Reactivity of Zinc Cations under Spontaneous Accumulation of Hydrophobic Coexisting Cations in Hydrophobic Nanoporous Silicon

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ABSTRACT: The ion enrichment behavior due to surface-induced phase separation and the concomitant phase transition of electrolyte solutions between a liquid and a solid confined within nanopores of porous silicon is examined using concentrated aqueous solutions. We performed open-circuit potential measurements and differential scanning calorimetry (DSC) while varying the concentration of aqueous tetraethylammonium chloride (TEACl) solution. Open-circuit potential measurements revealed that the local OH$^{-}$ concentration within the nanopores increases as the bulk TEACl concentration increases. DSC measurements indicated that TEA$^{+}$ cations are enriched within the nanopores and an extremely high concentration of TEA$^{+}$ remarkably increases the local OH$^{-}$ concentration. This increase in the local pH should realize the selective precipitation of metal hydroxides within the nanopores. However, such precipitation was not observed in our investigations using aqueous solutions containing zinc cations. The experimental results suggest that ionic species within the nanopores of porous silicon are more stable than those in a bulk solution due to the formation of ion pairs with enhanced stability as well as kinetic factors that increase the activation energy for precipitation.

INTRODUCTION

Highly concentrated aqueous solutions possess unique functions, which are advantageous for electrochemical reactions and the development of electrochemical devices. For example, water decomposition is suppressed by reducing the amount of water in aqueous solutions. In the case of an extremely high concentration, such solutions are referred to as the so-called hydrate melts.1−3 Since it was reported that lithium bis(trifluorosulfonyl)amide hydrate melts (21 mol kg$^{-1}$) exhibit a remarkable expansion of the electrochemical window,4 several studies have attempted to apply hydrate melts to batteries and electric double capacitors.5−7 In addition, concentrated solutions with suppressed hydrogen evolution have been applied to electrodeposition processes.8−10 Adachi et al. demonstrated chrome plating with a high current efficiency using a calcium chloride (CaCl$_2$) or lithium chloride (LiCl) hydrate melt based on trivalent chromium baths.8 Increasing the electrolyte concentration also affects the ionic interactions. Smith et al. demonstrated that the Debye length increases as the concentration of the sodium chloride (NaCl) aqueous solution increases.11 Nanoconfinement also induces other unique properties in aqueous solutions. The properties of solutions confined within nanopores with various shapes, such as cylindrical, spongy, cage-like, and dendritic, have gained prominence in diverse fields such as biology and nanotechnology.12−16 According to the IUPAC definition, pores can be divided into three categories as macropores being pores larger than 50 nm in diameter, mesopores being those with 2−50 nm, and micropores being those smaller than 2 nm. In such studies including the present study, pores with a diameter smaller than 50 nm were often utilized as nanoporous materials. As a striking example, the decreased water activity in DNA nanocages affects the folding of DNA structures.12 In nanotechnology, Raman spectroscopy revealed a remarkable increase in the melting points of water inside carbon nanotubes with ca. 1 nm diameter.15 Otake et al. also reported high proton conduction in water confined within metal−organic nanotubes.16

Porous materials with numerous nanopores exhibit unique phenomena, which are associated with aqueous media. Our previous studies focused on the hydrophobic effect that induced anomalous behavior in aqueous solutions confined
within nanopores.\textsuperscript{17–21} Surface-induced phase separation can occur in the vicinity of a hydrophobic surface (i.e., the vicinity of the surface is filled with a second phase, which has a high concentration of the hydrophobic solute) even when the bulk is stable as a single phase, as suggested by Kinoshita based on theoretical analysis.\textsuperscript{22,23} In particular, longer alkyl chains of hydrophobic alkylammonium cations were reported to induce a more rapid and larger shift in the local pH.\textsuperscript{21} It should be noted that the term surface-induced phase transition has often been used instead of surface-induced phase separation. However, the present study deals with the phase transition between a liquid and a solid. To avoid confusion, the term surface-induced phase separation is used to denote the accumulation of hydrophobic solutes into hydrophobic nanopores. These studies on the surface-induced phase separation in porous silicon have examined the behaviors only when using dilute solutions with concentrations less than 0.1 M of the alkylammonium cations.

To date, studies are yet to observe surface-induced phase separation using highly concentrated aqueous solutions with anomalous properties. Here, we investigate the effect of the bulk concentration of an aqueous solution containing alkylammonium cations on the ion enrichment behavior within nanopores of porous silicon due to surface-induced phase separation, especially in view of extremely high concentrations in the bulk. We conducted electrochemical measurements and thermal analyses to evaluate the local increase in the pH as well as the reactivity of hydrated zinc ions confined within nanopores where the surface-induced phase separation of hydrophobic ions is anticipated. Although the original motivation of the present study is to fabricate sophisticated p–n junction devices by filling n-type zinc oxide within the nanopores of p-type silicon driven by the local pH change, the precipitation reaction of zinc oxide is extremely hard within the nanopore of porous silicon as reported later. Thus, in the present paper, we focus our attention on the understanding of the physicochemical mechanism of the low reactivity of zinc cations confined within the hydrophobic nanopores of porous silicon.

\section*{RESULTS}

\textbf{Electrochemical Detection of the Local Increase in pH within the Hydrophobic Nanopores.} The open-circuit potential was determined by the simultaneous progress of silicon oxidation (SiO\textsubscript{2} + 4H\textsuperscript{+} + 4e\textsuperscript{−} = Si + 2H\textsubscript{2}O; \(E^\circ = -0.86 \text{ V vs SHE}\)) and proton reduction (2H\textsuperscript{+} + 2e\textsuperscript{−} = H\textsubscript{2}; \(E^\circ = 0 \text{ V vs SHE}\)). The electrode potentials of both reactions shifted by a function of pH. Figure 1 shows the time development of the open-circuit potential can be regarded as the mixed potential as the potential negatively shifted. The penetration of TEA\textsuperscript{+} from the adding the TEACl solution to the electrochemical cell, the electrode in a 1.0 M TEACl solution. Immediately after open-circuit potential measured on a nanoporous silicon with 1.0 M TEACl solution. The arrow indicates the maximum potential shift.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c04127)

**Figure 1.** Time development of the potential measured on nanoporous silicon in a 1.0 M TEACl solution. The potential before 0 s is measured in pure water, while the potential after 0 s is measured in the 1.0 M TEACl solution. The arrow indicates the maximum potential shift.

### Table 1. Bulk pH for TEACl Solutions with Various Concentrations

| bulk concentration/M | pH   |
|----------------------|------|
| 0.0                  | 5.4  |
| 0.001                | 6.2  |
| 0.005                | 6.1  |
| 0.01                 | 5.6  |
| 0.02                 | 5.6  |
| 0.05                 | 5.5  |
| 0.1                  | 5.5  |
| 0.2                  | 5.7  |
| 0.3                  | 5.7  |
| 0.5                  | 5.5  |
| 1.0                  | 5.6  |
| 1.5                  | 5.5  |
| 2.0                  | 5.3  |
| 3.0                  | 5.3  |

solutions at various concentrations. Although the TEACl solution was weakly acidic, the local pH of the solutions confined within the nanopores increased to balance the charge neutrality due to the difference between the concentrations of Cl\textsuperscript{−} and accumulated TEA\textsuperscript{+}. The negative potential shift was the largest when the TEA\textsuperscript{+} concentration within the nanopores was the highest because the large potential shift corresponded to the large increase in the TEA\textsuperscript{+} concentration.

Here, we focus on the maximum negative potential shift and evaluate the amount of TEA\textsuperscript{+} enriched within the nanopores as a function of the TEA\textsuperscript{+} concentration in the bulk. Figure 2 shows the dependence of the bulk concentration on the potential shift. The maximum potential shift increased as the bulk TEA\textsuperscript{+} concentration increased. In addition, the maximum potential shift changed linearly with the logarithm of the bulk concentration. The shift increased by \(ca. 120 \text{ mV}\) when the bulk concentration was 10 times higher. Since the open-circuit potential should be determined by the pH of the solution, the change in the local pH was estimated based on the Nernst equation. According to this equation, the open-circuit potential shifted to \(-0.059 \text{ V per pH change of 1.0}\). The local increase of pH in the confined solution was \(ca. 2.0\) when the bulk TEA\textsuperscript{+} concentration was 10 times higher. Thus, as the bulk TEA\textsuperscript{+} concentration became higher, the local pH of the confined
solution increased rapidly, which was triggered by the significant TEA⁺ enrichment within the nanopores with hydrophobic surfaces. Similarly, the maximum potential shift increased as the bulk concentration increased when using TBACl as the more hydrophobic case. This result indicates that the local pH within the nanopores increases with increasing bulk TBA⁺ concentration.

Thermal Detection of the Local Increase in pH within the Hydrophobic Nanopores. Here, the melting behaviors of the bulk and confined solutions within the nanopores are evaluated by differential scanning calorimetry (DSC) measurements to verify the TEA⁺ enrichment within the nanopores (Figure 3). Figure 3a,b shows the DSC melting curves of the bulk TEACl solution and the solution confined within the porosified silicon membrane, respectively. It should be noted that the porosified silicon membrane contained the confined solution within the nanopore as well as an excess bulk solution outside the membrane. Several thermoporometry studies using porous silica have adopted the extrapolated onset temperature of the endothermal peak in the heating curve as the melting point of the solid phase. Since the endothermal peaks marked with black circles in Figure 3b were detected only when the measurements were performed using the porosified membrane, they were attributed to the phase transition from solid to liquid with regard to the solution confined within the nanopores from solid to liquid. In the case of pure water, the peak derived from the melting of the confined solution was detected at a lower temperature than that derived from the melting of the bulk solution at 0 °C. This drop in the melting point was attributed to the Gibbs–Thomson effect, which appears when confining the solution within the nanopores. Several studies have demonstrated the melting point of pure solvents confined within the nanopores of porous materials decreases due to the Gibbs–Thomson effect. The shift in the melting point of pure solvents due to the nanoconfinement, \( \Delta T_{m} \), can be calculated by the Gibbs–Thomson equation as

\[
\Delta T_{m} = T_{m,bulk} - T_{m,confined} = 2T_{m,bulk} \gamma_{d} \rho_{l} / (r_{pore} \Delta H_{d}) \quad (1)
\]

where \( T_{m,bulk} \) and \( T_{m,confined} \) represent the transition temperatures of the bulk solvent and the solvent confined within the nanopores, respectively, \( \gamma_{d} \) is the surface excess free energy of the solid–liquid interface, \( \rho_{l} \) is the molar volume of the solvent, \( \Delta H_{d} \) is the molar melting enthalpy of the bulk, and \( r_{pore} \) is the average pore radius.

According to eq 1, the average diameter can be estimated once \( \Delta T_{m} \) is experimentally obtained. The reported values of \( \gamma_{d} \) and \( \Delta H_{d} \) of pure water were 25 mJ m⁻² and 6.01 kJ mol⁻¹, respectively. In the present analysis, the average pore diameter, \( 2r_{pore} \), was calculated from the peak temperature of the endothermal peak. The peak temperature using pure water was −4.7 °C, and the calculated average pore diameter was ca. 17 nm, which agrees well with the actual pore size reported in previous studies.

When the bulk concentration was 0.1 M or less, the extrapolated temperature of the confined solution was 7–10 °C lower than that of the bulk solution. The difference between the extrapolated temperatures of pure water was 9.2 °C. Hence, in the case of dilute TEACl solutions, the dominant extrapolated temperatures of the endothermal peaks in Figure 3 as the onset of solution melting (Table 2). In Figure 3a, the

| bulk concentration/M | \( T_{m,bulk} \) in °C | \( T_{m,confined} \) in °C |
|----------------------|----------------------|----------------------|
| 0.0                  | 0.3                  | −9.5                 |
| 0.01                 | 0.0                  | −7.5                 |
| 0.05                 | −1.0                 | −8.6                 |
| 0.1                  | −1.2                 | −9.2                 |
| 0.5                  | −4.6                 | −24                  |
| 1.0                  | −8.2                 | −24                  |
| 2.0                  | −24                  | −38                  |
| 3.0                  | −24                  | −40                  |

Figure 2. Bulk TEA⁺ concentration as a function of the maximum potential shift. The bulk TEA⁺ concentration is varied from 0.001 to 3.0 M.

Figure 3. DSC melting curves of TEACl solutions with various concentrations. (a, b) Melting curves in the absence and presence of the porosified layer of nanoporous silicon, respectively. Black and red broken lines indicate the eutectic temperatures of TEACl–H₂O (−24.5 °C) and TEAOH–H₂O (−35.7 °C), respectively. Black circles indicate endothermal peaks that appear only in the presence of the porosified layer. The scan rate of DSC measurement is 2 °C min⁻¹.
factor of the drop in the melting point is the Gibbs–Thomson effect and not solute enrichment.

On the other hand, the endothermal peak derived from the confined solution appeared near the TEACl–H₂O eutectic temperature when the bulk concentration was 0.5 M or higher (Figure 3b). Comparing with Figure 3a, this endothermal peak indicates that the TEACl concentration within the nanopores increased to ca. 2.0 M using a 0.5 M TEACl solution. For the case of the 0.5 M TEACl solution, the difference of the extrapolated temperatures between the bulk and the confined solutions was ca. 20 °C, which is much larger than that using dilute solutions. The larger difference in the melting behavior among the concentrated solutions indicated that the drop in the melting point for the confined solution was not only due to the Gibbs–Thomson effect but also due to another factor. The hydrophobic solutes enriched within the nanopores due to the surface-induced phase separation had a nontrivial impact on the expansion of the drop in the melting point. In other words, the DSC thermograms suggest enrichment behavior of hydrophobic solutes within the nanopores with hydrophobic surfaces.

Furthermore, in the presence of the porosified layer, another endothermal peak appeared below the TEACl−H₂O eutectic temperature when the bulk concentration was 1.0 M or higher (Figure 3b). The extrapolated temperature of the peak agrees well with the reported value of TEAOH−H₂O eutectic temperature as −35.4 °C. The eutectic point did not appear without the porosified layer. The DSC thermograms revealed not only a simple solute enrichment within the nanopores but also a remarkable increase in the concentration of OH⁻ to maintain the charge balance due to the accumulation of TEA⁺.

Reactivity of Zn Cations Confined within the Hydrophobic Nanopores. Both electrochemical and DSC measurements confirmed the increase in the OH⁻ concentration within the nanopore of porous silicon. Hence, controlling the local pH should selectively precipitate metal hydroxide. Here, we chose zinc hydroxychloride precipitation to evaluate the reactivity of zinc cations. According to the thermodynamic data, water-insoluble Zn(OH)₂Cl₂ precipitated when the pH of the 0.2 M ZnCl₂ solution exceeded 5.7. First, the pH of the 0.2 M ZnCl₂ solution was adjusted to 5.0 and the nanopore was filled with the solution. Then, 2.0 M TEACl was injected to promote the increase in the local pH within the nanopores. Note that the volumes of the abovementioned solutions were the same as those before mixing so that the solutions had a final concentration that was half of the initial concentration.

Figure 4 shows the energy-dispersive X-ray (EDX) mapping images of the porosified layer of nanoporous silicon after immersion in a 0.2 M ZnCl₂ solution after 10 min without cleaning. The white line indicates 20 μm.

Figure 5 shows the time development of the open-circuit potential measured on nanoporous silicon in the 0.1 M TEACl solution after immersion in the 0.2 M ZnCl₂ solution for 10 min. Potential before 0 s is measured in the 1.0 M TEACl solution. The arrow indicates the potential shift, and the value is −0.20 V.

cleaned to confirm the detection of zinc and chlorine within the nanopores when the TEA⁺ cations penetrated. Zinc and chlorine were detected in the porosified layer after adding the TEACl solution. Hence, a certain zinc compound exists within the nanopores after the TEA⁺ penetration.

To confirm whether the detected zinc compound is soluble or insoluble in water, the cross section of a sample was prepared using the same scheme as the sample in Figure 6 except it was cleaned with ultrapure water, was analyzed (Figure 7). Zinc and chlorine were not detected in the nanopores, indicating that the zinc compound detected in Figure 6 is water-soluble zinc chloride. This result is contradictory to the expectation based on the thermodynamic data of the bulk solution. In the case of nanoporous silicon with ca. 2 nm pore size, zinc hydroxychloride did not precipitate as well within the nanopores despite the fact that the local OH⁻ concentration increased similarly to the case of nanoporous silicon.

In this study, two types of nanoporous silicon were used: one with 17 nm diameter and 36 μm thickness and another with 2 nm diameter and 2 μm thickness. In the case of 17 nm diameter, the unique property of the confined solutions is
considered to become more dominant with increasing thickness of the porosified layer. This is because the area fraction of pore surfaces increases compared to the top surface of the layer that contacts the bulk solution. Therefore, the thickness should have an effect on the unique property of the aqueous solutions confined within the nanopores. On the other hand, in the case of 2 nm diameter, the thickness is considered to exhibit a weak effect on the property of the confined solution because the area fraction is high enough with the thickness being 2 μm.

DISCUSSION

Dissolution State of Zinc Cations within Hydrophobic Nanopores. According to the EDX mappings in Figure 4, zinc and chlorine are detected throughout the porosified layer after immersion in the 0.2 M ZnCl₂ solution for 10 min. Because hydrated Zn²⁺ and Cl⁻ are hydrophilic due to their large charge densities, these ions should be unstable within the hydrophobic nanopores of porous silicon. For this reason, Figure 4 seems to contradict the instability of hydrophilic ions within hydrophobic nanopores. A recent analysis on the potential of the mean force between oppositely charged particles in ionic liquids revealed that a particle pair becomes weakly solvophobic when they are coupled. The positive and negative particle pair behaves as if it is a single particle with low surface charge density. The high ion concentration and the short mean distance between oppositely charged ions lead to a similar coupling between Zn²⁺ and Cl⁻, resulting in the formation of a hydrophobic pair with low surface charge density (Figure 8). According to the thermodynamics data, this coupling may lead to the formation of complex ions such as ZnCl³⁻. Therefore, this pair between Zn²⁺ and Cl⁻ is stabilized within the hydrophobic nanoporous silicon and diffuses to all of the hydrophobic nanopores.

Comparison between the Experimental and Theoretical Results for TEA⁺ Enrichment within the Hydrophobic Nanopores. The DSC thermograms shown in Figure 3 indicate that the endothermal peak of the TEACl–H₂O eutectic point appears when the bulk TEACl concentration is higher than 2.0 or 0.5 M in the absence or presence of the nanoporous layer, respectively. The TEA⁺ concentration within the nanopores increases ca. 4 times compared to the bulk concentration. Theoretical analyses in our previous studies using a statistical mechanical theory showed that the
The concentration of the hydrophobic ions in nanoporous silicon can be orders of magnitude higher than that in the bulk. The present thermal analysis shows that the hydrophobic ions are certainly enriched within the nanopores, but the extent is several times higher at most.

**Reactivity of Zn Cations Confined in Nanoporous Silicon.** Due to the formation of the ion pairs between Zn$^{2+}$ and Cl$^{-}$ within the hydrophobic nanopores, the isolation of Cl$^{-}$ from Zn$^{2+}$ is more difficult. This is due to the enhanced stability of the ion pairs. The reason for the suppressed precipitation of zinc hydroxychloride may be related to kinetic factors as well as the increased stability of the ion pairs. There are two possible kinetics factors: the kinetic salt effect and the rigid cagelike structure between the water molecules on hydrophobic surfaces. TEA$^+$ enriched within the nanopores, which is not related to this precipitation, induces the kinetic salt effect. The enriched TEA$^+$ cations weaken the Coulomb interaction between the reactants such as the ion pairs and OH$^-$ anions, suppressing precipitation. Moreover, hydrogen-bonding networks between water molecules within the nanopores can suppress this precipitation due to the relatively low mobility of the networks within the nanopores caused by the rigid cagelike structure between water molecules on hydrophobic surfaces. These factors may inhibit the isolation of Cl$^{-}$ from the ion pairs, increasing the activation energy for the precipitation. According to the enhanced stabilities of the ion pairs and these kinetics factors, the precipitation of zinc hydroxychloride does not occur in nanoporous silicon. It is doubtless that the length of the alkyl chain does not show a significant impact on the suppression of precipitation. This is because the kinetic salt effect is applicable to the cations with different alkyl chain lengths as well. It should be noted the precipitation of zinc hydroxychloride is suppressed when the Zn$^{2+}$ concentration is low.

Considering the solubility product for the precipitation of zinc hydroxychloride, the pH required for this precipitation shifts to a higher value when the local Zn$^{2+}$ concentration within the nanopores becomes low. The present study uses the solution of 0.2 M ZnCl$_2$. If the Zn$^{2+}$ concentration within the nanopores becomes one-hundredth of the bulk solution, this is equivalent to a shift of the equilibrium pH to 7.5. According to the electrochemical measurements, the expected pH after the TEA$^+$ penetration is 8.4. This suggests that the precipitation must occur within the nanopores if the thermodynamics of the bulk solution is simply applicable to the system confined within the nanopores. However, precipitation of zinc compounds is not detected in the nanopores, strongly suggesting that the enhanced stability of the ionic species in the nanopores is derived from the formation of the hydrophobic ion pairs and the above kinetic factors.

**CONCLUSIONS**

We investigated the enrichment behavior of hydrophobic ions and the phase transition within the nanopores of porous silicon as a function of the bulk TEAICI concentration. Open-circuit potential measurements revealed an increase in the local pH within the nanopores with the bulk TEACl concentration. DSC thermograms indicated that TEA$^+$ cations are enriched and the concentration of OH$^-$ remarkably increases within the nanopores when the bulk TEA$^+$ concentration is extremely high. Therefore, the ion enrichment behavior and the phase transition within the nanopores become more prominent when the bulk concentration of TEA$^+$ is high. The DSC thermograms strongly suggest that the enrichment of the hydrophobic TEA$^+$ is not high compared with our expectation based on our theoretical analyses, which we previously reported. We also attempted the selective precipitation of metal hydroxide within the nanopores where the local pH increases. However, contrary to our expectation from the thermodynamics applied in the bulk solution, the precipitation expected was not observed in our investigations using aqueous solutions containing zinc cations. This contradiction originates from the formation of the hydrophobic ion pairs with enhanced stability and the kinetics factors with the increased activation energy for precipitation. The enhanced stability and the increased activation energy can explain the low reactivity for the precipitation of zinc hydroxychloride in the nanopores. In previous studies, we have discussed the enrichment of hydrophobic solutes within the hydrophobic nanopores based only on the thermodynamics. The newly found physicochemical point to be discussed in this paper is the low reactivity of dissolved species within the nanopores affected by the kinetics factors as well as the thermodynamics. Although low reactivity is not preferable to design a porous material as a host matrix for reactions, it certainly provides important insights. Namely, the thermodynamics of bulk solutions cannot be applied directly to nanoporous systems. This result will open further studies on the design of highly concentrated aqueous solutions using nanoporous materials. As mentioned in the Introduction section, highly concentrated aqueous solutions without precipitation have attracted keen attention. We believe that the combination between the design of nanoporous materials and the control of the liquid state in view of their hydration properties is an important strategy to design novel rechargeable batteries whose electrolyte solutions work under the condition where metal oxides are expected to be precipitated in the bulk condition.

**EXPERIMENTAL SECTION**

**Materials.** Tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), and zinc chloride (ZnCl$_2$) were purchased from Nacalai Tesque. All reagents were used as received. Their aqueous solutions were prepared with ultrapure water (18.2 MΩ cm, Millipore, Milli-Q Reference A+).

**Fabrication of Porous Silicon.** Nanoporous silicon substrates with dendritic pores growing perpendicular to the substrate surface were prepared by electrochemical anodization of p-type silicon (100) with a resistivity of 0.005–0.03 Ω cm in a 22 wt % hydrogen fluoride (HF) solution (48 wt %, HF/ethanol (≥95.0% purity in volume) = 1:1.7 in volume). Before anodization, the silicon wafer was dipped in a 5 wt % HF solution to remove the native oxide. Electrochemical anodization was performed at an anodic current density of 40 mA cm$^{-2}$ for a pore diameter of ca. 20 nm. The duration was tuned to create a membrane thickness of ca. 36 µm. The anodized area was 0.79 cm$^2$. The substrate and the membrane of porous silicon were kept wet during the washing process because the solutions for ion enrichment cannot infiltrate the pores if they are dry.

Nanoporous silicon substrates with 2 nm in diameter were also prepared by electrochemical anodization of p-type silicon (100) with a resistivity of 1.0–4.5 Ω cm in a 22 wt % HF solution. The substrate also possessed dendritic pores. After
using a 5 wt % HF solution to remove the native oxide, and anodization was performed at an anodic current density of 2 mA cm$^{-2}$. The duration is tuned to fabricate a porousified layer thickness of ca. 2 μm because a thick layer cannot be fabricated. The nanoporous silicon substrate with 2 nm in diameter was similarly kept wet during the washing process.

Open-Circuit Potential Measurements. The open-circuit potential of nanoporous silicon was measured using a potentiostat (SP-150, Bio-Logic Science Instruments) in aqueous solutions containing alkylammonium cations. In the case of TEACl solutions, the concentration was varied from 0.001 to 3.0 M. In the case of TBACl solutions, the concentration was varied from 0.001 to 1.0 M because the solubility of TBACl was lower compared to that of TEACl. A specific amount of a solution containing alkylammonium cations, whose concentration was 1.11 times higher than the target concentration, was added into the electrochemical cell with nanoporous silicon immersed in pure water to observe the ion penetration in the nanopores. In this observation, nanoporous silicon was immersed into a small amount of water to realize aqueous solutions with high concentrations.

The open-circuit potential was also measured in the case of dipping in a ZnCl$_2$ solution prior to adding the TEACl solution. In this case, the measurement was performed using a 1.0 M TEACl solution. The nanoporous silicon was immersed in a specific amount of the 0.2 M ZnCl$_2$ solution for 10 min. The pH of the ZnCl$_2$ solution was adjusted to 5.0 using HCl. In these ZnCl$_2$ solutions, Zn$^{2+}$ cations exist as a hydrated ion and do not coordinate with Cl$^{-}$ anions in the bulk. After immersion, the same amount of TEACl solutions but twice as concentrated was added into the electrochemical cell with porous silicon. After the measurement, cross-sectional views of the porousified layer were observed with a scanning electron microscope (SEM; VE-7800, KEYENCE) and analyzed by energy-dispersed X-ray (EDX) spectroscopy (Element EDS system, EDAX). To examine the dependence of the pore size on the precipitation of the zinc hydroxochloride within the nanopores, we also performed the same observations using nanoporous silicon substrates with 2 nm in diameter.

Thermal Analysis. Differential scanning calorimetry (DSC) measurements were performed on a standard DSC apparatus (DSC8231, Rigaku). A self-supported porousified layer was detached from the substrate by applying an anodic current density of 500 mA cm$^{-2}$ for 1 s immediately after anodization. The layer was dipped into the TEACl solution at various concentrations for 10 min. The layer was broken into fragments of a few square millimeters and put in an aluminum capsule with a few milligrams of electrolyte prior to hermetically sealing the capsule. For comparison, measurements using TEACl solutions without the porousified layer were also performed. We focused only on the melting behavior of electrolytes because the freezing behavior was not reproducible due to overcooling. Melting was measured at a scanning rate of 2 °C min$^{-1}$.

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Author Contributions

S.I. and K.F. designed the experiments. S.I. performed the electrochemical measurements, SEM observations, and DSC measurements. These data were analyzed by all of the authors. S.I. and K.F. coauthored the first draft of the paper. All of the authors contributed to the preparation of the final manuscript.

Notes

The authors declare no competing financial interest.

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