Electrochimica Acta 224 (2017) 56–63

Contents lists available at ScienceDirect

Electrochimica Acta

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

Microwave-Assisted Synthesis of Pt-Au Nanoparticles with Enhanced Electrocatalytic Activity for the Oxidation of Formic Acid

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ARTICLE INFO

Article history:
Received 13 October 2016
Received in revised form 15 November 2016
Accepted 5 December 2016
Available online 7 December 2016

Keywords:
PtAu alloy
electrocatalysis
formic acid oxidation
microwave hydrothermal synthesis
potential oscillations

ABSTRACT

We report the microwave-assisted hydrothermal synthesis of bimetallic Pt-Au nanoparticles with different Pt/Au mole ratio, and investigate their performance towards the electro-oxidation of formic acid. The as-synthesized Pt-Au sol was dispersed on a graphite electrode, without any binding agents, which allowed us to control the mass of alloy deposited. Pt-Au alloys showed better activity than bulk Pt and/or Pt nanoparticles towards the oxidation of formic acid, as evidenced by the decrease in the onset potential and the higher currents in the corresponding cyclic voltammograms. The higher activity is due both to atomic-ensemble effects, which lead the reaction through the so-called direct pathway with insignificant CO poisoning, and to electronic effects, which optimised the interaction between the catalyst surface and the reactive intermediate in the direct path. Further insight into the individual contributions of atomic-ensemble and electronic effects and their effect on the catalytic activity was provided by the analysis of galvanostatic potential oscillations.

1. Introduction

Formic acid is an attractive fuel candidate for polymer electrolyte membrane fuel cells (PEMFCs) converting liquid fuel due, among other reasons, to its lower crossover diffusion through the membrane [1], its better oxidation kinetics and also because the onset potential for the formic acid oxidation reaction is lower compared to that of other C1 and C2 alcohols, such as methanol and ethanol [2]. Although Pt is very active towards the formic acid oxidation reaction (FAOR), it is susceptible of being strongly poisoned by intermediate reaction products, particularly CO, which has been traditionally explained by the so-called dual-path reaction mechanism [3,4]. For this reason, alloying of Pt with other metals has been attempted in order to improve its catalytic properties.

A second metal can promote several effects in Pt-bimetallic surfaces [5]. For instance, gold has been extensively used to influence the activity and selectivity of Group VIII metals due to its intrinsic stability [6–8]. Alloying changes the electronic structure of both metals in the alloy, as in the case of Group VIII metals combined with Group IB metals [9]. The resulting changes in the adsorption energy of reactants, intermediates and products may result in enhanced reaction rates, that can be electrochemically detected by an increase in the current density at low potentials [10]. Additionally, alloying can lead to, purely geometric, atomic-ensemble effects, that can channel the reaction through one of two or more possible pathways [11,12]. For example, the alloying metal may disrupt sites composed of three contiguous Pt, which have been shown to be necessary for the dehydration of formic acid to adsorbed CO [13]. In principle, alloying will always give rise to both electronic and atomic-ensemble effects, although their weight in the final properties of the alloy will depend on the actual metal employed and on the atomic fraction of each material at the surface. However, it is difficult to obtain homogeneous and reproducible materials with traditional methods of synthesis.

The catalytic activity of bimetallic nanoparticles depends both on their composition and their structural properties, such as size, shape and morphology, which may be tuned via the synthesis method. Due to the potential technologic applications of

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http://dx.doi.org/10.1016/j.electacta.2016.12.022
0013-4686/

nanoparticles, systematic studies of their physicochemical properties, both intrinsic (like, e.g., their atomic structure), and extrinsic (like, e.g., their size and porosity) are required. Classical methods of synthesis involve the reduction of metal precursor salts under heating conditions to promote the interdiffusion of the cations inside the metal lattice. These processes have slow rates and, consequently, long heating times are required. Processes which facilitate the synthesis of these materials by reducing the energy consumption and the reaction times are highly desirable. For instance, despite the high efficiencies obtained in the synthesis of Au [14–16] and Pt [17] nanomaterials by conventional methods, it is still necessary to optimize control over nucleation and growth, to impede agglomeration [18] (in order to obtain nanostructured materials with high surface area and good electrochemical properties), and to develop cleaner and more efficient processes according to the Green Chemistry Principle [19]. Among all modern methods of synthesis, the application of microwaves has attracted attention, due to easy handling and sample preparation, as well as to its diverse applications in organic synthesis, solid state reactions, and preparation of nanostructured materials [20–24]. The fundamental distinctive advantage of the application of microwaves to synthesis processes is linked to its high efficiency and low cost, since microwave energy is absorbed directly by the reactants instead of being absorbed by the vessel or reactor, like in conventional methods. Thus, uniform heating leads to more homogeneous nucleation and shorter crystallization times. Preparation of metastable phases not accessible by conventional methods of synthesis has also been reported, [25,26] although microwave-specific thermal effects, as well as microwave non-thermal effects, are still a controversial matter. In this way, microwave-hydrothermal processes are gaining significance due to the feasibility of controlling the structure of the materials and the reaction selectivity by simply controlling temperature, reaction time and pressure. In consequence, this is a broad interdisciplinary field that is growing rapid and steadily.

This paper reports the synthesis, using microwave-assisted hydrothermal synthesis, of Pt-Au nano-alloys with high electrocatalytic activity for the FAOR.

1.1. Chemicals

All solutions were prepared using analytical grade reagents (purchased from Aldrich in the purest commercially available grade) and Milli-Q water (18.2 MΩ cm, Millipore). Solutions were degassed using nitrogen (99%, White Martins) and all measurements were carried out at room temperature.

2. Experimental

2.1. Instrumentation

All electrochemical experiments were performed with an Autolab PGSTAT302 electrochemical workstation (Eco Chemie) in a three-compartment electrochemical glass cell. The working electrode was a highly porous graphite electrode and the auxiliary electrode was a platinum wire. All potentials are reported versus the reversible hydrogen electrode (RHE). Synthesis of nanoparticles was performed in a microwave reactor Monowave 400 (Anton Paar). Scanning electron microscopy (SEM) images were obtained with a Supra-35 ZEISS FESEM system. Transmission electron microscopy with high resolution (HR-TEM) was performed with a Tecnai G2, FEI microscope. X-ray diffraction data were obtained using a Shimadzu diffractometer model XRD-6000, electrode voltage 30 kV, Cu Kα radiation, in θ–2θ mode, at $1^\circ s^{-1}$. XPS data from the nanoparticles and the corresponding electrodes were recorded with a nine channeltron Phoibos-150 hemispherical analyzer (specs) under a vacuum better than 1×10^{-9} mbar using Mg Kα radiation and a constant pass energy of 20 eV. The binding energy scale was referenced to the C 1 s signal of the adventitious carbon layer which was set at 284.6 eV.

2.2. Nanoparticles synthesis and working electrode preparation

Pt-Au nanoalloys were synthesized by chemical reduction of the precursor salts (hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot 6H_2O$) and hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$)) with trisodium citrate dehydrate ($Na_3C_6H_5O_7$, TSC) under microwave radiation, controlling the $[PtCl_6]^{2-}$ and $[AuCl_4]^-$ ratios in order to obtain Pt, Pt_3Au, PtAu, $PtAu_3$ and $PtAu_9$ nanoparticles. All reagents were added to the microwave reactor, without any previous treatment, and were heated at 150 °C for 6 minutes (10 bar). The obtained sol was centrifuged and washed several times with deionized water and dried at 60 °C. 1 mg of the nanoparticles was dispersed in ethanol, dropped on the graphite electrode and dried at 100 °C. The as-prepared electrodes were activated by cyclic voltammetry in 0.5 M H_2SO_4 until a *quasi* steady-state was reached. For the CO stripping measurements, CO was adsorbed at 0.3 V for 20 min and the adsorbed CO was oxidized at a scan rate of 20 mV s^{-1} after eliminating the dissolved CO from the solution with N_2 for 30 min. Successive scans were carried out to verify the absence of CO in solution. The electrochemical active surface area (EASA) of platinum was calculated from the hydrogen adsorption/desorption charge assuming a charge of 210 μC cm^{-2} for a monolayer of adsorbed hydrogen, and compared with the charge of CO stripping, assuming a charge of 420 μC cm^{-2} for a monolayer of adsorbed CO.

3. Results and Discussion

3.1. Structural characterization: SEM, HR-TEM and XRD

Structural parameters are crucial in determining the reactivity of the nanoparticles, as they affect both electronic and geometric effects [5]. Therefore, a deep characterization of all these parameters may lead us to a better understanding of their catalytic performance. Electronic effects can be described based on the energy distribution of the d band density of states (DOS), and all other effects can be explained by geometric factors. We have performed SEM, HR-TEM and XRD measurements in order to study the correlation between the lattice parameters and the electronic structure, as examined with XPS (see below), in these systems. Fig. 1 shows the SEM (A-E), HR-TEM (F-J) and the selected-area electron diffraction (SAED) pattern for the Pt, Pt_3Au, PtAu, $PtAu_3$ and $PtAu_9$ nanoparticles, respectively. All samples (Fig. 1A–E) show small nanoparticles with similar size distributions. Clearly, aggregation of the nanoparticles increased with gold content. As shown by the HR-TEM images and the corresponding SAED patterns, all nanoparticles show hexagonal shape and high crystallinity, with predominantly (111) facets (inset), which we attribute to a combination of the experimental conditions and synthesis method employed. [27–29] The measured distances between two adjacent atomic rows for Pt nanoparticles was approximately 0.23 nm, which are characteristic of the separation between (111) planes of *fcc* Pt. Increasing the gold content led to an increase of defects. It was not possible to determine changes in the crystal lattice spacing related to the increase in the gold content, because the lattice parameters for platinum and gold (3.920 Å and 4.080 Å, respectively) are very close to each other.

The XRD pattern of the nanoparticles is shown in Fig. S1. All XRD peaks could be indexed as face centered cubic (*fcc*) structure, and no peaks corresponding to other phases were detected. The sharp peaks indicate good crystallinity and the wide peaks, in