Utilization of renewable energy has been proposed for solution of the Global Warming. Electroreduction of CO2 into valuable chemicals using renewable electricity is a promising technology. Electroreduction of CO2 to CO and CH4 was studied using the polymer-electrolyte-membrane (PEM) gas cell. The electrocatalyst prepared by partial pyrolysis of Co-4,4'-dimethyl-2,2'-bipyridine supported on KEJENBLACK at 673 K (Co-dmbpy/KB(673 K)) has been found for selective reduction of CO2 to CO. Screening of co-catalysts to promote formation of CH4 during the CO2 reduction by the Co-dmbpy/KB(673 K) cathode was conducted in this work. An effective Ni/KB co-catalyst prepared by H2 reduction at 673 K was found. Suitable preparation conditions and methods of the cathode and effects of cathode potentials on the CO2 reduction to CO and CH4 were studied. The reaction path for the formation of CH4 in the CO2 reduction was studied and the successive reduction of CO2 to CO on the Co-dmbpy/KB(673 K) catalyst and CO to CH4 on the Ni/KB(673 K) co-catalyst was determined.

KEY WORDS: CO2 reduction; CO and CH4 formation; Co–N–C electrocatalyst; Ni co-electrocatalyst.
electrocatalyst using the impregnation method and the heat-treatment in inert gas has been already reported.\textsuperscript{15,16} A brief procedure is as following, KETJENBLACK ECP (KB) powder is added to ethanol solutions of dmbpy (4,4'-dimethyl-2,2'-bipyridine) and Co(NO\textsubscript{3})\textsubscript{2}: 6H\textsubscript{2}O. The mixtures are evaporated at 343 K and the precursor is obtained. The precursor is activated by heat-treatments 673 K in He for 1 h. The electrocatalyst abbreviated as Co-dmbpy/KB(673K) is obtained and the loading of Co was 1.0 wt%.

Various co-electrocatalysts were prepared form metal salts (NiCl\textsubscript{2}: 6H\textsubscript{2}O, FeCl\textsubscript{2}: 4H\textsubscript{2}O, CuCl\textsubscript{2}: 2H\textsubscript{2}O, CeCl\textsubscript{2}: 7H\textsubscript{2}O, ZnCl\textsubscript{2}, H\textsubscript{2}AuCl\textsubscript{4}: 4H\textsubscript{2}O, Mn(NO\textsubscript{3})\textsubscript{2}: 6H\textsubscript{2}O, Pb(NO\textsubscript{3})\textsubscript{2}, AgNO\textsubscript{3}) and KB powder by using a conventional impregnation method and reduction with H\textsubscript{2} at 773 K, as abbreviated metal/KB(773K). Loadings of metals were 10.0 wt%.

2.2. Electrode Preparation and Fabrication of Membrane Electrode Assembly (MEA)

2.2.1. Electrode Preparation

Mixing Method: A cathode was prepared by a mixing method using the 1wt%Co-dmbpy/KB(673K) electrocatalyst powder (9.0 mg), a 10wt%Metal/KB co-electrocatalyst (9.0 mg), a vapor-grown-carbon-fiber powder (VGCF, Showa Denko Co, 30.0 mg) as an electroconductive additive and a PTFE powder (F-104, Daikin Co., 3.0 mg) as a binder. The four powders were well mixed and kneaded to a clay-like ball using a mortar and pestle, pressed and shaped to a round sheet (2 cm\textsuperscript{2}, 0.8–0.9 mm thickness). The Co loading of 1wt%Co-dmbpy/KB(673K) is 45 μg cm\textsuperscript{-2} and 0.75 μmol cm\textsuperscript{-2} of Co. The anode was prepared from 50 wt% Pt/KB (25 mg), VGCF (25 mg), PTFE (5 mg) powders.

Coating Method: The catalyst ink was made from the 1wt%Co-dmbpy/KB(673K) electrocatalyst (5 mg), 10wt%Ni/KB(773K) (5 mg) and the Naftion solutions (10wt% Naftion solution 100 μL, acetone 1 000 μL) by ultrasonic mixing for 10 min.\textsuperscript{15} The ink was homogeneously coating on a gas-diffusion-electrode sheet (2 cm\textsuperscript{2}, SIGRACET\textsuperscript{\textregistered} GDL-25BC) and dried in vacuum. The Co loading of 1wt%Co-dmbpy/KB(673K) is 25 μg cm\textsuperscript{-2} and 0.42 μmol cm\textsuperscript{-2} of Co.

2.2.2. MEA Fabrication

A membrane electrode assembly (MEA) was prepared by a hot-press method. A Naftion electrode (Naftion 117) was pressed between the cathode and anode at 413 K at 59 MPa and then immersed in deionized water for 5 min. The formed MEA was set in a gas-electrolysis cell.

2.3. Electrochemical Reduction of CO\textsubscript{2}

Figure 1 shows the gas-electrolysis cell for CO\textsubscript{2} reduction.\textsuperscript{14–16} Pure H\textsubscript{2} gas (20 mL min\textsuperscript{-1}) and pure CO\textsubscript{2} gas (10 mL min\textsuperscript{-1}) were introduced into the anode and cathode compartments, respectively. In addition, to humidify the Naftion membrane, a 0.5 mL of deionized water was introduced in the cell and H\textsubscript{2} bubbled through deionized water. Potentiostatic electrolysis was performed using an electrochemical measurement system (Hokuto Denko Co. HZ-5000) at 273 K. Potentials were indicated basis on SHE. Constant potentials from −0.50 to −0.75 V (SHE) were applied to the cathode. Products were analyzed by using two gas-chromatograph equipments (H\textsubscript{2} analysis: a TCD detector, an activated-carbon column with Ar; CO analysis: a molecular-sieves-5A column with He).

In electroreduction of CO\textsubscript{2} at cathode, formation of CO and CH\textsubscript{4} are expected and unfavorable one is H\textsubscript{2}. A conversion of CO\textsubscript{2}, formation rates of CO, CH\textsubscript{4} and H\textsubscript{2}, Conv(CO), FR(CO), FR(CH\textsubscript{4}) and FR(H\textsubscript{2}) respectively, were calculated form average yields for 30 min. The faradic efficiencies of CO, CH\textsubscript{4} and H\textsubscript{2} formations, CE(CO), CE(CH\textsubscript{4}) and CE(H\textsubscript{2}) respectively, were calculated on a basis of a coulomb for each product formation against a sum of coulomb (Eq. (4)).

\[
CE = \frac{\text{coulomb for product formation}}{\text{sum coulomb}} \times 100\% \quad \text{(4)}
\]

3. Results & Discussion

3.1. Effect of co-electrocatalyst Addition on CH\textsubscript{4} Formation

The Co-dmbpy/KB(673K) electrocatalyst was active for the reduction of CO\textsubscript{2} to CO and a trace amount of CH\textsubscript{4} was produced. At −0.70 V(SHE), typical data were \(i_0 = 16.9\) mA cm\textsuperscript{-2}, FR(CO) = 254 μmol h\textsuperscript{-1} cm\textsuperscript{-2}, CE(CO) = 78%, FR(CH\textsubscript{4}) = 0.16 μmol h\textsuperscript{-1} cm\textsuperscript{-2}, CE(CH\textsubscript{4}) = 0.2%, FR(H\textsubscript{2}) = 69 μmol h\textsuperscript{-1} cm\textsuperscript{-2}, CE(H\textsubscript{2}) = 22% over the Co-dmbpy/KB(673K)-GDL cathode prepared by the coating method.\textsuperscript{15} Effects of co-catalysis of metal (10 wt%) supported on KB (metal: Mn, Fe, Co, Ni, Cu, Zn, Ce, Ag, Au, Pb) were studied for electroreduction of CO\textsubscript{2} by the Co-dmbpy/KB(673K) cathode prepared by the mixing method at −0.70 V (SHE) in Table 1. A 9 mg of metal/KB(773K) co-catalyst was mixed into a 9 mg of the Co-dmbpy/KB(673K) electrocatalyst and a 30 mg of VGCF powder, which was prepared to a cathode by the hot-press method as described in the experimental section. Cathodes made from various co-catalysts and the Co-dmbpy/KB(673K) electro-
catalyst were applied for CO2 reduction. Products were CO2, H2 and CH4 for all case. A sum of CEs was almost 100% within experimental errors. A cathode prepared by addition of KB powder to the Co-dmbpy/KB(673K) electrocatalyst was tested as a reference in run1. Though a formation of H2 was enhanced and Conv and FR(CO) values were decreased a little by addition of KB, the major reduction of CO2 to CO and the minor reduction to CH4 were conformed as mentioned above. Among the additives tested in the Table 1, significant enhancing effects on FR(CH4) or CE(CH4) were observed for co-catalysts of Ni/KB(773K) in run 5, Zn/KB(773K) in run 7 and Au/KB(773K) in run 10. On the Ni/KB(773K) and Zn/KB(773K) co-catalysts, the both FR(CH4) and CE(CH4) increased with holding the electrocatalytic activity of the CO formation of the reference cathode (run 1). On the Au/KB(773K) co-catalyst, the FR(CH4) significantly increased but FR(CO) decrease a little and the FR(H2) drastically increased. Therefore, the small increase in CE(CH4) and the large decrease in CE(CO) were observed for the Au/KB co-catalyst. Other additives were not effective for the CO2 reduction. In addition, the Co/KB(773K) additive in run 4 enhanced the FR(H2) and suppressed the FR(CO). This indicated that Co0 was not the active site for the CO2 reduction on the Co-dmbpy/KB(673K) cathode.

### 3.2. Effects of Cathode Potentials on CO and CH4 Formations

As described above, the Ni/KB(773K), Zn/KB(773K) and Au/KB(773K) co-catalysts accelerated the formation of CH4 through the electroreduction of CO2 at −0.70 V(SHE). Effects of cathode potentials on the CO2 reduction at the Co-dmbpy/KB(673K)+ Ni/KB(773K), Zn/KB(773K) or Au/KB(773K) cathodes were studied in Fig. 2(a) (a) FR(CO) and FR(CH4), (b) CE(CO) and CE(CH4). As shown in Fig. 2(a), Tafel plots (log i vs. potential) for the Ni/KB(773K), Zn/KB(773K) or KB(773K)-modified cathodes were almost on the same line. On the other hand, the similar plot for the Au/KB(773K)-modified cathode was on a different line. The FRs(CO) of the all cathodes increased with decreasing in the potentials on the same exponential curve, whereas the FRs(CH4) of the cathodes increased on different exponential curves, as shown in Fig. 2(b). An onset potential around −0.4 V for the formation of CH4 at the Au/KB-modified cathode was higher than that around −0.5 V at other cathodes. Fairly high FRs(CH4) were observed around −0.7 V; however the electroreduction of CO2 could not be conducted by an explosive formation of H2 under −0.75 V. The FR(CH4) on the Ni/KB(773K)-modified cathode increased with decreasing in potentials and a high FR(CH4) of 3.9 μmol h⁻¹ cm⁻² was obtained at −0.8 V(SHE). In the case of the Zn/KB(773K)-modified cathode, the electroreduction could not be done by the explosive formation of H2. A low FR(CH4) of 0.34 μmol h⁻¹ cm⁻² on the KB(773K)-modified cathode was observed at −0.8 V(SHE). As described above, the FRs(CO) were very similar among the four cathodes but CEs(CO) were different. Especially, the CE(CO) at the Au/KB-modified cathode was very low to compare with that at other cathodes. This low CE(CO) was due to fast formation of H2 on the Au/KB-modified cathode. Therefore, CEs(CH4) on the Au/KB(773K)-modified cathode were very low though the FRs(CH4) were fairly high. On the other hand, the Ni/KB(773K)-modified cathode showed a fairly high CE(CH4) of 2.2% at −0.80 V.

From the screening test of co-catalysts to the Co-dmbpy/KB(673K) electrocatalyst, the Ni/KB(773K) co-catalyst showed a good ability to promote formation of CH4 during the CO2 electroreduction because of the higher FR(CH4) and CE(CH4) with keeping high FR(CO) and CE(CO) at −0.80 V.

### 3.3. Improvement of the Co-dmbpy/KB(673K)+Ni/KB Cathode on CH4 Formation

In order to improve electrocatalytic activity of the cathode, effects of reduction temperature of Ni/KB co-catalyst were studied in run 2, 12, 13 of Table 2. The Ni/KB co-catalyst used in Fig. 1 and Table 1 was reduced with H2 at 773 K, as abbreviated Ni/KB(773K). The Ni/KB(773K) material was characterized by XRD analysis and formation.
of Ni\(^0\) crystal as 17.1 nm crystal size was determined from XRD pattern and the Scherrer’s equation. To expect enhancing co-catalysis of Ni\(^0\) by reduction of the crystal size, the reduction temperature with H\(_2\) was decreased from 773 K to 673 and 573 K and crystal sizes of 12.1 and 6.7 nm were obtained, respectively. Electrocatalytic reduction activity for CO\(_2\) on the Co-dmbpy/KB(673K)+Ni/KB(673K) and Ni/KB(573K) cathodes at −0.70 V(SHE) were indicated in runs 12 and 13, respectively. The \(i_d\) values largely increased but the reduction rate of CO\(_2\) did not drastically change. The FR(CH\(_4\)) was enhanced from 0.67 to 1.23 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\), 2 times, by mixing the Ni/KB(673K) co-catalyst and 1.5 times by mixing Ni/KB(573K) co-catalyst though their CE(CO) and CE(CH\(_4\)) were low. The Ni/KB(673K) co-catalyst was suitable for the CH\(_4\) formation.

In run 14, Nafion solutions were painted on the surface of the Co-dmbpy/KB(673K)+Ni/KB(673K) cathode because an increase in an area of electrochemical active site and an improvement in electrocatalysis of the cathode were expected. Though the large increase in the \(i_d\) value corresponded to a large increase in FR(H\(_2\)), the FR(CH\(_4\)) increased from 1.23 to 4.17 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) and the CE(CH\(_4\)) increased from 0.86 to 1.74% by the Nafion painting. In run 15, the catalyst ink of Co-dmbpy/KB(673K) and Ni/KB(673K) was coated on the GDL-25BC gas-diffusion-electrode as described in the experimental section. Remarkable increases in FR(CH\(_4\)) of 11.69 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) and in CE(CH\(_4\)) of 2.25% were observed against the results in run 12, though a large increase in the \(i_d\) value corresponded to FR(H\(_2\)). The sums of CE(H\(_2\)), CE(CO) and CE(CH\(_4\)) were almost 100% within experimental error (2%) in all cases of Table 2. In addition, ethane, ethylene and propane formations were observed in run 15 as below, FR(C\(_2\)H\(_6\)) = 0.25 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) CE(C\(_2\)H\(_6\)) = 0.08%, FR(C\(_2\)H\(_4\)) = 0.05 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) CE(C\(_2\)H\(_4\)) = 0.01%, FR(C\(_3\)H\(_8\)) = 0.04 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\) CE(C\(_3\)H\(_8\)) = 0.02%. The FR and CE of higher hydrocarbons on the dmbpy/KB(673K) cathode are very low but are very interesting because of no formation of higher hydrocarbons on the Co-dmbpy/KB(673K) cathode. Synergy of Co-dmbpy/KB(673K) and

| run | Cathode preparation | \(\text{Ni}^0/\text{KB}\) | \(i_d/\text{mA cm}^{-2}\) | Conv. % | FR/\(\mu\)mol h\(^{-1}\) cm\(^{-2}\) | CE/% |
|-----|---------------------|---------------------|---------------------|---------|---------------------|-------|
| 12 mixing | 773 | 17.1 | 18.3 | 1.74 | 212.0 | 0.67 | 66.8 | 0.79 |
| 12 mixing | 573 | 6.9 | 27.4 | 1.55 | 188.9 | 1.05 | 14.0 | 0.3 |
| 14 Nafion painting | 673 | 12.7 | 51.4 | 1.52 | 181.5 | 4.17 | 18.9 | 1.74 |
| 15 coating | 673 | 12.7 | 116.7 | 3.01 | 357.0 | 11.69 | 16.4 | 2.15 |

Table 2. Effects of co-catalyst addition to the Co-dmbpy/KB(673K) electrocatalyst on electroreduction of CO\(_2\) at −0.70 V(SHE) and 273 K.

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626
Ni/KB(673K) would be expected for the formation of higher hydrocarbons.

3.4. Reaction Path for CH₄ Formation on the Co-dmbpy/KB(673K) + Ni/KB(673K) Cathode

As described so far, the electroreduction of CO₂ to CO and CH₄ proceeded on the Co-dmbpy/KB(673K) + Ni/KB(673K) cathode. In order to know reaction path for CH₄ formation, (i) electroreduction of CO on the Co-dmbpy/KB(673K) cathode, (ii) electroreduction of CO₂ on the Ni/KB(673K) cathode, and (iii) electroreduction of CO on the Ni/KB(673K) cathode were conducted at −0.70 V (SHE) and 273 K. It was revealed that (i) the electroreduction of Ni/KB(673K) cathode were conducted at −0.70 V (SHE) and 273 K, formation of CH₄ was not observed. In other words, the hydrogenation of CO with H₂ to CH₄ does not proceed on Ni/KB(673K) catalyst. In order to know reaction path for CH₄ formation, (i) electroreduction of CO to CH₄ did not proceed on the Co-dmbpy/KB(673K) cathode, (ii) the electroreduction of CO₂ to CO and CH₄ did not proceed on the Ni/KB(673K) cathode, and (iii) the electroreduction of CO to CH₄ proceeded on the Ni/KB(673K) cathode. In addition, when a gas mixture of CO (0.5 atm) and H₂ (0.5 atm) was introduced over the Ni/KB(673K) at 273 K, formation of CH₄ was not observed. In other words, the hydrogenation of CO with H₂ to CH₄ does not proceed by the Ni/KB(673K) catalyst. Figure 3 shows effects of potentials at the Ni/KB(673K) cathode on the electroreductions of CO₂ and CO, (a) iᵣ and (b) FR(CH₄), CE(CH₄). As mentioned above, the electroreduction of CO₂ to CO did not proceed on the Ni/KB(673K) cathode from −0.30 to −0.80 V though higher iᵣ values corresponding to H₂ formation were observed. However, very low formation of CH₄ was observed at lower potentials from −0.70 to 0.80 V as shown in Fig. 3(b). On the other hand, the electroreduction of CO to CH₄ proceeded on the Ni/KB(673K) cathode from −0.60 to −0.80 V. The iᵣ values in CO were suppressed to compare with that in CO₂. The CEs(CH₄) were not so good and below 6% though 1 atm of CO, high concentration of CO₂ was flowed.

The above results suggested that CO₂ was reduced to CO on the Co-dmbpy/KB(673K) (Eq. (1)) and this CO was successively reduced to CH₄ on the Ni/KB(673K) (Eq. (5)) in the cathode. Remarkable reduction of iᵣ values in CO at the Ni/KB(673K) cathode indicated that CO strongly adsorbed on Ni⁰ surface and suppressed the H₂ formation.

CO + 6H⁺ + 6e⁻ → CH₄ + H₂O  E° = +0.26 V  .... (5)

4. Conclusion

Effects of co-catalysts on the reduction of CO₂ by the Co-dmbpy/KB(673K) cathode were studied. Various co-catalysts were screened and the enhancing effects of Ni/KB(773K), Au/KB(773K) and Zn/KB(773K) co-catalysts on the formation of CH₄ during the CO₂ electroreduction were found. The Ni/KB(773K) co-catalyst was most effective for the formation of CH₄ among the three co-catalysts. Effects of reduction temperatures of the Ni/KB precursor with H₂, of the mixing and coating methods for cathode preparation, and of cathode potentials on the CO₂ reduction with H₂, of the mixing and coating methods for cathode preparation, and of cathode potentials on the CO₂ reduction were clarified and the most suitable cathode was only 2.15% at −0.70 V, the cathode was the GDL electrode coated the 10wt%Ni/KB(673K) co-catalyst and 1wt%Co-dmbpy/KB(673K) catalyst with and Nafion solutions. Although the maximum CE(CH₄) on the suitable cathode was only 2.15% at −0.70 V, the cathode showed the unique electrocatalysis for the formations of C₃H₈ with 0.08% CE, C₅H₁₀ with 0.01%, C₆H₁₄ with 0.02%. Reaction paths for the formations of CO and CH₄ on the Co-dmbpy/KB(673K) + Ni/KB(673K) cathode were studied and the successive reduction scheme of CO₂ to CO on the Co-dmbpy/KB(673K) co-catalyst and CH₄ on the Ni/KB(673K) co-catalyst was clarified.

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