

## Electrocatalytic Reduction of CO<sub>2</sub> in Water by [Re(bpy)(CO)<sub>3</sub>Br] and [Re(terpy)(CO)<sub>3</sub>Br] Complexes incorporated into Coated Nafion Membrane (bpy = 2,2'-bipyridine; terpy = 2,2':6',2''-terpyridine)

Tsukasa Yoshida,<sup>a</sup> Koji Tsutsumida,<sup>b</sup> Shousuke Teratani,<sup>b</sup> Katsutoshi Yasufuku<sup>a</sup> and Masao Kaneko<sup>\*a</sup>

<sup>a</sup> The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

<sup>b</sup> Tokyo Gakugei University, Koganei, Tokyo 184, Japan

[Re(bpy)(CO)<sub>3</sub>Br] (bpy = 2,2'-bipyridine) and [Re(terpy)(CO)<sub>3</sub>Br] (terpy = 2,2':6',2''-terpyridine) complexes can work as efficient catalysts for CO<sub>2</sub> electroreduction to produce formic acid and CO in an aqueous medium when incorporated into a coated Nafion membrane.

It is important for basic science as well as for future solar energy conversion to mimic the photosynthetic reaction.<sup>1</sup> Since in photosynthesis the electrons which reduce the CO<sub>2</sub> molecule are provided by water oxidation, it is important to achieve CO<sub>2</sub> reduction in an aqueous medium as a part of artificial photosynthesis.<sup>2,3</sup> Various metal complexes have been studied as catalysts for the electroreduction of CO<sub>2</sub>;<sup>4-13</sup> without catalyst CO<sub>2</sub> reduction requires a high overpotential [CO<sub>2</sub>/CO<sub>2</sub><sup>•-</sup>, -2.21 V vs. normal hydrogen electrode(NHE) in dimethylformamide (DMF)].<sup>14</sup> However, most of the complexes were effective only in a non-aqueous medium because proton reduction instead of CO<sub>2</sub> reduction usually prevails in water. [Re(bpy)(CO)<sub>3</sub>X] (bpy = 2,2'-bipyridine, X = Cl<sup>-</sup>, Br<sup>-</sup>) and its derivatives are known as efficient catalysts for CO<sub>2</sub> reduction to produce CO both photochemically<sup>4</sup> and electrochemically<sup>5-8</sup> in non-aqueous media; however, they have never been used in a pure aqueous medium.

We report the first electrocatalytic reduction of CO<sub>2</sub> by [Re(bpy)(CO)<sub>3</sub>Br] as well as [Re(terpy)(CO)<sub>3</sub>Br] (terpy = 2,2':6',2''-terpyridine) in an aqueous medium by incorporating them into a coated Nafion membrane, which provides a

hydrophobic environment around the catalysts to suppress proton reduction.

The complexes were synthesized according to the literature.<sup>15</sup> A 10 μl solution (DMF-alcohol mixture) containing 2.6 mmol dm<sup>-3</sup> complex and 2.5 wt% Nafion was cast onto the surface of a BPG (basal-plane pyrolytic graphite) electrode (effective area = ca. 0.2 cm<sup>2</sup>) and dried at room temperature under air. The coated BPG was subsequently dipped in distilled water.<sup>16</sup> A phosphate buffer (pH ~7) was used as an aqueous electrolyte solution for the electrocatalysis. Gaseous products were analysed after potentiostatic electrolysis on a gas chromatograph (Shimadzu GC-4CPT) equipped with a 5 Å molecular sieve column using Ar carrier gas at 50 °C. The product dissolved in the liquid phase was analysed by a high-performance liquid chromatograph (Hitachi D-6000) equipped with a cation-exchange resin packed column (Shodex KC-811) at 40 °C using 0.1% phosphoric acid aqueous solution as eluent.

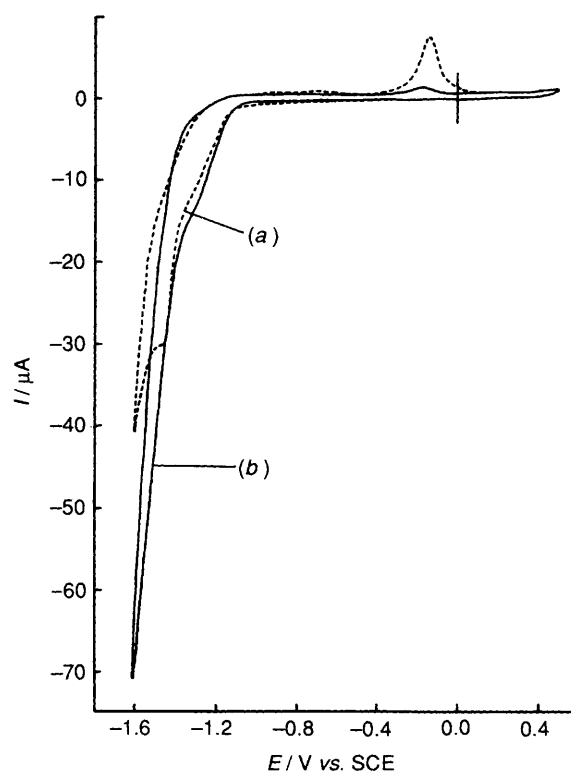
The cyclic voltammograms of the electrode coated with a [Re(bpy)(CO)<sub>3</sub>Br]-Nafion membrane in a phosphate aqueous buffer solution under Ar as well as CO<sub>2</sub> are shown in

Fig. 1. Two cathodic shoulder waves and one distinct but irreversible anodic peak were observed at about  $-1.3$ ,  $-1.45$  and  $-0.15$  V under Ar, respectively. The first reduction wave was assigned to the initial one electron reduction of the complex,  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}] + \text{e}^- \rightarrow [\text{Re}(\text{bpy}^{\cdot-})(\text{CO})_3\text{Br}]$ , which was observed at  $-1.34$  V vs. saturated calomel electrode (SCE) in DMF solution by a separate experiment. It has been reported that the reduced complex loses  $\text{Br}^-$  to form a five-coordinated complex and subsequently the complex dimerizes by forming a Re-Re bond in a homogeneous non-aqueous solution system under Ar  $\{[\text{Re}(\text{bpy}^{\cdot-})(\text{CO})_3\text{Br}] \rightarrow [\text{Re}(\text{bpy})(\text{CO})_3] + \text{Br}^-, 2[\text{Re}(\text{bpy})(\text{CO})_3] \rightarrow [\text{Re}(\text{bpy})(\text{CO})_3]_2\}$ .<sup>6,8</sup> We have carried out an *in situ* spectroelectrochemical study on the redox behaviour of the complex dissolved in DMF and confirmed these reactions. We have also observed clear reversible spectral changes accompanying the reduction of the dimer complex,  $[\text{Re}(\text{bpy})(\text{CO})_3]_2 + \text{e}^- \rightleftharpoons [\text{Re}(\text{bpy})(\text{CO})_3]_2^{\cdot-}$ , at  $-1.47$  V vs. SCE in DMF and found that the dimer complex is stable in DMF until it is oxidized to recover the six-coordinated complex by the reaction,  $[\text{Re}(\text{bpy})(\text{CO})_3]_2 - 2\text{e}^- \rightarrow 2[\text{Re}(\text{bpy})(\text{CO})_3\text{X}]$  at  $-0.11$  V vs. SCE in DMF. Details of the spectroelectrochemical measure-

ment will be reported elsewhere.<sup>17</sup> On considering these results, the second reduction wave in Fig. 1 (under Ar) can be assigned to the reduction of the dimer complex formed in the membrane. The irreversible anodic peak at  $-0.15$  V can be assigned to the oxidation of the zerovalent dimer  $\{[\text{Re}(\text{bpy})(\text{CO})_3]_2\}$ , although the reoxidation of the reduced dimer  $\{[\text{Re}(\text{bpy})(\text{CO})_3]_2^{\cdot-} \rightarrow [\text{Re}(\text{bpy})(\text{CO})_3]_2 + \text{e}^-\}$  which should take place at around  $-1.4$  V is obscure in this cyclic voltammogram (CV) because of the high proton reduction current at this potential range.

When the solution was saturated with  $\text{CO}_2$  gas, the cathodic current in the negative scan direction becomes greater than that under Ar (see Fig. 1) and it sharply increases afterwards at more negative potentials showing no distinct cathodic wave. The anodic peak at  $-0.15$  V is noticeably smaller than that under Ar indicating that dimerization of the complex is prohibited under  $\text{CO}_2$ . These differences in the CV under Ar and  $\text{CO}_2$  are explained as being due to the catalytic reduction of  $\text{CO}_2$ . The absence of the peaks due to the dimer complex would be explained by the coordination of the  $\text{CO}_2$  molecule to the vacant site of the five-coordinated complex produced electrochemically as reported for a homogeneous solution system.<sup>6,17</sup>

The results of the product analysis are summarized in Table 1. Although it is known that CO is selectively produced in a homogeneous non-aqueous solution of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]$  even when a small amount of water is added,<sup>5</sup> formic acid was produced in the present system, BPG-Nafion- $[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]$ -aqueous electrolyte solution, in addition to CO. The selectivity for the  $\text{HCO}_2\text{H}$  and CO formation depended strongly on the applied potentials. Hydrogen was also detected as a byproduct. In the electrolysis at more negative potentials, the catalytic  $\text{CO}_2$  reduction became faster and larger turnover numbers of the catalyst were achieved, e.g. turnover number (TN) of 346 for  $\text{CO}_2$  reduction to produce CO and formic acid in the electrolysis for about 2 h at  $-1.5$  V. However, proton reduction also becomes faster at this potential range, which lowers the selectivity for  $\text{CO}_2$  reduction, although it is uncertain whether the proton reduction is catalytic or not. On the other hand, higher selectivity for  $\text{CO}_2$  reduction can be achieved in the electrolysis at more positive potentials. The highest Faradic efficiency (48%) for formic acid production was obtained at  $-1.3$  V, and the highest efficiency for CO production was 28.5% at  $-1.4$  V. It should be mentioned that the fraction of the electrochemically reactive complex in the membrane is rather low; only 5% of the complex in the membrane is electrochemically active as estimated from the CV measured at a slow scan rate ( $1 \text{ mV s}^{-1}$ ). This is probably because a large part of the complex aggregates during solvent evaporation process due to its low solubility and also by its hydrophobic interaction with each other, which could lead to electrochemically inactive clusters. The catalytic activity of the polymer confined complex was stable. The potentiostat catalysis was repeated three times on the same modified electrode and approximately the same results on  $\text{CO}_2$  reduction could be obtained. The complex dispersed in the polymer membrane is much more active for



**Fig. 1** Cyclic voltammograms at BPG coated with Nafion membrane (thickness =  $5 \mu\text{m}$ ) incorporating  $2.63 \times 10^{-8} \text{ mol } [\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]$  dipped in  $0.030 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4$ - $0.030 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$  aqueous buffer solution (pH  $\sim 7$ ) under Ar (a) or  $\text{CO}_2$  (b). Scan rate =  $20 \text{ mV s}^{-1}$ .

**Table 1** Products of potentiostatic electrolysis at BPG electrodes coated with Nafion membrane incorporating metal complexes in  $0.8 \text{ ml}$  phosphate aqueous buffer solution saturated with  $\text{CO}_2$  (pH  $\sim 7$ )

Complex	Applied potential/ V vs. SCE	t/h	Charge passed/mC	Faradic efficiency (%)			Turnover number <sup>a</sup>		Selectivity for $\text{CO}_2/\text{H}^+$ reduction
				$\text{HCO}_2\text{H}$	CO	$\text{H}_2$	$\text{HCO}_2\text{H}$	CO	
$[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]$	$-1.60$	2.38	238	7.1	8.3	68	134	155	0.23
	$-1.50$	2.08	150	11.8	16.7	77.8	148	198	0.37
	$-1.40$	4.27	71	12.4	28.5	52.9	70	162	0.77
	$-1.30$	4.30	26	48.0	16.5	39	98	34	1.65
$[\text{Re}(\text{terpy})(\text{CO})_3\text{Br}]$	$-1.60$	3.19	354	14.5	trace	51	401	—	0.22
	$-1.50$	3.04	86	8.1	0	82	28	0	0.08

<sup>a</sup> Based on coverage  $\{1.32 \times 10^{-9} \text{ mol } [\text{Re}(\text{bpy})(\text{CO})_3\text{Br}], 1.31 \times 10^{-9} \text{ mol } [\text{Re}(\text{terpy})(\text{CO})_3\text{Br}]\}$  as estimated from CV.

the catalysis (TN about  $166 \text{ h}^{-1}$ ) compared to the complex in a homogeneous solution (TN about  $21 \text{ h}^{-1}$ ).<sup>5</sup>

A  $[\text{Re}(\text{terpy})(\text{CO})_3\text{Br}]$ -Nafion membrane was also active as a catalyst for the  $\text{CO}_2$  electroreduction and the product was mainly formic acid (Table 1). This complex was found to require larger overpotential than the bpy complex for  $\text{CO}_2$  reduction; the efficiency for the formic acid production (14.5%) was highest in the electrolysis at  $-1.6 \text{ V}$  and decreases at more positive potentials in spite of its more positive potential for one electron reduction in DMF (*ca.*  $1.2 \text{ V}$  vs. SCE) than the bpy complex.

It is important to study further details on the catalysis of the polymer confined complex especially with respect to the difference of the products between the present system and the homogeneous non-aqueous system. We are currently studying these aspects by *in situ* spectroelectrochemical measurements.<sup>18</sup>

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