RE: Habilitation thesis of Dr. Ivan Khalakhan

Dear habilitation committee,

This evaluation letter concerns the habilitation thesis of Mgr. Ivan Khalakhan PhD titled 'Platinum-based bimetallic cathode catalysts for proton-exchange membrane fuel cells'. In this habilitation work a new family of Pt based electrocatalyst materials prepared by magnetron sputtering is being evaluated for the use in PEMFCs. In the first part multiple ex-situ and in-situ/operando characterization techniques have been used to determine the electronic and morphological structure of the deposited bimetallic thin layers and to relate to their performance in both liquid half cells and PEMFC single cell devices. The second part describes the research performed on the similar bimetallic catalyst, but the focus is on evaluation of their stability following various accelerated stress tests designed to mimic the use of the materials under periodic load.

In the introduction the author goes in great depth explaining the need and the state of the art for PEMFC electrocatalyst research. Personal mobility as the most promising application for FC is mainly discussed, while to some extent marginalizing the future use in other sectors, such as stationary applications and power grid shaping, heavy duty transport, where in fact the technology is projected to be used most (1). There is one large problem with PEMFCs and the hydrogen cycle in general, which the author forgot to mention, is its low efficiency compared to electrochemical batteries, which precludes the widespread use in portable application, automotive industry, large scale grid storage and others (2). While the picture could be depicted rosy, I would expect a bit more critical view as this is important in order to properly direct future research. The author also discusses the reasons behind the strategies to increase the utilization and activity of the catalysts. The standard d-band theory is followed in length, nicely explaining the rationale of the d-band shifts and relation to the bonding energy of different reaction intermediates. However the author misses on certain details regarding the defects design and its relation to local strain, which leads to several misleading claims and misunderstanding in the thesis (e.g. jagged Pt nanowires activity origin). Mainly that the same strain effect and great increase in activity due to alloying can be in fact achieved with only a minimal fraction of alloying elements, just using local strains as a vehicle for d-band shifts (3). Which brings me to another critique and that is the combination of different characterization tools in the thesis. While the author tries to give an impression in Fig. 11 that those are the most important tools (indeed they are very important), he omits some other in-situ/operando tools developed decades ago and perfectly suited for the catalyst characterization. Those are for example the electrochemical tools such as CV, EIS, EQCM, SECM, CO desorption or XRD. The latter is mentioned in the thesis but in my opinion marginalized and unnecessary unutilized in the work. Finally the author very clearly states that in-situ/operando studies are needed to progress our understanding of the real device, it would be interesting to know more in detail what the author exactly means, what problems are in his opinion needed to solve and how. I think a broader perspective in this respect should be provided, for example regarding the triple phase boundary.

According to the author, the main motivation to use magnetron sputtering as a preparation method is to lower the Pt loading while keeping the catalyst preparation cost down. In the first part of the results the author is able to show that indeed magnetron sputtering can be effectively used for catalyst layer preparation. This by itself is a very nice finding and the given that the author shows this for various bimetallic systems only underlines the versatility of the technique. However, while the author suggests that magnetron sputtering is superior to other means of catalyst preparation (e.g. wet chemistry) any kind of analysis and comparison in this respect is missing. For example, is it really cheaper? Is the activity better in comparison to different types of low loading catalysts? Because of that, this section feels as a section of unfulfilled promises. For example the power obtained in P1 of 125 mW/cm^2 is a bit disappointing compared to later films (P3) which is getting closer to the standards in the field. But it is very difficult to judge as the metric is not unified and the comparison to work of others is not given. Interesting point for more discussion would also be the effect of dealloying on the measured activity and surface morphology/strain evolution (e.g. P3). It is well known that the dealloyed materials show reasonably good activities and this is why they are the closest for widespread commercialization. So the question arises about to what extent the enhancement is due to the alloying and to what extent to dealloying and could be critically assessed given the latest literature on the topic.

Nevertheless, I find the second part of the thesis devoted to the studies of the stability and degradation mechanism of a high quality providing an interesting insight into the degradation of the Pt based alloy electrocatalysts. In fact it is one of the first systematic studies looking into the degradation of these materials, combining findings from the Pt surfaces with the use of in-situ/operando characterization to extend the knowledge to the bimetallic systems. Particularly interesting findings are from the gas phase experiments, where the authors use gas phase reduction and oxidation to understand the changes in electronic structure and their relation to the degradation mechanism. The only critique I have for this section is that the author could compare his findings with the vast knowledge of degradation phenomena of nanoparticulate catalysts and put his research into a wider perspective.

In summary, this thesis successfully describes findings of important research into ORR bimetallic catalysts prepared by magnetron sputtering and their stability in a simulated PEMFC environment and it tackles fundamental questions about the interplay between different processes responsible for the degradation phenomena. The first part regarding the performance of these catalysts is missing a broad picture of this enormous field and where are the new materials in the landscape regarding the activity and longevity. Second part provides an interesting insight into the ageing phenomena of those materials and is in general of a high quality and original. The utilization of the in-situ/operando characterization techniques covers the broad range needed to properly describe the materials. While the author goes to great length discussing the need for the hydrogen economy, the thesis lacks a critical view of the field and its problems (e.g. difference between the idealized liquid environment and three phase boundary present in the actual PEMFC device) and ideas where the future research should be directed are given. Even though there are some issues to be discussed and the thesis could be improved, in overall it is sufficient for the habilitation for Dr. Ivan Khalakhan and I recommend it to be accepted. I have gone through the check of originality of the thesis done by the system Turnitin and it is clear that the thesis represents an original work with the only overlap with the existing literature written by the author.

Best regards,

Jakub Drnec, PhD

1. Energy Technology Perspectives 2020 [Internet]. [cited 2021 Oct 21]. Available from: https://www.iea.org/reports/energy-technology-perspectives-2020
2. Clerjon A, Perdu F. Matching intermittency and electricity storage characteristics through time scale analysis: an energy return on investment comparison. Energy Environ Sci. 2019;12(2):693–705.
3. Chattot R, Asset T, Bordet P, Drnec J, Dubau L, Maillard F. Beyond Strain and Ligand Effects: Microstrain-Induced Enhancement of the Oxygen Reduction Reaction Kinetics on Various PtNi/C Nanostructures. ACS Catal. 2017 Jan 6;7(1):398–408.