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Comparative study of aliphatic alcohols electrooxidation on zero-valent palladium complex for direct alcohol fuel cells

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ABSTRACT

In this paper, bis (dibenzylidene acetone) palladium (0), Pd (DBA)₂, was used as an effective catalyst for the electrooxidation of different aliphatic alcohols such as ethylene glycol (EG), ethanol (EtOH), glycerol (Gly), methanol (MeOH)) in the alkaline media. The activity and stability of Pd (DBA)₂ were assessed for the electrooxidation of the mentioned alcohols using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA). Pd (DBA)₂ exhibited significantly high anodic current density and lower onset potential in EtOH oxidation compared to EG, Gly and MeOH. CV and CA results demonstrated that Pd (DBA)₂ is still active even after 200 CV cycles. The tolerance of Pd (DBA)₂ against poisoning intermediate products in case EtOH was higher than other mentioned alcohols. Finally, Pd (DBA)₂ successfully employed as an anode catalyst in a passive air breathing direct alcohol fuel cell (DAFC). The maximum power density (MPD) of 30, 31, 25 and 18 mW cm⁻² were achieved for EG, EtOH, Gly and MeOH, respectively. These results indicated that Pd (DBA)₂ can be a promising anode catalyst for DAFCs.

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Introduction

Compared to H₂-fueled fuel cells, direct alcohol fuel cells (DAFCs) have attracted enormous attention due to the simple production, storage of liquid fuels and fuel purification [1,2]. Liquid fuels such as; ethylene glycol (EG), ethanol (EtOH), glycerol (Gly) and methanol (MeOH) not only are more easily stored and transported but also, have a higher volumetric energy density and more energy efficiency than gaseous fuels [3]. The volumetric energy density of EG, EtOH, Gly and MeOH at 20 MPa is 5.79, 6.31, 6.26 and 4.82 (kWh L⁻¹), respectively. They are much higher than hydrogen (0.53 kWh L⁻¹).

Nevertheless, DAFCs have suffered slow kinetics of the alcohols electrooxidation reaction on the surface of synthesized catalysts in spite of great efforts, which have been made for development of catalyst materials.

Pt and Pt-based catalysts have been extensively investigated and recognized as the traditional catalysts with suitable catalytic efficiency for the alcohols electrooxidation reaction [4–6]. However, the toxic intermediate species of the alcohols electrooxidation reaction would reduce catalytic performance of the mentioned catalysts. In addition, the high cost and limited supply of Pt would restrict its application in DAFCs.

As compared to the electrooxidation of MeOH, the oxidation of EG, EtOH and Gly not only depend on the ability of the

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catalyst in oxidative removal of poisoning intermediates, but also depend on its activity in C–C and C–H bond breakage [7]. Obviously, it is necessary to find high active and stable catalysts for electrooxidation of alcohols in DAFCs.

Notable works have been done for replacing of the Pt-based catalysts with Pd-based catalysts toward alcohols oxidation in DAFCs because, it is more abundant and less expensive than Pt. Also, Pd-based catalysts have been used successfully for the alcohols electrooxidation reaction in the alkaline environment. For example, many researchers have devoted to investigating of large variety of conductive materials for the support of the Pd nanoparticles in alcohols oxidation, including Vulcan XC-72R carbon black [8], tungsten carbides/carbon nanotubes [9], ultrahigh-surface hollow carbon spheres [10], carbonized TiO₂ nanotube [11] and carbon microspheres [12]. Pd nanoparticles supported on multi-walled carbon nanotubes were scrutinized for the oxidation of EtOH, Gly or MeOH in the 2 M KOH solution in half cells [13]. The catalyst was very active for the electrooxidation of all alcohols, with Gly providing the best performance in terms of the specific current density and EtOH showing the lowest onset potential.

Compositing or alloying Pd with other elements such as Sn [14,15], Au [14,16], Ag [17], Ni [18,19], Pt [20–22] and Bi [23] could potentially enhanced the catalysts activity, lower degradation of the active surface and overcome the poisoning effects by reducing surface coverage by adsorbed CO. Chen et al. [24] found that the catalytic activity of Pd–Ru is considerably higher than that of Pd toward the electrooxidation of EG, EtOH, and MeOH. The activity sequence of Pd–Ru toward the alcohol electrooxidation was EtOH > EG > MeOH, and Pd–Ru with 1:1 atomic ratio exhibited the highest activity. They also compared the activities of Pd–Ru and Pt–Ru catalysts for alcohol electrooxidations in alkaline media. For the electrooxidation of MeOH and EG, the activity of Pd–Ru was lower than that of Pt–Ru. For the EtOH electrooxidation reaction, instead, the activity of Pd–Ru was higher than that of Pt–Ru.

To diminishing the CO poisoning effect on the catalyst surface, metal oxides (CeO₂, NiO, Co₃O₄ and Mn₃O₄) were added into Pd-based catalysts in electrooxidation of alcohols [25–27]. The results indicated that addition of the metal oxide remarkably improves the activity and CO tolerance of the Pd-based catalysts in alcohols electrooxidation. All investigations suggested that Pd-based catalysts could make up for the deficiency of Pt-based catalysts in DAFCs.

All zero-valent complexes with d¹⁰ electronic configurations have considerable catalytic interest toward alcohols oxidation. Specially, zero-valent Pd complexes are efficient catalysts in the field of organic synthesis and in all reactions involving aryl, vinyl and allelic derivatives because of their good nucleophilic properties [28]. Among factors influencing the reactivity, electronic effects are very important, namely oxidizing of the metal center and tuning the donor/acceptor properties of the π -coordinated unsaturated hydrocarbon ligands and other co-ligands to vary the distribution of the electron density in the complexes [29].

In our previous work [30], we have successfully employed on first time zero-valent Pd complex, Pd (DBA)₂, as an catalyst toward the Gly electrooxidation reaction. Results showed that

Pd (DBA)₂ exhibits a superior catalytic performance with high long-term stability for the direct Gly fuel cell in alkaline media.

Pd (DBA)₂ was synthesized in 1970 [31]. Different substitution and addition reactions have been reported along with an investigation of the potential utility of the Pd (DBA)₂ as a catalyst [32,33]. The complex structure of Pd (DBA)₂ is shown in Fig. 1.

In the present work, the performance of Pd (DBA)₂ in electrooxidation of different aliphatic alcohols (EG, EtOH, Gly and MeOH) have been investigated in the half cell by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) techniques in the alkaline medium. To determine the performance of Pd (DBA)₂ in real alkaline DAFCs, membrane electrode assembly (MEA) was fabricated by using the Pd (DBA)₂ catalyst in the anode electrode. All the obtained results from the half and whole cell indicate that Pd (DBA)₂ represents an acceptable activity and performance for DAFCs in the alkaline medium.

Experimental

Half-cell electrochemical investigation

Deposition of Pd (DBA)₂ on the glassy carbon

A thin film of the catalyst layer on the glassy carbon (GC) electrode was prepared as follows: a mixture containing 2.0 mg of Pd (DBA)₂ (Aldrich, molecular weight of 575 g mol⁻¹, melting point of 150 °C), 1 mL of 2-propanol, 1 mL of the ultra pure water (MilliQ, Millipore) and 0.01 mL of 5 wt.% Nafion solution (Aldrich) were sonicated for 5 min. The well-dispersed catalyst ink was then quantitatively transferred onto the surface of the GC electrode by using a micropipette, and finally was dried in the oven at 60 °C for 15 min. The catalyst loading on the electrode surface was 0.033 mg cm⁻². All chemical materials (Merck) were analytical grade.

CV, EIS and CA measurements

The electrochemical activity and stability of Pd (DBA)₂ in alcohol electrooxidation reaction were investigated by CV, EIS and CA techniques. Electrochemical measurements were carried out with a conventional three-electrode cell and an

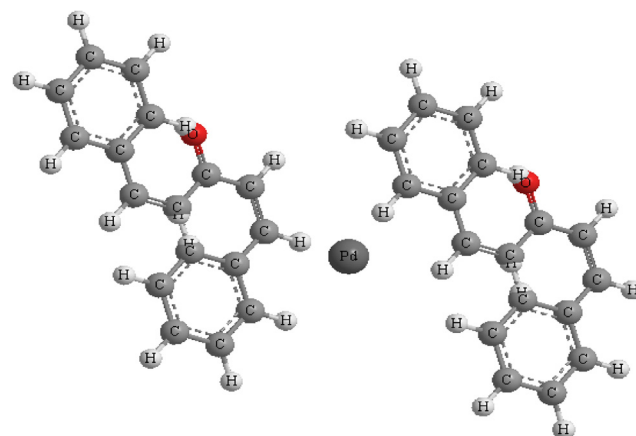


Fig. 1 – Structure of Pd (DBA)₂ catalyst.

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