Observation and Evaluation of Proton Diffusion in Porous Media by the pH-Imaging Microscope Using a Flat Semiconductor pH Sensor

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The diffusion of protons in porous media was observed and evaluated using a pH-imaging microscope with a flat semiconductor. Small particles were packed on the sensing surface of the flat sensor, followed by the addition of a lactic acid droplet on the top of the packed particle layer. The pH distribution accompanied by the diffusion of lactic acid was visualized at the bottom of the layer using the flat sensor. The difference in the diffusion property was confirmed depending on the particle type. The effective diffusion coefficients of the lactic acid in some porous media were estimated by combining the experimental results and mathematical calculation.

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Introduction

We have been developing a pH-imaging microscope using a flat semiconductor pH sensor based on photocurrent characteristics of semiconductor silicon, which we call a Scanning Chemical Microscope.¹⁻⁹ The sensor utilized in this microscope functions by light illumination to the opposite side of pH sensing.¹⁰ The sensor also functions as an array of multiple pH sensing parts by focussing and scanning the light illumination two dimensionally. The pH values obtained at each pH-measurement point on the sensor are converted to a color scale, and the color scale of each pH value is displayed as pH images by the microscope. Taking advantage of the use of the sensor with a flat pH-sensing surface and capability of multiple-point pH measurement, we have demonstrated a new type of surface characterization of solid samples using this microscope.³⁻⁵ In this characterization, a thin agar film is placed on the flat sensor with the sample surface contacting the top of the agar film. Multiple-point pH measurements enable the pH distribution formed in the agar film to be imaged. Since the pH distribution in the agar film was formed by the contact of the sample to the agar film, the pH image reflects the surface chemical condition of the sample. Thus, the surface chemical information of the sample can indirectly be obtained. As an application of this unique surface analysis, we successfully imaged the surface of some biological samples, such as plant leaves and sliced human teeth. We also visualized the generation and expansion of electrochemically formed pH distributions while taking advantage of the use of a sensor with a flat pH-sensing surface and the capability of multiple-point pH measurements in this microscope.² Simple electrolysis was conducted in agar film formed on the flat sensor using a platinum anode and cathode.

The resulting lower and higher pH regions and their expansions were repeatedly visualized. Iwasaki *et al.* also conducted similar experiments in solutions with high viscosity, evaluating the diffusion coefficients of protons and hydroxide in solution with various viscosities.⁹

In this research, we successfully observed proton diffusion in a porous environment using our pH-imaging microscope. The porous environment was formed by packing small particles on the flat sensor of the microscope with an electrolyte solution. Such an environment is regarded as an imitated soil system; thus, the observation of proton diffusion in the soil system was estimated in this research. The pH distribution formed in the bottom of the layer was repeatedly imaged after adding acid droplets on the top of the particle packed layer. The set of pH images obtained by repeated imaging showed the difference in the diffusion characteristics of acid inside the packed particle layer.¹¹ In addition, these pH images allowed the effective diffusion coefficient of the acid, which was an important parameter in diffusion in porous media, to be calculated combined with a simple mathematical method.

Some other pH-imaging methods have also been available with significant research results demonstrated so far. One method uses a scanning electrochemical microscope (SECM)¹² with a miniaturized ion-selective potentiometric electrode as a sensing probe. As an application of this microscopy, a wide variety of reactions, such as corrosion, enzyme, and cell metabolism, were presented. The other is a fluorescence microscope combined with a pH-sensitive fluorescent dye. As an application of this method, the pH distribution around the metal electrodes during water reduction and during corrosion was imaged with a relatively short time scale.¹² These present methods have a higher spatial and time resolution than our presented pH-imaging microscope. However, our pH-imaging microscope requires neither scanning of the sensing probe in side the sample nor the addition of a pH-sensitive fluorescent dye. This characteristic of our microscope is very important,

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Fig. 1 a) Light addressable potentiometric sensor (LAPS): A, electrolyte; B, insulator ($\text{Si}_3\text{N}_4/\text{SiO}_2$); C, silicon; D, light illumination; E, photocurrent. b) pH-Imaging sensor. The sensor is functionally divided into multiple sensing parts based on the photocurrent characteristics of LAPS.

depending on the sample to be measured, even though the spatial and time resolution are lower. The use of a flat pH sensor was also advantageous in conducting the measurement using the packed particle layer. In this paper, sets of pH images and mathematical calculations are described, obtained as the result of proton diffusion in such porous media.

Experimental

Instrument

The pH-imaging microscope (SCHEM-100 Horiba Ltd, Japan) utilizes a silicon pH sensor with a flat sensing area of $2.5 \text{ cm} \times 2.5 \text{ cm}$. This sensor is based on a Light Addressable Potentiometric Sensor (LAPS)¹⁰ made up of a $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ structure (Fig. 1). The proton-sensitive Si_3N_4 surface was made to contact with an electrolyte, and a modulated light beam was illuminated from the Si side with a bias voltage applied between the electrolyte and the Si side. The characterization of the AC photocurrent induced by the modulated illumination from the Si side depends on the amount of protons at the Si_3N_4 side, thus enabling pH measurements to be made. Since this sensor can only detect protons located in the illuminated region, the sensor can function as if it were divided into an array of small independent sensors by focusing and scanning the light illumination, though it is a single monolithic sensor. The modulation and scanning of light illumination, the application of a bias voltage and the data-acquisition function are all controlled by a computer. A computer connected to the microscope converts the pH values obtained by the sensor at each pH-measurement point to a color scale, and then displays the color scale of each pH value as pH images. The spatial resolution and pH resolution of the imaging are $100 \mu\text{m}$ and 0.1 pH , respectively.¹

Measurement set-up and procedure

A packed particle layer was formed by packing silica sand ($425 - 600 \mu\text{m}$ in diameter) or glass-beads particles ($400 \mu\text{m}$ in diameter) on a pH-imaging sensor (Fig. 2). The area and height of the layer were $25 \text{ mm} \times 25 \text{ mm}$ and 4 mm , respectively. A 0.1 M potassium chloride solution was filled into the packed particles, followed by the addition of a $10 \mu\text{l}$ lactic acid solution from the top surface of the layer. The pH distribution in a $20 \text{ mm} \times 20 \text{ mm}$ area was imaged with a $400 \mu\text{m}$ spatial resolution. The time required for obtaining a single pH image was 120 s . The imaging was repeated in 150 s intervals.

Porosity of the particle packed layer

The porosity (ϕ) of the packed particle layer was obtained by

Fig. 2 Experimental set-up for observing proton transport in a porous environment. X, pH imaging sensor; Y1 and Y2, electrodes for electric signals; Z, sensor holder; A, potassium chloride solution; B, drop of acid solution; C, packed particles (glass beads, silica sand). The arrows indicate the movement of the acid solution.

poring deionized water in an acrylic pipe followed by packing of the particles in a pipe.¹⁴ ϕ was calculated to be $38 - 39\%$ according to

$$\phi = \{(V_w - (V_t - V_s))/V_s \times 100, \quad (1)$$

where V_w is the actual volume of the deionized water, V_t the apparent volume of the deionized water when the particles were packed, and V_s the apparent volume of the packed particle layer, respectively.

Results and Discussion

The formation and expansion of a lower pH region was confirmed in a set of pH images obtained after the addition of lactic acid (Fig. 3). The shape of the lower pH region at each pH image was distorted compared to the round and uniform lower pH regions obtained by previous studies using agar film as a matrix.^{1,2} The distorted lower pH region shows that the particles were not packed completely uniformly, and that the protons could move faster in a relatively wider gap between each particle. The acid diffused faster in the case of glass beads, though the size of the particle was almost the same as that of silica sand. The faster proton diffusion in the glass beads layer can be explained by the difference in the tortuosity between the particles originating from the particle shape. The diffusion of the solute in porous media was estimated from the solute concentration measured at only one point of the layer combined with mathematical calculations in most present studies.^{6,10} Unlike these present researches, we enabled a clear visualization of proton diffusion in such a complicated environment by our pH-imaging microscope.

The diffusion of the acid was evaluated quantitatively based on the pH images shown in Fig. 3. The effective diffusion coefficient (D_e) of the acid was obtained by the following procedure. First, the ratio of the detected total proton amount (Q_t) over the induced proton amount (Q_m) was calculated based on the obtained pH images. Q_t was calculated based on

$$Q_t = \sum_{i=1, j=1}^{i_m, j_m} c_{i,j} x_c y_c H \phi \rho \quad (2)$$

where $c_{i,j}$ is the proton concentration obtained by the pH value at each measurement point; i_m and j_m are the numbers of measuring points ($i_m = j_m = 50$); x_c and y_c are the resolutions of the measuring points ($x_c = y_c = 400 \mu\text{m}$), H is the height of the packed-particle layer and ρ is the density of the acid, respectively. The ratio (Q_t/Q_m) is plotted in Fig. 4. Then, the ratio (Q_t/Q_m) was theoretically calculated using the three-

Fig. 3 pH distributions formed in a packed-particle bead and agar gel. a) Glass beads (400 μm). b) Silica sand (425 – 600 μm); image size, 20.0 mm $\times$ 20.0 mm; measured points, 40 $\times$ 40. The number at each image shows the time imaging started.

Fig. 4 Dependence of Q/Q_m on the particle types measured in a packed bead of glass beads or silica sands.

dimensional proton concentration changes which could be expected according to the following diffusion equation using the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) of the lactic acid (D_e) in a porous environment:

$$\frac{\partial c}{\partial t} = D_e \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (3)$$

Here, c is the concentration of protons (kg m^{-3}), t is time (s), and, x and y are the axes (m). The theoretical Q/Q_m value could be calculated in the case of various D_e values, and is shown in Fig. 4. By curve fitting between the experimental and theoretical Q/Q_m values, the D_e under each experimental condition could be estimated (listed in Table 1). Considerable accordance between the D_e and D values was confirmed in the case of both glass beads and silica sand, though the diffusion of the acid was influenced by the surface conditions, such as the wettability, shape and surface area of the packed particles in the packed-particle layer. The diffusion coefficients of some other organic acids are also listed in Table 1.

The diffusion of chemical substances occurs not only in uniform media, but also in more complicated environments.^{17–20} For example, chemical pollutants diffuse in a subsurface

Table 1 Simulated diffusion coefficient of lactic acid in a packed-particle layer ($10^{-9} \text{ m}^2/\text{s}$)

	Particle type and size	
	Glass beads	Silica sand
D_e^a	1.5	1.0
D^b		1.10
$D(\text{HCOOH})^c$		1.42
$D(\text{CH}_3\text{COOH})^d$		1.08

- a. D_e : simulated effective diffusion coefficient of lactic acid in packed-particle layer (room temperature).
- b. D : diffusion coefficient of lactic acid in aqueous solution (25°C).¹⁵
- c. $D(\text{HCOOH})$: diffusion coefficient of HCOOH in aqueous solution (25°C).¹⁶
- d. $D(\text{CH}_3\text{COOH})$: diffusion coefficient of CH_3OOH in aqueous solution (25°C).¹⁶

environment, which is regarded as a porous medium consisting of mineral, solution and gas phases. These phases interact with each other. The effective diffusion coefficient of the solute is

one of the most important parameters in order to assume the movement of solute in the porous media. Our method described in this paper will be applied to evaluate the effective diffusion coefficients of acids in various particle types, enabling us to contribute to the understanding of mass transfer in porous media. As a promising feature of our pH-imaging analysis described in this paper, applicability to a laboratory-scale evaluation of the bioremediation process²¹ or a microbiological-enhanced oil recovery process^{22,23} is expected. In order to conduct these processes efficiently, understanding both nutrient diffusion and the behavior of microbiology in a porous environment is important. A preliminary experiment using *Lactobacillus casei* is now underway.

Conclusion

We have proposed a new method to evaluate proton diffusion in a packed particle layer using pH-imaging analysis. The dependence of proton transport on the particle type was clearly imaged qualitatively. As a quantitative evaluation, an effective diffusion coefficient of lactic acid was obtained. The established method can be used for understanding mass transport in soil systems under laboratory conditions, thus contributing to fundamental research involving the transport of chemicals in soil systems.

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References

1. S. Nomura, M. Nakao, T. Nakanishi, S. Takamatsu, and K. Tomita, *Anal. Chem.*, **1997**, 69, 977.
2. T. Yoshinobu, H. Iwasaki, S. Nomura, M. Nakao, T. Nakanishi, S. Takamatsu, and K. Tomita, *Jpn. J. Appl. Phys.*, **1998**, 37, L353.
3. Y. Kitasako, T. Nikaido, J. Tagami, K. Ikeda, K. Mitsunari, and S. Nomura, *Bunseki Kagaku*, **2000**, 2, 325.
4. S. Nomura, K. Mitsunari, M. Nakao, Y. Kohno, and R. Matsuki, *G.I.T IMAGING & MICROSCOPY*, **2000**, 2, 59.
5. Y. Kitasako, N. Hiraishi, M. Nakajima, T. Nikaido, J. Tagami, and S. Nomura, *Jpn. J. Conserv. Dent.*, **2001**, 44, 56.
6. M. Nakao, T. Yoshinobu, and H. Iwasaki, *Jpn. J. Appl. Phys.*, **1994**, 33, L394.
7. M. Nakao, T. Yoshinobu, and H. Iwasaki, *Sens. Actuators*, **1994**, B20, 119.
8. M. Nakao, S. Inoue, R. Oishi, T. Yoshinobu, and H. Iwasaki, "Tech. Digest, 8th. Conf. Solid-state Sensors & Actuators (Transducers '95)", 451.
9. T. Yoshinobu, A. B. M. Ismail, T. Harada, and H. Iwasaki, *Jpn. J. Appl. Phys.*, **2000**, 39, L400.
10. D. J. Hafeman, J. W. Parce, and H. M. McConnell, *Science*, **1988**, 240, 1182.
11. S. Nomura, M. Nakao, S. Takamatsu, Y. G. Yang, C. Inoue, and T. Chida, *Bunseki Kagaku*, **1999**, 48, 763.
12. B. R. Horrocks, M. V. Mirkin, D. T. Pierce, A. J. Bard, G. Nagy, and K. Toth, *Anal. Chem.*, **1993**, 65, 1213.
13. R. C. Engstrom, S. Chaffari, and H. Qu, *Anal. Chem.*, **1992**, 64, 2525.
14. J. Bear and J. M. Buchlin, "Modeling and applications of transport phenomena in porous media", **1987**, Kluwer Academic Publishers, 344 - 345.
15. T. J. Chresand, B. E. Dale, and S. L. Hanson, *Biotechnol. Bioeng.*, **1988**, 32, 1029.
16. "Chemical data table", **1993**, Maruzen, Tokyo, II-93.
17. J. Brakel and P. M. Heertjes, *Int. J. Heat Mass Transfer*, **1974**, 17, 1093.
18. J. A. Ochoa-Tapia, P. Stroeve, and S. Whitaker, *Chem. Eng. Sci.*, **1991**, 46, 177.
19. M. Victor, M. Lobo, and A. J. M. Valente, *Intern. J. Polymeric. Matter.*, **1994**, 25, 139.
20. Q. Hu and M. L. Brusseau, *Water Resources Res.*, **1995**, 31, 1637.
21. R. M. Maier, I. L. Pepper, and C. P. Gerba, "Environmental Microbiology", **2000**, Academic Press, 61.
22. H. Mulder, A. M. Breure, and W. H. Rulkens, *Chemosphere*, **2001**, 42, 285.
23. Y. G. Yang, Y. Niibori, C. Inoue, and T. Chida, Proceedings of the IASTED International Conference on Applied Modeling and Simulation, **1999**.