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Electrochemical CO₂ Reduction Using Gas Diffusion Electrode Loading Ni-doped Covalent Triazine Frameworks in Acidic Electrolytes

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ABSTRACT

Ni-doped covalent triazine frameworks (Ni-CTF) has been known as an efficient electrocatalysts that achieve conversion of carbon dioxide (CO₂) to carbon monoxide (CO) with the faradaic efficiency (FE) exceeding 90% in neutral electrolytes. Here we report that the FE can reach 60% even in acidic electrolytes, where the hydrogen evolution can proceed competitively, by loading Ni-CTF on gas diffusion electrode (GDE). In the presence of Zn(II) ions, zinc hydroxide analogues that can be formed only in alkaline conditions were deposited on the GDE during the CO₂ reduction in an electrolyte with a bulk pH of 2. On the other hand, when a normal plate electrode (PE) was used, the FE was only 1.2% in an electrolyte with the same pH, and the zinc hydroxide analogues were not formed. These results indicate that the local pH around GDE increased during the cathodic process, which led to an increasing FE of CO₂ reduction even in an acidic electrolyte.

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Keywords : CO₂ Reduction, Covalent Organic Frameworks, Gas Diffusion Electrode

1. Introduction

Covalent organic frameworks (COFs) is a kind of porous organic polymer networks which has been regarded as one of the promising catalyst platforms due to the high density of possible coordination sites.^{1–4} Covalent triazine frameworks (CTFs) constitute a special and emerging class of COF, which are synthesized by trimerization reaction of carbonitriles and adopted triazine ring (C₃N₃H₃) as a building units.^{5,6} In a recent work, we have successfully synthesized CTFs hybridized with conductive carbon nanoparticles by introducing carbon particles during the polymerization to improve the pristine poor electrical conductivity.⁷ To obtain various catalytic activity, introducing the metal species as active site for catalytic reaction via impregnation process is a common method.⁸ Due to the large amount of N sites, various metals can be atomically-dispersed on CTFs.^{9–14} For example, we have reported catalytic activities of alcohol oxidation on ruthenium-doped CTF in acids,¹¹ nitrate reduction on copper-doped CTF in acids,¹² and oxygen reduction on platinum and copper-doped CTF both in acidic and alkaline solutions.^{13,14} Furthermore, it was also shown that cascade reactions could also be activated by loading CTFs carrying several different metal species.¹⁵

We have recently reported that nickel-doped covalent triazine framework (Ni-CTF) can serve as an effective electrocatalyst for converting carbon dioxide (CO₂) to carbon monoxide (CO), a

component of syngas, at an electrolyte pH of 6.8.¹⁶ In the examined potential range (–0.6 to –1.1 V vs. RHE) the maximum faradaic efficiency (FE) for electrochemical CO₂/CO conversion reached 90%. The FE of Ni-CTF was significantly higher than that of the Ni-doped fourfold-coordinated porphyrin, which was attributed to the larger adsorption energy of the key intermediate on the unsaturated Ni in CTF.¹⁶

Although we have thus revealed that Ni-CTF could serve as an efficient electrocatalyst for CO₂ reduction reaction (CRR), not only higher FE but the larger current density is important for electrochemical CRR. Use of a gas-diffusion electrode (GDE), which can overcome the problem of mass transport limitation due to the low solubility of CO₂, is an effective way to accelerate the CRR.^{17–24} A typical GDE has three-dimensional microstructures, by which the electrochemically active surface area at the triple-phase boundary, where the catalyst material, electrolyte, and gas pores intersect, is maximized. Although studies for electrochemical CRR have been generally conducted in neutral or alkaline solutions, it is worth investigating the CRR in wide pH range, because some of the CRR products are expected to be further converted to higher-value compounds in various downstream processes. In the present work, considering that Ni-CTF is stable enough in a wide pH range, we investigated electrochemical CRR on GDE loading Ni-CTF (hereafter called Ni-CTF/GDE).

2. Experimental

2.1 Synthesis of electrocatalysts

Ni-CTF and cobalt-modified CTF (Co-CTF) were prepared as CRR electrocatalysts, using a previously reported method.^{13,14,16} Briefly, a glass vacuum tube containing 2,6-pyridinedicarbonitrile (129 mg, Sigma-Aldrich), Ketjen Black (129 mg; EC600JD, Lion Corp.) and anhydrous ZnCl_2 (1.37 g, Wako) was heated to 400 °C over the period of an hour and then held for 40 h. The as-prepared powder was washed with deionized water, 1 M HCl solution (Wako), tetrahydrofuran (THF; Wako) and acetonitrile (Wako). Then the CTF powder was dispersed in a 10 mM aqueous solution of NiCl_2 or CoCl_2 and stirred at 80 °C in an oil bath for 3 h. The product was thoroughly washed with deionized water to remove residual metal salt, and then collected by vacuum filtration and transferred to a vacuum oven for drying at 60 °C overnight.

2.2 Electrochemical measurements

GDEs loaded with the CTF catalysts (Ni-CTF/GDE and Co-CTF/GDE) were prepared as follows. Typically, 21 mg of the as-prepared CTF-based catalyst mixed with 2.1 mL of ethanol and 199.5 μL of 5% Nafion 117 solution (Sigma-Aldrich) was sonicated for 30 min to obtain a homogenous catalyst ink. The catalyst ink was spin-coated (800 rpm, 8 s) on a polytetrafluoroethylene (PTFE)-treated carbon paper with a gas diffusion layer (Sigracet, 38BC) repeatedly to achieve a mass loading of ca. 0.4 mg cm^{-2} , and was then dried prior to use. Glassy-carbon plate electrodes loaded with the same amount of CTF catalysts (Ni-CTF/PE and Co-CTF/PE) were also prepared for comparison by the same preparation method using the glassy-carbon plate instead of carbon paper.

Electrochemical measurements were performed using an electrochemical station (HZ-5000, Hokuto Denko) and a two or three-compartment electrochemical cell in conjunction with three electrodes. A Ag/AgCl electrode (with saturated KCl as the internal solution) was used as the reference electrode (RE), and platinum wire as the counter electrode (CE). RE and CE compartments were separated by a Nafion membrane (Sigma-Aldrich, Nafion 117). The geometrical working electrode area was ca. 2 cm^2 . The CO_2 flow rate was set at 3 mL min^{-1} for the GDE. Electrolyte solutions were prepared from 0.1 M NaClO_4 (Wako) and specific volume of HClO_4 (Wako) based on the pH of the electrolyte. For pH = 14 condition, the electrolyte is 1 M KOH solution (Wako). To analyze the FE of product, the discharge gas would be collected by a PTEE bag for further characterization of possible products after an hour test. 0.1 M ZnCl_2 (Wako) was added to the electrolyte as a Zn^{2+} ions source for the verification of the local pH near the electrode. All potentials measured against the Ag/AgCl electrode were converted to the reversible hydrogen electrode (RHE) scale without ohmic drop compensation.

2.3 Characterization

X-ray photoelectron spectroscopy (XPS; Axis Ultra, Kratos Analytical Co.) was performed with monochromated $\text{AlK}\alpha$ X-rays. The results of as-prepared Ni-CTF powders characterization by XPS are shown in Fig. S1 and Table S1. Cross-sectional analysis of GDE was obtained with a Hitachi S-5000 scanning electron microscope (SEM). The surface of GDE tested in electrolyte with Zn ions analyzed by XPS spectra, scanning electron microscope equipped with energy dispersive spectroscopy (SEM-EDS, Miniscope TM3000 and Swift ED3000), X-ray diffraction (XRD, Rigaku miniflex with $\text{CuK}\alpha$ radiation) and Raman spectra (JASCO, NRS-3100 with a laser excitation wavelength of 785 nm).

2.4 Analyses of CRR products

The gas products were analyzed using gas chromatography-mass spectrometry (GC-MS; GCMS-QP 2010 Plus, Shimadzu, Japan),

calibrated using CO and H_2 samples diluted with CO_2 to various concentrations. A 0.5 mL sample of electrolyte after electrolysis was mixed with 0.1 mL D_2O containing 10 part per million dimethyl sulfoxide (DMSO; Wako) as an internal standard for characterization of the products in the liquid phase using nuclear magnetic resonance spectroscopy (NMR; Varian 500 MHz, Agilent). $^1\text{D } ^1\text{H}$ NMR spectra were measured with solvent suppression using a pre-saturation method.

3. Results and Discussion

3.1 Electrochemical CRR on Ni-CTF/GDE

Figure 1a shows a schematic diagram of the electrochemical reactor, which is composed of three compartments: (1) electrolyte compartment with CE, (2) electrolyte compartment with RE, and (3) gas compartment. The working electrode (i.e., GDE or PE) was placed at the boundary between compartment (2) and (3). The gas (CO_2 or Ar) was flowed in compartment (3) when the GDE was used, whereas it was bubbled into the electrolyte in compartment (2) when the PE was used. A proton exchange membrane was set at the boundary of compartments (1) and (2). The representative cross-sectional scanning electron microscopy (SEM) image of the Ni-CTF/GDE in Fig. 1b shows a ca. 4 μm thick catalyst layer was formed on the microporous layer of the GDE. Characterization results for the Ni-CTF/GDE can be found in Fig. S1 and Table S1, and also in our previous paper.¹⁶

Figure S2 shows cyclic voltammograms (CVs) obtained for Ni-CTF/GDE in electrolytes with initial pH = 14 electrolyte under Ar (black) and CO_2 (red) supply conditions. The absolute value of the current density (j_{abs}) exceeding 200 mA cm^{-2} was obtained, indicating that the use of GDE overcome the problem of the low solubility of CO_2 , as expected. CO was obtained as the main product of the electrochemical CRR in agreement with our previous study on Ni-CTF/PE.¹⁶ the FE reached 74% at 300 mA cm^{-2} (Fig. S2b). The above fact indicates that the Ni-CTF/GDE we have prepared have an ideal structure that provides the same level of performance as the general GDE. The Ni-CTF/GDE thus prepared was used for the experiments conducted in acidic electrolytes as shown below.

3.2 CRR activity in acidic solutions

Next, we examined the CRR activity on GDE and PE in acidic solutions. For both Ni-CTF/GDE and Ni-CTF/PE, CO_2 supply had little impact on the current density-potential curves at pH = 1 (Figs. 2a and b). For both cases, the j_{abs} started to increase at around -0.5 V, and the curves in both the absence and presence of CO_2 were almost overlapped. The active site for hydrogen evolution reaction is expected lower density on GDE than on PE, because the half side of the GDE is exposed to gas phase where no proton exists. In fact, j_{abs} on GDE was confirmed to be smaller than on PE. In contrast to the case at pH = 1, the Ni-CTF/GDE and Ni-CTF/PE exhibited contrasting behavior at pH = 2 and 3. On Ni-CTF/GDE, a larger j_{abs} was obtained under CO_2 -supply conditions than under Ar-supply conditions, in the potential region more negative than ca. -1.0 V (Figs. 2c and e). Conversely, a larger j_{abs} was observed on Ni-CTF/PE under Ar-supply conditions than under CO_2 -supply conditions (Figs. 2d and f).

CRR products taken from the liquid and gas compartments (i.e., compartments (2) and (3) in Fig. 1a) after application of -1.0 V for 1 h were quantitatively analyzed by ^1H NMR and GC-MS, respectively (typical results are shown in Fig. S3). In the present experiments, the applied potential was set to be much higher (and therefore j_{abs} was lower) than typical experimental conditions for the CRR on a GDE where a large current flows.^{18,20,25,26} As is the case with our previous research conducted in an electrolyte with pH = 6.8, it was confirmed that CO was the only detectable product

Figure 1. (a) Schematic diagram of two- or three-compartment cells. (b) Cross-sectional SEM image and diagram of the metal-modified CTF/GDE architecture. (c) Schematic illustration of metal-doped CTF.

from the CRR on both the Ni-CTF/GDE and Ni-CTF/PE in this pH range (pH = 1–3). Partial current densities for H₂ and CO generation from the Ni-CTF/GDE and Ni-CTF/PE at –1.0 V are plotted against pH in Fig. S4. The absolute value of the partial current for hydrogen evolution reaction (HER) for the Ni-CTF/GDE (solid line) was smaller than that for the Ni-CTF/PE (dashed line) at all pHs examined, and the difference was the largest at pH = 1 (Fig. S4a). In contrast, the absolute value of the partial current for CO generation from the Ni-CTF/GDE (solid line) was equal to or larger than that from the Ni-CTF/PE (dashed line), as shown in Fig. S4b.

Figure 2. Cyclic voltammetry (CV) results of Ni-CTF using a GDE and PE with different pH electrolytes under Ar (black) and CO₂ (red) supply; (a, b) pH = 1, (c, d) pH = 2, and (e, f) pH = 3. The scan rate was 10 mV s^{–1}.

Figure 3. FE for CO and H₂ generation under electrochemical conditions using the Ni-CTF/PE (left column) and Ni-CTF/GDE (right column) in electrolytes with different pH.

The FE at pH = 1, 2, and 3 with an applied potential of –1.0 V are summarized in Fig. 3. The HER was the dominant reaction at pH = 1 for both the Ni-CTF/GDE and Ni-CTF/PE, as expected. However, the Ni-CTF/GDE and Ni-CTF/PE exhibited contrasting behavior at pH = 2 and 3. Although the HER was still dominant for the Ni-CTF/PE at pH = 2, the FE for the CRR increased and reached 60% for the Ni-CTF/GDE. The FE for the CRR increased for the Ni-CTF/PE at pH = 3, but it was still lower than that for the Ni-CTF/GDE. From the results given in Figs. 3 and S4, it can be concluded that significant suppression of the HER led to improve-

Figure 4. (a) Total current density, and H₂ and CO partial current densities. (b) Corresponding FEs for H₂ and CO generation with the Ni-CTF/GDE under different applied potentials and an electrolyte of pH = 2.

ment of the FE for the CRR on the GDE at pH = 2 and 3. These results suggest that the local pH around the catalysts is largely different between Ni-CTF/GDE and Ni-CTF/PE, which will be discussed later in detail.

Qualitatively the same results shown in Figs. 3 and S4 were also confirmed for the gas diffusion and plate electrode loading cobalt (Co-CTF/GDE and Co-CTF/PE) as shown in Figs. S5, S6, and S7, which indicates that the GDE structure rather than the catalyst is the origin of the unusual increase in the FE for the CRR at pH = 2 and 3.

3.3 Potential dependence

In addition to the electrolyte pH, the electrode potential is another key factor that determines the FE for the CRR. Figure 4a shows the partial current density for the HER (red) and the CRR (green) for the Ni-CTF/GDE over a wide potential range from -1.8 V to -0.8 V vs. RHE. These experiments were conducted in pH = 2 electrolyte, in which clear difference was obtained between the GDE and PE. CO was obtained as the sole detectable product in this potential region. Corresponding FE values calculated from Fig. 4a are shown against the applied potential in Fig. 4b. Both H₂ and CO were detected as the reaction products at -0.8 and -1.0 V, whereas CO was detected as the sole product at potentials more negative than -1.0 V vs. RHE. The Co-CTF/GDE also exhibited similar potential dependence as the Ni-CTF/GDE, as shown in Fig. S8.

Figure 5. SEM images and photographs (insets) of GDE surfaces after one hour of the CRR in electrolytes with added Zn²⁺ ions at (a) pH = 1 and (b) pH = 2.

3.4 Verification of local pH increase

In acidic electrolytes, the HER is dominant;^{20,24,27–30} therefore, the FE of the CRR inevitably becomes small. However, as shown in Fig. 4, the CRR produced CO with FEs as high as 60% using the GDE, even at pH = 2. This result suggests that the local pH around the catalyst increases during cathodic reactions that consume protons (Eq. (1) and (2)).

Notably, the increase of the local pH is more significant when microstructured electrodes, such as those with porous, roughened, nanowires, or inverse opal structures, are used, because protons can be more easily depleted inside the confined microstructures.^{31–36} The increased local pH commonly leads to improvement of the FE for the CRR via suppression of the competitive HER.^{18,20,24,27–29} Based on these previous studies, it is expected that the local pH in the vicinity of a GDE would also be significantly increased due to the 3D microstructured interface, even if there is no difference in the current density between the Ni-CTF/GDE and Ni-CTF/PE.

Therefore, we next attempted to experimentally verify the increase in the local pH at the GDE surface by observing the formation of zinc hydroxides analogues from zinc ions (Zn(II)) that can only proceed in an alkaline solution. Zn(II) becomes solid-state zinc hydroxides analogues on a cathode, even in acidic electrolytes, when the local pH is increased by cathodic reactions, such as reduction reactions of protons, oxygen, nitrate, and hydrogen peroxide.^{37–40} Therefore, if the present hypothesis is true, zinc hydroxide analogues should be formed only on the GDE in electrolytes with pH = 2 and 3.

Figures 5a and b show SEM images and photographs of the Ni-CTF/GDE surface removed from the electrolyte after electrolysis for 1 h in the presence of Zn(II) at pH = 1 and 2, respectively. At pH = 1 (Fig. 5a), there was no deposit other than precipitated salts that could not be completely washed out. In contrast, it was confirmed that the GDE electrode surface was covered with numerous deposits at pH = 2. XPS analyses of the crystals revealed two peaks assignable to Zn-2p_{3/2} and Zn-2p_{1/2} both for the samples

Figure 6. Schematic illustration of the local pH increase in the vicinity of the GDE surface.

obtained at pH = 1 and 2 (Fig. S9). The atomic ratio of zinc on the electrode obtained at pH = 2 reached 22%, which was significantly larger than that on the sample obtained at pH = 1 (Table S2). Figure S10 shows SEM image and energy dispersive X-ray spectroscopy (EDX) elemental maps of the GDE surface, in which zinc and oxygen were confirmed to be homogeneously distributed and the atomic ratio of Zn reached 20% (Table S3). However, Zn was not detected by EDX when the PE was used. X-ray diffraction (XRD) and Raman spectroscopic analyses revealed that the deposits on the GDE at pH = 2 were composed of $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, which cannot be formed in acidic electrolytes (Fig. S11).^{41–43} The experimental results thus indicated that the local pH in the vicinity of the GDE became alkaline, even when the bulk pH was set to 2.

Finally, let us consider the possible influence of the local CO_2 concentration on the difference in the FE between GDE and PE. As shown in Figs. 3 and 5, despite that there is no difference in the CO_2 supply, in contrast to the case at pH = 2, both the CO and zinc hydroxide analogues were not formed at pH = 1 using same GDE. Furthermore, although CO and zinc hydroxide analogues were formed on GDE at pH = 2, they were not observed on PE in the electrolyte with the same pH. Thus, the formation of CO and zinc hydroxide analogues were always synchronized. The above results clearly show that the difference in the FE between on GDE and PE is not due to the difference in the local CO_2 concentration but in the local pH. Although the local pH can be generally larger when cathodic reactions proceed, the current density on the PE was at the same level as that on the GDE. Besides, it is known that protons can be more easily depleted inside the confined microstructures. Taken all together, this indicates that the increase of the local pH for the GDE is not based on the large current but on the structural features of the GDE, as schematically shown in Fig. 6.

4. Conclusion

In conclusion, we have revealed (1) that high CRR rate exceeding 300 mA cm^{-2} with 74.1% FE of CO could be achieved on Ni-CTF/GDE in an alkaline solution and (2) that the FE reached 60% even in a pH = 2 solution by using GDE. CO was generated as a main product in a wide potential region. The improved FE was attributed to an increase of the local pH, which is specifically induced at the GDE because of the extremely thin electrolyte layer at the triple phase boundary. Although many factors of GDE, including the porosity, hydrophobicity/hydrophilicity, amount of catalyst loading, and the thickness of the microparticle layer, can affect local pH, the general trend on pH dependence revealed in this study should be held regardless of the detailed structure of the GDE used.

The increase of the FE of the CRR via the suppression of the HER achieved with a GDE is advantageous to lower the voltage required for the CRR. Various hydrocarbons can be obtained with electrochemical CRR by the selection of appropriate catalysts, which can then be further converted to higher-value compounds in the downstream processes. For example, alcohols and acids can be used as substrates of oxygen fuel cells that are typically operated in acidic electrolytes. Furthermore, aldehyde compounds can be further converted to complex organics via acid-base reactions, such as Aldol condensation catalyzed by protons. Thus, expansion of the pH range to acidic conditions by the use of a GDE could be beneficial when considering secondary uses of the CRR products.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-64036>.

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