アカデミックプログラム［B講演］｜21. エネルギーとその関連化学，地球・宇宙化学：口頭B講演

2024年3月21日(木) 9:00 ~ 11:30 A1455(14号館 [5階] 1455)

[A1455-4am] 21. エネルギーとその関連化学，地球・宇宙化学

座長：前田 和彦、鳥本 司

日本語
9:00 ~ 9:20
[A1455-4am-01]
膜蒸留と気液交換を融合したHTOのH_2Oからの効率的分離

○三好 弘一[1]、藤原 正浩[2] (1. 徳島大学、2. 大阪大学)

英語
9:20 ~ 9:40
[A1455-4am-02]
Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

○Susmita Roy[1], Masayoshi Higuchi Higuchi[1], Sanjoy Mandal[1] (1. National Institute for Materials Science (NIMS), 1 -1 Namiki)

英語
9:40 ~ 10:00
[A1455-4am-03]
有機薄膜太陽電池材料における自発的対称性の破れによる電荷分離

○在間 嵩朗[1,2]、大田 航[1,2]、春田 直毅[1,2]、 上島 基之[3]、大北 英生[2]、佐藤 徹[1,2] (1. 京大福井セ、2. 京大院工、3. （株）MOLFEX)

英語
10:00 ~ 10:20
[A1455-4am-04]
Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

○Wentao Zhang[1], Kazutaka Akiyoshi[1], Tatsuya Kameyama[1], Tsukasa Torimoto[1] (1. Nagoya University)

10:20 ~ 10:30
休憩

英語
10:30 ~ 10:50
[A1455-4am-05]
層状ペロブスカイト酸フッ化物$Pb_3Fe_2O_5F_2$を電極触媒とした水の酸化反応

○水落 隆介[1]、菅原 勇貴[1]、山口 猛央[1]、前田 和彦[1] (1. 東京工業大学)

日本語
10:50 ~ 11:10
[A1455-4am-06]
CO_2と水からギ酸を生成する電気化学リアクタの長期耐久性向上

○加藤 直彦[1]、河合 泰明[1]、野尻 菜摘[1]、塩澤 真人[1]、菊澤 良弘[1]、鈴木 伸明[1]、小坂 悟[1]、濱口 豪[1]、竹田 康彦[1] (1. 株式会社　豊田中央研究所)

日本語

11:10 ~ 11:30

[A1455-4am-07]

光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

○竝木 裕司[1,2]、田部 博康[1]、堀毛 悟史[1] (1. 京大、2. ポーラ化成工業)

膜蒸留と気液交換を融合したHTOのH_2Oからの効率的分離

(徳島大放セ [1]・阪大環境安全セ [2]) ○三好 弘一 [1]・藤原 正浩 [2]
Efficient separation of HTO from H_2O by membrane distillation using gas-liquid exchange ([1] *Adv. Rad. Res., Edu., Mgmt. Ctr., Tokushima University*, [2]*Res. Ctr. Environ. Preserv., Osaka University*) ○Hirokazu Miyoshi,[1] Masahiro Fujiwara[2]

H_2O containing HTO loaded on a hydrophobic membrane with a photothermal black dye was exposed to an artificial sunlight for 1.5 h. The heat generated from the sunlight vaporized the water to penetrate the vapor through the membrane. The water vapor thus permeated was mixed in H_2O impregnated in hydrophilic filters under the membrane. Gas-liquid exchange occurred in these filters to decrease the content of HTO in the recovered water under all filters. The increases both of the filter number and the water content of the hydrophilic filters further enhanced the separation effect of HTO. When four hydrophobic membranes and four water-containing hydrophilic filters were set alternately, the ratio of HTO recovered under these filters was reduced to 12%.

Keywords：Tritiated water; Membrane distillation; Light irradiation; Gas-liquid exchange; rectification

光熱変換性の色素ソルベントブラック 5(SB-5)を塗布した疎水性膜(PTFE 製 PF100)上に HTO 含有水(HTO 濃度: 3026 Bq/mL)を導入し、上方から人工太陽光(994 Wm^{-2})を 1.5 時間照射した（図左)。光熱変換効果により HTO 含有水は蒸気となり疎水性膜を透過する。その際、膜下にセットした含水の親水性フィルター中で気液交換が起き、全てのフィルター下部に回収された水中の HTO 濃度は減少していた。親水性フィルターの枚数や含水量を増やすことで、回収水中の HTO 濃度をさらに下げることができた。親水性フィルターであるガラスフィルター(GB-140)に H_2O を約 2.5 g 含水させた場合、フィルター下部に回収された水中の HTO 濃度は約 77%まで減少した。さらに、含水ガラスフィルターと疎水性膜の組み合わせを 4 セット計 8 枚まで増やしたところ、HTO 量を約 12%までに減少させることに成功した（図右)。一方、水を含まないフィルターでは HTO 濃度はほとんど減少しなかった。

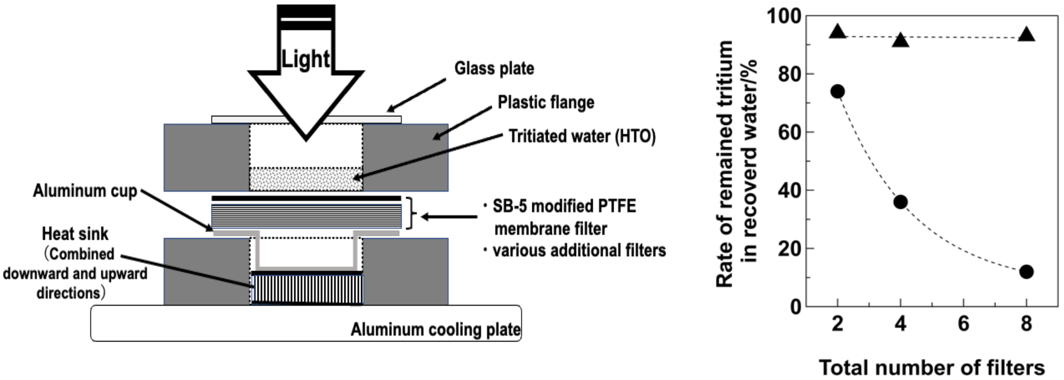

Figure (Left) Schematic diagram of experimental apparatus of tritiated water separation. (Right) Relation between the remained tritiated water rate in recovered water and the total number of PF100 and GB-140. ▲: Dry GB-140. ●: GB-140 with 1 g of water.

Highly Durable Electrochromic Devices for More Than 100000 Cycles with Fe(II)-Based Metallo-Supramolecular Polymer by Optimization of the Device Conditions

([1]*National Institute for Materials Science (NIMS), 1 -1 Namiki*) ○Susmita Roy,[1] Sanjoy Mandal,[1] Masayoshi Higuchi[1]

Keywords: Electrochromism; Metallo-supramolecular Polymer; Electrochromic Device; Durable Electrochromic Device; Electrochromic memory

An solid-state electrochromic device (ECD) of Fe(II)-based metallo-supramolecular polymer (polyFe) with excellent durability was fabricated by incorporating Nickel hexacyanoferrate (NiHCF) as a charge-balancing layer. The solid-state ECD displayed bleaching and coloring at small potential window, with maximum optical contrast. The minimalization of the potential difference during EC changes enabled ultra-high cycle stability and improved optical memory. For the further improvement of the EC properties, it was revealed that the optimization of the film thickness of the polyFe and NiHCF is critical to maintaining the charge balance between the working and counter electrodes. At last, the cyclic stability for the repeated color changes over 100,000 cycles were achieved.[1] This finding will help engineers and scientists to fabricate a low-voltage-driven, long-lasting ECD for real-life application in smart electrochromic window technology.

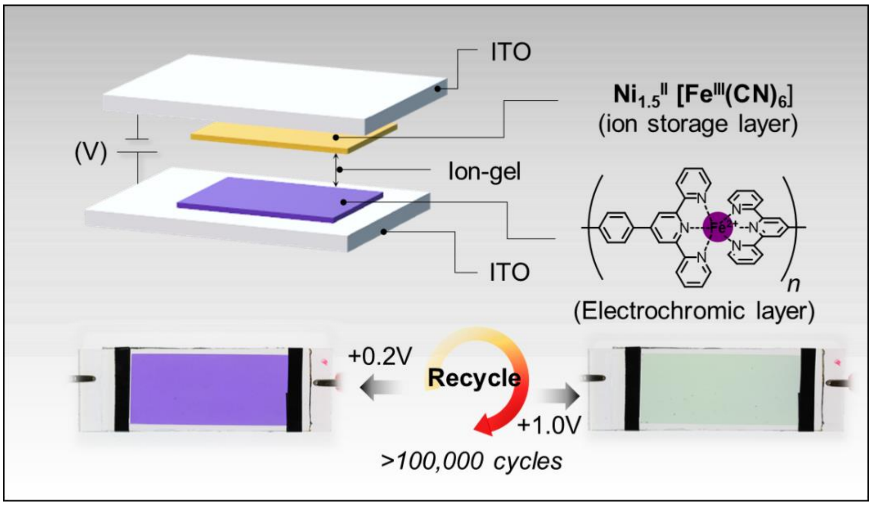

Figure 1. Highly Durable Electrochromic Device of Fe(II)-Based Metallo-Supramolecular Polymer

1) S. Mondal, S. Roy, Y. Fujii, M. Higuchi *ACS Appl. Electron. Mater.* **2023**, *5*, 6677–6685.

Spontaneous-Symmetry-Breaking Charge Separation in Organic Photovoltaic Material

([1]*Fukui Institute for Fundamental Chemistry, Kyoto University,* [2]*Graduate School of Engineering, Kyoto University,* [3]*MOLFEX, Inc.*) ○Takeaki Zaima,[1,2] Wataru Ota,[1,2] Naoki Haruta,[1,2] Motoyuki Uejima,[3] Hideo Ohkita,[2] Tohru Sato[1,2]

Keywords: Photovoltaic conversion; ITIC; Density functional theory; Pseudo-Jahn–Teller effect; Vibronic coupling

In organic photovoltaics (OPV), the driving force of the charge separation has been considered to be an energy offset, i.e., the LUMO (or HOMO) energy difference between donor and acceptor materials.[1] However, highly efficient OPV materials with small energy offsets were recently reported.[2,3] In such OPV materials, the driving force of the charge separation remains unclear. Symmetry-breaking charge separation (SB-CS) that causes the intra- or intermolecular charge separation between identical fragments could be an initial charge separation step in small offset systems.[4] This study aims to theoretically identify the driving force of charge separation in the small offset system using ITIC[3], a non-fullerene acceptor material for OPV devices.[5]

In the previous study, ITIC has been considered packed through the terminal π-π stacking.[6] Hence, we constructed the edge-stacking dimer model of ITIC. According to our density functional theory calculations, the pseudo-Jahn–Teller (PJT) distortion[4] of the S_1 excimer state induces spontaneous SB-CS (SSB-CS) between the identical ITIC molecules even without the asymmetry of the surrounding environment (Fig. 1). The strong PJT effect arises from the vibronic coupling between the pseudo-degenerate S_1 and S_2 excited states with different irreducible representations, i.e., A_u for S_1 and A_g for S_2, via the asymmetric vibrational mode of A_u. The vibrational mode responsible for the spontaneous polarization is the intramolecular C-C stretching vibration between the core IT and terminal IC units. These results suggest that the charge separation efficiency in the initial photovoltaic conversion process can be improved by controlling the PJT effect.

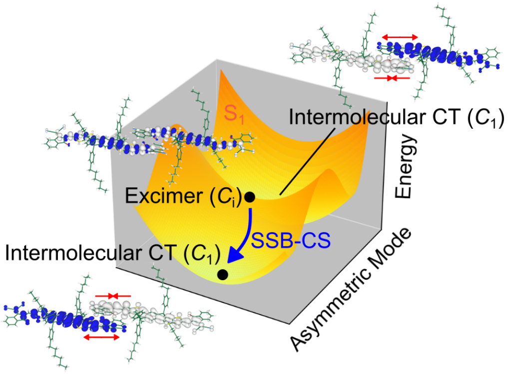

Fig. 1: Schematic illustration of the SSB-CS in ITIC dimer.

1) P. Peumans *et al.*, *J. Appl. Phys.* **2003**, *93*, 3693. 2) K. Kawashima *et al.*, *Nat. Commun.* **2015**, *6*, 1. 3) Y. Lin *et al.*, *Adv. Mater.* **2015**, *27*, 1170. 4) A. N. Bartynski *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 5397. 5) T. Zaima *et al.*, *J. Phys. Chem. Lett.* **2023**, *14*, 9706. 6) G. Han *et al.*, *J. Mater. Chem. C* **2017**, *5*, 4852. 7) I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, 1989).

Preparation of Size- and Composition-controlled Ag-Bi-S Quantum Dots for Application in Sensitized Solar Cells

(*Graduate School of Engineering, Nagoya University*) ○Wentao Zhang, Kazutaka Akiyoshi, Tatsuya Kameyama, Tsukasa Torimoto

Keywords: Semiconductor nanocrystal; Quantum size effect; $AgBiS_2$; Light energy conversion; Low toxicity

The energy structure and light absorption properties of semiconductor quantum dots (QDs) can be controlled by changing their size and composition. The QDs have been intensively investigated for the application to photovoltaic, photocatalysis, and bio-imaging. In recent years, I-V-VI semiconductors (e.g. $NaBiS_2$[1], $AgBiS_2$[2]), composed of low-toxic elements, are regarded as potential alternatives to toxic IV-VI and II-VI semiconductors (PbSe[3], CdS[4]). Notably, $AgBiS_2$ QDs are expected to be an excellent light absorber for photovoltaic application due to their remarkable light-harvesting capabilities from the visible to the near-IR regions. However, there are limited reports on controlling their particle size and composition to enhance light-electricity conversion efficiency. In this study, we report a solution-phase synthesis of Ag-Bi-S QDs and their utilization in sensitized solar cells.

Ag-Bi-S QDs were prepared by heating the precursors of Ag(OAc), $Bi(OAc)_3$ and S in a mixture solution of oleylamine and dodecane thiol at different temperatures. As the preparation temperature increased from 100 °C to 200 °C, the particle size increased from 2.7 to 8.1 nm, accompanied by the change in particle composition from Ag-deficient ones to the stoichiometric $AgBiS_2$. The energy gap of QDs decreased from 1.45 to 1.05 eV with an increase in the particle size from 2.7 to 8.1 nm.

Figure 1a shows the electronic energy structure of Ag-Bi-S QDs prepared at different temperatures. The level of valence band was negatively shifted with an increase in the reaction temperature, while the level of conduction band was almost constant. The level of defect sites in the energy gap was evaluated by measuring the photocurrent onset potential of QD-immobilized electrodes: The defect sites were present in the energy gap for QDs prepared at 100 and 120 °C, but they were absent for the QDs with almost the stoichiometric composition, prepared at temperatures higher than 150 °C. Sensitized solar cells were fabricated by immobilizing Ag-Bi-S QDs on porous TiO_2 electrodes. Figure 1b shows the *J-V* curves of resulting cells. The use of the QDs prepared at 150 °C gave the highest performance, the power conversion efficiency reaching 0.76%.

[1] J. Vela *et al.*, *Chem. Mater.* **2020**, *32*, 6085. [2] Y. Wang *et al*, *Nat. Photon.* **2022**, *16*, 235. [3] S. Liu *et al.*, *ACS Nano* **2021**, *15*, 3376. [4] R. Zeng *et al.*, *Anal. Chem.*, **2019**, *91*, 2447.

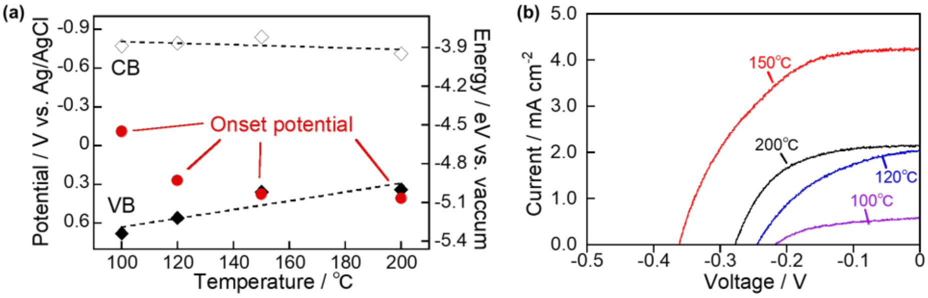

Fig. 1 (a) Energy structures of Ag-Bi-S QDs. (b) *J-V* curves of Ag-Bi-S QD-sensitized solar cells under the irradiation of AM1.5G simulated solar light.

Electrochemical water oxidation by layered-perovskite oxyfluoride $Pb_3Fe_2O_5F_2$

([1]*School of Science, Tokyo Institute of Technology*, [2]*Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology*) ○Ryusuke Mizuochi,[1] Yuuki Sugawara,[2] Takeo Yamaguchi,[2] Kazuhiko Maeda[1]

Keywords: Electrochemical water splitting; Oxygen evolution reaction electrocatalyst; Layered material; Mixed-anion compound

Hydrogen production by water electrolysis has attracted attention as a sustainable way to achieve carbon neutrality in the future, with a strong focus on oxygen evolution reaction (OER), compared to hydrogen evolution reaction (HER). It is because the OER is more sluggish with four-electron transfer than the HER. An OER electrocatalyst without noble metal is desired from the viewpoint of industrial application for cost-effectiveness. We have focused on iron-based oxyfluorides as OER electrocatalysts and, indeed, found that a lead-iron oxyfluoride, $PbFeO_2F$, achieved the functionality.[1] Oxyfluorides are mixed anion compounds, which include oxide and fluoride anions coordinated to a metal center. They have physical and chemical properties, which do not appear in a single anion counterpart (i.e., oxides and fluorides).[2] In this study, we investigated another lead-iron oxyfluoride, $Pb_3Fe_2O_5F_2$, with layered double perovskite structure as an OER electrocatalyst. 2D-layered compounds have attracted attention not only as electrocatalysts but also in other applications due to their unique structural and electronic properties. However, there is no report utilizing a single-phase 2D-layered oxyfluoride as an OER electrocatalyst. Therefore, we focused on the 2D-layered $Pb_3Fe_2O_5F_2$ as the OER electrocatalyst and compared to the $PbFeO_2F$ with 3D-cubic perovskite structure.

Electrodes of the lead-iron oxyfluorides were fabricated by drop-casting oxyfluoride particle suspension with a conductive carbon support onto a carbon substrate. Electrochemical OER activities and properties were investigated for the as-prepared electrodes. It was found that $Pb_3Fe_2O_5F_2$ had relatively high OER activity and superior electrochemical property compared to $PbFeO_2F$ and even general iron-based perovskite oxides (such as $SrFeO_3$, $LaFeO_3$ and $BiFeO_3$). Comparison between $Pb_3Fe_2O_5F_2$ samples with different parameters in the synthesis revealed that the presence of (0*k*0) crystal facets on the $Pb_3Fe_2O_5F_2$ enhanced the OER activity. Furthermore, density functional theory calculations in the OER process indicated that the higher activity of $Pb_3Fe_2O_5F_2$ than $PbFeO_2F$ was attributed to the greater exposed area of the crystal facets with lower OER overpotential, supporting the results confirmed by the above electrochemical investigation.

1) R. Mizuochi, K. Izumi, Y. Inaguma, K. Maeda, *RSC Adv.* **2021,** *11*, 25616.

2) H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun.* **2018,** *9*, 772.

CO_2と水からギ酸を生成する電気化学リアクタの長期耐久性向上

（豊田中研[1]）○加藤直彦[1]・河合康明[1]・野尻菜摘[1]・塩澤真人[1]・菊澤良弘[1]・鈴木伸明[1]・小坂悟[1]・濱口豪[1]・竹田康彦[1]

Improvements in long-term durability of electrochemical reactors producing formate from CO_2 and water

([1] Toyota Central R&D Labs., Inc.) ○Naohiko Kato*, Yasuaki Kawai, Natsumi Nojiri, Masahito Shiozawa, Yoshihiro Kikuzawa, Nobuaki Suzuki, Satoru Kosaka, Tsuyoshi Hamaguchi and Yasuhiko Takeda.

We previously developed a 1 m^2-sized artificial photosynthetic cell consisting of an electrochemical (EC) reactor featuring a Ru-complex polymer (RuCP) cathode catalyst integrated with Si solar cells to convert CO_2 to formate, and realized a solar-to-chemical energy conversion efficiency of 10.5%[1,2]. In this study, we improved the durability of the EC reactor. A pyrrole derivative containing amino group introduced in the RuCP and carboxyl group created on the carbon supports by a UV-ozone treatment formed strong chemical bond, reducing the detachment of the RuCP catalyst. A newly developed chemically-resistant graphite adhesive prevented the carbon supports from peeling off from the conductive substrates. We constructed 75 cm^2-sized EC reactors facing the cathodes and durable IrO_x-TaO_x/Pt-Metal oxide/Ti anodes with porous separators between them. High Faradaic efficiency (*FE*) of formate production over 80% was secured under inclined installation even after 3000 h intermittent operation (Figure 1).

Keywords: Solar fuels; Long-term durability; Artificial photosynthesis; Electrochemical reactors; Solar-driven CO_2 reduction; Formate.

我々は、これまでに、Ru 錯体ポリマー（RuCP）からなる CO_2 還元触媒を用いた電気化学(EC)リアクタと Si 太陽電池を組み合わせた 1 m^2 サイズの人工光合成セルを構築し、太陽光-化学エネルギー変換効率 10.5%を達成した[1,2]。今回、EC リアクタの耐久性を向上させた。アミノ基を含むピロール誘導体を RuCP に導入し、炭素担体への UV オゾン処理により生成するカルボキシル基と化学結合させることによって、RuCP の脱離を抑制した。更に、高化学耐性のグラファイト接着剤を開発し、炭素担体の導電基板からの剥離を防止した。対向させたカソードと高耐久性の IrO_x-TaO_x/Pt-Metal oxide/Ti アノードの間に多孔質セパレータを挿入した 75cm^2 の EC リアクタを、屋外環境を想定した傾斜設置で間欠動作させた 3000 時間後にギ酸生成ファラディー効率（*FE*）80%以上が維持された（図 1）。

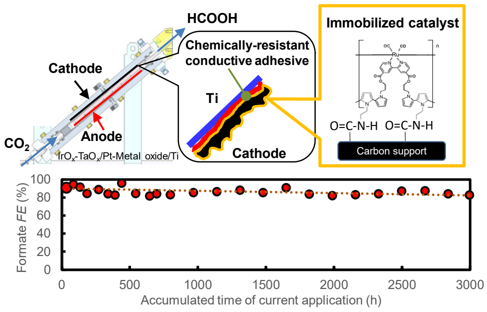

Fig.1 EC reactor designed for integration with solar cells and *FE* of formate production for 3000 h.

1)N. Kato, et al., *Joule*, **2021**, 5, 687. 2)N. Kato, et al., *ACS Sustain. Chem. Eng.*, **2021**, 9,16031.

光触媒型膜-電極接合体へのプロトン伝導性配位高分子の適用

（京大院工[1]・ポーラ化成[2]・京大高等研究院[3]・京大院理[4]）○竝木 裕司[1,2]・田部 博康[3]・堀毛 悟史[4]

Photocatalytic membrane electrode assemblies with proton conductive coordination polymers

([1]*Graduate School of Engineering, Kyoto University*, [2]*POLA Chemical Industries, Inc.*,[3]*Institute for Advanced Study, Kyoto University*, [4]*Graduate School of Science, Kyoto University*,) ○Yuji Namiki[1,2], Hiroyasu Tabe[3], Satoshi Horike[4]

Photocatalytic solar cells are a promising power supply system because of their higher cell voltage than conventional solar cells.[1] The photocatalytic solar cells consist of membrane-electrode assemblies composed by electrolyte membranes, electrodes, and photocatalysts. In this study, we used proton (H^+)-conductive coordination polymers as solid electrolytes.[2,3] Electric power was generated under the solar irradiation by MEAs with coordination polymers consisting of Zn^{2+} ions, phosphate ions, and alkylamines for 72 hrs, while the current decrease was observed in the MEAs consisting of conventional electrolyte membranes such as Nafion®.

Keywords : Photocatalytic reaction, Coordination polymer, Proton conductivionl, Solar cell

従来の太陽電池と比べ高い起電力を特長とする光触媒式太陽電池に注目が集まっている1)。光触媒式太陽電池は、電解質膜と光触媒電極によって構成される膜ー電極接合体（MEA）からなり、負極側に加湿アルゴンを、正極側に加湿酸素をフローさせ、太陽光を照射することで作動する。光触媒式太陽電池の安全面や省スペース性を向上させるには、固体電解質の利用が望ましい。本研究では機械的耐久性と耐湿性に優れ、光触媒との融合も近年報告された配位高分子（CP）を固体電解質として適用した2)。亜鉛イオン、リン酸イオン、アルキルアミンからなるCP3)から構築されるMEAに疑似太陽光を照射したところ72時間にわたり安定に発電できることを確認した（図1）。一方、Nafion®を適用すると、72時間後の電流出力は初期値と比較して75%低下した。

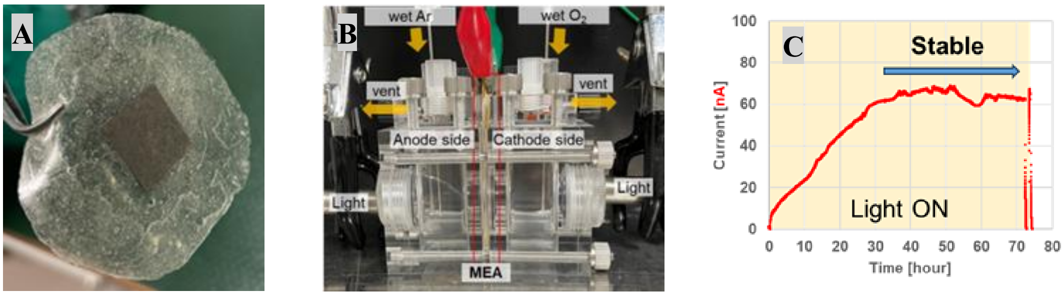

Figure 1. MEA with CP(A), H-type cell system(B), Stability test of MEA with CP(C)

1) Y. Ogura, S. Okamoto, T. Itoi, Y. Fujishima, Y. Yoshida, Y. Izumi, *Chem. Commun.*, **2014**, *50*, 3067.
2) H. Izu, H. Tabe, Y. Namiki, H. Yamada, S. Horike, *Inorg. Chem.*, **2023**, *62*, 11342.
3) T. Ogawa, K. Takahashi, S. S. Nagarkar, K. Ohara, Y. Hong, Y. Nishiyama, S. Horike. *Chem. Sci.*, **2020**, *11*, 5175.