Academic Program [Oral B] | 20. Materials Chemistry -Basic and Application-：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:40 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:40 AM UTC
[G]3402(3402, Bldg. 3, Area 4 [4F])

[[G]3402-1pm] 20. Materials Chemistry -Basic and Application-

Chair: Keigo Tashiro, Naoki Tanaka

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[G]3402-1pm-01]

Boosting desorption of confined water in metal-organic frameworks using oligomeric liquids

○Meles Zenawi Gebrekidan[1], Yuto Toki[1], Arisa Fukatsu[1], Kenji Okada[1], Masahide Takahashi[1] (1. Osaka Metropolitan University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[G]3402-1pm-02]

THz wave absorption properties of Rb-encapsulated Prussian blue analogue films

○Yuuki Mineo[1], Koji Nakabayashi[1], Asuka Namai[1], Kenta Imoto[1], Marie Yoshikiyo[1], Hiroko Tokoro[2], Shin-ichi Ohkoshi[1] (1. The University of Tokyo, 2. Univerity of Tsukuba)

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC

Break

Japanese
1:50 PM - 2:10 PM JST | 4:50 AM - 5:10 AM UTC
[[G]3402-1pm-03]

Medium-range order structure of sodium silicate glass

○Shigeo Sasahara[1], Yuito Kamijo[1], Sujimo Ozeki[2] (1. Fuji Chemical Co. Ltd.,, 2. Shinshu Univ.)

Japanese
2:10 PM - 2:30 PM JST | 5:10 AM - 5:30 AM UTC
[[G]3402-1pm-04]

Band gap and crystal size engineering of metal-organic framework and single-walled carbon nanotube composites

○Naoki Tanaka[1,2], Koshin Tanaka[1], Tsuyohiko Fujigaya[1,2,3] (1. Grad. Sch. Eng., Kyushu Univ., 2. WPI-I2CNER, 3. Center for Molecular Systems)

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

Break

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[G]3402-1pm-05]

Asymmertric mixed-matrix membranes for CO_2 separation

○Xin Zheng[1,2], Jieru Chen[2], Shin-ichiro Noro[1,2] (1. Faculty of Environmental Earth Science, Hokkaido Univ., 2. Graduate School of Environmental Science)

Japanese
3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC
[[G]3402-1pm-06]

One pot synthesis of metal-porous silica core-shell nanoparticles by using only sources of the particles and tannic acid

○Yoshiki Aoto[1], Kazuki Maeda[1], Satoru Doshi[1] (1. Osaka Research Institute of Industrial Science and Technology)

🏷 Japanese

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[[G]3402-1pm-07]

Electrolysis of Pure Water Resulting from Proton Conduction over Surface of Beta-type Zeolite with Silanol Nests

○Keigo Tashiro[1,2], Taisei Saito[2], Kojiro Goto[2], Shuhei Shimoda[3], Nao Tsunoji[4], Takashi Toyao[3], Ken-ichi Shimizu[3], Hiroshige Matsumoto[5], Shigeo Satokawa[2] (1. Shizuoka Univ., 2. Seikei Univ., 3. Hokkaido Univ., 4. Hiroshima Univ., 5. Kyushu Univ.)

Boosting desorption of confined water in metal-organic frameworks using oligomeric liquids

([1]*Graduate School of Engineering, Osaka Metropolitan University*) ○Meles Gebrekidan[1], Yuto Toki[1], Arisa Fukatsu[1], Kenji Okada,[1] and Masahide Takahashi [1]

Keywords: Atmospheric water harvesting, water desorption, metal-organic framework, liquid oligomer, composite material

MOF-303, (AlOH)(pzdc), pzdc^{2-}=1-*H*-pyrazole-3,5-dicarboxylate) is a metal-organic framework (MOF) recently picked as one of the best water sorbent materials, [1] due to its high surface area, maximum uptake, and moderate temperature water release. However, further studies are required to reduce the desorption temperature of this material to release water molecules without applying heat. Previously, efficient water recovery was achieved in polyether based liquid adsorbents due to the hydrophilicity difference-induced water transfer mechanism, (HWT). [2,3]

In this work we tried to decrease the desorption temperature of MOF-303 through MOF-oligomer composites. First, sorption and thermal properties of composites consisting of MOF-303 along with hydrophobic and hydrophilic oligomers (such as polypropylene glycol, PPG-400, polyethylene glycol, PEG-300, polyethyleneimine, PEI-600, and glycerol derivatives) were compared. Among the composites considered, MOF-303+ PPG-400 showed higher desorption efficiency when mixed at normal conditions with a 1:1 weight ratio. The thermodynamic behavior of water desorption in MOF-PPG composites were investigated and exhibit about 40-50% reduction in water desorption temperature compared to pure MOFs optimizing material properties to lower the energy demand. As the PPG-400 weight percentage increased in the composite, the desorption temperature of the pure MOF-303 was decreased from 85–100 °C to 49–53 °C.

The in-situ ATR-FTIR based water isotherm and cyclic gravimetric adsorption measurement results combined imply that the water kinetics of MOF-303+PPG-400 showed that a 100% release of the adsorbed water after 3 hrs. Whereas, the pure MOF-303 desorption rate was slow and only 45-50% of the adsorbed water was desorbed at 45 °C.

Finally, as shown in Fig. a) the DTA measurement, and b) cyclic sorption results agreed that the hydrophilicity difference induced water transfer mechanism accelerated water desorption after mixing polyglycerol glycol, PPG-400 to the pure MOF-303.

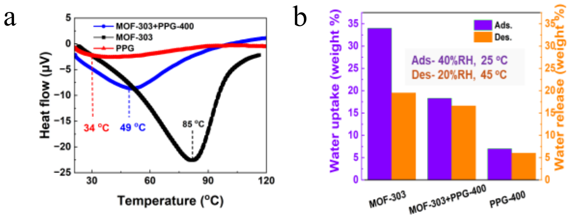


Fig: a. DTA after adsorption at 40% RH, 25 °C b. Cyclic water adsorption and desorption.

1) W. Xu, O. Yaghi, ACS Cent Sci. 2020, 26;6(8):1348–54. 2) D. Ikegawa, A. Fukatsu, K. Okada, M. Takahashi, ACS Omega 2024 9 (1), 1084-1091 3) D. Ikegawa, A. Fukatsu, K. Okada, M. Takahashi. ACS ES&T Water 2024 4 (11), 5169-5177

THz wave absorption properties of Rb-encapsulated Prussian blue analogue films

([1]*Graduate School of Science, The University of Tokyo*, [2]*Faculty of Pure and Applied Sciences, University of Tsukuba*) ○Yuuki Mineo,[1] Koji Nakabayashi,[1] Asuka Namai,[1] Kenta Imoto,[1] Hiroko Tokoro,[1, 2] Marie Yoshikiyo,[1] Shin-ichi Ohkoshi[1]

Keywords: Terahertz spectroscopy, cyanido-bridged metal assembly, Prussian blue analogue

Rubidium manganese hexacyanoferrate is known as one of functional cyanido-bridged metal assemblies exhibiting a charge-transfer phase transition induced by thermal, photo-irradiation, or pressure application.[1-3] Owing to the crystal structure encapsulating Rb^+ ions in the interstitial sites of the three-dimensional cyanido-bridged framework, the compound shows THz wave absorption around 1 THz mainly attributed to the phonon modes of confined Rb^+ ions.[4] Recently, THz waves have been used in a wide range of fields, such as security, pharmaceutical science, and wireless communication. In this context, THz wave absorption materials are practical for controlling THz waves. Especially, highly efficient absorption is desirable in such applications. Therefore, in this study, thin film samples of rubidium manganese hexacyanoferrate dispersed in resin were fabricated based on the calculation.

$Rb_{0.97}Mn[Fe(CN)_6]_{0.99}\cdot 0.3H_2O$ (**RbMnFe**), polyvinylidene fluoride (PVDF) resin, dispersant, and dispersion solvent were mixed under vacuum, applied at constant thickness and dried on a hot plate to obtain RbMnFe-PVDF composite film sample. In order to estimate the film thickness d which exhibits intense absorption around 1 THz, a metal-backed sample was considered. When the thickness d is set to a specific value determined by permittivity and permeability (here set to 1) of the absorber materials, both reflected waves from the metal plate and the absorber cancel each other out, which allows the incident wave to enter the absorber without interference from the reflected wave, *i.e.*, phase matching condition is achieved, resulting in improved absorption efficiency. Using the permittivity of RbMnFe-PVDF composite film measured using THz-Time domain spectroscopy, the calculation was performed to show the maximum absorption peak at 1 THz appears when d = 79 μm. Based on the result, a 79 μm-thick RbMnFe-PVDF composite film was fabricated in practice. THz reflection measurement with a metal plate revealed that the film exhibited more than 99.99% absorption at 0.98 THz. Such film sample has potential to realize efficient THz wave absorption.

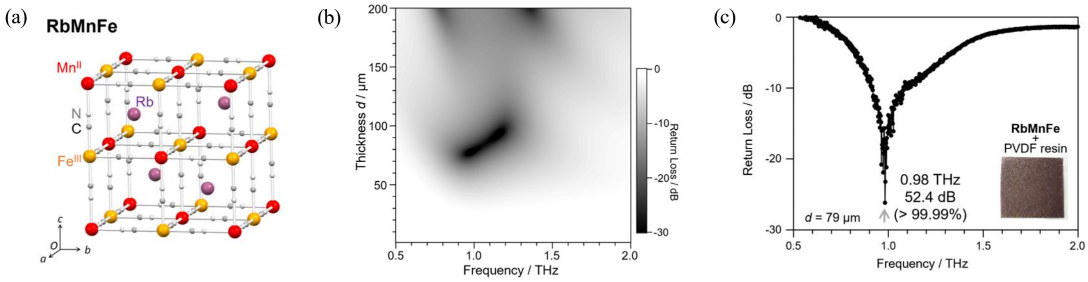


Figure. (a) Crystal structure of **RbMnFe**. (b) Frequency- and thickness-dependent calculated return loss values of RbMnFe-PVDF composite film. (c) Observed reflection spectrum of 79-μm thick RbMnFe-PVDF composite film.

1) S. Ohkoshi, *et al.*, *Chem. Mater.* **2005**, 17, 81. 2) H. Tokoro, S. Ohkoshi, *et al.*, *J. Appl. Phys.* **2005**, 97, 10M508. 3) S. Ohkoshi, *et al.*, *Nat. Commun.* **2023**, 14, 8466. 4) Y. Mineo, S. Ohkoshi, *et al.*, *Eur. J. Inorg. Chem.* **2024**, 27, e202400301.

ナトリウムシリカガラスの中距離秩序構造

（富士化学(株)[1]・信大理[2]）○笹原 茂生[1]・上條 由人[1]・尾関 寿美男[2]
Medium-range order structure of sodium silica glass. ([1]*Fuji Chemical co., Ltd.*, [2]*Graduate School of Science, Shinshu University*) ○Shigeo Sasahara,[1] Yuito Kamijo,[1] Sumio Ozeki[2]

Silicate glasses has long been used in many applications. In recent years, the glass can be analyzed in detail by X-ray scattering and TDA. First peak which observed at low *q* value of *S*(*q*) is called FSDP. The plane aligned through the voids in the glass is considered to be the medium-range structure which is the origin of FSDP. In this study, X-ray scattering experiments were performed on silicate glasses with different Na_2O concentrations to analyze the FSDP (Fig. 1, 2). The periodicity *D* (=2π/q_{FSDP}) estimated from *q* value of FSDP was decreased with increasing Na_2O concentration. The effect of Na on the silicate ring structure will be reported in more detail by TDA of the structure obtained from HRMC method.

Keywords : silicate glass, medium-range order stracture, HRMC method, persistent homology

ケイ酸塩ガラスは多くの用途で古くから利用されている材料である。近年では、ガラスは X 線散乱とトポロジカルデータ解析 (TDA) により詳細な構造解析が可能である。X 線散乱から得られる *S*(*q*) の低 *q* 値で観測されるピークは FSDP (First Sharp Diffraction Peak) と呼ばれる。ガラス中の空隙越しにそろった面が FSDP の起源となる中距離構造と考えられている。本研究では Na_2O 濃度を変えたケイ酸塩ガラスについて X 線散乱実験を行い、FSDP の解析を行った (Fig. 1, 2)。FSDP の *q* 値から見積もった周期 *D* (=2π/q_{FSDP}) は Na_2O 濃度が増加すると減少した。これはケイ酸の骨格が形成する空隙に Na^+がパッキングして Si-O ネットワーク中の O 原子間距離が縮んだためと考えられる。HRMC 法による解析により得られた構造について TDA をすることで、Na がケイ酸のリング構造に与える影響についてより詳細に報告する。

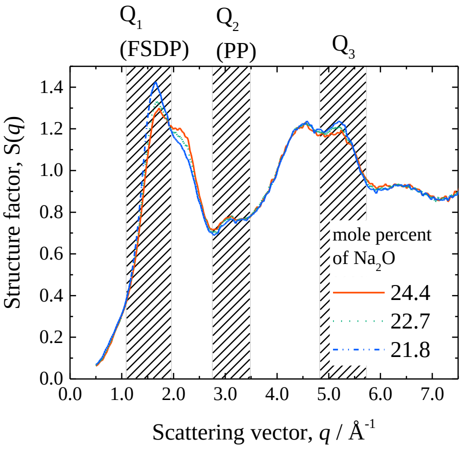


Fig. 1 Variations of *S*(*q*) of sodium silicate glasses with Na_2O concentrations.

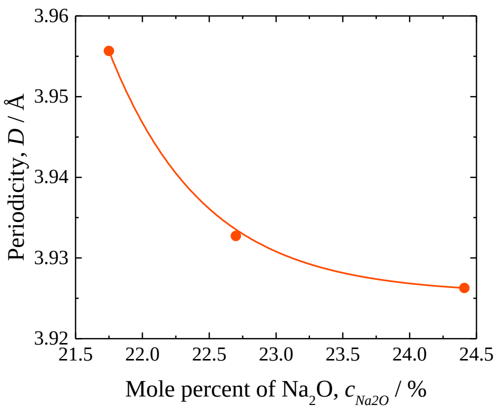


Fig. 2 The periodicity *D* (=2π/q_{FSDP}) of sodium silicate glasses.

金属有機構造体と単層カーボンナノチューブ複合材料のバンドギャップと結晶サイズ制御技術の開発

（九大院工 [1]・I^2CNER[2]・九大 CMS[3]）○田中 直樹 [1,2]・田中 航慎 [1]・藤ヶ谷 剛彦 [1,2,3]

Band gap and crystal size engineering of metal-organic framework and single-walled carbon nanotube composites

([1]*Graduate School of Engineering, Kyushu University*, [2]*I^2CNER*, [3]*Center for Molecular Systems*) ○Naoki Tanaka,[1,2] Koshin Tanaka,[1] Tsuyohiko Fujigaya,[1,2,3]

Composites of single-walled carbon nanotubes (SWCNTs) and metal-organic frameworks (MOFs) serve as gas sensors due to the resistance change of SWCNT from molecular adsorption and MOF’s selective gas adsorption. The gas-sensing properties depend on MOF crystal size and the electronic structure of SWCNT; however, composites with controlled properties have not yet been reported. In this study, we demonstrated that the band gap and crystal size were tuned by polymer-wrapping of SWCNT and controlling the concentration of MOF precursors. In addition, we report on identifying an optimal structure for gas sensors.

Polybenzimidazole (PBI) and polyvinylpyrrolidone (PVP) were used to coat SWCNTs. Ultraviolet and inverse photoemission spectroscopy revealed that PBI-SWCNT has a narrower band gap than PVP-SWCNT. ZIF-8 (one of the MOF) crystals (20 nm at low precursor concentrations and 40 nm at high concentrations) were formed on PBI- and PVP-SWCNTs. Resistance measurements showed that PBI-SWCNT composites with smaller ZIF-8 crystals had improved CO_2 response sensitivity and speed (**Fig. 1**). These findings highlight the critical role of band gap and crystal size control in enhancing gas-sensing performance.

Keywords : Single-Walled Carbon Nanotube, Metal-Organic Framework, Band Gap, Polymer Coating, Gas Sensor

単層カーボンナノチューブ (SWCNT) と金属有機構造体 (MOF) の複合体 (SWCNT/MOF) は、SWCNT の分子吸着による抵抗変化と MOF の選択的なガス吸着特性により、ガスセンサーとして機能する[1]。その検出能は、MOF の結晶サイズと SWCNT の電子構造が影響すると予想されるが、これらを制御した複合体の作製手法はない。そこで本研究では、両者を制御した複合体を作製し、ガス応答能への影響を明らかにすることを目的とした。

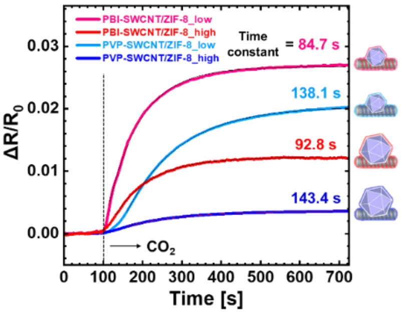


Fig. 1. Dynamic response signals of PBI-SWCNT/ZIF-8_low (pink), PBI-SWCNT/ZIF-8_high (red), PVP-SWCNT/ZIF-8_low (light blue) and PVP-SWCNT/ZIF-8_high (blue) for CO_2 at a total flow rate of 200 sccm.

MOF には、ゼオライト系イミダゾレート構造体 (ZIF-8) を採用し、前駆体濃度制御によるサイズ制御を図った。一方で、ポリベンゾイミダゾール (PBI) とポリビニルピロリドン (PVP) をそれぞれ SWCNT に被覆することで SWCNT の電子構造制御を狙った。各複合体は、SWCNT 分散液に大小 2 種類の濃度の ZIF-8 前駆体をそれぞれ加えることで作製した。電子顕微鏡観察 (SEM) の結果から、前駆体が低濃度で約 20 nm、高濃度で約 40 nm の ZIF-8 が確認された。ゼーベック係数測定から、PBI 複合体では p 型半導体、PVP 複合体では n 型半導体を示す値が観測された。また、CO_2 吸着による抵抗変化を観察したところ、ZIF-8 サイズが小さく、p 型半導体を示す複合体で応答感度と速度の向上が明らかになった (**Fig. 1**)。

[1] S. Kim *et al., ACS Sens.* **2022**, *7*, 3846.

Asymmetric mixed-matrix membranes for CO_2 separation

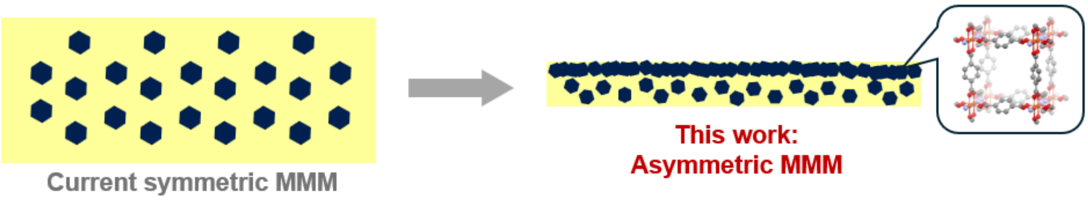
([1]*Faculty of Environmental Earth Science, Hokkaido University,* [2]*Graduate School of Environmental Science, Hokkaido University*) ○Xin Zheng[1,2], Jieru Chen[2], Shin-ichiro Noro[1,2]

Keywords: Mixed-matrix membranes; Metal-Organic Framework; Gas Separation

Mixed-matrix membranes (MMMs) are innovative composite membranes consisting of a polymer matrix and a dispersed filler phase. MMMs synergistically integrate the advantages of polymer matrices and inorganic fillers, offering improved separation performance, tunable properties, and cost-effectiveness for a wide range of applications, including gas separation, water treatment, and pervaporation.[1] Despite these benefits, interfacial compatibility, filler dispersion, mechanical stability, and fabrication complexity remain significant barriers to their practical implementation.

Conventional MMMs exhibit a symmetric structure, with fillers uniformly distributed throughout the matrix. However, this design often leads to suboptimal filler utilization and considerable membrane thickness, which can limit their practical applicability. Recently, asymmetric MMMs have emerged as a promising alternative. This innovative design not only reduces filler consumption but also enhances molecular permeance.[2]

In this study, we successfully fabricated a series of asymmetric MMMs using metal-organic frameworks (MOFs) as fillers to optimize filler utilization and enable the production of thinner membranes. The MOFs employed, known as the JAST series, feature a jungle gym-like structure constructed from Cu(II) ions, 1,4-diazabicyclo[2.2.2]octane (dabco) ligands, and derivatives of terephthalic acid.[3] Using a straightforward dip-coating process, nanoscale JAST particles were grown within the polymer matrix, forming compact layers and yielding asymmetric MMMs of approximately 1 μm thickness. These MMMs demonstrated significant improvements in CO_2 permeance and enhanced selectivity for CO_2/N_2 and CO_2/O_2 separations. Detailed gas separation performance data will be presented.



1) G. Dong, H. Li, V. Chen. *J. Mater. Chem. A*, **2013**, *1*, 4610, 2) H. Zhu, L. Wang, X. Jie, D. Liu, Y. Cao, *ACS Appl. Mater. Interfaces* **2016**, *34*, 22696. 3) R. Matsuda, W. Kosaka, R. Kitaura, Y. Kubota, M. Takata and S. Kitagawa, *Microporous Mesoporous Mater.*, **2014**, *189*, 83

ナノ粒子の原料とタンニン酸のみを用いた金属-多孔性シリカ コア-シェルナノ粒子のワンポット合成

（大阪技術研[1]）○青戸 義希[1]・前田 和紀[1]・道志 智[1]

One pot synthesis of metal-porous silica core-shell nanoparticles by using only sources of the particles and tannic acid ([1]*Osaka Research Institute of Industrial Science and Technology*)
○Yoshiki Aoto,[1] Kazuki Maeda,[1] Satoru Dohshi[1]

The synthesis of core-shell nanoparticles involves multiple steps, including synthesis of core particles, washing, and coating of core particles. One-pot synthesis methods of the particles have been developed to reduce the number of steps in the synthesis process1). However, each steps requires many chemicals such as reductants and capping agents to control morphology of the particles. There have been only few cases of reducing not only the number of steps but also the number of chemicals used in the synthesis process2).

In this study, metal-silica core-shell nanoparticles were successfully synthesized using only tannic acid, metal precursor, 3-aminopropyl trimethoxysilane (APTMS), and water as solvent. In this method, tannic acid was found to play all four roles as reductants of the metal precursor, capping agents of the synthesized core particles, promoters to form silica shell, and templates of micropore in the silica shell. When the core particles were gold, the average size of the core particles was controlled in the range of 9 ~ 12 nm by appropriately setting the addition rate of the metal precursor solution, the reaction temperature, and the molar ratio of the metal precursor to tannic acid.

Keywords：Core-Shell Nanoparticles, Tannic Acid, One-Pot Synthesis

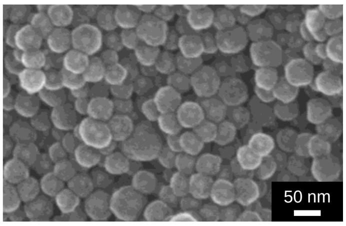


Fig. 1 A FE-SEM image of synthesized gold-silica core-shell nanoparticles.

コア-シェルナノ粒子の合成では、コア粒子の合成、洗浄、コア粒子の被覆、など多段階のステップを必要とする。合成プロセス中のステップ数を削減するためにワンポット合成法が開発されてきたが 1)、粒子の形態制御のために還元剤、保護剤など多くの化学薬品を必要とする。合成プロセス中のステップ数だけでなく、使用する薬品数も削減した例は少ない 2)。

本研究では、タンニン酸、金属前駆体、3-aminopropyl trimethoxysilane(APTMS)、および溶媒として水のみを用いた金属-シリカ コア-シェルナノ粒子のワンポット合成に成功した。この手法においてタンニン酸は、金属前駆体の還元剤、合成したコア粒子の保護剤、シリカシェル形成の促進剤、およびシリカシェル中に形成されるマイクロ孔の鋳型、の役割を全て果たすことがわかった。また、コア粒子が金の場合、金属前駆体の添加速度、反応温度、および金属前駆体とタンニン酸のモル比、を適切に設定することで 9 ~ 12 nm の範囲でコア粒子の平均粒径を制御することができた。

1) Junchen Chen, et. al., *Nano Research*, **2013**, 6, 871-879
2) Shan Zhang, et. al., *RSC Advances*, **2019**, 9, 17674-17678

シラノールネスト含有ベータ型ゼオライト表面でのプロトン伝導を用いた純水の電気分解

(静大院総科[1]・成蹊大院理工[2]・北大触媒研[3]・広島大院先進理工[4]・九大 I2CNER[5])
○田代 啓悟[1]・斉藤 大成[2]・後藤 光次郎[2]・下田 周平[3]・津野地 直[4]・鳥屋尾 隆[3]・清水 研一[3,5]・松本 広重[5]・里川 重夫[2]

Electrolysis of Pure Water Resulting from Proton Conduction over Surface of Beta-type Zeolite with Silanol Nests

([1]*Graduate School of Integrated Science and Technology, Shizuoka University*, [2]*Graduate School of Science and Technology, Seikei University,* [3]*Graduate School of Advanced Science and Engineering, Hiroshima University,* [4]*Institute for Catalysis, Hokkaido University,* [5]*International Institute for Carbon Neutral Energy Research, Kyushu University*)
○Keigo Tashiro,[1] Taisei Saito,[2] Kojiro Goto,[2] Shuhei Shimoda,[3] Nao Tsunoij,[4] Takashi Toyao,[3] Ken-ichi Shimizu,[3,5] Hiroshige Matsumoto,[5] Shigeo Satokawa[2]

Electrolysis of pure water by the cell containing of proton conductive solid electrolyte is one of the most suitable approaches to afford green hydrogen. We succeeded in the water electrolysis at neutral pH resulting from the effective proton conduction proceeding by the exchange of hydrogen bonding in the water network generated on zeolite surface in which the balance of hydrophilicity and hydrophobicity was adjusted by the dealumination treatment of beta-type zeolite. The silanol nest generated by the dealumination treatment has a crucial role in both adsorption of water and the formation of hydrogen-bonded water network on the surface. Water electrolysis efficiency was in linear relationship to the proton conductivity.

Keywords : Water Electrolysis; Proton Conduction; Zeolite; Silanol Nest; Water Network

安価にグリーン水素を製造するためには、中性でプロトンを効率よく伝導できる電解質を含むセルを用いた水電解が必要である。本研究では、脱アルミニウム処理を施すことでゼオライト表面の親疎水性を制御し、表面に水の水素結合ネットワークを効果的に形成させることで、中性領域で高いプロトン伝導を示すシステムを開発した。1) 純水中でのゼオライト表面におけるプロトン伝導度は、適度な親疎水性表面を持つ Si/Al 比のときに最大となった。脱アルミニウムを施していないベータ型ゼオライト **H-Beta-17.8** と最も疎水的な脱アルミニウム処理後の **H-Beta-da-84.7** の水蒸気吸着等温線を解析したところ、脱アルミニウム処理を施すことでゼオライト表面で水の水素結合ネットワークが形成され、プロトン伝導が促進されることが明らかになった。また、純水の電解効率はプロトン伝導度に直線関係を有しており、新たな手法で中性領域での水素製造技術の開発に成功した。

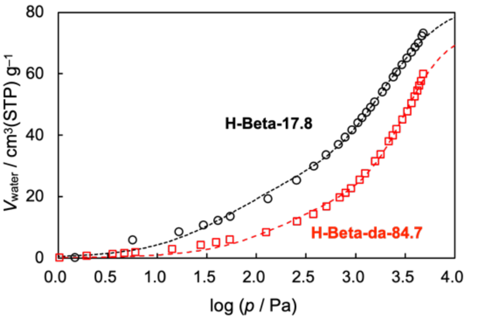


Figure 1. Water vapor adsorption isotherms at 80 °C of non-dealuminated **H-Beta-17.8** and dealuminated **H-Beta-da-84.7** possessing the highest hydrophobic surface among samples in this study.

1) K. Tashiro, T. Saito, K. Goto, J. Masuda, T. Miyakage, S. Shimoda, T. Toyao, N.Tsunoji, K. Shimizu, H. Matsumoto, S. Satokawa, *ChemCatChem* **2024**, *16*, e202301297.