Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene)-supported Pd-Sn nanoparticles dispersed on Au electrode for formic acid oxidation

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PdSn nanoparticles dispersed on polycrystalline Au electrode and poly(3,4-ethylenedioxythiophene)-modified polycrystalline Au electrode for the electro-oxidation of formic acid were synthesized using electrochemical methods.

Pd and Sn nanoparticles on polycrystalline Au electrode were synthesized via successive potentiodynamic electrodeposition. For the electrosynthesis of PdSn/PEDOT-modified polycrystalline Au electrode, PEDOT polymer was electrodeposited on polycrystalline Au via potentiostatic polymerization. Then, same electrodeposition procedure was done for PdSn deposition on PEDOT-modified Au electrode. Afterwards, the electrosynthesized electrocatalysts were subjected to electrochemical characterization using cyclic voltammetry (CV). Lastly, the electrocatalysts were subjected to formic acid electro-oxidation by potential cycling.

PdSn dispersed on Au and PdSn on PEDOT-modified Au electrode were successfully electrosynthesized. The first oxidation peak of formic acid shifted at lower potential when Sn is added. Moreover, the PdSn/PEDOT-modified Au electrode has a more enhanced electrooxidation towards formic acid oxidation than the Pd/Au and PdSn/Au catalyst due to the shift in the oxidation potential.

Keywords: polycrystalline Au, poly(3,4-ethylenedioxythiophene), formic acid, potentiostatic electropolymerization, potentiodynamic deposition, Pd, Sn

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INTRODUCTION

Nowadays, fuel cells are widely known for being an attractive device in obtaining electrical energy directly from chemical reaction. Low temperature fuel cells (e.g., direct alcohol fuel cell (DAFC), direct formic acid fuel cell (DFAFC), direct dimethyl ether fuel cell (DDEFC)) have made progress in recent years [1]. In particular, aqueous solution of formic acid is a potentially attractive fuel for fuel cell due to its several advantages: less toxicity, low crossover effects with formic acid, use of high concentration of formic acid (~15 M) in DFAFCs and higher power density than methanol [1, 2]. Also, formic acid is relatively benign and non-explosive especially when dissolved in water which makes it facile in distribution and handling as compared to hydrogen. Moreover, it can be activated even on neat platinum, and then decomposes to smaller fragments — CO₂, protons and electrons — at very high efficiency as compared to methanol and has lower energy content than hydrogen and methanol [3].

For recent years, Pt and Pt-based electrocatalysts were synthesized for formic acid electrooxidation [1, 2, 4]. However, these electrocatalysts can be easily poisoned by CO-like intermediates formed in the formic acid oxidation. Gojkovic´ and Obradovic´ [5] postulated that Pt nanoparticles dissolve in the presence of CO on the surface and in the electrolyte, and successively deposit on Au substrate. These results indicate the instability of Pt nanoparticles in the presence of CO in formic acid electrooxidation. Fortunately, several studies showed that Pd metal was more active than Pt for formic acid oxidation and it has demonstrated that Pd catalysts exhibits high catalytic activity for formic acid and overcomes CO poisoning effect [2, 6]. However, Pd catalysts have several drawbacks as an anodic catalyst. Pd catalyst is unstable and when used for long formic acid oxidation process, the oxidation current greatly decreases [1]. Upon further investigation, the addition of another metal such as Au, Ir, Co, Sn, and Pb can improve not only the stability of the Pd catalyst but also the catalytic activity [1–4].

Additional advancement in DFAFCs is the incorporation of conducting polymer matrix as a support for the metal nanoparticles for formic acid oxidation. A thin film of an electronically conducting polymer could act as a good dispersion medium for catalyst particles, which could improve the interfacial properties between the electrode and the electrolyte [7]. From the study of Patten and colleagues [8], ultrathin PEDOT film support was used for the dispersion of Pt nanoparticles for methanol and formic acid electro-oxidation. It was reported that it gave an enhanced oxidation towards formic acid [8].

In this study, the electrochemically synthesized PdSn nanoparticles on polycrystalline Au and PEDOT-modified polycrystalline Au electrodes were subjected to formic acid oxidation and their electrocatalytic effects towards formic acid electro-oxidation were evaluated. In addition, the stability of the electrochemically-prepared catalysts was also investigated.

EXPERIMENTAL

Materials and chemicals. 3,4-ethylenedioxythiophene (EDOT) was purchased from Sigma-Aldrich (USA) and was used as received. Pd particles and Sn particles were synthesized from PdCl₂ (>99.9%, Merck Germany), SnSO₄ and SnCl₂, respectively. Perchloric acid (HClO₄), hydrochloric acid (HCl), and sulfuric acid (H₂SO₄) are of suprapur grade and were purchased from Merck, Germany. Electrocatalytic activities of the modified electrodes were studied using analytical grade formic acid (Scharlau, Spain). Aqueous solutions were prepared using ultrapure water (TOC < 5.00 ppb; Resistivity = 18.2 MΩcm; Analytic Waters, Philippines). Gold wire (diameter: 1 mm; purity 99.95%) was purchased from Nilaco,
Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene)

Corporation, Japan and the gold disk (area: 0.0366 cm²) was purchased from Metrohm, Switzerland.

**Instrumentation.** All electrochemical measurements were performed in a conventional 3-electrode electrochemical cell at room temperature and were carried out using EDAQ potentiostat (Australia) under control of software (EChem, EDAQ) in a three-compartment electrochemical cell under an atmosphere of nitrogen (CIGI, Inc.). Pt rod and Ag/AgCl (sat. 3 M KCl) were used as counter and reference electrode, respectively. The working electrodes used were Pd/Au, PdSn/Au, and PdSn/PEDOT-Au. All potentials reported in this paper are presented in the Ag/AgCl scale. Also, surface characterization of the catalyst was done using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS).

**Procedure.** PdSn particles dispersed on polycrystalline Au electrodes were prepared via electrochemical deposition of palladium and tin. Successive electrodeposition of Pd and Sn were done using 5:1 optimum molar ratio, respectively, using potential cycling from −0.4 V to 0.85 V at 10 mV/s for 24 and six cycles, respectively.

PdSn particles dispersed on PEDOT-modified Au electrodes were prepared in two steps, namely: (a) aqueous electropolymerization of EDOT, and (b) electrochemical deposition of palladium and tin. Firstly, electropolymerization of 0.01 M EDOT in 0.10 M HClO₄ on a Au disk electrode was done via potentiostatic method at 1.10 V for 540 sec. Then, same procedure for the electrodeposition of PdSn on polycrystalline Au electrode was used.

Evaluation of the electrocatalytic activity towards formic acid was done using 1.0 M formic acid in 0.5 M H₂SO₄ by cyclic voltammetry from E = 0.0 to 1.0 V at a scan rate of 50 mV·s⁻¹.

The surface morphology of the catalysts was done via SEM and EDXS.

**RESULTS AND DISCUSSION**

**Au-supported electrocatalysts.** The modification of the polycrystalline Au electrode was done by electrodepositing monometallic Pd using potentiodynamic method. The Au electrode was subjected first to electrochemical characterization using 1.0 M HCOOH in 0.5 M H₂SO₄ in order to assess the electrocatalytic activity. As shown in Fig. 1, there are no peaks from E = −0.2 to 1.0 V, which means that Au has no electrocatalytic effect towards formic acid oxidation in acidic medium and can be used as a suitable support. When the Au electrode was electrodeposited with Pd, it was seen that the electrode has oxidation peaks at A₁ = 0.18 V, A₂ = 0.37 V, and A₃ = 0.55 V. This means that Pd has an electrocatalytic effect towards formic acid. Peak A₁ portion corresponds to the deprotonation of the formic acid species and the adherence to the Pd surface. The second peak, A₂, is the primary oxidation of formate species to CO₂ then lastly, peak A₃ is the other oxidation peak of formic acid where another formate species is oxidized to yield another CO₂ molecule [1].

The EDXS analysis of the electrocatalysts attests for the presence of several components of the catalyst. Based on the EDXS profile...
presented (Fig. 2), the presence of Pd was confirmed (with an elemental percentage of 69.61%) which means that Pd was successfully electrodeposited on the polycrystalline Au surface. The presence of Au in the EDXS profile suggests that Pd did not fully cover the Au surface and thus, the electrocatalysts are porous.

Even though Pd has electrocatalytic activity towards formic acid, it is unstable because the Pd particles were poisoned by CO species. To compensate for that, the addition of another metal at the surface of Pd is seen as a solution. In this study, it is observed that Sn can be a great promoter for the Pd catalyst even though it is non-catalytic when used solely. Sn enhances the electronic properties of Pd, thus increasing the electrocatalytic activity towards formic acid electro-oxidation [1, 7]. As seen in Fig. 3, the second and third oxidation peaks increased by 14 and 4 mA/cm², respectively, which suggests for the significant increase in the electrocatalysis of formic acid when Sn is added. Also, the oxidation potential shifted by 0.08 V to the left of the voltammogram, which indicates more ease of oxidation of formic acid. This is due to the enhanced electronic properties of Pd by the addition of promoter Sn [1].

**PEDOT-modified Au-supported electrocatalysts.** For the PEDOT-modified Au-supported electrode, the modification of Au surface was done by electropolymerizing EDOT using 0.01 M EDOT in 0.1 M HClO₄ using potentiostatic method. Potentiostatic electropolymerization is a good method because it uses a constant potential; therefore, it does not over-oxidize the polymer, which could decrease its conducting properties unlike potentiodynamic method of electropolymerization [10]. As seen in Fig. 4, the EDXS profile of PEDOT/Au electrode suggests the presence of O, S, Cl, and Au. This means that PEDOT was successfully electropolymerized on the Au surface because of the presence of the elements O and S, which are PEDOT constituents. Even though PEDOT does not contain Cl constituents, Cl is present in the EDXS analysis. This is due to the electrolyte used in dissolving the EDOT monomer which is HClO₄. The presence of Au suggests that PEDOT is porous. Moreover, the SEM image of PEDOT shows a cauliflower morphology.

When PdSn particles were electrodeposited on PEDOT-modified Au electrode support, it is observed that it has electrocatalytic activity towards formic acid.
Electrochemical synthesis and characterization of poly(3,4-ethylenedioxythiophene)

When PdSn bimetallic system is incorporated, two pronounced oxidation peaks are seen. Compared to Pd/PEDOT-Au electrocatalyst, PdSn on PEDOT-modified Au electrode still has better electrocatalytic activity towards formic acid electro-oxidation. Also, the oxidation peaks were more pronounced compared to the PEDOT-modified Au electrode dispersed with Pd particles.

Based on the SEM images in Fig. 6, it is seen that PdSn particles still form islands on the polymer surface and the metal particles could not be differentiated from each other. However, the EDXS profile of PdSn/PEDOT-Au electrode can prove the presence of Pd, Sn and PEDOT constituents. Even though Sn has an insignificant percentage it is observed that Sn still plays a major role in the electrocatalysis of formic acid as seen in Fig. 5. Based on Fig. 7, the dispersion of the metal particles are more...

Figure 4. (A) SEM image of PEDOT-modified Au electrode and (B) its EDXS profile indicating the presence of constituents of the polymer.

Figure 5. Cyclic voltammetric profile of Pd/PEDOT-Au (Inset, stability graph) and PdSn/PEDOT-Au towards formic acid oxidation via potential cycling from –0.20 to 1.00 V at 50 mV/s for 20 cycles.

Figure 6. SEM image and EDXS profile of PdSn/PEDOT-Au electrocatalyst.

Figure 7. SEM image and EDXS profile of PdSn/PEDOT-Au electrocatalyst.
uniform on the polymer-based support rather than on the metal-based support because of the higher surface area of the polymer.

**CONCLUSIONS**

The electrochemically synthesized Pd-based catalyst is a good catalyst for formic acid oxidation. The addition of promoter, such as Sn, enhances the electrocatalytic activity and stability of Pd catalyst towards formic acid oxidation. In addition, the oxidation peak is shifted at lower potential when Sn is added. Interestingly, the PdSn/PEDOT-modified Au electrode was seen to have an electrocatalytic effect towards formic acid electro-oxidation. Subsequently, the presence of PEDOT as a support matrix stabilizes the Pd particles leading to a more enhanced catalytic activity. Also, PdSn catalyst enhances the second oxidation peak of the formic acid electro-oxidation.

**REFERENCES**


