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# Gas phase electrocatalysis on metal/Nafion membranes

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## Abstract

The interest in metal/Nafion membranes for gas phase electrochemical reactors is pointed out, the preparation of metal deposits examined by various experimental procedures is briefly described, and their applications in various electrooxidation or electroreduction processes are reviewed.

## 1. Introduction

A porous metallic film formed by small particles of Pt, Au, etc., embedded in a solid polymer electrolyte membrane like Nafion® (Du Pont de Nemours) is a unique electrode material making it possible to carry out electrocatalytic reactions in the gas phase. A gaseous reactant can be contacted directly to it, thereby eliminating the problems associated with reactant solubility, supporting electrolyte side reactions, and mass transfer limitations found in a typical electrochemical reactor.

By imposing a voltage gradient across the membrane, $OH^-$ or $H^+$ ions can be electrically pumped to or from the metallic film, allowing oxidation or reduction reactions to be performed. The working electrode potential can therefore be used as the kinetic driving force instead of the more severe conditions of high temperature or pressure typically found in ordinary chemical reactors.

In addition, ionic pumping across the membrane, and fast diffusion of reactants and products to or from the electrode can occur. Moreover, the reactivity of the organic compounds in the gas phase is higher than in the liquid phase because the levelling-off effect of the solvent has no role.

## 2. Experimental

### 2.1. Deposition methods of metals on Nafion

Nafion, which is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether, has been widely used as a metallized membrane due to its advantageous features: it has a high ionic conductivity, an excellent permselectivity, an outstanding chemical and thermal stability, and a good mechanical strength. Nafion 117 (cation exchange type) sheets of suitable size are the supports most used. They are initially treated for 1 h at 100°C in 6 M $HNO_3$ and subsequently kept under pure, often renewed, Milli Q water.

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The electroless deposition of a thin, porous, metallic layer is obtained by exposing one side of the membrane to a solution containing an appropriate (0.01 M) concentration of the metallic salt (eventually containing a convenient ligand), while the other side faces an alkaline (1 M NaOH) solution of 0.1 M $NaBH_4$, or of $N_2H_4$ as reducing agent.

The principle of Pt deposition is given in Fig. 1a. The optimum deposition conditions (concentrations, pH, temperature, deposition time, etc.) may change from one metal to another.

Porous metallic deposits of Ag [1,2], Cu [3,4], Au [5–7,2], Pt [8–17,2], Ru [4,2], Co, Fe, Ni, Rh, Pd, Re, Os, Ir [2] have been obtained by this method of chemical reduction which leads to a predominant deposition of the metal *outside* Nafion.

In contrast, by the impregnation–reduction method shown in Fig. 1b, a predominantly plati-num deposition is obtained *within* Nafion [16,17] because the dominant reduction mechanism is expected to shift during the film growth from a chemical to an electroless reduction. By both these methods, polycrystalline platinum particles, without any preferred orientation are obtained, but their water environment is different because metallic particles are mostly *outside* or respectively *within* Nafion and this can lead to selective reactions, as in the case of partial oxidation of methanol [17].

The amount of platinum can be considerably lowered (from 2 mg $cm^{-2}$ to 0.35 mg $cm^{-2}$) without a loss of efficiency, by using highly dispersed Pt/C (Prototech) catalysts hot pressed (at 50–60 atm and 120–130°C) onto the Nafion 117 membrane [18,19]. More recently very active thin film catalyst layers containing only 0.17 mg Pt $cm^{-2}$ have been cast from solutions of sus-
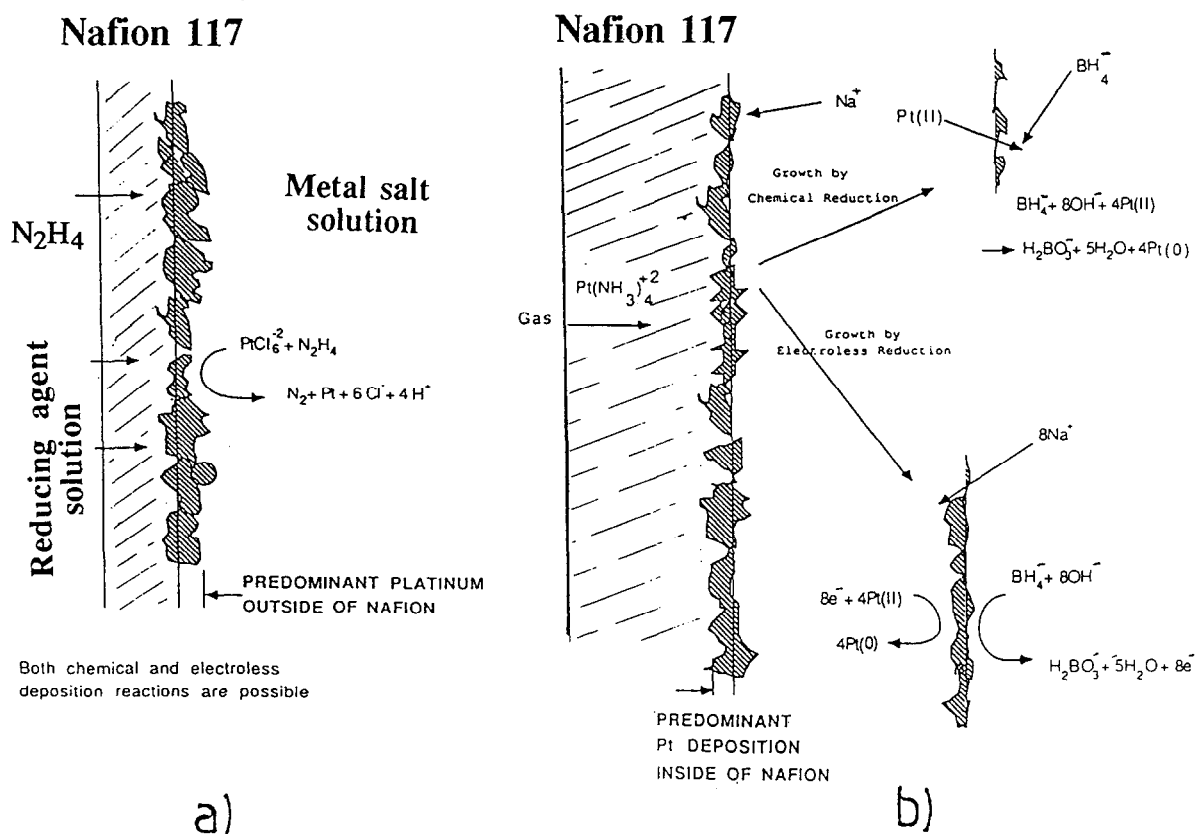


Fig. 1. Schematic diagrams of the deposition of metals on Nafion by (a) chemical reduction, or (b) impregnation–reduction methods.
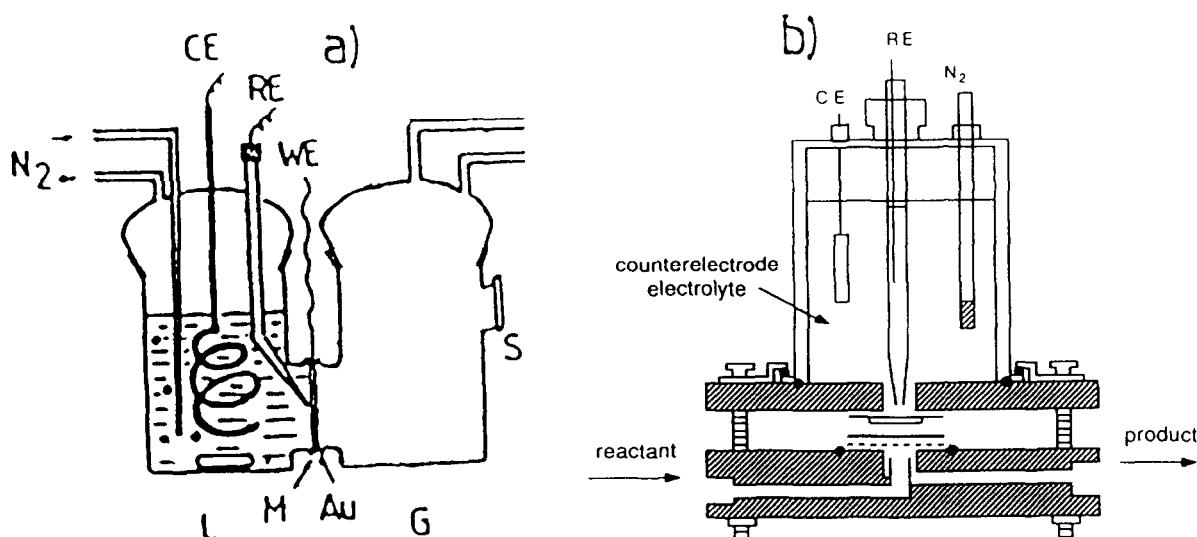
Fig. 2. Electrochemical cells. (a) Metallic deposit facing the gas phase; (b) facing the gas through a carbon-cloth/Pt gauze current collector.
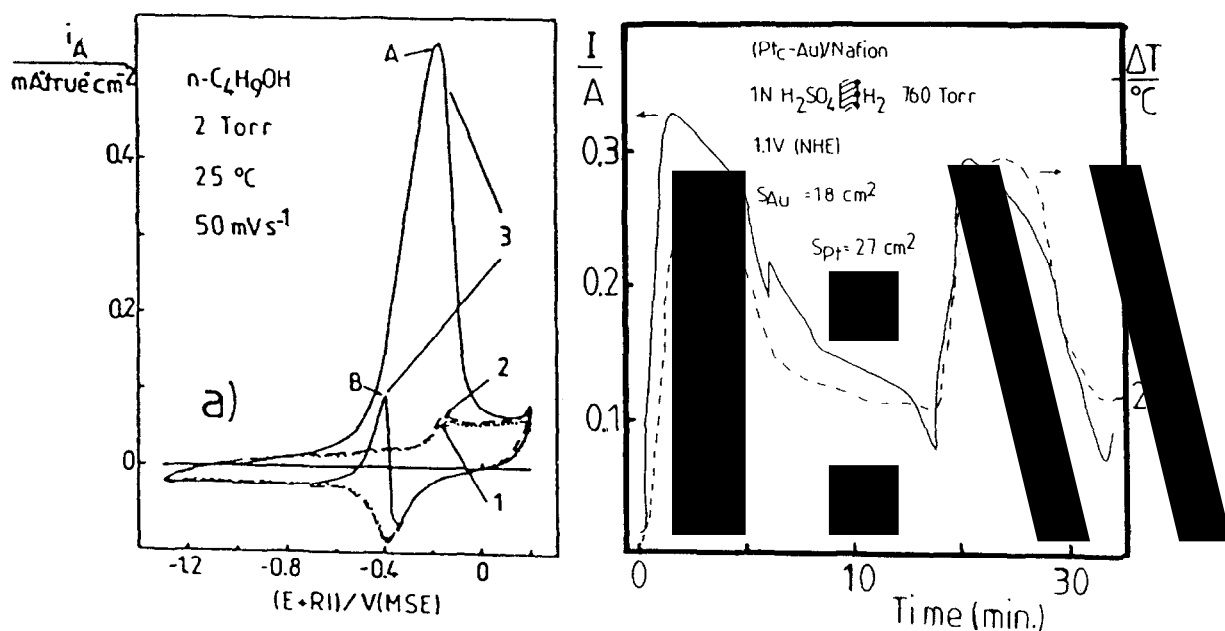


Fig. 3. (a) $I/E$ profiles of Au/Nafion (61.5 cm$^2$) in 1 M NaOH (1), under N$_2$ flow (2) or with n-butanol vapors (3); (b) current–time (left scale) and $\Delta T$–time (right scale) plots for hydrogen oxidation on (Pt–Au)/Nafion anodes.

pended Pt/C catalyst and solubilized Nafion ionomer, brushed on a Teflon support, baked, hot pressed to a Nafion membrane and finally peeled off together with the Nafion membrane [20,21].

A routine characterization of metal/Nafion deposits by electron microscopy (morphology, size of particles and thickness of the film), voltammetry (real active area, the roughness factor),

or chemical analysis (mg of metal per cm$^2$), is a prerequisite.

## 2.2. Electrochemical cells

Metal/Nafion samples are used as separation membranes with the metal facing the gas phase in the two-compartment electrochemical cells (Fig. 2). In the counterelectrolyte compartment filled with 1 M NaOH, 1 N H$_2$SO$_4$, or any other convenient electrolyte, a high area counter electrode (CE) is introduced, while the reference electrode (RE) is usually connected through a Luggin capillary. The current collector is a C ribbon ring in the first cell (Fig. 2a), while in the second a carbon cloth is compressed to the metallic deposit by a Pt gauze (Fig. 2b). Such a carbon cloth/Pt gauze current collector may modify the access of reactants to the reaction layer but improves the geometry of the cell and permits the use of thin metallic deposits.

## 2.3. Measurements

Various electrochemical (voltammetric, galvanostatic, open circuit or imposed potential sequences), chemical (GC and HPLC analysis of reactants and products), or physical measurements (increase of the local temperature, $\Delta T$, of the metallic film), can be simultaneously or alternatively performed.

$I/E$ profiles as those shown Fig. 3a show the high activity of Au deposits in the electrooxidation of very small amounts of butanol vapors, while current–time and $\Delta T$–time dependencies given in Fig. 3b present the characteristic oscillations found in the case of hydrogen oxidation on mixed (Pt–Au)/Nafion deposits. Plots of current density versus the partial pressure of vapors, current or current density versus the applied potential, oxidation current versus the local temperature variations, etc. are also very often used to follow such electrochemical processes.

## 3. Results

### 3.1. Electrooxidation processes

In most cases, the complete oxidation of H$_2$ or CH$_3$OH to H$_2$O or CO$_2$ + H$_2$O was investigated in relation with fuel cell applications; only a very few studies have been devoted to the partial oxidation of methanol [17], and to the electroactivity of alkyl alcohols or alkylamines [22].

*Hydrogen* [8,23,24,18–21] is today considered as the most convenient fuel for fuel cells using metal/Nafion membranes and consequently its electrooxidation has been extensively studied. High performance was obtained with Pt deposits [8,23] and Pt/C catalysts [18–21], despite the low platinum content used in the latter case.

More recently, a comparative study of Pt and Pd and Rh deposits has shown that, under the same conditions, Pd can be the most active metal (Fig. 4a), presumably due to the penetration of hydrogen in its crystalline network [23,24].

*Carbon monoxide* [5] cannot be regarded as a convenient fuel due to its high toxicity, but its oxidation, found to be 100 times more efficient on Au/Nafion anodes than on bare gold in aqueous solutions, was examined in order to obtain a better insight into the mechanism making it possible to obtain such a high (90%) current efficiency.

*Methanol* [6,10,12,13,17] may be in the future an alternative fuel: the oxidation of CH$_3$OH vapor on Pt and Au deposits was found to be quite efficient but occurred only at relatively high anodic polarisations ( > 1 V NHE), which makes it useless in combination with the actual Pt cathodes.

The partial oxidation of methanol may lead to methylformate [6], formaldehyde and methylal [17], through reactions sensitive to temperature, methanol partial pressure and electrode morphology. High temperature, a low methanol pressure and the use of Pt deposits prepared by the impregnation–reduction procedure (which permit the growth *within* Nafion of particles with a low water-content environment), lead to a selective production of formaldehyde [17].
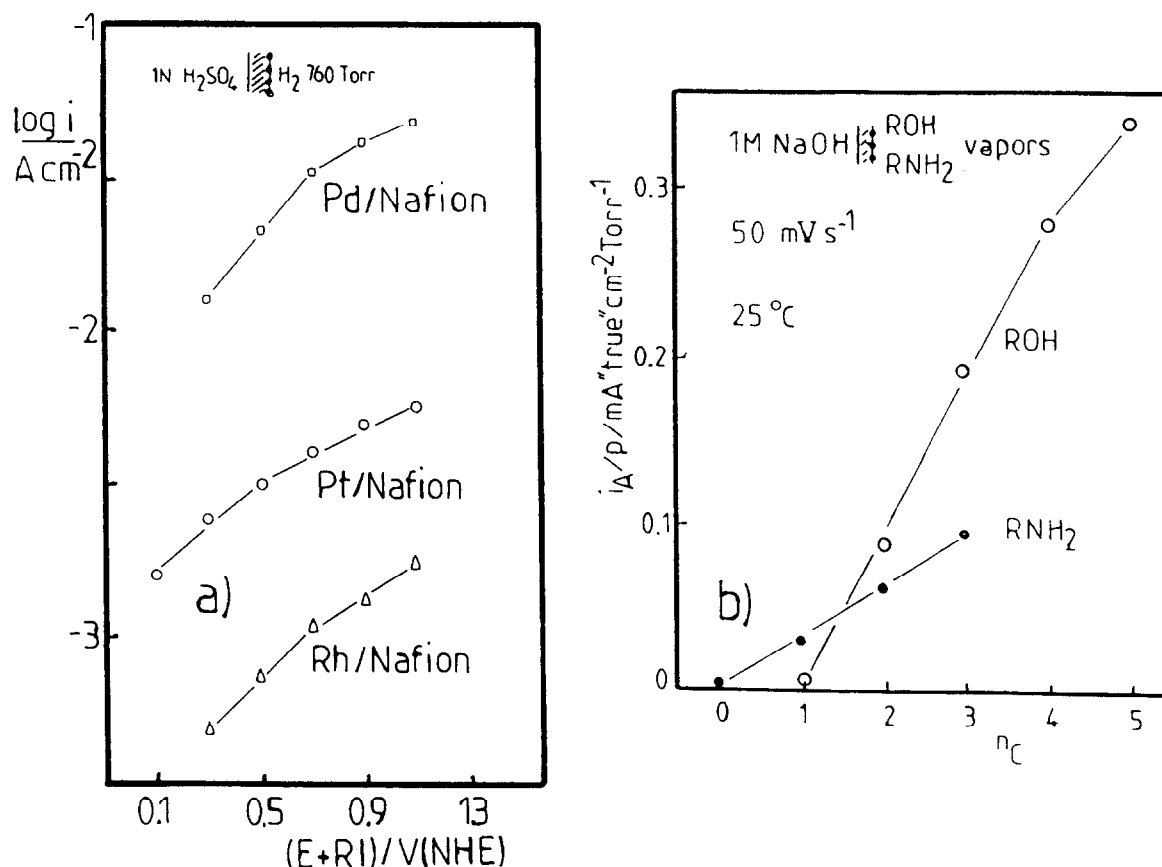
Fig. 4. Dependence of the electrooxidation processes on: (a) the kind of the metallic deposit used to oxidize hydrogen; (b) the length of the alkyl chain in ROH and RNH$_2$ compounds.

*Alkylalcohols* and *alkylamines* [22] have been studied in order to obtain a better insight into the relation between the electroactivity of these molecules and their molecular structure. The oxidation current densities (divided by the 'true' surface area and the partial vapor pressures) were found to depend linearly on the number of C atoms in the alkyl chain (Fig. 4b).

## 3.2. Electroreductions

*Oxygen* [7,8,15,25], as pure gas or mixed with nitrogen (in air), is an important fuel cell component. The reduction of O$_2$ on Pt/Nafion, briefly studied in 1983 [8], has been investigated in more detail on Au/Nafion deposits in the presence of under potential deposits of Bi and Pb [7]: both

have been found to enhance the electroreduction process to a large extent. Platinum gauze electrodes coated with Nafion [26] and Pt/C catalysts hot-pressed on Nafion [18,19], have been also considered in relation to the use of O$_2$ in fuel cell applications.

*Nitrogen* [4] reduction to ammonia on Ru/ Nafion 417 deposits occurs with a very low Faradaic efficiency (0.0015%). Other ruthenium containing substrates appear to be necessary to increase the N$_2$ dissociative adsorption coverage prior to the Faradaic hydrogenation reaction [4].

*Carbon dioxide* [3,2] electroreduction to hydrocarbons was tested on several metals (Cu, Co, Fe, Ni, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au) deposited on Nafion membranes. The relative rates of methane formation was found [2] to

increase in the order Ni > Ru > Rh > Au, but the highest Faradaic efficiency is below 0.25%. On Pt/Nafion membranes, reduction appears to involve interaction of $CO_2$ with electrochemically generated hydrogen and proceeds via a formate intermediate, resulting in strongly chemisorbed products that do not desorb and thus the active sites are blocked. In the case of Ru, Rh and Au deposits, only $CH_4$ was found as a reaction product, while with Ni/Nafion, $C_2H_4$ and $C_2H_6$ have also been obtained [2].

Cu/Nafion 115 membranes allow the reduction of $CO_2$ to $CH_4$ and $C_2H_4$ with a Faradaic efficiency of 10%, a value which is half of that obtained with bare Cu in aqueous solutions: high acidities in the counter-solution promote competitive proton reduction at Cu/Nafion, while higher pHs lead to proton starvation at the Cu electrode [3].

*Ethylene* [27] reduction at 50°C was found to proceed rather efficiently to $C_2H_6$ at Pt/Nafion deposits prepared by the impregnation–reduction method. The limiting current density was proportional to the pressure of $C_2H_4$ and has slightly increased [27] with temperature up to a value of approximately 50 mA cm$^{-2}$.

## 4. Conclusions

A vast amount of knowledge is presently available on the preparation of very thin metallic deposits on Nafion and their characterization by microscopic, chemical or electrochemical techniques, on the electroactivity of such materials towards various types of organic or inorganic molecules and on the influence of the various experimental factors (temperature, morphology of the deposit, partial pressure of vapors, etc.). This knowledge, mostly derived from fuel cells investigations, can now be helpful in using metal/Nafion membranes in gas phase processes for producing, with good efficiency and selectivity, valuable products. Different gas phase electrochemical reactors, involving various types of metallized membranes, can now be realized, as

for instance that having a phosphoric acid containing silica-wool disk as a proton conducting membrane which was recently found to be very efficient and selective [28] in the hydrogenation of acetylene to ethylene at 80°C.

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