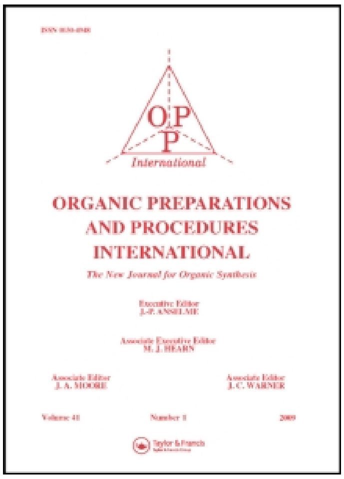

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ELECTROCATALYTIC HYDROGENATION ON HYDROGEN-ACTIVE ELECTRODES. A REVIEW

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INTRODUCTION

Successful electrosynthesis processes are dependent on finding efficient electrode materials which give the required selectivity for the intended chemical change. Electrocatalytic hydrogenations (ECH) have been carried out since the beginning of the century.[1] It has been suggested quite early[2] that electrochemical reductions on transition metal cathodes might involve reaction of an unsaturated substrate with adsorbed hydrogen atoms or molecules produced at the cathode by the discharge of protons with electrons. However, ECH has never achieved the same success as the widely used hydrogenation with heterogeneous catalysts. The main reason is the poor catalytic activity of regular electrode materials - usually massive transition metals electrodes - which requires very low current densities for efficient reactions. The situation is currently very different with respect to the development of catalytic electrodes, in particular Raney nickel cathodes and noble metals deposited on carbon. The literature does have now some potentially useful examples of ECH. A relevant one is the paired oxidation (to gluconic acid) and reduction (to sorbitol) of glucose in an undivided cell.[3]

Electrocatalytic hydrogenation of unsaturated organic molecules in aqueous media involves first the formation of chemisorbed hydrogen by reduction of water or proton (from an organic acid for example) at a cathode with a low hydrogen overvoltage, *i.e.* a transition metal electrode M (Eq. 1). Hydrogenation then proceeds by reaction of the adsorbed substrate S with adsorbed hydrogen (Eq. 2), as in catalytic hydrogenation.

$$\mathrm{M} \xrightarrow{H^+,\, e^-} \mathrm{M(H)} \qquad (1)$$

$$\mathrm{M} \xrightarrow{S} \mathrm{M(S)} \xrightarrow{2\,M(H)} \mathrm{SH_2} \qquad (2)$$

$$2\ \mathrm{M(H)} \longrightarrow \mathrm{H_2} \qquad (3)$$

$$\mathrm{M(H)} \xrightarrow{H^+,\, e^-} \mathrm{H_2} \qquad (4)$$

ECH must be distinguished from the electronation-protonation mechanism (Eq. 5).

$$\mathrm{S} \xrightarrow{e^-} \mathrm{S}^{\bullet -} \xrightarrow{H^+} \mathrm{SH}^{\bullet} \xrightarrow{e^-} \mathrm{SH}^- \xrightarrow{H^+} \mathrm{SH_2} \qquad (5)$$

Electrohydrogenation could only be expected with easily reducible compounds, since it requires an initial electron transfer to the substrate. Thus, electrohydrogenation normally occurs at a more negative potential than ECH. The two mechanisms have been clearly differentiated.[4] They may be simply controlled by measuring the reduction potential of the substrate used in a given experiment.[5] Common features and differences between catalytic, electrocatalytic and electrochemical hydrogenation have been thoroughly discussed.[6,7]

ECH has several advantages over catalytic hydrogenation. The electrochemical production of hydrogen directly at the surface of the catalyst avoids the use of hydrogen gas. Thus, the kinetic barrier for mass transport and splitting of the poorly soluble hydrogen molecule are completely bypassed. Elevated temperatures and high pressures can be avoided and the reaction conditions are much milder than in regular hydrogenation on heterogeneous catalysts. Furthermore, the cathodic potential applied to the catalyst in ECH could minimize or even prevent the problems of poisoning,[8] maintaining the catalytic activity for longer periods.

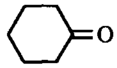
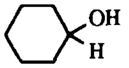
The efficiency of electrocatalytic hydrogenation is determined by the competition between hydrogenation of an unsaturated substrate (Eq. 2) and H_2 evolution (Eqs. 3 or 4). The relative rates of these two processes are affected by several factors, mainly by the activity of chemisorbed hydrogen but also by the current density and the presence of any other molecule (co-solvent, supporting electrolyte) that can be adsorbed on the electrode in preference to the substrate to be hydrogenated.

The objective of this review is to present useful synthetic reactions carried out using the ECH technique. Apart conventional cathodes like platinized platinum and the more recently developed hydrogen active electrodes (*i.e.* Raney nickel or metal deposited on carbon), new catalytic cathodes based on transition metal particles dispersed in polymeric matrices are promising electrode materials. Furthermore, recent developments show that ECH can be carried out on carbon electrodes modified with metal complexes-based polymeric films.

I. CONVENTIONAL MASSIVE ELECTRODE MATERIALS

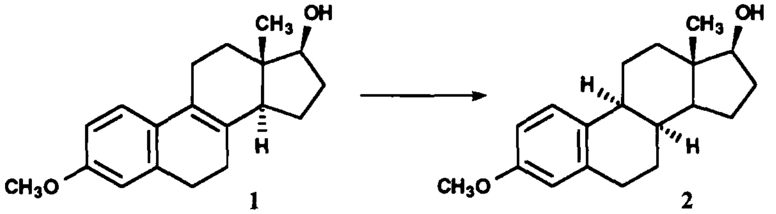
Cathodes were initially prepared from sheets, wires, gauzes, rods or wool of numerous metals, alloys or amalgams.[9] Platinum appeared to be the most widely used metal, especially in its platinized platinum (Pt/Pt) form. While a rough cathode has a lower overvoltage than a smooth one, it also has a greater surface area and the depolarizer, *i.e.* an unsaturated organic substrate has more opportunity to react with hydrogen on it. As an example, cinnamic acid failed to undergo hydrogenation at a smooth platinum electrode but reacted at a Pt/Pt cathode.[10] These electrode materials often give excellent yields, with good current efficiencies, for the reduction of functional groups such as carbon-oxygen and carbon-nitrogen double bonds,[11] as shown by some results in Table 1. It should be noted that these hydrogenations have been carried out in alkaline methanol at reasonable current densities over 10 mA cm^{-2}. Obviously, the current efficiency drops slowly with increasing current density. For example, the current efficiency for the hydrogenation of acetophenone to 1-phenylcyclohexanol is 90% and 78% at 25 and 200 mA cm^{-2} respectively.[11] It should be noted that the course of the reaction is strongly dependent on the electrolyte composition, the major product being ethybenzene in acidic alcohol.[12] This hydrogenation is an acceptable electrochemical analogue for the classical Clemmensen reduction.

TABLE 1. Hydrogenation[a] at a Pt/Pt Electrode[11]

Substrate[b]	Product	Yield (%)	Current Efficiency[c] (%)
$C_6H_5COCH_3$	$C_6H_5CH(OH)CH_3$	99	85
$CH_3C_6H_4COCH_3$	$CH_3C_6H_4CH(OH)CH_3$	98	83
$C_6H_5COC_6H_5$	$C_6H_5CH(OH)C_6H_5$	99	90
		95	98
C_6H_5CHO	$C_6H_5CH_2OH$	96	75
$CH_3OC_6H_4CHO$	$CH_3OC_6H_4CH_2OH$	98	86
$C_6H_5NO_2$	$C_6H_5NH_2$	86	72[d]
$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH_2NHC_6H_5$	93	79

a) In CH_3OH/CH_3ONa at 50 mA cm^{-2} b) 0.5 M c) Measured after 2 electrons per molecule have been passed d) After 6 electrons per molecule.

High area palladium cathodes, obtained upon electroreduction of palladium chloride on Pd, Pt, Au or Cu-foil have been shown of interest for the hydrogenation of carbon-carbon double bonds in the steroid field.[13] Estratetraene (**1**) was stereoselectively reduced to 8CL-estradiol methyl ether (**2**) (Eq. 6); the 8β-isomer was obtained on increasing the reaction temperature. Several examples of stereoselective hydrogenationsof steroids have also been described.[13]



1 2 (6)

In order to prepare more active cathode materials and to reduce cost, the use of carbon as the conductive base for the catalyst was recently introduced.[14] Carbon rods were electroplated in acidic aqueous solutions of noble metals salts and tested for electrocatalytic hydrogenation of several aromatic compounds to the corresponding cyclohexyl derivatives. Special attention was given to phenol reduction. The hydrogenation of phenol to cyclohexanol in dilute H_2SO_4 was initially shown to be much more efficient on Pt/C than on Pt/Pt, but the yield of product remained low (54%). On a Rh/C electrode the yield was much higher, producing 92% cyclohexanol with a good current efficiency (79%), thus establishing it as a satisfactory method for the synthesis of cyclohexanol. The observed difference between platinum and rhodium is reminiscent of results obtained in regular catalytic hydrogenation where Pt is known to result in considerable hydrogenolysis of phenol to benzene and cyclohexane, compared to Rh.[15] However, the pronounced decrease in catalytic activity due to the addition of an organic co-solvent limits this method. Only water soluble aromatic substrates could be satisfactorily hydrogenated.

In the same way, a high surface area palladium electrode prepared by electrodeposition of Pd on a graphite plate has been reported as a convenient electrocatalytic system for the cleavage of protected peptides.[16] Electrocatalytic hydrogenation of benzyloxycarbonyl derivatives of morpholine chosen as a model compound, and peptides yields the corresponding deprotected products quantitatively (Eq. 7), with current efficiencies greater than 70%. This procedure may be carried out in very mild conditions, at room temperature or below and the isolation of products is straightforward from the electrolysis medium.

$$RR'NCO_2CH_2C_6H_5 \xrightarrow[\text{MeOH/AcOH/NaClO}_4]{\text{Pd/C, -006 to -1 V SCE}} RR'NH + CO_2 + C_6H_5CH_3 \qquad (7)$$

RR'NH = amine, amino and peptide

Electrodeposition of nickel on graphite or glassy carbon electrodes leads also to hydrogen active surfaces. An attractive approach is the use of an electrolyte containing a low concentration of nickel ions.[17] Thus, the metal catalyst is deposited *in situ* in an oxygen free medium, at potentials where the coating is cathodically protected. Such deposit would be free of corrosion coating. Moreover, the surface of the catalyst would be continuously renewed by further electrodeposition, giving stable and reproducible cathodes. These electrodes have been tested for the electrocatalytic hydrogenation of aromatic ketones in acidic water ethanol mixtures.[17] Since organic compounds strongly inhibit the nucleation and growth of Ni(O) centers, it is necessary to form the catalytic surface prior to the introduction of the organic substrate in the catholyte. The presence of nickel ions in the medium maintains the activity of the cathode which shows good selectivity to products from a bielectronic reduction, giving almost exclusively the corresponding alcohols.[17] The major problem is the low catalytic activity of these nickel surfaces. Hence the current densities were below 5 mA cm^{-2} and a significant H_2 evolution was observed.

II. HYDROGEN ACTIVE POWDER CATHODES

1. Raney Nickel Electrodes and Related Materials

The use of Raney nickel (R-Ni) as the cathode material was mentioned several years ago,[18] but the last ten years have seen an increasing number of papers on this subject which demonstrate its usefulness for the hydrogenation of organic compounds.

The catalytic cathodes could be prepared simply by spreading the R-Ni powder onto a nickel plate which serves as the electrical contact. This design is not really satisfactory from a practical point of view, because of the powdery property of the cathode. Extraction of the hydrogenated product and recovery of the catalyst is less easy than with a solid electrode. More recently, Lessard and coworkers proposed more convenient Raney nickel cathodes.[19] The electrodes are prepared in the following manner: nickel plates are electroplated in a bath containing nickel ions and a dispersion of unleached powdered Raney alloy. The electrodes then are activated by leaching the particles of alloy embedded in the deposited nickel, according to procedures drawn from regular preparations of R-Ni. On that way, efficient and easily handled R-Ni cathodes were obtained. Devarda copper electrodes were also prepared by a similar procedure.[19]

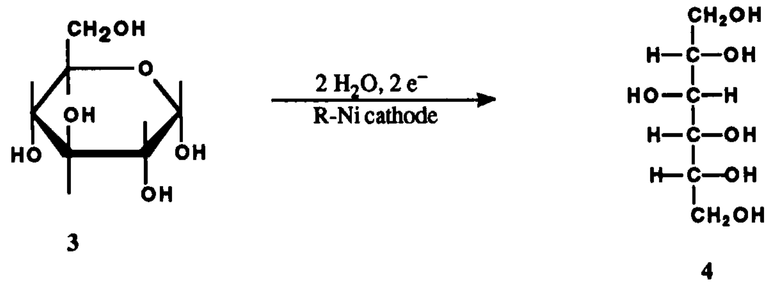
Hydrogenation in MeOH/MeONa of 39 unsaturated compounds including ketones, aromatic aldehydes, Schiff's bases, oximes, nitriles, nitro-aromatic, olefinic and acetylenic compounds on R-Ni powder (2 g per 0.1 mol of substrate) electrodes has been reported by Chiba and coworkers.[20] The course of the reaction ressembled that taken by regular catalytic hydrogenation with R-Ni and elemental hydrogen. This method seemed to be especially attractive in that these hydrogenations could be carried out at room temperature and atmospheric pressure, giving products in yields often greater than 60%.

The electrocatalytic hydrogenation of polycyclic aromatics compounds to dihydro, tetrahydro and octahydro derivatives clearly demonstrates the efficiency of this method,[19,21] since their catalytic hydrogenation on R-Ni require both elevated temperatures and high pressures. Efficient reduction at Raney nickel and Devarda copper electrodes of nitrobenzene, phenylhydroxylamine, azoxybenzene, azobenzene and hydrazobenzene to aniline in aqueous methanolic electrolytes and in high yields has also been reported.[22] More, the Devarda copper cathode could effectively reduce a nitroaliphatic compound, *i. e.* nitrocyclohexane to cyclohexylamine.[19] It is noteworthy that these hydrogenations cannot be performed on massive nickel or copper electrodes. The R-Ni powder cathode provided also selective hydrogenation of several nitriles.[23] In this way benzonitrile, hexanenitrile and 2,2-dimethylpropanenitrile were reduced to the corresponding primary amines in high yields.

Improvement of current efficiency of hydrogenation at R-Ni cathodes has been observed in aqueous micellar solutions obtained with cetyltrimethylammonium bromide.[24] which favored the ECH process over the hydrogen evolution reaction. The role of organic salts as supporting electrolytes during the electrocatalytic hydrogenation of aromatic compounds on R-Ni was investigated very recently.[25] In the presence of tetraethylammonium *p*-toluenesulfonate, benzene, aniline and nitrobenzene were hydrogenated to corresponding cyclohexane derivatives. With sodium *p*- toluenesulfonate as supporting electrolyte, only the nitro group of nitrobenzene was reduced. It was believed that benzene and its derivatives are solubilized in the hydrophobic quaternary ammonium ions film formed at the R-Ni electrode-electrolyte interface and remain on the catalytic surface for sufficiently long periods of time to react fully with six hydrogen atoms.

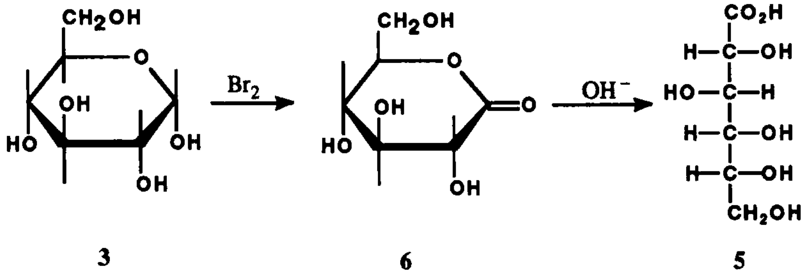
Useful compounds have been synthesized by the convenient paired electrolysis way in undivided packed bed flow-through reactors. In such a paired synthesis, α-D glucose **3** is electrohydrogenated to sorbitol **4** at a R-Ni powder cathode (Eq. 8) and glucose is indirectly oxidized by electrogenerated HOBR (Eq. 9) to gluconic acid **5**, *via* a δ-gluconolactone **6** intermediate (Eq. 10).

Under these conditions, the yields of sorbitol and of gluconic acid were very high, as well as the current efficiencies (80-100% and 100% respectively with an applied current of 250-500 mA per 10 g of R-Ni powder). Owing to the lower cathode potentials and the better current efficiencies



(8)

$$2\ \mathrm{Br}^- \xrightarrow[\text{graphite anode}]{2\,e^-} \mathrm{Br}_2 \xrightarrow{\mathrm{H_2O}} \mathrm{HOBr} + \mathrm{Br}^- + \mathrm{H}^+ \qquad (9)$$



(10)

observed, the R-Ni powder electrode appeared to be an attractive alternative to the high hydrogen overpotential cathodes such as Zn(Hg) or Pd(Hg), which were usually used in the commercial production of sorbitol by electrochemical reduction of glucose. A similar efficient electrocatalytic process for production of xylitol and xylonic acid directly from D-xylose has also been developed very recently.[27] Others paired electrosynthesis with R-Ni cathodes have been described, including a one-pot reaction addition of an alcohol to a carbon-carbon double bond[28] and the hydrogenation of 1,4-dimethoxybenzene to 1,4-cyclohexane dione.[29] In both cases, plausible reaction mechanisms involve reduction at the R-Ni cathode of an intermediate-formed at the anode.

The enantioselective catalytic hydrogenation by modified R-Ni has been successfully achieved.[30] Thus, it could be expected that a modified R-Ni cathode would give high optical purity and chemical yield in the reduction of carbonyl compounds. As a matter of fact, ECH of methyl acetoacetate on a R-Ni powder cathode modified with (R,R)-(+)-tartaric acid[31] afforded 3-hydroxylbutyrate with a chemical yield of 90% and a purity yield of 28.5%. In a similar way, enantioselective ECH of aliphatic ketones was attained,[32] but optical purities were quite unsatisfactory (2-6%).

2. Platinum and Palladium on Carbon Powder Electrodes

In comparison with Riney nickel electrodes, very little ttention has been paid to catalytic cathodes based on Pd-C and Pt-C powders dispersed on a metal plate which serves as the electrical contact. The ECH of 2-cyclohexen-1-one was used as a test reaction to compare the efficiency and the selectivity of the different catalytic powders: R-Ni, Pd-C and Pt-C.[33] The selectivity for the formation of cyclohexanone was very high on Pd-C and R-Ni (90-100%), whereas appreciable amounts of cyclohexanol were formed on Pt-C. It should be noted that Pd-C is superior to R-Ni, from a current efficiency point of view when water is used as the proton source instead of a weak organic acid. Hydrogenation of some others conjugated enones have been studied.[33b] This study was another demonstration of the similarity in reactivity of ECH to the ordinary catalytic hydrogenation. In addition, the Pd-C cathode afforded preferable results to the R-Ni cathode odth respect to the selective hydrogenation of 4-nitrobenzonitrile to 4-aminobenzonitrile.[23]

III. HYDROGEN ACTIVE CATHODES BASED ON METAL PARTICLES DISPERSED IN POLYMERIC FILM ELECTRODES

The reason for incorporating metallic particles into porous matrices is to increase the specific area of these materials and improve catalytic efficiency. Furthermore, the adsorption of a polymer on the surface of metal particles is known to prevent aggregation of the particles by steric interactions,[34] as well as physical or chemical loss of the catalyst[35]. This could improve the long term stability of the catalytic system. Thus, metal microparticles deposited on polymer coated electrodes and photoelectrodes, has recently attracted considerable interest for potential applications in electrocatalysis. It has been demonstrated that the inclusion of platinum and related metals microparticles in polymeric films, such as viologen (N,N′-dialkyl-4,4′-bipyridinium)[36] and cobaltocenium[37] based redox polymers, poly(vinylacetic acid),[35] poly(3-methylthiophene),[38] poly(4-vinylpyridine),[39] Nafion,[40] polyaniline[41] and poly(mercaptohydroquinone or benzoquinone)[42] results in improved photo- or electrocatalytic generation of hydrogen in aqueous media.

Recently, we reported that carbon electrodes coated by polypyrrole-pendant viologen (4,4′-bipyridinium salt) films containing Pd(O), Pt(O) or Rh(O) microparticles are efficient catalytic electrodes for the electrohydrogenation of unsaturated organic compounds in aqueous media.[43-45] In these

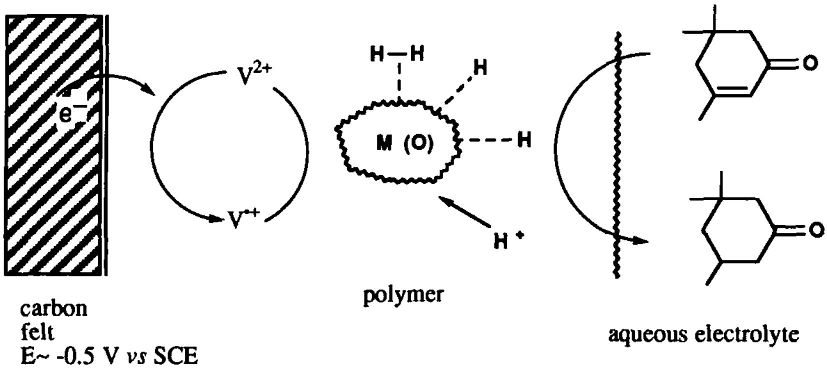


Fig. 1
Electrocatalytic Hydrogenation of an Olefin on a C/poly(pyrrole-viologen)-M(O) electrode; M is Pd, Pt or Rh; $V^{2+}/V^{\cdot+}$ is the 4,4′-bipyridinium dication/radical cation redox system linked to the polypyrrolic matrix.

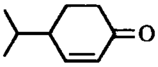
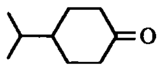
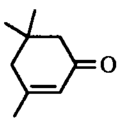
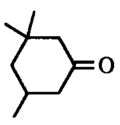
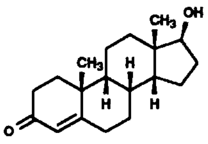
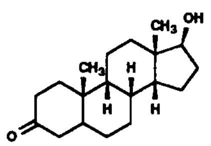
polymers, viologen groups ensure a stable transport of electrons at a potential (≅ 0.5 V *vs* SCE) where the reduction of protons to hydrogen is thermodynamically viable at pH ≤ 4. This reduction is catalyzed by the noble metals microparticles, on which the hydrogen formed is adsorbed and the organic substrate hydrogenated (Fig. 1).

Some relevant examples of ECH on these cathodes are presented in Table 2. Carbon-carbon double and triple bonds conjugated with an aromatic ring or a carbonyl group were readily hydrogenated. Steric hindrance markedly decreases the catalytic efficiency, as shown by the poor electric yield measured (13%) for the reduction of isophorone on Pd (entry 6). Better results could be obtained by using low amounts of Rh (current yield 37%, entry 7). The metal loading has also a pronounced effect on the catalytic efficiency of the cathode. The current yield increased with the amount of Rh in the polymer, reaching a maximum of 73% (entries 8 and 9). Quantitative and selective hydrogenation of testosterone on a Pt-containing polymer electrode was carried out with a current yield around 20% (entry 16). Only 1% of the carbonyl group was reduced, whatever the metal used. The influence of the catalyst is only a reciable on the comparative yield of a- and 3- isomers formed (entries 14, 15 and 17).

The high catalytic efficiency of these metal microparticles in polymer films with respect to that of solid metal electrodes is demonstrated with the hydrogenation of styrene (entries 10, 11 and 12) and benzonitrile (entry 13). While the Pt-based cathode readily hydrogenates styrene to ethylbenzene, a platinized platinum electrode was ineffective.[11] The Pd-based cathode has an efficiency similar to that of the Pd/C powder cathode.[11] It is noteworthy that benzonitrile could not be hydrogenated at Pt/Pt and Pd/C massive electrodes, while Pd in polyviologen films supports its conversion to benzylamine in a fair yield. Finally, these new cathodes have exhibited excellent long term stability and a high catalytic efficiency inspite of low metal loading. As a matter of fact, they could be reused numerous times without Pt/Pt or metal/C cathodes (see for example the hydrogenation of styrene and benzonitrile), easier to handle and more selective (see the hydrogenation of conjugated enones) than the R-Ni powder electrodes.

The application in ECH of non-redox active polymer films has also been reported. The use of palladium Black, deposited on a wettable porous polytetrafluoroethylene film electrode, has been studied for electrocatalytic hydrogenation of ethylene.[46] Hydrogenation of olefinic double bonds could also be achieved by the solid polymer electrolyte (*spe*) electrolysis method.[47] Various *spe* composite electrodes prepared by electrodes deposition of Au, Pt and Au-Pt on each side of a Nafion membrane were used. In this system, the cell is divided by the *spe* electrode. Oxygen and protons are produced in the anodic compartment. Protons migrate through the *spe* composite to be reduced to hydrogen on the other side (cathode) of the membrane where olefins are hydrogenated (Fig. 2). The advantage of the *spe* method is that no supporting electrolyte is required, thereby facilitating product separation and pypification. Electrocatalytic hydrogenation of diethyl maleate, cyelooctene and α-methylstyrene for example occured with better efficiencies on Pt-Au-*spe* than on Pt-*spe*. This may be attributed to a more uniform current distribution in the former composite. However, fairly low current efficiencies were observed, inspite of the low current densities (mainly below 5 mA/cm^2) used.

TABLE 2. Electrochemical Hydrogenation[a] on C/poly(pyrrole-viologen)-metal Electrodes

Entry	Substrate	Amount. (mmol)	Metal cat. (μmol)	consumed current electron molecule^{-1}	Product	Yield (%) (current efficiency %)
1	$C_6H_5CH{=}CHCO_2H$	7	Pd(33)	2	$C_6H_5CH_2CH_2CO_2H$	95 (95)
2		15	Pd(33)	2		100 (100)
3	$C_6H_5C{\equiv}CC_6H_5$	3	Pd(33)	4	$C_6H_5CH_2CH_2C_6H_5$	98 (98)
4	C_6H_5CHO	4	Pd(33)	2	$C_6H_5CH_2OH$	100 (100)
5	$C_6H_5NO_2$	8	Pd(42)	6	$C_6H_5NH_2$	86 (86)
6		15	Pd(33)	2		13 (13)
7			Rh(9)	2		37 (37)
8			Rh(31)	2		63 (63)
9			Rh(48)	2		73 (73)
10	$C_6H_5CH{=}CH_2$	10	Pd(42)	2	$C_6H_5CH_2CH_3$	65 (65)
11			Pd(45)	2		58 (58)
12			Rh(43)	2		56 (56)
13	$C_6H_5C{\equiv}N$	10	Pd(17)	4	$C_6H_5CH_2NH_2$	68 (68)
14		3.5	Pd(50)	2		38[b] (38)
15			Pt (48)	2		37[c] (37)
16				10		99 (20)
17			Rh(35)	2		32[d] (32)

a) Experiments carried out in water/alcohol mixtures at pH 1, on 20 x 20 x 10 mm carbon felt electrodes coated by polypyrrole films containing $2^{-5} \times 10^{-5}$ mol of viologen units and various amounts of metal catalyst; currents from 100 to 300 mA were obtained at - 0.4 to - 0.5 V *vs* SCE 5α/5β ratio: (b) 0.85 (c) 0.64 (d) 1.04.

Catalytic cathodes prepared by the electrodeposition of nickel microparticles in a Nafion film coated on a graphite or nickel plate were applied to ECH in a conventional electrochemical cell.[48] These electrodes have shown higher activity for hydrogenation of 2-cyclohexen-1-one than a Raney-nickel powder cathode, giving a high selectivity for cyclohexanol formation.

We have recently reported the dispersion of zerovalent palladium and rhodium catalysts in conducting anion-exchange polymers, coated on carbon felt electrodes by oxidative electropolymerization of pyrrole monomers containing alkylammonium or pyridinium groups.[49] Incorporation of metal catalysts in polymeric films was effected either by impregnation of $PdCl^{2}_{4}{}^{-}$ or $RhCl^{3}_{4}{}^{-}$ complexes followed by an electroreductive precipitation to Pd(O) or Rh(O), or by electroreduction of polymer coated electrodes immersed in K_2PdCl_4 or Na_3RhCl_6 aqueous solutions. A study of the electrocatalytic activity in hydrogenation of isophorone of various electrodes differing in loading level and

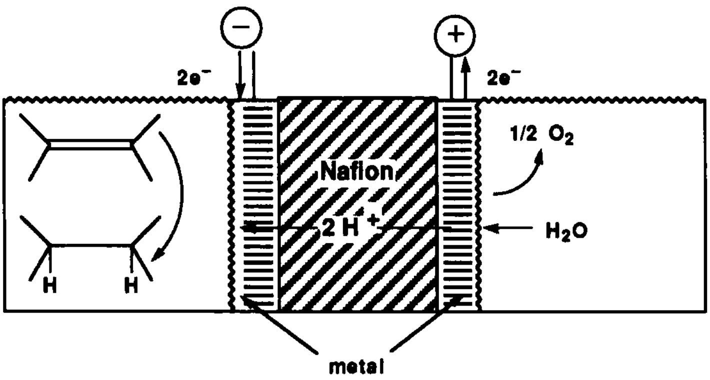


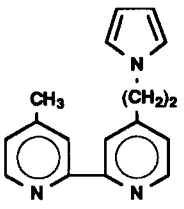
Fig. 2
ECH of an Olefin using the *spe* Electrolysis Method

incorporation method of metal catalyst was performed.[49] The most efficient electrodes were those obtained by incorporation of rhodium using the former preparation method which may lead to the formation of smaller metal clusters dispersed throughout the polymer film. Electron microscopy (SEM) showed a dispersion of metal particles from 100-200 nm on the polymer surface and a large accumulation of metal at the carbon substrate/polymer interface. These results were confirmed by Auger (AES) depth profile analysis, which also demonstrated that metal catalyst is dispersed throughout the polymer overlayer. These catalyic cathodes have also shown a high activity for the selective hydrogenation of organic azides to the corresponding amines.[50]

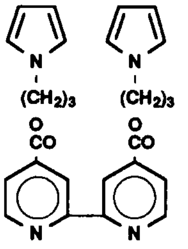
IV. MOLECULARLY-BASED ELECTRODE MATERIALS

The different cathodes above mentioned can be considered as electrochemical analogues for regular heterogeneous hydrogenation catalysts. The use of homogeneous catalysts such as metal complexes is a more a ealing route, their ability to coordinate substrates in a specific manner leading to high activity, regio- and stereospecificity in the ensuing catalytic reaction.[51] It thus appears attractive to realize hydrogen active cathodes by immobilizing on electrodes transition metal complexes having a well known activity in catalytic hydrogenation. Such heterogenisation of homogeneous catalysts could overcome difficulties coming from contamination of reaction products and recovery of the catalyst.

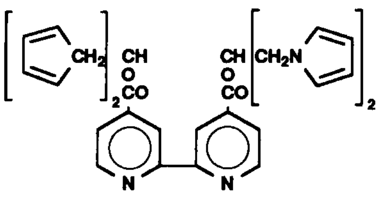
Surprisingly, transition metal complexes have only been used very recently as catalysts for the electrochemical hydrogenation of organic compounds. However, the literature has some relevant examples of efficient photoreduction[52,53] and electroreduction[54] of protons to hydrogen using rhodium complexes as catalysts. Reduction of protons or water with the metal complex in a low valence state leads to a metal-hydrogen intermediate from which hydrogen gas is evolved.[52] Such intermediate would be similar to that obtained from an hydrogenation catalyst and hydrogen gas. Thus, hydrogenation of an unsaturated organic substrate could be expected in the presence of a suitable metal complex electrochemically reduced in aqueous or proton-donor media. Such an electrocatalytic system would constitute a new concept iri the field of ECH. With this goal in mind, electrodes modified by polymeric films containing pendant polypyridyl complexes of RH(III)$^{54-56}$ and Pd(II) were prepared recently in our laboratory.[57] These electrode materials were synthesized from electropolymerization on glassy carbon plate or felt of metal complexes containing pyrrole-substituted 2,21-bipyridine ligands L_1, L_2 or L_3.



L_1

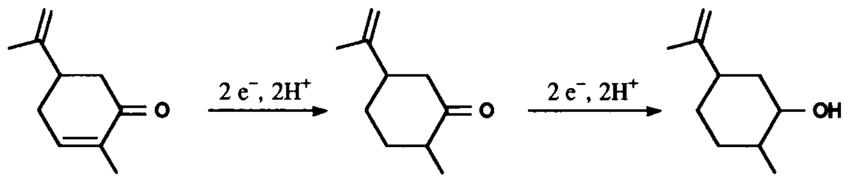


L_2



L_3

Preliminary results have shown that the C/poly[Ph^{III} $(L_2)_2Cl_2]^+$ electrode could hydrogenate cyclohexanone to cyclohexanol quantitatively in aqueous media, at a potential where catalytic active Rh(I) species are formed. Further investigations[58] demonstrated that this electrode is able to reduce numerous substituted cyclohexanone and 2-cyclohexen-1-one derivatives with high current and product yields. For example, the hydrogenation of carvone **7** gave mainly dihydrocarveol **8**, with the intermediate formation of dihydrocarvone **9** (Eq. 11). It is noteworthy that the distribution of dihydrocarveol diastereoisomers is quite different to that obtained in a comparative ECH experiment carried out with a similar Rh(III) complex in solution . On the modified cathode, the (lR, 2R, 5R), (lS, 2R, 5R) and (lS, 2S, 5R) isomers were formed in a 9:8:5 ratio, while the former diastereoisomer was the main product (yield 80%) obtained in the homogeneous experiment.[58] Thus, the microenvironment of the polymeric matrice in which the complex is embedded has a strong influence on its selectivity. It should be noted that these catalytic systems do not need large amounts catalyst to give viable syntheses, since turnovers of 10^3 (mol of substrate hydrogenated per mol of complex immobilized) were easily attained. Finally, it must be emphasized that such electrode materials allow to carry out hydrogenation in media where the metal complex is poorly or fully insoluble.



(11)

Electrode materials synthesized from electropolymerization of the $[Pd^{II}(L_1)_2]^{2+}$ complex have also been shown active for the selective hydrogenation of the carbon-carbon double bond of a series of enones,[57] including 2-cyclohexenone derivatives, (citral and cinnamaldehyde. Electrochemical observations demonstrate that the catalytic species is a Pd(O) form of the complex. However, catalytic activity and selectivity of this purely molecular electrode material is highly different to that ofpalladium particles dispersed in polymer film electrodes.[43,44]

V. CONCLUSION AND PERSPECTIVES

The development of catalytic cathodes having high activity and long term stability should call the attention of organic chemists to electrocatalytic hydrogenation processes and to electrosynthesis from a general point of view. Compared to catalytic hydrogenation, ECH does have some attractive features. Its main characteristic is the mild conditions required for efficient reactions. Very recent results demonstrate the possibility to synthesize catalytic cathodes by immobilizing molecular hydrogenation catalysts on conducting surfaces. These new electrode materials offer several advantages, including (satalyst saving and the possibility to avoid solubility problems. In addition, fixation of the metal complex onto an electrode surface, *i.e.* at the reducing agent (electron) source could minimize its degradation, thus increasing turnovers. In connection with the growing interest in electrosynthesis using metal complexes as catalysts in solution[59] or coated on an electrode surface,[45,60] the realization of molecularly-based electrode materials would elicit new interest in electrocatalytic hydrogenation. In particular, stereoselective hydrogenations using polymeric electrode materials based on chiral metal complexes would provide an ideal way to attain stereoselective electrosyntheses, a goal which has been sometimes attempted but never satisfactorily achieved.

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