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A Metal–Organic Framework as an Electrocatalyst for Ethanol Oxidation

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Direct alcohol fuel cells (DAFCs) have aroused great interest for portable electronic devices and electric vehicles due to their high power density output and low pollutant emissions. Ethanol is the most attractive of the possible low-molecular-weight alcohols that can be used, because it is a sustainable fuel that can be produced in large volumes by the fermentation of biomass. Furthermore, compared with methanol, ethanol is less toxic and more convenient, has a higher energy density, and appears to fulfill most fuel requirements for low-temperature fuel cells.[1] Even though platinum and platinum-based catalysts show a high efficiency towards ethanol electrooxidation,[2] the high cost and limited supply of platinum prevent the commercial development of direct ethanol fuel cells (DEFCs). Therefore, the search for efficient, durable, and most importantly, inexpensive alternative materials to Pt-based catalysts is of utmost importance.[3]

Metal–organic frameworks (MOFs) show promising catalytic activities for alcohol oxidation, in hydrogenation reactions, Knoevenagel condensations, ring opening of epoxides, and epoxidation of olefins.[4] We believe the following unique properties of MOFs make them good candidates as catalysts for the above-mentioned specific reactions. First, they possess various pore sizes (3–35 Å) and surface areas (500–6500 $m^2\,g^{-1}$).[5] Second, their surface properties can be manipulated using a variety of organic ligands, affording unique functionalities on the channel surface. For example, specific gas adsorption sites can be introduced into MOFs, and these can then show versatile storage capacities and selectivity for adsorbents.[6] Third, since each constituent of an MOF is exposed, they can provide unique catalytic sites for chemical reactions. Finally, adsorbent molecules can be confined in the nanospaces.[7] When molecules are confined in such spaces and undergo stress caused by the deviation from the thermodynamically and kinetically stable structures of the ambient surroundings, this stress brings about an effective energy conversion, and new chemical reactions occur.[8] However, to our knowledge, no example of MOFs exhibiting electrocatalytic activity has been reported to date. This lack is mainly due to the small number of MOF materials that display high electron conductivity, which is essential for electrocatalytic reactions.

The MOF material *N*,*N*′-bis(2-hydroxyethyl)dithiooxamidatocopper(II) [$(HOC_2H_4)_2$dtoaCu] (target compound, Figure 1 a) is a two-dimensional framework composed of dimeric Cu units and bridging ligands $(HOC_2H_4)_2dtoa^{2-}$.[9] This material is a good proton and electron conductor. Its proton conductivity is $3.3\times10^{-4}\,S\,cm^{-1}$. The effective pore size is around 7.8 Å, as estimated from the N_2 adsorption isotherm. It is insoluble, even in 1 M sulfuric acid at 80 °C, and is thermally stable below 165 °C. Furthermore, the active copper species have free binding sites in the nanospaces, which will facilitate the formation of adducts with electroactive molecules.[10] Such unique properties may provide benefits that make [$(HOC_2H_4)_2$dtoaCu] a good candidate for ethanol oxidation in fuel cells.[11] Herein, we report the first example

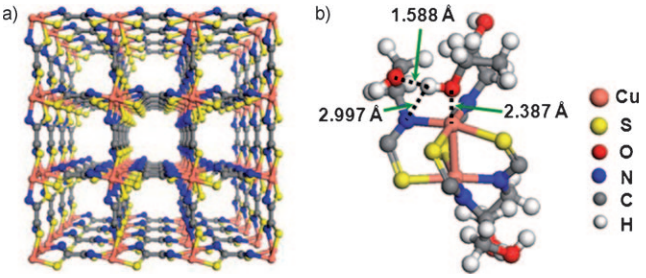

Figure 1. a) The crystal structure of [$(HOC_2H_4)_2$dtoaCu] (Ref. [9]). For clarity, the $HOC_2H_4^-$ group has been omitted. b) An interaction structure for [$(HOC_2H_4)_2$dtoaCu] and ethanol obtained from DFT calculations. Only a part of the unit structure is shown, while calculations were performed on the periodic structure.

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using this noble-metal-free MOF as the catalyst for ethanol electrooxidation reactions (EERs).

We first evaluated the ethanol sorption properties of $[(HOC_2H_4)_2dtoaCu]$, because the electrooxidation process in fuel cells involves consecutive adsorption and electrooxidation reactions. Figure 2 shows the adsorption and desorption isotherms at 298 K for ethanol on evacuated $[(HOC_2H_4)_2dtoaCu]$. An initial low uptake was followed by enhanced uptake of ethanol ($P/P_0 = 0.6$). The low uptake of ethanol at low pressure is probably due to the pore aperture constriction effect. The isotherms showed that $[(HOC_2H_4)_2dtoaCu]$ adsorbs about 0.8 mol of ethanol per 1.0 mol of the target compound (based on the Cu dimer; $P/P_0 = 0.95$). Interestingly, the desorption of ethanol shows large hysteresis,[12] suggesting that a strong chemical interaction between $[(HOC_2H_4)_2dtoaCu]$ and ethanol molecules occurs. To investigate this interaction, density functional theory (DFT) was employed, for which the dimer of the formula unit was used as the model. A stable interactive structure between ethanol and $[(HOC_2H_4)_2dtoaCu]$ was found (Figure 1b). In this structure, there are several interactions between ethanol and $[(HOC_2H_4)_2dtoaCu]$. The O atom of ethanol is coordinated to the Cu atom of $[(HOC_2H_4)_2dtoaCu]$, and at the same time, the H atom of the OH group of ethanol interacts with the O and N atoms of $[(HOC_2H_4)_2dtoaCu]$ through hydrogen bonds. The interaction energy for the structure was estimated to be 40 kJ mol^{-1}. Such a strong interaction will activate the ethanol molecule and facilitate its electrooxidation.

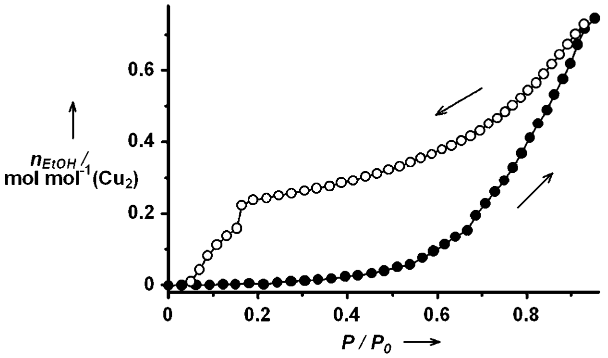

Figure 2. The ethanol sorption isotherms of $[(HOC_2H_4)_2dtoaCu]$ at 298 K. The molar value of ethanol sorption was calculated based on the molecular weight of the Cu dimer. P/P_0 is the relative pressure, where P_0 is the saturated vapor pressure of the adsorbent at 298 K. ● adsorption, ○ desorption.

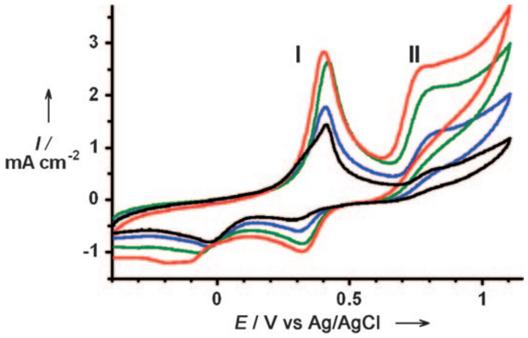

Figure 3. Cyclic voltammograms of a glassy carbon electrode coated with $[(HOC_2H_4)_2dtoaCu]$ in 0.5 M H_2SO_4 containing different concentrations of ethanol (black 0.0, blue 0.5, green 1.0, red 2.0 M ethanol). Sweep rate = 100 mV s^{-1}.

The catalytic activity of $[(HOC_2H_4)_2dtoaCu]$ was evaluated in acidic media by cyclic voltammetry. Figure 3 shows the voltammograms in a solution containing 0.5 M H_2SO_4 and different concentrations of ethanol in the potential range from −0.40 to 1.10 V at 100 mV s^{-1}. For comparison, the voltammogram in the absence of ethanol is also shown. Before adding ethanol, a quasi-reversible oxidation couple with a half-wave potential of 0.35 V (peak I, $E_{pa} = 0.41$ V and $E_{pc} = 0.29$ V, E_{pa}: anodic peak potential, E_{pc}: cathodic peak potential) and an irreversible wave with $E_p = 0.71$ V (peak II) were observed, which were assigned to the metal-based oxidation of $[(HOC_2H_4)_2dtoaCu]$. The first couple was assigned to the Cu^I/Cu^{II} oxidation. Similarly, the peak occurring at 0.71 V probably originates from the Cu^{II}/Cu^{III} oxidation couple.[13] The irreversible behavior is indicative of a structural rearrangement.[14] The cathodic peak calculated at $E_{pc} = -0.04$ V probably originated from another reduced form of Cu^{II} that is different from the one with $E_{pc} = 0.29$ V.

Upon adding ethanol to the electrolyte, a considerable enhancement in the oxidative current density occurring at peak I was observed during the positive scan. To clarify whether or not this enhancement is related to the EER, electrolysis with controlled potential (0.39 V) combined with gas chromatography analysis was conducted to determine the oxidation products. In this analysis, acetaldehyde was detected as an oxidation product with a maximum conversion ratio of 6.8 % within a period of 20 min (based on the area ratio of acetaldehyde and ethanol), in which the initial concentration of ethanol was 0.5 M and the electrolyte volume was 20 mL. However, acetic acid was not detected. From these results, the increase in the oxidative current of peak I is attributable to a catalytic EER by the oxidized $[(HOC_2H_4)_2dtoaCu]$ (Cu^{II}) species.

To obtain insight into the EER mechanism, we analyzed the interaction between ethanol and $[(HOC_2H_4)_2dtoaCu]$ further by DFT calculations. The DFT calculations show that the strong interactions between ethanol and $[(HOC_2H_4)_2dtoaCu]$ result in the elongation of the ethanol OH bond from 0.97 to 1.02 Å. This finding indicates that the EER is initiated by the loss of an H atom from the OH group of ethanol. However, no charge-transfer reaction was detected for the interacting structure. Therefore, the H-extracted structure was studied assuming that the extracted H atom attached itself to the N atom of $[(HOC_2H_4)_2dtoaCu]$, while the O atom of the ethanol molecule still interacted with the Cu atom of $[(HOC_2H_4)_2dtoaCu]$. Then, a charge transfer from the ethanol molecule to one of the Cu atoms in the $[(HOC_2H_4)_2dtoaCu]$ dimer in this assumed structure was found. The charges of the two Cu atoms in this model were 0.24 and 0.30, while charges of the two Cu atoms in the structure were both 0.30. This state is considered to be involved in the Cu^I/Cu^{II} oxidation process at peak I.

As can be seen from Figure 3, the oxidation current density occurring at peak II was also enhanced when ethanol was added to the electrolyte. Gas chromatography was carried out on the freshly prepared electrolyte solution after scanning from 0.60 to 1.10 V, and a considerable amount of acetaldehyde was detected. Combining the above results, we concluded that ethanol was oxidized to acetaldehyde in the potential ranges of both peaks I and II. The significant enhancement in current density at peak II can be attributed to the electrocatalytic oxidation of ethanol by the active Cu^{III} species, as it has higher oxidation potential than the Cu^{II} species.

The ethanol electrooxidation on this MOF material is dependent on the ethanol concentration. With an increasing ethanol concentration, the current density at peaks I and II increased continuously (Figure 3). It is noteworthy that even when the ethanol concentration was as high as 2 M, no plateau was observed, thus indicating that this catalyst is tolerant to the oxidation products of ethanol. This behavior is different from that of Pt-based catalysts, which are easily poisoned by the oxidation products of ethanol, such as CO and other intermediates.[15] A current density as high as about 3 $mA\,cm^{-2}$ can be achieved when the ethanol concentration is 2 M. It is also noticeable that the EER potential on the $[(HOC_2H_4)_2dtoaCu]$ catalyst is lower than some of the reported EER potential values on the Pt-based catalysts in acidic media, such as Pt–Sn,[16] Pt/MWNT,[17] and Pt nanocrystals.[18]

The effect of the potential sweep rate on the behavior of ethanol oxidation was also investigated. Figure 4 shows the cyclic voltammograms at various sweep rates in a 0.5 M H_2SO_4 + 0.5 M ethanol solution. It can be seen that with increasing sweep rate, the peak current densities of peaks I and II increase gradually. This behavior confirms that the catalytic reaction is a fast reaction.[19]

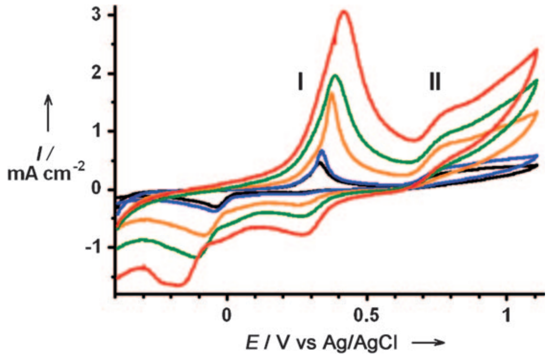

Figure 4. Cyclic voltammograms of a glassy carbon electrode coated with $[(HOC_2H_4)_2dtoaCu]$ with different sweep rates in a 0.5 M H_2SO_4 + 0.5 M EtOH solution (black 5, blue 10, orange 50, green 100, red 200 $mV\,s^{-1}$).

In conclusion, this work demonstrates the first example of the utilization of a noble-metal-free MOF material, $[(HOC_2H_4)_2dtoaCu]$, as an electrocatalyst for EER. Although ethanol is only partially oxidized to acetaldehyde under the present conditions, the performance in terms of oxidation potential and current density is comparable with Pt-based catalysts. We believe that this EER performance could be improved further by using a hybrid catalyst.

Experimental Section

Materials and reagents: The ethanol and sulfuric acid used were purchased as high quality and were used as received without further purification. Nafion (20 wt %) in a lower aliphatic alcohols and water mixture was purchased from Aldrich Chemicals. Millipore water (18.2 MΩ cm) was used to prepare the electrolyte. The $[(HOC_2H_4)_2dtoaCu]$ was synthesized using a literature method.[20]

Ethanol sorption isotherms: The ethanol sorption isotherms were measured at 298 K using a BEL SORP-18 volumetric adsorption apparatus (Bel Japan, Inc.). The sample was pretreated at 90 °C under reduced pressure (ca. 2 Pa) for a period of 46 h. The equilibrium time for the isotherms is 1000 s.

EER evaluation: An ALS/CHI 720A potentiostat connected to an ALS RRDE-2 analyzer was used in the electrochemical measurements. Electrochemical measurements were carried out at room temperature in a three-electrode cell. A glassy carbon (GC) rod (diameter 3 mm, geometric area 0.071 cm^2) implanted in polyether ether ketone (PEEK) was purchased from ALS and was coated with the catalyst as follows: The catalyst (2.5 mg) was ultrasonicated in a mixture of isopropyl alcohol (0.3 g) and Nafion (0.3 g) until a uniform ink was achieved. Then, 100 μL of the suspension was transferred quantitatively onto the GC electrode, which had been previously polished. The electrode was dried at room temperature until the solvent disappeared and was finally dried in an 80 °C oven to remove the solvent further. The GC electrode coated with the catalyst was used as the working electrode, and a platinum wire and an Ag/AgCl (KCl saturated) electrode were used as the counter and reference electrodes, respectively. The modified electrode was immersed in 0.5 M H_2SO_4 and cycled several times between a potential of −0.40 and 1.10 V until a steady-state voltammogram was reached. Because accurate determination of the catalyst surface area was difficult, the geometric area was used in density calculations. All potentials are referenced to a KCl saturated Ag/AgCl electrode.

Oxidation product determination: Gas chromatography analysis was performed using an Agilent 6850 chromatograph to identify the electrooxidation products. The chromatographic separations were carried out using a J&W HP-1 column (30 m, inner diameter 0.32 mm, film thickness 0.25 μm, Agilent) with helium as the carrier gas. The detector was a hydrogen flame ionization detection (FID) system. Products were identified by comparing the retention times with those of commercially available standards.

Theoretical study: The crystal structure of $[(HOC_2H_4)_2dtoaCu]$ was reproduced using the periodic boundary condition. The geometry optimizations were calculated using the local density approximation (LDA) with the Vosko–Wilk–Nusair (VWN) functional. After geometry optimization, single-point calculations were performed for the total energy refinement using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional. The effective core potential (ECP) was employed for the Cu atoms to take relativistic effects into account, while all electrons were considered for the C, N, O, S, and H atoms. Double numerical atomic basis sets augmented with the polarization function (DNP) were used to describe the valence electrons. All calculations were performed using the $DMol^3$ software package.[21]

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