

## **Referee report on the doctoral thesis “Research and development of platinum-based cathode catalysts for proton exchange membrane fuel cells” by Ms. Xianxian Xie**

The submitted doctoral thesis is a summary of carefully conducted studies that address the composition-activity-stability relationship of various Pt based oxygen reduction reaction (ORR) electrocatalysts for application in proton-exchange membrane fuel cells (PEMFCs). The author identified stabilization effects of Au in bi-metallic PtAu and ternary PtNiAu alloy catalysts. On the other hand, too high Au concentrations lead to a loss of catalytic activity. Importantly, the author provides a new mechanistic picture of the stabilization and deactivation mechanisms. Furthermore, the author demonstrates that dissolution of CeO<sub>x</sub> in Pt-C-CeO<sub>x</sub> catalysts during electrochemical activation leads to catalyst structures with increased activity and stability compared to monometallic Pt reference catalysts. Finally, it should be emphasized that the studies were not only performed as idealized half-cell reactions, but the composition-activity-stability relationships were tested in PEMFC assemblies in a complementary manner, bridging the complexity gap between mechanistic studies in fundamental science and application.

The thesis begins with a general motivation for energy storage and focuses subsequently on fuel cells and specifically on PEMFCs, discussing the corresponding working principles, the current status and the resulting challenges. In particular, the need for suitable ORR catalysts is emphasized and challenges regarding activity and stability are discussed. The introduction is well-structured and has a clear central theme.

Subsequently, the experimental methods are listed and the corresponding working principles are explained in a comprehensible manner.

The chapter Results is divided into 3 subsections. The first subsection focuses on the composition-activity-stability relationship of bimetallic PtAu alloys with different compositions (Pt, PtAu5, PtAu10, PtAu20, and Au). The second subsection extends the complexity of the system to ternary alloy systems, specifically PtNi-Au alloys with varying Au concentrations (PtNi, PtNiAu3, PtNiAu7, PtNiAu15), keeping the PtNi ratio constant (1:1). The thesis is completed by a study on Pt-C-CeO<sub>x</sub> catalysts, which were activated by potential cycling, dissolving the ceria. This pretreatment leads to porous structures increasing the electrochemically active surface area (ECSA) and the stability of the catalyst compared to its conventional Pt system.

All samples were prepared by magnetron sputtering and systematically characterized using a variety of complementary analysis tools namely X-ray and synchrotron radiation photoelectron spectroscopy (XPS, and SRPES), X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), cyclic voltammetry (CV) and CO stripping. Catalytic activities of the ORR were determined using rotating disc electrodes. The stability of the systems was investigated in situ using online ICP-MS and tested in accelerated degradation tests (ADT) both as half-cell reactions and in PEMFC assemblies. The study on PtAu catalysts (Subsection 1) was also complemented by computational simulations (Monte Carlo (MC) and density functional theory (DFT)) providing a deeper mechanistic understanding.

The conclusions drawn from the experimental results in this thesis are adequate. The selection and use of the above-listed methods, as well as the corresponding interpretation of the data, prove the author's ability for creative scientific work at a very high level. This resulted in 2 first author publications in high-impact journals (ACS Appl. Mater. Interfaces and Adv. Mater. Interfaces). The author planned and carried out the research in cooperation with an international team and reported her results in a very clear way.

**Thereby, I recommend Ms. Xianxian Xie to be awarded the title PhD.**

**Questions:**

- 1) Section 3.1.5: A very interesting point in the data presented in Figure 3.10, which was not further discussed in the thesis, is the decreasing Au dissolution with increasing Au concentration in the alloy. I think the discussion of this point can further strengthen the mechanistic picture presented in the thesis. Can the author discuss possible contributions to this phenomenon and how the different contributions could be distinguished?
- 2) Section 3.1.3: In the description of Figure 3.6b it is written: "In addition, a small tail in the CO-stripping voltammogram of monometallic Pt is observed at about 0.71 V<sub>RHE</sub>, which is related to the lower coordinated Pt atoms according to the literature [94-97]. The corresponding tail becomes smaller for the PtAu5 sample and then vanishes for PtAu10 and PtAu20 samples which might indicate that Au atoms are preferably located at coordinatively-unsaturated sites [98-100]." I agree with the observation that the tail in the CO stripping peak is not observable for PtAu10. For PtAu20, however, I see a distinct broadening of the peak and the appearance of a shoulder at higher potentials. What is the origin of this contribution, if it is not assigned to low coordinated Pt adsorption sites?

**Comments and corrections:**

- The reaction arrow in equilibrium reactions must be  $\rightleftharpoons$  instead of the incorrectly used = sign. (page 3, 8, 11, 12, formula (1) – (12)).
- The author should indicate clearly which of the presented results were obtained by her and which results were provided by cooperation partners.
- Please indicate the primary and secondary degradation mechanism directly in Figure 1.8.

Erlangen, 05.04.2024

Dr. Olaf Brummel