

Electrochemical deposition of metal
on microporous silicon electrodes
influenced by hydration structures of solutes
and electrode surfaces

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General Introduction

1 Porous electrode

The structure which has many pores is called porous structure. Porous structures can be used as porous electrodes when porous structures are composed of conductors or semiconductors. Porous electrodes are very important in the range of technologies. They have extremely larger surface area than flat electrodes. The specific surface area of porous electrodes is associated with the pore size, porosity and pore depth. Total amount of the product in an electrochemical reaction depends on electrode area as well as applied potential and duration of electrolysis. Therefore the porous electrodes have been used for conventional electrolytic industries. For instance nitrogen trifluoride is produced by an electrolytic process using porous electrodes.¹ Water is electrochemically decomposed through porous electrodes.² In addition, they are utilized for various modern electrochemical devices. For example, the graphite having porous structure is used as a cathode for lithium ion batteries.³ Porous electrodes that are composed of activated carbons are used for fuel cells and electric double layer capacitors.^{4,5} Titanium oxide porous electrodes are utilized for dye-sensitized solar cells.⁶

A porous electrode is characterized by the porosity, pore diameter, specific surface area and property of materials. Especially specific surface area which mainly depends on the pore size and porosity is an important parameter of porous electrodes. According to the IUPAC classification of pore size, pores are classified as micropore, macropore and mesopore when its average pore size is under 2 nm, over 50 nm and in between these two values, respectively. The smaller the pore diameter is, the larger the specific surface area is if the number of pores is the same. Therefore, the specific surface area in

a microporous structure is larger than the specific surface area in a macroporous structures if the number of pores is the same.

Some methods to prepare porous electrodes have been reported. For instance, some conducting porous electrodes are prepared by sintering, pressurizing or using a binder from conductive particles such as conductive ceramics or carbon particles. Gold porous electrodes are prepared by immersing gold-silver alloy in nitric acid.⁷ In a similar way nickel porous electrodes are prepared by immersing nickel-aluminum alloy in alkali solution.⁸ Pores are spontaneously formed by anodization on various plates such as gold⁹, silver, copper, iron, nickel¹⁰, aluminum¹¹, titanium¹² and silicon.¹³ Porous electrodes prepared by anodization are utilized for various technologies. Porous titanium oxide is used for photocatalytic electrodes.¹² The porous gold electrodes exhibit high electrochemical activities for glucose oxidation.¹⁴ Porous indium-phosphorus is used as an anode for lithium ion batteries.¹⁵ Also, porous electrodes are utilized for various devices. In particular, one of the remarkable applications is the utilization as a template to produce nanomaterials by filling metal in the porous electrode.

2 Metal deposition in porous silicon

By dissolving a porous template after filling metal in the template, transferred metal structures can be obtained. For example, metal rods or wires whose short axis and long axis correspond to the pore diameter and thickness of the porous layer, respectively, can be formed in the pores when metal is deposited only in the columnar pores.^{16,17} Metals with ordered columnar structures can be prepared by depositing metal in the pores with continued deposition to form a film on top of the porous electrode.^{18,19} The metals with ordered columnar structures can be used for sensing 4,4'-bipyridine with surface-enhanced Raman scattering¹⁶ and polarization control of a vertical cavity surface emitting laser.²⁰ Especially porous silicon has significant advantages in utilizing as a template. Metal can be electrochemically deposited

in porous silicon without pretreatments since silicon is a semiconductor. Porous silicon is chemically dissolved in alkali solution.¹⁸ Thus metal structures are easily prepared and the template is easily removed, when porous silicon is utilized as the templates. In addition, the pore wall surface can be covered with organic molecules.²¹ The modification with organic molecules change the property of pore wall surface.²²

Control of metal deposition in porous structures is important to prepare such metal structures. The accumulation of knowledge to control metal deposition in pores is indispensable. The metal deposition in mesoporous silicon and macroporous silicon has already reported to be controllable. Kobayashi et al. carried out nickel and copper electrodeposition in macroporous silicon.¹⁸ Foell et al. achieved metal deposition in macroporous silicon by adjustment of potential and current density.²³ Xu et al. tried nickel deposition experiments from the viewpoint of comparison with simulation.^{24, 25} Fukami et al. focused on the composition of electrolyte.²⁶ Matsumoto et al. deposited noble metal such as platinum, gold and silver, and they reported that noble metal deposition in macroporous silicon is affected by the rate of metal displacement deposition.²⁷ The supply of metal ions into mesopores is strongly inhibited by the presence of pore walls compared with that into macropores. Hamadache et al. focused on current density and the kind of metal ions, and they carried out nickel and iron deposition in mesopores.²⁸ Fukami et al. made it possible to deposit platinum and copper in the mesopores at extremely small current density as well as by stabilizing metal ions.^{19,29}

A few studies about metal deposition in microporous silicon has been reported.³⁰⁻³² However, the aim of these studies is not the control of metal deposition but the improvement of electroluminescent efficiency^{30,31} and conversion efficiency as catalysts.³² Therefore the mechanism of metal deposition in microporous silicon is not well understood. Generally the reactive species such as metal ions are supplied to reactive sites by diffusion. However if the pore diameter is small, the presence of pore walls inhibit the sup-

ply of reactive species. The reactive species such as metal ions are not abundantly supplied into the pores and metal deposition preferentially proceeds on the pore opening where the supply of metal ions by diffusion is favorable. The inhibition effect originating from the presence of pore walls is stronger with decreasing the pore diameter.³³ Therefore, metal deposition in micropores has not been fully controlled. In order to achieve the complete filling, the reactive species has to be sufficiently supplied. The supply of those ions should be accomplished by means other than diffusion to control metal deposition in the micropores since the diffusion is determined by the geometry. In other words, supply of chemicals into micropores based on another mechanism is strongly desired.

3 Properties of solute and solvent near solid surface

It is reported that the properties of liquid such as density, structure and viscosity in a confined space such as micropores are different from that in a bulk.³⁴⁻⁴⁰ An aqueous solution in the microscopic space have a ordered structure by the effect of pore walls according to the force profile along the direction normal to the pore wall measured with a surface force apparatus.^{34,35} In this case, an aqueous solution have more ordered structure on a hydrophilic plate such as mica or glass plate than a hydrophobic graphite plate.³⁶ The properties of solution in microscopic space are different depending on the kind of solution.³⁷⁻⁴⁰ In addition, it was revealed by numerical simulation that an aqueous solution in micropores has an ice-like structure despite at room temperature.⁴¹ The overlapping of the interaction potentials between a pore wall and molecule is predominant in micropores due to the presence of the opposite pore walls. Consequently the properties of liquid in micropores are different from that in a bulk. Therefore, to control the supply of solute such as ions into micropores, the properties of solute and solvent such as density and structure near the solid surface have to be investigated.

The properties of the solute and solvent near a solid surface have been analyzed by some analytical methods. Shen et al. analyzed the structure of an

aqueous solution near hydrophobic quartz modified by octadecyltrichlorosilane with sum-frequency generation spectroscopy. A free OH group which is not bonded to other H₂O molecules by hydrogen bonds exists in an aqueous solution near the hydrophobic quartz.^{42,43} The oxygen position of H₂O molecules near a hydrophilic mica plate was revealed by X-ray reflectivity technique.⁴⁴⁻⁴⁶ The interaction of hydrogen bonds between H₂O molecules and the surface has an influence on the oxygen position of H₂O molecules on the mica.⁴⁴ Besides, a gap exists between the hydrophobic surface of octadecyltriethoxysiloxane (or octadecyltrichlorosilane monolayer) and H₂O molecules.^{45,46} The gap cannot be found near a hydrophilic surface.⁴⁴ In addition, the viscosity of water near a hydrophilic surface measured by an atomic force microscope (AFM) is higher than that of bulk. In contrast the viscosity near a hydrophobic surface is lower than that of bulk.³⁶

Kimura et al. revealed by force curves near a solid surface that H₂O molecules are adsorbed or structured on the hydrophilic solid surface.⁴⁷⁻⁵⁰ The more hydrophilic the solid surface is, the more significantly the structure forms.^{51, 52} This AFM technique can be applied to other molecules as well.⁵³ Alcohol is affected not only by van der Waals interaction from a solid surface but also by the hydrogen bond from the surface.^{54,55} Atkin et al. measured the structure of ionic liquids near a solid surface.⁵⁶⁻⁵⁸ An ionic liquid regularly forms a stronger and layered structure near a quartz and mica plate compared to a graphite.⁵⁶ In addition, the layered structure is affected by the potential of the electrode surface.^{57,58}

The structure analysis of solute and solvent near a solid surface was performed not only experimentally but also theoretically. It was reported using molecular dynamics method that the viscosity and diffusion of water near a charged surface (hydrophilic) are different from those near an uncharged surface (hydrophobic).⁵⁹ The structure of ionic liquids on a carbon nanotube was investigated, and it was clarified that the structure of ionic liquids near the carbon material depends on a kind of ionic liquid.⁶⁰ In aqueous systems, the concentration of large size ions such as Cs⁺ and I⁻ becomes high near a

carbon material/H₂O interface. The concentration is different from small size ions such as Li⁺ and F⁻.⁶¹ It was revealed by an angle-dependent integral equation theory that large size ions in an aqueous solution are enriched near an uncharged surface (hydrophobic).⁶² It was reported by both experimental⁴² and theoretical⁶² analyses that the structure of a solute and solvent near a solid surface is different from the structure in bulk. This structure is especially affected by the affinity between the solid surface and solvent, in other words hydrophilic or hydrophobic.

The properties of ions and solute in micropores are mainly determined by the influence from pore walls due to a confined space. It is necessary to clarify the behavior of ions and solvent in micropores to control metal deposition in micropores. Therefore, it is necessary to investigate the effect of pore wall properties on metal deposition in micropores.

4 The outline of the present thesis

The properties of solute and solvent such as density and structure in micropores are different from those in a bulk, and mainly determined by the interactions between the solute, solvent and pore walls since the pore diameter is extremely small. This thesis focuses on these interactions. The main aim of the work is to investigate the effect of the interactions on metal deposition and clarify the properties of ions in micropores. The concentration of metal ions in micropores is related to the density of deposited metal. Therefore the deposition behavior such as the density of deposited metal and site of the deposits is investigated.

In chapter 1, platinum deposition is carried out on two types of microporous silicon with different hydration properties (hydrophilic or hydrophobic). Here, two kinds of platinum complex ions with different hydration properties are also used. Platinum deposition occurs only in the micropores having the hydrophobic pore walls. In addition, when the interaction between the metal ions and H₂O molecules is weak, platinum is densely depos-

ited in the micropores. The theoretical analysis based on a statistical-mechanical theory for molecular liquids revealed that the concentration of the metal ions in the immediate vicinity of the surface is higher than that in the bulk. This originates from the surface-induced hydration structure of the metal ions which is dependent on the hydration properties.

In chapter 2, platinum deposition is carried out in micropores with several concentrations of metal ions in the bulk to elucidate this mechanism in detail. There exists a threshold concentration at which the deposition behavior exhibited a sudden change, leading to drastic acceleration of the platinum deposition in the micropores. According to the statistical-mechanical theory, at the threshold the micropores are abruptly filled with the second phase in which the ion concentration is significantly higher than that in the bulk.

In chapters 2, it has been elucidated that the micropores are filled with the second phase. In chapter 3, effects of cation species coexisting with the metal complex anions in electrolyte are examined, and the effect of the cations on metal deposition in micropores is elucidated. With increasing the size of cation species, the threshold concentration, beyond which the electrochemical deposition within micropores is drastically accelerated, is low. According to the statistical-mechanical theory, it is clearly shown that not only anions but also cations are remarkably enriched in the second phase. In addition, the larger the size of cation is, the lower the threshold concentration to form the second phase of anion in micropores is.

In chapter 4, zinc electrodeposition is carried out in micropores at a current density higher than the diffusion-limited current density measured on a flat substrate. Zinc is densely deposited in the micropores even at a current density higher than the diffusion-limited current measured on a flat substrate. This result suggests that the metal ions are enriched in the micropores by the hydration properties as discussed in the preceding chapters.

In chapter 5, electordepotion in micropores is carried out to clarify the effect of overpotential to deposit metal onto a bare silicon upon the deposi-

tion behavior in the micropores. In case of metal requiring high over potential to deposit on a bare silicon such as platinum, deposition does not occur in micropores if platinum deposition proceeds on the pore openings. On the other hand, In case of metal requiring low over potential to deposit on it such as silver, deposition proceeds into the micropores even if silver deposits on the pore openings.

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1 Platinum electrodeposition in porous silicon: The influence of surface solvation effects on a chemical reaction in a nanospace

A chemical reaction in a nanospace is decelerated once a diffusion-limited condition is reached due to the difficulty in supply of reactants from the bulk. We illustrate how to overcome this problem for platinum electrodeposition within nanoporous silicon electrodes. The surface-induced hydration structure of reactants is essential. We make nanopore surfaces hydrophobic by covering them with organic molecules and adopt platinum complex ions with sufficiently large sizes as reactants. Due to the resulting fact that the ions are strongly excluded from the bulk solution to the surface, the ion concentration is greatly enriched within nanopores. This enrichment accelerates the reaction.

1.1 Introduction

A chemical reaction occurring in a nanospace is an important process enabling development of novel science and technology or highly functional materials and devices. However, the control of the reaction is difficult to achieve in a conventional way using the temperature and concentration of reactants in bulk solution¹⁻⁷. A typical problem is that the reaction in a nanospace can remarkably be decelerated due to a diffusion-limited condition reached (i.e., the difficulty in supply of reactants from the bulk through mass transfer). In modeling and understanding the reaction mechanism in a nanospace, the solvent confined by a surface or surfaces should play crucially important roles. It has been shown that the structure of ionic liquid or organic solvent near a nanosurface is substantially different from that in bulk⁸⁻¹⁰. Here we show that the surface-induced solvation structure of reactants has surprisingly large effects on the reaction process. By adjusting the affinity of surfaces for the solvent and the solvation properties of reactants, the reaction process can be controlled in a

variety of manners, for instance, to overcome the deceleration problem mentioned above. A statistical-mechanical theory for confined molecular liquids provides a useful guide to the control that can be achieved by manipulating the affinity of electrode surfaces for water and varying the ion size.

In the present study, porous silicon and platinum electrodeposition are used as platforms of a nanospace and a chemical reaction, respectively. The pore diameter is ~ 5 nm at its maximum and ~ 3 nm on the average. With platinum electrodeposition, we can visualize the past record of reaction process by investigating the density and distribution of platinum deposit within the porous structure (deposited platinum is stable against the spontaneous dissolution). In this case, the solvent is water and the reactants are platinum complex ions. The important point is that the hydration properties of reactants in the aqueous solution confined on the scale of a nanometer are substantially different from those in the bulk aqueous solution. More specifically, the surface-induced hydration structure of reactants, which has never been considered explicitly in electrochemical research, is experimentally explored by covering the nanopores with organic molecules to make their surface hydrophilic or hydrophobic and by testing different ion sizes of reactants. Theoretical analyses based on a molecular model (not a dielectric continuum model) for water are also employed. As a striking result, the physical factor that the ions are excluded from the bulk water to the surface comes into play when the surface is hydrophobic, leading to enrichment of the ion concentration within nanopores. Moreover, the degree of this enrichment is remarkably influenced by the ion size.

1.2 Experimental Method

Nanoporous silicon electrodes were prepared by anodization of a p-Si (100) wafer (Shin-Etsu Astech Co. Ltd.). The resistivity of the silicon was 10-20 Ω cm. All chemicals purchased from Nacalai Tesque, Inc. with analytical grade were used without further purification. The anodization was performed in 22 wt.% HF ethanolic solution at current density of 2.0 mAcm^{-2} for 20 min with

a conventional potentio/galvanostat (Hokuto Denko, HZ-3000). The anodized area was 0.78 cm^2 (1 cm in diameter).

After washing the as-anodized nanoporous silicon with water and ethanol, the substrate was immersed for 15 h in *n*-hexane containing 0.2 M propiolic acid or 0.2 M methyl propiolate to cover the pore-wall surfaces with the organic molecules¹¹. We note that it is better to graft almost similar molecules which show the opposite hydration properties, i.e., hydrophobic and hydrophilic, to understand the effect of surface-induced hydration structures. This is because the molecules on the pore wall strongly affect the electrochemical behavior, meaning that analyses of the electrochemical property become quite complex if one uses molecules with substantially different structures. Propiolic acid and methyl propiolate form one of the best combinations for the present study from this point of view. The chemically-modified nanoporous silicon substrate was analyzed using a Fourier-transform infrared spectrometer (JASCO, FT/IR-460 Plus; FT-IR) with a diffuse-reflection mode. The contact angles of the porous layers were evaluated using a contact-angle measure (KSV Instruments, CAM 200).

The deposition bath was aqueous solution containing 0.1 M K_2PtCl_4 and 0.5 M NaCl. Aqueous solution containing 0.1 M K_2PtBr_4 and 0.5 M KBr was also used to examine the ion-size effect. The platinum electrodeposition was carried out cathodically at current density of $-6.4 \mu\text{Acm}^{-2}$ (the minus sign means “cathodic” current density). The cross-sectional views of the platinum deposited nanoporous silicon were observed with FE-SEM (JEOL, JSM-6500F; SEM) and analyzed by an energy-dispersive X-ray spectrometer (EDS) equipped in the SEM. The nanoscopic images of the cross-section were observed with a scanning transmission microscope (JEOL, JEM-2200FS; STEM). To prepare the samples for the STEM observation, the porous layers were sliced into thin films using a focused ion beam (JEOL, JIB-4500; FIB). The schematic illustration shown in Figure 1.1 explains how the STEM samples were prepared and which part of the sample was considered for the observation by STEM.

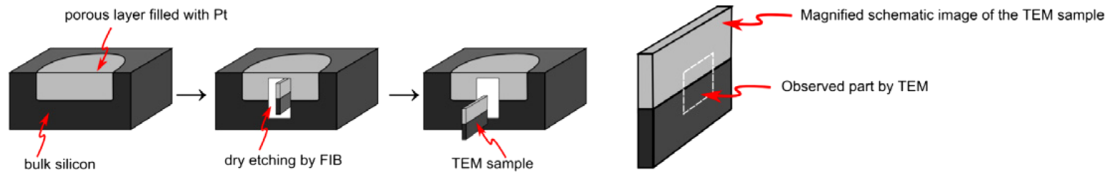


Figure 1.1: Schematic illustration explaining how the TEM sample was prepared and which part of the sample was considered for the observation by TEM.

1.3 Theoretical Method

It is required that a molecular model be employed for water to investigate the effects of the ion size. A water molecule is modeled as a hard sphere with diameter $d_S=0.28$ nm in which a point dipole and a point quadrupole of tetrahedral symmetry are embedded¹². The influence of molecular polarizability of water is included by employing the self-consistent mean field (SCMF) theory¹². Hard spherical cations and anions with diameters d_+ and d_- , respectively, are immersed in water. The water-water and water-ion correlations are then dependent not only on the distance between centers of the particles but also on the particle orientations. We analyze the structure of electrolyte solution at an extended, uncharged (hydrophobic) or charged (hydrophilic) surface. The water-surface correlations are also dependent on the orientations of water molecules.

We employ the angle-dependent integral equation theory¹²⁻¹⁵, a statistical-mechanical theory for molecular liquids. A macroparticle with diameter $d_M=30d_S$ (d_S is the diameter of water molecules, 0.28 nm) mimicking an extended surface is immersed in aqueous electrolyte solution. The subscripts, “S”, “+”, “-”, and “M” respectively, represent “solvent (water)”, “cations”, “anions”, and “macroparticle”. The Ornstein-Zernike (OZ) equation for the mixture comprising water molecules, cations, and anions can be written as¹²⁻¹⁷

$$\eta_{\alpha\beta}(12) = \{1/(8\pi^2)\} \sum_{\gamma} \rho_{\gamma} [c_{\alpha\gamma}(13) \{ \eta_{\gamma\beta}(32) + c_{\gamma\beta}(32) \} d(3)], \quad (1a)$$

$$\eta_{\alpha\beta}(12) = h_{\alpha\beta}(12) - c_{\alpha\beta}(12); \quad \alpha, \beta = S, +, -, M \quad (1b)$$

where h and c are the total and direct correlation functions, respectively, (ij) represents $(\mathbf{r}_{ij}, \mathbf{\Omega}_i, \mathbf{\Omega}_j)$, $\mathbf{r}_{ij}$ is the vector connecting the centers of particles i and j , $\mathbf{\Omega}_i$ denotes the three Euler angles describing the orientation of particle i , $\int d(3)$ represents integration over all position and angular coordinates of particle 3, and ρ is the number density. The closure equation is expressed by¹²⁻¹⁷

$$c_{\alpha\beta}(12) = \int_{r_{12}}^{\infty} [h_{\alpha\beta}(12) \partial \{ w_{\alpha\beta}(12) - b_{\alpha\beta}(12) \} / \partial r'_{12}] dr'_{12} - u_{\alpha\beta}(12)/(k_B T) + b_{\alpha\beta}(12), \quad (2a)$$

$$w_{\alpha\beta}(12) = -\eta_{\alpha\beta}(12) + u_{\alpha\beta}(12)/(k_B T), \quad (2b)$$

where u is the pair potential, b is the bridge function, and $r_{12} = |\mathbf{r}_{12}|$. In the present analysis, the hypernetted-chain (HNC) approximation is employed ($b=0$). We assume that the macroparticle is present at infinite dilution ($\rho_M \rightarrow 0$). The calculation process can then be split into two steps:

Step (i). Solve Eqs. (1) and (2) for bulk aqueous electrolyte solution. Calculate the correlation functions X_{SS} , X_{S+} , X_{S-} , X_{++} , X_{+-} , and X_{--} ($X=h, c$).

Step (ii). Solve Eqs. (1) and (2) for the macroparticle-aqueous electrolyte solution system using the correlation functions obtained in step (i) as input data. Calculate the correlation functions X_{MS} , X_{M+} , and X_{M-} ($X=h, c$).

For the numerical solution of Eqs. (1) and (2), the pair potentials and correlation functions are expanded in a basis set of rotational invariants (i.e., Wigner's generalized spherical harmonics), and the basic equations are reformulated in terms of the projections $X^{mnl}_{\mu}(r)$ occurring in the rotational-invariant

expansion of X^{12-17} . The expansion considered for $m, n \leq n_{\max}=4$ gives sufficiently accurate results. The basic equations are then numerically solved using the robust, highly efficient algorithm developed by Kinoshita and coworkers^{14, 18}. In the numerical treatment, a sufficiently long range r_L is divided into N grid points ($r_i = i\delta r, i=0, 1, \dots, N-1; \delta r = r_L/N$) and all of the projections are represented by their values on these points. The grid width and the number of grid points are set at $\delta r = 0.01d_s$ and $N=4096$, respectively.

In the real porous structure, the solution is confined within pores having various sizes whose surfaces are concave. However, the analyses on the solution confined by an extended surface provide fundamental information which can readily be applied to the solution confined between two extended surfaces, between two concave surfaces, or within a nanopore in a qualitative sense. The microstructure (heterogeneity) of the surface is not taken into account in the theoretical calculation. However, it has been shown that it has no essential effects on the conclusion as long as the *averaged* properties of the surface-induced structure are discussed¹⁹.

1.4 Results and Discussion

1.4.1 Electrodeposition in aqueous solution of $[\text{PtCl}_4]^{2-}$

First, platinum electrodeposition was carried out in aqueous solution of $[\text{PtCl}_4]^{2-}$ using the hydrophobic and hydrophilic nanoporous silicon electrodes. Figure 1.2 shows images of contact angle measurements, cross-sectional SEM images, and mappings of Si and Pt by EDS using the hydrophilic and hydrophobic porous silicon electrodes. The contact angles of the chemically-modified porous silicon electrodes in Figures 1.2a and b are 78° and 122° , respectively. The modifications of porous silicon were also characterized by FT-IR measurements (see supplementary content). As shown in Figures 1.2c, e, and g, platinum deposits are mainly observed on the top of the porous silicon when the hydrophilic porous electrode is employed. On the contrary, in Figures 1.2d, f, and h, platinum is uniformly deposited within the porous layer by the use of the hydrophobic porous electrode.

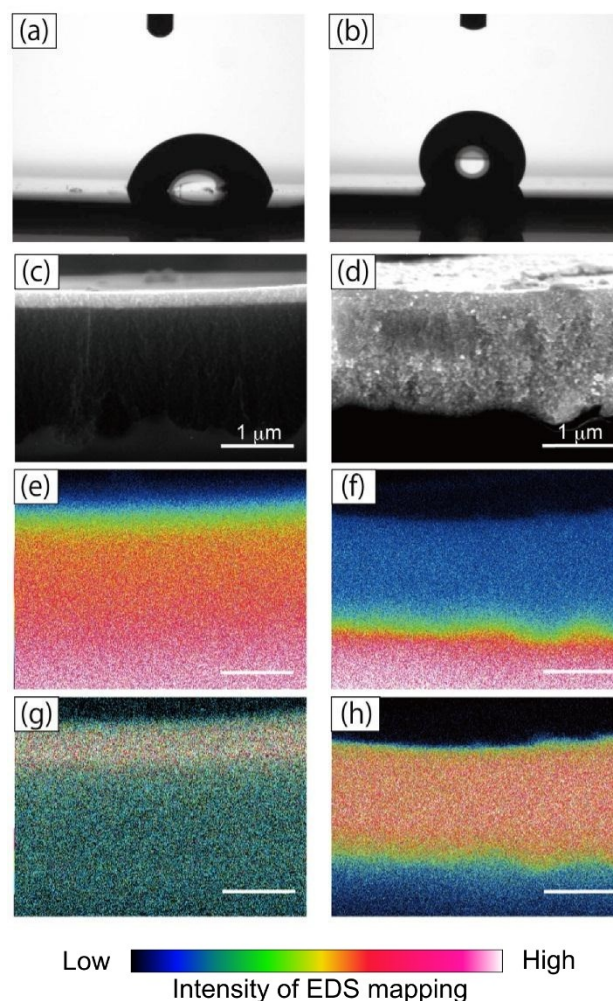


Figure 1.2: Strong effect of surface properties of porous silicon electrodes on platinum electrodeposition in which $[\text{PtCl}_4]^{2-}$ is used as platinum source. The electrode surfaces are hydrophilic in (a), (c), (e), and (g) whereas they are hydrophobic in (b), (d), (f), and (h). Images of contact angle measurements are shown in (a) and (b), cross-sectional SEM images in (c) and (d), EDS mappings of Si in (e) and (f), and EDS mappings of Pt in (g) and (h) after the platinum electrodeposition. The gradation bar in the bottom of the figure indicates the relative intensity of each element detected in the mapping. A marked difference in the electrodeposition behavior is observed between (g) and (h).

Current density-potential (i - E) curve measurements were performed to understand the electrodeposition behavior on various surfaces (Figure 1.3). A

platinum plate, a bare p-Si(100), and chemically-modified p-type silicon (100) substrate were used as the working electrodes. According to the i - E curves, the chemically-modified electrodes require much higher overpotential than a platinum plate electrode. However, the difference in the overpotential between the propiolic acid-modified p-Si and the methyl propiolate-modified one is not large, meaning that the electrochemical properties of these electrodes are similar. The amounts of deposited platinum are the same for the hydrophilic and hydrophobic porous silicon electrodes, but the preferential deposition sites are completely different. This, in turn, means that the difference between them in deposition behavior (Figure 1.2) originates solely from the surface-induced hydration structure of $[\text{PtCl}_4]^{2-}$ which is dependent on the surface properties. We have performed an additional experiment. The amount of platinum deposited on as-anodized nanoporous silicon, whose surface (it is not modified with the organic molecules) shows the highest hydrophobicity, is drastically larger as depicted in Figure 1.4. Because the electrochemical properties are different from those of the modified electrodes (Figure 1.3), one cannot compare the results in a simple way. However, it has been verified that the hydrophobic pore wall enhances the deposition reaction within the nanopores. Further, as discussed in the latter part of this paper (see Figure 1.6), the electrodeposition with a different platinum complex ion exhibits the same behavior as that with $[\text{PtCl}_4]^{2-}$, i.e., platinum deposition is substantially enhanced within the hydrophobic porous layer. These results indicate that the behavior is quite general and the specific chemical properties of functional groups on the modified surface and metal ions are not relevant.

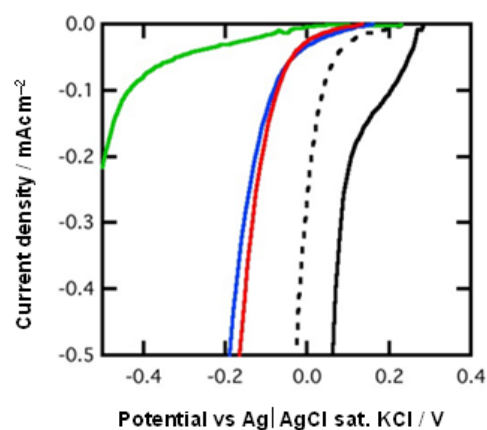


Figure 1.3: Current density-potential curves measured on various electrodes. The black, black-dotted, red, and blue curves were measured using a platinum plate, bare p-Si (100), propionic acid-modified p-Si (100), and methyl propiolate-modified p-Si (100), respectively. The measurements were carried out in aqueous solution containing 0.1 M K_2PtCl_4 and 0.5 M NaCl. The green curve was also measured with a methyl propiolate-modified p-Si (100), but in an aqueous solution containing 0.1 M K_2PtBr_4 and 0.5 M KBr. The scan rate of potential was 10 mVs^{-1} .

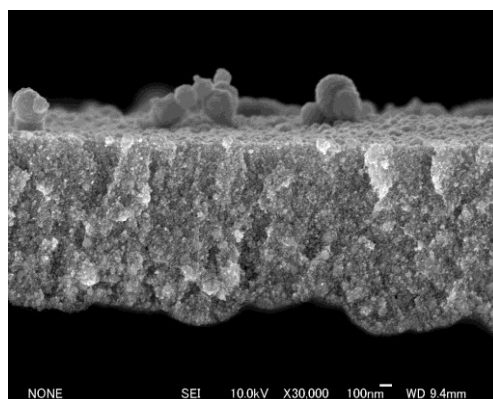


Figure 1.4: Cross-sectional SEM image of as-anodized nanoporous silicon after platinum electrodeposition. The condition for electrodeposition was the same as that in Figure 1.2, but the pore surface was not modified with organic molecules. Platinum is densely deposited within the porous layer. The pore surface is hydrogen-terminated, meaning that it is more hydrophobic than methyl propiolate.

1.4.2 Theoretical analyses

The above result was elucidated by our statistical-mechanical theory for confined molecular liquids. Our principal concern is the normalized number-density profile of anions $g(h)=\rho(h)/\rho_-$ where h is the distance from the surface, $\rho(h)$ is the number-density profile of anions, and ρ_- is the number density of anions in the bulk: $g(h)$ represents the surface-induced hydration structure of anions and $g(h)\rightarrow 1$ as $h\rightarrow\infty$. Our experience in theoretical analyses for alkali-halide ions has shown that the profile is rather insensitive to the ion concentration in the bulk over its wide range (<3 M)¹⁵. It is far more sensitive to the ion size. It is not significantly influenced by the species of the coexisting cations. On the basis of this information, the aqueous solution is treated as water containing K_2PtCl_4 at 1 mM. The anion, $[\text{PtCl}_4]^{2-}$, is modeled as a spherical ion within which the point charge of $-2|e|$ (e is the electronic charge) is placed at the center. The point charge of K^+ placed at its center is $|e|$. The cation size d_+ is set at 0.3 nm. As the anion size d_- , 0.60 nm is adopted for $[\text{PtCl}_4]^{2-}$. The size of $[\text{PtCl}_4]^{2-}$ was approximately calculated from the molecular weight and density of K_2PtCl_4 in solid state with the tetragonal crystal structure.

First, we show $g(h)$ near a hydrophobic surface in Figure 1.5. Two more values, 0.65 nm and 0.70 nm, are tested for d_- to look at the size effect. The anion concentration is enriched in the immediate vicinity of the surface. This strong enrichment occurs only within the first layer of the particles ($((h-d_-/2)/d_s\sim 1)$). Even in Figure 1.5c, $g(h)$ reduces quite rapidly as h increases, and the values of $g(h)$ are only 2.7 and 1.1 within the second ($((h-d_-/2)/d_s\sim 2)$) and third ($((h-d_-/2)/d_s\sim 3)$) layers, respectively. The physical interpretations of the enrichment and the great dependence on the anion size are given as follows.

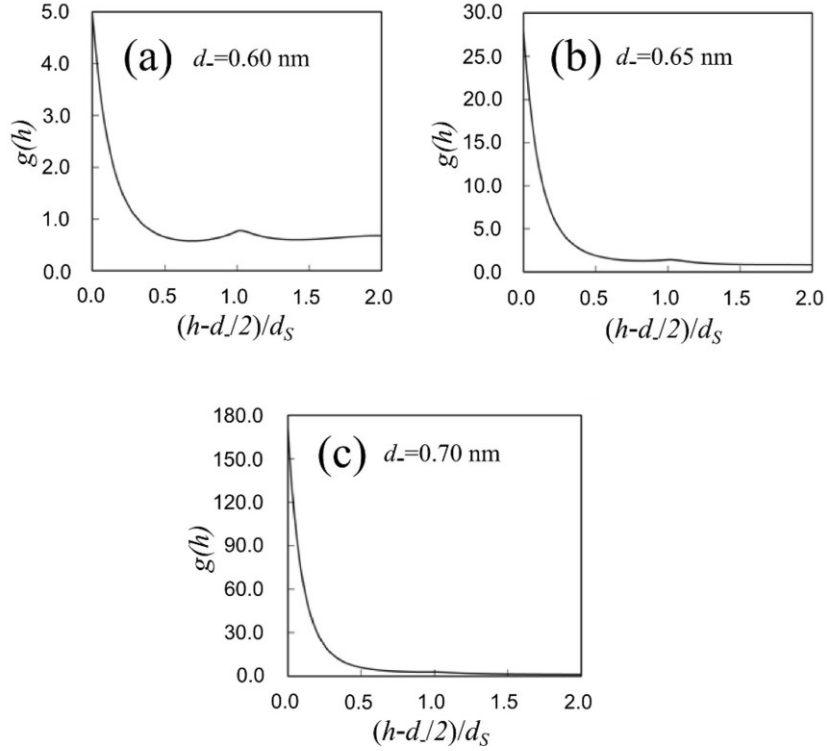


Figure 1.5: Remarkable effect of anion size on surface-induced hydration structure of anions: Normalized number-density profile of anions $g(h)$ near an extended hydrophobic surface for the three different values of d_- , 0.60 nm (a), 0.65 nm (b), and 0.70 nm (c). The anions in (a) and (c) correspond to $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, respectively. The profile exceeding 1 near the surface indicates the enrichment of anion concentration. Our experience in analyses on confined electrolyte solutions has shown the following [15]: As for the solution confined between two extended surfaces, when the surface separation becomes smaller than a few times of the diameter of a water molecule, not only $g(h)$ for all h exhibits an upward shift but also the anion-size effect becomes larger. The upward shift and the enhancement of anion-size effect are more appreciable when the surface separation is smaller or the surface is concave and its curvature is larger (see “Entropic enrichment originating from packing force” of SI). By the interplay of these physical factors, the enrichment of anion concentration and the anion-size effect become remarkable when the solution is confined within a pore having the size of a nanometer.

(1) $d_- = 0.60$ nm.

We consider system 1 where the charges of ions and the point dipole and quadrupole of water molecules are all switched to zero: A mixture of hard spheres with three different diameters (d_s , d_+ , and d_-) forms the solution. The surface is made by a hard wall. In this system, all of the allowed system configurations share the same energy and the system behavior is purely entropic in origin. The measure of the enrichment, $g(d_-/2)$, is ~ 30 . This entropic enrichment arises from “the packing force” (see supplementary content)²⁰. We then consider system 2 where only the charges of ions are set at zero. A binary mixture of hard spheres with different diameters (d_+ and d_-), which form hydrophobic solutes, is immersed in water. $g(d_-/2)$ reaches ~ 67000 . Energetically, water molecules do not want to accommodate a solute which cannot participate in the hydrogen bonding. The number of water molecules surrounding such a hydrophobic solute N_C is an important quantity. N_C for the solute in contact with the surface is half of N_C for the solute in the bulk. Therefore, the solutes are strongly excluded from water to the surface, which forms those with smaller N_C . When the charges are given to the ions (system 3: the model aqueous solution specified in the last paragraph), $g(d_-/2) \sim 5$ as observed in Figure 1.5a. This value is smaller than 30 in system 1, and the anions with $d_- = 0.60$ nm are rather favored by water: they are weakly hydrophilic.

(2) $d_- = 0.70$ nm.

It has been found that $g(d_-/2) \sim 44$ in system 1 and $g(d_-/2) \sim 170$ in system 3 as observed in Figure 1.5c. The latter value is larger than the former one, and the anions with $d_- = 0.70$ nm are unfavorable for water: they are rather hydrophobic despite that the charge carried by them is as large as $-2|e|$. This property is ascribed to the large anion size.

As explained in the caption for Figure 1.5, the enrichment becomes larger as the pore diameter decreases. For a pore having the size of a nanometer, the anion concentration within the whole nanospace is made far higher than that in the bulk.

We repeat that $g(h)$ and $g(d/2)$ remain roughly constant against a change in the anion concentration in the bulk C_- . However, the number-density profile and the number density of anions near the surface *themselves* (not normalized) increase in proportion with C_- . Actually, in our experiments, the electrodeposition behavior of platinum within the hydrophobic porous layer displayed a rather abrupt change at around the $[\text{PtCl}_4]^{2-}$ concentration of ~ 10 mM. Below this concentration, the electrodeposition occurred preferentially on the top of the hydrophobic porous layer, which is indicative that the concentration of $[\text{PtCl}_4]^{2-}$ near the surface is not high enough to deposit platinum despite almost the same degree of the enrichment. It is interesting that such a threshold value exists for C_- .

We then discuss the theoretical result for a hydrophilic surface. When the surface is negatively charged (i.e., hydrophilic) as in our experiments described above, within the surface-induced layer the anions are largely depleted ($g(d/2) \ll 1$). The depletion becomes more remarkable as the pore diameter decreases. There are two reasons for this behavior. The first reason is that the anions are repelled from the surface through electrostatic interaction. The second one is that the number density of water molecules is higher within a nanopore and the insertion of rather hydrophobic ions into the nanopore is less allowed.

1.4.3 Electrodeposition in aqueous solution of $[\text{PtBr}_4]^{2-}$

Figure 1.5 indicates that the enrichment of anion concentration is drastically enhanced by a minor increase in the anion size. To demonstrate this size effect, the deposition experiment was carried out in the bath containing $[\text{PtBr}_4]^{2-}$. The size difference between $[\text{PtBr}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ can be set at the double of that between Br^- and Cl^- with the result that the size of $[\text{PtBr}_4]^{2-}$ is ~ 0.7 nm which corresponds to Figure 1.5c²¹. Figure 1.6 depicts the microscopic structures of the deposited platinum in the $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$ baths. In Figures 1.6a and b, platinum is deposited as nanoparticles with ~ 4 nm in diameter, which is almost the same as the diameter of the original pores of porous silicon. These

are images of the interfaces between bulk silicon and the hydrophobic porous layer (Figure 1.2), showing that platinum complex ions were continuously supplied to the bottom and platinum electrodeposition occurred smoothly. As predicted by our theory, the deposition behavior exhibited a drastic change when platinum deposition was carried out in the $[\text{PtBr}_4]^{2-}$ bath. The density of platinum nanoparticles is obviously increased when $[\text{PtBr}_4]^{2-}$ is used as platinum source (Figures 1.6c and d). Strikingly, the electrochemical properties of $[\text{PtCl}_4]^{2-}$ bath are different from those of $[\text{PtBr}_4]^{2-}$ bath in the respect that the latter requires much higher overpotential than the former (see Figure 1.3). It follows that the deposition of $[\text{PtCl}_4]^{2-}$ would be much easier than that of $[\text{PtBr}_4]^{2-}$ from the electrochemical viewpoint. Nevertheless, $[\text{PtBr}_4]^{2-}$ produces much higher density of platinum particles within the hydrophobic porous electrode than $[\text{PtCl}_4]^{2-}$. This result strongly suggests that in cases of nanopores the surface-induced hydration structure of platinum complex ions plays dominant roles in the reaction mechanism.

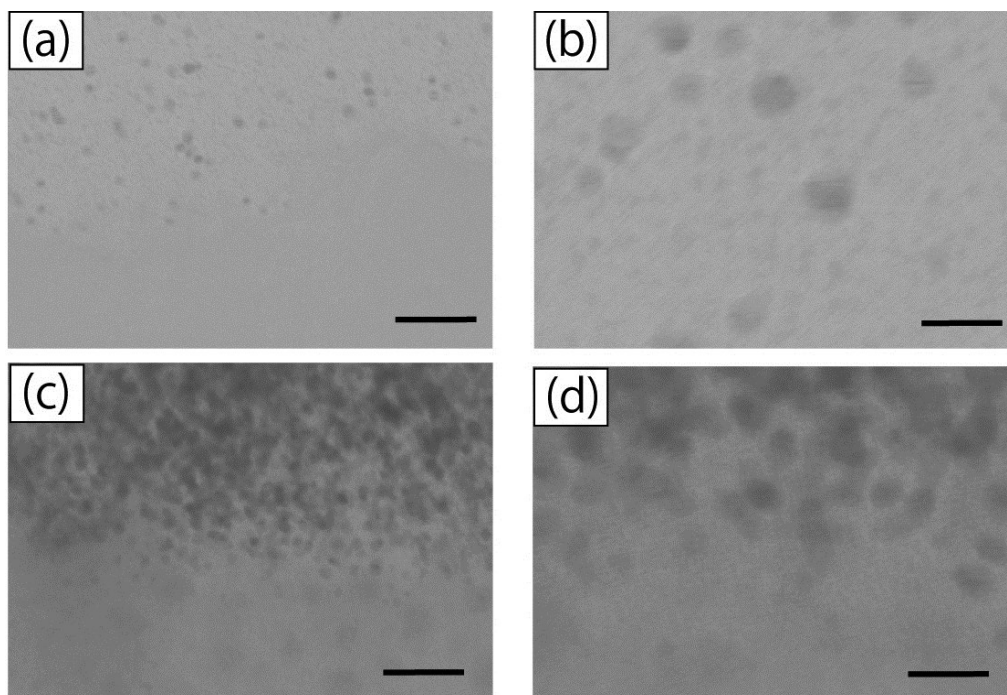


Figure 1.6: Substantially large increase in the density of platinum nanoparticles in the case where $[\text{PtBr}_4]^{2-}$ is used as platinum source: Cross-sectional STEM images of the hydrophobic porous silicon after the electrodeposition of platinum. The samples of (a, b) and (c, d) are deposited in deposition baths containing $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, respectively. The images (b, d) are magnified images of (a, c). The scale bars in (a, c) and (b, d) indicate 30 nm and 10 nm, respectively.

1.5 Concluding Remarks

We have illustrated how to control a chemical reaction occurring in a nanospace for platinum electrodeposition within nanoporous silicon electrodes as an example. The surface-induced hydration structure of reactants is shown to be crucially important. A statistical-mechanical theory for confined molecular liquids provides a useful guide to the control that can be achieved by manipulating the affinity of electrode surfaces for water and varying the ion size.

The important point is that when $d_{\perp}$ (size of platinum complex ions) is large enough, there is a physical factor excluding the anions from the bulk to the surface. This factor becomes stronger as $d_{\perp}$ increases. Moreover, the strength

is extremely sensitive to $d_{\perp}$. When the surface is hydrophobic, this factor dominates with the result that the anion concentration remains enriched in the immediate vicinity of the surface. For a pore having the size of a nanometer, the enrichment is kept remarkable within the whole nanospace. Thus, by modifying the silicon surface to make it hydrophobic and using platinum complexes with considerably large $d_{\perp}$, we have succeeded in promoting electrodeposition within pores which are deep and extremely small in diameter. Without the physical factor, the reaction within such pores would be decelerated to a remarkable extent after a short time due to a diffusion-limited condition reached. Even when a pore is considerably large in diameter and the enrichment occurs only in the immediate vicinity of the pore surface, the continuous supply of reactants into the pore could be driven by *surface diffusion* arising from the concentration gradient formed along the surface. Once sufficiently large nuclei of platinum are formed on the electrode surface, the electrodeposition proceeds quite easily.

To date, a variety of porous structures and solvents have been utilized in many applications. The present study, which has shown that the solvation properties of reactants in solvent confined on the scale of a nanometer play crucially important roles, sheds new light on design and control of highly efficient, chemical systems in a nanospace combined with proper solvents and reactants.

1.6 Supplementary Information

1.6.1 FT-IR characterization of chemically-modified nanoporous electrodes

Figure 1.7 shows FT-IR spectra of the bare and chemically-modified nanoporous silicon electrodes. As-anodized nanoporous silicon mainly shows Si-H modes. After the modification with propiolic acid, the Si-H modes are still not low, but broad OH and C=O modes appear. When the modification with methyl propiolate is performed, CH and C=O modes appear together with the high Si-H modes [11]. According to these spectra, the modifications with the

chemicals certainly occurred. In Ref. 11, an atomically-flat silicon substrate was used, and then the authors obtained a relatively high coverage of the organic molecules. In our case, the grafting of the molecules was performed onto porous silicon that has complex three-dimensional structure. The grafting is definitely affected by steric hindrance. Thus, our porous silicon samples still show high S-H signals even after the grafting was saturated in 15 h. However, the intensities of the absorption are very high compared with those in the case of flat silicon. In addition, we kept the modified nanoporous silicon electrodes in air with 95% humidity and measured the difference in weight. The hydrophilic nanoporous silicon showed 38% increase in weight relative to the weight of the porous layer. This result indicates that the pore walls were successfully modified with propionic acid. In fact, the contact angles of the hydrophilic and hydrophobic porous silicon substrates exhibit a clear difference. Further, the experimental results from *the hydrophilic and hydrophobic surfaces* are completely consistent with the theoretical results as described in the main text.

It should be noted that the FT-IR spectra after the electrodeposition of platinum did not show a broad OH absorption peak at $\sim 3600\text{ cm}^{-1}$. The hydrolysis of the ester did not occur during the electrodeposition.

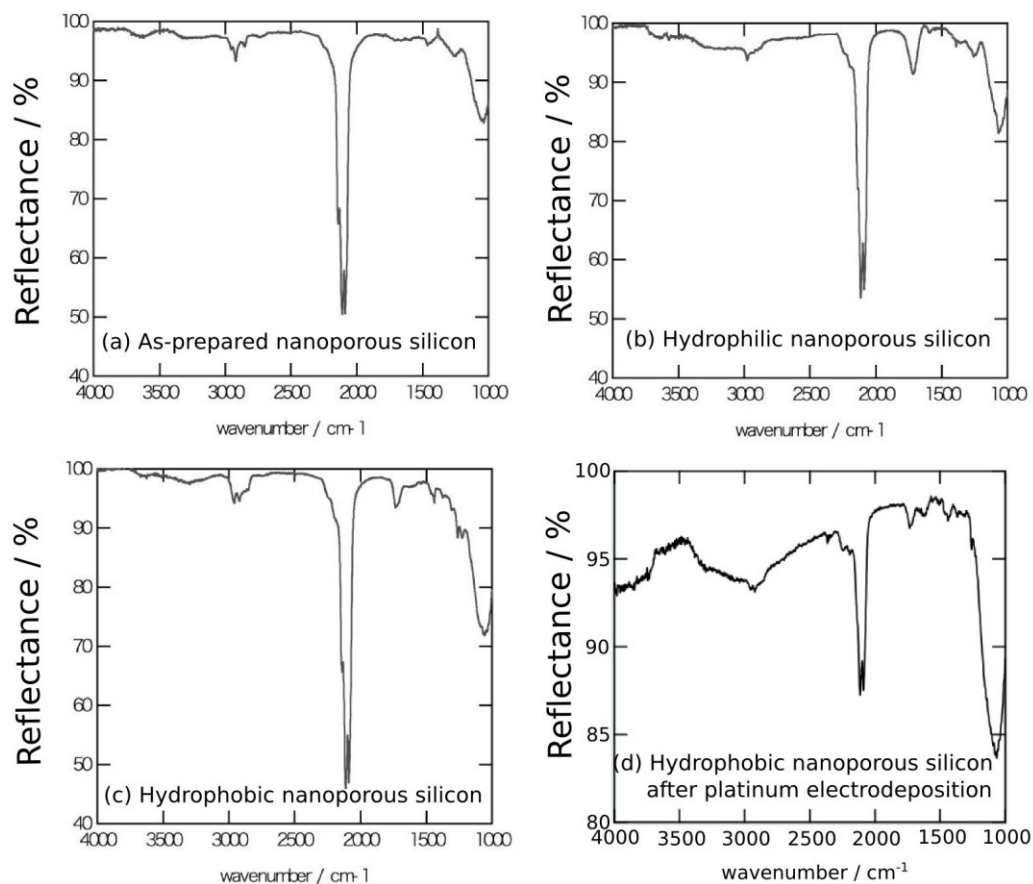


Figure 1.7: FT-IR spectra of as-anodized, hydrophilic and hydrophobic nanoporous silicon electrodes. The spectra of (a), (b), (c) and (d) show those obtained with as-anodized, hydrophilic, hydrophobic nanoporous silicon electrodes, and hydrophobic nanoporous silicon after platinum electrodeposition, respectively. The peaks are assigned as follows: C=O 1708.1 and 1728 cm^{-1} , SiH_x 2071.1 and 2083.7 cm^{-1} , OH 3600 cm^{-1} (broad), CH₃ 2962 and 2872 cm^{-1} .

1.6.2 Entropic enrichment originating from packing force

We consider hard spheres near an extended surface of a hard wall. In this system, all of the allowed system configurations share the same energy and the system behavior is purely entropic in origin²²⁻²⁶. The presence of the hard wall generates an excluded volume which the centers of hard spheres cannot enter. The presence of a hard sphere also generates an excluded volume for the other hard spheres. The excluded volumes are shadowed in Figure 1.8. When a hard sphere contacts the hard wall, the two excluded volumes overlap as illustrated in the figure: The overlapped volume is indicated by red dashes. The total excluded volume decreases by the overlapped volume, leading to a corresponding increase in the total volume available to the translational displacement of the other hard spheres. The solute contact leads to an increase in the number of accessible configurations of the other hard spheres, which is followed by a gain in the translational entropy of the other hard spheres. Thus, each hard sphere is entropically driven to contact the hard wall. The physical factor driving each hard sphere to contact the hard wall can be called “the packing force”²⁰. This factor competes with the other factor that hard spheres wish to move around as freely as possible in the space. The density of hard spheres rises in the vicinity of the hard wall and degree of this rise is determined by the interplay of the two factors. When a mixture of hard spheres with two different diameters is near a hard wall, the rise is stronger for hard spheres with larger diameter²⁶: The concentration of hard spheres with larger diameter is enriched near the wall.

When the wall surface is concave, it is apparent from Figure 1.8 that the overlapped volume becomes larger. Moreover, it is further enlarged as the curvature of the concave surface increases. A larger overlapped volume leads to a stronger packing force. This is a principal reason for the upward shift of $g(h)$ in the case of a concave surface (see the caption for Figure 1.5 in the main text).

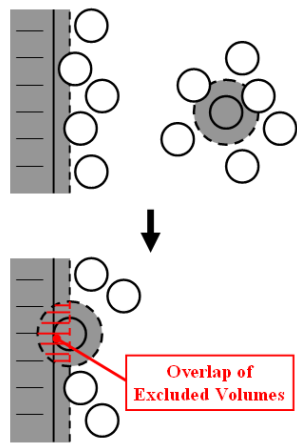


Figure 1.8 Contact of a hard sphere to a hard wall.

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2 Electrochemical deposition of platinum within nanopores on silicon: Drastic acceleration originating from surface-induced phase transition

An electrochemical reaction within nanopores is remarkably decelerated once a diffusion-limited condition is reached due to the difficulty in supply of reactants from the bulk. Here, we report a powerful method of overcoming this problem for electrochemical deposition of platinum within nanopores formed on silicon. We made the pore wall surface of the silicon electrode hydrophobic by covering it with organic molecules and adopted platinum complex ions with sufficiently large sizes. Such ions, which are only weakly hydrated, are excluded from the bulk aqueous electrolyte solution to the surface and rather hydrophobic in this sense. When the ion concentration in the bulk was gradually increased, at a threshold the deposition behavior exhibited a sudden change, leading to drastic acceleration of the electrochemical deposition. Using our statistical-mechanical theory for confined molecular liquids, we show that this change originates from a surface-induced phase transition: The space within nanopores is abruptly filled with the second phase within which the ion concentration is orders of magnitude higher. When the affinity of the surface with water was gradually reduced with fixing the ion concentration, qualitatively the same transition phenomenon was observed, which can also be elucidated by our theory. The utilization of the surface-induced phase transition sheds new light on the design and control of a chemical reaction in nanospace.

2.1 Introduction

Porous electrodes have become important materials in science and technology. They are utilized as sensing devices, host matrices for catalysts, and electrodes for batteries.¹⁻⁶ Although the specific surface area becomes larger with an increase in the porosity, it is difficult in chemical or electrochemical reactions

to elicit suitably high performance originating from the large specific surface area. This is because the reaction efficiency within nanoporous media is lowered by the difficulty in supply of reactants from the bulk and in ejection of products to the bulk. By applying the diffusion equation to the description of supply and ejection, we know that they are strongly disturbed by the porous structure and this disturbance is more serious whose pores are deeper and smaller in diameter.⁷ As a consequence, chemical or electrochemical reactions occur primarily on the top surface of porous structure which is advantageous in terms of supply of reactants from the bulk. Thus, the control of such reactions within nanoporous media is much more difficult than one simply imagines.

It was reported that the local structure of ionic liquid or organic solvent in a confined nanospace is substantially different from that in the bulk.⁸⁻¹⁰ Recently, we have revealed experimentally and theoretically that the surface-induced hydration structure of platinum complex ions has large effects on the enhancement of platinum deposition within nanoporous silicon electrodes.¹¹ The surface-induced hydration structure plays crucially important roles in the design and control of chemical reactions in nanoporous electrodes. When the pore wall surface was made hydrophobic and platinum complex ions with sufficiently large sizes were adopted, the ion concentration was greatly enriched at the surface due to rather hydrophobic properties of the ions. Since such large ions are only weakly hydrated, they are excluded from the bulk to the surface and rather hydrophobic in this sense. (As the anion size becomes larger with its charge kept constant, hydrogen atoms in a water molecule with positive partial charges cannot come closer to it, leading to weaker stabilization by the electrostatic attractive interaction. That is, a larger anion exhibits weaker affinity with water and becomes less hydrophilic.) However, it was reported that the structure had only monolayer thickness of the ions. In such a case, it was not clear how the diffusion limitation of reactants was overcome in the confined nanospace (i.e., nano-sized pores).

In the present study, we carry out a detailed investigation on the effects due

to the concentration of platinum complex ions in the bulk aqueous electrolyte solution and the affinity of the pore wall surface with water. A surprising finding is as follows. When the ion concentration in the bulk was gradually increased, at a threshold concentration the deposition behavior exhibited a sudden change, leading to drastic acceleration of the electrochemical deposition. This result is strongly suggestive of the occurrence of a transition phenomenon. When the affinity of the surface with water was gradually reduced (i.e., the hydrophobicity of the surface was gradually strengthened) with fixing the ion concentration, qualitatively the same phenomenon was observed. With the aid of our statistical-mechanical theory for confined molecular liquids, we attribute the finding to a surface-induced phase transition upon which the confined nanospace is filled with the second phase: The ion concentration is orders of magnitude higher in the second phase. We emphasize that the bulk aqueous electrolyte solution is thermodynamically stable as a single phase and subject to no phase transition. The transition in the present case is induced by the surface. A liquid mixture confined in nanospace behaves quite differently from the bulk. Thus, we have newly found that the elimination of the diffusion-limited condition, under which supply of reactants (i.e., platinum complex ions) from the bulk to nanospace is remarkably decelerated, originates not from the simple enrichment of the reactants at the surface but from the surface-induced phase transition. The theoretical analysis in our earlier work¹¹ was made only for a very low ion concentration which was far from the threshold for the phase transition.

In the present paper, we first present the striking experimental results of the electrochemical deposition behavior within porous silicon electrodes whose pore diameter is ~ 3 nm on an average, showing the existence of thresholds for the concentration of platinum complex ions in the bulk and the affinity of pore wall surface with water. Beyond the threshold, the drastic acceleration of platinum deposition within the porous layer is clearly observed from the density distribution of the platinum deposit. We then perform theoretical analyses based on statistical mechanics for confined molecular liquids to

elucidate the experimental results. It is shown that the transition behavior with thresholds is semi-quantitatively reproduced in the analyses, suggesting that the surface-induced phase transition is responsible for the drastic acceleration of platinum deposition. To the best of our knowledge, a surface-induced phase transition has never been reported for an aqueous electrolyte solution near a hydrophobic surface, which contains only weakly hydrated ions. Moreover, it is the first time that a surface-induced phase transition is clearly visualized in electrodeposition within porous silicon and studied by a combination of experimental and theoretical approaches. The present work is expected to stimulate the progress of an interesting new field, i.e., chemical physics of a liquid or liquid mixture confined in nanospace. It will also have a strong impact not only on the fundamental understanding of such reactions within nanopores but also on the design and control of the reactions in nanoporous media. We believe that the surface-induced phase transition will play essential roles in the adjustment of the distribution of chemicals within nanopores, enabling precise control of materials, such as fast response time of sensors, high efficiency of catalytic reactions, and quick recharge of batteries.

2.2 Materials and methods

Porous silicon electrodes were prepared by anodization of p-type silicon (100) with a resistivity of 10-20 Ωcm . The diameters of the pores were less than 5 nm, and the average diameter was ~ 3 nm. The anodization was carried out in HF/ethanol solution under a constant current density of 2.0 mAcm^{-2} . The duration for the electrochemical dissolution of silicon was tuned so that two porous layers different in thickness could be obtained. A thicker layer possesses deeper pores, and we can explore the effect of pore depth. The porous silicon electrode was dipped into *n*-hexane containing methyl propiolate (hydrophobic) and/or propiolic acid (hydrophilic). To obtain a hydrophobic porous silicon electrode, *n*-hexane solution of 0.2 M methyl propiolate without propiolic acid was used, and for the hydrophilic nanoporous silicon the recipe was the other way around.¹¹ Mixture of methyl

propiolate and propiolic acid prepared at different relative concentrations was used to adjust the affinity of the pore wall surface with water (i.e., to change the degree of hydrophilicity or hydrophobicity). Details are written in the caption of each figure.

Electrochemical deposition of platinum using the hydrophobic and hydrophilic porous silicon electrodes was performed at a constant current density of $-6.4 \mu\text{Acm}^{-2}$ (the minus sign means the cathodic current density). Aqueous electrolyte solution of K_2PtCl_4 and 0.5 M NaCl was used as the deposition bath. In some cases, aqueous electrolyte solution of K_2PtBr_4 and 0.5 M KBr was used instead of the chloride bath. The platinum complex ions are $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$. Concentrations of the platinum sources were tuned from 0.001 M to 0.1 M. The cross-sectional views of the nanoporous silicon were observed by a field-emission type scanning electron microscope (JEOL JSM-6500F).

2.3 Experimental results

2.3.1 Effect of concentration of platinum complex ions

Using the pore wall surface modified only with methyl propiolate to make it hydrophobic, we investigated the effect of the concentration of platinum complex ions on the deposition behavior. Electrochemical deposition of platinum was performed with gradually increasing the concentration of $[\text{PtCl}_4]^{2-}$ from 0.001 M (the increment was 0.001 M). A drastic change in the deposition behavior was observed at a threshold concentration: The behavior for 0.010 M becomes markedly different from that for 0.009 M. The drastic change can be appreciated from Figure 2.1b and c. Platinum deposition is not observed at all within the porous layer when the ion concentration is 0.009 M or lower. In contrast, platinum is uniformly distributed in the nanoporous silicon electrode when the ion concentration is 0.010 M or higher. The microscopic structure of the platinum deposited is the same as that reported in our previous paper. Namely, platinum was deposited not as continuous platinum fibars but as isolated nanometer-sized particles. Thus, there exists a

threshold (between 0.009 M and 0.010 M) in the concentration of $[\text{PtCl}_4]^{2-}$ for the deposition within the nanoporous layer. We note that the amount of platinum deposited is constant under the present experimental condition. Even if the electrochemical deposition within the porous layer is suppressed, the same amount of platinum is deposited mostly on the top surface of the porous layer.

Our earlier work showed that the electrochemical deposition of platinum in the porous silicon electrodes is remarkably enhanced when $[\text{PtCl}_4]^{2-}$ is replaced by $[\text{PtBr}_4]^{2-}$. This is because larger ions become more hydrophobic and tend to be excluded from the bulk to a hydrophobic surface to a stronger extent. The effect of ion size on the deposition behavior is revisited in the present study. Figure 2.1e, f, g and h depict the deposition behavior observed after the electrochemical deposition using $[\text{PtBr}_4]^{2-}$. There also exists a threshold in the concentration of $[\text{PtBr}_4]^{2-}$ between 0.004 M and 0.005 M which is considerably lower than in the case of $[\text{PtCl}_4]^{2-}$ (Figure 2.1f and g).

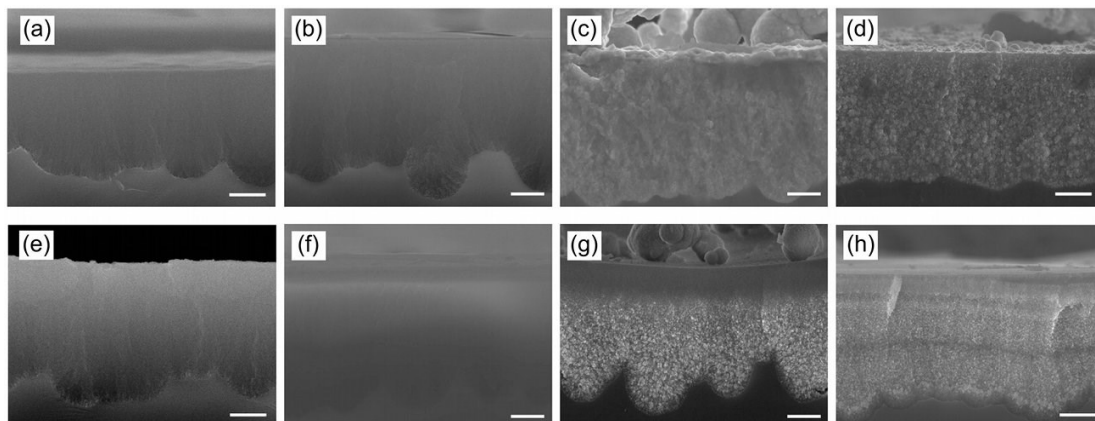


Figure 2.1: Cross-sectional SEM images of the porous silicon electrodes after electrochemical deposition of platinum. The electrochemical deposition was carried out in the $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$ baths for (a-d) and (e-h), respectively. Concentrations of platinum ions were (a) 0.001M, (b) 0.009 M, (c) 0.010 M and (d) 0.100 M for $[\text{PtCl}_4]^{2-}$, and (e) 0.002 M, (f) 0.004, (g) 0.005M and (h) 0.100 M for $[\text{PtBr}_4]^{2-}$. The drastic change in the electrodeposition within the porous layer can be appreciated from (b) and (c) for $[\text{PtCl}_4]^{2-}$ and from (f) and (g) for $[\text{PtBr}_4]^{2-}$. White bars in the figures indicate 0.5 μm .

2.3.2 Effect of affinity of pore wall surface with water

The surface-induced structure of platinum complex ions is dependent upon the affinity of the pore wall surface with water. In this experiment, the concentration of $[\text{PtCl}_4]^{2-}$ was kept constant at 0.1 M, but the affinity was controlled by modifying the surface in mixture *n*-hexane solutions of methyl propiolate and propiolic acid with various molar ratios. The total concentration of methyl propiolate and propiolic acid was kept constant at 0.2 M. When the porous electrode modified with 0.13 M methyl propiolate and 0.07 M propiolic acid was used, no platinum deposited was observed in the porous layer as shown in Figure 2.2a. Platinum can be observed on the top surface of the porous layer (or slightly inside the porous layer from the top). This electrode had the contact angle of 83° with ultra pure water before the electrochemical deposition (Figure 2.2c). Interestingly, the deposition behavior showed a drastic change when the electrode was modified with 0.14 M methyl propiolate and 0.06 M propiolic acid. Because the relative concentration of propiolic acid was slightly higher, the contact angle exhibited only a minor increase from 83° to 86° as shown in Figure 2.2d. The deposition behavior for 86° becomes markedly different (i.e., an abrupt change is displayed) from that for 83° . The electrochemical deposition within the porous layer was promoted far more strongly when the porous electrode with the contact angle of 86° was used (Figure 2.2b). The very small increase in the contact angle or in the surface hydrophobicity is effective enough to induce such a drastic change in the deposition behavior. Again, there exists a threshold degree of the affinity of the pore wall surface with water.

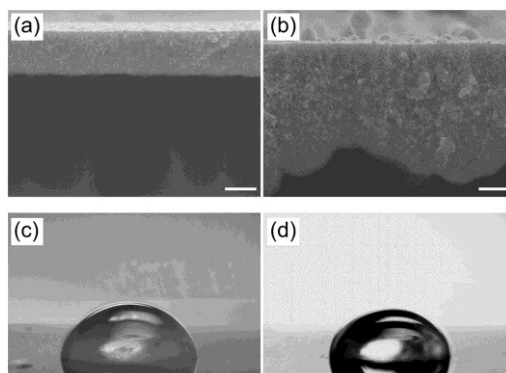


Figure 2.2: Cross-sectional SEM images (a, b) of the porous silicon electrodes modified with both propiolic acid and methyl propiolate under different molar ratios. Images shown in (c, d) are snapshots of contact angle measurements. Concentrations of propiolic acid and methyl propiolate were 0.07 M and 0.13 M, respectively, for (a, c), while they were 0.06 M and 0.14 M, respectively, for (b, d). The electrodes shown in (a, c) were only slightly more hydrophilic than those shown in (b, d). The cross-sectional images were taken after electrochemical deposition of platinum. White bars in the figures (a, b) indicate 0.5 μm .

2.3.3 Effect of depth of nanopores

We investigate the effect of pore depth on the electrochemical deposition behavior for the hydrophobic surface. If supply of the ions was made through mass transfer, the deposition behavior would be influenced by the pore depth. The pore depth (or equivalently, the thickness of the porous layer) can be tuned by changing the anodization time for preparing the porous silicon electrodes. Although the porous-layer thickness (i.e., the pore depth) of $\sim 2\ \mu\text{m}$ in the experiment described above could be sufficiently large, a silicon electrode with even much deeper pores (the thickness reaches $\sim 5\ \mu\text{m}$) was also tested in the $[\text{PtCl}_4]^{2-}$ or $[\text{PtBr}_4]^{2-}$ bath. The concentration of the platinum complex ions was 0.1 M. As shown in Figure 2.3, for both of $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, platinum is uniformly deposited and distributed within the pores as in the case of shallow pores. Surprisingly, no voids are found in the deposit. The amount of platinum deposited on the top surface is smaller for $[\text{PtBr}_4]^{2-}$

than for $[\text{PtCl}_4]^{2-}$, which is independent of the pore depth. From these results, we can conclude that supply of the ions is made not through mass transfer but through another physical factor.

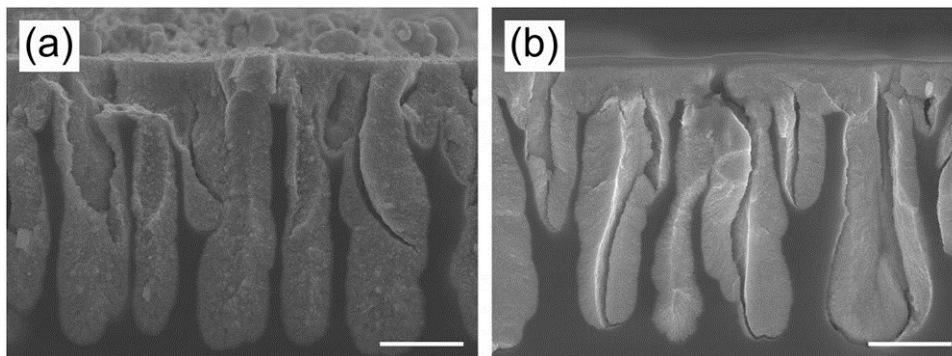


Figure 2.3: Cross-sectional SEM images of thicker porous silicon electrodes after electrochemical deposition of platinum. The electrochemical deposition was carried out in the $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$ baths for (a) and (b), respectively. The concentration of the platinum complex ions was 0.1 M. The thickness of the porous layer was $\sim 5 \mu\text{m}$. White bars in the figures indicate $2 \mu\text{m}$.

2.3.4 Summary of experimental results

We have found that there exists a threshold for the concentration of platinum complex ions. The behavior of platinum deposition within nanopores on silicon falls into one of two completely distinct categories in terms of whether the concentration is lower or higher than the threshold. This result is strongly suggestive of the occurrence of a transition phenomenon. A threshold degree of the affinity of the pore wall surface with water also exists. Once the ion concentration or the degree of surface hydrophobicity exceeds the threshold, drastic acceleration of the electrochemical deposition occurs within nanometer-sized pores irrespective of their depth. The existence of such thresholds cannot be explained by the simple consideration of the electrochemical reaction coupled with mass transfer. It should be noted that porous silicon with $\sim 20 \text{ nm}$ in diameter could be fabricated by electrochemical dissolution of highly doped silicon wafers. However, the pore size is

considerably dependent on the doping level, and the electrodeposition behavior becomes different between ~2 nm-sized pores and ~20 nm-sized pores in terms of electrochemical properties. Hence, it is not straightforward to examine the pore-size effect from an experimental viewpoint.

In earlier work, we gave the following remarks: The surface-induced hydration structure of platinum ions is crucial for controlling the electrochemical deposition; the ion concentration is enriched within a thin layer (its thickness is almost equal to the ion size) at the surface; but the average ion concentration within the layer increases only in proportion to the bulk concentration. Hence, the existence of such thresholds cannot be explained by these previous remarks. As argued below, we identify the striking phenomenon as a surface-induced phase transition occurring within the nanometer-sized pores. The theoretical analysis in our earlier work¹¹ was made only for a very low ion concentration which was far from the threshold argued in the present work.

2.4 Theoretical analyses

2.4.1 Analysis on phase transition in bulk fluid or liquid mixture

The concepts of the phase transition of a pure fluid¹²⁻¹⁶ or a liquid mixture¹⁷⁻¹⁹ in the bulk have already been established on the basis of the integral equation theories using the hypernetted-chain (HNC) and Percus-Yevick (PY) approximations. As an example system, let us consider a pure bulk fluid, wherein the fluid particles interact through Lennard-Jones potential, at a sufficiently low temperature.^{12,14} The Fourier transform of the total correlation function $h(r)$, $H(k)$, is expressed by

$$H(k) = 4\pi \int_0^{\infty} r^2 h(r) \{\sin(kr)/(kr)\} dr. \quad (1a)$$

$H(0)$ ($H(k)$ at zero wave vector ($k=0$)),

$$H(0)=4\pi\int_0^{\infty} r^2 h(r)dr, \quad (1b)$$

is an important parameter: When the number density ρ is gradually increased from a gas-phase value, at a threshold ρ_G^* , $H(0)$ exhibits an abrupt increase toward an extremely large value. That is, $h(r)$ becomes long ranged. When ρ is gradually decreased from a liquid-phase value, qualitatively the same behavior is observed at a threshold ρ_L^* . It is not quite definite whether at the threshold $H(0)$ truly diverges (the divergence of $H(0)$, which is equivalent to that of the isothermal compressibility or the correlation length, implies that $h(r)$ becomes infinitely long ranged) or remains finite, because the integral equation theory is solved not analytically but numerically. In either case, however, the abrupt increase can well be qualified as a signal of the spinodal instability: In the region, $\rho_G^* < \rho < \rho_L^*$, the fluid cannot exist as a single phase even in a metastable state; and the thresholds are the spinodal points for the liquid-gas phase separation beyond which the second phase unavoidably appears. In the real system, the transition occurs at a number density lower than ρ_G^* (ρ_G^+) or higher than ρ_L^* (ρ_L^+) ($\rho_G^+ < \rho < \rho_G^*$ and $\rho_L^* < \rho < \rho_L^+$ are the metastable regions). When the temperature is sufficiently high, there is no transition occurring.

We then consider a two-component liquid mixture¹⁷⁻¹⁹ which is immiscible unless the concentration of one of the components is sufficiently low (e.g., a mixture of water and cyclohexane). When the concentration of component 1 is gradually increased from zero, at a threshold C_1^* the Fourier transforms of the total correlation functions for the like pairs at zero wave vector ($H_{11}(0)$ and $H_{22}(0)$) simultaneously exhibit abrupt increases toward extremely large values (the Fourier transforms of the total correlation function for the unlike pair at zero wave vector, $H_{12}(0)$, displays an abrupt decrease toward an extremely large, negative value).¹⁹ Qualitatively the same behavior is encountered at a threshold C_2^* when the concentration of component 2 is gradually increased from zero. This *divergent* behavior, though it may not be a true divergence, gives a signal of the spinodal instability: The thresholds, C_1^* and C_2^* , are the

spinodal points for the demixing (liquid-liquid phase separation) beyond which the second phase unavoidably appears.

2.4.2 Analysis on surface-induced phase transition

The well-established concept for the phase transition of a pure fluid or a liquid mixture in the bulk has been extended by Kinoshita to a surface-induced phase transition using some different versions of the integral equation theory (IET) combined with simple-liquid models.²⁰⁻²⁵ A very large spherical particle (this is referred to as “macroparticle”) is usually employed to mimick an extended surface. In the simple-liquid model, the potential is dependent only on the distance between centers of two particles. The surface-induced phase transition is most likely to occur for water containing a low concentration of hydrophobic solute near a hydrophobic surface or for nonpolar liquid containing a low concentration of hydrophilic solute near a hydrophilic surface. The concentration of hydrophobic solute is enriched near the surface in the former while the concentration of hydrophilic solute is enriched near the surface in the latter. As the solute concentration in the bulk C increases, the enrichment becomes stronger, but the thickness of the enriched layer is microscopic in the sense that it is comparable with the solute size. However, near a threshold value of C , C^* , the Fourier transform of the surface-solute total correlation function at zero wave vector exhibits an abrupt increase toward infinity. (Since the integral equation theory is numerically solved, the abrupt increase may not be a true divergence but the behavior is highly divergent.) This can be identified as a signal of a transition phenomenon, a sudden growth of the enriched layer: The thickness of the layer grows from a microscopic scale to a submicroscopic one (much larger than the solute size but not a macroscopic scale because the bulk is thermodynamically stable as a single phase), and the solute concentration within the layer becomes much higher. This transition is referred to as the *partial-wetting transition* representing the partial wetting of the surface by the solute.^{20,21,25,26} C^* is the spinodal point beyond which the liquid near the surface cannot exist as a

single phase even as a metastable state. The second phase unavoidably appears at the surface. Beyond C^* the IET possesses no solutions. In the real system, the transition occurs at a concentration (C^+) that is lower than C^* ($C^+ < C < C^*$ is the metastable region). Let the thickness of the second phase be δ . The average solute concentration in the second phase and δ should be increasing functions of $C > C^*$ though they cannot be calculated by the IET.²⁵ The analysis on the partial-wetting transition has been extended to a molecular liquid near a surface.²⁶

The physical quantity, whose gradual increase eventually gives rise to the spinodal behavior, is not necessarily the solute concentration. For example, in the case of water containing a low concentration of hydrophobic solute near a surface, it can be the degree of the surface hydrophobicity. The spinodal point is encountered when the surface hydrophobicity is gradually strengthened, if the solute concentration is sufficiently high. When the HNC closure neglecting the bridge function is employed, however, it is often that the IET loses its solutions before the Fourier transform of the surface-solute total correlation function at zero wave vector exhibits the divergent behavior: It displays a significantly large increase but no abrupt increase toward infinity; and it certainly remains finite at the threshold.^{13,15,16} Thus, the HNC closure is often incapable of reproducing the spinodal behavior completely. Nevertheless, the significantly large increase accompanying the loss of the solutions can doubtlessly be regarded as a signal of the transition phenomenon (see the last paragraph in Sec. 2.5.2).

When the liquid is confined between two surfaces, if the surface separation L is sufficiently small, the confined domain is unavoidably filled with the second phase beyond a threshold value of C , C^{**} , which is referred to as the *bridging transition* (the two enriched layers bridge each other).²²⁻²⁵ In the case of $L \sim 2\delta$, the spinodal point of the bridging transition C^{**} is approximately equal to C^* : $C^{**} \sim C^*$. For $L < 2\delta$, however, it is lower than C^* ; it becomes lower as L decreases; and for very small L , the transition occurs at a remarkably low solute concentration in the bulk. It should be noted that the transition

phenomenon is *induced by the surface*. As the pore diameter decreases, the liquid confined within the pore is more influenced by the surface properties. It can thus be understood and has been verified by theoretical analyses that the surface-induced transition can occur more readily for a smaller pore. We emphasize that the surface-induced phase transition occurs even when the bulk is quite stable as a single phase. As a striking example, a nanopore (a pore whose diameter is a scale of a few nanometers) can be filled with the second phase at an unexpectedly low solute concentration in the bulk.

The concept of the surface-induced phase transition proposed by Kinoshita²⁰⁻²⁶ has been supported by a computer-simulation study. By using Grand Canonical Monte Carlo simulations, Greberg and Patey²⁷ verified the occurrence of the bridging transition for model systems mimicking water containing a low concentration of hydrophobic solute confined between hydrophobic surfaces and nonpolar liquid containing a low concentration of water confined between hydrophilic surfaces. In our view, the following experimental result is relevant to the concept. Kurihara and coworkers²⁸ studied cyclohexane-ethanol binary liquid near a single silica surface. Their system corresponds to nonpolar liquid (cyclohexane) containing a low concentration of hydrophilic solute (ethanol) near a hydrophilic surface (silica surface). They gradually increased the ethanol concentration from zero: They observed an abrupt formation of an ethanol layer whose thickness reached ~15 nm at the ethanol concentration of ~0.1 mol%. This manifests the existence of the partial-wetting transition.

2.4.3 Angle-dependent integral equation theory for molecular liquid near a surface

It is crucial to adopt a molecular model for water in the investigation of the ion-size effects. A water molecule is modeled as a hard sphere with diameter $d_S=0.28$ nm in which a point dipole and a point quadrupole of tetrahedral symmetry are embedded.^{29,30} The influence of molecular polarizability of water is included by employing the self-consistent mean field (SCMF)

theory.^{29,30} At the SCMF level the many-body induced interactions are reduced to pairwise additive potentials involving an effective dipole moment. Hard spherical cations and anions with diameters d_+ and d_- , respectively, are immersed in our model water. The water-water and water-ion correlations are then dependent not only on the distance between centers of the particles but also on the orientations of water molecules. We analyze the structure of aqueous electrolyte solution at an extended, uncharged or only weakly charged (hydrophobic) surface. The water-surface correlations are also dependent on the orientations of water molecules.

We employ the angle-dependent integral equation theory (ADIET), a statistical-mechanical theory for molecular liquids.^{26,29-45} A large, spherical particle with diameter $d_L=30d_s$ mimicking an extended surface is immersed in our model aqueous electrolyte solution. The subscripts, “S”, “+”, “-”, and “L” respectively, represent “solvent (water)”, “cations”, “anions”, and “large particle”. The large particle carries the charge Q_L placed at its center (the surface charge density is $Q_L/(\pi d_L^2)$). The Ornstein-Zernike (OZ) equation for the mixture comprising the large particle, water molecules, cations, and anions can be written as

$$\eta_{\alpha\beta}(12)=\{1/(8\pi^2)\} \sum_{\gamma} \rho_{\gamma} \int c_{\alpha\gamma}(13) \{ \eta_{\gamma\beta}(32)+c_{\gamma\beta}(32) \} d(3), \quad (2a)$$

$$\eta_{\alpha\beta}(12)=h_{\alpha\beta}(12)-c_{\alpha\beta}(12); \alpha, \beta=S, +, -, L \quad (2b)$$

where h and c are the total and direct correlation functions, respectively, (ij) represents $(\mathbf{r}_{ij}, \mathbf{\Omega}_i, \mathbf{\Omega}_j)$, $\mathbf{r}_{ij}$ is the vector connecting the centers of particles i and j , $\mathbf{\Omega}_i$ denotes the three Euler angles describing the orientation of particle i , $\int d(3)$ represents integration over all position and angular coordinates of particle 3, and ρ is the number density. The closure equation is expressed by

$$c_{\alpha\beta}(12) = \int_{r_{12}}^{\infty} [h_{\alpha\beta}(12) \partial \{w_{\alpha\beta}(12) - b_{\alpha\beta}(12)\} / \partial r'_{12}] dr'_{12} - u_{\alpha\beta}(12)/(k_B T) + b_{\alpha\beta}(12), \quad (3a)$$

$$w_{\alpha\beta}(12) = -\eta_{\alpha\beta}(12) + u_{\alpha\beta}(12)/(k_B T), \quad (3b)$$

where u is the pair potential, b is the bridge function, and $r_{12} = |\mathbf{r}_{12}|$. In the present analysis, the hypernetted-chain (HNC) approximation is employed ($b=0$). We assume that the macroparticle is present at infinite dilution ($\rho_L \rightarrow 0$). The calculation process can then be split into two steps:

Step (i). Solve Eqs. (2) and (3) for bulk aqueous electrolyte solution. Calculate the correlation functions X_{SS} , X_{S+} , X_{S-} , X_{++} , X_{+-} , and X_{--} ($X=h, c$).

Step (ii). Solve Eqs. (2) and (3) for the macroparticle-aqueous electrolyte solution system using the correlation functions obtained in step (i) as input data. Calculate the correlation functions X_{LS} , X_{L+} , and X_{L-} ($X=h, c$).

For the numerical solution of Eqs. (2) and (3), the pair potentials and correlation functions are expanded in a basis set of rotational invariants (i.e., Wigner's generalized spherical harmonics), and the basic equations are reformulated in terms of the projections $X^{mnl} \mu\nu(r)$ (r is the distance between centers of two particles) occurring in the rotational-invariant expansion of X . The expansion considered for $m, n \leq n_{\max}=4$ gives sufficiently accurate results. The basic equations are then numerically solved using the robust, highly efficient algorithm developed by Kinoshita and coworkers.^{35,37} In the numerical treatment, a sufficiently long range r_L is divided into N grid points ($r_i = i\delta r$, $i=0, 1, \dots, N-1$; $\delta r = r_L/N$) and all of the projections are represented by their values on these points. The grid width and the number of grid points are set at $\delta r = 0.01d_S$ and $N=4096$, respectively.

In the real system treated in the present study, the solution is confined within pores having various sizes whose surfaces are concave. However, the analyses

on the solution confined by an extended surface provide fundamental information which can readily be applied to the solution confined between two extended surfaces, between two concave surfaces, or within a nanopore in a semi-quantitative sense. The microstructure (heterogeneity) of the surface is not taken into account in the theoretical calculation. However, it has been shown that it has no essential effects on the conclusion as long as the *averaged* properties of the surface-induced structure are discussed.⁴⁶

The aqueous electrolyte solution in the present system is modeled as follows. It is treated as water containing K_2PtCl_4 or K_2PtBr_4 at C M. The anion (i.e., the platinum complex ion), $[PtCl_4]^{2-}$ or $[PtBr_4]^{2-}$, is modeled as a spherical ion within which the point charge of $-2e$ (e is the elementary electric charge) is placed at the center. The point charge of K^+ placed at its center is e . The cation size d_+ is set at 0.3 nm. As the anion size d_- , 0.60 nm is adopted for $[PtCl_4]^{2-}$. The size of $[PtCl_4]^{2-}$ was approximately calculated from the molecular weight and density of K_2PtCl_4 in solid state with the tetragonal crystal structure. The size difference between $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$ can be set at the double of the size difference between Br^- and Cl^- , with the result that $d_- = 0.70$ nm is adopted for $[PtBr_4]^{2-}$.⁴⁷ A cation and an anion carry the charges e and $-2e$, respectively, and $\rho_+ = 2\rho_-$.

The versatility and reliability of the ADIET was demonstrated in our earlier works. For example, the hydration free energies of nonpolar solutes calculated by the ADIET with the multipolar model are in quantitatively excellent agreement with those from Monte Carlo computer simulations.⁴³ The dielectric constant of bulk water calculated, which is a good measure of the validity of a molecular theory, is ~ 83 that is in good accord with the experimental value ~ 78 . The ADIET has successfully been applied to detailed analyses on bulk water and aqueous electrolyte solution,^{29,30} electrical double-layer,³¹⁻³⁴ water or aqueous electrolyte solution near a hydrophobic surface,^{35,38,40-42} interaction between colloidal particles in aqueous electrolyte solution,³⁶ metal-aqueous electrolyte solution interface,³⁹ negative heat capacity of hydrophilic hydration,⁴⁵ weakening of the hydrophobicity at low

temperatures,⁴⁸ and rotational component of (i.e., contribution from the restriction of rotational freedom of water molecules near the solute to) the hydration entropy.⁴⁴

2.4.4 Application to the present system, aqueous electrolyte solution near a hydrophobic surface: A surface-induced layer whose thickness is comparable with anion size

First, we show $g_{L+}(\xi)$ (ξ is the distance from the surface) as well as $g_{L-}(\xi)$ near a hydrophobic surface ($Q_L=0$) in Figure 2.4. C is set at 0.005 M that is much lower than the spinodal concentration. The two values, 0.60 nm and 0.70 nm, are tested for d_- . The concentration of anions (i.e., platinum complex ions) is enriched in the immediate vicinity of the surface. As discussed in our recent publication,¹¹ the anions are not strongly hydrated due to the large anion size despite that the charge carried by them is as large as $-2e$. As a consequence, the anions are excluded from the bulk to the surface. This effect is stronger for $[\text{PtBr}_4]^{2-}$ than for $[\text{PtCl}_4]^{2-}$: The degree of the enrichment is remarkably sensitive to the anion size. By contrast, the cations are highly hydrophilic due to their small size and they are preferentially and strongly hydrated in the bulk, with the result that they are depleted near the surface. Of course, the local charge neutrality does not hold near the surface.

The strong enrichment of the anion concentration occurs only within the first layer, $0 \leq (\xi - d_-/2)/d_s < 1$. $g_{L-}(\xi)$ reduces quite rapidly as ξ increases. In this sense, the layer within which the anion concentration is enriched is microscopic. Our experience in analyses on confined aqueous electrolyte solutions has shown the following. Let us consider the solution confined between two extended surfaces. When the surface separation L is not small, the solution around the center is very much like that in the bulk and the normalized number-density profile of anions near each of the surfaces is close to that near a single surface. As L becomes smaller, the solution for all ξ is more influenced not only by the nearest surface but also by the other surface. When L becomes smaller than a few times of the diameter of a water

molecule, the normalized number-density profile for all ξ exhibits an upward shift and the anion-size effect becomes larger. As discussed in our recent publication, the upward shift and the enhancement of anion-size effect are more appreciable when L is smaller or the surface is concave and its curvature is larger. By the interplay of these physical factors, the enrichment of anion concentration and the anion-size effect become larger when the solution is confined within a pore having the size of a nanometer.

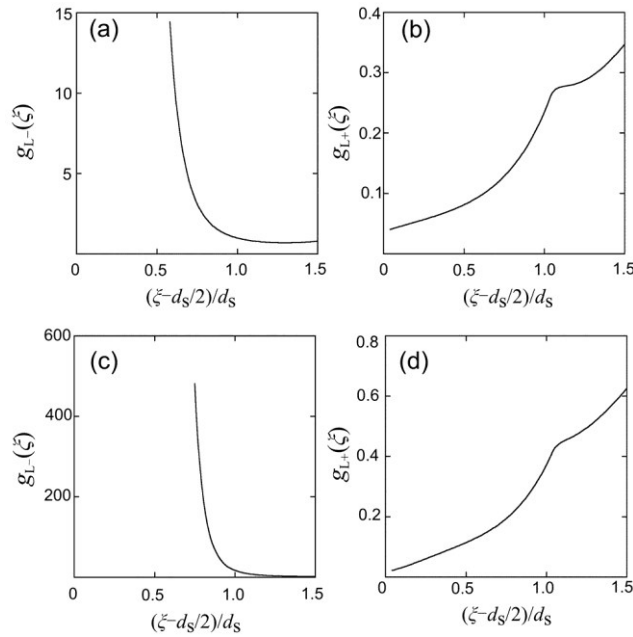


Figure 2.4: Normalized number-density profiles of anions $g_{L-}(\xi)$ (a, c) and cations $g_{L+}(\xi)$ (b, d) near an extended hydrophobic surface for $d_-=0.60$ nm (a, b) and $d_-=0.70$ nm (c, d). The anions are platinum complex ions, $[\text{PtCl}_4]^{2-}$ or $[\text{PtBr}_4]^{2-}$, and the cations are potassium ions, K^+ . $d_-=0.60$ nm and $d_-=0.70$ nm correspond to $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, respectively. It is indicated that the anion concentration is enriched near the surface whereas the cations are depleted.

2.4.5 Partial-wetting transition in the present system

In order to investigate the partial-wetting transition in the present system, we monitor the two quantities, $g_{L-}(d_-/2)$ and $H_{L-}(0)$. Here, $g_{L-}(\xi) = \rho_{L-}(\xi)/\rho_-$ where ξ is the distance from the surface, $\rho_{L-}(\xi)$ is the number-density profile of anions, and ρ_- is the number density of anions in the bulk. $g_{L-}(\xi)$ represents the

surface-induced hydration structure of anions and $g_{L-}(\xi) \rightarrow 1$ as $\xi \rightarrow \infty$. $H_{L-}(k)$ is the Fourier transform of $h_{L-}(r)$ ($g_{L-}(r) = h_{L-}(r) + 1$):

$$H_{L-}(k) = 4\pi \int_0^{\infty} r^2 h_{L-}(r) \{\sin(kr)/(kr)\} dr. \quad (4a)$$

$H_{L-}(0)$ expressed by

$$H_{L-}(0) = 4\pi \int_0^{\infty} r^2 h_{L-}(r) dr \quad (4b)$$

gives a signal of the transition phenomenon as described above, but $g_{L-}(d_-/2)$ also gives an equivalent signal.

The theoretical analysis is made for the partial-wetting transition near a single, extended hydrophobic surface. Figure 2.5 shows the plot of $g_{L-}(d_-/2)$ or $H_{L-}(0)$ against the anion concentration in the bulk denoted by C . The two values, 0.60 nm ($[\text{PtCl}_4]^{2-}$) and 0.70 nm ($[\text{PtBr}_4]^{2-}$), are tested for d_- . As observed in the figure, both $g_{L-}(d_-/2)$ and $H_{L-}(0)$ tend to diverge at $C^* \sim 0.0255$ M for $d_- = 0.60$ nm and at $C^* \sim 0.0095$ M for $d_- = 0.70$ nm. This divergent behavior is a signal of the partial-wetting transition, a sudden growth of the enriched layer from a microscopic scale to a submicroscopic one. C^* is the spinodal point (the spinodal concentration) explained above.

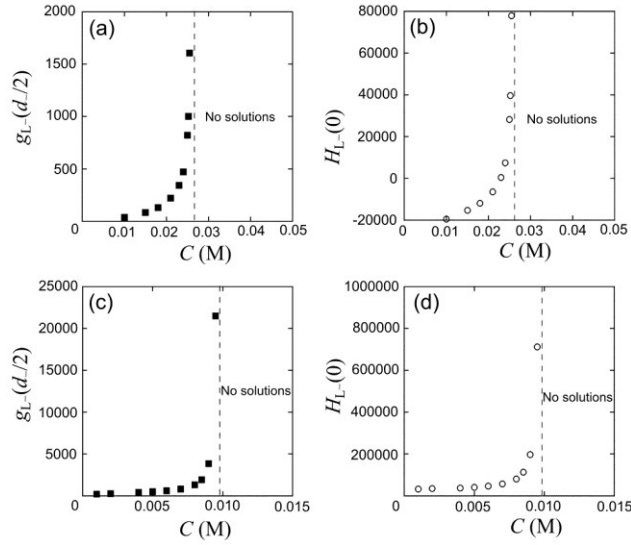


Figure 2.5: Relation between $g_L(d/2)$ (a, c) or $H_L(0)$ (b, d) and C (the concentration of anions, platinum complex ions) near an extended hydrophobic surface for $d=0.60$ nm (a, b) and $d=0.70$ nm (c, d). $d=0.60$ nm and $d=0.70$ nm correspond to $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, respectively. Both $g_L(d/2)$ and $H_L(0)$ diverge at $C^*\sim 0.0255$ M for $d=0.60$ nm and at $C^*\sim 0.0095$ M for $d=0.70$ nm. Beyond C^* (in the region indicated by “No Solutions”), the theory possesses no solutions.

2.5 Comparison between experimental and theoretical results

When the ADIET combined with the molecular model for water is employed, it is difficult to directly analyze the bridging transition. However, the analysis of the partial-wetting transition provides useful information on the bridging transition as well. As argued in Sec. 2.4.2, both of the two types of transitions have been investigated (not only theoretically²⁰⁻²⁶ but also experimentally^{27,28}) in detail for the same system consisting of simple-liquid models, and the connection between them is rather straightforward.

2.5.1 Threshold for concentration of platinum complex ions (anion concentration) in bridging transition

The spinodal concentration for the partial-wetting transition is $C^*\sim 0.0255$ M for $[\text{PtCl}_4]^{2-}$ and at $C^*\sim 0.0095$ M for $[\text{PtBr}_4]^{2-}$. The pore diameter of our

porous silicon is ~ 3 nm on the average. The spinodal concentration for the bridging transition within such a narrow pore, C^{**} , should be considerably lower than C^* . The anion concentration at which the bridging transition occurs, C° , is even lower than C^{**} . The threshold values observed in our experiments, ~ 0.0095 M for $[\text{PtCl}_4]^{2-}$ and ~ 0.0045 M for $[\text{PtBr}_4]^{2-}$, correspond to C° . Thus, the theoretical results are in agreement with the experimental observations in a semi-quantitative sense.

2.5.2 Threshold for affinity of pore-wall surface with water (strength of surface hydrophobicity) in bridging transition

By fixing C at 0.0260 M for $d=0.60$ nm ($[\text{PtCl}_4]^{2-}$; $C > C^*$), we analyze the effect of Q_L (this is a negative quantity) on $g_L(d/2)$ or $H_L(0)$. The essential matter is to set C at a value higher than C^* . Q_L is a measure of the hydrophobicity of the surface. As Q_L becomes closer to zero, the surface hydrophobicity becomes stronger. We gradually increase Q_L from the initial value, $-100e$. Figure 2.6 shows the plot of $g_L(d/2)$ or $H_L(0)$ against Q_L . Both $g_L(d/2)$ and $H_L(0)$ continue to increase until $Q_L \sim -50e$ though the increases are not divergent. For $Q_L > -50e$, the ADIET possesses no solutions. This result is indicative that the partial-wetting transition occurs beyond threshold strength of the surface hydrophobicity, which is qualitatively consistent with the experimental result.

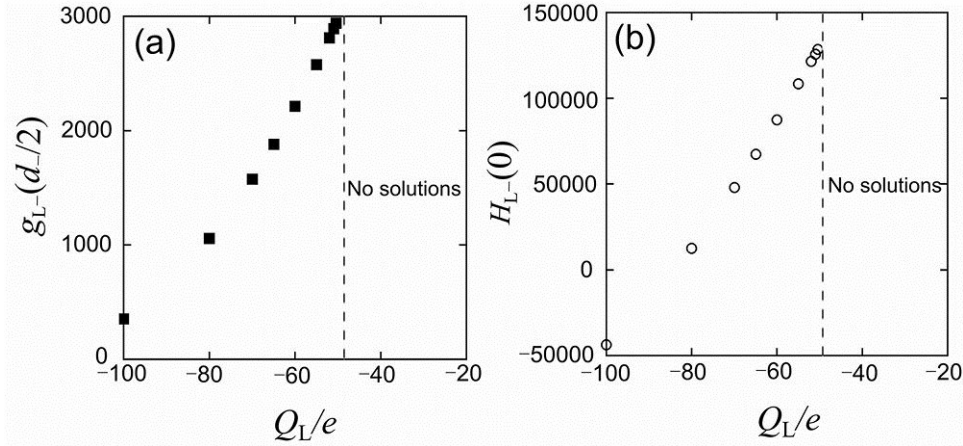


Figure 2.6: Relation between $g_{L-}(d-/2)$ (a) or $H_{L-}(0)$ (b) and Q_L/e (e is the elementary electric charge) near an extended surface for $d_-=0.60$ nm corresponding to $[\text{PtCl}_4]^{2-}$. $|Q_L/e|$ is a measure of strength of hydrophobicity of the surface: Smaller $|Q_L/e|$ implies weaker hydrophobicity. Both $g_{L-}(d-/2)$ and $H_{L-}(0)$ continue to increase, but beyond $Q_L/e \sim -50$ (in the region indicated by “No Solutions”), the theory possesses no solutions.

2.5.3 Properties of the second phase

The second phase appearing in the present system comprises the anions, water molecules, and cations. The anion concentration in the second phase should be orders of magnitude higher than C . Water molecules and cations are required for screening the electrostatic repulsive interactions among the anions. In fact, near the spinodal concentration C^* , $g_{LS}(d_s/2)$ and $g_{L+}(\xi)$ ($\xi \sim d_- + d_+/2$) also exhibit rather abrupt increases. The peaks of $g_{L-}(d-/2)$ and $g_{L+}(d_- + d_+/2)$ are indicative that the cations preferentially come into contact with the anions. The abrupt increase in $g_{L-}(d-/2)$ is more striking for $[\text{PtBr}_4]^{2-}$ than for $[\text{PtCl}_4]^{2-}$, implying that the anion concentration in the second phase is substantially higher for $[\text{PtBr}_4]^{2-}$. This result is in marked contrast with the case of water containing a nonpolar solute near a hydrophobic surface: In this case, the partial wetting of the surface by the solute accompanies the partial drying of the surface by water; and the second phase is formed by the solute molecules almost exclusively.^{23,25,26}

The ion concentration in the second phase filling a narrow pore should be

much higher than that formed at a single surface. Only if the pores are filled with the second phase, the electrodeposition is drastically accelerated because it is completely free from the diffusion-limited condition. Filling a pore with the second phase takes place as long as its diameter is sufficiently small regardless of its depth, which was proved by our experimental result illustrated in Figure 2.3.

2.5.4 Irrelevance to mass-transfer effect

The mass-transfer efficiency is not necessarily proportional to the anion concentration especially in nanospace. However, even such nonlinear behavior is not relevant to the transition phenomena by which the second phase abruptly appears and completely fills the whole space within nanopores. The phenomena arise from the long-range nature of the surface-anion correlation length. The mass transfer, whose driving force is the concentration gradient of the anions, is incapable of reproducing such transition phenomena. It is shown in our experiments that the whole space within nanopores is abruptly filled with the second phase even when the affinity of the surface with water is continuously reduced with fixing the ion concentration. This gives another evidence of the unrelevance to the mass-transfer effect.

2.5.5 Effect of electrochemical factors

Electrochemical factors are not taken into account in our theoretical analyses. What we have shown in the present study is as follows: Before the electrodeposition is started, the nanopores are filled with the second phase within which the anion concentration is orders of magnitude higher than in the bulk solution; and the anions are continuously supplied to the nanopores as they are consumed by the electrodeposition. The filling occurs quite rapidly just as the phase separation of a bulk liquid into two immiscible phases. The supply of the anions also occurs quite rapidly as long as the transition concentration of the anions is maintained in the bulk, which is consistent with the experimental observation that the porous layers is uniformly filled with the deposited plati-

num. We remark that the impact of the surface-induced phase transition is remarkable. Presumably, the surface is positively charged at the potential of platinum electrodeposition, and a positive electric field is emanated from the surface. Due to the field, the anions are attracted to the surface, acting in the direction where the transition phenomena are even enhanced. The neglect of the field is another factor leading to overestimation of C^* (see Sec. 2.5.1), but it does not vitiate the agreement between the experimental and theoretical results. Even if the surface is negatively charged, unless the surface-charge density is high, the surface-induced phase transition persists as shown in a theoretical study²⁶: It persists even at weakly charged (hydrophilic) surfaces immersed in water containing a low concentration of hydrophobic solute. A statistical-mechanical theory incorporating the electric field³⁹ has been developed, and the application of such a theory to the present case is a task for the future.

2.6 Concluding remarks

We have found the existence of thresholds for the concentration of platinum complex ions and the affinity of the pore wall surface with water in the electrochemical deposition of platinum within silicon electrode nanopores. The drastic change in the deposition behavior, which is exhibited beyond the threshold, cannot be explained by the consideration of the electrochemical reaction coupled with mass transfer. Also, the enrichment of the ion concentration within a thin layer at the surface is not capable of elucidating the drastic change, either. With the aid of statistical-mechanical theory for confined molecular liquids, we have revealed that the drastic change originates from a surface-induced phase transition. In our case, it occurs when the pore wall surface is sufficiently hydrophobic and the ion size is large enough for the ions to exhibit rather hydrophobic properties. As the ion size increases, for a fixed ion concentration the transition occurs even within larger pores, and for a fixed pore size it occurs at lower ion concentration in the bulk. Upon the transition, the nanopores are filled with the second phase within which the ion

concentration is orders of magnitude higher than in the bulk. The problem of the diffusion-limited condition, under which supply of the ions from the bulk becomes difficult, is completely overcome by the transition phenomenon. Once sufficiently large nuclei of platinum are formed on the electrode surface, the electrodeposition proceeds quite easily.

A surface-induced phase transition in nanospace was predicted by previous theoretical studies^{20-27,49,50}. Also, an experimental result²⁸ which should be relevant to the transition phenomenon is found in the literature. However, it has been investigated, for the first time, for the same system from both experimental and theoretical viewpoints in the present study. Moreover, its occurrence has never been reported for an aqueous electrolyte solution near a hydrophobic surface, which contains only weakly hydrated ions. It is interesting to look at some more different aqueous electrolyte solutions in future studies. Although the nanoporous materials have become important platforms for electrochemical reactions, the mass transfer of chemicals to and within nanopores has not yet been understood as emphasized in a recent review⁵¹. A surface-induced phase transition can take place even when the bulk liquid mixture is thermodynamically stable as a single phase, and it should be one of the crucial factors for controlling the electrochemical reactions that is substantially different from the mass transfer. It can be applied to other chemical reactions within nanometer-sized porous media: The transition filling nanospace with a solution containing reactants at orders of magnitude higher concentration will enable us to design and control novel materials possessing nanoporous structure. At the same time, the present results will stimulate the pioneering work in an interesting field for a liquid or liquid mixture confined in nanospace.

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3 Effect of cation species on surface-induced phase transition observed for platinum complex anions in platinum electrodeposition using nanoporous silicon

In an earlier work [K. Fukami et al. , J. Chem. Phys.138, 094702 (2013)], we reported a transition phenomenon observed for platinum complex anions in our platinum electrodeposition experiment using nanoporous silicon. The pore wall surface of the silicon electrode was made hydrophobic by covering it with organic molecules. The anions are only weakly hydrated due to their large size and excluded from the bulk aqueous solution to the hydrophobic surface. When the anion concentration in the bulk was gradually increased, at a threshold the deposition behavior exhibited a sudden change, leading to drastic acceleration of the electrochemical deposition. It was shown that this change originates from a surface-induced phase transition: The space within a nanopore is abruptly filled with the second phase in which the anion concentration is orders of magnitude higher than that in the bulk. Here we examine how the platinum electrodeposition behavior is affected by the cation species coexisting with the anions. We compare the experimental results obtained using three different cation species: K^+ , $(CH_3)_4N^+$, and $(C_2H_5)_4N^+$. One of the cation species coexists with platinum complex anions $[PtCl_4]^{2-}$. It is shown that the threshold concentration, beyond which the electrochemical deposition within nanopores is drastically accelerated, is considerably dependent on the cation species. The threshold concentration becomes lower as the cation size increases. Our theoretical analysis suggests that not only the anions but also the cations are remarkably enriched in the second phase. The remarkable enrichment of the anions alone would give rise to the energetic instability due to electrostatic repulsive interactions among the anions. We argue that the result obtained cannot be elucidated by the prevailing view based on classical electrochemistry. It is necessitated to consult a statistical-

mechanical theory of confined aqueous solutions using a molecular model for water.

3.1 Introduction

Porous materials play imperative roles in the development of such devices as sensors, catalysts, fuel cells, rechargeable batteries, and capacitors.¹⁻⁷ In the utilization of porous structure for a reaction field, a larger specific surface area brought by decreasing the pore diameter and increasing the porosity can lead to higher performance of chemical or electrochemical reactions. To prepare porous structure with high performance, the pore size needs to be sufficiently small, i.e., of the scale of a few nanometers. In solution (i.e., solvent in which reactants are dissolved as solutes), however, the mass transfer of reactants within such nanopores is geometrically hindered, and the extent of the hindrance becomes prominent with a decrease in the pore diameter. This is particularly true for deep pores. As a salient example, an electrochemical reaction within nanopores is remarkably decelerated once a diffusion-limited condition is reached due to the difficulty in supply of reactants from the bulk.^{8,9} Thus, it is often difficult in chemical or electrochemical reactions to elicit suitably high performance even when quite a large specific surface area is conferred to the porous structure. Design and control of injection into and ejection from nanopores is an important, challenging issue in modern nanotechnology.

Let us consider liquid or liquid mixture confined by a surface. The structure near the surface, which is referred to as “surface-induced structure,” is substantially different from that in the bulk. This is evidenced in, for instance, recent studies on ionic liquids near solid surfaces by scanning probe microscopy, nuclear magnetic resonance, ellipsometry, and X-ray reflectometry.¹⁰⁻¹⁴ Theoretical studies¹⁵⁻¹⁸ have argued that the surface-induced structure is largely influenced by the surface-liquid affinity. The solute concentration near the surface can remarkably be different from that in the

bulk. The details of the difference are determined by complex interplay of the solvent-solute, surface-solvent, and surface-solute affinities.^{19–24} Liquid, liquid mixture, or solution confined between two surfaces, when the surface separation is sufficiently small, may exhibit the structure and properties which are entirely different from those in the bulk. When it is confined within a nanopore, its structure and properties can be diverse, depending upon the pore diameter and the solvent, solute, and pore wall surface characteristics.

In recent works,^{25,26} we have investigated platinum electrodeposition within nanoporous silicon electrode (the pore diameter is ~ 3 nm on the average). The electrode is immersed in aqueous solution containing platinum complex ions (these are anions). The pore wall surface of the electrode is made hydrophobic by covering it with organic molecules and platinum complex ions with sufficiently large sizes, $[\text{PtCl}_4]^{2-}$, are adopted. Such ions are only weakly hydrated and excluded from the bulk with the result that the ionic concentration is largely enriched near the hydrophobic surface: They are rather hydrophobic in this sense. When the ion concentration in the bulk is gradually increased, at a threshold the deposition behavior exhibits a sudden change, leading to drastic acceleration of the electrochemical deposition.²⁶ Using our statistical-mechanical theory for confined molecular liquids, we have shown that this change originates from a surface-induced phase transition: The space within a nanopore is abruptly filled with the second phase in which the ion concentration is orders of magnitude higher than that in the bulk.²⁶ The threshold concentration is lowered when the ionic size is made larger (that is, $[\text{PtCl}_4]^{2-}$ with $d_-=0.60$ nm (d_- is the anion diameter) is replaced by $[\text{PtBr}_4]^{2-}$ with $d_-=0.70$ nm; the latter is more hydrophobic).^{25,26} When the pore wall surface is made hydrophilic, by contrast, there is no such striking behavior observed: It seems that the enrichment of the ionic concentration near the hydrophilic surface does not occur and the electrochemical deposition within nanopores does not proceed irrespective of the ionic concentration in the bulk. Near the hydrophilic surface, the concentration of the hydrophobic solute is not enriched but the number density of water is considerably heightened.

In the platinum electrodeposition experiment described above, we have been successful in producing platinum nanoparticles whose diameters are smaller than the pore diameter (~ 3 nm).²⁶ Below the threshold concentration, only filmy deposition is achieved on the top surface of porous silicon with essentially no deposition within nanopores. Above the threshold concentration, the nanoparticles are always deposited within nanopores. The surface-induced phase transition is thus crucial in the production of nanoparticles. Another significant finding is that the packing fraction of the nanoparticles produced within a nanopore can readily be controlled by adjusting the size of platinum complex ions.^{25,26} In the second phase filling nanopores, the ion concentration for $[\text{PtBr}_4]^{2-}$ is considerably higher than that for $[\text{PtCl}_4]^{2-}$, even when the ion concentrations in the bulk share the same value. Therefore, each nanopore is more densely packed with nanoparticles as the ion size is increased. It should be noted that this type of control is substantially different from the conventional one manipulating the applied potential, current density, or temperature of the electrochemical cell.

In the present study, we examine the effect of cations coexisting with $[\text{PtCl}_4]^{2-}$ on the platinum electrodeposition behavior. We compare the experimental results obtained using three different cation species: K^+ , $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$. It is shown that the threshold concentration, beyond which the electrochemical deposition within nanopores is drastically accelerated, is considerably dependent on the cation species which coexists with platinum complex anions. It follows that the cation species and its concentration in the bulk are also useful manipulated variables for controlling the deposition behavior. These results, which can hardly be expected from the standpoint of classical electrochemistry, are analyzed using our statistical-mechanical theory combined with a molecular model for water. The conclusion thus drawn is the following: The surface-induced phase transition for an anion species with a large size is substantially influenced by a coexisting cation species with a large size; and the influence becomes stronger as the cation size increases.

3.2 Materials and methods

Silicon wafers were purchased from Shin-Etsu Astech Co., Ltd., and all the chemicals were purchased from Nacalai Tesque, Inc. with analytical grade. Porous silicon electrodes were prepared by anodization of p-type silicon (100) with a resistivity in the range 3–5 Ω cm. The anodization was carried out in 22 wt. % HF solution (48 wt. % HF: ethanol = 1: 1.7 in volume) at 2.0 mA cm⁻² for 20 min. The average diameter of the pores was about $\sim$ 3 nm (the maximum diameter was $\sim$ 5 nm), and the thickness of porous layer was 1 μ m.

Displacement deposition of platinum (see Sec. 3.3.1) was performed using the porous silicon as the working electrode. Platinum complex (K_2PtCl_4) and one of the three salts, potassium chloride (KCl), tetramethylammonium chloride ($(\text{CH}_3)_4\text{NCl}$), and tetraethylammonium chloride ($(\text{C}_2\text{H}_5)_4\text{NCl}$), were added to ultra pure water (Millipore Reference A⁺, the resistivity of water was 18.2 M Ω cm). Each of the resultant solutions was used for the platinum deposition bath: K^+ , $(\text{CH}_3)_4\text{N}^+$, or $(\text{C}_2\text{H}_5)_4\text{N}^+$ coexisted with $[\text{PtCl}_4]^{2-}$ in the solution. The concentration of KCl, $(\text{CH}_3)_4\text{NCl}$, or $(\text{C}_2\text{H}_5)_4\text{NCl}$ (i.e., that of K^+ , $(\text{CH}_3)_4\text{N}^+$, or $(\text{C}_2\text{H}_5)_4\text{N}^+$) in the bulk was fixed at 0.5 M and that of K_2PtCl_4 (i.e., that of $[\text{PtCl}_4]^{2-}$) in the bulk was changed from 0.006 M to 0.010 M with the increment of 0.001 M. Thus, we looked at the deposition behavior for the 15 different solutions. In all the experiments, the displacement deposition was carried out for 2 h. As described in Sec. 3.3.1, the open circuit potential was measured after a porous silicon electrode was simply immersed in the deposition bath.

The cross-sectional views of the microporous silicon electrode after platinum displacement deposition were observed by a field-emission type scanning electron microscope (JEOL, JSM-6500F; SEM).

3.3 Experimental results and discussion

3.3.1 Concept of displacement deposition in porous silicon

In our earlier works,^{25,26} the surface of porous silicon was made hydrophobic by covering it with organic molecules. For the as-prepared porous silicon used

in the present study, such treatment is not necessary because its surface is terminated by Si–H bonds and inherently hydrophobic. The as-prepared porous silicon can spontaneously be oxidized in aqueous solution containing $[\text{PtCl}_4]^{2-}$. This spontaneous oxidation occurs together with the deposition of platinum on the silicon surface. Such deposition is categorized as *displacement deposition*.²⁷ The redox reactions can be written as follows: $[\text{PtCl}_4]^{2-} + 2\text{e}^- \rightarrow \text{Pt} + 4\text{Cl}^-$ and $\text{Si} + 2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{SiO}_2 + 4\text{H}^+$. Under the condition where a nanopore is filled with the second phase due to the surface-induced phase transition, the displacement deposition occurs drastically on the porous silicon wall, and platinum nanoparticles whose diameters are determined by the nanopore diameter are spontaneously produced without an external bias. Platinum is deposited within nanopores by this displacement deposition scheme in our experiment of the present study.

The oxidation of silicon during the displacement deposition should lead to only a slight change in the surface hydrophobicity. This is because the oxidation of silicon starts not from that of “Si–H” to “Si–OH” but from the backbond oxidation yielding “Si–O–Si”:²⁸ Most of the Si–H bonds still remain on the surface, leading to the persistence of the surface hydrophobicity during our deposition experiment.

3.3.2 Effect of coexisting cations on displacement deposition of platinum in porous silicon

Figure 3.1 shows cross-sectional SEM images of nanoporous silicon after the displacement deposition of platinum under a prescribed concentration of $[\text{PtCl}_4]^{2-}$ in the bulk with the three species of coexisting cations. At $C=0.006$ M (C is the concentration of $[\text{PtCl}_4]^{2-}$ in the bulk), the deposition does not proceed at all within the nanoporous layer in all the K^+ , $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$ solutions as observed in Figures 3.1(a)–3.1(c). At $C=0.007$ M (Figures 3.1(d)–3.1(f)), platinum is successfully deposited within nanopores only in $(\text{C}_2\text{H}_5)_4\text{N}^+$ solution. At $C=0.008$ M (Figures 3.1(g)–3.1(i)) and 0.009 M (Figures 3.1(j)–3.1(l)), the platinum deposition is achieved within the

nanoporous layer in $(\text{CH}_3)_4\text{N}^+$ and $(\text{C}_2\text{H}_5)_4\text{N}^+$ solutions but not in K^+ solution. At $C=0.010$ M (Figures 3.1(m)–3.1(o)), the platinum deposition is successful in all the K^+ , $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$ solutions.

Taken together, the platinum deposition in nanoporous silicon is suddenly accelerated at a threshold concentration C^{ex} in each of the three different solutions. The values of C^{ex} for K^+ , $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$ solutions are, respectively, in the ranges 0.009–0.010 M, 0.007–0.008 M, and 0.006–0.007 M. The threshold concentration is dependent upon the cation species which coexists with $[\text{PtCl}_4]^{2-}$.

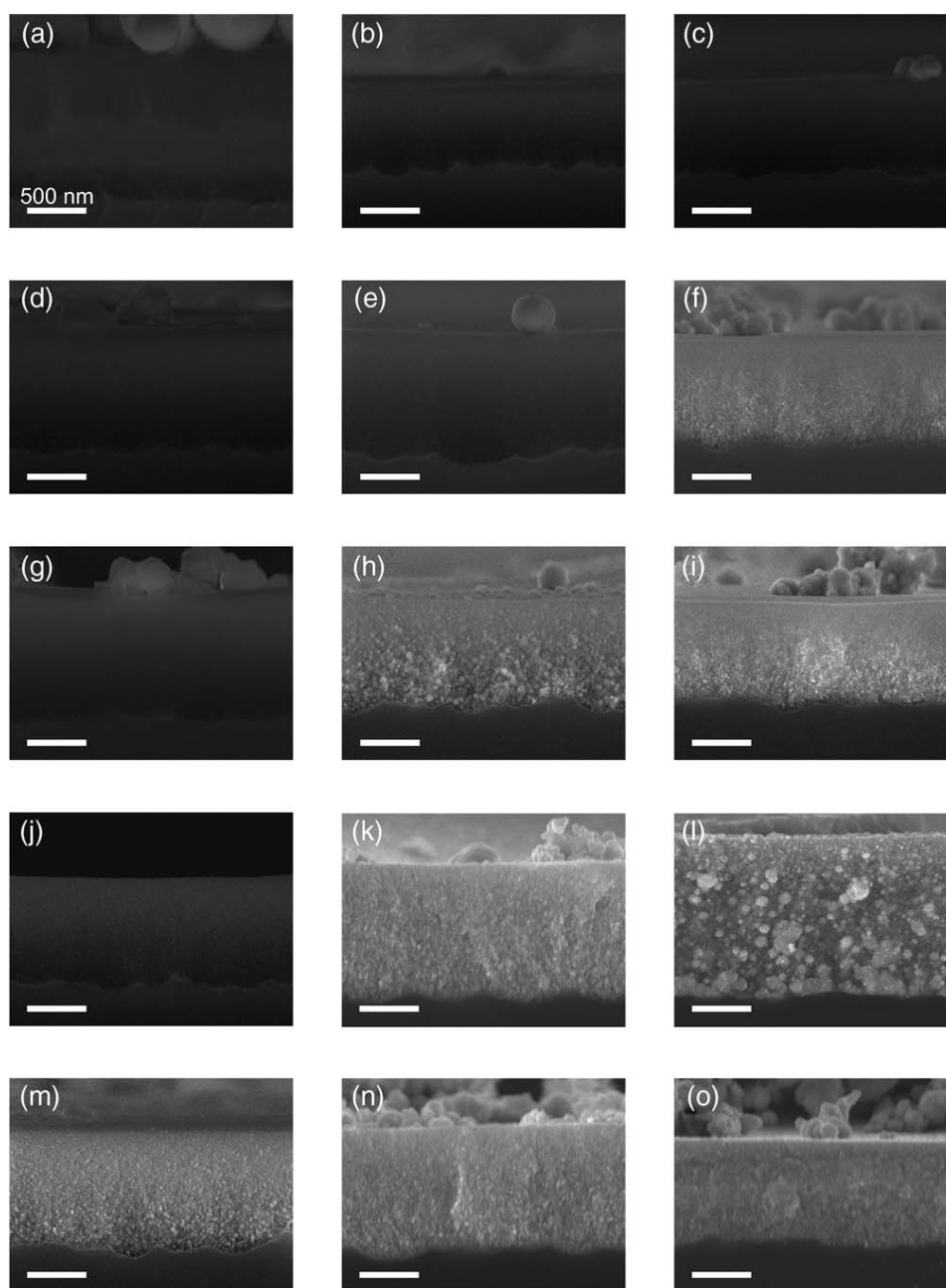


Figure 3.1: Cross-sectional SEM images of porous silicon after platinum displacement deposition. Samples on the left column (a, d, g, j, and m), middle column (b, e, h, k, and n), and right column (c, f, i, l, and o) were prepared, respectively, in 0.5 M of KCl, $(\text{CH}_3)_4\text{NCl}$, and $(\text{C}_2\text{H}_5)_4\text{NCl}$ solutions containing $[\text{PtCl}_4]^{2-}$ at the five different concentrations: 0.006 M (a, b, and c), 0.007 M (d, e, and f), 0.008 M (g, h, and i), 0.009 M (j, k, and l), and 0.010 M (m, n, and o). The scale bar indicates 500 nm.

3.3.3 Electrochemical behavior in platinum deposition analyzed using prevailing view

We measured the relation between current density and electrode potential for a flat silicon electrode, that is, the so-called i - E curve. The measurement serves as one of the typical methods to evaluate the electrochemical behavior. Figure 3.2 shows i - E curves measured for the flat silicon electrode in K^+ , $(CH_3)_4N^+$, and $(C_2H_5)_4N^+$ solutions containing $[PtCl_4]^{2-}$ at $C=0.008$ M. We emphasize that the experiment described in Sec. 3.2 was performed not for a flat surface but for nanopores. In Figure 3.2, all the curves are essentially indistinguishable, implying that the electrochemical behavior remains almost the same, being independent of the species of coexisting cations. This result indicates that the partial-wetting transition (see Sec. 3.4.1) does not occur for a *flat surface* at $C=0.008$ M in the aqueous solution employed in our experiment. The sudden acceleration of platinum deposition within nanopores at a threshold concentration of $[PtCl_4]^{2-}$ (Figure 3.1), which manifests a transition phenomenon, should originate not from the electrochemical behavior but from the surface-induced phase transition.

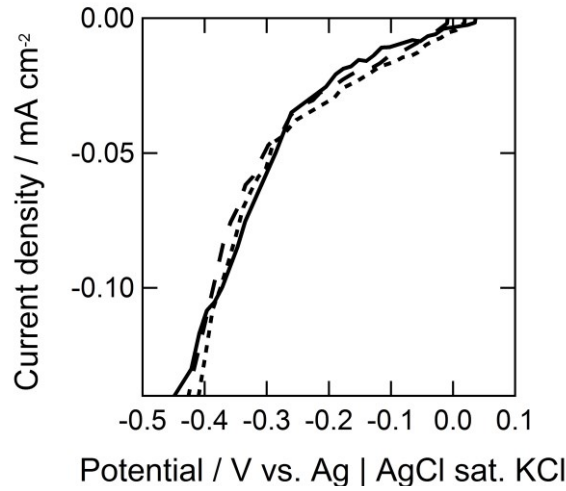


Figure 3.2: Current density versus potential curves measured for a flat silicon electrode in aqueous solutions containing 0.5 M of KCl (solid line), $(\text{CH}_3)_4\text{NCl}$ (dotted line), and $(\text{C}_2\text{H}_5)_4\text{NCl}$ (dashed line). The concentration of $[\text{PtCl}_4]^{2-}$ was 0.008 M. Scan rate was 10 mV/s. Although all the curves are almost perfectly overlapped, the platinum deposition within nanopores behaved quite differently (see Figures. 3.1(g)–3.1(i)).

The reaction rate of platinum displacement deposition is defined using the electrode potential where the reduction of platinum and the oxidation of silicon are balanced with each other. In other words, the net electric current flowing through the external circuit is zero. The current for the platinum deposition can be expressed by the equation,

$$i_{\text{Pt}} = n F A C_{\text{PtCl}} k(\phi) \quad (1)$$

where I_{Pt} denotes the current arising from the reduction of platinum that is balanced with the oxidation of silicon, n the number of electrons per a platinum complex ion reduced, F the Faradaic constant, A the surface area, $C_{[\text{PtCl}_4]^{2-}}$ the $[\text{PtCl}_4]^{2-}$ concentration at the surface, and $k(\phi)$ the reaction rate constant which is a function of the electrode potential ϕ . The diameters and depths of nanopores in silicon should remain unchanged during our experiment. This means that A as well as n and F is a constant. According to the result shown in Figure 3.2, the current is independent of the cation species

coexisting with $[\text{PtCl}_4]^{2-}$. A flat (non-porous) silicon electrode was employed in the i - E curve measurement. The electrochemical reaction took place on a single surface for which the partial-wetting transition could not occur as described above. The concentration of the platinum complex anions at the surface is not significantly influenced by the cation species with the result that $k(\phi)$ is not, either. It follows that I_{Pt} is dependent upon $C_{[\text{PtCl}_4]^{2-}}$ alone. Thus, the prevailing view based on classical electrochemistry applied to a flat electrode is incapable of elucidating the essential effect of the cation species.

As described above and in our earlier publications,^{25,26} the behavior of platinum deposition within nanopores in porous silicon is strongly influenced by the surface-water affinity (i.e., hydrophobicity or hydrophilicity of the pore wall surface), size of platinum complex anions (i.e., $[\text{PtCl}_4]^{2-}$ or $[\text{PtBr}_4]^{2-}$; even when the ionic strength is the same), and cation species coexisting with the anions in the aqueous solution. Moreover, the deposition behavior does not change monotonically as the anion concentration in the bulk increases: It exhibits a sort of transition phenomenon. Elucidation of this sophisticated result is made possible only by consulting a liquid-state theory based on statistical mechanics. In what follows, we review the surface-induced phase transition phenomena for solutions confined by a single surface or two surfaces and for solutions constrained within a nanopore. Model analysis which is closely related to the phenomena observed in the present experiment is also implemented.

3.4 Theoretical analysis

3.4.1 Concept of surface-induced phase transition

The concept of the surface-induced phase transition has been developed by Kinoshita^{19–24,29} using some different versions of the integral equation theory (IET). The surface-induced phase transition is most likely to occur for water containing a low concentration of hydrophobic solute near a hydrophobic surface or for nonpolar liquid containing a low concentration of hydrophilic solute near a hydrophilic surface. In the former, the hydrophobic solute, which

cannot participate in the hydrogen bonding of water, is excluded from water and its concentration is enriched near the hydrophobic surface. In the latter, the hydrophilic solute, which feels quite uncomfortable in nonpolar liquid, preferentially comes to the hydrophilic surface with the result of the enrichment of its concentration.

As the solute concentration in the bulk C increases, the enrichment mentioned above becomes stronger, whereas the thickness of the enriched layer is microscopic in the sense that it is comparable with the solute size. However, near a threshold value of C , C^* , the Fourier transform of the surface-solute total correlation function at zero wave vector exhibits an abrupt increase toward infinity, which indicates that the surface-solute correlation becomes quite intense and long ranged. This can be identified as a signal of a transition phenomenon exhibiting a sudden growth of the enriched layer: The thickness of the layer grows from a microscopic scale to a submacroscopic one, and the solute concentration within the layer becomes much higher. We note that the thickness is not of a macroscopic scale because the bulk is thermodynamically stable as a single phase. The transition is referred to as the *partial-wetting transition* representing the partial wetting of the surface by the solute.^{19,20,24,29} C^* is the spinodal point beyond which the microscopic surface-induced layer becomes unstable. Beyond C^* the IET possesses no solutions. In the real system, the transition occurs at the concentration that is lower than C^* , C^+ ($C^+ < C < C^*$ is the region which is metastable for the microscopic surface-induced layer). Let the thickness of the surface-induced layer be δ . The average solute concentration in the layer and δ should be increasing functions of $C > C^*$ though they cannot be calculated by the IET.

We then consider the solution confined between two surfaces (e.g., water containing a low concentration of hydrophobic component (i.e., solute) confined between two hydrophobic surfaces) with the surface separation L that is sufficiently small. When the solute concentration in the bulk C is gradually increased, the confined domain is unavoidably filled with the second phase (e.g., hydrophobic component containing a low concentration of water)

beyond a threshold value of C , C^{**} , which is referred to as the *bridging transition* implying that the two enriched layers bridge each other.^{21–24} In the case of $L \sim 2\delta$, the spinodal point of the bridging transition C^{**} is approximately equal to C^* : $C^{**} \sim C^*$. For $L < 2\delta$, however, it is lower than C^* for a single surface ($C^{**} < C^*$); it becomes lower as L decreases; and for very small L , the transition occurs at a remarkably low solute concentration in the bulk. Actually, the transition occurs at $C = C^{++}$ ($C^{++} < C^{**}$, $C^{++} \leq C^+$). Beyond C^{**} , the system without the second phase cannot exist even as the metastable state. $C^{++} < C < C^{**}$ is the region which is metastable for the system without the second phase. As for the liquid confined within a nanopore with diameter d_p , its behavior is more influenced by the surface properties than the behavior of the liquid confined between two surfaces with the surface separation $L = d_p$. The region which is metastable for the system without the second phase is represented by $C^{+++} < C < C^{***}$ (C^{***} is the spinodal concentration, the actual transition occurs at $C = C^{+++}$, $C^{***} < C^{**}$, and $C^{+++} < C^{++}$). Further, the influence becomes larger as d_p decreases. The transition, upon which the pore is unavoidably filled with the second phase, occurs at a lower solute concentration in the bulk for smaller d_p . In the present article, the transition occurring within a nanopore is also referred to as the bridging transition.

The two types of surface-induced phase transitions, partial-wetting and bridging transitions, occur even when the bulk is quite stable as a single phase. The existence of these transitions has been reproduced by computer-simulation and experimental studies. By using Grand Canonical Monte Carlo simulations, Greberg and Patey³⁰ verified the occurrence of the bridging transition for model systems mimicking water containing a low concentration of hydrophobic solute confined between hydrophobic surfaces and nonpolar liquid containing a low concentration of water confined between hydrophilic surfaces. Kurihara and co-workers³¹ experimentally studied cyclohexane-ethanol binary liquid near a single silica (SiO_2) surface. Their system corresponds to nonpolar liquid (cyclohexane) containing a low concentration of hydrophilic solute (ethanol) near a hydrophilic surface (silica surface). They

gradually increased the ethanol concentration from zero: They observed an abrupt formation of an ethanol layer whose thickness reached ~ 15 nm at the ethanol concentration of ~ 0.1 mol. %. This manifests the existence of the partial-wetting transition.

We have recently demonstrated the existence of the bridging transition for the aqueous electrolyte solution, water containing K_2PtCl_4 or K_2PtBr_4 , confined within a pore with a scale of a few nanometers.²⁶ The pore surface is made hydrophobic. The platinum complex anions, $[\text{PtCl}_4]^{2-}$ and $[\text{PtBr}_4]^{2-}$, behave as rather hydrophobic solutes due to their large sizes. As the anion size becomes larger with its charge kept constant, hydrogen atoms in water molecules with positive partial charges cannot come closer to it, leading to weaker stabilization by the electrostatic attractive interaction. That is, a sufficiently large anion possesses only weak affinity with water. We have shown the following: When the anion concentration in the bulk is gradually increased, at a threshold the space within a nanopore is abruptly filled with the second phase in which the anion concentration is remarkably higher than in the bulk. The threshold concentration for $[\text{PtBr}_4]^{2-}$ is lower than that for $[\text{PtCl}_4]^{2-}$.

3.4.2 Angle-dependent integral equation theory for molecular liquid near a surface

It is crucial to adopt a molecular model for water in the investigation of the ion-size effects. A water molecule is modeled as a hard sphere with diameter $d_S=0.28$ nm in which a point dipole and a point quadrupole of tetrahedral symmetry are embedded.^{32,33} The influence of molecular polarizability of water is included by employing the self-consistent mean field (SCMF) theory.^{32,33} At the SCMF level the many-body induced interactions are reduced to pairwise additive potentials involving an effective dipole moment. Hard spherical cations and anions with diameters d_+ and d_- , respectively, are immersed in our model water. The water-water and water-ion correlations are then dependent not only on the distance between centers of the particles but also on the orientations of water molecules. We analyze the structure of

aqueous electrolyte solution at an extended, uncharged (hydrophobic) surface. The water-surface correlations are also dependent on the orientations of water molecules.

We employ the angle-dependent integral equation theory (ADIET),^{29,32-49} a statistical-mechanical theory for molecular liquids. A large, spherical particle (neutral hard sphere) with diameter $d_L=30d_S$ mimicking an extended hydrophobic surface is immersed in our model aqueous electrolyte solution. The subscripts, “S,” “+,” “-,” and “L,” respectively, represent “solvent (water),” “cations,” “anions,” and “large particle.” The Ornstein-Zernike (OZ) equation for the mixture comprising the large particle, water molecules, cations, and anions can be written as^{29,32-49}

$$\eta_{\alpha\beta}(12)=\{1/(8\pi^2)\} \sum_{\gamma} \rho_{\gamma} \int c_{\alpha\gamma}(13) \{ \eta_{\gamma\beta}(32)+c_{\gamma\beta}(32) \} d(3), \quad (2a)$$

$$\eta_{\alpha\beta}(12)=h_{\alpha\beta}(12)-c_{\alpha\beta}(12); \alpha, \beta=S, +, -, L \quad (2b)$$

where h and c are the total and direct correlation functions, respectively, (ij) represents $(\mathbf{r}_{ij}, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$, $\mathbf{r}_{ij}$ is the vector connecting the centers of particles i and j , $\boldsymbol{\Omega}_i$ denotes the three Euler angles describing the orientation of particle i , $\int d(3)$ represents integration over all position and angular coordinates of particle 3, and ρ is the number density. The closure equation is expressed by^{29,32-49}

$$c_{\alpha\beta}(12)=\int_{r_{12}}^{\infty} [h_{\alpha\beta}(12) \partial \{w_{\alpha\beta}(12)-b_{\alpha\beta}(12)\} / \partial r'_{12}] dr'_{12} - u_{\alpha\beta}(12)/(k_B T) + b_{\alpha\beta}(12), \quad (3a)$$

$$w_{\alpha\beta}(12)=-\eta_{\alpha\beta}(12)+u_{\alpha\beta}(12)/(k_B T), \quad (3b)$$

where u is the pair potential, b is the bridge function, and $r_{12}=|\mathbf{r}_{12}|$. In the present analysis, the hypernetted-chain (HNC) approximation is employed ($b=0$). We assume that the macroparticle is present at infinite dilution ($\rho_L \rightarrow 0$). The calculation process can then be split into two steps:

Step (i). Solve Eqs. (2) and (3) for bulk aqueous electrolyte solution. Calculate the correlation functions X_{SS} , X_{S+} , X_{S-} , X_{++} , X_{+-} , and X_{--} ($X=h$, c).

Step (ii). Solve Eqs. (2) and (3) for the macroparticle-aqueous electrolyte solution system using the correlation functions obtained in step (i) as input data. Calculate the correlation functions X_{LS} , X_{L+} , and X_{L-} ($X=h$, c).

For the numerical solution of Eqs. (2) and (3), the pair potentials and correlation functions are expanded in a basis set of rotational invariants (i.e., Wigner's generalized spherical harmonics), and the basic equations are reformulated in terms of the projections $X_{\alpha\beta}^{mnl}{}_{\mu\nu}(r)$ (r is the distance between centers of two particles) occurring in the rotational-invariant expansion of $X_{\alpha\beta}$ (12). The expansion considered for m , $n \leq n_{\max}=4$ gives sufficiently accurate results. The basic equations are then numerically solved using the robust, highly efficient algorithm developed by Kinoshita and co-workers.^{38,40} In the numerical treatment, a sufficiently long range r_L is divided into N grid points ($r_i = i\delta r$, $i = 0, 1, \dots, N-1$; $\delta r = r_L/N$) and all of the projections are represented by their values on these points. The grid width and the number of grid points are set at $\delta r = 0.01d_S$ and $N = 4096$, respectively. The versatility and reliability of the ADIET was demonstrated in our earlier works on a variety of subjects (more details were described in our last publication²⁶ treating the electrochemical deposition of platinum within nanoporous silicon).

In the real system treated in the present study, the solution is confined within pores having various sizes whose surfaces are concave. However, the analysis on the solution confined by an extended surface and the partial-wetting transition provides fundamental information which can readily be applied to the solution confined between two extended surfaces and the solution within a nanopore in a semi-quantitative sense (see Sec. 3.4.1). The microstructure (heterogeneity) of the surface is not taken into account in the theoretical calculation. However, it has been shown that it has no essential effects on the

conclusion as long as the *averaged* properties of the surface-induced structure are discussed.⁵⁰

3.4.3 Model aqueous electrolyte solution considered

$[\text{PtCl}_4]^{2-}$ is considered as the platinum complex anion. Following our last publication²⁶ treating the electrochemical deposition of platinum within nanoporous silicon, we model $[\text{PtCl}_4]^{2-}$ as a hard sphere within which the point charge of $-2e$ (e is the elementary electric charge) is placed at its center. The size of $[\text{PtCl}_4]^{2-}$ is approximately calculated from the molecular weight and density of K_2PtCl_4 in solid state with the tetragonal crystal structure: We obtain $d_-/d_s=2.16$. As described in Sec. 3.4.2, only a single salt species can be treated in our computer program based on the ADIET. We therefore consider water containing X_2PtCl_4 whose concentration in the bulk is C . The cation X^+ is modeled as a hard sphere within which the point charge of e is placed at its center. The diameter of $(\text{CH}_3)_4\text{N}^+$ is roughly estimated from the molecular weight and density of $(\text{CH}_3)_4\text{NCl}$ in solid state by assuming that it possesses the close-packed structure and $(\text{CH}_3)_4\text{N}^+$ is spherical: The result is $d_+/d_s \sim 2$. We note that $(\text{C}_2\text{H}_5)_4\text{N}^+$ is larger than $(\text{CH}_3)_4\text{N}^+$. In our theoretical analysis, the three different values of d_+ are tested: $d_+/d_s=1.08$, 1.80 , and 2.00 . $d_+/d_s=1.08$ corresponds to the value for K^+ .²⁶ Though $d_+/d_s=1.80$ and 2.00 do not strictly correspond to $(\text{CH}_3)_4\text{N}^+$ or $(\text{C}_2\text{H}_5)_4\text{N}^+$, they are useful in examining the effect of the size of coexisting cations d_+ . A cation and an anion carry the charges e and $-2e$, respectively, and $\rho_+=2\rho_-$.

In our last publication mentioned above,²⁶ we analyzed water containing K_2PtCl_4 near a hydrophobic surface and found the occurrence of the partial-wetting transition in which the hydrophobic solute is $[\text{PtCl}_4]^{2-}$. In the present study, we consider X_2PtCl_4 ($d_+/d_s=1.08$, 1.80 , and 2.00) to know how the spinodal concentration C^* is affected by the size of X^+ , d_+ . When the concentration of X_2PtCl_4 , C , is given, ρ_+ and ρ_- are automatically determined. Since C is very low, ρ_s is fixed at the pure-water value.

3.4.4 Aqueous electrolyte solution near a hydrophobic surface: A surface-induced layer

We restate that all the calculations are performed for uncharged surfaces. The concentration profile of cations or anions is described by $g_{Lj}(\xi) = h_{Lj}(\xi) + 1 = \rho_{Lj}(\xi) / \rho_j$ ($j = +, -$) where ξ is the distance from the surface in the surface-normal direction, $\rho_{Lj}(\xi)$ is the number-density profile of cations or anions, and ρ_j is the number density of cations or anions in the bulk ($g_{Lj}(\xi) \rightarrow 1$ as $\xi \rightarrow \infty$). Even when C is much lower than the spinodal concentration, ions with large sizes are largely enriched near the hydrophobic surface. The degree of the enrichment follows the order: X^+ with $d_+/d_S = 2.00 > X^+$ with $d_+/d_S = 1.80 > [PtCl_4]^{2-}$. These ions, which behave as rather hydrophobic solutes, are often referred to as “ions exhibiting negative hydration.” For more information, in the case of $C = 0.00605$ M, $g_{L-}(0) = 29.99$ for $[PtCl_4]^{2-}$ and $g_{L+}(0) = 166.4$ for X^+ with $d_+/d_S = 1.80$; in the case of $C = 0.00189$ M, $g_{L-}(0) = 39.61$ for $[PtCl_4]^{2-}$ and $g_{L+}(0) = 656.0$ for X^+ with $d_+/d_S = 2.00$. The strong enrichment of the ion concentration occurs only in the vicinity of the surface. $g_{Lj}(\xi)$ reduces quite rapidly as ξ increases (a more detailed discussion on $g_{Lj}(\xi)$ is given in Sec. 3.4.6). In this sense, the layer within which the ion concentration is enriched is microscopic. On the other hand, ions with small sizes are preferentially hydrated in the bulk, with the result that they are depleted near the hydrophobic surface. These ions, which behave as highly hydrophilic solutes, are often referred to as “ions exhibiting positive hydration.” X^+ with $d_+/d_S = 1.08$, K^+ , and Cl^- (with $d_-/d_S = 1.16$) belong to these ions.

Our experience in analyses on confined aqueous electrolyte solutions has shown the following. Let us consider the solution confined between two extended surfaces. When the surface separation L is not small, the solution around the center within the confined space is very much like that in the bulk and the normalized number-density profile of ions near each of the surfaces is close to that near a single surface. As L becomes smaller, the solution for all ξ is more influenced not only by the nearest surface but also by the other surface. For ions with large sizes, for example, when L becomes smaller than a few

times of the diameter of a water molecule, the normalized number-density profile for all ξ exhibits an upward shift and the ion-size effect becomes larger. As discussed in our recent publication,²⁶ the upward shift and the enhancement of ion-size effect are more appreciable when L is smaller or the surface is concave and its curvature is larger. By the interplay of these physical factors, the enrichment of ion concentration and the ion-size effect becomes even larger when the solution is confined within a pore having the size of a nanometer.

3.4.5 Analysis on partial-wetting transition

In order to investigate the partial-wetting transition^{19,20,24,29} in the present system, we monitor the two quantities, $H_{Lj}(0)$ ($j=+, -$). $H_{Lj}(k)$ is the Fourier transform of $h_{Lj}(r)$:

$$H_{Lj}(k) = 4\pi \int_0^{\infty} r^2 h_{Lj}(r) \{\sin(kr)/(kr)\} dr. \quad (4a)$$

$H_{Lj}(0)$ expressed by

$$H_{Lj}(0) = 4\pi \int_0^{\infty} r^2 h_{Lj}(r) dr \quad (4b)$$

gives a signal of the transition phenomenon as described above. Divergence of $H_{Lj}(0)$ at the spinodal concentration C^* implies that the surface-cation or surface-anion correlation becomes quite intense and long ranged (i.e., not of a microscopic scale).

3.4.6 Partial-wetting transition: Effect of cation size

The theoretical analysis is made for the partial-wetting transition near a single, extended hydrophobic surface. For $d_+/d_s=1.08$, Figure 3.3(a) or 3.3(b) shows the plot of $H_{L+}(0)$ or $H_{L-}(0)$ against the concentration of $[\text{PtCl}_4]^{2-}$ in the

bulk denoted by C . It is found that $H_{L+}(0)$ and $H_{L-}(0)$ simultaneously exhibit the divergent behavior at the spinodal concentration C^* . This is true even for $d_+/d_s=1.08$. As observed in the figure, they tend to diverge at $C^* \sim 0.0254$ M. This behavior is a signal of the partial-wetting transition, a sudden growth of the enriched layer from a microscopic scale to a submicroscopic one. C^* is the spinodal point (the spinodal concentration) explained above. The divergence of $H_{L-}(0)$ is followed by that of $H_{L+}(0)$. As C approaches C^* , the normalized density profiles of cations and anions in the vicinity of the surface ($g_{L+}(\xi)$ and $g_{L-}(\xi)$, respectively; ξ is the distance from the surface in the surface-normal direction) make the changes illustrated in Figure 3.4. Near C^* , $g_{L+}(\xi)$ ($\xi \sim d_- + d_+/2$) as well as $g_{L-}(0)$ exhibits an abrupt increase but $g_{L+}(0)$ remains almost zero. This result is indicative that *the cations preferentially come into contact with the anions in contact with the surface.*

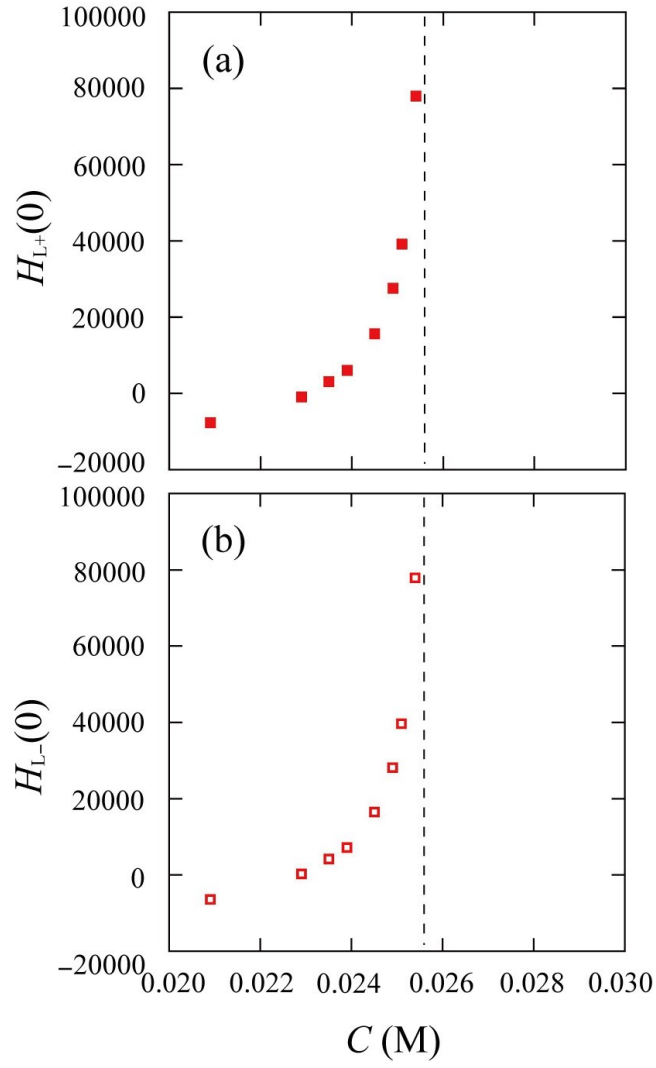


Figure 3.3: (a) $H_{L+}(0)$ plotted against C . (b) $H_{L-}(0)$ plotted against C . C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_s=1.08$ (d_+ denotes the diameter of X^+). The definition of $H_{Lj}(0)$ ($j=+, -$) is given by Eq. (4b). Beyond the spinodal concentration indicated by the broken line, the angle-dependent integral equation theory possesses no solutions.

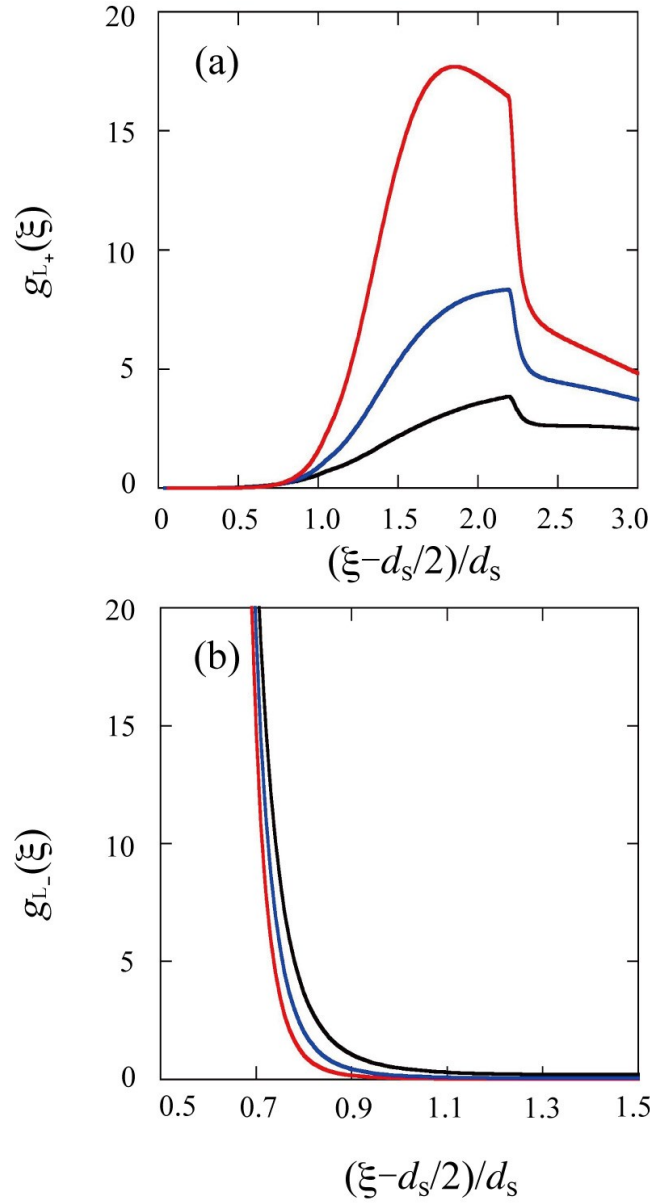


Figure 3.4: Normalized density profiles of cations (a) and anions (b) in the vicinity of the surface ($g_{L+}(\xi)$ and $g_{L-}(\xi)$, respectively; ξ is the distance from the surface in the surface-normal direction). Black: $C=0.0245$ M, blue: $C=0.0251$ M, and red: $C=0.0254$ M. C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_s=1.08$ (d_+ denotes the diameter of X^+). The contact values, $g_{L+}(d_+/2)$, in the three bulk concentrations are all zero and the contact position is at $(\xi - d_s/2)/d_s=0.04$. The contact values, $g_{L-}(d_-/2)$ ($d_-=2.16d_s$ denotes the diameter of $[PtCl_4]^{2-}$), in the three bulk concentrations are 630.4, 1002, and 1606, respectively, and the contact position is at $(\xi - d_s/2)/d_s=0.58$.

Similar plots for $d_+/d_s=1.80$ and $d_+/d_s=2.00$, respectively, are shown in Figures. 3.5 through 3.8. $H_{L+}(0)$ and $H_{L-}(0)$ simultaneously exhibit the divergent behavior at $C=C^*$. The simultaneous divergent behavior occurs at lower C^* as d_+ increases. The spinodal concentration C^* varies as follows: $C^* \sim 0.00825$ M and ~ 0.00258 M for $d_+/d_s=1.80$ and 2.00 , respectively. Near C^* , $g_{L+}(0)$ and $g_{L-}(0)$ exhibit simultaneous, abrupt increases. This result suggests that *the cations as well as the anions are in contact with the surface*.

We remark that cares must be taken in drawing Figures. 3.3, 3.5, and 3.7. Since the basic equations of the ADIET are solved not analytically but numerically, quite a robust numerical solution algorithm like ours is necessitated with very severe convergence criterion when C approaches C^* . The abrupt increases in $H_{L+}(0)$ and $H_{L-}(0)$ toward infinitely large values can then be traced out. As observed in the figures, it can be concluded that the ADIET possesses no solutions beyond C^* indicated by the broken line.

When the ADIET combined with the molecular model for water is employed, it is difficult to directly analyze the bridging transition because of the mathematical complexity. However, the analysis of the partial-wetting transition provides useful information on the bridging transition as well. We have investigated both of the two types of transitions in detail for the same system consisting of simple-liquid models, and the connection between them is rather straightforward. The pore diameter of our porous silicon is ~ 3 nm on the average. The spinodal concentration for the bridging transition within such a narrow pore, C^{***} , should be considerably lower than C^* . The salt concentration at which the bridging transition actually occurs, C^{+++} , is even lower than C^{***} . The threshold value observed in our experiment for X^+ with $d_+/d_s=1.08$, K^+ , which is in the range from 0.009 M to 0.010 M corresponds to C^{+++} . Thus, the theoretical results for X^+ with $d_+/d_s=1.08$ are in agreement with the experimental observations in a semi-quantitative sense. This type of argument does not hold in the cases of X^+ with $d_+/d_s=1.80$ and 2.00 as described in the first paragraph of Sec. 3.5.3.

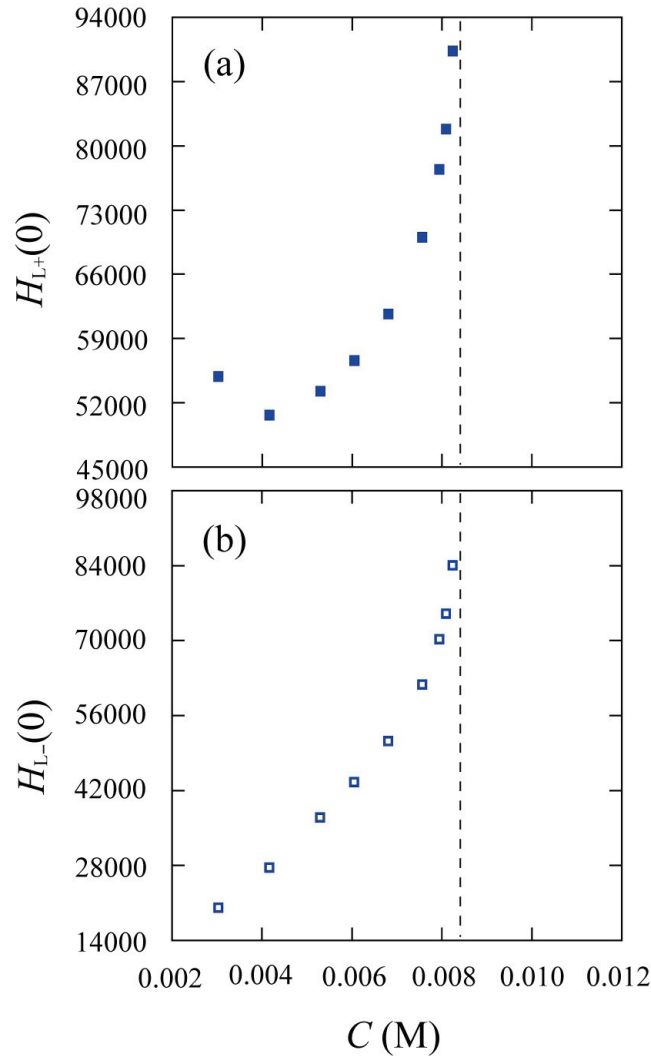


Figure 3.5: (a) $H_{L+}(0)$ plotted against C . (b) $H_{L-}(0)$ plotted against C . C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_S=1.80$ (d_+ denotes the diameter of X^+). The definition of $H_{Lj}(0)$ ($j=+, -$) is given by Eq. (4b). Beyond the spinodal concentration indicated by the broken line, the angle-dependent integral equation theory possesses no solutions.

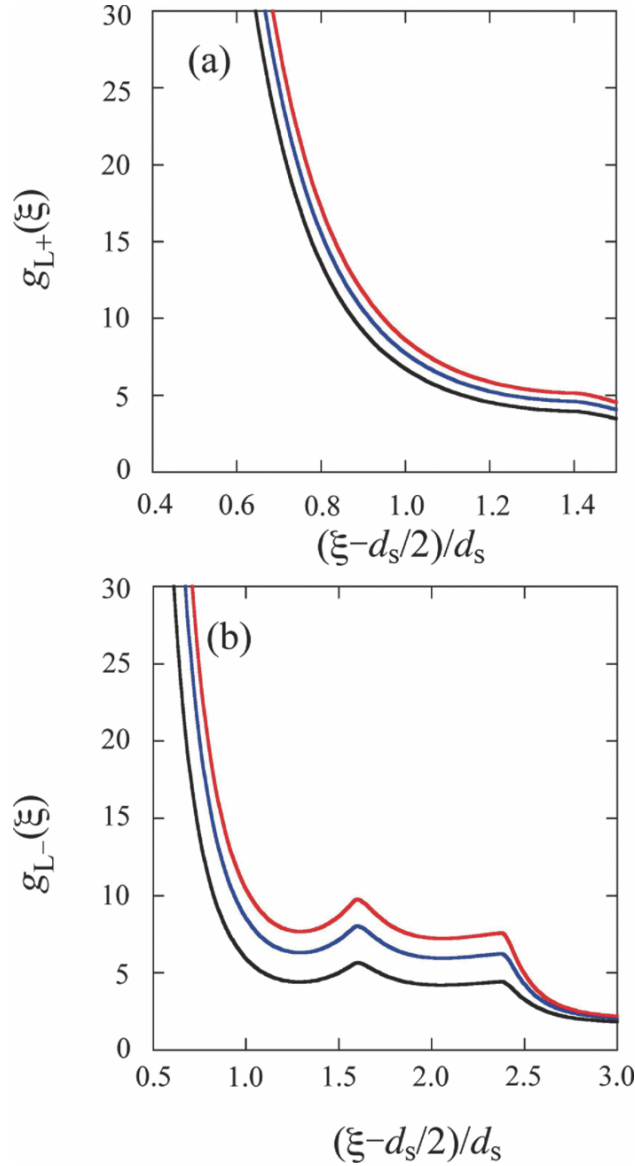


Figure 3.6: Normalized density profiles of cations (a) and anions (b) in the vicinity of the surface ($g_{L+}(\xi)$ and $g_{L-}(\xi)$, respectively; ξ is the distance from the surface in the surface-normal direction). Black: $C=0.00681$ M, blue: $C=0.00794$ M, and red: $C=0.00824$ M. C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_s=1.80$ (d_+ denotes the diameter of X^+). The contact values, $g_{L+}(d_+/2)$, in the three bulk concentrations are 172.7, 194.2, and 212.7, respectively, and the contact position is at $(\xi - d_s/2)/d_s=0.40$. The contact values, $g_{L-}(d_-/2)$ ($d_-=2.16d_s$ denotes the diameter of $[PtCl_4]^{2-}$), in the three bulk concentrations are 36.56, 53.42, and 65.50, respectively, and the contact position is at $(\xi - d_s/2)/d_s=0.58$.

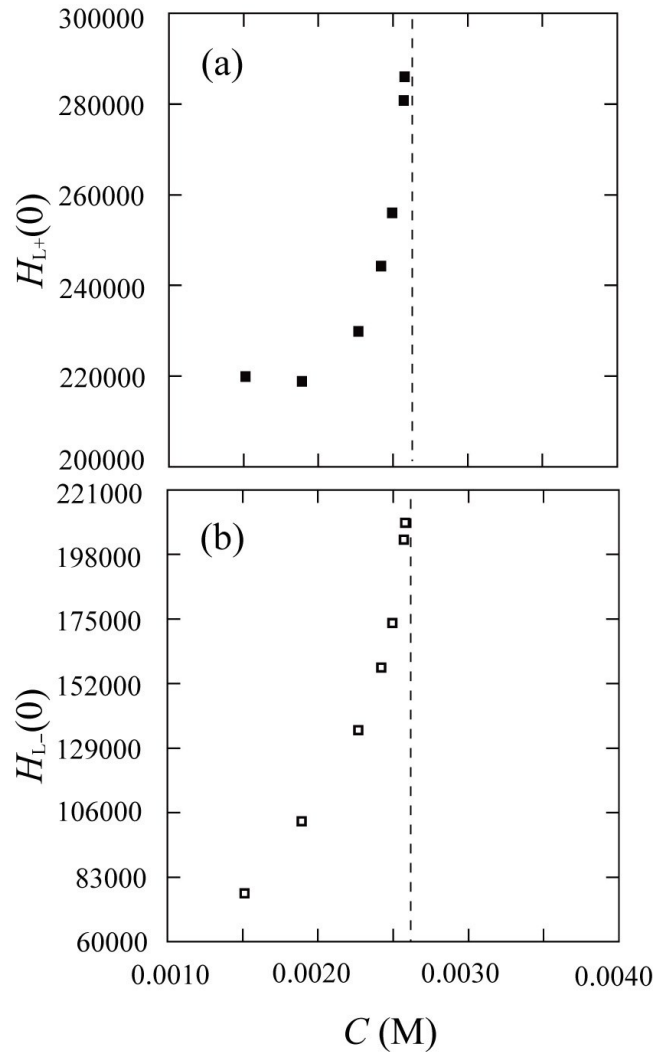


Figure 3.7: (a) $H_{L+}(0)$ plotted against C . (b) $H_{L-}(0)$ plotted against C . C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_s=2.00$ (d_+ denotes the diameter of X^+). The definition of $H_{Lj}(0)$ ($j=+, -$) is given by Eq. (4b). Beyond the spinodal concentration indicated by the broken line, the angle-dependent integral equation theory possesses no solutions.

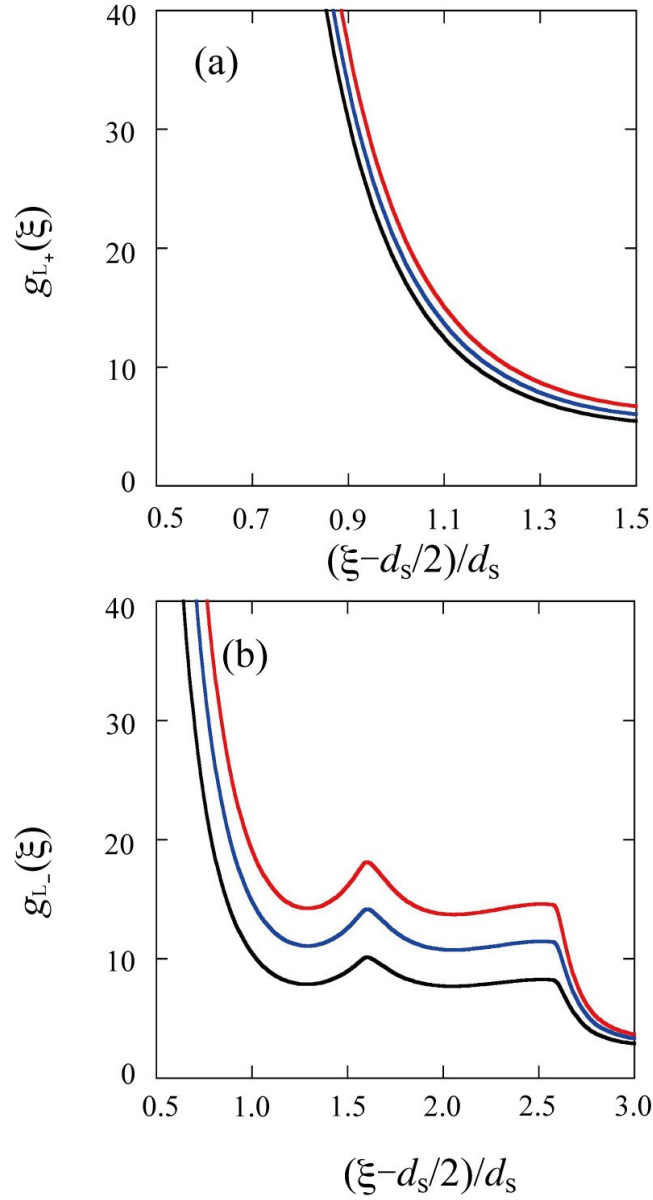


Figure 3.8: Normalized density profiles of cations (a) and anions (b) in the vicinity of the surface ($g_{L+}(\xi)$ and $g_{L-}(\xi)$, respectively; ξ is the distance from the surface in the surface-normal direction). Black: $C=0.00227$ M, blue: $C=0.00250$ M, and red: $C=0.00258$ M. C is the concentration of X_2PtCl_4 in the bulk, and $d_+/d_s=2.00$ (d_+ denotes the diameter of X^+). The contact values, $g_{L+}(d_+/2)$, in the three bulk concentrations are 681.5, 739.3, and 805.3, respectively, and the contact position is at $(\xi - d_s/2)/d_s=0.50$. The contact values, $g_{L-}(d_-/2)$ ($d_-=2.16d_s$ denotes the diameter of $[PtCl_4]^{2-}$), in the three bulk concentrations are 57.07, 80.15, and 103.3, respectively, and the contact position is at $(\xi - d_s/2)/d_s=0.58$.

3.5 Comparison between experimental and theoretical results

3.5.1 Real system treated in experiment

In the experiment, one of KCl, $(\text{CH}_3)_4\text{NCl}$, and $(\text{C}_2\text{H}_5)_4\text{NCl}$ is dissolved in water at the fixed concentration 0.5 M. K_2PtCl_4 is also dissolved and its concentration C in the bulk is gradually increased as an important parameter. The result manifests that the pores are abruptly filled with the second phase, in which the concentration of $[\text{PtCl}_4]^{2-}$ is remarkably enriched, at $C=C^{\text{ex}}$ (the superscript “ex” denotes “experimental”). The values of C^{ex} for KCl, $(\text{CH}_3)_3\text{NCl}$, and $(\text{C}_2\text{H}_5)_3\text{NCl}$ are, respectively, in the ranges from 0.009 M to 0.010 M, from 0.007 M to 0.008 M, and from 0.006 M to 0.007 M.

As explained above, $(\text{C}_2\text{H}_5)_4\text{N}^+$ and $(\text{CH}_3)_4\text{N}^+$ are even more hydrophobic than $[\text{PtCl}_4]^{2-}$. $(\text{C}_2\text{H}_5)_4\text{N}^+$, for example, is smaller than $[\text{PtCl}_4]^{2-}$ but the former carries only the charge e while the latter carries the charge $-2e$. Here, let us compare K_2PtCl_4 solution and $(\text{CH}_3)_4\text{NCl}$ solution. For each solution, only a single salt species is dissolved in water, and C denotes the concentration of K_2PtCl_4 or $(\text{CH}_3)_4\text{NCl}$ in the bulk. In K_2PtCl_4 solution, the theoretical result shows that the spinodal concentration for the partial-wetting transition $C^* \sim 0.0254$ M. Since $(\text{CH}_3)_4\text{N}^+$ is more hydrophobic than $[\text{PtCl}_4]^{2-}$, C^* in $(\text{CH}_3)_4\text{NCl}$ solution should be considerably lower than this value (both K^+ and Cl^- ions exhibit positive hydration, and these ions are not likely to affect C^*). C^{+++} in $(\text{CH}_3)_4\text{NCl}$ solution is further smaller. Therefore, the surface-induced phase transition occurs at the concentration of $(\text{CH}_3)_4\text{NCl}$ that is much lower than 0.5 M: At $C=0.5$ M, the pores are filled with the second phase in which the concentration of $(\text{C}_2\text{H}_5)_4\text{N}^+$ is remarkably enriched. The surface-induced phase transition is accompanied by remarkable enrichment of Cl^- . When K_2PtCl_4 is added to the solution and its concentration is gradually increased, it is probable that the anions of Cl^- are *abruptly* replaced by those of $[\text{PtCl}_4]^{2-}$ at $C=C^{\text{ex}}$. Qualitatively the same argument can be made for $(\text{C}_2\text{H}_5)_4\text{NCl}$ solution because $(\text{C}_2\text{H}_5)_4\text{N}^+$ is more hydrophobic than $(\text{CH}_3)_4\text{N}^+$.

3.5.2 Model system considered in theoretical analysis

In the theoretical analysis, only a single salt species X_2PtCl_4 is dissolved in water and its concentration C in the bulk is gradually increased as an important parameter. It is observed that the partial wetting occurs for both X^+ and $[PtCl_4]^{2-}$. The values of the spinodal concentration C^* for $X=K$, $(CH_3)_4N$, and $(C_2H_5)_4N$ are, respectively, ~ 0.0254 M, ~ 0.00825 M, and ~ 0.00258 M. The partial wetting originates from the remarkable enrichment of the concentration of ions with large sizes (i.e., ions exhibiting negative hydration) near the hydrophobic surface. Namely, it is caused by only $[PtCl_4]^{2-}$ for $X=K$, whereas by the interplay of $[PtCl_4]^{2-}$ and $(CH_3)_4N^+$ or $(C_2H_5)_4N^+$ for $X=(CH_3)_4N$ or $(C_2H_5)_4N$. Even in the case of K_2PtCl_4 , however, the partial wetting of $[PtCl_4]^{2-}$ is accompanied by that of K^+ . It is probable that the partial wetting of $[PtCl_4]^{2-}$ alone would give rise to the energetic instability due to electrostatic repulsive interactions among the platinum complex anions. In general, the partial wetting of large cations or large anions is accompanied by that of ions carrying charges with the opposite sign irrespective of the ion size.

3.5.3 Information concerning cation-size effect

Because of the differences between the real and model systems described above, the experimental and theoretical results cannot be compared quantitatively. Nevertheless, the following important point is demonstrated from both experimental and theoretical viewpoints: The surface-induced phase transition for an anion species with a large size is substantially influenced by a coexisting cation species with a large size; and the influence becomes stronger as the size of the cation species increases.

In the prevailing view based on classical electrochemistry, the anion concentration near the surface is normally determined by a balance of the electrochemical consumption and the supply by diffusion. The theory of electric double layer, in which the cation effect is taken into consideration only in terms of its ionic strength, is not capable of explaining the effect of cation species or cation size. Therefore, tuning an electrochemical reaction by the

choice of the cation species coexisting with the anions is not common knowledge. By contrast, the present study shows that our theory based on statistical mechanics for confined molecular liquids is a powerful tool which enables us to reveal the microscopic mechanism of the effect of cation species. Such tuning is feasible, which has been demonstrated for a nanoporous electrode using the displacement deposition experiment and the statistical-mechanical theory for confined aqueous solutions combined with a molecular model for water.

3.6 Concluding remarks

We have investigated the effect of cation species (K^+ , $(CH_3)_4N^+$, or $(C_2H_5)_4N^+$) coexisting with platinum complex anions ($[PtCl_4]^{2-}$) on electrochemical platinum deposition in nanoporous silicon. The pore diameter is ~ 3 nm on the average and the pore wall surface is hydrophobic. Platinum complex (K_2PtCl_4) and one of the three salts, KCl , $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$, are added to ultra pure water: Each of the resultant solutions is used for the platinum deposition bath. The concentration of K^+ , $(CH_3)_4N^+$, or $(C_2H_5)_4N^+$ in the bulk is fixed at 0.5 M. The deposition experiment was performed by gradually increasing the concentration of $[PtCl_4]^{2-}$ in the bulk from 0.006 M with the increment of 0.001 M.

At a threshold concentration of $[PtCl_4]^{2-}$ in the bulk, the platinum deposition within nanopores is drastically accelerated with the result that a nanopore is densely packed with platinum nanoparticles. We find that the threshold concentration becomes lower as the cation size increases. The prevailing view based on classical electrochemistry is not capable of elucidating the observed effect of coexisting cations. The elucidation is made possible only by consulting a liquid-state theory based on statistical mechanics. In particular, it is crucial to employ a molecular model for water and treat confined aqueous solutions.

Our analysis using the angle-dependent integral equation theory^{29,32-49} has suggested the following: The nanopores are abruptly filled with the second

phase in which the ion concentration is orders of magnitude higher than that in the bulk; and not only the anions but also the cations are remarkably enriched in the second phase. This result, which was not noticed in our earlier work,²⁶ is not straightforward because the charge neutrality is not necessarily satisfied within the confined aqueous solution. Presumably, the remarkable enrichment of the anions alone would give rise to the energetic instability due to electrostatic repulsive interactions among the anions. The ions with large sizes, $[\text{PtCl}_4]^{2-}$, $(\text{CH}_3)_4\text{N}^+$, and $(\text{C}_2\text{H}_5)_4\text{N}^+$, are only weakly hydrated and excluded from the bulk to a hydrophobic surface. The threshold concentration is influenced only by a cation species possessing a sufficiently large size. Replacement of K^+ by Na^+ , for example, would cause no change in the threshold concentration.

The present study provides important results from both scientific and practical viewpoints. It stimulates the researches in a new, very interesting field for liquid, liquid mixture, or aqueous solution confined in nanospace. More information is now available concerning the phase transition induced by a hydrophobic surface for aqueous electrolyte solutions containing only weakly hydrated ions. For further development of fuel cells, batteries, and capacitors in which nanoporous electrodes play essential roles, it may be an inevitable strategy to tune the behavior of electrochemical reaction for a particular ion species in solution using a coexisting ion species.

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4 A physical mechanism for suppression of zinc dendrites caused by high efficiency of the electrodeposition within confined nanopores

A strategy for the suppression of zinc dendrites in electrodeposition controlled by a physical factor has been proposed and demonstrated. Zinc electrodeposition within confined nanopores shows a high current efficiency even at a current density higher than the diffusion-limited current measured on a planar substrate. Our results suggest that the electrodeposition is free from the diffusion-limitation problem only when the electrodeposition occurs within the confined nanopores.

4.1 Introduction

Dendrite growth in metal electrodeposition is a typical reaction-diffusion system whose dynamics is described by differential equations of positive and negative feedback species.¹⁻⁵ Since diffusion of metal ions plays a significant role in dendrite formation, understanding of mass-transfer during metal electrodeposition is important. From an electrochemical viewpoint, dendrite growth is crucially important and must be suppressed in the development of rechargeable batteries. Strategies to suppress such dendrites have been proposed and demonstrated.⁶⁻⁸ A problem in these strategies was that the suppression was controlled by chemical factors such as additives and surfactants. Effective additives and surfactants differ depending upon the types of metal depositions. A general strategy for the suppression of dendrites by physical factors, which is applicable to any metal electrodes, is urgently desired.

Recently, we have reported that the electrochemical deposition was drastically accelerated when using hydrophobic porous silicon, while it was surprisingly decelerated when using hydrophilic one.⁹ Such a substantial

difference within confined nanopores is due to the fact that metal ions having a large diameter behave as hydrophobic solutes and tend to be excluded from the bulk to the hydrophobic pore wall. This exclusion of metal ions (a physical factor) results in a great enrichment of the ions in the confined nanopores. This enrichment leads to the idea that diffusion-limited electro-deposition, in which dendrites grow, is hard to be achieved within confined and hydrophobic nanopores.

In this letter, we report that growth of zinc dendrites is suppressed by the physical factor (exclusion of zinc toward hydrophobic nanopore walls) using porous silicon whose pore size is ~ 3 nm. The present study is fundamentally of great importance for the suppression of dendrites caused by a physical factor.

4.2 Experimental

Porous silicon, whose pore diameter was ~ 3 nm and thickness was $2\text{ }\mu\text{m}$, was prepared by anodization. An n-type silicon (100) substrate with a resistivity of $7\text{--}20\text{ }\Omega\text{ cm}$ was used. As shown later, the porous silicon looks like a macropore structure, which is so-called skeleton and completely filled with a microporous silicon body.¹⁰ A mixture of 22 wt.% HF/ethanol was used as electrolyte solution. Anodization was carried out for 20 min at 2 mA cm^{-2} under illumination. In some experiments, a thicker porous silicon with $3\text{ }\mu\text{m}$ was used. The thicker porous silicon was prepared by anodization for 30 min.

Zinc electrodeposition was carried out under the galvanostatic mode. A zinc plate, flat silicon and porous silicon were used as the working electrode for comparison. The zinc plate was polished with alumina powders ($3\text{ }\mu\text{m}$ and $0.3\text{ }\mu\text{m}$). The counter and reference electrodes were a platinum rod and Ag|AgCl saturated KCl electrodes, respectively. All the potential shown in the present paper are referred to this electrode. $0.1\text{ M ZnSO}_4 + 0.5\text{ M Na}_2\text{SO}_4$ aqueous solution, whose pH was adjusted to 4.0 by adding a small amount of H_2SO_4 , was used as deposition bath. When measuring

current density vs. potential (i - E) curves, potential was scanned at a rate of 10 mV s^{-1} .

Surfaces and cross-sections of the specimen were observed using a scanning electron microscope (SEM). To measure current efficiency on the planar silicon wafer and porous silicon, deposited zinc was dissolved by immersing the substrate in a dilute HNO_3 . This solution was diluted with ultra-pure water and the concentration of zinc ions in the dilute solution was measured using an inductively coupled plasma atomic emission spectrometer (ICP).

4.3 Results and discussion

An i - E curve using a zinc plate was measured to determine the diffusion-limited current density (i_{diff}). Potential scan was started at -1.0 V to negative. A cathodic current due to zinc electrodeposition starts to flow at -1.1 V and it reaches a plateau at -9 mA cm^{-2} . Such an i - E curve is also obtained on a flat silicon wafer. These results show that the i_{diff} in this electrolyte condition is $\sim 9 \text{ mA cm}^{-2}$. The dashed line shows an i - E curve on porous silicon. The behavior looks similar to the others, except that the cathodic current in high overpotential region starts to flow at a higher potential (-1.6 V). Figure 4.1b and c show SEM images of zinc deposits on the zinc plates formed at -6.4 mA cm^{-2} ($|i| < |i_{\text{diff}}|$) and -12.8 mA cm^{-2} ($|i| > |i_{\text{diff}}|$). Zinc deposited under $|i| < |i_{\text{diff}}|$ shows a flat and compact structure, whereas zinc dendrites are observed under $|i| > |i_{\text{diff}}|$.

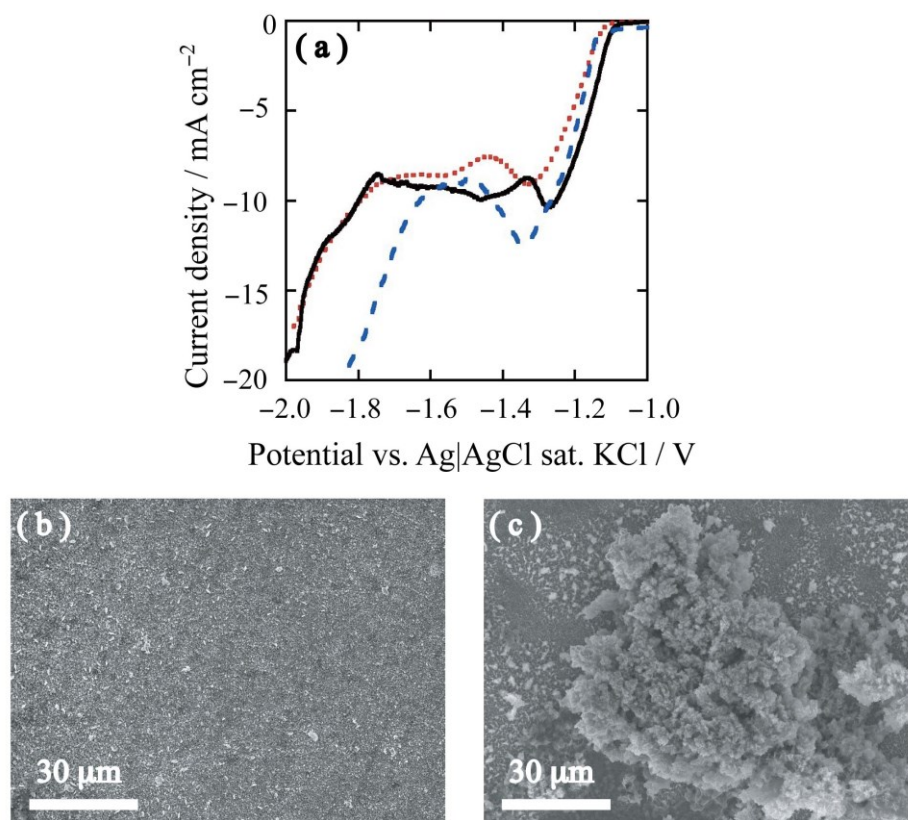


Figure 4.1: (a) Current density vs. potential curves measured on a zinc plate (black and solid curve), flat silicon wafer (red and dashed curve) and porous silicon (blue and dashed curve) at a scan rate of 10 mV s^{-1} in $0.1 \text{ M ZnSO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution. Images in (b, c) show the surface after zinc electrodeposition on zinc plates at -6.4 mA cm^{-2} for 2 min and at -12.8 mA cm^{-2} for 1 min.

A zinc plate, flat silicon wafer and porous silicon were used to investigate the effect of substrates on the dendrite growth. Zinc electrodeposition was carried out for 30 s on each electrode at a cathodic current density of -12.8 mA cm^{-2} ($|i| > |i_{\text{diff}}|$). Figures 4.2a, b and c show surface morphologies of zinc deposited on the electrodes. There are no significant differences between the zinc plate and flat silicon wafer. Zinc dendrites of height up to several micrometers are observed on the surfaces. By contrast, no dendrites are formed on the surface of porous silicon, but hexagonal crystals are observed. From the cross-sectional view (Figure 4.2e), zinc deposits are observed within the porous layer. The potential development in Figure 4.2g

on the zinc plate shows that a sudden shift in potential after 7 s of deposition, and then the potential reaches -1.8 V (hydrogen evolution). When the flat silicon wafer is used, the development shows very similar trend as on the zinc plate electrode. The sudden shift in potential on the porous silicon occurs a little bit later. This delay suggests that it takes longer to consume zinc ions and to shift to hydrogen evolution using the porous electrode. A thicker porous silicon was also used for the comparison. SEM images in Figures 4.2d and f show that zinc dendrites are suppressed and the amount of the hexagonal deposits on the top surface is smaller than the thinner porous silicon (Figures 4.2c and d). The potential shift shows the delay of ten seconds from that of the shallow porous silicon, and the shift in potential with the thicker porous silicon is much gentler. Note that the effect of displacement deposition was evaluated prior to the electrodeposition experiments, and we found that the contribution of displacement deposition to the increase in the electrode weight is very low (0.9%). We have confirmed that no nucleation and growth of zinc within the pores were observed in the present case. In addition, the i - E curve measured on porous silicon shows relatively similar to the others in low overpotential region (-1.1 V to -1.3 V). Therefore, chemical contribution to the electrodeposition seems to be very small. Zinc electrodeposition within the nanopores cannot be explained by simply considering chemical effects such as the reactivity of hydrogen-terminated porous silicon.

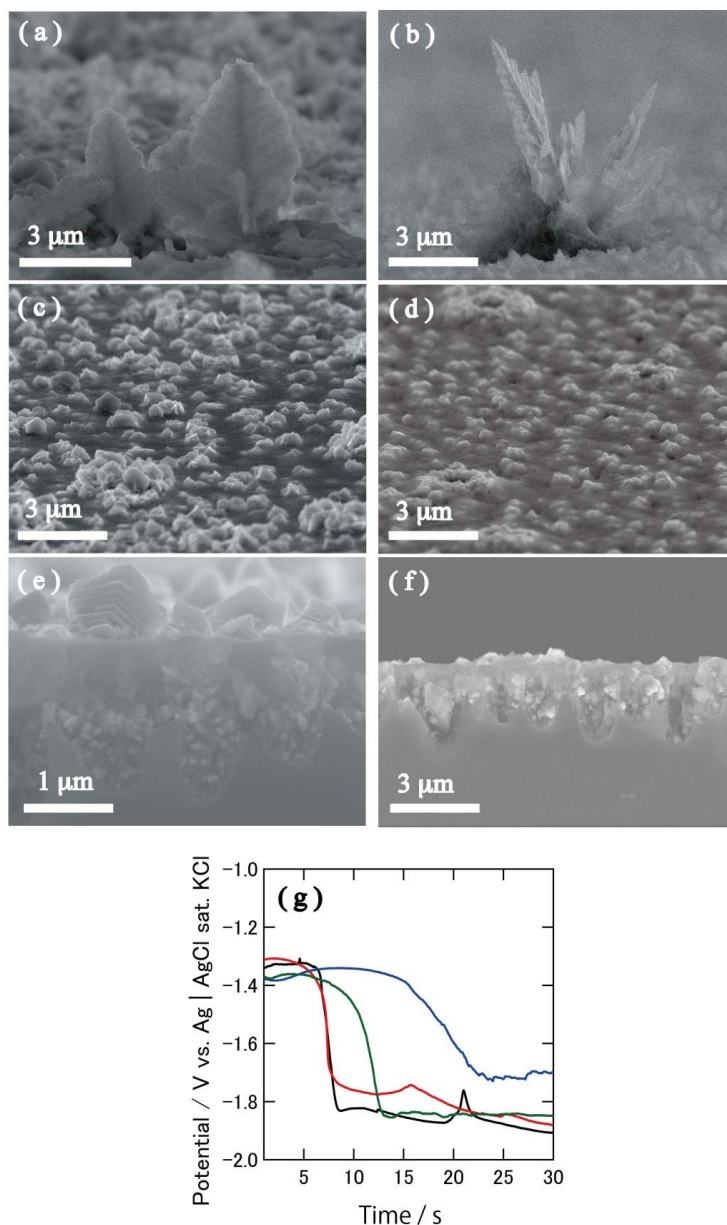


Figure 4.2: Images in (a, b, c, d) show the surfaces after the electrodeposition on a zinc plate (a), flat silicon wafer (b), shallower porous silicon with 2 μm depth (c) and deeper porous silicon with 3 μm depth (d). The images in (e, f) show cross-sectional views of the samples shown in (c, d). Time developments in potential using the substrates are shown in (g). Curves in black, red, green and blue indicate the results measured on the zinc plate, flat silicon, shallower porous silicon and deeper porous silicon, respectively.

Figure 4.3 shows current efficiencies measured on the flat and porous silicon. For 5 s of deposition, both the flat and porous silicon show high efficiencies. Since $|i| > |i_{\text{diff}}|$, the potential shift occurs after 7 s of deposition on the flat silicon as observed in Figure 4.2g. After this potential shift, the efficiency starts to decrease on the flat silicon. By contrast, the current efficiency on the porous silicon stays higher than that on the flat silicon. The differences in current efficiency between these electrodes become remarkable with prolonging the deposition time. As observed in Figure 4.2g, the potential shift is observed after 12 s of deposition (green curve). The efficiency measured on the porous silicon decreases after the potential shift. In Figure 4.2g, the potential shift is delayed from 12 s to 20 s when the thickness of the porous layer is changed from 2 μm to 3 μm . We think that this delay in the potential shift is simply due to the increase in the volume for the filling with zinc deposits.

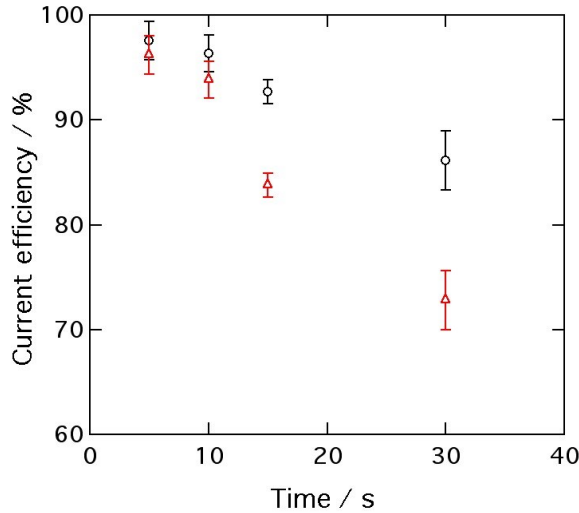


Figure 4.3: Current efficiencies measured after the electrodeposition on a flat silicon (red) and porous silicon (black).

Metal dendrites grow under diffusion-limited condition. This means that the suppression of dendrites in electrodeposition conflicts with the deposi-

tion at $|i| > |i_{\text{diff}}|$. This is only the case that the supply of metal ions is described by the diffusion equation. If supply of metal ions is achieved by another process, there exists a possibility to suppress them. The effect of hydration property of pore wall has been investigated in detail by modifying porous silicon with two different organic molecules to make the porous silicon hydrophobic and hydrophilic.⁹ We found that platinum electrodeposition within confined nanopores shows a drastic acceleration of the deposition when using the hydrophobic nanopores and larger platinum ions. In principle, smaller pore diameter results in an inhibition of diffusion, which leads to a low efficiency of reactions in nanopores. Our theoretical analyses revealed that the surface-induced hydration structure in confined nanopores plays a significant role for the great enrichment of metal ions in the nanopores, leading to a high efficiency of metal electrodeposition.⁹ Note that such enrichment is expected only when using pores with several nanometers in diameter. Electrodeposition within mesoporous silicon (~ 30 nm in diameter) did not show such a drastic acceleration of the deposition.¹¹ Judging from Figure 4.2e and f, complete filling of the porous silicon with zinc has not been achieved so far. We think that further tuning of the surface-induced hydration structure by the affinities of zinc ion and pore wall with water will result in higher density of zinc deposits within the nanopores. The high concentration in confined nanopores, which is the origin of the high current efficiency in the present system and suppression of dendrites, is achieved not by diffusion but by the other physical factor (exclusion of zinc ions to the hydrophobic pore wall).

4.4 Conclusions

Due to the fact that a higher concentration of zinc ions is expected in the hydrophobic nanopores, zinc dendrites are suppressed even at $|i| > |i_{\text{diff}}|$ when the electrodeposition primarily occurs within the confined nanopores. The present study is fundamentally important for further development of rechargeable batteries without the dendrite problem.

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5 Electrodeposition of platinum and silver into chemically modified microporous silicon electrodes

Electrodeposition of platinum and silver into hydrophobic and hydrophilic microporous silicon layers was investigated using chemically-modified microporous silicon electrodes. Hydrophobic microporous silicon enhanced the electrodeposition of platinum in the porous layer. Meanwhile, hydrophilic one showed that platinum was hardly deposited within the porous layer, and a film of platinum on the top of the porous layer was observed. On the other hand, the electrodeposition of silver showed similar deposition behavior between these two chemically modified electrodes. It was also found that the electrodeposition of silver started at the pore opening and grew toward the pore bottom, while a uniform deposition from the pore bottom was observed in platinum electrodeposition. These electrodeposition behaviors are explained on the basis of the both effect, the difference in overpotential for metal deposition on silicon and on the deposited metal, and displacement deposition rate of metal.

5.1 Background

Porous silicon has some properties such as high specific surface area and semiconductivity which allow metal electrodeposition within the porous layer without special treatment. Such properties are advantageous to the preparation of metal/semiconductor hybrid materials and catalyst-dispersed porous structures. However, there is a difficulty in metal electrodeposition within porous silicon that plugging often occurs before it is fully and/or homogeneously filled with metal¹⁻⁴. Inhibition of plugging during metal deposition is indispensable for controlling the filling of metal by electrodeposition. For macroporous silicon, it was reported that the plugging often occurred in some metal deposition systems due to a high rate of displacement deposition which preferentially occurred at the pore opening and electrodeposition preferentially proceeded on

the deposits⁵. Such an effect is not observed in the case of microporous silicon having hydrophobic pore wall, although the diameter of microporous silicon is much smaller than that of macroporous silicon. Another mechanism, which is different from the case of macroporous silicon, seems to control the deposition behavior in microporous silicon. Recently, we have found that the hydrophobic and hydrophilic properties of microporous silicon have strong effects on the platinum electrodeposition⁶. Only the hydrophobic microporous silicon accelerates the platinum deposition in the porous layer. Considering the surface hydration effect of platinum complex ions in the porous layer could explain this behavior.

In this study, electrodeposition behaviors of platinum and silver in chemically modified hydrophobic and hydrophilic microporous silicon are compared. The hydrophobic property of microporous silicon has a strong effect on platinum electrodeposition, while the silver electrodeposition is not affected by the hydrophobic and hydrophilic properties. The growth modes of the deposits show a clear difference between platinum and silver. These behaviors are explained on the basis of the both effects, the difference in overpotential for platinum and silver electrodeposition on silicon, and the difference in displacement deposition rate between platinum and silver.

5.2 Methods

5.2.1 Sample preparation

Two types of microporous silicon having various pore depths were prepared by anodization. *p*-type silicon (100) with a resistivity of 10 to 20 Ω cm was used. A mixture of 22 wt.% hydrogen fluoride/ethanol solution (47 wt.% hydrogen fluoride aqueous solution:ethanol = 1:1.7 in volume) was used for the electrolyte. Anodization was carried out for 20 and 60 min at 2 mA cm⁻². The depth of microporous structure was ca. 2 and 7 μ m, which was controlled by the duration of anodization. When the sample was anodized for 60 min under this condition, the microporous structure showed a macropore-like structure filled with microporous silicon⁷. We call this structure ‘skeleton structure.’

After anodization, microporous silicon substrates were immersed for 15 h in *n*-hexane containing 0.2 M methyl propiolate and 0.2 M propiolic acid to make the pore wall hydrophobic and hydrophilic by hydrosilylation reaction, respectively⁸.

Platinum and silver were electrodeposited on the chemically modified microporous silicon electrodes. A platinum rod was used as the counter electrode. Platinum electrodeposition was carried out using 0.1 M K₂PtCl₄ + 0.5 M NaCl solution, and silver electrodeposition was carried out using 0.1 M AgNO₃ + 0.5 M KNO₃ solution. Current density for the electrodeposition was set at a constant value of $-6.4 \mu\text{A cm}^{-2}$ in all the cases.

5.2.2 Characterization

Current density-potential (*i*-*E*) curves were measured. A platinum plate, bare *p*-type silicon, and chemically modified *p*-type silicon were used as the working electrodes, where plain silicon was employed without porosification. The counter electrode was a platinum rod, and the reference electrode was an Ag/AgCl saturated KCl electrode. Scan rate of potential was set at 10 mV s⁻¹.

A scanning electron microscope (JEOL, JSM-6500 F, JEOL Ltd., Tokyo, Japan) was employed to obtain secondary electron images (SEI) and back scattered electron images (BEI) of the cross-sectional microporous silicon after metal electrodeposition. SEI illustrates the morphology. On the other hand, BEI provides atomic number contrast: platinum and silver deposits appear brighter than silicon in the images.

5.3 Results

5.3.1 Characterization of platinum and silver bath

i-*E* curves were measured to understand the electrodeposition behavior of the platinum and silver baths on various electrodes. Figure 5.1 indicates that the *i*-*E* curves measured on flat silicon modified by the propiolic acid and methyl propiolate in both solutions are similar in shape. These results show that the difference in overpotential between the chemically modified silicon electrodes is not large for platinum electrodeposition. Compared to the platinum plate,

the i - E curves of the chemically modified flat silicon shift to negative potential in the platinum bath (Figure 5.1a). As a result, higher overpotential is necessary at the chemically modified silicon compared with the platinum plate.

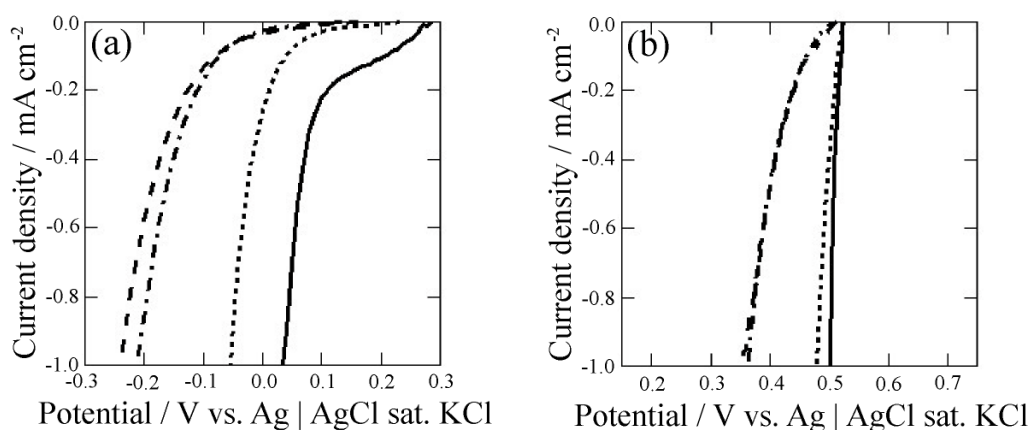


Figure 5.1: Current density-potential curves measured of various electrodes. The black, red, blue, and green curves were measured on a platinum or silver plate, bare *p*-type silicon, *p*-type silicon modified by propiolic acid, and *p*-type silicon modified by methyl propiolate, respectively. The scan rate of potential was 10 mV s⁻¹. (a) 0.1 M K₂PtCl₄ + 0.5 M NaCl, (b) 0.1 M AgNO₃ + 0.5 M KNO₃.

The i - E curves measured in silver bath behave at two differently modified silicon electrodes like the platinum case (Figure 5.1b). However, unlike the platinum case, a slight shift to negative potential is observed at the silicon electrodes compared with the silver plate. The result suggests that, in case of silver, the silicon electrodes do not require a higher overpotential than the case of platinum.

5.3.2 Metal electrodeposition in chemically modified microporous silicon

Platinum and silver electrodeposition was carried out for chemically modified microporous silicon with the depth of 2 μm. The cross-sectional images of microporous silicon after electrodeposition of platinum are shown in Figure

5.2a,b. When the pore wall is hydrophilic, platinum is deposited only on the top of microporous silicon. On the other hand, when the pore wall is hydrophobic, platinum is deposited inside microporous silicon as reported elsewhere⁶.

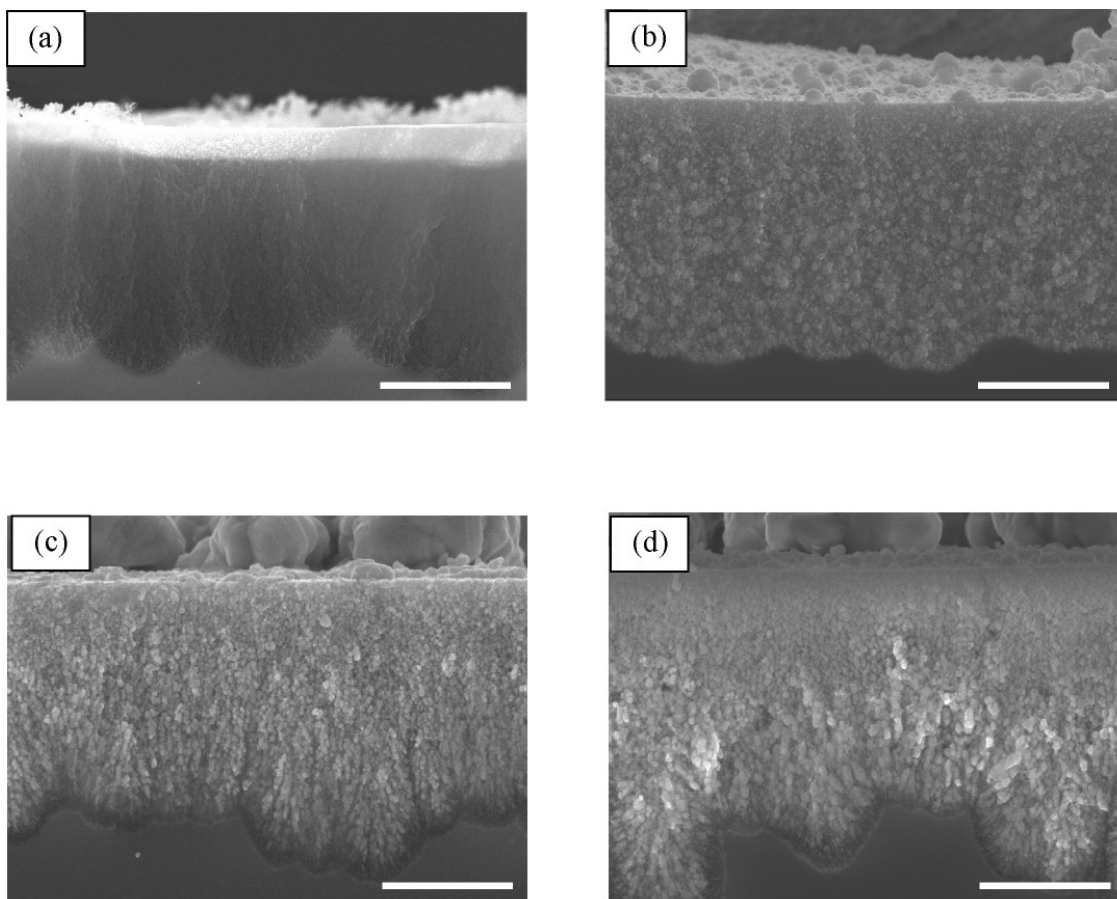


Figure 5.2: Cross-sectional SEI of microporous silicon after the electrodeposition of platinum and silver. After the electrodeposition of platinum and silver. Images of (a) and (b) are the cross-sections of platinum deposition in 0.1 M K_2PtCl_4 + 0.5 M NaCl, and those of (c) and (d) are of silver deposition in 0.1 M $AgNO_3$ + 0.5 M KNO_3 . The images in (a, c) and (b, d) show the samples of the hydrophilic and hydrophobic microporous silicon, respectively.

However, when silver electrodeposition was carried out, deposition proceeds uniformly both in the chemically modified hydrophobic and hydrophilic

microporous silicon (Figure 5.2c,d). Electrodeposition of silver is hard to be affected by the hydration properties of pore wall, such as hydrophobic or hydrophilic.

5.3.3 Time development of silver electrodeposition

To investigate the reason why the hydrophobic and hydrophilic properties of microporous silicon do not affect the electrodeposition behavior of silver, time development of silver electrodeposition in a chemically modified hydrophobic microporous silicon with the pore depth of ca. 7 μm was studied. Figures 5.3 and 5.4 show cross-sectional views of the samples after electrodeposition for 1 and 2 min, respectively. After electrodeposition for 1 min, silver is deposited from the pore opening to the middle depth of the pore, which is independent of hydrophobic and hydrophilic properties. After 2 min electrodeposition, silver is uniformly deposited in both microporous silicon. The uniform deposition is also independent of hydrophobic and hydrophilic properties. These results show that silver deposition proceeds from the pore opening to the pore bottom, and these phenomena are independent of the hydration properties of pore wall, such as hydrophobic or hydrophilic.

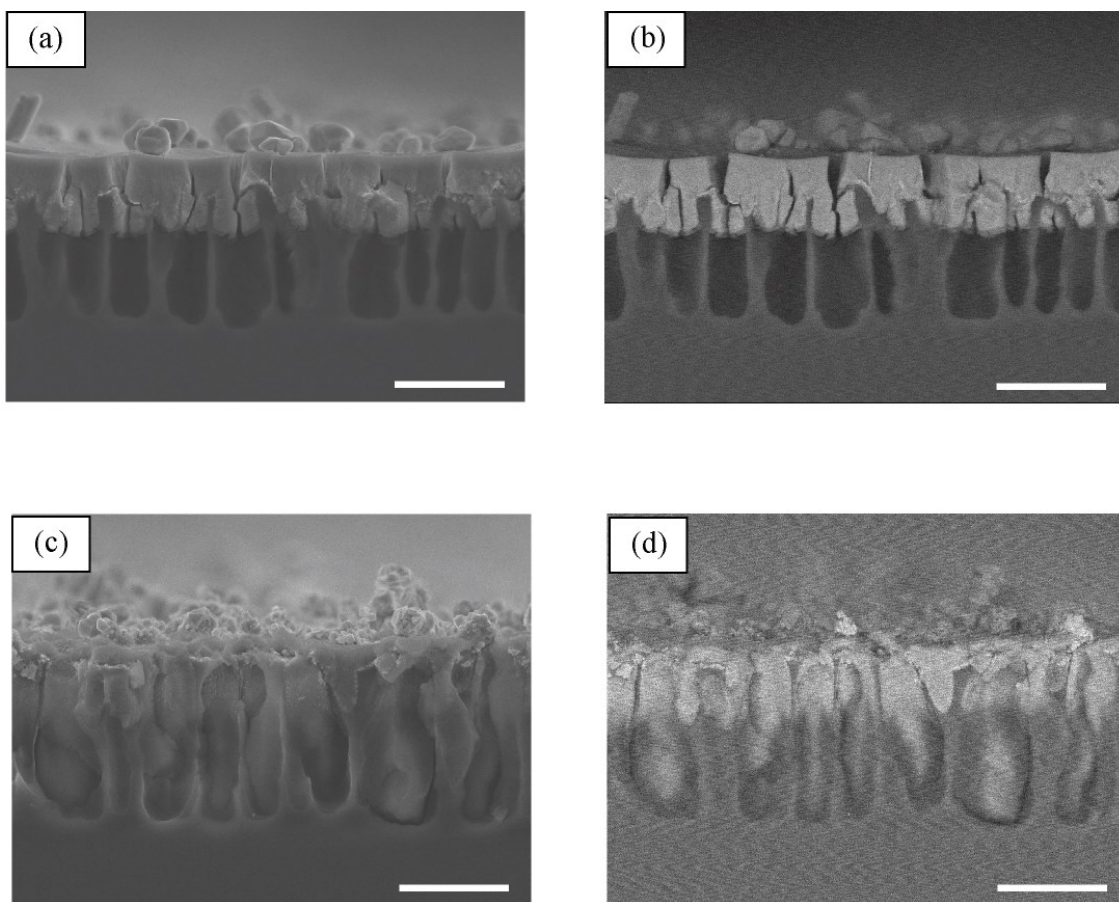


Figure 5.3: Cross-sectional views of microporous silicon after the electrodeposition of silver for 1 min. Images of (a, b) and (c, d) show the samples of hydrophilic and hydrophobic microporous silicon substrates, respectively. The images in (a) and (c) illustrate the SEI, and (b) and (d) illustrate the BEI.

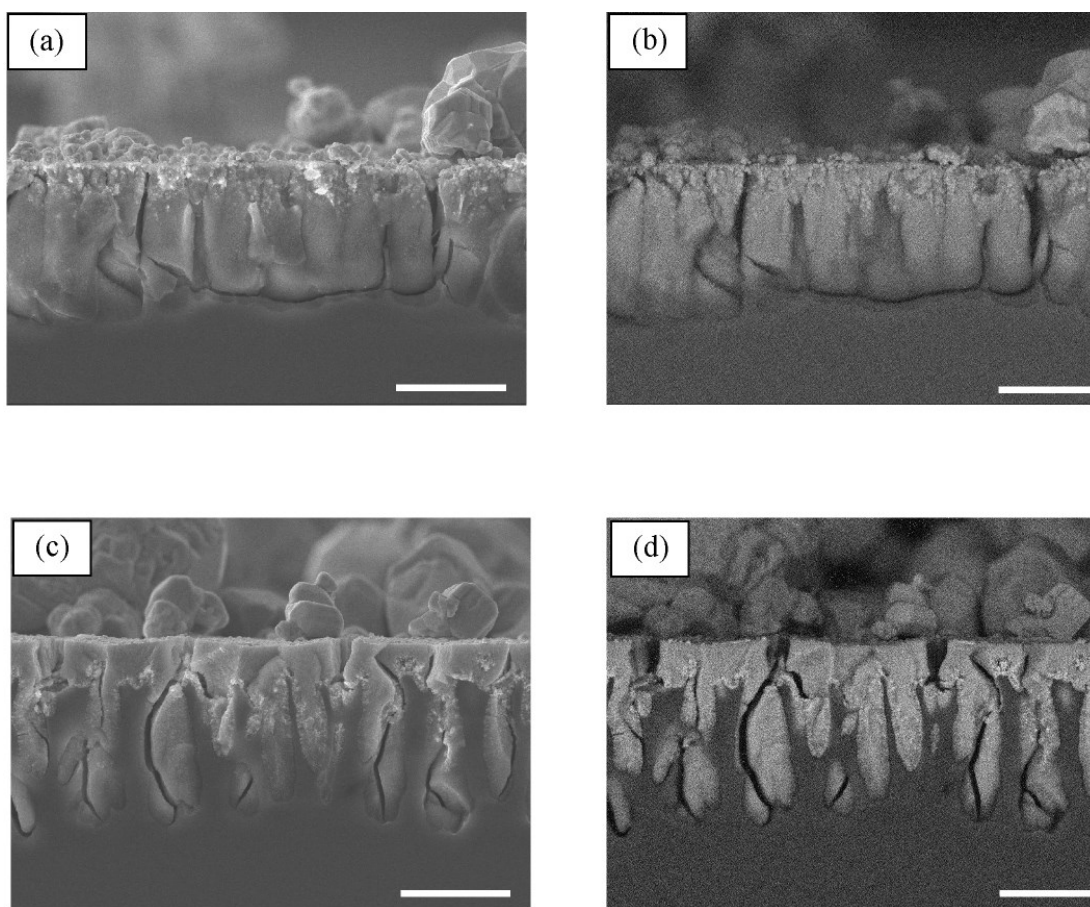


Figure 5.4: Cross-sectional views of microporous silicon after the electrodeposition of silver for 2 min. Images of (a, b) and (c, d) show the samples of hydrophilic and hydrophobic microporous silicon, respectively. The images in (a) and (c) illustrate the SEI, and (b) and (d) illustrate the BEI.

5.4 Discussion

5.4.1 Difference in metal growth direction between platinum and silver

Current mainly flows from the pore bottom when the electrodeposition is carried out on the porous silicon substrate. In addition, the resistivity of the microporous part is high. From these points of view, metal deposition should occur from the direction of the pore bottom to the opening. In fact, platinum deposition starts at the pore bottom of microporous structure in the present case. However, when silver electrodeposition is carried out on microporous silicon substrate, such growth does not appear, and silver deposition proceeds from the pore opening to the pore bottom (Figures 5.3 and 5.4). As discussed

below, the effect of displacement deposition occurring during electrodeposition and the different polarization behaviors on silicon and deposited metal can explain the difference in the growth direction.

Electrodeposition is often accompanied by displacement deposition during noble metal electrodeposition in porous silicon. In case of platinum, the electrodeposition is prevailing compared to displacement deposition because the rate of platinum displacement deposition on silicon substrate is slow⁴. Pore bottom is more favorable to electrodeposition than the opening in high resistive microporous silicon, as mentioned above; hence, the deposition proceeds from the direction of the pore bottom to the opening. This type of growth is observed for the hydrophobic porous silicon surface.

Figure 5.1a shows that platinum deposition on a silicon electrode needs much higher overpotential than that on a platinum electrode. Supposing that platinum deposition occurs on the top surface, the reaction preferentially proceeds on the top, and platinum is not deposited inside the porous layer. In addition, it was reported that, when the nucleation of metal starts at the pore opening in the initial stage of the metal electrodeposition, the metal is preferentially deposited there, and the pore opening is plugged soon^{1,2}. This type of growth is observed in porous silicon with the hydrophilic surface.

On the other hand, in case of silver, displacement deposition rate is extremely fast on silicon. Therefore, even though electrodeposition is carried out, displacement deposition proceeds preferentially compared to electrodeposition. It was reported that metal displacement deposition proceeds from the pore opening to the pore bottom in the macroporous structure³. Thus, silver electrodeposition also proceeds from the pore opening to the pore bottom in microporous structure because the effect of displacement deposition is stronger than that of electrodeposition. In addition, the potentials of silver deposition on the silicon electrode and silver electrode are similar (Figure 5.1b). These results show that, in the silver system, overpotential difference for silver electrodeposition on the silicon electrode and deposited silver is very small. Silver is deposited with almost equal rate on silver nuclei and bare

silicon surface. The reaction does not preferentially proceed on the deposited surface at the pore opening. Therefore, pore opening is hard to be plugged, and silver ions can diffuse into the porous structure.

5.4.2 Why is silver not affected by property of the pore wall?

Platinum is deposited within the hydrophobic microporous silicon in Figure 5.2. However, when the pore wall is hydrophilic, platinum deposition occurs only on the top of the porous layer. These results can be explained by the affinity of the pore wall to water molecules. Platinum complex ion ($[\text{PtCl}_4]^{2-}$) behaves like a molecule with lower polarity due to its large size. Therefore, platinum ions have high affinity to the hydrophobic pore wall compared with water molecules to the pore wall, and hence, platinum ions are excluded from bulk to the pore wall⁶. In case of platinum, platinum ions pass through a bare silicon surface because deposition proceeds toward the pore opening from the pore bottom. Therefore, platinum deposition behavior is affected by the hydration property of pore wall. In hydrophilic microporous silicon, once deposition occurs at the pore opening, platinum is not deposited into pores but on the top surface due to the need of high overpotential on the bare silicon.

However, silver deposition is not affected by the hydration properties of the pore wall. These results can be explained by the growth direction of deposition. Metal ions have to reach to the frontier of the deposition site and pass through not a bare silicon surface but the surface on which metal is deposited when metal deposition proceeds toward the pore bottom. Once the metal is deposited on the pore wall, the hydration property of pore wall changes due to the metal covering. Therefore, silver is uniformly deposited in microporous layer without relation to the hydration properties of the pore wall.

5.5 Conclusions

When the pore diameter of porous silicon is extremely small, platinum deposition is strongly affected by the hydration property of pore wall. On the other hand, silver deposition is not affected by the property. The results could

be explained by the difference in overpotential between the deposition on the metal surface and that on the silicon surface, and by the difference in intrinsic displacement deposition rate of metal. When metal electrodeposition is carried out in microporous silicon, the effect of the overpotential and the displacement deposition rate should be considered together with the hydration property of the metal ions.

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General Conclusion

Porous electrode is expected to be utilized as a template for metal nanostructure formation. To realize this technique, the procedure to control metal deposition in micropores should be established. However, the supply of reactants are strongly inhibited by the presence of pore walls by which the pore volume is confined to an extremely small space. This problem will be solved if we can enhance the supply of the reactant drastically. In the present work we have focused on the hydration properties of the surface of the pore wall and the solutes in the solution.

In chapters 1 and 2 we have found that the hydration property of the pore walls and solute has a strong influence on metal deposition in the micropores. In chapter 2 the surface-induced phase transition, which can result in very high concentration of the reactant in micropores, is revealed. Such transition is caused purely by the hydration properties, and hence, can appear regardless of the sign of the ion charge, i.e., cation or anion. Therefore, the hydration property of counter-cations coexisting with metal complex anions, which is to be deposited to fill the pores, has an effect on the surface-induced phase transition in the micropores as well (chapter 3). Metal is preferentially deposited in the micropores, rather than to the pore openings, even at a current density higher than the diffusion-limited current. This is attributed to the enrichment of metal ions in the micropores due to the hydration properties (chapter 4). Finally, in chapter 5, the effect of the overpotential on metal deposition behavior in the microporous silicon is investigated. In case of low over potential to deposit on it such as silver, deposition proceeds into the micropores even if silver deposits on the pore openings.

In this thesis, the work is focused only on metal deposition reactions. However, the phenomenon found in the present work is rather general. The control of the deposition reaction based on the hydration properties of the

surface and solutes can be applied to many electrochemical systems using porous electrodes, such as capacitors, lithium ion batteries, and so on. A higher efficiency in the electrochemical devices is attained by controlling the hydration properties, as is suggested in the present work.

List of Publications

Chapter 1: Platinum electrodeposition in porous silicon: The influence of surface solvation effects on a chemical reaction in a nanospace

Kazuhiro Fukami, Ryo Koda, Tetsuo Sakka, Tomoko Urata, Ken-ichi Amano, Hikaru Takaya, Masaharu Nakamura, Yukio Ogata, and Masahiro Kinoshita

Chemical Physics Letters **542**, 99-105 (2012).

Chapter 2: Electrochemical deposition of platinum within nanopores on silicon: Drastic acceleration originating from surface-induced phase transition

Kazuhiro Fukami, Ryo Koda, Tetsuo Sakka, Yukio Ogata, and Masahiro Kinoshita

Journal of Chemical Physics **138**, 094702/1-10 (2013).

Chapter 3: Effect of cation species on surface-induced phase transition observed for platinum complex anions in platinum electrodeposition using nanoporous silicon

Ryo Koda, Akira Koyama, Kazuhiro Fukamim, Naoya Nishi, Tetsuo Sakka, Takeshi Abe, Atsushi Kitada, Kuniaki Murase, and Masahiro Kinoshita

Journal of Chemical Physics **141**, 074701/1-11 (2014).

Chapter 4: A Physical Mechanism for Suppression of Zinc Dendrites Caused by High Efficiency of the Electrodeposition within Confined Nanopores

Ryo Koda, Kazuhiro Fukami, Tetsuo Sakka, and Yukio H Ogata

ECS Electrochemistry Letters **2**, D9-D11 (2013).

Chapter 5: Electrodeposition of platinum and silver into chemically modified microporous silicon electrodes

Ryo Koda, Kazuhiro Fukami, Tetsuo Sakka, Yukio H Ogata

Nanoscale Research Letters **7**, 330/1-5 (2012).

The following publication is not included in this thesis

Selective optical response of hydrolytically stable stratified Si rugate mirrors to liquid infiltration

Tero Jalkanen, Vicente Torres-Costa, Ermei Mäkilä, Martti Kaasalainen, Ryo Koda, Tetsuo Sakka, Yukio H. Ogata, Jarno Salonen
ACS Applied Materials & Interfaces **6**, 2884-2892 (2014).

On-Site Quantitative Elemental Analysis of Metal Ions in Aqueous Solutions by Underwater Laser-Induced Breakdown Spectroscopy Combined with Electrodeposition under Controlled Potential

Ayumu Matsumoto, Ayaka Tamura, Ryo Koda, Kazuhiro Fukami, Yukio H. Ogata, Naoya Nishi, Blair Thornton, Tetsuo Sakka
Analytical Chemistry **87**, 1655-1661 (2015).

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March, 2015 Ryo Koda