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Report of the manuscript "**Electron Microscopy and Spectroscopy Study of Nanostructured Thin Film Catalysts for Micro-fuel Cell Application**" proposed by Jaroslava LAVKOVA in order to obtain the joint PhD diploma of UNIVERSITE DE BOURGOGNE and CHARLES UNIVERSITY.

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The manuscript presented by Jaroslava Lavkovà is an extensive investigation of the magnetron sputtering of ceria thin films on various supports with the aim to optimize the porous character which should be ideal for the desired catalytic activity. The investigated topic concerns catalysts of the type: Proton Exchange Membrane Fuel Cell (PEMFC). It falls in the search for new energy sources with the announced advantages of high efficiency, absence of moving parts, no noise pollution, no emissions of environmental pollutants, and with the only exhaust as pure water. The aim of the PhD work is to overcome the important advantage which is still hindering the wide development of the PEMFCs, their high price by decreasing the Pt load.

The work proposes to bring about new solutions to optimize the use of the most efficient metal catalyst 'Pt' through a detailed structural and spectroscopic analysis, of first the ceria as support, and next its interaction with the metal. It is carried out by studying the morphology, structure and composition of the thin films of ceria which are generated during the magnetron sputtering on silicon substrates which are either covered by pure carbon, or nitrogenated carbon fimls. It is shown that the magnetron plasma strongly etches the carbon which may be partially protected by the depositing ceria, this leads to the formation of a porous catalytic support where the largest surface areas are obtained inside nitrogenated carbon (50-100% N) support. High resolution transmission electron microscopy (TEM) is extensively used in order to determine the local structure of the nanocrystals and the local composition is analyzed by EDS and EELS, this is complemented by the more global and surface sensitive XPS.

After the detailed scrutiny of the catalyst ceria support, the porous materials were used in order to analyze the relationship with platinum which is introduced during a co-deposition using the same magnetron sputtering technique. For fixing the amount of platinum in the catalyst, the author has positioned one to three wires of the metal on the ceria support to be sputtered. It appears that the result of the co-sputtering is highly complex, as it leads to the formation of various phases. Indeed, for the lowest Pt concentrations, a reaction between Pt, Cerium and

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oxygen is pointed out with the formation of alloys and oxides, whereas for the highest concentration (3 wires), Pt nanoparticles of small sizes are reported.

Finally, the developed method is used to modify a commercial gas diffusion layer (GDL) by co-sputtering of Pt (1 wire) and 100 nm thick CNx50% film, it shown that the differences between the nanoGDL coated by CNx50% film before and after the Pt-CeOx layer deposition are considerable. Therefore, this work demonstrated that the deposition of Pt-CeOx catalyst layer, along with the simultaneous carbon etching by oxygen plasma, leads to the porous structure with a highly increased surface area ideal for the desired catalytic activity.

The manuscript is clearly written and divided into three chapters, where chapter I introduces the topic through an extensive bibliographic analysis of the fuel cells, thus also justifying the investigation of platinum which is presented as the most active catalyst for the targeted application. Chapter II presents the tools used during the PhD research work, they cover many techniques of electron microscopy, going from the sample preparation through the use of a Focused Ion beam machine to imaging with the conventional, high resolution and STEM modes. Extensive high resolution imaging has been applied to identify the lattice distances and help to segregate between nanocrystals. The analytical methods of TEM EDS and EELS, which have been applied, are also presented, this is done along with larger scale observation using scanning electron microscopy. The XPS technique is also described in this chapter. Very importantly, the PhD candidate shows clearly in this chapter that she has mastered all these techniques in order to carry out a detailed characterization of the materials she had to optimize throughout a search of the most adequate deposition conditions which are also described in this chapter.

Chapter III, is the largest piece of work, it is a detailed account of the whole experimental process which has taken place along the PhD work. In this part, Jaloslava Lavkovà, clearly shows here contribution to the topic of developing a Ceria-Pt catalyst material for the next generation of Fuel cell materials and, as such, I am highly supporting her for the defense of her work with the aim to obtain the PhD degree from l'Université de Bourgogne and Charles University.

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