



Polymer electrolyte fuel cell supplied with carbon dioxide. Can be the reductant water instead of hydrogen?

Motoharu Morikawa^a, Naveed Ahmed^b, Yuta Ogura^a, Yasuo Izumi^{b,*}

^a Department of Nanomaterial Science, Graduate School of Advanced Integration Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

^b Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

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ABSTRACT

Polymer-electrolyte fuel cell supplying CO₂ was demonstrated. Using a PEFC, 95 mol% of methanol was selectively formed by supplying H₂ to Pt catalyst and CO₂ to Zn-Cu-Ga layered double hydroxide catalyst accompanying protons and electrons transfer, i.e. H₂ → 2H⁺ + 2e⁻ at anode followed by CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O at cathode. Using PEFC, CO₂ reduction with water was also enabled to methanol (100–86 mol%) in contrast that negligible amount of methanol was formed if mixed oxidation and reduction catalysts were under CO₂ and moisture. At anode, water was dissociated over Pt catalyst to provide protons (H₂O → OH(adsorbed) + H⁺ + e⁻) that transferred to Zn-Cu-Ga catalysts at cathode on which CO₂ was progressively reduced to methanol (CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O).

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1. Introduction

Chemical/biological conversion of carbon dioxide is attracting greater attentions to reduce one of the major green house gases [1]. Solar-driven thermal dissociation of CO₂ was reported with water utilizing cerium oxide [2]. The photocatalytic CO₂ conversion is also investigated to solve global environmental problem [1,3,4]. The choice of reductant, e.g. hydrogen or water and the selectivity to fuels, e.g. methanol are keys for the practical application. Especially, CO₂ conversion with water is a difficult problem and this situation hampers environmental application of catalysts to CO₂ removal.

In this work, the CO₂-reducing catalyst was separated from a reductant (hydrogen or water) and the oxidation catalyst by polymer electrolyte (PE) film and thus exclusive methanol formation was enabled. In the analogy to PE fuel cells (FC), Pt/C catalyst was chosen for the oxidation of H₂ and moisture [5]. The Zn-Cu-Ga-based reduction catalyst was chosen based on the elemental composition of industrial methanol synthesis catalysts starting from CO and/or CO₂ [6–8]. When hydrogen was used, PEFC using CO₂ was enabled for the first time. Even when water was used, partial oxidation of water and CO₂ reduction to methanol successfully

proceeded owing to the separation of the two half-reactions by the PE film.

The catalytic reaction mechanism was also investigated by changing the oxidation catalysts (Pt/C, C only), reduction catalysts (Zn-Cu-Ga/C, Zn-Cu-Ga only), and the reactant (H₂ and/or water). In addition, the kinetic tests using PEFC were compared to tests in a Pyrex reactor under CO₂ + H₂ gas or CO₂ + H₂O gas.

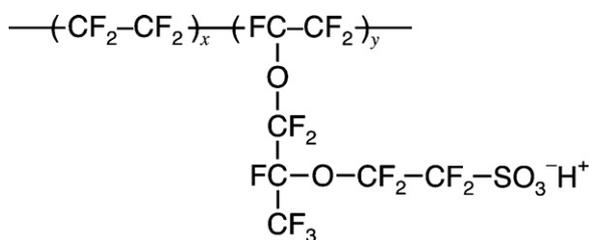
2. Experimental

50 μm thick perfluorosulfonic acid ionomer Nafion (Scheme 1; NR-212, Dupont; >95%, acid capacity >9.2 × 10⁻⁴ equivalent g⁻¹) was pasted with 20 wt% of Pt/C (19 mg; Vulcan XC72, Cabot) attached on water-repellent C paper (EC-20-10-7, Electrochem) or with C powder (Vulcan XC72R, 19 mg) attached on water-repellent C paper on one side and also layered double hydroxide [Zn_{1.5}Cu_{1.5}Ga(OH)₈]⁺₂(CO₃)₂⁻·mH₂O (abbreviated as Zn-Cu-Ga LDH, m ~ 4; 6.9–10 mg) [8,9] and/or Vulcan XC72R (6.9 mg) on the other side. The area of both catalysts was 3.8 cm². After adding 0.4 mL of 3% Nafion dispersion solution (DE521-CS, Wako Pure Chemical) to each side, the membrane-electrode assembly (MEA) was pressed with 2.0 MPa at 393 K for 10 min using Model SA-302, Tester Sangyo Co.

Catalytic CO₂ reduction tests were conducted using a PEFC based on a Model PEM-004 (Chemix Co.). To the Pt/C or C catalyst, 10 mL min⁻¹ of H₂ (101 kPa) or 50 mL of N₂ (101 kPa) was

* Corresponding author. Tel.: +81 43 290 3696; fax: +81 43 290 2783.

E-mail address: yizumi@faculty.chiba-u.jp (Y. Izumi).



Scheme 1. The structure of perfluorosulfonic acid ionomer used in this study (Nafion).

flowed via glass filter with pores of 5–10 μm filled in water set at 343 K. The tube between the glass filter bubbler and the inlet to PEFC was kept at 348 K. To the Zn-Cu-Ga LDH catalyst with/without C, 240 mL min^{-1} of CO_2 (2.6 kPa) [$+\text{H}_2$ (27 kPa)] + balance He to 101 kPa or 240 mL min^{-1} of He (101 kPa) was circulated in a loop of 172 mL.

The PEFC was maintained at 413 K for 5 h and the products at the cathode were analyzed using an online gas chromatograph (GC) with thermal conductivity detector (Shimadzu, Model GC8A) equipped with 2 m of polyethylene glycol-6000 supported on Flusin P and 3 m of Molecular Sieve 13X-S columns (GL Sciences).

The outlet gas from the anode was trapped in a flask cooled in liquid N_2 bath and obtained aqueous solution (~ 3 mL) was mixed with 15 μL of 30 wt% $\text{Ti}(\text{SO}_4)_2$ solution (Wako Pure Chemical). The concentration of H_2O_2 was evaluated based on the UV absorption intensity at 404 nm using a UV-visible spectrophotometer (JASCO, Model V-650). The MEA was washed with 5 mL of water after catalysis test and the wash was analyzed on UV-visible spectrometer in a similar manner.

Alternatively, 10 mL min^{-1} of CO_2 (101 kPa) was flowed via the water bubbler (343 K) and the tube between the bubble and PEFC was set at 348 K. 240 mL min^{-1} of water (2.8 kPa) + He (99 kPa) was circulated in a loop to the Pt/C catalyst. During the catalytic tests, the MEA was maintained as wet. The products at the anode were analyzed using the online MS 13X-S column. Control tests using the physical mixture of Zn-Cu-Ga (6.9 mg) + Pt/C (19 mg) and Zn-Cu-Ga (6.9 mg) alone were performed in a Pyrex reactor in CO_2 (2.7 kPa) + H_2O (2.0 kPa) and CO_2 (2.7 kPa) + H_2 (27 kPa), respectively.

3. Results

The result of CO_2 reduction test over Zn-Cu-Ga/C catalyst separated from Pt/C catalyst under H_2 + moisture is listed in Table 1a. Methanol was the major product (95 mol%, C-basis) accompanied with minor CO. The average current for the reaction of 5 h was 88 $\mu\text{mol-e}^- \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$, corresponding to 97% of the summation of six and two electrons required to reduce CO_2 into methanol and CO, respectively (Fig. 1a and Scheme 2a). In our knowledge, this is the first report of the feasibility of PEFC supplied with CO_2 and produce methanol at the same time.

Compared to the entry a, negligible current was monitored when moisture only was fed to Pt/C catalyst (Table 1b). Methanol was produced with the rate of 35% compared to that in entry a. The methanol selectivity was >86 mol% if the detection limit of CO using GC was considered. The methanol formation was enabled even from CO_2 and water utilizing PEFC in entry b.

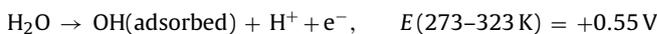
Two thermally reversible transitions are known below 423 K and above 513 K for Nafion [10]. Below 423 K, short-range segmental motions (glass transition) within a static network occur while above 513 K the long-range molecular mobility begins due to destabilization of the electrostatic network. Though the reaction temperature in this study (413 K) was near the first reversible transition, the structure was stable until 493–553 K in aqueous

system and the sulfate ligand (Scheme 1) is enough thermally stable [10–12]. Furthermore, reversible shape memory effect of Nafion was demonstrated at 413 K [10].

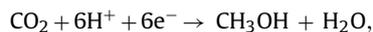
To confirm the stability, reaction tests of entries a and b at 373–413 K were repeated in total 45 h (35 h at 413 K) keeping the MEA always in moisture. The methanol formation rate for fresh MEA for entry b negligibly changed within 3% compared to a repeated test for the condition of entry b at the end of 45 h of use. This fact excludes the possibility that the significant irreversible change of Nafion affected the catalysis at 413 K in the presence of moisture.

As for the reaction mechanism in entry b, overall reaction of $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 1.5\text{O}_2$ was assumed, however, O_2 evolution was not detected at the anode ($<0.2 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$; Table 1b). By assuming another reaction mechanism via H_2O_2 , H_2O_2 was monitored during the PEFC test. The amount was less than the detection limit of 20 nmol at the outlet of anode and in the washing of used MEA, excluding the possibility of water disproportionation [13]. Further, the electronic state of Pt in the MEA during entry b was investigated by Pt $L_{3\text{-edge}}$ X-ray absorption fine structure at SPring-8, Ako, Japan (white line peak intensity, EXAFS curve fits). The molar ratio of population of Pt^0 and $\text{Pt}^{\text{IV}}\text{O}_2$ sites was 0.81:0.19 before the PEFC test and essentially unchanged at 0.78:0.22, 0.83:0.17, and 0.81:0.19 at 2, 5, and 20 h of reaction, respectively. Thus, the possibility that sacrificial oxidation of Pt surface produced H species from water was also denied.

Therefore, partial oxidation of water should proceed following the equation (onset, in SHE [14])



on Pt/C catalyst and subsequent reaction at cathode (in SHE [15,16])



occurred. Based on the standard redox potential values for the anodic and cathodic reactions, this cell reduction did not proceed spontaneously, but required a catalyst for CO_2 reduction. The available protons in Nafion ($\sim 5.0 \times 10^{-5}$ equivalent) were by more than one order greater than the amount of H needed to form methanol and CO in the entries a–g. Thus, consumed protons of Nafion in proximity to cathode catalyst (Zn-Cu-Ga/C) would be compensated from ones generated from water in proximity to anode catalyst (Pt/C; Scheme 2b). The protons apparently moved from anode to cathode side in Nafion, and the negative charge consumed for the CO_2 reduction at cathode could be also compensated as the apparent move of hydroxy ions in the same direction (Scheme 2b). Due to this situation, negligible current was monitored in entry b. The overall reaction was expressed as $\text{CO}_2 + 5\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 6\text{OH}(\text{ads})$.

When H_2 was added to CO_2 at the cathode (entry c), the test result was essentially identical with that of entry a. The direct reaction from $\text{CO}_2 + \text{H}_2$ was predominant.

Next, the selective methanol formation using Pt/C catalyst for activating water and Zn-Cu-Ga/C catalyst for activating CO_2 (entry b) was compared to entry d where the Pt content was depleted. The methanol formation rate ($0.7 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) was only 13% of that in the presence of Pt and the current was also negligible (Table 1b and d). Thus, Pt was found to be essential for the activation of water. The protons in Nafion could be consumed to form methanol at cathode, but protons were not compensated from water at anode in the absence of Pt.

In comparison to the entry a where 97% of FC current was monitored during the CO_2 conversion to methanol and CO, pure Zn-Cu-Ga LDH was set in the cathode, not mixed with C (Table 1e). In the entry e, PEFC current was negligible. Thus, mixed C at cathode

Table 1Results of CO₂ reduction tests for 5 h using the Zn-Cu-Ga catalyst separated from Pt/C or C catalyst by Nafion and using Zn-Cu-Ga and/or Pt/C catalyst(s) in a Pyrex reactor.

Ent. ^a	Anode		Cathode		Average formation rate ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$)			Methanol selectivity (mol%, C-base)	Current ($\mu\text{mol}\cdot\text{e}^{-} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$)/6 ^{b,d}
	Catalyst	Reactant	Catalyst	Reactant	Methanol ^b	CO ^b	O ₂ ^c		
a	Pt/C	H ₂ + H ₂ O	Zn-Cu-Ga/C	CO ₂	14.7	0.7	–	95	14.7
b	Pt/C	H ₂ O	Zn-Cu-Ga/C	CO ₂	5.1	<0.8	<0.2	>86	–0.10
b'	–	–	Zn-Cu-Ga/C + Pt/C	CO ₂ + H ₂ O	0.7	<0.04	–	>95	–
c	Pt/C	H ₂ O	Zn-Cu-Ga/C	CO ₂ + H ₂	15.3	<0.8	–	>95	1.1
c'	–	–	Zn-Cu-Ga	CO ₂ + H ₂	14.6 ^e	<0.04 ^e	–	>99	–
d	C	H ₂ O	Zn-Cu-Ga/C	CO ₂	0.7	<0.8	–	>46	0.17
e	Pt/C	H ₂ + H ₂ O	Zn-Cu-Ga	CO ₂	4.5	<0.8	–	>85	0.18
f	Pt/C	H ₂ O	Zn-Cu-Ga	CO ₂	5.6	<0.8	–	>88	0.12
g	Pt/C	H ₂ O	Zn-Cu-Ga/C	(He)	0.9	<1.0	–	>47	–0.10

^a Entries a–g were done in PEFC. Entries b' and c' were tested in Pyrex glass system.^b Values per 1 g of Zn-Cu-Ga catalyst.^c Values per 1 g of Pt/C catalyst.^d Divided by 6 to compare to six electron reduction rates from CO₂ to methanol. The current sign is positive if electrons moved from anode to cathode.^e Average rates in 2 h.

was essential for PEFC supplied with CO₂ (Scheme 2a). Interestingly, the methanol formation rate ($4.5 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) was in the same order as that for the entry b ($5.1 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) where C was mixed with Zn-Cu-Ga LDH catalyst but only moisture was supplied to the Pt/C catalyst.

Compared to entry e, only moisture was fed to Pt/C catalyst in entry f. The current value and methanol formation rate were essentially identical to those in the entry e (Table 1f). Thus, the protons generated on Pt surface derived either from H₂O or H₂ should have transferred to the Zn-Cu-Ga catalyst, suggesting similar reaction

mechanism including apparent protons/hydroxy species transfer from anode to cathode side in Nafion in entries b, e, and f.

In the comparison of entries a and e supplying H₂ for anode, mixed C in cathode was critical for external current and faster methanol formations. In contrast, entries b and f supplying moisture for anode, mixed C exhibited essentially no catalytic difference. In fact, in entries b and f, effective electron flow was not initiated at the Pt/C electrode (Scheme 2b) on which the half reaction $\text{H}_2\text{O} \rightarrow \text{OH}(\text{adsorbed}) + \text{H}^+ + \text{e}^-$ occurred but the electrons would be unfortunately trapped at electronegative OH(adsorbed) species.

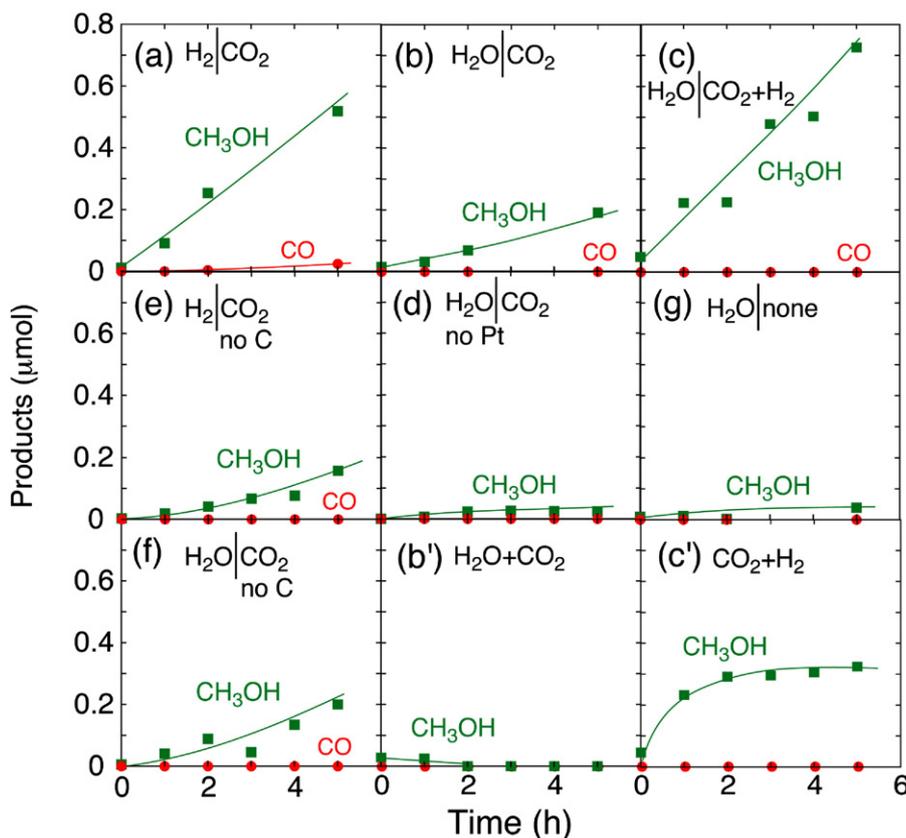
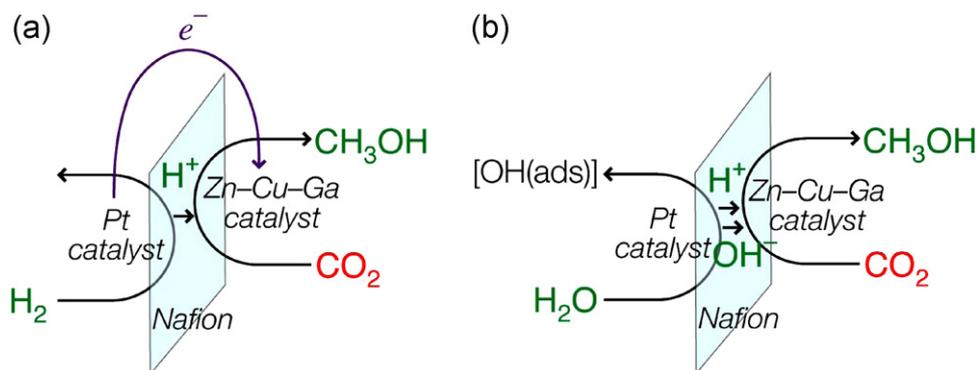


Fig. 1. Time course of CO₂ reduction tests using PEFC. (a) H₂ + moisture fed to Pt/C and CO₂ fed to Zn-Cu-Ga LDH/C, (b) moisture to Pt/C and CO₂ to Zn-Cu-Ga/C, (c) moisture to Pt/C and CO₂ + H₂ to Zn-Cu-Ga/C, (d) moisture to C and CO₂ to Zn-Cu-Ga/C, (e) H₂ + moisture to Pt/C and CO₂ to Zn-Cu-Ga, (f) moisture to Pt/C and CO₂ to Zn-Cu-Ga, and (g) moisture to Pt/C and He to Zn-Cu-Ga/C. CO₂ pressure: 2.6 kPa. Moisture pressure: 31 kPa. H₂ pressure: 101 kPa except for (c) (27 kPa). Control reaction tests in a Pyrex reactor in CO₂ (2.7 kPa) + H₂O (2.0 kPa) (b') and in CO₂ (2.7 kPa) + H₂ (27 kPa) (c').



Scheme 2. Proposed reaction mechanism using PEFC starting from H_2 and CO_2 (a) and from H_2O and CO_2 (b).

Thus, mixed C in cathode in entry b did not have a chance to conduct current.

As a blank test to entry b, He was fed to Zn-Cu-Ga/C catalyst instead of CO_2 (Table 1 g). The current was negligible, and the methanol formation rate ($0.9 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) was 17% of that for entry b. The C source was carbonates those were intercalated between Zn-Cu-Ga cation layers. Two thirds of carbonates of LDH catalyst remain at the reaction temperature 413 K, corresponding to 4.9–7.2 μmol per 6.9–10 mg of Zn-Cu-Ga LDH [8]. The amount was greater than the methanol obtained in the entry g.

In a Pyrex reactor filled with Zn-Cu-Ga LDH catalyst in $\text{CO}_2 + \text{H}_2$ (entry c'), the methanol formation rate was essentially equivalent to that in entry a. The selective catalysis to methanol was also possible in Pyrex reactor, but FC current was obtained in entry a (Scheme 2a). In the Pyrex reactor filled with the physical mixture of Zn-Cu-Ga/C and Pt/C in $\text{CO}_2 + \text{H}_2\text{O}$ (entry b'), negligible reaction proceeded.

4. Discussion

In the comparison of Table 1a and c, the efficient catalysis proceeded in similar rates if the H_2 and CO_2 supply was separated by Nafion film to generate current in entry a. The PEFC supplied with $\text{H}_2 + \text{CO}_2$ at 413 K in this work will be further developed to photo-PEFC supplied with CO_2 or air at 290 K because the cathode catalyst in this work worked at 290 K under UV–visible light to convert CO_2 into methanol [8,9].

The feasibility of PEFC supplied with $\text{H}_2\text{O} + \text{CO}_2$ at 413 K could not be demonstrated as current, but methanol was selectively produced. Partial decomposition $\text{H}_2\text{O} \rightarrow \text{OH}(\text{adsorbed}) + \text{H}^+ + \text{e}^-$ should proceed, but the rate was slower than proton transfer rate in Nafion and CO_2 reduction reaction over Zn-Cu-Ga catalyst. The rate balance of reaction steps in PEFC disabled stoichiometric current based on Scheme 2a, and charges transferred in Nafion. Nevertheless, photo-PEFC supplied with $\text{H}_2 + \text{CO}_2$ at 290 K is possible in principle [17], if excellent water-splitting photocatalyst consisting of deeper bandgap energy is used to form O_2 [18].

The partial oxidation of water at anode in entry b can be supported by previous reports. The O–H bond dissociation over Pt surface was reported to be relatively easy (72 kJ mol^{-1} on Pt(1 1 1) face) compared to over Cu, Au, Ni, or Pd surface [19]. The dissociative adsorption of water was reported to be less stable only by 6.3 kJ mol^{-1} compared to non-dissociative adsorption on Pt(1 1 1) face [20]. In the comparison of kinetic tests in entries a–g, O–H bond of water was dissociated over Pt surface and the protons transferred to cathode Zn-Cu-Ga LDH catalyst to reduce CO_2 into methanol.

5. Conclusions

Stoichiometric current was obtained when H_2 and CO_2 were fed to Pt/C and Zn-Cu-Ga LDH catalysts at anode and cathode, respectively, in PEFC. The PEFC supplied with CO_2 simultaneously produced methanol. When moisture and CO_2 were fed, owing the separation of oxidation and reduction catalysts by the PE film, methanol synthesis was enabled. If the PE film was not used, negligible reaction proceeded. In PEFC, water partially decomposed to $\text{OH}(\text{adsorbed}) + \text{H}^+ + \text{e}^-$ and transferred protons in Nafion reduced CO_2 to methanol in cathode.

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