

Polymers of Platinum Metals Complexes Immobilised on Electrodes

THEIR USE IN ELECTROCATALYTIC PROTON REDUCTION AND HYDROGENATION OF ORGANICS

By Alain Deronzier and Jean-Claude Moutet

Laboratoire d'Electrochimie Organique et de Photochimie Rédox,

Université Joseph Fourier, Grenoble, France

Interest is growing in using polymeric electrode materials containing platinum group metals complexes in molecular electrochemistry. Here, the synthesis of functionalised polypyrrole film electrodes, formed by the oxidative electropolymerisation of pyrrole-substituted rhodium, iridium and palladium complexes is reviewed, and recent results are presented concerning the electrocatalytic reduction of protons and the hydrogenation of unsaturated organic substrates in aqueous electrolyte. Metal hydride intermediates and their involvement in reactions at the electrodes are considered, as are preliminary results of asymmetric electrosynthesis on a molecular electrode material.

The deliberate modification of electrode surfaces by polymer films containing transition metal complexes is a new field of study. It combines co-ordination-, polymer- and electrochemistry, and aims at developing new materials for electrocatalysis, electroanalysis and photoelectrochemistry (1, 2). As the electrode is the key component in all electrochemical systems, the development of new electrode materials possessing the high activity and selectivity of transition metal catalysts is important for many uses.

Recently, rhodium, iridium and palladium complexes have been electrochemically transformed to their hydride derivatives and used for proton electroreduction and electrocatalytic hydrogenation of organics. Immobilising these homogeneous platinum metals catalysts on electrodes improves product and catalyst recovery, and operational stability. Reactions using very small amounts of reagents can then be performed.

Electroreductive Generation of Hydrido Complexes

The relevance of transition metal hydride complexes in co-ordination chemistry is now well recognised, particularly in chemical catalysis

(3). Additionally, it has been postulated that transition metal hydride complexes are the key intermediates in a number of electrocatalytic and photocatalytic systems, for instance, in the photoreduction and electroreduction of protons to dihydrogen (4), and in the electrochemical regeneration of the coenzyme NADH (nicotinamide adenine dinucleotide) from NAD^+ (5).

Electrochemical investigations of metal hydrides may be able to explain their activation by electron transfer and may lead to the development of new synthetic routes for the formation of transition metal hydrides. In fact, the successful electroreductive generation of transition metal hydride complexes in homogeneous media has recently been demonstrated for a number of metal complexes, including those of ruthenium (6), osmium (7), tungsten (8), iridium (7, 9), and rhodium (10, 11).

As an example, Figure 1 shows that the reduction of the cationic iridium(III) complex, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{bpy})\text{Cl}]^+$, in an organic electrolyte before (Curve (a)) and after (Curve (b)) the addition of formic acid which is the proton source, leads to the formation of its stable

hydrido derivative $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy})(\text{H})]^+$ (9). The latter exhibits a characteristic one-electron, reversible bpy ligand-based reduction (Figure 1, Curve (b)). Its quantitative production (Figure 1, Curve (c)) by the oxidative addition of a proton to the reduced $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{bpy})]^0$ complex, Equation (i), has been further corroborated from ^1H NMR

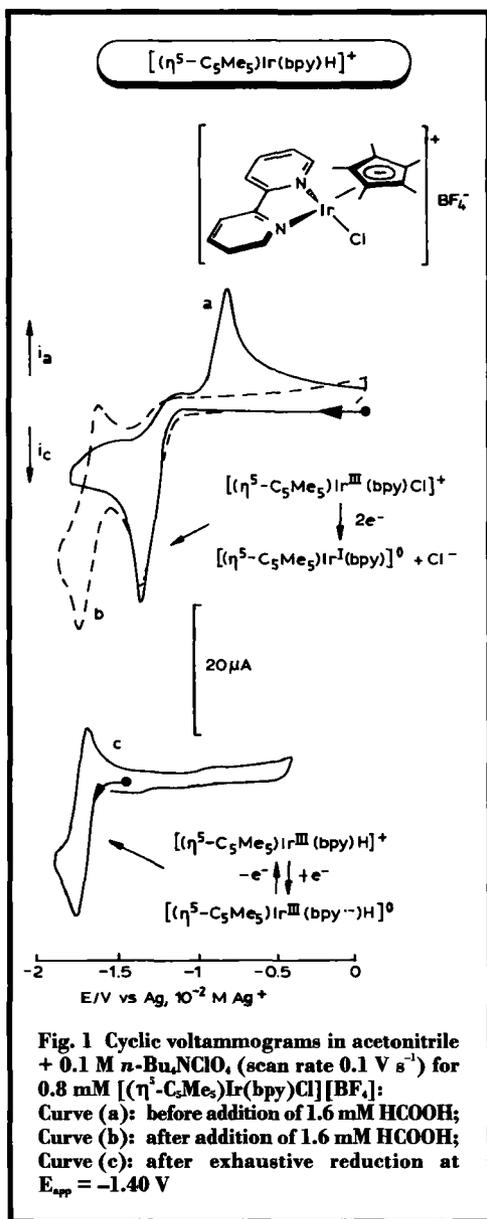


Fig. 1 Cyclic voltammograms in acetonitrile + 0.1 M *n*-Bu₄NClO₄ (scan rate 0.1 V s⁻¹) for 0.8 mM $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{bpy})\text{Cl}][\text{BF}_4]$: Curve (a): before addition of 1.6 mM HCOOH; Curve (b): after addition of 1.6 mM HCOOH; Curve (c): after exhaustive reduction at $E_{\text{app}} = -1.40$ V

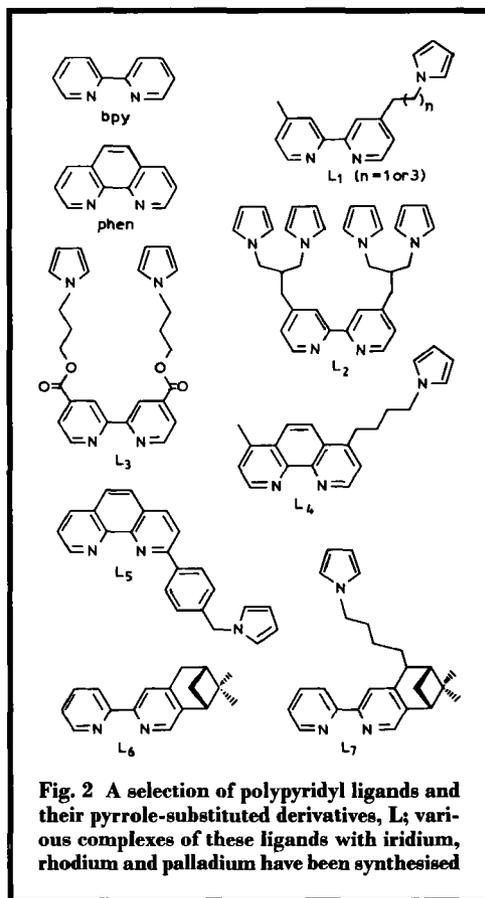
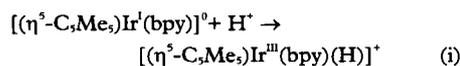


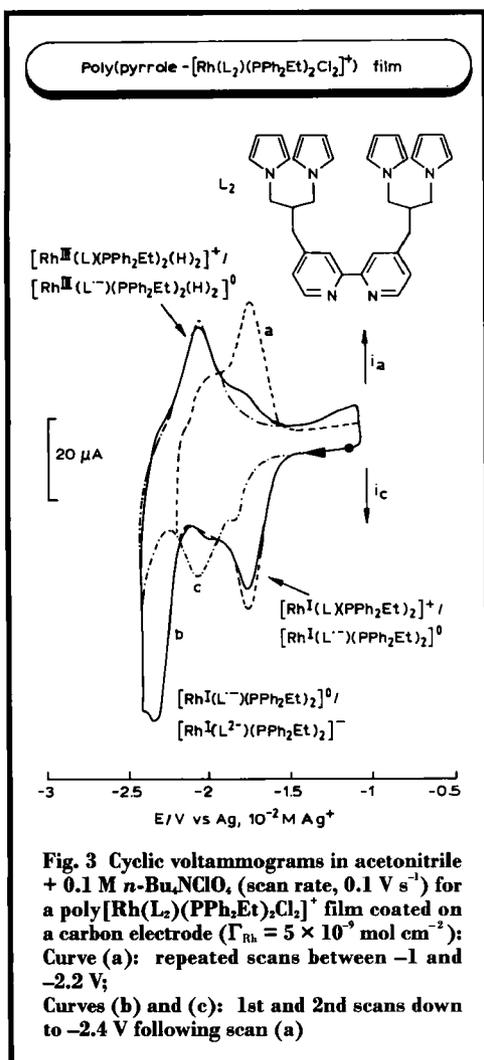
Fig. 2 A selection of polypyridyl ligands and their pyrrole-substituted derivatives, L; various complexes of these ligands with iridium, rhodium and palladium have been synthesised

(nuclear magnetic resonance) analysis of the resulting solution:



In addition, electrochemical and ^{31}P NMR data have demonstrated the electroreductive generation of the rhodium dihydro complex $[\text{Rh}(\text{bpy})(\text{PPh}_2\text{Et})_2(\text{H})_2]^+$, in acidic acetonitrile electrolyte, from its dichloro parent complex $[\text{Rh}(\text{bpy})(\text{PPh}_2\text{Et})_2(\text{Cl})_2]^+$ (10). Formation of the dihydro complex takes place via its corresponding monohydrido complex, $[\text{Rh}(\text{bpy})(\text{PPh}_2\text{Et})(\text{Cl})(\text{H})]^+$.

As in homogeneous solution, the electroreductive build-up of hydrido complexes in polymer films containing rhodium and iridium chloro parent complexes has been well established.

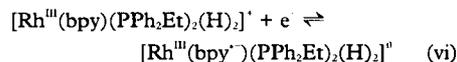
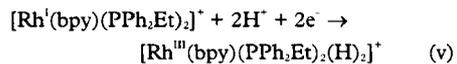
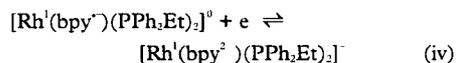
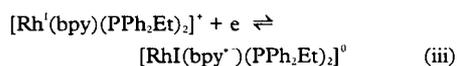
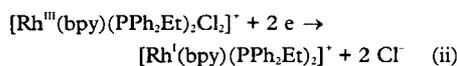


These studies have been carried out using electrodes modified by polymer film, synthesised by the oxidative electropolymerisation of complexes, such as $[(\eta^5-C_5Me_5)M(L)Cl]^+$ ($M = Ir$ (12) and Rh (11, 13)) and $[Rh(L)(PPh_2Et)_2(Cl)_2]^+$ (10), where L is a pyrrole-substituted polypyridyl ligand, see Figure 2.

A striking example of hydrido complex formation is shown in Figure 3, for a film of a cationic Rh(III) complex containing both phosphine and nitrogen ligands (10). In acetonitrile electrolyte, the reduced Rh(I) complex, Equation

(ii), is characterised by a reversible, one-electron bpy-centred redox wave (Equation (iii); Figure 3, Curve (a)) which remains stable during repeated scans.

By contrast, a fast and efficient transformation of this complex to its dihydro derivative, Equation (v), is obtained by scanning down to the second bpy-localised reduction (Equation (iv); Figure 3, Curve (b)), which forms a more strongly reducing intermediate, able to react with traces of water contained in the electrolyte. The dihydro complex is easily characterised from its reversible one-electron reduction wave (Equation (vi); Figure 3, Curve (c)).

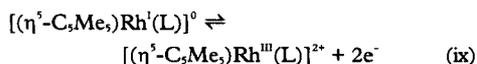
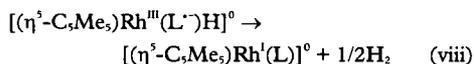
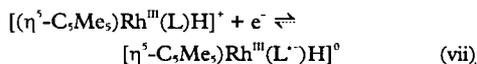


Electrocatalytic Activity of Films for Proton Reduction

Hydrido complexes of the type $[(\eta^5-C_5Me_5)Ir(L)H]^+$ ($L = bpy$ or $phen$) when studied by cyclic voltammetry, in neutral acetonitrile, are characterised by a reversible one-electron, L-centred reduction (see Figure 1, Curve (c), for example). This occurs in homogeneous solution (9) and in films (12).

However, reduction of the parent rhodium (III) complex $[(\eta^5-C_5Me_5)Rh^{III}(L)H]^+$, Equation (vii), is only partially reversible (11, 13), due to the higher instability of its reduced form. The complex $[(\eta^5-C_5Me_5)Rh^{III}(L^{\cdot-})H]^0$ decomposes to give dihydrogen and the rhodium complex $[(\eta^5-C_5Me_5)Rh^I(L)]^0$, see Equation (viii). This is shown in Figure 4 for a film of poly $[(\eta^5-C_5Me_5)Rh(L)H]^+$, where the gradual growth of the reversible two-electron wave corresponding to the $[(\eta^5-C_5Me_5)Rh(L)]^{0/2+}$ redox

couple (Equation (ix), Figure 4, Curves (b)) is seen upon repeated scanning, at the expense of the hydride reduction wave.



These films, therefore, exhibit a strong electrocatalytic activity towards proton reduction and hydrogen generation in protic media, that is, in acidic organic and aqueous electrolytes, see Figure 5A, for example. The experimental data agree with the catalytic cycle shown in Figure 5B, which involves the spontaneous decomposition of the reduced hydride complex, Path (a), and its reaction with protons, Path (b), both resulting in the release of dihydrogen. These studies clearly demonstrate that metal hydride species are the key species in the electroreduction of protons catalysed by such platinum metal complexes.

When preparative-scale electrolysis is carried out, in acidic organic and aqueous electrolytes, on vitreous carbon plate electrodes of area 5 cm² modified with poly[($\eta^5\text{-C}_5\text{Me}_5$)Ir(L)Cl]⁺ films (L = L₃, L₄), dihydrogen is produced in quasi-quantitative yields, with turnovers as high as 1000 without appreciable loss of activity by the catalytic material (12). Similar behaviour occurs with cathodes modified by polymer films derived from a number of platinum metals complexes, including [($\eta^5\text{-C}_5\text{Me}_5$)Rh(L)Cl]⁺ (11, 13–15), [Rh(L)₂Cl]⁺ (16), [Rh(L)(PPh₂Et)₂(Cl)₂]⁺ (10) and [Rh(L)(COD)]⁺ (17), where L = bpy or phen derivatives.

Electrocatalytic Hydrogenation of Organics

These new materials have attractive potential applications for electrosynthetic processes, such as the electrocatalytic hydrogenation (ECH) of organic molecules (18). ECH is the reaction of an unsaturated substrate with the hydrogen produced at a cathode by discharging protons with

electrons. ECH can thus be considered as the electrochemical analogue of conventional catalytic hydrogenation using a catalyst and molecular hydrogen; its main advantages are the in situ production of hydrogen at the surface of the catalyst (thus avoiding the use of hydrogen gas in cylinders) and much milder reaction

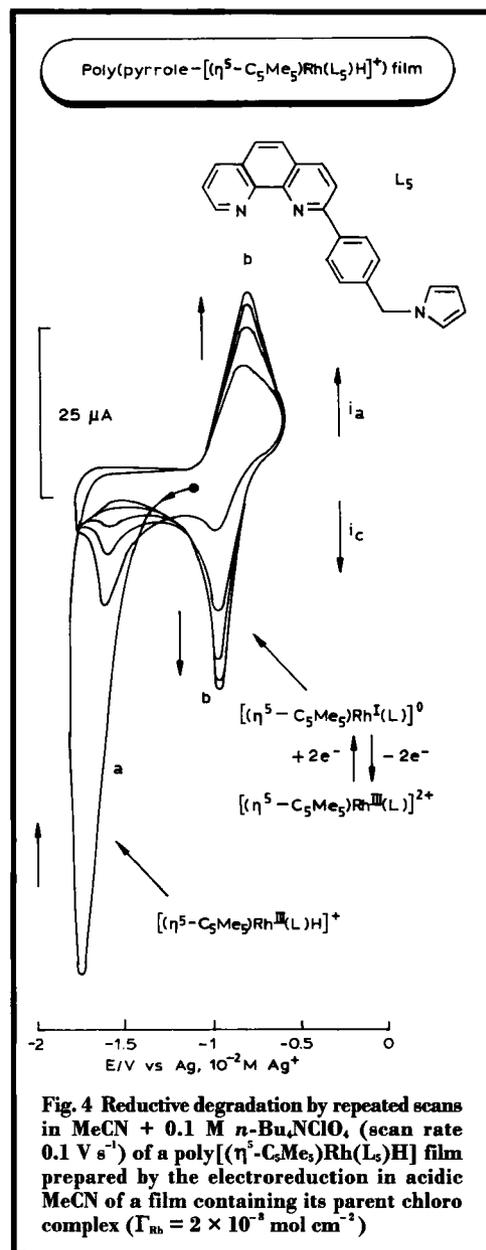
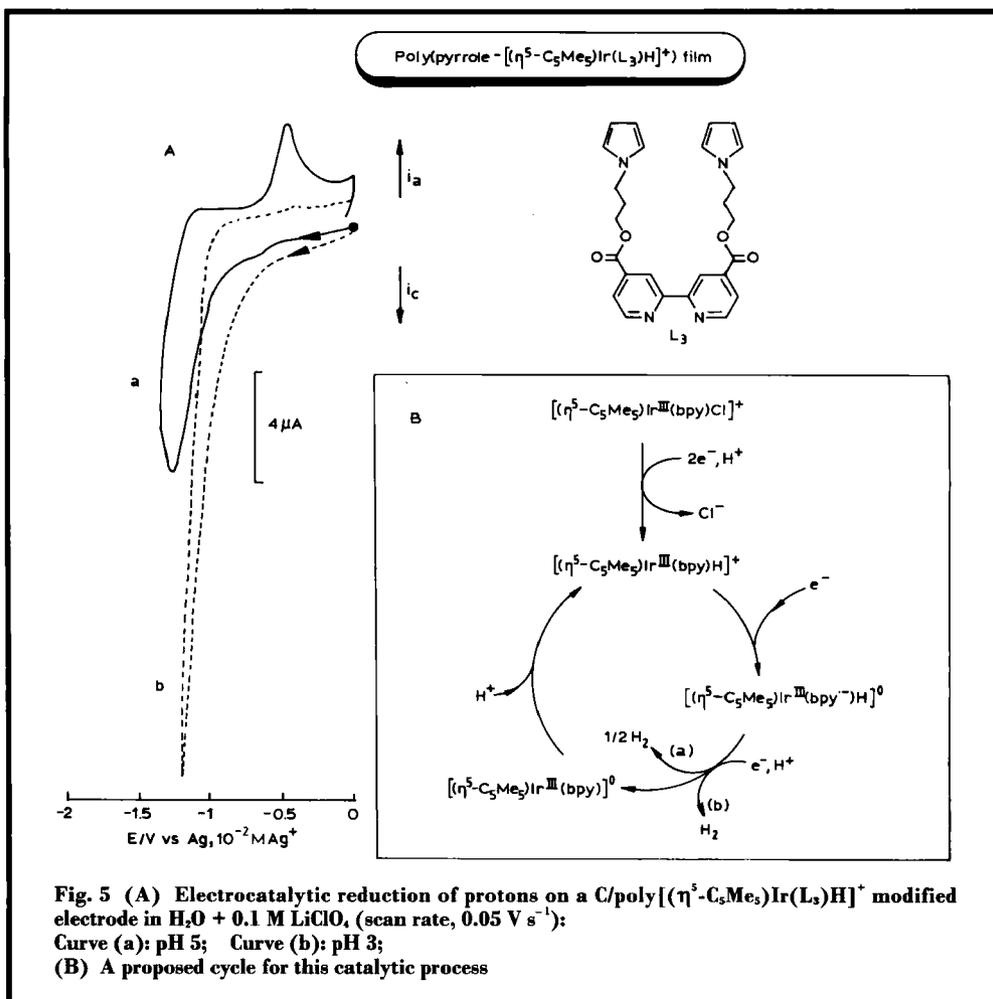


Fig. 4 Reductive degradation by repeated scans in MeCN + 0.1 M *n*-Bu₄NClO₄ (scan rate 0.1 V s⁻¹) of a poly[($\eta^5\text{-C}_5\text{Me}_5$)Rh(L₃)H] film prepared by the electroreduction in acidic MeCN of a film containing its parent chloro complex ($\Gamma_{\text{Rh}} = 2 \times 10^{-5} \text{ mol cm}^{-2}$)



conditions, since the kinetic barrier for mass transport and splitting of the barely soluble hydrogen molecule is bypassed. However, the hydrogen consuming hydrogenation reaction is in competition with hydrogen evolution, and efficient ECH processes need to use cathodes that are more active than the conventional solid transition metal cathodes. Catalytic cathodes based on Raney nickel and noble metal particles deposited on carbon or dispersed in polymers have been developed for this purpose, and applied to a number of potentially useful electrosyntheses (18). However, the use of immobilised molecular hydrogenation catalysts, such as metal complexes, is a more appealing route, as their

ability to co-ordinate substrates in a specific manner leads to high activity, regio- and stereospecificity in the ensuing catalytic reaction.

Hydrogenation on Poly $[\text{Rh}(\text{L})_2\text{Cl}_2]^+$ Film Electrodes

Platinum metals complexes have only recently been used as catalysts for the ECH of organic compounds. Undeniably, the best results have been obtained with polymer films grown on carbon electrodes by oxidative electropolymerisation of $[\text{Rh}(\text{L})_2\text{Cl}_2][\text{BF}_4]$ complexes ($\text{L} = \text{L}_1, \text{L}_3, \text{L}_4$). These materials are very active for the hydrogenation of ketones and enones in aqueous electrolytes (16, 19, 20). Some striking

results are summarised in the Table; these show that hydrogenated products can be produced in high yields, and with good current efficiencies.

One important factor is the good operational stability of the cathodes, which could be re-used several times to hydrogenate millimolar amounts of different substrates, despite the low amounts (a few μmol) of immobilised catalyst, see the Table. Turnovers as high as 5000 have been reached with polymer films based on complexes containing ligands L_1 and L_4 , see Figure 2, without significant loss of catalytic activity at the cathodes (20).

Comparative experiments, performed with similar complexes in homogeneous solution, have shown that the modified electrode is a more efficient system, as higher currents are obtained with lower amounts of catalyst. These observations can be explained by the high concentration of the active catalyst (up to 1 M) at the electron source, when the complex is polymerised onto the electrode surface.

Furthermore, differences between regio- and diastereoselectivity have been noted in homogeneous systems and polymer supported electrodes during ECH, especially with bulky substrates. For example, the main isomer formed upon catalytic hydrogenation of 4-*tert*-butylcyclohexanol on catalytic cathodes is always the *trans*-alcohol, while the major product in homogeneous catalysis is the *cis*-alcohol (19, 20). Changes in diastereoselectivity have also been

observed during the hydrogenation of carvone to dihydrocarveol, because of polymer crosslinking, which has resulted in restricted permeability of the polymer matrix. This forced selectivity is attributed to the modification of the steric environment around the catalytic centre in the polymerised complexes; access and conformational mobility of the substrate being controlled by the polymeric matrix.

Enantioselective Electrocatalytic Hydrogenation

Of the methods reported for electrochemical asymmetric induction (21), the use of electrodes that are chemically modified by chiral complexes display the best results, as they can achieve asymmetric induction with extremely small amounts of the inducing reagent. It is expected that polymer films containing transition metal complexes with optically active ligands can be used in the preparation of catalytically active and chiral electrode/electrolyte interfaces, which can then be applied to asymmetric electrosynthesis.

The validity of this approach has recently been demonstrated using catalytic cathodes synthesised from $[\text{Rh}(\text{L}_7)_2\text{Cl}_2][\text{BF}_4]$, where L_7 is a pyrrole-substituted chiral 2,2'-bipyridine (22), see Figure 2. Hydrogenations carried out with aryl ketones, such as acetophenone, 1-tetralone and 1-indanone, have shown that the corresponding alcohols are produced in moderate optical yields (5 to 12 per cent; the prevailing configuration

Electrocatalytic Hydrogenation on C/poly $[\text{Rh}(\text{L})_2\text{Cl}_2]^+$ Modified Electrodes ^a					
Ligand	Amount of complex, μmol	Substrate, amount, mmol	Product	Yield	Current efficiency, % ^b
L_1	1.1			100	66
L_4	1.4			100	87
L_1	5.3			99	52
L_3	6.6			98	63

^a Carried out at -1.2 to -1.4 V vs SCE in water-ethanol mixtures, pH 8, containing 0.1 M LiClO_4 , on modified carbon felt electrodes of dimensions $15 \times 15 \times 4$ mm

^b The ratio mol of product to mol of electron passed ^c R(-)-Carvone ^d Mixture of diastereoisomers of dihydrocarveol

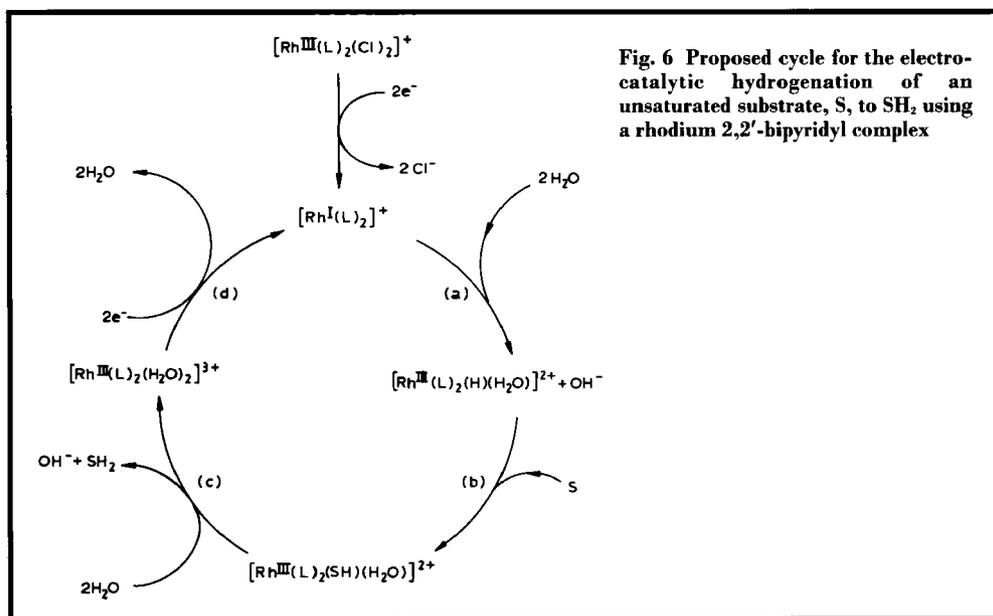


Fig. 6 Proposed cycle for the electrocatalytic hydrogenation of an unsaturated substrate, S, to SH₂ using a rhodium 2,2'-bipyridyl complex

was always (*S*). Results compare well with those obtained from hydrogen transfer promoted by homogeneous rhodium catalysts with various chiral bipyridines (23), which give a maximum enantiomeric excess of 15 per cent.

Comparative experiments performed in homogeneous solutions with $[\text{Rh}(\text{L}_6)_2\text{Cl}_2]^+$ as the electrocatalyst have shown that the enantioselectivity of the rhodium complex was fully retained in the films. Acetophenone was hydrogenated to (*S*)-phenylethanol with the same stereoselectivity (enantiomeric excess 12 per cent) on the L₇-based modified electrode and with the soluble catalyst containing L₆. This preliminary study clearly shows that for asymmetric electrocatalytic hydrogenation, effective use can be made of the selectivity of a chiral platinum metal complex, in homogeneous solution, or better still, on a polymer film modified electrode.

Role of Hydride Complexes in the Mechanism of Electrocatalytic Hydrogenation

The electrocatalytic hydrogenation of organics using 2,2'-bipyridine rhodium(III) complexes can be explained either by the catalytic reaction of an unsaturated compound with molecular hydrogen produced at the cathode, or by its

reaction with a rhodium hydride intermediate. The former hypothesis can be ruled out by taking into account the poor solubility of hydrogen in aqueous media; also quantitative current yields (close to 100 per cent) have been reached for the hydrogenation of a number of substrates. This means that all the dihydrogen, or "hydrogen equivalents" produced have been consumed. However, hydrogenation via a reactive rhodium hydride intermediate is likely to take place, by analogy with the mechanism postulated for hydrogen transfer catalysed by $[\text{Rh}(\text{bpy})_2]^+$ complexes in 2-propanol/KOH (23). A plausible electrocatalytic cycle is depicted in Figure 6. The hydride complex, formed by reaction of the electrochemically reduced Rh(I) complex with water, Step (a), reacts with a substrate S, Step (b). In Step (c), the hydrogenated product SH₂ and a Rh(III) complex are released following attack by water. In Step (d), the Rh(III) complex is then reduced at the applied potential, to regenerate $[\text{Rh}^{\text{I}}(\text{L})_2]^+$, which can then enter a new cycle.

This rhodium hydride complex has been postulated as the key intermediate in other catalytic reactions, such as photochemical water reduction (24) and electrochemical regeneration of

NADH from NAD^+ (5) with rhodium polypyridyl complexes. However, under these catalytic conditions it is too reactive to be detected, although its formation upon protonation of $[\text{Rh}(\text{bpy})_2]^+$ has been well established (25).

The participation of metal hydride complexes in the electrocatalytic hydrogenation process has been further corroborated by study of the electrocatalytic activity of different rhodium and iridium complexes. Indeed, it has been unambiguously demonstrated that complexes of $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}^{\text{III}}(\text{L})\text{Cl}]^+$ ($\text{M} = \text{Rh}$ and Ir) and $[\text{Rh}(\text{L})(\text{PPh}_2\text{Et})_2\text{Cl}_2]^+$ in polymer films are readily transformed to their hydride derivatives upon electroreduction in protic electrolytes, see above. Their ability to act as electrocatalysts for the hydrogenation of unsaturated organic substrates in aqueous electrolytes (10, 11) is in good agreement with a mechanism involving hydride species. These complexes appeared much less active than $[\text{Rh}(\text{L})_2\text{Cl}_2]^+$ complexes. Thus, the electrocatalytic activity of such transition metal complexes for the hydrogenation of organics is strongly dependent on the stability of their hydrido derivatives.

A similar trend has been observed for the electrocatalytic reduction of carbon dioxide into formate by $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{bpy})\text{Cl}]^+$ complexes ($\text{M} = \text{Rh}$ and Ir), where it appears that the best catalyst is the rhodium complex which gives the less stable, thus more reactive, reduced hydrido species (13).

Catalytically Active Films of Other Platinum Metal Complexes

Polymer materials derived from other platinum metal complexes, such as $[\text{Rh}^{\text{I}}(\text{bpy})(\text{COD})]^+$ (17) and $[\text{Pd}^{\text{II}}(\text{bpy})_2]^{2+}$ (26), have also been applied to the ECH reaction. In particular, modified electrodes synthesised by oxidative electropolymerisation of $[\text{Pd}(\text{L}_1)_2][2\text{BF}_4]$ are active for the selective hydro-

genation of activated olefins in aqueous media (26). The latter reaction is likely to proceed via a metal hydride species, formed from the doubly reduced $\text{Pd}(0)$ complex.

However, there is no experimental evidence for such an intermediate hydrido complex. It must be emphasised that the reduced form of the palladium complex is stable in its polymerised form, as well as in organic and aqueous electrolyte, while it decomposes to metallic palladium and free bpy in homogeneous electrolytes. This increased stability of the polymerised complex could result from a slower decoordination reaction associated with electron transfer in the polymeric matrix.

Conclusions

The development of catalytic cathodes by immobilising molecular hydrogenation catalysts on conducting surfaces may elicit new interest in the electrocatalytic hydrogenation process, alongside the already growing interest in electrosynthesis using metal complexes. These new electrode materials offer several advantages over the same complexes used in homogeneous solution: greater stability in the immobilised form, smaller amounts of catalyst and the possible avoidance of solubility problems in aqueous media. Furthermore, entrapping a metal complex in a polymer film coated onto an electrode surface improves its operational stability, and increases turnover. Stereoselective hydrogenations using electrode materials based on chiral metal complexes may also provide a way to asymmetric electrosyntheses, a goal that has been attempted, but not yet satisfactorily achieved.

Lastly, further development could make use of grouping, in the same polymer matrix, different selected catalytic partners, with a view to achieving electrocatalytic syntheses which involve multielectronic steps.

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Structural Nickel-Doped Iridium-Aluminium Materials

Materials used in high temperature structural applications are now required to withstand higher operating temperatures than ever before in the drive for more efficient function of equipment and plant. This is particularly true for materials used in high performance gas turbine engines where the nickel-based superalloys currently used reach their operational limit at < 1200°C. One focus of work in this area for the next generation of materials has been the ordered intermetallics, and Nb₃Al has been intensively investigated, but it shows poor ductility and low oxidation resistance.

Now, scientists at Iwate University in Japan report on the high temperature strength and ductility of ordered intermetallics, based on iridium, specifically IrAl and Ir_{1-x}Ni_xAl (with $x = 0-0.8$) at temperatures of 25 to 1400°C (A. Chiba, T. Ono, X. G. Li and S. Takahashi, *Intermetallics*, 1998, **6**, (1), 35-42). The high melting point of iridium at 2243°C may impart excellent high temperature strength, while the formation of a surface film of Al₂O₃ is anticipated to give good oxidation resistance.

Compression testing confirmed the postulated high room-temperature strength of IrAl at ~1900 MPa but revealed little ductility below 800°C. The ductile-brittle transition occurs between 800 and 1000°C, and above this there is pronounced compressive ductility resulting in steady state deformation after yield. The Ir_{0.2}Ni_{0.8}Al exhibits good ductility above 800°C but work hardens during deformation at 1000°C. Below 800°C its ductility is inferior to that of IrAl.

Adding nickel improves the ductility of IrAl, but the ductile-brittle transition temperature decreases with increasing nickel. At yielding IrAl is an order of magnitude stronger than NiAl, and Ir_{0.2}Ni_{0.8}Al shows improved strength by a factor of ~5. Generally, the strength of Ir_{1-x}Ni_xAl decreases with increased nickel content.

The creep behaviour of the materials also differs markedly. Both IrAl and NiAl exhibit normal primary creep where the creep rate decreases with increasing strain, but Ir_{0.2}Ni_{0.8}Al exhibits inverse primary creep. The steady state secondary creep of Ir_{0.2}Ni_{0.8}Al was measured between 950 and 1100°C, giving an activation energy, Q_c , of 400 kJ mol⁻¹ and steady-state exponent $n = 3.2$, typical of class I behaviour. Microstructural analysis revealed that only Ir_{0.2}Ni_{0.8}Al and NiAl exhibited a single-phase type B2 structure; IrAl contained secondary phase precipitates, contradicting earlier reports of an ordered single-phase structure from 48 to 52 mol%. The authors postulate that this may be due to deficiencies in their homogenisation heat treatments, and thus could not accurately produce the activation energy and exponent for IrAl. However, an exponent of 4.2 and class II behaviour are suggested. Creep strengths of IrAl and Ir_{0.2}Ni_{0.8}Al were four orders of magnitude higher than for NiAl for a given applied stress.

Overall, results are promising for the IrAl/NiAl based systems, although the relatively low temperatures of the present study would suggest that further evaluative work would be of considerable benefit.

R. B. MCGRATH