



Formic acid oxidation on Pt–Au nanoparticles: Relation between the catalyst activity and the poisoning rate

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ABSTRACT

Pt–Au nanoparticles supported on high area carbon were prepared by simultaneous reduction of Au and Pt precursors and by reduction of Pt precursor on already prepared Au nanoparticles. The first method produced a solid solution of Pt in Au containing ~5% Pt with the remaining Pt on the nanoparticles' surface. For the Pt:Au precursor ratio of 1:4 and 1:9, the surface ratio was found to be 0.70:0.30 and 0.55:0.45, respectively. By the second method with the Pt:Au precursors ratio of 1:12, the surface ratio was 0.30:0.70. The voltammetric peaks of Pt–oxide reduction and CO_{ads} oxidation demonstrated electronic modification of Pt by Au in all catalysts. With decreasing Pt:Au surface ratio the activity for HCOOH oxidation increases and surface coverage by CO_{ads} decreases. The highest activity under potentiodynamic and quasi steady-state conditions without poisoning by CO_{ads} was observed for the catalyst with the lowest Pt:Au surface ratio. Chronoamperometric test showed that its high catalytic activity is associated with a high deactivation rate. It was postulated that too strong adsorption of a reactive or non-reactive intermediate caused by electron modification of Pt by underlying Au, is responsible for the deactivation. This result stresses that high Pt dispersion, necessary for promotion of the dehydrogenation path in HCOOH oxidation, can produce too strong adsorption of intermediates causing deactivation of the catalyst.

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) using formic acid as a fuel, i.e. direct formic acid fuel cell (DFAFC), has been attracting significant attention since recognition of its advantages over direct methanol fuel cell (DMFC): crossover of HCOOH through the polymer membrane is lower and the equilibrium and the onset potential of the oxidation of HCOOH is less positive compared to CH₃OH [1,2].

Pt is not suitable electrocatalyst for HCOOH oxidation because it is prone to the poisoning by CO_{ads} formed in dehydration path. This makes most of the Pt surface unavailable for HCOOH oxidation through dehydrogenation path [3]. The initial activity of Pd is much higher comparing to Pt, but deactivation of Pd over time is significant [4] and Pd is not stable in acid media [5]. A solution of the problem of HCOOH oxidation catalysis is to use Pt-based bimetal catalysts. Although bifunctional mechanism and electronic effect can influence oxidative removal of CO_{ads} from the Pt sites, the

better approach is to prevent CO_{ads} formation by employing ensemble effect, i.e. to increase selectivity of Pt toward dehydrogenation path. This is based on the recent study of HCOOH oxidation on Pt(1 1 1) modified by cyanide ions performed by Cuesta et al. [6] in which they established that at least three contiguous Pt sites are necessary for dehydration of HCOOH, while at most two Pt sites are required for dehydrogenation of HCOOH.

After early work of Rach and Heitbaum [7], many articles published in the last several years confirmed that HCOOH on Pt–Au surfaces exhibits high current densities at low potentials with much less CO_{ads} on the surface than single Pt catalyst [8–16]. Although some other metals like Bi [17] and Pb [18] showed similar promotion of the dehydrogenation path on Pt, Pt–Au catalysts are more promising for practical application in DFAFC because of great chemical stability of Au.

General feature of the HCOOH oxidation catalysis on Pt–Au bimetal surfaces is that decreasing Pt content in the catalyst favors dehydrogenation path. In our previous work [13] we used bulk Pt electrode modified by submonolayers of Au and Au electrodes modified by submonolayers of Pt to demonstrate that increased selectivity toward dehydrogenation path in HCOOH oxidation is mainly caused by an ensemble effect. The electronic modification

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of Pt by Au, which might increase interaction of HCOOH molecule with Pt, probably contributes to rather low onset potential of the reaction [8,10]. Among several types of Pt–Au nanocatalysts, the best performance (high current density without CO_{ads} poisoning) was exhibited by Pt-decorated Au nanoparticles with Pt: Au ratio of 1:8 [10] and by Pt decorated nanoporous Au, previously annealed to enable surface alloying and good dispersion of Pt and Au [12].

This paper reports the synthesis of Pt–Au nanoparticles supported on high area carbon by simultaneous reduction of Au and Pt precursors and by reduction of Pt precursor on already prepared Au nanoparticles; and compares their activity for HCOOH oxidation. For the first time the reaction orders with respect to HCOOH and H⁺ ions were determined for the Pt surface unpoisoned by CO_{ads}. A problem of rapid deactivation of Pt–Au nanocatalyst with high initial activity is observed and discussed.

2. Experimental

2.1. Preparation of the catalysts

Au and bimetallic Pt–Au nanoparticles supported on high area carbon were prepared by microwave-assisted polyol method [19,20]. The advantage of microwave over conventional heating during nanoparticles synthesis is uniform heating of the substrate by the electromagnetic waves leading to a more homogeneous nucleation and shorter aggregation time. Another type of Pt–Au nanoparticles was prepared by decoration of Au nanoparticles with Pt by using ascorbic acid (C₆H₈O₆) as the reducing agent [8,21]. It was found that ascorbic acid as a weak reducing agent with a slower reduction rate in respect to NaBH₄ or NH₂OH, forms nanoparticles with better monodispersity and morphology [21].

In the first synthesis carbon black (Vulcan[®] XC-72R, produced by Cabot Corp., BET specific surface area 246 m² g⁻¹) was added in ethylene glycol and ultrasonicated over 1 h. Then HAuCl₄ (10% solution, Alfa Aesar), or a mixture of H₂PtCl₆ (10% solution, Alfa Aesar) and HAuCl₄ was added in the suspension of carbon black in ethylene glycol. pH of the suspension was adjusted to ~8. After heating for 60 s in the microwave oven (Samsung, 2450 MHz, 600 W), the suspension was vacuum-filtered and the powder was washed with 0.02 M NH₄OH, as it was shown that chloride anions can be eliminated from the samples by washing with ammonia solution of low concentration [22]. All the prepared samples were dried in Ar atmosphere at 80 °C over 8 h. The Pt–Au/C catalysts of two different compositions were prepared by mixing precursors in Pt: Au atomic ratio of 1:4 and 1:9. The corresponding catalysts are labeled according to the preparation method (polyol – P) and overall ratio of Pt and Au atoms as P-1:4 and P-1:9.

Prepared Au/C was modified with Pt in accord to a typical preparation of core–shell Au–Pt colloid [4,8]. A suspension containing 1.0 mg cm⁻³ Au/C was mixed with 0.20 M H₂PtCl₆ solution in the amount to get 1:1 ratio of surface Au atoms and Pt(IV) ions. The surface of Au nanoparticles was estimated from the average Au grain size determined in XRD measurements. This Pt: Au ratio correspond to the overall composition ratio of 1:12. Next, 0.1 M solution of ascorbic acid was added to the suspension. The molar ratio of ascorbic acid and Pt ions was 4:1. After stirring for 20 h, the suspension was precipitated, washed, and dried in Ar atmosphere at 80 °C over 8 h. The prepared electrocatalyst is also labeled according to the preparation method (ascorbic acid, AA) and overall Pt: Au atomic ratio, as AA-1:12.

For a comparison of voltammetric features and electrocatalytic activity, a sample of Pt nanoparticles supported on XC-72R carbon (Pt/C), manufactured by E-Tek, was used. According to Esparbé et al. [23], this catalyst consists of Pt nanoparticles with an

average diameter of 2.5 nm and electrochemically active surface area of 73 m² g Pt⁻¹.

2.2. Thermogravimetric analysis

Metal loading of the Au and Pt–Au/C samples was determined by thermogravimetric analysis (TGA) [24] using a SDT Q600 TGA/DSC instrument (TA Instruments). Several milligrams of the sample were heated to 800 °C at the heating rate of 20 °C min⁻¹ in the air atmosphere (flow rate 100 cm³ min⁻¹). Upon measuring of metal mass in the residual ash, metal loading was calculated to be between 12 and 19 mass%, and these data were used for calculation of specific surface area of the catalysts.

2.3. XRD and TEM characterization

The synthesized samples were examined by X-ray diffraction (XRD) in order to determine phase composition and to estimate particle size. The measurements were carried out with a SIEMENS D500 diffractometer operated with a CuK α source at 35 kV and 20 mA in the 2 θ range from 10° to 100° with 0.02° 2 θ s⁻¹. High resolution transmission electron microscopy (HRTEM) was used to characterize morphology and size of the nanoparticles and their distribution on the carbon support. The measurements were performed at the National Center for Electron Microscopy using the TEAM I TEM/STEM double-aberration-corrected electron microscope at 80 kV equipped with the Gatan 2k × 2k CCD cameras.

2.4. Electrochemical characterization

For electrochemical characterization, the Pt/C, Au/C, and Pt–Au/C powders were applied on a glassy carbon (GC) substrate in the form of a thin-film [25]. The GC electrode (Tacussel rotating disk electrode, 5 mm in diameter) was polished with 1, 0.3, 0.05 μ m Al₂O₃ slurry and washed ultrasonically with high purity water (Millipore, 18 M Ω cm resistivity) before use. The catalyst inks were made by mixing of 2.0 mg of the powder with 1 cm³ of high purity water and 50 μ L of the Nafion[®] solution (5 wt.%, 1100 E.W., Aldrich). After 1 h of agitation in an ultrasonic bath, 10 μ L of the suspension was placed onto the GC electrode and left to dry overnight. This procedure of film preparation gave 0.10 mg of powder per cm² of the GC surface.

A three-compartment electrochemical glass cell was used with a Pt wire as the counter electrode and a saturated calomel electrode as the reference electrode. All the potentials reported in the paper are expressed on the scale of the reversible hydrogen electrode (RHE). The cyclic voltammetry was carried out in 0.05–1.0 M H₂SO₄ (Merck) prepared with high purity water. The electrolytes were deaerated by the N₂ bubbling. Upon immersion into the electrolyte, a thin-film electrode was pre-conditioned by the potential cycling between 0.05 and 1.46 V at 0.1 V s⁻¹. After ten cycles the scan rate was reduced to 0.05 V s⁻¹ and the second cycle was recorded and used for the surface characterization.

The electrochemical active area of Au was determined from the reduction of the monolayer of gold oxide formed under the potential cycling with the anodic limit just before the onset of oxygen evolution, i.e. at the Burshtein's minimum [26]. The charge of the reduction of monolayer gold oxide was taken to be 400 μ C cm⁻² [12,27].

The electrochemically active area of Pt in Pt/C catalyst was calculated from the hydrogen desorption charge corrected for the double-layer charging assuming 210 μ C cm⁻² for monolayer hydrogen adsorption. However, for Pt–Au surfaces, especially those with low Pt content, this method was found to be unreliable because hydrogen adsorption/desorption features were barely seen or even absent, although the peak for Pt–oxide reduction and a

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