

PDF issue: 2025-07-26

Aqueous solution reaction during liquid-phase deposition and its application in electrochemical materials

Mizuhata, Minoru

(Citation)

Journal of the Ceramic Society of Japan, 130(9):752-761

(Issue Date) 2022-09-01

(Resource Type) journal article

(Version) Version of Record

(Rights)

© 2022 The Ceramic Society of Japan This is an Open Access article distributed under the terms of the Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the origina...

(URL)

https://hdl.handle.net/20.500.14094/0100478250





SPECIAL ARTICLE-ACADEMIC ACHIEVEMENTS

The 71th CerSJ Awards for Academic Achievements in Ceramic Science and Technology: Review

Aqueous solution reaction during liquid-phase deposition and its application in electrochemical materials

Minoru Mizuhata^{1,2,†}

¹Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University,

1–1 Rokkodai-cho, Nada, Kobe 657–8501, Japan

²Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30–387 Kraków, Poland

The study systematically attempts to synthesize a number of metal oxides using a liquid-phase deposition method and hydrolysis reaction of metal fluoride complexes. Instead of the conventional empirical optimization, the insolution equilibrium is precisely analyzed and desired oxides possessing nano-order structures and thin-film geometries are synthesized. By synthesizing oxides with ordered structures and large specific surface areas, materials with a high affinity for electrochemical reactions is developed, which contributes to the development of the science of such reactions.

©2022 The Ceramic Society of Japan. All rights reserved.

Key-words : Liquid phase deposition, Hydrolysis equilibrium reaction of metalfluoro complex, Liquid phase infiltration into nanostructured materials, Surface modification for electrochemical materials, Active materials, Nanoceramics

[Received May 5, 2022; Accepted June 7, 2022]

1. Introduction - Positioning liquid-phase deposition methods in soft solution

Metal oxide thin films have been widely used as inorganic functional materials owing to their promising electrical, optical, and magnetic properties. According to a previous study,¹⁾ conventional ceramic synthesis processes consist of "two-steps," i.e., the synthesis-fabrication processes in high temperatures that consume tremendous amounts of energy. The vapor phase process widely used in various industrial fields such as chemical vapor deposition, physical vapor deposition, and metal organic chemical vapor deposition requires a huge, complicated device for the operation under low pressure.²⁾ Therefore, softsolution processes are promising methods to achieve a reduction in the cost and energy consumption for fabrication and operation because of their advantages such as precise control of the equilibrium and kinetics and thermochemical (chemical) potential for the dissolving spices in related compound. There are various kinds of soft-solution processes that are conducted in ambient temperature and pressure through direct deposition, such as the metal complex deposition,¹⁾⁻³⁾ liquid-phase deposition (LPD),⁴⁾⁻⁶⁾ chemical bath deposition (CBD),⁷⁾⁻⁹⁾ and successive ionic layer adsorption and reaction,¹⁰⁾⁻¹²⁾ owing to their handling ease, low cost operations, and simplicity of required

equipment. Not only oxides but also other chalcogenide compounds are prepared using soft-solution processes.^{7)–12)} Various reactions of the metal complex have been studied using the solution reaction. Recently, the reaction mechanism in LPD has been reported in a study as a soft-solution process. As it resembles the hydrolysis reaction process, the LPD reaction is usually regarded as a subset of the CBD.^{13),14)} However, various kinds of oxides can be prepared using a combination of a metal-fluoro complex and a F⁻ scavenger, determined through the comparison of a relative stability constant of each fluorine complex.¹⁵⁾ Although many studies have attempted to fabricate various oxides using the LPD process, there has been limited research to understand the reaction process in a solution phase.¹⁵⁾⁻²⁰⁾ The LPD reaction spontaneously proceeds at ambient conditions through a balance of two equilibrium reactions-the hydrolysis equilibrium (ligand-exchange) reaction of a metal fluoride complex species [Eq. (1)] and F⁻ consumption reaction with boric acid or aluminum ion as an F⁻ scavenger [Eqs. (2) or (3)].

$$MFx^{(x-2n)-} + nH_2O \Leftrightarrow MO_n + xF^- + 2nH^+ (1) H_3BO_3 + 4HF \to BF_4^- + H_3O^+ + 2H_2O (2)$$

$$Al^{3+} + 6HF \rightarrow H_3AlF_6 + 3/2H_2$$
 (3)

©2022 The Ceramic Society of Japan

Deki et al. had employed the LPD method to fabricate various kinds of films, such as TiO₂,⁵ V₂O₅,²¹ VO₂,²² β -FeOOH,²³ Nb₂O₅,²⁴ ZrO₂,²⁵ CuFeO₂,²⁶ α -Ni(OH)₂,²⁷⁾ h-MoO₃,²⁸ H₂WO₄·H₂O,²⁹⁾ and other multi-component metal oxide films.²³ However, optimization of the com-

[†] Corresponding author: M. Mizuhata; E-mail: mizuhata@ kobe-u.ac.jp

position has not been fully achieved for a small amount of fluorine incorporated into the synthesized thin film, resulting in a poor reproducibility for the synthesis of transition metal oxides, especially copper and nickel oxides. In fact, the Fe-Ni binary oxide was synthesized using an iron fluoro-complex with aqueous Ni(NO₃)₂ solution as the "doping" reagent^{30),31)} owing to the low stability constant of the metal-fluoro complex, though whose deposition mechanism was still unclear. The understanding of the LPD reaction mechanism is indispensable for optimization, high-yield synthesis, and improvement of the physical properties of thin films. Additionally, the equilibrium reaction expressed in Eq. (1) involves not only the metal fluoro-complex but also hydrolysis. Hence, the LPD reaction is often misunderstood to be similar to a usual hydrolysis reaction, such as the sol-gel process, which requires pyroprocessing. It is often debated that these two equilibria dominate the reaction in the LPD method.^{18),19)} Certain studies have mentioned that the pH equilibrium condition predominantly determines the deposition process.³²⁾ However, by comparing the kinetic condition of the metal fluoro-complex and hydrolysis, the dissociation rate of the metal-fluoro complex is observed to be very low and predominant, which is estimated from the LPD reaction time of 12-24 h in ambient temperature. Therefore, in this study, the kinetic interpretation of the LPD process is considered in addition to the equilibrium reaction.

This study aims to understand the deposition mechanism by applying quantitative nuclear magnetic resonance (NMR) analysis to the LPD reaction solutions for preparing titanium oxide films under various reaction conditions.³³⁾ Moreover, the optimum conditions for the syntheses of 3d transition metal oxide thin films were investigated by controlling the pH and concentration of reacting species.³⁴⁾ From the results, a precise rate control is established for the LPD process using various nano-ordered materials, such as MCM-41,³⁵⁾ Nafion membrane with ionic clustering structure,³⁶⁾ and porous Si,³⁷⁾ applied to electrochemical materials. This study summarizes my involvement in the research of ceramics synthesis using aqueous solutions and progression to the latest research on nanostructured materials.

2. LPD research history before the author's involvement

I was involved in the LPD method and wrote my first paper on the deposition of TiO₂ films on porous silicon using the Deep-RIE method in 2008.38) I first gained an understanding of the difficult-to-handle metal-fluoride equilibria by observing my senior and junior students dealing with them. At that time, the behavior of hydrolysis equilibrium in fluoride complexes was known, but the idea of using it for the synthesis of metal oxides came from a technique called H-coating, which was initiated at Nippon Sheet Glass Co.³⁹⁾ An interesting fact about our laboratory was that, while we knew it was common to synthesize thin films while conducting research on ceramic synthesis, we assumed that such synthesis is done by the companies. Therefore, we disregarded repeating it, and rather appreciated the importance of understanding the reaction mechanism. Thus, we commenced research on the reaction mechanism of metal fluoride complex solutions by spectroscopic analysis. We began identifying the dissolved species by analysis, and measuring the activity of water as a solvent using a transpiration vapor pressure measuring apparatus as shown in Fig. 1.40),41)

At the time, I was trying to compile a doctoral dissertation on a different topic, "physical properties and behavior of electrolyte solutions in solid-liquid coexistence systems,"⁴²⁾ but I had several discussions with the authors of Ref. 41) who were involved with LPD on a daily basis. I believed that those discussions were quite useful, not only for the present precise synthesis of LPD method but also for the activity of dissolving species from the results of both the transpiration method and NMR measurements.⁴³⁾

It is undeniable that the most important fundamental aspect of ceramic research is the synthesis of ceramics. However, the resulting ceramics are the remnants of the reaction with less information available to comprehend the reaction mechanism. I believe that if a reaction was carried out in an aqueous solution, we only need to evaluate at the solution. Therefore, we can carry out reactions in real time. As I was mainly interested in electrolyte solutions and solid–liquid coexistence systems, and particu-



Fig. 1. Vapor pressure measurement system for determination of water and SiF_4 formed by hydrolysis reaction of hydrofluoric acid.⁴¹⁾



Fig. 2. Dissemination of research on LPD process to academia and industry.

larly in the behavior of dissolved species in aqueous solutions of fluorine complexes, I still have not changed this belief.

Furthermore, there are various advantages for synthesizing metal oxides by LPD. For example, in batteries and sensors using ceramics as active materials for redox reactions, the objective is to synthesize ceramics that will serve as the reaction field. If the LPD reaction itself is the subject of research, it is sufficient to develop the reaction on a flat plate, such as glass, and measure the physical properties. However, the shape of the base material would not necessarily be a flat plate, and the structure of the base material may vary by various orders of magnitude. In many cases, substrates with complex shapes and properties are used. In addition, most ceramic substrates that appear to be flat have a nano-scale roughness so they must be able to conform to the shape of the substrate. The application of LPD to substrates with complex geometries had been tackled before I was involved, as shown in Fig. 2, indicating that the surface treatment by LPD was expected to be used for numerous applications.44)-54)

In particular, the liquid-phase infiltration method, in which the oxide is filled into the voids of complex shapes, has made it possible to synthesize metal oxides with various hierarchical structures.⁵⁵⁾ This method utilizes the LPD method's excellent substrate shape-following property to fill the solid pore with oxide, which is evidently observed during the reaction as shown in **Fig. 3**.^{53),54)}

I became directly involved in the LPD method after a series of large-scale projects implemented in my laboratory, particularly, the research and development of sensors for volatile organic compounds and hydrogen in collaboration with New Cosmos Electric Co. Ltd. and Nippon Sheet Glass Co.⁵⁵⁾

To apply metal oxide thin films to sensors, it is not enough to simply create the oxides; various elemental technologies and devices to realize them are required as shown in **Fig. 4**. However, more important than the implementation technology was the precise fabrication of the thin film and control of its composition. Semiconductors such as WO_3 and SnO_2 are often used in sensors, but their oxides have rarely been synthesized by LPD. Furthermore, the shape control of these oxides at the nano- and microorder level to mount them on sensors was an important concern. My role was to conduct basic research on these issues in parallel with discussions with the students.

During this project, me and my coworkers published papers on the synthesis of WO_3 ,²⁹⁾ SnO_2 ,⁵⁷⁾ and thin films on silicon substrates,³⁸⁾ which led me to research on the deposition reaction of metal oxides in nanostructures.

Equilibrium and kinetics of fluorotitanium complex during LPD process for synthesis of TiO₂

I was appointed to my current laboratory in 2011, which gave me the opportunity to reconsider my approach to



prior to LPD reaction



after 5 hours



after 7.5 hours



after 10 hours

after 20 hours

Fig. 3. Reaction process of TiO_2 deposition on Si substrate with 200 nm diameter pores by LPD method. It can be seen that all the pores are filled after about 20 h. Composition of reaction solution, $(NH_4)_2 TiF_6$: 0.1 mol L⁻¹, H₃BO₃: 0.2 mol L⁻¹. Temperature: 30 °C.



Fig. 4. Material arrangement of the H_2 sensor with YSZ electrodes locally tuned by the liquid phase deposition method.⁵⁶⁾ The reference electrode is a glass-encapsulated YSZ, and the potential is measured by potentiometry; a lithographically patterned Pt electrode is placed on an Al₂O₃ substrate and heated to 600 °C.

Line & Pitch: 3µm

LPD. As anyone may have experienced, when one takes upon a research theme that has been studied for a long time and makes it one's own, criticism is unavoidable, particularly about second-guessing one's predecessor, unless one has a clear sense of originality. In other words, it was necessary to organize the thinking on the LPD method and clarify what is being pursued as a scientific principle. I decided to understand the LPD reaction mechanism from the viewpoint of equilibrium in solution, based on the belief that the underlying explanation would be obtained through a precise reaction analysis, which had not been attempted before. Of course, the fundamentals of each of these methods had been developed in previous LPD research, but each of them required some kind of breakthrough. The contents of these themes are introduced below using multinuclear NMR spectroscopy.³³⁾

Titanium dioxide (TiO₂) is one of the most typical species fabricated by the LPD process because it has been wide applicability, such as in photocatalyst,^{58)–61} antire-flection and self-cleaning technology,⁶² and electrochemical reaction,^{63),64} second only to SiO₂ films^{65),66} synthesized from the LPD process. The reaction control is relatively easy for the fabrication of these oxide thin films as the equilibrium constants of the fluorocomplexes of Ti and Si are in the middle range as shown in **Scheme 1**.⁶⁷⁾ Here, the equilibrium constant, β , is defined as:

$$\beta = k_1 k_2 k_3 \dots k_n \tag{4}$$



Scheme 1. Stability constants of various kinds of metalfluoro complex in aqueous solution summarized from the data in Ref. 67).

where $k_1, k_2, ..., k_n$ are obtained from the following sequential formation reactions of metal-fluoro complex:

$$M^{x+} + F^{-} \rightleftharpoons MF^{(x-1)+} \qquad \qquad k_{1} = \frac{[MF^{(x-1)+}]}{[M^{x+}][F^{-}]} \qquad (5a)$$
$$MF^{(x-1)+} + F^{-} \rightleftharpoons MF_{2}^{(x-2)+} \qquad \qquad k_{2} = \frac{[MF^{(x-2)+}]}{[M^{(x-1)+}][F^{-}]} \qquad (5b)$$

$$MF_{(n-1)}{}^{(x-n+1)+} + F^{-} \rightleftharpoons MF_{n}{}^{(x-n)+} \quad k_{n} = \frac{[MF^{(x-n)+}]}{[M^{(x-n+1)+}][F^{-}]}$$
(5c)

Boric acid (indicated as BO_3^{3-}) and Al^{3+} have high stability constants and act as typical F-scavengers from the other fluorine complexes. This results in the difficulty to obtain an Al_2O_3 film. Several kinds of F-scavengers, such as FeOOH, have been used for the LPD process for TiO₂ synthesis.¹⁵⁾ The LPD reaction should first proceed through the sequential defluorate reaction at the beginning of the deposition reaction, called the induction period.⁶⁸⁾ To the best of my knowledge, limited research has been done for reaction analysis in reaction solution, especially for each intermediate species of TiF_x(OH)_{6-x} and BF_x(OH)_{4-x}. Therefore, the reaction process is investigated using multinuclear NMR which can partially classify the dissolving species during the reaction solution.³³⁾

The $(NH_4)_2 TiF_6$ concentrations of the parent solutions for the TiO₂ thin film synthesis were 0.025, 0.1, and 0.2 mol L⁻¹, and the H₃BO₃ concentration was fixed at 0.2 mol L⁻¹. The degreased glass substrates were suspended vertically into the parent solution and reacted at 30 °C. The ¹⁹F NMR spectra were obtained by a Varian INOVA 400 NMR spectrometer.

Figure 5 shows a representative ¹⁹F-NMR spectra of the reaction time dependence of the LPD reaction solution at initial concentrations of 0.1 mol L⁻¹ (NH₄)₂TiF₆ and 0.2 mol L⁻¹ H₃BO₃. From the spectrum of the (NH₄)₂TiF₆ solution, only one signal due to TiF₆²⁻ was observed, which indicates that TiF₆²⁻ anions were quite stable in water. However, a quartet with an unusual intensity ratio



Fig. 5. ¹⁹F NMR spectra of $0.1 \text{ mol } L^{-1}$ (NH₄)₂TiF₆ aq. and reaction time dependence of LPD reaction solution. (NH₄)₂TiF₆ aq: $0.1 \text{ mol } L^{-1}$. H₃BO₃ aq: $0.2 \text{ mol } L^{-1}$.

was observed at -149 ppm after 1 h of LPD reaction, and a doublet with asymmetrical intensities was observed at -156 ppm after 6 h of LPD reaction; these signals can be assigned to BF₃(OH)⁻ and BF₄⁻, respectively.⁶⁶⁾ Free F⁻ anions which were produced by the hydrolysis reaction of TiF₆²⁻ were completely scavenged by H₃BO₃. Hence, the signal due to free F⁻ ions was not detected in the LPD reaction solution at each reaction time. The signals derived from BF(OH)₃⁻ and BF₂(OH)₂⁻ could not be observed because the ligand exchange of these species is much faster than the NMR time scale.

To quantitatively understand the deposition mechanism of titanium oxide thin films by the LPD process, the concentrations of the dissolving species in the LPD reaction solutions were determined by comparing them with the integrated intensity values of ¹⁹F NMR signals of external reference. The NMR is a powerful tool used not only for determining the dissolving species but also for their quantitative analysis because the integrated intensity is directly proportional to the number of resonant nuclei. Figure 6 shows the time dependence of the concentrations of the dissolving species in the LPD reaction solutions. The relationships between the concentrations of the reactant (TiF_6^{2-}) and products [BF₃(OH)⁻ and BF₄⁻] indicate that the most rapid reaction occurred when the initial concentration of $(NH_4)_2 TiF_6$ was $0.025 \text{ mol } L^{-1}$ and the agglomeration of particles as the precursor of a hazy TiO₂ film was depos-



Fig. 6. Reaction time dependence of the concentration of the dissolving species in LPD reaction solutions. $(NH_4)_2 \text{TiF}_6 \text{ aq.:}$ (a) $0.025 \text{ mol } \text{L}^{-1}$, (b) $0.10 \text{ mol } \text{L}^{-1}$, (c) $0.20 \text{ mol } \text{L}^{-1}$. $H_3 \text{BO}_3 \text{ aq.:} 0.20 \text{ mol } \text{L}^{-1}$. \blacksquare : $\text{BF}_3(\text{OH})^-$, \blacktriangle : BF_4^- .

ited. Unexpectedly, the concentration of BF₃(OH)⁻ was higher than that of the BF₄⁻ during the whole reaction. Thus, a boron molecule will scavenge, not four, but three F⁻ anions. Because the ¹⁹F NMR signals for only TiF₆²⁻, BF₃(OH)⁻, and BF₄⁻ species were observed and if TiF₆²⁻ ions released all the F⁻ ions by the hydrolysis reaction as per Eq. (1), then the following relationship will be established:

$$6[\text{TiF}_6^{2-}]_{\text{con}} = 3[\text{BF}_3(\text{OH})^-]_{\text{pro}} + 4[\text{BF}_4^-]_{\text{pro}}$$
(6)

where $[\text{TiF}_6^{2-}]_{\text{con}}$ represents the concentration of TiF_6^{2-} consumed by the LPD reaction, and $[\text{BF}_3(\text{OH})^-]_{\text{pro}}$ and $[\text{BF}_4^-]_{\text{pro}}$ represent the concentrations of $\text{BF}_3(\text{OH})^-$ and BF_4^- produced by the F⁻ consuming reaction, respectively. However, the concentration of F⁻ released from TiF_6^{2-} is much higher than that of the F⁻ scavenged by H₃BO₃ under all concentrations. This result suggests that TiF_6^{2-} does not release all F⁻ ions, indicating the existence of hydrolysis intermediate species $[\text{TiF}_x(\text{OH})_y(\text{H}_2\text{O})_{6-x-y}]^{(4-x-y)+}$ which could not be detected by ¹⁹F NMR owing to the rapid ligand exchange in the LPD reaction solutions. The complicated equilibrium behavior of these various intermediate species in the LPD reaction solutions subsequently affect the chemical composition, crystal structures, and final yields of the metal oxide thin films.

4. Obtaining transition metal oxides from fluorocomplexes having lower stability constants

Our knowledge of the equilibrium reactions of metal fluoride complexes in solution has helped in the systematic synthesis of a variety of metal oxides, especially transition metal oxides that were previously synthesized in a haphazard manner, except aluminum oxide which has the highest stability constant with fluorine ions. While some oxides such as TiO₂, SiO₂, ZrO₂, and SnO₂,⁶⁹⁾ are easily obtained from metal fluorocomplexes having mid-ranged stability constants, it is difficult to obtain the divalent or a part of trivalent transition metal oxides with lower stability constants. The fluorocomplexes of these transition metals are unstable and easily hydrolyzed. It is necessary to add plenty of fluoric acid solution to stabilize the fluorocomplex prior to the LPD reaction. Adding large amounts of



Fig. 7. (a) Various kinds of transition metal oxide thin films prepared by the liquid phase deposition process using wellcontrolled precursor reaction solutions and SEM images of α -Ni(OH)₂ thin films deposited on (b) glass substrate and (c) α -Al₂O₃ powder.

the F^- scavenger to reduce the excess amount of free fluoric ion in transition metal fluorocomplex causes a rapid and uniform hydrolysis reaction, resulting in the precipitation of hydroxide and oxides. Subsequently, I tried to precisely control the concentration and pH values of reaction solution to maintain the stability of complex. Most of the oxides of 3d transition metals, such as Ti, V, Mn, Fe, Co, and Cu, are obtained employing LPD solutions, as shown in **Fig. 7**.

In our studies for the synthesis of nickel hydroxide, α -Ni(OH)₂,²⁷⁾ and Ni–Al layered double hydroxide (NiAl-LDH),³⁴⁾ the pH values of the precursor solutions of NiF₆²⁻ are maintained at a particular value once NiF₆²⁻ is prepared from the Ni(OH)₂ and HF solutions. Considering the stoichiometry of these species, the following neutralization is expected:

 $Ni(OH)_2 + 6HF aq. \rightarrow NiF_6^{2-} + 2H^+ + 2H_2O$ (7)

As the low solubility of the commercialized hydroxide for HF (weak acid) aqueous solution hindered the parent solution preparation of nickel fluorocomplex solution, the Ni(NO₃)₃·6H₂O and NH₃ aqueous solutions were used to obtain the Ni(OH)₂ for the neutralization reaction. The rinsed wet precipitation of hydroxide, β -Ni(OH)₂, is easily dissolved in the HF solution. According to the measurements of free F⁻ concentration using a F⁻ selective electrode, the F-activity gradually decreased monotonically with the aging time of 48 h. The slow fluorocomplex formation and lower stability of the fluorocomplex resulted in a low reproducibility in obtaining nickel hydroxide, even after allowing a 48 h aging time to prepare the reaction solution. After completing the equilibrium reaction of nickel fluorocomplex, we add the aluminum nitrate solution to initiate the hydrolysis reaction. The Al ionic species were inserted into the Ni/Al pillar structure for at least 24 h to form a NiAl-LDH. This material is utilized as an active material in Ni-MH secondary batteries^{70)–72)} and gel sheets that includes the anticorrosive ionic species.⁷³⁾

Synthesis mechanism of chromium(III) oxide thin films in the LPD process

Chromium(III) oxide, which is another 3d transition metal oxide, has many applications in catalytic chemistry, photolithography process, and as an electrode material. We also investigated the optimization of the synthesis condition of the chromium(III) oxide thin film.⁷⁴) Because the solubility product of Cr(OH)₃ is 6.3×10^{-31} , it can be expected that Cr(OH)₃, which is a precursor of the chromium(III) oxide thin film, precipitates in pH > 4.6 at $[Cr^{3+}] = 7.5 \text{ mmol } L^{-1.67}$ For the syntheses of Cr_2O_3 thin films, the Cr(NO₃)₃ and HF concentrations of the parent solutions were set to be 0.05 and $0.15 \text{ mol } \text{L}^{-1}$, respectively. The pH of the parent solutions was controlled by NH₃(aq), and the H₃BO₃ solution was added to the final solution with a concentration of $0.25 \text{ mol } \text{L}^{-1}$. The degreased glass substrates were suspended vertically into the parent solution, and reacted for 24 h at 30 °C.

The NH₃ concentration dependence of Cr³⁺–HF and Cr³⁺–HNO₃ mixture solutions with the pH of the LPD parent solutions is shown in Fig. 8. The Cr(OH)₃ precipitated at a pH > 4.6 as expected from the solubility product in the Cr^{3+} -HNO₃ solutions, whereas in the case of the Cr^{3+} -HF solution, the Cr(OH)₃ precipitated at a pH > 6.1 against expectations. This indicates that the F⁻ anions which coordinate with the Cr³⁺ inhibits the formation of Cr(OH)₃. Hence, it can be inferred that the chromium(III) oxide thin film is synthesized by the LPD process when the hydrolysis of Cr^{3+} is inhibited by the coordination of F⁻ anions. In other words, the addition of H₃BO₃ as a fluorine scavenger when the fluorine inhibits the hydrolysis of Cr³⁺ causes a slow desorption of fluorine from the Cr³⁺, and the subsequent LPD reaction leads to the deposition of chromium(III) oxide thin film.

Figure 9 shows the NH₃ concentration dependence of the deposition amounts of chromium on the glass substrates by the LPD reaction and the initial and final pHs of the LPD reaction solutions. The depositions of chromium(III) oxide thin films were observed when the hydrolysis reaction of the complex was inhibited by the coordination of F^- , i.e., when pH > 4.6. Therefore, it was revealed that the LPD reaction optimization can be carried out by con-



Fig. 8. Various pH of Cr^{3+} -HF and -HNO₃ aq. with various [NH₃]. [Cr] = 7.5 mmol L⁻¹, [HF, HNO₃] = 150 mmol L⁻¹, [NH₃] = 0–240 mmol L⁻¹, dash line: dissolution, solid line: precipitation.



Fig. 9. Various deposition amounts of Cr on substrates by LPD reaction with various $[NH_3]$. $[Cr] = 7.5 \text{ mmol } L^{-1}$, $[HF] = 150 \text{ mmol } L^{-1}$, $[NH_3] = 0-130 \text{ mmol } L^{-1}$, reaction temp.: 30 °C and reaction time: 24 h.

trolling the concentrations of the reaction species and pH. The formation of the thin film of ca. 100 nm in the membrane was confirmed by the surface observation using the scanning electron microscope (SEM), and the composition was amorphous Cr_2O_3 with X-ray diffraction and Raman spectrometry.

6. Application of liquid-phase deposition method to nanostructures

Using a thin film, metal oxides can increase their reaction interfaces or have a unique structure at the interface. Several applications that take advantage of the additional functionality provided by metal oxide thin films are introduced in this study.

6.1 Synthesis of ceramic nanoparticles using local reaction fields

In the usual LPD method, the reaction field is the substrate surface, which has a small potential difference relative to the bulk of the liquid-phase. This results in the formation of ceramic nanoparticles such as TiO_2 and SnO_2 with extremely high dispersibility as shown in **Fig. 10**.^{75),76)} Using this method, we synthesized highly dispersed nanoparticles and applied them to the anode material of lithiumion batteries by compositing them with carbon materials.

6.2 Synthesis of microstructured ceramic thin films by the LPD method

Hydrolysis reactions due to the pH shifts and solubility differences are often so rapid that they are virtually irre-





versible. In addition, there are restrictions on substrate geometry such as the need for post-processing (e.g., heating and sintering of precursors in sol-gel reactions for substrates with nm-order size) and difficulty of wrapping around reaction gases in gas-phase methods. Using the LPD method, which allows an easy control of the reaction rate, we have realized ceramic structure substrates with complex interfaces using electrolithography. We also fabricated ceramic composites with an inverted opal structure and observed anisotropy related to their fluorescence enhancement phenomenon and optical properties.⁷⁷⁾ Moreover, we have succeeded in depositing TiO₂ particles in the cluster structures within perfluorosulfonic acid films known as MCM-4178) and Nafion[®], 79) which have pores of a few nm as shown in Fig. 11. In particular, the Nafion/ TiO₂ composite membrane shows a remarkable improvement from the conventional moisture retention performance, and the results are expected to contribute to lowtemperature operation of fuel cells.

7. Summary

In this study, an LPD method is introduced to synthesize ceramics at ambient conditions for the preparation of nanostructures for electrochemistry, solution chemistry, and analytical chemistry. For researchers in the related fields, to achieve a greater control over the various factors of the reaction process to produce the desired shape was a major concern, rather than the resulting ceramics. The author hopes that these results will lead to new scientific



Fig. 11. Composite prepared by deposition of (a) porous silica (MCM41)⁷⁸⁾ and in (b) Nafion membrane⁷⁹⁾ by LPD process and its reaction mechanism.

theories on the synthesis of ceramics at room temperature and help readers in their future research efforts.

Acknowledgment The author dedicates this paper to Professor Shigehito Deki who passed away in October 2021. He had been encouraging me over the years on research methods and concepts related to aqueous solution reactions. The author would like to express my sincere gratitude to the co-authors listed in the following references for their guidance and cooperation from the conception of the study to the compilation of the results. A part of this study was supported by the Energy and Environment Technologies Development Projects "Development of an Electric Energy Storage System for Grid-connection with New Energy Resources" supported by Kawasaki Heavy Industries (KHI) Ltd. and New Energy and Industrial Technology Organization (NEDO), and partially Grant-in-Aid for Scientific Research (B) (No. 22350094) by JSPS, Japan.

References

- 1) M. Yoshimura, J. Mater. Sci., 41, 1299–1306 (2006).
- M. Kakihana, M. Kobayashi, K. Tomita and V. Petrykin, B. Chem. Soc. Jpn., 83, 1285–1308 (2010).
- 3) S. Yin, J. Ceram. Soc. Jpn., 123, 823-834 (2015).
- H. Nagayama, H. Honda and H. Kawahara, J. Electrochem. Soc., 135, 2013–2016 (1988).
- S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, 25, 433–434 (1996).
- K. Tsukuma, T. Akiyama and H. Imai, J. Non-Cryst. Solids, 210, 48–54 (1997).
- N. R. Pavaskar, C. A. Menezes and A. P. B. Sinha, J. Electrochem. Soc., 124, 743–748 (1977).
- R. A. Boudreu and R. D. Rauh, J. Electrochem. Soc., 130, 513–516 (1983).
- S. M. Pawara, B. S. Pawara, J. H. Kima, O.-S. Joob and C. D. Lokhande, *Curr. Appl. Phys.*, 11, 117–161 (2011).
- Y. F. Nicolau, *Appl. Surf. Sci.*, 22–23, 1061–1074 (1985).
- 11) H. M. Pathan and C. D. Lokhande, *B. Mater. Sci.*, 27, 85–111 (2004).
- S. Sonia, P. S. Kumar, N. D. Jayram, Y. Masuda, D. Mangalaraj and C. Lee, *RSC Adv.*, 6, 24290–24298 (2016).
- H. Parikh and M. R. de Guire, J. Ceram. Soc. Jpn., 117, 228–235 (2009).
- 14) T. P. Niesen and M. R. de Guire, J. Electroceram., 6, 169–207 (2001).
- D. Gutiérrez-Tauste, X. Domènech, M. A. Hernández-Fenollosa and J. A. Ayllón, *J. Mater. Chem.*, 16, 2249– 2255 (2006).
- 16) A. Hishinuma, T. Goda, M. Kitaoka, S. Hayashi and H. Kawahara, *Appl. Surf. Sci.*, 48–49, 405–408 (1991).
- 17) C. J. Huang, M. P. Houng, Y. H. Wang, N. F. Wang and J.-R. Chen, *J. Vac. Sci. Technol. A*, **16**, 2646 (1998).
- K. Shimizu, H. Imai, H. Hirashima and K. Tsukuma, *Thin Solid Films*, 351, 220–224 (1999).
- Y. Masuda, T. Sugiyama, W. S. Seo and K. Koumoto, *Chem. Mater.*, 15, 2469–2476 (2003).
- 20) J.-C. Chiou, S.-W. Tsai, Y.-S. Liu and C.-T. Huang, Sensor. Mater., 20, 425–433 (2008).
- S. Deki, Y. Aoi, Y. Miyake, A. Gotoh and A. Kajinami, *Mater. Res. Bull.*, 31, 1399–1406 (1996).

- S. Deki, Y. Aoi and A. Kajinami, J. Mater. Sci., 32, 4269–4273 (1997).
- S. Deki, Y. Aoi, J. Okibe, H. Yanagimoto, A. Kajinami and M. Mizuhata, J. Mater. Chem., 7, 1769–1772 (1997).
- 24) H. Y. Y. Ko, M. Mizuhata, A. Kajinami and S. Deki, J. Fluorine Chem., 120, 157–163 (2003).
- 25) K. Kuratani, M. Uemura, M. Mizuhata, A. Kajinami and S. Deki, *J. Am. Ceram. Soc.*, 88, 2923–2927 (2005).
- S. Deki, H. Miki, M. Sakamoto and M. Mizuhata, *Chem. Lett.*, 36, 518–519 (2007).
- 27) S. Deki, A. Hosokawa, A. B. Béléké and M. Mizuhata, *Thin Solid Films*, 517, 1546–1554 (2009).
- 28) S. Deki, A. B. Béléké, Y. Kotani and M. Mizuhata, J. Solid State Chem., 182, 2362–2367 (2009).
- 29) S. Deki, A. B. Béléké, Y. Kotani and M. Mizuhata, *Mater. Chem. Phys.*, 123, 614–619 (2010).
- 30) S. Deki and Y. Aoi, J. Mater. Res., 13, 883-890 (1998).
- S. Deki, S. Iizuka, K. Akamatsu, M. Mizuhata and A. Kajinami, *J. Am. Ceram. Soc.*, 88, 731–736 (2005).
- 32) H. Kozuka, J. Mater. Res., 28, 673-688 (2013).
- H. Maki, Y. Okumura, H. Ikuta and M. Mizuhata, J. Phys. Chem. C, 118, 11964–11974 (2014).
- 34) H. Maki, Y. Mori, Y. Okumura and M. Mizuhata, *Mater. Chem. Phys.*, 141, 445–453 (2013).
- 35) T. Hasegawa, S. Matsumoto and M. Mizuhata, *Chem. Lett.*, 41, 1262–1264 (2012).
- 36) T. Hasegawa, A. B. Béléké and M. Mizuhata, J. Power Sources, 233, 148–156 (2013).
- 37) M. Mizuhata, A. Katayama and H. Maki, J. Fluorine Chem., 174, 62–69 (2015).
- M. Mizuhata, T. Miyake, Y. Nomoto and S. Deki, *Microelectron. Eng.*, 85, 355–364 (2008).
- 39) H. Nagayama, H. Honda and H. Kawahara, J. Electrochem. Soc., 135, 2013–2016 (1998).
- 40) W. Davis, Jr. and H. J. de Bruin, *J. Inorg. Nucl. Chem.*, 26, 1069–1083 (1964).
- 41) M. Mizuhata, Y. Saito, M. Takee and S. Deki, *J. Ceram. Soc. Jpn.*, 117, 335–339 (2009).
- 42) M. Mizuhata, Properties of the liquid phase in highly concentrated solid/liquid coexisting dispersion system, Kobe University Doctoral Dissertation (1992), https:// doi.org/10.11501/2964523.
- H. Maki, R. Sogawa, M. Fukui, S. Deki and M. Mizuhata, *Electrochemistry*, 87, 139–141 (2019).
- 44) N. Kimizuka, M. Tanaka and T. Kunitake, *Chem. Lett.*, 28, 1333 (1999).
- E. A. Whitsitt and A. R. Barron, *Nano Lett.*, 3, 775–778 (2003).
- 46) H. Yu, S. C. Lee, C. H. Ao and J. Yu, J. Cryst. Growth, 280, 612–619 (2005).
- 47) T. Hamaguchi, N. Yabuki, M. Uno, S. Yamanaka, M. Egashira, Y. Shimizu and T. Hyodo, *Sensor. Actuat. B-Chem.*, 113, 852–856 (2006).
- 48) M. Tatemichi, M. Sakamoto, M. Mizuhata, S. Deki and T. Takeuchi, J. Am. Chem. Soc., 129, 10906–10910 (2007).
- Y. Aoi, H. Kambayashi, T. Deguchi, K. Yato and S. Deki, *Electrochim. Acta*, 53, 175–178 (2007).
- R. E. Cochran, J.-J. Shyue and N. P. Padture, *Acta Mater.*, 55, 3007–3014 (2007).
- S. Deki, S. Iizuka, K. Akamatsu, M. Mizuhata and A. Kajinami, *J. Mater. Chem.*, 11, 984–986 (2001).

- 52) M. Mizuhata, Y. Kida and S. Deki, J. Ceram. Soc. Jpn., 115, 724–728 (2007).
- 53) S. Deki, S. Iizuka, A. Horie, M. Mizuhata and A. Kajinami, *Chem. Mater.*, 16, 1747 (2004).
- 54) S. Deki, S. Iizuka, A. Horie, M. Mizuhata and A. Kajinami, *J. Mater. Chem.*, 14, 3127 (2004).
- S. Deki, A. Nakata and M. Mizuhata, *Electrochemistry*, 72, 452–454 (2004).
- 56) S. Deki, M. Mizuhata, T. Ito, T. Maekawa and N. Yamanaka, JP Patent No. 4552008 (2004).
- Y. Saito, Y. Sekiguchi, M. Mizuhata and S. Deki, J. Ceram. Soc. Jpn., 115, 856–860 (2007).
- 58) A. Fujishima and H. Honda, Nature, 238, 37–38 (1972).
- H. Kishimoto, K. Takahana, N. Hashimoto, Y. Aoi and S. Deki, *J. Mater. Chem.*, 8, 2019–2024 (1998).
- S. Deki, S. Iizuka, M. Mizuhata and A. Kajinami, J. Electroanal. Chem., 584, 38–43 (2005).
- 61) G. Jiang, Z. Lin, C. Chen, L. Zhu, Q. Chang, N. Wang, W. Wei and H. Tang, *Carbon*, 49, 2693–2701 (2011).
- 62) L. Yao and J. He, Prog. Mater. Sci., 61, 94–143 (2014).
- H. Xiong, M. D. Slater, M. Balasubramanian, C. S. Johnson and T. Rajh, J. Phys. Chem. Lett., 2, 2560–2565 (2011).
- 64) H. S. Hwang, J. B. Lee, J. Jung, S. Lee, J. H. Ryu and S. M. Oh, *J. Power Sources*, 330, 204–210 (2016).
- T. Homma, T. Katoh, Y. Yamada and Y. Murao, J. Electrochem. Soc., 140, 2410–2414 (1993).
- Y. Chen, S. Zhong, M. Tan and W. Shen, *Front. Energy*, 11, 52–59 (2017).

- R. M. Smith and A. E. Martell, "Critical Stability Constants", Inorganic Complexes, Vol. 4, Plenum Press, NY (1976) p. 96.
- 68) S. Deki, Y. Aoi, Y. Asaoka, A. Kajinami and M. Mizuhata, J. Mater. Chem., 7, 733–736 (1997).
- 69) R. E. Mesmer and A. C. Rutenberg, *Inorg. Chem.*, 12, 699–702 (1973).
- 70) A. B. Béléké and M. Mizuhata, J. Power Sources, 195, 7669–7676 (2010).
- 71) A. B. Béléké, E. Higuchi, H. Inoue and M. Mizuhata, *J. Power Sources*, 225, 215–220 (2013).
- 72) A. B. Béléké, E. Higuchi, H. Inoue and M. Mizuhata, *J. Power Sources*, 247, 572–578 (2014).
- 73) K. Kamon, N. Uchida, H. Maki, M. Matsui and M. Mizuhata, *Electrochemistry*, 89, 111–117 (2021).
- 74) M. Mizuhata, H. Ikuta, Y. Okumura and H. Maki, Proc. Int. Conf. Nanomaterials: Applications and Properties (NAP-2013) (2013) 2(1), 01001.
- M. Mizuhata, Y. Umekage, A. Nakata, R. Kumaresan and S. Deki, *Chem. Lett.*, 38, 974–975 (2009).
- 76) A. Nakata, M. Mizuhata and S. Deki, *Electrochim. Acta*, 53, 179–185 (2007).
- 77) M. Mizuhata, Y. Kida and S. Deki, J. Ceram. Soc. Jpn., 115, 724–728 (2007).
- 78) T. Hasegawa, S. Matsumoto and M. Mizuhata, *Chem. Lett.*, 41, 1262–1264 (2012).
- 79) T. Hasegawa, A. B. Béléké and M. Mizuhata, *J. Power Sources*, 233, 148–156 (2013).



Minoru Mizuhata is a Professor of Kobe University, Japan. He earned his Ph.D. degree in Science (1992) from the Graduate School of Science and Technology, Kobe University. After working as a researcher at the Osaka National Research Institute, AIST (now the Kansai Center of the National Institute of Advanced Industrial Science and Technology, AIST) (1992–1996), a Research Associate at the Faculty of Engineering, Kobe University (1996), and an Associate Professor (2005), he has been a Full Professor since 2011. His research interests include inorganic materials synthesis and electrochemistry, especially ionic conduction and interfacial electrochemistry from the viewpoint of solution properties at the solid–liquid interface. He has published about 200 peer-reviewed papers in these research areas. He was appointed as a visiting professor at the Jagiellonian University, Poland (2019). He received the 2005 Excellent Paper Award from The Electrochemical Society of Japan and the 2015 Molten Salt Prize from Molten Salt Committee, The Electrochemical Society of Japan.