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

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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.

Keywords

Nanoporous, nanoparticles, deposition, platinum, XAFS

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 $[\text{PtBr}_4]^{2-}$ 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 22wt% HF solution (48wt% HF:ethanol = 1:1.7 v/v). The silicon wafer was anodized at a current density of 2.0 mA cm^{-2} for 20 minutes. 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 K_2PtCl_4 and 0.5 M NaCl or 0.1 M K_2PtBr_4 and 0.5 M KBr. Reduction of $[\text{PtX}_4]^{2-}$ (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 (11564 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 $15 \text{ \AA}^{-1}$. 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 an 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 Figures 1a and 1b. The main edge (white-line) peak area can be directly related to the PtO₂ 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 PtO₂. The temporal dependency of the main peak area was calculated and is presented in Figure 1c. The peak area decreased gradually with time, meaning that the relative content of PtO₂ decreased and the particle size increased. Particles grew faster in the [PtBr₄]²⁻ bath compared with the [PtCl₄]²⁻ bath. After 2 minutes of the reaction, most of the Pt in the nanoporous silicon electrode was metallic in the [PtBr₄]²⁻ bath. On the other hand, it took about five times longer to reach the equivalent chemical state with deposition from [PtCl₄]²⁻. As observed in Figures 1a and 1b, the phase stability of Pt deposited from the [PtCl₄]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

Figures 2a and 2b show the Fourier-transformed EXAFS data obtained from the Pt-filled nanoporous silicon prepared in [PtBr₄]²⁻ and [PtCl₄]²⁻ baths, respectively. In the case of the [PtBr₄]²⁻ bath (Figure 2a), the time evolution of the spectra showed a broad peak for the short time condition (centered at ~2.2 Å). As deposition time increased, this broad peak revealed two more contributions at ~1.8 Å and ~2.6 Å. The intensity of these contributions increased progressively with time as well as a fourth contribution at ~3.4 Å. These contributions were attributed to the Pt-O shell at ~1.8 Å, the Pt-Pt shell of the metallic phase at ~2.6 Å, and Pt-Pt in PtO₂ at ~3.4 Å. Regarding the samples prepared in the [PtCl₄]²⁻ bath, a different evolution of the contributions was

observed (Figure 2b). Variations in the relative intensity in the Pt-O, Pt-Pt (metallic Pt), and Pt-Pt (PtO₂) contributions were detected. The PtO₂ contribution that was intense in the initial stage of deposition vanished almost complete for deposition times longer than 3 minutes. The Pt-Pt contribution maintained its relative intensity from the initial to latter stages of deposition.

3.3 Fitting of the EXAFS data

As shown in Figure 2c (for [PtBr₄]²⁻), the fraction of metallic Pt was maintained at 0.7 from 20 to 40 s. Similar behavior was observed in Figure 2d (for [PtCl₄]²⁻) from 120 to 180 s, where the fraction was maintained at 0.85. When the temporal changes in electrode potential were overwritten, it was clearly observed that the duration of the stable fraction of Pt was matched with the potential plateau. The emergence of the potential plateau has been explained previously [10]. In brief, Pt complex anions penetrate into nanopores during the plateau. The dynamics of the penetration of Pt complex anions is related to the nucleation dynamics of Pt in the nanopores. During the potential plateau, the fraction of metallic Pt phase was higher in the [PtCl₄]²⁻ bath than in the [PtBr₄]²⁻ bath. If one considers the core-shell model with Pt covered with PtO₂, it was suggested that the particle size was much smaller in the case of [PtBr₄]²⁻ than in the [PtCl₄]²⁻ bath at equivalent stages of the potential plateau.

It was noticed for short deposition times, the Fourier transformed data presented as a broad peak at shorter distances (2.2 Å), which was a convoluted peak of the Pt-O and Pt-Pt (metallic Pt) contributions, but also showed a contraction in the bond distances of both shells with respect to the crystallographic values. Quantitative analysis of EXAFS showed that in the best fit the mean Pt-Pt distance in the metallic phase for the short deposition time shifted to shorter distances by ~0.1 Å. In Figures 3a-3c, the

results of the bounding mean distances of the first shells of Pt and PtO₂ are depicted as a function of deposition time. Because it was envisaged qualitatively in some of the spectra from the Fourier transformed data, there was a displacement of the Pt-Pt shell from shorter distances to longer as a function of deposition time (as the particle size increased). This expansion was a common behavior in all the shells in cases of Pt grown in the [PtBr₄]²⁻ bath. A closer examination of the temporal evolution of the shell distance revealed that the Pt-Pt shells of the metallic and oxide had a similar slope. This is different from the results obtained with the [PtCl₄]²⁻ bath, where temporal dependence of the shell distance is much less pronounced, even undetectable for the shortest deposition time conditions with the current experimental sensitivity.

The temporal evolution of the Debye-Waller (DW) factor was calculated for the first shells as in Figure 3d. Regarding the Pt-Pt shell of the metallic phase, relatively high values for a crystalline structure were obtained at 5 s, but after 10 s of deposition, the DW factor values were reduced to ~0.04 Å². However, the disorder decreased progressively to values within more standard ranges (below 0.01 Å² and reaching values of ~0.005 Å² by the last measurement). In the case of the PtO₂ phase, a relatively high atomic disorder was also observed below 10 s of deposition. The disorder in the Pt-O shell decreased as well around 40 s of deposition. After 40 s, it was not possible to detect the oxide phase.

4. Discussion

In the initial stages of growth, large amounts of PtO₂ were detected. Assuming a core-shell structure of Pt particles covered with PtO₂, the ratio between PtO₂ and metallic Pt directly correlated with the size of Pt clusters and nanoparticles. As observed in Figures 2c and 2d, the ratio of metallic Pt was low just after the start of deposition,

but it increased gradually. It was clear that it took much less time to reach fully metallic Pt when using $[\text{PtBr}_4]^{2-}$ compared with $[\text{PtCl}_4]^{2-}$. This result indicated that the size of Pt nanoparticles increased rapidly in the $[\text{PtBr}_4]^{2-}$ bath upon reaching a bulk-like metallic structure. It should be noted that the maximum size of nanoparticles cannot be larger than the size of the nanopores (~ 4 nm).

The greater contribution of PtO_2 and the structural parameters supported the hypothesis of the existence of very small Pt clusters formed in the shortest deposition times in the case of Pt grown from the $[\text{PtBr}_4]^{2-}$ bath. Shell radius contraction in all the shells is a well-documented effect in the case of sub-nanometric Pt particles [16]. As reported previously by Sun et al., sub-nanometric Pt particles present a collapsed structure and they exhibited an amorphous structure. According to the temporal dependence behavior of the DW factors of the Pt-Pt shells of both the metallic and oxide phases, we considered that such a situation was achieved in the case of the $[\text{PtBr}_4]^{2-}$ bath. The amorphization of the structure was highly compatible with the very high DW values observed for the short deposition times (smaller particles).

In previous studies, we reported that the local concentration of $[\text{PtBr}_4]^{2-}$ in the nanopores was much higher than that of $[\text{PtCl}_4]^{2-}$ [7, 8]. We considered that the larger number of Pt nucleation seeds from $[\text{PtBr}_4]^{2-}$, which cannot be achieved on a flat electrode, resulted in the formation of smaller amorphous Pt clusters, particularly in the initial stage of deposition. To the best of our knowledge, there have been no other studies that reported the formation of amorphous Pt by electrochemical deposition in a porous electrode.

5. Conclusions

Although the penetration of $[\text{PtBr}_4]^{2-}$ was much faster than that of $[\text{PtCl}_4]^{2-}$

and it was advantageous for electrochemical deposition in nanoporous electrodes, the formation of amorphous Pt clusters was detected only at the initial stage of deposition from $[\text{PtBr}_4]^{2-}$. Because $[\text{PtBr}_4]^{2-}$ was reported to be highly accumulated within the nanopores, we suggested that the amorphization was an intrinsic feature when depositing in conditions of high accumulation of the Pt precursor. Because such an amorphous cluster might be undesirable for applications in catalysis, there needs to be more attention paid to the preparation of nanoparticles by electrochemical techniques in nanoporous electrodes. Such unexpected chemical states of deposits are formed due to confined environments of nanoporous electrodes. This viewpoint is crucially important also in the development of electrochemical devices using nanoporous electrodes.

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References

- [1] S. Schauermann, N. Nilius, S. Shaikhutdinov, H.-J. Freund, Nanoparticles for heterogeneous catalysis: New mechanistic insights, *Acc. Chem. Res.* 46 (2013) 1673-1681.
- [2] X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo, X. Bao, Enhanced ethanol production inside carbon-nanotube reactors containing catalytic particles, *Nat. Mater.* 6 (2007) 507-511.

- [3] R.J. White, R. Luque, V.L. Budarin, J.H. Clark, D.J. MacQuarrie, Supported metal nanoparticles on porous materials, methods and applications, *Chem. Soc. Rev.* 38 (2009) 481-494.
- [4] Y. Nagai, K. Dohmae, Y. Ikeda, N. Takagi, T. Tanabe, N. Hara, G. Guilera, S. Pascarelli, M.A. Newton, O. Kuno, H. Jiang, H. Shinjoh, S. Matsumoto, In situ redispersion of platinum autoexhaust catalysts: An on-line approach to increasing catalyst lifetimes? *Angew. Chem. Int. Edit.* 47 (2008) 9303-9306.
- [5] N. Huang, Y. Xu, D. Jiang, High-performance heterogeneous catalysis with surface-exposed stable metal nanoparticles, *Sci. Rep.* 4 (2014) 7228.
- [6] Y.H. Ogata, K. Kobayashi, M. Motoyama, Electrochemical metal deposition on silicon, *Curr. Opin. Solid State Mater. Sci.* 10 (2006) 163-172.
- [7] K. Fukami, R. Koda, T. Sakka, T. Urata, K.-I. Amano, H. Takaya, M. Nakamura, Y. Ogata, M. Kinoshita, Platinum electrodeposition in porous silicon: The influence of surface solvation effects on a chemical reaction in a nanospace, *Chem. Phys. Lett.* 542 (2012) 99-105.
- [8] K. Fukami, R. Koda, T. Sakka, Y. Ogata, M. Kinoshita, Electrochemical deposition of platinum within nanopores on silicon: Drastic acceleration originating from surface-induced phase transition, *J. Chem. Phys.* 138 (2013) 094702.
- [9] R. Koda, A. Koyama, K. Fukami, N. Nishi, T. Sakka, T. Abe, A. Kitada, K. Murase, M. Kinoshita, Effect of cation species on surface-induced phase transition observed for platinum complex anions in platinum electrodeposition using nanoporous silicon, *J. Chem. Phys.* 141 (2014) 074701.
- [10] A. Koyama, K. Fukami, T. Sakka, T. Abe, A. Kitada, K. Murase, M. Kinoshita, Penetration of platinum complex anions into porous silicon: Anomalous behavior caused by surface-induced phase transition, *J. Phys. Chem. C.* 119 (2015) 19105-19116.

- [11] G. Castro, Optical design of the general-purpose spanish X-ray beamline for absorption and diffraction, *J. Synchrot. Radiat.* 5 (1998) 657-660.
- [12] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrot. Radiat.* 12 (2005) 537-541.
- [13] R.W.G. Wyckoff, *Crystal Structures*, 2 ed., Krueger Pub Co., 1982.
- [14] K.-J. Range, F. Rau, U. Klement, A.M. Heyns, β -PtO₂: High pressure synthesis of single crystals and structure refinement, *Mater. Res. Bull.* 22 (1987) 1541-1547.
- [15] A. Ankudinov, B. Ravel, J. Rehr, S. Conradson, Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure, *Phys. Rev. B.* 58 (1998) 7565-7576.
- [16] Y. Sun, L. Zhuang, J. Lu, X. Hong, P. Liu, Collapse in crystalline structure and decline in catalytic activity of pt nanoparticles on reducing particle size to 1 nm, *J. Am. Chem. Soc.* 129 (2007) 15465-15467.

Figure captions

Figure 1. XANES of Pt L₃-edge spectra of Pt-filled nanoporous silicon prepared in [PtBr₄]²⁻ (a) and [PtCl₄]²⁻ (b) baths. The plots in (c) show temporal changes in the peak area of XANES presented in (a) and (b).

Figure 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 [PtBr₄]²⁻ and [PtCl₄]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 [PtBr₄]²⁻ and [PtCl₄]²⁻ baths, respectively.

Figure 3. Time evolution of the EXAFS parameters considering a mixture of metallic Pt and PtO₂ in the case of the [PtBr₄]²⁻ bath. (a-c) First shell distances of Pt-Pt in metallic Pt, Pt-O in PtO₂, and Pt-Pt in PtO₂. The shell distances in the bulk Pt, Pt-O in PtO₂, and Pt-Pt in PtO₂ were 2.772 Å, 1.999 Å, and 3.136 Å, respectively. (d) Time evolution of DW factors. The blue and red plots indicate those of Pt-Pt in metallic Pt and Pt-O in PtO₂, respectively.

Figure %

Figure 8

Figure 3