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Evaluation of the habilitation thesis of Dr. Ivan Khalakhan

„Platinum-based bimetallic cathode catalysts for proton-exchange membrane fuel cells“

1. *Essence and Importance of the thesis*

In last several decades, economic, environmental and social drivers have stimulated an intense transition from fossil fuel to renewables based economy in many countries. A representative example is Germany, where federal government has promised to switch to 100% renewable energies electricity by 2050. In this scenario, electrochemical energy conversion technologies like fuel cells and water electrolysis are considered to smooth out the variability of wind or solar electricity production. State of the art are technologies based on acidic electrolytes, which indeed have reached commercialization already. These technologies, however, come with a high price tag that is amongst others due to the use of expensive and rare noble metals as electrocatalysts able to withstand aggressive corrosive environment of acidic electrolytes and corrosive potentials. The proton-exchange membrane fuel cell (PEMFC) technology, which is the core of the discussion in the habilitation thesis, is exactly at this stage at the moment, i.e. despite being utilized already in small fleets of passenger cars and trucks, the use of Pt-based materials renders them too expensive for a large scale commercialization. Therefore, major research efforts over the last decade have been attempting to improve the efficiency of energy conversion by i) enhancing the catalyst activity, ii) reducing the amount of Pt catalyst or even replacing Pt, iii) increasing the stability of the catalyst, or iv) enhancing the performance of the catalyst in the electrode layer. The current thesis focuses on Pt-bimetallic catalysts and respective electrode structures and basically covers all above aspects of the central international research agenda in fuel cell technology. Some Pt-bimetallic catalysts have previously shown to enhance the specific performance by a factor of more than 10 compared to

standard pure Pt, which is equivalent of being able to reduce noble metal usage by an order of magnitude at same power density. Moreover, specifically designed structures of Pt-alloy catalysts, i.e. core-shell type materials, have shown that the Pt amount can be significantly further reduced, cases of even up to 50% and more have been reported. However, instability particularly of the alloying elements has been a key challenge for such catalysts, with de-alloying as a crucial aspect that might also lead to further degradation processes. In addition, a particular challenge has been for Pt-alloy catalyst to transfer the superior fundamental specific performance to the electrode scale, where further complex factors come into play. Overall, despite significant advances in the field over the last decade, the fundamental understanding is still lacking to a certain degree, hindering the knowledge-based development of improved catalysts and electrodes. Considering the societal challenges of climate change and the energy transition, as well as the scientific-technical challenges of renewable energy conversion in fuel cells, the thesis covers both, extremely timely and highly important topics.

2. *Scientific content of the thesis*

Dr. Khalakhan focuses in his thesis on two major scientific challenges of electrocatalysis of the oxygen reduction reaction in PEMFCs, activity and stability. In a first part he utilizes physical vapor deposition by magnetron sputtering for the preparation of thin catalyst films of Pt and alloying materials. The advantage of this approach is that it offers quite some flexibility in composition over the deposition parameters, it is precise and environmentally friendly as it circumvents the usage of surfactants and/or hazardous solutions, and most importantly it can be potentially scaled for the production of large area electrodes. He demonstrates the applicability of this approach via Pt-Co cathode catalysts with very good performance at low overall loading. In order to achieve more control over processing parameters, he continues to investigate structural parameters of the thin-films in more detail, complemented by theoretical investigations of the effect of catalytic enhancement by the alloying element. The power of the magnetron sputtering approach was shown especially in the in-depth study of Pt-Ni films with different composition ranging from 25 to 100%; a clear trend in specific activity could be identified and related to structure and composition. Further studies towards activity enhancement were performed with Y as the alloying element, which had previously been identified as the to date best promoter of ORR. The superior performance of PtY could be verified also with magnetron sputtering as preparation, both for thin-films as well as electrodes, and utilizing in-situ characterization and theoretical calculations the effect was explained. While all the catalysts of this first section were already known to a certain extent, the value is clearly in the application of a novel process to prepare thin films and even electrodes based on the materials. So besides the additional scientific insights gained into their activity-structure relationships, magnetron sputtering was

confirmed as an exciting technical approach with many advantages over conventional strategies. In the second part of the work, Dr. Khalakhan focuses on the stability of Pt-alloy catalyst films and its characterization via powerful in-situ/operando methods. In particular, using accelerated aging tests and electrochemical atom force microscopy he investigates the morphological changes in the relevant potential ranges of fuel cell cathode operation (including potential excursions due to start/stop events). He reveals the drastic destruction of alloy catalyst surface caused by dissolution at potentials above 1,0V, as well as the coarsening and crack formation that occurs as a direct consequence. EC-AFM also enabled him to quantify coarsening kinetics of pure Pt films during electrochemical degradation. In continuation of these efforts, a special electrochemical cell for small angle X-ray scattering was developed, which enabled the detailed in-situ study of Pt and Pt-Ni degradation within electrode structures. Already Pt by itself dissolves and re-deposits upon potential excursions at highly positive potentials, forming a thinner but extended structure. Adding Ni to the system leads to additional de-alloying, which can thanks to the in-situ methods clearly be correlated to different upper potential limits of the accelerated aging tests. Also in this second part on stability some of the effects have been already hypothesized in literature, yet the thesis clearly extends this knowledge by high-quality in-situ data and discussions on the time-evolution of bimetallic alloys under simulated PEMFC operating conditions that have not been accessible before.

3. *Content aspects of the thesis*

Based on the presented thesis and especially his main publications, it is obvious that Dr. Khalakhan is very methodological in both planning and carrying out his experimental work, as well as very systematic in working with literature. As follows from the literature overview part, he knows the most important papers published on the topics related to PEM fuel cells and electrocatalysis and can selectively pick up the main messages for further analysis. He is able to identify challenges, to find means to address such challenges and to extract important findings from the obtained experimental results. This ability is especially visible in the discussion parts of the main individual research papers in the appendix. The presented scientific results and discussion are on a very high scientific level, particularly the extensive use of complex in-situ and operando methods is impressive. This is reflected already in the scientific papers published by Dr. Khalakhan. Overall, 13 papers that are part of the cumulative thesis were published in prestigious international journals like J. Phys. Chem. C, Electrochimica Acta, Applied Surface Science, etc. with him as first (7) or essential co-author (6). All of these papers present important results that are interesting by themselves, yet dispersed in different journals like pieces of a puzzle and now brought together in this thesis. Several more manuscripts that were published by him over the same timeframe on adjacent topics did not find its way in the thesis, which shows that Dr. Khalakhan can clearly focus his works in a scientific

meaningful way. Two aspects could have been however addressed in more detail. Firstly, Dr. Khalakhan could have more explicitly highlighted his contributions to the individual manuscripts, and focus in the results section more on his own achievements within the individual manuscripts rather than summarizing the outcome of the whole works. While his contributions are rather clear in his first author papers, it is less in his works as co-author. Independent of this, the storyline could have been more individual, which is my second point. An overarching critical analysis of the works is missing, and the personal conclusion and outlook of the combined body of work in the very end of the main part falls rather short and general. Nevertheless, it is without doubt that the individual works towards the habilitation are technically and scientifically excellent.

4. *Form of the thesis*

The cumulative thesis compiles an introduction to the background and the state-of-the-art of PEM fuel cells and catalysis of oxygen reduction, i.e. the more relevant of the two electrode reactions. In the main part the most important results of Dr. Khalakhan's individual works over the last years is presented, which is in the end summarized in a short section. Attached one can find a total of 13 manuscripts with him as the main author that are all published in international, peer-reviewed journals. The thesis presents a clear motivation and literature overview, the required experimental procedures and the main results with discussions including also general conclusions can be found in the individual papers. Despite the complexity and broad nature of this topic, it is quite straightforward to read. The amount of figures and tables is well balanced in the papers, only in the results section there could have been more visually appealing parts summarizing the main achievements. The quality of the figures, including those from literature and collaborative works, and the overall layout are at high level and show that, besides the scientific content, Dr. Khalakhan put a lot of efforts to find a most optimal way to deliver his work to the readers. The thesis is written in very good English, which is a natural outcome of the international scientific environment he has been part. I have also 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 minimum overlap with the existing literature, except for the works that have been published by the author himself.

5. *Conclusion*

The thesis by Dr. Khalakhan comprises an important contribution to the fuel cell and electrocatalysis communities and thus our sustainable energy oriented society. The scientific insights into stability of Pt-alloy electrocatalysts and the overall performance of magnetron sputtered electrodes with low Pt amount

has been a highly valuable contribution. The quality of the scientific results presented in this work is excellent, so that I recommend the University to accept the thesis for habilitation.

Sincerely,

Prof. Karl J.J. Mayrhofer