Electrocatalytic Reduction of CO_2 in Water on a Polymeric $[\{Ru^0(bpy)(CO)_2\}_n]$ (bpy = 2,2′-bipyridine) Complex Immobilized on Carbon Electrodes

Marie-Noëlle Collomb-Dunand-Sauthier,[a] Alain Deronzier[a] and Raymond Ziessel[b]

[a] *Laboratoire d'Electrochimie Organique et de Photochimie Rédox (URA CNRS 1210), Université Joseph Fourier Grenoble 1, BP 53, 38041 Grenoble Cédex 9, France*

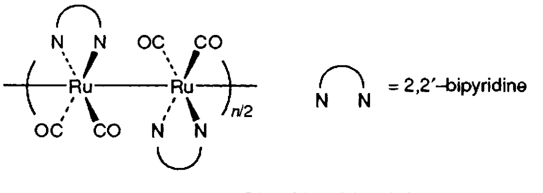
[b] *Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, Institut de Physique et de Chimie des Matériaux, Groupe des Matériaux Inorganiques, URM CNRS 46, 1 rue Blaise Pascal, BP 296F, 67008 Strasbourg Cédex, France*

The electrocatalytic reduction of CO_2 on a carbon/$[\{Ru^0(bpy)(CO)_2\}_n]$ (bpy = 2,2′-bipyridine) modified electrode, prepared by electrochemical reduction of $[Ru^{II}(bpy)(CO)_2Cl_2]$, leads to the selective and quantitative formation of CO even in pure aqueous electrolyte; the stability of the modified cathode is improved by using a preformed polypyrrolic film functionalized with this complex.

There is considerable interest in the electrocatalytic reduction of CO_2 with a view to constructing artificial photosynthetic systems.[1] A large number of metal complexes have been examined as electrocatalysts;[2] however, few appear to be effective in pure aqueous electrolyte because the accompanying reduction of protons is usually observed.[3–5] One solution to the problem could be to use complexes in a polymer-confined system deposited on cathode surfaces. Some attempts have been reported recently, and the results were moderately good in terms of selectivity and current efficiency.[6–8]

The complex *trans*-(Cl)-$[Ru^{II}(bpy)(CO)_2Cl_2]$ is an efficient homogeneous catalyst for the reduction of CO_2 to produce formate photochemically (in non-aqueous media)[9] and CO electrochemically (in aqueous MeCN).[10] We report here an efficient electrocatalytic system based on films prepared by electrochemical reduction of $[Ru^{II}(bpy)(CO)_2Cl_2]$. The cyclic voltammogram of $[Ru^{II}(bpy)(CO)_2Cl_2]$ (10^{-3} mol dm^{-3} in MeCN solution†) exhibits an intense irreversible cathodic peak at −1.48 V associated with an anodic peak at −0.74 V on the reverse scan,[10,11] typical of an electrodeposition–redissolution phenomena. Controlled-potential electrolysis of this solution at −1.65 V leads to the formation of a dark blue, air-sensitive and strongly adherent electroactive film on the working electrode (Pt or C for instance). FTIR, UV-VIS spectroscopy, elemental analysis and electrochemical properties suggest that these films have a polymeric nature with a basic chemical structure $[\{Ru^0(bpy)(CO)_2\}_n]$ containing metal–metal bonds.‡ A possible structure for electrodeposited $[\{Ru(bpy)(CO)_2\}_n]$ film is shown in Scheme 1.

The FTIR spectrum shows no $\nu_{Ru\text{-}Cl}$ stretching vibrations {observed at 338 cm^{-1} in *trans*-(Cl)-$[Ru^{II}(bpy)(CO)_2Cl_2]$} but the presence of a new band at 170 cm^{-1}. This stretching vibration might be indicative of the presence of metal–metal bonds. When studied under the same experimental conditions (polyethylene pellets) $Ru_3(CO)_{12}$ presented a band at 171 cm^{-1}. Others have recently reported the photochemical preparation[12] and structure determination[13] of a polymeric form of $[\{Ru^0(CO)_4\}_n]$. In our case, the electrochemical formation of the polymeric $[\{Ru^0(bpy)(CO)_2\}_n]$ film results from the addition of two electrons per mol of $[Ru^{II}(bpy)(CO)_2Cl_2]$ (established by coulometry) associated with the loss of two Cl^- ligands (estimated from the intensity of the anodic peak of the Cl^- ion released in solution) [eqn. (1)], as revealed by an exhaustive reduction.



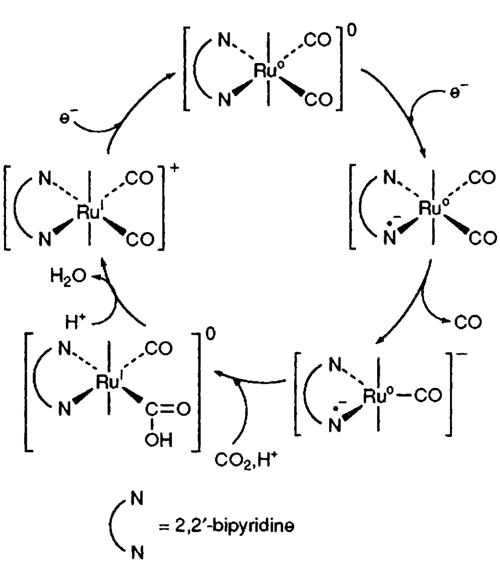
Scheme 1 Proposed structure of $[\{Ru^0(bpy)(CO)_2\}_n]$ polymeric film

$$n[Ru^{II}(bpy)(CO)_2Cl_2] + 2ne^- \rightarrow [\{Ru^0(bpy)(CO)_2\}_n] + 2nCl^- \quad (1)$$

Moreover, desorption and dissolution of the film by two successive oxidations at 0 and 1.1 V in MeCN solution leads to the quantitative formation of the $[Ru(bpy)(CO)_2(MeCN)_2]^{2+}$ complex. This means unambiguously that the basic structure of the initial complex is retained in the film.

These modified electrodes appear to be electroactive as a consequence of the reduction of the bipyridine ligand to the $bpy^{\cdot-}$ and bpy^{2-} levels and exhibit two reversible peak systems at −0.90 and −1.55 V under an argon atmosphere [Fig. 1(*a*)]. Note that only 8% of the bipyridine sites are electroactive in the polymer (doping level) as evaluated from the ratio of integrated currents for the signals in the film and the total charge involved in the preparation of the film. Obviously prior their utilization these modified electrodes are oxidized at −0.80 V into the pure $[\{Ru(bpy)(CO)_2\}_n]$ state (undoped level).

Fig. 1(*c*) shows a cyclic voltammogram of a vitreous carbon/$[\{Ru^0(bpy)(CO)_2\}_n]$ modified electrode in MeCN solution saturated with CO_2 in the presence of 5% of H_2O. A strong enhancement of the cathodic current from −1.3 V is observed.§ Preparative-scale electrolyses using a carbon felt electrode (10 × 10 × 4 mm^3, from Le Carbone Lorraine) modified with different amounts of $[\{Ru^0(bpy)(CO)_2\}_n]$, varying from 0.5 to 1.5 C charge passed, confirms its great catalytic activity. Electrolyses were conducted at −1.55 V in MeCN–5% H_2O and any gaseous products were analysed by gas chromatography. For all runs CO is obtained with a 100%



Scheme 2 Proposed mechanism for the electrocatalytic reduction of CO_2 on carbon/$[\{Ru^0(bpy)(CO)_2\}_n]$ modified electrode (only the electroactive site of the complex in the film is represented)

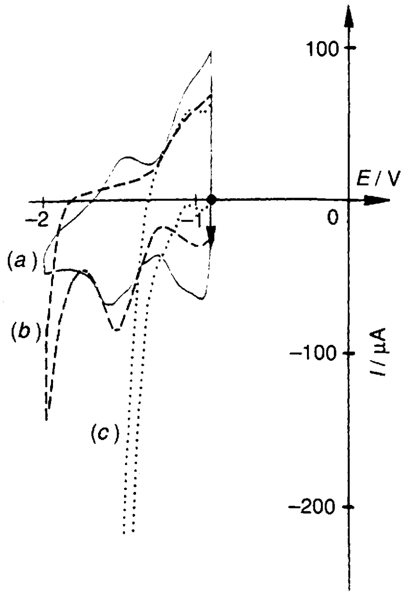


Fig. 1 Cyclic voltammograms of a carbon/[{$Ru^0(bpy)(CO)_2$}$_n$] modified electrode prepared by electrolysis at −1.6 V (Q = 5 mC) of a solution of [$Ru(bpy)(CO)_2Cl_2$] (10^{-3} mol dm^{-3}) in Bu_4NClO_4–MeCN (0.1 mol dm^{-3}): (*a*) under N_2; (*b*) containing H_2O (5%) under N_2; (*c*) containing H_2O (5%) after bubbling of CO_2 for 20 min; v = 100 mV s^{-1}

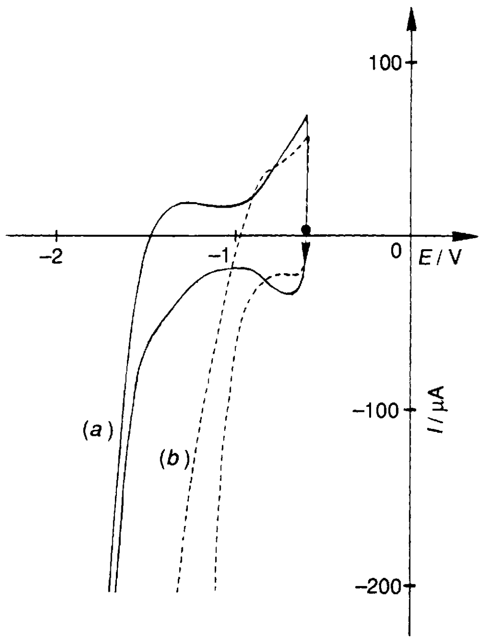


Fig. 2 Cyclic voltammograms in $LiClO_4$–H_2O (0.1 mol dm^{-3}) of a carbon/[{$Ru^0(bpy)(CO)_2$}$_n$] modified electrode prepared by electrolysis at −1.6 V (Q = 5 mC) of a solution of [$Ru(bpy)(CO)_2Cl_2$] (10^{-3} mol dm^{-3}) in Bu_4NClO_4–MeCN (0.1 mol dm^{-3}) under (*a*) N_2 and (*b*) CO_2; v = 100 mV s^{-1}

current efficiency after 60 C has been passed (3×10^{-4} mol of CO is formed). As expected, the electrolysis time decreases as the amount of polymer deposited increases. The current drops and reaches a pseudo-plateau more or less rapidly depending on the amount of the polymer, probably indicating that some desorption of the film occurs at the beginning of the electrolysis.

Similar experiments in pure aqueous solution ($LiClO_4$–H_2O, 0.1 mol dm^{-3}) show that the carbon/[{$Ru^0(bpy)(CO)_2$}$_n$] modified electrode is also an effective and selective catalyst for CO_2 reduction into CO, in water. Fig. 2 shows the cyclic voltammogram under N_2 and CO_2 of the film in an aqueous medium. The electroactivity of the modified electrode remains almost identical to that observed in MeCN; bubbling CO_2 induces a strong increase of the cathodic current. Electrolysis at −1.20 V on a carbon felt electrode coated with [{$Ru^0(bpy)(CO)_2$}$_n$] (prepared by passing 1.5 C) produces CO with current efficiency >97% after 60 C has been consumed. By this time, the electrolysis current had dropped to 40% of its initial value and a pseudo-plateau was reached.

Taking into account the proposed structure of the polymeric film we suggest the mechanism shown in Scheme 2 for the electrocatalytic cycle. The initial step involves a one-electron reduction of the electroactive [$Ru(bpy)(CO)_2$] site in the polymeric film to give [$Ru(bpy^{\cdot -})(CO)_2$]. This species is not fully stable and may liberate CO, generating a pentacoordinated species [$Ru(bpy^{\cdot -})(CO)$]. In the presence of CO_2, the latter coordinates this species to produce ($Ru(bpy)(CO)_2$]$^+$ *via* [$Ru(bpy)(CO)(CO_2H)$] in the presence of water, which acts as a proton source. At that potential [$Ru(bpy)(CO)_2$]$^+$ is reduced back to [$Ru(bpy)(CO)_2$], which is ready for participation in another electrocatalytic cycle. Electrogeneration of pentacoordinated metallic carbonyl complexes like [$Ru^0(bpy)_2CO$] and [$Re^I(bpy)(CO)_2Cl$]$^-$ has been postulated previously as a key species in some homogeneous electrocatalytic processes.[10,14]

The stability of these molecular cathodes can be improved by using a preformed functionalized polypyrrolic films. We have previously reported that polypyrrolic films containing a [$Ru^{II}(bpy)(CO)_2Cl_2$] core can be prepared by electropolymerization of the corresponding monomeric complex [$Ru^{II}(L_1)(CO)_2Cl_2$] having a 4-(2-pyrrol-1-ylethyl)-4′-methyl-2,2′-bipyridine ligand (L_1).[15] Electropolymerization was accomplished for instance by maintaining the working electrode at 0.95 V in MeCN. Continuous cycling of this poly-[$Ru^{II}(L_1)(CO)_2Cl_2$] modified electrode in the cathodic region (−0.9 to −2.0 V) induces a further modification, which is attributed to formation of the putative metal–metal bonds in the film with simultaneous chloride-ion loss, *via* a mechanism similar to that proposed for [{$Ru^0(bpy)(CO)_2$}$_n$] formation from [$Ru(bpy)(CO)_2Cl_2$]. A series of pseudo-reversible peak systems is then observed at $E_{1/2}$ = −1.12, −1.51 and −1.68 V. When the solution is purged with CO_2 a large catalytic current is observed from −1.50 V in MeCN–5% of H_2O or in pure aqueous electrolyte H_2O–$LiClO_4$ (0.1 mol dm^{-3}). Bulk electrolysis carried out with a poly-[$Ru^{II}(L_1)(CO)_2Cl_2$] film deposited on a carbon felt electrode (E_{appl} = −1.60 V in MeCN and −1.35 V in aqueous solution) results in the production of CO in very high yield (90% and 80% current efficiency, respectively). In pure aqueous electrolyte H_2 has been also detected as side-product (20%). Note that the current after 60 C had been consumed remained identical to its initial value even in pure aqueous electrolyte.

We are currently investigating the influence of the pH of the aqueous electrolyte on the catalytic effect and on the life of these new molecular cathodes.

Received, 20th July, 1993; Com. 3/04259F

Footnotes

† All potentials are referenced *vs.* Ag/Ag$^+$ (10^{-2} mol dm^{-3}) as reference electrode in Bu_4NClO_4–MeCN (0.1 mol dm^{-3}) or Bu_4NClO_4–MeCN + 5% H_2O (0.1 mol dm^{-3}) medium and *vs.* SCE in pure aqueous medium. Potentials referenced to the Ag/Ag$^+$ system can be converted to the SCE by adding 0.3 V.

‡ FTIR (KBr pellets): ν_{CO} 2017 and 1977 cm^{-1}; UV–VIS (optically transparent indium oxide electrode), 475, 600 and 760 nm; elemental analysis C, 45.63%, H, 2.45%, N, 8.71%. FAB-MS data using *m*-nitrobenzylalcohol (*m*-NBA)–acetonitrile as matrix are consistent with the hypothesis of a polymeric or oligomeric structure. Fragments are observed at *m/z* 1137 [$Ru_3(bpy)_3(CO)_6$(*m*-NBA)(MeCN) + H], 966 [$Ru_2(bpy)_3(CO)_5$(*m*-NBA) + H], 794 [$Ru_2(bpy)_2(CO)_3$(*m*-NBA)]. The lack of solubility of the films in organic solvents like DMF or DMSO is also in favour of a polymeric structure.

§ Note that under N_2 the presence of 5% water does not alter the electrochemical behaviour of the film. The redox system at −1.55 V appears to be less reversible, probably because of the catalytic reduction of water starting from −1.9 V [Fig. 1(*b*)].

References

1 R. Ziessel, in *Photosensitization and Photocatalysis using Inorganic and Organometallic Compounds*, ed. K. Kalyanasundaram and M. Grätzel, Kluwer, Dordrecht, 1993, pp. 217–240.

2 J.-P. Collin and J.-P. Sauvage, *Coord. Chem. Rev.*, 1989, **93**, 245.

3 K. Takahashi, K. Hiratsuka, H. Sasaki and S. Toshima, *Chem. Lett.*, 1979, 305.

4 S. Kapusta and N. Hackerman, *J. Electrochem. Soc.*, 1984, **131**, 1511.

5 M. Beley, J.-P. Collin, R. Ruppert and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1984, 1315; *J. Am. Chem. Soc.*, 1986, **108**, 7461.

6 K. Ogura, K. Mine, J. Yano and H. Sugihara, *J. Chem. Soc., Chem. Commun.*, 1993, 20.

7 T. Yoshida, T. Iida, T. Shirasagi, R.-J. Lin and M. Kaneko, *J. Electroanal. Chem.*, 1993, **344**, 355.

8 T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1993, 631.

9 J.-M. Lehn and R. Ziessel, *J. Organometal. Chem.*, 1990, **382**, 157.

10 H. Ishida, K. Fujiki, T. Ohba, K. Ohkubo, K. Tanaka, T. Tereda and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1990, 2155.

11 M.-N. Collomb-Dunand-Sauthier, A. Deronzier and R. Ziessel, *J. Electroanal. Chem.*, 1993, **350**, 43.

12 W. Ross Hastings and M. C. Baird, *Inorg. Chem.*, 1986, **25**, 2913.

13 N. Masciocchi, M. Moret, P. Cairati, F. Ragaini and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1993, 471.

14 J. Hawecker, J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990.

15 M.-N. Collomb-Dunand-Sauthier, A. Deronzier and R. Ziessel, *J. Phys. Chem.*, 1993, **97**, 5973.