Electrodeposited Pt Catalyst on Zirconium-based Metal–organic Frameworks Modified Carbon Nanotubes to Enhance Catalyst Efficiency for Direct Alcohol Fuel Cells

Panawut Audthangkhai[1,2], Surin Saipanya[1,2,3], Burapat Inceesungvorn[1,2,3], Satita Sudrungruang[1,2], Suwaphid Themsirimongkon[1,2,4], Napapha Promsawan[1,2], Jaroon Jakmunee[1,3] and Paralee Waenkaew[1,2,3*]

[1]*Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand*

[2]*Laboratory of Vantage Electromaterials (LOVEs), Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand*

[3]*Materials Science Research Center, Chiang Mai University, Chiang Mai, 50200, Thailand*

[4]*Office of Research Administration, Chiang Mai University, Chiang Mai, 50200, Thailand*

[*]*Corresponding author's e-mail address: paralee.w@cmu.ac.th*

ABSTRACT

Fuel cells are a promising clean energy technology, with direct alcohol fuel cells (DAFCs) offering notable advantages such as high energy density, low operating temperature, and simple fuel handling. However, their performance is often limited by sluggish alcohol oxidation kinetics and CO poisoning. In this study, Zirconium-based Metal-organic Frameworks modified carbon nanotubes (Zr-MOFs/CNT) were employed as an advanced support material to enhance the dispersion, stability, and CO tolerance of Pt catalysts. Pt nanoparticles were electrodeposited onto carbon nanotubes (CNT) supports containing varying Zr-MOFs loadings (1, 5, 10, and 20 wt%) to enhance catalyst efficiency. Electrochemical performance was studied by the cyclic voltammetry (CV) technique for the electro-oxidation of various alcohols, including methanol, ethanol, *n*-propanol, *n*-butanol, ethylene glycol, and glycerol. The optimized Pt/10 wt% Zr-MOFs/CNT catalyst has higher current densities compared to Pt/CNT, with methanol and ethanol oxidation currents increasing nearly threefold, and notable improvements were also observed for polyols such as ethylene glycol and glycerol. These enhancements are attributed to improved Pt active surface area and the synergistic effect of Zr-MOFs, which mitigates CO poisoning and stabilizes the catalyst. These findings highlight that Zr-MOFs/CNT composites provide a synergistic effect with Pt, offering improved alcohol oxidation kinetics and CO tolerance. Overall, Pt/10 wt% Zr-MOFs/CNT emerges as a highly efficient and stable catalyst, underscoring their potential for advancing the DAFCs.

INTRODUCTION

Direct alcohol fuel cells (DAFCs) are promising clean-energy technologies due to their high energy density and low operating temperature. However, their performance is limited by sluggish alcohol oxidation kinetics and CO poisoning of Pt catalysts, leading to reduced catalytic activity and long-term stability.

Carbon materials are widely used as catalyst supports because of their high electrical conductivity, low density, and chemical stability. Among them, CNT offer superior advantages, including large surface area, excellent electron transport, and strong structural integrity, which promote improved Pt dispersion and enhanced catalytic performance.

Zirconium-based Metal-organic Frameworks (Zr-MOFs), particularly UiO-66(Zr), possess high surface area, excellent chemical stability, and tunable porosity. When integrated with CNT, Zr-MOFs introduce additional active sites and improve CO tolerance, forming an effective hybrid support for advanced Pt-based catalysts in DAFC applications.

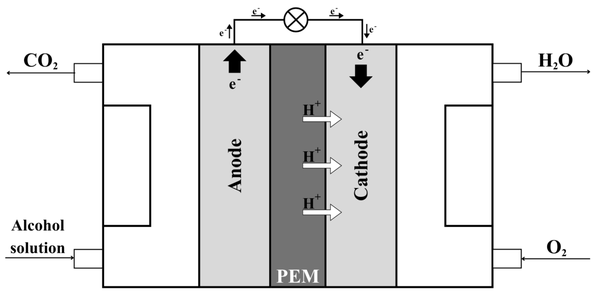


Fig. 1. Schematic diagram of a direct alcohol fuel cell

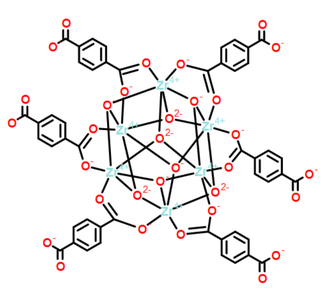


Fig. 2. Structure of Zr-MOFs

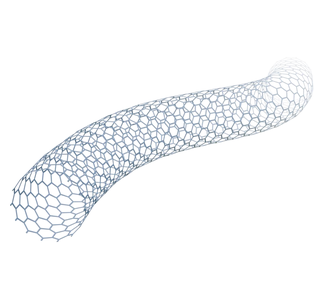
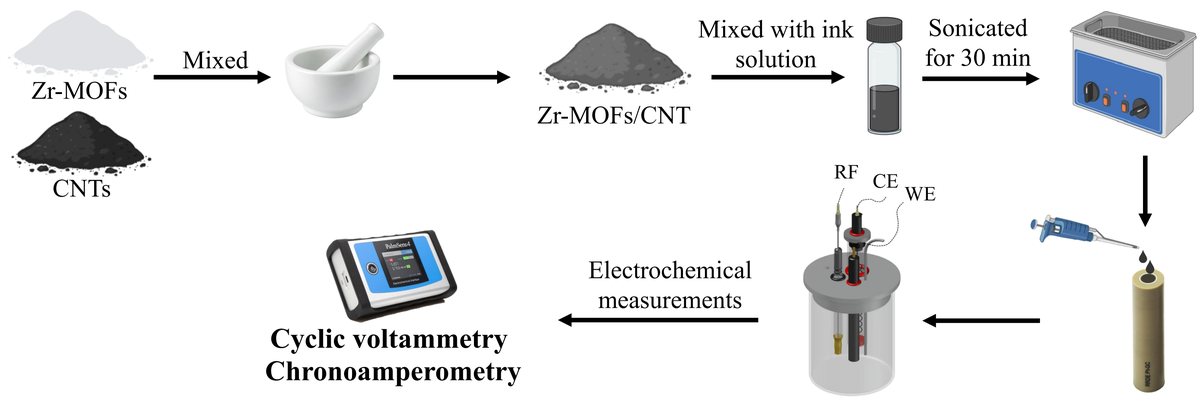


Fig. 3. Structure of CNT

OBJECTIVES

- To develop Pt catalysts supported on Zr-MOFs-modified CNT with enhanced Pt dispersion, stability, and CO tolerance
- To investigate the effect of Zr-MOFs loading (1–20 wt%) on the electrocatalytic performance using cyclic voltammetry for various alcohol fuels
- To evaluate and compare the activity and stability of the optimized Pt/Zr-MOFs/CNT catalyst with a conventional Pt/CNT catalyst for DAFC applications

METHODOLOGY



CONCLUSIONS

DAFCs offer clean energy advantages but are hindered by slow oxidation kinetics and CO poisoning. This study employed Zr-MOF-modified CNTs as advanced supports for Pt catalysts, with varying Zr-MOF loadings (1–20 wt%). The optimized Pt/10 wt% Zr-MOF/CNT catalyst exhibited a threefold improvement in catalytic activity compared to Pt/CNT for methanol and ethanol oxidation. This enhancement is attributed to its highest ECSA of 1.28 $m^2\ g^{-1}$, which provides abundant active sites and superior Pt dispersion. Notably, ethylene glycol showed the highest current density, while methanol exhibited the lowest onset potential. These results indicate that catalytic activity strongly depends on alcohol molecular size, structure, and catalyst composition. The synergistic effect between Zr-MOFs and CNT effectively mitigates CO poisoning, making this catalyst a highly efficient and durable anode material for DAFC technology.

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RESULTS AND DISCUSSION

Catalyst Performance Across Zr-MOFs Loadings

Electrodeposited Pt nanoparticles on CNT supports with varying Zr-MOF loadings (1–20 wt%) exhibited different electrocatalytic activities toward methanol oxidation. As shown in Fig. 4, low loadings (1–5 wt%) enhanced the current density relative to Pt/CNT, whereas 10 wt% Zr-MOF delivered the highest catalytic performance, suggesting optimal Pt dispersion. However, excessive loading (20 wt%) decreased the catalytic efficiency due to partial surface coverage, which restricted access to active sites.

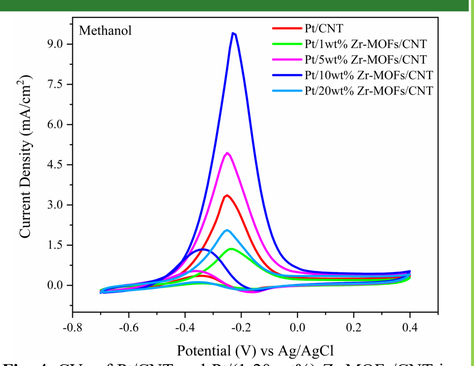


Fig. 4. CVs of Pt/CNT and Pt/(1-20 wt%) Zr-MOFs/CNT in 0.5 M KOH + 0.5 M methanol, within the potential range of -0.7 V to 0.4 V at a scan rate of 50 $mV \cdot s^{-1}$.

Determination of Electrochemical Active Surface Area (ECSA)

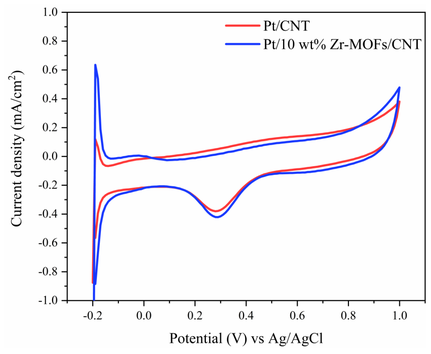


Fig. 5. CVs of hydrogen adsorption/desorption of Pt/CNT and Pt/10 wt% Zr-MOFs/CNT catalysts in 0.5 M H_2SO_4, within the potential range of -0.2 V to 1.0 V at a scan rate of 50 $mV \cdot s^{-1}$.

Table 1. Hydrogen Adsorption/Desorption Electrochemical Values of Pt/CNT and Pt/10 wt% Zr-MOFs/CNT.

Catalysts	m_{pt} (μg /cm²)	Q_H (μC)	ESA (cm^2)	ECSA (m^2/g)
Pt/CNT	6.32	4.17	0.0199	0.31
Pt/10 wt% Zr-MOFs/CNT	6.22	16.70	0.0795	**1.28**

Pt/10 wt% Zr-MOFs/CNT exhibited the highest ECSA **(Fig. 5 and Table 1)**. This result indicates that the hybrid support (Zr-MOFs/CNT) facilitates superior Pt dispersion and suppresses nanoparticle agglomeration. Consequently, more accessible active sites are generated on the Pt surface, leading to enhanced alcohol oxidation performance, as reflected by higher current density and catalytic activity.

Cyclic Voltammetry (CV)

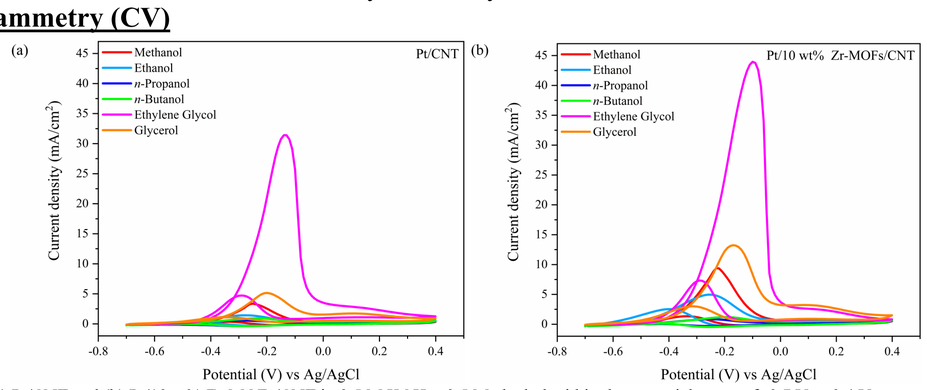


Fig. 6. CVs of (a) Pt/CNT and (b) Pt/10wt% Zr-MOFs/CNT in 0.5 M KOH + 0.5 M alcohol within the potential range of -0.7 V to 0.4 V at a scan rate of 50 $mV \cdot s^{-1}$.

As shown in **Fig. 6 and Table 2**, Pt/10 wt% Zr-MOFs/CNT exhibits a lower onset potential (E_{onset}) and higher current density (I_f) than Pt/CNT, indicating superior catalytic performance. This enhancement arises from strong Pt-support interactions and the synergistic effects of Zr-MOFs and CNT, which improve Pt dispersion, electrical conductivity, and charge-transfer efficiency. Among the tested alcohols, ethylene glycol produced the highest current density, whereas methanol displayed the lowest E_{onset}, highlighting the strong dependence of catalytic activity on alcohol molecular size, structure, and catalyst composition.

Chronoamperometry (CA)

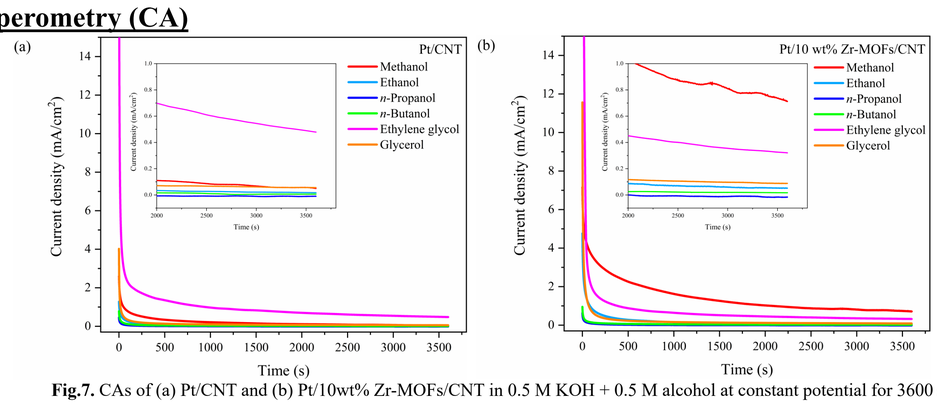


Fig.7. CAs of (a) Pt/CNT and (b) Pt/10wt% Zr-MOFs/CNT in 0.5 M KOH + 0.5 M alcohol at constant potential for 3600 s

CA results (**Fig. 7**) show that Pt/10wt% Zr-MOFs/CNT delivers higher electrocatalytic activity and better long-term stability than Pt/CNT, especially for methanol and ethylene glycol oxidation, due to the synergistic role of Zr-MOFs in enhancing Pt dispersion and suppressing the buildup of inhibitory intermediates.

Table. 2. Electrochemical parameters of Pt/CNT and Pt/10 wt% Zr-MOFs/CNT catalysts in alcohol oxidation.

Catalyst	Fuel types (Alcohol)	E_{onset} (V)	Forward scan		Backward scan		Stability ($mA\ cm^{-2}$)
			I_f ($mA\ cm^{-2}$)	E_f (V)	I_b ($mA\ cm^{-2}$)	E_b (V)	
Pt/CNT	Methanol	-0.49	3.36	-0.25	0.36	-0.34	0.049
	Ethanol	-0.52	1.43	-0.28	0.37	-0.46	0.017
	n-Propanol	-0.52	0.55	-0.29	-0.15	-0.54	-0.011
	n-Butanol	-0.47	0.92	-0.23	-0.06	-0.48	0.006
	Ethylene glycol	-0.50	31.40	-0.13	4.73	-0.29	0.479
	Glycerol	-0.45	5.15	-0.20	1.10	-0.35	0.056
Pt/10 wt% Zr-MOFs/CNT	Methanol	-0.58	9.41	-0.23	1.34	-0.34	0.712
	Ethanol	-0.56	4.96	-0.25	2.54	-0.40	0.051
	n-Propanol	-0.52	0.85	-0.25	0.05	-0.43	-0.016
	n-Butanol	-0.48	1.20	-0.20	0.10	-0.43	0.017
	Ethylene glycol	-0.53	43.96	-0.10	7.33	-0.29	0.320
	Glycerol	-0.51	13.24	-0.17	3.00	-0.32	0.088