Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

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Original Research Paper

Synthesis, characterization, and enhanced formic acid electrooxidation activity of carbon supported MnO_x promoted Pd nanoparticles

Ahmet Bulut [a], Mehmet Yurderi [a], Orhan Alal [b], Hilal Kivrak [b],*, Murat Kaya [c], Mehmet Zahmakiran [a]

[a] Nanomaterials and Catalysis (NanoMatCat) Research Laboratory, Department of Chemistry, Van Yüzüncü Yıl University, 65000 Van, Turkey
[b] Department of Chemical Engineering, Van Yüzüncü Yıl University, 65000 Van, Turkey
[c] Department of Chemical Engineering and Applied Chemistry, Atilim University, 06836 Ankara, Turkey

ARTICLE INFO

Article history:
Received 7 December 2017
Received in revised form 23 February 2018
Accepted 1 March 2018
Available online xxxx

Keywords:
Formic acid
Hydrogen
Fuel cell
Palladium
Manganese oxides

ABSTRACT

Formic acid (HCOOH) is one of the promising fuels for direct liquid fed fuel cells. However, CO poisoning is a major challenge for the development of effective catalytic system for formic acid electrooxidation (FAEO). Herein, a novel CO-resistive activated carbon supported Pd-MnO_x bimetallic catalyst (Pd-MnO_x/C) was presented for FAEO. Pd-MnO_x/C catalyst was prepared via simple and reproducible surfactant-free deposition-reduction technique. The characterization of this novel Pd-MnO_x/C catalyst was performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), bright field transmission electron microscopy (BFTEM), high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and scanning transmission electron microscope-energy dispersive X-ray spectroscopy (STEM-EDX). The characterization results revealed that Pd and MnO_x nanoparticles (NPs) were well dispersed and separately nucleated with a mean diameter of 2.9 nm on the surface of active carbon. FAEO studies were performed on both Pd-MnO_x/C and Pd/C catalysts to comprehend the effect of separately formed MnO_x on the electrocatalytic activity of Pd NPs. The electrochemical measurements were carried out by using Cyclic Voltammetry (CV) and Chronoamperometry (CA), CO-Strriping Voltammetry, Lineer Sweep Voltammetry (LSV), Electrochemical impedance spectroscopy (EIS) techniques. Electrochemical results revealed that FAEO was activated by the addition of MnOx. $Pd_{0.6}$-$Mn_{0.4}$ exhibited the optimum catalytic activity with 0.95 A/mg Pd current density. The sum of their results clearly points that the existence of MnO_x NPs enhances the electrocatalytic activity of Pd NPs by increasing their CO-resistivity and durability throughout the FAEO.

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are commonly regarded as a competent substitute to batteries for portable power devices. Along this line, hydrogen fuel cells (H_2-PEM) and direct methanol fuel cells (DMFCs) have gained intensive research interest [1–5]. The critical limitations for commercialization of H_2-PEM are the high cost of miniaturized H_2 containers, potential dangers in the transportation of H_2, and low gas-phase energy density of H_2. Although, liquid methanol (CH_3OH) has superior energy density compared to H_2, the toxicity of methanol vapor is still a remaining concern for commercialization of DMFCs for on-board systems. In this respect, formic acid (HCOOH; FA) is a potential fuel for Direct formic acid fuel cells (DFAFCs) because it is non-toxic and non-flammable and formed in biomass processing. As compared to DMFCs, DFAFCs have higher electromotive force (1.45 V) and smaller crossover flux through the proton exchange membrane [6–9]. Considering these enhanced properties of DFAFCs, one could note that DFAFCs are promising alternative power sources for portable device applications.

In DFAFCs, FAEO proceeds via dehydrogenation ($HCOOH \rightarrow H_2 + CO_2$) pathway to form CO_2 and dehydration ($HCOOH \rightarrow H_2O + CO$) pathway to form CO followed by further oxidation to CO_2 at higher potentials [6–9]. Pt and Pd are two mainly used active metals for FAEO. Pt surface is readily poisoned due to CO formation as a result of the dehydration of FA. CO formation hinders the dehydrogenation at lower potentials on Pt surfaces, while FA dehydrogenation prevails to form CO_2 on Pd surfaces. In this context, Pd gains more

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* Corresponding author.
E-mail address: hilalkivrak@yyu.edu.tr (H. Kivrak).

https://doi.org/10.1016/j.apt.2018.03.003
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Please cite this article in press as: A. Bulut et al., Synthesis, characterization, and enhanced formic acid electrooxidation activity of carbon supported MnO_x promoted Pd nanoparticles, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.03.003

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attention in consequence of its lower cost and higher reactivity. However, monometallic Pd is deactivated because of CO adsorption resulting from the reduction of CO_2 at H-adsorbed Pd surfaces [10]. Hence, the development of novel Pd based catalysts with improved activity and stability has great importance for the practical applications of DFAFCs systems [11,12].

The literature survey exposes that the incorporation of secondary metal increases the CO resistance of Pd and avoids CO-deactivation of Pd active sites. Various Pd based bimetallic alloys (Pd-M) [13] and core@shell (M@Pd) [14,15] nanostructures have been tested in FAO and enhanced activities with respect to monometallic Pd have been reported by these studies. Of particular importance, in our recent work [16], we have reported that amine-grafted silica supported catalytically inactive MnO_x NPs (NPs) drastically increase the activity of Pd NPs, which exist on the same support as physical mixture, in the dehydrogenation of aqueous FA solution. The preliminary investigation of this phenomenon was done by CO-stripping voltammetry studies conducted on both Pd/NH_2-SiO_2 and Pd-MnO_x/NH_2-SiO_2. Results indicates that both CO poisoning resistance and the activity of Pd NPs are significantly enhanced by the existence of separately nucleated MnO_x NPs that act as CO-sponge around the catalytically active Pd NPs.

Herein, it is present a facile synthesis Pd-MnO_x NPs supported on active carbon, referred to as Pd-MnO_x/C, and their excellent catalysis for FAEO. Pd-MnO_x/C catalyst was prepared by simultaneous reduction method. Furthermore, it was characterized by ICP-OES, P-XRD, BFTEM, HRTEM, and STEM-EDX point analyses. The sum of the results of these multi-pronged analyses shows that the formation of well-dispersed separately nucleated Pd(0) and MnO_x NPs with an average size of 2.9 ± 1.2 nm on the surface of activated carbon.

FAEO activity measurements were performed via Cyclic voltammetry (CV), Chronoamperometry (CA), and CO stripping voltammetry, and Lineer sweep voltammetry (LSV) Electrochemical impedance spectroscopy (EIS) techniques. Their results clearly reveal that the existence of MnO_x NPs improves the electrocatalytic activity of Pd NPs by increasing their CO-resistivity and durability throughout the FAEO and the optimum catalyst composition was found to be $Pd_{0.6}Mn_{0.4}$.

2. Experimental

2.1. Materials

Palladium(II) nitrate dihydrate ($Pd(NO_3)_2{\cdot}2H_2O$), manganese(II) chloride dihydrate ($MnCl_2{\cdot}2H_2O$), sodium borohydride ($NaBH_4$) and activated carbon (C) were purchased from Sigma-Aldrich®. FA (CH_2O_2, >96%) was obtained from Merck®.Milli-Q Water Purification System was employed to take distilled water.

2.2. Preparation and characterization of catalysts

Pd-MnO_x/C catalyst was prepared by the conventional impregnation method and subsequent reduction steps [17]. First of all, 5 mL aqueous solution of $Pd(NO_3){\cdot}2H_2O$ (12.35 mg, 46.3 µmol Pd), $MnCl_2{\cdot}2H_2O$ (3.1 mg, 19.1 µmol Mn), and C (140 mg) were mixed during 3 h. Following this, 1.0 mL aqueous solution of $NaBH_4$ (39 mg, 0.98 mmol) was added to this mixture and further stirred for half an hour. Then, the resulting mixture was centrifugated at 6000 rpm for 5 min. After centrifugation, it was washed with copious water, filtrated, and dryed in oven at 373 K. As a result of this procedure, Pd-MnO_x/C catalyst was obtained. These catalysts were prepared at varying Pd:MnO_x atomic ratios.

The metal contents of the catalysts were measured by ICP-OES. Crystal structure of these catalysts samples was determined via XRD (MAC Science MXP 3TZ, Cu-Kα radiation, wavelength 1.54 Å). Prior to microscopy measurements, samples were prepared by taking and adding on a copper grid by drop wise from dilute catalyst suspension. The conventional TEM images of these samples were taken at 120 kV by using a JEOL JEM-200CX transmission electron microscope. In addition, HRTEM, STEM, and HAADF-STEM measurements were accomplished via at 200 kV JEOL JEM-2010F transmission electron microscope. STEM-EDX system is connected to Oxford EDX system and the Inca software to collect the data and to operate. The XPS measurements were performed by a Physical Electronics 5800 XP spectrometer (Al-Kα X-ray source, 1486.6 eV, 15 kV, 350 W, with pass energy of 23.5 eV).

2.3. Electrochemical measurements

The Pd-MnOx catalysts were prepared and their electrochemical measurements were performed in a conventional three-electrode cell with a CHI 660E potentiostat. A Pt wire employed as a counter electrode and Ag/AgCl as a reference electrode. Furthermore, a modified glassy carbon electrode (GCE) was used as a working electrode. GCE surface was cleaned polished with alumina prior to use. In order to prepare the modified GCE electode, 5–6 mg catalyst was dispersed in 1 mL Aldrich 5% Nafion solution and a catalyst ink was obtained. Afterward, 4 µL ink was dispersed on the GCE surface and GCE surface was dried at room temperature. Before the CV, CA, CO stripping, EIS, and poisoning measurements, the electrolyte was saturated by nitrogen and the electrode surface was activated in 0.5 M H_2SO_4. First of all, CV measurements were carried out in 0.5 M H_2SO_4 solution on Pd-MnOx catalysts. CVs were taken at −0.25 to 1 V potentials with a scan rate of 20 mV s^{-1}. Furthermore, CVs were recorded at −0.25 to 0.8 V with a scan rate of 10 mV s^{-1} in 0.5 M H_2SO_4 + 0.5 M HCOOH for Pd-MnOx catalysts to examine their FAEO activities. To investigate the FAEO stability of Pd-MnOx catalysts, CAs were recorded in 0.5 M H_2SO_4 + 0.5 M HCOOH at 0.2 V for 200 s with 1000 s pulse width and 2 s quiet times. One could see that current values were given as normalized per gram of Pd because the FA adsorption and dehydrogenation occurs on Pd sites. CO stripping voltammetry measurements of Pd-MnOx catalysts were carried out in 0.5 M H_2SO_4 and CO purged solution. Firstly, to remove the dissolved oxygen, 0.5 M H_2SO_4 solution was bubbled with pure nitrogen for 30 min and then, CO was then purged into solution for 20 min at 0 V. After 20 min, excess CO was then purged with nitrogen for 30 min. LSV technique was employed to investigate the poisoning capacity of these catalysts. Before to LSV measurements, surface was pretreated and the details of surface pretreatment were given in literature [18,19]. Then, potential was held constant at −0.1 V. Finally, LSV measurements were taken at 0.0 V in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at 10 mV s^{-1}.

Electrochemical impedance spectroscopy (EIS) as a dynamic method was used to examine the electrochemical behavior of carbon supported Pd based catalysts. EIS measurements were recorded between 100 kHz and 0.01 Hz in 0.5 M H_2SO_4 + 0.5 M HCOOH at amplitude of 10 mV at varying electrode potentials. The electrode potential was varied from 0 to 400 mV vs. NHE for these catalysts.

3. Results and discussion

3.1. Preparation and characterization of Pd-MnO_x/C catalyst

Pd-MnO_x/C catalyst were prepared by following $NaBH_4$ reduction in water at room temperature at varying Pd:Mn atomic ratios. Then, these catalysts were prepared by ICP-OES, P-XRD, XPS, BFTEM, and STEM-EDX-line analyses. The metal content of the

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