DISSERTATION INFORMATION

Title: **SYNTHESIS AND CHARACTERIZATION OF M-DOPED TIO_2 (M=W, Ir) MATERIALS AS SUPPORTS FOR PLATINUM NANOPARTICLES TO IMPROVE CATALYTIC ACTIVITY AND DURABILITY IN FUEL CELLS**

Major: **Chemical Engineering**

Major code: **62520301**

PhD student: **Tai Thien Huynh**

Advisors: **1. Assoc.Prof. Dr. Van Thi Thanh Ho**

2. Dr. Son Truong Nguyen

University: **University of Technology, Vietnam National University – Ho Chi Minh City**

Contributions of this dissertation:

This dissertation has discovered and designed the novel M-doped TiO_2 (M = W, Ir) nanostructured support with novel catalytic functionality for Pt used as advanced nanoelectrocatalyst for fuel cells. The novel M-doped TiO_2 (M = W, Ir) supports exhibited good properties that not only physically separate the catalytic particles and decrease their agglomeration rate but also are proven specific catalytic properties. More specifically, this approach can solve the above main issues of catalyst for PEMFC and DMFC such as the carbon corrosions, the slow rate of the oxygen reduction reaction and instability of Pt on the cathode side, the key factors limiting its wide application. The properties of new catalyst supports were well characterized by many cutting edge techniques such as XRD, BET, TEM, HR-TEM, SEM, EDX, XRF, XPS, and electrochemical measurements. The contributions of this dissertation related to the objectives are listed below:

- The $Ti_{0.7}W_{0.3}O_2$ support was synthesized using a single-step solvothermal process, at low temperature as a low energy consuming fabrication technique that did not employ a surfactant or stabilizer. The relatively uniform distribution Pt on $Ti_{0.7}W_{0.3}O_2$ with a diameter of approximately 3 nm was obtained via the rapid and facile microwave-assisted polyol route. The cyclic voltammetry results indicated that the 20 wt. % $Pt/Ti_{0.7}W_{0.3}O_2$ catalyst was a promising catalyst toward MOR. For instance, the onset potential of 20 wt. % $Pt/Ti_{0.7}W_{0.3}O_2$ catalyst was more negative than that of the 20 wt. % Pt/C, which suggested the better methanol oxidation of the 20 wt. % $Pt/Ti_{0.7}W_{0.3}O_2$ catalyst. The I_f/I_b value of 20 wt. % $Pt/Ti_{0.7}W_{0.3}O_2$ catalyst was found to be ~2.33 indicating the high tolerance possibility with carbonaceous species of the 20 wt. % $Pt/Ti_{0.7}W_{0.3}O_2$ catalyst.

- For the first time, $Ti_{0.7}Ir_{0.3}O_2$ was prepared by means of a one-pot hydrothermal route as a support for Pt nanocatalysts. The homogeneous distribution of Pt nanoparticles over $Ti_{0.7}Ir_{0.3}O_2$

NRs' surface could be achieved by using a facile chemical reduction method. The large electrochemically active surface area (ECSA) was observed for 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NRs catalyst (~81.45 $m^2.g^{-1}Pt$). More importantly, after loading 2000 cycles, there was only a minor decrease in ECSA to be observed, suggesting the high durability of $Ti_{0.7}Ir_{0.3}O_2$ NRs supports. Regarding the catalytic activity for ORR, the large onset potential (~1.02 V) was found for 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NRs catalyst, which was higher compared to that of 20 wt. % Pt/C (E-TEK) (~0.94 V). These results suggested that 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NRs catalyst could be a prospective candidate for replacing the 20 wt. % Pt/C catalyst in PEMFC.

- Additionally, we introduce the Pt anchored on the $Ti_{0.7}Ir_{0.3}O_2$ NPs as a robust electrocatalyst toward MOR. The ECSA of the 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NPs catalyst was ~96.89 $m^2.g^{-1}Pt$. For MOR, the 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NPs catalyst possessed the high methanol oxidation current density (~21.69 $mA.cm^{-2}$) and the I_f/I_b ratio (~1.72) versus the 20 wt. % Pt/C catalyst. Furthermore, after the 2000-cycling test, the 20 wt. % Pt/$Ti_{0.7}Ir_{0.3}O_2$ NPs catalyst showed the decay of the methanol electro-oxidation current density to be around 8.34%, which was ~2.8-time lower than that of the 20 wt. % Pt/C (E-TEK). We also demonstrated that the electronic transmission from $Ti_{0.7}Ir_{0.3}O_2$ to Pt nanocatalyst leading to the modified surface electronic structure of Pt which could interpret for the unique characterization of $Ti_{0.7}Ir_{0.3}O_2$ supported Pt.

- Furthermore, the novel $Ti_{0.9}Ir_{0.1}O_2$ NPs with a low doping iridium concentration possessed the 10^5-fold enhanced electric conductivity compared to undoped TiO_2. It is worth noting that the 20 wt. % Pt/$Ti_{0.9}Ir_{0.1}O_2$ catalyst possessed the higher methanol oxidation current density, the lower onset potential as well as the higher I_f/I_b ratio in comparison with the 20 wt. % Pt/C (E-TEK) catalyst. The chronoamperometry results indicated the superior durability of the 20 wt. % Pt/$Ti_{0.9}Ir_{0.1}O_2$ compared to that of the 20 wt. % Pt/C (E-TEK) catalysts. The research orientation of lowering the amount of dopants in support materials offered in this work also creates a new economic trend for fabricating other materials that can apply in several fields such as solar cells, biosensors, and photocatalysts.

Advisors **PhD student**

Assoc.Prof. Van Thi Thanh Ho Dr. Son Truong Nguyen Tai Thien Huynh