Electrocatalytic Alcohol Oxidation on Pt/Caffeine/GO and Pt/Caffeine/CNTs: Carbon–Molecule Synergy for Fuel Cell Applications

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ABSTRACT

Two carbon-based electrocatalytic systems, Pt/caffeine/GO and Pt/caffeine/CNTs, were developed for efficient alcohol (*e.g.* ethylene glycol) oxidation by combining graphene oxide (GO) or carbon nanotubes (CNTs) with caffeine, followed by Pt-electrochemical deposition. The surface modification with caffeine enhanced the interaction between the carbon supports and Pt, leading to improved dispersion and catalytic activity. Cyclic voltammograms (CVs) demonstrated that the Pt/caffeine/GO and the Pt/caffeine/CNTs catalysts exhibited higher current density, lower onset potential, and reduced potential at maximum current intensity, compared with their non-modified counterparts, with the Pt/caffeine/CNTs showing the highest activity. Chronoamperograms (CAs) confirmed the long-term durability of the catalysts, maintaining high current intensity even after 3600 s of continuous operation. These results indicate that both Pt/caffeine/GO and Pt/caffeine/CNTs are promising electrocatalysts for direct alcohol fuel cell applications, with caffeine serving as an effective molecular modifier to enhance catalytic efficiency and stability.

INTRODUCTION

Direct alcohol fuel cells (DAFCs), including direct ethylene glycol fuel cells, are promising energy conversion systems but are limited by the activity and durability of Pt-based electrocatalysts. Carbon supports such as graphene oxide (GO) and carbon nanotubes (CNTs) offer high surface area and conductivity, yet weak Pt–support interactions reduce catalytic efficiency. In this work, caffeine was used as a molecular modifier to enhance Pt–carbon interactions. Two electrocatalysts, Pt/caffeine/GO and Pt/caffeine/CNTs, were prepared via caffeine functionalization followed by Pt electrochemical deposition. The caffeine-modified catalysts show improved activity and stability for alcohol (e.g. ethylene glycol) oxidation, highlighting their potential for DAFC applications.

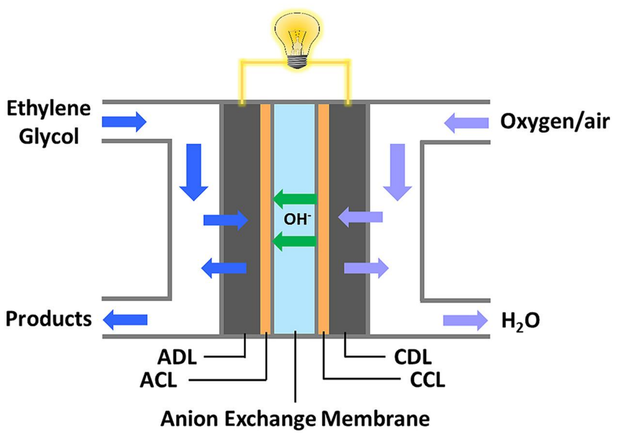


Fig. 1. Schematic diagram of a direct ethylene glycol fuel cell

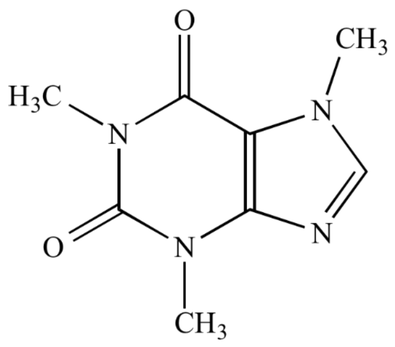


Fig. 2. Caffeine structure

Anode (EG Oxidation): $C_2H_6O_2 + 10\ OH^- \rightarrow 2CO_3^{2-} + 8H_2O + 6e^-$

Cathode (Oxygen Reduction): $5/2O_2 + 5H_2O + 10e^- \rightarrow 10\ OH^-$

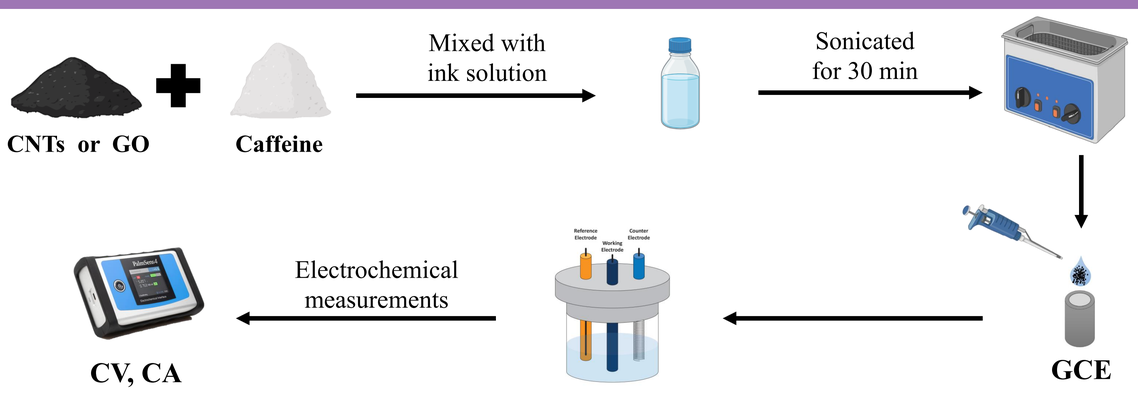
Overall cell reaction (Alkaline DEGFC): $C_2H_6O_2 + 3/2O_2 + 4OH^- \rightarrow 2CO_3^{2-} + H_2O$

This overall reaction corresponds to the 10-electron oxidation of ethylene glycol at the anode, coupled with the oxygen reduction reaction at the cathode.

OBJECTIVES

- To develop caffeine-modified carbon-supported Pt electrocatalysts (Pt/caffeine/GO and Pt/caffeine/CNTs) for alcohol oxidation.
- To evaluate the potential of caffeine-modified Pt catalysts for direct alcohol fuel cell applications
- To compare the electrocatalytic activity and durability of Pt/caffeine/GO and Pt/caffeine/CNTs toward alcohol oxidation using cyclic voltammetry and chronoamperometry

EXPERIMENTAL



CONCLUSIONS

Caffeine was successfully incorporated into Pt-based catalysts without forming new covalent bonds, while effectively enhancing electrochemical performance toward ethylene glycol oxidation. Pt/10%Caf/CNTs exhibited the highest activity and stability due to improved Pt dispersion and the high conductivity of CNTs, whereas excessive caffeine on GO partially blocked active sites, leading to reduced performance.

ACKNOWLEDGEMENTS

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RESULTS AND DISCUSSION

FT-IR Spectroscopy

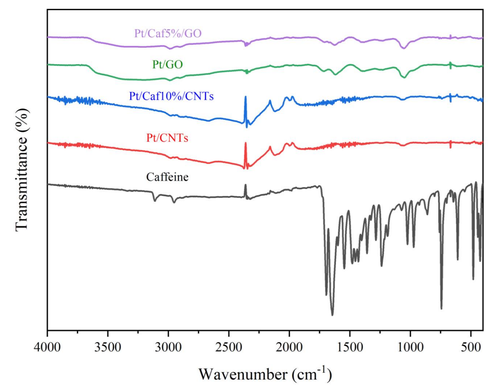


Fig. 3. FTIR Spectra of Caffeine, Pt/CNTs, Pt/GO, Pt/Caf10%/CNTs and Pt/Caf5%/GO.

The FTIR spectra of caffeine show characteristic bands at ~1700–1650 cm^{-1} (C=O stretching) and ~1550–1450 cm^{-1} (C–N and ring vibrations), while Pt/GO and Pt/CNTs exhibit bands near ~3400 cm^{-1} (O–H stretching) and ~1600 cm^{-1} (C=C graphitic structure); after caffeine modification, Pt/5%Caf/GO and Pt/10%Caf/CNTs retain these caffeine-related bands with reduced intensity and slight shifts, indicating successful caffeine incorporation via interfacial interactions rather than covalent bond formation.

Cyclic Voltammetry (CV)

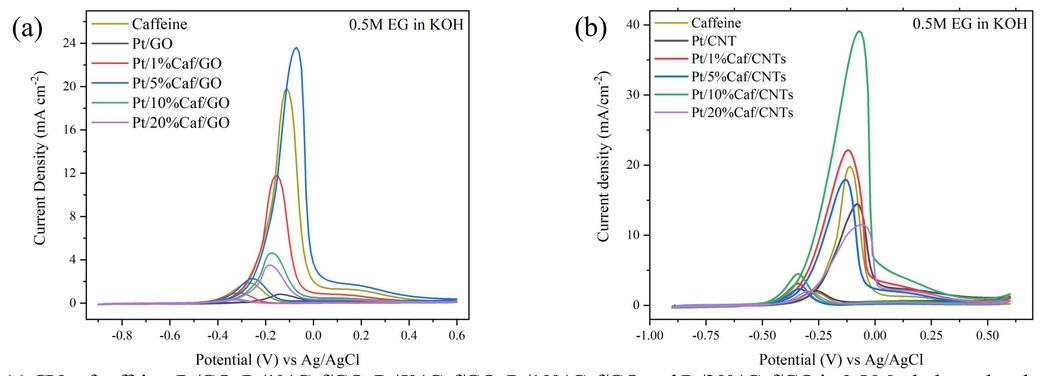


Fig. 4. (a) CVs of caffeine, Pt/GO, Pt/1%Caf/GO, Pt/5%Caf/GO, Pt/10%Caf/GO and Pt/20%Caf/GO in 0.5 M ethylene glycol, (b) CVs of Caffeine, Pt/CNTs, Pt/1%Caf/CNTs, Pt/5%Caf/CNT, Pt/10%Caf/CNTs and Pt/20%Caf/CNTs in 0.5 M ethylene glycol.

Table 1. Electrochemical performance parameters of Pt/Caf/C catalysts toward ethylene glycol oxidation.

Catalyst	E_{onset} (V)	Anodic scan		Cathode scan		I_f/I_b ratio
		I_f (mA cm^{-2})	E_f (V)	I_b (mA cm^{-2})	E_b (V)	
Caffeine	-0.41	19.41	-0.11	1.79	-0.27	10.84
Pt/CNTs	-0.47	13.71	-0.08	2.02	-0.27	6.79
Pt/1%Caf/CNTs	-0.57	21.94	-0.12	3.00	-0.35	7.31
Pt/5%Caf/CNTs	-0.54	17.62	-0.13	2.30	-0.34	7.66
Pt/10%Caf/CNTs	-0.61	36.77	-0.08	4.30	-0.34	8.55
Pt/20%Caf/CNTs	-0.52	11.38	-0.06	2.01	-0.29	5.66
Pt/GO	-0.30	19.73	-0.11	1.83	-0.27	10.78
Pt/1%Caf/GO	-0.35	11.65	-0.16	0.95	-0.31	12.26
Pt/5%CafGO	-0.36	22.31	-0.08	2.15	-0.26	10.39
Pt/10%Caf/GO	-0.36	4.91	-0.18	0.37	-0.34	13.21
Pt/20%Caf/GO	-0.35	3.36	-0.19	0.29	-0.33	11.62

Moderate caffeine loading enhances Pt/GO activity for ethylene glycol oxidation, with Pt/5%Caf/GO showing the highest current density, while excess caffeine reduces performance due to surface blocking.

Pt/Caf/CNTs exhibits higher electrocatalytic activity than Pt/Caf/GO, with Pt/10%Caf/CNTs achieving the highest current density due to the high conductivity and favorable structure of CNTs.

Chronoamperometry (CA)

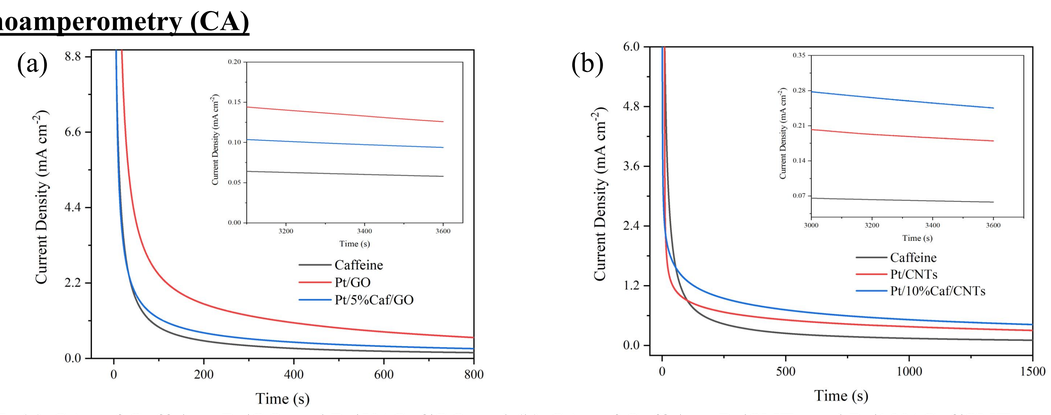


Fig. 5. (a) CAs of Caffeine, Pt/GO and Pt/5%Caf/GO and (b) CAs of Caffeine, Pt/CNTs and Pt/10%Caf/CNTs.

The chronoamperometric curves show a rapid initial current decay followed by a quasi-steady state, indicating diffusion-controlled behavior. Pt/10%Caf/CNTs exhibits the highest current density throughout the measurement, reflecting enhanced electrochemical activity and stability due to improved Pt dispersion and increased active sites.

All electrodes display a similar initial current decay, with Pt/GO delivering the highest current density, highlighting efficient electron transfer on the GO support. The slightly lower current of Pt/5%Caf/GO is attributed to partial blockage of Pt active sites by caffeine, although it still shows better performance and stability than caffeine alone.

Table 2. CA of Pt-based and Caffeine-modified Catalysts in 0.5 M EG + 0.5 M KOH at -0.85 V

Catalyst	Stability (mA cm^{-2})
Caffeine	0.0566
Pt/CNTs	0.1840
Pt/10%Caf/CNTs	0.2406
Pt/GO	0.1273
Pt/5%Caf/GO	0.0990