Aqueous electrocatalytic CO$_2$ reduction using metal complexes dispersed in polymer ion gels

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Experimental

Materials

All reagents and solvents were purchased from Sigma Aldrich and used without further purification. \(\text{fac-}[\text{Re(bpy)(CO)}_3\text{Cl}]\) ([Re-Cl]) and \([\text{Ir(tpy)(ppy)Cl}]\) ([Ir]) were synthesized according to literature methods.$^{1,2,33}$
Preparation of Polymer Ion Gel Electrodes

[Re]-PIG/CC Electrode

The precursor solution was made by combining monomer and [Re-Cl] in dichloromethane (CH\(_2\)Cl\(_2\)). [Re-Cl] (8 mg, 0.017 mmol), ammonium trifluoromethanesulfonate (38 mg) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 ml) were dissolved in 1 mL of CH\(_2\)Cl\(_2\) solution containing silicone rubber (20 mg mL\(^{-1}\)). Then, 50 µL of formic acid (HCOOH) and Tetraethyl orthosilicate (TEOS, 38 µL) were added, and the solution was stirred for five minutes. Dimethylacrylamide/methylenebisacrylamide (0.4 mol % dimethylacrylamide) solution (0.17 mL) and 2,2’-azodiisobutyronitrile (12 mg) as a radical initiator were added to the solution. 0.1 mL of the precursor solution was drop cast onto carbon cloth (CC) on a Teflon seat. The area of CC was about 2.0 cm\(^2\) (1.0 cm × 2.0 cm). The coating procedure was repeated three times (to yield approximately 1.49 µmol cm\(^{-2}\) of [Re-Cl]), and the resulting polymer solution on CC was heated on a hot plate at 393 K for twelve hours, after which the [Re]-PIG was rinsed with distilled water and dried for 1 day. Copper wire was connected to the [Re]-PIG/CC electrode using copper tape, and the edges of the electrode and all connection points were coated with hot glue. A schematic illustration of the [Re]-PIG electrode is shown in Scheme S1.

[Re]/CC Electrode

[Re-Cl] (8 mg) and ammonium trifluoromethanesulfonate (38 mg) were dissolved in 1 mL of CH\(_2\)Cl\(_2\). Then, 50 µL of formic acid (HCOOH) and TEOS (38 µL) were added, and the solution
was stirred for 5 minutes. After stirring, 0.1 mL of solution was drop cast on CC. The area of CC was about 2.0 cm$^2$ (1.0 cm × 2.0 cm). The coating procedure was repeated three times, and the resulting electrode was heated on a hot plate at 393 K for 12 hours. The [Re]/CC electrode was then rinsed with distilled water and dried for 1 day. Copper wire was connected to the [Re]/CC electrode using copper tape, and the edges of the [Re]/CC electrode and the connection points were coated with hot glue.

**PIG/CC Electrode**

Ammonium trifluoromethanesulfonate (38 mg) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 mL) were dissolved in 1 mL of CH$_2$Cl$_2$ containing silicone rubber (20 mg/ml). Then, 50 µL of formic acid (HCOOH) and TEOS (38 µL) were added, and the solution was stirred for five minutes. After stirring, dimethylacrylamide/methylenebisacrylamide (0.4 mol % in dimethylacrylamide) solution (0.17 ml) and 2,2'-azodiisobutyronitrile (12 mg) as a radical initiator were added. The precursor mixed solution (0.1 mL) was drop cast on CC. The area of CC was about 2.0 cm$^2$ (1.0 cm × 2.0 cm). The coating procedure was repeated three times, and the resulting electrode was heated on a hot plate at 393 K for 12 hours, after which the PIG/CC electrode was rinsed with distilled water and dried for 1 day. Copper wire was connected to the electrode using copper tape, and the edges of the electrode and the connection points were covered with hot glue.
[Ir]-PIG/CC Electrode

[Ir] (4 mg, 0.0052 mmol) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 ml) were dissolved in 1 mL of CH$_2$Cl$_2$ containing silicone rubber (20 mg mL$^{-1}$). Then, 50 µL of formic acid (HCOOH) and TEOS (38 µL) were added, and the solution was stirred for five minutes. After stirring, dimethylacrylamide/methylenebisacrylamide (0.4 mol % dimethylacrylamide) solution (0.17 mL) and 2,2'-azodiisobutyronitrile (12 mg) as a radical initiator were added. The solution (0.1 mL) was drop cast on CC. The area of the CC electrode was about 2.0 cm$^2$ (1.0 cm × 2.0 cm). The coating procedure was repeated three times (to yield an approximately 0.45 µmol cm$^{-2}$ of [Ir]), and the resulting electrode was heated on a hot plate at 393 K for 12 hours. Then, the electrode was rinsed with distilled water and dried for 1 day. Copper wire was connected to the electrode using copper tape, and the edges of the [Ir]-PIG electrode and the connection points were coated with hot glue.

CoO(OH)/CP Electrode

CoO(OH) nanoparticles were synthesized according to literature procedure.$^{40}$ CoCl$_2$·6H$_2$O (0.095 g, 0.4 mmol) was dissolved in 125 mL of distilled water. The solution was purged with nitrogen for 30 minutes, after which the solution was heated at 60 °C for 15 minutes. NaOH (0.64 M in H$_2$O, 12.5 mL) and H$_2$O$_2$ (2.4 % in H$_2$O, 5 mL) were added to the solution while stirring at 60 °C. Then, the reaction solution was cooled to room temperature. CoO(OH) nanoparticles were coated on hydrophilic treatment carbon paper (CP) by immersion of the CP into the CoO(OH) reaction
solution. The CoO(OH)/CP electrode was dried overnight, and the electrode was annealed at 423 K for one hour in atmosphere, followed by rinsing with distilled water. Copper wire was connected to the CoO(OH)/CP electrode using copper tape, and the edges of the electrode and the connection points were coated with hot glue. A schematic illustration of the CoO(OH)/CP electrode is shown in Scheme S2.

**Electrochemistry**

Electrocatalytic reactions were performed at atmospheric pressure in a flow reactor with a Bio-Logic VSP-300 potentiostat. The [Re]-PIG, [Re]/CC, PIG/CC, [Ir]-PIG/CC and CoO(OH)/CP electrodes (electrode size of about 1.0 × 2.0 cm, reaction area of about 0.9–1.1 cm²) were used as the working electrode. A leak less Ag/AgCl reference electrode and platinum wire counter electrode were used. A Pyrex glass cell was used as the electrochemical cell, and 0.1 M potassium hydroxide (KOH)/0.1 M potassium carbonate (K₂CO₃) aqueous solution was used as the electrolyte. CO₂ or N₂ gas was bubbled into the reactor for 60 minutes prior to the measurement and allowed to flow at 20 sccm during the measurement period. The amounts of CO, H₂, and O₂ gas produced were determined in situ using a flow reactor combined with a gas chromatograph (SRI Instruments Multiple Gas Analyzer TCD-FID) and oxygen sensor (NeoFOX Oxygen Sensor, Ocean Optics). CO₂ reduction coupled to water oxidation was conducted using a two electrode configuration (Figure 3a). The [Re]-PIG/CC cathode and CoO(OH)/CP anode were connected with a potentiostat in a single compartment flow reactor.
**Calculation of Potential Values vs. RHE**

Potential values expressed versus RHE were obtained using the following equation:

\[
E_{a \ (v s. \ RHE)} = E_a + 0.059 \times pH + 0.199 \ V \ (f o r \ Ag/AgCl)
\]

where \( E_a \) is the applied potential.

The pH of the 0.1 M KOH + 0.1 M K\(_2\)CO\(_3\) solution saturated with CO\(_2\) was approximately 7.2. The pH of the 0.1 M KOH + 0.1 M K\(_2\)CO\(_3\) solution saturated with N\(_2\) was approximately 11.8.
Figure S1. Bulk electrolysis for 24 hours at -0.68 V vs. RHE in a solution of CO$_2$-saturated 0.1 M KOH + 0.1 M K$_2$CO$_3$. (a) The plot shows the volume of carbon monoxide (gray) produced and Faradaic efficiency for CO production (blue) using the [Re]-PIG electrocatalyst. (b) Chronoamperograms using [Re]-PIG electrode for 24 h.

Figure S2. IR spectra of [Re]-PIG electrode before (black) and after 8h reaction (red).
**Figure S3.** Electrocatalytic activity of [Ir]-PIG electrode in 0.1 M KOH + 0.1 M K$_2$CO$_3$ mixed solution. Bulk electrolysis for one hour at -0.68 V vs. RHE in a solution of CO$_2$-saturated 0.1 M KOH + 0.1 M K$_2$CO$_3$ indicating volume of carbon monoxide (black) and hydrogen (blue) produced using the [Ir]-PIG electrocatalyst.

**Figure S4.** (a) Chronoamperograms using [Co(TPP)]-PIG electrode for 1 h at -0.59 V (vs. RHE) under CO$_2$ atmosphere in 0.1 M K$_2$B$_4$O$_7$ + 0.2 M K$_2$SO$_4$ mixed solution. (b) Time courses of H$_2$ (blue) and CO (black) production during electrolysis at -0.59 V vs RHE for 1h under CO$_2$ atmosphere in 0.1 M K$_2$B$_4$O$_7$ + 0.2 M K$_2$SO$_4$ mixed solution.
Figure S5. Cyclic voltammograms of the CoO(OH)/CP (black) and [Re]-PIG (red) electrodes in CO$_2$-saturated 0.1 M KOH + 0.1 M K$_2$CO$_3$ solution.

Figure S6. Chronoamperometry for CO$_2$ reduction coupled to water oxidation using [Re]-PIG and CoO(OH)/CP electrodes at 2.5 V cell bias in 0.1 M KOH + 0.1 M K$_2$CO$_3$ solution under CO$_2$. 
Figure S7. (A) Current efficiency for CO formation as a function of oxygen concentration in CO₂ flow over [Re]-PIG electrode and Ag foil in 0.1M KOH + 0.1M K₂CO₃ mix solution (for [Re]-PIG) and 0.1 M KHCO₃ solution (for Ag foil). Bulk electrolysis for one hour at -0.78 V vs. RHE.
**Figure S8.** MS spectra of bulk electrolysis for 1 hours at -0.68 V vs. RHE. (a) MS spectrum under CO$_2$ in 0.1 M KOH + 0.1 M K$_2$CO$_3$; (b) MS spectrum under $^{13}$CO$_2$ in 0.1 M KOH + 0.1 M K$_2$$^{13}$CO$_3$. 
Figure S9. Chronoamperometry of CO$_2$ reduction by [Re]-PIG electrodes at various bias voltages [-0.58 V (black), -0.68 V (blue) and -0.78 V (red)].

Table S1. Summary of electrocatalytic CO$_2$ reduction using PIG based electrodes at several concentrations of [Re-Cl]. Electrocatalytic CO$_2$ reduction for one hour using [Re]-PIG electrodes at -0.68 V vs. RHE in 0.1 M KOH + 0.1 M K$_2$CO$_3$ purged with CO$_2$.

| Electrode | Amount of Catalyst / µmol cm$^{-2}$ | FE of CO / % | FE of H$_2$ / % | Current Density / mA cm$^{-2}$ |
|-----------|-------------------------------------|--------------|-----------------|--------------------------------|
| [Re]-PIG  | 0.75                                | 55.4         | 33.8            | 0.77                           |
| [Re]-PIG  | 1.49                                | 90.8         | trace           | 1.19                           |
| [Re]-PIG  | 2.24                                | 92.1         | trace           | 1.08                           |
Scheme S1. Schematic illustration of [Re]-PIG electrode preparation. (Capitalize the T in OTf)

Scheme S2. Schematic illustration of CoO(OH)/CP electrode preparation.