

Abstract

The development of palladium (Pd) electrocatalysts supported on graphene oxide (GO) modified with three aza-BODIPY compounds (DA, DM and DP) has been carried out to enhance efficiency of oxidation reaction in direct alcohol fuel cells (DAFCs). The synthesis of the catalysts involved ultrasonic dispersion and chemical reduction. The electrochemical activity and stability of the synthesized catalysts were investigated using cyclic voltammetry (CV) and chronoamperometry (CA), respectively. The results showed that the electrochemical surface area of the modified catalysts (GO-DA/Pd, GO-DM/Pd and GO-DP/Pd) significantly increased compared to that of the unmodified catalyst (GO/Pd). Additionally, the GO-DM/Pd exhibited the highest current density of 0.328 mA.cm⁻² for methanol oxidation and 0.257 mA.cm⁻² for ethanol oxidation. For butanol oxidation, the GO-DA/Pd showed the highest current density of 0.177 mA.cm⁻². This improvement in catalytic efficiency resulted from the synergistic effect between palladium and the modified graphene oxide support. From the CA study, the GO-DM/Pd catalyst has greater stability than the GO-DA/Pd, GO-DP/Pd and the unmodified catalysts (GO/Pd). In addition, the GO-DM/Pd catalyst demonstrated the highest electrocatalytic activity and stability for methanol and ethanol oxidation reactions.

Introduction

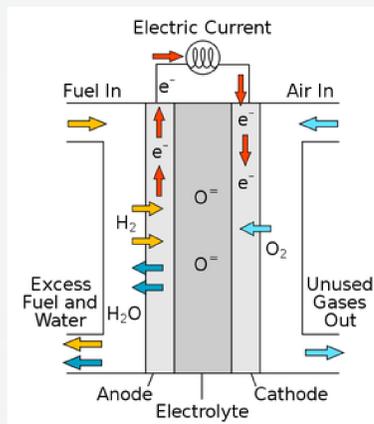


Fig. 1 Scheme of a proton exchange membrane fuel cells (PEMFC)

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- + (1/2)O_2 \rightarrow H_2O(l)$

Overall: $H_2 + 0.5O_2 \rightarrow H_2O(l)$

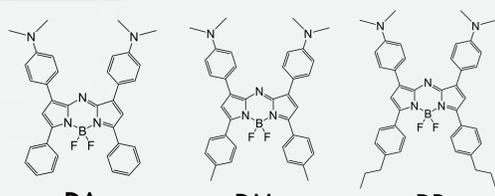


Fig. 2 Structure of Aza-BODIPYs (Aza-boron-dipyrromethene)

A Direct Alcohol Fuel Cell (DAFC) generates electricity by oxidizing alcohol (eg. methanol or ethanol) directly, using an alkaline electrolyte like potassium hydroxide (KOH). Palladium (Pd) is a promising alternative to platinum (Pt) for alcohol oxidation in alkaline solutions due to its cost-effectiveness, good catalytic activity, enhanced stability, and higher tolerance to CO poisoning. While Pd may have lower intrinsic activity than Pt, it can be optimized through nano-structuring to improve its performance in alkaline solution, making it a viable option for efficient, cost-effective portable power applications in DAFCs.

Results

Cyclic voltammetry (CV)

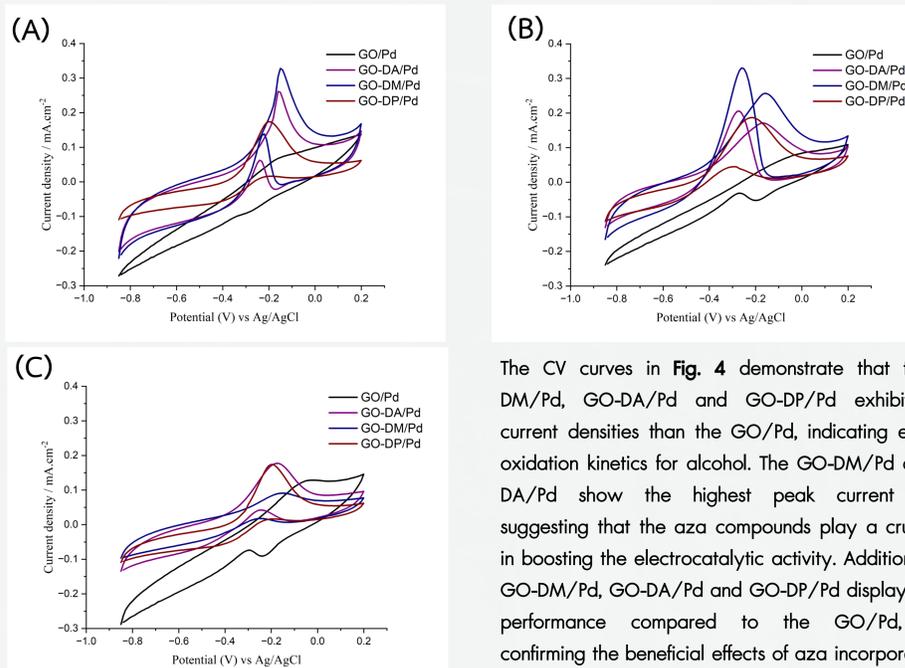
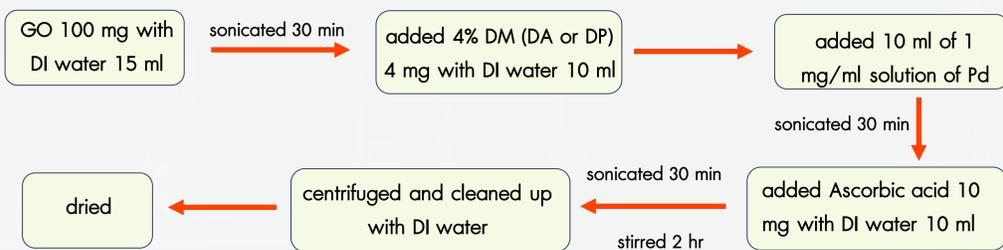


Fig. 4 CV curves of the catalysts conducted in an electrolyte of 0.5 M KOH at a scan rate of 50 mV s⁻¹ with (A) 0.5 M methanol (B) 0.5 M ethanol and (C) 0.5 M n-butanol

The CV curves in Fig. 4 demonstrate that the GO-DM/Pd, GO-DA/Pd and GO-DP/Pd exhibit higher current densities than the GO/Pd, indicating enhanced oxidation kinetics for alcohol. The GO-DM/Pd and GO-DA/Pd show the highest peak current density, suggesting that the aza compounds play a crucial role in boosting the electrocatalytic activity. Additionally, the GO-DM/Pd, GO-DA/Pd and GO-DP/Pd display superior performance compared to the GO/Pd, further confirming the beneficial effects of aza incorporation.

Methodology



Results

Cyclic voltammetry (CV)

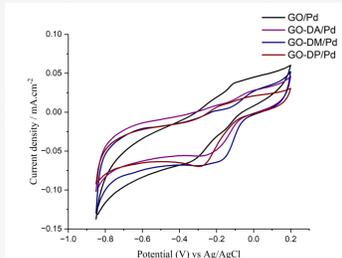


Fig. 3 CV curves of the catalysts conducted in an electrolyte of 0.5 M KOH at a scan rate of 50 mV s⁻¹

Table 1 The electrical measurements of hydrogen adsorption and desorption of the prepared catalysts

| catalysts | Q _H | ESA(cm ²) | ECSA (cm ² mg ⁻¹) | RF |
|-----------|----------------|-----------------------|--|-------|
| GO/Pd | 6.84 | 0.033 | 2873 | 0.465 |
| GO-DA/Pd | 7.65 | 0.036 | 3213 | 0.520 |
| GO-DM/Pd | 9.22 | 0.044 | 3872 | 0.627 |
| GO-DA/Pd | 1.15 | 0.005 | 4830 | 0.078 |

Table 2 The electrical measurements of catalysts conducted in an electrolyte of 0.5 M KOH with 0.5 M alcohol solution

| Solution | Catalys | Eonset (V) | If (mA.cm ⁻²) | Ef (V) | Ib (mA.cm ⁻²) | Eb (V) | If/Ib |
|-----------|----------|------------|---------------------------|--------|---------------------------|--------|--------|
| methanol | GO/Pd | -0.41 | 0.024 | -0.25 | -0.082 | -0.27 | -0.295 |
| | GO-DA/Pd | -0.33 | 0.094 | -0.15 | 0.063 | -0.24 | 1.490 |
| | GO-DM/Pd | -0.31 | 0.328 | -0.15 | 0.139 | -0.22 | 2.365 |
| | GO-DP/Pd | -0.26 | 0.102 | -0.12 | 0.016 | -0.2 | 6.221 |
| ethanol | GO/Pd | -0.38 | 0.191 | -0.06 | 0.184 | -0.2 | 1.036 |
| | GO-DA/Pd | -0.41 | 0.073 | -0.09 | 0.206 | -0.27 | 0.353 |
| | GO-DM/Pd | -0.50 | 0.257 | -0.16 | 0.330 | -0.26 | 0.778 |
| | GO-DP/Pd | -0.38 | 0.188 | -0.08 | 0.045 | -0.3 | 4.210 |
| n-butanol | GO/Pd | -0.35 | 0.121 | -0.07 | -0.082 | -0.21 | -1.481 |
| | GO-DA/Pd | -0.18 | 0.177 | -0.14 | 0.042 | -0.25 | 4.198 |
| | GO-DM/Pd | -0.22 | 0.040 | -0.19 | 0.018 | -0.25 | 2.249 |
| | GO-DP/Pd | -0.49 | 0.028 | -0.23 | 0.023 | -0.21 | 1.215 |

Chronoamperometry (CA)

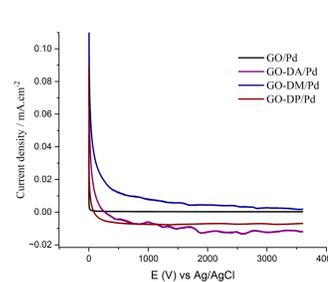


Fig. 5 CA curves at -0.85 V in 0.5 M KOH with 0.5 M methanol at a scan rate of 50 mV s⁻¹

The CA curves in Fig. 5 show that the GO/Pd and GO-aza/Pd initially exhibit the highest current density but decline over 3600 seconds, indicating poor stability. In contrast, the GO-DM/Pd, GO-DA/Pd and GO-DP/Pd show more stable current retention, suggesting better durability. The addition of aza compounds enhances the catalytic activity and also reduces catalyst degradation, leading to a longer electrocatalyst lifespan.

Conclusions

- 1) Pd-electrocatalysts on the modified GO (GO-DA/Pd, GO-DM/Pd and GO-DP/Pd) provided significantly improved electrochemical surface area (ECSA) in the range of 3213 – 4830 cm²/mg⁻¹, compared to that of the non-modified catalyst (GO/Pd) of 2873 cm²/mg⁻¹, indicating a remarkable enhancement.
- 2) The GO-DM/Pd catalyst exhibited the highest current density of 0.328 mA.cm⁻² for methanol oxidation and 0.257 mA.cm⁻² for ethanol oxidation. For butanol oxidation, the GO-DA/Pd showed the highest current density of 0.177 mA.cm⁻².
- 3) The GO-DM/Pd catalyst has greater stability than the GO-DA/Pd, GO-DP/Pd and the unmodified catalysts (GO/Pd).

References

- 1) S. Lia, J. Shua, S. Maa, H. Yanga, J. Jina, X. Zhangb, R. Jin. *Appl. B: Environ.*, **2020**, 280, 119464.
- 2) S. Luangphai, P. Thuptimdang, S. Buddhiranon, K. Chanawanno, *Spectrochim Acta A Mol. Biomol. Spectrosc.*, **2024**, 322, 124806.

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- 2) Department of Chemistry, Faculty of Science, Chiang Mai University