. page 81/83/92: Fig. 5.3, 5.5 and 5.9 should appear after their mentioning in the text.

Erlangen, 20.08. 2016



Armin Neitzel, PhD.