

Electroreduction of Carbon Dioxide to Carbon Monoxide by Co-phthalocyanine Electrocatalyst under Ambient Conditions

Ichiro YAMANAKA,* Kyosuke TABATA, Wataru MINO and Takeshi FURUSAWA

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo, 152-8552 Japan.

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Electrochemical reduction of carbon dioxide using a gas-electrolysis cell reactor was studied. A new electrocatalyst has been screened and Co-phthalocyanine (Co-Pc) supported on carbon support was found to reduce CO_2 to CO. Effects of reaction conditions on a formation rate of CO and a selectivity to CO corresponding to a current efficiency (CE) were studied. Loadings of Co-Pc, kinds of carbon materials as a support, reaction temperatures and cathode potentials strongly affected the performance of the electroreduction of CO_2 to CO. A maximum CE to CO formation was achieved to 70% with 14 mA cm^{-2} by use of 0.1 wt% Co-Pc supported vapor-grown-carbon-fiber (VGCF) electrocatalyst at -0.90 V (Ag/AgCl) and 273 K. The reaction model of electroreduction of CO_2 was proposed in this work.

KEY WORDS: reduction of carbon dioxide; electrochemical reduction; carbon monoxide; Co electrocatalyst.

1. Introduction

Reduction of carbon dioxide emission and suppression of energy consumption are very serious subject for iron making process from a viewpoint of the global warming problem. Kato has proposed application of the Active Carbon Recycle Energy System (ACRES) to iron making process for reduction of CO_2 emission (iACRES). The iACRES uses recycling CO for reduction of iron oxides. CO is produced by CO_2 reduction using non-fossil energy, ca. nuclear energy by high-temperature gas-cooled reactor or renewable energy by solar and wind power.^{1,2)} Conventional catalytic reduction of CO_2 to CO and various chemicals using solid catalysts have been reported. For example, Mitsui Chemical Co. in Japan has been already developed a new process of methanol synthesis from CO_2 and H_2 at 673 K by a solid catalyst, Cu and Zn oxide modified catalyst.^{3,4)} Methanol can store as chemical stock and we will use as artificial resource. The catalytic process is primary candidate for CO_2 conversion to CO, useful chemicals and fuel. This catalytic CO_2 recycling system will be realized if enough heat energy and reducing agent such as H_2 could be continuously supplied to the process. The catalytic process is not suitable for utilization of the renewable energy because it fluctuates widely in day and season. Catalytic chemical process cannot stop at short intervals because of deactivation of catalysts by repeat thermal stress. On the other hand, electrochemical reaction proceeds under mild conditions and can be immediately stopped by turnoff switch. The reaction rate can be easily controlled by electrode potential to correspond to the fluctuation of renewable energy. Thus, electroreduction of CO_2 using renewable electric energy from solar panels and wind

power generation is secondary candidate for the CO_2 recycling system, which can incorporate to the iACRES.

Hori and co-workers first reported electroreduction of CO_2 to CO, CH_4 , C_2H_4 and higher hydrocarbons by Cu-plate cathode.^{5,6)} Then, a lot of works were reported electroreduction of CO_2 ; however, most of all works were conducted under severe reaction conditions, slow formation rates of products, low faradic efficiency.^{7–14)} Purposes of this work are to develop a gas-electrolysis cell for CO_2 reduction and to find new electrocatalyst to reduce CO_2 with a high formation rate and faradic efficiency in mild conditions.

2. Experimental

Reduction of carbon dioxide was conducted using a gas-electrolysis cell, as shown in Fig. 1.^{15,16)} A diaphragm was

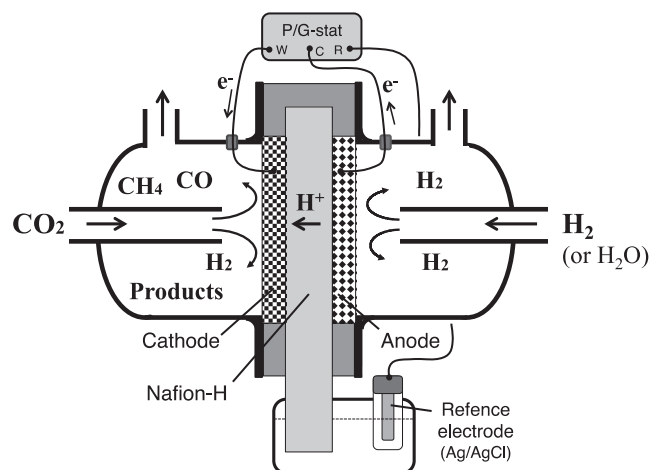


Fig. 1. Schematic diagram of a gas-electrolysis cell.

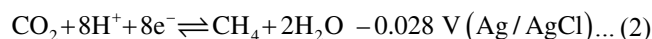
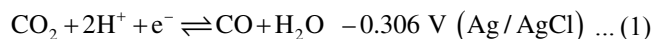
* Corresponding author: E-mail: yamanaka@cms.titech.ac.jp
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attached at middle of the electrolysis cell. The diaphragm was assembled using three membranes of a cathode membrane, Nafion-117 membrane and anode membrane, which functioned an electrolysis unit in the gas phase. CO₂ gas (101 kPa, 10 mL min⁻¹) and H₂ gas (101 kPa, 10 mL min⁻¹) were respectively introduced in the cathode and anode compartments. The electrolysis of CO₂ with H₂ was conducted under ambient conditions.

The cathode membrane was prepared from three powders of electrocatalyst, vapor-grown-carbon-fiber (VGCF, 13 m² g⁻¹, Showa Denko Co) as an electroconductive additive and PTFE (F-104, Daikin Co.) as a binder by a hot-press method. Preparation procedure of the electrode membrane in detail has been described in previous report;^{17,18)} therefore, it was briefly explained as follows. The three powders were well mixed and kneaded to a clay-like ball using a mortar and pestle, pressed and shaped to a round sheet. The anode membrane was also prepared from Pt supported carbon black of Vulcan XC-72 (XC72, 245 m² g⁻¹, Cabot Co.), VGCF and PTFE powders. The three membranes were layered and hot-pressed.

The electrocatalyst was prepared by an impregnation method. For example, Co-phthalocyanine (Co-Pc) supported on VGCF electrocatalyst described later was prepared as below; (i) Co-Pc (8.73 mg) dissolved in pyridine (50 mL), (ii) VGCF (291.27 mg) added to the Co-Pc/pyridine solutions and stirred over night, (iii) the mixture was heated on a hot-plate at 150°C in a draft-hood and was well mixed by mixing with a glass rod. The mixture was dried up well to remove pyridine solvent. The Co-Pc/VGCF electrocatalyst was prepared. Co-Pc loading based on Co was 0.3 wt% versus whole weight of the material. Other carbon supports for Co-Pc, activated carbon (AC, 1560 m² g⁻¹), XC-72, and graphite (Gr, 7 m² g⁻¹) were used in this work.

The potentiostatic electrolysis of CO₂ was conducted at each potentials for 30 min and products were analyzed using on-line GC. Cathode potential was varied from -0.2 to -1.0 V versus a Ag/AgCl reference electrode. All electrochemical controls and measurements were conducted by use of a computed electrochemical instrument (Hokuto Denko HZ-5000). Major products were CO and H₂ by two-electron reaction (Eq. (1)), and a trace amount of CH₄ by eight-electron reduction (Eq. (2)) was detected. H₂ was also produced (Eq. (3)) which was simple electrochemical pumping of H₂ from the anode to cathode.



Quantities of products were determined by GC technics (Shimadzu GC-8APT with TCD, CO and CH₄; Porapac-Q column (4φ × 2 m) with He carrier gas, H₂: Activated Carbon column (4φ × 2 m), Ar carrier gas). When other products such as CH₃OH, HCHO, HCO₂H, etc. were produced, we could detect using other GC and HPLC instruments.

Current efficiency (CE) of product was calculated from the charge for product formation (Eqs. (1) and (2)) and the sum of charge passed through Eq. (4). The CE is a very important factor to evaluate electrocatalytic activity.

$$\text{CE} = (\text{charge for product formation})$$

$$/(\text{sum of charge passed}) \times 100\% \quad \dots (4)$$

3. Results and Discussion

Electrocatalytic activities of various metal complexes such as Mn, Fe, Co, Ni, Cu, Zn-phthalocyanine (Pc), -tetraphenyl porphyrin (TPP) and -N,N'-ethylenebis(salicylimine) (Salen) for reduction of CO₂ were studied. First, candidates as electrocatalyst were loaded on activated carbon (AC) support (0.3 wt% loading based on metal). The metal-complex/AC materials were used for roughly screening of electroreduction of CO₂ at 298 K by applying a cathode potential of -0.80 V (Ag/AgCl) which was a sufficiently negative potential compared with the standard redox potentials of CO₂ to CO (Eq. (1)) and CH₄ (Eq. (2)). Then, a brief conclusion of capable element as Co was obtained from the roughly screening. Electrocatalytic activities of Co-complexes/AC, current density (*i_d*), formation rate of CO, CE for CO formation, formation rate of H₂, CE for H₂ formation, were indicated at runs 1–3 in **Table 1**. In addition, results used a 0.3wt%Pt/AC electrocatalyst were added. Reduction currents were observed for three cathodes prepared from Co-Pc/AC, Co-TPP/AC and Co(salen)/AC electrocatalysts. The current densities (*i_d*) were very different, Co(salen)/AC >> Co-Pc/AC > Co-TPP/AC. Though a major product at the cathodes was H₂ (H₂ pumping from anode to cathode), significant formation of CO was observed. The formation rates of CO were Co-Pc/AC > Co-TPP/AC >> Co(salen)/AC (none) and the CEs at the Co-Pc/AC and Co-TPP/AC cathodes were low values of 4.5 and 3.6%, respectively. Remain CEs were for the formation of H₂. The sum of CEs for the CO and H₂ formation were almost 100% within experimental error. When the Pt/AC electrocatalyst was used for the CO₂ reduction, no formation of CO was observed (run 4). The Co-Pc/AC electrocatalyst has a unique electrocatalysis.

Effects of carbon supports, AC, XC-72, VGCF and Gr,

Table 1. Electrocatalytic activities of Co complexes loaded on activated carbon support for electroreduction of CO₂ using a polymer-electrolyte-membrane electrolysis cell.

Run	Electrocatalyst	<i>i_d</i> /mA cm ⁻²	CO formation		H ₂ formation	
			Rate/μmol cm ⁻² h ⁻¹	CE/%	Rate/μmol cm ⁻² h ⁻¹	CE/%
1	Co-Pc/AC	10.7	8.9	4.5	190.1	95.2
2	Co-TPP/AC	5.6	3.8	3.6	99.8	95.5
3	Co(salen)/AC	75.3	0.0	0.0	1398.5	99.6
4	Pt/AC	85.2	0.0	0.0	1580.1	99.4
5	Co-Pc/VGCF	16.3	93.5	30.5	210.0	69.1
6	Co-Pc/XC72	16.1	8.0	3.0	292.4	97.3
7	Co-Pc/Gr	8.9	14.5	8.7	151.0	91.0

i_d: current density, CE: current efficiency.

T: 298 K, electrolysis potential: -0.8 V (Ag/AgCl).

Cathode compartment: Co-complex/carbon cathode, P(CO₂): 1 atm.

Anode compartment: Pt/XC72 anode, P(H₂): 1 atm.

for Co-Pc/carbon electrocatalysts (0.3 wt% Co loading) on the reduction of CO_2 were studied at -0.8 V, as indicated at runs 1 and 5–7 in Table 1. The four Co-Pc/carbon cathodes showed fairly high current densities and were active for CO formation. The formation rate of CO at Co-Pc/VGCF cathode was remarkably higher than these of other cathodes. Effective supports for CO formation were $\text{VGCF} \gg \text{Gr} > \text{AC}, \text{XC72}$. On a viewpoint of the CEs for CO formation, a remarkable high CE of 30.5% at the Co-Pc/VGCF cathode was to be note and effective supports were as same order as that for the CO formation. The remnant currents were for the formation of H_2 . The sum of CEs for the CO and H_2 formation were almost 100%.

These data clearly indicate that the Co-Pc/VGCF electrocatalyst is suitable for reduction of CO_2 to CO among the electrocatalyst screened in Table 1. The turnover frequency of Co for the CO formation was 203 h^{-1} and the CE was 30.5% at -0.8 V and 298 K. The VGCF support was chosen for Co-Pc electrocatalyst, hereafter. In addition, a carbon support having a higher surface area, AC ($1470 \text{ m}^2 \text{ g}^{-1}$) and XC72 ($245 \text{ m}^2 \text{ g}^{-1}$), seems to be not suitable for electroreduction of CO_2 but suitable for the H_2 formation. In addition, a carbon support having a lower surface area, VGCF ($13 \text{ m}^2 \text{ g}^{-1}$) and Gr ($7 \text{ m}^2 \text{ g}^{-1}$), may be better for reduction of CO_2 because of suppression of H_2 evolution. Carbon surface has several functional groups such as carboxyl, carbonyl, phenolic hydroxyl and alcoholic hydroxyl groups. These functional groups promote electrochemical formation of H_2 .¹⁹⁾ A carbon support having a large surface area has a larger amount of functional groups; therefore, formation of H_2 is relatively accelerated to compare the formation of CO by the Co-Pc electrocatalyst.

Figure 2 shows effect of Co-Pc loading at the VGCF support on electroreduction of CO_2 to CO at -0.80 V and 298 K; (a) formation rate of CO and CE, (b) electrolysis current density and turnover frequency (TOF) of Co, (c) formation rate of H_2 and CE. Of course, VGCF without Co-Pc loading did not show electrocatalytic activity for reduction of CO_2 and formation of H_2 at -0.8 V. When a small amount of Co-Pc of 0.05 wt% was loaded, a low electrocatalytic activity was observed and CO was formed with a low CE of 7%. When the Co-Pc loading was increased to 0.1 wt%, the formation rate of CO increased remarkably and the CE was also increased to 24%. However, the formation rates of CO at 0.2 and 0.3 wt% loadings were slightly lower than that at 0.1 wt%. The CEs were increased with the loadings and a maximum as 31% at 0.3 wt% loading. On the other hand, the TON of 660 h^{-1} at 0.1 wt% loading was higher than that of 314 h^{-1} at 0.2 wt% and 203 h^{-1} at 0.3 wt% loading. When the Co-Pc loading was increased to 0.5 wt%, the formation rate of CO and the CE were obviously decreased. The byproduct was H_2 as indicated in Fig. 2(c). The VGCF anode no Co-Pc loading was inactive for formation of H_2 . The formation rate of H_2 increased with Co-Pc loadings and a maximum formation rate was obtained at 0.10 wt%. The formation rate gradually decreased with the loadings. The sum of CEs for the CO and H_2 formation were almost 100% within experimental error ($\pm 2\%$) at all Co loadings.

The VGCF surface is inactive for electrochemical reduction of CO_2 to CO and H^+ to H_2 . The Co-Pc adsorbed on VGCF surface is active site for the electrochemical reduc-

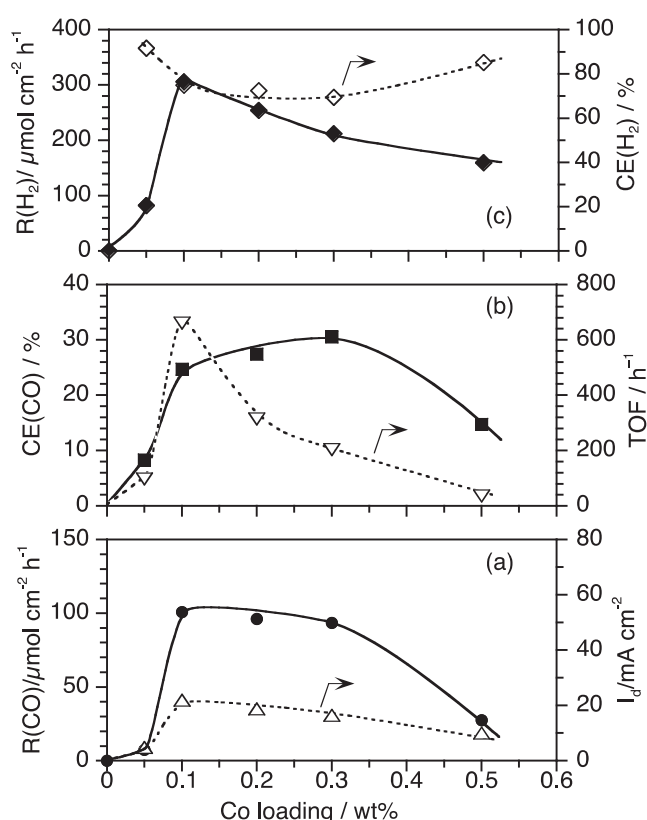


Fig. 2. Effects of Co loadings on (a) formation rate of CO and current density, (b) current efficiency and turn-over frequency for CO formation, (c) formation rate and current efficiency of H_2 for potentiostatic electrolysis of CO_2 using the gas-electrolysis cell. T: 298 K. Cathode potential: -0.80 V (Ag/AgCl). Cathode compartment: Co-Pc/VGCF cathode, CO_2 1 atm. Anode compartment: Pt/XC72 anode, H_2 1 atm.

tions. The loadings from 0.1 to 0.3 wt% were suitable to study effects of reaction conditions on the electroreduction of CO_2 to CO. We choose the 0.3wt%Co-Pc/VGCF cathode on evaluation of a higher CE with a higher formation rate.

Figure 3 shows effects of cathode potential on the electroreduction of CO_2 by 0.3wt%Co-Pc/VGCF cathode at 298 K; (a) formation rate of CO and CE, (b) i_d and TOF of Co, (c) formation rate of H_2 and CE. A reduction current flowed from -0.70 V and small amounts of CO and H_2 formation were observed. The current density increased exponentially with decreasing the cathode potential until -0.90 V. The formation rate of CO increased with decreasing the potential and showed a maximum at -0.85 V. A 10% CE to the CO formation at -0.70 V was low. The CE increased over 30% at -0.75 and -0.80 V. At -0.90 V, the formation rate of CO and the CE decreased but the current density increased because of acceleration of the H_2 formation. The formation rate of H_2 increased remarkably with decreasing cathode potentials and the CE also increased. The sum of CEs for the CO and H_2 formation were almost 100%.

The above data indicated that CO and H_2 formation were competitive. How to suppress the H_2 formation at negative potentials is essential to realize fast and efficient electroreduction of CO_2 to CO.

Figure 4 shows effects of reaction temperatures on electroreduction of CO_2 as a function of potentials at the 0.3wt%Co-Pc/VGCF cathode; (a) formation rate of CO, (b)

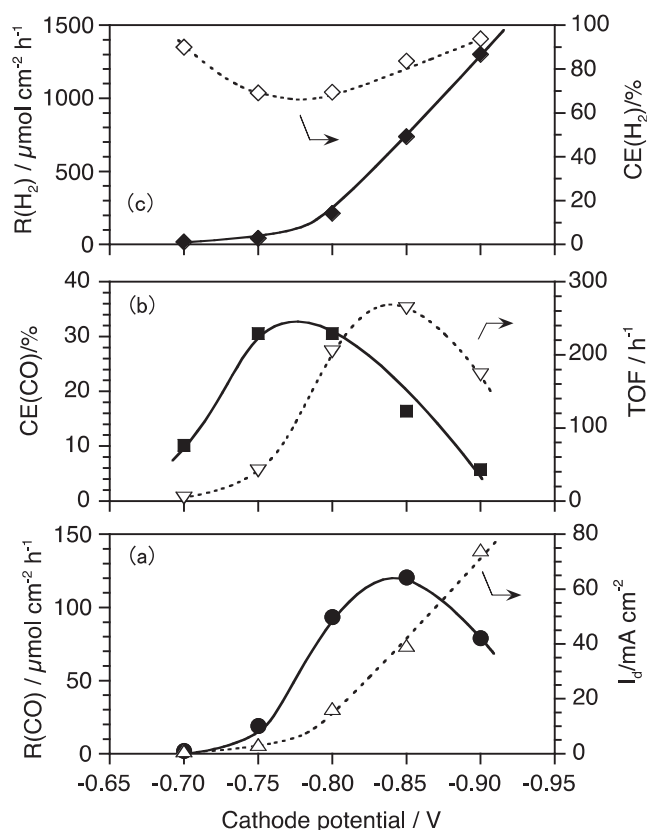


Fig. 3. Effects of cathode potential on (a) formation rate of CO and current density, (b) current efficiency and turn-over frequency for CO formation, (c) formation rate and current efficiency of H₂ for the potentiostatic electrolysis of CO₂. T: 298 K. Cathode compartment: 0.3wt%Co-Pc/VGCF cathode, CO₂ 1 atm. Anode compartment: Pt/XC72 anode, H₂ 1 atm.

CE of CO formation, (c) formation rate of H₂. At 303 K, a very similar performance of the reduction of CO₂ to that in Fig. 3 at 298 K was obtained. When reaction temperature was increased to 313 K, large reduction currents were observed at lower potentials than -0.70 V. At -0.80 V, the formation rate of CO at 313 K was remarkably higher than that at 303 K; however, the formation rate decreased at -0.85 V and the formation rate of H₂ dramatically increased, as shown in Fig. 4(c). The CEs to the CO formation were lower than 20% at 313 K. When the reaction temperature was decreased to 283 and 273 K, on set cathode potentials for the CO formation shifted to negative about -0.05 V. Thus, the formation rates of CO at 283 and 273 K at -0.80 V were lower than that at 303 K. The formation rate of CO decreased with decreasing in reaction temperatures. However, the formation rate of CO at 273 K increased with decreasing in potentials lower than -0.80 V. A maximum formation rate of CO at 273 K was obtained at -0.90 V. The formation rates of H₂ at 273 K were suppressed even at -0.90 and -0.95 V; therefore, the CE increased with decreasing in potentials and reached to a maximum of 63% at -0.90 V. While, the H₂ formation at 303 K was already major even at -0.85 V.

As described above, the reaction temperature strongly affects the electrocatalysis of Co-Pc/VGCF cathode. Acceleration of CO formation and suppression of H₂ formation at negative potentials were especially to be note; therefore, we

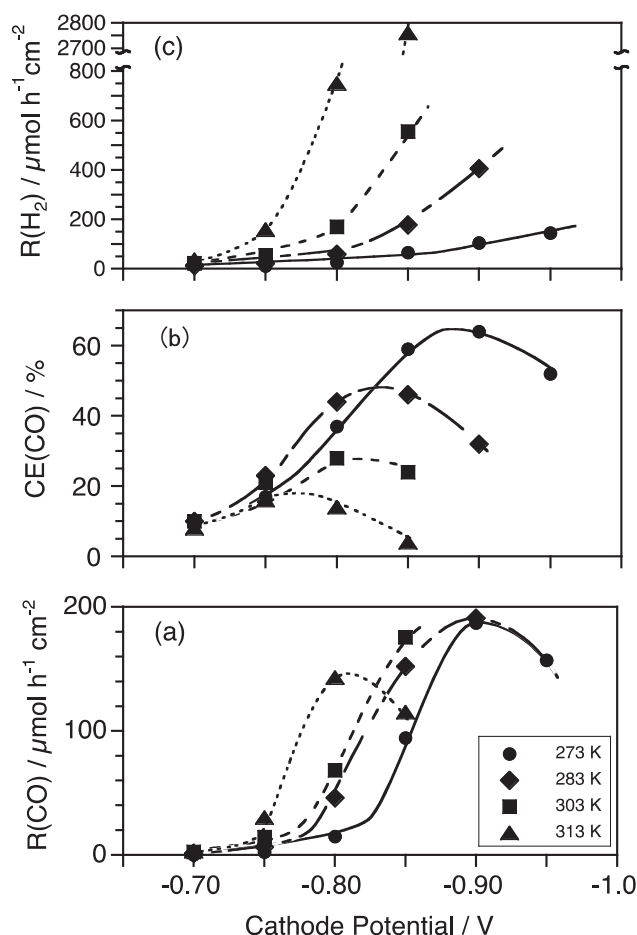


Fig. 4. Effects of reaction temperature on the potentiostatic electrolysis of CO₂, (a) formation rate of CO, (b) current efficiency of CO and (c) formation rate of H₂. T: 273–313 K. Cathode compartment: 0.3wt%Co-Pc/VGCF cathode, CO₂ 1 atm. Anode compartment: Pt/XC72 anode, H₂ 1 atm.

confirmed again effects of Co loadings of Co-Pc/VGCF electrocatalyst under suitable electrolysis conditions of -0.9 V and 273 K.

Figure 5 shows effects of Co loadings between 0.05 and 0.50 wt% on the electroreduction of CO₂; (a) the formation rates of CO and CEs and (b) the formation rates of H₂ and CEs. The Co-Pc/VGCF electrocatalysts loaded from 0.10 to 0.30 wt% showed high electrocatalytic activity and the formation rates of CO and CEs were very similar. The maximum CE of 70% was obtained at 0.10 wt% loading that was higher than 63% CE obtained in Fig. 2. When the Co loading increased 0.5 wt%, CO and H₂ formation rates and i_d decreased. In addition, the sum of CEs for CO and H₂ formation was almost 100%. Under suitable conditions at -0.90 V and 273 K, the 0.10wt%Co-Pc/VGCF electrocatalyst was most effective for the electroreduction of CO₂ to CO in this work.

The 0.10 wt% Co-loading of Co-Pc (3–4 nm² molecule⁻¹) is enough to cover the surface of VGCF (13 m² g⁻¹) as monolayer. Co-Pc molecules may stack and aggregate on the VGCF surface at the higher Co-Pc loading of 0.50 wt%. The excess loading of 0.50 wt% Co-Pc on VGCF decreases the CO and H₂ formation rates and CEs, as described in Figs. 2 and 5. The isolated Co-Pc on the VGCF surface is

active site for electroreduction of CO_2 to CO. The VGCF surface is very smooth because VGCF is prepared at a higher temperature of 1400 K. Therefore, Co-Pc could be adsorbed and isolated on the surface. How to disperse Co-Pc molecular on carbon surface of higher surface area may be key process for preparation of more active and selective electrocatalyst.

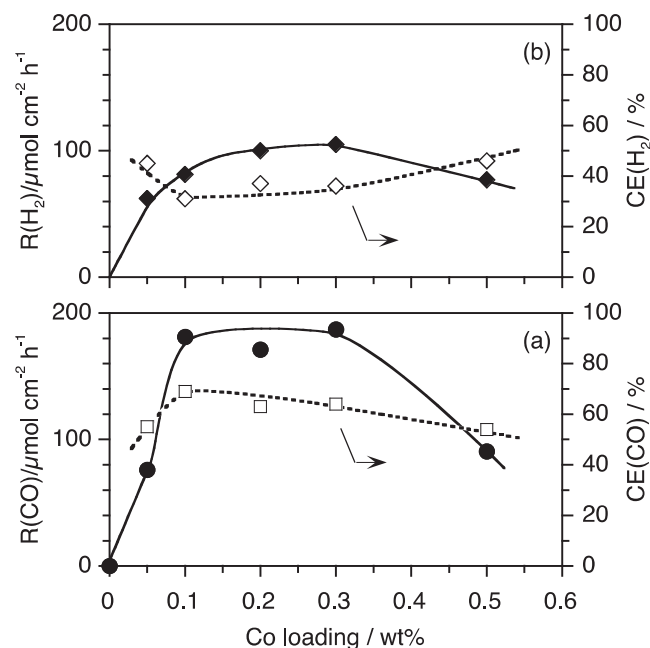


Fig. 5. Effects of Co-loading of Co-Pc/VGCF electrocatalyst on (a) formation rate of CO and current efficiency and (b) formation rate of H_2 and current efficiency for the potentiostatic electrolysis of CO_2 at -0.90 V and 273 K. Cathode compartment: Co-Pc/VGCF cathode, CO_2 1 atm. Anode compartment: Pt/XC72 anode, H_2 1 atm.

4. Conclusions

As described above, we have developed the gas-electrolysis cell applying a fuel cell reactor and found the new electrocatalyst of 0.10wt%Co-Pc/VGCF for selective reduction of CO_2 to CO. The maximum CE to the CO formation was 70%. The TOF of Co for the CO formation was 1097 h^{-1} and Co-Pc on VGCF functioned very well. The suppression of H_2 formation at the cathode is essential to achieve more selective and fast reduction of CO_2 to CO.

REFERENCES

- 1) Y. Kato: *ISIJ Int.*, **50** (2010), 181.
- 2) Y. Kato: *ISIJ Int.*, **52** (2012), 1433.
- 3) Mitsui Chemicals Media Center: News Releases, (2008), <http://www.mitsuiichem.com/release/2008/080825e.htm> (accessed 2014-12-28).
- 4) A. Bansode and A. Urakawa, *J. Catal.*, **309** (2014), 66.
- 5) Y. Hori, A. Murata and R. Takahashi: *J. Chem. Soc., Faraday Trans. I*, **85** (1989), 2309.
- 6) Y. Hori: In *Modern Aspects of Electrochemistry*, Vol. 42, eds. C. G. Vayenas, R. E. White and M. E. Gamboa-Aldeco, Springer, New York, (2008), 89.
- 7) A. Yamaguchi, M. Yamamoto, K. Takai, T. Ishii, K. Hashimoto and R. Nakamura: *Electrochim. Acta*, **141** (2014), 311.
- 8) J. Xie, Y. Huang, W. Li, X. Song, L. Xiong and H. Yu: *Electrochim. Acta*, **139** (2014), 137.
- 9) R. Kas, R. Kortlever, A. Milbrat, M. Koper, G. Mul and J. Baltrusaitis: *Phys. Chem. Chem. Phys.*, **16** (2014), 12194.
- 10) T. V. Magdesieva, K. P. Butin, T. Yamamoto, D. A. Tryk and A. Fujishima: *J. Electrochem. Soc.*, **150** (2003), E608.
- 11) T. Abe, H. Imai, T. Yoshida, S. Tokita, D. Schlettwein, D. Wöhrle and M. Kaneko: *J. Porphyr. Phthal.*, **1** (1997), 315.
- 12) K. Hara, A. Kudo and T. Sakata: *J. Electroanal. Chem.*, **421** (1997), 1.
- 13) Y. Kushi, H. Nagao, T. Nishioka, K. Isobe and K. Tanaka: *Chem. Lett.*, **23** (1994), 2175.
- 14) M. Schwartz, M. E. Vercauteren and A. F. Sasmells: *J. Electrochem. Soc.*, **141** (1994), 3119.
- 15) K. Otsuka, and I. Yamanaka: *Catal. Today*, **41** (1998), 311.
- 16) K. Otsuka and I. Yamanaka: *Catal. Today*, **57** (2000), 71.
- 17) I. Yamanaka, T. Hashimoto, R. Ichihashi and K. Otsuka: *Electrochim. Acta*, **53** (2008), 4824.
- 18) I. Yamanaka, S. Tazawa, T. Murayama and S. Takenaka: *ChemSusChem*, **3** (2010), 59.
- 19) T. Murayama and I. Yamanaka: *J. Phys. Chem. C*, **115** (2011), 5792.