# Electrocatalytic Reduction of $CO_2$ at a Chemically Modified Electrode

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When electropolymerized, the complex $Re(vbpy)(CO)_3Cl$ (vbpy = 4-vinyl-4′-methyl-2,2′-bipyridine), as a polymeric film on a Pt electrode, electrocatalytically reduces $CO_2$ to CO with turnover numbers greatly exceeding those observed for the analogous electrocatalytic reduction of $CO_2$ by $Re(bpy)(CO)_3Cl$ in homogeneous solution (bpy = 2,2′-bipyridine).

The discovery by Lehn and coworkers[1] that a system based on $Re(bpy)(CO)_3Cl$ (bpy = 2,2′-bipyridine) photocatalytically reduces $CO_2$ has led to interest in similar systems. Further studies[2] have shown that $Re^I(bpy)(CO)_3X$ ($X = Cl^-$, MeCN) and a variety of other complexes electrocatalytically reduce $CO_2$ at moderate overvoltages. More recently, work on the thermal and photochemical reactivity of $Re^I(bpy)(CO)_3L$ ($L = H^-, D^-$) has provided insight into the mechanism of $CO_2$ insertion into the Re–H or Re–D bond.[3]

Electrochemically-initiated polymerization of metal complexes of 4-vinyl-4′-methyl-2,2′-bipyridine (vbpy) groups is a versatile technique to form chemically active polymeric films on electrodes.[4] Chemically modified electrodes for electrocatalysis have potential advantages over homogeneous systems in that only small amounts of catalyst are necessary for efficient electrolysis, and enhanced reactivities might be realized by blocking normal solution deactivation pathways. We have electropolymerised the complex $Re(vbpy)(CO)_3Cl$,† to yield electroactive films on platinum electrodes, and have demonstrated efficient reduction of $CO_2$ to CO using it.

Figure 1(a) shows the course of an electropolymerization reaction carried out by cycling the potential of a Pt disc electrode between 0.00 and −1.70 V *vs.* saturated sodium calomel electrode (s.s.c.e.) in an MeCN solution which was (typically) 0.1 M in electrolyte ($Bu_4NPF_6$ or $Et_4NClO_4$) and 2 mM in $Re(vbpy)(CO)_3Cl$. The voltammetry shows a reductive wave which is localized on the bipyridine ligand followed by a second wave which is metal-based, as shown from studies on a variety of $Re^I(bpy)(CO)_3L$ complexes.[2] Subsequent potential scans show enhanced currents indicative of formation of a polymeric film which can be charged and discharged and which can further reduce reactive monomers. Removal of the electrode from the polymerizing solution and rinsing with MeCN reveals a greenish-gold film which, upon standing in air, becomes yellow.

A typical cyclic voltammogram (c.v.) of the yellow film in fresh MeCN–electrolyte solution is shown in Figure 1(b). There are no distinct reversible reductive waves, and so we have estimated the coverage of polymerized complex from the final voltammetric scan of the electropolymerization. Since it has been shown[2] that $Re(bpy)(CO)_3Cl$ undergoes $Cl^-$ loss (albeit slowly) upon reduction at the first wave with formation

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† vbpy was synthesized *via* a modification of the method of Abruna *et al.* (ref. 5). The complex $Re(vbpy)(CO)_3Cl$ was synthesized (ref. 6) by heating vbpy (1 equiv.) with $Re(CO)_5Cl$ (1 equiv., Pressure Chemical Co.) at reflux in pentane for 5 h. The yellow complex was filtered out of the solution in essentially quantitative yield and was used without further purification.

of a metal–metal bonded dimer, it might be expected that the electropolymerized polymer is either the MeCN complex or is the dimer. It is not possible to determine electrochemically whether this is the case. The oxidation feature appearing at −0.15 V during the electropolymerization in Figure 1(a) is characteristic of reoxidation of the Re–Re bonded dimer.[3b] The initial green colour of the electropolymerized film is thought to be due to residual amounts of this dimer, which decomposes to a monomer in air. *X*-Ray photoelectron spectral data collected on a film electropolymerized in $Bu_4NPF_6$ on a Pt flag electrode show only a small amount of F present; the MeCN complex would have $PF_6^-$ as a counterion. In addition, u.v.-visible spectra obtained from a film on a NaCl plate sputter-coated with an optically transparent film of Pt gave λ 291 and 380 nm, indicative of $Re(bpy)(CO)_3X$ (X = anion). While not conclusive, these results are consistent with most of the metal sites in the film as having retained the $Cl^-$ ligand.

The electrocatalysis experiment shown in Figure 1(b) is typical of the behaviour of films deposited on Pt electrodes. The c.v. in $N_2$-saturated MeCN–electrolyte is contrasted with the c.v. of the same electrode after the solution has been purged with $CO_2$ for 5 min. The observed current enhancement (dashed line) is characteristic of such electrocatalytic systems. Experiments using modified rotating disc electrodes show that the currents do not depend on electrode rotation rate. This is plausible given that $CO_2$ is very soluble in MeCN and has a high diffusion coefficient; the result suggests that $CO_2$ permeates the film rapidly and that its mass transport is not rate-limiting in the catalysis.

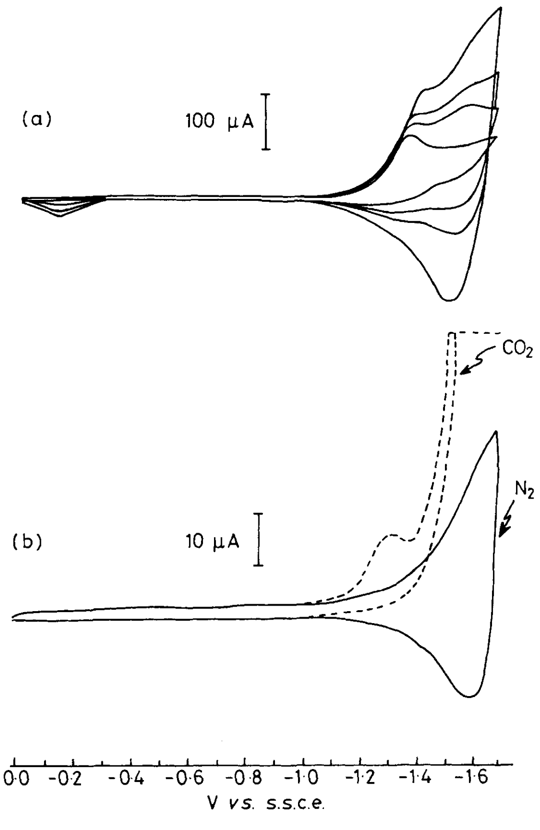

**Figure 1.** (a) C.v. of the electropolymerization of $Re(vbpy)(CO)_3Cl$ in MeCN solution with $Bu_4NClO_4$ as supporting electrolyte at a Pt disc electrode. Sweep rate was 200 mV $s^{-1}$. (b) C.v. under $N_2$ (——) and $CO_2$ (– – – –) of a Pt disc electrode with poly-$Re(vbpy)(CO)_3Cl$, in MeCN–0.1 M $Bu_4NClO_4$ at 100 mV $s^{-1}$.

In order to characterize the gaseous products and the efficiency of the catalysis, $Re(vbpy)(CO)_3Cl$ was electropolymerized onto a platinum gauze electrode. An upper limit on the total amount of electroactive material on this electrode was estimated to be $5 \times 10^{-7}$ mol (from the integrated current under the last voltammetric scan of the polymerization). The electrode was placed in a gas-tight cell in MeCN–$Bu_4NPF_6$ saturated with $CO_2$. Potentiostating the electrode at −1.55 V *vs.* s.s.c.e. for 80 min led to the formation of 6.3 ml of CO at an overall current efficiency of 92.3% (as measured by g.c. and coulometry). Based on the estimated amount of catalyst in the polymer, this represents 516 turnovers as compared to 20—30 turnovers in 80 min for an electrocatalysis experiment performed with the corresponding monomer in solution[2,3b] and at the same electrode potential. In both electrolyses the current had decayed to a small value after 80 min. C.v.'s after the modified electrode experiment was completed showed that the electroactive material was lost from the surface.

There are two important differences in the 80 min electrocatalysis experiments with electropolymerized Re(vbpy)-$(CO)_3Cl$ and with a $Re(bpy)(CO)_3Cl$ solution. First, the electropolymerized catalyst executed 20—30 times more turnovers per site (at a minimum). Secondly, no $CO_3^{2-}$ product was observed with electropolymerized Re(vbpy)-$(CO)_3Cl$ whereas equal amounts of CO and $CO_3^{2-}$ were produced[2,3b] in the solution experiment for electrolysis at −1.55 V. Conducting the electrocatalytic reaction in the polymerized medium apparently enhances an alternate, more reactive pathway and may also stabilise the catalyst toward decomposition. The results described here combined with earlier results on $CO_2$ reduction by adsorbed $Co^{II}$ phthalocyanines[7,8] are encouraging examples of the application of chemically modified electrodes to the oxidation/reduction of small molecules.

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