Enhanced Methanol Oxidation Catalysis Using Platinum Supported on Carbon Black with Polypyrrole Mixed with Copper and Nickel

Parisa Klanarong[a], Suwaphid Themsirimongkon[a], Paralee Waenkaew[a,b], Surin Saipanya[a,b*]

[a]Department of Chemistry, Faculty of Science, Chiang Mai University. Chiang Mai 50200, Thailand
[b]Laboratory of Vantage Electromaterials (LOVE), Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

ABSTRACT

This study investigates the preparation of catalysts for the methanol oxidation reaction (MOR) by synthesizing polypyrrole (Ppy) mixed with copper (Cu), nickel (Ni), and a combination of both copper and nickel (Cu-Ni) on carbon black (CB) as a support material to enhance the electrodeposited Pt catalyst's ability. The catalysts were prepared as follows: platinum on carbon black with polypyrrole mixed with copper (CB/Cu-Ppy/Pt), platinum on carbon black with polypyrrole mixed with nickel (CB/Ni-Ppy/Pt), and platinum on carbon black with polypyrrole mixed with copper and nickel (CB/Cu-Ppy-Ni/Pt). Electrochemical analysis using cyclic voltammetry (CV) and chronoamperometry (CA) revealed that the CB/Cu-Ppy/Pt catalyst exhibited the highest current density for methanol oxidation (2.01 $mA \cdot cm^{-2}$) and a forward-to-backward current ratio (If/Ib) of 3.85. These results suggest that the CB/Cu-Ppy/Pt catalyst is effective in promoting methanol oxidation and facilitating the oxidation of poisoning intermediates. However, it does not significantly enhance the stability of the MOR.

INTRODUCTION

A direct methanol fuel cell (DMFC) consists of several key components:

1.Anode: Where methanol (CH_3OH) is oxidized, releasing electrons and protons. The methanol is typically mixed with water to facilitate the reaction.

2.Cathode: Where oxygen (from the air) is reduced, combining with electrons from the external circuit and protons that pass through the electrolyte to form water (H_2O).

3.Electrolyte: A proton-conducting membrane, typically made of materials like Nafion, that allows the protons generated at the anode to travel to the cathode while preventing the mixing of methanol and oxygen.

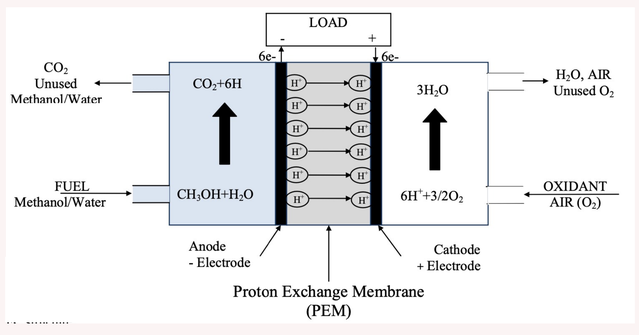


Fig.1. Scheme of a Direct methanol fuel cell (DMFC)
ref. Giorgi L, Leccese F. *Send Orders of Reprints at Reprints@benthamscience.Net Fuel Cells: Technologies and Applications.*

Working Principle:

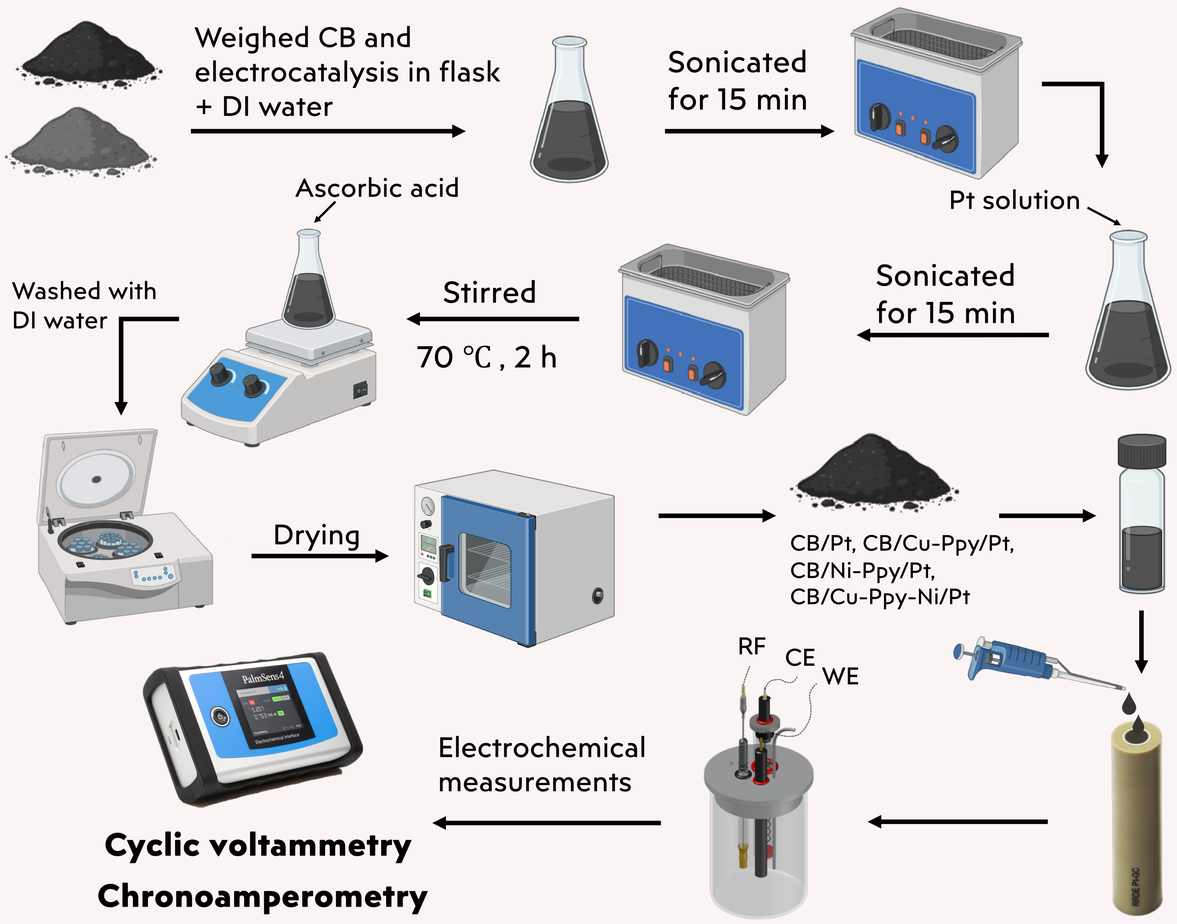
Liquid methanol is injected into the anode, where it is oxidized to CO_2, protons (H^+), and electrons (e^-). Protons move through the Nafion membrane to the cathode, while electrons flow through an external circuit, generating electricity. At the cathode, protons, electrons, and oxygen combine to produce water (H_2O).

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Overall: $CH_3OH + H_2O + 3/2O_2 \rightarrow CO_2 + 3H_2O$

OBJECTIVES

- To improve the efficiency of the platinum catalyst and carbon black to enhance performance.
- To compare the performance of different synthesized catalysts in catalyzing the oxidation reaction of methanol.
- To compare the stability of different types of catalysts.

METHODOLOGY



Acknowledgements: This work has been deliberately developed by members of Laboratory of Vantage Electrochemical (LOVE), Department of Chemistry, Faculty of Science, Chiang Mai University.

RESULTS AND DISCUSSIONS

Determination of electrochemical active surface area (ECSA) by CVs

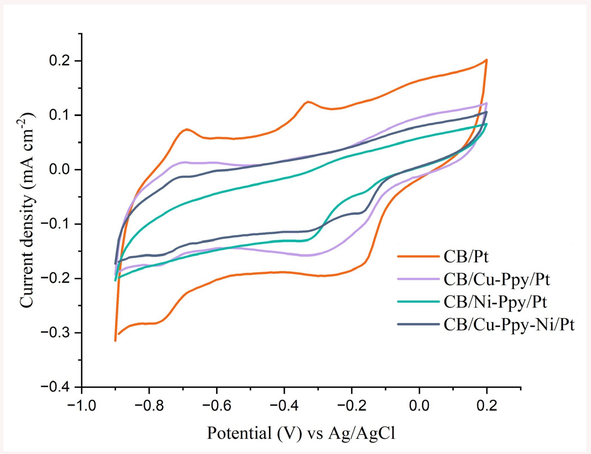


Fig.2. CVs of CB/Pt, CB/Cu-Ppy/Pt, CB/Ni-Ppy/Pt, CB/Cu-Ppy-Ni/Pt electrocatalyst were analyzed in 0.5M KOH by the potential range of -0.9V to 0.2V at scan rate of. 50 mVs^{-1}

Table.1. Q_H and ECSA of catalysts in 0.5 M KOH solution

Catalysts	Hydrogen adsorption /desorption	
	Q_H (μC)	ECSA (cm^2mg^{-1})
CB/Pt	1.06	10.09
CB/Cu-Ppy/Pt	1.22	11.62
CB/Ni-Ppy/Pt	1.07	10.19
CB/ Cu-Ppy-Ni/Pt	1.16	11.05

Cyclic voltammetry

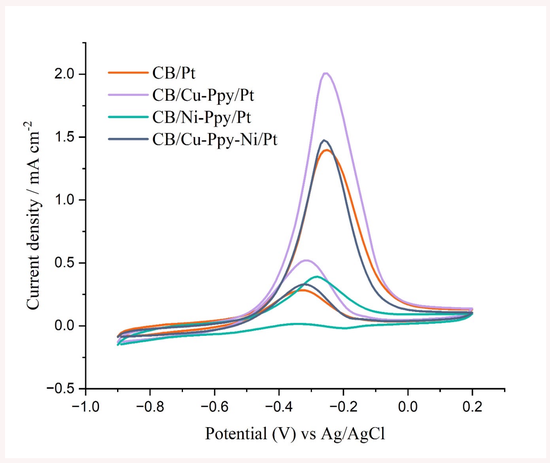


Fig.3. CVs of electrocatalyst were analyzed in 0.5M methanol + 0.5M KOH by the potential range of -0.9V to 0.2V at scan rate of. 50 mVs^{-1}

Chronoamperometry

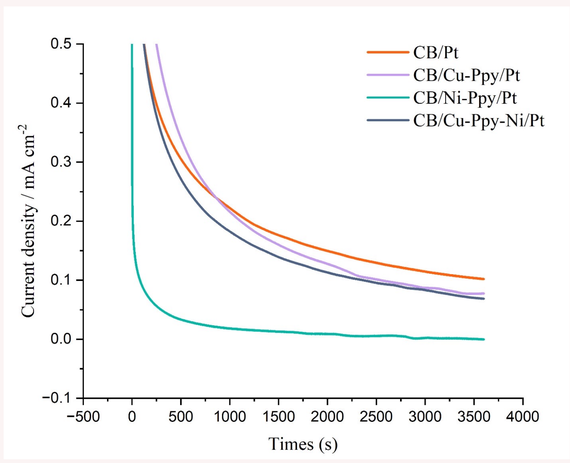


Fig.4. Chronoamperograms of selected catalysts at E_{max} for 3600s in 0.5 M KOH + 0.5 M methanol solution

Table.2. The electrical measurements of catalysts conducted in an electrolyte of 0.5 M KOH with 0.5 M MeOH

catalyst	E_{onset} (V)	Anodic scan		Cathodic scan		I_f/I_b
		I_f ($mA\ cm^{-2}$)	E_f (V)	I_b ($mA\ cm^{-2}$)	E_b (V)	
CB/Pt	-0.54	1.270	-0.250	0.267	-0.310	4.756
CB/Cu-Ppy/Pt	-0.51	2.007	-0.250	0.520	-0.310	3.855
CB/Ni-Ppy/Pt	-0.56	0.389	-0.280	0.015	-0.350	24.930
CB/ Cu-PpyNi/Pt	-0.51	1.475	-0.260	0.329	-0.320	4.474

CONCLUSIONS

A catalyst, consisting of a carbon support and metal as the main catalytic component, was prepared by modifying CB with Ppy and incorporating two metals, Cu and Ni, to support Pt. Electrochemical measurements of the methanol oxidation reaction revealed that the CB/Cu-Ppy/Pt catalyst exhibited high electrochemical activity. However, the CB/Cu-Ppy/Pt catalyst still suffers from low stability compared to the CB/Pt catalyst.

REFERENCES

1. Adeyanju A, Agboola O. Fuel Cells: An Overview of Its Green Value and Readiness Levels. Published online September 6, 2023. doi:10.26434/chemrxiv-2023-gg8q7
2. Giorgi L, Leccese F. *Send Orders of Reprints at Reprints@benthamscience.Net Fuel Cells: Technologies and Applications.*