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PHYSIQUE & CHIMIE | NANOSCIENCES - PHOTONIQUE – SCIENCES & ANALYSE DES MATERIAUX

Report on the PhD thesis manuscript submitted by Mgr. Ivan KHALAKHAN

Mgr. Ivan Khalakhan submitted a PhD thesis, the title of which is: “Preparation and Characterization of Novel Oxide Catalysts for Fuel Cell Applications”. This PhD thesis is concerned with topics of high scientific interest from both a fundamental point of view and potential applications in the Polymer Electrolyte Membrane Fuel Cell (PEMFC) domain. Actually, in PEMFC, platinum based catalysts are used for both reactions on anode and cathode sides and this leads to quite expensive catalysts. Search for reducing the cost involves at the same time maximizing the surface area, minimizing the catalyst amount and developing novel catalysts having the right properties. Ivan Khalakhan PhD work comes within this scope.

The purpose of this thesis is thus the study of the physico chemical properties, mainly morphology and stoichiometry, of novel oxide catalysts prepared by magnetron sputtering deposition for fuel cell applications.

In a first part, Ivan Khalakhan gives some insight on the basic principles of PEMFC as well as a state of the art on the existing Pt-based catalysts and on the supports which are mainly used. This introduction is rather short but provides good basis on the subject thanks to the references.

In a second part of his manuscript Ivan Khalakhan presents the different experimental techniques he used for his work as well for preparation of the samples and for their characterizations. Techniques are presented in the right way, without too many details which could be found elsewhere, but providing what is necessary to know for understanding the results.

The major part of the thesis describes the results Ivan Khalakhan obtained on novel catalysts based on cerium oxide thin films. The influence of different preparation parameters is fully described through results obtained on both morphological and chemical properties of the catalysts. Characterizations of the morphology of the samples by SEM and AFM and of their composition mainly by XPS are systematically done for each deposition conditions. It is clearly shown that morphology and stoichiometry of the catalyst film vary with deposition parameters such as the deposition angle, the film thickness, the deposition rate… allowing to tune catalyst film specific area and stoichiometry by simply changing the deposition parameters.

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In particular very porous structures can be obtained on carbon substrates thanks to simultaneous deposit growth and oxygen plasma etching of carbon during the sputtering process. These catalysts are demonstrated as being very interesting in fuel cell tests with a maximum specific power much higher than the one obtained for commercial classical catalysts. In addition Ivan Khalakhan demonstrates that this fact is not only related to the high surface area of the prepared catalyst film but also to the formation of fully cationic platinum within the oxide film.

In order to go further in the understanding of the role of the platinum properties on performances in fuel cell tests, platinum oxide films were also investigated. They were prepared by magnetron sputtering under oxygen on different substrates. In addition, the role of H_2 exposure on the platinum oxide film properties was also studied in the case of platinum oxide films deposited on naturally oxidized Si(111) substrate. It was shown that the film which initially presented a very low surface roughness is cracked after exposure to hydrogen. In this case, even if platinum is totally reduced as shown in XPS experiments, the very high roughness of the reduced film leads to high performance in fuel cell tests. This method may be a new way of preparing platinum catalyst with very high surface area interesting as a catalyst for PEM fuel cell due to the possible low platinum loading.

In conclusion, I think that Ivan Khalakhan PhD work is very interesting in the sense it proposes new ways for developing platinum based catalysts having high performance in fuel cell tests but lower platinum loading.

This PhD work is well written and results are presented in a logic and rigorous manner. In addition, all the results Ivan Khalakhan has obtained led to eleven already published papers referenced in the Web of Science.

In conclusion I consider that this work meets, without any doubt, the requirements for a PhD thesis.

Dijon, 21/05/2013

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