Fabrication of nanoporous metals by dealloying of ternary alloys: evaluation of electrocatalytic properties

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ABSTRACT

Novel nanoporous structures have been formed by electrochemical dealloying of ternary precursors (i.e., Ag-Au-Pt with a platinum content of ca. 1, 2 and 4 at.% and 77 at.% of silver) in acidic media. Dealloying is a common corrosion process in which the less-noble element is selectively dissolved from the metallic solid solution, leaving behind a nanoporous sponge composed almost entirely of the more noble alloy constituents. The presence of Pt, even in such a small concentrations, reduces the feature size of the nano-structure (< 7 nm), minimizes coarsening of the porosity and helps preserve the structural integrity of the structure. Furthermore, these structures show greater catalytic activity for methanol electro-oxidation reaction in alkaline solutions, if compared with the nanoporous structure formed from Ag-Au alloy (77 at.% of silver). This enhancement is exemplified by a broad and high anodic peak during the positive scan and two secondary oxidation peaks in the subsequent reverse scan.

Keywords: dealloying, ternary alloys, platinum, methanol electrooxidation

1 INTRODUCTION

The development of new and more robust materials for applications in chemical processes, sustainable energy, remediation of the environment and many other fields is one of the biggest challenges in the 21st century. Porous materials, such as zeolites, aerogels or even porous metals, offer versatile properties and characteristics (e.g., pore sizes, morphology, conductivity) that have been found very useful in a variety of fields [1-3]. Particularly, porous precious metals, with pore size distribution below 10 nm, are useful in electrocatalysis, catalysis, sensing and other applications. Dealloying is, among possible methods to make porous precious metals, a very effective technique. Typically, one starts with a monolithic alloy in any form (e.g., bulk or thin films) and selectively dissolves the less noble element from the alloy leaving an interconnected ligament/pore structure with high surface area and with a very good control of porosity and size [4-6].

Nanoporous gold (NPG), typically formed by dealloying of silver-gold alloys, has dominated the literature in this area because these alloys display single-phase solid solubility across the entire range of compositions, and produce a structure with open porosity [5,7,8]. Unfortunately, NPG suffers from a major limitation: coarsening of the porosity by surface self-diffusion of Au, which becomes a limiting factor for long term functionality in applications like catalysis [9]. Additionally, NPG has relatively limited catalytic activity, although nanoscale gold does have catalytic abilities not shown by the bulk metal [10,11]. Recently, it has been reported that adding platinum to the silver-gold precursor is beneficial in reducing the coarsening of the nanoporous layer [12]. Platinum, which does not dissolve, is immobile relative to Au and blocks step edges, creating a porous structure with a smaller length scale. Furthermore, the presence of Pt may induce distinctive catalytic properties.

Our main objective in the present study is to characterize the effect that small amounts of Pt has on the nanoporous structure. For that purpose, a comparison between the nanostructure formed from binary (Ag-Au) and ternary (Ag-Au-Pt) precursors, with the same silver content and with a systematic variation in Pt content, is made. Besides the comparison of the quatitative morphology of the different structures, their average composition and the amount of exposed Pt on the surface, the electrocatalytic activity towards methanol oxidation is evaluated.

2 EXPERIMENTAL

Ag-Au alloy with 23 at.% Au was obtained as cold-rolled 200 µm sheet from Goodfellow Metals, Cambridge, UK. Ag-Au-Pt alloys with approximately 1, 2 and 4 at.% Pt and 77 at.% Ag were obtained as cold-rolled 200 µm sheet from Ames National Laboratory, Iowa, USA. The composition of all alloys were verified before any electrochemical experiment by electron probe X-ray microanalyzer (EPMA – CAMECA SX-50/51) equipped with 3 wavelength dispersive spectrometers (WDS) and operated at 20 kV and 15 nA. All the specimens were annealed and then used in the as-annealed condition without any further surface preparation.

All electrochemistry was performed using a Gamry 600 potentiostat. Dealloying was carried out in 0.77 M $HClO_4$ solution prepared from Analar grade $HClO_4$ (Alfa-Aesar, 62%). All solutions were prepared with 18 MΩ cm de-ionized water. An electrochemical cell was used in all cases with a platinum counter electrode and saturated

mercury/mercury sulfate reference electrode (MSE, 640 mV vs. SHE), which was housed in a separate compartment and connected to the electrochemical cell via a Luggin probe. Prior to any dealloying, the solutions were de-aerated by high-purity nitrogen purging. The true area of the electrodes was determined by means of voltammetric profiles in 1 M $HClO_4$ solution. Immediately after dealloying, cyclic voltammetry (CV) in the double layer region of potentials (-240 to 50 mV vs. MSE) was done at different scan rates. In all cases, the capacity of 1 cm^2 of Au and Pt was considered equal to 28 µF [13]. The surface area was normalized by dividing the true area of the electrode by the mass of the dealloyed layer.

BET surface area and pore size distribution were carried out using the Autosorb-1 Analyzer (Quantachrome Instruments). Nitrogen adsorption/desorption isotherms were obtained at 77 K. The BET surface area was later normalized by mass of the dealloyed layer (DL). In order to assess the presence of Pt on the surface of the nanoporous structure, under-potential-deposition (UPD) of hydrogen was used [14,15]. Immediately after the specimen was dealloyed and rinsed with de-ionized water, it was immersed in 1 M H_2SO_4 solution (EMD, 95-98%) in a three-electrode cell with a MSE reference electrode, a Pt wire as a counter electrode and the dealloyed specimen as a working electrode. The solution was de-aerated for 15 min before the experiment. CV curves were obtained at 25 °C between -630 and 0 mV vs. MSE, at 20 mV s^{-1}. The charge associated with the monolayer formation was assumed to be 210 µC cm^{-2}_{Pt} [16].

For the microstructural characterization (e.g., ligament size), dealloyed samples from all alloys were broken in air and the fracture surface was photographed using high magnification scanning electron microscopy (SEM - Hitachi S-5200). Cross-sectional metallographic specimens were prepared for the determination of the dealloyed layer thickness. In all the cases, specimens were polished up to 0.05 µm using alumina powder. To determine the average chemical composition of the dealloyed layer, a scanning electron microscope (SEM - JEOL JSM6610-Lv) complemented by an Oxford INCA X-sight energy dispersive X-ray spectrometer (EDS) was used. The composition profile across the layer was determined with a transmission electron microscope (TEM - Hitachi HD-2000), complemented by Oxford INCA X-sight EDS, using ultra-microtomed samples of 30-50 nm thickness.

For the methanol electro-oxidation experiments, samples were immersed in a solution of methanol (Caledon, 99.8%) in 5 M KOH (Aldrich, 90%). The counter electrode was platinum helical wire. A mercury/mercury oxide reference electrode (Hg/HgO - 20% KOH, 100 mV vs. SHE) was used for these experiments. Prior to any measurement, the solution was de-aerated by high-purity nitrogen purging. CV was performed between -900 and 650 mV vs. Hg/HgO at 15 mV s^{-1}. All currents were normalized by the true area of the electrode.

3 RESULTS

Recently, there has been a resurgence of interest in dealloying, thanks to the remarkable properties of the nanoporous products such as the resulting interconnected porosity (as shown in Figure 1), high surface to volume ratio and distintive mechanical properties [17-19].
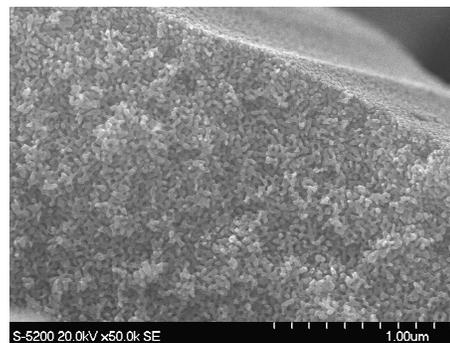

Figure 1: Morphology of Ag_{77}:Au_{23} dealloyed in 0.77 M $HClO_4$ at 40 °C and 550 mV vs. MSE showing an interconnected ligament/pore structure.

The effect of a ternary element in dealloying has been demonstrated to be practically important [12,20]. However, to assess in greater detail the impact of the Pt on the nanoporous structure, Ag-Au-Pt alloys with ca. 1, 2 and 4 at.% Pt and 77 at.% Ag were evaluated. Their compositions (measured by EPMA-WDS) were very close to the nominal compositions. As shown in Figure 2, just by adding 1 at.% of Pt, the feature size in the structure changes significantly. In the case of NPG, the ligament size is approximately 14 nm. The structure formed from an alloy with only 1 at.% Pt shows a ligament width of ca. 7 nm. The higher the Pt content, the smaller the ligament size, as shown in Table 1. The average residual silver content in the dealloyed layer (also shown in Table 1), increases with the Pt content. This retained silver must exist buried in the core of the ligaments with a shell comprised of gold and platinum. While dealloying is progressing and silver is removed from the dealloying front, the Ag removal from the already formed ligaments continues; however, because Pt reduces Au mobility, the post-porosity coarsening is hindered, resulting in higher Ag contents. In other words, the small silver content in the NPG is due to exposure of buried silver to the electrolyte during coarsening behind the dissolution front. This was confirmed by comparing the silver content gradient across the dealloyed layer (measured by TEM EDS). It was determined that in the binary alloy the silver profile increases from ca. 28 at.% (close to the surface of the sample) to around 57 at.% close to the dealloying front. On the ternary alloys, on the other hand, the profile is less pronounced, increasing from ca. 47 at.% at the edge of the sample to ca. 58 at.% at the dealloying front. Consequently, the dealloyed layer is thicker in the ternary alloys (see Table 1).
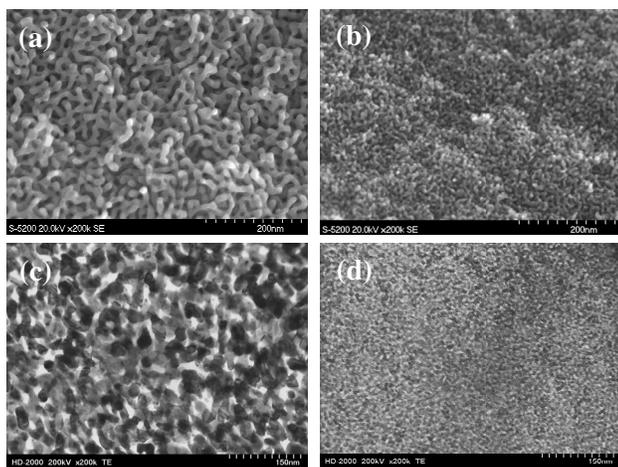
Figure 2: SEM and TEM images of $Ag_{77}:Au_{23}$ (a, c) and $Ag_{77}:Au_{22}:Pt_1$ (b, d) nanoporous structures grown in 0.77 M $HClO_4$. Charge density: 5 C cm^{-2}. Dealloying potential: 550 mV vs. MSE. Temperature: 25 °C.

Precursor	Ligament width (nm)	Thickness of layer (µm)	Residual Ag (at. %)
$Ag_{77}:Au_{23}$	13.8 (0.7)	7.8 (0.2)	36.0 (0.4)
$Ag_{77}:Au_{22}:Pt_1$	6.8 (0.4)	8.9 (0.9)	53.1 (1.1)
$Ag_{77}:Au_{21}:Pt_2$	6.0 (0.2)	9.0 (0.2)	56.4 (0.4)
$Ag_{77}:Au_{19}:Pt_4$	4.3 (0.2)	8.7 (0.5)	60.1 (0.9)

Table 1: Physical characteristics and residual silver of different nanoporous structures developed at 25 °C and 550 mV vs. MSE in 0.77 M $HClO_4$. Charge density: 5 C cm^{-2}. The numbers in brackets represent the 95% CI.

The pore size distributions of all the nanostructures are shown in Figure 3. As expected, the NPG has a wider pore size distribution, with a peak pore size in the range of 17 nm. With the presence of Pt, the pore size is reduced; in the case of the sample with 1 at.% Pt, the peak pore size is in the range of 11 nm. Based on the working model of porosity evolution [21], it has been suggested that during dealloying the Pt should segregate to the edges of the growing islands, stabilize them and ultimately reducing the length scale of porosity [12]. As observed by TEM, (Figures 2c and 2d) the pore sizes (light regions) show good agreement with the BET method.

The effect of the Pt content on the surface area of the developed structure (measured by three different methods) is shown in Figure 4. The surface area (given per mass of dealloyed layer) doubled just by adding 1 at.% of Pt to the precursor (from ca. 15 m^2 g$^{-1}_{DL}$ to almost 29 m^2 g$^{-1}_{DL}$). By adding more Pt, the surface area keeps increasing; however, it shows a decreasing dependence upon Pt concentration.

The presence of Pt on the surface of the ligaments was quantified by UPD of hydrogen, showing a nominal Pt surface area of ca. 1.1, 2.6 and 5.6% of the true surface area

of the nanoporous structures (e.g., BET surface area) for the alloys with 1, 2 and 4 at.% of Pt respectively. XPS analyses yielded similar Pt contents.
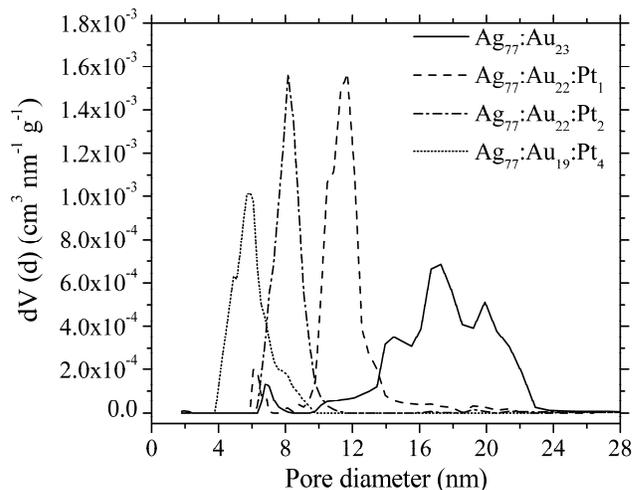

Figure 3: Pore size distribution of freshly-formed nano-structures in 0.77 M $HClO_4$. Charge density: 5 C cm^{-2}.
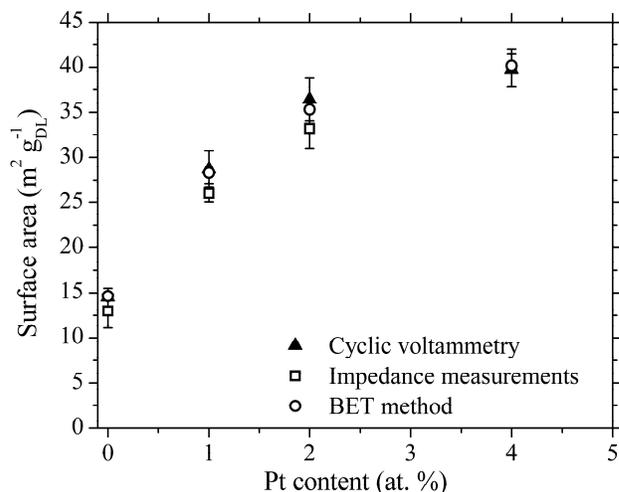

Figure 4: Surface area as a function of the Pt content in the nanoporous structure. Error bars represent the 95% CI calculated from triplicate runs.

Nanoporous materials, in which the interconnected interstices and channels extend in three dimensions, have a desirable structure for catalysis allowing the flow of molecules and electrons. Additionally, it is well-known that alloying Pt with other metals often improves its catalytic activity, as well as reducing the cost of the overall material [22]. Au-Pt alloys clearly display interesting properties [23,24]. Thefore, exploring the electrocatalytic properties of nanoporous gold with small amounts of platinum has an important place in the search for novel nanocatalysts, even if eventually such materials would be too expensive. Besides the presence of Pt that is exposed to the surface,

the strong chemisorption of oxygen species on the porous gold will provide many oxygenated species which promote further oxidation of carbonaceous intermediates typically absorbed on the Pt surface, which may also reduce the poisoning effect [25].

Freshly prepared structures (with and without Pt) were characterized in alkaline solution by means of CV. Figure 5 shows CV profiles of NPG and the structure with 1 at.% Pt. As reported before, on Au electrodes two reactions can occur; at lower potentials (below ~0.3 V vs. Hg/HgO) methanol is oxidized to formates via a four-electron transfer reaction, whereas at higher potentials, methanol molecules are oxidized to carbonates with the exchange of six electrons [26]. By comparing the two catalysts, it is clear that there is a significant difference in the current density and peak potentials between the two structures. The sharp rising current in the forward scan can be ascribed to the characteristic methanol oxidation on the surface (based on CV profiles recorded in the supporting electrolyte – not shown here). The current density on the ternary alloy is significantly higher than that on the binary Ag-Au alloy, and the onset of methanol oxidation starts at more negative potentials (ca. 400 mV more negative than that of NPG). During the reverse sweep, the reduction peaks occuring at 0.1 V (a and b in Figure 5) are related to the reduction of gold surface oxides and the oxidation peaks (c and d) are related to the reactivation of methanol oxidation.
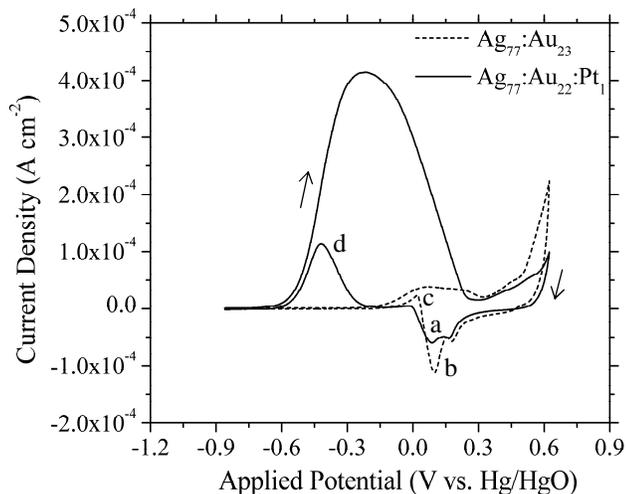

Figure 5: CVs of NPG formed on $Ag_{77}:Ag_{23}$ and $Ag_{77}:Au_{22}:Pt_1$ in a solution of 5 M KOH - 2 M MeOH. Potential scan rate: 15 mV s^{-1}. Temperature: 25 °C.

For the alloy with 1 at.% Pt, the highest anodic peak current per unit mass catalyst was ~120 A g$^{-1}_{DL}$.

In summary, nanoporous metals formed from ternary alloys with small amounts of Pt represent a new class of materials, in which their morphology is stabilized and their pore size is significantly reduced. Additionally, Pt also helps to significantly enhance their catalytic behaviour towards methanol electro-oxidation. The presence of Pt

and the smaller feature size clearly contribute in the enhanced performance.

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