

# Reduction of Carbon Dioxide with Platinum Metals Electrocatalysts

## A POTENTIALLY IMPORTANT ROUTE FOR THE FUTURE PRODUCTION OF FUELS AND CHEMICALS

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*The reduction of carbon dioxide to fuels and chemicals can be accomplished by the use of electrocatalysts of the platinum group metals. Worthwhile products include carbon monoxide, formate, methanol, methane, oxalate and even higher hydrocarbons depending on the catalyst type and environment. Three classes of electrocatalysts have been identified: catalytic metal surfaces, monomeric solution complexes, and chemically modified electrodes; the latter being a novel hybrid of solid state, surface and homogeneous solution chemistry.*

Transition metal complexes have great potential as catalysts for the production of high energy fuels and chemicals. The strategy of using redox reactions in solution, or at the surfaces of chemically modified electrodes, is the modern equivalent of high temperature, high pressure homo- or heterogeneous catalysis but it offers the promise of results that will far outstrip the older methods. In an electrocatalytic cell, electricity is the energy source used to drive desirable reactions such as  $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{O}_2$ . In an ideal cell configuration, the reduction product, methanol, and the oxidation product, oxygen, are generated at separate electrodes in separate cell compartments using either solar or nuclear energy input. The energy stored in this reaction is recovered by combustion in a fuel cell which completes a closed cycle in which there is net carbon dioxide balance. There is growing interest in such cycles triggered in part by the growing environmental concern over carbon dioxide accumulation in the environment. In a more general sense, the electrocatalytic cell approach could have an impact on technology in that other target molecules, such as nitrogen, nitrogen oxides, or sulphur oxides could be converted to useful, recyclable materials, once

the principles of electrocatalyst design are understood.

Inherent to this approach is the replacement of conventional substrate hydrogenation reactions involving hydrogen gas with those that utilise coupled electron/proton transfers. The latter reactions can be used as the cathodic half-cell reaction in an electrocatalytic cell. As I will illustrate here for carbon dioxide reduction, appropriate homogeneous solution and heterogeneous phase catalytic systems are found extensively for the platinum group metals.

The strategies for electrocatalysis include the use of platinum group metal solid surfaces, monomeric solution complexes, and catalytic sites that are immobilised in polymeric thin films. When the latter type of catalytic system is attached to a conductive surface like a platinum or a glassy carbon electrode, it is commonly referred to as a chemically modified electrode. Figure 1 illustrates three approaches.

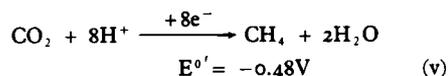
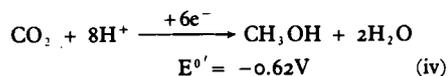
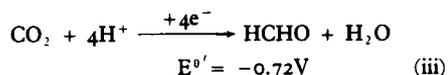
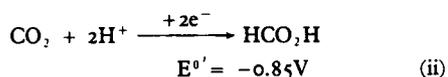
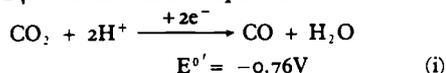
### Thermodynamics and Pathways of Carbon Dioxide Reduction

Carbon dioxide reduction can yield a variety of useful products, such as single carbon species like carbon monoxide, formate, methanol and methane, or  $\text{C}_2$  products like

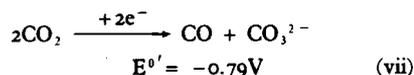
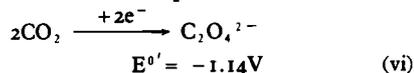
oxalate, glycolate, ethanol, ethane and ethylene. The potential importance of the products is apparent from current uses, for example, carbon monoxide in hydroformylation, formate as a precursor to organic esters, methanol as a significant solvent or fuel cell component, and methane as a stable, storable and transportable energy source. Oxalate is somewhat special in that it could serve as a precursor to ethylene or ethylene glycol, both of which are significant for further industrial chemical synthesis.

The thermodynamic requirements for the electrochemical reactions leading to simple organic compounds involving incorporation of hydrogen in the form of protons are shown in equations (i) to (v) where it is apparent that reduction potentials of between about  $-0.5$  and

$-0.8$  V (versus SCE at pH 7) are required (1). The choice of the saturated calomel electrode (SCE) as the reference state for the equations follows from the necessity to compare aqueous and nonaqueous thermodynamic and kinetic data. Conversion of the potentials to the normal hydrogen electrode can be done by adding  $+0.24$  V to the values reported here:



Equations (vi) and (vii) show two important, nonaqueous routes for carbon dioxide reduction, one giving carbon monoxide and the other oxalate as the ultimate product:



The potentials required for the reactions in Equations (i) to (vii) contrast quite sharply with the one-electron potential for the production of the carbon dioxide radical anion,  $-2.21$  V, which has been determined by Saveant and coworkers (acetonitrile solution at a platinum metal electrode) (2). Clearly, catalysis is necessary to surmount this barrier. The products of a bulk electrolysis at this potential are carbon monoxide, carbonate and oxalate under strictly anhydrous conditions, with formate forming in the presence of a proton source such as water (3). The overpotential lowering necessary to achieve the thermodynamic reduction to these products according to Equations (i), (ii), (vi) and (vii) is between 1.0 and 1.5 V.

The very cathodic electrolysis potentials at a platinum electrode probably reflect the energy

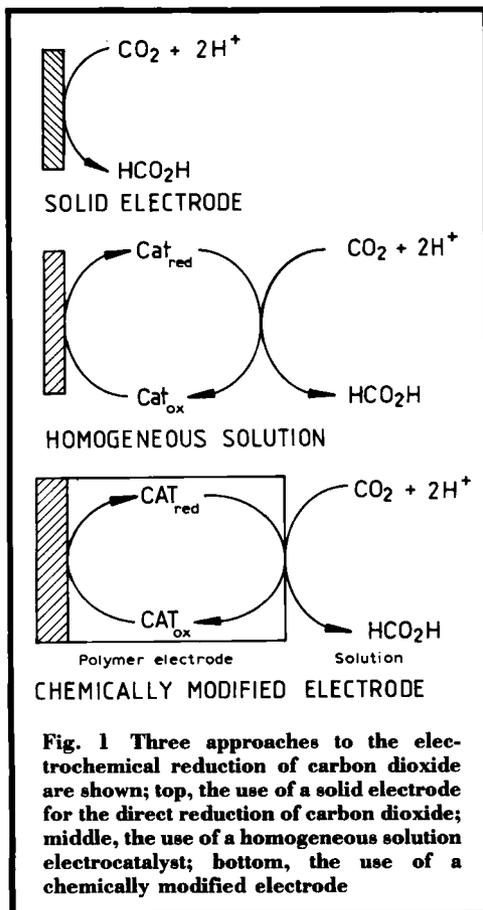
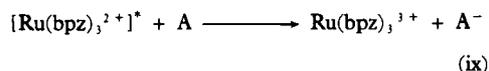
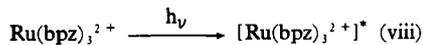


Fig. 1 Three approaches to the electrochemical reduction of carbon dioxide are shown; top, the use of a solid electrode for the direct reduction of carbon dioxide; middle, the use of a homogeneous solution electrocatalyst; bottom, the use of a chemically modified electrode

required to place electrons into  $\pi^*$  orbitals of weakly adsorbed carbon dioxide molecules plus the energy necessary for bond reorganisation in the radical anion products. Less severe potential requirements exist for ruthenium metal electrodes, that apparently point to surface catalysis. In fact, for ruthenium metal deposited on a carbon substrate in aqueous solution, mechanistic pathways exist which give up to about 30 per cent methane (4). Apparently, the ruthenium surface sites that are occupied by both carbon dioxide and hydrogen react to lead to hydrogenated intermediates and eventually methane. Thus it appears that the generation of surface hydrides using water as the proton source followed by reaction with adsorbed carbon dioxide are crucial steps in the catalytic function of ruthenium metal. Of course, hydride formation is a feature of the platinum group metals that results in their facile catalytic behaviour for substrates such as alkenes.

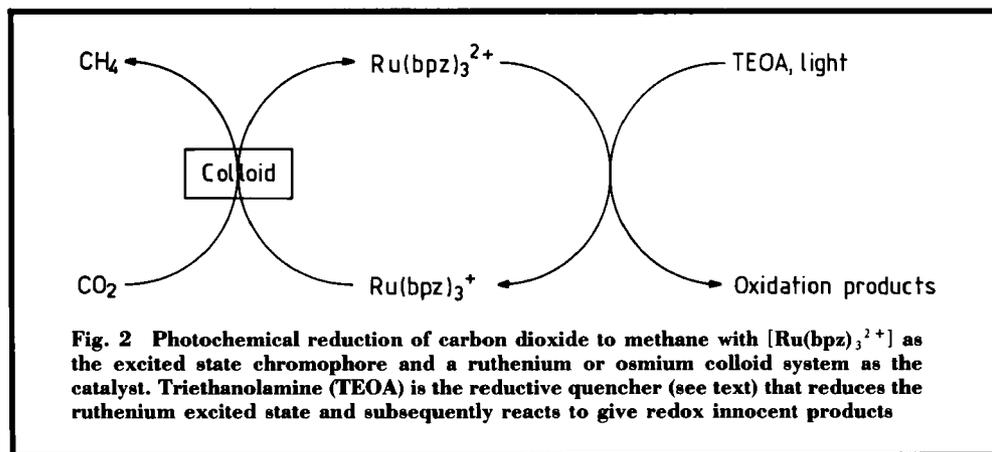
In an approach that also relies on catalytic metal surface structures, ruthenium and osmium colloids have been used to produce methane from carbon dioxide in a photochemical system that exploits the electrochemical properties of known photosensitisers such as  $\text{Ru}(\text{bpy})_3^{2+}$  or  $\text{Ru}(\text{bpz})_3^{2+}$  (where bpy is 2,2'-bipyridine and bpz is 2,2'-bipyrazine)(5). As depicted in Equations (viii) to (x), the use of metal-to-ligand charge

transfer (MLCT) excited states to produce potent redox reagents is a means of photochemically driving electrocatalysis (6).



This is accomplished by reductive or oxidative quenching in the following manner. Visible light excitation of the MLCT transition ( $d_\pi(\text{Ru})-\pi^*(\text{bpz})$ ) generates  $[\text{Ru}(\text{bpz})_3^{2+}]^*$  which can be oxidatively quenched, by an acceptor, A, to give the reductant  $\text{A}^-$  that can be the source of reducing equivalents for the reduction of the catalysis precursor. Alternatively,  $[\text{Ru}(\text{bpz})_3^{2+}]^*$  can be reductively quenched by a donor, D, to give the reduced complex  $\text{Ru}(\text{bpz})_3^+$ , which will function in the same fashion.

An example of a photocatalytic cycle is presented in Figure 2 which shows that photoexcitation of  $\text{Ru}(\text{bpz})_3^{2+}$  produces an excited state that is immediately quenched in a chemically irreversible step to yield the powerful reductant  $\text{Ru}(\text{bpz})_3^+$ . At this point, rapid electron transfer from  $\text{Ru}(\text{bpz})_3^+$  to the colloid catalyst gives methane from surface bound carbon dioxide and its intermediates. A feature of



**Fig. 2** Photochemical reduction of carbon dioxide to methane with  $[\text{Ru}(\text{bpz})_3^{2+}]$  as the excited state chromophore and a ruthenium or osmium colloid system as the catalyst. Triethanolamine (TEOA) is the reductive quencher (see text) that reduces the ruthenium excited state and subsequently reacts to give redox innocent products

importance in the  $\text{Ru}(\text{bpz})_3^{2+}$ /metal colloid system is the selective reduction of carbon dioxide to methane in the presence of water. Unfortunately, little is known concerning the mechanism of reduction at the colloid surface.

Photomethanation of carbon dioxide at room temperature and atmospheric pressure can also be accomplished by the use of highly dispersed ruthenium/ruthenium oxides on a titania support (7). In this case, the method relies on hydrogen gas, although photoexcitation in the presence of a sacrificial electron donor in the presence of water might also be capable of giving a similar result, since excitation of the semiconductor titania surface will generate highly oxidising valence band holes concomitant with conduction band electrons capable of transfer to the ruthenium catalytic sites.

### Electrocatalysis by Monomeric Complexes

A strategy for electrocatalytic carbon dioxide reduction in homogeneous solution is to use monomeric complexes that have, as prerequisites, redox active sites and at least one open co-ordination site at which a reaction with carbon dioxide can take place. The majority of homogeneous solution catalysts involve platinum group metals, these include,  $\text{Pd}(\text{porphyrin})$  (porphyrin is tetraphenyl- or tetramethylporphine) (8),  $\text{Ru}(\text{bpy})_2(\text{CO})\text{L}^{n+}$  (bpy is 2,2'-bipyridine;  $\text{L} = \text{Cl}$ ,  $n = 1$ ;  $\text{L} = \text{CO}$ ,  $n = 2$ ) (9, 10),  $\text{Ru}(\text{trpy})(\text{dppene})\text{L}^{n+}$  (trpy is 2,2',2''-terpyridine; dppene is *cis*-1,2-diphenylphosphinoethylene;  $\text{L}$  is  $\text{Cl}$  or  $\text{CH}_3\text{CN}$ ) (11,12),  $\text{M}(\text{bpy})_2(\text{CO})\text{H}^+$  ( $\text{M} = \text{Ru}$ ,  $\text{Os}$ ) (12,13),  $\text{Pd}(\text{triphos})\text{L}^{2+}$  (triphos is  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh})_2$ ;  $\text{L}$  is  $\text{CH}_3\text{CN}$  or tertiary phosphine or phosphite) (14),  $\text{Rh}(\text{bpy})_2\text{X}_2^+$  ( $\text{X}$  is  $\text{Cl}$  or trifluoromethanesulfonate) (11,12,15), and  $\text{Rh}(\text{diphos})_2^+$  (diphos is 1,2-diphenylphosphinoethane) (16). In these later three systems I wish to illustrate the mechanisms of reduction, the understanding of which gives insight into the control of product selectivity and overpotential requirements for electrocatalysis.

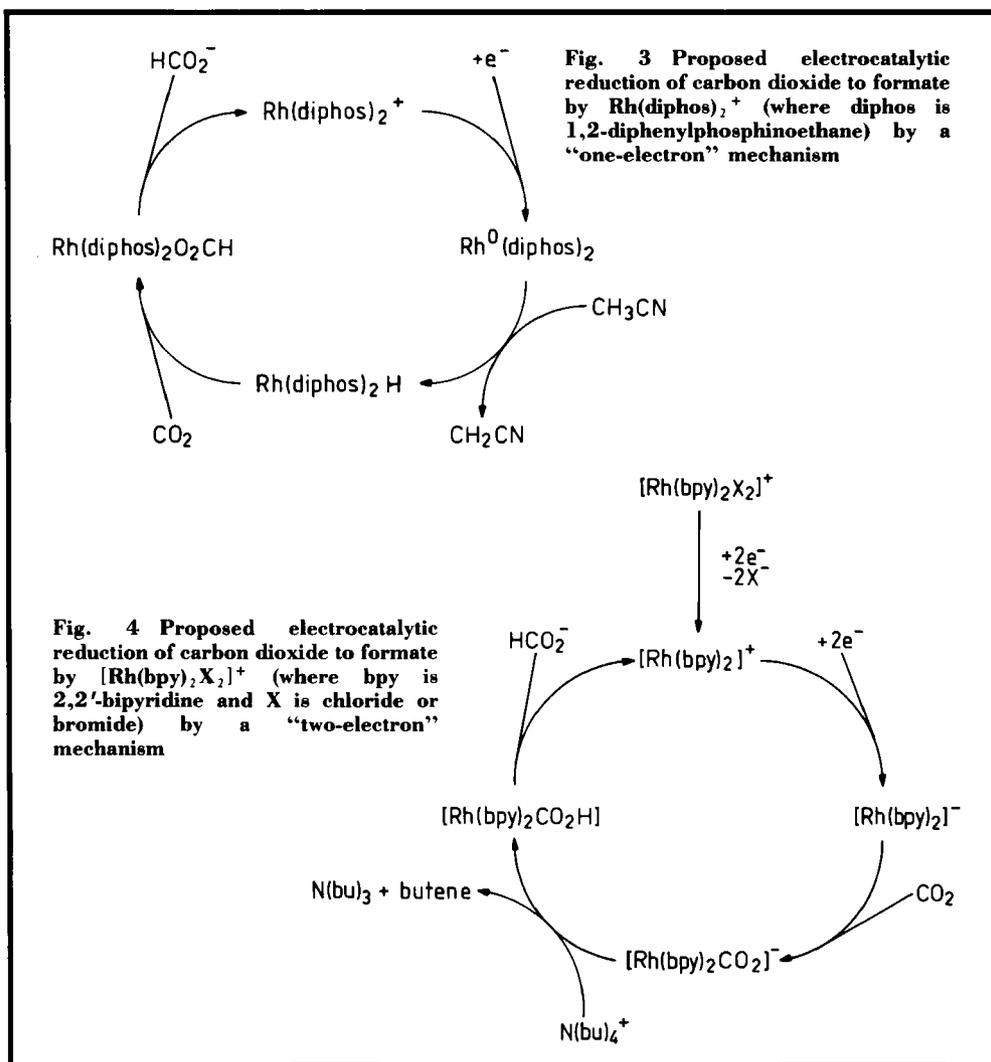
Electrocatalytic carbon dioxide reduction by

$\text{Pd}(\text{triphos})\text{L}^{2+}$  complexes gives carbon monoxide at relatively low potentials and under mild conditions (about  $-0.9$  V in acetonitrile solution at a platinum electrode in the presence of fluoroboric acid). From a series of studies, several mechanisms have been considered, including the stepwise reduction of  $\text{Pd}(\text{II})$  to  $\text{Pd}(\text{0})$  concomitant with binding of carbon dioxide to the reduced complex followed by protonation to give formate, or, prior protonation of the  $\text{Pd}(\text{0})$  intermediate resulting in a hydrido species which then reacts with carbon dioxide to give formate. Despite the mechanistic complexity, these complexes are the only examples of electrocatalysts that operate close to the thermodynamic potential of the carbon dioxide/formic acid couple (14).

With the square planar complex  $\text{Rh}(\text{diphos})_2^+$  the electrocatalytic reduction of carbon dioxide to formate can be effected at fairly negative potentials (about  $-1.5$  V). However, this example provides valuable mechanistic information on the reduction process for metal complexes in solution as shown in the proposed electrocatalytic cycle in Figure 3. The catalysis precursor  $\text{Rh}(\text{diphos})_2^+$  takes up a single electron to give as a first reaction intermediate the nineteen electron radical  $\text{Rh}(\text{diphos})_2$ . This species abstracts hydrogen from the solvent to form a second reaction intermediate  $\text{Rh}(\text{diphos})_2\text{H}$  which then inserts carbon dioxide to form a third reaction intermediate, the formate complex,  $\text{Rh}(\text{diphos})_2\text{O}_2\text{CH}$ . Dissociation of formate ion from  $\text{Rh}(\text{diphos})_2\text{O}_2\text{CH}$  regenerates the catalysis precursor and closes the cycle (16).

This work demonstrates that single-electron pathways can be used to effect net two-electron reduction of carbon dioxide, a point that also has been made for some complexes of rhenium (12). Of particular interest is that metal-based radical chemistry is involved in these cases, which opens the possibility of devising electrocatalytic cycles that couple a hydrogen radical donor to other useful chemistry.

Recent work on complexes of the type  $\text{Rh}(\text{bpy})_2\text{X}_2^+$  shows that a mechanistic scheme which involves reduction of ligand



based orbitals can be used to produce formate from carbon dioxide. As shown in Figure 4, the proposed mechanism involves the initial two-electron reduction of the catalysis precursor  $\text{Rh}(\text{bpy})_2\text{X}_2^+$  to form  $\text{Rh}(\text{bpy})_2^+$  which then reduces in two sequential, single-electron steps at the bpy ligands to give the reactive intermediate  $[\text{Rh}(\text{bpy})_2]^-$ . This basic anion then binds carbon dioxide to produce  $[\text{Rh}(\text{bpy})_2\text{CO}_2]^-$  which abstracts a proton from the electrolyte, tetra-*n*-butylammonium hexafluorophosphate, resulting in the Hofmann degradation and, the formate complex,

$[\text{Rh}(\text{bpy})_2\text{O}_2\text{CH}]$ . Then dissociation of  $[\text{Rh}(\text{bpy})_2\text{O}_2\text{CH}]$  into  $[\text{Rh}(\text{bpy})_2]^+$  and free formate completes the catalytic cycle. A key feature of this mechanistic scheme is the reduction of the bpy ligands, which act as "electron reservoirs" (17), that indirectly increase the electron density at the metal to provide reactivity channels for carbon dioxide binding (11,15).

The mechanistic schemes in Figures 3 and 4, both based on rhodium but containing dissimilar ligand systems, demonstrate that radical "one-electron" pathways and polar "two-electron" pathways can yield the net two

electron reduction of carbon dioxide to formate.

Photochemical activation and reduction of carbon dioxide to formate by a homogeneous solution system has been achieved through the reductive quenching of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  by triethanolamine in dimethylformamide. Although the mechanism is not completely understood, it appears that photochemical ligand loss from  $[\text{Ru}(\text{bpy})_3]^{2+}$  leads to  $\text{Ru}(\text{bpy})_2(\text{CO})\text{H}^+$  as the active catalyst, and that triethanolamine acts as a reductive quencher during the photoreduction process described for the ruthenium colloid system (18).

### Electrocatalysis by Thin Polymeric Films

Compared to homogeneous systems electrode immobilised catalysts have many advantages including:

[a] increased current density due to a high local concentration of catalyst,

[b] the use of only small amounts of expensive chemical materials,

[c] avoidance or minimisation of catalyst deactivation pathways,

[d] the ability to achieve chemical selectivity toward mixed substrates as a consequence of molecular shape, size, and charge of the pendant polymer sites,

[e] the ability to alter mechanistic pathways by selectively inhibiting or facilitating bimolecular reactions between redox active polymer sites,

[f] the possibility of using bi- or multilayer configurations in order to accomplish spatial segregation of different catalytic tasks, and,

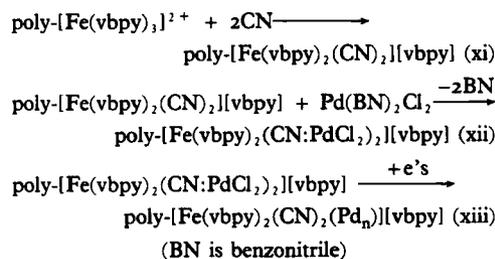
[g] easier product separation that offers the convenience of flow-through electrochemical cell designs.

We have pursued the synthesis and electrocatalytic properties of thin polymeric films that contain metal particles embedded in the interstitial regions of redox active polymers, that is by using the strategy of chemically modified electrodes (19). If properly constructed these materials could provide ligating groups that bind small metal particles but leave unsatisfied

valences at which catalytic reactions can occur. An early study has used palladium particles embedded in a non-co-ordinating matrix involving silanised polymers of 4-4'-dimethylbipyridinium cations on a platinum surface to produce formate from carbon dioxide in aqueous solution (20).

We have used two strategies in the formation of electrocatalytic polymeric films, these are: [i] the reductive electropolymerisation of vinyl containing metal complexes with an exchange labile metal (21), for example,  $[\text{Rh}^{\text{I}}(\text{vbpy})(\text{COD})]^+$  (vbpy is vinyl bipyridine, COD is 1,5-cyclooctadiene), followed by reduction of Rh(I) to Rh(0), and [ii] the reductive electropolymerisation of precursors with ligating sites followed by binding of metal cations in the film and in situ reduction.

Formation of palladium metal-containing films can be accomplished according to the synthetic route shown in Equations (xi) to (xiii) by using a preformed film of poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2][\text{vbpy}]$ , which has available both cyano groups and a vbpy chelate as potential co-ordinating sites (22). Cyclic voltammetry, u.v.-visible spectroscopy, infrared spectroscopy and ESCA all point to the formulations of the films as poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2][\text{vbpy}][\text{PdCl}_2]_2$  and poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2][\text{vbpy}][\text{Pd}_x]$  ( $x < 2$ ) in Equations (xi) to (xiii) (23).



Bulk electrolysis of polymeric films of poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2][\text{vbpy}][\text{Pd}_x]$  in carbon dioxide saturated acetonitrile with tetra-n-butylammonium ion as supporting electrolyte in the presence of water yields up to 10 per cent Faradaic efficiency hydrocarbon products, principally methane, ethylene and ethane (23).

Films of poly- $[\text{Rh}(\text{bpy})(\text{COD})]^+$  which are

electrolysed on platinum or carbon electrodes in the presence of excess  $[\text{Rh}(\text{COD})\text{Cl}]_2$  in acetonitrile solution with tetra-*n*-butylammonium salts as supporting electrolyte form a new thin film which is probably of the type poly-[vbpy]/Rh that is an electrocatalyst for carbon dioxide reduction (24). Characterisation of the new film has been accomplished by using cyclic voltammetry and ESCA which shows a typical thin film to have a surface ratio of rhodium:nitrogen of about 7–8.

Like the palladium film, bulk electrolysis studies of carbon dioxide reduction in aqueous acetonitrile results in a hydrocarbon product distribution, however,  $\text{C}_3$  and  $\text{C}_4$  skeletons make up an increasing fraction of the Faradaic yield, which now approaches 25 per cent of the current (24). This extraordinary chemistry is apparently the consequence of an electrochemically-driven Fischer-Tropsch reaction where the thermal chemistry of carbon monoxide and hydrogen is replaced with carbon dioxide and coupled electron/proton steps.

## Summary

Thus far the platinum group metals have played a dominant role in the electrocatalytic reduction of carbon dioxide, and this trend is

likely to continue. In this review I have attempted to focus on two new areas of great promise, the use of homogeneous solution electrocatalysts, and the use of polymeric films on electrode surfaces (chemically modified electrodes) that contain embedded electrocatalytic sites, especially metal particles. From the former approach a clear understanding of the intimate mechanistic details of carbon dioxide reduction is beginning to emerge, while with the latter, the possibility of multielectron products past the two-electron stage is a reality.

Some of the future challenges are to be found in the development of chemically modified electrodes that are specific to oxalate or formate, the understanding of mechanisms in the chemically modified electrode environment, the unravelling of the role of carbon dioxide complexes in both homogeneous and chemically modified electrode electrocatalysis, and, in the discovery of new methods for the electrocatalytic formation of functionalised organic compounds (25).

## Acknowledgements

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## The Clean-Up of Fusion Reactor Waste Gases

### A STUDY OF THE EFFECTS OF IMPURITIES ON SILVER-PALLADIUM

The viability of nuclear fusion reactors will depend, in part, upon the effectiveness of the fuel clean-up system. One of the purposes of this system is to separate hydrogen isotopes from impurities in the exhaust emanating from the plasma. Such treatment can be achieved by cryogenic techniques, but these are made more effective if a preliminary removal of impurities can be performed. The technique favoured for this first stage is diffusion through palladium alloy membranes, which has been used commercially for many years to produce high purity hydrogen for use in a wide range of industrial applications including the electronics industry.

The alloy most commonly used for hydrogen purification is silver-palladium, with silver contents in the range 20 to 25 weight per cent. The operating regime is predominantly hydrogen rich, at pressures between 1 and 2 MPa and temperatures between 570 and 720K. Under these conditions no loss of activity of the alloy membrane surface due to carbon monoxide, carbon dioxide or water present as impurities has been reported.

In the potential fusion reactor fuel application the aim is to separate the hydrogen isotopes from impurities such as  $C(H,D,T)_4$ ,  $(H,D,T)_2O$  and  $N(H,D,T)_3$ , as well as from carbon monoxide, carbon dioxide, oxygen and nitrogen. Thus it is desirable to restrict operating temperatures and pressures as far as possible, in order to limit diffusion through the structural components of the system. Under such conditions, however, loss of membrane activity due to poisoning by impurities is possible; the most likely cause being related to chemisorption onto active alloy sites of impurity molecules, with a subsequent loss of these sites for the promotion of through-membrane diffusion. A reduction in the operating temperature will promote chemisorption, but at the expense of desorption, and there has been a lack of information about the effect of large amounts of impurities upon

membrane behaviour. However, a recent paper from the Centre d'Etudes Nucléaires de Saclay gives experimental data for the diffusion of hydrogen through palladium-silver in the presence of the impurities expected to occur in fusion reactor waste gases (J. Chabot, J. Lecomte, C. Grumet and J. Sannier, *Fusion Technol.*, 1988, **14**, (2), part 2A, 614-618).

The French team investigated palladium-23 silver under partial pressures of hydrogen of 14 kPa, and temperatures between 420 and 725K. Their findings indicate that methane and carbon dioxide have a depressing effect upon the hydrogen permeability at temperatures below 425K, when present in concentrations of 9 volume per cent in a carrier of helium. However, carbon monoxide at 0.2 volume per cent was found to severely degrade hydrogen permeability, under the same conditions. The detrimental effect of carbon monoxide was found to extend up to 570K, as the concentration was increased to 9.5 volume per cent. No synergism between the various impurity gases was observed, and the effect of carbon monoxide in mixtures was primarily that equivalent to the concentration of carbon monoxide alone. Regeneration of the membrane was found to be possible by thermal treatment, either in vacuo at 523K or by surface oxidation/reduction treatments.

A second valuable finding from this work is that a significant carbon monoxide/hydrogen reaction was observed at temperatures in excess of 650K, with the formation of methane, carbon dioxide and water, probably as a result of the catalytic activity of the alloy membrane surface. Thus this work has defined limits within which the utilisation of palladium alloy membranes for the purification of fusion reactor feed gas appears to be feasible, that is within the temperature range 475 to 650K.

The same group are currently considering the influence of other gaseous contaminants on this process.

D.R.C.