



Short communication

# A comparison of alloyed and dealloyed silver/palladium/platinum nanoframes as electrocatalysts in oxygen reduction reaction

Chien-Liang Lee<sup>\*</sup>, Kun-Lung Huang, Yao-Lung Tsai, Yi-Ju Chao

Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan

## ARTICLE INFO

## Article history:

Received 6 May 2013

Received in revised form 9 July 2013

Accepted 9 July 2013

Available online 18 July 2013

## Keywords:

Nanoring

Alloy

Dealloy

Cathodic catalyst

Oxygen reduction reaction

## ABSTRACT

Ag-rich Ag–Pd–Pt nanoframes and their dealloyed nanoframes were compared successfully as catalysts in oxygen reduction reaction (ORR). Supported by electrochemical quartz crystal microbalance results, the dealloying process was complete and a Pd–Pt-rich surface for the ternary nanoframes was obtained by a cyclic voltammetric method in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte after the second cycle. Comparing the data of mass activity analyses in 1 M NaOH electrolyte showed that the ternary catalysts without dealloying can show faster kinetics in ORR.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The mass activities of Pt in oxygen reduction reactions (ORRs) by Cu/Pt [1] and Ag/Pt [2,3] nanoparticles prepared via electrochemical dealloying can be enhanced to be greater than those of commercial Pt catalysts. Electrochemical dealloying approach of the selective removal of Cu or Ag from alloyed nanoparticles by an etching process is effective for the adequate exposure of active Pt shell on bimetallic surface [3]. However, it is recognized that high OH<sup>−</sup> coverage on Pt can cause the suppression of ORR in an alkaline electrolyte [4]. According to general scientific opinion, a highly effective catalyst in a four-electron ORR process must have optimal OH coverage [5]. One promising way to reach this goal is to introduce strongly OH-adsorbing atoms with Pt atoms on the surface of catalyst. These strongly OH-adsorbing atoms, such as Ir, Rh, and Pd atoms, show higher adsorption strength for hydroxyls than Pt atoms do [6], thus decreasing the OH-coverage of Pt-rich catalytic surface via repulsion effect [5]. This difference in OH-coverage possibly results from the behaviour of native Pd and Pt, as the Pd–Pt system just forms weak alloys [7]. For Pt–Pd catalysts with Pd-enriched surface, there is still a problem in improving the ORR activity. Ag, which adsorbs hydroxyl ions weakly, can usually be mixed with Pd to make a uniform alloy [8] for improving the ORR activity [8] while being partly soluble with Pt [9]. This metallurgical behaviour provides a possibility for adjusting the OH-adsorbing strength of a ternary catalyst.

The goal of the present study is to demonstrate a method for preparing Ag–Pd–Pt nanoframes with Ag-rich Pd–Pt shell, and successfully dealloying these nanoframes to a Pd–Pt shell by cyclic voltammetric

method. The dealloying pathway was successfully monitored by electrochemical quartz crystal microbalance (EQCM). Subsequently, supported by thin-film electrode analyses, the mass activities of Ag–Pd–Pt nanoframes and kinetics of generated HO<sub>2</sub><sup>−</sup> were studied in a NaOH electrolyte and compared to those of dealloyed nanoframe catalysts.

## 2. Experimental

Ag nanoplates as reactants were synthesized using a previously reported modified seed-growth method [10] to increase their yield. Approximately 25 μL of 1.11 × 10<sup>−2</sup> M Pd(CH<sub>3</sub>COO)<sub>2</sub> solution (2.78 × 10<sup>−7</sup> moles) was added to 3 mL of well-stirred Ag nanoplate solution at a constant temperature of 25 °C and let to react for 70 min. Next, 25 μL of 1.11 × 10<sup>−2</sup> M H<sub>2</sub>PtCl<sub>6</sub> solution was added to this Ag–Pd nanoplate solution at 25 °C. Ag–Pd–Pt nanoframes were obtained after another 70 min. The synthesized Ag–Pd–Pt nanoframes in solution (3 mL) were separated by centrifugation at 700 rpm and redispersed in 3 mL of deionized water to reduce the interactions with AgCl produced during the displacement period. 0.05 mmole H<sub>2</sub>PdCl<sub>4</sub> solution and 1 mmole HCl solution were added in 10 mL 12.5 × 10<sup>−2</sup> mmole hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB) solution. Then, 0.36 mmole NaBH<sub>4</sub> solution was dropped to reduce Pd nanoparticles at 95 °C. Based on the same method, Pt nanoparticles were prepared when 0.05 mmole H<sub>2</sub>PdCl<sub>4</sub> was replaced by 0.01 mmole H<sub>2</sub>PtCl<sub>6</sub> and 1 mmole C<sub>16</sub>TAB solution (10 mL) was used.

For recording the dealloying kinetics, EQCM (Autolab PGATAT 30 combined with Seiko EG&G QCA 922) was employed and the ternary catalysts were applied at constant load of 50 μg cm<sup>−2</sup> onto an Au electrode. A three-electrode cell consisting of an Au working electrode, a Pt

<sup>\*</sup> Corresponding author. Fax: +886 7 3830674.

E-mail addresses: [cl\\_lee@url.com.tw](mailto:cl_lee@url.com.tw), [cl\\_lee@kuas.edu.tw](mailto:cl_lee@kuas.edu.tw) (C.-L. Lee).

counter electrode, and an Ag/AgCl reference electrode was used for cyclic voltammetry (CV).

The microstructure and composition analyses of Ag–Pd–Pt catalysts before and after dealloying were conducted by using a transmission electron microscope (TEM) combined with energy-dispersive X-ray spectroscopy (EDX), and crystalline structures were detected using X-ray diffraction analysis (XRD).

The activity of Ag–Pd–Pt catalysts was evaluated by performing rotating ring-disk electrode (RRDE) measurements. The samples were prepared by dropping a solution containing 40  $\mu\text{g}$  of the catalyst and 3  $\mu\text{L}$  of 5% Nafion onto a 0.196  $\text{cm}^2$  glassy carbon electrode (GCE) disk. RRDE measurements were performed using a combination of an RRDE system (AFMSRCE, Pine Co., Ltd.) and a bipotentiostat (CHI 727D). A catalyst-modified rotating GCE disk/platinum ring electrode (ring area = 0.11  $\text{cm}^2$ ) was used as a working electrode. In addition, a Pt counter electrode and a Ag/AgCl (3 M KCl) reference electrode were used for the polarization measurements in a  $\text{N}_2$  or  $\text{O}_2$  saturated aqueous 1 M NaOH solution. Disk potential was varied from 0 to  $-0.8$  V, while the ring potential was maintained at 0.145 V in order to oxidize the  $\text{HO}_2^-$  produced by the  $\text{O}_2$  reduction at the disk electrode. The collection efficiency (N) of ring electrode obtained by reducing ferricyanide at the disk electrode was detected and approximately 0.192.

### 3. Results and discussion

Fig. 1A shows the TEM image of Ag–Pd–Pt nanoframes. The crystal structures of prepared catalysts were identified through their XRD patterns, and the results are shown in Fig. 1B. A strong peak at  $38.21^\circ$  was assigned to the (111) diffraction similar to Ag (111), and negligible peaks of (200), (220) and (311) planes were detected in the nanoframes with an Ag-rich structure. Ag nanoplates are typically composed of (111) basal and edge planes [11]. The resulting XRD spectrum suggests a galvanic displacement reaction, where the Pd and Pt atoms were deposited and crystals were grown on the enclosed planes of Ag nanoplates. Some quasi-spherical particles separated from nanoframes in the Fig. 1A by centrifugation are composed of ternary alloy. Additionally, according to the results from the EDX analysis of a single nanoframe, the weight percentages for Ag, Pd, and Pt are 78.48%, 13.81%, and 7.71%, respectively, confirming the Ag-rich composition of the alloyed nanoframe suggested by the XRD result.

Fig. 2 shows the CV curves and corresponding mass changes of Ag–Pd–Pt nanoframes experiencing dealloying in the first, second, third, and 25th cycle using EQCM. It should be noted that the two initial cycles clearly reveal the advancing of the dealloying process. The first cycle clearly shows two stronger peaks between 0.4 V and 0.9 V for the anodic reaction associated with oxidative dissolution and Ag leaching [2]. The mass change of this anodic dissolution in the first cycle is  $22.25 \mu\text{g cm}^{-2}$ . Sharp peaks at 0.4 V to 0.9 V and a corresponding mass change of  $7.82 \mu\text{g cm}^{-2}$  are obtained in the second cycle. In the first cycle, the broadening of the peaks for Ag dissolution probably suggest that Ag located with Pt and Pd was removed, and particularly the Ag atoms on the surface [2]. Next, for the third and the 25th cycle, the peak representing the removal of Ag is absent and the curve of the corresponding mass change is flat. This indicates that the Ag dissolution reaction stopped before this cycle. Significant peaks for the hydrogen adsorption and desorption in the catalysis were obtained. The result from the EDX analysis of a single dealloyed nanoframes shows that the weight percentage for Ag, Pd and Pt are 50%, 31.41% and 18.59%, respectively. This result means  $9.96 \mu\text{g/cm}^2$  for Ag in a dealloyed catalyst, confirming the obtained EQCM data. Additionally, broad (111) peaks for the dealloyed nanoframes are observed in Fig. 1B and the location of this peak is at  $39.09^\circ$ , which is higher than that of the nanoframes before dealloying. This implies that the crystal size of the catalysts is reduced and Pd–Pt is enriched on the surface of the ternary alloy nanoframes after removing most of the Ag.

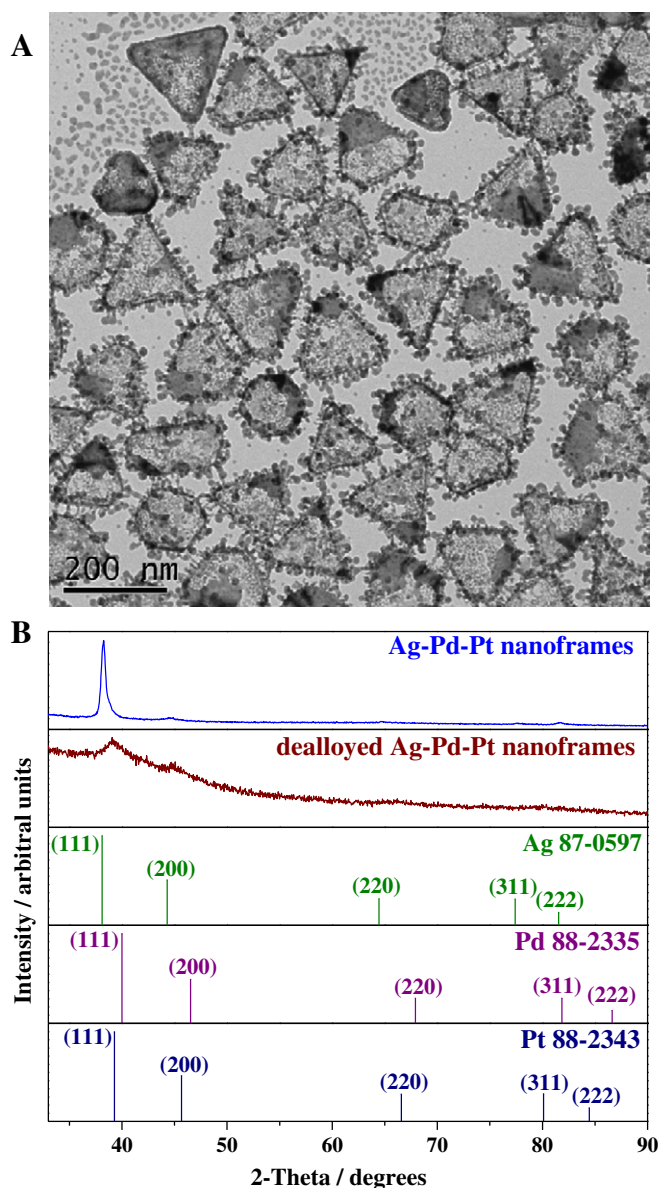


Fig. 1. (A) TEM image of Ag–Pd–Pt nanoframes, and (B) XRD patterns of Ag–Pd–Pt nanoframes and dealloyed nanoframes.

The catalytic properties of alloyed and dealloyed nanoframes in the ORR were examined, and their electrochemical properties were initially measured using CV. Fig. 3A shows a comparison of CV curves after measuring the electrochemical property of the nanoframes before and after the dealloying in aqueous 1 M NaOH solutions saturated with  $\text{N}_2$ . With Ag-rich nanoframes, the sharp oxidation peak at 0.2 V can be ascribed to the formation of  $\text{Ag}_2\text{O}$  [12]. The subsequently observed cathodic peak at approximately 0.1 V is attributed to the reduction of  $\text{Ag}_2\text{O}$ . The reduction of Pd–Pt alloy oxides occurred at approximately  $-0.36$  V, similar to the CV features of Pd–Pt nanoparticles [13]. It should be noted that for dealloyed nanoframes, the individual reduction of PtO and PdO is observed at  $-0.2$  V and  $-0.27$  V, respectively, which can be confirmed from the cyclic voltammograms of Pt and Pd nanoparticle, as shown in the inset. This suggests that Pt atoms and Pd atoms do not mix on the dealloyed surface and that Ag atoms are likely to alloy and bridge with Pt atoms and Pd atoms in the original nanoframe. This similar result for Au is observed in Au–Pd [14].

The kinetic properties and activities of these catalysts compared with those of nanoparticles were studied by RRDE experiments. Fig. 3B shows the polarization curves of  $\text{O}_2$  reduction catalysed by alloyed and

Download English Version:

<https://daneshyari.com/en/article/6601569>

Download Persian Version:

<https://daneshyari.com/article/6601569>

[Daneshyari.com](https://daneshyari.com)