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Evaluation Report on the Habilitation Dissertation Submitted by Dr. Ivan KHALAKHAN

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

Our unsustainable consumption of fossil energy resources is one of the most conspicuous acts of anthropogenic impact on global warming and its environmental outcomes. If the European Union's policy on the green deal shows the road ahead, Dr. I. Khalakhan dissertation provides key information on the hydrogen fuel cell vehicle (HFCV). Although Toyota (with Mirai) and other manufacturers are following suit, European ones are progressing very timidly. Indeed, as Dr. I. Khalakhan describes it so well, hydrogen fuel cells have the advantage of providing energy, heat, and no noise pollution, since the electrical energy is obtained by direct conversion of the chemical energy contained in the H-H bond. The only product released by the vehicle is water, which avoids all the pollutants from fossil sources such as COx, NOx and SOx.

Nevertheless, the core of a fuel cell, described in this dissertation, requires a membrane which is expensive, electrode materials which are essentially composed of either precious metals (PGMs) or critical raw materials (CRMs). Two strategies are to be adopted:

- either to replace the critical materials (CRMs) and the precious ones (PGMs)
- or to reduce their content, while keeping constant or improving electrocatalytic performance, through preparing innovative electrode materials.

Dr. I. Khalakhan describes the challenges and the key points of the second strategy which are rather in the cathode compartment where occurs the reaction of reduction of air or oxygen (ORR): the development of bimetallic catalysts based on Pt (Pt-M, where M = Co, Ni, Cu...) to reduce the metal loading of the precious element (Pt). Further progress in decreasing the cathode loading must be made, even though this has decreased considerably over the last ten years, since the Pt content is the primary approach for reducing the PEMFC costs (in short term, *i.e.*, by 2025, the total Pt content in a PEMFC should decrease by almost three times its current content). Although the opponent/reader understands the scientific approach of the applicant, he would have liked him to mention the ethical problems of using the cobalt element (extracted by children in some countries in war); moreover, the EU considers Co as a CRM.

The dissertation of Dr. I. Khalakhan, in the framework of his Habilitation, focuses on the preparation of this cathode material, the comprehension of the mechanisms of its degradation and thus those of its stability/durability under severe conditions of a PEMFC. He proposes a synthesis method that can be transposed to research and development (*i.e.*, on an industrial scale). As a laboratory investigation cannot be carried out at the same number of cyclings as one would like to see a cathode in a vehicle (*ca.* 5,000 - 80,000 operating hours), the impetus conducted studies of 2,000 cyclings where the behavior of the cathode could be extrapolated and transferred. This consists of accelerated aging tests (AST) under operating conditions as close as possible to reality. It is also a question of developing stable/durable bimetallic catalysts by setting them up in the 0.8 - 1.5 V vs RHE potential range, in an acidic environment (with M = Ni, Co...). If it can be considered that H2 oxidation (HOR) occurs at low potential without major corrosion problems and with a reasonable Pt loading, the whole PEMFC paradigm is focused on the ORR catalyst. Indeed, it is necessary to drastically decrease the noble metal content of the cathode, to increase, if possible, its activity around 1 V vs RHE without dissolution/detachment of Pt, nor dissolution of the co-catalyst (M = Ni, Co, Cu...)

In building a strategy to find a viable performance solution of a PEMFC, Dr. I. Khalakhan addresses approaches suggested by several research teams, *i.e.*, the fabrication of PGM-free or shape-controlled Pt cathodes (nanowires, nanotubes, nanorods, hollows...). Notwithstanding, Dr. I. Khalakhan moderates these approaches which, although lead to better Pt utilization efficiency, they are currently complex and expensive fabrication processes at the research & development scale.

After having written a consistent state-of-the-art introduction on the ORR catalysts, Dr. I. Khalakhan focused the main part of his habilitation dissertation on the development of a bimetallic material composed of Pt and Ni. He chose to fabricate it by Magnetron Sputtering, a method that can be transposed to Research & Development. The investigations carried out, described, and commented, result from 13 publications of which he is often the main author (or first author).

I note that if the input of the Turnitin system has resulted in a high percentage of coincidences of terms, this is not expressed in terms of plagiarism, but rather it is the result of an editing from these 13 peer-reviewed articles already published in very prestigious journals of the discipline related to PEMFCs. Thereby, the Turnitin report has not shown any serious scientific misconduct regarding copying.

The studies undertaken by Dr. I. Khalakhan focused on understanding the degradation mechanisms of this cathode under severe operating conditions. To achieve this objective, it was necessary to implement new techniques involving in situ/operando electrochemical/spectroscopic measurements (sometimes by coupling and/or associated with modeling), to investigate the ageing process of the electrode. This has required many local collaborations at Charles University, and especially external ones illustrated by a mobility of Dr. I. Khalakhan (Spain, Austria, Sweden, Germany, Italy...).

The work of Dr. I. Khalakhan is well done and allows to elucidate the PtNi material ageing in the ORR of a PEMFC, which proceeds mechanistically by a first step of coalescence of the particles followed by an Oswald ripening, which fatally leads to a loss of the catalytic surface (ECSA) and as consequence, to its activity.

Nevertheless, I am wondering about the content of the article P-13 in which the material was exposed to a temperature of 523 K to simulate its ageing, supposedly under reducing (H_2) and oxidizing (O_2) conditions. Why was this experiment carried out without any applied potential? Does the impetus think that under potential (1 - 1.5 V/RHE) this would have influenced the same particle coarsening (coalescence/Oswald ripening)?

Based on my evaluation, the dissertation of Dr. I. Khalakhan who co-authored 87 peer-reviewed articles according to Web of Science, meets all the requirements for a Habilitation Thesis.

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Professor K. Boniface KOKOH