VIET NAM NATIONAL UNIVERSITY - HCMC
HO CHI MINH CITY UNIVERSITY OF TECHNOLOGY

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DISSERTATION INFORMATION

Title:	**Study on methanol oxidation ability of PtRuX (X = Fe, Co, Ni) materials on carbon - carbon nanotubes composite substrate for application in fuel cells.**
Major:	**Engineering Physics** Major code: **9520401**
PhD candidate:	**Dang Long Quan**
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Major Contributions of This Dissertation

Developing new energy technologies is one of the urgent issues that must be addressed to protect the environment. Among them, direct methanol fuel cell (DMFC) are one of the promising candidates because of their compact size, easy production and storage of methanol (CH_3OH), high energy density, and low-temperature operation. However, the commercialization of DMFC remains a challenge due to several barriers. Specifically, carbon monoxide (CO) poisoning at the anode surface causes the cell performance to decrease gradually over time, and platinum (Pt) used as a catalyst at the electrode is very expensive. In this thesis, the PtRuX (X = Fe, Co, Ni)/C-MWCNTs catalysts have been fabricated and studied both experimentally and theoretically to find the most suitable catalyst for use in the anode electrode of DMFC that can partially overcome the above two disadvantages.

In our experimental studies, the mass ratio of carbon Vulcan to multi-walled carbon nanotubes (C:MWCNTs) in the composite support was first investigated to find the most optimized ratio. The mass percentage of C:MWCNTs in the composite support was changed respectively: 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, and 0:100. The survey results showed that the catalyst with the mass ratio of C:MWCNTs = 70:30 had the highest methanol oxidation capacity and the smallest electron transfer resistance. Therefore, the composite support with this mass ratio was used for subsequent studies. Next, the PtRuX (X

= Fe, Co, Ni)/C-MWCNTs catalysts (mass ratio C:MWCNTs = 70:30) were fabricated and investigated to find the most effective third metal (Fe/Co/Ni) substitutions. With the largest methanol oxidation capacity and the least electron transfer resistance, the PtRuCo/C-MWCNTs catalyst was proposed for use in methanol fuel cell electrodes. Finally, to optimize the metal ratio in the PtRuCo alloy, the $Pt_1Ru_1Co_y$ (y = 0, 0.5, 1, 2, 3, 4)/C-MWCNTs catalysts (mass ratio C:MWCNTs = 70:30) were synthesized and studied. The results showed that the catalyst with the atomic ratio Pt:Ru:Co = 1:1:2 was the optimal choice. Thus, $Pt_1Ru_1Co_2/C_{70}MWCNTs_{30}$ catalyst is best for the DMFC anode.

In our theoretical study, density functional theory (DFT) was used to calculate and investigate $PtRuFe_3$/C-MWCNTs and $PtRuCo_3$/C-MWCNTs catalysts. We chose these two catalysts because our experimental work showed that, among the studied catalysts, the first one has the best resistance to CO poisoning. Meanwhile, the second one exhibited the highest methanol oxidation reaction activity. The numerical results showed that the CO adsorption strength on the $PtRuCo_3$/C-MWCNTs was higher than on the $PtRuFe_3$/C-MWCNTs. This result agreed with our experimental study that the anti-CO poisoning of $PtRuFe_3$/C-MWCNTs was higher than that of $PtRuCo_3$/C-MWCNTs. Notably, we clarified the methanol oxidation mechanisms on the surfaces of the catalysts. Gibbs free energy calculations showed that the most favorable methanol oxidation pathway for both supports was: $CH_3OH \rightarrow CH_3OH^* \rightarrow CH_2OH^* \rightarrow CH_2O^*/CHOH^* \rightarrow CHO^* \rightarrow CHOOH^* \rightarrow CHOO^*/COOH^* \rightarrow CO_2^*$, which doesn't go through the formation of CO* on the catalysts' surface.

Advisors **PhD candidate**

Le Huu Phuoc **Do Ngoc Son** **Dang Long Quan**