



Accelerated growth from amorphous clusters to metallic nanoparticles observed in electrochemical deposition of platinum within nanopores of porous silicon



Álvaro Muñoz-Noval ^{a,*}, Kazuhiro Fukami ^{b,*}, Akira Koyama ^b, Dario Gallach ^c, Daniel Hermida-Merino ^d, Giuseppe Portale ^{d,e}, Atsushi Kitada ^b, Kuniaki Murase ^b, Takeshi Abe ^f, Shinjiro Hayakawa ^a, Tetsuo Sakka ^f

^a Department of Applied Chemistry, Hiroshima University, Hiroshima 739-8527, Japan

^b Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

^c Department of Applied Physics, Universidad Autonoma de Madrid, Madrid, Spain

^d DUBBLE CRG BM26, The European Synchrotron Radiation Facility, Grenoble, France

^e Faculty of Mathematics and Natural Sciences, University of Groningen, Netherlands

^f Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto 615-8510, Japan

ARTICLE INFO

Article history:

Received 5 July 2016

Received in revised form 22 July 2016

Accepted 27 July 2016

Available online 28 July 2016

Keywords:

Nanoporous
Nanoparticles
Deposition
Platinum
XAFS

ABSTRACT

This study examined the formation of amorphous platinum (Pt) clusters in nanopores of porous silicon at an initial stage of pore filling. The time dependency of the chemical state and local structure of Pt in the nanoporous silicon were characterized by X-ray absorption fine structure spectroscopy (XAFS). Initially, the Pt deposits showed non-negligible amounts of PtO₂, formed by surface oxidation from the atmosphere, suggesting that the particle size was quite small. Deep analysis of extended XAFS (EXAFS) strongly suggested that Pt at the early stage of deposition was amorphous. The mechanism of amorphous Pt formation is discussed based on the confinement effect for Pt complex anions in nanopores.

© 2016 Published by Elsevier B.V.

1. Introduction

Platinum (Pt) is a key material in the heterogeneous catalysis of hydrocarbons and other energy-related compounds. Supporting and anchoring of reactive metals in porous scaffolds greatly increases the available active surface area in catalytic devices [1–3]. It also offers the possibility of the durability of catalysts by avoiding particle agglomeration [4,5].

Fine-tuning of metal nanoparticles is easily achieved by electrochemical deposition. Porous silicon is a candidate porous electrode that can deposit metals by applying a potential or by reducing metal ions coupled with the oxidation of porous silicon itself [6]. When using a porous electrode, homogeneous distribution of metal nanoparticles along the porous layer is normally difficult to achieve. Recently, we succeeded in generating a uniform deposition of Pt within a nanoporous silicon layer by tuning the hydration properties of porous electrodes as well as Pt complex anions [7–10]. Pt precursors with a larger ionic size (lower charge density) are highly accumulated in hydrophobic nanopores. This accumulation helps uniform deposition in nanopores.

Because the properties of the solution for Pt deposition in nanopores are markedly different from those in the bulk state, deposits of Pt within nanopores may show some peculiar states that are not obtained on a flat

electrode in a bulk solution. The purpose of this study was to identify the chemical state of Pt deposited from highly accumulated [PtBr₄]²⁻ in nanopores using XAFS.

2. Experimental

2.1. Synthesis and electrochemical measurements

Nanoporous silicon substrates whose pore diameter was ~3 nm were prepared by anodization of p-type Si (100) with a resistivity of 10–20 Ω cm. Electrolyte solutions for anodization was 22 wt% HF solution (48 wt% HF:ethanol = 1:1.7 v/v). The silicon wafer was anodized at a current density of 2.0 mA cm⁻² for 20 min. The porosity of the porous layer was determined gravimetrically to be 76%. After washing the pores by pure water to extract residual fluorides, displacement deposition of Pt was conducted by immersing the prepared porous silicon into an aqueous solution of 0.1 M K₂PtCl₄ and 0.5 M NaCl or 0.1 M K₂PtBr₄ and 0.5 M KBr. Reduction of [PtX₄]²⁻ (X = Cl, Br) spontaneously proceeds with an oxidation of silicon [6]. Temporal change of potential was measured using an Ag|AgCl sat. KCl reference electrode.

2.2. XAFS measurements

XAFS measurements were performed at the Pt L_3 -edge (11,564 eV) in fluorescence yield mode at the branch A of BM25-Spline at the European Synchrotron [11]. The spectra were acquired as photoelectron wave-vector values of 15 \AA^{-1} . Extended XAFS (EXAFS) data were reduced applying standard procedures using the Demeter package [12]. The fits of all the spectra were performed both in real and photoelectron wave-vector (k) space from k^3 -weighted signals using theoretical functions for the paths of the FCC Pt and rutile PtO_2 computed using standard crystallographic references for Pt [13] and PtO_2 [14] with FEFF8.4 code [15].

3. Results

3.1. XANES of Pt-filled nanoporous silicon

Although Pt deposited in the nanoporous Si electrode by the displacement reaction is metallic in origin, atmospheric exposure caused rapid oxidation at the surface to form a PtO_2 layer over the metallic Pt structure. The X-ray absorption near edge structure (XANES) of Pt at the different deposition stages for the two baths are presented in Fig. 1a and b. The main edge (white-line) peak area can be directly related to the PtO_2 content in the case of metallic Pt nanoparticles [4]. A correlation of the area (height) of this peak and the particle size can be understood if we consider a core-shell model structure of the deposited particles because Pt was covered with PtO_2 . The temporal dependency of the main peak area was calculated and is presented in Fig. 1c. The peak area decreased gradually with time, meaning that the relative content of PtO_2 decreased and the particle size increased. Particles grew

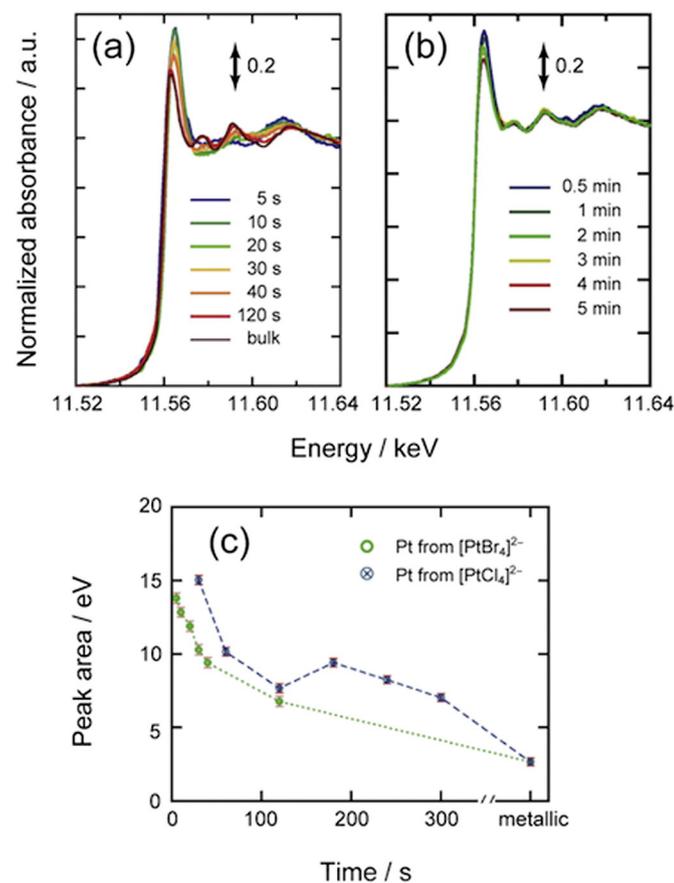


Fig. 1. XANES of Pt L_3 -edge spectra of Pt-filled nanoporous silicon prepared in $[\text{PtBr}_4]^{2-}$ (a) and $[\text{PtCl}_4]^{2-}$ (b) baths. The plots in (c) show temporal changes in the peak area of XANES presented in (a) and (b).

faster in the $[\text{PtBr}_4]^{2-}$ bath compared with the $[\text{PtCl}_4]^{2-}$ bath. After 2 min of the reaction, most of the Pt in the nanoporous silicon electrode was metallic in the $[\text{PtBr}_4]^{2-}$ bath. On the other hand, it took about five times longer to reach the equivalent chemical state with deposition from $[\text{PtCl}_4]^{2-}$. As observed in Fig. 1a and b, the phase stability of Pt deposited from the $[\text{PtCl}_4]^{2-}$ bath was observed not only with a smaller oscillation in the peak area that overlapped each other but also in the edge position of the spectra, which did not present a noticeable relative shift between conditions.

3.2. EXAFS of Pt-filled nanoporous silicon

Fig. 2a and b show the Fourier-transformed EXAFS data obtained from the Pt-filled nanoporous silicon prepared in $[\text{PtBr}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ baths, respectively. In the case of the $[\text{PtBr}_4]^{2-}$ bath (Fig. 2a), the time evolution of the spectra showed a broad peak for the short time condition (centered at $\sim 2.2 \text{ \AA}$). As deposition time increased, this broad peak revealed two more contributions at $\sim 1.8 \text{ \AA}$ and $\sim 2.6 \text{ \AA}$. The intensity of these contributions increased progressively with time as well as a fourth contribution at $\sim 3.4 \text{ \AA}$. These contributions were attributed to the Pt-O shell at $\sim 1.8 \text{ \AA}$, the Pt-Pt shell of the metallic phase at $\sim 2.6 \text{ \AA}$, and Pt-Pt in PtO_2 at $\sim 3.4 \text{ \AA}$. Regarding the samples prepared in the $[\text{PtCl}_4]^{2-}$ bath, a different evolution of the contributions was observed (Fig. 2b). Variations in the relative intensity in the Pt-O, Pt-Pt (metallic Pt), and Pt-Pt (PtO_2) contributions were detected. The PtO_2 contribution that was intense in the initial stage of deposition vanished almost completely for deposition times longer than 3 min. The Pt-Pt contribution maintained its relative intensity from the initial to latter stages of deposition.

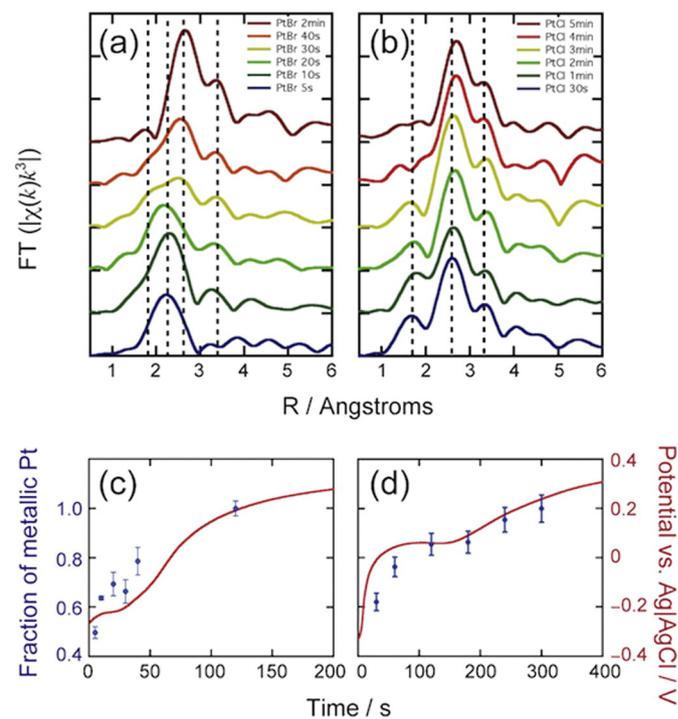


Fig. 2. (a, b) Fourier transformation of EXAFS data of Pt in Pt-filled nanoporous silicon at different stages of deposition. The spectra shown in (a) and (b) were obtained from samples prepared in the $[\text{PtBr}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ baths, respectively. (c, d) Blue plots indicate the fraction of metallic Pt against total Pt in both systems. Red lines show the temporal changes in potential measured during Pt deposition. Results in (c) and (d) were obtained from the $[\text{PtBr}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ baths, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/178608>

Download Persian Version:

<https://daneshyari.com/article/178608>

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