Electrocatalytic Reduction of CO₂ to CO and CH₄ by Co–N–C Catalyst and Ni co-catalyst with PEM Reactor

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(Received on August 10, 2018; accepted on September 25, 2018)

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(673K)) 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(673K) 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(673K) catalyst and CO to CH₄ on the Ni/KB(673K) co-catalyst was determined.

KEY WORDS: CO₂ reduction; CO and CH₄ formation; Co–N–C electrocatalyst; Ni co-electrocatalyst.

1. Introduction

Inhibition of global warming is essential problem for sustainable society and human life. Emission of CO₂ is major factor for the global warming and must be reduced. Utilization of renewable energy instead of fossil fuels has been proposed for the reduction of the CO₂ emission. In this regard, electrochemical reduction of CO₂ into valuable chemicals such as carbon monoxide (CO) and methane using renewable electricity is a promising technology.¹⁻⁴) Kato has proposed application of the Active Carbon Recycle Energy System (ACRES) to iron making process for reduction of CO₂ emission.⁵⁻⁶) In the previous work, the Co–N–C electrocatalyst was prepared by partial pyrolysis of Co(dmbpy)₃ (dmbpy = 4,4’-dimethyl-2,2’-bipyridine) complex supported on carbon materials (c.a. KETJENBLACK) in inert gas (He) at 673 K, as abbreviated Co-dmbpy/KB(673K). Electrocatalytic activity of the Co-dmbpy/KB(673K) cathode for the CO₂ reduction strongly depended on reaction conditions; however, the major product was always CO and byproduct was H₂. The sum selectivity of CO and H₂, corresponding to the current efficiency, was > 99.5%. However, a trace amount of CH₄ formation (< 0.5% current efficiency) was sometimes observed. CH₄ can be utilized as a reductant for the Iron making; therefore, direct formation of CH₄ by electroreduction of CO₂ would be attractive topic. Purposes of this study is to increase the formation rate of CH₄ during the electroreduction of CO₂ by modification of the Co-dmbpy/KB(673K) electrocatalyst by addition of co-catalysts and to study reaction scheme for the CH₄ formation.

2. Experimental

2.1. Preparation of Co–N–C Electro catalyst and co-electrocatalysts

The standard preparation procedure of the Co–N–C...
electrocatalyst using the impregnation method and the heat-treatment in inert gas has been already reported.\textsuperscript{15,16}
A brief procedure is as follows, KETJENBLACK ECP (KB) powder is added to ethanol solutions of dmbpy (4,4'-dimethyl-2,2'-bipyridine) and Co(NO$_3$)$_2$·6H$_2$O. The mixtures are evaporated at 343 K and the precursor is obtained. The precursor is activated by heat-treatment 673 K 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$_2$·6H$_2$O, FeCl$_3$·4H$_2$O, CuCl$_2$·2H$_2$O, CeCl$_3$·7H$_2$O, ZnCl$_2$, HAuCl$_4$·4H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O, Pb(NO$_3$)$_2$), AgNO$_3$) and KB powder by using a conventional impregnation method and reduction with H$_2$ 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$^2$, 0.8–0.9 mm thickness). The Co loading of 1wt%Co-dmbpy/KB(673K) is 45 μg cm$^{-2}$ and 0.75 μmol cm$^{-2}$ of Co. The anode was also 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 Nafion solutions (10wt% Nafion solution 100 μL, acetone 1 000 μL) by ultrasonic mixing for 10 min.\textsuperscript{15,16} The ink was homogeneously coating on a gas-diffusion-electrode sheet (2 cm$^2$, SIGRACET® GDL-25BC) and dried in vacuum. The Co loading of 1wt%Co-dmbpy/KB(673K) is 25 μg cm$^{-2}$ and 0.42 μmol cm$^{-2}$ of Co.

2.2.2. MEA Fabrication

A membrane electrode assembly (MEA) was prepared by a hot-press method. A Nafion membrane (Nafion 117) was pressed between the cathode and anode at 413 K at 59 MPa and then immersed in deionized water for 5 min. After that, it 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$_2$

Figure 1 shows the gas-electrolysis cell for CO$_2$ reduction.\textsuperscript{14–16} Pure H$_2$ gas (20 mL min$^{-1}$) and pure CO$_2$ gas (10 mL min$^{-1}$) were introduced into the anode and cathode compartments, respectively. In addition, to humidify the Nafion membrane, 0.5 mL of deionized water was introduced in the cell and H$_2$ 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$_2$ analysis: a TCD detector, an activated-carbon column with Ar; CO analysis: a molecular-sieves-5A column with He).

In electroreduction of CO$_2$ at cathode, formation of CO and CH$_4$ are expected and unfavorable one is H$_2$.

Cathode: CO$_2$ + 2H$^+$ + 2e$^-$ → CO + H$_2$O  E° = −0.11 V ......................................(1)
CO$_2$ + 8H$^+$ + 8e$^-$ → CH$_4$ + 2H$_2$O  E° = +0.17 V ..................................(2)
2H$^+$ + 2e$^-$ → H$_2$ (side reaction)  E° = ±0.00 V ................................(3)

A conversion of CO$_2$, formation rates of CO, CH$_4$ and H$_2$, Conv, FR(CO), FR(CH$_4$) and FR(H$_2$) respectively, were calculated form average yields for 30 min. The faradic efficiencies of CO, CH$_4$ and H$_2$ formations, CE(CO), CE(CH$_4$) and CE(H$_2$) respectively, were calculated on a basis of a coulomb for each product formation against a sum of coulomb (Eq. (4)).

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

3. Results & Discussion

3.1. Effect of co-electrocatalyst Addition on CH$_4$ Formation

The Co-dmbpy/KB(673K) electrocatalyst was active for the reduction of CO$_2$ to CO and a trace amount of CH$_4$ was produced. At −0.70 V(SHE), typical data were \(i_{\text{d}} = 16.9\) mA cm$^{-2}$, FR(CO) = 254 μmol h$^{-1}$ cm$^{-2}$, FE(CO) = 78%, FR(CH$_4$) = 0.16 μmol h$^{-1}$ cm$^{-2}$, CE(CH$_4$) = 0.2%, FR(H$_2$) = 69 μmol h$^{-1}$ cm$^{-2}$, CE(H$_2$) = 22% over the Co-dmbpy/KB(673K)-GDL cathode prepared by the coating method.\textsuperscript{15,16} 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$_2$ 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 power, 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 CE 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 CH₂ were confirmed as mentioned above. Among the additives tested in the Table 1, significant enhancing effects on FR(CH₄) and FR(CH₄) were observed around −0.7 V; however the electroreduction of H₂ could not be conducted by an 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). 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 and suppressed the FR(CO). This indicated that Co⁶⁺ 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-catalyst increased 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). Tafel plots (log iₐ vs. potential) for the Ni/KB(773K), Zn/KB(773K) or Au/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 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 and suppressed the FR(CO). This indicated that Co⁶⁺ was not the active site for the CO₂ reduction on the Co-dmbpy/KB(673K) cathode.

### Table 1. Effects of metal/KB(773K) co-catalyst addition to the Co-dmbpy/KB(673K) electrocatalyst on electroreduction of CO₂ at −0.70 V(SHE) and 273 K.

<table>
<thead>
<tr>
<th>run</th>
<th>co-catalyst</th>
<th>iₐ mA cm⁻²</th>
<th>Conv. %</th>
<th>Formation Rate μmol h⁻¹ cm⁻²</th>
<th>Current Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KB</td>
<td>16.1</td>
<td>1.74</td>
<td>206.5 0.16 94.5</td>
<td>68.8 0.21 31.5 100.5</td>
</tr>
<tr>
<td>2</td>
<td>Mn/KB</td>
<td>16.4</td>
<td>1.58</td>
<td>193.5 0.21 112.0</td>
<td>63.2 0.28 36.6 100.1</td>
</tr>
<tr>
<td>3</td>
<td>Fe/KB</td>
<td>17.0</td>
<td>1.49</td>
<td>182.3 0.16 145.9</td>
<td>53.5 0.28 46.0 99.8</td>
</tr>
<tr>
<td>4</td>
<td>Co/KB</td>
<td>38.1</td>
<td>0.70</td>
<td>85.9 0.31 620.4</td>
<td>12.7 0.17 87.3 100.2</td>
</tr>
<tr>
<td>5</td>
<td>Ni/KB</td>
<td>18.3</td>
<td>1.74</td>
<td>212.0 0.67 110.2</td>
<td>66.8 0.79 32.3 99.9</td>
</tr>
<tr>
<td>6</td>
<td>Cu/KB</td>
<td>28.0</td>
<td>0.97</td>
<td>118.3 0.20 343.5</td>
<td>34.7 0.15 65.2 100.6</td>
</tr>
<tr>
<td>7</td>
<td>Zn/KB</td>
<td>19.4</td>
<td>1.72</td>
<td>210.8 0.37 149.6</td>
<td>58.2 0.41 41.3 99.9</td>
</tr>
<tr>
<td>8</td>
<td>CeO₂/KB</td>
<td>29.2</td>
<td>1.54</td>
<td>188.6 0.16 359.8</td>
<td>34.6 0.12 66.0 100.8</td>
</tr>
<tr>
<td>9</td>
<td>Ag/KB</td>
<td>29.6</td>
<td>1.61</td>
<td>196.8 0.13 355.0</td>
<td>35.7 0.09 64.3 100.1</td>
</tr>
<tr>
<td>10</td>
<td>Au/KB</td>
<td>116.5</td>
<td>1.50</td>
<td>180.5 3.17 1999.8</td>
<td>8.3 0.58 92.0 100.0</td>
</tr>
<tr>
<td>11</td>
<td>Pb/KB</td>
<td>16.9</td>
<td>1.69</td>
<td>206.6 0.19 97.0</td>
<td>68.8 0.23 30.8 99.8</td>
</tr>
</tbody>
</table>

Cathode: Co-dmbpy/KB(673K)+metal/KB(773K), CO₂: 1atm 20 mL min⁻¹. Anode: Pt/KB, H₂ 1am, 20 mL min⁻¹.

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 μmol 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 μmol 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 μmol 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 μmol h\(^{-1}\) cm\(^{-2}\) CE(C\(_2\)H\(_6\)) = 0.08%, FR(C\(_2\)H\(_4\)) = 0.05 μmol h\(^{-1}\) cm\(^{-2}\) CE(C\(_2\)H\(_4\)) = 0.01%, FR(C\(_3\)H\(_8\)) = 0.04 μmol h\(^{-1}\) cm\(^{-2}\) CE(C\(_3\)H\(_8\)) = 0.02%. The FR and CE of higher hydrocarbons on the dmbpy/KB(673K) co-catalyst were 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

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.

<table>
<thead>
<tr>
<th>run</th>
<th>Cathode preparation</th>
<th>T/K</th>
<th>size/ nm</th>
<th>(i_d)/ mA cm(^{-2})</th>
<th>Conv. %</th>
<th>FR/μmol h(^{-1}) cm(^{-2})</th>
<th>CE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>mixing</td>
<td>773</td>
<td>17.1</td>
<td>18.3</td>
<td>1.74</td>
<td>212.0</td>
<td>0.67</td>
</tr>
<tr>
<td>12</td>
<td>mixing</td>
<td>673</td>
<td>12.7</td>
<td>30.7</td>
<td>2.21</td>
<td>269.5</td>
<td>70.0</td>
</tr>
<tr>
<td>13</td>
<td>mixing</td>
<td>573</td>
<td>6.9</td>
<td>72.4</td>
<td>1.55</td>
<td>188.9</td>
<td>10.0</td>
</tr>
<tr>
<td>14</td>
<td>Nafion painting</td>
<td>673</td>
<td>12.7</td>
<td>51.4</td>
<td>1.52</td>
<td>181.5</td>
<td>18.9</td>
</tr>
<tr>
<td>15</td>
<td>coating</td>
<td>673</td>
<td>12.7</td>
<td>116.7</td>
<td>3.01</td>
<td>357.0</td>
<td>16.4</td>
</tr>
</tbody>
</table>

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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) the electroreduction of Ni/KB(673K) cathode were conducted at −0.70 V(SHE) 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) KB(673K) cathode, and (iii) electroreduction of CO on the Co-dmbpy/KB(673K) cathode. In order to know reaction path for CH₄ formation, (i) electroreduction of CO 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) iₓ 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 iₓ 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 iₓ values in CO were suppressed to compare with that in CO₂. The CEs(CH₄) were not so good and below 6% though 1atm 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 iₓ values in CO at the Ni/KB(673K) cathode indicated that CO strongly adsorbed on Ni⁰ surface and suppressed the H₂ formation.

\[
\text{CO} + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{E}^\circ = +0.26 \text{ V} \quad (5)
\]

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 to CO and CH₄ were clarified and the most suitable cathode was the GDL electrode coated the 10wt%Ni/KB(673K) co-catalyst and 1wt%Co-dmbpy/KB(673K) catalyst with and Naftion solutions. Although the maximum CE(CH₄) on the suitable cathode was only 2.15% at −0.70 V, the cathode appeared the unique electrocatalysis for the formations of C₂H₆ with 0.08% CE, C₃H₈ with 0.01%, C₄H₁₀ 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) and CO to CH₄ on the Ni/KB(673K) co-catalyst was clarified.

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