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Aqueous electrocatalytic CO_2 reduction using metal complexes dispersed in polymer ion gels

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We use *fac*-[Re(bpy)(CO)$_3$Cl] ([Re-Cl]) dispersed in polymer ion gel (PIG) ([Re]-PIG) to carry out electrocatalytic CO_2 reduction in water. Electrolysis at −0.68 V vs. RHE in a CO_2-saturated KOH and K_2CO_3 solution produces CO with over 90 % Faradaic efficiency. The PIG electrode is readily combined with water oxidation catalysts to generate a full electrochemical cell. Additionally, we provide evidence that the PIG electrode can be implemented with other molecular catalysts.

Development of photoelectrochemical catalysts for reduction of CO_2 is an increasingly important area of research due to the shortage of fossil fuels and global warming. Developing a photosynthetic system for solar fuel generation which produces organic products from CO_2, H_2O, and sunlight is one of the most promising technologies to help overcome these issues.

fac-[Re(bpy)(CO)$_3$Cl] ([Re-Cl]) is one of the most famous electrochemical and photochemical catalysts for CO_2 reduction. Since the report of [Re-Cl] by Lehn et al. in 1983,[1] a multitude of studies have been conducted on [Re-Cl] and its derivatives as potent photo-/electrocatalytic CO_2 reduction catalysts.[2-20] For example, [Re-Cl] can act as a photocatalyst in a DMF/TEOA solution under 365 nm UV light. The selectivity of CO production is over 99% with a turnover number (TON) of 15 and ca. 15% quantum yield for CO_2 reduction.[2] However, it has been shown that CO_2 reduction activity by nearly all Re complex catalysts is suppressed by the addition of water.[3,4] The majority of studies of photo- and electrocatalytic CO_2 reduction using Re complexes have been carried out in organic solvent.[1-20] Additionally, Re complex catalysts have not been successfully implemented in a full cell with water oxidation at the anode. Recently, there have been a few reports of CO_2 reduction in aqueous solution using Re or other molecular catalysts appended with hydroxyl groups to increase aqueous solubility.[21,22] However, this strategy limits catalyst design.

Polymer ion gels (PIG) are composed of an ionic liquid and a polymer and have unique properties compared to hydrogels. Previous studies have used PIGs as CO_2 gas separation films,[23,24] as actuators,[25] as electrolytes for lithium-ion batteries,[26] and as high mechanical strength gels.[27] Recently, PIGs were embedded with [Re-Cl] and used for electrocatalytic CO_2 reduction under CO_2 atmosphere in the absence of additional solvent.[28] However, due to the lack of a proton source, the current density of the PIG/[Re-Cl] composite was smaller than that observed in organic solvent.

CO_2 reduction activity is drastically affected by both the solvent and the supporting electrolyte.[4,29] Although [Re-Cl] can act as a photocatalyst for CO_2 reduction in DMF/TEOA solution, hydrogen is the main product from [Re-Cl] in a THF/TEOA solution.[4] Recently, it was reported that electrocatalytic CO_2 reduction activity can be improved by combining molecular catalysts with carbon-based supports.[30-32] For instance, [Re{4,4'-di(1H-pyrrolyl-3-propyl carbonate)-2,2'bipyridine}(CO)$_3$(Cl)] cannot act as a CO_2 reduction photo- or electrocatalyst in organic solvent, because the reduction potential of the catalyst is too small. However, this Re complex can act as an electrocatalyst for CO_2 reduction in water in the presence of a carbon support.[32] Previous reports have also shown how ionic liquids can improve electrocatalytic CO_2 reduction activity of metal complexes, making PIGs good candidates as solid supports for CO_2 reduction.[13,14,33]

This paper describes the electrocatalytic CO_2 reduction of [Re-Cl] using a PIG support in aqueous solution. The PIG is composed of acrylamide polymer with silicone rubber and ionic liquid, imparting stability to the gel in aqueous solution. Herein, we demonstrate that [Re-Cl] embedded in a PIG electrode ([Re]-PIG) selectively catalyzes CO_2 reduction at the same applied potential as that observed in non-aqueous systems. Thus, stable CO_2 reduction activity in aqueous solution can be improved by PIG supports, opening the way for use of other molecular catalysts in aqueous solution and in tandem CO_2 reduction and water oxidation systems.

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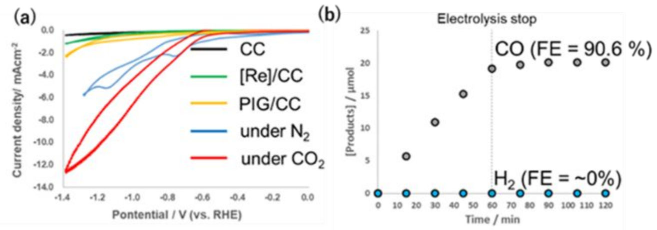

Figure 1. (a) Cyclic voltammograms of CC (black), [Re]/CC (green), PIG/CC (yellow) and [Re]-PIG (red) electrocatalyst in CO_2-saturated 0.1 M KOH + 0.1 M K_2CO_3 solution, and [Re]-PIG electrocatalyst in N_2-saturated 0.1 M KOH + 0.1 M K_2CO_3 solution (blue). (b) Evolution of CO (black) and H_2 (blue) production during electrolysis at -0.68 V vs RHE for one hour under CO_2 atmosphere in 0.1 M KOH + 0.1 M K_2CO_3 solution.

Table 1. Summary of electrocatalytic CO_2 reduction using PIG electrodes at several applied potentials. All trials report electrochemical CO_2 reduction for one hour using [Re]-PIG electrodes at -0.58 to -0.78 V (vs. RHE) in 0.1 M KOH + 0.1 M K_2CO_3 purged with CO_2 or N_2.

Electrode	Applied potential /V (vs. RHE)	FE of CO / %	FE of H_2 / %	Current density / mA cm^{-2}
[Re]-PIG[a]	-0.58	44.8	trace	0.19
[Re]-PIG[a]	-0.68	90.8	trace	1.19
[Re]-PIG[a]	-0.78	98.7	trace	2.54
[Re]-PIG[b]	-0.68	n.d.	88.9	0.47
PIG/CC	-0.68	0.5	87.1	0.92
[Re]/CC	-0.68	44.2	51.9	0.28
CC	-0.68	n.d.	trace	~0.05

[a] Chronoamperograms for [Re]-PIG electrode shown in Figure S9. [b] Electrolysis was conducted under N_2

[Re-Cl] was synthesized according to literature precedent.[1,2] Polymer ion gels with [Re-Cl] electrode ([Re]-PIG) were prepared by drop casting polymer solution on carbon cloth (CC). The polymer solution consisted of 1-butyl-3-methylimidazoluim triflate (BMI), dichloromethane, silicone rubber, [Re-Cl], electrolyte, tetraethyl orthosilicate, formic acid (HCOOH), dimethylacrylamide, methylenebisacrylamide, and azobisisobutyronitrile. Experimental details are given in the ESI and Scheme S1.

Figure 1a depicts the cyclic voltammetry of [Re]-PIG, [Re-Cl] on CC without PIG ([Re]/CC), PIG on CC without [Re-Cl] (PIG/CC), and CC with CO_2 or N_2 in 0.1 M KOH and 0.1 M K_2CO_3 aqueous solution. A clear difference in cathodic current occurs at potentials negative of -0.58 V vs. RHE in the presence of CO_2. The [Re]-PIG electrode catalyzes CO_2 reduction to form CO in 0.1 M KOH and 0.1 M K_2CO_3 aqueous solution (pH = 7.2, saturated with CO_2). Figure 1b shows the electrocatalytic formation of CO on the [Re]-PIG electrode at −0.68 V vs. RHE using an electrochemical flow cell over one hour. The main product detected by GC-FID-TCD was CO, with a Faradaic efficiency (FE) of 90 ± 5%. H_2 was not detected during electrolysis. To assess the durability of the [Re]-PIG electrode, electrolysis was performed for 24 hours (Figure S1). Although FE for CO production was over 90% in the first six hours, CO efficiencies decreased to about 50% after 24 hours. [Re-Cl] may have decomposed during electrolysis, as evidenced by a color change from yellow to colorless. We also identified by ATR-IR that the CO peaks of [Re-Cl] decreased in intensity after electrolysis, further supporting catalyst decomposition (Figure S2). However, the TON for CO was 76 after 24 hours in aqueous solution, which is higher than any TON observed for [Re-Cl] in non-aqueous solvent (TON = 15).[1-4]

The results for electrochemical CO_2 reduction conducted at various overpotentials for [Re]-PIG, [Re]/CC, PIG/CC and CC are shown in Table 1. The [Re]-PIG electrode under N_2 atmosphere and the PIG/CC and CC electrodes under CO_2 atmosphere did not produce any quantifiable CO_2 reduction products. Only H_2 production was observed for these electrodes. Although CO production was observed using the [Re]/CC electrode, H_2 was the primary product, and the current density was lower than [Re-Cl]/PIG at the same overpotential.

Carbon-based supports such as carbon cloth are known to improve CO_2 reduction activity for molecular catalysts.[30-32] It is well known that the CO_2 reduction activity of [Re-Cl] is greatly decreased in aqueous environments. In contrast, the [Re]-PIG electrode had a higher selectivity and current density than other electrodes. The [Re]-PIG electrode can act as an electrocatalyst for CO_2 reduction at potentials cathodic of -0.68 V vs. RHE, which is near the reduction potential of [Re-Cl].[34] On the other hand, it shows poor CO_2 reduction activity at -0.58 V vs, RHE because the potential is smaller than the reduction potential of [Re-Cl]. A current density of 1.19 mA cm^{-2} and an FE value of 90.8 % for CO were achieved at −0.68 V vs. RHE over [Re]-PIG electrode, accompanied by the generation of 20.1 µmol of CO after electrolysis for one hr. At −0.78 V vs. RHE, the current density was 2.54 mA cm^{-2}, which generated 46.6 µmol of CO with a FE of 98.7 % after electrolysis for one hour. Although there is one report for electrocatalytic CO_2 reduction in water using $Re(bpy)(CO)_3Br$ ([Re-Cl] and [$Re(bpy)(CO)_3Br$] exhibit similar behavior for CO_2 reduction) with Nafion, H_2 was the primary product (FE for CO production was less than 30%).[35] These results suggest that PIG drastically improves the CO_2 reduction activity of [Re-Cl] in aqueous solution.

The [Re]-PIG electrode can act as an electrocatalyst for CO_2 reduction at nearly the same reduction potential as [Re-Cl]. It has been reported that ionic liquids can lower the overpotential of CO_2 reduction.[13,14] The suppression of H_2 production can also be explained by the presence of ionic liquid in the PIG support.[13,14,33] Two mechanisms for electrocatalytic CO_2 reduction by [Re-Cl] exist in the literature.[22] The first is the one electron reduction pathway, which is two molecular reactions of Re complexes. The other pathway is the two electron reduction pathway. CO_2 reduction in [Re]-PIG electrode can operate by the one electron reduction pathway, because CO_2 reduction is able to proceed at the first reduction potential of [Re-Cl]. Assuming the reaction proceeds by the one electron reduction pathway, electrocatalytic activity should depend on the concentration of catalyst because this mechanism requires two Re complexes.

Table S1 shows the results of CO_2 reduction using several concentrations of [Re-Cl] in the PIG electrode. A low concentration of [Re]-PIG electrode resulted in poor CO_2 reduction activity. Due to the low concentration of Re complex and low diffusion coefficients of PIG,[28] the Re carbonate dimer cannot be produced efficiently due to the low concentration of Re complexes. Based on these results, we propose that the reaction mechanism of [Re]-PIG electrode proceeds by the one electron reduction pathway with some involvement of the ionic liquid in facilitating CO_2 reduction.

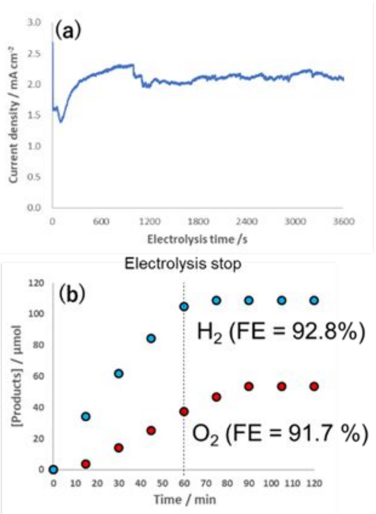

Figure 2. (a) Chronoamperograms using CoO(OH)/CP for one hour at +1.82 V (*vs.* RHE) under CO_2 atmosphere in 0.1 M KOH + 0.1 M K_2CO_3 mixed solution. (b) Time courses of H_2 (blue) and O_2 (red) production during electrolysis at +1.82 V vs RHE for one hour under CO_2 atmosphere in 0.1 M KOH + 0.1 M K_2CO_3 mixed solution with an electrode area of 3 cm^2.

The PIG support is applicable to CO_2 reduction with other molecular catalysts because it imparts favorable conditions for CO_2 reduction in aqueous solution. To demonstrate the applicability of the PIG support on molecular catalysts, we also tested an Ir catalyst, [Ir(tpy)(ppy)Cl] ([Ir], tpy: terpyridine, ppy: 2-phenylpyridine). Similar to [Re-Cl], [Ir] acts as a photocatalyst for CO_2 reduction in non-aqueous solvents.[36] [Ir] with PIG ([Ir]-PIG, method of preparation given in ESI) exhibited electrocatalytic CO_2 reduction activity in aqueous solution (Figure S3). The PIG support can also be implemented with cobalt tetraphenylporphyrin (Co(TPP)), another CO_2 reduction catalyst (Figure S4). Thus, the PIG support can also be implemented with other catalysts for aqueous CO_2 reduction.

One of the goals of CO_2 reduction technology is to develop a full electrochemical cell with water oxidation at the anode to create a biomimetic system. To this end, we attempted to combine the [Re]-PIG electrode and a water oxidation catalyst. Numerous water oxidation catalysts have been reported in the literature.[37-39] For example, Ni foam electrodes exhibit good electrocatalytic activity for water oxidation in basic solution.[38] However, the water oxidation activity of Ni foam in neutral pH has been shown to be drastically attenuated.[40-43] Thus, we selected CoO(OH), which has been shown to catalyze water oxidation under neutral pH conditions.[41] Figure 2a shows the chronoamperomogram of CoO(OH) on carbon paper (CoO(OH)/CP; detail of preparation in ESI) electrode in 0.1 M KOH and 0.1 M K_2CO_3 aqueous solution under CO_2 atmosphere at +1.82 V vs. RHE. Stable current was observed under CO_2 atmosphere and oxygen production was confirmed after electrolysis for one hour (Figure 2b). Combined with a [Re]-PIG cathode, a cell potential over 2.3 V can be obtained (Figure S5).

Tandem electrocatalytic CO_2 reduction and water oxidation was carried out using a full cell system (schematic illustration of full cell system in Figure 3a). A current density of −2.3 to −1.7 mA cm^{-2} was obtained at a cell voltage of 2.5 V for one hour (Figure S6). CO and O_2 were produced during electrolysis, generating 30.45 μmol of CO and 15.97 μmol of O_2 (Figure 3b). The FEs for CO and O_2 production were 90.4 % and 94.6 %, respectively. Generally, CO_2 reduction is disturbed by the reduction of O_2 as a competitive reaction. However, we found that the amount of O_2 was approximately stoichiometric with the amount of CO produced. Therefore, the PIG can act as a catalyst support and prevent parasitic O_2 reduction at the cathode, similar to molecular catalyst-carbon materials.[30,43] This behaviour is also consistent with the utility of PIG films as CO_2 gas separation films.[23,24] Therefore, we confirmed that the electrocatalytic CO_2 reduction using [Re]-PIG electrode proceeds even in the presence of oxygen (Figure S7). These results suggest that the PIG support can provide a platform for integrating selective CO_2 reduction and water oxidation in a two-electrode configuration.

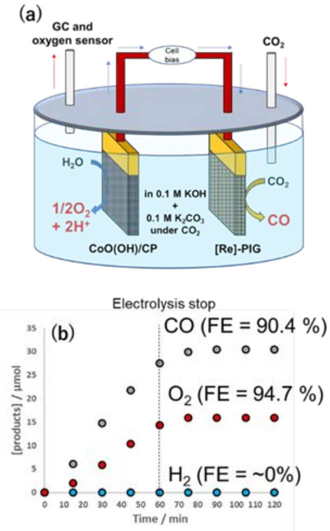

Figure 3. (a) Schematic illustration of the full-cell configuration for CO_2 reduction using water as the electron donor. (b) Time courses of CO (black), H_2 (blue) and O_2 (red) production during electrolysis at 2.5 V for one hour under CO_2 atmosphere in 0.1 M KOH + 0.1 M K_2CO_3 mixed solution.

To verify the carbon source for the generation of CO, an isotope tracer experiment with $^{13}CO_2$ was performed using [Re]-PIG electrode (Figure S8). CO (m/z = 29) was the main product, confirming that the CO detected in these electrocatalytic reactions over [Re]-PIG did not originate from any other source of carbon.

Conclusions

We have demonstrated that the PIG support provides a favorable environment for CO$_2$ reduction, allowing [Re-Cl] to perform electrocatalytic CO$_2$ reduction in aqueous solution. Without the PIG support, hydrogen production was mainly observed. However, the [Re]-PIG composite generated CO with high efficiency at -0.68 V (vs RHE), near the first reduction potential of [Re-Cl]. The PIG electrode can be successfully combined with water oxidation in a full cell system, with the water produced from CO$_2$ reduction used as an electron donor for oxygen evolution. The PIG support can be applied to variety molecular catalysts for CO$_2$ reduction in water, opening the way to more extensive studies on aqueous, electrocatalytic CO$_2$ reduction.

Conflicts of interest

There are no conflicts to declare.

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‡ Full experimental section and additional data are provided in ESI.

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