



A novel nano-palladium complex anode for formic acid electro-oxidation



Gumaa A. El-Nagar^{a,b,*}, Ahmed F. Darweesh^a, Ibrahim Sadiék^{a,c}

^a Department of Chemistry, Faculty of Science, Cairo University, Egypt

^b Institut für Chemie und Biochemie Physikalische und Theoretische Chemie, Freie Universität Berlin, Berlin, Germany

^c Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, 24118, Kiel, Germany

ARTICLE INFO

Article history:

Received 8 July 2016

Accepted 26 August 2016

Available online 28 August 2016

Keywords:

Nano-Pd-complex

Electrocatalysis

Fuel cells

ABSTRACT

This study introduces a novel nano-sized palladium complex with high electrocatalytic activity and stability as a catalyst for the anodic reaction of direct Formic acid fuel cell (DFAFC). Morphologically, as prepared Pd-complex has intersected nano-rod like structure with an average particle size of 7 nm. Nano-Pd-complex modified GC electrode showed 10 times higher electrocatalytic activity and 16 times higher stability compared with the traditional Pd nanoparticles modified GC electrode with the same Pd weight. This significant improvement may be attributed to its small size and bulky structure that hinders the sintering of the active Pd atoms (i.e., obstructs the growth of Pd particle size) and impedes the adsorption of poisoning intermediate species (e.g., CO) and/or formation reversible surface hydride as evidenced by the DFT calculations. This study introduces a new promising category of Pd-based catalyst with high activity, catalyst utilization and durability for DFAFCs applications.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Direct formic acid fuel cells (DFAFCs) received a great attention in the recent years as an efficient and eco-friendly promising alternative power source for electronic applications. This is due to their numerous attractive features such as higher energy efficiency, power density, theoretical electromotive force as well as the faster oxidation kinetics, lower toxicity and lower crossover of FA through Nafion[®] membrane compared to methanol fuel cells [1–8].

Pd-based nanostructured materials have commonly been used as excellent anode for DFAFCs generally due to their high electrocatalytic activity and power densities compared with Pt-based electrodes. However, their low durability due to poisoning with a strong adsorbed carbon monoxide (CO) intermediates and the sintering of the catalyst (this is also true for nanoparticles) have seriously limited their practical and commercial application [9,10]. To this end, various approaches have been used to improve the activity and stability of Pd-based catalysts. For instance, efficient

promoters such as second metals, nonmetals, and metal oxides have been proposed to enhance the catalytic properties of Pd-based catalysts via synergetic effect [11–17]. Despite of the huge scientific literature, the electrocatalytic activity and stability of the Pd-based catalysts used in DFAFCs still remain unsatisfactory and need further improvement.

Herein, a novel nano-Pd-complex catalyst of (2-[1-(Benzyloxymino) ethyl] benzothiazole-κ²N,Ndichloropalladium(II)) is used as alternative to the traditional Palladium nanoparticles (PdNPs) catalysts for formic acid oxidation (FAO). This catalyst is used as a precatalyst for synthesis of some organic compounds via Suzuki reactions [18]. Physical and electrochemical characterization methods were used to explore its electrocatalytic activity and stability. DFT quantum chemical calculations have been performed to model and characterize the interactions between FA and the Pd-complex. This study introduces a new solution for the dilemma of the activity and the stability of traditional Pd catalysts based on catalyst design and Pd-complex structure-catalytic activity relationship.

2. Experimental

Glassy carbon (GC with geometric area of 0.07 cm²), Ag/AgCl/KCl (sat.), and a spiral Pt wire served as a working, reference and counter electrodes, respectively. All chemicals were of analytical

* Corresponding author at: Department of Chemistry, Faculty of Science, Cairo University, Egypt.

E-mail addresses: gumaa.elnagar@fu-berlin.de, elnagar087@yahoo.com (G.A. El-Nagar).

grade. They were purchased from Merck and Sigma Aldrich and used as received without further purification. All solutions were prepared using second distilled water. Pd-complex was prepared as described elsewhere [18].

Pd-complex modified GC electrodes (next noted as: Nano-Pd-complex/GC) was prepared as following: A suspension of Pd-Complex, for being anchored on GC, was prepared by adding the proper weight of the Complex powder in a test tube containing 5 ml ethanol and one drop of Nafion solution (5% in water). Then, the mixture was sonicated for 35 min in an ice bath. Finally, 20 μL of a freshly prepared suspensions casted onto the cleaned GC electrode surface and left overnight for drying in air. Different volumes were casted onto GC surface to prepare electrodes with different Pd-complex loading level. Pd nanoparticles modified GC electrodes (next noted as: PdNPs/GC) were performed by electrodeposition from an acidic solution of 0.1 M H_2SO_4 containing 1.0 mM $\text{Pd}(\text{CH}_3\text{COO})_2$ solution at a constant potential electrolysis of 0.0V. The loading of PdNPs was estimated from the amount of charge used for the electrodeposition process.

All measurements were performed at room temperature ($25 \pm 1^\circ\text{C}$) using an EG&G potentiostat (model 273A) operated with Echem 270 software. The electrocatalytic activity of PdNPs/GC electrodes towards FAO were examined in an aqueous solution of 0.3 M FA, at pH3.5. A field emission scanning electron microscope, FE-SEM, (QUANTA FEG 250) coupled with an energy dispersive X-ray spectrometer (EDX) unit was employed to evaluate the electrode's morphology and surface composition. Fourier

transform infrared spectroscopy (FTIR), ^1H NMR ^{13}C NMR and X-ray diffraction (XRD) have been performed to investigate the change in the nano-Pd complex after the FAO reaction.

The density functional Theory (DFT) approach has been used to model the interaction of FA with the Pd-complex. All the calculations have been performed using *Gaussian 09* suite of programs [19]. All the geometries were optimized first at HF/3-21G level of theory. The second geometry optimization step was performed using the Density Functional three-parameter hybrid (B3LYP) model by implementing the 6-311++G(d, p) basis set for all the atoms except Pd atom, we used the LanL2DZ basis set. A number of 10 water molecules have been explicitly used in the modeling of the interaction of FA with the Pd-complex. Frequency calculations have been carried out at the same level of theory to characterize the global minima.

3. Results and discussions

3.1. Material, electrochemical, and geometrical characterizations

The morphological characterization of the nano-Pd-complex/GC and PdNPs/GC electrodes, using FE-SEM, is shown in Fig. 1A and B, respectively. As seen in Fig. 1A the casted nano-Pd-complex has intersected nano-rods structure with an average length of ~ 7 nm which is homogeneously distributed over the entire GC surface (size measured from TEM see S1 in supplementary materials). In the other hand the electrodeposited Pd nanoparticles has a grained

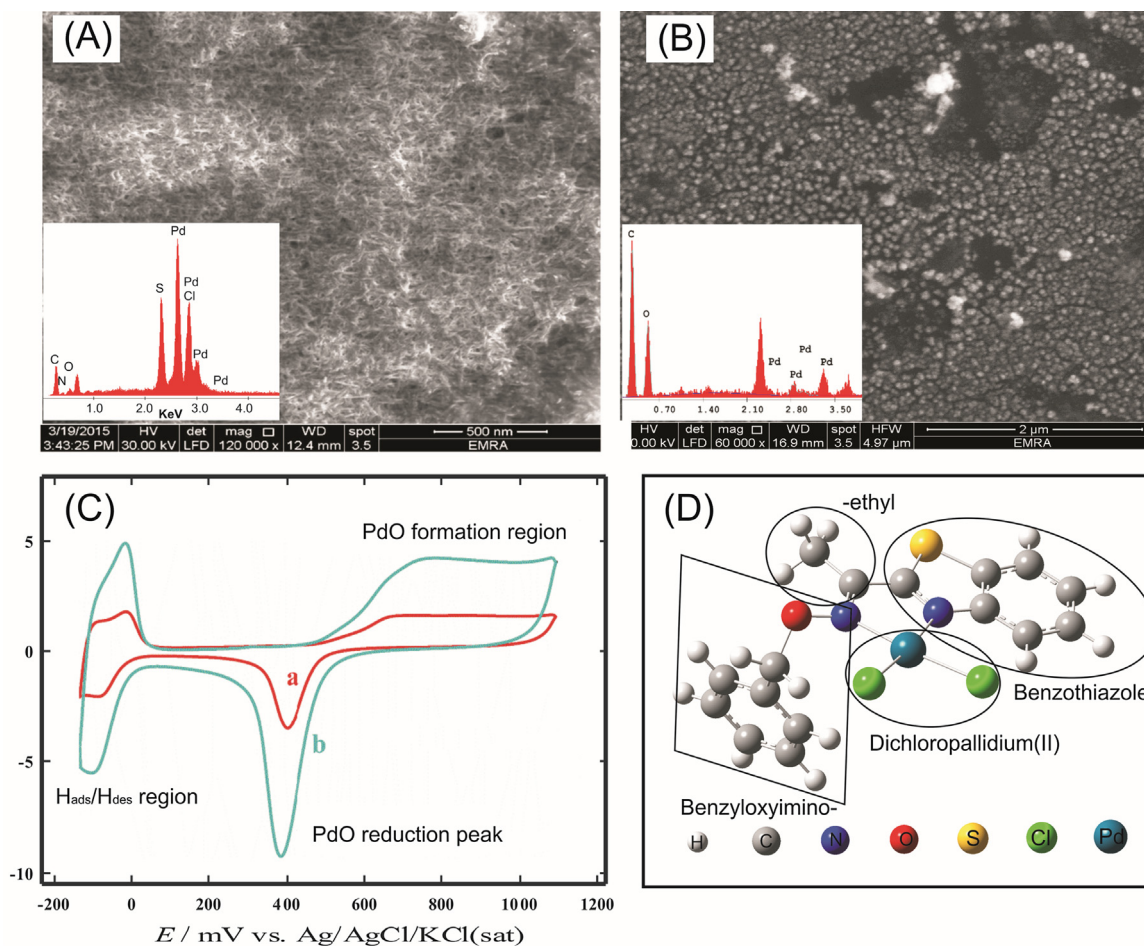


Fig. 1. (A) FE-SEM (inset shows EDX pattern), (B) TEM, (C) CV measured in 0.5 M H_2SO_4 with scan rate of 0.1 V/s at PdNPs/GC (curve a) and nano-Pd-complex/GC (curve b), and (D) The optimized structure calculated at the B3LYP/6-311++G(d, p)/LanL2DZ level of theory of nano-Pd-complex.

Download English Version:

<https://daneshyari.com/en/article/6473156>

Download Persian Version:

<https://daneshyari.com/article/6473156>

[Daneshyari.com](https://daneshyari.com)