アカデミックプログラム［Ｂ講演］｜09. 錯体化学・有機金属化学：口頭Ｂ講演

2025年3月28日(金) 9:00 ~ 11:20 [B]A307(第2学舎 1号館 [3階] A307)

[[B]A307-3am] 09. 錯体化学・有機金属化学

座長：吉成 信人、田中 大輔

英語
9:00 ~ 9:20
[[B]A307-3am-01]
低配位Cuを用いた融解する金属シアニド

○岩井 優大[1]、大谷 亮[1]、大場 正昭[1] (1. 九州大学)

英語
9:20 ~ 9:40
[[B]A307-3am-02]
CuCrプルシアンブルー類似体における圧力印加水滴生成

○赤木 慎太郎[1]、田中 万由子[1]、Junhao Wang[1]、木内 久雄[2]、原田 慈久[2]、井元 健太[2]、大越 慎一[2]、所 裕子[1] (1. 筑波大院数理、2. 東大)

英語
9:40 ~ 10:00
[[B]A307-3am-03]
配位高分子ガラスにおける負の熱膨張の機構解明

○西口 大智[1]、堀毛 悟史[1] (1. 京大)

英語
10:00 ~ 10:20
[[B]A307-3am-04]
金属錯体八面体の自己集合による柔軟な多孔性ナノファイバーの合成

○宮田 彩名[1,2]、徳田 駿[1,2]、古川 修平[1,2] (1. 京大院工、2. 京大アイセムス)

日本語
10:20 ~ 10:40
[[B]A307-3am-05]
一次元配位高分子ガラスが示す異方的構造の発現と制御

○津田 修斗[1]、西口 大智[1]、堀毛 悟史[1] (1. 京大)

英語
10:40 ~ 11:00
[[B]A307-3am-06]
R-dpa三座配位子の銅(II)錯体によるH_2O_2活性化： 配位子構造によるH_2O_2活性化と活性種の制御

○藤川 恭祐[1]、Alexander Granichny[2]、Siegfried Schindler[2]、北岸 宏亮[1]、小寺 政人[1] (1. 同志社大学大学院、2. Justas-Liebig university)

日本語
11:00 ~ 11:20
[[B]A307-3am-07]
CO2濃淡電池

〇山田 鉄兵[1]、柿澤 彩花[1]、若山 悠有佑[1]、杉山 高康[1]、伊東 みのり[1]、米川 真由[1]、Kunyi Leng[1]、周 泓遥[1] (1. 東大)

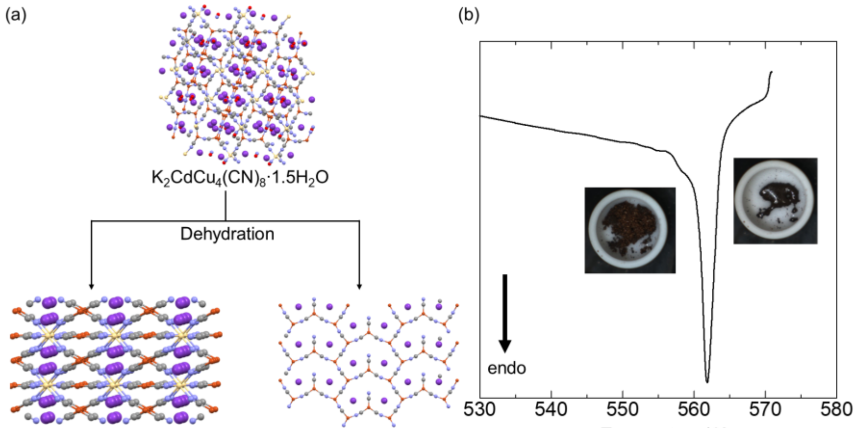
Melting metal cyanidos with low-coordinate copper center

([1]*Department of Chemistry, Faculty of Science, Kyushu University,*) ○Yuudai Iwai,[1] Ryo Ohtani,[1] Masaaki Ohba[1]

Keywords: *Metal cyanidos, Coordination polymer, melting*

Metal cyanide is a kind of coordination polymer constructed from only metal ions and cyanide linkers. The representative example, Prussian blue, was first synthesized in 1704 and has long been studied since then, with reports of ferromagnetic transitions at room temperature[1] and adsorption of certain alkali metals[2]. However, despite more than a century of research, only three melting metal cyanidos have been obtained. They all consist of one-dimensional structures, and no melting two- (2D) or three-dimensional (3D) metal cyanides have ever been reported. Herein, we successfully synthesized a composite of melting 3D $KCd[Cu(CN)_2]_3$ and 2D $K_2Cu_3(CN)_5$.[3] These compounds melted at around 570 K and 565 K.

First, we synthesized a hydrated precursor $K_2CdCu_4(CN)_8{\cdot}1.5H_2O$.[4] Then, $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ were obtained as orange powder via structural transformation by simple dehydration. Uniquely, these compounds coexisted in the single particle. The crystal structure of these compounds were determined by micro-ED. DSC measurement and real-view system revealed $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ melted at around 567 K. Thus, variable temperature powder X-ray diffraction measurements demonstrated that diffraction peaks of $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ disappeared at 570 K and 565 K, respectively. Moreover, molecular-dynamics simulation clarified the cause of melting is geometrical flexibility of tow-coordinate Cu^I center. The coordination number and geometry of Cu^I varied at high temperature resulting in increase of ΔS and the reduction of melting point.



1) S. Ferlay, *et al.*, *Nature*, **1995**, *378*, 701. 2) T. Guo, *et al.*, *Desalin. Water Treat.*, **2022**, *272*, 118. 3) A. H. pohl, *et al.*, *Solid State Sci.*, **2006**, *8*, 379–387. 4) S.-I. Nishikori, *J. Coord. Chem.*, **1996**, *37*, 23-38.

Pressure-induced water formation in a CuCr Prussian blue analog

([1]*University of Tsukuba*, [2]*The University of Tokyo*) ○Shintaro Akagi,[1] Mayuko Tanaka,[1] Junhao Wang,[1] Hisao Kikuchi,[2] Yoshihisa Harada,[2] Kenta Imoto,[2] Shin-ichi Ohkoshi,[2] Hiroko Tokoro[1]

Keywords: MOF, Puressure-induced water production, Prussian-blue analog, Cyanide-bridged complex

Cyanido-bridged complexes have attracted attention as materials that exhibit functionality in response to various external stimuli.[1, 2] Herein, we demonstrate an example of pressure-induced water production using a copper–chromium Prussian blue analog (CuCr PBA).

CuCr PBA was prepared by adding 50 cm^{-3} of an aqueous solution of $CuCl_2$ (45 mmol dm^{-3}) to 50 cm^{-3} of an aqueous solution of $K_3[Cr(CN)_6]$ (30 mmol dm^{-3}), yielding a green powder. Elemental analysis was performed using ICP-MS and CHN analysis. The crystal structure was determined using powder X-ray diffraction (PXRD). Soft X-ray absorption (XAS) and emission spectroscopy (XES) were measured by synchrotron radiation at SPring-8 BL07LSU.

Elemental analysis of the obtained powder revealed a formula of $Cu_{1.5}[Cr(CN)_6]\cdot 6.4H_2O$ at 26°C and 27% relative humidity. When a uniaxial pressure of 1 GPa was applied to the CuCr PBA, the incorporated water molecules were expelled, forming droplets on the surface. Collecting the water droplets with a pipette revealed that approximately 240 g of water was obtained per 1 kg of CuCr PBA. From the IR spectra before and after pressure application, it was observed that the peak intensity attributed to OH stretching mode decreased with pressure. In addition, the peak at 2180 cm^{-1} attributed to CN stretching mode decreased and the peak intensity at 2115 cm^{-1} increased. This change suggests that the pressure application modified the Cu–NC–Cr bonding state. PXRD patterns before and after pressure application revealed no drastic changes in the diffraction positions and intensity ratios. This indicates that the CuCr PBA maintained its cubic framework before and after pressure application. XAS and XES measurements revealed that pressure induces partial electron transfer from ligand water oxygen to copper, while Cr^{III} state remained unchanged. One possible mechanism of water production could be the hydrophobization of pores at defect sites based on partial electron transfer from the oxygen of the ligand water to copper upon pressure application.

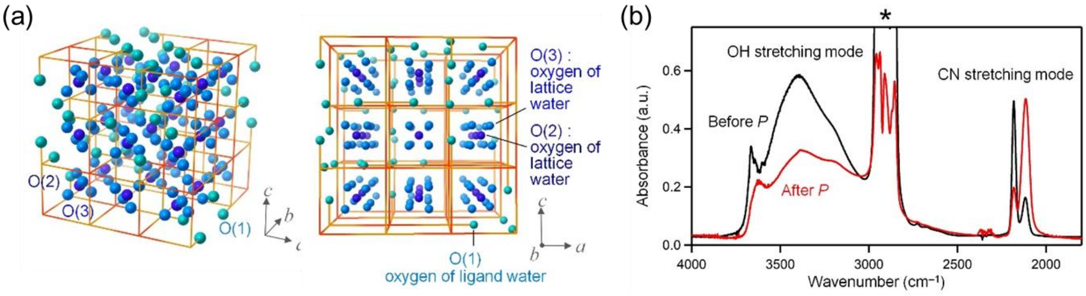


Figure 1. (a) Crystal structure of CuCr PBA, (b) IR spectra before (black) and after (red) pressure application. Regions marked with asterisks indicate signals from fluid paraffin.

1) S. Ohkoshi, et al, *Nat. Chem.*, **2020**, *12*, 338. 2) S. Ohkoshi, et al, *Nat. Photonics* **2014**, *8*, 65.

Mechanism of Negative Thermal Expansion in Coordination Polymer Glass

([1]*Graduate School of Engineering, Kyoto University*, [2]*Graduate School of Science, Kyoto University*) ○Taichi Nishiguchi,[1] Satoshi Horike[2]

Keywords: Coordination polymer, Glass, Negative thermal expansion

Negative thermal expansion, referring to contraction upon temperature increase, has been extensively studied in a wide variety of materials. However, NTE in glassy materials are poorly known, and the understanding of glassy NTE has been limited.[1] Coordination polymers (CPs) are crystalline materials constructed from metal cations and molecular linkers. In recent years, glassy states of CPs have emerged as a platform for studying glassy properties based on molecular design and diverse coordination geometries.[2]

We synthesized $Li_2(TFSI)_2(SN)_3$ (**1c**, $TFSI^-$ = bis(trifluoromethanesulfonyl)imide, SN = succinonitrile). Single-crystal X-ray diffraction (SC-XRD) revealed the two-dimensional sheet-forming structure with the Li^+–SN–Li^+ linkage (Fig. a). Differential scanning calorimetry (DSC) confirmed the formation of a glassy state (**1g**) below 225 K upon melt-cooling processes. Dilatometry and synchrotron X-ray diffraction observed an NTE behavior with a linear thermal expansion coefficient of -140×10^{-6} K^{-1}, reaching three orders of magnitude larger than SiO_2 glass (Fig. b). Raman spectra indicated the $TFSI^-$ replacing the Li^+–SN coordination, forming Li^+–$TFSI^-$–Li^+ linkage in **1g**. Synchrotron X-ray-based pair distribution function (PDF) analyses observed the contraction of $TFSI^-$ in **1g** upon heating from 160 to 220 K (Fig. c). These suggest the NTE mechanism originating from the soft molecular network formation in the glassy state.

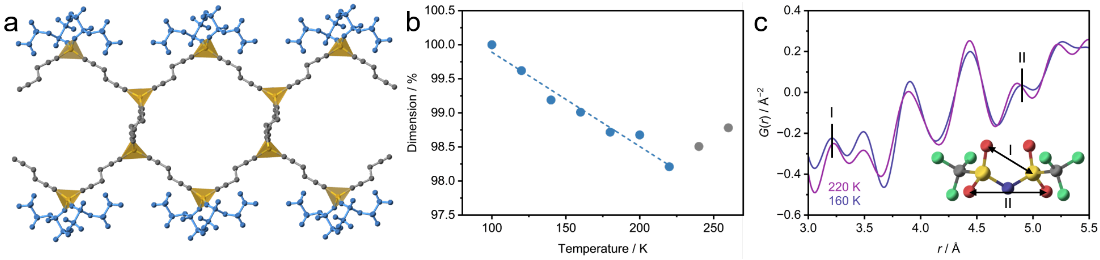


Figure. (a) SC-XRD structure of **1c**. Li: yellow, $TFSI^-$: blue, SN: grey. (b) Relative dimension of **1g** determined by synchrotron X-ray diffraction. (c) PDF analyses.

1) G. D. Barrera, J. A. O. Bruno, T. H. K. Barron and N. L. Allan, *J. Phys. Condens. Matter* **2005**, *17* R217. 2) N. Ma and S. Horike, *Chem. Rev.* **2022**, *122*, 4163.

Flexible Porous Nanofibers Assembled from Metal-Organic Octahedra

([1]*Graduate School of Engineering, Kyoto University*, [2]*Institute for Integrated Cell-Material Sciences, Kyoto University*) ○Ayana Miyata,[1,2] Shun Tokuda,[1,2] Shuhei Furukawa [1,2]

Keywords: Supramolecule; Self-assembly; Non-covalent interaction; Structural chemistry; Porous materials

Porous materials such as synthetic zeolites and metal-organic frameworks (MOFs) are widely known to possess uniform pores, excellent structure tunability, and high surface areas, making them ideal for many applications, such as gas separation, catalysis, drug delivery, and molecular sensing. However, their rigid structures, formed by strong covalent or coordination bonds, are easily damaged by mechanical stress, limiting their potential for further processing and application. Herein, we synthesized mechanically flexible porous materials by assembling metal-organic polyhedra (MOPs) into one-dimensional nanofibers through van der Waals (vdW) interactions.

We selected an octahedral MOP family of $[\mathrm{Cu}_{12}(\mathrm{NDI}_\mathrm{R})_{12}]$ (NDI_R = naphthalenediimide (NDI)-based dicarboxylates), in which dinuclear copper paddlewheel motifs are located at the six vertices of octahedrons, and twelve NDI_R molecules link them at the edges.[1,2,3] We used L-isoleucine (R = Ile) or 2-cyclohexyl-L-glycine (R = Chg) as an amino acid for the synthesis of NDI_R linkers. Through the reaction of these linkers with copper(II) nitrate trihydrate, two MOP molecules were obtained ($\mathbf{MOP}_{\mathbf{Ile}}$, and $\mathbf{MOP}_{\mathbf{Chg}}$, respectively). These MOPs were further assembled into uniform one-dimensional fibers with widths of several tens of nm and lengths of several μm. These fibers entangled together and eventually formed a free-standing gel. These gels exhibited sol–gel transitions in response to mechanical stress. Additionally, these gels seem to be in a metastable phase, and they underwent a morphological transition to crystal when left at room temperature. Single-crystal X-ray diffraction experiments revealed these MOPs were aligned one-dimensionally in their crystal structures. Corresponding aerogels were obtained when these gels were dried with supercritical CO_2 before the crystal formation. The nitrogen adsorption isotherm of these aerogels showed high adsorption in the low-pressure region (at P/P_0 = 0.1, 123 cm^3/g for $\mathbf{MOP}_{\mathbf{Ile}}$ and 120 cm^3/g for $\mathbf{MOP}_{\mathbf{Chg}}$), confirming the microporosity. The mechanical properties of the aerogel were evaluated via uniaxial compression measurements. Until a strain value of 27%, the aerogel exhibited elastic behavior, and after that point, it underwent plastic deformation. However, even when compressed up to 85%, no fracture point was observed. This result demonstrated that aerogels synthesized in this study possess excellent flexibility under mechanical stress.

1) S. K. Ghosh et al., *Angew. Chem. Int. Ed.* **2019**, *58*, 1041. 2) D. R. Turner et al., *Chem. Eur. J.* **2019**, *25*, 8489. 3) S. Tokuda, S. Furukawa, *ChemRxiv*. **2023**, DOI: 10.26434/chemrxiv-2023-j7m58.

一次元配位高分子ガラスが示す異方的構造の発現と制御

（京大理 [1]・京大院工 [2]・京大院理 [3]）○津田 修斗 [1]・西口 大智 [2]・堀毛 悟史 [3]
Control of Anisotropic Structures in One-dimensional Coordination Polymer Glasses ([1]*Faculty of Science, Kyoto University.*, [2]*Graduate School of Engineering, Kyoto University.*, [3]*Graduate School of Science, Kyoto University.*) ○Shuto Tsuda,[1] Taichi Nishiguchi,[2] Satoshi Horike[3]

Macroscopic anisotropy in glasses induced unique properties including birefringence and uniaxial elasticity1). Coordination polymers have emerged as novel functional glasses, and microstructures have been controlled by external stimuli such as shear stress2). However, the structural control on a macroscopic scale is still to be explored.

We studied the anisotropy of a glassy state of Li(TFSI)(bpp) (**1**, Li(TFSI) = Lithium bis(trifluoromethanesulfonyl)imide, bpp = 1,3-Bis(4-pyridyl)propane). Single-crystal X-ray diffraction analysis revealed that **1** has a one-dimensional chain structure in the crystalline state (Fig. a, b). **1** melted at 139 °C (T_m) and formed a glassy state below 11 °C (T_g) (Fig. c). We controlled the anisotropic structures of the glass of **1** by external stimuli such as elongation.

Keywords : Melting; Glass; Coordination polymer

ガラスにおける巨視的な構造異方性は、複屈折や方向性をもった弾性など異方的な特性を実現する 1)。近年、配位高分子がガラス化することが見出され、剪断応力など外的刺激を用いた微視的な構造制御が試みられてきたが、巨視的な異方性をもった配位高分子ガラスは未開拓である 2)。

本研究では配位高分子 Li(TFSI)(bpp) (**1**) のガラスにおいて異方性を検討した。単結晶 X 線構造解析から、**1** は一次元鎖状構造をもつことを明らかにした (Fig. a, b)。また、示差走査熱量測定から **1** は 139 °C (T_m) で融解し、続く冷却により 11 °C (T_g) でガラス化することを確認した (Fig. c)。**1** に伸延などの外部刺激を加えることでガラス構造の異方性の制御を試みた。

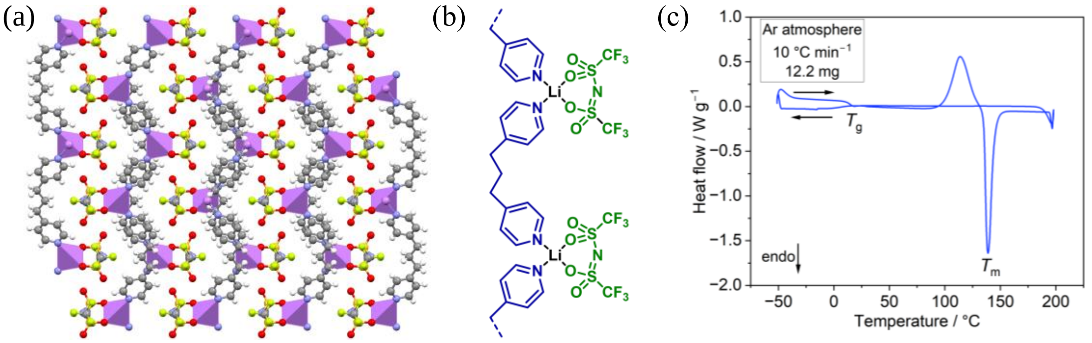


Fig. (a, b) Crystal structure of **1**. (c) DSC profile of **1**. Melting (T_m) and glass transition (T_g) points are indicated.

1) J. Endo *et al.*, *J. Am. Ceram. Soc.* **2015**, *98*, 2767.
2) T. Nishiguchi, S. Horike *et al.*, *Chem. Sci.* **2025**, *16*, 621.

H_2O_2 activation by Cu(II) complexes with R-dpa tridentate ligand: Control of H_2O_2 activation and the active species by the ligand structures

([1]Department of Molecular Chemistry and Biochemistry, Doshisha University, [2]Institute of Inorganic and analytical Chemistry, Justus Liebig University Giessen) ○Kyosuke Fujikawa,[1] Alexander Granichny,[2] Seigfried Schindler,[2] Hiroaki Kitagishi,[1] Masahito Kodera[1]

Keywords: H_2O_2 activation; Alkane oxidation; Copper-Oxo species; Copper complexes

The direct oxidation of inert alkane to alcohol or aldehyde is one of the key processes for the efficient synthesis of various chemical products. This is a difficult chemical process because it requires cleavage of the strong C-H bond. Meanwhile, methane monooxygenases (MMO) in methanotrophs can catalyze the conversion of methane to methanol under ambient conditions. Recently, DFT studies proposed that the active species of pMMO is Cu^{II}_2-μ-O• dicooper species having a high reactivity to the C-H band cleavage of methane.[1] Thus, Cu complexes able to form the Cu^{II}_2-μ-O• species can be promising bioinspired catalysts for the C-H bond activation.

The DFT study proposed the dioxygen activation mechanism by dicopper site of pMMO where $Cu^{II}_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2)$ species is reduced by Tyr374 in the second coordination sphere to form the Cu^{II}_2-μ-O• active species.[1] Thus, the reduction of dicopper-oxygen intermediate is the key process for Cu^{II}_2-μ-O• formation. Itoh reported that monocopper(II) complex of phenethyldpa tridentate ligand forms dicopper-oxygen intermediate.[2] Since H_2O_2 can be a reductant, the reaction of such copper complexes with H_2O_2 may enable the formation and reduction of dicopper-oxygen intermediate to give Cu^{II}_2-μ-O• active species.

Here, the reactions of monocopper(II) complexes ($\mathbf{1^R}$) of *N*-alkyl-di(pycolyl)amine (R-dpa) ligands (R = Me, phenethyl (Phe), *t*-Bu) with H_2O_2 were examined by the stopped-flow studies at low-temperature. It was found that $\mathbf{1^{Me}}$ and $\mathbf{1^{\textit{t}\text{-}Bu}}$ produced the monocopper intermediate Cu^{II}-OOH, and $\mathbf{1^{Phe}}$ formed the dicopper intermediate $[Cu^{III}(\mu\text{-}O)]_2$. In the reaction of $\mathbf{1^{Me}}$ and $\mathbf{1^{\textit{t}\text{-}Bu}}$, Cu^{II}-OOH forms HO• in the Fenton-type reaction to oxidatively decompose the ligand and reduce the catalytic turnover number. On the other hand, in the reaction of $\mathbf{1^{Phe}}$, complex-based active species may be formed via $[Cu^{III}(\mu\text{-}O)]_2$ to suppress the nonspecific ligand oxidation by HO• and increase the catalytic turnover number. These results showed that the formation of dicopper intermediates is a key process for the efficient alkane oxidation.

1) K. Yoshizawa, et. al., *Inorg. Chem.* **2013**, *52*, 7907−7917. 2) S. Itoh, et al., *Angew. Chem.,* **2002**, *114*, 4501-4504.

CO_2 濃淡電池

（東大院理）○山田 鉄兵・柿澤 彩花・若山 悠有佑・杉山 高康・伊東 みのり・米川 真由・Kunyi Leng・周 泓遥

A CO_2 Concentration Cell (*Department of Chemistry, The University of Tokyo*), ○Teppei Yamada Ayaka Kakizawa, Yusuke Wakayama, Takayasu Sugiyama, Minori Ito, Mayu Yonekawa, Kunyi Leng, Hongyao Zhou

Waste gas through the burning of fossil fuels contains 10% to 20% of the CO_2 and its release to atmosphere with low CO_2 concentrations dissipates Gibbs free energy. We propose an electrochemical system, a CO_2 concentration cell, which converts the Gibbs energy derived from this CO_2 concentration difference into electric energy. The scheme of the CO_2 concentration cell is shown in Fig. 1. It is composed of a copper electrode and aqueous solutions of ethylenediamine (EDA) and copper nitrate. The cell has three equilibria: CO_2 adsorption by EDA, coordination of EDA to copper ions and redox reactions of the copper electrode. The first equilibrium shifts by the difference in CO_2 concentration between the two electrodes, which causes the shift of redox potential of copper. CO_2 and nitrogen gases were introduced into a couple of separate electrolytes, and a voltage of up to 300 mV was obtained. The formation of carbamate by the reaction of EDA and CO_2 and the resultant formation of copper aqua complex were confirmed by spectroscopic method. In addition, a solution-type CO_2 concentration cell was also achieved by using N,N'-bis(2-aminoethyl)-4,4'-bipyridine.

Keywords : A CO_2 Concentration Cell; $Cu(en)_2$; bis(2-aminoethyl-4,4'-bipyridine)

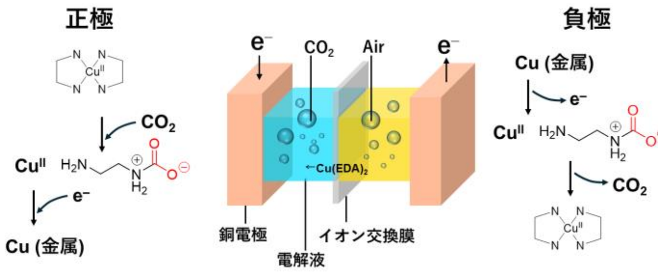


Figure 1. The scheme of a CO_2 concentration cell.

化石資源の燃焼により CO_2 を排出する過程において、10%~20%の濃度の CO_2 を低濃度の大気へと放出しており、濃度差に基づくギブスエネルギーを散逸している。本発表ではこの CO_2 の濃度差に由来するギブスエネルギーを電気エネルギーに変換する電気化学システム、CO_2 濃淡電池を提案する。

CO_2 濃淡電池の概要を図 1 に示す。本電池は銅電極と、エチレンジアミン（EDA）および硝酸銅の水溶液から構成される。電池内には EDA の CO_2 吸着、銅イオンと EDA の配位および銅電極の酸化還元反応の 3 つの平衡が連動している。両電極間の CO_2 濃度の差によって平衡がシフトし、電気エネルギーを得る。実際に両極に CO_2 および窒素を吹き込んだ電解液を導入すると、最大で 300 mV の電圧が得られた。また CO_2 の導入に伴い、EDA のカーバメートへの反応と、銅アクア錯体の生成が確認された。さらに、N,N'-ビス（2-アミノエチル）-4,4'ビピリジンを合成し、電解液に用いることで、溶液型 CO_2 濃淡電池も作成したので合わせて報告する。